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Selective Derivatization and Characterization of Bifunctional "Janus-Type" Cyclotetrasiloxanes

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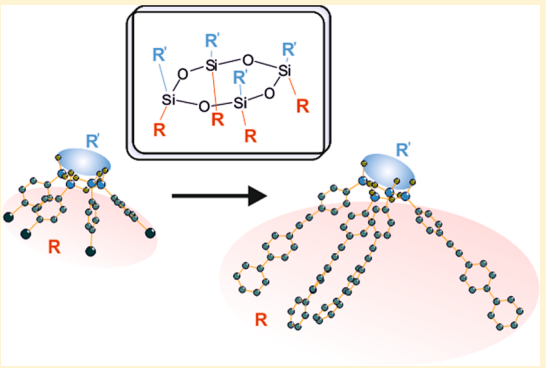
Supporting Information

ABSTRACT: Stereoregular all-*cis* cyclotetrasiloxanes $[R\text{-}Si(O)\text{-}R']_4$ with different functional groups attached to the opposite faces of the ring skeleton were derivatized without stereoisomerization or cleavage of the $(SiO)_4$ ring and with high selectivity using standard synthetic methods. The solid-state structures obtained for the iodophenyl-substituted starting material **16** ($[p\text{-}I\text{-}C_6H_4\text{-}Si(O)\text{-}OSiMe_2Vin]_4$) and for the coupling product **21** ($[biphenyl\text{-}CC\text{-}C_6H_4\text{-}Si(O)\text{-}OSiMe_2Vin]_4$) show a pronounced differentiation in the steric requirements of the different sides of the ring, resulting in characteristic crystal packing. In combination with the observed high thermal and chemical stability, these data demonstrate the high potential of cyclotetrasiloxanes for a wide range of applications.



INTRODUCTION

The design and synthesis of new materials based on functionalized oligosilsesquioxanes have recently received a great deal of attention. Cage-type siloxanes of the general formula $Si_8O_8R_8$ (T_8R_8) in particular have found numerous applications.[1]

Due to their unique characteristics as well-defined nanoscale molecules, silsesquioxanes offer the intriguing perspective of controlling the spatial arrangement of functional groups. By varying the type of substituents and directing the substitution pattern around a silsesquioxane framework, the macroscopic properties of a nanostructured material might be predicted and controlled.

Stereoregular all-*cis* cyclooligosiloxanes in particular are a class of promising building blocks with the desired properties. The first examples of phenyl-substituted cyclooligosiloxanes were synthesized and characterized as siloxanolate complexes of metal cations by Shchegolikhina.[2−5] Most of the work in the literature focuses on the synthesis of cyclotetrasiloxanolates, which are formally half-cage structures, but also key intermediates[6] for the formation of T_8 derivatives. Metal-free cyclotetrasiloxanes (CTS) such as a trimethylsilyloxy derivative[5] or tetrasilanols[7,8] were obtained via reaction of the Na- or K-cyclosiloxanolates with chlorotrimethylsilane ($[R\text{-}Si(O)\text{-}R']_4$, R = Ph, R′ = $OSiMe_3$)[9] or acids, respectively. Following these early studies, the range of substituents attached to the $(SiO)_4$ ring was significantly extended. CTS derivatives with nonfunctional alkyl groups (R = ^{i}Pr,[8] R = Me, Et,[10,11] R = butyl[12]), but also with synthetically useful functional alkyl groups (R = Vin,[10,12] R′ = $OSiMe_2Vin$[13]) and various functionalized aryl substituents including chloro- and bromophenyl groups (R = $Hal\text{-}C_6H_4$[12−14]) or styryl substituents (R = $Vin\text{-}C_6H_4$[12,14]) were reported.

Despite the fact that simple, but yet potentially functionalizable, CTS derivatives were obtained in reasonable yields, examples of successful derivatizations of cyclotetrasiloxanes by standard synthetic methods are scarce. Makarova[15] reported the hydrosilylation of different stereoisomers of $[Ph\text{-}Si(O)\text{-}OSiMe_2H]_4$ with a mesogenic group as a route toward siloxanes with liquid-crystalline properties.

As part of our continuing interest in the chemistry of novel silsesquioxane derivatives,[16,17] we envisaged the application of cyclotetrasiloxanes as potential building blocks of nanostructured materials. The presence of different functional groups attached to the opposite sides of the ring skeleton of all-*cis* cyclotetrasiloxanes may offer the possibility of an orthogonal and selective derivatization of each face and therefore serve as a general synthetic route toward a wide variety of Janus-type cyclotetrasiloxanes. While the complete functionalization of T_8R_8 derivatives has been extensively studied,[1,18,19] the precise control of the substitution pattern of

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different substituents around a silsesquioxane skeleton has not been achieved yet.

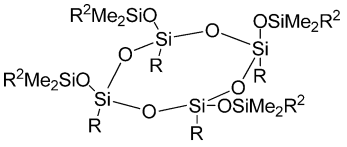
The herein proposed concept is of potentially high practical importance. As a consequence of the inert inorganic $(SiO)_4$ core, the resulting products are expected to have a relatively high thermal and chemical stability. The small ring size forces the substituents attached to the ring in close vicinity to each other and possibly results in significant intramolecular interactions, both sterically and electronically.[20] Depending on the type of the substituent, both faces of the ring and therefore the spatially directed midrange environment of the molecules can be endowed with very different characteristics, for example different polarity or Lewis-acidity/Lewis-basicity. Another possible scenario is attaching substituents with a high selectivity for a substrate of interest on one face of the molecule, while the opposite face remains available for further reactions. As a result, the three-dimensional structure and the macroscopic properties of a material can be controlled in a predictable way. For example, the possibility of forming well-ordered structures, such as micellar structures, extended three-dimensional networks, or monolayers on surfaces for various coating applications, is an intriguing goal.

In this paper we present the functionalization of a dimethylvinylsilyl-capped phenylcyclotetrasiloxane ($[Ph\text{-}Si(O)\text{-}OSiMe_2Vin]_4$, **1**) via a Heck-type coupling and demonstrate the selective derivatization of stereoregular all-*cis* iodophenyl-substituted cyclotetrasiloxanes in the presence of potentially reactive vinyl groups attached to the opposite side of the ring.

RESULTS AND DISCUSSION

In order to develop a general preparative scheme toward the synthesis of stereochemically pure cyclotetrasiloxanes that offer the possibility of attaching various different functional groups to the different faces of the $(SiO)_4$ ring, a careful choice of the substituents in the starting material is important. Suitable substituents have to allow a highly selective and orthogonal derivatization under reaction conditions that do not lead to stereoisomerization or cleavage of the ring skeleton, give the desired products in high yields, and do not require a complicated separation procedure from byproducts. These requirements prompted us to focus on transition-metal-catalyzed reactions, as they generally offer the advantage of mild reaction conditions, can be carried out at room temperature in short reaction times, and avoid strongly acidic or basic media. On the basis of these considerations, we decided to investigate the feasibility of an orthogonal and selective derivatization of haloaryl groups attached to one side of the ring and terminal alkenes or SiH groups on the other side of the ring. Furthermore, an independent optimization of the reaction conditions of each of the envisaged couplings in the absence of the second functional groups appeared to be a sensible strategy.

In the first step we investigated the functionalization of the previously reported CTS **1**,[13] in order to explore the range of compatible reactions with a higher tolerance of functional groups. Following the procedures reported by Shchegolikhina[5] and Kawakami,[12] alkaline hydrolysis of $PhSi(OMe)_3$ gave the expected all-*cis* phenylcyclotetrasiloxanolate, which was converted into **1** by reaction with chloro(dimethyl)vinylsilane in the presence of pyridine as a base. No further purification of **1** was necessary.



R = Ph	R^2 = Vin	**1**
Ph	Allyl	**2**
p-Cl-C_6H_4	Me	**5**
p-Br-C_6H_4	Me	**6**

Initial attempts to derivatize the vinyl groups in **1** via cross-metathesis with styrene in the presence of Grubb's first-generation catalyst were not successful, and only starting materials were isolated. This finding is in agreement with results obtained by Marciniec,[21] who observed the irreversible deactivation of the catalyst by alkyl-substituted vinylsilanes, while alkoxyvinylsilanes could be converted in high yields. It is interesting to note, however, that the attempted functionalization of the homologous allyl-substituted CTS derivative **2** also failed.[22,23]

In general, Heck reactions involving vinylsilanes and aryl halides are quite uncommon due to the high reactivity of the Si−C bond resulting in a decrease of the yield of the desired Heck-type product and an increase of the amount of side products such as styrene derivatives. Several modifications of the original protocol aiming to suppress the undesired Si−C bond cleavage were published. Hallberg[24,25] reported the use of silver nitrate as an additive, while Jeffery successfully applied a tetraalkylammonium salt-based catalyst system.[26] Both methods use aryl iodides as the most reactive coupling reagents. In our case, however, these methods proved to be unsatisfactory. The desired arylated CTS derivatives were obtained only in low yields as mixtures of inseparable products.

