For Supporting Information:

Gold Nanoparticles Stabilized by Cationic Carbosilane Dendrons: Synthesis, Characterization and Biological Properties

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S1. Experimental Section

S1.1. General Considerations. All reactions were carried out under inert atmosphere and solvents were purified with MBraun SPS purification system. Thiol-ene reactions were carried out employing a HPK 125W Mercury Lamp from Heraeus Noblelight with maximum energy at 365 nm, in normal glassware under inert atmosphere. 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 (^{1}H), 100.60 (^{13}C), 79.49 (^{29}Si) MHz). Chemical shifts (δ) are given in ppm. ^{1}H and ^{13}C resonances were measured relative to solvent peaks considering TMS = 0 ppm, meanwhile ^{15}N and ^{29}Si resonances were measured relative to external NH_3(l) and TMS, respectively. When necessary, assignment of resonances was done from HSQC, HMBC, COSY and TOCSY NMR experiments. Elemental analyses were performed on a LECO CHNS-932. Mass Spectra were obtained from an Agilent 6210 TOF LC/MS for ESI-TOF in MeOH/H_2O with (NH_4)(HCO_2), and an AB Sciex QSTAR for ESI-POS in H_2O/MeOH. The UV-visible absorption measurements were performed using a Perkin-Elmer Lambda 18 spectrophotometer. The spectra were recorded by measuring dilute samples in a quartz cell with a path length of 1 cm. Compounds $NaHCO_3$, MeI, Amberlite@ IRA-Cl, HCl (MeOH solution), $NaAuCl_4$, and $NaBH_4$ were obtained from commercial sources. Compounds $MeCOSG_n(S\text{-}NMe_2{\cdot}HCl)_m$ and $HSG_n(S\text{-}NMe_2{\cdot}HCl)_m$ were synthesized as published.[1]

S1.2. Synthesis of compounds.

$MeCOSG_1(S\text{-}NMe_2)_2$ (1). To a THF solution (ca. 5 mL) of $MeCOSG_1(S\text{-}NMe_2{\cdot}HCl)_2$ (0.957 g, 1.87 mmol) was added $NaHCO_3$ (0.628 g, 7.48 mmol) and the mixture was stirred at 25ºC during 12 hours. Afterwards, volatiles were removed under vacuum and the residue was dissolved in Et_2O. Subsequently brine was added, the organic phase was separate and the aqueous phase was extracted twice with Et_2O. The organic phase was washed with brine and dried over $MgSO_4$. The solution was filtered through celite and the volatiles were removed under vacuum, yielding **1** as orange oil (0.706 g, 86 %).

Data for **1**: NMR ($CDCl_3$): ^{1}H NMR: δ -0.00 (s, 3 H, SiC*H*$_3$), 0.53 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 0.87 (m, 4 H, $SiCH_2CH_2S$), 1.34 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 1.56 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.27 (s, 12 H, NC*H*$_3$), 2.29 (s, 3 H, C*H*$_3$COS), 2.49 (m, 8 H, $SiCH_2CH_2S$, SCH_2CH_2N), 2.52 (m, 4 H, SCH_2CH_2N), 2.83 (t, J = 7.3 Hz, 2 H, MeCOSC*H*$_2$); ^{13}C NMR{^{1}H}: δ -5.4 (Si*C*H$_3$), 13.1

($SCH_2CH_2CH_2\mathit{C}H_2Si$), 14.5 ($Si\mathit{C}H_2CH_2S$), 22.9 ($SCH_2CH_2\mathit{C}H_2CH_2Si$), 27.7 ($S\mathit{C}H_2CH_2N$), 28.6 ($MeCOS\mathit{C}H_2$), 29.6 ($SiCH_2\mathit{C}H_2S$), 30.7 ($\mathit{C}H_3COS$), 33.1 ($SCH_2\mathit{C}H_2CH_2CH_2Si$), 45.2 ($N\mathit{C}H_2$), 59.1 ($SCH_2\mathit{C}H_2N$), 195.9 ($CH_3\mathit{C}OS$); ^{15}N NMR: δ 27.8; ^{29}Si NMR: δ 2.8 ($\mathit{Si}CH_3$). MS: $[M + H]^+$: 439.23. Anal. Calcd.: $C_{19}H_{42}N_2OS_3Si$ (438.83): Calcd.: C, 52.00; H, 9.65; N, 6.38; S, 21.92; Obt.: C, 49.73; H, 9.13; N, 6.99; S, 21.03.

MeCOS)G_2(S-NMe_2)$_4$ (2). Following the procedure described for compound **1**, compound **2** was obtained as orange oil (1.473 g, 98 %) from the reaction of $MeCOSG_2(S\text{-}NMe_2\cdot HCl)_4$ (1.762 g, 1.13 mmol) with $NaHCO_3$ (1.161 g, 13.82 mmol). Data for **2**: NMR ($CDCl_3$): ^1H NMR: δ -0.01 (s, 3 H, $SiC\mathit{H}_3$), -0.003 (s, 6 H, $SiC\mathit{H}_3$), 0.55 (m, 10 H, $SCH_2CH_2CH_2C\mathit{H}_2Si$, $SiC\mathit{H}_2CH_2C\mathit{H}_2Si$), 0.87 (m, 8 H, $SiC\mathit{H}_2CH_2S$), 1.31 (m, 6 H, $SCH_2CH_2C\mathit{H}_2CH_2Si$, $SiCH_2C\mathit{H}_2CH_2Si$), 1.56 (m, 2 H, $SCH_2C\mathit{H}_2CH_2CH_2Si$), 2.23 (s, 24 H, $NC\mathit{H}_3$), 2.30 (s, 3 H, $C\mathit{H}_3COS$), 2.57 (m, 24 H, $SiCH_2C\mathit{H}_2S$, $SC\mathit{H}_2CH_2N$), 2.67 (m, 4 H, $SCH_2C\mathit{H}_2N$), 2.80 (t, J = 7.3 Hz, 2 H, $SC\mathit{H}_2CH_2CH_2CH_2Si$); ^{13}C NMR{^1H}: δ -5.4 (1 $Si\mathit{C}H_3$), -5.2 (2 $Si\mathit{C}H_3$), 13.3 ($SCH_2CH_2CH_2\mathit{C}H_2Si$), 14.5 ($Si\mathit{C}H_2CH_2S$), 18.2, 18.3, 18.5 ($Si\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2Si$), 22.6 ($SCH_2CH_2\mathit{C}H_2CH_2Si$), 27.1 ($S\mathit{C}H_2CH_2N$), 28.2 ($S\mathit{C}H_2CH_2CH_2CH_2Si$), 29.2 ($SiCH_2\mathit{C}H_2S$), 30.1 ($\mathit{C}H_3COS$), 32.6 ($SCH_2\mathit{C}H_2CH_2CH_2Si$), 44.8 ($N\mathit{C}H_3$), 58.7 ($SCH_2\mathit{C}H_2N$), 195.4 ($CH_3\mathit{C}OS$); ^{29}Si NMR: δ 1.7 (1 $\mathit{Si}CH_3$), 2.0 (2 $\mathit{Si}CH_3$); ^{15}N NMR: δ 27.4. MS: $[M + H]^+$: 873.50. Anal. Calcd.: $C_{39}H_{88}N_4OS_5Si_3$ (873.72): Calcd.: C, 53.61; H, 10.15; N, 6.41; S, 18.35; Obt.: C, 53.69; H, 10.20; N, 6.49; S, 18.40.

(MeCOS)G_3(S-NMe_2)$_8$ (3). Following the procedure described for compound **1**, compound **3** was obtained as orange oil (0.920 g, 94 %) from the reaction of $MeCOSG_3(S\text{-}NMe_2\cdot HCl)_8$ (1.139 g, 0.56 mmol) with $NaHCO_3$ (0.752 g, 8.96 mmol). Data for 3: NMR ($CDCl_3$): ^1H NMR: δ 0.10 (s, 9 H, $SiC\mathit{H}_3$), 0.01 (m, 12 H, $SCH_2CH_2CH_2C\mathit{H}_2Si$), 0.52 (m, 26 H, $SCH_2CH_2CH_2C\mathit{H}_2Si$, $SiC\mathit{H}_2CH_2C\mathit{H}_2Si$), 0.88 (m, 16 H, $SiC\mathit{H}_2CH_2S$), 1.27 (m, 14 H, $SCH_2CH_2C\mathit{H}_2CH_2Si$, $SiCH_2C\mathit{H}_2CH_2Si$), 1.55 (m, 2 H, $SCH_2C\mathit{H}_2CH_2CH_2Si$), 2.25 (s, 48 H, $NC\mathit{H}_3$), 2.30 (s, 3 H, $C\mathit{H}_3COS$), 2.56 (m, 48 H, $SiCH_2C\mathit{H}_2S$, $SC\mathit{H}_2C\mathit{H}_2N$), 2.85 (t, J = 7.3 Hz, 2 H, $SC\mathit{H}_2CH_2CH_2CH_2Si$); ^{13}C NMR{^1H}: δ -5.3 (3 $Si\mathit{C}H_3$), -5.0 (4 $Si\mathit{C}H_3$), 12.2 ($SCH_2CH_2CH_2\mathit{C}H_2Si$), 14.7 ($Si\mathit{C}H_2CH_2S$), 18.4, 18.5, 18.9 ($Si\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2Si$), 23.3 ($SCH_2CH_2\mathit{C}H_2CH_2Si$), 26.9 ($S\mathit{C}H_2CH_2N$), 28.8 ($S\mathit{C}H_2CH_2CH_2CH_2Si$), 29.8 ($SiCH_2\mathit{C}H_2S$), 30.4 ($\mathit{C}H_3COS$), 33.3 ($SCH_2\mathit{C}H_2CH_2CH_2Si$), 45.4 ($N\mathit{C}H_3$), 59.2 ($SCH_2\mathit{C}H_2N$), not observed ($CH_3\mathit{C}OS$); ^{29}Si

NMR: δ 1.8 (3 *Si*CH_3), 2.2 (4 *Si*CH_3); ^{15}N NMR: δ 27.6. MS: $[M + H]^+$: 1743.9. Anal. Calcd.: $C_{79}H_{180}N_8OS_9Si_7$ (1743.51): Calcd.: C, 54.42; H, 10.41; N, 6.43; S, 16.55; Obt.: C, 55.47; H, 10.69; N, 6.41; S, 15.87.

(MeCOS)G$_1$(S-NMe$_3$I)$_2$ (4I). To a THF solution (ca.10 mL) of **1** (1.659 g, 3.78 mmol) was added CH_3I (2.576 g, 18.15 mmol) and the mixture was stirred at 25ºC for 12 hours. Volatiles were removed under vacuum and the residue was purified by nanofiltration (MWCO = 500), yielding compound **4I** as orange solid (2.599 g, 95%).

