Chemistry 605 (Hans J. Reich)

THIRD HOUR EXAM

Mon. May 14, 2012

Question/Points

R-11P_____/15

R-11Q_____/15

R-11R_____/20

R-11S_____/10

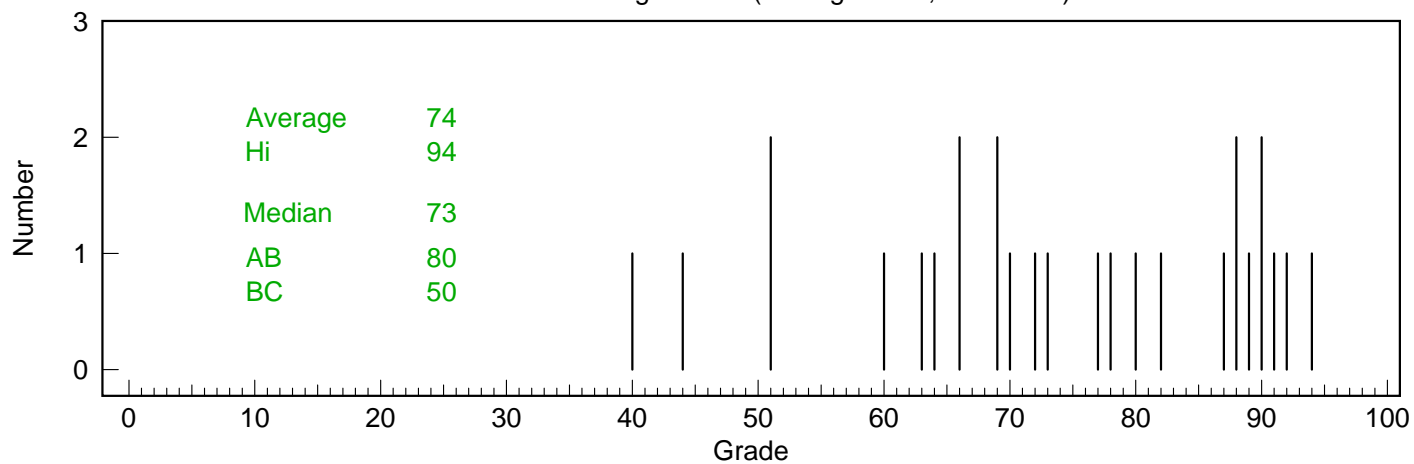R-11T_____/20

R-11U_____/20

Total _____/100

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.

Distribution from grade list (average: 73.5; count: 27)

Average	74
Hi	94
Median	73
AB	80
BC	50

Problem R-11P (C$_8$H$_8$F$_2$Si. Below is a 300 MHz ^{1}H NMR spectrum of vinyl difluorophenylsilane (source: Josh Dykstra/Burke). Analyze the spectrum, and label the spectrum with coupling trees, and label them with H$_g$, H$_c$ and H$_t$. Report all coupling in the standard format ($^nJ_{X-Y}$ = 00.0 Hz). Apart from intensities, the spectrum is basically first order .
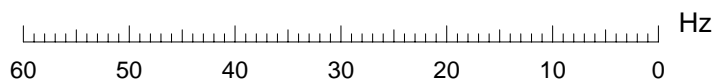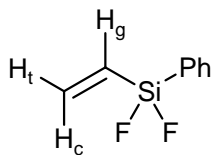
5 pts each
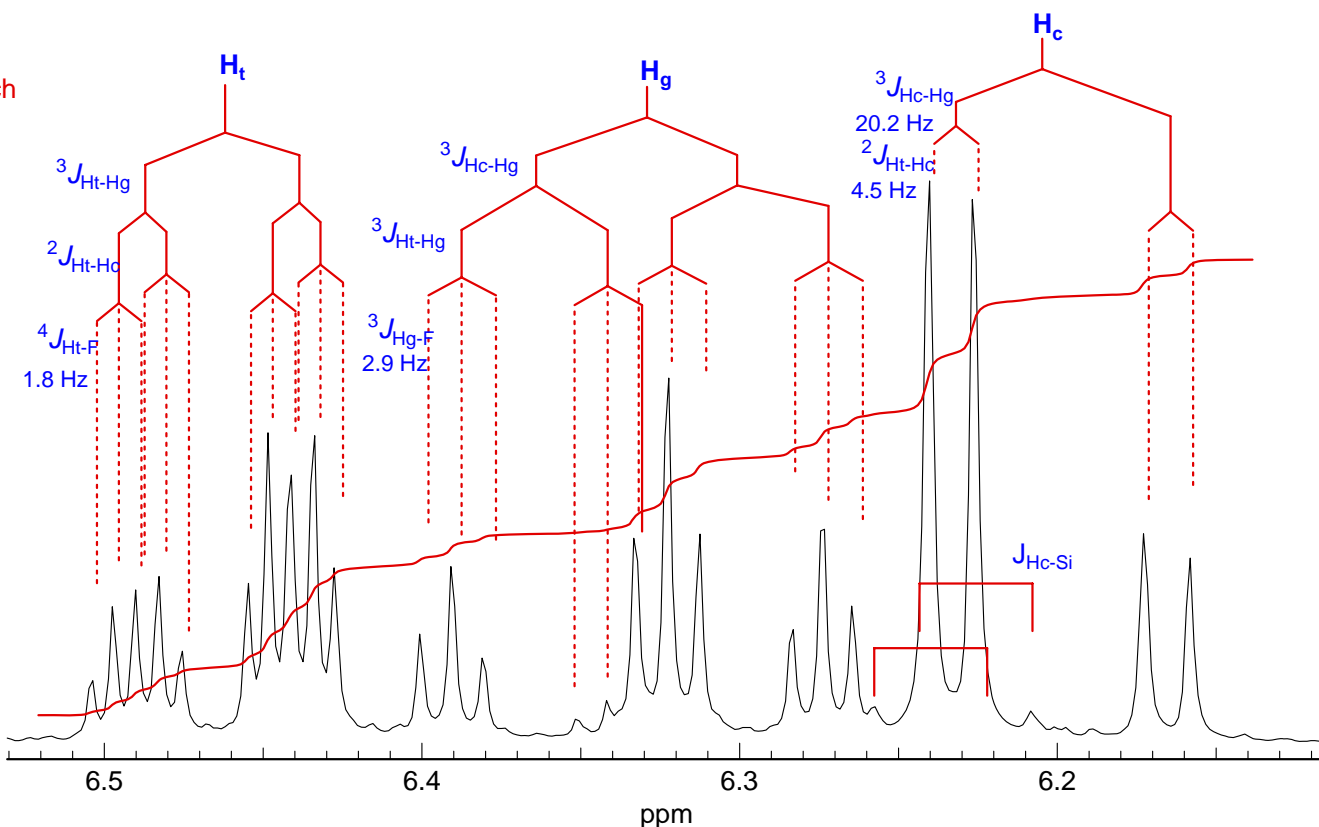
$^2J_{Ht-Hc}$ = 4.5 Hz

