# **ORGANOMETALLICS**

# Thiol-Ene Synthesis of Cationic Carbosilane Dendrons: a New Family of Synthons

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**Supporting Information** 

**ABSTRACT:** A variety of neutral and cationic carbosilane dendrons containing a wide range of active groups, such as  $-N_3$ , -OH,  $-NH_2$ , and -SH, at the focal points were synthesized from carbosilane vinyl dendrons  $BrG_nV_m$  from generations 1-3 by substitution of the bromine atom at the focal point and functionalization of the vinyl groups via thiol-ene click chemistry with  $HS(CH_2)_2NMe_2$ ·HCl. These dendritic wedges were characterized by NMR, MS, and elemental analysis.

# 1. INTRODUCTION

Dendritic molecules have been studied for several applications such as catalysis, material sciences, and nanobiotechnology for their well-defined and uniform branching structure, multivalency, and variety of typologies.<sup>1–17</sup> Two main topologies define these macromolecules: spherical dendrimers, which usually show a symmetric distribution around a core, and dendritic wedges or dendrons, which are cone-shaped molecules with two different functions, one in the periphery and another at the focal point. The presence of these two potentially different moieties gives dendrons an entity by themselves, thus giving the design of dendrons its own place in macromolecular chemistry, as it allows the precise combination of several properties in a single molecule. Dendrons have been used to modify properties of polymers,<sup>18</sup> stabilize nanoparticles,<sup>19–23</sup> and improve biological activity of functional molecules,<sup>24–27</sup> as well as other purposes.<sup>4,28</sup>

The synthesis of dendrimers follows an iterative procedure of at least two different types of reactions, which should have high yields, be regioselective, be reproducible, and, if possible, produce the minimum number of byproducts in order to be useful for higher generations. Click chemistry refers to a type of reaction characterized by easy initiation, high yields, minimal product purification, and high tolerance to a variety of solvents and functional groups. For that reason the number of dendrimers synthesized using this kind of reaction has increased over the last few years.<sup>29–34</sup> One of these reactions is the addition of thiols to olefins, known as thiol-ene click chemistry.<sup>35,36</sup>

Heterofunctionalization of dendrons would require, on one hand, the presence of adequate focal points that bind to the target molecule. In this sense, several moieties are widely deserving of being candidates for their selectivity shown toward a particular fragment, such as alkyne, azide, and thiol, related



with click chemistry coupling, or primary amines and carboxylic acids related with amide bond formation, as these functions are present in a wide range of biomolecules and are also important coordinative groups for transition metals. On the other hand, proper functionalization of the dendron periphery would provide the properties required for the use their development calls for.<sup>37–39</sup>

Our group is interested in biomedical applications of dendritic molecules. For this use, these molecules should not only show low cytotoxicity but also be preferably soluble in aqueous media.<sup>40</sup> However, in the particular case of carbosilane dendrimers, the macromolecule is endowed with high hydrophobicity due to the low polarity of the C–C and C–Si bonds in its scaffold. To enable them to be water-soluble, the periphery has to be modified with polar moieties, anionic or cationic, or neutral, such as carbohydrates, thus making them suitable for biomedical applications.<sup>17,31,41–58</sup> Carbosilane dendrimers bearing cationic groups have already been tested for gene therapy,<sup>17,31,41–43,46,48</sup> bactericides,<sup>44,45,47</sup> and immune response inhibitors<sup>49,50</sup> and have also been shown to interact with drugs.<sup>51</sup>

These promising results of carbosilane dendrimers in biomedical applications have triggered our search for new systems, in which we aim to cut down the synthetic steps and also look for new properties. In this sense, only a few carbosilane dendrons have been described so far, <sup>59–61</sup> some of which were designed for biomedical applications, such as sialic acid terminated dendrons against influenza viruses<sup>58</sup> or as guest molecules with amino acids at the focal point.<sup>62</sup> The growth of carbosilane dendrons requires the presence of terminal olefins; thus the thiol-ene approach is very interesting for the

Received: December 17, 2012 Published: March 12, 2013

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Scheme 1. Synthesis of Neutral and Cationic Dendrons<sup>a</sup>



<sup>*a*</sup>Conditions: (i)  $ClMg(C_2H_3)$ ; (ii) MX (M = Na, X = N<sub>3</sub>; M = K, X = Pht, MeC(O)S) or 1,4-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>; (iii) HS(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>·HCl, *hv*, DMPA; (iv) H<sub>2</sub>NNH<sub>2</sub>; (v) HCl.

functionalization of these molecules, as previously shown for spherical dendrimers.<sup>63,64</sup> However, no carbosilane dendrons have yet been synthesized by this methodology. Hence, in this work we report the application of this procedure to the synthesis of carbosilane dendrons bearing amine or ammonium functions in the periphery and versatile focal points that show the orthogonality of this approach. The thiol-ene addition also saves the final hydrosilylation steps, which carbosilane dendrimers usually undergo during growth, diminishing undesirable side reactions.<sup>65</sup> Finally, the aim of decorating the dendron periphery with ammonium moieties is to provide water solubility to these wedges, as required for biomedical applications, and also to offer the same features as other related carbosilane dendrimers that are being applied in biomedicine (vide supra).

