

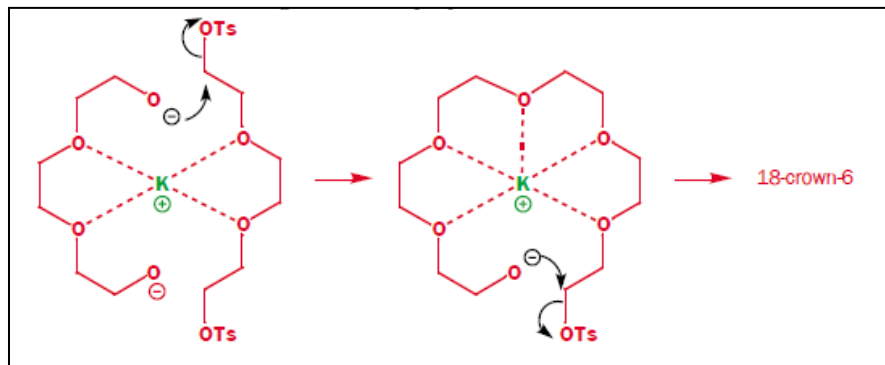
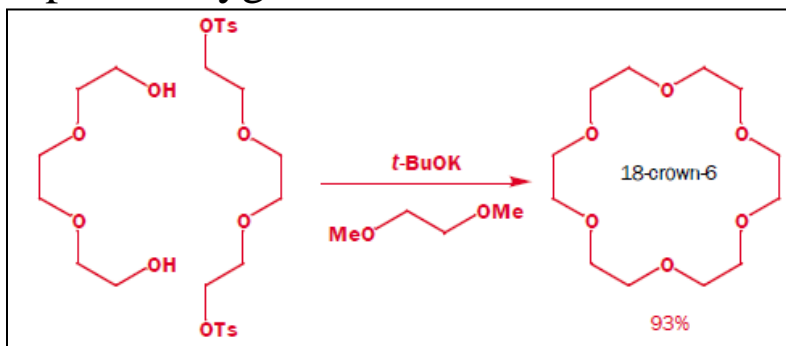
**Crown ethers** are cyclic compounds that have several ether linkages. A crown ether specifically binds certain metal ions or organic molecules, depending on the size of its cavity.

### Polymerization by the $S_N2$ reaction

In principle, co-polymerization of a 1,2-diol and a 1,2-dihalide might lead to a polyether.



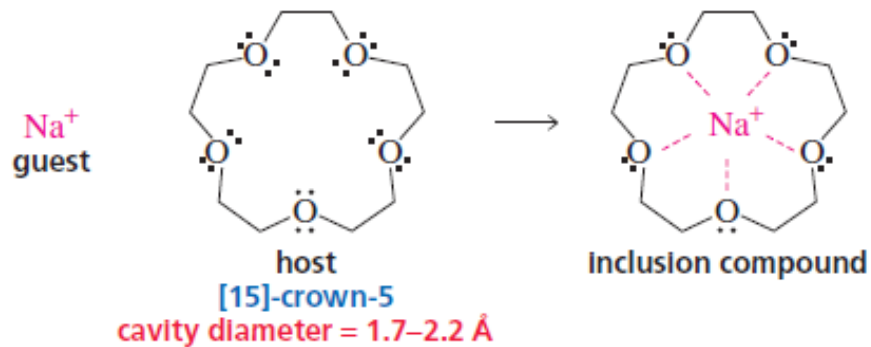
One molecule of base is consumed for each new C–O bond made, and these reactions terminate quickly before long chains are made. It is more useful for making the cyclic oligomers called ‘**crown ethers**’. 18-Crown-6 has an eighteen-membered ring with six evenly spaced oxygen atoms.