Recent advances in Heck chemistry, however, enabled the use of less active bromo- or even chloroarenes instead of aryl iodides or triflates.[27] More importantly, the specific reaction conditions for this type of coupling are compatible with siloxane chemistry, as demonstrated by several groups.[28−30] Following this methodology, we succeeded in coupling various bromoarenes to the dimethylvinylsilyloxy-modified CTS **1** (Scheme 1). The reactions were carried out in a mixture of toluene/dioxane (2:1) in the presence of 3.0 mol % bis(tri-*tert*-butylphosphine)palladium(0) as catalyst and dicyclohexylmethylamine as a base/HBr scavenger (1.6 equivalents per SiVin group) with a slight excess of bromoarene (1.03 equivalents per SiVin group) at 50 °C for 12 h. Reaction monitoring by ^1H NMR spectroscopy (disappearance of the vinyl multiplet) after that period of time indicated the complete conversion of the CTS starting material. Aqueous workup gave the crude product, which could be purified by column chromatography using silica gel (eluent hexane/$CHCl_3$).

We were able to isolate various arylated products and characterize them by multinuclear NMR spectroscopy and mass spectrometry. The results clearly confirm the formation of arylated, all-*cis* configured cyclotetrasiloxanes as the exclusive products. The representative examples of compounds reported herein (**3**: R^3 = *p*-F-C_6H_4, **4**: R^3 = 9-phenanthrenyl) also show the tolerance of the coupling reaction to steric and electronic factors. Both the electron-poor *p*-fluorophenyl-substituted and the electron-rich, sterically demanding phenanthrenyl-substituted CTS derivatives were obtained in comparable, but moderate yields.

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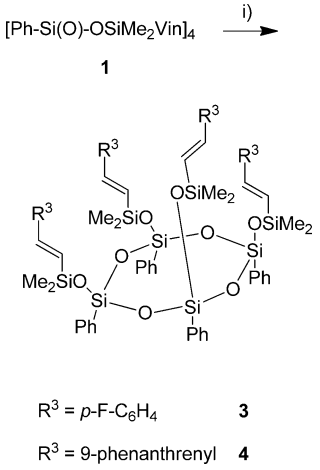
Scheme 1. Functionalization of Vinyl-Substituted CTS 1 via a Heck Coupling[a]



[a]Reaction conditions: (i) Br-R^3, $Pd(P^tBu_3)_2$, Cy_2NMe, toluene/dioxane, 50 °C, 12 h.

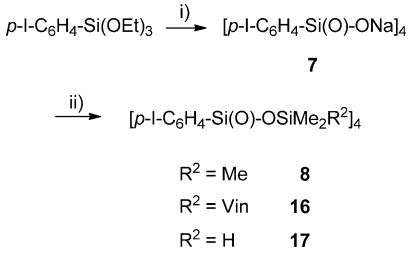
The observed ^{29}Si NMR chemical shifts for **3** and **4** are almost identical. The peak at higher field was assigned to the Si centers of the $(SiO)_4$ ring structure ($\delta^{29}Si$ = −78.4 for **3** and $\delta^{29}Si$ = −78.3 for **4**); the signal at lower field belongs to the dimethylsilyloxy groups ($\delta^{29}Si$ = 0.4 for **3** and $\delta^{29}Si$ = 0.1 for **4**). The transformation of the vinyl groups can be monitored by the disappearance of the vinyl multiplet of the starting material (δ^1H = 5.74−6.24) in the ^1H NMR spectrum and the appearance of one of the proton resonances of an internal alkene (δ^1H = 6.18, $^3J_{HH}$ = 18.9 Hz for **3**, and δ^1H = 6.44, $^3J_{HH}$ = 19.2 Hz for **4**). ^1H NMR spectroscopy also shows the formation of the *E* isomer as the only product, while the *Z* isomer could not be detected. The remaining CH peak of the alkene could not be assigned due to overlapping with the signals of the aryl groups. The ^{13}C NMR spectra change significantly as a result of the arylation. While the signal of the vinylic methylene group ($\delta^{13}C$ = 132.2 in **1**) disappears, the signal assigned to the CH group ($\delta^{13}C$ = 138.7 in **1**) is shifted characteristically to lower field ($\delta^{13}C$ = 143.5 for **3**, $\delta^{13}C$ = 142.5 for **4**). New signals at $\delta^{13}C$ = 132.1 (**4**) and $\delta^{13}C$ = 127.3 (**3**) could be assigned to the CH group of an internal alkene. It is worth noting that the CH resonance for **3** is split into a doublet with a $^5J_{CF}$ coupling constant of 2.4 Hz. Mass spectrometry confirmed the characterization, and the MALDI-TOF spectra showed only the M^+ peak.

Following our initially proposed strategy toward an orthogonal modification of the two opposite sides of a CTS structure, we turned our focus to the optimization of methods for the functionalization of the remaining face of the ring. Haloaryl-substituted compounds, such as the previously reported chlorophenyl (**5**) and bromophenyl (**6**) substituted cyclotetrasiloxanes,[12−14] appeared to be suitable starting materials. Both siloxanolates were obtained by alkaline hydrolysis of the corresponding triethoxysilanes in *n*-butanol. Reaction with chlorotrimethylsilane in the presence of pyridine in toluene yielded the target compounds for the coupling studies, **5** and **6**, in high purity.

Our attempts to functionalize the chlorophenyl- and bromophenyl-substituted cyclotetrasiloxanes (**5** and **6**) were not successful. In the case of **5**, neither a Ni-catalyzed coupling with alkyl Grignard reagents[31] nor the recently developed Fe-catalyzed cross-coupling procedure[32] gave the desired alkylated products; instead inseparable mixtures of unidentified siloxanes were obtained. All attempts to apply the previously successful Heck coupling conditions to the vinylation of the bromophenyl moieties of **6** failed. Various modifications to the protocol, such as higher catalyst loadings (up to 10 mol %), prolonged reaction times, and higher temperatures (up to 48 h, 100 °C) or an excess of the base (5 equivalents per Me_2SiVin group) also did not give the desired products. The failure of the Heck coupling is probably due to the inherently low reactivity of these groups in combination with steric hindrance as a result of the presence of four haloaryl groups in close vicinity to each other.

As iodophenyl groups are generally more reactive under most transition-metal-catalyzed reaction conditions, a CTS derivative with iodophenyl substituents seemed to be a promising candidate. Starting from 4-(triethoxysilyl)iodobenzene,[33] siloxanolate **7** could obtained by alkaline hydrolysis in a concentrated solution in *n*-butanol as a white precipitate after 4 days at room temperature (Scheme 2). ^1H NMR spectroscopy indicated that the resulting dry powder contained varying amounts of *n*-butanol. The hygroscopic product can be stored at ambient conditions over a few months without notable change.

Scheme 2. Synthesis of Iodophenyl-Substituted CTS 8 and 16[a]



[a]Reaction conditions: (i) NaOH, H_2O, *n*-butanol; (ii) Me_3SiCl/$Me_2SiVinCl$/Me_2SiHCl pyridine, toluene.

Capping of the siloxanolate **7** with chlorotrimethylsilane gave the desired starting material for functionalization studies, CTS **8**. It was obtained as a colorless solid in chemically and stereoisomerically pure form, as indicated by NMR spectroscopy, and could be used for subsequent reactions without further purification.

The iodophenyl group proved to be highly reactive under standard Sonogashira conditions. The reaction of **8** with terminal alkynes in the presence of dichloropalladium(II)bis(triphenylphosphine) as catalyst, copper(I) iodide, and triethylamine as base in THF gave the expected coupling products (Scheme 3). Notable were the mild reaction conditions: the starting material was completely consumed after 12 h at room temperature. After aqueous workup the crude product was purified by column chromatography using silica gel (eluent hexane/$CHCl_3$).

A series of coupling products (**9**−**15**) with various groups on one side of the ring structure and trimethylsilyloxy groups on the other side could be synthesized and characterized in moderate to high yields. As summarized in Scheme 3 and Table 1, the range of possible substituents includes alkyl, benzyl, and aryl groups and, most importantly, a synthetically valuable trimethylsilyl group (CTS **15**). The yield of the methox-

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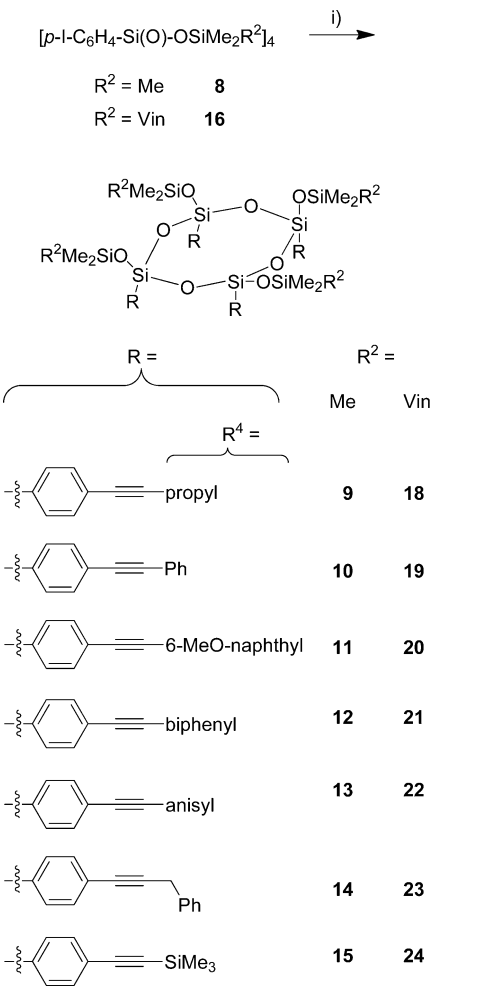
Scheme 3. Functionalization of Iodophenyl-Substituted CTS 8 and 16[a]



[a]Reaction conditions: (i) alkyne HC≡CR^4, $Cl_2Pd(PPh_3)_2$, CuI, NEt_3, THF, 12 h at room temperature.

