CHEM 344 Fall 2014 Spectroscopy Quiz – A (50 pts)

Name:

TA Name:

Directions for analyzing spectra:

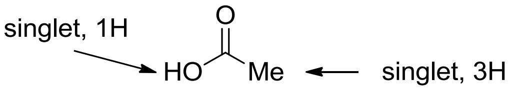
- Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. Assign each **^{1}H-NMR** signal and write your assignments directly onto the spectrum. Justify your assignments by use of the empirical chemical shift parameters (Curphy-Morrison parameters) or chemical shift tables found at the end of the exam.

- Identify each **^{13}C-NMR** signal as either alkyl, vinyl, alkynyl, aryl, nitrile, imine, or carbonyl (you do not need to assign individual carbon atoms to each signal).

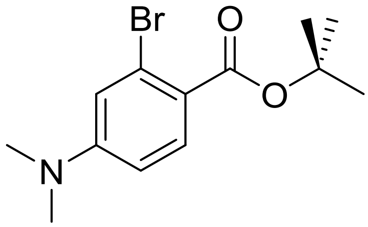
- Assign each key **IR** absorption band >1500 cm^{-1} to a specific functional group.

- Draw fragments for all labeled peaks in the **EI-MS** directly onto the spectrum (you do not need to show the fragmentation mechanism unless directed to do so).

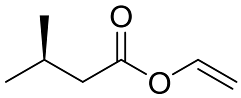
1) Predict the multiplicity and integration value of all signals in the ^{1}H-NMR spectrum of each molecule shown below. **(8 pts total)** See the example below.



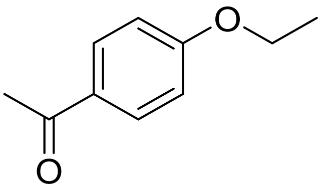
a)



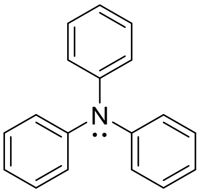
b)

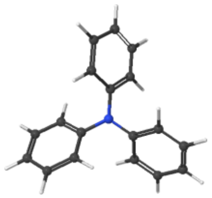


2) For the molecule below, use the empirical (Curphy-Morrison) parameters available at the end of the exam to predict the chemical shift of each unique ^{1}H-nucleus. **(4 pts total)**



3) The ^{1}H-NMR spectrum of triphenylamine is on the subsequent page. An expansion of the aromatic region is included for clarity. **(13 pts total)**





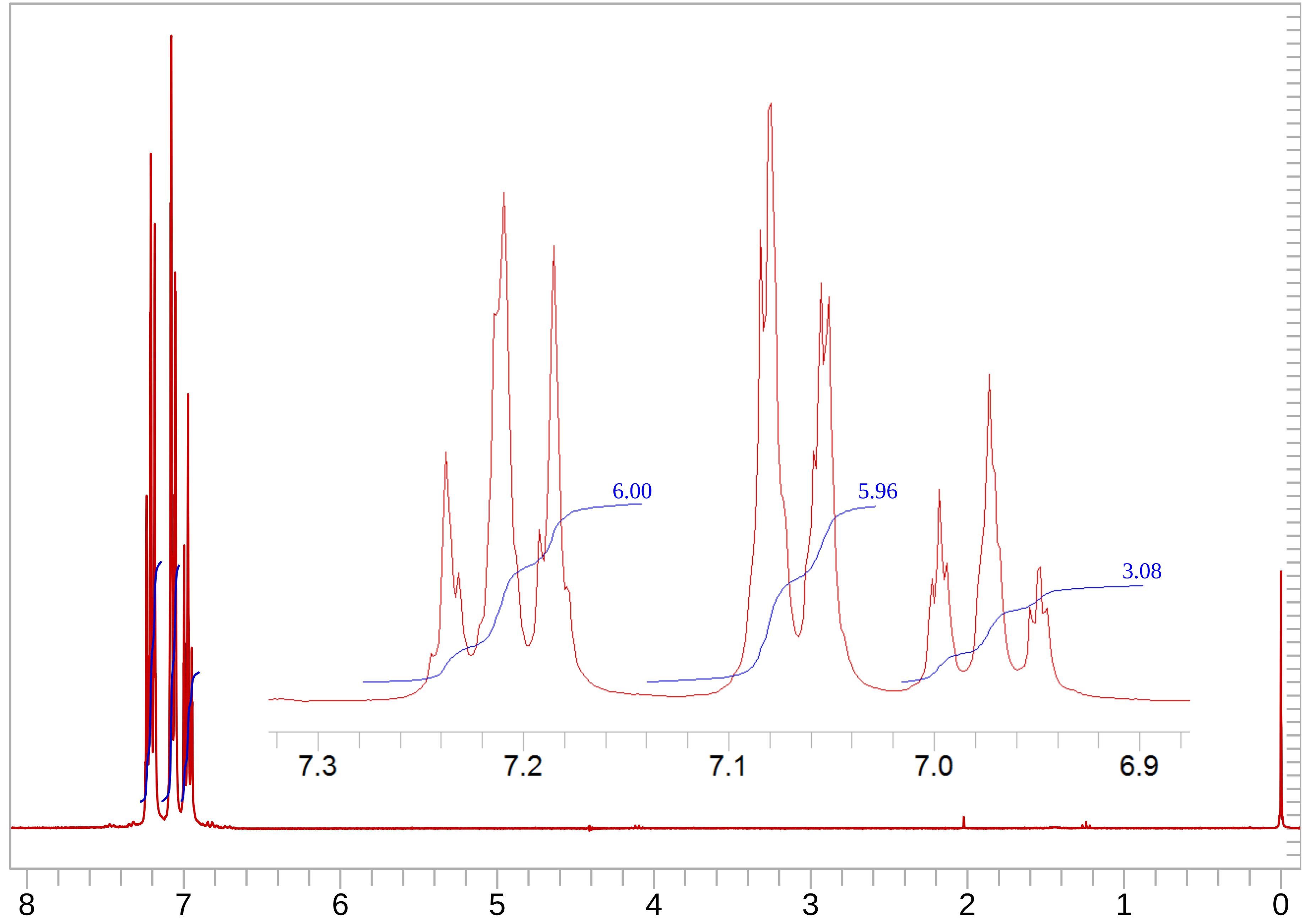
a) Assign the ^{1}H-nuclei of triphenylamine to the appropriate signals in the ^{1}H-NMR spectrum. **Draw your assignments directly onto the ^{1}H-NMR spectrum using the H_a, H_b etc. convention shown in the lectures and practice problem sets. (3 pts)**

