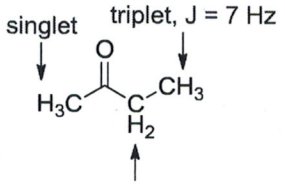
Chemistry 344: Spectroscopy Problem Set 2

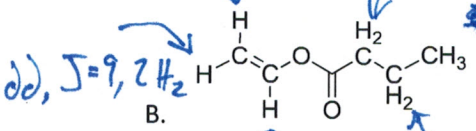
Name (print): _____ **(Not for credit)**

TA Name (print): _____

I. For each of the following molecules and fragments below, predict the multiplicity of each of the signals that you would expect to see in an ^{1}H-NMR spectrum. Include an approximation of the expected coupling value in Hz. See the example below.

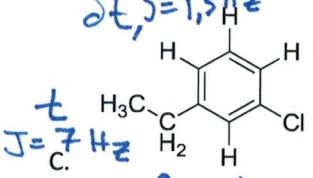


A.



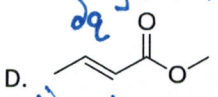
B.

dd, J = 15, 2 Hz
triplet, J = 7 Hz
dd, J = 9, 2 Hz
triplet, J = 7 Hz
sextet, J = 7 Hz
dd, J = 15 Hz, 9 Hz



C.

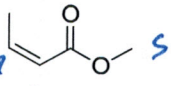
t, J = 9 Hz
dt, J = 9, 3 Hz
dt, J = 9, 3 Hz
t, J = 7 Hz
q
t, J = 3 Hz
J = 7 Hz



D.

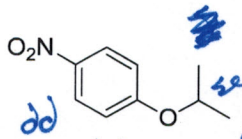
J = 15, 7 Hz
dq
s
dd
dq, J = 15, 2 Hz
J = 7, 2

dd, J = 7, 2 Hz



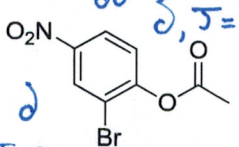
E.

dq
s
J = 9, 7 Hz
dq, J = 9, 2 Hz



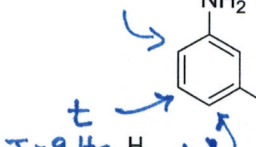
F.

septet, J = 7 Hz
dd
d, J = 7 Hz
dd



G.

dd, J = 9, 3 Hz
d, J = 9 Hz
d
s
J = 3 Hz

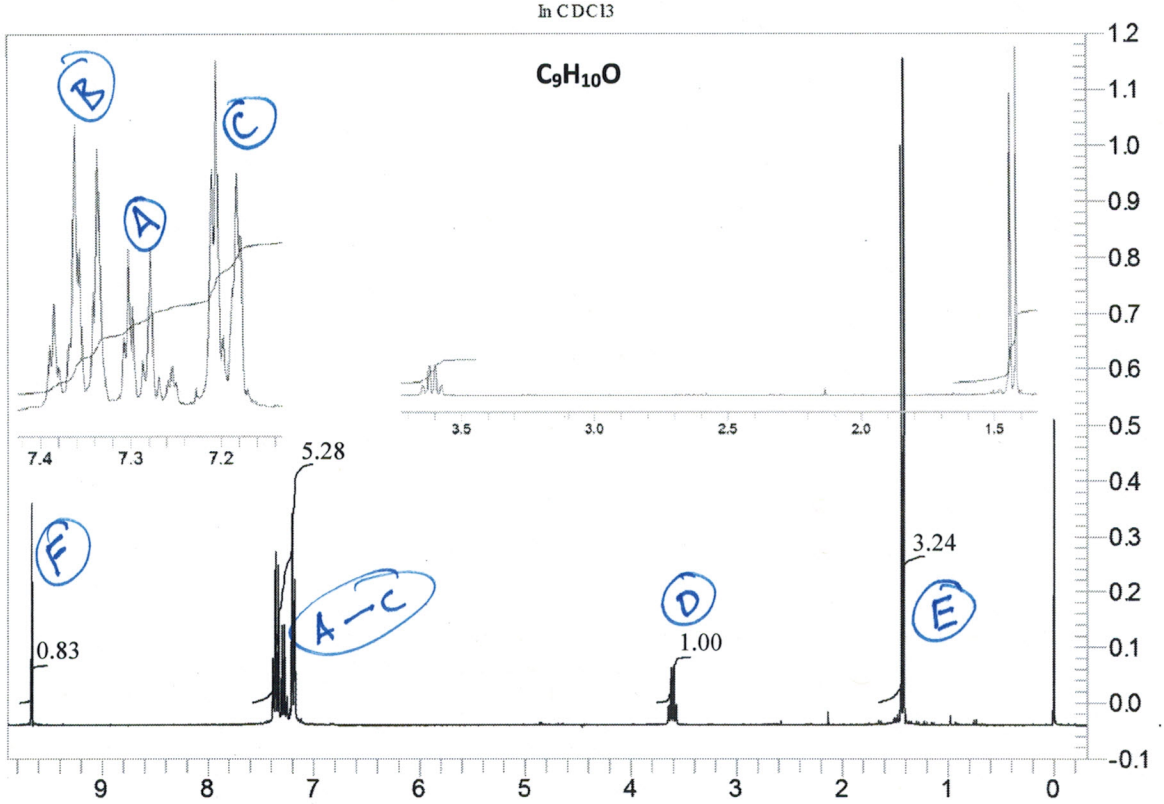


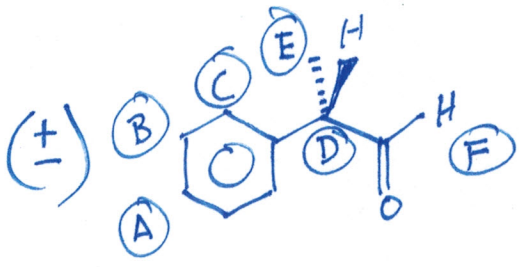
H.

dt, J = 9, 3 Hz
t, J = 3 Hz
t
s
J = 9 Hz
dt
J = 9, 3 Hz

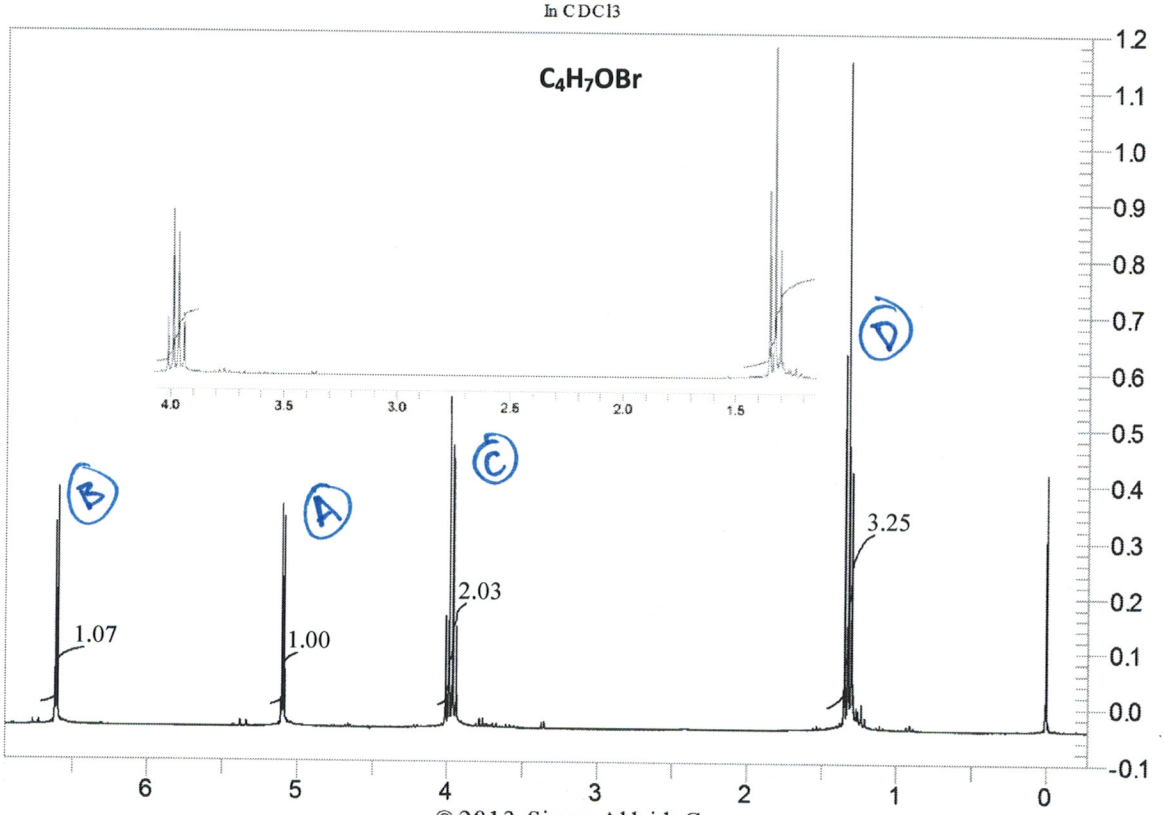
II. For each of the ^{1}H-NMR spectra below, determine the structure of the molecule responsible for it and assign the protons in the molecule to its corresponding ^{1}H-NMR signal.

