

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 353

TUESDAY MARCH 10th, 2009

Time: 2 Hours

PLEASE WRITE YOUR NAME AND FULL STUDENT I.D. NUMBER ON BOTH YOUR COMPUTER ANSWER SHEET and on the ANSWER BOOKLET provided.

READ ALL THE INSTRUCTIONS CAREFULLY

The exam consists of Parts 1 - 7, each of which should be attempted. Note that some Parts provide you with a choice of questions, e.g. 5 out of 6. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 4 will be computer graded, and Parts 5, 6 and 7 are to be answered **IN THE BOOKLET PROVIDED**. A periodic table with atomic numbers and atomic weights and spectroscopic data tables are included with this examination paper.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 34 which are to be answered on the computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a soft 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.

Absolutely no electronic devices are allowed.

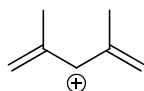
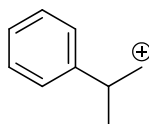
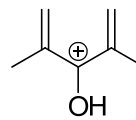
PART 1: RELATIVE PROPERTIES**16% ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.**

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

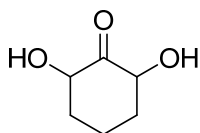
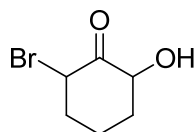
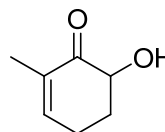
Use the following code to indicate your answers.

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

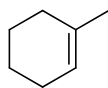
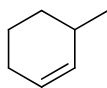
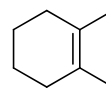
1. The relative stability of each of the following:

**(i)****(ii)****(iii)**

2. The number of configurational isomers of each of the following: (most to least)

**(i)****(ii)****(iii)**

3. The relative reactivity of the following alkenes with $\text{CH}_3\text{CO}_3\text{H}$:

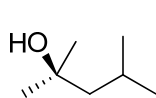
**(i)****(ii)****(iii)**

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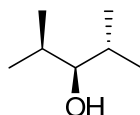
Use the following code to indicate your answers.

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

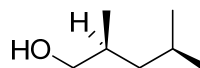
4. The relative yield of each of the following from the hydroboration, oxidation reaction of 2,4-dimethyl-2-pentene:



(i)

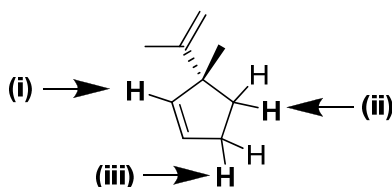


(ii)

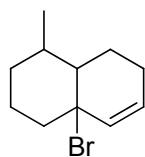


(iii)

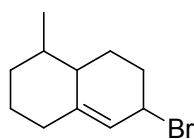
5. The relative acidity of the hydrogens indicated from most acidic to least acidic:



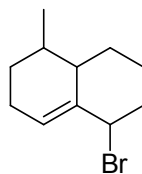
6. The relative yields of the HBr addition reaction carried out at 100 °C on the diene shown below: (highest to lowest)



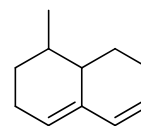
(i)



(ii)



(iii)

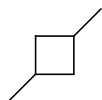
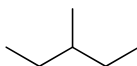
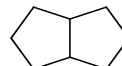


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Use the following code to indicate your answers.

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

7. The number of different mono-alkene starting materials that could give rise to the following products after a Pt catalysed hydrogenation: (most to fewest):

**(i)****(ii)****(iii)**

8. The relative reactivity of each of the following acids with (Z)-3,4-dimethyl-2pentene:

HCl

(i)

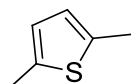
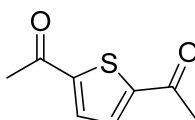
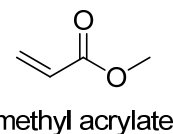
HI

(ii)

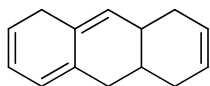
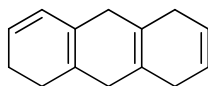
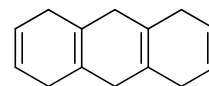
HF

(iii)

9. The relative reactivity of methyl acrylate (shown below) with each of the following:

**(i)****(ii)****(iii)**

10. The relative resonance energies of each of the following: (highest to lowest):

**(i)****(ii)****(iii)**

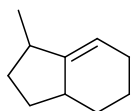
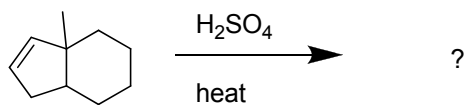
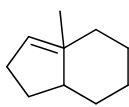
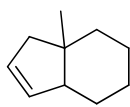
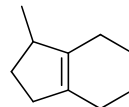
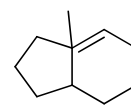
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PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS

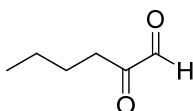
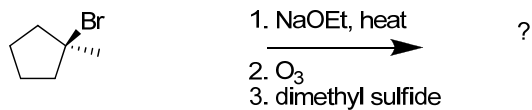
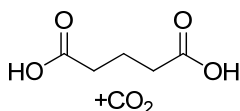
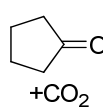
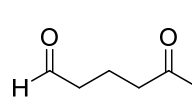
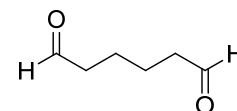
14% ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.

