

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAMINATION
CHEMISTRY 351

Version
1

December 10th 2018

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

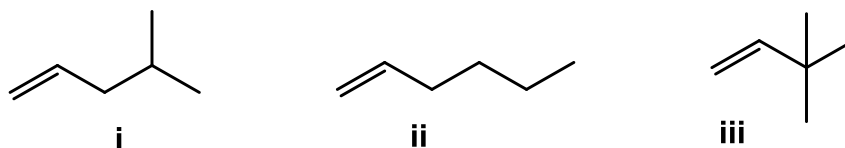
15% PART 1: RELATIVE PROPERTIES**ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.****Arrange the items in questions 1-12 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.**

Use the following code to indicate your answers.

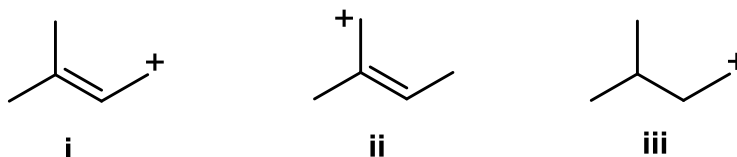
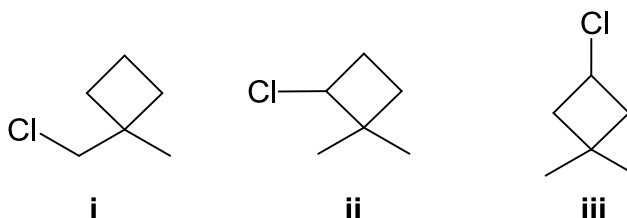
A. i > ii > iii
B. i > iii > ii
C. ii > i > iii

D. ii > iii > i
E. iii > i > ii
AB. iii > ii > i

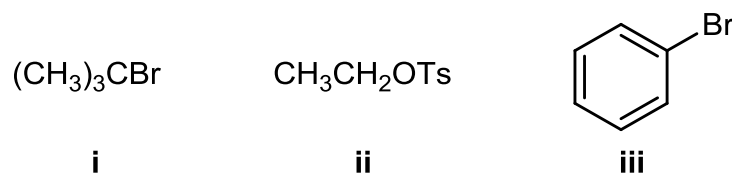
1. The relative boiling points of the following alkenes :



2. The relative stability of the following carbocations :

3. The relative amount of the following products formed by the reaction 1,1-dimethylcyclobutane with Cl_2 / uv light:

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



Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

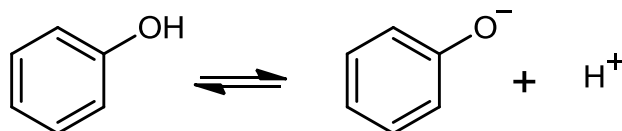
C. ii > i > iii

D. ii > iii > i

E. iii > i > ii

AB. iii > ii > i

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



$\text{CH}_3\text{CH}_2\text{ONa}$

i

$(\text{CH}_3)_3\text{N}$

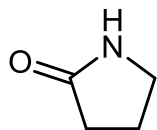
ii

$\text{LiN}(\text{iPr})_2$

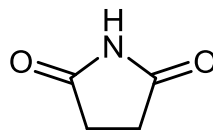
iii

iPr = isopropyl

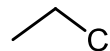
6. The relative acidity of the most acidic proton in each of the following structures :



i



ii



iii

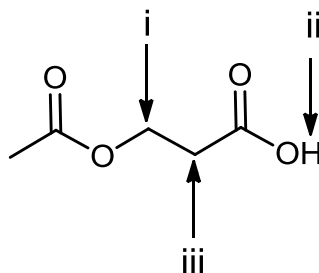
7. The relative rate of reaction when each of the following was heated with H_2SO_4 :

i. 1-butanol

ii. 2-butanol

iii. t-butanol

8. The relative $^1\text{H-NMR}$ chemical shifts for the proton nuclei indicated by arrows in the following structure:



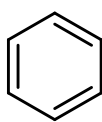
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

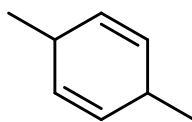
9. The relative intensity of the peaks in the electron impact mass spectrum of chlorobenzene :

- i.** $m/z = 112$ **ii.** $m/z = 113$ **iii.** $m/z = 114$

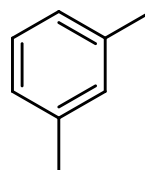
10. The number of types of hydrogen in each of the following:



i

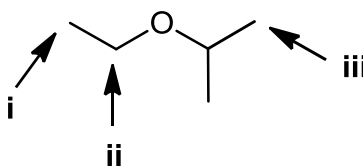


ii

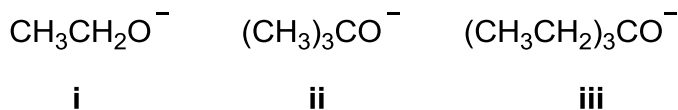


iii

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

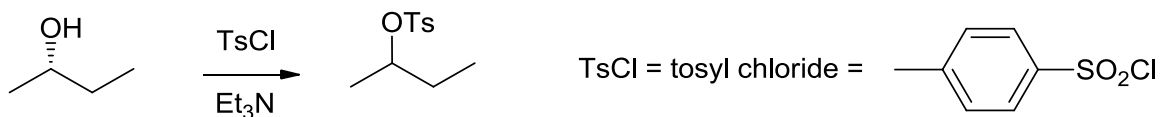


12. The relative yield of the pent-2-ene produced when 2-bromopentane is heated with each of the following :

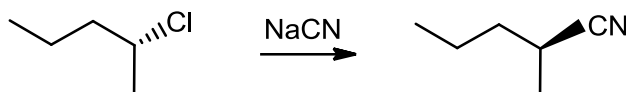


12% **PART 2: MOLECULAR PROPERTIES****ANSWER ALL SIX (6) OF THE QUESTIONS 13 TO 18.**In questions 13-17 choose the single option that provides the best answer.

