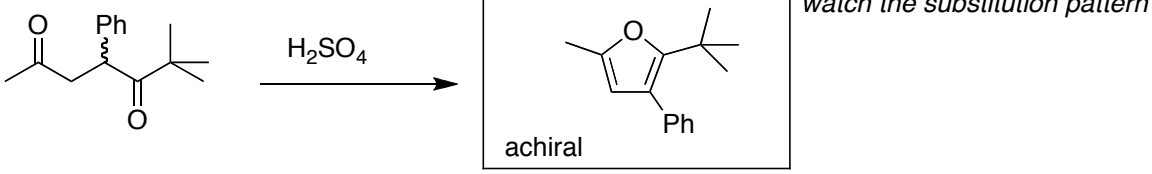
Problem set 6
Chapters 43, and 44.

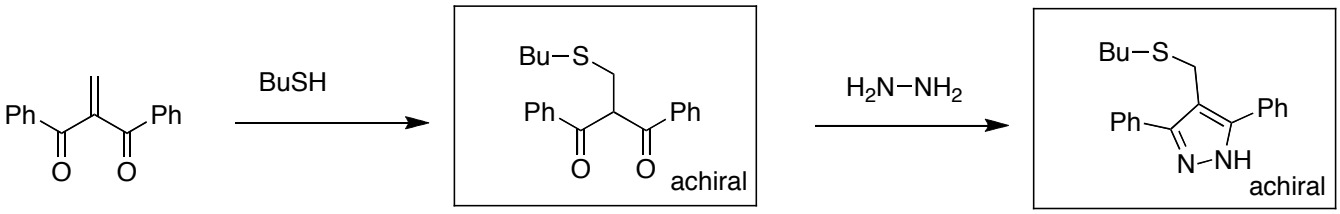
1. Fill in the boxes with the reagents required to produce the stereoisomer shown, or with the MAJOR stereoisomer produced by the reaction conditions given. For **all structures**, indicate whether the structure is achiral, a single enantiomer, or racemic.

a)



watch the substitution pattern

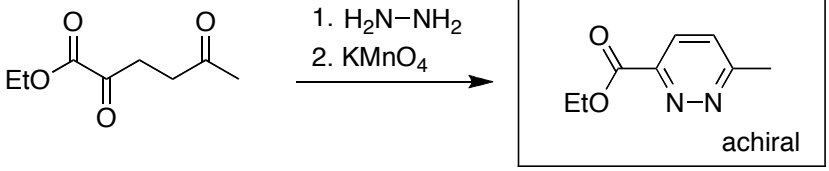
b)



soft Nu, soft electrophile = conjugate addition

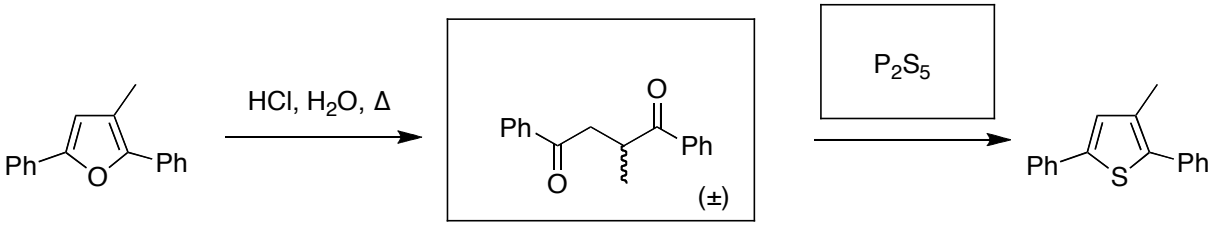
1,3-dicarbonyl to pyrazole

c)

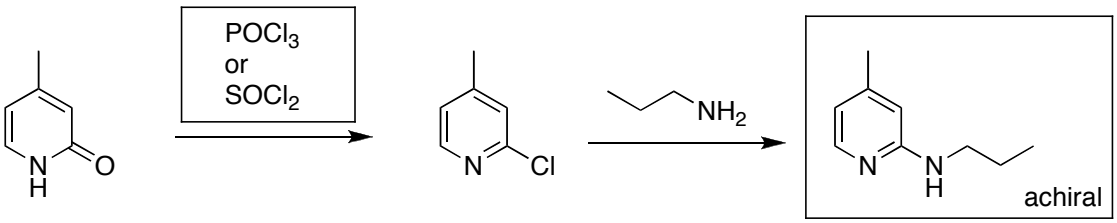


first the 6-membered ring forms with only two double bonds, then is oxidized to the aromatic product

