Chemistry 605 (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

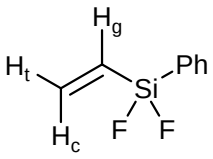
Practice Exam 3

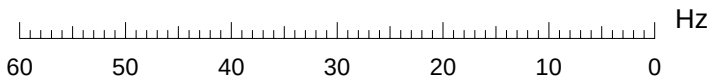
Name_____

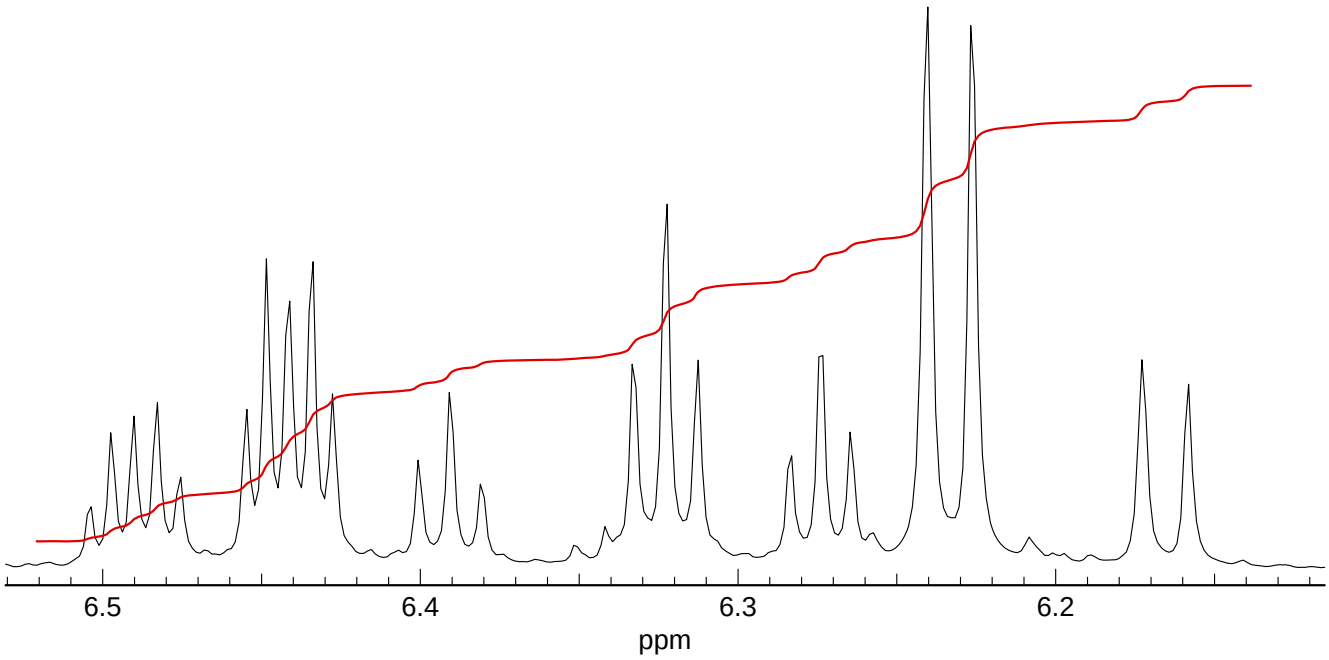
If you place answers anywhere else except in the spaces provided, (e.g. on the spectra or on extra pages) clearly indicate this on the answer sheets.

15

Problem R-11P ($C_8H_8F_2Si$. Below is a 300 MHz ^1H NMR spectrum of vinyl difluorophenylsilane, 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 ($^nJ_{X\text{-}Y}$ = 00.0 Hz). Apart from intensities, the spectrum is basically first order.

