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# Synthesis of calix[4]arene-based polycarboxylate ligands and their chemical immobilization onto controlled-pore glass

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## ABSTRACT

Three new calix[4]arene-based carboxylate ligands with an appended allyl function have been synthesized, chemically immobilized onto a controlled-pore glass (CPG), and the extracting ability of selected materials towards Sr<sup>2+</sup> in solid-liquid extraction was examined. The calixarenes were characterized by elemental analysis, mass spectrometry, IR and NMR spectroscopy, and where appropriate by X-ray crystallography. Four functionalized CPGs were prepared by radical thiol addition of the corresponding 5-allylcalix[4]arenes to  $\gamma$ -mercaptopropyl-modified CPG. Analysis by <sup>13</sup>C and <sup>29</sup>Si cross polarization/magic angle spinning (CP/MAS) NMR spectroscopy clearly showed the covalent fixation of the calix[4]arenes to CPG. The calix[4]arene phases were found to be stable up to 200 °C by simultaneous thermal analysis (STA). The extraction performance of the modified CPGs towards Sr<sup>2+</sup> were found to be superior over the unmodified CPGs as demonstrated by radiotracing using the short-lived radio nuclide <sup>85</sup>Sr.

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## 1. Introduction

Calix[4]arenes are easily accessible from base-catalyzed condensation reactions of *p*-substituted phenols with formaldehyde.<sup>1</sup> Due to their ease of synthesis calix[4]arenes have been extensively used as scaffolds for the construction of ionophores for alkali and alkaline earth metal ions, where the conformational properties were exploited to control efficiency and selectivity in metal ion recognition.<sup>2–6</sup> Thus, Ungaro and co-workers have shown that bis- and tetrakis(carbonylmethoxy)calix[4]arenes are quite effective in the liquid–liquid extraction of alkali and alkaline earth metal cations.<sup>7,8</sup>

Calix[4]arenes have also been immobilized on solid supports, such as silica gel.<sup>9</sup> These materials are of potential use as solid phase extractants in solid–liquid extraction processes and other applications.<sup>10–14</sup> The allyl group has turned out to be a versatile group for immobilization of calixarenes. Glennon and co-workers immobilized calix[4]arenes and calix[6]arenes bearing upper rim allyl functions onto silica gel via radical thiol addition or hydrosilylation.<sup>15–18</sup> The fixation of a 1,3-alternate calix[4]arene crown ether onto silica gel via two lower rim

substituents has also been reported.<sup>19</sup> Recently, Zhang and co-workers applied a multi-step route to immobilize highly metal-ion selective calix[4]arene ligands via an upper rim allyl function onto silica gel.<sup>20,21</sup>

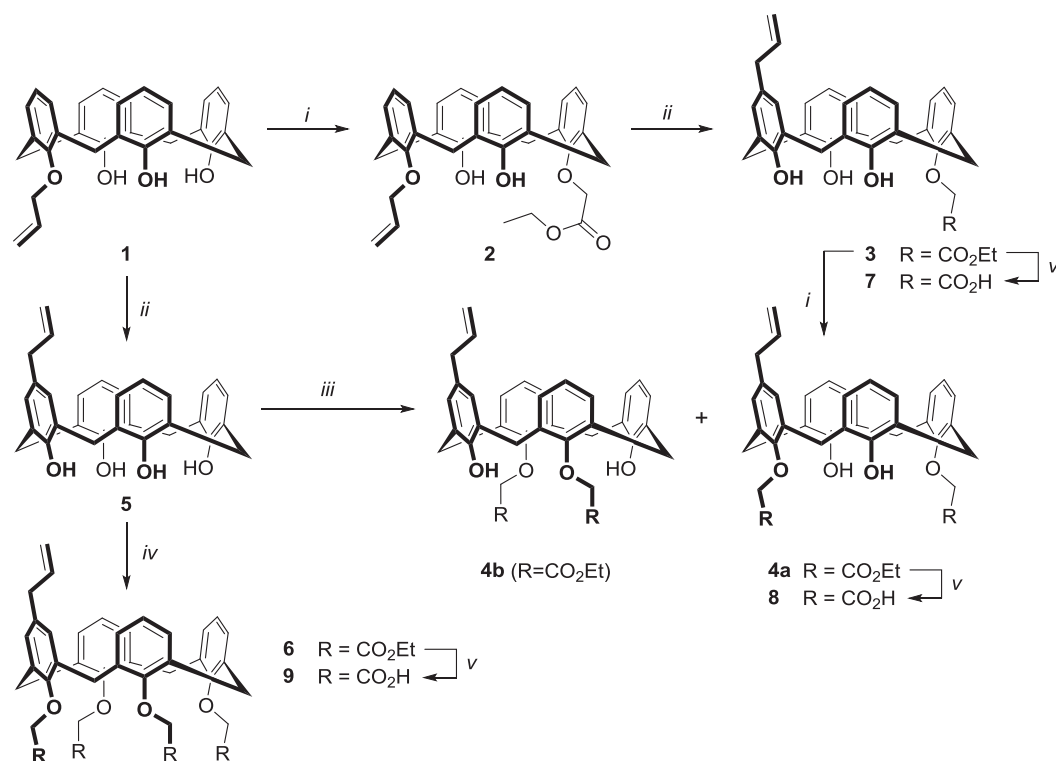
Our group is interested in the liquid-liquid extraction behavior of polycarboxylate ligands based on calix[4]arene scaffolds. It has been established that the diacid *p*-*tert*-butyl-25,27-bis(carboxymethoxy)calix[4]arene is a quite potent ligand for extracting Sr<sup>2+</sup> even from a synthetic ground water.<sup>22</sup> Herein, we present the synthesis and characterization of the allylated ligand system and its immobilization onto a controlled-pore glass (CPG). The CPG was used instead of silica gel due to its higher stability in basic media.<sup>23</sup> Silica gel decomposes above pH 8.<sup>24</sup> The synthesis of the analogous mono- and tetraacid is also described along with orienting extraction experiments.

