UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 15th 2011 Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON ***BOTH*** YOUR EXAM ANSWER BOOKLET AND COMPUTER ANSWER SHEET.

The examination consists of Parts 1 - 9, each of which should be attempted. Note that some Parts provide you with a choice of questions, *i.e*. answer 4 out of 5. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and Parts 6 - 9 are to be answered in the answer booklet provided. A periodic table with atomic numbers and atomic weights, and spectroscopic tables are appended to this examination paper.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 42, which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

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

Absolutely no other electronic devices are allowed.

Cont'd -->

15% PART 1: RELATIVE PROPERTIES

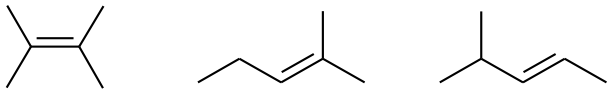
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

Arrange the items in questions 1-12 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.

Use the following code to indicate your answers.

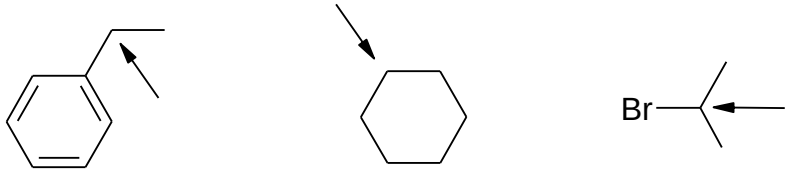
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of the following alkenes:



i **ii** **iii**

2. The number of lines in the H-NMR signals for the H atoms at the positions indicated in each of the following:



i **ii** **iii**

3. The relative leaving group ability of the **bold group** in each of the following:

R—**I** R—**NH_2** R—**OH**

i **ii** **iii**

4. The relative basicity of each of the following:

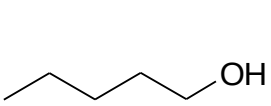
CH_3CH_2OH $CH_3CH_2CH_3$ $CH_3CH_2NH_2$

i **ii** **iii**

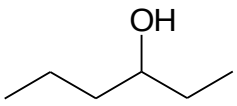
Use the following code to indicate your answers.

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

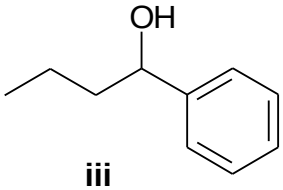
5. The relative rate of reaction of each of the following when heated with sulfuric acid:



i



ii

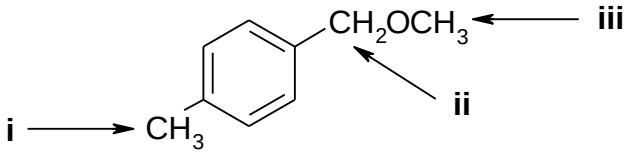


iii

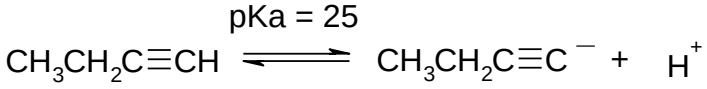
6. The relative rate of reaction of each of the following with NaI / acetone (propan-2-one):

i. 2-bromo-2-methylpropane **ii**. 2-bromopropane **iii**. bromobenzene

7. The ^{1}H-NMR chemical shifts for the groups indicated in the following structure:



8. The relative amount of the conjugate base of but-1-yne formed by the reaction of 1 mole equivalent of each of the following:

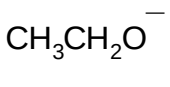


CH_3^-	HO^-	NH_2^-
i	**ii**	**iii**

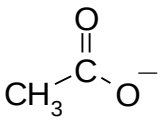
Use the following code to indicate your answers.

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

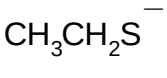
9. The relative nucleophilicity of the following in a polar, protic solvent:



i

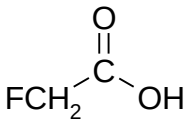


ii

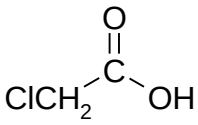


iii

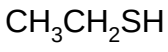
10. The relative acidity of each of the following:



i

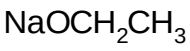


ii



iii

11. The relative yields of the Zaitsev (or Saytzeff) product produced by the reaction of 3-bromo-3-methylpentane with each of the following:

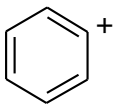


i

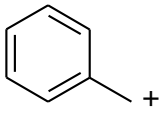
ii

iii

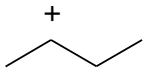
12. The relative stability of the following carbocations:



i



ii



iii

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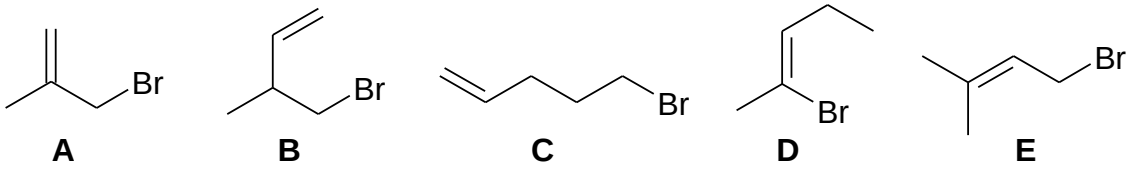
9% **PART 2: MOLECULAR PROPERTIES**

ANSWER ANY SIX (6) OF THE QUESTIONS 13 TO 20.

