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Selective O-alkylations with glycol chlorohydrins via the Mitsunobu reaction. A versatile route to calix[4]- and 1,1′-binaphthocrowns

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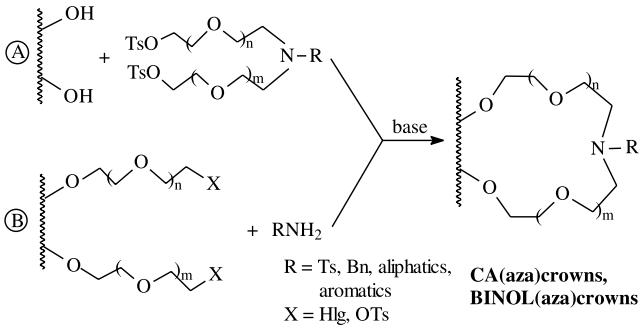
Dedicated to Professor Károly Lempert on his 80th birthday

Abstract—Selective monoalkylation of *p-tert*-butylcalix[4]arene and BINOL with oligoethylene glycol chlorohydrins was achieved under the Mitsunobu protocol using DEAD/TPP. The method provides a simple access to ether precursors capable of cyclising to various crowns.

1. Introduction

In the last decade a large number of supramolecular systems combining the unique properties of calixarenes (CA) and crowns have been described[1,2] and applied in analytical and separation chemistry.[3,4] Recently, calix[4](aza)crowns have attracted great interest due to the easy and versatile derivatisation of the nitrogen atom in the crown ring. N-Alkylation provides a convenient route to the introduction of various side-chains, most frequently additional binding sites or sensing (chromo/fluorophore) units.[5–12]

Although the classical synthesis of azacrown ethers (route A) has also been utilised in the access to calix(aza)crowns,[7] the cyclisation of ω-chloro or tosyloxy-glycolethers with different amine derivatives is preferred (route B)[5,6,8] (Scheme 1). The protecting groups (R=Ts, Bn) can then be removed by reductive methods to afford a free NH in the symmetric position of the crown ring (n=m), which can be further derivatised.[6,8] Although the complexation characteristics of calix(aza)crowns should be infuenced by the position of the nitrogen atom in the ring, asymmetric analogues (where $m \neq n$), still have not been studied. This kind of structure was also found to be essential in chiral 1,1′-binaphtho(crowns), where the recognition of primary amine enantiomers was improved by an asymmetric crown ether binding site.[13] Apart from calix(aza)crowns, the respective 1,1′-binaphthyl analogues have only been examplified by a few racemic derivatives,[14] though these chiral molecules may have potential in designing chromoionophores for the optical recognition of ammonium salt enantiomers.[15]



Scheme 1. Synthetic routes to monoazacrowns.

The synthesis of asymmetric CA- and BINOL-azacrown hosts ($m \neq n$) require precursors with two different ω-halogen/(tosyloxy)ether chains which cannot be introduced either in the CA or in the BINOL molecule by simple stepwise base-promoted alkylations. In both cases protection/deprotection methods[16–18] have to be used to obtain the target compounds. To overcome the inconvenience and low overall yields of the four-step procedures, a rapid alkylation method is herein reported for the selective etherification of *p-tert*-butylcalix[4]arene and BINOL with oligoethylene glycol chlorohydrins.

Keywords: Calix[4]arene; BINOL; O-Alkylation; Mitsunobu reaction; Crown ethers.
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2. Results and discussion

Recently, we have described the convenient application of the Mitsunobu reaction in the selective 1,3-dialkylation- and cycloalkylation of *p-tert*-butylthiacalix[4]arene (TCA) with alcohols and glycols.[19,20] We have shown that quite different results were achieved with the calix[4]arene (CA) counterpart in the same reactions.[20] The higher reactivity and lower selectivity of TCA versus CA were attributed to the more acidic (and less differences in pK_a) OHs and to the 15% larger cavity size. Actually, mono-alkylation of TCA with any alcohols could not be attained, and 1,3-diethers or tetraethers always being formed.[19] These observations prompted us to investigate the possibility of selective alkylation of CA and BINOL[21] with oligoethylene glycol derivatives under the standard Mitsunobu protocol using triphenylphosphine (TPP) and diethyl azodicarboxylate (DEAD) coupling agents (Scheme 2).

2.1. Synthesis of CA- and BINOL mono- and diethers

The reactions were performed at ambient temperature treating CA **1** or (±)-BINOL **2** with glycol chlorohydrins **3a**-**c** and TPP/DEAD (Caution! DEAD may explode if exposed to shock, friction, or heating) in toluene using different molar ratios: (1) **1/3**/(TPP/DEAD)=1:2:2.2, (2) **2/3**/(TPP/DEAD)=1:1.2–1.5:1.3–1.6, respectively. After 2 h reaction (0.5 h was sufficient for **2**) the starting material was consumed and exclusively monoethers **5b**,**c** and **7b**,**c** were formed when **3b**,**c** had been used. In this way, (*S*)-**7b** was prepared in enantiomerically pure form from (*S*)-BINOL. The more reactive **3a** afforded a separable mixture of monoethers **5a** (with a small amount of diether **9a**), and **7a** with diether **10a** in 2:1 ratio, respectively. The generally moderate yields of monoethers (35–50%) refer to 1 mmol scale and can be increased by scaling-up (in 5 mmol scale **5b** and **7b** were obtained in yields of 65–70%).

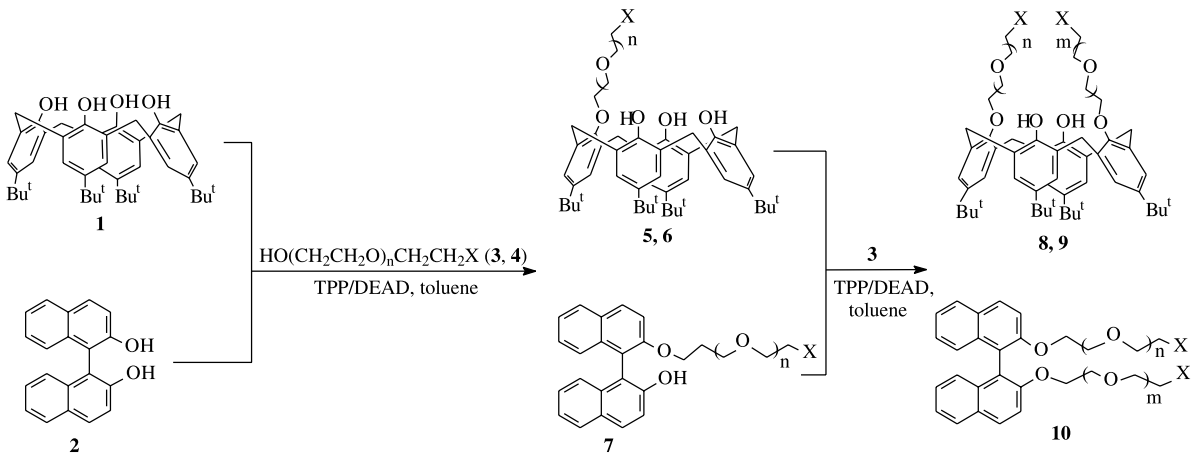
Symmetrical diethers **8a**,**b** and **10a**,**b** were cleanly obtained under the same protocol by increasing the molar ratios to **1**, **2/3**/(TPP/DEAD)=1:3:3.5. On the use of **3b**, however, 1 h reflux was required to complete the reaction. As expected, the long chain chlorohydrin **3c** was not sufficiently reactive to afford CA or BINOL diethers even under vigorous conditions. Making use of the high reactivity of **3a**,**d**, mixed diethers **9a**-**c** and **10c**,**d** including (*S*)-**10c** could easily be prepared by the treatment of monoethers **5b**,**c** and **7b** with 1.5 equiv. of **3a** or **3d** at room temperature. In contrast, the reaction of **7c** with **3a** did not lead to complete conversion even at elevated temperature, and pure asymmetric diether could not be separated from the mixture.

