Chemistry 605 (Reich)

FIRST HOUR EXAM

Thur, March 9, 2012

Question/Points

R-11A_____/7

R-11B_____/10

R-11C_____/5

R-11D_____/25

R-11E_____/20
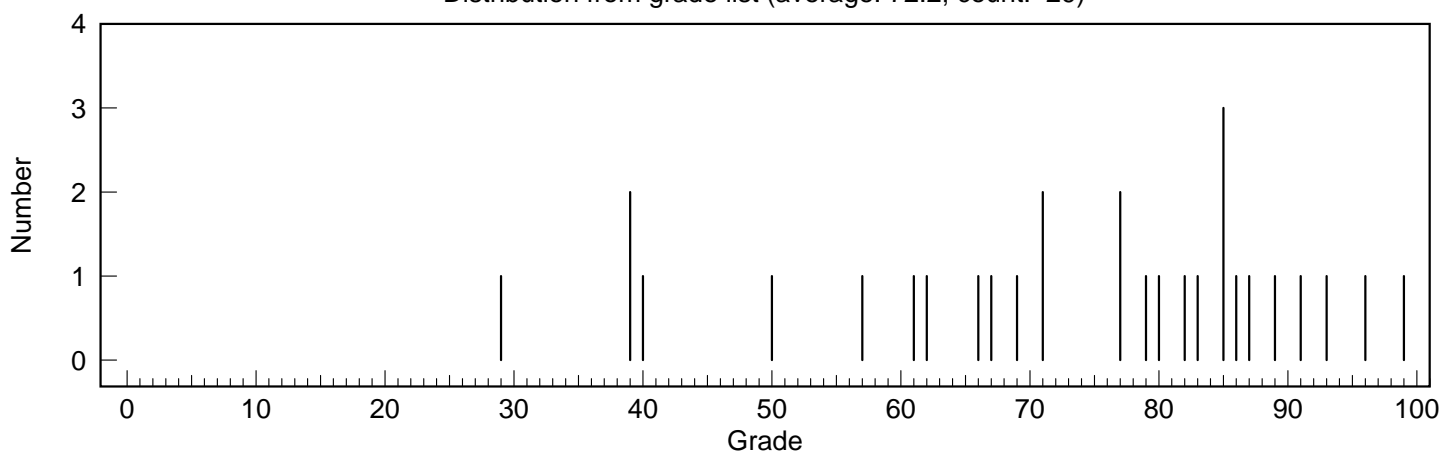
R-11F_____/20

R-11G_____/13

Total _____/100

Hi	99
Average	72
Median	77
AB	82
BC	50
CD	40

Distribution from grade list (average: 72.2; count: 29)


Grading Copy

Name_____

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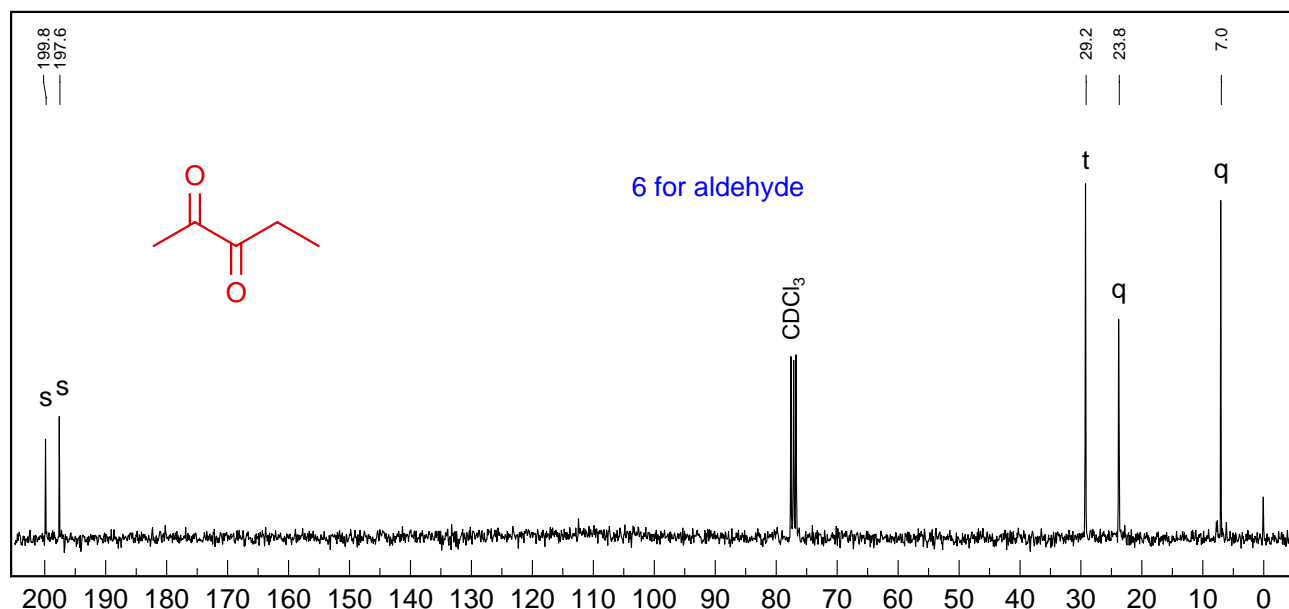or on extra pages) clearly indicate this on the answer sheets.

Problem R-11A. Analyze the muiltiplet below, and report in the standard format

ddt, 17, 11, 5

Suggest a part structure that fits the multiplet, indicate which proton is being observed, and label the structure with J values

7

Hz
40 30 20 10 0

6.15   6.10   6.05   6.00
ppm
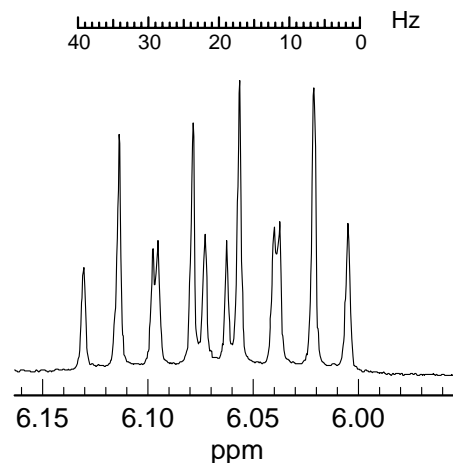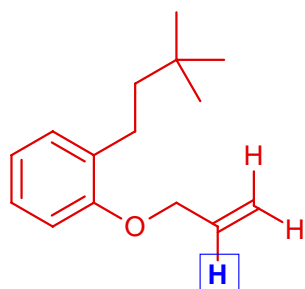
Problem R-11B Determine the structure of the compound $C_5H_8O_2$ whose 75 MHz ^{13}C NMR spectrum is shown below. Assign the carbons.