$^3J_{Ht-Hg}$ = 20.2 Hz

$^3J_{Hg-F}$ = 2.9 Hz

$^4J_{Ht-F}$ = 1.8 Hz

There are also a number of small peaks from ^{29}Si coupling to the various protons. Pretty indistinct - hard to be sure which might be impurities because usually can't see both satellites.

The strange intensities of the middle peak is confirmed by a simulation
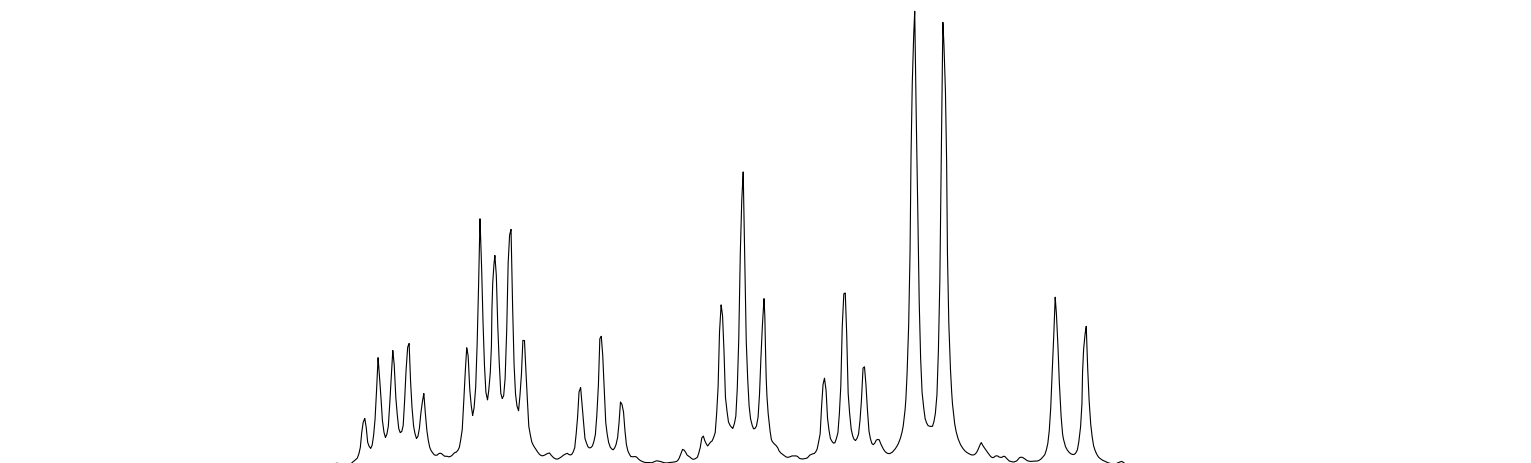
Problem R-11Q ($C_{11}H_{19}NO_8$). This problem requires you to determine the stereochemistry of