THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

March 1st , 2000 Time: 2 Hours*

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER AND SECTION NUMBER (01 for MWF lectures and 02 for TR lectures) **ON YOUR COMPUTER ANSWER SHEET** and on the **WRITTEN ANSWER PAGES** provided.

Read the instructions carefully. The exam consists of Parts 1 - 9, each of which should be attempted. Note that some Parts provide you with a choice of questions. Parts 1 - 6 will be computer graded, and Parts 7, 8 and 9 are to be answered **ON THE PAGES PROVIDED** in this examination booklet. A periodic table with atomic numbers and atomic weights and spectroscopic data tables are appended to the exam.

Parts 1 - 6 consist of a series of multiple choice questions numbered 1 - 46 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. 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***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.

* Due to our participation in a research study you will be allowed **3 hours**

PART 1: RELATIVE PROPERTIES

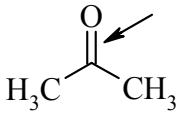
12% **ANSWER ANY SIX (6) OF QUESTIONS 1-8**.

Arrange the items in the questions in this section in **DECREASING ORDER** (greatest first) with respect to the indicated property.

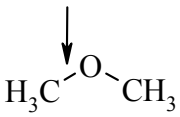
Use the following code to indicate your answers.

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

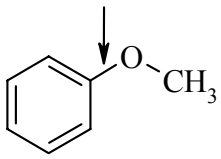
1. The IR stretching frequencies in cm^{-1} of the following CO bonds:



(i)

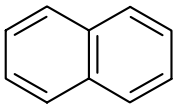


(ii)

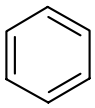


(iii)

2. The resonance energies of each of the following:



(i)



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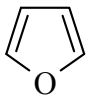
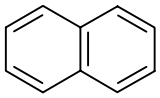


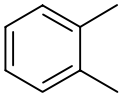
(iii)

3. The number of signals seen in the broadband decoupled 13C nmr of the following:

(i)



(ii)



(iii)

4. The number of peaks in the signal for the **H** in the H nmr spectra of the following:

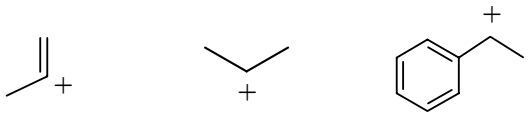
$C\mathbf{H}_3CH_3$ $C\mathbf{H}_3CH_2CH_2CH_3$ $(C\mathbf{H}_3)_3CH$

(i) (ii) (iii)

Use the following code to indicate your answers.

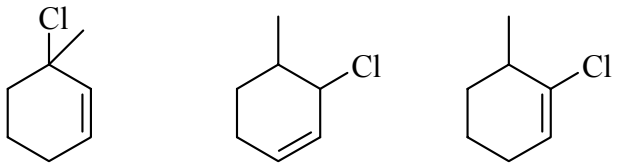
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

5. The relative stability of the following carbocations:



(i) (ii) (iii)

6. The relative yield of the following products from the reaction of HCl with 1-methyl-1,3-cyclohexadiene at 50 ^{o}C:



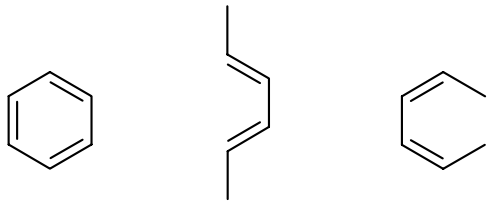
(i) (ii) (iii)

7. The chemical shift (δ in ppm) for the methyl groups in each of the following:

$(CH_3)_4Si$ $(CH_3)_2O$ $(CH_3)_2CO$

(i) (ii) (iii)

8. The relative reactivity towards 1-buten-3-one of the following:



(i) (ii) (iii)

PART 2: LABORATORY

9% **ANSWER ANY NINE (9) OF THE QUESTIONS 9-18.**

For each of the questions 9-18, decide whether the whole statement is true or false. If it is true then blacken **A**. If it is false then blacken **B**.

