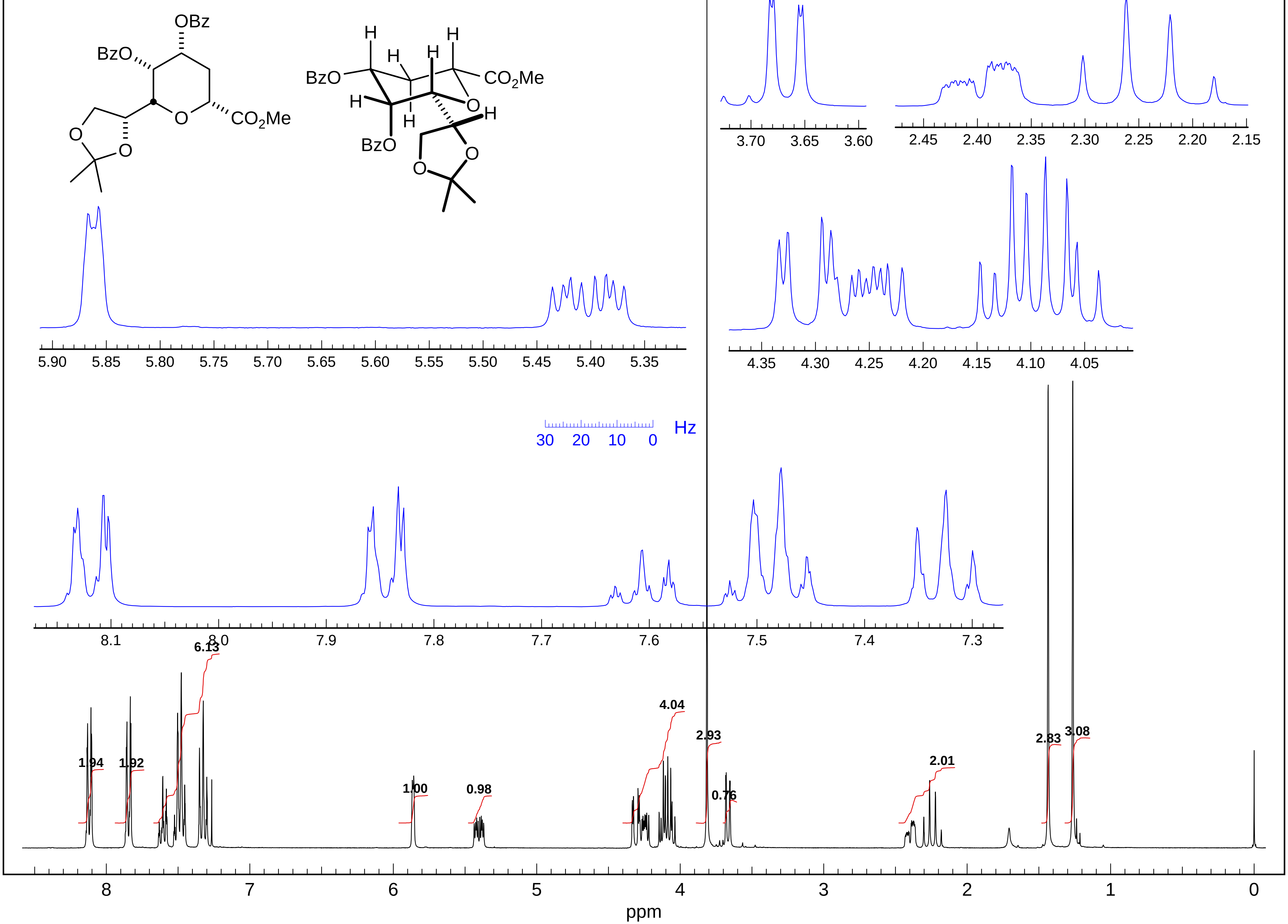
Problem R-10J ($C_{24}H_{28}O_9$)
300 MHz ^1H NMR spectrum in $CDCl_3$
Source: Geoffrey Sametz/Burke



