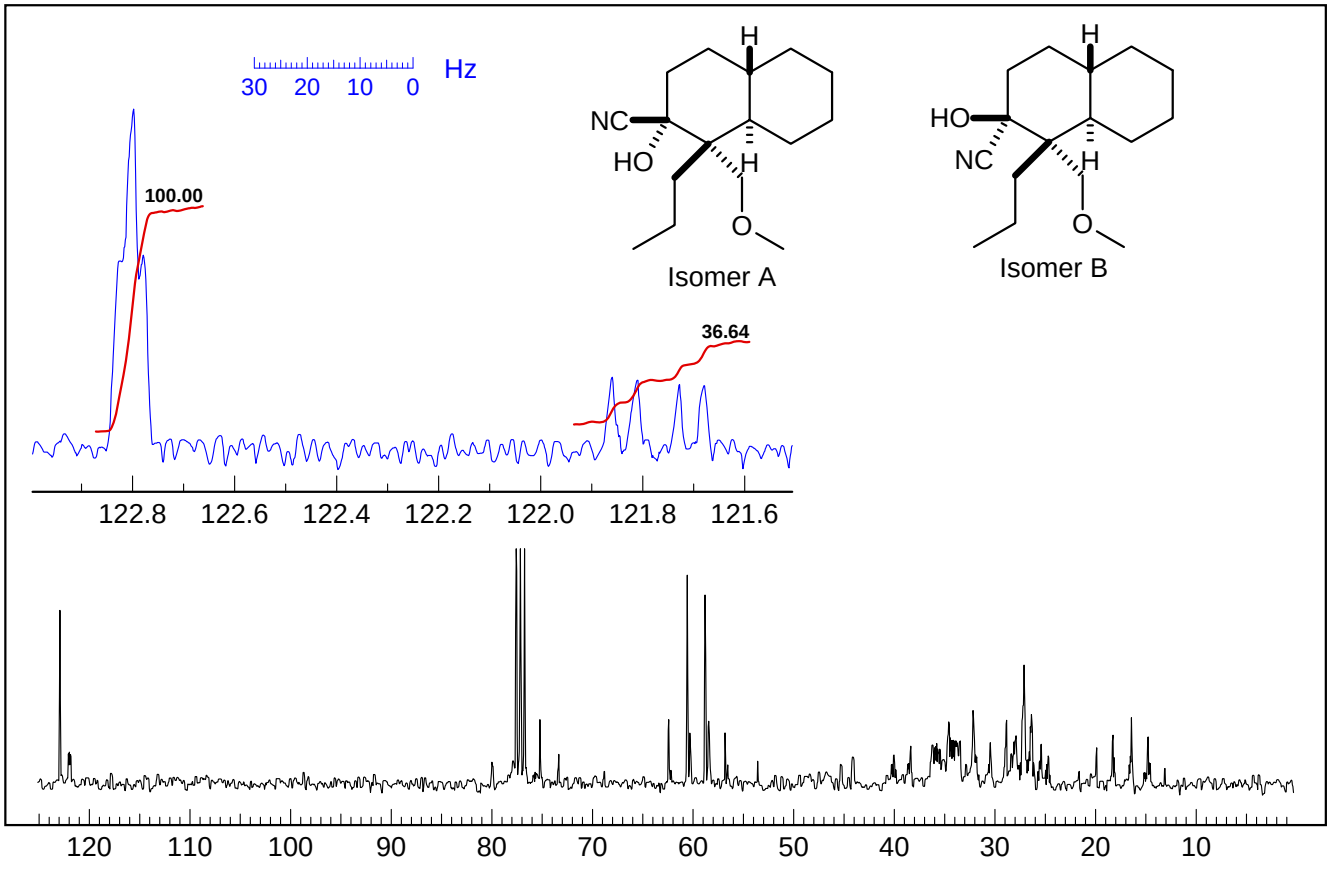
Problem R-13l ($C_{16}H_{27}NO_2$). This problem requires that you determine the stereochemistry of a cyanohydrin (R. Corcaran). The fully coupled 75.6 MHz ^{13}C NMR spectrum ($CDCl_3$) shown below is of a ≈1:3 mixture of two isomers. Source: R, Corcoran, U. Wyoming.



(a) Which carbons are responsible for the signals near 122 ppm? Analyze them.

(b) Which isomer is the major one? Explain your reasoning using a conformational drawing.

