UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 2008 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 -->

20% PART 1 RELATIVE PROPERTIES

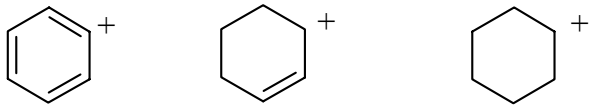
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

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.

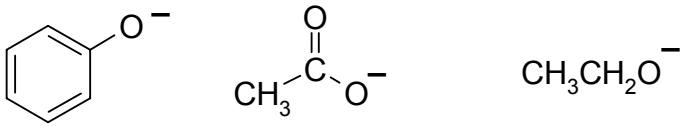
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of the following carbocations:



i **ii** **iii**

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



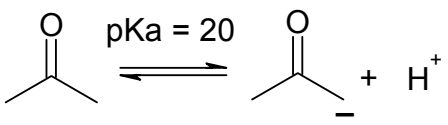
i **ii** **iii**

3. The relative basicity of the following:

CH_3CH_2OH $(CH_3)_2NH$ $CH_3CH_2CH_3$

i **ii** **iii**

4. The relative amount of the conjugate base of 2-propanone formed by the reaction of 1 mole equivalent of each of the following:



H_2O $CH_3CH_2O^-$ NH_2^-

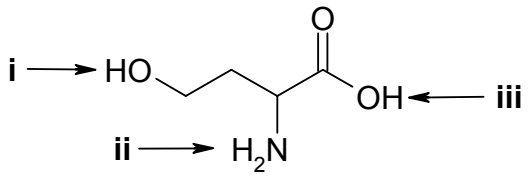
i **ii** **iii**

Cont'd -->

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**

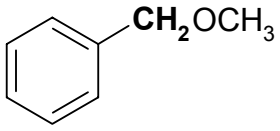
5. The relative acidity of the atoms indicated in the following structure:



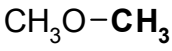
6. The relative rate of reaction of each of the following with $AgNO_3$ / aq. ethanol:

i 2-Bromo-2-methylpropane
ii 2-Bromopropane
iii Bromobenzene

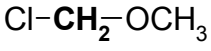
7. The ^{1}H-NMR chemical shifts for the groups shown in **bold** in each of the following structures:



i

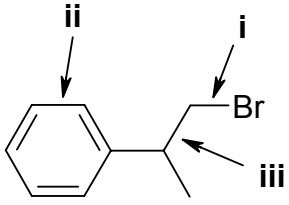


ii



iii

8. The relative bond length of the indicated bond:



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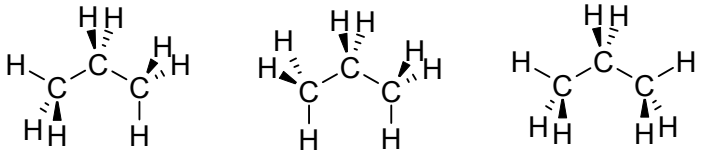
Use the following code to indicate your answers.

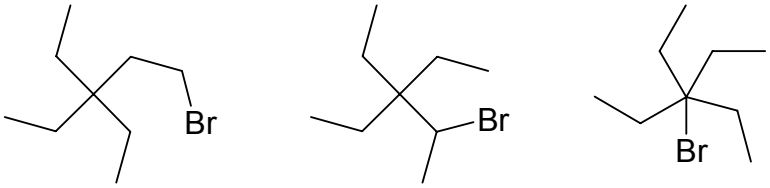
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

9. The relative energies of the conformations shown below:



i **ii** **iii**

10. The relative yields of the following products produced by the reaction of Br_2 / uv light with 3,3-diethylpentane:

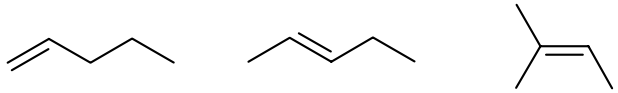


i **ii** **iii**

11. The number of possible alkene isomers that could be produced by the reaction of each of the following by heating with ethanolic KOH:

i 1-bromopentane
ii 2-bromopentane
iii 2-chloro-3-methylbutane

12. The heats of formation of the following alkenes **(most exothermic to least exothermic)**:



i **ii** **iii**

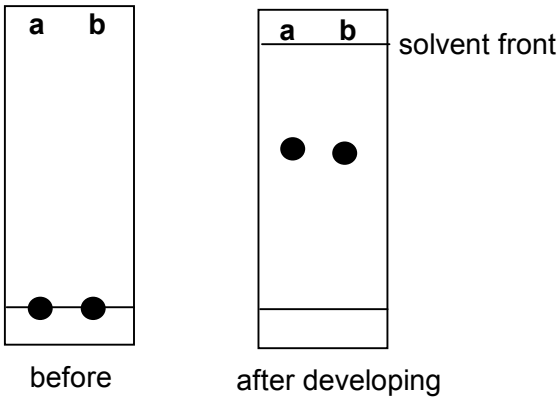
Cont'd -->

9% PART 2: LABORATORY

ANSWER ALL FIVE (5) OF THE QUESTIONS 13-17.

Questions 13-17 are based on the laboratory component of the course.

In order to clarify that two white solids labeled "**a**" and "**b**" are the same molecule, you decide to analyse them using thin layer chromatography (TLC).



