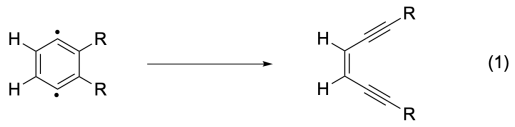
T6. Carbon Nanorings

7%							
6.1	6.2	6.3	6.4	6.5	6.6	6.7	∑
10	11	2	12	24	20	4	83

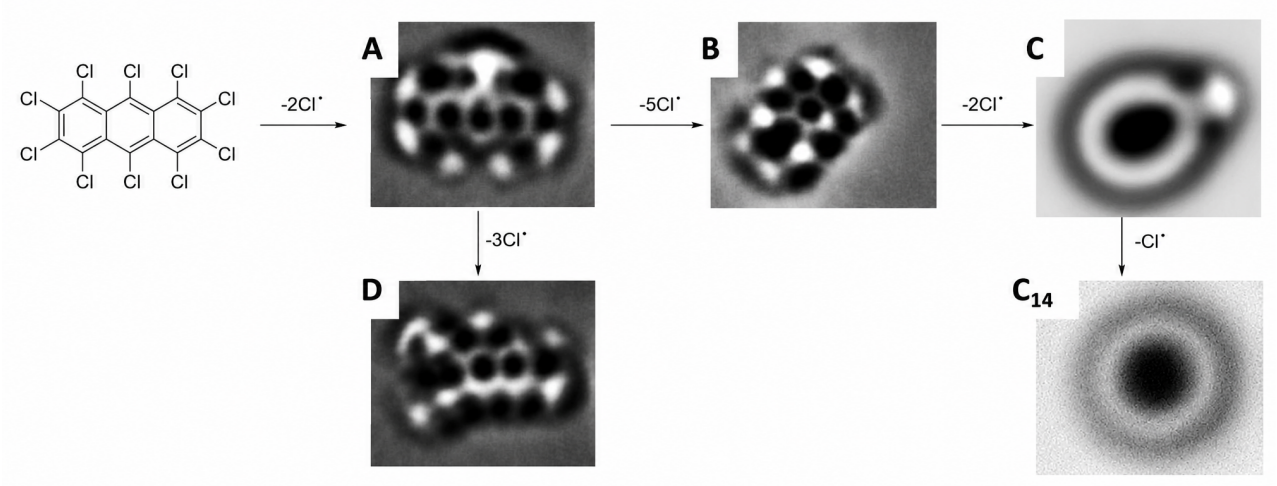
In 2019, C_{18}, the first example of a new class of carbon allotropes called cyclo[n]carbons (C_n) was detected. Cyclocarbons are monocyclic, all-carbon compounds with high strain energy and low stability. They can be generated and analysed by bond-resolved Atomic Force Microscopy (AFM). Cyclocarbons have interesting aromatic properties based on their π systems. C_{13} has triplet ($^3C_{13}$, spin $S = 1$), and singlet ($^1C_{13}$, spin $S = 0$) forms.

6.1 Based on Hückel's *r*ule, **fill in** the table with the number of distinct aromatic (**A**) and anti-aromatic (**AA**) π-systems present in each of C_{18}, C_{16}, $^3C_{13}$, and $^1C_{13}$. **Fill in all blanks.** 10.0 pt

Later, cyclo[n]carbons C_{10}, C_{12}, C_{14}, C_{20}, and C_{26} were generated by a combination of dehalogenation and retro-Bergman (1) reactions on a surface. AFM images taken during the synthesis of C_{14} are shown below:



(1)

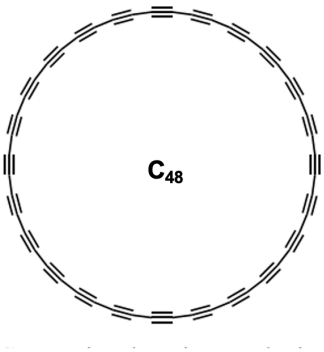


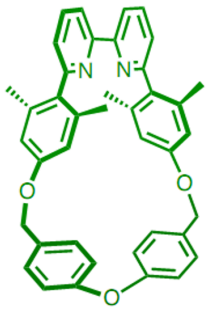
6.2 **Draw** structures **B-D**. Note they may contain one or more unpaired electrons. The structure of **A** is given as an example. 11.0 pt

6.3 The voltages applied during the AFM-mediated synthesis of C_n may vary. Using the given C–X bond energies, **choose** the possible halogen(s) in the halogenated reagent for C_{18} synthesis via a retro-Bergman reaction with a voltage of 2.5 V acting on the electrons. 2.0 pt

Bond (C–X)	Bond Dissociation Energy / $\mathrm{kJ\ mol^{-1}}$
C–F	467
C–Cl	346
C–Br	290
C–I	228

In 2025, the first relatively stable cyclo[48]carbon was synthesised. The molecule was stabilised by catenation (forming interlocking rings) with macrocycle **E** and was first characterised by electrospray mass spectrometry in positive mode.



