

## Design and synthesis of calixarene

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Calixarenes are versatile macromolecules in the field of supramolecules because of its synthetic feasibility and extensive analytical applications. This paper reviews synthesis of calixarenes and related derivatives containing heterocycles, polymers, crown-ethers, and fullerenes. Various analytical applications of calixarenes are discussed.

**Keywords:** Calixarenes, Crown-ethers, Fullerenes, Polymers

### Introduction

Calixarene is a macrocycle or cyclic oligomer based on a hydroxyl alkylation product of phenols and aldehydes<sup>1</sup>. Calixarenes have hydrophobic cavities that can hold smaller molecules or ions and belong to the class of cavitands known as host-guest chemistry. In 1940s, Zinke & Ziegler<sup>2</sup> discovered base-induced reaction of *p*-alkylphenols with formaldehyde, which yields cyclic oligomers. Then, synthesis of cyclic oligomers was reported<sup>3</sup>. Calixarenes can be used as ion sensitive electrodes or sensors<sup>4</sup>, optical sensors<sup>5</sup>, chiral recognition devices for solid phase extraction, as a stationary phase and modifiers<sup>6</sup>. Several books<sup>7-12</sup> and reviews<sup>13-17</sup> covered synthesis, properties and applications of calixarenes. Some studies<sup>18-20</sup> reported structures and properties of calixarene. This review presents five types of calixarenes.

### I. Modified Calixarenes

There are two places (phenolic hydroxyl groups and *p*-positions) for modification of calixarenes. Methylene bridges may be substituted with aromatic system of phenolic units as a whole or may lead to replacement of OH-function by other groups. Functional groups introduced in a first step may be further modified by subsequent reactions including migration. Usually

upper rim substitution of calixarene is carried out by de-*t*-butylation of *p*-*tert*-butyl group followed by subsequent reaction. Substitution of hydroxamic acid group<sup>21-24</sup> and bromination<sup>25</sup> is reported. Similarly, *p*-bromination of calix[4]arenemethylether<sup>26</sup> and bromination of tetramethoxycalix[4]arene is also reported<sup>27</sup>. *Ips*o-bromination<sup>28</sup> has been carried out under a variety of reaction parameters. Optimized conditions give *p*-bromocalixarenes and methylene bridge brominated calix[*n*]arene directly<sup>28</sup>. Single step, one-pot procedure is also given (Scheme 1) for conversion of *p*-*tert*-butylcalix[*n*]arenes (Table 1) to their *p*-acyl derivatives; thus (2) and (3) has been prepared<sup>29</sup>. *Ips*o-substitution is also possible with more than one substitution (Table 2)<sup>30</sup>. Calixarenes having larger cavity size like calix[8]arenes can also be *ip*so substituted<sup>31</sup>.

Calixarenes of varying cavity size can form variety of host-guest type of inclusion complexes similar to cyclodextrins. However, calixarene host molecules have a unique composition that include benzene groups, which provide Å-Å interaction and hydroxyl groups for hydrogen bonding, which is generally water insoluble. Shinkai *et al* synthesized water-soluble calixarenes having sulfonate groups<sup>32</sup>. Calixarene cavity is capable for molecular recognition in solution, and can be applied in remediation of contaminated groundwater and industrial effluents. Intercalation of water-soluble *p*-sulfonated calix[4]arene (CS<sub>4</sub>) in interlayer of Mg-Al and Zn-Al lactate dehydrogenase (LDHS) (M<sub>2</sub>+/Al = 3) by co-precipitation method<sup>33</sup> showed adsorption ability for benzyl alcohol (BA) and *p*-nitrophenol (NP) in aqueous solutions, which

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Table 1—Substitutions for *p*-acyl derivatives prepared from *p*-*t*-butylcalixarene

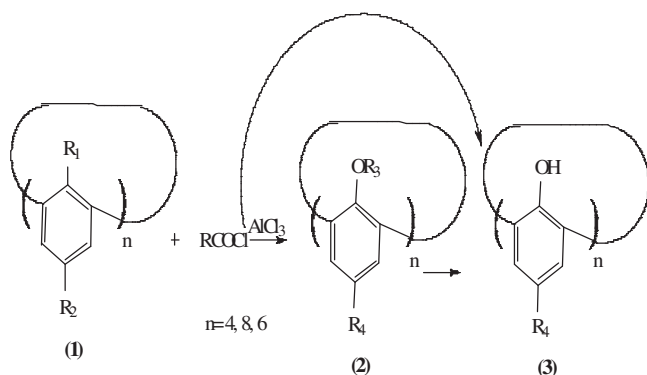
R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub> (3)	R <sub>4</sub> (4)
OH	H	CO-C <sub>6</sub> H <sub>5</sub>	CO-C <sub>6</sub> H <sub>5</sub>	CO-C <sub>6</sub> H <sub>5</sub>
OH	<i>t</i> -Bu	CO-C(CH <sub>3</sub> ) <sub>3</sub>	CO-C(CH <sub>3</sub> ) <sub>3</sub>	CO-C(CH <sub>3</sub> ) <sub>3</sub>
OMe	<i>t</i> -Bu	CO-CH <sub>3</sub>	<i>t</i> -Bu	CO-4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>
		CO-CH <sub>3</sub> CH <sub>2</sub>	<i>t</i> -Bu	

Table 2—*ipso*-substitution group for calix[4]arene

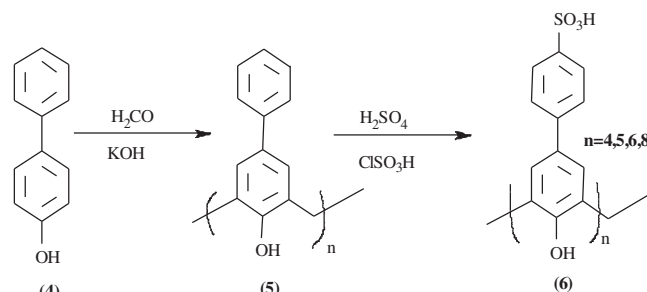
Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
1	H	H	H	H
2	H	H	H	Me
3	H	COMe	H	Me
4	H	H	H	COMe
5	Me	COMe	H	H
6	Me	H	H	COMe
7	Me	H	H	CoMe

are also larger in Zn-Al/CS<sub>4</sub>/LDH than in Mg-Al/CS<sub>4</sub>/LDH because of effective use of parallel arranged cavity only in Zn-Al/CS<sub>4</sub>/LDH. CS<sub>4</sub>/LDHs have possibility as new organic-inorganic hybrid adsorbents.

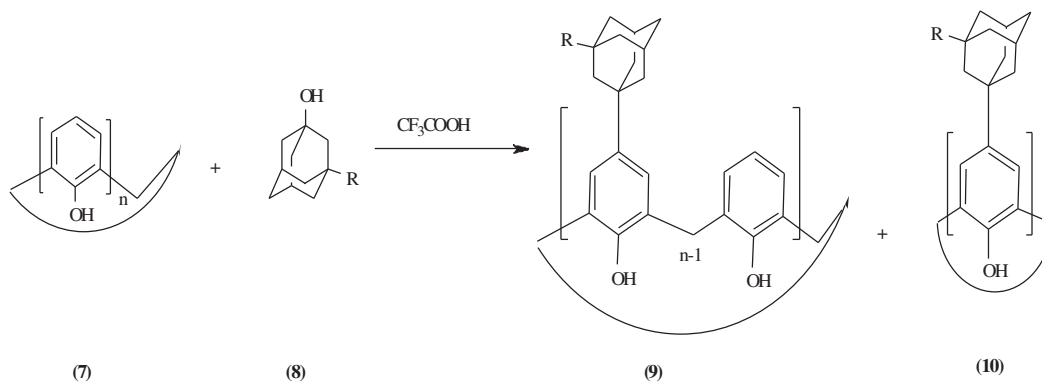
Makha & Rasston<sup>34</sup> synthesized water soluble calixarenes using *p*-phenyl calix[*n*]arene and sulfonate derivatives (Scheme 2), which have exciting possibilities as a phase transfer catalyst in transport processes. To increase size of a hydrophobic cavity, calix[*n*]arenes (Scheme 3) consist of different bulky groups. Functional groups present in adamantane fragment (9) and (10)