Data for **4I**: NMR (D_2O): ^{1}H NMR: δ 0.02 (s, 3 H, SiC*H$_3$*), 0.56 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 0.89 (m, 4 H, $SiCH_2CH_2S$), 1.30 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 1.52 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.28 (s, 3 H, CH_3COS), 2.69 (m, 4 H, $SiCH_2CH_2S$), 2.81 (t, J = 7.1 Hz, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.95 (m, 4 H, SCH_2CH_2N), 3.13 (s, 18 H, NC*H$_3$*), 3.56 (m, 4 H, SCH_2CH_2N); ^{13}C NMR {^{1}H}: δ -4.9 (Si*C*H_3), 12.9 ($SCH_2CH_2CH_2CH_2Si$), 14.5 ($SiCH_2CH_2S$), 22.7 ($SCH_2CH_2CH_2CH_2Si$), 24.3 (SCH_2CH_2N), 27.8 ($SiCH_2CH_2S$), 28.8 ($SCH_2CH_2CH_2CH_2Si$), 30.9 (CH_3COS), 32.8 ($SCH_2CH_2CH_2CH_2Si$), 53.5 (N*C*H_3), 65.7 (SCH_2CH_2N), 198.5 (CH_3COS); ^{15}N NMR: δ 49.2; ^{29}Si NMR: δ 3.0 (*Si*CH_3). MS: $[M - I^-]^+$: 595.19, $[M - 2\ I^-]^+$: 234.14. Anal. Calcd.: $C_{21}H_{48}I_2N_2OS_3Si$ (722.71): Calcd.: C, 39.40; H, 6.69; N, 3.88; S, 13.31; Obt.: C, 38.93; H, 6.43; N, 3.78; S, 12.99.

(MeCOS)G$_2$(S-NMe$_3$I)$_4$ (5I). Following the procedure described for compound **4I**, compound **5I** was obtained as orange solid (1.705 g, 98 %) from the reaction of **2** (1.052 g, 1.21 mmol) with CH_3I (1.642 g, 11.57 mmol). Data for **5I**: NMR (D_2O): ^{1}H NMR: δ -0.06 (s, 3 H, SiC*H$_3$*) 0.18 (s, 6 H, SiC*H$_3$*), 0.49 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 0.64 (m, 8 H, $SiCH_2CH_2CH_2Si$) 1.01 (m, 8 H, $SiCH_2CH_2S$), 1.36 (m, 6 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 1.55 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.33 (s, 3 H, CH_3COS), 2.82 (m, 10 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2S$), 3.07 (m, 8 H, SCH_2CH_2N), 3.27 (s, 36 H, NC*H$_3$*), 3.74 (m, 8 H, SCH_2CH_2N); ^{13}C NMR {^{1}H}: δ -4.2 (1 Si*C*H_3), -4.0 (2 Si*C*H_3), 13.8 ($SCH_2CH_2CH_2CH_2Si$), 15.1 ($SiCH_2CH_2S$), 18.6, 18.8 ($SiCH_2CH_2CH_2Si$), 23.3 ($SCH_2CH_2CH_2CH_2Si$), 24.7 (SCH_2CH_2N), 28.2 ($SiCH_2CH_2S$), 30.1 ($SCH_2CH_2CH_2CH_2Si$), 31.3 (CH_3COS), 33.3 ($SCH_2CH_2CH_2CH_2Si$), 53.8 (N*C*H_3), 65.8 (SCH_2CH_2N), 195.7 (CH_3COS); ^{15}N NMR: δ 50.9; ^{29}Si NMR: δ 1.7 (1 *Si*CH_3)., 2.6 (2 *Si*CH_3). MS:

$[M - 2\ I^-]^{2+}$: 593.20, $[M - 3\ I^-]^{3+}$: 356.16, $[M - 4\ I^-]^{4+}$: 233.15. Anal. Calcd.: $C_{43}H_{100}I_4N_4OS_5Si_3$ (1441.48): Calcd.: C, 35.83; H, 6.99; N, 3.89; S, 11.12; Obt.: C, 35.93; H, 7.05; N, 3.86; S, 11.03.

(MeCOS)G$_3$(S-NMe$_3$I)$_8$ (6I). Following the procedure described for compound **4I**, compound **6I** was obtained as orange solid (1.397 g, 96 %) from the reaction of **3** (0.878 g, 0.51 mmol) with CH_3I (1.372 g, 9.67 mmol). Data for **6I**: NMR (D_2O): ^{1}H NMR: δ - 0.07 (s, 9 H, SiC*H$_3$*), 0.15 (s, 12 H, SiC*H$_3$*), 0.55 (m, 26 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 0.97 (m, 16 H, $SiCH_2CH_2S$), 1.32 (m, 14 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 1.50 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.28 (s, br, 3 H, CH_3COS), 2.79 (m, 18 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2S$), 3.05 (m, 16 H, SCH_2CH_2N), 3.23 (s, 72 H, NCH_3), 3.71 (m, 16 H, SCH_2CH_2N); ^{13}C NMR {^{1}H}: -4.4 (3 $SiCH_3$), -4.1 (4 $SiCH_3$), 13.7 ($SCH_2CH_2CH_2CH_2Si$), 15.0 ($SiCH_2CH_2S$), 18.6, 18.8 ($SiCH_2CH_2CH_2Si$), 23.3 ($SCH_2CH_2CH_2CH_2Si$), 24.7 (SCH_2CH_2N), 28.1 ($SiCH_2CH_2S$), 28.8 ($SCH_2CH_2CH_2CH_2Si$), 31.5 (CH_3COS), 33.3 ($SCH_2CH_2CH_2CH_2Si$), 53.7 (NCH_3), 65.8 (SCH_2CH_2N); ^{15}N NMR: δ 51.2; ^{29}Si NMR: δ 1.8 (3 *Si*CH_3), 2.8 (4 *Si*CH_3). MS: $[M - 2\ I^-]^{2+}$: 1311.28, $[M - 3\ I^-]^{3+}$: 831.93, $[M - 4\ I^-]^{4+}$: 592.74, $[M - 5\ I^-]^{5+}$: 448.81. Anal. Calcd.: $C_{87}H_{204}I_8N_8OS_9Si_7$ (2879.02): Calcd.: C, 36.29; H, 7.14; N, 3.89; S, 10.02; Obt.: C, 36.64; H, 6.88; N, 3.66; S, 9.90.

(MeCOS)G$_1$(S-NMe$_3$Cl)$_2$ (4Cl). To an aqueous solution of compound **4I** (1.325 g, 1.83 mmol) was added Amberlite IRA-402, Cl-form ion-exchange resin (6.625 g) and the mixture was stirred for 12 hours. The solution was filtered and evaporated under vacuum affording **4Cl** as yellow solid (0.932 g, 94 %).

Data for **4Cl**: NMR (D_2O): ^{1}H NMR: δ - 0.05 (s, 3 H, SiC*H$_3$*), 0.56 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 0.84 (m, 4 H, $SiCH_2CH_2S$), 1.30 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 1.50 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.26 (s, 3 H, CH_3COS), 2.61 (m, 4 H, $SiCH_2CH_2S$), 2.85 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.90 (m, 4 H, SCH_2CH_2N), 3.02 (s, 18 H, NCH_3), 3.45 (m, 4 H, SCH_2CH_2N). MS: $[M - 2\ Cl^-]^{2+}$: 234.44, $[M - Cl^-]^+$: 503.22. Anal. Calcd.: $C_{21}H_{48}Cl_2N_2OS_3Si$ (539.79): Calcd.: C, 46.73; H, 8.96; N, 5.19; S, 17.82; Obt.: C, 46.58; H, 8.82; N, 5.05; S, 17.70.

(MeCOS)G$_2$(S-NMe$_3$Cl)$_4$ (5Cl). Following the procedure described for compound **4Cl**, compound **5Cl** was obtained as yellow solid (0.262 g, 98 %) from the reaction of **5I** (0.306 g, 0.25 mmol) with Amberlite IRA-402, Cl-form ion-exchange resin (g). Data for **5Cl**: ^{1}H NMR: δ -0.09 (s, 3 H, SiC*H$_3$*), 0.04 (s, 6 H, SiC*H$_3$*), 0.57 (m, 10 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$) 0.90 (m, 8 H, $SiCH_2CH_2S$), 1.34

(m, 6 H, $SCH_2CH_2C\mathit{H}_2CH_2Si$, $SiCH_2C\mathit{H}_2CH_2Si$), 1.55 (m, 2 H, $SCH_2C\mathit{H}_2CH_2CH_2Si$), 2.33 (s, 3 H, $C\mathit{H}_3COS$), 2.68 (m, 8 H, $SiCH_2C\mathit{H}_2S$), 2.86, (m, 2 H, $SC\mathit{H}_2CH_2CH_2CH_2Si$), 2.95 (m, 8 H, $SC\mathit{H}_2CH_2N$), 3.11 (s, 36 H, $NC\mathit{H}_3$), 3.52 (m, 8 H, $SCH_2C\mathit{H}_2N$).). MS: $[M - 4\ Cl^-]^{4+}$: 233.15, $[M - 3\ Cl^-]^{3+}$: 322.52, $[M - 2\ Cl^-]^{2+}$: 502.27, $[M - Cl^-]^{+}$: 1039.48. Anal. Calcd.: $C_{43}H_{100}Cl_4N_4OS_5Si_3$ (1075.67): Calcd.: C, 48.01; H, 9.37; N, 5.21; S, 14.90; Obt.: C, 47.89; H, 9.48; N, 5.41; S, 15.02.

$(MeCOS)G_3(S\text{-}NMe_3Cl)_8$ (6Cl). Following the procedure described for compound **4Cl**, compound **6Cl** was obtained as yellow solid (0.435 g, 99 %) from the reaction of **6I** (0.588 g, 0.20 mmol) with Amberlite IRA-402, Cl-form ion-exchange resin (g). Data for **6Cl**: ^{1}H NMR: δ -0.08 (s, 9 H, $SiC\mathit{H}_3$), 0.05 (s, 12 H, $SiC\mathit{H}_3$), 0.55 (m, 22 H, $SCH_2CH_2CH_2C\mathit{H}_2Si$, $SiC\mathit{H}_2CH_2C\mathit{H}_2Si$), 0.89 (m, 16 H, $SiC\mathit{H}_2CH_2S$), 1.31 (m, 16 H, $SCH_2CH_2C\mathit{H}_2CH_2Si$, $SiCH_2C\mathit{H}_2CH_2Si$), 1.57 (m, 2 H, $SCH_2C\mathit{H}_2CH_2CH_2Si$), 2.33 (s, br, 3 H, $C\mathit{H}_3COS$), 2.65 (m, 16 H, $SiCH_2C\mathit{H}_2S$), 2.93 (m, 18 H, $SC\mathit{H}_2CH_2CH_2CH_2Si$, $SC\mathit{H}_2CH_2N$), 3.07 (s, 72 H, $NC\mathit{H}_3$), 3.50 (m, 16 H, $SCH_2C\mathit{H}_2N$). MS: $[M - 6\ Cl^-]^{6+}$: 322.2, $[M - 5\ Cl^-]^{5+}$: 393.3, $[M - 4\ Cl^-]^{4+}$: 501.30, $[M - 3\ Cl^-]^{3+}$: 680.00, $[M - 2\ Cl^-]^{2+}$: 1037.50. Anal. Calcd.: $C_{87}H_{204}Cl_8N_8OS_9Si_7$ (2147.38): Calcd.: C, 48.66; H, 9.58; N, 5.22; S, 13.44; Obt.: C, 48.66; H, 9.22; N, 5.10; S, 12.44.