13. Which of the following statements are correct ?

A The molecules were more polar BEFORE developing the TLC plate

B Sample "**a**" appears to have eluted slightly more rapidly than sample "**b**"

C TLC has proven that sample "**a**" and "**b**" are identical

D TLC indicates that sample "**a**" and "**b**" would have similar melting points

E The *r.f.* of sample "**a**" is greater than 0.5, but less than 1.0

14. "*r.f.*" is short for:

A Relative fraction

B Retardation factor

C Relative factor

D Ratio of fraction

E Ratio to the solvent front

Cont'd -->

In questions 15-17 select the ALL statements that are true. In some questions, MORE THAN ONE STATEMENT MAY BE TRUE.

15. Based on the molecular solubility exercise, which of the following solvents would dissolve methoxybenzene ?

    A Water

    B Diethyl ether

    C Aqueous sodium hydroxide

    D Aqueous sodium bicarbonate

    E Aqueous hydrochloric acid

16. Which of the following statements from the experiment "Reactivity in Substitution Reactions" using aqueous ethanolic silver nitrate are true ?

    A ethanol is an example of a non-polar, protic solvent.

    B ethanol acts as the electrophile.

    C positive reactions were identified by observation of a silver nitrate precipitate.

    D bromides are more reactive than chlorides.

    E it was concluded that tertiary carbocations were more stable than primary carbocations.

17. Which of the following statements about laboratory techniques are true ?

    A the observed boiling point of a liquid in Calgary would be higher than its boiling point at sea level.

    B silica gel is a common mobile phase for TLC.

    C a filtering funnel can be used for removing drying agent from organic liquids.

    D charcoal can be used to remove water from organic solutions.

    E a separating funnel can be used to separate two miscible liquids.

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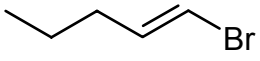
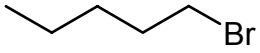
10% PART 3: MOLECULAR PROPERTIES

ANSWER ALL TEN (10) of the questions 18-27

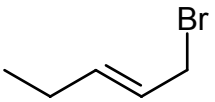
Use the structures below to answer questions 18 – 21



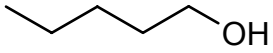
A



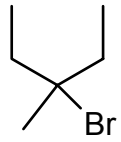
B



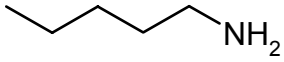
C



D



E



AB

18. Which structure has the most acidic hydrogen atom ?

19. When heated with concentrated H_2SO_4, which structure(s) will produce greatest number of different alkenes ?

20. When reacted with NaCN in DMSO, which structure will react the fastest ?

21. Select any two structures that are constitutional isomers of each other ?

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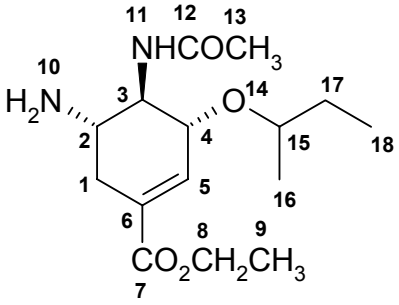
Questions 22 – 27 refer to the structure of Tamiflu:



Tamiflu

22. What is the IHD of Tamiflu ?

A. 1 **B.** 2 **C.** 3 **D.** 4 **E.** 5

23. In Tamiflu, of the carbons at **C5**, **C7**, **C8**, **C9** and **C18**, which is the most downfield in the ^{13}C NMR spectrum ?

