

UNIVERSITY OF CALGARY  
FACULTY OF SCIENCE  
MIDTERM EXAMINATION  
CHEMISTRY 353

WEDNESDAY MARCH 3rd, 2010

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. answer any 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.**

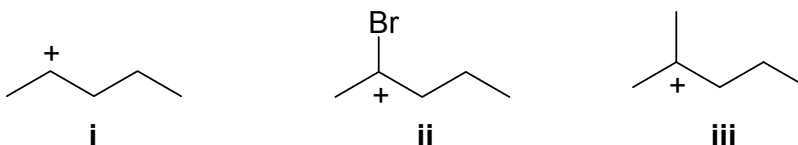
**PART 1: RELATIVE PROPERTIES****16% ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.**

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

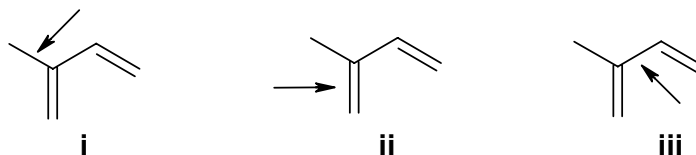
Use the following code to indicate your answers.

- |           |                           |            |                           |
|-----------|---------------------------|------------|---------------------------|
| <b>A.</b> | <b>i &gt; ii &gt; iii</b> | <b>D.</b>  | <b>ii &gt; iii &gt; i</b> |
| <b>B.</b> | <b>i &gt; iii &gt; ii</b> | <b>E.</b>  | <b>iii &gt; i &gt; ii</b> |
| <b>C.</b> | <b>ii &gt; i &gt; iii</b> | <b>AB.</b> | <b>iii &gt; ii &gt; i</b> |

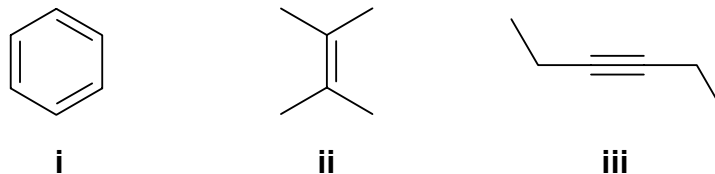
1. The relative stability of each of the following:



2. The relative strengths of the CC bonds indicated in each of the following:



3. The relative reactivity of each of the following towards H<sub>2</sub>/ Pd :

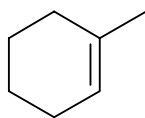


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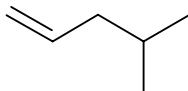
Use the following code to indicate your answers.

- |           |                           |            |                           |
|-----------|---------------------------|------------|---------------------------|
| <b>A.</b> | <b>i &gt; ii &gt; iii</b> | <b>D.</b>  | <b>ii &gt; iii &gt; i</b> |
| <b>B.</b> | <b>i &gt; iii &gt; ii</b> | <b>E.</b>  | <b>iii &gt; i &gt; ii</b> |
| <b>C.</b> | <b>ii &gt; i &gt; iii</b> | <b>AB.</b> | <b>iii &gt; ii &gt; i</b> |

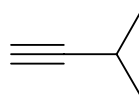
4. The relative rate of reaction of each of the following towards aq.  $\text{H}_2\text{SO}_4$ :



**i**

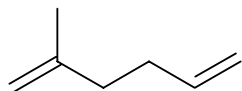


**ii**

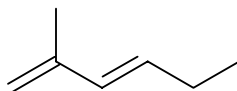


**iii**

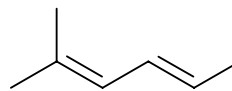
5. The relative heats of hydrogenation of the following (most endothermic to most exothermic, *i.e.* most +ve to most -ve):



**i**



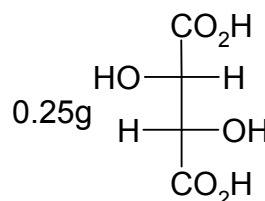
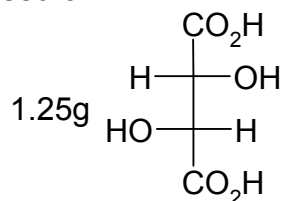
**ii**



**iii**

6. The optical purity of the following samples of tartaric acid given that (R,R)-tartaric acid  $[\alpha]_D = +12.7$  :

**i** a mixture composed of :



**ii** a sample whose observed rotation =  $+ 1.27^\circ$  when 2.00g of a mixture was dissolved in 10mL and measured in a standard 10cm polarimeter cell

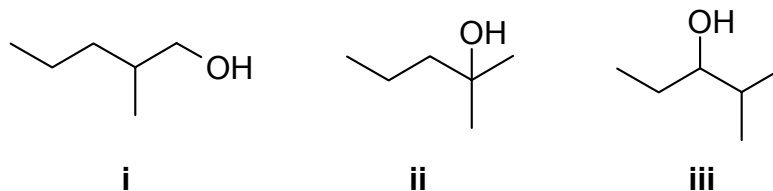
**iii** a racemic mixture

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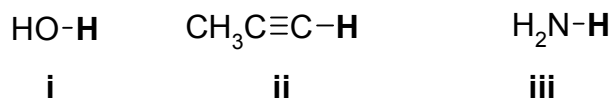
Use the following code to indicate your answers.