b) ***In the space below***, draw all important resonance structures of triphenylamine to justify your signal assignments. Clearly show all formal charges and lone pairs. **(6 pts)**

c) Assuming that resonance structures are sufficient to predict the chemical shifts of the H-nuclei in this molecule, provide a brief written explanation of your assignments. **(4 pts)**

300 MHz ^{1}H NMR

In CDCl3

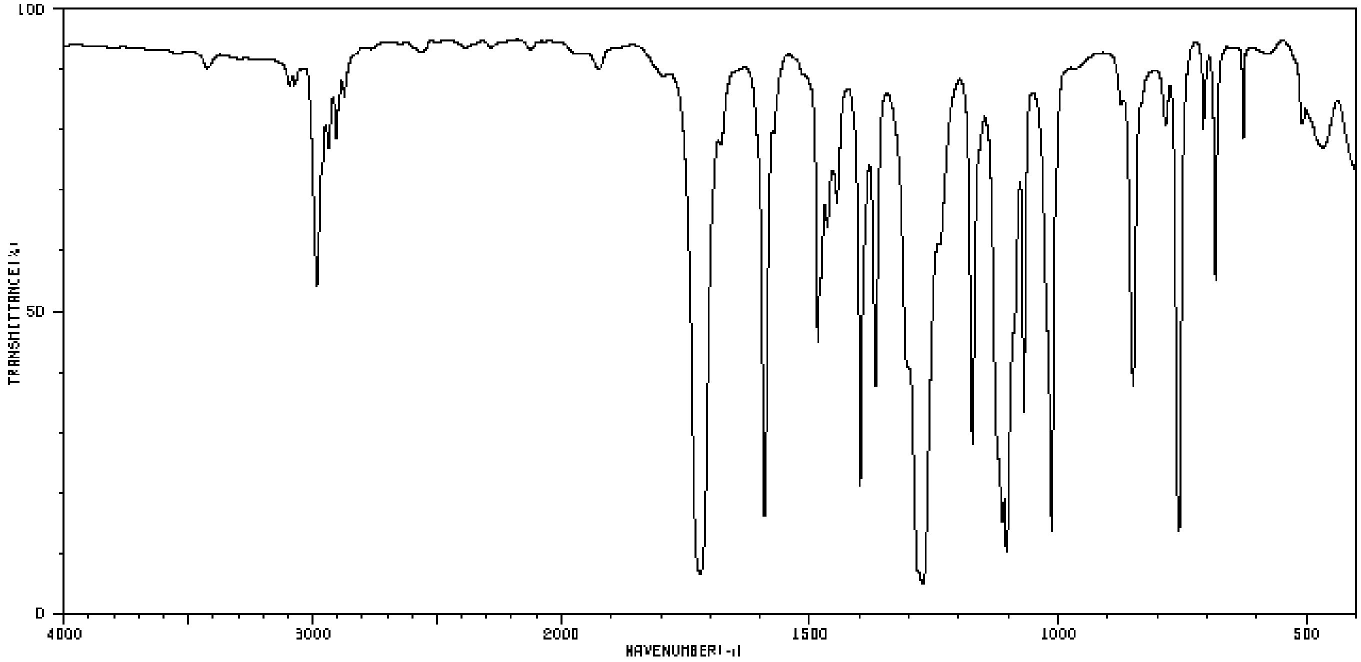


4) The spectra below were obtained from a brominated organic molecule ($C_9H_9BrO_2$). Determine the structure of the molecule using the spectra provided and by answering the questions below. **(25 pts total)**

