UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 10th 2007

Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **<u>BOTH</u>** 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, <u>but</u> <u>NOT programmable calculators</u>.

Absolutely no other electronic devices are allowed.

20% PART 1 RELATIVE PROPERTIES

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

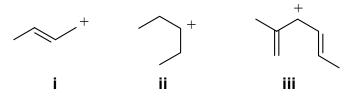
Arrange the items in questions 1-12 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.

Use the following code to indicate your answers.

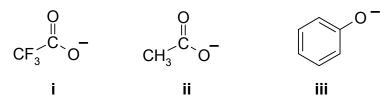
- A.
 i > ii > iii
 D.
 ii > iii > i

 B.
 i > iii > ii
 E.
 iii > i > ii

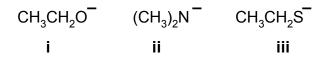
 C.
 ii > i > iii
 AB.
 iii > ii > i
- 1. The relative stability of the following carbocations:



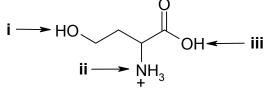
2. The relative nucleophilicity of the following in a polar, protic solvent:



3. The relative basicity of the following:



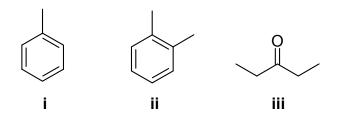
4. The relative acidity of the **atoms** indicated in the following structure :



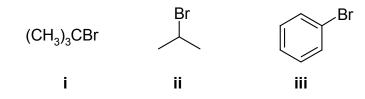
Use the following code to indicate your answers.

Α.	i > ii > iii	D.	ii > iii > i
Β.	i > iii > ii	Ε.	iii > i > ii
С.	ii > i > iii	AB.	iii > ii > i

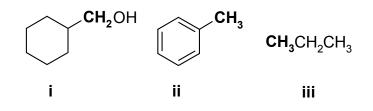
5. The number of peaks seen in the normal broadband decoupled ¹³C nmr spectrum for each of the following:



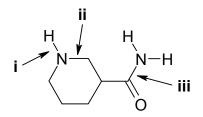
6. The relative rate of reaction of each of the following with Nal / acetone:



7. The number of peaks in the normal H nmr spectra in the coupling pattern corresponding to the group in **bold** in each of the following:



8. The relative bond length of the indicated bond:

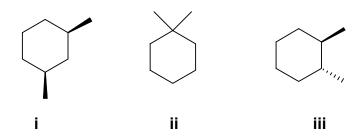


Chem 351 cont'd.

Use the following code to indicate your answers.

Α.	i > ii > iii	D.	ii > iii > i
Β.	i > iii > ii	Ε.	iii > i > ii
С.	ii > i > iii	AB.	iii > ii > i

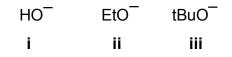
9. The relative energies of the most stable conformation of the following molecules:



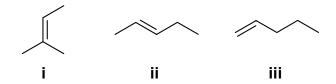
10. The relative importance of the following resonance contributors to CH₂N₂ (all required charges are shown):

$$\dot{C}H_2 - N = \overline{N}$$
 $CH_2 = \dot{N} = \overline{N}$ $CH_2 = N \equiv N$
i ii iii

11. The relative yields of the Zaitsev product produced by the reaction of each of the following with 2-bromobutane at 80°C:



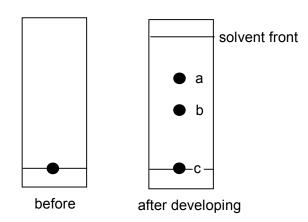
12. The heats of combustion of the following alkenes (most endothermic to most exothermic):



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.



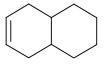
13. What is the Rf value for the sample spot "a" shown on the normal chromatographic plate after development (see diagram above) ?

A 1.5 **B** 0.75 **C** 0.67 **D** 0.5 **E** 0.25

- 14. Which of the following 3 statements about the normal chromatographic plate shown above are correct ?
 - i the original sample is probably impure.
 - ii sample "b" is more polar than "c"
 - iii sample "a" eluted more rapidly than sample "b"
 - A only i is trueB only ii is trueC only iii is trueD only i and ii are trueE only i and iii are trueAB i, ii and iii are true

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 models exercise, which of the following statements are true ?
 - A 1,2,4,5-tetramethylbenzene has an index of hydrogen deficiency = 4
 - **B** 1,3-dimethylbenzene has 4 types of carbon.
 - **C** the following molecule has 4 types of hydrogen.



