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Functionalisation of the upper rim of calix[4]arene via alcoholysis and hydrosilylation reactions

Kazem D. Safa *, Yones Mosaei Oskoei

Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 5166616471 Tabriz, Iran

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ABSTRACT

Metalation of 5,17-dibromo-25,26,27,28-tetra propoxy calix[4]arene (**1**) with *n*-BuLi in THF at −78 °C gave organolithium reagent, which reacted with Me_2HSiCl to give 5,17-bis(dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**2**). The Si–H groups of calixarene **2** were treated with methanol, ethanol, propanol, butanol, pentanol, hexanol, 2-propanol and 2-methyl propanol in the presence of Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex, solution in xylene) to give the corresponding 5,17-bis(alkoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**3**). Moreover, calixarene **2** was easily functionalized with a variety of alkenes using Karstedt catalyst to give the corresponding organosilylated calix[4]arene (**4**).

1. Introduction

Calixarenes, the cyclic products of the condensation of molecules such as para-substituted phenol and formaldehyde, represent a class of receptors which are readily available in varying ring sizes [1]. Organosilylated calixarenes are of potential interest for molecular recognition of anions [2] because silicon can expand its coordination shell to become pentacordinate or hexacordinate, especially when bonded to electronegative atoms [3], but few such calixarenes have hitherto been reported [4–10].

The dehydrocoupling reaction between hydrosilane and alcohol is a typical well-known method for the preparation of Si–O bonds using transition metal catalyst [11]. Since calixarenes containing alkoxysilane introduce a new field in the calixarene chemistry, it multiplied our great interest in the preparation of calix[4]arene molecules containing two alkoxydimethylsilyl groups appended to the upper rim of the cone conformation.

The hydrosilylation of alkenes is an important industrial process, but is also extremely valuable in laboratory scale synthesis as well. The hydrosilylation reaction also provide an easy method for introducing different functionality on the upper rim of calix[4]arenes. Many metal complexes are known to be catalysts for the reaction [12]. Si–C bonds are often prepared by platinum-catalyzed hydrosilylation reactions in which, the anti-Markovnikov addition of a Si–H bond across a C=C double bond is usually observed [13]. The silylated calix[4]arenes were designed to function as ditopic receptor molecules that will bind cations through the oxygen atoms at the lower rim and anions through the silicon atoms on the upper rim [8].

In this work, we report the use of the dehydrocoupling and hydrosilylation reactions as new methods for functionalization of the upper rim of calix[4]arenes, which cannot be achieved via other methods.

2. Results and discussion

The precursor 5,17-dibromo-25,26,27,28-tetra propoxy calix[4]arene (**1**) was obtained in 75% yield according to Scheme 1 [14]. The starting point for the synthesis of calixarenes containing organosilicon derivatives on the upper rim was the preparation of 5,17-bis(dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene **(2)**, which was obtained in 72% yield (Scheme 2). The organolithium reagent of calixarene was prepared from dibromo calixarene **1** by halogen–lithium exchange using an excess of *n*-BuLi in THF at −78 °C for 15 min. Quenching with Me_2HSiCl gave 5,17-bis(dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene **2**.

Calixarene **2** having hydrosilane (Si–H) substituents are potentially useful for the preparation of new derivatives of calixarene containing organosilicon groups. The addition of the hydrosilane to alcohol is an attractive route to silylethers because the only side-product is hydrogen gas.

$$R_{4-x}SiH_x + xR'OH \xrightarrow{\text{catalyst}} R_{4-x}Si(OR'_x) + xH_2$$

The alcoholysis requires a catalyst because alcohols are not generally sufficiently nucleophilic to attack hydrosilanes [15,16]. Since we were interested in extending of the applied methodology in

* Corresponding author. Tel.: +98 411 3393124; fax: +98 411 3340191.
E-mail address: dsafa@tabrizu.ac.ir (K.D. Safa).

