Table 1- Typical 2D NMR experiments used for molecular structure determination (*)

Experiment	Typical quantity (mg)	Exp. Time*	What kind of information is obtained?
COSY	5 mg	5 to 30 min	Establishes correlation between spins with scalar coupling (J) but does not determine coupling constants.
Long-range COSY	5 mg	5 to 30 min	Emphasize correlation with small Js.
COSY-45	5 mg	5 to 30 min	Decreases the intensity of the diagonal peaks with respect to the correlation peaks, thus identifying correlation between strongly coupled spins.
DQ-COSY	5 mg	10 to 60 min	Establishes correlation between spins with scalar coupling (J); can be used to measure Js. Singlets are removed (CH_3 signals, for example) and solvent (H_2O) by means of filtration of the correlation signals with a double quantum filter.
Relayed-COSY or RELAY	5 mg	5 to 30 min	Magnetization transfer to 1 or 2 chemical bonds beyond those of the COSY transfer to determine coupled spin systems (only via J).
TOCSY	5 mg	5 to 30 min	Show correlation among all the spins that have a common coupling partner, e.g., A $\rightarrow$ B $\rightarrow$ C, where J_{AB}, $J_{BC} \neq 0$, BUT $J_{AC} = 0$.
NOESY	10 mg	1 to 2 hours	Stereochemical information via dipolar coupling using cross-relaxation (longitudinal); determination of chemical exchange processes.
ROESY	10 mg	1 to 2 hours	Stereochemical information via dipolar coupling using cross-relaxation (transversal); adequate for molecules with average MW in the range of 1000-3000 and/or when $\omega\tau_c \sim 1.12$ (where ω is the spectrometer frequency and τ_c the correlation time).
HETCOR (1-bond)	20 mg	1 to 2 hours	Heteronuclear assignment
HMQC/HSQC (1 bond)	10 mg	0.5 to 2 hours	Heteronuclear assignment using inverse detection, i.e., using ^{1}Hs to detect heteronuclear frequencies (more often) or using a nucleus with larger (to detect a low-(nucleus (e.g. use of ^{19}F to detect ^{13}C frequencies).
HETCOR (n-bond)	20 mg	4 to 12 hours	H-X long range heteronuclear assignment (via $^2J_{XH}$ and $^3J_{XH}$).
HMBC (n-bond)	10 mg	2 to 12 hours	H-X long range heteronuclear assignment (via $^2J_{XH}$ and $^3J_{XH}$) using inverse detection.
HMQC-TOCSY	10 mg	0.5 to 2 hours	H-X long range heteronuclear assignment (via $^2J_{XH}$ e $^3J_{XH}$) using inverse detection and protonated Xs
INADEQUATE	100 mg	24-72 hours	Establishes ^{13}C-^{13}C connectivities. For structural elucidation of organic molecules, it is the most powerful experiment, but with the lowest sensitivity.

(*) The acquisition times and quantities mentioned above are for phase-cycled 2D experiments, i.e., experiments that require a minimum number of transients in F_2 to eliminate axial peaks and make quadrature detection. The experiments with pulsed field gradients tend to be faster than the phase-cycled ones.

