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Incorporation of Substituents at the Methylene Linkages of the Calix[5]arene Skeleton

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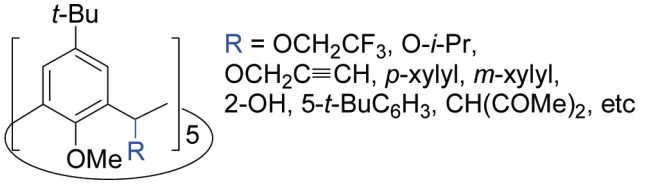
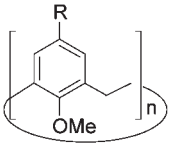
Received July 7, 2009



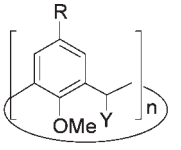
Under S_N1 reaction conditions, the bromine atoms of the pentabromo *p-tert*-butylcalix[5]arene **6** were replaced by alkoxy, electron-rich aryl, and acetylacetonate groups.

Although numerous synthetic routes have been developed for the functionalization of the aromatic rings of the calixarenes,[1] only a handful of methods are available for the chemical modification of the methylene bridges.[2−7] Radical bromination of the calixarene methyl ethers **1a**,**b** and **2** affords derivatives incorporating bromine groups at the bridges (**3a**,**b** and **4a**, respectively).[8,9] We have recently reported that the bromocalixarene derivatives **3a**,**b** and **4a** react with O-, N-, and even some C-nucleophiles under S_N1 reaction conditions, yielding fully monosubstituted methylene-functionalized calix[4]- and calix[6]arenes.[9,10] Attractive features of this facile reaction are (i) Lewis acid or dry solvents are not required and (ii) purification of the product is typically conducted by simple recrystallization. In most cases, the *all-cis* isomer product was isolated, while a mixture of isomers was obtained in the reaction of **3a** with the reactive and sterically unhindered nucleophiles SCN^- or N_3^-.[9b]

Incorporation of substituents at the bridges of the calix scaffold is of interest since these groups may be involved in stabilizing interactions with a putative guest, thus affecting the binding properties of the macrocycle. The substituents at the bridge may affect the binding properties of the calixarene in an indirect fashion by modifying the intrinsic conformational preferences of the calixarene scaffold. For example, whereas tetramethoxycalix[4]arene **1** exists in $CDCl_3$ solution as a conformational mixture where the partial cone form is the major conformer,[11] NMR data of the *rccc* form of the methylene-functionalized calix[4]arene **3c** are consistent with a pinched cone conformation. Additionally, the presence of substituents at the bridges may affect the rigidity of the system. In contrast to the parent **2**, NMR data indicate that the pinched cone conformation of hexamesityl calix[6]arene **4b** is conformationally rigid.



1a: R = *t*-Bu, n = 4
1b: R = H, n = 4
2: R = *t*-Bu, n = 6



3a: R = *t*-Bu, Y = Br, n = 4
3b: R = H, Y = Br, n = 4
3c: R = *t*-Bu, Y = 2-methylfuranyl, n = 4
4a: R = *t*-Bu, Y = Br, n = 6
4b: R = *t*-Bu, Y = 2,4,6-$Me_3C_6H_2$, n = 6
4c: R = *t*-Bu, Y = $CH(COMe)_2$, n = 6

The present study was conducted to examine whether this synthetic methodology can also be applied to the functionalization of the methylene bridges of the calix[5]arene skeleton. Calix[5]arenes are attractive potential hosts since their cavity is larger than that of calix[4]arenes, but in contrast to the larger calixarenes, they still may adopt nearly symmetric cone conformations.

Bromination of Pentamethoxy *p-tert*-Butylcalix[5]arene. The pentabromo *p-tert*-butylcalix[5]arene derivative **6** was

(1) For reviews on calixarenes see: (a) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713. (b) Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, UK, 1998. (c) Böhmer, V. In *The Chemistry of Phenols*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 2003; Chapter 19. (d) Gutsche, C. D. *Calixarenes. An Introduction*, 2nd ed.; Royal Society of Chemistry: Cambridge, UK, 2008.