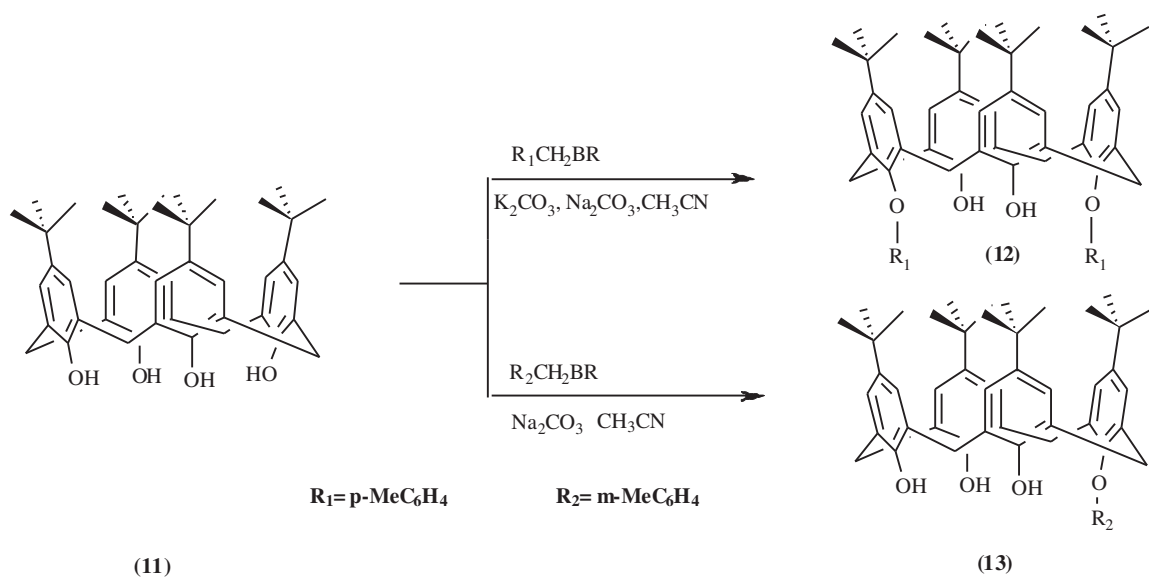
Scheme 1



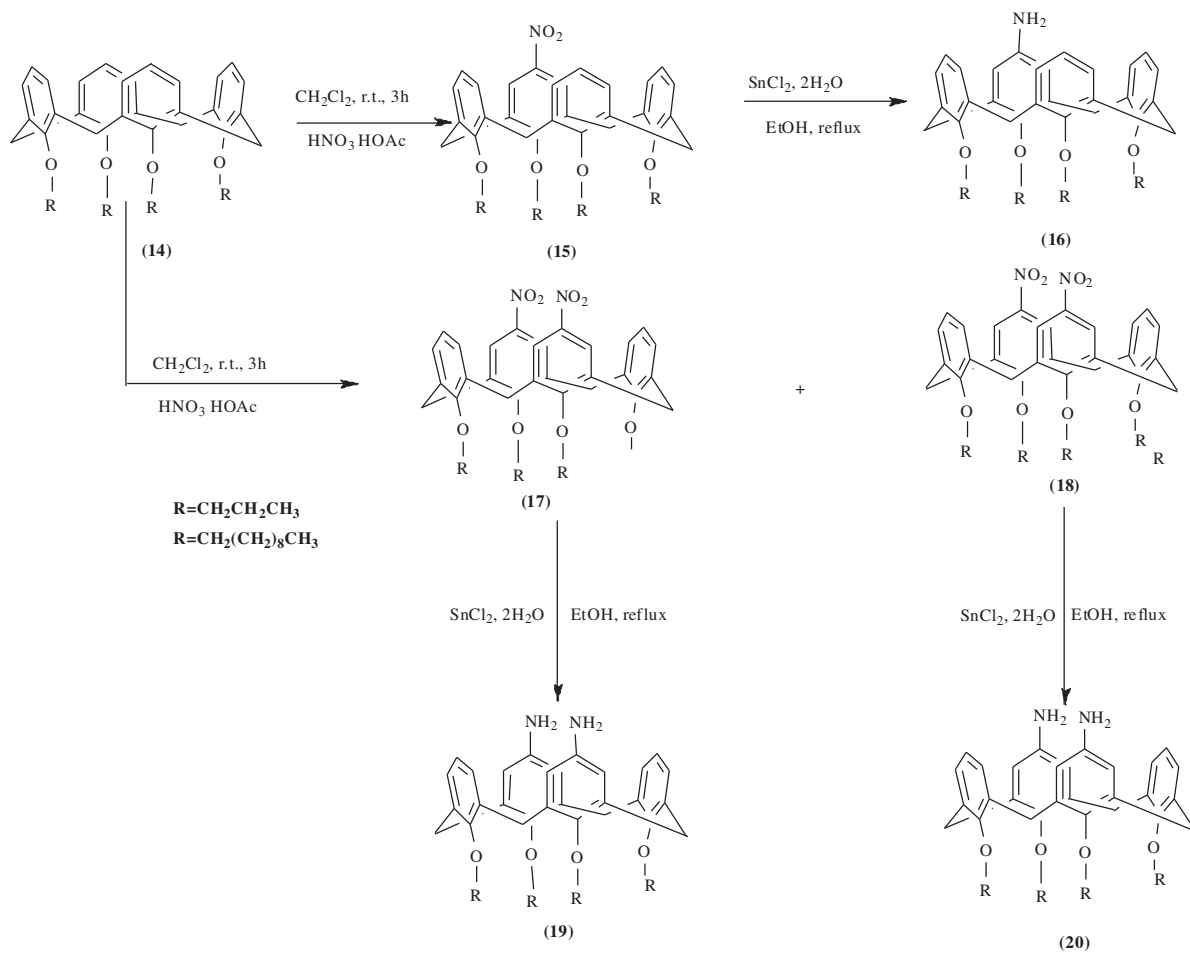
Scheme 2



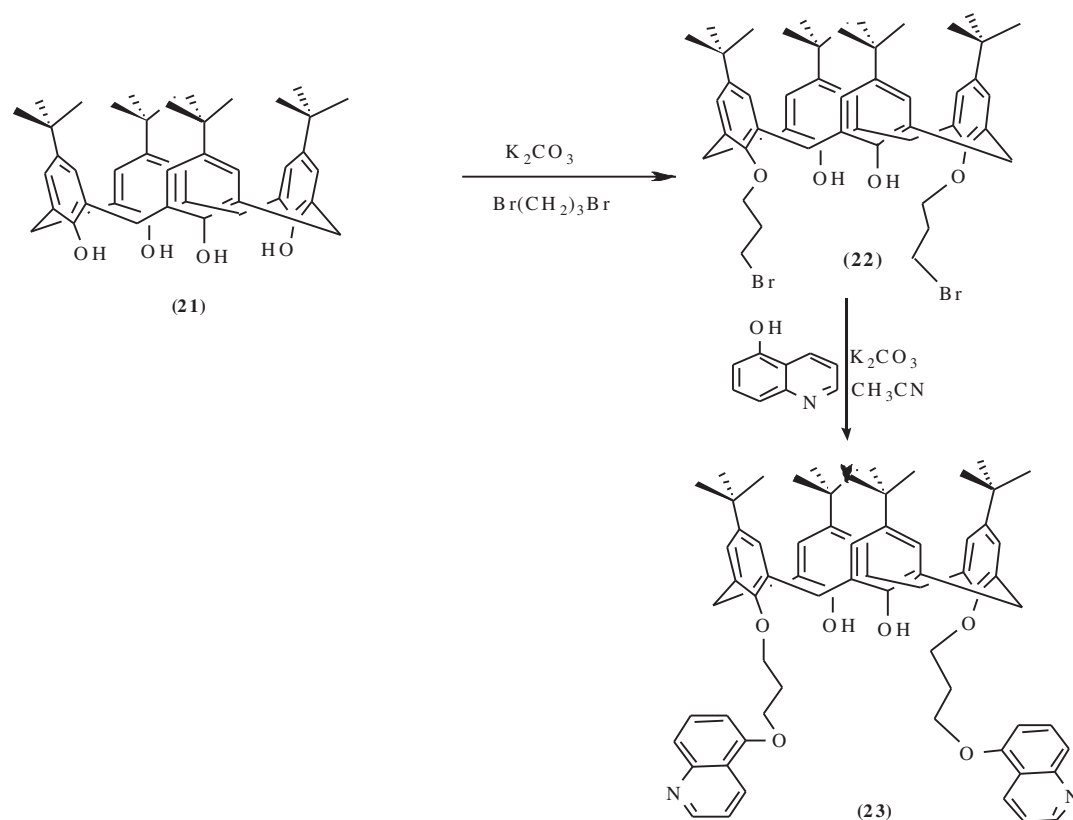
Scheme 3



Scheme 4



Scheme 5



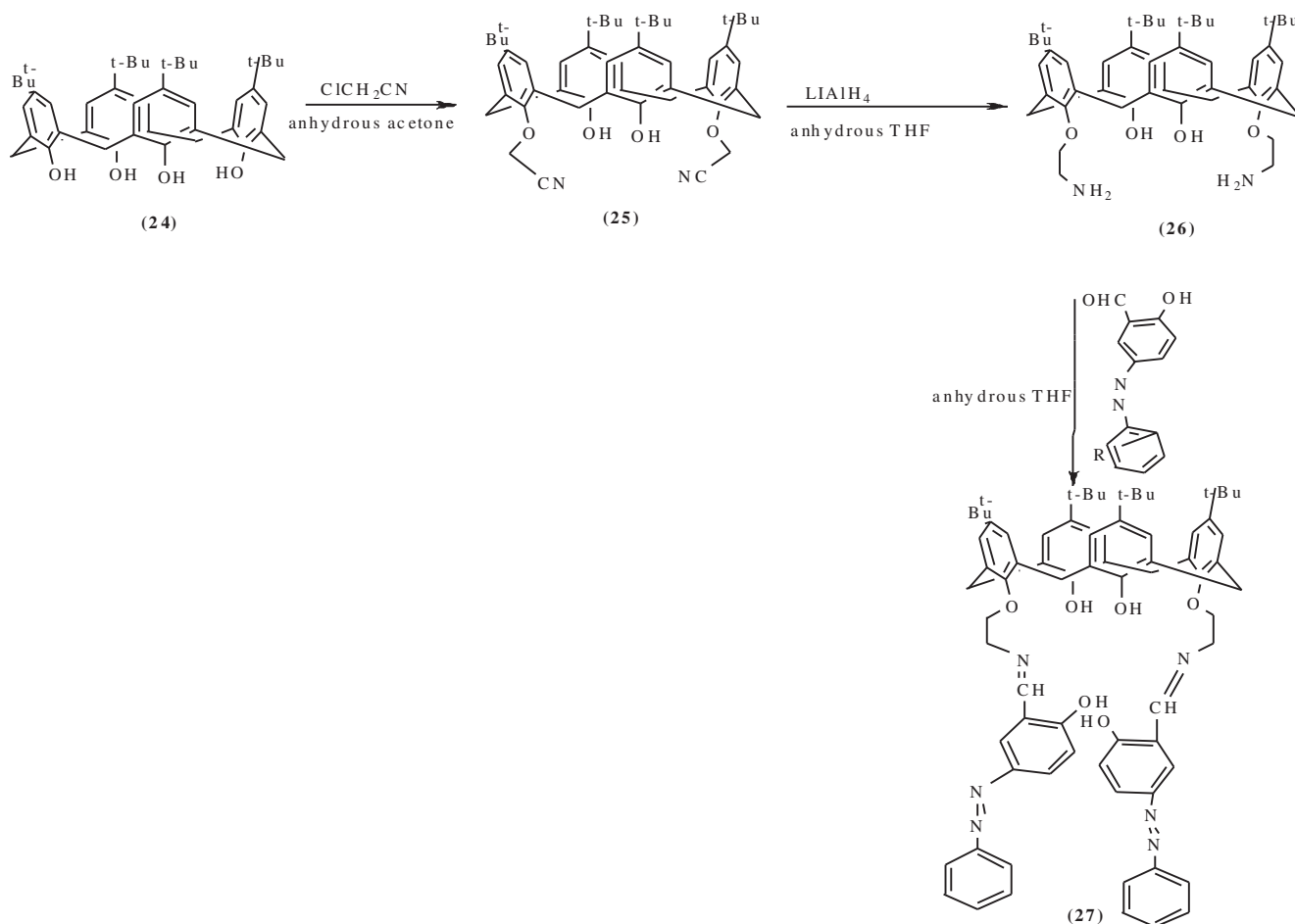
Scheme 6

should provide possibility for further modification and conformational organization of molecule<sup>35-37</sup>. Self-assembly of tetradentate ligand 5,5-bipyrimidine with *c*-methyl calix[4]resorcinarene is reported<sup>38,39</sup>. It modulates volume and periphery of cavity in a predictable fashion by changing size, flexibility and composition of spacer between pyrimidyl units.

Introduction of bulky substituents as *m*-methyl benzyl groups incorporate and remove protective groups in synthesis of calixarenes with three different substituents in molecule. In presence of sodium and potassium carbonates, reaction of calixarene with *p* and *m*-methyl benzyl bromides gives compounds (12) and (13) that affect composition, current conformations, and yield of products (Scheme 4)<sup>40-43</sup>. Calix[4]arene nucleoside base (19) and (20) receptors provide ion pairing complex<sup>44</sup> (Scheme 5). Novel bis (8-hydroxyquinoline)calix[4]arene (23) is a versatile building block of supramolecular chemistry (Scheme 6). This ligand is specially designed for photo physical applications in metalo-supramolecular chemistry<sup>45-47</sup>. Liu *et al*<sup>48</sup> synthesized bis(azo-phenol)calix[4]arenes (27), which

possesses multiple chromogenic donors (Scheme 7) and is useful for alkali metal ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ . Bis and tetrakis-tetrazole derivatives of calix[4]arene (32) have ability to bind cations of transition metals (Scheme 8). Result of structural investigation of macrocycle and its complex with palladium dichloride is also reported<sup>49-51</sup>.

Separation of amino acids is a key technology for downstream processing in bio-industrial complex. Tabaksi *et al*<sup>52</sup> carried out a reaction of *p*-tert-butylcalix[4]arene and *p-h*-calix[4]arene with (S)-(-)-1-phenylethylamine (37) (Scheme 9), which forms useful host molecule for quantitative extraction of  $\pm$ -amino acid methyl esters and  $\pm$ -phenylethylamines in a liquid-liquid extraction system. Specified applications of calixarenes can be possible by substitution of selected groups either on upper or lower rim. Several picoline binding groups at upper or lower rim of calix[*n*]arenes (39) (*n* = 4, 6, 8) have been synthesized for extraction of actinides (Scheme 10)<sup>53</sup>. Fluorescence chemosensors, calix[4]arene containing tetraamide derivative (43) (Scheme 11)<sup>54</sup>, exhibit high selectivity for  $\text{H}_2\text{PO}_4^-$  over a wide range of anions;



Scheme 7— (THF, Tetrahydrofuran)

selectivity for  $\text{H}_2\text{PO}_4^-$  is more than 2700-fold higher than for  $\text{F}^-$ .

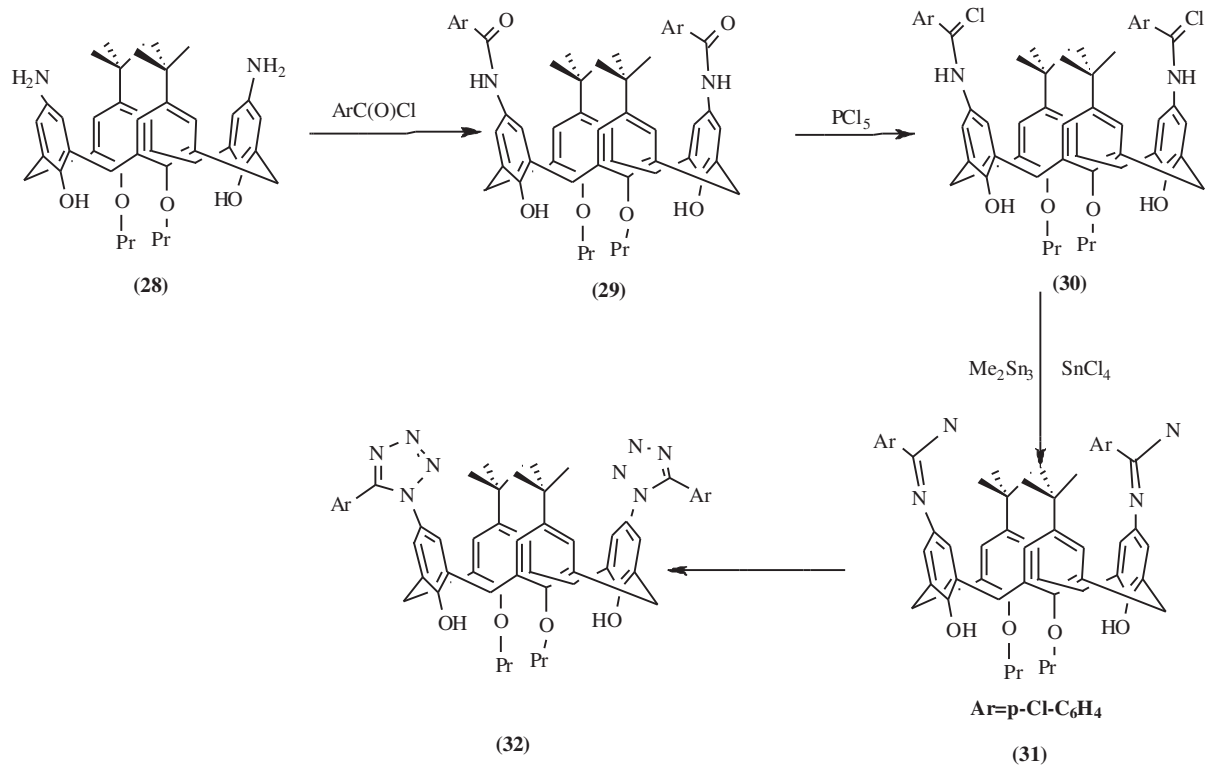
Fluorescence-labeled calix[4]arene substituted with peptides serve as a useful platform to produce artificial receptors using peptides and various types of other building blocks<sup>55</sup>. Upper rim, c-linked and cbz-protected cone calix[4]arene bis-l-alanyl derivative have been synthesized to prepare self-assembled nanotubes in solid state through a two-dimensional network of hydrogen bonds between amide chains of adjacent conformers<sup>56</sup>. A new type of inherently chiral calix[5]arene has been obtained from significant inherently chiral calix[5]arene derivatives using (R)-BINOL and their racemates (Scheme 12)<sup>57-59</sup>. Calix[8]quinone derivative (**48**) has also been synthesized (Scheme 13) through a protection-deprotection procedure<sup>60</sup>.

