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# Suzuki–Miyaura coupling on the three upper rims of hexahomotrioxacalix[3]arenes

Kazunori Tsubaki,* Masahide Sakakibara, Yuki Nakatani and Takeo Kawabata

*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

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**Abstract**—The efficient functionalization of three upper rims based on Suzuki–Miyaura coupling to temporarily lower rim-protected hexahomotrioxacalix[3]arenes was developed. After deprotection of the three protecting groups, the three upper rim-functionalized and lower rim-free hexahomotrioxacalix[3]arenes **5a**–**5m** were synthesized.

## 1. Introduction

Hexahomotrioxacalix[3]arene is a member of the calixarene family and has structural features of both a calixarene and an 18-crown-6 ether, having a cavity composed of a $C_3$-symmetric 18-membered ring (similar to 18-crown-6 ether), and also a three-dimensional cavity, which can adopt cone and/or partial-cone conformations (by analogy with calixarenes).[1] Hexahomotrioxacalix[3]arene skeleton having such features would be expected to be a useful platform for selective and specific function or host–guest recognition properties. However, functionalization of the upper or lower rim of hexahomotrioxacalix[3]arenes, especially the transformation of functional groups on the upper rim in the presence of a phenolic hydroxy group on the lower rim, is quite difficult due to structural weakness attributed to the combination of three dibenzyletheral linkages and phenolic hydroxyl groups (Fig. 1). To overcome these synthetic difficulties, we developed a stepwise construction of hexahomotrioxacalix[3]arenes based on cyclization of the corresponding linear trimers[2] as well as several functional group transformations at one of the three upper rim aryl groups of hexahomotrioxacalix[3]arenes using the so-called ‘Mannich route’ in calixarene chemistry.[3] However, the Mannich route is not suitable for transformation of the three upper rims in one operation because the yield of each reaction is around 50%. In this paper, we report functionalization of the three upper rims based on Suzuki–Miyaura coupling[4] to temporarily lower rim-protected hexahomotrioxacalix[3]arenes.

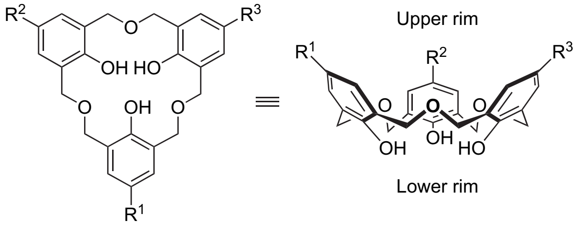
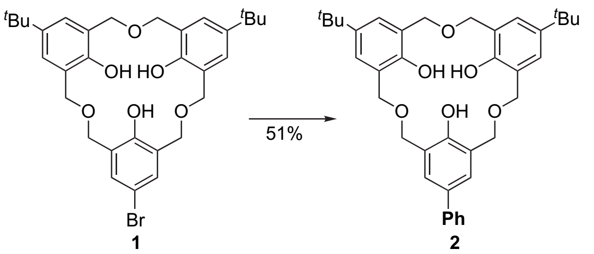


**Figure 1**. Hexahomotrioxacalix[3]arenes.

## 2. Results and discussion

Since there have been a few reports on the Suzuki–Miyaura coupling of the three upper rims of lower rim-alkylated hexahomotrioxacalix[3]arenes,[5] we applied this coupling to the mono-brominated hexahomotrioxacalix[3]arene **1**.[2a] First, we tried the modified Suzuki–Miyaura coupling reported by Buchwald et al.[6] on one of the three upper rims of **1** (Scheme 1).



**Scheme 1**. Conditions: (2-biphenyl) di-*tert*-butylphosphine, $Pd(OAc)_2$, and KF.

Hexahomotrioxacalix[3]arene with one bromine on the upper rim **1** was reacted with 1.5 equiv of boric acid in the presence of (2-biphenyl) di-*tert*-butylphosphine (10 mol %),

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* Corresponding author. Tel.: +81 774 38 3191; fax: +81 774 38 3197; e-mail: tsubaki@fos.kuicr.kyoto-u.ac.jp

