UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

Version 1

December 12th 2019 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

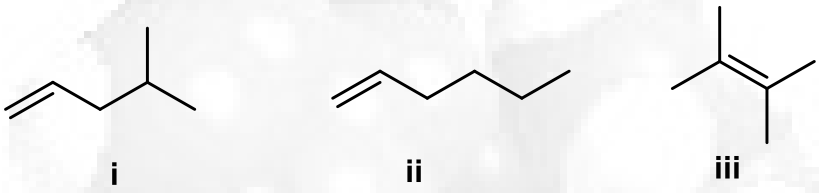
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

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

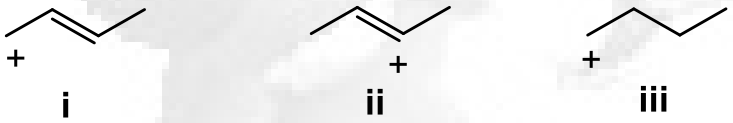
Use the following code to indicate your answers.

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

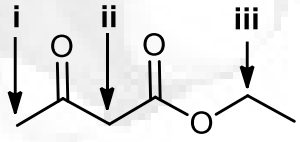
1. The relative stability of the following alkenes :



2. The relative stability of the following carbocations :



3. The relative acidity of the hydrogens indicated:



4. The relative rate of reaction when each of the following was treated with NaCN / DMF:

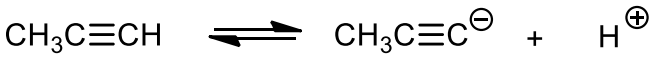
$(CH_3)_2CHBr$	$CH_3CH_2CH_2I$	$(CH_3)_2CHI$
i	**ii**	**iii**

 Cont'd -->

Use the following code to indicate your answers.

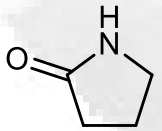
A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

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

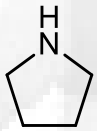


$(CH_3CH_2)_3N$ **i** CH_3CH_2ONa **ii** $LiN(iPr)_2$ **iii** iPr = isopropyl

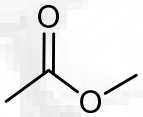
6. The relative acidity of the most acidic proton in each of the following structures :



i



ii

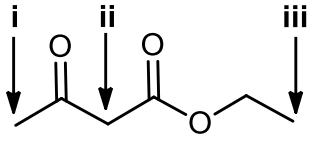


iii

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

i. n-butanol **ii**. sec-butanol **iii**. t-butanol

8. The relative ^{1}H-NMR chemical shifts for the hydrogen atoms indicated by arrows in the following structure:



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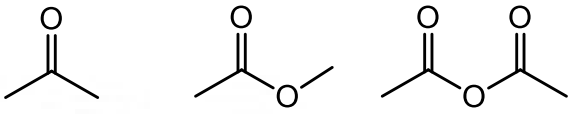
Use the following code to indicate your answers.

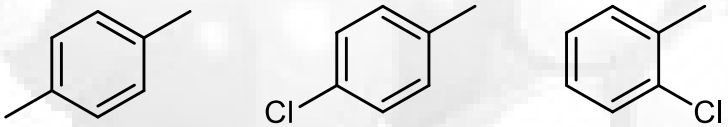
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

9. The relative frequency of the C=O stretching vibration in the IR spectra of each of the following:



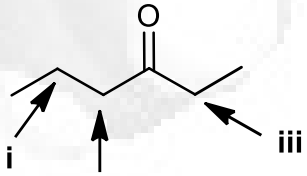
i **ii** **iii**

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



i **ii** **iii**

11. The number of lines observed in the ^{1}H-NMR spectra for the H atoms at the positions indicated in each of the following :



12. The relative yield of the anti-Zaitsev product formed when 2-bromopentane is heated with each of the following :

$CH_3CH_2O^-$ $(CH_3)_3CO^-$ HO^-

i **ii** **iii**

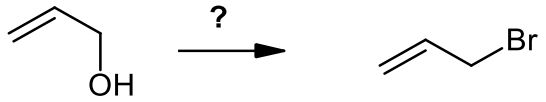
Cont'd -->

12% PART 2: MOLECULAR PROPERTIES

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

In questions 13-18 choose the single option that provides the best answer.

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



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

B. Br_2/UV is required because the reaction is a radical bromination

C. NaBr is required because the reaction is a S_N2 nucleophilic substitution.

D. HBr is required because the reaction is a S_N1 nucleophilic substitution.

E. PBr_3/Et_3N is required because the reaction is a S_N1 nucleophilic substitution.

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

A. They have equal priority because both attach at C atoms

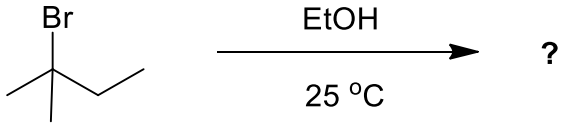
B. **I** because it has a 6 carbon chain

C. **I** because it has a mass of 85 compared to **II** = 57

D. **II** because there are 3 C attached to the first C

E. **II** because 3 methyl groups out rank the 1 methyl group in **I**

15. Which of the following is the major product of the following reaction ?



A. **I** because EtOH is a strong base.

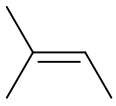
B. **II** because EtOH is a strong nucleophile.

C. **I** due to steric effects.

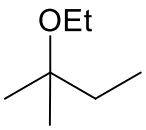
D. **II** because EtOH is a weak base

E. **I** and **II** are formed in approximately equal amounts

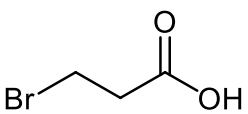
I



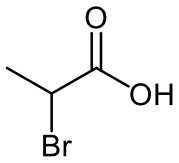
II



16. In the 13C-NMR spectra, which of the following predictions is true regarding to the **chemical shift** of the **C atom in the carbonyl groups**?