$HSG_1(S\text{-}NMe_3I)_2$ (7I). To a MeOH solution (ca. 10 mL) of **4I** (0.997 g, 1.38 mmol) was added HCl in ether (2 M, 3.9 mL, 7.74 mmol) and the mixture was stirred at 55°C overnight. Afterward, volatiles were removed under vacuum yielding **7I** as orange solid (0.824 g, 88 %).

Data for **7I**: ^{1}H NMR: δ -0.03 (s, 3 H, $SiC\mathit{H}_3$), 0.53 (m, 2 H, $SCH_2CH_2CH_2C\mathit{H}_2Si$), 0.86 (m, 4 H, $SiC\mathit{H}_2CH_2S$), 1.34 (m, 2 H, $SCH_2CH_2C\mathit{H}_2CH_2Si$), 1.53 (m, 2 H, $SCH_2C\mathit{H}_2CH_2CH_2Si$), 2.47 (m, 2 H, $MeCOSC\mathit{H}_2$) 2.62 (m, 4 H, $SiCH_2C\mathit{H}_2S$), 2.89 (m, 4 H, $SC\mathit{H}_2CH_2N$), 3.06 (s, 18 H, $NC\mathit{H}_3$), 3.46 (m, 4 H, $SCH_2C\mathit{H}_2N$); ^{13}C NMR {^{1}H}: δ -5.7 ($Si\mathit{C}H_3$), 12.4 ($SCH_2CH_2CH_2\mathit{C}H_2Si$), 14.0 ($Si\mathit{C}H_2CH_2S$), 21.9 ($MeCOS\mathit{C}H_2$), 23.5 ($SCH_2CH_2\mathit{C}H_2CH_2Si$), 23.8 ($S\mathit{C}H_2CH_2N$), 27.4 ($SiCH_2\mathit{C}H_2S$), 38.0 ($SCH_2\mathit{C}H_2CH_2CH_2Si$), 53.0 ($N\mathit{C}H_3$), 65.6 ($SCH_2\mathit{C}H_2N$); ^{15}N NMR: δ 48.2; ^{29}Si NMR: δ 2.86 ($\mathit{Si}CH_3$). MS: $[M - I^-]^{+}$: 553.16, $[M - 2\ I^-]^{2+}$: 213.13. Anal. Calcd.: $C_{19}H_{46}I_2N_2OS_3Si$ (680.67): Calcd.: C, 33.53; H, 6.81; N, 4.12; S, 14.13; Obt.: C, 33.46; H, 7.80; N, 4.11; S, 13.96.

$HSG_2(S\text{-}NMe_3I)_4$ (8I). Following the procedure described for compound **7I**, compound **8I** was obtained as orange solid (0.611 g, 90 %) from the reaction of **5I** (0.702 g, 0.05 mmol) with HCl in ether (2

M, 0.5 mL, 1.0 mmol). Data for **8I**: NMR (D_2O): ^{1}H NMR: δ - 0.06 (s, 3 H, SiC*H*$_3$) 0.16 (s, 6 H, SiC*H*$_3$), 0.47 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 0.62 (m, 8 H, $SiCH_2CH_2CH_2Si$) 0.98 (m, 8 H, $SiCH_2CH_2S$), 1.36 (m, 6 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 1.58 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.49 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.80 (m, 8 H, $SiCH_2CH_2S$), 3.05 (m, 8 H, SCH_2CH_2N), 3.23 (s, 36 H, NC*H*$_3$), 3.71 (m, 8 H, SCH_2CH_2N); ^{13}C NMR {^{1}H}: δ -4.4 (1 Si*C*H$_3$), -4.1 (2 Si*C*H$_3$), 13.6 ($SCH_2CH_2CH_2CH_2Si$), 14.8 ($SiCH_2CH_2S$), 18.5, 18.6 ($SiCH_2CH_2CH_2Si$), 22.7 ($SCH_2CH_2CH_2CH_2Si$), 24.2 ($SCH_2CH_2CH_2CH_2Si$), 24.4 (SCH_2CH_2N), 27.9 ($SiCH_2CH_2S$), 37.7 ($SCH_2CH_2CH_2CH_2Si$), 53.4 (N*C*H$_3$), 65.6 (SCH_2CH_2N); ^{15}N NMR: δ 50.2; ^{29}Si NMR: δ 1.79 (1 *Si*CH$_3$), 2.60 (2 *Si*CH$_3$). MS: $[M - 2\ I^-]^{2+}$: 572.20. Anal. Calcd.: $C_{41}H_{98}I_4N_4OS_5Si_3$ (1399.44): Calcd.: C, 35.19; H, 7.06; N, 4.00; S, 11.46; Obt.: C, 35.96; H, 7.50; N, 4.08; S, 11.60.

HSG_3(S-NMe_3I)$_8$ (9I). Following the procedure described for compound **7I**, compound **9I** was obtained as orange solid (1.802 g, 86 %) from the reaction of **6I** (2.126 g, 0.74 mmol) with HCl in ether (4 M, 1.1 mL, 4.43 mmol). Data for **9I**: NMR (D_2O): ^{1}H NMR: δ - 0.04 (s, 9 H, SiC*H*$_3$) 0.18 (s, 12 H, SiC*H*$_3$), 0.64 (m, 26 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$) 1.01 (m, 16 H, $SiCH_2CH_2S$), 1.37 (m, 14 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 1.59 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.46 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.82 (m, 16 H, $SiCH_2CH_2S$), 3.07 (m, 16 H, SCH_2CH_2N), 3.26 (s, 72 H, NC*H*$_3$), 3.75 (m, 16 H, SCH_2CH_2N); ^{13}C NMR {^{1}H}: δ -4.2 (1 Si*C*H$_3$), -3.97 (2 Si*C*H$_3$), 13.4 ($SCH_2CH_2CH_2CH_2Si$), 15.1 ($SiCH_2CH_2S$), 18.6, 18.7 ($SiCH_2CH_2CH_2Si$), 22.8 ($SCH_2CH_2CH_2CH_2Si$), 24.4 ($SCH_2CH_2CH_2CH_2Si$), 24.8 (SCH_2CH_2N), 28.1 ($SiCH_2CH_2S$), 37.9 ($SCH_2CH_2CH_2CH_2Si$), 53.8 (N*C*H$_3$), 65.8 (SCH_2CH_2N); ^{15}N NMR: δ 51.2; ^{29}Si NMR: δ 1.21, 2.68 (*Si*CH$_3$). MS: $[M - 5\ I^-]^{5+}$: 440.21. Anal. Calcd.: $C_{85}H_{202}I_8N_8OS_9Si_7$ (2836.99): Calcd.: C, 35.99; H, 7.18; N, 3.95; S, 6.93; Obt.: C, 35.86; H, 7.91; N, 4.13; S, 7.03.

HSG_1(S-NMe_3Cl)$_2$ (7Cl). Following the procedure described for compound **7I**, compound **7Cl** was obtained as yellow solid (0.088 g, 100 %) from the reaction of **4Cl** (0.095 g, 0.18 mmol) with HCl in ether (2 M, 0.5 mL, 1.06 mmol).

Data for **7Cl**: NMR (D_2O): δ - 0.05 (s, 3 H, SiC*H*$_3$), 0.51 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 0.84 (m, 4 H, $SiCH_2CH_2S$), 1.32 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 1.52 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.45 (m, 2 H,

SC*H*$_2$CH$_2$CH$_2$CH$_2$Si), 2.60 (m, 4 H, SiCH$_2$C*H*$_2$S), 2.87 (m, 4 H, SC*H*$_2$CH$_2$N), 3.04 (s, 18 H, NC*H*$_3$), 3.43 (m, 4 H, SCH$_2$C*H*$_2$N). ^{13}C NMR {^{1}H}: δ -6.4 (Si*C*H$_3$), 11.7 (SCH$_2$CH$_2$CH$_2$*C*H$_2$Si), 13.6 (Si*C*H$_2$CH$_2$S), 21.5 (S*C*H$_2$CH$_2$CH$_2$CH$_2$Si), 23.2 (SCH$_2$CH$_2$*C*H$_2$CH$_2$Si), 23.4 (S*C*H$_2$CH$_2$N), 27.1 (SiCH$_2$*C*H$_2$S), 36.4 (SCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 52.8 (N*C*H$_3$), 65.5 (SCH$_2$*C*H$_2$N); ^{15}N NMR: δ 48.2; ^{29}Si NMR: δ 2.86 (*Si*CH$_3$). MS: [M – 2 Cl$^-$]$^{2+}$: 213.44, [M – Cl$^-$]$^+$: 461.23, [M]$^+$: 499.24. Anal. Calcd.: $C_{21}H_{48}Cl_2N_2OS_3Si$ (497.77): Calcd.: 45.85; H, 9.31; Cl, 14.24; N, 5.63; S, 19.33; Obt.: C, 43.74; H, 8.89; N, 5.59; S, 17.70.

HSG$_2$(S-NMe$_3$Cl)$_4$ (8Cl). Following the procedure described for compound **7I**, compound **8Cl** was obtained as yellow solid (0.275 g, 93 %) from the reaction of **5Cl** (0.306 g, 0.29 mmol) with HCl in ether (2 M, 0.9 mL, 1.71 mmol). Data for **8Cl**: NMR (D$_2$O): ^{1}H NMR: δ - 0.11 (s, 3 H, SiC*H*$_3$) 0.01 (s, 6 H, SiC*H*$_3$), 0.45 (m, 2 H, SCH$_2$CH$_2$CH$_2$C*H*$_2$Si), 0.58 (m, 8 H, SiC*H*$_2$CH$_2$C*H*$_2$Si) 0.87 (m, 8 H, SiC*H*$_2$CH$_2$S), 1.32 (m, 6 H, SCH$_2$CH$_2$C*H*$_2$CH$_2$Si, SiCH$_2$C*H*$_2$CH$_2$Si), 1.55 (m, 2 H, SCH$_2$C*H*$_2$CH$_2$CH$_2$Si), 2.48 (m, 2 H, SC*H*$_2$CH$_2$CH$_2$CH$_2$Si), 2.65 (m, 8 H, SiCH$_2$C*H*$_2$S), 2.92 (m, 8 H, SC*H*$_2$CH$_2$N), 3.08 (s, 36 H, NC*H*$_3$), 3.49 (m, 8 H, SCH$_2$C*H*$_2$N). MS: [M – 4 Cl$^-$]$^{4+}$: 222.65, [M – 3 Cl$^-$]$^{3+}$: 308.52, [M – 2 Cl$^-$]$^{2+}$: 480.76. Anal. Calcd.: $C_{41}H_{98}Cl_4N_4OS_5Si_3$ (1033.64): Calcd.: C, 47.64; H, 9.56; N, 5.42; S, 15.51;Obt.: C, 47.40; H, 9.28; N, 5.54; S, 13.58.