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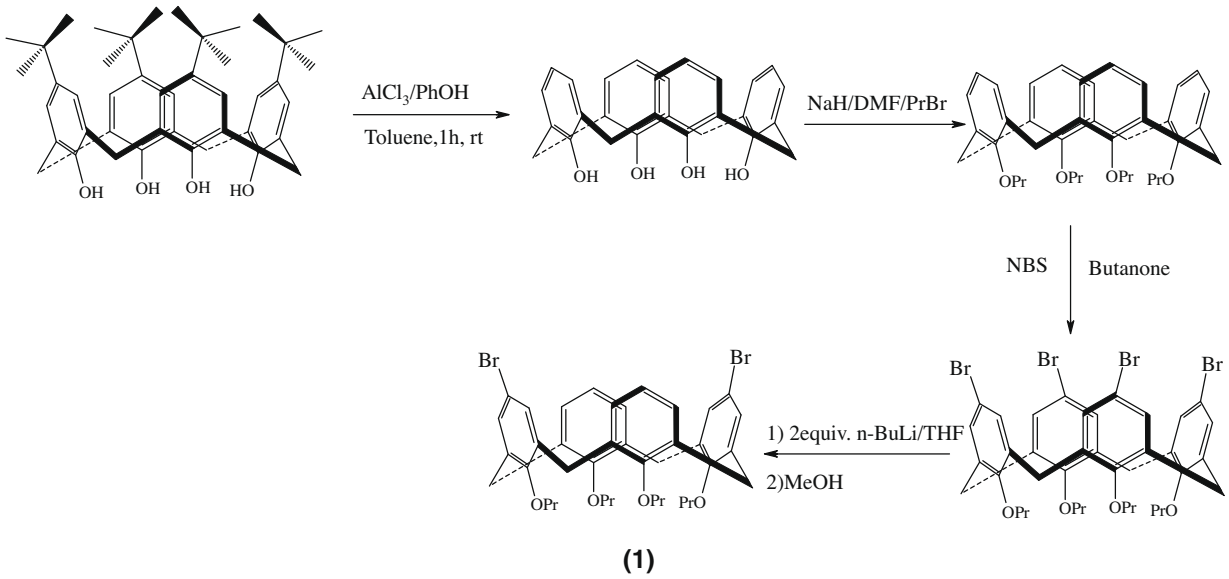
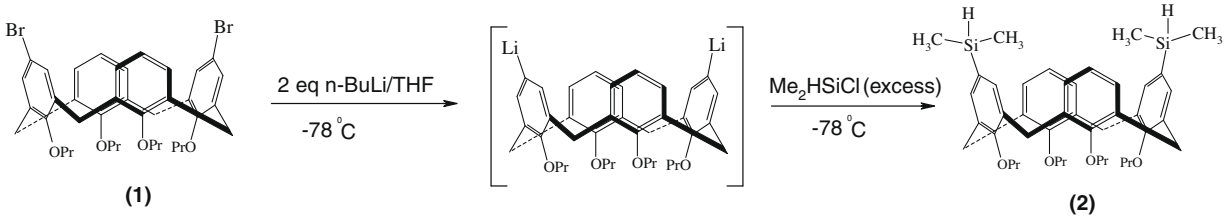
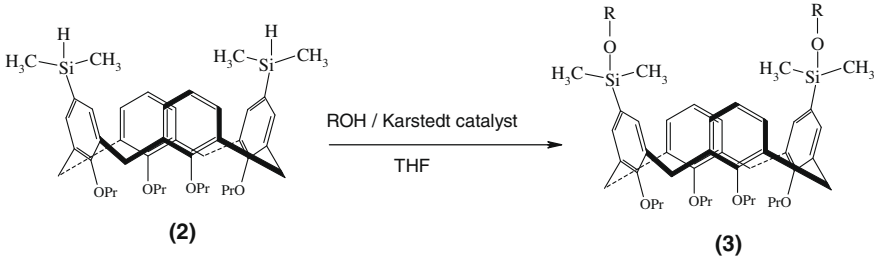


Scheme 1. Preparation of calixarene **1**.



Scheme 2. Preparation of calixarene **2**.



Scheme 3. Preparation of calixarene **3**.

the grafting of calixarene containing Si–H group **2** to various alcohols, it was decided to study the dehydrocoupling reaction between compound **2** and some alcohols under different conditions (Scheme 3).

Monofunctional alcohols (methanol, ethanol, propanol and butanol) were treated with **2** in the presence of $H_2PtCl_6{\cdot}6H_2O$ as the catalyst in air under reflux condition. The related 5,17-bis(alkoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arenes were produced, but the reaction time was long ($t > 24$ h) under reflux condition. In order to optimize the alcoholysis of calixarene **2**, the Karested catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex, solution in xylene) was decided to be used which is more active than Speier catalyst ($H_2PtCl_6{\cdot}6H_2O$). Calixarene **2** was insoluble in alcohols, therefore high reaction temperature was applied. For this reason, calixarene **2** was disolved in 5 ml of dry THF and the corresponding alcohol was added to the reaction mixture. Then Karstedt catalyst was added (20 μl, [Pt]/[Si–H] = 3.1×10^{-6}). The colorless reaction mixture gradually turned to homogenous black-colored solution, indicating the generation of colloidal Pt° particles. These reactions occurred in air. In contrast, most reported alcoholysis reactions prompted by transition metal catalysts have been carried out under inert atmospheres such as argon or nitrogen. Reaction of calixarene **2** with primary alcohols gave higher yields than analogous reactions with secondary alcohols, probably because of the increase in steric hindrance (Table 1).

The reaction progress was monitored by FTIR spectroscopy on the basis of absorption measurements at the Si–H stretching bond frequency (2114 cm^{-1}). For instance, the FTIR spectrum of the obtained calixarene **3a** does not show a sharp peak at 2114 cm^{-1}, indicating the absence of Si–H bond, and concomitant appearance of Si–O peak at 1085 cm^{-1} (Fig. 1). In addition the ^1H NMR spectrum of calixarene **3a** shows the complete disappearance of Si–H at 4.43 ppm and concomitant appearance of signals assigned to OCH_3 at 3.44 ppm (Fig. 2). Similar results were observed for other alcohols.

Table 1
Yields of alcoholysis of various hydroxyl compounds with calixarene **2** in the presence of the Karstedt catalyst.

Compound	Hydroxy compound	Yields (%)
3a	CH_3OH	77
3b	CH_3CH_2OH	75
3c	$CH_3CH_2CH_2OH$	75
3d	$CH_3CH_2CH_2CH_2OH$	70
3e	$CH_3CH_2CH_2CH_2CH_2OH$	67
3f	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	65
3g	$(CH_3)_2CHOH$	62
3h	$(CH_3)_2CHCH_2OH$	60

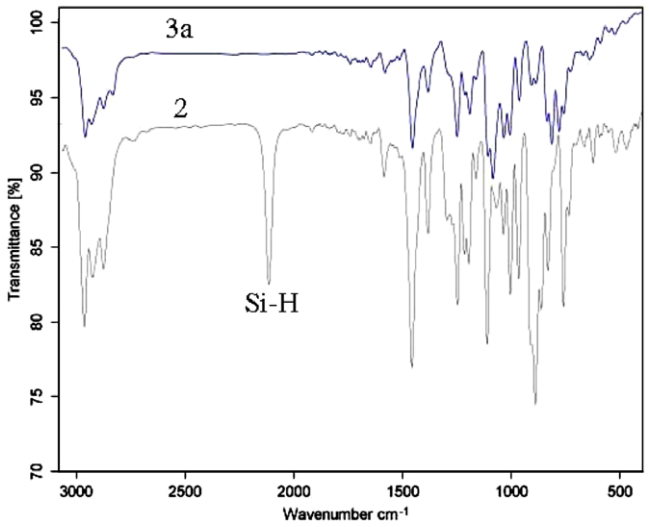


Fig. 1. Comparing the FTIR spectra of the compound **2** and **3a**.