(2) Fragment condensation: (a) Tabatabai, M.; Vogt, W.; Böhmer, V. *Tetrahedron Lett.* **1990**, *31*, 3295. (b) Sartori, G.; Maggi, R.; Bigi, F.; Arduini, A.; Pastorio, A.; Porta, C. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1657. (c) Biali, S. E.; Böhmer, V.; Cohen, S.; Ferguson, G.; Grüttner, C.; Grynszpan, F.; Paulus, E. F.; Thondorf, I.; Vogt, W. *J. Am. Chem. Soc.* **1996**, *118*, 2261. (d) Tsue, H.; Enyo, K.; Hirao, K. *Org. Lett.* **2000**, *2*, 3071. (e) For a review on the synthesis of calixarenes via the stepwise and fragment condensation methods see: Böhmer, V. *Liebigs Ann./Recl.* **1997**, 2019.

(3) Spirodienone route: Agbaria, K.; Biali, S. E. *J. Am. Chem. Soc.* **2001**, *123*, 12495.

(4) Homologous anionic ortho Fries rearrangement: Middel, O.; Greff, Z.; Taylor, N. J.; Verboom, W.; Reinhoudt, D. N.; Snieckus, V. *J. Org. Chem.* **2000**, *65*, 667.

(5) Lithiation/alkylation: Scully, P. A.; Hamilton, T. M.; Bennett, J. L. *Org. Lett.* **2001**, *3*, 2741.

(6) Addition of organolithium reagents to ketocalixarenes: Kuno, L.; Seri, N.; Biali, S. E. *Org. Lett.* **2007**, *9*, 1577.

(7) Oxidation of the methylene bridges: (a) Görmar, G.; Seiffarth, K.; Schultz, M.; Zimmerman, J.; Flämig, G. *Macromol. Chem.* **1990**, *191*, 81. (b) Matsuda, K.; Nakamura, N.; Takahashi, K.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 5550. (c) Seri, N.; Simaan, S.; Botoshansky, M.; Kaftory, M.; Biali, S. E. *J. Org. Chem.* **2003**, *68*, 7140. (d) Kogan, K.; Biali, S. E. *Org. Lett.* **2007**, *9*, 2393.

(8) Bromination of the methylene bridges: (a) Klenke, B.; Näther, C.; Friedrichsen, W. *Tetrahedron Lett.* **1998**, *39*, 8967. (b) Kumar, S. K.; Chawla, H. M.; Varadarajan, R. *Tetrahedron Lett.* **2002**, *43*, 7073.

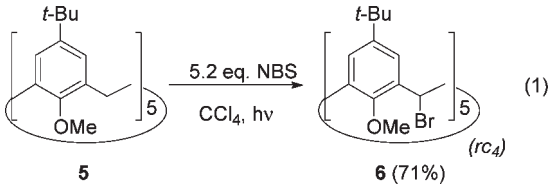
(9) (a) Columbus, I.; Biali, S. E. *Org. Lett.* **2007**, *9*, 2927. (b) Columbus, I.; Biali, S. E. *J. Org. Chem.* **2008**, *73*, 2598. (c) Kogan, K.; Columbus, I.; Biali, S. E. *J. Org. Chem.* **2008**, *73*, 7327.

(10) For examples of silver-mediated substitutions in bromodienone calix-arene derivatives see: Troisi, F.; Pierro, T.; Gaeta, C.; Neri, P. *Org. Lett.* **2009**, *11*, 697.

(11) Harada, T.; Rudzinski, J. M.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2109.

Published on Web 08/25/2009 DOI: 10.1021/jo901450x

prepared via photochemical bromination of pentamethoxy *p-tert*-butylcalix[5]arene **5**[12] (eq 1).



In principle, four isomeric forms are possible for a derivative of **5** in which the five bridges are monosubstituted by a single substituent (Figure 1). ^{1}H NMR analysis of the crude mixture indicated that the major product displays a simple signal pattern (one singlet each for the *t*-Bu, methoxy, methine, and aromatic protons), consistent with an rc_4 (*all-cis*) disposition of stereocenters.[13]

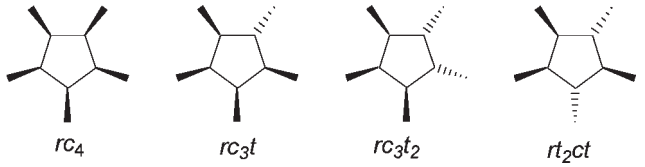


FIGURE 1. Four possible patterns of stereocenters for a derivative of **5** in which the five bridges are monosubstituted by a given substituent.

