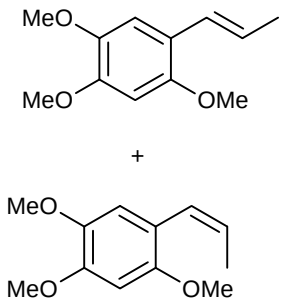
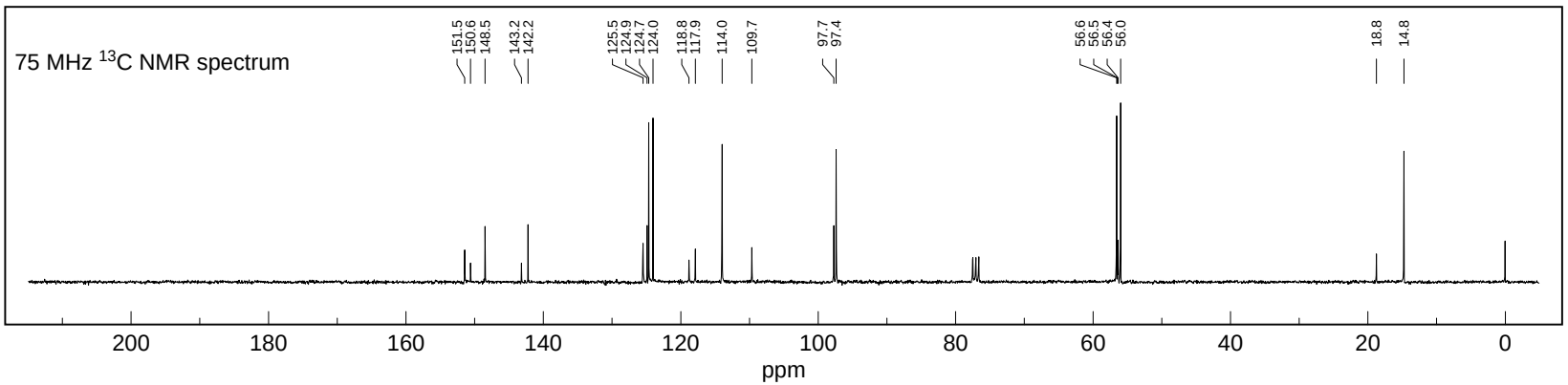
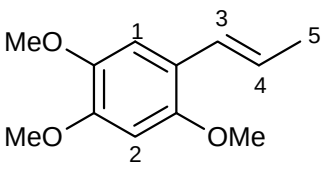
Problem R-08E ($C_{12}H_{16}O_3$)
300 MHz NMR spectrum in $CDCl_3$
Source: Aldrich Spectra Collection/Reich g



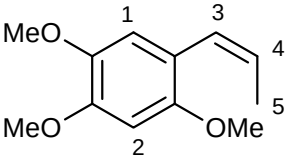


PLT ex-1-2008-09-gq.plt

Problem R-08E. You are given the ^{1}H and ^{13}C NMR spectra of a mixture of stereoisomers.

