CHEM 344 Summer 2014 Midterm Quiz (100 pts)

Name:

TA Name:

Directions for analyzing spectra:

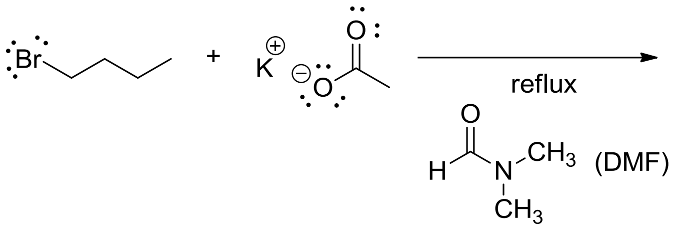
- Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. Assign each **^{1}H-NMR** signal and write your assignments directly onto the spectrum. Justify your assignments by use of the empirical chemical shift parameters (Curphy-Morrison parameters) or chemical shift tables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

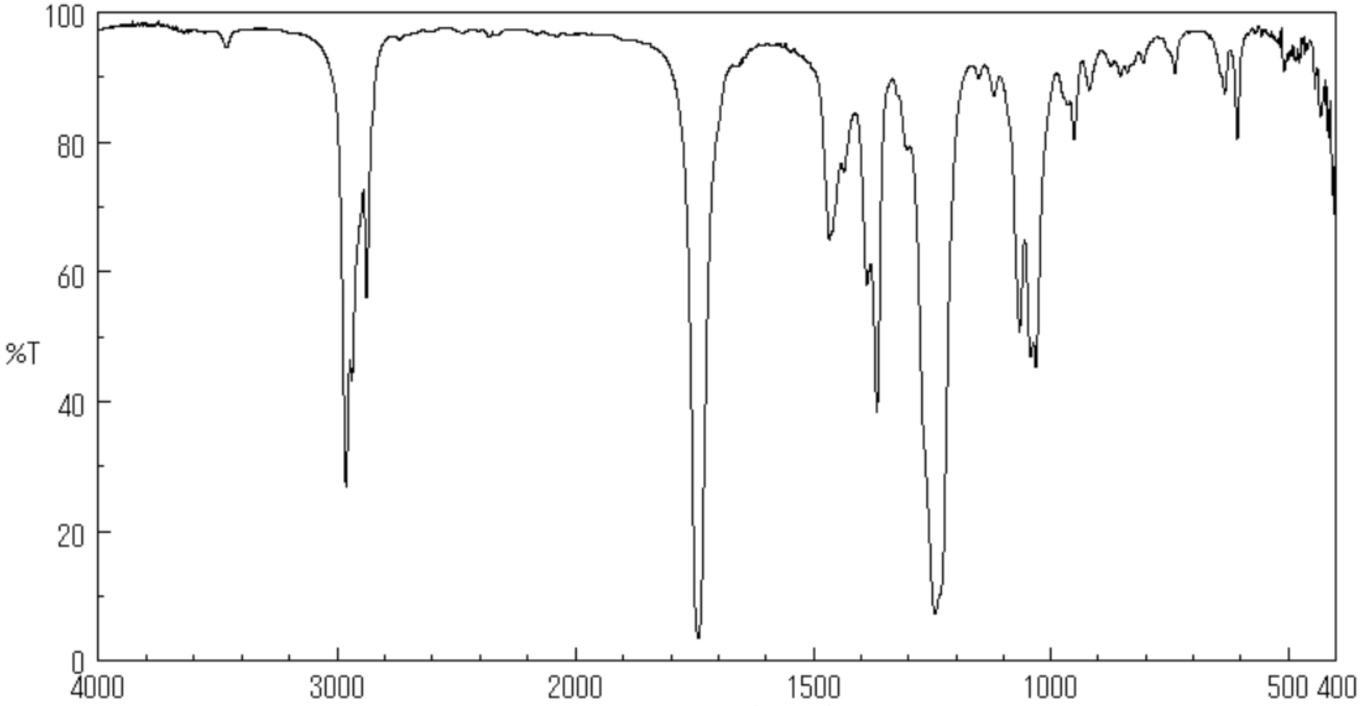
- Assign each key **IR** absorption band >1500 cm^{-1} to a specific functional group.