Two polyether moieties, two urea sites, and two bipyridine units containing novel multi-responsive host (**54**) has been synthesized and its ion binding sites are

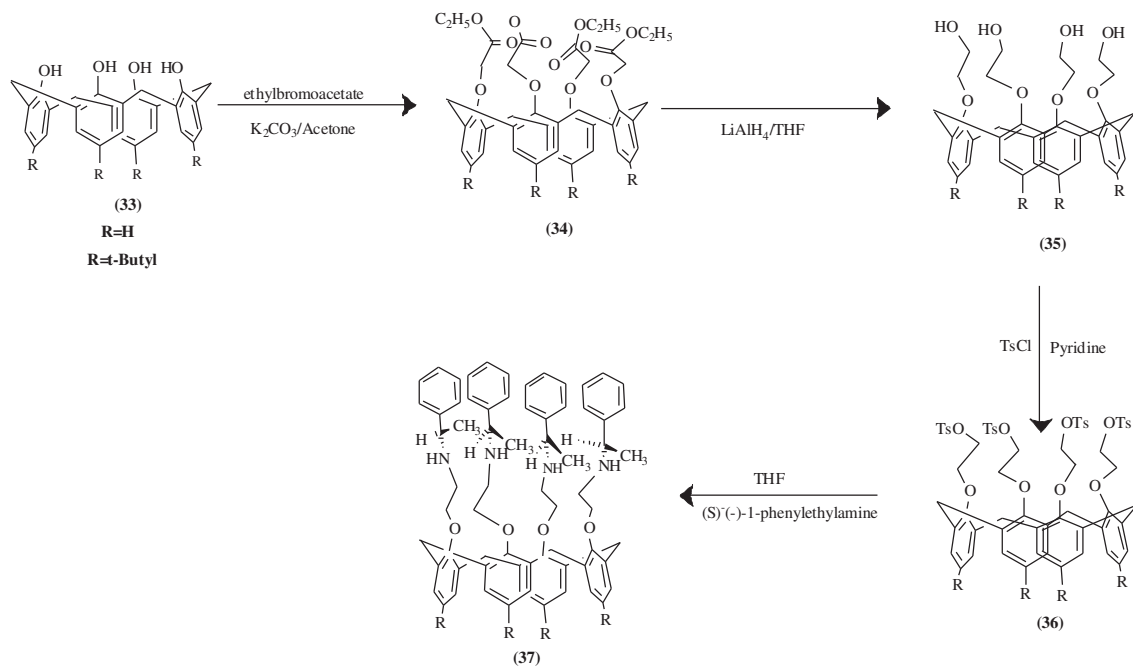
arranged on calix[4]arene skeleton<sup>61</sup>. Compound (**54**) (Scheme 14) recognizes  $\text{Na}^+$  and  $\text{Ag}^+$  simultaneously as well as quantitatively and captures an anionic guest. Ability of (**54**) to recognize anions including  $\text{CF}_3\text{SO}_3^-$  and  $\text{BF}_4^-$  remarkably increases using  $\text{Na}^+$  and  $\text{Ag}^+$ . Yang *et al*<sup>62</sup> and Tilki *et al*<sup>63</sup> synthesized oxo-calixarenes (**57**), (**58**) (Scheme 15), which have unique applications in molecular recognition studies and for enhancement of  $\text{Ag}^+$  and  $\text{Hg}^+$  ion selectivity by minimizing side arm effect. However, extraction results of bisazocalix[4]arenes show no selectivity toward heavy metal ions but effect of bis-structure on color and selectivity of bisazocalix[4]arenes have been discussed; dyeing behavior, performance on solvent and framework effect are assessed<sup>63-65</sup>.

## II. Bridged Calixarenes

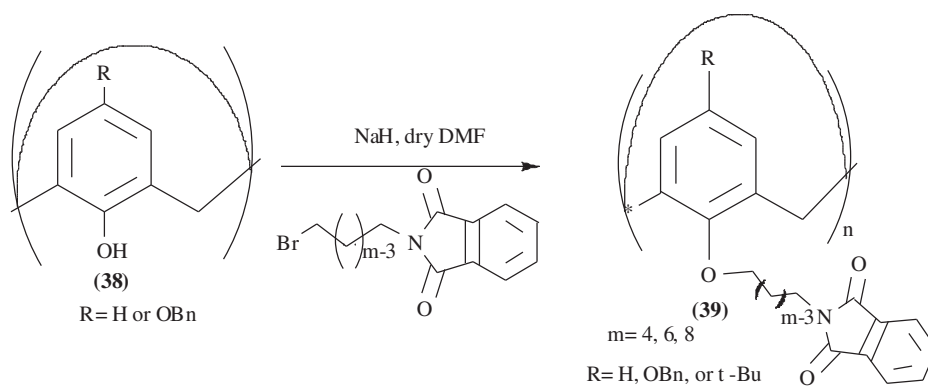
Remarkable regio-selectivities have been observed in bridging reactions of calixarenes. If a bridge contains functional groups like S, N, O, then it is easy to get



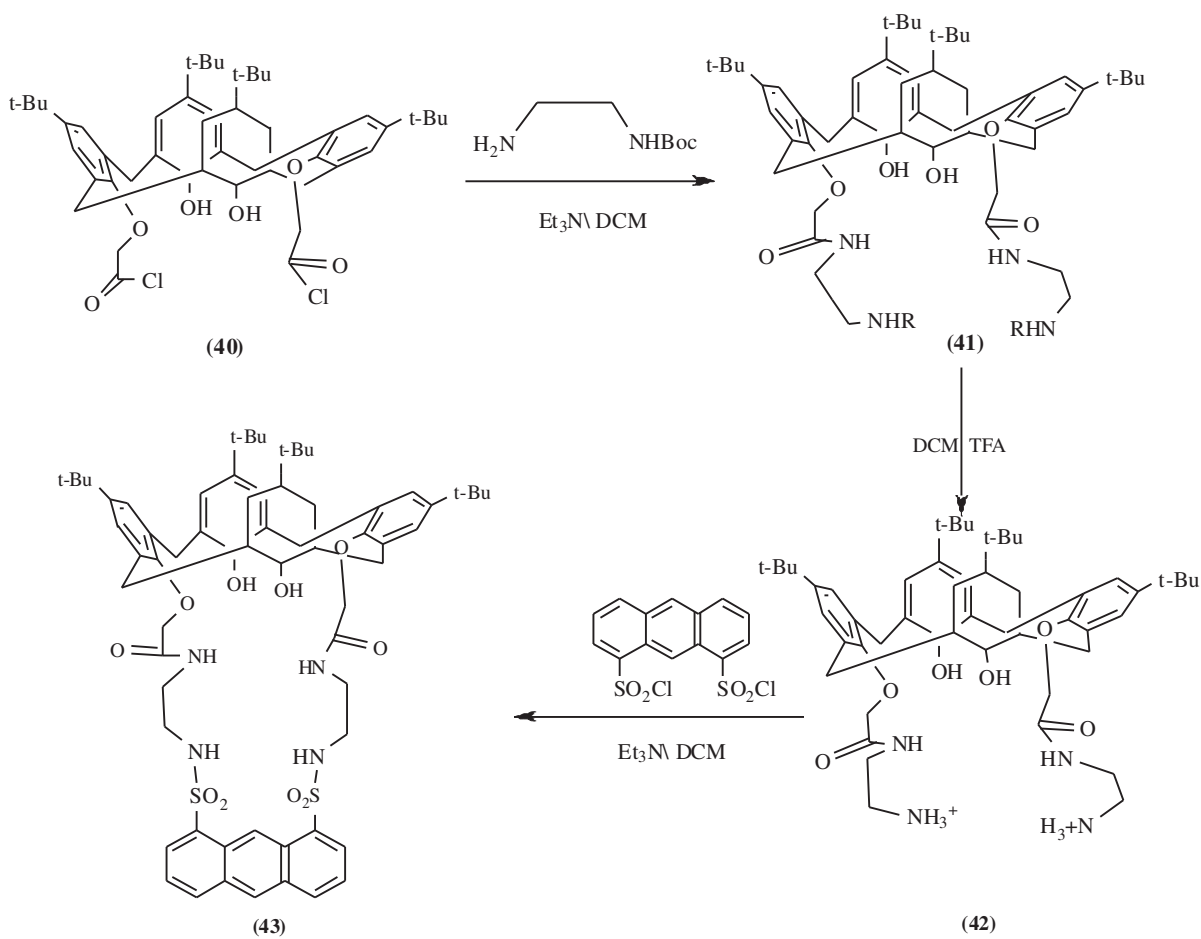
Scheme 8



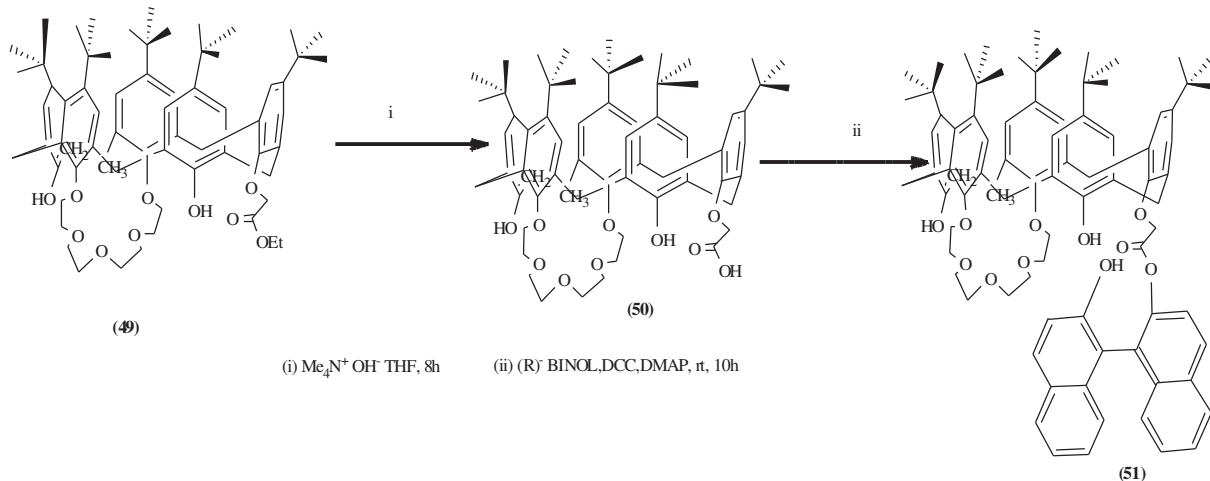
Scheme 9— (THF, Tetrahydrofuran)



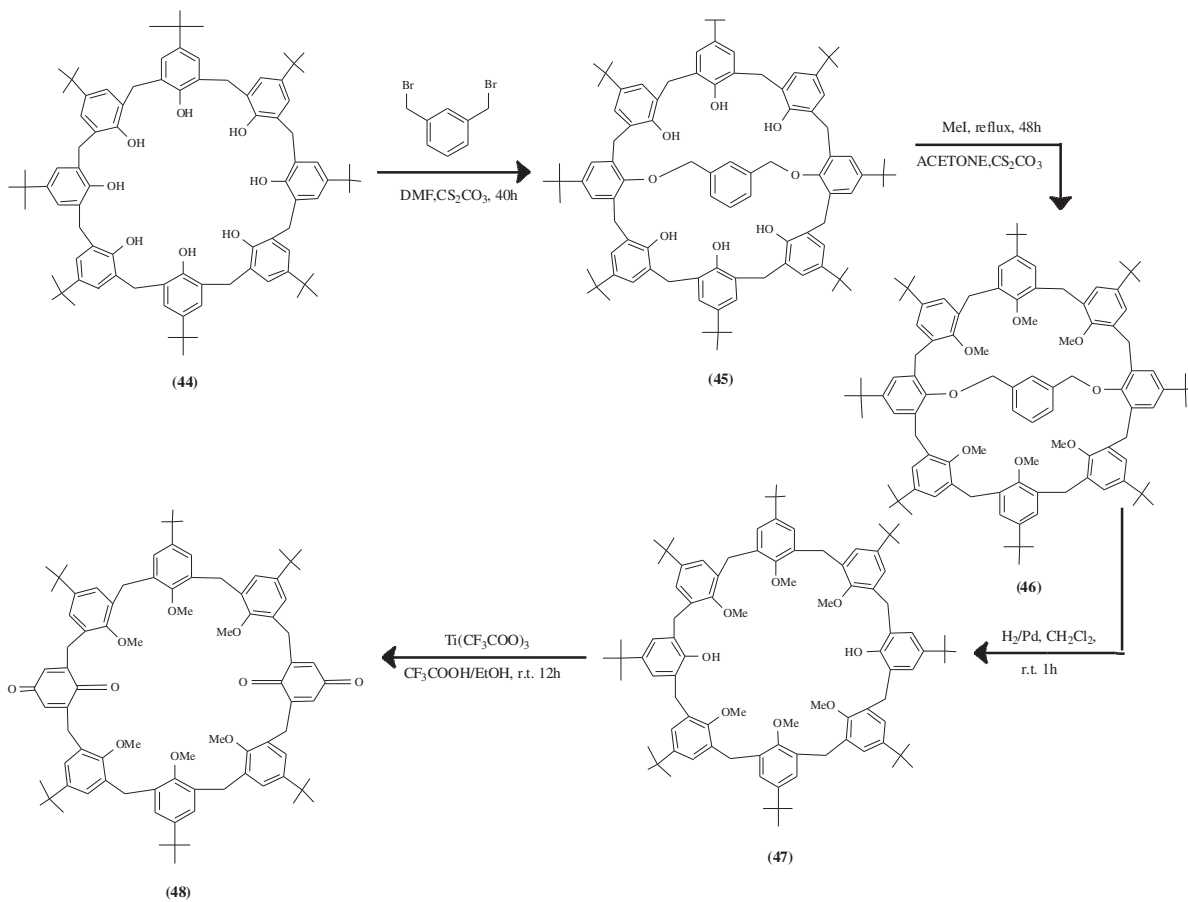
Scheme 10— (DMF, Dimethyl formamide)