Use the structures below to answer questions 13-15.



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

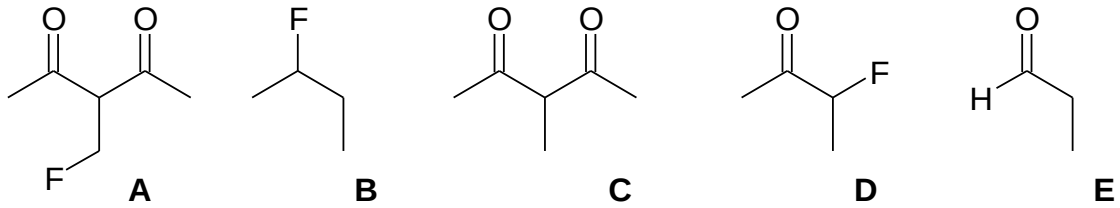
Which of the above structures:

13. Undergoes the *fastest* reaction with $AgNO_3$ in CH_3CH_2OH / H_2O solution ?

14. Undergoes the *slowest* reaction when treated with NaI in acetone ?

15. Forms the most stable diene when heated with potassium t-butoxide in t-butanol ?

Use the structures below to answer questions 16-18.



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

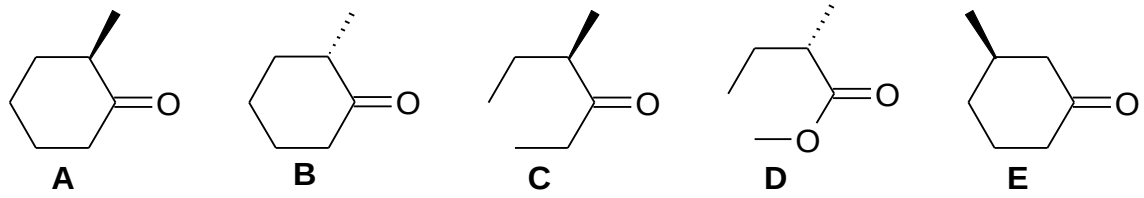
Which of the above structures:

16. Has the H with the most deshielded chemical shift in its H NMR spectrum ?

17. Has the most acidic hydrogen ?

18. Is most likely to undergo an E1cB reaction when heated with sodium methoxide ?

Use the structures below to answer questions 19-20.



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

19. Select any two molecules that would have the same melting point.

20. Which of the above structures is a constitutional isomer of methoxycyclohexane ?

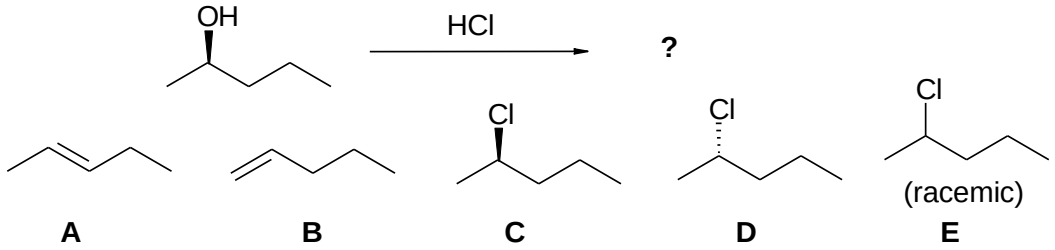
Cont'd -->

14% PART 3: REACTIONS

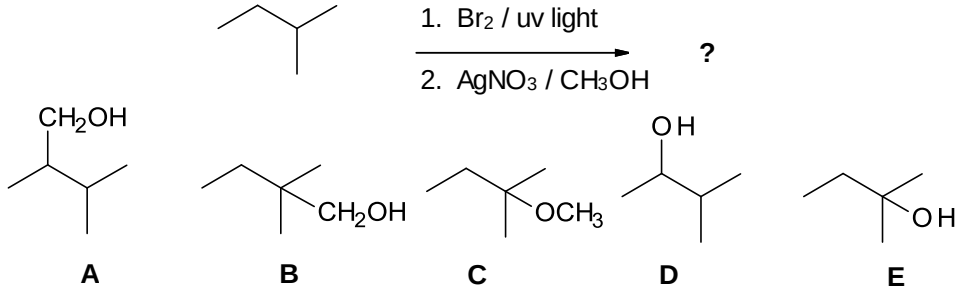
ANSWER ANY SEVEN (7) OF QUESTIONS 21 TO 28.

For each of questions 21-28 select the MISSING component (the best starting material, the major product or the best reagents) required in order to BEST complete each of the reaction schemes.

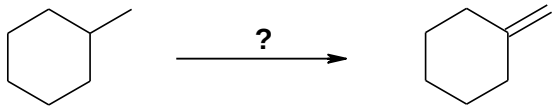
21.



22.



23.



A 1. Br_2 / uv light
2. NaCN, cold

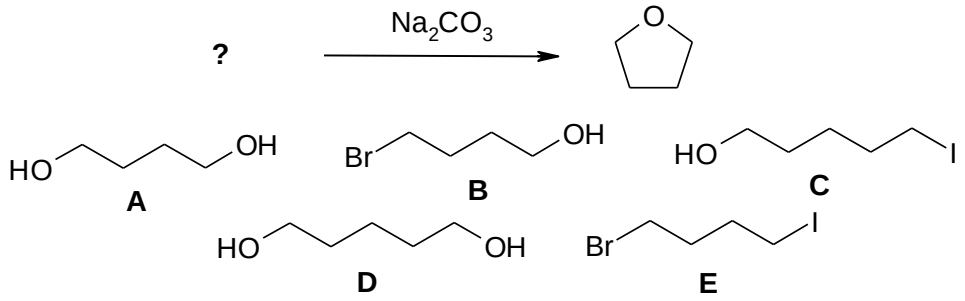
B 1. Cl_2 / uv light
2. NaOEt / EtOH / heat

C H_2SO_4 / heat

D 1. Br_2 / uv light
2. KO^tBu / ^tBuOH / heat

E NaOEt / EtOH / heat

24.



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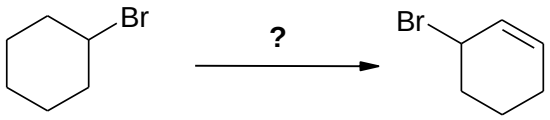
25.



A Br_2 / $FeBr_3$

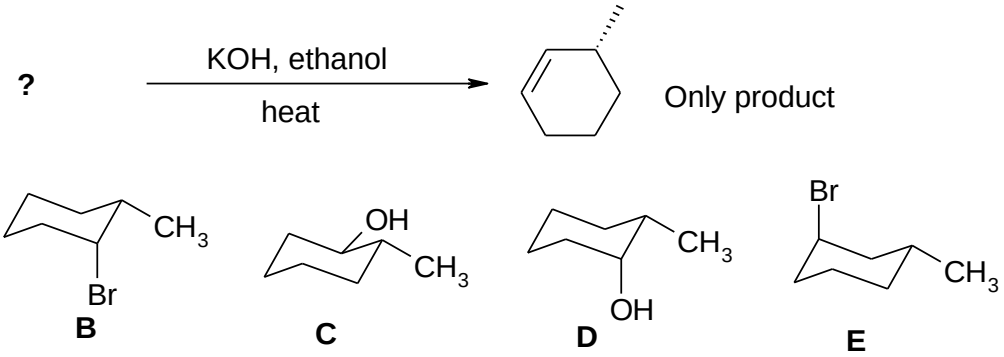
B NaOEt / EtOH / heat

C 1. KO^{t}Bu / ^{t}BuOH / heat
2. Br_2 / uv light

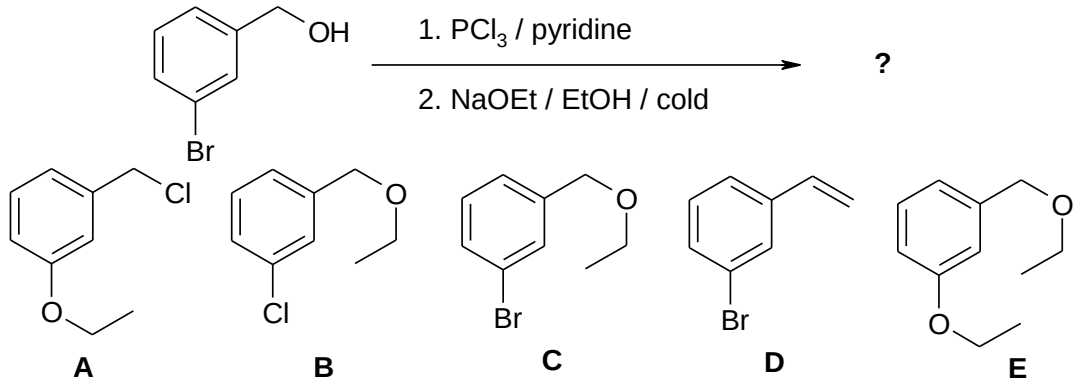
D 1. KO^{t}Bu / ^{t}BuOH / heat
2. Br_2

E 1. NaOEt / EtOH / cold
2. Br_2 / uv light

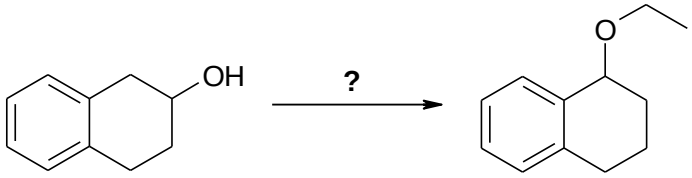
26.



27.



28.



A 1. TsCl / pyridine
2. NaOEt / HOEt / cold

B 1. HBr
2. NaOEt / HOEt / cold

C 1. H_2SO_4 / heat
2. Br_2
3. EtOH

D EtOH / heat

E 1. $SOCl_2$ / NEt_3
2. ethyl iodide

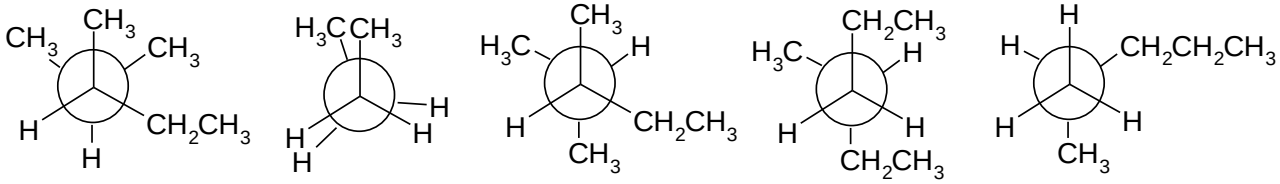
Cont'd -->

12% PART 4: CONFORMATIONAL ANALYSIS

ANSWER SIX (6) OF THE QUESTIONS 29 TO 36.