# 2. RESULTS AND DISCUSSION

Carbosilane dendrons with a Br atom at the focal point and vinyl functions in the periphery were synthesized following the procedure described for analogous dendrons decorated with allyl groups<sup>66</sup> from  $BrG_n(SiCl_2)_m$  (n = 1, m = 1; n = 2, m = 2; n= 3, m = 4) and ClMg(C<sub>2</sub>H<sub>3</sub>), thus giving the corresponding vinyl dendrons  $BrG_n V_m$  (*n* = 1, *m* = 2 (1); *n* = 2, *m* = 4 (2); *n* = 3, m = 8 (3)) as colorless oils in high yields (Scheme 1). In general, dendrons are named in this work according to the  $XG_n(Y)_m$  nomenclature, where X indicates the nature of the focal point,  $G_n$  the dendron generation, and  $(Y)_m$  the peripheral function and its number (Figure 1). The reason for synthesizing these vinyl-terminated dendrons was the fact that the related allyl compounds showed very little reactivity toward the thiolammonium derivative used in this work. The most important NMR data of these compounds showed resonances arising from the CH<sub>2</sub>Br group at the focal point, one triplet at  $\delta$  ca. 3.40 in the <sup>1</sup>H NMR spectra and one signal at  $\delta$  ca. 33.0 in the <sup>13</sup>C NMR spectra and from the peripheral vinyl groups two multiplets at  $\delta$  ca. 5.70 and 6.05 in the <sup>1</sup>H NMR spectra and two resonances at  $\delta$  ca. 133.0 and 137.0 in the <sup>13</sup>C NMR



Figure 1. Dendron skeletons  $(G_1-G_3)$  described in this work.

spectra. Furthermore, the <sup>29</sup>Si NMR gave rise to one resonance at  $\delta$  ca. -13.5 due to the outer Si atom.

Our next goal was to substitute the focal point of dendrons 1-3 with active groups that play an important role in different areas of chemistry, such as  $-N_{3}$ ,  $-OH_{2}$ ,  $-NH_{2}$ , and -SH. The azide moiety was introduced by a direct method, as this group did not interfere with the subsequent thiol-ene reaction. Dendrons 1-3 reacted with NaN<sub>3</sub> upon heating in acetone to afford the dendrons  $N_3G_nV_m$  (n = 1, m = 2 (4); n = 2, m = 4(5); n = 3, m = 8 (6)) in high yields as colorless oils (Scheme 1). NMR spectroscopy clearly confirmed modification of the focal point (Figure 2), as the resonances of the initial  $CH_2Br$ group were not observed. The presence of the new CH<sub>2</sub>N<sub>3</sub> fragment was identified as one triplet at  $\delta$  ca. 3.20 in the <sup>1</sup>H NMR spectra and at  $\delta$  ca. 51.0 in the <sup>13</sup>C NMR spectra. Furthermore, <sup>1</sup>H-<sup>15</sup>N NMR spectroscopy showed two cross peaks belonging to the nitrogen atoms NCH<sub>2</sub> and N=NCH<sub>2</sub> at  $\delta$  ca. -308 and -131, respectively, whereas the external N atom could not be detected.

With respect to the introduction of a hydroxyl group at the focal point, mixtures of dendrons 1-3 were directly heated in the presence of an excess of hydroquinone and K<sub>2</sub>CO<sub>3</sub>. Thus, the compounds HOG<sub>n</sub>V<sub>m</sub> (n = 1, m = 2 (7); n = 2, m = 4 (8); n = 3, m = 8 (9)) were obtained as colorless oils in moderate yields (Scheme 1). The change at the focal point (Figure 2) was confirmed by means of <sup>1</sup>H NMR spectroscopy, giving







Figure 3. Representative dendrons of the third generation synthesized in this work.

resonances at  $\delta$  ca. 3.90 due to the new CH<sub>2</sub>O group and a broad singlet at  $\delta$  ca. 4.75 for the OH terminal, and also by the resonances of the two different aromatic CH groups, which were observed as a multiplet at  $\delta$  ca. 6.75. The <sup>13</sup>C NMR spectra showed a peak for the CH<sub>2</sub>O group at  $\delta$  ca. 68.3 and in the case of the four different aromatic C atoms peaks for the CH groups at  $\delta$  ca. 132.9 and 136.8 and for the C<sub>ipso</sub> atoms at  $\delta$ ca. 149.3 and 153.2. However, in the case of the  $-NH_2$  and -SH groups, precursors acting as protective groups, such as phthalimide (Pht) for primary amines  $-NH_2$  and thioacetate (MeCOS) for terminal thiols -SH, had to be used. In this sense, addition of KPht to solutions of dendrons  $BrG_nV_m$  (1–3) led to the corresponding modified dendrons  $PhtG_nV_m$  (n = 1, m = 2 (10); n = 2, m = 4 (11); n = 3, m = 8 (12)) in high yields upon heating in DMF (Scheme 1). As above, the introduction of the phthalimide group at the focal point was confirmed by NMR

spectroscopy (Figure 2), showing one triplet at  $\delta$  ca. 3.65 for the CH<sub>2</sub>N group in the <sup>1</sup>H NMR spectra and one resonance at  $\delta$  ca. 37.5 for the carbon atom of this group in the <sup>13</sup>C NMR spectra. Furthermore, <sup>15</sup>N NMR spectroscopy proved the presence of the phthalimide group, showing one resonance at  $\delta$ ca. -216.

The thioacetate group was introduced by reaction of dendrons 1–3 with HSC(O)Me and  $K_2CO_3$  in acetone at 55 °C, to give the new dendrons  $MeC(O)SG_nV_m$  (n = 1, m = 2 (13); n = 2, m = 4 (14); n = 3, m = 8 (15)) as orange oils in high yields (Scheme 1). NMR spectroscopy showed the exchange of the Br atom for the MeC(O)S function at the focal point (Figure 2) by means of the <sup>1</sup>H NMR resonances at  $\delta$  ca. 2.82 and 2.30 for the CH<sub>2</sub>S and the MeC(O) groups, respectively, and the <sup>13</sup>C NMR resonances at  $\delta$  ca. 28.7 for the CH<sub>2</sub>S group and at  $\delta$  ca. 30.6 and 196.0 for the Me and CO groups of the MeC(O) moiety, respectively.

