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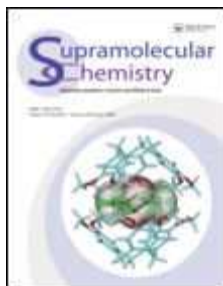
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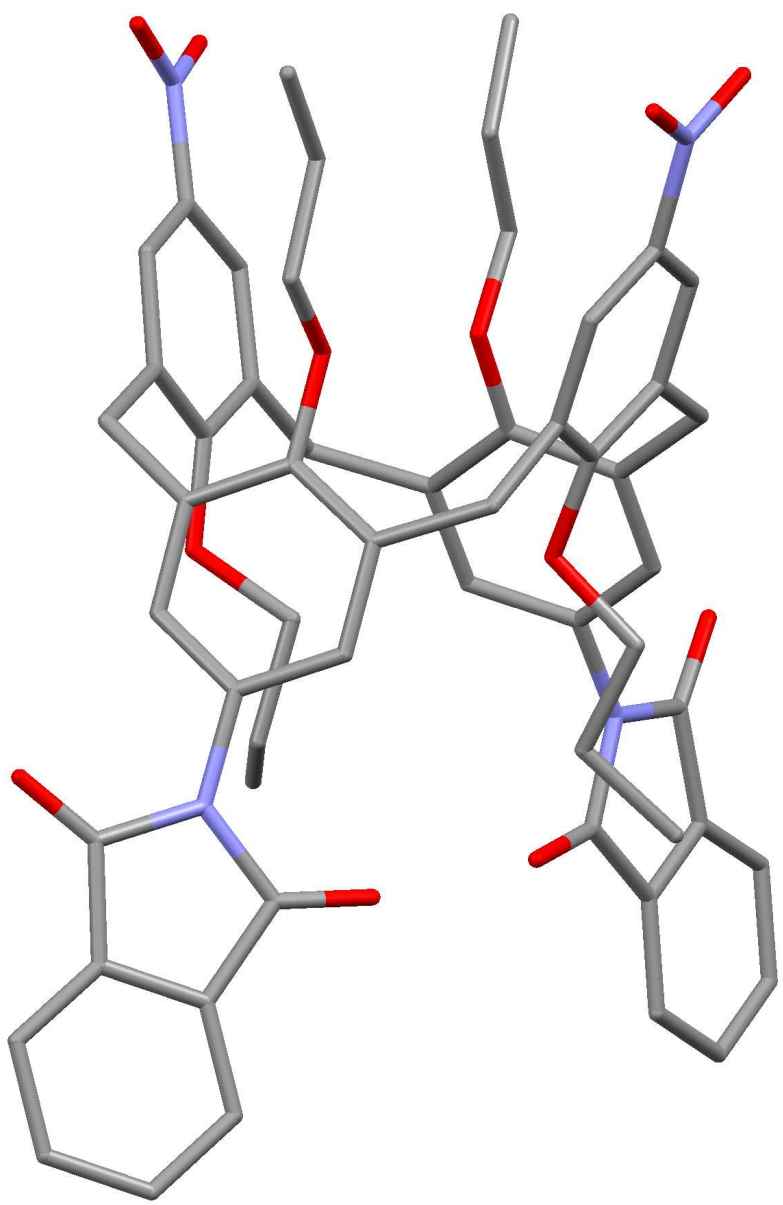


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# Tetra-CMPO-Derivatives of Calix[4]arenes fixed in the 1,3-Alternate Conformation

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## Abstract.

Calix[4]arene derivatives fixed in the 1,3-alternate conformation and substituted at one side by four carbamoylmethylphosphine oxide residues (=CMPO) were synthesized. Two CMPO groups are directly attached to the wide rim while the second pair is bound to the narrow rim via a tri- or tetramethylene spacer. Similar compounds, in which two CMPO groups at the wide rim are combined with two picolinamide groups or two ionisable carboxylic groups at the narrow rim were also prepared. Some of these calixarene derivatives were studied as extractants for lanthanides (La<sup>3+</sup>, Eu<sup>3+</sup>, Yb<sup>3+</sup>) and thorium (Th<sup>4+</sup>) from acidic solution to methylenechloride. For selected samples stability constants in methanol were determined by spectrophotometric titrations. Three compounds (**1b'**, **13**, **17**) in the 1,3-alternate conformation and one intermediate in the cone conformation (**18**) were confirmed by a crystal structure.

## Keywords:

Lanthanides, calix[4]arenes, complexation, extraction, crystal structures.

## Introduction

Carbamoylmethylphosphine oxides (CMPOs) are efficient extractants for actinides (and lanthanides) and especially the N,N-diisobutyl derivative is used on a technical scale (TRUEX-process).<sup>1</sup> CMPO is a bidentate ligand, and a trivalent cation surely binds more than one molecule of the ligand in its complex. Thus it appeared reasonable to attach several CMPO functions to a common platform. In fact tri-CMPO derivatives of triphenylmethanes<sup>2</sup> and tetra-CMPO derivatives of calix[4]arenes<sup>3</sup> are much more efficient extractants than CMPO itself. This is true for compounds, where the CMPO functions are attached to the wide rim<sup>4</sup> or to the narrow rim<sup>5</sup> Better extraction results are even obtained with linear<sup>6</sup> oligo-CMPOs and with calix[4]arenes bearing only two or three CMPO functions.<sup>7</sup>

Calix[4]arenes bearing ether residues equal to or larger than propyl are fixed in one of the four basic conformations (cone, partial cone, 1,2- and 1,3-alternate). Nearly all calix[4]arene derived ligands of the podand-type are based on the cone conformation<sup>8</sup> where all oxygens (and all *p*-positions) point in the same direction, although rare examples with other conformations are known<sup>9, 10, 11</sup> It should be possible, however, to use also the 1,3-alternate conformation as scaffold<sup>12</sup>, if the ligating groups are attached alternately to the wide and to the narrow rim, where an appropriate spacer could bring them to the same level. The 1,3-alternate skeleton is more rigid compared to the cone isomers, which still can change between two „pinched“ cone conformations. Considering the fact that a tetra-CMPO derived from a rigid biscrown-3 calix[4]arene is by a factor of 10 more efficient as extractant,<sup>13</sup> this rigidity could be even advantageous.

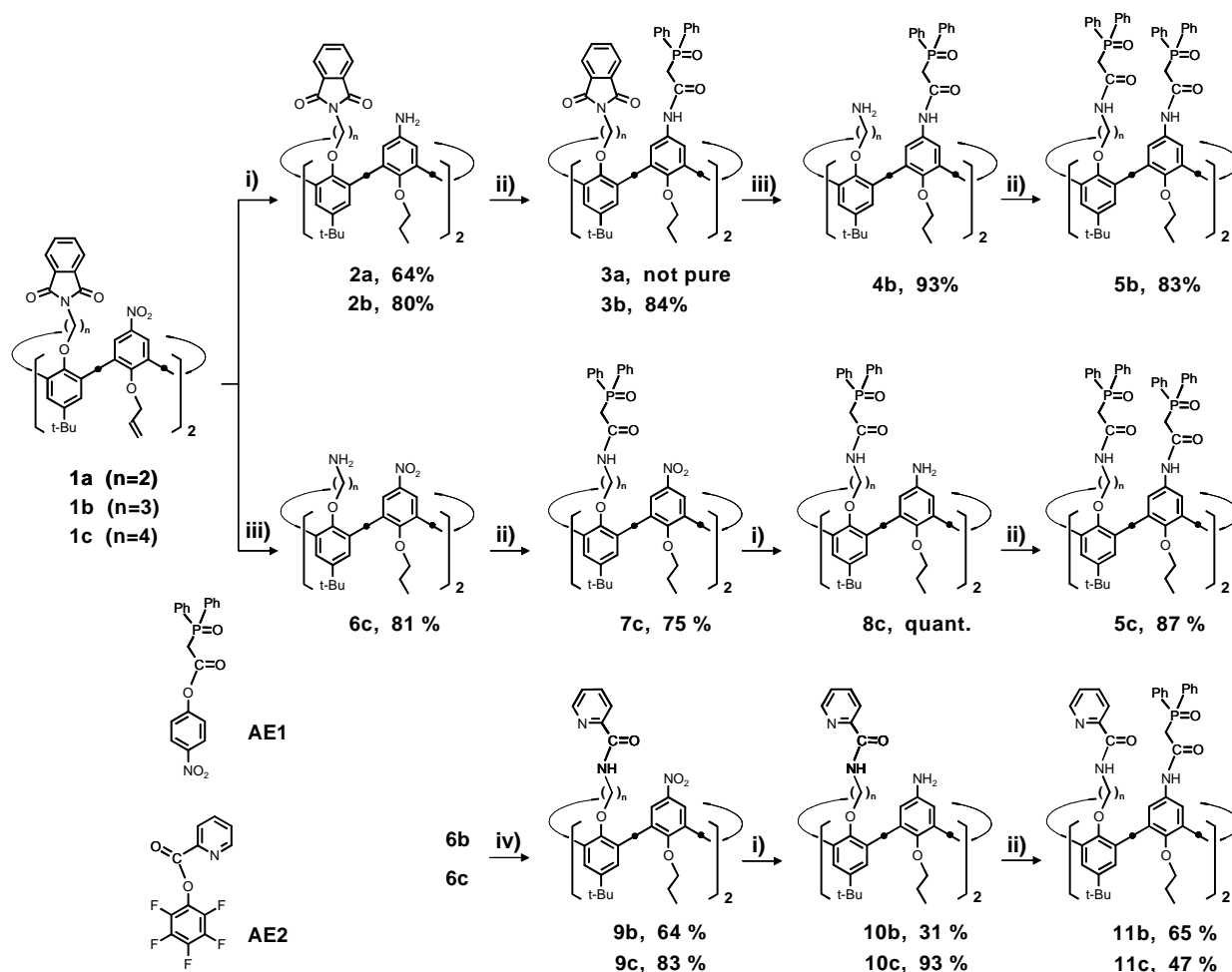
It should be also worthwhile to attach different ligating functions to the wide and narrow rim of the calix[4]arene in its 1,3-alternate conformation. Picolinamide groups, for instance, should lead to a better selectivity than CMPO functions alone.<sup>14, 15, 16</sup> Carboxylic acids could potentially act as anion exchanger and reduce the number of nitrate anions to be extracted into the organic phase. Lipophilic carboxylic acids are often used as synergisers for neutral ligands in nuclear waste treatment,<sup>17</sup> while polycarboxylic acids were proven to efficiently complex actinide<sup>18</sup> and lanthanide<sup>19</sup> cations.<sup>20</sup>