D the amino acid glycine (below) is non-superimposable on it's mirror image.

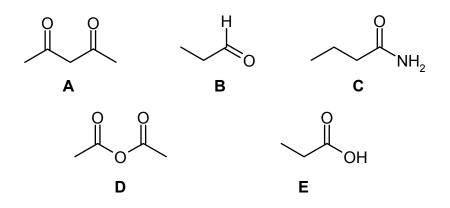


- **E** trans-1,3-dimethylcyclohexane is non-superimposable on it's mirror image.
- 16. Which of the following statements from the experiment "Reactivity in Substitution Reactions" using aqueous ethanolic silver nitrate are true ?
 - **A** ethanol is an example of a polar, protic solvent.
 - **B** the nitrate ion is a good nucleophile.
 - **C** positive reactions were identified by observation of a silver halide precipitate.
 - **D** bromides are less reactive than chlorides.
 - **E** t-butyl bromide reacted more rapidly than n-butyl bromide.
- 17. Which of the following statements about laboratory techniques are true ?
 - **A** the observed boiling point of a liquid in Calgary is higher than at sea level.
 - **B** silica gel is a common mobile phase for TLC.
 - **C** a Buchner funnel is used for vacuum filtrations.
 - **D** charcoal can be used to remove water from organic solutions.
 - **E** a filtering funnel can be used to separate two immiscible liquids.

10% PART 3: MOLECULAR PROPERTIES

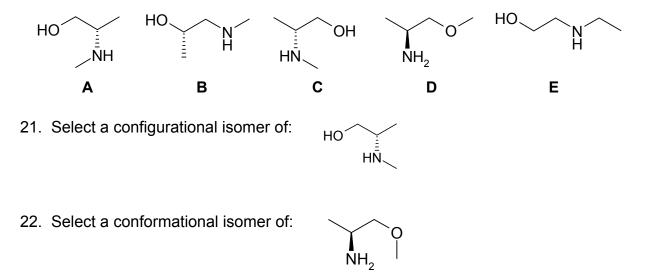
ANSWER ALL TEN (10) of the questions 18-27

Use the following information and structures A-E to answer questions 18 - 20

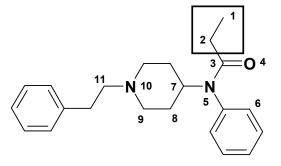


- 18. Which structure has the most acidic hydrogen atom ?
- 19. Which structure has the hydrogen with the most shielded chemical shift in its proton NMR spectrum ?
- 20. Which structure has the carbonyl group that gives the IR absorption with the lowest frequency ?

Use the following list of structures to answer questions 21 and 22.



For each of the questions about FENTANYL (right), select the answer from those provided.



23. How many chiral carbons are there in FENTANYL ?

A. 0 B. 1 C. 2 D. 3 E. 4

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

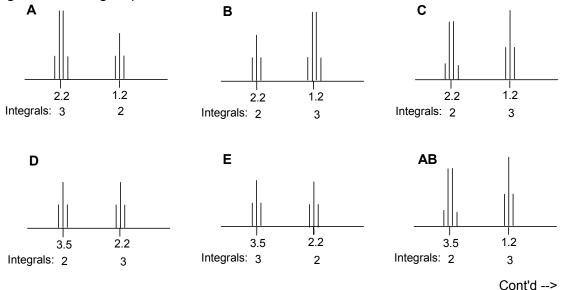
A. 12 **B**. 15 **C**. 16 **D**. 18 **E**. 22

25. In FENTANYL, what are the hydridisations of O4, N10, and C6 respectively:

- 26. In **FENTANYL**, which of the following best describes the orbital the lone pair on **N5** occupies ?

A. s **B**. p **C**. sp³ **D**. sp² **E**. sp

27. In a ¹H-NMR spectrum of **FENTANYL**, which of the following figures best match the signals for the group in the box ?