199.8
197.6

29.2
23.8

7.0

t

q

6 for aldehyde

CDCl₃

q

10

S S

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Problem R-11C. Are the two one-proton multiplets below coupled to each other? What criteria are you using?

No - the leaning is not pronounced enough

This should be halfway between the two if they are coupled to each other

5

8.10 8.05 8.00 7.95 7.90 7.85
ppm
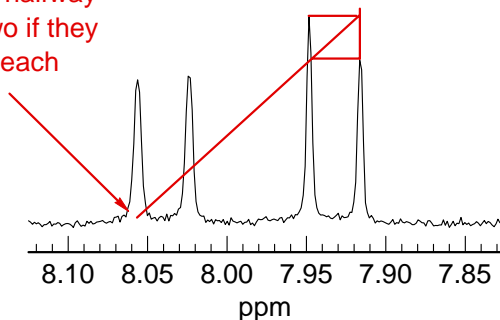
Problem R-11D (C_5H_8O). Determine the structure of **R-10E** from the ^1H NMR, ^{13}C NMR and IR spectra provided.

2   (a) DBE ___2___   (b) What information can you obtain from the IR spectrum (give frequency and peak assignment).

4
3400 cm^{-1} O-H stretch
2120 cm^{-1} C≡C stretch
3300 H-C≡C stretch (not very distinct)

(c) Analyze the ^1H NMR spectrum. For each of the groups of signals marked on the spectrum, report the multiplet structure in the standard format (e.g., 0.0 δ, dtd, J = 0.0, 0.0, 0.0 Hz, 2H) and any part structure you could obtain from the signal(s).

A   δ 1.29, d, J = 6 Hz   CH₃-C̲ H

B   δ 1.93, d J = 5 Hz   H̲-O-C-H   H̲-C-C-H

C   δ 2.08, t J = 3 Hz   H̲-C≡C-CH₂ (small coupling)

7

D   δ 2.34, 2.42, A̲BXY system, J$_{AB}$ = 17, J$_{AX}$ = 6.6 Hz, J$_{AY}$ = 2.5 Hz J$_{BX}$ = 5 Hz, J$_{BY}$ = 2.5 Hz,
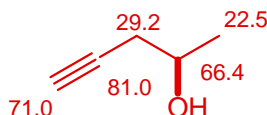
Diastereotopic CH₂, coupled to two protons, one long range, one vicinal

E   δ 3.99, Apparent septet, J= 6 Hz (actually dddq, with all coupling very similar in size)

3.
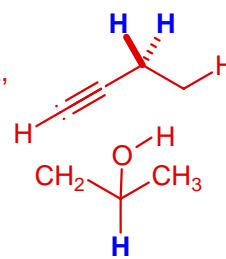
(d) Give your answer below. If more than one structure fits the data, draw them, but indicate your best choice by circling the structure

6

29.2   22.5
81.0   66.4
71.0   OH

(e) The ^{13}C NMR chemical shifts are listed below. Write the δ values on your structure.

δ
22.5
29.2
66.4
71.0
81.0

2

(f) To confirm your assignment (and structure) calculate the chemical shifts of the carbons in your structure assigned to the 29.2 and 66.4 signals. Use a suitable model compound, and appropriate chemical shift Δδ values.

4

H
68.2
83.6
20.1
22.1
13.1

20.1 + β(OH)-iso = 20.1 + 8 = 28.1 (obs 29.2)
      (if use "iso" value, don't need branching - already included)

22.1 + α(OH)iso = 22.1 + 42 = 64.1 (obs 66.4)

JMR-76-521
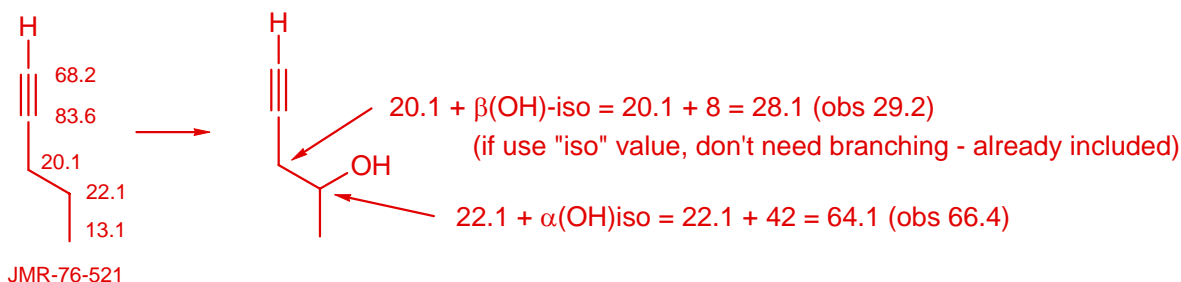
Problem R-11D (C$_5$H$_8$O)

300 MHz ^{1}H NMR Spectrum in CDCl$_3$

(Source: Rob Risi/Burke 03/42)