## Results and discussion

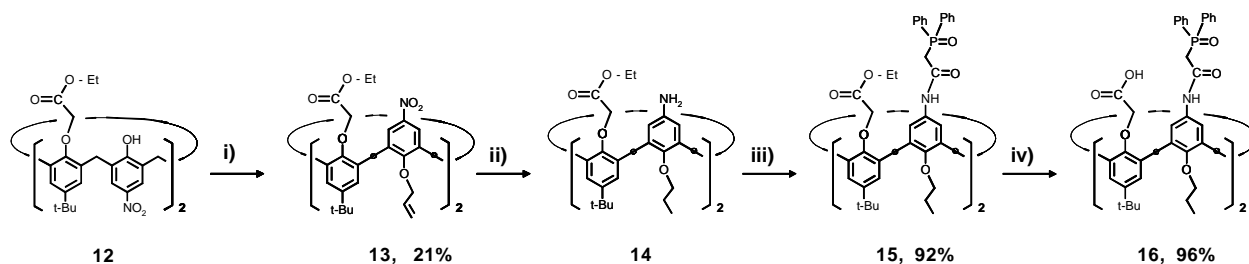
**Syntheses.** Aminogroups attached to the wide rim of a calix[4]arene are usually obtained by reduction of nitrogroups which are often introduced via ipso-nitration.<sup>21</sup> For the attachment at the narrow rim the alkylation by N-( $\omega$ -bromoalkyl)phthalimides (or by  $\omega$ -bromoalkylnitriles) followed by hydrazinolysis of the phthalimide groups (or by reduction of the nitrile groups) are convenient methods.

Since selective substitutions are possible only at the wide rim distinguishing phenol and phenoether units<sup>22</sup> the following two pathways (Scheme 1) were checked, starting with the known 1,3-alternate derivative **1**.<sup>23</sup>

**a):** Catalytic hydrogenation leads in excellent yields to the propoxy aniline derivative (amino propyl ether) **2a,b** ( $n=3,4$ ) which was acylated by the active ester **AE1**<sup>3, 24</sup> to give **3b** in 84%. (For  $n=2$  the product could not be sufficiently purified, for  $n=4$  this pathway was not further followed.) Cleavage of the phthalimide by hydrazine (93% of **4b**) and acylation of the aliphatic amino groups by **AE1** (83% of **5b** ( $n=3$ )) occurred without problems.



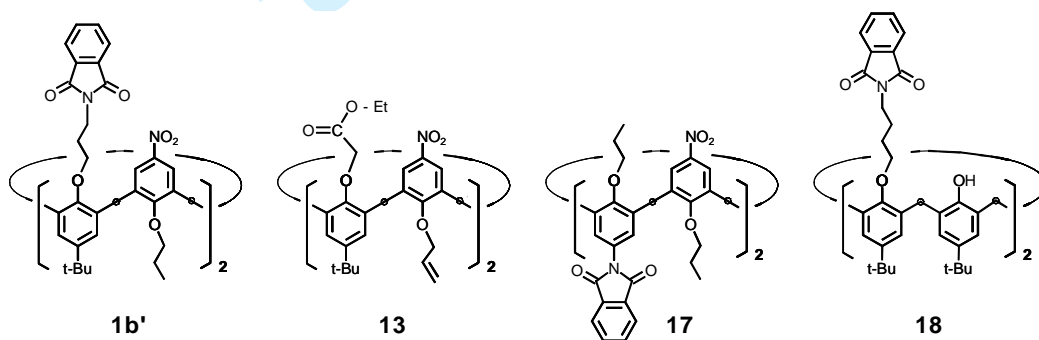
**Scheme 1** Syntheses of tetra-CMPO derivatives of calix[4]arenes in the 1,3-alternate conformation and of compounds bearing two CMPO and two picolinamide residues. i)  $H_2$ , Raney-Ni, THF, rt; ii) **AE1**,  $CH_2Cl_2$ , rt; iii) hydrazine, EtOH, reflux; iv) **AE2**,  $CH_2Cl_2$ , rt.



**Scheme 2** Synthesis of 1,3-alternate derivatives combining two CMPO with two carboxylic groups. i) allylbromide,  $\text{Cs}_2\text{CO}_3$ , DMF,  $50^\circ\text{C}$ ; ii)  $\text{H}_2$ , Raney-Ni, THF, rt; iii) **AE1**,  $\text{CH}_2\text{Cl}_2$ , rt; iv) LiOH, THF/MeOH, rt.

**b**): Alternatively (as studied for  $n=4$ ), cleavage of the phthalimide groups (of **1c**) with hydrazine occurred with the simultaneous hydrogenation of the allyl groups to give 81% of **6c**. Subsequent acylation by **AE1** (75% of **7c**) followed by quantitative hydrogenation of the nitro groups to **8c** and a second acylation step by **AE1** (87% of **5c** ( $n=4$ )) was also possible without any problems. It should be mentioned that the allyl groups must not be quantitatively hydrogenated during the cleavage of the phthalimide groups, since this will be completed in the next step. It is important, however, that the cleavage of the phthalimide groups is quantitative while nitro groups remain unchanged.

A direct conversion of **1** to the respective tetra amine (simultaneous or subsequent cleavage of the phthalimide groups and reduction of the nitro groups) was not attempted, although it should be more economic for those cases, where only one acyl-residue has to be attached.



**Table 1** Extraction of selected lanthanides and thorium by tetra-CMPOs **5**,  $c_L = 10^{-3}$  M ( $c_L = 10^{-4}$  M); values for a narrow and a wide rim tetra-CMPO fixed in the cone conformation are included for comparison.

		$\text{La}^{3+}$	$\text{Eu}^{3+}$	$\text{Yb}^{3+}$	$\text{Th}^{4+}$
<b>5b</b>	%E	11	11	9	(17)
	D	0.12	0.12	0.09	(0.2)
<b>5c</b>	%E	12	10	11	48 (12) <sup>a</sup>
	D	0.13	0.11	0.12	0.92 (0.13) <sup>a</sup>
narrow rim <sup>5</sup> ( $n=3$ )	%E	70	68	37	(96)
	D	2.33	2.12	0.58	(24)
wide rim <sup>6,7</sup>	%E	98	64	6.6	(61.8)
	D	49	1.78	0.07	(1.62)

<sup>a</sup> Values for  $c_L = 10^{-4}$  M.

**Table 2** Stability constants ( $\log \beta \pm \sigma_{n-1}$ ) for complexes of tetra-CMPOs **5** with some lanthanides in methanol at  $25^\circ\text{C}$  ( $I = 10^{-2}$  M,  $\text{Et}_4\text{NNO}_3$ ). Data for a wide rim tetra-CMPO in the cone conformation are included for comparison.

		$\text{La}^{3+}$	$\text{Eu}^{3+}$	$\text{Yb}^{3+}$
<b>5b</b>	1:1	$5.5 \pm 0.2$	$4.7 \pm 0.2$	$5.1 \pm 0.2$
	2:1	10.6	11.0	8.6
<b>5c</b>	1:1	$4.2 \pm 0.2$	$3.9 \pm 0.2$	$3.2 \pm 0.2$
	2:1	6.0	5.6	3.5
wide rim <sup>26</sup>	1:1	6.0	5.6	3.5
	2:1	10.6	11.0	8.6

Two similar calixarene derivatives combining two picolinamide functions<sup>25</sup> at the narrow rim (attached via three or four methylene groups) with two CMPO functions at the wide rim, were prepared in analogy to pathway **b**). Acylation of **6b,c** with **AE2**, the hexafluorophenyl ester of  $\alpha$ -picolinic acid<sup>27</sup> (64%/83% of **9b,c**), reduction of the nitro groups

(31%/93% of **10b,c**) and acylation with **AE1** (65%/47% of **11b,c**). The partly striking difference in the yield for the last steps indicates that the reaction conditions are not optimized. These syntheses of extractants **5** and **11** are summarized in Scheme 1.

