Study on the Esterification of *p-tert*-Butylcalix[8]arene

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Introduction

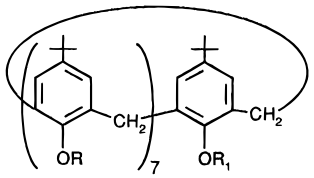
Synthetic effort in calixarene chemistry has mainly been directed toward the functionalization of the phenolic OH groups at the so-called *lower rim*, with the major aim of modifying the host−guest properties of these macrocycles.[1] Most of the studies in this field have been done on the smaller members of the family, calix[4]arenes and, more recently, calix[6]arenes.[1] The larger calix[8]arenes have received less attention, in spite of their potential for the complexation of medium-sized molecules.[2]

Esterification of phenolic groups is a simple way to introduce new functions at the lower rim of calixarenes. Application of these reactions to calix[4]arenes has been largely explored by Gutsche, who evidenced the effect of the relative rate of aroylation and conformational interconversion in the atropisomeric distribution of tetraester derivatives.[3] In addition, several procedures for the selective di- and trisubstitution of calix[4]arenes have been developed.[3bc,4,5] These studies have been expanded to include *p-tert*-butylcalix[5]arene[6] and *p-tert*-butylcalix[6]arene. For this last compound, 1,2,4,5-tetrasubstitution can be obtained in high yields using NaH as base.[7] As regards calix[8]arene, aside from some octaesters,[5b,8] only a few partial esters (di-, tetra-, and hexa-) of uncertain structure have been reported.[9]

As part of our program[2] on the selective functionalization of *p-tert*-butylcalix[8]arene (**1**), the typical representative of this class of macrocyclic compounds, we have examined its aroylation and we wish to report here the results obtained.

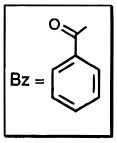
Results and Discussion

Esterification of *p-tert*-butylcalix[8]arene has been carried out using three different procedures: (i) reaction with aroyl chloride in pyridine, (ii) reaction with aroyl chloride in THF in the presence of NaH, (iii) reaction with a free acid in $CHCl_3$ in the presence of dicyclohexylcarbodiimmide (DCC) and 4-(dimethylamino)pyridine (DMAP). The NaH-induced aroylation is the procedure of choice to obtain octasubstituted derivatives **2a-h**, which are formed in high yield using moderate excess of acyl chloride (Table 1). When the acylating agent is used in less than stoichiometric amounts for the complete esterification, mixtures of partially derivatized compounds are obtained, too complex to be amenable to chromatographic separation.



1 R = R_1 = H
2a-i R = R_1
3a-g R_1 = H

	R
a	*p-t*-Bu-Bz
b	*p*-Me-Bz
c	*p*-MeO-Bz
d	Bz
e	*p*-Br-Bz
f	*p*-CN-Bz
g	*p*-NO_2-Bz
h	*p*-C_6H_5-Bz



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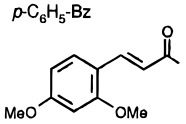

Reaction in pyridine with a large excess of acyl chloride (from 24 to 32 equiv, depending on its reactivity) also affords octaesters **2a-h** in good yields (Table 1). In this case reduction of the amount of the acylating agent (to ca. 10 moles per mole of *p-tert*-butylcalix[8]arene) with a concurrent shortening of the reaction time allowed for the preparation of heptaesters **3a-g** in satisfying yields (45−80%). This procedure is comparable to the preparation of calix[4]arene tribenzoate developed by Gutsche and Lin.[4a] In these reactions, besides heptaesters **3a-g**, variable amounts of octasubstituted derivative were usually formed, depending on the aroyl chloride reactivity. A reduction of reaction time caused a decrease in the yield of octaester, while concurrently a mixture of hexasubstituted derivatives (unresolved by TLC) increased. A reduction of the relative amount of acyl halide again led to intractable mixtures.

In the attempt to find synthetic procedures useful for the preparation of calix[8]arenes with a lower degree of esterification, we were induced to use weak bases such as K_2CO_3 or CsF which had been proved valuable in the partial alkylation of *p-tert*-butylcalix[8]arene.[2] In these reactions a higher selectivity was observed with apparently simpler mixtures on TLC. However, the difficulties encountered in their chromatographic separation precluded any structural characterization of the components.

