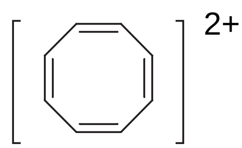
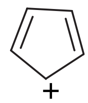
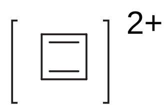
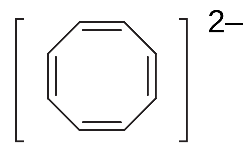
Chem 332, PS 6 answers, Spring 2003, Prof. Fox

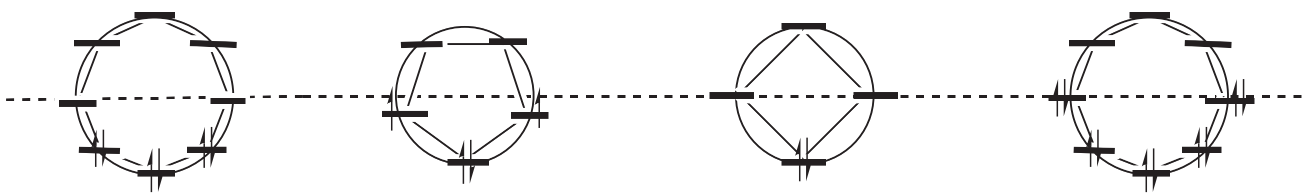
1. Which of the following are aromatic. Draw "Frost Circles" that support your answers











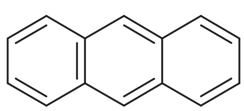
all bonding MO's
are filled
aromatic

although all electrons
are in bonding orbitals,
two bonding MO's are
only half-filled
anti-aromatic

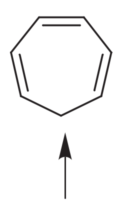
all bonding MO's
are filled
aromatic

this is an interesting case: this is a 4n+2 molecule, and it is flat--characteristic of aromatic molecules. However, it has four electrons in non-bonding orbitals, so we might have considered this to be non-aromatic. So it comes down to how you define aromaticity. For now we will call it aromatic with a question mark.

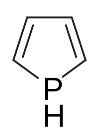
2. Which of the following are aromatic. Use the Huckel rule to support your answer



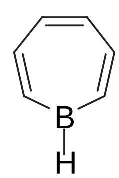
14 electrons, **aromatic**



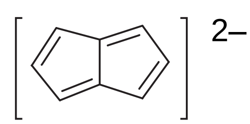
sp^3 center
not conjugated
and **not aromatic**



6 electrons
(filled sp^2 on
phosphorus)
aromatic



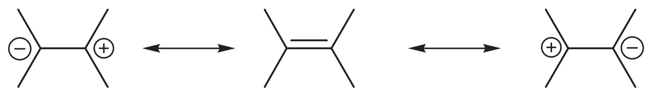
6 electrons
(empty sp^2 on
boron)
aromatic



10 electrons
aromatic

3. Compound **1** has an unusually large dipole moment for an organic hydrocarbon. Explain why (consider resonance structures for the central double bond)

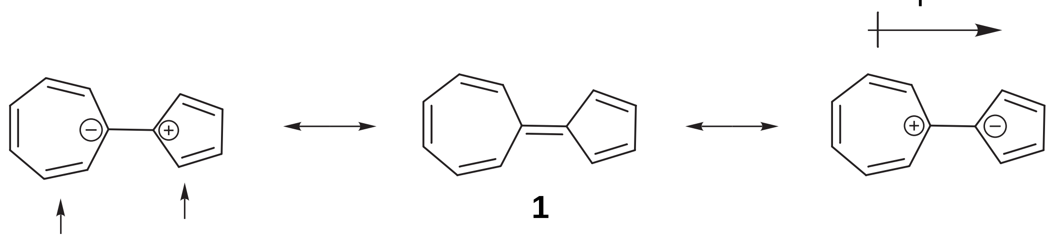
We need to remember that for any double bond compound, we can draw two polar resonance structure. Normally, these resonance structures are unimportant



unimportant unimportant

However, for **1** the story is different because there is a polar resonance form that has two aromatic components. In other words, 'breaking' the double bond gives rise to aromaticity, and therefore the polar resonance structure is important and leads to the observed dipole.