In order to (partly) compensate the positive charge of the extracted cation we prepared compound **16**, where two CMPO functions are combined with two carboxyl groups. The synthesis starts with the known<sup>28</sup> diester **12** which is fixed in the 1,3-alternate conformation as di-allylether **13** (isolated yield 21%, together with 39% of the isomer in the partial cone conformation). Reduction/hydrogenation and direct acylation of the crude diamine **14** furnished the diester **15** (92%) which was hydrolysed by aqueous LiOH to give the di-CMPO-di-acid **16** with 96% yield. (see Scheme 2).

**Extraction and Complexation.** The extraction of selected cations (lanthanides and thorium) from 1.0 M nitric acid into dichloromethane was studied for two tetra-CMPO compounds (**5b**, **5c**). The respective extraction percentages %E and distribution coefficients D are given in Table 1 and compared with values previously obtained<sup>5-7</sup> for calixarenes fixed in the cone conformation and substituted at the wide or narrow rim by four CMPO-functions. These data show that the extraction ability of lanthanides is similar for **5b** and **5c** (and practically identical for La<sup>3+</sup>, Eu<sup>3+</sup>, Yb<sup>3+</sup>), but five to twenty times lower than for the analogues in the cone conformation. The stability constants of the complexes, however, are distinctly higher (by factors of 6 to 80) for **5b** than for **5c** (Table 2).

By all criteria, however, wide as well as narrow rim tetra-CMPOs in the cone conformation are better extractants/ligands than the derivatives in the 1,3-alternate conformation, which in addition are more difficult to synthesize. Both data sets show no real selectivity within the lanthanide series in contrast with the lower and especially the upper rim derivatives.

**Crystal structures.** Single crystals suitable for X-ray diffraction were obtained for three compounds fixed in the 1,3-alternate conformation, **1b'** (obtained from **1b** by selective hydrogenation of the allyl groups, or by direct alkylation, using propyl- instead of allylbromide), **13**, and **17** (a derivative with two different precursor functions for amino groups at the wide rim<sup>23</sup>). A crystal structure was also determined for the 1,3-diether **18** in the cone conformation,<sup>29</sup> the very first step in the synthesis of **1c**.

**18** assumes the usual pinched cone conformation where the aryl residues of the phenolic units are bent outwards, including angles of 148.7° and 132.2° with the reference plane defined by the four methylene bridge carbons. Consequently the two ether aryl units are bent towards the cavity, with angles of 114.7° and 108.9°. This conformation (with interplanar angles between opposite calix[4]arene aryl planes of 100.9° and 43.6°) permits a slightly larger distance between the (bulky) ether residues (distances O12-O32 = 4.534 Å and O22-O42 = 3.222 Å). The orientation of the phthalimide planes is obviously mainly determined by packing requirements, since the (CH<sub>2</sub>)<sub>4</sub>-linker (tetramethylene linker) allows for conformational freedom.

**Table 3** Comparison of some typical data taken from the crystal structures of three different calix[4]arene derivatives in the 1,3-alternate conformation (**1b'**, **13**, **17**) and **one** in the cone conformation (**18**).

Compounds:		<b>1b'</b>	<b>13</b> · CHCl <sub>3</sub>	<b>17</b>	<b>18</b> 2 H <sub>2</sub> O	
Distances (Å) within the reference plane	C1 - C2	5.139	5.108	5.145	5.120	
	C2 - C3	5.110	5.137	5.134	5.105	
	C3 - C4	5.185	5.130	5.109	5.129	
	C4 - C1	5.144	5.125	5.123	5.105	
	C1 - C3	7.266	7.061	6.944	7.291	
	C2 - C4	7.278	7.365	7.412	7.173	
	opposite phenolic oxygens	O12-O32	3.588	4.471	4.180	4.534
		O22-O42	4.149	4.585	4.546	3.222
opposite <i>p</i> -C atoms		C15-C35	7.989	7.481	7.487	7.466
	C25-C45	7.377	6.326	6.580	9.548	
Angles (°) with main plane	<i>p</i> - <i>t</i> Bu	112.3	113.1	120.6 <sup>a</sup>	148.7	
		131.9	109.5	104.5 <sup>a</sup>	132.2	
		112.0	107.4	111.2	114.7	
	<i>p</i> -NO <sub>2</sub>	115.4	99.9	100.7	108.9	
		64.2	42.7	45.2	43.6	
		47.4	27.4	31.9	100.9	
between opposite planes	<i>p</i> - <i>t</i> Bu					
	<i>p</i> -NO <sub>2</sub>					
within main plane	folding C1-C3	4.8	15.0	21.7	2.5	
	folding C2-C4	4.8	15.6	23.1	2.5	

<sup>a</sup> Phthalimide instead of *t*-butyl.

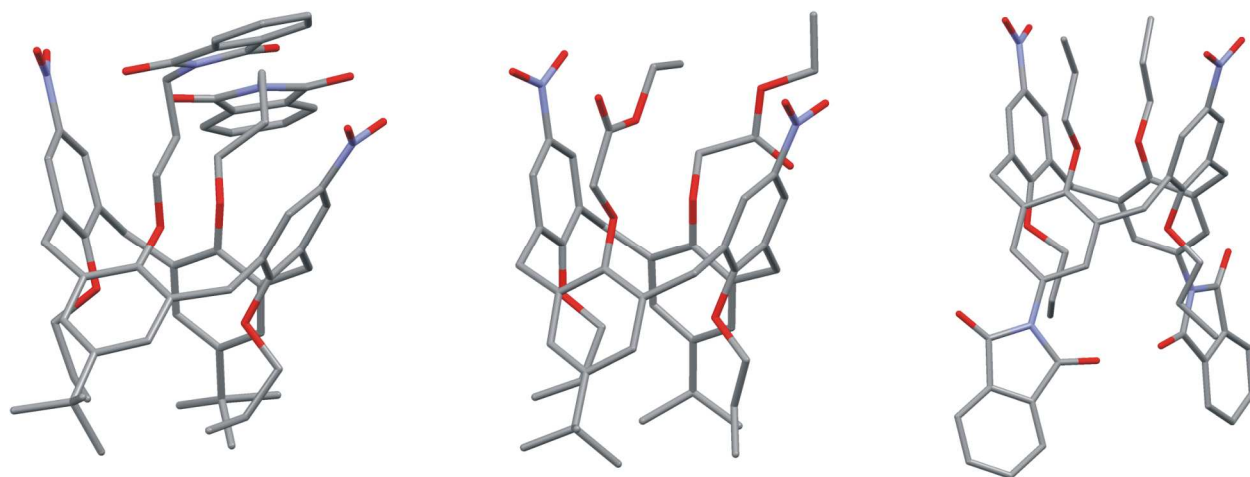
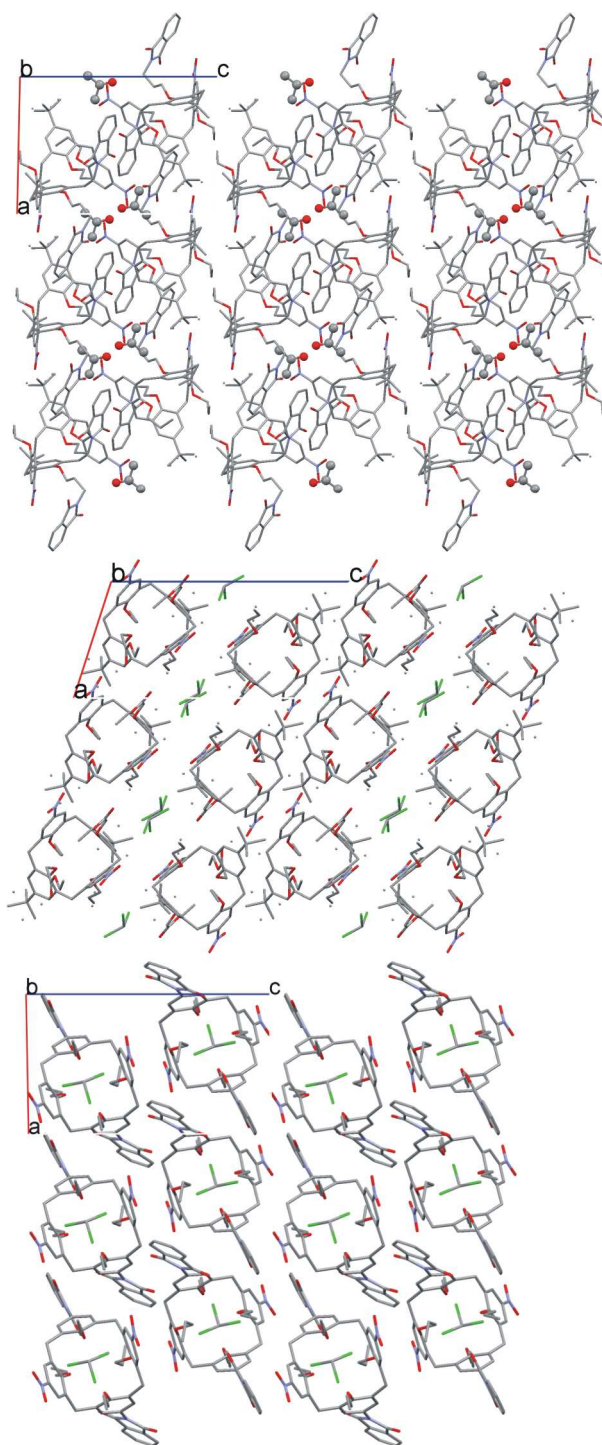


Fig. 1 Molecular conformation of the three 1,3-alternate derivatives **1b'**, **13**, and **17** (from the left to the right)





**Fig. 2** Packing of molecules seen along the b-axis in the lattice of **1b'**, **13** and **17** (from the top to the bottom); for **1b'** the included acetone molecules are shown as "ball and stick" models. .

