CHEM 344 Summer 2014 Final Quiz (100 pts)

Name:

TA Name:

Directions for analyzing spectra:

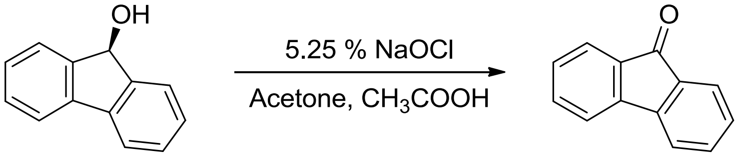
- Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. Assign each **^{1}H-NMR** signal and write your assignments directly onto the spectrum. Justify your assignments by use of the empirical chemical shift parameters (Curphy-Morrison parameters) or chemical shift tables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

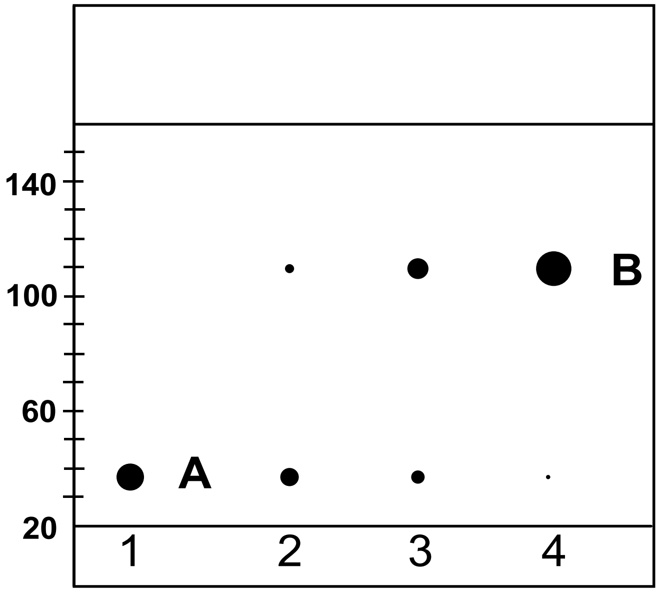
1) A sample of 50 mg of 9-fluorenol is dissolved in 3 mL of acetone in a 10-mL round-bottom flask. To the 9-fluorenol, 0.12 mL of glacial acetic acid is added, followed by the addition of 0.4 mL of 5.25 % sodium hypochlorite solution (commercial bleach). After 5 minutes the progress of the reaction is determined by normal phase TLC and additional bleach is added in 0.4 mL increments as needed. Once TLC indicates completion of the reaction, the reaction mixture is extracted twice with 2 mL of hexane and then washed with 1 mL of 5% $NaHCO_3$ solution and 2 mL of water. Recrystallization is carried out using a small portion of hexane and the product is characterized by ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy. **(34 pts total)**



9-fluorenol

9-fluorenone

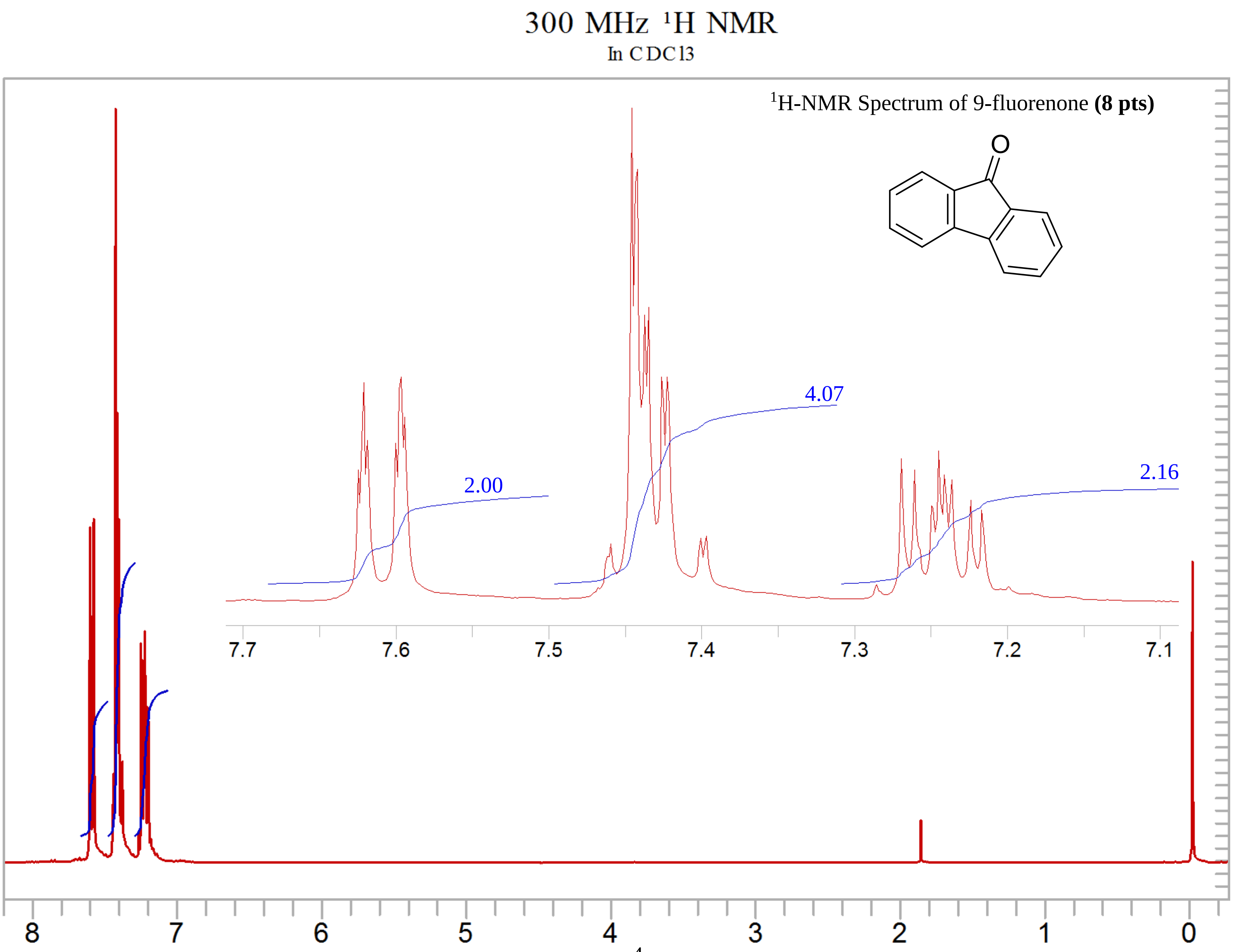
a) The progress of the reaction was tracked using TLC, shown below. Spot 1 shows the starting material and spots 2-4 are at 5 min intervals after the reaction was started. Showing all work, calculate the R_f values (as decimals) for compounds A and B. **(6 pts)**



b) What can be concluded from the TLC plate at the final time point 4? Explain, how you would proceed. **(4 pts)**

c) Provide the balanced chemical equation that accounts for the production of the active oxidizing agent. **(2 pts)**