For each of questions 11-18 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

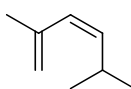
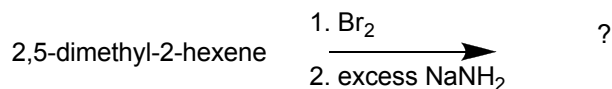
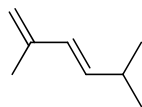
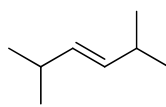
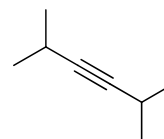
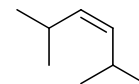
11.

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

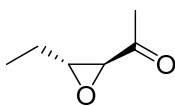
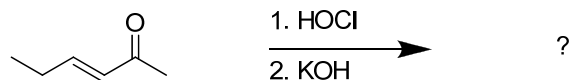
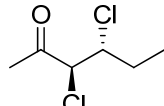
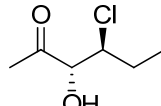
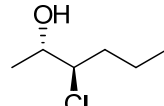
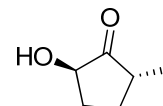
12.

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

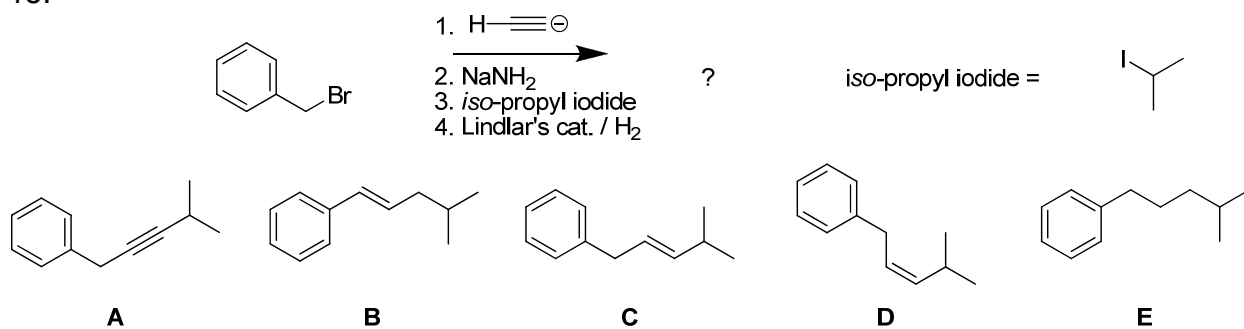
13.

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

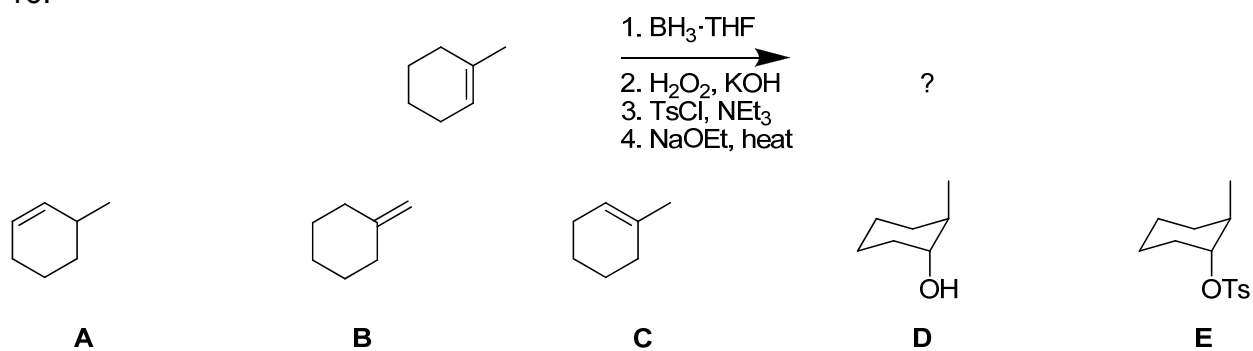
14.

**A****B****C****D****E****CONTINUED -->**

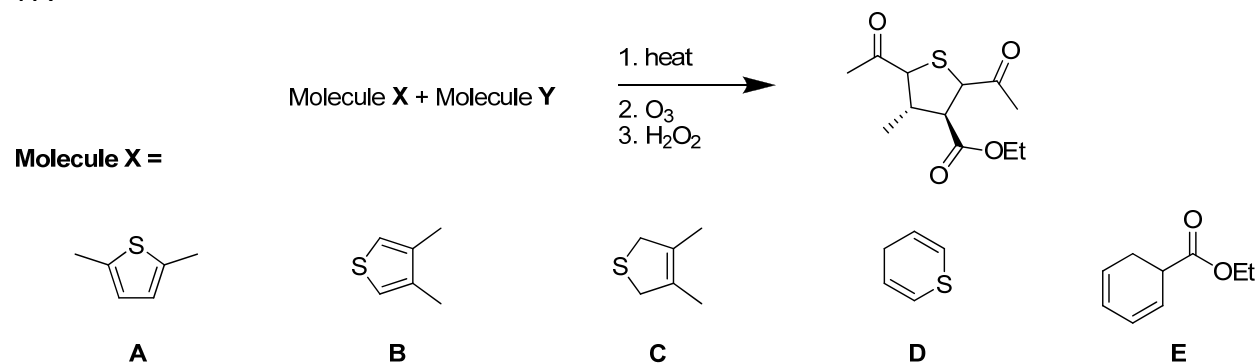
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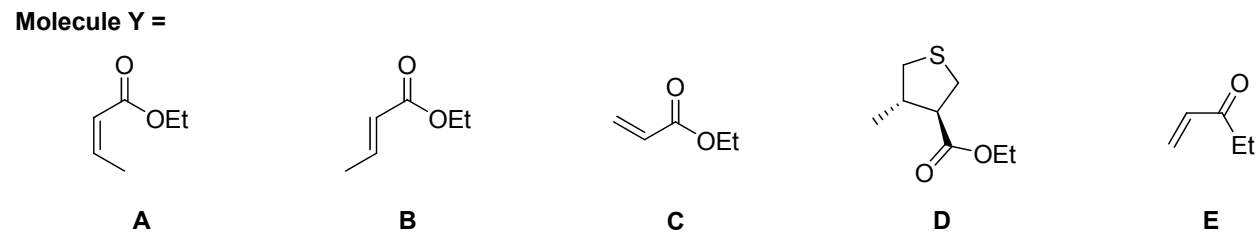
16.



