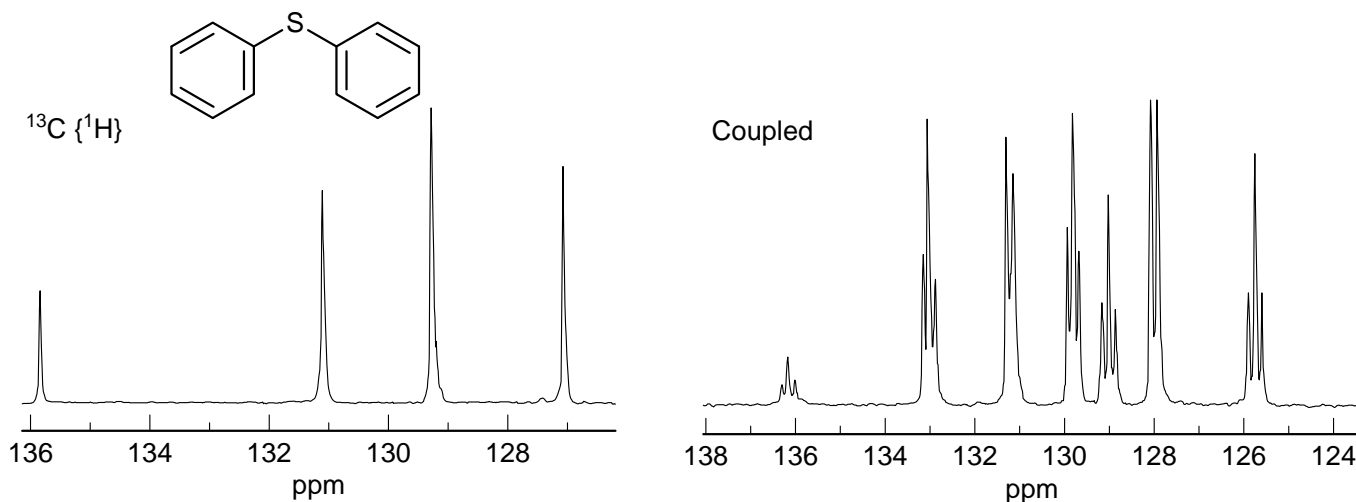
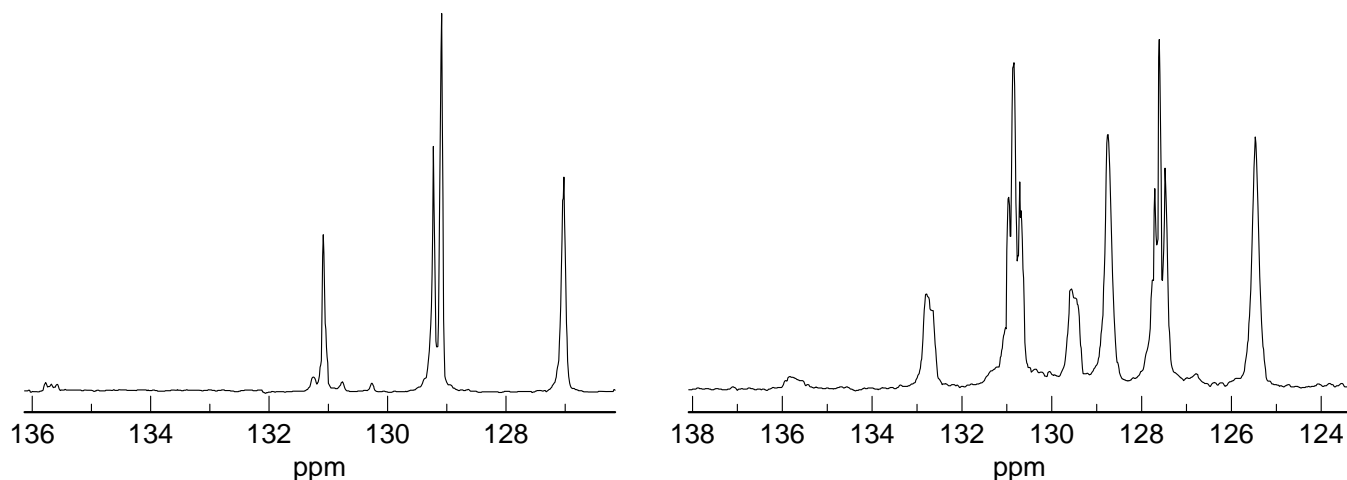