two isomers of sialic acid (**A** and **B**). Below is shown a portion of the 126 MHz ^{13}C NMR spectrum (D_2O solvent) of a 10:1 mixture of two isomers (Hori, H.; Nakajima, T.; Nishida, Y.; Ohrui, H.; Meguro, H. *Tetrahedron Lett.* **1988**, *29*, 6317). Spectrum 1 is the fully proton decoupled. Spectrum 2 has the decoupler turned off.
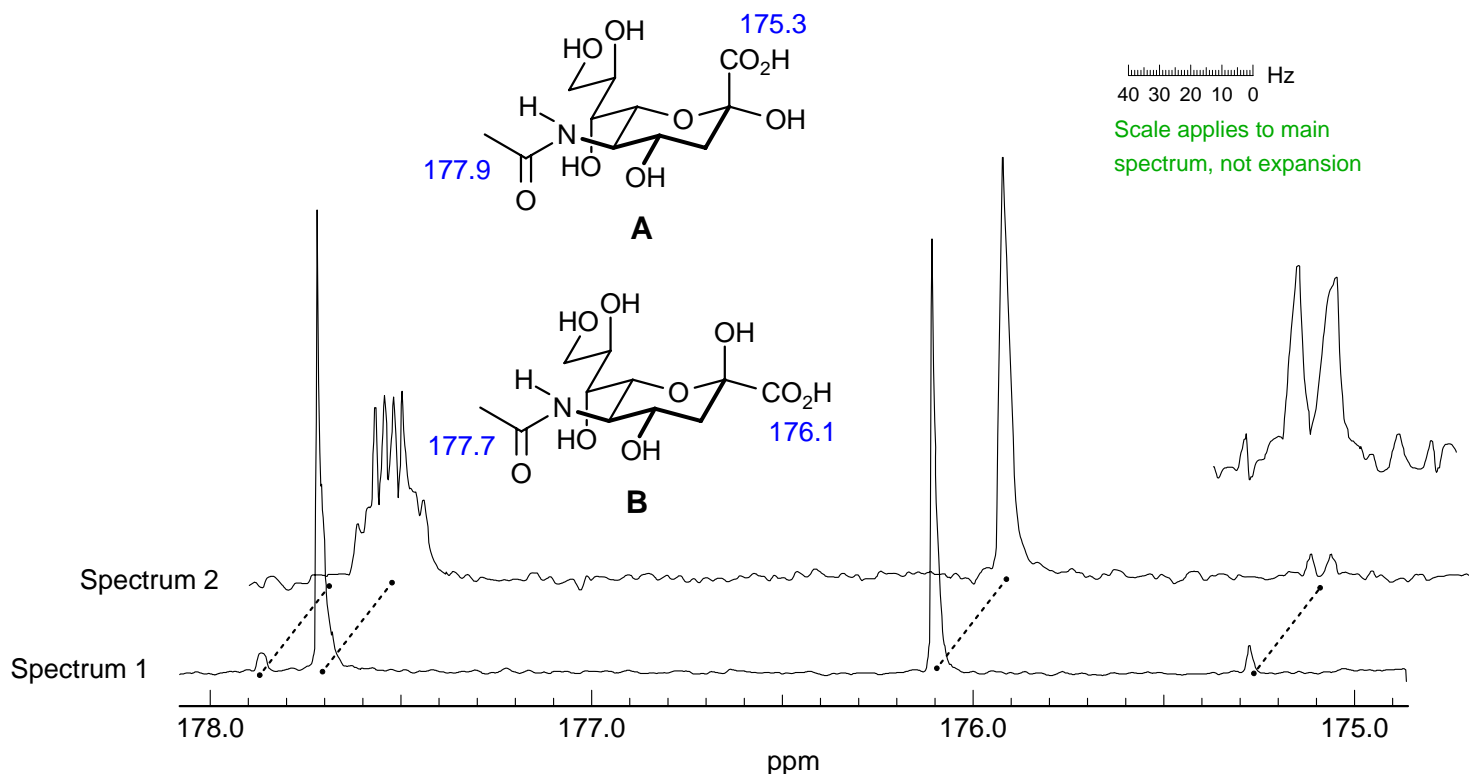
(a) Which carbons of the sialic acid are being shown here? Mark the shifts on the structures.

