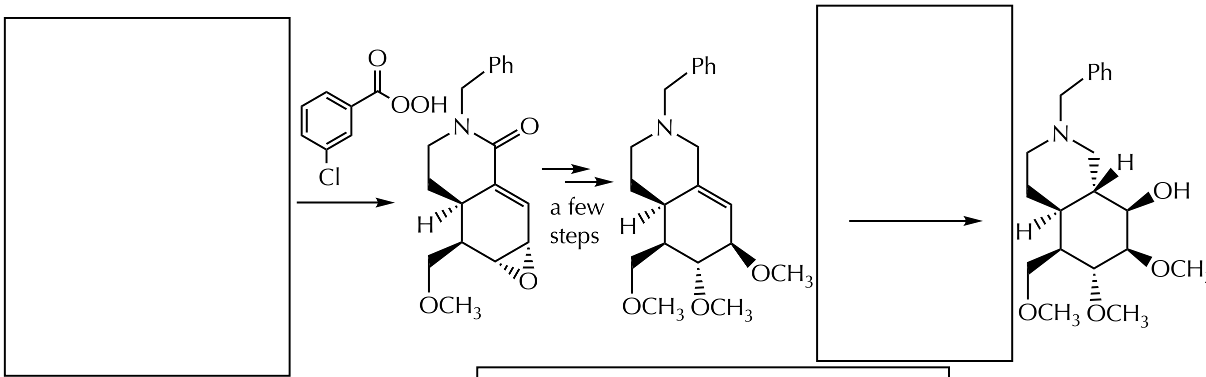
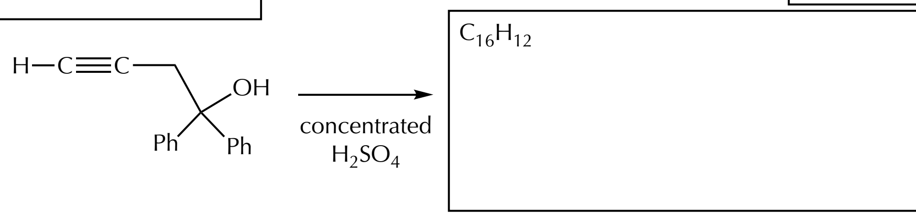
*Thinking in Blue #13 - featuring EQ 03.19*

Complete the following as required. Complete structures should be shown, not abbreviations or acronyms. Sequential experimental steps should be numbered.

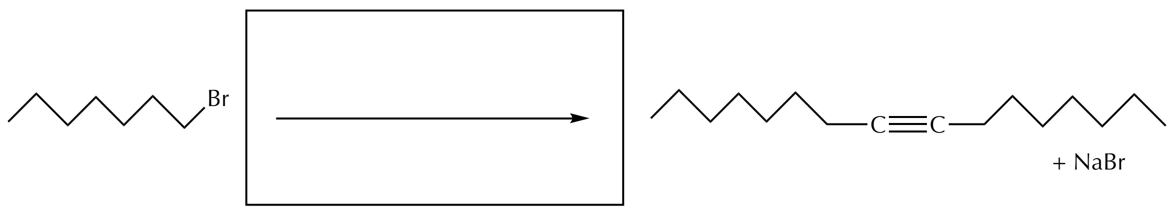
(a)



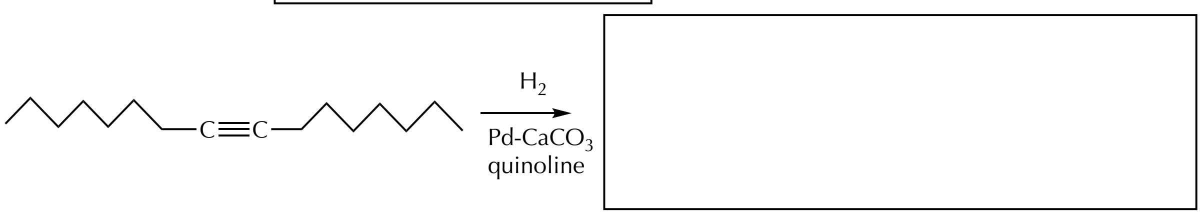

(b)