300 MHz ^{1}H NMR
In CDCl3

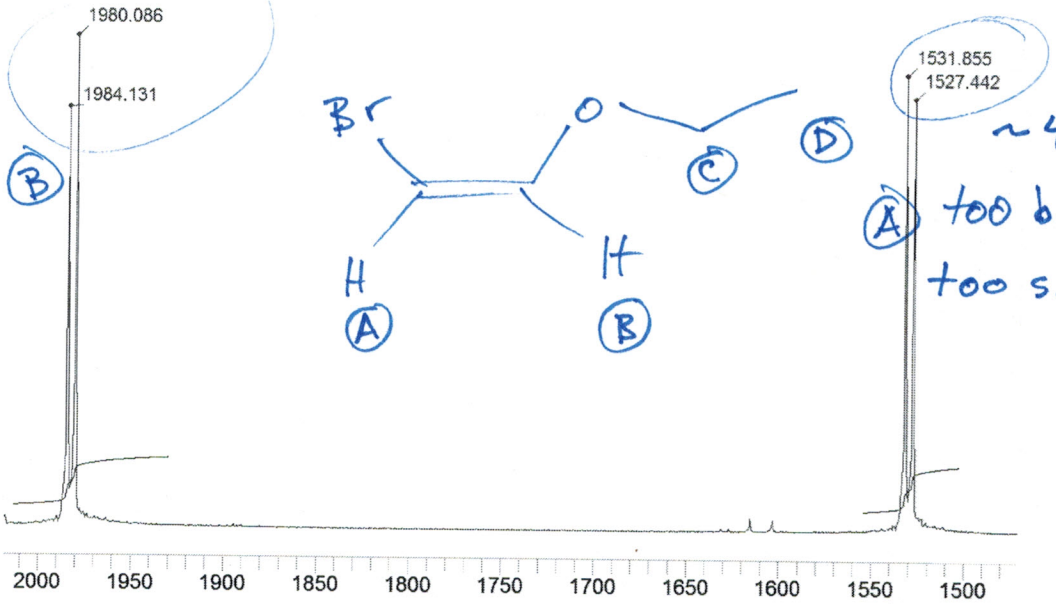




300 MHz ^{1}H NMR
In CDCl3



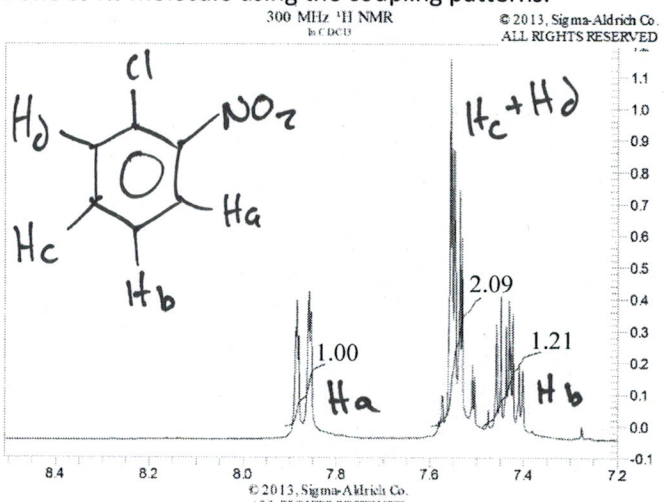
The signals at δ 6.60 and δ 5.10 ppm are shown below with an axis Hz to assist in determining the coupling constant.



III. The three ^{1}H-NMR spectra below from 7.0 – 7.7 ppm correspond to three chloronitrobenzenes. Assign each one to its molecule using the coupling patterns.

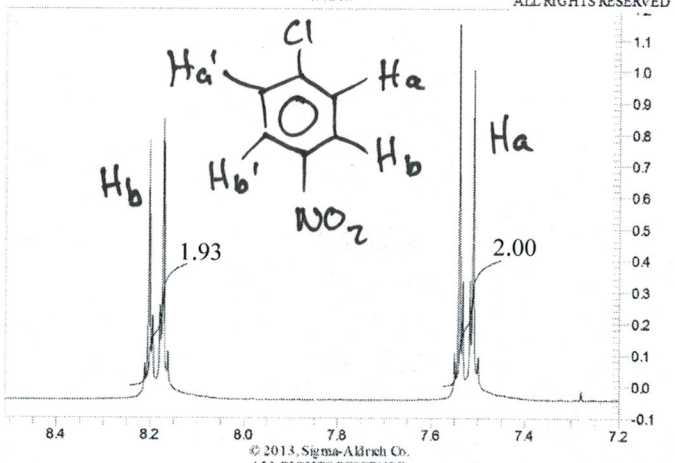
Curphy-Morrison Estimates

A.



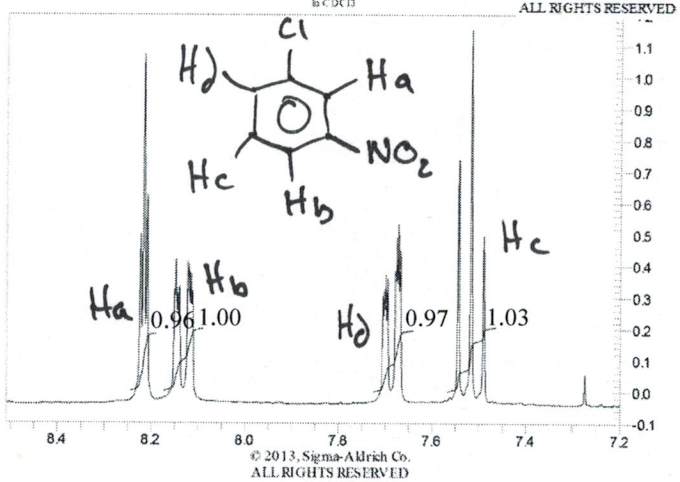
H_a = 8.16
H_b = 7.43
H_c = 7.64
H_d = 7.54

B.



