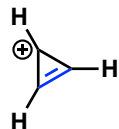
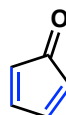


Problem Set 4
Chem 2211

1. a. Label the following compounds as either aromatic, not aromatic or antiaromatic. Explain your reasoning.



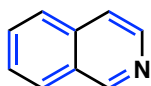
aromatic; fully conjugated pi system with 2 electrons with $4n + 2 = 2$, $n = 0$.



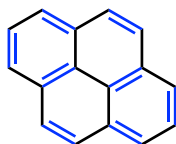
antiaromatic; not fully conjugated pi system in ring and for pi bonds in ring, $4n = 4$, so $n = 1$



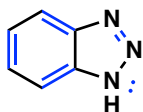
this resonance structure explains the lack of aromaticity and participation of only 4 pi electrons



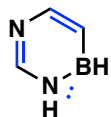
aromatic; fully conjugated pi system with 10 electrons with $4n + 2 = 10$, $n = 2$.



antiaromatic; fully conjugated pi system with 16 electrons with $4n = 16$, $n = 4$.

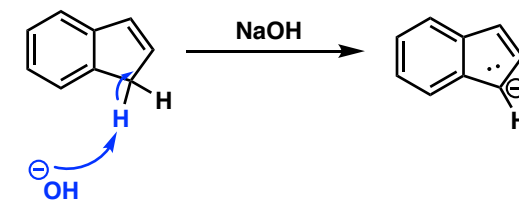
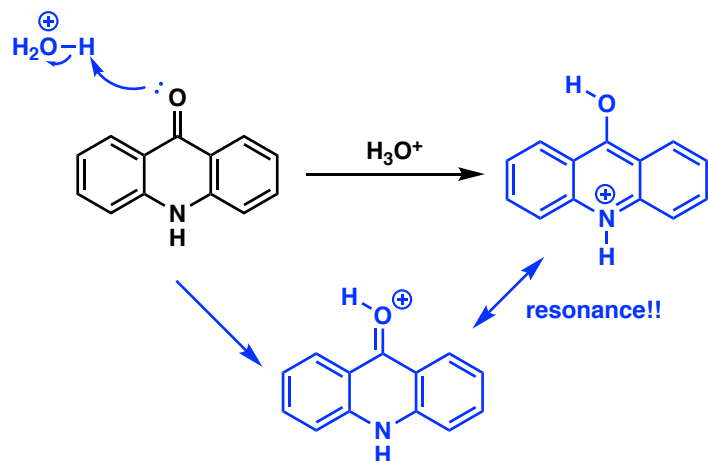


aromatic; fully conjugated pi system with 10 electrons with $4n + 2 = 10$, $n = 2$.

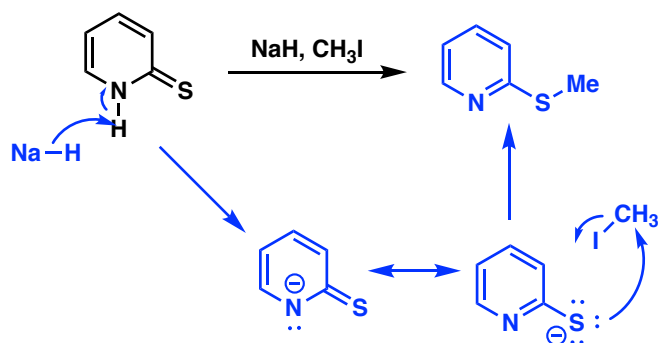
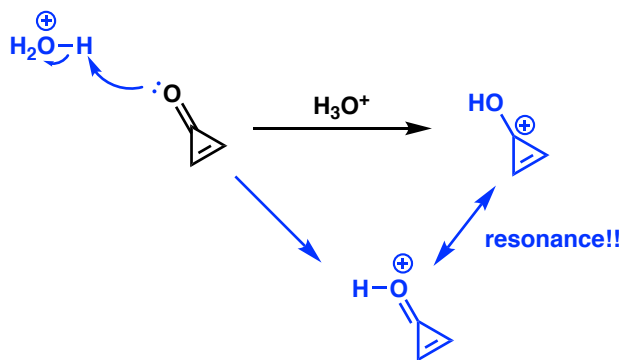


aromatic; fully conjugated pi system with 6 electrons with $4n + 2 = 6$, $n = 1$.

