1. 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.

\[ \text{singlet, } J = 7 \text{ Hz} \]

A. quartet, $J = 7$ Hz

\[ \text{triplet, } J = 7 \text{ Hz} \]

B. triplet, $J = 7$ Hz

\[ \text{dd, } J = 15 \text{ Hz}, 9 \text{ Hz} \]

C. dq, $J = 15, 7$ Hz

\[ \text{dq, } J = 15, 2 \text{ Hz} \]

D. dd, $J = 15, 2$ Hz

\[ \text{dd, } J = 15, 1 \text{ Hz} \]

E. dd, $J = 15, 2$ Hz

\[ \text{dd, } J = 9, 2 \text{ Hz} \]

F. dd, $J = 9, 2 \text{ Hz}$

\[ \text{dd, } J = 9, 3 \text{ Hz} \]

G. dd, $J = 9, 3 \text{ Hz}$

\[ \text{dd, } J = 9, 3 \text{ Hz} \]

H. $J = 9, 3 \text{ Hz}$

\[ J = 9, 3 \text{ Hz} \]
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

$\text{C}_9\text{H}_{10}\text{O}$
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.

A. 

Ha = 8.16
Hb = 7.43
Hc = 7.64
Hd = 7.54

B. 

Ha = Ha' ≈ 7.54
Hb = Hb' ≈ 8.16

C. 

Ha = 8.21
Hb = 8.10
Hc = 7.49
Hd = 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 $\delta$ 8.10 ppm (36.61 H) is due to two H-atoms in the major product and the signals at $\delta$ 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?

\[
\frac{1H \text{ Major}}{1H \text{ Minor}} = \frac{36.61}{5.67} = 3.22 \text{ major: minor}
\]
a) $\text{C}_4\text{H}_8\text{O}_2$: $\delta$ 1.15 (triplet, 3H), $\delta$ 2.33 (quartet, 2H), and $\delta$ 3.67 (singlet, 3H)

\[ \text{O} \]

methyl propanoate

b) $\text{C}_9\text{H}_{10}\text{O}$: $\delta$ 1.22 (triplet, 3H), $\delta$ 2.98 (quartet, 2H), $\delta$ 7.43 (multiplet, 2H), $\delta$ 7.53 (triplet of triplets, 1H), and $\delta$ 7.94 (multiplet, 2H)

\[ \text{O} \]

propiophenone

c) $\text{C}_{10}\text{H}_{14}$: $\delta$ 1.3 (singlet, 9H), $\delta$ 7.17 (triplet of triplets, 1H), $\delta$ 7.29 (triplet, 2H), and $\delta$ 7.38 (doublet, 2H)

\[ \text{CH}_3 \text{C}_6\text{H}_4 \text{CH}_3 \]

tert-butyl benzene

d) $\text{C}_{10}\text{H}_{12}\text{O}_2$: $\delta$ 2.01 (singlet, 3H), $\delta$ 2.92 (triplet, 2H), $\delta$ 4.27 (triplet, 2H), and $\delta$ 7.21 (multiplet, 5H) IR spectrum contains a strong absorption at 1740 cm$^{-1}$ MS contains a strong signal at $m/z = 43$

\[ \text{O} \]

phenethyl acetate

e) $\text{C}_8\text{H}_7\text{N}$: $\delta$ 3.70 (singlet, 2H), and $\delta$ 7.3 (multiplet, 5H) IR spectrum contains a strong absorption at $\sim 2250$ cm$^{-1}$

\[ \text{CH}_3 \text{C}_6\text{H}_4 \equiv \text{N} \]

phenylacetonitrile

f) $\text{C}_4\text{H}_6\text{Cl}_2\text{O}_2$: $\delta$ 1.36 (triplet, 3H), $\delta$ 4.34 (quartet, 2H), and $\delta$ 5.96 (singlet, 1H)

\[ \text{Cl} \]

phenylacetonitrile

g) $\text{C}_7\text{H}_{14}\text{O}$: $\delta$ 0.91 (triplet, 6H), $\delta$ 1.60 (sextet, 4H), and $\delta$ 2.37 (triplet, 4H)

\[ \text{CH}_3 \text{C}_6\text{H}_4 \text{CH}_3 \]

4-heptanone

h) $\text{C}_5\text{H}_{10}\text{O}_2$: $\delta$ 1.23 (doublet, 6H), $\delta$ 2.02 (singlet, 3H), and $\delta$ 4.99 (septet, 1H)

\[ \text{O} \]

isopropyl acetate
i) $\text{C}_6\text{H}_{12}\text{O}_2$: $\delta$ 1.44 (singlet, 9H), and $\delta$ 1.96 (singlet, 3H)

\[
\text{O} \quad \text{O}
\]