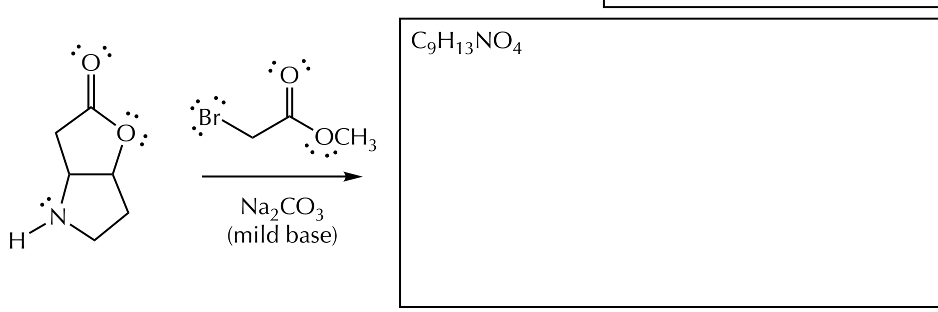

(c)



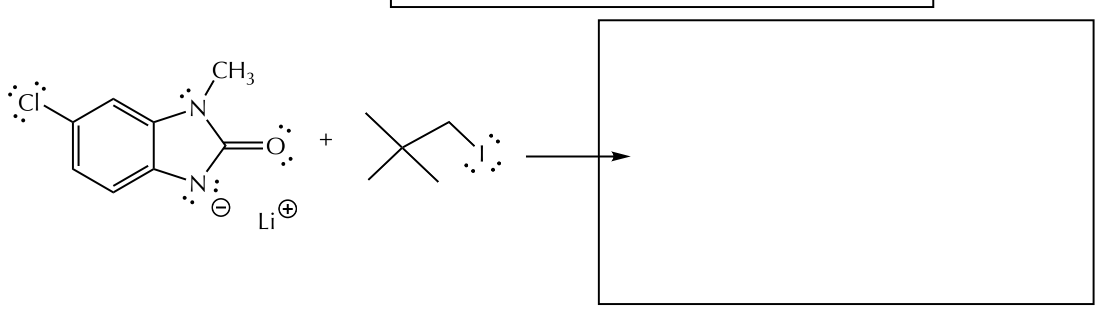

(d)




(e)



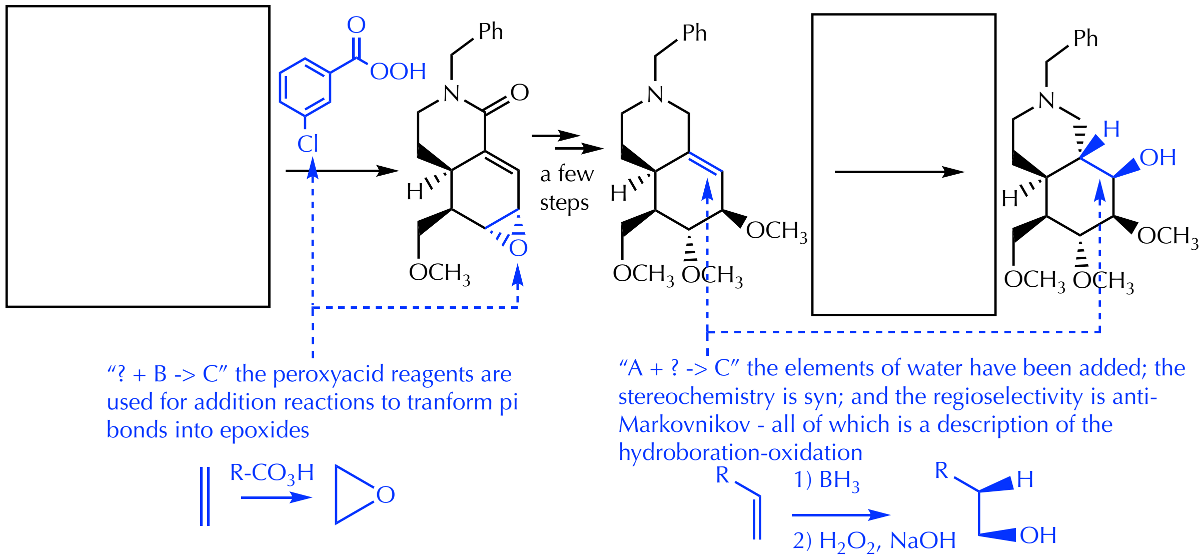

(f)