Once vinyl dendrons with adequate focal points were obtained, we proceeded to modify their periphery via thiolene addition. Thus, solutions of dendrons  $XG_nV_m$  (X = N<sub>3</sub> (4-6), HO (7-9), Pht (10-12), MeC(O)S (13-15)) and 2dimethylethylenethiol hydrochloride, HS(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>·HCl, in THF/MeOH stirred under UV irradiation (see the Experimental Section) afforded the new wedges  $XG_n(S (CH_2)_2 NMe_2 HCl)_m (X = N_3, n = 1, m = 2 (16), n = 2, m =$ 4 (17), n = 3, m = 8 (18); X = OH, n = 1, m = 2 (19), n = 2, m= 4 (20), n = 3, m = 8 (21); X = Pht; n = 1, m = 2 (22), n = 2,m = 4 (23), n = 3, m = 8 (24); X = MeC(O)S; n = 1, m = 2(25), n = 2, m = 4 (26), n = 3, m = 8 (27)) (Scheme 1 and Figure 3), which were obtained as white solids in high yields. These reactions required the presence of a photoinitiator, which in our case was 2,2'-dimethoxy-2-phenylacetophenone (DMPA). The addition of the thiol to the vinyl groups was regioselective at the  $\beta$ -position (vide infra). These compounds were thus soluble in water and other polar solvents, such as alcohols and DMSO.

The NMR spectroscopic and analytical data for derivatives 16-27 were consistent with their proposed structures. The presence of the new chain Si(CH<sub>2</sub>)<sub>2</sub>S was confirmed by TOCSY <sup>1</sup>H NMR, which showed two multiplets at  $\delta$  ca. 0.88 and 2.60 for the protons of the SiCH<sub>2</sub> and the CH<sub>2</sub>S groups, respectively, whereas the outer chain  $S(CH_2)_2N$  gave rise to two multiplets at  $\delta$  ca. 3.00 and 3.30 for the protons of the SCH<sub>2</sub> and the CH<sub>2</sub>N groups, respectively. Furthermore, a singlet at  $\delta$  ca. 3.30 confirmed the presence of the NMe<sub>2</sub>H fragment. The carbon atoms of the CH<sub>2</sub> groups of the Si(CH<sub>2</sub>)<sub>2</sub>S chain were observed in the <sup>13</sup>C NMR spectra at  $\delta$  ca. 13.5 for the SiCH<sub>2</sub> group and at  $\delta$  ca. 26.0 for the CH<sub>2</sub>S group, whereas those belonging to the S(CH<sub>2</sub>)<sub>2</sub>N chain arose at  $\delta$  ca. 24.5 for the SCH<sub>2</sub> group and at  $\delta$  ca. 55.5 for the CH<sub>2</sub>S group. The NMe<sub>2</sub>H group was also detected at  $\delta$  ca. 41.4 by <sup>13</sup>C NMR spectroscopy. <sup>29</sup>Si NMR spectra showed one resonance for the Si atom of this outer group at  $\delta$  ca. 2.4. Finally, <sup>15</sup>N NMR spectra resolved one resonance at about  $\delta$  -338.3 for the NMe<sub>2</sub>·HCl group. The  $\alpha$  addition was only observed in firstgeneration dendrons, by means of a doublet at about 1.20 ppm in the <sup>1</sup>H NMR spectra; this signal was overlapped with the resonances of the intermediate alkyl chains in higher generations. The integration of this resonance indicated ca. 2.5% formation of this function.

Removal of the protecting Pht group of dendrons to generate others with a  $-NH_2$  function at the focal point was achieved by addition of hydrazine to dendrons **22–24**, which gave the

neutral dendrons NH<sub>2</sub>G<sub>n</sub>(S(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>)<sub>m</sub> (n = 1, m = 2 (**28**); n = 2, m = 4 (**29**); n = 3, m = 8 (**30**) in good yields. In this process, deprotonation of the ammonium groups was also produced by basic hydrazine. This change led to the isolation of these wedges as oils, which were soluble in organic solvents but not in water. The presence of the new focal point NH<sub>2</sub>CH<sub>2</sub>- in dendrons **28**-**30** was clearly identified by NMR spectroscopy, showing a new triplet at  $\delta$  ca. 2.65 in the <sup>1</sup>H NMR for the CH<sub>2</sub>N at the focal point and a resonance at  $\delta$  ca. 41.9 in the <sup>13</sup>C NMR spectra for the carbon atom of this group. Furthermore, a shifting to lower frequency was observed for the resonances corresponding to the CH<sub>2</sub>NMe<sub>2</sub> groups, as a consequence of charge neutralization of the nitrogen atoms.

For the synthesis of dendrons with -SH functions at the focal point, excess HCl in dioxane was added to solutions of dendrons 25-27 to give the compounds  $HSG_n(S-(CH_2)_2NMe_2\cdotHCl)_m$  (n = 1, m = 2 (31); n = 2, m = 4 (32); n = 3, m = 8 (33)) as pale yellow solids in moderate yields (ca. 70%) which were soluble in polar organic solvents and in water. NMR spectroscopy confirmed that the thioacetate group had disappeared and that the thiol  $HSCH_2-$  moiety had been formed. The <sup>1</sup>H NMR spectra showed one triplet at  $\delta$  ca. 2.46 for the CH<sub>2</sub> group, and the resonance for the SH proton appeared at  $\delta$  ca. 1.33, as detected by COSY, since it is overlapped with the resonances of the carbosilane fragment, while in the <sup>13</sup>C NMR spectra a resonance for the CH<sub>2</sub>SH carbon atom at  $\delta$  ca. 25.0 was observed.