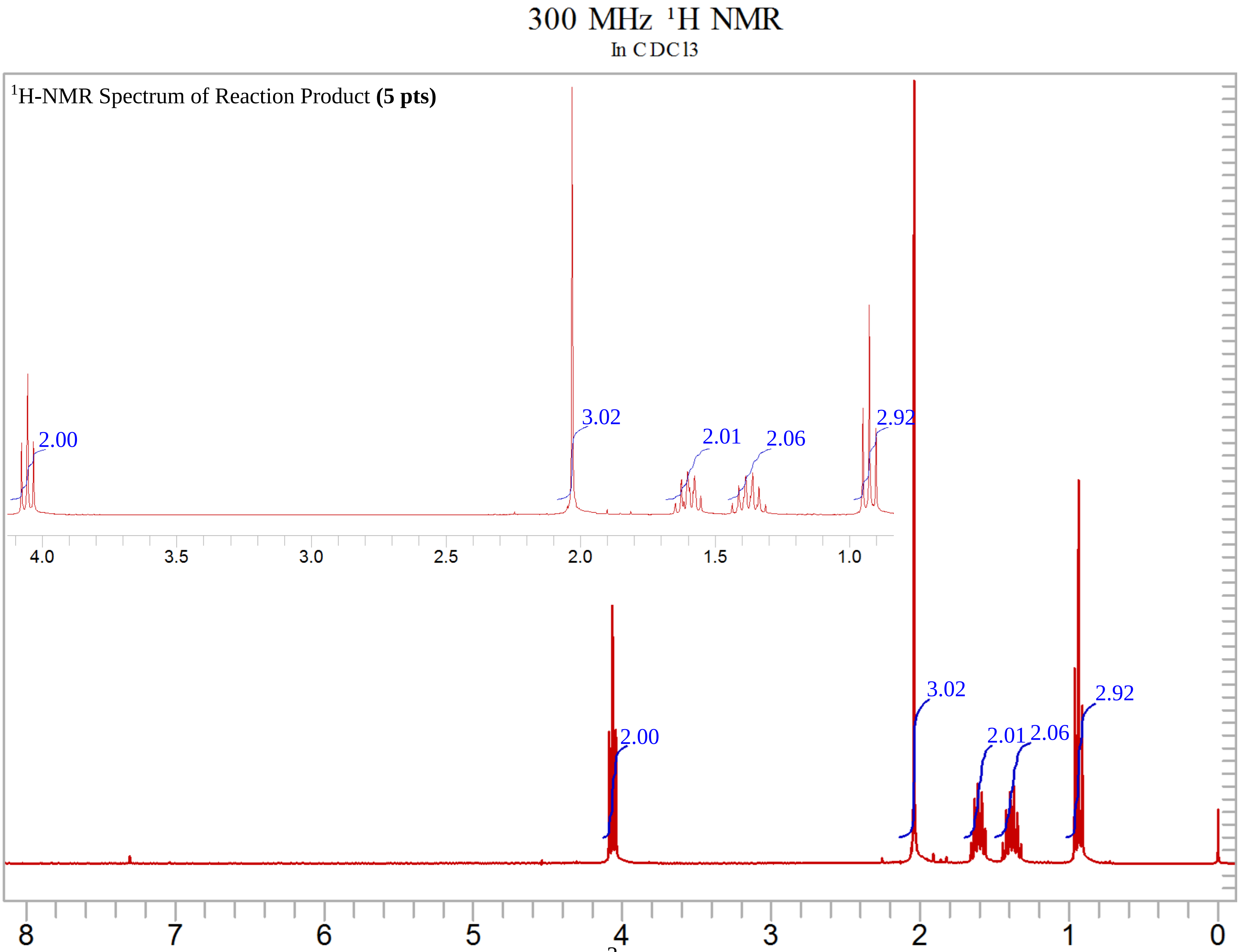
- Draw fragments for all labeled peaks in the **EI-MS** directly onto the spectrum (you do not need to show the fragmentation mechanism unless directed to do so).

1) A mixture of 0.5 g (5.1 mmol) of potassium acetate, 1 mL, 9.3 mmol, ρ = 1.276 g/cm^3 of 1-bromobutane, and 3 mL of N,N-dimethylformamide (DMF, ρ = 0.949 g/cm^3) and a few boiling chips were added to a 5-mL round-bottom flask equipped with a reflux condenser. The heterogeneous mixture is then heated until the DMF (bp 156 ºC) and 1-bromobutane (bp 100–104 ºC) begins to gently boil. Most, but not all, of the potassium acetate dissolves prior to achieving reflux. After a few minutes the mixture thickens significantly upon the formation of a white solid. The gentle reflux is maintained for a total of 15 minutes and then the solution is cooled to room temperature and diluted with approximately 50 mL of water. The organic products were isolated by extraction with two 15-mL portions of hexane (ρ = 0.66 g/cm^3). Anhydrous sodium sulfate (Na_2SO_4) was added to the combined organic layers and the mixture stirred for 5 min. Following gravity filtration, the solvent was removed by evaporation to give the crude product. This sample is then used for ^{1}H-NMR, IR, and GC-MS analysis; the spectra are provided below and on the subsequent pages. Analyze the spectra and answer the follow up questions. **(39 pts total)**



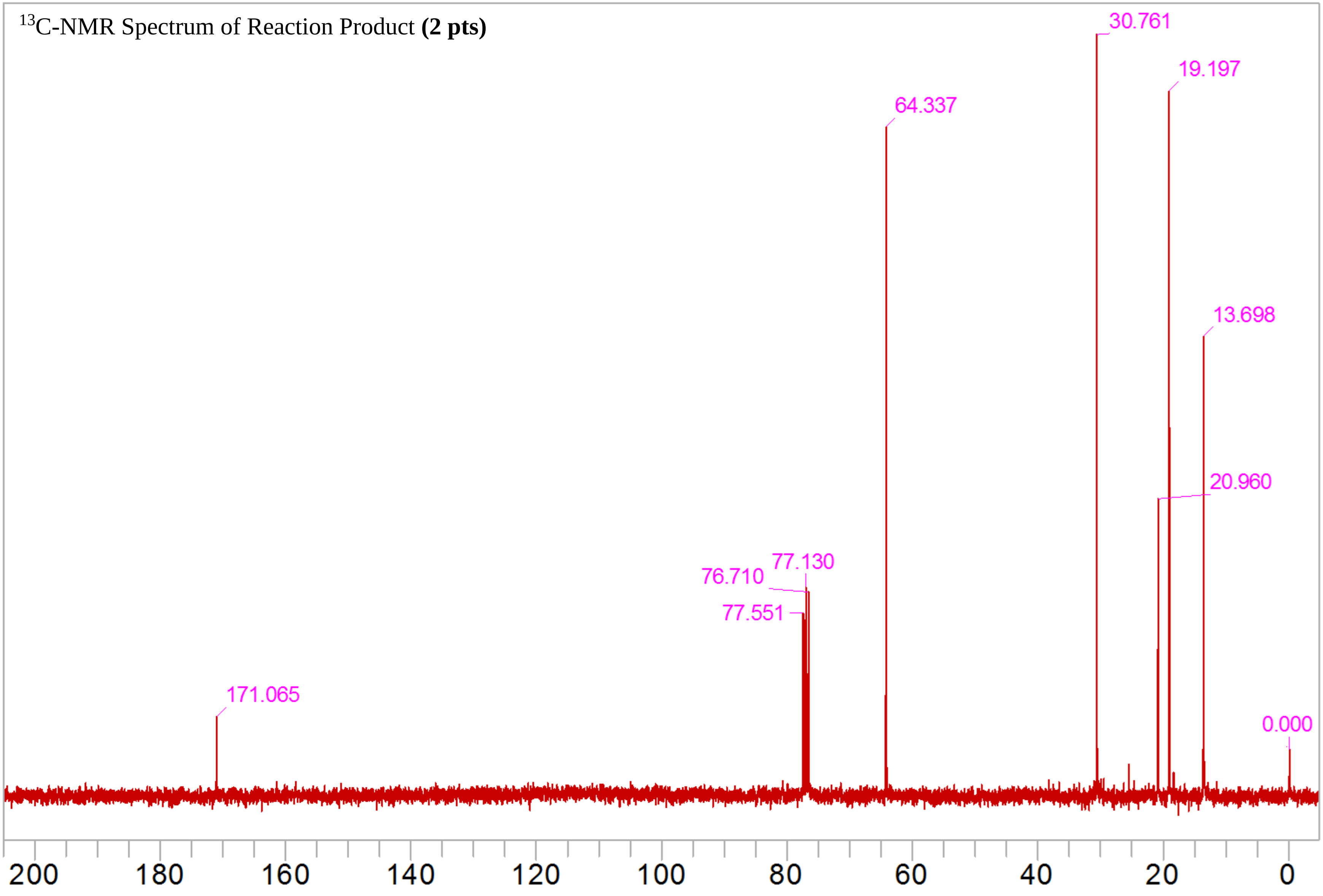
IR Spectrum of Reaction Product **(2 pts)**



