For Supporting Information

Structure-Activity Relationship Study of Cationic Carbosilane Dendritic Systems as Antibacterial Agents

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S.1. Experimental Section

S.1.1. General Considerations. All reactions were carried out under inert atmosphere and solvents were purified from appropriate drying agents when necessary. NMR spectra were recorded on a Varian Unity VXR-300 (300.13 (^{1}H), 75.47 (^{13}C) MHz) or on a Bruker AV400 (400.13 (1H), 100.60 (^{13}C), 40.56 (^{15}N), 79.49 (^{29}Si) MHz). Chemical shifts (δ) are given in ppm. ^{1}H and ^{13}C resonances were measured relative to internal deuterated solvent peaks considering TMS = 0 ppm, meanwhile ^{15}N and ^{29}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. Mass Spectra were obtained from a Bruker Ultraflex III and an Agilent 6210. 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. Compounds, $HS(CH_2)_2NH_2{\cdot}HCl$ (Acros), $HS(CH_2)_2NMe_2{\cdot}HCl$ (Acros), 2,2'-dimethoxy-2-phenylacetophenone (DMPA) (Aldrich), MeI (Aldrich), $HSiMeCl_2$ (Aldrich), K_2CO_3 (Panreac) were obtained from commercial sources. Compounds G_nSiV_m,[1] $[G_nSi(Si\text{-}NMe_3)_m]^{m+}$ (**7Si-9Si**),[2] $[G_nO_3(Si\text{-}NMe_3)_m]^{m+}$ (**34Si-36Si)**,[3] $[G_nO_3(S\text{-}NMe_3)_m]^{m+}$ (**34S-36S**) and $G_nO_3(S\text{-}NH_3)_m]^{m+}$ (**37S-39S**),[4] BrG_nV_m,[5] $XGn(NMe_2{\cdot}HCl)_m$ (X = N_3, HOC_6H_4O, Pht),[5] $[NH_2G_n(S\text{-}NMe_3)_m]^{m+1}$ (**31S-33S**),[6] and $[G_0Si(S\text{-}NH_3)_4]^{2+}$ (**10S**)[7] were synthesized as published.

S.1.2. Synthesis of compounds.

$G_0Si(S\text{-}NMe_2{\cdot}HCl)_4$ (1S). This dendrimer was prepared from G_0SiV_4 (0.250 g, 1.84 mmol), 2-(Dimethylamino)ethanethiol hydrochloride (1.042 g, 7.36 mmol), 2,20-dimethoxy-2-phenylacetophenone, DMPA (0.188 g, 0.74 mmol), and a 1:2 THF/methanol solution (3 mL). The reaction mixture was deoxygenated using an argon flow and then irradiated for 1.5 h with UV light at 365 nm. Next, DMPA was again added (5 % mol per vinyl group) and the reaction mixture was irradiated for another 1.5 h. ^{1}H-NMR monitorization allows checking the disappearance of vinyl groups. Afterward, the initial reaction mixture

was concentrated via rotator evaporation and solved in MeOH. Then, the product was precipitated in Et_2O under continuous stirring, eliminating the DMPA remains. After filtering the solution, the precipitate was again solved in water and nanofiltration with membranes of MW = 500 was performed in order to eliminate the excess of disulfide. Then, nanofiltration with membranes of MW = 500 was performed. The pure product was dried in vacuo to afford **1S** as a white solid (0.400 g, 31 %).

^{1}H-NMR (DMSO-d_6): δ 0.98 (t, J = 8.5 Hz, 8 H, SiC*H*$_2$CH$_2$S), 2.61 (t, J = 8.5 Hz, 8 H, SiCH$_2$C*H*$_2$S), 2.70 (s, 24 H, -N*Me*$_2$HCl), 2.86 (t, J = 7.8 Hz, 8 H, SC*H*$_2$CH$_2$N), 3.16 (t, J = 7.9 Hz, 8 H, SCH$_2$C*H*$_2$N), 10.68 (sa, 4 H, -NMe$_2$*H*$^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ 11.9 (Si*C*H$_2$CH$_2$S), 24.3 (S*C*H$_2$CH$_2$N), 25.6 (SiCH$_2$*C*H$_2$S) 41.6 (-N*Me*$_2$), 55.4 (SCH$_2$*C*H$_2$N). ^{15}N-NMR (DMSO-d_6): -338.2 (-*N*Me$_2$H$^+$). ^{29}Si-NMR (DMSO-d_6): 2.6 (G_0–SiMe). MS: [M-3HCl-Cl$^-$]$^+$ = 557.32 uma (calcd. = 557.32 uma); [M-1HCl-2Cl$^-$]$^{2+}$ = 297.10 uma (calcd. = 297.16 uma). Anal. Calcd. $C_{24}H_{60}Cl_4N_4S_4Si$ (702.92 g/mol): C, 41.01; H, 8.60; N, 7.97; S, 18.25; Exp.: C, 40.48; H, 8.38; N, 7.38; S, 18.88.

G_1Si(S-NMe$_2$·HCl)$_8$ (2S). This dendrimer was obtained following the synthetic procedure described for **1S** from G_1SiV_8 (0.501 g, 0.86 mmol), 2-(dimethylamino)ethanethiol hydrochloride (1.071 g, 7.18 mmol) and DMPA (0.176 g, 0.69 mmol) to be obtained as a white solid (1.183 g, 80 %).

^{1}H-NMR (DMSO-d_6): δ 0.03 (s, 12 H, Si*Me*), 0.56 (m, 8 H, SiC*H*$_2$CH$_2$C*H*$_2$Si), 0.63 (m, 8 H, C*H*$_2$SiC$_2$H$_4$S), 0.88 (t, J = 8.4 Hz, 16 H, SiC*H*$_2$CH$_2$S), 1.29 (m, 8 *H* SiCH$_2$C*H*$_2$CH$_2$Si), 2.61 (t, J = 8.2 Hz, 16 H, SiCH$_2$C*H*$_2$S), 2.75 (s, 48 H, -N*Me*$_2$HCl), 2.89 (t, J = 8.3 Hz, 16 H, SC*H*$_2$CH$_2$N), 3.22 (t, J = 8.3 Hz, 16 H, SCH$_2$C*H*$_2$N), 10.70 (bs, 8 H, -NMe$_2$*H*$^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.6 (Si*Me*), 13.6 (Si*C*H$_2$CH$_2$S), 16.4, 17.4 and 17.6 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 24.2 (S*C*H$_2$CH$_2$NMe$_2$), 26.0 (SiCH$_2$*C*H$_2$S), 41.3 (-N*Me*$_2$H$^+$), 55.2 (SCH$_2$*C*H$_2$NMe$_2$). ^{15}N-NMR (DMSO-d_6): δ -338.2 (-*N*Me$_2$H$^+$). ^{29}Si-NMR (DMSO-d_6): δ 1.1 (G_0–*Si*Me), 2.4 (G_1–*Si*Me). Anal. Calcd. $C_{64}H_{156}Cl_8N_8S_8Si_5$ (1718.55 g/mol): C, 44.73; H, 9.15; N, 6.52; S, 14.93; Exp.: C, 44.23; H, 9.26; N, 6.36; S, 13.84.

$G_2Si(S\text{-}NMe_2{\cdot}HCl)_{16}$ (3S). This dendrimer was obtained following the synthetic procedure described for **1S** from G_2SiV_{16} (0.225 g, 0.15 mmol), 2-(dimethylamino)ethanethiol hydrochloride (0.380 g, 2.55 mmol) and DMPA (0.062 g, 0.24 mmol) to be obtained as a white solid (0.571 g, 83 %).

^{1}H-NMR (DMSO-d_6): δ -0.09 (s, 12 H, Si*Me*), 0.02 (s, 24 H, Si*Me*), 0.54 (m, 24 H, SiC*H*$_2$CH$_2$C*H*$_2$Si), 0.61 (m, 16 H, C*H*$_2$SiC$_2$H$_4$S), 0.88 (t, J = 8.4 Hz, 32 H, SiC*H*$_2$CH$_2$S), 1.29 (m, 24 H, SiCH$_2$C*H*$_2$CH$_2$Si), 2.60 (t, J = 8.4 Hz, SiCH$_2$C*H*$_2$S), 2.75 (s, 96 H, (-N*Me*$_2$H$^+$), 2.89 (m, 32 H, SC*H*$_2$CH$_2$NMe$_2$), 3.22 (m, 32 H, SCH$_2$C*H*$_2$NMe$_2$), 10.70 (sa, 16 H, -NMe$_2$*H*$^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.7 and -5.4 (Si*C*H$_3$), 13.6 (Si*C*H$_2$CH$_2$S), 17.4–17.8 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 24.2 (S*C*H$_2$CH$_2$NMe$_2$), 26.0 (SiCH$_2$*C*H$_2$S), 41.3 (-N*Me*$_2$H$^+$), 55.2 (SCH$_2$*C*H$_2$NMe$_2$). ^{15}N-NMR (DMSO-d_6): -338.2 (-*N*Me$_2$H$^+$). ^{29}Si-NMR (DMSO-d_6): δ 1.1 (G_1–*Si*Me), 2.4 (G_2–*Si*Me). Anal. Calcd. $C_{144}H_{348}Cl_{16}N_{16}S_{16}Si_{13}$ (3749.81 g/mol): C, 46.12; H, 9.35; N, 5.98; S, 13.68; Exp.: C, 45.16; H, 8.76; N, 5.37; S, 13.89.

$G_0Si(S\text{-}NMe_2)_4$ (4S). To a $H_2O/CHCl_3$ (1:1, 20 mL) solution of **1S** (0.124 g, 0.18 mmol), a NaOH aqueous solution was added drop by drop (0.028 g, 0.70 mmol). The reaction mixture was stirred for 15 minutes at room temperature, and finally the aqueous phase was removed. The organic phase was dried using Na_2SO_4 and finally filtered and evaporated to obtain **4S** as a pale yellow oil (0.078 g, 80 %).

^{1}H-NMR ($CDCl_3$): δ 0.80 (t, J = 8.6 Hz, 8 H, SiC*H*$_2$CH$_2$S), 2.21 (s, 24 H, -N*Me*$_2$), 2.40 (m, 8 H, SCH$_2$C*H*$_2$N), 2.43 (m, 8 H, SiCH$_2$C*H*$_2$S, overlapped), 2.45 (m, 8 H, SC*H*$_2$CH$_2$N, overlapped). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 13.0 (Si*C*H$_2$CH$_2$S), 27.3 (SiCH$_2$*C*H$_2$S), 29.9 (S*C*H$_2$CH$_2$N), 45.3 (-N*Me*$_2$), 59.1 (SCH$_2$*C*H$_2$N). ^{15}N-NMR ($CDCl_3$): δ -352.1 (-*N*Me$_2$). ^{29}Si-NMR ($CDCl_3$): δ 2.2 (G_0–*Si*Me). MS: $[M+H]^+$ = 557.32 uma (calcd. = 557.40 uma). Anal. Calcd. $C_{24}H_{56}N_4S_4Si$ (557.07 g/mol): C, 51.74; H, 10.13; N, 10.06; S, 23.02; Exp.: C, 52.65; H, 9.46; N, 9.46; S, 22.07.

$G_1Si(S\text{-}NMe_2)_8$ (5S). This dendrimer was obtained following the synthetic procedure described for **4S**, starting from **2S** (0.887 g, 0.52 mmol) and NaOH (0.198 g, 4.95 mmol) to be obtained as a yellowish oil (0.605 g, 82 %).

^{1}H-NMR ($CDCl_3$): δ -0.09 (s, 12 H, *SiMe*), 0.45 (t, J = 9.0 Hz, 8 H, SiC*H*$_2$CH$_2$CH$_2$Si), 0.51 (t, J = 8.2 Hz, 8H, C*H*$_2$SiC$_2$H$_4$S), 0.80 (t, J = 8.6 Hz, 8 H, SiC*H*$_2$CH$_2$S), 1.19 (m, 8 H, SiCH$_2$C*H*$_2$CH$_2$Si), 2.14 (s, 48 H, -N*Me*$_2$), 2.40 (m, 8 H, SCH$_2$C*H*$_2$N), 2.43 (m, 8 H, SiCH$_2$C*H*$_2$S, overlapped), 2.45 (m, 8 H, SC*H*$_2$CH$_2$N, overlapped). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.4 (Si*Me*), 14.4 (Si*C*H$_2$CH$_2$S), 17.3, 18.2 and 18.4 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 27.5 (SiCH$_2$*C*H$_2$S), 29.6 (S*C*H$_2$CH$_2$N), 45.2 (N*Me*$_2$), 59.1 (SCH$_2$***C***H$_2$NMe$_2$). ^{15}N-NMR ($CDCl_3$): δ -352.1 (-*N*Me$_2$). ^{29}Si-NMR ($CDCl_3$): δ 1.0 (G_0–*Si*Me), 2.0 (G_1-*Si*Me). Anal. Calcd. $C_{64}H_{148}N_8S_8Si_5$ (1426.86 g/mol): C, 53.87; H, 10.45; N, 7.85; S, 17.98; Exp.: C, 54.45; H, 10.80; N, 7.83; S, 18.06.

G_2Si(S-NMe$_2$)$_{16}$ (6S). This dendrimer was obtained following the synthetic procedure described for **4S**, starting from **3S** (0.400 g, 0.11 mmol) and NaOH (0.088 g, 2.20 mmol) to be obtained as a yellowish oil (0.334, 99 %).

^{1}H-NMR ($CDCl_3$): δ -0.11 (s, 12 H, Si*Me),* -0.01 (s, 24 H, Si*Me*), 0.55 (m, 48 H, SiC*H*$_2$CH$_2$C*H*$_2$Si), 0.87 (t, J = 8.6 Hz, 32 H, SiC*H*$_2$CH$_2$S), 1.26 (m, 24 H, SiCH$_2$C*H*$_2$CH$_2$Si), 2.22 (s, 96 H, -N*Me*$_2$), 2.47 (m, 24 H, SCH$_2$C*H*$_2$N), 2.53 (m, 24 H, SiCH$_2$C*H*$_2$S), 2.59 (m, 24 H, SC*H*$_2$CH$_2$N). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.2 and -5.0 (Si*Me*), 14.6 (Si*C*H$_2$CH$_2$S), 17.7–19.2 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 27.7 (SiCH$_2$*C*H$_2$S), 29.8 (S*C*H$_2$CH$_2$N), 45.4 (-N*Me*$_2$), 59.3 (SCH$_2$*C*H$_2$NMe$_2$). ^{15}N-NMR ($CDCl_3$): δ -352.1 (-*N*Me$_2$). ^{29}Si-NMR ($CDCl_3$): δ 2.0 (G_2–*Si*Me). Anal. Calcd. $C_{144}H_{332}N_{16}S_{16}Si_{13}$ (3166.44 g/mol): C, 54.62; H, 10.57; N, 7.08; S, 16.20; Exp.: C, 54.65; H, 9.88; N, 6.58; S, 15.59.

G_0Si(S-NMe$_3$I)$_4$ (7S). To a diethyl ether (20 mL) solution of **4S** (0.078 g, 0.14 mmol) a MeI solution was added (0.05 mL, 0.80 mmol). The resulting solution was stirred for 16 h at room temperature and then evaporated under reduced pressure and washed twice with hexane (20 mL). **7S** is got after drying as a white solid (0.115 g, 70 %).