We also investigated the synthesis of calixarenes substituted with organosilicon groups on the upper rim. Thus calixarene **2** containing Si–H groups were easily functionalized with a variety of alkenes using Karstedt catalyst to give the corresponding product (**4**) (Scheme 4). All of the hydosilylation reactions were carried out in freshly distilled dry THF and catalyzed by the addition of Karstedt catalyst. Typically 5 mol equivalents of alkene were added per Si–H group. Hydrosilylation of alkenes with **2** proceeded very fast in the presence of Karstedt catalyst in THF at room temperature. After a short initial period (about 5 min) an exothermic reaction took place. The reaction mixture turned black due to the formation of colloidal platinum. FTIR spectrum recorded after 15 min, proved the complete disappearance of Si–H bond. It is worth noting that the Speier catalyst was less active than the Karstedt catalyst at room temperature. The best result was obtained using Karstedt catalyst (25 μl, $[Pt]/[Si–H] = 3.9 \times 10^{-6}$) in dry THF at room temperature. Hydrosilylation of styrene derivatives (styrene, *p*-chloro methyl styrene, α-methyl styrene) and allyl glycidyl ether were successful with Karstedt catalyst. However, with acrylate derivatives (glycidyl methacrylate, butylacrylate), allylbromide and 1,1-dichloroethene, the hydrosilylation reactions were unsuccessful and we were not able to identify the products (Table 2).

The ^{1}H NMR spectrum of the calixarene **4d** (Fig. 3) shows the complete disappearance of the Si–H resonance at 4.43 ppm and the concomitant disappearance of the allyl group in allyl glycidyl ether at 5.5 and 6.6 ppm. In addition, the peaks at $\delta = 0.7$, 1.7 and 3.5 ppm are the resonance peaks of the silyl propyl group, while those at $\delta = 2.6$, 2.8 and 3.1 ppm represent the resonance peaks of the epoxide group. These results clearly indicate that the hydrosilylation reaction of **4d** was successful.

3. Conclusion

In conclusion, this paper reports that a series of new calixarenes substituted with organosilicon groups on the upper rim were obtained in good yields from the catalytic reaction of calixarene **2** with several alcohols. It was found that using the Speier catalyst, alcoholysis rate was low under reflux condition, but in the presence of the Karstedt catalyst, alcoholysis took place during 1–2 h in high yields at room temperature. It should be mentioned that the primary alcohols gave higher yields than the secondary alcohols, which might be the result of the increase in the steric hindrance. Hydrosilylation of calixarene **2** with functionalized alkenes such as styrene, methylstyrene, *p*-chloromethyl styrene and allyl glycidyl ether in the presence of Karstedt catalyst, insert

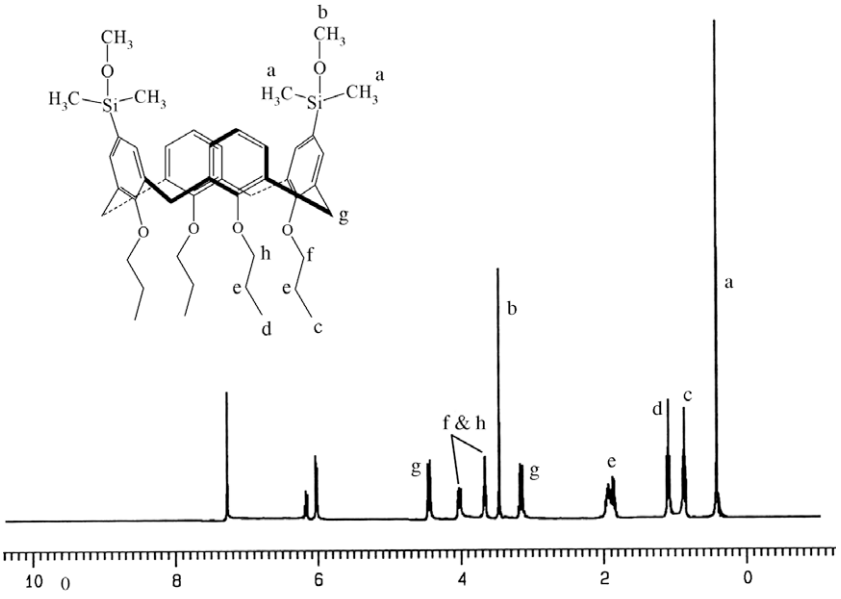
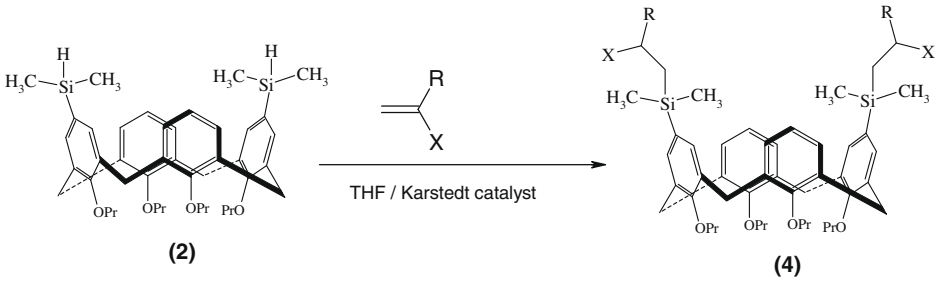
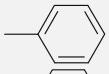
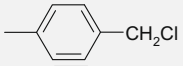
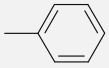
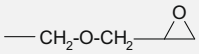
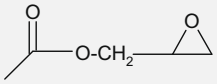
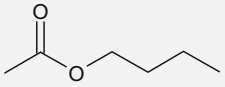


Fig. 2. The ^{1}H NMR spectrum of the calixarene **3a**.