Scheme 11— (DCM, Dichloromethane; TFA, Trifluoroacetic acid)

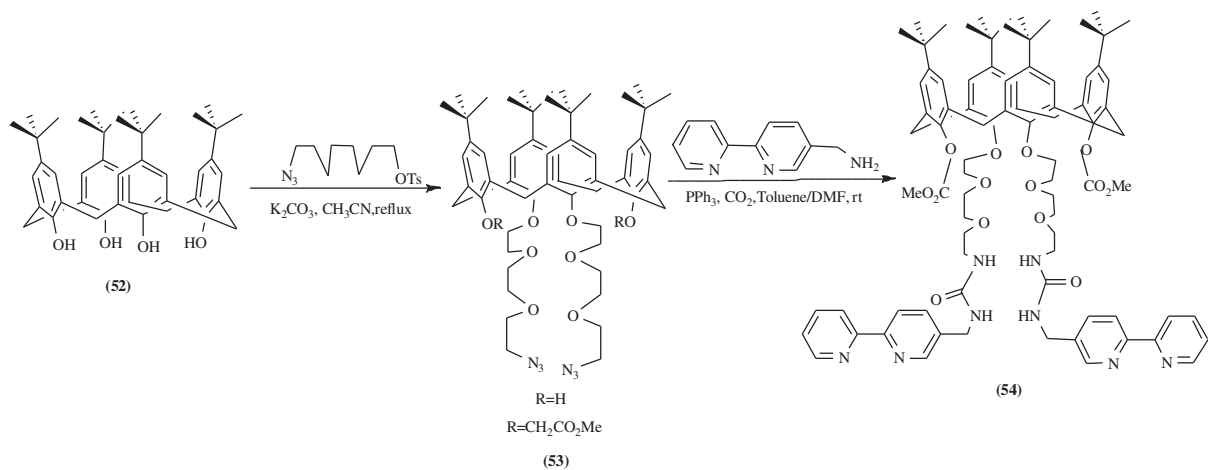


Scheme 12— (DCC, Dicyclohexyl carbodimide; DMAP, 4-Dimethylaminopyridine)

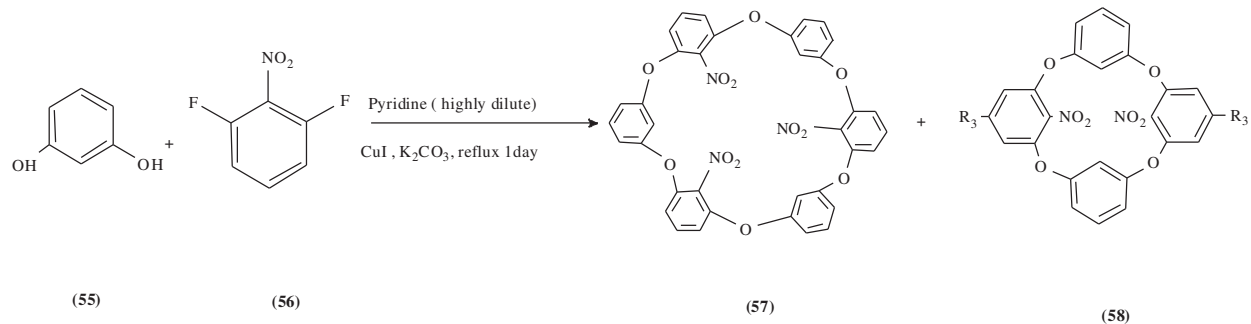


Scheme 13— (DMF, Dimethyl formamide; MeI, Methyl iodide)

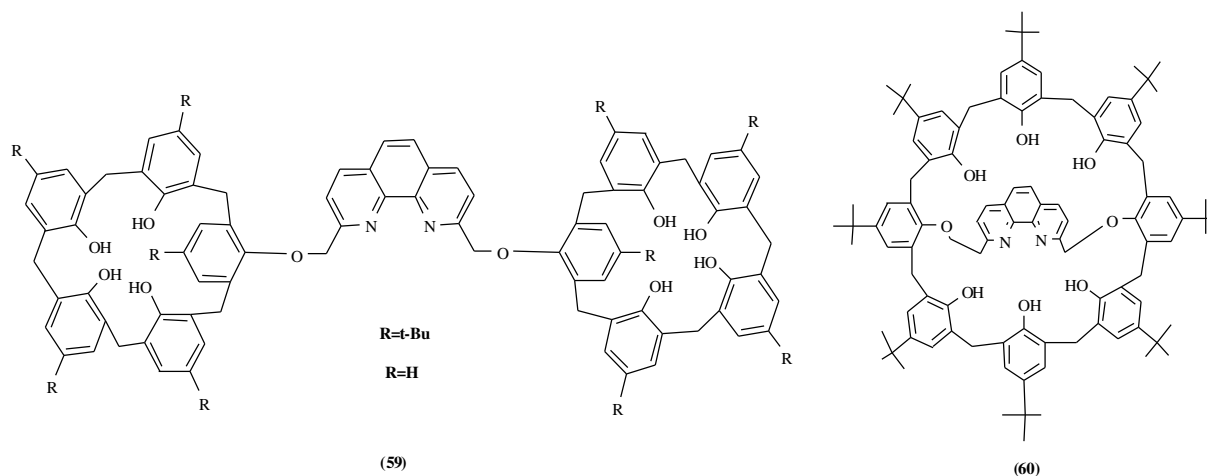




Scheme 14

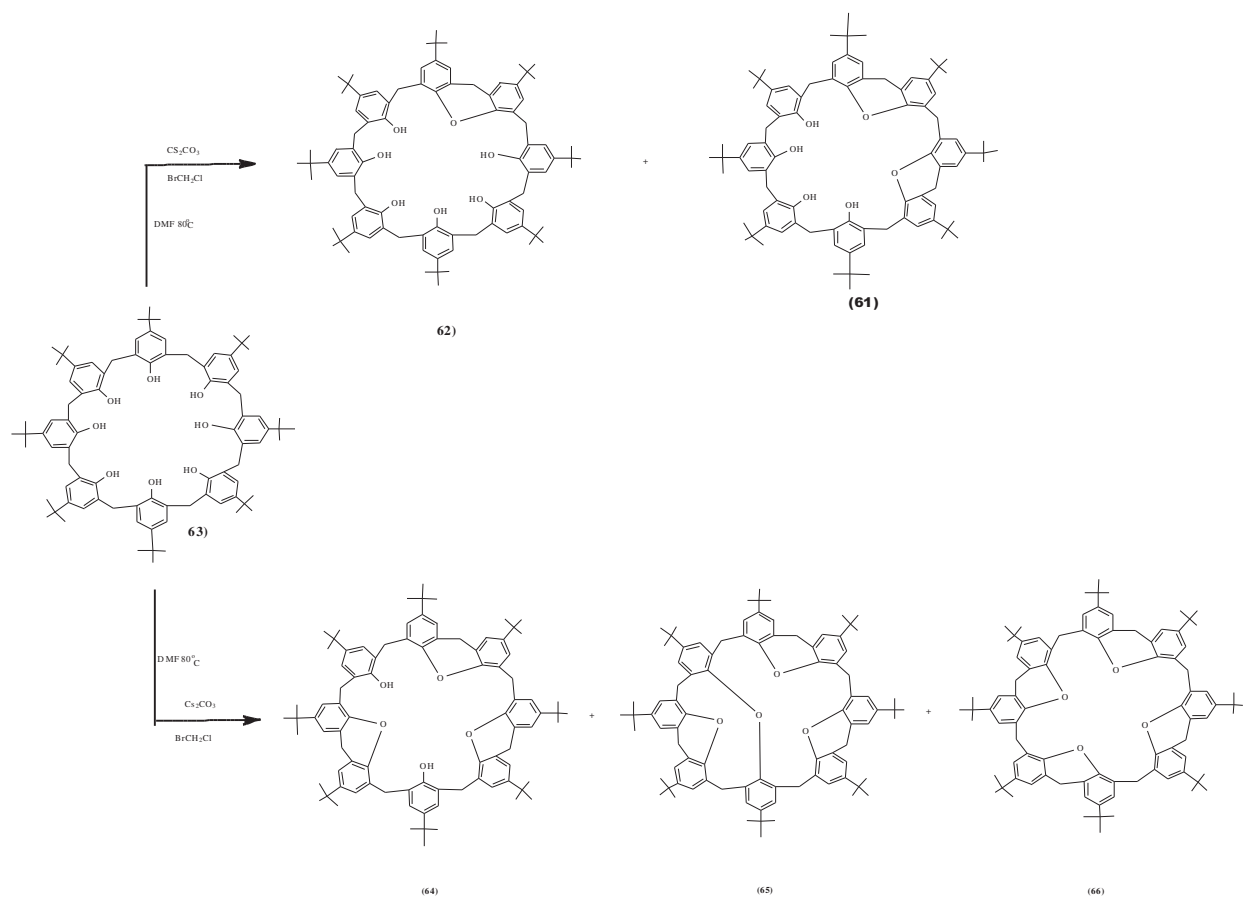


Scheme 15

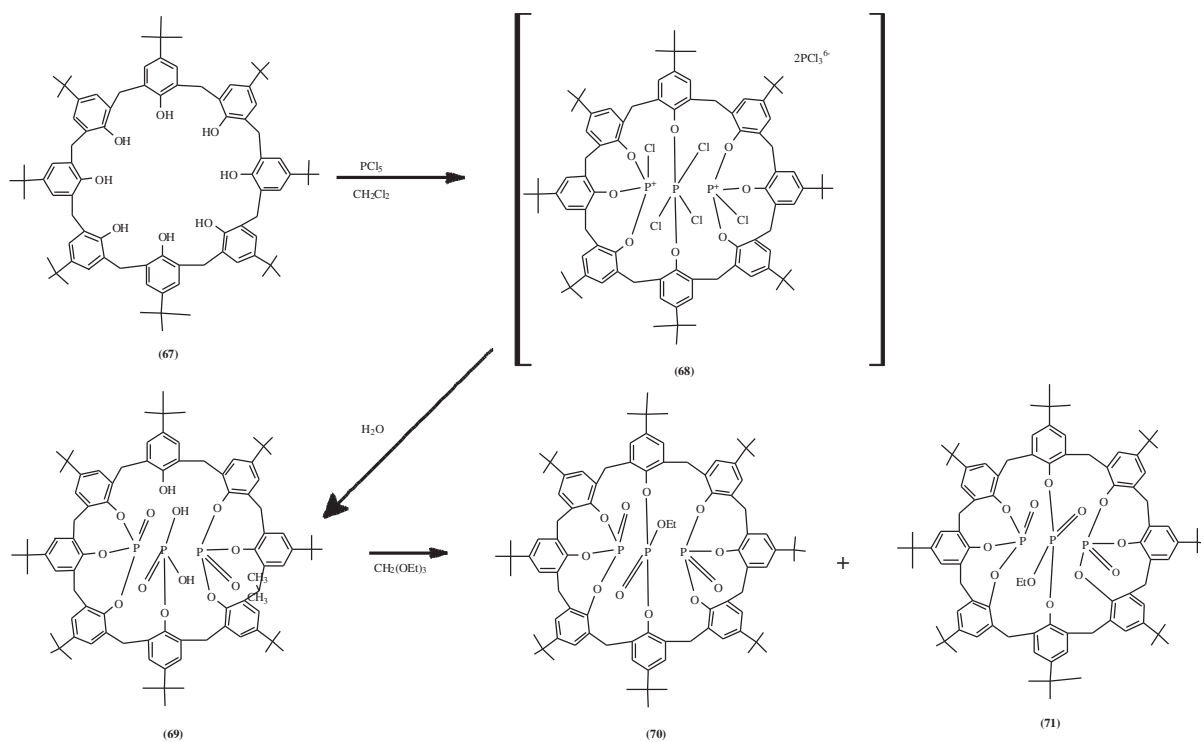


sterically shielded reagents. Size of macrocycles affects selectivity towards metal ions. Bigger cavity size calixarenes are more selective to heavy metal ions than other calixarenes. Calix[5]arene and calix[8]arene react with bis(bromomethyl)-substituted heterocyclic such as 1,10-phenanthroline to give [2+1] dicalixarenes (59) and