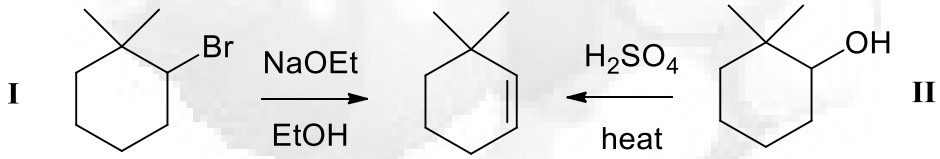
I



II

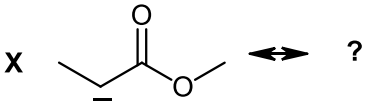
A. **I** should be higher than **II**, because of the deshielding effect of the Br in **II**
B. **I** should be higher than **II**, because of the shielding effect of the Br in **II**.
C. **II** should be higher than **I**, because compound **II** is a stronger acid.
D. **II** should be higher than **I**, because of greater inductive effect in **II**
E. There is no difference between the C=O groups of the two compounds because both are carboxylic acids.

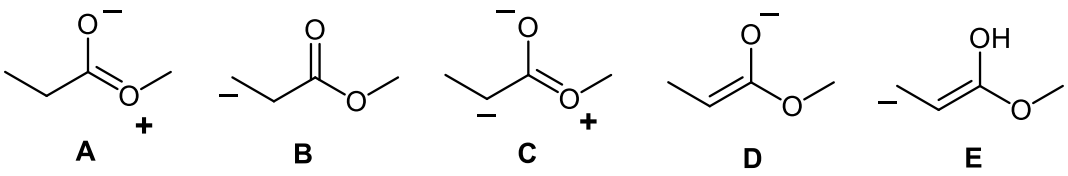
17. Which of the following reactions is more efficient for producing the alkene shown ?



A. **I** because the reaction is more likely to be E2
B. **II** because the reaction is more likely to be E2
C. **I** because the reaction is more likely to be E1
D. **II** because the reaction is more likely to be E1
E. The routes are equally efficient at producing the alkene

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



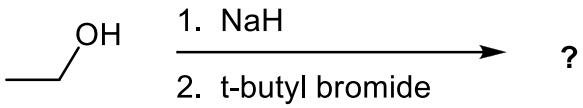


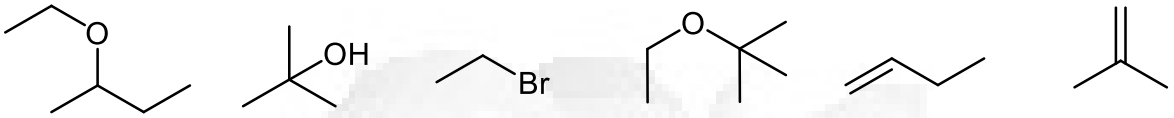
14% PART 3: REACTIONS

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

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

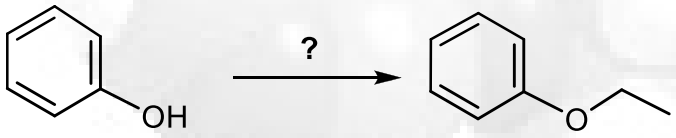
19.





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

20.



A 1. $SOCl_2$ / Et_3N;
2. $NaOCH_2CH_3$

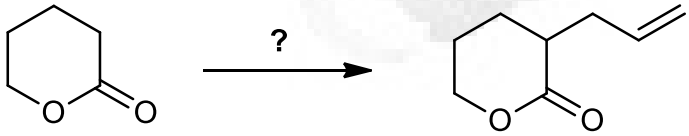
B H_2SO_4 / bromoethane

C Na_2CO_3 / bromoethane

D 1. p-TsCl / Et_3N
2. Chloroethane

E 1. Cl_2 / uv light
2. Ethanol

21.



A 1. $LiN(i\text{-}Pr)_2$; 2. allyl acohol

B 1. Br_2/UV; 2. allyl alcohol

C 1. $LiN(i\text{-}Pr)_2$; 2. allyl bromide

D 1. H_2SO_4; 2. allyl bromide

E 1. Cl_2 / uv light; 2. allyl bromide

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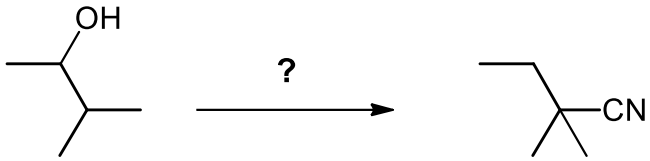
22.



A 1. Thionyl chloride / Et_3N
2. NaCN

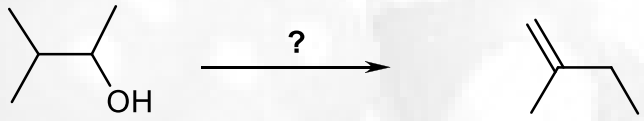
B 1. Br_2 / UV
2. NaCN

C 1. Cl_2, uv light
2. NaCN

D 1. HBr
2. NaCN

E 1. TsCl / Et_3N
2. NaCN

23.



A 1. Br_2
2. KO ^{t}Bu / t-BuOH / heat

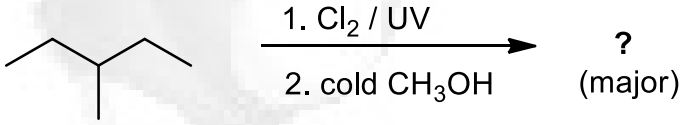
B 1. $SOCl_2$ / Et_3N
2. KOH / EtOH / heat

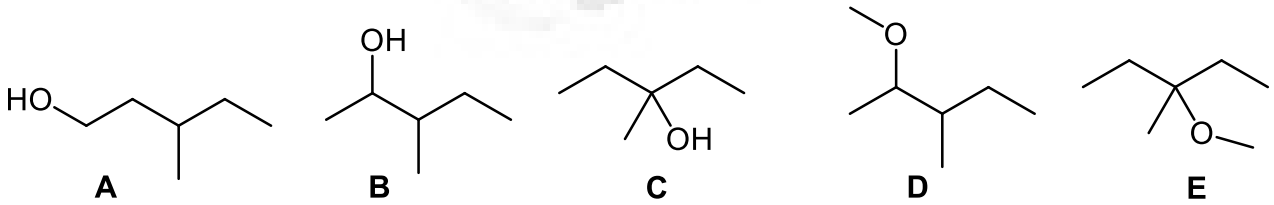
C 1. PBr_3 / Et_3N
2. KO ^{t}Bu / t-BuOH / heat

D 1. HBr
2. KO ^{t}Bu / t-BuOH / heat

E Conc. H_2SO_4 / heat

24.





