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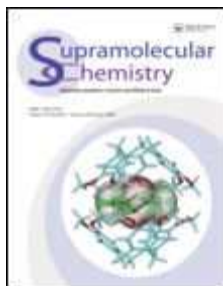
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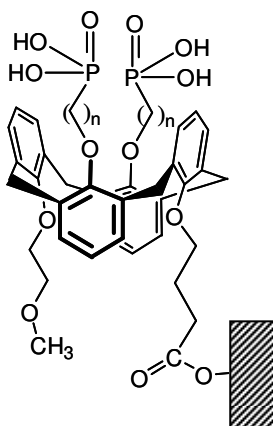


**Synthesis of phosphorylated calix[4]arene derivatives  
for the design of solid phases immobilizing uranyl cations.**

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Keywords:	: Phosphorous-Calix[4]arenes, Uranyl immobilization, Solid supports, Anchoring arms

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With the aim of developing supports for uranyl cation immobilization, new 1,3-alternate bearing both phosphonic acid functions as chelating site and N-succinimide-4-oxabutyrate as anchoring arm were synthesized. These compounds were proved to be coupled on a hydrazide gel and to complex uranium successfully.



Elias Bou Maroun, Agnès  
Hagège, Christian Basset,  
Eric Quéméneur, Claude  
Vidaud, Zouhair Asfari

Synthesis of new  
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Synthesis of phosphorylated calix[4]arene derivatives  
for the design of solid phases immobilizing uranyl cations.

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## Abstract

With the aim of developing supports for uranyl cations immobilization, new 1,3-alternate calix[4]arenes bearing both phosphonic acid functions as chelating sites and N-succinimide-4-oxabutyrate as the anchoring arm were synthesized in good yields. The coupling of such calixarenes to a gel was performed and a successful immobilization of uranyl cations was obtained.

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*Keywords: Phosphorous-Calix[4]arenes; Uranyl cations immobilization; Solid supports; Anchoring arms*

## Introduction

Uranium, especially under its uranyl ion form (UO<sub>2</sub><sup>2+</sup>), is widespread in the environment, naturally occurring in various minerals but also resulting from both nuclear civil and military uses. Regarding to the complexity of biological matrices, studying its speciation *in vivo* still requires innovative tools. Thus, the design and synthesis of macrocyclic ligands which could preorganize uranyl chelating functions is of primary importance in the development of such tools.

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Among them, calixarenes represent an interesting class of macrocycles. On the one hand, they might adopt pseudoplanar configuration. However, in contrast to homooxalix[4]arenes and tetrathiacalix[4]arenes [1-3], the crystal structure of the complex between the simple calix[4]arene and UO<sub>2</sub><sup>2+</sup> evidenced that the 1,3-oxygen atom distance is far from the ideal distance required for an internal complex [3]. On the other hand, calix[4]arenes can adopt an 1,3-alternate conformation where the uranyl cation binding sites can be remote from the anchoring arm designed for a covalent bond to a polymer support.

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Calix[4]arenes functionalized by various complexing groups were then used as extractants of uranyl ion, i.e. carboxylic acid [4-8], carboxylic acid-amide [9,10], ester [11], hydroxamate [12] or semicarbazone functions [13]. Phosphoryl groups have also been proved to be suitable for

uranyl [cation](#) complexation. The solvent extraction of uranium(VI) was widely studied by neutral or acid organo-phosphorus extractants [14-21]. A recent work of Taran *et al.* reported that bis-phosphonates were powerful uranyl ligands [22]. Several papers described the synthesis of phosphonatocalix[4]arenes [23-31]. Some of them were also functionalized with an anchoring arm to be immobilized on solid supports [7,8,13]. However, none of these phosphorus-containing calixarenes were used to extract the uranyl ion.

Consequently, the purpose of the present work was also to provide bifunctional ligands which could simultaneously bind uranium and be immobilized on solid supports.

In this work, the synthesis of two phosphorus-containing calix[4]arenes in the 1,3 alternate conformation bearing both phosphonic acid and N-hydroxysuccinimide ester entities is reported. Their incorporation into a macromolecular matrix is also demonstrated.

## Results and discussion

### 1. Conception of uranyl [cation](#) immobilizing agents: Synthesis of several (phosphonic acid)calix[4]arenes

[Phosphorus containing calixarenes](#), [modified to](#) provide an N-hydroxysuccinimide moiety able to react with  $\text{NH}_2$  groups of a solid support [were synthesized](#). As it is established that the 1,3-alternate conformation of calixarenes seems to be the most favorable for metal complexation [32-34], the synthesis was [designed to produce](#) the new calixarenes [with this preferred](#) conformation.

Calixarenes **6** and **9** were obtained via a five-step synthesis. The synthetic pathway is illustrated in Fig.4.

[insert figure 1 about here]

Calix[4]arene **1** was first O-alkylated in the presence of  $\text{K}_2\text{CO}_3$  with 1 equivalent of methoxyethoxy-p-toluenesulfonate to obtain the monoalkoxycalix[4]arene **2** in a 68 % yield. The cone conformation, [stabilized by hydrogen bonds](#), [was revealed by the presence of two AB](#) systems [at 4.49 and 3.48 ppm \( \$J = 13.0\$  Hz\) and at 4.31 and 3.46 ppm \( \$J = 13.0\$  Hz\), in the  \$^1\text{H}\$ -](#)

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3 | [NMR spectrum](#), attributed to the methylenic protons ArCH<sub>2</sub>Ar. The calixarene derivative **2** was  
4 then functionalized by reacting 1 equivalent of ethyl-4-bromobutyrate to obtain compound **3** in a  
5 56 % yield. The cone conformation was proved to be maintained by the <sup>1</sup>H NMR spectrum of  
6 compound **3** which revealed two AB systems at 4.42 and 3.38 ppm ( $J = 13.0$  Hz) and at 4.28  
7 and 3.38 ppm ( $J = 13.0$  Hz), attributed to the methylenic protons ArCH<sub>2</sub>Ar.