9. Sucrose is a disaccharide of glucose and galactose.

10. The rate law for a first order reaction is given by rate = k [R-X]

11. Steam distillation is described by Raoult's Law.

12. Anhydrous sodium sulphate is an example of a drying agent.

13. Casein is a protein.

14. Hydrolysis of ester bonds in proteins gives amino acids.

15. Lactose is an example of a carbohydrate.

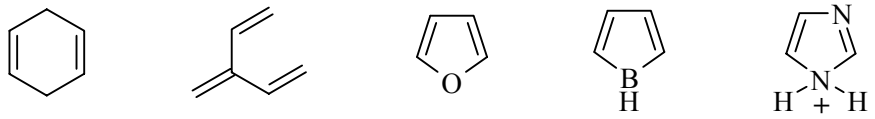
16. When compared to soaps, detergents less readily precipitate when sulphuric acid is added because they are weaker bases.

17. Chemically, saponification is the alkaline hydrolysis of an ester.

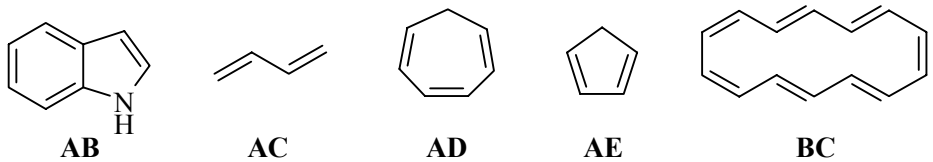
18. On hydrolysis, carboxylic esters give carboxylic acids and alcohols.

PART 3: AROMATICITY AND RESONANCE

12% **ANSWER ANY SIX (6) of the questions 19-25.**



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



AB **AC** **AD** **AE** **BC**

For each of the questions **19-25** select a compound from the list above that is **best** described as:

19. A 6π-electron, aromatic system.

20. An aromatic system because n=3 in the Huckel 4n+2 rule.

21. A non-aromatic, conjugated 6π-electron system

22. A non-conjugated hydrocarbon.

23. Non-aromatic as drawn but has a neutral aromatic conjugate base.

24. Non-aromatic as drawn, but can form an aromatic carbanion when treated with a base.

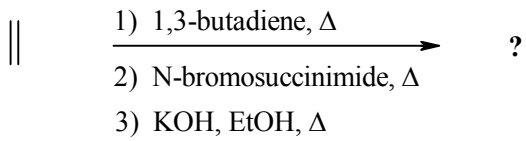
25. Aromatic as drawn and also has an aromatic conjugate acid.

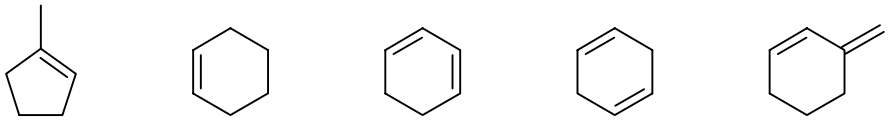
PART 4: REACTIONS

12% **ANSWER ANY SIX (6) OF QUESTIONS 26-32.**

For each of questions **26-32** select either the major product or the starting material required in order to complete the reaction schemes.

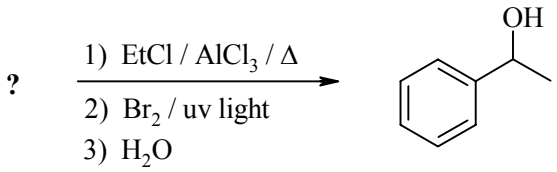
26.

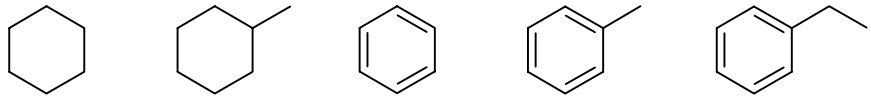




A **B** **C** **D** **E**

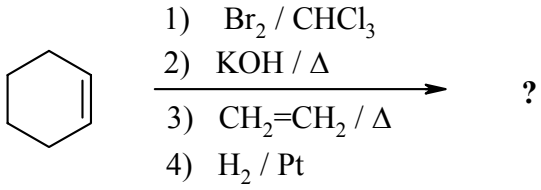
27.

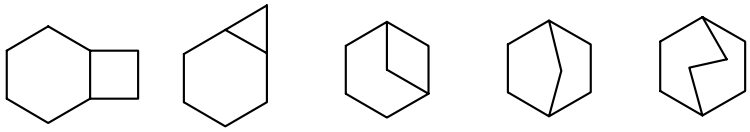




A **B** **C** **D** **E**

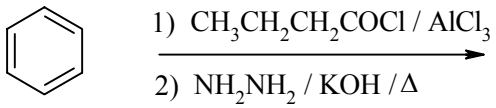
28.