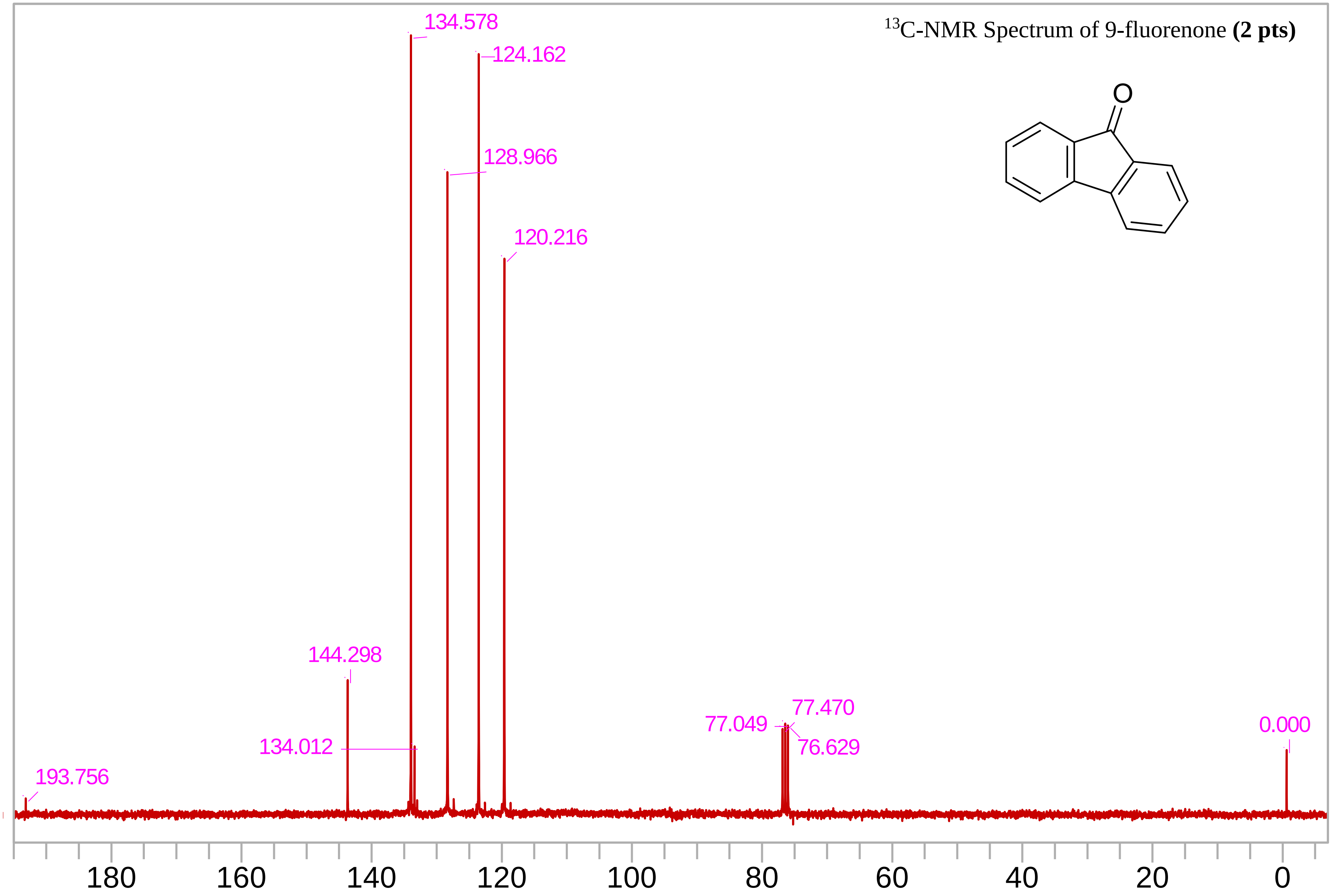
d) What is the purpose of washing the crude product with 1 mL of 5 % $NaHCO_3$ solution? Include a balanced chemical equation in your answer. **(4 pts)**



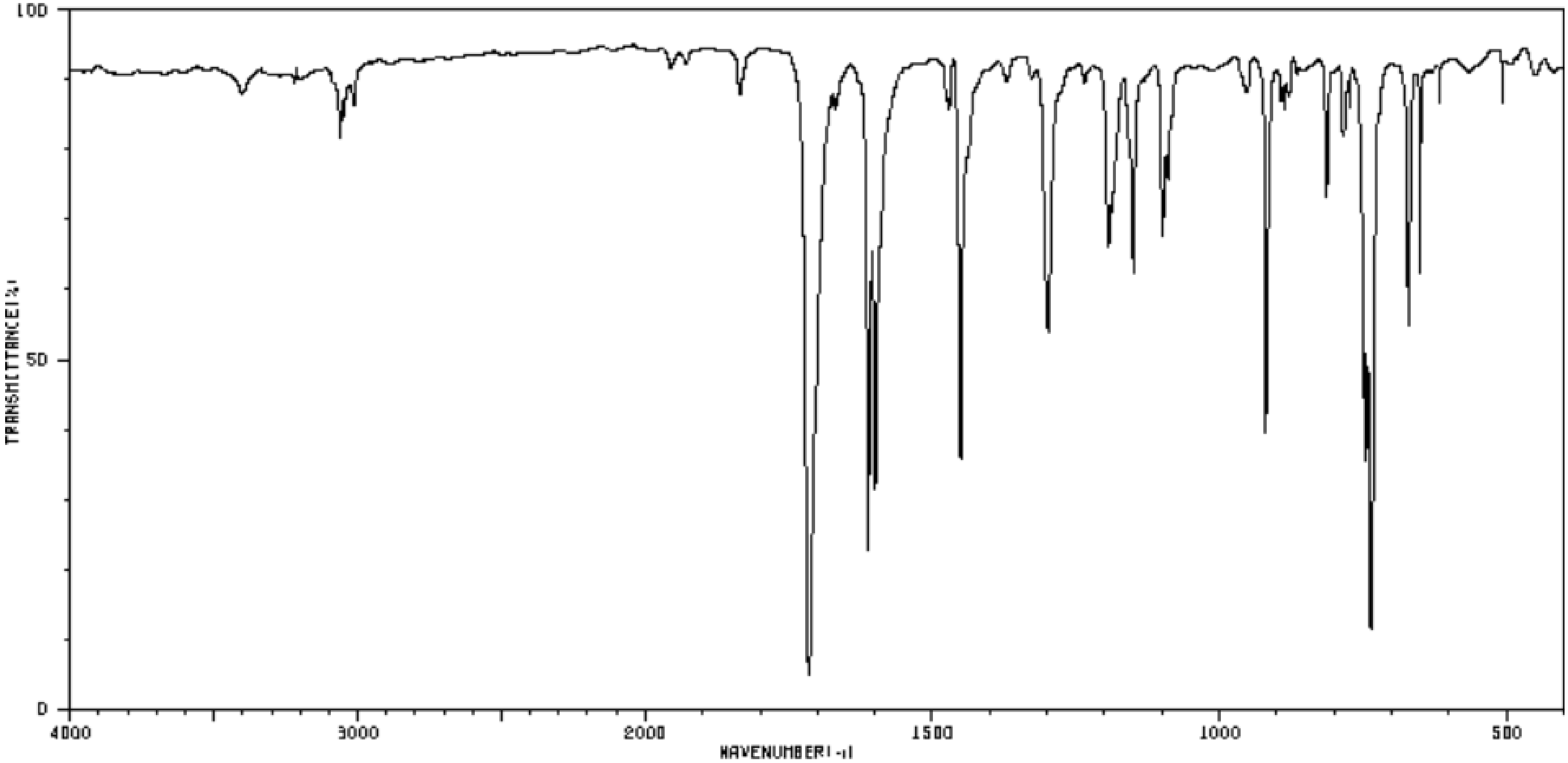
^{1}H-NMR Spectrum of 9-fluorenone **(8 pts)**