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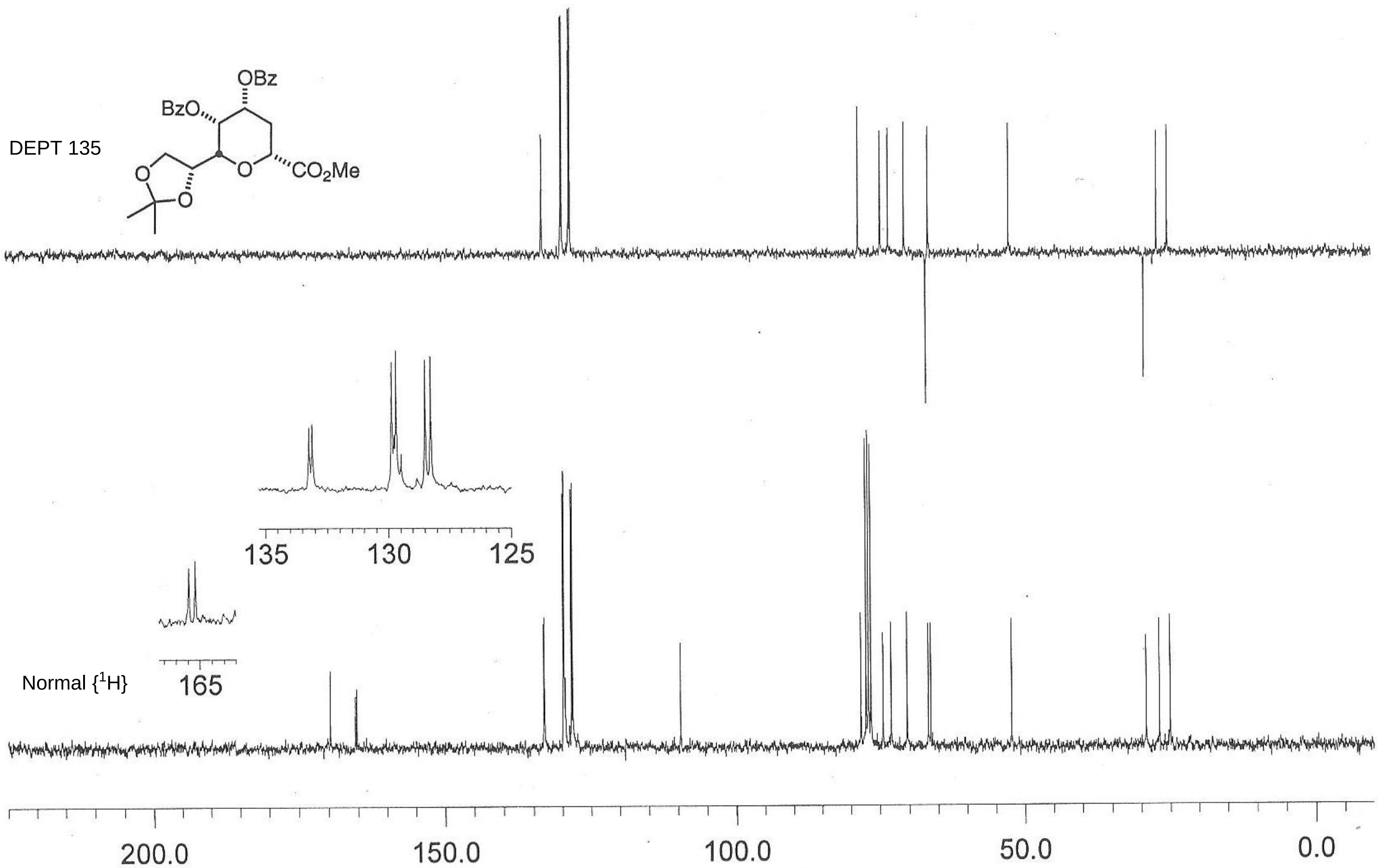
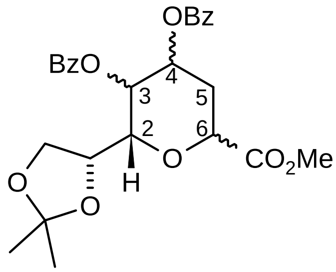
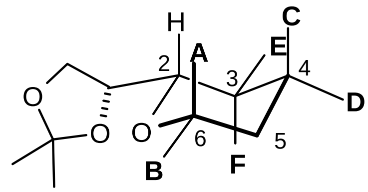
75 MHz ^{13}C NMR spectrum in $CDCl_3$



PLT ex-2-2010-11-gq.plt

Problem R10J ($C_{24}H_{28}O_9$). This problem requires you to analyze part of the ^{1}H NMR spectrum of a tetrahydropyran, and determine the stereochemistry at three centers. A planar projection and conformational drawing is shown below.