From a synthetic point of view it was of interest to check the reactivity of tosylates **4a** and **4b** under similar conditions. Both analogues reacted more sluggishly with CA **1** as compared with the respective chlorohydrins **3** requiring two molar excess of reagents for the monoether derivatives **6a**,**b**, and four molar excess of reagents for the diethers **8c**,**d** under 2 h reflux in both cases. Notably, these reactions took place in the BINOL series, too, but we failed to obtain pure tosylethers due to separation problems. The molecules containing reactive tosylate end-groups in the chain are regarded as valuable intermediates, albeit they are accessible otherwise, but in significantly longer multi-step reactions.

None of the mono and diethers prepared in this study have been described until now, except for the debutylated analogue of **8a**, which was obtained in a slow, base-promoted alkylation of the parent CA with diethylene glycol monochlorohydrin tosylate.[10]

2.2. Cyclisations of mono- and diethers

The calixarene- and BINOL monoethers and diethers in hand provided a simple access to crowns and azacrowns of different type by self-condensation (monoethers) or by cyclising with *p*-toluenesulfonamide (diethers). Although these reactions were not optimised, they offer a useful synthetic alternative for the preparation of certain crowns.



3a (X = Cl, n = 1)
3b (X = Cl, n = 2)
3c (X = Cl, n = 3)
3d (X = Br, n = 0)
4a (X = TsO, n = 1)
4b (X = TsO, n = 2)

	5a	5b	5c	6a	6b	7a	7b	7c	8a	8b	8c	8d	9a	9b	9c	10a	10b	10c	10d
X	Cl	Cl	Cl	TsO	TsO	Cl	Cl	Cl	Cl	Cl	TsO	TsO	Cl, Br	Cl	Cl	Cl	Cl	Cl	Cl, Br
n	1	2	3	1	2	1	2	3	1	2	1	2	3	2	3	1	2	2	3
m	-	-	-	-	-	-	-	-	1	2	1	2	0	1	1	1	2	1	0
%	83	43	45	47	50	65	43	50	81	77	50	59	42	81	76	64	70	58	53

Scheme 2. Synthesis of CA and BINOL mono- and diethers via the Mitsunobu reaction.

2.3. Calix[4]- and 1,1′-binaphthocrowns

Monoethers **5a**-**c**, and **7b**,**c** exposed to basic conditions underwent intra- and/or intermolecular cyclisations depending on the chain length, affording calix- and binaphthocrowns **11**-**13** (Fig. 1).

The reactions were conducted in MeCN (48 h reflux) using a large excess of K_2CO_3 (equimolar KI was added). Compound **5a** possessing a short chain cyclised to 1,2-calix[4](crown-3) **11a**,[22] while **5c** with a long chain afforded exlusively 1,3-calix[4](crown-5) **12b**.[23] Compound **5b**, which has a medium chain length, gave predominantly also the 1,3-calix[4](crown-4) **12a**[24] with traces of the 1,2-isomer **11b**.[25] Interestingly, we have obtained the same results, when CA was treated with di-, tri- and tetraethylene glycol under the Mitsunobu protocol.[20] The structure of regioisomers **11** and **12** has been determined earlier by others with the aid of the ^{1}H NMR spectra, which display characteristic differences in the splitting pattern of the bridging methylene protons for the proximally-coupled **11**[22,25] versus the distally-coupled **12**.[23,24]

Notably, Shinkai et al.[24] investigated the reaction of calix[4]arene tetrols and triethylene glycol ditosylate in the presence of various alkali carbonate bases to optimise the yield of the 1,3-calix[4](crown-4) **12a**. In these reactions a complex mixture was obtained containing the target **12a** and several side-products, among others 1,2-calixcrown-4 **11b**, non-cyclised intermediate and dimers in comparable amounts. In the light of these results, our indirect method, after optimisation, may have advantages over the traditional direct cyclisations.

Racemic BINOL monoether **7b** and its enantiomer (*S*)-**7b** were smoothly cyclised exclusively to bis(binaphtho-crown-8) (±)-**13b** and (*S*)-**13b**, respectively, which were also the major products in the direct ring closure of 1,1′-bi-2-naphthol with triethylene glycol ditosylate.[26] Compound **7c**, however, gave a 2:1 mixture of mono-(binaphtho-crown-5) **13a** and bis(binaphtho-crown-10) **13c** indicating that the longer tetraethyleneoxy chain of **7c** allows simultaneous intra- and intermolecular reaction pathways. That is the reason why only a low yield of **13a** was achieved in the cyclisation of **2** with tetraethylene glycol ditosylate.[14] Better results were reported for the Okahara cyclisation of *O*,*O*-bis(2-hydroxyethoxyethoxy)-1,1′-bi-2-naphthol.[27]

2.4. Calix[4]- and 1,1′-binaphtho(aza)crowns

Di-chloroethers **8**-**10** were cyclised with *p*-tosylamide ($TsNH_2$) to 1,3-calix[4]- and 1,1′-binaphtho(aza)crown-5,-6, and 7 (**14**, **15**), respectively. This base-promoted ring closure has been used mainly in the case of 1,3-calix[4]arene (bis)chloroethers not containing free phenolic OH groups, probably to avoid a possible self-condensation. Indeed, when the debutylated analogue of **14a** was synthesized by this method using Cs_2CO_3 in DMF solvent, a low yield was reported.[28] Since the N-alkylation of $TsNH_2$ can effectively be performed in the presence of a weaker base, we used a 5-fold excess of K_2CO_3 in DMF at 100 °C (48 h) to effect the cyclisation. Under these conditions the expected N-cyclised products were obtained in good yields. Thus, compounds **8a**,**b** gave the symmetric calix[4](aza)-crowns **14a**,**b**, while **9b** resulted in the asymmetric analogue **14c**. Analogously, BINOL diethers **10a**-**c** cleanly furnished the symmetric- and asymmetric binaphtho(azacrowns) (±)-**15a**-**c** and (*S*)-**15c**. The latter molecule is an appropriate candidate for the synthesis of chiral receptors. Notably, in these experiments, self-cyclised side-products were not formed due to the much higher acidity of the tosylamide NH's versus the remaining calixarene OH's.