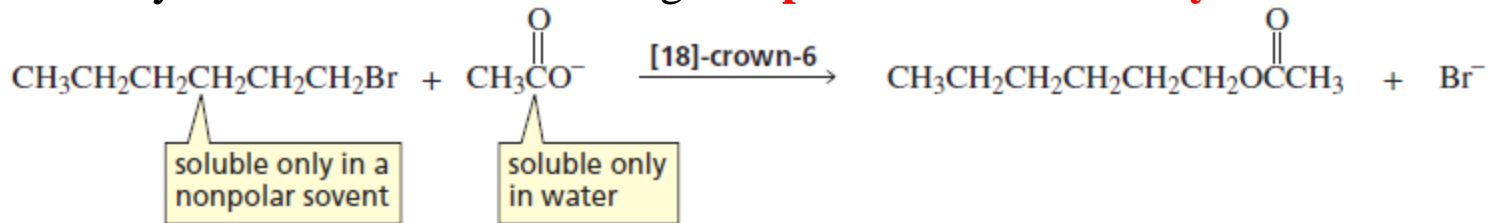
These crown ethers have cavities ideal for complex formation with metal ions. They can even carry metal ions into solution in organic solvents. **18-crown-6** is the right size for potassium ions, and a solution of KMnO<sub>4</sub> and 18-crown-6 in benzene, so-called ‘purple benzene’, is a useful oxidizing agent. The high-yielding oligomerization is a template reaction with a potassium ion holding the two reagents together.

## APPLICATION

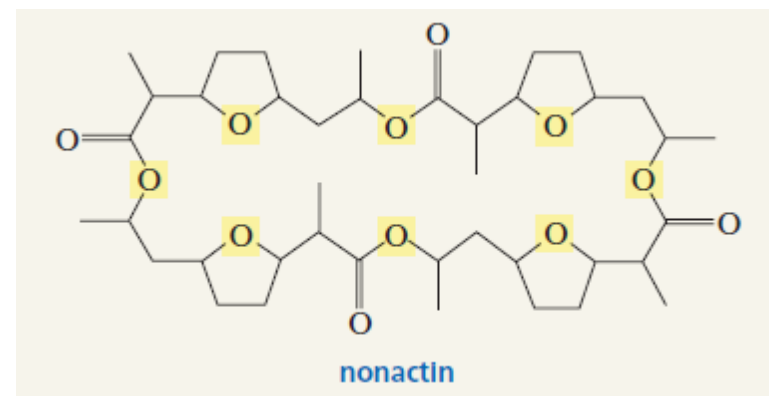
1) The *crown-guest complex* is called an **inclusion compound**.



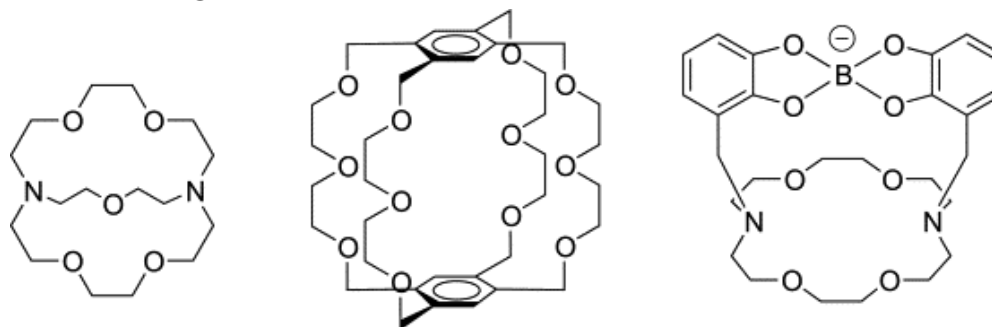
2) Potassium acetate can be dissolved in a nonpolar solvent such as benzene if [18]-crown-6 is added to the solution. The crown ether binds potassium in its cavity, and the nonpolar crown ether-potassium complex dissolves in benzene, along with the acetate ion, to maintain electrical neutrality. The crown ether is acting as a **phase-transfer catalyst**



3) **Nonactin** is a naturally occurring antibiotic that owes its biological activity to its ability to disrupt the carefully maintained electrolyte balance between the inside and outside of a cell. Nonactin disrupts this gradient by acting like a crown ether. Nonactin's diameter is such that it specifically binds potassium ions.

