

## Synthesis of Calix[4]arenylvinylene and Calix[4]arenylphenylene Oligomers by Stille and Suzuki Cross-Coupling Reactions

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Recent work in our laboratory has focused on the synthesis of bisphenol A copolyethers and copolyesters containing lower-rim bound calix[4]arenes on the main chain.<sup>1</sup> The successful polymerization of upper-rim derivatized calix[4]arenes with terephthaloyl chloride was reported by Blanda and Adou to give two new calixarene-based polyesters.<sup>2</sup> The polymers described by us and Blanda represent the first examples of incorporation of calixarene monomers in polymer backbones because the earlier products were carrying calixarene units as appendages of the main chains.<sup>3</sup> The increasing interest in calixarene-based polymers arises from the potential to develop new materials suitable for the construction of chemical and biochemical sensor devices<sup>4</sup> and membranes for the selective transport of ions.<sup>5</sup> Moreover, other applications may include antioxidants and light stabilizer additives for polymer commodities.<sup>6</sup> It appears that calixarene insertion in a macromolecular system such as a polymer chain may enhance the intrinsic properties of the macrocycle. For instance, the calixarene–bisphenol A copolyether<sup>1</sup> exhibited a 10-fold higher binding affinity for silver ions relative to calix[4]arene tetrapropyl ether.<sup>1b</sup> Given the well-known receptor properties of substituted calixarenes toward various cations and some anions,<sup>7</sup> the effects calixarene incorporation into polymer chains may have on such properties now become of interest.

We have explored synthetic approaches to other calixarene-based polymers and report here the synthesis of oligomers in which 1,3-(distal)calix[4]arenes are linked to 1,2-vinylene and *p*-phenylene units by a single carbon–carbon bond merging from the upper rim of the macrocycle. The main structural unit in these products is

similar to that occurring in poly(phenylenevinylene) (PPV) and poly(paraphenylene) (PPP) polymers, two classes of extensively conjugated systems that are receiving considerable attention as promising materials for the construction of electronic and optoelectronic devices, such as light-emitting diodes (LED).<sup>8</sup>

Syntheses of PPV and PPP polymers and analogues have been reported by various carbon–carbon bond-forming reactions including the palladium-catalyzed cross-coupling of aryl halides with bis-stannylethylenes (Stille reaction),<sup>9,10</sup> aryl bis-boronic acids (Suzuki reaction),<sup>11,12</sup> and divinylbenzenes (Heck reaction).<sup>13,14</sup> For the application of these reactions in our polymerization studies, the 1,3-dihalocalix[4]arene derivatives **2** (R = Br) and **3** (R = I) were prepared by regioselective halogenation of the known<sup>15</sup> calix[4]arene dipropyl ether **1**. The bromination of **1** proceeded readily under the same conditions described for the dimethyl ether analog<sup>16</sup> to give the 1,3-dibromo upper-rim substituted calix[4]arene **2** in very high yield. On the other hand, a lower yield of pure diiodo derivative **3** was obtained by the use of benzyltrimethylammonium dichloroiodate<sup>17</sup> (BTMAICl<sub>2</sub>) as iodinating agent.<sup>18</sup> Both compounds **2** and **3** were characterized as being in the cone conformation at room temperature by the presence of two doublets ( $J \approx 13$  Hz) in their <sup>1</sup>H NMR spectra for the bridging methylenes at  $\delta \sim 3.3$  and 4.2.<sup>19</sup>