17.



18.

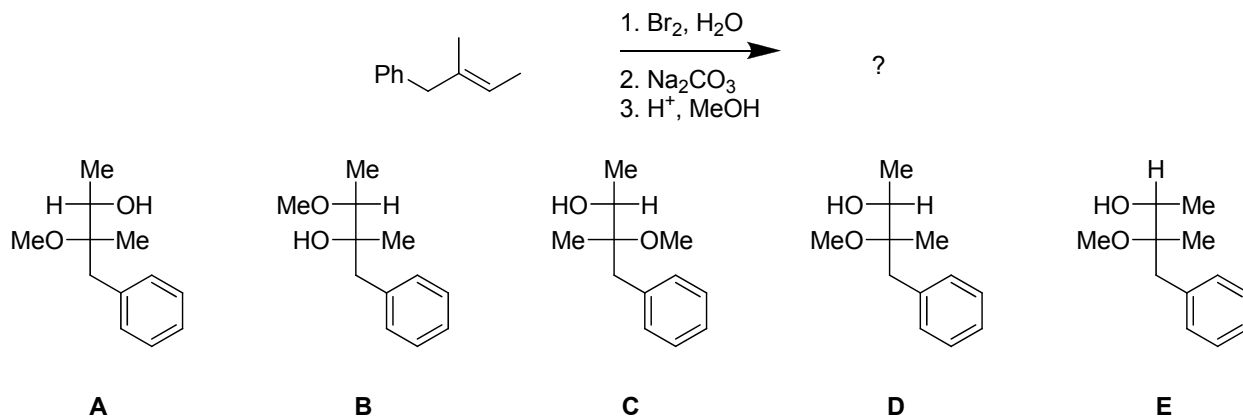


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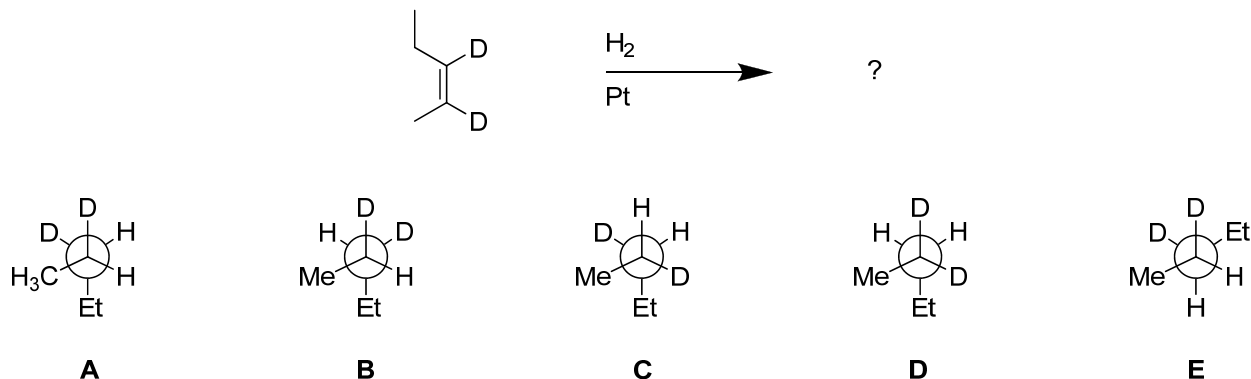
PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS**18% ANSWER ANY SIX (6) OF QUESTIONS 19-25.**

For each of the questions 19-25, select the structure(s) required to complete the reaction shown. If two products are equally abundant, then you must indicate both for full marks. If two starting materials will give the same product, then you must indicate both for full marks. In order to indicate more than one structure, blacken the spaces corresponding to each one.