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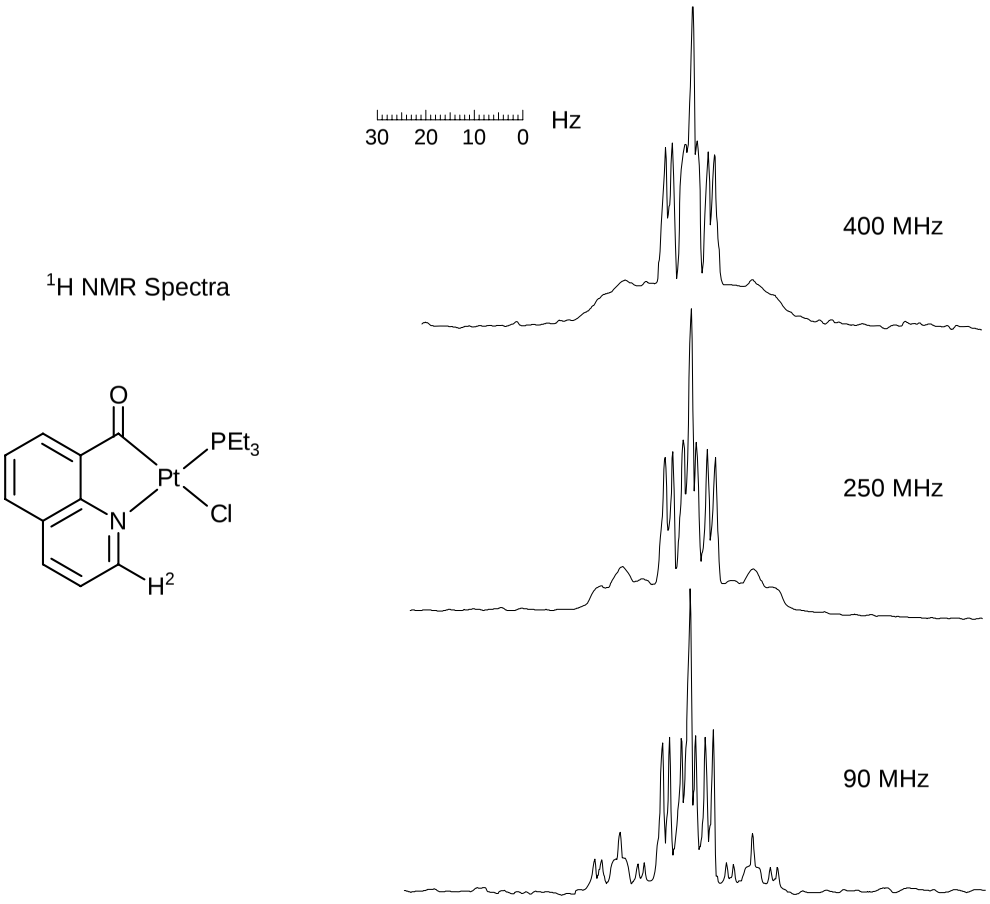
Problem R-12O ($C_{16}H_{21}ClNOPPt$). Shown below are partial ^1H NMR spectra of a platinum complex at several field strengths. All three spectra are at the same Hz scale. Only the signal for H^2 is shown (source: *Magn. Res. Chem.* **1985**, *23*, 671).



(a) Explain the small outer peaks of the multiplet.

(b) Analyze the multiplet. Give approximate coupling constants, report them in the form $^nJ_{XY}$ = __ Hz. Assign the couplings.

(c) Why do the small outer peaks become broad at higher field strength? This is not a fluxional molecule, and there is no ligand exchange under these conditions.