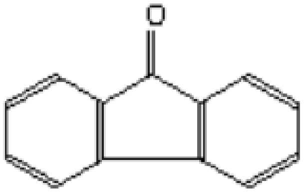
75 MHz ^{13}C NMR

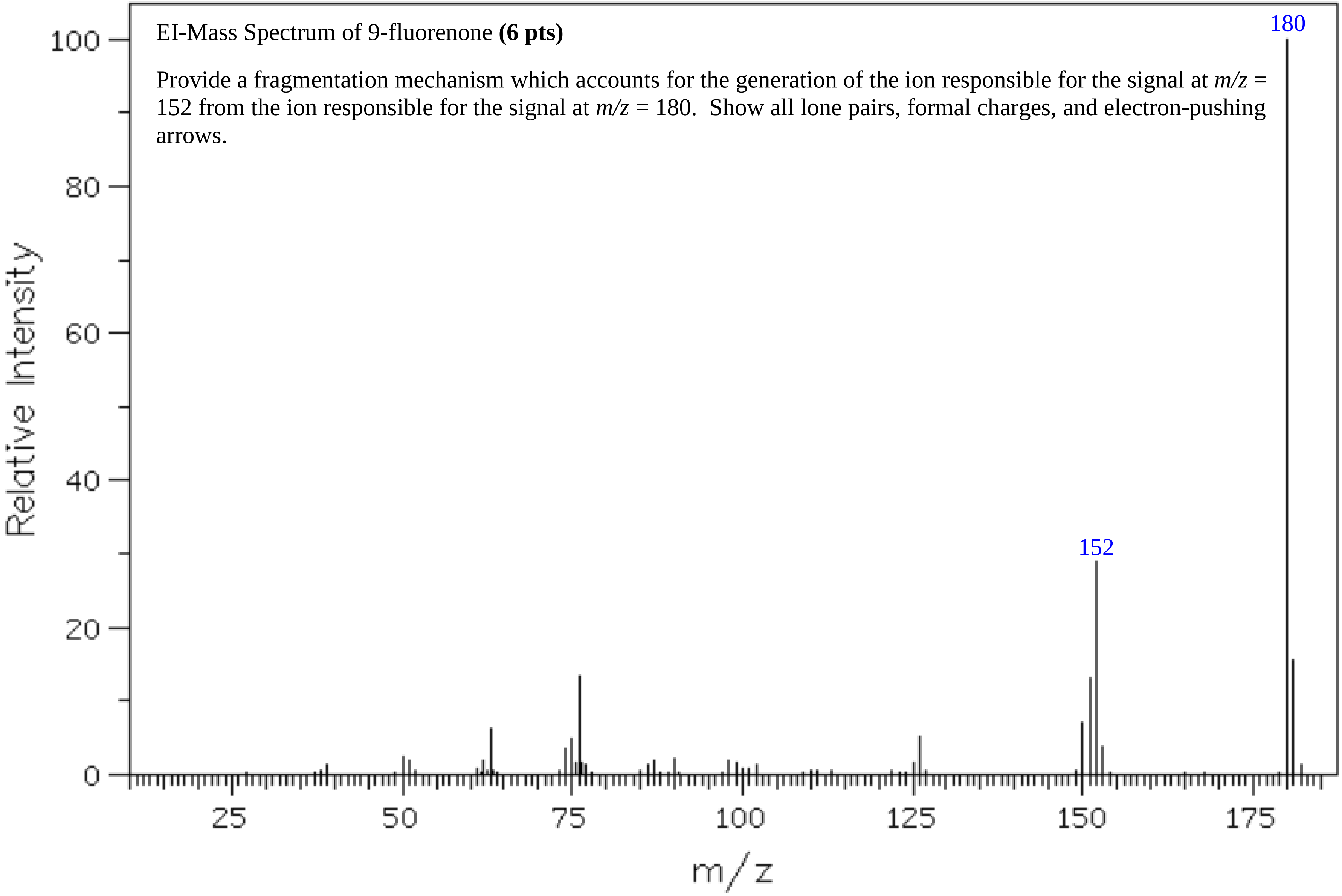
In CDCl3



IR Spectrum of 9-fluorenone **(2 pts)**



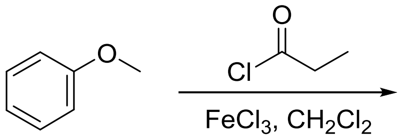
3401	84	1666	84	1236	86	962	84	774	64	
3061	79	1612	21	1194	64	920	37	745	34	
3047	81	1600	30	1187	88	893	64	736	10	
3013	84	1476	84	1168	77	887	81	672	62	
1834	84	1471	81	1151	60	879	84	651	60	
1715	4	1451	34	1098	84	815	70	617	64	
1671	81	1299	62	1090	72	786	78	607	84	



EI-Mass Spectrum of 9-fluorenone **(6 pts)**

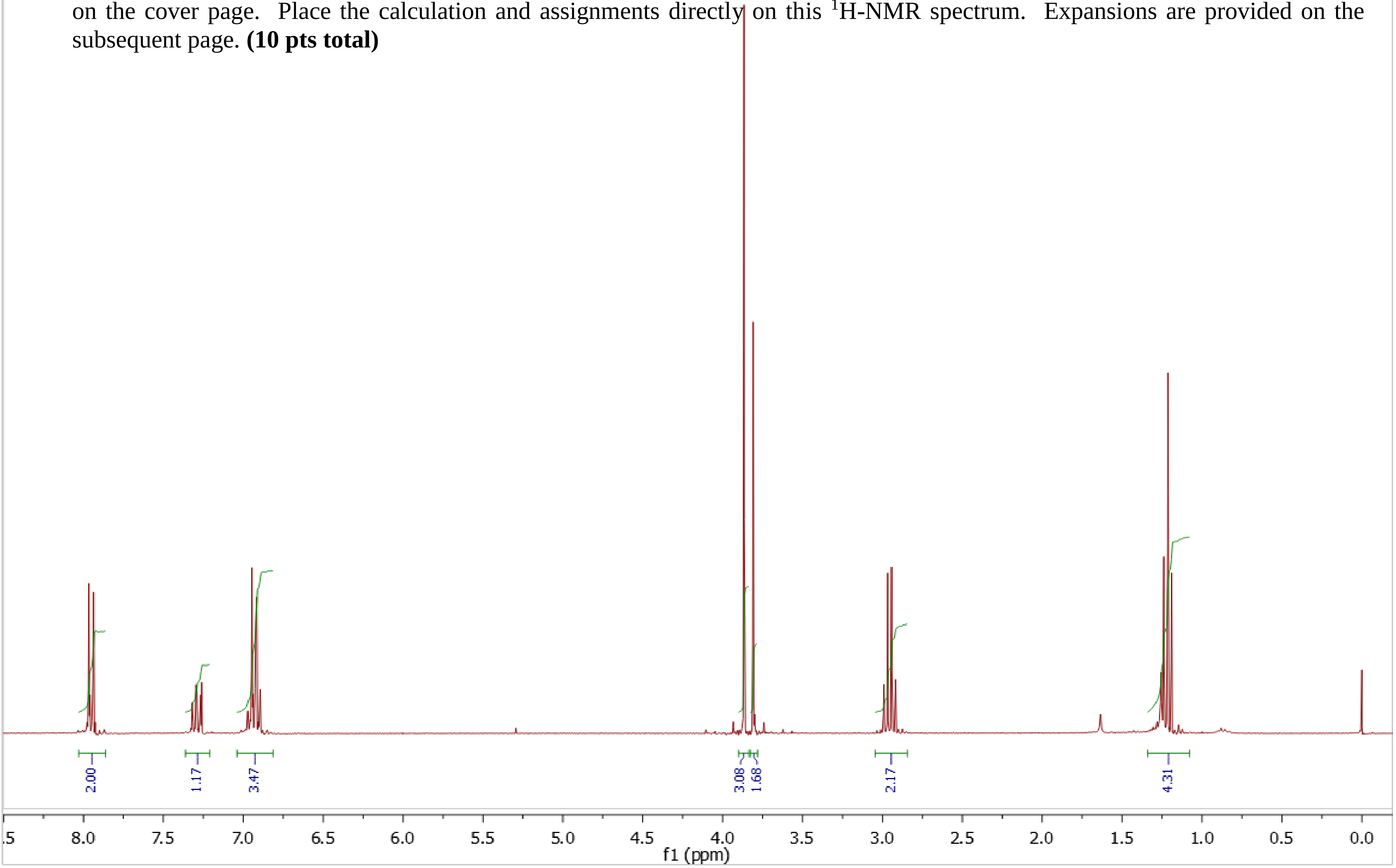
Provide a fragmentation mechanism which accounts for the generation of the ion responsible for the signal at *m/z* = 152 from the ion responsible for the signal at *m/z* = 180. Show all lone pairs, formal charges, and electron-pushing arrows.

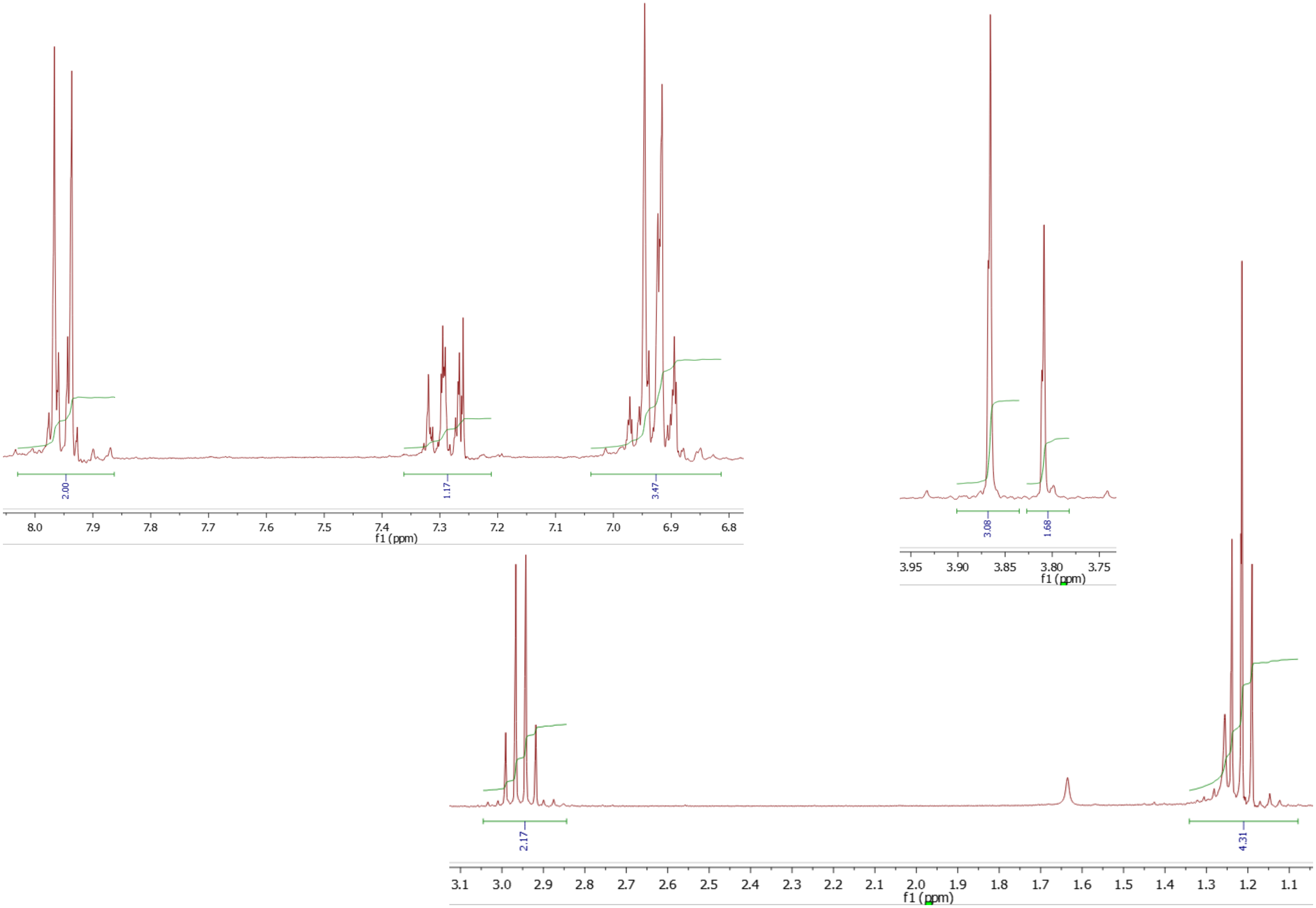
2) Anisole can react with propionyl chloride in the presence of a Lewis acid catalyst in an electrophilic aromatic substitution to produce one or more anisole derivatives. **(18 pts total)**