The third procedure, an application of the Steglich's methodology for esterification of phenols,[10] can be used

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0022-3263/96/1961-2195$12.00/0

Table 1. Compound Yield in the Esterification of *p-tert*-Butylcalix[8]arene

entry	procedure	equiv of acylating agent	reaction time (h)	purification	compd (yield, %)	mp, °C
1	A	32	48 rt +18 reflux	cryst	**2a** (84)	298−300
2	A	32	48	cryst	**2b** (80)	254−256
3	B	10	4.5	cryst	**2b** (92)	
4	C	20	24	TLC	**2b** (48)	
5	A	32	43	cryst	**2c** (80)	258−260
6	B	10	4	cryst	**2c** (83)	
7	A	24	20	cryst	**2d** (80)	261−263
8	A	32	48	cryst	**2e** (76)	290−292
9	A	32	48	cryst	**2f** (78)	286−288
10	A	24	24	cryst	**2g** (80)	296−298
11	B	10	5	TLC	**2h** (31)	248−250
12	C	20	18	TLC	**2i** (76)	183−185
13	A	16	6	cryst	**3a** (75)	288−290
14	A	16	12	TLC	**3b** (50)	193−195
15	A	16	12	TLC	**3c** (45)	196−198
16	A	14	12	TLC	**3d** (45)	220−222
17	A	10	3	cryst	**3e** (80)	242−244
18	A	14	3	TLC	**3f** (50)	258−260
19	A	10	2	TLC	**3g** (65)	238−240

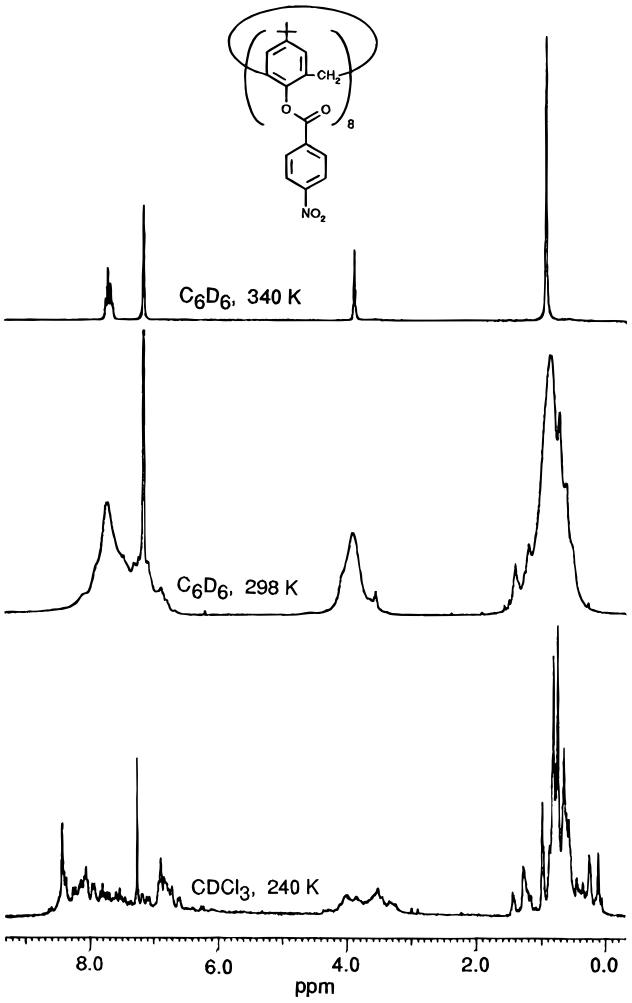

Figure 1. ^{1}H NMR spectra (250 MHz) of octaester **2g** at the given conditions.

advantageously when the acyl chloride is not readily available and octasubstituted compounds are obtained. This is exemplified by the easy preparation of calix[8]-arene *trans*-2,4-dimethoxycinnamoyl octaester **2i**, isolated in 76% yield (entry 12, Table 1).