13. In the following reaction, the stereochemistry of the product:



- A. is racemic because the reaction is SN1 and takes place with inversion
- B. is (R)- because the reaction is SN2 and takes place with inversion.
- C. is racemic because the reaction is SN1 and occurs via a carbocation intermediate.
- D. is (S)- because the reaction does not break the C-O bond.
- E. is irrelevant because the alcohol does not have a chirality center.
14. In the reaction shown below, the rate of reaction is markedly increased when the reaction is carried out in DMSO compared to methanol. This is because:

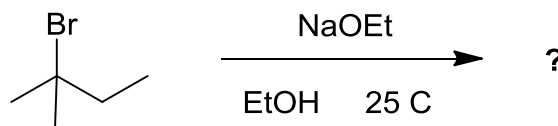


- A. DMSO is a polar solvent.
- B. DMSO is a polar protic solvent which stabilizes the carbocation intermediate
- C. DMSO is a polar aprotic solvent which stabilizes the carbocation intermediate
- D. DMSO enhances the leaving group ability of the chlorine.
- E. The cyanide ion is a better nucleophile in DMSO than MeOH.
15. Which of the following is formed when ethanal reacts with a strong base ?

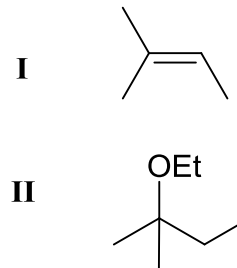


- A. **I** because the -ve charge can be resonance delocalized to the oxygen.
- B. **II** because the -ve charge can be resonance delocalized to the oxygen.
- C. **I** because the negative charge is further from the electronegative oxygen
- D. **II** because the negative charge is closer to the more electronegative oxygen
- E. **II** based on the pKa of ethanal.

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



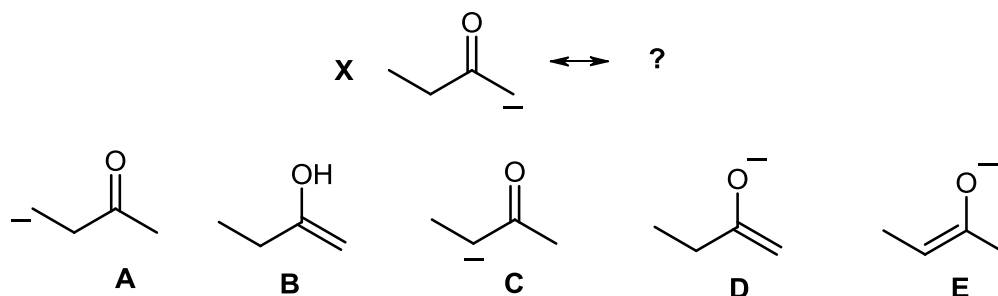
- A. **I** because EtO^- is a strong base.
 B. **II** because EtO^- is a strong nucleophile.
 C. **I** due to steric effects.
 D. **II** due to steric effects.
 E. **I** and **II** are formed in approximately equal amounts



17. In the ^{13}C -NMR of propan-2-one, the carbonyl carbon is observed at 206 ppm, while the carbonyl in ethyl ethanoate is at 171 ppm. Which of the following statements best explains this observation ?

- A. The methyl group in 2-propanone is an electron donating group which has a deshielding effect.
 B. The methyl group in 2-propanone is an electron donating group which has a shielding effect.
 C. The methyl group in 2-propanone is an electron withdrawing group which has a deshielding effect.
 D. The ethoxy group in ethyl ethanoate is an electron withdrawing group which has a deshielding effect.
 E. The ethoxy group in ethyl ethanoate is an electron donating group which has a shielding effect.

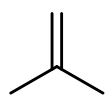
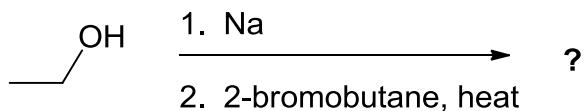
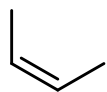
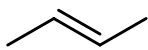
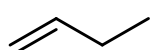
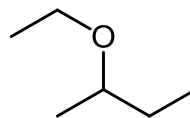
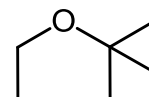
18. Which of the following is/are resonance structures of the structure **X** ? (**select all that apply**)



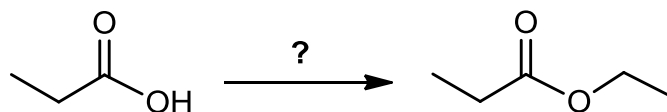
14% **PART 3: REACTIONS****ANSWER ANY SEVEN (7) OF QUESTIONS 19 TO 26.**

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.

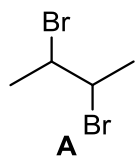
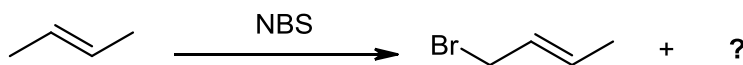
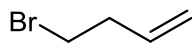
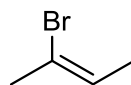
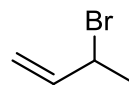
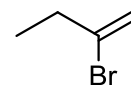
**A** NaOH / ethanol**B** H₂SO₄ / bromoethane**C** Na₂CO₃ / bromoethane**D** 1. Cl₂ / uv light

2. Chloroethane

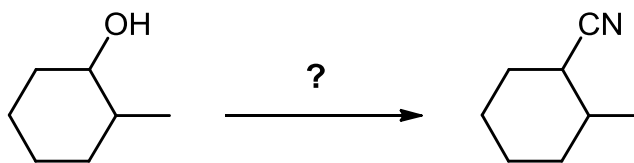
E 1. Cl₂ / uv light

2. Ethanol

21.

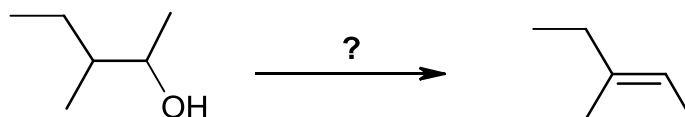
**A****B****C****D****E**

22.