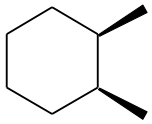
For each of the questions 29-36 select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

29. Which of the following Newman projections represent conformations of 2-methylpentane ?



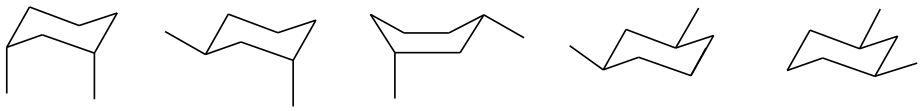
A **B** **C** **D** **E**

30. What is the **torsional** angle between the two methyl groups in the most stable conformation of the substituted cyclohexane shown below ?



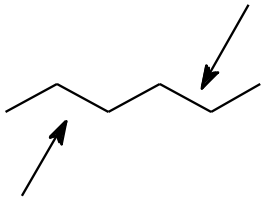
A 0° **D** 109.5°
B 60° **E** 120°
C 90° **AB** 180°

31. Which of the following structures represents the lowest energy conformations of trans-1,3-dimethylcyclohexane ?



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

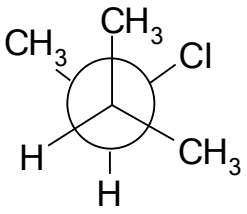
32. Which of the following terms **best** describes the relative position of the two indicated bonds in the hexane conformation shown below?

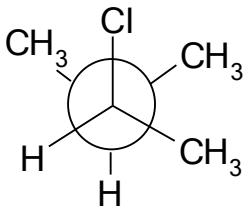


A eclipsed
B staggered
C anti
D cis
E gauche
AB trans
AC flagpole

Cont'd -->

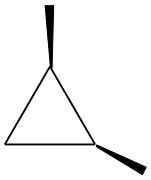
33. Which of the following terms **best** describes the relationship between the two molecules shown below ?





A constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB meso
AC not isomers

34. Which of the following term(s) can be used to describe the strain(s) present in cis-1,2-dimethylcyclopropane ?

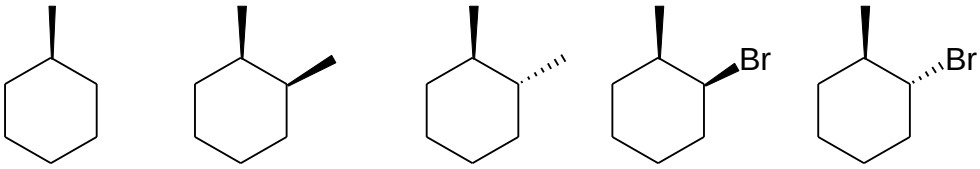


A Van der Waals
B Torsional (eclipsing)
C 1,3-Diaxial
D Flagpole
E Ring

35. Which of the following C_5H_{10} isomers has the most exothermic heat of formation ?

A cis-1,2-dimethylcyclopropane
B trans-1,2-dimethylcyclopropane
C 1,1-dimethylcyclopropane
D methylcyclobutane
E cyclopentane

36. Which of the following structures have two chair conformations of equal energy ?



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

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12% PART 5: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 37 TO 42.

For each of questions 37-42 select the compound from the list provided that corresponds BEST with the spectroscopic data provided. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, p= pentet, m = multiplet.

37. **^{1}H NMR** : δ 3.7 ppm (singlet, 3 H), 7.0 ppm (singlet, 1 H).
IR = 1735 cm^{-1}

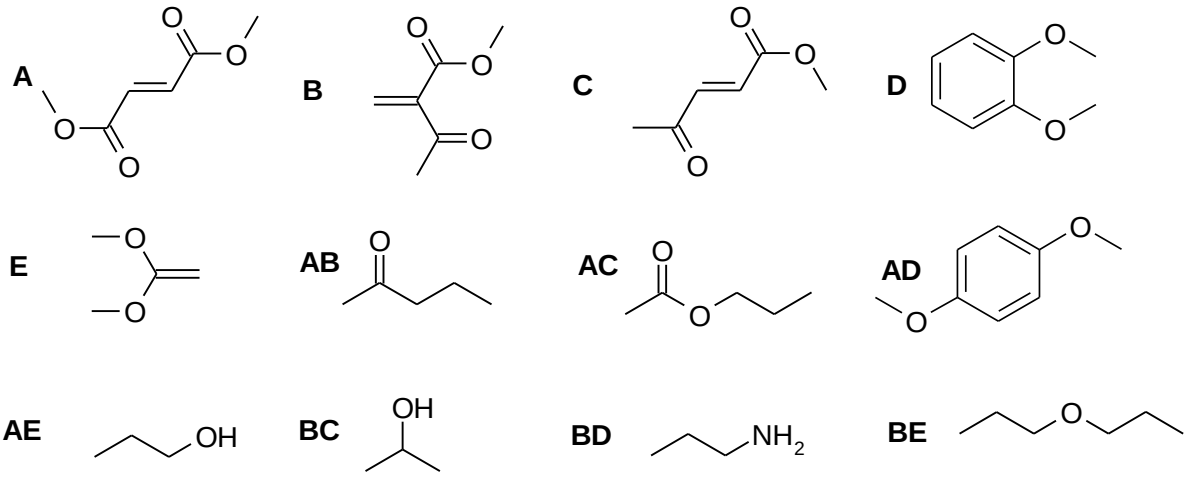
38. **^{1}H NMR** : δ 1.0 ppm (triplet, 3 H), 1.6 ppm (sextet, 2 H), 2.0 ppm (singlet, 3 H), 4.1 ppm (triplet, 2 H).
IR = 1745 cm^{-1}

39. **^{1}H NMR** : δ1.0 ppm (triplet, 3 H), 1.5 ppm (sextet, 2 H), 3.4 ppm (triplet, 2 H).

