Pergamon

Tetrahedron Letters 43 (2002) 1225–1229

TETRAHEDRON LETTERS

Water-soluble *para*-sulfonated 1,2;3,4-calix[4]arene-biscrowns in the cone conformation

Alexandre Mathieu,* Zouhair Asfari* and Jacques Vicens*

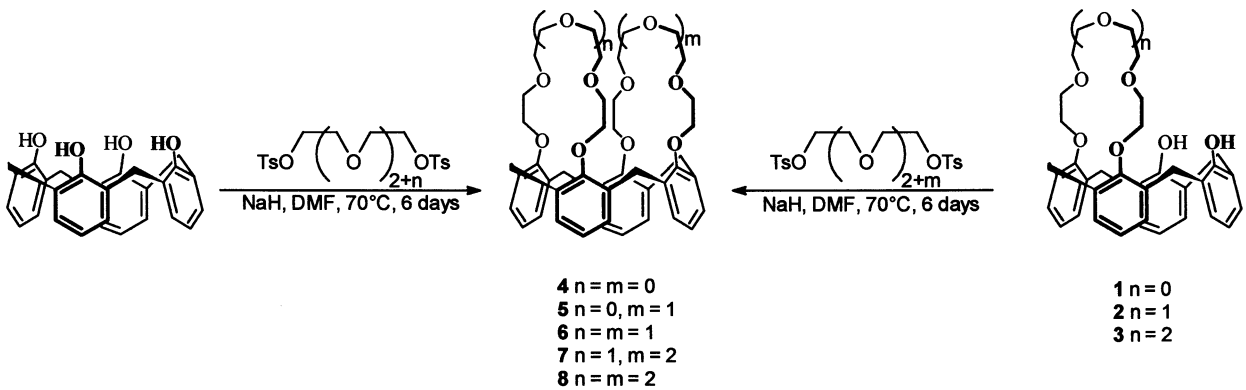
ECPM, Laboratoire de Chimie des Interactions Moléculaires Spécifiques (CNRS UMR 7512), 25, rue Becquerel, F-67087 Strasbourg, France

Received 25 October 2001; revised 19 December 2001; accepted 20 December 2001

Abstract—Water-soluble 1,2;3,4-calix[4]arene-biscrowns (**14**)–(**18**) have been synthesized in two or three steps via chlorosulfonation. Cs^+-ligand interactions were studied in aqueous media by ^1H NMR.

Several families of macrocyclic molecules are at the origin of the present wide development of supramolecular chemistry. Among them, calix[4]arene–crown ethers or calix[4]crowns are one of the most widely investigated classes of cation ligands based on calixarenes.[1] They show considerable interest as selective ion transport agents more particularly for the *cesium* cation.[1] Related water-soluble 1,3-calix[4]arene-biscrown-6 in the *1,3-alternate conformation* derivatives, functionalized at the *para* positions with sulfonic acid or sulfonamide groups, present affinities for this cation and it has been proposed to use such ligands in nanofiltration techniques for the removal of radioactive cesium ions from nuclear wastes.[2] Subsequently, 1,2;3,4-calix[4]arene-biscrowns in the *1,2-alternate conformation* have been shown to present pronounced Cs^+/Na^+ selectivities depending on the number of oxygen donor atoms in the crown ether loops.[3]

In order to compare the complexation properties in this series of calix[4]-biscrowns, we report in this paper the synthesis and complexing properties of water-soluble 1,2;3,4-calix[4]arene-biscrowns (**14**)–(**18**) in the *cone conformation*. The procedure reported here allowed us to prepare *symmetrical* 1,2;3,4-calix[4]arene-biscrowns (**14**), (**16**) and (**18**) in which the two loops are the same and *unsymmetrical* 1,2;3,4-calix[4]arene-biscrowns (**15**) and (**17**) in which the two loops are different. *Symmetrical* precursors 1,2;3,4-calix[4]-biscrowns (**4**),[4] (**6**)[5,6] and (**8**) were prepared from the calix[4]arene while *unsymmetrical* 1,2;3,4-calix[4]-biscrowns (**5**) and (**7**) were prepared from 1,2-calix[4]arene-monocrown-5.[3] The final



Scheme 1. Synthesis of 1,2;3,4-calix[4]arene-biscrowns **4**–**8**.

Keywords: water-soluble calixarenes; calixcrowns; cesium complexation.