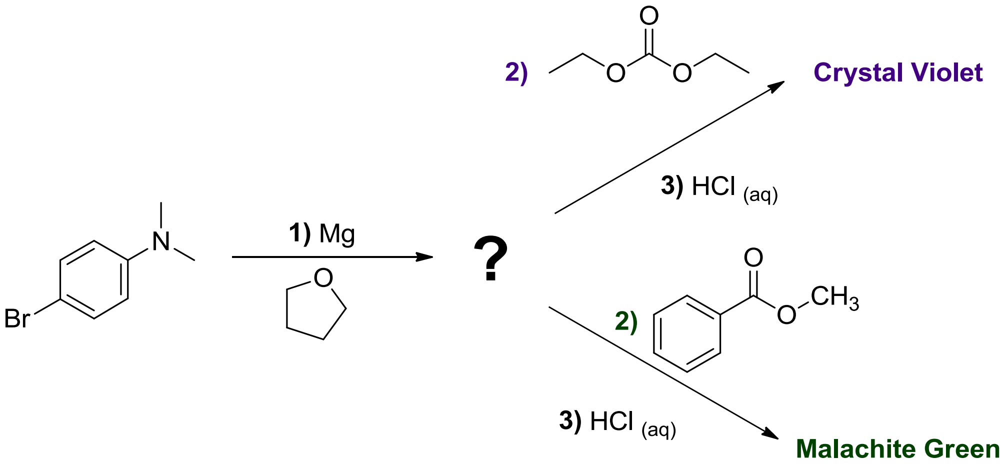
b) The regiochemical outcome of the reaction is governed by the kinetic favorability of one reaction pathway over another. Draw a potential energy surface showing the formation of the possible regioisomeric arenium intermediates from the starting material. For the arenium intermediate on the lowest-energy pathway, justify its stability relative to the other arenium cation intermediates. **(8 pts total)**

b) An authentic reaction sample may contain more than one molecule as evidenced by the ^{1}H-NMR spectrum. Using the spectrum, determine the % of the mixture that is the major product of the reaction and assign all integrated NMR signals as per the instructions on the cover page. Place the calculation and assignments directly on this ^{1}H-NMR spectrum. Expansions are provided on the subsequent page. **(10 pts total)**

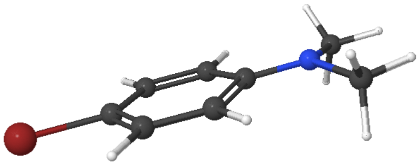


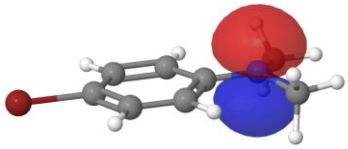

2.00
1.17
3.47
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
3.08
1.68
3.95
3.90
3.85
3.80
3.75
f1 (ppm)
2.17
4.31
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
f1 (ppm)

3) A Grignard synthesis can be used to make triarylmethane dyes such as **Malachite Green** and **Crystal violet** in reasonable yield and is shown in the synthetic route below. Crystal violet has a varied usage history including high school and undergraduate kinetic experiments, treating athlete's foot, staining gram-positive bacteria, and ink-jet printers. Malachite green is a controversial antifungal used in commercial aquaculture that has been used to dye bacteria, silk, leather, and paper. **(24 pts total)**

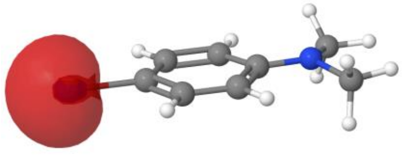


a) The B3LYP/6-31G(d) optimized 4-bromo-N,N-dimethylaniline (precursor to both **Crystal Violet** and **Malachite Green**) structure is presented below along with images of all four of its lone pair orbitals calculated using NBO. Circle one or more lone pairs that are in conjugation with the aromatic π system. **(2 pts)**

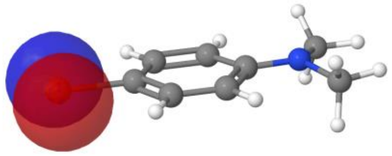




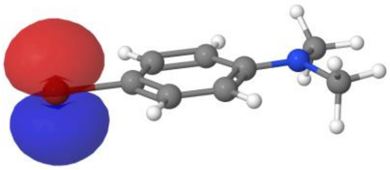
#70



#71



#72



#73

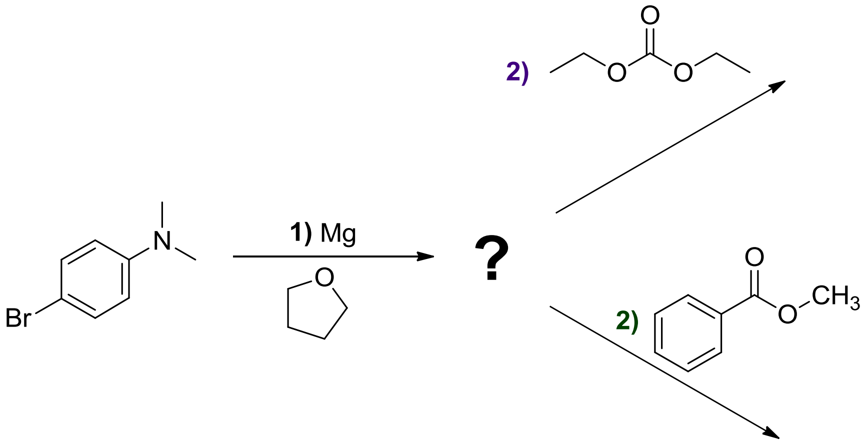
70	LP(1)N2 s(2.10%)p46.66(97.89%)d0.01(0.01%)
71	LP(1)Br15 s(86.27%)p0.16(13.73%)d0.00(0.00%)
72	LP(2)Br15 s(0.00%)p1.00(99.99%)d0.00(0.01%)
73	LP(3)Br15 s(0.00%)p1.00(99.98%)d0.00(0.02%)

Step 1 of the dye preparation is carried out in a 250-mL round bottomed flask equipped with a reflux condenser. The flask and condenser are rinsed with a few milliliters of anhydrous THF, then the flask is charged with magnesium (0.80 g), anhydrous THF (45 mL), 4-bromo-N,N-dimethylaniline (5.0 g), and a few drops of 1,2-dibromoethane. The mixture is warmed gently to reflux, and maintained there for 30 min, during which time the original dark color changes to the typical "dirty dishwater" shade of the Grignard reagent. In **step 2**, the flask is cooled to room temperature (ice- water bath), then diethyl carbonate (0.49 g) to make **crystal violet** or methyl benzoate (0.85 g) to make **malachite green** in 5mL of THF is added in one portion. The mixture is warmed to reflux for an additional 5 min, then cooled again to room temperature (ice-water bath). In **step 3**, Aqueous hydrochloric acid (15mL of a 10% solution) is added slowly (the reaction with the remaining magnesium is vigorous). The result is a muddy purple (**crystal violet**) or cloudy green (**malachite green**) mixture. The product was prepared for ^{1}H-NMR, ^{13}C-NMR, IR, and UV/VIS analysis.