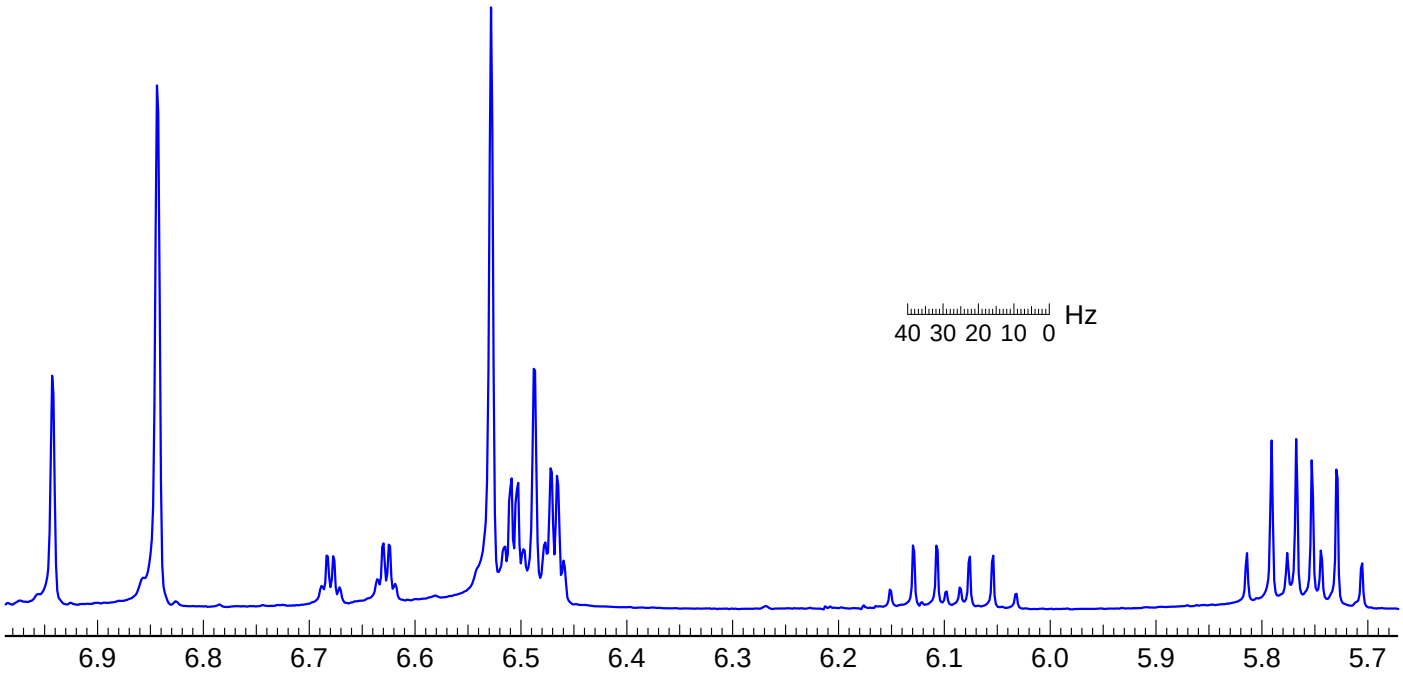


E



Z

(a) Identify which is the major and which the minor isomer in the ^{1}H NMR spectrun, and place assignments (E-1, E-2, Z-3, Z-4, etc) over the appropriate peaks in the expansion below.



(b) Explain specifically how you made the E/Z assignment. Describe the multiplets you used (eg. td J=7, 3 Hz at δ 3.4) for each isomer.

(c) Identify a feature of the ^{13}C NMR spectrum which allows a firm structure assignment.

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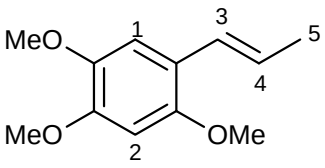
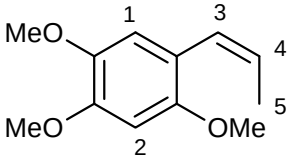
Problem R-08E. You are given the 300 MHz ^{1}H NMR spectrum of a mixture of stereoisomers. The full spectrum is on the next page, but you only need to deal with the expansion on this page.