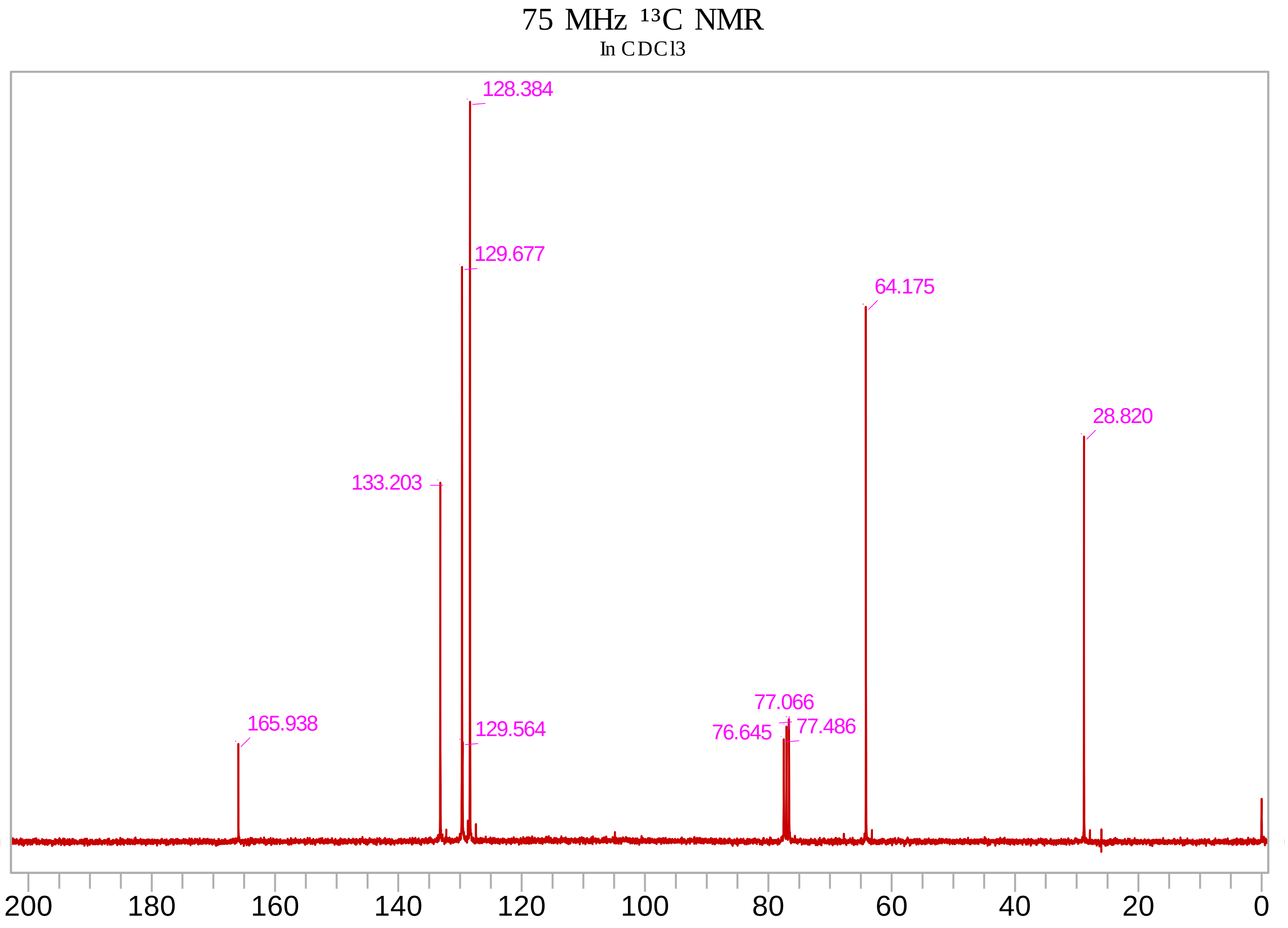
a) Calculate the number of double bond equivalencies, unsaturation number, or the index of hydrogen deficiency for this molecule using the equation provided. **(2 pt)**

$$IHD = \frac{2C + N - H - X + 2}{2}$$

b) Based upon the chemical formula, index of dehydration, and the IR spectrum below, what organic functional groups are possible/likely in this molecule? **(3 pts)**