*tert*-butyl acetate

j) $\text{C}_9\text{H}_{10}\text{O}_2$: $\delta$ 2.08 (singlet, 3H), $\delta$ 5.09 (singlet, 2H), and $\delta$ 7.34 (multiplet, 5H)

\[
\text{O} \quad \text{O}
\]

benzyl acetate

k) $\text{C}_{10}\text{H}_{12}\text{O}_2$: $\delta$ 1.23 (triplet, 3H), $\delta$ 3.60 (singlet, 2H), $\delta$ 4.13 (quartet, 2H), and $\delta$ 7.28 (multiplet, 5H)

\[
\text{O} \quad \text{O}
\]

ethyl phenylacetate

l) $\text{C}_{10}\text{H}_{12}\text{O}_2$: $\delta$ 1.52 (doublet, 3H), $\delta$ 2.05 (singlet, 3H), $\delta$ 5.87 (quartet, 1H), and $\delta$ 7.30 (multiplet, 5H) IR spectrum contains a strong absorption at 1742 cm$^{-1}$

\[
\text{O} \quad \text{O}
\]

1-phenylethyl acetate

m) $\text{C}_4\text{H}_8\text{O}_2$: $\delta$ 1.39 (doublet, 3H), $\delta$ 2.22 (singlet, 3H), $\delta$ 3.91 (broad singlet, 1H), and $\delta$ 4.27 (quartet, 1H) IR spectrum contains a strong absorption at 3451 cm$^{-1}$

\[
\text{O} \quad \text{OH}
\]

3-hydroxy-2-butanone

n) $\text{C}_{10}\text{H}_2\text{O}$: $\delta$ 1.01 (triplet, 3H), $\delta$ 2.45 (quartet, 2H), $\delta$ 3.67 (singlet, 2H), and $\delta$ 7.24 (multiplet, 5H)

\[
\text{O}
\]

1-phenyl-2-butanone

o) $\text{C}_2\text{H}_4\text{Br}_2$: $\delta$ 2.46 (doublet, 3H), and $\delta$ 5.84 (quartet, 1H)

\[
\text{Br} \quad \text{Br}
\]

1,1-dibromoethane

p) $\text{C}_3\text{H}_6\text{Br}_2$: $\delta$ 2.35 (quintet, 2H), and $\delta$ 3.56 (triplet, 4H)

\[
\begin{array}{c}
\text{Br} \\
\text{Br} \\
\end{array}
\]

1,3-dibromopropene
q) \( \text{C}_8\text{H}_9\text{Br} \): \( \delta \ 2.02 \text{ (doublet, 3H)}, \delta \ 5.18 \text{ (quartet, 1H)}, \delta \ 7.29 \text{ (asymmetrical doublet, 2H)}, \) and \( \delta \ 7.41 \text{ (multiplet, 3H)} \)

(1-bromoethyl)benzene

r) \( \text{C}_{14}\text{H}_{14} \): \( \delta \ 2.90 \text{ (singlet, 4H)}, \delta \ 7.17 \text{ (multiplet, 6H)}, \) and \( \delta \ 7.26 \text{ (multiplet, 4H)} \)

bibenzyl

s) \( \text{C}_{11}\text{H}_{17}\text{N} \): \( \delta \ 1.04 \text{ (triplet, 6H)}, \delta \ 2.51 \text{ (quartet, 4H)}, \delta \ 3.56 \text{ (singlet, 2H)}, \) and \( \delta \ 7.33 \text{ (multiplet, 5H)} \)

N,N-diethylbenzylamine

t) \( \text{C}_3\text{H}_5\text{ClO}_2 \): \( \delta \ 1.74 \text{ (doublet, 3H)}, \delta \ 4.45 \text{ (quartet, 1H)}, \) and \( \delta \ 12.2 \text{ (singlet, 1H)} \)

2-chloropropionic acid

u) \( \text{C}_3\text{H}_5\text{ClO}_2 \): \( \delta \ 2.87 \text{ (triplet, 2H)}, \delta \ 3.76 \text{ (triplet, 2H)}, \) and \( \delta \ 11.8 \text{ (singlet, 1H)} \)