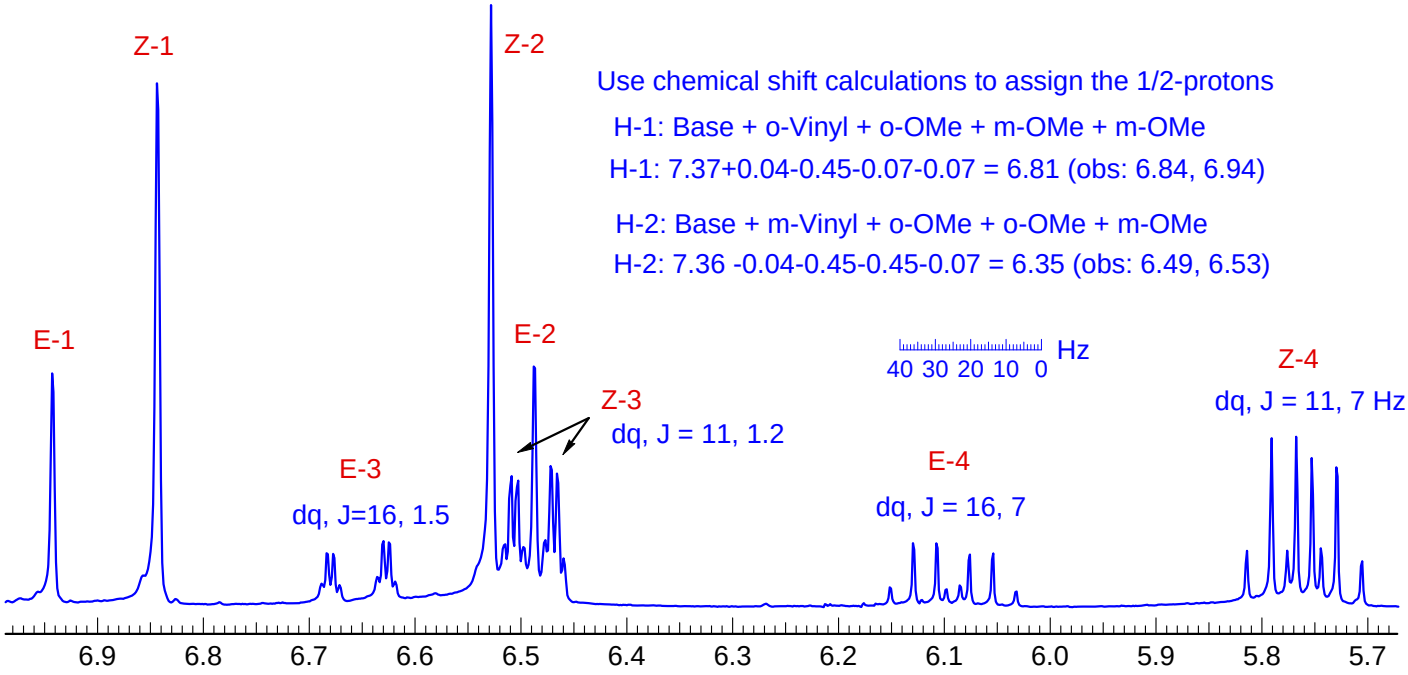


E



Z

(a) Identify which is the major and which the minor isomer, and place assignments (E-1, E-2, Z-3, Z-4, etc) over the appropriate peaks in the expansion below.



Use chemical shift calculations to assign the 1/2-protons

H-1: Base + o-Vinyl + o-OMe + m-OMe + m-OMe

H-1: 7.37+0.04-0.45-0.07-0.07 = 6.81 (obs: 6.84, 6.94)

H-2: Base + m-Vinyl + o-OMe + o-OMe + m-OMe

H-2: 7.36 -0.04-0.45-0.45-0.07 = 6.35 (obs: 6.49, 6.53)

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(b) Explain specifically how you made the E/Z assignment. Describe the multiplets you used (eg. td J=7, 3 Hz at δ 3.4) for each isomer.

7 The minor isomer has a dq, J = 16, 7 at δ 6.09, and a dq, J=16, 1.5 at δ 6.65, thus these protons are trans on the double bond

The major isomer has the corresponding coupling of 11 Hz (δ 5.76, dq, J = 11, 7 Hz; 6.48, dq, J = 11, 1.2 Hz)), thus the cis isomer

(c) Identify a feature of the ^{13}C NMR spectrum which allows a firm structure assignment.

5 The CH_3 carbons should show a substantial (several ppm) difference between the *E* and *Z*-isomers, with the *Z*-isomer upfield (cis gamma-effedct). Indeed, the major isomer (*Z*) has the CH_3 at δ 14.8, the minor at δ 18.8.