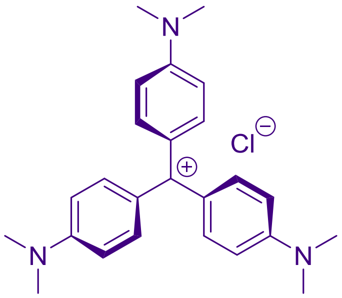
b) Draw the Grignard reagent that forms by reaction of magnesium to 4-bromo-N,N-dimethylaniline. Provide an additional halogentated starting material that would likely work as well for this reaction and one that would not work effectively for this reaction. Justify your selections. **(5 pts)**

c) The glassware is rinsed with a few milliliters of anhydrous THF and 45 mL is used for the reaction. Why is THF an effective solvent for Grignard reagent formation and Grignard reactions? Why does it need to be anhydrous? **(4 pts)**

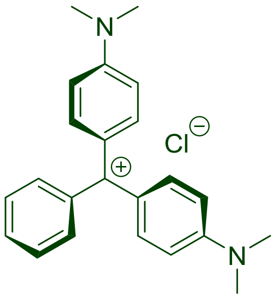
d) The esters (diethyl carbonate or methyl benzoate) allow for three or two additions of the Grignard reagent respectively. For each case, show the product at the **end of step 2** before the addition of 15 mL 10 % HCl **(step 3)**. **(2 pts)**



e) **Step 3**, the addition of 15 mL 10 % HCl serves more than one purpose in this synthesis. It is used to workup the reaction mixture and to protonate and dehydrate the product at the end of step two. This dehydrated product is crystal violet or malachite green depending on the synthesis. Show an electron-pushing mechanism depicting how this protonation and dehydration occurs for **crystal violet**. You may use –Ar for aromatic substituents not involved in a specific mechanistic step. **(4 pts)**



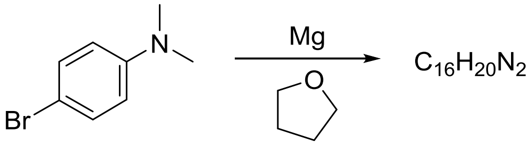
Crystal Violet



Malachite Green

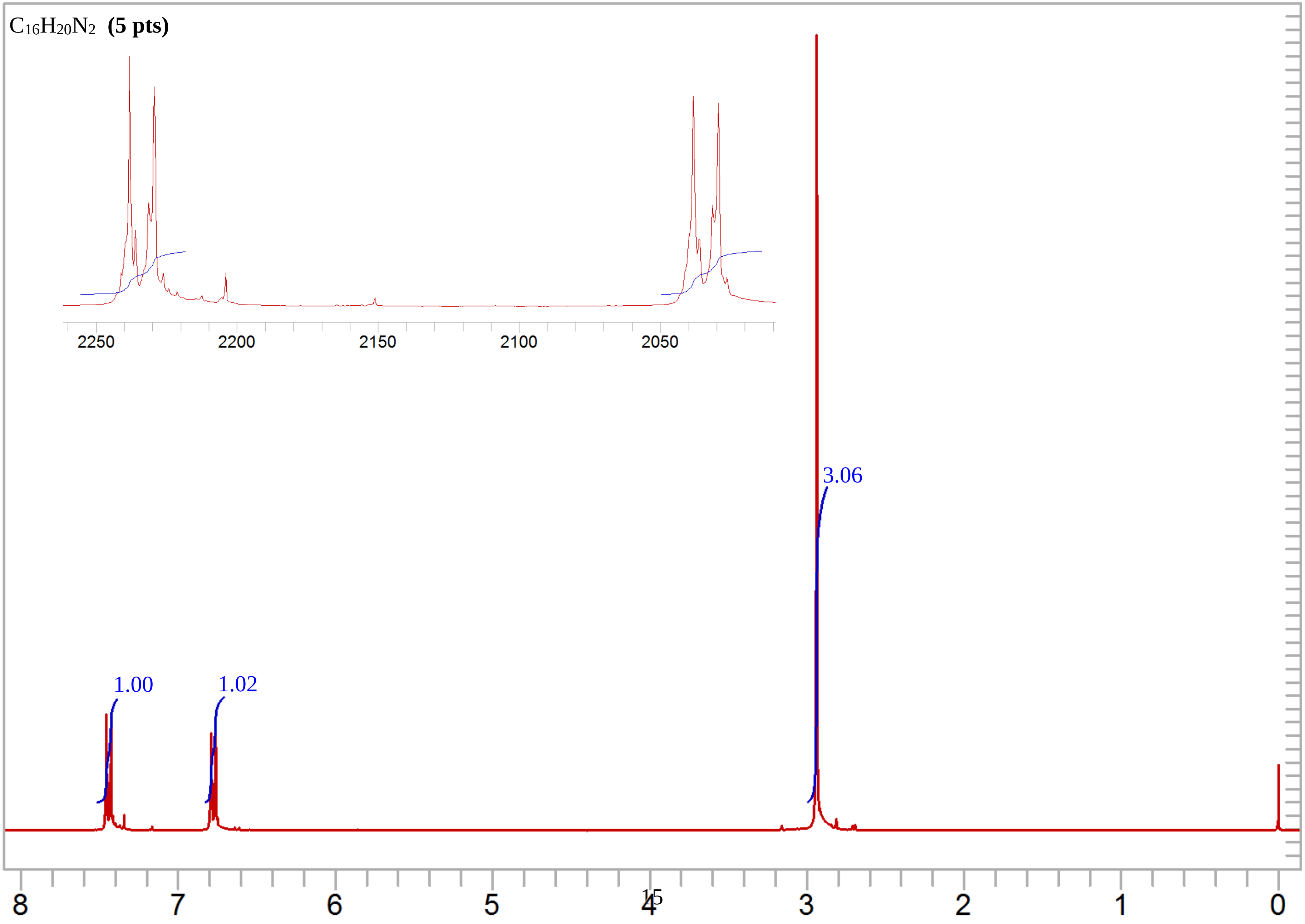
f) The extended conjugated π systems of triarylmethane dyes are responsible for the most intense absorption features in their UV/Vis spectra and their bright colors. For **crystal violet** and **malachite green**, identify the total number of atoms in π conjugation. **(2 pts)**

g) A common byproduct of Grignard reagent formation, highlighting that the mechanism is more complicated than often depicted, is a combination of two Grignard reagents. Use the provided ^{1}H-NMR spectrum to determine the byproduct of this Grignard reaction. Place your final answer directly on the spectrum and assign the ^{1}H-NMR signals.