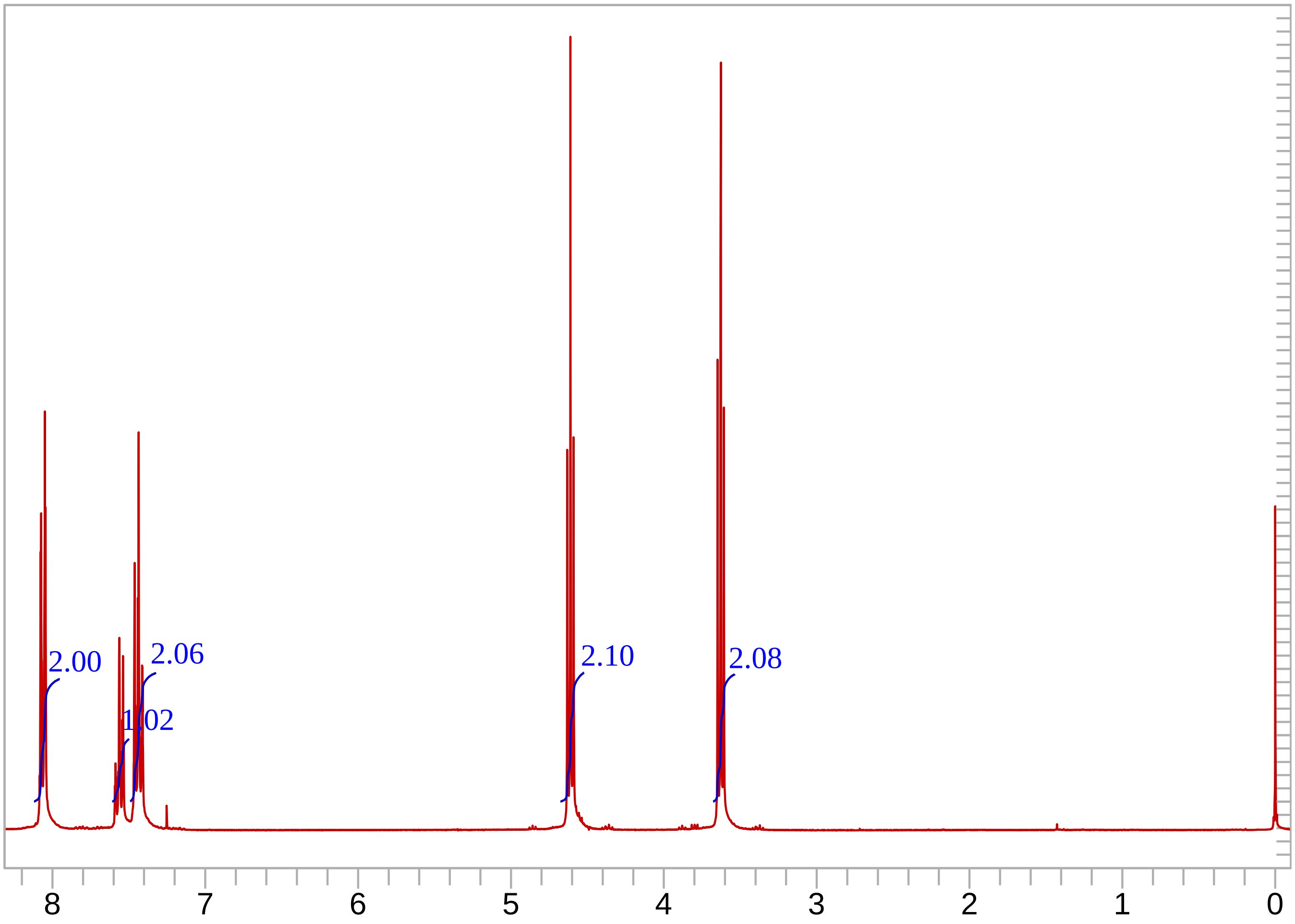


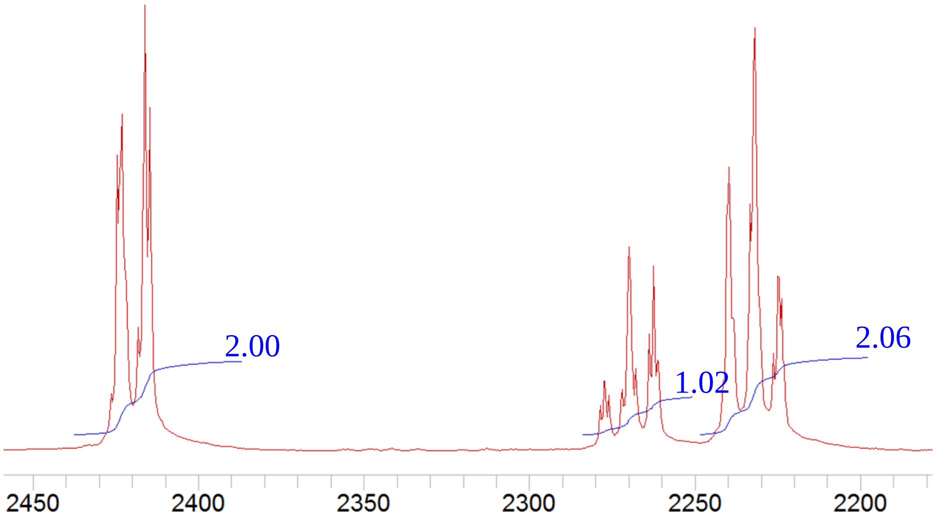
c) Use the ^{13}C-NMR spectrum below, collected in $CDCl_3$, to identify each ^{13}C-atom as either alkyl, vinyl, alkynyl, aryl, nitrile, imine, or carbonyl. **(3 pts)**



d) Use the information from parts a – c and the ^{1}H-NMR spectrum (collected in $CDCl_3$) below, to determine the structure of the molecule and assign each ^{1}H-atom. Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. **(10 pts)**

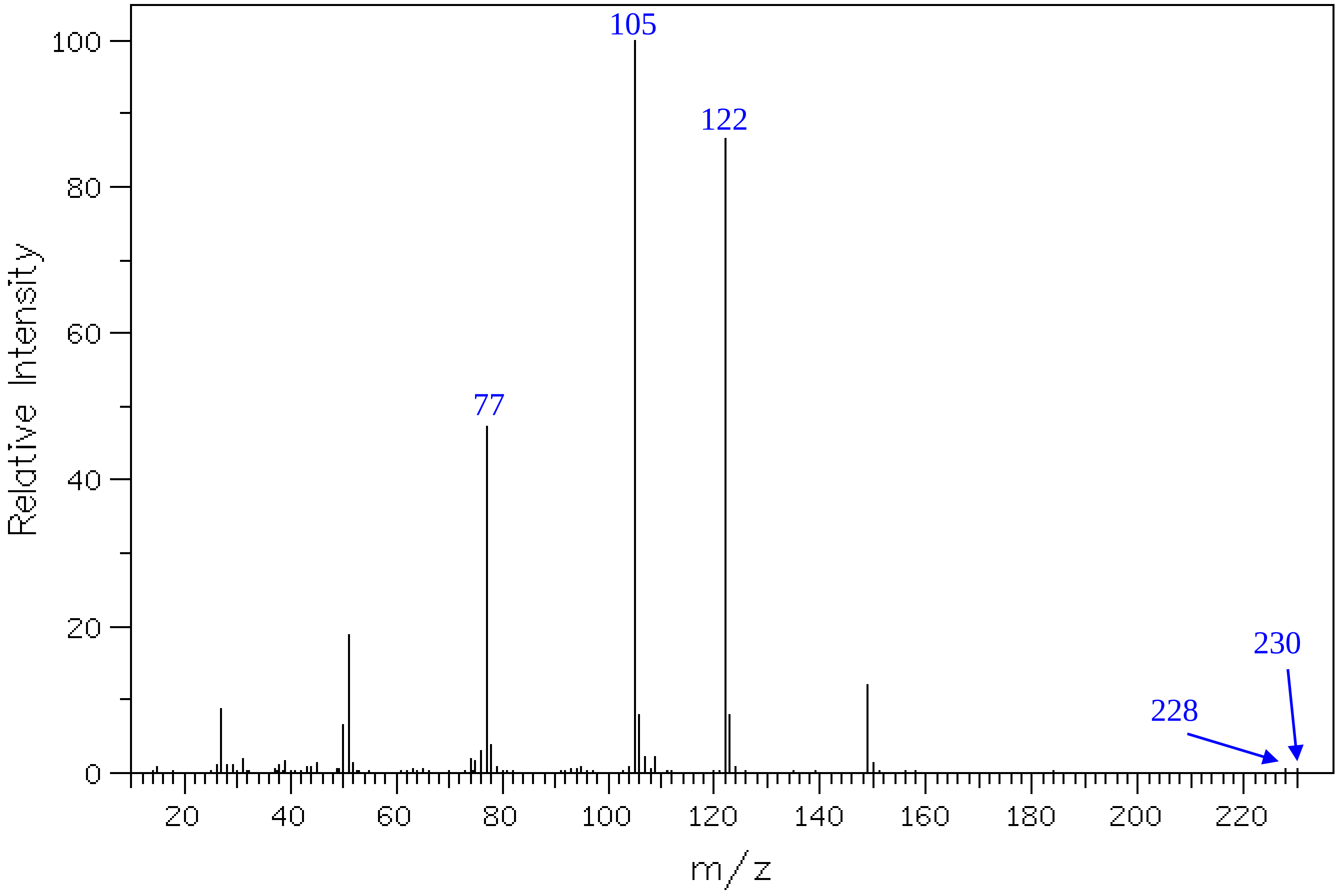
300 MHz ^{1}H NMR
In CDCl3





e) Confirm your structure determination by use of the EI-Mass spectrum provided below. **(7 points total)**

i. Provide the most likely ions responsible for the signals at *m/z* = 230, 228, 122, 105, and 77. Draw the fragments on the spectrum and clearly label them. Show all lone pairs and formal charges. **(5 points)**



ii. Which of the signals in the EI-Mass spectrum contain the bromine atom? Circle one or more signals on the EI-Mass spectrum that contain bromine. Explain briefly how you can identify presence of bromine atoms in the species responsible for these signals. **(2 points)**

