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Stilbene-bridged 1,3-alternate calix[4]arene crown ether for selective alkali ion extraction

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Abstract—A series of stilbene-bridged calix[4]arenes was synthesized through an intramolecular reductive McMurry coupling of bis-benzaldehyde calix[4]arene in high yields. Tetra- and pentaethylene glycol chains were tethered to the phenolic groups of calix[4]arene to form stilbene-bridged calix[4]arene crown-5 and crown-6, respectively. The presence of stilbene bridge over the calix[4]arene rim effectively prevented the connection of the polyether chains in the cone conformation resulting in the exclusive formation of 1,3-alternate stilbene-bridged calix[4]arene crown product. Compared to the cone analogues, the 1,3-alternate calix[4]arene crown ethers showed a greater extraction ability and selectivity toward Cs^+.

1. Introduction

Since its discovery, calix[4]arene has been extensively used as a molecular platform to construct artificial ionophores.[1] Thanks to its preorganized basket structure and readily functionalizable phenolic groups, calix[4]arene-based ionophores with variety of cavity shapes and sizes were readily synthesized.[2] Calix[4]arene crown ethers, a class of calix[4]arene derivatives containing polyether chain tethered across opposite phenolic rings, are known to be more selective alkali ionophores than their crown ethers counterparts.[3] Both crown ether chain length and calixarene conformation play important roles in regulating the complextion with metal ions.[4] The applications of calix[4]arene crown ethers for Na^+/K^+ pump mimicking,[5] Rb^+ transportation in radiopharmaceutical treatments,[6] and the removal of Cs^+ radioactive wastes were reported.[7]

We have recently synthesized and studied a series of azobenzene-bridged and stilbene-bridged *tert*-butylcalix[4]arenes as photoswitchable ionophores[8] and molecular receptors.[9] We found that the incorporation of different isomers of rigid azobenzene or stilbene bridge on the narrow phenolic rim can regulate the calix[4]arene cavity shape. In this work, we would like to report the use of stilbene bridge to direct the synthesis of calix[4]arene crown ethers in a 1,3-alternate conformation for selective alkali ion extraction.

2. Results and discussion

Using reductive McMurry intramolecular coupling of bis-benzaldehyde calix[4]arenes **1** followed by condensation with the ditosylate ester of tetra- and pentaethylene glycol, stilbene-bridged calix[4]arene crown-5 and crown-6 were synthesized (Scheme 1). The reductive coupling yielded stereoisomeric mixtures of *cis* and *trans* stilbene **2** of which the cis isomer was predominant. By using a high dilution condition (7 mM of bisbenzaldehydes) and a large excess of $TiCl_4$ and Zn (20 equiv), the yields of stilbene products were markedly improved from our previous work.[9] The mixtures of *cis* and *trans* stilbene-bridged calix[4]arene were separated by column chromatography and used in the next condensation step. Only cis form of the final products from the condensation were successfully synthesized except for *o*-**3** that the trans isomer was also obtained. The characteristic singlet NMR signal of the calix[4]arene methylene protons observed in the spectra of **3** and **4** indicated that the stilbene-bridged calix[4]arene crowns were formed in the 1,3-alternate conformation.[10]

To our surprise, the attempts to prepare *m*-*trans*-**3** and *m*-*trans*-**4** from *m*-*trans*-**2** by the same approach have

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Keywords: Crown ether; Extraction; Calix[4]arene; Alkali ion.

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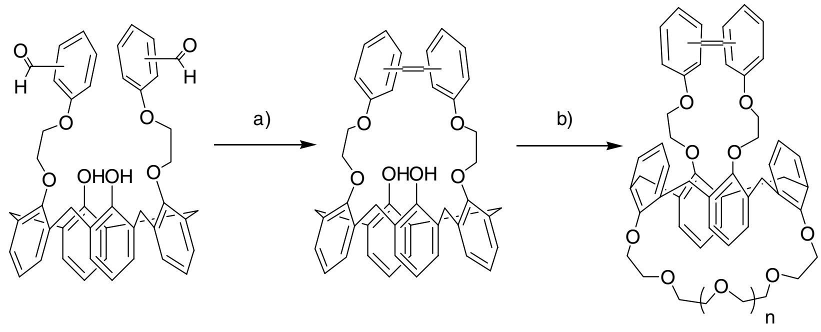


