THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 20th, 2006 Time: 3 Hours

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** ON THE **COMPUTER ANSWER SHEET** AND THE **BOOKLET** FOR THE WRITTEN ANSWER QUESTIONS.

READ THE INSTRUCTIONS CAREFULLY

The examination consists of Parts 1 - 10, each of which should be attempted. Note that some Parts provide you with a choice of questions, *e.g*. answer 5 out of 6. These will be graded in order the answers appear until the required number have been completed, ***regardless*** of whether they are right or wrong.

Parts 1 - 7 will be computer graded, and only Parts 8, 9 and 10 are to be answered in the booklet. Parts 1 - 7 consist of a series of multiple choice questions numbered 1 - 58 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***.

A periodic table with atomic numbers and atomic weights and tables of spectroscopic data are provided at the end of the examination paper.

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

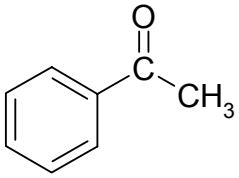
12% PART 1: RELATIVE PROPERTIES

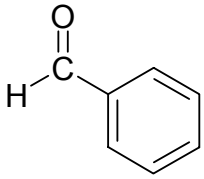
ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.

Arrange the items in questions **1-10** 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 reactivity towards lithium aluminum hydride in tetrahydrofuran (THF) of each of the following:


i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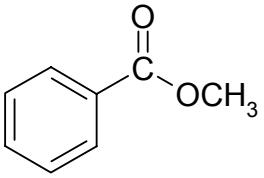
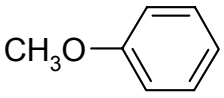
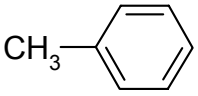

iii

2. The relative reactivity towards $(CH_3)_3CCl$ / $AlCl_3$ of each of the following:


i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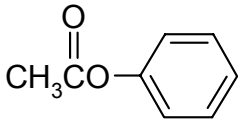
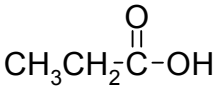

iii

3. The relative acidity of the most acidic hydrogen in each of the following: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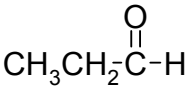
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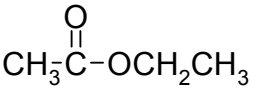
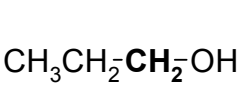

iii

4. The relative oxidation state of the **C** atom in each of the following: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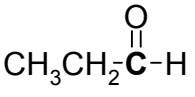
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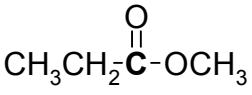
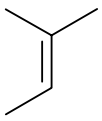

iii

5. The relative reactivity towards HBr (dark, N_2) of each of the following :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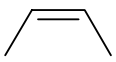
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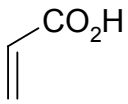
iii

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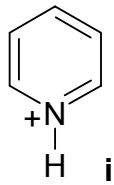
Value

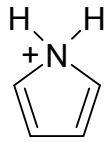
Use the following code to indicate your answers:

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

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



i



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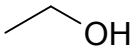
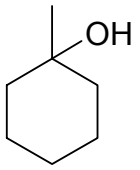
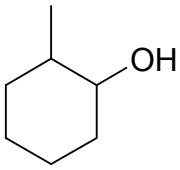


iii

7. The relative yields of the following products from the reaction of (1) BH_3 then (2) aq. NaOH / H_2O_2 with 1-methylcyclohexene :



i



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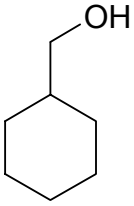
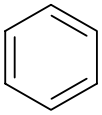


iii

8. The resonance energies of each of the following:

i



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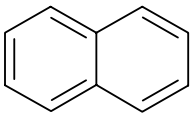


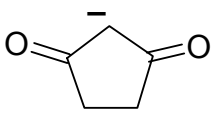
iii

9. The relative reactivity of the following towards benzaldehyde in dry THF:

CH_3MgBr CH_3Li CH_3OH

i **ii** **iii**

10. The relative basicity of the following carbanions :



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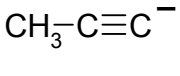

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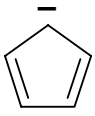

iii

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9% **PART 2: LABORATORY**

ANSWER ANY SIX (6) OF THE QUESTIONS 11-18.

The questions **11-13**, refer to the answers below:

A Water
B 5% $NaHCO_3$ (aq.)
C 5% NaOH (aq.)
D 5% HCl (aq.)
E None of the above

11. Select **all** solvents that would completely dissolve acetophenone.

12. Select **all** solvents that would completely dissolve aniline.

13. Select **all** solvents that would completely dissolve phenol.

The questions **14-18**, refer to the following functional groups:

A	Alcohol	**AB**	Amine
B	Aldehyde	**AC**	Carboxylic Acid
C	Alkane	**AD**	Ester
D	Alkene	**AE**	Ketone
E	Amide	**BC**	Phenol

14. A functional group that gives a positive result with Tollen's test.

15. A functional group that gives a positive iodoform test.

16. A functional group that gives a positive ferric chloride test.

17. A functional group that would react with phenyl isocyanate to yield a phenyl urethane.

18. A functional group that would readily react with hydroxylamine to yield an oxime.

CONTINUED -->

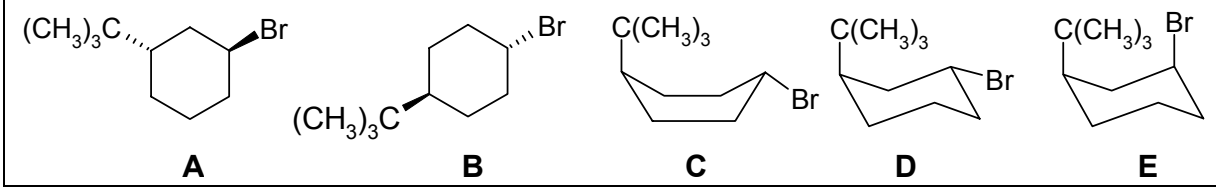
Value

10 % **PART 3: STRUCTURE AND PROPERTIES**

ANSWER ANY TEN (10) OF THE QUESTIONS 19-29.