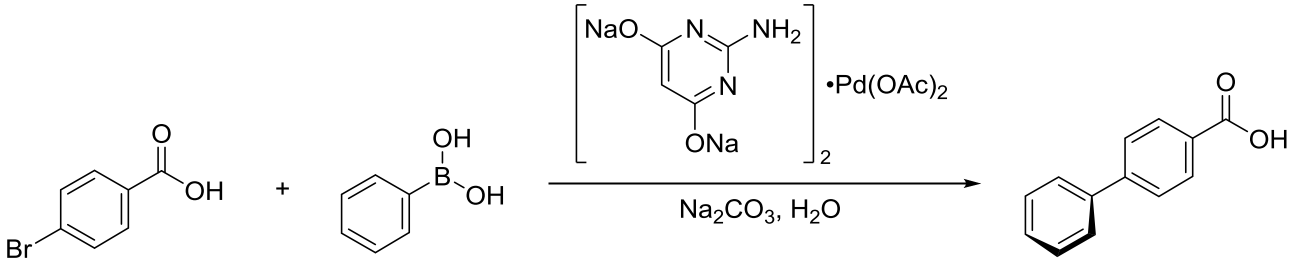


300 MHz ^{1}H NMR

In CDCl3

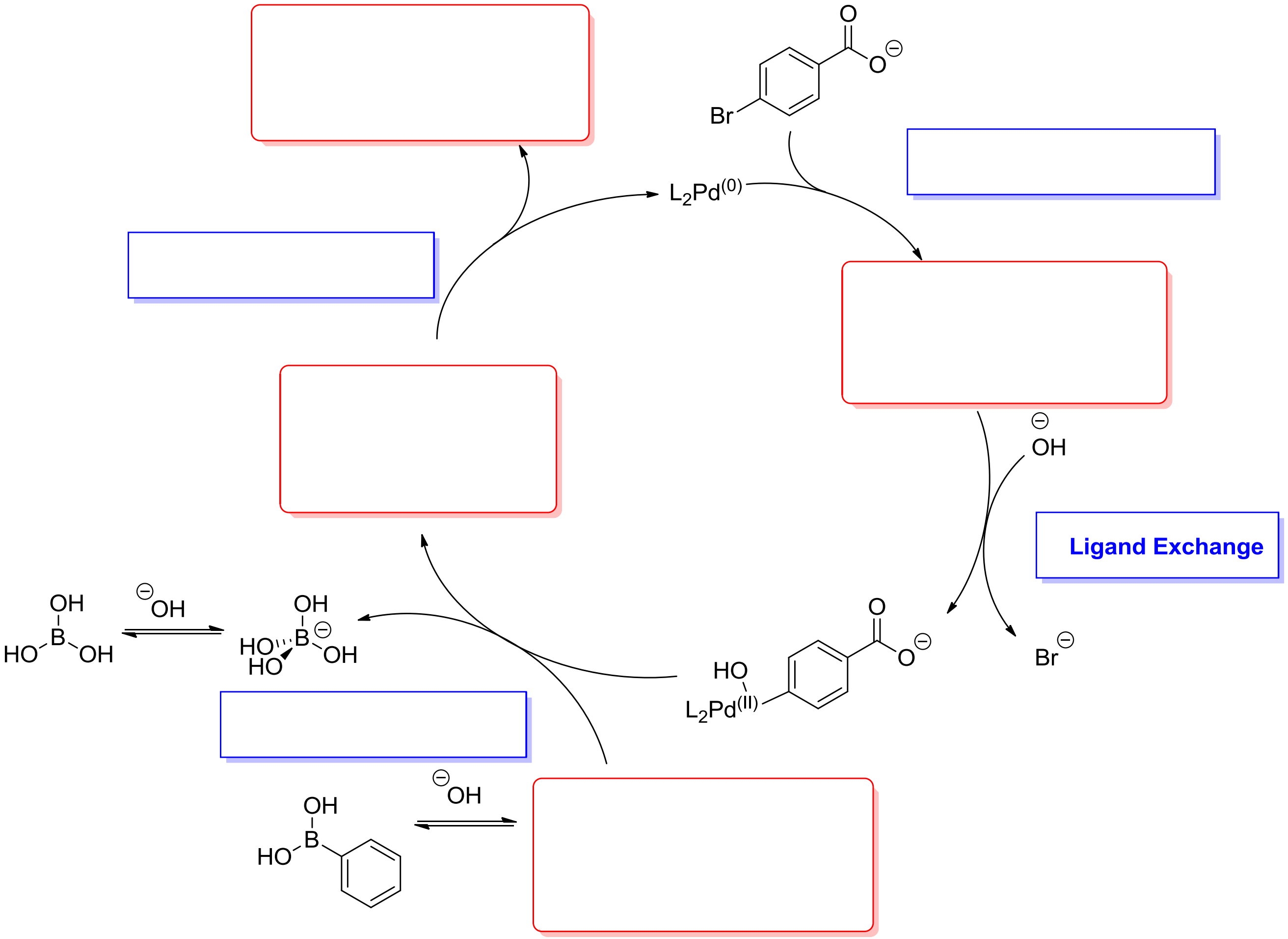


4) Described as an operationally simple aqueous Suzuki-Miyaura cross-coupling reaction, 4-phenylbenzoic acid can be synthesized in greater than 50% yield from phenylboronic acid and *para*-bromobenzoic acid. **(24 points total)**

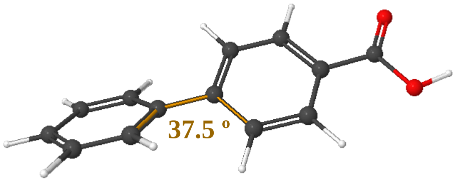


Dissolve 0.80 g of sodium carbonate (7.5 mmol) in 15 mL of deionized water and add it to 0.50 g of 4-bromobenzoic acid (2.5 mmol) and 0.37 g of phenylboronic acid (3.0 mmol) to a 125 mL Erlenmeyer flask containing a stirring bar. After 10 min. of stirring add 1.0 mL palladium (0.01 mol %) catalyst solution. Heat the reaction to a temperature of about 70 ºC for 30 minutes. Allow the reaction cool to room temperature and place it in an ice bath. Position the flask and ice bath so that the mixture is still stirred efficiently. Add 25 mL of 1M HCl dropwise and stir for 5 minutes. Isolate the crude product by vacuum filtration and recrystallize in a 1 to 10 ratio of 1M HCl and EtOH. Prepare the sample for IR, ^{1}H-NMR, and ^{13}C-NMR analysis.

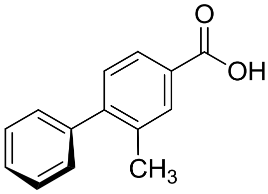
a) An incomplete catalytic cycle for this Suzuki-Miyuara coupling is shown below. Fill in the missing terms and molecules. (**Blue boxes = missing terms**; **red boxes = missing structures**.) **(7 points)**



b) The B3LYP/6-31G(d) optimized structure of the carboxylic acid product is shown below with the inter-ring dihedral angle labeled. Clearly explain the factor or factors that result in this 37.5 º dihedral angle. **(4 points)**



c) Would you expect the dihedral angle to be greater or lesser in the molecule below compared to the product of the reaction shown above in 2b. Justify your answer. **(2 points)**



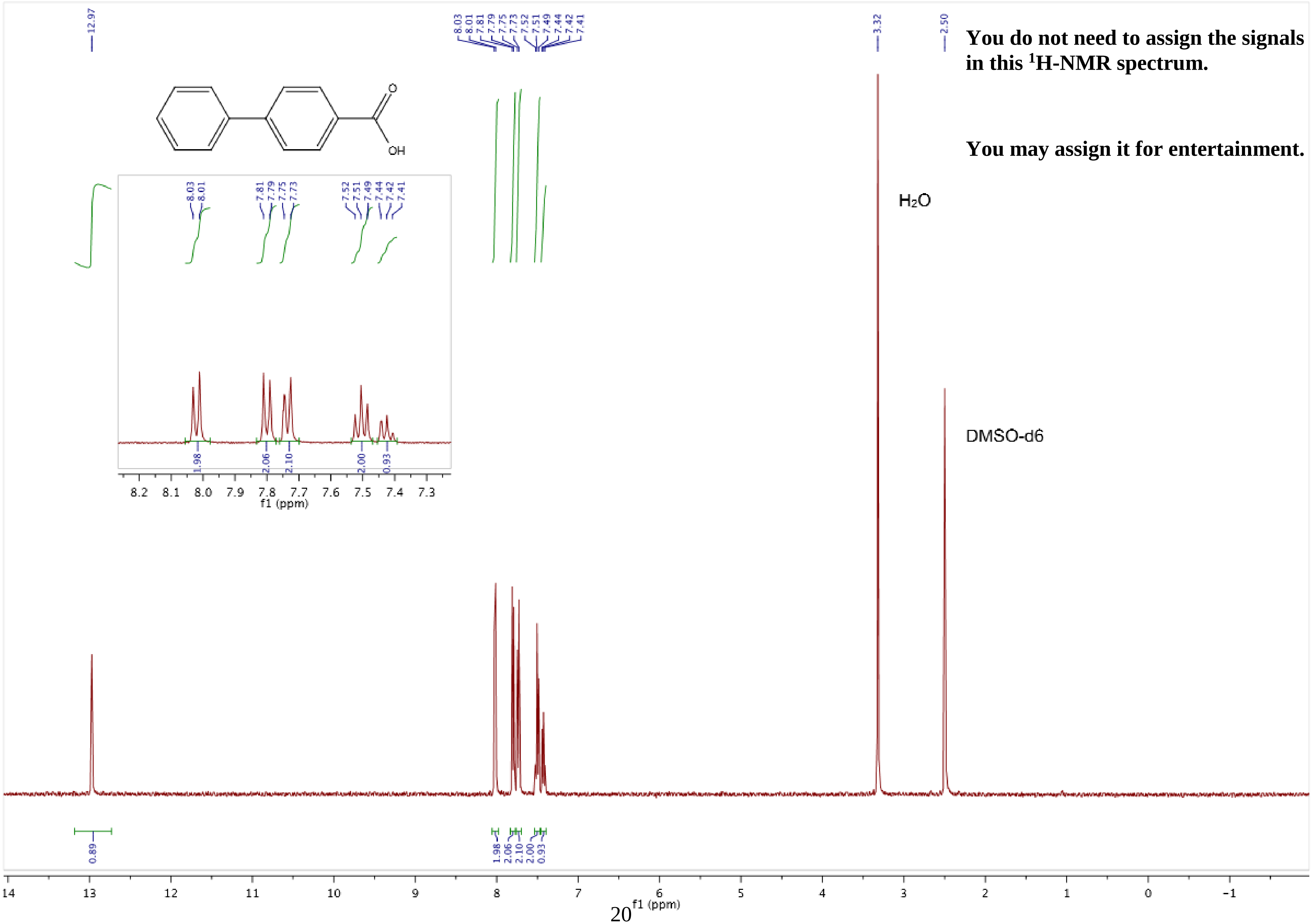
d) The ^{1}H-NMR Spectrum in $CDCl_3$/DMSO-d_6 of the product (on the subsequent page) contains a signal at δ 13.0 ppm with an integration of 0.89. Provide a rationale for why this signal has an integration less than one. **(3 pts)**

e) The crude biaryl product can be purified by recrystallization in acidic ethanol and vacuum filtration. Draw a series of diagrams that explain how this process works. Clearly identify where the product and impurities will be located at each stage of purification. **(4 pts)**

f) The crude biaryl product could be purified readily by another method. Suggest an alternate method of purification and draw a series of diagrams that explain how this process works. Clearly identify where the product and impurities will be located at each stage of purification. **(4 points)**

You do not need to assign the signals in this ^{1}H-NMR spectrum.