4

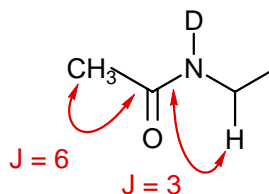Carbonyl peaks - amide at 177.7 and 177.9 ppm, carboxylic acid at 176.1 and 175.3 ppm

(b) Interpret the multipicity of the signal at 177.7 ppm in the coupled spectrum (2). Estimate coupling constants, and assign them.
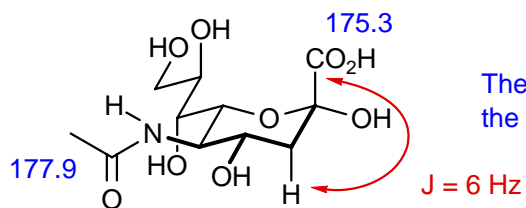
4

qd, J = 6, 3 Hz

Thus this must be the amide carbonyl - coupled to CH_3 (6 Hz) and the N-C-H proton (3 Hz). Coupling cannot be to N-H proton since in D_2O this would be N-D.
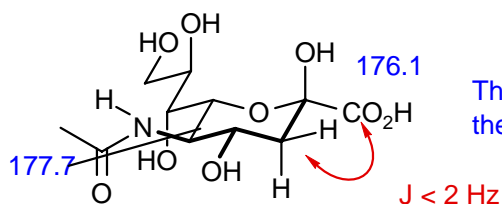

4 (c) Which is the major isomer (A or B)?___**B**___ Give your reasoning below. Be specific and brief.

3

The minor isomer (δ 175.3) has a $^3J_{CH}$ coupling between the vicinal axial C and the axial H of 6 Hz.

The major isomer has no significant ^3J coupling to either of the vicinal C-H protons - Karplus angle is ca 60°

Problem R-11R ($C_{18}H_{22}Se_2$) You are given the structure, and asked to interpret the spectrum (complete spectrum on next page).

(a) Analyze the multiplet at δ 2.1 and report couplings.

4

Septet of doublets, $^3J_{H\text{-}H}$ = 6.5, 3 Hz (H_D)

No Se satellites due to $^3J_{HD\text{-}Se}$ can be seen here (satellites of the larger inner peaks are buried under the outer ones)
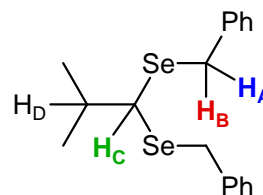
(b) Analyze the multiplet at δ 3.7. Identify all peaks. Obtain exact shifts and report all shifts and couplings in the form: δ 0.00, $^nJ_{XY}$ = 00 Hz. An enlarged copy of the multiplet is shown below. The Hz values are from TMS at 0 Hz.

6 Main feature is the AB quartet (H_A, H_B) of the diastereotopic $Se\text{-}CH_2\text{-}Ph$ group.

764, 753, 749, 738 Hz (marked with • and •)

J_{AB} = 754-753 = 11Hz; 749-738 = 11 Hz

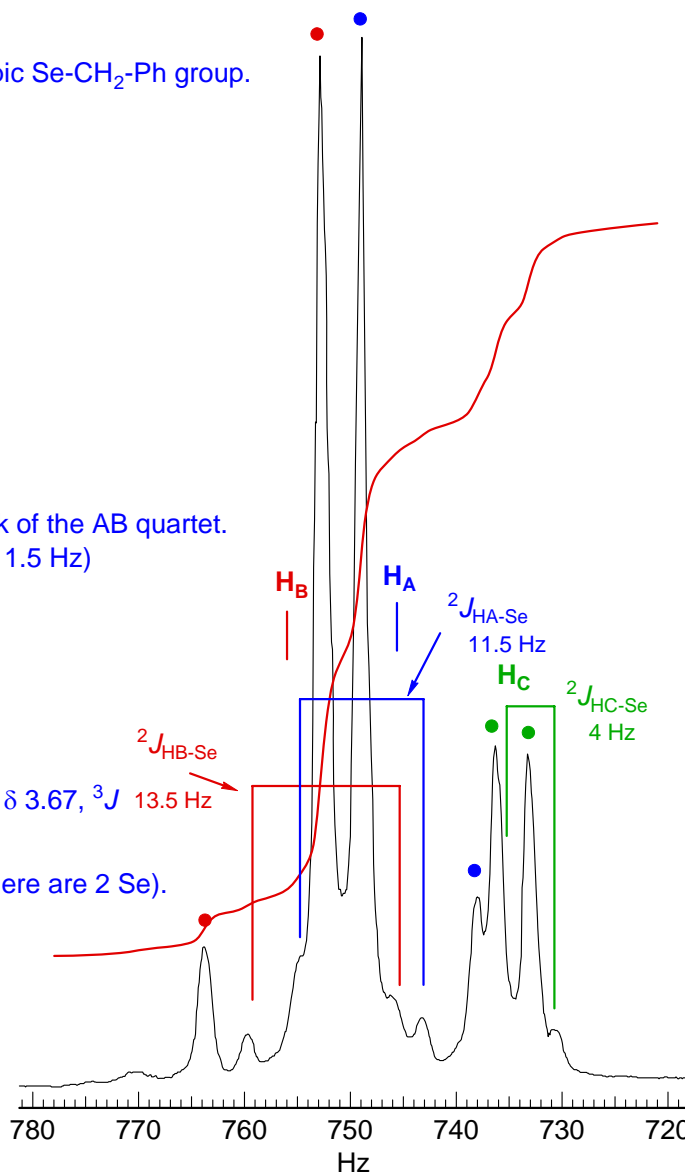Solve the AB quartet:

ν_{AB} = 10.2 Hz, ν_{center} = 751 Hz

ν_A = 751-5.1 = 746 Hz, δ 3.73

ν_B = 751+5.1 = 756 Hz, δ 3.78

5

There are selenium satellites on both sides of each peak of the AB quartet. The $^2J_{HSe}$ if slightly larger for H_B (13.5 Hz) than for H_A (11.5 Hz)

3

There is also a doublet for H_C at 735 Hz (marked with •) δ 3.67, ^3J 13.5 Hz = 3 Hz (to H_D)

2

One satelline only is visible (double intensity because there are 2 Se). It is about 2 Hz from central peak, so $^2J_{HC\text{-}Se}$ = 4 Hz.

