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Stereoselective dialkylation of the proximal hydroxy groups of calix- and thiacalix[4]arenes

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Treatment of *p-tert*-butylcalix[4]arene (**C1**) and its sulfur-bridged analog **T1** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in the presence of imidazole gives proximally *O*,*O*′-disiloxane-1,3-diyl-bridged calixarenes **C2** and **T2** in excellent yields, respectively. Subsequent base-catalyzed etherification of the remaining hydroxy groups with alkyl halides gives *syn*- and *anti*-*O*″,*O*‴-dialkylated products, the stereoselectivity of which varies depending on the nature of the macrocycle, as well as the metal cation of the base employed. Thus, conventional calixarene **C2** preferentially affords *syn* compounds of 1,2-alternate conformation (**C3**) with the aid of *tert*-BuOK and K_2CO_3 and *anti* counterparts of partial-cone conformation (**C4**) with Cs_2CO_3. On the other hand, thiacalixarene **T2** affords *syn* compounds of 1,2-alternate conformation (**T3**) with any of the bases. The disiloxanediyl bridge of the resulting products can readily be removed by treatment with tetrabutylammonium fluoride. Thus, the net process provides an efficient method for the regio- and stereoselective synthesis of proximally dialkylated calix[4]arenes.

Introduction

The calix[4]arene skeleton is an extensively utilized scaffold for the construction of synthetic receptors of metal ions and neutral molecules, taking advantage of easy availability and feasibility of various modifications at the phenolic hydroxy groups (lower rim), as well as at the *para* positions (upper rim), to develop varying functions.[1,2] It is well known in calixarene chemistry that dialkylation of calix[4]arenes with alkyl halides in the presence of a base occurs preferentially at the distal hydroxy groups by virtue of a circular intramolecular hydrogen bonding in the monoalkylated intermediate,[3] which provides an easy access to distally *O*,*O*′-dialkylated calix[4]arenes. On the other hand, a general protocol for the regioselective *O*,*O*′-dialkylation at the proximal hydroxy groups, which is highly desirable for the development of synthetic receptors,[4–7] has yet to be established despite efforts toward this end.[5–10]

Among such endeavors, a promising approach may be to block only one or two adjacent hydroxy groups of the starting calixarenes with a proper protective group before alkylation.[10] Shinkai *et al*. examined alkylation of mono-*O*-benzyl-protected *p-tert*-butylcalix[4]arene with 1-bromopropane to obtain, after debenzylation of the resulting triether, *syn*-*O*,*O*′-dipropyl ether.[6] On the other hand, Böhmer *et al*. proposed *O*,*O*′-bridging of calixarene **C1** with phthaloyl dichloride to protect two adjacent hydroxy groups.[7] However, the derivatization suffered from low yield and subsequent alkylation with ethyl bromoacetate gave, after hydrolysis, a mixture of *syn*- and *anti*-*O*,*O*′-diethers. Alternatively, Lattman *et al*. prepared *O*,*O*′-dimethylsilylene-bridged *p-tert*-butylcalix[4]arene, attempted proximal dimethylation of which with butyllithium and methyl trifluoromethanesulfonate resulted in failure, giving not the desired product but a doubly *O*,*O*′- and *O*″,*O*‴-silylene-bridged compound, accompanied by the formation of tetramethyl ether of calixarene **C1**.[9] During the course of our studies on the development of novel functions of thiacalixarene **T1**,[11] we have found that the 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl (TIPDS) moiety is quite useful as a protective group for the proximal dialkylation to give *syn*- and *anti*-*O*″,*O*‴-dialkylated products stereoselectively, depending on the reaction conditions.[12] Herein we report the net proximal dialkylation of calix- and thiacalix[4]arenes **C1** and **T1** with high stereoselectivity *via* TIPDS derivatives **C2** and **T2** in detail. Also reported is the mechanism of the high *syn*/*anti* selectivity deduced from a detailed study of stepwise alkylation monitored by ^{1}H NMR spectroscopy.

Results and discussion

Synthesis of *syn*- and *anti*-*O*,*O*′-dialkylcalixarenes

Calixarenes **C1** and **T1** were treated with an excess of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in DMF in the presence of imidazole at room temperature to give, after one crystallization from dichloromethane–methanol, proximally *O*,*O*′-bridged derivatives **C2** and **T2** in 90 and 92% yields, respectively (Scheme 1). It is of interest to note that the reaction gave neither detectable amounts of *O*,*O*″-bridged isomer nor intermolecularly bridged oligomers without relying on a high-dilution technique (see Experimental section). It seems that the short chain length of three atoms, with the aid of the steric bulk of the four isopropyl substituents, prevented the dichloride from such unwanted bridging.

The dialkylation of the TIPDS derivatives **C2** and **T2** was performed by treatment with an alkyl halide in THF in the presence of a base at appropriate temperatures (Scheme 2, Table 1). The reaction gave the corresponding *syn*- (**C3** and **T3**) and *anti*-*O*″,*O*‴-dialkylated products (**C4** and **T4**) in good to excellent yields except the cases of iodobutane with K_2CO_3 (entries 5 and 15). The product ratio varied depending on the substrate, as well as the metal cation of the base employed. Thus, in the dialkylation of conventional calixarene **C2**, *tert*-BuOK gave *syn* compound **C3** exclusively with no detectable amount of *anti* counterpart **C4** (entries 1–3). A weaker base bearing potassium

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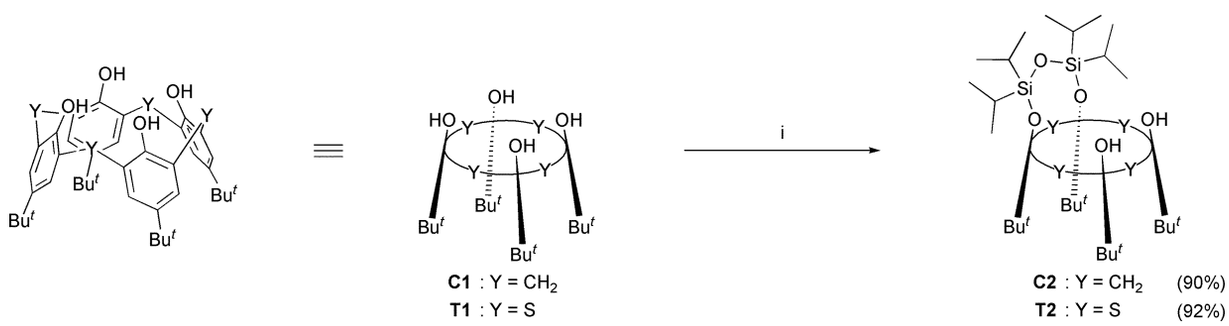
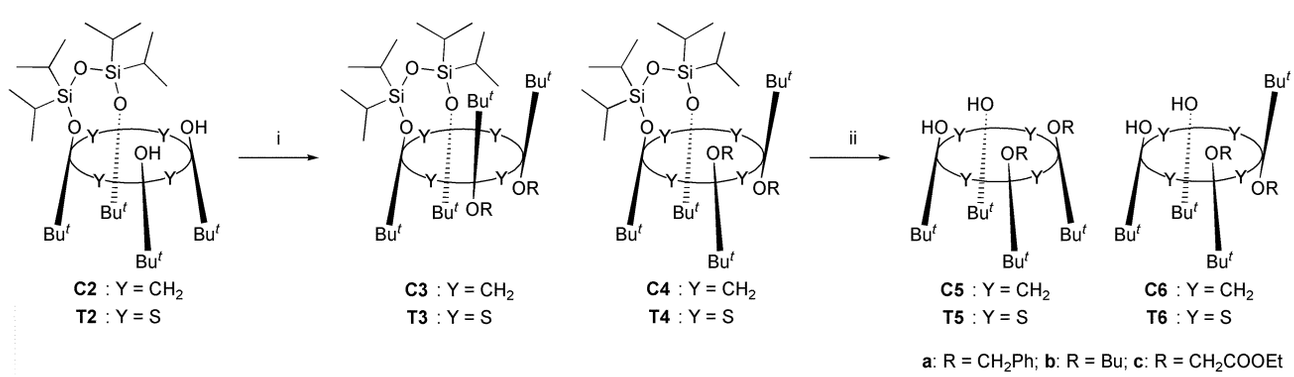
Table 1 Dialkylation of TIPDS derivatives **C2** and **T2** with RX in THF

Entry	Starting material	RX (mol equiv.)	Base (mol equiv.)	Temp./°C	Time	Yield (%) [Product] **C3** or **T3**	**C4** or **T4**
1	**C2**	$BrCH_2Ph$ (6.0)	*tert*-BuOK (3.0)	0	1 h	90 [**C3a**]	0 [**C4a**]
2		BuI (6.0)	*tert*-BuOK (3.0)	0	2 h	67 [**C3b**]	0 [**C4b**]
3		$BrCH_2COOEt$ (6.0)	*tert*-BuOK (3.0)	0	2 h	52 [**C3c**]	0 [**C4c**]
4[a]		$BrCH_2Ph$ (20.0)	K_2CO_3 (20.0)	Reflux	5 days	61 [**C3a**]	6 [**C4a**]
5[b]		BuI (20.0)	K_2CO_3 (20.0)	Reflux	5 days	13 [**C3b**]	0 [**C4b**]
6		$BrCH_2COOEt$ (6.0)	K_2CO_3 (6.0)	Reflux	12 h	79 [**C3c**]	16 [**C4c**]
7		$BrCH_2Ph$ (8.0)	Cs_2CO_3 (6.0)	Reflux	12 h	2 [**C3a**]	94 [**C4a**]
8		BuI (8.0)	Cs_2CO_3 (6.0)	Reflux	18 h	2 [**C3b**]	85 [**C4b**]
9		$BrCH_2COOEt$ (6.0)	Cs_2CO_3 (6.0)	Reflux	6 h	69 [**C3c**]	25 [**C4c**]
10[c]		$BrCH_2COOEt$ (6.0)	Cs_2CO_3 (6.0)	Reflux	4 h	28 [**C3c**]	68 [**C4c**]
11	**T2**	$BrCH_2Ph$ (6.0)	*tert*-BuOK (3.0)	RT	2 days	63 [**T3a**]	0 [**T4a**]
12[d]		BuI (6.0)	*tert*-BuOK (3.0)	RT	4 days	58 [**T3b**]	0 [**T4b**]
13		$BrCH_2COOEt$ (6.0)	*tert*-BuOK (3.0)	RT	4	67 [**T3c**]	0 [**T4c**]
14		$BrCH_2Ph$ (20.0)	K_2CO_3 (20.0)	Reflux	24	81 [**T3a**]	8 [**T4a**]
15[e]		BuI (20.0)	K_2CO_3 (20.0)	Reflux	5 days	26 [**T3b**]	0 [**T4b**]
16		$BrCH_2COOEt$ (6.0)	K_2CO_3 (6.0)	Reflux	9	88 [**T3c**]	0 [**T4c**]
17		$BrCH_2Ph$ (6.0)	Cs_2CO_3 (6.0)	Reflux	4	74 [**T3a**]	9 [**T4a**]
18		BuI (8.0)	Cs_2CO_3 (6.0)	Reflux	9	88 [**T3b**]	0 [**T4b**]
19		$BrCH_2COOEt$ (6.0)	Cs_2CO_3 (6.0)	Reflux	4	88 [**T3c**]	trace [**T4c**]

[a] Monoalkylated compound **C8a** was obtained in 21% yield. [b] Monoalkylated compound **C7b** and **C8b** were obtained in 64 and 13% yields, respectively. [c] The reaction was carried out in THF–DMF (4:1). [d] Monoalkylated compound **T7b** was obtained in 24% yield. [e] Monoalkylated compound **T7b** was obtained in 63% yield.