^{1}H-NMR (DMSO-d$_6$): δ 1.00 (t, J = 8.3 Hz, 8 H, SiC*H*$_2$CH$_2$S), 2.68 (t, J= 8.4 Hz, 8 H, SiCH$_2$C*H*$_2$S), 2.93 (t, J = 8.1 Hz, 8 H, SC*H*$_2$CH$_2$N$^+$), 3.25 (s, 36 H, -N*Me*$_3^+$), 3.57 (t, J = 8.2 Hz, 8 H, SCH$_2$C*H*$_2$N$^+$). ^{13}C{^{1}H}-NMR (DMSO-d$_6$): δ 12.3 (Si*C*H$_2$CH$_2$S), 23.2 (S*C*H$_2$CH$_2$N$^+$), 26.2 (SiCH$_2$*C*H$_2$S), 51.8 (-N*Me*$_3^+$),

64.0 ($SCH_2CH_2N^+$). ^{15}N-NMR (DMSO-d_6): δ -330.0 (-*N*Me_3I). ^{29}Si-NMR (DMSO-d_6): δ 2.7 (G_0–*Si*Me_2). MS: $[M-3I]^{3+}$ = 248.00 uma (calcd. = 247.77 uma). Anal. Calcd. $C_{28}H_{68}I_4N_4S_4Si$ (1124.83 g/mol): C, 29.90; H, 6.09; N, 4.98; S, 11.40; Exp.: C, 29.80; H, 6.31; N, 4.29; S, 10.40.

G_1Si(S-NMe_3I)$_8$ (8S). This dendrimer was obtained following the synthetic procedure described for **7S** from **5S** (0.416 g, 0.29 mmol) and MeI (0.18 mL, 2.80 mmol) to be obtained as a white solid (0.66 g, 88 %).

^{1}H-NMR (DMSO-d_6): δ 0.05 (s, 12 H, Si*Me*), 0.54 (m, 8 H, $SiCH_2CH_2CH_2Si$), 0.64 (m, 8 H, $CH_2SiC_2H_4S$), 0.86 (t, J = 8.3 Hz, 16 H, $SiCH_2CH_2S$), 1.28 (m, 8 H, $SiCH_2CH_2CH_2Si$), 2.65 (t, J= 8.4 Hz, 16 H, $SiCH_2CH_2S$), 2.91 (t, J = 8.1 Hz, 16 H, $SCH_2CH_2N^+$), 3.13 (s, 72 H, -NMe_3^+), 3.59 (t, J = 8.2 Hz, 96 H, $SCH_2CH_2N^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): -5.5 (Si*Me*), 13.7 ($SiCH_2CH_2S$), 17.3–18.0 ($SiCH_2CH_2CH_2Si$), 23.2 ($SCH_2CH_2NMe_3^+$), 26.5 ($SiCH_2CH_2S$), 51.8 (-NMe_3^+), 64.0 ($SCH_2CH_2NMe_3^+$). ^{15}N-NMR (DMSO-d_6): δ -330.0 (-*N*Me_3^+). ^{29}Si-NMR (DMSO-d_6): δ 0.9 (G_0–*Si*Me), 2.4 (G_1–*Si*Me_2). Anal. Calcd. $C_{72}H_{172}I_8N_8S_8Si_5$ (2562.37 g/mol): C, 33.75; H, 6.77; N, 4.37; S, 10.01; Exp.: C, 33.18; H, 6.90; N, 4.29; S, 9.40.

G_2Si(S-NMe_3I)$_{16}$ (9S). This dendrimer was obtained following the synthetic procedure described for **7S**, starting from **6S** (0.134 g, 0.04 mmol) and MeI (0.05 mL, 0.80 mmol) to be obtained as a white solid (0.165 g, 72 %).

^{1}H-NMR (DMSO-d_6): δ -0.09 (s, 12 H, Si*Me*), 0.05 (s, 24 H, Si*Me*), 0.52 (m, 32 H, $SiCH_2CH_2CH_2Si$), 0.62 (m, 16 H, $CH_2SiCH_2CH_2S$), 0.85 (t, J_a = 7.6 Hz, 32 H, $SiCH_2CH_2S$), 1.25 (m, 24 H, $SiCH_2CH_2CH_2Si$), 2.65 (t, J_a = 7.5 Hz, 32 H, $SiCH_2CH_2S$), 2.91 (t, J_b = 6.9 Hz, 32 H, -NMe_3^+), 3.15 (s, 144 H, $SCH_2CH_2NMe_3I$), 3.60 (m, 32 H, SCH_2CH_2N). ^{13}C{^{1}H}-NMR (DMSO-d_6): *δ* -5.5 (Si*Me*), 13.7 ($SiCH_2CH_2S$), 17.3–18.0 ($SiCH_2CH_2CH_2Si$), 23.2 (SCH_2CH_2N), 26.5 ($SiCH_2CH_2S$), 51.8 (-NMe_3^+), 64.0 ($SCH_2CH_2NMe_3^+$). ^{15}N-NMR (DMSO-d_6): *δ* -330.0 (-*N*Me_3^+). ^{29}Si-NMR (DMSO-d_6): *δ* 2.4 (G_2–*Si*Me). ESI: q=4 (1231.35 $[M-4I]^{4+}$), q=5 (959.68 $[M-5I]^{5+}$), q=6 (778.55 $[M-6I]^{6+}$). Anal. Calcd.

$C_{160}H_{380}I_{16}N_{16}S_{16}Si_{13}$ (5437.45 g/mol): C, 35.34; H, 7.04; N, 4.12; S, 9.44; Exp.: C, 35.07; H, 6.98; N, 4.01; S, 8.82.

$G_0Si(S\text{-}NH_2\cdot HCl)_4$ (10S). This compound was prepared following the procedure described by Rissing *et al*.[7]

$G_1Si(S\text{-}NH_2\cdot HCl)_8$ (11S). This dendrimer was obtained following the synthetic procedure described for **1S** from G_1SiV_8 (0.925 g, 1.59 mmol), cysteamine hydrochloride (1.442 g, 12.72 mmol) and DMPA (0.328 g, 1.28 mmol) to be obtained as a white solid (1.564 g, 66 %).

^{1}H-NMR (DMSO-d_6): δ 0.54 (m, 8 H, SiCH_2), 0.62 (m, 8 H, CH_2SiC$_2$H$_4$S, overlapped) 0.85 (t, J = 8.5 Hz, 8 H, SiCH_2CH$_2$S), 1.28 (m, 8 H, SiCH$_2$CH_2CH$_2$Si) 2.58 (t, J = 8.5 Hz, 16 H, SiCH$_2$CH_2S), 2.77 (t, J = 7.8 Hz, 16 H, SCH_2CH$_2$N$^+$), 2.94 (t, J = 7.9 Hz, 16 H, SCH$_2$CH_2N$^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.7 (Si*Me*), 13.5 (Si*C*H$_2$CH$_2$S), 16.4, 17.4 and 17.6 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 25.9 (SiCH$_2$*C*H$_2$S), 27.2 (S*C*H$_2$CH$_2$N$^+$), 38.0 (SCH$_2$*C*H$_2$N$^+$). ^{15}N-NMR (DMSO-d_6): -342.4 (-*N*H$_3^+$). ^{29}Si-NMR (DMSO-d_6): δ 1.1 (G_0–SiMe), 2.4 (G_1–SiMe). MALDI: [M-5HCl-3Cl]$^{3+}$ = 401.20 uma (calcd. = 401.21 uma); [M-4HCl-3Cl]$^{3+}$ = 413.20 uma (calcd. = 413.20 uma); [M-2HCl-3Cl]$^{3+}$ = 437.19 uma (calcd. = 437.18 uma); [M-6HCl-2Cl]$^{2+}$ = 601.31 uma (calcd. = 601.30 uma); [M-7HCl-Cl]$^+$ = 1201.61 uma (calcd. = 1201.60 uma); [M-6HCl-Cl]$^+$ = 1237.58 uma (calcd. = 1237.58 uma); [M-8HCl+K]$^+$ = 1239.56 uma (calcd. = 1239.56 uma) Anal. Calcd. $C_{48}H_{124}Cl_8N_8S_8Si_5$ (1494.12 g/mol): C, 38.59; H, 8.37; N, 7.50; S, 17.17; Exp.: C, 37.77; H, 8.36; N, 7.10; S, 16.48.

$G_2Si(S\text{-}NH_2\cdot HCl)_{16}$ (12S). This dendrimer was obtained following the synthetic procedure described for **1S** from G_2SiV_{16} (0.130 g, 0.09 mmol), cysteamine hydrochloride (0.157 g, 1.38 mmol) and DMPA (0.028 g, 0.11 mmol) to be obtained as a white solid (0.264 g, 89 %).

^{1}H-NMR (DMSO-d_6): δ -0.1 (s, 12 H, Si*Me*), 0.00 (s, 24 H, SC$_2$H$_4$Si*Me*), 0.53 (m, 32 H, SiCH_2), 0.60 (m, 16 H, CH_2SiC$_2$H$_4$S, overlapped) 0.86 (t, J = 8.3 Hz, 32 H, SiCH_2CH$_2$S), 1.29 (m, 24 H, SiCH$_2$CH_2CH$_2$Si), 2.58 (t, J = 8.2 Hz, 32 H, SiCH$_2$CH_2S), 2.80 (t, J = 6.4 Hz, 32 H, SCH_2CH$_2$N$^+$), 2.94 (t, J = 6.7 Hz, 32 H, SCH$_2$CH_2N$^+$). ^{13}C{^{1}H}-NMR (DMSO): δ -5.7, -5.2 (Si*Me*), 13.5 (Si*C*H$_2$CH$_2$S), 16.6 –

17.8 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 25.9 (SiCH$_2$*C*H$_2$S), 27.2 (S*C*H$_2$CH$_2$N$^+$), 38.0 (SCH$_2$*C*H$_2$N$^+$). ^{15}N-NMR (DMSO): -342.4 (-*N*H$_3^+$). ^{29}Si-NMR (DMSO): δ 1.1 (G$_1$–SiMe), 2.4 (G$_2$–SiMe). MALDI: [M-9HCl-7Cl]$^{7+}$ = 388.66 uma (calcd. = 388.64 uma); [M-10HCl-6Cl]$^{6+}$ = 453.26 uma (calcd. = 453.24 uma); [M-11HCl-5Cl]$^{5+}$ = 543.71 uma (calcd. = 543.69 uma); [M-12HCl-4Cl]$^{4+}$ = 679.38 uma (calcd. = 679.36 uma); [M-13HCl-3Cl]$^{3+}$ = 905.49 uma (calcd. = 905.47 uma); [M-14HCl-2Cl]$^{2+}$ = 1357.71 uma (calcd. = 1357.70 uma). Anal. Calcd. $C_{112}H_{284}Cl_{16}N_{16}S_{16}Si_{13}$ (3300.96 g/mol): C, 40.75; H, 8.67; N, 6.79; S, 15.54; Exp.: C, 40.43; H, 8.61; N, 6.41; S, 14.94.

N$_3$G$_1$(S-NMe$_2$)$_2$ (13S). This dendron was obtained following the synthetic procedure described for **4S** from N$_3$G$_1$(SNMe$_2$·HCl)$_2$ (0.218 g, 0.46 mmol) and Na$_2$CO$_3$ (0.145 g, 1.37 mmol) to be obtained as a yellowish oil (0.174 g, 94 %).

^{1}H-NMR (CDCl$_3$): δ 0.01 (s, 3 H, *SiMe*), 0.56 (t, J$_a$ = 8.5 Hz, 2 H, NCH$_2$CH$_2$CH$_2$C*H*$_2$Si), 0.90 (t, J$_b$ = 9.4 Hz, 4 H, SiC*H*$_2$CH$_2$S), 1.36 (m, 2 H, NCH$_2$CH$_2$C*H*$_2$), 1.60 (m, 2 H, NCH$_2$C*H*$_2$), 2.24 (s, 12 H, -N*Me*$_2$), 2.50 (m, 4 H, SCH$_2$C*H*$_2$N), 2.56 (m, 4 H, SiCH$_2$C*H*$_2$S, overlapped), 2.59 (m, 4 H, SC*H*$_2$CH$_2$N, overlapped), 3.25 (t, J$_c$ = 7.0, 2 H, NC*H*$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ -5.4 (Si*Me*), 13.2 (N$_3$CH$_2$CH$_2$CH$_2$C*H*$_2$), 14.4 (Si*C*H$_2$CH$_2$S), 20.9 (N$_3$CH$_2$CH$_2$C*H*$_2$), 27.5 (SiCH$_2$*C*H$_2$S), 29.8 (S*C*H$_2$CH$_2$N), 32.5 (N$_3$CH$_2$C*H*$_2$), 45.3 (SiCH$_2$CH$_2$N*Me*$_2$), 50.9 (N$_3$C*H*$_2$), 58.8 (SCH$_2$*C*H$_2$NMe$_2$). ^{15}N-NMR (CDCl$_3$): δ -352.1 (-*N*Me$_2$), -306.9 (N=*N*=N-CH$_2$), -131.5 (*N*=N=N-CH$_2$). ^{29}Si-NMR (CDCl$_3$): δ 2.78 (G$_1$-*Si*Me). IR (KBr, cm^{-1}): 2095, υ(N$_3$). [M+H]$^+$ = 406.2 uma (calcd. = 406.2 uma). Anal. Calcd. $C_{17}H_{39}N_5S_2Si_7$ (405.74 g/mol): C, 50.32; H, 9.69; N, 17.26; S, 15.81; Exp.: C, 52.03; H, 10.95; N, 15.39; S, 15.35.

N$_3$G$_2$(S-NMe$_2$)$_4$ (14S). This dendrimer was obtained following the synthetic procedure described for **4S** from N$_3$G$_2$(SNMe$_2$·HCl)$_4$ (0.135 g, 0.14 mmol) and Na$_2$CO$_3$ (0.058 g, 0.55 mmol) to be obtained as a yellowish oil (0.124 g, 98 %).

^{1}H-NMR (CDCl$_3$): δ -0.11 (s, 3 H, *SiMe*), 0.00 (s, 6 H, *SiMe*), 0.55 (m, 10 H, NCH$_2$CH$_2$CH$_2$C*H*$_2$Si and SiC*H*$_2$CH$_2$C*H*$_2$Si), 0.86 (t, J$_a$ = 8.7 Hz, 8 H, SiC*H*$_2$CH$_2$S), 1.34 (m, 6 H, NCH$_2$CH$_2$C*H*$_2$ and SiCH$_2$C*H*$_2$CH$_2$Si), 1.58 (m, 2 H, NCH$_2$C*H*$_2$), 2.22 (s, 24 H, -N*Me*$_2$), 2.45 (m, 8 H, SCH$_2$C*H*$_2$N), 2.52 (m, 8

H, $SiCH_2CH_2S$, overlapped), 2.60 (m, 8 H, SCH_2CH_2N, overlapped), 3.24 (t, J_c = 6.8, 2 H, NCH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ -5.4 and -5.2 (Si*Me*), 13.4 ($NCH_2CH_2CH_2CH_2$), 14.6 ($SiCH_2CH_2S$), 18.2, 18.4 and 18.6 ($SiCH_2CH_2CH_2Si$), 21.1 ($NCH_2CH_2CH_2$), 27.6 ($SiCH_2CH_2S$), 29.8 (SCH_2CH_2N), 32.6 (NCH_2CH_2), 45.3 ($SiCH_2CH_2NMe_2$), 51.0 (NCH_2), 59.2 ($SCH_2CH_2NMe_2$). ^{15}N-NMR ($CDCl_3$): δ -352.0 (-NMe_2), -306.8 (N=N=N-CH_2), -131.4 (N=N=N-CH_2). ^{29}Si-NMR ($CDCl_3$): δ 1.5 (G_1–*Si*Me), 1.9 (G_3-*Si*Me). MALDI: $[M+2H]^{2+}$ = 420.76 uma (calcd. = 420.76 uma), $[M+H+NH_4]^{2+}$ = 428.75 uma (calcd. = 428.76 uma). IR (KBr, cm^{-1}): 2093, υ(N_3). Anal. Calcd. $C_{37}H_{85}N_7S_4Si_3$ (840.63 g/mol): C, 52.86; H, 10.19; N, 11.66; S, 15.26; Exp.: C, 52.70; H, 9.77; N, 10.93; S, 13.96.