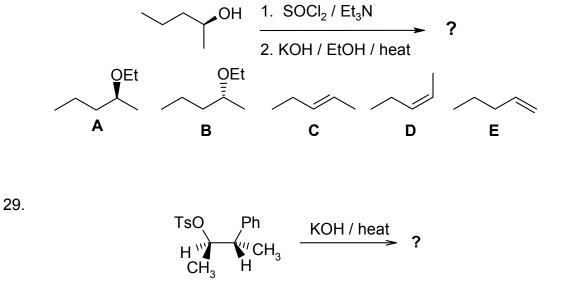


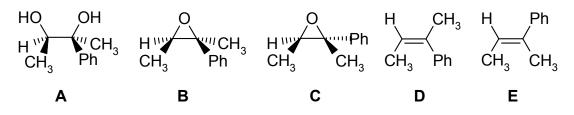
12% PART 4: REACTIONS

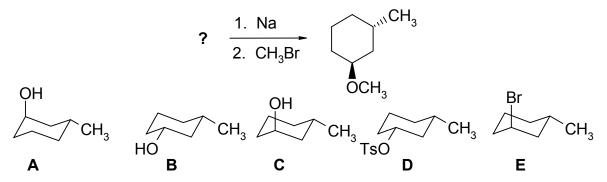
ANSWER ANY EIGHT (8) OF QUESTIONS 28-36.

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.

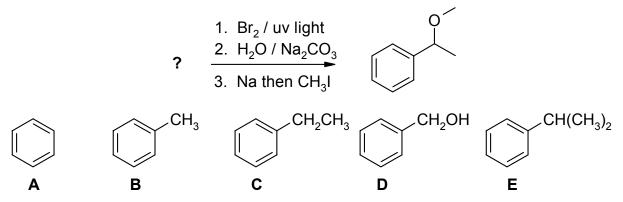
28.



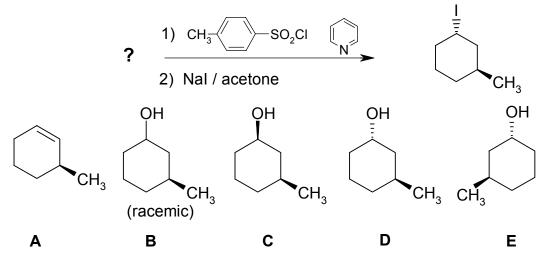


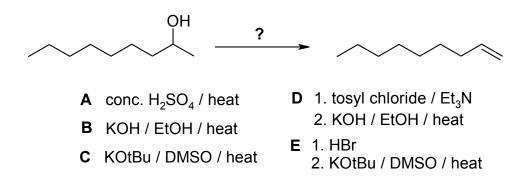


31.

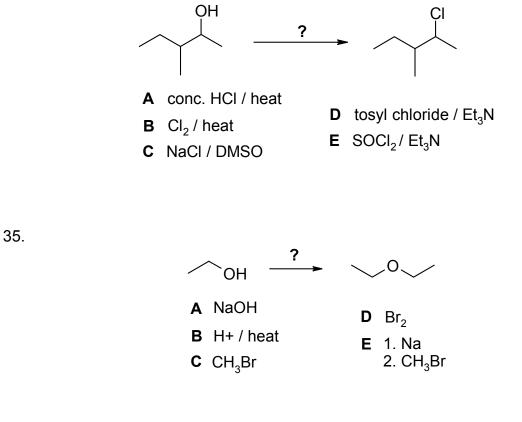


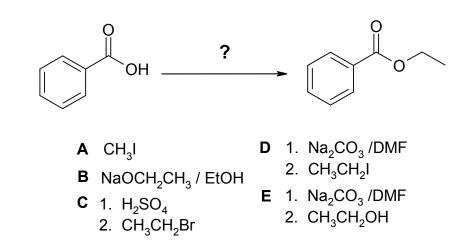
32.





34.