11 The introduction of the phosphorus-containing functions was performed by O-alkylation with  
12 2.1 equivalents of diethylphosphonoyl-methoxy-*p*-toluenesulfonate (**a**) or  
13 diethylphosphonoyl-propoxy-*p*-toluenesulfonate (**b**) in the presence of K<sub>2</sub>CO<sub>3</sub> to yield calixarene  
14 **4** and a mixture of compounds **7** and **7'** respectively. The 1,3-alternate conformation of  
15 compound **4** was confirmed by the presence in the <sup>1</sup>H NMR spectrum of a singlet for the  
16 methylenic protons ArCH<sub>2</sub>Ar at 3.49 ppm and by the <sup>31</sup>P NMR spectrum which showed a singlet  
17 at 21.8 ppm. Compounds **7** and **7'** were further separated by gel chromatography and were  
18 shown to be the expected diethylphosphonate calix[4]arene in two different conformations.  
19 Compound **7** was proved to be in the 1,3-alternate conformation, confirmed by the absence of  
20 any AB system in the <sup>1</sup>H NMR spectrum for the methylenic protons ArCH<sub>2</sub>Ar and the presence  
21 of a singlet at 33.5 ppm in the <sup>31</sup>P NMR spectrum indicating the presence of two equivalent  
22 phosphorous atoms. Compound **7'** was shown to be in the partial cone conformation. The <sup>1</sup>H  
23 NMR spectrum revealed an AB system at 4.05 ppm and at 3.09 ppm ( $J = 13.0$  Hz),  
24 corresponding to 4 methylenic protons ArCH<sub>2</sub>Ar. The singlet corresponding to the other 4  
25 methylenic protons ArCH<sub>2</sub>Ar was located in the multiplet at 3.92-3.57 ppm. The <sup>31</sup>P NMR  
26 spectrum confirmed this conformation, revealing two singlets at 34.1 ppm and 33.1 ppm for the  
27 two different phosphorous atoms.

30 Calixarenes **5** and **8** were obtained by transesterification using trimethylbromosilane and  
31 subsequent hydrolysis of the trimethylsilylestere in a nearly quantitative yield. Finally, the  
32 activation of the carboxylic groups was performed using 2 equivalents of NHS and 2 equivalents  
33 of EDC to obtain calixarenes **6** and **9** with a 64 % and a 45% yield respectively. For all these  
34 compounds, the absence of any AB system in the <sup>1</sup>H NMR spectra confirmed that the 1,3-  
35 alternate conformation was maintained.

## 2. Immobilization of calixarenes 6 and 9 on a gel column

Immobilization was performed by incubating the Ultralink hydrazide gel (15  $\mu\text{mol NH}_2$  functions per g) with calixarenes quantities corresponding to 20% of the total amount of  $\text{NH}_2$  groups.

Since the calixarenes synthesized in this paper are based on a succinimide ester that is commonly used for reactive amine crosslinking, the ester hydrolysis is a limiting factor. Two buffers were tested for the coupling: a HEPES buffer (pH 8.0) and a borate buffer (pH 9.2). A higher pH was shown to favor the nucleophilic attack to the detriment of the ester hydrolysis, and pH 9.2 was thus used in further experiments.

The repeatability of the coupling was then evaluated on 2 different gels using compound **6**. An average value of  $(32 \pm 2)\%$  (% mol) of coupled calixarene **6** was found.

The same experiment conducted with calixarene **9** led to 28.5% (% mol), which seems to indicate that the alkyl chain length has no influence on the coupling.

Improvement of the coupling extent was investigated by performing successive calixarene **6** additions and incubations. Results are reported in Table 1 and show that a maximum of 2  $\mu\text{mol}$  calixarene **6** / g gel is obtained.

## 3. Immobilization of uranyl ions on a gel column

Assessment of the complexation efficiency on a modified gel was performed. 1 g of the Ultralink hydrazide gel coupled with 2  $\mu\text{mol}$  calixarene **6** / g was incubated overnight in the presence of 5 equivalents of uranyl acetate. A similar experiment was also conducted with the same quantity of a non-coupled gel. The uranyl cation content in the eluates was quantified and found to be 7.5  $\mu\text{mol}$  for the eluates of the gel bound with calixarene **6** and 9.9  $\mu\text{mol}$  for the blank. Consequently,  $(2.4 \pm 0.1)$   $\mu\text{mol}$  uranyl cation / g were immobilized on the modified gel, which corresponds to a 100% immobilization (referring to the calixarene). For the non-coupled gel, the immobilized concentration was found to be as low as  $(0.1 \pm 0.1)$   $\mu\text{mol}$  uranyl cation / g. It seems then that the immobilization of the uranyl cation occurs through the formation of a 1:1 (uranyl:calixarene) complex. The total release of the uranyl cation from the blank gel shows the absence of non specific interactions and reinforces this assumption.

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## Conclusion

The synthesis of new phosphorous-containing calix[4]arenes bearing phosphonic acid functions on one side and NHS activated carboxylic functions on the other side, was achieved. With the aim of providing solid supports, the coupling of these compounds to a solid support was performed. A coupling extent of 2  $\mu\text{mol}$  calixarene **6** / g gel was obtained. Under the used conditions, a quantitative immobilization of uranyl cations was shown to occur through the formation of an 1:1  $\text{UO}_2^{2+}$ :calixarene **6** complex.

Further studies will be performed to improve the coupling extent of calixarene **6** on such support. However, the use of these heterofunctional macrocycles for many other usages into supramolecular devices could be further envisioned.