Problem R-11R $C_{18}H_{22}Se_2$
200 MHz ^1H NMR spectrum.
Solvent $CDCl_3$.
(Source: Bob Dykstra/HJR 12/25)

Hz
30   20   10   0

3.9   3.8   3.7   3.6
ppm

2.2   2.0

1.0   0.9

10.26

5.09

1.11

6.00

9   8   7   6   5   4   3   2   1   0
ppm
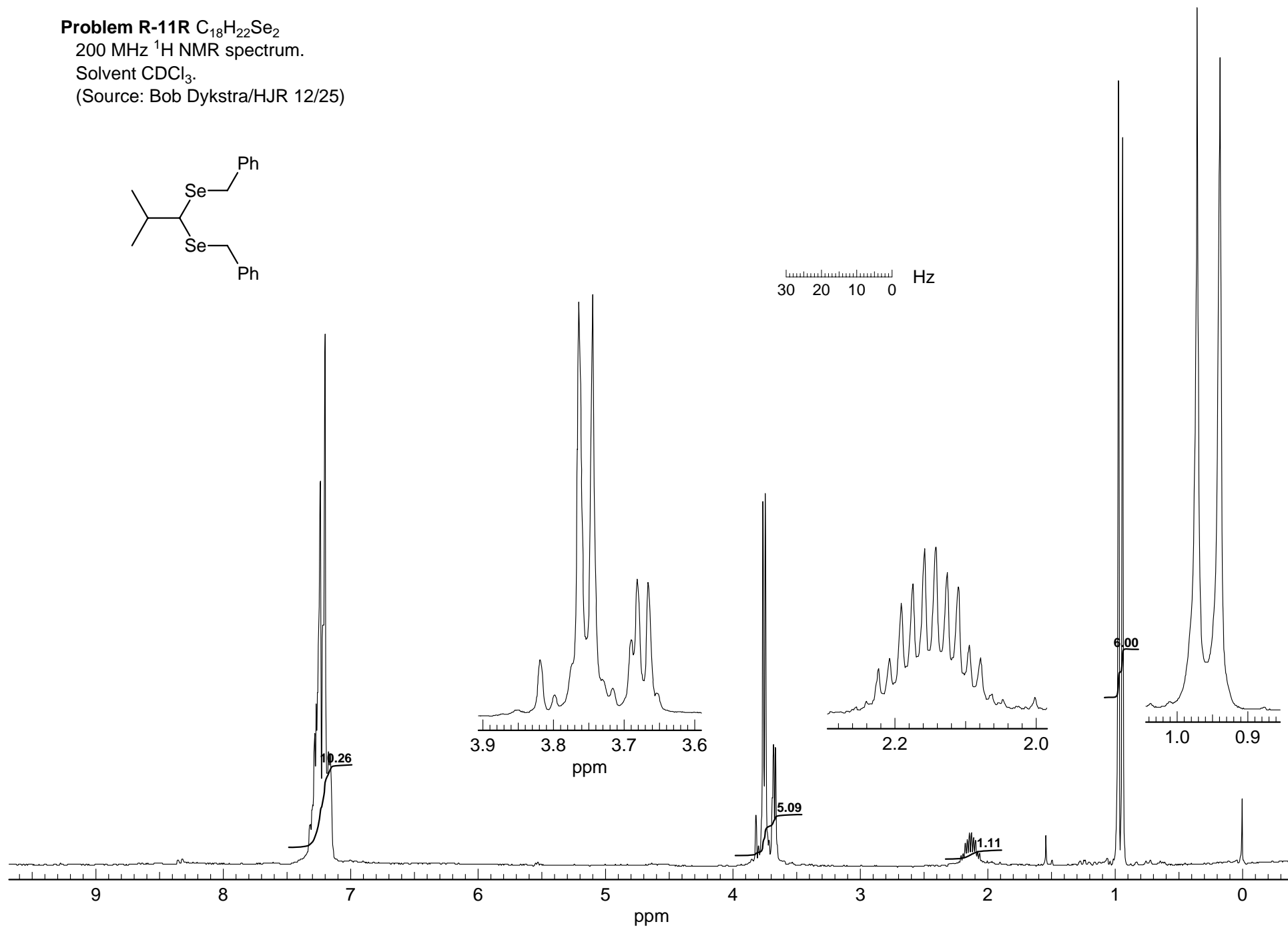