In some cases more than one answer may be correct and all compounds that apply must be selected for full credit.

SET 1:



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

Answer questions **19-22** by selecting the compounds from **SET 1** above.

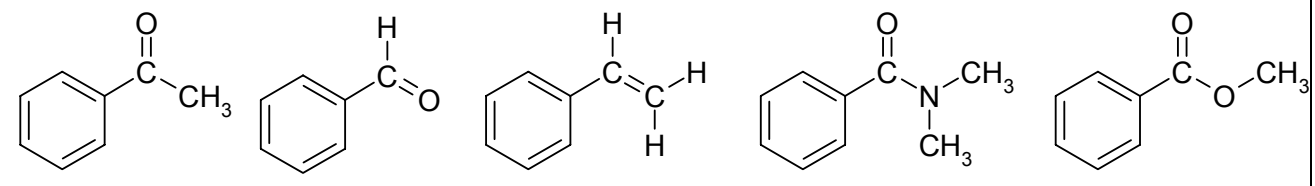
19. Which compound (in its most stable conformation) would react the fastest with KO^tBu ?

20. Select two compounds that represent a pair of enantiomers

21. Select two compounds that are conformational isomers

22. Select a compound with an (S,S) configuration

SET 2:



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

Answer questions **23-26** by selecting the compounds from **SET 2** above.

23. Which compound most readily forms an acetal when reacted with ethylene glycol in the presence of a catalytic amount of an acid ?

24. Which compound(s) has (have) enolisable hydrogens ?

25. Which compound is **not** readily reduced by $LiAlH_4$?

26. Which compound would react with a Schiffs reagent to give a magenta colour ?

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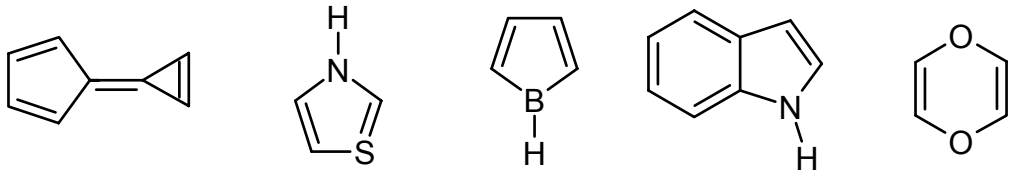
SET 3



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

Answer questions **27-29** by selecting the compounds from **SET 3** above.

27. Which structure(s) is (are) aromatic as drawn ?

28. Which aromatic structure(s) has (have) an aromatic conjugate acid ?

29. Which structure(s) is (are) non-aromatic as drawn, but has (have) an important aromatic resonance structure ?

CONTINUED -->

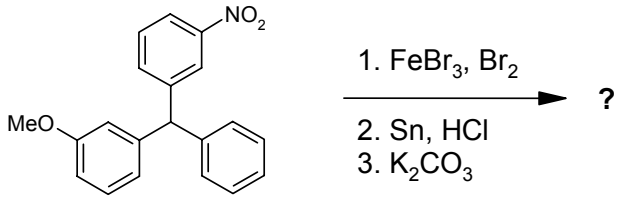
Value

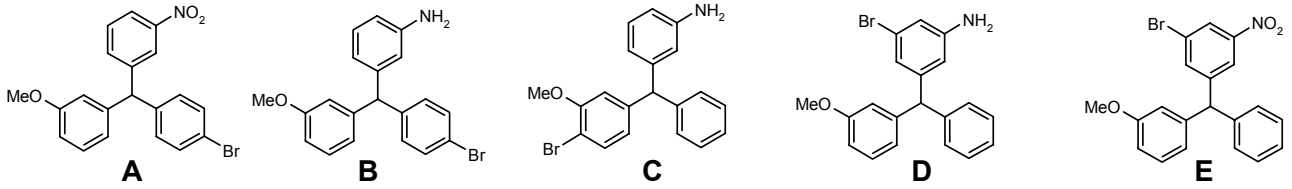
9% **PART 4: PRODUCTS OF SYNTHESIS**

ANSWER ANY SIX (6) OF QUESTIONS 30-36.

For each of the questions **30-36** identify the **major product** obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

30.





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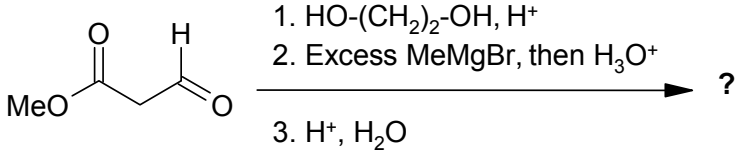

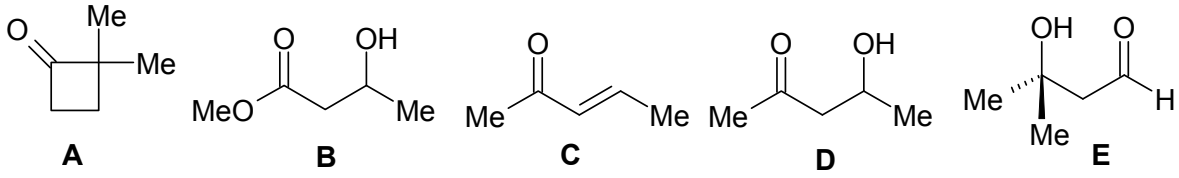

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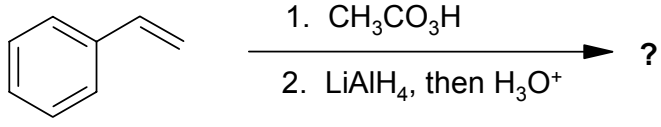