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Name:

TA Name:

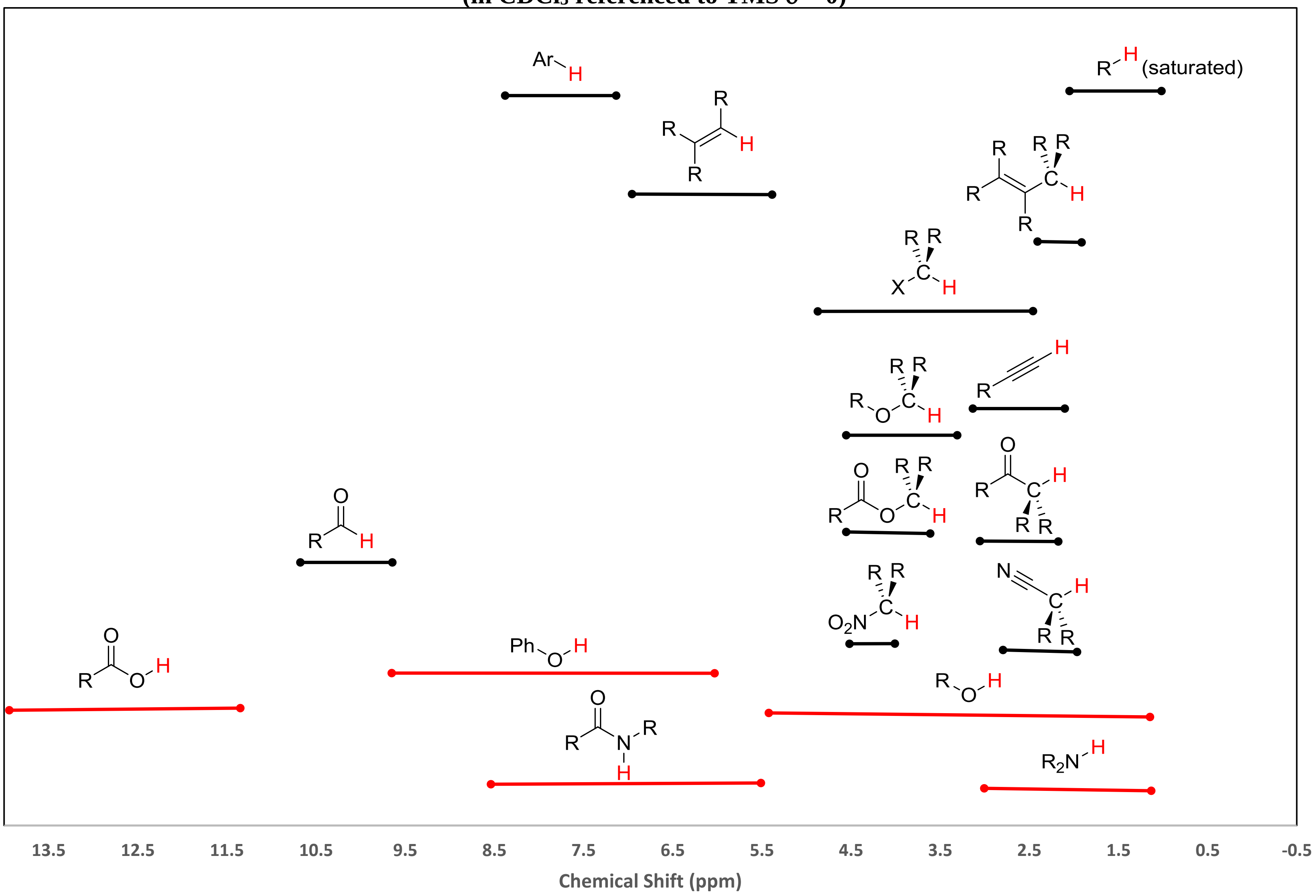
1) ______ /8

2) ______ /4

3) ______ /13

4) ______ /25

Total = ______ /50



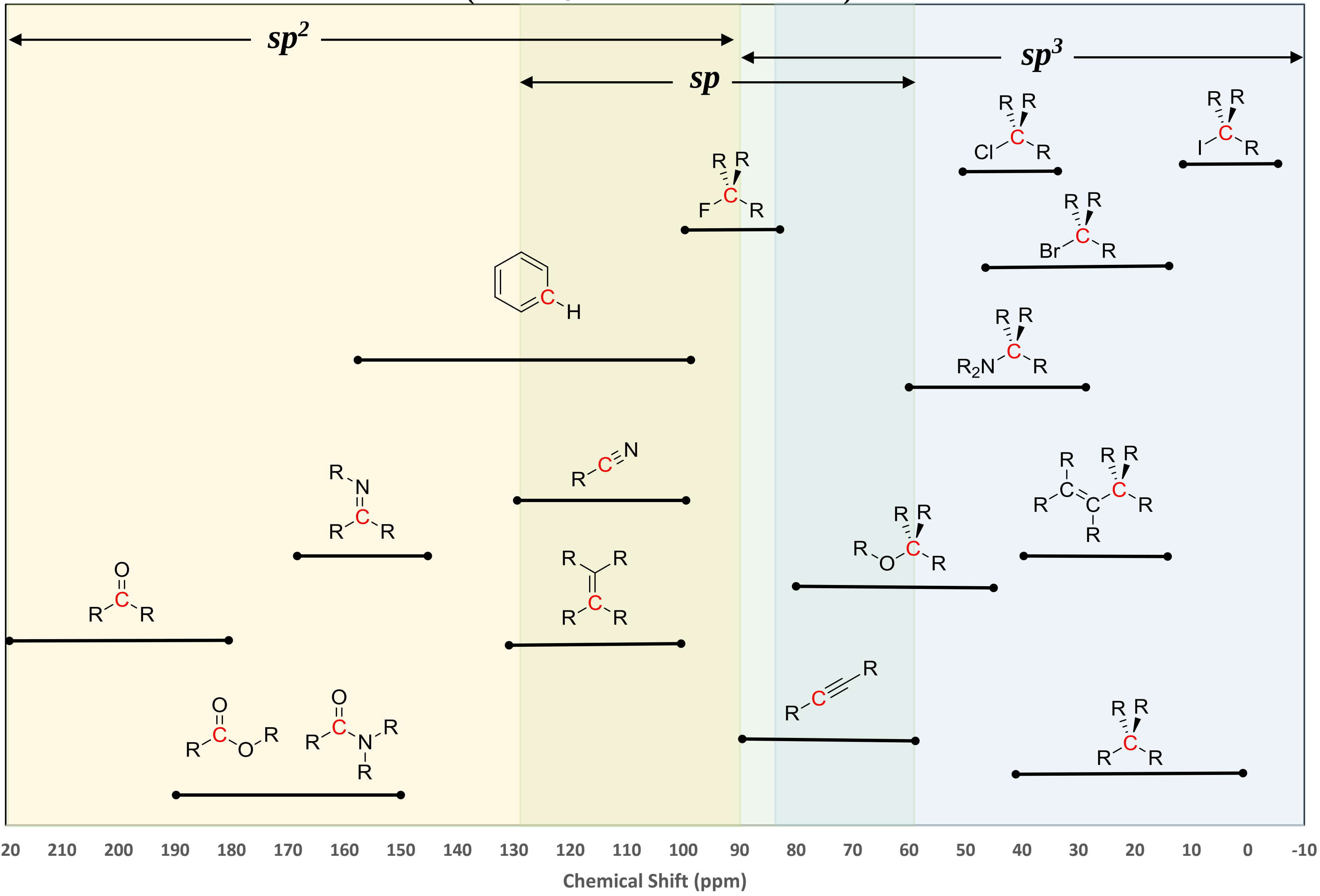
Typical ^{1}H-NMR Chemical Shift Ranges

(in $CDCl_3$ referenced to TMS δ = 0)

F

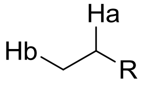
Typical ^{13}C-NMR Chemical Shift Ranges

(in $CDCl_3$ referenced to TMS δ = 0)



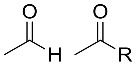
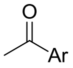
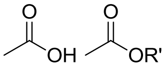
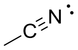
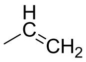
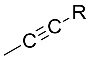
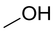
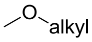
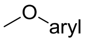
Curphy-Morrison Additivity Constants for Proton NMR

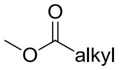
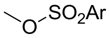
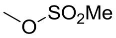
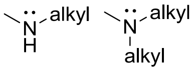
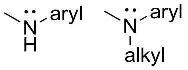
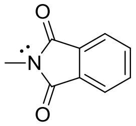