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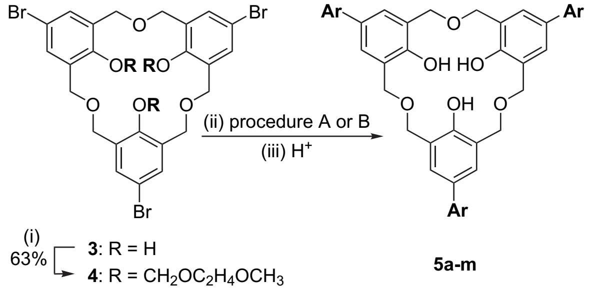
palladium acetate (5 mol %), and potassium fluoride (3 equiv) in THF at 50 °C to give **2** in 51% yield. However, our attempt to introduce three phenyl groups to the three upper rims on **3**[7] was not successful due to the formation of inseparable and complicated product mixtures. Therefore, we changed our synthetic strategy, so that active hydroxy groups at the lower rim were temporarily protected by methoxyethoxymethyl (MEM) groups (Scheme 2). Tribromohexahomotrioxacalix[3]arene **3** was treated with 10 equiv of MEMCl and sodium hydride in THF at room temperature to give the desired **4** in 63% yield. Shinkai and co-workers reported that ring-inversion of hexahomotrioxacalix[3]arenes took place through oxygen-through-the-annulus rotation, and cone/partial-cone ring-inversion was inhibited by introducing butyl and bulkier groups to the lower rim.[8] Based on the results of $^1$H NMR, MEM-protected **4** is fixed in a partial-cone conformation.



**Scheme 2**. Conditions: (i) MEMCl and NaH; (ii) procedure A: ArB(OH)$_2$, Pd(OAc)$_2$, (2-biphenyl) di-*tert*-butylphosphine; procedure B: ArB(OH)$_2$, Pd(PPh$_3$)$_4$; (iii) 0.2 N HCl.

Suzuki–Miyaura coupling of the three upper rims of lower rim-protected **4** was investigated. Among the several procedures reported on modified Suzuki–Miyaura coupling,[5] two procedures (procedures A and B; see Section 3 and Table 1) were suitable for introducing aromatic rings to the three upper rims of MEM-protected **4**. Procedure A was suitable for *para*-substituted boric acids (entries 1–4), and procedure B was suitable for boric acids possessing a strong electron-withdrawing group and/or *ortho*-substitution (entries 5–13). After a coupling reaction through procedure A or B, deprotection of the three MEM groups was successively performed for concise purification of the lower rim-free hexahomotrioxacalix[3]arenes **5**, and the yields in Table 1 were calculated in two steps based on isolated **5**. Since procedure A had milder reaction conditions, the combined yields (74–90%) were generally higher than those using procedure B (36–78%).

**Table 1**. Suzuki–Miyaura coupling on the three upper rims of hexahomotrioxacalix[3]arenes **4**

| Entry | Ar | Product | Procedure[a] | Yield (%)[b] |
|---|---|---|---|---|
| 1 | Ph | **5a**[9] | A | 77 |
| 2 | *p*-Me–C$_6$H$_4$ | **5b** | A | 90 |
| 3 | *p*-MeO–C$_6$H$_4$ | **5c** | A | 89 |
| 4 | *p*-F–C$_6$H$_4$ | **5d** | A | 74 |
| 5 | *o*-NC–C$_6$H$_4$ | **5e** | B | 36 |
| 6 | *p*-CHO–C$_6$H$_4$ | **5f** | B | 59 |
| 7 | *p*-O$_2$N–C$_6$H$_4$ | **5g** | B | 62 |
| 8 | *o*-MeO–C$_6$H$_4$ | **5h** | B | 78 |
| 9[c] | *o*-HO–C$_6$H$_4$ | **5i** | B | 67 |
| 10 | *o*-EtO$_2$C–C$_6$H$_4$ | **5j** | B | 63 |
| 11[c] | *o*-MeCONH–C$_6$H$_4$ | **5k** | B | 43 |
| 12 | 3-Pyridinyl | **5l** | B | 50 |
| 13 | 4-Pyridinyl | **5m** | B | 60 |

[a] Procedure A: ArB(OH)$_2$ (10 equiv), Pd(OAc)$_2$ (10 mol %), (2-biphenyl) di-*tert*-butylphosphine (20 mol %), rt, 2 days. Procedure B: ArB(OH)$_2$ (10 equiv), Pd(PPh$_3$)$_4$ (20 mol %), 80 °C, 6–19 h.

