In-Class Exercise Solutions:
Through-Space Correlations with 2D NOESY

a. Using the numbering scheme on the triene shown below, and rotating either the C(2)-C(3) or the C(4)-C(5) bond,

rotate C2-C3 bond   *rotate C4-C5 bond*

NOE   *NOE*   *NOE*

NOE   *NOE*

If the original structure is correct, we should expect NOE's between -C(1')H$_3$ and H(4), and between -C(3')H$_3$ and H(6), in addition to neighboring H-H and CH$_3$-CH$_3$ correlations.

b. The ^{1}H NMR has three 1H-intensity resonances in the alkene (δ = 5-7 ppm) region of the spectrum, four 3H resonances in the C=C-CH$_3$ region (δ = ~2 ppm), and one giant 12H peak at δ = 1.5 ppm. The giant peak must be from the four equivalent boronate methyl groups. In addition, one of the methyl resonances is split into a doublet (δ = 1.71 ppm), and one of the alkene protons (δ = 5.46 ppm) is split into a quartet; these two must be the H(6) and C(6')H$_3$ that are coupled to one another.

Unfortunately, that's all we can do with the 1D ^{1}H NMR alone. Looking at the NOESY spectrum that correlates H's with CH$_3$'s, we can start with H(6) at 5.46 ppm. This is correlated through space with C(6')H$_3$ (no surprise there) and then with one other CH$_3$ group. For a moment, let's assume that is C(3')H$_3$, as shown on the right side above. This methyl group shows another NOE to a different proton, which we'll guess is H(2) (left side above), and H(2) shows NOE to the boronate methyls. This is actually great--H(2) should be the only alkene proton with NOE to the boronate. To recap what I just wrote on the NOESY spectrum itself,

The only H we haven't assigned above is H(4), which must be the middle one. That assignment is confirmed by the other NOESY closeup, where H(4) is the only one of the three alkene protons to show through-space correlations with both of the others.

So then between C(1')H$_3$ and C(5')H$_3$, which resonance goes with which methyl group? Unfortunately, the region of the NOESY that would show methyl-methyl NOE's was not very clear, so we don't have any more info to go on. Based purely on NOE intensity (not a great measure), I would guess that the δ = 1.76 ppm peak would belong to C(1')H$_3$, because the distance in the conformation shown above is so short. But this assignment isn't clear.

c. The spectra are consistent with the all-*trans* stereoisomer that Susan wanted.