$N_3G_3(S\text{-}NMe_2)_8$ (15S). This dendrimer was obtained following the synthetic procedure described for **4S** from $N_3G_3(SNMe_2{\cdot}HCl)_8$ (0.487 g, 0.24 mmol) and Na_2CO_3 (0.265 g, 2.50 mmol) to be obtained as a yellowish oil (0.362 g, 87 %).

^1H-NMR ($CDCl_3$): δ -0.11 (s, 9 H, *SiMe*), 0.00 (s, 12 H, *SiMe*), 0.51 (m, 24 H, $NCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$), 0.88 (t, J_a = 8.8 Hz, 16 H, $SiCH_2CH_2S$), 1.26 (m, 12 H, $NCH_2CH_2CH_2$ and $SiCH_2CH_2CH_2Si$), 1.59 (m, 2 H, NCH_2CH_2), 2.23 (s, 48 H, -NMe_2), 2.48 (m, 16 H, SCH_2CH_2N), 2.53 (m, 16 H, $SiCH_2CH_2S$, overlapped), 2.60 (m, 16 H, SCH_2CH_2N, overlapped), 3.24 (t, J_c = 6.7, 2 H, NCH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ -5.2 and -5.0 (Si*Me*), 13.6 ($NCH_2CH_2CH_2CH_2$), 14.7 ($SiCH_2CH_2S$), 18.4-18.9 ($SiCH_2CH_2CH_2Si$), 21.2 ($NCH_2CH_2CH_2$), 27.7 ($SiCH_2CH_2S$), 29.8 (SCH_2CH_2N), 32.6 (NCH_2CH_2), 45.4 ($SiCH_2CH_2NMe_2$), 51.0 (NCH_2), 59.3 ($SCH_2CH_2NMe_2$). ^{15}N-NMR ($CDCl_3$): δ -352.2 (-NMe_2), -307.0 (N=N=N-CH_2), -131.6 (N=N=N-CH_2). ^{29}Si-NMR ($CDCl_3$): δ 0.9 (G_2–*Si*Me), 1.6 (G_1–*Si*Me), 2.0 (G_3-*Si*Me). IR (KBr, cm^{-1}): 2094, υ(N_3). Anal. Calcd. $C_{77}H_{177}N_{11}S_8Si_7$ (1710.42 g/mol): C, 54.07; H, 10.43; N, 9.01; Exp.: C, 54.61; H, 9.82; N, 8.32.

$(HOC_6H_4O)G_1(S\text{-}NMe_2)_2$ (16S). This dendrimer was obtained following the synthetic procedure described for **4S** from $HOC_6H_4OG_1(SNMe_2{\cdot}HCl)_2$ (0.498 g, 0.91 mmol) and Na_2CO_3 (0.193 g, 1.82 mmol) to be obtained as a yellowish oil (0.409 g, 96 %).

^{1}H-NMR ($CDCl_3$): δ -0.02 (s, 3 H, *SiMe*), 0.53 (m, 2 H, $OCH_2CH_2CH_2CH_2Si$), 0.83 (t, J_a = 8.7 Hz, 4 H, $SiCH_2CH_2S$), 1.41 (m, 2 H, $OCH_2CH_2CH_2$), 1.71 (m, 2 H, OCH_2CH_2), 2.26 (s, 12 H, -NMe_2), 2.46 (m, 4 H, SCH_2CH_2N), 2.50 (m, 4 H, $SiCH_2CH_2S$, overlapped), 2.56 (m, 4 H, SCH_2CH_2N, overlapped), 3.92 (t, J_b = 7.0 Hz, 2 H, OCH_2), 6.69 and 6.74 (m, 4 H, C_6H_4, C-*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.3 (Si*Me*), 13.0 ($OCH_2CH_2CH_2CH_2$), 14.5 ($SiCH_2CH_2S$), 20.1 ($OCH_2CH_2CH_2$), 27.6 ($SiCH_2CH_2S$), 29.5 (SCH_2CH_2N), 32.9 (OCH_2CH_2), 45.2 ($SiCH_2CH_2NMe_2$), 59.2 ($SCH_2CH_2NMe_2$), 67.9 (OCH_2), 115.9 and 116.7 (C_6H_4, *C*-H), 150.3 and 152.7 (C_6H_4, C_{ipso}-O). ^{15}N-NMR ($CDCl_3$): δ -352.1 (-*N*Me_2). ^{29}Si-NMR ($CDCl_3$): δ 2.3 (G_1–*Si*Me). MALDI: $[M+H]^+$ = 473.1 uma (calcd. = 473.3 uma). Anal. Calcd. $C_{23}H_{44}N_2O_2S_2Si$ (472.82 g/mol): C, 58.42; H, 9.38; N, 5.92; S, 13.56; Exp.: C, 56.87; H, 8.99; N, 6.56; S, 12.65.

$(HOC_6H_4O)G_2(S\text{-}NMe_2)_4$ (17S). This dendrimer was obtained following the synthetic procedure described for **4S** from $HOC_6H_4OG_1(SNMe_2{\cdot}HCl)_2$ (0.996 g, 0.94 mmol) and Na_2CO_3 (0.200 g, 1.89 mmol) to be obtained as a yellowish oil (0.686 g, 80 %).

^{1}H-NMR ($CDCl_3$): δ -0.11 (s, 3 H, *SiMe*), -0.04 (s, 6 H, *SiMe*), 0.52 (m, 10 H, $SiCH_2CH_2CH_2Si$ and $OCH_2CH_2CH_2CH_2Si$), 0.83 (t, J_a = 8.6 Hz, 8 H, $SiCH_2CH_2S$), 1.24 (m, 4 H, $SiCH_2CH_2CH_2Si$), 1.42 (m, 2 H, $OCH_2CH_2CH_2$), 1.71 (m, 2 H, OCH_2CH_2), 2.24 (s, 24 H, -NMe_2), 2.47 (m, 8 H, SCH_2CH_2N), 2.50 (m, 8 H, $SiCH_2CH_2S$, overlapped), 2.60 (m, 8 H, SCH_2CH_2N, overlapped), 3.88 (m, 2 H, OCH_2), 6.66 and 6.71 (m, 4 H, C_6H_4, C-*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.3 and -5.0 (Si*Me*), 14.6 ($OCH_2CH_2CH_2CH_2$), 14.7 ($SiCH_2CH_2S$), 18.3, 18.4 and 18.7 ($SiCH_2CH_2CH_2Si$), 20.1 ($OCH_2CH_2CH_2$), 27.7 ($SiCH_2CH_2S$), 29.8 (SCH_2CH_2N), 30.9 (OCH_2CH_2), 45.4 (-NMe_2), 59.3 ($SCH_2CH_2NMe_2$), 67.7 (OCH_2), 115.8 and 116.5 (C_6H_4, *C*-H), 150.8 and 152.4 (C_6H_4, C_{ipso}-O). ^{15}N-NMR ($CDCl_3$): δ -352.0 (-*N*Me_2). ^{29}Si-NMR ($CDCl_3$): δ 1.5 (G_1–*Si*Me), 1.9 (G_2–*Si*Me). Anal. Calcd. $C_{43}H_{90}N_4O_2S_4Si_3$ (907.72 g/mol): C, 56.90; H, 9.99; N, 6.17; S, 14.13; Exp.: C, 55.46; H, 8.83; N, 5.74; S, 13.21.

$(HOC_6H_4O)G_3(S\text{-}NMe_2)_8$ (18S). This dendrimer was obtained following the synthetic procedure described for **4S** from $HOC_6H_4OG_3(SNMe_2{\cdot}HCl)_8$ (0.504 g, 0.24 mmol) and Na_2CO_3 (0.103 g, 0.98 mmol) to be obtained as a yellowish oil (0.349 g, 80 %).

^{1}H-NMR ($CDCl_3$): δ -0.07 (s, 9 H, *SiMe*), 0.02 (s, 12 H, *SiMe*), 0.58 (m, 26 H, Si*C*$H_2$$CH_2CH_2$Si and $OCH_2CH_2CH_2$CH_2Si), 0.90 (t, J_a = 8.6 Hz, 16 H, Si*C*$H_2$$CH_2$S), 1.30 (m, 12 H, $SiCH_2$C$H_2$$CH_2$Si), 1.45 (m, 2 H, OCH_2CH_2CH_2), 1.78 (m, 2 H, OCH_2CH_2), 2.28 (s, 48 H, -N*Me*$_2$), 2.53 (m, 16 H, SCH_2CH_2N), 2.54 (m, 16 H, $SiCH_2$CH_2S, overlapped), 2.65 (m, 16 H, SC$H_2$$CH_2$N, overlapped), 3.91 (t, J_b = 6.1 Hz, 2 H, OCH_2), 6.69 and 6.75 (m, 4 H, C_6H_4, C-*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.3 and -5.0 (Si*Me*), 13.5 ($OCH_2CH_2CH_2$*C*H_2), 14.6 (Si*C*$H_2$$CH_2$S), 18.3-18.8 (Si*C*$H_2$*C*$H_2$*C*$H_2$Si), 20.5 ($OCH_2CH_2$*C*$H_2$), 27.6 ($SiCH_2$*C*$H_2$S), 29.7 (S*C*$H_2$$CH_2$N), 33.1 ($OCH_2$*C*$H_2$), 45.3 ($SiCH_2CH_2$N*Me*$_2$), 59.2 ($SCH_2$*C*$H_2NMe_2$), 68.2 (O*C*$H_2$), 115.6 and 116.3 ($C_6H_4$, *C*-H), 150.9 and 152.3 (C_6H_4, *C*$_{ipso}$-O). ^{15}N-NMR ($CDCl_3$): δ -352.2 (-*N*Me$_2$). ^{29}Si-NMR ($CDCl_3$): δ 1.0 (G_2-*Si*Me), 1.9 (G_3–*Si*Me). Anal. Calcd. $C_{83}H_{182}N_8O_2S_8Si_7$ (1777.50 g/mol): C, 56.08; H, 10.32; N, 6.30; S, 14.43; Exp.: C, 54.78; H, 9.23; N, 5.78; S, 13.38.

(HOC$_2$H$_4$O)G$_1$V$_2$. An excess of ethylenglycol (46 µl, 0.84 mmol) was treated with NaH (0.040 g, 1.01 mmol) in dried THF at 0 ºC for 1 hour. Afterwards, a solution of BrG_1V_2 (0.380 g, 0.42 mmol), 18-C-6 (0.053 g, 0.20 mmol) and NaI in dried THF was added dropwise under argon atmosphere and stirred for 18 hours at 100 ºC. Solvents were removed and the crude product was extracted in Et_2O to provide the desired product as a yellowish oil (0.253 g, 84 %).

^{1}H-NMR ($CDCl_3$): δ 0.13 (s, 3 H, Si*Me*), 0.66 (t, J_a = 7.5 Hz, 2 H, CH_2Si), 1.39 (m, 2 H, C$H_2$$CH_2$Si), 1.62 (m, 2 H, OCH_2CH_2), 2.27 (sa, 1 H, *H*O-), 3.47 (t, 2 H, OCH_2), 3.52 (t, 2 H, $HOCH_2$CH_2O, overlapped), 3.71 (m, 2 H, HOC$H_2$$CH_2$O), 5.71 and 6.08 (m, 6 H, Si*CHCH*$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.4 (Si*Me*), 13.8 ($OCH_2CH_2CH_2$*CH*$_2$Si), 20.2 (OCH_2CH_2*C*$H_2$$CH_2$Si), 33.2 ($OCH_2$*C*$H_2$$CH_2CH_2$Si), 61.8 (HO*C*$H_2$$CH_2$O), 70.9 (O*C*$H_2$$CH_2CH_2CH_2$Si), 71.7 ($HOCH_2$*C*$H_2$O), 132.8 ($SiCH$*C*$H_2$), 136.8 (Si*C*$HCH_2$). ^{29}Si-NMR ($CDCl_3$): δ -12.8 ($G_1$–SiMe). IR (KBr, cm^{-1}): 3429, υ(OH). MALDI: [M+Na$^+$]$^+$ = 237.13 uma (calcd. = 237.14). Anal. Calcd. $C_{11}H_{22}O_2Si$ (214.38 g/mol): C, 61.63; H, 10.34; Obt.: C, 59.11; H, 9.88.

$(HOC_2H_4O)G_2V_4$. This dendron was prepared following the synthetic procedure described for $HOC_2H_4OG_1V_2$ from BrG_2V_4 (0.955 g, 2.03 mmol), ethylene glycol (0.23 mL, 4.17 mmol), NaH (0.200 g, 5.00 mmol) and 18-C-6 (0.110 g, 0.42 mmol) to be obtained as a yellowish oil (0.832 g, 91 %).

^{1}H-NMR ($CDCl_3$): δ -0.09 (s, 3 H, Si*Me*), 0.12 (s, 6 H, Si*Me*), 0.56 (m, 6 H, C*H*$_2$Si), 0.70 (m, 4 H, C*H*$_2$SiC$_2$H$_3$, overlapped), 1.34 (m, 6 H, C*H*$_2$CH$_2$Si), 1.59 (m, 2 H, OCH$_2$C*H*$_2$), 2.26 (sa, 1 H, *H*O-), 3.46 (m, 2 H, OC*H*$_2$), 3.52 (m, 2 H, HOCH$_2$C*H*$_2$O, overlapped), 3.72 (m, 2 H, HOC*H*$_2$CH$_2$O), 5.81 and 6.07 (m, 6 H, SiC*H*CH$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.2 and -5.1 (Si*C*H$_3$), 13.8 (OCH$_2$CH$_2$CH$_2$*CH*$_2$Si), 18.2–18.7 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 20.0 (OCH$_2$CH$_2$*C*H$_2$CH$_2$Si), 33.5 (OCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 61.8 (HO*C*H$_2$CH$_2$O), 71.1 (O*C*H$_2$CH$_2$CH$_2$CH$_2$Si), 71.7 (HOCH$_2$*C*H$_2$O), 132.6 (SiCH*C*H$_2$), 137.1 (Si*C*HCH$_2$). ^{29}Si-NMR ($CDCl_3$): δ 1.8 (G_1–SiMe), -13.4 (G_2–SiMe). IR (KBr, cm^{-1}): 3429, υ(OH). MS: $[M+Na]^+$ = 461.28 uma (calcd. = 461.28 uma). Anal. Calcd. $C_{23}H_{46}O_2Si_3$ (438.87 g/mol): C, 62.95; H, 10.56; Obt.: C, 63.24; H, 10.34.