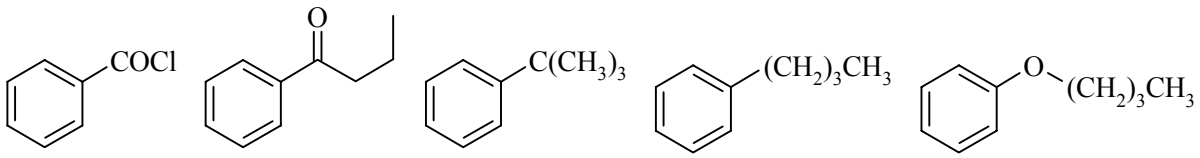




A **B** **C** **D** **E**

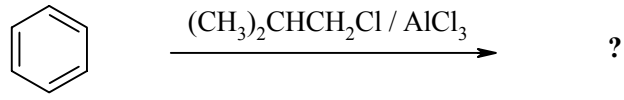
29.

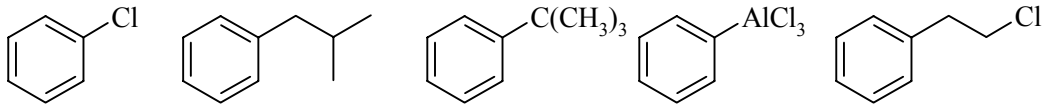




A **B** **C** **D** **E**

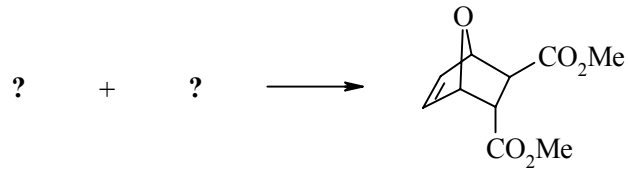
30.



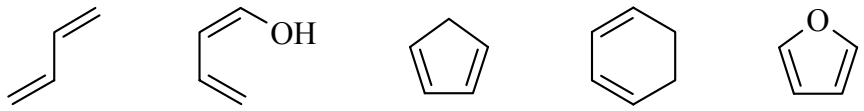


A **B** **C** **D** **E**

The last two questions both apply to the following reaction scheme:

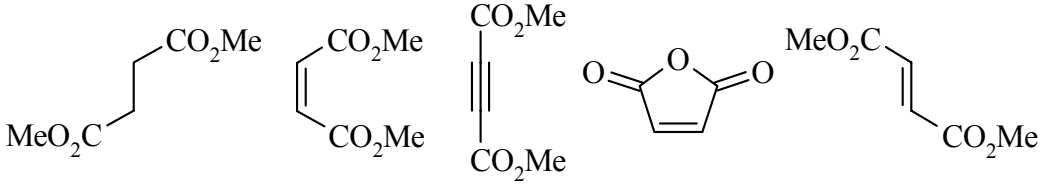


31.



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

32.