**Problem R-64** ( $C_{12}H_{10}S$ ). Below are four  $^{13}C$  NMR spectra (50 MHz). The upper spectra are of diphenyl sulfide ( $Ph_2S$ ). The lower spectra are of  $Ph_2S$  partially deuterated. The left set of spectra are proton-decoupled, the right set is fully coupled. Source: S.-K. Chung, K. Sasamoto *JOC* **1981**, 46, 4950 (DOI: 10.1021/jo00335a062)

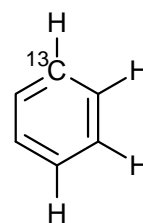
(a) Assign the resonances in the unlabelled spectra ( $C^1$ ,  $C^2$ ,  $C^3$ ,  $C^4$ ).



(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.



$$^1J_{CH} = 159 \text{ Hz}$$

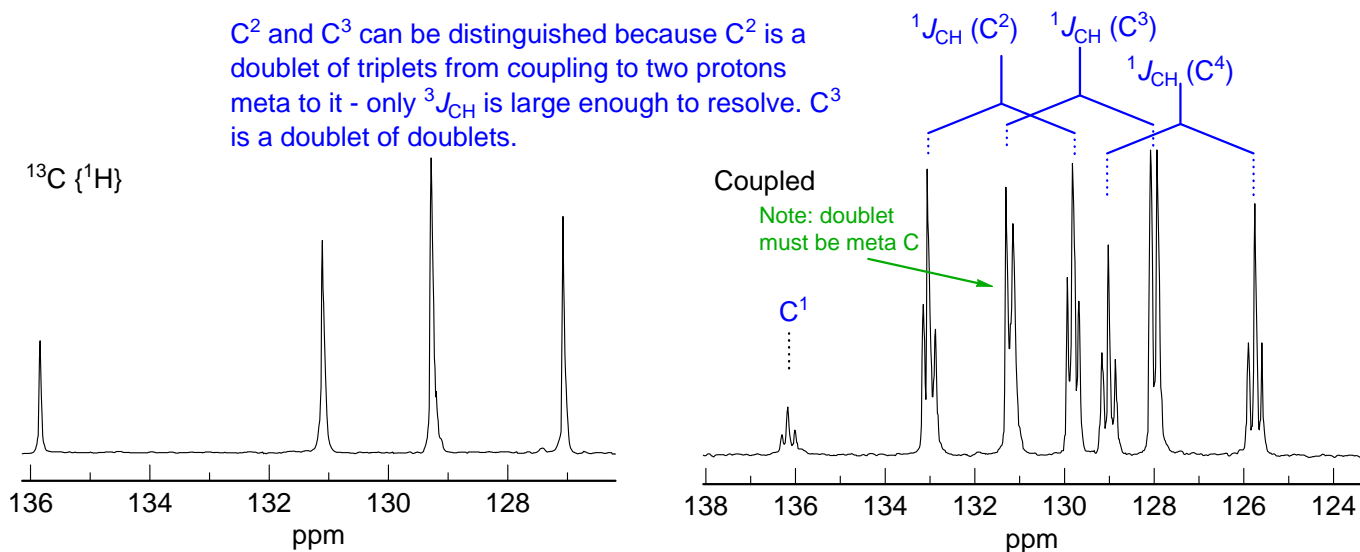
$$^2J_{CH} = 1.0 \text{ Hz}$$

$$^3J_{CH} = 7.4 \text{ Hz}$$

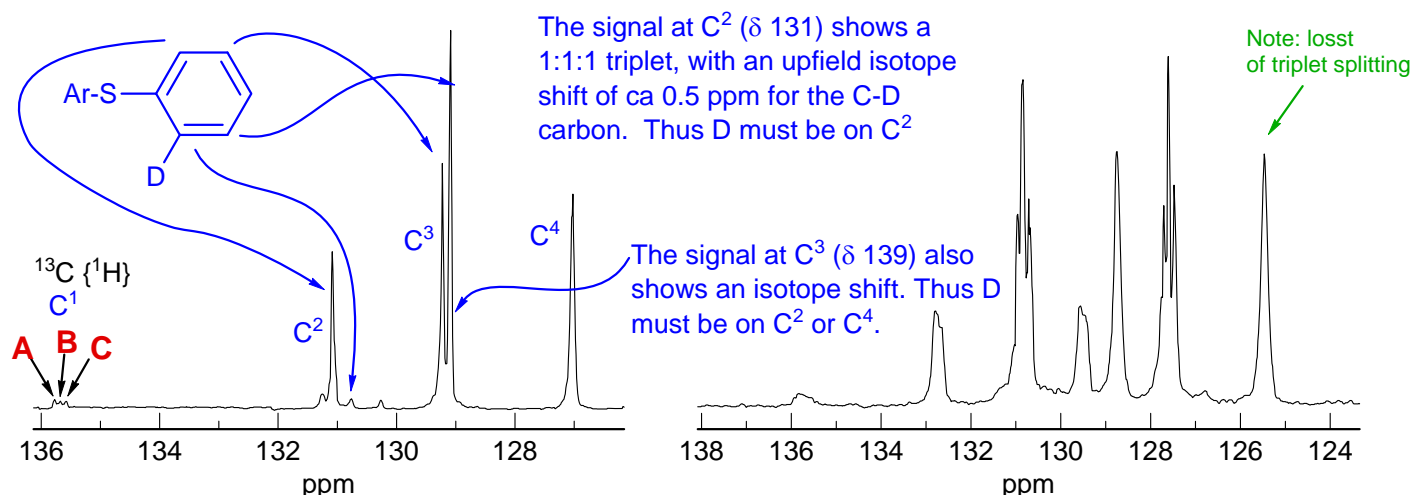
$$^4J_{CH} = -1.1 \text{ Hz}$$

**Problem R-64** ( $C_{12}H_{10}S$ ). Below are four  $^{13}C$  NMR spectra (50 MHz). The upper spectra are of diphenyl sulfide ( $Ph_2S$ ). The lower spectra are of  $Ph_2S$  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)

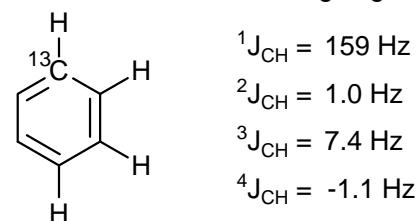
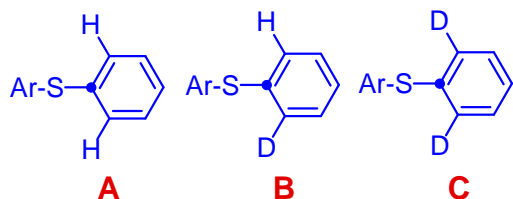
(a) Assign the resonances in the unlabelled spectra ( $C^1$ ,  $C^2$ ,  $C^3$ ,  $C^4$ ).



(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.



The three peaks for  $C^1$  (labelled A, B, C) are separated by 6 Hz. These cannot be due to  $^3J_{CD}$  since this would be at most  $1/6 \times 7.4 \text{ Hz}$  (if D was meta), or to  $^2J_{CD}$ , if D was ortho (as it actually is) since it would be only  $1/6 \times 1.0 \text{ Hz}$ . 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  $C^2$  (this is the only carbon that shows  $^1J_{CD}$ ). The best estimate of the level of labelling at  $C^2$  is probably from the two peaks at  $C^3$  (two-bond isotope shift), (60% D, 40% H). There must be a significant amount of 2,6-dideutero, to account for peak C at  $C^1$ , and very little 2,6-diproto (structure A), otherwise peak A at  $C^1$  would be taller. Peaks B and especially C are very weak because they would have long  $T_1$  due to loss of  $\underline{CH}$  DD relaxation, leading to saturation, and possible loss of NOE enhancement.