1

o-**2** *cis* 62% *trans* 15%
m-**2** *cis* 37% *trans* 37%
p-**2** *cis* 87%

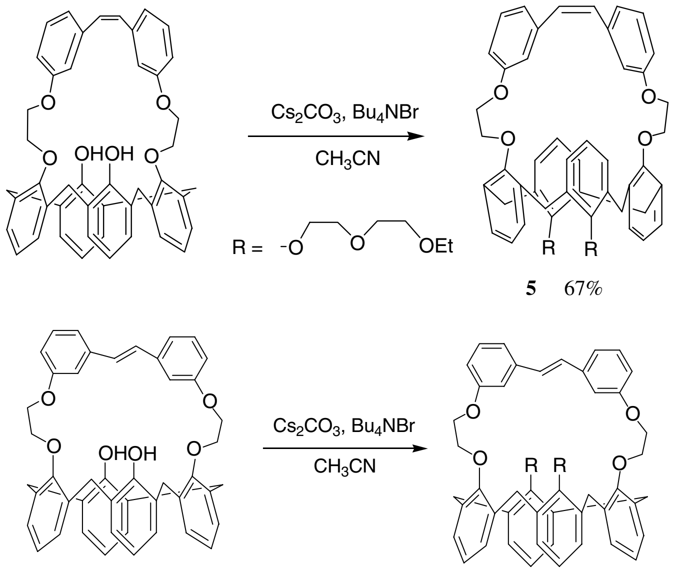
n=1 *o-cis*-**3** 80%
o-trans-**3** 67%
m-cis-**3** 84%
p-cis-**3** 80%
n=2 *o-cis*-**4** 75%
m-cis-**4** 68%
p-cis-**4** 70%

Scheme 1. Synthesis of stilbene calix[4]arene crown ether **3**, **4**.[11] Reagents: (a) $TiCl_4$, Zn, THF; (b) $TsO(CH_2CH_2O)_{(3+n)}Ts$, Cs_2CO_3, Bu_4NBr, CH_3CN.

been so far fruitless, yielding only intractable materials. To clarify these puzzling results, both *cis*- and *trans*-*m*-**2** were condensed with 2 equiv of *p*-toluenesulfonate ester of diethyleneglycol monoethylether (Scheme 2). The products from *m*-*cis*-**2** was the expected 1,3-alternate *m*-*cis*-**5** but the reaction of *m*-*trans*-**2** gave only a poor yield of the unexpected cone *m*-*trans*-**6**. The cone conformation was assigned according to the characteristic NMR signals of the doublet pairs of the calix[4]arene methylene protons. The results suggested that the phenol ring flipping process required for the conversion of the conformation from cone to 1,3-alternate was somehow disallowed in *m*-*trans*-**2**. Although our previous work has predicted that the calix[4]arene rims in *m*-*trans*-**2** were distorted from the normal circular shape into an oval shape[9] we have never thought that this distortion would totally prevent the ring flipping process.

For comparison in the extraction study, calix[4]arene crowns without the stilbene bridge (**7** and **8**) containing the same crown sizes as **3** and **4** were also synthesized (Scheme 3). Without the stilbene bridge, calix[4]arene crowns were obtained in the cone conformation exclusively.

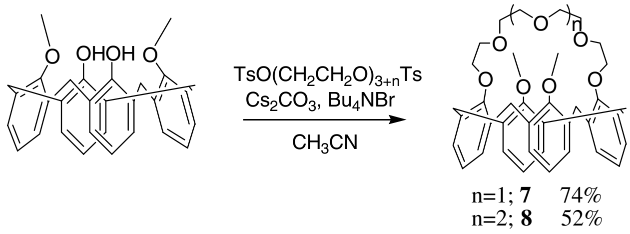
The alkali metal ion extraction at the aqueous $CHCl_3$ interface by stilbene-bridged calix[4]arene crowns **3** and **4** were investigated in comparison with compounds **5**, **7**, **8**, and 18-crown-6. The extraction was carried out by thorough mixing a chloroform solution (5 mM, 1 mL) of the ligand with an aqueous solution of the metal picrate (5 mM, 1 mL) for 24 h. After centrifugation, the aqueous phase (35 μL) was pipetted out and diluted to 5 mL. The concentration of the remaining metal ion in the aqueous phase was determined from



5 67%

6 20%

Scheme 2. Synthesis of stilbene calix[4]arene crown ether **5**, **6**.