* Corresponding authors. E-mail: mathieua@ecpm.u-strasbg.fr; asfariz@ecpm.u-strasbg.fr; vicens@chimie.u-strasbg.fr

0040-4039/02/$ - see front matter
PII: S0040-4039(01)02399-1

step was to introduce the sulfonate groups by chlorosulfonation and hydrolysis to obtain *para*-sulfonated 1,2;3,4-calix[4]arene-biscrowns (**14**)–(**18**) in the cone conformation. Preliminary complexation studies were made by ^{1}H NMR spectroscopy.

Symmetrical 1,2;3,4-calix[4]arene-biscrowns (4), (6) and (8). The general pathway to **4**, **6** and **8** is presented in Scheme 1. Calix[4]arene was heated at 70°C for 6 days under nitrogen with 2.4 equiv. of tri-, tetra- and pentaethylene glycol ditosylates (added in two equal batches) in dimethylformamide in the presence of sodium hydride in excess to afford corresponding **4**, **6** and **8**.[7,8] Compound **4** was precipitated with ethanol and obtained in 17% yield, **6** and **8** were purified by column chromatography (95/5 dichloromethane/acetone) and obtained in 13 and 20% yields, respectively.

^{1}H NMR, FAB-MS spectra and microanalysis were in agreement with the presence of one calix[4]arene and two polyether elements.[8] The *cone* conformation was assigned due to the presence of two AB systems in a 1:1 ratio for the $ArC\underline{H}_2Ar$ methylene protons of the calix[4]arene unit (see Table 1). Compound **4** has been shown to be in cone conformation in the crystal state.[4]

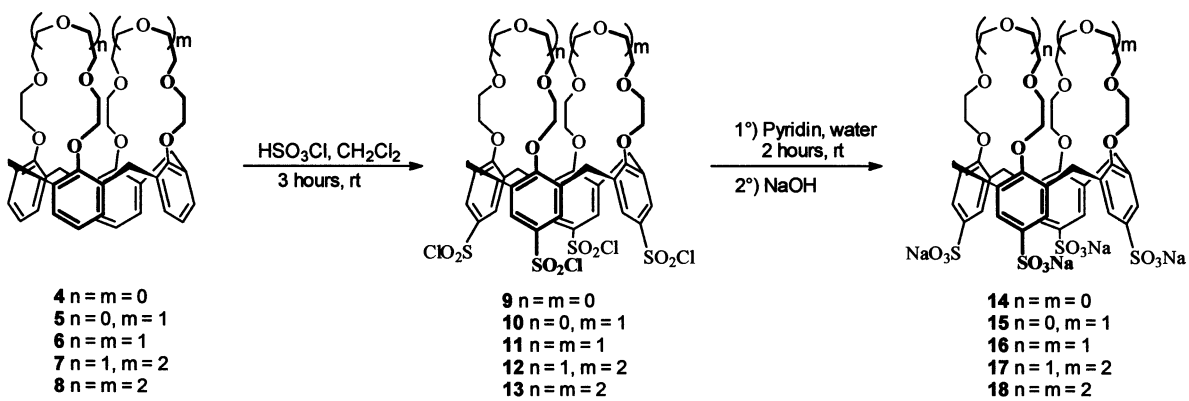
Unsymmetrical 1,2;3,4-Calix[4]arene-biscrowns. In similar conditions, 1,2-calix[4]arene-monocrown-5 (**2**)[3] was heated at 70°C for 6 days under nitrogen with 2.4 equiv. of tri- and pentaethylene glycol ditosylates (added in two equal crops) in dimethylformamide in the presence of sodium hydride in excess to give the corresponding 1,2;3,4-calix[4]arene-crowns-4;crown-5 (**5**) and 1,2;3,4-calix[4]arene-crowns-5;crown-6 (**7**). **5** and **7** were purified by column chromatography (eluent for **5**: 95/5 dichloromethane/acetone and for **7**: 80/20 dichloromethane/acetone) and obtained in 13 and 14% yields, respectively. ^{1}H NMR, FAB-MS spectra and microanalysis were in agreement with the presence of one calix[4]arene and two polyether elements.[8] The *cone* conformation was assigned due to the presence of three AB systems (ratio 1:2:1) for the $ArC\underline{H}_2Ar$ methylene protons of the calix[4]arene unit. The presence of three AB systems is due to the two different glycolic chains (see Table 1).

***p*-Sulfonated-1,2;3,4-calix[4]arene-biscrowns (14)–(18)**. The preparation of **14**–**18** was conducted by introduction of chlorosulfonyl functions on the *para* positions on the calixarene units as already described.[2,3] Compounds **4**–**8** were reacted with HSO_3Cl (in excess and

Table 1. ^{1}H NMR data for the bridged methylene protons (the numbers in parentheses are the coupling constants J in Hz)

Compounds						
4	4.98, (13.0)	–	[a]	–	3.22, (13.5)	3.11, (13.0)
5	4.99, (13.0)	4.54, (13.0)	4.37, (13.0)	3.19, (13.0)	3.12, (13.0)	3.10, (13.0)
6	–	4.58, (13.5)	4.38, (13.5)	3.18, (13.5)	3.13, (13.5)	–
7	4.61, (13.0)	4.60, (13.5)	4.39, (13.5)	[a]	[a]	[a]
8	–	4.58, (13.0)	4.39, (13.0)	–	3.15, (13.0)	3.15, (13.0)
9	–	5.24, (13.5)	[a]	3.54, (14.0)	3.38, (13.5)	–
10	5.31, (13.5)	5.30, (13.5)	4.53, (13.5)	3.50, (13.5)	3.39, (13.5)	3.37, (13.5)
11	–	4.92, (13.5)	4.52, (13.5)	3.47, (13.5)	3.39, (13.5)	–
12	4.97, (13.5)	4.99, (14.0)	4.66, (13.5)	[a]	[a]	[a]
13	–	4.91, (14.0)	4.84, (13.5)	[a]	[a]	–
14	–	4.81, (13.0)	4.72, (13.0)	3.34, (13.0)	3.19, (13.0)	–
15	[a]	[a]	[a]	[a]	[a]	[a]
16	–	[a]	[a]	3.30, (14.5)	3.23, (14.0)	–
17	[a]	[a]	[a]	[a]	[a]	[a]
18		[a]	[a]	[a]	[a]	

[a] The AB system is in a multiplet.



Scheme 2. Synthesis of *p*-sulfonated 1,2;3,4-calix[4]arene-biscrowns (**14**)–(**18**).

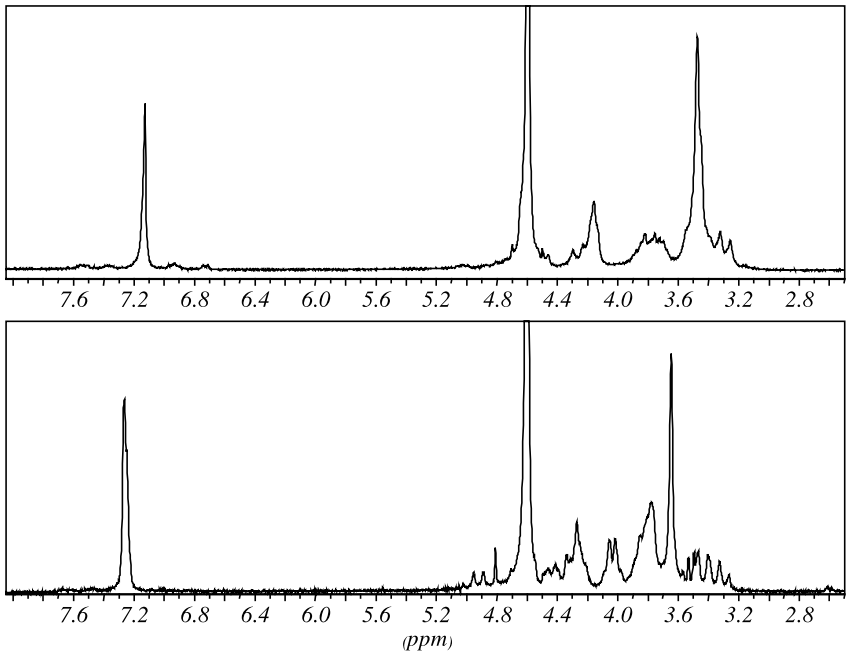


Figure 1. ^{1}H NMR spectra of **18** (top) and of **18** in the presence of $CsNO_3$ (bottom).

added at −10°C) in methylene chloride at room temperature for 3 h[9] (see Scheme 2). Chlorosulfonyled 1,2;3,4-calix[4]arene-biscrowns (**9**)–(**13**) were used directly for subsequent hydrolysis.[10] Compounds **9**–**13** were treated with water (in excess) in pyridine at room temperature for 2 h and salts were formed with NaOH. Compounds **14**–**18** were purified by crystallization from acetone. The yields were quantitative. Electro spray-MS and microanalysis showed that four sulfonate groups were introduced with Na^+ as counter ion because of the use of NaOH during isolation. The ^{1}H NMR spectra of **14**–**18** in D_2O were similar to those of **4**–**8** indicating that the cone conformation was maintained during the introduction of the sulfonate groups (see Table 1).