Hz

40 30 20 10 0

3.43

D   C   B

2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10 2.05 2.00 1.95 1.90 1.85

ppm

2.13

0.95 0.96

E

A

4.05 4.00 3.95 3.90

ppm

1.00

1.30 1.25

ppm

E   D C B   A

9   8   7   6   5   4   3   2   1   0

ppm
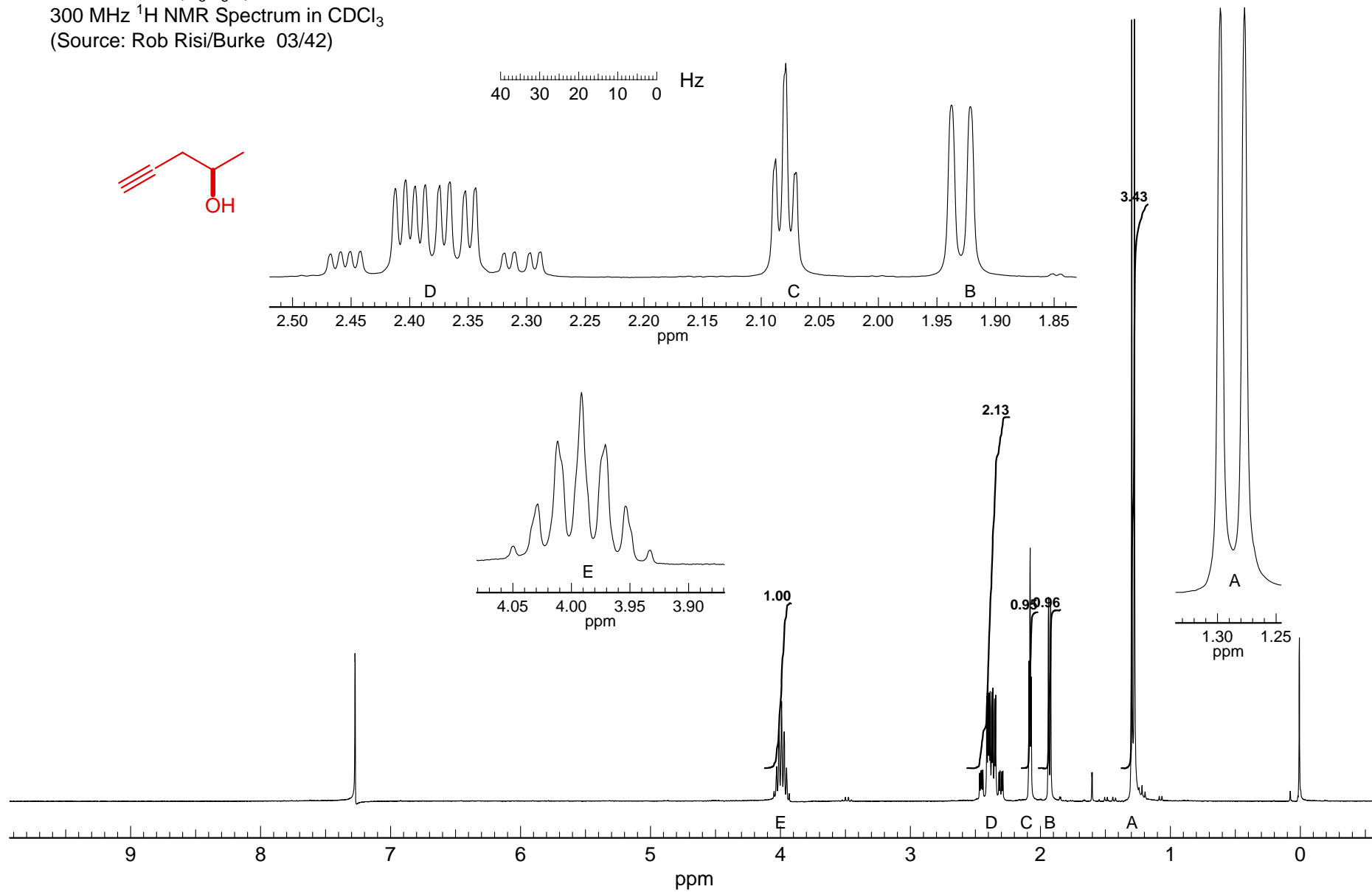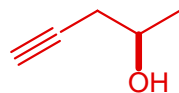
Problem R-11D (C_5H_8O)
 75.4 MHz ^{13}C NMR Spectrum in $CDCl_3$
 (Source: Rob Risi/Burke 03/42)

81.0
71.0
66.4
29.2
22.5

ppm

200   180   160   140   120   100   80   60   40   20   0
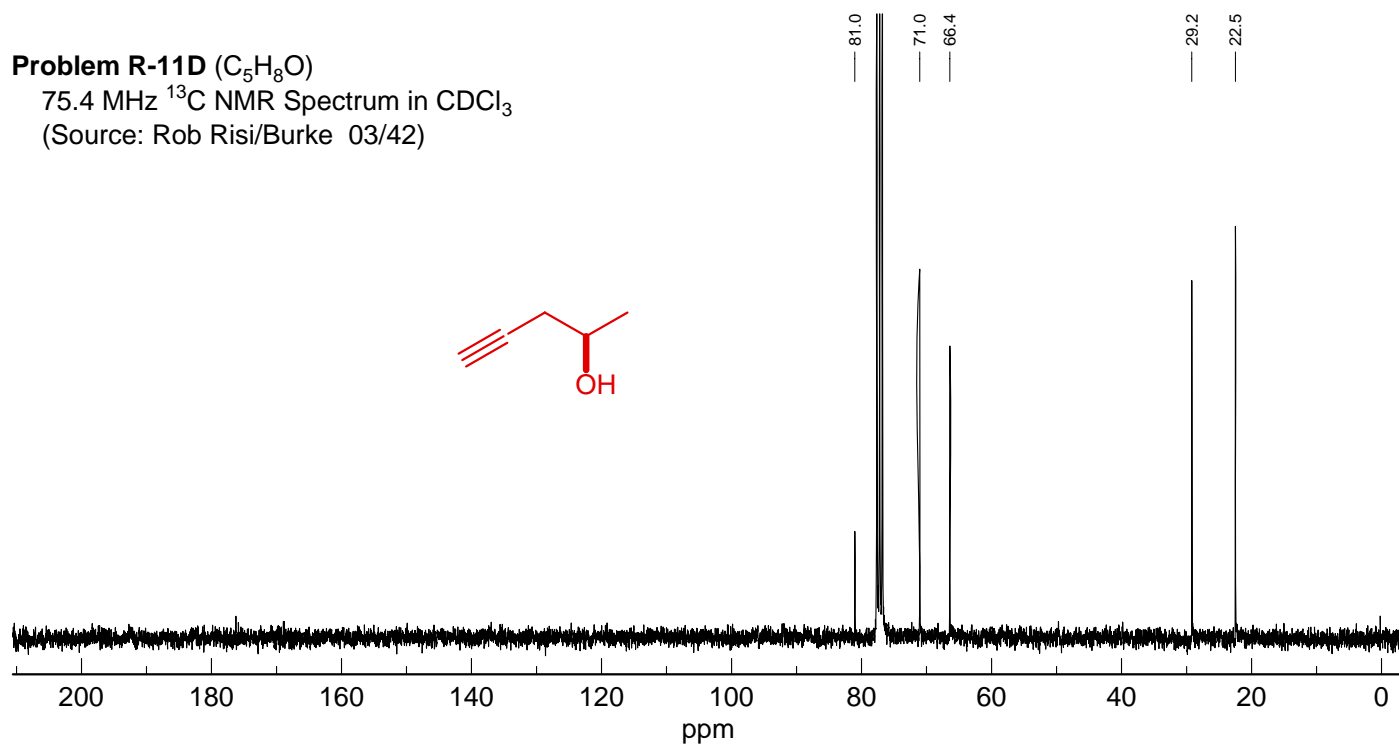
Problem R-11D (C_5H_8O)
 IR Spectrum (neat liquid)
  (Source: Rob Risi/Burke 03/42)