The best plane through the C-atoms of the bridging methylene groups is a suitable reference plane also for the derivatives in the 1,3-alternate conformation, although the deviation from this common plane reaches 0.357 Å for **17**, with the four carbon atoms laying alternately on both sides (for **13** and **1b'** this deviation is 0.243 and 0.076 Å). The shape of the molecule may be characterised then by the angle between the aromatic planes and this reference plane (see Table 3). The deviation of the reference plane from an geometrically exact plane can be characterised also by the angle between two triangles obtained by folding along the diagonal (C1-C3 or C2-C4). These angles are small (4.75°) for **1b'**, but larger for **13** (15.00/15.64°) and **17** (21.70/23.12°).

However, this folding does not entirely explain the strong differences found for the distances of opposite phenolic

oxygen (largest for **1b'**,  $\Delta = 0.561 \text{ \AA}$ ) and opposite *p*-aryl carbons (largest for **13**,  $\Delta = 1.155 \text{ \AA}$ ). Most probably also packing effects are responsible for such deviations in the exact shape of the 1,3-alternate skeleton, since especially the *p*-substituents (*t*-butyl, nitro, phthalimido) are rather different in size, shape and polarity.

Further distances and angles of the three molecules with 1,3-alternate conformation are compared in Table 3, which contains also data for two compounds (precursors) in the cone conformation. The molecular conformation of compounds **1b'**, **13** and **17** is compared in Fig. 1, while their packing is compared in Fig. 2.

In the crystal lattice **13**·CHCl<sub>3</sub> forms columns with alternating directionality parallel to the *b*-axis. Within the *a*-*b*-plane these columns form double layers separated by channels which contain the chloroform molecules (Fig. 2, middle). **17**·CHCl<sub>3</sub> forms similar columns along the *b*-axis, but here the molecules within each column are separated by solvent molecules, which are "included" in the cavity surrounded by the phthalimide and the nitro groups. The larger size of this cavity, compared with **13**, may be the reason for this inclusion. Otherwise both structures are rather similar. A description of the packing of **1b'** is more complicated. Fig. 2 (left) shows a view along the *b*-axis in which the included acetone molecules are shown in "ball and stick" representation.

## Experimental Part

**Syntheses.** Compounds **1b**, **1c**, **2b** and **6b** were prepared as described earlier. **Error! Bookmark not defined.**

**5,17-Di-*t*-butyl-11,23-dinitro-26,28-diphthalimidoethoxy-25,27-di-allyloxy-calix[4]arene 1a.** Compound **1a** was obtained (together with its partial cone isomer) as described for the analogous compounds **1b** and **1c** from the dinitro compound. A suspension of 5,17-Di-*t*-butyl-11,23-dinitro-26,28-diphthalimidoethoxy-calix[4]arene (2.9 g, 2.98 mmol) in dry DMF (40 ml) and Cs<sub>2</sub>CO<sub>3</sub> (7.8 g, 23 mmol) was stirred under nitrogen at 50 °C for 6 days. Water (50 ml) was added to stop the reaction and after several washing (3x50 ml water) the organic phase was dried over MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure. Colourless crystals (0.05 g, 2%) of the desired 1,3-alternate isomer **1a** were isolated by column chromatography (chloroform/hexane, 1:2) together with the *partial cone* isomer (0.27 g, 9%). Clearly these yields are not optimized.

**1a:** m.p. 251-253 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.78 (s, 18H, *t*-Bu), 3.72, 3.86 (2d, 4/4H, <sup>2</sup>*J* = 15.6 Hz, Ar-CH<sub>2</sub>-Ar), 3.79 (m, 8H, O-CH<sub>2</sub>-, -CH<sub>2</sub>-N), 4.10 (d, 4H, <sup>2</sup>*J* = 5.16 Hz, CH<sub>2</sub>=CH-CH<sub>2</sub>-O-), 5.08 (m, 4H, CH<sub>2</sub>=CH-), 5.75 (m, 2H, CH<sub>2</sub>=CH-), 6.95, 8.28 (2s, 4/4H, ArH), 7.66-7.85 (m, 8H, Phth-H).

**partial cone isomer of 1a:** m.p. 215-217 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.00 (s, 18H, *t*-Bu), 3.24 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, Ar-CH<sub>2</sub>-Ar), 3.70-4.25 (m, 18H, O-CH<sub>2</sub>-, -CH<sub>2</sub>-N, Ar-CH<sub>2</sub>-Ar, -O-CH<sub>2</sub>-CH=CH<sub>2</sub>), 4.85, 5.22 (2m, 2/2H, CH<sub>2</sub>=CH-), 5.56, 5.88 (2m, 1/1H, CH<sub>2</sub>=CH-), 6.57, 6.88 (2d, 2/2H, <sup>4</sup>*J*=2.2 Hz, ArH), 7.82 (m, 8H, Phth-H), 8.00, 8.42 (2s, 2/2H, ArH).

**5,17-Di-*t*-butyl-11,23-diamino-26,28-diphthalimidoethoxy-25,27-dipropoxy-calix[4]arene 2a.** The diamine **2a** was prepared as described earlier for **2b**. **Error! Bookmark not defined.** A clear solution of **1a** (50 mg, 0.04 mmol) in THF (15 ml) was hydrogenated under normal pressure with Raney-Ni. The catalyst was filtered off, the solvent was evaporated and the dry residue was dissolved in CHCl<sub>3</sub> (3 ml) and reprecipitated with hexane to give **2a** as yellow powder (30

mg, 64%); mp 315°C; <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>)  $\delta$  0.57 (t, 6H, <sup>3</sup>*J* = 7.16 Hz, CH<sub>3</sub>-CH<sub>2</sub>-), 1.23 (s, 18H, *t*-Bu), 3.17 (bt, 4H, -NH<sub>2</sub>), 3.45-3.60 (2bt, 4/4H, -CH<sub>2</sub>-N, O-CH<sub>2</sub>-), 3.74, 3.84 (2d, 4/4H, <sup>2</sup>*J* = 12.2 Hz, Ar-CH<sub>2</sub>-Ar), 6.88, 6.95 (2s, 4/4H, ArH), 7.68-7.79 (2m, 8H, Phth-H).

**5,17-Di-*t*-butyl-11,23-diCMPOamido-26,28-diphthalimidopropoxy-25,27-dipropoxy-calix[4]arene 3b.** *p*-Nitrophenyl carbamoylmethyl diphenyl phosphine oxide (**AE1**, 0.25 g, 0.65 mmol) was added to a clear solution of diamine **2b** (0.28 g, 0.27 mmol) and few drops of NEt<sub>3</sub> in dichloromethane (30 ml). The mixture was stirred at ambient temperature over night. The *p*-nitrophenol formed during the acylation was extracted with an aqueous solution of NaOH (5%, 3 x 100 ml). After drying over MgSO<sub>4</sub> the solvent was evaporated under reduced pressure, the residue was dissolved in dichloromethane (5 ml). Compound **3b** was obtained as white powder by reprecipitation from hexane; 0.4 g, 84%; m.p. 194-196 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  0.65 (t, 6H, <sup>3</sup>*J* = 7.3 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.20 (m, 22H, *t*-Bu, -CH<sub>2</sub>-), 1.51 (m, 4H, -CH<sub>2</sub>-), 3.26-3.69 (m, 24H, Ar-CH<sub>2</sub>-Ar, O-CH<sub>2</sub>-, -CH<sub>2</sub>-P, -CH<sub>2</sub>-N), 6.90, 6.95 (2s, 8H, ArH), 7.40-7.75 (m, 28H, *m*, *p*-Ph<sub>2</sub>H, *o*-Ph<sub>2</sub>H, Phth-H), 8.84 (bs, 2H, NH); FD-MS, (M<sup>+</sup>+H) *m/z* = 1508.9.