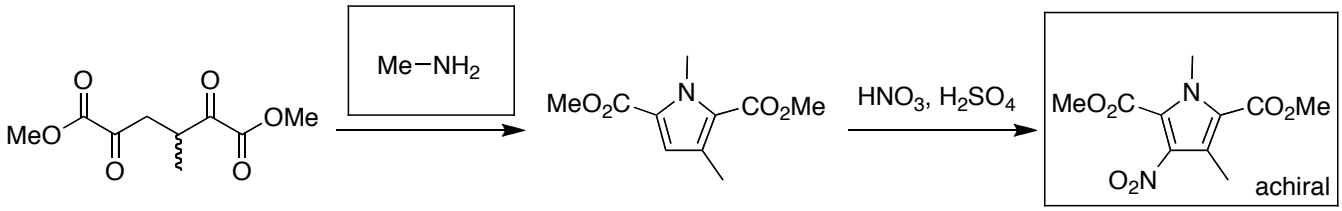
d)



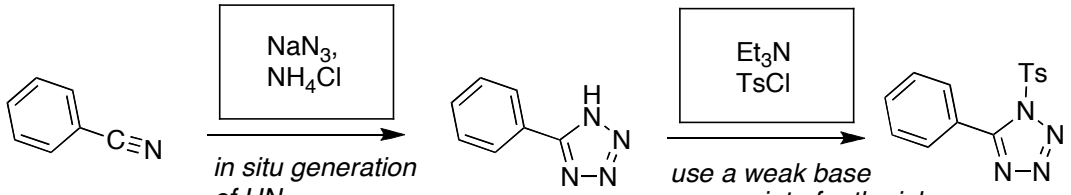
e)



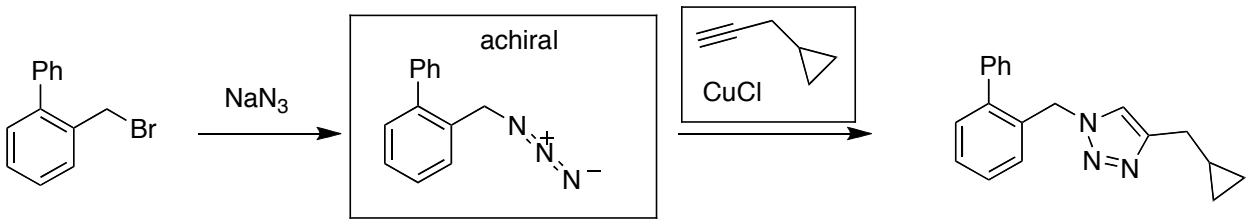
f)



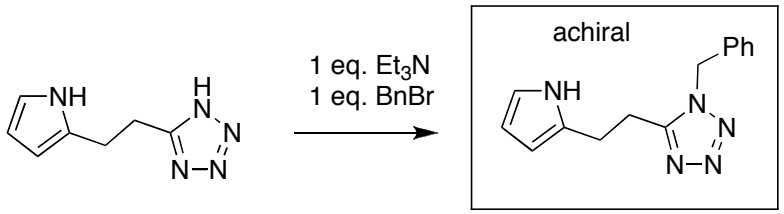
g)



h)

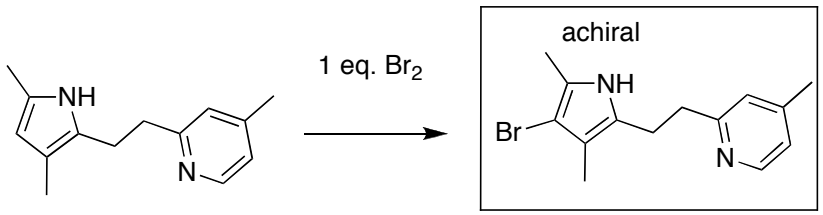


i)



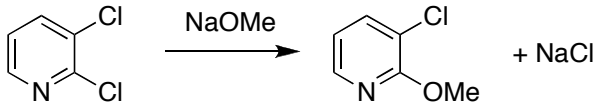
tetrazole NH far more acidic than pyrrole NH

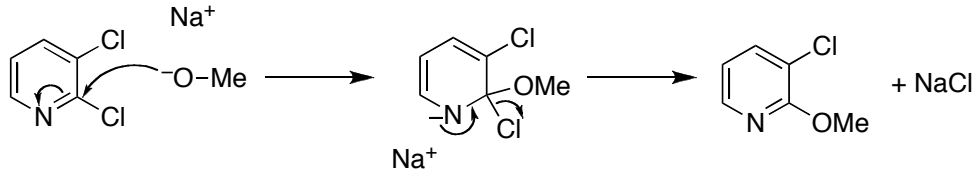
j)