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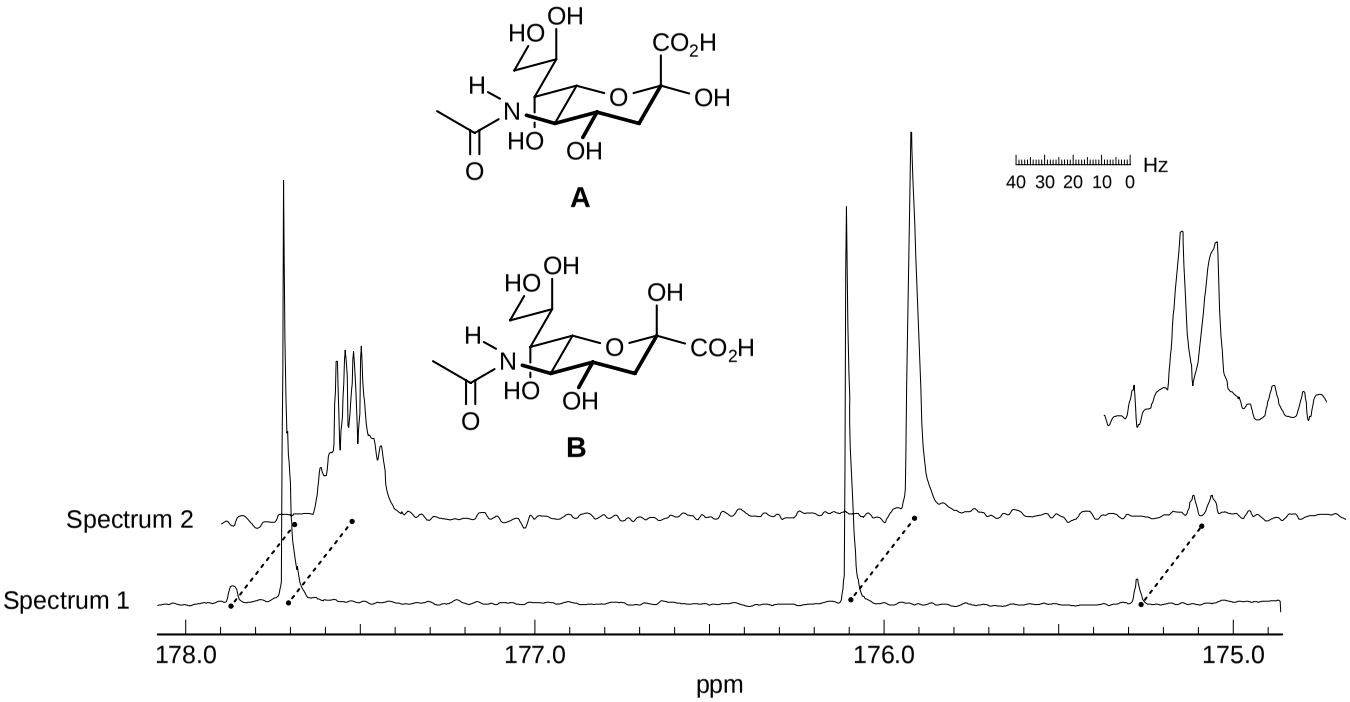
Problem R-11Q ($C_{11}H_{19}NO_8$). This problem requires you to determine the stereochemistry of two isomers of sialic acid (**A** and **B**). Below is shown a portion of the 126 MHz ^{13}C NMR spectrum (D_2O solvent) of a 10:1 mixture of two isomers (Hori, H.; Nakajima, T.; Nishida, Y.; Ohrui, H.;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

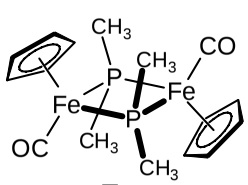


(a) Which carbons of the sialic acid are being shown here? Mark the shifts on the structures.

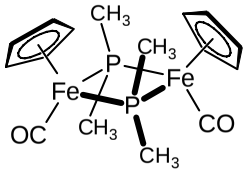
(b) Interpret the multipicity of the signal at 177.7 ppm in the coupled spectrum (2). Estimate coupling constants, and assign them.