Table 1. Comparison of Yields Obtained for CTS 9−15 and 18−24

	R^2 = Me		R^2 = Vin	
entry	product	yield (%)	product	yield (%)
1	**9**[a]	54	**18**[a]	77
2	**10**[b]	81	**19**[b]	36
3	**11**[c]	45	**20**[c]	31
4	**12**[d]	65	**21**[d]	62
5	**13**[e]	90	**22**[e]	23
6	**14**[f]	72	**23**[f]	55
7	**15**[g]	74	**24**[g]	83

[a]R^4 = propyl. [b]R^4 = phenyl. [c]R^4 = 6-methoxynaphthyl. [d]R^4 = biphenyl. [e]R^4 = anisyl. [f]R^4 = benzyl. [g]R^4 = $SiMe_3$.

ynaphthyl-substituted alkyne **11** is significantly lower than that for the rest of the products, probably due to the increased steric demand of the methoxynaphthyl group (Table 1, entry 3). The observed ^{29}Si NMR chemical shifts do not change significantly as a result of the coupling (δ^{29}Si = −79.4 and 11.6 for **8**), are independent of the R^4 group, and indicate the presence of only one stereoisomer. The main characteristic of the coupling products is the complete disappearance of the signal assigned to the C−I group of the starting material (δ^{13}C = 97.5 in **8**), while two new signals within the chemical shift range from δ^{13}C = 80 to δ^{13}C = 105, depending on the substituent, indicate the presence of an internal triple bond. MALDI-TOF, ESI, and EI mass spectra provide further evidence for the successful coupling and the isolation of products with four identical substituents attached to the siloxane ring. Although silsesquioxane derivatives bearing substituents with high π-electron density generally show reasonably good ionization efficiencies, we encountered difficulties with some of the compounds, even as their corresponding Na^+ or Ag^+ ions. All methods, however, gave the M^+ peak, and the experimentally observed isotope patterns matched the calculated isotope patterns. A representative example of the ^{29}Si NMR spectrum and mass spectrum of CTS **9** are shown in Figure 1.

The presence of a triple bond is of high preparative value, as it offers the intriguing perspective of subsequent organic transformations at groups adjacent to the CTS ring. One of the most interesting reactions is "click chemistry". In contrast to terminal alkynes, which can be coupled with azides in the presence of a Cu(I) catalyst,[34,35] internal alkynes require the use of a Ru-based catalyst system.[36] Our preliminary results demonstrate that the synthesized alkynes are reactive toward simple azides in the presence of Cp*RuCl(COD), although the final products have not been isolated and fully characterized. As the Cu(I)-catalyzed cycloaddition of terminal alkynes generally has proven to be more reliable than the cycloaddition of internal alkynes, subsequent efforts focused on cleaving the trimethylsilyl group in **15** in order to obtain a terminal triple bond. Although a series of experiments revealed a relatively high stability of the siloxane ring framework, the selective cleavage of the $SiMe_3$ group in the presence of the CTS appeared to be difficult. For example, while the reaction of **15** with potassium carbonate and water (up to 10 equivalents per $CCSiMe_3$ group) in THF affected neither the cyclotetrasiloxane framework nor the $SiMe_3$ group attached to the triple bond, reaction with tetrabutylammonium fluoride in THF proceeded with stereoisomerization of the ring. In general, the reactivity of the ring toward acidic or basic conditions significantly depends on the amount of acid or base, the reaction time, and the presence of nucleophiles.[37,38] The ring remained unchanged in the presence of equimolar amounts of trifluoroacetic acid for 24 h, while the reaction with a 2-fold excess for one week resulted in rearrangement of the $(SiO)_4$ skeleton. The reaction with methanolic HCl and potassium carbonate in MeOH also gave a mixture of stereoisomerized products.

Having successfully demonstrated the possibility of an independent derivatization of each of the two sides of the ring structure, i.e., the modification of the iodophenyl groups on one side via Sonogashira coupling and of the dimethylvinylsilyloxy groups on the other side via Heck coupling, we were encouraged to investigate the synthetic potential of these reactions in the presence of a second, potentially reactive group at the remaining side of the ring. As starting materials for a stepwise, orthogonal functionalization, two CTS derivatives (**16** and **17**) with iodophenyl groups on one face of the ring and functional groups on the other side were obtained. The dimethylvinylsilyloxy groups in **16** were expected to serve as reactive sites for a Heck-type cross coupling; the dimethylsilyloxy groups in **17**, as reactive groups for hydrosilylation. ^{29}Si NMR spectroscopy indicated the presence of one stereoisomer; only one signal for the four equivalent ring-forming Si centers (δ^{29}Si = −79.3 for **16**, δ^{29}Si = −78.7 for **17**) and only one signal

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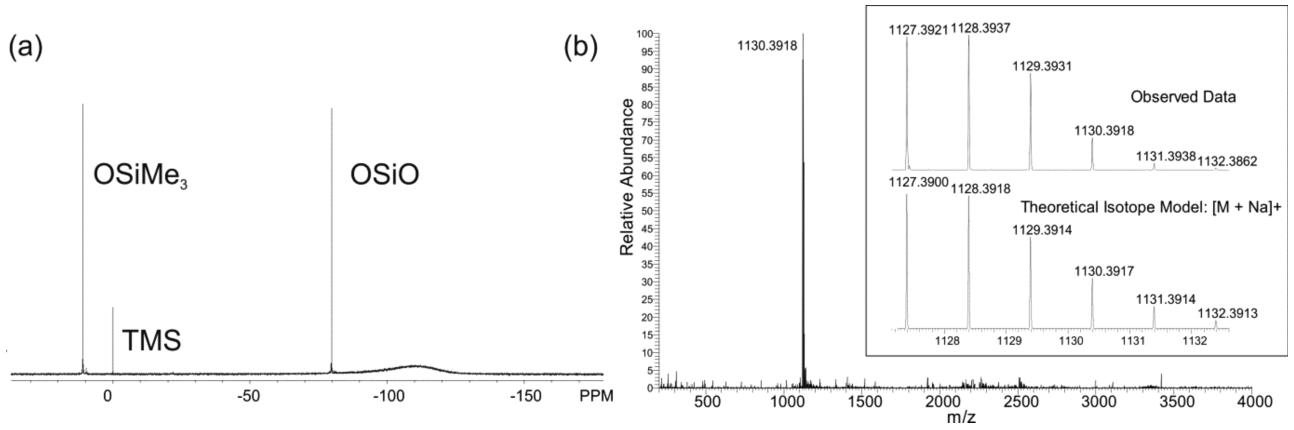

Figure 1. (a) $^{29}Si\{^{1}H\}$ NMR spectrum of **9**. (b) High-resolution ESI mass spectrum of **9**. The inset shows the comparison of the experimental isotope distribution with the calculated isotope pattern.

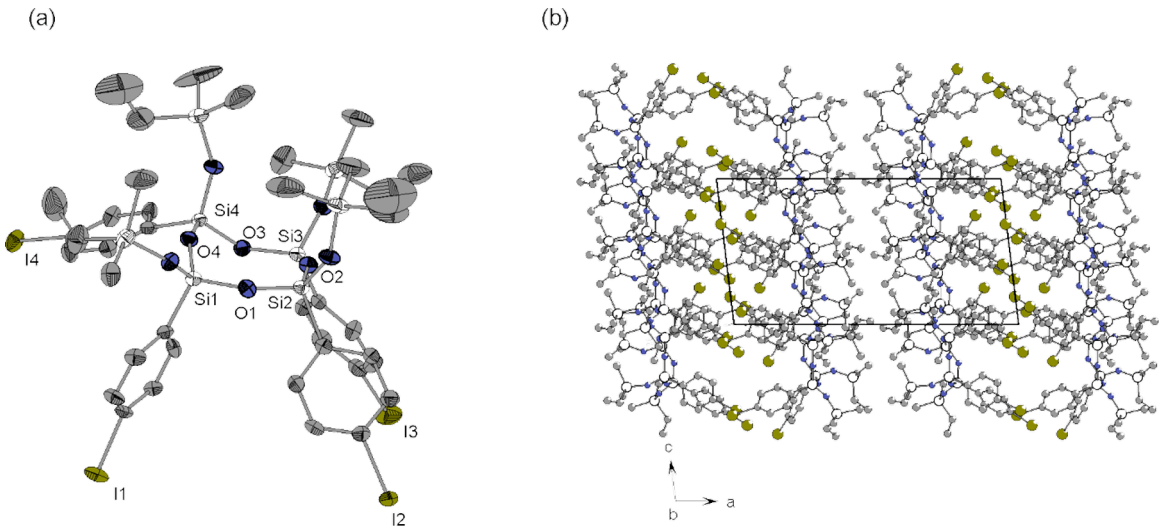

Figure 2. (a) Molecular structure of **16**. Only one component of the positional disorder of the Me_2SiVin groups is shown. (b) Packing diagram of **16**, view along the crystallographic *b*-axis. Color code: I brown, Si white, O blue, C gray. H atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

for the dimethylsilyloxy groups (δ^{29}Si = 0.1 for **16**, δ^{29}Si = −3.0 for **17**) were observed.