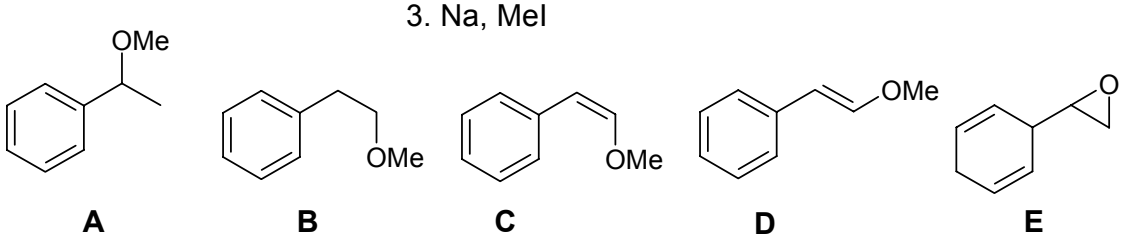

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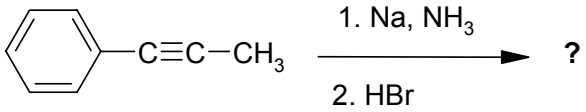

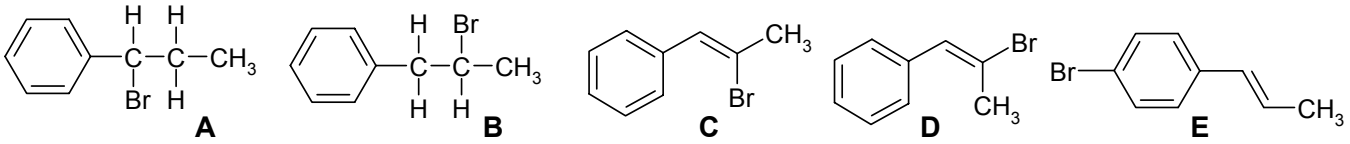

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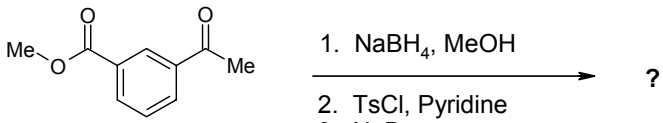

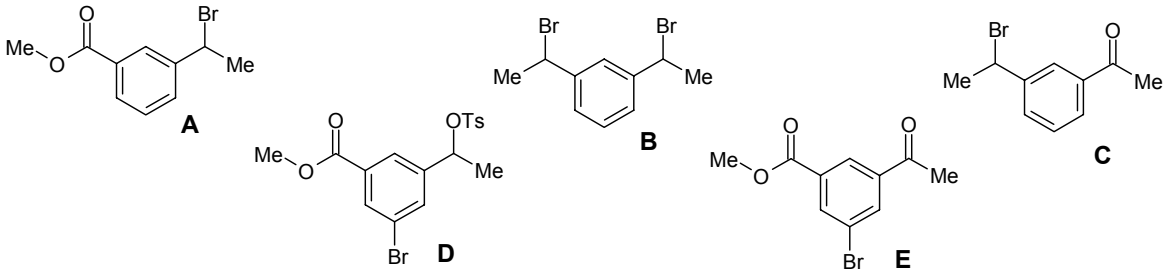

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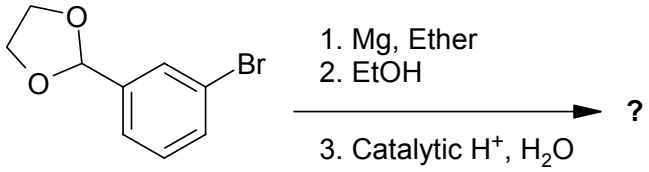

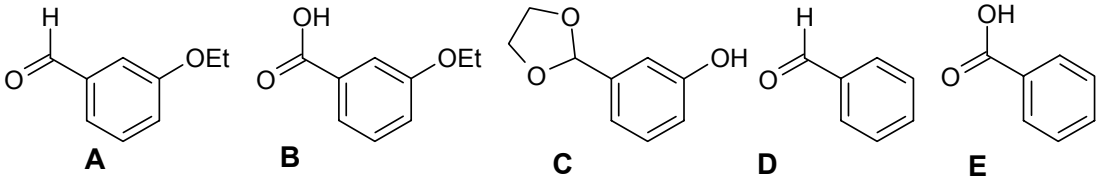

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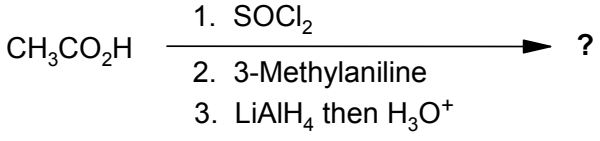