Transmittance [%]

BRUKER

3299.21
2974.38
2933.77
2915.05
2119.56
1636.07
1457.51
1420.51
1377.58
1350.56
1309.57
1215.97
1116.88
1087.73
958.49
937.33
829.91
629.99

3500   3000   2500   2000   1500   1000

Wavenumber cm-1
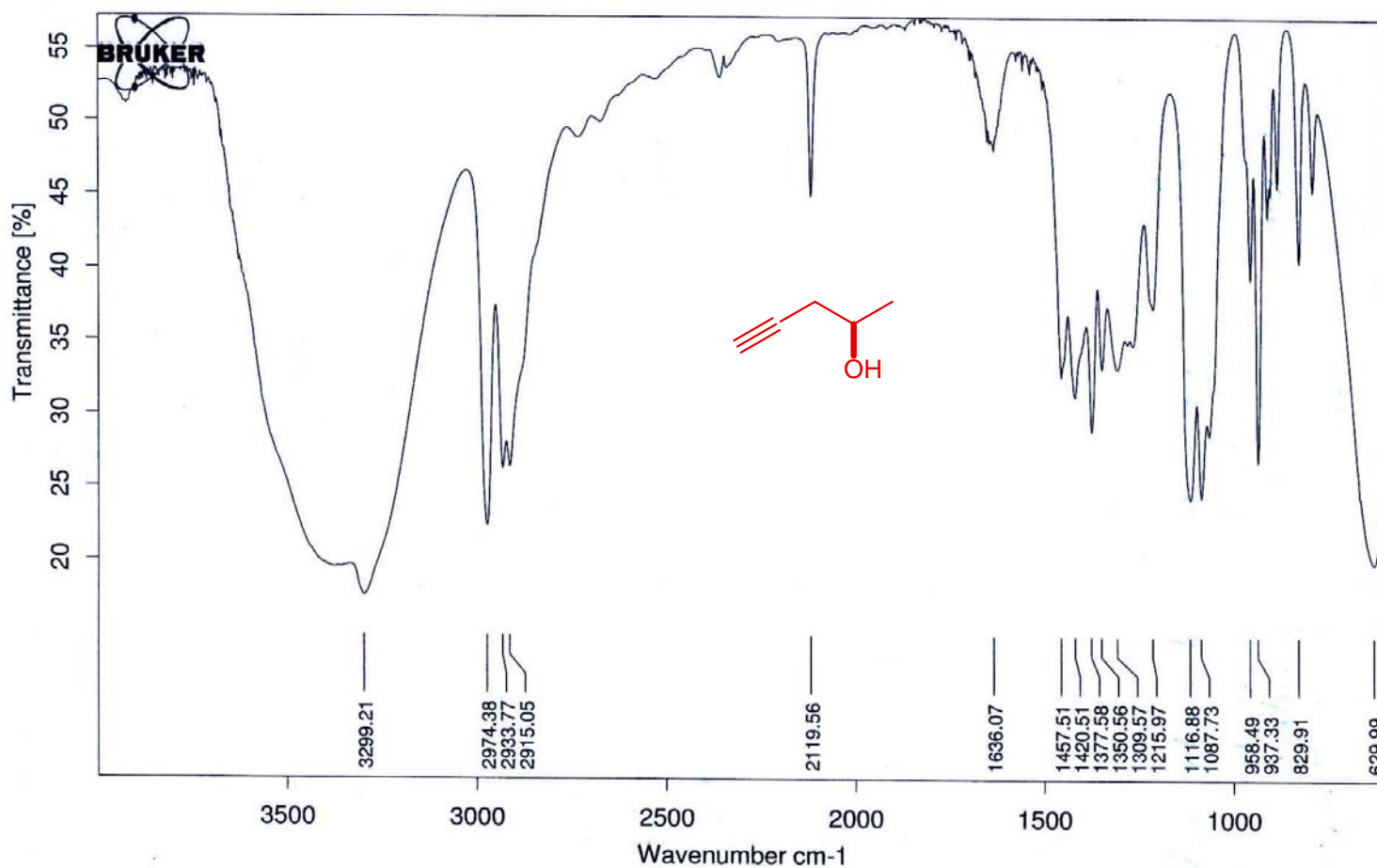
Problem R-11E ($C_{11}H_9IO$). You are provided the ^1H NMR spectrum of a disubstituted naphthalene (**the substituents are methoxy and iodo**). You are required to analyze the NMR spectrum, and determine the structure or structures.
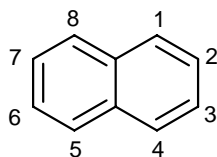
(a) For each of the 8 positions on the naphthalene as defined above, give either the substituent at that position, or the NMR signal (δ, multiplicity and J values). If there is more than one plausible structure assignment, draw the alternative structure, and indicate your preference. To make grading easier, **please place the methoxy substituent at either 1 or 2**.

key multiplet

10 points for considering both

8 points for one or the other

1	7.03, d, J = 2.5 Hz
2	**OCH₃**
3	7.19, dd, J = 9, 2.5 Hz
4	7.97. d (t), J = 9 (<1) Hz
5	**I**
6	7.90, dd, J = 7.5, 1.5
7	7.07, dd, J = 8, 7,5
8	7.68, d(t), J = 8 (~1) Hz

8

8 points for considering both

6 points for one or the other

key multiplet

or

(b) Briefly describe the key evidence that led to your structure assignment.