Scheme 4. Preparation of calixarene **4**.

Table 2
Hydrosilylation of various alkenes with calixarene **2** in the presence of the Karstedt catalyst.

Compound	R	X	Yield (%)
4a	H		80
4b	H		65
4c	CH_3		72
4d	H		85
4e	CH_3		[a]
4f	H		[a]
4g	H	CH_2Br	[a]
4h	Cl	Cl	[a]

[a] The Si–H peak disappeared in the 1H NMR and the FTIR spectra but the products have not been identified.

new functional groups to calixarene moieties which cannot be achieved via other methods. On the other hand, the insertion of acrylates to the upper rim of calixarene with this method was unsuccessful. These compounds may be used as ditopic receptor molecules that will bind cations through the oxygen atom at the lower rim and anions through the silicon atom on the upper rim.

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 calixarene **2**, viz, *p*-tert-butyl phenol, formaldehyde 35–40%, NaH, DMF, 1-bromopropane, NBS, 2-butanone, Me_2HSiCl and all alcohols used in alcoholysis, also all alkenes used in hydrosilylation reactions were purchased from Merck and Fluka and NBS, Me_2HSiCl, all alcohols and alkenes purified by standard methods. Karstedt catalyst was purchased from Aldrich.

4.2. Spectra

The ^1H NMR 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 FTIR spectra were recorded on a Bruker–Tensor 270 spectrometer. Elemental analyses were carried out with a Heareus CHN-ORAPID instrument.

4.3. Preparation of the 5,17-dibromo-25,26,27,28-tetra propoxy calix[4]arene (*1*)

This was synthesized according to the literature [14].

4.4. Preparation of the 5,17-bis(dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (2)

To the stirred solution of 5.3 mmol calixarene **1** in 200 ml dry THF at −78 °C was added 9.3 ml (1.51 M, 14 mmol) *n*-BuLi/hexane. The yellow solution was stirred at −78 °C for 15 min, quenched with Me_2HSiCl (10 ml) and stirred for another 30 min. The reaction mixture was poured into ice cold 2 M hydrochloric acid (200 ml) and extracted with $CHCl_3$ (2 × 100 ml). The organic phase was washed with 100 ml water and dried with Na_2SO_4, and the solvent was removed in vacuum to yield a solid. The raw product was recrystallized from MeOH gave **2** in 72% yield as a white crystals: m.p. 180–181 °C; FTIR (KBr,cm^{-1}): 3062(HC═), 2114 (Si–H), 1585, 1457 (Ph), 1248, 890 (Si–CH_3); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.3 (d, 12H, $^3J_{HH}$ = 3.5 Hz, 2 × $SiMe_2$), 0.88 (t, 6H, *J* = 7.4 Hz, 2×$CH_3CH_2CH_2O$), 1.09 (t, 6H, *J* = 7.4 Hz, 2×$CH_3CH_2CH_2O$), 1.85–1.97 (m, 8H, 4 × $CH_3CH_2CH_2O$), 3.1 (d, 4H, *J* = 13.4 Hz, 4 × Ar*CH*Ar), 3.69 (t, 4H, *J* = 7 Hz, 2 × $CH_3CH_2CH_2O$), 4.01 (t, 4H, *J* = 8.1 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, *J* = 13.5 Hz, 4 × Ar*CH*Ar), 4.42–4.46 (m, overlapped with doublet, 2H, 2 × Si–H), 6.0 (d, 4H, *J* = 7.6 Hz, aromatic), 6.2 (t, 2H, *J* = 7.6 Hz, aromatic), 7.21 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −3.4 (SiMe), 9.8, 10.8, 23.0, 23.4, 31.0, 76.4, 76.6, 122.0, 127.3, 129.4, 133.3, 134.8, 136.4, 155.2, 159.1 ppm; *Anal.* Calc. for $C_{44}H_{60}O_4Si_2$: C, 74.5%; H, 8.5. Found: C, 74.3; H, 8.4%.

4.5. General procedure for the synthesis of 5,17-bis(alkoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene

A 50 ml round-bottom two-neck flask with magnetic stirring was charged with 0.20 g (0.28 mmol) calixarene **2**, 1 ml ROH, and 5 ml dry THF as a solvent. Then 20 μl of Karstedt catalyst ([Pt]/[Si–H] = 3.1 × 10^{-6}) was added. To follow the reaction progress, several samples were taken at different times and were analyzed by FTIR spectroscopy. The reaction mixture was stirred at room temperature until the complete disappearance of Si–H bond in FTIR spectroscopy. The alcohols and THF were evaporated under reduced pressure and the residue purified by column chromatography (*n*-hexane-ethylacetate, 10:1) to give the corresponding products.