$H_a = H_{a'} \approx$ 7.54
$H_b = H_{b'} \approx$ 8.16

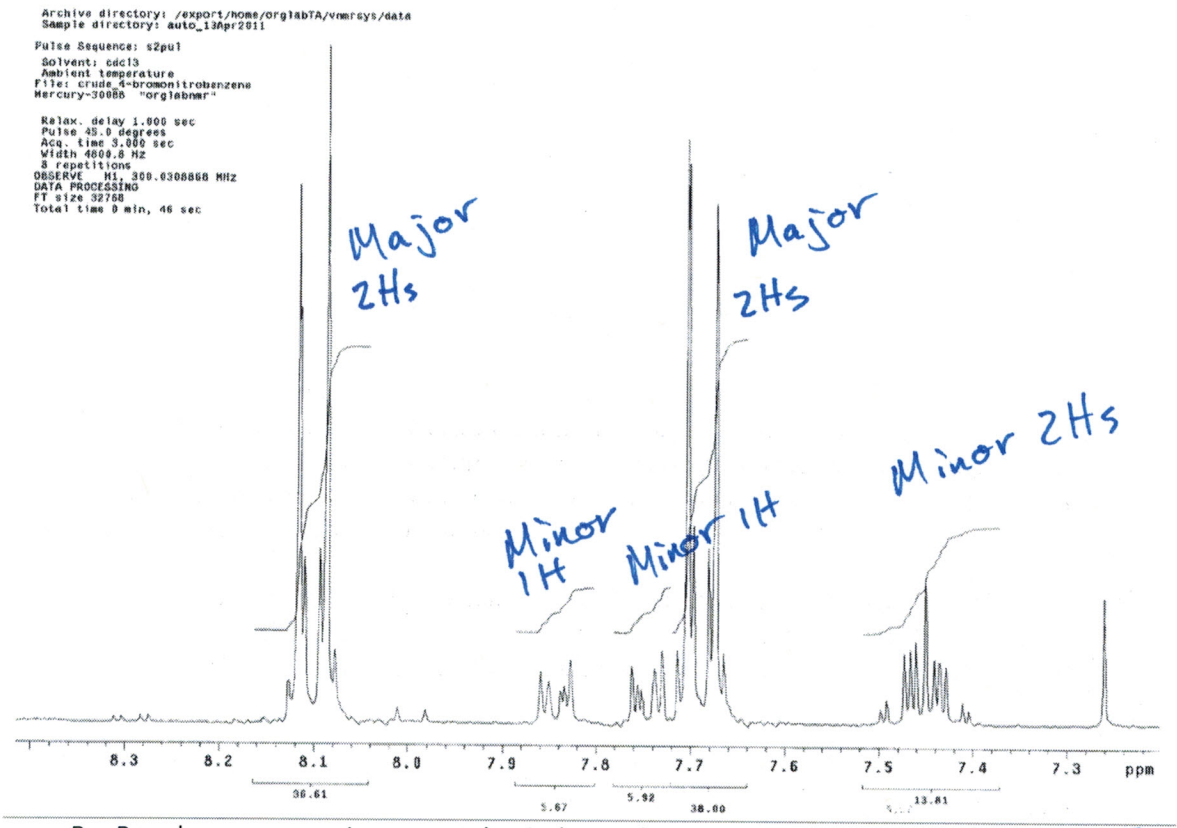
C.



H_a = 8.21
H_b = 8.10
H_c = 7.49
H_d = 7.69

IV. While ^{1}H-NMR is a powerful tool in structure determination, it can also be used to determine the relative ratio of two molecules in a mixture. This is particularly useful for determining product ratios in chemical reactions where more than one product is generated. The following ^{1}H-NMR spectrum is of a crude mixture of two isomers.

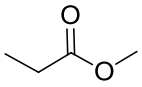
A. Given that the signal at δ 8.10 ppm (36.61 H) is due to two H-atoms in the major product and the signals at δ 7.85 is due to a single H-atom in the minor product, assign the remaining signals to either the major or minor isomer.



B. Based upon your assignments, what is the product ratio of major to minor isomer?

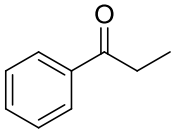
$$\frac{1\text{ H Major}}{1\text{ H Minor}} = \frac{36.61/2}{5.67} = 3.22 \text{ major : minor}$$

a) **$C_4H_8O_2$**: δ 1.15 (triplet, 3H), δ 2.33 (quartet, 2H), and δ 3.67 (singlet, 3H)



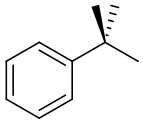
methyl propanoate

b) **$C_9H_{10}O$**: δ 1.22 (triplet, 3H), δ 2.98 (quartet, 2H), δ 7.43 (multiplet, 2H), δ 7.53 (triplet of triplets, 1H), and δ 7.94 (multiplet, 2H)



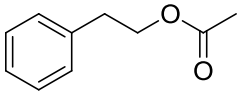
propiophenone

c) **$C_{10}H_{14}$**: δ 1.3 (singlet, 9H), δ 7.17 (triplet of triplets, 1H), δ 7.29 (triplet, 2H), and δ 7.38 (doublet, 2H)



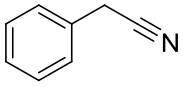
tert-butyl benzene

d) **$C_{10}H_{12}O_2$**: δ 2.01 (singlet, 3H), δ 2.92 (triplet, 2H), δ 4.27 (triplet, 2H), and δ 7.21 (multiplet, 5H) IR spectrum contains a strong absorption at 1740 cm^{-1} MS contains a strong signal at *m*/z = 43



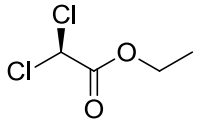
phenethyl acetate

e) **C_8H_7N:** δ 3.70 (singlet, 2H), and δ 7.3 (multiplet, 5H) IR spectrum contains a strong absorption at ~2250 cm^{-1}



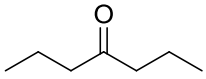
phenylacetonitrile

f) **$C_4H_6Cl_2O_2$**: δ 1.36 (triplet, 3H), δ 4.34 (quartet, 2H), and δ 5.96 (singlet, 1H)



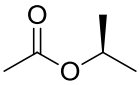
phenylacetonitrile

g) **$C_7H_{14}O$**: δ 0.91 (triplet, 6H), δ 1.60 (sextet, 4H), and δ 2.37 (triplet, 4H)



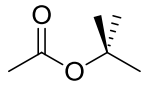
4-heptanone

h) **$C_5H_{10}O_2$**: δ 1.23 (doublet, 6H), δ 2.02 (singlet, 3H), and δ 4.99 (septet, 1H)



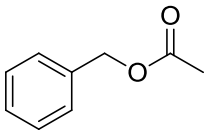
isopropyl acetate

i) **$C_6H_{12}O_2$**: δ 1.44 (singlet, 9H), and δ 1.96 (singlet, 3H)



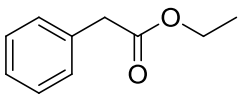
tert-butyl acetate

j) **$C_9H_{10}O_2$**: δ 2.08 (singlet, 3H), δ 5.09 (singlet, 2H), and δ 7.34 (multiplet, 5H)



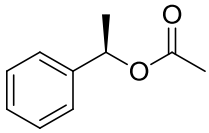
benzyl acetate

k) **$C_{10}H_{12}O_2$**: δ 1.23 (triplet, 3H), δ 3.60 (singlet, 2H), δ 4.13 (quartet, 2H), and δ 7.28 (multiplet, 5H)



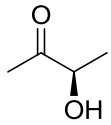
ethyl phenylacetate

l) **$C_{10}H_{12}O_2$**: δ 1.52 (doublet, 3H), δ 2.05 (singlet, 3H), δ 5.87 (quartet, 1H), and δ 7.30 (multiplet, 5H) IR spectrum contains a strong absorption at 1742 cm^{-1}



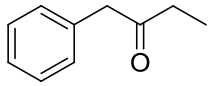
1-phenylethyl acetate

m) **$C_4H_8O_2$**: δ 1.39 (doublet, 3H), δ 2.22 (singlet, 3H), δ 3.91 (broad singlet, 1H), and δ 4.27 (quartet, 1H) IR spectrum contains a strong absorption at 3451 cm^{-1}