## Experimental

### 1. Synthesis

All reagents and solvents were commercial and were used without further purification. Reagents for the synthesis were all Sigma-Aldrich and Prolabo products Calix[4]arene was prepared according to the literature [35]. Chromatography used  $\text{SiO}_2$  columns with Kieselgel Merck (art. 11567). The melting points were taken on a Büchi 535 apparatus in capillaries sealed under nitrogen.  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra were respectively recorded at 300 MHz and 400 MHz on a Bruker Avance spectrometer. For  $^1\text{H}$  NMR spectra,  $\text{CHCl}_3$  ( $\delta = 7.26$  ppm) was used as an internal standard in  $\text{CDCl}_3$  and  $\text{CHD}_2\text{OD}$  ( $\delta = 3.31$  ppm) was used as an internal standard in  $\text{CD}_3\text{OD}$ . For  $^{31}\text{P}$  NMR spectra, 85 %  $\text{H}_3\text{PO}_4$  was used as an external reference. MALDI-TOF mass spectra were obtained with a Bruker Autoflex II equipped with a  $\text{N}_2$  laser ( $\lambda = 337\text{nm}$ ) using  $\alpha$ -cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg.

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3 **1.1 Synthesis of 1,3-[di-(oxamethyl-phosphonic acid)], 2-(N-succinimide-4-oxabutyrate),**  
4 **4-(methoxyethoxy)-calix[4]-arene (6).**  
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8 **1.11. Mono-methoxyethoxy-calix[4]arene (2).** A suspension of calix[4]arene **1** (12.73 g, 30.0  
9 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.16 g, 15.6 mmol) in acetonitrile (500 mL) was stirred for 30 min at room  
10 temperature under a nitrogen atmosphere. Methoxyethyl *p*-toluenesulfonate (6.91 g, 12.0 mmol)  
11 was then added and the mixture was stirred and refluxed for 4 days. After removal of the  
12 solvent, 400 mL of CH<sub>2</sub>Cl<sub>2</sub> and 400 mL of water were added and the mixture was stirred and  
13 acidified with HCl 1M. The organic layer was recovered and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After  
14 removal of the solvent, compound **2** was purified by column chromatography (SiO<sub>2</sub>, eluent:  
15 CH<sub>2</sub>Cl<sub>2</sub>) and obtained as a white powder.  
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18 Yield: 9.91 g (68%) mp 224-225 °C. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) δ (ppm): 9.86 (s, 1H, ArOH), 9.24  
19 (s, 2H, ArOH), 7.12-7.00 (m, 8H, ArH<sub>meta</sub>), 6.89 (t, 1H, J = 7.5 Hz, ArH<sub>para</sub>), 6.72-6.65 (m, 3H,  
20 ArH<sub>para</sub>), 4.49 (d, 2H, J = 13.0 Hz, ArCH<sub>2</sub>Ar), 4.35-4.32 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 4.31 (d, 2H, J =  
21 13.0 Hz, ArCH<sub>2</sub>Ar), 4.04-4.01 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.62 (s, 3H, OCH<sub>3</sub>), 3.48 (d, 2H, J = 13.0  
22 Hz, ArCH<sub>2</sub>Ar), 3.46 (d, 2H, J = 13.0 Hz, ArCH<sub>2</sub>Ar). Anal. Calcd. for C<sub>31</sub>H<sub>30</sub>O<sub>5</sub> (%): C, 77.16; H,  
23 6.27. Found C, 77.43; H, 6.00  
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33 **1.12. 1-(Ethyl-4-oxabutyrate), 3-(methoxyethoxy)-calix[4]arene (3).** Mono-methoxyethoxy-  
34 calix[4]arene **2** (4.83 g, 10.0 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.72 g, 5.2 mmol) were suspended in  
35 acetonitrile (200 mL) and stirred for 1 h at room temperature under a nitrogen atmosphere.  
36 Br(CH<sub>2</sub>)<sub>3</sub>C(O)OCH<sub>2</sub>CH<sub>3</sub> (2.34 g, 12.0 mmol) was then added and the resulting solution was  
37 refluxed for 4 days. After evaporation of the solvent in vacuo, the residue was taken up in  
38 CH<sub>2</sub>Cl<sub>2</sub> (300 mL) and in water (300 mL) and the resulting mixture was acidified then separated  
39 in order to recover the organic layer which was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation  
40 of the solvent, compound **3** was purified by column chromatography (SiO<sub>2</sub>, eluent:  
41 CH<sub>2</sub>Cl<sub>2</sub>/acetone 98/2 v/v) and obtained as a white powder.  
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48 Yield: 3.36 g (56%), mp 165-166 °C. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) δ (ppm): 7.93 (s, 2H, ArOH),  
49 7.06 (d, 4H, J = 7.5 Hz, ArH<sub>meta</sub>), 6.90 (d, 4H, J = 7.5 Hz, ArH<sub>meta</sub>), 6.76-6.71 (m, 2H, ArH<sub>para</sub>),  
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6.65 (t, 2H,  $J = 7.5$  Hz,  $ArH_{para}$ ), 4.42 (d, 2H,  $J = 13.0$  Hz,  $ArCH_2Ar$ ), 4.28 (d, 2H,  $J = 13.0$  Hz,  $ArCH_2Ar$ ), 4.23-4.16 (m, 4H,  $COOCH_2CH_3 + CH_2CH_2OCH_3$ ), 4.07 (t, 2H,  $J = 6.1$  Hz,  $CH_2CH_2CH_2COOEt$ ), 3.95-3.92 (m, 2H,  $CH_2CH_2OCH_3$ ), 3.56 (s, 3H,  $CH_2OCH_3$ ), 3.38 (d, 4H,  $J = 13.0$  Hz,  $ArCH_2Ar$ ), 2.90 (t, 2H,  $J = 7.4$  Hz,  $CH_2COOEt$ ), 2.41-2.32 (m, 2H,  $CH_2CH_2CH_2COOEt$ ), 1.29 (t, 3H,  $J = 7.2$  Hz,  $COOCH_2CH_3$ ). Anal. Calcd. for  $C_{37}H_{40}O_7$  (%): C, 74.47; H, 6.76. Found C, 74.68; H, 6.52

**1.13. Diethylphosphonoylmethoxy-*p*-toluenesulfonate (a).** A solution of triethylamine (10.12 g, 100.0 mmol) in  $CH_2Cl_2$  (50 mL) was added dropwise to a stirred mixture of diethyl(hydroxymethyl)phosphonate (8.41 g, 50.0 mmol) and *p*-toluenesulfonyl chloride (10.01 g, 52.5 mmol) in  $CH_2Cl_2$  (450 mL) at ca. 0°C. The resulting mixture was cooled to room temperature and stirred for 15 h. It was then extracted with 300 mL of acidified aqueous solution and dried over anhydrous  $Na_2SO_4$ . After removal of the solvent, the residue was purified by column chromatography on silica gel.  $CH_2Cl_2$  was used as the first mobile phase then  $CH_2Cl_2$ /acetone (98/2, v/v). Compound **a** was recovered as a viscous liquid.

Yield: 12.93 g (80%).  $^1H$ -NMR (300MHz,  $CDCl_3$ )  $\delta$  (ppm): 7.79 (d, 2H,  $J = 8.1$  Hz,  $ArH$ ), 7.36 (d, 2H,  $J = 8.1$  Hz,  $ArH$ ), 4.19-4.09 (m, 6H,  $SO_3CH_2P + POOCH_2CH_3$ ), 2.45 (s, 3H,  $CH_3Ar$ ), 1.31 (t, 6H,  $J = 7.1$  Hz,  $POOCH_2CH_3$ ).

**1.14. 1,3-[Di-(oxamethyl-diethylphosphonate)], 2-(ethyl-4-oxabutyrate), 4-(methoxyethoxy)-calix[4]arene (4).** A suspension of 1-(ethyl-4-oxabutyrate), 3-(methoxyethoxy)-calix[4]arene **3** (1.79 g, 3.0 mmol) and  $K_2CO_3$  (4.15 g, 30.0 mmol) in acetonitrile (100 mL) was stirred for 2 h at room temperature under nitrogen atmosphere. Diethylphosphonoylmethoxy-*p*-toluenesulfonate **a** (2.03 g, 6.3 mmol) was then added and the mixture was refluxed for 10 days. After filtration of the mixture, the solvent was removed under vacuo and the residue was taken up in  $CH_2Cl_2$  (200 mL). 200 mL of water were added and the mixture was acidified with 1 M HCl. The organic layer was separated, dried over anhydrous  $Na_2SO_4$ , filtered and concentrated. The resulting residue was purified by column

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chromatography (SiO<sub>2</sub>, eluent: CH<sub>2</sub>Cl<sub>2</sub>/acetone 90/10 v/v). Compound **4** was obtained as a pure yellow viscous liquid.

Yield: 1.69 g (63%). <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) δ (ppm): 7.25-7.21 (m, 4H, ArH<sub>meta</sub>), 7.11-7.08 (m, 2H, ArH<sub>meta</sub>), 6.99-6.96 (m, 2H, ArH<sub>meta</sub>), 6.68-6.57 (m, 4H, ArH<sub>para</sub>), 4.29-4.17 (m, 6H, ArOCH<sub>2</sub> + COOCH<sub>2</sub>CH<sub>3</sub>), 4.07 (d, 4H, J = 9.2 Hz, ArOCH<sub>2</sub>P), 3.91-3.88 (m, 2H, CH<sub>2</sub>OCH<sub>3</sub>), 3.77-3.64 (m, 8H, POOCH<sub>2</sub>), 3.59 (s, 3H, CH<sub>2</sub>OCH<sub>3</sub>), 3.49 (s, 8H, ArCH<sub>2</sub>Ar), 2.53 (t, 2H, J = 7.2 Hz, CH<sub>2</sub>COOEt), 2.20 (q, 2H, J = 7.2 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOEt), 1.42 (t, 12H, J = 7.1 Hz, POOCH<sub>2</sub>CH<sub>3</sub>), 1.24 (t, 3H, J = 7.1 Hz, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 21.8. Anal. Calcd. for C<sub>47</sub>H<sub>62</sub>O<sub>13</sub>P<sub>2</sub> (%): C, 62.94; H, 6.97. Found C, 62.76; H, 7.14.

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**1.15. 1,3-[Dj-(oxamethyl-phosphonic acid)], 2-(4-oxabutyric acid), 4-(methoxyethoxy)-calix[4]arene (5).** Bromotrimethylsilane (5.64 g, 36.83 mmol) was added to a solution of compound **4** (1.10 g, 1.23 mmol) in 20 mL acetonitrile. The reaction mixture was stirred for 24 h at room temperature under nitrogen atmosphere. It was then evaporated under reduced pressure and a mixture of 10 mL of methanol/water (50/50, v/v) was added to the residue. The resulting solution was stirred at room temperature overnight. After removal of methanol and water, the residue was evaporated twice with 10 mL of dry toluene and filtered to obtain compound **5** as a pink solid.

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Yield: 0.91 g (98 %), mp 158-159 °C. <sup>1</sup>H-NMR (300MHz, CD<sub>3</sub>OD) δ (ppm): 7.17 (d, 4H, J = 7.5 Hz, ArH<sub>meta</sub>), 7.05-7.02 (m, 2H, ArH<sub>meta</sub>), 6.95-6.92 (m, 2H, ArH<sub>meta</sub>), 6.62-6.53 (m, 4H, ArH<sub>para</sub>), 3.76-3.50 (m, 18H, ArOCH<sub>2</sub>CH<sub>2</sub> + ArCH<sub>2</sub>Ar + ArOCH<sub>2</sub>P + CH<sub>2</sub>OCH<sub>3</sub>), 3.22 (s, 3H, CH<sub>2</sub>OCH<sub>3</sub>), 2.47-2.39 (m, 2H, CH<sub>2</sub>COOH), 2.03-1.92 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COOH). <sup>31</sup>P NMR (400 MHz, CD<sub>3</sub>OD) δ (ppm): 19.9. Anal. Calcd. for C<sub>37</sub>H<sub>42</sub>O<sub>13</sub>P<sub>2</sub> (%): C, 58.73; H, 5.59. Found C, 58.47; H, 5.44. Mass spectrum (MALDI-TOF): m/z = 755.2 [M-H].

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**1.16. 1,3-[Dj-(oxamethyl-phosphonic acid)], 2-(N-succinimide-4-oxabutyrate), 4-(methoxyethoxy)-calix[4]arene (6).** Compound **5** (1.14 g, 1.5 mmol), EDC [1-Ethyl-3-(3-dimethyl-aminopropyl)-carbodiimide] (0.58 g, 3.0 mmol) and NHS (N-hydroxysuccinimide) (0.35 g, 3.0 mmol) were dissolved in DMF (90 mL) and the mixture was stirred overnight at room

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temperature and then for 3 h at 55 °C. After removal of the solvent, the residue was treated with acetonitrile to obtain compound **6** as white solid.

Yield: 0.82 g (64 %), mp 109-111 °C. <sup>1</sup>H-NMR (300MHz, DMSO-d<sub>6</sub>) δ (ppm): 7.24 (d, 4H, *J* = 7.4 Hz, Ar*H*<sub>meta</sub>), 7.02-6.99 (m, 2H, Ar*H*<sub>meta</sub>), 6.93-6.90 (m, 2H, Ar*H*<sub>meta</sub>), 6.57-6.52 (m, 4H, Ar*H*<sub>para</sub>), 3.75-3.55 (m, 12H, ArOCH<sub>2</sub>CH<sub>2</sub> + ArCH<sub>2</sub>Ar), 3.37 (s, 3H, CH<sub>2</sub>OCH<sub>3</sub>), 3.03-2.89 (m, 6H, ArOCH<sub>2</sub>P + CH<sub>2</sub>OCH<sub>3</sub>), 2.71 (s, 4H, NHS), 1.99-1.95 (m, 2H, CH<sub>2</sub>COONHS), 1.76-1.71 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COONHS). <sup>31</sup>P NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 16.4. Anal. Calcd. for C<sub>41</sub>H<sub>45</sub>NO<sub>15</sub>P<sub>2</sub> (%): C, 57.68; H, 5.31; N, 1.64. Found C, 57.39; H, 5.45; N, 1.81. Mass spectrum (MALDI-TOF): *m/z* = 855.1 [MH<sup>+</sup>].

## 1.2. Synthesis of 1,3-[di-(oxapropyl-phosphonic acid)], 2-(*N*-succinimide-4-oxabutyrate), 4-(methoxyethoxy)-calix[4]arene (**9**).

**1.21. Diethylphosphonoylpropoxy-*p*-toluenesulfonate (b).** Diethyl 3-bromopropylphosphonate (5.18 g, 20.0 mmol) and silver *p*-toluenesulfonate (11.16 g, 40.0 mmol) were dissolved in 200 mL acetonitrile and stirred at room temperature for 3 days. The solution was then filtered and the solvent was evaporated to dryness under reduced pressure. The residue was then taken up in CH<sub>2</sub>Cl<sub>2</sub> (400 mL) and water (400 mL). The organic layer was recovered and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by column (SiO<sub>2</sub>, eluent: CH<sub>2</sub>Cl<sub>2</sub>/acetone 80/20 v/v). Compound **b** was recovered as a viscous liquid.

Yield: 1.75 g (25 %). <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) δ (ppm): 7.78 (d, 2H, *J* = 8.2 Hz, Ar*H*), 7.34 (d, 2H, *J* = 8.2 Hz, Ar*H*), 4.12-3.99 (m, 6H, CH<sub>3</sub>ArSO<sub>3</sub>CH<sub>2</sub> + POOCH<sub>2</sub>CH<sub>3</sub>), 2.44 (s, 3H, CH<sub>3</sub>Ar), 2.01-1.87 (m, 2H, SO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.81-1.69 (m, 2H, SO<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.29 (t, 6H, *J* = 7.1 Hz, POOCH<sub>2</sub>CH<sub>3</sub>).

**1.22. 1,3-[Di-(oxapropyl-diethylphosphonate)], 2-(ethyl-4-oxabutyrate), 4-(methoxyethoxy)-calix[4]arene (**7 and 7'**).** The synthesis was performed as for compound **4**.

Calix[4]arene derivative **3**: 1.43 g, 2.4 mmol; K<sub>2</sub>CO<sub>3</sub>: 3.32 g, 24.0 mmol; acetonitrile: 100 mL; diethylphosphonoylpropoxy-*p*-toluenesulfonate **b**: 1.77 g, 5.0 mmol; CH<sub>2</sub>Cl<sub>2</sub>: 200 mL; H<sub>2</sub>O: 200

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mL. Column chromatography (SiO<sub>2</sub>, eluent: CH<sub>2</sub>Cl<sub>2</sub>/acetone 80/20 v/v). Compounds **7** and **7'** were obtained as yellow viscous liquids.

Compound **7** (1,3-alternate), yield: 0.53 g (23 %). <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) δ (ppm): 7.09-7.06 (m, 2H, ArH<sub>meta</sub>), 7.02-7.00 (m, 6H, ArH<sub>meta</sub>), 6.75-6.70 (m, 4H, ArH<sub>para</sub>), 4.21-4.09 (m, 10H, ArOCH<sub>2</sub> + COOCH<sub>2</sub>CH<sub>3</sub>), 3.75-3.55 (m, 16H, POOCH<sub>2</sub>CH<sub>3</sub> + ArCH<sub>2</sub>Ar), 3.37-3.35 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.34 (s, 3H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.26 (t, 2H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOEt), 1.92-1.66 (m, 10H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>POOEt + CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOEt), 1.37 (t, 12H, *J* = 7.1 Hz, POOCH<sub>2</sub>CH<sub>3</sub>), 1.30 (t, 3H, *J* = 7.1 Hz, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 33.5 ppm. Anal. Calcd. for C<sub>51</sub>H<sub>70</sub>O<sub>13</sub>P<sub>2</sub> (%): C, 64.27; H, 7.40. Found: C, 64.17; H, 7.29. Mass spectrum (MALDI-TOF): *m/z* = 975.4 [MNa<sup>+</sup>].

