CHEMISTRY HONOURS EXAMINATION: JUNE 2018

MODULE: CEM 8X04- INSTRUMENTAL ANALYSIS

UNIVERSITY OF JOHANNESBURG

Examiners: Prof R. Meijboom, Dr E.M. Mmutlane and Dr N.S. Bingwa

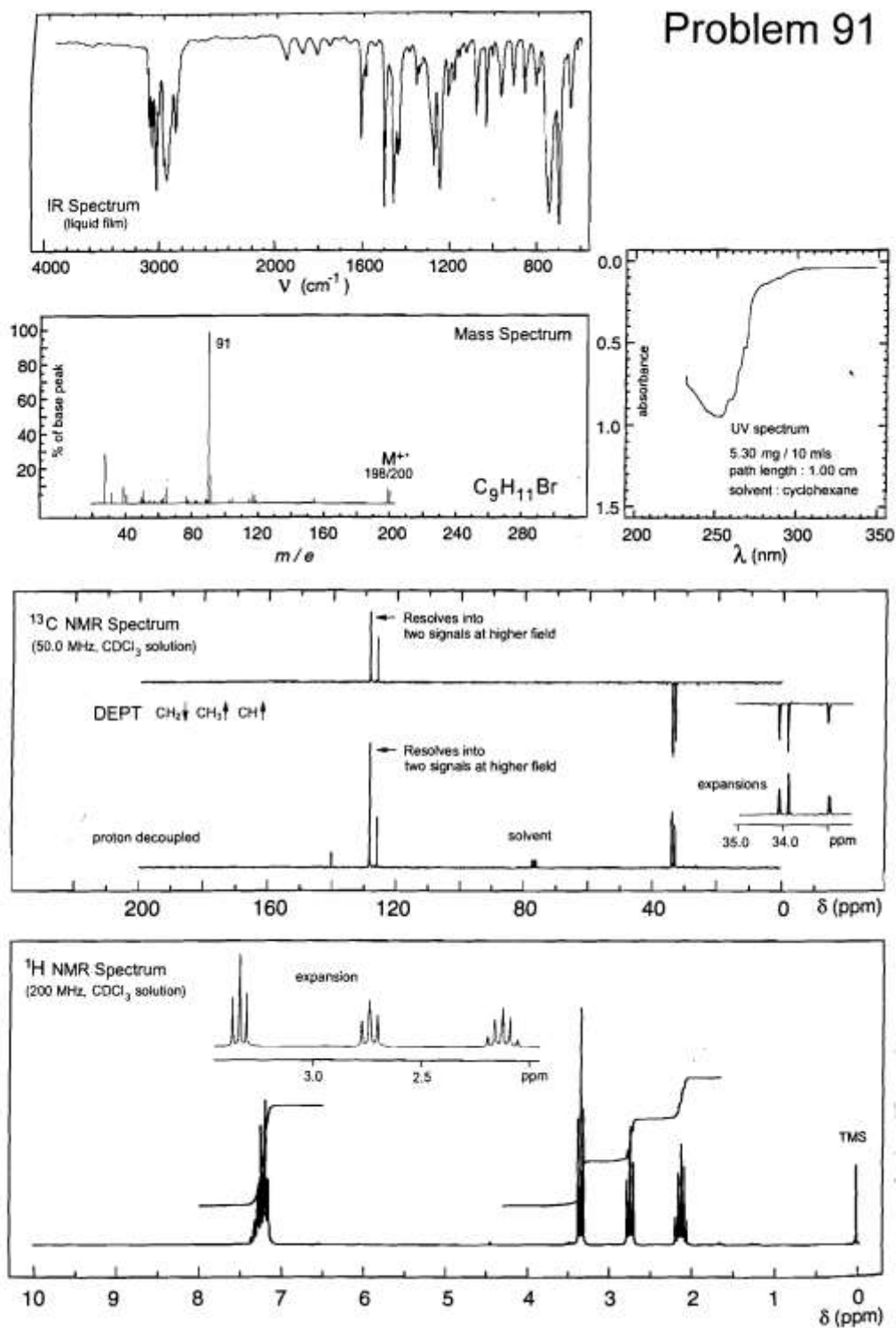**Moderator:** Dr R. Mampa (University of Limpopo)

INSTRUCTIONS

(i) This examination is out of a Total of 100 Marks and you have 3 Hours (180 Minutes) to complete it. No extra time will be allowed for any reason.