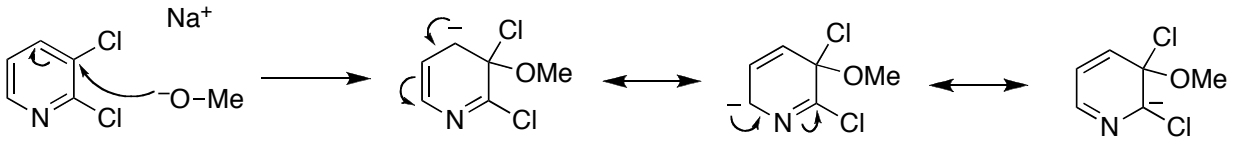
pyrrole is the most electron rich ring, therefore the best at electrophilic aromatic bromination

2. Explain the regioselectivity of the reaction below using text and diagrams.





Anionic intermediate stabilized by placement of negative charge on electronegative nitrogen atom



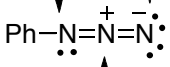
No resonance structure can be drawn with negative charge on nitrogen atom

3. a) Give the Lewis structure of phenyl azide (PhN_3), showing all lone pairs, bonds orders, and charges.

N with 3 bonds, 1 lone pair = total 5 e⁻, so it's neutral

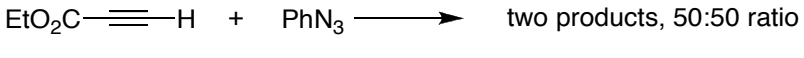
N with 2 bonds, 2 lone pairs = total 6 e⁻, so negatively charged

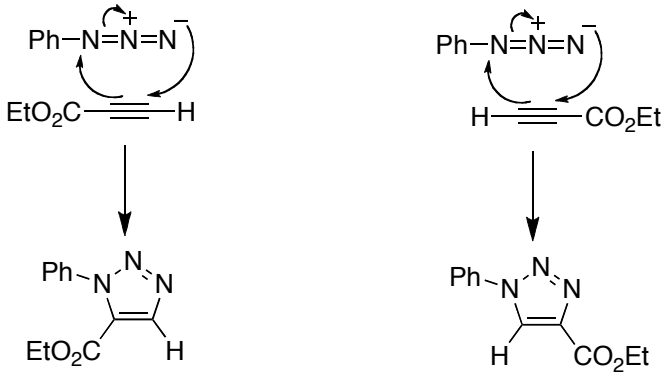
Nitrogen normally has 5 valence electrons.



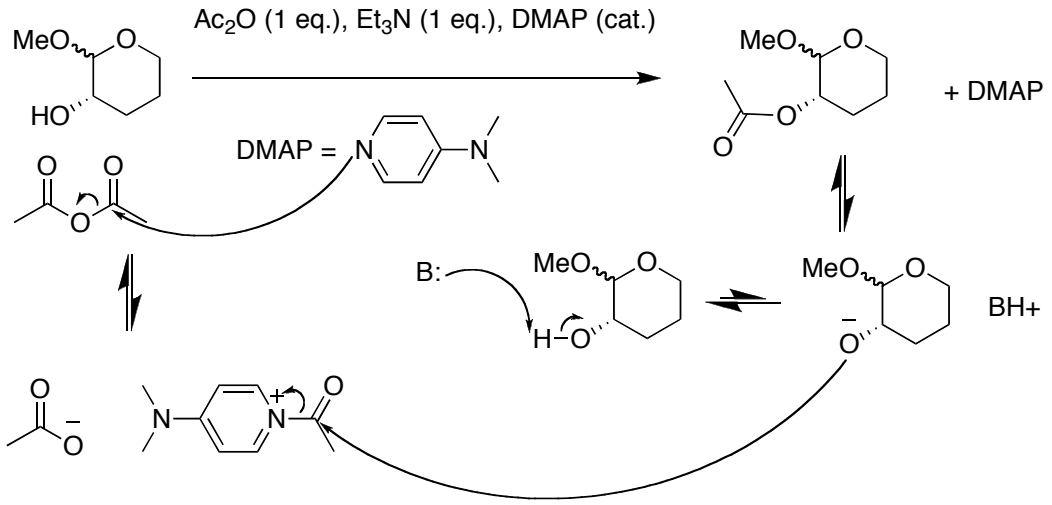
N with 4 bonds, no lone pairs total 4 e⁻, so positively charged

b) Give the products and detailed mechanism for the following transformations. Be precise about arrows and charges.

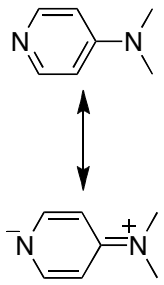




4. Give a detailed mechanism for the following transformation, and explain why the reaction is faster in the presence of DMAP.



Pyridine is a much poorer catalyst for this reaction. Why is the dimethylamino group on DMAP important?



The resonance-donating dimethylamino group puts more electron density on the ring nitrogen, making it a better nucleophile.