While siloxane **17** could not be crystallized despite various attempts, single crystals suitable for X-ray diffraction studies were obtained from a toluene/dichloromethane solution (1 mL/2 mL, 100 mg **16**) of siloxane **16** (Figure 2) by slow evaporation. The latter compound crystallizes in the monoclinic crystal system, space group $P2_1/c$. In the crystal, **16** packs in a layer structure; the aryl groups of molecules in one layer are facing the aryl substituents of molecules of a different layer (Figure 2b). The significant interdigitation of the C−I groups leads to several rather close contacts between molecules belonging to different layers: the closest interlayer I···I distance was measured as d(I···I) = 379.2(1) pm (sum of the van der Waals radii $\sum r_{I-I}$ = 396 pm[39]), and the closest C···I contact as 372.2(1) pm (sum of the van der Waals radii $\sum r_{C-I}$ = 368 pm[39]). Notably, both distances are slightly shorter than the sum of the van der Waals radii, indicating a close packing.

Both the packing and the molecular structure resemble the structural data obtained by Pizzotti[14] for the CTS derivative **6**, bearing bromophenyl groups. The $(SiO)_4$ ring shows only small deviations from planarity; only the atoms Si4 and O4 are located at a distance of 86 and 76 pm away from the least-squares plane formed by the atoms Si1−3/O1−3. As a consequence of this rather unusual[14] conformation of the eight-membered ring, three of the aryl substituents point in approximately the same direction, while the remaining group attached to Si4 is aligned almost parallel to the ring plane, as indicated by the small dihedral angle between the C_6H_4 plane and the ring least-squares plane of 24°. Overall, the conformations of both the iodophenyl groups and the rather bulky dimethylvinylsilyloxy substituents are clearly a result of the requirement to reduce steric hindrance between the R groups. No evidence for attractive π-stacking interactions could be found. The closest contacts between aryl groups of the same molecule are quite long, with C···H distances of d(C···H) = 297.1(1.1) pm (C12−H14) and d(C···H) = 301.3(0.9) pm (C7−H14). Within the margins of experimental error, the mean Si−O distances in **16** and **6** are almost identical; the terminal Si−O bonds are slightly shorter (d(SiO) = 160.9(6) pm for **16**, 160.1(1) pm for **6**) than the bridging Si−O bonds (162.1(7) pm for **16**, 161.3(4) pm for **6**).

Interestingly, siloxane **17** is of very little synthetic use. Neither the hydrosilylation of the Si−H group with various simple alkenes such as 1-hexene using both Speier's and Karstedt's catalyst and less common reagents such as platinum

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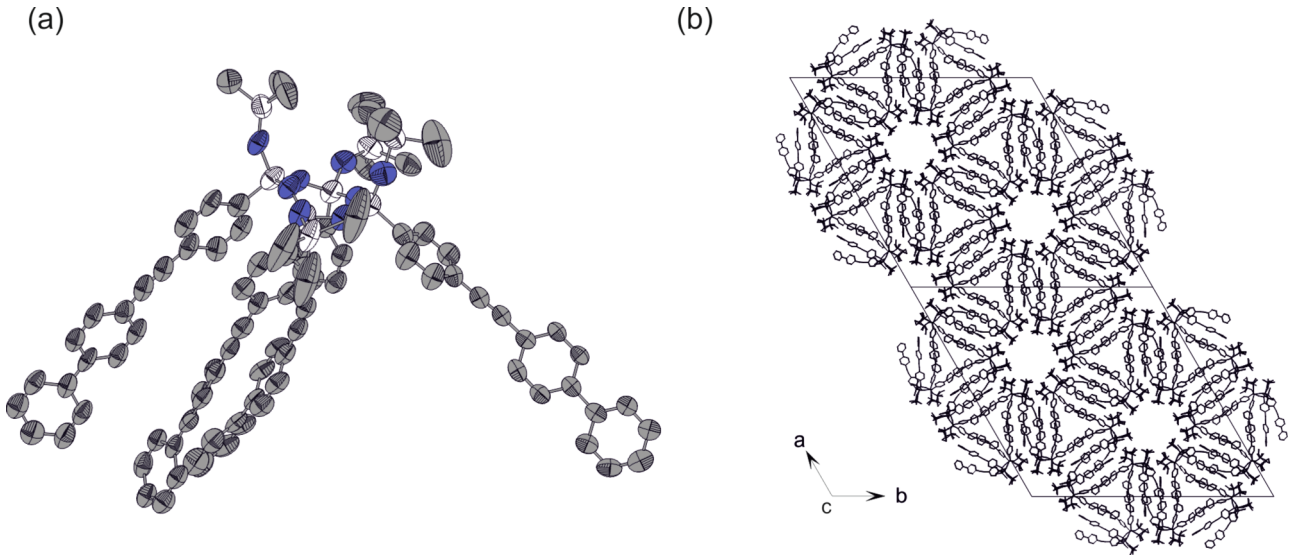

Figure 3. (a) Molecular structure of **21**. For clarity, some atoms of the highly disordered Me_2SiVin groups are omitted. See Supporting Information for details. (b) Packing diagram of **21**, view along the crystallographic *c*-axis. Color code: Si white, O blue, C gray. H atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

dioxide nor a Sonogashira-type coupling, as described previously, gave the expected products. In the case of an attempted hydrosilylation, only traces of the starting material reacted, whereas the reaction under Sonogashira conditions gave a mixture of inseparable products. The finding that **17** was partially converted only in the presence of a large excess of hydrosilylation catalyst might indicate an irreversible deactivation by the reactive C−I functionalities. Similarly, the observed result under Sonogashira conditions suggests a reaction of both the C−I groups and the Si−H moieties.

In contrast, functionalization of **16** via Sonogashira coupling could be carried out successfully under the same reaction conditions as described for the series with trimethylsilyloxy groups (CTS **9**−**15**). A series of CTS derivatives (CTS **18**−**24**, Scheme 3) with alkyl, aryl, and silyl substituents on one side of the molecule was obtained as stereoisomerically pure substances in fair to excellent yields. The yields were mostly comparable with the trimethylsilyloxy series (CTS **9**−**15**), although significantly lower yields were obtained for **19**, **20**, and **22**. This result might be rationalized by the higher steric requirements of the dimethylvinylsilyloxy moieties, which force the substituents on the other side of the ring skeleton to be much closer to each other, therefore resulting in a lower yield of the desired product.

The ^{1}H NMR spectra clearly show the presence of vinyl groups in the isolated product with the expected ratios between the $SiMe_2$ proton resonances and the newly introduced substituents on the other side of the ring, indicating the isolation of pure tetrafunctionalized products. All acquired ^{29}Si{^{1}H} NMR spectra show only minor variations in the NMR chemical shifts, compared with the starting material. The presence of one signal at δ^{29}Si = −80 with a small half-height width of $\nu_{1/2}$ = 1.2 Hz is characteristic for a stereoisomerically pure CTS compound; the signal around δ^{29}Si = −0.4 can be assigned to the dimethylvinylsilyloxy group. Diagnostic for the successful coupling are the disappearance of the resonance assigned to the C−I group at δ^{13}C = 97.5, the presence of signals in the range δ^{13}C = 80 to δ^{13}C = 105 assigned to internal triple bonds, and signals arising from unreacted vinyl groups at δ^{13}C = 132.5 (CH_2) and δ^{13}C = 138.4 (CH). All signals in the ^{13}C NMR spectra are reasonably sharp with small half-height widths ($\nu_{1/2}$ = 1.7 Hz for **24**). Mass spectrometric studies support the characterization: the MALDI-TOF spectra show only the expected $(M + Na)^+$ or the M^+ peak.

Despite numerous attempts, crystals suitable for single-crystal X-ray diffraction could be obtained only from the biphenyl-substituted CTS derivative **21** (Figure 3) from a chloroform solution by slow evaporation. The latter compound crystallizes in the trigonal space group $R\bar{3}$. In contrast to the iodophenyl -substituted starting material **16**, CTS **21** shows a more complicated packing (Figure 3b). A view along the crystallographic *c*-axis reveals the hexagonal arrangement of six molecules of **21** as the most noteworthy feature of the packing. While the aryl groups of different molecules show a significant overlapping and are still well separated from each other (closest intermolecular distance between aryl groups: d(C···C) = 374.4(3) pm between C33−C73), the dimethylvinylsilyloxy groups point to the inside of large (approximate diameter 1.2 nm) voids. The absence of close intermolecular interactions between Me_2SiVin groups at the inside of these cavities results in significant disorder of the silyl substituents and therefore is one of the reasons for the low overall quality of the solid-state structure (R1 = 0.1019). Additionally, the cavities are not empty, but are filled with highly disordered solvent molecules (see Experimental Section and Supporting Information for details). In contrast, the atom positions of the $(SiO)_4$ skeleton itself and the aryl substituents are well-defined. The molecular structure (Figure 3a) is similar to the structure of iodophenyl-substituted CTS **16**. The $(SiO)_4$ ring forms a distorted envelope conformation, leading to an almost parallel alignment of three of the substituents, while the orientation of the remaining substituent is almost perpendicular to the average ring plane.