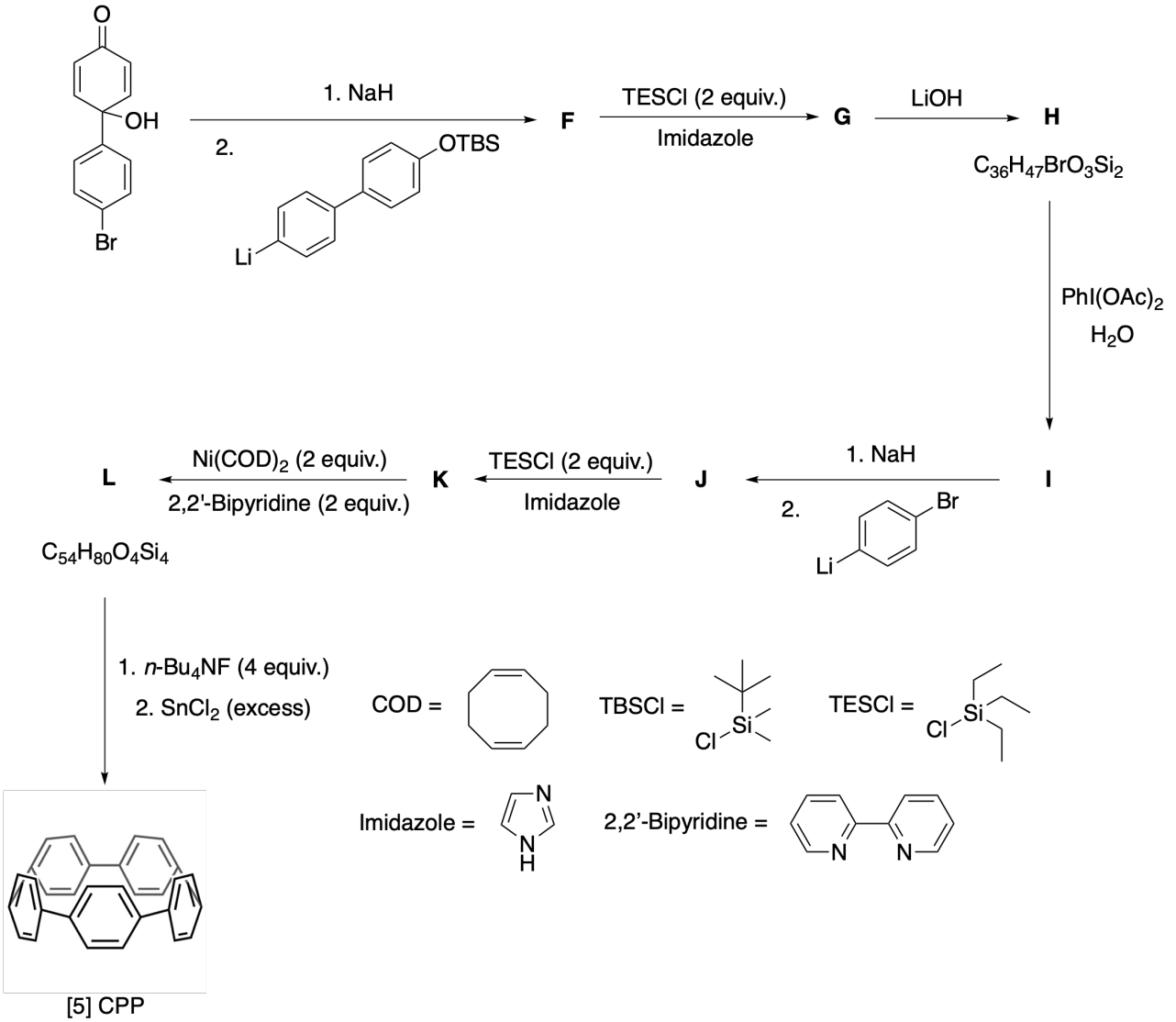


E

$C_{40}H_{34}N_2O_3$

6.4 In the mass spectrum obtained, four intense peaks were observed *m/z*: 591, 783, 879, and 1174. **Suggest** the identity of these ions. **Use** integer atomic masses and **assume** no fragmentation happened. The ion corresponding to *m/z* = 591 is given as an example. 12.0 pt