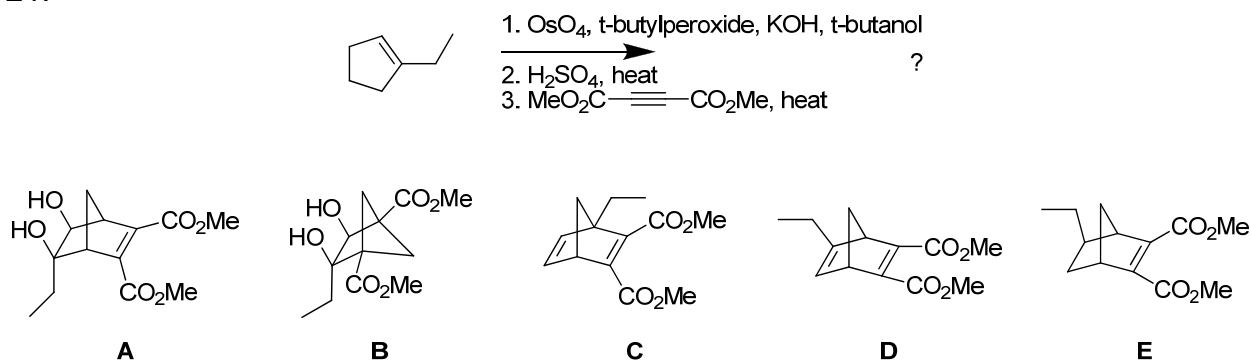
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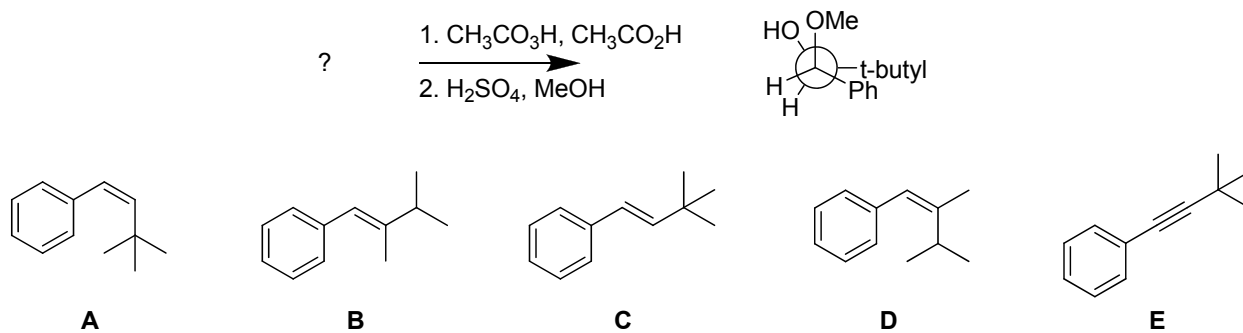
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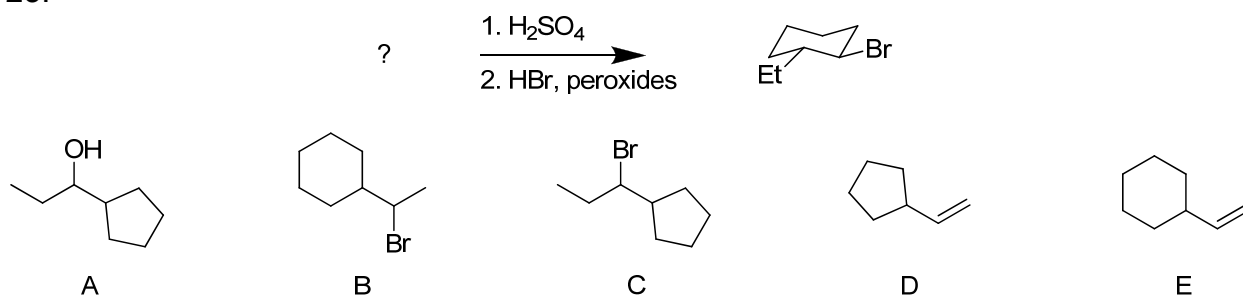
21.

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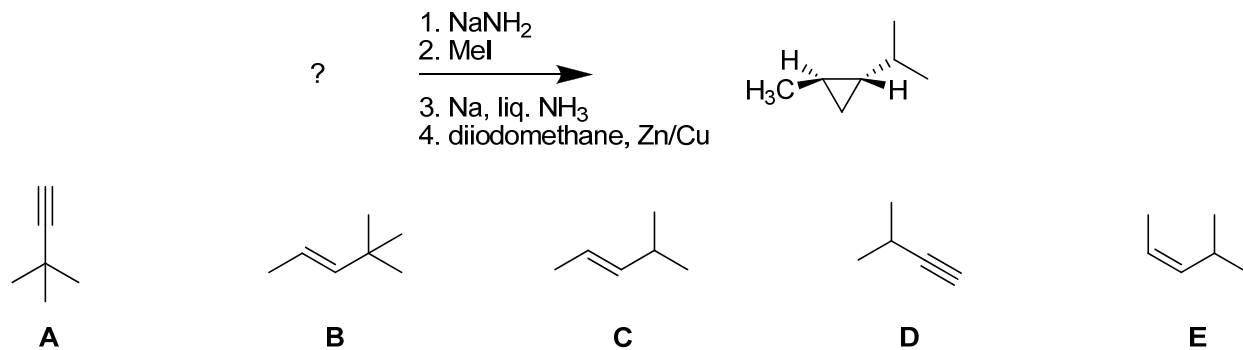
22.