(ii) The Exam comprises 2 Sections. PLEASE ANSWER EACH SECTION IN A SEPARATE BOOK.

(iii) The use of cell phones and other electronic communication devices is forbidden and they must be switched off. No data/image storing devices, including calculators capable of such, are permitted in this examination.

(iv) This is a closed book examination. You are NOT allowed to have any book, memorandum, notes, paper, photographs, document or written/printed material other than the question paper and the answer books provided by the examiner/invigilator. If you need paper for rough work, an additional exam answer sheet will be given to you, which must be clearly labelled as rough work: not for marking, and handed in together with the question paper and all your answer books.

QUESTION 1   **[38]**

Consider the following spectra:

Problem 91

IR Spectrum (liquid film)

Mass Spectrum

M⁺·
198/200

$C_9H_{11}Br$

UV spectrum
5.30 mg / 10 mls
path length : 1.00 cm
solvent : cyclohexane

¹³C NMR Spectrum
(50.0 MHz, CDCl₃ solution)

DEPT CH₂↓ CH₃↑ CH↑

Resolves into two signals at higher field

Resolves into two signals at higher field

proton decoupled

solvent

expansions

¹H NMR Spectrum
(200 MHz, CDCl₃ solution)

expansion

TMS

180

a) Determine the degree of unsaturation **(2)**

The molecular formula is $C_9H_{11}Br$ so one can determine the degree of unsaturation. Replace the Br by H to give an effective molecular formula of C_9H_{12} (C_nH_m) which gives the degree of unsaturation as (n - $m/2$ +I) = 9 - 6 + I = 4. The compound must contain the equivalent or 4 TC bonds and/or rings. This degree of unsaturation would be consistent with one aromatic ring (with no other elements of unsaturation).

b) Identify the structural elements based on the Mass Spectrum. **(4)**

From the molecular ion, the molecular weight is 198/200. The molecular ion has two peaks of equal intensity separated by two mass units. This is the characteristic pattern for a compound containing one bromine atom.

198 – 91 = 107. One peak for 107, obviously loss of Br (no double peak); Br = 79; 28 = C_2H_4

c) Calculate the extinction coefficient **(2)**

$$\varepsilon_{255} = \frac{199 \times 0.95}{0.53 \times 1.0} = 357$$

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d) What structural elements does the UV-vis spectrum suggest? **(2)**

The ultraviolet spectrum shows a typical benzenoid absorption without further conjugation or auxochromes. This would also be consistent with the Ph-CH_2- group.

e) Identify the structural elements based on the IR spectrum. **(4)**

There is no useful additional information from infrared spectrum, other than C-H stretching frequency at around 3000 cm^{-1} (2 pt) and the four overtones for a monosubstituted aromatic between 1640 and 2000 (2 pt).

f) Estimate the integrals for each proton and tabulate them **(4)**

δ 1H (ppm)	integral	Relative No of H	Rounded No of H

δ ^1H (ppm)	Integral (mm)	Relative No. of hydrogens (rounded)
~ 7.2	19	4.9 (5H)
~ 3.3	8	2 (2H)
~ 2.8	8	2 (2H)
~ 2.2	8	2 (2H)

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g) What structural elements do the ^1H NMR spectra suggest? **(8)**

From the ^1H NMR, there are 5 protons near δ ~7.2 which strongly suggests a monosubstituted benzene ring, consistent with MS and UV-vis data. The Ph-CH_2- group is confirmed. (2 pt)

3

The triplet at approximately δ 3.3 ppm of intensity 2H suggests a CH_2 group. The downfield chemical shift suggests a -CH_2-X group with X being an electron withdrawing group (probably bromine). The triplet splitting indicates that there must be another CH_2 as a neighbouring group. (2 pt)

In the expanded proton spectrum 1 ppm = 42 mm and since this is a 200 MHz NMR spectrum, therefore 200 Hz = 42 mm. The triplet spacing is measured to be 1.5 mm *i.e.* 1 Hz and this is typical of vicinal coupling ($^3J_{HH}$).