Scheme 3. Synthesis of calix[4]arene crown ether **7**, **8**.

the UV absorbance of picrate ion at 354 nm in the diluted solution. The % extraction was calculated from $([A_0 - A]/[A_0]) \times 100$, whereas A_0 and A were the absorbance of the aqueous metal picrate solutions before and after extraction, respectively.

Calix[4]arene crowns (**3**, **4**, and **7**) and 18-crown-6 generally showed a good extractability toward alkali ions larger than Na^+ (Fig. 1). While the calix[4]arene crown-5 such as **3** and **7** showed a significantly greater K^+/Cs^+ selectivity than that of 18-crown-6, the calix[4]arene crown-6 (compound **4**) displayed impressively high Cs^+/K^+ selectivity. Stilbene-bridged calix[4]arene **5** in which structure contains two linear diethylene glycol chains has poor extractability toward all alkali ions.

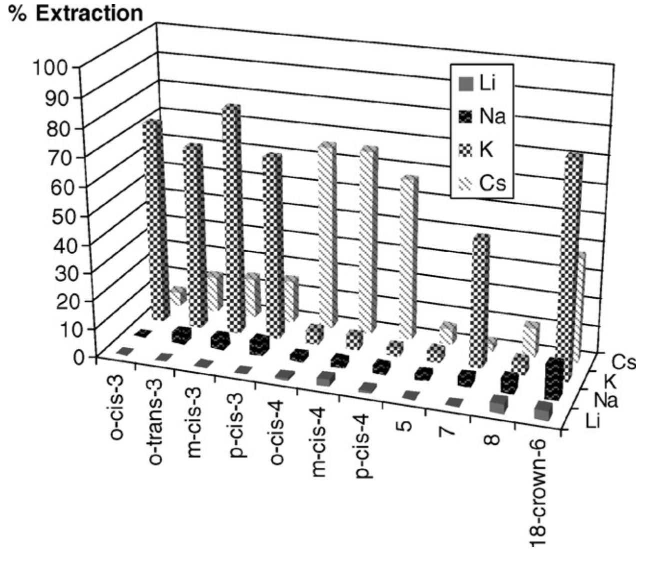


Figure 1. Extraction percentage of alkali metal picrates from water to chloroform by calix[4]arene derivatives and 18-crown-6 at room temperature.

The result indicated that neither the six oxygen atoms present in the diethylene glycol chains nor in the crown oxygens on the same side with the stilbene bridge are suitable for hosting the alkali ions. The cone calix[4]arene crown **8** has relatively much lower Cs^+ extractability compared to the 1,3-alternate stilbene-bridged calix[4]arene crown **4**. The 1,3-alternate calix[4]arene crown was reported to have a suitable orientation of aromatic rings for cation/π interaction participating in the binding of Cs^+.[11]

Having a high extracting ability, ligands **3** and **4** were also tested for solid–liquid extraction. An excess amount of potassium picrate was added into a solution of **3** or **4** in $CDCl_3$ and the mixture was sonicated. The color of the solution gradually changed from colorless to yellow indicating the dissolution of metal picrate into $CDCl_3$, which is normally nonsolvent for picrate salts. The changes in ^1H NMR spectra were used to justify the nature of complexation. For example, a new set of proton signals was clearly observed after 1 h of sonication *p*-*cis*-**3** with potassium picrate salt (compare Fig. 2a and b) suggesting a partial association of the ligand to K^+, to form the expecting host–guest complex, in the slow exchange process. This new set of signals became stronger with the expenses of the original set of signals as the sonication prolonged. The original signals *p*-*cis*-**3** were completely replaced by the signals of the complex after 3 h of sonication (Fig. 2c) signifying a full complexation of the host molecules to K^+ in the solid–liquid extraction.

Upon complexation with K^+, the signals of the methylene protons in the crown ether moiety of *p*-*cis*-**3** were shifted significantly downfield while the other signals were shifted only slightly (Fig. 3a) indicating that K^+ situated mostly within the crown ether loop. For the complexation between *p*-*cis*-**4** and Cs^+, significant shifts of various signals including the calixarene aromatic protons were observed (Fig. 3b) suggesting the possibility of cation–π interaction involving in the complexation.