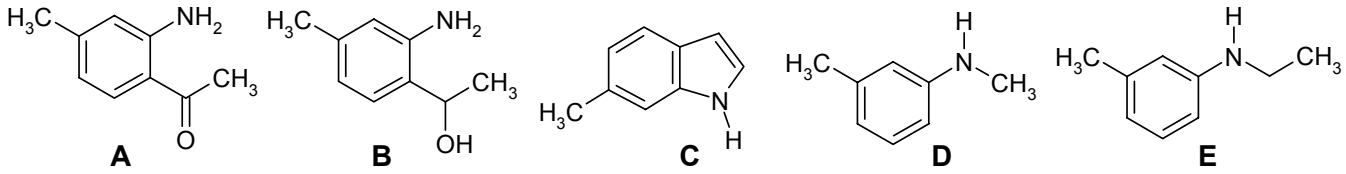

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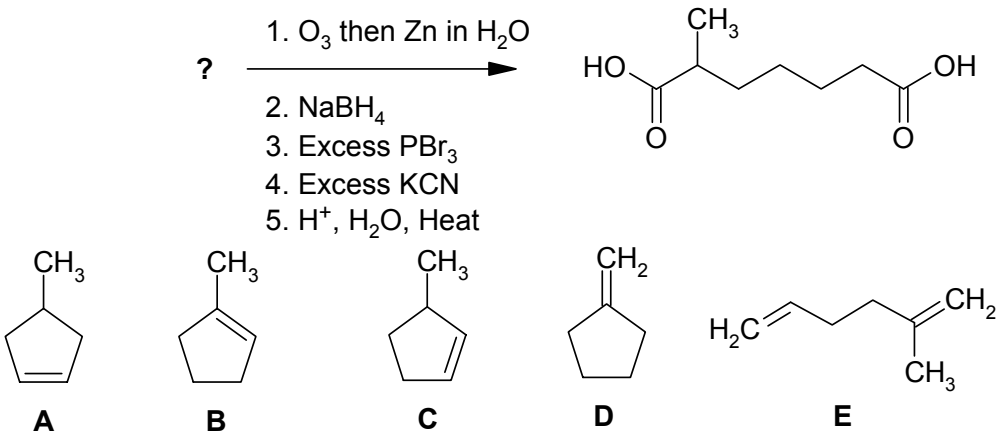
9% PART 5: STARTING MATERIALS FOR SYNTHESIS

ANSWER ANY SIX (6) OF QUESTIONS 37-43.

For each of the questions **37-43**, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

37.



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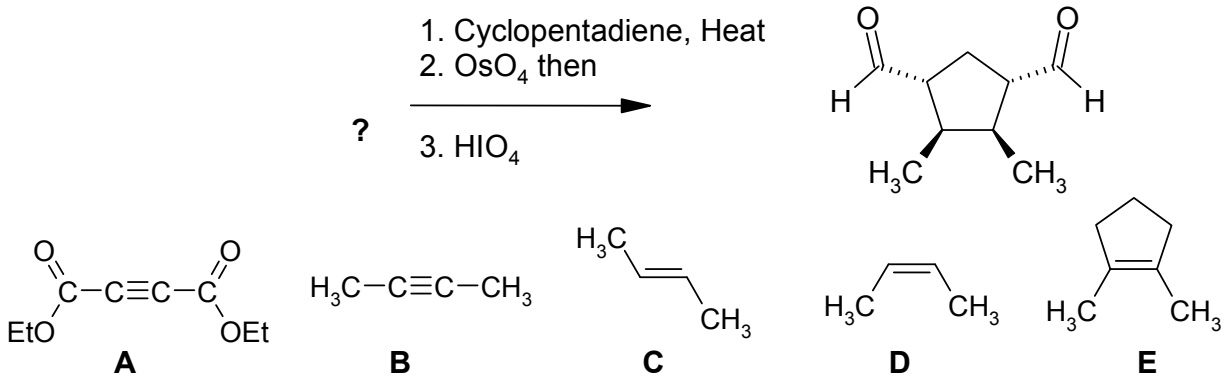

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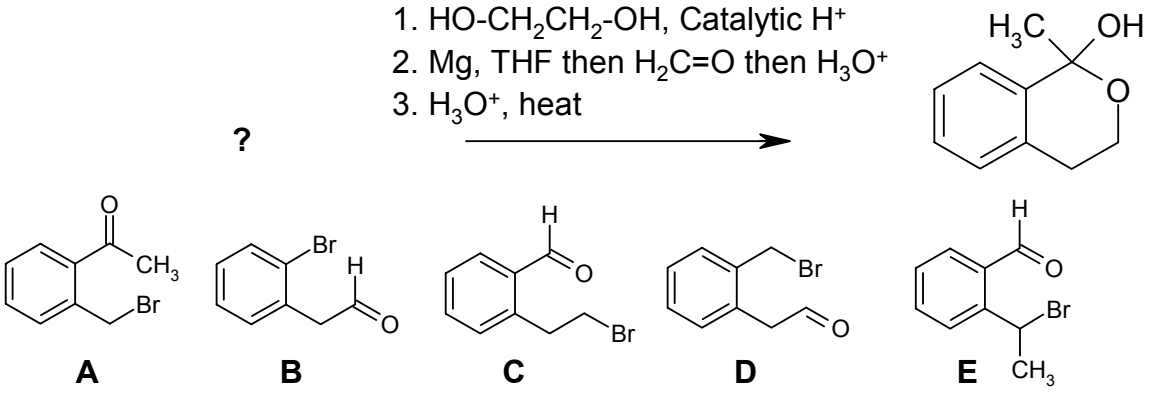