### 3. CONCLUSIONS

A versatile and simple procedure has been developed for the synthesis of a library of carbosilane dendrons containing ammonium or amine groups in the periphery and reactive groups, such as  $-N_{32}$   $-OH_{22}$   $-NH_{22}$  and  $-SH_{22}$  at the focal point, which are attractive for a variety of applications. The new dendritic wedges were obtained in good to high yields from carbosilane dendrons with a C-Br bond at the focal point and vinyl groups in the peripheral dendrons by modification of the focal point followed by thiol-ene addition. For the preparation of the -NH<sub>2</sub> and -SH derivatives protective groups had to be introduced prior to the thiol-ene reaction. The cationic carbosilane wedges thus obtained were water-soluble, which is an important requirement for biomedical applications. Hence, these new families of synthons displaying focal points to which different biomolecules such as drugs, peptides, antibodies, or also chromophores may be conjugated and a cationic ammonium periphery are promising building blocks for biomedical applications.

## 4. EXPERIMENTAL SECTION

**4.1. General Considerations.** All reactions were carried out under an inert atmosphere, and solvents were purified from appropriate drying agents when necessary. Thiol-ene reactions were carried out employing a HPK 125 W mercury lamp from Heraeus Noblelight with maximum energy at 365 nm, in normal glassware under an inert atmosphere. NMR spectra were recorded on a Varian Unity VXR-300 (300.13 (<sup>1</sup>H), 75.47 MHz (<sup>13</sup>C)) or on a Bruker AV400 instrument (400.13 (<sup>1</sup>H), 100.60 (<sup>13</sup>C), 40.56 MHz (<sup>15</sup>N), and 79.49 MHz (<sup>29</sup>Si)). Chemical shifts ( $\delta$ ) are given in ppm. <sup>1</sup>H and <sup>13</sup>C resonances were measured relative to solvent peaks considering TMS at 0 ppm; meanwhile <sup>15</sup>N and <sup>29</sup>Si resonances were measured relative to external MeNO and TMS, respectively. When necessary, assignment of resonances was done from HSQC, HMBC, COSY, TOCSY, and NOESY NMR experiments. Elemental analyses were performed on a LECO CHNS-932 instrument. Mass spectra were obtained from

a Bruker Ultraflex III instrument for MALDI-TOF in dithranol, an Agilent 6210 TOF LC/MS instrument for ESI-TOF in MeOH/H<sub>2</sub>O with (NH<sub>4</sub>)(HCO<sub>2</sub>), and an AB Sciex QSTAR instrument for ESI-POS in H<sub>2</sub>O/MeOH. The compounds ClMg(C<sub>2</sub>H<sub>3</sub>), NaN<sub>3</sub>, (HO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, KPht, MeC(O)SH, HS(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>·HCl, 2,2'-dimethoxy-2-phenylacetophenone (DMPA), H<sub>2</sub>NNH<sub>2</sub>, and HCl (4 M in dioxane) (Aldrich) and K<sub>2</sub>CO<sub>3</sub> (Panreac) were obtained from commercial sources. The compounds BrG<sub>n</sub>(SiCl<sub>2</sub>)<sub>m</sub> (n = 1, m = 1; n = 2, m = 2; n = 3, m = 4)<sup>66</sup> were synthesized as reported.

4.2. Synthesis of Compounds. 4.2.1.  $BrG_1V_2$  (1). An Et<sub>2</sub>O solution of ClMg(C2H3) (33.3 mL, 53.28 mmol) was added drop by drop to a BrG<sub>1</sub>(SiCl<sub>2</sub>) solution (5.550 g, 22.20 mmol) in Et<sub>2</sub>O cooled to 0 °C, and then the mixture was stirred overnight at room temperature. Afterward a water solution of NH<sub>4</sub>Cl was added (12%, 40 mL), organic phase was separated, and the aqueous phase was extracted twice with Et<sub>2</sub>O. Finally the organic phase was washed with brine and dried over MgSO4 and SiO2. The solution was filtered, and the volatiles were removed under vacuum, yielding 1 as a colorless liquid (4.66 g, 90%). Data for 1 are as follows. NMR (CDCl<sub>3</sub>): <sup>1</sup>H NMR  $\delta$  0.13 (s, 3 H, SiMeC<sub>2</sub>H<sub>3</sub>), 0.63 (m, 2 H, CH<sub>2</sub>SiC<sub>2</sub>H<sub>3</sub>), 1.46 (m, 2 H, BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.85 (m, 2 H, BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 3.39 (t, J = 6.6 Hz, 2 H, BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 5.71 (m, 2 H, SiCHCH<sub>2</sub>), 6.03 (m, 4 H, SiCHCH<sub>2</sub>;  ${}^{13}C{}^{1}H{}$  NMR  $\delta$  -5.4 (SiMe), 13.1 (BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 22.3 (BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 33.6 (BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 36.2 (BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 133.1 (SiCHCH<sub>2</sub>), 136.6 (SiCHCH<sub>2</sub>); <sup>29</sup>Si NMR  $\delta$  –13.5 (SiCHCH<sub>2</sub>). Anal. Calcd for C<sub>9</sub>H<sub>17</sub>BrSi (233.22 g/mol): C, 46.35; H, 7.35. Found: C, 46.83; H, 7.65.