- |           |                           |            |                           |
|-----------|---------------------------|------------|---------------------------|
| <b>A.</b> | <b>i &gt; ii &gt; iii</b> | <b>D.</b>  | <b>ii &gt; iii &gt; i</b> |
| <b>B.</b> | <b>i &gt; iii &gt; ii</b> | <b>E.</b>  | <b>iii &gt; i &gt; ii</b> |
| <b>C.</b> | <b>ii &gt; i &gt; iii</b> | <b>AB.</b> | <b>iii &gt; ii &gt; i</b> |

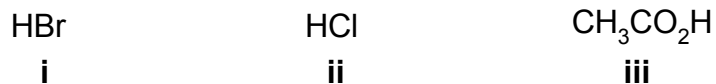
7. The relative yields of the following products from the reaction of 2-methyl-2-pentene with  $\text{BH}_3$  followed by the normal work-up with aq.  $\text{NaOH} / \text{H}_2\text{O}_2$  :



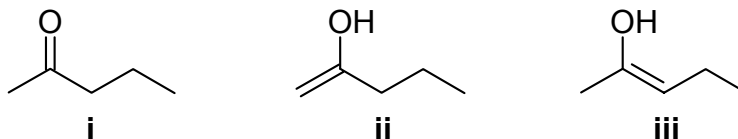
8. The relative acidity of the **H** atom in each of the following:



9. The relative reactivity of each of the following towards 1-hexene:



10. The relative stability of each of the following:



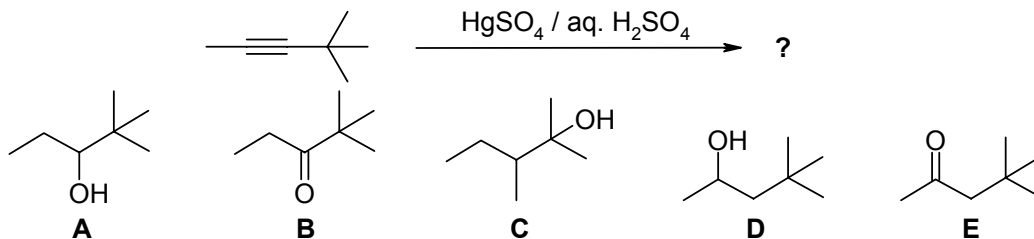
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**PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS**

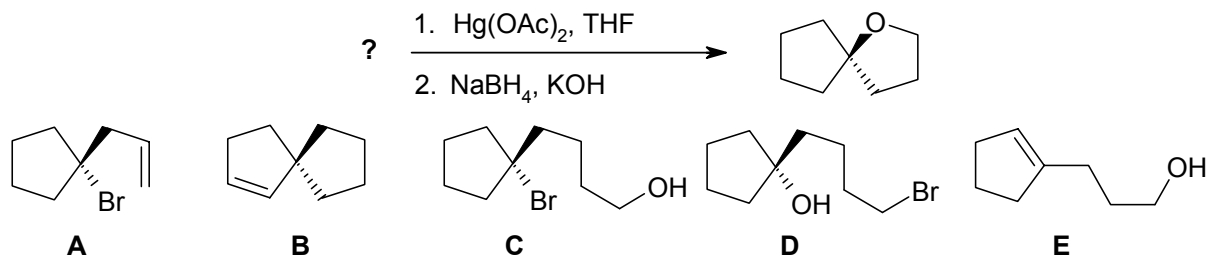
14% ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.

For each of questions 11-18 select the MISSING component(s) (the starting material, the product or the reagents) required in order to complete each of the reaction schemes. In order to indicate more than one structure, blacken the spaces corresponding to each one.

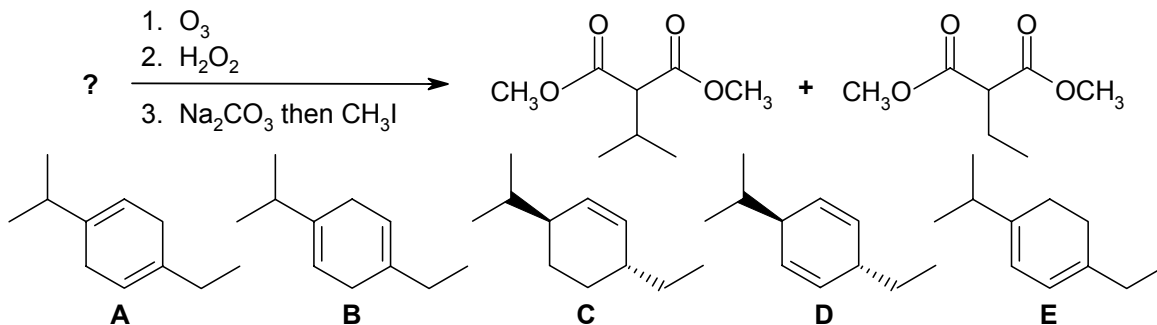
11.