40. **^{1}H NMR** : δ 2.3 ppm (singlet, 3 H), 3.8 ppm (singlet, 3 H), 6.9 ppm (doublet, *J*=16 Hz, 1 H), 7.3 ppm (doublet, *J* = 16 Hz, 1 H).
IR = 1725, 1675 and 1645 cm^{-1}

41. **^{1}H NMR** : δ 0.9 ppm (triplet, 3H) 1.6 ppm (sextet, 2 H), 2.3ppm (broad singlet, exchangeable, 1H), 3.6 ppm (triplet, 2H)
IR = ~ 3400 cm^{-1} (broad)

42. **^{1}H NMR** : δ 0.92 ppm (triplet, 3H) 1.24ppm (broad singlet, exchangeable, 2H) 1.45 ppm (sextet, 2 H), 2.65 ppm (triplet, 2H)
IR = ~ 3370, 3291 cm^{-1}



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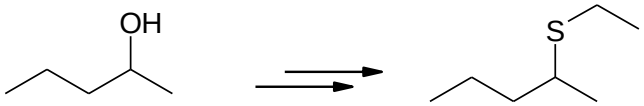
8% PART 6: SYNTHESIS

DESIGN EFFICIENT SYNTHESES OF ANY TWO (2) of the following target molecules from the indicated starting materials. In addition, you are allowed to use any hydrocarbon with three or fewer carbon atoms, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the carbon skeleton in the product. More than one step will be required for each synthesis. Clearly show the required reagents and the product of each step.

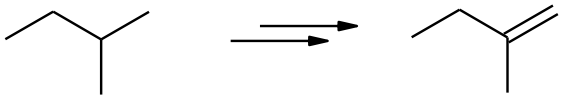
WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

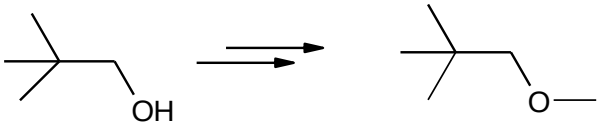
A.



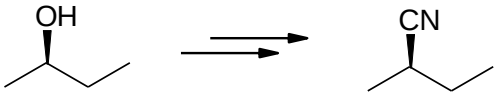
B.



C.



D.

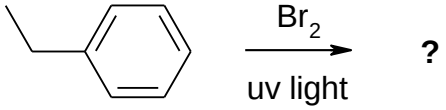


9% PART 7: MECHANISMS

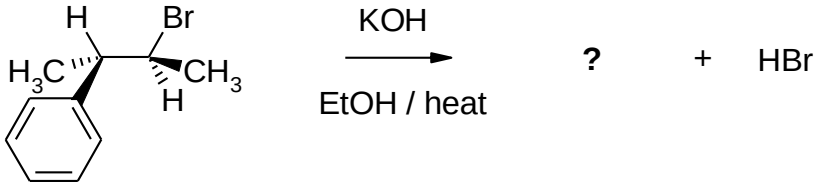
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Use curly arrows to show the mechanism in order to explain **ANY TWO** of the following:

A Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



B Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



C Draw the mechanism to explain the following reaction.