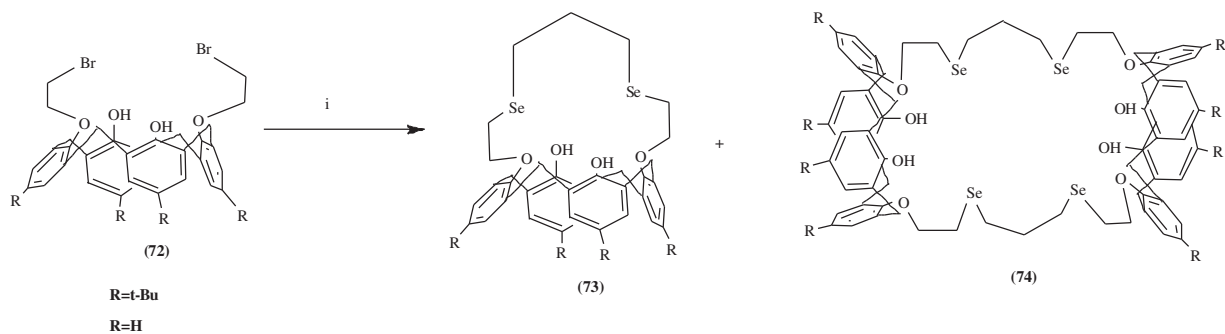
[1+1] condensation products (60). Resulting heterocycles are selective ligand for copper (I) ions and also show remarkable synthetic selectivity<sup>66-68</sup>. These compounds due to bulky group inside cavity could not be much elongated but elongation of calix[8]arenes could be possible by bridging such calixarenes with ethers,



