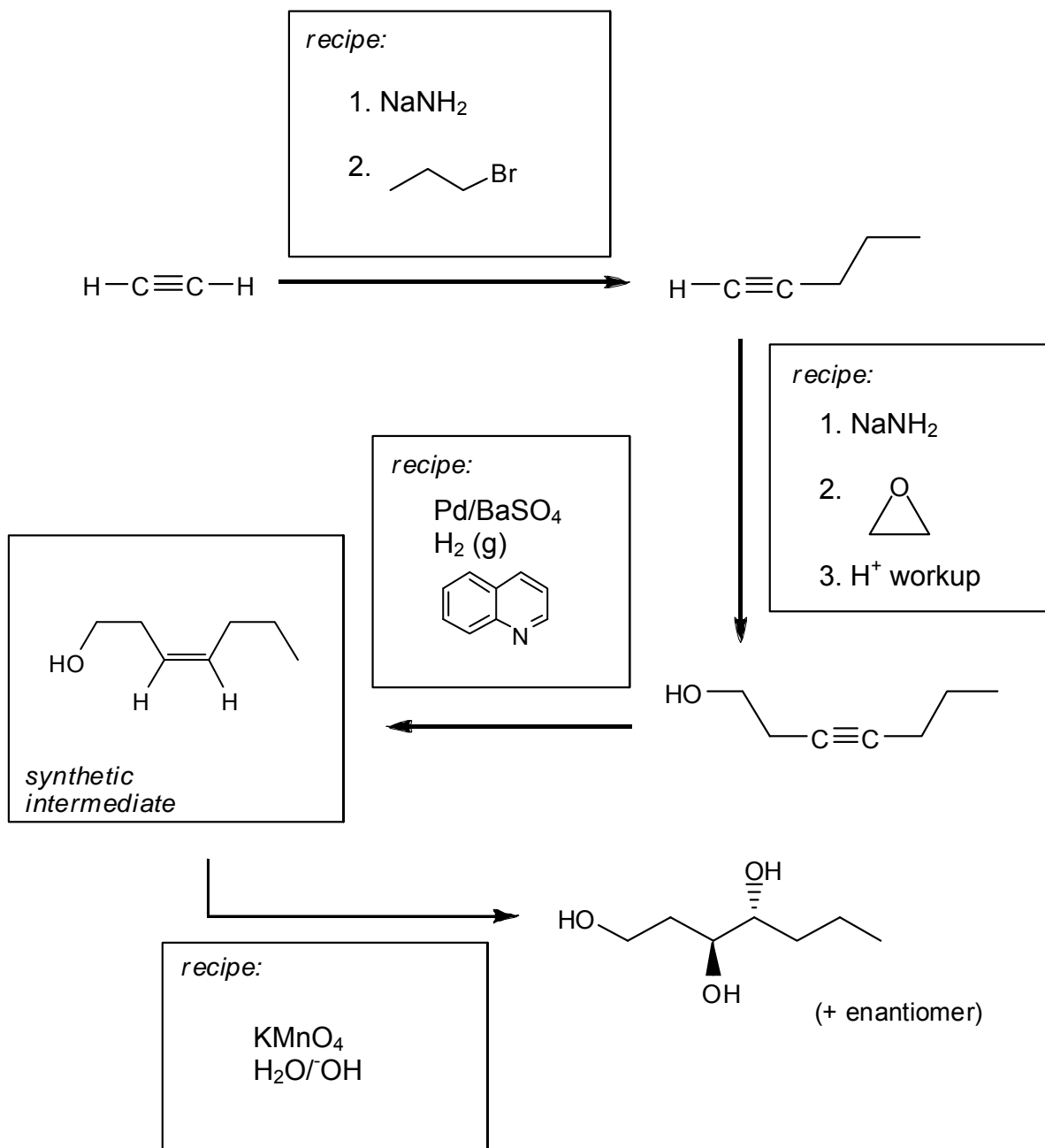
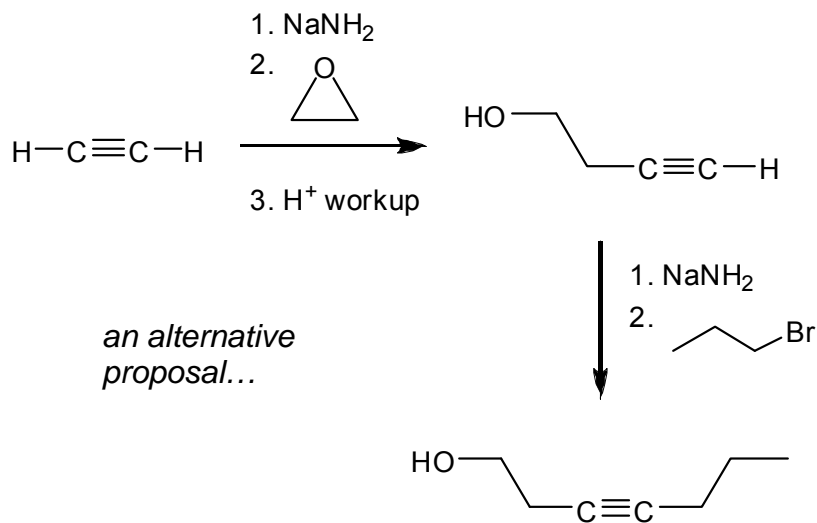
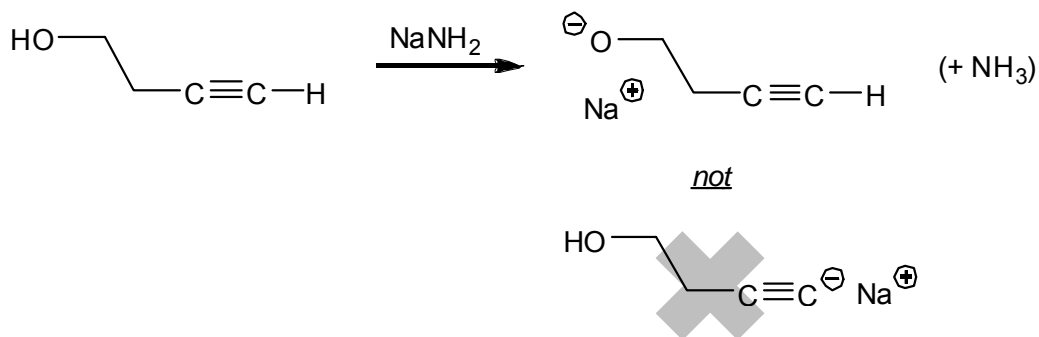


