Chemistry 605 (Reich)

THIRD HOUR EXAM

Mon. May 10, 2010

Question/Points

R-09N_____/20

R-09O_____/15

R-09P_____/15

R-09Q_____/15

R-08R_____/25

R-08S_____/10

Total _____/100

|	
Average	72
Hi	91
Median	73
AB	78
BC	55

Answers

Name_____

If you place answers anywhere else except in the spaces provided, (e.g. on the spectra
or on extra pages) clearly indicate this on the answer sheets.

Problem R-09N (C_5H_9DO) Yes, that's a deuterium. Determine the structure from the 200 MHz ^1H NMR spectrum.

1

(a) DBE __1__ (b) Interpret the multiplets at δ 4.95 and δ 5.95. Report coupling in the standard format ($^nJ_{x-y}$ = 00 Hz). Show part structure(s) suggested by these peaks

δ 4.95   d $^3J_{H-H}$ = 10.5

H   H
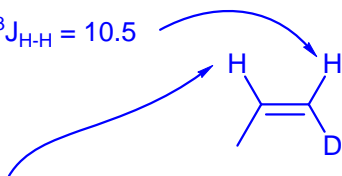
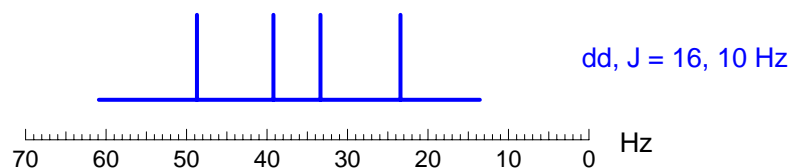The protons must be cis on the double
bond to give a 10 Hz coupling

D

5

δ 5.95   d 1:1:1 t, $^3J_{H-H}$ = 10.5, $^3J_{H-D}$ = 2.5 Hz

The 1:1:1 triplet 2.5 Hz is J_{HD}, J_{HH} = 2.5 x 100/15.35 = 16.3 Hz
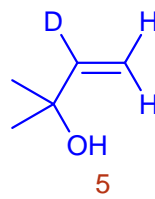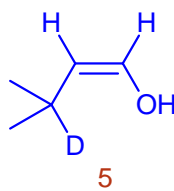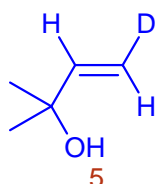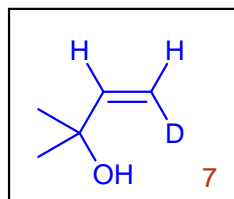
$$J_{HH} = J_{HD} \times \gamma_H/\gamma_D$$

(c) On the Hz scale below sketch what the proton at δ 5.95 would look like in the undeuterated compound ($C_5H_{10}O$)

dd, J = 16, 10 Hz

3

70   60   50   40   30   20   10   0   Hz

(d) Draw the structure of R-09N. If more than one structure is possible, then draw them, but circle the one you prefer.

7

H   H

D

OH   7

H   D

H

OH

5

H   H

OH

D

5

D   H

H

OH

5

(e) The boxed inset between δ 5.1 and 5.3 (reproduced below) is an 8x vertical expansion. Suggest what these small impurities might be due to, and assign the peaks..

30   20   10   0   Hz

d, J = 16.5 Hz

dd, J = 16.5, 1.5 Hz

4

5.3   5.2   5.1
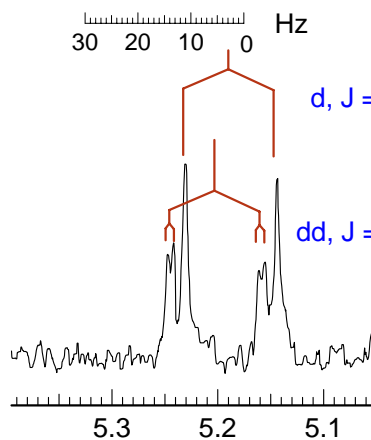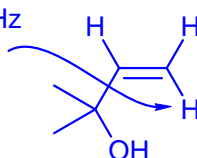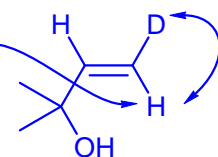
$^2J_{H-D}$ is too small to detect (ca 0.4 Hz)

H   D

H

OH

The impurities are a mixture of the undeuterated compund, and the compound with D in the cis position

H   H

H

OH

There is a small H/D isotope shift, with the deuterated compound being slightly upfield of the protio

Problem R-09N C_5H_9DO
200 MHz ^1H NMR spectrum.
Solvent $CDCl_3$.
(Source: Ken Yelm/HJR 12/15)

30 20 10 0   Hz

5.95

4.95   H   OH

D

d J = 10.5

8x vertical expansion

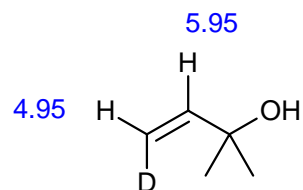d, J = 16.5 Hz

dd, J = 16.5, 1.5 Hz

d 1:1:1 t, J=10.5, 2.5
The 1:1:1 triplet 2.5 Hz is J_{HD}, J_{HH} = 2.5 x 100/15.35 = 16.3 Hz