[b] Isolated yield.

[c] Corresponding pinacol ester of boric acid was used.

In summary, efficient functionalization of the three upper rims of (lower rim-free) hexahomotrioxacalix[3]arenes based on Suzuki–Miyaura coupling was developed. We believe that products **5a–5m**, which have deep cavities and binding sites on peripheral aromatic rings, will contribute to the field of host–guest chemistry. In particular, further studies on products **5e** and **5j** with regard to fluorescence and complexation with various guest molecules are now in progress.

## 3. Experimental

### 3.1. General

Nuclear magnetic resonance (NMR) spectra were taken at 200 or 300 MHz in CDCl$_3$ with chemical shifts being reported as $\delta$ ppm from tetramethylsilane as an internal standard and couplings are expressed in hertz. Preparative TLC was carried out with silica gel 60 F$_{254}$ plates (Merck).

### 3.2. Phenylhexahomotrioxacalix[3]arene 2

A mixture of **1**[2a] (50.0 mg, 0.083 mmol), phenylboric acid (15.3 mg, 0.125 mmol), 2-(di-*tert*-butylphosphino)biphenyl (3.0 mg, 0.008 mmol), and KF (14.6 mg, 0.25 mmol) was heated with a heat gun under vacuum and flushed with argon. A solution of palladium acetate (1.0 mg, 0.004 mmol) in dry THF (1 ml) was added to the mixture and stirred overnight at 50 °C. To the reaction mixture, 0.1 N aqueous hydrochloric acid and EtOAc were added. The organic layer was separated, and washed successively with water, aqueous sodium carbonate solution, and brine. After being dried over sodium sulfate, the solvent was evaporated in vacuo. The residue was purified by PTLC to furnish pure **2** (25.4 mg) in 51% yield. Mp=118–120 °C; IR (KBr) 3348, 2957, 1611, 1486, 1361 cm$^{-1}$; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 1.25 (s, 18H), 4.74 (s, 4H), 4.75 (s, 4H), 4.76 (s, 4H), 7.14 (s, 4H), 7.20–7.50 (m, 5H), 7.35 (s, 2H), 8.58 (s, 2H), 8.87 (s, 1H); HRMS (EI$^+$) calcd for $C_{38}H_{44}O_6$ (M$^+$): 596.3138. Found: 596.3145. Anal. Calcd for $C_{38}H_{44}O_6 \cdot 0.5H_2O$: C, 75.34; H, 7.49. Found: C, 75.03; H, 7.37.

### 3.3. MEM-protected hexahomotrioxacalix[3]arene 4

To a solution of **3**[7] (33.9 mg, 0.053 mmol) in THF (3 ml) were added sodium hydride (28.3 mg, 0.71 mmol, 60% oil dispersion in mineral oil) and 2-methoxyethoxymethyl chloride (60 μl, 0.53 mmol), and the mixture was stirred for 5 h at room temperature. Aqueous ammonium chloride solution and EtOAc were added to the reaction mixture. The organic layer was separated, and washed successively with water, sodium hydrogen carbonate solution, and brine. After being dried over sodium sulfate, the solvent was evaporated in vacuo. The residue was purified by PTLC (hexane/EtOAc=2/3) to give **4** as a colorless oil (29.9 mg, 63%

