1. (10 pts) Chapters 12 and 13 teach us that aromatic systems do not undergo addition reactions like conventional alkenes. Instead, electrophilic reagents (often generalized as “$\text{E}^+$”) react to replace a proton (“$\text{H}^+$”) on the aromatic ring. Of course, a proton (or a deuteron) is an electrophile (Lewis acid) itself. So it is possible to exchange deuterium into aromatics in much the same way that we saw in the acid-catalyzed exchange of D into alkenes (remember Elvira’s study of Igor’s acid-catalyzed hydration of alkenes). So…Elvira sets out to make the fully deuterated analogue of anisole (methoxybenzene), but decides to “watch” the reaction in progress via NMR. She notices that the deuterium is incorporated into the 2-, 4-, and 6-positions much faster than into the 3- and 5-positions, although the 3-incorporation does eventually happen as well (we don’t have to worry about the H’s in the CH$_3$ group; they don’t exchange at all). Explain the relative rates of reaction in terms of the electrophilic substitution mechanism.

![Diagram showing the incorporation of deuterium into anisole](image.png)
2. (5 pts) Realizing that she is really observing a competition among the ortho, meta, and para sites in the anisole, Elvira wonders how to simplify the system so that all the ring C-H sites in the compound would exchange at the same rate. She considers the following three disubstituted benzenes A, B, and C, but ultimately settles on only one. Can you predict her answer? Which of these compounds (circle your choice) will have the same rates of H/D exchange at all sites? Explain.

Only C has all four sites equivalent in terms of symmetry and thus reactivity.

3. (5 pts) Now predict which of the compounds A, B, or C above would have the fastest H/D exchange rate for the first exchange, and explain your reasoning.

Compound B has three sites that are doubly activated. Both OCH$_3$ groups in B contribute stabilization for attack at the same three sites, marked with arrows at left. So H/D exchange at those sites will be faster than on any sites in A or C. Even though all attacks must be ortho to at least one OCH$_3$, steric effects are not important for small electrophiles like H$^+$/D$^+$. 