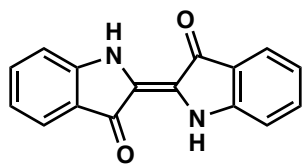
b. Some compounds can be made more aromatic by performing a simple transformation on them. Provide a mechanism and a justification for why the product compound is more aromatic.



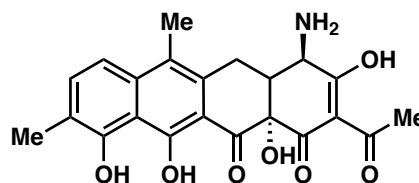
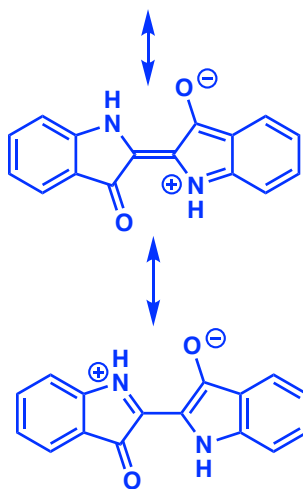
pKa of indene (starting molecule above) is 20 due to thermodynamic preference to be aromatic!



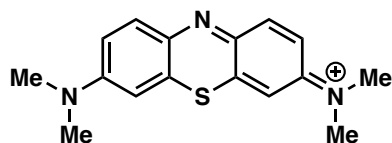
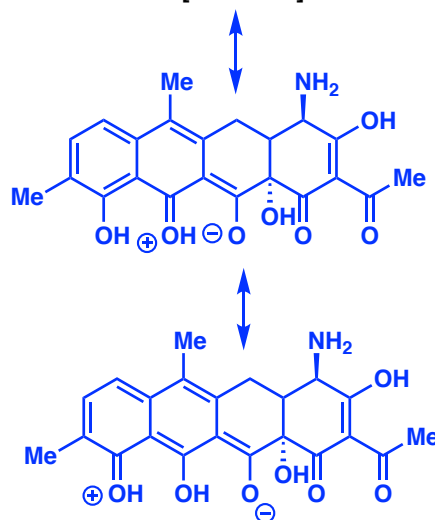
2. a. Molecules that contain aromatic groups can have drastic resonance effects. Propose 2 major resonance contributors for the following compounds not including their given parent structures.



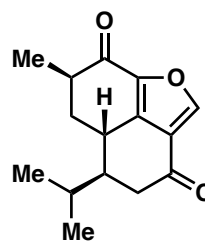
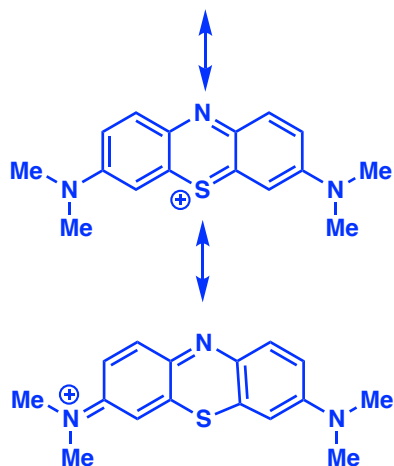
indigo
[ingredient of denim]



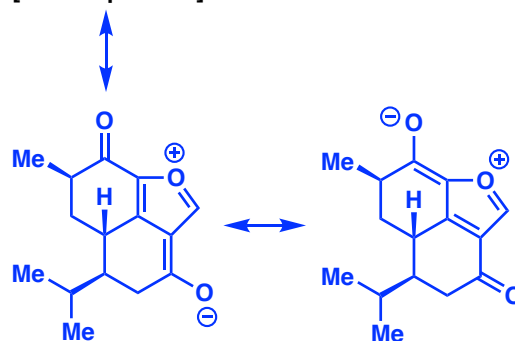
chelocardin
[antibiotic]



