Journal of Organometallic Chemistry 695 (2010) 26–31

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis of novel calix[4]arenes containing organosilicon groups

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ARTICLE INFO

Article history:
Received 5 August 2009
Received in revised form 6 September 2009
Accepted 10 September 2009
Available online 17 September 2009

Keywords:
Calixarene
Sterically hindered groups
Vinylsilanes
Organosilicon

ABSTRACT

Metalation of $(RSiMe_2)_3CH$ (**1a** R = H, **1b** R = Me, **1c** R = Ph) with lithium diisopropylamide (LDA) or methyllithium in THF gave organolithium reagents $(RSiMe_2)_3CLi$, which reacted with the formylated calixarene (**2**), to give the corresponding 5,17-bis[2,2-bis(organosilyl)-1-ethenyl]-25,26,27,28-tetrapropoxycalix[4]arenes (**3a, 3b** and **3c**) via the Peterson olefination. The compounds $(RSiMe_2)_3CLi$ were treated with 25,26,27,28-tetrakis(4-bromobutoxy)calix[4]arene (**4**) to give 25,26,27,28-tetrakis[4-(tris(dimethylsilyl)methyl)butoxy] calix[4]arene (**5a**) and 25,26,27,28-tetrakis[4-(tris(trimethylsilyl)methyl)butoxy] calix[4]arene (**5b**) via nucleophilic substitution reactions. However the compound 25,26,27,28-tetrakis[4-(tris(dimethylphenylsilyl)methyl)butoxy] calix[4]arene (**5c**) was not obtained, presumably because $(PhSiMe_2)_3C$- is highly sterically hindered and the reactivity of its derivatives is low. The compound **5a** has potential as a core for dendrimers.

1. Introduction

Calixarenes have been widely used as building blocks in the design and synthesis of new materials for molecular recognition and supramolecular chemistry [1]. Calixarenes bearing organosilicon substituents have potential for the recognition of anionic and nucleophilic substances [2–4], but few such calixarenes have hitherto been reported [4–8].

1,1-Bis(organosilyl)-1-alkenes constitute an important class of organosilicon reagents which are currently widely used as potential intermediates in organic and organometallic synthesis. Their use as precursors for the preparation of ketones, as well as variety of organosilicon intermediates such as acylsilanes, epoxysilanes, 1-halovinylsilanes, silylenolethers, (E)-alkenylsilanes, and silylenolacetates, stimulates interest in their synthetic availability [9–17]. Therefore, the preparation of calixarenes containing the organosilylvinyl substituents is important.

Organosilicon compounds containing bulky groups, such as $(RSiMe_2)_3C$– (**a** R = H, **b** R = Me, **c** R = Ph) have been widely used previously [18–24]. In this work, new calixarenes containing organosilylvinyl substituents at the upper rim and calixarenes bearing bulky organosilicon groups on the lower rim have been prepared. The compound **5a** has 12 Si–H bonds that might be used for the preparation of dendrimers.

2. Results and discussion

The precursor $(HSiMe_2)_3CH$ was made by the reaction of $CHBr_3$ and Mg with $HSiMe_2Cl$ in THF [23,24]. The organolithium reagent $(HSiMe_2)_3CLi$, was obtained by treatment of $(HSiMe_2)_3CH$ with LDA at room temperature [24]. The precursor $(Me_3Si)_3CH$ was prepared from the reaction between $CHCl_3$, Li and Me_3SiCl in THF. The organolithium reagent, $(Me_3Si)_3CLi$ was obtained by treatment of $(Me_3Si)_3CH$ with MeLi under reflux in THF [25]. The precursor $(PhSiMe_2)_3CH$, obtained by the reaction of $PhMe_2SiCl$ with $CHBr_3$ in the presence of *n*-BuLi at −78 °C, was metalated with MeLi under the conditions used for $(Me_3Si)_3CH$ [26] (Scheme 1).

By using the Peterson olefination reaction, synthetically useful 2,2-bis(organosilyl)ethenyl groups can be prepared by the reaction of tri(organosilyl)methylmetals with non-enolizable aromatic aldehydes using a direct addition–elimination process [17,27,28]. The starting point for the synthesis of calixarenes containing 2,2-bis(organosilyl)ethenyl groups was the preparation of 5, 17-diformyl-25,26,27,28-tetrapropoxycalix[4]arene **2**, which was obtained in 75% yield according to Scheme 2 [29].