5.3   5.2   5.1

6.28

6.2   6.1   6.0   5.9   5.8   5.7   5.6   5.5   5.4   5.3   5.2   5.1   5.0   4.9

0.92

1.00   1.00

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

ppm
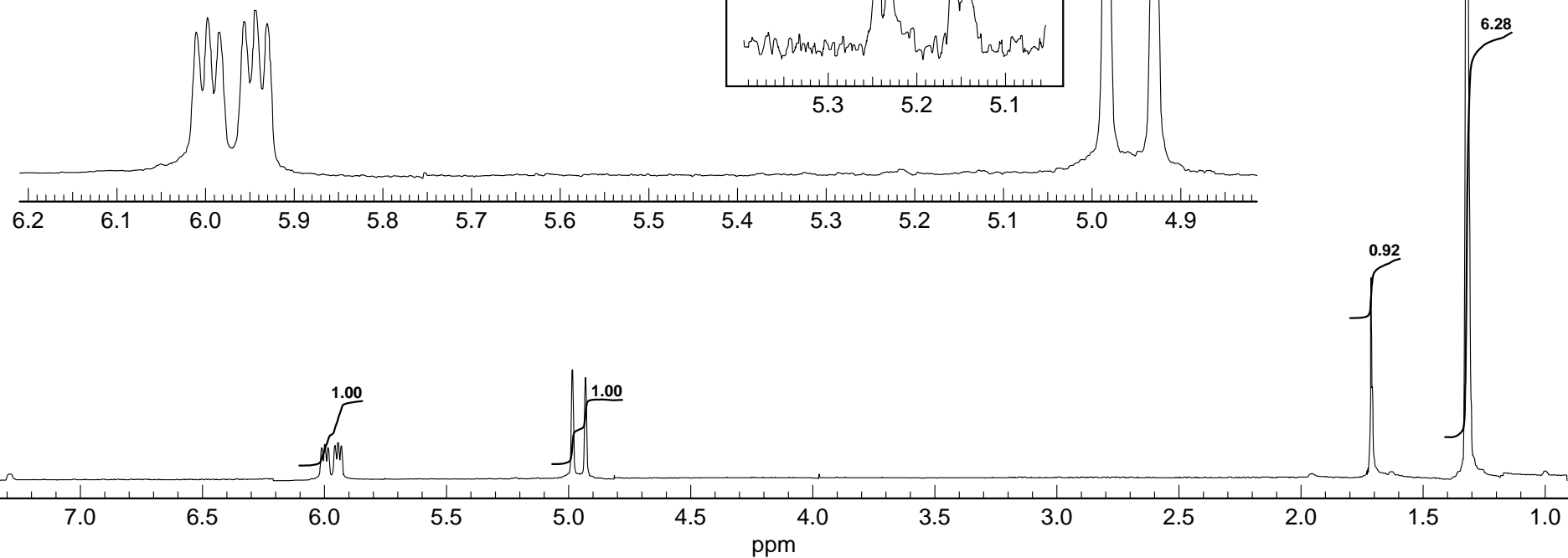
Problem R-09O ($C_{10}H_7NO$). Shown below is the 250 MHz proton homonucear shift correlated spectrum (H,H-COSY) of quinoline 8-carboxaldehyde. The aldehyde proton at δ 9.5 is not shown.
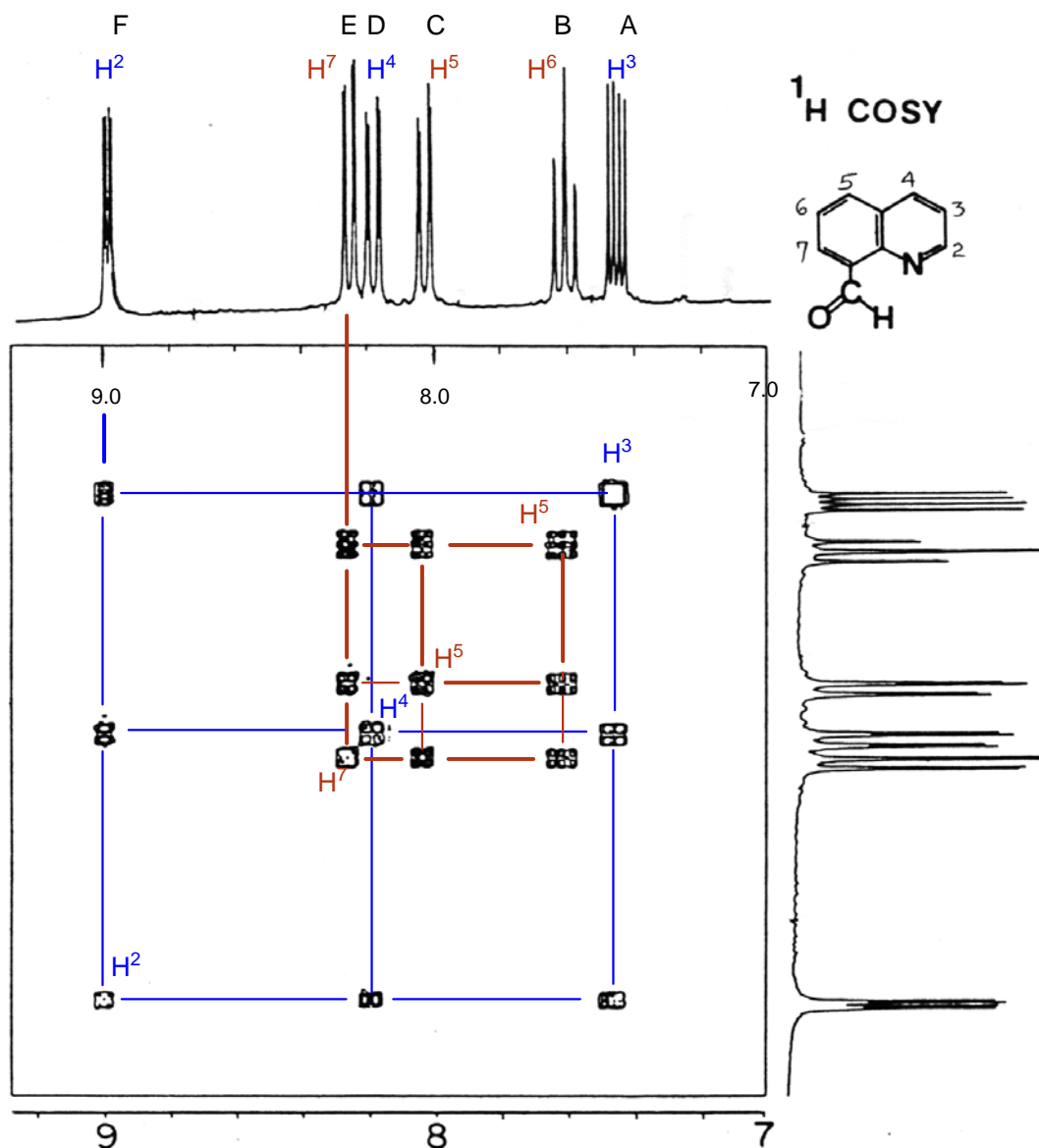
Asign the proton signals A through F to the protons H^2 to H^7.