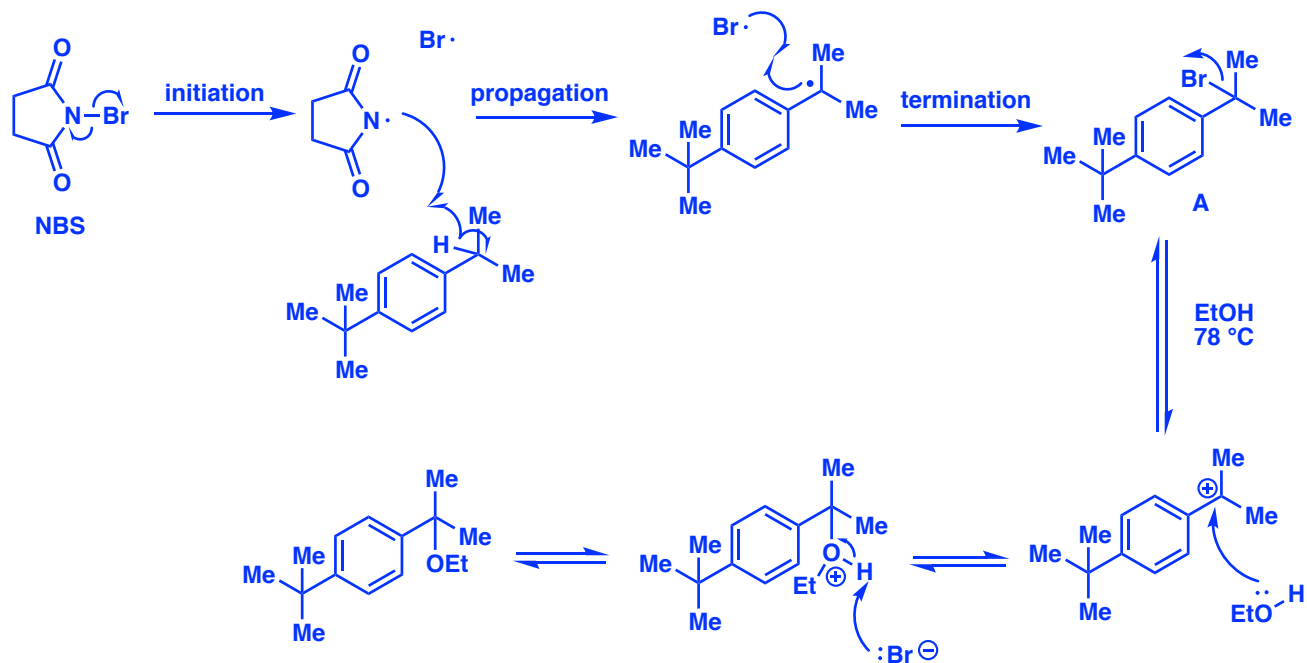
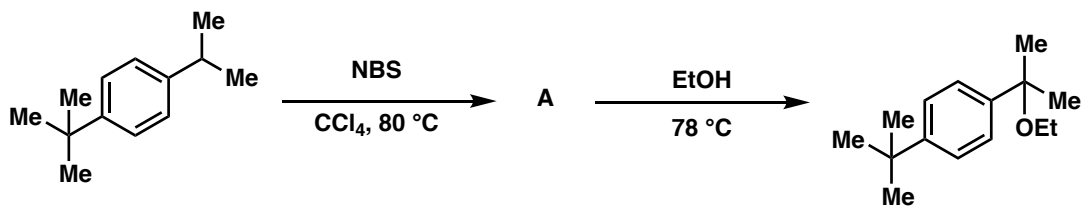
methylene blue
[colored dye]



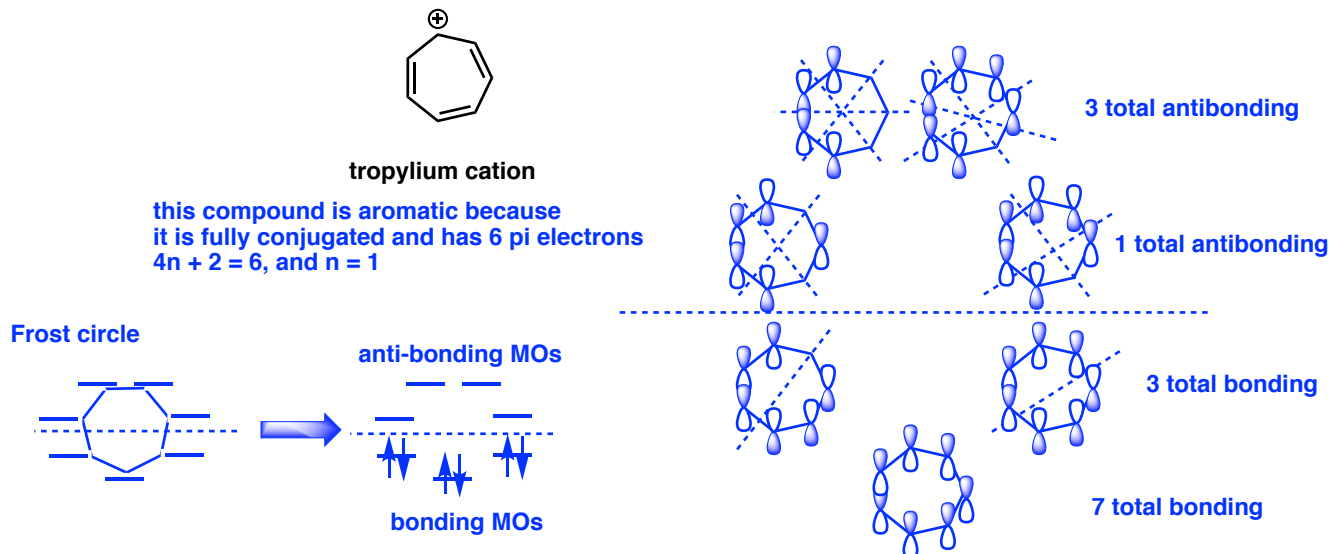
hibiscone C
[natural product]