$(HOC_2H_4O)G_3V_8$. This dendron was prepared following the synthetic procedure described for $HOC_2H_4OG_1V_2$, but heating at 120 ºCfrom BrG_3V_8 (1.057 g, 1.16 mmol), ethylene glycol (0.13 mL, 2.33 mmol), NaH (0.112 g, 2.80 mmol) and 18-C-6 (0.062 g, 0.23 mmol) to be obtained as a yellowish oil (0.941 g, 91 %).

^{1}H-NMR ($CDCl_3$): δ -0.11 (s, 9 H, Si*Me*), 0.10 (s, 12 H, Si*Me*), 0.56 (m, 18 H, C*H*$_2$Si), 0.71 (m, 8 H, C*H*$_2$SiC$_2$H$_3$, overlapped), 1.24 (m, 14 H, C*H*$_2$CH$_2$Si), 1.58 (m, 2 H, OCH$_2$C*H*$_2$), 2.25 (sa, 1 H, *H*O-), 3.47 (m, 2 H, OC*H*$_2$), 3.53 (m, 2 H, HOCH$_2$C*H*$_2$O, overlapped), 3.73 (m, 2 H, HOC*H*$_2$CH$_2$O), 5.80 and 6.07 (m, 6 H, SiC*H*CH$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.2, -5.1 and -5.0 (Si*C*H$_3$), 13.9 (OCH$_2$CH$_2$CH$_2$*CH*$_2$Si), 18.3–18.9 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 20.5 (OCH$_2$CH$_2$*C*H$_2$CH$_2$Si), 33.6 (OCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 61.9 (HO*C*H$_2$CH$_2$O), 71.1 (O*C*H$_2$CH$_2$CH$_2$CH$_2$Si), 71.7 (HOCH$_2$*C*H$_2$O), 132.6 (SiCH*C*H$_2$), 137.2 (Si*C*HCH$_2$). ^{29}Si-NMR ($CDCl_3$): δ 1.8 (G_1–SiMe), 0.9 (G_2–SiMe), -13.3 (G_3–SiMe). IR (KBr, cm^{-1}): 3429, υ(OH). MS: $[M+Na]^+$ = 909.56 uma (calcd. = 909.56 uma). Anal. Calcd. $C_{47}H_{94}O_2Si_7$ (887.85 g/mol): C, 63.58; H, 10.67; Obt.: C, 64.67; H, 11.00.

$(HOC_2H_4O)G_1(S\text{-}NMe_2)_2$ (19S). Thiol-ene addition was performed as described for compound **1S** from $HOC_2H_4OG_1V_2$ (0.181 g, 0.84 mmol), 2-(dimethylamino)ethanethiol hydrochloride (0.239 g, 1.69 mmol) and DMPA (0.043 g, 0.17 mmol). Basification was performed without further purification following the synthetic procedure described for **4S** and using Na_2CO_3 (0.123 g, 1.16 mmol) to obtain the product as a yellowish oil (0.217 g, 88 %).

^{1}H-NMR ($CDCl_3$): δ -0.04 (s, 3 H, *SiMe*), 0.51 (t, J_a = 8.5 Hz, 2 H, $OCH_2CH_2CH_2CH_2Si$), 0.85 (t, J_b = 8.8 Hz, 4 H, $SiCH_2CH_2S$), 1.31 (m, 2 H, $OCH_2CH_2CH_2$), 1.55 (m, 2 H, OCH_2CH_2), 2.19 (s, 12 H, $-NMe_2$), 2.43 (m, 4 H, SCH_2CH_2N), 2.46 (m, 4 H, $SiCH_2CH_2S$, overlapped), 2.58 (m, 4 H, SCH_2CH_2N, overlapped), 3.41 (m, 2 H, OCH_2), 3.45 (m, 2 H, $HOCH_2CH_2O$, overlapped), 3.65 (m, 2 H, $HOCH_2CH_2O$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.4 (Si*Me*), 13.2 ($OCH_2CH_2CH_2CH_2Si$), 14.4 ($SiCH_2CH_2S$), 20.2 ($OCH_2CH_2CH_2$), 27.5 ($SiCH_2CH_2S$), 29.5 (SCH_2CH_2N), 33.3 (OCH_2CH_2), 45.2 ($SiCH_2CH_2NMe_2$), 59.1 ($SCH_2CH_2NMe_2$), 61.6 ($HOCH_2$), 70.6 ($OCH_2CH_2CH_2$), 72.0 ($HOCH_2CH_2O$). ^{15}N-NMR ($CDCl_3$): δ -352.3 ($-NMe_2$). ^{29}Si-NMR ($CDCl_3$): δ 2.7 (G_1-*Si*Me). MALDI: $[M+H]^+$ = 425.27 uma (calcd. = 425.27 uma). Anal. Calcd. $C_{19}H_{44}N_2O_2S_2Si$ (424.78 g/mol): C, 53.72; H, 10.44; N, 6.59; S, 15.10; Exp.: C, 53.88; H, 10.31; N, 6.84; S, 16.27.

$(HOC_2H_4O)G_2(S\text{-}NMe_2)_4$ (20S). This product was synthesized following the synthetic procedure described for **19S** but the final product was purified using a size exclusion chromatography. The reaction was performed from $HOC_2H_4OG_2V_4$ (0.832 g, 1.90 mmol), 2-(dimethylamino)ethanethiol hydrochloride (1.074 g, 7.58 mmol) and DMPA (0.194 g, 0.76 mmol). Afterwards Na_2CO_3 (0.804 g, 7.58 mmol) was added to obtain the product after size exclusion chromatography as a yellowish oil (1.346 g, 82 %).

^{1}H-NMR ($CDCl_3$): δ -0.01 (s, 3 H, *SiMe*), 0.03 (s, 6 H, *SiMe*), 0.56 (m, 10 H, $SiCH_2CH_2CH_2Si$ and $OCH_2CH_2CH_2CH_2Si$), 0.86 (t, J_a = 8.7 Hz, 8 H, $SiCH_2CH_2S$), 1.26 (m, 4 H, $SiCH_2CH_2CH_2Si$), 1.57 (m, 2 H, $OCH_2CH_2CH_2$), 1.81 (m, 2 H, OCH_2CH_2), 2.22 (s, 24 H, $-NMe_2$), 2.49 (m, 8 H, SCH_2CH_2N), 2.58 (m, 8 H, $SiCH_2CH_2S$, overlapped), 2.60 (m, 8 H, SCH_2CH_2N, overlapped), 3.44 (m, 2 H, OCH_2), 3.49 (m, 2 H, $HOCH_2CH_2O$, overlapped), 3.68 (m, 2 H, $HOCH_2CH_2O$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.3 and -5.1 (Si*Me*),

13.7 ($OCH_2CH_2CH_2\mathit{C}H_2$), 14.6 ($SiCH_2CH_2S$), 17.7-18.9 ($SiCH_2CH_2CH_2Si$), 20.5 ($OCH_2CH_2\mathit{C}H_2$), 27.7 ($SiCH_2\mathit{C}H_2S$), 29.8 ($SCH_2CH_2N$), 33.5 ($OCH_2\mathit{C}H_2$), 45.3 (-N$\mathit{Me}_2$), 59.2 ($SCH_2\mathit{C}H_2NMe_2$), 61.7 ($HOCH_2CH_2O$), 71.0 ($OCH_2CH_2CH_2CH_2Si$), 71.9 ($HOCH_2\mathit{C}H_2O$). ^{15}N-NMR ($CDCl_3$): δ -352.3 (-$\mathit{N}Me_2$). ^{29}Si-NMR ($CDCl_3$): δ 1.7 ($G_1$–$\mathit{Si}$Me), 2.0 ($G_2$–$\mathit{Si}$Me). MALDI: $[M+H]^+$ = 859.6 uma (calcd. = 859.5 uma). Anal. Calcd. $C_{39}H_{90}N_4O_2S_4Si_3$ (859.67 g/mol): C, 54.49; H, 10.55; N, 6.52; Exp.: C, 55.35; H, 9.77; N, 6.86.

$(HOC_2H_4O)G_3(S\text{-}NMe_2)_8$ (21S). This product was synthesized following the synthetic procedure described for **20S**. The reaction was performed from $HOC_2H_4OG_3V_8$ (0.553 g, 0.62 mmol), 2-(dimethylamino)ethanethiol hydrochloride (0.713 g, 5.03 mmol) and DMPA (0.128 g, 0.50 mmol). Afterwards Na_2CO_3 (0.528 g, 4.98 mmol) was added to obtain the product after size exclusion chromatography as a yellowish oil (0.631 g, 59 %).

^{1}H-NMR ($CDCl_3$): δ -0.10 (s, 9 H, *SiMe*), 0.00 (s, 12 H, *SiMe*), 0.52 (m, 26 H, $SiC\mathit{H}_2CH_2C\mathit{H}_2Si$ and $OCH_2CH_2CH_2C\mathit{H}_2Si$), 0.88 (t, J_a = 8.6 Hz, 16 H, $SiC\mathit{H}_2CH_2S$), 1.28 (m, 12 H, $SiCH_2C\mathit{H}_2CH_2Si$), 1.59 (m, 2 H, $OCH_2CH_2C\mathit{H}_2$), 1.79 (m, 2 H, $OCH_2C\mathit{H}_2$), 2.23 (s, 48 H, -NMe_2), 2.47 (m, 16 H, $SCH_2C\mathit{H}_2N$), 2.54 (m, 16 H, $SiCH_2C\mathit{H}_2S$, overlapped), 2.62 (m, 16 H, $SC\mathit{H}_2CH_2N$, overlapped), 3.46 (m, 2 H, $OC\mathit{H}_2$), 3.50 (m, 2 H, $HOCH_2C\mathit{H}_2O$, overlapped), 3.70 (m, 2 H, $HOC\mathit{H}_2CH_2O$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ -5.2 and -5.0 (Si*Me*), 13.6 ($OCH_2CH_2CH_2\mathit{C}H_2$), 14.7 ($SiCH_2CH_2S$), 18.4-18.9 ($SiCH_2CH_2CH_2Si$), 20.6 ($OCH_2CH_2\mathit{C}H_2$), 27.7 ($SiCH_2\mathit{C}H_2S$), 29.8 ($SCH_2CH_2N$), 33.7 ($OCH_2\mathit{C}H_2$), 45.4 (-N$\mathit{Me}_2$), 59.3 ($SCH_2\mathit{C}H_2NMe_2$), 61.7 ($HOCH_2CH_2O$), 71.1 ($OCH_2CH_2CH_2CH_2Si$), 72.0 ($HOCH_2\mathit{C}H_2O$). ^{15}N-NMR ($CDCl_3$): δ -352.1 (-$\mathit{N}Me_2$). ^{29}Si-NMR ($CDCl_3$): δ 1.6 ($G_1$–$\mathit{Si}$Me), 1.0 ($G_2$-$\mathit{Si}$Me), 1.9 ($G_3$–$\mathit{Si}$Me). MALDI: $[M+Na]^+$ = 1749.9 uma (calcd. = 1750.0 uma), $[M+H]^+$ = 1727.9 uma (calcd. = 1728.1 uma). Anal. Calcd. $C_{79}H_{182}N_8O_2S_8Si_7$ (1729.46 g/mol): C, 54.86; H, 10.61; N, 6.48; Exp.: C, 54.86; H, 9.42; N, 6.84.

$N_3G_1(S\text{-}NMe_3I)_2$ (22S). This dendron was obtained following the synthetic procedure described for **7S** from **13S** (0.066 g, 0.16 mmol) and MeI (0.02 mL, 0.38 mmol) to obtain the product as a white solid (0.074 g, 66 %).

^{1}H-NMR (DMSO-d_6): 0.04 (s, 3 H, Si*Me*), 0.59 (t, J_a = 7.2 Hz, 2 H, $NCH_2CH_2CH_2CH_2Si$), 0.87 (t, J_b = 8.3 Hz, 4 H, $SiCH_2CH_2S$), 1.33 (m, 2 H, $NCH_2CH_2CH_2CH_2CH_2Si$), 1.55 (m, 2 H, $NCH_2CH_2CH_2CH_2CH_2Si$), 2.63 (t, J_b = 8.2 Hz, 4 H, $SiCH_2CH_2CH_2S$), 2.89 (t, J_c = 7.8 Hz, 4 H, $SCH_2CH_2NMe_3^+$), 3.08 (s, 20 H, $SCH_2CH_2NMe_3^+$ and N_3CH_2, overlapped), 3.55 (t, J_c = 7.2 Hz, 4 H, $SCH_2CH_2NMe_3^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.85 (Si*Me*), 11.9 ($N_3CH_2CH_2CH_2CH_2Si$), 13.5 ($SiCH_2CH_2S$), 19.9 ($N_3CH_2CH_2CH_2CH_2Si$), 23.0 ($SCH_2CH_2N^+$), 26.2 ($SiCH_2CH_2S$), 31.4 ($N_3CH_2CH_2CH_2CH_2Si$), 49.7 (N_3CH_2), 51.7 (-N*Me*$_3^+$), 63.9 (CH_2N^+). ^{15}N-NMR (DMSO-d_6): δ -338.3 (-*N*Me_2H^+), -308.5 (N=*N*=N-CH_2), -131.8 (*N*=N=N-CH_2). ^{29}Si-NMR (DMSO-d_6): δ 2.9 (G_1–*Si*Me). IR (KBr, cm^{-1}): 2094, υ(N_3). MS: [M–I]$^+$ = 562.3 uma (calcd. = 562.2 uma). Anal. Calc. $C_{19}H_{45}I_2N_5S_2Si$ (689.62 g/mol): C, 33.09; H, 6.58; N, 10.16; S, 9.30; Obt.: C, 31.15; H, 6.24; N, 7.12; S, 9.66.

N_3G_2(S-NMe_3I)$_4$ (23S). This dendron was obtained following the synthetic procedure described for **7S** from **14S** (0.125 g, 0.14 mmol) and MeI (0.04 mL, 0.64 mmol) to obtain the product as a white solid (0.165 g, 85 %).

^{1}H-NMR (DMSO-d_6): -0.08 (s, 3 H, Si*Me*), 0.03 (s, 6 H, Si*Me*), 0.55 (m, 10 H, $NCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2$), 0.86 (m, 8 H, $SiCH_2CH_2S$), 1.31 (m, 6 H, $NCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2$), 1.53 (m, 2 H, $NCH_2CH_2CH_2CH_2CH_2Si$), 2.63 (m, 8 H, $SiCH_2CH_2CH_2S$), 2.90 (m, 8 H, $SCH_2CH_2NMe_3^+$), 3.10 (s, 36 H, $SCH_2CH_2NMe_3^+$ and N_3CH_2, overlapped), 3.55 (m, 8 H, $SCH_2CH_2NMe_3^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.7 and -5.5 (Si*Me*), 12.4 ($N_3CH_2CH_2CH_2CH_2Si$), 13.6 ($SiCH_2CH_2S$), 16.8, 17.4 and 17.6 ($SiCH_2CH_2CH_2Si$), 20.2 ($N_3CH_2CH_2CH_2CH_2Si$), 23.1 ($SCH_2CH_2N^+$), 26.3 ($SiCH_2CH_2S$), 31.5 ($N_3CH_2CH_2CH_2CH_2Si$), 49.7 (N_3CH_2), 51.7 (-N*Me*$_3^+$), 63.9 (CH_2N^+). ^{15}N-NMR (DMSO-d_6): δ -329.3 (-*N*Me_3^+), -308.6 (N=*N*=N-CH_2), -131.8 (*N*=N=N-CH_2). ^{29}Si-NMR (DMSO-d_6): δ 1.6 (G_1–*Si*Me), 2.3 (G_2–*Si*Me). IR (KBr, cm^{-1}): 2094, υ(N_3). ESI: q=2 (576.71 [M-2I]$^{2+}$), q=3 (342.17 [M-3I]$^{3+}$), q=4 (224.90 [M-4I]$^{4+}$). Anal. Calc. $C_{41}H_{97}I_4N_7S_4Si_3$ (1408.39 g/mol): C, 34.96; H, 6.94; N, 6.96; S, 9.11; Obt.: C, 33.95; H, 6.30; N, 5.66; S, 7.32.