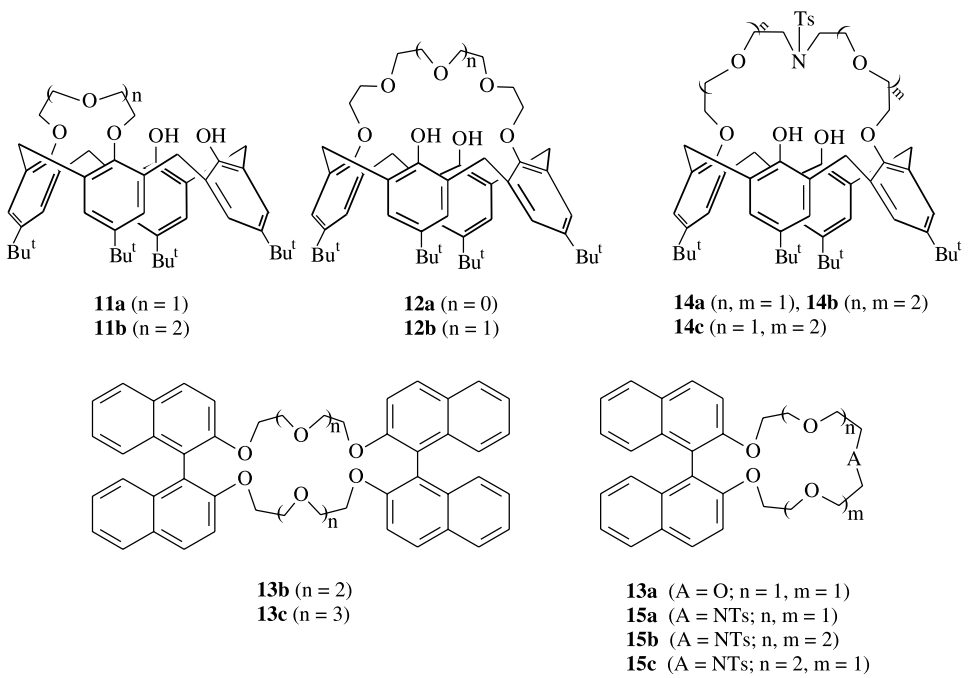


Figure 1. Survey of cyclisation products obtained from monoethers **5**, **7** and diethers **8**-**10**.

With mixed diethers **9a**, **9c** and **10d** an inseparable mixture was obtained and we failed to recover the expected cyclised products. These examples clearly show that the success of ring closure is not dependent on the size of the crown ring being formed, rather on the difference between the chain lengths (n, m) of the precursors. In case of $n-m>1$, for example, in **9c** (2), **9a** and **10d** (3), the cyclisation is not preferred.

3. Conclusions

A series of calixarene- and BINOL mono- and diethers comprised of oligoethylene glycol chains supplied with reactive terminal groups have been synthesized via the Mitsunobu reaction. This selective and rapid alkylation with glycol derivatives provides an easy access to precursors capable of cyclising to various calix[4]- and 1,1′-bi-2-naphthocrowns.

4. Experimental

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ at 500:125 MHz on a Bruker Avance DRX-500 spectrometer. Pre-coated silica gel plates (Merck 60 F_{254}) were used for analytical TLC and Kieselgel 60 for column chromatography. All chemicals were reagent grade and used without further purification. TPP, **3a**,**d** were purchased from Merck. *p-tert*-Butylcalix[4]arene **1**,[29] BINOL **2**,[30] glycol chlorohydrins **3b**,**c**[31] tosylates **4**[32] and DEAD[33] were prepared as described in the literature.

4.1. General procedure for the synthesis of monoethers 5, 6, 7 and diethers 8, 9, 10

To the mixture of CA **1** (0.65 g, 1 mmol), glycol derivatives **3** or **4** (2 mmol) and TPP (0.6 g, 2.3 mmol) in toluene (25 ml), a 40% toluene solution of DEAD (1.05 ml, 2.3 mmol) was added dropwise with stirring at room temperature. After 2 h reaction the solution was evaporated to dryness and the residue was separated by column chromatography on silica. The same procedure was applied for the monoalkylation of BINOL **2** (2 mmol) using **3** (1.2 mmol), TPP/DEAD (0.4 g/0.75 ml, 1.5 mmol each) in 0.5 h reactions.

During the synthesis of symmetric diethers **8a**,**b** and **10a**,**b** an enhanced reagent ratio of **1** or **2/3**/(TPP/DEAD)=1:3:3.5 was used. The less reactive **3b** required 0.5 h reflux for completion of the reaction. Mixed diethers **9a**-**c** and **10c**,**d** were prepared by the treatment of monoethers **5b**,**c** or **10b** (1 mmol) with **3a** or **3d** (0.19 g, 1.5 mmoI each) and TPP/DEAD (045 g/0.85 ml, 1.7 mmol each) at ambient temperature.

Tosylethers **6a**,**b** and **8c**,**d** were prepared following the procedures above but using reagent ratios of **1/4a**,**b**/(TPP/DEAD)=1:3:3 (monoethers) and **1/4a**,**b**/(TPP/DEAD)=1:6:6 (diethers), respectively, under 2 h reflux in both cases.

4.2. Calix[4]- and BINOL monoethers

4.2.1. 25-(1-Chloro-3-oxapent-5-yl)oxy-26,27,28-trihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (5a). White solid, mp 162–166 °C, (triturated with MeOH); ^{1}H NMR: δ 10.25 (s, 1H, O*H*), 9.38 (s, 2H, O*H*), 7.09 (s, 2H, Ar*H*), 7.05 (m, 4H, Ar*H*), 6.98 (d, 2H, J=2.5 Hz, Ar*H*), 4.47 (d, 2H, J=13 Hz, ArCH_2Ar), 4.31 (m, 2H, CH_2), 4.26 (d, 2H, J=13.5 Hz, ArCH_2Ar), 4.13 (m, 2H, CH_2), 3.97 (t, 2H, J=6 Hz, CH_2), 3.78 (t, 2H, J=5.5 Hz, CH_2), 3.43 (d, 2H, J=14 Hz, ArCH_2Ar), 3.40 (d, 2H, J=14 Hz, ArCH_2Ar), 1.22 (s, 9H, C(CH_3)$_3$), 1.21 (s, 18H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$); FAB-MS m/z (%): 754.4 (M($^+$(24) (Calcd 754.4). Anal. Calcd for $C_{48}H_{63}O_5Cl$ (755.47): C, 76.31; H, 8.41, found: C, 76.05; H, 8.45%.

4.2.2. 25-(1-Chloro-3,6-dioxaoct-8-yl)oxy-26,27,28-trihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (5b). White solid, mp 162–165 °C (eluent: hexane/EtOAc=8:2); ^{1}H NMR: δ 10.27 (s, 1H, O*H*), 9.40 (s, 2H, O*H*), 7.09 (s, 2H, Ar*H*), 7.05 (m, 4H, Ar*H*), 6.98 (d, 2H, J=2 Hz, Ar*H*), 4.47 (d, 2H, J=13 Hz, ArCH_2Ar), 4.32 (m, 2H, CH_2), 4.26 (d, 2H, J=13.5 Hz, ArCH_2Ar), 4.11 (m, 2H, CH_2), 3.87 (m, 2H, CH_2), 3.82 (m, 2H, CH_2), 3.76 (t, 2H, J=6 Hz, CH_2), 3.54 (t, 2H, J=5.5 Hz, CH_2), 3.43 (d, 2H, J=14 Hz, ArCH_2Ar), 3.39 (d, 2H, J=13 Hz, ArCH_2Ar), 1.22 (s, 9H, C(CH_3)$_3$), 1.21 (s, 18H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$); ^{13}C NMR: δ 149.6, 148.5, 148.3, 148.2, 143.8, 143.3, 133.9, 128.5, 127.9, 126.6, 126.0, 125.9 (Ar*C*), 75.3, 71.7, 71.1, 71.0, 70.3, 42.9 (*C*H$_2$), 34.4, 34.2, 34,1 (*C*CH$_3$), 33.3, 32.3 (Ar*C*H$_2$Ar), 31.7, 31.5 (C*C*H$_3$); FAB-MS m/z (%): 821.5 (M+Na)$^+$ (100) (Calcd 821.5). Anal. Calcd for $C_{50}H_{67}O_6Cl$ (799.53): C, 75.11; H, 8.45, found: C, 74.62; H, 8.38%.

