Selective Upper Rim Functionalization and Lower Rim Bridge Building with Calix[4]arenes and Calix[6]arenes[1]

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Selective upper rim functionalization of calix[6]arenes has been achieved by selective lower rim benzoylation at the 1,2,4,5 positions followed by $AlCl_3$-induced removal of the *tert*-butyl groups of the unesterified aryl residues and introduction of various functionalities into the vacated *para* positions, including bromo (**5**), dialkylamino, (**7**−**11**) cyanomethyl (**12**), and (propargyloxy)methyl (**13**) groups. Lower rim bridge building has been achieved via oxidative coupling reactions between the aryne moieties of calix[4]arenes and calix[6]arenes in which *O*-benzyl groups carry one (from **23** and **24**) or two (from **25**) propargyloxy residues. In the calix[4]arene series both a single-spanned (**32**) and a double-spanned (**33**) double-cavity calixarene were obtained. In the calix[6]arene series only a single-spanned double cavity calixarene (**36**) could be characterized.

Calixarenes are macrocyclic compounds comprising 4−16 or more phenolic moieties joined in cyclic array at the *meta* positions by methylene groups. Although most of the attention during the past 15 years has been devoted to the calix[4]arenes,[2] increasing attention is being devoted to some of the larger members, particularly the calix[6]arenes. The present work falls primarily in the latter category and deals with the selective introduction of functional groups at the upper rim and the building of bridges at the lower rim.

Only a few cases of selective upper rim functionalization of preformed calix[6]arenes have appeared in the literature. Kanamathareddy and Gutsche[3] prepared a tetraester of *p-tert*-butylcalix[6]arene and selectively removed the two *tert*-butyl groups *para* to the free phenolic groups but did not report the introduction of functional groups into these positions. de Mendoza et al.[4] selectively removed the *tert*-butyl groups *para* to the phenolic moieties in partially methylated *p-tert*-butylcalix-[6]arenes and then introduced bromo and nitro groups into the vacated *para* positions. In similar fashion, Takeshita et al.[5] selectively removed three *p-tert*-butyl groups from the 1,3,5-trimethyl ether of *p-tert*-butylcalix-[6]arene, methylated the remaining OH groups, and introduced chloromethyl groups into the three available *para* positions.

The present approach, which is similar to those described above, starts with the selective lower rim conversion of *p-tert*-butylcalix[6]arene (**1b**) to the 1,2,4,5-*tetra-p*-nitrobenzoyl ester (**2**)[3] followed by selective de-*tert*-butylation of the unesterified phenolic residues to give **3** (Scheme 1). Hydrolysis of **3** then yields the pivotal compound **4** into which a variety of functional groups have been introduced, including bromine to give **5** in 85% yield and various amino moieties via the Mannich base reaction[6] to give **7**−**11** in 85−90% yields. Compound **11**, in turn, can be converted to its quaternary ammonium salt with MeI and treated with NaCN or propargyl alcohol and NaH to provide **12** and **13** via the quinone methide route[6] in yields of 35% and 20%, respectively. The rather low yield of **13**, however, discouraged its use for building upper rim bridges, and attention was therefore turned to bridge building at the lower rim.

The appropriately-substituted arylmethyl bromides for reaction at the lower rim were synthesized from 3-hydroxybenzoic acid (**14**), 4-hydroxybenzoic acid (**15**), and 3,5-dihdroxybenzoic acid (**16**) by treatment with propargyl bromide to yield **17**, **18**, and **19**, respectively. Lithium aluminum hydride reduction of the esters yielded the benzyl alcohols **20**−**22** which were treated with methanesulfonyl chloride followed by LiBr to afford the mono- and bis-propargyl ethers **23**−**25**. Elemental analysis along with mass spectral data showed that some samples of **24** and **25** contained *ca.* 10% of the corresponding aryl chloride, the result of displacement of the methanesulfonyl group by chloride from the triethylammonium chloride formed in the mesylation reaction. Although compounds **17**−**25** are quite simple in structure, a number are not in the literature or have been only briefly described.[7]

The 1,3-dibenzyl ether of *p-tert*-butylcalix[4]arene (**26**)[8] and the 1,3,5-trimethyl ether of *p-tert*-butylcalix[6]arene (**27**)[9] were treated with the bis-propargyl ether **25** and converted to **28** and **29**, respectively, in *ca* 70% yield

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(1) Paper 44 in the series Calixarenes. For paper 43, cf. Gibbs, C. G.; Sujeeth; P. K.; Rogers, J. S.; Stanley, G. G., Krawiec, M.; Watson, W. H.; Gutsche, C. D. *J. Org. Chem.* **1995**, *60*, 8394.

(2) (a) Gutsche, C. D. Calixarenes. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: London, 1989. (b) *Calixarenes, A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer: Dordrecht, 1991. (c) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713−745. (d) Gutsche, C. D. *Aldrichimica Acta* **1995**, *28*, 3−9.

(3) Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem.* **1992**, *57*, 3160.

(4) de Mendoza, J.; Carramolino, M.; Cuevas, F.; Nieto, P. D.; Prados, P.; Reinhoudt, D. N. Verboom, W.; Ungaro, R.; Casnati, A. *Synthesis* **1994**, 47.

(5) Takeshita, M.; Nishio, S.; Shinkai, S. *J. Org. Chem.* **1994**, *59*, 4032.

(6) Gutsche, C. D.; Nam, K. C. *J. Am. Chem. Soc.* **1988**, *110*, 6153.