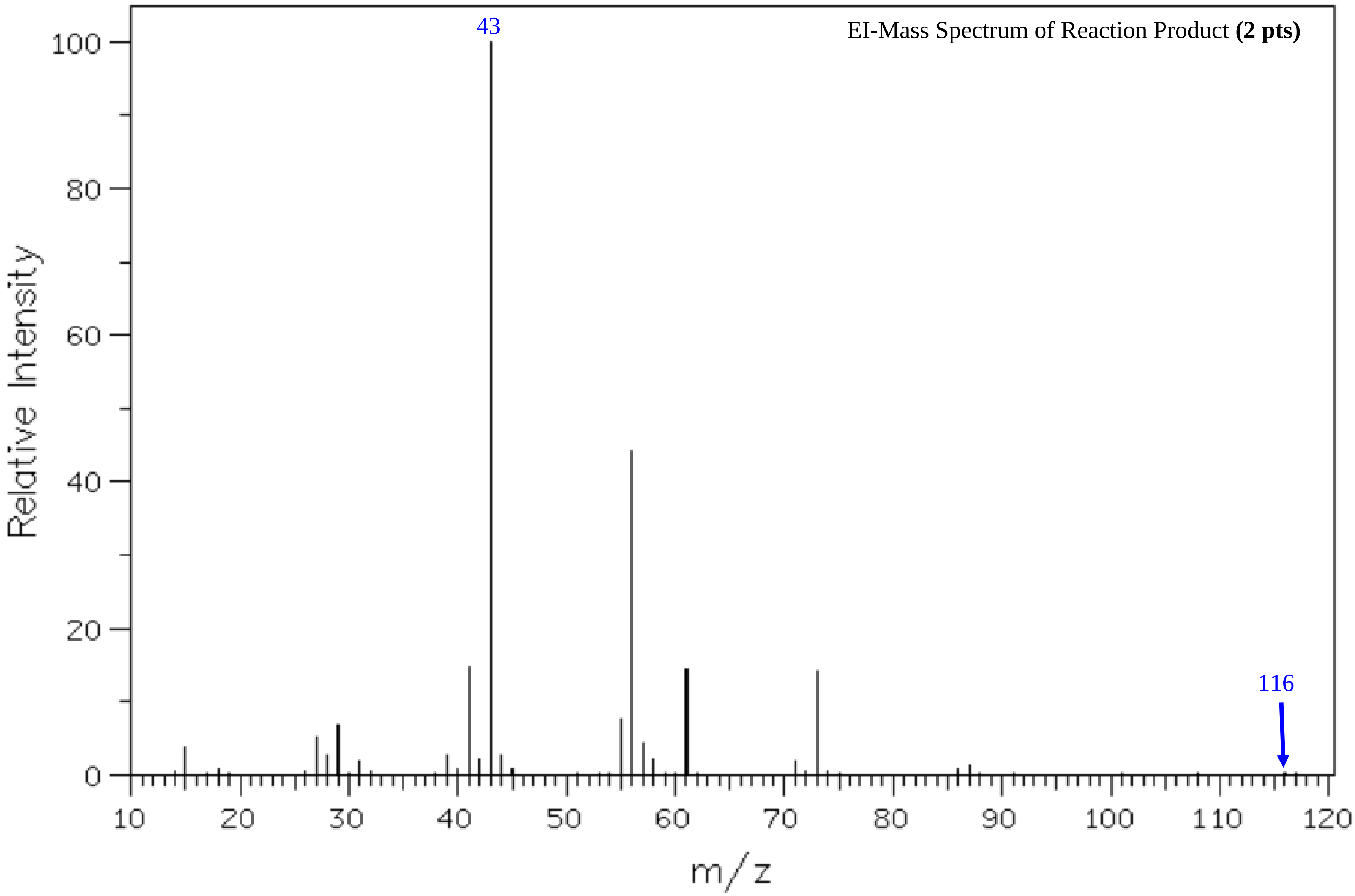


300 MHz ¹H NMR
In CDCl3
¹H-NMR Spectrum of Reaction Product **(5 pts)**
2.00
3.02
2.01
2.06
2.92
4.0
3.5
3.0
2.5
2.0
1.5
1.0
3.02
2.92
2.00
2.01
2.06
8
7
6
5
4
3
2
1
0

75 MHz ^{13}C NMR
In CDCl3



^{13}C-NMR Spectrum of Reaction Product **(2 pts)**


EI-Mass Spectrum of Reaction Product **(2 pts)**
43
116
Relative Intensity
0
20
40
60
80
100
m/z
10
20
30
40
50
60
70
80
90
100
110
120

a) Draw an electron-pushing mechanism for the reaction of *n*-bromobutane with potassium acetate. Identify the limiting reagent. Identify the white solid byproduct. Explicitly show all lone pairs and important resonance contributors. **(4 pts)**

b) This reaction is carried out with potassium acetate (weak base) dissolved in DMF. Could the same reaction, potassium acetate with 1-bromobutane, be effectively carried out in a strongly acidic environment? Use a chemical reaction in your answer. **(3 pts)**