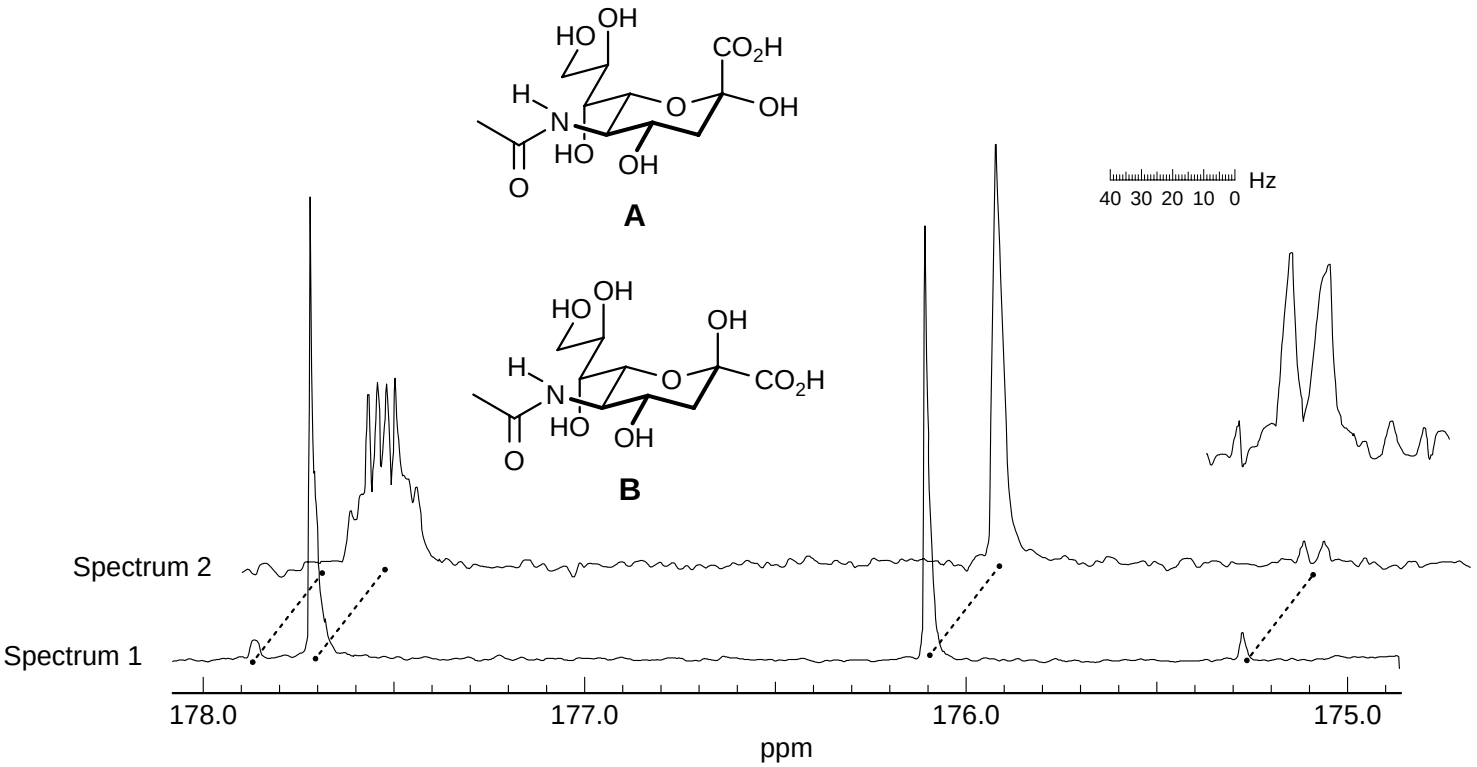






15

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.



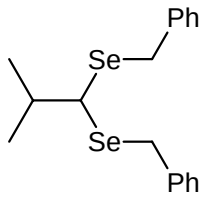
(a) Which carbons of the sialic acid are being shown here? Mark the shifts on the structures.