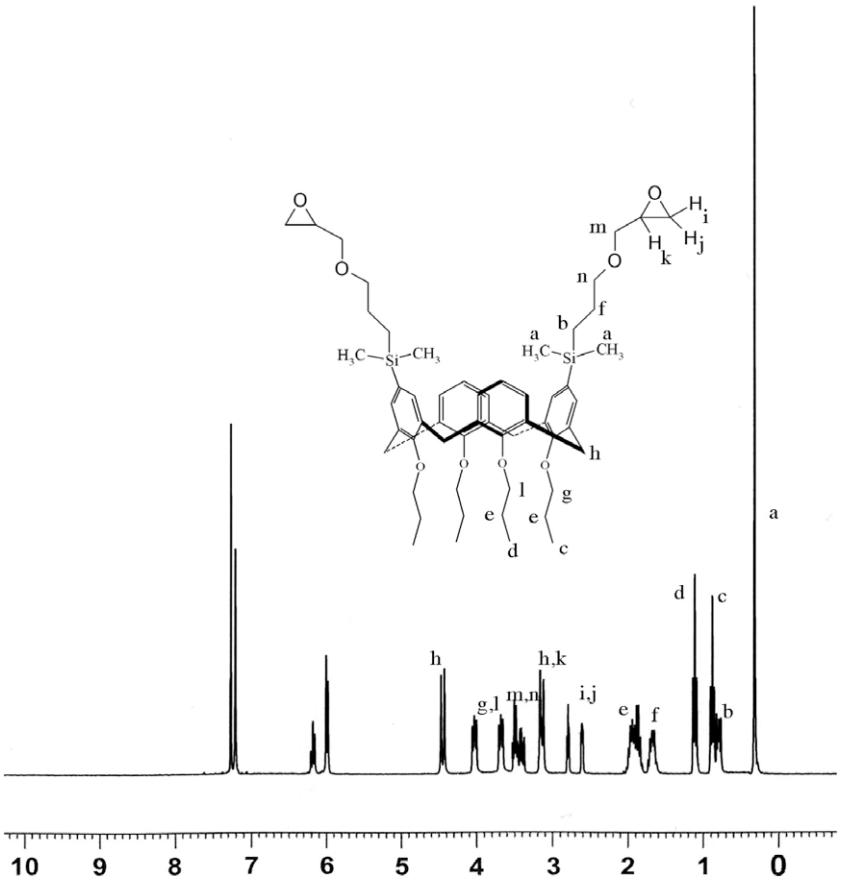


Fig. 3. The ^{1}H NMR spectrum of the calixarene **4d**.

*4.5.1. 5,17-Bis(methoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**3a**)*

Yield 77%; m.p. 127–129 °C; FTIR (KBr, cm^{-1}): 3061 (HC═), 1581, 1454 (Ph), 1249 (Si–CH_3), 1084 (Si–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.39 (s, 12H, 2 × $SiMe_2$), 0.85 (t, 6H, J = 7.5 Hz, 2 × $CH_3CH_2CH_2O$), 1.07 (t, 6H, J = 7.4 Hz, 2 × $CH_3CH_2CH_2O$), 1.82–1.95 (m, 8H, 4 × $CH_3CH_2CH_2O$), 3.1 (d, 4H, J = 13.4 Hz, 4 × Ar*CH*Ar), 3.44 (s, 6H, 2 × CH_3O), 3.6 (t, 4H, J = 6.7 Hz, 2 × $CH_3CH_2CH_2O$), 4.00 (t, 4H, J = 8.1 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.3 Hz, 4 × Ar*CH*Ar), 6.0 (d, 4H, J = 7.5 Hz, aromatic), 6.1 (t, 2H, J = 7.3 Hz, aromatic), 7.26 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −3.0 (SiMe), 8.9, 9.9, 22.1, 22.6, 30.1, 49.7, 75.5, 75.8, 121.2, 126.4, 128.6, 132.3, 133.5, 135.6, 154.2, 158.7 ppm; *Anal.* Calc. for $C_{46}H_{64}O_6Si_2$: C, 71.8; H, 8.4. Found: C, 71.5; H, 8.5.

*4.5.2. 5,17-Bis(ethoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**3b**)*

Yield 75%; m.p. 115–117 °C; FTIR (KBr, cm^{-1}): 3059 (HC═), 1584, 1456 (Ph), 1251 (Si–CH_3), 1109 (Si–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.31 (s, 12H, 2 × $SiMe_2$), 0.86 (t, 6H, J = 7.5 Hz, 2 × $CH_3CH_2CH_2O$), 0.9 (t, 6H, J = 8 Hz, 2 × CH_3CH_2O), 1.1 (t, 6H, J = 7.3 Hz, 2 × $CH_3CH_2CH_2O$), 1.82–1.94 (m, 8H, 4 × $CH_3CH_2CH_2O$), 3.1 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 3.45 (t, 4H, J = 8 Hz, 2 × CH_3CH_2O), 3.65 (t, 4H, J = 6.7 Hz, 2 × $CH_3CH_2CH_2O$), 4.00 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 6.0 (d, 4H, J = 7.5 Hz, aromatic), 6.1 (t, 2H, J = 7 Hz, aromatic), 7.33 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.8 (SiMe), 9.0, 10.0, 22.1, 22.6, 22.7, 30.1, 57.12, 75.4, 75.7, 121.0, 126.2, 128.4, 132.0, 133.4, 135.2, 154.0, 158.4 ppm; *Anal.* Calc. for $C_{48}H_{68}O_6Si_2$: C, 72.3; H, 8.6. Found: C, 72.1; H, 8.4%.

*4.5.3. 5,17-Bis(propoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**3c**)*

Yield 75%; m.p. 106–108 °C; FTIR (KBr, cm^{-1}): 3060 (HC═), 1584, 1457 (Ph), 1251 (Si–CH_3), 1085 (Si–O);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.43 (s, 12H, 2 × $SiMe_2$), 0.83–0.94 (m, 12, 2 × $CH_3CH_2CH_2O$ overlapped with 2 × $CH_3CH_2CH_2OSi$), 1.10 (t, 6H, J = 7.2 Hz, 2 × $CH_3CH_2CH_2O$), 1.56–1.58 (m, 4H, 2 × CH_3-CH_2CH_2O), 1.84–1.95 (m, 8H, 4 × $CH_3CH_2CH_2O$), 3.1 (d, 4H, J = 13.3 Hz, 4 × Ar*CH*Ar), 3.59 (t, 4H, J = 7 Hz, 2 × $CH_3CH_2CH_2O$), 3.68 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.04 (t, 4H, J = 8.5 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.2 Hz, 4 × Ar*CH*Ar), 6.0 (d, 4H, J = 7.8 Hz, aromatic), 6.1 (t, 2H, J = 7.5 Hz, aromatic), 7.31 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.8 (SiMe), 9.7, 10.2, 10.9, 22.7, 23.2, 23.7, 30.3, 68.1, 76.5, 76.7, 121.6, 127.2, 128.7, 132.5, 134.1, 135.1, 154.5, 158.4 ppm; *Anal.* Calc. for $C_{50}H_{72}O_6Si_2$: C, 72.8; H, 8.8. Found: C, 72.5; H, 8.6%.