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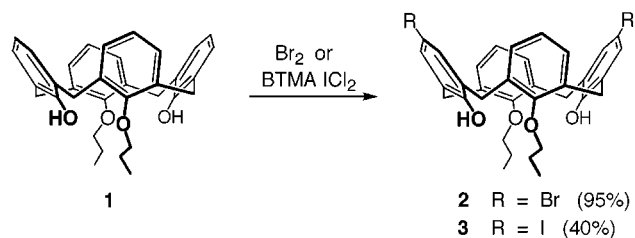
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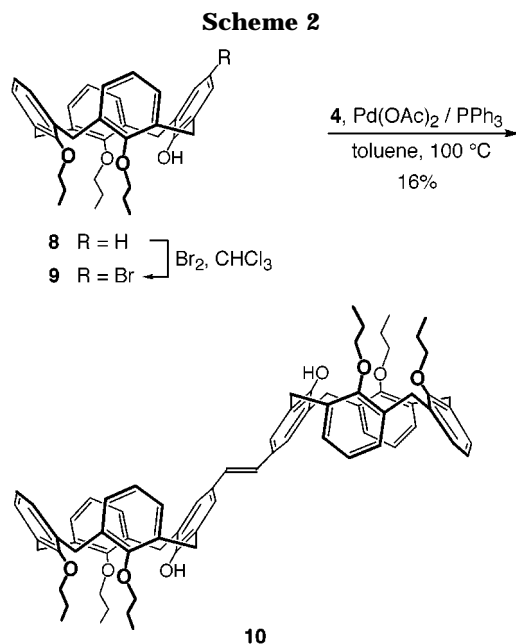
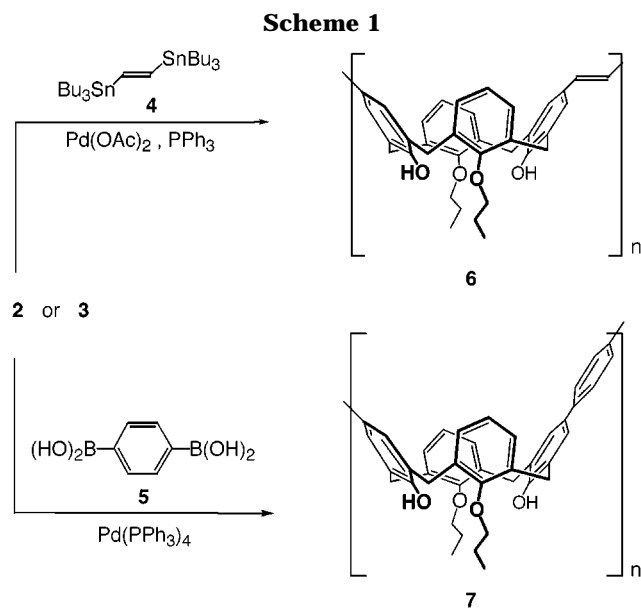
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Both calixarene monomers **2** and **3** were first reacted<sup>20</sup> with (*E*)-1,2-bis(tributylstannyl)ethylene (**4**) under the conditions of the Stille cross-coupling reaction<sup>10d</sup> [Pd(OAc)<sub>2</sub> with 4-fold PPh<sub>3</sub>, toluene, 100 °C] (Scheme 1). Both monomers were used in equimolar amounts, while the palladium salt was 4 mol %. After the complete consumption of the reagents (5 days, TLC analysis), the product **6** was isolated by evaporation of the solvent and purified by trituration with boiling *n*-hexane. Comparable yields of isolated **6** were obtained starting from either the dibromo monomer **2** (52%) or the diiodo derivative **3** (64%). The use of equimolar amounts of palladium salt,<sup>21</sup> higher reaction temperature (140 °C in cumene), and longer reaction time (14 days) gave similar results. It was established by GPC analysis (THF, 45 °C, refractive index detection) that the product **6** is a mixture of calix[4]arenylvinylene oligomers with an average molecular weight (*M<sub>w</sub>*) ranging between 1740 and 1030 and a polydispersity (*M<sub>w</sub>*/*M<sub>n</sub>*) between 1.3 and 1.2 depending on whether the starting calixarene monomer was **2** or **3**. However, the GPC analysis under different conditions (CHCl<sub>3</sub>, 35 °C, UV detection) gave for the oligomer **6** prepared from **2** a *M<sub>w</sub>* value of 2040. The calibration of the molecular weights was obtained by comparison of the MALDI-TOF mass spectrum of **6** with its GPC chromatograms. The mass spectrum of **6** showed the presence of a main product with molecular weight ranging from 2268 to 2370, corresponding to a tetramer with different chain ends. Thus, we estimated calibration factors of ca. 1.3 and 1.1 relative to the molecular weights determined by GPC analysis in THF and CHCl<sub>3</sub>, respectively. We assumed that these calibration factors were also valid for the overall GPC data obtained from the other oligomers.

Although the <sup>1</sup>H NMR spectrum of **6** was rather complex due to the presence of the various oligomers, the cone conformation of the calixarene moieties was safely established from the presence of signals for the bridging methylenes similar to those of the monomers **2** and **3**. On the other hand, the *trans* olefinic linkage was assigned in analogy with the results of the 2-fold Stille cross-coupling polymerization of the bis-stannylethylene **4** with diiodoarenes.<sup>10d</sup> These assignments were confirmed by considering the structure of the 1,2-bis(calix[4]arene) ethylene **10** that was obtained, although in low



yield (16%),<sup>22</sup> by the Stille cross-coupling reaction of **4** with the upper-rim monobromocalix[4]arene tripropyl ether **9** (Scheme 2). The *C*<sub>2</sub>-symmetrical compound **10** showed a well resolved first-order <sup>1</sup>H NMR spectrum with a single set of signals for both the calixarene and vinyl protons. Similar to *trans*-stilbene, a sharp signal corresponding to the vinyl protons appeared at 7.04 ppm. Moreover, the cone conformation was substantiated by the characteristic chemical shift ( $\delta = 3.22, 3.35$  and  $4.40, 4.46$ ) and coupling constant values ( $J \approx 13$  Hz) of the two types of diastereotopic proton signals of the methylene bridges.