H^2 = __F__

H^3 = __A__

H^4 = __D__

H^5 = __C__

H^6 = __B__

H^7 = __E__

H^2 can be assigned to F on the basis of chemical shift. It is correlated to A and D. A is a dd with two large couplings, so must be H^3, and thus $D = H^4$

H^7 can be assigned to E on the basis of chemical shift (ortho shift of CHO larger than para shift). It is correlated to C and B. B is a triplet (two large couplings), so must be H^6, and thus $C = H^5$

Magn. Reson. Chem 1985, 23, 672

15

Problem R-09P ($C_{14}H_{20}O_2S$). Spectrum (1) is a normal 400 MHz ^1H NMR spectrum of one of the isomers shown. Impurity peaks are marked with x. Spectra (2) and (3) are difference spectra, in which the normal spectrum is subtracted from the spectrum obtained by preirradiating for a few seconds at the frequency shown by the arrow

A   or   **B**

(3)

(2)

(1) Normal 400 MHz ^1H NMR spectrum
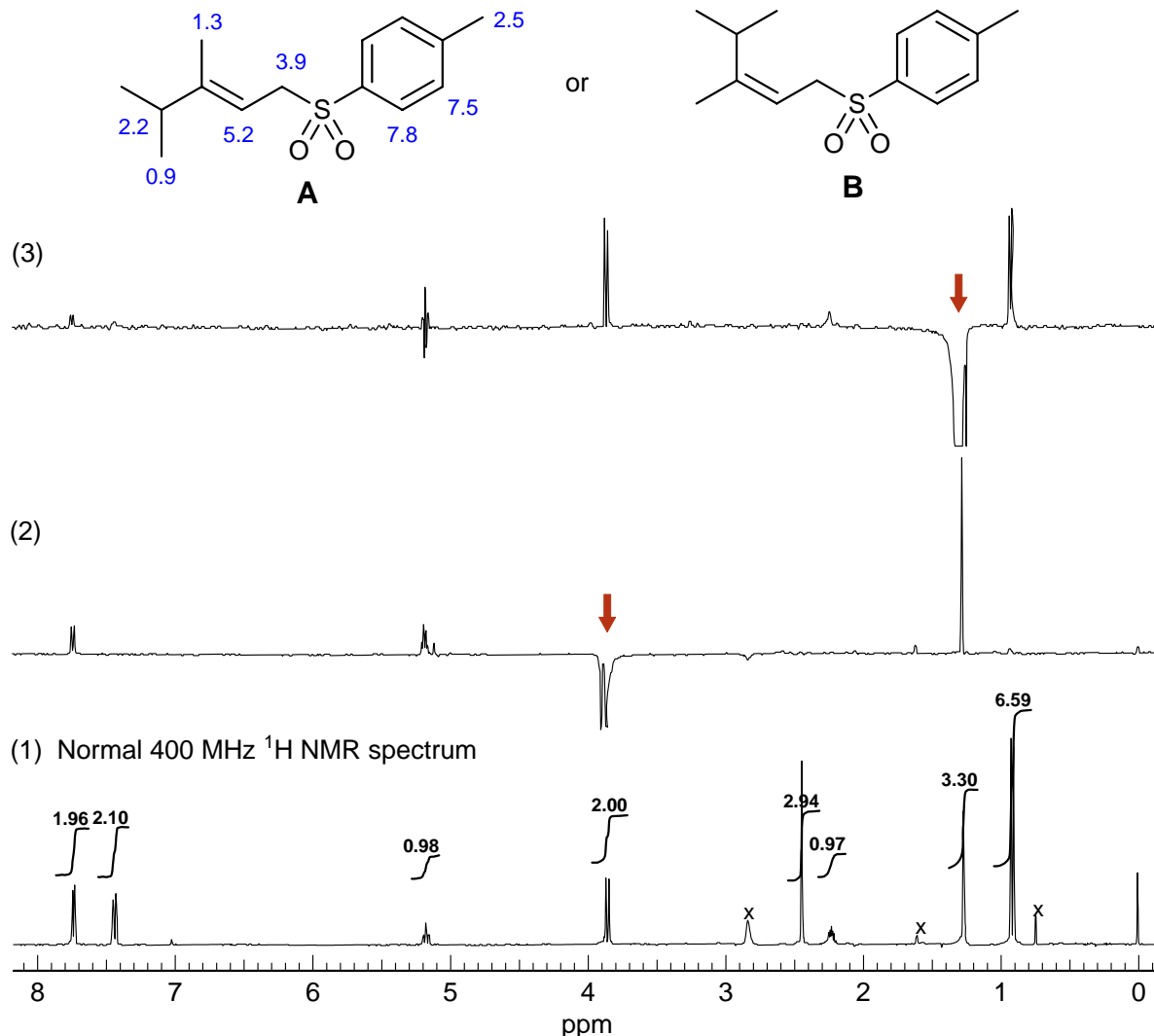
(a) What kind of experiment is being done here?