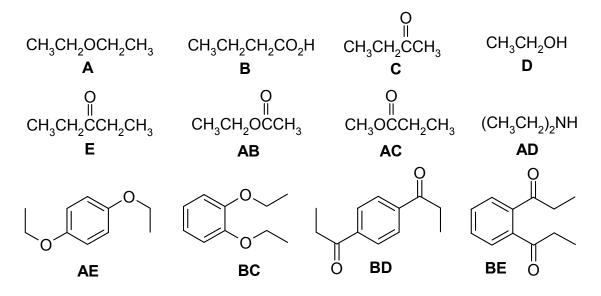


12% PART 5: SPECTROSCOPY

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

- ¹H NMR : δ/ppm 1.1 (t, 3H), 2.1 (s, 3H), 2.4 (q, 2H)
 ¹³C-NMR: δ/ppm 7.9, 29.4, 36.9, 209.3
 IR : 1718 cm⁻¹
- ¹H NMR : δ/ppm 1.2 (t, 3H), 2.3 (q, 2H), 3.7 (s, 3H)
 ¹³C-NMR: δ/ppm 9.2, 27.5, 51.5, 174.9
 IR : 1741 cm⁻¹
- ¹H NMR : δ/ppm 1.1 (t, 3H), 2.4 (q, 2H)
 ¹³C-NMR: δ/ppm 7.9, 35.5, 212.1
 IR : 1716 cm⁻¹
- 40. ¹H NMR : δ/ppm 1.4 (t, 3H), 4.0 (q, 2H), 6.9 (m, 2H) ¹³C-NMR: δ/ppm 14.9, 64.6, 114.0, 121.1, 149.0
- ¹H NMR : δ/ppm 1.3 (t, 3H), 2.0 (s, 3H) 4.1 (q, 2H)
 ¹³C-NMR: δ/ppm 14.3, 21.0, 60.4, 171.0
 IR : 1743 cm⁻¹
- ¹H-NMR: δ/ppm 1.0 (t, 3H), 1.7 (sextet, 2H), 2.3 (t, 2H), 11.5 (s, 1H, D₂O exchange)
 ¹³C-NMR: δ/ppm 13.7, 18.4, 36.2, 180.7
 IR: 2700-3300, 1712 cm⁻¹

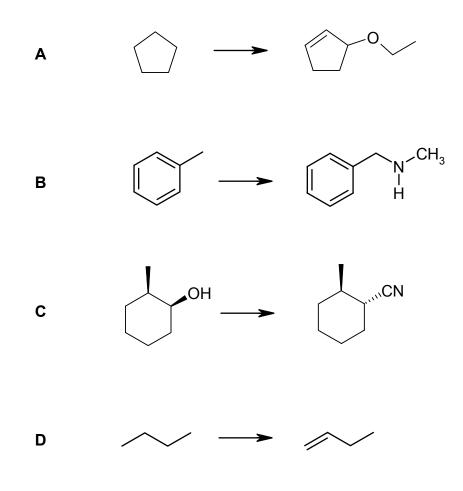


6% PART 6: SYNTHESIS

DESIGN EFFICIENT SYNTHESES OF <u>ANY TWO (2)</u> of the following target molecules from the starting material indicated. In addition, you are allowed to use any other hydrocarbon with three or less carbon atoms and any solvent or inorganic reagent that does not become part of the <u>carbon</u> skeleton in the <u>product</u>.

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.



9% PART 7: MECHANISMS

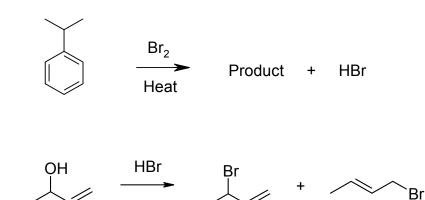
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

ANSWER ANY THREE (3) OF THE QUESTIONS I to IV.

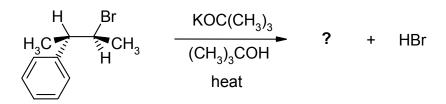
Use CURLY ARROW MECHANISMS to explain any THREE (3) of the following reactions / observations (curly arrow mechanisms are required in order to get full marks).

I.