The substituents must be in different rings, otherwise would see two td (o,o,m) from protons in the unsubstituted ring

2
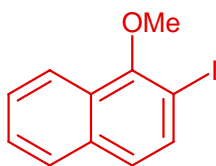
The d (J=2.3 Hz) at 7.03 means that one substituent must be at a β position, the upfield shift means this is ortho to OMe (δ_o = -0.45 in benzene, -0.7 in naphthalene)

The big dd (J = 8, 7.5) means the other substituent has to be at peri position (5 or 8). Deciding among these is hard, since only long-rang couplings distinguish them.

Problem R-11E (C₁₁H₉IO)
  250 MHz ¹H NMR Spectrum in CDCl₃
  (Source: Adam Fiedler/Reich 10/29)

This is only d that
matches J with the
7.07 dd - thus 3

6 is coupled only to
7 and 8 - no other
long range
coupling

8 has more long-range
coupling opportunities
(to 4 and 1)
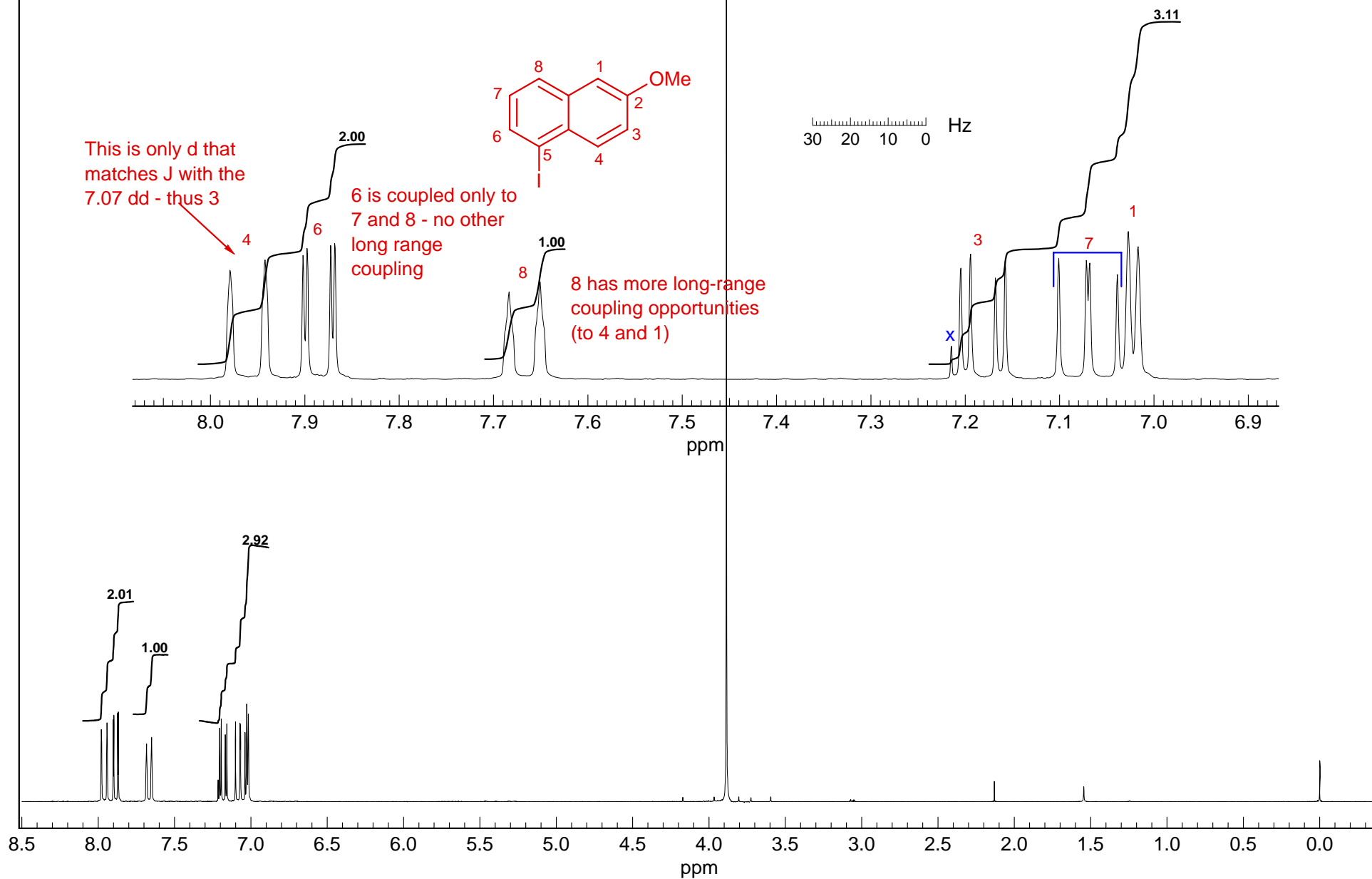
Problem R-11F ($C_5H_5ClN_2$). The 300 MHz NMR spectrum of of a disubstituted pyridine is shown below (the complete spectrum on the next page. This means there are three aromatic protons, which form an ABX pattern.
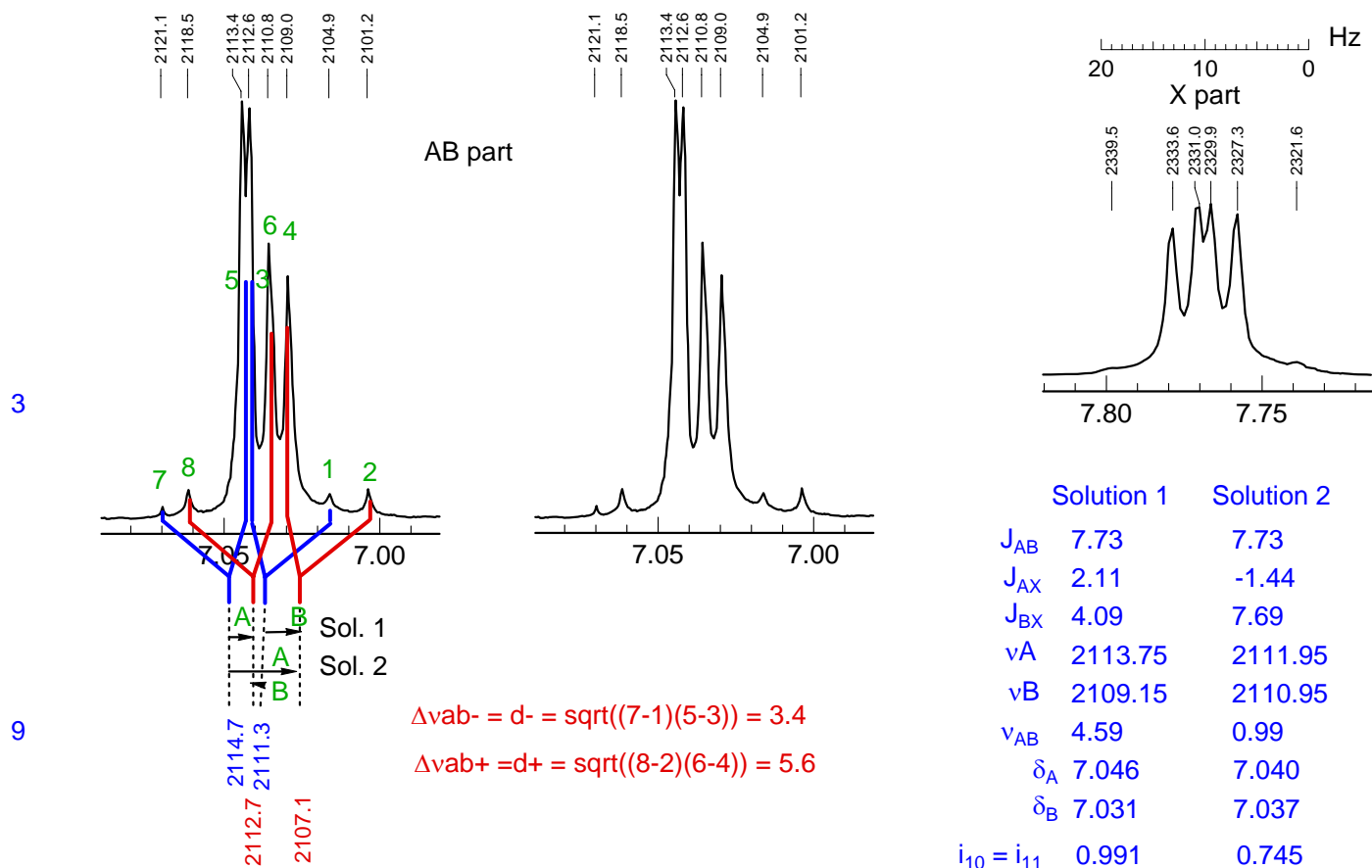
(a) Do an accurate calculation and determine couplings and chemical shifts, and **tabulate your results in an easily readable format**. If there are two solutions, report them both, and draw coupling trees on the spectra. For your convenience two copies of the AB part of the spectrum are shown.

