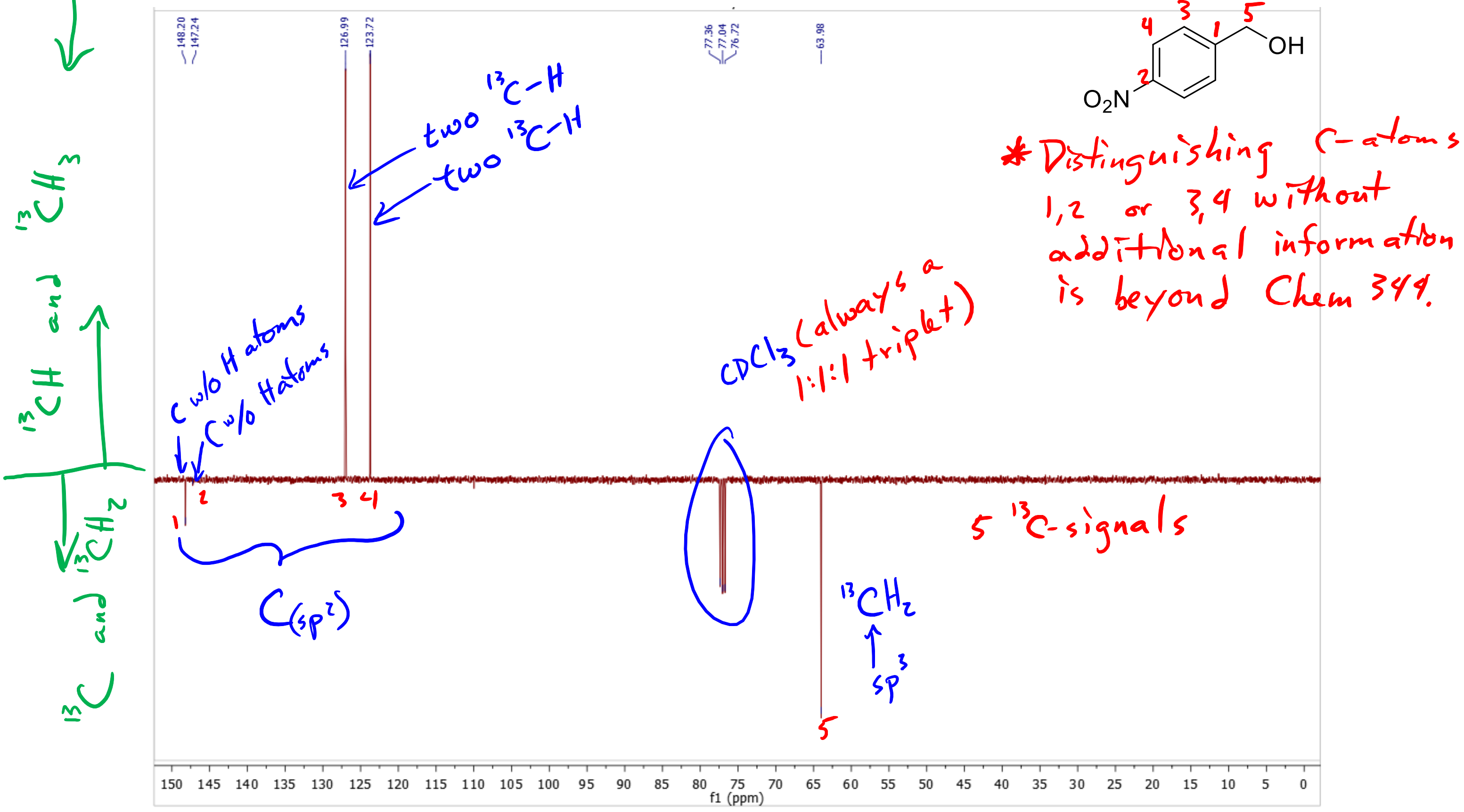
Chemistry 344: Spectroscopy and Spectrometry Problem Set 3

Name (print): ____

TA Name (print): _____________________________________

I. The NMR spectra of *p*-nitrobenzyl alcohol are provided below.

A. In the ^{13}C-NMR APT spectrum, assign the hybridization of the ^{13}C-atoms in *p*-nitrobenzyl alcohol responsible for each signal. Identify any key functional group signals and label each ^{13}C-atom signal with the number of H-atoms attached.



* Distinguishing C-atoms 1,2 or 3,4 without additional information is beyond Chem 344.

B. Predict the ^{1}H-NMR chemical shift for each ^{1}H-atom in the molecule using empirical (Curphy-Morrison) parameters.

H_A

7.36 ppm $C_{aryl} - H$

−0.07 ppm meta $-CH_2OH$

+0.87 ppm ortho $-NO_2$

8.16 ppm

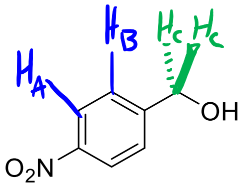
H_B

7.36 ppm $C_{aryl} - H$

−0.07 ppm ortho $-CH_2OH$

+0.20 ppm meta $-NO_2$

7.49 ppm



H_C

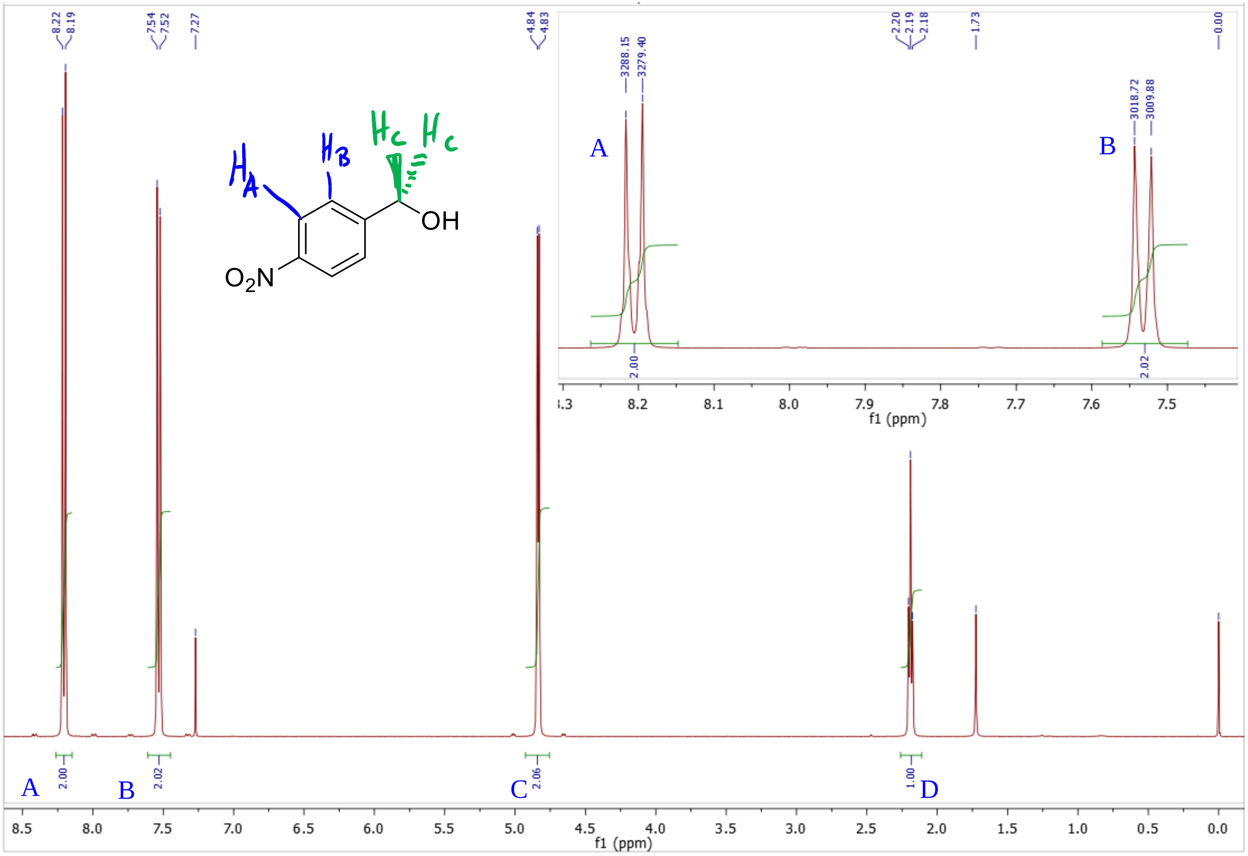
1.20 ppm $-CH_2-$

+2.30 ppm α OH

+1.45 ppm α Ar

4.95 ppm

C. Assign the ^{1}H-atoms in the molecule to their corresponding signals in the ^{1}H-NMR spectrum.

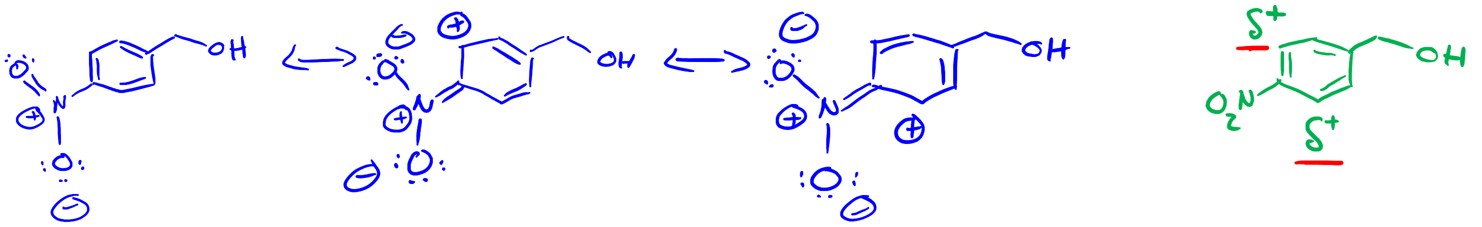


D. How well do the Curphy-Morrison parameters predict the observed ^{1}H-NMR chemical shifts?

	Empirical Prediction (ppm)	Observed (ppm)
A	8.16	8.23
B	7.49	7.54
C	4.95	8.84

The agreement is s

E. Rationalize the intense deshielding and resultant downfield shift of the ^{1}H-atoms attached *ortho* to the nitro group by providing a series of resonance structures. *For all resonance structures in Chem 344, you must properly show all lone pairs and formal charges*.



$-NO_2$ groups are EWG and deshield their ortho ^{1}H-atom neighbors

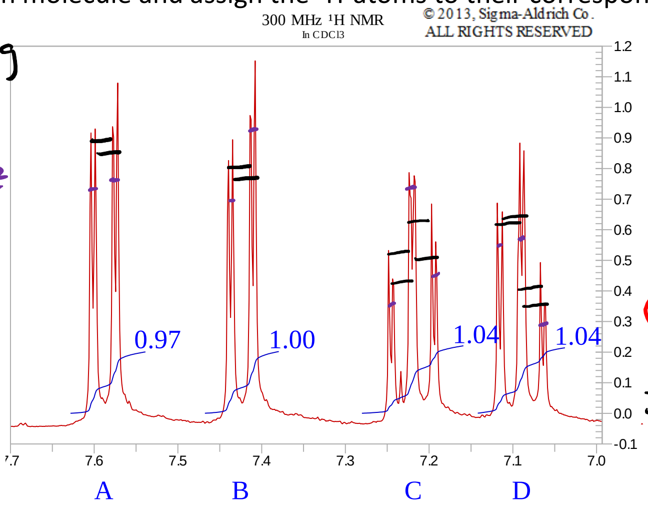
(empirical estimates)

II. The three ^{1}H-NMR spectra below from 7.0 – 7.7 ppm correspond to three bromochlorobenzenes; identify each molecule and assign the ^{1}H-atoms to their corresponding signals.

ignore p-coupling

J ortho ≈ 10 Hz

J meta ≈ 2 Hz



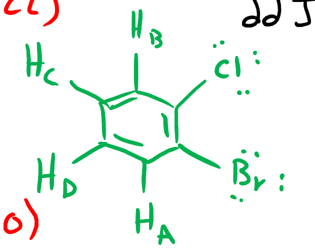
A.

ddd J = ortho, ortho, meta

(7.21)

(7.22)

dd J = ortho, meta



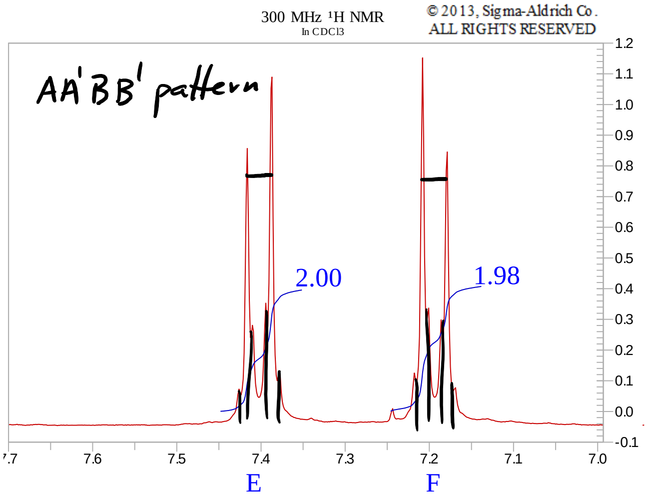
(7.10)

ddd

J = ortho, ortho, meta

(7.42)

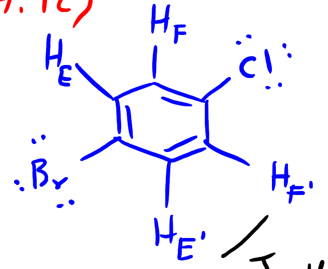
dd J = ortho, meta



B.