The introduction of eight aroyloxy groups in *p-tert*-butylcalix[8]arene causes a considerable reduction of the conformational mobility in solution, since conformational interconversion via the *oxygen through the annulus route* is hampered. This is evident in the ^{1}H NMR spectrum of **2g** taken at room temperature, which exhibits extreme signal broadening (Figure 1). In general, the full interpretation of the ^{1}H NMR spectra of aroylated *p-tert*-butylcalix[8]arene **2a-i** required heating at 355 K, in order to observe the expected resonances. Analogously, a good resolution of the ^{13}C NMR spectra requires heating at 330 K. However, a complete inhibition of the conformational interconversion cannot be obtained whatever the size of the appended aroyl groups, since the alternative *tert-butyl through the annulus route* is always operating.[11] At low temperatures the ^{1}H NMR spectra became progressively more sharpened, but splitting of each singlet in a very large number of resonances was observed (more than 14 for the *tert*-Bu groups of **2d** or **2g** at 240 K, see Figure 1) pointing to freezing of several conformations without any preference.[12]

Similarly, heptaaroylated derivatives **3a**−**g** have a reduced conformational mobility and therefore the ^{1}H NMR signal pattern expected from their molecular symmetry, containing five *tert*-butyl signals in a 2:1:2:2:1 ratio and four singlets of equal intensity for the $ArCH_2$-Ar groups, becomes evident only at high temperature (usually 355 K, Figure 2). However, the aromatic region remains uninterpretable due to extensive overlapping. In the ^{13}C NMR spectra the similarity of the four types of aroylated aromatic rings gives rise to several accidental isochronies reducing the number of the observed resonances. Thus, the bridging methylenes resonate in the 29.7−31.2 ppm region and are often unresolved and obscured by the broad signal of *t*-Bu groups attached to esterified phenolic rings (δ 31.0−31.2), whereas the single OH bearing ring is sufficiently different to give a distinct resonance for its *t*-Bu group (δ 31.5−31.6).

In brief, acylation of *p-tert*-butylcalix[8]arene appears to be less selective than alkylation, and heptaesters are the only partially functionalized derivatives prepared in satisfying to good yields with the procedures used in the

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(11) It has been demonstrated that this route is operating even in the smaller *p-tert*-butylcalix[6]arenes: Otsuka, H.; Araki, K.; Sakaki, T.; Nakashima, K.; Shinkai, S. *Tetrahedron Lett.* **1993**, *34*, 7275. van Duynhoven, J. P. M.; Janssen, R. G.; Verboom, W.; Franken, S. M.; Casnati, A.; Pochini, A.; Ungaro, R.; de Mendoza, J.; Nieto, P. M.; Prados, P.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1994**, *116*, 5814. Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem.* **1994**, *59*, 3871.

(12) See for comparison the behavior of the octakis(trimethylsilyl) ether of **1** described in ref 8.

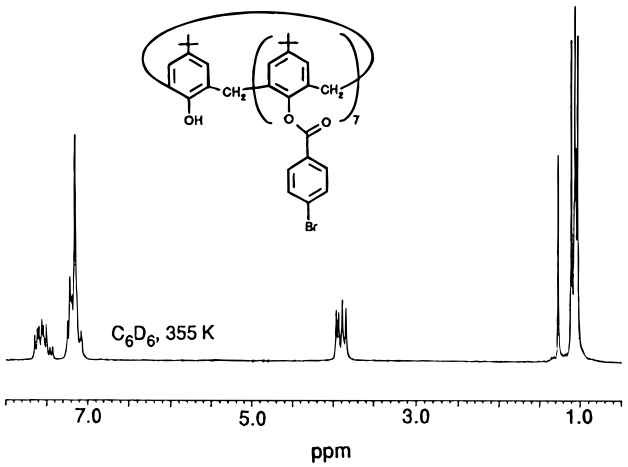

Figure 2. ^{1}H NMR spectrum (250 MHz) of heptaester **3e**.

present work. These compounds, in analogy to Gutsche's calix[4]arene tribenzoate,[4a] can be used as "protected" *p-tert*-butylcalix[8]arene in the synthesis of monoalkyl derivatives, when the alkylating agent is hardly obtainable and therefore high yields are strongly desirable.