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

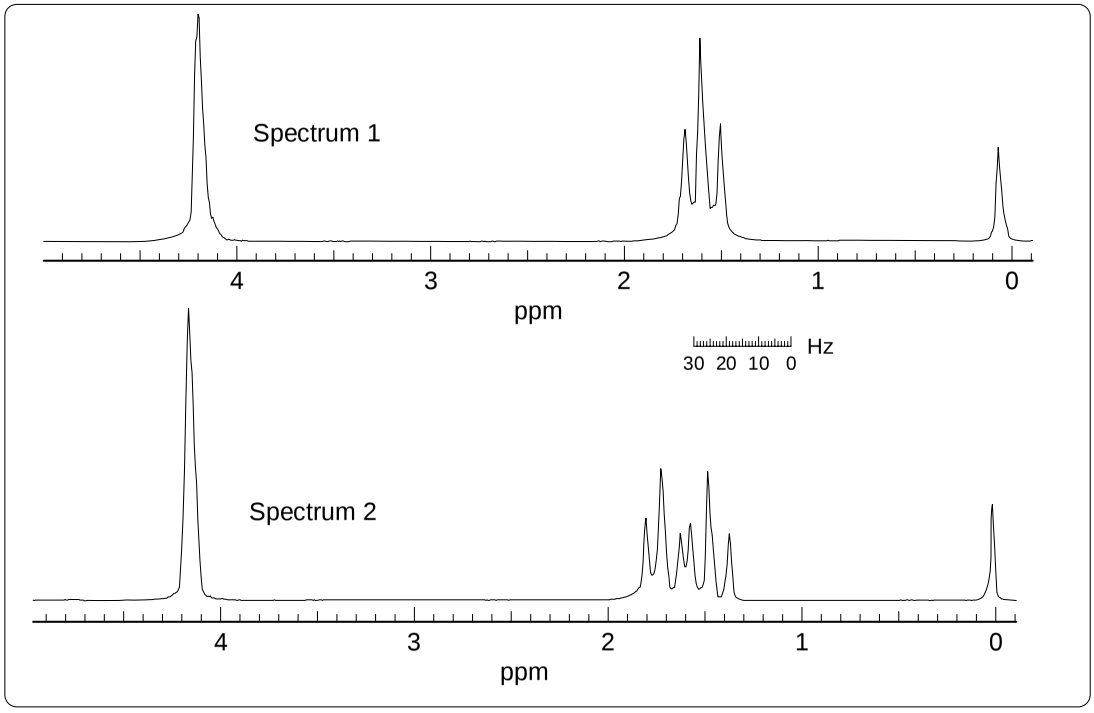
Problem R-11S ($C_{16}H_{22}Fe_2O_2P_2$). Below are the 60 MHz ^1H NMR spectra of two stereoisomers (E and Z) of the iron Cp complexes shown (*J. Am. Chem. Soc* **1963**, *85*, 3120).



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)?