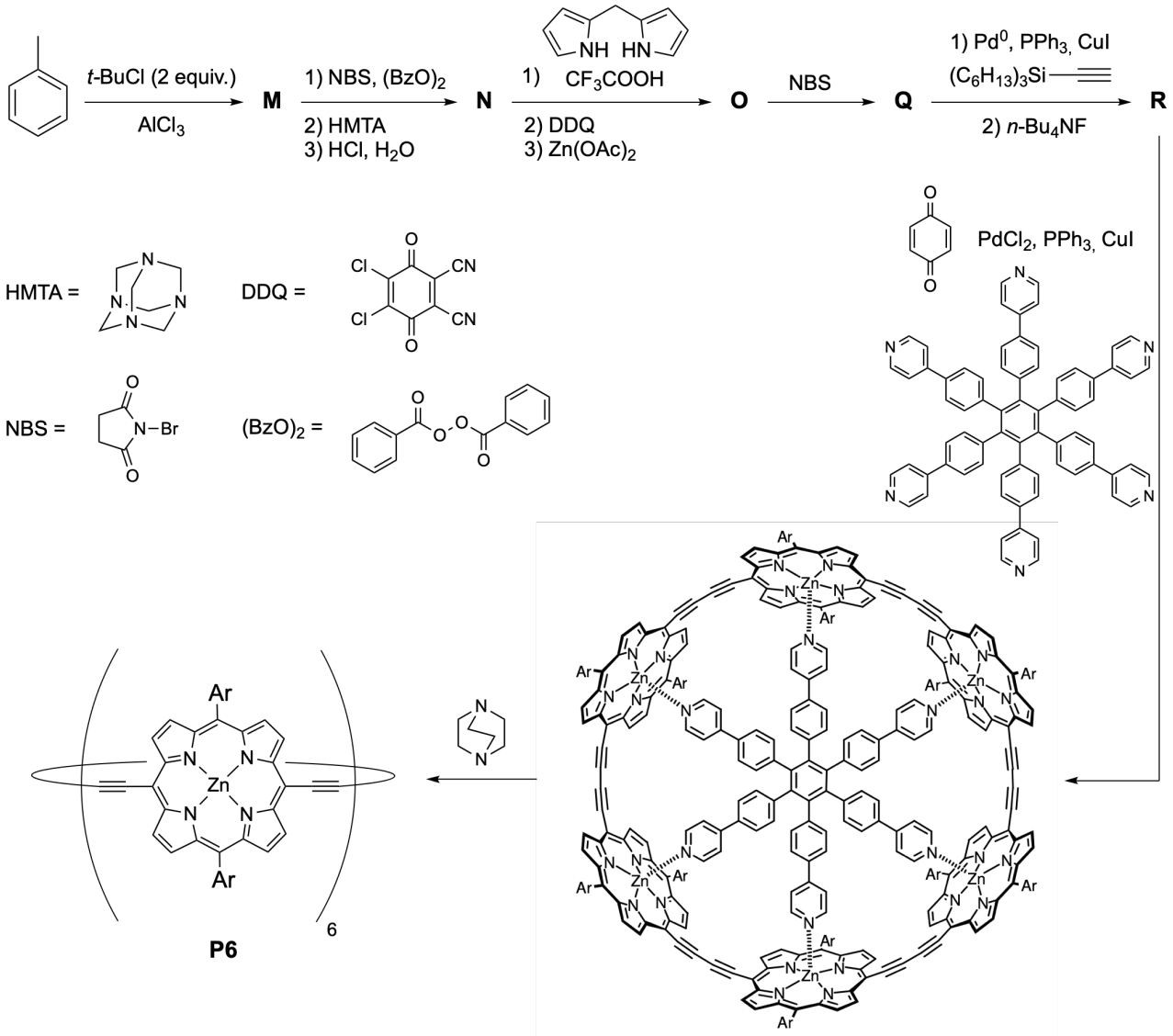
Cycloparaphenylene (CPP) is another cyclic, highly-strained molecule commonly called a carbon nanohoop. The synthesis of the smallest known member, [5]CPP, is shown below, where $PhI(OAc)_2$ acts as a two electron oxidant.



(equiv. = Equivalent, excess = Excess)

6.5	**Draw** the structures of **F-L**.	24.0 pt

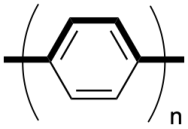
Next generation nanobelts were constructed from porphyrin rings and triple bonds using the template synthesis method. *Hint:* **M** is the thermodynamic product and has four types of protons.



(equiv. = Equivalent)

6.6	**Draw** the structures of **M-R**.	20.0 pt

When aromatic rings are joined to form a macrocycle, oxidation or reduction can produce global aromaticity, in which π electrons are delocalised around the entire macrocycle. Only the π system forming the continuous conjugated pathway around the ring participates in this delocalisation. As an example, [n]CPPs can become globally aromatic upon addition or removal of electrons. The number of π electrons is counted only along the bold pathway shown below.



When **P6** is oxidised, it can exhibit global aromaticity and global anti-aromaticity.

6.7	Based on Hückel's rule, **find** the minimum number of electrons, $n(e)$, from **P6** that should be removed to achieve global aromaticity. **Write** the total number of π electrons, $n(t)$, in the global aromatic system.	4.0 pt