Experimental Section

General Comments. Melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were taken at 250.13 MHz in C_6D_6 (355 K) and at 62.9 MHz in $CDCl_3$ (330 K), respectively. FAB(+) MS spectra were recorded using 3-nitrobenzyl alcohol as matrix. Elemental analyses were obtained from the Institute of Pharmaceutical Chemistry of the University of Catania. Preparative TLC was performed using silica gel plates (Kieselgel 60 F_{254}, 1 mm, Merck). Recrystallization of products was from MeOH/CH_2Cl_2. All chemicals were reagent grade and were used without further purification. Anhydrous pyridine, THF, and $CHCl_3$ were purchased from Aldrich; *p-tert*-butylcalix[8]arene was either from a commercial source or prepared following a literature procedure.[13]

General Procedures. Procedure A. A suspension of 0.250 g (0.192 mmol) of *p-tert*-butylcalix[8]arene and aroyl chloride in 5 mL of dry pyridine was stirred at room temperature for the time indicated for each individual compound (only in the preparation of **2a**, completion of the reaction required a period of refluxing). The mixture was poured into 50 mL of 2 N HCl, and the precipitate was collected by filtration. After washing with 2 N NaOH (50 mL) followed by H_2O and finally MeOH (20 mL), the crude product was purified by TLC or recrystallization.

Procedure B. A suspension of 0.250 g (0.192 mmol) of *p-tert*-butylcalix[8]arene in 25 mL of dry THF was refluxed under stirring until a clear solution was obtained (20 min), and then 0.074 g (3 mmol) of NaH was added under N_2. The mixture was allowed to stir for 15 min, and then the aroyl chloride (1.92 mmol) in 5 mL of dry THF was introduced and stirring under reflux was continued for 4-5 h. THF was removed under vacuum, and the solid residue was triturated with 50 mL of 2 N HCl. The insoluble material was collected by filtration and washed with 20 mL of MeOH and purified by recrystallization or TLC.