yield). IR (film) 2876, 1579, 1454, 1361, 1200 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 3.17–3.20 (m, 2H), 3.32–3.36 (m, 2H), 3.36 (s, 9H), 3.46–3.51 (m, 4H), 3.67–3.72 (m, 4H), 4.17 (s, 2H), 4.19 (d, $J$=10.3 Hz, 2H), 4.20 (d, $J$=12.8 Hz, 2H), 4.32 (d, $J$=11.2 Hz, 2H), 4.39 (d, $J$=11.4 Hz, 2H), 4.62 (d, $J$=11.2 Hz, 2H), 4.68 (d, $J$=11.2 Hz, 2H), 4.85 (s, 4H), 7.37 (d, $J$=2.4 Hz, 2H), 7.41 (d, $J$=2.4 Hz, 2H), 7.47 (s, 2H); HRMS (FAB$^+$) calcd for $C_{36}H_{45}O_{12}{}^{79}Br_3Na$ (M+Na$^+$): 929.0359. Found: 929.0380, calcd for $C_{36}H_{45}O_{12}{}^{79}Br_2{}^{81}BrNa$ (M+Na$^+$): 931.1034. Found: 931.0357, calcd for $C_{36}H_{45}O_{12}{}^{79}Br^{81}Br_2Na$ (M+Na$^+$): 933.0318. Found: 933.0338, calcd for $C_{36}H_{45}O_{12}{}^{81}Br_3Na$ (M+Na$^+$): 935.0298. Found: 935.0320. Anal. Calcd for $C_{36}H_{45}O_{12}Br_3\cdot H_2O$: C, 46.62; H, 5.11. Found: C, 46.37; H, 4.83.

### 3.4. Procedure A for the synthesis of compounds 5a–5d

The synthesis of **5a** is typical. A solution of **4** (35.3 mg, 0.039 mmol), phenylboric acid (47.3 mg, 0.388 mmol), 2-(di-*tert*-butylphosphino)biphenyl (1.7 mg, 0.008 mmol), palladium acetate (0.9 mg, 0.004 mmol) in degassed toluene (2 ml), and 2 M aqueous sodium carbonate (0.23 ml) was stirred for 2 days at room temperature under an Ar atmosphere. Water and EtOAc were added to the reaction mixture. The organic layer was separated, and washed successively with 0.1 N aqueous hydrochloric acid, water (twice), and brine. After being dried over sodium sulfate, the solvent was evaporated in vacuo. The residue was dissolved in EtOAc (10 ml) and 4 N hydrogen chloride in EtOAc (0.5 ml) was added to the solution and stirred overnight. The reaction mixture was poured into a mixture of ethyl acetate and water. The organic layer was separated, washed successively with water (twice) and brine, dried over $Na_2SO_4$, and evaporated in vacuo to give a pale yellow viscous oil. The residue was purified by PTLC ($CHCl_3$/hexane=3/1) to furnish pure **5a** (19.0 mg) in 77% yield.

**3.4.1. Hexahomotrioxacalix[3]arene 5a.** Known.[9]

**3.4.2. Hexahomotrioxacalix[3]arene 5b.** Mp=229–231 °C; IR (KBr) 3361, 1611, 1479, 1361, 1193 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 2.37 (s, 9H), 4.81 (s, 12H), 7.20 (d, $J$=8.2 Hz, 6H), 7.35 (s, 6H), 7.39 (d, $J$=8.2 Hz, 6H), 8.83 (s, 3H); HRMS (FAB$^+$) calcd for $C_{45}H_{42}O_6$ (M$^+$): 678.2981. Found: 678.2989. Anal. Calcd for $C_{45}H_{42}O_6\cdot 0.5H_2O$: C, 78.58; H, 6.30. Found: C, 78.37; H, 6.24.

**3.4.3. Hexahomotrioxacalix[3]arene 5c.** Mp=134–136 °C; IR (KBr) 3347, 1609, 1519, 1360, 1181 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 3.83 (s, 9H), 4.80 (s, 12H), 6.93 (d, $J$=8.8 Hz, 6H), 7.32 (s, 6H), 7.42 (d, $J$=8.4 Hz, 6H), 8.81 (s, 3H); HRMS (FAB$^+$) calcd for $C_{45}H_{42}O_9$ (M$^+$): 726.2829. Found: 726.2834. Anal. Calcd for $C_{45}H_{42}O_6\cdot 0.5H_2O$: C, 73.45; H, 5.89. Found: C, 73.09; H, 5.84.

**3.4.4. Hexahomotrioxacalix[3]arene 5d.** Mp=137–139 °C; IR (KBr) 3342, 1605, 1481, 1361, 1223 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.81 (s, 12H), 7.03–7.12 (m, 6H), 7.31 (s, 6H), 7.39–7.47 (m, 6H), 8.84 (s, 3H); HRMS (FAB$^+$) calcd for $C_{42}H_{33}F_3O_6$ (M$^+$): 690.2229. Found: 690.2219. Anal. Calcd for $C_{42}H_{33}F_3O_6\cdot H_2O$: C, 71.18; H, 4.98. Found: C, 71.37; H, 4.82.