**5,17-Di-*t*-butyl-11,23-di-CMPOamido-26,28-diaminopropoxy-25,27-dipropoxy-calix[4]arene 4b.** Hydrazine (1.6 ml) was added to a solution of **3b** (0.33 g, 0.2 mmol) in ethanol (15 ml). After 2 h under reflux the reaction mixture was evaporated under reduced pressure; the residue was dissolved in chloroform (10 ml) and washed three times with water. The organic phase was dried over MgSO<sub>4</sub> and evaporated. The desired diamine was obtained as white powder by reprecipitation from chloroform (5 ml) and hexane (25 ml). 0.25 g, 93%; m.p. 212-214 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  0.60 (t, 6H, <sup>3</sup>*J* = 6.8 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.00 (m, 4H, -CH<sub>2</sub>-), 1.19 (s, 18H, *t*-Bu) 1.46 (m, 4H, -CH<sub>2</sub>-), 3.22-4.03 (m, 28H, NH<sub>2</sub>, Ar-CH<sub>2</sub>-Ar, O-CH<sub>2</sub>-, -CH<sub>2</sub>-P, -CH<sub>2</sub>-N), 6.98, 7.23 (2s, 8H, ArH), 7.55-7.92 (m, 20H, *m*, *p*-Ph<sub>2</sub>H, *o*-Ph<sub>2</sub>H), 10.24 (bs, 2H, NH); FD-MS, (M<sup>+</sup>+H) *m/z* = 1250.7.

**5,17-Di-*t*-butyl-11,23-diCMPOamido-26,28-diCMPOamidopropoxy-25,27-dipropoxy-calix[4] arene 5b.** The tetra-CMPO **5b** was prepared by the same acylation procedure described above for **3b**. Starting from a solution of diamine **4b** (0.22 g, 0.14 mmol) in dichloromethane (30 ml) and **AE1** (0.16 g, 0.42 mmol), **5b** was obtained as white

powder, 0.2 g, 83 %; m.p. 152 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.61 (t, 6H,  $^3J = 7.7$  Hz,  $-\text{CH}_2-\text{CH}_3$ ), 1.20 (m, 22H, *t*-Bu,  $-\text{CH}_2-$ ), 2.75 (m, 4H,  $-\text{CH}_2-$ ), 2.72 (t, 4H,  $^3J = 7.0$  Hz,  $-\text{CH}_2-\text{N}$ ), 3.20 (t, 4H,  $^3J = 7.3$  Hz,  $\text{O}-\text{CH}_2-$ ), 3.50, 3.56 (2d, 8H,  $^2J = 15.8$  Hz,  $\text{Ar}-\text{CH}_2-\text{Ar}$ ), 3.61 (m, 8H,  $\text{O}-\text{CH}_2-$ ,  $-\text{CH}_2-\text{P}$ ), 3.76 (d, 4H,  $^2J = 10.3$  Hz,  $-\text{CH}_2-\text{P}$ ), 6.87, 7.09 (2s, 8H,  $\text{ArH}$ ), 7.38-7.81 (m, 40H, *m*, *p*- $\text{Ph}_2\text{H}$ , *o*- $\text{Ph}_2\text{H}$ ), 8.96, 10.05 (2bs, 2/2H,  $\text{NH}$ ); FD-MS, ( $\text{M}^+ + \text{H}$ )  $m/z = 1732.5$ .

**5,17-Di-*t*-butyl-11,23-diCMPOamido-26,28-diCMPOamidobutyloxy-25,27-dipropoxy-calix[4]arene 5c.** Tetra-CMPO **5c** was prepared as described for **5b**. 100 mg (0.078 mmol) diamine **8c** in 10 ml dichloromethane were acylated with and **AE1** (72 mg, 0.18 mmol). After purification by column chromatography ( $\text{CHCl}_3/\text{MeOH}$  98:2) 0.138 g (87 %) of **5b** were obtained as pink powder; m.p. 152 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.65 (t, 6H,  $^3J = 7.7$  Hz,  $-\text{CH}_2-\text{CH}_3$ ), 1.01-1.23 (m, 26H, *t*-Bu, 3x- $\text{CH}_2-$ ), 2.93 (t, 4H,  $^3J = 7.0$  Hz,  $-\text{CH}_2-\text{N}$ ), 3.08, 3.27 (2t, 8H,  $^3J = 7.3$  Hz, 2xO- $\text{CH}_2-$ ), 3.37, 3.67 (2d, 4H,  $^2J = 14.3$  Hz,  $\text{CH}_2-\text{P}$ ), 3.65, 3.69 (2d, 8H,  $^2J = 15.5$  Hz,  $\text{Ar}-\text{CH}_2-\text{Ar}$ ), 6.92, 7.27 (2s, 8H,  $\text{ArH}$ ), 7.38-7.74 (m, 40H, *m*, *p*- $\text{Ph}_2\text{H}$ , *o*- $\text{Ph}_2\text{H}$ ), 8.31, 10.20 (2bs, 2/2H,  $\text{NH}$ ).

**5,17-Di-*t*-butyl-11,23-dinitro-26,28-diaminopropoxy-25,27-dibutyloxy-calix[4]arene 6c.** 0.45 g (0.43 mmol) of the bis-phthalimide **1c** were dissolved in EtOH (30 ml), hydrazine (3 ml) was added and the reaction mixture was refluxed for 2 h. After the usual work up the diamine **6c** was obtained as yellow oil (0.3 g, 81 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.80 (t, 6H,  $^3J = 7.4$  Hz,  $-\text{CH}_2-\text{CH}_3$ ), 1.23 (m, 22H, *t*-Bu,  $-\text{CH}_2-$ ), 1.47 (m, 4H,  $-\text{CH}_2-$ ), 2.28 (bs, 4H,  $-\text{NH}_2$ ), 2.69 (bt, 4H,  $-\text{CH}_2-$ ), 3.51 (t, 4H,  $^3J = 7.4$  Hz,  $\text{N}-\text{CH}_2-$ ), 3.59 (bt, 4H,  $\text{O}-\text{CH}_2-$ ), 3.63, 3.71 (2d, 4/4H,  $^2J = 15.2$  Hz,  $\text{Ar}-\text{CH}_2-\text{Ar}$ ), 6.98, 7.94 (2s, 4/4H,  $\text{ArH}$ ).

**5,17-Di-*t*-butyl-11,23-dinitro-26,28-diCMPOamidobutyloxy-25,27-dipropoxy-calix[4]arene 7c.** The acylation of diamine **6c** by **AE1** was carried out at rt over night as follows: 0.3 g **6c** (0.35 mmol) dissolved in dichloromethane (15 ml) were reacted with 0.32 g (0.84 mmol) **AE1**; 0.35 g (75 %) of diCMPOamide **7c** were obtained as white powder; m.p. 142 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.80 (t, 6H,  $^3J = 7.4$  Hz,  $-\text{CH}_2-\text{CH}_3$ ), 1.22 (m, 26H, *t*-Bu, 2x- $\text{CH}_2-$ ), 3.13 (m, 4H,  $-\text{CH}_2-$ ), 3.07 (bt, 4H,  $-\text{CH}_2-\text{N}$ ), 3.48 (2t, 4/4H, 2x  $\text{O}-\text{CH}_2-$ ), 3.66 (d, 4H,  $^2J = 13.7$  Hz,  $-\text{CH}_2-\text{P}$ ), 3.66, 3.75 (2d, 8H,  $^2J = 15.2$  Hz,  $\text{Ar}-\text{CH}_2-\text{Ar}$ ), 6.96, 7.88 (2s, 4/4H,  $\text{ArH}$ ), 7.38-7.81 (m, 22H, *m*, *p*- $\text{Ph}_2\text{H}$ , *o*- $\text{Ph}_2\text{H}$ ,  $\text{NH}$ ).

**5,17-Di-*t*-butyl-11,23-diamino-26,28-diCMPOamidobutyloxy-25,27-dipropoxy-calix[4]arene 8c.** A solution of **7c** (110 mg, 0.082 mmol) and hydrazine (1 ml) in ethanol (15 ml) was refluxed for 2 h with Raney/Ni as catalyst. The solvent was evaporated under reduced pressure; the formed residue was dissolved in chloroform (10 ml) and washed three times with water. The organic phase was dried over  $\text{MgSO}_4$ , the solvent was evaporated under reduced pressure. The diamine **8c** was obtained as yellow oil which was used in the next step without further purification.