The triplet at approximately δ 2.8 ppm of intensity 2H in the ^1H NMR spectrum suggests a CH_2 with one CH_2 as a neighbour. The spacing of this triplet is almost identical with that observed for the triplet near δ 3.3 ppm. (2 pt)

The quintet at approximately δ 2.2 ppm. of intensity 2H has the same spacings as observed in the triplets near δ 2.8 and δ 3.3 ppm. This signal is consistent with a CH_2 group coupled to *two* flanking CH_2 groups. A sequence -CH_2-CH_2-CH_2- is revealed. (2 pt)

h) What structural elements does the ^{13}C NMR suggest?   **(6)**

From the ^{13}C spectrum there are 7 carbon environments: 4 carbons are in the typical aromatic/olefinic chemical shift range and 3 carbons in the aliphatic chemical shift range. The molecular formula is C9H11Br so there must be an element (or elements) of symmetry to account for the 2 carbons not apparent in the ^{13}C spectrum. (2 pt)

From the ^{13}C DEPT spectrum there are 3 CH resonances in the aromatic/olefinic chemical shift range and 3 CH_2 carbons in the aliphatic chemical shift range. (2 pt)

From the ^{13}C NMR spectrum, there is one resonance in the $^{13}C\{^1H\}$ spectrum which does not appear in the ^{13}C DEPT spectrum. This indicates one quaternary (non-protonated) carbon. There are 4 resonances in the aromatic region, 3 x CH and 1 x quaternary carbon, which is typical of a monosubstituted benzene ring. (2 pt)

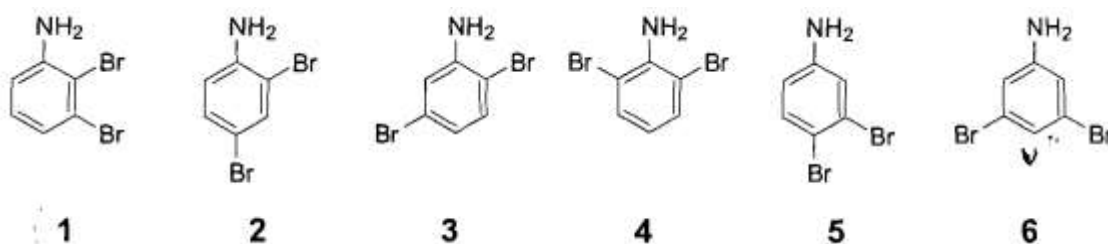i) Draw and name the structure which is consistent with the above analysis.   **(6)**
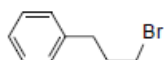
1-bromo-3-phenylpropane

$C_9H_{11}Br$

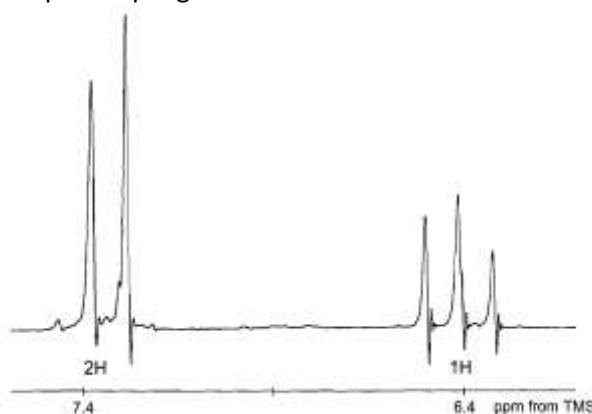# QUESTION 2   [4]
A portion of the 90 MHz ^1H NMR spectrum (5% in CDCl$_3$) of one of the six possible isomeric dibromoanilines is given below. Only the resonances of the aromatic protons are shown.

Determine which is the correct structure for this compound using arguments based on symmetry and the magnitudes of spin-spin coupling constants.

Of the 6 isomeric anilines, only compounds **4** and **6** have the correct symmetry to give a spectrum with only two chemical shifts in the aromatic region, in the ratio 2:1. (2 pt)

Both **4** and **6** would give A2X spin systems. The measured coupling constant is 7.7 Hz which is in the range for protons which are *ortho* to each other. Compound **4** is the correct answer. (2 pt)

QUESTION 3 [20]

An organic compound has the molecular formula $C_{12}H_{17}NO$. Identify the compound using the spectroscopic data given below.

v_{max} (KBr disc): 3296 m, 1642 s cm^{-1}.