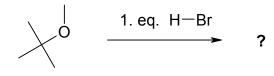
Ш



III. Predict the major product of this reaction by showing the mechanism of the reaction:



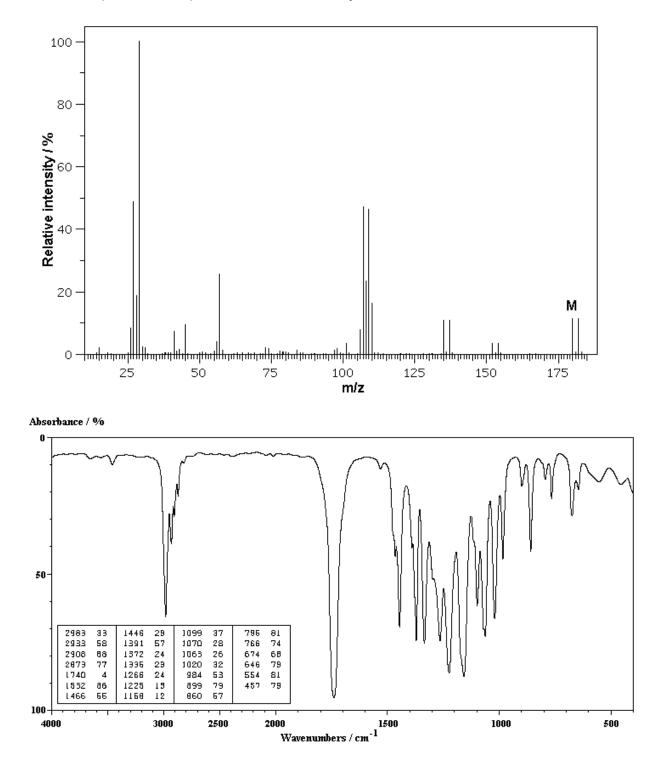
IV. Predict the major product of this reaction by showing the mechanism of the reaction:

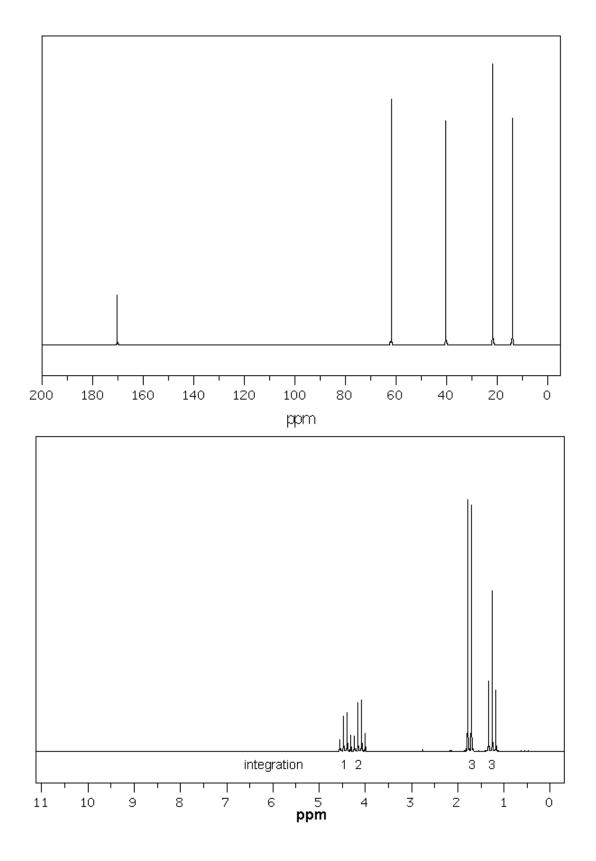


10% PART 8: SPECTROSCOPY

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.





12% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Compound **A**, $C_6H_{12}O$, (IR : 3500cm⁻¹, broad) was reacted with PBr₃ / Et₃N to give **B** $C_6H_{11}Br$ as the major product. **B** was observed to react quite slowly with aqueous ethanolic silver nitrate but rapidly with sodium iodide in acetone. When **B** was reacted with either hot KOH / EtOH or KOtBu / DMSO it gave the same product, **C**, C_6H_{10} (IR : 1650cm⁻¹).

In contrast, when **B** was reacted with cold aq. NaOH solution the major product was **A**.

When **A** was heated with conc. H_2SO_4 , two constitutional isomer of **C** were obtained, **D** and **E**. Catalytic hydrogenation of either **C** or **D** was found to give methylcyclopentane but **E** gave a different alkane.

When **A** was treated with HBr the reaction gave **F** and **G**, constitutional isomers of **B**. **F** was observed to react rapidly with aqueous ethanolic silver nitrate but very slowly (if at all) with sodium iodide in acetone while G reacted at a moderate rate with both reagents. **F** could also be obtained on reaction of methylcyclopentane with bromine / uv light.

In a ¹³C nmr spectroscopic analysis of the isomeric compounds, **C**, **D** and **E** it was found that **E** had only 3 peaks, **C** had 4 peaks and **D** had 6 peaks.

None of the compunds **A** - **G**, have chirality centers.