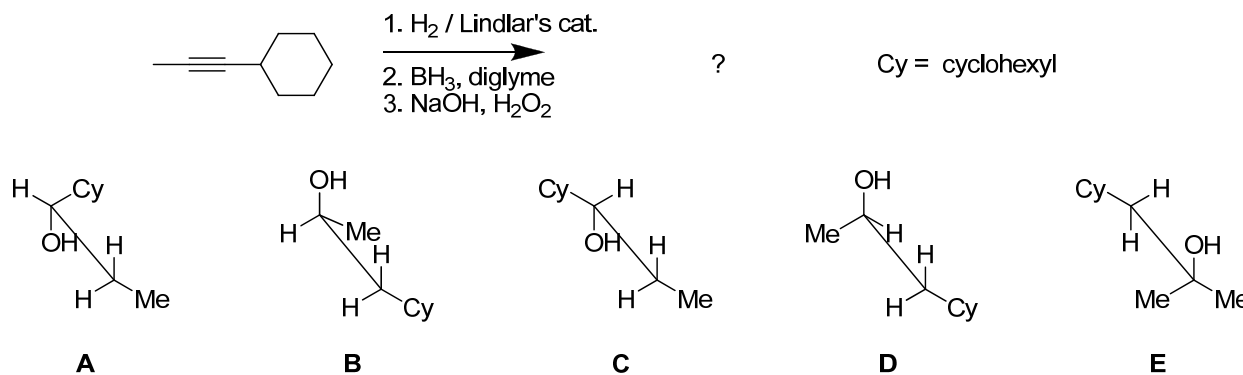
23.



24.



25.



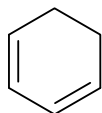
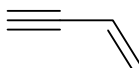
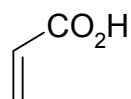
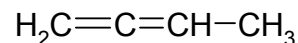
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PART 4: PI SYSTEMS

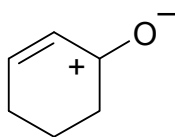
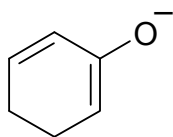
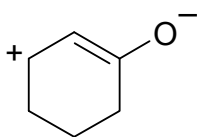
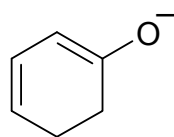
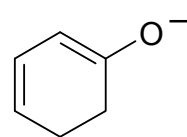
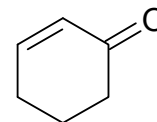
16% ANSWER ANY EIGHT (8) of the questions 26 - 34.

For each of the questions 26-34 select the appropriate answer from the answers provided. In questions 26-29 more than one selection may be required for full credit.

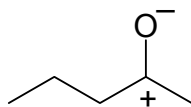
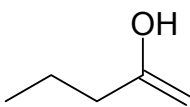
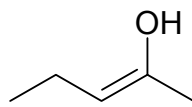
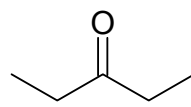
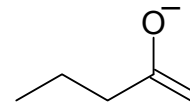
26. Which of the following molecules contain conjugated systems? **(select all that apply)**

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

27. Which of the following systems are resonance contributors of cyclohex-2-enone (shown below right) ? **(select all that apply)**

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

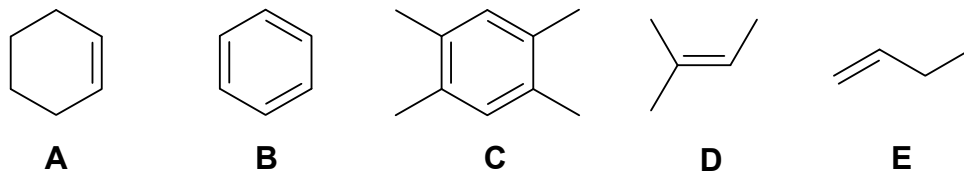
28. Which of the following systems are tautomers of 2-pentanone ? **(select all that apply)**

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

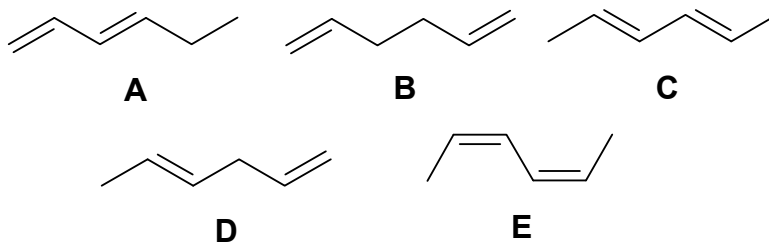
29. Which of the following compounds used in the Chem 353 laboratory experiments are contain C=C ? **(select all that apply)**

A. sucrose**B.** biodiesel**C.** terephthalic acid (the monomer recovered from PETE depolymerisation)**D.** nylon**E.** benzoic acid**CONTINUED -->**

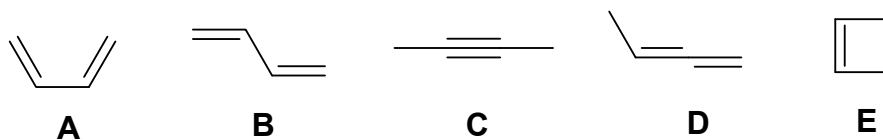
30. Which of the following systems has the **most** allylic hydrogens ?



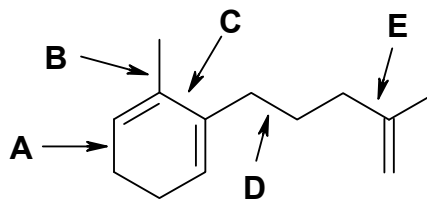
31. Which of the following isomers is the **most** stable ?