Bz = PhC(=O)-

(a) Determine the stereochemistry at C-6. Explain what signal(s) you used, give their shift and multiplicity (e.g. δ 0.00, tq, J =0, 0) and briefly describe how you made the stereochemical assignment using the data:

A =______ , B =_______ (**H** or **CO_2Me**).

(b) Determine the stereochemistry at C-4. Explain what signal(s) you used, give their shift and multiplicity and briefly describe how you made the stereochemical assignment using the data:

C =______ , D =_______ (**H** or **OBz**).

(c) Determine the stereochemistry at C-3. Explain what signal(s) you used, give their shift and multiplicity and briefly describe how you made the stereochemical assignment using the data:

E =______ , F =_______ (**H** or **OBz**).

Problem R-10J ($C_{24}H_{28}O_9$)
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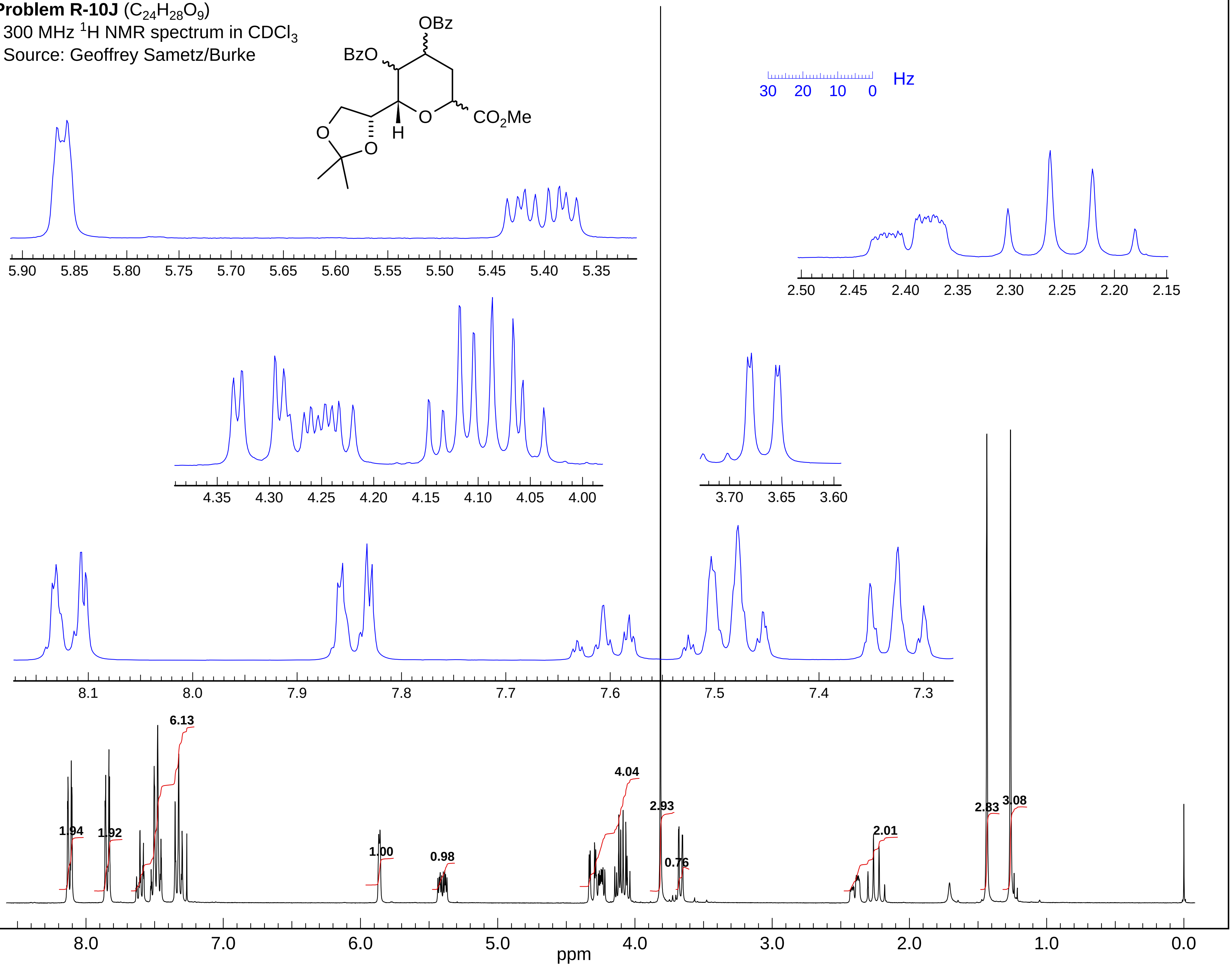