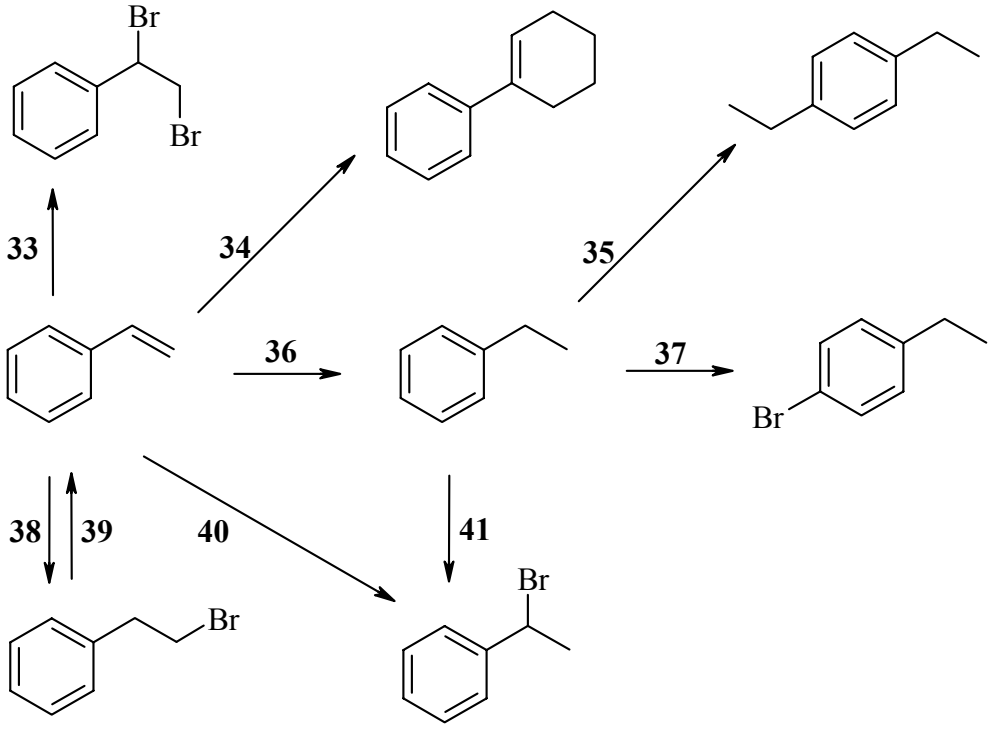


A. **B.** **C.** **D.** **E.**

PART 5: REAGENTS FOR REACTIONS

9% **ANSWER ANY SIX (6) OF QUESTIONS 33-41**.

For each of questions **33-41**, choose from the list provided the best reagent combination to produce the product shown:



Reagents

A. Br_2
B. NaBr / acetone
C. Br_2 / uv light
D. Br_2 / $FeBr_3$
E. HBr / dark
AB. HBr / light
AB. EtBr
AC. EtBr / $AlCl_3$
AD. KOH / EtOH / Δ
AE. $CH_2CHCHCH_2$ / Δ
BC. H_2SO_4
BD. H_2 /Pd

PART 6: SPECTROSCOPY

10% **ANSWER ANY FOUR (4) OF QUESTIONS 42-46**

Listed below are the H-NMR and ^{13}C-NMR chemical shift data (in ppm) for 5 isomers of $C_9H_{10}O_2$. For the ^{13}C-NMR data, the multiplicity of the off-resonance decoupled signals, and for the H-NMR data, the multiplicity and integrals, are given in brackets to the right of each chemical shift. Standard abbreviations are used.

In each question, select the structure from the list, that matches the chemical shift data.

42. 1.4 (3H, t), 4.4 (2H, q), 7.4-7.8 (5H, m)
166 (s), 132 (d), 130 (s), 129 (d), 128 (d), 61 (t), 14 (q)

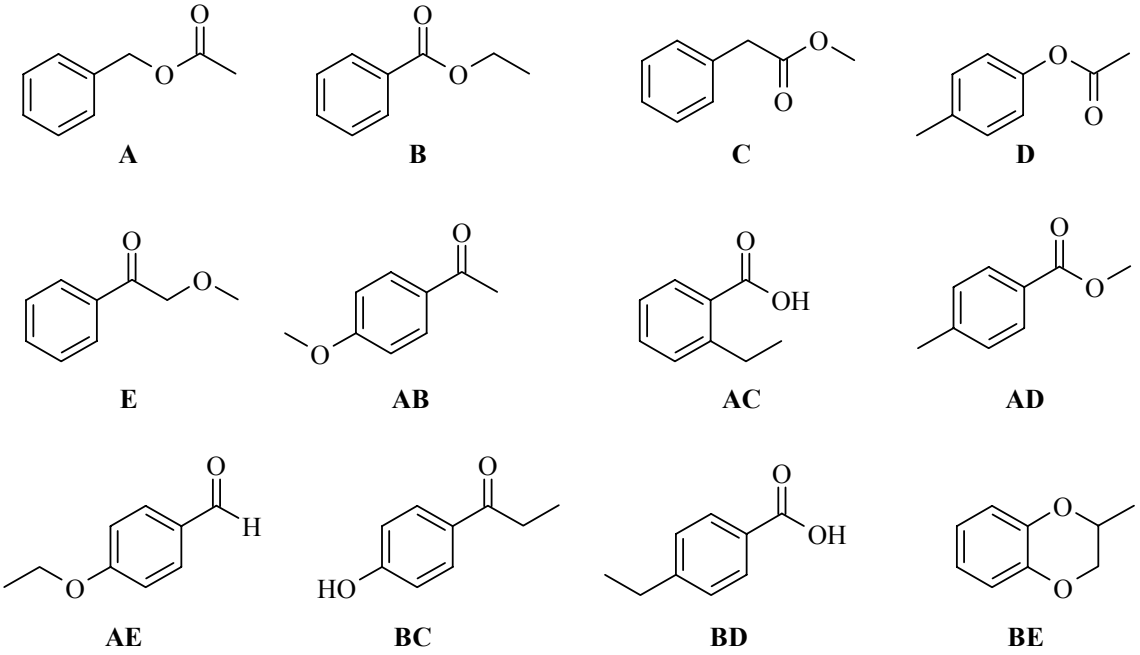
43. 2.0 (3H, s), 5.1 (2H, s), 7.3 (5H, m)
170 (s), 136 (s), 129 (d), 128 (d), 127 (d), 66 (t), 21 (q)