*4.5.4. 5,17-Bis(butoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**3d**)*

Yield 70%; m.p. 90–92 °C; FTIR (KBr, cm^{-1}): 3065 (HC═), 1583, 1457 (Ph), 1252 (Si–CH_3), 1087 (Si–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.41 (s, 12H, 2 × $SiMe_2$), 0.86 (t, 6H, J = 7.5 Hz, 2 × $CH_3CH_2CH_2O$), 0.89 (t, 6H, J = 7.3 Hz, 2 × $CH_3CH_2CH_2CH_2O$), 1.10 (t, 6H, J = 7.4 Hz, 2 × $CH_3CH_2CH_2O$), 1.31–1.38 (m, 4H, 2 × $CH_3CH_2CH_2CH_2O$), 1.50–1.57 (m, 4H, 2 × $CH_3CH_2CH_2CH_2O$), 1.84–1.96 (m, 8H, 4 × $CH_3CH_2CH_2O$), 3.1 (d, 4H, J = 13.4 Hz, 4 × Ar*CH*Ar), 3.63–3.68 (m, 8H, 2 × $CH_3CH_2CH_2O$ overlapped with 2 × $CH_3CH_2CH_2CH_2O$), 4.03 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.3 Hz, 4 × Ar*CH*Ar), 6.0 (d, 4H, J = 7.5 Hz, aromatic), 6.14 (t, 2H, J = 7.4 Hz, aromatic), 7.30 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.6 (SiMe), 8.7, 9.8, 12.8, 18.0, 21.9,

22.5, 30.0, 33.8, 61.8, 75.6, 75.8, 120.9, 126.2, 128.0, 132.1, 133.4, 135.1, 154.0, 158.6 ppm; *Anal.* Calc. for $C_{52}H_{76}O_6Si_2$: C, 73.2; H, 8.9. Found: C, 72.9; H, 8.7%.

4.5.5. 5,17-Bis(pentoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**3e**)

Yield 67%; m.p. 89–91 °C; FTIR (KBr, cm^{-1}): 3062 (HC=), 1584, 1457 (Ph), 1250 (Si–CH_3), 1090 (Si–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.41 (s, 12H, 2 × $SiMe_2$), 0.87–0.94 (m, 12H, 2 × $CH_3CH_2CH_2O$ overlapped with 2 × $CH_3(CH_2)_3CH_2O$), 1.10 (t, 6H, J = 7.3 Hz, 2 × $CH_3CH_2CH_2O$), 1.27–1.33 (m, 8H, 2 × $CH_3(CH_2)_2$-CH_2CH_2O), 1.53–1.57 (m, 4H, 2 × $CH_3(CH_2)_2CH_2CH_2O$), 1.87–1.96 (m, 8H, 4 × $CH_3CH_2CH_2O$), 3.1 (d, 4H, J = 13.4 Hz, 4 × Ar*CH*Ar), 3.64 (t, 4H, J = 6.8 Hz, 2 × $CH_3(CH_2)_2CH_2CH_2O$), 3.66 (t, 4H, J = 7 Hz, 2 × $CH_3CH_2CH_2O$), 4.03 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.4 Hz, 4 × Ar*CH*Ar), 5.99 (d, 4H, J = 7.5 Hz, aromatic), 6.11 (t, 2H, J = 7.5 Hz, aromatic), 7.30 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.6 (SiMe), 8.7, 9.8, 13.0, 21.4, 22.0, 22.5, 27.0, 30.0, 31.4, 62.0, 75.6, 75.8, 120.9, 126.2, 127.7, 132.8, 133.6, 135.5, 154.0, 158.6 ppm; *Anal.* Calc. for $C_{54}H_{80}O_6Si_2$: C, 73.6; H, 9.1. Found: C, 73.4; H, 8.7%.

4.5.6. 5,17-Bis(hexoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**3f**)

Yield 65%; m.p. 85–87 °C; FTIR (KBr, cm^{-1}): 3066 (HC=), 1586, 1460 (Ph), 1253 (Si–CH_3), 1110 (Si–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.41 (s, 12H, 2 × $SiMe_2$), 0.85–0.91 (m, 12H, 2 × CH_3CH_2-CH_2O overlapped with 2 × $CH_3(CH_2)_4CH_2O$), 1.10 (t, 6H, J = 7 Hz, 2 × $CH_3CH_2CH_2O$), 1.27–1.35 (m, 12H, 2 × $CH_3(CH_2)_3CH_2CH_2O$), 1.54–1.57 (m, 4H, 2 × $CH_3(CH_2)_3CH_2CH_2O$), 1.86–1.94 (m, 8H, 4 × $CH_3CH_2CH_2O$), 3.1 (d, 4H, J = 13.4 Hz, 4 × Ar*CH*Ar), 3.62 (t, 4H, J = 7 Hz, 2 × $CH_3(CH_2)_3CH_2CH_2O$), 3.68 (t, 4H, J = 6.8 Hz, 2 × CH_3-CH_2CH_2O), 4.04 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.4 Hz, 4 × Ar*CH*Ar), 6.0 (d, 4H, J = 7.5 Hz, aromatic), 6.1 (t, 2H, J = 7.6 Hz, aromatic), 7.30 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.6 (SiMe), 8.7, 9.8, 13.0, 21.6, 22.0, 22.5, 24.5, 28.6, 30.0, 31.6, 62.2, 75.4, 75.6, 120.9, 126.2, 127.7, 132.4, 133.4, 135.5, 154.0, 158.6 ppm; *Anal.* Calc. for $C_{56}H_{84}O_6Si_2$: C, 73.9; H, 9.3. Found: C, 73.5; H, 8.9%.

