Answer all questions as completely as you can. Clearly show your work and reasoning.

(1) Two mechanisms are shown below for the reaction of singlet oxygen (generated photochemically from normal, triplet oxygen) with tetramethylethylene. Mechanism A gives a zwitterion, while mechanism B gives a cyclic per-epoxide; the intermediates then swiftly react by hydrogen abstraction to give the final product. Please note that the per-epoxide is expected to be geometrically rigid.

Isotopically substituted versions of tetramethylethylene were used to try to differentiate the two mechanisms. The isotope effects are shown below, relative to tetramethylethylene itself. Which mechanism do you think is more likely, based on the isotope effects observed? Briefly explain your answer. (50 pts)

\[
\begin{align*}
\text{H}_3\text{C} &\text{CH}_3 &\text{O} &\text{O} &\text{H}_3\text{C} \\
\text{H}_3\text{C} &\text{CH}_3 &\text{mechanism} &\text{A} &\text{H}_3\text{C} \\
\text{H}_3\text{C} &\text{CH}_3 &\text{mechanism} &\text{B} &\text{H}_3\text{C}
\end{align*}
\]

KINETIC ISOTOPE EFFECT EXPERIMENTS

\[
\begin{align*}
\text{H}_3\text{C} &\text{CD}_3 &\text{CD}_3 &\text{H}_3\text{C} \\
\text{H}_3\text{C} &\text{CD}_3 &\text{H}_3\text{C} \\
\text{H}_3\text{C} &\text{CD}_3 &\text{H}_3\text{C}
\end{align*}
\]

\[
\begin{align*}
k_{\text{H}}/k_{\text{D}} &= 1.44 \\
k_{\text{H}}/k_{\text{D}} &= 1.02 \\
k_{\text{H}}/k_{\text{D}} &= 1.04
\end{align*}
\]

(2) Are the effects described in (1) above primary or secondary isotope effects? Briefly explain your answer. (20 pts)

(3) Briefly describe a cross-over labeling experiment. You may use the reaction shown below as an example for your description (30 pts).