AB part

Labels on AB spectrum: 2121.1, 2118.5, 2113.4, 2112.6, 2110.8, 2109.0, 2104.9, 2101.2

X part labels: 20 10 0 Hz

X part peak labels: 2339.5, 2333.6, 2331.0, 2329.9, 2327.3, 2321.6

7.80   7.75

7.05   7.00

A   B   Sol. 1
A   Sol. 2
B

2114.7 2111.3
2112.7 2107.1

$\Delta\nu ab- = d- = \sqrt{((7-1)(5-3))} = 3.4$

$\Delta\nu ab+ = d+ = \sqrt{((8-2)(6-4))} = 5.6$

|	Solution 1	Solution 2
J_{AB}	7.73	7.73
J_{AX}	2.11	-1.44
J_{BX}	4.09	7.69
νA	2113.75	2111.95
νB	2109.15	2110.95
ν_{AB}	4.59	0.99
δ_A	7.046	7.040
δ_B	7.031	7.037
$i_{10} = i_{11}$	0.991	0.745

(b) If you are proposing two solutions, suggest at least one criterion which allows you to identify the correct one.

This must be solution 1:

1. The outer peaks would have to be 25% of the tallest peaks, they are barely visible
2. One of the couplings would have to be negative, in pyridines all couplings are positive
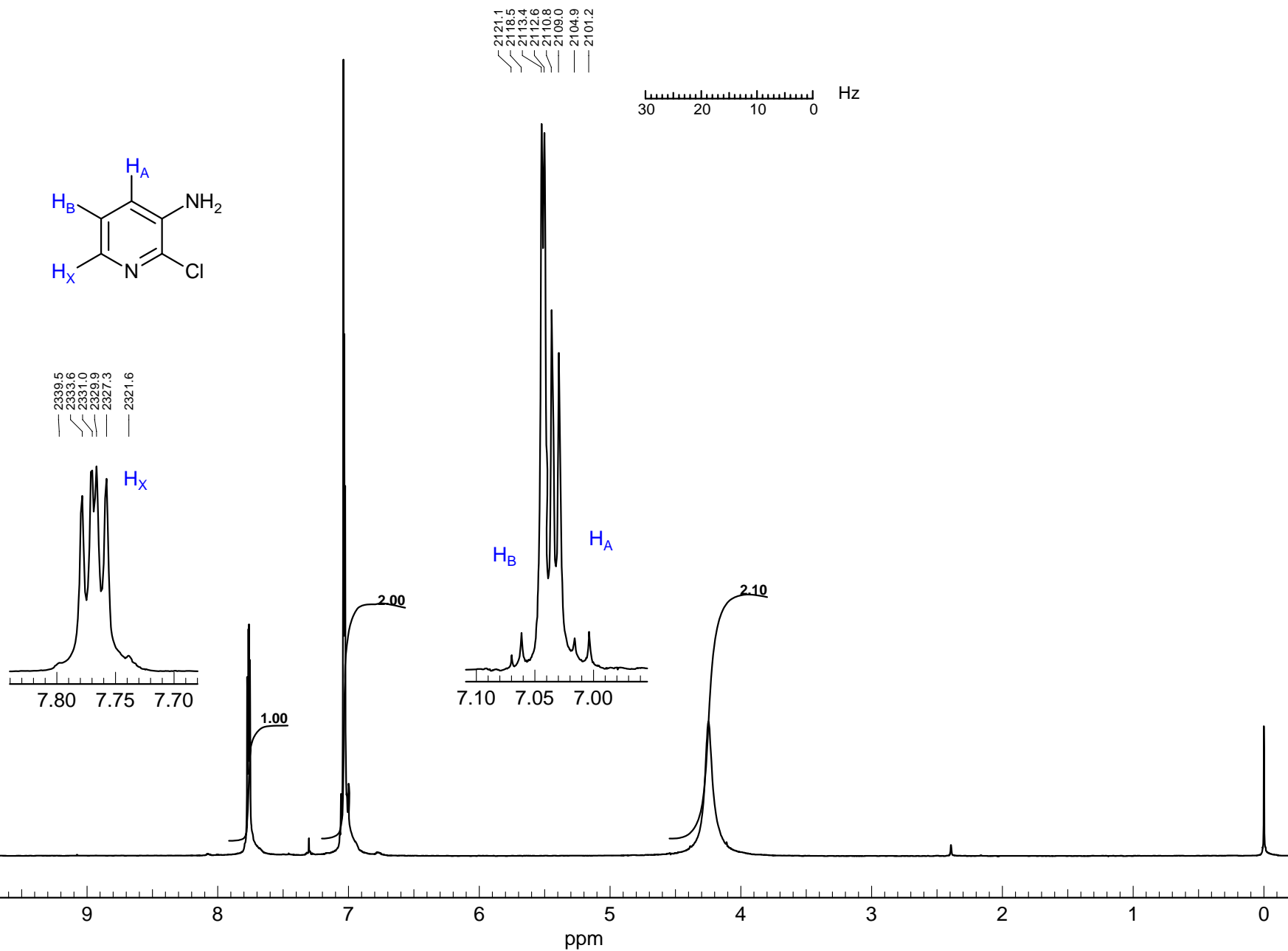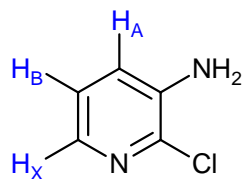3. Size of the ortho-couplings fits better - J2,3 is small, Sol 2 requires both be large - 7.73 and 7.66

(c) Which of the following structures best fits the NMR J and δ values?. Label your preferred structure with H_A, H_B and H_X. For your convenience, the typical coupling constants in pyridines are reproduced below.
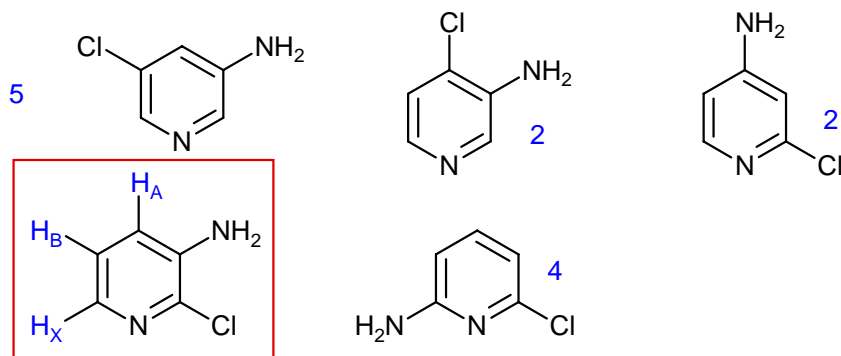