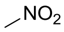
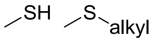
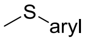
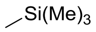
α and β Substituent Effects on:



Standard Shift: Methyl (-CH_3) 0.90 δ, Methylene (-CH_2-) 1.20 δ, Methine (-CH-) 1.55 δ

Shift Estimate: δ_H = Standard Shift + $\Sigma_{\alpha\text{-shifts}} + \Sigma_{\beta\text{-shifts}}$

Substituent (R)		α-shift	β-shift
Cl	-CH_3	2.30	0.60
	-CH_2-	2.30	0.55
	-CH-	2.55	0.15
Br	-CH_3	1.80	0.80
	-CH_2-	2.15	0.80
	-CH-	2.20	0.25
I	-CH_3	1.80	0.80
	-CH_2-	2.15	0.80
	-CH-	2.20	0.25
Aryl	-CH_3	1.45	0.35
	-CH_2-	1.45	0.55
	-CH-	1.35	----
	-CH_3	1.25	0.25
	-CH_2-	1.10	0.30
	-CH-	0.95	----
	-CH_3	1.70(6)	0.28(4)
	-CH_2-	1.64(10)	0.50(3)
	-CH-	1.76(2)	0.76(1)
	-CH_3	1.20	0.25
	-CH_2-	1.00	0.30
	-CH-	0.95	----
	-CH_3	1.10	0.45
	-CH_2-	1.10	0.40
	-CH-	0.95	----
	-CH_3	0.90	0.05
	-CH_2-	0.75	0.10
	-CH-	0.65	----
	-CH_3	0.90	0.15
	-CH_2-	0.80	0.05
	-CH-	0.35	----
	-CH_3	2.45	0.40
	-CH_2-	2.30	0.20
	-CH-	2.10	----
	-CH_3	2.45	0.30
	-CH_2-	2.30	0.15
	-CH-	2.10	----
	-CH_3	2.95	0.40
	-CH_2-	2.65(11)	0.45
	-CH-	3.06(2)	----