(7.42)

(7.21)

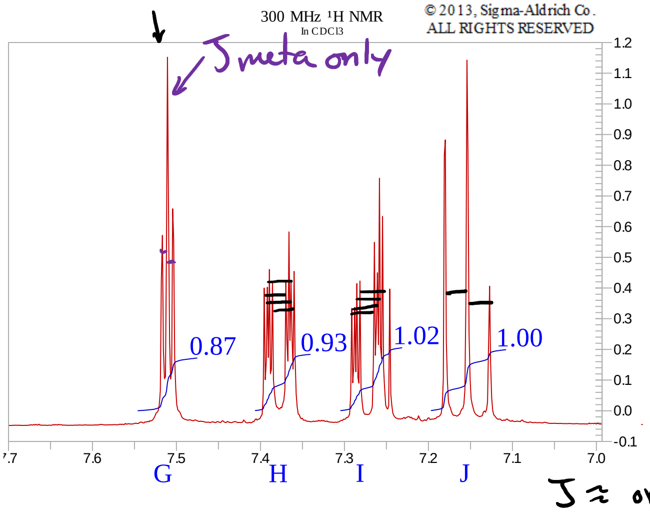


J ortho ≈ 10 Hz

No J ortho

J = ortho, ortho

J = ortho, meta, meta



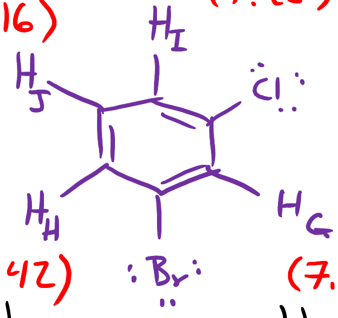
C.

dd or t

ddd

(7.26)

(7.16)



(7.42)

(7.47)

ddd

dd or t

J ≈ ortho, meta, meta

J = meta, meta

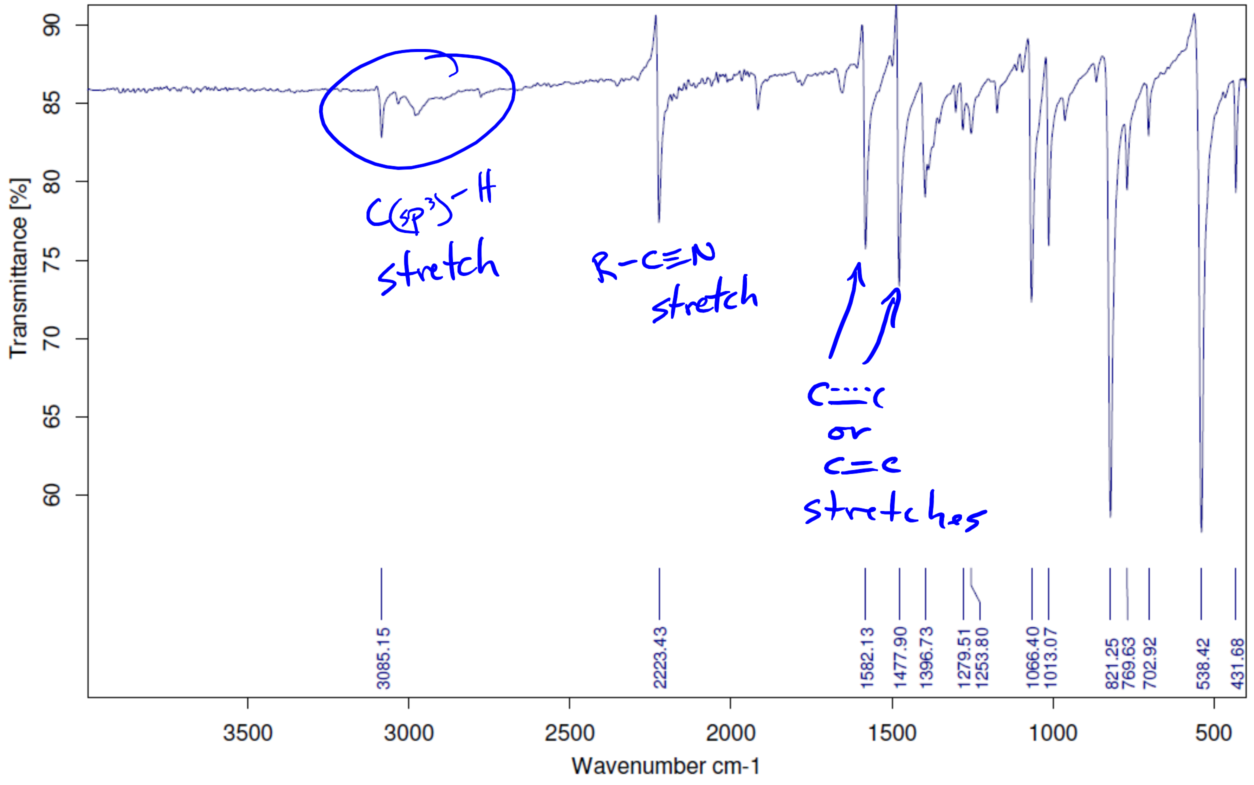
III. For the IR, ^{1}H-NMR and ^{13}C-NMR spectra shown below for C_7H_4BrN, analyze the structure and each of the spectra as instructed.

A. What is the unsaturation number (**U**) or index of hydrogen deficiency (**IHD**)? What does this indicate about which functional groups are possible for this molecule?

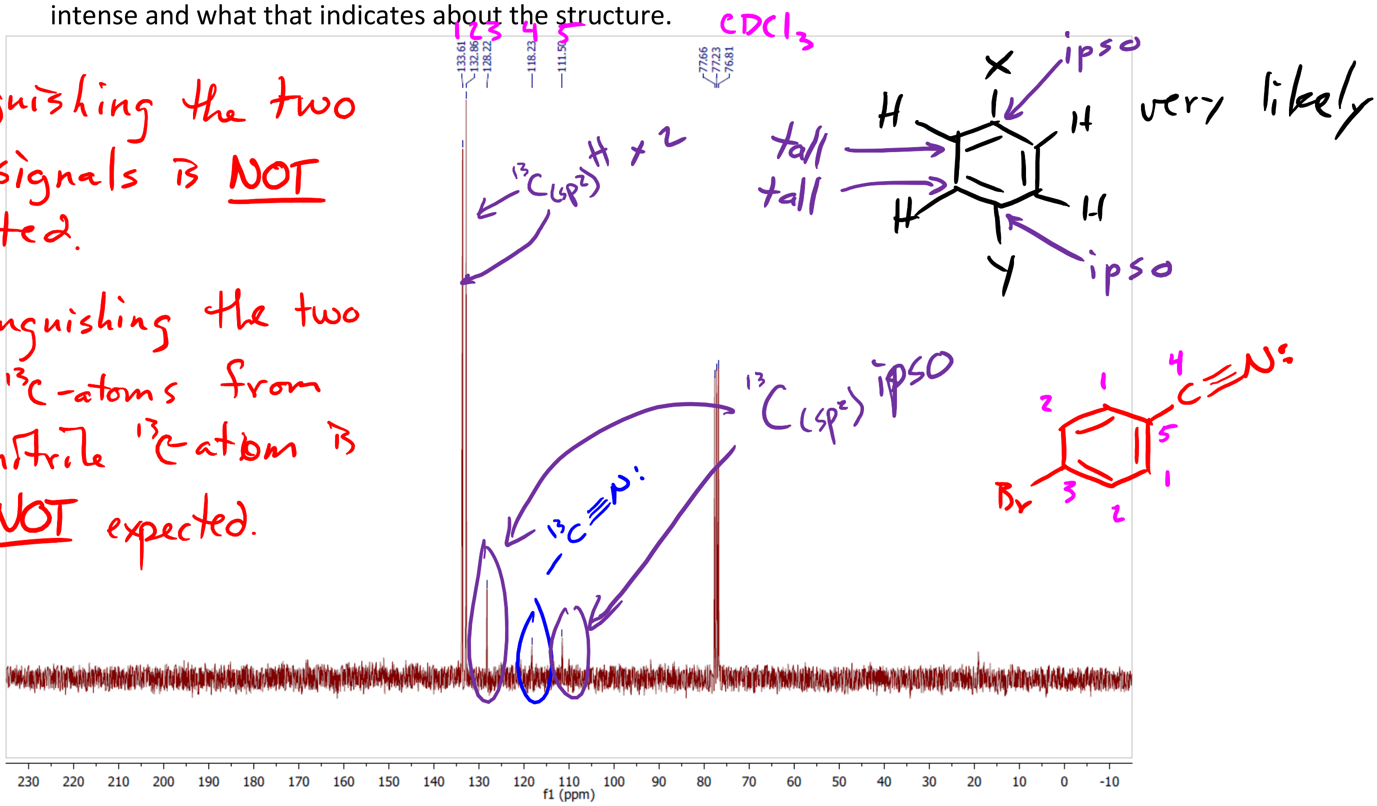
* lots of rings and/or π bonds

$$U = IHD = \frac{2C + 2 + N - H - X}{2} = 6$$

B. The IR spectrum of C_7H_4BrN is provided below; identify any key absorptions that will assist in the determination of its structure.



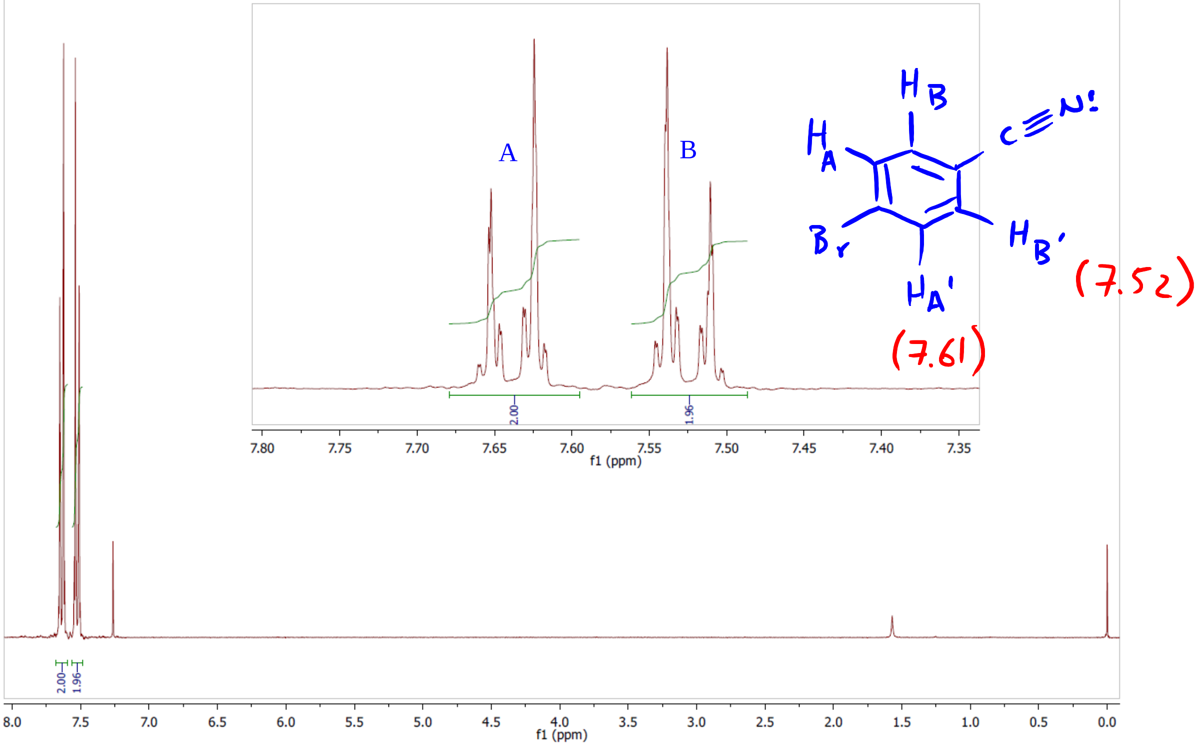
C. The ^{13}C-NMR spectrum of C_7H_4BrN is provided below; identify the hybridization and likely functional group identity of each ^{13}C-atom signal. Explain why the signals at 133.61 and 132.86 ppm are so intense and what that indicates about the structure.



* Distinguishing the two ^{13}C-H signals is NOT expected.

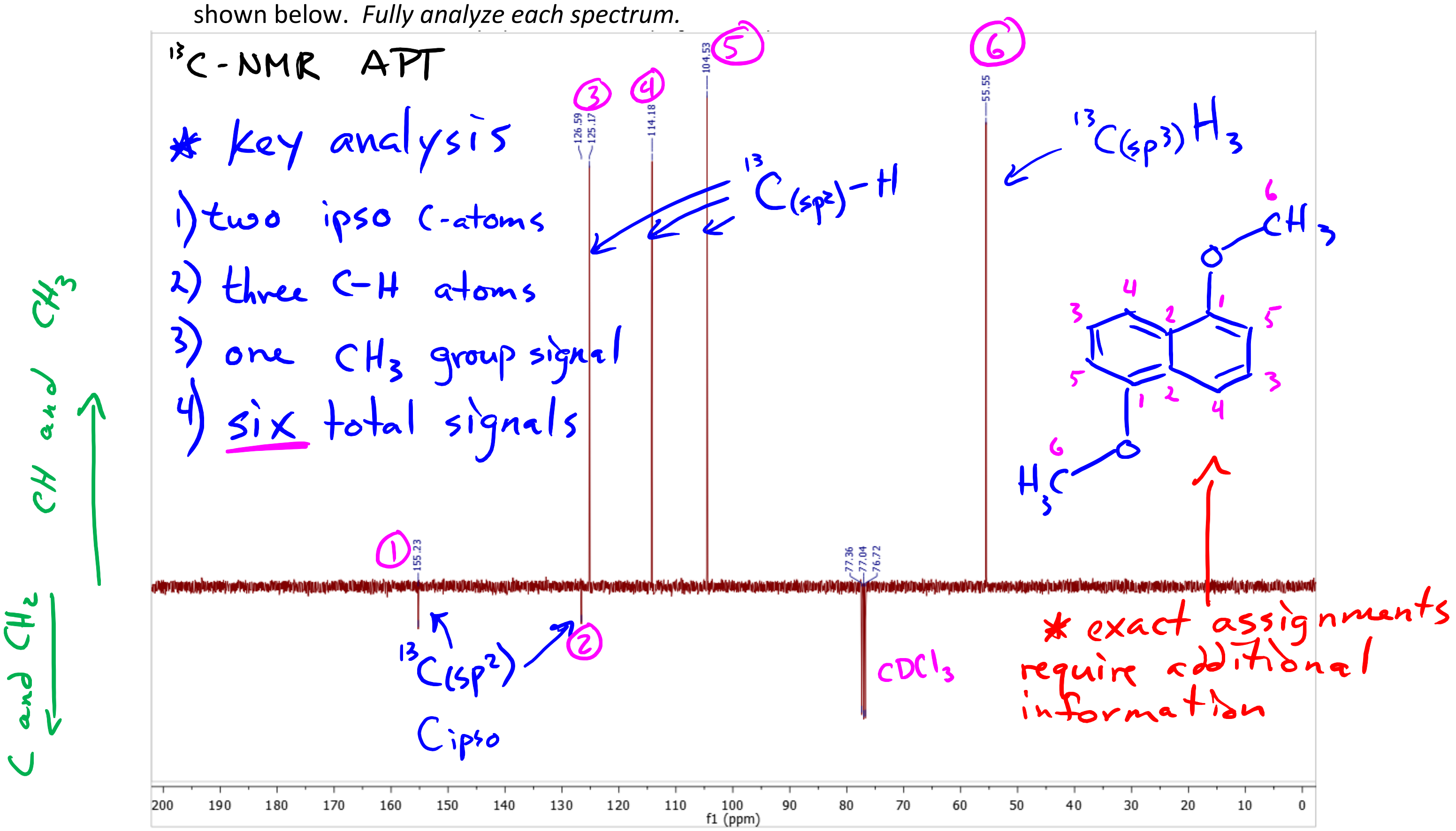
* Distinguishing the two ipso ^{13}C-atoms from the nitrile ^{13}C atom is also NOT expected.