The pentabromo derivative **6** was crystallized from a $CHCl_3$/MeOH mixture and submitted to X-ray crystallography. The crystal structure (Figure 2) shows that the product obtained is the *all-cis* isomer, which adopts in the crystal a distorted cone conformation. All the bromine atoms are located at the sterically unencumbered equatorial positions. A single methoxy group (O1−C36) is oriented "in" (toward the cavity center) while the rest of the methoxy groups are oriented "out".

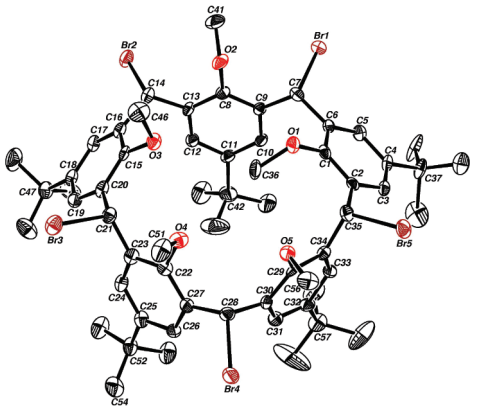
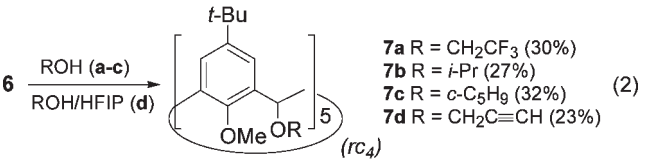


FIGURE 2. Crystal structure of the pentabromocalix[5]arene **6**.

Reactions of the Pentabromo Derivative 6. The reactivity of **3a** and **4a** differs toward solvolysis under S_N1 conditions. Whereas the bromine atoms of **4a** can be replaced by primary and secondary alkoxy groups simply by refluxing the calixarene in the appropriate alcohol, the less reactive **3a** requires the presence of an ionizing solvent (e.g., 2,2,2-trifluoroethanol (TFE)).



Heating of **6** in TFE, 2-propanol, or cyclopentanol at reflux afforded the corresponding pentaalkoxy derivatives **7a**−**c** (eq 2).[14] In each case, the NMR spectra of the major products indicated 5-fold symmetry under the NMR time scale, and on this basis the *all-cis* configuration is assigned to these products. X-ray diffraction of the pentaisopropoxy derivative **7b** corroborated this configurational assignment (Figure 3). Similar to **6**, the macrocycle adopts a distorted cone conformation with a single methoxy group oriented "in".

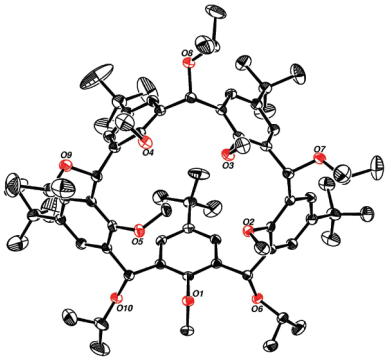


FIGURE 3. Crystal structure of the pentaisopropoxy derivative **7b**.

The reaction of **6** with propargyl alcohol is of interest, since after reaction of the alcohol functionality, additional reactions can be conducted at the triple bond, allowing further modification of the substituents at the bridges. The reaction with propargyl alcohol was conducted with HFIP (1,1,1,3,3,3-hexafluoroisopropanol) as the ionizing solvent and afforded **7d** in 23% yield.

Reaction with C-Nucleophiles. a. Friedel−Crafts Reactions. We have previously shown that solvolytic Friedel−Crafts alkylation reactions (in the absence of a Lewis acid)[15] can be conducted for the derivatives **3a**,**b** and **4a**. The reaction involves a competition between reaction of the carbocation generated by heterolytic cleavage of the C−Br bonds with the ionizing solvent and with the aromatic substrate. For electron-rich, aromatic substrates (e.g., 2-methylfuran) the reaction was conducted in TFE, while the less nucleophilic HFIP was used for less activated substrates such as *m*-xylene.

The solvolytic Friedel−Crafts reaction of **6** was examined with benzene derivatives substituted by electron-donating groups. Under solvolytic conditions in HFIP, **6** reacted with *m*-xylene, *p*-xylene, *tert*-butylphenol, and

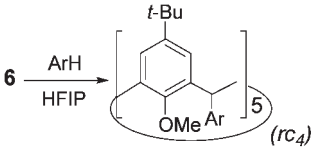
(12) Stewart, D. R.; Krawiec, M.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *J. Am. Chem. Soc.* **1995**, *117*, 586.

