

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 353

Version

1

Time: 2 Hours

THURSDAY MARCH 10th, 2022

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR BLUE BOOKLET AND OPTICAL SCORE ANSWER SHEET.

ENTER VERSION NUMBER 1 ON THE OPTICAL SCORE ANSWER SHEET

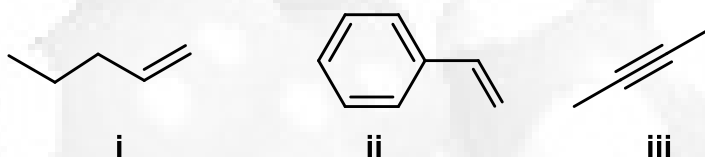
The exam consists of **Parts 1 - 7**, each of which should be attempted. Note that some Parts provide you with a choice of questions, e.g. answer any 5 out of 6. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. **Parts 1 - 4** will be computer graded, and **Parts 5, 6 and 7** are to be answered **IN BLUE OR BLACK INK IN THE BLUE 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 optical score answer sheet. Indicate your answer by blackening out the appropriate space(s) A, B, C, D or E on the answer sheet. Use a soft / dark 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**.

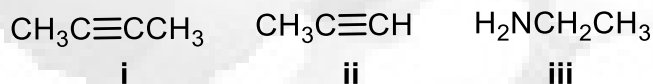
Molecular models are permitted during the exam; calculators are also permitted, **but NOT programmable calculators**. **Absolutely no other electronic devices are allowed.**

16% **PART 1: RELATIVE PROPERTIES****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.**

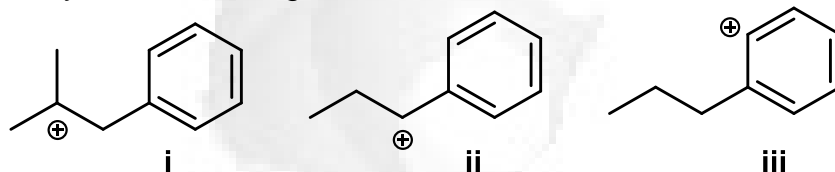
- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

1. The relative reactivity of each of the following towards aq. H₂SO₄:

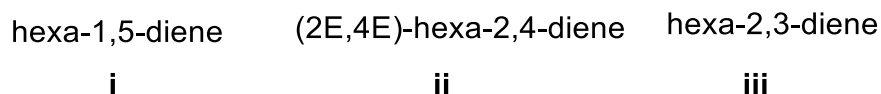
2. The relative acidity of each of the following:



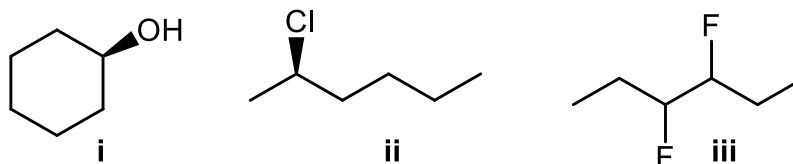
3. The relative stability of the following carbocations:



4. The relative stability of each of the following isomers:



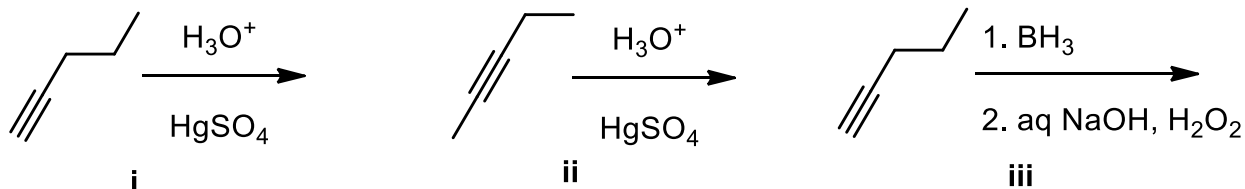
5. The number of configurational isomers of each of the following:



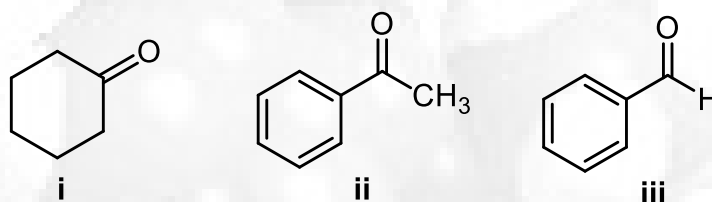
Use the following code to indicate your answers.

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

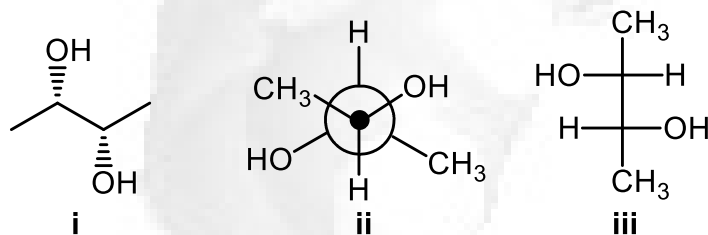
6. The relative yields of pentan-2-one from each of the following reactions:



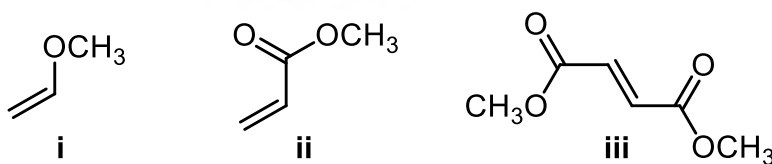
7. The number of alpha-H in each of the following:



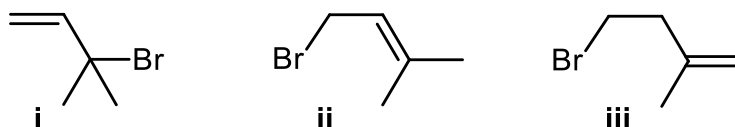
8. The specific rotations of each of the following molecules given that (2R,3R)-butan-2,3-diol has an $[\alpha]_D = -13.2^\circ$:



9. The relative reactivity towards 1,3-butadiene of each of the following:



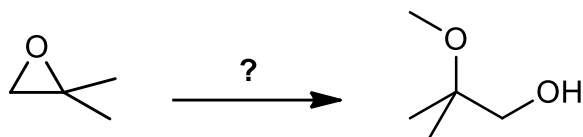
10. The relative yields of each of the following from the reaction of HBr / dark / N₂ with 2-methylbuta-1,3-diene at 60 °C:



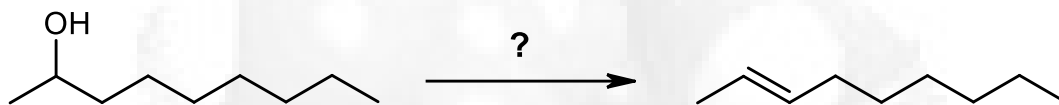
14% **PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS****ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**

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.

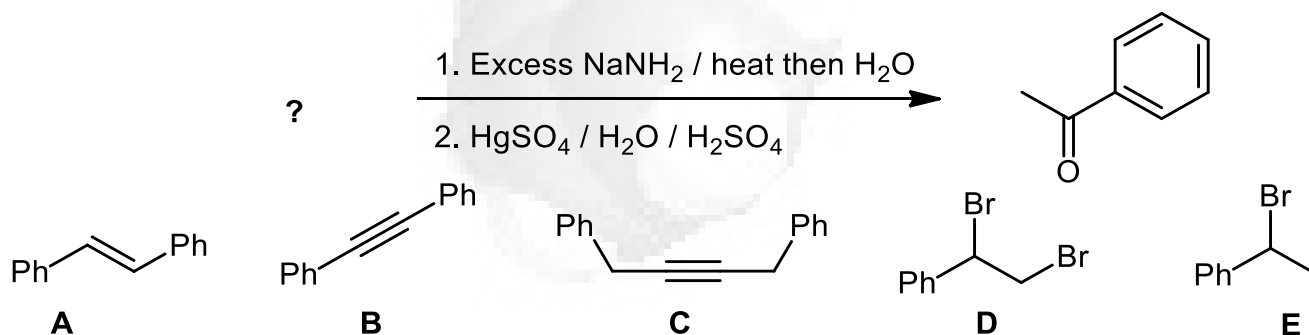
11.

**A** NaOH / ethanol**B** aq. H₂SO₄**C** CH₃OH / H⁺**D** aq. NaOH**E** CH₃ONa / CH₃OH

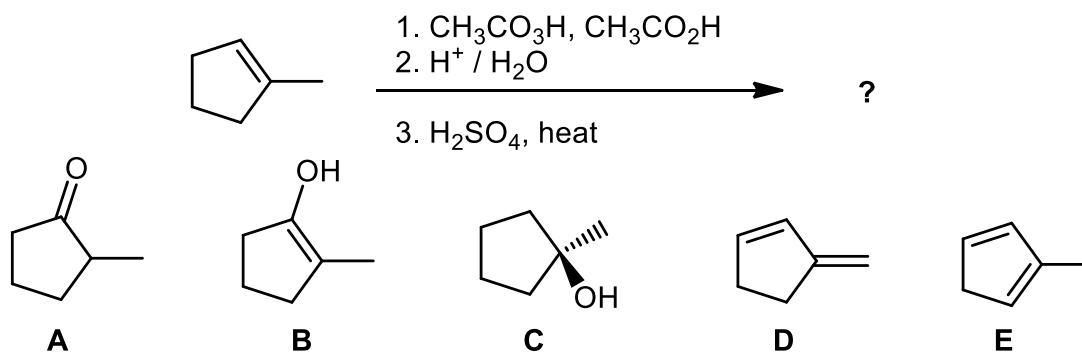
12.

**A.** conc. H₂SO₄ / heat**B.** HBr / heat**C.** NaOH / heat**D.** 1. H₂O / H₂SO₄
2. NaOH / heat**E.** 1. Br₂
2. KO^tBu / heat

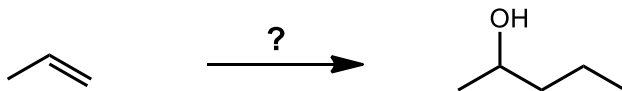
13.



14.



15.



