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Selective Synthesis of Oxacalix[6]arenes and Mixed Oxacalix[4]arenes

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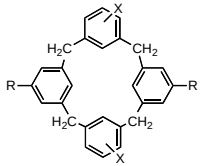
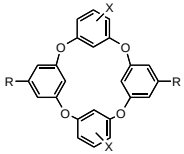
Introduction and Overview:

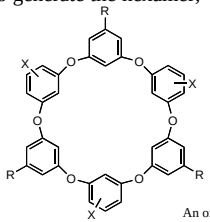
Calixarenes are macrocycles composed of benzene rings meta linked to each other by one carbon atom. These exotic compounds can be used for a variety of purposes including metal leaching for environmental cleanup, surface technology, luminescent probes, nuclear waste treatment, among others. A variety of calixarenes exist, including azacalix[n]arenes thiocalix[n]arenes (where n = the number of benzene rings) and oxacalix[n]arenes; these macrocycles use nitrogen, sulfur and oxygen, respectively, as the atom which links the benzene rings together. My research has focused on synthesizing oxacalix[6]arenes ("hexamer") in high yield, which is a synthetic challenge because it is generally accepted that oxacalix[n>4]arenes will thermodynamically decompose to the oxacalix[4]arene ("tetramer"); i.e. heating the reaction mixture will yield the tetramer, not the hexamer. To generate the hexamer, "trimer" precursors have been synthesized, in the hopes of facilitating hexamer ring closure.



A calix[4]arene (where x = azacycle)

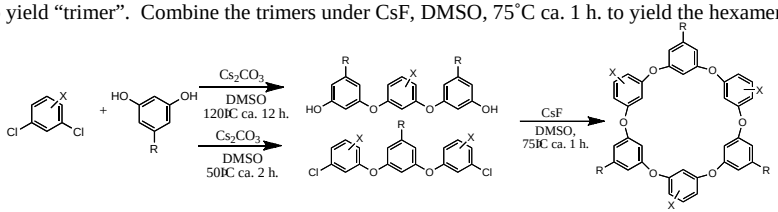


An oxacalix[4]arene, the "tetramer"

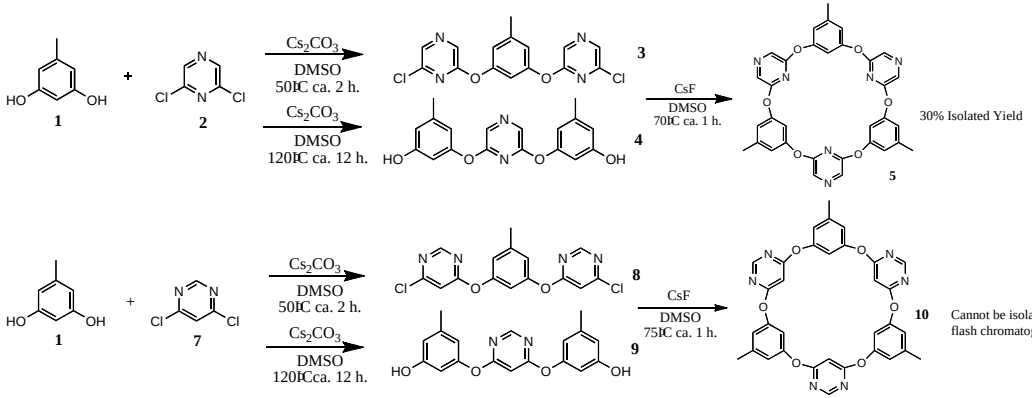


An oxacalix[6]arene, the "hexamer"

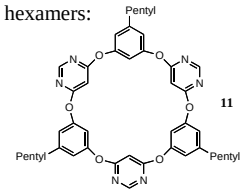
The General Concept for Oxacalix[6]arenes: Combine nucleophile and electrophile in a 2:1 and 1:2 stoichiometric ratio to yield "trimer". Combine the trimers under CsF, DMSO, 75˚C ca. 1 h. to yield the hexamer



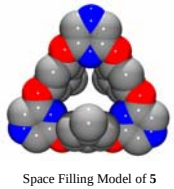
Specific Trimer Synthesis and Hexamer Formation:



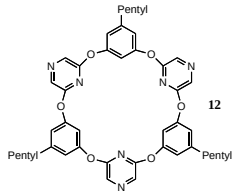
Other synthesized hexamers:



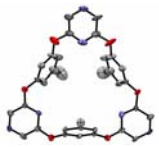
22% Isolated Yield



Space Filling Model of **5**

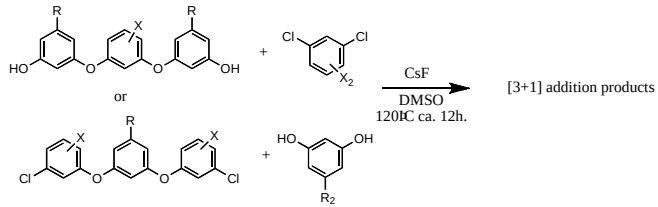


Cannot be isolated via flash chromatography

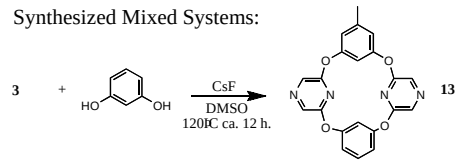


X-Ray Structure of **5**

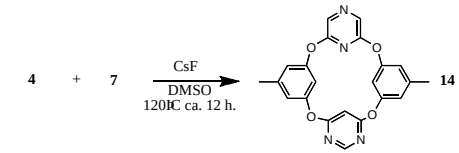
The General Concept for Mixed Oxacalix[4]arenes: Combine a dihydroxy- or dichloro-trimer with a different electrophile or nucleophile monomer, respectively, to yield a mixed [3+1] addition tetramer under DMSO, 120˚C ca. 12 h.



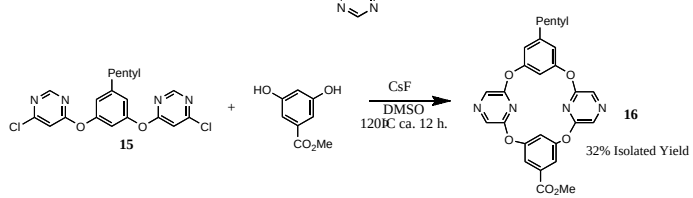
Synthesized Mixed Systems:



47% Isolated Yield



15% Isolated Yield



32% Isolated Yield