### 3.5. Procedure B for the synthesis of compounds 5e–5m

The synthesis of **5e** is typical. A solution of **4** (57.6 mg, 0.063 mmol), 2-cyanophenylboric acid (93.1 mg, 0.63 mmol), $Pd(PPh_3)_4$ (14.6 mg, 0.013 mmol), and 2 M aqueous sodium carbonate (0.38 ml) in toluene (2 ml) and methanol (2 ml) was stirred for 17 h at 80 °C under an Ar atmosphere. Water and EtOAc were added to the reaction mixture. The organic layer was separated, and washed successively with 0.1 N aqueous hydrochloric acid, water (twice), and brine. After being dried over sodium sulfate, the solvent was evaporated in vacuo. The residue was dissolved in EtOAc (10 ml) and 4 N hydrogen chloride in EtOAc (0.5 ml) was added to the solution and stirred overnight. The reaction mixture was poured into a mixture of ethyl acetate and water. The organic layer was separated, washed successively with water (twice) and brine, dried over $Na_2SO_4$, and evaporated in vacuo to give a pale yellow viscous oil. The residue was purified by PTLC ($CHCl_3$/EtOAc=20/1) to furnish pure **5e** (16.3 mg).

**3.5.1. Hexahomotrioxacalix[3]arene 5e.** Mp=145–148 °C; IR (KBr) 3340, 2223, 1612, 1473, 1362 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.83 (s, 12H), 7.36 (s, 6H), 7.36–7.45 (m, 6H), 7.56–7.63 (m, 3H), 7.72 (d, $J$=7.6 Hz, 3H), 9.01 (s, 3H); HRMS (FAB$^+$) calcd for $C_{45}H_{34}N_3O_6$ (M+H$^+$): 712.2447. Found: 712.2444. Anal. Calcd for $C_{45}H_{33}N_3O_6\cdot 0.5CHCl_3$: C, 70.84; H, 4.38; N, 5.45. Found: C, 70.84; H, 4.69; N, 5.11.

**3.5.2. Hexahomotrioxacalix[3]arene 5f.** Mp=157–159 °C; IR (KBr) 3340, 1696, 1602, 1480, 1388 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.85 (s, 12H), 7.45 (s, 6H), 7.87 (d, $J$=8.0 Hz, 6H), 7.92 (d, $J$=8.0 Hz, 6H), 8.95 (s, 3H), 10.03 (s, 3H); HRMS (FAB$^+$) calcd for $C_{45}H_{36}O_9$ (M$^+$): 720.2359. Found: 720.2347. Anal. Calcd for $C_{45}H_{36}O_9\cdot 1/3CHCl_3$: C, 71.59; H, 4.82. Found: C, 71.91; H, 5.04.

**3.5.3. Hexahomotrioxacalix[3]arene 5g.** Mp=236–238 °C; IR (KBr) 3340, 1595, 1514, 1476, 1343 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.86 (s, 12H), 7.44 (s, 6H), 7.65 (d, $J$=8.6 Hz, 6H), 8.27 (d, $J$=8.6 Hz, 6H), 8.97 (s, 3H); HRMS (FAB$^+$) calcd for $C_{42}H_{33}N_3O_{12}Na$ (M+Na$^+$): 794.1962. Found: 794.1944. Anal. Calcd for $C_{42}H_{33}N_3O_{12}\cdot CHCl_3$: C, 57.96; H, 3.85; N, 4.72. Found: C, 57.75; H, 3.89; N, 4.54.

**3.5.4. Hexahomotrioxacalix[3]arene 5h.** Mp=115–117 °C; IR (KBr) 3351, 1601, 1478, 1360, 1243 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.77 (s, 9H), 4.79 (s, 12H), 6.92–7.01 (m, 6H), 7.20–7.31 (m, 6H), 7.30 (s, 6H), 8.90 (s, 3H); HRMS (FAB$^+$) calcd for $C_{45}H_{42}O_9$ (M$^+$): 726.2829. Found: 726.2818. Anal. Calcd for $C_{45}H_{42}O_9\cdot 1.5H_2O$: C, 71.70; H, 6.02. Found: C, 72.09; H, 5.74.