Scheme: 16

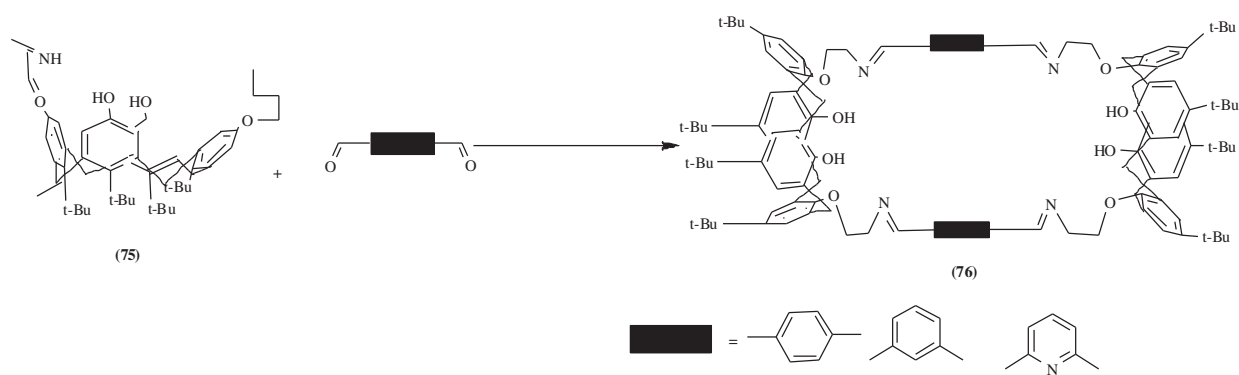


Scheme: 17

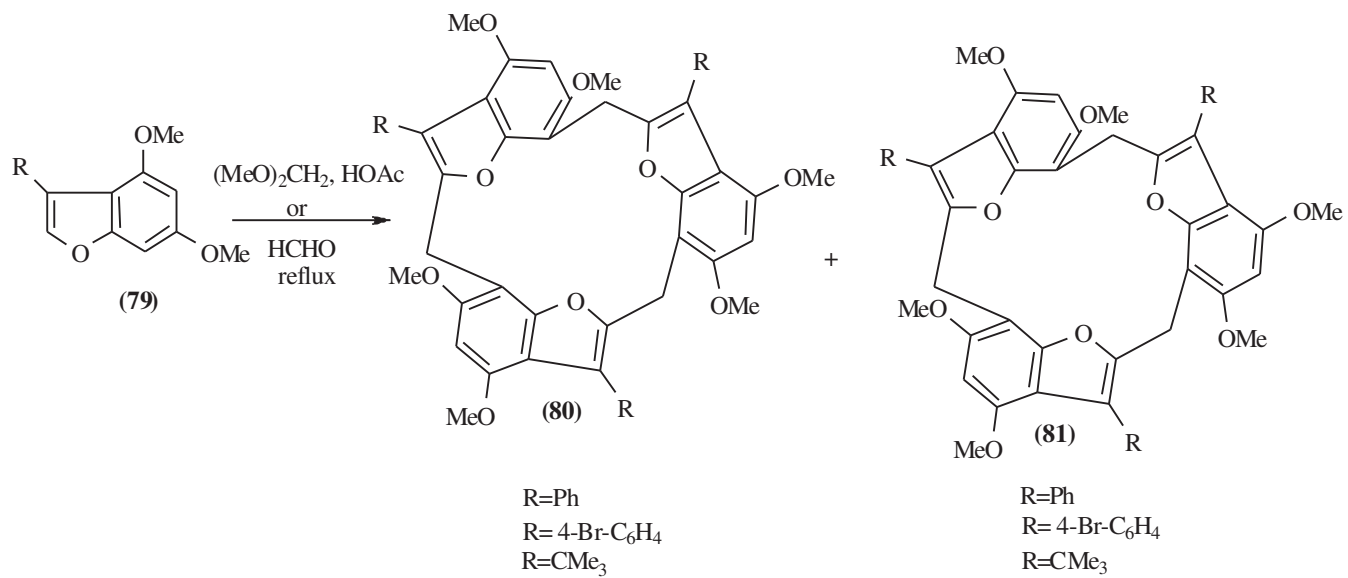


*i* = Disodium salts of 1, 3 propanediol, ethanol, THF, reflux 6h

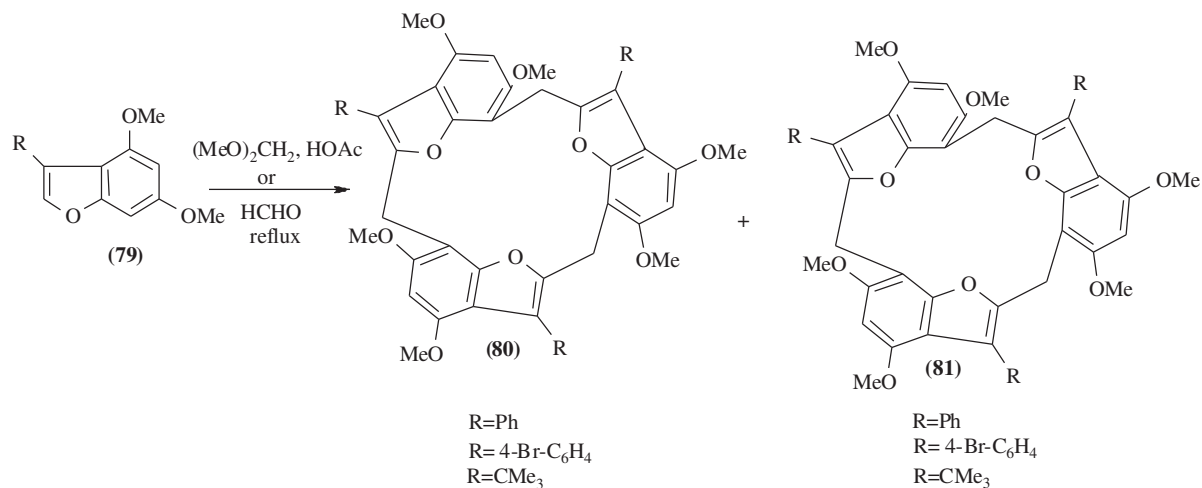
Scheme:18



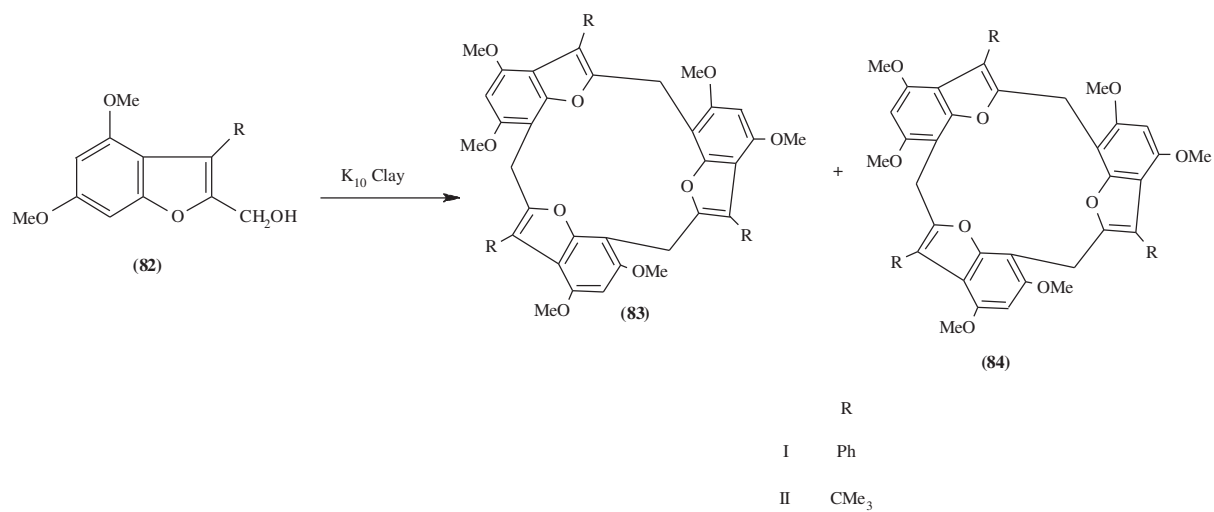
Scheme:19



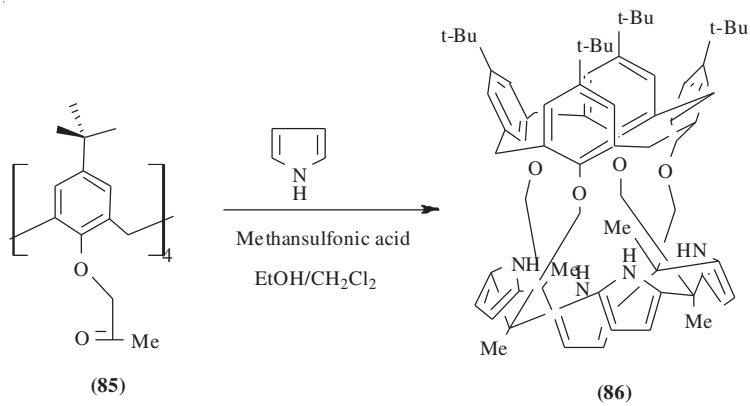
Scheme:20



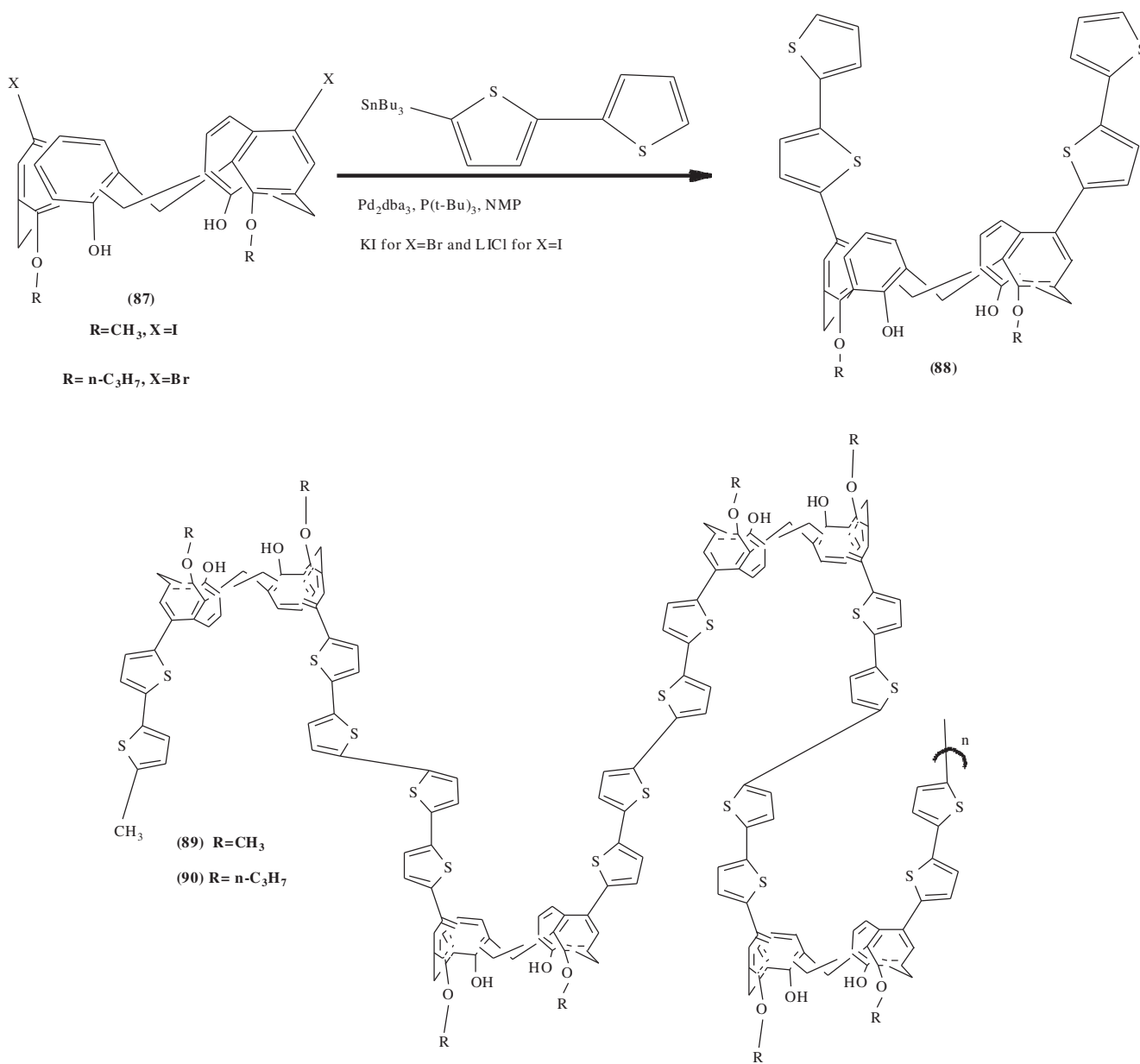
Scheme 21



Scheme 22



Scheme 23

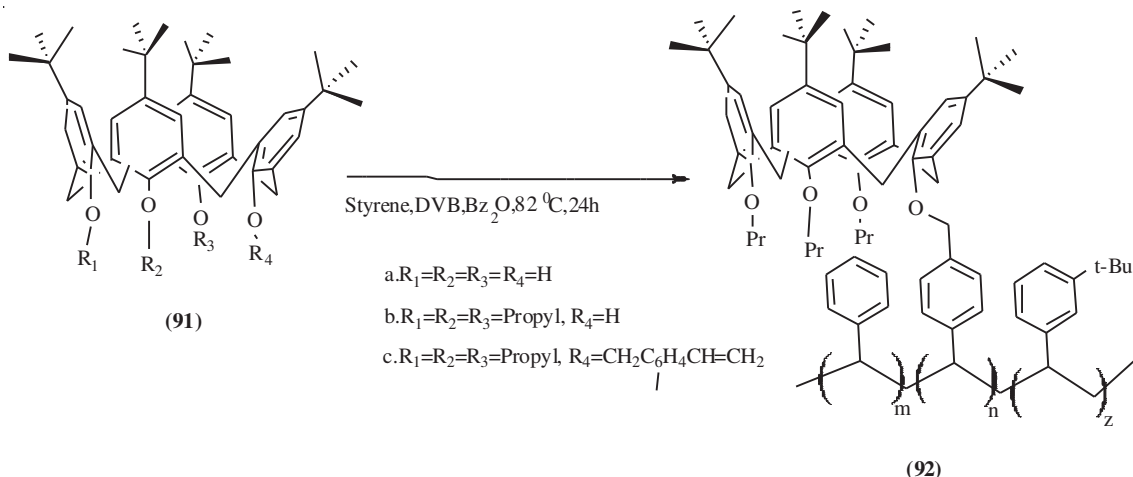


Scheme 24— (NMP, N-methylpyrrolidine)

phosphoryls and aza groups. Depending on length and nature of bridges, they possess better encapsulating properties toward alkali metal ions, rare earths and heavy metal ions. Such calixarenes have been prepared from *p*-*tert*-butylcalix[8]arenes by using two step alkylation procedure<sup>69-74</sup>.

Mono to tetra-dioxamethylene bridged calix[8]arene derivatives<sup>75</sup> [(64), (65), (66)] have been synthesized (Scheme 16). *p*-*tert*-Butylcalix[8]arene (67) with 5 equivalent of  $\text{PCl}_5$  in  $\text{CH}_2\text{Cl}_2$  gives compound (68) whose

subsequent hydrolysis gives compound (69) (Scheme 17)<sup>76</sup>. Series of tweezer-like calix[4]arene derivatives containing S, N and O atoms exhibit a good  $\text{Ag}^+$  selectivity against interfering ions. Zeng *et al* synthesized two calix[4](diseleno)crown ethers (74) from compound (72) and (73) (Scheme 18)<sup>77-79</sup>. Selenium schiff base<sup>81</sup> and hydroxamic acid<sup>80</sup> containing bis-calixarenes are versatile compounds in calixarene chemistry, and show silver-ion selectivity by two-phase extraction and transportation. Bis-calix[4]arene (76) forms silver-



Scheme 25

selective PVC membrane due to electrostatic interaction between metal ion and aza crown cavity composed of oxygen and nitrogen atoms as donors (Scheme 19)<sup>81</sup>.

### III. Hetero Calixarenes

Heterocalixarenes or calixhetarenes are built from heterocyclic moieties. Another class is heterocalixarenes (aza, oxa and thia-calixarenes), in which bridges between phenol units contain heteroatoms (N, O or S). This review reports hetero-calixarenes built from benzofuran moieties and from other heterocycles. Formation of cone conformers of calix[3]indoles has been discussed<sup>82</sup>. An isomeric series has also been obtained with combination of an indole with bis (hydroxymethyl)-2, 2'-di-indolylmethane (Scheme 20)<sup>83</sup>.

3-Substituted 4, 6-dimethoxyindoles possess two reactive sites for electrophilic substitution, and can react with aryl aldehydes in presence of phosphoryl chloride to give calix[3]indoles (**77**). As a part of expanding range of calixarenes from other activated heterocycles, calix [3]benzofurans have been prepared from 3-substituted 4,6-dimethoxybenzofurans (**79**) (Scheme 21) and 2-7-hydroxymethylbenzofurans (**82**) (Scheme 22) with formaldehyde and aryl- aldehydes in presence of acetic acid and phosphoryl chloride<sup>84-85</sup>.

Like indoles and furans, pyridines and pyrroles can play a major role in heterocyclic calixarene chemistry. Calix(4)pyrroles are effective and selective receptors for anions and neutral guest species and find applications as coordination complexes, catalytic materials, nano-sponges, molecular machines, nano entities and semi

conducting materials<sup>86</sup>. Bipyridyl group containing calixarenes are useful for binding various metal ions. Bipyridyl containing calixarenes<sup>87</sup> are extensively used to form complexes with various metal ions<sup>88-93</sup>. Two new meso-indanyl-substituted calix[4]pyrrole receptors have been synthesized<sup>94</sup> using MCM-41. For expansion of calixarenes, pseudo-dimer (**86**) of calix[4]arene and calix[4]pyrroles (Scheme 23) have been synthesized as a good anion receptors<sup>95</sup>.

### IV. Polymeric Calixarenes

Polymer supported calixarenes have variety of applications. Polyethyleneimine supported calix[6]arenes can extract uranium from seawater<sup>96</sup>, polyacryloyl chloride and chloromethyl polystyrene supported calix[4]arenes have been used to extract iron<sup>97</sup> and lead<sup>98</sup>. Methacrylate<sup>99</sup> acrylonitrile and styrene<sup>100</sup> derived calix[4]arenes have been polymerized to make calixarene oligomers. Proton-doped segmented polymers, Poly(**89**) and Poly(**90**), are based upon a calix[4]arene scaffold and increase conductivity of calixarene polymers (Scheme 24)<sup>101</sup>. These compounds are attractive candidates for design of sensing and actuating materials<sup>102</sup>.

Utility of calix[4]arenes for phase transfer reactions, adsorbents or for fabricating membranes and sensors, copolymer and homopolymer containing calix[4]arene moieties on polymer backbone were successfully synthesized from monomer and styrene<sup>103</sup>. Both polymers show good selectivity towards Hg<sup>+</sup> ion. In a related study<sup>104</sup>, radical polymerization of styrene has been carried out in presence of a novel calix[4]arene

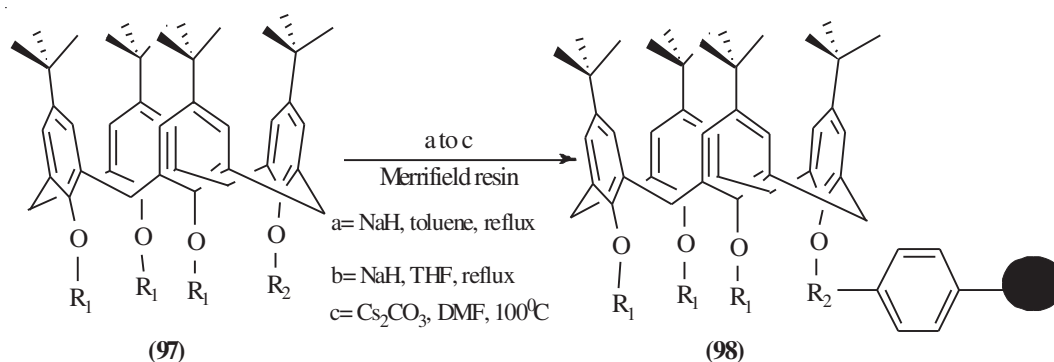
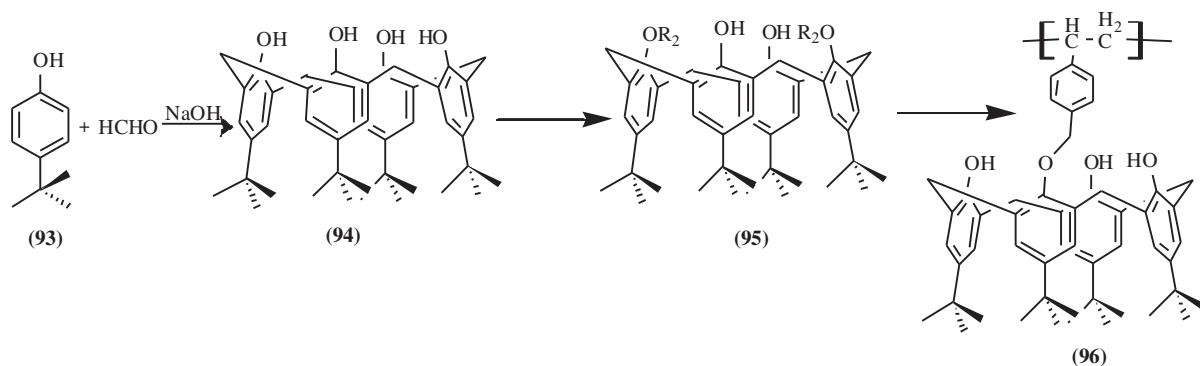


Table 3—Substitution groups to prepare polymerizable calixarene derivatives

	R <sub>1</sub>	R <sub>2</sub>
95a	CH <sub>2</sub> CN	CH <sub>2</sub> CN
96a	CH <sub>2</sub> CN	CH <sub>2</sub> CN
95b	H	CNC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>
96b	CNC <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	CNC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>
95c	H	CNC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>
96c	CNC <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	CNC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>

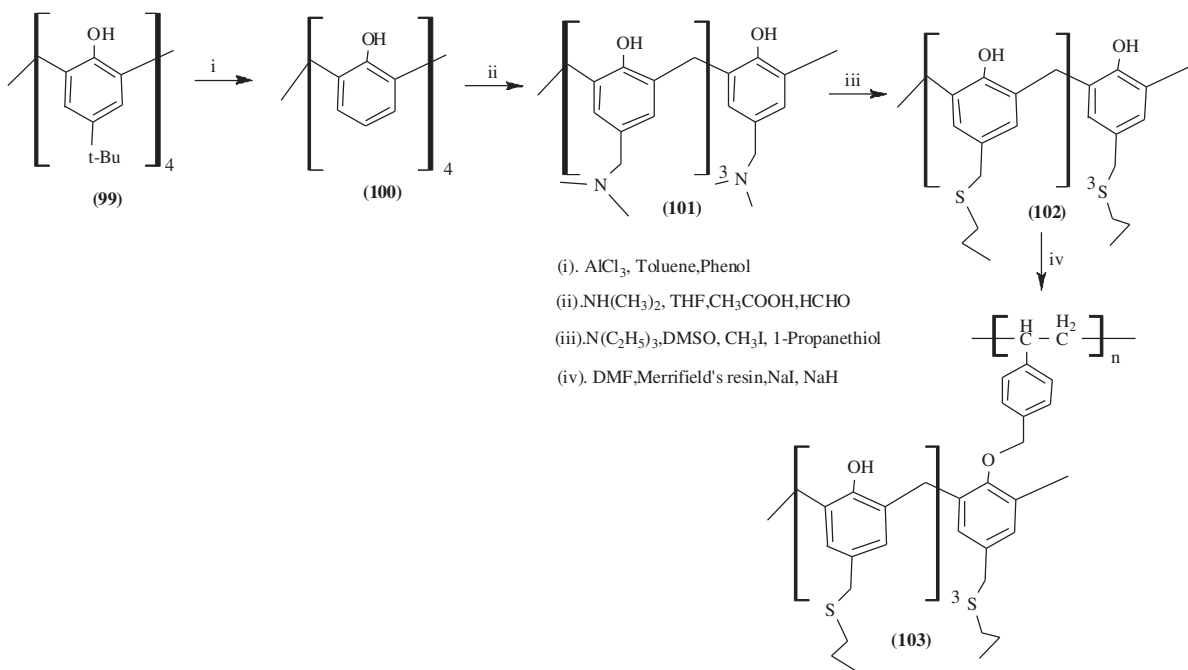
Table 4—Substitution groups for Merrifield resin containing calixarene