3-hydroxy-2-butanone

n) **$C_{10}H_{12}O$**: δ 1.01 (triplet, 3H), δ 2.45 (quartet, 2H), δ 3.67 (singlet, 2H), and δ 7.24 (multiplet, 5H)

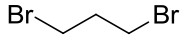


1-phenyl-2-butanone

o) **$C_2H_4Br_2$**: δ 2.46 (doublet, 3H), and δ 5.84 (quartet, 1H)

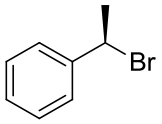
1,1-dibromoethane

p) **$C_3H_6Br_2$**: δ 2.35 (quintet, 2H), and δ 3.56 (triplet, 4H)



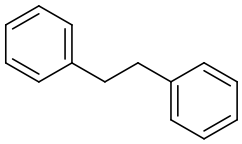
1,3-dibromopropane

q) **C_8H_9Br**: δ 2.02 (doublet, 3H), δ 5.18 (quartet, 1H), δ 7.29 (asymmetrical doublet, 2H), and δ 7.41 (multiplet, 3H)



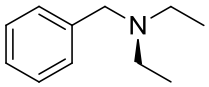
(1-bromoethyl)benzene

r) **$C_{14}H_{14}$**: δ 2.90 (singlet, 4H), δ 7.17 (multiplet, 6H), and δ 7.26 (multiplet, 4H)



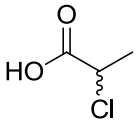
bibenzyl

s) **$C_{11}H_{17}N$**: δ 1.04 (triplet, 6H), δ 2.51 (quartet, 4H), δ 3.56 (singlet, 2H), and δ 7.33 (multiplet, 5H)



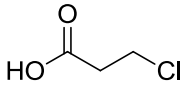
N,N-diethylbenzylamine

t) **$C_3H_5ClO_2$**: δ 1.74 (doublet, 3H), δ 4.45 (quartet, 1H), and δ 12.2 (singlet, 1H)



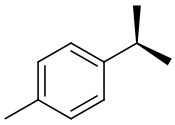
2-chloropropionic acid

u) **$C_3H_5ClO_2$**: δ 2.87 (triplet, 2H), δ 3.76 (triplet, 2H), and δ 11.8 (singlet, 1H)



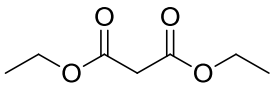
3-chloropropionic acid

v) **$C_{10}H_{14}$**: δ 1.22 (doublet, 6H), δ 2.30 (singlet, 3H), δ 2.86 (septet, 1H), and δ 7.0 (symmetrical multiplet, 4H)



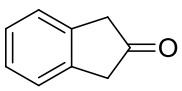
p-cymene

w) **$C_7H_{12}O_4$**: δ 1.29 (triplet, 6H), δ 3.36 (singlet, 2H), and δ 4.22 (quartet, 4H)



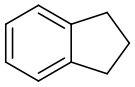
diethyl malonate

x) **C_9H_8O**: δ 3.54 (singlet, 4H), and δ 7.26 (symmetrical multiplet, 4H)



2-indanone

y) **C_9H_{10}**: δ 2.04 (quintet, 2H), δ 2.90 (triplet, 4H), δ 7.10 (multiplet, 2H), and δ 7.20 (multiplet, 2H)

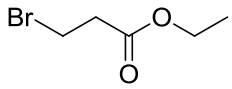


indan

z) **$C_3H_4O_2$**: δ 3.55 (triplet, 2H), and 4.28 (triplet, 2H)

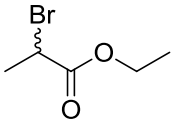
2-oxetanone

aa) **$C_5H_9BrO_2$**: δ 1.29 (triplet, 3H), δ 2.92 (triplet, 2H), δ 3.58 (triplet, 2H), and δ 4.19 (quartet, 2H)



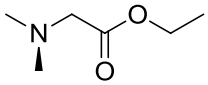
ethyl 3-bromopropionate

bb) **$C_5H_9BrO_2$**: δ 1.17 (triplet, 3H), δ 1.63 (doublet, 3H), δ 3.79 (quartet, 1H), and δ 3.91 (quartet, 2H)



ethyl 2-bromopropionate

cc) **$C_6H_{13}NO_2$**: δ 1.29 (triplet, 3H), δ 2.36 (singlet, 6H), δ 3.16 (singlet, 2H), and δ 4.20 (quartet, 2H) IR spectrum contains a strong absorption at 1749 cm^{-1}



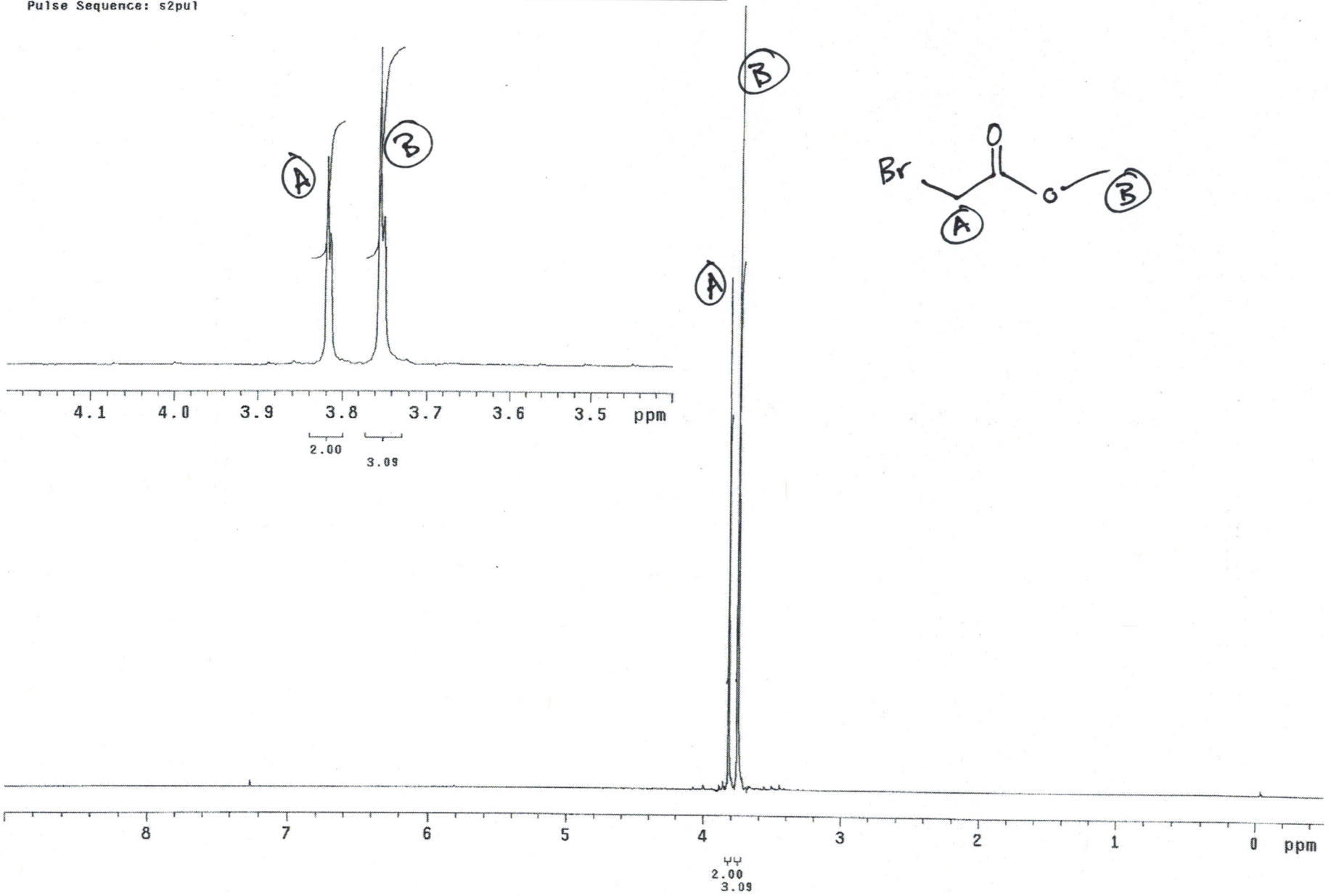
ethyl (dimethylamino)acetate

CHEM 344 Unknown W

Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_21Jan2013

Pulse Sequence: s2pul

Unknown W
$C_3H_5O_2Br$ ^{1}H-NMR



Unknown W

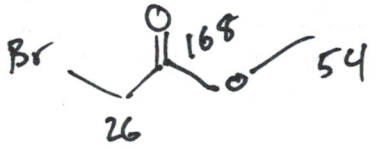
Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_21Jan2013