4.2.3. 25-(1-Chloro-3,6,9-trioxaundec-11-yl)oxy-26,27,28-trihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]-arene (5c). White solid, mp 103–105 °C (eluent: hexane/EtOAc=7:3); ^{1}H NMR: δ 10.28 (s, 1H, O*H*), 9.40 (s, 2H, O*H*), 7.08 (s, 2H, Ar*H*), 7.05 (m, 4H, Ar*H*), 6.97 (d, 2H, J=2 Hz, Ar*H*), 4.46 (d, 2H, J=13 Hz, ArCH_2Ar), 4.32 (m, 2H, CH_2), 4.26 (d, 2H, J=13.5 Hz, ArCH_2Ar), 4.10 (m, 2H, CH_2), 3.86 (m, 2H, CH_2), 3.81 (m, 2H, CH_2), 3.72 (m, 4H, CH_2), 3.59 (m, 4H, CH_2), 3.43 (d, 2H, J=13.5 Hz, ArCH_2Ar), 3.39 (d, 2H, J=13 Hz, ArCH_2Ar), 1.22 (s, 9H, C(CH_3)$_3$), 1.21 (s, 18H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$); FAB-MS m/z (%): 865.5 (M+Na)$^+$ (46) (Calcd 865.5), 842.5 (M)$^+$ (49); (Calcd 842.5). Anal. Calcd for $C_{52}H_{71}O_7Cl$ (843.58): C, 74.04; H, 8.48, found: C, 73.98; H, 8.31%.

4.2.4. 25-(1-*p*-Toluenesulfonyloxy-3-oxapent-5-yl)oxy-26,27,28-trihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]-arene (6a). White solid, mp 81–84 °C (eluent: hexane/EtOAc=8:2); ^{1}H NMR: δ 10.22 (s, 1H, O*H*), 9.37 (s, 2H, O*H*), 7.80 (d, 2H, J=8 Hz, Ar*H*), 7.25 (d, 2H, J=8 Hz, Ar*H*), 7.08 (s, 2H, Ar*H*), 7.04 (m, 4H, Ar*H*), 6.97 (d, 2H, J=1 Hz, Ar*H*), 4.36 (d, 2H, J=13 Hz, ArCH_2Ar), 4.32 (t, 2H, J=4.5 Hz, CH_2), 4.24 (m, 2H, CH_2), 4.18 (d, 2H, J=14 Hz, ArCH_2Ar), 4.05 (m, 2H, CH_2), 3.91 (t, 2H, J=4.5 Hz, CH_2), 3.39 (d, 2H, J=13.5 Hz, ArCH_2Ar), 3.37 (d, 2H, J=13 Hz, ArCH_2Ar), 2.39 (s, 3H, CH_3), 1.22 (s, 9H, C(CH_3)$_3$), 1.21 (s, 18H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$);

FAB-MS *m/z* (%): 890.5 (M(+ (71) (Calcd 890.5). Anal. Calcd for $C_{55}H_{70}O_8S$ (891.21): C, 74.12; H, 7.94, found: C, 74.22; H, 7.86%.

4.2.5. 25-(1-1-*p*-Toluenesulfonyloxy-3,6-dioxaoct-8-yl)oxy-26,27,28-trihydroxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene (6b). White solid, mp 160–163 °C (eluent: hexane/ EtOAc=7:3); ^{1}H NMR: δ 10.24 (s, 1H, O*H*), 9.38 (s, 2H, O*H*), 7.78 (d, 2H, *J*=8 Hz, Ar*H*), 7.29 (d, 2H, *J*=8 Hz, Ar*H*), 7.08 (s, 2H, Ar*H*), 7.05 (m, 4H, Ar*H*), 6.97 (d, 2H, *J*=2 Hz, Ar*H*), 4.43 (d, 2H, *J*=13 Hz, ArCH_2Ar), 4.28 (m, 2H, CH_2), 4.23 (d, 2H, *J*=13.5 Hz, ArCH_2Ar), 4.08 (m, 4H, CH_2), 3.79 (m, 2H, CH_2), 3.72 (m, 4H, CH_2), 3.41 (d, 2H, *J*=14 Hz, ArCH_2Ar), 3.38 (d, 2H, *J*=13.5 Hz, ArCH_2Ar), 2.40 (s, 3H, CH_3), 1.22 (s, 9H, C(CH_3)$_3$), 1.20 (s, 18H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$); FAB-MS *m/z* (%): 957.5 (M+Na)$^+$ (65) (Calcd 957.5). Anal. Calcd for $C_{57}H_{74}O_9S$ (935.26): C, 73.20; H, 7.97, found: C, 72.84; H, 8.03%.

4.2.6. (±)-*O*-(1-Chloro-3-oxapent-5-yl)-1,1′-bi-2-naphthol (7a). Yellow oil (eluent: toluene/MeOH=95:5); ^{1}H NMR: δ 8.02 (d, 1H, *J*=9 Hz, Ar*H*), 7.88 (m, 3H, Ar*H*), 7.45 (d, 1H, *J*=9 Hz, Ar*H*), 7.39–7.20 (m, 6H, Ar*H*), 7.04 (d, 1H, *J*=8.5 Hz, Ar*H*), 5.08 (s, 1H, O*H*), 4.19 (m, 1H, CH_2), 4.10 (m, 1H, CH_2), 3.55 (t, 2H, *J*=4.5 Hz, CH_2), 3.23–3.10 (m, 4H, CH_2); FAB-MS *m/z* (%): 392.1 (M(+ (30) (Calcd 392.1). Anal. Calcd for $C_{24}H_{21}O_3Cl$ (392.88): C, 73.37; H, 5.39, found: C, 73.63; H, 5.44%.

4.2.7. (±)-*O*-(1-Chloro-3,6-dioxaoct-8-yl)-1,1′-bi-2-naphthol (7b). Yellow oil (eluent: hexane/EtOAc=6:4); ^{1}H NMR: δ 7.99 (d, 1H, *J*=9 Hz, Ar*H*), 7.86 (m, 3H, Ar*H*), 7.45 (d, 1H, *J*=9 Hz, Ar*H*), 7.37–7.16 (m, 6H, Ar*H*), 7.04 (d, 1H, *J*=8 Hz, Ar*H*), 5.32 (s, 1H, O*H*), 4.25 (m, 1H, CH_2), 4.10 (m, 1H, CH_2), 3.55 (t, 2H, *J*=4.5 Hz, CH_2), 3.50–3.34 (m, 4H, CH_2), 3.30–3.19 (m, 4H, CH_2); ^{13}C NMR: δ 155.5, 151.6, 134.2, 134.1, 130.9, 129.8, 129.7, 129.3, 128.3, 128.2, 127.4, 126.5, 125.3, 125.1, 124.5, 123.4, 118.1, 116.9, 115.7, 115.6 (Ar*C*), 71.3, 70.6, 70.0, 69.6, 42.6 (*C*H$_2$); FAB-MS *m/z* (%): 436.1 (M)$^+$ (10) (Calcd 436.1). Anal. Calcd for $C_{26}H_{25}O_4Cl$ (436.93): C, 71.47; H, 5.77, found: C, 71.22; H, 5.82%.