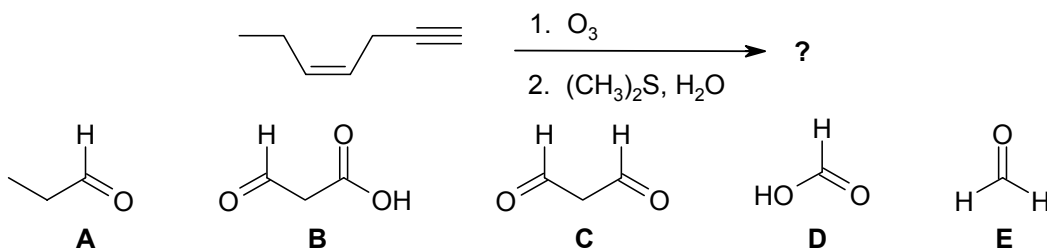
12.



13.

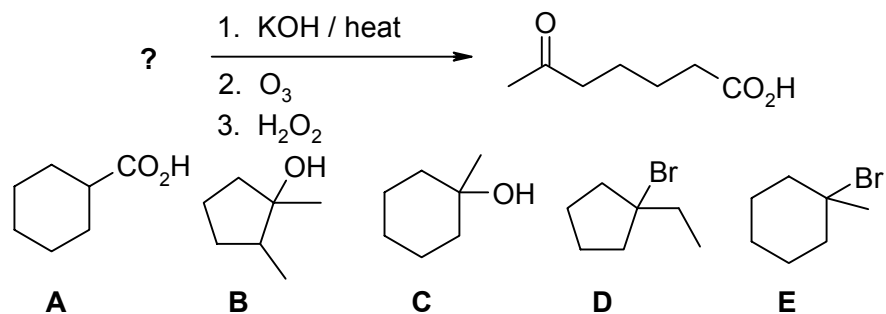


14.

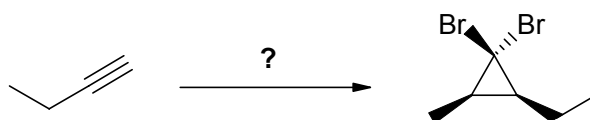


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15.

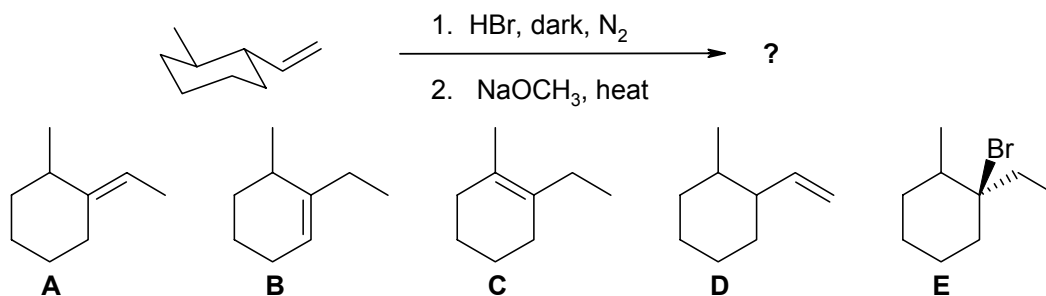


16.

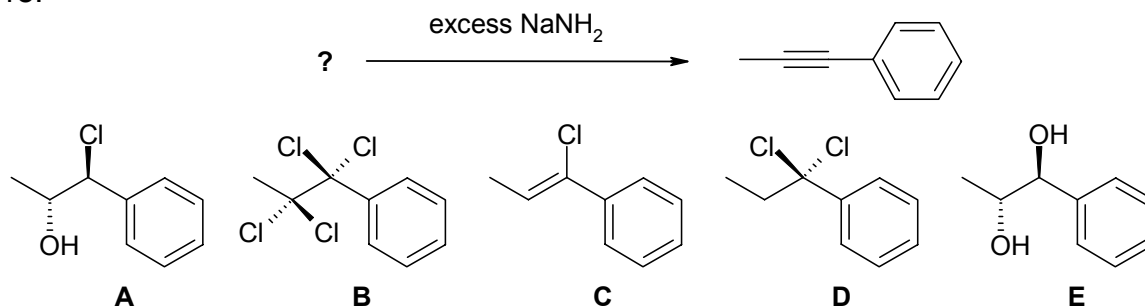


- A** 1.  $\text{NaNH}_2$  then  $\text{CH}_3\text{I}$     2.  $\text{H}_2$  / Lindlar's catalyst    3.  $\text{CH}_2\text{Br}_2$  / Zn Cu  
**B** 1.  $\text{Na} / \text{NH}_3$                 2.  $\text{NaNH}_2$  then  $\text{CH}_3\text{I}$             3.  $\text{CH}_2\text{Br}_2$  / Zn Cu  
**C** 1.  $\text{NaNH}_2$  then  $\text{CH}_3\text{I}$     2.  $\text{Na} / \text{NH}_3$                         3.  $\text{CH}_2\text{Br}_2$  / Zn Cu  
**D** 1.  $\text{NaNH}_2$  then  $\text{CH}_3\text{I}$     2.  $\text{Na} / \text{NH}_3$                         3.  $\text{CHBr}_3$  /  $\text{KOC}(\text{CH}_3)_3$   
**E** 1.  $\text{NaNH}_2$  then  $\text{CH}_3\text{I}$     2.  $\text{H}_2$  / Lindlar's catalyst    3.  $\text{CHBr}_3$  /  $\text{KOC}(\text{CH}_3)_3$

17.



18.