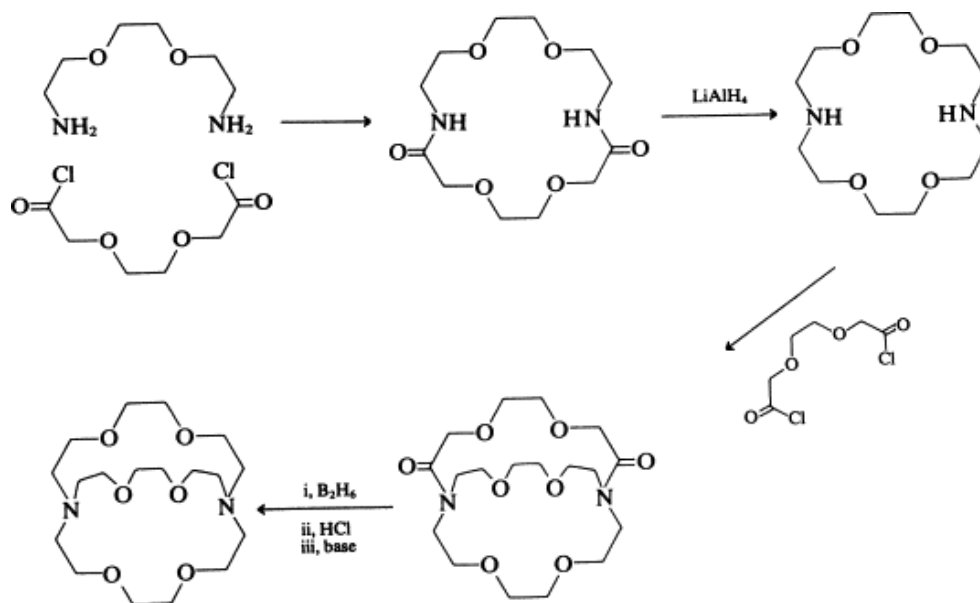


**Cryptands** are macro-bi- or -poly-cycles able to encapsulate an ion by providing it higher protection because of their cagelike structures.

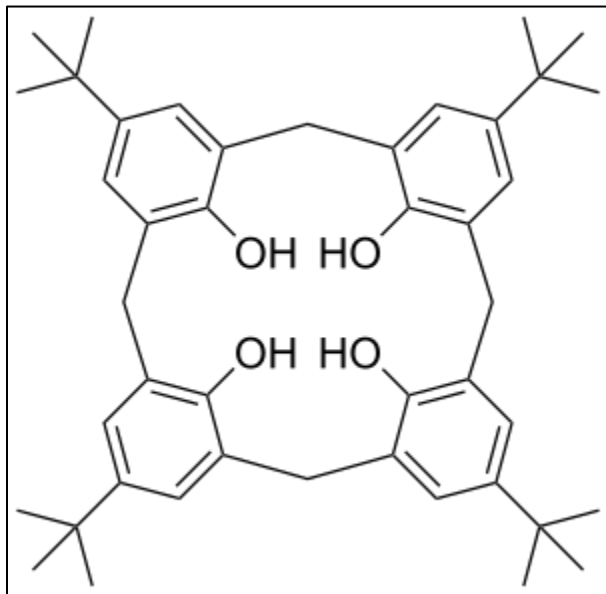


## Lehn Cryptand Synthesis

The amide formation and reduction sequence allowed the ready introduction of different heteroatoms and rigidifying groups into the macrobicycle. However, high dilution conditions were necessary and total yields were low. These basic routes have been applied to many diverse cryptands.