4.2.2.  $N_3G_1V_2$  (4). A solution of 1 (0.500 g, 2.15 mmol) in acetone (60 mL) was heated to 60 °C in the presence of an excess of NaN<sub>3</sub> (0.965 g, 4.30 mmol) and 18-crown-6 (0.061 g, 0.24 mmol) for 16 h. After this time, volatiles were removed and the mixture was extracted with H2O/Et2O. The organic phase was dried over Na2SO4 and dried under vacuum to give 4 as a colorless oil (0.39 g, 93%). Data for 4 are as follows. NMR (CDCl<sub>3</sub>): <sup>1</sup>H NMR  $\delta$  0.13 (s, 3 H, SiMeC<sub>2</sub>H<sub>3</sub>), 0.64  $(t, J = 8.2 Hz, 2 H, CH_2SiC_2H_3), 1.40 (m, 2 H,$ N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.61 (m, 2 H, N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 3.32 (t, J = 6.9 Hz, 2 H, N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 5.70 and 6.06 (m, 6 H, SiCHCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  - 5.4 (SiMe), 13.6 (N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 20.9 (N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 32.4  $(N_3CH_2CH_2CH_2CH_2Si)$ , 51.0  $(N_3CH_2CH_2CH_2CH_2Si)$ , 133.1 (SiCHCH<sub>2</sub>), 136.6 (SiCHCH<sub>2</sub>). <sup>15</sup>N NMR :  $\delta$  -308.7 (N=N= NCH<sub>2</sub>), -131.9 (N=N=NCH<sub>2</sub>); <sup>29</sup>Si NMR  $\delta$  -12.9 (SiCHCH<sub>2</sub>). MS: [M + H]<sup>+</sup> 196.12 amu (calcd 196.12 amu). Anal. Calcd for C<sub>9</sub>H<sub>17</sub>N<sub>3</sub>Si (195.34 g/mol): C, 55.34; H, 8.77; N, 21.51. Found: C, 55.63; H, 8.49; N, 21.89.

4.2.3.  $HOArG_1V_2$  (7). 1,4-(HO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (2.860 g, 25.68 mmol), 1 (0.600 g, 2.57 mmol), K<sub>2</sub>CO<sub>3</sub> (0.710 g, 5.14 mmol), and crown ether 18-C-6 (0.070 g, 0.26 mmol) were stirred in acetone (70 mL) at 90 °C in a sealed ampule for 2 days under vacuum. Afterward, the volatiles were removed under vacuum and a water solution of NH<sub>4</sub>Cl (12%, 50 mL) and CH<sub>2</sub>Cl<sub>2</sub> were added. The organic phase was separated, and the aqueous phase was extracted twice with Et<sub>2</sub>O. The organic phase was dried over MgSO<sub>4</sub> and for an extra 10 min also with SiO<sub>2</sub>. The solution was filtered, and the volatiles were removed under vacuum. Then alumina column chromatography was performed using several ethyl acetate/hexane mixtures with an increasing polarity gradient. At 60% acetate, compound 7 was obtained as a colorless oil (0.40 g, 60%). Data for 6 are as follows. NMR (CDCl<sub>3</sub>): <sup>1</sup>H NMR  $\delta$  0.14 (s, 3 H, SiMe), 0.68 (t,  $J_a = 8.5$  Hz, 2 H, CH<sub>2</sub>Si), 1.48 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>Si), 1.77 (m, 2 H, OCH<sub>2</sub>CH2), 3.88 (t, J<sub>b</sub> = 6.4 Hz, 2 H, OCH<sub>2</sub>), 4.65 (bs, 1 H, HOAr-), 5.71 and 6.08 (m, 6 H, SiCHCH<sub>2</sub>), 6.75 (m, 4 H,  $C_6H_4O_2$ ; <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  -5.4 (SiMe), 13.7 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 20.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 32.9 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 68.3 (OCH<sub>2</sub>), 115.6 and 115.9 (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>; CH), 132.9 (SiCHCH<sub>2</sub>), 136.8 (SiCHCH<sub>2</sub>), 149.3 and 153.2  $(C_6H_4O_2; CO)$ ; <sup>29</sup>Si NMR  $\delta$  -12.8 (G<sub>1</sub>-SiMe). Anal. Calcd for C15H22O2Si (262.42 g/mol): C, 68.65; H, 8.45. Found: C, 69.08; H, 8.53.

4.2.4.  $PhtG_1V_2$  (10). To a DMF solution (25 mL) of wedge 1 (0.270 g, 1.16 mmol) were added the commercial reagent KPht (0.875 g, 98.00 mmol) and 10% NaI. The reaction mixture was heated to 80 °C for 16 h in a Teflon-valved ampule. Then a Et<sub>2</sub>O/H<sub>2</sub>O extraction was performed, and after the organic phase was dried over MgSO4 and the volatiles were evaporated, compound 10 was obtained as a yellowish oil (0.21 g, 61%). Data for 10 are as follows. NMR (CDCl<sub>3</sub>): <sup>1</sup>H NMR  $\delta$  0.11 (s, 3 H, SiMe), 0.67 (t, J = 8.8 Hz, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.36 (m, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.68 (m, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 3.64 (t, J = 7.3 Hz, 2 H, NCH<sub>2</sub>), 5.69 and 6.05 (m, 6 H, SiCHCH<sub>2</sub>), 7.68 and 7.81 (m, 4 H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  -5.5 (SiMe), 13.4 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 21.0 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 32.0 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 37.6 (NCH<sub>2</sub>), 123.0 ( $C_6H_4$ , CH), 132.1 ( $C_6H_4$ ,  $C_{ipso}$ ), 132.9 (SiCHCH<sub>2</sub>), 133.7 ( $C_6H_4$ , CH), 136.6 (SiCHCH<sub>2</sub>), 168.3 (C=O); <sup>15</sup>N NMR  $\delta$  -216.7; <sup>29</sup>Si NMR  $\delta$  –12.8 (G<sub>1</sub>–SiMe). MS: [M + H]<sup>+</sup> 300.15 amu (calcd 300.14 amu). Anal. Calcd for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub>Si (299.44 g/mol): C, 68.19; H, 7.07; N, 4.68. Found: C, 68.67; H, 7.16; N, 4.67.