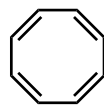


b. Resonance in aromatic systems also provides opportunity for reactions at the benzylic position. Provide a mechanism for the following transformations and predict the structure of **A**.



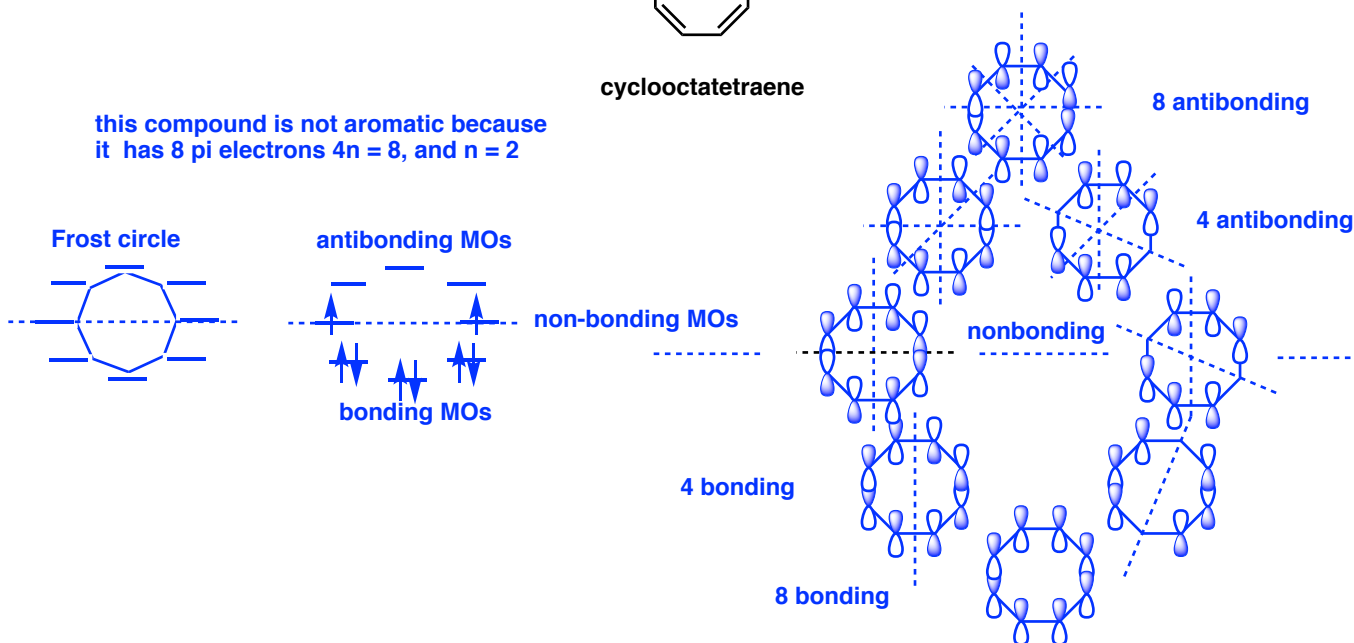
3. Draw the molecular orbital diagrams for the tropylium ion and cyclooctatetraene and explain why they are aromatic or not. Hint: use a Frost circle to help.