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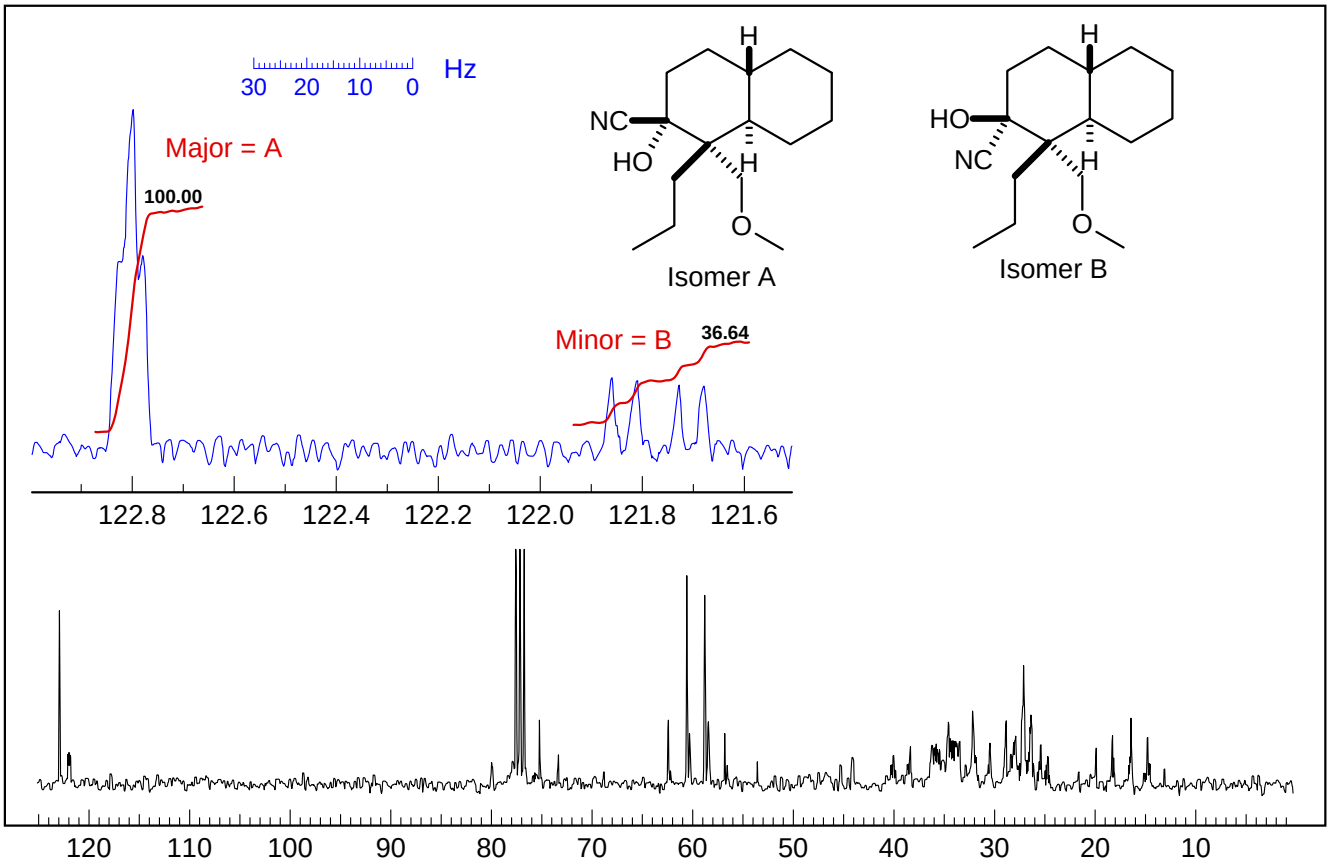
Problem R-13I ($C_{16}H_{27}NO_2$). This problem requires that you determine the stereochemistry of a cyanohydrin (R. Corcaran, U. Wyoming). The fully coupled 75.6 MHz ^{13}C NMR spectrum ($CDCl_3$) shown below is of a ≈1:3 mixture of two isomers.



(a) Which carbons are responsible for the signals near 122 ppm? Analyze them.

This is the CN group. The C would be coupled only to the adjacent CH_2 protons - all other Hs are 4 or more bonds away.

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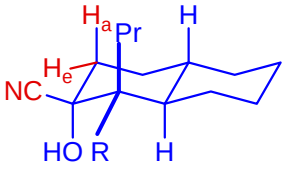
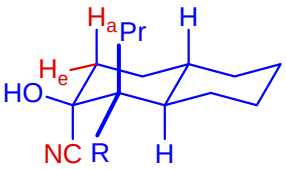
122.8 CN carbon, t, $^3J_{CH}$ = 1.7 Hz (major isomer)

121.7 CN carbon, dd, $^3J_{CH}$ = 9.0, 3.7 Hz (minor isomer)

(b) Which isomer is the major one? Explain your reasoning using a conformational drawing.



Isomer A Major



Isomer B Minor

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The CN carbon should show approximately equal small couplings ($^3J_{CeqHeq}$ and $^3J_{CeqHax}$) to the CH_2 ax and eq protons. The major isomer has an approximate triplet, with J = 1.7 Hz.

The CN carbon should show one large ($^3J_{CaxHax}$) and one small ($^3J_{CaxHeq}$) coupling to the CH_2 ax and eq protons. The minor isomer has a dd, J = 9.0 and 3.7 which fits this pattern.

A second argument can be made based on gamma effect on the CN chemical shift: isomer B has an axial CN group, which should therefore be upfield of the equatorial one. This leads to same assignment - Minor is B. However, the chemical shift difference is only 1.1 ppm, so this argument is not as strong as the coupling argument, and one would need some confirmation that γ-effects operate reliably on CN carbons