D. The ^{1}H-NMR spectrum of C_7H_4BrN is provided below; determine the structure. Assign each of the ^{1}H-atoms in the molecule to a signal on the spectrum using the key provided. (empirical estimate)



IHD = 7 (lots of rings and/or π bonds)

IV. Determine the structure of the molecule with formula $C_{12}H_{12}O_2$ that corresponds to the spectra shown below. *Fully analyze each spectrum.*



* key analysis

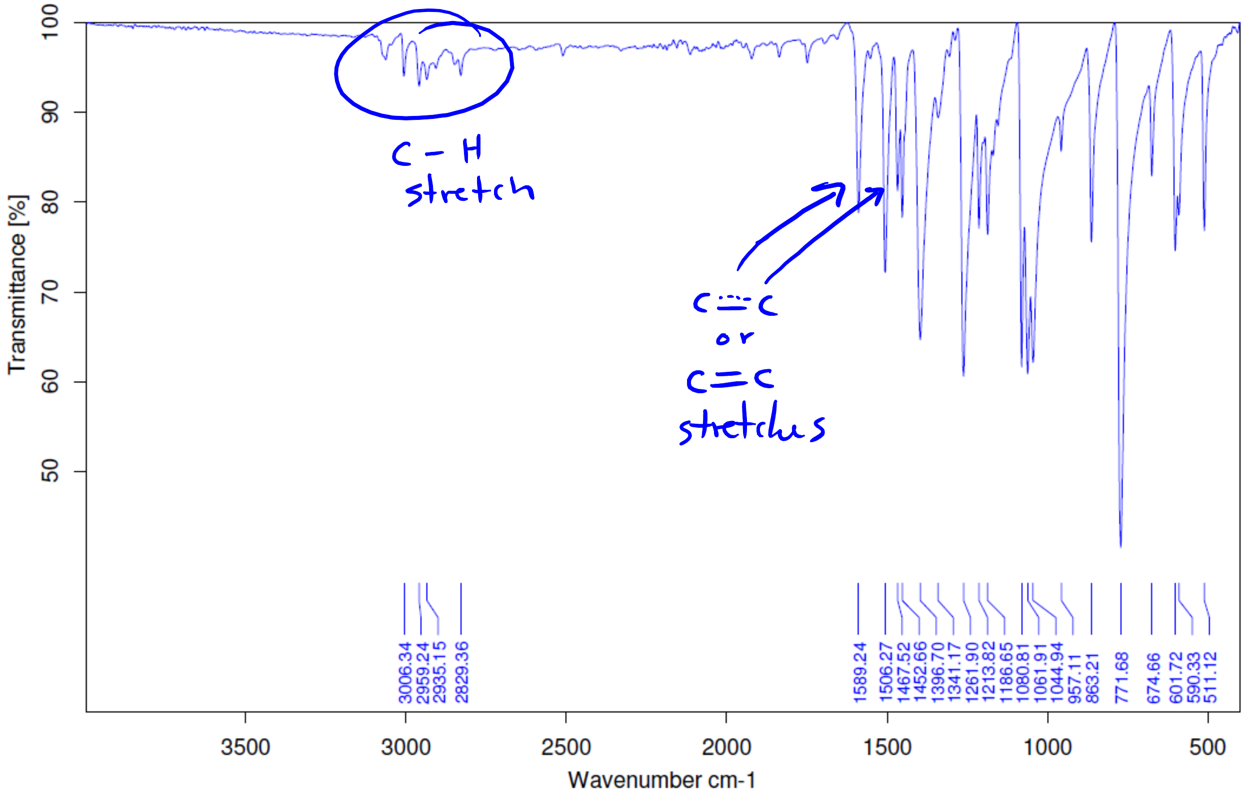
1) two ipso C-atoms

2) three C–H atoms

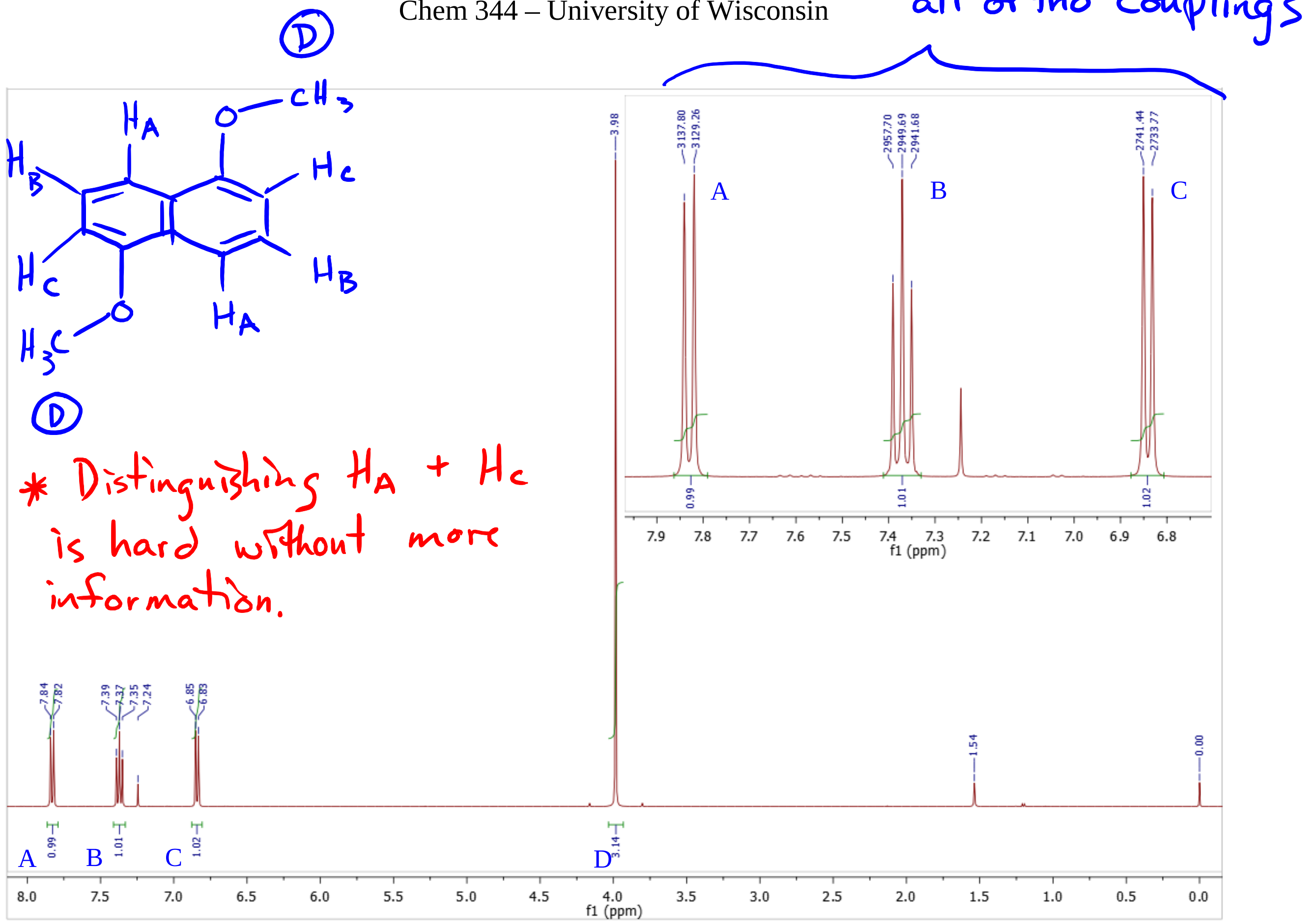
3) one CH_3 group signal

4) six total signals

* exact assignments require additional information

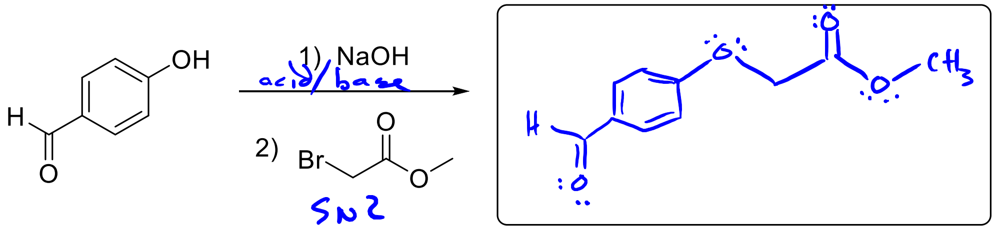


all ortho couplings



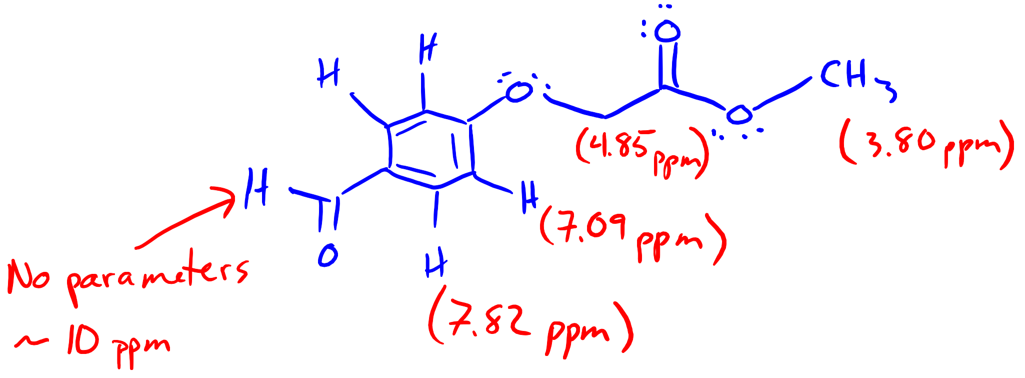
* Distinguishing H_A + H_C is hard without more information.

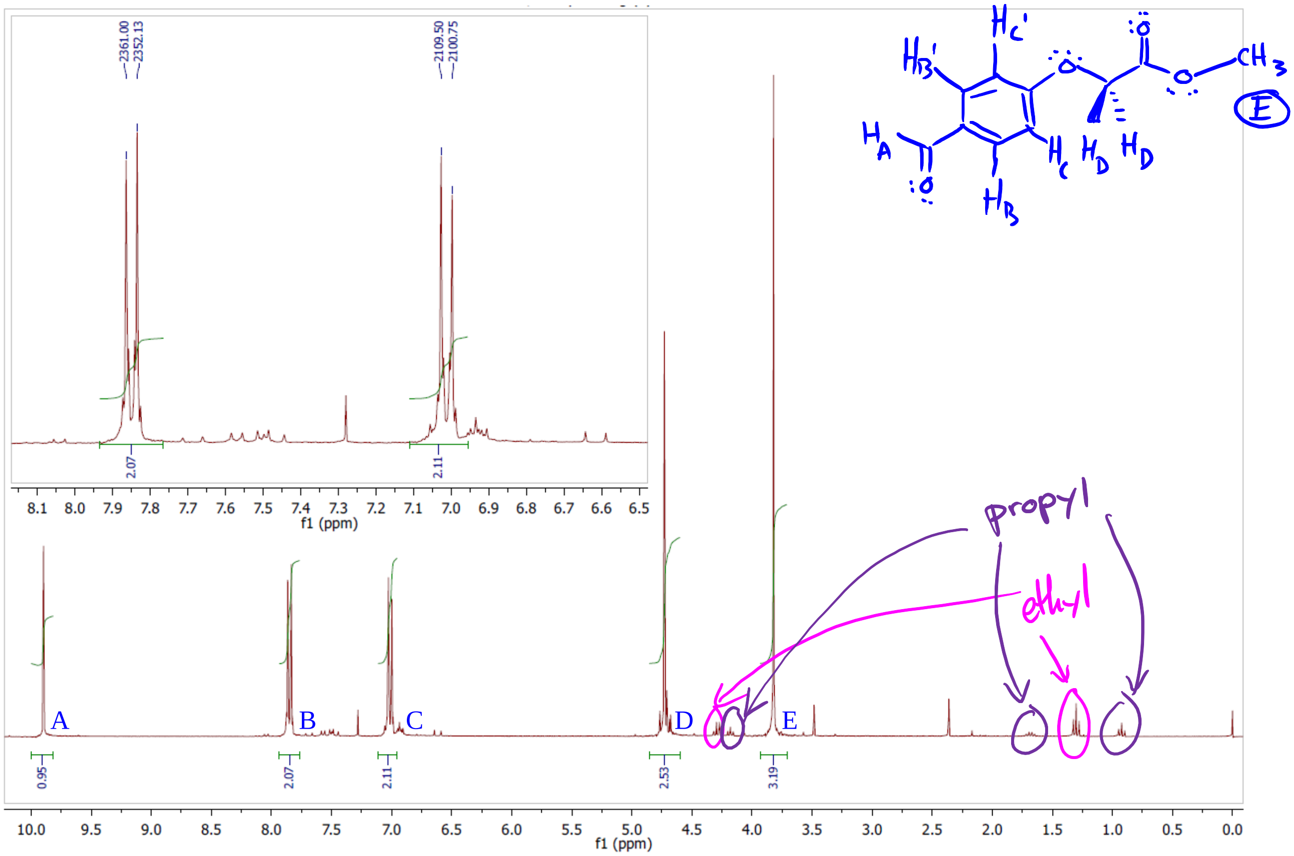
V. The subsequent IR, EI-Mass, ^{1}H-NMR and ^{13}C-NMR spectra were obtained from the product of an S_N2 reaction of 4-hydroxybenzaldehyde and methyl bromoacetate. Predict the product, determine its structure and fully analyze the spectra.



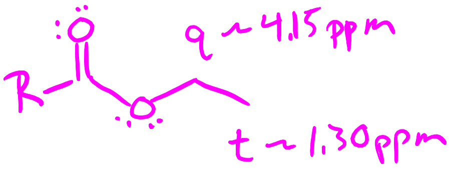
Williamson ether synthesis

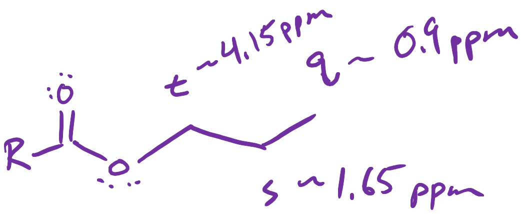
A. Predict the structure of the product and the ^{1}H-NMR chemical shifts of its ^{1}H-atoms using either empirical parameters or a series of resonance structures.