In summary, the incorporation of stilbene bridge to calix[4]arenes provided a sensible approach to synthesize calix[4]arene crown-5 and crown-6 in 1,3-alternate conformation. These 1,3-alternate calix[4]arene crowns have a greater extractability and selectivity than those of the corresponding cone calix[4]arene crowns. The stilbene-bridged calix[4]arene crown-5 has an excellent K^+/Cs^+ selectivity while the stilbene-bridged calix[4]arene

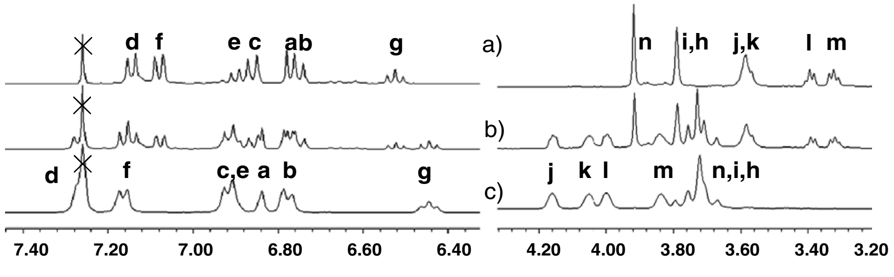


Figure 2. The ^1H NMR spectra of (a) *p*-*cis*-**3**, (b) partial complexation between *p*-*cis*-**3** and potassium picrate, and (c) full complexation between *p*-*cis*-**3** and potassium picrate.

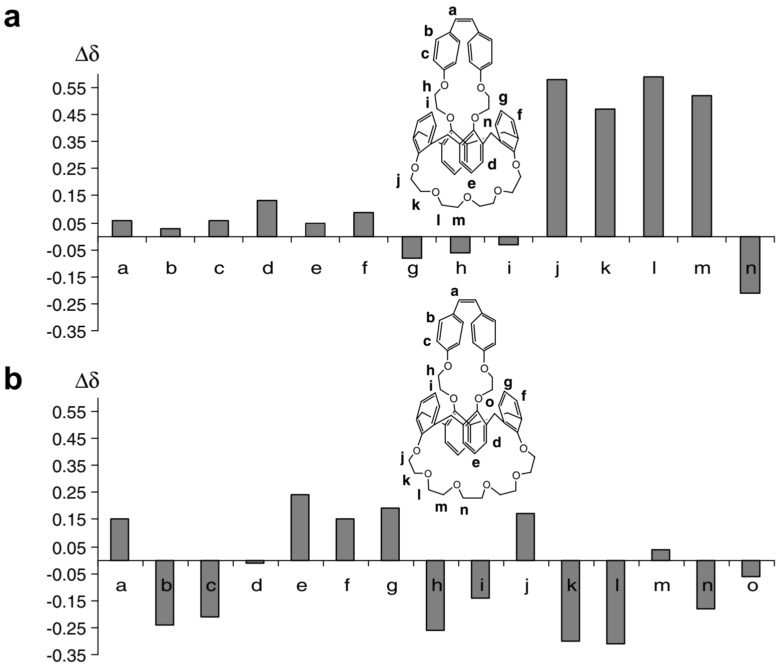


Figure 3. (a) Δ*δ* of *p-cis*-**3** complexed with potassium picrate and (b) Δ*δ* of *p-cis*-**4** complexed with cesium picrate.

crown-6 has an excellent Cs^+/K^+ selectivity in the aqueous chloroform extraction. The metal selectivities of 1,3-alternate calix[4]arene crowns also significantly outperform 18-crown-6.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.01.026.