R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>
H	CH <sub>2</sub>	H	H
CH <sub>2</sub> CO <sub>2</sub> Et	CH <sub>2</sub>	Propyl	H
CH <sub>2</sub> CO <sub>2</sub> H	CH <sub>2</sub>	CH <sub>2</sub> CO <sub>2</sub> Et	CH <sub>2</sub> CO <sub>2</sub> Et
CH <sub>2</sub> CO <sub>2</sub> Na	CH <sub>2</sub>	CH <sub>2</sub> CO <sub>2</sub> H	CH <sub>2</sub> CO <sub>2</sub> H
CH <sub>2</sub> CO <sub>2</sub> H	C(O)OCH <sub>2</sub>	Propyl	H

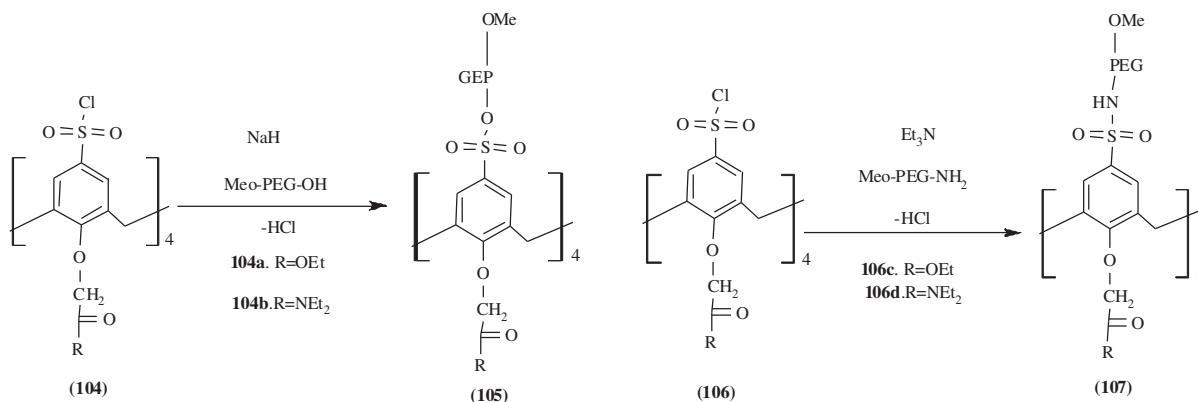
derivative bearing two distal benzyl-vinyl groups in lower rim. Such terpolymer (**92**) exhibits good thermal stability and good yield (Scheme 25)<sup>105</sup>. Nitrile functionality at lower rim of calix[4]arenes, synthesized via nucleophilic substitution reactions, have an effective binding character for particular set of cations and can be useful for laboratory, clinical, environmental, and industrial process analysis<sup>106</sup>.

A novel benzyl-terminated dendron based sol-gel coating has been developed for capillary micro extraction

(CME). Characteristic branched design of dendron makes them structurally superior extraction media compared to traditional linear polymeric counterparts<sup>107</sup>. Other higher molecular weight moieties that are also useful for many specialized applications like new polymer-supported calix[6]arene hydroxamic acid have been synthesized<sup>108</sup>. Resin was used for chromatographic separation of U (VI), Th (IV) and Ce (IV). Versatile starting materials for synthesis of polymerizable calixarene derivatives (**95**) have been



Scheme 28 — (DMSO, Dimethylsulfoxide; DMF, Dimethyl formamide)



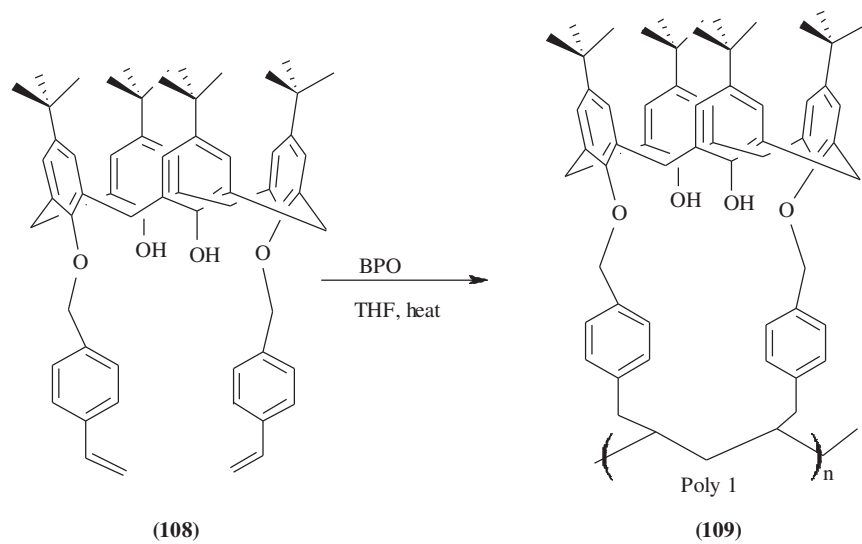
Scheme 29— (PEG, Polyethyleneglycol)

synthesized for extraction of cations as well as for anions (Table 3, Scheme 26). Depending on oxidative stability, it is observed that ionophore (**95a**) is selective for  $\text{Hg}^{2+}$ , whereas ionophores [(**95b**) and (**95c**)] are selective for both  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ <sup>109</sup>. Immobilized calix[4]arene (**98**) containing merrifield resin is a very useful polymeric scaffold for synthesis of various lower rim derivatives (Table 4, Scheme 27) demonstrated with preparation of triacid<sup>110</sup>.

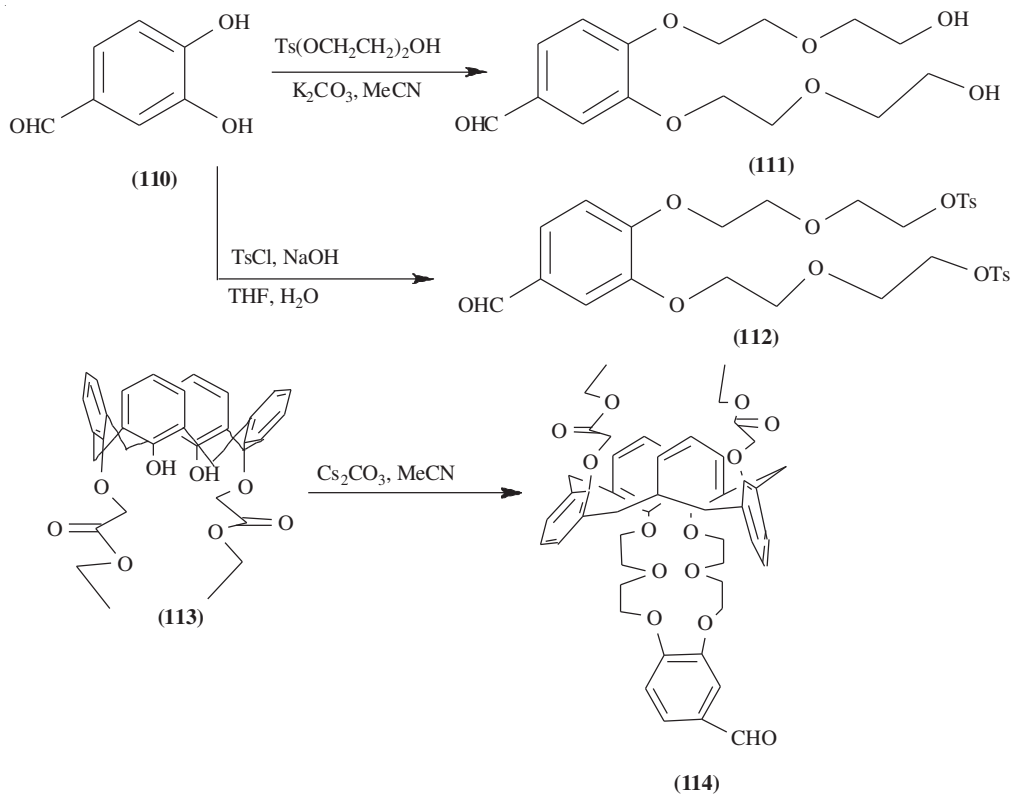
Thio-ether functionalized calix[4]arene based polymeric resin compounds (**102**), which are versatile starting materials for synthesis of polymerizable calixarene derivatives<sup>111</sup>, are suitable for extraction of

toxic heavy metal cations as well as for dichromate anions (Scheme 28). In case of more than one functionalization of polymeric groups on calix[4]arenes (**107**), both ligating and methoxy poly(ethylene glycol) groups are introduced for formation of sulfonyl ester groups on wide rim (Scheme 29), schiff base derivatives on narrow rim, and thioether groups on both wide and narrow rims<sup>112</sup>, which are non-toxic, non-flammable, biphasic and hydrophilic. It can also be potentially useful for simultaneous extraction of both metals and organics that are commonly present in soil and water. Cyclo-polymerizability of calix[4]arene monomer is also a favorable interaction that occurs between two vinyl benzyl

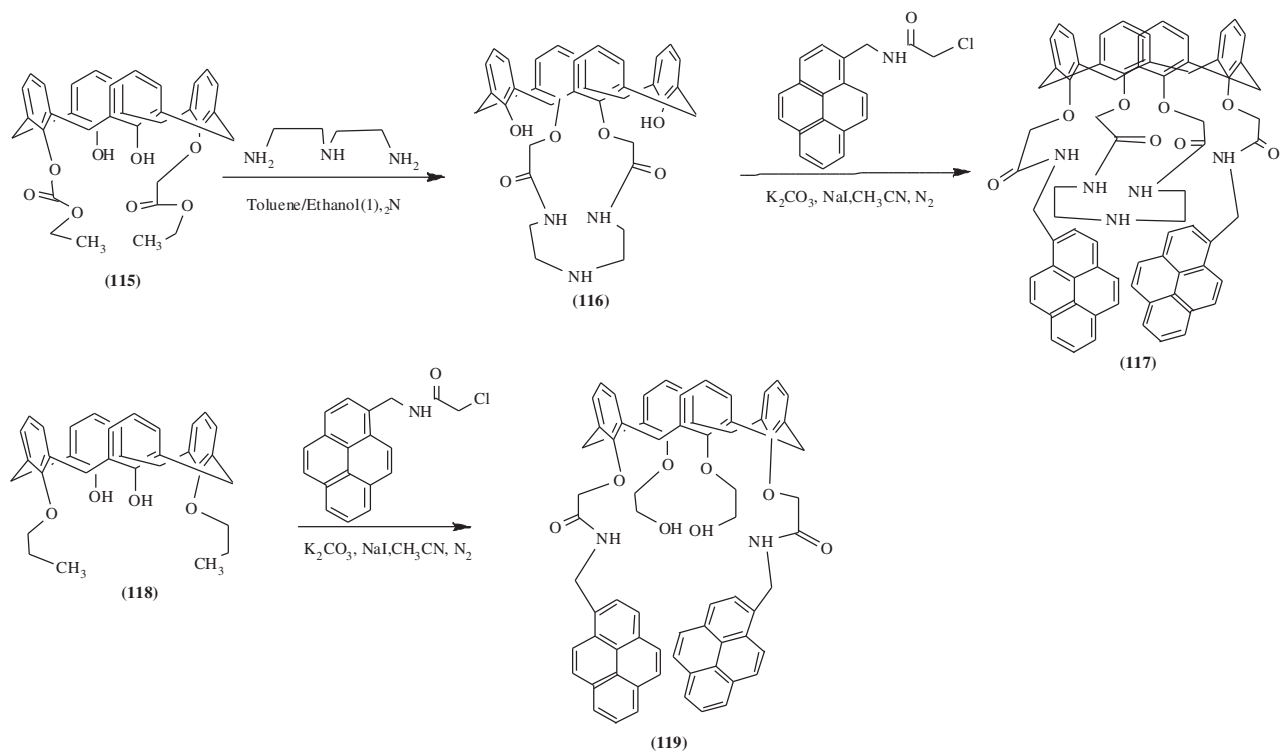




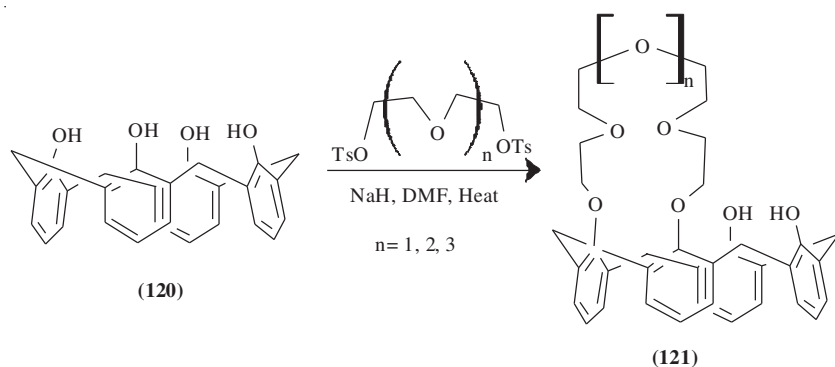
Scheme 30— (BPO, Benzoyl peroxide)



