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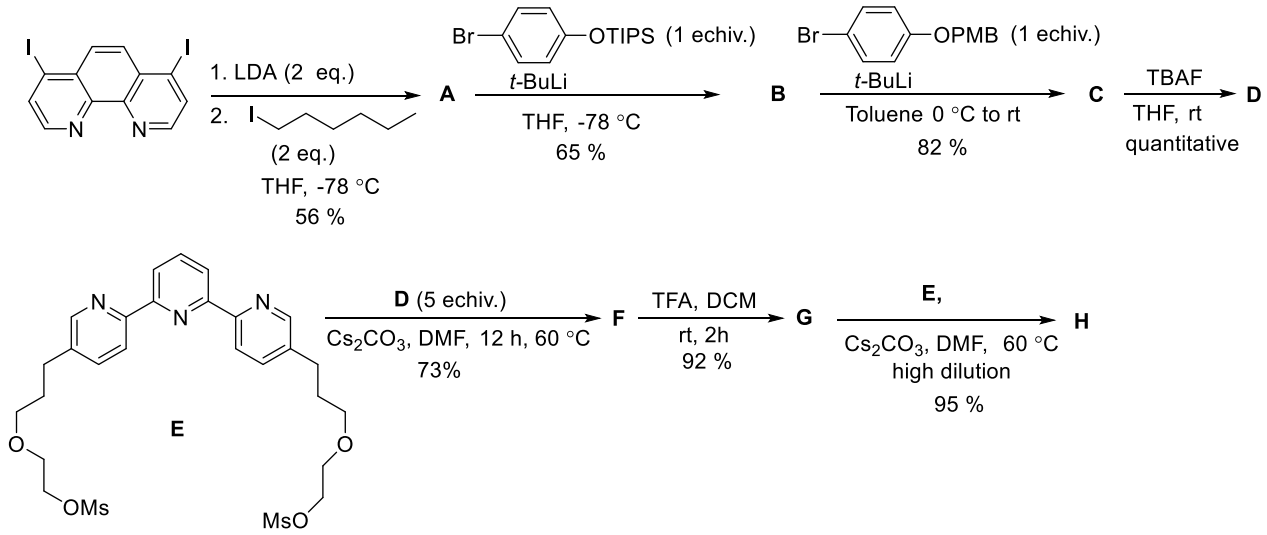
# Synthesis of a molecular muscle

A special class of molecular machines is represented by contractile and extensible molecules called "molecular muscles". Such an example is compound **H**, synthesized by Nobel Laureate prof. Jean-Pierre Sauvage, shown in the scheme 1.




LDA=lithium diisopropylamine, TIPS=triisopropylsilane, PMB=*p*-methoxybenzyl, TBAF=tetra-*n*-butylammonium fluoride, Ms –mesyl, TFA= trifluoroacetic acid

Scheme 1. Synthesis of **H**

**Queries**:

**a)** Identify the structures of compounds **A**–**H** in Scheme 1.

**b)** The molecular contraction and expansion motion in case of compound **H** can be achieved through complexation – decomplexation – recomplexation processes.

Using $Fe(OTf)_2$, $[Cu(CH_3CN)_4][PF6]$, $Cs_2CO_3$ and KCN, write the equilibria that describe the molecular muscle behavior of compound **H**.

Note: Treating the iron(II) complex with $Cs_2CO_3$ in DMF causes the disappearance of the characteristic purple color. Treating the Cu(I) complex with KCN in water/acetonitrile led to the discoloration of the solution to deep red.

**c)** Treating compound **H** with $[Cu(CH_3CN)_4][PF_6]$ in acetonitrile led to formation of a dark red solution which over time, in presence of oxygen, turns green. Explain the observed changes using chemical reactions.

References: works of JP Sauvage

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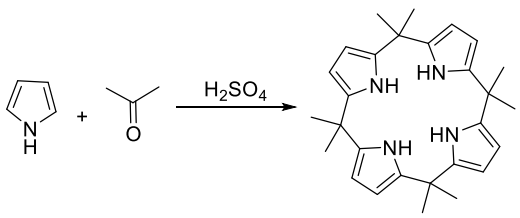
# Octamethylcalix[4]pyrol in practice

Since the discovery that calix[4]pyrrole can complex anions and other species that can form hydrogen bonds with the NH groups of pyrroles, this macrocyclic system has been intensively studied due to its potential applications in various fields, including molecular recognition, detection, catalysis, self-assembly and fabrication of smart materials. Anions play a key role in the biological world and, therefore, anion receptors have been studied as potential drugs due to their ability to transport anions across membranes. Both antibacterial and cytotoxic effects against some cancer cells have been reported for macrocycles that transport chloride ions. In addition, calixpyrrole derivatives show genotoxic effects and, therefore, a cytotoxic action that is not correlated with anion transport.

In this task you will combine theory with practical details. Your task is to perform the following reaction.



You will use 5 mmol of pyrrole, a 1:1 ratio of the starting materials, methanol as solvent and a catalytic amount of sulfuric acid. The following reagents are also available for your experiment: tetra-*n*-butylammonium 4-nitrophenolate, tetra-*n*-butylammonium fluoride, ethyl acetate, *n*-pentane and all is necessary to perform thin layer chromatography.

Queries:

1. Describe a working procedure for this reaction in as much detail as you can. Justify your choices for glassware and equipment (stirring/heating), reaction monitoring, isolation of the compound from the crude reaction mixture and purification.
2. Describe what changes you could observe by mixing octamethylcalix[4]pyrol with each ammonium salt.