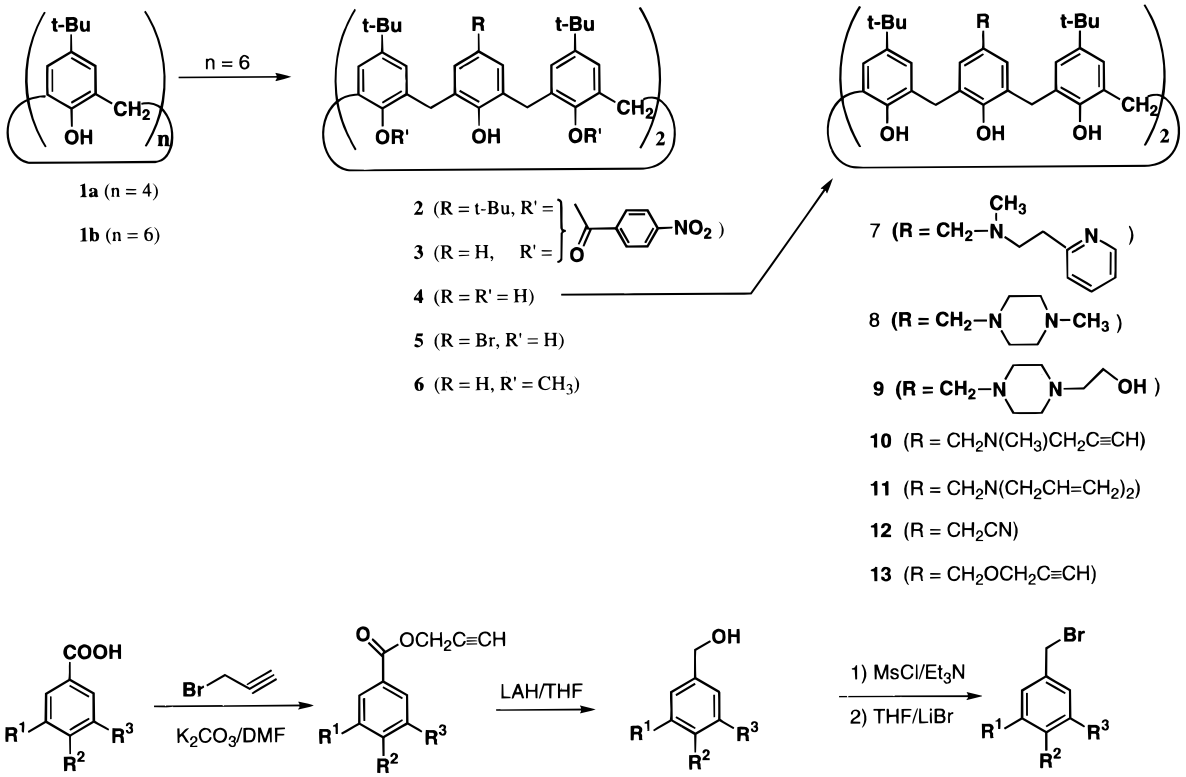
(7) Compound **21** has been described with brief experimental detail (Miura, M.; Gabel, D.; Oenbrink, G.; Fairchild, R. G. *Tetrahedron Lett.* **1990**, *31*, 2247). Compound **22** has been reported in the patent literature [Karrer, F.; Farooq, S.; Drabek, J.; Meyer, W.; Gsell, L. Ger. Offen. 2,654,293 (*Chem. Abstr.* **1977**, *87*, 84693k); Sumitomo Chemical Co., Ltd. Fr 2,043,019 (*Chem. Abstr.* **1972**, *76*, 3557s)]. Compound **23** has been reported in the patent literature [Henrick. C. A.; Garcia, B. A. Ger. Offen. 2,812,169 (*Chem. Abstr.* **1979**, *90*, 122072d); US 4,243,-819 (*Chem. Abstr.* **1982**, *96*, 123297s)]. 2,5-Bis(propargyloxy)benzoic esters have been reported by Brown, A. B.; Whitlock, H. W., Jr. *Synth. Commun.* **1993**, *23*, 23.

(8) Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K. E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, Ugozzoli, Ghidini, E. *J. Am. Chem. Soc.* **1989**, *111*, 7567. Gutsche, C. D.; Reddy, P. A. *J. Org. Chem.* **1991**, *56*, 4783.

(9) Casnati, A.; Minari, P.; Pochini, A.; Ungaro, R. *J. Chem. Soc. Chem.Commun.* **1991**, 1413. Kanamathareddy, S.; Gutsche, C. D. *J. Am. Chem. Soc.* **1993**, *115*, 6572.

0022-3263/96/1961-2511$12.00/0

Scheme 1

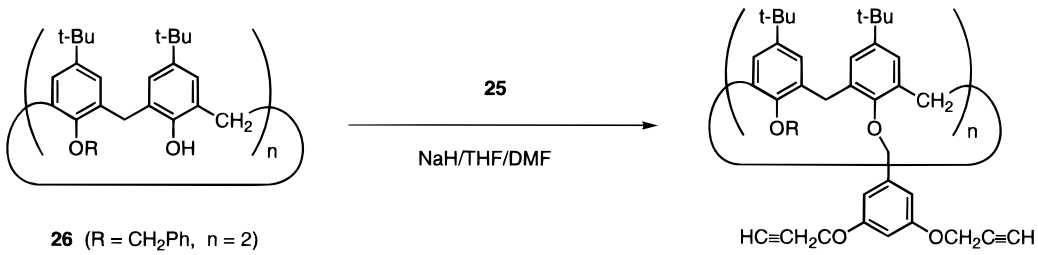


14 ($R^1 = R^2 = H, R^3 = OH$) **17** ($R^1 = R^2 = H, R^3 = OCH_2C{\equiv}CH$) **20** ($R^1 = R^2 = H, R^3 = OCH_2C{\equiv}CH$) **23** ($R^1 = R^2 = H, R^3 = OCH_2C{\equiv}CH$)

15 ($R^1 = R^3 = H, R^2 = OH$) **18** ($R^1 = R^3 = H, R^2 = OCH_2C{\equiv}CH$) **21** ($R^1 = R^3 = H, R^2 = OCH_2C{\equiv}CH$) **24** ($R^1 = R^3 = H, R^2 = OCH_2C{\equiv}CH$)

16 ($R^1 = R^3 = OH, R^2 = H$) **19** ($R^1 = R^3 = OCH_2C{\equiv}CH, R^2 = H$) **22** ($R^1 = R^3 = OCH_2C{\equiv}CH, R^2 = H$) **25** ($R^1 = R^3 = OCH_2C{\equiv}CH, R^2 = H$)

Scheme 2



26 ($R = CH_2Ph$, n = 2)

27 ($R = CH_3$, n = 3)

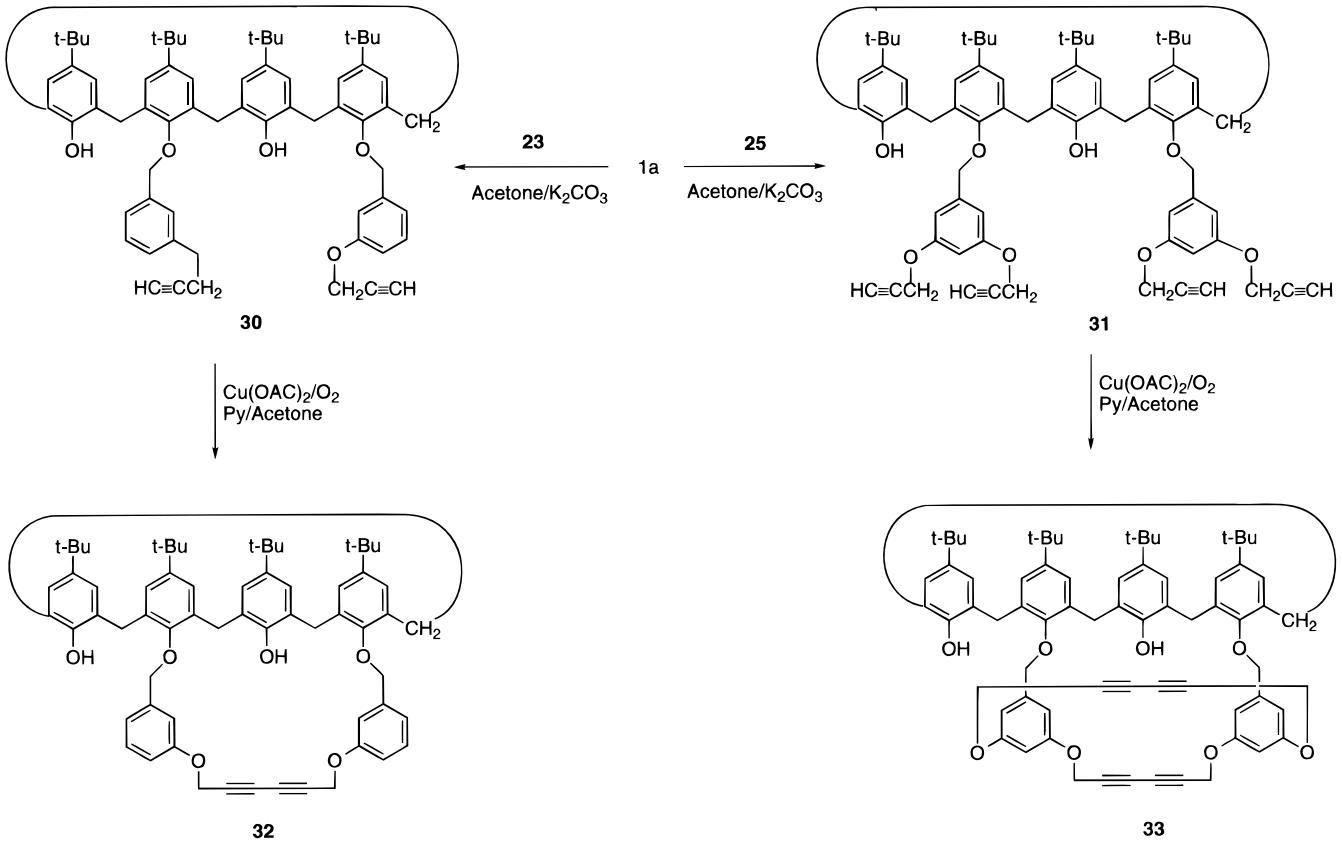
28 ($R = CH_2Ph$, n = 2)