Scheme 1 *Reagents:* i, 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane, imidazole, DMF.



Scheme 2 *Reagents:* i, RX, base, THF; ii, tetrabutylammonium fluoride, THF.

cations, K_2CO_3, also gave *syn* compound **C3** preferentially, though it was less active than *tert*-BuOK (entries 4–6). Alternation of the base to Cs_2CO_3, however, drastically shifted the stereoselectivity toward the *anti* counterpart **C4** (entries 7–10). Almost perfect *anti*-selective dialkylation was achieved with bromomethylbenzene and iodobutane (entries 7 and 8), compensating well the *syn* selectivity achieved by the use of *tert*-BuOK (entries 1 and 2). Thus, a practical synthesis of both the stereoisomers is now available only by changing the base. Although the dialkylation with ethyl bromoacetate still preferred the formation of *syn* isomer **C3c** even by using Cs_2CO_3, an addition of DMF greatly improved the *anti* selectivity (entries 9 and 10). On the other hand, the stereoselectivity in the dialkylation of thiacalixarene **T2** was not altered by the metal cation, giving *syn* isomer **T3** selectively (entries 11–19). Addition of DMF had no effect on the stereoselectivity in this case.

Desilylation of the dialkylated products was carried out by a simple treatment with tetrabutylammonium fluoride in THF to liberate the corresponding proximally *O*,*O*′-dialkylated calix[4]arenes quantitatively (Scheme 2).

Structural analyses of compounds C2–6 and T2–6

The TIPDS derivative **C2** showed the molecular ion peak at 891 (M^+) in the FAB mass spectrum, indicating that it is an intramolecularly bridged compound. Its ^1H NMR spectrum in $CDCl_3$ showed two singlets (18 H each) for the *tert*-butyl protons and four doublets (2 H each) for the aryl protons to

support *O*,*O*′- rather than *O*,*O*″-bridged structures, as the latter should show only two singlets for the aryl protons. It is known that the chemical shift difference ($\Delta\delta$) between the geminal protons of a bridging methylene group of conventional calix[4]arenes varies depending on the circumstances.[1a] Thus, the methylene protons between two adjacent phenol units of *syn* conformation have the $\Delta\delta$ value of *ca.* 0.9 ppm in nonpolar solvents, whereas those between the units of *anti* conformation less than 0.5 ppm. Compound **C2** showed $\Delta\delta$ values of more than 0.9 ppm for all the methylene groups, indicating that it adopted a cone conformation in solution. The intramolecularly proximally bridged structure of the thiacalixarene analog **T2** was also deduced from the molecular ion peak at 963 (M^+) in the FAB mass spectrum and the resonance patterns of the *tert*-butyl and aryl protons in the ^{1}H NMR spectrum as described for compound **C2**. Although compound **T2** lacks methylene bridges which have been a probe for assigning the conformation of conventional calix[4]arenes, its conformation was rather safely deduced to be cone by comparing the chemical shifts of the methyl protons of the TIPDS moiety [four doublets (6 H each) at δ 0.80–1.38] with those of compound **C2** [four doublets (6 H each) at δ 0.79–1.37]; if compound **T2** adopted 1,2-alternate conformation, these protons should appear at a higher field (*ca.* 0.4 ppm) because of the anisotropic shielding effects by the facing benzene rings (*vide infra*).

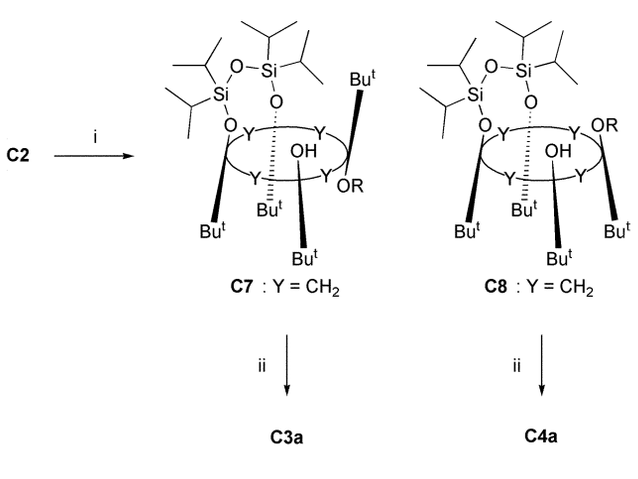
The stereochemistry of dialkylated compounds **C3**, **T3**, **C4** and **T4** was determined by ^{1}H and ^{13}C NMR analyses as exemplified by the cases of dibenzyl ethers **C3a** and **C4a** given below. The ^{1}H NMR spectrum of dibenzyl ether **C3a** showed two singlets (18 H each) for the *tert*-butyl protons and four doublets (2 H each) for the aromatic protons, indicating that the compound adopted either cone or 1,2-alternate conformation with the *syn* arrangement of the two benzyl moieties. The signals of the bridging methylene protons appeared as three pairs of doublets with an intensity ratio of 1 : 2 : 1. The double intensity signals, which are assigned to the methylenes between the benzene ring bearing a siloxy moiety and that bearing a benzyloxy moiety, had the $\Delta\delta$ value (0.2 ppm) of less than 0.5 ppm, indicating that the compound adopted 1,2-alternate conformation. The methyl signals of the TIPDS moiety appeared at a higher field [δ 0.31, 0.71, 0.95 and 0.99 (each 6 H)] than those of compound **C2** (δ 0.79, 1.10, 1.31 and 1.37), which was attributed to the shielding effects by the facing benzene rings. It has been reported that conformation of calix[4]arenes can be deduced from the ^{13}C NMR chemical shifts of the methylene signals. Thus, methylene carbons between two adjacent phenol units of *syn* conformation resonate at 30–32 ppm, whereas those between the units of *anti* conformation at 37–39 ppm.[13] Dibenzyl ether **C3a** showed three signals at δ 33.8, 34.0 and 39.2 for the bridging methylene carbons, which supported the assignment based on the ^{1}H NMR analysis. On the other hand, the ^{1}H NMR spectrum of compound **C4a** showed four singlets (9 H each) for the *tert*-butyl protons and eight doublets (1 H each) for the aromatic protons. The unsymmetrical spectral patterns unambiguously assigned the compound to the *anti* isomer of partial-cone conformation. The conformation of thiacalixarene derivatives **T3** was determined to be 1,2-alternate similarly to the case of the methylene-bridged analogs **C3** based on the splitting patterns of the *tert*-butyl and aromatic protons combined with the upfield shifts of the methyl signals of the TIPDS moiety in the ^{1}H NMR spectra. The NOESY spectrum of dibenzyl ether **T3a** revealed a correlation between the methyl protons of the TIPDS moiety and the *tert*-butyl protons to support the assignment.

Desilylated *syn*-diethers **C5** had $\Delta\delta$ values of larger than 0.9 ppm for all four methylene protons, indicating that the compounds adopted cone conformation in solution.[5,14] The ^{1}H NMR spectrum of the *anti* counterparts **C6** showed one singlet (2 H) for the hydroxy protons, two singlets (18 H each) for the *tert*-butyl protons and four doublets (2 H each) for the aryl protons, the magnetic equivalences suggesting C_2-symmetric structure. On the other hand, only one methylene carbon appeared around 32 ppm in the ^{13}C NMR spectra, indicating that only two aryl units adjacent to the methylene group statically adopted *syn* conformation. These observations indicate that *anti*-diethers **C6** rapidly interconvert between two partial-cone conformations in solution. Although sulfur-bridged analogs **T5** and **T6** lack structural information from the bridging moieties in the NMR analysis, their conformations are expected to be the same as those of the corresponding methylene-bridged ones, considering the similarities in their ^{1}H NMR spectra.

Mechanistic consideration of the dialkylation reaction

In order to gain insight into the origin of the high stereoselectivity in the dialkylation, a stepwise alkylation of the TIPDS derivative **C2** was examined (Scheme 3, Table 2). Monoalkylation of compound **C2** could be achieved by decreasing molar equivalences of the alkyl halide and the base to the substrate and reducing the reaction time to give compounds **C7** and **C8**. Both compounds (*e.g.* **C7a** and **C8a**) showed four singlets (9 H each) for the *tert*-butyl protons and eight doublets (1 H each) for the aryl protons in the ^{1}H NMR spectra in accordance with their unsymmetrical structures. All the $\Delta\delta$ values of the methylene protons of compound **C8a** were larger than 0.9 ppm, indicating that the compound adopted cone conformation and thus the benzyl group was introduced from the same side to the TIPDS moiety in regard to the mean plane of the macrocycle. On the other hand, the conformation of counterpart **C7a** could not be deduced from its NMR spectra, though it is apparent that the benzyl group was introduced from the opposite side to the TIPDS moiety, considering the fact that benzylation of this compound gave dibenzyl ether **C3a** with 1,2-alternate conformation (*vide infra*). The stereoselectivity of the monoalkylation was strongly affected by the base employed. Thus, K_2CO_3 preferentially gave compound **C7** (entries 1 and 2), while Cs_2CO_3 gave compound **C8** except the alkylation with ethyl bromoacetate (entries 3–5). Monobenzyl ethers **C7a** and **C8a** were then treated with bromomethylbenzene (6 mol equiv.) in the presence of Cs_2CO_3 (6 mol equiv.) in THF to give dibenzyl ethers **C3a** and **C4a** in 92 and 88% yields, respectively, as single stereoisomers (Scheme 3). These observations should indicate that the second alkylation in the one-pot dialkylation occurs from the opposite side to the TIPDS moiety regardless of the stereochemistry of the monoalkylated intermediates and that the net stereochemistry of the dialkylation is determined at the first alkylation step.

The reaction mechanism was supported by ^{1}H NMR analyses of metal salts formed by treatment of the substrates with the



Scheme 3 *Reagents:* i, RX, base, THF; ii, bromomethylbenzene, Cs_2CO_3, THF.

Table 2 Monoalkylation of TIPDS derivative **C2** with RX in THF at reflux

Entry	RX (mol equiv.)	Base (mol equiv.)	Time/h	Yield (%) [Product]	
				C7	**C8**
1	$BrCH_2Ph$ (6.0)	K_2CO_3 (6.0)	8	70 [**C7a**]	18 [**C8a**]
2	BuI (12.0)	K_2CO_3 (12.0)	30	78 [**C7b**]	18 [**C8b**]
3	$BrCH_2Ph$ (2.0)	Cs_2CO_3 (2.0)	4	0 [**C7a**]	89 [**C8a**]
4	BuI (4.0)	Cs_2CO_3 (2.0)	6	3 [**C7b**]	77 [**C8b**]
5[a]	$BrCH_2COOEt$ (1.1)	Cs_2CO_3 (1.0)	10	34 [**C7c**]	21 [**C8c**]

[a] Dialkylated compound **C3c** was obtained in 28% yield.