4.5.7. 5,17-Bis(1-methyl ethoxydimethylsilyl)-25,26,27,28- tetra propoxy calix[4]arene (3g)

Yield 62%; m.p. 79–81 °C; FTIR (KBr, cm^{-1}): 3068 (HC=), 1582, 1457 (Ph), 1250 (Si–CH_3), 1112 (Si–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.45 (s, 12H, 2 × $SiMe_2$), 0.91 (t, 6H, J = 7.2 Hz, 2 × $CH_3CH_2CH_2O$), 1.09 (t, 6H, J = 7 Hz, 2 × $CH_3CH_2CH_2O$), 1.18 (d, 12H, J = 6.3 Hz, 2 × $(CH_3)_2CHO$), 1.85–1.95 (m, 8H, 4 × CH_3CH_2-CH_2O), 3.1 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 3.68 (t, 4H, J = 6.6 Hz, 2 × $CH_3CH_2CH_2O$), 4.03–4.10 (m, 6H, 2 × $CH_3CH_2CH_2O$ overlapped with 2 × $(CH_3)_2CHO$), 4.4 (d, 4H, J = 13.2 Hz, 4 × Ar*CH*Ar), 6.06 (d, 4H, J = 7.5 Hz, aromatic), 6.15 (t, 2H, J = 7.6 Hz, aromatic), 7.30 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −1.2 (SiMe), 9.7, 10.9, 23.0, 23.5, 25.6, 29.6, 65.11, 76.3, 76.5, 121.9, 127.2, 130.8, 133.1, 134.5, 136.5, 155.0, 159.5, ppm; *Anal.* Calc. for $C_{50}H_{72}O_6Si_2$: C, 72.8; H, 8.8. Found: C, 72.5; H, 8.6%.

4.5.8. 5,17-Bis(2-methyl propoxydimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (3h)

Yield 60%; m.p. 82–84 °C; FTIR (KBr, cm^{-1}): 3059 (HC=), 1585, 1459 (Ph), 1252 (Si–CH_3), 1087 (Si–O); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.42 (s, 12H, 2 × $SiMe_2$), 0.85–0.94 (m, 18H, 2 × CH_3CH_2-CH_2O overlapped with 2 × $(CH_3)_2CHCH_2O$), 1.12 (t, 6H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 1.7–1.8 (m, 10H, 4 × $CH_3CH_2CH_2O$ overlapped with 2 × $(CH_3)_2CHCH_2O$), 3.1 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 3.4 (d, 4H, J = 7 Hz, 2 × $(CH_3)_2CHCH_2O$), 3.68 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.06 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.2 Hz, 4 × Ar*CH*Ar), 6.04 (d, 4H, J = 7.5 Hz, aromatic), 6.11 (t, 2H, J = 7 Hz, aromatic), 7.3 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −1.5 (SiMe), 8.7, 9.9, 18.2, 21.9, 22.5, 29.7, 30.1, 67.1, 76.4, 76.6, 120.5, 126.3, 128.0, 131.3, 131.5, 136.2, 153.9, 158.3 ppm; *Anal.* Calc. for $C_{52}H_{76}O_6Si_2$: C, 73.2; H, 8.9. Found: C, 72.8; H, 8.7%.

4.6. General procedure for the hydrosilylation of 5,17-bis(dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**2**) with various alkenes

In 50 ml round-bottom two-neck flask with a magnetic stirring under argon 2.8 mmol of alkene was dissolved in 5 ml of freshly distilled dry THF. To this solution was added 25 μl ([Pt]/[Si–H] = 3.9×10^{-6}) of Karstedt catalyst, 0.28 mmol of calixarene **2** in 5 ml dry THF was added via syringe and the reaction was stirred at room temperature until all of the starting material was consumed (10–15 min). After a short initial period, the reaction mixture turned black due to the formation of colloidal platinum. Several samples were taken at different times and were analyzed by FTIR spectroscopy. After the reaction was complete, activated carbon was added to the solution to help remove the colloidal platinum and the solution was filtered and concentrated under reduced pressure to provide viscous oil. The products were recrystallized (CH_2Cl_2–MeOH, 10:90) to yield the analytical pure samples.

4.6.1. 5,17-Bis(2-phenyl ethyl dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (4a)

Yield 80%; m.p. 106–108 °C; FTIR (KBr, cm^{-1}): 3060 (HC=), 1584, 1455 (Ph), 1248 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.35 (s, 12H, 2 × $SiMe_2$), 0.89 (t, 6H, J = 7.5 Hz, 2 × $CH_3CH_2CH_2O$), 1.14 (t, 6H, J = 6.8 Hz, 2 × $CH_3CH_2CH_2O$), 1.18 (t, 4H, J = 5 Hz, 2 × CH_2CH_2Si), 1.84–1.99 (m, 8H, 4 × $CH_3CH_2CH_2O$), 2.67 (m, 4H, 2 × $PhCH_2CH_2$), 3.1 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 3.68 (t, 4H, J = 6.6 Hz, 2 × $CH_3CH_2CH_2O$), 4.05 (t, 4H, J = 8.1 Hz, 2 × CH_3CH_2-CH_2O), 4.4 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 6.0 (d, 4H, J = 7.5 Hz, aromatic), 6.1 (t, 2H, J = 7.2 Hz, aromatic), 7.16–7.27 (m, 14H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.8 (SiMe), 9.7, 10.8, 18.5, 23.0, 23.5, 30.2, 31.0, 76.3, 76.5, 122.0, 125.4, 127.1, 127.7, 128.2, 131.1, 133.1, 134.4, 136.5, 146.5, 155.1, 158.