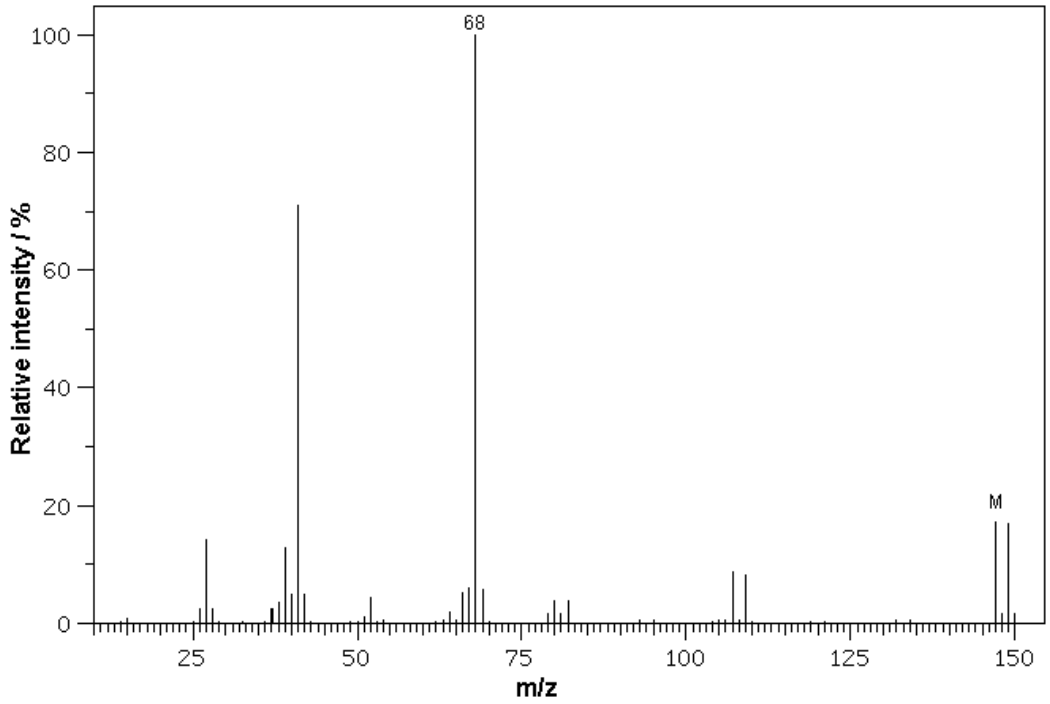
Cont'd -->

10% **PART 8: SPECTROSCOPY**

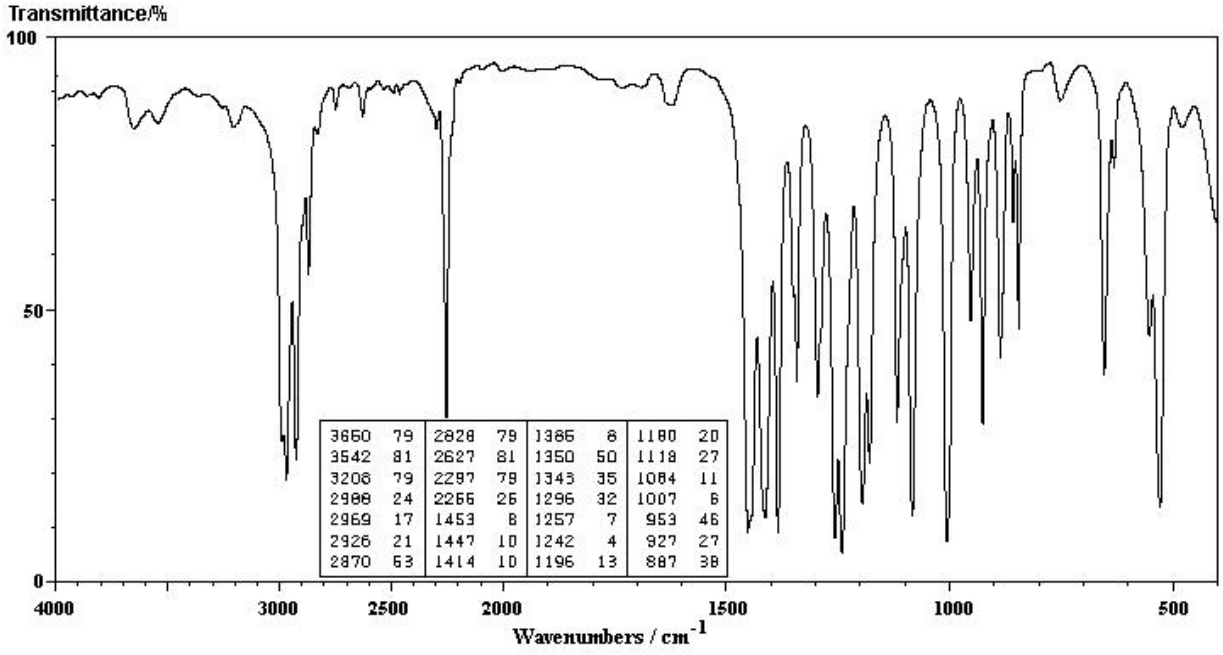
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

From the spectral data provided below, identify the structure of the "unknown" molecule.

Mass Spectrum:

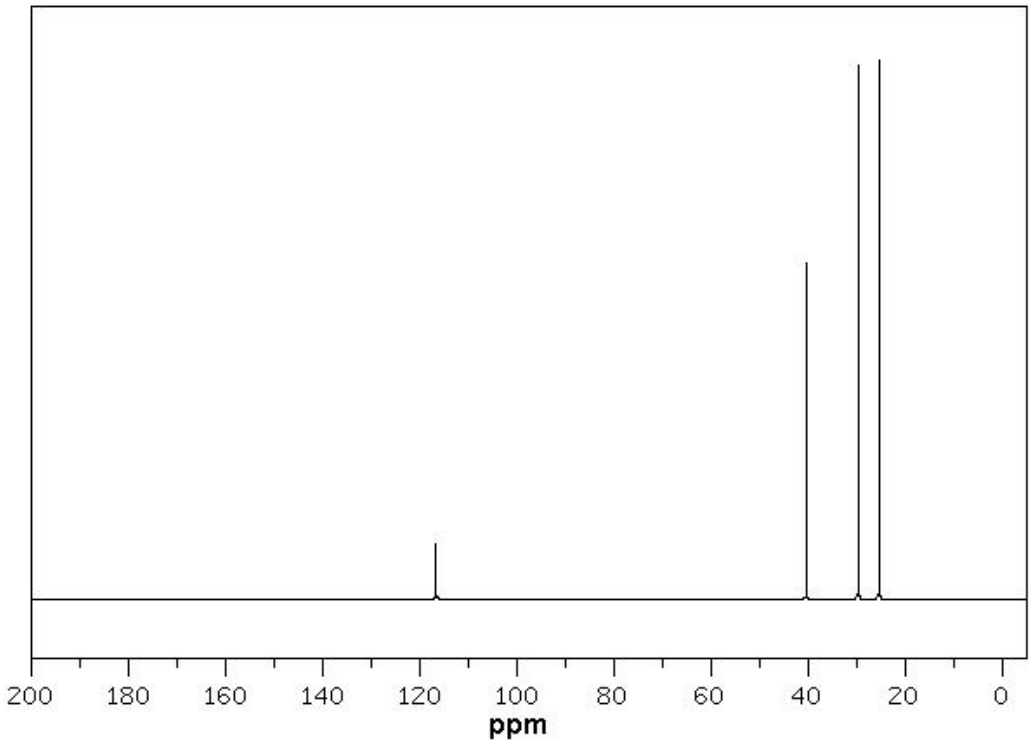


IR Spectrum:

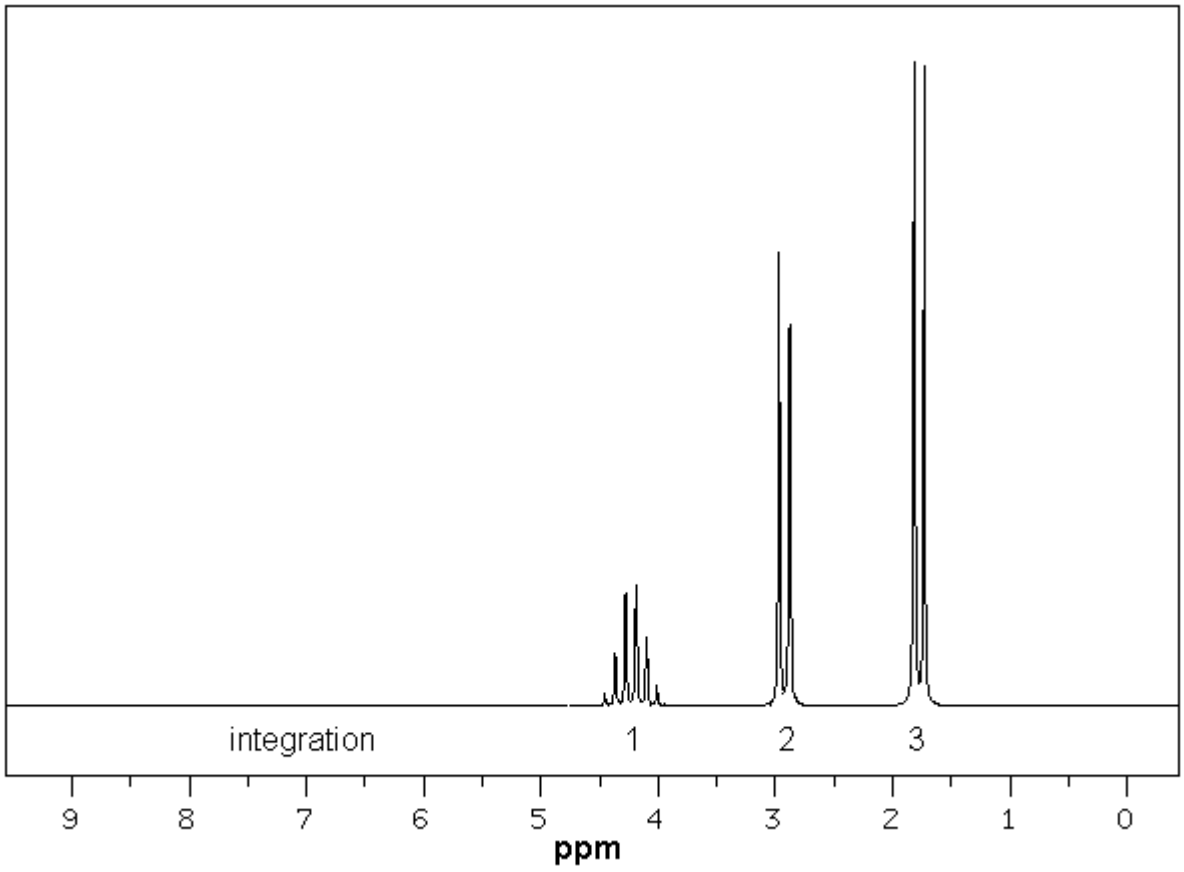


Cont'd -->

^{13}C-NMR:



^{1}H-NMR:



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11% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

An alkyl bromide **A**, $C_5H_{11}Br$, which contains a chiral centre, was reacted with aqueous Na_2CO_3 solution to give **B** $C_5H_{12}O$ (IR : 3500cm^{-1}, broad) as the major product.

Reaction of **B** with HBr gave **C** a constitutional isomer of **A**. When **C** was heated with KOH / ethanol, the major product was **D**, C_5H_{10} (IR : 1650cm^{-1}). **C** could also be obtained on reaction of 2-methylbutane with bromine / uv light.

In contrast, reaction of **A** with KOtBu / t-butanol/ heat gave **E**, which was a constitutional isomer of **D**. Reaction of **C** with KOtBu / t-butanol/ heat gave **F**, another constitutional isomer of **D**

i. Identify **A-F** (only structures are needed)