Procedure C. DMAP (0.471 g, 3.84 mmol), *p-tert*-butylcalix[8]arene (0.250 g, 0.192 mmol), and DCC (0.7 g, 3.84 mmol) were added at room temperature to a stirred solution of carboxylic acid (3.84 mmol) in 15 mL of dry $CHCl_3$. Stirring was maintained for 18 h under reflux. Removal of $CHCl_3$ left a residue which was triturated with 0.5 N HCl. The insoluble material was collected by filtration, washed with water, dried, and purified by TLC.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[(4-*tert*-butylbenzoyl)oxy]calix[8]arene (2a) (procedure A; entry 1, Table 1): 420 mg (84.5%), white powder, mp 298−300 °C; ^{1}H NMR δ 1.056, 1.057 (s, 72 H each), 3.96 (bs, 16 H), 7.07 (s, 16 H), 7.13 and 7.94 (AB, J = 8.5 Hz, 32 H); ^{13}C NMR δ 31.1 (q, t, overlapped), 34.1, 35.0 (s), 125.4, 126.3, 130.2 (d), 126.4, 132.2, 145.9, 148.3, 156.6, 164.7 (s); FAB(+) MS 2579 (MH^+). Anal. Calcd for $C_{176}H_{208}O_{16}$: C, 81.95; H, 8.13. Found: C, 81.85; H, 8.16.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[(4-methylbenzoyl)oxy]calix[8]arene (2b) (procedure B; entry 3, Table 1): 401 mg (92%), white powder, mp 254−256 °C; ^{1}H NMR δ 1.09 (s, 72 H), 3.99 (bs, 16 H), 7.24 (s, 16 H), 6.79 and 7.74 (AB, J = 7.7 Hz, 32 H); ^{13}C NMR δ 21.5 (q), 30.3 (t), 31.2 (q), 34.2 (s), 126.1, 129.0, 130.1 (d), 126.1, 131.6, 143.9, 145.4, 148.0, 164.7 (s); FAB(+) MS 2224 (MH^+). Anal. Calcd for $C_{152}H_{160}O_{16}$: C, 81.40; H, 7.19. Found: C, 81.35; H, 7.16.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[(4-methoxybenzoyl)oxy]calix[8]arene (2c) (procedure B; entry 6, Table 1): 382 mg (83.6%), white powder, mp 258−260 °C; ^{1}H NMR δ 1.08 (s, 72 H), 3.34 (s, 24 H), 4.02 (bs, 16 H), 7.23 (s, 16 H), 6.56 and 7.79 (AB, J = 8.5 Hz, 32 H); ^{13}C NMR δ 29.7, 30.3 (t), 31.3 (q), 34.2 (s), 55.3 (q), 113.7, 125.9, 132.3 (d), 121.5, 133.1, 145.9, 148.1, 154.6, 163.7 (s); FAB(+) MS 2370 (MH^+). Anal. Calcd for $C_{152}H_{160}O_{24}$: C, 77.00; H, 6.80. Found: C, 77.08; H, 6.76.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis(benzoyloxy)calix[8]arene (2d) (procedure A; entry 7, Table 1): 329 mg (80.2%), white powder, mp 261−263 °C (lit.[5b] mp 246−248 °C); ^{1}H NMR δ 1.09 (s, 72 H), 3.94 (bs, 16 H), 6.91 and 6.94 (AB, J = 7.4 Hz, 16 H), 7.06 (m, 8 H), 7.21 (s, 16 H), 7.75 (d, J = 7.4 Hz, 16 H); ^{13}C NMR δ 31.2 (q), 31.6 (t), 34.3 (s), 126.2, 128.4, 130.0, 133.1 (d), 129.2, 131.7, 145.7, 148.4, 164.6 (s); FAB(+) MS 2130 (MH^+). Anal. Calcd for $C_{144}H_{144}O_{16}$: C, 81.17; H, 6.81. Found: C, 81.09; H, 6.78.