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Compound **7'** (partial cone), yield: 0.43 g (19 %). <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) δ (ppm): 7.35-7.33 (m, 1H, ArH<sub>meta</sub>), 7.25-7.22 (m, 1H, ArH<sub>meta</sub>), 7.10-7.07 (m, 2H, ArH<sub>meta</sub>), 7.01-6.88 (m, 4H, ArH<sub>meta</sub>), 6.49-6.42 (m, 2H, ArH<sub>para</sub>), 6.32-6.26 (m, 2H, ArH<sub>para</sub>), 4.21-4.10 (m, 10H, ArOCH<sub>2</sub> + COOCH<sub>2</sub>CH<sub>3</sub>), 4.05 (d, 2H, *J* = 13.0 Hz, ArCH<sub>2</sub>Ar), 3.92-3.57 (m, 12H, POOCH<sub>2</sub>CH<sub>3</sub> + ArCH<sub>2</sub>Ar), 3.45 (s, 3H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.09 (d, 2H, *J* = 13.0 Hz, ArCH<sub>2</sub>Ar), 2.61-2.43 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.23-2.14 (m, 4H, CH<sub>2</sub>POOEt + CH<sub>2</sub>COOEt), 1.96-1.84 (m, 2H, CH<sub>2</sub>POOEt), 1.76-1.53 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>POOEt + CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOEt), 1.43-1.34 (m, 12H, POOCH<sub>2</sub>CH<sub>3</sub>), 1.26 (t, 3H, *J* = 7.1 Hz, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 34.1 and 33.1 ppm. Anal. Calcd. for C<sub>51</sub>H<sub>70</sub>O<sub>13</sub>P<sub>2</sub> (%): C, 64.27; H, 7.40. Found C, 64.17; H, 7.29

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**1.23. 1,3-[Di-(oxapropyl-phosphonic acid)], 2-(4-oxabutyric acid), 4-(methoxyethoxy)-calix[4]arene (8).** The synthesis was performed as for compound **5**.

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Calix[4]arene derivative **7**: 0.29 g, 0.3 mmol; bromotrimethylsilane: 1.38 g, 9.0 mmol; acetonitrile: 10 mL; methanol/water (50/50, v/v): 5 mL. Pink solid, yield: 0.24 g (98%); mp > 290 °C. <sup>1</sup>H-NMR (300MHz, CD<sub>3</sub>OD) δ (ppm): 7.15-7.03 (m, 8H, ArH<sub>meta</sub>), 6.92-6.77 (m, 4H, ArH<sub>para</sub>), 3.84-3.49 (m, 18H, ArOCH<sub>2</sub> + ArCH<sub>2</sub>Ar + CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.31 (s, 3H, CH<sub>2</sub>OCH<sub>3</sub>), 2.12-1.98 (m, 2H, CH<sub>2</sub>COOH), 1.72-1.45 (m, 10H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>POOH + CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH). <sup>31</sup>P NMR (400 MHz, CD<sub>3</sub>OD) δ (ppm): 33.5 ppm. Anal. Calcd. for C<sub>41</sub>H<sub>50</sub>O<sub>13</sub>P<sub>2</sub> (%): C, 60.59; H, 6.20. Found C, 60.46; H, 6.13.

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1.24. 1,3-**[Dj-(oxapropyl-phosphonic acid)]**, 2-(N-succinimide-4-oxabutyrate), 4-(methoxyethoxy)-calix[4]arene (**9**). The synthesis was performed as for compound **6**.

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Calix[4]arene derivative **8**: 0.22 g, 0.27 mmol; EDC: 0.10 g, 0.54 mmol; NHS: 0.06 g, 0.54 mmol; DMF: 16 mL. Brown solid, yield: 0.11 g (45%); mp > 290 °C. <sup>1</sup>H-NMR (300MHz, DMSO-d<sub>6</sub>) δ (ppm): 7.13-6.94 (m, 8H, ArH<sub>meta</sub>), 6.79-6.69 (m, 4H, ArH<sub>para</sub>), 3.66-3.46 (m, 18H, ArOCH<sub>2</sub> + ArCH<sub>2</sub>Ar + ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.36 (s, 3H, CH<sub>2</sub>OCH<sub>3</sub>), 2.71 (s, 4H, NHS), 1.99-1.88 (m, 2H, CH<sub>2</sub>COONHS), 1.57-1.21 (m, 10H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>POOH + CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COONHS). <sup>31</sup>P NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 32.1. Anal. Calcd. for C<sub>45</sub>H<sub>53</sub>NO<sub>15</sub>P<sub>2</sub> (%): C, 59.40; H, 5.87; N, 1.54. Found C, 59.18; H, 5.60; N, 1.60. Mass spectrum not available due to the poor solubility in solvents compatible with mass spectrometry.

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## 2. Coupling on the solid support

A column was packed with 1 g Ultralink hydrazide gel according to the protocol described by the manufacturer and conditioned with a 50 mM sodium borate buffer at pH 9. 40 mg/mL solutions of compound **6** and compound **9** were prepared in DMSO. Five successive additions of these solutions were performed in order to obtain a final concentration of 3 μmol/g calixarene and the coupling was performed during 2.5 h under agitation.

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The column was then washed with 2 x 2 mL coupling buffer and 2 mL coupling buffer containing 1M NaCl and the eluates were analyzed using a fluorimeter CARY-Eclipse (Varian) at λ<sub>exc</sub> = 268 nm and λ<sub>em</sub> = 310 nm. λ<sub>exc</sub> and λ<sub>em</sub> were previously determined from a calixarene solution and the calixarene amount in the eluates was quantified from a calibration curve (0; 1.86; 3.70; and 7.36 x 10<sup>-4</sup> M).

The calixarene content was determined from the mass-balance, by difference between the initial number of moles of calixarene and that found in the eluate fractions.