**5,17-Di-*t*-butyl-11,23-dinitro-26,28-dipicolinamidopropoxy-25,27-dipropoxy-calix[4]arene 9b.** The active ester **AE2** (0.21 g, 0.73 mmol) was added to a suspension of diamine **6b** (0.25 g, 0.3 mmol) in chloroform (30 ml). The mixture was stirred at room temperature until the tlc shows that no starting material was left. The pentafluorophenol formed during the reaction was extracted with a solution of  $\text{Na}_2\text{CO}_3$  (5 %, 4 x 100 ml) and the organic phase was dried over  $\text{MgSO}_4$ . The solvent was evaporated under reduced pressure, the residue was dissolved in dichloromethane (5 ml) from which the desired compound was obtained by reprecipitation with hexane as yellow powder; 0.2 g (64 %); m.p. 127-129 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.78 (t, 6H,  $^3J = 7.35$  Hz,  $-\text{CH}_2-\text{CH}_3$ ), 1.21 (s, 18H, *t*-Bu), 1.41 (m, 4H,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ), 1.71 (m, 4H,  $-\text{CH}_2-\text{CH}_3$ ), 3.45-3.50 (m, 8H,  $-\text{CH}_2-\text{N}$ ,  $\text{O}-\text{CH}_2-$ ), 3.65-3.81 (m, 12H,  $\text{Ar}-\text{CH}_2-\text{Ar}$ ,  $\text{O}-\text{CH}_2-$ ), 6.95 (s, 4H,  $\text{ArH}$ ), 7.40 (m, 2H,  $H_b$ ), 7.80 (m, 2H,  $H_c$ ), 7.99 (s, 4H,  $\text{ArH}$ ), 8.17 (m, 2H,  $H_d$ ), 8.29 (bt, 2H,  $-\text{NH}$ ), 8.58 (m, 2H,  $H_a$ ).

**5,17-Di-*t*-butyl-11,23-dinitro-26,28-dipicolylamidobutyloxy-25,27-dipropoxy-calix[4]arene 9c.** Starting from diamine **6c** (0.25 g), containing traces of compounds which has unhydrogenated allyl groups the desired compound **9c** was obtained as the analogous mixture with the respective allyl compounds as described for **9b**; 0.25 g (83 %) were isolated as a white powder. The signals belonging to the protons of **9c** are listed below.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (t, 6H,  $^3J = 7.35$  Hz,  $-\text{CH}_2-\text{CH}_3$ ), 1.21 (s, 18H, *t*-Bu), 1.20-1.66 (m, 12H,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_3$ ), 3.46-3.86 (m, 20H,  $-\text{CH}_2-\text{N}$ , 2x  $\text{O}-\text{CH}_2-$ ,  $\text{Ar}-\text{CH}_2-\text{Ar}$ ), 6.96 (s, 4H,  $\text{ArH}$ ), 7.39 (m, 2H,  $H_b$ ), 7.81 (m, 2H,  $H_c$ ), 7.92 (s, 4H,  $\text{ArH}$ ), 8.20 (m, 2H,  $H_d$ ), 8.25 (bt, 2H,  $-\text{NH}$ ), 8.56 (m, 2H,  $H_a$ ).

**5,17-Di-*t*-butyl-11,23-diamino-26,28-di-picolinamidopropoxy-25,27-dipropoxy-calix[4]arene 10b.** Raney/Ni was added to a clear solution of **9b** (740 mg, 0.70 mmol) in THF (20 ml), and the reaction mixture was stirred under hydrogen during 4 days. When the hydrogen uptake was complete the catalyst was filtered off and the solvent evaporated under reduced pressure. The residue was dissolved in chloroform (10 ml) and the desired amine was precipitated with hexane (15 ml) as a white powder, 200 mg, 31 %; m.p. 120 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.59 (t, 6H,  $^3J = 7.7$  Hz,  $-\text{CH}_2-\text{CH}_3$ ), 1.01-1.08 (m, 4H,  $-\text{CH}_2-$ ), 1.22 (s, 18H, *t*-Bu), 1.55-1.59 (m, 4H,  $-\text{CH}_2-$ ), 2.89 (bs, 4H,  $-\text{NH}_2$ ), 3.17-3.22 (m, 8H,  $-\text{CH}_2-\text{N}$ ,  $-\text{CH}_2-\text{O}$ ), 3.51 (t, 4H,  $^3J = 7.3$  Hz,  $\text{O}-\text{CH}_2-$ ), 3.65, 3.74 (2d, 4/4H,  $^2J = 15.8$  Hz,  $\text{Ar}-\text{CH}_2-\text{Ar}$ ), 6.48, 6.92 (2s, 4/4H,  $\text{ArH}$ ), 7.38 (m, 2H,  $H_b$ ), 7.80 (m, 2H,  $H_c$ ), 8.13 (m, 2H,  $H_d$ ), 8.26 (bt, 2H,  $-\text{NH}$ ), 8.51 (m, 2H,  $H_a$ ).

**5,17-Di-*t*-butyl-11,23-diamino-26,28-dipicolinamidobutyloxy-25,27-dipropoxy-calix[4]arene 10c.** Diamine **10c** was prepared analogously. For a solution of mixture **9c** (0.25 g) in THF (20 ml) the hydrogenation was complete after 30 h. The diamine was reprecipitated from chloroform/hexane (~20 ml, 1:3) as white powder, 220 mg, 93 %; m.p. 132

°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.64 (t, 6H, <sup>3</sup>J = 7.7 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.09-1.22 (m, 26H, 2x-CH<sub>2</sub>-, t-Bu), 1.82-1.86 (m, 4H, -CH<sub>2</sub>-), 3.21-3.73 (m, 20H, -CH<sub>2</sub>-N, -CH<sub>2</sub>-O, Ar-CH<sub>2</sub>-Ar), 6.42 (s, 4H, -NH<sub>2</sub>), 6.92, 6.97 (2s, 4/4H, ArH), 7.38 (m, 2H, H<sub>b</sub>), 7.81 (m, 2H, H<sub>c</sub>), 8.18 (m, 2H, H<sub>d</sub>), 8.30 (bt, 2H, -NH), 8.54 (m, 2H, H<sub>a</sub>).

**5,17-Di-*t*-butyl-11,23-diCMPO-26,28-dipicolinamidopropoxy-25,27-dipropoxy-calix[4]arene 11b.** The final acylation was done as described above e.g. for **6b**. 200 mg of diamine **10b** (0.20 mmol) dissolved in dichloromethane (30 ml) were reacted with 490 mg (2.4 mmol) of active ester **AE1**. 170 mg of **11b** (65 %) were isolated as white powder; m.p. 108-109 °C; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ 0.93 (t, 6H, <sup>3</sup>J = 7.2 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.18 (s, 18H, t-Bu), 1.44 (m, 4H, -CH<sub>2</sub>-), 3.05-3.78 (m, 24H, -CH<sub>2</sub>-N, -CH<sub>2</sub>-O, Ar-CH<sub>2</sub>-Ar, -CH<sub>2</sub>-P), 6.32 (s, 2H, -NH), 6.95, 7.12 (2s, 4/4H, ArH), 7.49-7.99 (m, 22H, *m*, *p*-Ph<sub>2</sub>H, *o*-Ph<sub>2</sub>H, H<sub>b</sub>), 8.34 (m, 2H, H<sub>c</sub>), 8.50 (m, 2H, H<sub>d</sub>), 8.73 (bt, 2H, -NH), 9.77 (m, 2H, H<sub>a</sub>).

**5,17-Di-*t*-butyl-11,23-diCMPO-26,28-dipicolinamidobutyloxy-25,27-dipropoxy-calix[4]arene 11c.** 220 mg diamine **10c** (0.23 mmol) in dichloromethane (30 ml) were reacted analogously with 325 mg (0.55 mmol) **AE1** to yield 160 mg (47 %) of **11c** as white powder; m.p. 117-119 °C; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>) δ 0.60 (t, 6H, <sup>3</sup>J = 7.2 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.21 (m, 30H, t-Bu, -CH<sub>2</sub>-), 3.06-3.72 (m, 24H, -CH<sub>2</sub>-N, -CH<sub>2</sub>-O, Ar-CH<sub>2</sub>-Ar, -CH<sub>2</sub>-P), 6.90, 7.06 (2s, 4/4H, ArH), 7.40-7.80 (m, 22H, *m*, *p*-Ph<sub>2</sub>H, *o*-Ph<sub>2</sub>H, H<sub>b</sub>), 8.11 (m, 2H, H<sub>c</sub>), 8.34-8.50 (m, 6H, H<sub>d</sub>,-NH, H<sub>a</sub>), 9.45 (s, 2H, NH).

**5,17-Di-*t*-butyl-11,23-dinitro-25,27-diallyloxy-26,28-diethoxycarbonylmethoxy-calix[4]arene 13 (1,3-alternate) and 13a (partial cone).** A stirred suspension of dinitro-calixarene **12** (1.3 g, 1.6 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (4 g, 12.8 mmol) in dry DMF (40 ml) was heated to 40 °C under nitrogen. After 1 h allylbromide (1.1 ml, 12.8 mmol) was added and the reaction was continued for 7 days. The DMF was removed under reduced pressure and the residue was treated with chloroform (25 ml) and water (75 ml). The organic phase was washed with water (2x75 ml), dried (MgSO<sub>4</sub>) and the solvent was evaporated to give a yellow oil. Analysis by t.l.c showed the presence of two compounds, which were separated and purified by column chromatography (CHCl<sub>3</sub>) and identified by NMR as the *1,3-alternate* and the *partial cone* isomers.