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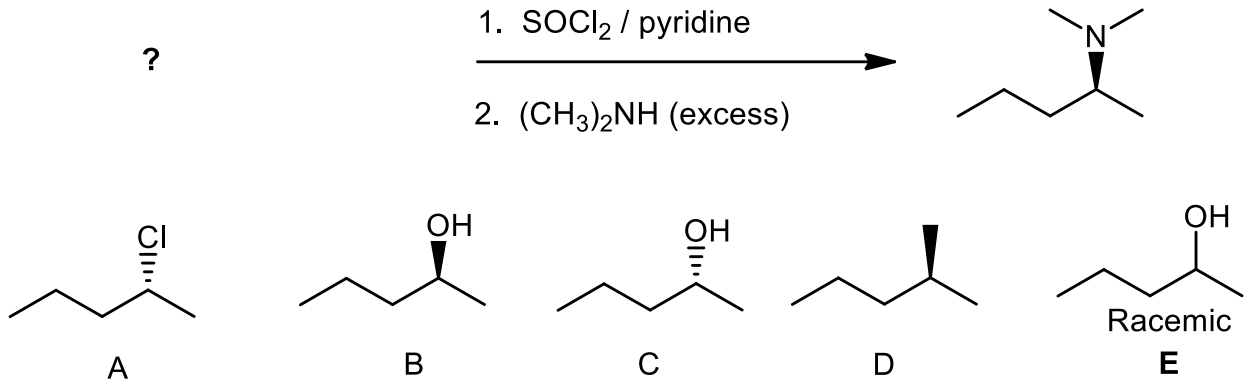
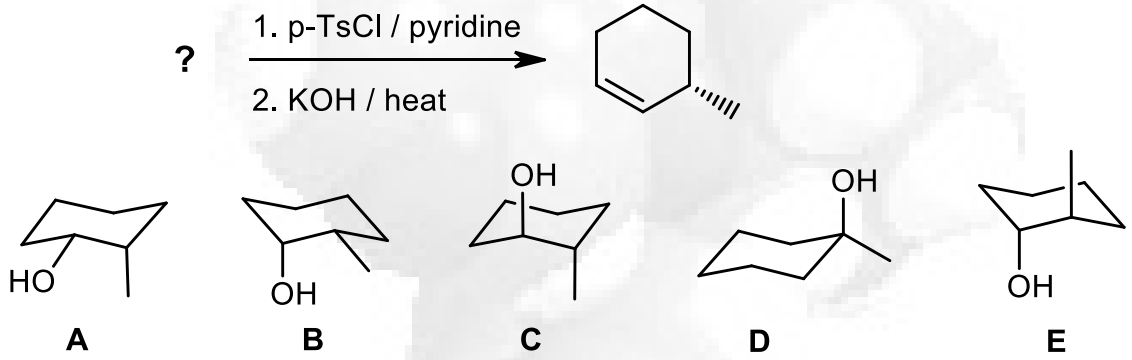
25.



26.



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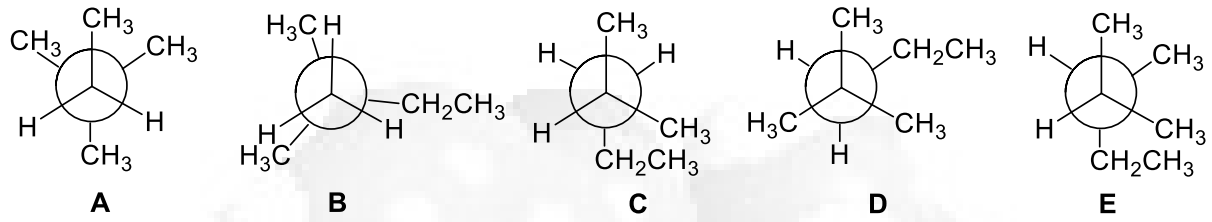
9% PART 4: CONFORMATIONAL ANALYSIS

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.

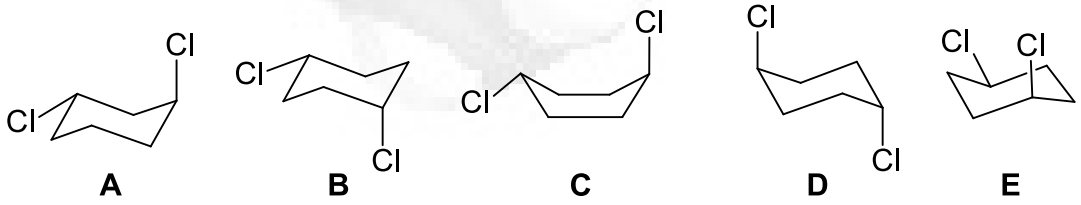
27. Which of the Newman projections represent conformations of 2,2-dimethylpentane ? (**select all that apply**)



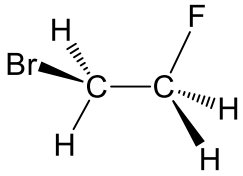
28. What is the **torsional** angle between the two methyl groups in the conformation of *cis*-1,2-dimethylcyclohexane shown below ?

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

29. Which of the following structures represent conformations that can be adopted by *trans*-1,4-dichlorocyclohexane ? (**select all that apply)**

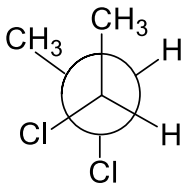


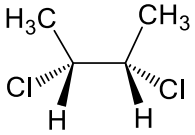
30. Which of the following terms **best** describes the relative position of the two halogen atoms in the conformation of the molecule shown below?