The herein reported structural data of cyclotetrasiloxanes **16** ($[p$-I-C_6H_4-Si(O)-$OSiMe_2Vin]_4$) and **21** ([biphenyl-CC-C_6H_4-Si(O)-$OSiMe_2Vin]_4$) clearly demonstrate the significant influence of having different environments on the two sides of the ring. In both cases, characteristic patterns are observed: a layer structure for **16** and a hexagonal packing for **21**. The

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aromatic substituents tend to overlap, while the ring and the silyloxy groups are more separated from each other, resulting in the formation of predominantly "organic" and "inorganic" domains in the crystal.

This work represents an important result in the chemistry of functionalized cyclotetrasiloxanes, as it demonstrates for the first time the highly selective derivatization of only one of two potentially reactive groups present in an oligosiloxane. Our work does not give any evidence of side reactions involving the dimethylvinylsilyloxy moieties. Following the initial strategy toward a stepwise modification, our subsequent synthetic efforts focused on attempts to functionalize the CTS compounds **18**–**24** via a Heck-type coupling. However, the expected coupling products could not be obtained as pure substances. Characterization of the resulting crude products by NMR spectroscopy and mass spectrometry did not indicate the formation of tetra-arylated siloxanes in high yields. Instead the coupling experiments gave mostly unreacted starting materials in varying yields along with mono- and diarylated products and yet unidentified siloxanes, but only small amounts (<10%) of tri- and tetra-arylated compounds. Our preliminary attempts to optimize the reaction conditions of the cross-coupling, e.g., by changing the reaction time, temperature, or ratio of the catalyst, additives, and reagents, did not give the expected tetra-arylated CTS as the predominant products.

Considering the high potential of functionalized cyclotetrasiloxanes for a vast number of applications, an investigation of the chemical stability and the thermal properties is essential. In order to assess the scope and limitations of these newly synthesized molecules, selected compounds were characterized by thermogravimetric analysis (TGA). Our results revealed remarkably high thermal stabilities of the investigated siloxanes (**4**, **9**, **10**, **12**, **15**, **18**, **19**, **21**, **24**). The temperatures at which 5% weight loss occurred (T_{d5}) and the final weight loss under N_2 are summarized in Table 2. The highest T_{d5} temperatures

Table 2. Summary of Thermal Properties of CTS Derivatives[a]

entry	product	T_{d5} [°C]	final weight %[b]
1	**4**[c]	422	25
2	**9**[d]	307	57
3	**10**[e]	525	78
4	**12**[f]	533	64
5	**15**[g]	320	55
6	**18**[h]	460	74
7	**19**[i]	543	80
8	**21**[j]	516	74
9	**24**[k]	345	67

[a]Thermogravimetric analysis under N_2 at a heating rate of 10 °C/min. [b]Obtained at 1000 °C. [c]R = Ph, R^3 = −(HC═CH)-phenanthrenyl. [d]R^2 = Me, R^4 = propyl. [e]R^2 = Me, R^4 = Ph. [f]R^2 = Me, R^4 = biphenyl. [g]R^2 = Me, R^4 = $SiMe_3$. [h]R^2 = Vin, R^4 = propyl. [i]R^2 = Vin, R^4 = Ph. [j]R^2 = Vin, R^4 = biphenyl. [k]R^2 = Vin, R^4 = $SiMe_3$.

were observed for compounds with rather inert aryl groups attached to the triple bond, while compounds with alkyl or silyl groups suffer from weight loss at significantly lower temperatures (Figure 4). CTS derivatives with dimethylvinylsilyloxy groups are thermally more stable than their trimethylsilyloxy analoges, as indicated by higher T_{d5} temperatures. Aryl-substituted molecules (**10** and **19**) and the alkyl-substituted CTS **18** show a weight loss that occurs in one step. In the case

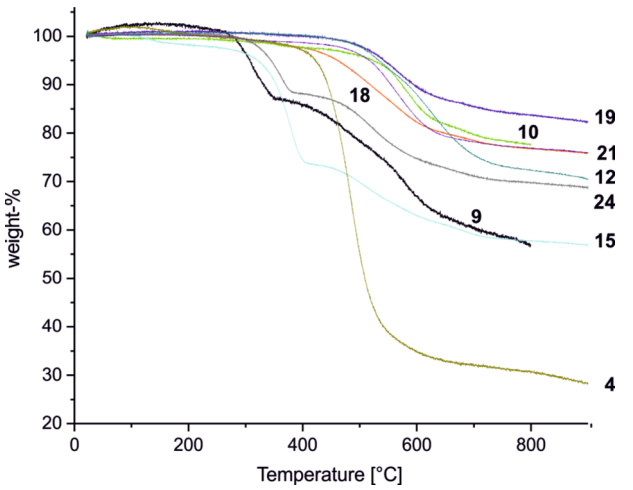

Figure 4. TGA curves for selected cyclotetrasiloxanes.

of the silyl-substituted (**15** and **24**) compounds and the propyl-substituted (**9**) compounds weight loss is a two-step process. The compound showing the largest weight loss is the Heck coupling product **4** with phenanthrenyl substituents.

The observed remarkable thermal stability can be compared with that of the isopropyl-substituted CTS $(^iPr_2SiO)_4$, which is characterized by a significantly lower T_{d5} of 205 °C, or ladder siloxanes reported by Unno,[40] for example, a pentacyclic siloxane with T_{d5} = 296 °C.

CONCLUSIONS

In this paper we report the selective functionalization of stereoregular all-*cis* cyclotetrasiloxanes **1** ([Ph-Si(O)-OSi-Me_2Vin]$_4$), **8** ([*p*-I-C_6H_4-Si(O)-$OSiMe_3$]$_4$), and **16** ([*p*-I-C_6H_4-Si(O)-$OSiMe_2$Vin]$_4$) using standard synthetic methods, i.e., a Heck-type coupling for the functionalization of **1** and a Sonogashira protocol for the modification of **8** and **16**. Using CTS **8** and **16** as starting materials, a series of cyclotetrasiloxanes (**9**–**15**, **18**–**24**) with various substituents having different steric and electronic characteristics was obtained under mild reaction conditions and, most notably, without stereoisomerization reactions or cleavage of the $(SiO)_4$ ring skeleton. Of particular interest is the selective derivatization of **16** via Sonogashira coupling in the presence of a vinylsilyl group. This result demonstrates the intriguing possibility of a stepwise and orthogonal modification of the opposite faces of all-*cis* cyclotetrasiloxanes, which is the subject of current studies in our laboratories. Preliminary investigations using differential scanning calorimetry, polarized optical microscopy, and X-ray diffraction methods also revealed liquid-crystalline properties of some of the CTS derivatives. A full account on the mesomorphic properties will be published elsewhere.

The combined structural data obtained for **16** and **21** ([biphenyl-CC-C_6H_4-Si(O)-$OSiMe_2$Vin]$_4$) and the observed high thermal and chemical stabilities of the herein reported CTS derivatives demonstrate the unique suitability of the siloxane ring as a versatile scaffold for the combination of functional groups with different properties in one molecule. Our findings support the initially proposed high potential of functionalized CTS derivatives as a general strategy toward the controlled synthesis of nanomaterials. Further investigations on the potential applications of CTS derivatives, e.g., as surface modifiers, are currently under way in our laboratories.

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EXPERIMENTAL SECTION

4-(Triethoxysilyl)iodobenzene was prepared according to a literature procedure.[33] The synthesis of tetraphenyl cyclotetrasiloxanolate [Ph-Si(O)-ONa]$_4$ was carried out using the method reported by Kawakami.[12] CTS **5** and **6** were obtained by a modified literature procedure using *n*-BuOH instead of EtOH as solvent.[14]

CTS 1. Pyridine (1.61 g, 20.3 mmol) was added to a suspension of 2.24 g of tetraphenyl cyclotetrasiloxanolate [Ph-Si(O)-ONa]$_4$ in 35 mL of toluene. The reaction mixture was cooled to 0 °C, and 2.41 g (20.3 mmol) of chloro(dimethyl)vinylsilane was added slowly via a syringe. The white suspension was stirred for 12 h at room temperature and quenched with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated to yield 1.51 g (1.7 mmol, 49%) of a colorless oil. ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.24 (s, 24H, $SiMe_2$), 5.74−6.24 (m, 12H, vinyl), 7.07−7.32 (m, 20H, Ar-H). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): δ 0.3 ($SiMe_2$), 127.3 (CH), 129.7 (CH), 132.2 (C=$\underline{C}H_2$), 132.9 (Cq), 134.1 (CH), 138.7 (C=$\underline{C}$H). ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ −79.3 (OSiO), 0.1 ($SiMe_2$). Anal. Calcd for $C_{40}H_{56}O_8Si_8$: C 54.01, H 6.35. Found: C 53.64, H 6.30.