References and notes

1. (a) Gutsche, C. D. *Acc. Chem. Res.* **1983**, *16*, 161–170; (b) Gutsche, C. D. *Calixarenes* Revisited. In *Monograph in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1989; (c) Böhmer, V. *Angew. Chem., In. Ed. Engl.* **1995**, *34*, 713–745; (d) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713–1734; (e) Gutsche, C. D. *Calixarenes* Revisited. In *Monograph in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: London, 1998; (f) Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J. *Calixarenes 2001*; Kluwer Academic: Dordrecht, Holland, 2001.
2. (a) Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767–2777; (b) Matsumoto, H.; Shinkai, S. *Tetrahedron Lett.* **1996**, *37*, 77–80; (c) Arduini, A.; Domiano, L.; Pochini, A.; Secchi, A.; Ungarro, R.; Ugozzoli, F.; Struck, O.; Verboom, W.; Reinhoudt, D. N. *Tetrahedron* **1997**, *53*, 3767–3776; (d) Bodenant, B.; Weil, T.; Businelli-Pourcel, M.; Fages, F.; Barbe, B.; Pianet, I.; Laguerre, M. *J. Org. Chem.* **1999**, *64*, 7034–7039; (e) Beer, P. D.; Hopkins, P. K.; McKinny, J. D. *Chem. Commun.* **1999**, 1253–1254; (f) Guillon, J.; Leger, J.-M.; Sonnet, P.; Jarry, C.; Robba, M. *J. Org. Chem.* **2000**, *65*, 8283–8289; (g) Tuntulani, T.; Poompradub, S.; Thavornyutikarn, P.; Jaiboon, N.; Ruangpornvisuti, V.; Chaichit, N.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **2001**, *42*, 5541–5544; (h) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516; (i) Liu, J.-M.; Zheng, Q.-Y.; Yang, J. L.; Chen, C.-F.; Huang, Z.-T. *Tetrahedron Lett.* **2002**, *43*, 9209–9212; (j) Yilmaz, A.; Memon, S.; Yilmaz, M. *Tetrahedron* **2002**, 7735–7740; (k) Cao, Y.-D.; Zheng, Q.-Y.; Chen, C.-F.; Huang, Z.-T. *Tetrahedron Lett.* **2003**, *44*, 4751–4755.
3. (a) Gbidini, E.; Ugozzoli, F.; Ungaro, R.; Harkema, S.; El-Fadl, A.; Reinhoudt, D. *J. Am. Chem. Soc.* **1990**, *112*, 6979–6985; (b) Nijenhuis, W. F.; Buitenhuis, E. G.; de Jong, F.; Sudholter, E. J. R.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 7963–7968; (c) Yamamoto, H.; Shinkai, S. *Chem. Lett.* **1994**, 1115–1118; (d) Asfari, Z.; Bressot, C.; Vicens, J.; Hill, C.; Dozol, J.; Rouquette, H.; Eymard, S.; Lamare, V.; Toumois, B. *Anal. Chem.* **1995**, *67*, 3133–3139; (e) Geraci, C.; Chessari, G.; Piattelli, M.; Neri, P. *Chem. Commun.* **1997**, 921; (f) Kim, J.; Lee, W.; Suh, I.; Kim, J.; Yoon, I.; Lee, J. *J. Org. Chem.* **2000**, *65*, 7215–7217.
4. (a) Bocchi, C.; Careri, M.; Casnati, A.; Mori, G. *Anal. Chem.* **1995**, *67*, 4234–4238; (b) Asfari, Z.; Bressot, C.; Vicens, J.; Hill, C.; Dozol, J.; Rouquette, H.; Eymard, S.; Lamare, V.; Tournois, B. *Anal. Chem.* **1995**, *67*, 3133–3139; (c) Arnaud-Neu, F.; Caccamese, S.; Fuangswasdi, S.; Pappalardo, S.; Parisi, M. F.; Petringa, A.; Principato, G. *J. Org. Chem.* **1997**, *62*, 8041–8048; (d) Kim, J. S.; Pang, J. H.; Yu, I. Y.; Lee, W. K.; Suh, I. H.; Kim, J. K.; Cho, M. H.; Kim, E. T.; Ra, D. Y. *J. Chem. Soc., Perkin Trans. 2* **1999**, 837–840; (e) Casnati, A.; Ca, N. D.; Sansone, F.; Ugozzoli, F.; Ungaro, R. *Tetrahedron* **2004**, *60*, 7869–7876; (f) Luo, H.; Dai, S.; Bonnesen, P. V.;

Buchanan, A. C.; Holbrey, J. D.; Bridges, N. J.; Rogers, R. D. *Anal. Chem.* **2004**, *76*, 3078–3083; (g) van Leeuwen, F. W. B.; Beijleveld, H.; Miermans, C. J. H.; Huskens, J.; Verboom, W.; Reinhoudt, D. N. *Anal. Chem.* **2005**, *77*, 4611–4617.