A eclipsed
B staggered
C anti
D syn
E gauche

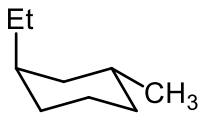
31. Which of the following terms **best** describes the relationship between the two molecules shown below ?



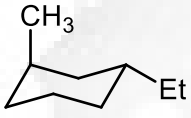


A constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB not isomers

32. Which of the following represents the **most** abundant conformation of *trans*-1-ethyl-3-methylcyclohexane at 25 °C?

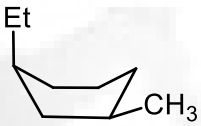


A

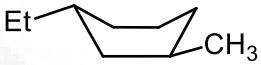


B

C

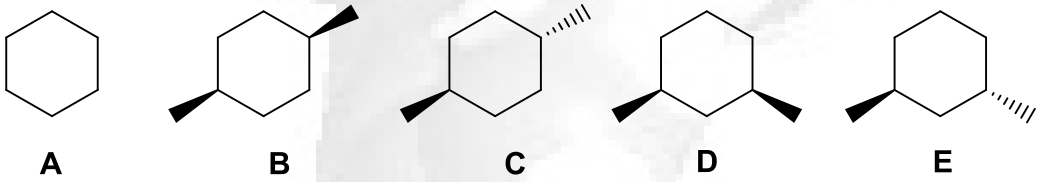


D



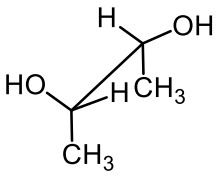
E

33. Which of the following structures have two chair conformations of equal energy ? (**select all that apply)**

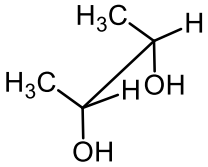


A **B** **C** **D** **E**

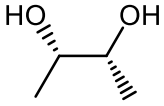
34. Which of the following represents a conformation of (2R,3R)-butane-2,3-diol?



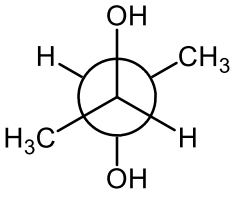
A



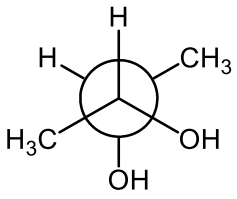
B



C



D



E

Cont'd -->

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. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet *etc*. .

35. **^{1}H NMR** : δ/ppm 1.1 (t, 3H), 2.1 (s, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 7.9, 29.4, 36.9, 209.3
IR : 1718 cm^{-1}

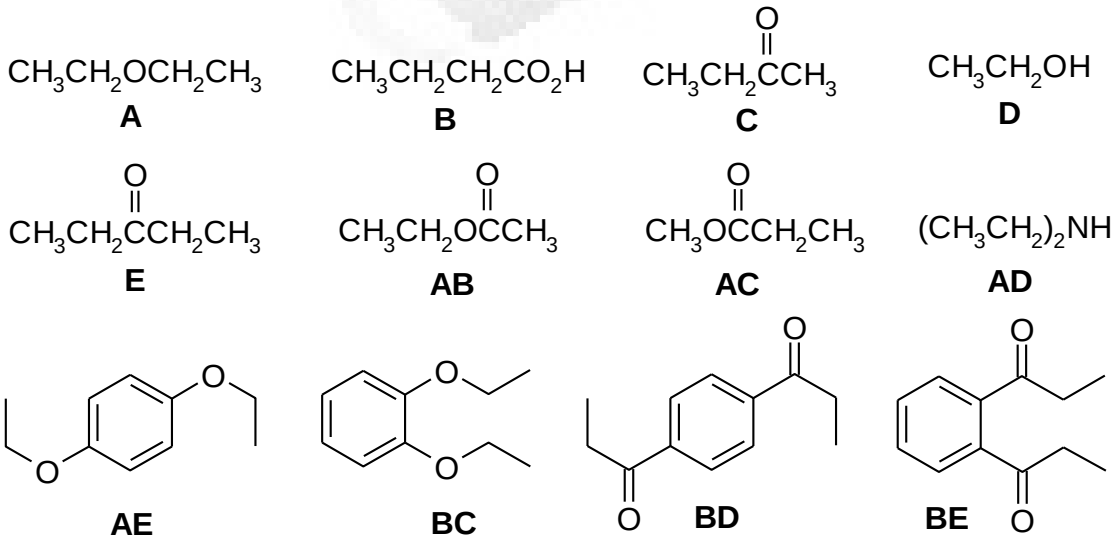
36. **^{1}H NMR** : δ/ppm 1.2 (t, 3H), 2.3 (q, 2H), 3.7 (s, 3H)
^{13}C-NMR: δ/ppm 9.2, 27.5, 51.5, 174.9
IR : 1741 cm^{-1}

37. **^{1}H NMR** : δ/ppm 1.1 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 7.9, 35.5, 212.1
IR : 1716 cm^{-1}

38. **^{1}H NMR** : δ/ppm 1.4 (t, 3H), 4.0 (q, 2H), 6.9 (m, 2H)
^{13}C-NMR: δ/ppm 14.9, 64.6, 114.0, 121.1, 149.0

39. **^{1}H NMR** : δ/ppm 1.3 (t, 3H), 2.0 (s, 3H) 4.1 (q, 2H)
^{13}C-NMR: δ/ppm 14.3, 21.0, 60.4, 171.0
IR : 1743 cm^{-1}

40. **^{1}H-NMR**: δ/ppm 1.0 (t, 3H), 1.7 (sextet, 2H), 2.3 (t, 2H), 11.5 (s, 1H, D_2O exchange)
^{13}C-NMR: δ/ppm 13.7, 18.4, 36.2, 180.7
IR: 2700-3300, 1712 cm^{-1}



8% PART 6: SYNTHESIS

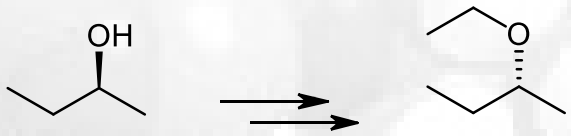
DESIGN TWO(2) EFFICIENT SYNTHESES, ONE from **PART A** and **ONE** from **PART B** of the following target molecules from the indicated starting material. In addition, you are allowed to use **any hydrocarbon with three or fewer carbon atoms**, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the carbon skeleton in the product. More than one step will be required for each synthesis. Clearly show the required reagents and the product of each step.