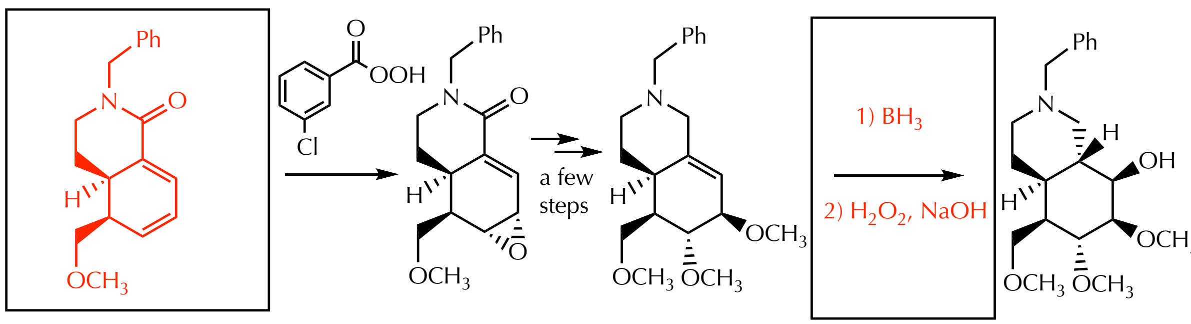


The previous Thinking in Blue question (Week 12) contains an extensive look at the kind of cumulative background knowledge is needed to answer these kinds of questions confidently. With that background, the strategy here is (a) to use the information present to identify and classify the reaction, then (b), access the general concepts associated with that type of reaction, and finally (c), to apply the general concept to the specific case.

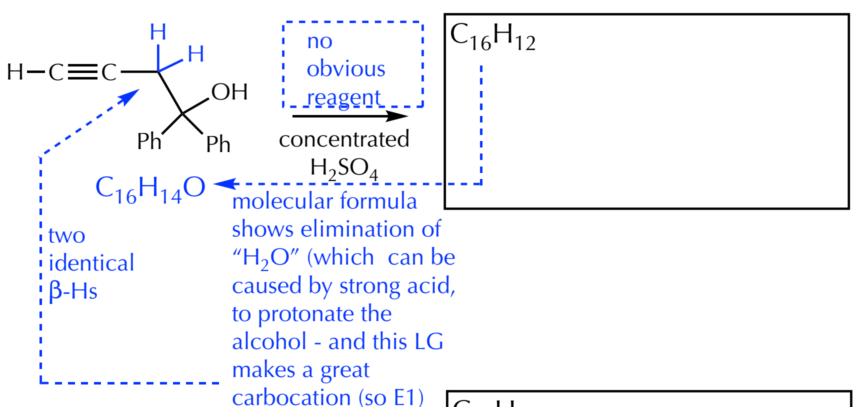
Complete the following as required. Complete structures should be shown, not abbreviations or acronyms. Sequential experimental steps should be numbered.

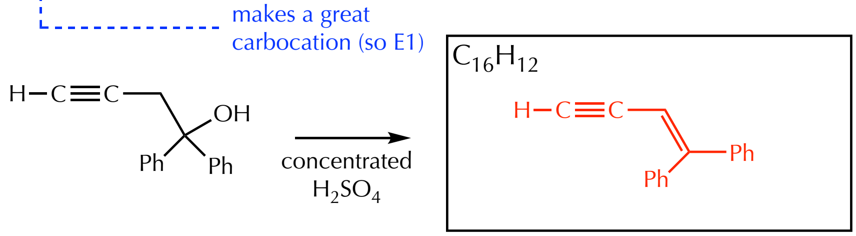
(a)



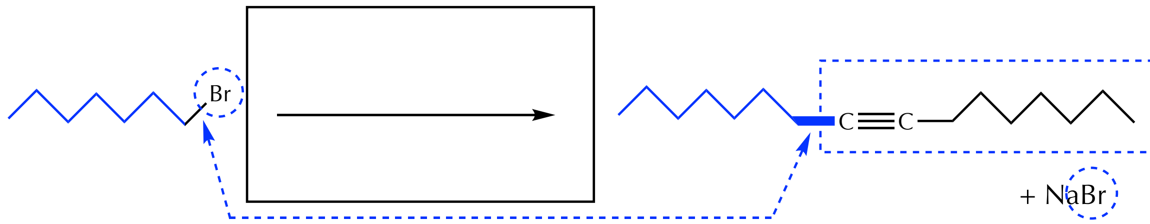




(b)