$(RSiMe_2)_3CLi$ (**1a, 1b** and **1c**) were treated with the non-enolisable formylated calixarene **2**. The Peterson reaction readily takes place on the upper rim of the calixarene skeleton and gives the corresponding 2,2-bis(organosilyl)-1-ethenyl calixarenes.

It has been postulated that when $(RSiMe_2)_3CLi$ is treated with a compound containing a carbonyl group, it initially forms the alkoxide intermediate (**A**), then an intramolecular alkoxide attack takes place and gives **3**. It seems likely that the intermediates A are unstable and swiftly convert into **3** with the elimination of RMe_2SiOLi [27] (Scheme 3).

The yields for **3a**, **3b** and **3c** are 76%, 62% and 45%, respectively. A comparison of the reactivities of **1a**, **1b** and **1c** toward the formylated calixarene shows that the Ph group provides much greater steric hindrance than the Me and H groups, and that the Me group provides greater hindrance than H. The rate of nucleophilic attack on the formyl group decreases with increasing size of R.

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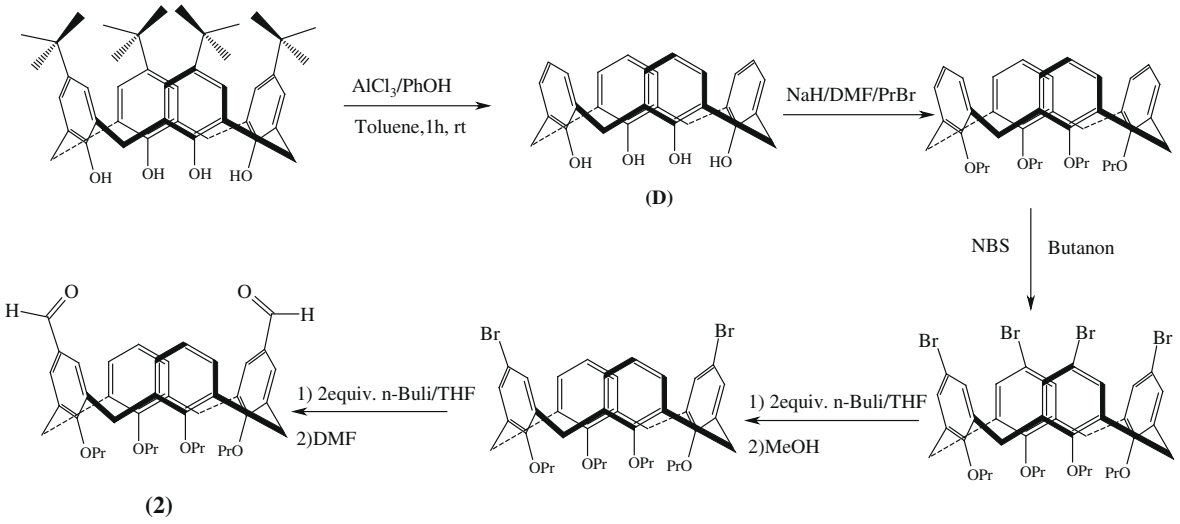
0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.09.021

$$HMe_2SiCl + CHBr_3 + Mg \xrightarrow{THF} (HSiMe_2)_3CH \xrightarrow[12h]{LDA} (HSiMe_2)_3CLi \quad \textbf{(1a)}$$