29 ($R = CH_3$, n = 3)

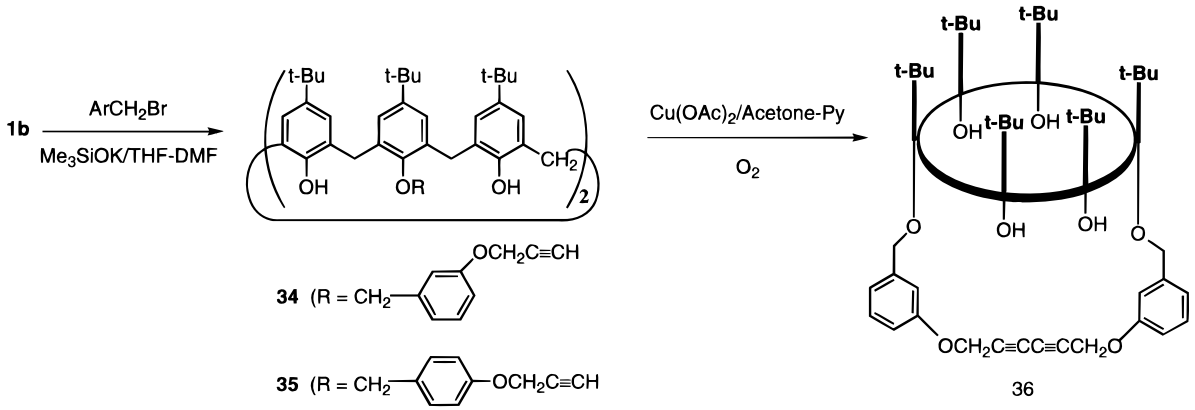
(Scheme 2). Attempts to achieve intramolecular oxidative coupling of the alkyne residues in these compounds, however, yielded only intractable products that could not be characterized. In further exploration of this type of cyclization process, compounds **30** and **31** were prepared in 90% yield by selective lower ring functionalization with **23** and **25**, respectively (Scheme 3). Surprisingly, both **30** and **31** underwent smooth oxidative coupling to afford the single-spanned double-cavity calixarene **32** in 75% yield and the double-spanned double-cavity calixarene **33** in 55% yield, analogous to the compounds previously prepared by Gutsche and See.[10] By following the course of the cyclization of **31** by TLC and ^{1}H NMR (disappearance of the resonance at δ 2.44 arising from the acetylenic proton), it was determined that the second bridge forms considerably more slowly than the first bridge, probably accounting for the somewhat lower yield. That the aryne coupling reactions are intra- rather than intermolecular was confirmed by mass spectral measurements. The single-spanned and double-spanned compounds **32** and **33** differ markedly with respect to the flexibility of their diaryne bridge(s). Whereas the ^{1}H NMR spectrum of **32** at ambient temperature shows a singlet arising from the $OCH_2C{\equiv}C$ methylene hydrogens, **33** shows a pair of doublets. Although the hydrogens of the methylene groups are diastereotopic in both compounds, they can become equivalent on a time-averaged basis as the result of a twisting of the bridge(s) and the attached aryl rings. However, molecular models of **32** and **33** show that the twisting is much more constrained in **33** as indicated by its variable temperature ^{1}H NMR spectral behavior in which the doublet pattern broadens somewhat as the

(10) Gutsche, C. D.; See, K. A. *J. Org. Chem.* **1992**, *57*, 4527.

Scheme 3



Scheme 4



temperature is raised to 125 °C in $C_2D_2Cl_4$ but which shows no indication of being near a coalescence point.

Encouraged by the results of the aryne coupling reactions with the cyclic tetramers **30** and **31**, comparable reactions were undertaken in the calix[6]arene series. The 1,4-diethers **34** and **35** were obtained by treatment of **1b** with arylmethyl bromides **23** and **24**, respectively (Scheme 4). In the case of **35** a single product was obtained for which the ^{1}H NMR spectrum (two pairs of doublets for the $ArCH_2Ar$ methylene hydrogens) is commensurate with a flattened cone conformation (**ou,**u,u,-ou,u,u[11]). In the case of **34**, however, the product was indicated by its ^{1}H NMR spectrum to be a *ca.* 1:1 mixture of the the flattened cone conformer (**ou**,u,u,ou,u,u) and the 1,2,3-alternate conformer (**u**,u,d,d,d,u). Both **34** and **35** were subjected to aryne coupling conditions, and both gave complex mixtures under a variety of conditions. Only after repeated attempts was it possible to convert **34** in 20−25% yield to the single-spanned double-cavity calix[6]arene **36**, the structure of which is based on its elemental analysis, mass spectrum, and ^{1}H NMR and ^{13}C NMR spectra. The presence of two pairs of doublets for the $ArCH_2Ar$ protons and two lines for the *tert*-butyl protons in the ^{1}H NMR spectrum of **36** indicates it to be the flattened cone conformer (**ou**,u,u,ou,u,u).

(11) For details of nomenclature, cf. Kanamathareddy, S.; Gutsche, C. D. *J. Am. Chem. Soc.* **1993**, *115*, 6572.