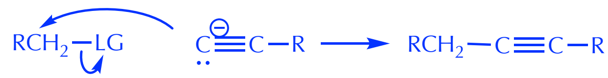


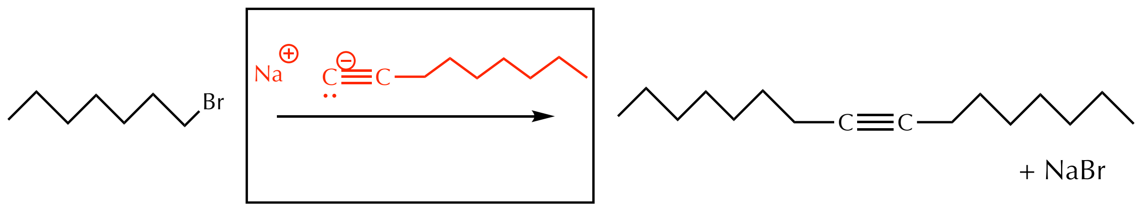



(c)

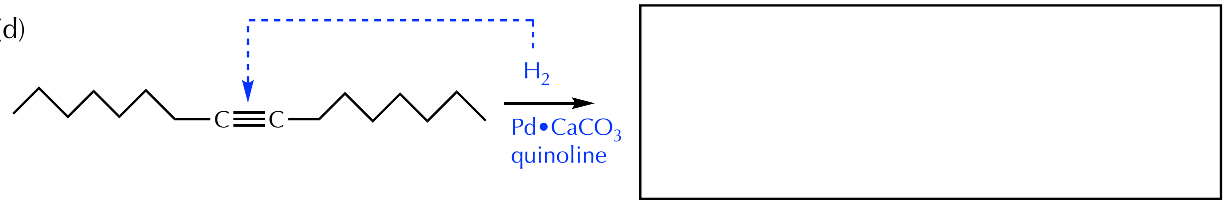



the 7-carbon chain with a 1˚ C-Br LG has undergone a substitution reaction to make this new C-C bond with an sp C atom; one bromide is shown, so only one of the chains in the product was placed during the reaction, not both of them (so the other one was intact); sp carbanions are excellent nucleophiles for $S_N2$ reactions with 1˚ C-LG bonds… the counterion is given to be a sodium ion (yet another reminder that this answer COULD have been generated based on core principles, on the first day of class!

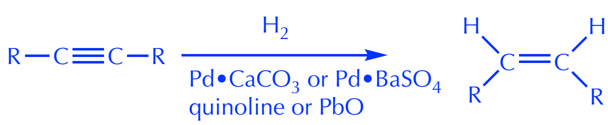


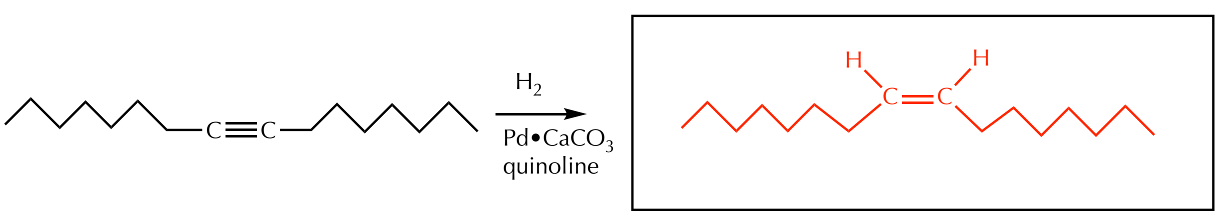

(d)



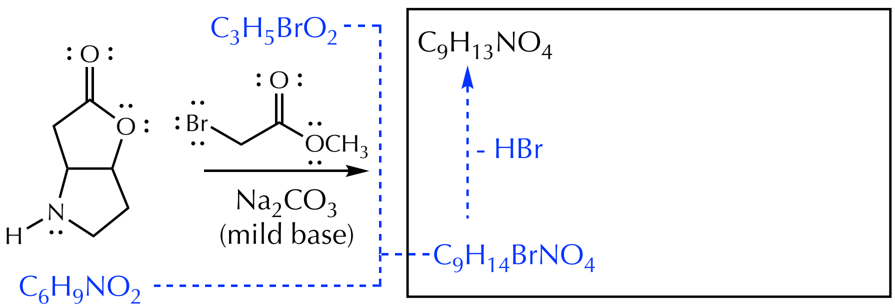

Addition of hydrogen to a triple bond can be done twice with a regular catalyst (Pd-C), once to give an (E)-double bond using $Na/NH_3$ or $Li/NH_3$, and once to give a (Z)-double bond using one of the “poisoned catalyst” conditions (which is what is shown here).



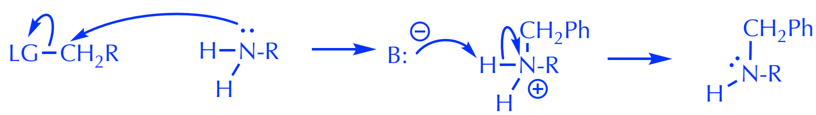

The molecular geometry of the new $sp^2$ atoms should be shown correctly.

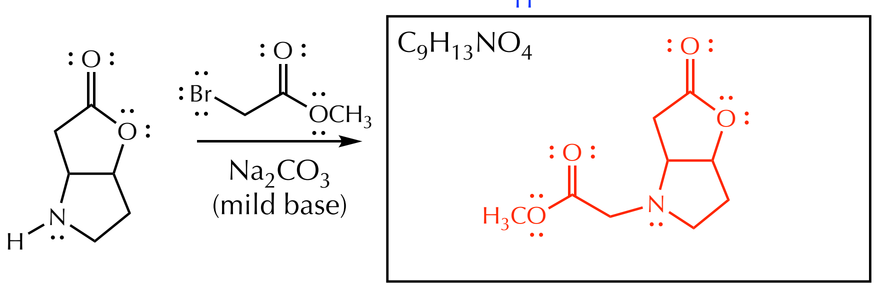


(e)

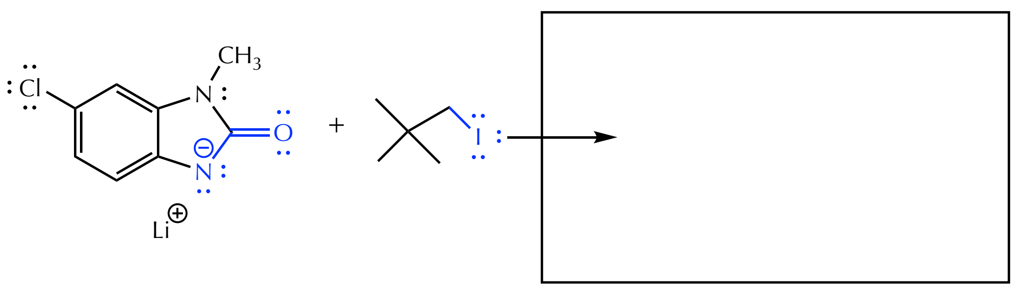



In general, molecular formulas are quite useful. The product is the sum of both reagents minus HBr. The loss of Br (particularly as bromide anion) is consistent with its being a leaving group, and because there are no b-Hs, the molecule can only have undergone substitution. As a 1˚ C-Br bond with no b-Hs, it favors Lewis bases for $S_N2$ that are anions whose conjugate acids are fairly weak … but there are no anions in the $C_6H_9NO_2$ component, and the indication of the mild base (sodium carbonate) is a reminder that getting an anion is not going to be easy. But uncharged $sp^3$ nitrogen, sulfur, and phosphorus atoms are also good Lewis bases for $S_N2$ reactions of 1˚ C-LG bonds, and there is an uncharged $sp^3$ nitrogen atom present. The general scheme would be:




(f)



The molecule on the right (once again) has a potential LG on a 1˚ C and no b-Hs. This time there is an anion, and the best match on the $pK_a$ table for its conjugate acid is about 15, so this is also a combination that can give $S_N2$ substitution.