^1H NMR ($CDCl_3$ solution): δ 7.23-7.42, m, 5H; 5.74, br s, exch. D_2O, 1H; 5.14, q, J 6.7 Hz, 1H; 2.15, t, J 7.1 Hz, 2H; 1.66, m, 2H; *1.48, d, J 6.7 Hz, 3H*; 0.93, t, J 7.3 Hz, 3H ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$ solution): δ 172.0 (C), 143.3 (C), 128.6, 127.3, 126.1, 48.5 (CH), 38.8 (CH_2), 21.7 (CH_3), 19.1 (CH_2), 13.7 (CH_3) ppm.

Mass spectrum: *m/e* 191 ($M^+·$, 40), 120 (33), 105 (58), 104 (100), 77 (18), 43 (46).

IR: C=O; OH or NH → can only be NH as only one O in molecule. (2 pt)

^1H NMR:

7.23-7.42: monosubstituted aromatic (2 pt)

5.74: NH (1 pt)

5.14 q couples with 1.48 d (methyl) suggests RR'CH-CH₃ Shifted upfield so probably attached to heteroatom. (2 pt)

5

2.15 t (2H); 1.66 m (2H), 0.93 t (3H) suggests $CH_2CH_2CH_3$; 2.15 typically for CH_2 next to C=O (2 pt)

^{13}C NMR:

172: C=O (1 pt)

143, 128, 127, 126: monosubstituted aromatic. (1 pt)

48: CH, confirms 5.14 in 1H NMR (1 pt)

21.7: methyl, confirms RR'CH-CH_3. Shifted upfield so probably attached to heteroatom. (1 pt)

38, 19, 13: $CH_2CH_2CH_3$; shifted upfield, typically for CH_2 next to C=O (1 pt)

Fragments to consider: C_6H_5-R; RR'CHCH_3 (one R is heteroatom); RC(=O)$CH_2CH_2CH_3$; RR'NH

Note: not a heteroatom next to C_6H_5… MS: 105 is fragment for C_8H_9, suggesting $C_6H_5CH(CH_3)$R (2 pt)

Suggested structure:
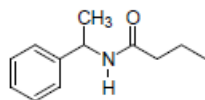
N-(1-methyl-1-phenylethyl)-
butyramide
$C_{12}H_{17}NO$

Question 4 [8]

How do DEPT experiments differ from normal NMR experiments? Distinguish between the various (3) DEPT techniques.

DEPT Spectra differentiate between CH, CH_2 and CH_3 groups in a compound and quaternary carbons (carbons C-4a, C-5 and C-8a in the structure) are always missing from DEPT spectra because the large one-bond heteronuclear coupling ($^1J_{XH}$) is used for polarization transfer. *DEPT 135*– yields spectra with CH (carbons C-1, C-3, C-6, C-7 and C-8 in the structure) and CH_3 (carbons C-9 and C-10 in the structure) in opposite (normal/positive) phase to CH_2 signals (carbon C-4). *DEPT 90*– yields spectra with only CH signals. *DEPT 45*- yields spectra with positive CH, CH_2, and CH_3 signals (all protonated carbons).
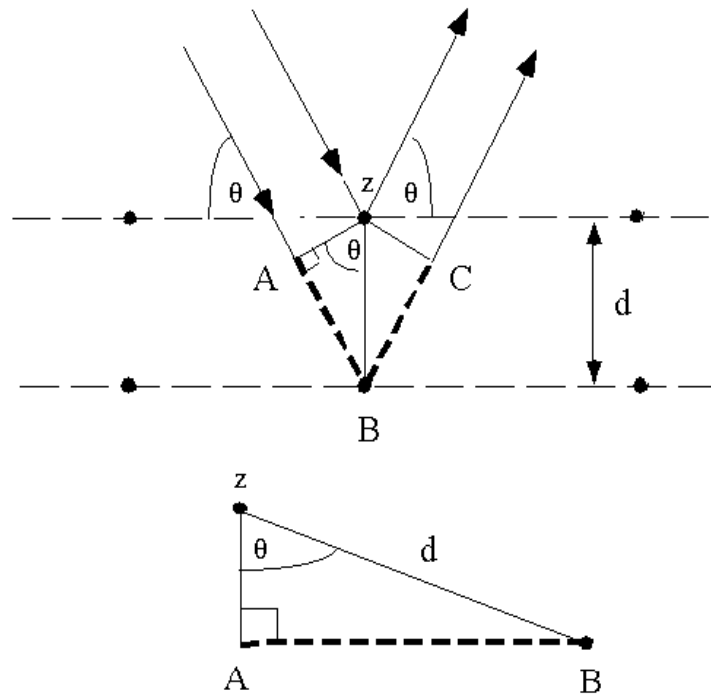