A. 1. aq. KMnO_4 / NaOH
2. Na / bromoethane

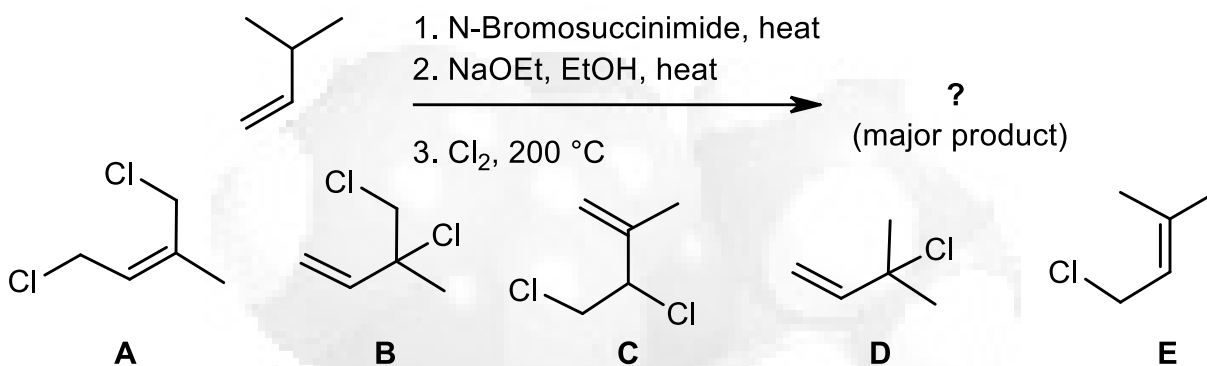
B. 1. HCl / H_2O
2. Na_2CO_3 / H_2O

C. 1. Na / bromoethane
2. HgSO_4 / H_2O / H_2SO_4

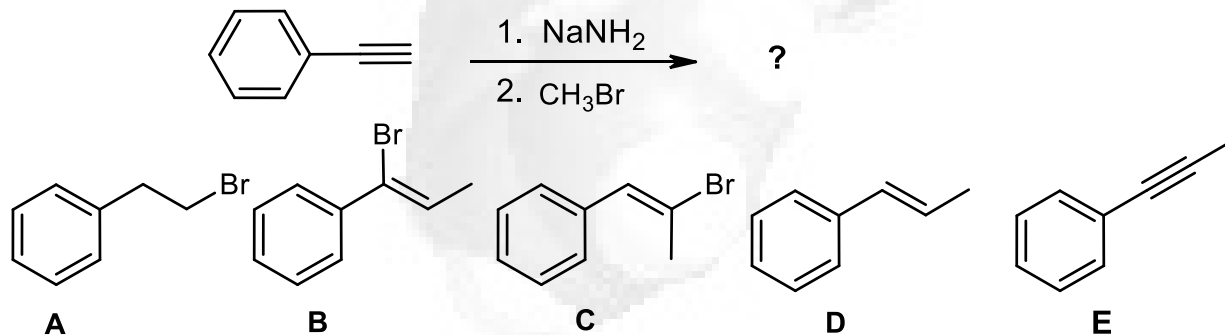
D. 1. $\text{CH}_3\text{CO}_3\text{H}$, $\text{CH}_3\text{CO}_2\text{H}$
2. $\text{HC}\equiv\text{CH}$ / NaNH_2 then H_2O
3. H_2 / Pd

E. 1. H_2 / Pd
2. O_3 then Me_2S
3. Na / bromoethane

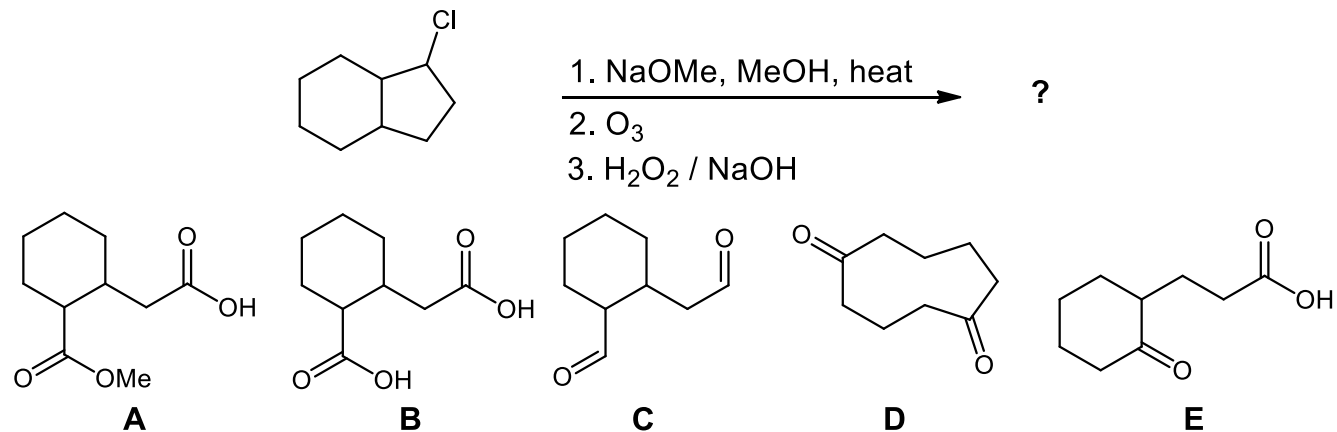
16.



17.



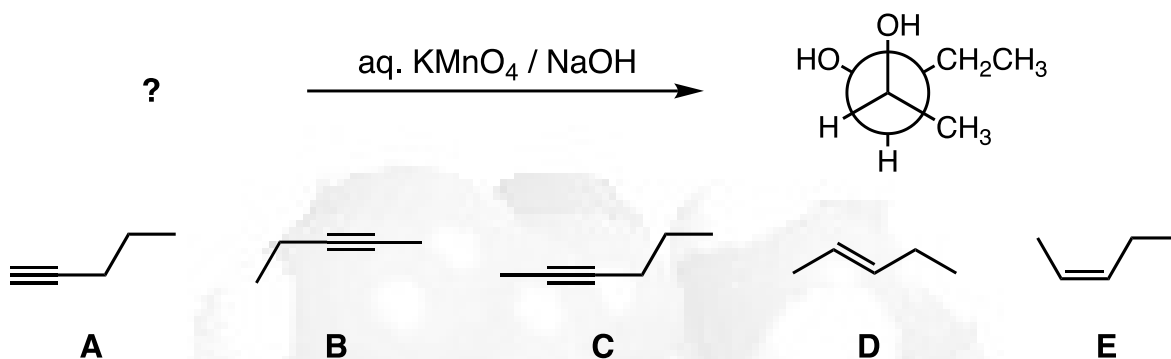
18.