CTS 2. Pyridine (1.61 g, 20.3 mmol) was added to a suspension of 2.24 g of tetraphenyl cyclotetrasiloxanolate [Ph-Si(O)-ONa]$_4$ in 35 mL of toluene. The reaction mixture was cooled to 0 °C, and 2.73 g (20.3 mmol) of allyl(chloro)dimethylsilane was added slowly via a syringe. The white suspension was stirred for 12 h at room temperature and quenched with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated to yield 1.25 g (1.3 mmol, 37%) of a colorless oil. ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.20 (s, 24H, $SiMe_2$), 1.67 (d, $^3J_{HH}$ = 8.3 Hz, 8H, CH_2), 4.83−4.90 (m, 8H, CH_2), 5.73−5.84 (m, 4H, CH), 7.07−7.13 (m, 8H, Ar-H), 7.27−7.31 (m, 12H, Ar-H). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): δ −0.3 ($SiMe_2$), 26.0 (CH_2), 113.8 (CH_2), 129.8 (CH), 132.7 (Cq), 134.0 (CH). ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ −79.5 (OSiO), 7.8 ($SiMe_2$). Anal. Calcd for $C_{44}H_{64}O_8Si_8$: C 55.88, H 6.82. Found: C 55.93, H 6.35.

CTS 3 and 4. **1** (0.41 g, 0.46 mmol) was dissolved in 6 mL of toluene and 3 mL of dioxane. After the addition of 8 mg (0.03 equivalent per SiVin group, 0.056 mmol) of Pd(P^tBu_3)$_2$, 0.57 g (1.6 equivalents per SiVin group, 2.9 mmol) of Cy_2NMe, and 1.89 mmol (1.03 equivalents per SiVin group) of bromoarene the reaction mixture was stirred for 12 h at 50 °C. Workup was carried out by diluting with chloroform, filtration through charcoal, and washing with diluted acetic acid and saturated sodium bicarbonate solution. The organic layer was dried over magnesium sulfate. The crude product was purified by column chromatography using gradient elution (hexane, hexane/$CHCl_3$ = 7:3 to hexane/$CHCl_3$ = 1:9).

CTS 3. ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.23 (s, 24H, $SiMe_2$), 6.18 (d, $^3J_{HH}$ = 18.9 Hz, 4H, C=C$\underline{H}$), 6.73−7.26 (m, 40H, Ar-H/C=C$\underline{H}$). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): δ 0.7 ($SiMe_2$), 115.3 (d, $^2J_{CF}$ = 21.2 Hz, CH, C^{ortho}F), 127.3 (d, $^5J_{CF}$ = 2.4 Hz, C=$\underline{C}$H), 127.4 (CH), 128.1 (d, $^3J_{CF}$ = 8.2 Hz, CH, C^{meta}F), 129.9 (CH), 132.7 (Cq), 134.1 (CH), 134.2 (d, $^4J_{CF}$ = 3.8 Hz, Cq, C^{para}F), 143.5 (C=$\underline{C}$H), 162.7 (d, $^1J_{CF}$ = 247.3 Hz, CF). ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ −78.4 (OSiO), 0.4 ($SiMe_2$). Yield: 0.17 g, 29%. R_f = 0.78 (hexane/$CHCl_3$ = 7:3). Colorless oil. Anal. Calcd for $C_{64}H_{68}F_4O_8Si_8$: C 60.72, H 5.41. Found: C 59.38, H 5.18. MS (MALDI): *m*/*z* 1287.123 (M + Na)$^+$.

CTS 4. ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.36 (s, $SiMe_2$, 24H), 6.44 (d, $^3J_{HH}$ = 19.2 Hz, 4H, C=C$\underline{H}$), 6.97 (m, 8H, Ar-H), 7.17 (s, 4H, Ar-H), 7.32−7.60 (m, 40H, Ar-H, C=C$\underline{H}$), 7.83 (m, 4H, Ar-H), 8.42−8.50 (m, 8H, Ar-H). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): δ 1.0 ($SiMe_2$), 122.3, 122.8, 124.4, 124.6, 126.4, 126.1, 126.4, 126.5, 127.5, 128.7, 129.9, 130.1 (Cq), 130.2 (Cq), 131.6 (Cq), 132.1 (C=$\underline{C}$H), 132.8 (Cq), 134.1, 135.1 (Cq), 142.5 (C=$\underline{C}$H). ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ −78.3 (OSiO), 0.1 ($SiMe_2$). Yield: 0.15 g, 20%. R_f = 0.23 (hexane/$CHCl_3$ = 7:3). Yellow solid, mp dec. Anal. Calcd for $C_{96}H_{88}O_8Si_8$: C 72.32, H 5.56. Found: C 72.46, H 5.64. MS (MALDI): *m*/*z* 1702.3 (M + Ag)$^+$.

CTS 5. Sodium hydroxide (0.55 g, 13.7 mmol) was dissolved in a mixture of 271 μL (15 mmol) of water and 20 mL of *n*-butanol. Then 3.77 g (13.7 mmol) of 4-(triethoxysilyl)chlorobenzene was added, and the reaction mixture was stirred for 2 days at room temperature. The resulting white precipitate was filtered off, washed with 15 mL of hexane, and dried under high vacuum to yield 2.70 g of a white powder, which typically contains varying amounts of *n*-butanol. The product was used for subsequent reactions without further characterization. Pyridine (1.61 g, 20.3 mmol) was added to a suspension of 2.70 g of [*p*-Cl-C_6H_4-Si(O)-ONa]$_4$ in 35 mL of toluene. The reaction mixture was cooled to 0 °C, and 2.2 g (20.3 mmol) of chlorotrimethylsilane was added slowly via a syringe. The white suspension was stirred for 12 h at room temperature and quenched with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated to yield CTS **5** as a colorless crystalline solid (1.9 g, 56%). ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.20 (s, 36H, $SiMe_3$), 7.17−7.32 (m, 16H, Ar-H). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): δ 1.8 ($SiMe_3$), 127.9 (CH), 131.1 (Cq), 135.1 (CH), 136.5 (Cq). ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ −79.9 (OSiO), 11.5 ($SiMe_3$). Anal. Calcd for $C_{36}H_{52}Cl_4O_8Si_8$: C 44.15, H 5.35. Found: C 44.21, H 5.46.

CTS 6. Sodium hydroxide (0.55 g, 13.7 mmol) was dissolved in a mixture of 271 μL (15 mmol) of water and 20 mL of *n*-butanol. Then 4.37 g (13.7 mmol) of 4-(triethoxysilyl)bromobenzene was added, and the reaction mixture was stirred for 2 days at room temperature. The resulting white precipitate was filtered off, washed with 15 mL of hexane, and dried under high vacuum to yield 2.05 g of a white powder, which typically contains varying amounts of *n*-butanol. The product was used for subsequent reactions without further characterization. Pyridine (1.61 g, 20.3 mmol) was added to a suspension of 2.05 g of [*p*-Br-C_6H_4-Si(O)-ONa]$_4$ in 35 mL of toluene. The reaction mixture was cooled to 0 °C, and 2.2 g (20.3 mmol) of chlorotrimethylsilane was added slowly via a syringe. The white suspension was stirred for 12 h at room temperature and quenched with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated to yield CTS **6** as a colorless crystalline solid (1.46 g, 59%). ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.22 (s, 36H, $SiMe_3$), 7.15−7.36 (m, 16H, Ar-H). ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ −79.9 (OSiO), 11.5 ($SiMe_3$). Anal. Calcd for $C_{36}H_{52}Br_4O_8Si_8$: C 37.37, H 4.53. Found: C 37.23, H 4.58.

CTS 7. Sodium hydroxide (0.55 g 13.7 mmol) was dissolved in a mixture of 271 μL (15 mmol) of water and 15 mL of *n*-butanol. Then 5.00 g (13.7 mmol) of 4-(triethoxysilyl)iodobenzene was added, and the reaction mixture was stirred for 4 days at room temperature. The resulting white precipitate was filtered off, washed with 15 mL of hexane, and dried under high vacuum to yield 3.66 g (12.8 mmol, 90%) of a white powder, which typically contains varying amounts of *n*-butanol. The product was used for subsequent reactions without further characterization.

CTS 8. Pyridine (1.61 g, 20.3 mmol) was added to a suspension of 3.66 g of **7** in 35 mL of toluene. The reaction mixture was cooled to 0 °C, and 2.21 g (20.3 mmol) of chlorotrimethylsilane was added slowly via a syringe. The white suspension was stirred for 12 h at room temperature and quenched with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated to yield 2.06 g (1.5 mmol, 47%) of a colorless crystalline solid, mp 38−42 °C. ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.15 (s, 36H, $SiMe_3$), 6.95 (d, $^3J_{HH}$ = 8.2 Hz, 8H, Ar-H), 7.49 (d, $^3J_{HH}$ = 8.2 Hz, 8H, Ar-H) ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): δ 1.8 ($SiMe_3$), 97.5 (C−I), 132.0 (C−Si), 135.2 (CH), 136.8 (CH). ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ −79.4 (OSiO), 11.6 ($SiMe_3$). Anal. Calcd for $C_{36}H_{52}I_4O_8Si_8$: C 32.15, H 3.90. Found: C 32.57, H 3.76.

