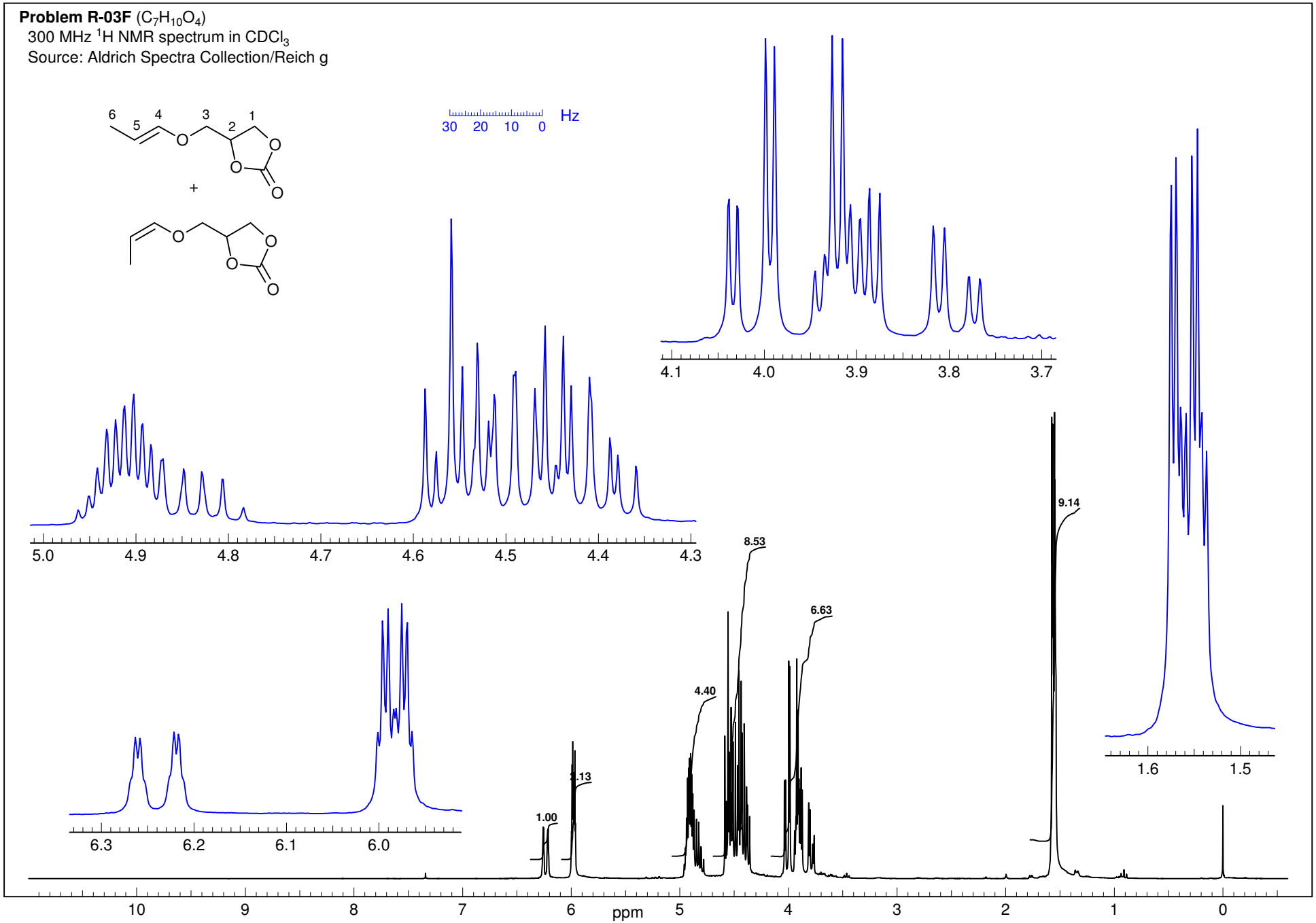
Exercize: This is a mixture of cis and trans isomers of the enol ether shown. Assign all of the proton signals, and extract coupling constants. First order analysis is appropriate. Which is the major isomer?



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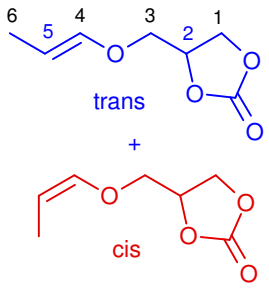
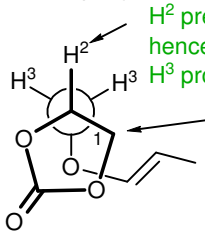
Problem R-03F ($C_7H_{10}O_4$)

This is a mixture of cis and trans isomers of the enol ether shown. Assign all of the proton signals, and extract coupling constants. You may use first order analysis.