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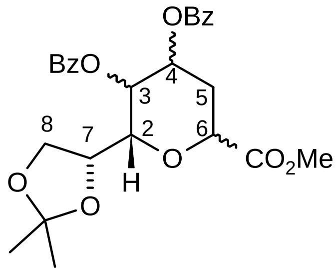
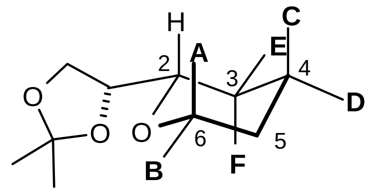
Problem R10J ($C_{24}H_{28}O_9$). This problem requires you to analyze part of the ^{1}H NMR spectrum of a tetrahydropyran, and determine the stereochemistry at three centers. A planar projection and conformational drawing is shown below.





Bz = PhC(=O)-

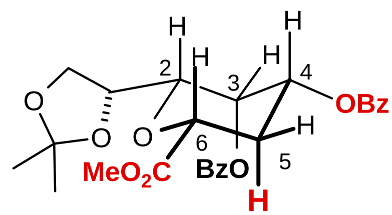
3 pts for correct answer
3 or 4 for reasoning

(a) Determine the stereochemistry at C-6. Explain what signal(s) you used, give their shift and multiplicity (e.g. δ 0.00, tq, J =0, 0) and briefly describe how you made the stereochemical assignment using the data:

A = H , B = CO_2Me (**H** or **CO_2Me**). **δ 4.31 (H^6)**

7 The quartet at δ 2.24 (q, J = 12 Hz) is the axial proton at C-5. The three large couplings must be a J_{gem} and two $J_{ax\text{-}ax}$, thus protons on both sides are axial, and the substituents at C-6 and C-4 must both be equatorial.

The couplings of the equatorial proton H^{5e} (dddd J = 12, 5, 2.5, 1 Hz) also help identify the H^4 (5.40, J = 5 Hz) and H^6 (4.31, J = 2.5 Hz) protons



(b) Determine the stereochemistry at C-4. Explain what signal(s) you used, give their shift and multiplicity and briefly describe how you made the stereochemical assignment using the data:

C = H , D = OBz (**H** or **OBz**). **δ 5.40 (H^4)**

6 See part (a)

The signal at 5.4 shows J = 12, 5, 3, so one axial-axial coupling (to H^5), and two ax-eq couplings to H^3 and H^5 (this also proves that H^3 must be equatorial)