Synthesis of CTS 9−15: Typical Procedure of the Sonogashira Coupling of 8. **8** (0.3 g 0.29 mmol) was dissolved in 6 mL of THF, and 12 mg (0.017 mmol) of $Cl_2Pd(PPh_3)_2$, 7 mg (0.037 mmol) of CuI, 0.89 g (8.8 mmol) of NEt_3, and 1.5 mmol of alkyne (dissolved in 1 mL of THF) were added. The reaction mixture was stirred at room temperature for 12 h. The brown solution was filtered through charcoal and washed with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated. The crude product was

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purified by column chromatography using gradient elution (hexane, hexane/$CHCl_3$ = 7:3 to hexane/$CHCl_3$ = 1:9).

CTS **9**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.15 (s, 36H, $SiMe_3$), 1.03 (t, $^3J_{HH}$ = 7.1 Hz, 12H, CH_3), 1.55−1.67 (m, 8H, CH_2), 2.36 (t, $^3J_{HH}$ = 7.1 Hz, 8H, CH_2), 7.12−7.19 (m, 16H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 1.8 ($SiMe_3$), 13.6 (CH_3), 21.4 (CH_2), 22.2 (CH_2), 80.8 (CC), 91.2 (CC), 125.5 (Cq), 130.5 (CH), 132.2 (Cq), 133.6 (CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.8 (OSiO), 11.0 ($SiMe_3$). Yield: 0.17 g, 54%. R_f = 0.95 (hexane/$CHCl_3$ = 7:3). Colorless solid, mp 83 °C. Anal. Calcd for $C_{56}H_{80}O_8Si_8$: C 60.82, H 7.29. Found: C 60.10, H 7.08. MS (ESI): m/z 1123.4391 $(M + NH_4)^+$.

CTS **10**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.20 (s, 36H, $SiMe_3$), 7.28−7.31 (m, 28H, Ar-H), 7.47−7.51 (m, 8H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 1.8 ($SiMe_3$), 89.3 (CC), 90.3 (CC), 123.1 (Cq), 124.8 (Cq), 128.2 (CH), 130.6 (CH), 131.6 (CH), 133.0 (Cq), 133.7 (CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.9 (OSiO), 11.3 ($SiMe_3$). Yield: 0.29 g, 81%. R_f = 0.83 (hexane/$CHCl_3$ = 7:3). Colorless solid, mp 179 °C. Anal. Calcd for $C_{68}H_{72}O_8Si_8$: C 65.76, H 5.84. Found: C 65.79, H 5.91. MS (EI): m/z 1241.5 (M^+).

CTS **11**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.23 (s, 36H, $SiMe_3$), 3.89 (s, 12H, OMe), 7.02−7.55 (m, 36H, Ar-H) 7.90 (s, 4H, CH). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 1.9 ($SiMe_3$), 55.3 (OMe), 89.1 (CC), 91.0 (CC), 105.7 (CH), 118.1 (Cq), 119.2 (CH), 125.0 (Cq), 126.8, 128.5 (Cq), 129.1, 129.4, 130.6, 131.3, 132.9 (Cq), 135.9, 133.8, 134.1 (Cq), 158.3 (Cq). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.8 (OSiO), 11.2 ($SiMe_3$). Yield: 0.20 g, 45%. R_f = 0.10 (hexane/$CHCl_3$ = 7:3). Brown solid, mp dec. Anal. Calcd for $C_{88}H_{88}O_{12}Si_8$: C 67.65, H 5.68. Found: C 67.13, H 5.36. MS (EI): m/z 1561.6 (M^+).

CTS **12**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.22 (s, 36H, $SiMe_3$), 7.28−7.56 (m, 52H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 1.8 ($SiMe_3$), 90.1 (CC), 90.4 (CC), 122.2 (Cq), 125.0 (Cq), 126.9, 126.9, 127.6, 128.8, 130.7, 132.2, 133.1 (Cq), 133.9, 140.3 (Cq), 140.9 (Cq). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.9 (OSiO), 11.3 ($OSiMe_3$). Yield: 0.29 g, 65%. R_f = 0.66 (hexane/$CHCl_3$ = 7:3). Yellow solid, mp dec. Anal. Calcd for $C_{92}H_{88}O_8Si_8$: C 71.46, H 5.74. Found: C 70.54, H 5.64. MS (MALDI-TOF): m/z 1545.5 (M^+).

CTS **13**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.13 (s, 36H, $SiMe_3$), 3.72 (s, 12H, OMe), 6.75−6.73 (m, 8H, Ar-H), 7.20−7.21 (m, 16H, Ar-H), 7.34−7.37 (m, 8H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 1.8 ($SiMe_3$), 55.2 (OMe), 88.2 (CC), 90.3 (CC), 113.9 (CH), 115.4 (Cq), 125.1 (Cq), 130.4 (CH), 132.7 (Cq), 133.1 (CH), 133.7 (CH), 159.6 (C−O). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.9 (OSiO), 11.1 ($SiMe_3$). Yield: 0.35 g, 90%. R_f = 0.16 (hexane/$CHCl_3$ = 7:3). Colorless solid, mp 202 °C. Anal. Calcd for $C_{72}H_{80}O_{12}Si_8$: C 63.49, H 5.92. Found: C 62.96, H 5.83. MS (MALDI-TOF): m/z = 1496.3 $(M + Ag)^+$.

CTS **14**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.19 (s, 36H, $SiMe_3$), 3.78 (s, 8H, CH2), 7.22−7.39 (m, 36H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 1.8 ($SiMe_3$), 25.7 (CH2), 82.7 (CC), 88.5 (CC), 125.2 (Cq), 126.6, 127.9, 128.5, 130.6, 132.6 (Cq), 133.7, 136.6 (Cq). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.9 (OSiO), 11.1 ($SiMe_3$). Yield: 0.27 g, 72%. R_f = 0.81 (hexane/$CHCl_3$ = 7:3). Brown solid, mp dec. Anal. Calcd for $C_{72}H_{80}O_8Si_8$: C 66.62, H 6.21. Found: C 66.24, H 5.76. MS (EI): m/z 1297.6 (M^+).

CTS **15**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.04 (s, 36H, $SiMe_3$), 0.12 (s, 36H, $SiMe_3$), 7.06−7.13 (m, 16H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ −0.1 ($SiMe_3$), 1.8 ($SiMe_3$), 95.2 (CC), 105.0 (CC), 124.6 (Cq), 131.0 (C−H), 133.3 (Cq), 133.5 (CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.8 (OSiO), −17.2 ($CSiMe_3$), 11.7 ($OSiMe_3$). Yield: 0.26 g, 74%. R_f = 0.93 (hexane/$CHCl_3$ = 7:3). Colorless solid, mp 165 °C. Anal. Calcd for $C_{56}H_{88}O_8Si_{12}$: C 54.85, H 7.23. Found: C 54.65, H 6.90. MS (ESI): m/z 1248.3595 $(M + Na)^+$.

Synthesis of CTS 16. Pyridine (1.61 g, 20.3 mmol) was added to a suspension of 3.66 g of **7** in 35 mL of toluene. The reaction mixture was cooled to 0 °C, and 2.45 g (20.3 mmol) of chloro(dimethyl)-vinylsilane was added slowly via a syringe. The white suspension was stirred for 12 h at room temperature and quenched with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated to yield 2.4 g (1.7 mmol, 54%) of a colorless crystalline solid, mp 33−35 °C. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.23 (s, 24H, $SiMe_2$), 5.74−6.19 (m, 12H, vinyl), 6.96 (d, $^3J_{HH}$ = 7.6 Hz, 8H, Ar-H), 7.51 (d, $^3J_{HH}$ = 7.6 Hz, 8H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 0.2 ($SiMe_2$), 97.5 (C−I), 131.7 (Cq), 132.6 (CH_2), 135.3 (CH), 136.7 (CH), 138.2 (C═CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.3 (OSiO), 0.1 ($SiMe_2$). Anal. Calcd for $C_{40}H_{52}I_4O_8Si_8$: C 34.49, H 3.76. Found: C 34.55, H 3.85. MS (ESI): m/z 1414.7878 $(M + Na)^+$. Crystallographic data:[41,42] formula $C_{40}H_{52}I_4O_8Si_8$, MW = 1393.14, monoclinic, space group $P2_1/c$, colorless crystals from a toluene/dichloromethane solution (1 mL/2 mL, 100 mg **16**) by slow evaporation, unit cell dimensions a = 2226.91(15) pm, α = 90°, b = 2196.69(8) pm, β = 96.973(7)°, c = 1152.15(4) pm, γ = 90°, Z = 4, V = 5.5944(5) nm^3, 22 316 reflections were collected, 9678 were unique (R_{int} = 0.0418). The final R factor was R1 = 0.0539 with wR2 = 0.1452 for 9678 reflections with $F^2 > 2\sigma(F^2)$, GOF = 1.128.

CTS 17. Pyridine (1.61 g 20.3 mmol) was added to a suspension of 3.66 g of **7** in 35 mL of toluene. The reaction mixture was cooled to 0 °C, and 1.92 g (20.3 mmol) of chlorodimethylsilane was added slowly via a syringe. The white suspension was stirred for 12 h at room temperature and quenched with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated to yield 1.55 g (1.2 mmol, 38%) of a colorless oil. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.26 (d, $^3J_{HH}$ = 2.7 Hz, 24H, $SiMe_2$), 4.83 (sept, $^3J_{HH}$ = 2.7 Hz, $^1J_{SiH}$ = 209.0 Hz, 4H, SiH), 7.00 (d, $^3J_{HH}$ = 7.2 Hz, 8H, Ar-H), 7.54 (d, $^3J_{HH}$ = 7.2 Hz, 8H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 0.2 ($SiMe_2$), 97.6 (C−I), 131.6 (Cq), 132.5 (CH_2), 135.4 (CH), 136.8 (CH), 138.1 (C═CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −78.7 (OSiO), −3.0 ($OSiMe_2H$). Anal. Calcd for $C_{32}H_{44}I_4O_8Si_8$: C 29.82, H 3.44. Found: C 29.51, H 3.62.