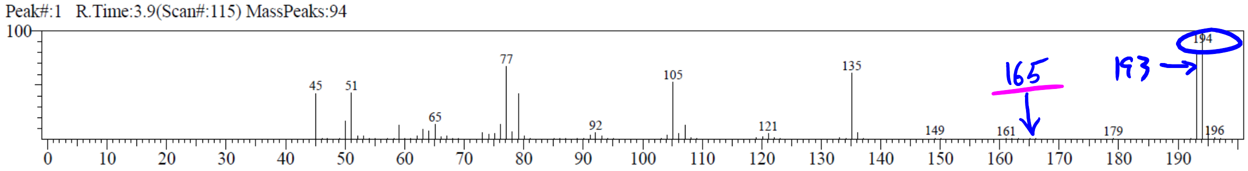


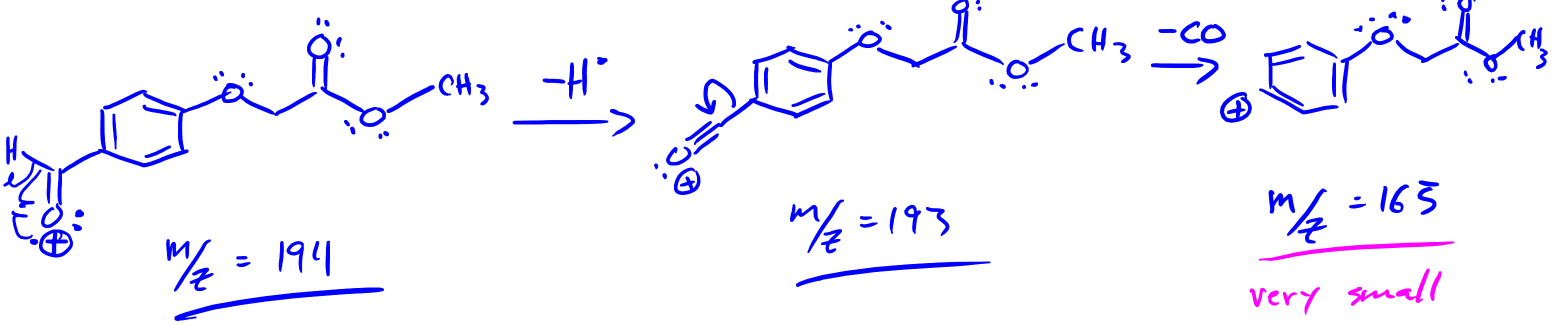


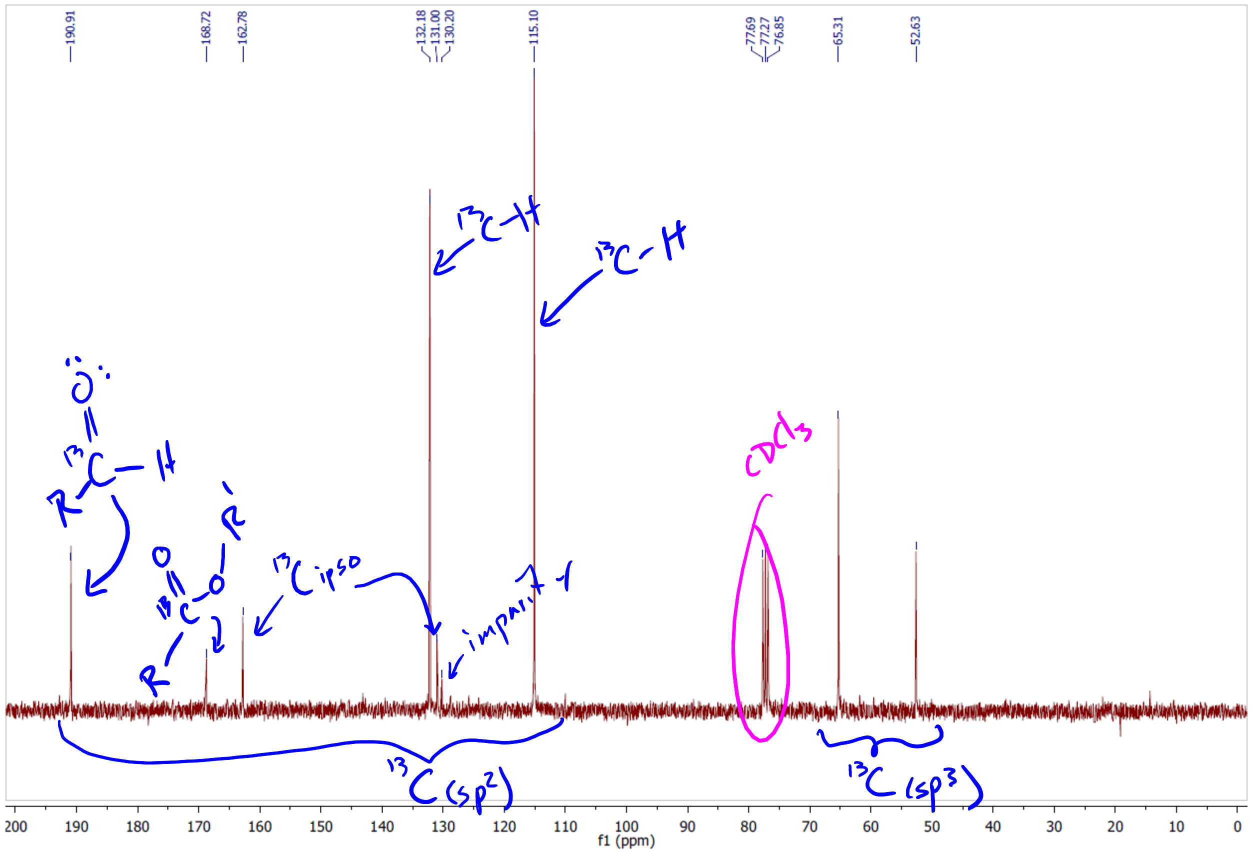
B. The ^{1}H-NMR spectrum contains a number of impurities. What evidence is present of an ethyl ester or propyl ester impurity?

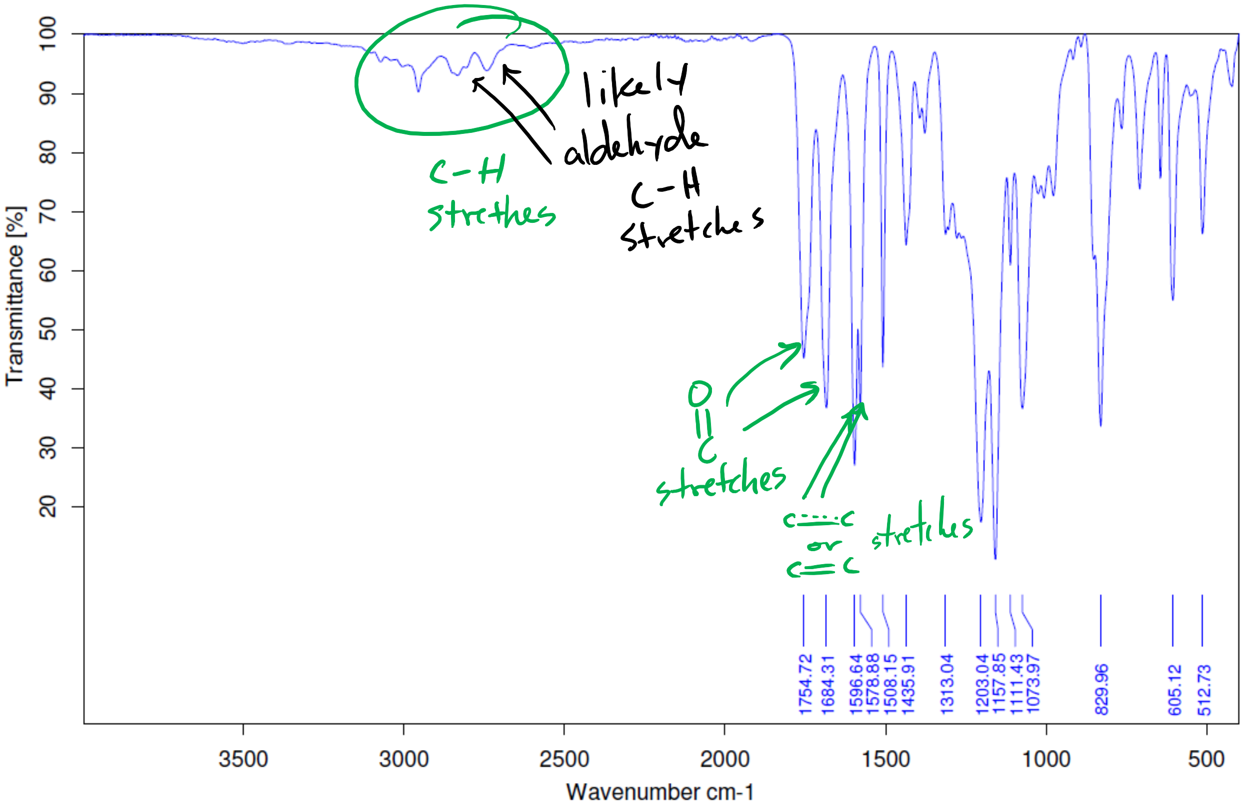




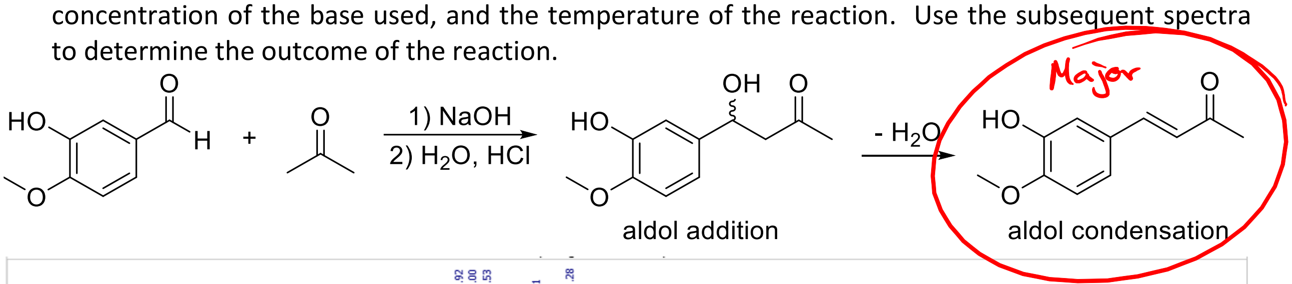


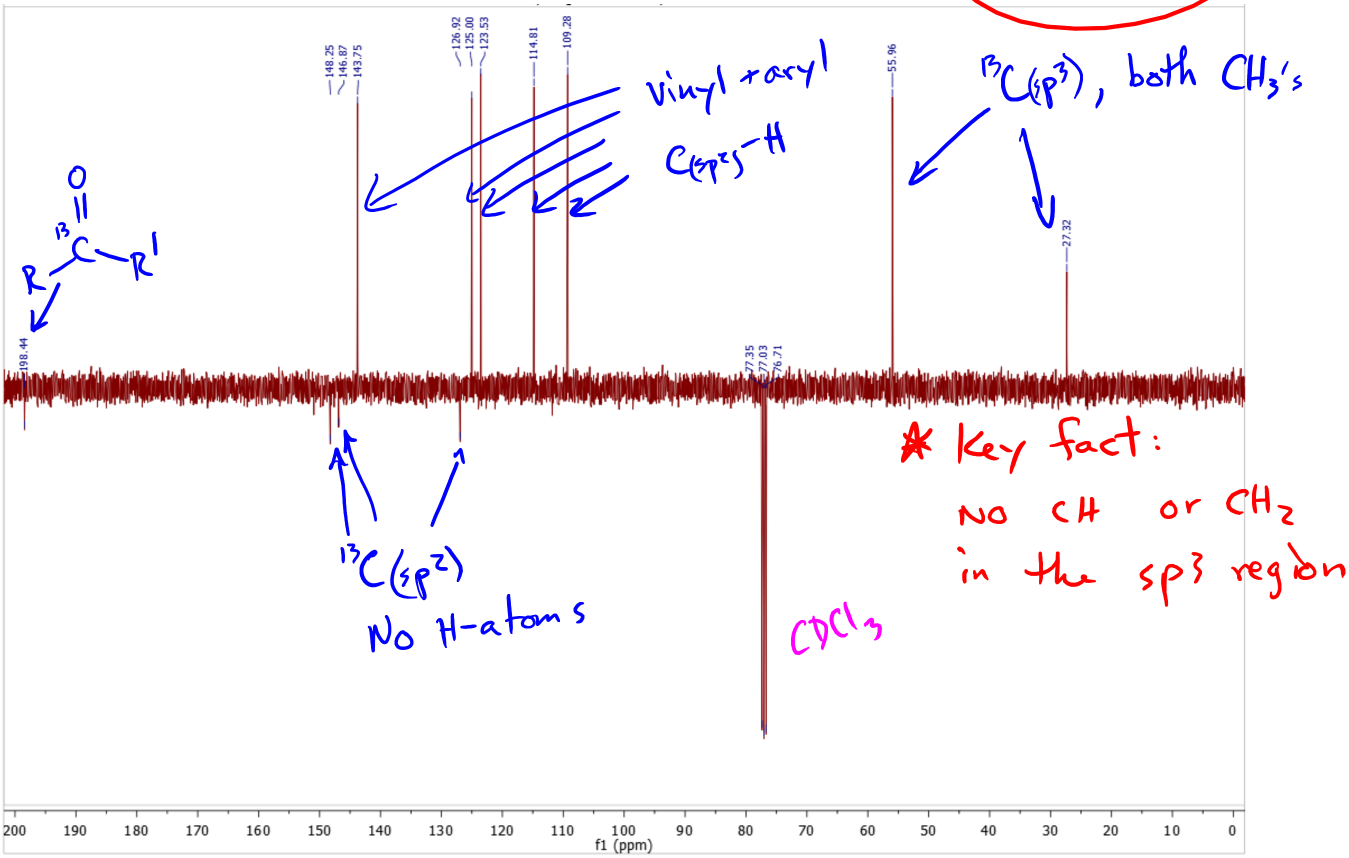



190.91
168.72
162.78
132.18
131.00
130.20
115.10
77.69
77.27
76.85
65.31
52.63
^{13}C-H
^{13}C-H
Ö:
‖
R–^{13}C—H
O
‖
R–^{13}C–O–R'
^{13}C ipso
impurity
$CDCl_3$
^{13}C (sp^2)
^{13}C (sp^3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

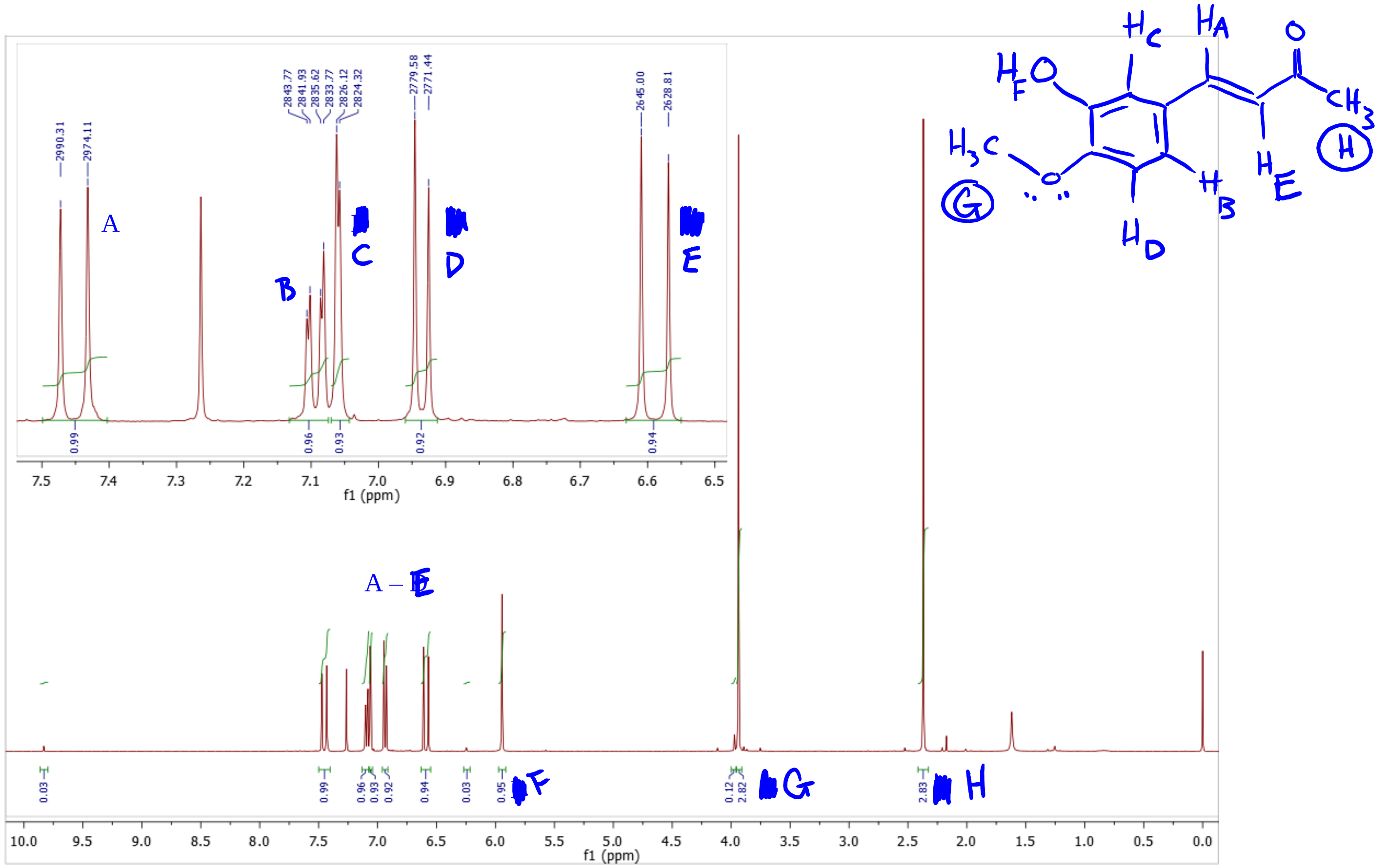

Transmittance [%]
100
90
80
70
60
50
40
30
20
C-H strethes
likely aldehyde C-H stretches
O
‖
C
stretches
C⋯C
or
C=C
stretches
1754.72
1684.31
1596.64
1578.88
1508.15
1435.91
1313.04
1203.04
1157.85
1111.43
1073.97
829.96
605.12
512.73
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

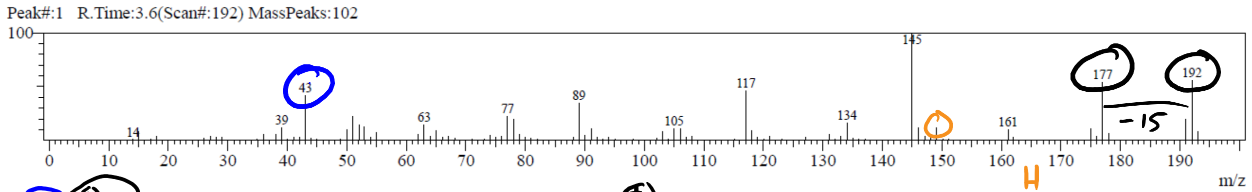
VI. Vanillin and acetone were reacted in basic aqueous conditions. Reactions such as these can lead to aldol addition or condensation products depending on the aldehyde and ketone chosen, the concentration of the base used, and the temperature of the reaction. Use the subsequent spectra to determine the outcome of the reaction.