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

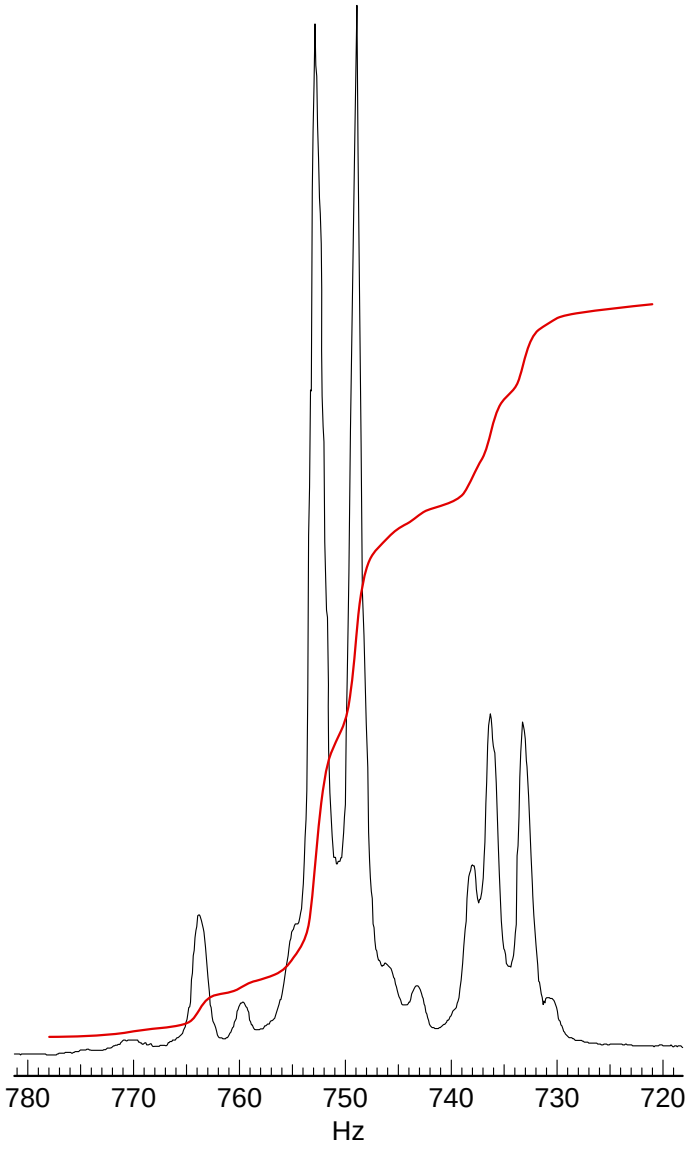
(c) Which is the major isomer (A or B)?_____ Give your reasoning below. Be specific and brief.

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.



(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, $^{n}J_{XY}$ = 00 Hz. An enlarged copy of the multiplet is shown below. The Hz values are from TMS at 0 Hz.

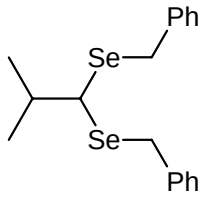


Problem R-11R $C_{18}H_{22}Se_2$

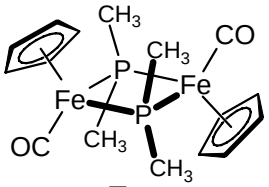
200 MHz ^1H NMR spectrum.

Solvent $CDCl_3$.

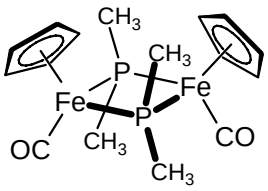
(Source: Bob Dykstra/HJR 12/25)



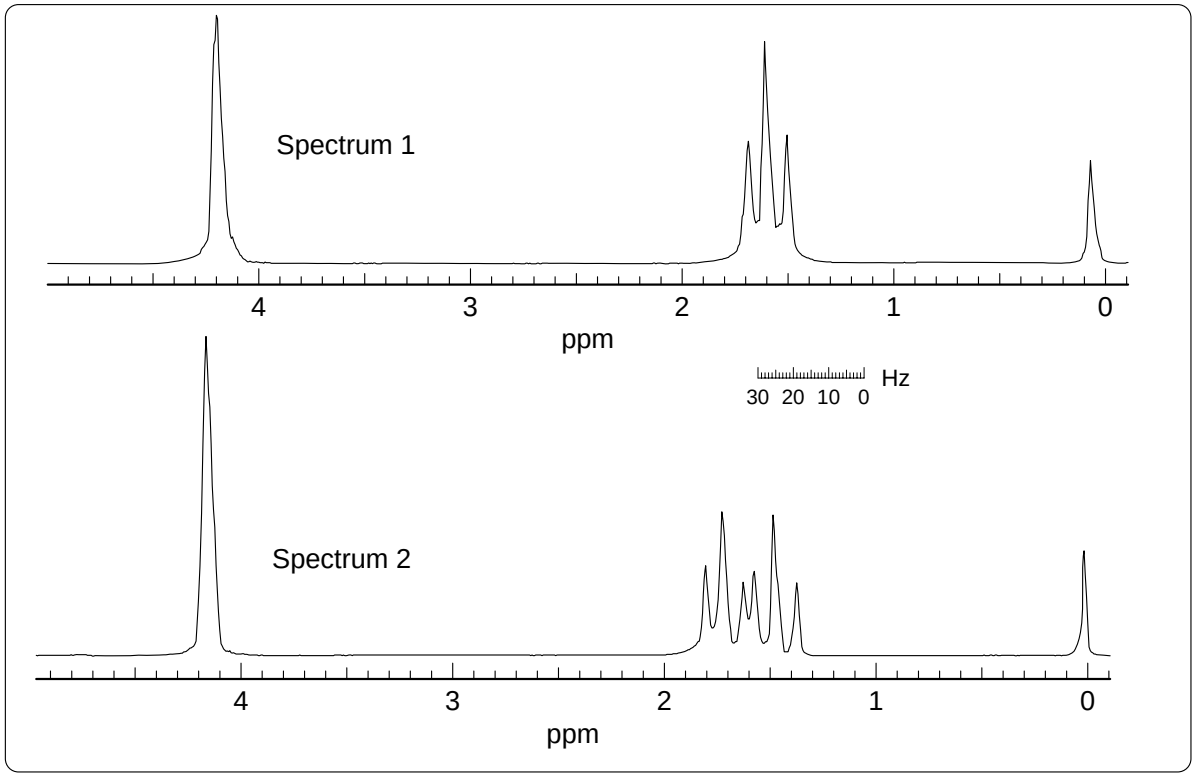
Problem R-11S ($C_{16}H_{22}Fe_2O_2P_2$). Below are the 60 MHz ^{1}H NMR spectra of two stereoisomers (E and Z) of the iron Cp complexes shown (*J. Am. Chem. Soc* **1963**, *85*, 3120).