A. C5 **B.** C7 **C.** C8 **D.** C9 **E.** C18

24. How many types of carbon are there in Tamiflu ?

A. 8 **B.** 11 **C.** 12 **D.** 13 **E.** 15

25. In Tamiflu, which of the following best describes the orbitals that the two lone pairs on **O14** occupy ?

A. sp^3, sp^3 **B.** sp^2, sp^2 **C.** sp, sp **D.** p, p **E.** p, sp^3

26. What is the oxidation state of **C12** ?

A. -3 **B.** -1 **C.** 0 **D.** +1 **E.** +3

27. In Tamiflu, which of the following bonds has the highest IR absorption frequency ?

A. H—C5 **B.** H—C9 **C.** H—N10 **D.** H—C13 **E.** H—C15

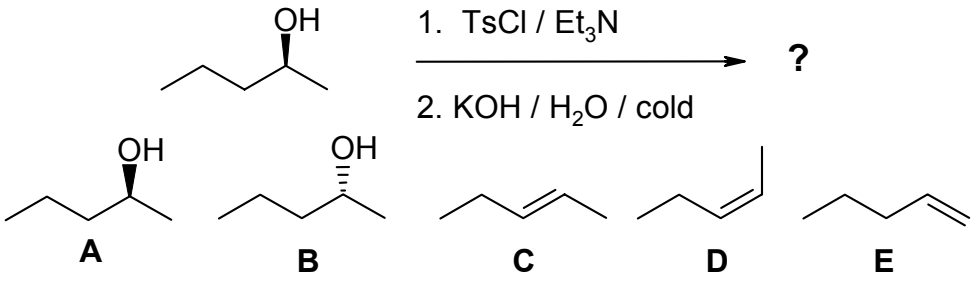
Cont'd -->

12% PART 4: REACTIONS

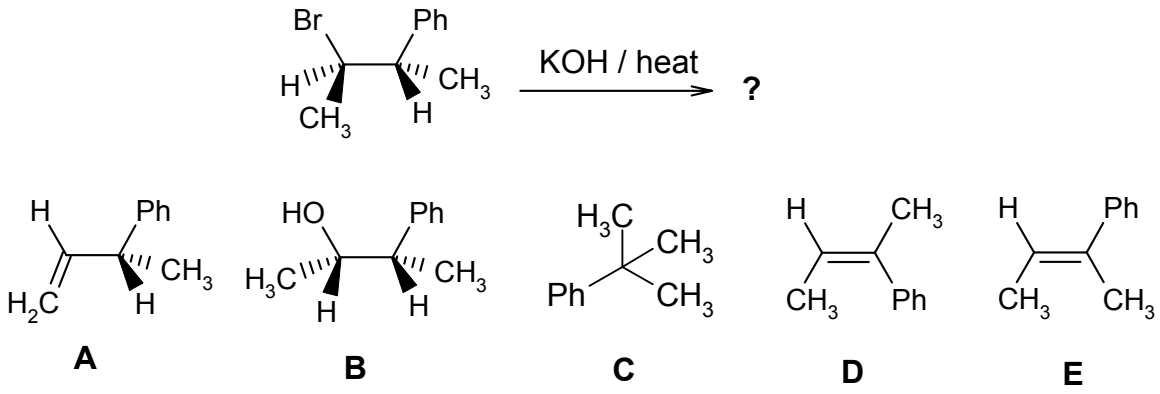
ANSWER ANY EIGHT (8) OF QUESTIONS 28-36.

For each of questions 28-36 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.

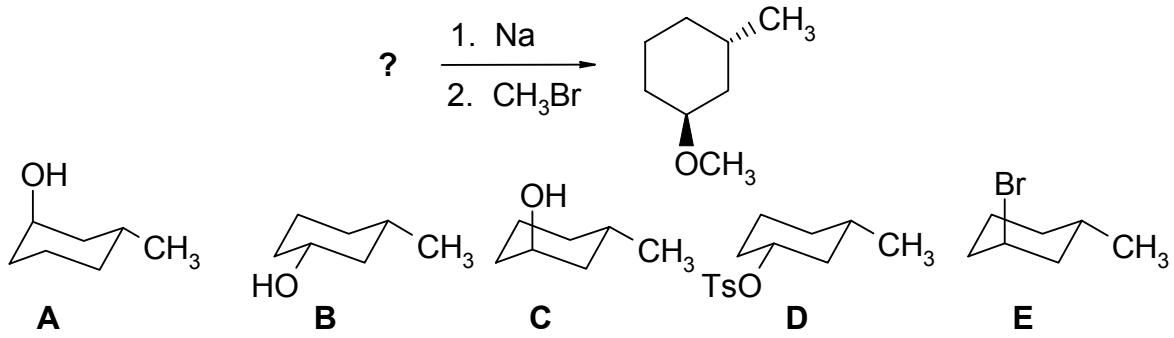
28.



29.



30.



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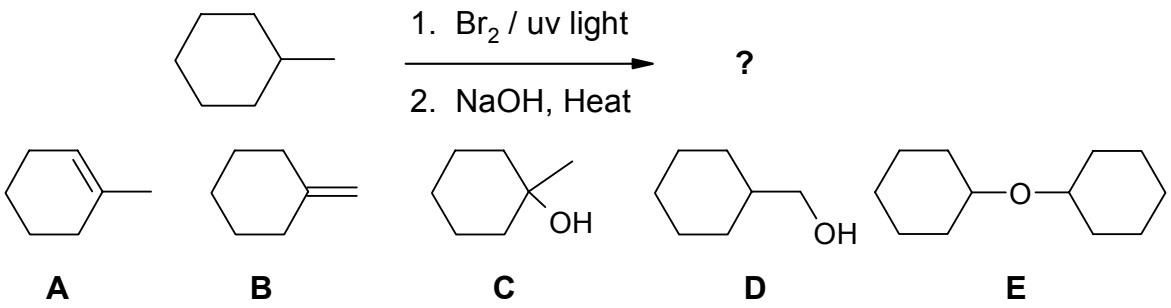
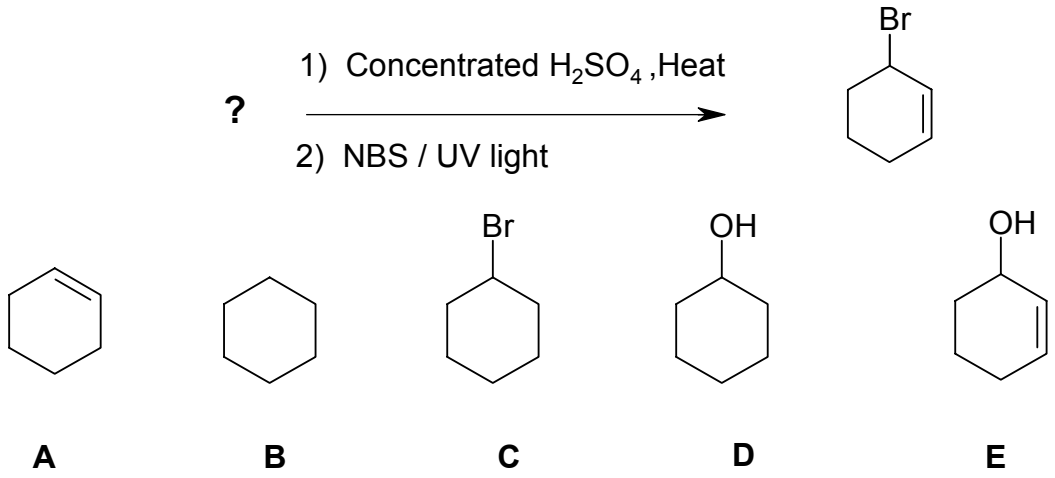
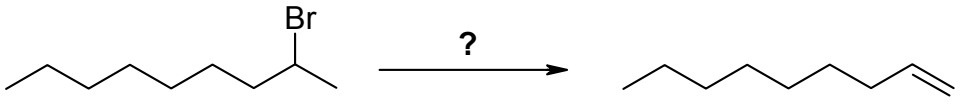
31.