2   Proton-proton NOE difference experiment

(b) Which of the isomers is the correct structure (**A** or **B**)?_____ **A**xplain briefly, but be specific.

5   Irradiation of the methyl group at δ 1.3 (spectrum 3) causes an NOE enhancement of the CH_2 doublet δ 3.9 - thus these must be cis, hence structure A. Conversely, irradiation at δ 3.9 (spectrum 2) causes NOE enhancement of the vinyl proton at δ 5.2, the ortho protons δ 7.8, and (most importantly), the methyl signal at δ 1.3, also consistent only with structure A

(c) Assign the protons by writing chemical shifts on the correct structure.

8

Problem R-09Q (C_1H_6ClN). Shown below is the 30 MHz ^1H NMR spectrum of 60% ^{15}N enriched $CH_3NH_3^+$ Cl^- in H_2O
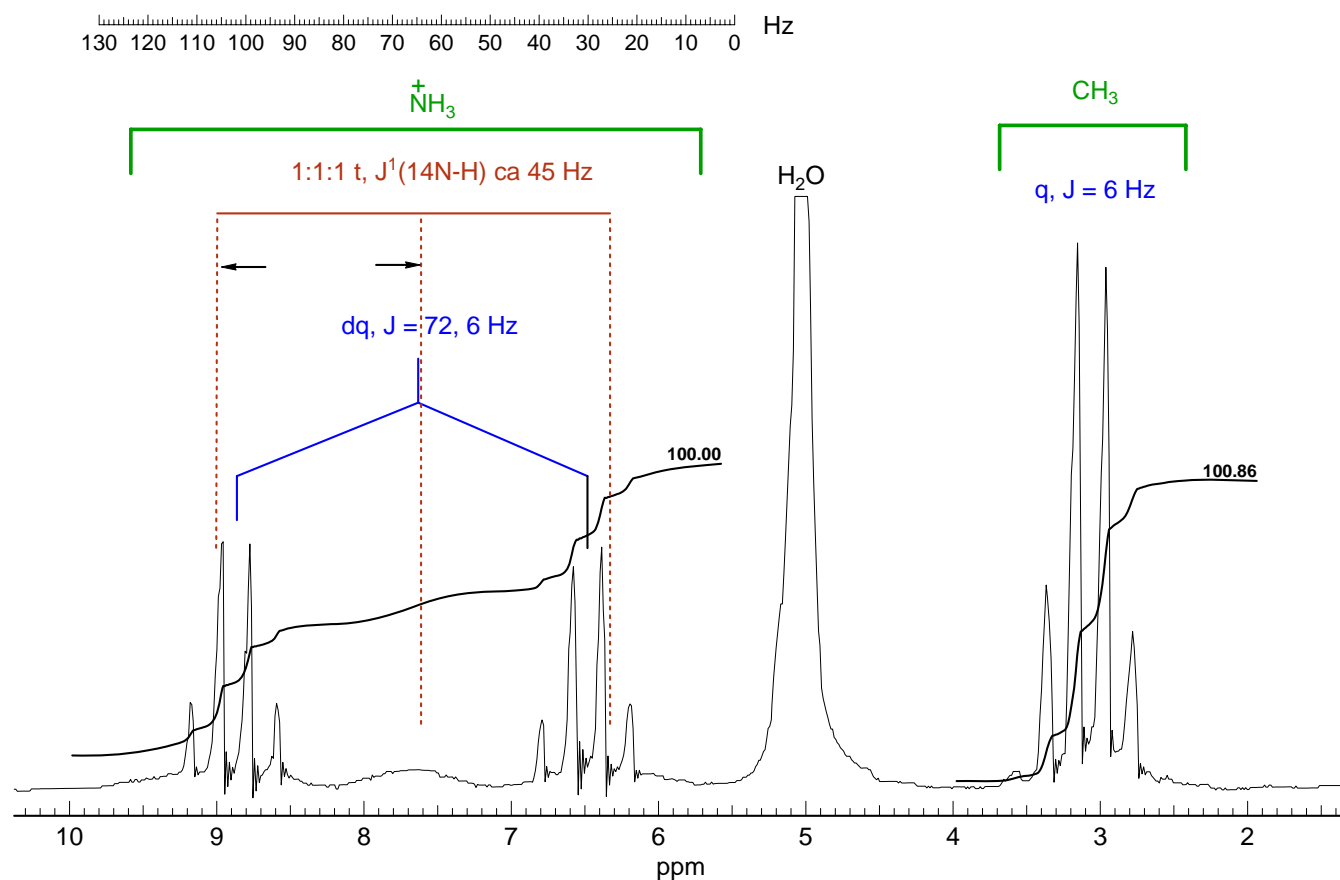
Identify all significant peaks by labelling the spectrum. Show all coupling constants in the standard format $^nJ_{x\text{-}y} = $ 00 Hz.