Problem R-11S ($C_{16}H_{22}Fe_2O_2P_2$). Below are the 60 MHz ^1H NMR spectra of two stereoisomers (E and Z) of the iron Cp complexes shown (*J. Am. Chem. Soc* **1963**, *85*, 3120).
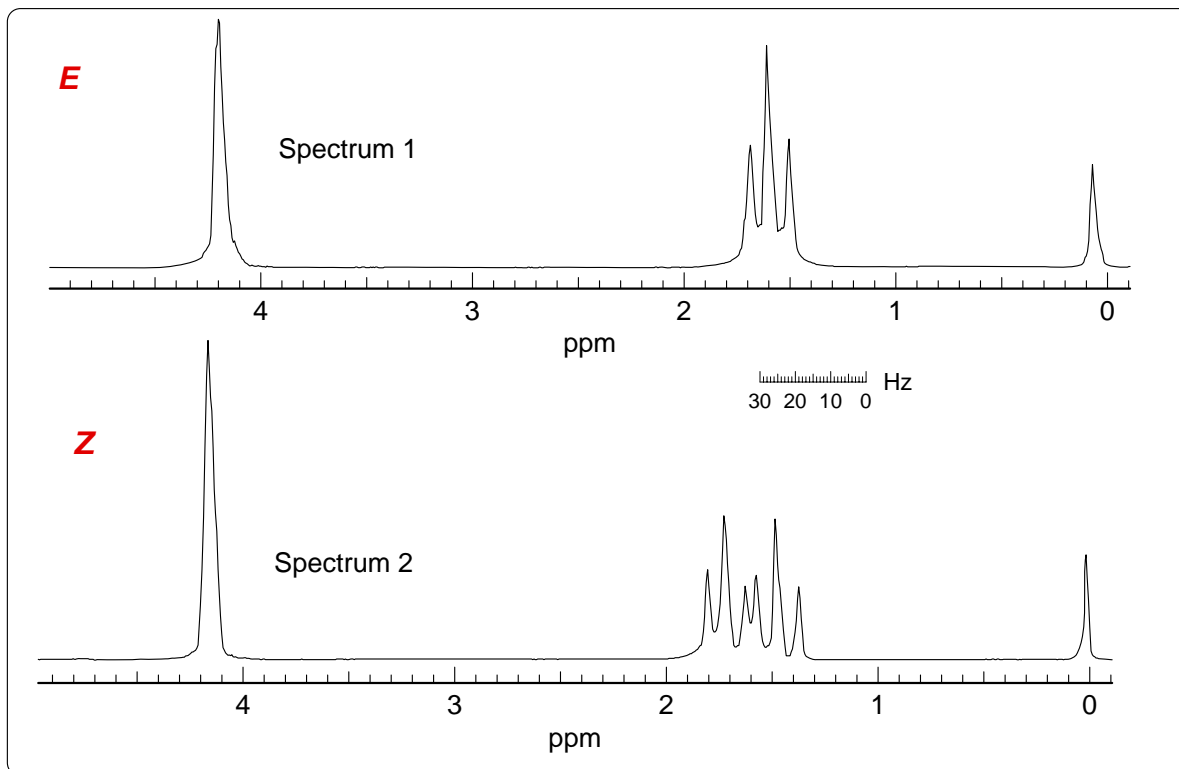
(a) Which isomer corresponds to Spectrum 1 __*E*__, and which to Spectrum 2 __*Z*__? Explain