Then we considered the synthesis of polymers having the calixarene units linked through a phenylene moiety by the Suzuki cross-coupling reaction.<sup>13b,c</sup> Unlike the Stille reaction, the palladium-catalyzed coupling of aryl-

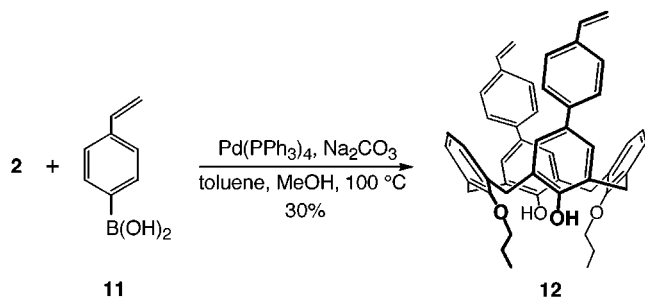
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(22) Pure compound **10** was isolated by chromatography from a complex mixture of side products arising from the 1-fold cross-coupling reaction and the decomposition of **9**. The use of benzene as a solvent gave similar results, while at lower temperature (50 °C) the formation of **10** did not occur.

boronic acids with bromocalixarene derivatives has been recently reported.<sup>23</sup> Thus, the reaction of the 1,3-dibromocalix[4]arene derivative **2** with 1,4-phenylenebis(boronic acid) **5** was carried out under the agency of Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst (Scheme 1). The monomers **2** and **5** and the palladium catalyst were used in equimolar amounts. The reaction afforded the product **7** (61% yield), which constituted a mixture of calix[4]arenyl-phenylene oligomers. The product **7** was purified by trituration with boiling diethyl ether and characterized by GPC (CHCl<sub>3</sub>, 35 °C, UV detection). Since this analysis gave  $M_w = 1580$  and  $M_w/M_n = 1.3$ , the most abundant fraction is constituted of trimers. The <sup>1</sup>H NMR spectrum showed the same signals for the methylene bridges as described above for **6** and **9**. Therefore, it was concluded that the calix[4]arene moieties in this material are also in the cone conformation.

As a second approach, we considered the Heck reaction<sup>15</sup> of the calixarene **2** with *p*-divinylbenzene in the presence of palladium catalyst and a base. No product from this cross-coupling reaction was obtained despite several attempts under different conditions.<sup>24</sup> Therefore, the calixarene **12** was designed as monomer for the 2-fold Heck reaction with a *p*-dihalobenzene. It was hoped that some reactivity would appear because the vinyl group was not directly linked to the upper rim of the macrocycle. Compound **12** was prepared in quite good yield by the Suzuki-type cross-coupling of **2** with the arylboronic acid **11** and adequately characterized by <sup>1</sup>H NMR spectroscopy. Unfortunately, the attempted Heck reaction of **11** with *p*-diiodobenzene likewise did not produce any extended coupling product.



The receptor properties toward silver ions of the oligomer **6**, 1,2-bis(calix[4]arene) ethylene **10**, and calix[4]arene *O*-tetrapropyl ether were investigated by <sup>1</sup>H NMR titration experiments as described by Shinkai and co-workers.<sup>25</sup> The relevant association constant values ( $K_{\text{assoc}}$ ) obtained from nonlinear least-squares computation<sup>26</sup> of the titration curves were the same for the three compounds (ca. 100 M<sup>-1</sup>). This value is lower than that reported by Shinkai for calix[4]arene *O*-tetrapropyl ether.<sup>25</sup> Thus, enhancement of binding properties arising from the calixarene insertion in polymeric chains is not realized in these oligomers as anticipated. Very likely,

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(24) Pd catalyst (from 4 to 100 mol %): Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(OAc)<sub>2</sub>/PPh<sub>3</sub>, Pd(OAc)<sub>2</sub>/dppe, Pd(OAc)<sub>2</sub>/P(*o*-tol)<sub>3</sub>. Solvent: DMF, pyridine, toluene. Base: NEt<sub>3</sub>, NEt(*i*-Pr)<sub>2</sub>, pyridine. Temperature and time: 80–110 °C, from 3 days to 2 weeks.

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this may be ascribed both to the modest length and high rigidity of the calix[4]arenylvinylene and phenylene oligomeric chains.