$N_3G_3(S\text{-}NMe_3I)_8$ (24S). This dendron was obtained following the synthetic procedure described for **7S** from **15S** (0.362 g, 0.21 mmol) and MeI (0.14 mL, 2.24 mmol) to obtain the product as a white solid (0.369 g, 61 %).

^{1}H-NMR (DMSO-d_6): -0.08 (s, 9 H, Si*Me*), 0.04 (s, 12 H, Si*Me*), 0.53 (m, 26 H, $NCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2$), 0.86 (m, 16 H, $SiCH_2CH_2S$), 1.25 (m, 14 H, $NCH_2CH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2$), 1.54 (m, 2 H, $NCH_2CH_2CH_2CH_2Si$), 2.64 (m, 16 H, $SiCH_2CH_2S$), 2.90 (m, 16 H, $SCH_2CH_2NMe_3^+$), 3.11 (s, 74 H, $SCH_2CH_2NMe_3^+$ and N_3CH_2, overlapped), 3.56 (m, 16 H, $SCH_2CH_2NMe_3^+$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.6 and -5.4 (Si*Me*), 12.5 ($N_3CH_2CH_2CH_2CH_2Si$), 13.6 ($SiCH_2CH_2S$), 17.5-17.8 ($SiCH_2CH_2CH_2Si$), 20.3 ($N_3CH_2CH_2CH_2CH_2Si$), 23.2 ($SCH_2CH_2N^+$), 26.4 ($SiCH_2CH_2S$), 31.4 ($N_3CH_2CH_2CH_2CH_2Si$), 49.6 (N_3CH_2), 51.7 ($-NMe_3^+$), 63.9 (CH_2N^+). ^{15}N-NMR (DMSO-d_6): δ -329.4 ($-NMe_3^+$), -308.5 ($N{=}N{=}N\text{-}CH_2$), -131.7 ($N{=}N{=}N\text{-}CH_2$). ^{29}Si-NMR (DMSO-d_6): δ 1.0 (G_2–*Si*Me), 2.4 (G_3–*Si*Me). IR (KBr, cm^{-1}): 2094, υ(N_3). Anal. Calc. $C_{85}H_{201}I_8N_{11}S_8Si_7$ (2845.93 g/mol): C, 35.87; H, 7.12; N, 5.41; Obt.: C, 35.38; H, 6.86; N, 5.24.

$(HOC_6H_4O)G_1(S\text{-}NMe_3I)_2$ (25S). This dendron was obtained following the synthetic procedure described for **7S** from **16S** (0.178 g, 0.38 mmol) and MeI (0.05 mL, 0.80 mmol) to obtain the product as a white solid (0.287 g, 95 %).

^{1}H-NMR (DMSO-d_6): δ 0.04 (s, 3 H, Si*Me*), 0.60 (m, 2 H, $CH_2SiC_2H_4S$), 0.87 (m, 4 H, $SiCH_2CH_2S$), 1.44 (m, 2 H, $OCH_2CH_2CH_2$), 1.67 (m, 2 H, OCH_2CH_2), 2.60 (m, 4 H, $SiCH_2CH_2S$), 2.86 (m, 4 H, $SCH_2CH_2N^+$), 3.06 (s, 18 H, $SCH_2CH_2NMe_3^+$), 3.50 (m, 4 H, CH_2N^+), 3.82 (m, 2 H, OCH_2), 6.65 and 6.69 (m, 4 H, HOC_6H_4O), 8.87 (s, 1 H, *H*O-). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -1.7 (Si*Me*), 14.1 ($OCH_2CH_2CH_2CH_2Si$), 15.5 ($SiCH_2CH_2S$), 18.7 ($OCH_2CH_2CH_2CH_2Si$), 23.0 ($SCH_2CH_2NMe_3^+$), 24.8 ($SiCH_2CH_2S$), 31.9 ($OCH_2CH_2CH_2CH_2Si$), 51.7 ($SiCH_2CH_2NMe_3^+$), 63.9 ($CH_2NMe_3^+$), 66.9 (OCH_2), 114.7 and 115.2 ($C_6H_4O_2$, *C*-H), 150.5 and 150.9 ($C_6H_4O_2$, *C*-O). ^{29}Si-NMR (DMSO-d_6): δ 3.1 (G_1–*Si*Me). ESI: q=1 (629.3 $[M\text{-}I]^+$). Anal. Calcd. $C_{25}H_{50}I_2N_2O_2S_2Si$ (756.70 g/mol): C, 39.68; H, 6.66; N, 3.70; S, 8.47; Exp.: C, 36.50; H, 5.49; N, 3.66; S, 8.14.

$(HOC_6H_4O)G_2(S\text{-}NMe_3I)_4$ (26S). This dendron was obtained following the synthetic procedure described for **7S** from **17S** (0.631 g, 0.70 mmol) and MeI (0.18 mL, 2.92 mmol) to obtain the product as a white solid (0.972 g, 98 %).

^{1}H-NMR (DMSO-d_6): δ -0.07 (s, 3 H, Si*Me*), 0.03 (s, 6 H, Si*Me*), 0.54 (m, 6 H, $OCH_2CH_2CH_2CH_2SiCH_2$), 0.63 (m, 4 H, $CH_2SiC_2H_4S$, overlapped), 0.85 (m, 8 H, $SiCH_2CH_2S$), 1.25 (m, 6 H, $SiCH_2CH_2$), 1.66 (m, 2 H, $OCH_2CH_2CH_2CH_2Si$), 2.62 (m, 8 H, $SiCH_2CH_2S$), 2.89 (m, 8 H, $SCH_2CH_2NMe_3^+$), 3.07 (s, 36 H, $SCH_2CH_2NMe_3^+$), 3.51 (m, 8 H, $SCH_2CH_2NMe_3^+$), 3.83 (m, 2 H, OCH_2), 6.66 and 6.69 (m, 4 H, HOC_6H_4O), 8.88 (s, 1 H, *H*O-). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.7 and -5.4 (Si*Me*), 12.6 ($OCH_2CH_2CH_2CH_2Si$), 13.6 ($SiCH_2CH_2S$), 17.2, 17.4 and 17.6 ($SiCH_2CH_2CH_2Si$), 19.6 ($OCH_2CH_2CH_2CH_2Si$), 23.1 ($SCH_2CH_2NMe_3^+$), 26.3 ($SiCH_2CH_2S$), 32.2 ($OCH_2CH_2CH_2CH_2Si$), 51.6 (-NMe_3^+), 63.9 ($CH_2NMe_3^+$), 67.0 (OCH_2), 114.9 and 115.2 ($C_6H_4O_2$, *C*-H), 150.6 and 150.9 ($C_6H_4O_2$, *C*-O). ^{15}N-NMR (DMSO-d_6): δ -329.9 (-*N*Me_3^+). ^{29}Si-NMR (DMSO-d_6): δ 1.9 (G_1–*Si*Me), 2.6 (G_2–*Si*Me). ESI: q=1 (1347.31 $[M\text{-}I]^+$), q=2 (610.22 $[M\text{-}2I]^{2+}$), q=3 (364.51 $[M\text{-}3I]^{3+}$), q=4 (241.66 $[M\text{-}4I]^{4+}$). Anal. Calcd. $C_{47}H_{102}I_4N_4O_2S_4Si_3$ (967.85 g/mol): C, 38.26; H, 6.97; N, 3.80; S, 8.69; Exp.: C, 36.98; H, 6.73; N, 4.17; S, 8.50.

$(HOC_6H_4O)G_3(S\text{-}NMe_3I)_8$ (27S). This dendron was obtained following the synthetic procedure described for **7S** from **18S** (0.427 g, 0.24 mmol) and MeI (0.14 mL, 0.27 mmol) to obtain the product as a white solid (0.622 g, 89 %).

^{1}H-NMR (DMSO-d_6): δ -0.09 (s, 9 H, Si*Me*), 0.04 (s, 12 H, Si*Me*), 0.53 (m, 18 H, $OCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$), 0.63 (m, 8 H, $CH_2SiC_2H_4S$), 0.86 (m, 16 H, $SiCH_2CH_2S$), 1.28 (m, 12 H, $SiCH_2CH_2$), 1.65 (m, 2 H, $OCH_2CH_2CH_2CH_2Si$), 2.63 (m, 16 H, $SiCH_2CH_2S$), 2.90 (m, 16 H, $SCH_2CH_2N^+$), 3.10 (s, 72 H, -NMe_3^+), 3.54 (m, 16 H, CH_2N^+), 3.78 (m, 2 H, OCH_2), 6.66 and 6.69 (m, 4 H, HOC_6H_4O), 8.89 (s, 1H, *H*O-). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.6 and -5.4 (Si*Me*), 13.6 ($SiCH_2CH_2S$), 17.3-17.8 ($SiCH_2CH_2CH_2Si$), 23.2 ($SCH_2CH_2N^+$), 26.4 ($SiCH_2CH_2S$), 51.7 (-NMe_3^+), 64.0 (CH_2N^+), 114.8 and 115.2 ($C_6H_4O_2$, *C*-H), 150.6 and 151.0 ($C_6H_4O_2$, *C*-O). ^{15}N-NMR (DMSO-d_6): δ -330.0 (-*N*Me_3^+). ^{29}Si-

NMR (DMSO-d_6): δ 2.0 (G_1–*Si*Me), 1.1 (G_2–*Si*Me), 2.5 (G_3–*Si*Me). ESI: q=2 (1328.32 $[M-2I]^{2+}$), q=3 (843.26 $[M-3I]^{3+}$), q=4 (600.72 $[M-4I]^{4+}$), q=5 (455.20 $[M-5I]^{4+}$). Anal. Calcd. $C_{91}H_{206}I_8N_8O_2S_8Si_7$ (2913.01 g/mol): C, 37.52; H, 7.13N, 3.85; S, 8.81; Exp.: C, 36.50; H, 7.11; N, 4.04; S, 8.31.

$(HOC_2H_4O)G_1(S\text{-}NMe_3I)_2$ (28S). This dendron was obtained following the synthetic procedure described for **7S** from **19S** (0.125 g, 0.29 mmol) and MeI (0.04 mL, 0.64 mmol) to obtain the product as a white solid (0.200 g, 96 %).

^{1}H-NMR (DMSO-d_6): δ -0.03 (s, 3 H, Si*Me*), 0.57 (t, J_a = 8.2 Hz, 2 H, $OCH_2CH_2CH_2CH_2Si$), 0.83 (t, J_b = 8.6 Hz, 4 H, $SiCH_2CH_2S$), 1.30 (m, 2 H, $OCH_2CH_2CH_2CH_2Si$), 1.51 (m, 2 H, $OCH_2CH_2CH_2CH_2Si$), 2.62 (t, J_b = 8.6 Hz, 4 H, $SiCH_2CH_2S$), 2.89 (t, J_c = 8.4 Hz, 4 H, $SCH_2CH_2NMe_3^+$), 3.08 (s, 18 H, $SCH_2CH_2NMe_3^+$), 3.37 (m, 4 H, $OCH_2CH_2CH_2$ and $HOCH_2CH_2$), 3.51 (m, 6 H, $SCH_2CH_2NMe_3^+$ and $HOCH_2$), 4.55 (m, 1 H, *H*OCH_2). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.8 (Si*Me*), 12.2 ($OCH_2CH_2CH_2CH_2Si$), 13.5 ($SiCH_2CH_2S$), 19.4 ($OCH_2CH_2CH_2CH_2Si$), 23.0 ($SCH_2CH_2NMe_3^+$), 26.2 ($SiCH_2CH_2S$), 32.5 ($OCH_2CH_2CH_2CH_2Si$), 51.7 ($SiCH_2CH_2NMe_3^+$), 59.7 ($HOCH_2$), 63.9 ($CH_2NMe_3^+$), 69.4 ($OCH_2CH_2CH_2CH_2Si$), 71.5 ($HOCH_2CH_2$). ^{15}N-NMR (DMSO-d_6): δ -329.3 (-*N*Me_3^+). ^{29}Si-NMR (DMSO-d_6): δ 3.0 (G_1–*Si*Me). MS: $[M–I]^+$ = 581.2 uma (calcd. = 581.3 uma). Anal. Calcd. $C_{21}H_{50}I_2N_2O_2S_2Si$ (708.66 g/mol): C, 35.59; H, 7.11; N, 3.95; Exp.: C, 32.56; H, 6.32; N, 4.04.

$(HOC_2H_4O)G_2(S\text{-}NMe_3I)_4$ (29S). This dendron was obtained following the synthetic procedure described for **7S** from **20S** (0.501 g, 0.58 mmol) and MeI (0.15 mL, 2.40 mmol) to obtain the product as a white solid (0.800 g, 96 %).

^{1}H-NMR (DMSO-d_6): δ -0.08 (s, 3 H, Si*Me*), 0.04 (s, 6 H, Si*Me*), 0.54 (m, 6 H, $OCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$, overlapped), 0.63 (m, 4 H, $CH_2SiC_2H_4S$, overlapped), 0.85 (t, J_a = 8.3 Hz, 8 H, $SiCH_2CH_2S$), 1.28 (m, 6 H, $OCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$), 1.49 (m, 2 H, $OCH_2CH_2CH_2CH_2Si$), 2.63 (t, J_a = 8.5 Hz, 8 H, $SiCH_2CH_2S$), 2.89 (t, J_b = 7.9 Hz, 8 H, $SCH_2CH_2NMe_3^+$), 3.09 (s, 36 H, $SCH_2CH_2NMe_3^+$), 3.36 (m, 4 H, $OCH_2CH_2CH_2$ and $HOCH_2CH_2$), 3.53 (m, 10 H, $SCH_2CH_2NMe_3^+$ and $HOCH_2$), 4.54 (*H*O-). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.7 and -5.4 (Si*Me*), 12.6

($OCH_2CH_2CH_2\mathit{C}H_2Si$), 13.6 ($Si\mathit{C}H_2CH_2S$), 17.1, 17.4 and 17.6 ($Si\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2Si$), 19.6 ($OCH_2CH_2\mathit{C}H_2CH_2Si$), 23.1 ($S\mathit{C}H_2CH_2NMe_3^+$), 26.3 ($SiCH_2\mathit{C}H_2S$), 32.6 ($OCH_2\mathit{C}H_2CH_2CH_2Si$), 51.6 ($SiCH_2CH_2N\mathit{Me}_3^+$), 59.7 ($HO\mathit{C}H_2$), 63.9 ($\mathit{C}H_2NMe_3^+$), 69.5 ($O\mathit{C}H_2CH_2CH_2CH_2Si$), 71.5 ($HOCH_2\mathit{C}H_2$). ^{15}N-NMR (DMSO-d_6): δ -329.4 (-$\mathit{N}Me_3^+$). ^{29}Si-NMR (DMSO-d_6): δ 1.7 (G_1–SiMe), 2.5 (G_2–SiMe). ESI: q=1 (1299.31 $[M-I]^+$), q=2 (586.22 $[M-2I]^{2+}$), q=3 (348.51 $[M-3I]^{3+}$). Anal. Calcd. $C_{43}H_{102}I_4N_4O_2S_4Si_3$ (1427.43 g/mol): C, 36.18; H, 7.20; I, 35.56; N, 3.93; O, 2.24; S, 8.99; Exp.: C, 35.64; H, 6.89; N, 3.94; S, 8.67.