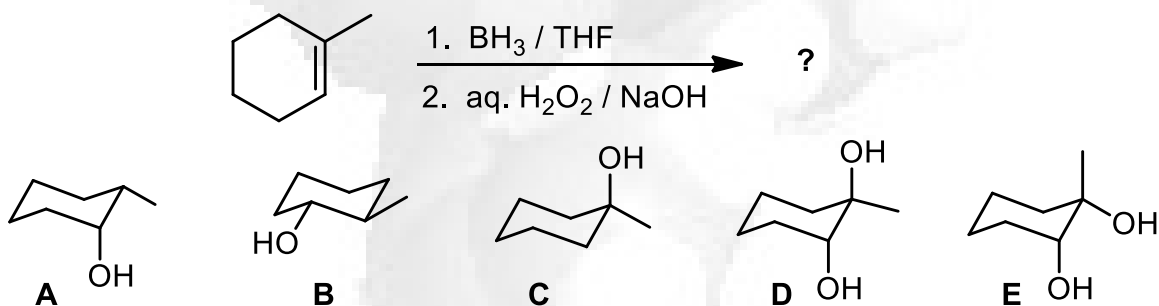
18% PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS**ANSWER ANY SIX (6) OF QUESTIONS 19-25.**

For each of the questions 19-25, select the **MISSING** component (the starting material, the product or the reagents) required in order to **BEST** complete each of the reaction schemes.

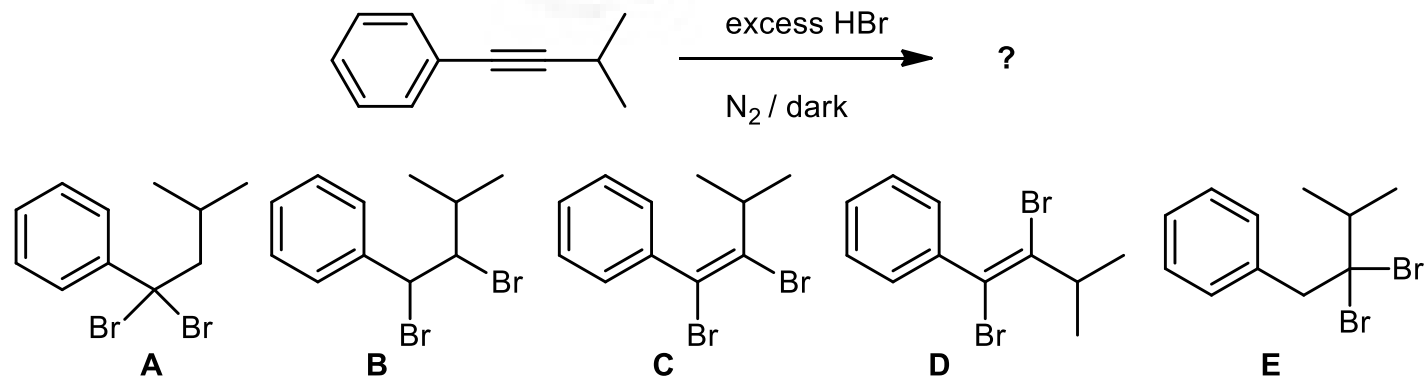
19.



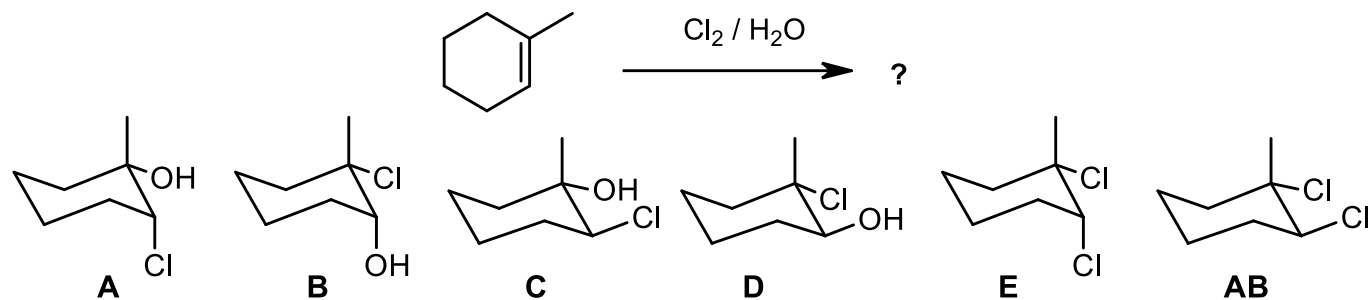
20.



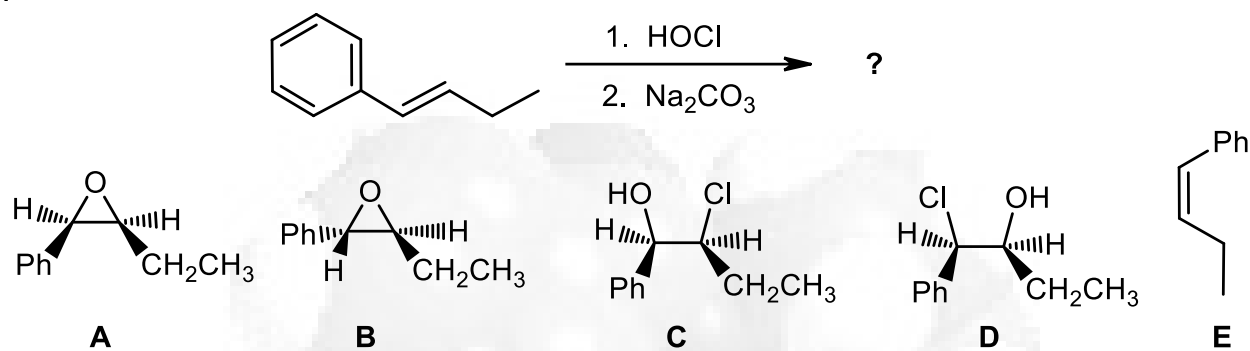
21.



