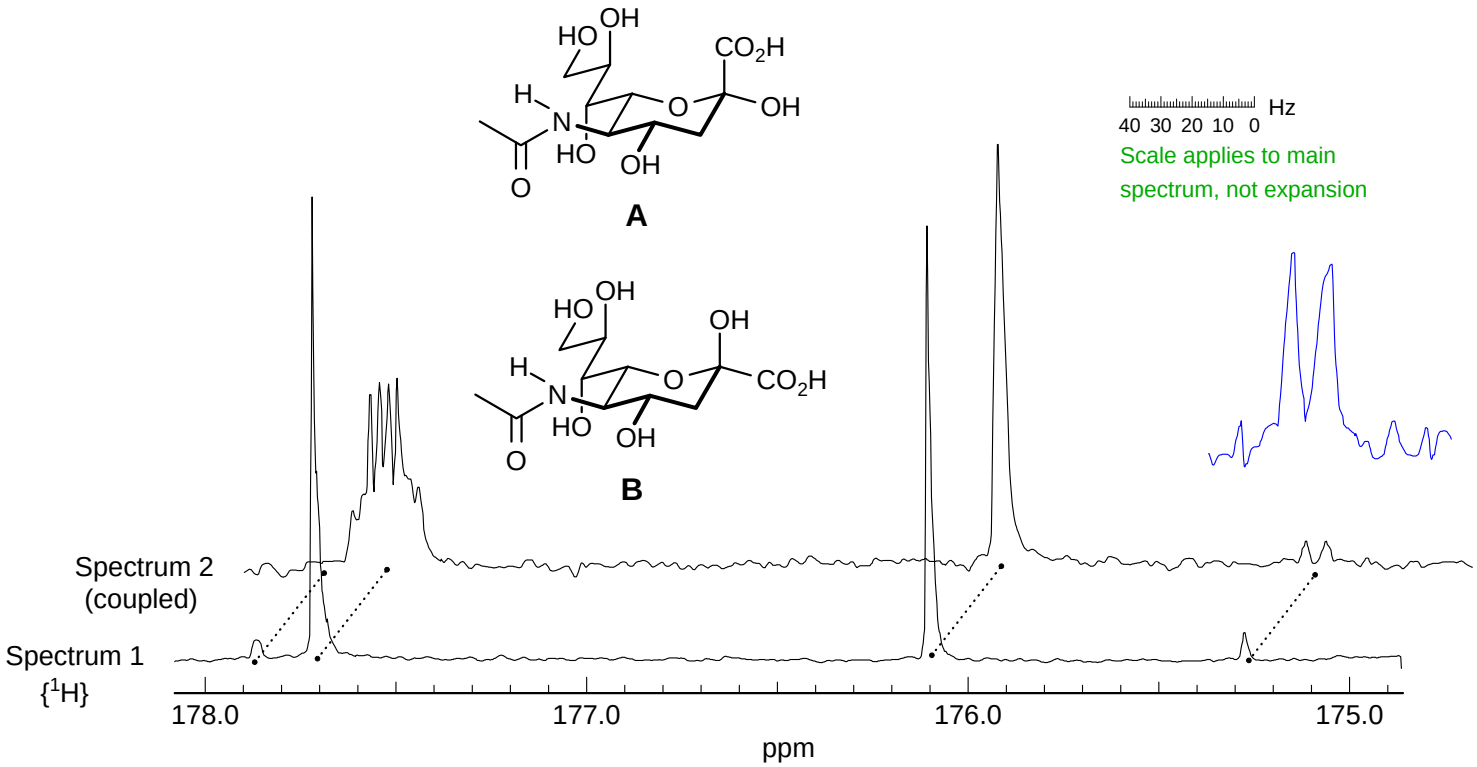
15

**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.

15

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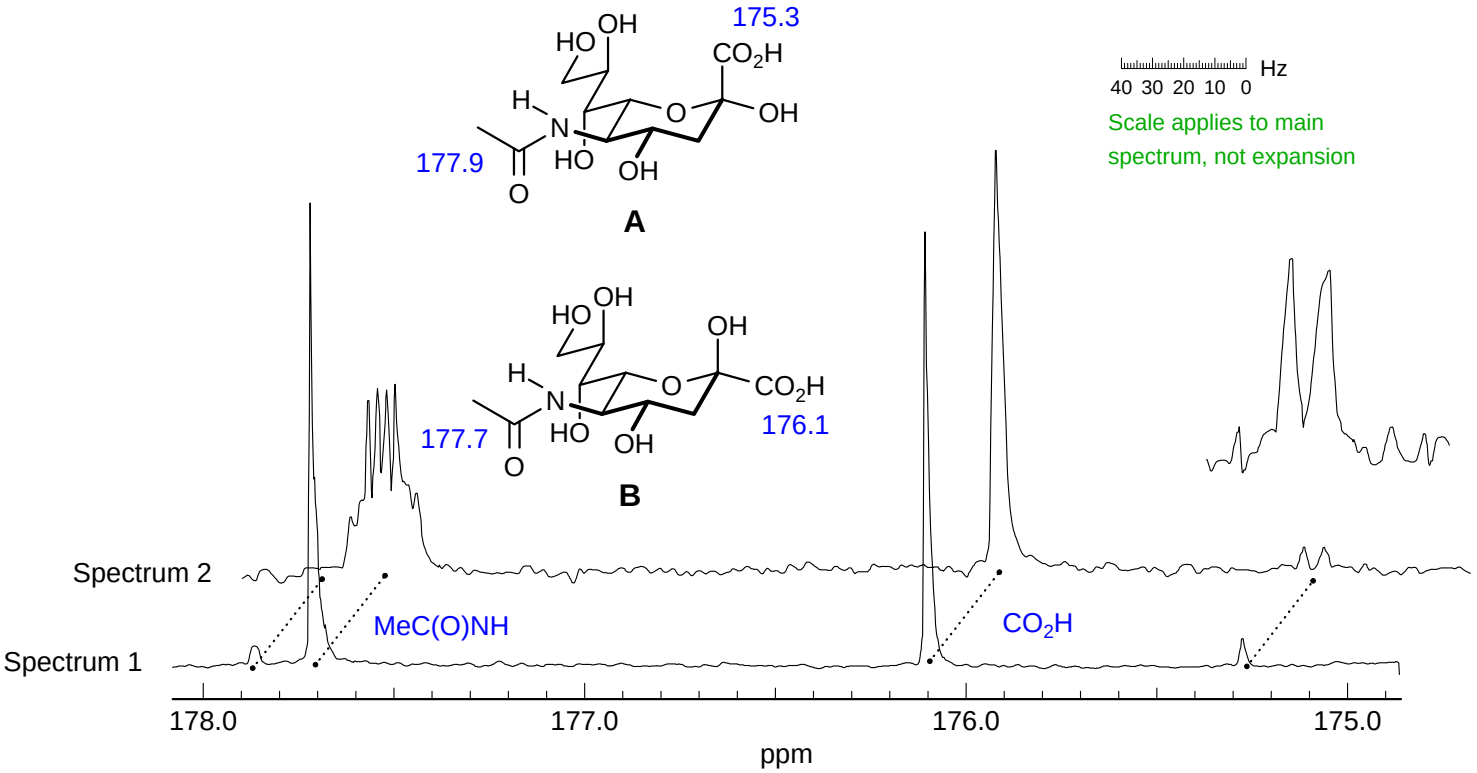



(a) Which carbons of the sialic acid are being shown here? Mark the shifts on the structures.

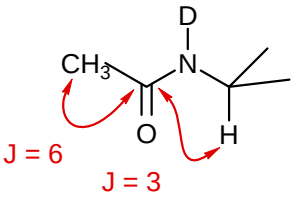
Carbonyl peaks - amide at 177.7 and 177.9 ppm, carboxylic acid at 176.1 and 175.3 ppm

4

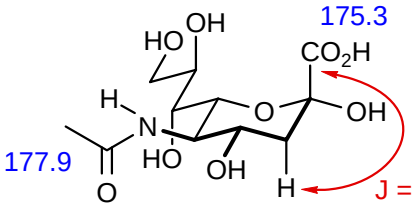
(b) Interpret the multipicity of the signal at 177.7 ppm in the coupled spectrum (2). Estimate coupling constants, and assign them.

qd, J = 6, 3 Hz

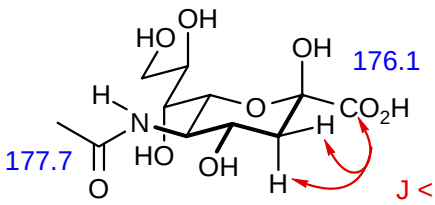
4 Thus this must be the amide carbonyl - coupled to $CH_3$ (6 Hz) and the N-C-H proton (3 Hz). Coupling cannot be to N-H proton since in $D_2O$ this would be N-D.




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 $CO_2H$ and the axial H of 6 Hz - Karplus angle is 180°.




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

PLT ex-3-11-12.plt