## 2. Results and discussion

### 2.1. Syntheses of calix[4]arenes

A set of 5-allylcalix[4]arene-based mono-, di- and tetracarboxylate ligands were prepared in this study using standard reactions.<sup>25–27</sup> Scheme 1 depicts the synthetic procedures. The regioselective distal substitution was achieved by treatment of **1** with 1 equiv ethyl bromoacetate in the presence of a weak base

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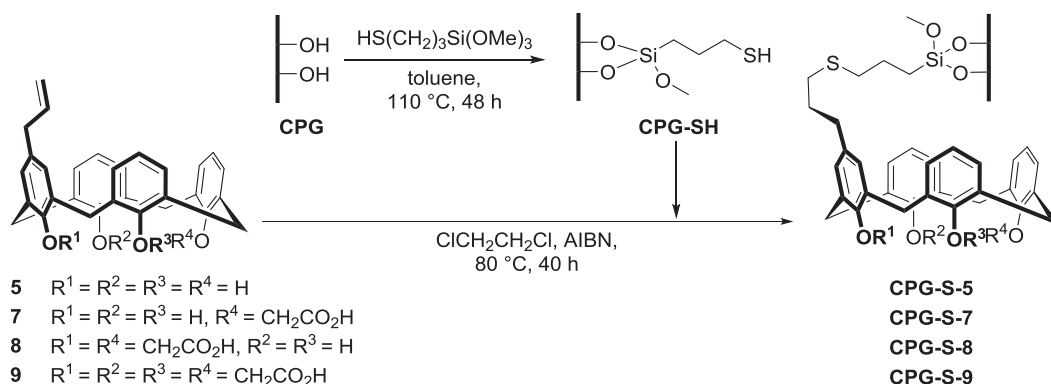


**Scheme 1.** Synthesis of calix[4]arene-based carboxylate ligands 7–9. Reagents and conditions: (i) 1 equiv  $\text{BrCH}_2\text{CO}_2\text{Et}$ , 1 equiv  $\text{Na}_2\text{CO}_3$ ,  $\text{CH}_3\text{CN}$ ,  $80^\circ\text{C}$ , 12 h; (ii) *N,N*-dimethylaniline,  $200^\circ\text{C}$ , 30 min; (iii) 2 equiv  $\text{BrCH}_2\text{CO}_2\text{Et}$ , 1 equiv  $\text{Na}_2\text{CO}_3$ ,  $\text{CH}_3\text{CN}$ ,  $80^\circ\text{C}$ , 12 h; (iv) 6 equiv  $\text{BrCH}_2\text{CO}_2\text{Et}$ , 10 equiv  $\text{Na}_2\text{CO}_3$ ,  $\text{CH}_3\text{CN}$ ,  $80^\circ\text{C}$ , 72 h; (v)  $\text{NaOH}$ ,  $\text{THF}/\text{EtOH}/\text{H}_2\text{O}$ ,  $80^\circ\text{C}$ , 12 h.

furnishing the ester **2** in 42% yield, which was subsequently Claisen rearranged to the corresponding 5-allylcalix[4]arene **3** in 85% yield.<sup>28,29</sup> The etherification of **3** with another equiv ethyl bromoacetate provided the diester **4a** as the sole product in 75% yield. Compound **4a** can also be accessed by etherification of 5-allylcalix[4]arene (**5**), however, in this case the isomer **4b** forms as a byproduct. Treatment of **5** with excess ethyl bromoacetate gave the tetraester **6**. All attempts to convert **1** to a triester failed. All esters could be saponified to provide the targeted acids in 68–88% yield. The compounds gave satisfactory elemental analysis and

## 2.2. Immobilization of calix[4]arene-based carboxylate ligands onto CPG

**Scheme 2** shows the route used for immobilization of the calix[4]arenes onto controlled-pore glass. Activated CPG was modified with  $\gamma$ -mercaptopropyl trimethoxysilane in refluxing toluene.<sup>10</sup> The so obtained **CPG-SH** was mixed with each of the calix[4]arenes **5**, **7–9** and subjected to conditions that promote radical thiol addition to the SH function of **CPG-SH** to obtain the corresponding **CPG-S-R** materials ( $\text{R}=\mathbf{5}, \mathbf{7}\text{--}\mathbf{9}$ ).



**Scheme 2.** Synthesis of CPG-bonded calix[4]arenes **CPG-S-R**.

their formulation was confirmed by ESI-MS,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

The cone conformation of the derivatized calix[4]arenes was confirmed by  $^1\text{H}$  NMR by the characteristic doublets at 3.35–3.56/4.25–4.50 ppm for the methylene protons  $\text{H}_{\text{eq}}$  and  $\text{H}_{\text{ax}}$ .<sup>30</sup> In case of **2** and **3** the cone conformation was also confirmed by single crystal X-ray crystallography ([Supplementary data](#)).

The calix[4]arene ligands **5**, **7–9** behaved very similar with respect to their loading efficiencies onto the CPG. Hence, the loadings were  $160\ \mu\text{mol/g}$  (**CPG-S-5**),  $185\ \mu\text{mol/g}$  (**CPG-S-7**),  $172\ \mu\text{mol/g}$  (**CPG-S-8**), and  $144\ \mu\text{mol/g}$  (**CPG-S-9**). The different loadings are presumably due to different reactivity imposed by the steric requirements of the calix[4]arenes. The loadings are otherwise comparable to those reported in the literature.<sup>13</sup>

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