Experimental Section[12]

5,11,23,29-Tetra-*tert*-butylcalix[6]arene-37,38,39,40,41,-42-hexol (4). A 5.85 g sample (4 mmol) of tetraester **3** prepared as previously described[3] was slurried in 100 mL of EtOH, and to this heterogeneous mixture was added 20 mL of 20% KOH. The contents were heated under reflux for 8 h, EtOH was removed under vacuum, and the brown reaction mixture was poured into 150 g of crushed ice. The precipitate was removed by filtration and treated with a mixture of 150

mL of CH_2Cl_2 and 100 mL of 2 N HCl, and the contents were stirred to bring the free calixarene into the CH_2Cl_2 layer. The organic layer was removed, washed with water and brine, and dried over Na_2SO_4. The residue after evaporation of the solvent was treated with MeOH to give 3.2 g (93%) of **4** as a white powder. Recrystallization from $CHCl_3$−MeOH yielded an analytical sample: mp 385−386 °C; ^{1}H NMR ($CDCl_3$) δ 10.60 (bs, 2), 10.44 (bs, 4), 7.14 (d, 4, J = 8.0 Hz), 7.13 (s, 8), 6.82 (t, 2, J = 8.0 Hz), 3.90 (bs, 12), 1.26 (s, 36); ^{13}C NMR ($CDCl_3$) δ 149.6, 147.2, 144.3, 129.3, 127.6, 126.9, 126.6, 126.3, 126.2, 121.7, 34.0, 32.8, 32.6, 31.5. Anal. Calcd for $C_{58}H_{68}O_6$: C, 80.89; H, 7.96. Found: C, 80.94; H, 7.87.

5,11,23,29-Tetra-*tert*-butyl-17,35-dibromocalix[6]arene-37,38,39,40,41,42-hexol (5). To a solution of 0.43 g (0.5 mmol) of **4** in 15 mL of 2-butanone was added 0.36 g (2 mmol) of NBS. The mixture was stirred at rt for 24 h, solvent was removed under vacuum, and the residue was stirred with 10 mL of 10% $NaHSO_3$. The pale yellow precipitate was removed by filtration, dried, and passed through silica gel to give 0.36 g (70%) of **5**. An analytical sample was obtained as a white powder after recrystallization from $CHCl_3$−MeOH: mp > 400 °C; ^{1}H NMR ($CDCl_3$) δ 10.64 (bs, 2), 10.25 (bs, 4), 7.26 (s, 4), 7.19 (d, 4, J = 2.4 Hz), 7.11 (d, 4, J = 2.4 Hz), 3.84 (bs, 12), 1.27 (s, 36). Anal. Calcd for $C_{58}H_{66}Br_2O_6$: C, 68.37; H, 6.53. Found: C, 68.57; H, 6.55.

5,11,23,29-Tetra-*tert*-butyl-37,38,39,40,41,42-hexamethoxycalix[6]arene (6). A sample of 1.30 g (1.5 mmol) of **4** was dissolved in 25 mL of THF containing 2 mL of DMF. To this was added 0.4 g (10 mmol) of 60% dispersion of NaH, the mixture was stirred for 15 min, and 0.77 mL (12 mmol) of CH_3I was introduced. The contents were heated at 70 °C for 6 h, THF was removed under vacuum, 50 mL of cold water was added, and the mixture was neutralized with dilute HCl. The white precipitate was removed by filtration, dried, and recrystallized from $CHCl_3$−MeOH to give 1.2 g (85%) of **6** as a white powder: mp 316−317 °C; ^{1}H NMR ($CDCl_3$) δ 6.98 (d, 4, J = 2.4 Hz), 6.90 (d, 4, J = 2.4 Hz), 6.83 (d, 4, J = 7.5 Hz), 6.72 (t, 2, J = 7.5 Hz), 3.96 (s, 12), 3.15 (s, 6), 3.02 (s, 12), 1.13 (s, 36); ^{13}C NMR ($CDCl_3$) δ 156.0, 153.7, 145.8, 134.7, 133.6, 133.4, 128.6, 126.2, 125.6, 123.2, 59.9, 34.1, 31.3, 30.4, 30.2. Anal. Calcd for $C_{64}H_{80}O_6 \cdot {}^1/_2H_2O$: C, 80.55; H, 8.55. Found: C, 80.30; H, 8.44.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis[(*N*-methyl-*N*-{2-pyridylethyl}amino)methyl]calix[6]arene-37,38,39,40,-41,42-hexol (7). To a solution of 1.72 g (2 mmol) of **4** in 40 mL of THF and 10 mL of AcOH were added 0.65 mL (8 mmol) of 37% HCHO and 1.08 g (8 mmol) of 2-(2-(methylamino)ethyl)-pyridine. The reaction mixture was stirred at rt for 40 h, the solvents were removed under vacuum, and the residue was dissolved in 100 mL of water and neutralized with 10% K_2CO_3. The white precipitate that formed was removed by suction filtration, dried, and purified by trituration with MeOH to give 1.04 g (90%) of **7** as a white powder: mp > 278 °C. The product is insoluble in common NMR solvents, and the spectrum that was recorded in a mixure of DMSO-d_6/$CDCl_3$ showed very broad peaks. Anal. Calcd for $C_{76}H_{92}N_4O_6 \cdot H_2O$: C, 77.65; H, 8.06. Found: C, 77.94; H, 7.78.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis[(*N*′-methyl-*N*-piperazino)methyl]calix[6]arene-37,38,39,40,41,42-hexol (8) was prepared from **4** using 1-methylpiperazine following the procedure described above for **7** and was isolated in 90% yield: mp > 260 °C; ^{1}H NMR (DMSO-d_6/$CDCl_3$) δ 7.05 (s, 4), 6.98 (s, 4), 6.91 (3, 4), 3.81 (bs, 12), 3.53 (s, 4), 2.58 (bs, 16), 2.35 (s, 6), 1.22 (s, 36). Anal. Calcd for $C_{70}H_{92}N_4O_6 \cdot H_2O$: C, 76.19; H, 8.59. Found: C, 76.42; H, 8.43.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis[(*N*′-(2-hydroxyethyl)-*N*-piperazino)methyl]calix[6]arene-37,38,39,40,41,42-hexol (9) was prepared from **4** using 1-(2-hydroxyethyl)-piperazine following the procedure described above for **7** and was isolated in 90% yield: ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 4), 7.12 (s, 4), 7.08 (s, 4), 3.85 (bs, 12), 3.59 (t, 4, J = 5.4 Hz), 3.40 (s, 4), two signals at 2.52 (bm) and 2.07 (bs) with less defined integral values, 1.25 (s, 36). Anal. Calcd for $C_{72}H_{96}N_4O_8 \cdot H_2O$: C, 74.32; H, 8.49. Found: C, 74.67; H, 8.22.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis[(*N*-methyl-*N*-propynylamino)methyl]calix[6]arene-37,38,39,40,41,42-hexol (10) was prepared from **4** using *N*-methylpropargylamine following the procedure described above for **7** and was isolated in 85% yield. An analytical sample was recrystallized from $CHCl_3$−MeOH: mp > 270 °C dec; ^{1}H NMR ($CDCl_3$) δ 10.48 (bs, 6), 7.16, 7.14 and 7.13 (3 × s, each 4), 3.90 (bs, 12), 3.46 (s, 4), 3.24 (d, 4, J = 2.2 Hz), 2.32 (s, 6), 2.26 (t, 2, J = 2.2 Hz), 1.25 (s, 36); ^{13}C NMR ($CDCl_3$) δ 149.0, 147.2, 144.4, 131.1, 130.0, 127.4, 127.0, 126.9, 126.7, 126.2, 78.5, 73.3, 59.3, 44.3, 41.7, 34.0, 32.8, 32.6, 31.5. Anal. Calcd for $C_{68}H_{82}N_2O_6 \cdot H_2O$: C, 78.43; H, 8.13. Found: C, 78.09; H, 8.16.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis((*N*,*N*-diallylamino)-methyl)calix[6]arene-37,38,39,40,41,42-hexol (11) was prepared from **4** using diallylamine following the procedure described above for **7** and was isolated in 90% yield: ^{1}H NMR ($CDCl_3$) δ 10.4 0 (bs, 6), 7.15 (s, 4), 7.12 (s, 4), 7.09 (s, 4), 5.85 (m, 4), 5.14 (m, 8), 3.90 (bs, 12), 3.47 (s, 4), 3.04 (d, 8, J = 6.4 Hz), 1.24 (s, 36). The amine **11** was used without further purification to make compounds **12** and **13** via quinone methide reactions as described below.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis(cyanomethyl)calix-[6]arene-37,38,39,40,41,42-hexol (12). A sample of 2.2 g (2 mmol) of **11** was dissolved in 30 mL of DMSO and 10 mL of THF, and to this mixture was added 0.35 mL (5 mmol) of CH_3I. The mixture was stirred at rt for 2 h, NaCN (1.0 g) was added to the quarternary salt, and the reaction mixture was heated at 110−120 °C for 6 h. It was then cooled to rt and poured into 100 mL of cold water and acidified with dilute HCl. The pale yellow precipitate was collected by suction filtration, dried, and purified by chromatography using CH_2Cl_2−hexane (80/20, v/v) to give 0.64 g (35%) of **12** as a white powder. Recrystallization from $CHCl_3$−MeOH yielded an analytical sample: mp > 300 °C dec; ^{1}H NMR ($CDCl_3$) δ 10.66 (bs, 2), 10.35 (bs, 4), 7.19 (d, J = 2.2 Hz), 7.14 (d, 4, J = 2.2 Hz), 7.09 (s, 4), 3.88 (bs, 12), 3.62 (s, 4), 1.26 (s, 36); ^{13}C NMR ($CDCl_3$) δ 149.4, 147.2, 144.7, 128.7, 128.5, 126.8, 126.6, 126.1, 122.8, 118.1, 34.1, 32.7, 32.5, 31.5, 22.8. Anal. Calcd for $C_{62}H_{70}N_2O_6$: C, 79.28; H, 7.51. Found: C, 79.37; H, 7.60.