4.2.5. MeCOSG<sub>1</sub>V<sub>2</sub> (13). MeCOSH (0.627 mL, 8.776 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.049 g, 8.98 mmol) were stirred in acetone (60 mL) at room temperature for 1 h. Afterward, BrG<sub>1</sub>V<sub>2</sub> (1; 2.000 g, 8.58 mmol) was added and the mixture was stirred at 55 °C for 22 h. Volatiles were removed under vacuum, and the residue was dissolved in Et<sub>2</sub>O. Subsequently brine was added, the organic phase was separated, and the aqueous phase was extracted twice with Et<sub>2</sub>O. The organic phase was washed with brine and dried over MgSO<sub>4</sub>. The solution was filtered through Celite, and the volatiles were removed under vacuum, yielding 13 as an orange oil (1.85 g, 95%). Data for 13 are as follows. NMR (CDCl<sub>3</sub>): <sup>1</sup>H NMR  $\delta$  0.11 (s, 3 H, SiCH<sub>3</sub>), 0.62 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.37 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.57 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 2.29 (s, 3 H, CH<sub>3</sub>COS), 2.83 (t, J = 7.2Hz, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 5.67 (m, 2 H, SiCHCH<sub>2</sub>), 6.01 (m, 4 H, SiCHCH<sub>2</sub>);  ${}^{13}C{}^{1}H{}$  NMR  $\delta -5.4$  (SiCH<sub>2</sub>), 13.5 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 22.9 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 28.7  $(SCH_2CH_2CH_2CH_2Si)$ , 30.6  $(CH_3COS)$ , 33.0 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 132.9 (SiCHCH<sub>2</sub>), 136.7 (SiCHCH<sub>2</sub>), 195.9  $(CH_3COS)$ ; <sup>29</sup>Si NMR  $\delta$  -13.0  $(CH_3Si)$ . Anal. Calcd for for C<sub>11</sub>H<sub>20</sub>OSSi (228.43): C, 57.84; H, 8.88; S, 14.04. Found: C, 58.20; H, 8.81; S, 14.17.

4.2.6. N<sub>3</sub>G<sub>1</sub>(SNMe<sub>2</sub>HCl)<sub>2</sub> (16). Compound 4 (0.089 g, 0.46 mmol), 2-(dimethylamino)ethanethiol hydrochloride (0.136 g, 0.91 mmol), 5 mol % of DMPA (0.020 g, 0.08 mmol), and a 1/2 THF/methanol solution (5 mL) were combined. The reaction mixture was deoxygenated and irradiated for 1.5 h. Another 5 mol % of DMPA was added, and the reaction mixture was irradiated for another 1.5 h and monitored by <sup>1</sup>H NMR. The initial reaction mixture was concentrated by rotary evaporation and redissolved in methanol. Afterward, it was precipitated in Et<sub>2</sub>O, and after the solvent was separated, the solid was dried under vacuum to afford 16 as a white solid (0.19 g, 86%). Data for 16 are as follows. NMR (DMSO): <sup>1</sup>H NMR  $\delta$  0.00 (s, 3H, SiMe), 0.55 (t,  $J_a$  = 8.57 Hz, 2 H,  $NCH_2CH_2CH_2CH_2Si$ ), 0.93 (t,  $J_b = 7.2$  Hz, 4H,  $SiCH_2CH_2S$ ), 1.34 (m, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.58 (m, 2 H,  $NCH_2CH_2CH_2CH_2Si$ ), 2.65 (t,  $J_b = 7.2$  Hz, 4 H,  $SiCH_2CH_2S$ ), 2.86 (s, 12 H,  $SCH_2CH_2NMe_2HCl$ ), 3.02 (t,  $J_c = 7.7$  Hz, 4 H, SCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>HCl), 3.27 (m, 6 H, SCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>HCl and NCH<sub>2</sub>);  ${}^{13}C{}^{1}H$  NMR  $\delta$  -5.4 (SiMe), 12.4 (N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 13.5 (SiCH<sub>2</sub>CH<sub>2</sub>S), 20.2 (N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 24.3  $(SCH_2CH_2N^+)$ , 26.0  $(SiCH_2CH_2S)$ , 31.5  $(N_3CH_2CH_2CH_2CH_2Si)$ , 41.4 ( $-NMe_2H^+$ ), 49.7 ( $N_3CH_2$ ), 55.3 ( $CH_2N^+$ ); <sup>15</sup>N NMR  $\delta$  -338.4  $(-NMe_2H^+)$ , -308.6  $(N=N=NCH_2)$ , -131.7  $(N=N=N-CH_2)$ ; <sup>29</sup>Si NMR  $\delta$  3.0 (G<sub>1</sub>-SiMe). MS: [M – Cl – HCl]<sup>+</sup> 406.25 amu (calcd 406.25 amu), Anal. Calcd for C<sub>17</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>5</sub>S<sub>2</sub>Si (478.66 g/mol): C, 42.66; H, 8.63; N, 14.63; S, 13.40. Found: C, 41.96; H, 8.05; N, 13.59; S, 14.30.

4.2.7.  $HOArG_1(NMe_2HCl)_2$  (19). This wedge was prepared from 7 (0.490 g, 1.87 mmol), 2-(dimethylamino)ethanethiol hydrochloride (0.557 g, 3.74 mmol), DMPA (0.010 g, 0.37 mmol), and a 1/2 THF/ methanol solution (3 mL) using the preparative procedure for 16. The product was dried in vacuo to afford 19 as a white solid (0.74 g, 73%).