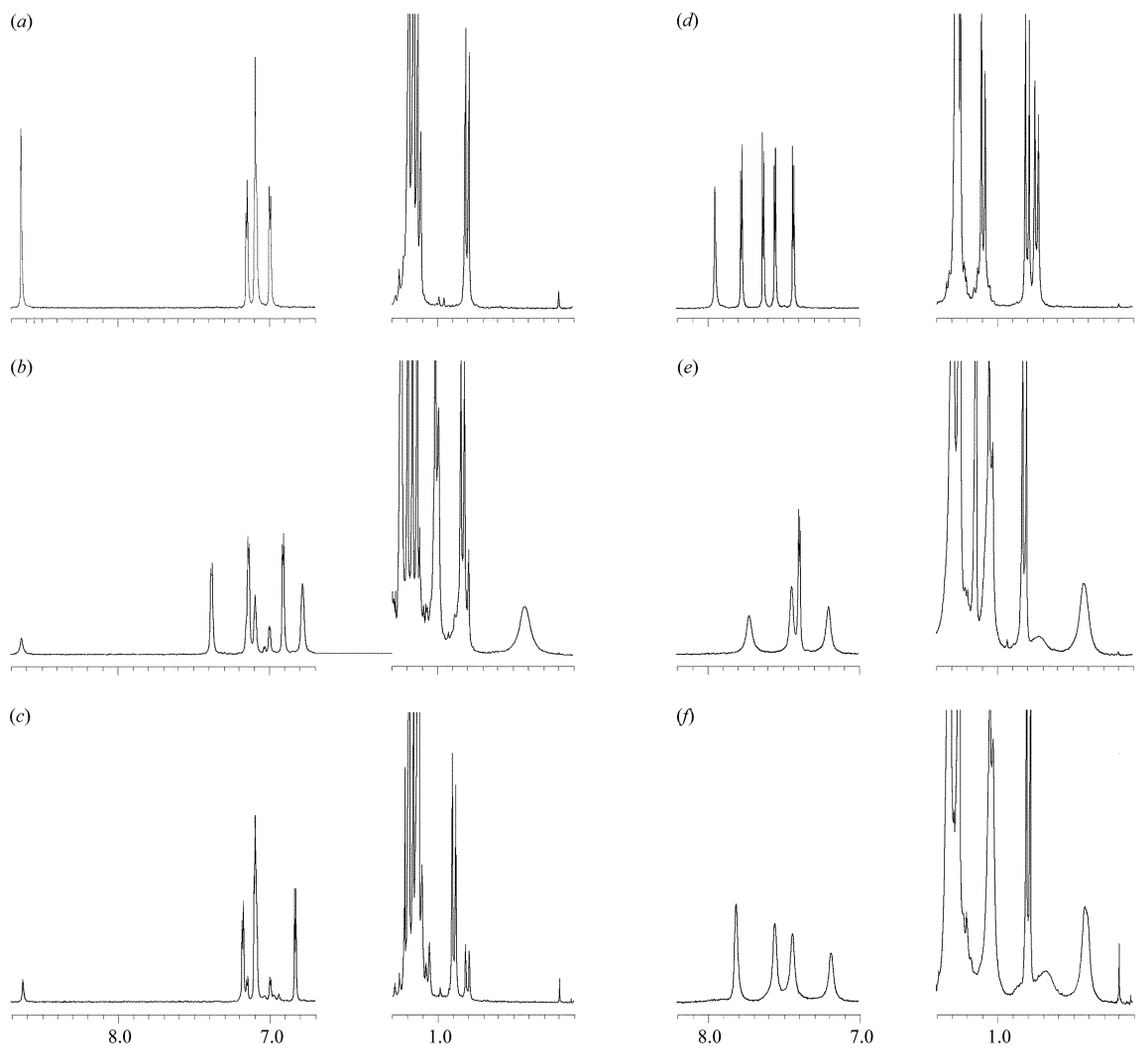
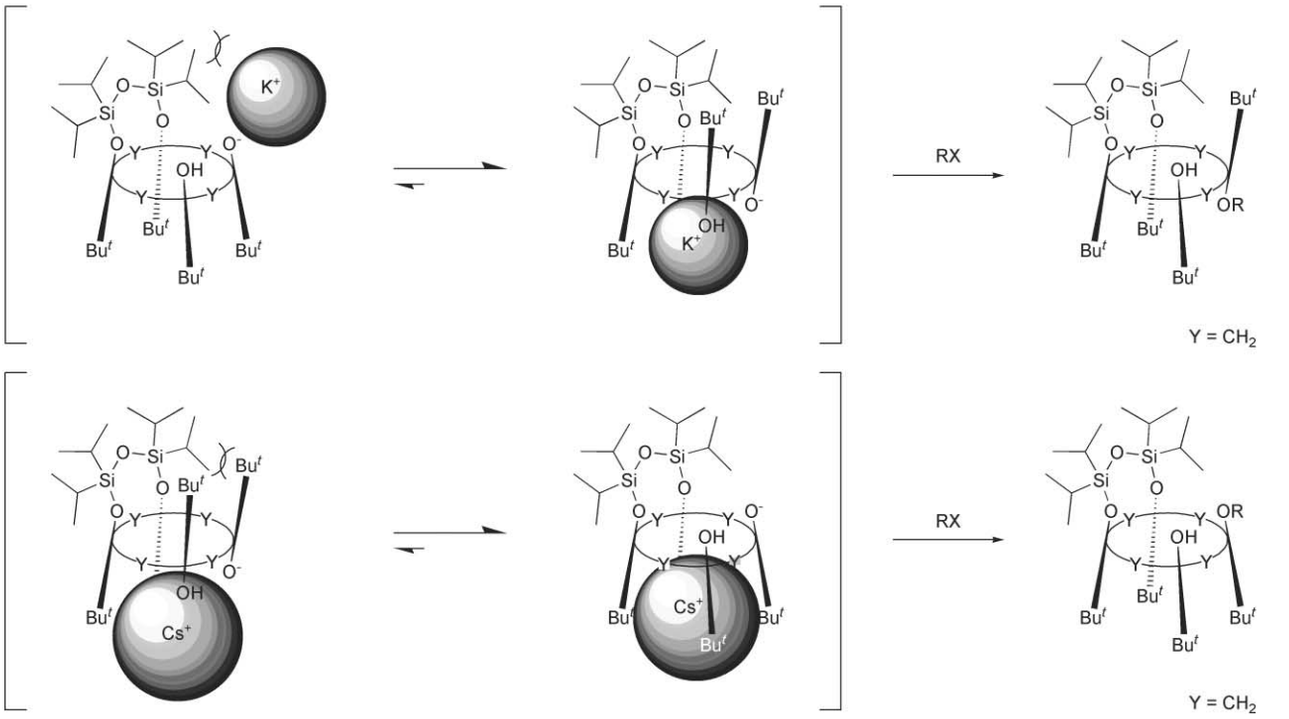


Fig. 1 ^{1}H NMR spectra (300 MHz) of 10.0 mM solution of TIPDS derivatives **C2** (*a*–*c*) and **T2** (*d*–*f*) in THF-d_8 in the presence or absence of a base at 20 °C: (*a* and *d*) no base; (*b* and *e*) *tert*-BuOK (1.0 mol equiv.); (*c* and *f*) Cs_2CO_3 (saturated).

bases. Fig. 1 shows the ^{1}H NMR spectra of compounds **C2** and **T2** measured in the presence or absence of a base in THF-d_8. The signals of the free calixarene decreased or even disappeared by addition of 1.0 mol equiv. of *tert*-BuOK or an excess of Cs_2CO_3 with the appearance of new signals, indicating the formation of a salt between the phenoxide and the metal cation. As mentioned above, TIPDS derivatives of 1,2-alternate conformation can be distinguished from those of the other conformations by ^{1}H NMR spectrum, where some of the methyl protons of the TIPDS moiety are strongly shielded by the facing benzene ring, appearing around 0.4 ppm. Based on this criteria, the conformation of the salt between the monoanion of compound **C2** and K^+ was assigned as 1,2-alternate (*b*). The monoanion seems to bind to a K^+ ion in this conformation to avoid steric repulsion imposed by the bulky TIPDS moiety, with the aid of coordination of the adjacent phenolic hydroxy group and cation-π interactions with the two benzene rings bridged by the TIPDS moiety.[15] On the other hand, the cesium salt of compound **C2** showed two singlets for the *tert*-butyl protons and four doublets for the aryl protons with no methyl signals of the TIPDS moiety around 0.4 ppm (*c*), indicating that the salt adopted a cone conformation. It has been reported that the monocesium salt of *p*-*tert*-butylcalix[4]arene adopts a cone conformation in the solid state and chloroform solution, the metal ion being included within the calixarene cavity through interactions with the π electrons of the aromatic rings.[16] Therefore, it seems likely that in the cone conformation of the monoanion of compound **C2**, the Cs^+ ion is also located within the cavity and the resulting cation-π interactions stabilize the cone conformation. The stereochemical course of the dialkylation can be rationalized by the conformations of these salts which should mediate the reaction (Scheme 4). Thus, the first alkylation of the potassium salt of 1,2-alternate conformation should occur from the opposite side to the TIPDS moiety to give monoalkyl-



Scheme 4

ated intermediate **C7**, while a similar reaction of the cesium salt of cone conformation will occur from the same side to give intermediate **C8**. The second alkylation seems to be allowed only from the opposite side to the TIPDS moiety in both cases because of the steric congestion, yielding the dialkylated products of *syn* (**C3**) and *anti* (**C4**) conformations for K^+ and Cs^+ ions, respectively.[7] On the contrary, because the metal salts of thiacalix[4]arene tend to form five-membered bischelate complexes by coordination of the adjacent hydroxy group and a bridging sulfur atom,[17] the cesium salt, as well as the potassium salt, adopts 1,2-alternate conformation like the potassium salt of conventional calixarene **C2**, as is clearly shown by the ^{1}H NMR analysis [Fig. 1, (*e*) and (*f*)]. Thus the first alkylation should occur from the opposite side to the TIPDS moiety, giving *syn* diether **T3**.

Conclusion

We have shown here that the 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl unit is very useful in protecting two adjacent hydroxy groups of calix[4]arenes; the *O,O′*-capping reaction, subsequent alkylation of the remaining hydroxy groups and final desilylation proceed quite smoothly with excellent yields to provide an efficient method for the net proximal dialkylation of calix[4]arenes. The *syn*/*anti* selectivity in the alkylation was very high and could be altered by the entity of the macrocycle and the metal cation of the base employed, the origin of which was ascribed to the conformation of the metal salt generated *in situ* from the macrocycle and the base.

Experimental

Mps were taken using a Mitamura Riken MP-P or Yamato IA-9000 apparatus. Samples for the mp measurement were routinely recrystallized from dichloromethane–methanol, unless otherwise noted. Microanalyses were carried out in the Microanalytical Laboratory of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. IR spectra were recorded on a JEOL JIR-3510 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400, DRX-500 or JEOL JNM-ECA300 spectrometer using tetramethylsilane (^{1}H NMR) or chloroform (^{13}C NMR) as an internal standard and $CDCl_3$ as a solvent, unless otherwise noted. *J*-values are given in Hz. Mass spectra were measured on a JEOL JMS-DX602 spectrometer. Silica gel columns were prepared by use of Merck silica gel 60 (63–200 μm). THF was distilled from sodium diphenylketyl just before use. Compound **C1** was prepared according to the Gutsche's procedure.[18] Compound **T1** was prepared as described previously.[11a] Other materials were used as purchased.