5. (a) Reinhoudt, D. N.; Dijkstra, P. J.; in't Veld, P. J. A.; Bugge, K.-E.; Harkema, S.; Ungaro, R.; Ghidini, E. *J. Am. Chem. Soc.* **1987**, *109*, 4761–4762; (b) Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K.-E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E. *J. Am. Chem. Soc.* **1989**, *111*, 7567–7575; (c) Beer, P. D.; Gale, P. A.; Chen, Z.; Drew, M. G. B.; Heath, J. A.; Ogden, M. I.; Powell, H. R. *Inorg. Chem.* **1997**, *36*, 5880–5893; (d) Bourgeois, J.-P.; Echegoyen, L.; Fibboli, M.; Pretsch, E.; Diederich, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2118–2121.
6. (a) Brewer, K. *J. Am. Chem. Soc.* **1938**, *60*, 691; (b) Anderson, C. J.; Welch, M. J. *Chem. Rev.* **1999**, *99*, 2219–2234.
7. (a) *Radioactive Waste Management and Disposal*; Cecille, L., Ed.; Elsevier: New York, 1991; (b) Asfari, Z.; Pulpoka, B.; Saadioui, M.; Wenger, S.; Nierlich, M.; Thuery, P.; Reynier, N.; Dozol, J.-F.; Vincens, J. In *J. Mol. Recognit. Inclusion, Proc. 9th Int. Symp.*; 1998; pp 173–178; (c) Hill, C.; Dozol, J.-F.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; Vincens, J.; Asfari, Z.; Bressot, C. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *19*, 399–408; (d) McDowell, W. J.; Case, G. N.; McDonough, J. A.; Bartsch, R. A. *Anal. Chem.* **1992**, *64*, 3013–3017.
8. (a) Pipoosananakaton, B.; Sukwattanasinitt, M.; Jaiboon, N.; Chaichit, N.; Tuntulani, T. *Tetrahedron Lett.* **2000**, *41*, 9095–9100; (b) Sukwattanasinitt, M.; Rojanathanes, R.; Tuntulani, T.; Sritana-anant, Y.; Ruangpornvisuti, V. *Tetrahedron Lett.* **2001**, *42*, 5291–5293; (c) Rojanathanes, R.; Pipoosananakaton, B.; Tuntulani, T.; Bhanthumnavin, W.; Orton, J. B.; Cole, S. J.; Hursthouse, M. B.; Grossel, M. C.; Sukwattanasinitt, M. *Tetrahedron* **2005**, *61*, 1317–1324.
9. Rojanathanes, R.; Tutulani, T.; Bhabthumnavin, W.; Sukwattanasinitt, M. *Org. Lett.* **2005**, *7*, 3401–3404.
10. Spectroscopic data of stilbene calix[4]arene crown-5 or 6 (**3** and **4**); compound *o-cis*-**3**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.06, 3.42 (t, $–OCH_2CH_2O$-crown, 8H), 3.11, 3.45 (t, $ArOCH_2CH_2O$-crown, 8H), 3.56 (br, $ArOCH_2CH_2OAr$, 8H), 3.87 (m, $ArCH_2Ar$, 8H), 6.86, 6.90 (t, calix-ArH, 4H), 6.79, 7.18 (d, stilbene-ArH, 4H), 6.90, 7.16 (t, stilbene-ArH, 4H), 6.55 (s, $CH=CH$, 2H), 6.98, 7.10 (d, calix-ArH, 8H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 38.1 ($ArCH_2Ar$), 68.3 (OCH_2), 68.8 (OCH_2), 69.7 (OCH_2), 69.8 (OCH_2), 70.7 (OCH_2), 72.7 (OCH_2), 122.8 (calix-ArC), 123.7 (calix-ArC), 129.2 (calix-ArC), 