Problem R-10J \((C_{24}H_{28}O_9)\)
300 MHz \(^1\)H NMR spectrum in CDCl\(_3\)
Source: Geoffrey Sametz/Burke

\[
\begin{align*}
\text{OBz} & & \text{BzO} \\
\text{CO}_2\text{Me} & & \text{CO}_2\text{Me} \\
\text{H} & & \text{H} \\
\text{H} & & \text{H} \\
\text{H} & & \text{H} \\
\text{O} & & \text{O} \\
\end{align*}
\]
75 MHz $^{13}$C NMR spectrum in CDCl$_3$

DEPT 135
**Problem R10J**  \((C_{24}H_{28}O_9)\). This problem requires you to analyze part of the \(^1H\) NMR spectrum of a tetrahydropyran, and determine the stereochemistry at three centers. A planar projection and conformational drawing is shown below.

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

\[A = \ldots, \ B = \ldots\ (H \text{ or } CO_2Me)\].

(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:

\[C = \ldots, \ D = \ldots\ (H \text{ or } OBz)\].

(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:

\[E = \ldots, \ F = \ldots\ (H \text{ or } OBz)\].
Problem R-10J \((\text{C}_{24}\text{H}_{28}\text{O}_9)\)

300 MHz \(^1\text{H} \) NMR spectrum in CDCl\(_3\)

Source: Geoffrey Sametz/Burke
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.

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

A = __________, B = ________CO_{2}Me (H or CO_{2}Me). $\delta$ 4.31 (H^6)

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

(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 = __________OBz (H or OBz). $\delta$ 5.40 (H^4)

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 = ________, F = ________OBz (H or OBz). $\delta$ 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 $J_{ax-ax}$.

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

The proton at H^2 ($\delta$ 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 coupling must be to H^3. Thus H^3 must be equatorial.
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300 MHz \(^{13}\text{C}\) NMR spectrum in CDCl\(_3\)
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\(\text{H}^3\)  
\(\text{H}^4\) ddd, \(J = 12, 5, 3\)

\(\text{H}^6\) dd, \(J = 9, 4\)  
\(\text{H}^8\) dd, \(J = 9, 6\)

\(\text{H}^7\) ddd, \(J = 8, 6, 4\)

\(\text{H}^2\) dd, \(J = 8, 2\)

\(\text{H}^{5a}\) q, \(J = 12\) Hz

\(\text{H}^{5e}\) dddd \(J = 12, 5, 2.5, 1\)

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