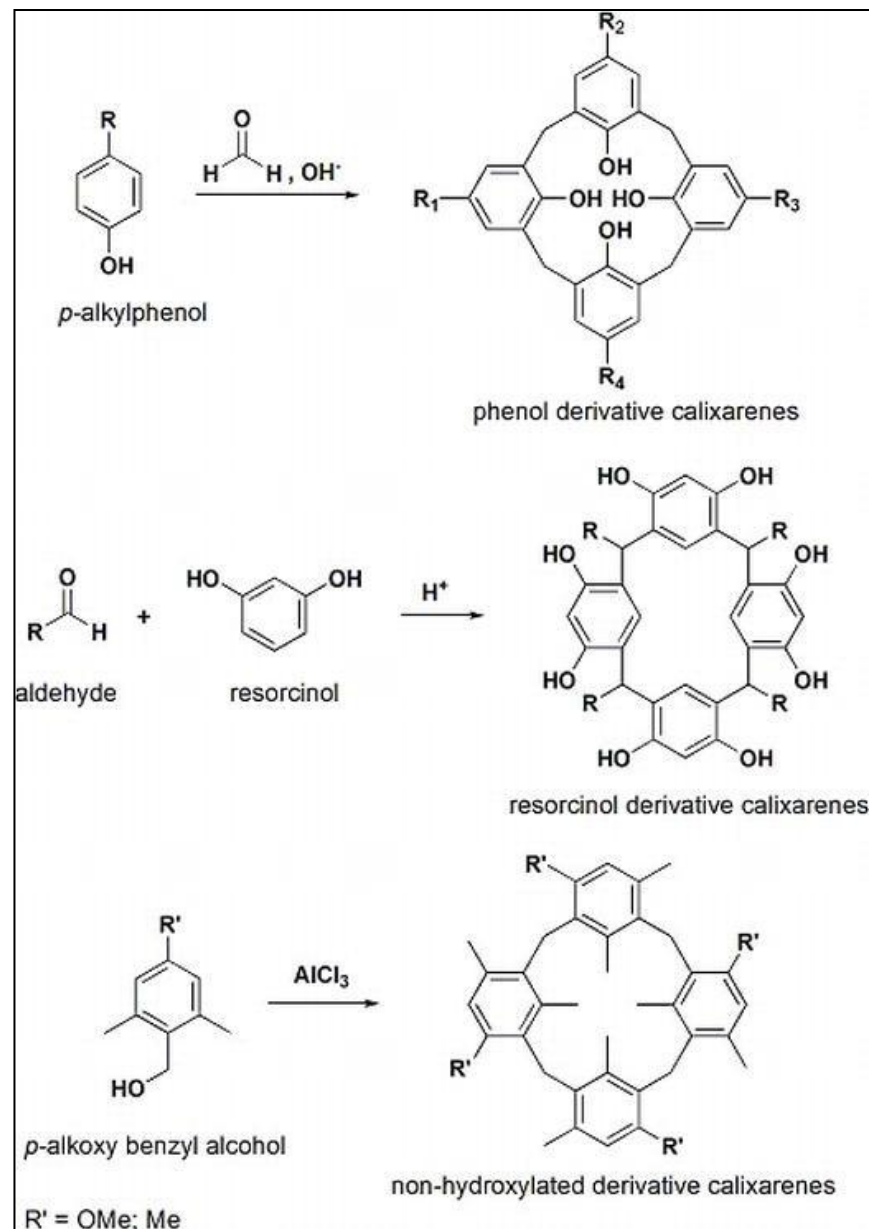


**Calixarene** is a macrocycle or cyclic oligomer based on a hydroxyalkylation product of a phenol and an aldehyde.



**Calix[4]arene with para-tert-butyl substituents**

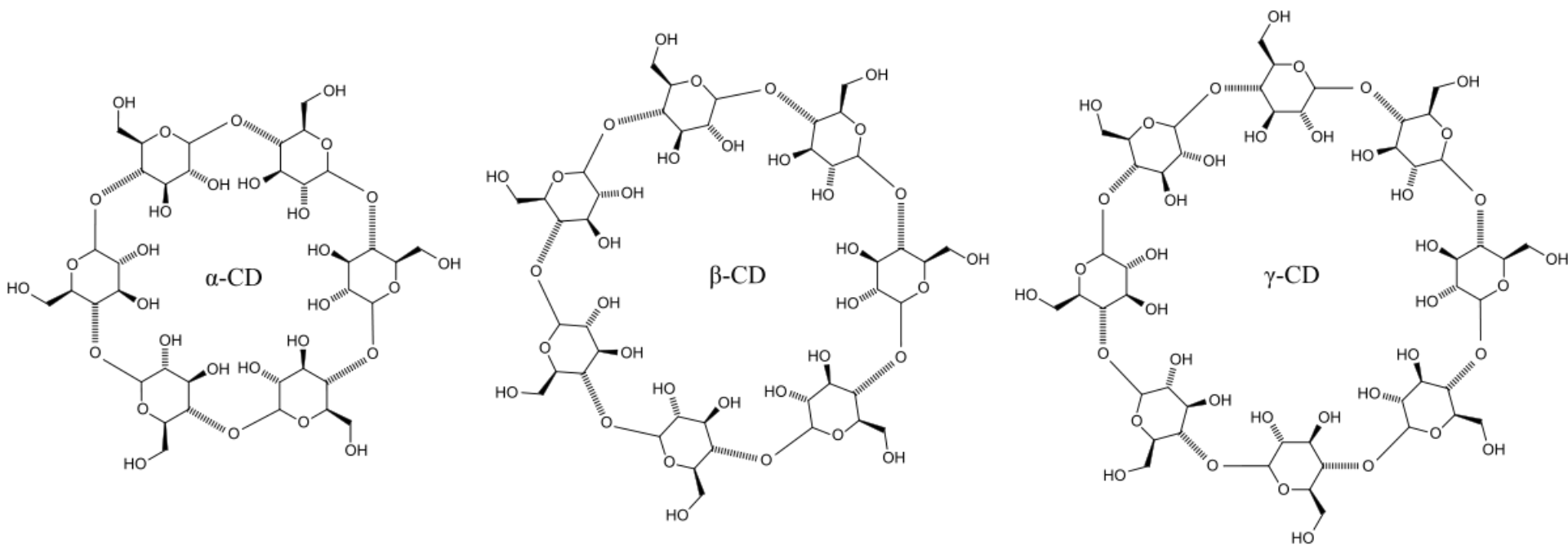
There are several products that use aromatic compounds in the forms of para-alkoxy-substituted benzyl alcohol derivatives, such as p-alkoxybenzyl alcohol, that when reacted with the aid of  $\text{AlCl}_3$  as a catalyst will result in non-hydroxylated calixarenes.