129.7 (calix-ArC), 133.4 (calix-ArC), 133.9 (calix-ArC), 156.1 (calix-ArC), 156.3 (calix-ArC), 129.1 (stilbene-ArC), 127.9 (stilbene-ArC), 117.3 (stilbene-ArC), 117.7 (stilbene-ArC), 121.7 (stilbene-ArC), 122.8 (stilbene-ArC), 127.9 (stilbene-ArC), 129.1 (stilbene-ArC), 156.9 (stilbene-ArC), 126.7 ($CH=CH$); mp = 124–126 °C; FTMS calcd for $C_{54}H_{54}O_9$ [ESI, M^+ NH_4]: 846.4106, found: 864.4091; compound *o-trans*-**3**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.16, 3.53 (t, OCH_2CH_2O-crown, 8H), 3.25, 3.65 (t, $ArOCH_2CH_2O$-crown, 8H), 3.57, 3.64 (br, $ArOCH_2CH_2OAr$, 8H), 3.88 (m, $ArCH_2Ar$, 8H), 6.65, 7.15 (d, calix-ArH, 8H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 37.9 ($ArCH_2Ar$), 65.8 (OCH_2), 68.1 (OCH_2), 68.3 (OCH_2), 69.8 (OCH_2), 70.5 (OCH_2), 72.6 (OCH_2), 129.3 (calix-ArC), 129.3 (calix-ArC), 133.9 (calix-ArC), 134.1 (calix-ArC), 134.1 (calix-ArC), 139.3 (calix-ArC), 156.2 (calix-ArC), 158.5 (calix-ArC), 111.1 (stilbene-ArC), 115.3 (stilbene-ArC), 122.6 (stilbene-ArC), 122.7 (stilbene-ArC), 129.1 (stilbene-ArC), 156.1 (stilbene-ArC), 121.4 ($CH=CH$) FTMS calcd for $C_{54}H_{54}O_9$ [ESI, M^+ NH_4]: 846.4106, found: 864.4099; compound *m-cis*-**3**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.16, 3.46 (t, OCH_2CH_2O-crown, 8H), 3.27, 3.52 (t, $ArOCH_2CH_2O$-crown, 8H), 3.60 (br, $ArOCH_2CH_2OAr$, 8H), 3.87 (m, $ArCH_2Ar$, 8H), 6.65, 6.91 (t, calix-ArH, 4H), 6.83, 6.89 (d, stilbene-ArH, 4H), 7.27 (t, stilbene-ArH, 2H), 6.63 (s, stilbene-ArH, 2H), 6.78 (s, $CH=CH$, 2H), 7.05, 7.13 (d, calix-ArH, 8H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 38.1 ($ArCH_2Ar$), 67.0 (OCH_2), 68.3 (OCH_2), 68.4 (OCH_2), 69.7 (OCH_2), 70.7 (OCH_2), 72.8 (OCH_2), 129.5 (calix-ArC), 129.8 (calix-ArC), 130.0 (calix-ArC), 134.1 (calix-ArC), 134.2 (calix-ArC), 138.5 (calix-ArC), 156.1 (calix-ArC), 158.5 (calix-ArC), 109.9 (stilbene-ArC), 111.5 (stilbene-ArC), 116.5 (stilbene-ArC), 122.3 (stilbene-ArC), 111.5 (stilbene-ArC), 156.0 (stilbene-ArC), 122.4 ($CH=CH$); mp = 206–207 °C; Anal. Calcd for $C_{54}H_{54}O_9$: C, 76.62; H, 6.38. Found: C, 76.68; H, 6.45; compound *p-cis*-**3**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.32, 3.39 (t, OCH_2CH_2O-crown, 8H), 3.59 (br, $ArOCH_2CH_2O$-crown, 8H), 3.79 (br, $ArOCH_2CH_2OAr$, 8H), 3.92 (s, $ArCH_2Ar$, 8H), 6.52, 6.89 (t, calix-ArH, 4H), 6.75, 6.86 (d, stilbene-ArH, 8H), 6.78 (s, $CH=CH$, 2H), 7.08, 7.14 (d, calix-ArH, 8H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 37.8 ($ArCH_2Ar$), 68.9 (OCH_2), 68.9 (OCH_2), 69.4 (OCH_2), 70.5 (OCH_2), 