5,11,23,29-Tetra-*tert*-butyl-17,35-bis((2-propynyloxy)-methyl)calix[6]arene-37,38,39,40,41,42-hexol (13) was obtained by following the procedure described above for **12**. In this experiment the nucleophile was prepared by dissolving 0.45 g (8 mmol) of propargyl alcohol in 10 mL of DMSO to which 0.32 g (8 mmol) of 60% dispersion of NaH was added. The contents were stirred for 10 min and then added to the quarternary salt. After chromatography of the resulting product, 0.4 g (20%) of **13** was obtained. Recrystallization from $CHCl_3$−MeOH yielded an analytical sample as a white powder: mp 368−370 °C; ^{1}H NMR ($CDCl_3$) δ 10.61 (bs, 2), 10.38 (bs, 4), 7.16 (s, 4), 7.14 (s, 8), 4.49 (s, 4), 4.06 (d, 4, J = 2.3 Hz), 3.85 (bs, 12), 2.44 (t, 2, J = 2.3 Hz), 1.26 (s, 36); ^{13}C NMR ($CDCl_3$) δ 149.5, 147.2, 144.4, 130.1, 129.4, 127.6, 126.9, 126.5, 126.4, 126.2, 79.7, 74.4, 70.9, 56.2, 34.0, 32.8, 32.6, 31.5. Anal. Calcd for $C_{66}H_{76}O_8$: C, 79.49; H, 7.68. Found: C, 79.28; H, 7.69.

2-Propynyl 3-(2-propynyloxy)benzoate (17) was prepared from 3-hydroxybenzoic acid (**15**) follwing the procedure described below for **19** and was isolated in 94% yield: mp 63−63.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.73−7.65 (m, 2), 7.38 (t, 1, J = 8.1 Hz), 7.22−7.18 (m, 1), 4.92 (d, 2, J = 2.4 Hz), 4.75 (d, 2, J =2.4 Hz), 2.55 (t, 1, J = 2.4 Hz), 2.52 (t, 1, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 165.5, 157.5, 130.7, 129.6, 123.1, 120.6, 115.5,

(12) Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. THF was freshly distilled from Na−benzophenone. The melting points of all compounds melting above 250 °C were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) with the use of a Fluka 51 K/J thermometer (John Fluke Mfg. Co., Inc., Everett, WA). ^{1}H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively. TLC analyses were carried out on Analtech silica gel plates (absorbent thickness 250 μm) containing a fluorescent indicator. TLC analyses were carried out on Analtech silica gel plates (absorbant thickness 250 μm) containing a fluorescent indicator. Chromatography was carried out with J. T. Baker silica gel JT7042-2 (40 μm particles) on columns 50 mm in diameter filled to a height of *ca.* 7 in. Elution rates were 2 in./min; fractions of 50 mL were collected. Analytical samples were dried at least 36 h at 100−140 °C and 1−2 mm of pressure.

78.1, 77.7, 76.0, 75.1, 55.9, 52.6; MS (EI)[13] m/z = 214.05 (M^+), 175.05 (base peak). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.86; H, 4.82.

2-Propynyl 4-(2-propynyloxy)benzoate (18) was prepared from 4-hydroxybenzoic acid (**14**) following the procedure described below for **19** and was isolated in 92% yield: mp 49 °C; ^{1}H NMR ($CDCl_3$) δ 8.04 (d, 2, J = 9.0 Hz), 7.01 (d, 2, J = 9.0 Hz), 4.90 (d, 2, J = 2.5 Hz), 4.75 (d, 2, J = 2.5 Hz), 2.55 (t, 1, J = 2.5 Hz), 2.50 (t, 1, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 165.3, 161.4, 131.8, 122.5, 114.5, 77.9, 77.7, 76.2, 74.9, 55.8, 52.2; MS (EI)[13] m/z = 214.15 (M^+), 131.15 (base peak). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.37; H, 4.72.

2-Propynyl 3,5-Bis(2-propynyloxy)benzoate (19). A mixture of 7.7 g (0.05 mol) of 3,5-dihydroxybenzoic acid (**16**), 21 g (0.15 mol) of K_2CO_3, and 16.5 mL (80% w/w solution in toluene) of propargyl bromide in 100 mL of DMF was stirred at rt for 24 h. The contents were poured into cold water, and the precipitate was removed by filtration, dried, and washed with hexane to give 13 g (97%) of **19**: mp 99−99.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.32 (d, 2, J = 2.3 Hz), 6.83 (t, 1, J = 2.3 Hz), 4.91 (d, 2, J = 2.4 Hz), 4.72 (d, 4, J = 2.4 Hz), 2.55 (t, 2, J = 2.4 Hz), 2.52 (t, 1, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 165.1, 158.5, 131.3, 109.1, 107.8, 77.9, 77.5, 76.1, 75.1, 56.1, 52.7; MS (EI)[13] m/z = 268.15 (M^+), 229.15 (base peak). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.52; H, 4.51.