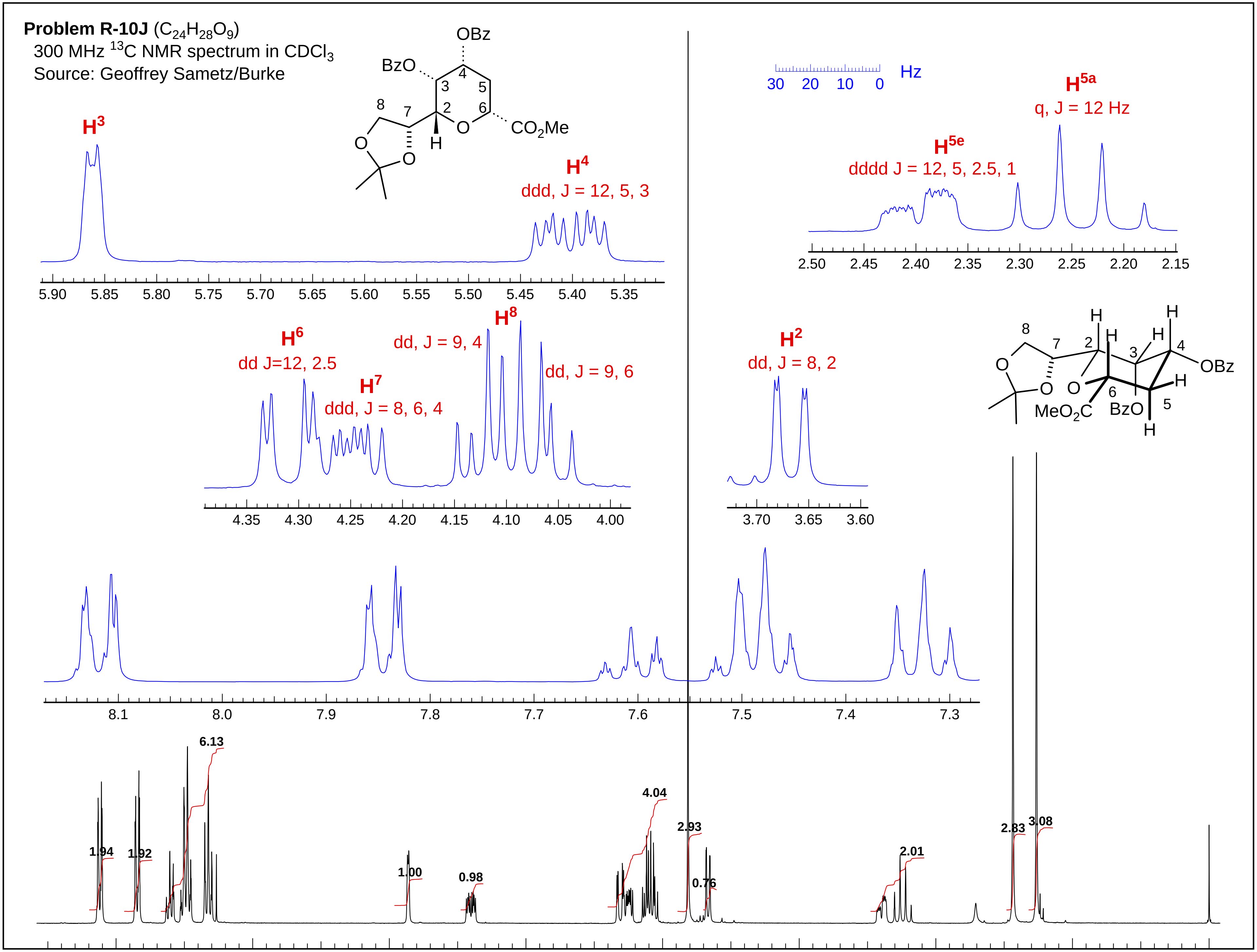
(c) Determine the stereochemistry at C-3. Explain what signal(s) you used, give their shift and multiplicity and briefly describe how you made the stereochemical assignment using the data:

E = H , F = OBz (**H** or **OBz**). **δ 5.86 (H^3)**

The "d" at 5.86 has to be H^3 - it shows only one obvious small coupling. Since H^2 is axial, this means that H^3 must be equatorial, or else it would show a large $J_{ax\text{-}ax}$

7 Could also use the axial proton at H^4 5.40, ddd, J = 12, 5, 3 Hz. The 12 Hz coupling is the $J_{ax\text{-}ax}$ to H^5, the two smaller coulings have to be the $J_{ax\text{-}eq}$ to H^3 and H^5, hence H^3 has to be equatorial

The proton at H^2 (δ 3.67, dd, J = 8, 2 Hz) has to be axial, if it were equatorial the ring would flip. The 8 Hz coupling is to H^7, the 2 Hz couping must be to H^3. Thus H_3 must be equatorial.



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