SECTION 2: SURFACE CHARACTERIZATION TECHNIQUES

QUESTION 5 [10]

a) From the diagrams below, if $n\lambda = AB + BC$, derive Bragg's equation. **(5)**
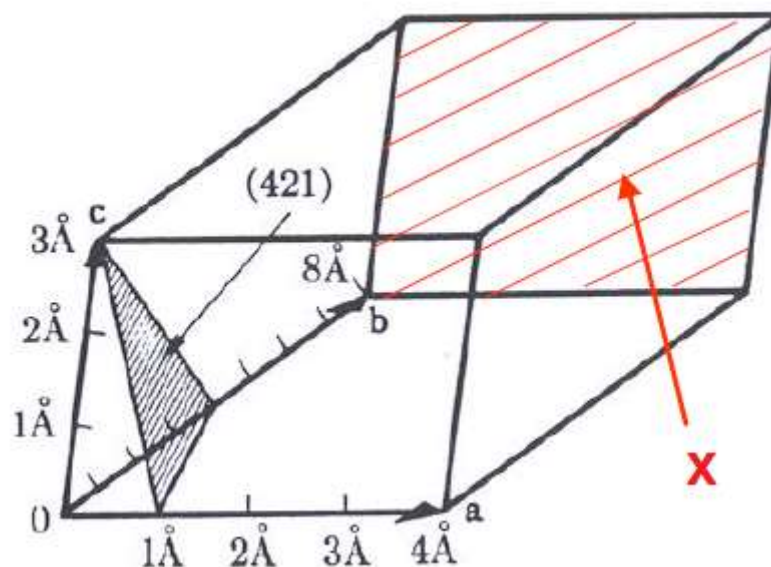
$$\theta_{X-ray1} = \theta_{X-ray2}$$

$$AB = BC$$

But $n\lambda = AB + BC$ this implies that $\qquad n\lambda = 2AB$

$$sin\theta = \frac{AB}{d}$$

$$AB = dsin\theta$$

Substitute AB by nλ/2 $\qquad\qquad n\lambda = 2dsin\theta$

b) If you are given the unit cell below with a triangle-like plane and plane X,

Complete the table below **(5)**

	Triangle-like plane			Plane X		
	a	b	c	A	B	c
Axial length (Å)	4	8	3	4	8	3
Intercept length (Å)	1	4	3	-	8	-
Fractional indices	1/4	1/2	1	0	1	0
Miller indices	4	2	1	0	1	0

QUESTION 6 [10]

a) What is an Auger electron? **(1)**

An Auger electron is an ejected electron as a result of ionization of a gas by bombardment with X-rays.

b) If a peak in an XPS spectrum is identified as 2p3/2. What is the electron's (i) orbital momentum (*l*), (ii) spin momentum (s), and the total momentum (j)? **(3)**

(i) orbital momentum (l) = 1

(ii) spin momentum (s) = 1/2

(ii) total momentum (j) = 3/2

c) Differentiate between the two photoelectron peaks of Pt, 4f7/2 and 4f5/2 **(3)**

4f7/2 has l = 3, s =1/2 and j = (3 + ½ = 7/2)

4f5/2 has l = 3, s = -1/2 and j = (3 – 1/2 =5/2)

d) Explain the increase in binding energy as the oxidation state of an atom increases. **(2)**
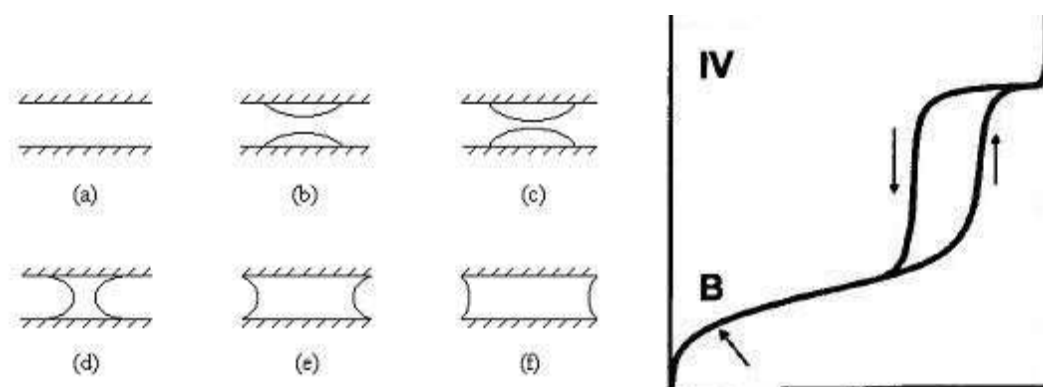
e) How can you eliminate Auger electron peaks from an XPS spectrum? **(1)**

