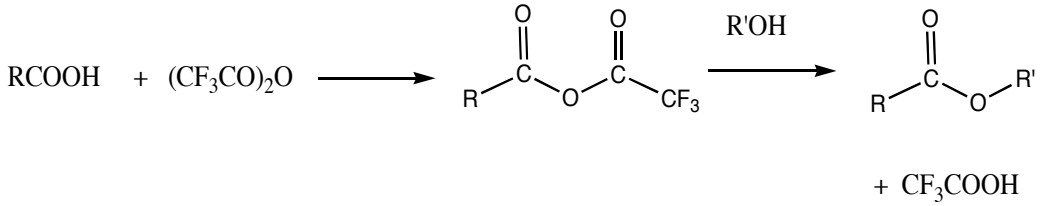
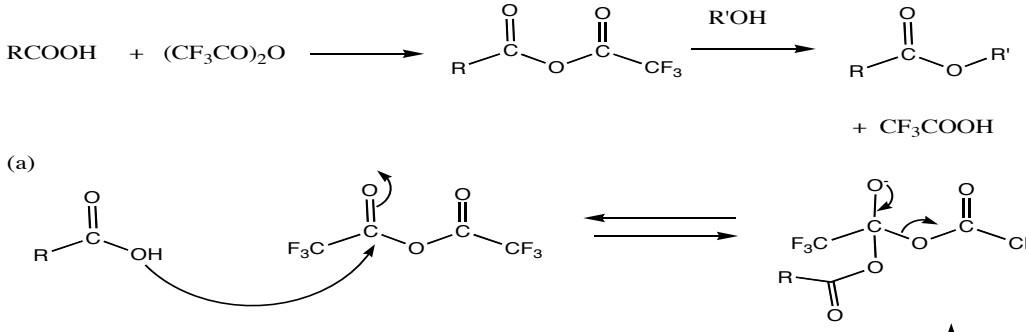
Problems for additional practice:

1. A particularly mild method of esterification involves the use of trifluoroacetic anhydride. Treatment of a carboxylic acid with trifluoroacetic anhydride leads to a mixed anhydride that rapidly reacts with alcohol:

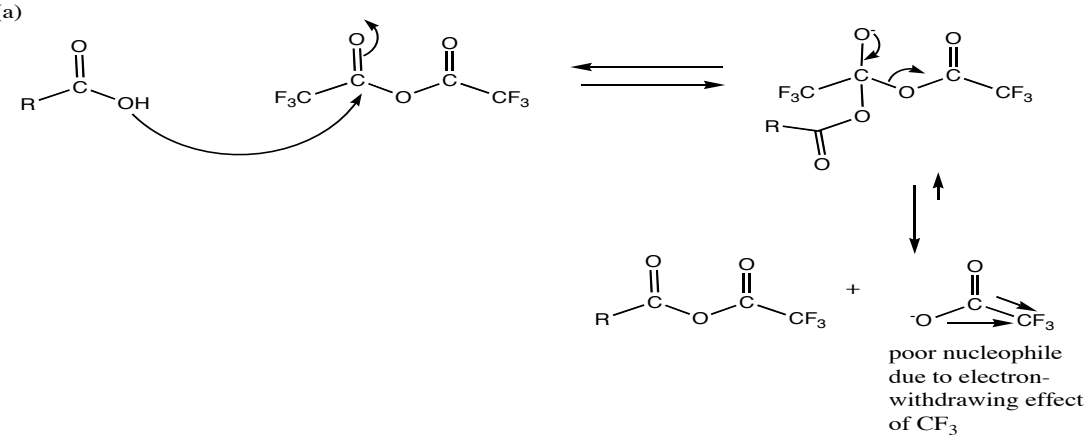


   (a) propose a mechanism for formation of the mixed anhydride

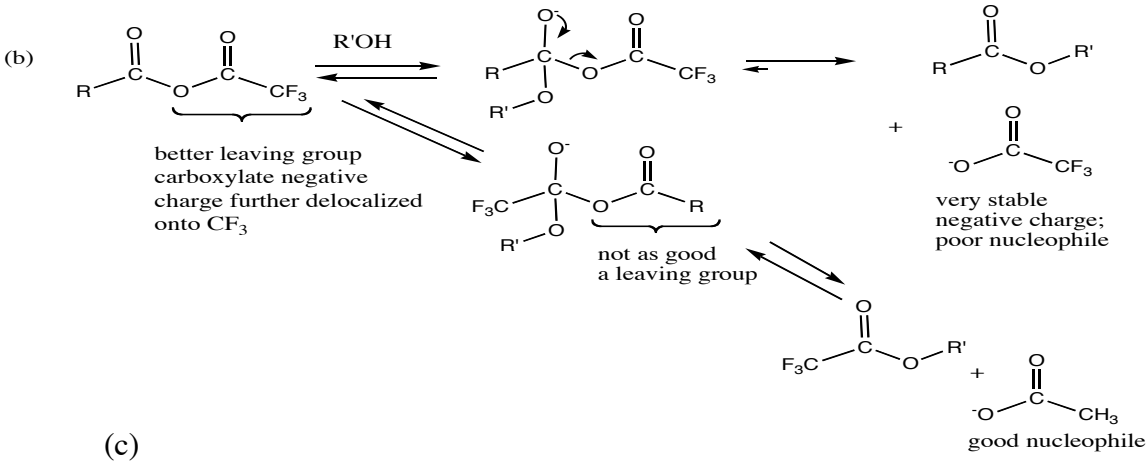
   (b) Why does the mixed anhydride react as indicated, rather than giving trifluoroacetate ester plus carboxylic acid?