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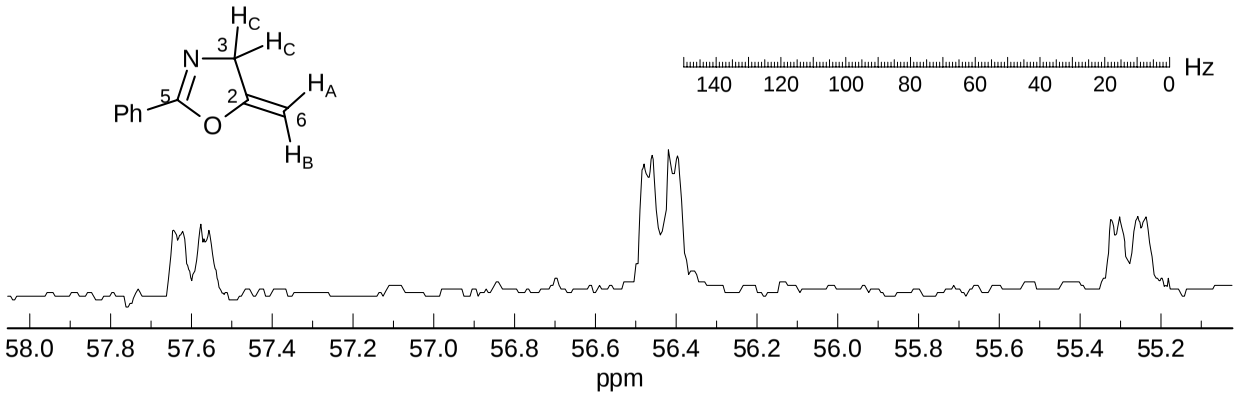
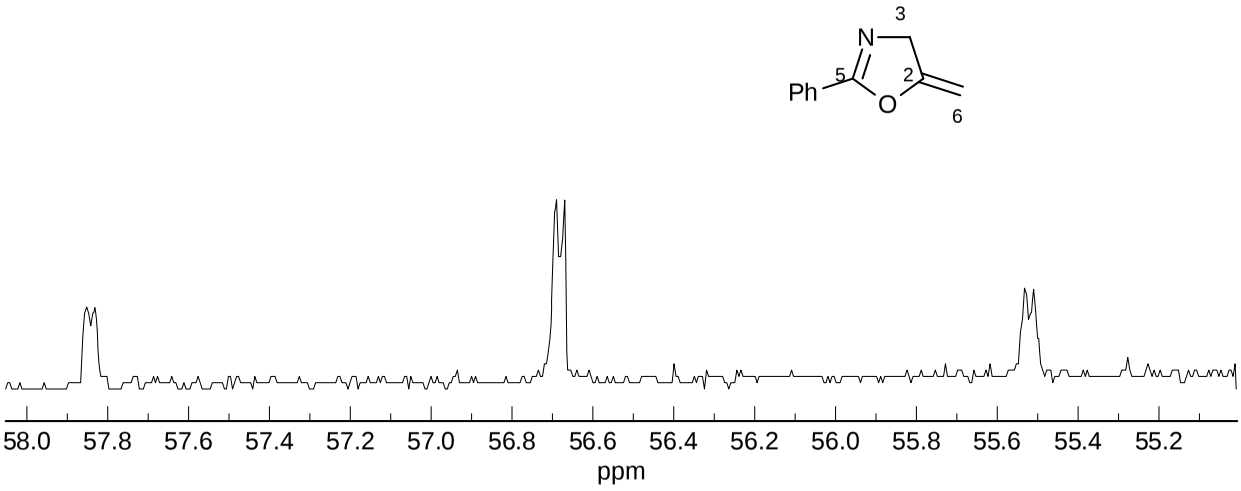
Problem R-12M. You are asked to interpret the coupled ^{13}C NMR spectrum of an oxazoline.

(a) Which carbon are we looking at? _____



(b) Analyze the spectrum, report all coupling constants in the standard format ($^{n}J_{X\text{-}Y}$ = 00.0 Hz).

(c) The spectrum below is of the same compound with one H replaced by D. Where is the deuterium? Place it on the structure, and explain briefly.