32.



33.



A conc. H_2SO_4 / heat

B KOH / EtOH / heat

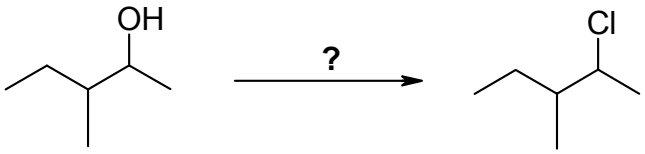
C KOtBu / DMSO / heat

D 1. tosyl chloride / Et_3N
2. KOH / EtOH / heat

E 1. HBr
2. KOtBu / DMSO / heat

Cont'd -->

34.



A conc. HCl

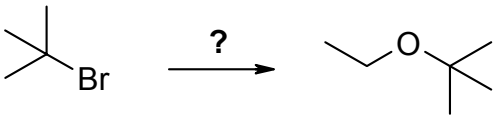
B Cl_2

C NaCl / DMSO

D tosyl chloride / Et_3N

E $SOCl_2$ / Et_3N

35.



A $AgNO_3$, ethanol

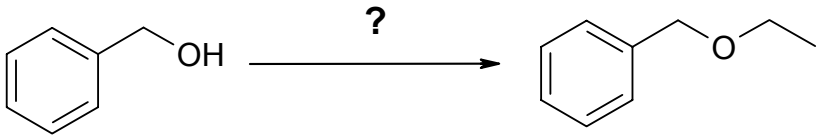
B H+ / ethanol

C NaOH, ethanol

D Acetone, NaI, ethanol

E 1. Na
2. Ethanol

36.



A $NaOCH_2CH_3$ / EtOH

B 1. Na_2CO_3 /DMF
2. CH_3CH_2OH

C 1. NaH /DMF
2. CH_3CH_2I

D 1. Na_2CO_3 /DMF
2. CH_3CH_2F

E 1. NaOH /DMF
2. CH_3CH_2OH

Cont'd -->

12% PART 5: SPECTROSCOPY

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

For each of questions 37-41 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/ppm 1.3 (s, 1H), 3.2 (s, 1H)
^{13}C-NMR: δ/ppm 24.0, 48.3, 100.0
IR : 1217, 1182, 1082, 1056 cm^{-1}

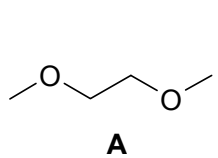
38. **^{1}H NMR** : δ/ppm 3.3 (s, 3H), 3.7 (s, 2H)
^{13}C-NMR: δ/ppm 59.0, 71.9
IR : 1110 cm^{-1}

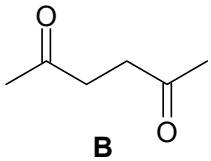
39. **^{1}H NMR** : δ/ppm 2.2 (s, 3H), 2.7 (s, 2H)
^{13}C-NMR: δ/ppm 29.8, 37.0, 206.9
IR : 1715 cm^{-1}

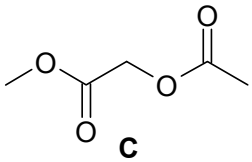
40. **^{1}H NMR** : δ/ppm 1.0 (d, 3H), 3.3 (s, 6H), 4.5 (q, 1H)
^{13}C-NMR: δ/ppm 18.8, 52.3, 101.2
IR : 1089, 1127 cm^{-1}

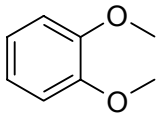
41. **^{1}H NMR** : δ/ppm 1.0 (d, 6H), 1.8 (s, 1H, D_2O exchange) 3.7 (septet, 1H)
^{13}C-NMR: δ/ppm 25.3, 64.0
IR : ~3400 cm^{-1}

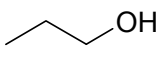
42. **^{1}H-NMR**: δ/ppm 3.7 (s, 6H), 6.4 (s, 1H), 6.5 (d, 2H), 7.2 (t, 1H)
^{13}C-NMR: δ/ppm 55.2, 100.7, 106.3, 130.0, 161.0
IR: 1606, 1152 cm^{-1}


A

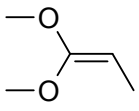

B


C


D


E


AB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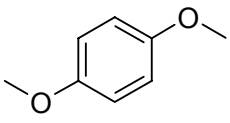
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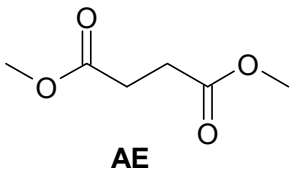
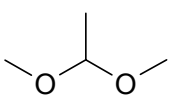
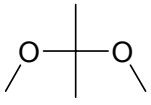
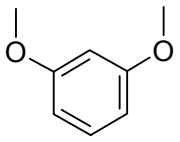

AE


BC


BD


BE

Cont'd -->

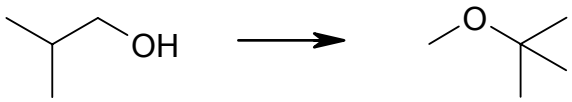
6% PART 6: SYNTHESIS

DESIGN EFFICIENT SYNTHESES OF ANY TWO of the following target molecules from the starting material indicated. In addition, you can use any other hydrocarbon with three or less carbon atoms and any solvent or inorganic reagent that does not become part of the carbon skeleton in the product.