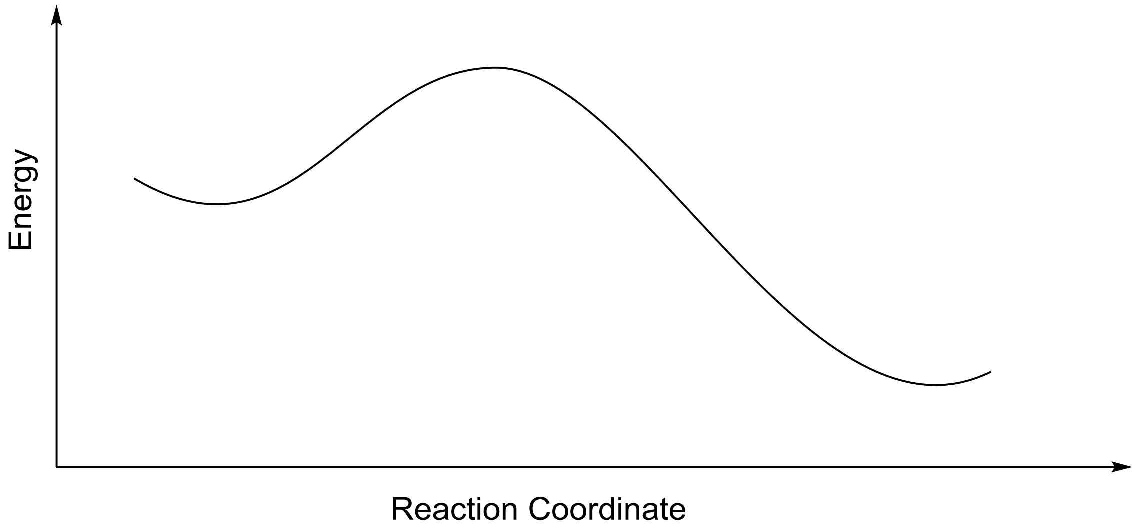
c) What is the purpose of allowing this reaction to undergo a gentle reflux for 15 minutes? Provide a chemical and physical justification for its use in this reaction. **(4 pts)**

d) Hexane is used to extract the product which effectively removes it from DMF. Provide several attributes makes hexane an effective extraction solvent for this reaction workup? **(3 pts)**

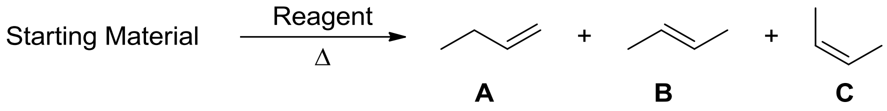
e) What is the purpose of anhydrous Na_2SO_4? Briefly describe chemically or physically how it accomplishes this. **(3 pts)**

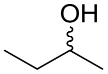
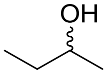
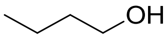
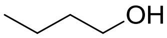
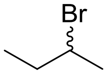
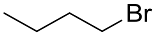
f) A separatory funnel is used to extract the product in hexane from DMF, H_2O, and the white solid mentioned in the procedure. On the image below, label the identity of each of the liquid layers. Indicate which layer will contain the product. Indicate which layer will contain the white solid byproduct mentioned above. **(5 pts)**

g) In order to better understand the reaction performed, the potential energy surface is explored computationally. On the potential energy surface below, draw the structures that would need to be optimized for the reactants, transition state and product. Computationally, what identifies a molecular structure as a transition state, differentiating it from a reactant or product? **(6 pts)**



2) In the laboratory, a series of elimination reactions were carried out in a variety of acidic or basic conditions to produce three isomeric butenes. All of the alkene products are exceptionally volatile care must be taken to collect the products; when analyzing these data assume no product was lost due to evaporation. Use the results to answer the questions below. **(29 pts total)**



	Starting Material	Reagent	% **A**	% **B**	% **C**
1		H_2SO_4/H_3PO_4	5	62	33
2		H_2SO_4	5	53	42
3		H_2SO_4/H_3PO_4	10	56	34
4		H_2SO_4	12	56	32
5		KOH/EtOH	10	49	41
6		KO*t*Bu	100	0	0

a) Would you expect both starting material molecules in reaction 1 to show up as a single spot on a TLC plate used to monitor the reaction? Explain briefly including drawings of each molecule. **(4 pts)**

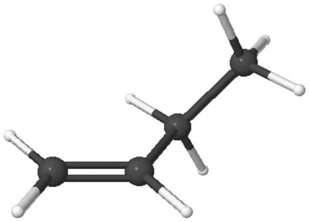
b) In error, a student used conc. HNO_3 rather than conc. H_2SO_4 in reaction 1. Predict the outcome of the experiment with this reagent substitution and briefly explain your reasoning. **(3 pts)**

c) Reactions 1 – 4 generate three isomeric alkenes (bp range from -6 to 3 ºC) and a stoichiometric byproduct of water. Given the volatility of the product, explain how the alkene products are obtained as a liquid and starting material/water during the course of the reaction. **(4 pts)**

d) Which of the reactions is most selective? Explain using the reaction mechanism why that is the case. **(6 pts)**

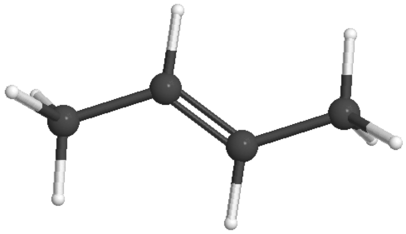
e) The three isomeric products were investigated using B3LYP/6-31G(d) calculations to determine their relative stability. Their optimized geometries are presented below along with their symmetry point groups and RB3LYP energies in Hartrees/Particle (1 Hartree/Particle = 627.509 kcal/mol). Determine the relative energy of each in kcal/mol referenced to the most stable molecule. **(3 pts)** Circle the most stable isomer and put a box around the least stable isomer. **(1 pt)**