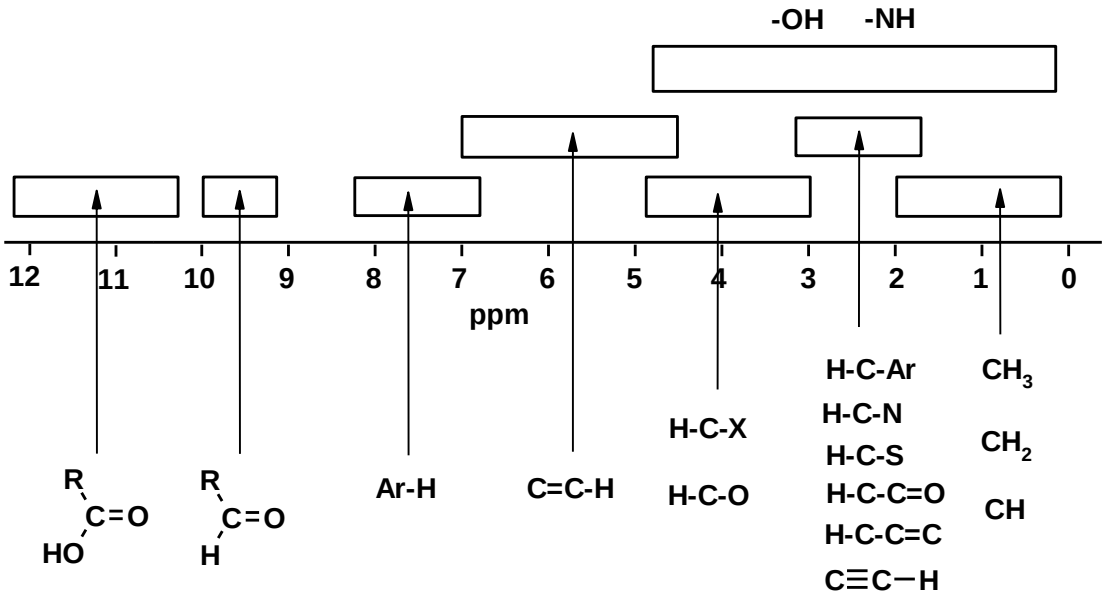
ii. Indicates how many types of carbon are present in then structures you have drawn for **A, D and F**

iii. Give the complete name of one enantiomer of **A**

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

SPECTROSCOPIC TABLES

^{1}H NMR



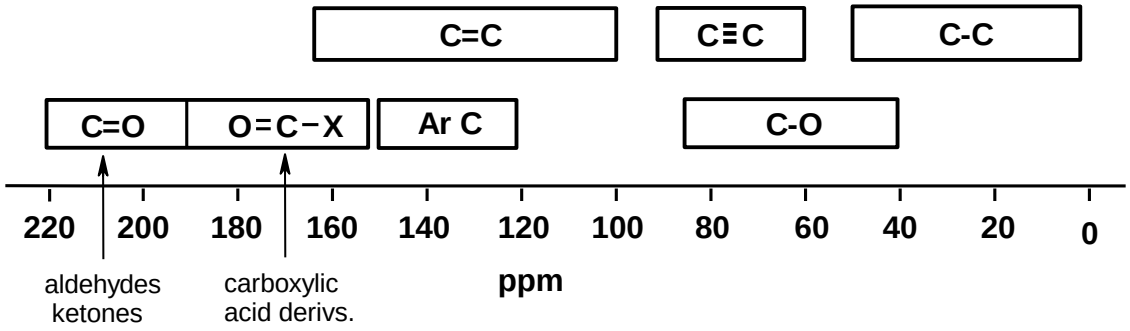
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	methyl CH_3-	methylene -CH_2-	methyne CH
R−C—	0.9	1.4	1.5
R C=C	1.6	2.3	2.6
O C R	2.1	2.4	2.5
R−N	2.2	2.5	2.9
R-Ar	2.3	2.7	3.0
R−Br	2.7	3.3	4.1
R−Cl	3.1	3.4	4.1
R−O—	3.3	3.4	3.7

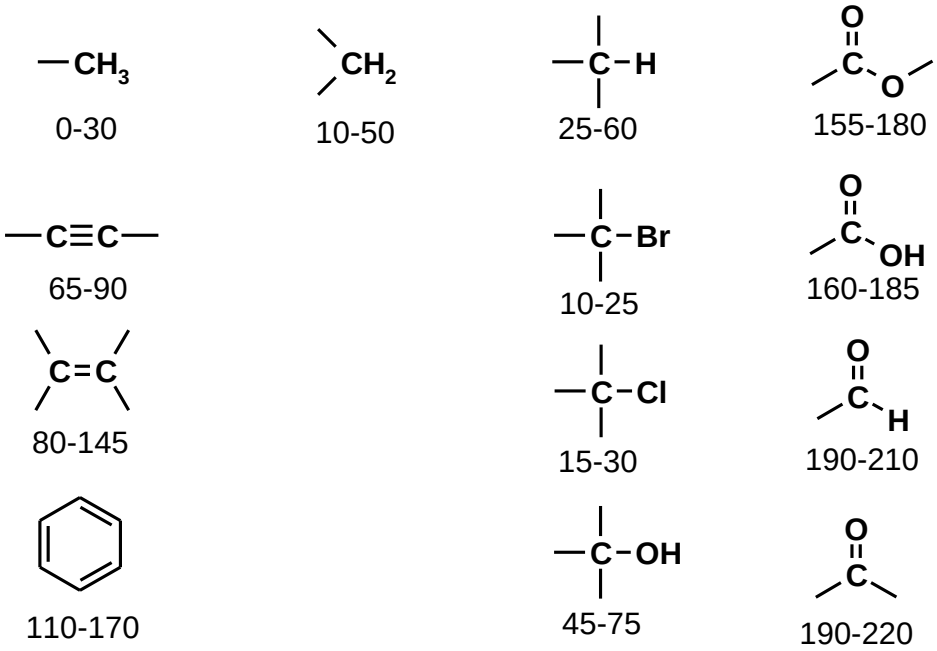
other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C H	5.5
Ar-H	7.3
O C R H	10
O C R OH	9-12

Cont'd -->

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
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 maybe very broad

Cont'd -->

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)