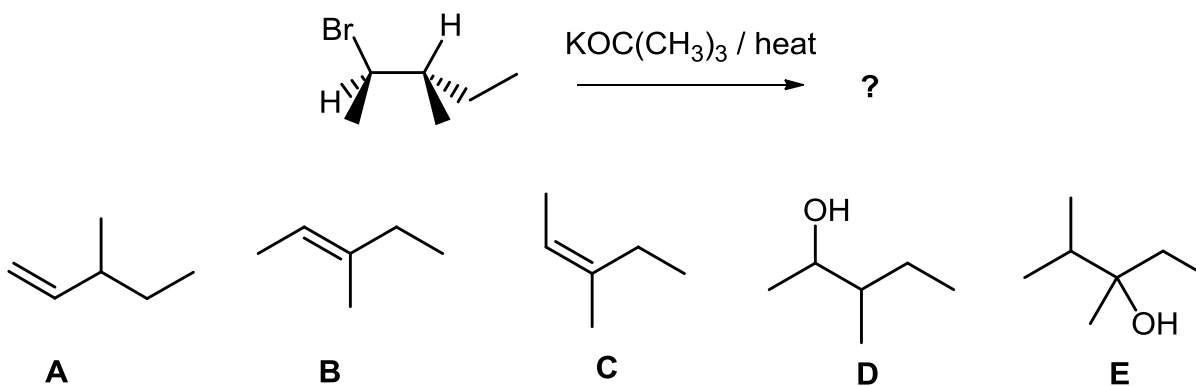
- A** 1. Thionyl chloride / Et₃N
 2. NaCN
- B** 1. Na
 2. NaCN
- C** 1. Br₂, uv light
 2. NaCN
- D** HCN
- E** 1. HBr
 2. NaCN

23.

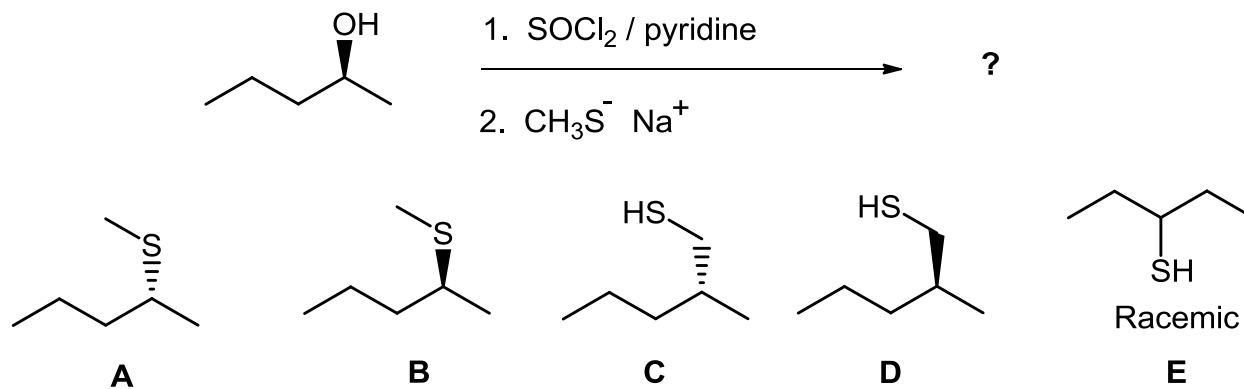


- A** KOH / EtOH / heat
- B** 1. H₂SO₄ / EtOH
 2. KOH / EtOH / heat
- C** KO^tBu / t-BuOH / heat
- D** 1. HBr
 2. Conc. H₂SO₄ / heat
- E** Conc. H₂SO₄ / heat

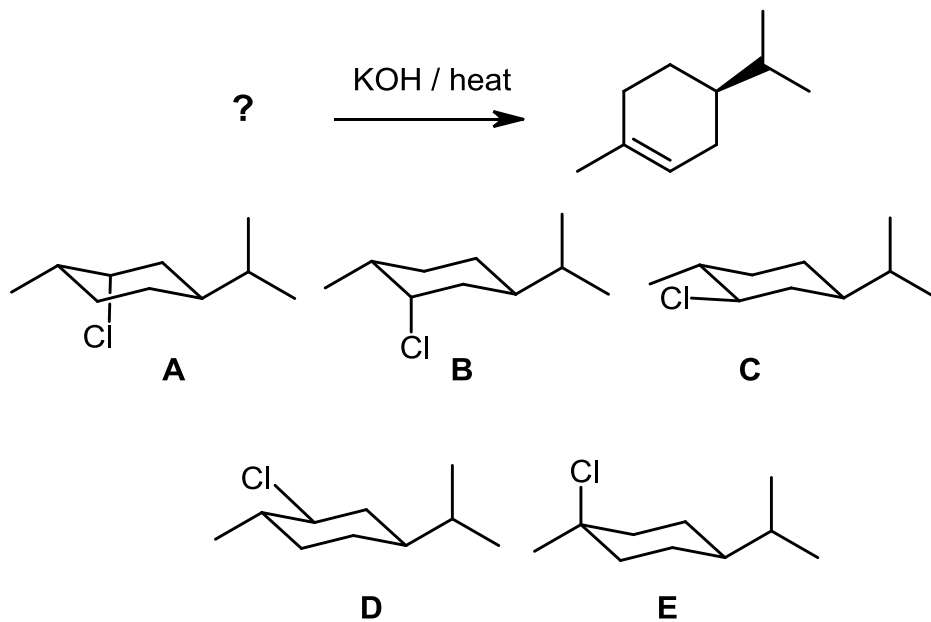
24.



25.



26.