## Experimental Section

All moisture-sensitive reactions were performed under a nitrogen atmosphere using oven-dried glassware. All solvents were dried over standard drying agents<sup>27</sup> and freshly distilled prior to use. Flash column chromatography<sup>28</sup> was performed on silica gel 60 (230–400 mesh). Reactions were monitored by TLC on silica gel 60 F<sub>254</sub> with detection by charring with sulfuric acid. Melting points were determined with a Mettler DSC 820 differential scanning calorimeter. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75 MHz) NMR were recorded at rt for CDCl<sub>3</sub> solutions, unless otherwise specified. Assignments were aided by homo- and heteronuclear two-dimensional experiments. MALDI-TOF mass spectra were acquired using 2,6-dihydroxybenzoic acid or 3,5-dimethoxy-4-hydroxycinnamic acid as the matrix. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) both in CHCl<sub>3</sub> at 35 °C and in THF at 45 °C (flow rate = 0.8 mL/min, sample concentration ranging from 0.1 to 0.5% w/v) using a chromatograph equipped with Waters pump model 515, Waters UV detector model 484, Waters RI detector model 410, and two gel mixed C (5 μm) microcolumns (purchased from Polymer Laboratories). A Pentium personal computer equipped with Millennium 32 software was used for data acquisition and elaboration and microcolumn calibration. The calibration was carried out using at least 10 narrow polydispersity polystyrene standards ranging from 5.8 × 10<sup>2</sup> to 2.0 × 10<sup>6</sup> for the different experimental conditions. Since the elemental analyses of calixarenes are very often uncorrected<sup>29</sup> (found carbon values considerably lower than the calculated ones), the identity and purity of the nonoligomeric new compounds were established by MS and NMR analyses. Tetraakis(triphenylphosphine)palladium<sup>30</sup> and bis-stannyethylene<sup>31</sup> **4** were prepared as described. Known<sup>16</sup> calixarene **1** was prepared as reported for the synthesis of the upper rim tetra-*tert*-butylated analogue.<sup>32</sup>

**5,17-Dibromo-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (2).** To a cooled (0 °C), stirred solution of **1** (1.00 g, 1.97 mmol) in anhydrous CHCl<sub>3</sub> (40 mL) was added a solution of Br<sub>2</sub> (0.20 mL, 3.94 mmol) in anhydrous CHCl<sub>3</sub> (40 mL) during 20 min. The solution was stirred at 0 °C for 1 h and at rt for 1 h and then concentrated to give **2** (1.30 g, 99%) as a white solid: mp 372 °C (from CHCl<sub>3</sub>); <sup>1</sup>H NMR δ 1.24 (t, 6 H, *J* = 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.01–2.12 (m, 4 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.34 and 4.23 (2 d, 8 H, *J* = 13.9 Hz, ArCH<sub>2</sub>Ar), 3.98 (t, 4 H, *J* = 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 6.81 (t, 2 H, *J* = 6.9 Hz, Ar), 6.93 (d, 4 H, *J* = 6.9 Hz, Ar), 7.18 (s, 4 H, Ar), 8.38 (s, 2 H, OH); <sup>13</sup>C NMR δ 10.8 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 23.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.2 (ArCH<sub>2</sub>Ar), 78.4 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 125.5, 129.3, 130.0, 130.7, 132.7, 151.9 (Ar); MALDI-TOF MS for C<sub>34</sub>H<sub>34</sub>Br<sub>2</sub>O<sub>4</sub> (666.46) *m/z* = 689.4 [M<sup>+</sup> + Na], 705.5 [M<sup>+</sup> + K].

**25,27-Dihydroxy-5,17-diiodo-26,28-dipropoxycalix[4]arene (3).** A mixture of **1** (250 mg, 0.49 mmol), benzyltrimethylammonium dichloroiodate (383 mg, 1.10 mmol), sodium hydrogencarbonate (200 mg, 2.38 mmol), anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and anhydrous CH<sub>3</sub>OH (2 mL) was stirred at rt for 7 h and then diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and filtered. The solution was washed with 10% aqueous NaHCO<sub>3</sub> (10 mL), water (10 mL), 10% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 mL), and water (10 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The residue was triturated at rt