In-Class Solutions:  
Alkynes in Synthesis

a. One might very well propose that the order of the first two steps could be reversed:

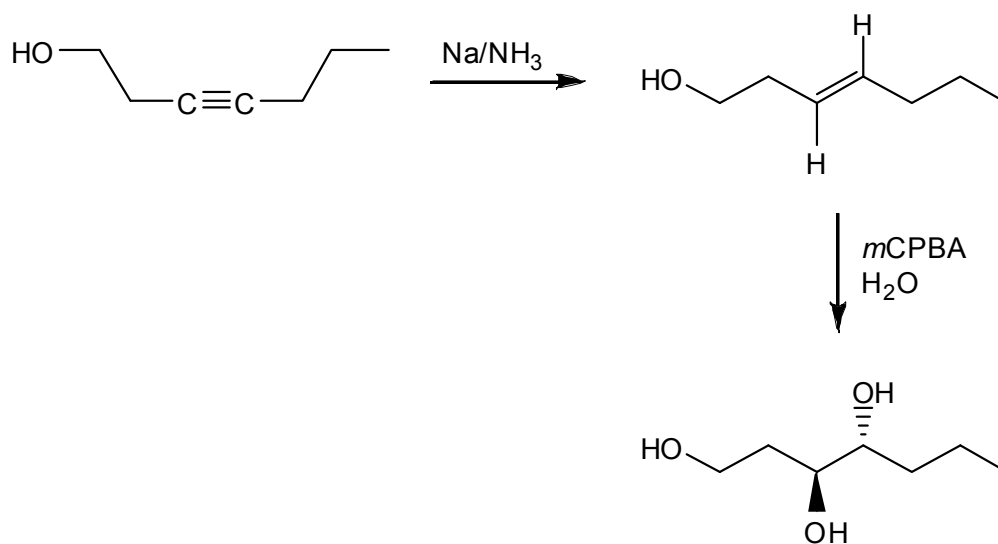


As written, this synthesis wouldn't work, because the second step would fail. NaNH<sub>2</sub> is a strong base, intended to be strong enough to deprotonate the alkyne (pK<sub>a</sub> ≈ 25). But that would also make it strong enough to deprotonate the alcohol (pK<sub>a</sub> ≈ 16, close to water), and because the alcohol is a stronger acid, it would be deprotonated first.

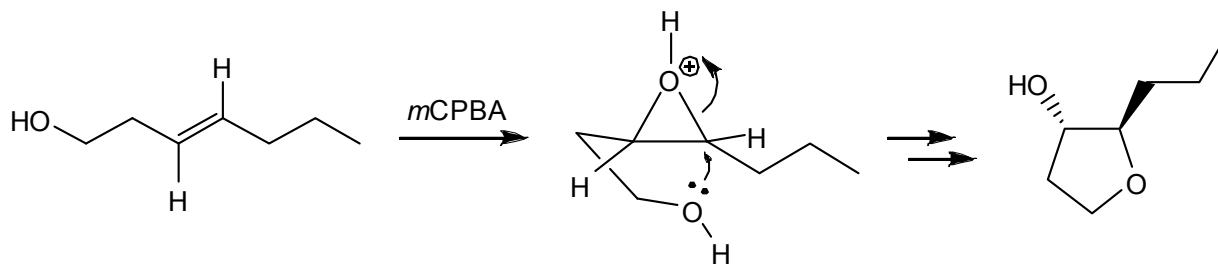


So, in the subsequent S<sub>N</sub>2 reaction, the alkoxide would act as the nucleophile, which definitely isn't what we want. The better way to do this, then, would be the way shown on the original synthesis—to add the alkyl halide first, and the epoxide second.

b. One way to do the last two steps is as I've shown it above—*syn*-hydrogenation of the alkyne with a poisoned catalyst, followed by *syn*-dihydroxylation of the *cis*-alkene with KMnO<sub>4</sub>. An alternative approach would be *anti*-hydrogenation of the alkyne with Na/NH<sub>3</sub>, followed by *anti*-dihydroxylation of the *trans*-alkene with *m*CPBA/H<sub>2</sub>O:



I don't like this route as much as the first one, because the terminal alcohol could serve as the nucleophile (instead of  $\text{H}_2\text{O}$ ) in the epoxide opening part of the second synthetic step:



This would be a potential side reaction of the second step of the route above, and the amount observed would depend on how much better  $\text{H}_2\text{O}$  was as a nucleophile compared with the alcohol. (I assume it wouldn't be any better.)