HSG$_3$(S-NMe$_3$Cl)$_8$ (9Cl). Following the procedure described for compound **7I**, compound **9Cl** was obtained as yellow solid (0.197 g, 90 %) from the reaction of **6Cl** (0.223 g, 0.10 mmol) with HCl in ether (2 M, 0.3 mL, 0.62 mmol). Data for **9Cl**: NMR (D$_2$O): δ - 0.08 (s, 9 H, SiC*H*$_3$) 0.05 (s, 12 H, SiC*H*$_3$), 0.58 (m, 26 H, SCH$_2$CH$_2$CH$_2$C*H*$_2$Si, SiC*H*$_2$CH$_2$C*H*$_2$Si) , 0.90 (m, 16 H, SiC*H*$_2$CH$_2$S), 1.32 (m, 14 H, SCH$_2$CH$_2$C*H*$_2$CH$_2$Si, SiCH$_2$C*H*$_2$CH$_2$Si), 1.57 (m, 2 H, SCH$_2$C*H*$_2$CH$_2$CH$_2$Si), 2.50 (m, 2 H, SC*H*$_2$CH$_2$CH$_2$CH$_2$Si), 2.67 (m, 16 H, SiCH$_2$C*H*$_2$S), 2.95 (m, 16 H, SC*H*$_2$CH$_2$N), 3.11 (s, 72 H, NC*H*$_3$), 3.52 (m, 16 H, SCH$_2$C*H*$_2$N). MS: [M – 4 Cl$^-$]$^{4+}$: 222.65, [M – 3 Cl$^-$]$^{3+}$: 308.52, [M – 2 Cl$^-$]$^{2+}$: 480.76. Anal. Calcd.: $C_{85}H_{202}Cl_8N_8OS_9Si_7$ (2105.34): Calcd.: C, 48.49; H, 9.67; N, 5.32; S, 13.71; Obt.: C, 48.52; H, 9.46; N, 5.43; S, 12.29.

HSG$_1$(S-NMe$_2$)$_2$ (10). To a THF solution (ca. 5 mL) of compound HSG$_1$(S-NMe$_2$·HCl)$_2$ (0.508 g, 1.24 mmol) was added NaHCO$_3$ (0.919 g, 4.98 mmol) and the mixture was stirred at 25ºC during 12 hours. Afterwards, volatiles were removed under vacuum and the residue was dissolved in Et$_2$O.

Subsequently brine was added, the organic phase was separate and the aqueous phase was extracted twice with Et_2O. The organic phase was washed with brine and dried over $MgSO_4$. The solution was filtered through celite and the volatiles were removed under vacuum, yielding **7** as orange oil (0.469 g, 95 %).

Data for **7**: NMR ($CDCl_3$): ^{1}H NMR: δ 0.01 (s, 3 H, SiC*H*$_3$), 0.54 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 0.89 (m, 4 H, $SiCH_2CH_2S$), 1.29 (m, 1 H, *H*S), 1.37 (m, 2 H, $SCH_2CH_2CH_2CH_2CH_2Si$), 1.61 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.24 (s, 12 H, NC*H*$_3$), 2.59 (m, 14 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2S$, SCH_2CH_2N); ^{13}C NMR{^{1}H}: δ -5.2 ($SiCH_3$), 13.0 ($SCH_2CH_2CH_2CH_2Si$), 14.4 ($SiCH_2CH_2S$), 22.2 ($SCH_2CH_2CH_2CH_2Si$), 24.1 ($SCH_2CH_2CH_2CH_2Si$), 25.3 (SCH_2CH_2N), 27.6 ($SiCH_2CH_2S$), 37.4 ($SCH_2CH_2CH_2CH_2Si$), 42.9 (NCH_3), 57.3 (SCH_2CH_2N); ^{15}N NMR: δ 27.8; ^{29}Si NMR: δ 2.25 ($SiCH_3$). MS: $[M + H]^+$: 396.22. Anal. Calcd.: $C_{17}H_{40}N_2S_3Si$ (396.79): Calcd.: C, 51.46; H, 10.16; N, 7.06; S, 24.24; Obt.: C, 51.09; H, 9.88; N, 7.09; S, 23.18.

$HSG_2(S\text{-}NMe_2)_4$ (11). Following the procedure described for compound **10**, compound **11** was obtained as orange oil (0.339 g, 70 %) from the reaction of $HSG_2(S\text{-}NMe_2{\cdot}HCl)_4$ (0.571 g, 0.55 mmol) with $NaHCO_3$ (0.392 g, 4.67 mmol). Data for **11**: ^{1}H NMR: δ -0.01 (s, 3 H, SiC*H*$_3$), 0.03 (s, 6 H, SiC*H*$_3$), 0.52 (m, 10 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 0.87 (m, 8 H, $SiCH_2CH_2S$), 1.18 (m, 1 H, *H*S), 1.29 (m, 6 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 1.60 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.23 (s, 24 H, NC*H*$_3$), 2.53 (m, 26 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2S$, SCH_2CH_2N), ^{13}C NMR{^{1}H}: δ -5.1 (1 $SiCH_3$), -5.1 (2 $SiCH_3$), 13.3 ($SCH_2CH_2CH_2CH_2Si$), 14.7 ($SiCH_2CH_2S$), 18.3, 18.5, 18.7 ($SiCH_2CH_2CH_2Si$), 22.7 ($SCH_2CH_2CH_2CH_2Si$), 24.2 ($SCH_2CH_2CH_2CH_2Si$), 27.7 (SCH_2CH_2N), 29.8 ($SiCH_2CH_2S$), 37.7 ($SCH_2CH_2CH_2CH_2Si$), 42.4 (NCH_3), 59.3 (SCH_2CH_2N)M; ^{29}Si NMR: δ 1.7 (1 $SiCH_3$), 2.0 (2 $SiCH_3$); ^{15}N NMR: δ 27.4. MS: $[M + H]^+$: 831.5. Anal. Calcd.:$C_{37}H_{86}N_4S_5Si_3$ (831.69): Calcd.: C, 53.43; H, 10.42; N, 6.74; S, 19.28; Obt.: C, 51.69; H, 9.93; N, 6.59; S, 18.20.

$HSG_3(S\text{-}NMe_2)_8$ (12). Following the procedure described for compound **10**, compound **12** was obtained as orange oil (0.317 g, 71 %) from the reaction of $HSG_3(S\text{-}NMe_2{\cdot}HCl)_8$ (0.526 g, 0.26 mmol) with $NaHCO_3$ (0.354 g, 4.22 mmol). Data for **12**: ^{1}H NMR: δ -0.07(s, 6 H, SiC*H*$_3$), 0.03 (s, 12 H, SiC*H*$_3$), 0.55 (m, 26 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 0.90 (m, 16 H, $SiCH_2CH_2S$), 1.21 (m, 1 H, *H*S), 1.27 (m, 14 H, $SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 1.64 (m, 2 H, $SCH_2CH_2CH_2CH_2Si$), 2.27 (s, 48 H,

NC*H*$_3$), 2.58 (m, 50 H, SC*H*$_2$CH$_2$CH$_2$CH$_2$Si, SiCH$_2$C*H*$_2$S, SC*H*$_2$C*H*$_2$N), ^{13}C NMR{^{1}H}: δ -5.3 (3 Si*C*H$_3$), -5.0 (4 Si*C*H$_3$), 13.3 (SCH$_2$CH$_2$CH$_2$*C*H$_2$Si), 14.6 (Si*C*H$_2$CH$_2$S), 18.3, 18.4, 18.8 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 22.6 (S*C*H$_2$CH$_2$CH$_2$CH$_2$Si), 24.2 (SCH$_2$CH$_2$*C*H$_2$CH$_2$Si), 27.6 (S*C*H$_2$CH$_2$N), 29.8 (SiCH$_2$*C*H$_2$S), 39.5 (SCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 45.3 (N*C*H$_3$), 59.2 (SCH$_2$*C*H$_2$N)M; ^{29}Si NMR: δ 0.91, 1.62 (3 *Si*CH$_3$), 1.99 (4 *Si*CH$_3$); ^{15}N NMR: δ 28.4. MS: $[M + H]^+$: 1701.9, $[M + Na]^+$: 1723.9. Anal. Calcd.: $C_{77}H_{178}N_8S_9Si_7$ (1699.00): Calcd.: C, 54.35; H, 10.54; N, 6.59; S, 16.96; Obt.: C, 53.25; H, 10.26; N, 6.19; S, 17.20.

AuNP(SG$_2$(S-NMe$_2$)$_4$). To an aqueous solution of HAuCl$_4$ (8.82 mL, 0.26 mmol, 29.5 mM) was added a solution of tetraoctylammonium bromide in toluene (21.2 mL, 1.06 mmol, 50 mM) the solution was stirred until the color was transferred to the organic layer. A solution of (0.26 mmol) in a minimal quantity of toluene was added to the mixture, followed by the dropwise addition of a freshly solution of NaBH$_4$ (6.25 mL, 1.30 mmol, 208 mM) under vigorous stirring, the mixture was stirred for a further 4 hours. Nanoparticles were precipitated from the solution and were just partially soluble in DMSO but not soluble in THF, Ether or CH$_2$Cl$_2$. Data for **AuNP(SG$_2$(S-NMe$_2$)$_4$)**: Mean diameter of gold core (TEM): D = 1.88 nm.

AuNP(SG$_1$(S-NMe$_3$Cl)$_2$) (13Cl). To an aqueous solution of HAuCl$_4$ (30 mL, 0.9 mmol, 30 mM) was added dropwise an aqueous solution of compound **7Cl** (80 mL, 1 mmol, 12.5 mM). Afterward, NaBH$_4$ in water (25 mL, 5 mmol, 200 mM) was added dropwise, and the mixture was stirred another 4 h. Nanoparticles were purified by dialysis (MWCO 10.000) affording **13Cl** (273 mg), which were stored in deionized water at 4 ºC.

Data for **13Cl**: NMR (D$_2$O): ^{1}H NMR: δ -0.07 (SiC*H*$_3$), 0.60 (SCH$_2$CH$_2$CH$_2$C*H*$_2$Si), 0.91 (SiC*H*$_2$CH$_2$S), 1.41 (SCH$_2$CH$_2$C*H*$_2$CH$_2$Si), 1.70 (SCH$_2$C*H*$_2$CH$_2$CH$_2$Si), 2.70 (SiCH$_2$C*H*$_2$S), 2.97 (SC*H*$_2$CH$_2$N), 3.10 (NC*H*$_3$), 3.51 (SCH$_2$C*H*$_2$N). Au/(l) reactant molar ratio = 1:1. TGA (%): Au, 54.80; (l), 45.20. Calc. molar ratio Au/(l) = 3.05:1 in nanoparticle. SPR (UV-Vis): 528.1 nm. Zeta Potential: +54.1. DLS (Z-average d.nm) = 13.81 nm. Mean diameter of gold core (TEM): D = 1.80 nm. Number of gold atoms: N_{Au} = 180; number of dendrons N_d = 59. Molecular formula: $Au_{1590}(C_{19}H_{45}Cl_2N_2S_3Si)_{442}$. Average *Mw* = 64761.64 gmol^{-1}.