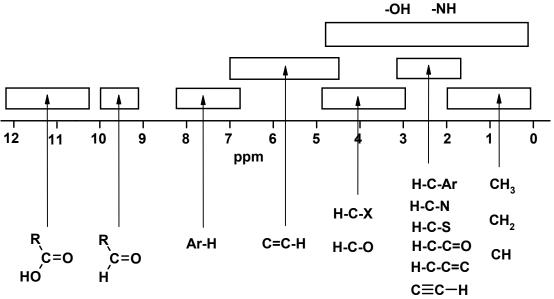
- Identify A-G (only structures are needed)
- Give the complete name of compound F.

**** THE END ****

IRH / AC / C-CL Dec 2007

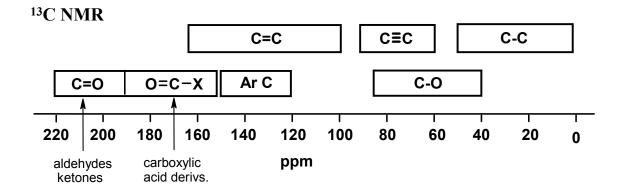
SPECTROSCOPIC TABLES



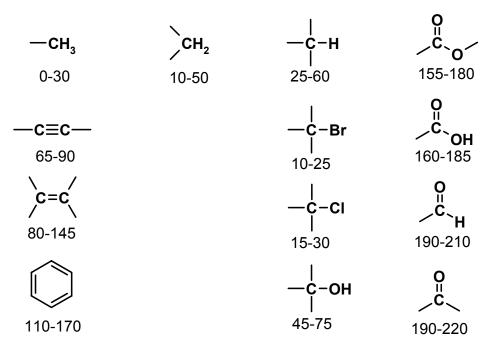


¹H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	methyl CH ₃ -	methylene -CH ₂ -	methyne CH	other	
R−C 	0.9	1.4	1.5	-OH 1-5	
	1.6	2.3	2.6	-NH 1-3 C≡CH 2.5	
O R C		2.4	2.5	Ar-H 7.3	
R-N	2.2	2.5	2.9	о " " "	
R-Ar	2.3	2.7	3.0		
R-Br	2.7	3.3	4.1	о "С с`он ⁹⁻¹²	2
R-CI	3.1	3.4	4.1		
R-0-	3.3	3.4	3.7		



¹³C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

	<u>TY</u>	PE OF VIBRATION	FREQUENCY (cm ⁻¹)	<u>WAVELENGTH</u> (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
	CH2	(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-0	Alcohols, Ethers	s, Esters,			
	Carboxylic acid	S	1300-1000	7.69-10.0	S
O-H	Alcohols, Pheno	ols			
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acid	s (2)	3300-2500	3.03-4.00	m
N–H	Primary and see	condary 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

100

Fm

(257)

99

Es

(252)

102

No

(259)

101

Md

(258)

103

Lr

(260)

1																	18
1A																	8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
3	4											5	6	7	8	9	10
Li	Be											В	С	Ν	0	F	Ne
6.941	9.012											10.81	12.01	14.01	16.00	19.00	20.18
11	12	2	4	=	(-	0	0	10	11	10	13	14	15	16	17	18
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	Р	S	Cl	Ar
22.99	24.31 20	21	22	23	24	25	26	27	28	29	30	26.98 31	28.09 32	30.97 33	32.07 34	35.45 35	39.95 36
19																	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.10	40.08	44.96	47.88	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38	69.72	72.59	74.92	78.96	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	Ι	Xe
85.47	87.62	88.91	91.22	92.91	95.94	(98)	101.1	102.9	106.4	107.9	112.4	114.8	118.7	121.8	127.6	126.9	131.3
55	56	57*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.9	137.3	138.9	178.5	180.9	183.9	186.2	190.2	192.2	195.1	197.0	200.6	204.4	207.2	209.0	(209)	(210)	(222)
87	88	89**	104	105	106	107	108	109	110	111							
Fr	Ra	Ac	Rf	На	Sg	Ns	Hs	Mt	Uun	Uuu							
(223)	226.0	(227)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)							
											-						
	Т	1	1	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Lant	hanio	aes *	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
												·					
				140.1	140.9	144.2	(145)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0

96

Cm

(247)

97

Bk

(247)

98

 $\mathbf{C}\mathbf{f}$

(251)

95

Am

(243)

PERIODIC TABLE

Actinides	**	

91

Pa

231.0

92

U

238.0

93

Np

237.0

94

Pu

(244)

90

Th

Last	Page
------	------