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
File: 5502
Mercury-300BB "orglabnmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
128 repetitions
OBSERVE C13, 75.4428085 MHz
DECOUPLE H1, 300.0323276 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 min, 49 sec

Unknown W
$C_3H_5O_2Br$ ^{13}C-NMR

See Course Website or Loudon page 622-629 for more information on ^{13}C-NMR.

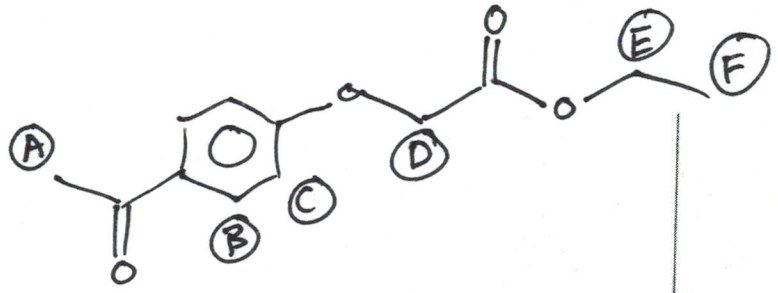


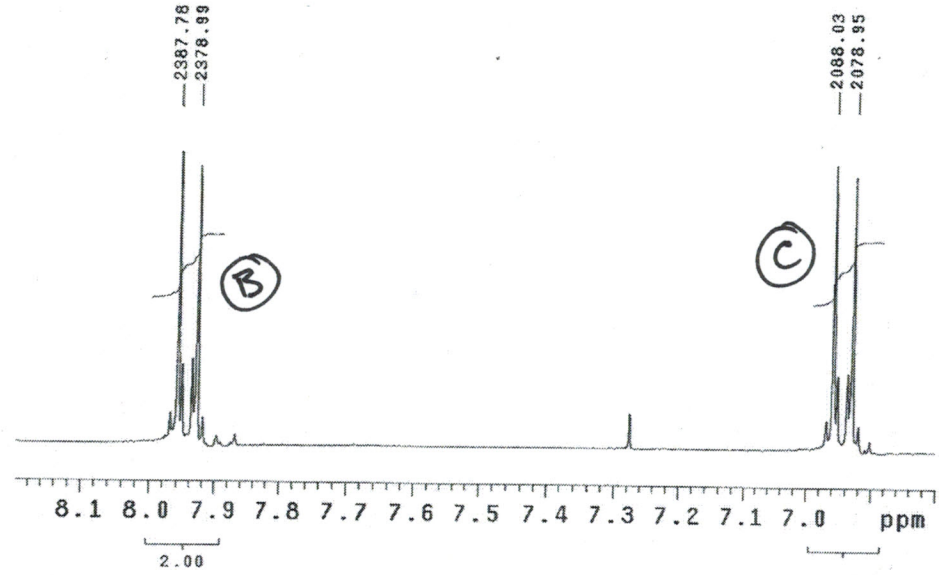
CHEM 344 Unknown K

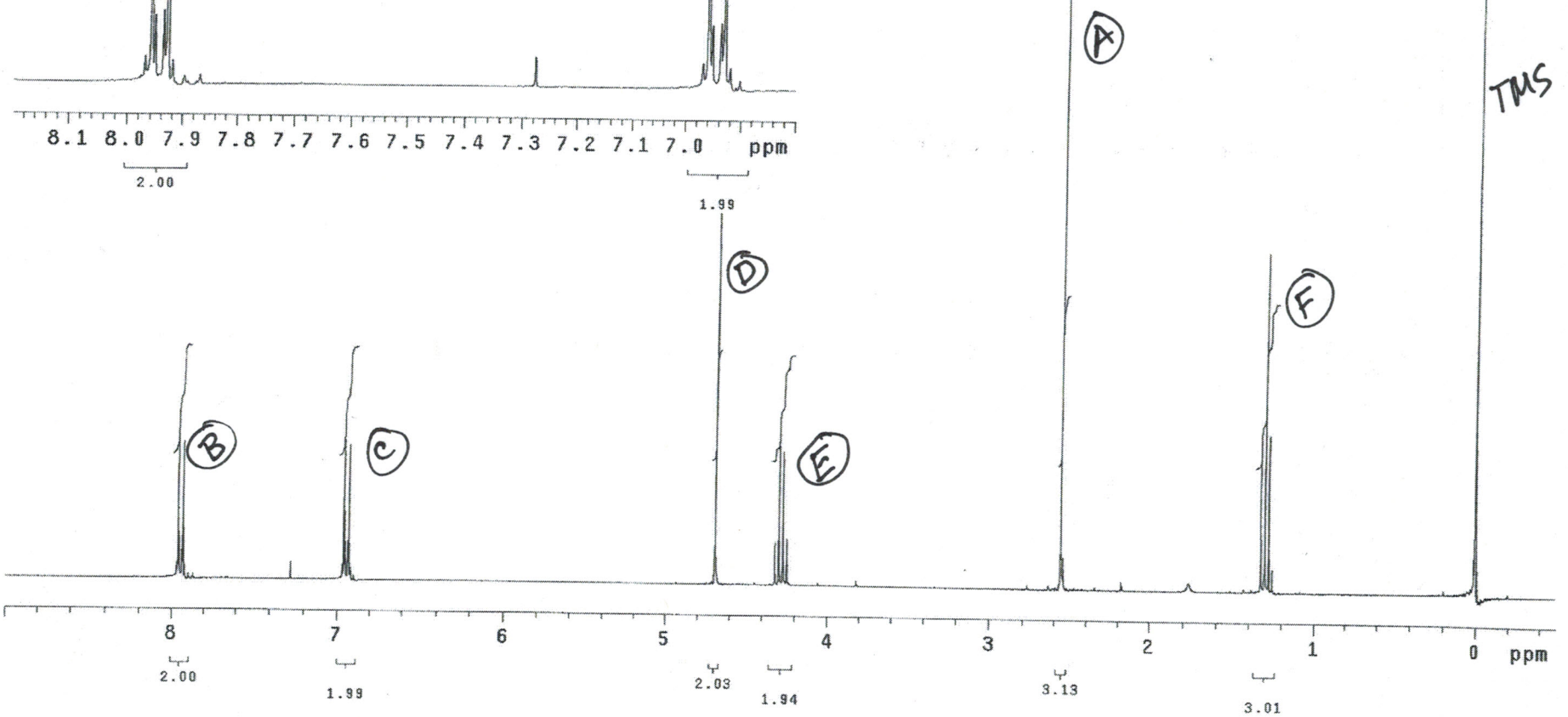
Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_13Jun2012