4.2.8. (*S*)-*O*-(1-Chloro-3,6-dioxaoct-8-yl)-1,1′-bi-2-naphthol ((*S*)-7b). Yellow oil (eluent: hexane/ EtOAc=6:4), yield: 79%, $[\alpha]_D^{20}$=+21.7 (*c*=1, $CHCl_3$).

4.2.9. (±)-*O*-(1-Chloro-3,6,9-trioxaundec-11-yl)-1,1′-bi-2-naphthol (7c). Yellow oil (eluent: hexane/EtOAc=7:3); ^{1}H NMR: δ 7.99 (d, 1H, *J*=9 Hz, Ar*H*), 7.85 (m, 3H, Ar*H*), 7.46 (d, 1H, *J*=9 Hz, Ar*H*), 7.37–7.17 (m, 6H, Ar*H*), 7.04 (d, 1H, *J*=8.5 Hz, Ar*H*), 5.50 (s, 1H, O*H*), 4.26 (m, 1H, CH_2), 4.10 (m, 1H, CH_2), 3.64–3.22 (m, 14H, CH_2); FAB-MS *m/z* (%): 503.2 (M+Na)$^+$ (16) (Calcd 503.2). Anal. Calcd for $C_{28}H_{29}O_5Cl$ (480.98): C, 69.92; H, 6.08, found: C, 69.31; H, 6.11%.

4.3. Symmetrical calix[4]- and BINOL diethers

4.3.1. 25,27-Bis(1-chloro-3-oxapent-5-yl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (8a). White solid, mp 110–113 °C (triturated with MeOH); ^{1}H NMR: δ 7.14 (s, 2H, O*H*), 7.07 (s, 4H, Ar*H*), 6.78 (s, 4H, Ar*H*), 4.34 and 3.31 (d+d, 4+4H, *J*=13 Hz, ArCH_2Ar), 4.16 (t, 4H, *J*=4 Hz, CH_2), 4.01 (t, 4H, *J*=4 Hz, CH_2), 3.98 (t, 4H, *J*=6 Hz, CH_2), 3.74 (t, 4H, *J*=6 Hz, CH_2), 1.30 (s, 18H, C(CH_3)$_3$), 0.95 (s, 18H, C(CH_3)$_3$); ^{13}C NMR: δ 150.5, 149.7, 146.9, 141.4, 133.3, 132.5, 127.8, 126.4, 125.6, 125.1 (Ar*C*), 75.5, 71.9, 70.3, 43.1 (*C*H$_2$), 34.2, 34,1 (*C*CH$_3$), 32,1, 31.3 (C*C*H$_3$), 31.8 (Ar*C*H$_2$Ar); FAB-MS *m/z* (%): 860.5 (M(+ (24) (Calcd 860.5). Anal. Calcd for $C_{52}H_{70}O_6Cl_2$ (862.03): C, 72.45; H, 8.18, found: C, 72.96; H, 8.10%.

4.3.2. 25,27-Bis(1-chloro-3,6-dioxaoct-8-yl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (8b). Yellow oil (eluent: hexane/EtOAc=7:3); ^{1}H NMR: δ 7.09 (s, 2H, O*H*), 7.05 (s, 4H, Ar*H*), 6.75 (s, 4H, Ar*H*), 4.36 and 3.28 (d+d, 4+4H, *J*=13 Hz, ArCH_2Ar), 4.23 (m, 4H, CH_2), 4.15 (t, 4H, *J*=4.5 Hz, CH_2), 3.96 (t, 4H, *J*=5 Hz, CH_2), 3.83 (m, 4H, CH_2), 3.76 (m, 4H, CH_2), 3.53 (t, 4H, *J*=6 Hz, CH_2), 1.31 (s, 18H, C(CH_3)$_3$), 0.93 (s, 18H, C(CH_3)$_3$). Anal. Calcd for $C_{56}H_{78}O_8Cl_2$ (950.13): C, 70.79; H, 8.27, found: C, 70.25; H, 8.36%.

4.3.3. 25,27-Bis(1-*p*-toluenesulfonyloxy-3-oxapent-5-yl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (8c). White solid, mp 160–163 °C (triturated with MeOH); ^{1}H NMR: δ 7.73 (d, 4H, *J*=7 Hz, Ar*H*), 7.20 (d, 4H, *J*=7 Hz, Ar*H*), 7.17 (s, 2H, O*H*), 7.05 (s, 4H, Ar*H*), 6.77 (s, 4H, Ar*H*), 4.25 (m, 4+4H, ArCH_2Ar, CH_2), 4.05 (m, 4H, CH_2), 3.89 (m, 8H, CH_2), 3.26 (d, 4H, *J*=13 Hz, ArCH_2Ar), 2.37 (s, 6H, CH_2), 1.30 (s, 18H, C(CH_3)$_3$), 0.94 (s, 18H, C(CH_3)$_3$). Anal. Calcd for $C_{66}H_{84}O_{12}S_2$ (1133.50): C, 69.94; H, 7.47, found: C, 69.44; H, 7.52%.

4.3.4. 25,27-Bis(1-*p*-toluenesulfonyloxy-3,6-dioxaoct-8-yl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (8d). Yellow oil (eluent: hexane/ EtOAc=7:3); ^{1}H NMR: δ 7.79 (d, 4H, *J*=7 Hz, Ar*H*), 7.34 (d, 4H, *J*=7 Hz, Ar*H*), 7.16 (s, 2H, O*H*), 7.06 (s, 4H, Ar*H*), 6.77 (s, 4H, Ar*H*), 4.35 and 3.29 (d+d, 4+4H, *J*=13 Hz, ArCH_2Ar), 4.12 (m, 8H, CH_2), 3.92 (m, 4H, CH_2), 3.77 (m, 4H, CH_2), 3.68 (m, 8H, CH_2), 2.43 (s, 6H, CH_2), 1.31 (s, 18H, C(CH_3)$_3$), 0.95 (s, 18H, C(CH_3)$_3$). Anal. Calcd for $C_{70}H_{92}O_{14}S_2$ (1221.61): C, 68.82; H, 7.59, found: C, 69.19; H, 7.63%.

4.3.5. (±)-*O*,*O*′-Bis(1-chloro-3-oxapent-5-yl)-1,1′-bi-2-naphthol (10a). Yellow oil (eluent: toluene/ MeOH=97:3); ^{1}H NMR: δ 7.94 (d, 2H, *J*=9 Hz, Ar*H*), 7.85 (d, 2H, *J*=8 Hz, Ar*H*), 7.41 (d, 2H, *J*=9.5 Hz, Ar*H*), 7.33 (t, 2H, *J*=7 Hz, Ar*H*), 7.23 (t, 2H, *J*=7 Hz, Ar*H*), 7.17 (d, 2H, *J*=8.5 Hz, Ar*H*), 4.15–4.05 (m, 4H, CH_2), 3.49 (t, 4H, *J*=4.5 Hz, CH_2), 3.15–3.06 (m, 8H, CH_2). Anal. Calcd for $C_{28}H_{28}O_4Cl_2$ (499.43): C, 67.34; H, 5.65, found: C, 67.86; H, 5.70%.