(13) The configuration of the stereocenters is designated by describing the cis (*c*) or trans (*t*) disposition of the substituents relative to the reference (*r*) substituent. For example, a calix[5]arene derivative possessing all bridges monofunctionalized, in which all substituents are in a cis disposition relative to the reference substituent is designated as rc_4.

(14) The reaction with MeOH or EtOH displayed poor stereoselectivity affording a complex stereoisomeric mixture.

(15) Hofmann, M.; Hampel, N.; Kanzian, T.; Mayr, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 5402.

thymol affording the corresponding pentaarylated derivatives **8a**−**d** (eq 3). In contrast to the reaction of **3b** under similar conditions, no cleavage of ArO−Me bonds was observed under the reaction conditions. No Friedel−Crafts product was obtained when the reaction was conducted with the crowded mesitylene.

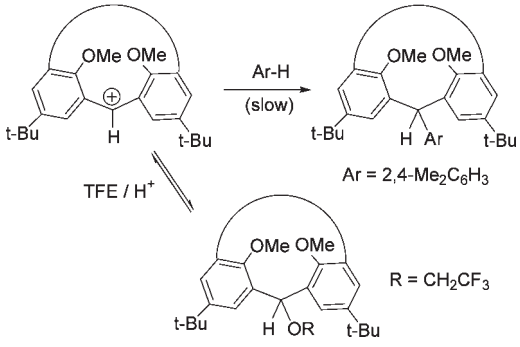


(3)

8a Ar = 2,5-$Me_2C_6H_3$ (39%) **8c** Ar = 2-OH,5-*t*-Bu-C_6H_3 (7%)
8b Ar = 2,4-$Me_2C_6H_3$ (60%) **8d** Ar = 2-Me,4-OH,5-*i*-Pr-C_6H_2 (20%)

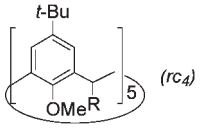
Since HFIP is substantially more expensive than TFE, we also examined the reaction of **6** in a TFE/*m*-xylene mixture containing an acid (HBr). Since TFE is more nucleophilic than *m*-xylene and is present in excess, it was expected that the carbocation would initially react with a TFE molecule. However, if the reaction is reversible under the acidic reaction conditions and the reaction with the aromatic ring is irreversible, we anticipated that the arylated product should eventually be formed (Scheme 1). Indeed, the only product obtained was the Friedel−Crafts product **8b**.

SCHEME 1



b. Reaction with *β*-Diketones. The Lewis acid-catalyzed alkylation of benzhydryl cations with compounds possessing active methylenes has been reported in the literature.[16] The introduction of the acetylacetonyl group at the bridges of the calixarene skeleton is of interest, since this group can bind metal cations and can be further transformed into a wide array of groups. We have shown that the carbocation derived from the heterolytic cleavage of the C−Br bonds of **4a** reacts with the enol form of 1,3-pentanedienone, yielding the acetylacetonate derivative **4c**.[9c]

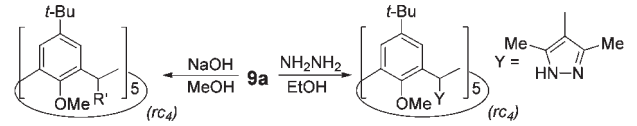
Heating of **6** in a 1,3-pentadienone/TFE mixture at reflux afforded the derivative **9a**. Reaction with dibenzoylmethane required reaction conditions similar to those used in the reaction with *m*-xylene (i.e., TFE /HBr) to yield **9b**. As observed previously for **4c**, no enolic form was detected in the ^{1}H NMR of **9a** and **9b** in $CDCl_3$, indicating that the compound exists almost exclusively in its keto form.



9a R = $CH(COMe)_2$ (23%)
9b R = $CH(COPh)_2$ (10%)

Acetylacetonyl groups undergo fragmentation in the presence of base affording a *β*-ketoalkyl chain.[17] Reflux of **9a** with NaOH in MeOH resulted in a 5-fold cleavage of the acetylacetonyl, and yielded the pentakis(2-propanonyl) derivative **10**. Reaction of **9a** with hydrazine hydrate/ethanol afforded **11** (Scheme 2).