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with  $\text{CH}_2\text{Cl}_2$  (2 mL) and then 2-butanone (2 mL) to give **3** (150 mg, 40%) as a yellow solid. An analytical sample was obtained by column chromatography on silica gel (3:2 cyclohexane- $\text{CH}_2\text{Cl}_2$ ): mp 360 °C;  $^1\text{H NMR}$   $\delta$  1.30 (t, 6 H,  $J = 6.9$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 2.02–2.10 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.32 and 4.24 (2 d, 8 H,  $J = 13.4$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.97 (t, 4 H,  $J = 6.9$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 6.82 (t, 2 H,  $J = 7.0$  Hz, Ar), 6.93 (d, 4 H,  $J = 7.0$  Hz, Ar), 7.37 (s, 4 H, Ar), 8.43 (s, 2 H, OH);  $^{13}\text{C NMR}$   $\delta$  10.9 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 23.5 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 31.0 ( $\text{ArCH}_2\text{Ar}$ ), 78.5 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 125.5, 129.3, 130.7, 132.7, 136.7 (Ar); MALDI-TOF MS for  $\text{C}_{34}\text{H}_{34}\text{I}_2\text{O}_4$  (760.45)  $m/z = 783.7$  [ $\text{M}^+ + \text{Na}$ ], 799.6 [ $\text{M}^+ + \text{K}$ ].

**1,4-Phenylenebis(boronic acid) (5).** To a stirred solution of butyllithium (2.1 mL of a ca. 2.5 M solution in hexane, ca. 5.8 mmol) in anhydrous  $\text{Et}_2\text{O}$  (5 mL) was added dropwise a solution of 1,4-dibromobenzene (0.50 g, 2.12 mmol) in anhydrous  $\text{Et}_2\text{O}$  (5 mL). The suspension was stirred at rt for 2.5 h and then cooled at  $-70$  °C and treated with trimethyl borate (2.19 g, 21.11 mmol). The mixture was stirred at rt for 5 h and then diluted with  $\text{Et}_2\text{O}$  (20 mL), washed with 1 M HCl (10 mL) and water (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated to give **5** (0.22 g, 63%) as a white solid: mp  $>300$  °C (from  $\text{Et}_2\text{O}$ );  $^1\text{H NMR}$  ( $\text{D}_2\text{O} + \text{NaOH}$ )  $\delta$  7.25 (s, 4 H, Ar). The NMR spectra in  $\text{CDCl}_3$  and the elemental analysis indicated that **5** was a mixture of anhydride and acid derivatives. These findings have already been reported for other arylboronic acids.<sup>12b</sup>

The compound **5** was heated at 100 °C for 2 h in neat 1,2-ethanediol (10 equiv) and then concentrated. The solid residue was triturated with  $\text{Et}_2\text{O}$  and then sublimated (150 °C, 0.05 mbar) to give pure bisethylene 1,4-phenylenebisboronate: mp 225–227 °C (in closed vial);  $^1\text{H NMR}$   $\delta$  4.40 (s, 8 H, 4  $\text{CH}_2$ ), 7.83 (s, 4 H, Ph);  $^{13}\text{C NMR}$   $\delta$  66.1 (4  $\text{CH}_2$ ), 130.5 (2 CB), 134.0 (4 CH). Anal. Calcd for  $\text{C}_{10}\text{H}_{12}\text{B}_2\text{O}_4$ : C, 55.14; H, 5.55. Found: C, 55.29; H, 5.60.

**Oligomer 6.** A mixture of calixarene **2** (300 mg, 0.45 mmol), triphenylphosphine (42 mg, 0.16 mmol), palladium(II) acetate (6 mg, 0.03 mmol), (*E*)-1,2-bis(tributylstannyl)ethylene (**4**, 272 mg, 0.45 mmol), and anhydrous toluene (25 mL) was stirred at 100 °C for 5 days in a nitrogen atmosphere and then cooled to rt, diluted with  $\text{CH}_2\text{Cl}_2$  (20 mL), washed with water (3  $\times$  20 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was triturated with boiling *n*-hexane (3  $\times$  5 mL) to give **6** (156 mg, 52 wt %) as a brown solid:  $^1\text{H NMR}$   $\delta$  1.22–1.42 (m, 6 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.98–2.18 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.28–3.43 and 4.23–4.38 (m, 8 H,  $\text{ArCH}_2\text{Ar}$ ), 3.88–4.02 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 6.62–7.72 (m, 12 H, Ar and  $\text{CH}=\text{CH}$ ), 8.21–8.42 (m, 2 H, OH);  $^{13}\text{C NMR}$   $\delta$  10.8 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 23.5 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 31.1–31.6 ( $\text{ArCH}_2\text{Ar}$ ), 78.4–78.6 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 125.2–133.4 (Ar and  $\text{CH}=\text{CH}$ ), 151.8–151.9 (Ar). Similar results were obtained using **3** instead of **2** as starting material.