3-(2-Propynyloxy)benzenemethanol (20) was prepared by the reduction of the ester **17** following the procedure described below for **22** and was isolated in 94% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.29 (t, 1, J = 8.2 Hz), 6.99−6.89 (m, 3), 4.70 (d, 2, J = 2.4 Hz), 4.66 (d, 2, J = 5.5 Hz), 2.53 (t, 1, J = 2.4 Hz), 1.95 (t, 1, J = 5.5 Hz, exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 157.6, 142.7, 129.6, 120.0, 113.9, 113.3, 78.7, 75.7, 64.6, 55.7; MS (EI)[13] m/z = 162.05 (M^+), 131.05 (base peak).

4-(2-Propynyloxy)benzenemethanol (21) was prepared by the reduction of the ester **18** following the procedure described below for **22** (the reaction was carried out at ice-bath temperature and the product was isolated after 30 min) and was isolated in 85% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.30 (d, 2, J = 8.5 Hz), 6.97 (d, 2, J = 8.5 Hz), 4.69 (d, 2, J = 2.4 Hz), 2.52 (t, 1, J = 2.5 Hz), 1.79 (bs, 1, OH); ^{13}C NMR ($CDCl_3$) δ 156.8, 134.0, 128.5, 114.8, 78.6, 75.7, 64.3, 55.7; MS (EI)[13] m/z = 162.15 (M^+), 131.15 (bae peak). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.52; H, 6.19.

3,5-Bis(2-propynyloxy)benzenemethanol (22). A 10.7 g (40 mmol) sample of the ester **19** was dissolved in 100 mL of dry THF, and to this was added 25 mL of 1 M THF solution (25 mmol) of $LiAlH_4$ under an atmosphere of N_2 (the reaction is slightly exothermic during the addition, and the temperature was maintained at 20−22 °C). The reaction mixture was left at rt for 4 h, EtOAc was added to decompose excess of $LiAlH_4$, and THF was removed under vacuum. Cold water (150 mL) was added to the contents of the flask, and the resulting mixture was acidified with dilute HCl. The product was extracted into CH_2Cl_2 (3 × 25 mL), washed with water and brine, and dried over Na_2SO_4. Removal of the solvent under vacuum gave 8.5 g (98%) of pure alcohol **22** which was recrystallized from hexane−CH_2Cl_2: mp 69−70 °C; ^{1}H NMR ($CDCl_3$) δ 6.63 (d, 2, J = 2.2 Hz), 6.54 (t, 1, J = 2.2 Hz), 4.68 (d, 4, J = 2.2 Hz), 4.64 (d, 2, J = 6.0 Hz), 2.53 (t, 2, J = 2.2 Hz), 1.7.5 (t, 1, J = 6.0 Hz, exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 158.8, 143.6, 106.2, 101.4, 78.4, 75.7, 64.9, 55.9; MS (EI)[13] m/z = 216.05 (M^+), 77.05 (base peak). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 71.87; H, 5.62.

1-(Bromomethyl)-3-(2-propynyloxy)benzene (23) was prepared from the alcohol **20** following the procedure described below for **25** and was obtained in 89% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.28 (t, 1, J = 7.8 Hz), 7.24−6.90 (m, 3), 4.70 (d, 2, J = 2.3 Hz), 4.46 (s, 2), 2.53 (t, 1, J = 2.3 Hz); ^{13}C NMR ($CDCl_3$) δ 157.7, 139.3, 129.9, 122.3, 115.6, 114.9, 78.4, 75.9, 55.9, 33.4; MS (EI)[13] m/z = 225.1 (M^+), 145.05 (base peak). Anal. Calcd for $C_{10}H_9BrO$: C, 53.36; H, 4.03. Found: C, 53.53; H, 4.20.

1-(Bromomethyl)-4-(2-propynyloxy)benzene (24) was prepared from the alcohol **21** following the procedure described for **25** and was isolated in 60% yield. The mesylate isolated appeared to be unstable and was treated with LiBr in THF at rt. Heating to 40 °C gave more polymeric material: ^{1}H NMR ($CDCl_3$) δ 7.35−7.32 (m, 2), 6.97−6.93 (m, 2), 4.69 (d, 2, J = 2.5 Hz), 4.57 (s), 4.50 (s), 2.53 (t, 1, J = 2.5 Hz). The presence of two signals at δ 4.57 and 4.50 arising from the $ArCH_2X$ protons in the ^{1}H NMR spectrum indicates that the product is a mixture of 1-(bromomethyl)-4-(2-propynyloxy)benzene and 1-(chloromethyl)-4-(2-propynyloxy)benzene formed during the mesylation reaction. This observation was further supported by MS (EI)[13]: m/z 180.15 (M^+ for the chloromethyl compound) and 225.05 (M^+ for the bromomethyl compound).

1-(Bromomethyl)-3,5-bis(2-propynyloxy)benzene (25). Alcohol **22** was dissolved in 150 mL of CH_2Cl_2. To this was added 8.4 mL (60 mmol) of triethylamine, and the reaction mixture was cooled to ice-bath temperature. A solution of 3.9 mL (50 mmol) of $MeSO_2Cl$ in 25 mL of CH_2Cl_2 was introduced into the reaction mixture over a period of 30 min. The reaction mixture was warmed to rt over a period of 30 min, thoroughly washed with water (3 × 30 mL) and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the mesylate which was dissloved in 100 mL of THF to which 5.16 g (60 mmol) of LiBr was added and the contents of the flask heated at 50 °C for 30 min. THF was removed under vacuum, and cold water (100 mL) was added to the residue. The product was extracted into CH_2Cl_2 (3 × 25 mL) which was washed with water (2 × 25 mL) and brine and dried over anhydrous Na_2SO_4. Removal of the solvent and recrystallization from hexane−CH_2Cl_2 gave 10 g of arylmethyl bromide **25** as white needles: mp 60 °C; ^{1}H NMR ($CDCl_3$) δ 6.55 (d, 2, J = 2.2 Hz), 6.55 (t, 1, J = 2.2 Hz), 4.68 (d, 4, J = 2.4 Hz), 4.42 (s, 2), 2.55 (t, 2, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 158.7, 139.9, 108.7, 108.2, 102.3, 102.2, 78.2, 75.9, 55.9, 33.2; MS (EI)[13] m/z = 279.0 (M^+, corresponding to the bromide), 199.05 (base peak), and 235.15, 236.15, and 237.15 (M^+, $M^+ + 1$, and $M^+ + 2$, respectively, corresponding to the chloride). Anal. Calcd for $C_{13}H_{11}BrO_2$: C, 55.94; H, 3.97. Found: C, 57.22; H, 4.12. The high carbon percentage in the elemental analysis and the presence of a molecular ion at 235.15 corresponding to 3,5-bis(2-propynyloxy)benzyl chloride indicates that *ca.* 10% of the benzyl chloride is formed during the mesylate formation.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(benzyloxy)-26,28-bis[[3,5-bis(2-propynyloxy)benzyl]oxy]calix[4]arene (28) was prepared in 70% yield from the previously described[9] 1,3-dibenzylcalix[4]arene **26** following the procedure described below for **29** and was obtained as a white powder. An analytical sample was obtained by recrystallization from $CHCl_3$−MeOH: mp 129−130 °C; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 10), 6.68 (s, 4), 6.67 (s, 4), 6.56 (t, 2, J = 2.2 Hz), 6.52 (d, 4, J = 2.2 Hz), 4.93 (s, 4), 4.83 (s, 4), 4.48 (d, 8, J = 2.4 Hz), 4.10 (d, 4, J = 12.7 Hz), 2.80 (d, 4, J = 12.7 Hz), 2.44 (t, 4, J = 2.4 Hz), 1.06 (s, 18), 1.04 (s, 18); ^{13}C NMR ($CDCl_3$) δ 158.6,152.8, 144.8,140.9, 138.5, 134.2, 130.1, 128.2, 127.8, 125.2, 109.6, 102.1, 78.8,76.7, 76.4, 75.8, 56.2, 34.1, 31.9, 31.7. Anal. Calcd for $C_{84}H_{88}O_8$: C, 82.32; H, 7.24. Found: C, 82.29; H, 7.21.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-tris[[3,5-bis(2-propynyloxy)benzyl]oxy]-38,40,42-trimethoxycalix[6]-arene (29). A sample of 1.01 g (1 mmol) of **27**[9] was dissolved in 25 mL of THF containing 2 mL of DMF. To this was added 0.24 g (6 mmol) of 60% dispersion of NaH, stirring was continued for 15 min, and 1.12 g (4 mmol) of the bromide **25** in 5 mL of THF was introduced. The contents were heated at 70 °C for 6 h, THF was removed under vacuum, 50 mL of cold water was added, and the mixture was neutralized with dilute HCl. The white precipitate was removed by filtration, dried, and recrystallized from $CHCl_3$−MeOH to give 1.1 g (73%) of **29**: mp 163−164 °C; ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 8), 6.48 (d, 6, J = 2.2 Hz), 6.67 (s, 4), 6.58 (t, 3, J = 2.2 Hz), 4.93 (s, 6), 4.69 (d, 12, J = 2.4 Hz), 4.59 (d, 6, J = 15.5 Hz), 3.38 (d, 6, J = 15.5 Hz), 2.50 (t, 6, J = 2.2. Hz), 2.27 (s, 9), 1.38 (s, 27), 0.80 (s, 27); ^{13}C NMR ($CDCl_3$) δ 158.7, 154.5, 151.5, 145.8, 145.7,