For the 60% ^{15}N, signals are a dq for the NH_3, and a q for the CH_3

$^1J(^{15}N\text{-}H)$ = 72 Hz.

$^3J(H\text{-}H)$ = 6 Hz.

Apparently the $^2J_{N\text{-}H}$ is too small to resolve, otherwise would see a qd for the Me group

For the 40% ^{14}N, signals are a broad 1:1:1 triplet for the NH_3 (the coupling to the Me group is not resolved because T_1 relaxation of ^{14}N is fast enough to cause broadening. The q for the CH_3 is superimposed on the signals of the ^{15}N isotopomer.

$^1J(^{14}N\text{-}H)$ ca 45 Hz.

The ratio of $^1J(^{15}N\text{-}H)$ and $^1J(^{14}N\text{-}H)$ should be 10.13/ 7.22, i.e.predict $^1J(^{14}N\text{-}H)$ = 51 Hz if $^1J(^{15}N\text{-}H)$ = 72

Common errors: Ignoring the ^{14}N entirely; mixing up CH_3 and NH_3

25

Problem R-09R. Interpret the proton noise decoupled 50.3 MHz ^{13}C NMR spectra of ^{13}C and ^{18}O labelled succinic acid. Only the carbonyl region is shown - the signals appear at δ 176.

There are 6 possible different ^{18}O labelled succinic acids (isotopomers), drawn as compounds 1-6 below. Under the conditions of the NMR experiment, proton/deuterium transfers of OH/OD are fast, so the protons/deuterons are not shown.

$O = {}^{16}O$

1 **2** **3** **4** **5** **6**
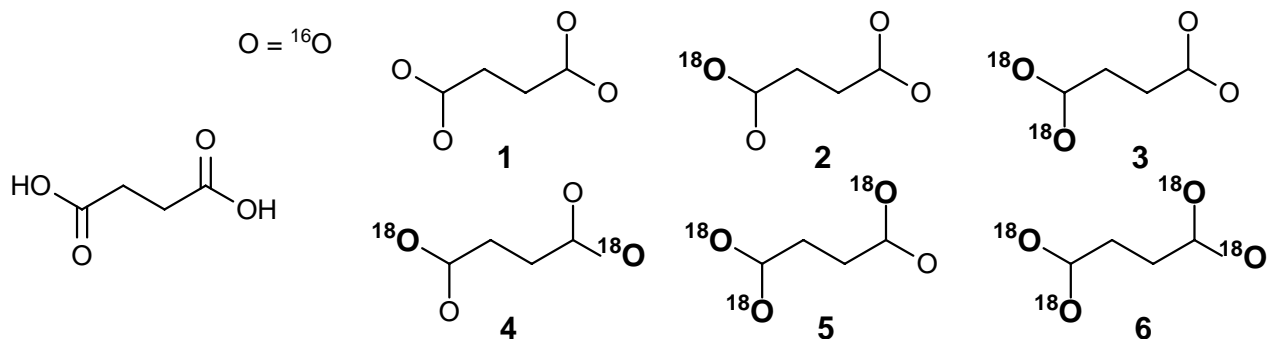
Spectrum (1) shows mono-^{13}C labelled succinic acid with ^{18}O at natural abundance (0.2%) (compound **1**).

(1)

100% ^{13}C

9 8 7 6 5 4 3 2 1 0
Hz
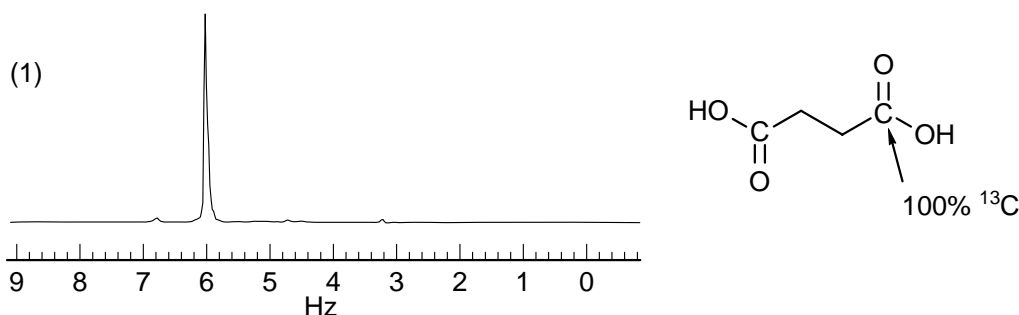
(a) Interpret spectrum (2) reproduced below. This sample was produced by heating a sample of succinic acid in $H_2{}^{18}O$ (ca 52% ^{18}O incorporation) and contains all 6 isotopomers (**1**-**6**). Show you understand the origin of the three peaks by sketching the signals you would expect to see for a sample of each pure isotopomer **2** to **6**.

Pure **6**

Pure **5**

Pure **4**

Pure **3**

Pure **2**

10
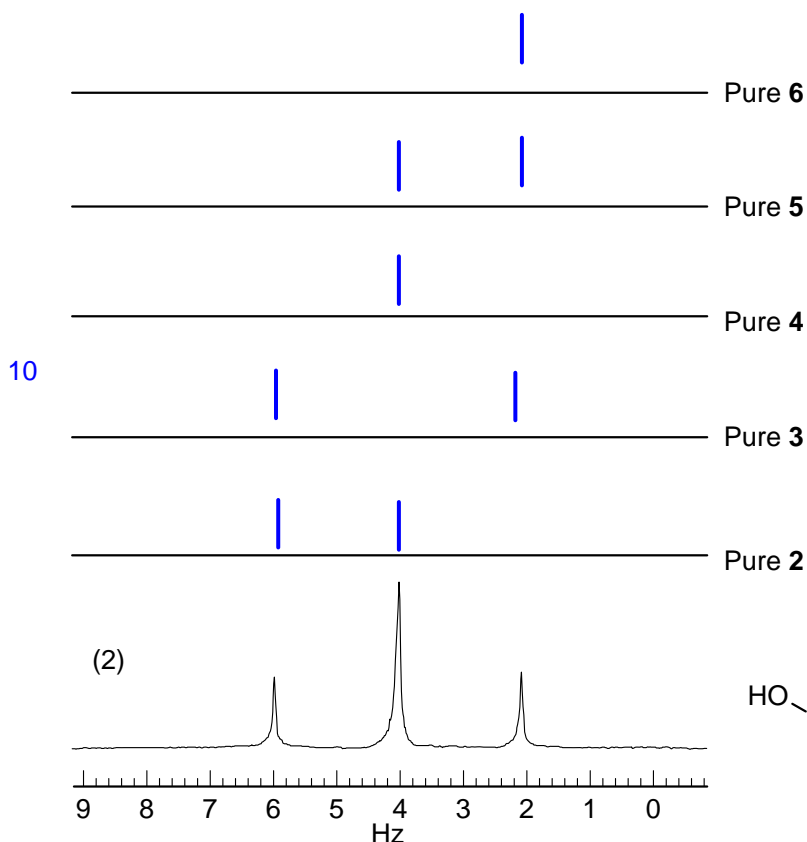
The ^{18}O will be randomly incorporated into both the ^{13}C enriched as well as ^{12}C carboxyl group

There is a carbon NMR isotope shift of 2 Hz upfield for ^{18}O vs ^{16}O. The shift is double (4 Hz) if both ^{16}Os are replaced by ^{8O}s

(2)

9 8 7 6 5 4 3 2 1 0
Hz

100% ^{13}C
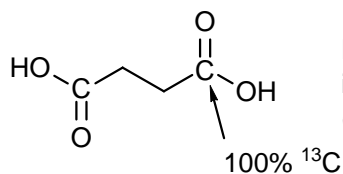
Mono-^{13}C labelled, after heating in $H_2{}^{18}O$ for some time (mixture of isotopomers **1** to **6**)

(b) The sample for spectrum (3) was prepared similarly to spectrum (2), except that succinic acid was used in which both carboxyl groups are labelled 100% with ^{13}C. To help you get started in your analysis, sketch the spectrum you would expect for a pure sample of isotopomer **2**.

$^3J_{C-C}$ 2.8 Hz

Pure **2**

6

9

(3)

HO, C, OH, O

100% ^{13}C
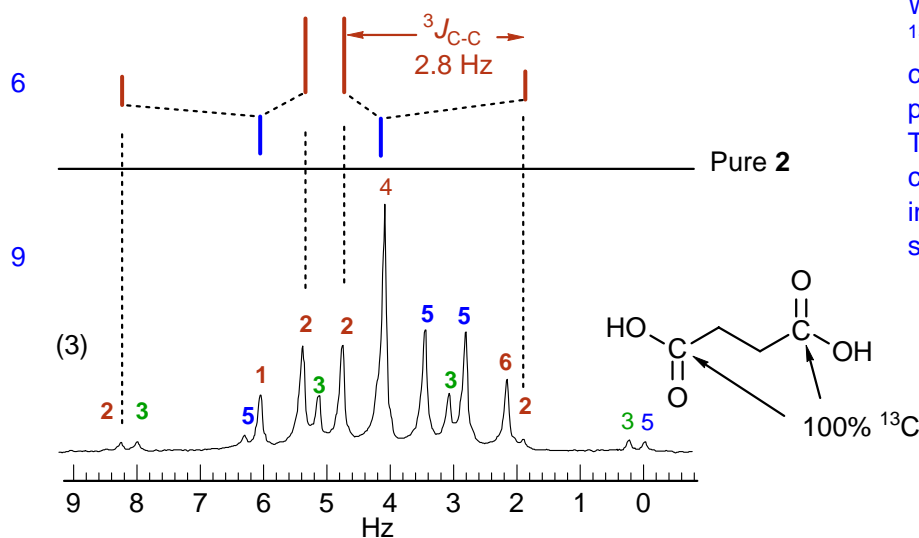
When both carbons are 100% enriched by ^{13}C, then each of the unsymmerically labelled compounds (those that have two peaks in part (a) **2**, **3** and **5**) will form an AB quartet. The $^3J_{CC}$ is 2.8 Hz. The symmetrical compounds (**1**, **4**, **6**) will show a singlet, just as in part (a). The three-bond $^{12}C/^{13}C$ isotope shift is too small to detect.

Double ^{13}C labelled, after heating in $H_2{}^{18}O$ for some time (mixture of isotopomers **1** to **6**)

(c) On spectrum (3), mark the peaks which correspond to isotopomers **1**, **2**, **3**, **4**, **5** and **6** by placing numbers on the appropriate peaks (amazingly, there are no superimposed peaks!). Make sure you account for the small peaks (i.e., those at 0.0, 0.3, 2.0, 6.3, 8.0 and 8.3 Hz). Report and identify any coupling constants you can measure.

Here is all the data in one place:

(1) Mono-^{13}C labelled, with ^{18}O at natural abundance (0.2%) (compound **1**).

100% ^{13}C

(2) Mono-^{13}C labelled, after heating in $H_2{}^{18}O$ for some time (mixture of isotopomers **1** to **6**)

100% ^{13}C

(3) Double ^{13}C labelled, after heating in $H_2{}^{18}O$ for some time (mixture of isotopomers **1** to **6**)
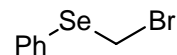
100% ^{13}C
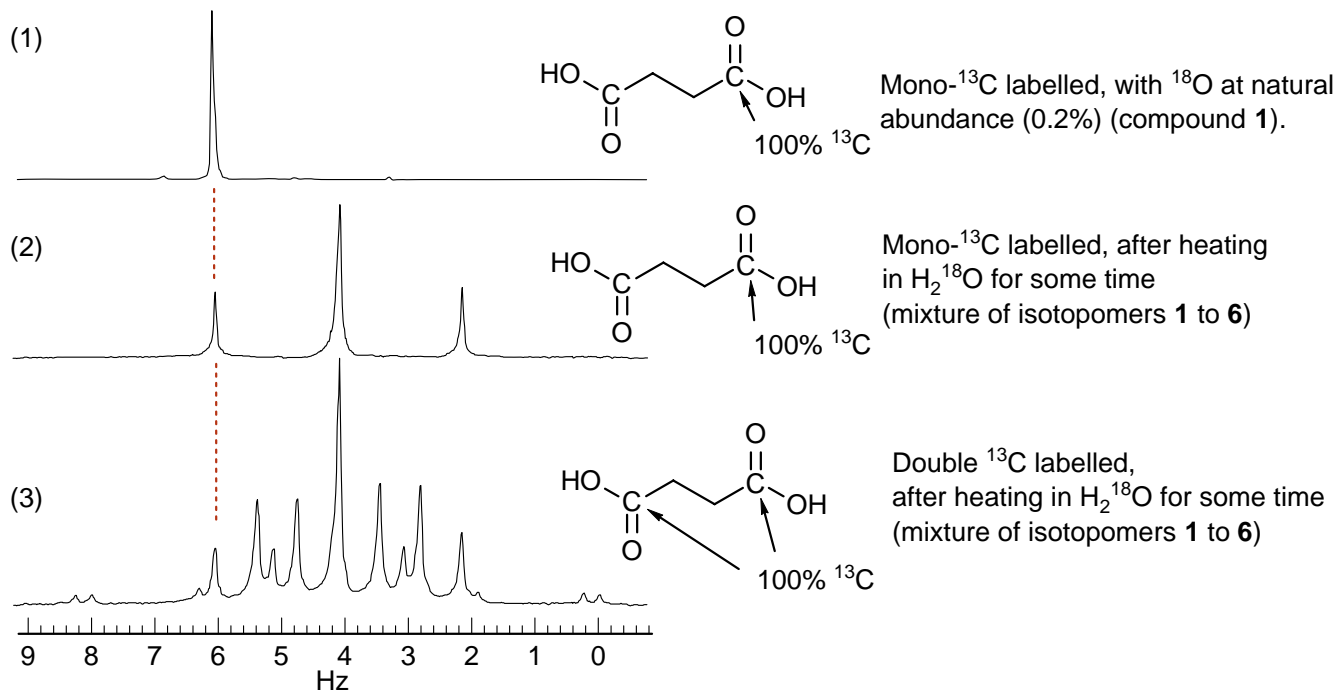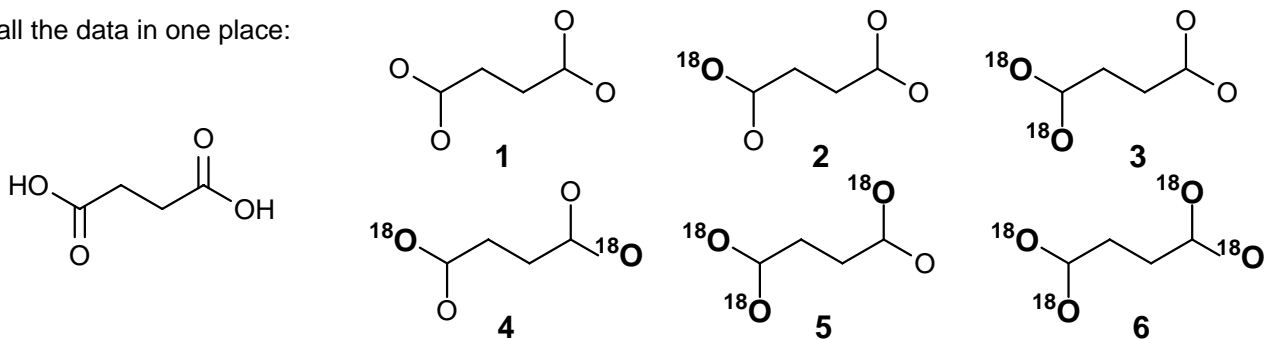
Problem R-09S. The 200 MHz ^{1}H NMR spectrum of a mixture of two selenides (approx a 2:1 ratio) is shown below. The compounds are bis(phenylseleno)methane and bromo(phenylseleno)methane.
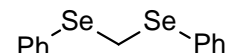
(a) Identify all of the peaks in the region δ 4 to δ 5. Give chemical shifts and any couplings you have identified.