General procedure for the preparation of TIPDS derivatives C2 and T2

To a suspension of calix[4]arene **C1** or **T1** (5.00 mmol) in dry DMF (50 cm^3) was added imidazole (1.02 g, 15.0 mmol) and the mixture was stirred at room temperature for 30 min. To the mixture was added dropwise a solution of TIPDSCl (1.90 g, 6.02 mmol) in DMF (25 cm^3) over 1 h and the resulting mixture was stirred for 11 h. The mixture was cooled to 0 °C and quenched by addition of 2 M HCl (100 cm^3) to liberate a precipitate, which was collected by filtration, washed with water and then purified by recrystallization from dichloromethane–methanol.

Compound C2. As a colorless powder (90%), mp 238–240 °C (Found: C, 75.2; H, 9.3. Calc. for $C_{56}H_{82}O_5Si_2$: C, 75.5; H, 9.3%); δ_H(500 MHz) 0.79 (6 H, d, *J* 7.4, CHCH_3 × 2), 1.10 (6 H, d, *J* 7.4, CHCH_3 × 2), 1.17 [18 H, s, C(CH_3)$_3$ × 2], 1.17–1.21 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.23 [18 H, s, C(CH_3)$_3$ × 2], 1.31 (6 H, d, *J* 7.4, CHCH_3 × 2), 1.37 (6 H, d, *J* 7.4, CHCH_3 × 2), 1.47–1.53 [2 H, m, CH(CH$_3$)$_2$ × 2], 3.33–3.42 (4 H, m, ArCHAr × 4), 4.20 (1 H, d, *J* 13.6, ArCHAr), 4.55 (1 H, d, *J* 13.3, ArCHAr), 4.60 (2 H, d, *J* 13.1, ArCHAr × 2), 6.95 (2 H, d, *J* 2.5, ArH × 2), 6.98 (2 H, d, *J* 2.3, ArH × 2), 7.02 (2 H, d, *J* 2.5, ArH × 2), 7.06 (2 H, d, *J* 2.3, ArH × 2) and 8.66 (2 H, s, OH × 2); *m*/*z* (FAB) 891 (M^+).

Compound T2. As a colorless powder (92%), mp 308–310 °C (Found: C, 64.7; H, 7.7; S, 13.3. Calc. for $C_{52}H_{74}O_5S_4Si_2$: C, C, 64.8; H, 7.7; S, 13.3%); δ_H(500 MHz) 0.80 (6 H, d, *J* 7.6, CHCH_3 × 2), 1.14–1.20 [14 H, m, CHCH_3 × 4 and CH(CH$_3$)$_2$ × 2], 1.16 [18 H, s, C(CH_3)$_3$ × 2], 1.24 [18 H, s, C(CH_3)$_3$ × 2], 1.32–1.39 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.38 (6 H, d, *J* 2.1, CHCH_3

× 2), 7.49 (2 H, d, *J* 2.5, ArH × 2), 7.51 (2 H, d, *J* 2.5, ArH × 2), 7.54–7.56 (4 H, m, ArH × 4) and 8.12 (2 H, s, OH × 2); *m*/*z* (FAB) 963 [(M + 1)$^+$].

General procedure for the alkylation of TIPDS derivatives C2 and T2 (Tables 1 and 2)

To a 50.0 mM solution of compound **C2** or **T2** in dry THF were added a base and an alkyl halide at 0 °C (Table 1, entries 1–3) or room temperature (the other entries) and the mixture was stirred at an appropriate temperature for 1 h to 5 days, after which it was cooled to 0 °C and quenched with 2 M HCl. The mixture was extracted with chloroform and the extract was washed successively with 2 M HCl and water, dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel by using the indicated eluent. See Tables 1 and 2 for the reaction conditions and the product yields.

Compound C3a. Dichloromethane–hexane (1 : 3) as the eluent; crystals, mp 238–239 °C (Found: C, 78.4; H, 8.8. Calc. for $C_{70}H_{94}O_5Si_2$: C, 78.5; H, 8.8%); δ_H(500 MHz) 0.31 (6 H, d, *J* 7.5, CHCH_3 × 2), 0.71 (6 H, d, *J* 7.0, CHCH_3 × 2), 0.74–0.82 [2 H, m, CH(CH$_3$)$_2$ × 2], 0.95 (6 H, d, *J* 7.0 Hz, CHCH_3 × 2), 0.99 (6 H, d, *J* 7.5, CHCH_3 × 2), 0.97–1.06 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.14 [18 H, s, C(CH$_3$)$_3$ × 2], 1.26 [18 H, s, C(CH$_3$)$_3$ × 2], 2.30 (1 H, d, *J* 12.3, ArCHAr), 3.32 (1 H, d, *J* 12.3, ArCHAr), 3.36 (1 H, d, *J* 13.3, ArCHAr), 3.75 (2 H, d, *J* 16.5, ArCHAr × 2), 3.96 (2 H, d, *J* 12.2, OCHPh × 2), 3.97 (2 H, d, *J* 16.5, ArCHAr × 2), 4.14 (2 H, d, *J* 12.2, OCHPh × 2), 4.43 (1 H, d, *J* 13.3, ArCHAr), 6.19 (4 H, d, *J* 7.3, OCH$_2$*Ph* × 2), 6.91 (2 H, d, *J* 2.4, ArH × 2), 6.94–6.97 (6 H, m, ArH × 2, OCH$_2$*Ph* × 2), 7.03–7.06 (4 H, m, ArH × 2, OCH$_2$*Ph* × 2) and 7.25 (2 H, d, *J* 2.4, ArH × 2); δ_C(125 MHz) 13.71, 14.02, 16.67, 16.87, 17.21, 17.68, 29.29, 31.29, 31.52, 33.72, 34.01, 34.17, 39.60, 73.59, 125.00, 125.05, 125.44, 125.56, 126.18, 127.35, 127.87, 129.36, 130.65, 132.10, 135.13, 137.82, 142.30, 144.28, 149.82 and 152.75; *m*/*z* (FAB) 1071 (M$^+$).

Compound C3b. Dichloromethane–hexane (1 : 3) as the eluent; crystals, mp 243–244 °C (Found: C, 76.6; H, 9.9. Calc. for $C_{64}H_{98}O_5Si_2$: C, 76.6; H, 9.8%); δ_H(300 MHz) 0.36 (6 H, d, *J* 7.2, CHCH_3 × 2), 0.56–0.72 (2 H, m, OCH$_2$CH × 2), 0.72–0.85 [14 H, m, CHCH_3 × 2, CH(CH$_3$)$_2$ × 2 and CH$_2$CH_3 × 2], 0.91–0.96 (12 H, m, CHCH_3 × 4), 0.92–1.18 [8 H, m, CH(CH$_3$)$_2$ × 2, OCH$_2$CH × 2 and CH$_2$CH_2CH$_3$ × 2], 1.27 [18 H, s, C(CH$_3$)$_3$ × 2], 1.30 [18 H, s, C(CH$_3$)$_3$ × 2], 3.07 (1 H, d, *J* 12.4, ArCHAr), 3.16–3.29 (5 H, m, OCH_2CH$_2$ × 2 and ArCHAr), 3.78 (2 H, d, *J* 16.1, ArCHAr × 2), 3.94 (2 H, d, *J* 16.5, ArCHAr × 2), 4.14 (1 H, d, *J* 12.0, ArCHAr), 4.31 (1 H, d, *J* 13.1, ArCHAr), 6.94 (2 H, d, *J* 2.1, ArH × 2), 6.98 (2 H, d, *J* 2.4, ArH × 2), 7.09 (2 H, d, *J* 2.4, ArH × 2) and 7.18 (2 H, d, *J* 2.8, ArH × 2); δ_C(75 MHz) 13.66, 13.90, 13.98, 14.23, 14.51, 16.96, 17.04, 17.36, 17.69, 19.06, 29.79, 30.04, 60.18, 61.60, 61.79, 31.91, 33.83, 34.07, 39.38, 73.50, 125.34, 125.40, 125.54, 125.66, 126.27,129.97, 132.17, 134.51, 141.84, 143.85, 149.96 and 154.24.

Compound C3c. Dichloromethane–hexane (1 : 1) as the eluent; crystals, mp 213–214 °C (Found: C, 72.05; H, 8.8. Calc. for $C_{64}H_{94}O_9Si_2$: C, 72.3; H, 8.9%); ν_{max}(KBr)/cm^{-1} 1761 (CO); δ_H(500 MHz) 0.42 (6 H, d, *J* 7.4, CHCH_3 × 2), 0.80 (6 H, d, *J* 7.1, CHCH_3 × 2), 0.93 (6 H, d, *J* 7.4, CHCH_3 × 2), 0.96 (6 H, d, *J* 7.1, CHCH_3 × 2), 0.97–1.06 [4 H, m, CH(CH$_3$)$_2$ × 4], 1.11 (6 H, t, *J* 7.0, OCH$_2$CH_3 × 2), 1.26 [18 H, s, C(CH$_3$)$_3$ × 2], 1.28 [18 H, s, C(CH$_3$)$_3$ × 2], 3.14 (1 H, d, *J* 12.8, ArCHAr), 3.30 (1 H, d, *J* 13.2, ArCHAr), 3.55 (2 H, d, *J* 16.3, OCHCO × 2), 3.93 (2 H, d, *J* 16.3, OCHCO × 2), 3.89–4.00 (8 H, m, ArCHAr × 4 and OCH_2CH$_3$ × 2), 4.33 (1 H, d, *J* 13.2, ArCHAr), 4.83 (1 H, d, *J* 12.8, ArCHAr), 6.94 (2 H, d, *J* 2.2, ArH × 2), 7.05–7.06 (4 H, m, ArH × 4) and 7.23 (2 H, d, *J* 2.5, ArH × 2); δ_C(125 MHz) 14.07, 14.15, 15.11, 17.05, 17.38, 17.60, 31.36, 31.48, 31.57, 31.71, 33.81, 34.02, 39.25, 59.93, 69.60, 125.59, 125.73, 125.85, 126.62, 129.46, 129.81, 131.83, 134.25, 142.01, 144.25, 149.61, 153.25 and 170.02; *m*/*z* (FAB) 1086 [(M+Na)$^+$].

Compound T3a. Dichloromethane–hexane (1 : 2) as the eluent; crystals, mp 287–288 °C (Found: C, 69.1; H, 7.5; S, 11.0. Calc. for $C_{66}H_{86}O_5S_4Si_2$: C, 69.3; H, 7.6; S, 11.2%); δ_H(500 MHz) 0.38 (6 H, d, *J* 7.5, CHCH_3 × 2), 0.74 (6 H, d, *J* 7.6, CHCH_3 × 2), 0.82–0.88 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.02 (6 H, d, *J* 7.6, CHCH_3 × 2), 1.12 (6 H, d, *J* 7.5, CHCH_3 × 2), 1.13–1.20 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.13 [18 H, s, C(CH$_3$)$_3$ × 2], 1.27 [18 H, s, C(CH$_3$)$_3$ × 2], 4.45 (2 H, d, *J* 12.2, OCHPh × 2), 4.14 (2 H, d, *J* 12.2, OCHPh × 2), 6.37 (4 H, d, *J* 7.4, OCH$_2$*Ph* × 2), 6.94 (4 H, t, *J* 7.6, OCH$_2$*Ph* × 2), 7.04 (2 H, t, *J* 7.3, OCH$_2$*Ph* × 2), 7.35 (2 H, d, *J* 2.5, ArH × 2), 7.45 (2 H, d, *J* 2.6, ArH × 2), 7.50 (2 H, d, *J* 2.6, ArH × 2) and 7.72 (2 H, d, *J* 2.5, ArH × 2); *m*/*z* (FAB): 1143 [(M + 1)$^+$].