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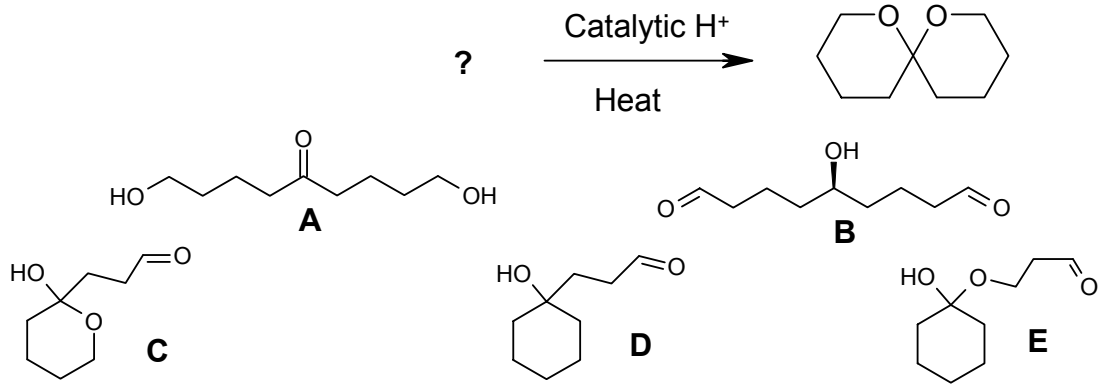
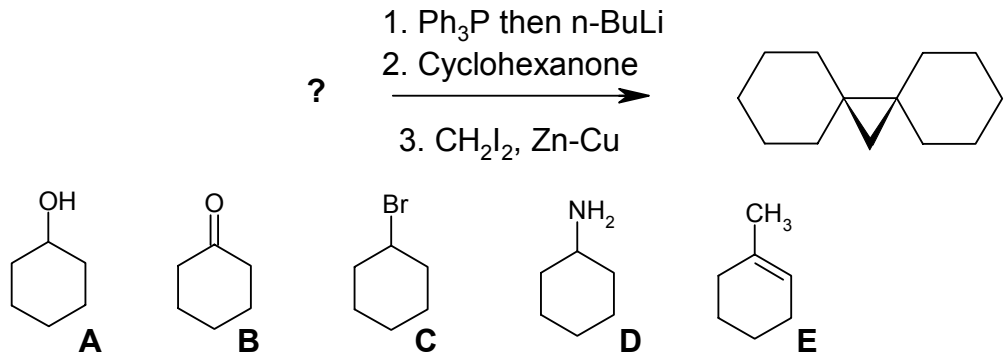
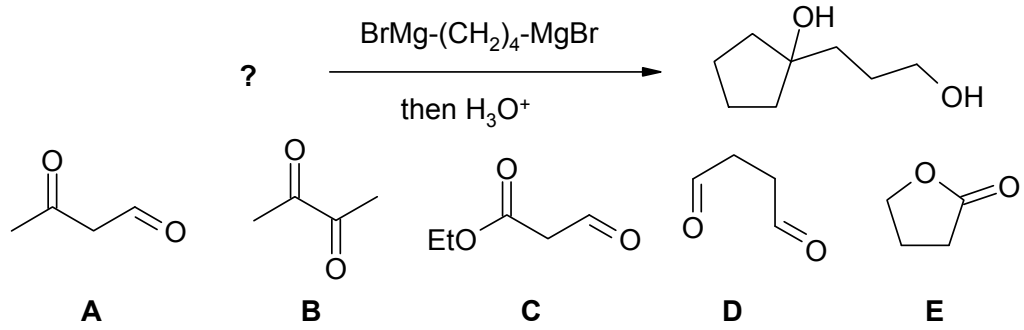


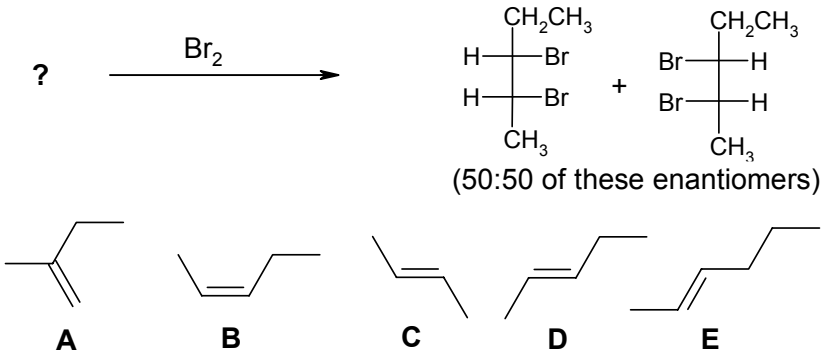
41.



42.



43.



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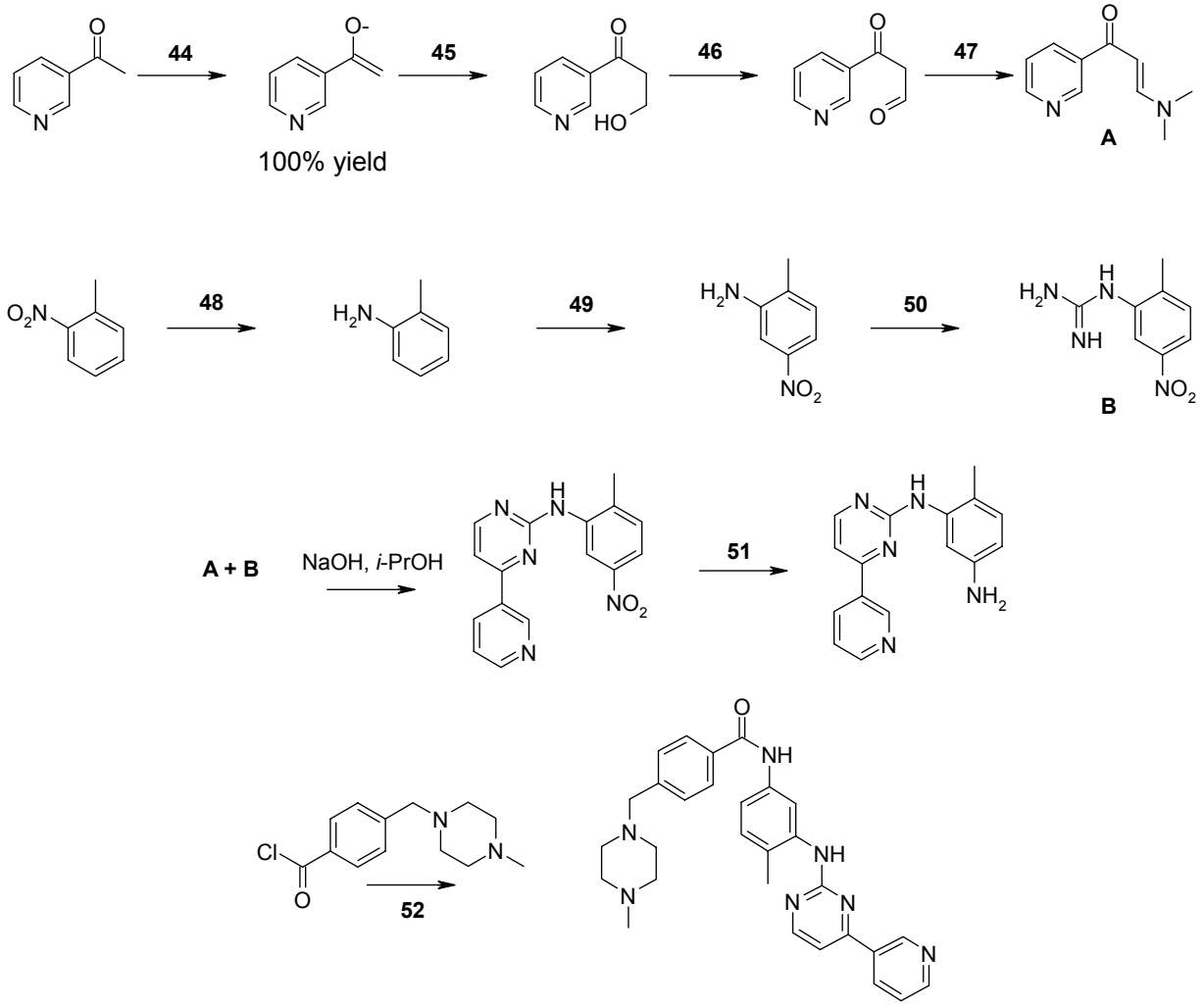
9% PART 6: REAGENTS FOR SYNTHESIS