**Oligomer 7.** A mixture of calixarene **2** (150 mg, 0.23 mmol), 1,4-phenylenebis(boronic acid) (**5**, 38 mg, 0.23 mmol), tetrakis(triphenylphosphine)palladium(0) (173 mg, 0.15 mmol), anhydrous toluene (5 mL), and anhydrous  $\text{CH}_3\text{OH}$  (0.5 mL) was stirred at 100 °C for 15 min and then treated with 2 M aqueous  $\text{Na}_2\text{CO}_3$  (1 mL). The suspension was stirred at 100 °C for 3 days, cooled to rt, diluted with  $\text{CH}_2\text{Cl}_2$  (10 mL), washed with water (10 mL), 1 M HCl (10 mL), and water (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was triturated with boiling  $\text{Et}_2\text{O}$  (3  $\times$  5 mL) to give **7** (91 mg, 61 wt %) as a brown solid:  $^1\text{H NMR}$   $\delta$  1.18–1.38 (m, 6 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.98–2.15 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.28–3.47 and 4.21–4.41 (m, 8 H,  $\text{ArCH}_2\text{Ar}$ ), 3.90–4.06 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 6.70–7.90 (m, 20 H, Ar and OH);  $^{13}\text{C NMR}$   $\delta$  10.9 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 23.5 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 31.2–31.7 ( $\text{ArCH}_2\text{Ar}$ ), 78.4 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 126.8–135.5 (Ar).

**25-Hydroxy-26,27,28-tripropoxycalix[4]arene (8).** To a stirred solution of 25,26,27,28-tetrahydroxycalix[4]arene (2.00 g, 4.70 mmol) in anhydrous DMF (40 mL) was added  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (5.20 g, 16.48 mmol),  $\text{BaO}$  (1.10 g, 7.17 mmol), and after 15 min, *n*-propyl iodide (13.8 mL, 141.5 mmol). The mixture was stirred at rt for 6 h, diluted with  $\text{CH}_2\text{Cl}_2$  (100 mL), washed with water (3  $\times$  50 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was eluted from a column of silica gel with 4:1 cyclohexane- $\text{CH}_2\text{Cl}_2$  to give **8** (1.22 g, 47%) as a white solid: mp 101–102 °C;  $^1\text{H NMR}$   $\delta$  0.96 (t, 3 H,  $J = 7.0$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.13 (t, 6 H,  $J = 7.0$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.90–1.93 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 2.24–2.29 (m, 2 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.22 and 4.44 (2 d, 8 H,  $J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.30 and 4.39 (2 d, 8 H,  $J = 13.7$  Hz,

$\text{ArCH}_2\text{Ar}$ ), 3.78 (t, 4 H,  $J = 7.0$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.82 (t, 2 H,  $J = 7.0$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 4.72 (s, 1 H, OH), 6.40 (m, 6 H, Ar), 6.78 (t, 1 H,  $J = 7.0$  Hz, Ar), 6.98 (t, 1 H,  $J = 7.0$  Hz, Ar), 7.11 (d, 2 H,  $J = 7.0$  Hz, Ar), 7.19 (d, 2 H,  $J = 7.0$  Hz, Ar);  $^{13}\text{C NMR}$   $\delta$  9.6 and 10.8 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 22.3 and 23.4 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 30.7 ( $\text{ArCH}_2\text{Ar}$ ), 71.0 and 77.4 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 119.3, 122.9, 127.7, 127.8, 128.4, 129.2, 131.2, 132.6, 133.4, 137.2, 153.3, 154.4, 156.8 (Ar). MALDI-TOF MS for  $\text{C}_{37}\text{H}_{42}\text{O}_4$  (550.74)  $m/z = 573.6$  [ $\text{M}^+ + \text{Na}$ ], 589.9 [ $\text{M}^+ + \text{K}$ ].

**5-Bromo-26,27,28-tripropoxy-calix[4]arene (9).** To a cooled (0 °C), stirred solution of **8** (268 mg, 0.49 mmol) in anhydrous  $\text{CHCl}_3$  (5 mL) was added a solution of  $\text{Br}_2$  (25  $\mu\text{L}$ , 0.49 mmol) in anhydrous  $\text{CHCl}_3$  (5 mL) during 20 min. The solution was stirred at 0 °C for 1 h and at rt for 1 h and then concentrated to give **9** (303 mg, 99%) as a white solid: mp 132–133 °C (from  $\text{CHCl}_3$ );  $^1\text{H NMR}$   $\delta$  0.93 (t, 3 H,  $J = 6.4$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.12 (t, 6 H,  $J = 6.4$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.82–1.92 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 2.20–2.30 (m, 2 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.21 and 4.40 (2 d, 8 H,  $J = 12.5$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.24 and 4.34 (2 d, 8 H,  $J = 12.5$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.72 (t, 4 H,  $J = 6.3$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.82 (t, 2 H,  $J = 6.3$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 4.78 (s, 1 H, OH), 6.35–6.44 (m, 6 H, Ar), 6.98 (t, 1 H,  $J = 7.0$  Hz, Ar), 7.18 (d, 2 H,  $J = 7.0$  Hz, Ar), 7.23 (s, 2 H, Ar);  $^{13}\text{C NMR}$   $\delta$  8.6 and 9.8 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 21.3 and 22.4 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 29.6 and 29.7 ( $\text{ArCH}_2\text{Ar}$ ), 75.6 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 122.2, 126.8, 127.3, 128.2, 129.8, 130.7, 132.2, 132.6, 136.1, 153.4 (Ar); MALDI-TOF MS for  $\text{C}_{37}\text{H}_{41}\text{BrO}_4$  (629.64)  $m/z = 652.5$  [ $\text{M}^+ + \text{Na}$ ], 668.8 [ $\text{M}^+ + \text{K}$ ].