Preliminary complexation studies. Gaubert et al.[11] have been developed a nanofiltration technique for separation in aqueous media. This technique requires a water-soluble ligand.[11] Because of the presence of -SO_3Na groups, **14**–**18** are susceptible to be used as complexing agents for this technique. The suitability of **14**–**18** as a ligand for Cs^+ was therefore checked by use of ^{1}H NMR spectroscopy. Preliminary experiments carried out in which solid $CsNO_3$ salt was added in excess to $\sim 10^{-3}$ M solutions of **14**–**18** in D_2O showed that only the ligand **18** complexed.

Fig. 1 gives the ^{1}H NMR spectra of **18** (Fig. 1 top) and of **18** in the presence of $CsNO_3$ saturated solution (Fig. 1 bottom). Although these spectra are difficult to assign one can notice the downfield shift of the singlet of the aromatic protons Ar–H from 7.12 to 7.25 ppm. This observation is rationalized in the following manner:

1. The ligand **18** is the only one which formed a complex, probably because the size of the loops is suitable for Cs^+ complexation.
2. By comparing with related molecules in the 1,2-alternate conformation,[3] which complexes Cs^+ whatever the number of oxygen atoms, π-Cs^+ interactions seem to be important in this case as already noted.[3]

The observation that $CsNO_3$ complexes only with a saturated solution seems to indicate that $CsNO_3$ is too highly solvated by water as well as **18** for the complexation to occur. One can assume the 1,2-alternate conformation to form a hydrophobic pocket excluding water molecules and facilitating the complexation of Cs^+. We are currently investigating the binding properties of these ligands with alkali metals and alkyl ammoniums in water. Further studies of nanofiltration experiments are also under investigation.

References

1. Casnati, A.; Ungaro, R.; Asfari, Z.; Vicens, J. In *Calixarenes 2001*; Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J., Eds.; Kluwer Academic: Dordrecht, 2001; Chapter 20.
2. Nicod, L.; Pellet-Rostaing, S.; Chitry, F.; Lemaire, M. *Tetrahedron Lett*. **1998**, *39*, 9443.
3. Mathieu, A.; Asfari, Z.; Thuéry, P.; Nierlich, M.; Faure, S.; Vicens, J. *J. Inclusion Phenom*. **2001**, *40*, 173.
4. The crystalline structure of **4** has been published without full description of its preparation, see: Thuéry, P.; Nierlich, M.; Mathieu, A.; Asfari, Z.; Vicens, J. *Z. Kristallogr. NCS* **2001**, *216*, 255.
5. The synthesis of **6** was made in presence of $CsCO_3$, acetone in 9% yield, see: Asfari, Z.; Astier, J. P.; Bressot, C.; Estienne, J.; Pèpe, G.; Vicens, J. *J. Inclusion Phenom*. **1994**, *19*, 291.

6. The crystal structure of **6** is described in: Pèpe, G.; Astier, J. P.; Estienne, J.; Bressot, C.; Asfari, Z.; Vicens, J. *Acta Crystallogr*. **1995**, *C51*, 726.