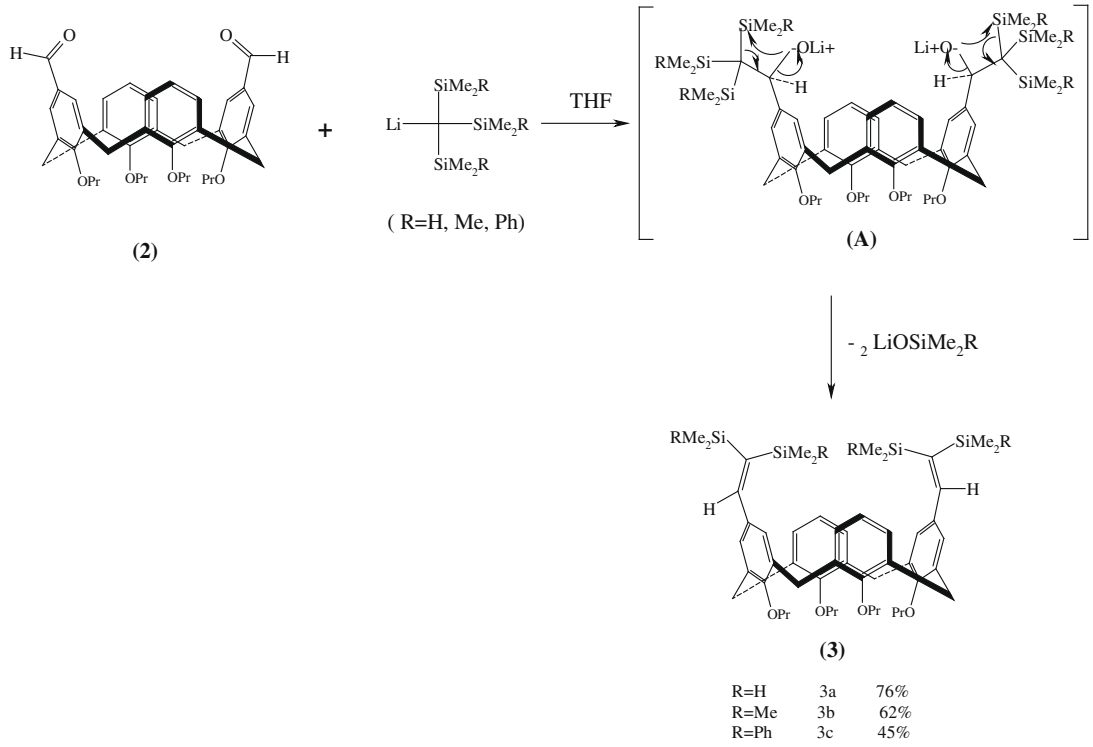
$$Me_3SiCl + CHCl_3 + Li \xrightarrow{THF} (Me_3Si)_3CH \xrightarrow[2h]{MeLi} (Me_3Si)_3CLi \quad \textbf{(1b)}$$

$$PhMe_2SiCl + CHBr_3 + n\text{-}BuLi \xrightarrow{THF} (PhSiMe_2)_3CH \xrightarrow[2h]{MeLi} (PhSiMe_2)_3CLi \quad \textbf{(1c)}$$

Scheme 1. Preparation of organolithium reagents.



Scheme 2. Preparation of the formylated calixarene **2**.



Scheme 3. Synthesis of calixarenes containing bis(organosilyl)ethenyl groups.

The ^{1}H NMR spectra of the calixarene **3a** show the complete disappearance of aldehydic proton resonance at 9.41 ppm and the concomitant appearance of signals assigned to *HC*=C at 7.81 ppm, Si*H* at 4.43–4.41 ppm and –$SiMe_2$ protons at 0.3 and