$(HOC_2H_4O)G_3(S\text{-}NMe_3I)_8$ (30S). This dendron was obtained following the synthetic procedure described for **7S** from **21S** (0.631 g, 0.36 mmol) and MeI (0.18 mL, 2.88 mmol) to obtain the product as a white solid (1.003 g, 96 %).

^{1}H-NMR (DMSO-d_6): δ -0.09 (s, 9 H, Si*Me*), 0.04 (s, 12 H, Si*Me*), 0.53 (m, 18 H, $OCH_2CH_2CH_2C\mathit{H}_2Si$ and $SiC\mathit{H}_2CH_2C\mathit{H}_2Si$), 0.63 (m, 8 H, $C\mathit{H}_2SiC_2H_4S$, overlapped), 0.86 (m, 16 H, $SiC\mathit{H}_2CH_2S$), 1.29 (m, 14 H, $OCH_2CH_2C\mathit{H}_2CH_2Si$ and $SiCH_2C\mathit{H}_2CH_2Si$), 1.51 (m, 2 H, $OCH_2C\mathit{H}_2CH_2CH_2Si$), 2.63 (m, 16 H, $SiCH_2C\mathit{H}_2S$), 2.90 (m, 16 H, $SC\mathit{H}_2CH_2NMe_3^+$), 3.10 (s, 72 H, $SCH_2CH_2N\mathit{Me}_3^+$), 3.36 (m, 4 H, $OC\mathit{H}_2CH_2CH_2$ and $HOCH_2C\mathit{H}_2$), 3.54 (m, 18 H, $SCH_2C\mathit{H}_2NMe_3^+$ and $HOC\mathit{H}_2$). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ -5.6 and -5.4 (Si*Me*), 12.7 ($OCH_2CH_2CH_2\mathit{C}H_2Si$), 13.6 ($Si\mathit{C}H_2CH_2S$), 17.4-17.8 ($Si\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2Si$) , 19.5 ($OCH_2CH_2\mathit{C}H_2CH_2Si$), 23.2 ($S\mathit{C}H_2CH_2NMe_3^+$), 26.4 ($SiCH_2\mathit{C}H_2S$), 32.7 ($OCH_2\mathit{C}H_2CH_2CH_2Si$), 51.7 (-$N\mathit{Me}_3^+$), 59.7 ($HO\mathit{C}H_2$), 63.9 ($\mathit{C}H_2NMe_3^+$), 69.3 ($O\mathit{C}H_2CH_2CH_2CH_2Si$), 71.4 ($HOCH_2\mathit{C}H_2$). ^{15}N-NMR (DMSO-d_6): δ -329.4 (-$\mathit{N}Me_3^+$). ^{29}Si-NMR (DMSO-d_6): δ 1.7 (G_1–SiMe), 1.1 (G_2–SiMe), 2.5 (G_3–SiMe). ESI: q=2 (1305.30 $[M-2I]^{2+}$), q=3 (827.26 $[M-3I]^{3+}$), q=4 (588.73 $[M-4I]^{4+}$). Anal. Calcd. $C_{87}H_{206}I_8N_8O_2S_8Si_7$ (2864.97 g/mol): C, 36.47; H, 7.25; N, 3.91; Exp.: C, 35.68; H, 7.27; N, 3.91.

S.2 Tables

	S. Aureus		*E. coli*	
	MIC	MBC	MIC	MBC
$[G_0Si(Si\text{-}NMe_3)_4]^{4+}$ (**7Si**)	3	12	12	12
$G_1Si(Si\text{-}NMe_3)_8]^{8+}$ (**8Si**)	11	21	43	85
$G_2Si(Si\text{-}NMe_3)_{16}]^{16+}$ (**9Si**)	20	20	162	162
$[G_0Si(S\text{-}NMe_3)_4]^{4+}$ (**7S**)	455	1821	910	1821
$[G_1Si(S\text{-}NMe_3)_8]^{8+}$ (**8S**)	50	400	50	200
$[G_2Si(S\text{-}NMe_3)_{16}]^{16+}$ (**9S**)	94	94	94	94
$[G_0Si(S\text{-}NH_3)_4]^{4+}$ (**10S**)	792	1583	792	1583
$[G_1Si(S\text{-}NH_3)_8]^{8+}$ (**11S**)	11	21	21	21
$[G_2Si(S\text{-}NH_3)_{16}]^{16+}$ (**12S**)	2482	2482	2482	2482

Table S1. Bacteriostatic (MIC) and bactericide (MBC) concentrations of dendrimers with a Si atom core. Data are in $[NR_3^+]$, which refers to the μM concentration of ammonium groups for each compound.

	S. Aureus		*E. coli*	
	MIC	MBC	MIC	MBC
$[G_1O_3(Si\text{-}NMe_3)_6]^{6+}$ (**34Si**)	6	6	45	90
$[G_2O_3(Si\text{-}$	10	10	158	158

$NMe_3)_{12}]^{12+}$ (**35Si**)				
$[G_3O_3(Si\text{-}NMe_3)_{24}]^{24+}$ (**36Si**)	39	39	156	156
$[G_1O_3(S\text{-}NMe_3)_6]^{6+}$ (**34S**)	6	6	6	12
$[G_2O_3(S\text{-}NMe_3)_{12}]^{12+}$ (**35S**)	6	6	23	23
$[G_3O_3(S\text{-}NMe_3)_{24}]^{24+}$ (**36S**)	22	22	45	45

Table S2. Bacteriostatic (MIC) and bactericide (MBC) concentrations of dendrimers with a polyphenoxo core 1,3,5-$(O)_3C_6H_3$. Data are in $[NR_3^+]$, which refers to the μM concentration of ammonium groups for each compound.

	S. Aureus		*E. coli*	
	MIC	MBC	MIC	MBC
$[N_3G_2(S\text{-}NMe_3)_4]^{4+}$ (**23S**)	23	23	23	23
$[(HOC_6H_4O)G_1(S\text{-}NMe_3)_2]^{2+}$ (**25S**)	85	169	85	169
$[(HOC_6H_4O)G_2(S\text{-}NMe_3)_4]^{4+}$ (**26S**)	5	11	11	11
$[(HOC_6H_4O)G_3(S\text{-}NMe_3)_8]^{8+}$ (**27S**)	44	44	176	176
$[(HOC_2H_4O)G_2(S\text{-}NMe_3)_4]^{4+}$ (**29S**)	11	11	11	22
$[(NH_2)G_2(S\text{-}NMe_3)_4]^{4+}$ (**32S**)	21	21	21	21

Table S3. Bacteriostatic (MIC) and bactericide (MBC) concentrations of dendrons. Data are in $[NR_3^+]$, which refers to the μM concentration of ammonium groups for each compound.

	ppm	μM $[NR_3^+]$
$G_0Si(Si\text{-}NMe_3^+)_4$ (**7Si**)	24	71
$G_1Si(S\text{-}NMe_3^+)_8$ (**8S**)	1074*	3353*
$G_1O_3(Si\text{-}NMe_3^+)_6$ (**34Si**)	2	6
$G_1O_3(S\text{-}NMe_3^+)_6$ (**34S**)	487	1415
$G_2O_3(S\text{-}NMe_3^+)_{12}$ (**35S**)	2	6
$G_1O_3(S\text{-}NH_3^+)_6$ (**37S**)	3	13
$G_2O_3(S\text{-}NH_3^+)_{12}$ (**38S**)	0.4	2

Table S4. HC_{20} of dendrimers in ppm (mg L^{-1}) and μM $[NR_3^+]$. HC_{20} is the concentration corresponding with 20 % hemolysis. $[NR_3^+]$ refers to concentration of ammonium groups for each compound.

	ppm	μM $[NR_3^+]$
$N_3G_2(S\text{-}NMe_3^+)_4$ (**23S**)	4	10
$HOC_6H_4OG_2(S\text{-}NMe_3^+)_4$ (**26S**)	184	499
$HOC_2H_4OG_2(S\text{-}NMe_3^+)_4$ (**29S**)	18	50
$NH_2G_2(S\text{-}NMe_3^+)_4$ (**32S**)	84	278

Table S5. HC_{20} of dendrons in ppm (mg L^{-1}) and μM $[NR_3^+]$. HC_{20} is the concentration corresponding with 20 % hemolysis. $[NR_3^+]$ refers to concentration of ammonium groups for each compound.

	IC_{50} HeLa cells	p-values
$G_0Si(S\text{-}NMe_3^+)_4$ (**7S**)	> 512	0.037654
$G_1Si(S\text{-}NMe_3^+)_8$ (**8S**)	390.2 ± 52.3	0.000011
$G_2Si(S\text{-}NMe_3^+)_{16}$ (**9S**)	15.9 ± 2.9	-
$G_0Si(Si\text{-}NMe_3^+)_4$ (**7Si**)	16.0 ± 2.8	0.001782
$G_1Si(Si\text{-}NMe_3^+)_8$ (**8Si**)	21.1 ± 1.0	
$G_2Si(Si\text{-}NMe_3^+)_{16}$ (**9Si**)	29.2 ± 0.4	-
$G_1O_3(S\text{-}NMe_3^+)_6$ (**34S**)	69.5 ± 7.1	0.000220
$G_2O_3(S\text{-}NMe_3^+)_{12}$ (**35S**)	26.9 ± 4.2	0.021894
$G_3O_3(S\text{-}NMe_3^+)_{24}$ (**36S**)	31.2 ± 3.8	0.159372
$G_1O_3(Si\text{-}NMe_3^+)_6$ (**34Si**)	24.3 ± 0.4	
$G_2O_3(Si\text{-}NMe_3^+)_{12}$ (**35Si**)	24.0 ± 3.3	-
$G_3O_3(Si\text{-}NMe_3^+)_{24}$ (**36Si**)	33.9 ± 1.6	-
$G_1O_3(S\text{-}NH_3^+)_6$ (**37S**)	6.2 ± 0.8	0.000078
$G_2O_3(S\text{-}NH_3^+)_{12}$ (**38S**)	8.5 ± 1.1	-
$G_3O_3(S\text{-}NH_3^+)_{24}$ (**39S**)	10.4 ± 0.7	-

Table S6. IC_{50} values on HeLa cells after 24 h of incubation (statistical analysis, t student by groups; $p < 0.05$). Cytotoxicity was evaluated using the microculture tetrazolium assay (MTT). Concentrations expressed in milligrams per liter (ppm).[8]

S.3 Hemolytic Figures

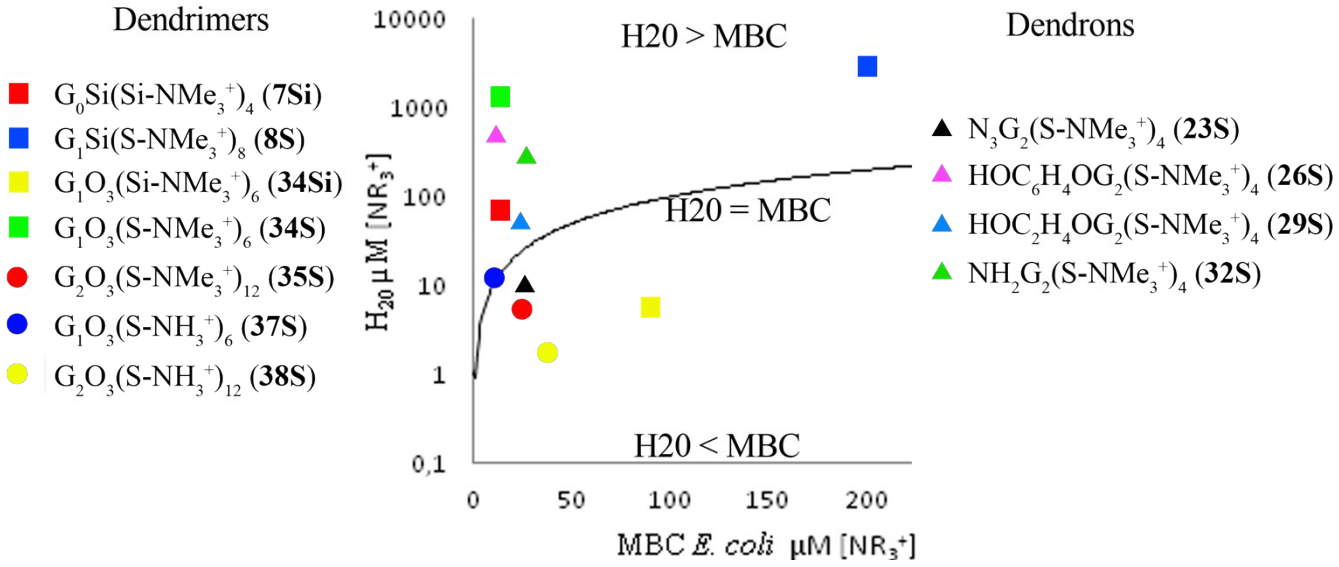

Figure S1. H_{20} vs MBC for selected compounds in *E. coli*. H_{20} refers to the concentration corresponding with 20 % hemolysis. $[NR_3^+]$ refers to the µM concentration of ammonium groups for each compound. The line represents equal values of toxicity (H_{20}) and activity (MBC).

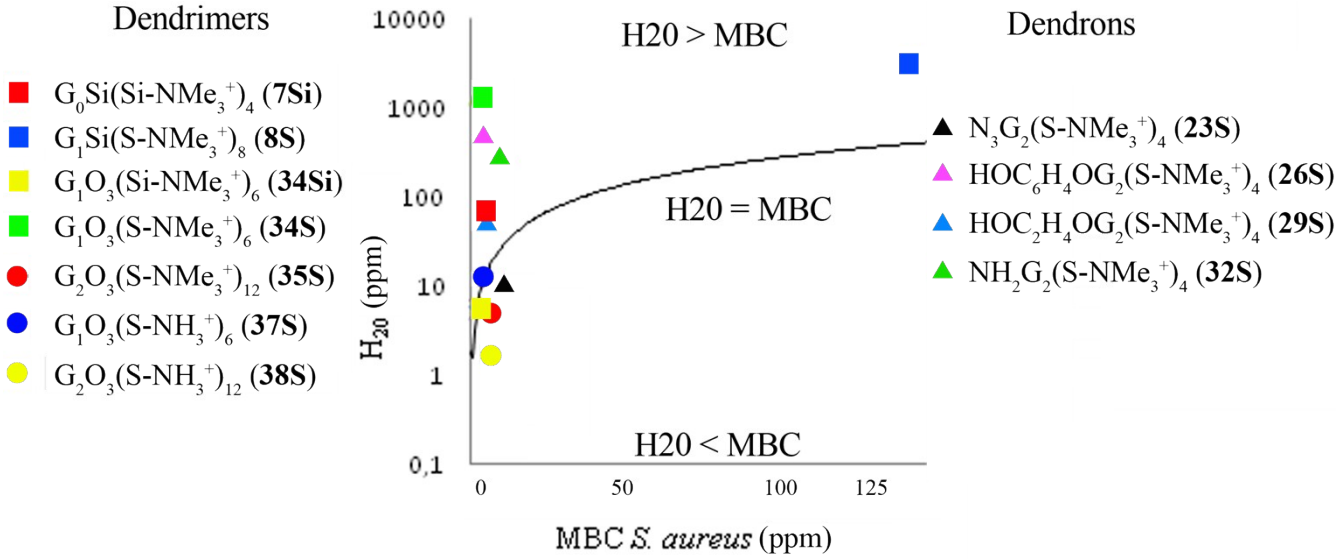

Figure S2. H_{20} vs MBC for selected compounds in *S. aureus*. H_{20} refers to the concentration corresponding with 20 % hemolysis. Data are in ppm. The line represents equal values of toxicity (H_{20}) and activity (MBC).