**Bis(25-hydroxy-26,27,28-tripropoxycalix[4]aren-5-yl)-ethylene (10).** A mixture of calixarene **9** (50 mg, 0.08 mmol), triphenylphosphine (8 mg, 0.03 mmol), palladium(II) acetate (~0.1 mg, ~0.3  $\mu\text{mol}$ ), (*E*)-1,2-bis(tributylstannyl)ethylene (**4**, 48 mg, 0.08 mmol), and anhydrous toluene (5 mL) was stirred at 100 °C for 18 h in a nitrogen atmosphere, cooled to rt, diluted with  $\text{CH}_2\text{Cl}_2$  (20 mL), washed with water (3  $\times$  20 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was eluted from a column of silica gel with 3:2 cyclohexane- $\text{CH}_2\text{Cl}_2$  (containing 0.3% of  $\text{Et}_3\text{N}$ ) to give **10** (14 mg, 16%) slightly contaminated by uncharacterized byproducts. An analytical sample was obtained by trituration with *n*-pentane (1 mL) and then  $\text{CH}_3\text{OH}$  (1 mL): mp 227–228 °C;  $^1\text{H NMR}$   $\delta$  0.92 (t, 6 H,  $J = 9.0$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.15 (t, 12 H,  $J = 9.0$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.82–1.98 (m, 8 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 2.22–2.38 (m, 4 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.22 and 4.46 (2 d, 8 H,  $J = 13.5$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.35 and 4.40 (2 d, 8 H,  $J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.70–3.88 (m, 8 H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 3.86 (t, 4 H,  $J = 9.0$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 4.82 (s, 1 H, OH), 6.32–6.49 (m, 12 H, Ar), 6.98 (t, 2 H,  $J = 7.7$  Hz, Ar), 7.04 (s, 2 H,  $\text{CH}=\text{CH}$ ), 7.18 (d, 4 H,  $J = 7.7$  Hz, Ar), 7.30 (s, 4 H, Ar);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  9.9 and 10.9 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 22.8 and 23.7 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 31.3 and 31.5 ( $\text{ArCH}_2\text{Ar}$ ), 76.8 and 77.6 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 123.5, 123.7, 126.9, 128.0, 128.3, 129.1, 129.3, 129.6, 130.2, 131.6, 132.9, 133.9, 137.6, 153.8, 154.9, 157.5 (Ar). MALDI-TOF MS for  $\text{C}_{76}\text{H}_{84}\text{O}_8$  (1125.51)  $m/z = 1126.0$  [ $\text{M}^+ + \text{H}$ ], 1148.6 [ $\text{M}^+ + \text{Na}$ ], 1166.2 [ $\text{M}^+ + \text{K}$ ].

**4-Styrylboronic Acid (11).** To a warmed (40 °C), stirred suspension of magnesium (1.20 g, 49.36 mmol) in anhydrous THF (10 mL) was slowly added a solution of 4-bromostyrene (6.06 g, 33.12 mmol) in anhydrous THF (20 mL). During the addition, the oil bath was removed in order to keep the mixture under a gentle reflux. The suspension was refluxed for 1 h, cooled to  $-78$  °C, and treated with trimethyl borate (4.57 g, 43.95 mmol). The mixture was stirred at rt for 20 min, diluted with  $\text{Et}_2\text{O}$  (100 mL), washed with 1 M HCl (50 mL) and water (50 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was crystallized with  $\text{Et}_2\text{O}$ -hexane to give **11** (3.80 g, 78%) as a white solid: mp 190 °C (dec);  $^1\text{H NMR}$  ( $\text{D}_2\text{O} + \text{NaOH}$ )  $\delta$  4.97 (d, 1 H,  $J = 11.6$  Hz,  $\text{CH}=\text{CH}_2$ ), 5.57 (d, 1 H,  $J = 18.2$  Hz,  $\text{CH}=\text{CH}_2$ ), 6.53 (dd, 1 H,  $J = 11.6$  Hz and  $J = 18.2$  Hz,  $\text{CH}=\text{CH}_2$ ), 7.15 (d, 2 H,  $J = 8.3$  Hz, Ar), 7.28 (d, 2 H,  $J = 8.3$  Hz, Ar). The NMR spectra in  $\text{CDCl}_3$  and the elemental analysis indicated that **11** was a mixture of anhydride and acid derivatives. These findings have been already reported for other arylboronic acids.<sup>12b</sup>