QUESTION 7 [10]

a) Explain the formation of hysteresis loop in the type IV isotherm. Use diagram(s) where necessary. **(2)**

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b) Derive the BET equation from first principles. **(5)**

$$\frac{p}{v} = \frac{1}{v_m b} + \frac{p}{v_m}$$

$$v = \frac{v_m C p}{(p_0 - p)[1 + (C - 1)\frac{p}{p_0}]}$$

c) Explain regions I,II and III in the type II isotherm shown below in terms of adsorption. Determine and briefly explain where you are most likely to get reliable surface area information in this isotherm. **(3)**
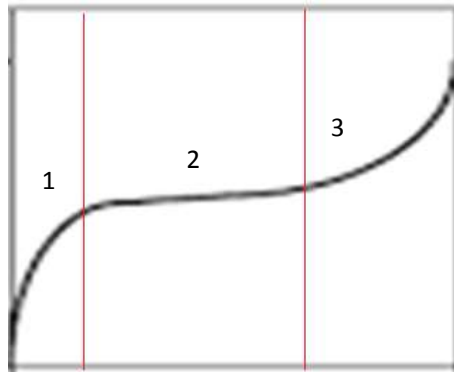
Region I: The rapid adsorption of gaseous molecules on the energetic regions of the solid.

Region II: Attachment of additional gas molecules on sites already occupied, i.e., additional layers are forming (multilayer formation)

Region III: Bulk condensation of gaseous molecules to a liquid.

REFERENCE TABLES

Table of Characteristic IR Absorptions

frequency, cm⁻¹	bond	functional group
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH₂X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp
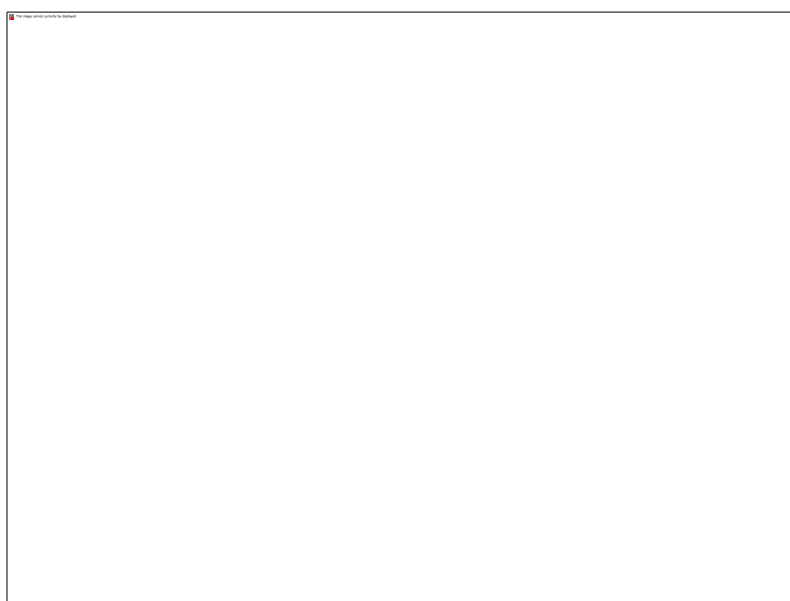
¹H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED ALKENES
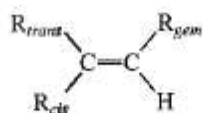
$$\delta_H \text{ ppm} = 5.25 + \delta_{gem} + \delta_{cis} + \delta_{trans}$$