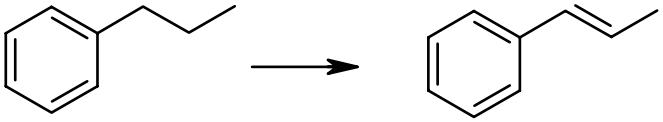
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

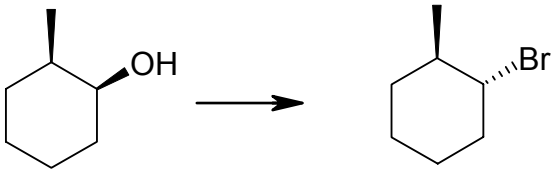
A



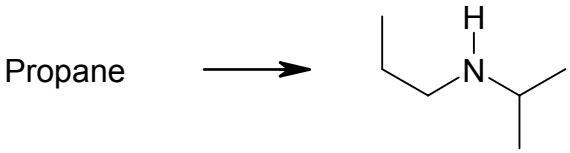
B



C



D



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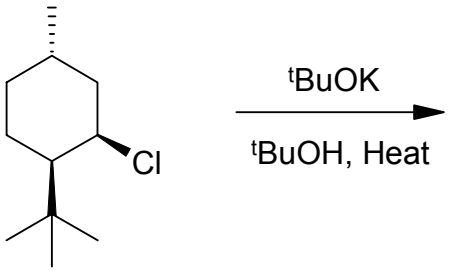
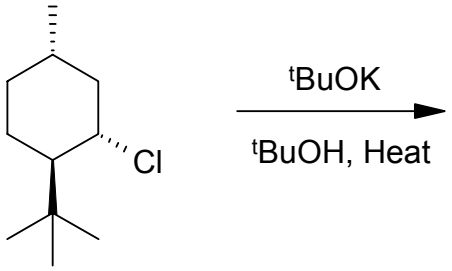
9% PART 7: MECHANISMS

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

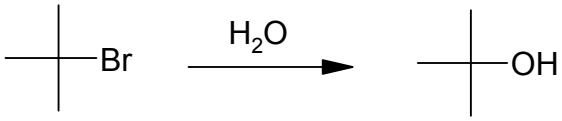
Use curly arrows to show the mechanism in order to explain **ANY TWO** of the following:

A Which of the following two substrates below reacts faster when heated with potassium *tert*-butoxide in *tert*-butanol ? Draw the reaction mechanism to explain your answer.

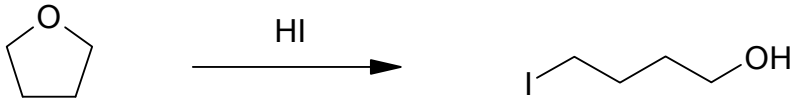




B Draw the reaction mechanism for the following:



C Draw the reaction mechanism for the following:



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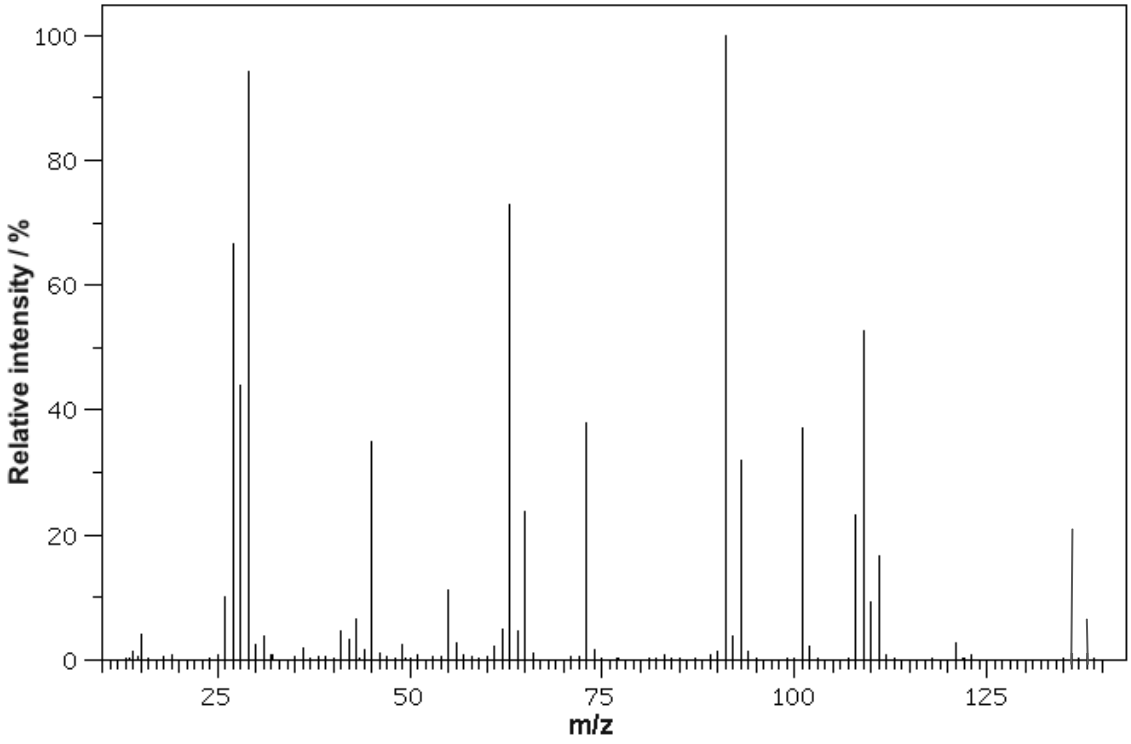
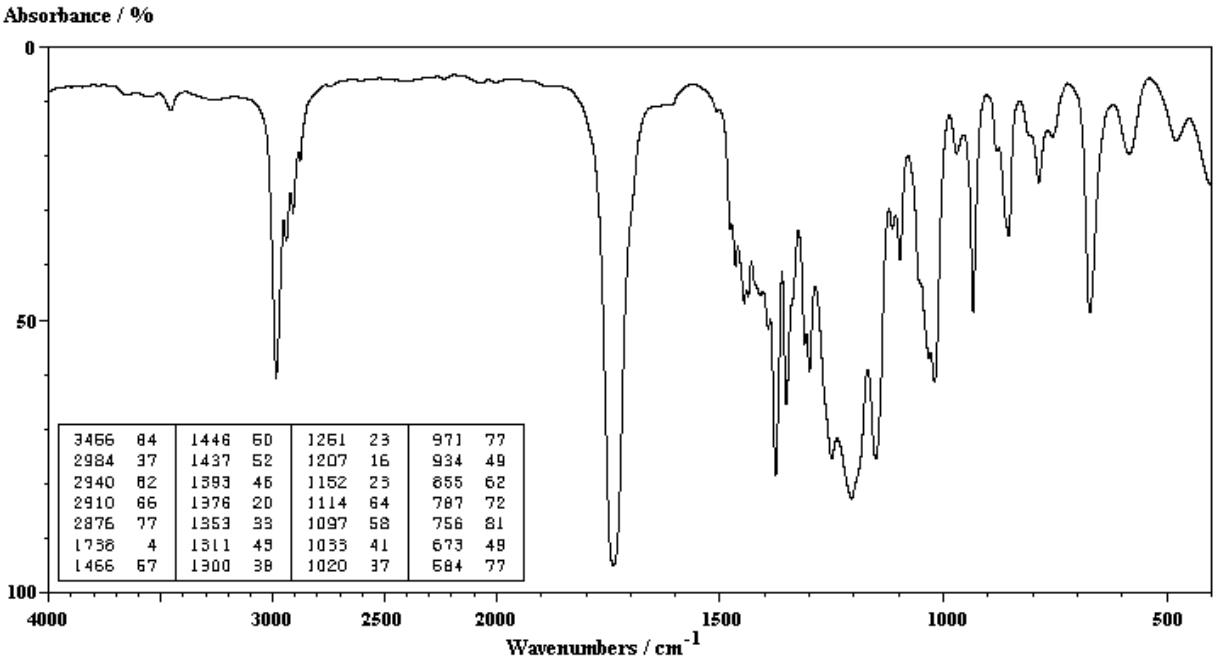
10% PART 8: SPECTROSCOPY

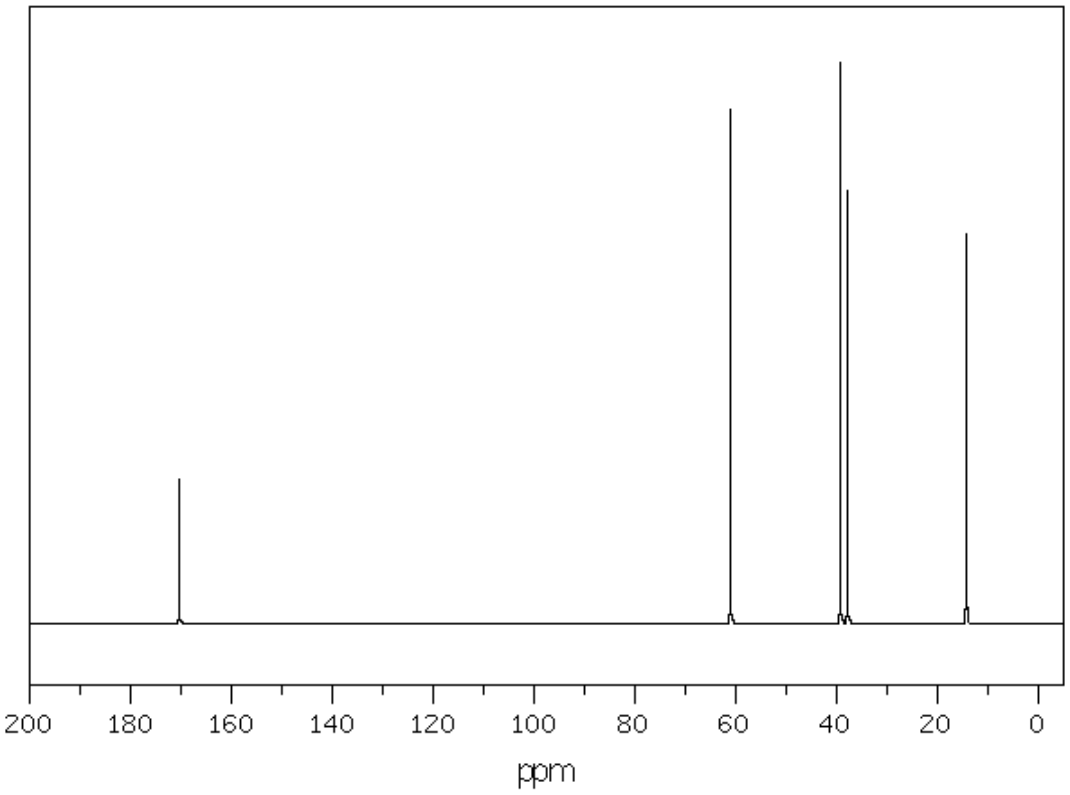
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