You may assign it for entertainment.



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Name:

TA Name:

1) ________ /34

Page 2 ________ /10
Page 3 ________ /6
Page 4 ________ /8
Page 5 – 7 ________ /10

2) ________ /18

Page 8 ________ /8
Page 9 – 10 ________ /10

3) ________ /24

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Page 12 ________ /9
Page 13 ________ /6
Page 14 – 15 ________ /7

4) ________ /24

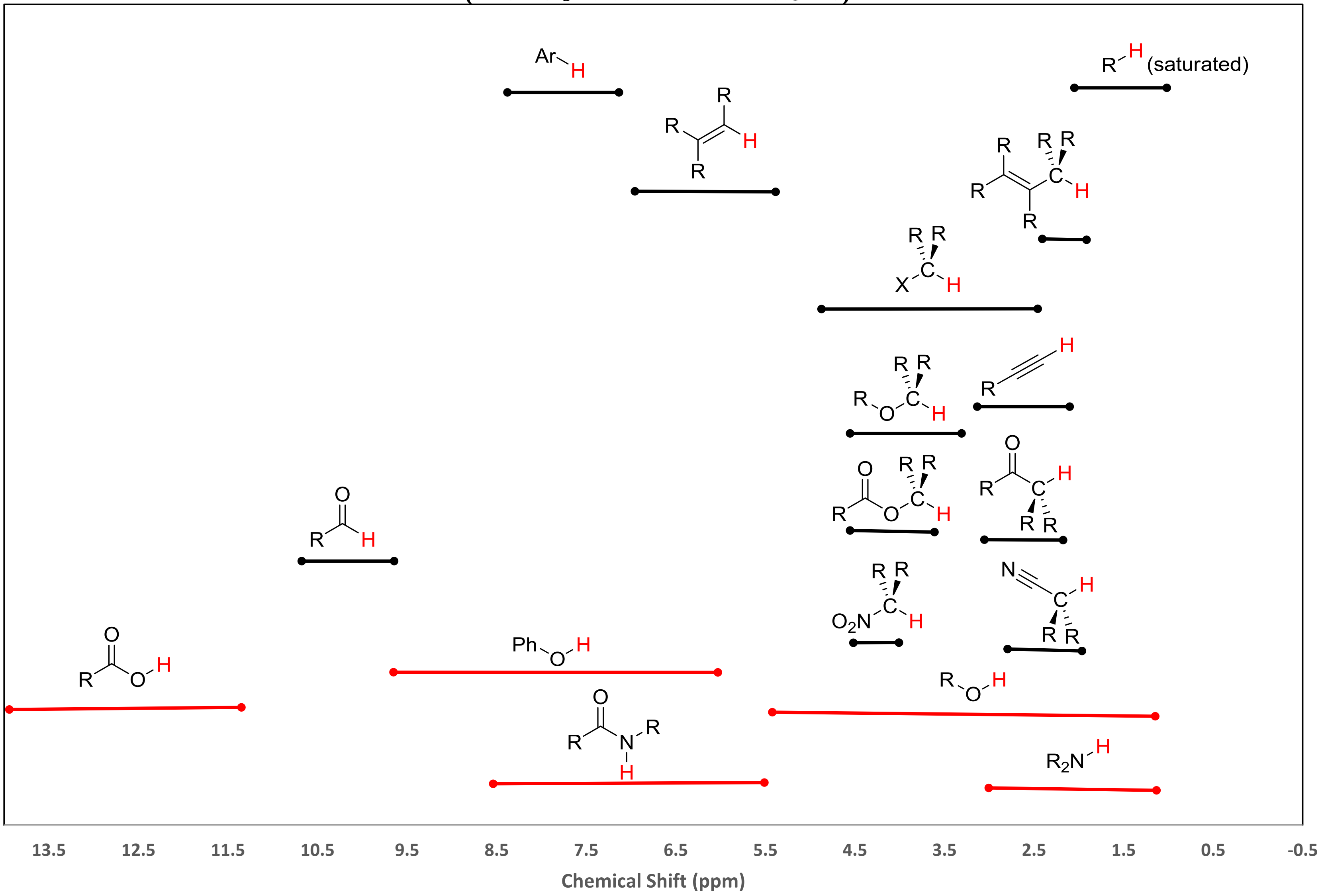
Page 16 ________ /7
Page 17 ________ /6
Page 18 ________ /7
Page 19 ________ /4

Total = ________ /100

Total = ________ /100 (math double-check)

Typical ^{1}H-NMR Chemical Shift Ranges

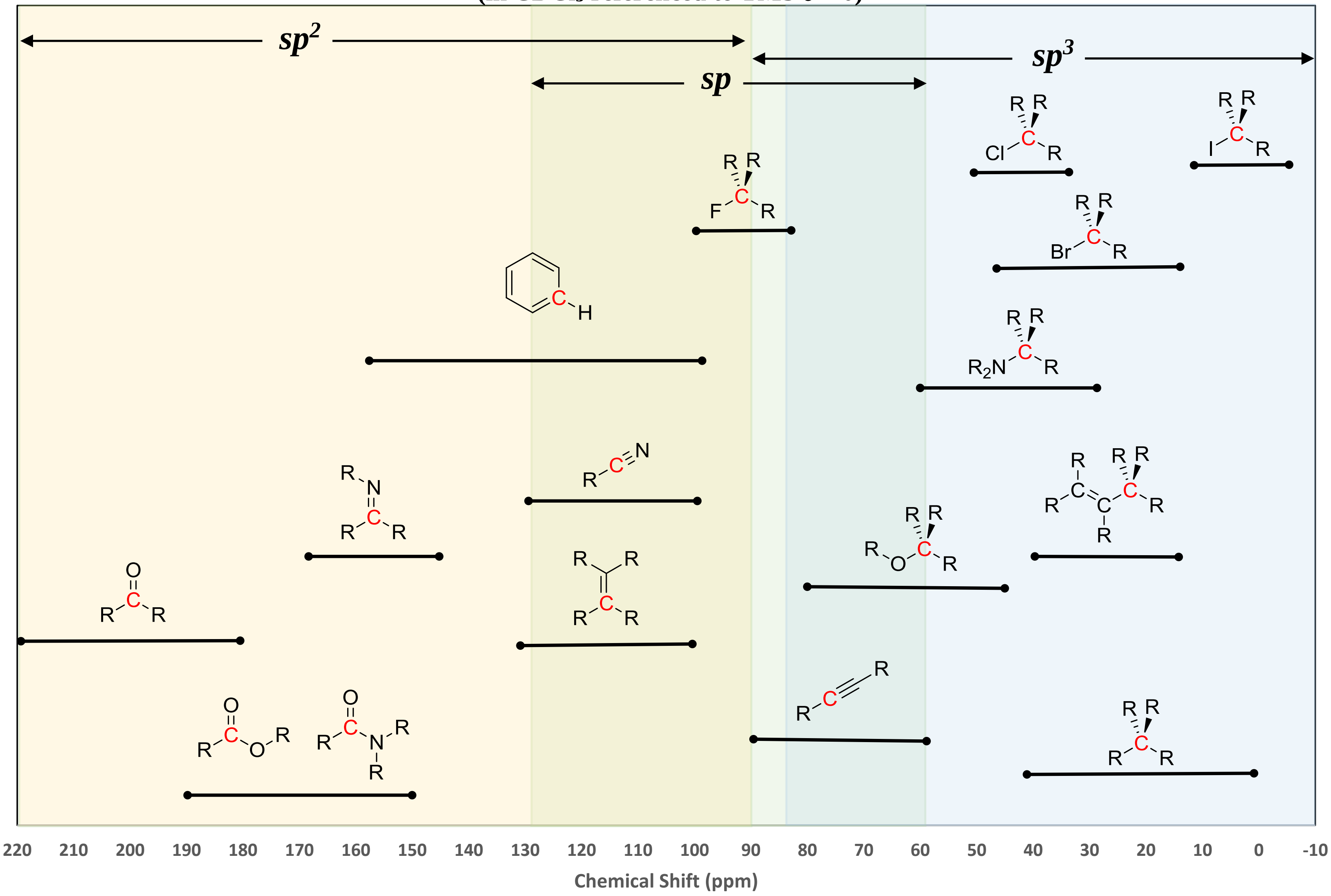
(in $CDCl_3$ referenced to TMS δ = 0)