Mixture:

2   δ 4.22, with Se satellites $^2J_{H-Se}$ = 12 Hz - CH$_2$ of PhSeCH$_2$SePh

2   δ 4.72, with Se satellites $^2J_{H-Se}$ = 14 Hz - CH$_2$ of PhSeCH$_2$Br

(b) Identify **two** distinct features of the spectrum which allow you to unambiguously assign which signal corresponds to which compound.

3   Method 1:

Size of the ^{77}Se satellites. The δ 4.22 signal has double-intensity ^{77}Se satellites, thus this signal must be PhSeCH$_2$SePh

3   Method 2:

Integrations: Because the two ortho protons at δ 7.54 and δ 7.64 are present in a ca 1:1 ratio, the compounds must be present in a 2:1 ratio, with twice as much PhSeCH$_2$Br as PhSeCH$_2$SePh, thus the larger CH$_2$ peak must be PhSeCH$_2$Br

Method 3:

Chemical shift calculations: PhSeCH$_2$SePh   PhSeCH$_2$Br

                               1.20   1.20
                               2.15 α-Br   1.55 α-PhSe
                               1.55 α-PhSe   1.55 α-PhSe
                               ⎯⎯⎯   ⎯⎯⎯
               Calculated: 4.90   4.30
               Observed: **4.72**   **4.22**

Method 4:

The integration of the aromatic vs the CH$_2$ protons defines which must be the major isomer: if Br is major then Ar = 5 + 10/2 = 10, CH$_2$ = 2 + 2/2 = 3, hence 3.33/1. If PhSe is major then ArH = 10 + 5/2 = 12.5, CH$_2$ = 2 + 2/2 = 3, hence 12.5/3 = 4.1. Observed is 100/33.66 = 3.06, much closer to Br being the major isomer.

Method 5:

The chemical shift of PhSeCH$_2$SePh is in the handouts!!

Problem R-09S $C_{13}H_{12}Se_2$
200 MHz ^{1}H NMR spectrum.
Solvent CDCl$_3$.
(Source: R. D. Dykstra/Reich 12/26)

PhSeCH$_2$Br

Mixture:

Ph-Se-Br

Ph-Se-Se-Ph

30 20 10 0 Hz

100.00

22.89

9.77

^{77}Se satellites
$^2J_{H\text{-}Se}$ = 14 Hz

PhSeCH$_2$SePh

^{77}Se satellites
$^2J_{H\text{-}Se}$ = 12 Hz

4.7   4.6   4.5   4.4   4.3   4.2
ppm

7.7 7.6 7.5 7.4 7.3 7.2
ppm

9   8   7   6   5   4   3   2   1   0
ppm