dipole



1

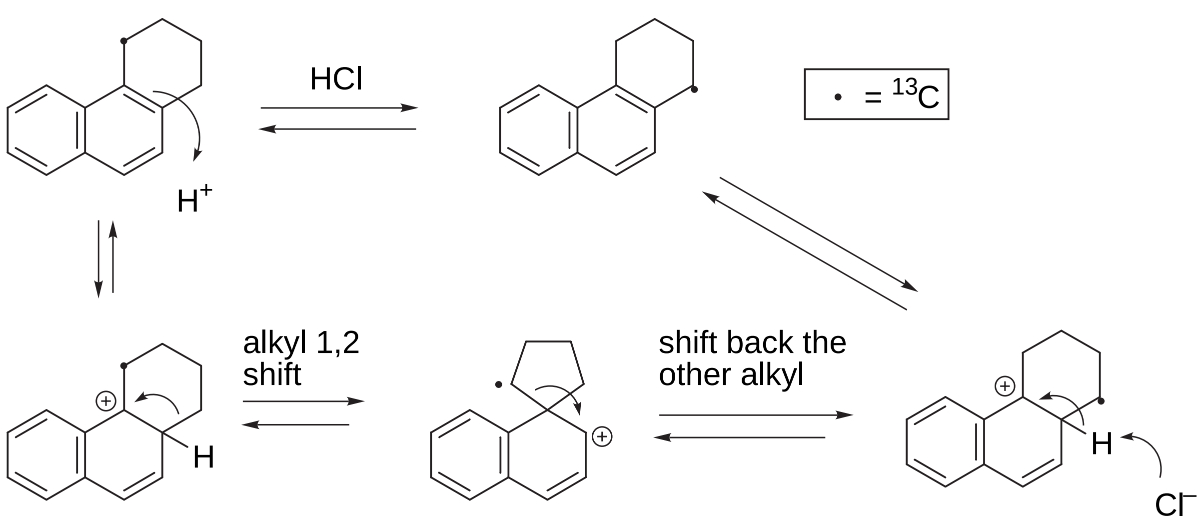
8 e$^-$ anti-aromatic | 4 e$^-$ anti-aromatic