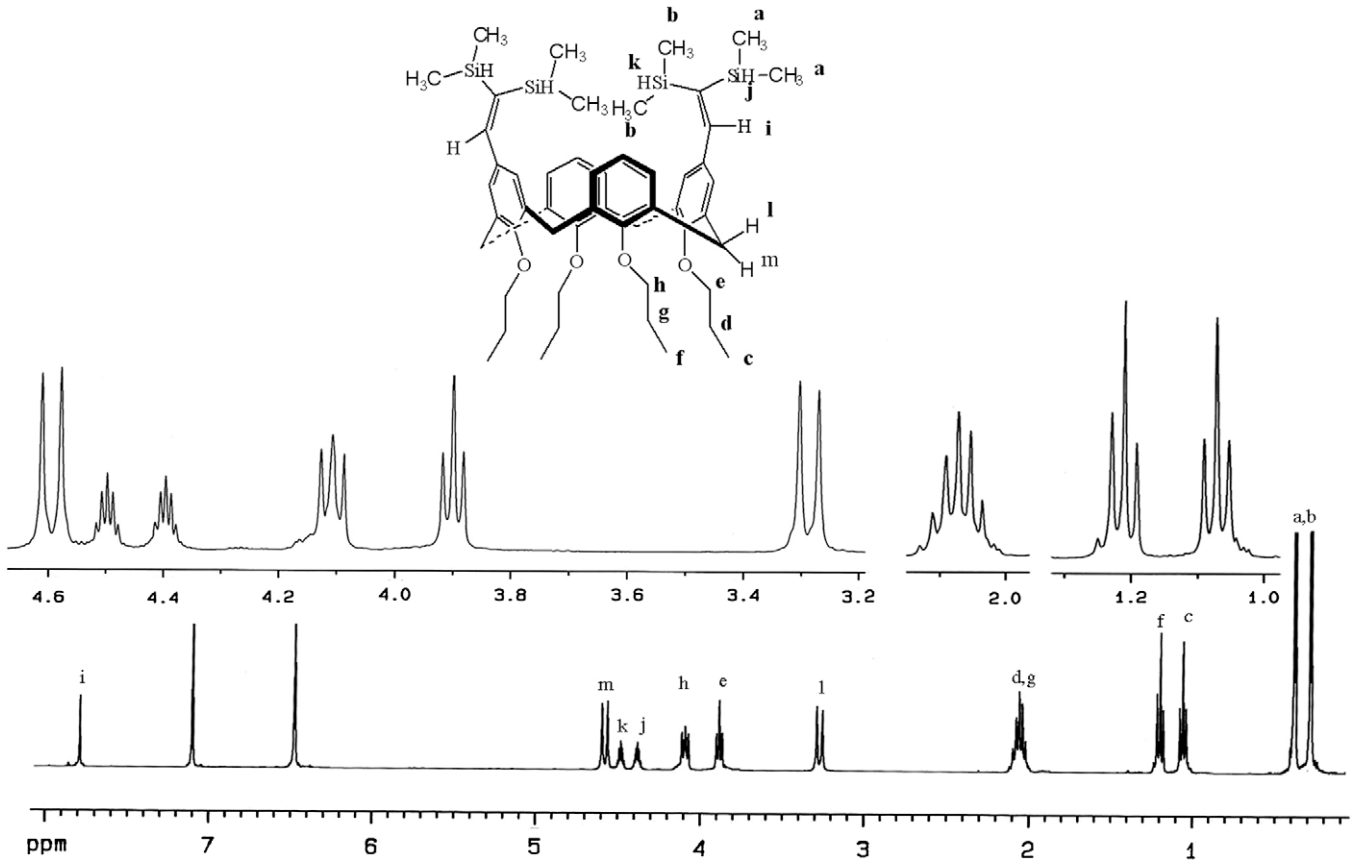


Fig. 1. ^{1}H NMR spectra of **3a**.

0.4 ppm (Fig. 1). Similar results were observed for **3b** and **3c**. In addition the FTIR spectra of the calixarenes **3a**, **3b** and **3c** do not show a sharp peak at 1696 cm^{-1}, indicating the absence of carbonyl groups. In the case of **3a**, there is a band to show the presence of Si–H at ca. 2100 cm^{-1}. According to the NMR spectrum and as expected, calixarenes **3** were in the flattened cone (or pinched cone) conformation [30].

We also investigated the synthesis of calixarenes bearing bulky organosilicon groups on the lower rim. Thus 25,26,27,28-tetrakis(4-bromobutoxy)calix[4]arene (**4**) was synthesized by treatment of the dealkylated calixarene (**D**) with an excess of NaH and 1,4-dibromobutane in DMF (Scheme 4). This symmetrical compound allowed for the incorporation of four sterically hindered groups on the lower rim. Compound **4** was treated with **1a** and **1b** and gave **5a** and **5b** with 82% and 60% yields, respectively. The reaction of **1c** with **4** did not take place under similar conditions or even under reflux for 36 h. All of the spectroscopic results indicated that the nucleophilic substitution on to **4** with **1a** and **1b** was complete.

3. Conclusion

The formylated calixarene **2** is converted to the corresponding 2,2-bis(organosilyl)-1-ethenylcalixarene derivatives in a one-pot procedure involving the addition of $(RSiMe_2)_3CLi$ to the carbonyl group. The calixarenes containing vinylsilane substituents on the upper rim are potential intermediates for the functionalization of calixarenes, which cannot be achieved via other methods. $(RSiMe_2)_3C$-groups (R = H or Me) were attached to the lower rim of the calixarene **4** by nucleophilic substitution with $(RSiMe_2)_3CLi$. It is worth noting that the compound **5a** is a potential core for dendrimers, since it has 12 Si–H bonds that could easily be converted to other functional groups.