Synthesis of CTS 18−24: Typical Procedure of a Sonogashira Coupling of CTS 16. 16 (0.4 g, 0.29 mmol) was dissolved in 6 mL of THF, and 12 mg (0.017 mmol) of $Cl_2Pd(PPh_3)_2$, 7 mg (0.037 mmol) of CuI, 0.89 g (8.8 mmol) of NEt_3, and 1.5 mmol of alkyne (dissolved in 1 mL of THF) were added. The reaction mixture was stirred at room temperature for 12 h. The brown solution was filtered through charcoal and washed with water. The organic layer was dried over magnesium sulfate, and the solvent evaporated. The crude product was purified by column chromatography using gradient elution (hexane, hexane/$CHCl_3$ = 7:3 to hexane/$CHCl_3$ = 1:9).

CTS **18**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.22 (s, 24H, $SiMe_2$), 1.05 (t, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3), 1.56−1.69 (m, 8H, CH_2), 2.38 (t, $^3J_{HH}$ = 6.9 Hz, 8H, CH_2), 5.72−6.21 (m, 12H, vinyl), 7.13−7.20 (m, 16H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 0.3 ($SiMe_2$), 13.6 (CH_3), 21.4 (CH_2), 22.2 (CH_2), 80.8 (CC), 91.2 (CC), 125.6 (Cq), 130.5 (CH), 131.9 (Cq), 132.4 (CH_2), 133.7 (CH), 138.5 (C═CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.3 (OSiO), −0.2 ($SiMe_2$). Yield: 0.26 g, 77%. R_f = 0.89 (hexane/$CHCl_3$ = 7:3). Colorless solid, mp 78 °C. Anal. Calcd for $C_{60}H_{80}O_8Si_8$: C 62.45, H 6.99. Found: C 61.58, H 6.90. MS (ESI): m/z 1176.3925 $(M + Na)^+$.

CTS **19**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.28 (s, 24H, $SiMe_2$), 5.79−6.25 (m, 12H, vinyl), 7.29−7.52 (m, 36H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 0.3 ($SiMe_2$), 88.3 (CC), 90.4 (CC), 123.2 (Cq), 124.8 (Cq), 128.2 (CH), 128.3(CH), 130.6 (CH), 131.7 (CH), 132.5 (C═CH_2), 132.8 (Cq), 133.8 (CH), 138.4 (C═CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.8 (OSiO), −0.4 ($SiMe_2$). Yield: 0.15 g, 36%. R_f = 0.75 (hexane/$CHCl_3$ = 7:3). Yellow solid, mp 165 °C. Anal. Calcd for $C_{72}H_{72}O_8Si_8$: C 67.04, H 5.63. Found: C 67.10, H 5.59. MS (MALDI): m/z 1288.3164 (M^+).

CTS **20**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.20 (s, 24H, $SiMe_2$), 3.82 (s, 12H, OMe), 5.70−6.19 (m, 12H, vinyl), 6.94−7.00 (m, 8H, Ar-H), 7.16−7.29 (m, 20H, Ar-H), 7.41−7.47 (m, 12H, Ar-H), 7.83 (s, 4H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 0.3 ($SiMe_2$), 55.2 (C-OMe), 89.1 (CC), 91.1 (CC), 105.7 (CH), 118.0 (Cq), 119.2 (CH), 125.1 (Cq), 126.7 (CH), 128.4 (Cq), 129.0 (CH), 129.3 (CH), 130.6 (CH), 131.3 (CH), 132.5 (CH_2), 132.6 (Cq), 133.8 (CH), 134.1 (Cq), 138.4 (CH), 158.2 (Cq). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.3 (OSiO), −0.1 ($SiMe_2$). Yield: 0.14 g, 31%. R_f = 0.07 (hexane/$CHCl_3$ = 7:3). Brown solid, mp dec. Anal. Calcd for $C_{92}H_{88}O_{12}Si_8$: C 68.62, H 5.51. Found: C 67.64, H 5.45.

CTS **21**. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.29 (s, 24H, $SiMe_2$), 5.78−6.26 (m, 12H, vinyl), 7.23−7.57 (m, 52H, Ar-H). $^{13}C\{^1H\}$ NMR

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(75.6 MHz, $CDCl_3$): δ 0.3 ($SiMe_2$), 90.1 (CC), 90.3 (CC), 122.1 (Cq), 124.9 (Cq), 126.9 (CH), 126.9 (CH), 127.6 (CH), 128.8 (CH), 130.6 (CH), 132.1 (CH), 132.6 (CH_2), 132.8 (CH), 133.8 (CH), 138.4 (CH), 140.2 (Cq), 140.9 (Cq). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.8 (OSiO), −0.4 ($SiMe_2$). Yield: 0.29 g, 62%. R_f = 0.59 (hexane/$CHCl_3$ = 7:3). Yellow solid, mp dec. Anal. Calcd for $C_{96}H_{88}O_8Si_8$: C 72.32, H 5.56. Found: C 72.18, H 5.35. MS (MALDI-TOF): m/z 1593.5 (M^+). Crystallographic data:[42] formula $C_{94}H_{90}O_8Si_8$, MW = 1572.38, trigonal, space group $R\bar{3}$, colorless crystals from a chloroform solution by slow evaporation, unit cell dimensions a = 6851.4(6) pm, α = 90°, b = 6851.4(6) pm, β = 90°, c = 1082.20(10) pm, γ = 120°, Z = 18, V = 43.994 34(871) nm^3, 140 449 reflections were collected, 19230 were unique (R_{int} = 0.0780). The final R factor was R1 = 0.1019 with wR2 = 0.2185 for 19 230 reflections with $F^2 > 2\sigma(F^2)$, GOF = 1.008.

CTS 22. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.24 (s, 24H, $SiMe_2$), 3.79 (s, 12H, OMe), 5.74−6.23 (m, 12H, vinyl), 6.79−6.82 (m, 8H, Ar-H), 7.22−7.29 (m, 16H, Ar-H), 7.40−7.23 (m, 8H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 0.3 ($SiMe_2$), 55.2 (C-OMe), 88.1 (CC), 90.4 (CC), 113.9 (CH), 115.3 (Cq), 125.1 (Cq), 130.4 (CH), 132.4 (Cq), 132.5 (CH_2), 133.1 (CH), 133.8 (CH), 138.5 (CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.8 (OSiO), −0.5 ($SiMe_2$). Yield: 0.09g, 23%. R_f = 0.13 (hexane/$CHCl_3$ = 7:3). Yellow solid, mp 188 °C. Anal. Calcd for $C_{76}H_{80}O_{12}Si_8$: C 64.73, H 5.72. Found: C 63.80, H 5.79. MS (MALDI-TOF): m/z = 1409.4 (M^+).

CTS 23. ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.22 (s, 24H, $SiMe_2$), 3.80 (s, 8H, CH2), 5.73−6.21 (m, 12H, vinyl), 7.21−7.41 (m, 36H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 0.3 ($SiMe_2$), 25.7 (CH_2), 82.7 (CC), 88.5 (CC), 125.2 (Cq), 126.6 (CH), 127.9 (CH), 128.5 (CH), 130.6 (CH), 132.3 (Cq), 132.4 (CH_2), 133.7 (CH), 136.6 (Cq), 138.5 (CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.4 (OSiO), −0.1 ($SiMe_2$). Yield: 0.21 g, 55%. R_f = 0.75 (hexane/$CHCl_3$ = 7:3). Yellow solid, mp dec. Anal. Calcd for $C_{76}H_{80}O_8Si_8$: C 67.81, H 5.99. Found: C 67.71, H 5.51.

CTS 24. ^1H NMR (300.5 MHz, $CDCl_3$) δ 0.20 (s, 24H, $SiMe_2$), 0.23 (s, 36H, $SiMe_3$), 5.70−6.18 (m, 12H, vinyl), 7.15−7.22 (m, 16H, Ar-H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ −0.1 (Me), 0.2 (Me), 95.2 (CC), 105.0 (CC), 124.6 (Cq), 130.9 (CH), 132.5 (CH_2), 133.0 (Cq), 133.6 (CH), 138.4 (C═CH). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ −79.7 (OSiO), −17.2 ($SiMe_3$), 0.0 ($SiMe_2$). Yield: 0.31 g, 83%. R_f = 0.88 (hexane/$CHCl_3$ = 7:3). Colorless solid, mp 137 °C. Anal. Calcd for $C_{60}H_{88}O_8Si_{12}$: C 56.55, H 6.96. Found: C 55.49, H 6.90. MS (MALDI): m/z = 1295.2958 (M^+).

■ ASSOCIATED CONTENT

Supporting Information

NMR, IR spectroscopic data, and mass spectra of the reported compounds; crystallographic data for CTS **16** and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(42) CCDC 910737 (**16**) and CCDC 911089 (**21**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.