4.6.2. 5,17-Bis(2-(p-chloromethyl phenyl) ethyl dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**4b**)

Yield 65%; m.p. 108–110 °C; FTIR (KBr, cm^{-1}): 3065 (HC=), 1585, 1456 (Ph), 1252 (Si–CH_3), ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.36 (s, 12H, 2 × $SiMe_2$), 0.90 (t, 6H, J = 7.5 Hz, 2 × $CH_3CH_2CH_2O$), 1.02 (t, 4H, J = 5 Hz, 2 × CH_2CH_2Si), 1.12 (t, 6H, J = 7.5 Hz, 2 × $CH_3CH_2CH_2O$) 1.85–1.98 (m, 8H, 4 × $CH_3CH_2CH_2O$), 2.69 (m, 4H, 2 × $PhCH_2CH_2$), 3.1 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 3.69 (t, 4H, J = 7 Hz, 2 × $CH_3CH_2CH_2O$), 4.06 (t, 4H, J = 8 Hz, 2 × CH_3CH_2-CH_2O), 4.4 (d, 4H, J = 13.2 Hz, 4 × Ar*CH*Ar), 4.58 (s, 4H, 2 × $ClCH_2Ph$), 6.0 (d, 4H, J = 7.8 Hz, aromatic), 6.1 (t, 2H, J = 7.2 Hz, aromatic), 7.19–7.32 (m, 12H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.7 (SiMe), 9.7, 10.3, 18.5, 23.0, 23.5, 30.0, 31.0, 46.2, 76.3, 76.5, 121.9, 122.0, 127.9, 128.5,128.8, 131.0, 133.1, 134.4, 136.5, 145.8, 155.1, 159.1 ppm.

4.6.3. 5,17-Bis(2-methyl-2-phenyl ethyl dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**4c**)

Yield 72%; m.p. 67–69 °C; FTIR (KBr, cm^{-1}): 3058 (HC=), 1586, 1458 (Ph), 1255 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.3 (s, 12H, 2 × $SiMe_2$), 0.88–0.94 (m, 12H, 2 × $CH_3CH_2CH_2O$ over lapped with 2 × $CH_2CH(CH_3)Ph$), 1.02 (t, 4H, J = 5 Hz, 2 × CH_2CH_2Si), 1.12 (t, 6H, J = 7.5 Hz, 2 × $CH_3CH_2CH_2O$) 1.86–1.98 (m, 8H, 4 × CH_3CH_2-CH_2O), 3.1 (d, 4H, J = 13.5 Hz, 4 × Ar*CH*Ar), 3.6 (t, 4H, J = 6.7 Hz,

2 × $CH_3CH_2CH_2O$), 4.02 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.2(m, 2H, 2 × $CH_2CH(CH_3)Ph$), 4.4 (d, 4H, J = 13.5 Hz, 4 × ArCHAr), 6.0 (d, 4H, J = 7.8 Hz, aromatic), 6.1 (t, 2H, J = 7.2 Hz, aromatic), 7.10–7.27 (m, 14H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.7 (SiMe), 9.5, 10.1, 14.0, 22.6, 22.9, 30.2, 31.9, 76.3, 76.5, 121.7, 121.8, 127.7, 128.0, 128.5, 130.8, 132.4, 134.2, 136.3, 145.7, 155.1, 158.1 ppm.

*4.6.4. 5,17-Bis(3-(2,3-epoxypropoxy)propyl dimethylsilyl)-25,26,27,28-tetra propoxy calix[4]arene (**4d**)*

Yield 85%; m.p. 76–78 °C; FTIR (KBr, cm^{-1}): 3060 (HC═), 1585, 1457 (Ph), 1251 (Si–CH_3), 1109 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.33 (s, 12H, 2 × $SiMe_2$), 0.79 (t, 4H, J = 7.8 Hz, 2 × $CH_2CH_2CH_2Si$), 0.88 (t, 6H, J = 7.2 Hz, 2 × $CH_3CH_2CH_2O$), 1.11 (t, 6H, J = 7.2 Hz, 2 × $CH_3CH_2CH_2O$), 1.6 (m, 4H, 2 × $CH_2CH_2CH_2Si$), 1.84–1.97(m, 8H, 4 × $CH_3CH_2CH_2O$), 2.6(q, 2H, J = 2.7 Hz, 2 × CH_2–CH(O)CH–H), 2.8 (t, 2H, J = 4 Hz, 2 × CH_2–CH(O)CH–H), 3.1 (m, 6H, 4 × ArCHAr over lapped with 2 × CH_2–CH(O)CH–H), 3.37–3.53(m, 8H, 2 × $CH_2CH_2CH_2OCH_2$–CH(O)CH–H overlapped with 2 × CH_2-$CH_2CH_2OCH_2$–CH(O)CH–H), 3.6 (t, 4H, J = 7 Hz, 2 × $CH_3CH_2CH_2O$), 4.03 (t, 4H, J = 8 Hz, 2 × $CH_3CH_2CH_2O$), 4.4 (d, 4H, J = 13.5 Hz, 4 × ArCHAr), 6.0 (d, 4H, J = 6.6 Hz, aromatic), 6.1 (t, 2H, J=7 Hz, aromatic), 7.27 (s, 4H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −2.6 (SiMe), 9.7, 10.8, 12.1, 23.0, 23.5, 24.2, 31.0, 44.3, 50.9, 71.4, 74.4, 76.3, 76.5, 122.0, 127.2, 131.3, 133.2, 134.4, 136.4, 155.1, 159.0 ppm.

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