Pulse Sequence: s2pul

Unknown K
$C_{12}H_{14}O_4$ ^{1}H-NMR





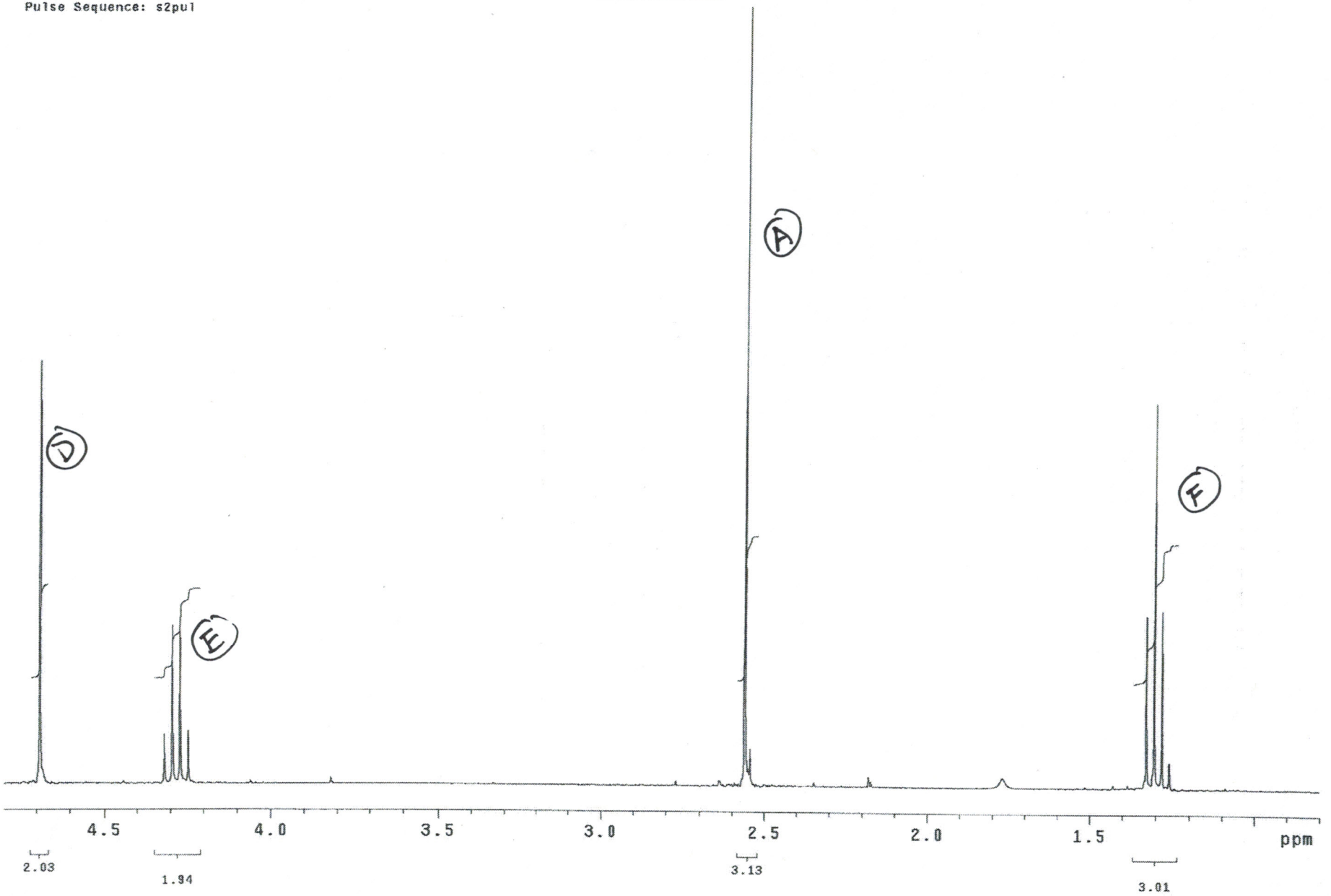


CHEM 344 Unknown K

Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_13Jun2012

Pulse Sequence: s2pul

Unknown K
$C_{12}H_{14}O_4$ ^{1}H-NMR

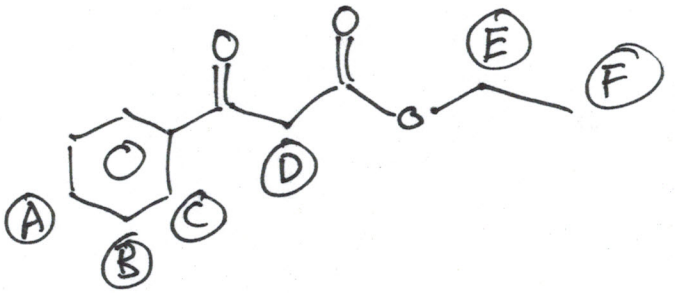


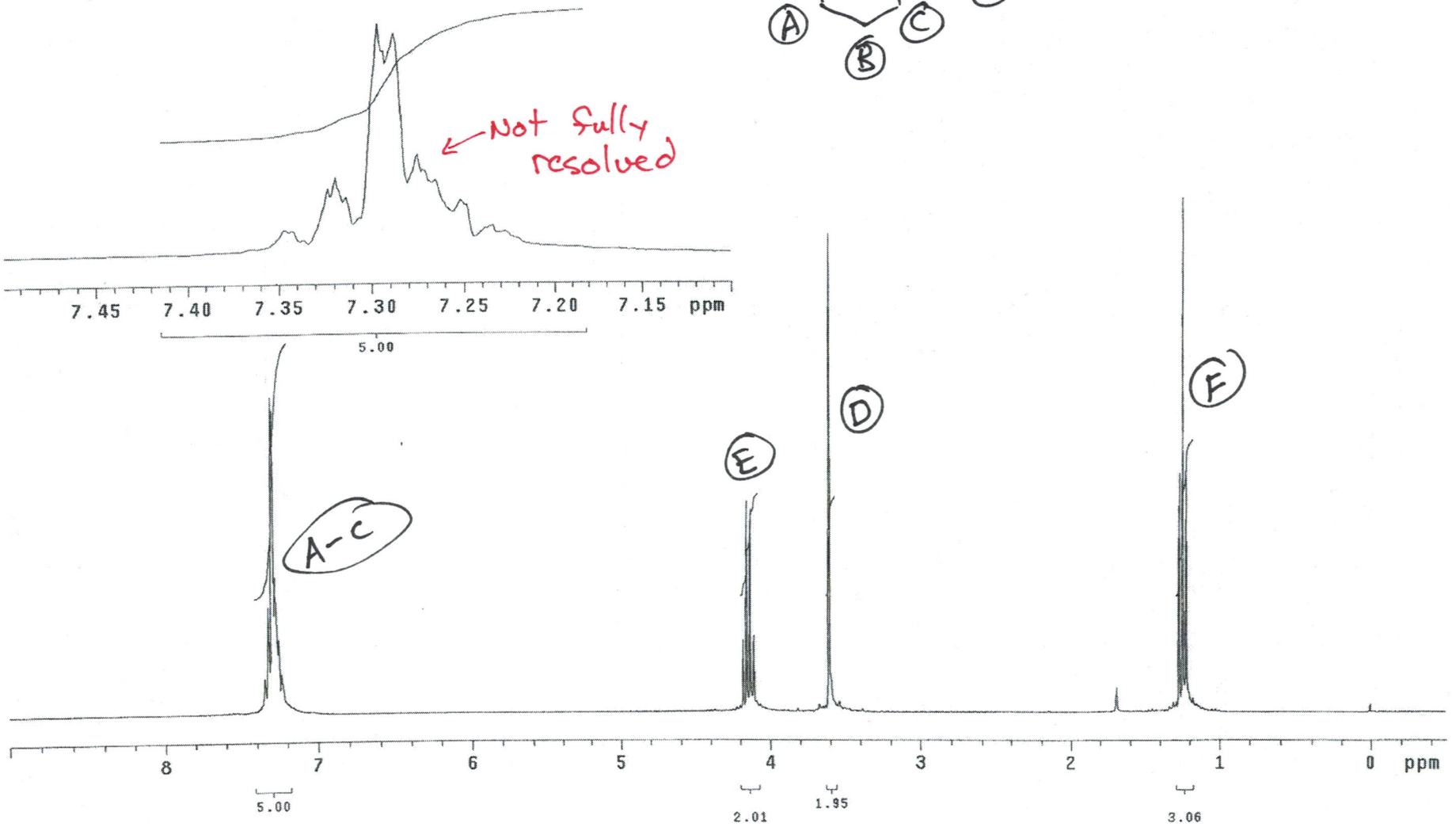
CHEM 344 Unknown I

Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_13Jun2008