**Basic synthesis of calixarene**

**Cyclodextrins** are a family of cyclic oligosaccharides, consisting of a macrocyclic ring of glucose subunits joined by  $\alpha$ -1,4 glycosidic bonds.

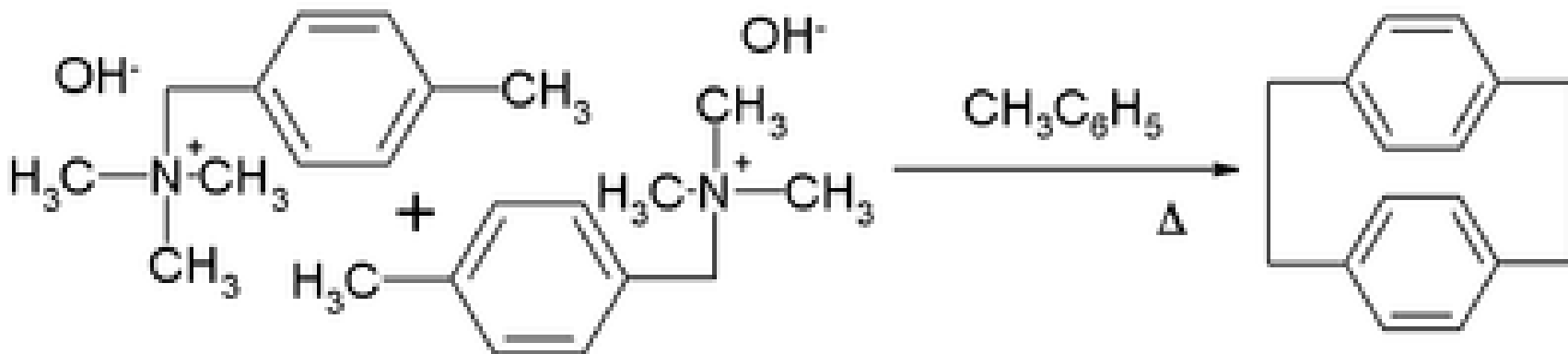
**Cyclodextrins** are prepared by enzymatic treatment of starch. Commonly, cyclodextrin glycosyltransferase (CGTase) is employed along with  $\alpha$ -amylase. First starch is liquified either by heat treatment or using  $\alpha$ -amylase, then CGTase is added for the enzymatic conversion. CGTases produce mixtures of cyclodextrins.