3-chloropropionic acid

v) \( \text{C}_{10}\text{H}_{14} \): \( \delta \ 1.22 \text{ (doublet, 6H)}, \delta \ 2.30 \text{ (singlet, 3H)}, \delta \ 2.86 \text{ (septet, 1H)}, \) and \( \delta \ 7.0 \text{ (symmetrical multiplet, 4H)} \)

\( p \)-cymene

w) \( \text{C}_{7}\text{H}_{12}\text{O}_4 \): \( \delta \ 1.29 \text{ (triplet, 6H)}, \delta \ 3.36 \text{ (singlet, 2H)}, \) and \( \delta \ 4.22 \text{ (quartet, 4H)} \)

diethyl malonate

x) \( \text{C}_3\text{H}_8\text{O} \): \( \delta \ 3.54 \text{ (singlet, 4H)}, \) and \( \delta \ 7.26 \text{ (symmetrical multiplet, 4H)} \)

2-indanone
y) $\text{C}_3\text{H}_8$: $\delta$ 2.04 (quintet, 2H), $\delta$ 2.90 (triplet, 4H), $\delta$ 7.10 (multiplet, 2H), and $\delta$ 7.20 (multiplet, 2H)

\[
\text{indan}
\]

z) $\text{C}_3\text{H}_4\text{O}_2$: $\delta$ 3.55 (triplet, 2H), and 4.28 (triplet, 2H)

\[
\text{2-oxetanone}
\]

aa) $\text{C}_3\text{H}_5\text{BrO}_2$: $\delta$ 1.29 (triplet, 3H), $\delta$ 2.92 (triplet, 2H), $\delta$ 3.58 (triplet, 2H), and $\delta$ 4.19 (quartet, 2H)

\[
\text{ethyl 3-bromopropionate}
\]

bb) $\text{C}_3\text{H}_5\text{BrO}_2$: $\delta$ 1.17 (triplet, 3H), $\delta$ 1.63 (doublet, 3H), $\delta$ 3.79 (quartet, 1H), and $\delta$ 3.91 (quartet, 2H)

\[
\text{ethyl 2-bromopropionate}
\]

c) $\text{C}_6\text{H}_{13}\text{NO}_2$: $\delta$ 1.29 (triplet, 3H), $\delta$ 2.36 (singlet, 6H), $\delta$ 3.16 (singlet, 2H), and $\delta$ 4.20 (quartet, 2H) IR spectrum contains a strong absorption at 1749 cm$^{-1}$

\[
\text{ethyl (dimethylamino)acetate}
\]
Unknown W
C₃H₅O₂Br 'H-NMR

Pulse Sequence: s2pul

Chemical shifts:
- A: 3.9 ppm
- B: 3.5 ppm

Structural formula:
- A: Carbon atom bonded to Br
- B: Carbon atom bonded to O
See Course Website or Loudon page 622-629 for more information on $^{13}$C-NMR.
Unknown K
C_{12}H_{14}O_{4} \text{ } ^1{H}-\text{NMR}

Pulse Sequence: s2pul
Unknown I
C\textsubscript{11}H\textsubscript{12}O\textsubscript{3} \textsuperscript{1}H-NMR

Not fully resolved

A-C

8 7 6 5 4 3 2 1 0 ppm

7.45 7.40 7.35 7.30 7.25 7.20 7.15 ppm

Pulse Sequence: m2pul
Unknown I
C₁₁H₁₂O₃ ¹H-NMR
Unknown T
C_{10}H_{10}O_4 ^1H-NMR

Unknown T
Base

[Chemical Structures and Spectra]

Pulse Sequence: s2pul
Unknown P
C₆H₅O₃Br 'H-NMR

C₆H₆ ← see lab manual

meta coupling

Not from unknown P

ortho and meta coupling

ortho coupling

p-substituted aromatic impurity: starting material?
Unknown P

C₅H₉O₃Br¹³C-NMR

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18067.3 Hz
256 repetitions

OBSERVE C13, 75.4428153 MHz
DECOUPLE H1, 300.6325456 MHz
Power 38 dB
continuously on

DATA PROCESSING
FT size 65536
Total time 6 min, 48 sec

all sp² c-atoms

all sp³ c-atoms
Unknown P

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

Pulse Sequence: s2pul
Solvent: CD6D
Ambient temperature
File: 5182
Mercury-300B "orglabmer"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 10867.5 Hz
256 repetitions
OBSERVE C13, 75.4428153 MHz
DECOUPLE H1, 366.8923546 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 8 min, 49 sec

C6H9O3Br13C-NMR

Unknown P