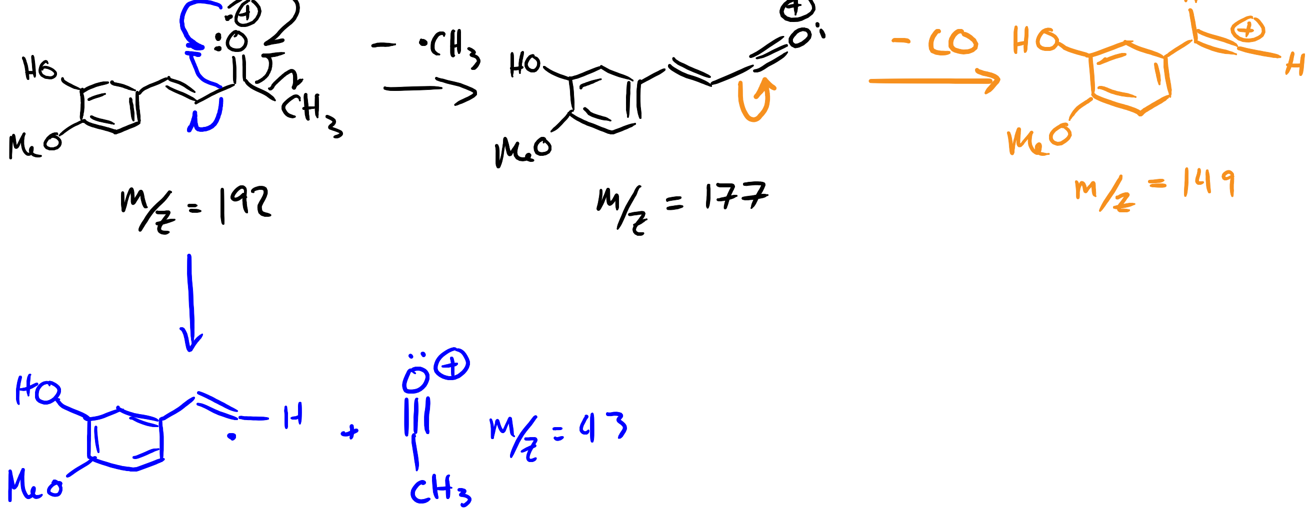




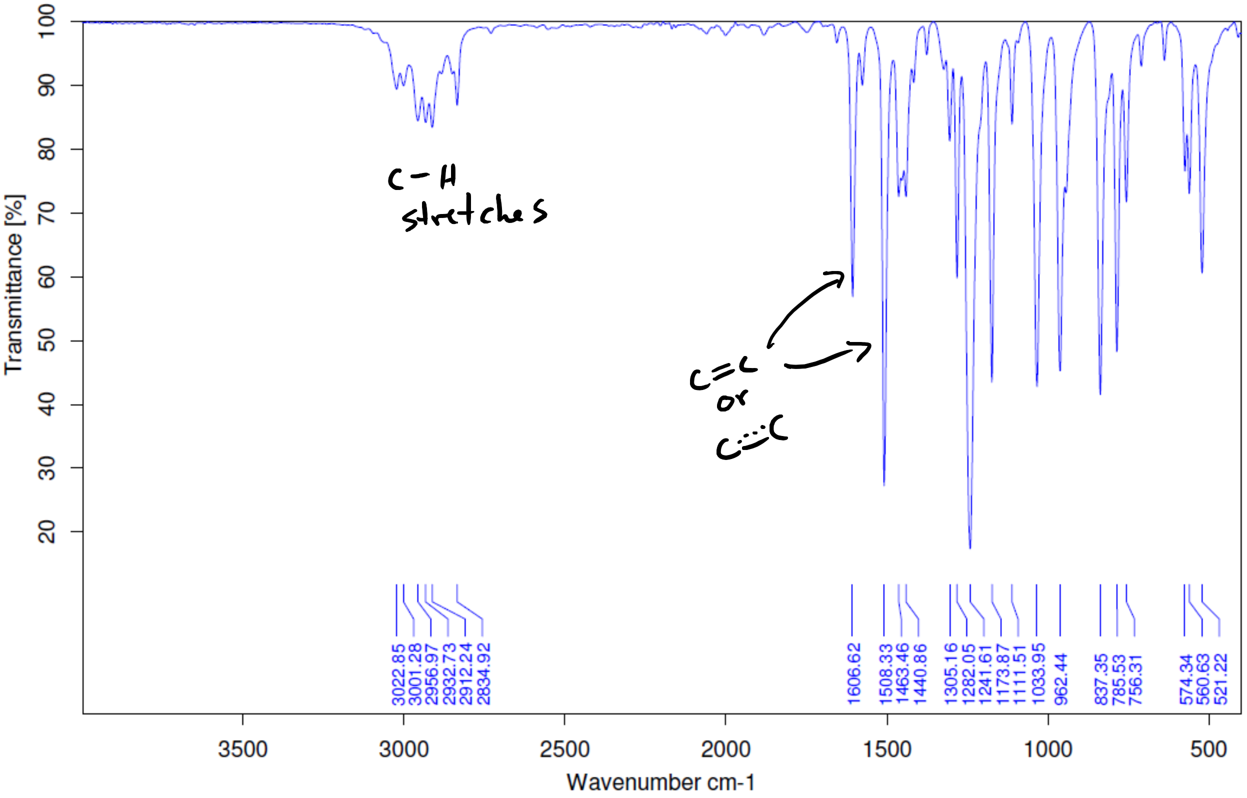
* Key fact:
NO CH or CH_2
in the sp^3 region

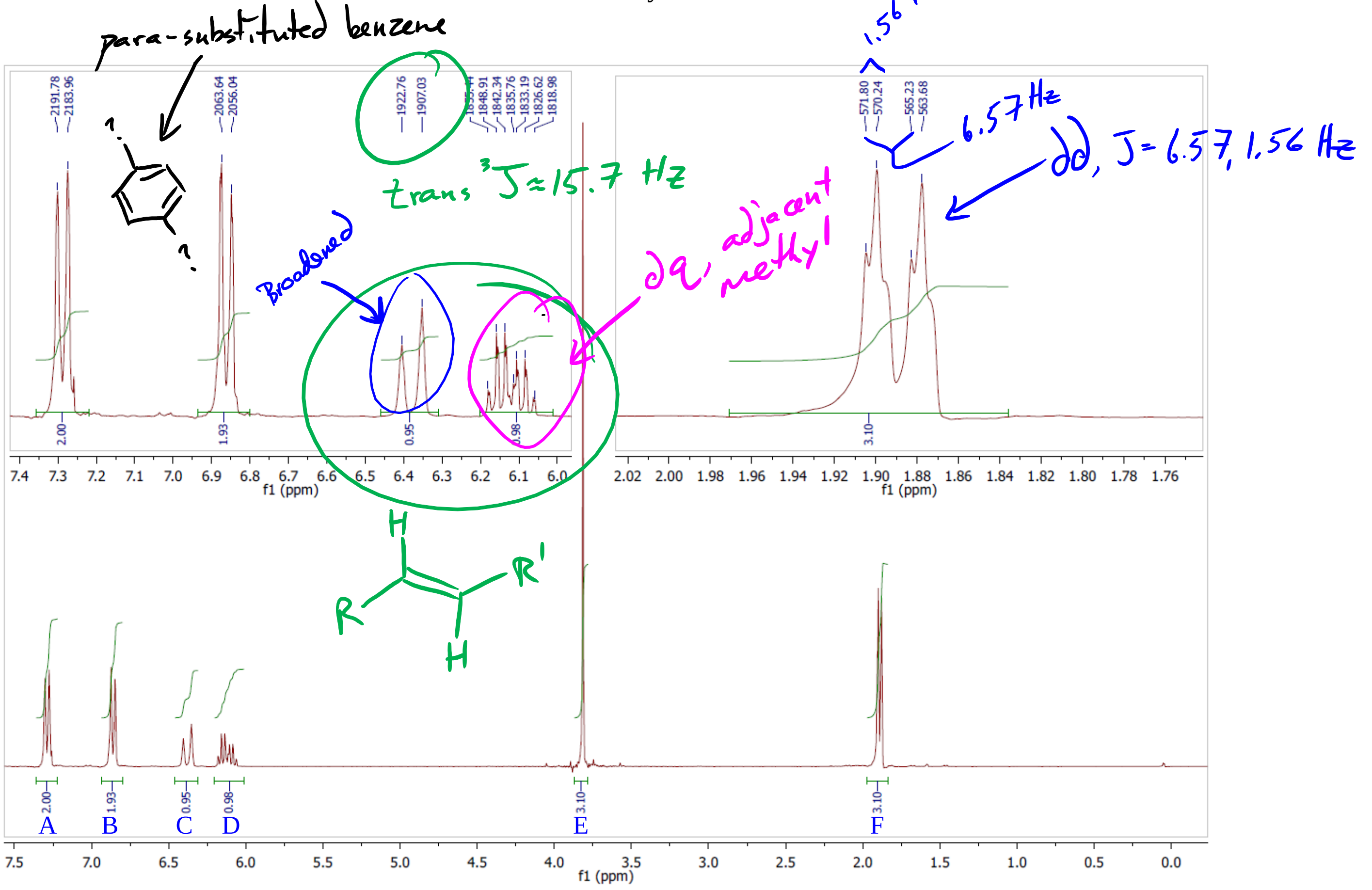

2990.31
2974.11
2843.77
2841.93
2835.62
2833.77
2826.12
2824.32
2779.58
2771.44
2645.00
2628.81
A
B
C
D
E
0.99
0.96
0.93
0.92
0.94
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
f1 (ppm)
A – E
0.03
0.99
0.96
0.93
0.92
0.94
0.03
0.95
F
0.12
2.82
G
2.83
H
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
H_F O
H_C
H_A
O
CH_3
H
H_3C
O
G
H_B
H_E
H_D

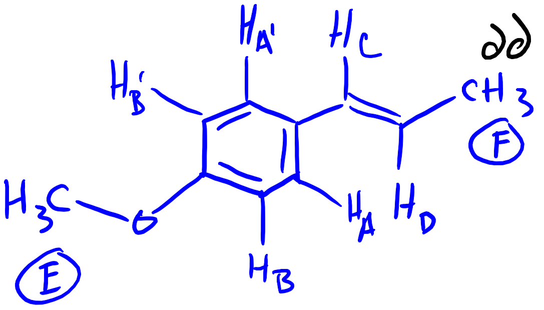

Peak#:1 R.Time:3.6(Scan#:192) MassPeaks:102
100
14
39
43
63
77
89
105
117
134
145
161
177
192
-15
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
m/z

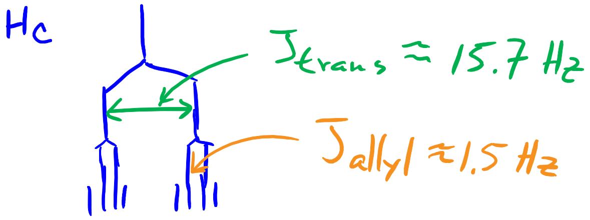

HO
MeO
O
CH_3
m/z = 192
- •CH_3
HO
MeO
O
m/z = 177
- CO
HO
MeO
H
H
m/z = 149
HO
MeO
H
+
O
CH_3
m/z = 43

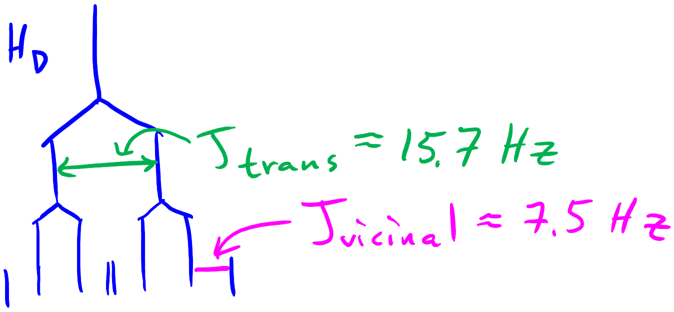
VII. Determine the structure of the molecule with formula $C_{10}H_{12}O$ that corresponds to the spectra shown below. Fully analyze each spectrum.

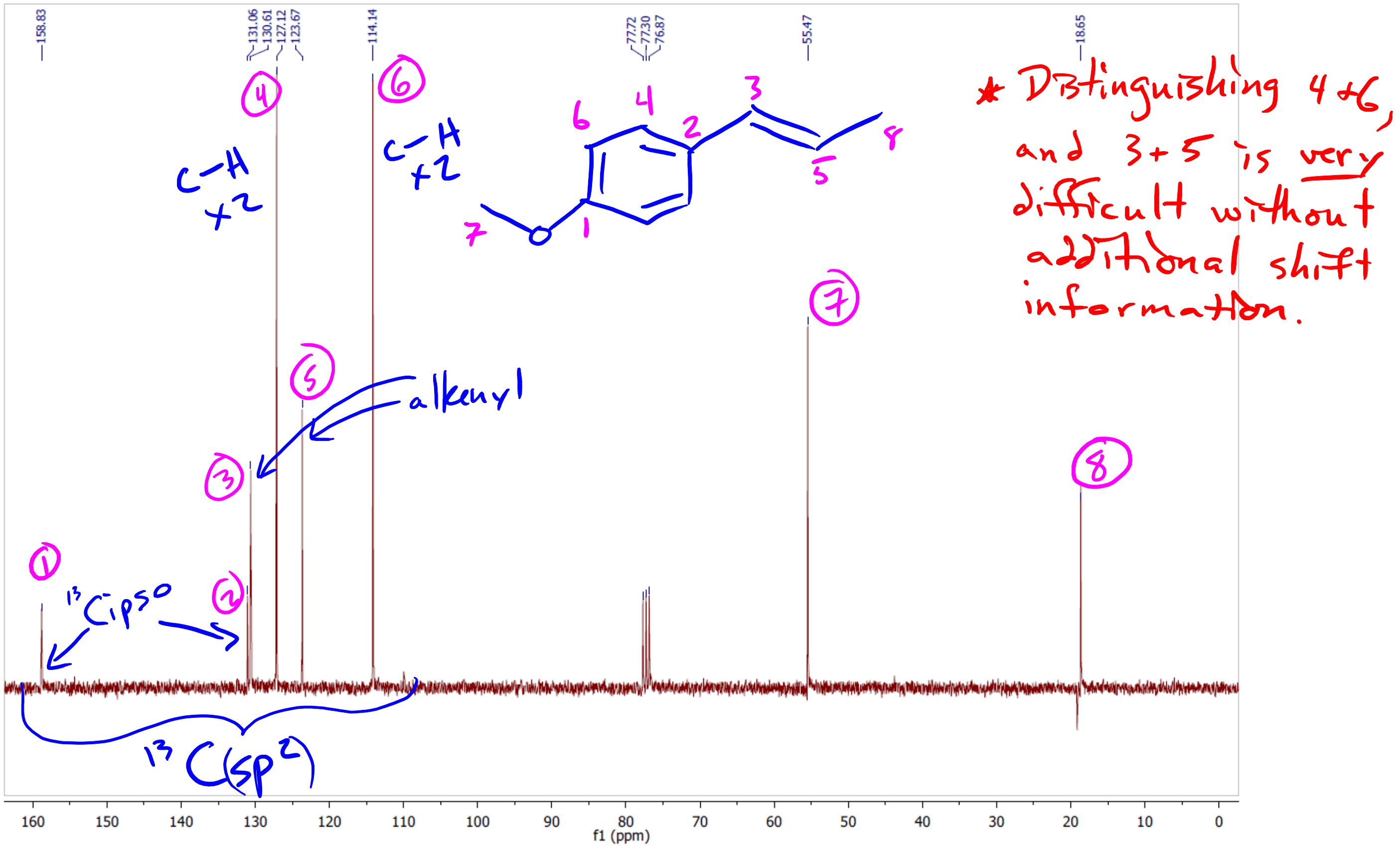



para-substituted benzene
?
?
2191.78
2183.96
2063.64
2056.04
1922.76
1907.03
1855.44
1848.91
1842.34
1835.76
1833.19
1826.62
1818.98
trans $^3J \approx 15.7$ Hz
Broadened
dq, adjacent methyl
2.00
1.93
0.95
0.98
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0
f1 (ppm)
1.56 Hz
571.80
570.24
565.23
563.68
6.57 Hz
dd, J = 6.57, 1.56 Hz
3.10
2.02 2.00 1.98 1.96 1.94 1.92 1.90 1.88 1.86 1.84 1.82 1.80 1.78 1.76
f1 (ppm)
H
R
R'
H
2.00
1.93
0.95
0.98
3.10
3.10
A
B
C
D
E
F
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