**13 (1,3-alternate):** White-yellow crystals, yield 0.3 g, 21 %; mp 199-201 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.24 (t, 6H, <sup>3</sup>J = 6.1 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.24 (s, 18H, t-Bu), 3.66, 4.07 (2d, 4/4H, <sup>2</sup>J = 14.7, 15.1 Hz, Ar-CH<sub>2</sub>-Ar), 3.99 (s, 4H, -CH<sub>2</sub>-O-), 4.19 (m, 8H, O-CH<sub>2</sub>), 5.14 (m, 4H, CH<sub>2</sub>=CH-), 5.78 (m, 2H, CH<sub>2</sub>=CH-), 6.98, 8.02 (2s, 4/4H, ArH).

**13a (partial cone):** Yellow powder, yield 0.54 g, 39 %; mp 222-223 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.00 (s, 18H, t-Bu), 1.31 (t, 6H, <sup>3</sup>J = 7.3 Hz -CH<sub>2</sub>-CH<sub>3</sub>), 3.22, 3.65, 4.07 (3d, 2/2/2H, <sup>2</sup>J = 13.6, 13.9, 13.6 Hz, Ar-CH<sub>2</sub>-Ar), 4.15-4.37 (m, 14H, 3xO-CH<sub>2</sub>-, Ar-CH<sub>2</sub>-Ar), 4.94, 5.40 (2m, 2/2H, -CH=CH<sub>2</sub>), 6.06, 6.12 (2m, 2/2H, -CH=CH<sub>2</sub>), 6.50, 6.88 (2d, 2/2H, <sup>4</sup>J = 2.5, 2.5 Hz, ArH), 8.03, 8.37 (2s, 2/2H, ArH).

**5,17-Di-*t*-butyl-11,23-diCMPO-25,27-dipropoxy-26,28-diethoxycarbonylmethoxy-calix[4]arene 15.** Pd/C (0.1 g) was added to a solution of the dinitro compound **13** (0.3 g, 0.34 mmol) in THF (15 ml) and the suspension was stirred under hydrogen atmosphere at rt. After the hydrogen uptake was complete, the catalyst was filtered off and the solvent was evaporated. The residue was dissolved in dichloromethane (15 ml) to form a clear solution. **AE1** (80 mg, 0.09 mmol) and few drops of triethylamine were added, and the mixture was stirred at rt for 12 h. An aqueous solution of NaOH (30 ml, 5 %) was added and the stirring was continued for additional 30 min. Then the organic phase was separated, washed three times with diluted aqueous NaOH (3 x 30 ml), dried over MgSO<sub>4</sub> and evaporated under reduced pressure. The product was reprecipitated from CHCl<sub>3</sub>/hexane (15 ml, 1:2) to give 0.11g (92 %) of a white powder; m.p. 210-212 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.73, 1.13 (2t, 6/6H, <sup>3</sup>J = 7.7, 7.3 Hz, 2x-CH<sub>2</sub>-CH<sub>3</sub>), 1.20 (m, 22H, t-Bu, -CH<sub>2</sub>-), 3.35, 4.01 (2t, 4/4H, <sup>3</sup>J = 7.7, 6.99 Hz, 2xO-CH<sub>2</sub>-), 3.44 (d, 4H, <sup>2</sup>J = 12.9 Hz, -CH<sub>2</sub>-P), 3.57 (s, 4H, O-CH<sub>2</sub>-), 3.64, 3.93 (2d, 4/4H, <sup>2</sup>J = 15.8 Hz, Ar-CH<sub>2</sub>-Ar), 6.92, 7.15 (2s, 4/4H, ArH), 7.43-7.78 (m, 20H, *m*, *p*-Ph<sub>2</sub>H, *o*-Ph<sub>2</sub>H), 9.06 (bs, 2H, NH).

**5,17-Di-*t*-butyl-11,23-diCMPO-25,27-dipropoxy-26,28-dicarboxymethoxy-calix[4]arene 16.** An aqueous solution of LiOH (98 mg/2 ml water) was added to the solution of **15** (0.11 g, 0.09 mmol) in THF (7 ml) and MeOH (4 ml) and the mixture was stirred at rt over night and neutralized with diluted HCl. The desired acid was isolated by precipitation with water. The white precipitate was filtered and washed with water and dried. 0.1 g (96 %) of diacid **16** were obtained as white powder; m.p. 264 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 0.65 (t, 6H, <sup>3</sup>J = 7.4 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.15 (m, 4H, -CH<sub>2</sub>-CH<sub>3</sub>), 1.23 (s, 18H, t-Bu), 1.96 (s, 2H, -COOH), 3.31 (t, 4H, <sup>3</sup>J = 7.4 Hz, O-CH<sub>2</sub>-), 3.67, 3.92 (2d, 4/4H, <sup>2</sup>J = 16.2 Hz, Ar-CH<sub>2</sub>-Ar), 3.76 (d, 4H, <sup>2</sup>J = 16.0 Hz, -CH<sub>2</sub>-P), 3.69 (s, 4H, O-CH<sub>2</sub>-), 7.00, 7.16 (2s, 4/4H, ArH), 7.51-7.84 (m, 20H, *m*, *p*-Ph<sub>2</sub>H, *o*-Ph<sub>2</sub>H), 9.46 (bs, 2H, NH).

**Binding studies.** Extraction experiments of lanthanide and thorium nitrates (C<sub>M</sub> = 10<sup>-4</sup> M) from 1 M nitric acid into dichloromethane were performed at 20 °C. A colorimetric method using Arsenazo-III was applied to determine the concentration of the metal ions before and after extraction in the aqueous phase. The full procedure, the starting materials and the calculations of the distribution coefficients (D) and the percentage extraction (%E) have already been described in detail.<sup>3</sup> Complexation data, i.e. the stoichiometry and the stability constants (log β) of the species formed in methanol, were derived from spectrophotometric titrations at 25 °C. The experimental procedure<sup>30</sup> and the

1  
2 data processing by program Specfit<sup>31</sup> have been previously published. The ligand concentrations were ranging  
3 between  $5 \times 10^{-5}$  and  $10^{-4}$  M and the ionic strength was settled as constant by using  $10^{-2}$  M  $\text{Et}_4\text{NNO}_3$  as background-  
4 electrolyte.

5 Stock solutions of lanthanide and thorium nitrates used in extraction and complexation experiments were  
6 standardized by complexometric titrations with EDTA in the presence of xylenol orange as coloured indicator.  
7

8 **Crystallographic data.** Single crystals were obtained from a solution in acetone/methanol (**1b'**) or  
9 chloroform/methanol (**13**, **17**, **18**) which was overlaid in a test tube by an excess of methanol. **The two molecules of**  
10 **water found per molecule 18 in its crystal structure were obviously uptaken from the atmosphere.**

11 Intensity data were collected on a STOE IPDS II two-circle diffractometer with graphite-monochromated  $\text{MoK}_\alpha$   
12 radiation at 173K. For **13** and **17** an empirical absorption correction was performed using the MULABS<sup>32</sup> option in  
13 PLATON.<sup>33</sup> The structures were solved by direct methods using the program SHELXS<sup>34</sup> and refined against  $F^2$  with  
14 full-matrix least-squares techniques using the program SHELXL. Error! Bookmark not defined. Hydrogen atoms were  
15 included at calculated positions with fixed displacement parameters. In **1b'**, one *tert*-butyl group is disordered over  
16 two positions (site occupation factors 0.491(6)/0.509(6)). In **13**, the two *tert*-butyl groups (site occupation factors  
17 0.449(6)/0.551(5) and 0.320(2)/0.680(2)) and the terminal two C atoms of a propenoxy group (site occupation factors  
18 0.40(2)/0.60(2)) are disordered over two positions. The C-C bond lengths in the disordered *tert*-butyl groups were  
19 restrained to 1.54(1)Å and the C=C double bonds in the propenoxy groups to 1.30(1)Å. In **18**, the water H atoms  
20 could not be located and were omitted from refinement. The geometric parameters of the side chain O32 to N324  
21 were restrained to be equal to those of O12 to N124.

22 Crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Data Centre:  
23 reference numbers: **1b'** CCDC 734171; **13** CCDC 734172; **17** CCDC 734173; **18** CCDC 734174.  
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**Table 4** Crystal Data and Structure Refinement Details for **1b'**, **13**, **17** and **18**; data collection with a Stoe-IPDS-II two-circle-diffractometer, solution and refinement with SHELXS and SHELXL.