Compound T3b. Dichloromethane–hexane (1 : 6) as the eluent; crystals, mp 322–323 °C (Found: C, 66.9; H, 8.4; S,12.2. Calc. for $C_{60}H_{90}O_5S_4Si_2$: C, 67.0; H, 8.4; S,11.9%); δ_H(300 MHz) 0.40 (6 H, d, *J* 7.5, CHCH_3 × 2), 0.77 (6 H, d, *J* 7.6, CHCH_3 × 2), 0.78 (6 H, t, *J* 7.2, CH$_2$CH_3 × 2), 0.79–0.89 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.01 (6 H, d, *J* 7.5, CHCH_3 × 2), 1.07 (6 H, d, *J* 7.2, CHCH_3 × 2), 1.04–1.21 [6 H, m, CH(CH$_3$)$_2$ × 2 and CH_2CH$_3$ × 2], 1.27 [18 H, s, C(CH$_3$)$_3$ × 2], 1.32 [18 H, s, C(CH$_3$)$_3$ × 2], 1.24–1.35 (4 H, m, OCH$_2$CH_2 × 2), 3.53–3.67 (4 H, m, OCH_2CH$_2$ × 2), 7.31 (2 H, d, *J* 2.4, ArH × 2), 7.52 (2 H, d, *J* 2.4, ArH × 2), 7.56 (2 H, d, *J* 2.4, ArH × 2) and 7.71 (2 H, d, *J* 2.8, ArH × 2).

Compound T3c. Dichloromethane as the eluent; crystals, mp 284–285 °C (Found: C, 63.2; H, 7.5; S, 11.3. Calc. for $C_{60}H_{86}O_9S_4Si_2$: C, 63.5; H, 7.6; S, 11.3%); ν_{max}/cm^{-1} 1765 (CO); δ_H(500 MHz) 0.47 (6 H, d, *J* 7.4, CHCH_3 × 2), 0.80 (6 H, d, *J* 7.6, CHCH_3 × 2), 0.85–0.95 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.03 (6 H, d, *J* 7.4, CHCH_3 × 2), 1.09 (6 H, d, *J* 7.6, CHCH_3 × 2), 1.14 (6 H, t, *J* 7.2, OCH$_2$CH_3 × 2), 1.14–1.22 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.27 [18 H, s, C(CH$_3$)$_3$ × 2], 1.30 [18 H, s, C(CH$_3$)$_3$ × 2], 3.62 (2 H, d, *J* 16.3, OCHCO × 2), 4.03 (4 H, q, *J* 7.2, OCH_2CH$_3$ × 2), 4.96 (2 H, d, *J* 16.3, OCHCO × 2), 7.33 (2 H, d, *J* 2.5, ArH × 2), 7.48 (2 H, d, *J* 2.5, ArH × 2), 7.58 (2 H, d, *J* 2.6, ArH × 2) and 7.75 (2 H, d, *J* 2.6, ArH × 2); *m*/*z* (FD) 1134 (M$^+$).

Compound C4a. Dichloromethane–hexane (1 : 4) as the eluent; crystals, mp 236–237 °C (Found: C, 78.7; H, 9.0. Calc. for $C_{70}H_{94}O_5Si_2$: C, 78.5; H, 8.8%); δ_H(500 MHz) 0.61 (3 H, d, *J* 7.3, CHCH_3), 0.70 [9 H, s, C(CH$_3$)$_3$], 0.75 [9 H, s, C(CH$_3$)$_3$], 0.78 (3 H, d, *J* 7.6, CHCH_3), 0.83–0.89 [1 H, m, CH(CH$_3$)$_2$], 0.85 (3 H, d, *J* 7.3, CHCH_3), 0.90 (3 H, d, *J* 7.3, CHCH_3), 1.01–1.06 (9 H, m, CHCH_3 × 3), 1.13–1.22 [2 H, m, CH(CH$_3$)$_2$ × 2], 1.30–1.36 [1 H, m, CH(CH$_3$)$_2$], 1.31 (3 H, d, *J* 7.1, CHCH_3), 1.34 [9 H, s, C(CH$_3$)$_3$], 1.40 [9 H, s, C(CH$_3$)$_3$], 2.88 (1 H, d, *J* 12.2, ArCHAr), 2.89 (1 H, d, *J* 13.4, CHPh), 3.09 (1 H, d, *J* 13.4, CHPh), 3.22 (1 H, d, *J* 13.2, ArCHAr), 3.47 (1 H, d, *J* 15.7, ArCHAr), 3.56 (1 H, d, *J* 15.7, ArCHAr), 3.68 (1 H, d, *J* 15.4, ArCHAr), 3.92 (1 H, d, *J* 15.4, ArCHAr), 4.25 (1 H, d, *J* 12.2, ArCHAr), 4.39 (1 H, d, *J* 12.2, ArCHAr), 4.66 (1 H, d, *J* 11.5, CHPh), 4.71 (1 H, d, *J* 11.5, CHPh), 5.93 (2 H, d, *J* 7.1, CH$_2$*Ph*), 6.47 (1 H, d, *J* 2.4, ArH), 6.62 (1 H, d, *J* 2.4, ArH), 6.77 (2 H, t, *J* 7.4, CH$_2$*Ph*), 6.78 (1 H, d, *J* 2.4, ArH), 6.85 (1 H, t, *J* 7.3, CH$_2$*Ph*), 6.88 (1 H, d, *J* 2.5, ArH), 7.00–7.03 (2 H, m, CH$_2$*Ph*), 7.05 (1 H, d, *J* 2.5, ArH), 7.10 (1 H, d, *J* 2.4, ArH), 7.12 (1 H, d, *J* 2.5, ArH), 7.14 (1 H, d, *J* 2.4, ArH), 7.21–7.25 (2 H, m, CH$_2$*Ph*) and 7.26–7.30 (1 H, m, CH$_2$*Ph*); *m*/*z* (FD) 1071 (M$^+$).

Compound C4b. Dichloromethane–hexane (1 : 4) as the eluent; crystals, mp 217–219 °C (Found: C, 76.8; H, 10.0. Calc. for $C_{64}H_{98}O_5Si_2$: C, 76.6; H, 9.8%); δ_H(500 MHz) 0.56–0.66

(7 H, m, $CH_2CH_2CH_3$), 0.66 (3 H, d, *J* 7.0, $CHCH_3$), 0.81 (3 H, d, *J* 7.5, $CHCH_3$), 0.87–1.07 [17 H, m, $CHCH_3 \times 4$, $CH(CH_3)_2 \times 2$ and CH_2CH_3], 1.09–1.21 [1 H, m, $CH(CH_3)_2$], 1.11 [3 H, d, *J* 7.5, $CH(CH_3)_2$], 1.14 [18 H, s, $C(CH_3)_3 \times 2$], 1.22–1.31 [6 H, m, $CHCH_3$, $CH(CH_3)_2$ and $CH_2CH_2CH_3$], 1.26 [9 H, s, $C(CH_3)_3$], 1.34 [9 H, s, $C(CH_3)_3$], 1.55–1.61 (2 H, m, OCH_2CH_2), 2.45–2.51 (1 H, m, $OCHCH_2$), 2.60–2.66 (1 H, m, $OCHCH_2$), 3.11 (1 H, d, *J* 12.2, ArCHAr), 3.20 (1 H, d, *J* 13.2, ArCHAr), 3.55–3.67 (2 H, m, OCH_2CH_2), 3.72 (1 H, d, *J* 15.3, ArCHAr), 3.74 (1 H, d, *J* 15.7, ArCHAr), 3.83 (1 H, d, *J* 15.7, ArCHAr), 3.91 (1 H, d, *J* 15.3, ArCHAr), 4.35 (1 H, d, *J* 13.2, ArCHAr), 4.46 (1 H, d, *J* 12.2, ArCHAr), 6.83 (1 H, d, *J* 2.3, ArH), 6.85 (1 H, d, *J* 2.4, ArH), 6.88 (1 H, d, *J* 2.4, ArH), 6.97 (1 H, d, *J* 2.4, ArH), 7.00 (1 H, d, *J* 2.3, ArH), 7.06 (1 H, d, *J* 2.1, ArH), 7.07 (1 H, d, *J* 2.4, ArH) and 7.10 (1 H, d, *J* 2.1, ArH); *m*/*z* (FD) 1004 [$(M + 1)^+$].

Compound C4c. Dichloromethane–hexane (2 : 1) as the eluent; crystals, mp 195–197 °C (Found: C, 72.2; H, 9.1. Calc. for $C_{64}H_{94}O_9Si_2$: C, 72.3; H, 8.9%); ν_{max}/cm^{-1} 1760 (CO); δ_H(400 MHz) 0.65 (3 H, d, *J* 7.3, $CHCH_3$), 0.77 (3 H, d, *J* 7.3, $CHCH_3$), 0.84 (3 H, d, *J* 7.6, $CHCH_3$), 0.78–0.84 [1 H, m, $CH(CH_3)_2$], 0.91 (3 H, d, *J* 7.5, $CHCH_3$), 1.02 (3 H, d, *J* 7.5, $CHCH_3$), 1.06 (3 H, d, *J* 7.6, $CHCH_3$), 1.08 [9 H, s, $C(CH_3)_3$], 1.09 [9 H, s, $C(CH_3)_3$], 1.15 (3 H, t, *J* 7.2, OCH_2CH_3), 1.13–1.16 [2 H, m, $CH(CH_3)_2$], 1.18–1.24 [1 H, m, $CH(CH_3)_2$], 1.27 (3 H, t, *J* 7.2, OCH_2CH_3), 1.27 (3 H, d, *J* 8.7, $CH(CH_3)_2$), 1.30 [9 H, s, $C(CH_3)_3$], 1.32 [9 H, s, $C(CH_3)_3$], 1.38–1.40 [3 H, br, $CH(CH_3)_2$], 2.75 (1 H, d, *J* 15.7, OCHCO), 3.07 (1 H, d, *J* 15.7, OCHCO), 3.15 (1 H, d, *J* 12.6, ArCHAr), 3.20 (1 H, d, *J* 13.2, ArCHAr), 3.85 (1 H, d, *J* 14.9, ArCHAr), 3.92 (1 H, d, *J* 14.9, ArCHAr), 3.91–4.03 (4 H, m, OCH_2CH_3 and ArCHAr × 2), 4.16 (2 H, q, *J* 7.2, OCH_2CH_3), 4.31 (1 H, d, *J* 13.2, $ArCH_2Ar$), 4.32 (1 H, d, *J* 15.8, OCH_2CO), 4.45 (1 H, d, *J* 15.8, OCH_2CO), 4.61 (1 H, d, *J* 12.6, $ArCH_2Ar$), 6.85 (1 H, d, *J* 2.5, ArH), 6.92 (1 H, d, *J* 2.4, ArH), 6.97 (2 H, d, *J* 2.5, ArH × 2), 7.01 (1 H, d, *J* 2.5, ArH), 7.08 (1 H, d, *J* 2.5, ArH), 7.10 (1 H, d, *J* 2.4, ArH) and 7.24 (1 H, d, *J* 2.4, ArH); *m*/*z* (FD) 1062 (M^+).