44. 2.25 (3H, s), 2.3 (3H, s), 6.9 (2H, d), 7.1 (2H, d)
170 (s), 149 (s), 135 (s), 130 (d), 121 (d), 21 (q), 20 (q)

45. 3.5 (3H, s), 4.7 (2H, s), 7.4-7.9 (5H, m)
196 (s), 135 (s), 133 (d), 129 (d), 128 (d), 75 (t), 59 (q)

46. 1.3 (3H, t), 2.7 (2H, q), 7.3 (2H, d), 8.0 (2H, d), 12.1 (1H, brd s)
172 (s), 151 (s), 130 (d), 128 (d), 127 (s), 29 (t), 15 (q)

List of possible structures

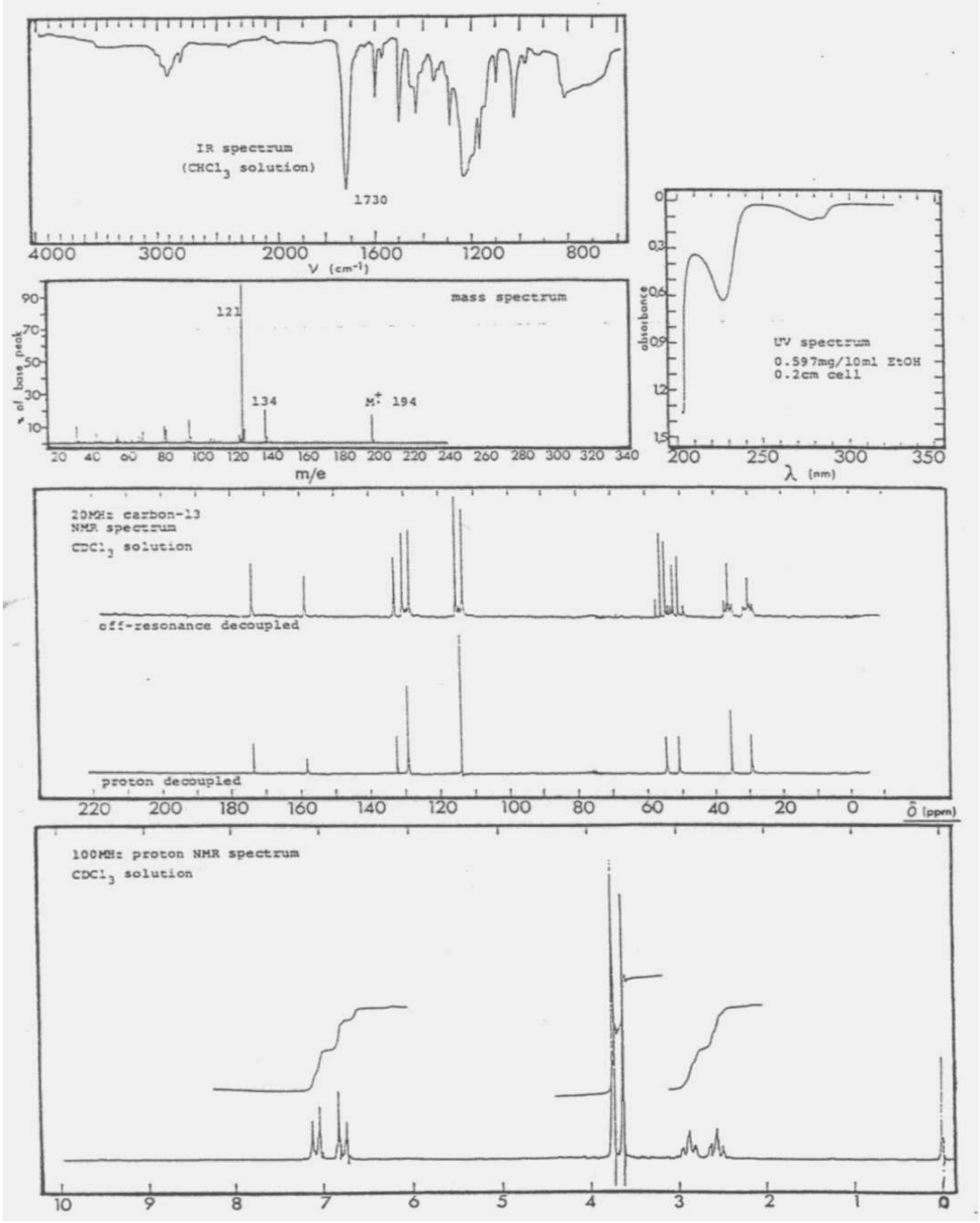


PART 6: SPECTROSCOPY

12% **WRITE YOUR ANSWERS ON THE PAGE PROVIDED**.

Show your workings as PARTIAL marks will be given.

The combustion analysis of an unknown molecule is 68.04 % C and 7.22 % H (by weight). From this data and the spectral data provided below, identify the structure of the molecule.



PART 7 : STRUCTURE DETERMINATION

12% **WRITE YOUR ANSWER ON PAGE PROVIDED**

Compound **A**, C_6H_{10}, showed 3 peaks in the broadband decoupled ^{13}C nmr spectrum. When **A** was heated in a sealed tube with **B**, C_3H_6 (also had 3 peaks in the ^{13}C nmr), product **C**, C_9H_{16} was produced as a pair of enantiomers. **C** was then reacted with N-bromosuccinimide to form isomers, **D** and **E**, both $C_9H_{15}Br$ and both as pairs of diastereomers.