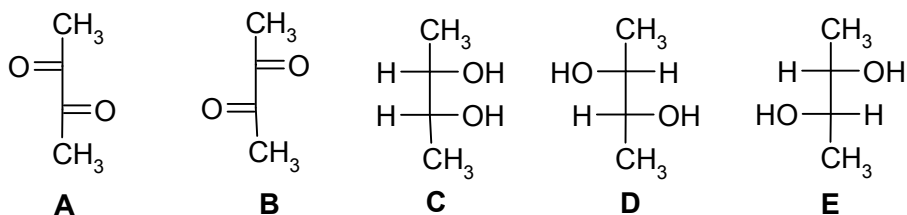
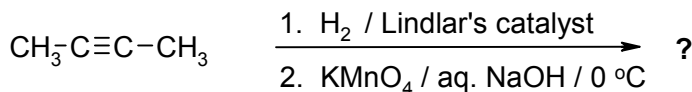


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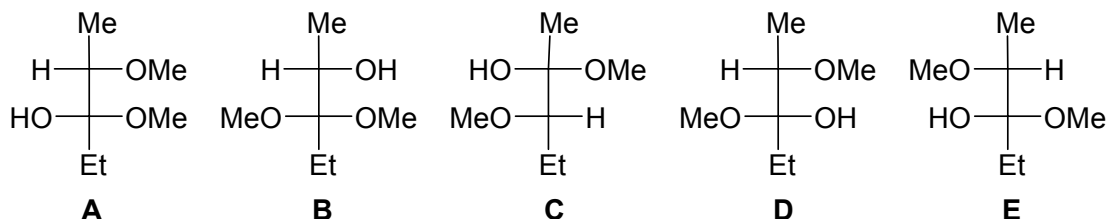
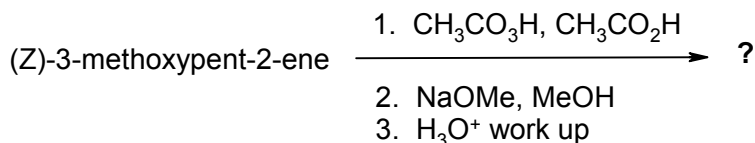
**PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS****18% ANSWER ANY SIX (6) OF QUESTIONS 19-25.**

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.

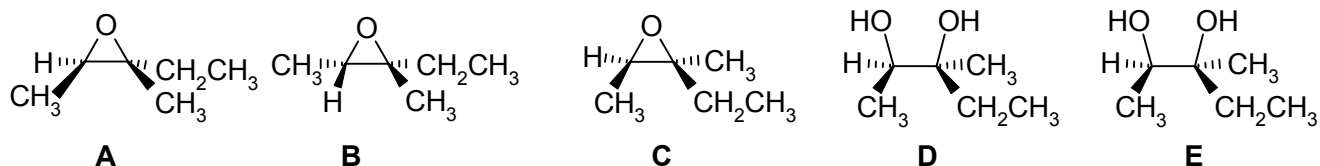
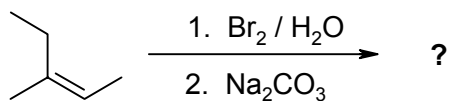
19.



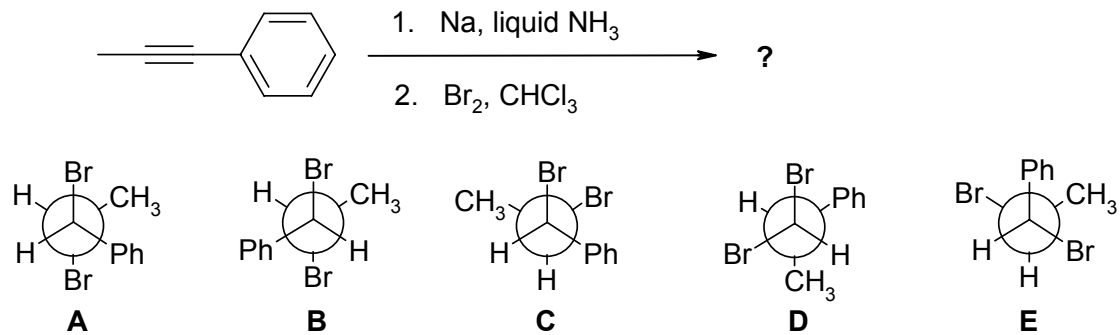
20.



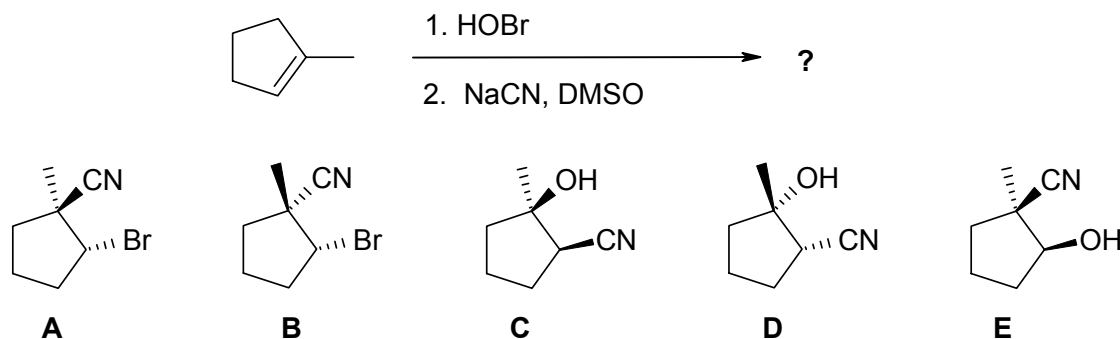
21.