4.3.6. (±)-*O*,*O*′-Bis(1-chloro-3,6-dioxaoct-8-yl)-1,1′-bi-2-naphthol (10b). Yellow oil (eluent: toluene/MeOH=95:5); ^{1}H NMR: δ 7.93 (d, 2H, *J*=9 Hz, Ar*H*), 7.85 (d, 2H, *J*=8 Hz, Ar*H*), 7.41 (d, 2H, *J*=9 Hz, Ar*H*), 7.32 (td, 2H, *J*=7 Hz, 1 Hz, Ar*H*), 7.21 (td, 2H, *J*=8 Hz, 1 Hz, Ar*H*), 7.15 (d, 2H, *J*=8.5 Hz, Ar*H*), 4.09 (m, 4H, CH_2), 3.55–3.45 (m, 12H, CH_2), 3.20 (t, 4H, *J*=4 Hz, CH_2), 3.15–3.05 (m,

4H, CH_2). Anal. Calcd for $C_{32}H_{36}O_6Cl_2$ (587.54): C, 65.42; H, 6.18, found: C, 65.08; H, 6.22%.

4.4. Mixed calix[4]- and BINOL diethers

4.4.1. 25-(1-Chloro-3,6,9-trioxaundec-11-yl)oxy-27-(2-bromoethoxy)-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (9a). White solid, mp 57–59 °C (eluent: hexane/EtOAc=7:3); ^{1}H NMR: δ 7.06 (d, 4H, J=0.5 Hz, Ar*H*), 7.01 (s, 2H, O*H*), 6.79 (s, 2H, Ar*H*), 6.73 (s, 2H, Ar*H*), 4.34 and 3.30 (dd, 4H+4H, J=13.5, 3 Hz, ArCH_2Ar), 4.30 (t, 2H, J=6.5 Hz, CH_2), 4.16 (t, 2H, J=4 Hz, CH_2), 4.00 (t, 2H, J=4.5 Hz, CH_2), 3.88 (t, 2H, J=4.5 Hz, CH_2), 3.81 (t, 2H, J=6.5 Hz, CH_2), 3.75 (t, 2H, J=4.5 Hz, CH_2), 3.68 (m, 4H, CH_2), 3.59 (m, 4H, CH_2), 1.30 (s, 18H, C(CH_3)$_3$), 0.96 (s, 9H, C(CH_3)$_3$), 0.90 (s, 9H, C(CH_3)$_3$). Anal. Calcd for $C_{54}H_{74}O_7BrCl$ (950.53): C, 68.23; H, 7.85, found: C, 68.65; H, 7.94%.

4.4.2. 25-(1-Chloro-3-oxapent-5-yl)oxy-27-(1-chloro-3,6-dioxaoct-8-yl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (9b). White solid, mp 80–82 °C (eluent: hexane/EtOAc=7:3); ^{1}H NMR: δ 7.11 (s, 2H, O*H*), 7.05 (s, 4H, Ar*H*), 6.76 (d, 4H, J=4 Hz, Ar*H*), 4.37 and 4.33 (d+d, 2H+2H, J=13.5 Hz, ArCH_2Ar), 4.15 (m, 4H, CH_2), 3.98 (m, 6H, CH_2), 3.87 (m, 2H, CH_2), 3.75 (m, 6H, CH_2), 3.52 (t, 2H, J=5.5 Hz, CH_2), 3.29 (d, 4H, J=13 Hz, ArCH_2Ar), 1.30 (s, 18H, C(CH_3)$_3$), 0.94 (s, 9H, C(CH_3)$_3$), 0.93 (s, 9H, C(CH_3)$_3$); ^{13}C NMR: δ 150.8, 150.0, 147.1, 141.6, 132.7, 128.0, 125.7, 125.3, (Ar*C*), 75.6, 72.0, 71.7, 71.2, 71.0, 70.3, 43.1, 43.0 (*C*H$_2$), 34.1, 34,0 (*C*CH$_3$), 32,0, 31.2 (C*C*H$_3$), 31.7 (Ar*C*H$_2$Ar). Anal. Calcd for $C_{54}H_{74}O_7Cl_2$ (906.08): C, 71.58; H, 8.23, found: C, 71.11; H, 8.28%.

4.4.3. 25-(1-Chloro-3-oxapent-5-yl)oxy-27-(1-chloro-3,6,9-trioxaundec-11-yl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (9c). Yellow oil (eluent: hexane/EtOAc=8:2); ^{1}H NMR: δ 7.12 (s, 2H, O*H*), 7.05 (s, 4H, Ar*H*), 6.76 (s, 4H, Ar*H*), 4.35 and 4.33 (d+d, 2H+2H, J=13.5 Hz, ArCH_2Ar), 4.14 (m, 4H, CH_2), 3.99 (m, 4H, CH_2), 3.95 (t, 2H, J=5 Hz, CH_2), 3.85 (t, 2H, J=4.5 Hz, CH_2), 3.72 (m, 4H, CH_2), 3.66 (m, 4H, CH_2), 3.58 (m, 4H, CH_2), 3.28 (dd, 4H, J=13.5, 2.5 Hz, ArCH_2-Ar), 1.29 (s, 18H, C(CH_3)$_3$), 0.94 (s, 9H, C(CH_3)$_3$), 0.93 (s, 9H, C(CH_3)$_3$). Anal. Calcd for $C_{56}H_{78}O_8Cl_2$ (950.13): C, 70.79; H, 8.27, found: C, 70.23; H, 8.32%.

4.4.4. (±)-*O*-(1-Chloro-3-oxapent-5-yl)-*O*′-(1-chloro-3,6-dioxaoct-8-yl)-1,1′-bi-2-naphthol (10c). Yellow oil (eluent: toluene/MeOH=95:5); ^{1}H NMR: δ 7.93 (d, 2H, J=9 Hz, Ar*H*), 7.85 (d, 2H, J=8 Hz, Ar*H*), 7.41 (t, 2H, J=8 Hz, Ar*H*), 7.32 (t, 2H, J=7 Hz, Ar*H*), 7.24–7.14 (m, 4H, Ar*H*), 4.09 (m, 4H, CH_2), 3.56–3.48 (m, 8H, CH_2), 3.21 (t, 2H, J=4.5 Hz, CH_2), 3.16–3.05 (m, 6H, CH_2); ^{13}C NMR: δ 154.5, 154.4, 134.3, 129.7, 129.6, 129.5, 128.0, 126.5, 125.7, 125.6, 124.0, 120.8, 120.7, 115.8, 115.7 (Ar*C*), 71.4, 71.3, 70.7, 70.6, 70.2, 70.1, 69.9, 69.8, 43.0, 42.8 (*C*H$_2$). Anal. Calcd for $C_{30}H_{32}O_5Cl_2$ (543.48): C, 66.30; H, 5.93, found: C, 66.02; H, 5.99%.

4.4.5. (*S*)-*O*-(1-Chloro-3-oxapent-5-yl)-*O*′-(1-chloro-3,6-dioxaoct-8-yl)-1,1′-bi-2-naphthol ((*S*)-10c). Yellow oil (94%), eluent: toluene/MeOH=95:5; $[\alpha]_D^{20}$=−45 (c=1, $CHCl_3$).