AuNP(SG_2(S-NMe_3Cl)$_4$) (14). Following the procedure described for compound **13**, compound **14** was obtained (111 mg) from the reaction of $HAuCl_4$ (5.3 mL, 0.16 mmol, 30 mM) with compound **8Cl** (14. mL, 0.17 mmol, 12.5 mM) and $NaBH_4$ (4.4 mL, 0.9 mmol, 200 mM) Nanoparticles were purified by dialysis (MWCO 10,000). Data for **14**: NMR (D_2O): δ - 0.01, 0.12 (SiC*H*$_3$), 0.64 ($SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$) 0.92 ($SiCH_2CH_2S$), 1.38 ($SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 2.72 ($SiCH_2CH_2S$), 2.98 (SCH_2CH_2N), 3.15 (NCH_3), 3.57 (SCH_2CH_2N). Au/(l) reactant molar ratio = 1:1. TGA: Au, 32.3; (l), 67.7. Calc. molar ratio Au/(l) = 2.5:1 in the nanoparticles. SPR (UV-Vis): 533.7 nm. Zeta potential (mV): +63.7. DLS (Z-average d.nm) = 15.69 nm. Mean diameter of gold core (TEM): D = 2.2 nm. N_{Au} = 329; N_{th} = 132. Molecular weight calculation: $Au_{329}(C_{41}H_{97}Cl_4N_4S_5Si_3)_{132}$. Average M = 201105.7 gmol^{-1}.

AuNP(SG_3(S-NMe_3Cl)$_8$) (15). Following the procedure described for compound **14**, compound **15** was obtained (217 mg) from the reaction of $HAuCl_4$ (5.0 mL, 0.15 mmol, 30 mM) with compound **9Cl** (13.3 mL, 0.17 mmol, 12.5 mM) and $NaBH_4$ (4.2 mL, 0.83 mmol, 200 mM) Nanoparticles were purified by dialysis (MWCO 10,000). Data for **15**: NMR (D_2O): δ -0.08, 0.05 (SiC*H*$_3$), 0.55 ($SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$) 0.90 ($SiCH_2CH_2S$), 1.35 ($SCH_2CH_2CH_2CH_2Si$, $SiCH_2CH_2CH_2Si$), 2.68 ($SiCH_2CH_2S$), 2.95 (SCH_2CH_2N), 3.11 (NCH_3), 3.54 (SCH_2CH_2N). TGA: Au, 15.8; (l), 84.2. Calc. molar ratio Au/(l) = 2.0:1 in the nanoparticles. SPR (UV-Vis): 543.1 nm. Zeta potential (mV): +59.6. DLS (Z-average d.nm) = 21.04 nm. Mean diameter of gold core (TEM): D = 2.0 nm. N_{Au} = 247; N_{th} = 123. Molecular weight calculation: $Au_{247}(C_{85}H_{201}Cl_8N_8S_9Si_7)_{123}$. Average M = 307482.9 gmol^{-1}.

Determination of the number of ligands in AuNPs. An example of procedure to obtain Au/dendron ratio and molecular weight is described:[2,3]

From TGA it is obtained information about percentage of non-volatile (metallic core) and volatile (dendron) fragments of NPs. For example for **AuNP(SG_1(S-NMe_3Cl)$_2$)** (**13Cl**): Au, 54.80 %; ligand (l, dendron), 45.20 %. These values correspond with a mass relationship Au/dendron.

From TEM it is obtained the average diameter of NPs metallic core (d_n = 1.80 nm for **13Cl**). Then, taking into account the density of this gold core (59 atoms nm^{-3} for bulk face-centered cubic (fcc)) and a spherical distribution of gold atoms (sphere volume (π/6) $(d_n)^3$), the approximate number of gold atoms in a cluster is $N_{Au} = 59(\pi/6)(d_n)^3$ = 180 (for **13Cl**).

From previous data we have obtained a mass relationship Au/dendron and the number of gold atoms in the NPs core. Then, these data can be related with the number of ligands on NPs surface considering that volatile material observed in TGA belongs to dendron. Thus, taking into account dendron formula weight, the number of ligands on NPs is N_d = 59 for **13Cl**, and finally the average molecular weight can be calculated (64761.64 $gmol^{-1}$ for **13Cl**).

S1.3 Thermogravimetric Analysis (TGA). The thermogravimetrics analyses were performed using a Q500 from TGA instruments. Dry and pure samples (2 - 10 mg) were placed into platinum sample holder under nitrogen atmosphere. The measurements were recorded from 25 to 1000 ºC, with heating rate of 10 ºC/min.

S1.4 Transmission electron microscopy (TEM). TEM were performed using a ZEISS EM10 TEM with 30 μm lens and a side-mounted 1K CCD Camera, operating at an acceleration voltage of 100 kV and with 0.2 nm resolution. The samples were prepared by dropping a dilute solution containing the nanoparticles on a carbon-coated copper grid (400 mesh) and dried before observation and measurement (particles size measurements were performed using Image J).

S1.5 Zeta Potential.

The zeta-potential of compounds were measured using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK) at 25 ºC in a disposable Malvern plastic cuvette. The solutions were prepared by solving 1 mg of each compound, previously dried, in 1 mL of MiLiQ water, which was previously filtered through 0.22 μm syringe filter.

S1.6 Dynamic Light Scattering (DLS).

Batch mode hydrodynamic size (diameter) measurements were performed on a Malvern Zetasizer Nano ZS (Malvern Instruments) equipped with Non-Invasive Backscatter optics (NBS). The solutions were prepared by solving 1 mg of each compound, previously dried, in 0.004 mL of MiLiQ water, which was previously filtered through 0.22 μm syringe filter. Before measurements equilibration (typically 5 minutes) at 25°C were performed and then minimum of three measurements per sample were made.

S1.7 Hemotoxicity

Blood from healthy donors was obtained from Central Blood Bank in Lodz. Blood was anticoagulated with 3% sodium citrate. Erythrocytes were separated from blood plasma and leukocytes by centrifugation (4000 g, 10 min) at 4 °C and washed three times with PBS (phosphate buffered saline; pH = 7.4). Erythrocytes were used immediately after isolation. To study the effect of dendrons $HSG_n(S\text{-}NMe_3^+)_m$ (**7-9**) and dendronized $AuNP(SG_n(S\text{-}NMe_3^+)_m)$ (**13-15**) on erythrocytes, AuNPs were added in the concentrations: 0.05; 0.5; 1; 5; 10; 20 μM to red blood cells of 2 % hematocrit and incubated at 37 °C. After 2 h and 24 h incubation suspensions were centrifuged (1000 g, 10 min). Hemolysis was determined by measuring the hemoglobin content in the supernatant at 540 nm. Percent of hemolysis was calculated from the formula:

Hemolysis [%]= (A/Ac) x 100%

Where A is the absorbance of the sample, Ac is the absorbance of the sample in water (100% hemolysis).

To study the effect of the presence of human serum albumin (HSA) in human blood on hemolysis caused by dendrons $HSG_n(S\text{-}NMe_3^+)_m$ (**7-9**) $AuNP(SG_n(S\text{-}NMe_3^+)_m)$ (**13-15**), 2 μg/l of HSA was added to a 5 μM and 10 μM AuNP solution, and after 5 min, red blood cells were added to 2% hematocrit. The samples were then incubated for 2 h and 24 h, and the percentage of hemolysis was determined on the basis of released hemoglobin in supernatants and measured spectrophotometrically from the absorbance at 540 nm.

S1.8 Platelets aggregation

Blood from healthy donors, anticoagulated with CPDA-1 (110 mM glucose; 55 mM mannitol; 25.8 mM K_2HPO_4; 14.7 mM KH_2PO_4; 17.9 mM potassium citrate), was obtained from the Republican Research & Practical Center for Transfusiology and Medical Biotechnologies of MH RB (Minsk, Republic of Belarus). Blood plasma was centrifuged at 360 g for 5 min to pellet the platelets, which were resuspended in 200 μl Tris buffer containing EDTA (0.12 M NaCl, 0.0154 M KCl, 0.006 M glucose, 0.0015 M Na_2EDTA, 0.0133 M Tris, pH 6.5).[4] The suspension was centrifuged at 360 g for 5 min. The supernatant was removed and the pellet was resuspended in the buffer at 2.0×10^9 cell/ml.

Aggregation of platelets was studied using an automatic aggregometer AP2110 (SOLAR, Belarus). In the assay, 400 μL phosphate-saline buffer containing Ca^{2+} (0.137 M NaCl, 0.0027 M KCl, 0.0087 M Na_2HPO_4, 0.00148 M KH_2PO4, 0.001 M $CaCl_2$, pH 7.35)[4] and 50 μL of platelet suspension were added to a thermostated (37°C) plastic tube at a final platelet concentration of 2.0×10^8 cells/ml. Thrombin Dendron or AuNP (10 μM) were then added to the platelet suspension.

S1.9 Lymphocyte proliferation

Blood from healthy donors, anticoagulated with 3% sodium citrate, was obtained from the Central Blood Bank (Lodz). Peripheral blood mononuclear cells (PBMC) were isolated using Histopaque 1077. Viability was approximately 99% as measured by the trypan blue exclusion assay. Lymphocyte proliferation was assayed according to previously published procedure.[4,5] After isolation, the cells were resuspended in RPMI 1640 supplemented with 10% FBS (heat inactivated), 2 mM L-glutamine, 100 U/ml penicillin, 100 lg/ml streptomycin sulfate at a density of 1 x 10^6 cells/ml, and 100 μl of the cell suspension per well was dispensed into a 96-well round-bottom plate. The isolated cells were incubated in a humidified 37ºC, 5% CO_2 incubator in the presence (test samples) or absence (control samples) of dendrons/AuNPs, and in the presence or absence of phytohemagglutinin (PHA-M) to assess the inhibition or induction of proliferation, respectively. After 72 h incubation, the samples were analyzed using Alamar Blue assay (resazurin in final concentration 12.5 μg/ml). The final concentration of PHA-M was 10 μg/ml and the final concentrations of the dendrons/AuNP were 0.05, 0.5, 1, 5, 10 μM. A PBMC suspension with PHA-M solution at a concentration of 10 μg/ml in cell culture medium was used for a positive (proliferating) control, and PBMC suspension with PBS was used as the negative (nonproliferating) control.

S1.10 Statistics

The Shapiro-Wilk test was used to check the normality of distribution.Variance homogeneity were verified using Levene's test. Results are presented as Mean±S.D. (standard deviation), N = 6. Data were analyzed by ANOVA test with *post-hoc*tests (indicated at the figures and tables).

S1.11 Dendriplex formation and gel electrophoresis

Dendriplexes were prepared by mixing equal volumes of siRNA and dendron **9** or AuNPs **13** dissolved in sterile water at concentrations depending on the -/+ charge ratios and molar concentrations desired at different times (2, 24, 48 and 120 hours). 2 Electrophoretic mobility of the mixtures were visualized on a 2% (w/v) agarose gel at 90 V in a Tris–acetate–EDTA, TAE buffer solution (40 mM Tris–HCl, 1% (v/v) acetic acid, and 1 mM EDTA. The gel bands were quantified using Quantity One 1D Analysis Software (Bio-Rad Laboratories, Inc., Hercules, CA, USA).