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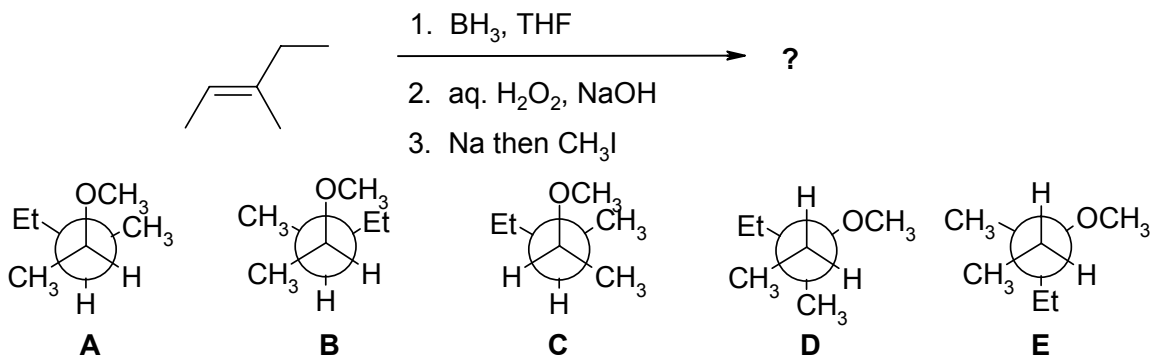
22.



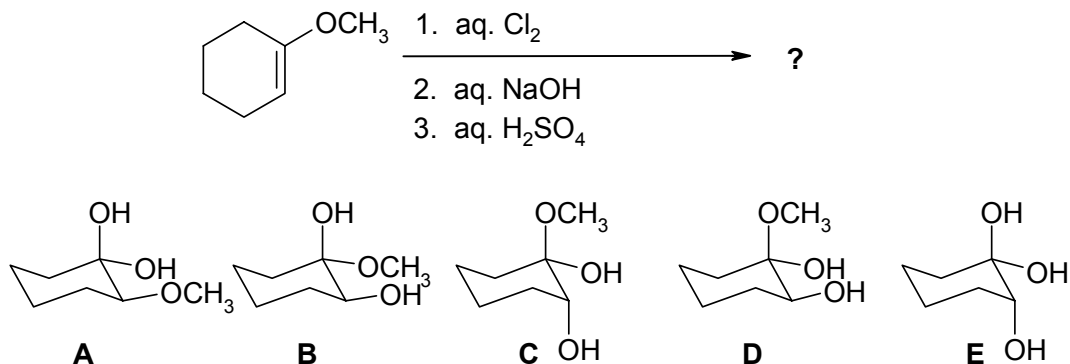
23.



24.



25.



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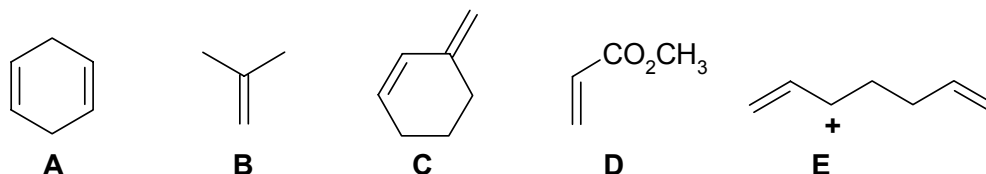


**PART 4: PI SYSTEMS**

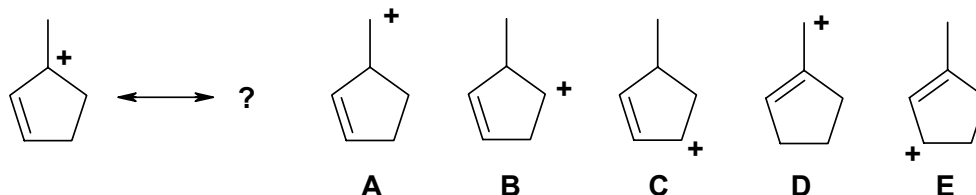
16% **ANSWER ANY EIGHT (8) of the questions 26 - 34.**

For each of the questions 26-34 select the appropriate answer from the answers provided. In questions 26-31 more than one selection may be required for full credit.