Data for 19 are as follows. NMR (DMSO): <sup>1</sup>H NMR  $\delta$  0.01 (s, 3 H, SiMe), 0.56 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.86 (t, J<sub>a</sub> = 8.3 Hz, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S), 1.31 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.66 (m, 2 H,  $OCH_2CH_2CH_2CH_2Si$ ), 2.59 (t,  $J_a = 9.0$  Hz, 4 H,  $SiCH_2CH_2S$ ), 2.70  $(s, 12 \text{ H}, \text{ SCH}_2\text{CH}_2\text{NM}e_2\text{H}^+), 2.86 (t, J_b = 8.0 \text{ Hz}, 2 \text{ H},$  $SCH_2CH_2NMe_2H^+$ ), 3.16 (t,  $J_b = 8.0$  Hz, 2 H,  $SCH_2CH_2NMe_2H^+$ ), 3.82 (t,  $J_c = 6.3$  Hz, 2 H, OCH<sub>2</sub>), 6.68 (m, 4H,  $C_6 H_4 O_2$ ); <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  -5.4 (SiMe), 12.7 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 13.5  $(SiCH_2CH_2S)$ , 19.6  $(OCH_2CH_2CH_2CH_2Si)$ , 24.3  $(SCH_{2}CH_{2}NMe_{2}H^{+}), 26.0 (SiCH_{2}CH_{2}S), 32.2$  $(OCH_2CH_2CH_2CH_2Si)$ , 41.4  $(SiCH_2CH_2NMe_2H^+)$ , 55.3 (S-1)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>H<sup>+</sup>), 67.0 (OCH<sub>2</sub>), 114.8 and 115.2 (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>; CH), 150.6 and 150.9 (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>; CO); <sup>29</sup>Si NMR  $\delta$  3.0 (G<sub>1</sub>-SiMe); <sup>15</sup>N NMR  $\delta$  -338.2 (SiCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>H<sup>+</sup>). MS: [M - HCl - Cl]<sup>+</sup> = 476.27 amu (calcd 476.27 amu). Anal. Calcd for C23H46Cl2N2O2S2Si (545.75 g/mol): C, 50.62; H, 8.50; N, 5.13; S, 11.75. Found: C, 50.78; H, 8.37; N, 4.95; S, 12.02.

4.2.8. PhtG<sub>1</sub>(NMe<sub>2</sub>HCl)<sub>2</sub> (22). Compound 10 (0.303 g, 1.01 mmol), 2-(dimethylamino)ethanethiol hydrochloride (0.287 g, 2.02 mmol), 5 mol % of DMPA (0.052 g, 0.20 mmol), and a 1/2 THF/methanol solution (5 mL) were combined. The reaction mixture was deoxygenated and irradiated for 1.5 h. Another 5 mol % of DMPA was added, and the reaction mixture was irradiated for another 1.5 h and monitored by <sup>1</sup>H NMR. After the reaction was completed, the volatiles were removed under vacuum and then the residue was dissolved in methanol. Afterward, it was precipitated in Et<sub>2</sub>O, and after the solvent was separated, the solid was dried under vacuum to afford 22 as a white solid (0.46 g, 78%). Data for 20 are as follows. NMR (DMSO): <sup>1</sup>H NMR  $\delta$  0.00 (s, 3 H, SiMe), 0.60 (m, 2 H, CH<sub>2</sub>SiC<sub>2</sub>H<sub>4</sub>S), 0.85 (m, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S). 1.28 (m, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.60 (m, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 2.58 (m, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S), 2.73 (s, 12 H, NMe<sub>2</sub>H<sup>+</sup>), 2.86 (m, 4 H, SCH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 3.16 (m, 4 H, SCH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 3.56 (m, 2 H, N-CH<sub>2</sub>), 7.84 (m, 4 H, C<sub>6</sub>H<sub>4</sub>), 10.79 (bs, 2 H, NMe<sub>2</sub>H<sup>+</sup>);  ${}^{13}C{}^{1}H{}$  NMR  $\delta - 5.9$ (SiMe), 11.9 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 13.4 (SiCH<sub>2</sub>CH<sub>2</sub>S), 20.2  $(NCH_2CH_2CH_2CH_2Si)$ , 24.0  $(SCH_2CH_2N^+)$ , 25.9  $(SiCH_2CH_2S)$ , 31.0 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 36.5 (NCH<sub>2</sub>), 41.2 (NMe<sub>2</sub>H<sup>+</sup>), 55.2 (CH<sub>2</sub>N<sup>+</sup>), 122.5 and 133.9 (C<sub>6</sub>H<sub>4</sub>, CH), 131.1 (C<sub>6</sub>H<sub>4</sub>, C<sub>ipso</sub>), 167.5 (C=O); <sup>15</sup>N NMR  $\delta$  -338.9  $(-NMe_2H^+)$ , -217.9  $((CO)_2NCH_2)$ .<sup>32</sup>Si NMR  $\delta$  3.0  $(G_1$ -SiMe). MS:  $[M - HCl - Cl]^+$ 510.26 amu (calcd 510.26 amu). Anal. Calcd for C25H45Cl2N3O2S2Si (582.77 g/mol): C, 51.52; H, 7.78; N, 7.21; S, 11.00. Found: C, 50.87; H, 7.94; N, 6.69; S, 11.80.