Compound **11** was heated at 100 °C for 10 min in neat 1,2-ethanediol (4 equiv), cooled to rt, diluted with  $\text{CH}_2\text{Cl}_2$ , washed three times with  $\text{H}_2\text{O}$ , dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was distilled using a Kugelrohr apparatus (80 °C, 0.1 mbar) to give pure ethylene 4-styrylboronate:  $^1\text{H NMR}$   $\delta$  4.39

(s, 4 H, 2 CH<sub>2</sub>), 5.31 (d, 1 H, *J* = 11.0 Hz, CH<sub>2</sub>=), 5.83 (d, 1 H, *J* = 17.5 Hz, CH<sub>2</sub>=), 6.74 (dd, 1 H, *J* = 11.0, 17.5 Hz, CH=), 7.78 and 7.44 (2 bd, 4 H, *J* = 8.0 Hz, Ph); <sup>13</sup>C NMR δ 65.9 (CH<sub>2</sub>), 115.0 (CH<sub>2</sub>=), 125.6 (2 C-3), 127.0 (C-1), 135.0 (2 C-2), 136.7 (CH=), 140.3 (C-4). Anal. Calcd for C<sub>8</sub>H<sub>9</sub>BO<sub>2</sub>: C, 64.94; H, 6.13. Found: C, 65.18; H, 6.19.

**25,27-Dihydroxy-26,28-dipropoxy-5,17-bis(4-styryl)calix-[4]arene (12).** A mixture of calixarene **2** (250 mg, 0.37 mmol), 4-styrylboronic acid (**11**, 54 mg, 0.37 mmol), tetrakis(triphenylphosphine)palladium(0) (280 mg, 0.25 mmol), anhydrous toluene (2.5 mL), and anhydrous CH<sub>3</sub>OH (1 mL) was stirred at 100 °C for 15 min and then treated with 2 M aqueous Na<sub>2</sub>CO<sub>3</sub> (1 mL). The suspension was stirred at 100 °C for 4 h, cooled to rt, diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), washed with 2 M aqueous Na<sub>2</sub>CO<sub>3</sub> (5 mL) containing 0.5 mL of concentrated NH<sub>3</sub> and then water (10 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The residue was eluted from a column of silica gel with 4:1 CCl<sub>4</sub>-CH<sub>2</sub>Cl<sub>2</sub> (containing 0.3% Et<sub>3</sub>N) to give **12** (80 mg, 30%) as a white solid: mp 239–240 °C; <sup>1</sup>H NMR δ 1.33 (t, 6 H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>-CH<sub>2</sub>), 2.04–2.13 (m, 4 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.46 and 4.38 (2 d, 8 H, *J* = 13.7 Hz, ArCH<sub>2</sub>Ar), 4.02 (t, 4 H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>),

5.25 (d, 2 H, *J* = 11.2 Hz, CH=CH<sub>2</sub>), 5.74 (d, 2 H, *J* = 18.7 Hz, CH=CH<sub>2</sub>), 6.70–6.78 (m, 4 H, CH=CH<sub>2</sub>, Ar), 7.10 (d, 4 H, *J* = 7.3 Hz, Ar), 7.29 (s, 4 H, Ar), 7.46 (q, 8 H, *J* = 8.0 Hz, Ar), 8.52 (s, 2 H, OH); <sup>13</sup>C NMR δ 10.0 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 30.7 (ArCH<sub>2</sub>Ar), 77.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 112.3 (CH=CH<sub>2</sub>), 124.4, 125.5, 126.1, 127.5, 128.2, 132.5, 135.6, 150.9, 152.3 (CH=CH<sub>2</sub>, Ar); MALDI-TOF MS for C<sub>50</sub>H<sub>48</sub>O<sub>4</sub> (712.93) *m/z* = 735.8 [M<sup>+</sup> + Na], 751.9 [M<sup>+</sup> + K].

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**Supporting Information Available:** <sup>1</sup>H NMR spectra of compounds **2**, **3**, **5**, and **8–12** as evidence of the degree of purity and <sup>1</sup>H and <sup>13</sup>C NMR spectra of the cyclic ethylene esters of **5** and **11** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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