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[(4-bromobenzoyl)oxy]calix[8]arene (2e) (procedure A; entry 8, Table 1): 406 mg (76.5%), white powder, mp 290−292 °C; ^{1}H NMR δ 1.07 (s, 72 H), 3.90 (s, 16 H), 7.19 (s, 16 H), 7.17 and 7.51 (AB, J = 8.4 Hz, 32 H); ^{13}C NMR δ 30.2 (t), 31.2 (q), 34.3 (s), 126.4, 131.5, 131.9 (d), 127.8, 128.7, 131.6, 145.5, 148.8, 163.8 (s); FAB(+) MS 2761 (MH^+). Anal. Calcd for $C_{144}H_{136}O_{16}Br_8$: C, 62.62; H, 4.96. Found: C, 62.58; H, 4.90.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[(4-cyanobenzoyl)oxy]calix[8]arene (2f) (procedure A; entry 9, Table 1): 333 mg (78%), white powder, mp 286−288 °C; ^{1}H NMR δ 0.97 (s, 72 H), 3.83 (s, 16 H), 7.08 (s, 16 H), 7.07 and 7.6 (AB, J = 7.8 Hz, 32 H); ^{13}C NMR δ 30.9 (q, t, overlapped), 34.1 (s), 126.4, 130.3, 132.2 (d), 126.5, 129.9, 131.4, 145.3, 149.1, 162.6 (s); FAB(+) MS 2330 (MH^+). Anal. Calcd for $C_{152}H_{136}N_8O_{16}$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.30; H, 5.82; N, 4.89.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[(4-nitrobenzoyl)oxy]calix[8]arene (2g) (procedure A; entry 10, Table 1): 382 mg (80%), yellow powder, mp 296−298 °C; ^{1}H NMR δ 0.93 (s, 72 H), 3.89 (s, 16 H), 7.15 (s, 16 H), 7.66 and 7.73 (AB, J = 8.5 Hz, 32 H); ^{13}C NMR δ 31.0 (q, t, overlapped), 34.2 (s), 123.5, 126.7, 131.1 (d), 131.6, 134.0, 145.5, 149.5, 151.1, 162.6 (s); FAB(+) MS 2490 (MH^+). Anal. Calcd for $C_{144}H_{136}N_8O_{32}$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.40; H, 5.42; N, 4.68.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[4-phenylbenzoyl)oxy]calix[8]arene (2h) (procedure B; entry 11, Table 1): 34 mg from TLC (AcOEt/cyclohexane 1:4) of 100 mg of reaction mixture (31%), white powder, mp 248−250 °C; ^{1}H NMR δ 1.01 (s, 72 H), 4.08 (s, 16 H), 7.12−7.17 (m, overlapped 40 H), 7.19 and 7.28 (AB, J = 6.7 Hz, 32 H), 7.83 (bs, 16 H); ^{13}C NMR δ 30.8 (t), 31.2 (q), 34.2 (s), 126.3, 127.1, 127.3, 128.1, 128.9, 130.6 (d), 127.7, 131.9, 140.0, 145.8, 146.1, 148.4, 164.6 (s); FAB(+) MS 2739 (MH^+). Anal. Calcd for $C_{192}H_{176}O_{16}$: C, 84.18; H, 6.48. Found: C, 84.09; H, 6.40.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55,56-octakis[(*trans*-2,4-dimethoxycinnamoyl)oxy]calix[8]-arene (2i) (procedure C; entry 12, Table 1): 83 mg from TLC (CH_2Cl_2/Et_2O 99:1) of 110 mg of reaction mixture (76%), white powder, mp 183−185 °C; ^{1}H NMR δ 1.05 (s, 72 H), 3.15 (s, 24 H), 3.35 (s, 24 H), 3.98 (s, 16 H), 6.06 (s, 8 H), 6.21 and 6.99 (AB, J = 8.3 Hz, 16 H), 6.49 and 8.01 (AB, J = 14.9 Hz, 16 H), 7.15 (s, 16 H); ^{13}C NMR δ 30.5 (t), 31.3 (q), 34.2 (s), 55.3 × 2C (q), 98.5, 105.4, 115.0, 126.1, 130.6, 141.4 (d), 116.9, 132.2, 145.9,