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

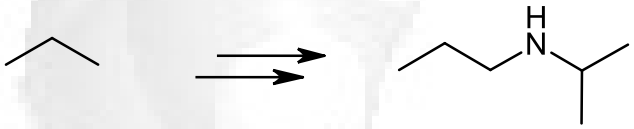
DO NOT SHOW MECHANISMS.

PART A

either

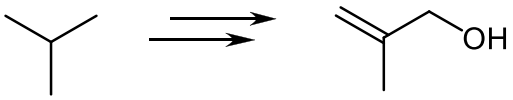


or

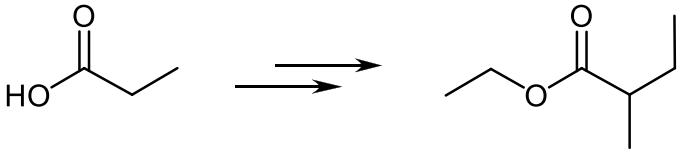


PART B

either



or



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10% PART 7: MECHANISMS

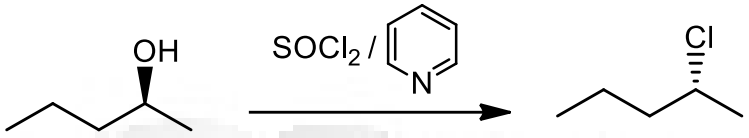
WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED

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

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.

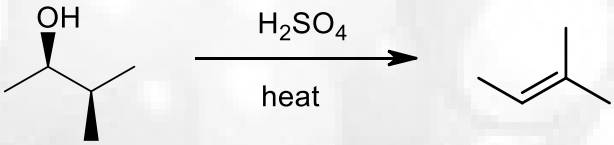
(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:

i.



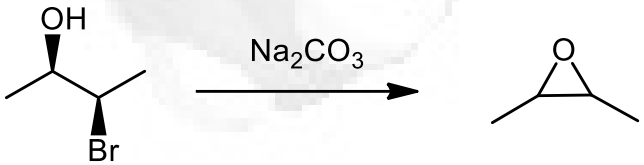
OR

ii.



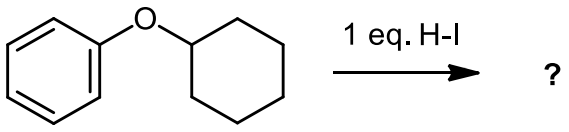
(5%) PART B: Use a curly arrow mechanism to explain ONE of the following:

i. A synthesis of an epoxide (an example of a cyclic ether) is shown below. Draw the curly arrow mechanism to account for the formation of the product (stereochemistry not shown) and **make sure to clearly show the required stereochemistry of the product**.



OR

ii. Predict the product of the reaction of the compound shown below with one equivalent of HI. Provide a clear and detailed curly arrow mechanism to account for this prediction.



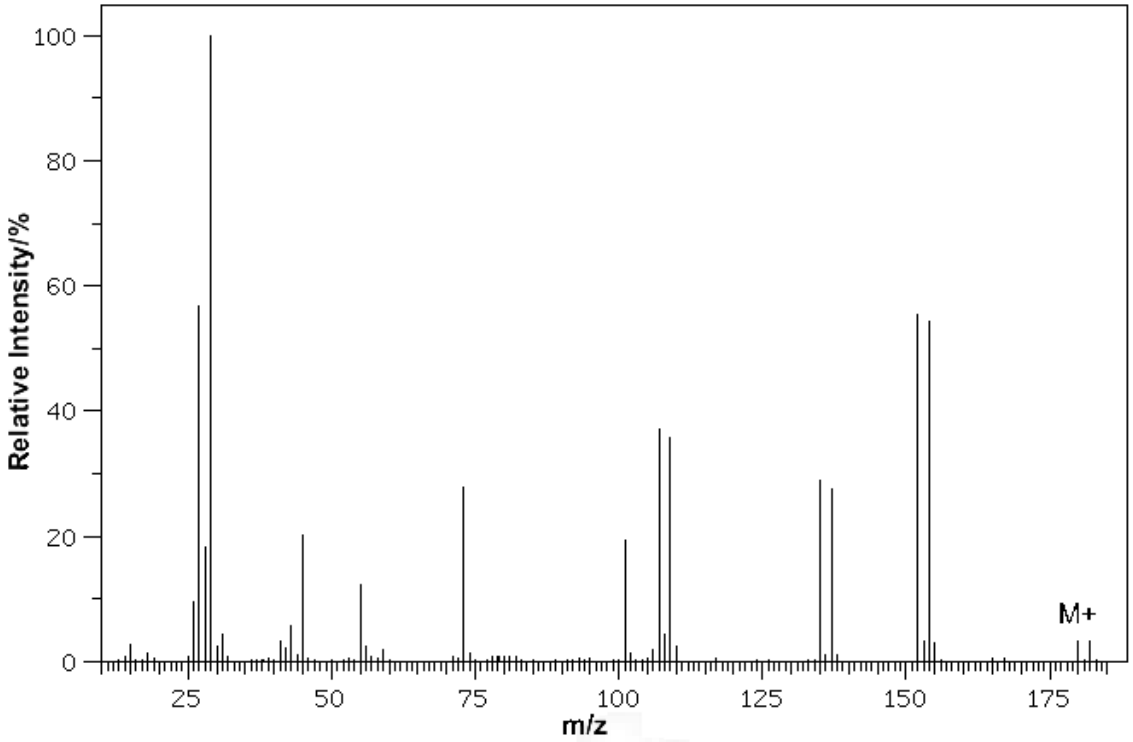
10% PART 8: SPECTROSCOPY

WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED.