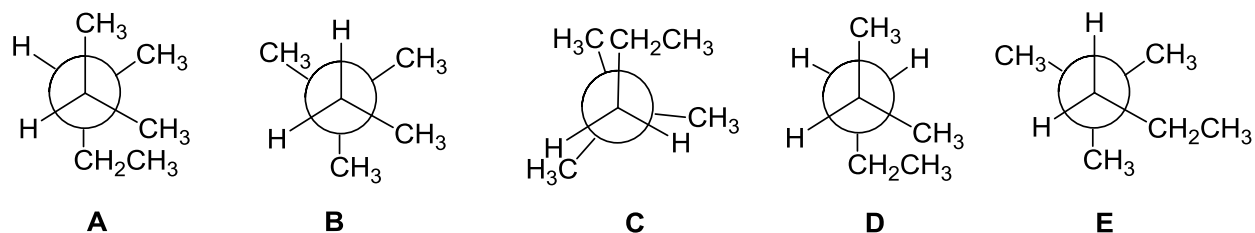


9% **PART 4: CONFORMATIONAL ANALYSIS**

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)

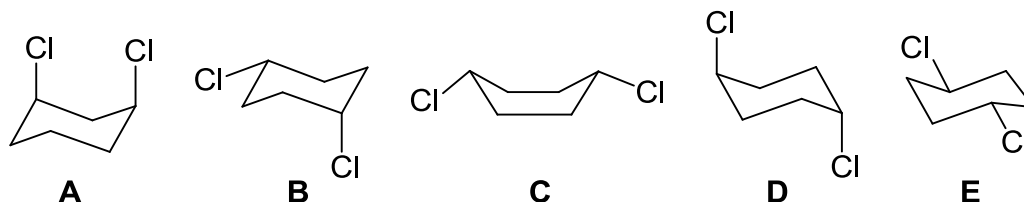


28. What is the **torsional** angle between the two methyl groups in the conformation of *trans*-1,2-dimethylcyclohexane shown below ?

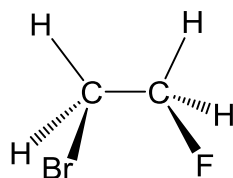


- | | | | |
|----------|------------|-----------|---------------|
| A | 0° | D | 109.5° |
| B | 60° | E | 120° |
| C | 90° | AB | 180° |

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

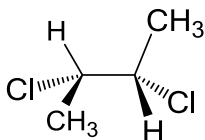
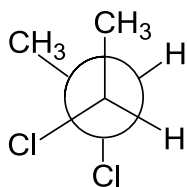


30. Which of the following terms **best** describes the relative position of the two halogen atoms in the conformation of the molecule shown below?



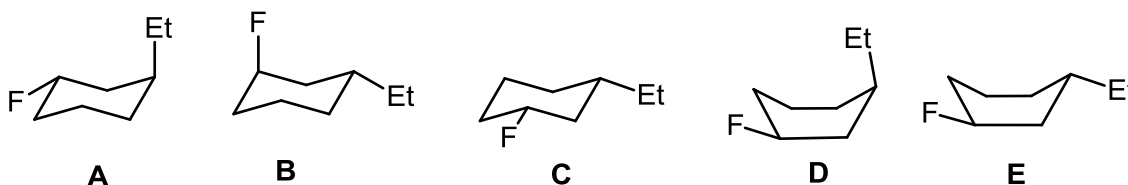
- | | |
|----------|-----------|
| A | eclipsed |
| B | staggered |
| C | anti |
| D | syn |
| E | gauche |

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

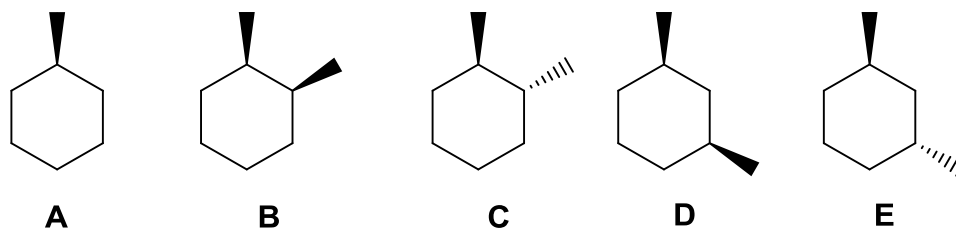


- A** constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB meso
AC not isomers

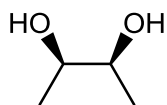
32. Which of the following represents the **most** abundant conformation of *trans*-1-ethyl-3-fluorocyclohexane at 25 °C?



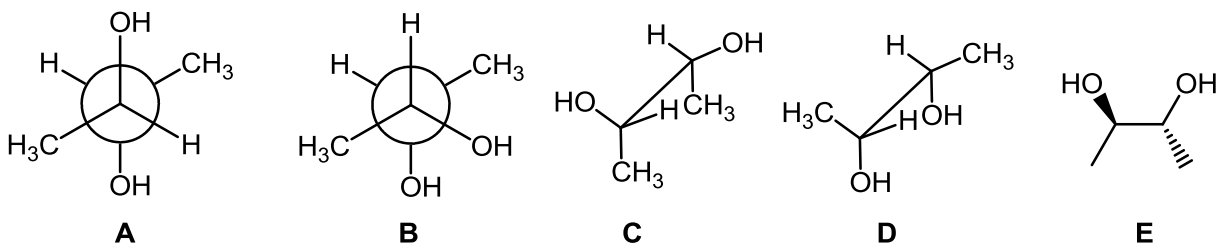
33. Which of the following structures have two chair conformations of equal energy



34. The structure of *meso*-butane-2,3-diol is depicted as follow, which of the following represents a conformation of *meso*-butane-2,3-diol?



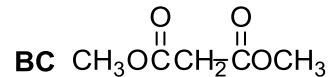
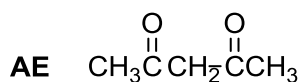
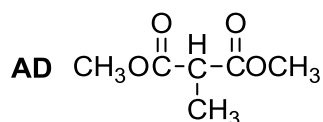
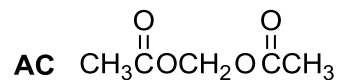
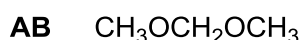
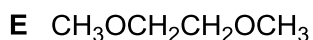
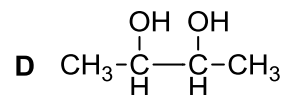
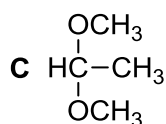
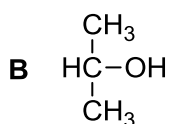
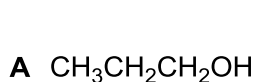
meso-butane-2,3-diol