4. Experimental

4.1. Solvents and reagents

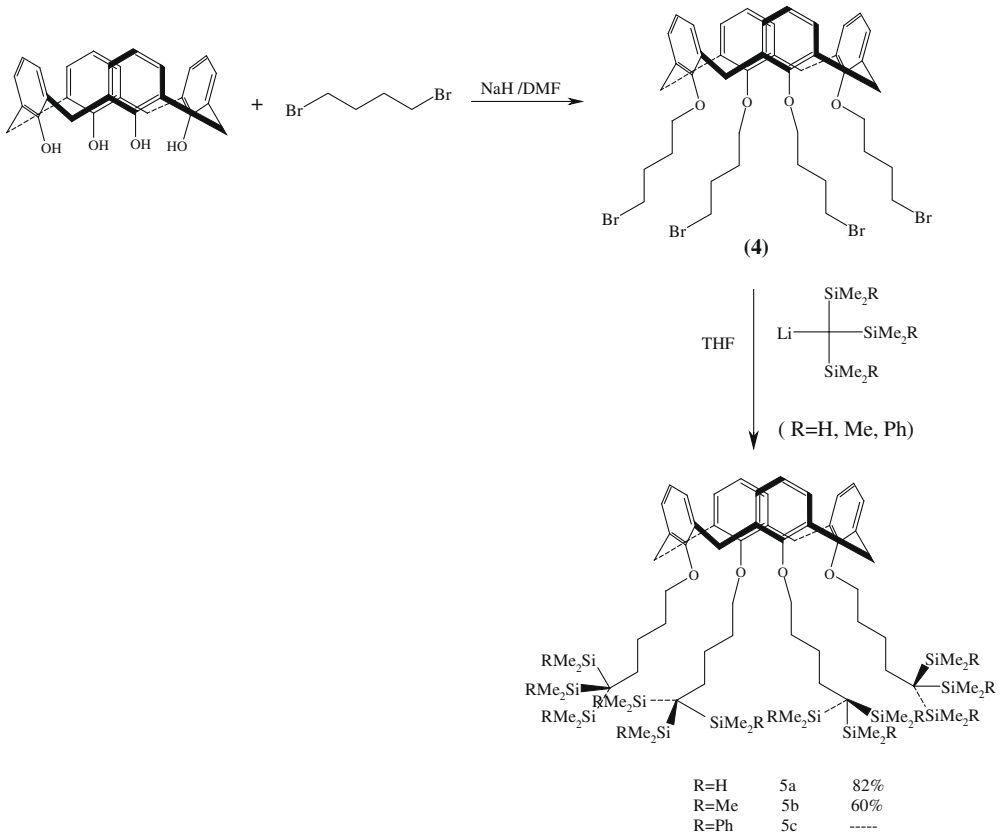
Reactions involving organolithium reagents were carried out under dry argon. Solvents were dried by standard methods. Substrates for preparation of $(RSiMe_2)_3CLi$, viz., $HSiMe_2Cl$, Mg, $CHBr_3$, Me_3SiCl, $CHCl_3$, Li, *n*-BuLi, PhBr, Me_2SiCl_2 and substrates for the preparation of the formylated calixarene, viz., *p-tert*-butylphenol, formaldehyde 35–40%, NaH, DMF, 1-bromopropane, NBS, and 1,4-dibromobutane were purchased from Merck and used without further purification.

4.2. Spectra

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and with $CDCl_3$ as a solvent. The mass spectra were obtained with a MALDI-TOF-PerSeptive Mass Spectrometer. The FTIR spectra were recorded on a Bruker Tensor 270 spectrometer. Elemental analyses were made with a Heareus CHN-ORAPID instrument.

4.3. Preparation of tris(dimethylsilyl)methyllithium, $(HSiMe_2)_3CLi$, solution in THF [24]

A 50 ml round-bottom flask, equipped with a stirrer, septum, and gas-inlet needle was charged with diisopropylamine (0.53 g, 5.3 mmol) and 15 ml of THF. The flask was placed in a water-ice



Scheme 4. Synthesis of **4** and calixarenes **5** bearing bulky organosilicon groups.

bath and then *n*-BuLi (3.8 ml, 1.5 M solution in hexane) was added dropwise via a syringe to give a clear yellow solution. The solution was stirred for an additional 30 min. The lithium diisopropylamide (LDA) solution was transferred into a dropping funnel and added dropwise to a 50 ml round-bottom flask containing tris(dimethylsilyl)methane, $(HSiMe_2)_3CH$, (1 g, 5.3 mmol) in 10 ml THF under argon atmosphere at room temperature. The orange-red solution was stirred at ambient temperature for 10 h.

4.4. Preparation of tris(trimethylsilyl)methyllithium, $(Me_3Si)_3CLi$, in THF

The reagent was prepared as described by Grobel and co-workers [25].