4

This is a simple symmetry argument - in the *Z* isomer the PMe$_2$ group is diastereotopic, so two triplets are seen. In the *E* they are identical (related by a C_2 axis).

(b) Explain the appearance of the multiplet at δ 1.6 (i.e. why does it look like this).

4

In the absence of other effects, the methyl groups should be coupled to one ^{31}P nucleus, hence a doublet. If the 4-bond coupling to the remote P was large enough, one would expect to see a dd. One sees a triplet because there is a large *J* between the two ^{31}P nuclei, so anything coupled to them will show "virtual coupling" effects - i.e. the methyl group *appears* to be coupled equally to both P.

(c) Would you expect the spectrum to look significantly different at 300 MHz (instead of the 60 MHz of the spectra shown)?

2

Apart from a larger separation between the two triplets in Spectrum 2, there would be no difference - the chemical shift between the P nuclei is zero at all fields, so the "virtual couplings" effect will always be there.

Problem R-11T ($C_{19}H_{25}FO_2$). Below are part of the 60 MHz ^{1}H NMR spectra of two stereoisomers (**A** and **B**) of the fluorinated steroids shown. To aid in your analysis, a conformational drawing is also provided (*J. Am. Chem. Soc.* **1963**, *85*, 3038).
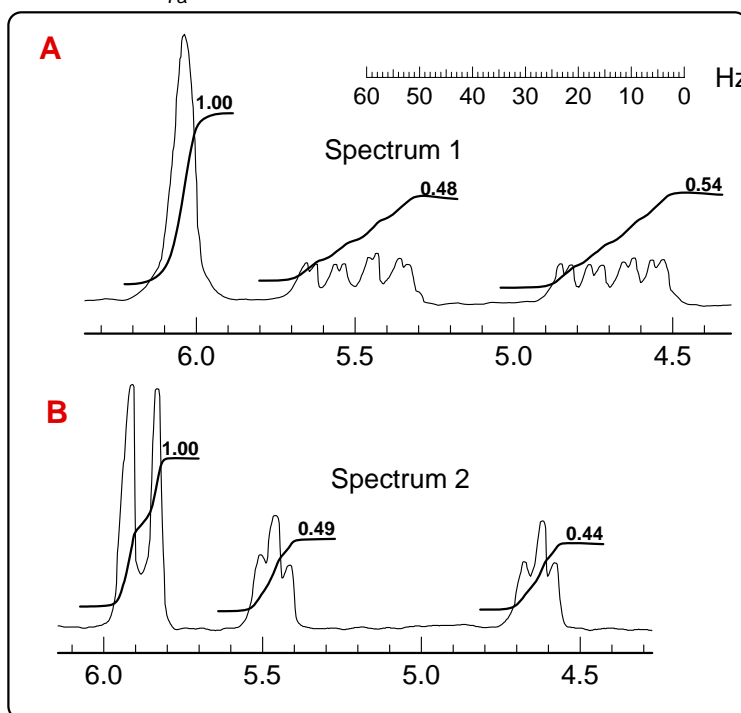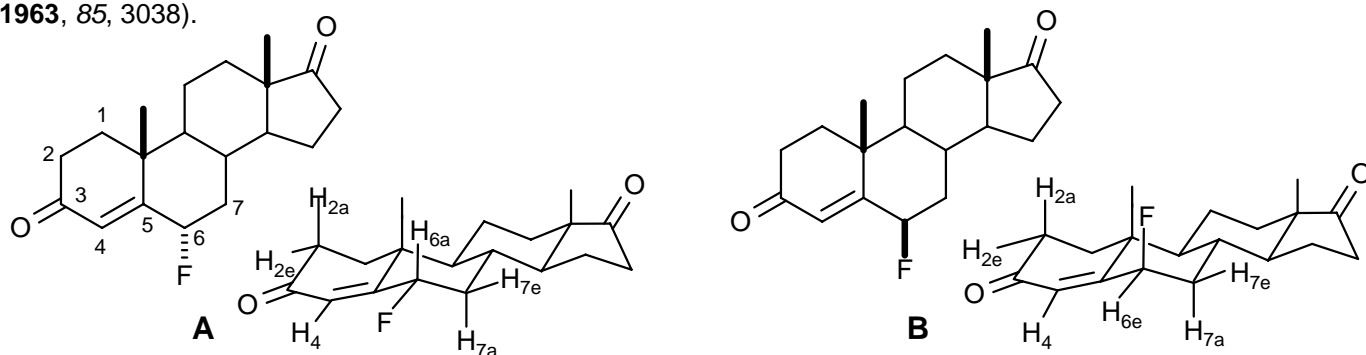
(a) Which protons are being shown here? Analyze the coupling, and report them in the standard format (give δ and identify any couplings you found).

Spectrum 1:

$^2J_{H6a-F} = 48$ Hz

$^3J_{H6a-7a} = 11$ Hz

6   δ 6.05, broad s, H^4

$^3J_{H6a-7e} = 6$ Hz

          δ 5.1, dddd, J = 48, 11, 6, 2

$^4J_{H6a-4} = 2$ Hz

Spectrum 2:

$^2J_{H6e-F} = 51$ Hz

$^3J_{H6e-7a} = 3$ Hz

7   δ 5.89, d, J = 5Hz

$^3J_{H6e-7e} = 3$ Hz

          δ 5.05, dt, J = 51, 3

$^4J_{H6e-4} < 2$ Hz

(b) Which isomer corresponds to Spectrum 1 __**A**__ , which to Spectrum 2 ___**B**__. Explain briefly.