SCHEME 2



R' = CH_2COMe
10 (57%)

11 (39%)

Conclusions

Reaction of the pentabromocalix[5]arene **6** under S_N1 conditions with the appropriate nucleophile affords calix[5]arene derivatives monosubstituted at all bridges. In all cases a single major product was formed (assigned to the *all-cis rc*$_4$ form) that could be purified by simple recrystallization.

Experimental Section

5,11,17,23,29-Penta-*tert*-butyl-31,32,33,34,35-pentamethoxy-2,8,14,20,26-pentabromocalix[5]arene (6). A mixture of **5**[12] (2.96 g, 3.36 mmol), NBS (3.11 g, 17.47 mmol) and 150 mL of CCl_4 was refluxed overnight while being irradiated with a spotlight (100 W). The organic phase was washed with aq $Na_2S_2O_5$ and water, dried ($MgSO_4$), and evaporated. The crude product was recrystallized from $CHCl_3$/MeOH giving 3.03 g of **6** (71%). Mp 302−304 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (s, 10H), 6.90 (s, 5H), 3.72 (s, 15H), 1.16 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.3, 147.0, 134.2, 127.2, 61.2, 41.8, 34.6, 31.2 ppm; HRMS (ESI) *m*/*z* 1275.1563 [$(M + H)^+$, calcd for $C_{60}H_{76}Br_5O_5$, 1275.1569]. Anal. Calcd for $C_{60}H_{75}Br_5O_5$: C, 56.49; H, 5.93. Found: C, 56.41; H, 5.92.

General Procedure for the Preparation of the Hexaalkoxy Calix[5]arene Derivatives. A mixture of **6** (0.10 g, 0.078 mmol) and 10 mL of the appropriate alcohol was refluxed overnight. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$/MeOH.

7a: yield 30%, mp 289−291 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (s, 10H), 6.20 (s, 5H), 3.88 (q, J = 8.5 Hz, 10H), 3.56 (s, 15H), 1.09 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.8, 146.9, 132.6, 124.5, 124.0 (q, J_{C-F} = 277.4 Hz), 72.7, 66.4 (q, J_{C-C-F} = 34.5 Hz), 62.2, 34.4, 31.2 ppm; HRMS (ESI) *m*/*z* 1393.5795 [$(M + Na)^+$, calcd for $C_{70}H_{85}F_{15}NaO_{10}$, 1393.5801]. Anal. Calcd for $C_{70}H_{85}F_{15}O_{10}$: C, 61.31; H, 6.25. Found: C, 61.51; H, 6.24.

7b: yield 27%, mp 279 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (s, 10H), 6.20 (s, 5H), 3.66 (h, J = 6.0 Hz, 5H), 3.57 (s, 15H), 1.22

(16) (a) Bisaro, F.; Prestat, G.; Vitale, M.; Poli, G. *Synlett* **2002**, 1823. (b) Jana, U.; Biswas, S.; Maiti, S. *Tetrahedron Lett*. **2007**, *48*, 4065. (c) Sanz, R.; Miguel, D.; Martinez, A.; Alvarez-Gutierrez, J. M.; Rodriguez, F. *Org. Lett*. **2007**, *9*, 727.

(17) Bray, D. J.; Jolliffe, K. A.; Lindoy, L. F.; McMurtrie, J. C. *Tetrahedron* **2007**, *63*, 1953.

(d, J = 6.0 Hz, 30H), 1.07 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.6, 145.6, 134.5, 124.4, 68.9, 68.4, 62.1, 34.3, 31.3, 22.4 ppm; HRMS (ESI) m/z 1193.7987 [$(M + Na)^+$, calcd for $C_{75}H_{110}NaO_{10}$, 1193.7997]. Anal. Calcd for $C_{75}H_{110}O_{10}$: C, 76.88; H, 9.46. Found: C, 76.45; H, 9.34.

7c: yield 32%, mp 325−327 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (s, 10H), 6.11 (s, 5H), 4.00 (m, 5H), 3.58 (s, 15H), 1.61 (m, 40H), 1.07 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.6, 145.5, 134.5, 124.4, 79.4, 69.7, 62.1, 34.3, 32.5, 31.3, 23.6 ppm; HRMS (ESI) m/z 1323.8804 [$(M + Na)^+$, calcd for $C_{85}H_{120}NaO_{10}$, 1323.8779].