4.5. Preparation of tris(dimethylphenylsilyl)methyllithium, $(PhSiMe_2)_3CLi$, in THF

The method for the preparation of tris(trimethylsilyl)methyllithium was used.

*4.6. Preparation of the formylated calixarene, 5,17-diformyl-25,26,27,28-tetrapropoxycalix[4]arene (**2**)*

This was synthesized according to the literature [29].

*4.7. Preparation of 25,26,27,28-tetrakis(4-bromobutoxy)calix[4]arene (**4**)*

A mixture of 3 g (7 mmol) dealkylated calixarene (**D**) and 2.4 g (60 mmol) NaH (60% in paraffin) in 100 ml of dry DMF was stirred at room temperature for 0.5 h. Subsequently 20 g (92 mmol) of 1,4-dibromobutane was added. The mixture was stirred at room temperature for 24 h. Then DMF was evaporated in vacuum, and the residue was taken up in $CHCl_3$ (200 ml) and the extract was washed with 1 N HCl (2×50 ml) and brine (50 ml), then dried ($MgSO_4$). After filtration the solvent was evaporated, and the residue was subjected to column chromatography (*n*-hexane/ethyl acetate, 4:1, $R_f = 0.80$), to yield **4** (4.00 g, 60 %) as a white solid. m.p. 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.96–2.15 (m, 16H, 4×$CH_2CH_2CH_2CH_2$), 3.2 (d, 4H, $J = 13.4$ Hz, 4×Ar*CH*Ar), 3.5 (t, 8H, $J = 6.3$ Hz, 4×$CH_2CH_2CH_2CH_2O$), 3.9 (t, 8H, $J = 6.9$ Hz, $CH_2CH_2CH_2CH_2Br$), 4.4 (d, 4H, $J = 13.3$ Hz, 4×Ar*CH*Ar), 6.55–6.72 (m, 12H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 27.9, 28.5, 29.8, 32.7, 72.9, 121.2, 127.2, 133.8, 155.0; MALDI-TOF MS *m/z*: $[M+Na]^+ = 987.61$; Anal. Calcd for $C_{44}H_{52}Br_4O_4$ (964.50): C, 54.79; H, 5.43. Found: C, 54.32; H, 5.15%.

*4.8. General procedure for the synthesis of 5,17-bis[2,2-bis(triorganosilyl)-1-ethenyl]-25,26,27,28-tetrapropoxy calix[4]arene (**3**)*

To a stirred solution of **1a**, **1b** or **1c** (5.3 mmol) in THF at room temperature was added formylated calix[4]arene **2** (1 mmol) in 10 ml THF, and the mixture was heated under reflux for 12 h. The mixture was poured into ammonium chloride solution (50 ml) and extracted with CH_2Cl_2 (2 × 50 ml). The organic phase was washed with water (100 ml) and dried (Na_2SO_4), and the solvent was removed in vacuum to yield a cream solid.

*4.8.1. Preparation of 5,17-bis[2,2-bis(dimethylsiyl)-1-ethenyl]-25,26,27,28-tetrapropoxycalix[4]arene (**3a**)*

A white solid 0.66 g (76%) was obtained by preparative TLC (silica gel, *n*-hexane, $R_f = 0.25$), m.p. 142–144 °C; FTIR (KBr, cm^{-1}):

3062 (HC=), 2111 (Si–H), 1598, 1490 (Ph), 1250, 888 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.3 (d, 12H, $^3J_{HH}$ = 3.8 Hz, 2×$SiMe_2$), 0.4 (d, 12H, $^3J_{HH}$ = 3.6 Hz, 2×$SiMe_2$), 1.07 (t, 6H, J = 7.4 Hz, 2×CH_3CH_2), 1.21 (t, 6H, J = 7.4 Hz, 2×CH_3CH_2), 2.03–2.11 (m, 8H, 4×$CH_3CH_2CH_2$), 3.3 (d, 4H, J = 13.3 Hz, 4×ArCHAr), 3.9 (t, 4H, J = 7.0 Hz, 2×CH_2CH_2O), 4.10 (t, 4H, J = 7.8 Hz, 2×CH_2CH_2O), 4.38–4.41 (m, 2H, 2×Si$H$$Me_2$), 4.48–4.51 (m, 2H, 2×Si$H$$Me_2$), 4.61 (d, 4H, J = 13.22 Hz, 4×ArCHAr), 6.49 (s, 6H, Ar), 7.11(s, 4H, Ar), 7.81 (s, 2H, 2×HC=); ^{13}C NMR(100 MHz, $CDCl_3$, ppm): δ −3.8, −3.2 ($SiMe_2$), 9.0, 9.6, 22.0, 22.3, 30.0, 75.8, 75.9, 121.2, 126.6, 128.1, 132.5, 133.3, 134.6, 136.5, 154.5, 155.4, 156.5; MALDI-TOF MS m/z: $[M+Na]^+$ = 899.39; Anal. Calcd for $C_{52}H_{76}O_4Si_4$ (876.48): C, 71.17; H, 8.73. Found: C, 70.92; H, 8.50%.