Pulse Sequence: s2pul

Unknown I
$C_{11}H_{12}O_3$ ^{1}H-NMR



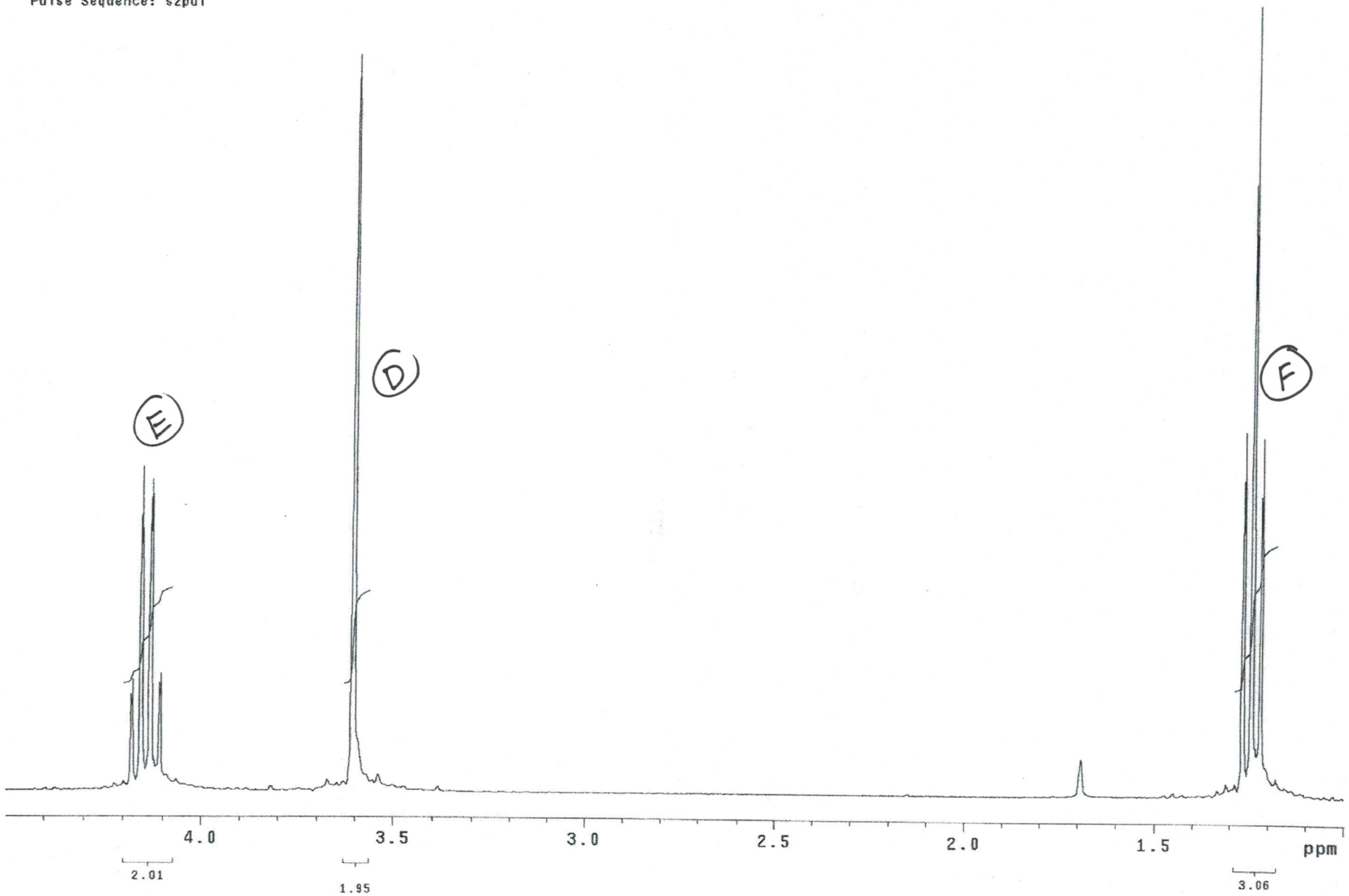


CHEM 344 Unknown I

Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_13Jun2008

Pulse Sequence: s2pul

Unknown I
$C_{11}H_{12}O_3$ ^{1}H-NMR

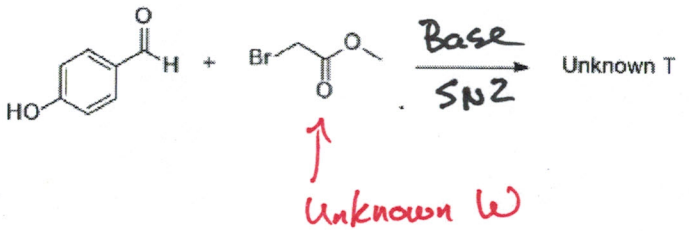


CHEM 344 Unknown T

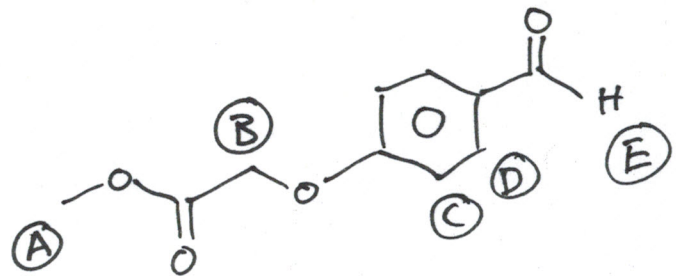
Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_20Sep2011