70.6 (OCH_2), 71.9 (OCH_2), 130.1 (calix-ArC), 130.5 (calix-ArC), 130.6 (calix-ArC), 131.3 (calix-ArC), 133.8 (calix-ArC), 134.0 (calix-ArC), 155.8 (calix-ArC), 156.4 (calix-ArC), 117.4 (stilbene-ArC), 121.8 (stilbene-ArC), 115.5 (stilbene-ArC), 158.0 (stilbene-ArC), 122.7 ($CH=CH$); mp = 211 °C; Anal. Calcd for $C_{54}H_{56}O$: C, 76.62; H, 6.38. Found: C, 76.60; H, 6.38; compound *o-cis*-**4**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.12 (t, OCH_2, 4H) 3.19 (t, OCH_2, 4H) 3.42 (t, OCH_2, 4H), 3.46 (t, OCH_2, 4H), 3.55 (t, OCH_2, 4H), 3.61 (m, OCH_2, 8H), 3.75 (t, $ArCH_2Ar$, 8H), 6.41 (s, $CH=CH$, 2H), 6.89, 7.02 (d, calix-ArH, 8H), 6.82, 7.09 (t, calix-ArH, 4H), 6.75 (m, stilbene-ArH, 2H), 6.77 (m, stilbene-ArH, 2H), 6.82 (m, stilbene-ArH, 2H), 7.20 (d, stilbene-ArH, 2H); mp = 116–118 °C; Anal. Calcd for $C_{56}H_{58}O_{10}$: C, 75.53; H, 6.51. Found: C, 75.54; H, 6.56; compound *m-cis*-**4**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.35 (t, OCH_2, 8H), 3.46 (t, OCH_2, 4H), 3.53 (t, OCH_2, 4H), 3.61 (t, OCH_2, 4H), 3.64 (t, OCH_2, 4H), 3.67 (t, OCH_2, 4H), 3.71 (t, OCH_2, 4H), 3.85 (s, $ArCH_2Ar$, 8) 6.63, 7.27 (t, calix-ArH, 4H), 7.07, 7.12 (d, calix-ArH, 8H), 6.82, 6.91 (d, stilben-ArH, 4H), 6.90 (t, stilben-ArH, 2H), 6.64 (s, stilben-ArH, 2H) 6.78 (s, $CH=CH$, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 38.0 ($ArCH_2Ar$), 61.7 (OCH_2), 66.9 (OCH_2), 68.3 (OCH_2), 68.9 (OCH_2), 69.4 (OCH_2), 72.7 (OCH_2), 1129.9 (calix-ArC), 130.1 (calix-ArC), 130.3 (calix-ArC), 134.0 (calix-ArC), 134.3 (calix-ArC), 138.5 (calix-ArC), 156.3 (calix-ArC), 158.4 (calix-ArC), 111.3 (stilbene-ArC), 116.4 (stilbene-ArC), 112.4 (stilbene-ArC), 122.6 (stilbene-ArC), 122.6 (stilbene-ArC), 156.0 (stilbene-ArC), 122.2 ($CH=CH$) FTMS calcd for $C_{56}H_{58}O_{10}$ [ESI, M^+ NH_4]: 908.4368, found: 908.4352; compound *p-cis*-**4**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.54 (t, OCH_2, 4H), 3.81 (t, OCH_2, 4H), 3.87 (t, OCH_2, 4H), 3.91 (t, OCH_2, 8H), 3.97 (t, OCH_2, 4H), 4.46 (t, OCH_2, 4H), 3.87 (s, $ArCH_2Ar$, 8H), 6.19, 6.78 (t, calix-ArH, 4H), 7.02, 7.19 (d, calix-ArH, 8H), 7.07, 7.14 (d, stilbene-ArH, 8H), 6.70 (s, $CH=CH$, 2H) mp = 256–257 °C; FTMS calcd for $C_{56}H_{58}O_{10}$ [ESI, M^+ NH_4]: 908.4368, found: 908.4375. The experimental details are available in Supplementary data.
11. (a) Lamare, V.; Dozol, J. F.; Ugozzoli, F.; Casnati, A.; Ungaro, R. *Eur. J. Org. Chem.* **1998**, *8*, 1559–1568; (b) Kim, J. S.; Ohki, A.; Ueki, R.; Ishizuka, T.; Shimotashiro, T.; Maeda, S. *Talanta* **1999**, *48*, 705–710.