(13) We are indebted to Wenfang Miao, Department of Chemistry, Texas Christian University, for providing this mass spectrum.

140.2, 133.8, 133.0, 127.9, 123.6, 107.1, 102.0, 78.4, 75.8, 74.2, 60.1, 55.9, 34.2, 33.9, 31.6, 31.4, 31.1, 29.8. Anal. Calcd for $C_{108}H_{120}O_{12}$: C, 80.56; H, 7.51. Found: C, 80.43; H, 7.62.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[[3-(2-propynyloxy)]-benzyl]oxy]calix[4]arene-26,28-diol (30). The 1,3-diether was prepared from *p-tert*-butylcalix[4]arene **1a** and aryl bromide **23** follwing the procedure described below for **31** and was obtained in 90% yield: mp 147−48 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 2, D_2O exchange), 7.29−7.22 (m, 6), 7.04 (s, 4), 6.95 (bd, 2), 6.79 (s, 4), 5.04 (s, 4), 4.53 (d, 4, J = 2.4 Hz), 4.27 (d, 4, J = 13.1 Hz), 3.26 (d, 4, J = 13.1 Hz), 2.42 (t, 2, J = 2.4 Hz), 1.28 (s, 18), 0.95 (s, 18); ^{13}C NMR ($CDCl_3$) δ 157.8, 150.7, 149.6, 147.0, 141.4, 138.6, 132.6, 129.6, 127.7, 125.5, 124.9, 120.3, 115.1, 113.1, 78.7, 77.8, 75.3, 55.6, 33.9, 33.8, 31.7, 31.6, 30.9. Anal. Calcd for $C_{64}H_{72}O_6$: C, 82.02; H, 7.74. Found: C, 82.27; H, 7.90.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[[3,5-bis(2-propynyloxy)benzyl]oxy]calix[4]arene-26,28-diol (31). A mixture of 1.3 g (2 mmol) of *p-tert*-butylcalix[4]arene (**1a**), 1.1 g (8 mmol) of K_2CO_3, and 1.4 g (4.5 mmol) of arylmethyl bromide **25** in 30 mL of acetone was stirred at 70 °C for 6 h. Acetone was removed under vacuum, cold water (100 mL) was added to the reaction flask, and the contents were acidified with dilute HCl. The product was extracted into CH_2Cl_2 (3 × 25 mL), and the combined organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was crystallized from hexane−CH_2Cl_2 to give 1.88 g (90%) of 1,3-diether **31** in the cone conformation as a white powder: mp 174−75 °C; ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 2, exchanged with D_2O), 7.05 (s, 4), 6.98 (d, 4, J = 2.2 Hz), 6.81 (s, 4), 6.58 (t, 2, J = 2.2 Hz), 5.01 (s, 4), 4.50 (d, 8, J = 2.3 Hz), 4.28 (d, 4, J = 13.0 Hz), 3.29 (d, 4, 13.0 Hz), 2.44 (t, 4, J = 2.3 Hz), 1.28 (s, 18), 0.95 (s, 18); ^{13}C NMR-($CDCl_3$) δ 158.9, 150.7, 149.4, 147.2, 141.6, 139.4, 132.6, 127.8, 125.6, 125.0, 106.2, 102.3, 78.6, 77.8, 75.4, 55.8, 33.9, 33.8, 31.7, 31.6, 31.0. Anal. Calcd for $C_{70}H_{76}O_8$: C, 80.43; H, 7.33. Found: C, 80.68; H, 7.21.

Bridged compound 32 was prepared by the oxidative coupling of **30** following the procedure described below for **33** and was obtained in 75% yield as a white powder. In this experiment the product was isolated soon after the addition was completed: mp > 260 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.30−7.24 (m, 4), 7.09 (m, 2), 7.05 (s, 4), 6.96 (bd, 2), 6.69 (s, 4), 6.62 (s, 2, exchanged with D_2O), 4.93 (s, 4), 4.79 (s, 4), 4.27 (d, 4, J = 13.2 Hz), 3.22 (d, 4, J = 13.2 Hz), 1.31 (s, 18), 0.88 (s, 18); ^{13}C NMR ($CDCl_3$) δ 157.5, 150.6, 150.3, 146.6, 141.2, 138.3, 132.2, 129.3, 127.9, 125.4, 124.9, 122.7, 116.3, 115.79, 78.6, 75.25, 71.9, 56.6, 33.8, 31.7, 31.6, 30.9; MS (FAB)[14] M^+ 935.6 (calcd 935.3). Anal. Calcd for $C_{64}H_{70}O_6$: C, 82.19; H, 7.54. Found: C, 82.11; H, 7.57.