(a)



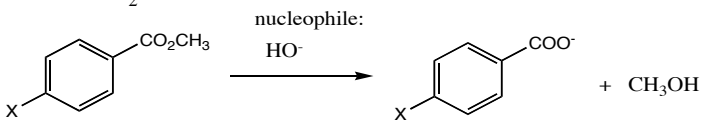
(b)



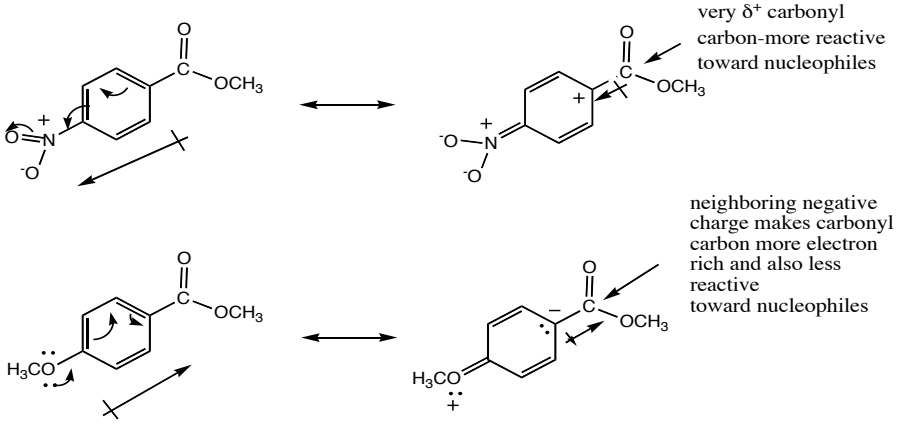
(c)

2. In the basic hydrolysis of para-substituted methyl benzoates

the following reactivity order has been found for X: NO_2>Br>H>CH_3>OCH_3. How can you explain this reactivity order?. Where would you expect X=CN, X=CHO and X=NH_2 to be in this list?



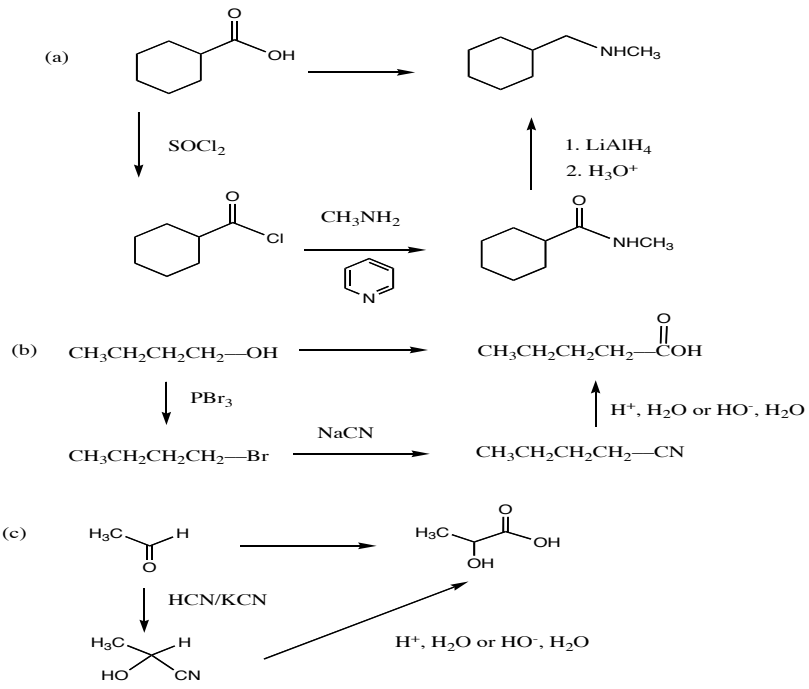
Reacitivity order parallels electron density of the aromatic ring:

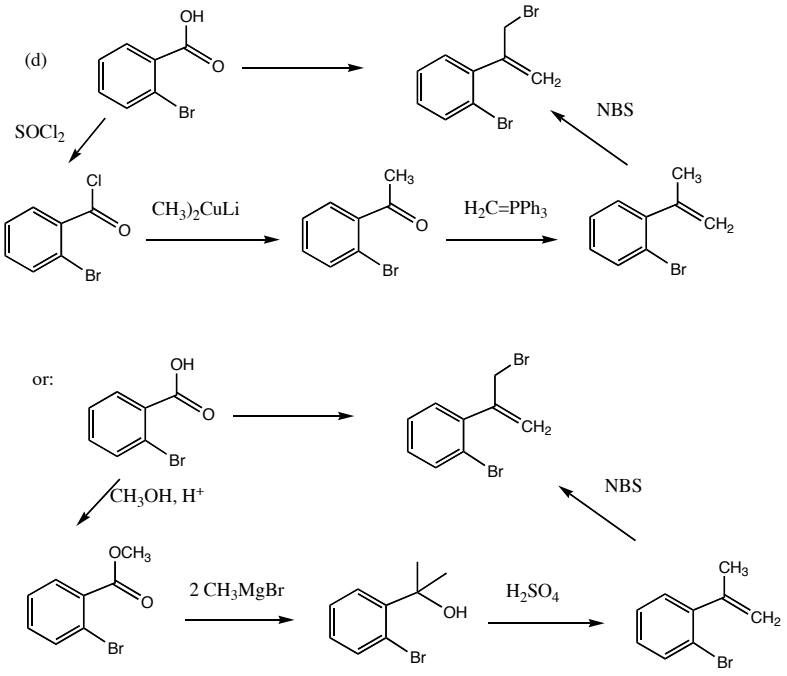


Thus, NO_2>Br>H>CH_3>OCH_3

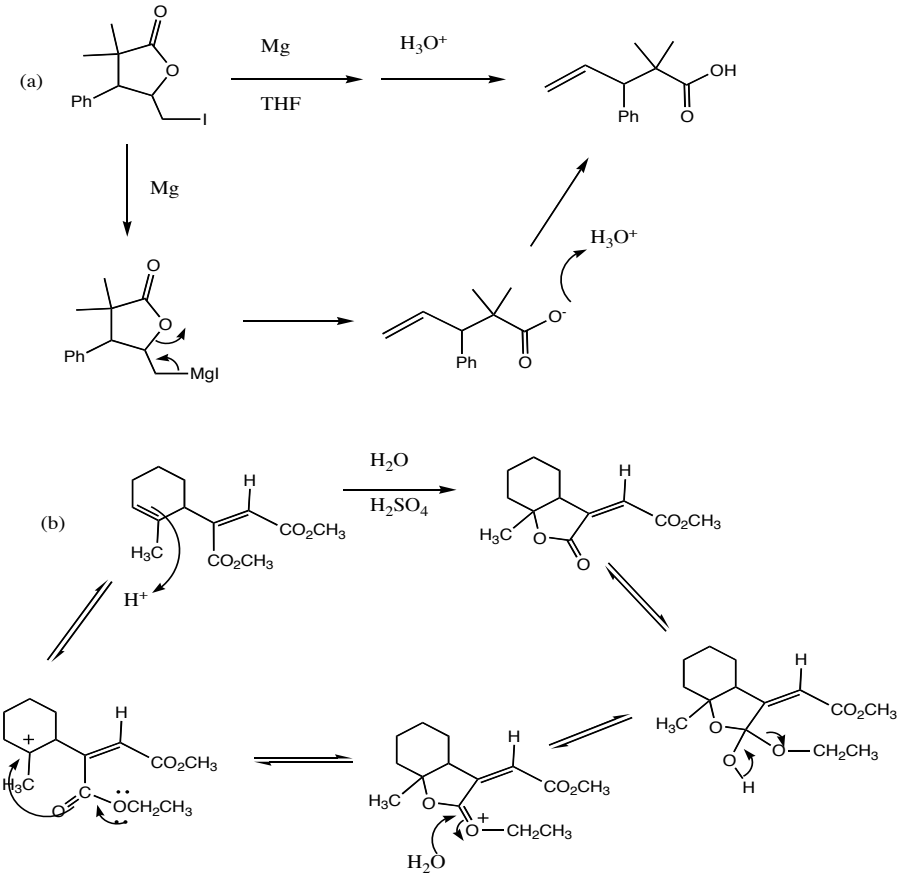
CN is electron-withdrawing, but not as much as the nitro group:
thus: NO_2>CN>Br>H>CH_3>OCH_3

3. Show a synthetic sequence to accomplish the following transformations:





4. Show a mechanism for the following transformations:



5. Outline a synthesis of each of the following compounds from the indicated starting material: