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

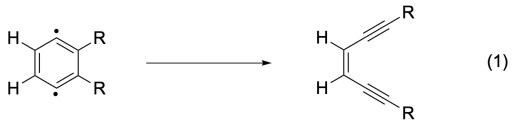
SOLUTION:

Number of Rings	C_{18}	C_{16}	$^3C_{13}$	$^1C_{13}$
A	2	0	0	1
AA	0	2	0	1

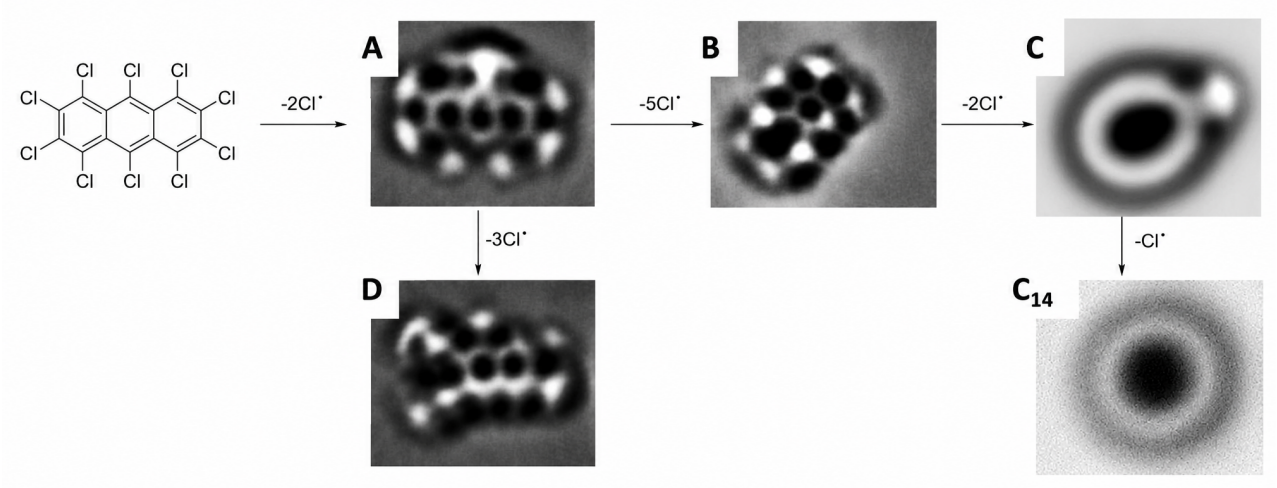
For C18 and C16: 2 pts each.
If both A and AA correct: 2 pts
If one correct, one blank: 1 pt
If one correct, one wrong: 0 pt
Both wrong: 0 pt

For triplet C13 and singlet C13: 3 pts each
If both A and AA correct: 3 pts
If one correct, one blank: 2 pt
If one correct, one wrong: 1 pt
Both wrong: 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:

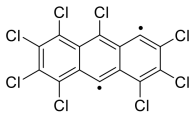
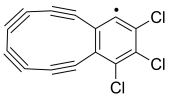
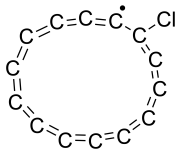
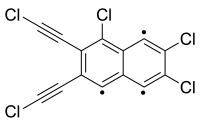


(1)



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

SOLUTION:

A 	**B** 
C 	**D** 

A is given to the students.
B is worth 4 points. 1 pt awarded to incorrect structure with 3 Cl. 1 pt awarded to incorrect structures with 2 alkynes in 1,5-relationship, indicating understanding of retro-Bergman. -1 pt if radicals missing or incorrect.
C is worth 3 points. Full points also given to alternating single and triple bonds. 1 pt awarded to incorrect structure with 1 Cl. -1 pt if radicals missing or incorrect.
D is worth 4 points. 1 pt awarded to incorrect structure with 5 Cl. 1 pt awarded to incorrect structures with two alkynes in 1,5-relationship, indicating understanding of retro-Bergman. -1 pt if radicals missing or incorrect.