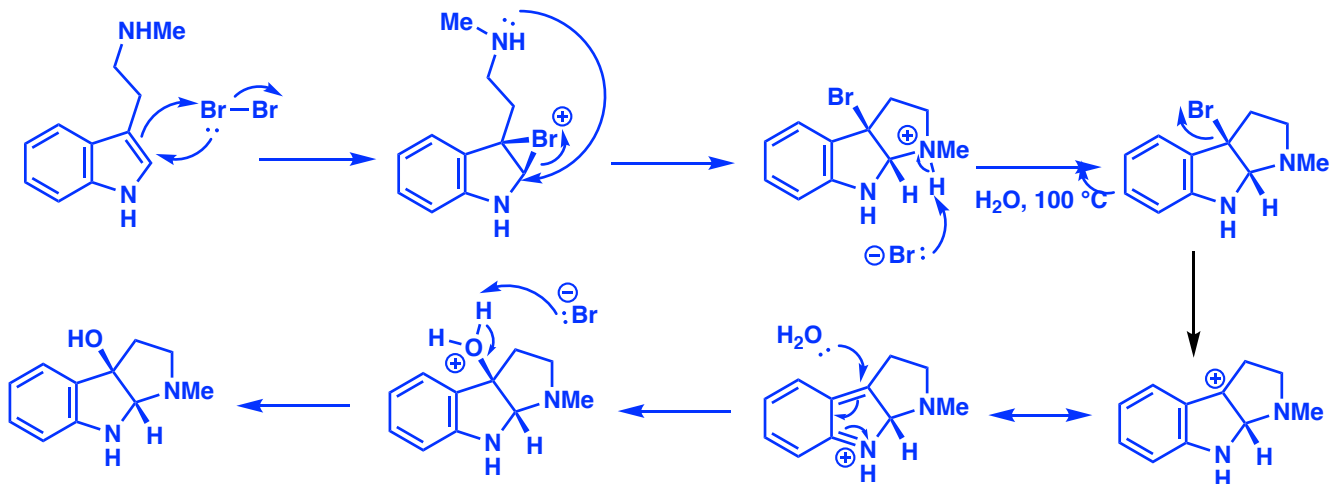
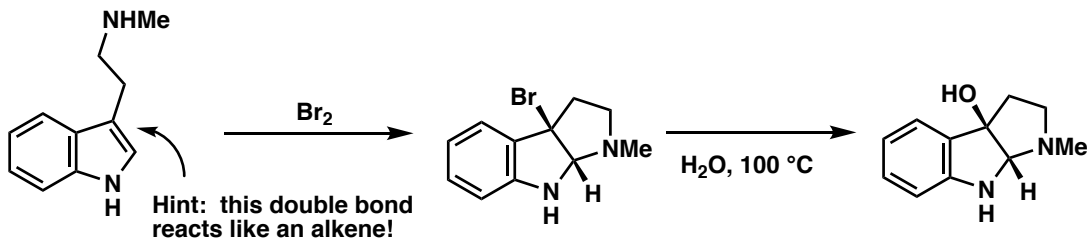