|	
$^3J_{34}$	6.9 to 9.1
$^3J_{23}$	4.0 to 6.0
$^4J_{24}$	0 to 2.7
$^4J_{35}$	0.5 to 1.8
$^4J_{26}$	0 to 0.6
$^5J_{25}$	0 to 2.3

All coupling constants are positive

Problem R-11F ($C_5H_5ClN_2$)
300 MHz ^{1}H NMR Spectrum in CDCl$_3$
Source: Aldrich Spectral Viewer/Reich

2121.1
2118.5
2113.4
2112.6
2110.8
2109.0
2104.9
2101.2

Hz
30   20   10   0

H$_A$
H$_B$
NH$_2$
H$_X$
N
Cl

2339.5
2333.6
2331.0
2329.9
2327.3
2321.6

H$_X$

H$_B$
H$_A$

2.00

2.10

7.80 7.75 7.70

7.10 7.05 7.00

1.00

1.00

10   9   8   7   6   5   4   3   2   1   0
ppm

Problem R-11G ($C_{24}H_{24}Se$) This problem requires you to determine which isomer is which from the ^{13}C NMR spectra of cis and trans 3,5-diphenyl-1-phenylselenocyclohexane.

(a) Assign the signals 0-50 ppm for both isomers (place the δ values on the structures below). Briefly explain how you made the assignments.

6

SePh
44.3
38.8
39.8
Ph   Ph
41.4

Spectrum A

SePh
41.8
41.2
45.1
Ph   Ph
41.0
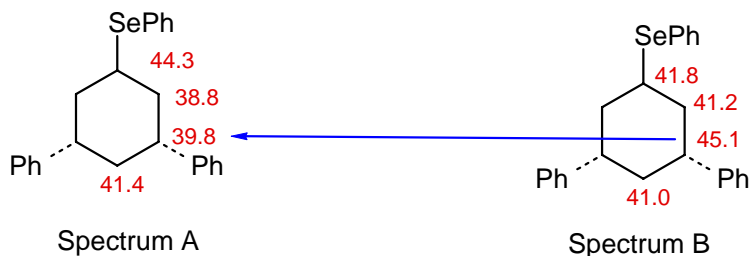
Spectrum B

Assignments are unambiguous - there is one double intensity CH, and one single-intensity CH, same for CH_2

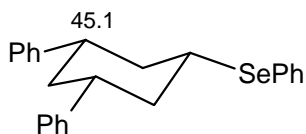(b) Identify a key feature in the spectra which allows identification of which spectrum corresponds to the cis isomer and which to the trans isomer. Explain your reasoning.