*4.8.2. Preparation of 5,17-bis[2,2-bis(trimethylsiyl)-1-ethenyl]-25,26,27,28-tetra propoxycalix[4]arene (**3b**)*

A white solid 0.57 g (62 %) was obtained by preparative TLC (silicagel, n-hexane, R_f = 0.25), m.p. 176–178 °C; FTIR (KBr, cm^{-1}): 3070 (HC=), 1590, 1459 (Ph), 1248, 891(Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.0 (d, 18H, $^5J_{HH}$ = 0.8 Hz, 2×$SiMe_3$), 0.19 (d, 18H, $^5J_{HH}$ = 0.7 Hz, 2×$SiMe_3$), 0.90 (t, 6H, J = 7.4 Hz, 2×CH_3CH_2), 1.08 (t, 6H, J = 7.5 Hz, 2×CH_3CH_2), 1.86–1.97 (m, 8H, 4×$CH_3CH_2CH_2$), 3.1 (d, 4H, J = 13.2 Hz, 4×ArCHAr), 3.71 (t, 4H, J = 6.9 Hz, 2×CH_2CH_2O), 3.98 (t, 4H, J = 7.9 Hz, 2×CH_2CH_2O), 4.4 (d, 4H, J = 13.2 Hz, 4×ArCHAr), 6.3 (s, 6H, Ar), 6.9 (s, 4H, Ar), 7.73 (s, 2H, 2×HC=); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −0.3, 1.2 ($SiMe_3$), 6.0, 9.6, 21.9, 22.4, 30.0, 75.5, 75.8, 121.0, 126.7, 127.4, 132.3, 134.8, 135.3, 143.1, 154.3, 154.6, 156.0; MALDI-TOF MS m/z: $[M+Na]^+$ = 955.41; Anal. Calcd for $C_{56}H_{84}O_4Si_4$(932.54): C, 72.04; H, 9.07. Found: C, 71.85; H, 8.90%.

*4.8.3. Preparation of 5,17-bis[2,2-bis(dimethylphenylsiyl)-1-ethenyl]-25,26,27,28-tetrapropoxycalix[4]arene (**3c**)*

A yellow viscous oil 0.53 g (45%) was obtained by preparative TLC (silica gel, n-hexane, R_f = 0.12); FTIR (KBr, cm^{-1}): 3066 (HC=), 2111(Si–H), 1589, 1458 (Ph), 1249, 867 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.49 (s, 12H, 2×$SiMe_2$), 0.86 (s, 12H, 2×$SiMe_2$), 1.29 (t, 6H, J = 7.4 Hz, 2×CH_3CH_2), 1.48 (t, 6H, J = 7.3 Hz, 2×CH_3CH_2), 2.22–2.37 (m, 8H, 4 ×$CH_3CH_2CH_2$), 3.29 (d, 4H, J = 13.3 Hz, 4×ArCHAr), 4.0 (t, 4H, J = 6.8 Hz, 2×CH_2CH_2O), 4.29 (t, 4H, J = 8.0 Hz, 2×CH_2CH_2O), 4.68 (d, 4H, J = 13.3 Hz, 4×ArCHAr), 6.39 (d, 4H, J = 7.5, Ar), 6.48–7.07 (m, 6H, Ar), 7.64–7.82 (m, 20H, Ar), 8.33 (s, 2H, 2×HC=); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −1.5, −0.05 ($SiMe_2$), 8.9, 9.7, 21.8, 22.4, 29.8, 75.3, 75.8, 120.9, 126.4, 126.5, 126.6, 127.0, 127.3, 127.6, 128.1, 132.0, 132.8, 133.1, 133.9, 134.1, 134.7, 137.3, 154.0, 156.5, 158.5; MALDI-TOF MS m/z: $[M+Na]^+$ = 1204.61; Anal. Calcd for $C_{76}H_{92}O_4Si_4$ (1181.61): C, 77.23; H, 7.85. Found: C, 76.90; H, 7.60%.