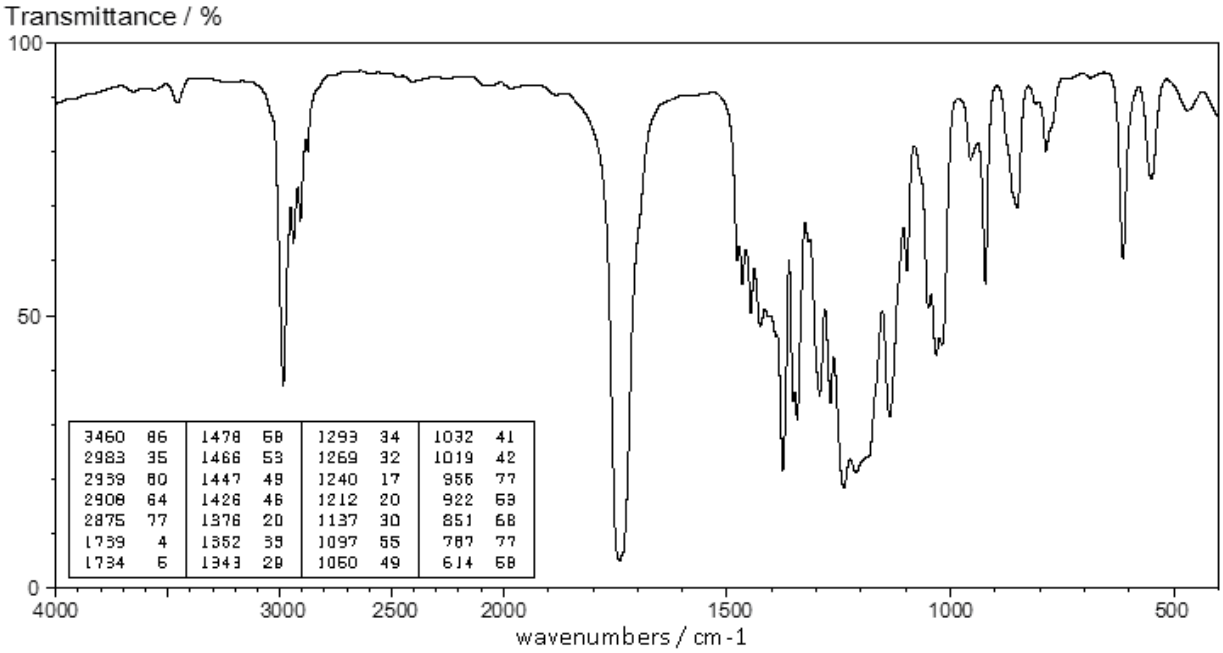
Show your workings as PARTIAL marks will be given.

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

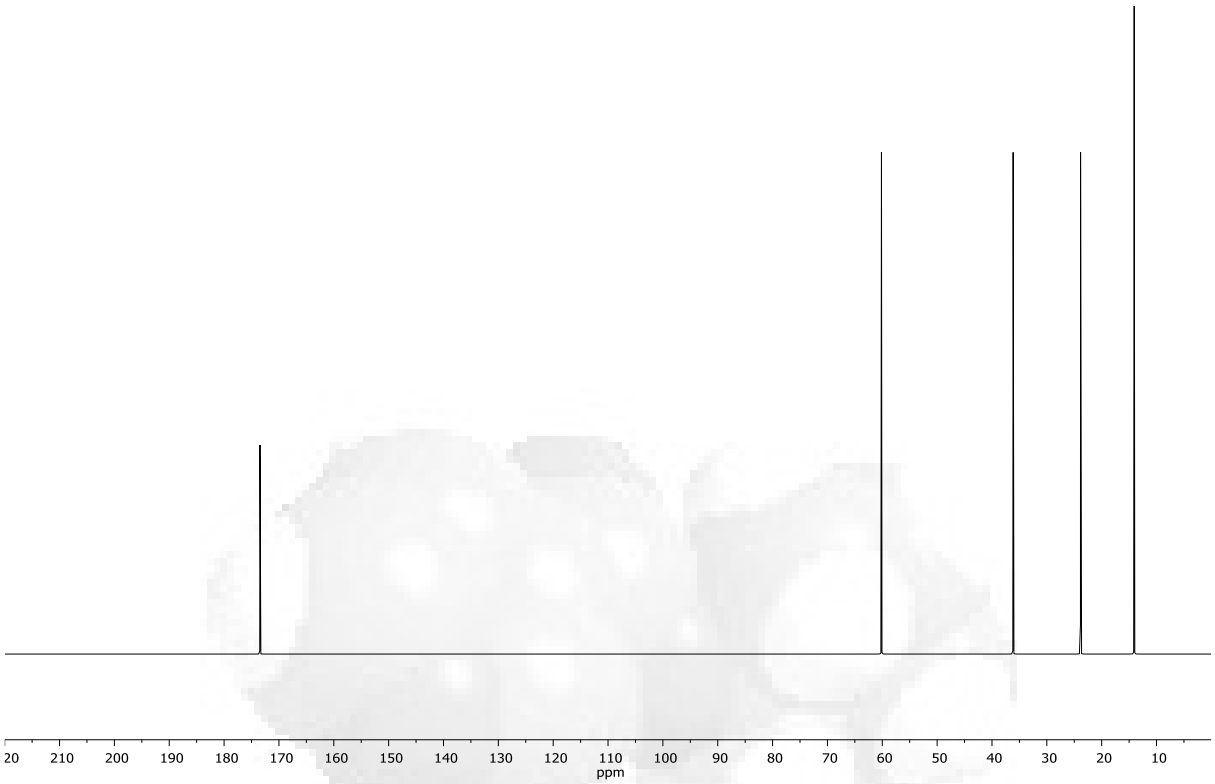
Mass Spectrum:



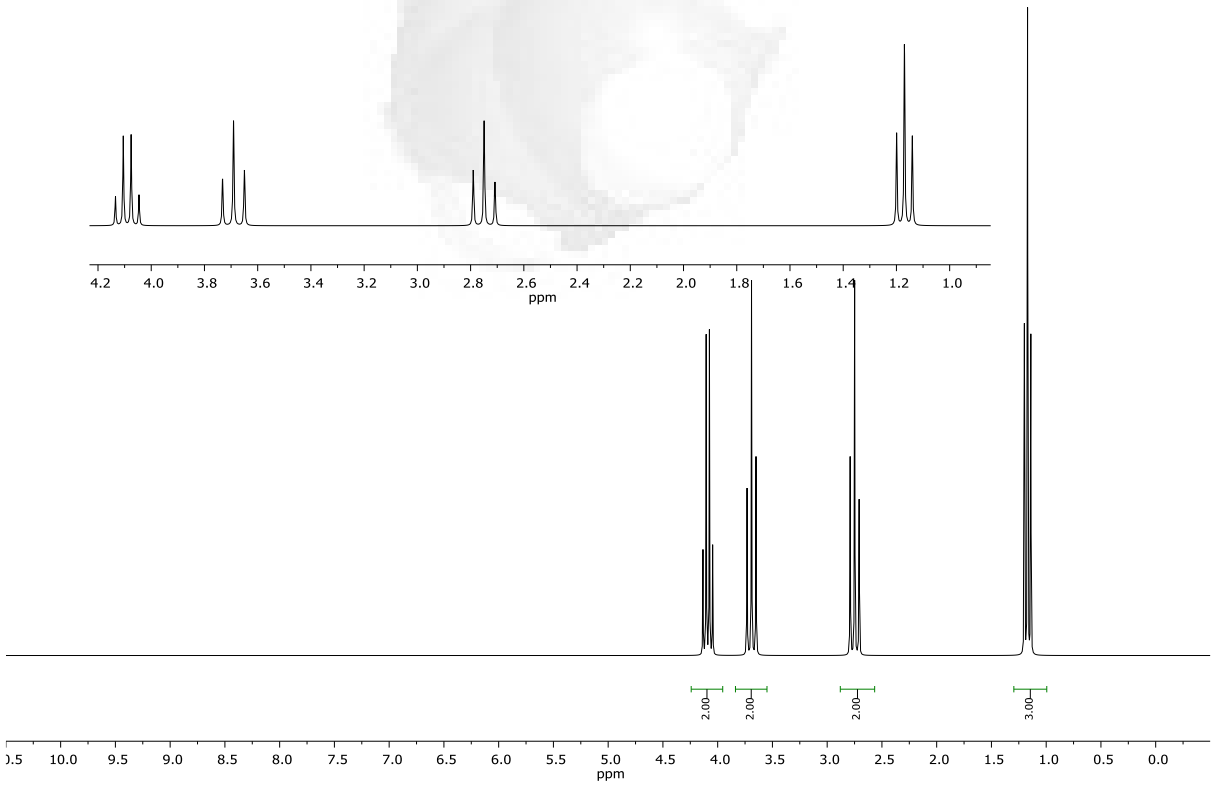
IR Spectrum:



^{13}C-NMR:



^{1}H-NMR:



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10% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED

Compound **A** with molecular formula $C_{10}H_{14}O$ (IR: 3500 cm^{-1}, broad) was reacted with HBr to give major product **B**.

When **B** was reacted with KOH / EtOH / heat it gave products **C** and **D**. **C** and **D** were found to be geometric isomers. In contrast, when **B** was reacted with KOtBu / DMSO / heat, it gave **E**, a constitutional isomer of **C** and **D** as the major product. **B** was found to react rapidly with aqueous $AgNO_3$ or aqueous Na_2CO_3 to give **F**, a constitutional isomer of **A**.

When **A** was reacted with PBr_3 / Et_3N , product **G** was obtained. **G** was found to be a constitutional isomer of **B**. When **G** was heated with KOtBu / DMSO / heat, it gave **H**, a constitutional isomer of **C**, **D** and **E**.

When *sec*-butylbenzene was reacted with Br_2 and heat, **B** was obtained as the major product.

Both **A** and **F** react with conc. H_2SO_4 and heat to form **C** (major) and **D** (minor).

In a 13C-NMR spectroscopic analysis of the compounds, **A** - **H** each had 8 peaks.

- Identify **A**-**H** (only structures are needed)
- Give the complete IUPAC name of **C.**

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

IRH / CCL / JvH 2019

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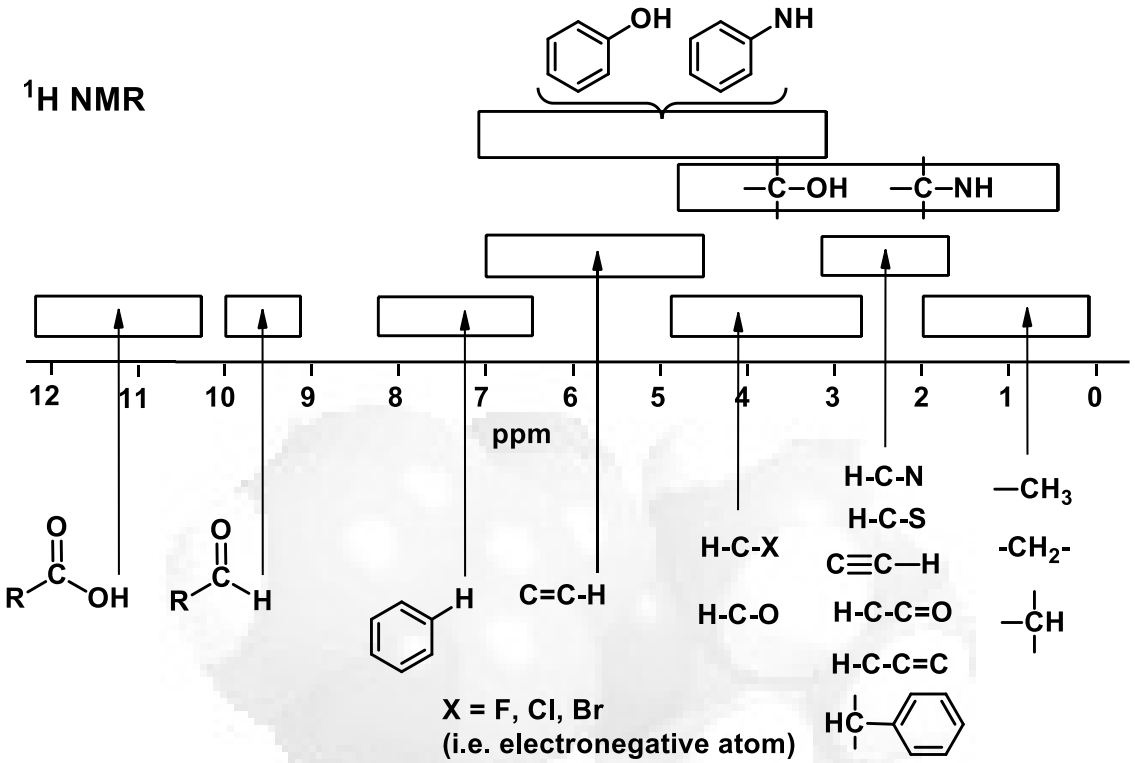
SPECTROSCOPIC TABLES