When **D** was heated in ethanolic KOH, **F**, C_9H_{14} was produced as a single compound. In contrast, when **E** was heated in ethanolic KOH, **G**, an isomer of **F**, was produced as a pair of enantiomers.

Repeating the cycle of reactions using N-bromosuccinimide then ethanolic / KOH / heat with either **F** or **G** gave a single product, **H**, C_9H_{12}, whose broadband decoupled ^{13}C-nmr showed the following peaks: 136.2, 135.1, 133.3, 130.5, 129.6, 126.5, 20.9, 19.6 and 19.2 ppm.

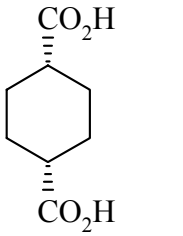
Identify **A - H**.

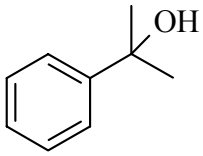
PART 8: SYNTHESIS

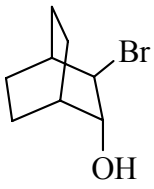
12% Using any of the starting materials shown, design efficient syntheses of any **THREE (3)** of the following molecules.

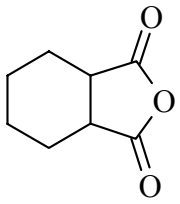
WRITE YOUR ANSWERS ON THE PAGE PROVIDED.

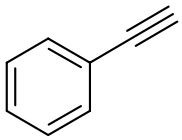
DO NOT SHOW MECHANISMS.

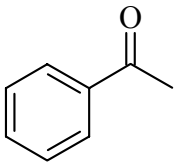


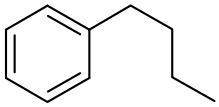


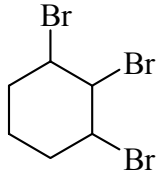




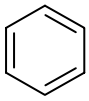


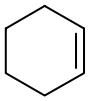






Allowed Starting Materials:





solvents
inorganic reagents
Any compounds with 4 or less C atoms