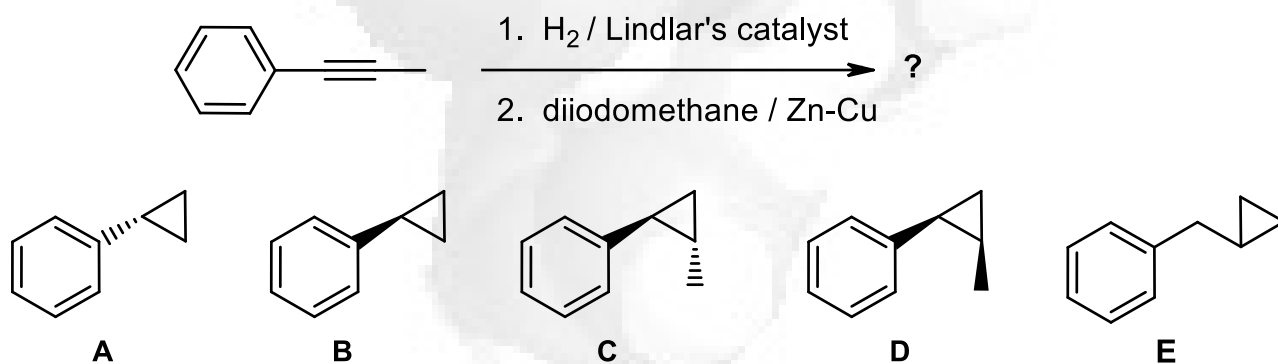
22.



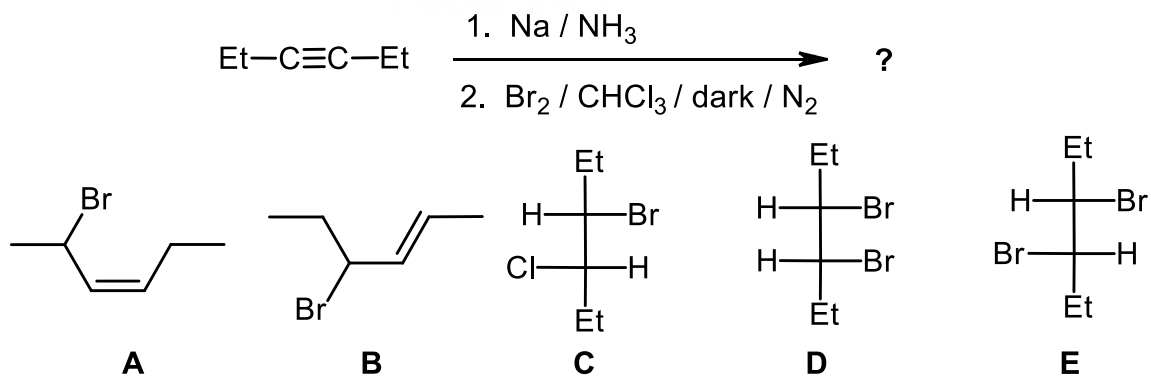
23.



24.



25.

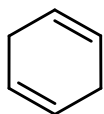


16% **PART 4: PI SYSTEMS**

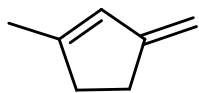
ANSWER ANY EIGHT (8) of the questions 26 - 34.

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

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



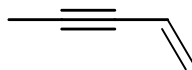
A



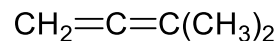
B



C



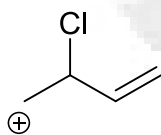
D



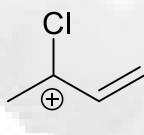
E

27. Which of the following systems are resonance contributors of the cation shown to the right ?

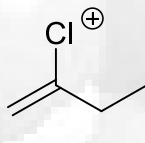
(select all that apply)



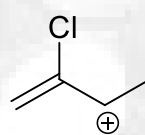
A



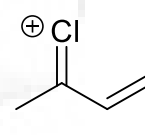
B



C

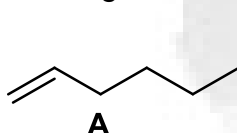


D

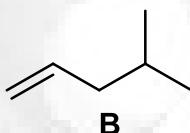


E

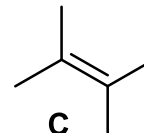
28. Which of the following isomers reacts **fastest** with HCl ?



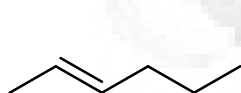
A



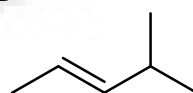
B



C

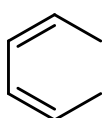


D

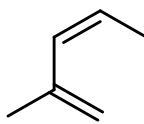


E

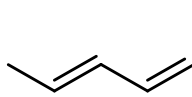
29. Which of the following isomers is the **least** stable as drawn ?