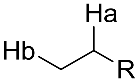
F

Typical ^{13}C-NMR Chemical Shift Ranges

(in $CDCl_3$ referenced to TMS δ = 0)

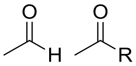
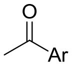
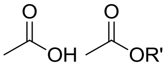
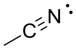
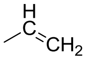
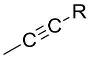
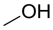
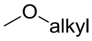
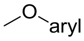


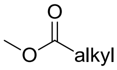
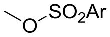
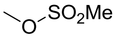
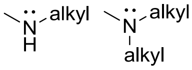
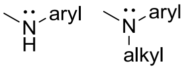
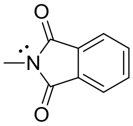
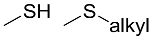
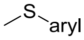
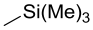
Curphy-Morrison Additivity Constants for Proton NMR

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

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)	----

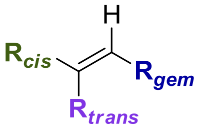
Substituent (R)		α-shift	β-shift
	$-CH_3$	2.90	0.40
	$-CH_2-$	2.95	0.45
	$-CH-$	3.45	----
	$-CH_3$	2.84	0.39(1)
	$-CH_2-$	2.66(6)	0.28(5)
	$-CH-$	3.16(3)	0.32(2)
	$-CH_3$	3.01	0.47(2)
	$-CH_2-$	2.90(5)	0.43(2)
	$-CH-$	2.64(1)	0.61(1)
	$-CH_3$	1.25	0.20
	$-CH_2-$	1.40	0.15
	$-CH-$	1.35	----
	$-CH_3$	2.08(8)	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: $\delta_{H\,(vinyl)} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$

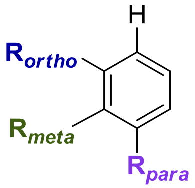
Substituent (R)	Z_{gem}	Z_{cis}	Z_{trans}	Substituent (R)	Z_{gem}	Z_{cis}	Z_{trans}
H	0.00	0.00	0.00	F	1.54	-0.40	-1.02
alkyl	0.45	-0.22	-0.28	Cl	1.08	0.18	0.13
Alkyl (cyclic)	0.69	-0.25	-0.28	Br	1.07	0.45	0.55
CH_2OH	0.64	-0.01	-0.02	I	1.14	0.81	0.88
CH_2SH	0.71	-0.13	-0.22	OR (R = aliphatic)	1.22	-1.07	-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	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}
H	0.00	0.00	0.00
CH_3	-0.18	-0.11	-0.21
*t*Bu	0.02	-0.08	-0.21
CH_2Cl	0.02	-0.01	-0.04
CH_2OH	-0.07	-0.07	-0.07
CF_3	0.32	0.14	0.20
CCl_3	0.64	0.13	0.10
$C{=}CH_2$	0.04	-0.04	-0.12
C=CHCOOH	0.19	0.04	0.05
C≡C-H	0.15	-0.02	-0.01
C≡C-Ph	0.17	-0.02	-0.03
Ph	0.23	0.07	-0.02
COOH	0.77	0.11	0.25
$C(O)OCH_3$	0.68	0.08	0.19
C(O)OPh	0.85	0.14	0.27
$C(O)NH_2$	0.46	0.09	0.17
C(O)Cl	0.76	0.16	0.33
$C(O)CH_3$	0.60	0.10	0.20
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
OPh	-0.36	-0.04	-0.28
$O\text{-}C(O)CH_3$	-0.27	-0.02	-0.13
O-C(O)Ph	-0.14	0.07	-0.09
$O\text{-}SO_2CH_3$	-0.05	0.07	-0.01
SH	-0.08	-0.16	-0.22
SMe	-0.08	-0.10	-0.24
SPh	0.06	-0.09	-0.15
SO_2Cl	0.76	0.35	0.45
NH_2	-0.71	-0.22	-0.62
NMe_2	-0.66	-0.18	-0.67
NEt_2	-0.68	-0.15	-0.73
$NMe_3^+\ I^-$	0.69	0.36	0.31
$NHC(O)CH_3$	0.14	-0.07	-0.27
$NH\text{-}NH_2$	-0.60	-0.08	-0.55
N=N-Ph	0.67	0.20	0.20
N=O	0.58	0.31	0.37
NO_2	0.87	0.20	0.35
$SiMe_3$	0.22	-0.02	-0.02

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	quartet	65.91 (CH_2)
	1.21	triplet	15.20 (CH_3)
ethanol	3.72	quartet	58.28 (CH_2)
	1.25	triplet	18.41 (CH_3)
n-hexane	1.26	2nd order multiplet	31.64 (CH_2)
	0.88	triplet	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)	singlet	137.8 (Ar)
	7.1 – 7.3 (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.

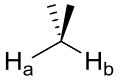
Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics*, **2010**,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

Typical ^{1}H-NMR Coupling Values*

Coupling

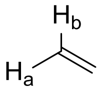
2-bond

gem alkyl



$^2J = 2 – 15$
(typical -12 Hz)

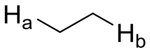
gem vinyl



$^2J = 1 – 3$

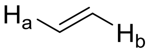
3-bond

vicinal alkyl



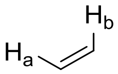
$^3J = 2 – 20$
(typical 7 Hz)

trans vinyl



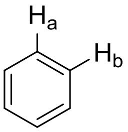
$^3J = 12 – 18$

cis vinyl



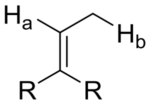
$^3J = 6 – 12$

ortho aryl



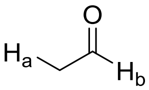
$^3J = 8 – 12$

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



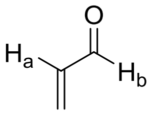
$^3J = 3 – 11$
(dihedral dependent)

vicinal aldehyde



$^3J = 1 – 3$

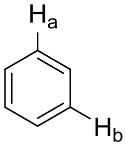
vicinal conjugated aldehyde



$^3J = 7 – 8$

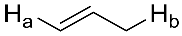
4-bond

meta aryl



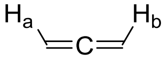
$^4J = 2 – 3$

allylic



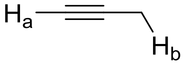
$^4J = 0 – 3$

allenic



$^4J = 6 – 7$

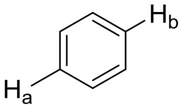
propargylic



$^4J = 2 – 4$

5-bond

para aryl



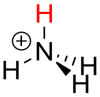
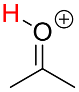
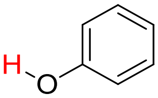
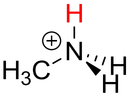
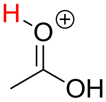
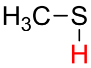
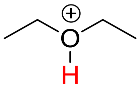
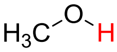
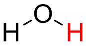
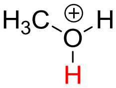
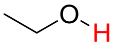
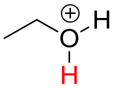
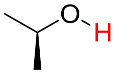
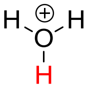
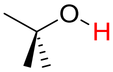
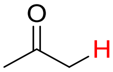
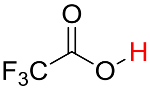
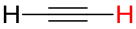
$^5J = 0 – 1$

*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	**pKa**	**Acid**	**pKa**
H–I	-10	H–CN	9.1
H–Br	-9		9.2
	-7.5		9.9
H–Cl	-7		10.6
	-6.2		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
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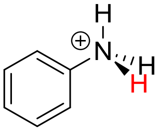
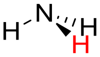
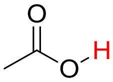
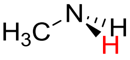
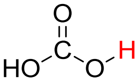
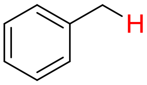
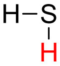
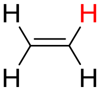
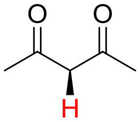
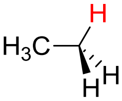
	4.6		38
	4.75		38
	6.35		41
	7.0		44
	9.0		50

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