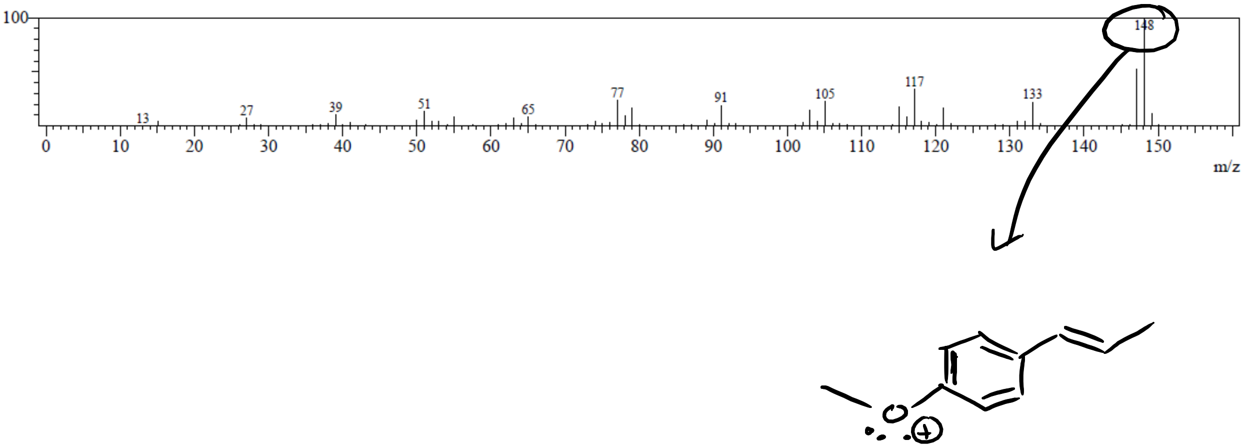

$H_{A'}$
H_C
dd
$H_{B'}$
CH_3
F
H_3C
O
H_A
H_D
E
H_B


H_C
$J_{trans} \approx 15.7$ Hz
$J_{allyl} \approx 1.5$ Hz

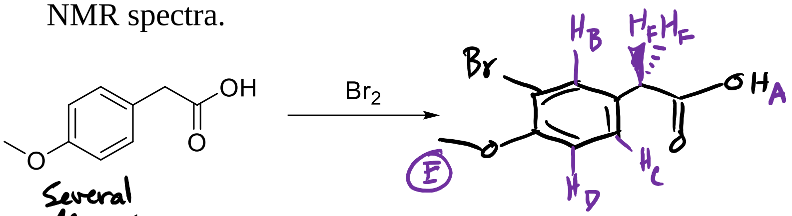

H_D
$J_{trans} \approx 15.7$ Hz
$J_{vicinal} \approx 7.5$ Hz



* Distinguishing 4 & 6, and 3 + 5 is very difficult without additional shift information.



VIII. In an electrophilic aromatic substitution, 4-methoxyphenylacetic acid reacts with bromine without the need for a catalyst. Use the ^{1}H-NMR and ^{13}C-NMR spectra that follow to determine the identity of the major product of the reaction. Assign the ^{1}H-NMR and ^{13}C-NMR spectra.



(most likely E.A.S. product)

A. ~~7~~ Several ^{1}H-NMR signals of the starting material are discernable in the ^{1}H-NMR and ^{13}C-NMR spectra. Identify and assign these signals. Using the ^{1}H-NMR spectrum calculate the approximate ratio of product to starting material.

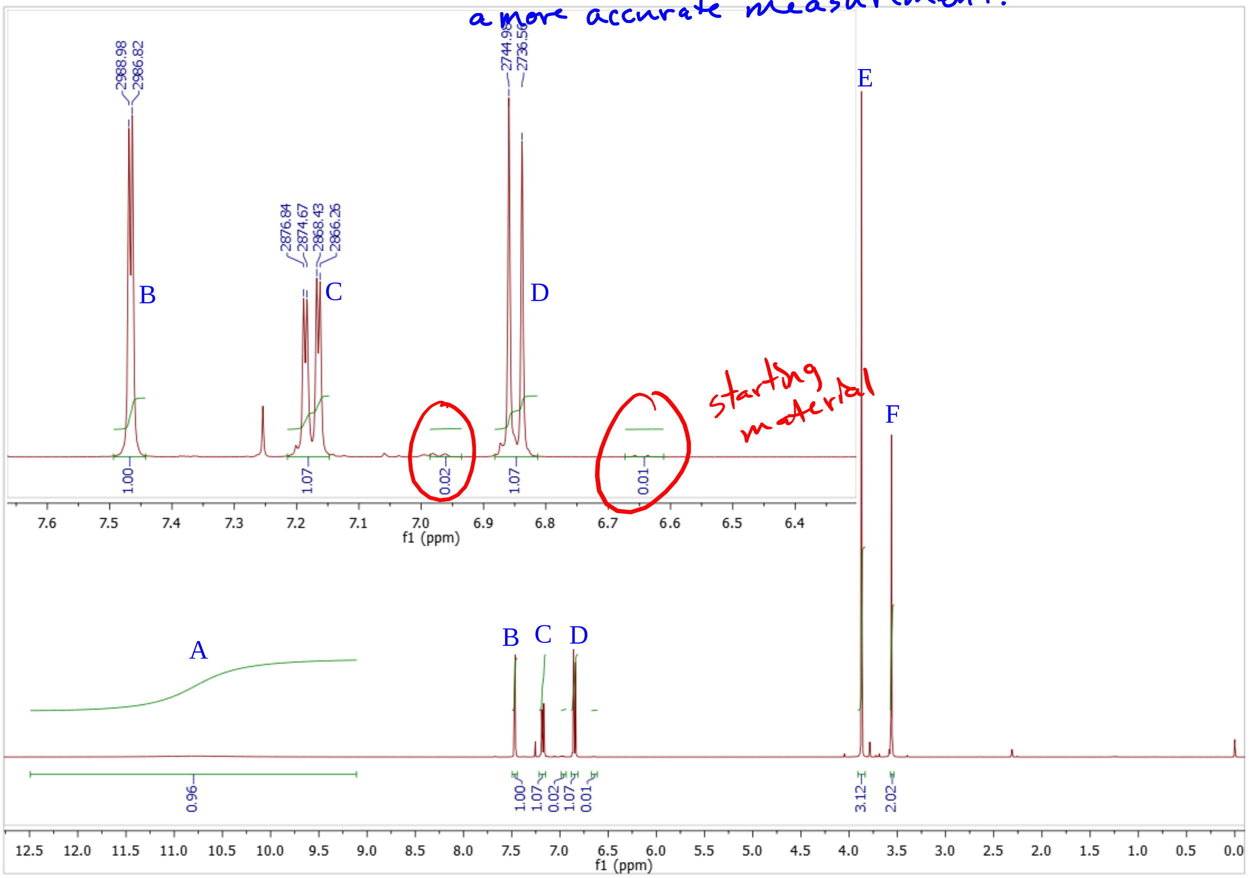
$\frac{1.00}{0.005}$ = 200 product : 1 starting material

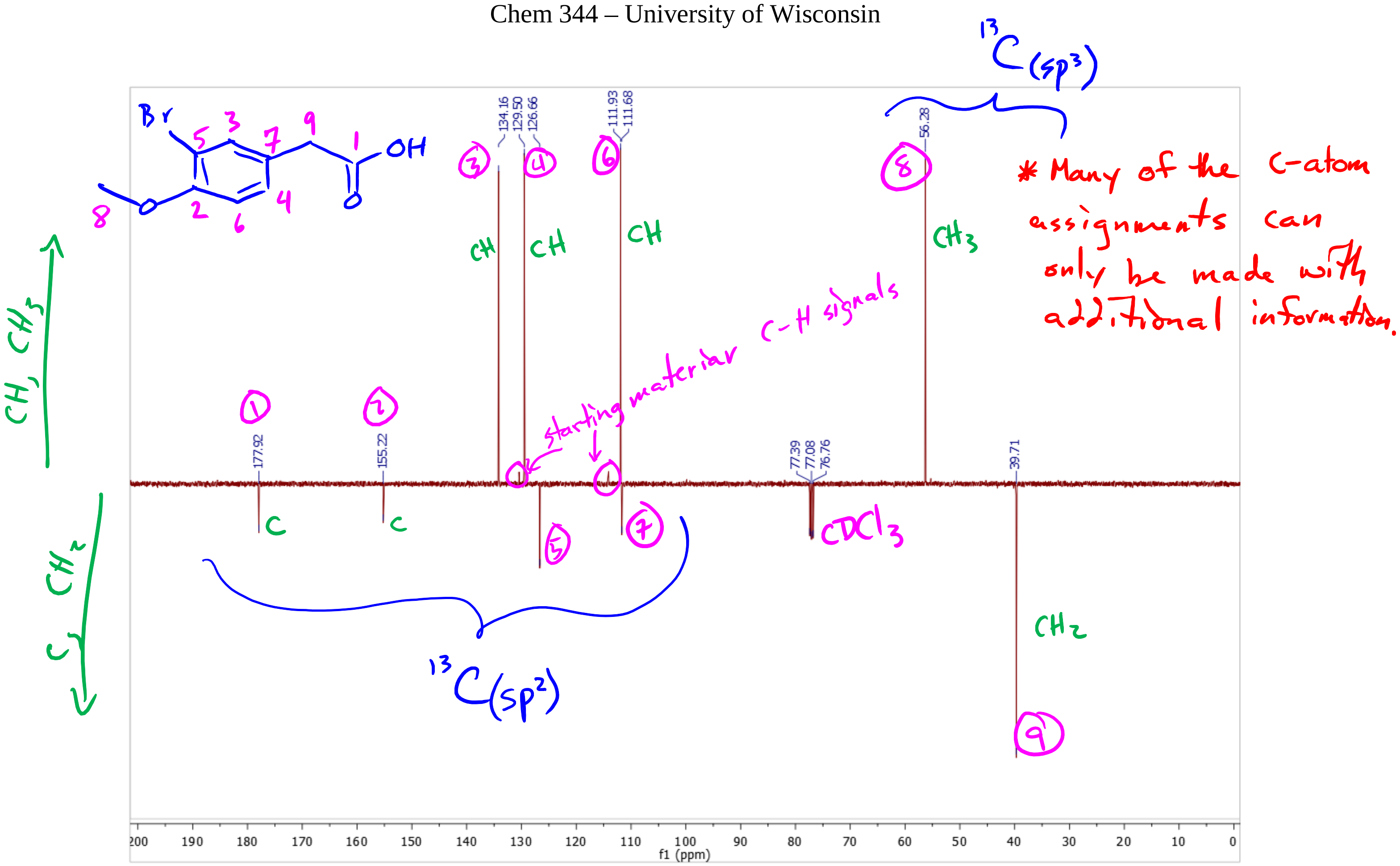
or

$\frac{1.00}{0.01}$ = 100 product : 1 s.m.

either is ok

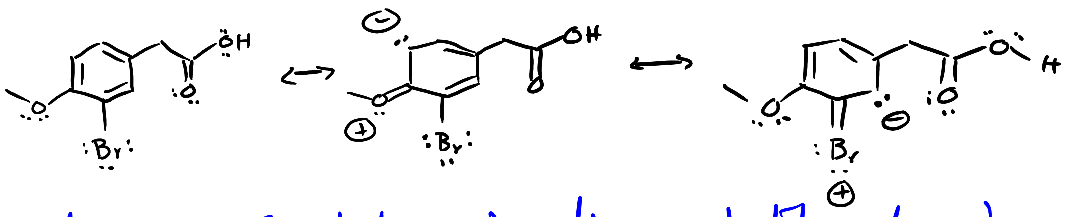
* clearly more sig. figs. would be needed for a more accurate measurement.





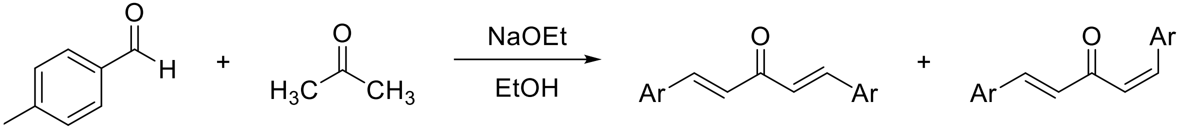
* Many of the C-atom assignments can only be made with additional information.

B. Rationalize the ^{1}H-NMR chemical shifts of each ^{1}H-atom attached to the aromatic ring of the product (relative to the ^{1}H-atoms in benzene) using a series of resonance structures. Clearly state how the charge distribution depicted in the resonance structures rationalizes the chemical shift of the ^{1}H-atoms.

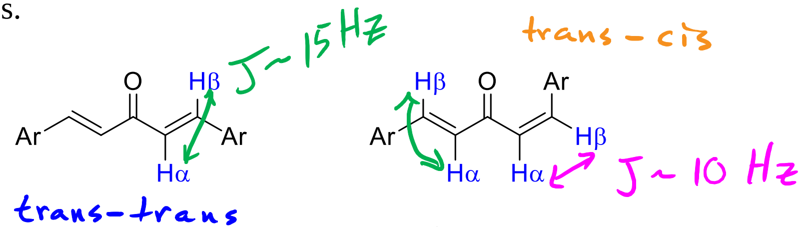


The two π electron-donating substituents donate electron-density to their ortho C-atoms as shown. The extra e⁻ density causes an increase in shielding for the attached H-atoms.

IX. An aldol condensation used in the organic laboratory at Madison College produced the stereoisomeric product mixture shown below.