ANSWER ALL OF THE QUESTIONS 44 - 52

The following synthesis shows a possible synthesis of Gleevec®, which is a drug produced by Novartis and used for cancer treatment. From the list of reagents provided in the table below, select the best reagent combination to carry out each of the reactions required at each numbered step.



A. HNO_3 / H_2SO_4, heat	**BD**. excess CH_3MgI then H_3O^+
B. NaOEt / EtOH	**BE.** formaldehyde, HC(O)H, heat.
C. CH_3ONa / CH_3OH	**CD**. NCS or Cl_2
D. $HN(CH_3)_2$. toluene, then CH_3CO_2H	**CE**. $LiAlH_4$ then H_3O^+
E. Fe / HCl	**DE**. $NaBH_4$
AB. 1. Sn / HCl 2. NaOH	**ABC**. $Ph_3P{=}CH_2$
AC. conc. H_2SO_4	**ABD.** LDA, $LiN(i\text{-}Pr)_2$
AD. BH_3 then aq. NaOH / H_2O_2	**ABE.** PCC, CH_2Cl_2
AE. H_2NCN / H_2O, heat	**BCD**. H_2O / $HgSO_4$ / H_2SO_4
BC. pyridine, room temperature	

CONTINUED -->

9% PART 7: EXPLANATION OF PHENOMENA

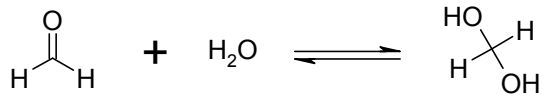
ANSWER ALL OF THE QUESTIONS 53 - 58.

CHOOSE THE SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.

53. The ^{1}H-NMR spectrum of N,N-dimethyl acetamide (DMA, ) shows two peaks for the methyl groups attached to the nitrogen. This is because:

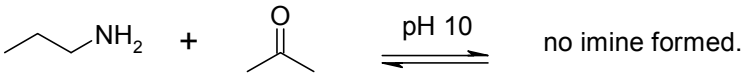
A The N atom has a lone pair and is more electronegative than C.
B The lone pairs on N and O participate in Hydrogen bonding.
C The bond between N and the carbonyl C has some double bond character.
D There is a tautomeric form of DMA where the methyl groups are not equivalent.
E The N is sp^3 hybridized.

54. Which side of the following equilibrium is favoured and why?



A The aldehyde because C=O bond is stronger than C-O bond.
B The aldehyde because formaldehyde is not soluble in H_2O.
C The hydrate because there is generally less steric hindrance in an sp^3 hybrid.
D The hydrate because it is the entropically favoured product.
E The hydrate because the formaldehyde carbon is electrophilic.

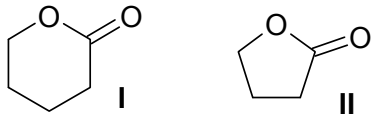
55. In the following unsuccessful imine reaction, why does the reaction not go to completion?



A At pH 10, the ketone will be protonated and the amine cannot attack the carbonyl.
B At pH 10, the ketone will form the enolate ion.
C At pH 10, the tetrahedral intermediate is protonated and H_2O leaves.
D At pH 10, the amine is ionic and the tetrahedral intermediate is deprotonated.
E At pH 10, the amine will be neutral and the tetrahedral intermediate cannot lose $^-$OH.

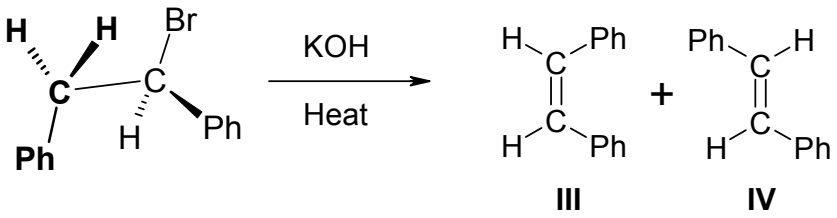
CONTINUED -->

56. For the rate of the saponification of the following lactones:



A. **I** reacts the fastest because the carbonyl is less stabilized
B. **I** reacts the fastest because the tetrahedral reaction intermediate is more stable due to staggered bonds
C. **II** reacts the fastest because the five membered ring has more strain
D. **II** reacts the fastest tetrahedral reaction intermediate is more stable due to eclipsed bonds
E. Both **I** and **II** do not react under these reaction conditions due to the enhanced stability of a cyclic ester

57. For the following reaction:



A. An approximately 50:50 mixture of **III** and **IV** are obtained under these conditions
B. A greater amount of **III** would be produced because it is formed the fastest (the kinetic product)
C. A greater amount of **III** would be produced because it is more stable (the thermodynamic product)
D. A greater amount of **IV** would be produced because it is formed the fastest (the kinetic product)
E. The reaction would not proceed because KOH is not a strong enough base

58. When added to water, hexachloroacetone…

A. Forms a biphasic mixture with water as the lower layer
B. Forms a biphasic mixture with water as the upper layer
C. Is rapidly hydrolysed to form two equivalents of acetic acid and HCl
D. Rapidly forms a hydrate
E. Rapidly forms an enol

CONTINUED -->

10% **PART 8: MECHANISM**

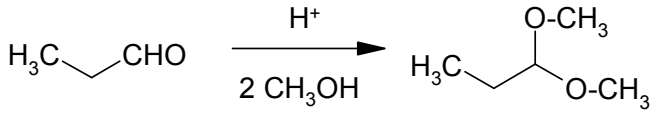
ANSWER TWO(2) QUESTIONS, ONE FROM PART A AND ONE FROM PART B.

