Question 1

Compound 1 has 18 π electrons of which 14 make up a contiguous cyclic set of p-orbitals perpendicular to the plane of the molecule and therefore constitute the aromatic system. The other 4 π electrons are in p-orbitals in the plane of the ring as the result of the sp hybridisation of the carbons shown 'dotted' in the picture.

NB. although this molecule must be represented by resonance forms in which there is a cumulene and an alkyne, it is in fact highly symmetrical and is correctly represented by the two resonance forms shown below. Hence it is referred to as a 1,8-bisdidehydro[14]annulene. the symmetry is perhaps most clearly apparent from orbital representation. The 1H NMR spectrum shows just three signals as indicated below.

see: Sondheimer et al. J. Am. Chem. Soc. 1962, 84, 4595 (DOI)

1H NMR: δ -5.54 (Hc, t), 8.43 (Ha, d), 9.65 (Hb, dd)

Question 2

Compound 2 is predicted to have a large dipole moment due to the significant contribution made to the structure by the dipolar resonance form shown below comprising an aromatic cyclopentadienyl anion portion and an aromatic cyclopropenyl cation portion. In fact, this compound, named calicene, has never been prepared although various derivatives have and these do indeed display large dipole moments (e.g. hexaphenylcalicene has a dipole moment of 6.3 D)

Question 3(a-d)

The following routes are suggested, alternatives are possible:

(a) \[ \text{CN} \rightarrow \text{NO}_2 \rightarrow \text{Sn-HCl or S(NH}_4\text{)}_2 \rightarrow \text{NaNO}_2 \rightarrow \text{HCl} \rightarrow \text{CuCl or KCl} \rightarrow \text{c.H}_2\text{SO}_4 \rightarrow \text{c.HNO}_3 \rightarrow \text{c.H}_2\text{SO}_4 \rightarrow \text{c.HNO}_3 \rightarrow \text{Br}_2 \rightarrow \text{FeBr}_3 \]

(b) \[ \text{MeCOCl} \rightarrow \text{O} \rightarrow \text{Zn-HCl or S(NH}_4\text{)}_2 \rightarrow \text{MeCOCl} \rightarrow \text{O} \rightarrow \text{Sn-HCl or S(NH}_4\text{)}_2 \rightarrow \text{HBr} \rightarrow \text{Br} \rightarrow \text{Cl} \rightarrow \text{HNO}_3 \rightarrow \text{c.H}_2\text{SO}_4 \]

(c) \[ \text{MeCOCl} \rightarrow \text{O} \rightarrow \text{H}_2\text{SO}_3 \rightarrow \text{MeCOCl} \rightarrow \text{O} \rightarrow \text{Zn-HCl or S(NH}_4\text{)}_2 \rightarrow \text{SO}_2 \rightarrow \text{Br} \rightarrow \text{Cl} \rightarrow \text{HNO}_3 \rightarrow \text{c.H}_2\text{SO}_4 \]

(d) \[ \text{MeCOCl} \rightarrow \text{O} \rightarrow \text{H}_2\text{SO}_3 \rightarrow \text{MeCOCl} \rightarrow \text{O} \rightarrow \text{Zn-HCl or S(NH}_4\text{)}_2 \rightarrow \text{SO}_2 \rightarrow \text{Br} \rightarrow \text{Cl} \rightarrow \text{HNO}_3 \rightarrow \text{c.H}_2\text{SO}_4 \]

Question 4a


Question 4b


Standard S$_x$Ar mechanism. Fluorine is highly electronegative (4.1, Pauling Scale) and facilitates initial nucleophilic attack on ipso-C (so-called 'element effect') which is the rate determining step (RDS). The nitro group stabilises the Meisenheimer intermediate by allowing negative charge to be delocalised onto its oxygens by resonance (NB. only possible at ortho- and para- positions relative to fluorine).
**Question 4c**


First: diazonium salt formation (via online N-amination)  
Second: EITHER S_N^- displacement (for KX) OR Sandmeyer-type S_N^+ displacement (for CuCN):

**Question 4d**


6 (X = F): use HBF_4 to form diazonium salt and then heat to effect Bälz Scheimann  
6 (X = CN): form diazonium salt then treat with CuCN (Sandmeyer reaction)