A. For each of the stereoisomers, estimate the expected coupling constant ($J_{\alpha\beta}$) for H_α - H_β for each of the molecules.

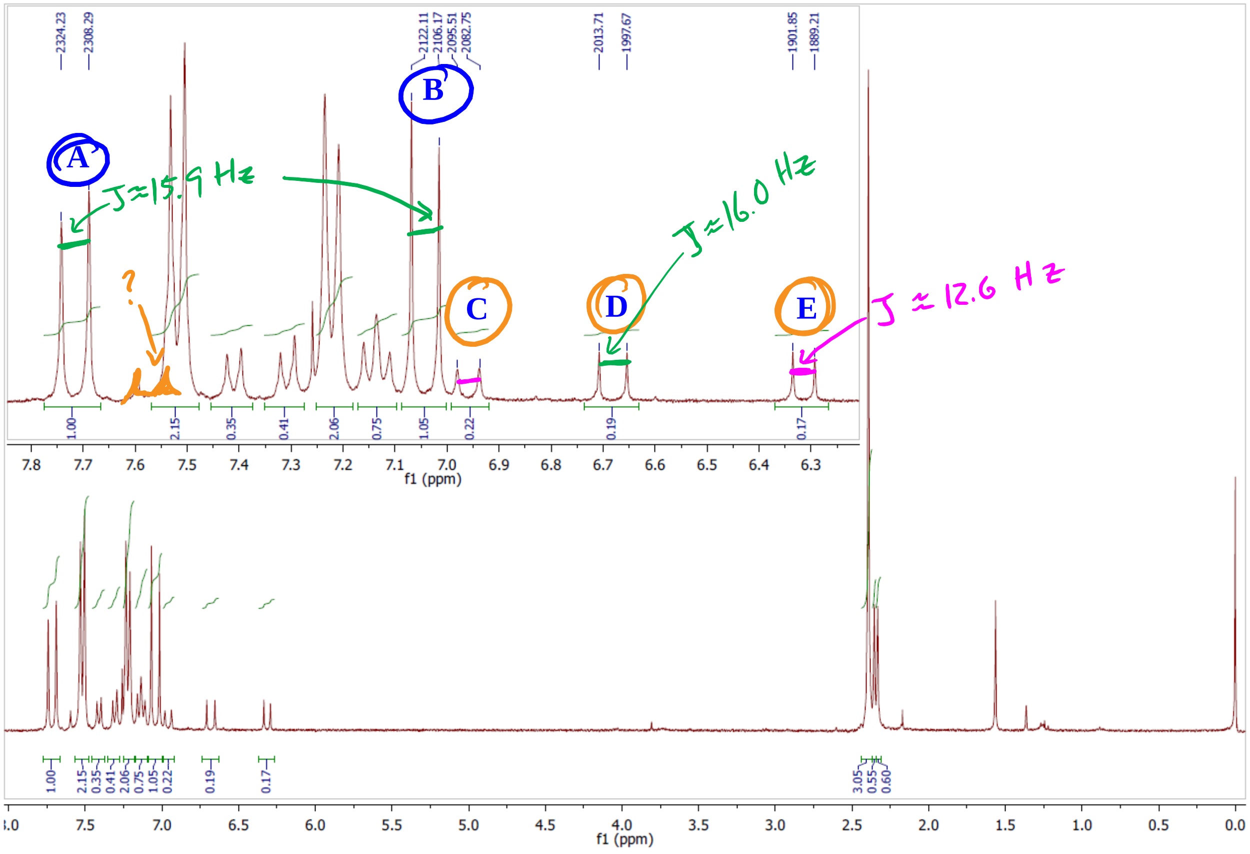


B. Unfortunately, only five of the six possible vinyl ^{1}H-atom signals (labeled A – E) are observable in the aromatic and vinyl regions of the product mixture. These integrals, however, are sufficient to determine the product ratio of this reaction. Use the coupling constants and integrals of the identified signals to estimate the product ratio. Use the most isolated signal integrals for each molecule.

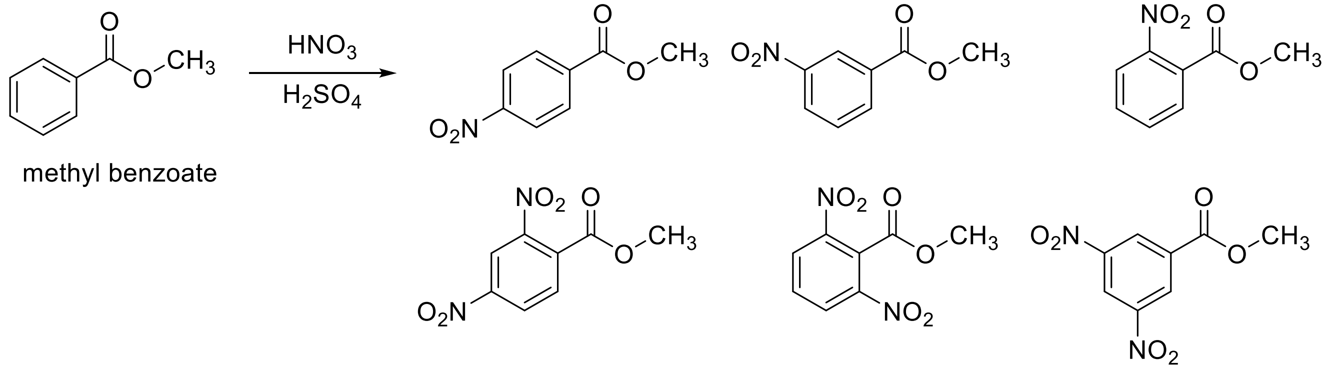
$\frac{1{,}00 \text{ Major } 2H}{0.38 \text{ Minor } 2H} \approx 2.6 \text{ major} : 1 \text{ minor}$

trans- trans

trans- cis



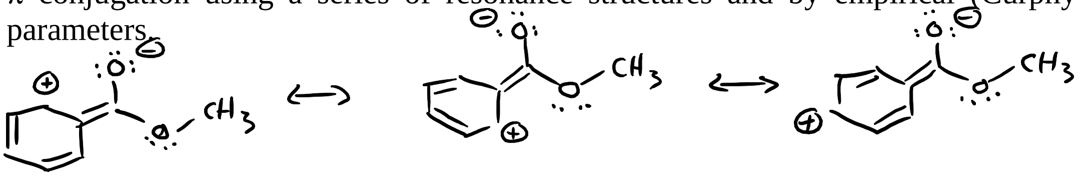
X. An electrophilic aromatic substitution, the sulfuric acid-catalyzed nitration of methyl benzoate, was carried out in the Organic Chemistry Bootcamp at UW-Waukesha. The spectra presented below are from authentic student samples. Analyze the spectra to understand the outcome of this reaction.

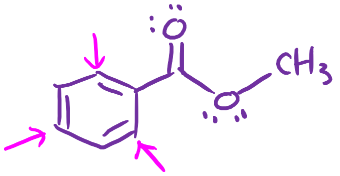


methyl benzoate

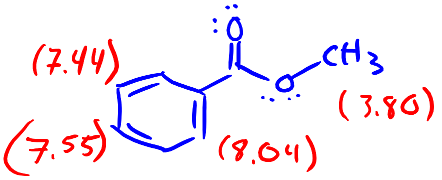
potential nitrated products

A. Estimate the ^{1}H-NMR chemical shifts of the ^{1}H-atoms in methyl benzoate by analysis of the π conjugation using a series of resonance structures and by empirical (Curphy-Morison) parameters.

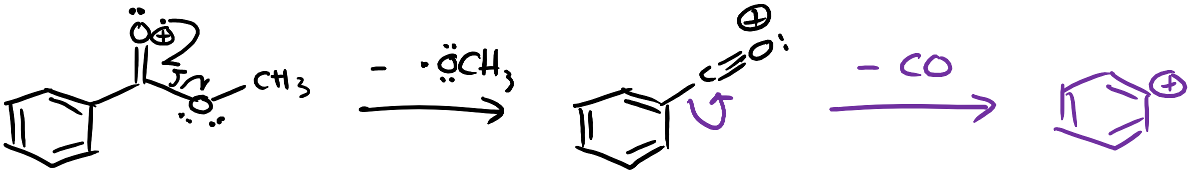




downfield relative to benzene



B. Predict the expected fragmentation pattern of the molecular ion of methyl benzoate in an EI-Mass Spectrometer and provide a complete electron-pushing mechanism.

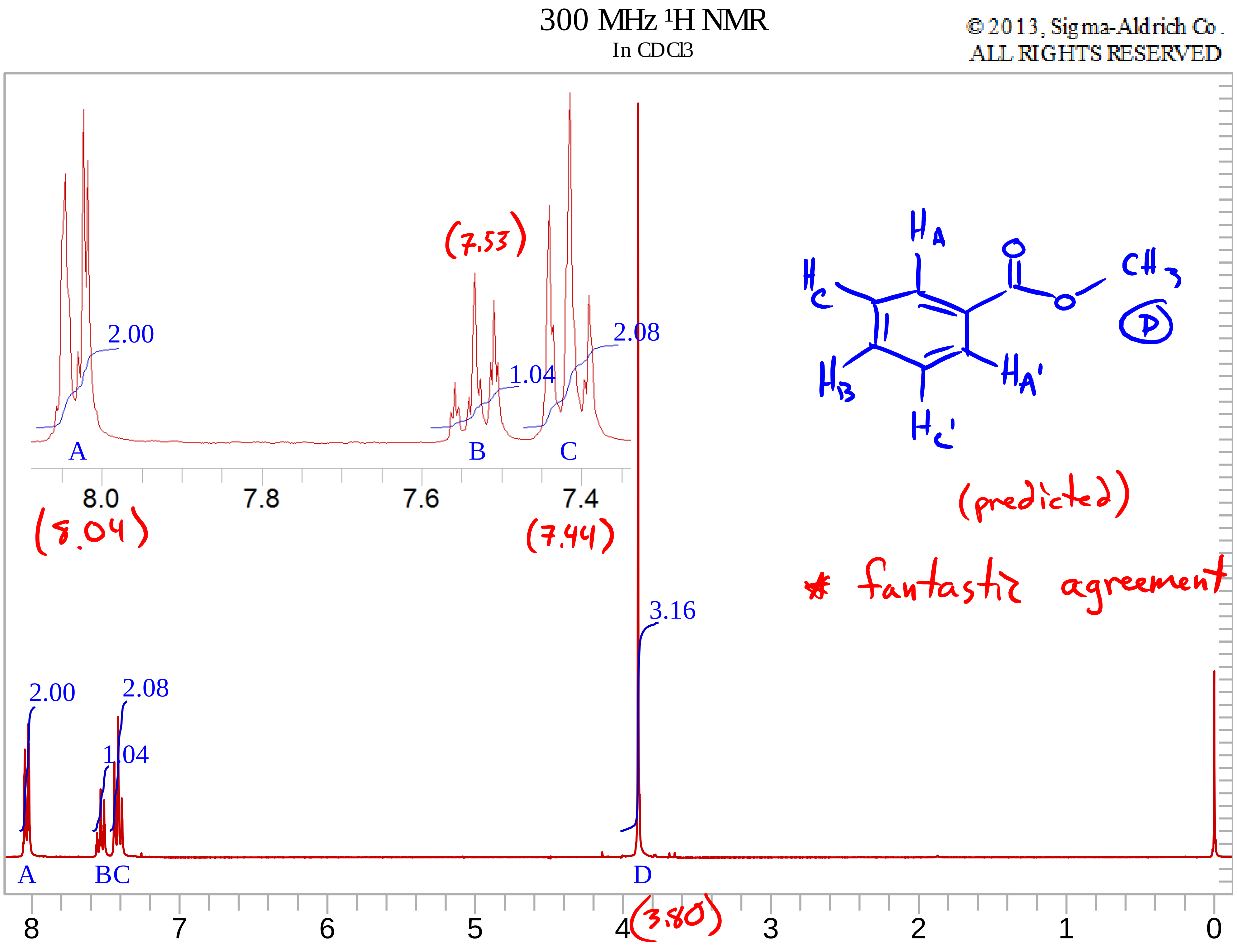


m/z = 136

m/z = 105

m/z = 77

C. The authentic ^{1}H-NMR spectrum of methyl benzoate is provided below from the Aldrich database. Assign each of the signals to its corresponding ^{1}H-atom in methyl benzoate. Comment on how well the resonance structures and empirical parameters predicted the ^{1}H-NMR spectrum.

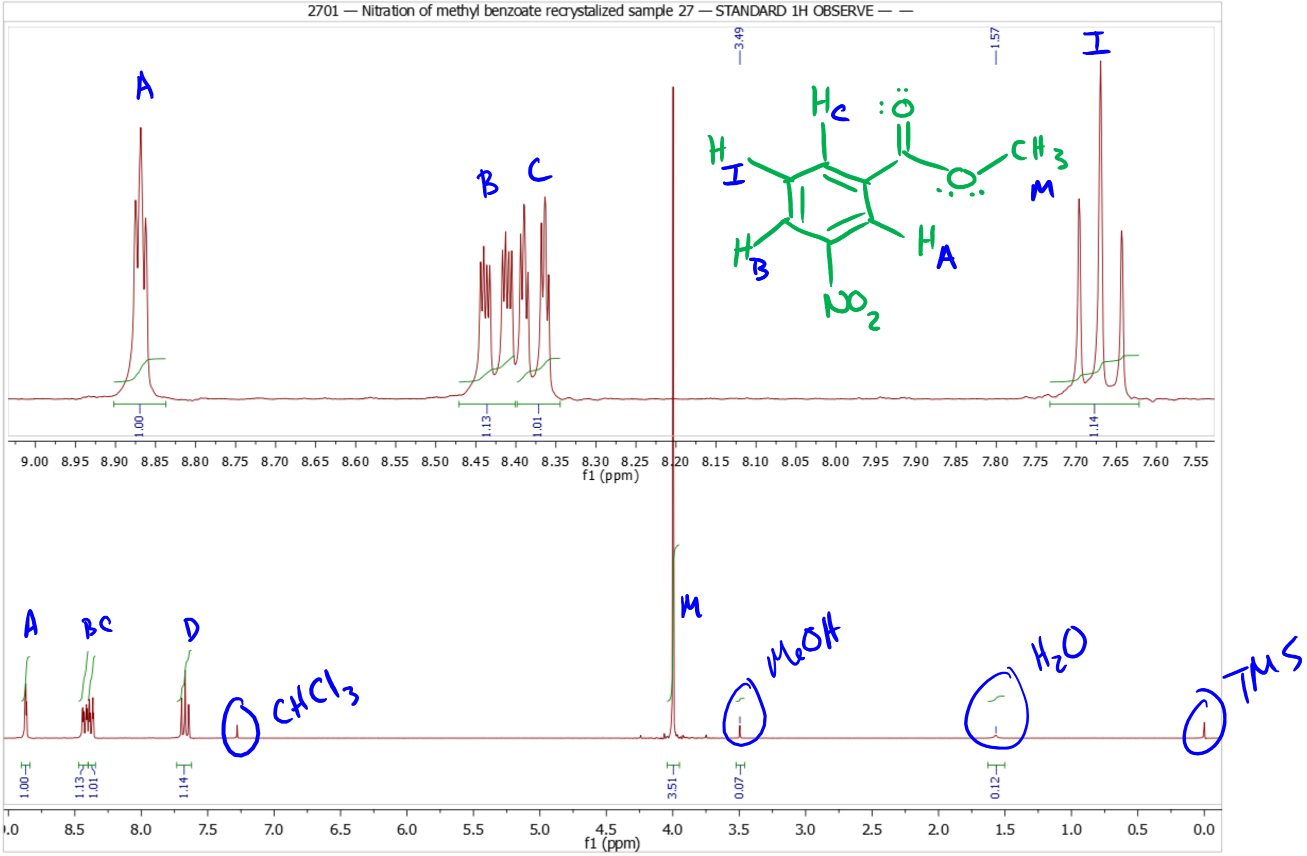


(predicted)

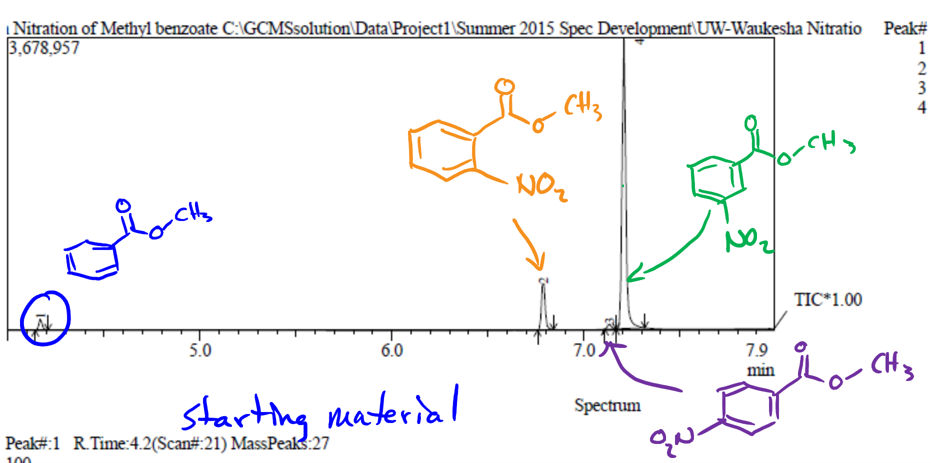
* fantastic agreement

D. The major product of the EAS nitration of methyl benzoate was obtained after recrystallization in methanol; its ^{1}H-NMR spectrum is shown below.