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

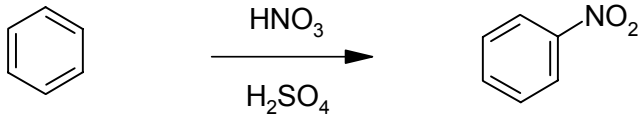
NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED FOR THESE QUESTIONS.

(4) PART A: Use a curly arrow mechanism to explain ONE of the following transformations :

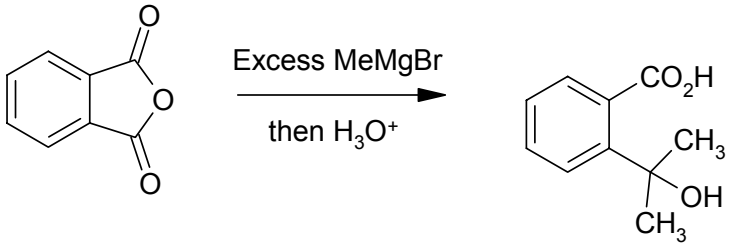
i



ii

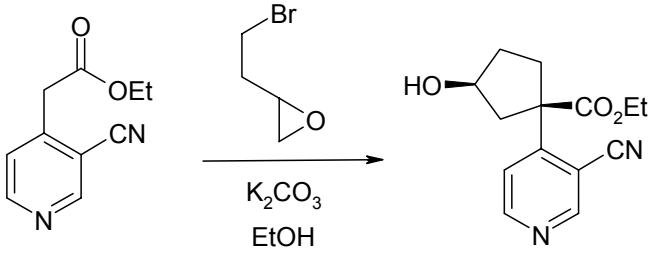


iii

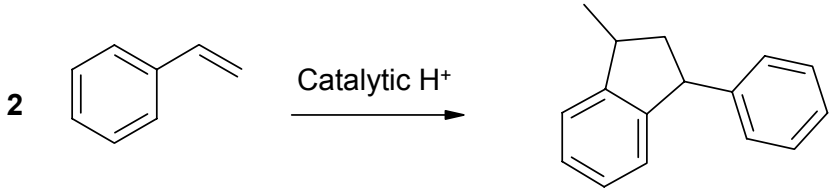


(6) PART B : Use a curly arrow mechanism to answer ONE of the following :

i. Provide a detailed mechanism showing all the steps for the following:



ii. Provide a detailed mechanism showing all the steps for the following:



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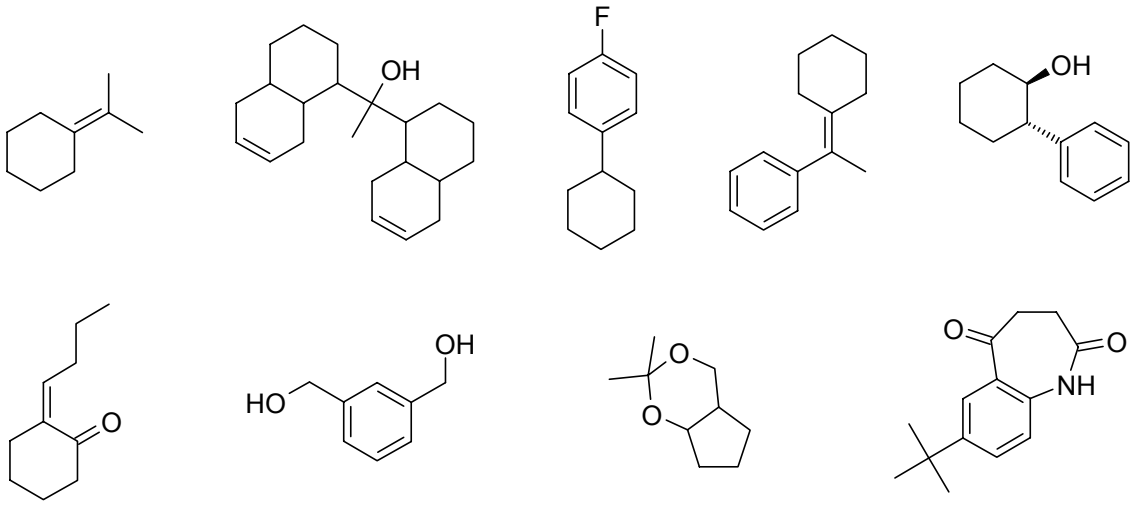
12% PART 9: TOTAL SYNTHESIS

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Design an efficient synthesis for any **THREE (3)** of the following target molecules using any of the starting materials and reagents given in the accompanying list. Show the product of each step and clearly identify the required reagents.

DO NOT SHOW MECHANISMS



Permitted Starting Materials and Reagents*

- Any inorganic materials
- Any organic compounds with no more than **FOUR** carbons
- triphenyl phosphine
- MCPBA
- Either of the following:

* **any materials that contribute carbon atoms to the target must come from this allowed list**.

CONTINUED -->

10% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Compound **A** was found to be 88.16% C and 11.84%H (from standard elemental analysis for CHN) and had a strong IR absorption at about 1600cm^{-1} and ^{13}C nmr spectra peaks at 18, 114, 117, 140 and 142ppm.

When **A** was heated in a sealed tube with ethene at 200^{o}C it gave compound **B** which reacted rapidly with Br_2 / $CHCl_3$ to give a colourless solution.