## 3. Uranyl cation binding



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3 Aliquots of gels (1 g) coupled with 2  $\mu\text{mol}$  calixarene **6** / g were washed with 4 x 2 mL 50 mM  
4 sodium acetate buffer pH 4.0. 5 x 20  $\mu\text{L}$  of a 0.1 M uranyl acetate solution ( i.e 10  $\mu\text{M}$ ) were  
5 then added to the column and contacted overnight under agitation at room temperature. The  
6 supernatant was recovered and the column was then rinsed using 3 x 2 mL 50 mM acetate  
7 buffer pH 4 and 3 x 2 mL 50 mM HEPES buffer pH 7.4  
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9 UV spectra of uranyl solutions, recorded on a CARY 50 (Varian), showed a maximum peak  
10 between 222 and 234 nm, correlated to the uranyl concentrations in the solutions. A calibration  
11 curve ( 0; 1.5; 3; and 6 x 10<sup>-4</sup> M) was used to quantify the uranyl amount in both supernatant  
12 and eluates. The amount of gel sorbed uranyl cation was determined by difference between its  
13 initial quantity and that measured in the liquid fractions.  
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## References

- [1] Thuéry, P.; Masci, B., *Dalton Trans.* **2003**, *12*, 2411-2417.
- [2] Masci, B.; Gabrielli, M.; Mortera, S. L.; Nierlich, M.; Thuéry, P. *Polyhedron* **2002**, *21*, 1125-1131.
- [3] Asfari, Z. ; Bilyk, A. ; Dunlop, J. W. C.; Hall, A. K. ; Harrowfield, J. M.; Hosseini, M. W.; Skelton, B. W. ; White, A. W. *Angew. Chem. Int. Ed.* **2001**, *40*, 721-723.
- [4] Montavon, G.; Duplatre, G.; Asfari, Z.; Vicens, J. *Solvent Extr. Ion Exch.* **1997**, *15*, 169-188.
- [5] Du, Z.; Zhang A.-Y.; Yang Z.-X.; Zhou Z.-M. *J. Radioanal. Nucl. Chem.* **1999**, *241*, 241-243.
- [6] Montavon, G.; Duplatre, G.; Asfari, Z.; Vicens, J. *Radioanal. Nucl. Chem.* **1996**, *210*, 87-103.
- [7] Hall, C.W.; Cockayne J.S.; Kan, M.J.; Nicholson G.P. *Green Chem.* **2001**, *3*, 114-122.
- [8] Evans, C.J.; Nicholson G.P., *Sensors and Actuators B* **2005**, *105*, 204-207.