E



Z

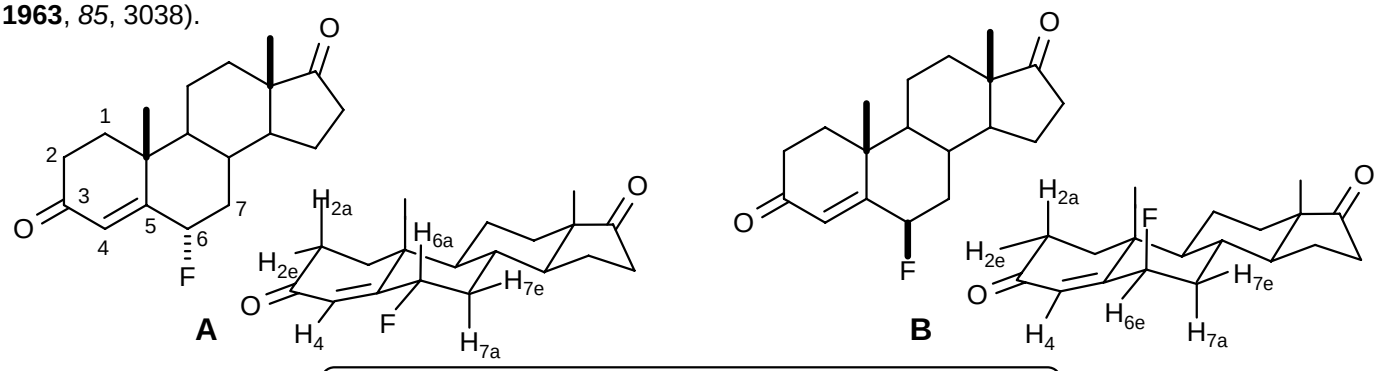


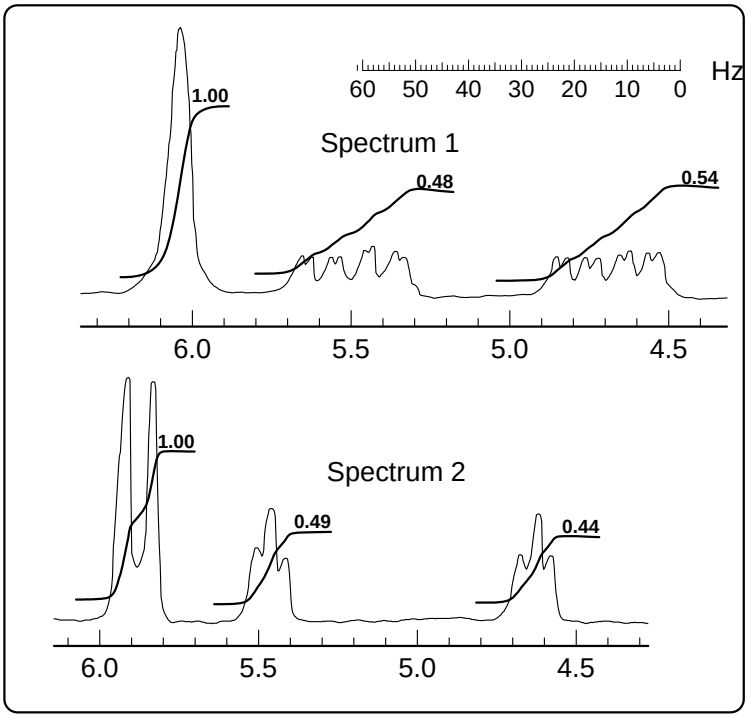
(a) Which isomer corresponds to Spectrum 1 ____, and which to Spectrum 2 ____? Explain

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

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

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).

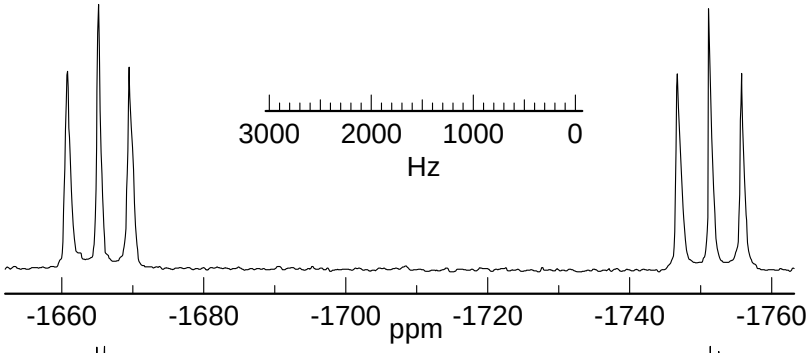
Spectrum 1:

Spectrum 2:

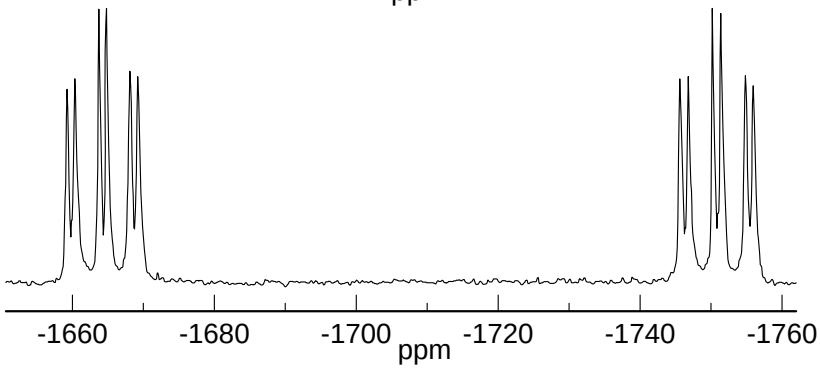