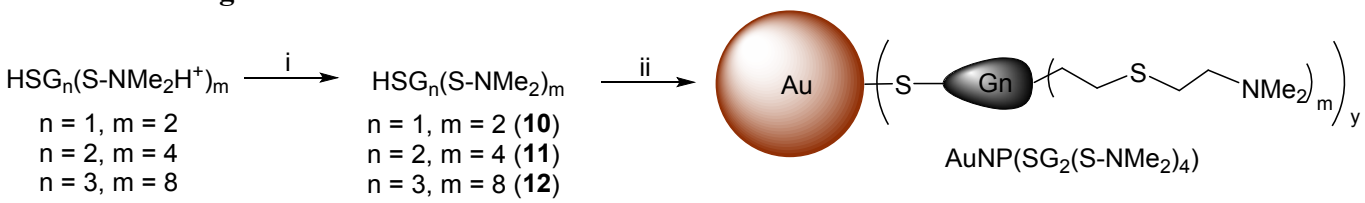
S1.12 Inhibition Assay

Peripheral Blood Mononuclear Cells (PBMCs) were stimulated with 1µg/ml of phytohemagglutinin (PHA), washed, counted and infected with X4-HIVNL4-3 strain at a dose of 20 ng of virus per million of cells during 2 hours. After that, cells were washed twice with medium, seeded (10^6 cells/ml) and treated with the dendriplexes at non-toxic concentrations obtained by MTT. Supernatants were collected after three days and p24 Ag production was quantified by ELISA kit according to the manufacturer's instructions (INNOTEST™HIV AntigenmAb, Innogenetics).

S1.11 References

1. E. Fuentes-Paniagua, C. E. Peña-González, Marta Galán, R. Gómez, F. J. de la Mata and J. Sánchez-Nieves, *Organometallics*, 2013, **32**, 1789−1796.
2. C. Park, H. Youn, H. Kim, T. Noh, Y. H. Kook, E. T. Oh, H. J. Park and C. Kim, *J. Mater. Chem. B*, 2009, **19**, 2310-2315.
3. M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293–346.
4. B. Ziemba, I. Halets, D. Shcharbin, D. Appelhans, B. Voit, I. Pieszynski, M. Bryszewska and B. Klajnert, *J. Biomed. Mat. Res. A.*, 2012, **100**, 2870-2880.
5. M. A. Dobrovolskaia, B. W. Neun, J. D. Clogston, H. Ding, J. Ljubimova and S. E. McNeil, *Nanomedicine (Lond)*, 2010, **5**, 555-562.

S2. Schemes and Figures



Scheme S1. Synthesis of neutral dendrons and AuNPs (G_n stands for dendron generation). i) $NaHCO_3$; ii) $[AuCl_4]^-$, $NaBH_4$.

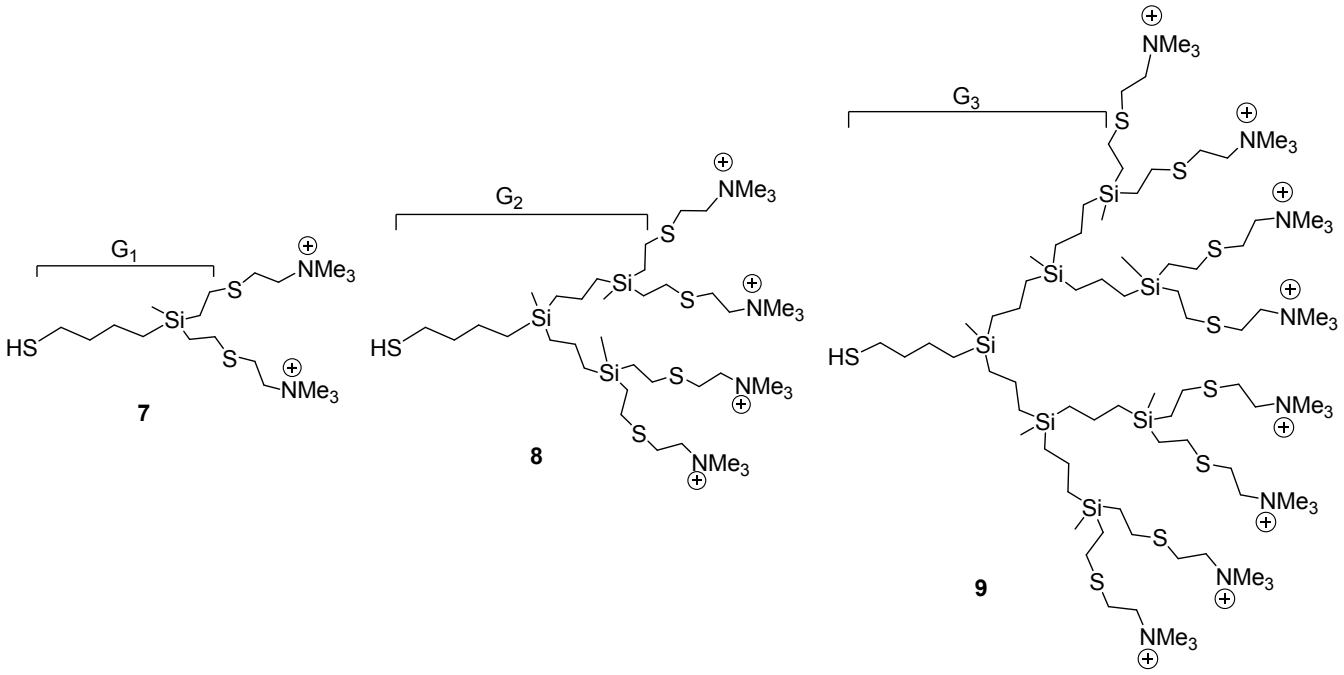


Figure S1. Drawing of cationic dendrons $HSG_n(S\text{-}NMe_3^+)_m$ (n = 1, m = 2 (**7**); n = 2, m = 4 (**8**); n = 3, m = 8 (**9**)). Anions have been omitted for clarity.

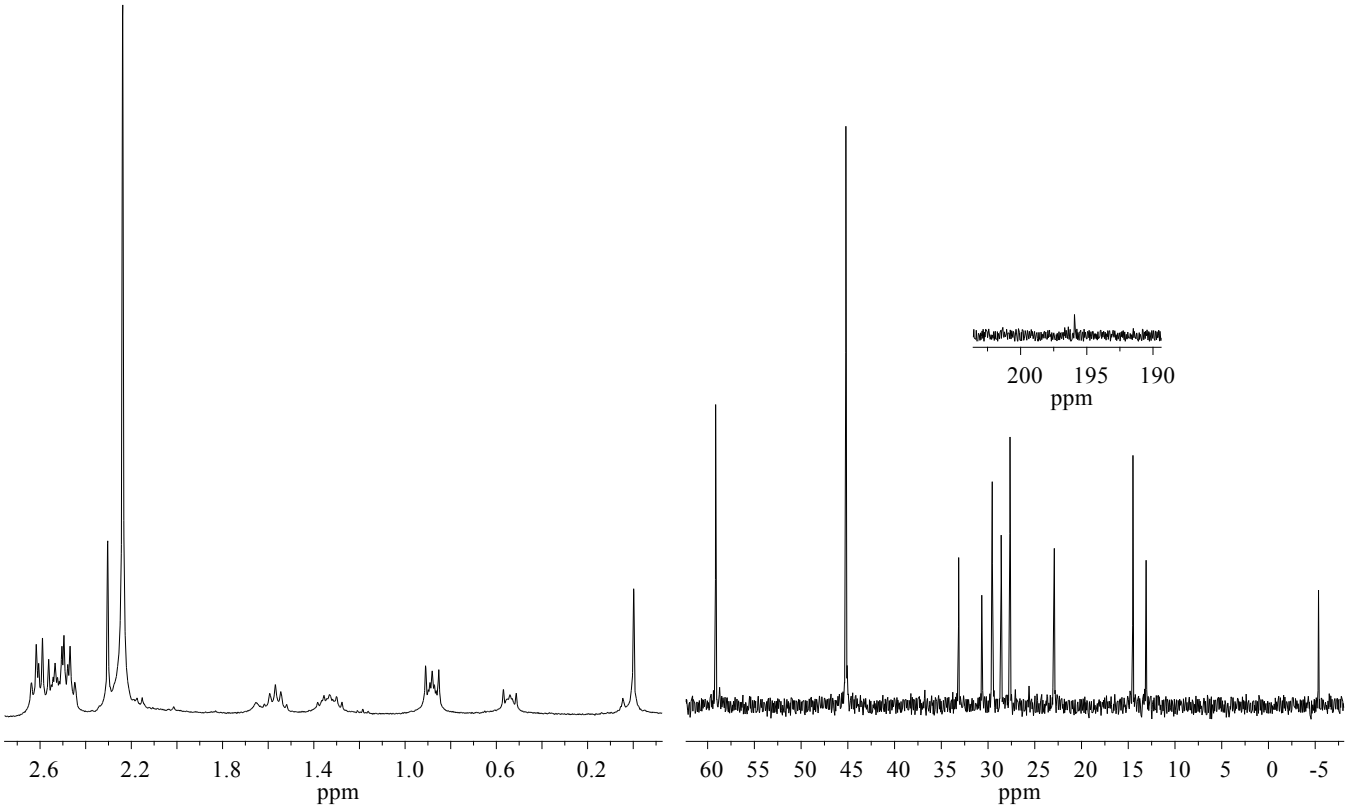


Figure S2. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **1**.