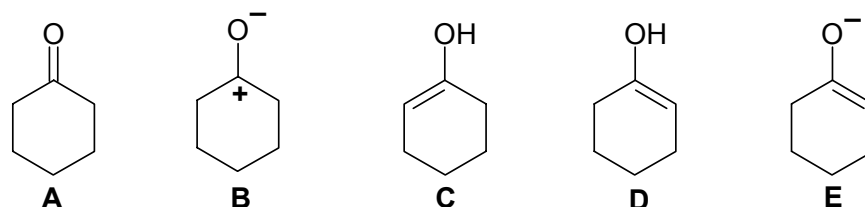
26. Which of the following molecules contain conjugated systems? (**select all that apply**)



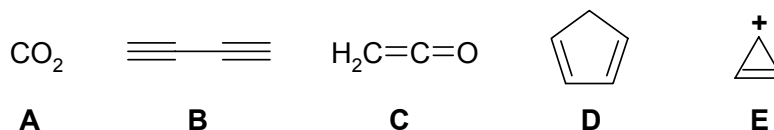
27. Which of the following systems are resonance contributors of the carbocation shown below? (**select all that apply**)



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

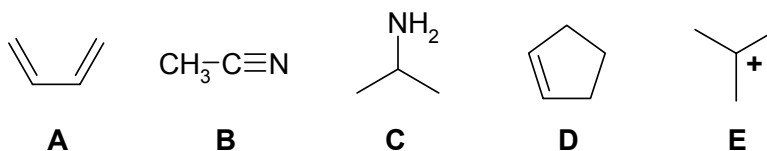


29. Which of the following molecules contain cumulated pi systems? (**select all that apply**)

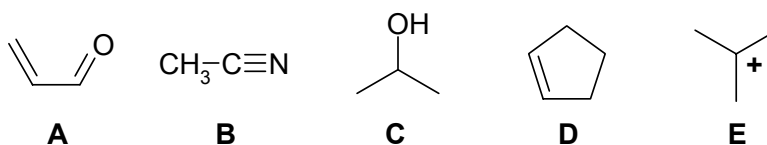


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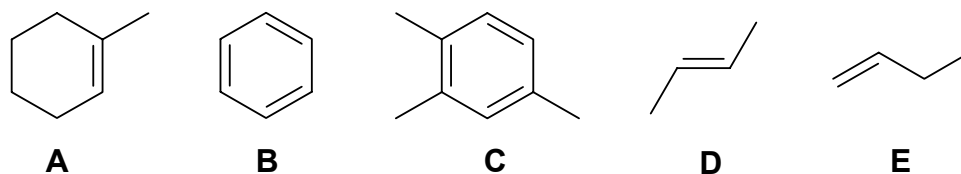
30. Which of the following molecules contain  $sp^2$  hybridised atoms ? (**select all that apply**)



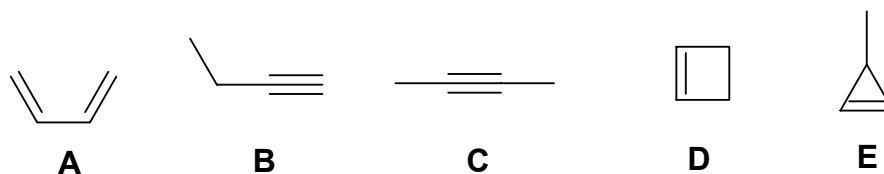
31. Which of the following molecules contain  $sp$  hybridised atoms ? (**select all that apply**)



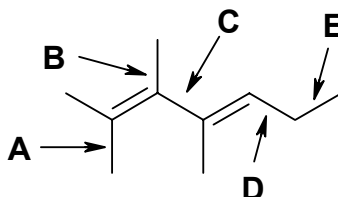
32. Which of the following systems has the **most** allylic hydrogens ?



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



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



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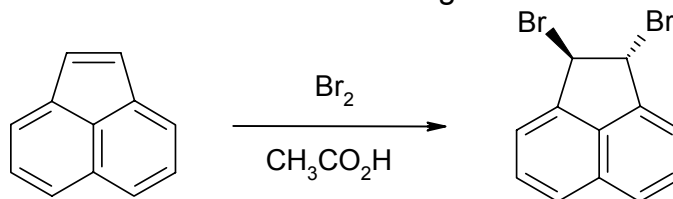
**PART 5: MECHANISMS**

10% ANSWER TWO (2) QUESTIONS, ONE FROM PART A and ONE FROM PART B

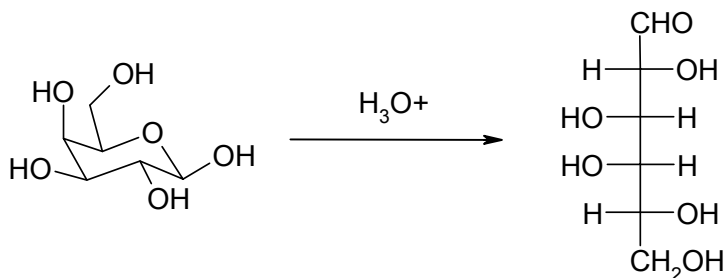
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Draw curly arrow mechanisms to explain the following reactions / observations.  
No other reagents are required.