(b) Which isomer corresponds to Spectrum 1 ____, which to Spectrum 2____. Explain briefly.

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)

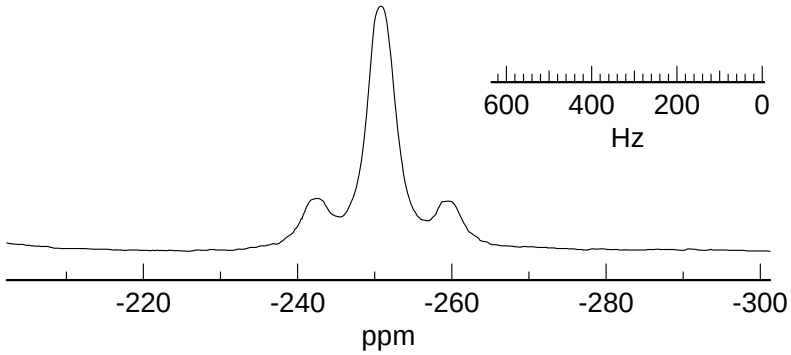
Spectrum 1. 69.56 MHz ^{129}Xe NMR spectrum of $[CH_3C{\equiv}N\text{-}Xe\text{-}F]^+$ AsF_6^- in HF at -10 °C



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



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



(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.

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