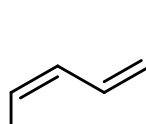
A



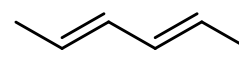
B



C

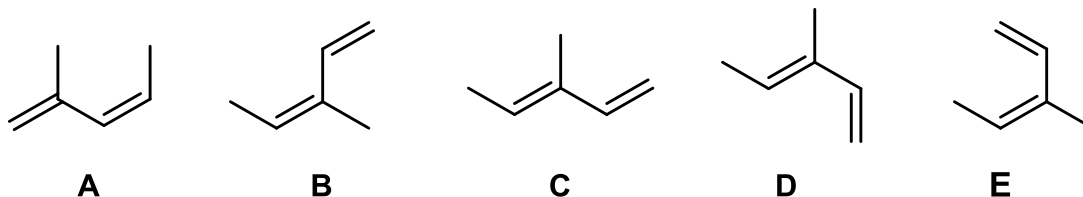


D

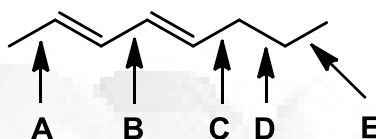


E

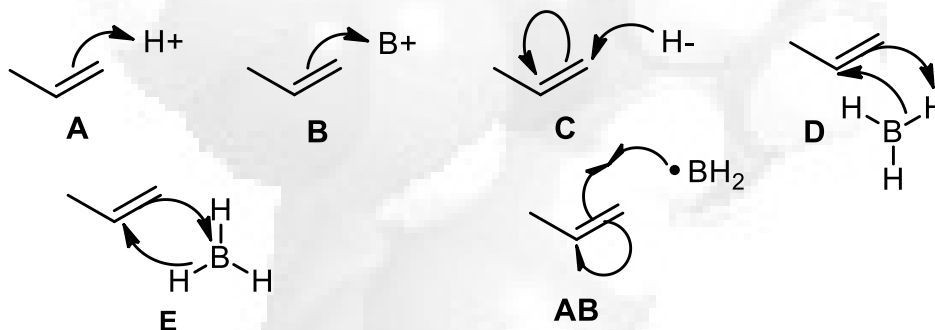
30. Which of the following molecules is the *s-trans* form of (3Z)-3-methylpenta-1,3-diene ?
(select all that apply)



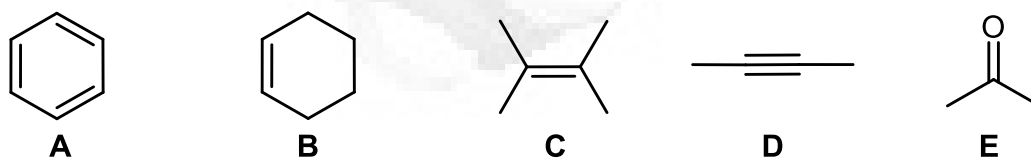
31. Which of the CC bonds indicated is the **shortest** ?



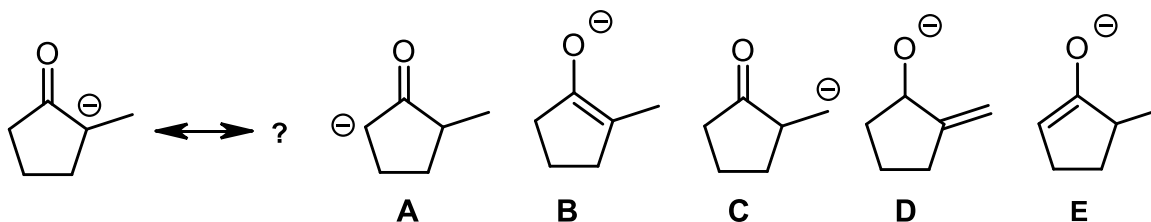
32. Which of the following **best** represents a step in the mechanism of the reaction of propene with BH_3 ?

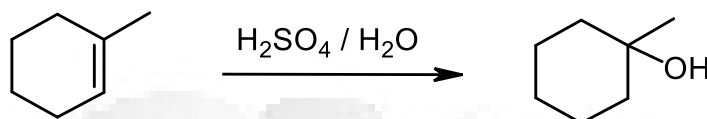
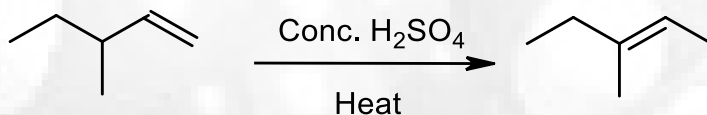
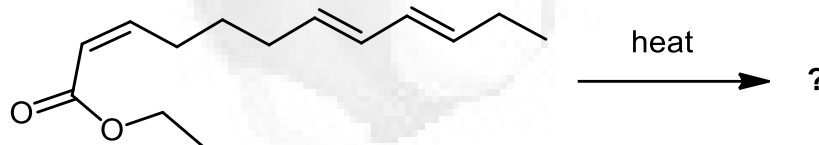
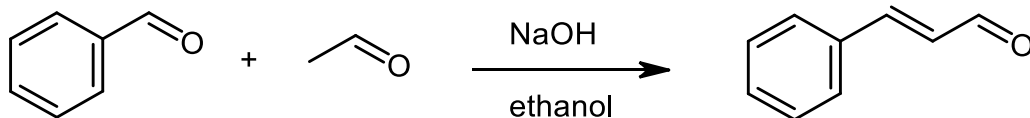


33. Which of the following systems would be the **most** reactive towards H_2 / Pd ?



34. Which of the following systems are resonance contributors of the anion shown below ?
(select all that apply)



10% **PART 5: MECHANISMS****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****AND****B.** Show the mechanism for **one** of the following reactions to give the major product and **briefly** justify the product formation :**OR**

15% PART 6: SYNTHESIS

ANSWER THREE (3) QUESTIONS, ONE FROM A, ONE FROM B AND ONE FROM C.