3   The large H-H coupling in Spectrum 1 requires that the proton at H^6 be axial, to get one large ax-ax coupling ($^3J_{H6a-7a} = 11$ Hz). The vicinal couplings in Spectrum 2 are all small (3 Hz) so only eq-eq and eq-ax coupling, hence H^6 must be equatorial.
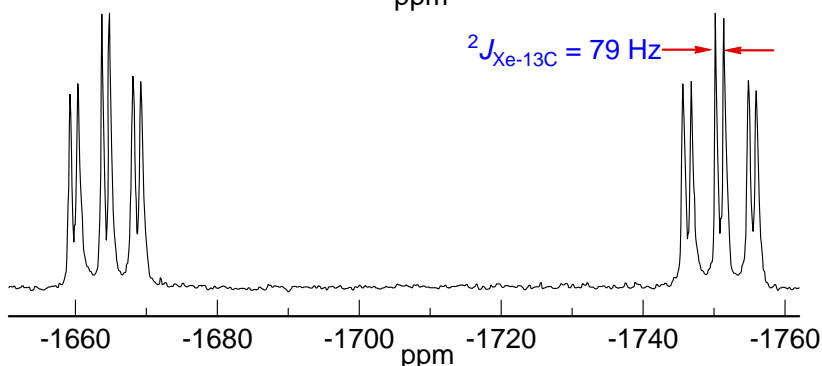
Problem R-11U ($C_{02}H_{03}AsF_7NXe$). This problem requires you to interpret the ^{129}Xe and ^{14}N spectra of $[CH_3C{\equiv}N\text{-}Xe\text{-}F]^+ AsF_6^-$ (Emara, A. A. A; Schrobilgen, G. J. *Chem. Commun.* **1987**, 1644)

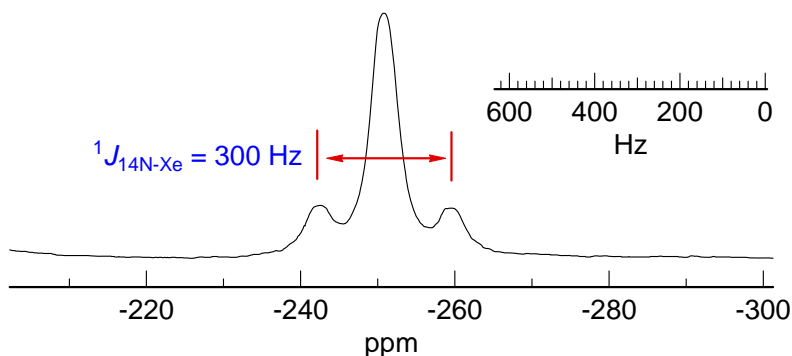Spectrum 1. 69.56 MHz ^{129}Xe NMR spectrum of $[CH_3C{\equiv}N\text{-}Xe\text{-}F]^+ AsF_6^-$ in HF at -10 °C

^{129}Xe, I = 1/2, 26.3% abundant

$^1J_{Xe\text{-}F}$ = 6020 Hz
$^1J_{Xe\text{-}14N}$ = 313 Hz
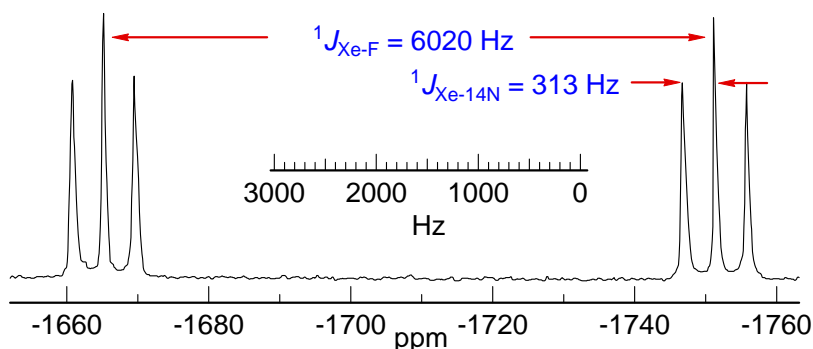
Spectrum 2. 69.56 MHz ^{129}Xe NMR spectrum of $[CH_3{}^{13}C{\equiv}N\text{-}Xe\text{-}F]^+$ AsF_6^- in HF at -10 °C

$^2J_{Xe\text{-}13C}$ = 79 Hz

Spectrum 3. 18.075 MHz ^{14}N NMR spectrum of $[CH_3C{\equiv}N\text{-}Xe\text{-}F]^+ AsF_6^-$ in HF at -10 °C

$^1J_{14N\text{-}Xe}$ = 300 Hz

(a) Analyze Spectrum **1** and **2**. Spectrum **2** is of a compound labeled >99% with ^{13}C at the CN carbon. Report coupling constants. Use the form $^nJ_{X\text{-}Y}$ = 00.0 Hz.

δ_{Xe} = 1708 ppm

12    $^1J_{Xe\text{-}F}$ = 6060 Hz

$^1J_{Xe\text{-}14N}$ = 313 Hz

$^2J_{Xe\text{-}13C}$ = 79 Hz

Spectrum 1: a doublet of 1:1:1 triplets, J = 6020, 313 Hz

Spectrum 2: a doublet of 1:1:1 triplets of doublets , J = 6020, 313, 79 Hz

(b) Analyze Spectrum **3**. Make sure you understand and explain the origin of all peaks. Why are the signals somewhat broadened?

Central peak: all of the isotopes of Xe except ^{129}Xe

5

Outer peaks: ^{129}Xe satelites due to ^{129}Xe - ^{14}N coupling, J ca 300 Hz

The signals are broadened because ^{14}N T_1 is quite short due to quadrupolar relaxation, so signals are boadened. There could also be broadening effects from unresolved coupling to F and CH_3.

3