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148.1, 160.0, 162.8, 166.2 (s). Anal. Calcd for $C_{176}H_{192}O_{32}$: C, 74.98; H, 6.86. Found: C, 74.92; H, 6.82.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55-heptakis[(4-*tert*-butylbenzoyl)oxy]calix[8]aren-56-ol (3a) (procedure A; entry 13, Table 1): 349 mg (75%), white powder, mp 288−290 °C; ^{1}H NMR δ 0.96 (bs, 18 H), 1.00 (s, 9 H), 1.02 (s, 18 H), 1.04 (s, 9 H), 1.10 (bs, 18 H), 1.20 (bs, 18 H), 1.22 (bs, 18 H), 1.25 (bs, 18 H), 1.28 (s, 9 H) 3.99 (s, 4 H), 4.02 (s, 4 H), 4.05 (s, 4 H), 4.13 (s, 4 H), 7.00−7.31 (overlapped, 30 H), 7.77 (d, J = 7.5 Hz, 2 H), 7.90 (d, J = 8.3 Hz, 4 H), 7.94 (d, J = 9.5 Hz, 4 H), 8.02 (d, J = 8.4 Hz, 4 H); ^{13}C NMR δ 31.1 (q, t, overlapped), 31.6 (q), 34.1, 35.0 (s), 124.7, 125.4, 125.9, 126.3, 126.5, 127.1, 127.6, 129.5, 130.2 (d), 131.7, 131.9, 132.2, 142.6, 145.5, 148.3, 148.5, 150.6, 156.8, 164.6, 164.8 (s); FAB(+) MS 2419 (MH^+). Anal. Calcd for $C_{165}H_{196}O_{15}$: C, 81.91; H, 8.17. Found: C, 81.84; H, 8.11.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55-heptakis[(4-methylbenzoyl)oxy]calix[8]aren-56-ol (3b) (procedure A; entry 14, Table 1): 35 mg from TLC (CH_2Cl_2/*n*-hexane 7:3) of 70 mg of reaction mixture (50%), white powder, mp 193−195 °C; ^{1}H NMR δ 1.05 (s, 18 H), 1.07 (s, 9 H), 1.09 (s, 18 H), 1.13 (s, 18 H), 1.26 (s, 9 H), 2.06 (bs, overlapped, 21 H), 3.96 (s, 4 H), 3.99 (s, 4 H), 4.00 (s, 4 H), 4.06 (s, 4 H), 6.79−6.92 (overlapped, 14 H), 7.10−7.25 (overlapped, 16 H), 7.71 (d, J = 8.3 Hz, 2 H), 7.78 (d, J = 7.9 Hz, 4 H), 7.83 (d, J = 8 Hz, 4 H), 7.88 (d, J = 7.7 Hz, 4 H); ^{13}C NMR δ 21.5 (bq), 29.7 (t), 31.1 (q, t, overlapped), 31.5 (q), 33.9, 34.1 (s), 124.6, 126.1, 127.3, 129.0, 130.2 (d), 131.6, 143.9, 145.2, 148.2, 164.7 (s); FAB(+) MS 2124 (MH^+). Anal. Calcd for $C_{144}H_{154}O_{15}$: C, 81.40; H, 7.31. Found: C, 81.36; H, 7.26.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55-heptakis[(4-methoxybenzoyl)oxy]calix[8]aren-56-ol (3c) (procedure A; entry 15, Table 1): 31 mg from TLC (CH_2Cl_2/Et_2O 99:1) of 70 mg of reaction mixture (45%), white powder, mp 196−198 °C; ^{1}H NMR δ 1.04 (s, 18 H), 1.07 (s, 9 H), 1.09 (s, 18 H), 1.14 (s, 18 H), 1.26 (s, 9 H), 3.33 (s, 6 H), 3.34 (s, 6 H), 3.35 (s, 3 H), 3.36 (s, 6 H), 3.98 (s, 4 H), 4.0 (s, 4 H), 4.02 (s, 4 H), 4.08 (s, 4 H), 6.54−6.68 (overlapped, 14 H), 7.10−7.28 (overlapped, 16 H), 7.78 (d, J = 8.9 Hz, 2 H), 7.83 (d, J = 8.1 Hz, 4 H), 7.90 (d, J = 6.4 Hz, 4 H), 7.92 (d, J = 5.9 Hz, 4 H); ^{13}C NMR δ 29.7 (t), 31.2 (q, t, overlapped), 31.6 (q), 34.2 (s), 55.3 (bq), 113.8 (d), 121.6 (s), 124.7, 125.9, 126.3, 127.4 (d), 127.8, 128.2 (s), 132.3 (d), 145.6, 148.3, 163.8, 163.9, 164.4, 164.5 (s); FAB(+) MS 2236 (MH^+). Anal. Calcd for $C_{144}H_{154}O_{22}$: C, 77.32; H, 6.94. Found: C, 77.24; H, 6.87.