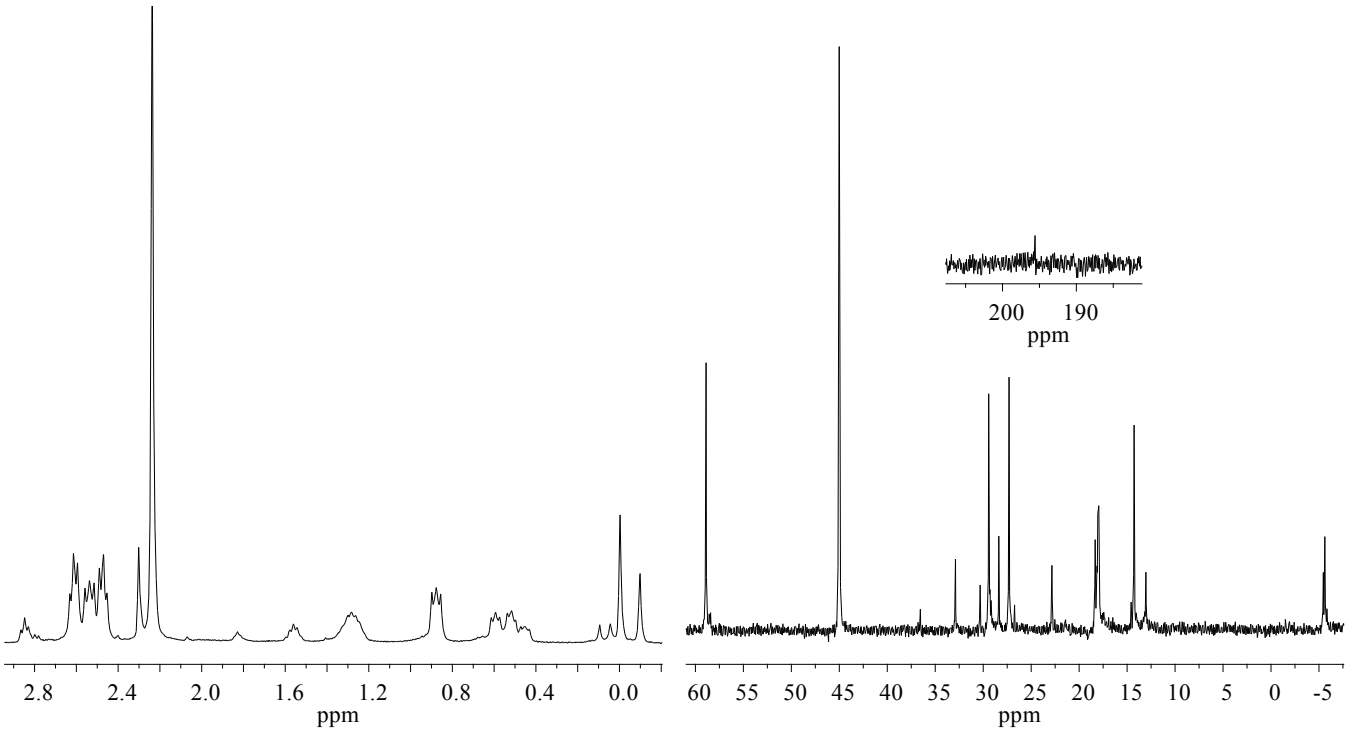


Figure S3. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **2**.

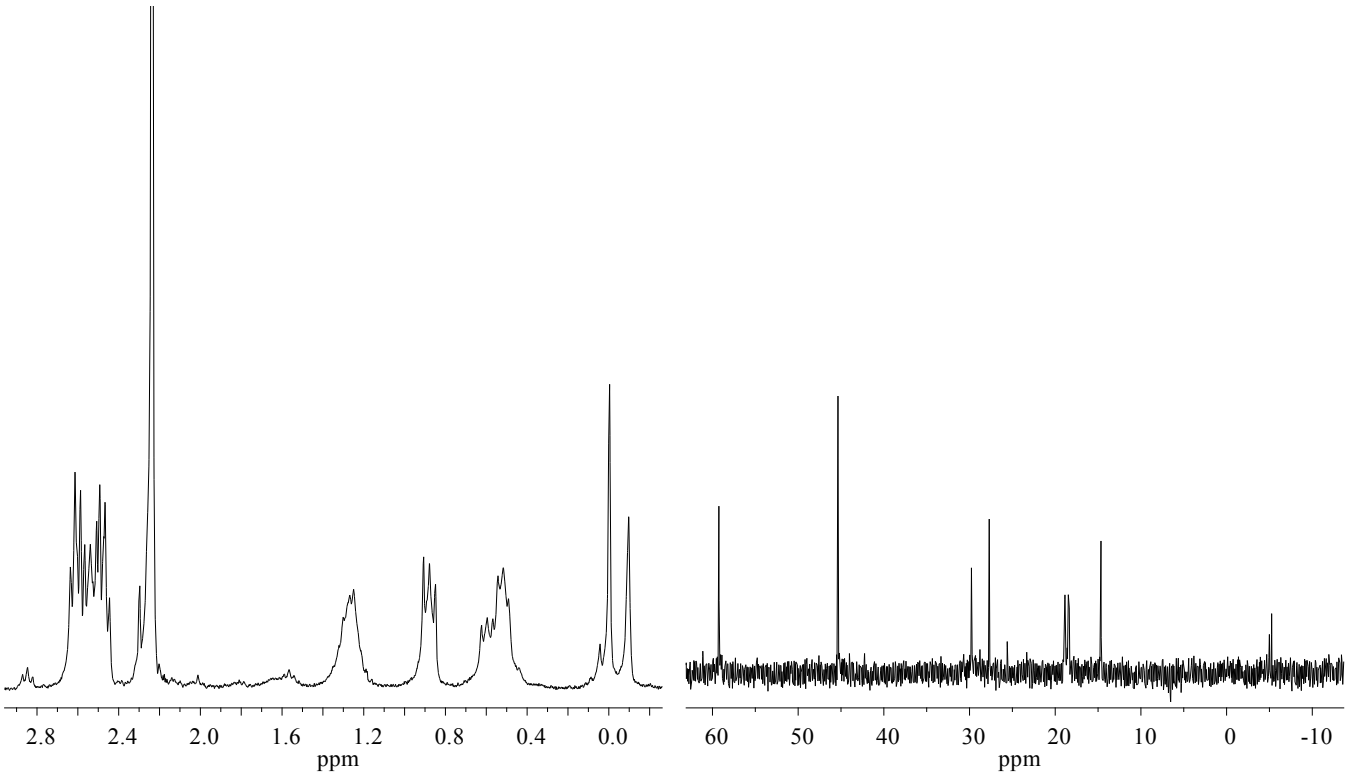


Figure S4. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **3**.

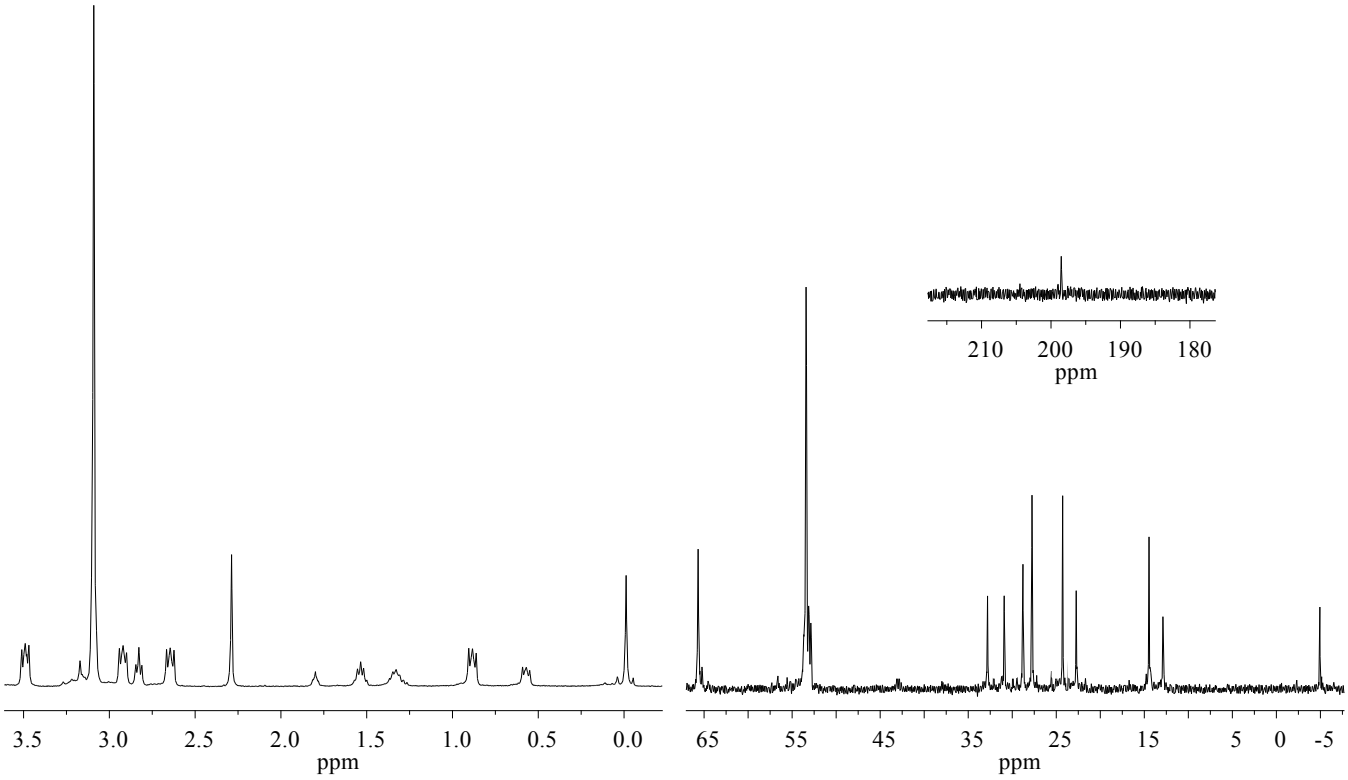


Figure S5. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **4I**.

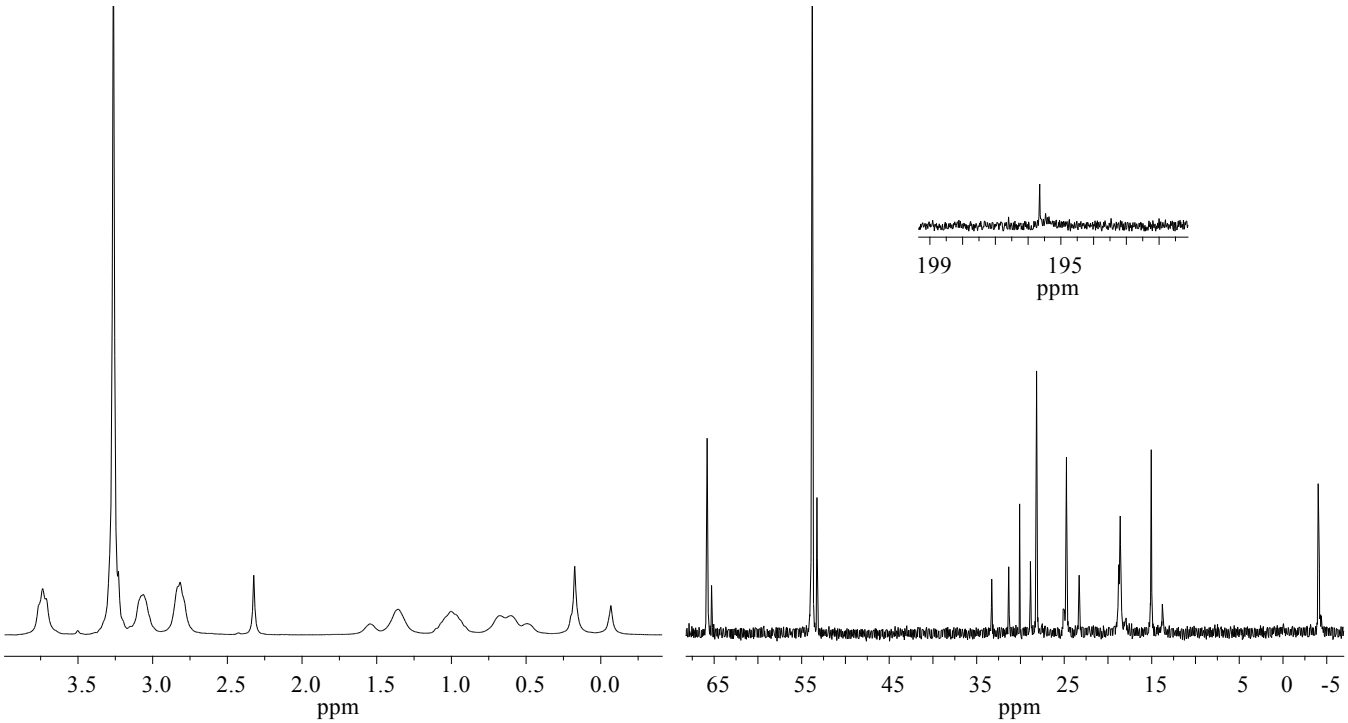


Figure S6. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **5I**.