7d: A mixture of **6** (0.10 g, 0.078 mmol), 8 mL of chloroform, 2 mL of HFIP, and 1 mL of propargyl alcohol was refluxed overnight. After evaporation of the solvents, the residue was recrystallized from $CHCl_3$/MeOH affording 21 mg (23%) of **7d**, mp 195−197 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (s, 10H), 6.40 (s, 5H), 4.22 (d, J = 2.5 Hz, 10H), 3.66 (s, 15H), 2.46 (t, J = 2.5 Hz, 5H), 1.09 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.1, 146.2, 133.2, 124.2, 80.2, 74.6, 70.3, 62.5, 56.0, 34.3, 31.3 ppm; HRMS (ESI) m/z 1173.6426 [$(M + Na)^+$, calcd for $C_{75}H_{90}NaO_{10}$, 1173.6432].

8a: A mixture of **6** (0.10 g, 0.078 mmol), 10 mL of HFIP, and 1 mL of *p*-xylene was refluxed overnight. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$/MeOH to afford 43 mg (39%) of **8a**, mp 248 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.96 (d, J = 7.6 Hz, 5 H), 6.90 (s, 5H), 6.87 (d, J = 7.8 Hz, 5H), 6.77 (s, 10H), 6.32 (s, 5H), 3.37 (s, 15H), 2.19 (s, 15H), 2.14 (s, 15H), 1.00 (s, 45H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.1, 144.5, 142.2, 135.7, 134.2, 133.7, 130.2, 130.0, 126.3, 125.3, 60.9, 40.5, 34.1, 31.2. 21.2, 20.2 ppm; MS (MALDI) m/z 1424.4006 [$(M + Na)^+$, calcd for $C_{100}H_{120}NaO_5$, 1424.9067].

8b: A mixture of **6** (0.10 g, 0.078 mmol), 10 mL of TFE, 2 drops of HBr, and 1 mL of *m*-xylene was refluxed overnight. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$/MeOH to afford 66 mg (60%) of **8b**, mp 268 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98 (d, J = 7.8 Hz, 5H), 6.89 (s, 5H), 6.87 (d, J = 7.9 Hz, 5H), 6.78 (s, 10H), 6.31 (s, 5H), 3.30 (s, 15H), 2.25 (s, 15H), 2.14 (s, 15H), 0.99 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.2, 144.6, 139.5, 136.6 135.8, 135.0, 131.3, 128.9, 125.9, 125.3, 60.9, 40.2, 34.1, 31.3, 20.8, 20.6 ppm; HRMS (ESI) m/z 1424.9059 [$(M + Na)^+$, calcd for $C_{100}H_{120}NaO_5$, 1424.9067].

8c: A mixture of **6** (0.10 g, 0.078 mmol), 10 mL of HFIP, and 0.10 g of *p*-*tert*-butylphenol was refluxed overnight. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$/MeOH to afford 9.1 mg (7%) of **8c**, mp 310−312 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12 (d, J_m = 2.5 Hz, 5H), 7.07 (d, J_o = 8.2 Hz, J_m = 2.5 Hz, 5H), 6.93 (s, 10H), 6.69 (d, J_o = 8.2 Hz, 5H), 6.48 (s, 5H), 5.00 (br s, 5H), 3.40 (s, 15H), 1.15 (s, 45H), 1.02 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.0, 151.4, 145.3, 142.6, 135.4, 129.2, 127.2, 125.5, 123.8, 115.5, 61.4, 37.3, 34.2, 34.0, 31.6, 31.3 ppm; HRMS (ESI) m/z 1645.0372 [$(M + Na)^+$, calcd for $C_{110}H_{140}NaO_{10}$, 1645.0378].

8d: A mixture of **6** (0.10 g, 0.078 mmol), 10 mL of HFIP, and 0.10 g of thymol was refluxed for 2.5 h. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$/MeOH to afford 25 mg (20%) of **8d**, mp 210 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.01 (s, 5H), 6.79 (s, 10H), 6.50 (s, 5H), 6.28 (s, 5H), 4.60 (br s, 5H), 3.28 (s, 15H), 3.09 (h, J = 6.9 Hz, 5H), 2.06 (s, 15H), 1.05 (d, J = 6.9 Hz, 30H), 1.00 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.0, 150.2, 144.5, 136.1, 135.2, 134.9, 130.5, 127.4, 125.2, 117.5, 60.9, 40.0, 34.1, 31.4, 26.4, 23.1, 20.1 ppm; HRMS (ESI) m/z 1645.0372 [$(M + Na)^+$, calcd for $C_{110}H_{140}NaO_{10}$, 1645.0378].