Bridged Compound 33. Oxygen was bubbled through a mixture of 125 mL of acetone and 25 mL of pyridine in a 1 L 3-necked flask for 10 min. To this solvent mixture was added 1.44 g (8 mmol) of $Cu(OAc)_2$, and the contents were heated to 65 °C (bath temperature) with stirring. A solution of 0.52 g (0.5 mmol) of **31** in 100 mL of acetone was added over a period of 4 h. After the addition was completed the reaction mixture was maintained at 65 °C for another 12 h with continued stirring. The solvent was removed under vacuum, cold water (150 mL) was added, and the contents were acidified with dilute HCl. The product was extracted into CH_2Cl_2 (3 × 25 mL), and the combined organic layer was washed with water and brine and dried over Na_2SO_4. Removal of the solvent under vacuum gave a dark brown residue which was chromatographed over silica gel (70−230 mesh) using CH_2Cl_2−hexane (60/40 v/v). The fractions containing the product were collected and recrystallized from $CHCl_3$−MeOH to give 0.29 g (55%) of **33** as a pale yellow powder: mp > 290 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.12 (s, 4), 6.82 (bs, 4), 6.71 (s, 4), 6.50 (bs, 2), 6.45 (s, 2, D_2O exchange), 4.81 (q or an overlapping doublet of doublets, 4), 4.79 (s, 4), 4.52 (d, 4, J = 13.1 Hz), 3.41 (d, 4, J = 13.1 Hz), 1.35 (s, 18), 0.88 (s, 18); ^{13}C NMR ($CDCl_3$) δ 163.1, 157.5, 150.7, 150.6, 146.5, 141.1, 138.6, 131.8, 127.8, 125.5, 125.0, 109.5, 78.5, 74.1, 71.1, 55.3, 33.9, 33.8, 31.7, 31.5, 30.9; MS(FAB)[14] M^+ 1041.9 (calcd 1041.3). Anal. Calcd for $C_{70}H_{72}O_8 \cdot {}^1/_2CHCl_3$: C, 76.91; H, 6.64. Found: C, 77.37; H, 6.65.

5,11,17,23,29,35-Hexa-*tert*-butyl-39,42-bis[[3-(2-propynyloxy)benzyl]oxy]calix[6]arene-37,38,40,41-tetrol (34). A sample of 0.97 g (1 mmol) of **1b** was dissolved in a mixture of 40 mL of THF and 10 mL of DMF. To this was added 0.77 g (6 mmol) of Me_3SiOK at ice-bath temperature, stirring was continued for 5 min, and a solution of 0.5 g (2.2 mmol) of 3-(2-propynyloxy)benzyl bromide (**23**) in 2 mL of THF was introduced. The reaction mixture was stirred at rt for 8 h, THF was removed under vacuum, cold water was added, and the mixture was acidified with dilute HCl. The precipitate was collected by suction filtration, dried, and triturated with MeOH to give 1.0 g (76%) of **34** as a white powder. Recrystallization from $CHCl_3$−MeOH yielded an analytical sample: mp 216−217 °C; ^{1}H NMR ($CDCl_3$) δ 7.87 and 7.84 (s, 2), 7.32−6.74 (m), 5.07 and 4.94 (s, 2), 4.65 and 4.47 (d, 2, J = 2.1 Hz), 4.28, 3.84, 3.62 and 3.52 (d, 4, J = 15.0 Hz), 4.05 (d, J = 15.0 Hz), 3.74 (s), 3.68 (d, J = 15.0 Hz), 2.47 and 2.18 (t, 2, J = 2.1 Hz), 1.24, 1.23, 1.17 and 1.00 (4s); ^{13}C NMR ($CDCl_3$) δ 157.7 and 157.5 (2s), 150.2−112.9 (30 lines), 78.5 and 78.2 (2 lines), 75.7 and 75.6 (2 lines), 55.9 and 55.7 (2 lines), 34.3−31.1 (11 lines). Anal. Calcd for $C_{86}H_{100}O_8$: C, 81.87; H, 7.99. Found: C, 81.99; H, 8.05.

5,11,17,23,29,35-Hexa-*tert*-butyl-39,42-bis[[4-(2-propynyloxy)benzyl]oxy]calix[6]arene-37,38,40,41-tetrol (35) was prepared using **24** following the procedure described above for **34** and was obtained as a white powder in 70% yield: mp 214−215 °C; ^{1}H NMR ($CDCl_3$) δ 7.95 (s, 4, OH), 7.42 (d, 4, J = 8.6 Hz), 7.07 (d, 4, J = 2.3 Hz), 7.05 (d, 4, J = 2.3 Hz), 6.97 (d, 4, J = 8.6 Hz), 6.86 (s, 4), 5.04 (s, 4), 4.65 (d, 4, J = 2.4 Hz), 4.25 (d, 4, J = 14.6 Hz), 3.80 (d, 2, J = 14.2 Hz), 3.66 (d, 2, J = 14.2 Hz), 3.52 (d, 4, J = 14.6 Hz), 2.50 (t, 2, J = 2.4 Hz), 1.24 (s, 36), 1.01 (s, 18); ^{13}C NMR ($CDCl_3$) δ 157.6, 150.2, 149.7, 147.4, 142.3, 132.2, 129.7, 129.3, 126.7, 126.1, 125.8, 125.6, 125.4, 115.0, 78.5, 75.5, 55.8, 34.1, 33.8, 32.0, 31.5, 31.1. Anal. Calcd for $C_{86}H_{100}O_8$: C, 81.87; H, 7.99. Found: C, 81.23; H, 8.01.

Bridged Compound 36. Oxygen was bubbled through a mixture of 125 mL of acetone and 25 mL of pyridine in a 1 L 3-necked flask for 10 min. To this was added 1.44 g (8 mmol) of $Cu(OAc)_2$, and the contents were heated to 65 °C (bath temperature) with stirring. A solution of 0.50 g (0.4 mmol) of **34** in 100 mL of acetone was then added over a period of 4 h. After the addition was completed the reaction mixture was left at 65 °C for another 2 h while stirring continued. The solvents were removed under vacuum, cold water (150 mL) was added, and the contents were acidified with dilute HCl. The pale white precipitate was removed by filtration, dried, and chromatographed over silica gel (70−230 mesh) using CH_2Cl_2−hexane (60/40 v/v). The fractions containing the product (as indicated by TLC) were collected and recrystallized from $CHCl_3$−MeOH to give 20−25% of **36**: mp > 250 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (s, 4, OH), 7.45 (bs, 2), 7.32 (m, 2), 7.11 (d, 4, J = 2.5 Hz), 7.05 (d, 4, J = 2.5 Hz), 6.99−6.90 (m, 4), 6.83 (s, 4), 5.16 (s, 4), 4.87 (s, 4), 4.30 (d, 4, J = 15.1 Hz), 4.05 (d, 2, J = 4.30 Hz), 3.58 (d, 4, J = 15.5 Hz), 3.54 (d, 2, J = 14.5 Hz), 1.24 (s, 36), 0.95 (s, 18); ^{13}C NMR ($CDCl_3$) δ 157.8, 150.1, 149.5, 147.6, 142.4, 137.7, 132.2, 129.6, 126.6, 125.9, 125.8, 125.4, 125.2, 119.9, 116.6, 112.2, 75.6, 74.9, 71.8, 56.5, 34.1, 33.9, 31.6, 30.9; MS(FAB)[14] M^+ 1259.4 (calcd 1259.7). Anal. Calcd for $C_{86}H_{98}O_8$: C, 82.00; H, 7.84. Found: C, 82.09; H, 7.87.

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