Compound	<b>1b'</b>	<b>13</b>	<b>17</b>	<b>18</b>
empirical formula	C <sub>64</sub> H <sub>68</sub> N <sub>4</sub> O <sub>12</sub> · CH <sub>3</sub> COCH <sub>3</sub>	C <sub>50</sub> H <sub>58</sub> N <sub>2</sub> O <sub>12</sub> · CHCl <sub>3</sub>	C <sub>56</sub> H <sub>52</sub> Cl <sub>3</sub> N <sub>4</sub> O <sub>12</sub> · CHCl <sub>3</sub>	C <sub>68</sub> H <sub>78</sub> N <sub>2</sub> O <sub>8</sub> · 2 H <sub>2</sub> O
color	colourless	Colourless	light yellow	colourless
shape	block	Block	block	block
fw [g/mol]	1143.30	998.35	1092.38	1087.36
temperature [K]	173	173	100	173
wave length [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	P-1	P-1	P-1	P2 <sub>1</sub> /c
Z	2	2	2	4
cell parameters				
a [Å]	12.924(3)	10.4879(6)	9.8020(7)	13.0264(9)
b [Å]	14.094(3)	14.0724(8)	15.6199(11)	24.5795(15)
c [Å]	17.881(4)	19.2015(11)	17.9197(13)	19.9439(16)
α [°]	78.44(3)	96.336(4)	72.276(6)	90
β [°]	87.30(3)	104.191(4)	88.546(6)	105.126(6)
γ [°]	70.72(3)	111.084(4)	88.444(6)	90
Volume [Å <sup>3</sup> ]	3011.5(10)	2501.0(2)	2612.0(3)	6164.4(8)
calcd density [Mg/m <sup>3</sup> ]	1.261	1.326	1.389	1.172
abs coeff [mm <sup>-1</sup> ]	0.088	0.247	0.244	0.078
crystal size [mm <sup>3</sup> ]	0.42 x 0.40 x 0.22	0.32 x 0.18 x 0.14	0.43 x 0.41 x 0.36	0.25 x 0.19 x 0.17
2θ <sub>max</sub> [°]	55.24	55.52	59.62	51.64
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -23 ≤ l ≤ 22	-13 ≤ h ≤ 13, -18 ≤ k ≤ 17, -25 ≤ l ≤ 25	-13 ≤ h ≤ 13, -21 ≤ k ≤ 19, -24 ≤ l ≤ 24	-15 ≤ h ≤ 15, -29 ≤ k ≤ 29, -23 ≤ l ≤ 24
no. of rflns collected	114465	66572	55297	64136
no. of indep rflns	13916	11731	14801	11636
R <sub>int</sub>	0.0786	0.0701	0.0777	0.1496
absorption correction	none	multi-scan	multi-scan	none
T <sub>min</sub> , T <sub>max</sub>	-	0.917, 0.970	0.902, 0.917	-
data / restraints /parameter	13916 / 1 / 787	11731 / 5 / 688	14801 / 0 / 685	11636 / 9 / 721
goodness of fit	1.017	1.010	0.896	0.961
R1,wR2 [I > 2σ(I)]	0.0659, 0.1758	0.0479, 0.1229	0.0464, 0.1104	0.1027, 0.2671
R1,wR2 [all data]	0.0822, 0.1873	0.0729, 0.1317	0.0793, 0.1189	0.1723, 0.3205
largst diff peak and hole, eÅ <sup>-3</sup>	0.883, -0.650	0.691, -0.542	0.474, -0.514	0.674, -0.751

## Conclusions

Calix[4]arenes fixed in the 1,3-alternate conformation have been used for the first time as basic skeleton for the attachment of four carbamoylmethyl phosphine oxide residues or of two CMPO functions in combination with two picolinamide or (potentially ionizable) carboxylic groups. Preliminary extraction and complexation studies with selected lanthanides showed, however, that this new arrangement does not lead to improved properties in comparison to narrow or wide rim tetra-CMPO derivatives of calix[4]arenes in the cone conformation. Most probably this is not caused by the more rigid scaffold, which might be even beneficial, but to an inappropriate mutual situation of the ligating functions. MD-simulations should be helpful to find their best arrangement.

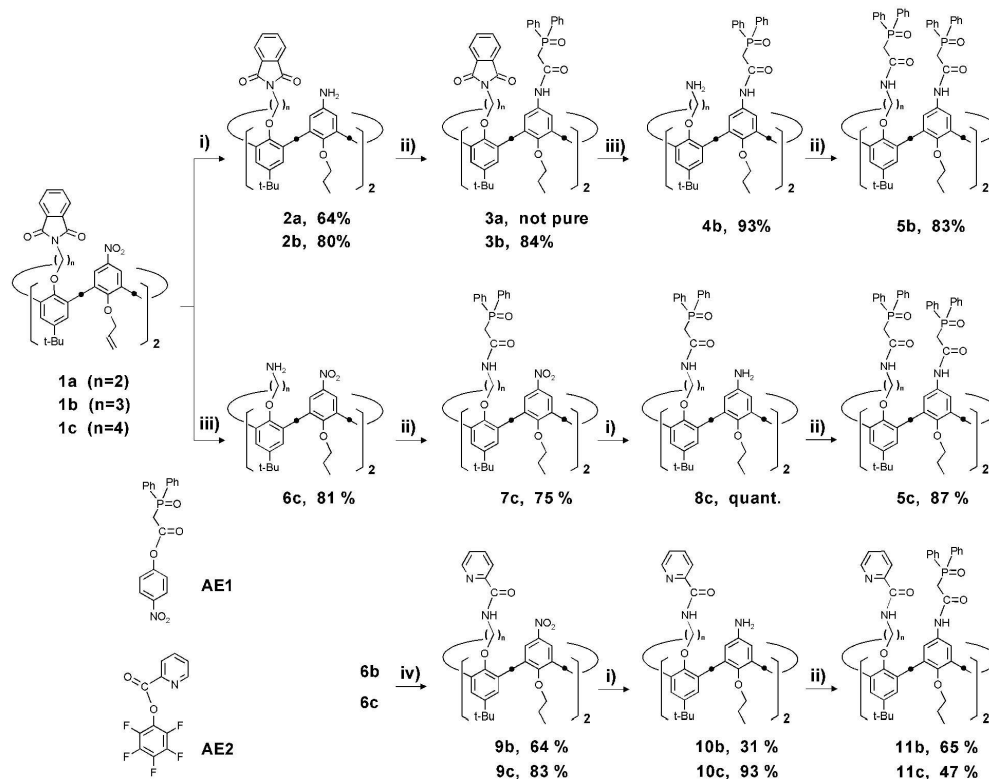
## Acknowledgements

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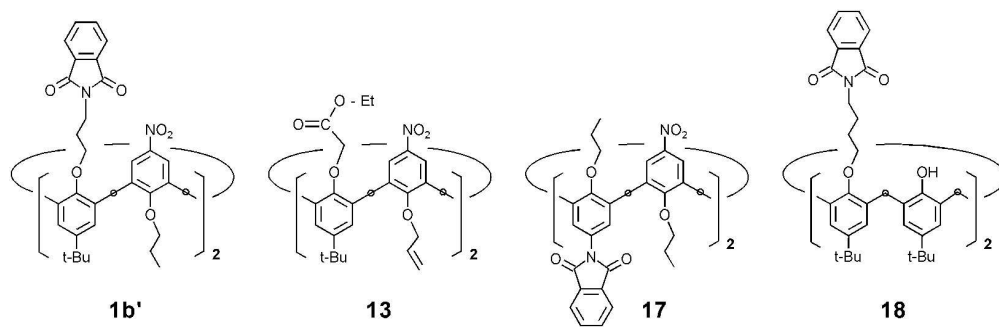
## Notes and references

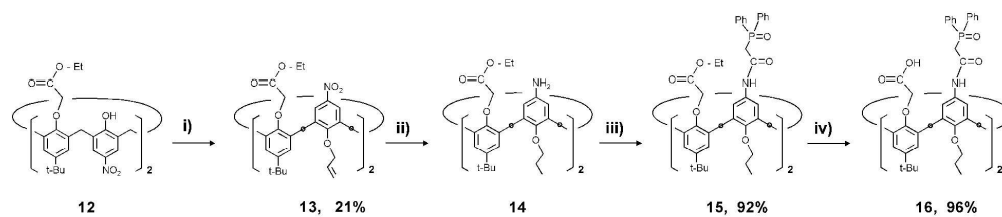
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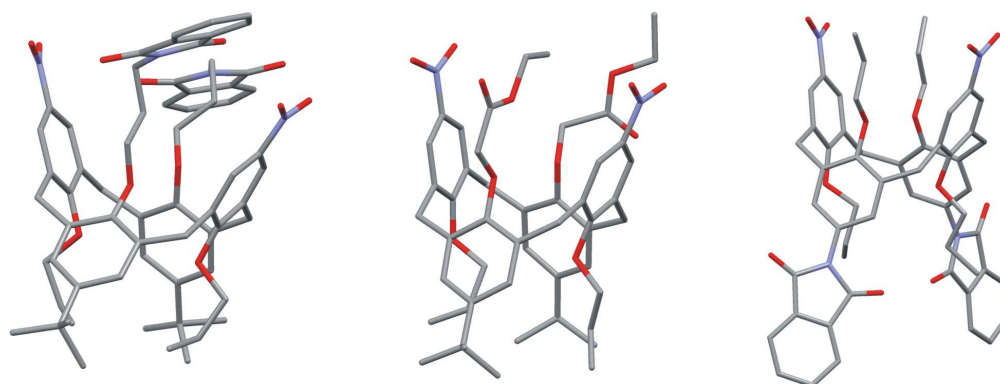
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