Product A (C_1)



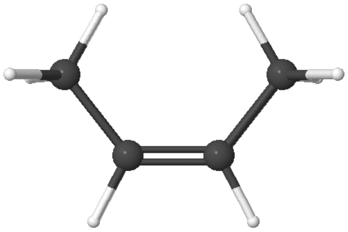
-157.221066977 Hartree

Product B (C_{2h})



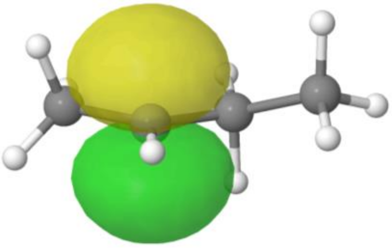
-157.226912213 Hartree

Product C (C_{2v})



-157.224768724 Hartree

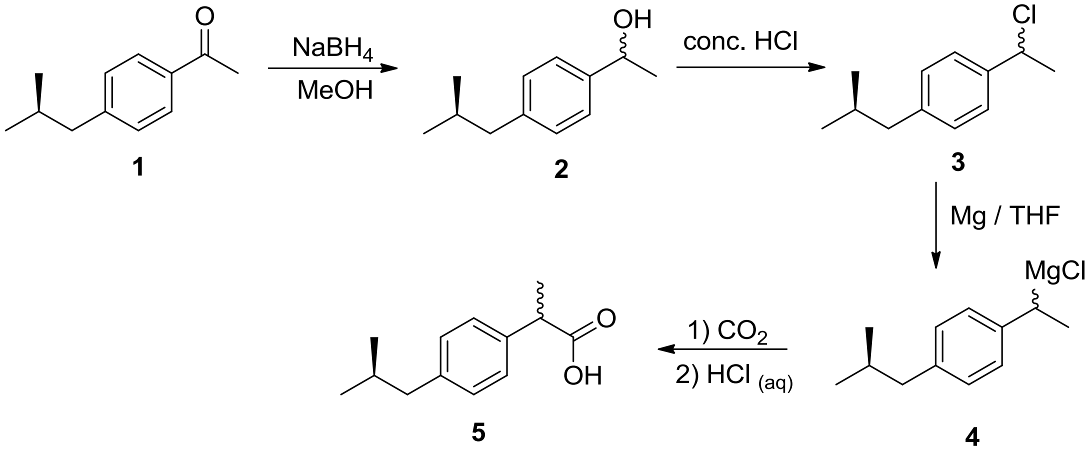
f) Reactions 1 – 4 generate two possible carbocations, one of which is depicted below. Approximate the hybridization of the depicted *empty* orbital and explain why its NBO electron occupancy is 0.396. Where does the electron density come from? **(2 pts)**



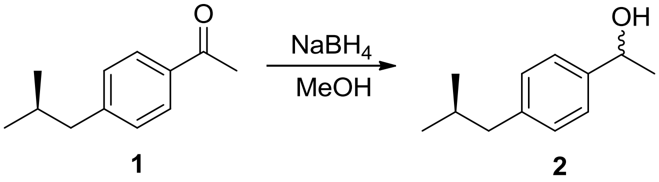
g) Explain why reactions # 3 and 4 produce more than twice the amount of A as reactions #1 and #2. **(4 pts)**

h) Of reactions 1 – 6, which are under thermodynamic control and which are under kinetic control? **(4 pts)**

3) A multi-step synthesis of ibuprofen (**5**) has been carried out in an undergraduate organic laboratory course using the following synthetic route from *p*-isobutylacetophenone (**1**). Answer the following questions about key steps in the procedure, reactants, and products. (Note, that some of the reactions utilized are from the 2nd half of CHEM 344; you will only asked about the reactions and concepts relevant to the 1st half of the course.) **(32 pts total)**

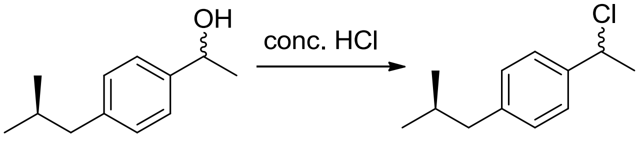


a) In the first reaction converting *p*-isobutylacetophenone (**1**) to 1-(4-Isobutylphenyl)ethanol (**2**), explain how the IR spectrum of the product mixture would be expected to change throughout the course of the reaction. Discuss the key IR spectral features of both the reactant and product. **(4 pts)**



b) The following excerpt is from the procedure for converting **2** to **3**: Use it for any of the subsequent questions.

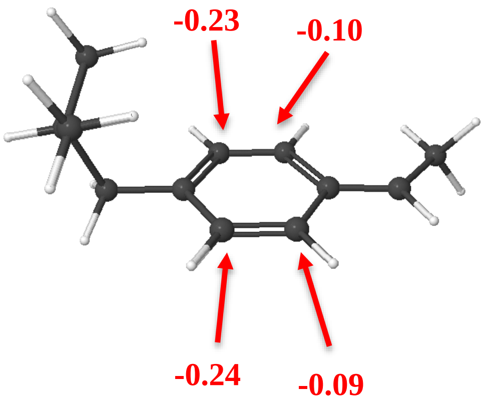
“While working in a fume hood, use a pipet to carefully transfer the 1-(4-isobutylphenyl)ethanol (**2**) into a separatory funnel and then use two 5-mL portions of 12 M HCl to help transfer any that remains in the flask and the pipet. Shake this mixture about 2 minutes. Extract the product (**3**) from this mixture with 3 x 5 mL of pentanes ($\rho = 0.64$ g/cm^3), and then swirled with Na_2SO_4. Gravity filter and remove the solvent by evaporation from a pre-weighed 50-mL round-bottomed flask, and then weigh to determine the yield. Record the ^{1}H NMR spectrum of one drop of this product in about 0.5 mL $CDCl_3$. Stopper the flask. Use a marker to write your name on it, and then hand it in on a cork ring.”