WRITE YOUR ANSWERS IN THE BLUE BOOKLET PROVIDED.

Design an efficient synthesis for THREE (3) of the following target molecules

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENTS REQUIRED AND PRODUCT OF EACH STEP.

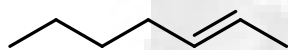
DO NOT SHOW MECHANISMS (*i.e.* curly arrows are NOT required)

Allowed starting materials and reagents :

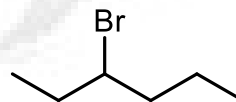
Any hydrocarbons with 5 or less C atoms

Any solvents or reagents that do not contribute carbon atoms to the final structure.

A

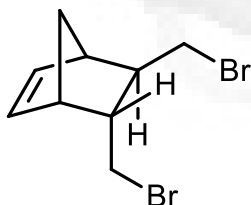


or

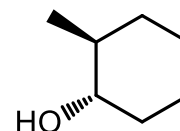


AND

B

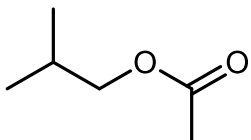


or

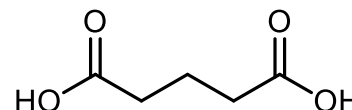


AND

C



or



11% PART 7: STRUCTURE DETERMINATION**WRITE YOUR ANSWER IN THE BLUE BOOKLET PROVIDED****Use the information in the following paragraph to answer the questions below.**

None of the materials **A - G** are chiral.

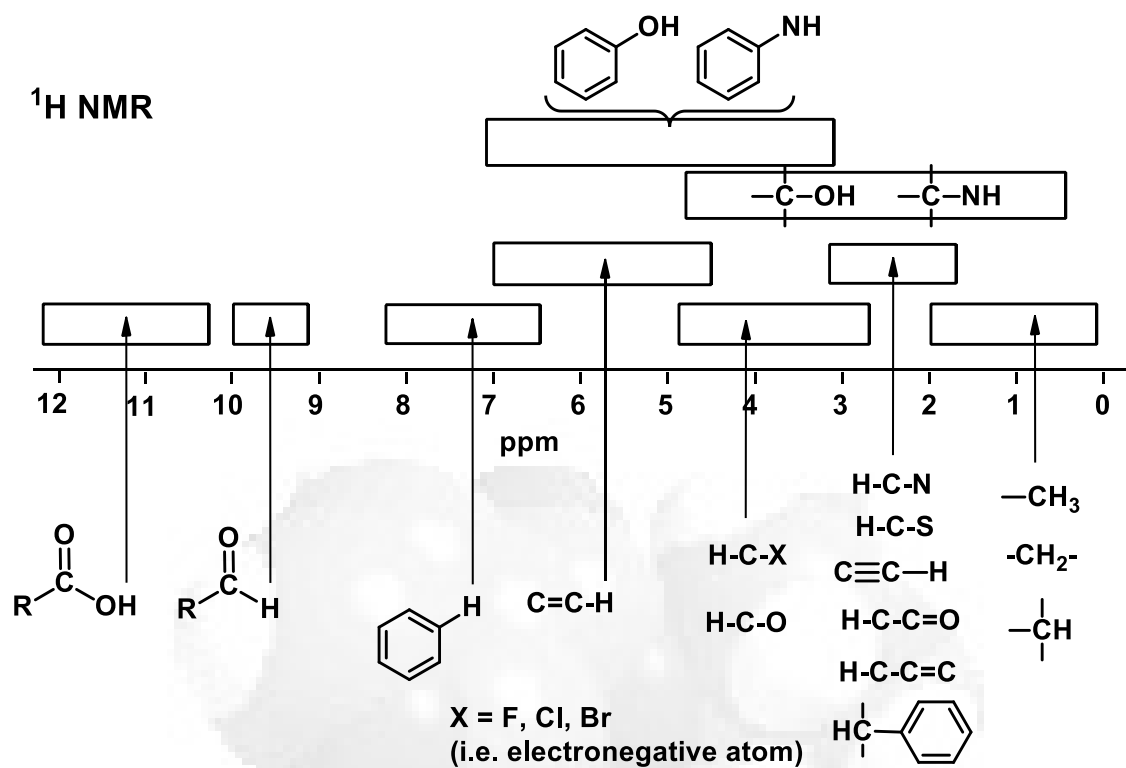
When **A**, $C_5H_{11}Br$, was reacted with hot, ethanolic KOH, **B**, C_5H_{10} was obtained, IR : 1680 cm^{-1} (w). **B** gave a colourless solution when tested with Br_2 in chloroform. Subsequent reaction of **B** with Br_2 under a uv lamp or with N-bromosuccinimide gave **C**, C_5H_9Br as the major product. When **B** was reacted BH_3 then aq. NaOH / H_2O_2 , **D** was the major product. Reaction of **D** with PBr_3 / Et_3N gave **A** as the major product. In contrast, reaction of **B** with aq. H_2SO_4 gave **E** as the major product. **E** spectral data : 1H -NMR: 1.8 ppm (broad, singlet, 1H), 1.5 ppm (quartet, 2H), 1.20 ppm (singlet, 6H) and 0.9 ppm (triplet, 3H), IR : 3500 cm^{-1} (very broad).