(d) What is the proton NMR frequency of the spectrometer they were using?_____

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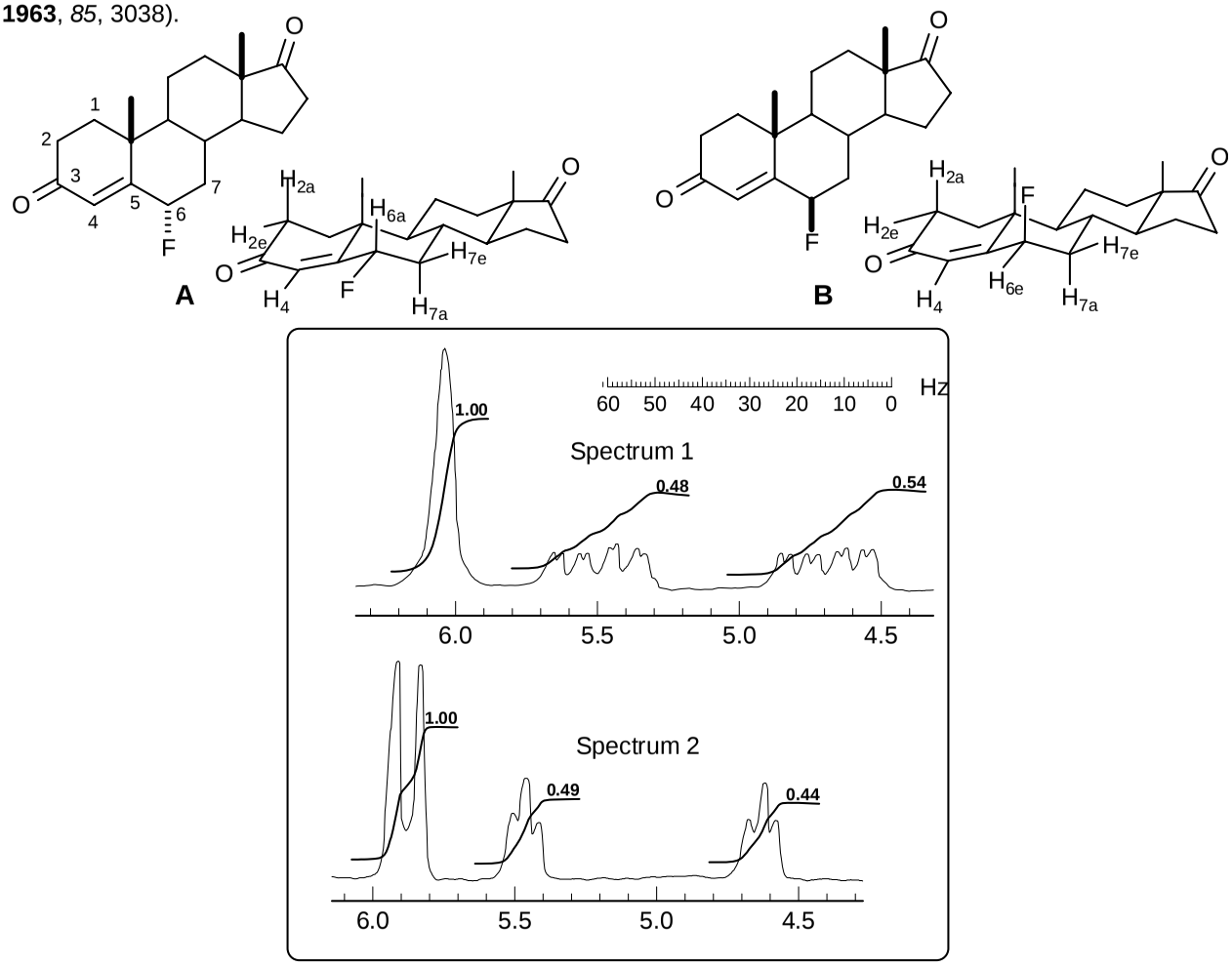
Problem R-11T ($C_{19}H_{25}FO_2$). Below are part of the 60 MHz ^{1}H NMR spectra of two stereoisomers (**A** and **B**) of the fluorinated steroids shown. To aid in your analysis, a conformational drawing is also provided (*J. Am. Chem. Soc.* **1963**, *85*, 3038).

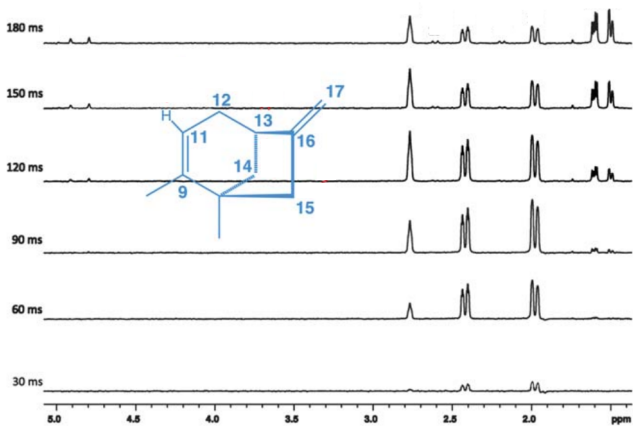


(a) Which protons are being shown here? Analyze the coupling, and report them in the standard format (give δ and identify any couplings you found).

Spectrum 1:

Spectrum 2:

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


180 ms
150 ms
120 ms
90 ms
60 ms
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H
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