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. $^1\text{H-NMR}$: δ/ppm 1.4 (d, 3H), 3.3 (q, 1H), 3.8 (s, 6H)
 $^{13}\text{C-NMR}$: δ/ppm 15, 41, 52, 170
 IR: 1737, 1200 cm^{-1}
36. $^1\text{H-NMR}$: δ/ppm 3.3 (s, 3H), 3.7 (s, 2H)
 $^{13}\text{C-NMR}$: δ/ppm 59, 72
37. $^1\text{H-NMR}$: δ/ppm 2.1 (s, 3H), 3.6 (s, 1H)
 $^{13}\text{C-NMR}$: δ/ppm 30, 58, 202
 IR: 1713 cm^{-1}
38. $^1\text{H-NMR}$: δ/ppm 1.3 (d, 3H), 3.3 (s, 6H), 4.5 (q, 1H)
 $^{13}\text{C-NMR}$: δ/ppm 19, 52, 102
39. $^1\text{H-NMR}$: δ/ppm 1.2 (d, 6H), 1.8 (broad s, 1H, D_2O exchange), 3.7 (septet, 1H)
 $^{13}\text{C-NMR}$: δ/ppm 25, 64
 IR: 3350 cm^{-1}
40. $^1\text{H-NMR}$: δ/ppm 0.9 (t, 3H), 1.6 (sextet, 2H), 2.3 (broad s, 1H, D_2O exchange), 3.6 (t, 2H)
 $^{13}\text{C-NMR}$: δ/ppm 10, 26, 64
 IR: 3340 cm^{-1}



8% PART 6: SYNTHESIS

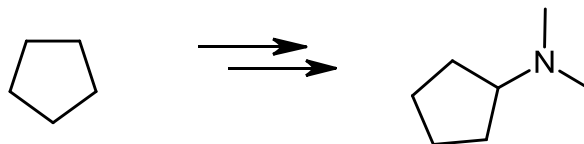
DESIGN TWO(2) EFFICIENT SYNTHESSES, ONE from PART A and ONE from PART B of the following target molecules from the indicated starting material. In addition, you are allowed to use **any hydrocarbon with three or fewer carbon atoms**, any solvents or inorganic reagents, and any organic reagents that do 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 EXAM BOOKLET PROVIDED.

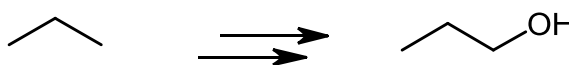
DO NOT SHOW MECHANISMS.

PART A

either



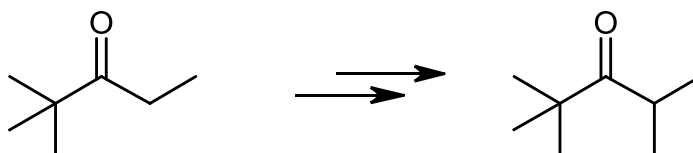
or

**PART B**

either



or



10% PART 7: MECHANISMS

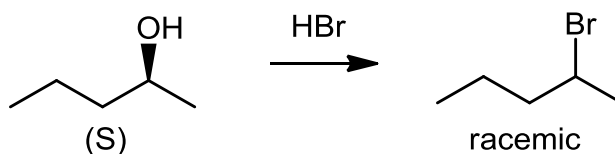
WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED

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

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.

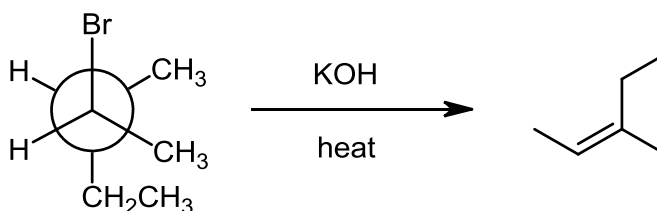
(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:

i.



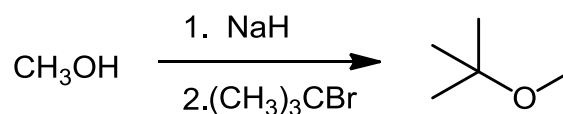
OR

ii.



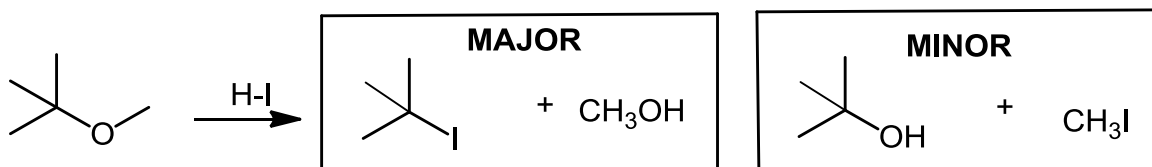
(5%) PART B: Use a curly arrow mechanism to explain ONE of the following:

- i. A potential synthesis of t-butyl methyl ether is shown below. Draw the curly arrow mechanism for this proposed synthesis. However, this reaction is not very efficient. What is the major organic by-product and show the curly arrow mechanism to account for its formation:



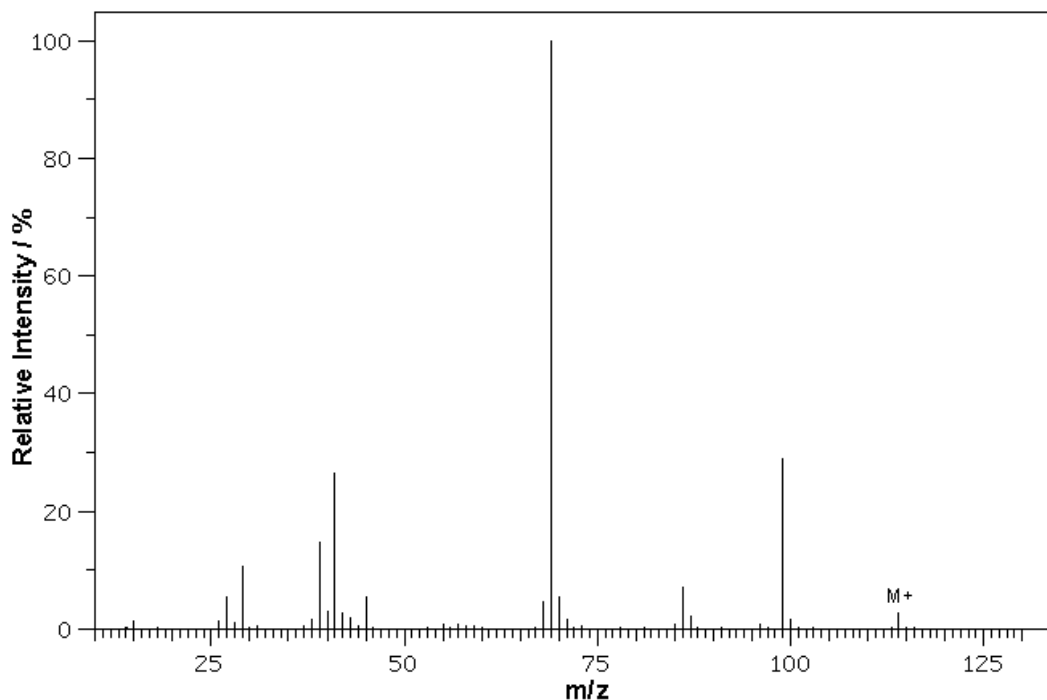
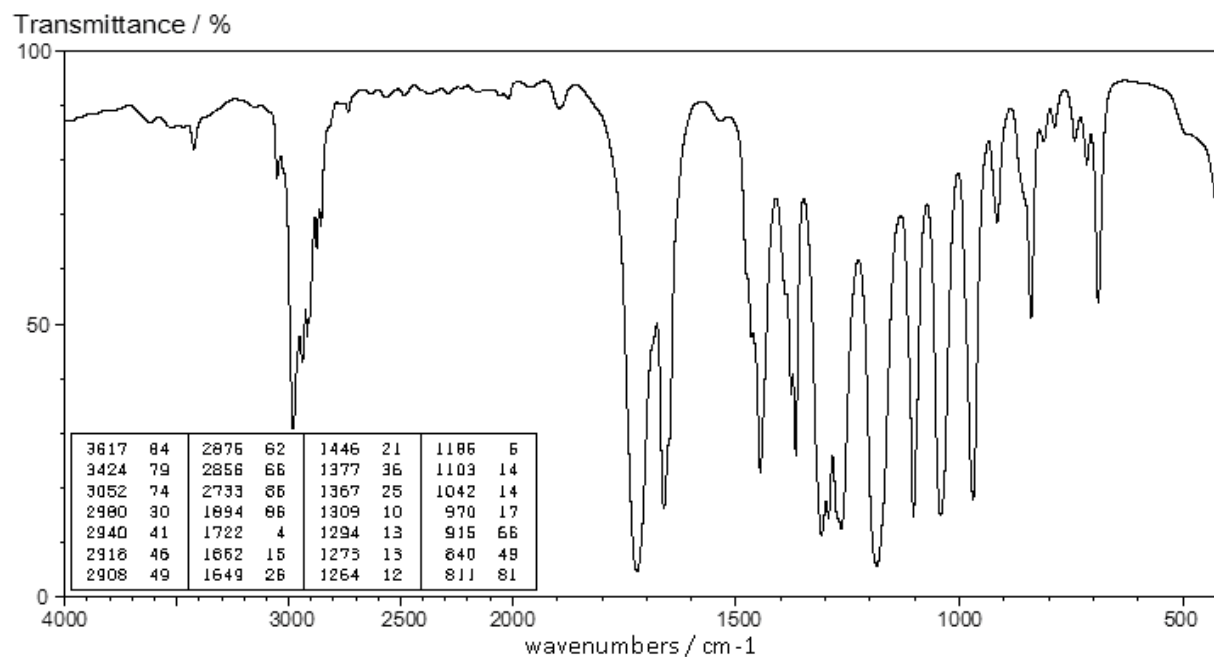
OR