cyclooctatetraene

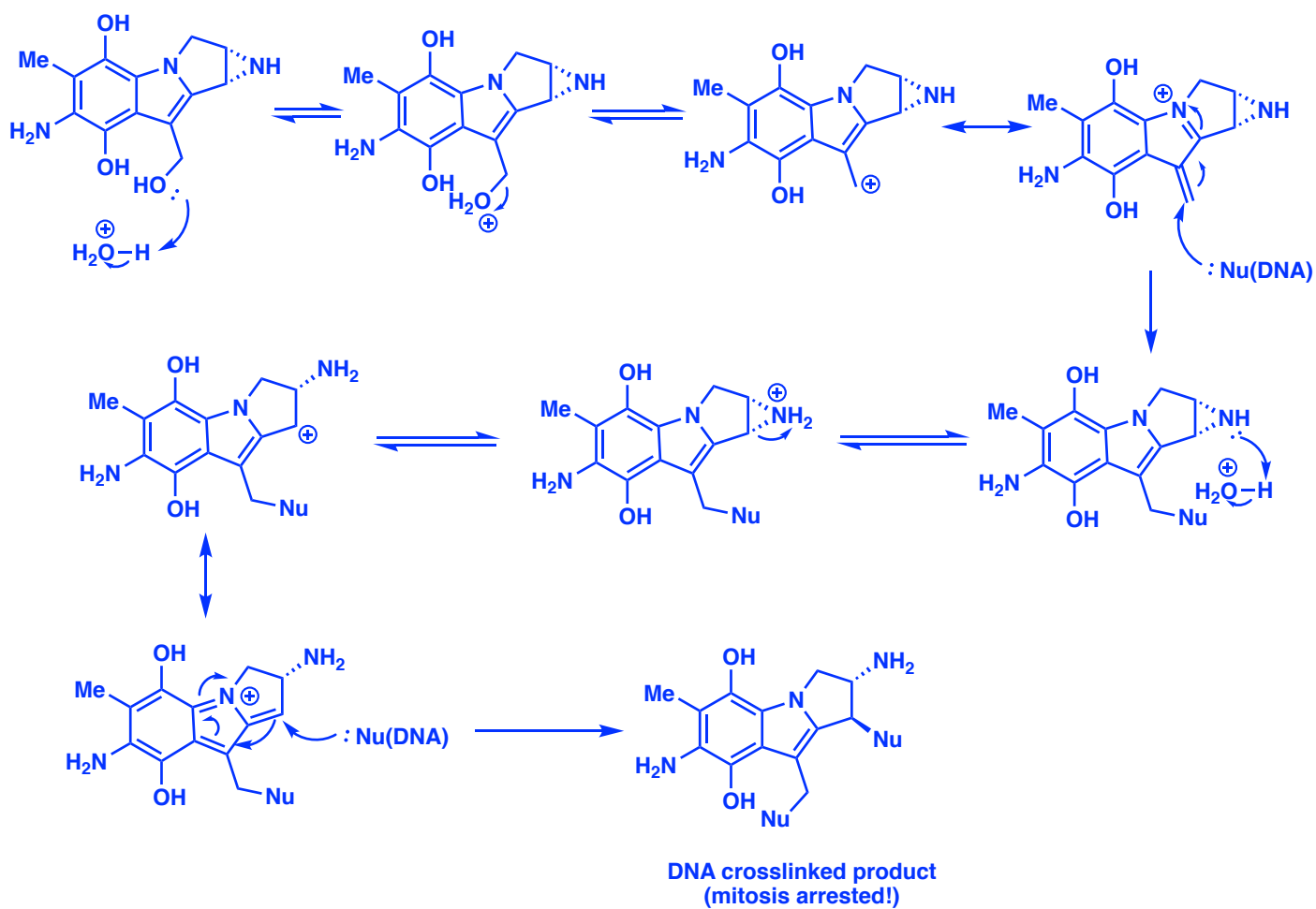
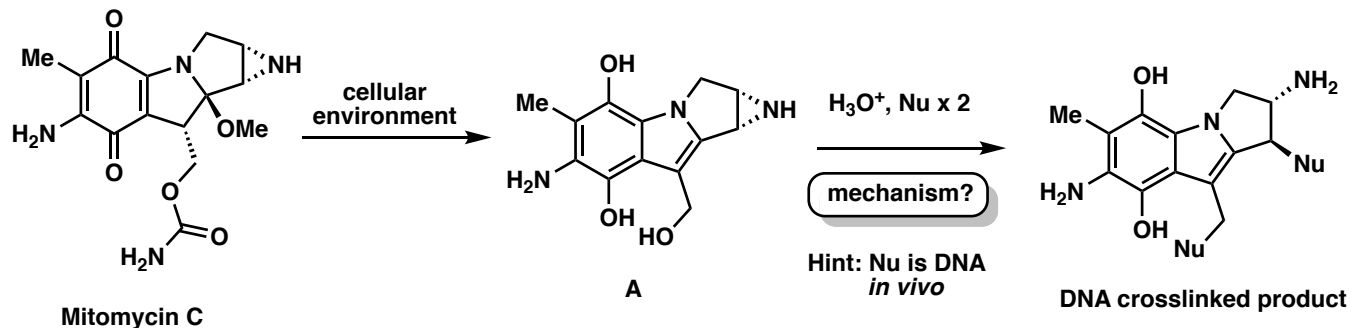
this compound is not aromatic because it has 8 pi electrons $4n = 8$, and $n = 2$



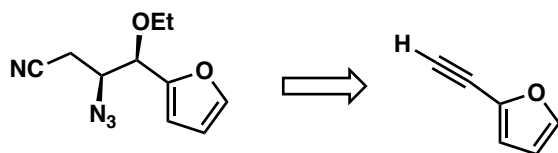
4. a. The indole is a privileged aromatic bicyclic system in biologically active compounds and natural products. This is so much so that it has been dubbed "lord of the rings." Using your knowledge of alkenes and arenes provide mechanisms for the following transformations.