Substituents (—R)	δ_{gem}	δ_{cis}	δ_{trans}
Saturated carbon groups			
Alkyl	0.44	−0.26	−0.29
—CH₂—O—	0.67	−0.02	−0.07
Aromatic groups			
—C₆H₅	1.35	0.37	−0.10
Carbonyl, acid derivatives, and nitrile			
COR	1.10	1.13	0.81
—COOH	1.00	1.35	0.74
—COOR	0.84	1.15	0.56
—C≡N	0.23	0.78	0.58
Oxygen groups			
—OR	1.18	−1.06	−1.28
—OCOR	2.09	−0.40	−0.67
Nitrogen groups			
—NR₂	0.80	−1.26	−1.21
—NO₂	1.87	1.30	0.62
Halogen groups			
—F	1.54	−0.40	−1.02
—Cl	1.08	0.19	0.13
—Br	1.04	0.40	0.55
—I	1.14	0.81	0.88

¹H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED BENZENE RINGS

$$\delta_H \text{ ppm} = 7.27 + \Sigma\delta$$
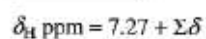
Substituents (—R)	δ_{ortho}	δ_{meta}	δ_{para}
Saturated carbon groups			
Alkyl	−0.14	−0.06	−0.17
—CH₂OH	−0.07	−0.07	−0.07
Aldehydes and ketones			
—CHO	0.61	0.25	0.35
—COR	0.62	0.14	0.21
Carboxylic acids and derivatives			
—COOH	0.85	0.18	0.34
—COOR	0.71	0.10	0.21
—C≡N	0.25	0.18	0.30
Oxygen groups			
—OH	−0.53	−0.17	−0.45
—OCH₃	−0.48	−0.09	−0.44
—OCOCH₃	−0.19	−0.03	−0.19
Nitrogen groups			
—NH₂	−0.80	−0.25	−0.65
—NO₂	0.95	0.26	0.38
Halogen groups			
—F	−0.29	−0.02	−0.23
—Cl	0.03	−0.02	−0.09
—Br	0.18	−0.08	−0.04
—I	0.38	−0.23	−0.01

¹³C NMR Correlation Chart
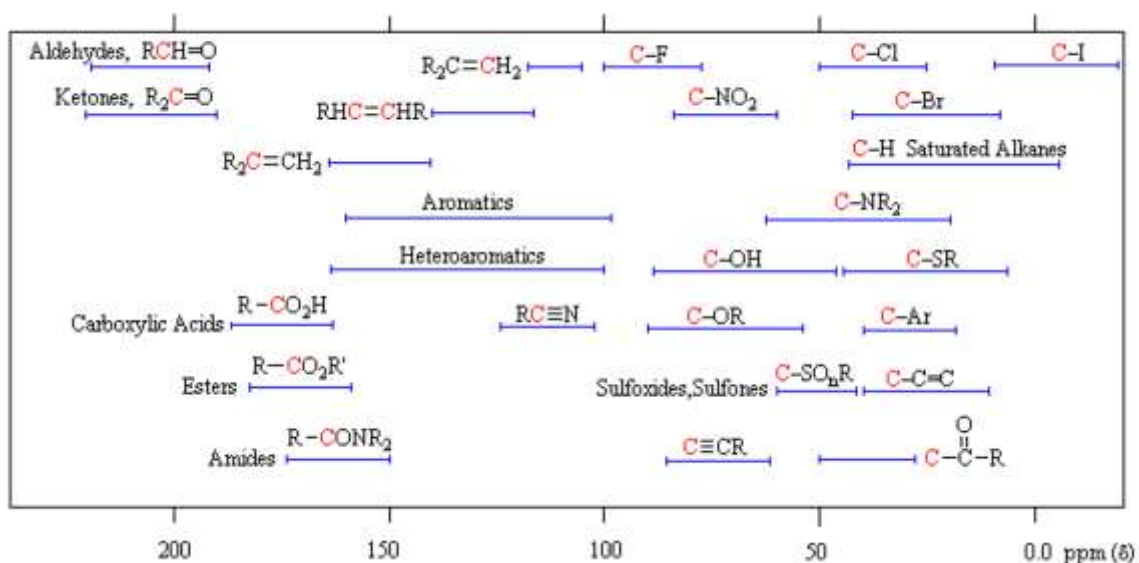
^{13}C SUBSTITUENT INCREMENTS FOR ALKENE (VINYL) CARBONS[a,b]

$$\gamma-\beta-\alpha \underset{\alpha}{\overset{}{\diagdown}} C=C \underset{\alpha'}{\overset{\alpha'-\beta'-\gamma'}{\diagup}}$$