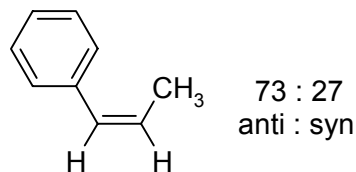
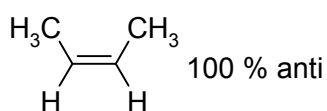
A. Show the mechanism for one of the following reactions:



OR

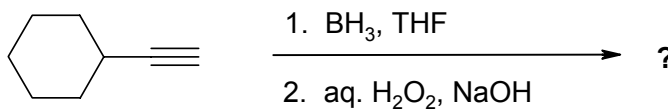


B. Provide a mechanistic explanation for the difference in the stereoselectivity of the addition of  $\text{Br}_2$  in  $\text{CH}_3\text{CO}_2\text{H}$  at 25 °C to the following alkenes:

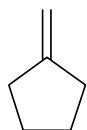
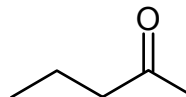
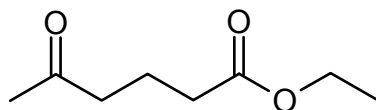
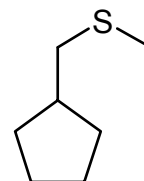
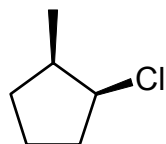


OR

Based on the hydroboration of alkenes and the hydration of alkynes, provide a mechanistic prediction of the product of the reaction shown below:



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**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)****Allowed starting materials and reagents****any compounds with 3 or less C atoms****In addition, you may use any solvents or 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.

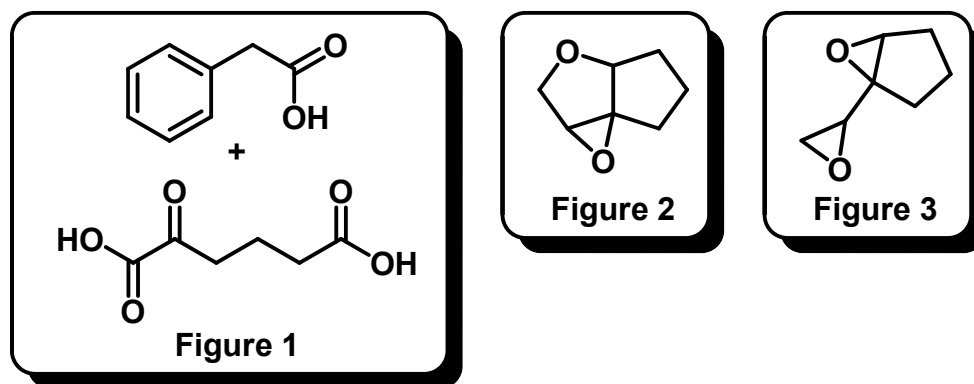
Compound **A** ( $C_7H_8$ ) was reacted with one equivalent of N-bromosuccinimide to produce **B** ( $C_7H_7Br$ ).

Compound **C** ( $C_7H_8$ ) was treated first with  $NaNH_2$  and then **B** to produce **D** ( $C_{14}H_{14}$ ). **D** underwent ozonolysis followed by an  $H_2O_2$  workup to give the two products shown in *figure 1*.

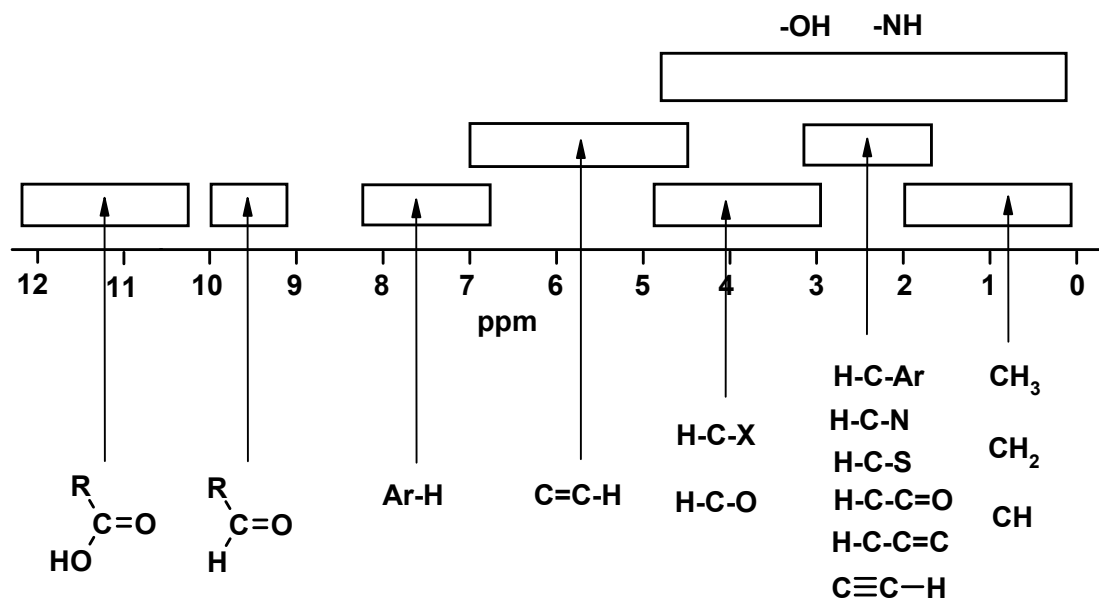
**C** was also reduced with sodium metal in liquid ammonia to give compound **E** ( $C_7H_{10}$ ). When **E** was reacted with one equivalent of  $Cl_2$  at  $-50\text{ }^\circ\text{C}$  it gave compound **F** ( $C_7H_{10}Cl_2$ ). However when **E** was reacted with one equivalent of  $Cl_2$  at  $80\text{ }^\circ\text{C}$  **G** was obtained. The help identify the regiochemistry of **F** and **G**, **F** was reacted with  $OsO_4$ ,  $(CH_3)_3COOH$  and excess  $KOH$  to give the product shown in *figure 2*. In contrast, when **G** was reacted with cold  $KMnO_4$  in excess  $KOH$  it gave the product shown in *figure 3*.