Compound T4a. Dichloromethane–hexane (1 : 2) as the eluent; crystals, mp 266–267 °C (Found: C, 69.4; H, 7.6; S, 11.4. Calc. for $C_{66}H_{86}O_5S_4Si_2$: C, 69.3; H, 7.6; S, 11.2%); δ_H(300 MHz) 0.61 (3 H, d, *J* 6.9, $CHCH_3$), 0.74 (3 H, d, *J* 7.6, $CHCH_3$), 0.76–0.80 (3 H, m, $CHCH_3$), 0.78 [9 H, s, $C(CH_3)_3$], 0.80 [9 H, s, $C(CH_3)_3$], 0.84 (3 H, d, *J* 7.2, $CHCH_3$), 0.99 (3 H, d, *J* 5.5, $CHCH_3$), 1.02–1.11 [1 H, m, $CH(CH_3)_2$], 1.06 (3 H, d, *J* 7.5, $CHCH_3$), 1.10 (3 H, d, *J* 7.2, $CHCH_3$), 1.15–1.40 [3 H, m, $CH(CH_3)_2 \times 3$], 1.28 (3 H, d, *J* 6.9, $CHCH_3$), 1.32 [9 H, s, $C(CH_3)_3$], 1.36 [9 H, s, $C(CH_3)_3$], 4.73 (2 H, s, OCH_2Ph), 4.92 (1 H, d, *J* 11.0, OCHPh), 5.13 (1 H, d, *J* 11.0, OCHPh), 6.22 (2 H, d, *J* 7.2, OCH_2Ph), 6.71 (2 H, t, *J* 7.5, OCH_2Ph), 6.89 (1 H, t, *J* 7.2, OCH_2Ph), 7.02 (1 H, d, *J* 2.4, ArH), 7.16 (1 H, d, *J* 2.4, ArH), 7.26–7.32 (5 H, m, ArH × 2 and OCH_2Ph), 7.35–7.40 (4 H, m, ArH × 2 and OCH_2Ph), 7.71 (1 H, d, *J* 2.7, ArH) and 7.78 (1 H, d, *J* 2.7, ArH).

Compound C7a. Dichloromethane–hexane (1 : 3) as the eluent; crystals, mp 193–194 °C (Found: C, 76.9; H, 9.2. Calc. for $C_{63}H_{88}O_5Si_2$: C, 77.1; H, 9.0%); δ_H(500 MHz) 0.23 (3 H, d, *J* 7.4, $CHCH_3$), 0.56 (3 H, d, *J* 7.5, $CHCH_3$), 0.68–0.75 [1 H, m, $CH(CH_3)_2$], 0.76 (3 H, d, *J* 7.5, $CHCH_3$), 0.80 (3 H, d, *J* 7.0, $CHCH_3$), 0.85 (3 H, d, *J* 7.4, $CHCH_3$), 0.79–0.89 [1 H, m, $CH(CH_3)_2$], 0.92–1.05 [7 H, m, $CHCH_3 \times 2$ and $CH(CH_3)_2$], 1.01 [9 H, s, $C(CH_3)_3$], 1.14 (3 H, d, *J* 7.5, $CHCH_3$), 1.08–1.15 [1 H, m, $CH(CH_3)_2$], 1.21 [9 H, s, $C(CH_3)_3$], 1.30 [9 H, s, $C(CH_3)_3$], 1.38 [9 H, s, $C(CH_3)_3$], 3.23 (1 H, d, *J* 13.9, ArCHAr), 3.39 (1 H, d, *J* 13.2, ArCHAr), 3.54 (1 H, d, *J* 13.9, ArCHAr), 3.76 (1 H, d, *J* 16.4, ArCHAr), 3.91 (1 H, d, *J* 16.5, ArCHAr), 4.01 (1 H, d, *J* 16.4, ArCHAr), 4.07 (1 H, d, *J* 12.1, CHPh), 4.14 (1 H, d, *J* 16.5, ArCHAr), 4.46 (1 H, d, *J* 13.2, ArCHAr), 4.63 (1 H, d, *J* 12.1, CHPh), 6.27 (1 H, s, OH), 6.33 (2 H, d, *J* 7.4, CH_2Ph), 6.86–6.88 (2 H, m, ArH × 2), 6.92 (1 H, d, *J* 2.4, ArH), 6.95 (2 H, t, *J* 7.3, CH_2Ph), 6.98 (1 H, d, *J* 2.3, ArH), 7.02 (1 H, t, *J* 7.3, CH_2Ph), 7.08 (1 H, d, *J* 2.2, ArH), 7.14 (1 H, d, *J* 2.3, ArH) and 7.26–7.28 (2 H, m, ArH × 2); δ_C(125 MHz) 13.63, 13.67, 14.28, 14.48, 16.29, 16.79, 17.02, 17.12, 17.22, 17.27, 17.42, 18.16, 31.27, 31.40, 31.51, 31.65, 31.87, 32.74, 33.71, 33.77, 34.05, 34.07, 34.25, 38.68, 39.84, 74.59, 124.24, 124.45, 125.24, 125.62, 125.91, 125.96, 126.00, 126.24, 126.33, 126.98, 127.64, 128.06, 129.34, 129.71, 129.96, 131.51, 132.61, 134.11, 136.29, 143.05, 143.11, 146.39, 149.52, 149.60, 150.69 and 151.60; *m*/*z* (FD) 981 (M^+).

Compound C7b. Dichloromethane–hexane (1 : 3) as the eluent; crystals, mp 191–193 °C (Found: C, 76.1; H, 9.7. Calc. for $C_{60}H_{90}O_5Si_2$: C, 76.1; H, 9.6%); δ_H(300 MHz) −0.13 (3 H, d, *J* 7.2, $CHCH_3$), 0.36–0.54 [2 H, m, $CH(CH_3)_2$ and OCH_2CH], 0.69 (3 H, d, *J* 7.6, $CHCH_3$), 0.69 (3 H, t, *J* 7.2, CH_2CH_3), 0.73–0.82 [6 H, m, $CHCH_3$, $CH(CH_3)_2$ and CH_2CH_3], 0.86 (3 H, d, *J* 7.6, $CHCH_3$), 0.88–1.04 [8 H, m, $CHCH_3 \times 2$, $CH(CH_3)_2$ and OCH_2CH], 1.01 (3 H, d, *J* 7.2, $CHCH_3$), 1.06–1.19 [1 H, m, $CH(CH_3)_2$], 1.10 (3 H, d, *J* 7.6, $CHCH_3$), 1.25 [9 H, s, $C(CH_3)_3$], 1.27 [9 H, s, $C(CH_3)_3$], 1.30 [9 H, s, $C(CH_3)_3$], 1.33 [9 H, s, $C(CH_3)_3$], 3.21–3.35 (2 H, m, OCH_2CH_2), 3.29 (1 H, d, *J* 13.1, ArCHAr), 3.34 (1 H, d, *J* 12.7, ArCHAr), 3.84 (1 H, d, *J* 16.8, ArCHAr), 3.85 (1 H, d, *J* 12.7, ArCHAr), 3.86 (1 H, d, *J* 17.5, ArCHAr), 4.04 (1 H, d, *J* 17.5, ArCHAr), 4.06 (1 H, d, *J* 15.8, ArCHAr), 4.36 (1 H, d, *J* 13.1, $ArCH_2Ar$), 6.42 (1 H, s, OH), 6.91–6.98 (3 H, m, ArH × 3), 6.99 (1 H, d, *J* 2.4, ArH), 7.04 (1 H, d, *J* 2.4, ArH), 7.17 (2 H, d, *J* 2.4, ArH × 2) and 7.32 (1 H, d, *J* 2.4, ArH); δ_C(75 MHz) 13.29, 13.50, 13.78, 14.46, 14.62, 15.90, 16.67, 17.03, 17.20, 17.26, 17.39, 17.51, 18.02, 18.68, 29.42, 31.47, 31.63, 31.78, 32.46, 33.51, 33.90, 34.18, 39.52, 39.84, 74.19, 124.15, 124.75, 124.83, 125.53, 125.57, 126.21, 126.26, 126.45, 127.54, 128.16, 128.69, 129.06, 131.24, 131.69, 131.73, 134.46, 141.74, 142.64, 142.82, 146.43, 148.80, 150.10, 150.44 and 151.62; *m*/*z* (FD) 946 (M^+).

Compound C7c. Dichloromethane–hexane (1 : 2) as the eluent; crystals, mp 228–230 °C (decomp.) (Found: C, 73.5; H, 9.2. Calc. for $C_{60}H_{88}O_7Si_2$: C, 73.7; H, 9.1%); ν_{max}/cm^{-1} 1745 (CO); δ_H(300 MHz) 0.29 (3 H, d, *J* 7.2, $CHCH_3$), 0.42 (3 H, d, *J* 7.2, $CHCH_3$), 0.69–0.84 [3 H, m, $CH(CH_3)_2 \times 3$], 0.77 (3 H, d, *J* 7.2, $CHCH_3$), 0.81 (3 H, d, *J* 6.5, $CHCH_3$), 0.91–1.02 (12 H, m, $CHCH_3 \times 3$ and OCH_2CH_3), 1.02–1.13 [1 H, m, $CH(CH_3)_2$], 1.05 (3 H, d, *J* 7.6, $CHCH_3$), 1.27 [18 H, s, $C(CH_3)_3 \times 2$], 1.28 [9 H, s, $C(CH_3)_3$], 1.29 [9 H, s, $C(CH_3)_3$], 3.32 (2 H, d, *J* 14.1, ArCHAr × 2), 3.56 (1 H, d, *J* 15.6, OCHCO), 3.79–4.11 (8 H, m, ArCHAr × 5, OCHCO and OCH_2CH_3), 4.37 (1 H, d, *J* 13.1, ArCHAr), 6.18 (1 H, s, OH), 6.93 (1 H, d, *J* 2.1, ArH), 6.97–7.03 (4 H, m, ArH × 4), 7.16 (1 H, d, *J* 2.1, ArH), 7.18 (1 H, d, *J* 2.8, ArH) and 7.26 (1 H, d, *J* 3.1, ArH); δ_C(75 MHz) 13.72, 13.82, 14.06, 14.13, 14.18, 16.47, 16.91, 17.03, 17.28, 17.40, 17.46, 17.90, 31.44, 31.61, 31.68, 31.86, 33.64, 33.85, 33.91, 34.22, 39.11, 39.59, 60.85, 69.92, 76.68, 124.48, 124.90, 125.14, 125.74, 126.10, 126.19, 126.37, 127.19, 128.95, 129.05, 130.25, 131.04, 132.19, 133.95, 140.99, 142.72, 142.80, 146.54, 149.16, 149.53, 150.68, 151.46 and 168.43; *m*/*z* (FD) 978 [$(M + 1)^+$].