4.9. General procedure for the synthesis of 25,26,27,28-tetrakis[4-(tris(silyl)methyl)butoxy]calix[4]arenes

To a stirred solution of **1a**, **1b** or **1c** (5.3 mmol) in THF at 0 °C was added 25,26,27,28-tetrakis(4-bromobutoxy)calix[4]arene (**4**) (1 mmol) in 10 ml THF, and the mixture was stirred for another 2 h at room temperature. The mixture was poured into ammonium chloride solution (50 ml) and extracted with CH_2Cl_2 (2 × 50 ml). The organic phase was washed with water (100 ml) and dried (Na_2SO_4), and the solvent was removed in vacuum to yield a viscous oil.

*4.9.1. Preparation of 25,26,27,28-tetrakis[4-(tris(dimethylsilyl)methyl)butoxy] calix[4]arene (**5a**)*

A white solid 1.15 g (82%) was obtained by preparative TLC (silica gel, n-hexane, R_f = 0.2), m.p. 59–61 °C; FTIR (KBr, cm^{-1}): 3061 (HC=), 2107 (Si–H), 1589, 1456 (Ph), 1252, 896 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.1 (d, 72 H, $^3J_{HH}$ = 3.7 Hz, 12×$SiMe_2$), 1.51–1.58 (m, 8H, 4×CCH_2CH_2), 1.66–1.71 (m, 8H, 4×$CCH_2CH_2CH_2$), 1.85–1.93 (m, 8H, 4×$CCH_2CH_2CH_2CH_2$), 3.1 (d, 4H, J = 13.4 Hz, 4×ArCHAr), 3.9 (t, 8H, J = 7.2 Hz, 4×CCH_2CH_2-CH_2CH_2O), 3.99–4.05 (m, 12H, 12×Si$H$$Me_2$), 4.4 (d, 4H, J = 13.3 Hz, 4×ArCHAr), 6.56–6.62 (m, 12H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −4.06 ($SiMe_2$), 0.58 ($C(SiMe_2H)_3$), 25.0, 29.5, 30.2, 30.6, 73.7, 120.9, 127.1, 133.8, 155.6; MALDI-TOF MS m/z: $[M+Na]^+$ = 1424.35; Anal. Calcd for $C_{72}H_{136}O_4Si_{12}$ (1400.77): C, 61.64; H, 9.77. Found: C, 61.25; H, 9.63%.

*4.9.2. Preparation of 25,26,27,28-tetrakis[4-(tris(trimethylsilyl)methyl)butoxy]calix[4]arene (**5b**)*

A white solid 0.94 g (60 %) was obtained by preparative TLC (silica gel, n-hexane, ethyl acetate 4:1 R_f = 0.60), m.p. 138–140 °C; FTIR (KBr, cm^{-1}): 3059 (HC=), 1587, 1455 (Ph), 1253, 839 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.1 (s, 108H, 12×$SiMe_3$), 1.52–1.56 (m, 8H, 4×CCH_2CH_2), 1.66–1.69 (m, 8H, 4×$CCH_2CH_2CH_2$), 1.85–1.89 (m, 8H, 4×$CCH_2CH_2CH_2CH_2$), 3.1 (d, 4H, J = 13.4 Hz, 4×ArCHAr), 3.9 (t, 8H, J = 6.6 Hz, 4×CCH_2-$CH_2CH_2CH_2O$), 4.4 (d, 4H, J = 13.3 Hz, 4×ArCHAr), 6.51–6.72 (m, 12H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 1.8 ($SiMe_3$), 5.1 ($C(SiMe_3)_3$), 26.1, 29.5, 29.9, 30.9, 73.7, 120.8, 127.1, 133.8, 155.6; MALDI-TOF MS m/z: $[M+Na]^+$ = 1592.4; Anal. Calcd for $C_{84}H_{160}O_4Si_{12}$ (1568.95): C, 64.21; H, 10.26. Found: C, 64.05; H, 9.95%.

4.9.3. Tris(dimethylphenylsilyl)methyllithium did not react with **4** under reflux in THF for 36 h.

Acknowledgment

We thank Dr. J.D. Smith for helpful comments.

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