Substituent	α	β	γ	α'	β'	γ'
Carbon	10.6	7.2	−1.5	−7.9	−1.8	−1.5
—C_6H_5	12			−11		
—OR	29	2		−39	−1	
—OCOR	18			−27		
—COR	15			6		
—COOH	4			9		
—CN	−16			15		
—Cl	3	−1		−6	2	
—Br	−8	0		−1	2	
—I	−38			7		

[a] In the upper chains, if a group is in the β or γ position, the preceding atoms (α and/or β) are assumed to be carbon atoms. Add these increments to the base value of ethylene (123.3 ppm).
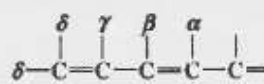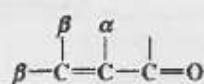
[b] Calculate C1 as shown in the diagram. Redefine C2 as C1 when estimating values for C2.

^{13}C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)[a]

Substituent Y	α (ipso)	o (ortho)	m (meta)	p (para)
—CH_3	9.3	0.7	−0.1	−2.9
—CH_2CH_3	11.7	−0.5	0	−2.6
—$CH(CH_2)_2$	20.1	−2.0	−0.3	−2.5
—$C(CH_3)_3$	18.6	−3.4	−0.4	−3.1
—CH=CH_2	9.1	−2.4	0.2	−0.5
—C≡CH	−6.2	3.6	−0.4	−0.3
—C_6H_5	8.1	−1.1	−0.5	−1.1
—CHO	8.2	1.2	0.6	5.8
—$COCH_3$	8.9	−0.1	−0.1	4.4
—COC_6H_5	9.1	1.5	−0.2	3.8
—COOH	2.1	1.6	−0.1	5.2
—$COOCH_3$	2.0	1.2	−0.1	4.3
—CN	−16.0	3.6	0.6	4.3
—NH_2	18.2	−13.4	0.8	−10.0
—$N(CH_3)_2$	16.0	−15.7	0.8	−10.5
—$NHCOCH_3$	9.7	−8.1	0.2	−4.4
—NO_2	19.6	−4.9	0.9	6.0
—OH	28.8	−12.7	1.6	−7.3
—OCH_3	33.5	−14.4	1.0	−7.7
—$OCOCH_3$	22.4	−7.1	−0.4	−3.2
—F	33.6	−13.0	1.6	−4.5
—Cl	5.3	0.4	1.4	−1.9
—Br	−5.4	3.4	2.2	−1.0
—I	−31.2	8.9	1.6	−1.1

[a] Add these increments to the base value for benzene-ring carbons (128.5 ppm).

EMPIRICAL RULES FOR ENONES

$$\overset{\beta}{\underset{|}{C}}=\overset{\alpha}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=O \qquad \overset{\delta}{\underset{|}{C}}=\overset{\gamma}{\underset{|}{C}}-\overset{\beta}{\underset{|}{C}}=\overset{\alpha}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=$$

Base values:		
Six-membered ring or acyclic parent enone		= 215 nm
Five-membered ring parent enone		= 202 nm
Acyclic dienone		= 245 nm
Increments for:		
Double-bond-extending conjugation		30
Alkyl group or ring residue	α	10
	β	12
	γ and higher	18
Polar groupings:		
—OH	α	35
	β	30
	δ	50
—OCOCH$_3$	α,β,δ	6
—OCH$_3$	α	35
	β	30
	γ	17
	δ	31
—Cl	α	15
	β	12
—Br	α	25
	β	30
—NR$_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39
Solvent correction		Variable
	λ_{max}^{EtOH} (calc) = Total	

EMPIRICAL RULES FOR UNSATURATED ACIDS AND ESTERS

Base values for:

$$\overset{\beta}{\underset{\beta}{\diagup}}C=C\overset{\alpha}{\underset{\diagdown COOR}{}} \qquad \overset{\beta}{\underset{\beta}{\diagup}}C=C\overset{\alpha}{\underset{\diagdown COOH}{}}$$
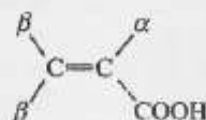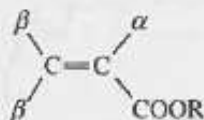
With α or β alkyl group	208 nm
With α,β or β,β alkyl groups	217
With α,β,β alkyl groups	225
For an exocyclic α,β double bond	Add 5 nm
For an endocyclic α,β double bond in a five- or seven-membered ring	Add 5 nm