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

SOLUTION:

First, we need to convert eV to kJ $\mathrm{mol^{-1}}$:

$$E_{given}[\mathrm{kJ\ mol^{-1}}] = 2.5 \times (1.602 \times 10^{-19} \times 6.022 \times 10^{23})/1000\ \mathrm{kJ\ mol^{-1}} \quad (1)$$

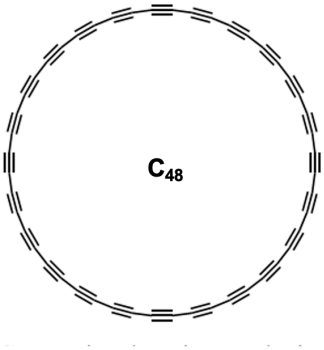
$$E_{given} = 2.5 \cdot 96.485\ \mathrm{kJ\ mol^{-1}} = 241.2\ \mathrm{kJ\ mol^{-1}} \quad (2)$$

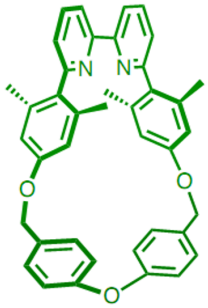
The only candidate with $BDE \leq E_{given}$ is the C–I bond.

X = I

1 point for unit transformation, 1 point for correct halogen choice.
(2 pts awarded if I is chosen with no working)
0 pts for other halogens or more than one halogen chosen.

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

SOLUTION:

Molecular weight of **E** is 590 ($C_{40}H_{34}N_2O_3$). Molecular weight of C_{48} is 576. The first signal is given and corresponds to $[\mathbf{E}+H]^+$. The catenane with one molecule of **E** would yield signal *m/z* 1161 which does not match with given signals. Hence we should consider the probability of di- and tri-catenation as well as dication and trication formation (question clearly states positive mode):

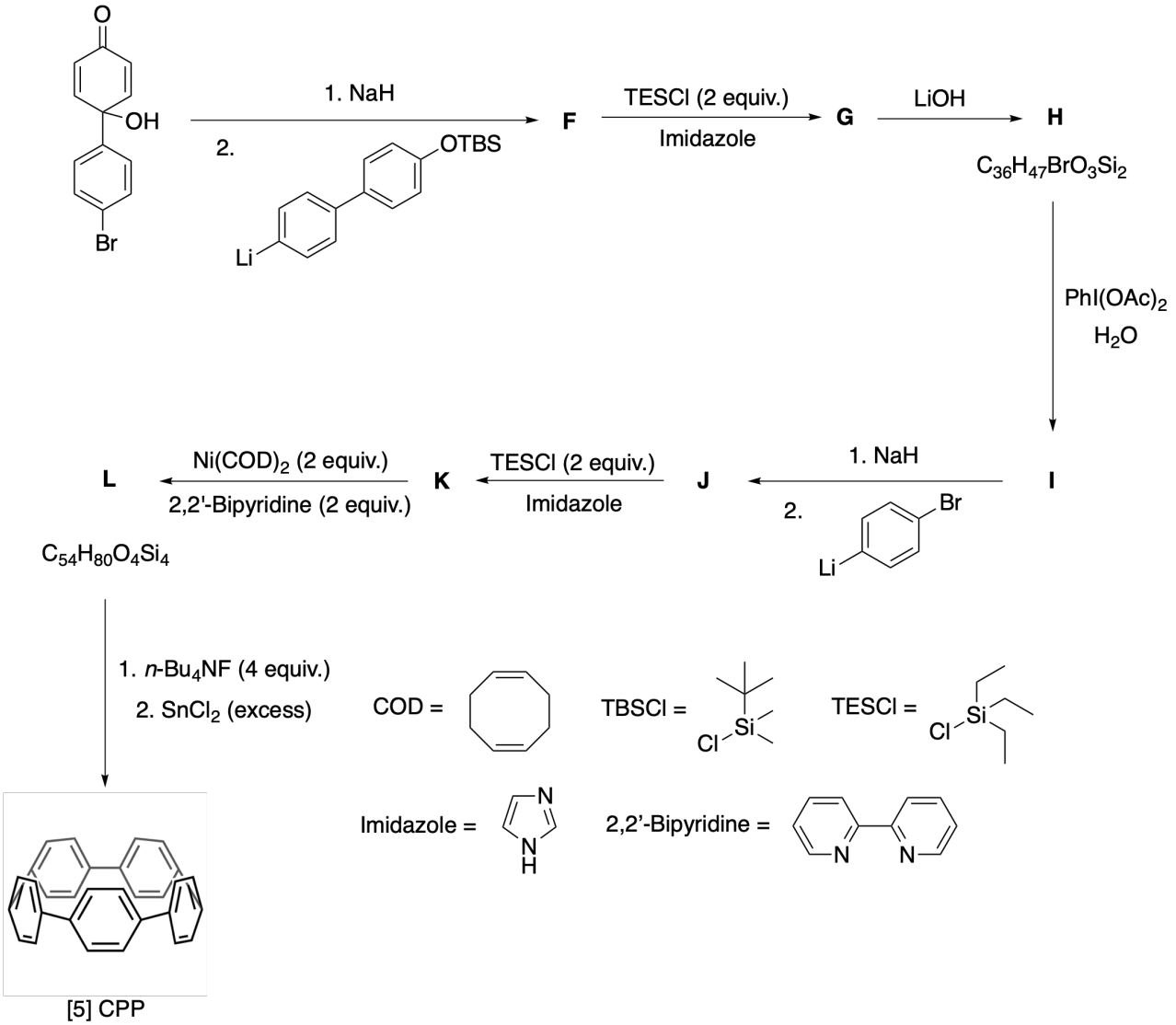
m/z	$+1H^+$	$+2H^+$	$+3H^+$
$C_{48}E$	1167	584	389.7
$C_{48}E_2$	1757	**879**	586.3
$C_{48}E_3$	2347	**1174**	**783**