7. **General**: All reagents and solvents were commercial and used without further purification. DMF is analytical grade from Prolabo. Calix[4]arene was prepared according to the literature.[12] The melting points were taken on Büchi apparatus in a capillary sealed under nitrogen. Chromatography, SiO_2 columns with Kieselgel Merck (art. 11567). ^1H NMR in $CDCl_3$ or in D_2O, Brucker SY200 (δ in ppm, J in Hz), FAB(+), VG-Analytical ZAB HF. Elemental analyses performed at the Service de Microanalyse of the Institut de chimie de Strasbourg. Compound **2**[3] was prepared as described elsewhere.
8. **Preparation of 4, 6 and 8**. Calix[4]arene (8.49 g, 20.00 mmol), NaH (2.40 g, 100.00 mmol), appropriated ethylene glycol ditosylate (24.00 mmol) and dimethylformamide (1800 ml) were heated at 50°C under N_2. After 3 days, the same quantities of NaH and ethylene glycol ditosylate were added. 3 days later, methanol and water were added and solvents were evaporated to dryness and the residue was dissolved in dichloromethane. The solution was acidified with conc. aq. HCl. The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. Compound **4** was precipitated with ethanol and **6** and **8** were purified by column chromatography. Compound **4** was obtained pure as a white solid by precipitation with ethanol. Mp 158–160°C. ^1H NMR (200 MHz, $CDCl_3$): 6.76–6.55 (m, 12H, ArH in *meta* and *para* position), 4.98 (d, $2H_{ax}$, $J=13.0$ Hz, $ArCH_2Ar$), 4.39–4.31 (m, 6H, $ArCH_2Ar$ and $ArOCHHCH_2O$), 4.26–4.15 (m, 4H, $ArOCHHCH_2O$), 3.96–3.67 (m, 16H, OCH_2CH_2O), 3.22 (d, $2H_{eq}$, $J=13.4$ Hz, $ArCH_2Ar$), 3.11 (d, $2H_{eq}$, $J=13.0$ Hz, $ArCH_2Ar$). Anal. calcd for $C_{40}H_{44}O_8\cdot C_2H_6O$: C, 72.17; H, 7.22. Found C, 72.22; H, 7.24. FAB MS $m/z=653.3$ (MH^+). Yield: 17%. Compound **6** was obtained pure as a white solid by chromatography (SiO_2, 95/5 dichloromethane/acetone as eluent). Same ^1H NMR as a sample of **6** obtained previously.[5] Mp 82–84°C. Mp lit. 206–207°C.[5] Yield: 13%. Compound **8** was obtained pure as a yellow oil by chromatography (SiO_2, 95/5 dichloromethane/acetone as eluent). ^1H NMR (200 MHz, $CDCl_3$): 6.67–6.53 (m, 12H, ArH in *meta* and *para* position), 4.58 (d, $2H_{ax}$, $J=13.2$ Hz, $ArCH_2Ar$), 4.39 (d, $2H_{ax}$, $J=13.2$ Hz, $ArCH_2Ar$), 4.22–3.63 (m, 40H, OCH_2CH_2O), 3.15 (d, $4H_{eq}$, $J=13.2$ Hz, $ArCH_2Ar$). Anal. calcd for $C_{48}H_{60}O_{12}$: C, 69.85; H, 7.24. Found C, 69.55; H, 7.30. FAB MS $m/z=829.5$ (MH^+). Yield: 20%. **Preparation of 5 and 7**. 1,2-Calix[4]-monocrown ($\sim$7.00 mmol), NaH (0.84 g, 35.00 mmol), appropriate ethylene glycol ditosylate (7.70 mmol) and dimethylformamide (1000 ml) were heated at 50°C under N_2. After 3 days, the same quantities of NaH and ethylene glycol ditosylate were added. 3 days later, methanol and water were added and solvents were evaporated to dryness and the residue was dissolved in dichloromethane. The solution was acidified with conc. aqueous HCl. The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. Compound **5** was obtained pure as a white solid by chromatography (SiO_2, 95/5 dichloromethane/acetone as eluent). Mp 210–212°C. ^1H NMR (200 MHz, $CDCl_3$): 6.70–6.54 (m, 12H, ArH in *meta* and *para* position), 4.99 (d, $1H_{ax}$, $J=13.0$ Hz, $ArCH_2Ar$), 4.54 (d, $1H_{ax}$, $J=13.0$ Hz, $ArCH_2Ar$), 4.37 (d, $2H_{ax}$, $J=13.2$ Hz, $ArCH_2Ar$), 4.37–3.72 (m, 28H, OCH_2CH_2O), 3.19 (d, $2H_{eq}$, $J=13.2$ Hz, $ArCH_2Ar$), 3.12 (d, $1H_{eq}$, $J=13.0$ Hz, $ArCH_2Ar$), 