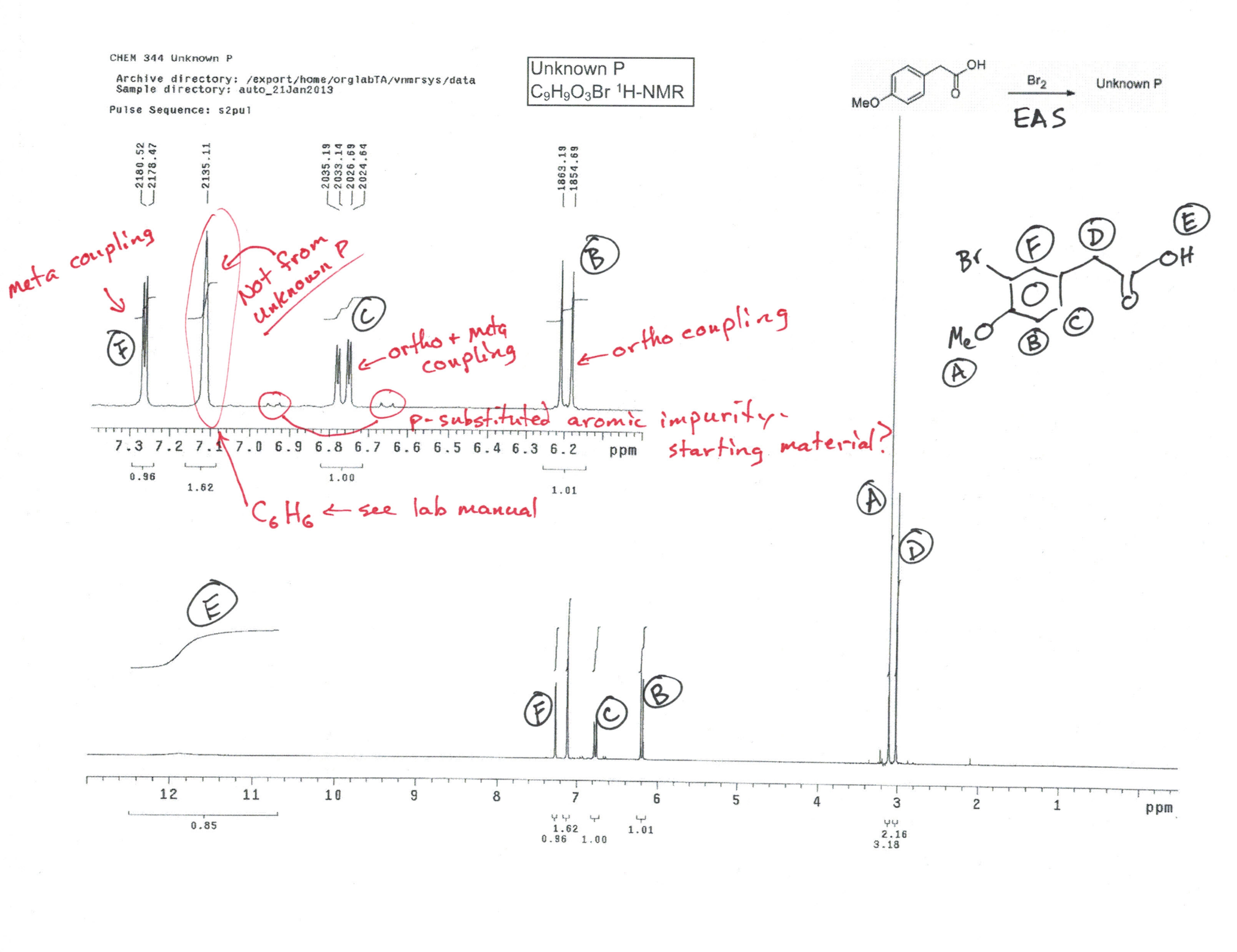
Pulse Sequence: s2pul

Unknown T
$C_{10}H_{10}O_4$ ^{1}H-NMR



Unknown W




CHEM 344 Unknown P
Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_21Jan2013
Pulse Sequence: s2pul
Unknown P
C9H9O3Br 1H-NMR
MeO
OH
O
Br2
Unknown P
EAS
2180.52
2178.47
2135.11
2035.19
2033.14
2026.69
2024.64
1863.19
1854.69
meta coupling
Not from unknown P
ortho + meta coupling
ortho coupling
p-substituted aromic impurity- starting material?
C6H6 ← see lab manual
Br
OH
Me
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 ppm
0.96
1.62
1.00
1.01
12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.85
1.62
0.96
1.00
1.01
2.16
3.18

Unknown P

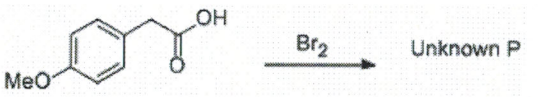
Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_21Jan2013

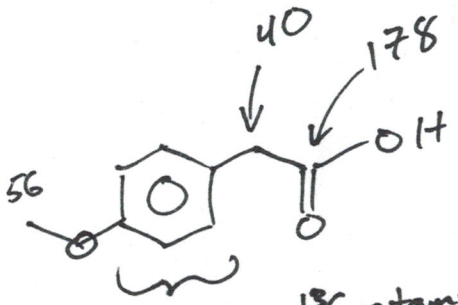
Pulse Sequence: s2pul

Solvent: C6D6
Ambient temperature
File: 5102
Mercury-300BB "orglabnmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4428153 MHz
DECOUPLE H1, 300.0323546 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 8 min, 49 sec

Unknown P
$C_9H_9O_3Br$ ^{13}C-NMR

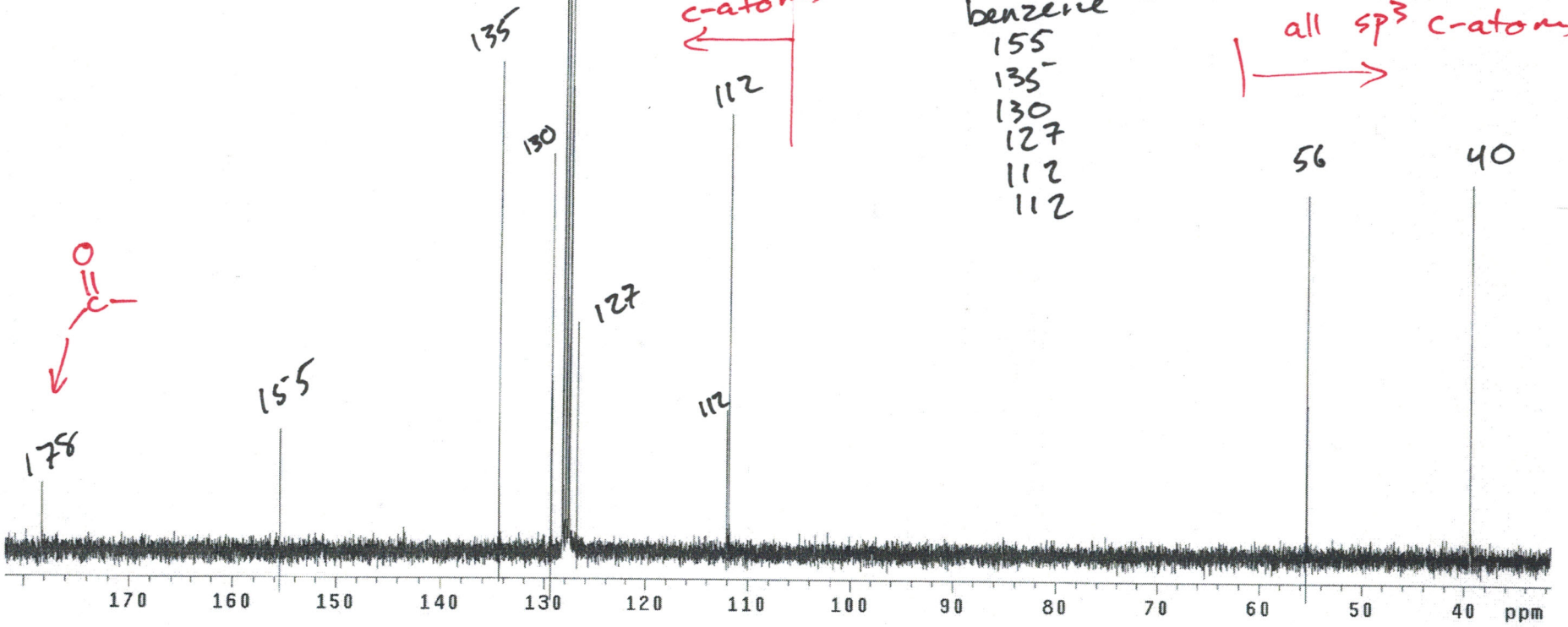




benzene ^{13}C-atoms
155
135
130
127
112
112

all sp^2 c-atoms

all sp^3 c-atoms



Unknown P

Archive directory: /export/home/orglabTA/vnmrsys/data
Sample directory: auto_21Jan2013

Pulse Sequence: s2pul

Solvent: C6D6
Ambient temperature
File: 5102
Mercury-300BB "orglabnmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4428153 MHz
DECOUPLE H1, 300.0323546 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 8 min, 49 sec

Unknown P
$C_9H_9O_3Br$ ^{13}C-NMR