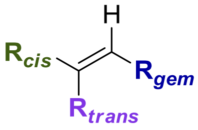
Substituent (R)		α-shift	β-shift
	-CH_3	2.90	0.40
	-CH_2-	2.95	0.45
	-CH-	3.45	----
	-CH_3	2.84	0.39(1)
	-CH_2-	2.66(6)	0.28(5)
	-CH-	3.16(3)	0.32(2)
	-CH_3	3.01	0.47(2)
	-CH_2-	2.90(5)	0.43(2)
	-CH-	2.64(1)	0.61(1)
	-CH_3	1.25	0.20
	-CH_2-	1.40	0.15
	-CH-	1.35	----
	-CH_3	2.08(8)	0.28(10)
	-CH_2-	2.03(12)	0.34(2)
	-CH-	2.33(2)	?
	-CH_3	2.08(8)	0.28(10)
	-CH_2-	2.03(12)	0.34(2)
	-CH-	2.33(2)	?
	-CH_3	3.50	0.65
	-CH_2-	3.15	0.85
	-CH-	3.05	----
	-CH_3	2.08(1)	0.45(1)
	-CH_2-	1.45(3)	0.46(1)
	-CH-	1.46(2)	-0.22(1)
	-CH_3	1.20	0.40
	-CH_2-	1.30	0.30
	-CH-	1.30	----
	-CH_3	1.47(2)	0.35(2)
	-CH_2-	1.45(8)	0.31(2)
	-CH-	1.60(4)	0.01(4)
	-CH_3	-0.90(1)	0.06(2)
	-CH_2-	-0.39(2)	?
	-CH-	-0.83(8)	?

Adapted from: P. L. Fuchs and C. A. Bunnell, "Carbon-13 NMR Based Spectral Problems," John Wiley, New York, 1979. Data with numbers in parentheses were added by H. J. Reich with limited number of examples (number is sample size).

(Adapted from Hans J. Reich, http://www.chem.wisc.edu/areas/reich/nmr/notes-9-hmr-5-curphy-morrison.pdf)

Curphy-Morrison Additivity Constants for Calculating Vinyl Chemical Shifts

Substituent Effects on:



Shift Estimate: $\delta_{H\ (vinyl)} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$

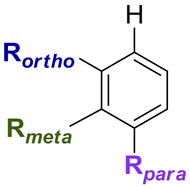
Substituent (R)	Z_{gem}	Z_{cis}	Z_{trans}	Substituent (R)	Z_{gem}	Z_{cis}	Z_{trans}
H	0.00	0.00	0.00	F	1.54	-0.40	-1.02
alkyl	0.45	-0.22	-0.28	Cl	1.08	0.18	0.13
Alkyl (cyclic)	0.69	-0.25	-0.28	Br	1.07	0.45	0.55
CH_2OH	0.64	-0.01	-0.02	I	1.14	0.81	0.88
CH_2SH	0.71	-0.13	-0.22	OR (R = aliphatic)	1.22	-1.07	-1.21
CH_2X (X = F, Cl, Br)	0.71	-0.13	-0.22	OR (R = conjugated)	1.21	-0.60	-1.00
CH_2NR_2	0.58	-0.10	-0.08	O-C(O)R	2.11	-0.35	-0.64
CF_3	0.66	0.61	0.32	NR_2 (R = aliphatic)	0.80	-1.26	-1.21
$C{=}CR_2$ (isolated)	1.00	-0.09	-0.23	NR_2 (R = conjugated)	1.17	-0.53	-0.99
$C{=}CR_2$ (conjugated)	1.24	0.02	-0.05	N=N-Ph	2.39	1.11	0.67
C≡C-R	0.47	0.38	0.12	NO_2	1.87	1.30	0.62
C≡N	0.27	0.75	0.55	N-C(O)R	2.08	-0.57	-0.72
COOH (isolated)	0.97	1.41	0.71	N_3	1.21	-0.35	-0.71
COOH (conjugated)	0.80	0.98	0.32	$SiMe_3$	0.77	0.37	0.62
COOR (isolated)	0.80	1.18	0.55				
COOR (conjugated)	0.78	1.01	0.46				
C(O)H (aldehyde)	1.02	0.95	1.17				
$C(O)NR_2$ (amide)	1.37	0.98	0.46				
C(O)Cl (acid chloride)	1.11	1.46	1.01				
C(O)R (ketone)	1.10	1.12	0.87				
C(O)R (conj. ketone)	1.06	0.91	0.74				
CH_2-C(O)R; CH_2-CN	0.69	-0.08	-0.06				
CH_2Ar (benzyl)	1.05	-0.29	-0.32				
Aryl	1.38	0.36	-0.07				
Aryl (*o*-substituted)	1.65	0.19	0.09				

The increments 'R conjugated' are to be used instead of 'R isolated' when either the substituent or the double bond is conjugated with further substituents. The increment alkyl (cyclic) is to be used when both the substituent and the double bond form part of a ring. (Data for compounds containing 3- and 4-membered rings have not been considered.) Numbers in parentheses represent the number of examples used to calculate the parameters.

[1] Pascual, C. *Helv. Chem. Acta* **1966**, *49*, 164.
[2] L'Abbe, G. *Chem. & Ind.* (London) **1971**, 278.

(Adapted from Hans J. Reich, http://www.chem.wisc.edu/areas/reich/nmr/notes-9-hmr-6-vinyl-aryl-shifts.pdf)

Curphy-Morrison Additivity Constants for Calculating Benzene Chemical Shifts



Substituent Effects on:

Shift Estimate: $\delta_{H\ (vinyl)} = 7.36 + Z_{ortho} + Z_{meta} + Z_{para}$

Substituent (R)	Z_{ortho}	Z_{meta}	Z_{para}	Substituent (R)	Z_{ortho}	Z_{meta}	Z_{para}
H	0.00	0.00	0.00	OPh	-0.36	-0.04	-0.28
CH_3	-0.18	-0.11	-0.21	O-C(O)CH_3	-0.27	-0.02	-0.13
*t*Bu	0.02	-0.08	-0.21	O-C(O)Ph	-0.14	0.07	-0.09
CH_2Cl	0.02	-0.01	-0.04	O-SO_2CH_3	-0.05	0.07	-0.01
CH_2OH	-0.07	-0.07	-0.07	SH	-0.08	-0.16	-0.22
CF_3	0.32	0.14	0.20	SMe	-0.08	-0.10	-0.24
CCl_3	0.64	0.13	0.10	SPh	0.06	-0.09	-0.15
C=CH_2	0.04	-0.04	-0.12	SO_2Cl	0.76	0.35	0.45
C=CHCOOH	0.19	0.04	0.05	NH_2	-0.71	-0.22	-0.62
C≡C-H	0.15	-0.02	-0.01	NMe_2	-0.66	-0.18	-0.67
C≡C-Ph	0.17	-0.02	-0.03	NEt_2	-0.68	-0.15	-0.73
Ph	0.23	0.07	-0.02	$NMe_3^+ I^-$	0.69	0.36	0.31
COOH	0.77	0.11	0.25	NHC(O)CH_3	0.14	-0.07	-0.27
C(O)OCH_3	0.68	0.08	0.19	NH-NH_2	-0.60	-0.08	-0.55
C(O)OPh	0.85	0.14	0.27	N=N-Ph	0.67	0.20	0.20
C(O)NH_2	0.46	0.09	0.17	N=O	0.58	0.31	0.37
C(O)Cl	0.76	0.16	0.33	NO_2	0.87	0.20	0.35
C(O)CH_3	0.60	0.10	0.20	$SiMe_3$	0.22	-0.02	-0.02
C(O)*t*Bu	0.44	0.05	0.05				
C(O)H	0.53	0.18	0.28				
C(NPh)H	0.60	0.20	0.20				
C(O)Ph	0.45	0.12	0.23				
C(O)C(O)Ph	0.62	0.15	0.30				
CN	0.29	0.12	0.25				
F	-0.29	-0.02	-0.23				
Cl	-0.02	-0.07	-0.13				
Br	0.13	-0.13	-0.08				
I	0.39	-0.21	0.00				
OH	-0.53	-0.14	-0.43				
OCH_3	-0.45	-0.07	-0.41				

Data in dilute $CDCl_3$ by Paul Schatz, UW-Madison. Original data from *J. Am. Chem. Soc.* **1956**, *78*, 3043 at 30 MHz with 50% solutions in cyclohexane.

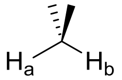
(Adapted from Hans J. Reich, http://www.chem.wisc.edu/areas/reich/nmr/notes-9-hmr-6-vinyl-aryl-shifts.pdf)

Typical ^{1}H-NMR Coupling Values*

Coupling

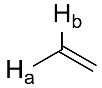
2-bond

gem alkyl



$^{2}J = 2 - 15$
(typical -12 Hz)

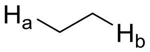
gem vinyl



$^{2}J = 1 - 3$

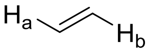
3-bond

vicinal alkyl



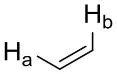
$^{3}J = 2 - 20$
(typical 7 Hz)

trans vinyl



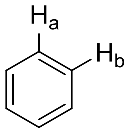
$^{3}J = 12 - 18$

cis vinyl



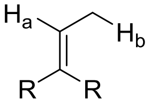
$^{3}J = 6 - 12$

ortho aryl



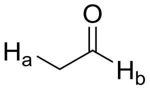
$^{3}J = 8 - 12$

vicinal C(sp^{2})-C(sp^{3})



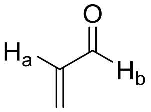
$^{3}J = 3 - 11$
(dihedral dependent)

vicinal aldehyde



$^{3}J = 1 - 3$

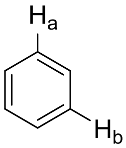
vicinal conjugated aldehyde



$^{3}J = 7 - 8$

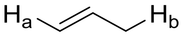
4-bond

meta aryl



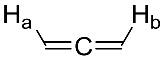
$^{4}J = 2 - 3$

allylic



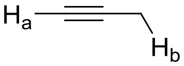
$^{4}J = 0 - 3$

allenic



$^{4}J = 6 - 7$

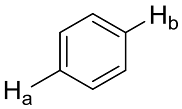
propargylic



$^{4}J = 2 - 4$

5-bond

para aryl



$^{5}J = 0 - 1$

*J values listed as absolute values of coupling in Hz

Infrared Correlation Chart

	Type of Vibration		Frequency (cm^{-1})	Intensity
C-H	Alkanes	(stretch)	3000-2850	s
	-CH$_3$	(bend)	1450 and 1375	m
	-CH$_2$-	(bend)	1465	m
	Alkenes	(stretch)	3100-3000	m
		(out-of-plane bend)	1000-650	s
	Aromatics	(stretch)	3150-3050	s
		(out-of-plane bend)	900-690	s
	Alkyne	(stretch)	~3300	s
	Aldehyde		2900-2800	w
			2800-2700	w
C-C	Alkane	not interpretatively useful		
C=C	Alkene		1680-1600	m-w
	Aromatic		1600 and 1475	m-w
C≡C	Alkyne		2250-2100	m-w
C=O	Aldehyde		1740-1720	s
	Ketone		1725-1705	s
	Carboxylic Acid		1725-1700	s
	Ester		1750-1730	s
	Amide		1670-1640	s
	Anhydride		1810 and 1760	s
	Acid Chloride		1800	s
C-O	Alcohols, Ethers, Esters, Carboxylic Acids, Anhydrides		1300-1000	s
O-H	Alcohols, Phenols			
	Free		3650-3600	m
	H-bonded		3500-3200	m
	Carboxylic Acids		3400-2400	m
N-H	Primary and Secondary Amines and Amides			
		(stretch)	3500-3100	m
		(bend)	1640-1550	m-s
C-N	Amines		1350-1000	m-s
C=N	Imines and Oximes		1690-1640	w-s
C≡N	Nitriles		2260-2240	m
X=C=Y	Allenes, Ketenes, Isocyanates, Isothiocyanates		2270-1950	m-s
N=O	Nitro (R-NO$_2$)		1550 and 1350	s
S-H	Mercaptans		2550	w
S=O	Sulfoxides		1050	s
	Sulfones, Sulfonyl Chlorides, Sulfates, Sulfonamides		1375-1300	s
C-X	Fluoride		1400-1000	s
	Chloride		800-600	s
	Bromide, Iodide		<667	s

Original Source Unknown. w = weak, m = medium, s= strong