Therefore, 783 and 1174 peaks correspond to tri-catenane $[C_{48}E_3 + 3H]^{3+}$ and $[C_{48}E_3 + 2H]^{2+}$ ions. Peak at 879 corresponds to dicatenane dication$[C_{48}E_2 + 2H]^{2+}$.

m/z	591	783	879	1174
	$[\mathbf{E}+H]^+$	$[C_{48}\mathbf{E}_3+3H]^{3+}$	$[C_{48}\mathbf{E}_2+2H]^{2+}$	$[C_{48}\mathbf{E}_3+2H]^{2+}$

4 points for each correct ionic species.
No partial credit as other answers will not have correct *m/z* ratios.

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.

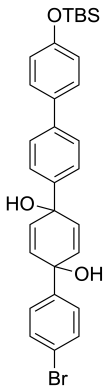


(equiv. = Equivalent, excess = Excess)

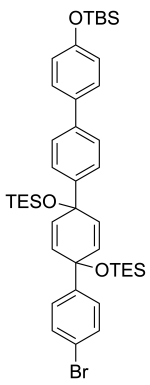
6.5 **Draw** the structures of **F-L**. 24.0 pt

SOLUTION:

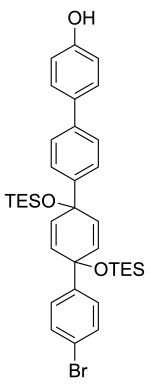
F



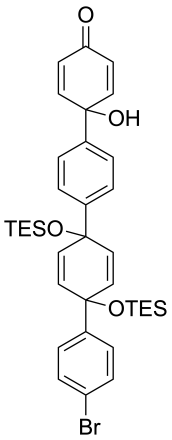
G



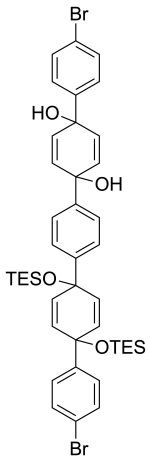
H



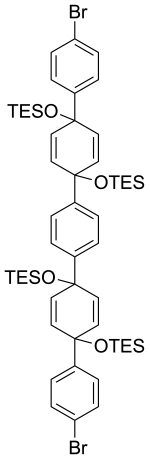
I



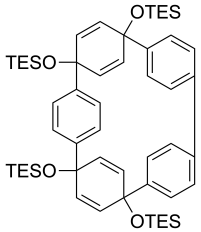
J



K



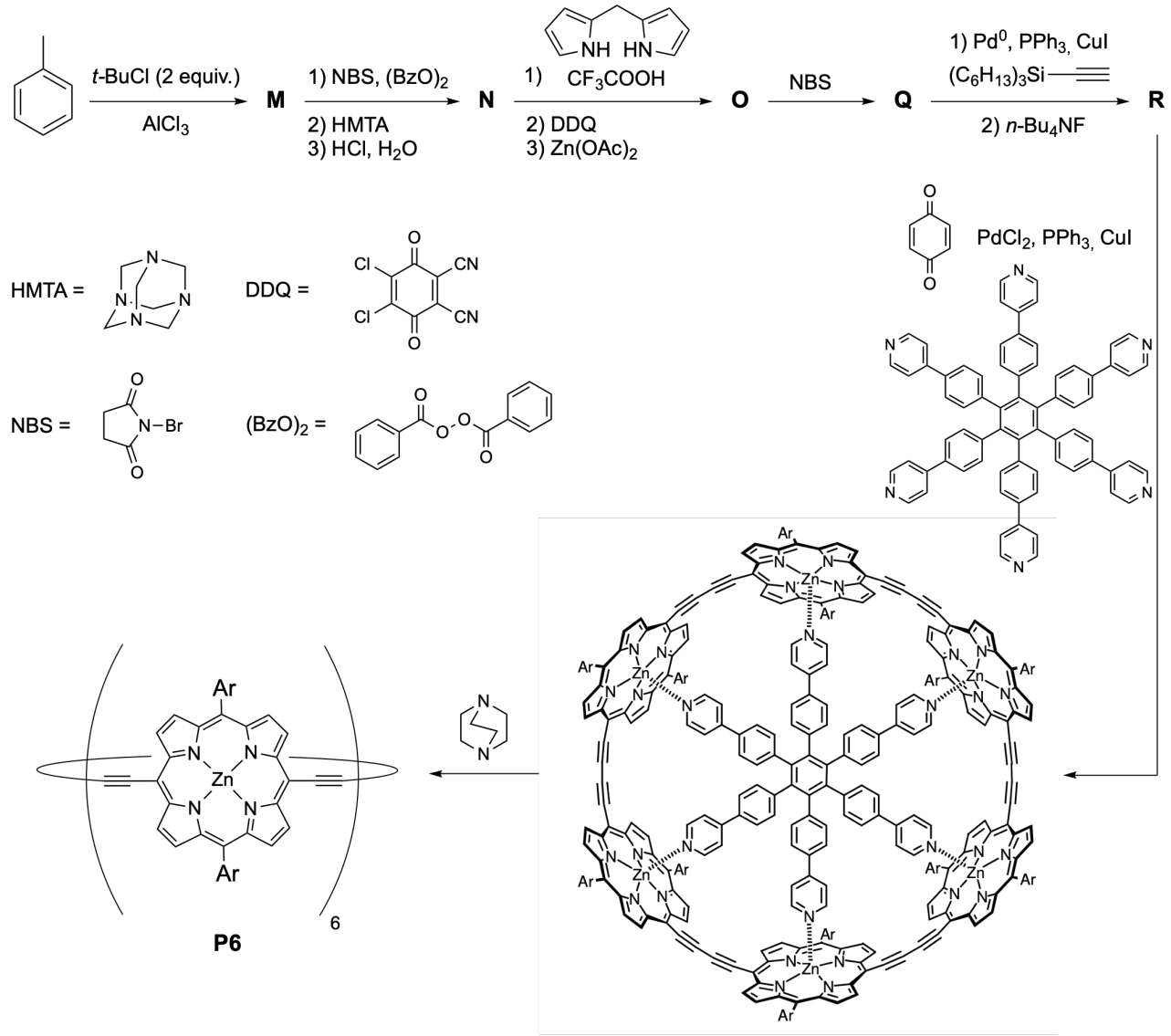
L



RUBRICS:

F: 4 pts
G: 3 pts
H: 3 pts
I: 4 pts
J: 3 pts
K: 3 pts
L: 4 pts
Error carry forward can be awarded if the desired reactivity is shown and the chemistry is sensible.
-1 pt for each mistake in a part of the molecule not undergoing reaction.
For **F** and **J**, the di-anion of the product or salts (OLi/ONa) will be accepted for full credit.
For **H,** the mono-anion of the product or salt (OLi) will be accepted for full credit.

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.

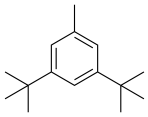


(equiv. = Equivalent)

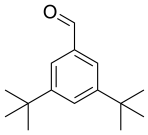
6.6 **Draw** the structures of **M-R**. 20.0 pt

SOLUTION:

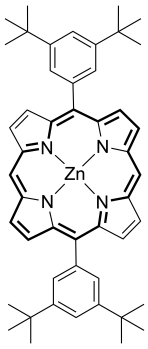
M



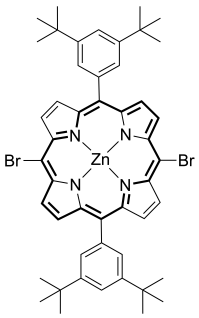
N



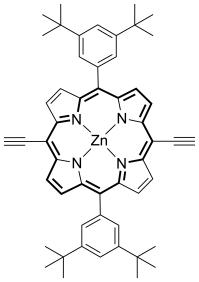
O



Q



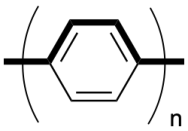
R



RUBRICS:

M: 4 pts
Substitution pattern should be determined with information on four types of proton.
1 pt for any structure with one *t*-Bu group.
3 pt for structure with *t*-Bu added at both *ortho* positions, 1 pt for any other structure with two *t*-Bu groups.
N: 4 pts
4 pts if amine is given instead of the aldehyde (Delepine reaction). Does not affect the grading of the rest of the parts.
1 pt if Br instead of aldehyde.
O: 4 pts
Q: 4 pts
R: 4 pts
- 1 pt if double bonds in porphyrin drawn incorrectly, this penalty will be applied at most once.
- 2 pt if Zn is missing, this penalty will be applied at most once.

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.

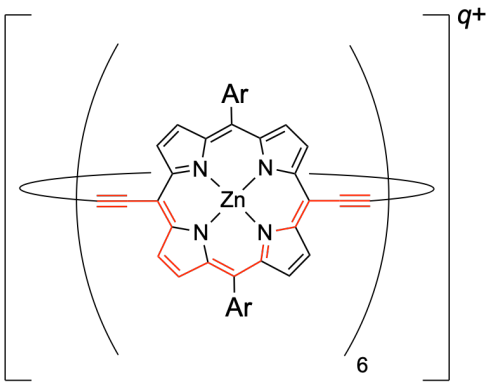


When **P6** is oxidised, it can exhibit global aromaticity and global anti-aromaticity.

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

SOLUTION:

We should count electrons around the abbreviated structure of **P6** as shown below:



The total number of π-electrons is $14 \times 6 = 84$ in the ground state.
To achieve global aromaticity by Hückel's rule, we need $4n + 2$ π-electrons.
The minimum number of π-electrons that need to be lost is two electrons and the total number of π-electrons is 82.

n(*e*)	**2**
n(*t*)	**82**

4 pts for fully correct.
2 pts if total number of electrons is wrong but it satisfies Hückel's $4n + 2$ rule.
No partial points for the loss of two electrons.