Scheme 31



Scheme 32



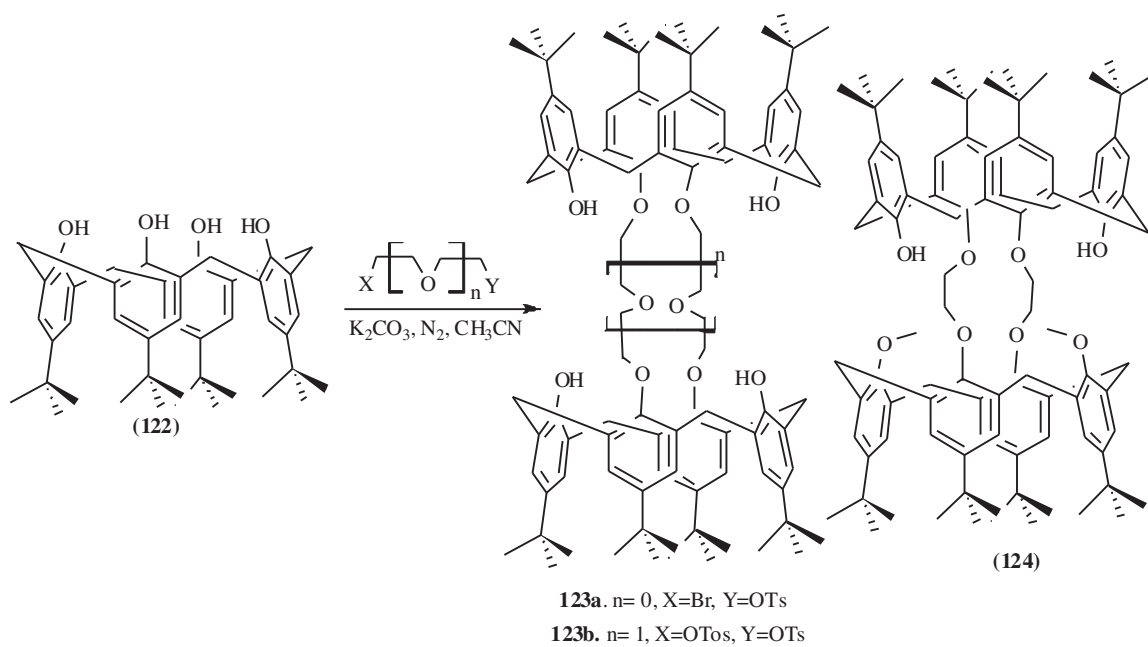
Scheme 33— (DMF, Dimethyl formamide)

units due to constrained conformation generated by calixarene moiety, which in turn drive intermolecular cyclization. Poly1 (**109**) represents a new type of highly organized macromolecule useful for widespread applications associated with single-handed helical polymers<sup>113</sup> (Scheme 30).

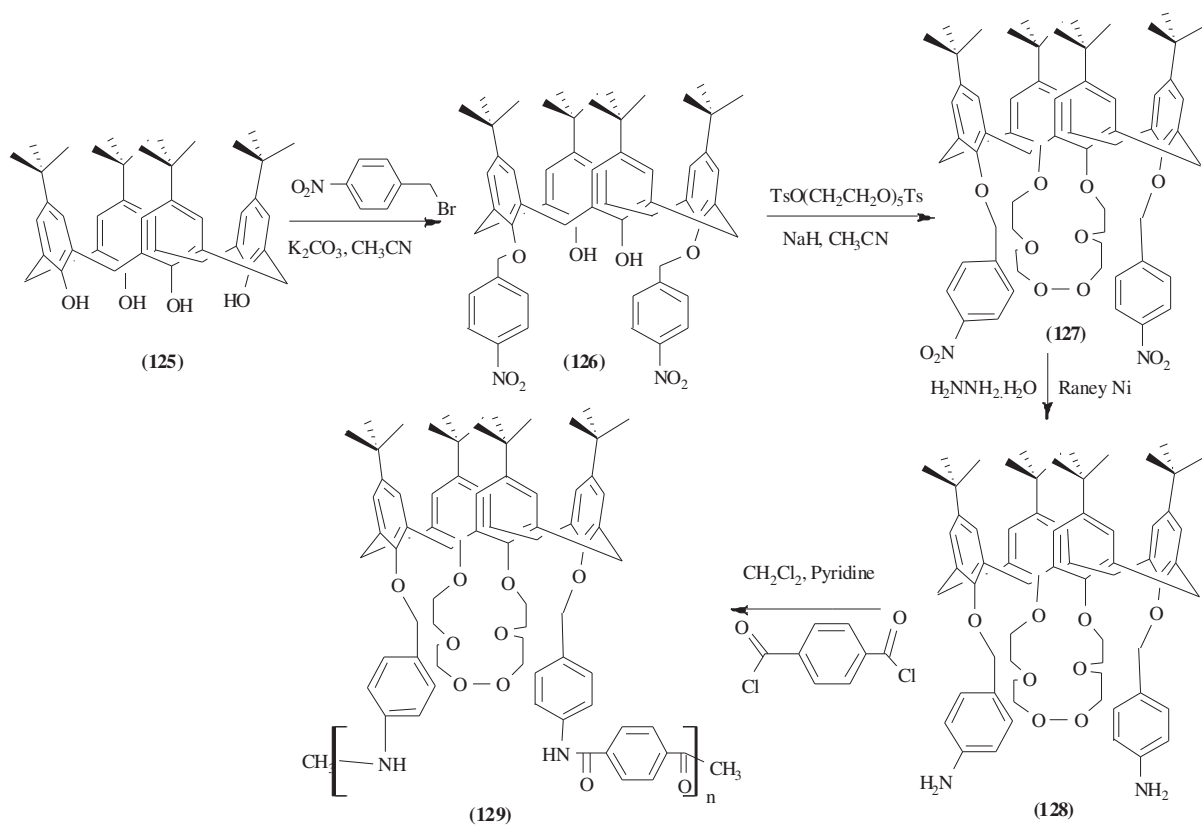
### V. Crown And Fullerene Bearing Calixarenes

Calix[*n*]crowns are macrocycles composed of subunits of a calix[*n*]arene and crown ether joined *via* phenolic oxygen of calix component. Chen *et al*<sup>114</sup>

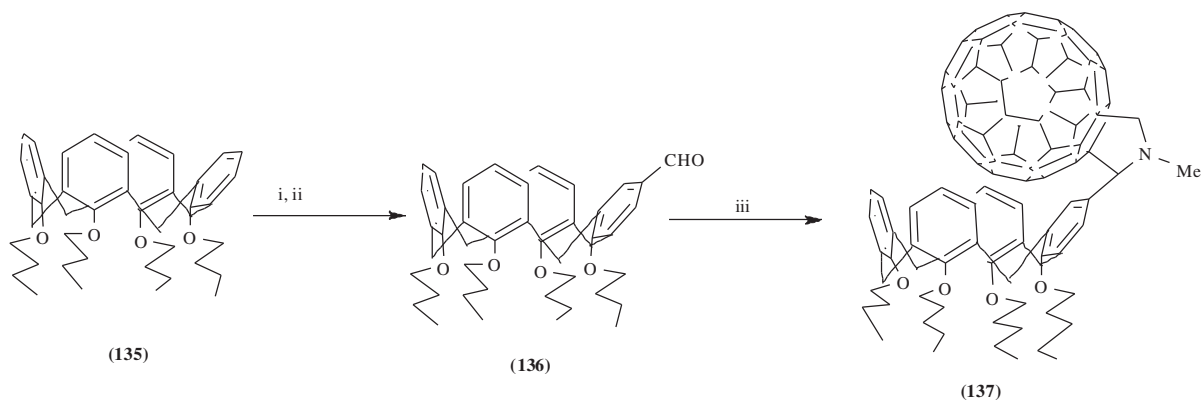
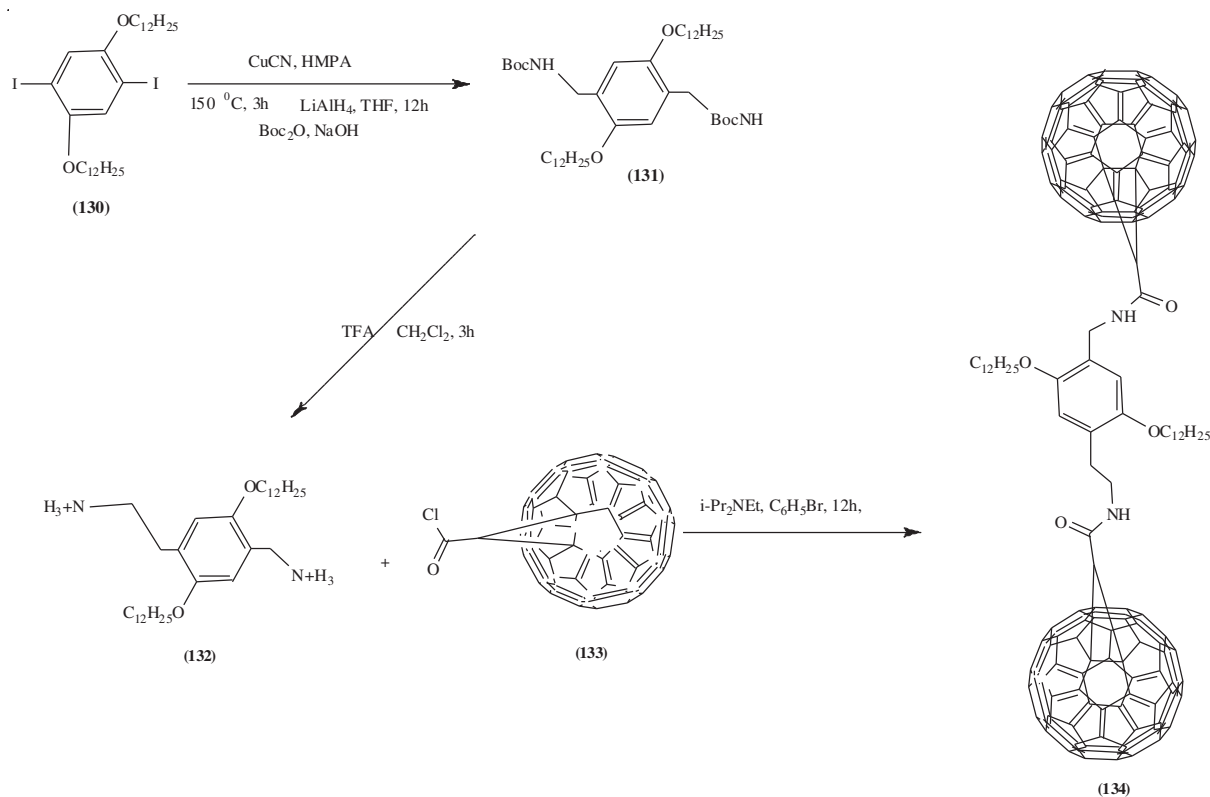
synthesized dendrimers from an excellent ionophore 1,3 calix[4]crown that gives multi metal recognition central dendrimer (Scheme 31). Moreover, 2<sup>nd</sup> generation dendrimers have also been synthesized from 1,3 calix[4]benzocrown-6 as repeat units<sup>115</sup>. 1,3-Calix[4]arene bis-crown-6 containing six oxygen donor atoms are also potential extractant for selective removal of cesium cation from radioactive liquid nuclear waste<sup>116</sup>. To increase complexation ability and for better analytical applications, one has to substitute calix[*n*]crown with different hetero or bulky groups. Lee *et al*<sup>117</sup> prepared a



Scheme 34



Scheme 35



new fluorogenic cone calix[4]triazacrown-5 (**117**) bearing two pyrene amide groups and its structural analogues (**119**) (Scheme 32). Such fluorescent chemosensors are effective useful tool to analyze and clarify roles of charged chemical species in living system as well as to measure amount of metal ions from sources contaminated<sup>118,119</sup>.

To perform selective extraction of metals, preparation of a series of *p*-sulfonated 1,2,3,4-calix[4]arene-biscrowns (**121**) are reported<sup>120</sup> for Cs<sup>+</sup>/Na<sup>+</sup> selectivity (Scheme 33). Kerdpaiboon *et al*<sup>121</sup> synthesized three new calix[4]quinines [(**123a**)<sup>122</sup>, (**123b**)<sup>123</sup>, (**124**)<sup>124</sup>] from corresponding double calix[4]arenes and complexation studies were carried

out with alkali metal ions such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> (Scheme 34). Substitution of oligomers increases liquid liquid extraction ability for calix[4]crown-6 monomers [(128) and (129)] (Scheme 35)<sup>125</sup> while aza crown based two new calix[4]arene ionophores increases complexation ability with metal ions<sup>126</sup>. Apart from crown ethers, covalent assemblies of fullerene and calixarenes have also been investigated to study polymeric nature appeared in solid phase<sup>127,128</sup> using calix[5]arenes (Scheme 36)<sup>129</sup>. Intramolecular association, self complexation and de-complexation properties using tetra-*o*-alkylated cone calix[4]arene (137) skeleton have also been examined (Scheme 37)<sup>130,131</sup>.

### Conclusions

Calixarenes are easy to synthesize and modify, and can form polymer, dendritic network particles and liquid crystalline systems. Development of new catalysts, non-linear optics and removal of heavy metal ions and/or uranyl ion is on.

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