**3.5.5. Hexahomotrioxacalix[3]arene 5i.** Mp=138–141 °C; IR (KBr) 3363, 1608, 1480, 1361, 1204 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.78 (s, 12H), 5.13 (s, 3H), 6.91–6.98 (m, 6H), 7.12–7.25 (m, 6H), 7.25 (s, 6H), 8.92 (s, 3H); HRMS (FAB$^+$) calcd for $C_{42}H_{36}O_9$ (M$^+$): 684.2360.

Found: 684.2371. Anal. Calcd for $C_{42}H_{36}O_9 \cdot 0.5CHCl_3$: C, 68.57; H, 4.94. Found: C, 68.86; H, 5.27.

**3.5.6. Hexahomotrioxacalix[3]arene 5j.** Mp=103–106 °C; IR (KBr) 3343, 1728, 1612, 1473, 1364 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.07 (t, *J*=7.0 Hz, 9H), 4.11 (q, *J*=7.0 Hz, 6H), 4.76 (s, 12H), 7.11 (s, 6H), 7.26–7.48 (m, 9H), 7.78 (d, *J*=7.4 Hz, 3H), 8.86 (s, 3H); HRMS (FAB$^+$) calcd for $C_{51}H_{48}O_{12}$ (M$^+$): 852.3146. Found: 852.3158. Anal. Calcd for $C_{51}H_{48}O_{12} \cdot 0.5H_2O$: C, 71.07; H, 5.73. Found: C, 71.15; H, 5.72.

**3.5.7. Hexahomotrioxacalix[3]arene 5k.** Mp=154–156 °C; IR (KBr) 3345, 1665, 1580, 1521, 1447 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.99 (s, 9H), 4.81 (s, 12H), 7.00 (s, 3H), 7.17 (br s, 12H), 7.30–7.40 (m, 3H), 8.24 (d, *J*=7.6 Hz, 3H), 8.96 (s, 3H); HRMS (FAB$^+$) calcd for $C_{48}H_{46}N_3O_9$ (M+H$^+$): 808.3234. Found: 808.3223. Anal. Calcd for $C_{48}H_{45}N_3O_9 \cdot 1/3CHCl_3$: C, 68.48; H, 5.39; N, 4.96. Found: C, 68.84; H, 5.57; N, 5.04.

**3.5.8. Hexahomotrioxacalix[3]arene 5l.** Mp=135–137 °C; IR (KBr) 3348, 2854, 1612, 1471, 1322 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.85 (s, 12H), 7.29–7.33 (m, 3H), 7.34 (s, 6H), 7.78 (d, *J*=7.6 Hz, 3H), 8.55 (d, *J*=3.8 Hz, 3H), 8.76 (s, 3H), 8.91 (s, 3H); HRMS (FAB$^+$) calcd for $C_{39}H_{34}N_3O_6$ (M+H$^+$): 640.2448. Found: 640.2450. Anal. Calcd for $C_{39}H_{33}N_3O_6 \cdot 0.5CHCl_3$: C, 67.83; H, 4.83; N, 6.01. Found: C, 68.12; H, 5.22; N, 5.86.

**3.5.9. Hexahomotrioxacalix[3]arene 5m.** Mp>300 °C; IR (KBr) 3332, 1600, 1548, 1477, 1317 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.85 (s, 12H), 7.43 (d, *J*=6.2 Hz, 6H), 7.46 (s, 6H), 8.61 (d, *J*=6.2 Hz, 6H), 8.97 (s, 3H); HRMS (FAB$^+$) calcd for $C_{39}H_{34}N_3O_6$ (M+H$^+$): 640.2448. Found: 640.2451. Anal. Calcd for $C_{39}H_{33}N_3O_6 \cdot 1.5H_2O$: C, 70.26; H, 5.44; N, 6.30. Found: C, 70.27; H, 5.32; N, 6.22.

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## Supplementary data

The $^1$H NMR spectra of **2**, **4**, and **5a–5m**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.08.073.

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