4.2.9. MeCOSG1(SNMe2·HCl)2 (25). A MeOH solution of HS- $(CH_2)_2NMe_2$ ·HCl (1.303 g, 9.20 mmol) was added to a THF solution of 13 (1.000 g, 4.38 mmol) in the presence of DMPA (10%) as catalyst and the mixture stirred under ultraviolet light  $(h\nu)$  for 4 h. Volatiles were removed under vacuum, the residue was dissolved in MeOH, excess Et<sub>2</sub>O was added, and the resulting precipitate was washed with Et<sub>2</sub>O, yielding 25 as a yellow solid (1.57 g, 70%). Data for 25 are as follows. NMR (D<sub>2</sub>O): <sup>1</sup>H NMR  $\delta$  –0.02 (s, 3 H, SiCH<sub>3</sub>), 0.53 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.87 (m, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S), 1.30 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.50 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 2.28 (s, 3 H, CH<sub>3</sub>COS), 2.62 (m, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S), 2.85 (m, 18 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, SCH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>3</sub>), 3.33 (t, J = 7.5 Hz, 4 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  – 5.6 (SiCH<sub>3</sub>), 12.7  $(SCH_2CH_2CH_2CH_2Si)$ , 13.9  $(SiCH_2CH_2S)$ , 22.6  $(SCH_2CH_2CH_2CH_2Si)$ , 26.9  $(SiCH_2CH_2S)$ , 28.7  $(SCH_2CH_2CH_2CH_2Si)$ , 30.6  $(CH_3COS)$ , (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 42.7 (SCH<sub>2</sub>CH<sub>2</sub>N), 42.8 (NCH<sub>3</sub>), 56.4  $(SCH_2CH_2N)$ , 199.0  $(CH_3COS)$ ; <sup>15</sup>N NMR  $\delta$  –339.0; <sup>29</sup>Si NMR  $\delta$ 2.9 (SiCH<sub>3</sub>). MS [M - HCl - Cl]<sup>+</sup> 439.23. Adequate analytical data could not be obtained for this compound because the final product showed a behavior very close to that of the starting HS-(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>·HCl.

4.2.10.  $NH_2G_1(NMe_2)_2$  (28). An excess of  $N_2H_4$  (0.03 mL, 0.96 mmol) was added to a solution of 22 (0.141 g, 0.24 mmol) in MeOH (10 mL). The reaction mixture was heated overnight at 80 °C in a sealed ampule. Afterward solvent and excess  $N_2H_4$  were removed and the product was extracted into  $CH_2Cl_2$ . After evaporation 28 was

obtained as a yellowish oil (0.10 g, 95%). Data for **20** are as follows. NMR (CDCl<sub>3</sub>): <sup>1</sup>H NMR δ –0.09 (s, 3 H, SiMe), 0.43 (t,  $J_a$  = 9.7 Hz, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.80 (t,  $J_b$  = 8.6 Hz, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S), 1.21 (m, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.38 (m, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 2.14 (s, 12 H, SCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 2.48 (m, 4 H, SCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 2.52 (m, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S), 2.57 (m, 4 H, SCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 2.55 (m, 2 H, NH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR δ –5.5 (SiMe), 13.2 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 14.3 (SiCH<sub>2</sub>CH<sub>2</sub>S), 20.9 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 27.4 (SCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 29.6 (SiCH<sub>2</sub>CH<sub>2</sub>S), 36.8 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 45.2 (SiCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>), 59.0 (SCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>); <sup>15</sup>N NMR δ –353.0 (-NMe<sub>2</sub>); <sup>29</sup>Si NMR δ 2.5 (G<sub>1</sub>-SiMe). Anal. Calcd for C<sub>17</sub>H<sub>41</sub>N<sub>3</sub>S<sub>2</sub>Si (379.74 g/mol): C, 53.77; H, 10.88; N, 11.07; S, 16.89. Found: C, 53.83; H, 10.20; N, 11.03; S, 16.13.

4.2.11. HSG<sub>1</sub>(SNMe<sub>2</sub>·HCl)<sub>2</sub> (31). To an MeOH solution of 25 (1.000 g, 1.96 mmol) was added HCl in dioxane (4 M, 2.9 mL, 11.73 mmol), and the mixture was stirred at 55 °C overnight. Afterward, volatiles were removed under vacuum, yielding 31 as a yellowish solid (0.69 g, 75%). Data for 31 are as follows. NMR (D<sub>2</sub>O): <sup>1</sup>H NMR  $\delta$ -0.05 (s, 3 H, SiCH<sub>3</sub>), 0.52 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.84 (m, 4 H, SiCH<sub>2</sub>CH<sub>2</sub>S), 1.33 (m, 3 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, HS), 1.53 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 2.46 (m, 2 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 2.58 (t, J = 8.0 Hz, 4 H,  $\text{SiCH}_2\text{CH}_2\text{S}$ ), 2.80 (m, 16 H,  $\text{SCH}_2\text{CH}_2\text{N}$ ,  $\text{NCH}_3$ ), 3.26 (t, J = 7.0 Hz, 4 H,  $\text{SCH}_2\text{CH}_2\text{N}$ ); <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  –6.5 (SiCH<sub>3</sub>), 11.7  $(SCH_2CH_2CH_2CH_2Si)$ , 13.5  $(SiCH_2CH_2S)$ , 23.2 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 25.1 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 26.6 (SiCH<sub>2</sub>CH<sub>2</sub>S) 36.4 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 42.6 (SCH<sub>2</sub>CH<sub>2</sub>N), 42.7  $(NCH_3)$ , 56.2  $(SCH_2CH_2N)$ ; <sup>15</sup>N NMR  $\delta$  -338.3; <sup>29</sup>Si NMR  $\delta$  2.9 (SiCH<sub>3</sub>). MS: [M - HCl - Cl]<sup>+</sup> 397.22. Anal. Calcd for C<sub>17</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>S<sub>3</sub>Si (469.72): C, 43.47; H, 9.01; N, 5.96; S, 20.48. Found: C, 42.99; H, 9.53; N, 5.97; S, 19.91.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Text giving the full experimental section and figures giving selected NMR spectra. 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.

# ACKNOWLEDGMENTS

This work was supported by the grants CTQ2011-23245 (MINECO) and Consortium NANODENDMED ref S2011/ BMD-2351 (CAM) awarded to R.G. and UAH2011/EXP-037 (University of Alcalá) awarded to F.J.d.I.M. This study was also supported by the CIBER-BBN financed by the *Instituto de Salud Carlos III*, with assistance from the European Regional Development Fund. E.F.-P. and M.G. acknowledge the Ministerio de Educación y Ciencia (Spain), and C.E.P.-G. acknowledges the Ministerio de Educación Superior, Ciencia y Tecnología (Dominican Republic), for a fellowship.

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