- i. Assign the methanol, $CHCl_3$ and TMS signals.
- ii. Determine the major product of the reaction and assign each of the ^{1}H-NMR signals to its corresponding ^{1}H-atom(s) in the major product.
- iii. Justify the assignments with use of empirical (Curphy-Morrison) parameters.

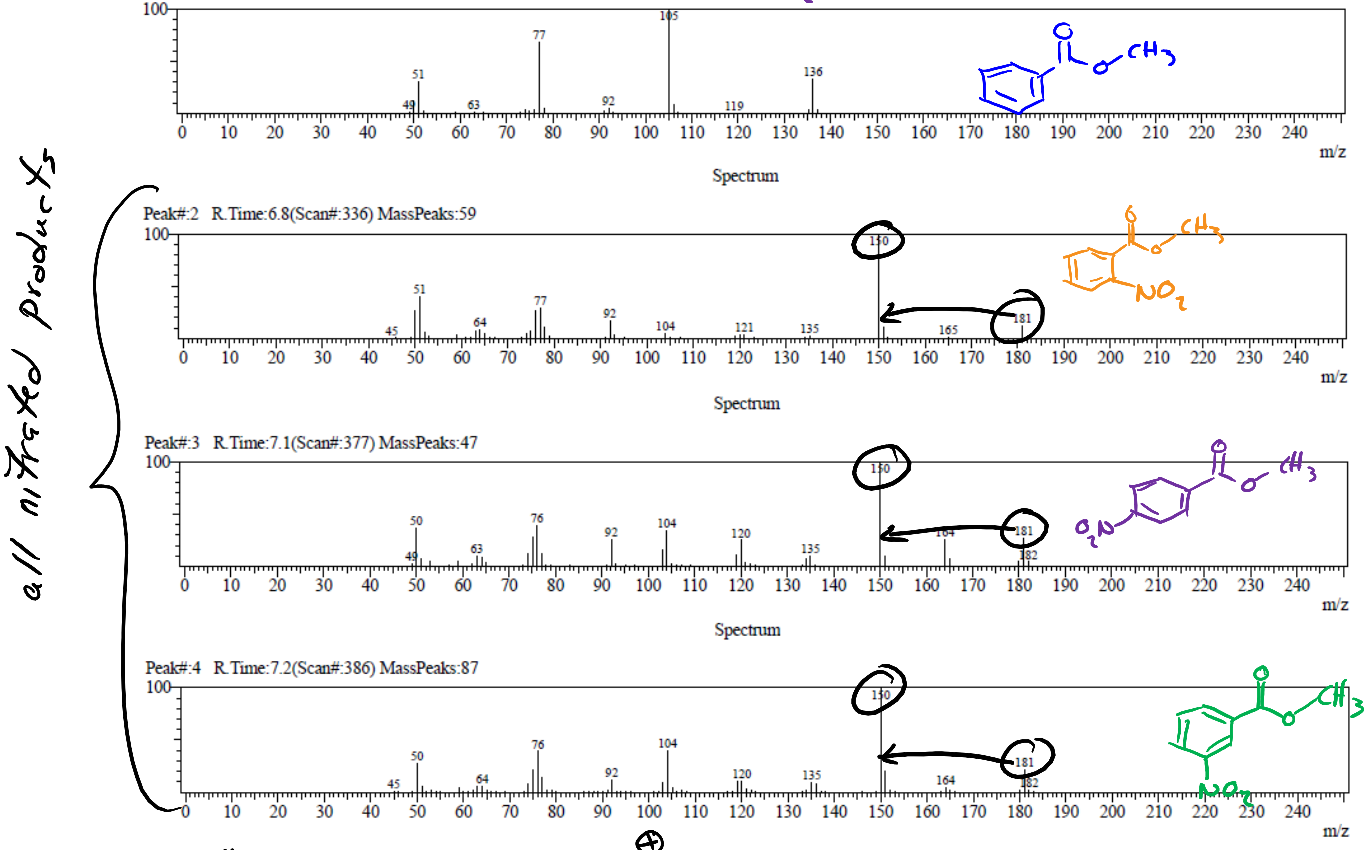


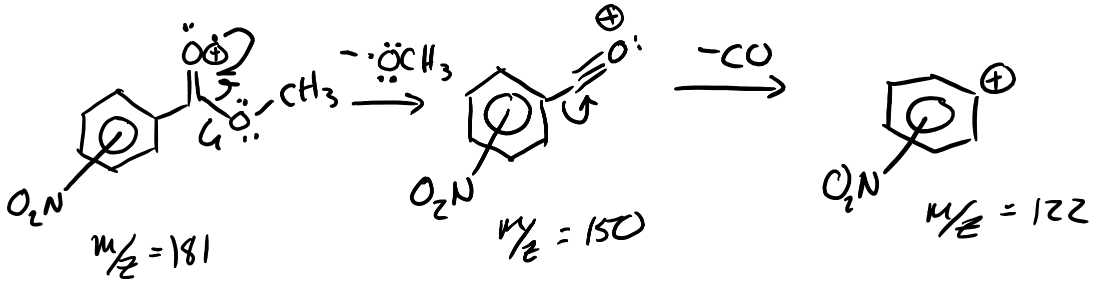
E. Prior to recrystallization, the crude product mixture was analyzed by GC-MS and the data are presented below. Determine the identity of the components of the mixture responsible for GC trace peaks 1 and 4. Provide a fragmentation mechanism to rationalize the major signals observed in the EI-Mass spectrum of component 4.



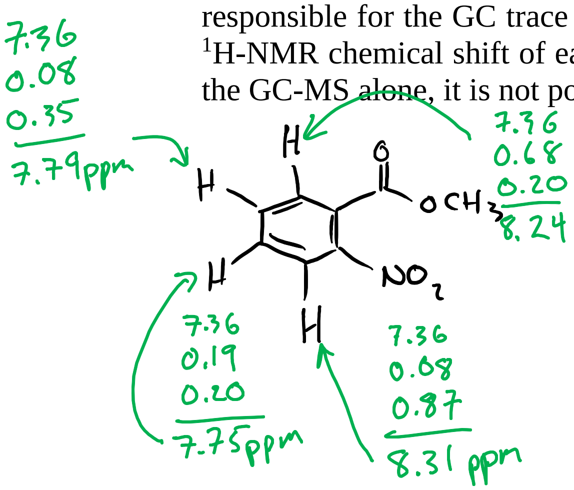
Peak Report TIC

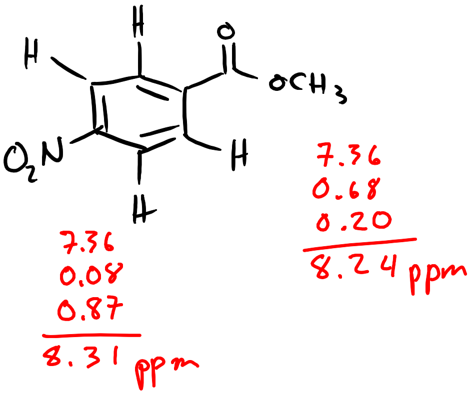
Peak#	R.Time	Area	Area%
1	4.168	173248	2.86
2	6.788	812211	13.43
3	7.133	89836	1.48
4	7.208	4974322	82.23
		6049617	100.00



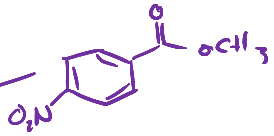


F. Based upon their EI-Mass spectra, propose the identity of the components of the mixture responsible for the GC trace peaks 2 and 3. Use Curphy-Morrison parameters to predict the ^{1}H-NMR chemical shift of each of the ^{1}H-atoms in the proposed components 2 and 3. From the GC-MS alone, it is not possible for you to distinguish between these two components.

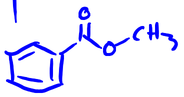


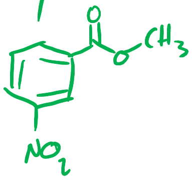


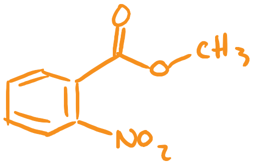
G. Use the GC-trace to determine the ratio of components in the product mixture in order of relative abundance in the form of X:Y:Z:1.



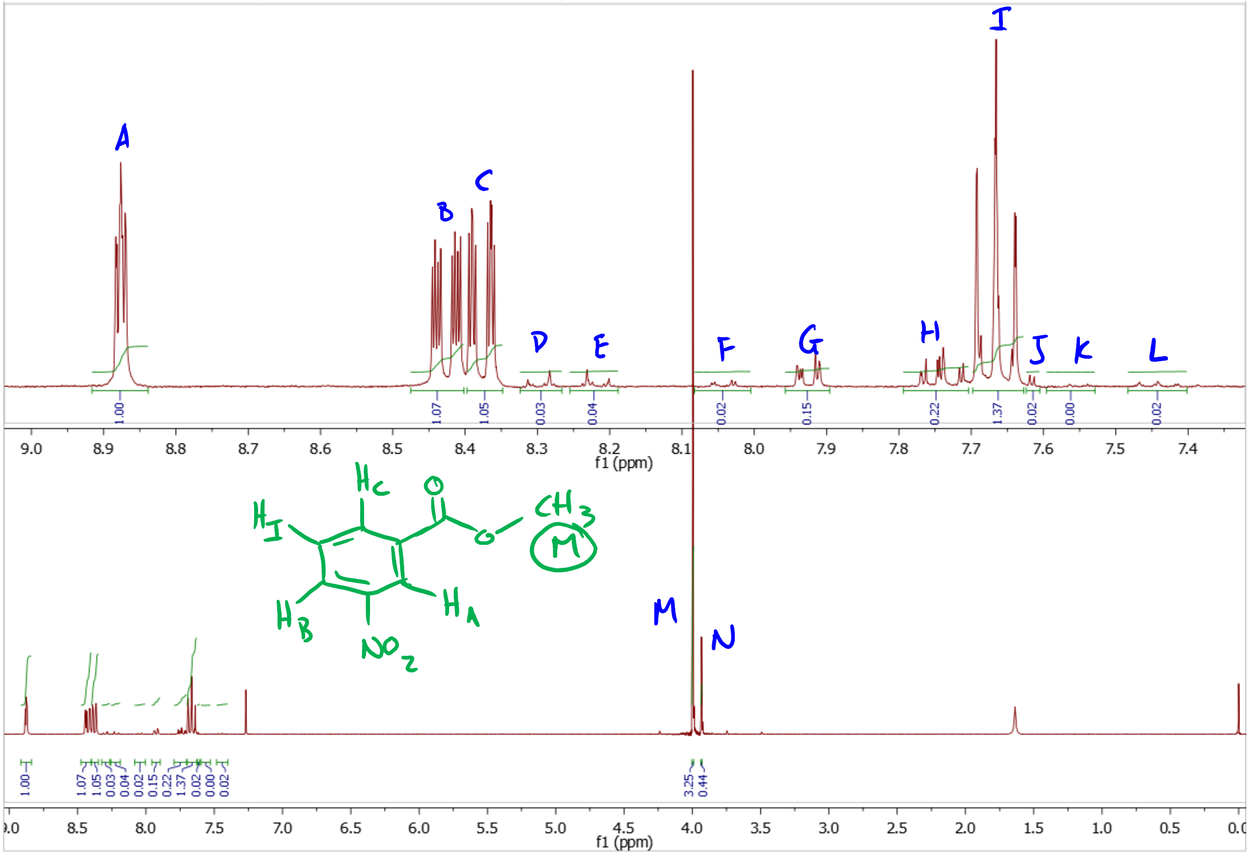
55.6 : 9.1 : 1.9 : 1.0

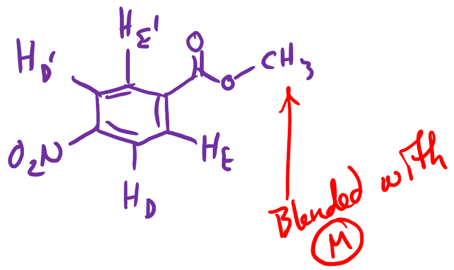


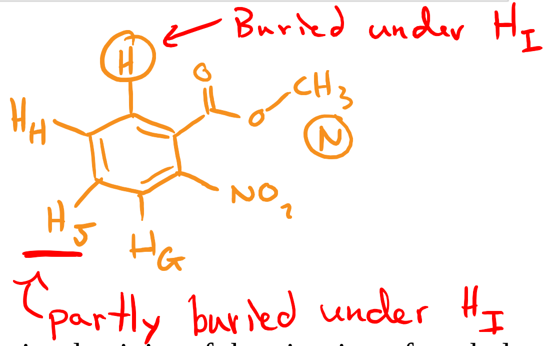




H. The ^{1}H-NMR spectrum of the crude mixture is shown below. Assign the ^{1}H-atoms for all of the integrated signals in the aromatic region of the ^{1}H-NMR spectrum.







I. Based upon the experimental data, comment on the regioselectivity of the nitration of methyl benzoate. Which product(s) are favored and which are disfavored?

The nitration of methyl benzoate is very selective for the meta regioisomer, but the ortho and para products are generated.

55.6 : 9.1 : 1.0
meta ortho para

J. The Curphy-Morrison predictions of the ^{1}H-NMR chemical shifts of which component matches the most poorly to its experimental spectrum? Explain why the parameters do not predict the ^{1}H-NMR chemical shifts of the ^{1}H-atoms in this molecule to the same degree of accuracy as in the other molecules.

In order for the empirical predictions (C-M parameters), to yield reasonable chemical shift predictions, the molecule of interest must be similar to the molecules used to generate the parameters. The parameters work well for methyl benzoate and the para- and meta-nitration products. Since the parameters predict the shift poorly for the ortho-nitration product, the structure must prevent the ester and nitro substituents from having their usual impact. The steric interaction forces the ortho substituents to twist. The twist reduces the π conjugation and changes the orientation of the substituent magnetic fields.