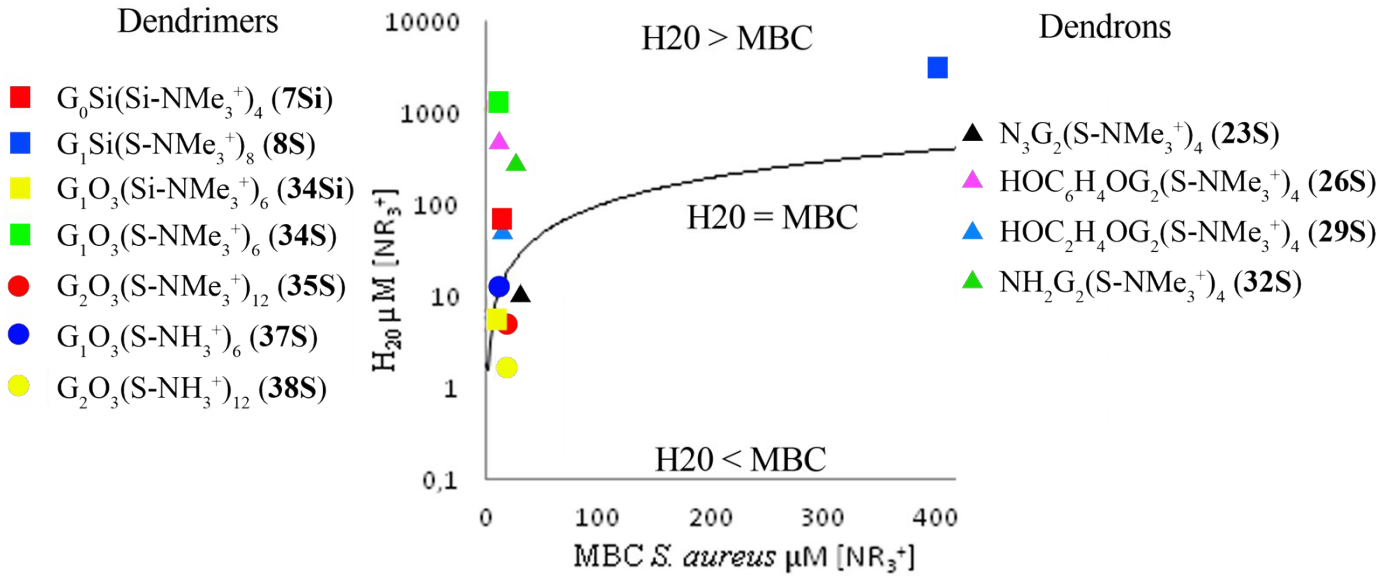

Figure S3. H_{20} vs MBC for selected compounds in *S. aureus*. H_{20} refers to the concentration corresponding with 20 % hemolysis. $[NR_3^+]$ refers to the µM concentration of ammonium groups for each compound. The line represents equal values of toxicity (H_{20}) and activity (MBC).

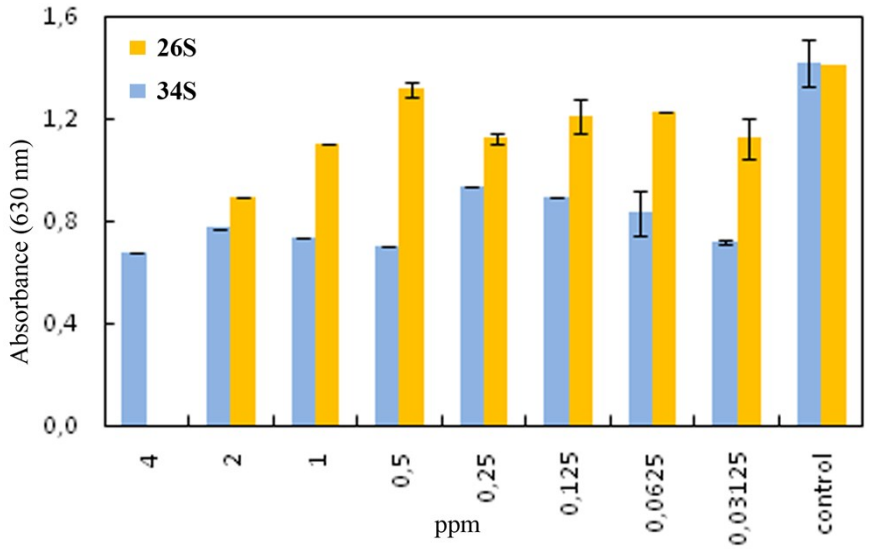

Figure S4. Absorbance at 630 nm corresponding to the crystal violet-stained biofilm in the pre-biofilm; assay at different concentrations of dendrimer (**34S**) and dendron (**26S**). Control: wells in the microtiter plates without dendritic compounds.

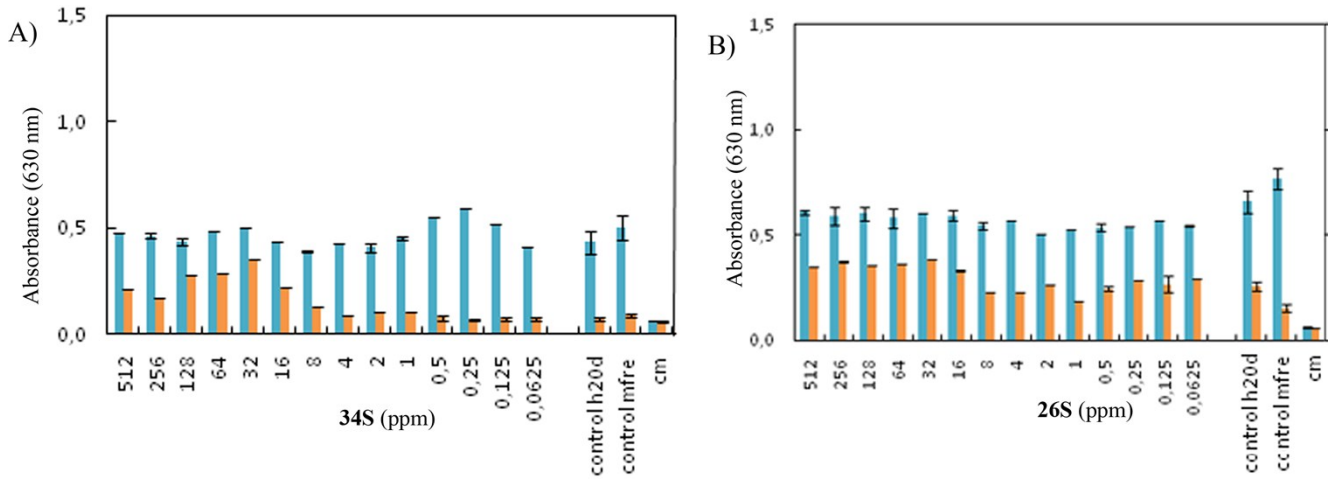

Figure S5. Post-biofilm effect of dendrimer **34S** (A) and dendron **26S** (B) in *S. aureus* biofilm. Control 1 and 2: wells where distilled water of fresh TSB medium has been added instead dendritic molecules; cm: wells only with culture medium.

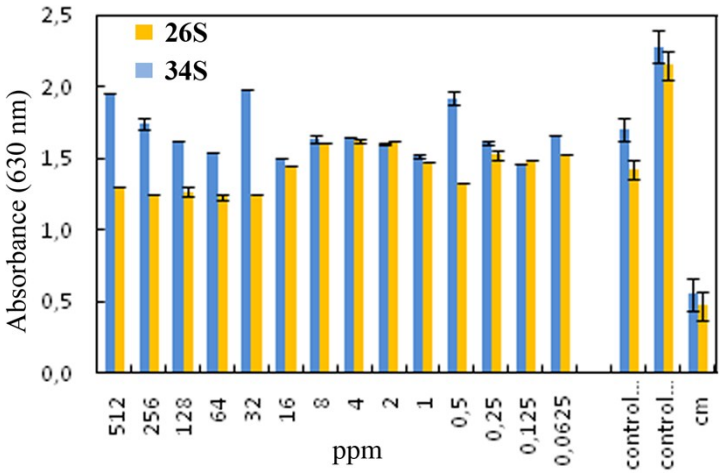

Figure S6. Absorbance at 630 nm corresponding to the crystal violet-stained biofilm in the post-biofilm assay at different concentrations of dendrimer (**34S**) and dendron (**26S**). Control 1 and 2: wells where distilled water of fresh TSB medium has been added instead dendritic molecules; cm: wells only with culture medium.

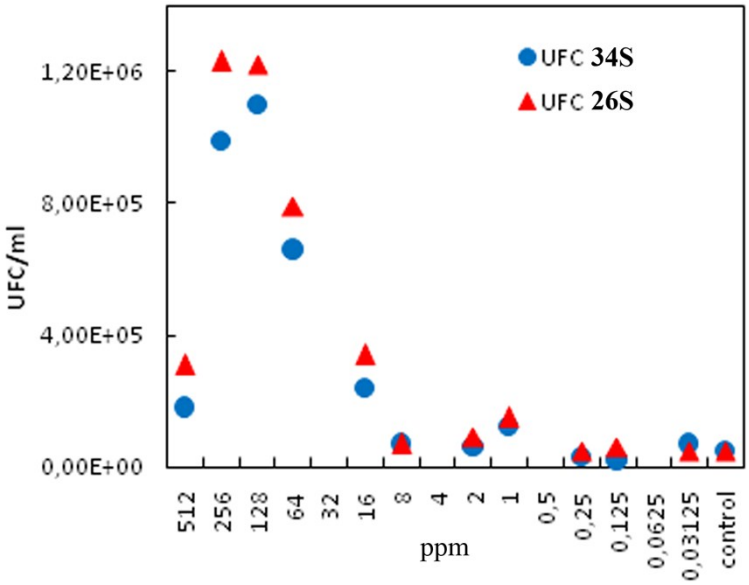

Figure S7. CFU counted in the wells at the end of the post-biofilm assay. Control: wells in the microtiter plates without dendritic compounds.

S.4 Selected NMR spectra

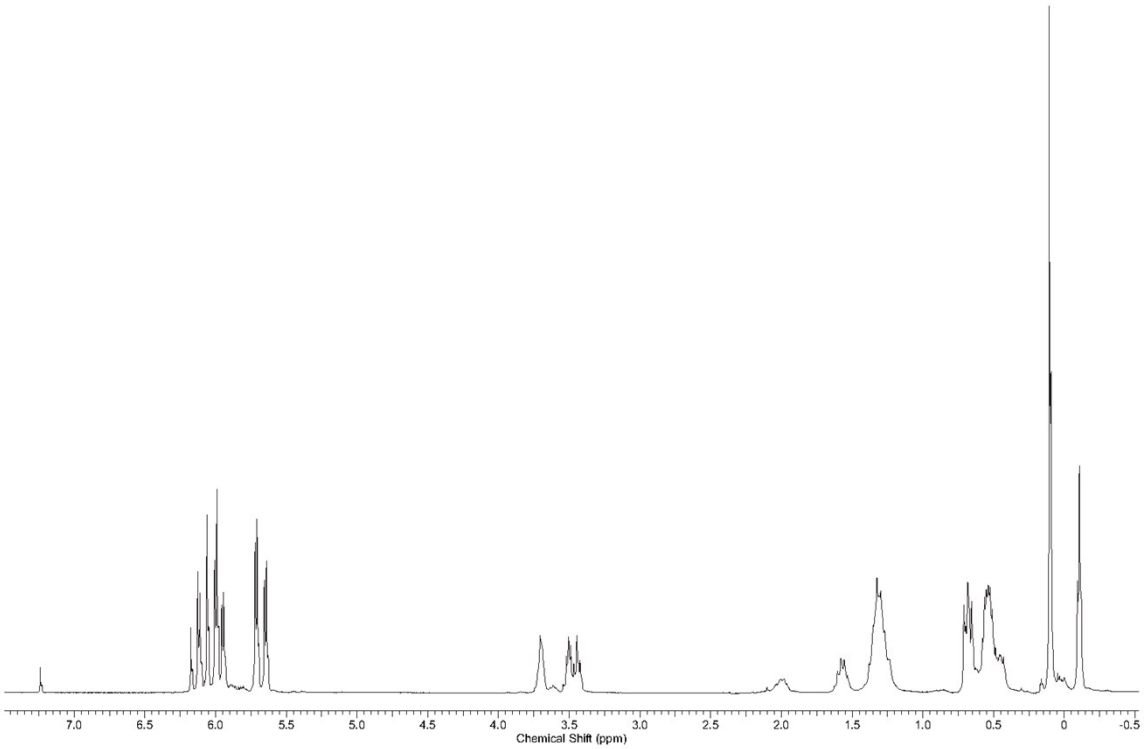

Figure S8. ^{1}H-NMR ($CDCl_3$) spectra of compound $HOC_2H_4OG_2V_4$.