Draw the structures of compounds **A** to **G**.

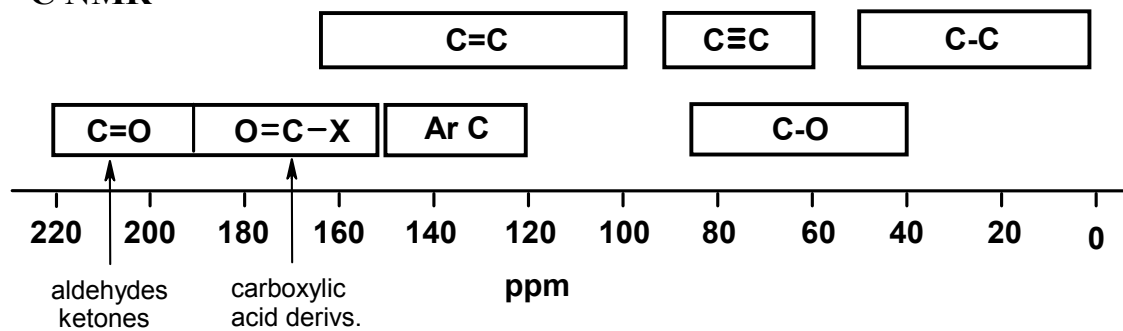
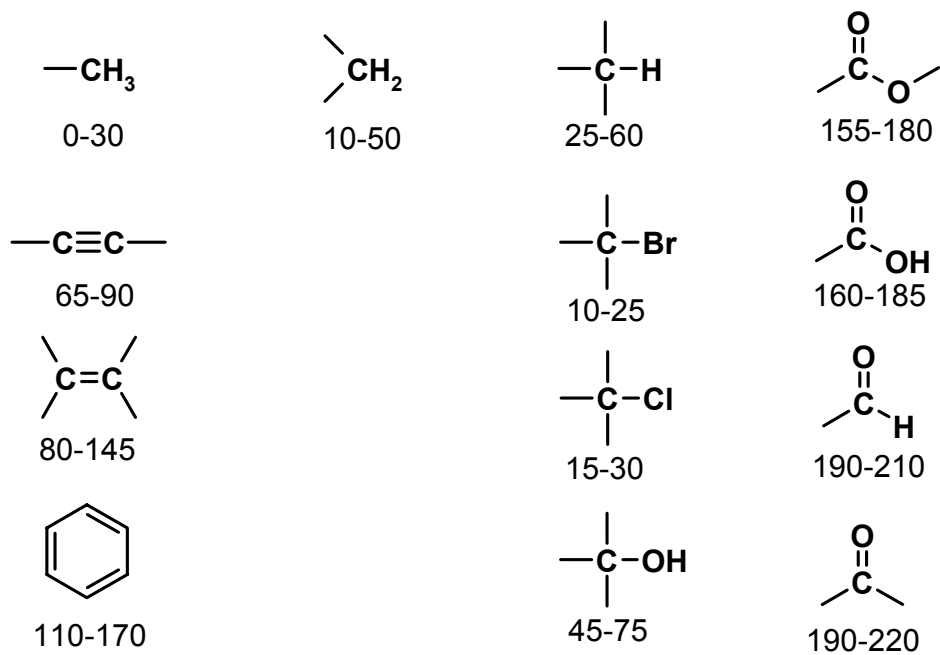
Is **F** the kinetic or thermodynamic product? Briefly justify your choice.



**\*\*\* THE END \*\*\***

**SPECTROSCOPIC TABLES** **$^1\text{H}$  NMR** **$^1\text{H}$  NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	methyl CH <sub>3</sub> -	methylene -CH <sub>2</sub> -	methyne CH	other	
$\begin{array}{c}   \\ \text{R}-\text{C}- \\   \end{array}$	0.9	1.4	1.5	-OH	1-5
$\begin{array}{c} \text{R} \\   \\ \text{C}=\text{C} \\   \end{array}$	1.6	2.3	2.6	-NH	1-3
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C} \end{array}$	2.1	2.4	2.5	C≡CH	2.5
$\begin{array}{c} \text{R}-\text{N} \\   \end{array}$	2.2	2.5	2.9	$\begin{array}{c} \text{H} \\   \\ \text{C}=\text{C} \\   \end{array}$	5.5
R-Ar	2.3	2.7	3.0	Ar-H	7.3
R-Br	2.7	3.3	4.1	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{H} \end{array}$	10
R-Cl	3.1	3.4	4.1	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{array}$	9-12
R-O-	3.3	3.4	3.7		

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

**INFRA-RED GROUP ABSORPTION FREQUENCIES**

		<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm<sup>-1</sup>)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>
C-H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	-CH <sub>3</sub>	(bend)	1450 and 1375	6.90 and 7.27	m
	-CH <sub>2</sub> -	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca. 3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C-C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
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 <sub>2</sub> )		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C-X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad.



## PERIODIC TABLE

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

## Lanthanides \*

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

## Actinides \*\*