unimportant resonance structure

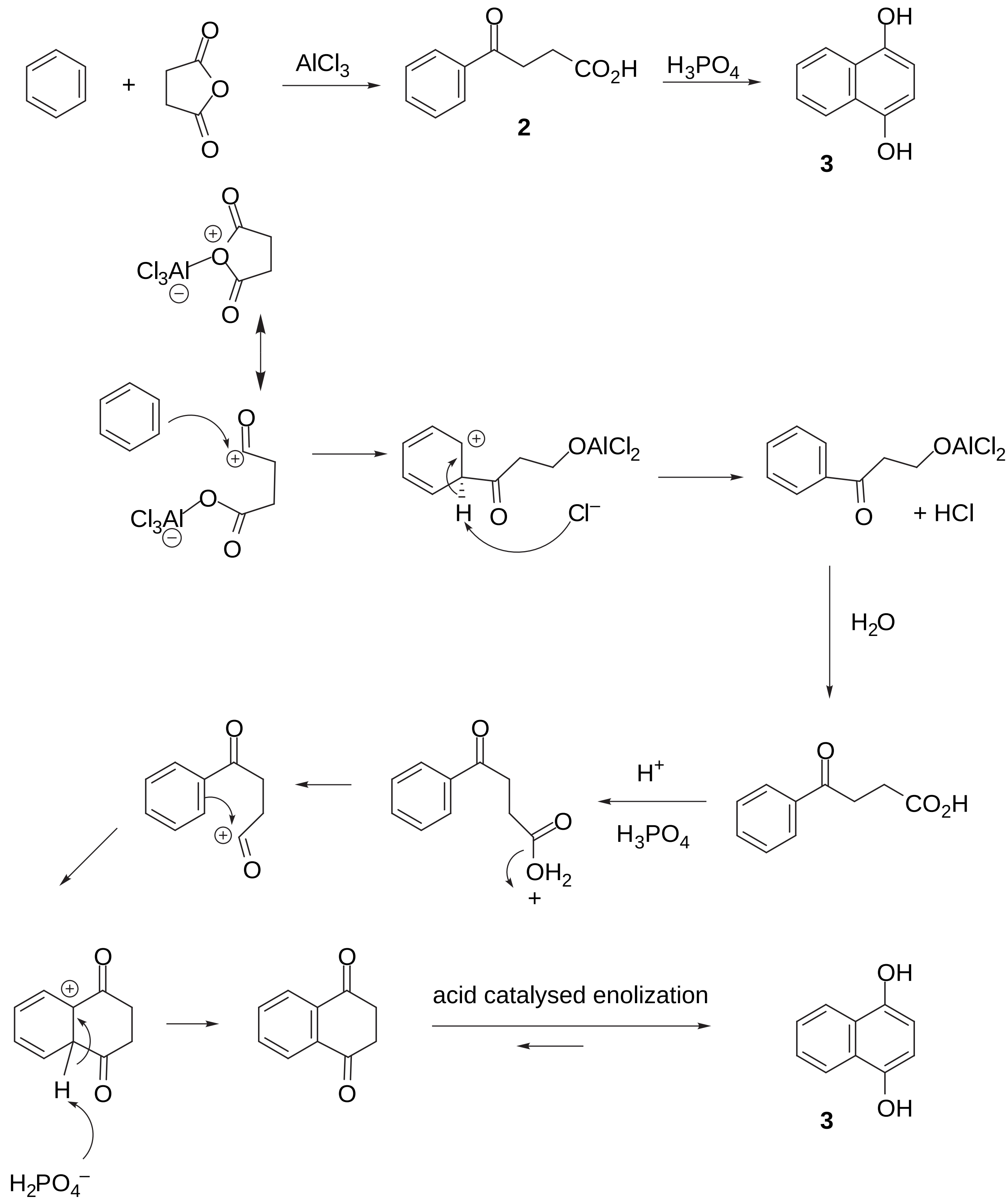
6 e$^-$ aromatic | 6 e$^-$ aromatic

important resonance structure

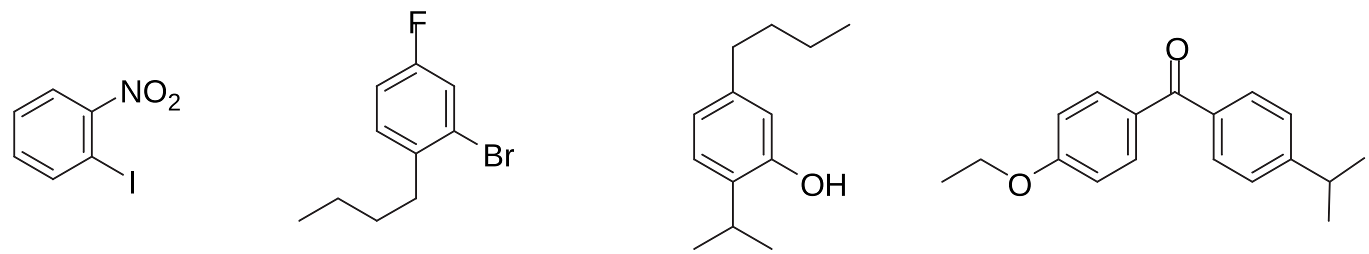
5. Provide a mechanism. This problem is easier than it looks!