Biwer, A., Antranikian, G. and Heinzle, E., 2002. Enzymatic production of cyclodextrins. *Applied microbiology and biotechnology*, 59(6), pp.609-617.

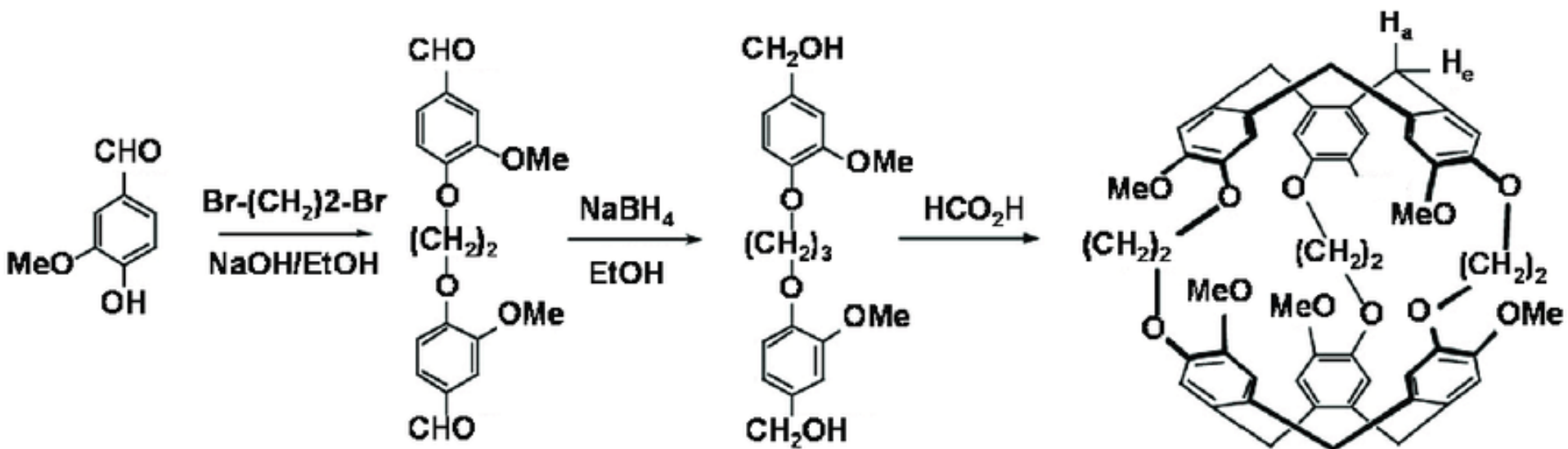
**Cyclophane** is a hydrocarbon consisting of an aromatic unit (typically a benzene ring) and an aliphatic chain that forms a bridge between two non-adjacent positions of the aromatic ring. More complex derivatives with multiple aromatic units and bridges forming cagelike structures are also known.

A well exploited member of the [n.n]paracyclophane family is [2.2]paracyclophane. One method for its preparation is by a 1,6-Hofmann elimination:



**Cryptophanes** are a class of organic supramolecular compounds studied and synthesized primarily for molecular encapsulation and recognition. One possible noteworthy application of cryptophanes is encapsulation and storage of hydrogen gas for potential use in fuel cell automobiles.

## SYNTHESIS



**Dendrimers** are repetitively branched molecules. This macromolecule is also commonly known by the name arborol.

The synthesis is started by nucleophilic substitution of 1-bromopentane by triethyl sodiomethanetricarboxylate in DMF and benzene. The ester groups were then reduced by  $\text{LiAlH}_4$  to a triol then to tosylate groups with tosyl chloride and pyridine. The reaction with the tricarboxylate, forming generation two. Further repetition of the two steps leads to higher generations of arborol