4.4.6. (±)-*O*-(1-Chloro-3-oxapent-5-yl)-*O*′-(2-bromoethoxy)-1,1′-bi-2-naphthol (10d). Yellow oil (53%), eluent: toluene/MeOH=95:5; ^{1}H NMR: δ 7.94 (t, 2H, J=9.5 Hz, Ar*H*), 7.85 (d, 2H, J=8 Hz, Ar*H*), 7.41 (m, 2H, Ar*H*), 7.32 (m, 2H, Ar*H*), 7.22 (m, 2H, Ar*H*), 7.14 (m, 2H, Ar*H*), 3.57 (m, 4H, CH_2), 3.48 (m, 4H, CH_2), 3.24–3.09 (m, 6H, CH_2). Anal. Calcd for $C_{30}H_{32}O_5BrCl$ (587.93): C, 61.29; H, 5.49, found: C, 61.11; H, 5.52%.

4.5. General procedure for the self-condensation of mono-chloroethers

The mixture of mono-chloroethers **5a**,**b**,**c** or **7b**,**c** (0.5 mmol), K_2CO_3 (0.7 g, 5 mmol) and KI (0.17 g, 0.5 mmol) in MeCN (20 ml) was stirred for 48 h under reflux. The solvent was then evaporated, the residue was extracted with CH_2Cl_2 (30 ml), washed with dilute aq. HCl, water and dried. The crude products were separated by column chromatography on silica to afford white solids (except for **13c**).

4.6. Calix[4]crowns

4.6.1. 25,26-(3-Oxapenta-1,5-diyl)oxy-27,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (11a). Yield: 69%, mp 152–155 °C (triturated with MeOH). The ^{1}H NMR data are identical to those reported in Ref. 22.

4.6.2. 25,27-(3,6-Dioxaocta-1,8-diyl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (12a). Yield: 55%, eluent: hexane/EtOAc=8:2, mp 235–237 °C (lit.[24] mp 259–262 °C). The ^{1}H NMR data are identical to those reported in Ref. 24.

4.6.3. 25,27-(3,6,9-Trioxaundeca-1,11-diyl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (12b). Yield: 35%, eluent: hexane/EtOAc=7:3, mp 224–226 °C (lit.[23] mp 246–248 °C). The ^{1}H NMR data are identical to those reported in Ref. 23.

4.7. 1,1′-Binaphthocrowns

4.7.1. (±)-1,1′-Bi-2-naphtho(17-crown-5) (13a). Yield: 36%, eluent: hexane/EtOAc=3:7, mp 103–105 °C (lit.[24] mp 114–115 °C); ^{1}H NMR: δ 7.92 (d, 2H, J=9 Hz, Ar*H*), 7.84 (d, 2H, J=8 Hz, Ar*H*), 7.47 (d, 2H, J=8.5 Hz, Ar*H*), 7.30 (t, 2H, J=7 Hz, Ar*H*), 7.19 (t, 2H, J=8 Hz, Ar*H*), 7.11 (d, 2H, J=8.5 Hz, Ar*H*), 4.25 (m, 2H, CH_2), 3.99 (m, 2H, CH_2), 3.65 (m, 2H, CH_2), 3.57–3.36 (m, 10H, CH_2); FAB-MS; m/z (%): 467.0 (M+Na)$^+$ (82) (Calcd 467.2). Anal. Calcd for $C_{28}H_{28}O_5$ (444.52): C, 75.66; H, 6.35, found: C, 75.23; H, 6.40%.

4.7.2. (±)-Bis(1,1′-bi-2-naphtho-28-crown-8) (13b). Yield: 21%, eluent: hexane/EtOAc=1:1, mp 119–122 °C; ^{1}H NMR: δ 7.93 (d, 4H, J=8.5 Hz, Ar*H*), 7.85 (d, 4H, J=8 Hz, Ar*H*), 7.49 (d, 4H, J=8.5 Hz, Ar*H*), 7.32–7.05 (m, 12H, Ar*H*), 4.11 (m, 4H, CH_2), 4.03 (m, 4H, CH_2), 3.50–3.34 (m, 8H, CH_2), 3.16 (m, 8H, CH_2); FAB-MS m/z (%): 822.9 (17) (M+Na)$^+$ (Calcd 823.3). Anal. Calcd for

$C_{52}H_{48}O_8$ (800.94): C, 77.98; H, 6.04, found: C, 78.44; H, 6.00%.

4.7.3. (*S*)-Bis(1,1′-bi-2-naphtho-28-crown-8) ((*S*)-13b). Yield: 56%; eluent: hexane/EtOAc=1:1, $[\alpha]_D^{20}=-119$ (c=1, $CHCl_3$).

4.7.4. (±)-Bis(1,1′-bi-2-naphtho-34-crown-10) (13c). Yellow oil (27%), eluent: hexane/EtOAc=3:7; ^{1}H NMR: δ 7.91 (d, 4H, J=9 Hz, Ar*H*), 7.83 (d, 4H, J=8 Hz, Ar*H*), 7.43 (d, 4H, J=9 Hz, Ar*H*), 7.30 (t, 4H, J=7 Hz, Ar*H*), 7.19 (t, 4H, J=8 Hz, Ar*H*), 7.13 (d, 4H, J=8.5 Hz, Ar*H*), 4.12 (m, 4H, CH_2), 4.02 (m, 4H, CH_2), 3.51 (m, 4H, CH_2), 3.42 (m, 4H, CH_2), 3.28–3.16 (m, 16H, CH_2); FAB-MS m/z (%): 927.3 $(M+K)^+$ (15) (Calcd 927.3). Anal. Calcd for $C_{56}H_{56}O_{10}$ (889.05): C, 75.66; H, 6.35, found: C, 75.19; H, 6.40%.

4.8. General procedure for the synthesis of (aza)crowns

The mixture of di-chloroethers **8a**,**b**, **9b** or **10a**-**c** (0.5 mmol), $TsNH_2$ (0.085 g, 0.5 mmol), K_2CO_3 (0.35 g, 2.5 mmol) in DMF (20 ml) was stirred at 100 °C for 48 h. The solvent was then evaporated, the residue was extracted with CH_2Cl_2 (30 ml), washed with dilute aq. HCl, water and dried. The crude products were separated by column chromatography on silica to afford white solids (except for **15b**,**c**).

4.9. Calix[4](aza)crowns

4.9.1. 25,27-(3,9-Dioxa-6-*N*-tosylazaundeca-1,11-diyl)-oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]-arene (14a). Yield: 31%, mp 127–129 °C (triturated with MeOH); ^{1}H NMR: δ 7.70 (d, 2H, J=13 Hz, Ar*H*), 7.32 (s, 2H, O*H*), 7.25 (d, 2H, J=13 Hz, Ar*H*), 7.03 (s, 4H, Ar*H*), 6.78 (s, 4H, Ar*H*), 4.29 and 3.27 (d+d, 4+4H, J=21.5 Hz, ArCH_2Ar), 3.99 (m, 12H, CH_2), 3.44 (t, 4H, J=10.5 Hz, CH_2), 2.37 (s, 3H, CH_3), 1.28 (s, 18H, C(CH_3)$_3$), 0.94 (s, 18H, C(CH_3)$_3$). Anal. Calcd for $C_{59}H_{77}NO_8S$ (960.32): C, 73.79; H, 8.08, found: C, 73.21; H, 8.0.2%.