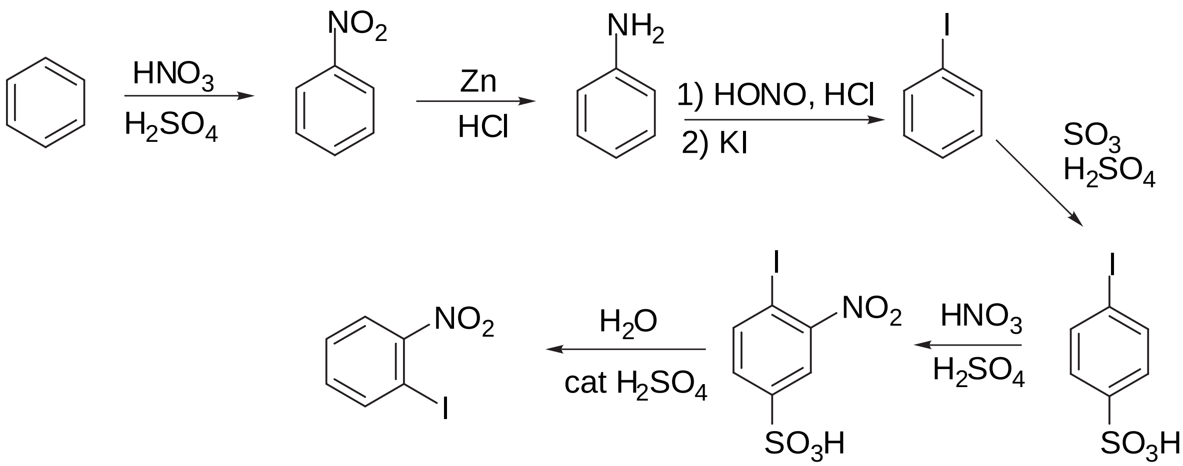


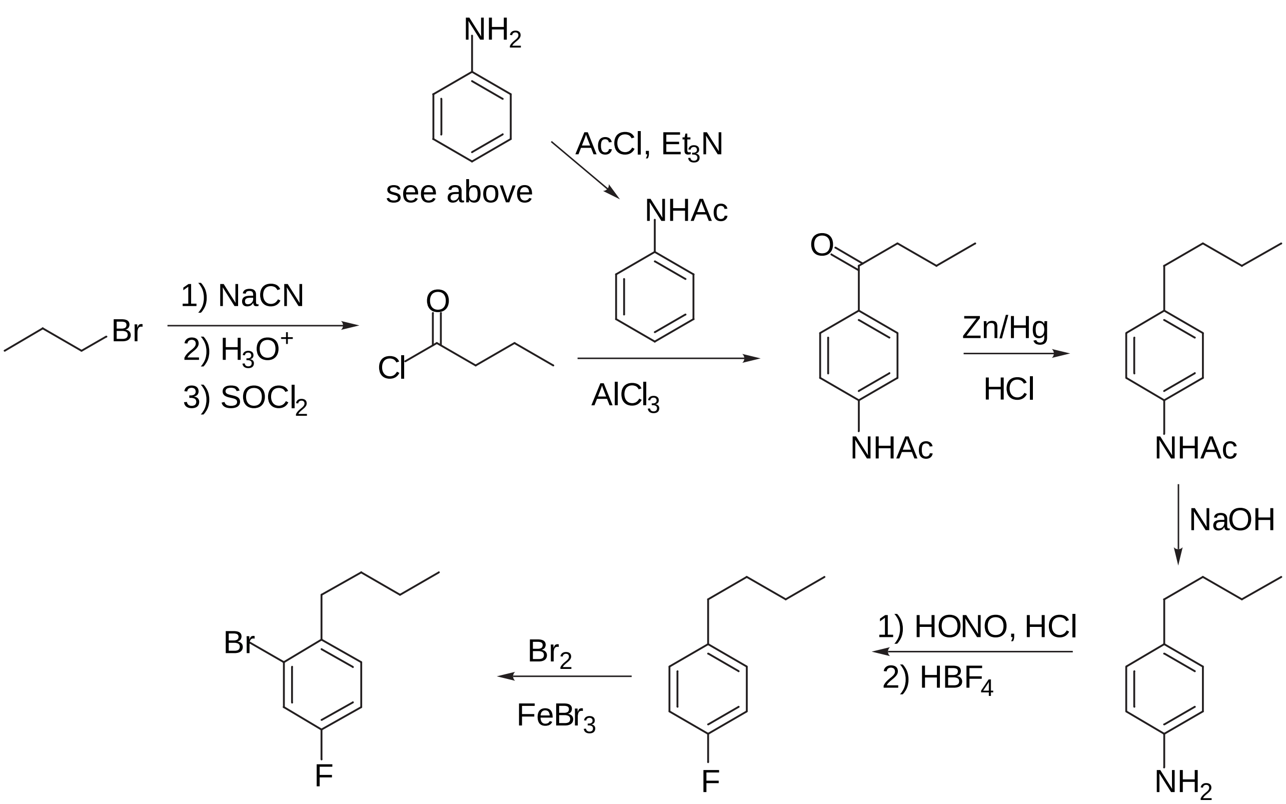
4. Provide mechanisms for the formation of **2** and **3**.

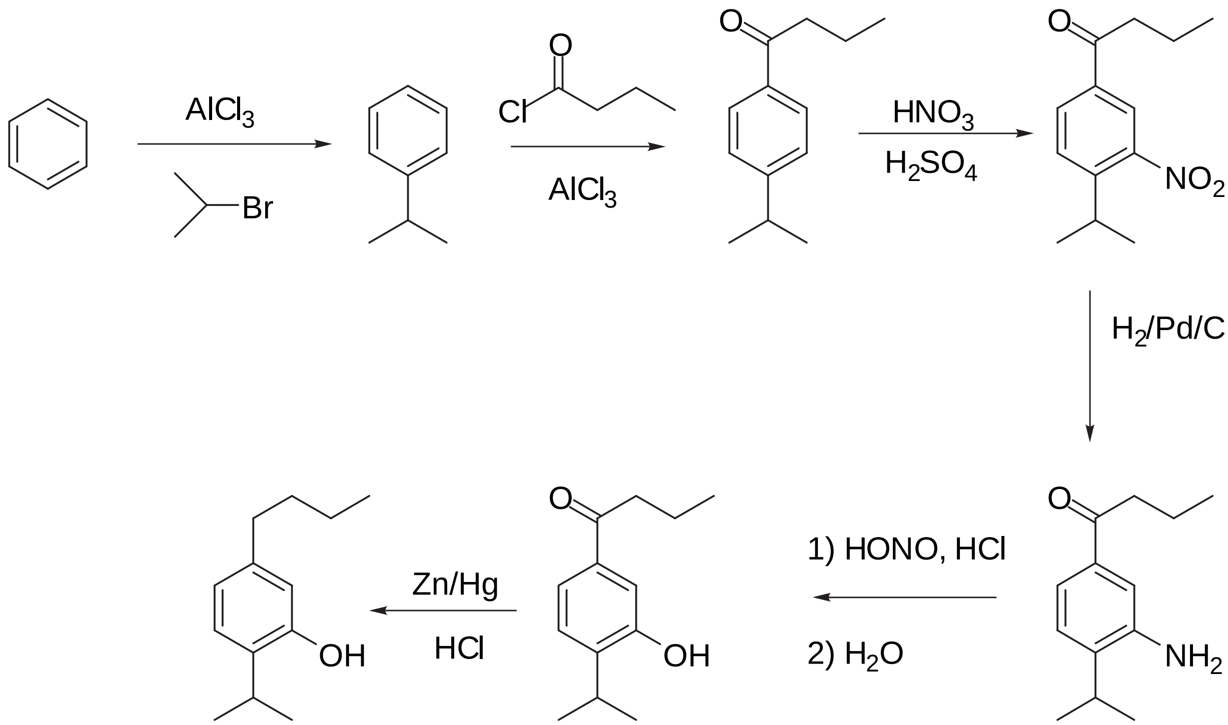


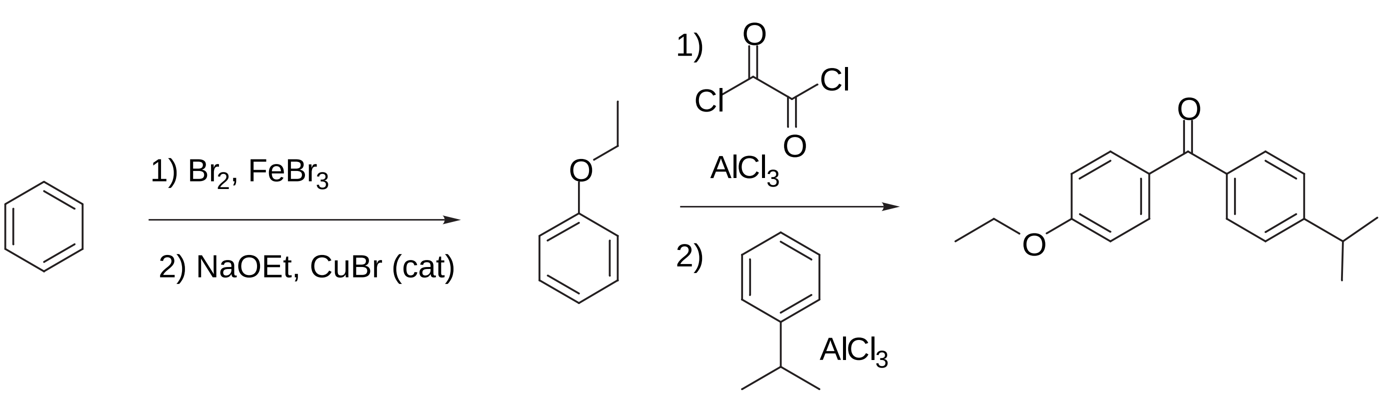
6. Devise syntheses of the following, using benzene and any other materials containing 3 carbons or less.








AlCl3
Br
O
Cl
AlCl3
O
HNO3
H2SO4
O
NO2
H2/Pd/C
O
NH2
1) HONO, HCl
2) H2O
O
OH
Zn/Hg
HCl
OH


1) Br2, FeBr3
2) NaOEt, CuBr (cat)
O
1)
O
Cl
Cl
O
AlCl3
2)
AlCl3
O
O