Compound T7b. Dichloromethane–hexane (1 : 6) as the eluent; crystals, mp 284–286 °C (Found: C, 65.6; H, 8.1; S,12.5. Calc. for $C_{56}H_{82}O_5S_4Si_2$: C, 66.0; H, 8.1; S,12.6%); δ_H(300 MHz) 0.12 (3 H, d, *J* 7.2, $CHCH_3$), 0.52 (3 H, d, *J* 7.5, $CHCH_3$), 0.56–0.67 (2 H, m, $CHCH_3$ and OCH_2CH), 0.69 (3 H, t, *J* 7.6, CH_2CH_3), 0.77 (3 H, d, *J* 7.2, $CHCH_3$), 0.71–0.82 [1 H, m, $CH(CH_3)_2$], 0.85 (3 H, d, *J* 7.6, $CHCH_3$), 0.97 (3 H, d, *J* 7.6, $CHCH_3$), 1.01 (3 H, d, *J* 7.2, $CHCH_3$), 1.05 (3 H, d, *J* 7.9, $CHCH_3$), 1.14 (3 H, d, *J* 7.6, $CHCH_3$), 0.93–1.17 [4 H, m, $CH(CH_3)_2$, OCH_2CH and CH_2CH_3], 1.22–1.33 [1 H, m, $CH(CH_3)_2$], 1.25 [9 H, s, $C(CH_3)_3$], 1.29 [9 H, s, $C(CH_3)_3$], 1.30

[9 H, s, $C(CH_3)_3$], 1.34 [9 H, s, $C(CH_3)_3$], 3.40–3.48 (1 H, m, OC*H*CH_2), 3.77–3.85 (1 H, m, OC*H*CH_2), 7.25 (1 H, s, OH), 7.28 (1 H, d, *J* 2.4, ArH), 7.35 (1 H, d, *J* 2.7, ArH), 7.40 (1 H, d, *J* 2.4, ArH), 7.50 (1 H, d, *J* 2.7, ArH), 7.60 (1 H, d, *J* 2.4, ArH), 7.61 (1 H, d, *J* 2.4, ArH), 7.66 (1 H, d, *J* 2.4, ArH) and 7.82 (1 H, d, *J* 2.4, ArH).

Compound C8a. Dichloromethane–hexane (1 : 4) as the eluent; crystals, mp 232–233 °C (Found: C, 76.9; H, 9.15. Calc. for $C_{63}H_{88}O_5Si_2$: C, 77.1; H, 9.0%); δ_H(300 MHz) 0.62 (3 H, d, *J* 6.8, CHC*H*$_3$), 0.78 [9 H, s, $C(CH_3)_3$], 0.88 (3 H, d, *J* 7.5, CHC*H*$_3$), 0.90–1.01 [10 H, m, CHC*H*$_3$ × 3 and C*H*$(CH_3)_2$], 0.96 [9 H, s, $C(CH_3)_3$], 1.10 (3 H, d, *J* 7.6, CHC*H*$_3$), 1.22–1.43 [9 H, m, CHC*H*$_3$ × 2 and C*H*$(CH_3)_2$ × 3], 1.30 [9 H, s, $C(CH_3)_3$], 1.31 [9 H, s, $C(CH_3)_3$], 3.14 (1 H, d, *J* 12.9, ArCHAr), 3.16 (1 H, d, *J* 12.4, ArCHAr), 3.25 (2 H, d, *J* 13.4, ArCHAr × 2), 4.33 (1 H, d, *J* 13.6, ArCHAr), 4.38 (1 H, d, *J* 13.2, ArCHAr), 4.42 (1 H, d, *J* 12.9, ArCHAr), 4.71 (1 H, d, *J* 12.4, ArCHAr), 4.79 (1 H, d, *J* 11.8, C*H*Ph), 4.90 (1 H, d, *J* 11.8, C*H*Ph), 6.47 (1 H, d, *J* 2.3, ArH), 6.61 (1 H, d, *J* 2.4, ArH), 6.66 (1 H, d, *J* 2.4, ArH), 6.69 (1 H, s, OH), 6.78 (1 H, d, *J* 2.5, ArH), 7.01 (1 H, d, *J* 2.4, ArH), 7.02 (1 H, d, *J* 2.6, ArH), 7.06 (1 H, d, *J* 2.3, ArH), 7.11 (1 H, d, *J* 2.4, ArH), 7.30–7.37 (3 H, m, CH_2*Ph*) and 7.59 (2 H, d, *J* 7.8, CH_2*Ph*); δ_C(125 MHz) 13.85, 13.90, 14.42, 14.78, 16.55, 17.24, 17.46, 17.47, 17.59, 17.87, 17.94, 17.99, 29.68, 31.12, 31.70, 31.76, 31.83, 32.17, 33.68, 33.72, 33.87, 33.91, 34.79, 77.60, 124.51, 124.76, 124.83, 125.16, 125.21, 125.40, 125.54, 125.64, 127.33, 127.54, 128.02, 128.15, 128.60, 129.36, 129.46, 131.71, 131.98, 132.46, 133.36, 138.27, 141.00, 143.44, 143.75, 144.83, 145.67, 148.70, 151.23 and 152.22; *m*/*z* (FD) 981 (M^+).

Compound C8b. Dichloromethane–hexane (1 : 6) as the eluent; crystals, mp 118–121 °C (Found: C, 75.7; H, 9.5. Calc. for $C_{60}H_{90}O_5Si_2$: C, 76.1; H, 9.6%); δ_H(300 MHz) 0.68 (3 H, d, *J* 7.0, CHC*H*$_3$), 0.77 [9 H, s, $C(CH_3)_3$], 0.89 (3 H, d, *J* 7.5, CHC*H*$_3$), 0.96 [9 H, s, $C(CH_3)_3$], 0.96 (3 H, t, *J* 7.4, CH_2CH_3), 0.99–1.05 [4 H, m, CHC*H*$_3$ and C*H*$(CH_3)_2$], 1.11 (3 H, d, *J* 7.6, CHC*H*$_3$), 1.25–1.35 [10 H, m, CHC*H*$_3$ × 3 and C*H*$(CH_3)_2$], 1.30 [9 H, s, $C(CH_3)_3$], 1.32 [9 H, s, $C(CH_3)_3$], 1.42 (3 H, d, *J* 7.4, CHC*H*$_3$), 1.41–1.46 [2 H, m, C*H*$(CH_3)_2$ and C*H*CH_3], 1.49–1.58 (1 H, m, C*H*CH_3), 1.58–1.65 [1 H, m, C*H*$(CH_3)_2$], 1.69–1.78 (1 H, m, OCH$_2$C*H*), 1.82–1.91 (1 H, m, OCH$_2$C*H*), 3.17–3.27 (4 H, m, ArCHAr × 4), 3.71 (1 H, dt, *J* 9.8 and 7.5, OC*H*CH_2), 3.90 (1 H, ddd, *J* 5.1, 8.2 and 9.8, OC*H*CH_2), 4.32 (1 H, d, *J* 13.1, ArCHAr), 4.38 (1 H, d, *J* 13.3, ArCHAr), 4.39 (1 H, d, *J* 13.2, ArCHAr), 4.66 (1 H, d, *J* 12.4, ArCHAr) 6.45 (1 H, d, *J* 2.4, ArH), 6.59 (1 H, d, *J* 2.4, ArH), 6.64 (1 H, d, *J* 2.5, ArH), 6.69 (1 H, s, OH), 6.75 (1 H, d, *J* 2.5, ArH), 7.01 (1 H, d, *J* 2.4, ArH), 7.02 (1 H, d, *J* 2.6, ArH), 7.05 (1 H, d, *J* 2.4, ArH) and 7.09 (1 H, d, *J* 2.6, ArH); δ_C(125 MHz) 13.64, 14.11, 14.73, 14.83, 16.41, 17.29, 17.41, 17.49, 17.60, 17.80, 18.12, 18.30, 19.50, 29.60, 31.09, 31.69, 31.77, 31.99, 33.59, 33.64, 33.80, 33.84, 34.83, 75.88, 124.53, 124.77, 124.87, 125.12, 125.35, 125.53, 127.74, 128.26, 128.82, 129.51, 131.87, 132.14, 133.14, 140.76, 143.29, 144.55, 145.97, 148.60, 151.18 and 152.29.

Compound C8c. Dichloromethane–hexane (1 : 2) as the eluent; crystals, mp 151–153 °C (Found: C, 73.7; H, 9.0. Calc. for $C_{60}H_{88}O_7Si_2$: C, 73.7; H, 9.1%); ν_{max}/cm^{-1} 1758 (CO); δ_H(300 MHz) 0.69–0.73 (3 H, m, CHC*H*$_3$), 0.71 [9 H, s, $C(CH_3)_3$], 0.90 (3 H, d, *J* 7.6, CHC*H*$_3$), 0.96 [9 H, s, $C(CH_3)_3$], 0.93–1.03 [4 H, m, CHC*H*$_3$ and C*H*$(CH_3)_2$], 1.12 (3 H, d, *J* 7.6, CHC*H*$_3$), 1.25–1.34 [13 H, m, CHC*H*$_3$ × 3, C*H*$(CH_3)_2$ and OCH$_2$C*H*$_3$], 1.31 [9 H, s, $C(CH_3)_3$], 1.32 [9 H, s, $C(CH_3)_3$], 1.35–1.50 [1 H, m, C*H*$(CH_3)_2$], 1.41 (3 H, d, *J* 7.2, CHC*H*$_3$), 1.52–1.65 [1 H, m, C*H*$(CH_3)_2$], 3.23 (1 H, d, *J* 12.7, ArCHAr), 3.25 (2 H, d, *J* 13.4, ArCHAr × 2), 3.26 (1 H, d, *J* 13.1, ArCHAr), 4.14–4.28 (2 H, m, OC*H*$_2$CH$_3$), 4.33 (1 H, d, *J* 13.7, ArCHAr), 4.38 (1 H, d, *J* 13.4, ArCHAr), 4.41 (1 H, d, *J* 13.1, ArCHAr), 4.48 (1 H, d, *J* 15.8, OCHCO), 4.55 (1 H, d, *J* 15.8, OCHCO), 4.77 (1 H, d, *J* 12.7, ArCHAr), 6.40 (1 H, d, *J* 2.4, ArH), 6.50 (1 H, d, *J* 2.4, ArH), 6.56 (1 H, s, OH), 6.66 (1 H, d, *J* 2.7, ArH), 6.79 (1 H, d, *J* 2.4, ArH), 7.00 (1 H, d, *J* 2.4, ArH), 7.04 (1 H, d, *J* 2.4, ArH), 7.08 (1 H, d, *J* 2.1, ArH) and 7.10 (1 H, d, *J* 2.4, ArH); δ_C(75 MHz) 13.31, 14.21, 14.36, 14.95, 16.29, 17.35, 17.51, 17.66, 17.80, 17.92, 18.20, 30.38, 30.99, 31.07, 31.70, 31.76, 32.14, 33.62, 33.80, 33.85, 34.64, 60.77, 72.12, 124.47, 124.67, 124.76, 125.10, 125.28, 125.48, 125.65, 125.72, 127.06, 128.30, 129.25, 131.32, 131.69, 131.90, 133.50, 140.83, 143.46, 143.75, 144.71, 145.55, 148.70, 151.06, 152.71 and 170.02; *m*/*z* (FD) 977 (M^+).

General procedure for the desilylation of dialkylated compounds C3,4 and T3,4

To a 50.0 M solution of dialkylated compound **C3,4** or **T3,4** in THF was added 1.0 mol equiv. of tetrabutylammonium fluoride (1.0 M in THF) and the mixture was stirred at room temperature for 1 h, after which it was cooled to 0 °C and quenched with 2 M HCl. The mixture was extracted with chloroform and the extract was washed with water, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel by using the indicated eluent.