When **C** was reacted with hot, ethanolic KOH, **F**, C_5H_8 was formed. **F** was found to have 5 peaks in the ^{13}C -NMR. When **F** was heated in a sealed tube with ethene, it gave **G**, C_7H_{12} , as the major product. **G**, IR : 1660 cm^{-1} , 7 peaks in the ^{13}C -NMR. **G** also gave a colourless solution with Br_2 in chloroform. Subsequent reaction of **G** with ozone followed by hydrogen peroxide work up gave 6-oxo-heptanoic acid.

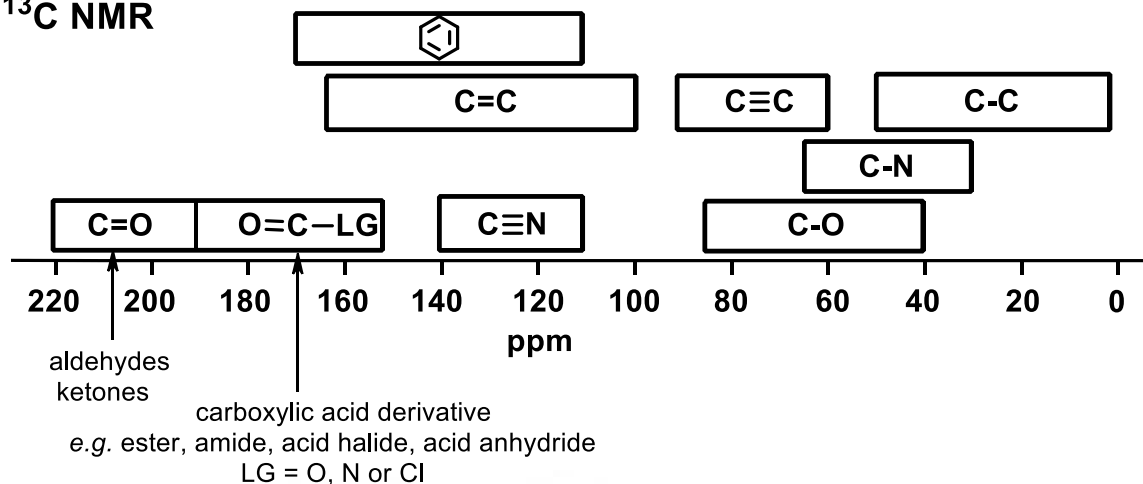
- Identify the compounds **A - G** (structures are sufficient)

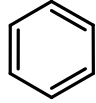
***** THE END *****

IRH / JvH / W22

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

	R = methyl	methylene	methylene	other
$\text{R}-\text{C}-$ CH_3	0.9	-CH ₂ - 1.4	-CH 1.5	sp ³ C-OH 1-5
$\text{R}-\text{C}=\text{C}$	1.6	2.3	2.6	sp ³ C-NH 1-3
$\text{R}-\text{C}(=\text{O})-$	2.1	2.4	2.5	$\text{C}\equiv\text{CH}$ 2.5
$\text{R}-\text{N}$	2.2	2.5	2.9	$\text{C}=\text{C}-\text{H}$ 4.5-6.5
$\text{R}-\text{C}_6\text{H}_5$	2.3	2.7	3.0	$\text{H}-\text{C}_6\text{H}_5$ 6.5-8
$\text{R}-\text{Br}$	2.7	3.3	4.1	$\text{R}-\text{C}(=\text{O})-\text{H}$ 9-10
$\text{R}-\text{Cl}$	3.1	3.4	4.1	$\text{R}-\text{C}(=\text{O})-\text{OH}$ 9-12
$\text{R}-\text{O}-$	3.3	3.4	3.7	

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

—CH_3 0-30	>CH_2 10-50	—C—H 25-60	—C(=O)—O— 155-180
$\text{—C}\equiv\text{C—}$ 65-90	>C=C< 80-145	—C—Br 10-40	—C(=O)—OH 160-185
 110-170		—C—Cl 20-50	—C(=O)—H 190-210
		—C—OH 45-75	—C(=O)— 190-220
		—C—N 30-65	$\text{—C}\equiv\text{N}$ 110-140

INFRA-RED GROUP ABSORPTION FREQUENCIES

		<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>	
C-H	Alkanes	(stretch)	3000-2850	3.33-3.51	s	
		-CH ₃	(bend)	1450 and 1375	6.90 and 7.27	m
		-CH ₂ -	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m	
		(bend)	1700-1000	5.88-10.0	s	
	Aromatics	(stretch)	3150-3050	3.17-3.28	s	
		(out-of-plane bend)	1000-700	10.0-14.3	s	
	Alkyne	(stretch)	ca. 3300	ca.3.03	s	
	Aldehyde		2900-2800	3.45-3.57	w	
			2800-2700	3.57-3.70	w	
C-C	Alkane	not usually useful				
C=C	Alkene		1680-1600	5.95-6.25	m-w	
	Aromatic		1600-1400	6.25-7.14	m-w	
C≡C	Alkyne		2250-2100	4.44-4.76	m-w	
C=O	Aldehyde		1740-1720	5.75-5.81	s	
	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	
	Acyl chloride		1800	5.55	s	
C-O	Alcohols, Ethers, Esters,					
	Carboxylic acids		1300-1000	7.69-10.0	s	
O-H	Alcohols, Phenols					
	Free		3650-3600	2.74-2.78	m	
	H-Bonded		3400-3200	2.94-3.12	m	
	Carboxylic acids (2)		3300-2500	3.03-4.00	m	
N-H	Primary and secondary amines		ca. 3500	ca. 2.86	m	
C≡N	Nitriles		2260-2240	4.42-4.46	m	
N=O	Nitro (R-NO ₂)		1600-1500	6.25-6.67	s	
			1400-1300	7.14-7.69	s	
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 may be 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
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 **