4.9.2. 25,27-(3,6,12,15-Tetraoxa-9-*N*-tosylazaheptadeca-1,17-diyl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (14b). Yield: 20% (eluent: hexane/EtOAc=6:4), mp 173–176 °C; ^{1}H NMR: δ 7.64 (d, 2H, J=7 Hz, Ar*H*), 7.25 (d, 2H, J=7 Hz, Ar*H*), 7.14 (s, 2H, O*H*), 7.02 (s, 4H, Ar*H*), 6.74 (s, 4H, Ar*H*), 4.36 and 3.26 (d+d, 4+4H, J=12.5 Hz, ArCH_2Ar), 4.12 (m, 4H, CH_2), 3.92 (m, 8H, CH_2), 3.68 (m, 8H, CH_2), 3.19 (m, 4H, CH_2), 2.40 (s, 3H, CH_3), 1.26 (s, 18H, C(CH_3)$_3$), 0.92 (s, 18H, C(CH_3)$_3$). Anal. Calcd for $C_{63}H_{85}NO_{10}S$ (1048.42): C, 72.17; H, 8.17, found: C, 71.73; H, 8.11%.

4.9.3. 25,27-(3,9,12-Trioxa-6-*N*-tosylazatetradeca-1,14-diyl)oxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (14c). Yield: 36% (eluent: hexane/EtOAc=7:3), mp 76–79 °C; ^{1}H NMR: δ 7.70 (d, 2H, J=8 Hz, Ar*H*), 7.24 (d, 2H, J=6 Hz, Ar*H*), 7.15 (s, 2H, O*H*), 7.05 (s, 4H, Ar*H*), 6.75 (d, 4H, J=2 Hz, Ar*H*), 4.32 (dd, 4H, J=12.5, 5 Hz, ArCH_2Ar), 4.06 (m, 4H, CH_2), 4.01 (m, 2H, CH_2), 3.88 (m, 6H, CH_2), 3.72 (t, 2H, J=5 Hz, CH_2), 3.68 (t, 2H, J=4.5 Hz, CH_2), 3.54 (t, 2H, J=6 Hz, CH_2), 3.49 (t, 2H, J=5 Hz, CH_2), 3.27 and 3.25 (d+d, 2+2H, J=13 Hz, ArCH_2Ar), 2.38 (s, 3H, CH_3), 1.29 (s, 18H, C(CH_3)$_3$), 0.92 (s, 18H, C(CH_3)$_3$); ^{13}C NMR: δ 150.9, 150.1, 150.0, 147.1, 143.2, 141.5, 137.3, 132.8, 132.7, 129.7, 128.0, 127.9, 127.4, 127.3, 125.7, 125.2 (Ar*C*), 76.2, 75.8, 71.3, 71.2, 70.9, 70.6, 70.0, 49.1, 49.0 (*C*H$_2$), 34.1, 34,0 (*C*CH$_3$), 31.9, 31.2 (C*C*H$_3$), 31.7, 31.6 (Ar*C*H$_2$Ar), 21.6 (*C*H$_3$); FAB-MS m/z (%): 1026.5 $(M+Na)^+$ (100) (Calcd 1026.5). Anal. Calcd for $C_{61}H_{81}NO_9S$ (1004.37): C, 72.95; H, 8.13, found: C, 73.24; H, 8.15%.

4.10. 1,1′-Binaphtho(aza)crowns

4.10.1. (±)-*O*,*O*′-(3,9-Dioxa-6-*N*-tosylazaundeca-1,11-diyl)-1,1′-bi-2-naphthol (15a). Yield: 70% (eluent: toluene/MeOH=97:3), mp 71–74 °C; ^{1}H NMR: δ 7.92 (d, 2H, J=9 Hz, Ar*H*), 7.84 (d, 2H, J=8 Hz, Ar*H*), 7.62 (d, 2H, J=8 Hz, Ar*H*), 7.44 (d, 2H, J=9 Hz, Ar*H*), 7.30 (t, 2H, J=7.5 Hz, Ar*H*), 7.24 (d, 2H, J=8.5 Hz, Ar*H*), 7.19 (t, 2H, J=7.5 Hz, Ar*H*), 7.10 (d, 2H, J=8.5 Hz, Ar*H*), 4.22 (m, 2H, CH_2), 3.93 (m, 2H, CH_2), 3.55 (m, 2H, CH_2), 3.46–3.36 (m, 6H, CH_2), 3.24–3.09 (m, 4H, CH_2), 2.40 (s, 3H, CH_3); FAB-MS m/z (%): 597.3 (M(+ (9) (Calcd 597.2). Anal. Calcd for $C_{35}H_{35}NO_6S$ (597.72): C, 70.33; H, 5.90, found: C, 69.89; H, 5.94%.

4.10.2. (±)-*O*,*O*′-(3,6,12,15-Tetraoxa-9-*N*-tosylazaheptadeca-1,17-diyl)-1,1′-bi-2-naphthol (15b). Yellow oil (51%), eluent: hexane/ EtOAc=3:7); ^{1}H NMR: δ 7.92 (d, 2H, J=9 Hz, Ar*H*), 7.84 (d, 2H, J=8 Hz, Ar*H*), 7.69 (d, 2H, J=8 Hz, Ar*H*), 7.43 (d, 2H, J=8.5 Hz, Ar*H*), 7.32–7.26 (m, 4H, Ar*H*), 7.18 (t, 2H, J=7.5 Hz, Ar*H*), 7.13 (d, 2H, J=8.5 Hz, Ar*H*), 4.15 (m, 2H, CH_2), 4.01 (m, 2H, CH_2), 3.64–3.54 (m, 6H, CH_2), 3.42–3.28 (m, 14H, CH_2), 2.41 (s, 3H, CH_3); FAB-MS m/z (%): 724.3 $(M+K)^+$ (35) (Calcd 724.2). Anal. Calcd for $C_{39}H_{43}NO_8S$ (685.83): C, 68.30; H, 6.32, found: C, 68.42; H, 6.28%.

4.11. (±)-*O*,*O*′-(3,9-Dioxa-6-*N*-tosylazaundeca-1,11-diyl)-1,1′-bi-2-naphthol (15c)

Yellow oil (37%), eluent: toluene/MeOH=95:5; ^{1}H NMR: δ 7.91 (t, 2H, J=8.5 Hz, Ar*H*), 7.84 (t, 2H, J=9 Hz, Ar*H*), 7.64 (d, 2H, J=8 Hz, Ar*H*), 7.43 (d, 2H, J=9 Hz, Ar*H*), 7.33–7.12 (m, 8H, Ar*H*), 4.16 (m, 2H, CH_2), 3.95 (m, 2H, CH_2), 3.66–3.16 (m, 16H, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR: δ 154.6, 143.3, 136.8, 134.3, 129.8, 129.7, 129.6, 129.5, 129.4, 128.1, 128.0, 127.4, 126.4, 125.6, 125.5, 123.9, 123.8, 121.0, 116.6, 116.4, 116.2 (Ar*C*), 71.0, 70.9, 70.8, 70.4, 70.3, 70.1, 69.8, 49.5, 49.4 (*C*H$_2$), 21.7 (*C*H$_3$); FAB-MS m/z (%): 664.2 $(M+Na)^+$ (59) (Calcd 664.2). Anal. Calcd for $C_{37}H_{39}NO_7S$ (641.77): C, 69.25; H, 6.13, found: C, 69.61; H, 6.07%.

4.12. (*S*)-*O*,*O*′-(3,9-Dioxa-6-*N*-tosylazaundeca-1,11-diyl)-1,1′-bi-2-naphthol (*S*)-15c

Yellow oil (44%), eluent: toluene/MeOH=95:5; $[\alpha]_D^{20}=-94.7$ (c=1, $CHCl_3$).

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