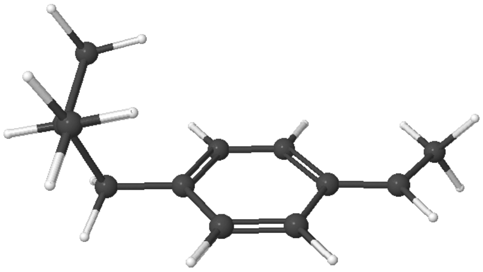


2 **3**

Draw an electron-pushing mechanism for this reaction. Show all lone pairs, intermediates, important resonance structures, etc. Label the rate-determining step with an (RDS) over the reaction arrow. **(8 pts)**

c) Explain the NBO charge data for the C-atoms shown below using a series of resonance structures and by a drawing of the π_1 molecular orbital. **(4 pts)**

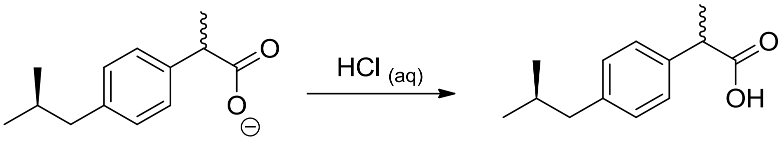




Draw π_1 on the molecule above.

d) A separatory funnel is used to extract 1-Chloro-1-(4-isobutylphenyl)ethane (**3**) in pentanes from an aqueous acidic solution. On the image below, label the identity of each of the liquid layers. Indicate which layer will contain **3**. **(4 pts)**

e) The reaction of **4** with carbon dioxide results in the formation of the carboxylate shown below. It is extracted in an ether layer as ibuprofen (**5**) by addition of 8 mL of 4 M HCl $_{(aq)}$. Explain how the solubility of ibuprofen (**5**) compares to the carboxylate in an aqueous solution and in an organic solvent. **(4 pts)**



5

f) If 1.00 mL of *p*-isobutylacetophenone (**1,** $\rho = 0.952\ \text{g/cm}^3$) is used to create 0.813 g of ibuprofen what was the overall yield of the synthesis? **Show all of your work. (4 pts)**

g) The crude ibuprofen can be purified (separated from impuritites) by recrystallization in ethanol and vacuum filtration. Draw a series of diagrams that explain how this process works. Clearly identify where the ibuprofen and impurities will be located after the procedure is complete. **(4 pts)**

CHEM 344 Summer 2014 Midterm Quiz (100 pts)

Name:

TA Name:

Q1 /39

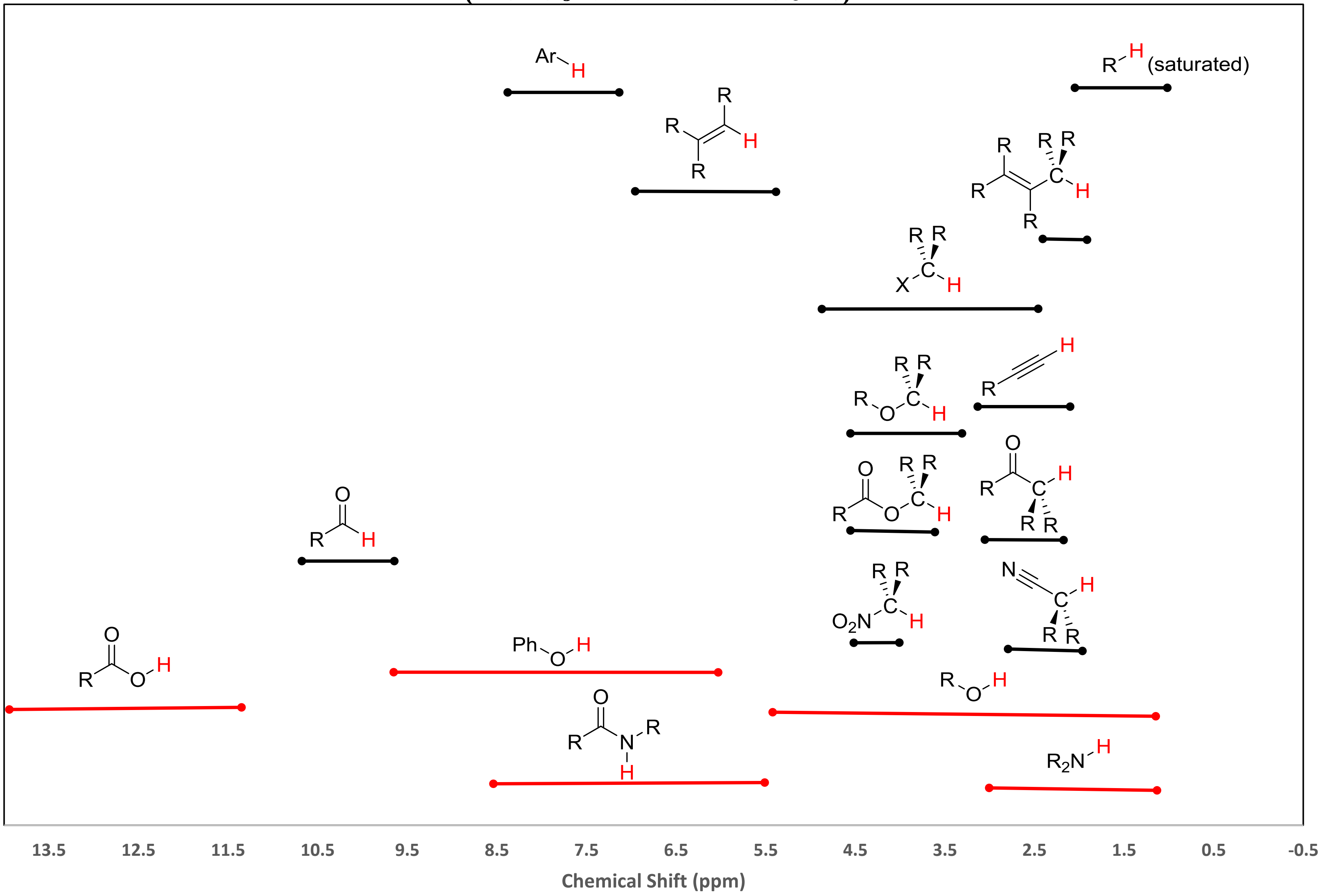
Q2 /29

Q3 /32

Total = /100

Typical ^{1}H-NMR Chemical Shift Ranges

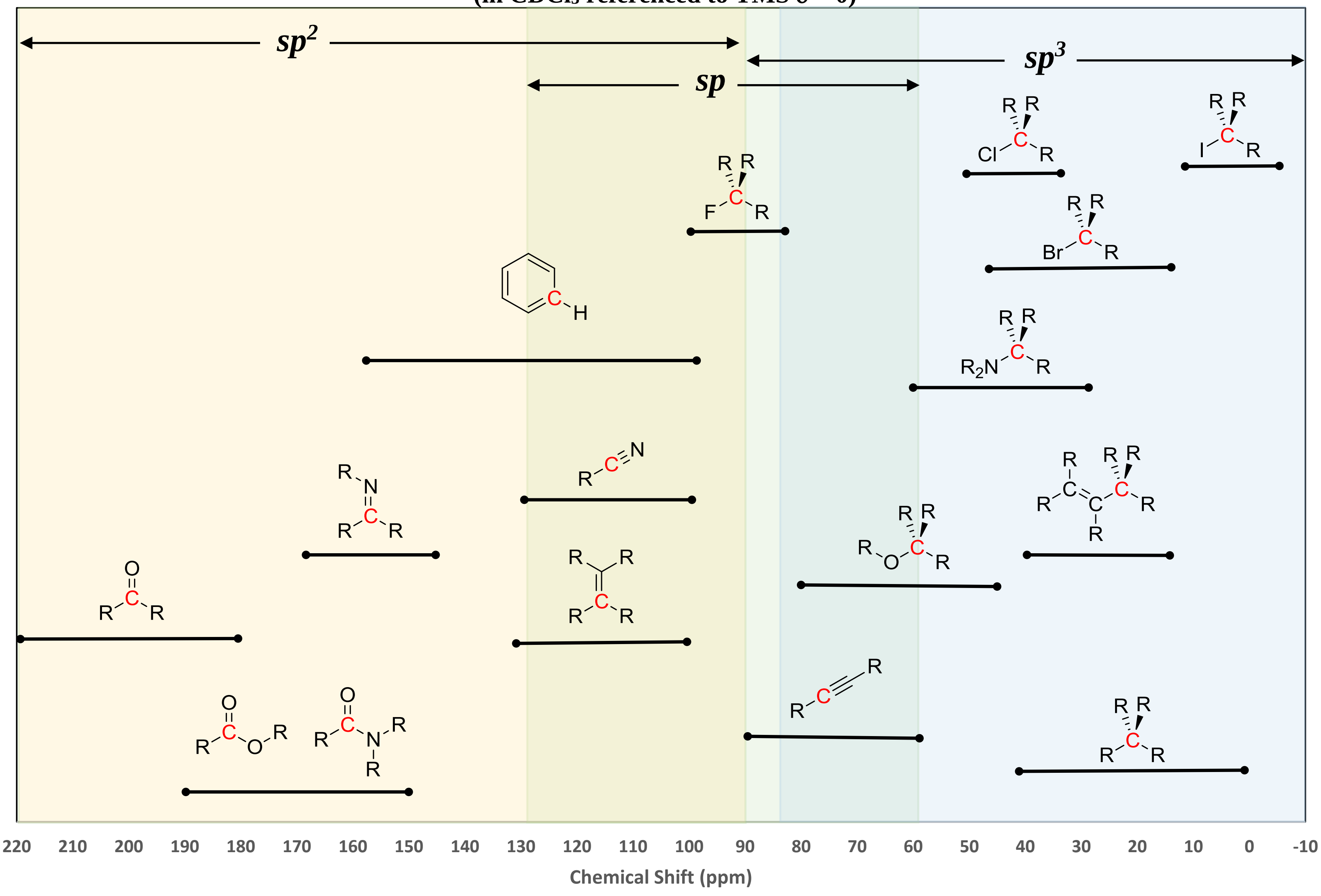
(in $CDCl_3$ referenced to TMS δ = 0)



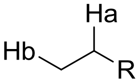
F

Typical ^{13}C-NMR Chemical Shift Ranges

(in $CDCl_3$ referenced to TMS $\delta = 0$)

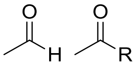
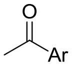
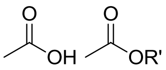
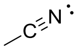
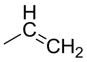
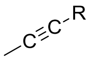
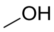
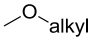
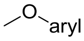
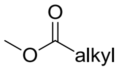
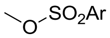
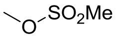
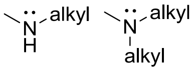
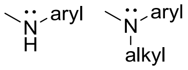
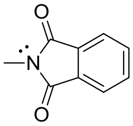
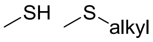
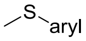
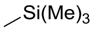


Curphy-Morrison Additivity Constants for Proton NMR

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 + $\Sigma_{\alpha\text{-shifts}} + \Sigma_{\beta\text{-shifts}}$

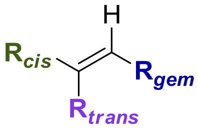
Substituent (R)		α-shift	β-shift
Cl	$-CH_3$	2.30	0.60
	$-CH_2-$	2.30	0.55
	-CH-	2.55	0.15
Br	$-CH_3$	1.80	0.80
	$-CH_2-$	2.15	0.80
	-CH-	2.20	0.25
I	$-CH_3$	1.80	0.80
	$-CH_2-$	2.15	0.80
	-CH-	2.20	0.25
Aryl	$-CH_3$	1.45	0.35
	$-CH_2-$	1.45	0.55
	-CH-	1.35	----
	$-CH_3$	1.25	0.25
	$-CH_2-$	1.10	0.30
	-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)	----
	$-CH_3$	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: $\delta_{H\ (vinyl)} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$