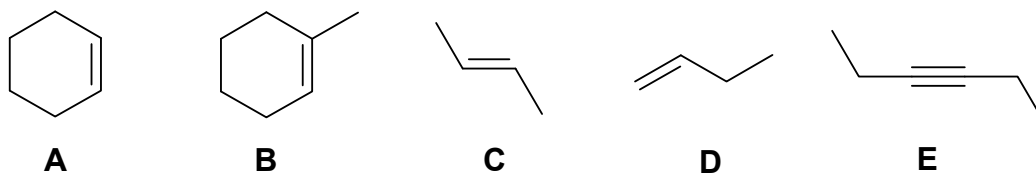
32. Which of the following isomers is the **most** stable ?



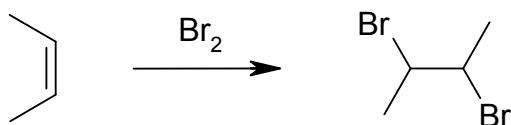
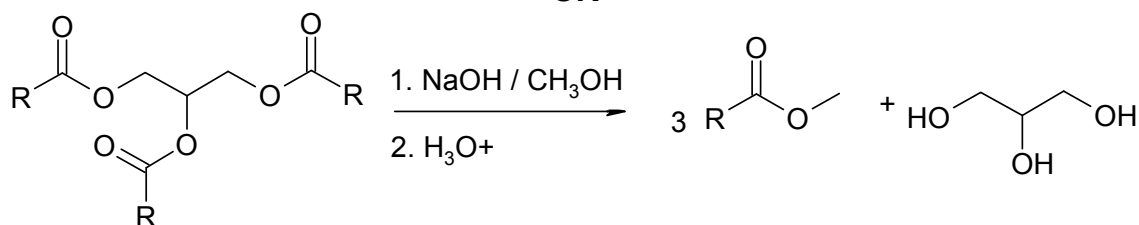
33. Which of the bonds indicated below is the **shortest** ?



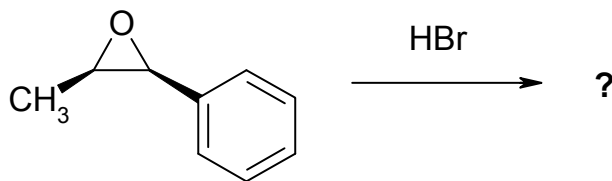
34. Which of the following systems would be the **most** reactive towards aq. H_2SO_4 ?



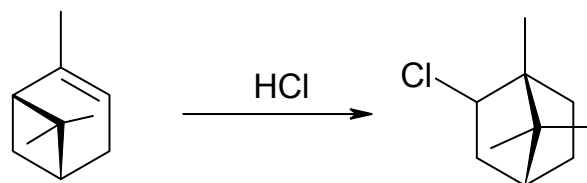
CONTINUED -->

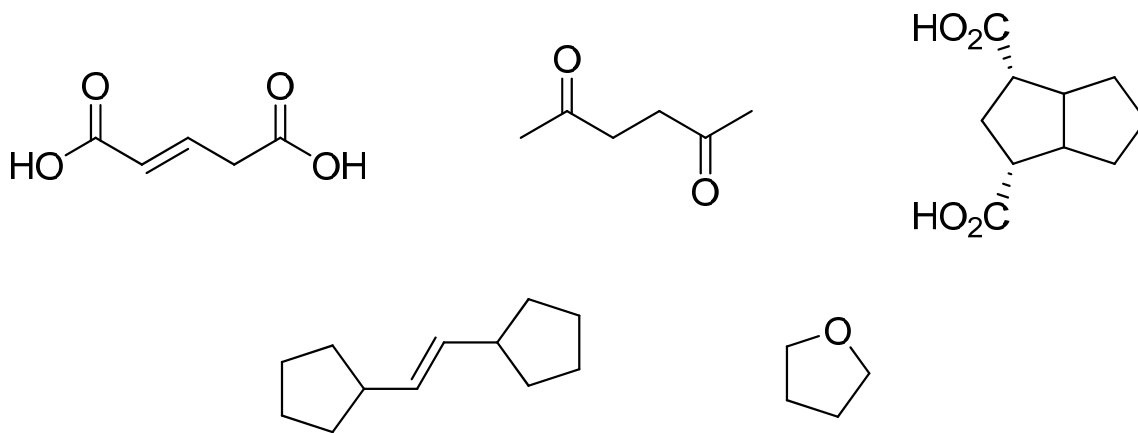
PART 5: MECHANISMS**10% ANSWER TWO (2) QUESTIONS, ONE FROM PART A and ONE FROM PART B****WRITE YOUR ANSWER IN THE BOOKLET PROVIDED****Draw curly arrow mechanisms to explain the following reactions / observations.
No other reagents are required.****A.** Show the mechanism for one of the following reactions:**OR**

(only show how one of the functional groups reacts)

B. Predict the product of the following reaction by showing the mechanism. Make sure to predict and justify the regiochemistry and stereochemistry.**OR**

Show the mechanism for the following reaction. Briefly justify why the product is thermodynamically favoured.

**CONTINUED -->**

PART 6: SYNTHESIS**15% ANSWER ANY THREE (3) OF QUESTIONS****WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.****Design an efficient synthesis for any THREE (3) of the following target molecules****SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE PRODUCT OF EACH STEP****DO NOT SHOW MECHANISMS (i.e. curly arrows are NOT required)****You may use cyclopentene and / or any hydrocarbon containing up to TWO carbon atoms as starting materials. In addition, you may use any solvents or inorganic reagents that do not contribute carbon atoms to the final structure.****CONTINUED -->**

PART 7: STRUCTURE DETERMINATION**11% WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

Use the information in the following paragraph to answer the questions below.