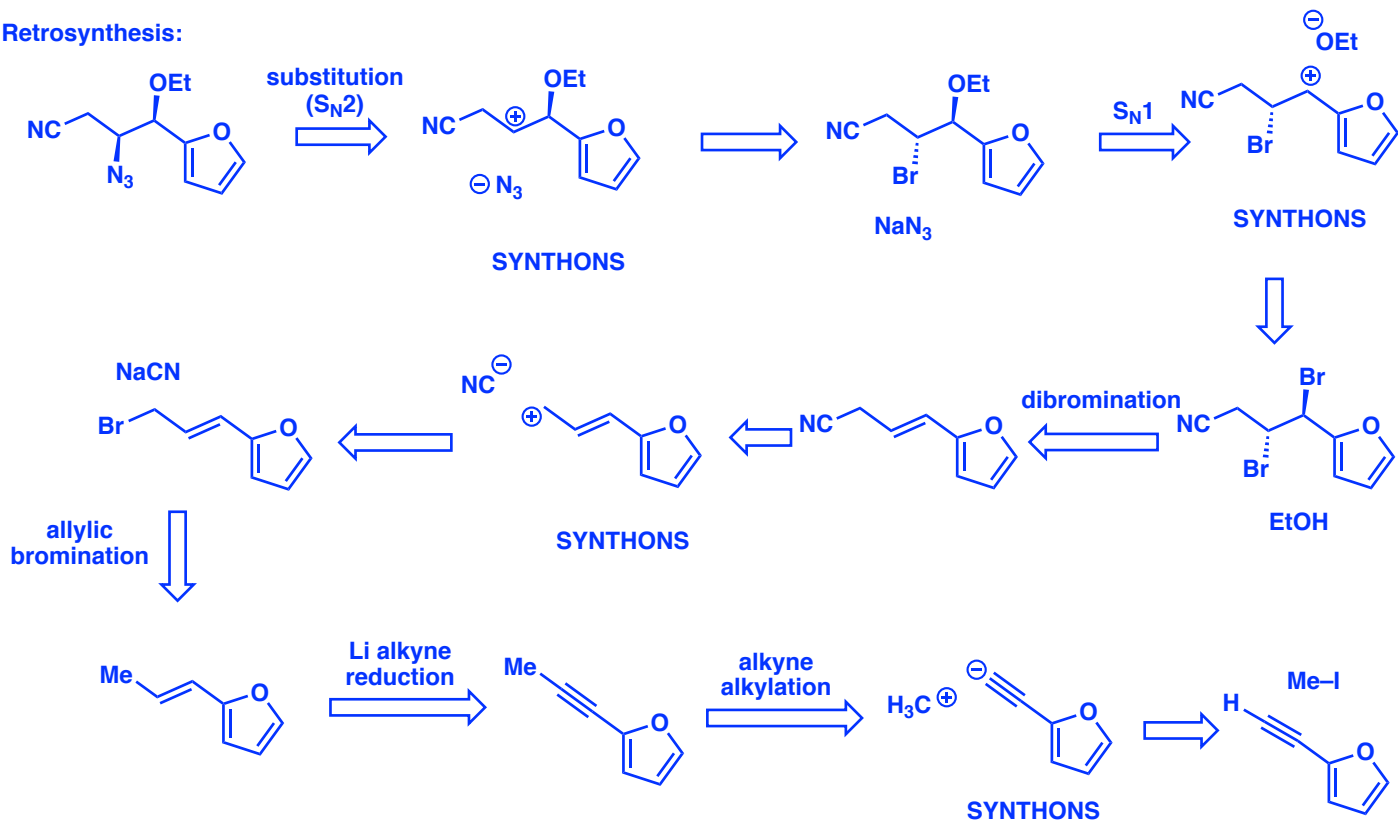
b. The anticancer therapeutic Mitomycin C is converted in the body to the indole structure **A** and then crosslinks double-stranded DNA to arrest the cell division cycle. Provide a mechanism of the DNA crosslinking events.



5. Provide a retrosynthetic analysis including synthons, transforms, and synthetic equivalents for the following target molecule from the given starting material. Then, provide a forward synthesis based off of your retrosynthesis.



Retrosynthesis:



Forward synthesis:

