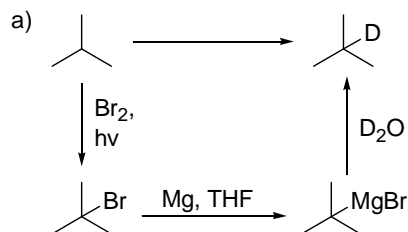
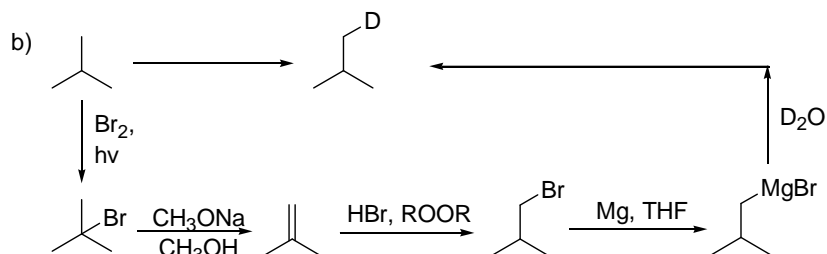


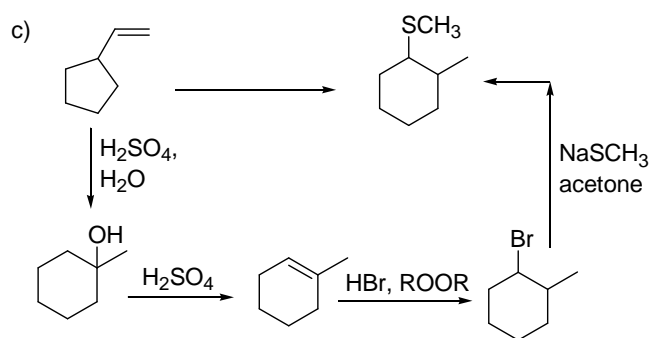
Design syntheses to create the target molecules from the given starting materials.



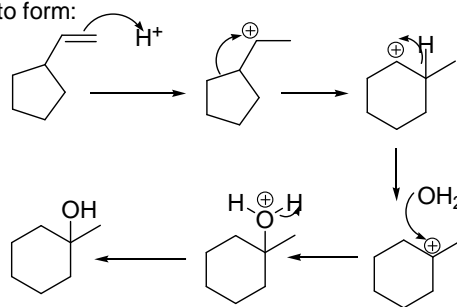
The starting material has no FGs at all, so you have to use the only reaction you know for alkanes: radical halogenation. Br₂ is the more selective choice. After that, you need to turn Br into the FG you want. D is pretty much a stand-in for H, so replace Br with D by turning it into a Grignard and then using D₂O.

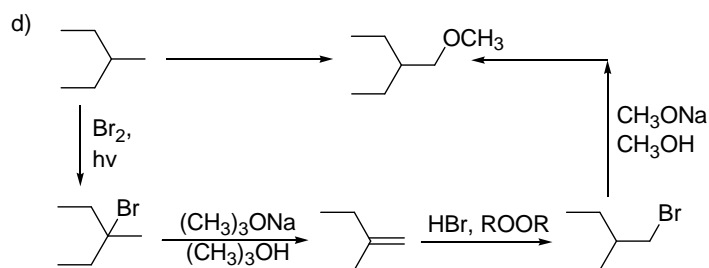


Again, a totally blank alkane means that you have to stick Br₂ on first. It only adds to the most substituted C so you'll need to eliminate and add back in if you want to access the carbon that's one away from there. Then finish up the reaction like before.

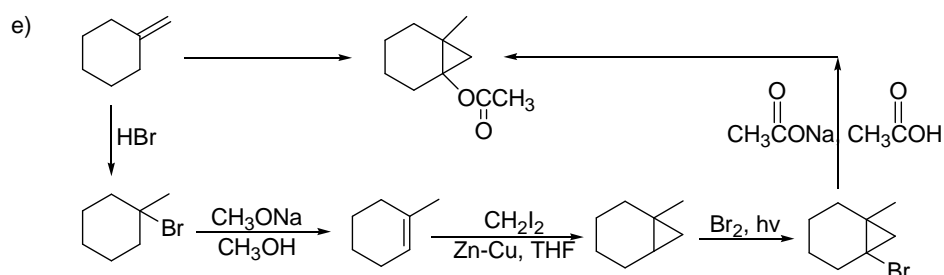


Seeing the entire carbon skeleton rearrange itself tells you that a carbocation is likely. You can hit the alkene directly with H₂SO₂ to get a carbocation to form:





This is pretty similar to (b), but the big difference is that there are multiple directions you can eliminate. You need to choose a strong base that will prefer anti-Zaitsev - in other words, tert-butoxide.



For this one, you need to add two new things to the carbon that ends up with the ester group hanging from it: you need to cyclopropanate there, and also add some sort of replaceable FG. We can do this by forming the double bond and cyclopropanating first, then using radical halogenation on the blank alkane that we get as a result. From there we just need to swap out the group.

I had a few people asking questions about this synthesis when it showed up on the previous handout. You know that the conditions in the last step should give you an $S_N1/E1$ mix, so why is S_N1 the only product? It has to do with ring strain. Being part of a three-membered ring means that the carbon (the one where the action is taking place) is constrained to hold 60 degree bond angles. But sp^3 carbon prefers angles of 109.5 degrees, so it's already pretty unstable. Doing the $E1$ pathway would create a double bond there, to an sp^2 carbon. In this case, the carbon would want bond angles of 120 degrees, so it would be less stable still. Given the choice between the two pathways, the molecule chooses not to make a bad situation worse, and just does the substitution reaction. This is related to something called Bredt's Rule - you can't make a double bond to a bridgehead carbon (one at the junction of multiple rings), especially when one or more of the rings is already strained.