Compound **A** is an achiral hydrocarbon, MS shows $M^+ = 84$. Reaction of **A** with Br_2 in chloroform produces a colourless solution which gives **B** as the major product. When **B** is heated with excess $KOH / EtOH$, **C** is the major product of the reaction.

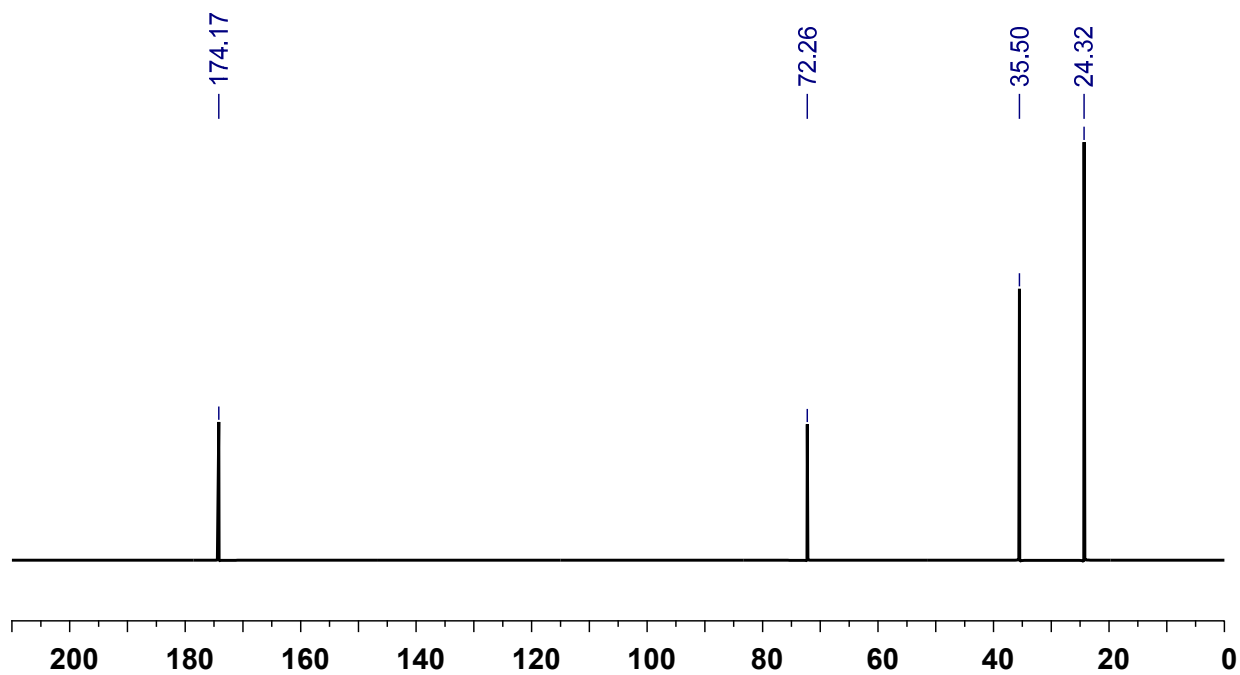
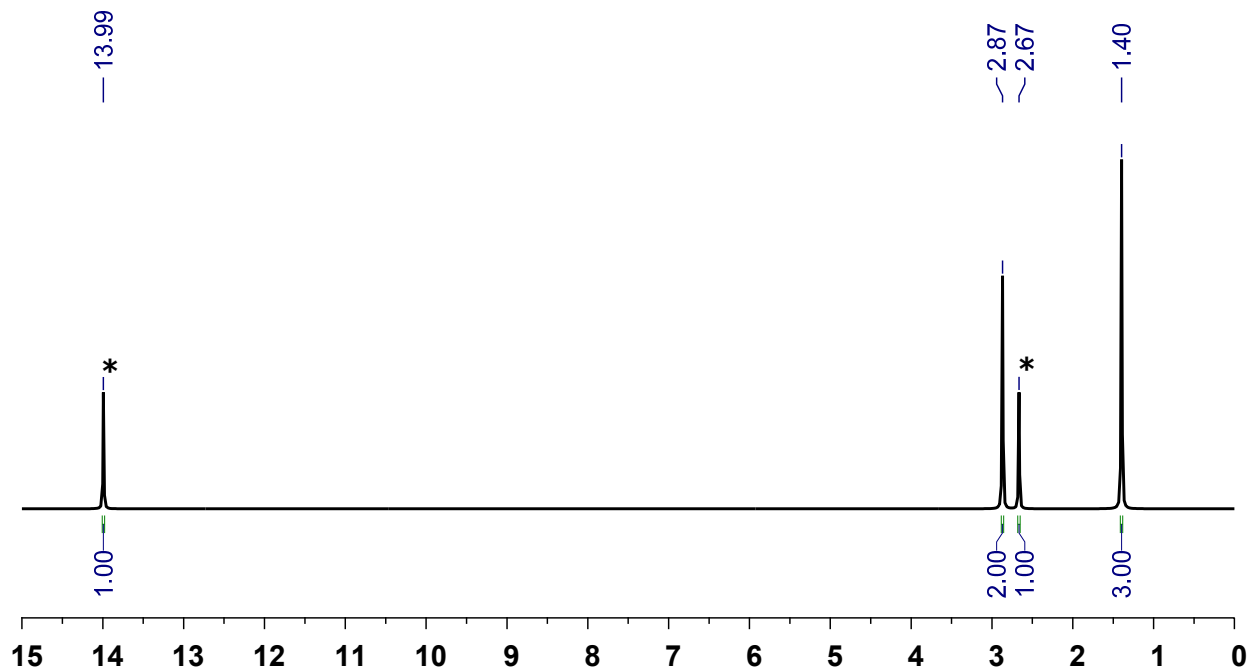
When **C** is heated with ethyne at high temperature and pressure, **D** is the major product. Careful reaction of **D** with one equivalent of CH_3CO_3H , gives **E**. **E** was then reacted with ozone followed by hydrogen peroxide work-up to give **F**. Reaction of **F** with aqueous acid gives a racemic mixture of (R,R)- and (S,S)-3,4-dihydroxy-3,4-dimethylhexan-1,6-dioic acid (the H-NMR and ^{13}C -NMR spectra of one of the enantiomers is shown on the following page).