3

cis isomer
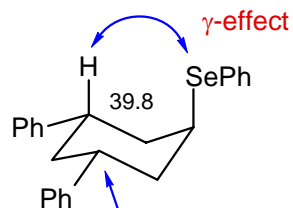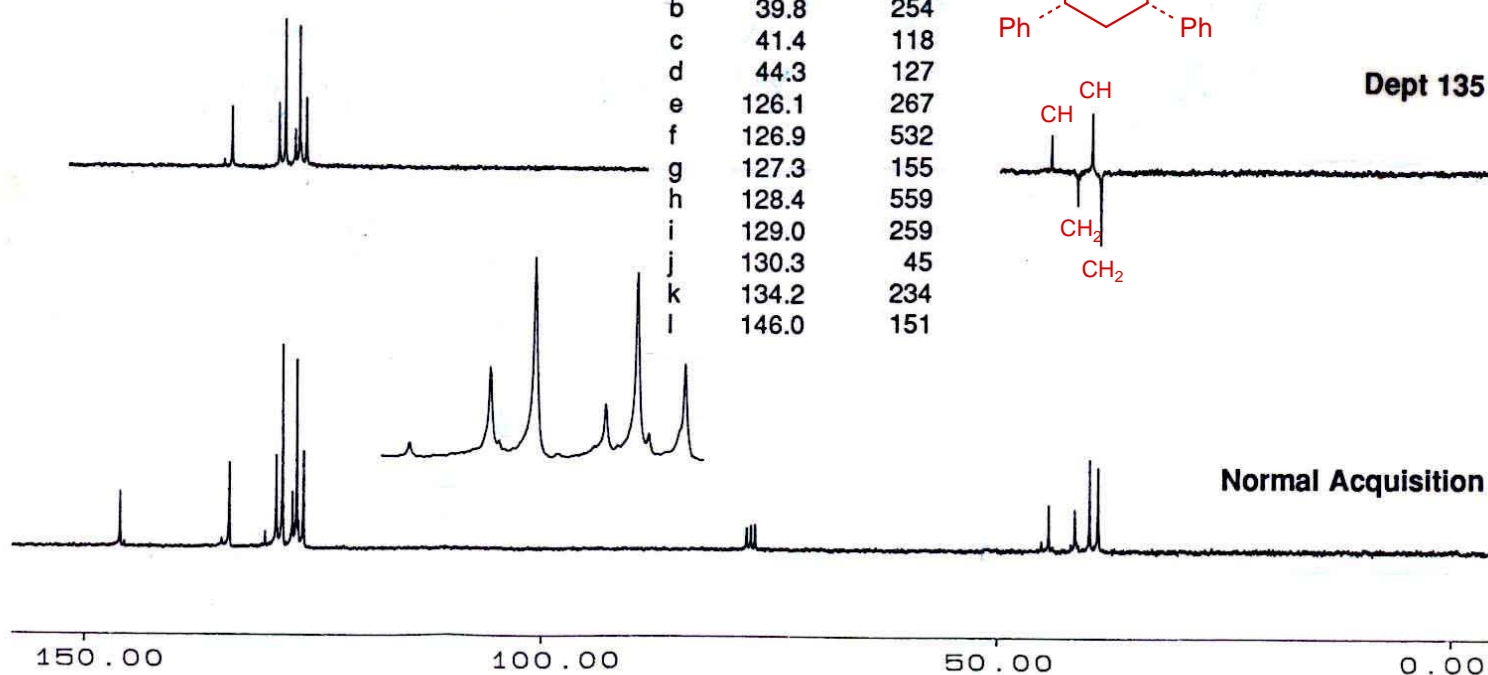SePh

Ph   Ph

Spectrum __B__

trans isomer
SePh

Ph   Ph

Spectrum __A__

4

45.1
Ph
SePh
Ph
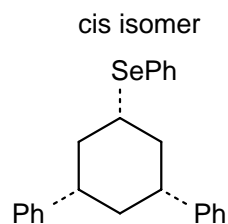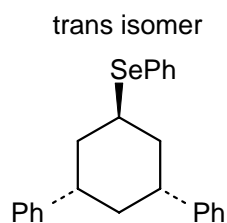
γ-effect
H   SePh
39.8
Ph
Ph

Arguments based on α and β effects are weaker

These should be upfield due to γ-effect of axial PhSe group

Problem R-11G ($C_{24}H_{24}Se$) **Isomer A**
  67.5 MHz ^{13}C NMR Spectra in $CDCl_3$
  The upper spectrum is a DEPT 135 spectrum
  (CH_2 negative, CH and CH_3 positive)
  (Source: Mike Bowe/Reich 12/20)

	δ	Intensity
a	38.8	232
b	39.8	254
c	41.4	118
d	44.3	127
e	126.1	267
f	126.9	532
g	127.3	155
h	128.4	559
i	129.0	259
j	130.3	45
k	134.2	234
l	146.0	151

Dept 135

Normal Acquisition

150.00   100.00   50.00   0.00

Problem R-11G ($C_{24}H_{24}Se$) **Isomer B**
  67.5 MHz ^{13}C NMR Spectra in $CDCl_3$
  The upper spectrum is a DEPT 135 spectrum
  (CH_2 negative, CH and CH_3 positive)
  (Source: Mike Bowe/Reich 12/20)

	δ	Intensity
a	41.0	104
b	41.2	181
c	41.8	94
d	45.1	188
e	126.2	209
f	126.7	406
g	127.5	108
h	128.4	419
i	128.5	82
j	128.9	206
k	135.0	183
l	145.6	115

Dept 135

Normal Acquisition

150.00   100.00   50.00   0.00