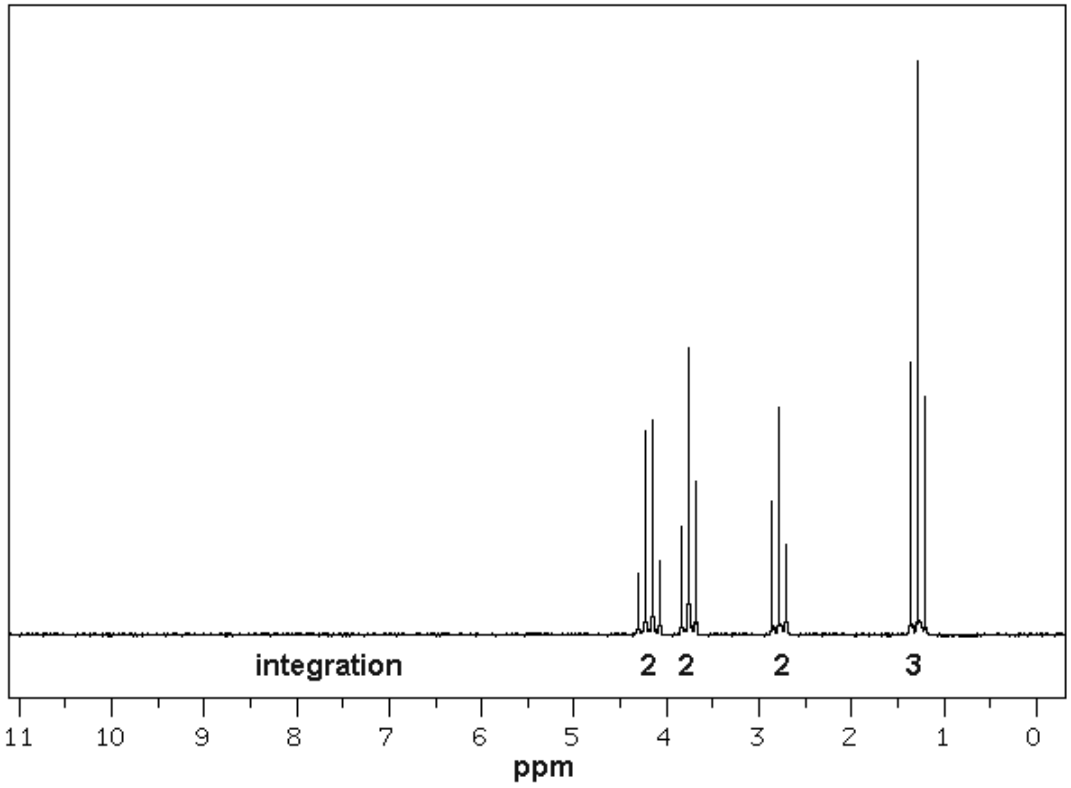
From the spectral data provided below, identify the structure of the "unknown" molecule.





Cont'd -->


200
180
160
140
120
100
80
60
40
20
0
ppm


integration
2
2
2
3
11
10
9
8
7
6
5
4
3
2
1
0
ppm

Cont'd -->

12% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

An achiral molecule **A**, C_9H_{12}, was reacted with Br_2 using UV light to give the mono-brominated major product **B**. When **B** was reacted with either KOH / EtOH/ heat or KOBu-*t* / DMSO / heat, it gave product **C** as the only product. **C** was found to react with *N*-bromosuccinimide to give **D** as the major product. When **D** was reacted with cold aq. NaOH solution, **E** was obtained. Reduction of **E** via catalytic hydrogenation (H_2 / Pd) gave the compound **F.** When **F** was reacted with PBr_3 / Et_3N, **G** was obtained and **G** was found to be the constitutional isomer of **B**. When **F** was treated was HBr, **B** was obtained as the major product. When **B** was treated with H_2O / Na_2CO_3, **H** was found to readily form. **H** is a constitutional isomer of **F**.

Of the compounds **A**-**H**, only **F** and **G** have chiral centers. ^{13}C NMR revealed that compound **A** has 6 peaks.
The ^{13}C NMR of **A** showed peaks at 148, 128, 126, 126, 34 and 24 ppm.

Identify **A**-**H** (only structures are needed)

Draw a structure showing the stereochemistry and give the complete name of one enantiomer of **G**.