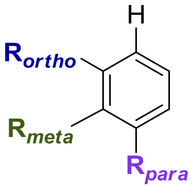
Substituent (R)	Z_{gem}	Z_{cis}	Z_{trans}	Substituent (R)	Z_{gem}	Z_{cis}	Z_{trans}
H	0.00	0.00	0.00	F	1.54	-0.40	-1.02
alkyl	0.45	-0.22	-0.28	Cl	1.08	0.18	0.13
Alkyl (cyclic)	0.69	-0.25	-0.28	Br	1.07	0.45	0.55
CH_2OH	0.64	-0.01	-0.02	I	1.14	0.81	0.88
CH_2SH	0.71	-0.13	-0.22	OR (R = aliphatic)	1.22	-1.07	-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	1.18	0.55	$SiMe_3$	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)

^{1}H- and ^{13}C-NMR Chemical Shifts for Common Solvents in $CDCl_3$

	^{1}H δ (ppm)	**^{1}H Signal Multiplicity**	**^{13}C δ (ppm)**
acetone	2.17	singlet	207.07(CO) 30.92 (CH_3)
chloroform	7.27	singlet	77.58 (CH) 77.44 (CH) 77.00 (CH)
dichloromethane	5.30	singlet	53.52 (CH_2)
diethyl ether	3.48 1.21	quartet triplet	65.91 (CH_2) 15.20 (CH_3)
ethanol	3.72 1.25	quartet triplet	58.28 (CH_2) 18.41 (CH_3)
n-hexane	1.26 0.88	2nd order multiplet triplet	31.64 (CH_2) 22.70 (CH_2) 14.14 (CH_3)
methanol	3.49	singlet	50.41 (CH3)
tetramethylsilane (TMS)	0.00	singlet	0.00
toluene	2.36 (CH_3) 7.1 – 7.3 (Ar)	singlet	137.8 (Ar) 129.0 (Ar) 128.2 (Ar) 125.3 (Ar) 21.46 (CH_3)
water	1.56	singlet	

Values obtained from the following:

Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J. Org. Chem.*, **1997**, *62*, 7512–7515.

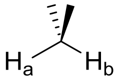
Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics*, **2010**, *29*, 2176–2179.

Typical ^{1}H-NMR Coupling Values*

Coupling

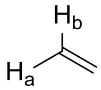
2-bond

gem alkyl



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

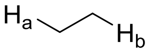
gem vinyl



$^2J = 1 - 3$

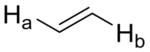
3-bond

vicinal alkyl



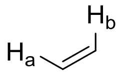
$^3J = 2 - 20$
(typical 7 Hz)

trans vinyl



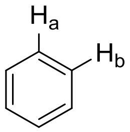
$^3J = 12 - 18$

cis vinyl



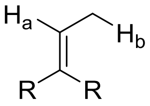
$^3J = 6 - 12$

ortho aryl



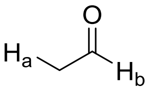
$^3J = 8 - 12$

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



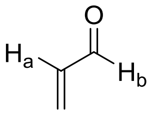
$^3J = 3 - 11$
(dihedral dependent)

vicinal aldehyde



$^3J = 1 - 3$

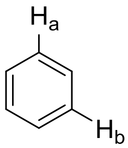
vicinal conjugated aldehyde



$^3J = 7 - 8$

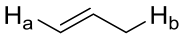
4-bond

meta aryl



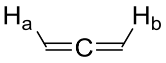
$^4J = 2 - 3$

allylic



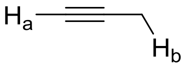
$^4J = 0 - 3$

allenic



$^4J = 6 - 7$

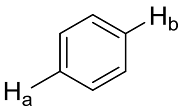
propargylic



$^4J = 2 - 4$

5-bond

para aryl



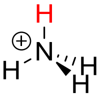
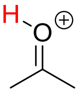
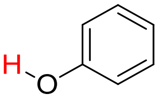
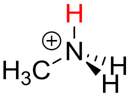
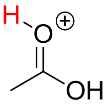
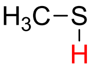
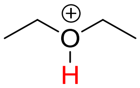
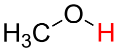
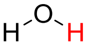
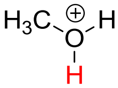
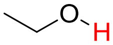
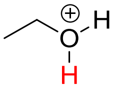
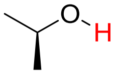
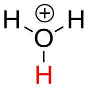
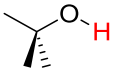
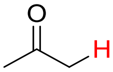
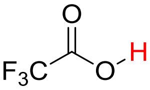
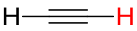
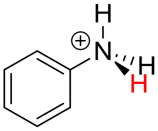
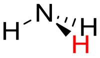
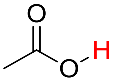
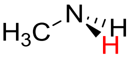
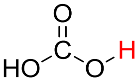
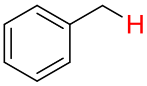
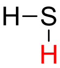
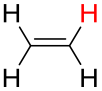
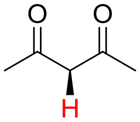
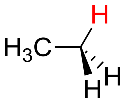
$^5J = 0 - 1$

*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

Acid	pK_a	Acid	pK_a
H–I	-10	H–CN	9.1
H–Br	-9		9.2
	-7.5		9.9
H–Cl	-7		10.6
	-6.2	 $H_3C{-}S{-}H$	10.7
	-3.8		15.5
$H{-}O{-}SO_3H$	-3*		15.7
	-2.5		16
	-2.4		16.5
	-1.74		18
$H{-}O{-}NO_2$	-1.4		19.2
	0.18		25
H–F	3.2	H–H	35
	4.6		38
	4.75		38
	6.35		41
 $H{-}S{-}H$	7.0		44
	9.0		50

*values differ widely depending on source from -9 to -3.