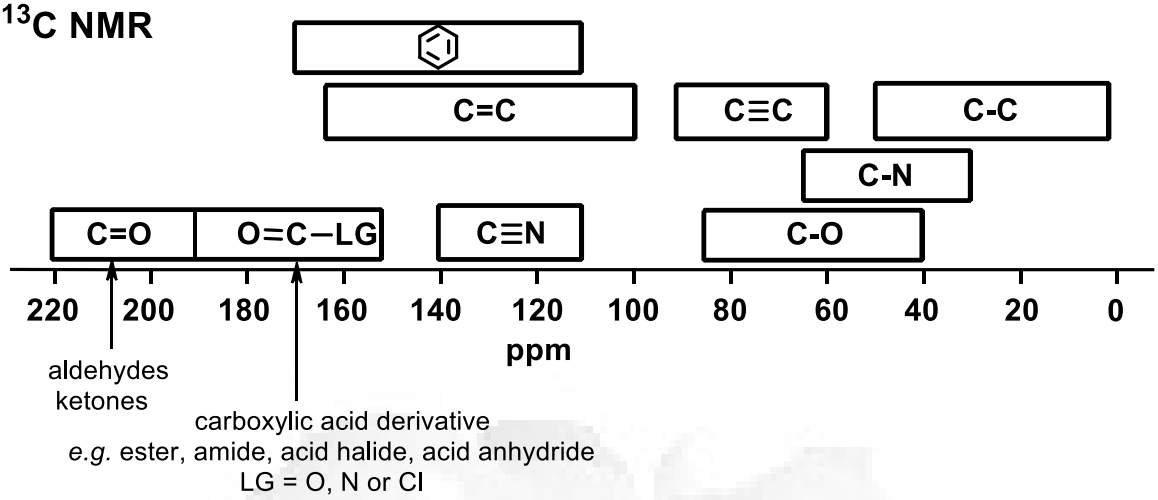
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

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

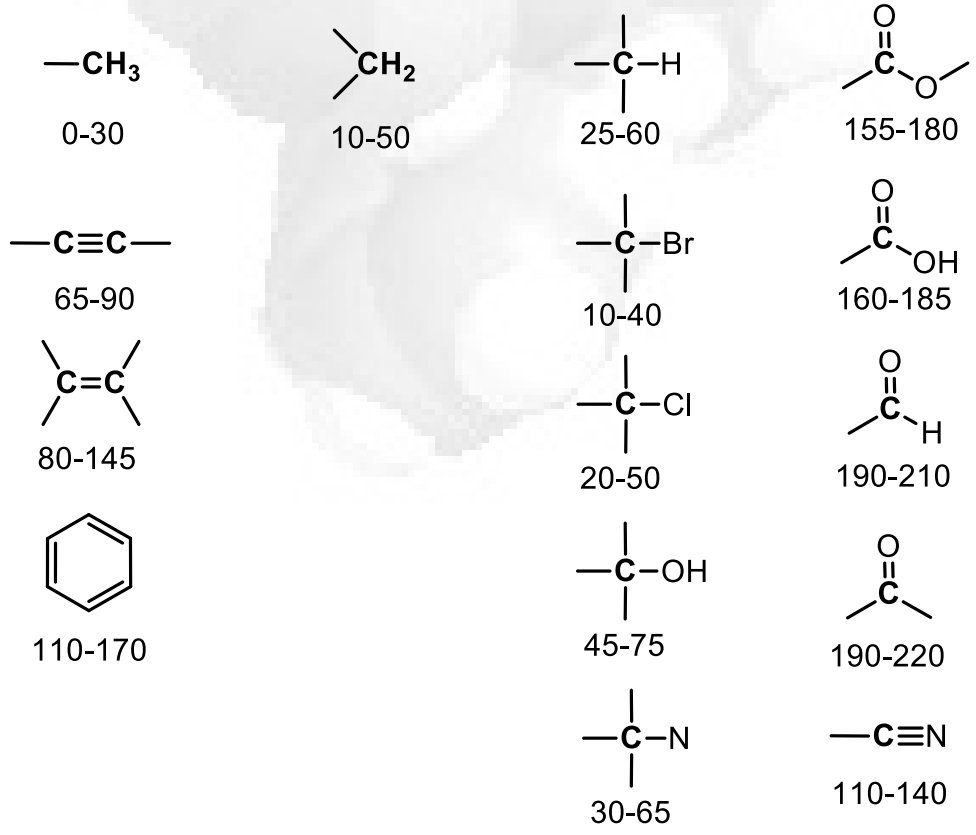
other	
sp^3C-OH	1-5
sp^3C-NH	1-3
C≡CH	2.5
C=C(H)	4.5-6.5
H–Ar	6.5-8
R–C(=O)–H	9-10
R–C(=O)–OH	9-12

Cont'd -->

^{13}C NMR



^{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		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																	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)