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2  
3 [9] Beer, P. D.; Brindley, G. D.; Danny Fox, O.; Grieve, A.; Ogden, M. I.; Szemes, F.; Drew, M.  
4 G. B. *J. Chem. Soc., Dalton Trans.* **2002**, 16, 3101-3111.  
5  
6 [10] Kan M.J.; Nicholson G.; Horn I., Williams G.; Beer P.D.; Schmitt P.; Heseck D.; Drew  
7 M.G.B.; Sheen P. *Nucl. Energy* **1998**, 37, 295-345.  
8  
9 [11] Felinto, M. C. F. C.; Almeida, V. F. J. *Alloys and Compounds* **2000**, 303-304, 524-528.  
10  
11 [12] Agrawal Y.K.; Sanyal M. *J. Radioanal. Nucl. Chem.* **1995**, 198, 349-358.  
12  
13 [13] Jain V.K.; Pandya R.A.; Pillai S.G.; Shrivastav P.S. *Talanta* **2006**, 70, 257-266.  
14  
15 [14] Ghiasvand, A. R.; Mohagheghzadeh, E., *Anal. Sci.* **2004**, 20, 917-919.  
16  
17 [15] Dogmane, S. D.; Singh, R. K.; Bajpai, D. D.; Mathur, J. N., *J. Radioanal. Nucl. Chem.* **2002**,  
18 253, 477-482.  
19  
20 [16] Sarkar, S. G.; Bandekar, S. V.; Dhadke, P. M. *J. Radioanal. Nucl. Chem.* **2000**, 243, 803-  
21 807.  
22  
23 [17] Singh, D. K.; Singh, H.; Gupta, C. K. *J. Radioanal. Nucl. Chem.* **2000**, 245, 575-580.  
24  
25 [18] Sun, G. X.; Yu, C.; Han, J. T.; Hua, S.; Bao, B. R. *J. Radioanal. Nucl. Chem.* **2000**, 246,  
26 431-432.  
27  
28 [19] Sameda, H. H.; El Zahhar, A. A.; Shehata, M. K.; El Nagggar, H. A. *J. of Radioanal. Nucl.*  
29 *Chem.* **1998**, 228, 37-41.  
30  
31 [20] Elias, A.; Rodehuser, L.; Azzouz, A.; Attou, M. *Hydrometallurgy* **1996**, 40, 189-194.  
32  
33 [21] Gatrone, R.C.; Horwitz, E. P.; Rickert P.G., Diamond, H. *Solvent Extr. Ion Exch.* **1989**, 7,  
34 793-811.  
35  
36 [22] Sawicki M., Siaugue J.-M., Jacopin C., Moulin C., Bailly T., Burgada R., Meunier S., Baret  
37 P., Pierre J.-L., Taran F., *Chem. Eur.*, **2005**, 11, 3689.  
38  
39 [23] Jurecka, P.; Vojtisek, P.; Novotny, K.; Rohovec, J.; Lukes, I. *J. Chem. Soc., Perkin Trans. 2*  
40 **2002**, 7, 1370-1377.  
41  
42 [24] Bochenska, M.; Hoffmann, M.; Lesinska, U. *J. Incl. Phenom.* **2004**, 49, 57-60.  
43  
44 [25] Matulkova, I.; Rohovec, J. *Polyhedron* **2005**, 24(2), 311-317.  
45  
46 [26] Ozegowski, S.; Coostisella, B.; Gloede, J. *Phosphorus, Sulfur and Silicon and Their*  
47 *Related Elements* **1996**, 119, 209-223.  
48  
49  
50  
51  
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54  
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2  
3 [27] Gloede, J.; Ozegowski, S.; Kockritz, A.; Keitel, I. *Phosphorus, Sulfur and Silicon and Their*  
4 *Related Elements* **1997**, *131*, 141-145.  
5  
6 [28] Cherenok, S.; Vovk, A.; Muravyova, I.; Shivanyuk, A.; Kukhar, V.; Lipkowski, J.; Kalchenko,  
7 *V. Organic Letters* **2006**, *8*, 549-552.  
8  
9 [29] Kyoda, M.; Maekawa, H.; Sadai, Y.; Nishiguchi, I. *Adv. Technol. Mat. Mat. Process. J.*  
10 **2004**, *6*, 29-36.  
11  
12 [30] Wiit, D.; Dziemidowicz, J.; Rachon, J. *Heteroat. Chem.* **2004**, *15*, 155-161.  
13  
14 [31] Hoffmann, M.; Konitz, A.; Lesinska, U.; Bochenska, M.; *J. Incl. Phenom.* **2003**, *47*, 137-142.  
15  
16 [32] Casnati, A.; Pochini, A.; Ungaro, R.; Bocchi, C.; Ugozzoli, F.; Egberink, R. J. M.; Struijk, H.;  
17 Lugtenberg, R.; de Jong, F.; Reinhoudt, D. N. *Chem. Eur. J.* **1996**, *2*, 436-445.  
18  
19 [33] Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M. J.;  
20 Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767-2777.  
21  
22 [34] Ungaro, R.; Casnati, A.; Ugozzoli, F.; Pochini, A.; Dozol, J. F.; Hill, C.; Rouquette, H.  
23 *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1506-1509.  
24  
25 [35] Gutsche, C. D.; Levine, J. A.; Sujeeth, P. K. *J. Org. Chem.* **1985**, *50*, 5802-5806.  
26  
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28  
29  
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5 **Captions:**  
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9 **Figure 1** : Synthetic pathway for phosphonic acid)calix[4]arenes possessing an anchoring arm.  
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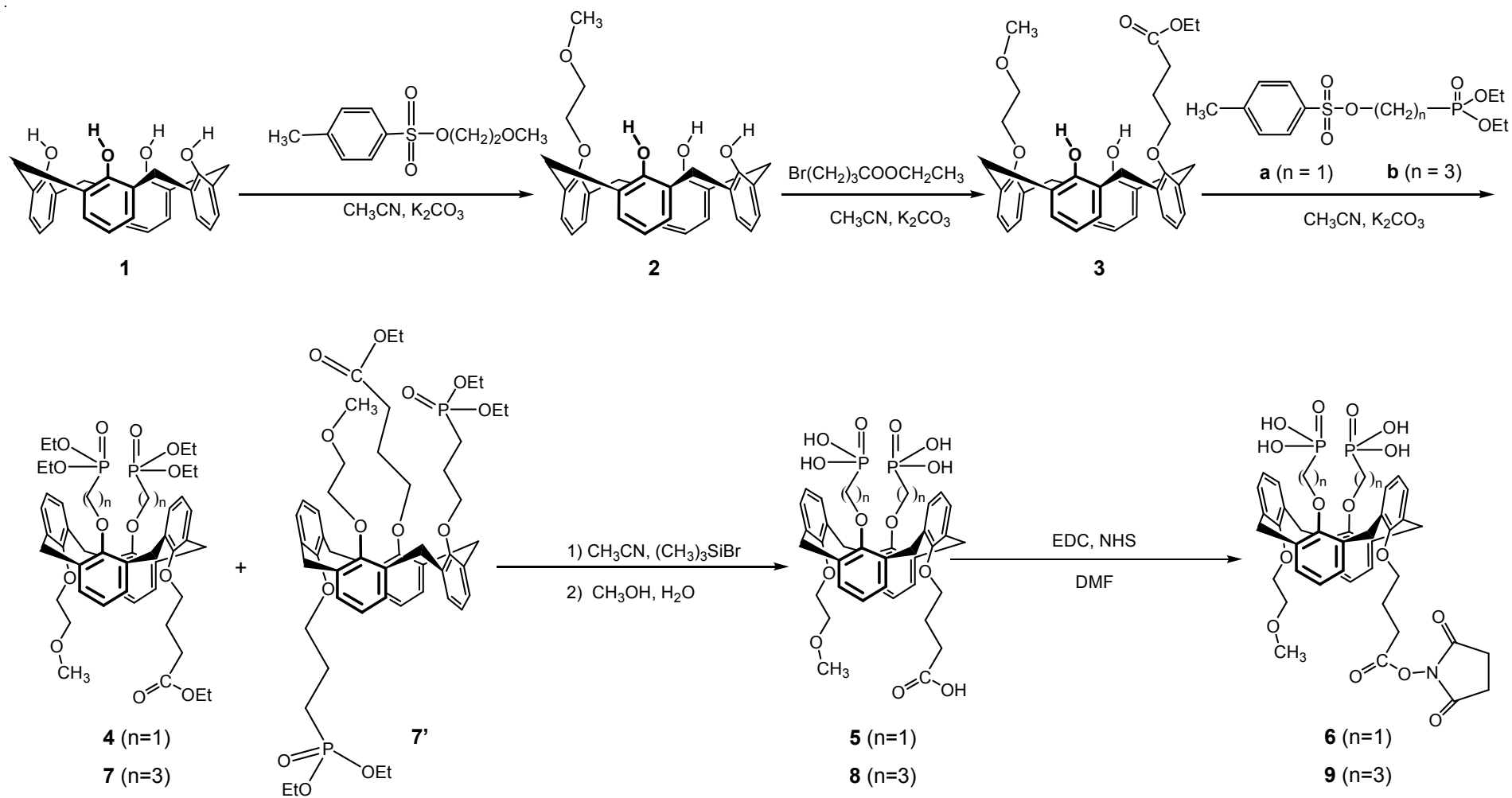


Table 1 : Successive couplings of calixarene 6 on the same gel

Experiment number	Addition of calixarene 6 ( $\mu\text{mol}$ )	Calixarene 6 found in the eluate ( $\mu\text{mol}$ )	% calixarene 6 coupled to the gel
1	2.99	1.99	33.5
2	2.99	1.97	34.1
3	6.00	6.15	-

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