3.10 (d, $1H_{eq}$, $J=13.0$ Hz, $ArCH_2Ar$). Anal. calcd for $C_{42}H_{48}O_9\cdot 1/2CH_2Cl_2$: C, 69.05; H, 6.68. Found C, 69.05; H, 6.95. FAB MS $m/z=697.1$ (MH^+). Yield: 13%. Compound **7** was obtained pure as a yellow oil by chromatography (SiO_2, 80/20 dichloromethane/acetone as eluent). ^1H NMR (200 MHz, $CDCl_3$): 6.66–6.57 (m, 12H, ArH in *meta* and *para* position), 4.61 (d, $1H_{ax}$, $J=13.1$ Hz, $ArCH_2Ar$), 4.60 (d, $1H_{ax}$, $J=13.5$ Hz, $ArCH_2Ar$), 4.39 (d, $2H_{ax}$, $J=13.5$ Hz, $ArCH_2Ar$), 4.20–3.87 (m, 16H, OCH_2CH_2O), 3.74–3.66 (m, 20H,OCH_2CH_2O), 3.20–3.10 (m, $4H_{eq}$, $ArCH_2Ar$). Anal. calcd for $C_{46}H_{56}O_{11}$: C, 70.39; H, 7.19. Found C, 70.23; H, 7.21. FAB MS $m/z=785.5$ (MH^+). Yield: 14%.
9. **Preparation of 9–13**. Calixarenes **4–8** (2.00 mmol), HSO_3Cl (9.32 g, 8.00 mmol) in 30 ml of dichloromethane were stirred at room temperature under N_2 for 3 h. Ice was added and the aqueous layer was washed three times with dichloromethane. The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness to afford the corresponding **9–13**. **9**: ^1H NMR (200 MHz, $CDCl_3$): 7.51 (s, 8H, ArH in *meta* position), 5.24 (d, $2H_{ax}$, $J=13.5$ Hz, $ArCH_2Ar$), 4.58–3.68 (m, 26H, $ArCH_2Ar$ and OCH_2CH_2O), 3.54 (d, $2H_{eq}$, $J=13.8$ Hz, $ArCH_2Ar$), 3.38 (d, $2H_{eq}$, $J=13.5$ Hz, $ArCH_2Ar$). Yield: quantitative. **10**: ^1H NMR (200 MHz, $CDCl_3$): 7.53–7.47 (m, 8H, ArH in *meta* position), 5.31 (d, $1H_{ax}$, $J=13.4$ Hz, $ArCH_2Ar$), 5.30 (d, $1H_{ax}$, $J=13.7$ Hz, $ArCH_2Ar$), 4.60–3.66 (m, 28H, OCH_2CH_2O), 4.53 (d, $2H_{ax}$, $J=13.4$ Hz, $ArCH_2Ar$), 3.50 (d, $2H_{eq}$, $J=13.4$ Hz, $ArCH_2Ar$), 3.39 (d, $1H_{eq}$, $J=13.7$ Hz, $ArCH_2Ar$), 3.37 (d, $1H_{eq}$, $J=13.4$ Hz, $ArCH_2Ar$). Yield: quantitative. **11**: ^1H NMR (200 MHz, $CDCl_3$): 7.49 (s, 8H, ArH in *meta* position), 4.92 (d, $2H_{ax}$, $J=13.6$ Hz, $ArCH_2Ar$), 4.52 (d, $2H_{ax}$, $J=13.7$ Hz, $ArCH_2Ar$), 4.45–3.87 (m, 32H, OCH_2CH_2O), 3.47 (d, $2H_{eq}$, $J=13.7$ Hz, $ArCH_2Ar$), 3.39 (d, $2H_{eq}$, $J=13.6$ Hz, $ArCH_2Ar$). Yield: quantitative. **12**: ^1H NMR (200 MHz, $CDCl_3$): 7.49 (s, 8H, ArH in *meta* position), 4.97 (d, $1H_{ax}$, $J=13.4$ Hz, $ArCH_2Ar$), 4.90 (d, $1H_{ax}$, $J=14.0$ Hz, $ArCH_2Ar$), 4.66 (d, $2H_{ax}$, $J=13.4$ Hz, $ArCH_2Ar$), 4.45–3.36 (m, 40H, OCH_2CH_2O and $ArCH_2Ar$). Yield: quantitative. **13**: ^1H NMR (200 MHz, $CDCl_3$): 7.49 (s, 8H, ArH in *meta* position), 4.91 (d, $2H_{ax}$, $J=13.9$ Hz, $ArCH_2Ar$), 4.84 (d, $2H_{ax}$, $J=13.4$ Hz, $ArCH_2Ar$), 4.46–3.33 (m, 44H, OCH_2CH_2O and $ArCH_2Ar$). Yield: quantitative.
10. **Preparation of 14–18**. Calixarenes **9–13** (1.80 mmol), pyridine (10 ml) and water (2.5 ml) were stirred at room temperature for 2 h. Solvents were evaporated to dryness. The residue was dissolved in a minimum amount of water and treated with a solution of 10% NaOH in water. Precipitation with acetone afforded **14** as a white solid. Mp >260°C. ^1H NMR (200 MHz, D_2O): 7.15 (s, 8H, ArH in *meta* position), 4.81 (d, $2H_{ax}$, $J=12.9$ Hz, $ArCH_2Ar$), 4.72 (d, $2H_{ax}$, $J=13.2$ Hz, $ArCH_2Ar$), 4.38–4.10 (m, 8H, $ArOCH_2CH_2O$), 3.82–3.56 (m, 16H, OCH_2CH_2O), 3.34 (d, $2H_{eq}$, $J=13.2$ Hz, $ArCH_2Ar$), 3.19 (d, $2H_{eq}$, $J=12.9$ Hz, $ArCH_2Ar$). Anal. calcd for $C_{40}H_{40}Na_4O_{20}S_4\cdot 3H_2O$: C, 43.09; H, 4.16. Found C, 43.09; H, 4.17. ES MS $m/z=1037.1$ ($M-Na^+$). Yield: quantitative. **15** as a white solid. Mp >260°C. ^1H NMR (200 MHz, D_2O): 7.16–7.14 (m, 8H, ArH in *meta* posi-