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55-heptakis(benzoyloxy)calix[8]aren-56-ol (3d) (procedure A; entry 16, Table 1): 27 mg from TLC (AcOEt/cyclohexane 15:85) of 60 mg of reaction mixture (45%), white powder, mp 220−222 °C; ^{1}H NMR δ 1.02 (s, 18 H), 1.05 (s, 18 H), 1.09 (s, 9 H), 1.12 (s, 18 H), 1.26 (s, 9 H), 3.87 (s, 4 H), 3.92 (s, 4 H), 3.97 (s, 4 H), 4.03 (s, 4 H), 6.83−7.20 (overlapped, 30 H), 7.63 (d, J = 7.8 Hz, 2 H), 7.74 (d, J = 7.9 Hz, 4 H), 7.85 (d, J = 7.5 Hz, 4 H), 7.89 (d, J = 8 Hz, 4 H); ^{13}C NMR δ 29.7, 30.6 (t), 31.1 (q, t, overlapped), 31.6 (q), 33.3, 34.2 (s), 124.8, 126.1, 126.4, 127.4, 128.2, 128.4, 130.0, 130.1, 133.2 (d), 129.1, 131.4, 131.9, 132.1, 145.5, 148.5, 150.6, 164.7, 164.8 (s); FAB(+) MS 2026 (MH^+). Anal. Calcd for $C_{137}H_{140}O_{15}$: C, 81.19; H, 6.96. Found: C, 81.12; H, 6.88.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55-heptakis[(4-bromobenzoyl)oxy]calix[8]aren-56-ol (3e) (procedure A; entry 17, Table 1): 397 mg (80%), white powder, mp 242−244 °C; ^{1}H NMR δ 1.03 (s, 18 H), 1.05 (s, 9 H), 1.06 (s, 18 H), 1.10 (s, 18 H), 1.26 (s, 9 H), 3.84 (s, 4 H), 3.88 (s, 4 H), 3.93 (s, 4 H), 3.96 (s, 4 H), 7.07−7.24 (overlapped, 30 H), 7.44 (d, J = 8.4 Hz, 2 H), 7.52 (d, J = 8.5 Hz, 4 H), 7.58 (d, J = 8.4 Hz, 4 H), 7.63 (d, J = 8.4 Hz, 4 H); ^{13}C NMR δ 29.7 (t), 31.1 (q, t, overlapped), 31.5 (q), 34.0, 34.2 (s), 125.1, 126.1, 126.4, 126.6, 131.5, 131.8, 132.4 (d), 127.8, 128.7, 145.3, 148.9, 163.8 (s); FAB-(+) MS 2578 (MH^+). Anal. Calcd for $C_{137}H_{133}O_{15}Br_7$: C, 63.81; H, 5.20. Found: C, 63.78; H, 5.16.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55-heptakis[(4-cyanobenzoyl)oxy]calix[8]aren-56-ol (3f) (procedure A; entry 18, Table 1): 35 mg from TLC (CH_2Cl_2/Et_2O 99:1) of 70 mg of reaction mixture (50%), white powder, mp 258−260 °C; ^{1}H NMR δ 0.99 (s, 27 H), 1.01 (s, 18 H), 1.05 (s, 18 H), 1.25 (s, 9 H), 3.77 (s, 4 H), 3.82 (s, 4 H), 3.90 (s, 4 H), 3.92 (s, 4 H), 7.00−7.21 (overlapped, 30 H), 7.51 (d, J = 6.9 Hz, 2 H), 7.60 (d, J = 8.3 Hz, 4 H), 7.68 (d, J = 8 Hz, 4 H), 7.76 (d, J = 8.3 Hz, 4 H); ^{13}C NMR δ 29.7 (t), 31.0 (q, t, overlapped), 31.5 (q), 34.0, 34.2 (s),117.1, 117.3, 124.2 (s), 125.2, 126.0, 126.5, 126.9, 127,9, 130.5 (d), 130.9, 131.5 (s), 132.2 (d), 145.2, 145.4, 149.5, 162.8, 162.9 (s); FAB(+) MS 2201 (MH^+). Anal. Calcd for $C_{144}H_{133}N_7O_{15}$: C, 78.56; H, 6.09; N, 4.45. Found: C, 78.50; H, 5.97; N, 4.53.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,-55-heptakis[(4-nitrobenzoyl)oxy]calix[8]aren-56-ol (3g) (procedure A; entry 19, Table 1): 45 mg from TLC (CH_2Cl_2) of 70 mg of reaction mixture (65%), white powder, mp 238−240 °C; ^{1}H NMR δ 0.92 (s, 18 H), 0.96 (s, 9 H), 0.98 (s, 18 H), 1.04 (s, 18 H), 1.25 (s, 9 H), 3.84 (s, 4 H), 3.86 (s, 4 H), 3.94 (s, 4 H), 3.97 (s, 4 H), 7.04−7.24 (overlapped, 22 H), 7.54−7.80 (overlapped, 22 H); ^{13}C NMR δ 29.7 (t), 31.0 (q, t, overlapped), 31.5 (q), 34.2 (s),123.3, 123.6, 126.2, 126.6, 131.0, 131.1 (d), 125.4, 127.9, 131.1, 133.9, 134.1, 145.3, 149.7, 150.9, 162.5 (s); FAB(+) MS 2341 (MH^+). Anal. Calcd for $C_{137}H_{133}N_7O_{29}$: C, 70.27; H, 5.73; N, 4.19. Found: C, 70.20; H, 5.66; N, 4.26.

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