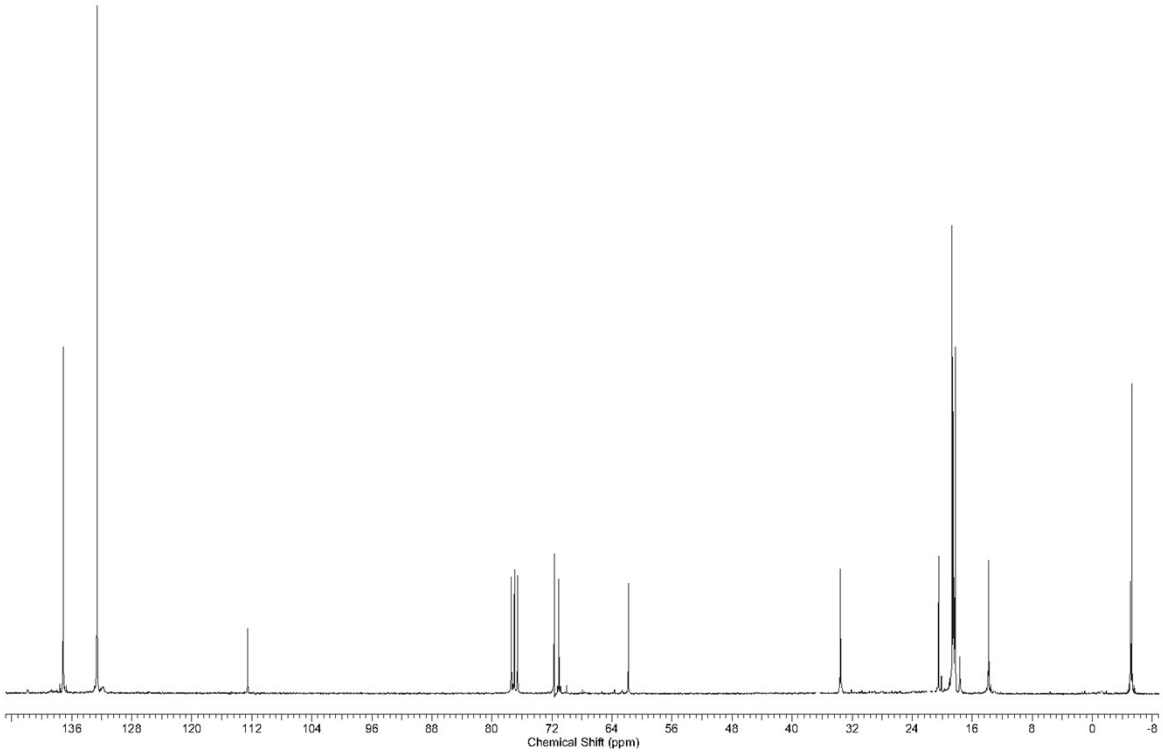

Figure S9. ^{13}C-NMR ($CDCl_3$) spectra of compound $HOC_2H_4OG_2V_4$.

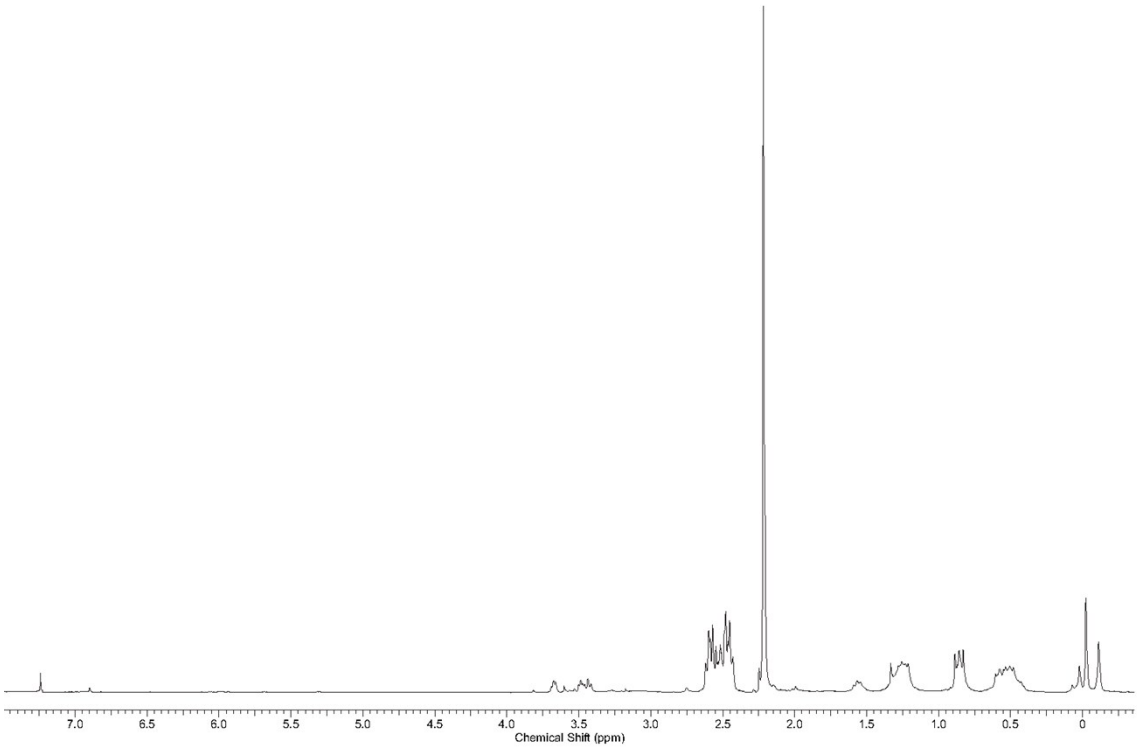

Figure S10. ^{1}H-NMR ($CDCl_3$) spectra of compound $HOC_2H_4OG_2(S\text{-}NMe_2)_4$ (**20S**).

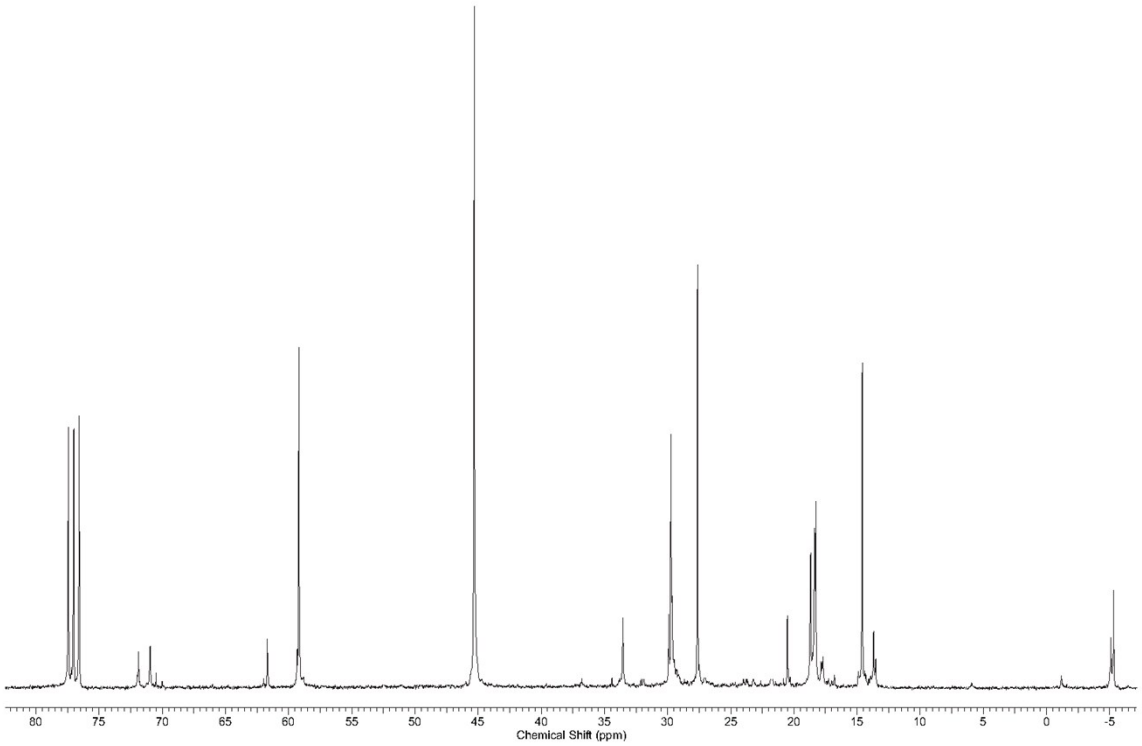

Figure S11. ^{13}C-NMR ($CDCl_3$) spectra of compound $HOC_2H_4OG_2(S\text{-}NMe_2)_4$ (**20S**).

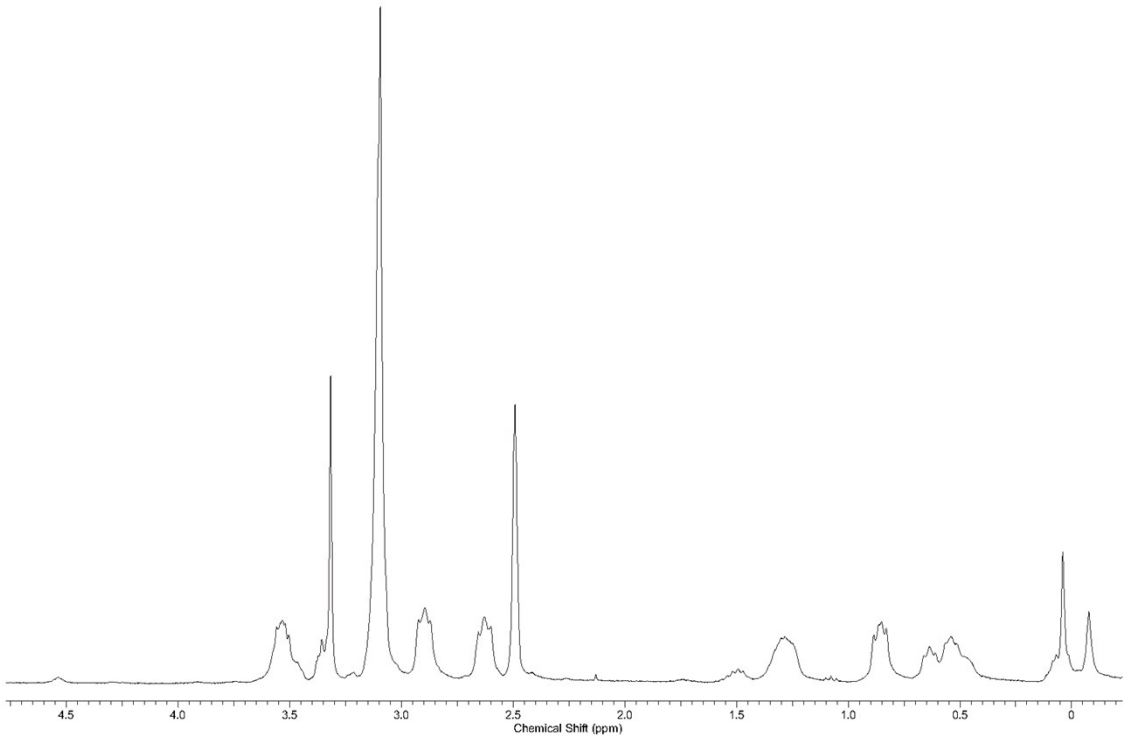

Figure S12. ^{1}H-NMR (DMSO-d_6) spectra of compound $HOC_2H_4OG_2(S\text{-}NMe_3I)_4$ (**29S**).

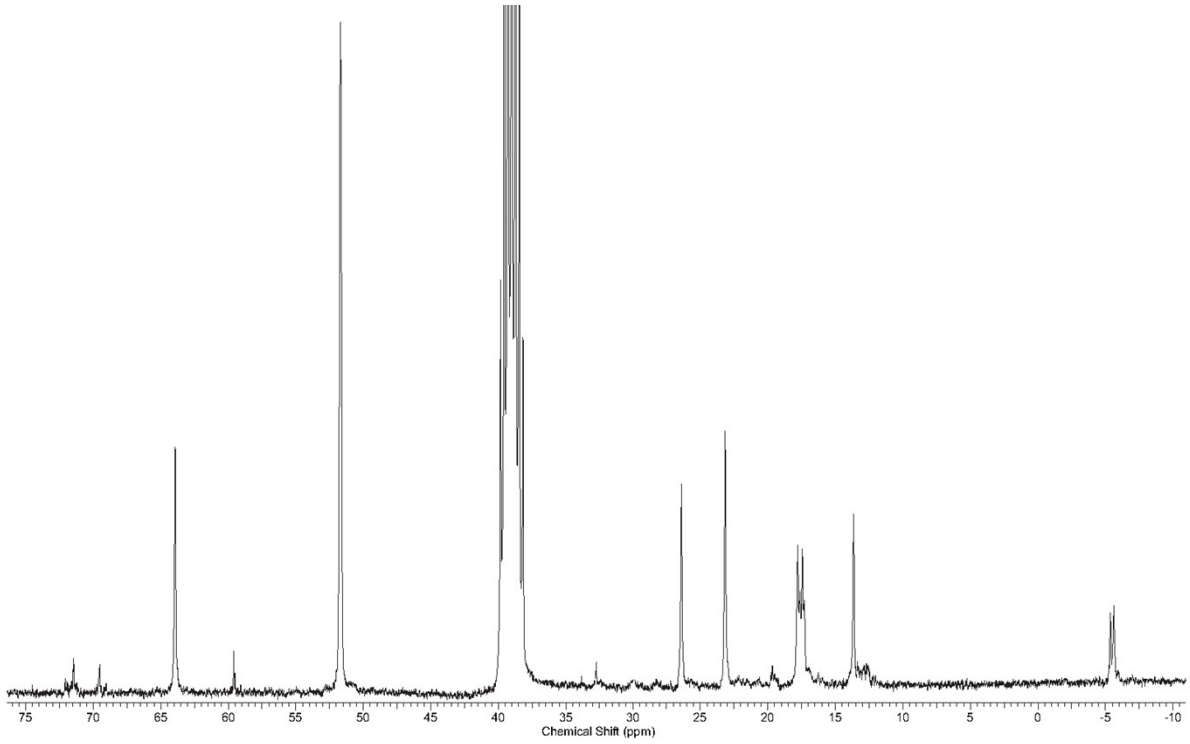

Figure S13. ^{13}C-NMR (DMSO-d_6) spectra of compound $HOC_2H_4OG_2(S\text{-}NMe_3I)_4$ (**29S**).

S.5. References

1. T. Strašák, J. Čermák, J. Sýkora, J. Horský, Z. Walterová, F. Jaroschik and D. Harakat, *Organometallics*, 2012, **31**, 6779-6786.
2. P. Ortega, M. Cobaleda, J. M. Hernández-Ros, E. Fuentes-Paniagua, J. Sánchez-Nieves, M. P. Tarazona, J. L. Copa-Patiño, J. Soliveri, F. J. de la Mata and R. Gómez, *Org. Biomol. Chem.*, 2011, **9**, 5238-5248.
3. E. Pedziwiatr-Werbicka, E. Fuentes-Paniagua, V. Dzmitruk, J. Sánchez-Nieves, M. Sudas, E. Drozd, A. Shakhbazau, D. Shcharbin, F. J. de la Mata, R. Gómez-Ramírez, M. Á. Muñoz-Fernández and M. Bryszewska, *Colloids Surf. B: Biointerfaces*, 2013, **109**, 183– 189.
4. E. Fuentes-Paniagua, J. M. Hernández-Ros, M. Sánchez-Milla, M. A. Camero, M. Maly, J. Pérez-Serrano, J. L. Copa-Patiño, J. Sánchez-Nieves, J. Soliveri, R. Gómez and F. J. de la Mata, *RSC Adv.*, 2014, **4**, 1256–1265.
5. E. Fuentes-Paniagua, C. E. Peña-González, M. Galán, R. Gómez, F. J. de la Mata and J. Sánchez-Nieves, *Organometallics*, 2013, **32**, 1789−1796.
6. Á. Martínez, E. Fuentes-Paniagua, A. Baeza, J. Sánchez-Nieves, R. Gómez, F. J. de la Mata, B. González and M. Vallet-Regí, *Chem. Eur. J.*, 2015, **21**, 15651-15666.
7. C. Rissing and D. Y. Son, *Organometallics*, 2008, **27**, 5394-5397.
8. I. Heredero-Bermejo, J. L. Copa-Patiño, J. Soliveri, E. Fuentes-Paniagua, F. J. de la Mata, R. Gómez and J. Pérez-Serrano, *Parasitol. Res.*, 2015, **114**, 473-486.