tion), 4.38–3.16 (m, 36H, $ArC\underline{H}_2Ar$ and $OC\underline{H}_2C\underline{H}_2O$). Anal. calcd for $C_{42}H_{44}Na_4O_{21}S_4 \cdot 10H_2O$: C, 39.25; H, 5.02. Found C, 39.04; H, 4.82. ES MS $m/z = 1082.2$ ($M-Na^+$). Yield: quantitative. **16** as a white solid. Mp >260°C. ^1H NMR (200 MHz, D_2O): 7.12 (s, 8H, $Ar\underline{H}$ in *meta* position), 4.20–3.55 (m, 36H, $ArC\underline{H}_2Ar$ and $OC\underline{H}_2C\underline{H}_2O$), 3.30 (d, $2H_{eq}$, $J = 14.4$ Hz, $ArC\underline{H}_2Ar$), 3.23 (d, $2H_{eq}$, $J = 13.9$ Hz, $ArC\underline{H}_2Ar$). Anal. calcd for $C_{44}H_{48}Na_4O_{22}S_4 \cdot 14H_2O$: C, 37.71; H, 5.47. Found C, 37.72; H, 5.27. ES MS $m/z = 1125.2$ ($M-Na^+$). Yield: quantitative. **17** as a white solid. Mp >260°C. ^1H NMR (200 MHz, D_2O): 7.15 (s, 8H, $Ar\underline{H}$ in *meta* position), 4.45–3.23 (m, 44H, $ArC\underline{H}_2Ar$ and $OC\underline{H}_2C\underline{H}_2O$). Anal. calcd for $C_{46}H_{52}Na_4O_{23}S_4 \cdot 11H_2O$: C, 39.71; H, 5.36. Found C, 39.76; H, 5.13. ES MS $m/z = 1170.2$ ($M-Na^+$). Yield: quantitative. **18** as a white solid. Mp >260°C. ^1H NMR (200 MHz, D_2O): 7.12 (s, 8H, $Ar\underline{H}$ in *meta* position), 4.30–3.23 (m, 48H, $ArC\underline{H}_2Ar$ and $OC\underline{H}_2C\underline{H}_2O$). Anal. calcd for $C_{48}H_{56}Na_4O_{24}S_4 \cdot 14H_2O$: C, 38.71; H, 5.68. Found C, 38.67; H, 5.48. ES MS $m/z = 1214.2$ ($M-Na^+$). Yield: quantitative.

11. Gaubert, E.; Barnier, H.; Nicod, L.; Favre-Reguillon, A.; Foos, F.; Bardot, C.; Lemaire, M. *Sep. Sci. Technol.* **1997**, *32*, 2309.
12. Gutsche, C. D.; Levine, J. A.; Sujeeth, P. K. *J. Org. Chem.* **1985**, *50*, 5802.