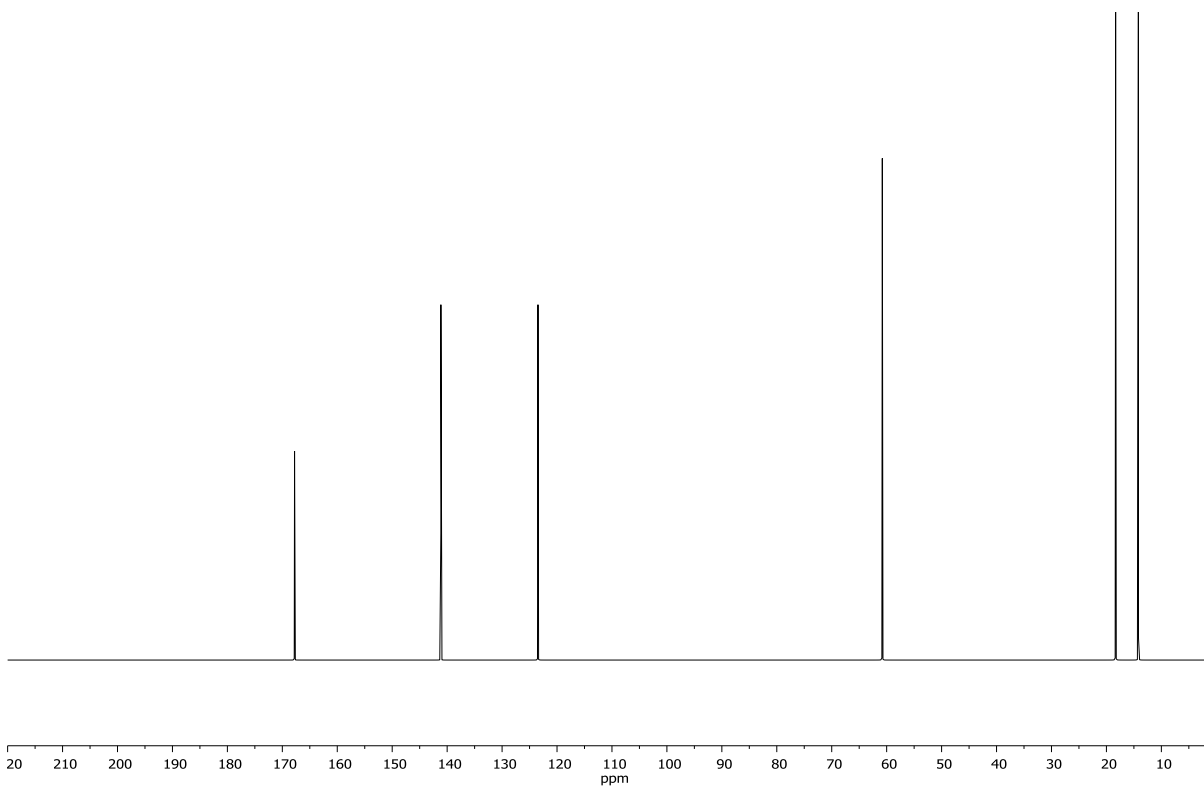
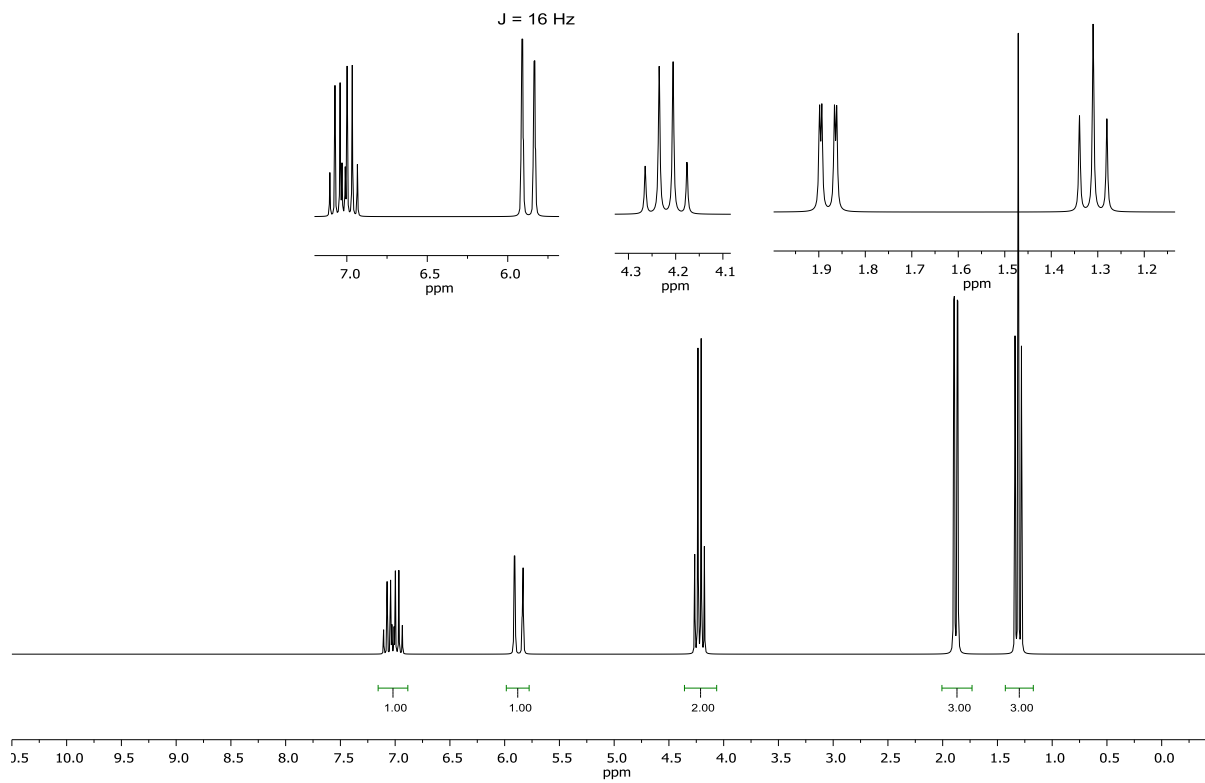
- ii. The reaction of hydrogen iodide and t-butyl methyl ether results in t-butyl iodide and methanol as the major products. Provide a clear and detailed curly arrow mechanism to account for this observation explanation.



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: **^1H -NMR:**

10% PART 9: STRUCTURE DETERMINATION**WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED**

A hydrocarbon **A**, C_6H_{14} , was heated with bromine to give **B**, $C_6H_{13}Br$, as the major product. **B** was observed to react at a moderate rate with either aqueous ethanolic silver nitrate or with sodium iodide in acetone. When **B** was reacted with either KOH / EtOH / heat or KOtBu / DMSO / heat it gave the same product, **C**, C_6H_{12} (IR: 1650cm^{-1}).

When **B** was reacted with cold aq. NaOH solution the major product was **D**, $C_6H_{14}O$ (IR : 3500cm^{-1} , broad).

When **D** was reacted with PBr_3 / Et_3N , **B** was obtained but when **D** was treated with HBr the reaction gave **E** as the major product. **E** was observed to react rapidly with aqueous ethanolic silver nitrate but very slowly (if at all) with sodium iodide in acetone. **E** was found to be a constitutional isomer of **B**. **E** could also be obtained on reaction of 2,3-dimethylbutane with bromine / uv light.