300 MHz ^{1}H NMR spectrum in $CDCl_3$

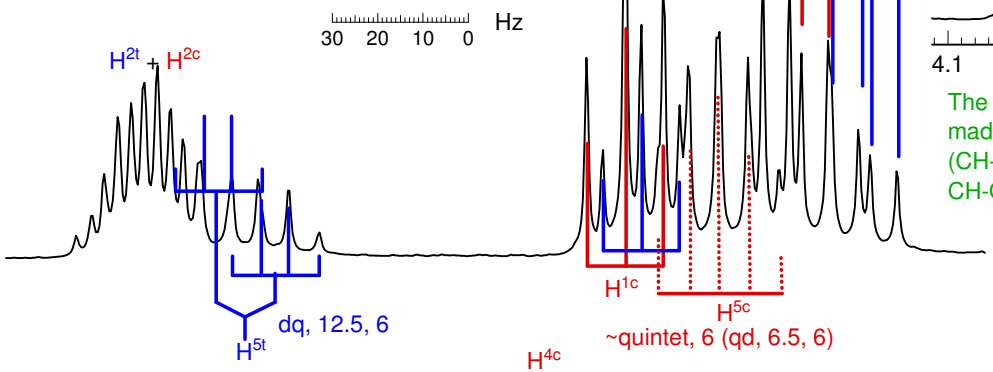
Source: Aldrich Spectral Viewer/Reich

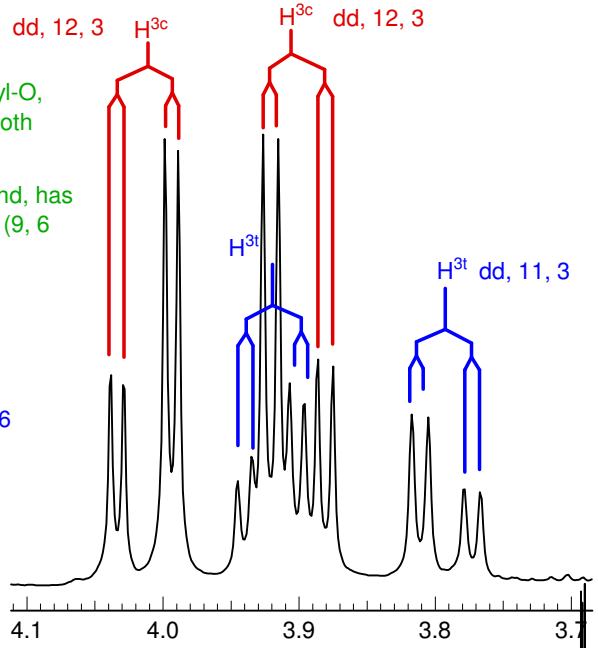




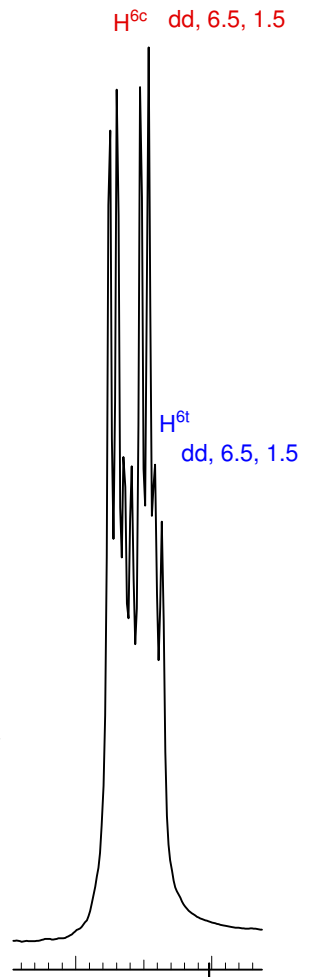
H^2 prefers to be anti to vinyl-O, hence small couplings to both H^3 protons

H^1, on the other hand, has the large couplings (9, 6 Hz) to H^2 typical of 5-membered rings

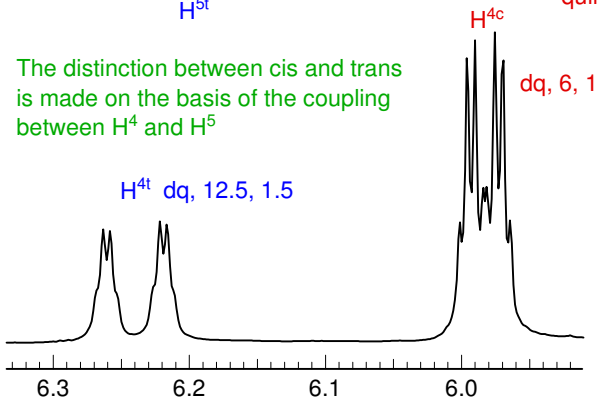




The distinction between H^1 and H^3 is made on the basis of chemical shift (CH-OR is 0.5-0.7 ppm upfield of CH-OC=O)



The distinction between cis and trans is made on the basis of the coupling between H^4 and H^5



Solution

1. H^{4c} and H^{4t} give the identity of the major (cis) and minor (trans) components.
2. CH_3 signals
3. H^3 - isolated AB of ABX for both isomers
4. H^5 - quintet for cis, dq for trans
5. H^1 - Both sets superimposed in each other, and on the quintet for H^5