Compound C5b. Dichloromethane–hexane (1 : 3) as the eluent; crystals (98%), mp 79–81 °C (Found: C, 82.1; H, 9.6. Calc. for $C_{52}H_{72}O_4$: C, 82.1; H, 9.5%); δ_H(300 MHz) 1.05 (6 H, t, *J* 7.2, CH_2CH_3 × 2), 1.11 [18 H, s, $C(CH_3)_3$ × 2], 1.21 [18 H, s, $C(CH_3)_3$ × 2], 1.51–1.64 (4 H, m, CH_2CH_3 × 2), 2.02–2.13 (4 H, m, OCH_2CH_2 × 2), 3.28–3.38 (4 H, m, ArCHAr × 4), 3.85–3.94 (2 H, m, OC*H*CH_2 × 2), 4.03–4.11 (2 H, m, OC*H*CH_2 × 2), 4.28–4.37 (3 H, m, ArCHAr × 3), 4.48 (1 H, d, *J* 12.4, ArCHAr), 6.91 (2 H, d, *J* 2.1, ArH × 2), 6.97 (2 H, d, *J* 2.4, ArH × 2), 6.99 (2 H, d, *J* 2.4, ArH × 2), 7.01 (2 H, d, *J* 2.4, ArH × 2) and 8.95 (2 H, s, OH × 2).

Compound T5a. Dichloromethane–hexane (1 : 2) as the eluent; crystals (93%), mp 114–116 °C (Found: C, 71.7; H, 6.7; S, 14.5. Calc. for $C_{54}H_{60}O_4S_4$: C, 72.0; H, 6.7; S, 14.2%); δ_H(500 MHz) 0.90 [18 H, s, $C(CH_3)_3$ × 2], 1.21 [18 H, s, $C(CH_3)_3$ × 2], 5.19 (2 H, d, *J* 10.9, C*H*Ph × 2), 5.54 (2 H, d, *J* 10.9, C*H*Ph × 2), 7.07 (2 H, d, *J* 2.5, ArH × 2), 7.15 (2 H, d, *J* 2.5, ArH × 2), 7.40–7.32 (6 H, m, CH_2*Ph* × 2), 7.48 (2 H, d, *J* 2.5, ArH × 2), 7.51 (2 H, d, *J* 2.5, ArH × 2), 7.64–7.61 (4 H, m, CH_2*Ph* × 2) and 8.35 (2 H, s, OH × 2); *m*/*z* (FAB) 901 [(M + 1)$^+$].

Compound T5b. Dichloromethane–hexane (1 : 3) as the eluent; crystals (95%), mp 96–98 °C (Found: C, 69.3; H, 7.8; S, 15.7. Calc. for $C_{48}H_{64}O_4S_4$: C, 69.2; H, 7.7; S, 15.4%); δ_H(500 MHz) 0.89 [18 H, s, $C(CH_3)_3$ × 2], 1.03 (6 H, t, *J* 7.6, CH_2-CH_3 × 2), 1.24 [18 H, s, $C(CH_3)_3$ × 2], 1.50–1.62 (4 H, m, CH_2CH_3 × 2), 1.84–2.12 (4 H, m, OCH_2CH_2 × 2), 4.18 (2 H, dt, *J* 5.9 and 8.9, OC*H*CH_2 × 2), 4.39 (2 H, dt, *J* 6.2 and 8.9, OC*H*CH_2 × 2), 7.03 (2 H, d, *J* 2.4, ArH × 2), 7.14 (2 H, d, *J* 2.8, ArH × 2), 7.54 (2 H, d, *J* 2.4, ArH × 2), 7.56 (2 H, d, *J* 2.4, ArH × 2) and 8.91 (2 H, s, OH × 2).

Compound T5c. Dichloromethane–hexane (1 : 1) as the eluent; crystals (93%), mp 194–195 °C (Found: C, 64.5; H, 6.8; S, 14.1. Calc. for $C_{48}H_{60}O_8S_4$: C, 64.5; H, 6.8; S, 14.4%); ν_{max}/cm^{-1} 1745 (CO); δ_H(500 MHz) 0.88 [18 H, s, $C(CH_3)_3$ × 2], 1.23 [18 H, s, $C(CH_3)_3$ × 2], 1.35 (6 H, t, *J* 7.2, OCH_2CH_3 × 2), 4.35–4.30 (4 H, m, OCH_2CH_3 × 2), 4.81 (2 H, d, *J* 16.5, OCHCO × 2), 5.31 (2 H, d, *J* 16.5, OCHCO × 2), 7.03 (2 H, d, *J* 2.5, ArH × 2), 7.12 (2 H, d, *J* 2.5, ArH × 2), 7.52 (2 H, d, *J* 2.5, ArH × 2), 7.54 (2 H, d, *J* 2.5, ArH × 2) and 9.14 (2 H, s, OH × 2); *m*/*z* (FAB) 893 [(M + 1)$^+$].

Compound C6a. Dichloromethane–hexane (1 : 2) as the eluent; crystals (96%), mp 239–241 °C (decomp.) (Found: C, 84.0; H, 8.5. Calc. for $C_{58}H_{68}O_4$: C, 84.0; H, 8.3%); δ_H(500 MHz) 1.01 [36 H, s, $C(CH_3)_3 \times 4$], 3.68 (2 H, s, $ArCH_2Ar$), 3.81 (2 H, d, *J* 15.4, ArCHAr × 2), 3.85 (2 H, d, *J* 15.4, ArCHAr × 2), 4.07 (2 H, s, $ArCH_2Ar$), 4.40 (2 H, d, *J* 11.6, OC*H*Ph × 2), 4.71 (2 H, d, *J* 11.6, OC*H*Ph × 2), 6.22 (4 H, d, *J* 7.6, OCH_2-*Ph* × 2), 6.78 (4 H, t, *J* 7.6, OCH_2*Ph* × 2), 6.84 (2 H, d, *J* 2.4, ArH × 2), 6.87 (2 H, d, *J* 2.3, ArH × 2), 6.94 (2 H, t, *J* 7.6, OCH_2*Ph* × 2), 6.94 (2 H, d, *J* 2.3, ArH × 2), 7.13 (2 H, d, *J* 2.4, ArH × 2) and 8.29 (2 H, s, OH × 2); δ_C(125 MHz) 31.16, 31.26, 32.40, 33.61, 33.89, 35.94, 39.47, 72.11, 124.36, 125.08, 125.33, 125.61, 126.16, 126.60, 127.29, 127.80, 128.5, 132.07, 133.65, 136.32, 142.65, 147.05, 149.08 and 151.50; *m*/*z* (FD) 828 (M^+).

Compound C6b. Dichloromethane–hexane (1 : 2) as the eluent; crystals (98%), mp 108–110 °C (Found: C, 81.9; H, 9.65. Calc. for $C_{52}H_{72}O_4$: C, 82.1; H, 9.5%); δ_H(500 MHz) 0.49 (6 H, t, *J* 7.3, $CH_2CH_3 \times 2$), 0.57–0.65 (4 H, m, $CH_2CH_3 \times 2$), 0.81–0.90 (2 H, m, $OCH_2CH \times 2$), 0.92–1.01 (2 H, m, $OCH_2CH \times 2$), 1.23 [18 H, s, $C(CH_3)_3 \times 2$], 1.34 [18 H, s, $C(CH_3)_3 \times 2$], 3.07 (2 H, dt, *J* 5.8 and 8.7, OC*H*$CH_2 \times 2$), 3.28 (2 H, dt, *J* 5.8 and 8.7, OC*H*$CH_2 \times 2$), 3.74 (2 H, d, *J* 14.7, ArCHAr × 2), 3.77 (2 H, s, $ArCH_2Ar$), 3.90 (2 H, d, *J* 14.7, ArCHAr × 2), 3.98 (2 H, s, $ArCH_2Ar$), 6.97 (2 H, d, *J* 2.4, ArH × 2), 7.03 (2 H, d, *J* 2.4, ArH × 2), 7.05 (2 H, d, *J* 2.5, ArH × 2), 7.20 (2 H, d, *J* 2.5, ArH × 2) and 8.18 (2 H, s, OH × 2); δ_C(125 MHz) 13.84, 18.37, 30.89, 31.56, 31.60, 33.90, 34.16, 35.66, 72.44, 124.63, 125.10, 125.86, 126.76, 127.81, 129.10, 132.53, 134.09, 142.84, 146.23, 149.19 and 152.28.

Compound C6c. Dichloromethane–hexane (1 : 1) as the eluent; crystals (92%), mp 154–155 °C (from MeOH) (Found: C, 75.95; H, 8.5. Calc. for $C_{52}H_{68}O_8$: C, 76.1; H, 8.4%); ν_{max}/cm^{-1} 1745 (CO); δ_H(500 MHz) 1.01 (6 H, t, *J* 7.1, $OCH_2CH_3 \times 2$), 1.21 (18 H, s, $C(CH_3)_3 \times 2$), 1.25 [18 H, s, $C(CH_3)_3 \times 2$], 3.38 (2 H, d, *J* 15.7, OCHCO × 2), 3.70 (2 H, d, *J* 14.7, ArCHAr × 2), 3.75 (2 H, s, $ArCH_2Ar$), 3.89 (2 H, d, *J* 15.7, OCHCO × 2), 3.92 (4 H, q, *J* 7.1, $OCH_2CH_3 \times 2$), 4.00 (2 H, s, $ArCH_2Ar$), 4.02 (2 H, d, *J* 14.7, ArCHAr × 2), 6.98 (2 H, d, *J* 2.4, ArH × 2), 7.00 (2 H, d, *J* 2.4, ArH × 2), 7.12 (2 H, d, *J* 2.5, ArH × 2), 7.21 (2 H, d, *J* 2.5, ArH × 2) and 7.66 (2 H, s, OH × 2); δ_C(125 MHz) 13.98, 31.43, 31.60, 32.43, 33.91, 34.17, 35.03, 38.56, 60.90, 68.73, 124.99, 125.35, 126.20, 127.28, 127.77, 129.04, 133.10, 134.17, 142.93, 157.05, 149.03, 151.59 and 168.88; *m*/*z* (FD) 820 (M^+).

Compound T6a. Dichloromethane–hexane (1 : 3) as the eluent; crystals (96%), mp 239–240 °C (Found: C, 71.95; H, 6.8; S, 14.1. Calc. for $C_{54}H_{60}O_4S_4$: C, 71.9; H, 6.7; S, 14.2%); δ_H(300 MHz) 0.99 [18 H, s, $C(CH_3)_3 \times 2$], 1.05 [18 H, s, $C(CH_3)_3 \times 2$], 4.83 (2 H, d, *J* 11.3, OC*H*Ph × 2), 5.29 (2 H, d, *J* 11.7, OC*H*Ph × 2), 6.38 (4 H, d, *J* 7.5, OCH_2*Ph* × 2), 6.71 (4 H, t, *J* 7.6, OCH_2*Ph* × 2), 6.91 (2 H, t, *J* 7.5, OCH_2*Ph* × 2), 7.14 (2 H, d, *J* 2.4, ArH × 2), 7.38 (2 H, d, *J* 2.4, ArH × 2), 7.44 (2 H, d, *J* 2.4, ArH × 2), 7.46 (2 H, d, *J* 2.4, ArH × 2) and 8.53 (2 H, s, OH × 2).

^{1}H NMR analyses of metal salts of compounds C2 and T2

Samples containing *tert*-BuOK were prepared from a 10.0 mM solution of compound **C2** or **T2** in THF-d_8 by simple addition of 1.0 mol equiv. of the base, while Cs_2CO_3-saturated samples were prepared by addition of 6.0 mol equiv. of the base to the THF-d_8 solution, followed by irradiation of the mixture with ultrasound (38 kHz, 80 W) for 30 min and subsequent filtration of the resulting suspension. These samples, together with the solutions of compounds **C2** and **T2** in THF-d_8, were analyzed by ^{1}H NMR spectroscopy (300 MHz) at 20 °C.

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