Problem R-64 (C_{12}H_{10}S). Below are four $^{13}$C NMR spectra (50 MHz). The upper spectra are of diphenyl sulfide (Ph$_2$S). The lower spectra are of Ph$_2$S partially deuterated. The left set of spectra are proton-decoupled, the right set is fully coupled. Source: S.-K. Chung, K. Sasamoto JOC 1981, 46, 4950 (DOI: 10.1021/jo00335a062)

(a) Assign the resonances in the unlabelled spectra ($C^1$, $C^2$, $C^3$, $C^4$).

(b) Assign the various peaks in the D-labelled spectra.

(c) Determine the position(s) and roughly estimate the extent of deuteration indicated by the upper spectra. Briefly give your reasoning. Hint: calculate the expected C-D couplings and compare to the observed ones before assigning the signals.

\[
\begin{align*}
{^{13}}C \{^1H\} & \quad \text{Coupled} \\
136 & 134 132 130 128 & 138 & 136 134 132 130 128 \quad \text{ppm} \\
136 & 134 132 & 130 128 \quad \text{ppm}
\end{align*}
\]
**Problem R-64** (C₁₂H₁₀S). Below are four $^{13}$C NMR spectra (50 MHz). The upper spectra are of diphenyl sulfide (Ph₂S). The lower spectra are of Ph₂S partially deuterated. The left set of spectra are proton-decoupled, the right set is fully coupled. Source: S'-K' Chung, K'Sasamoto JOC 1981, 46, 4950 (DOI: 10.1021/jo00335a062)

(a) Assign the resonances in the unlabelled spectra (C¹, C², C³, C⁴).

C² and C³ can be distinguished because C² is a doublet of triplets from coupling to two protons meta to it – only $^3$JCH is large enough to resolve. C³ is a doublet of doublets.

(b) Assign the various peaks in the D-labelled spectra.

The signal at C² (δ 131) shows a 1:1:1 triplet, with an upfield isotope shift of ca 0.5 ppm for the C-D carbon. Thus D must be on C².

The signal at C³ (δ 139) also shows an isotope shift. Thus D must be on C² or C⁴.

(c) Determine the position(s) and roughly estimate the extent of deuteration indicated by the upper spectra. Briefly give your reasoning. Hint: calculate the expected C-D couplings and compare to the observed ones before assigning the signals.

The three peaks for C¹ (labelled A, B, C) are separated by 6 Hz. These cannot be due to $^3$JCD since this would be at most 1/6 x 7.4 Hz (if D was meta), or to $^2$JCD, if D was ortho (as it actually is) since it would be only 1/6 x 1.0 Hz. The A/B/C peaks are from the 2-bond isotope shift due to the H/H, H/D and D/D isotopomers.

The deuterium seems to be almost entirely at C² (this is the only carbon that shows $^1$JCD). The best estimate of the level of labelling at C² is probably from the two peaks at C³ (two-bond isotope shift), (60% D, 40% H). There must a significant amount of 2,6-dideutero, to account for peak C at C¹, and very little 2,6-diprotio (structure A), otherwise peak A at C¹ would be taller. Peaks B and especially C are very weak because they would have long $T_1$ due to loss of CH DD relaxation, leading to saturation, and possible loss of NOE enhancement.