9a: A mixture of **6** (0.10 g, 0.078 mmol), 10 mL of TFE, and 1 mL of 2,4-pentanedione was refluxed overnight. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$/MeOH to afford 25 mg (23%) of **9a**, mp 293−295 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99 (s, 10H), 5.43 (d, J = 11.9 Hz, 5H), 4.52 (d, J = 11.9 Hz, 5H), 3.87 (s, 15H), 2.01 (s, 30H), 1.06 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.2, 153.0, 146.2, 134.4, 124.0, 74.7, 61.6, 37.3, 34.3, 31.2, 30.2 ppm; MS (MALDI) m/z 1393.4331 [$(M + Na)^+$, calcd for $C_{85}H_{110}NaO_{15}$, 1393.7742]. Anal. Calcd for $C_{85}H_{110}O_{15}$: C, 74.42; H, 8.08. Found: C, 74.24; H, 8.08.

9b: A mixture of **6** (0.10 g, 0.078 mmol), 10 mL of TFE, 2 drops of HBr, and 0.1 g of dibenzoylmethane was refluxed overnight. After evaporation of the solvent, the residue was chromatographed on silica gel first with petroleum ether (40−60 °C)/ethyl acetate (2:1 v/v) and finally with ethyl acetate neat to give a crude product. Recrystallization from $CHCl_3$/MeOH afforded 15 mg (10%) of **9b**, mp 225 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (d, J = 8.3 Hz, 20H), 7.31 (t, J = 7.3 Hz, 10H), 7.16 (t, J = 7.9 Hz, 20H), 6.95 (s, 10H), 6.16 (d, J = 10.2 Hz, 5H), 5.77 (d, J = 10.1 Hz, 5H), 3.74 (s, 15H), 0.79 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.3, 154.1, 144.4, 138.0, 134.7, 132.5, 128.5, 128.4, 124.5, 62.6, 61.8, 39.0, 34.1, 31.1 ppm; HRMS (ESI) m/z 2014.9338 [$(M + Na)^+$, calcd for $C_{135}H_{130}NaO_{15}$, 2014.9341].

10: A mixture of **9a** (0.068 g, 0.05 mmol), 10 mL of methanol, and 10 mL of 0.5 M NaOH was refluxed for 6 h. During this period the mixture was stirred vigorously. After vacuum filtration, the white solid was recrystallized from $CHCl_3$/MeOH to afford 33 mg (57%) of **10**, mp 283 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.87 (s, 10H), 5.30 (t, J = 8.1 Hz, 5H), 3.73 (s, 15H), 3.03 (d, J = 8.2 Hz, 5H), 2.07 (s, 15H), 1.00 (s, 45H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.2, 153.5, 145.9, 136.3, 122.7, 61.6, 50.0, 34.2, 32.7, 31.3, 30.1 ppm; HRMS (ESI) m/z 1183.7261 [$(M + Na)^+$, calcd for $C_{75}H_{100}NaO_{10}$, 1183.7214].

11: A mixture of **9a** (0.05 g, 0.04 mmol), 10 mL of ethanol, and 1 mL of hydrazine monohydrate was refluxed overnight. The white solid was vacuum filtered and washed several times with water to afford 19 mg (39%) of **11**, mp 310−312 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.87 (s, 10H), 5.96 (s, 5H), 3.24 (s, 15H), 1.80 (s, 30H), 0.96 (s, 45H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz, 343 K) δ 153.1, 143.7, 141.1, 135.5, 124.8, 115.8, 78.9, 60.2, 33.5, 30.7, 11.6 ppm; HRMS (ESI) m/z 1351.8733 [$(M + H)^+$, calcd for $C_{85}H_{111}N_{10}O_5$, 1351.8739].

Acknowledgment. We thank Dr. Shmuel Cohen (Hebrew University, Jerusalem) for the crystal structure determinations and Dr. Norbert Itzhak (Hebrew University, Jerusalem) and Dr. Ishay Columbus (Institute for Biological Research, Ness Ziona) for helpful discussions. This research was supported by the Israel Science Foundation (grant no. 257/07).

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **6**−**11** and crystal structures of **6** and **7b** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.