**** THE END ****

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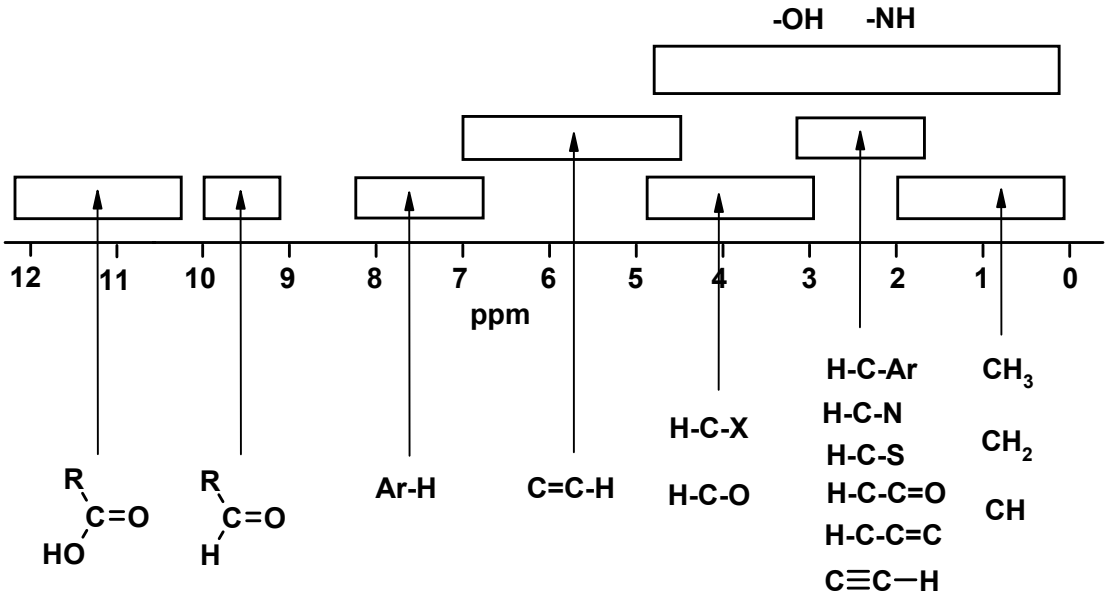
SPECTROSCOPIC TABLES

^{1}H NMR



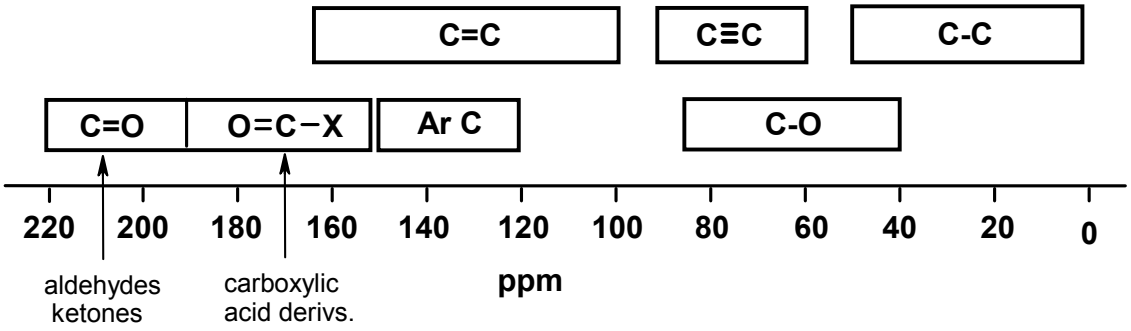
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	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

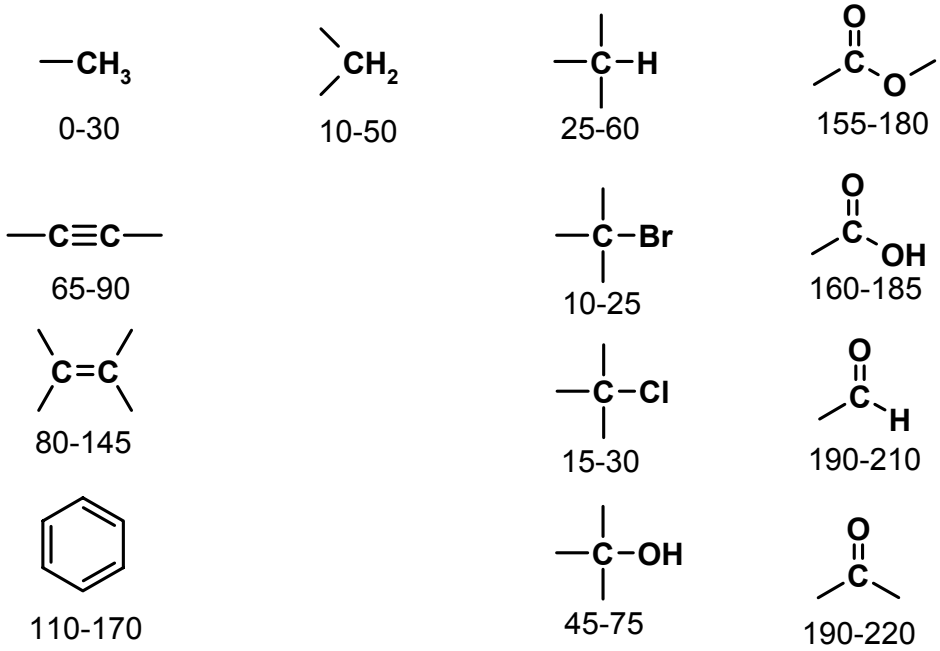
other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C H	5.5
Ar-H	7.3
O C R H	10
O C R OH	9-12

Cont'd -->

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



Cont'd -->

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
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)