When **B** was reacted with BH_3 and then H_2O_2 / aq. NaOH, compound **C** was formed, IR absorption near 3000cm^{-1} (broad). When **C** was reacted with acidic $K_2Cr_2O_7$ or PCC / CH_2Cl_2 compound **D**, $C_7H_{12}O$ was produced. The ^{13}C nmr spectra of **D** had 7 peaks, one at 213ppm and the rest were below 50ppm. The IR spectra of **D** had a strong absorption at 1712cm^{-1}. Reaction of **D** with CH_3CO_3H gave compound **E**, $C_7H_{12}O_2$ whose ^{13}C nmr spectra also had 7 peaks : 175, 70ppm and the rest below 50ppm. Reaction of **E** with $LiAlH_4$ / THF followed by a normal work-up gave racemic heptan-1,6-diol.

When **B** was reacted with O_3 followed with a H_2O_2 work-up it gave compound **F**, $C_7H_{12}O_3$. The IR spectra of **F** had strong absorptions near 3000 (broad) and 1710cm^{-1}.

Subsequent reaction of **F** with $NaBH_4$ / aq. EtOH followed by a normal work-up gave **E** again whereas reaction of **F** with $LiAlH_4$ / THF followed by a normal work-up gave racemic heptan-1,6-diol.

When **B** was reacted with O_3 followed with Zn / acid work-up it gave compound **G**, $C_7H_{12}O_2$. The IR spectra of **G** had a strong absorption at 1725cm^{-1}. Subsequent reaction of **G** with hot NaOH / EtOH gave 1-cyclopent-1-en-1-ylethanone.

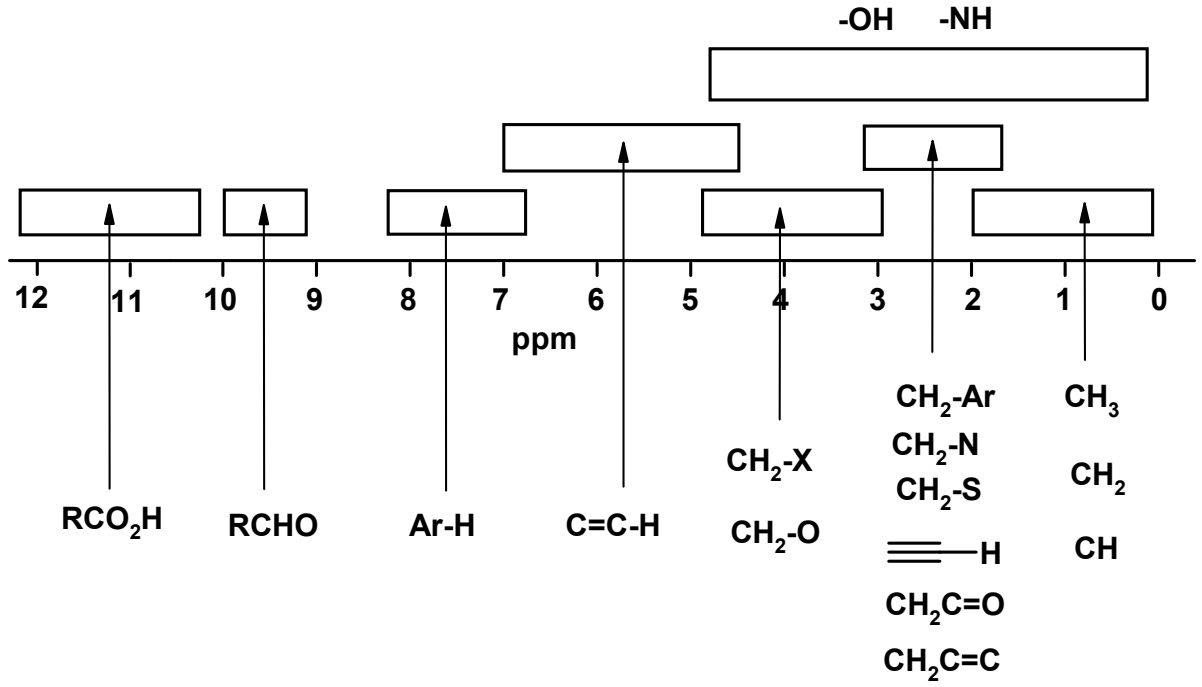
Compounds **C**, **D** and **E** were formed as a pair of enantiomers.

Identify the compounds **A**, **B**, **C**, **D**, **E**, **F** and **G** (structures are sufficient)

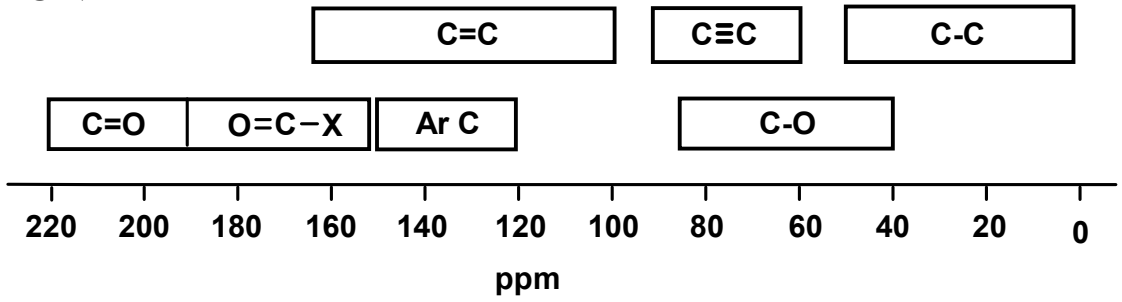
THE END

Schematic diagrams of NMR chemical shift data for H and ^{13}C NMR

^{1}H NMR



^{13}C NMR



A Correlation Table of Infra-Red Group Absorption Frequencies

	TYPE OF VIBRATION		FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY
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 interpretatively 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
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*		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

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

PERIODIC TABLE

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

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