Draw the structures of A to F.

Give the systematic IUPAC name for the molecule that you have drawn for D.

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

* = peaks exchange with D₂O



*** THE END ***

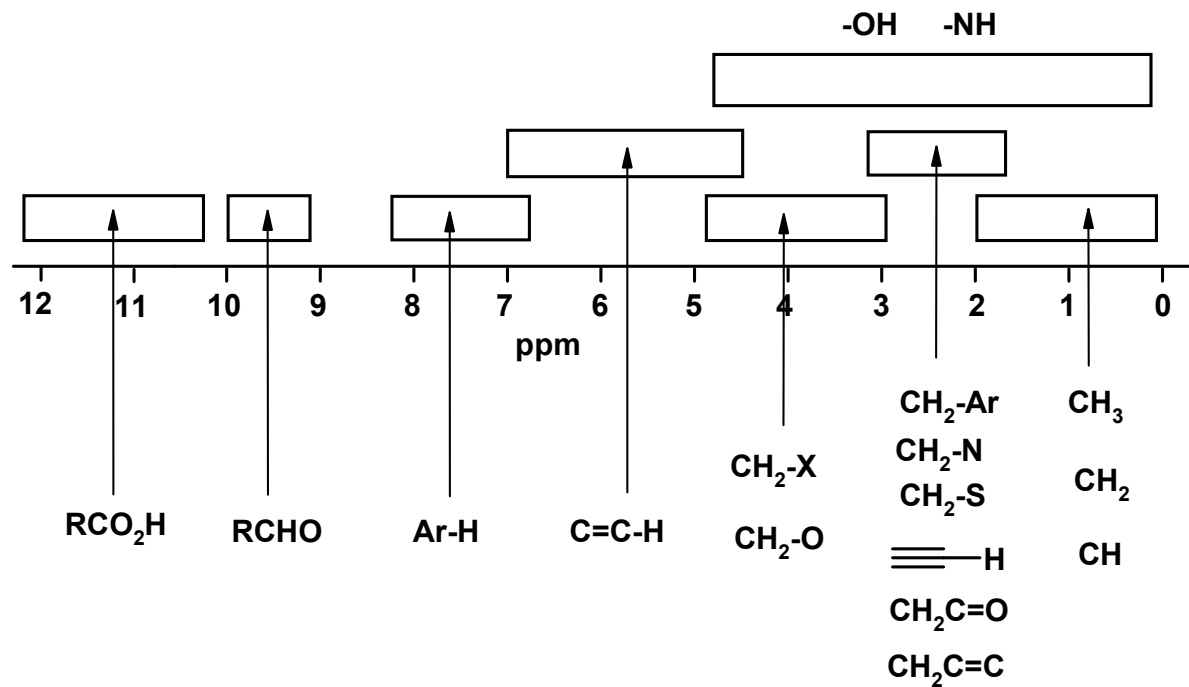
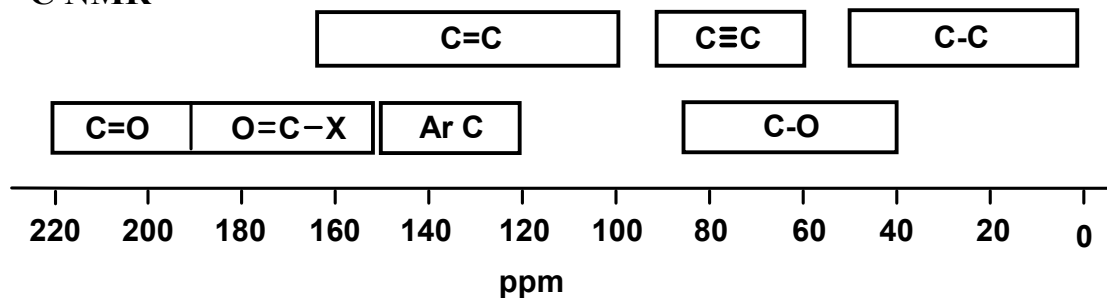
PERIODIC TABLE

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 **

Schematic diagrams of NMR chemical shift data for ^1H and ^{13}C NMR ^1H 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. 1760	ca. 5.52 ca. 5.68	s 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)