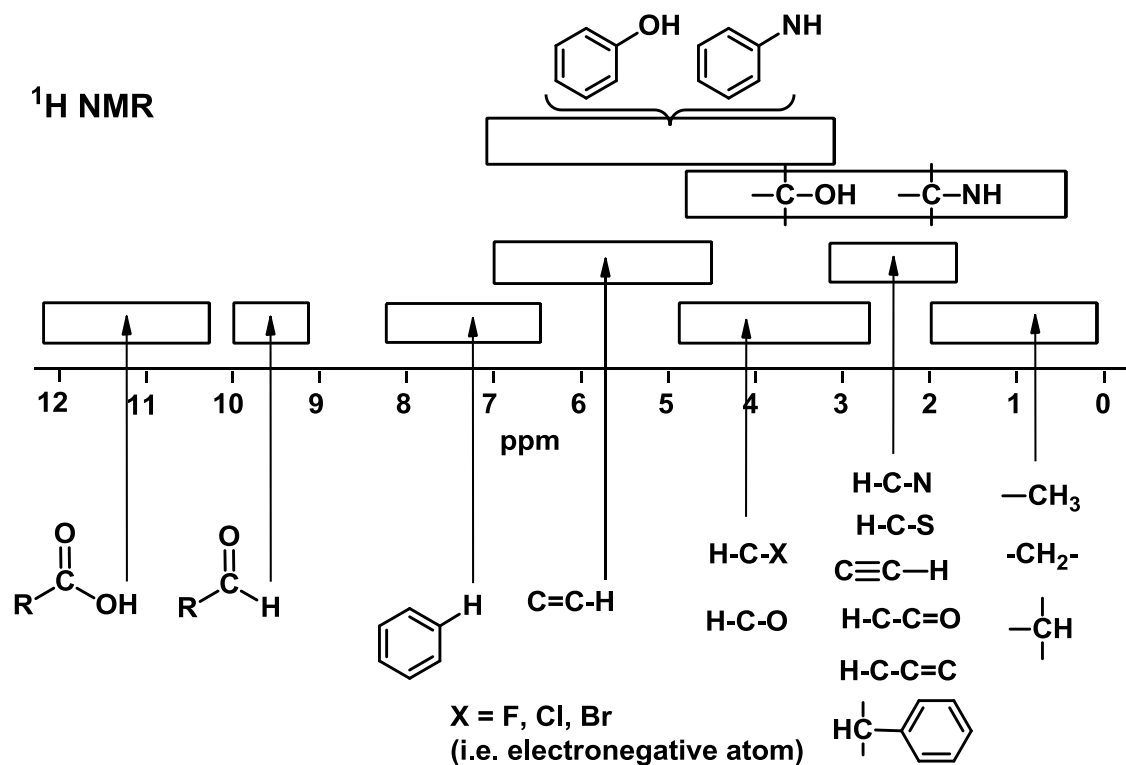
When **D** was heated with conc. H_2SO_4 , the major product was **F**, a constitutional isomer of **C**. **F** was also formed as the major product of the reaction of **E** with hot ethanolic KOH.

In a ^{13}C -NMR spectroscopic analysis of the compounds, **A** - **E** each had 4 peaks, while **F** had only 2 peaks.

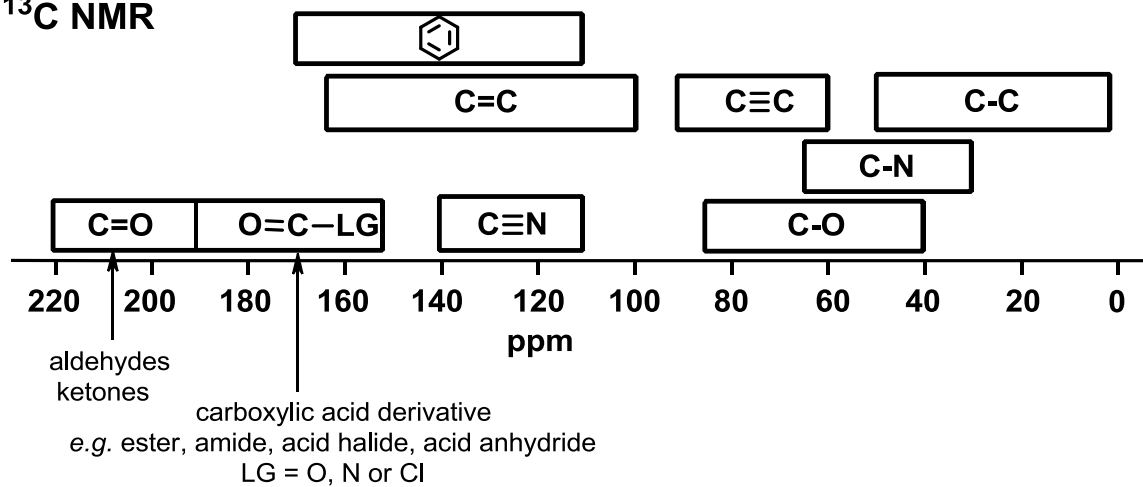
Of the compounds **A** - **F**, only **B** and **D** have chirality centers.

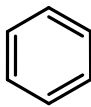
- Identify A-F (only structures are needed)
- Draw a structure showing the stereochemistry and give the complete name of one enantiomer of B.

**** THE END ****

SPECTROSCOPIC TABLES**¹H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	R = methyl	methylene	methyne	other
	-CH ₃ 0.9	-CH ₂ - 1.4	-CH 1.5	sp ³ C-OH 1-5
	1.6	2.3	2.6	sp ³ C-NH 1-3
	2.1	2.4	2.5	C≡CH 2.5
	2.2	2.5	2.9	
	2.3	2.7	3.0	H-benzene ring 6.5-8
R-Br	2.7	3.3	4.1	R-C(=O)H 9-10
R-Cl	3.1	3.4	4.1	R-C(=O)OH 9-12
R-O-	3.3	3.4	3.7	

^{13}C NMR **^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

—CH_3 0-30	>CH_2 10-50	$\text{—}\overset{ }{\text{C}}\text{—H}$ 25-60	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—O—}$ 155-180
$\text{—C}\equiv\text{C—}$ 65-90	>C=C< 80-145	$\text{—}\overset{ }{\text{C}}\text{—Br}$ 10-40	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—OH}$ 160-185
 110-170	$\text{—}\overset{ }{\text{C}}\text{—Cl}$ 20-50	$\text{—}\overset{ }{\text{C}}\text{—OH}$ 45-75	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ 190-220
	$\text{—}\overset{ }{\text{C}}\text{—N}$ 30-65	$\text{—C}\equiv\text{N}$ 110-140	

INFRA-RED GROUP ABSORPTION FREQUENCIES

		<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>	
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	
			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	
			1400-1000	7.14-10.0	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											18						
1A											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
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)

Actinides **