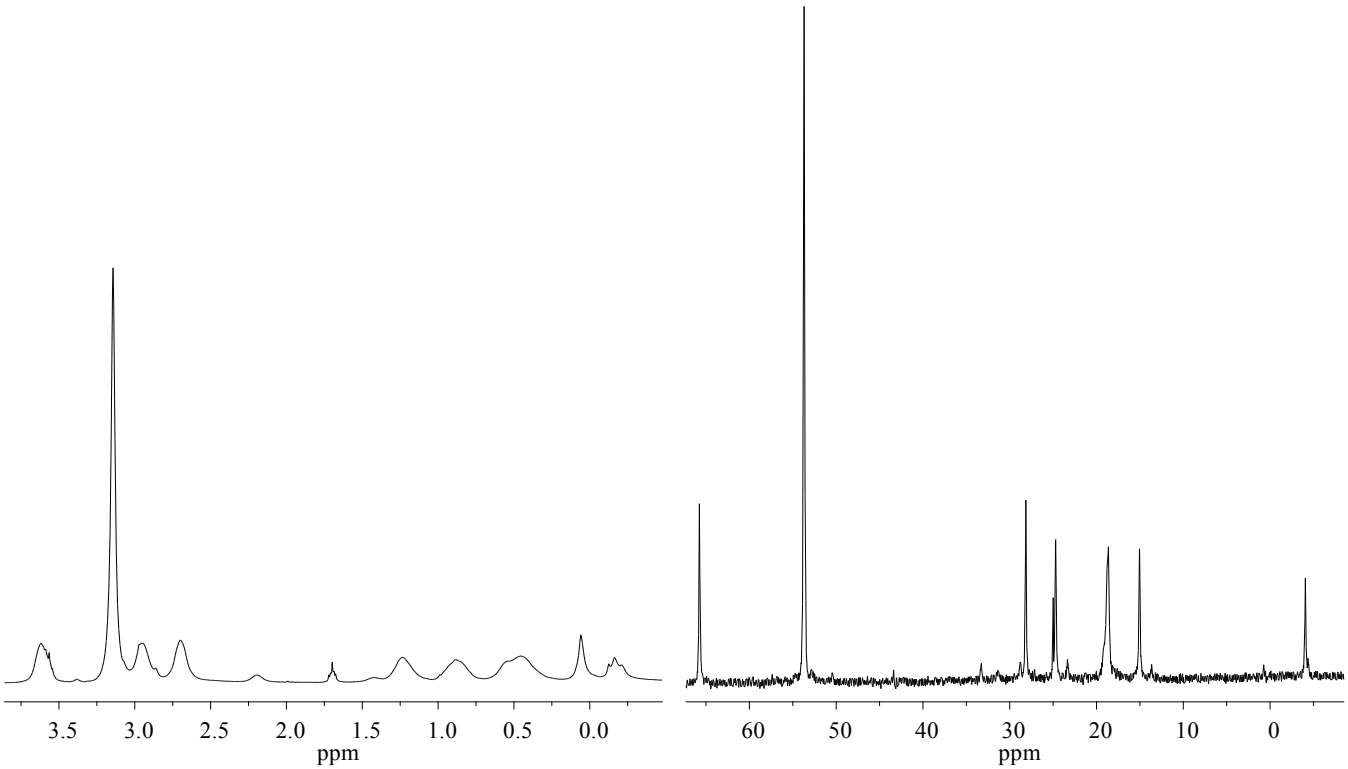


Figure S7. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **6I**.

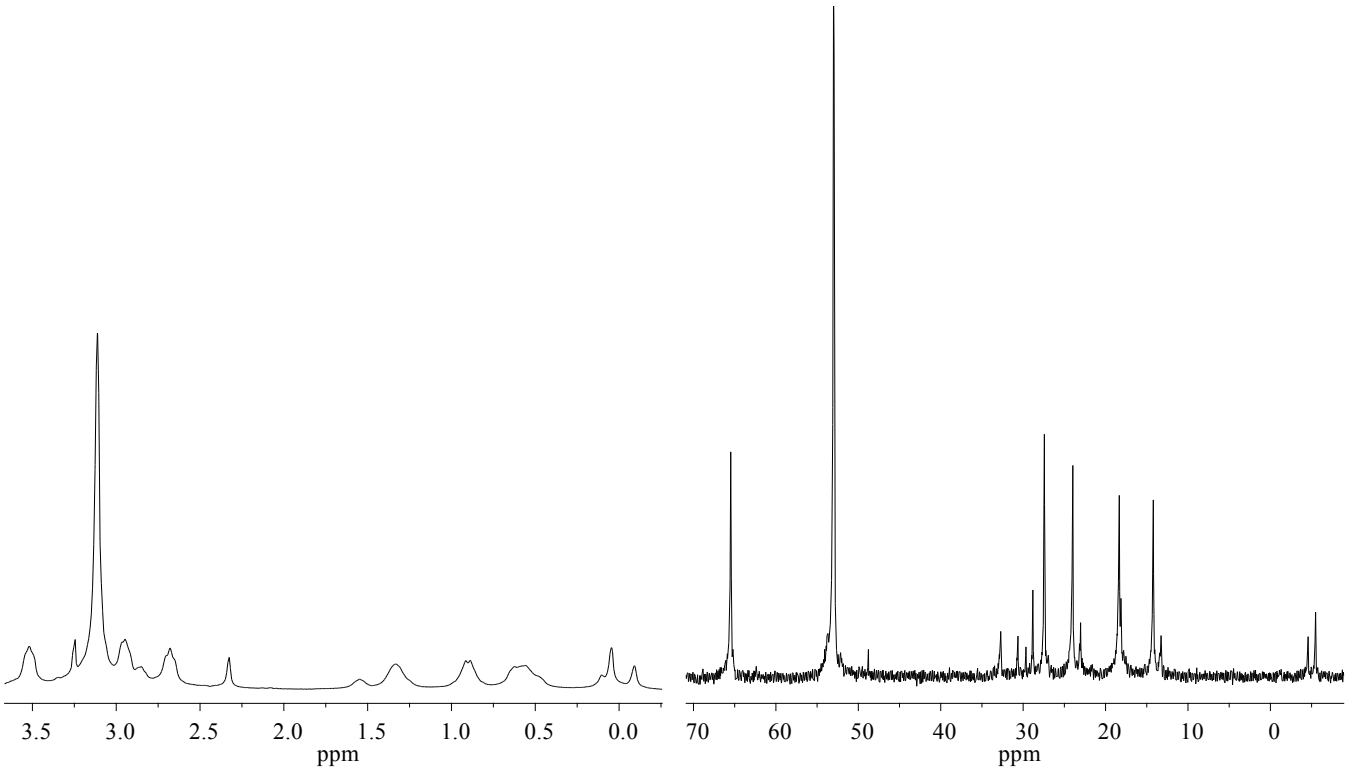


Figure S8. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **5Cl**.

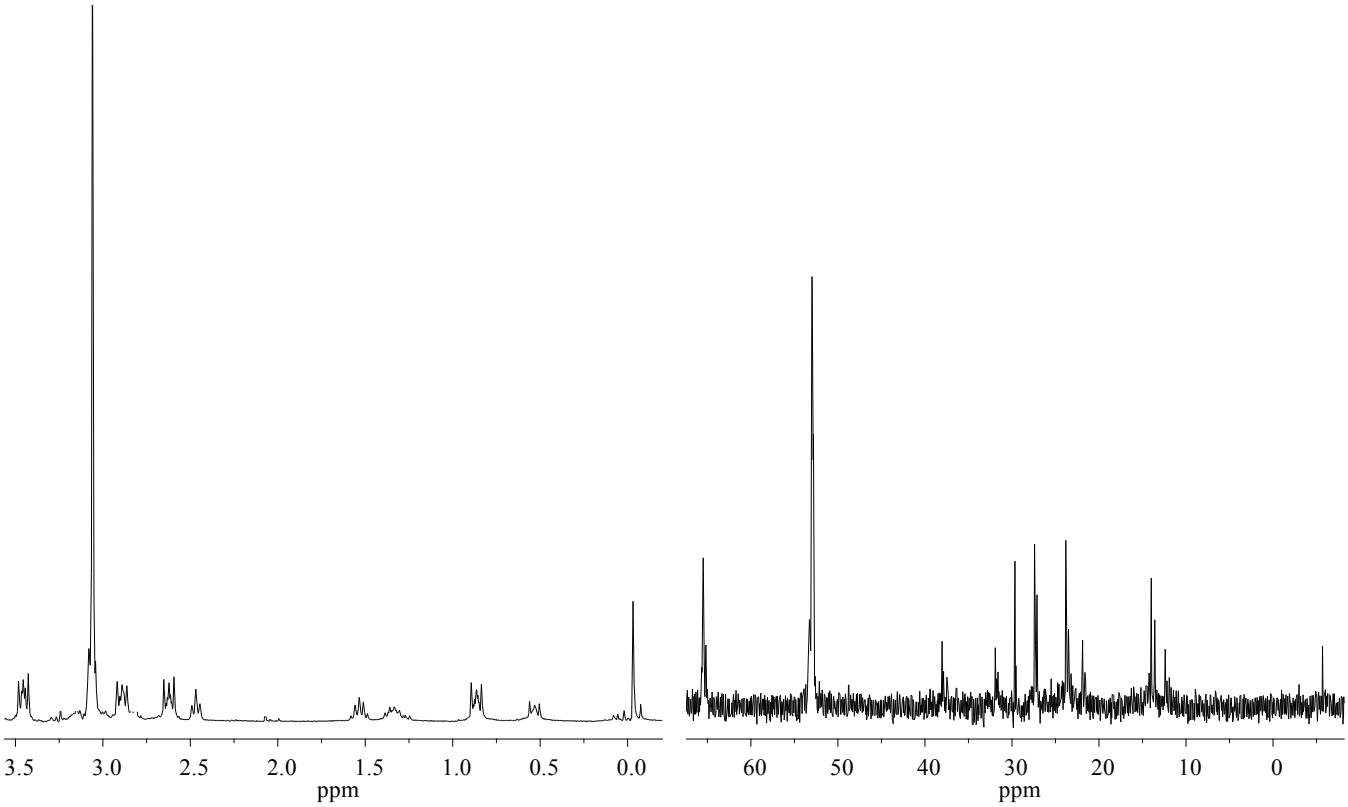


Figure S9. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **7I**.

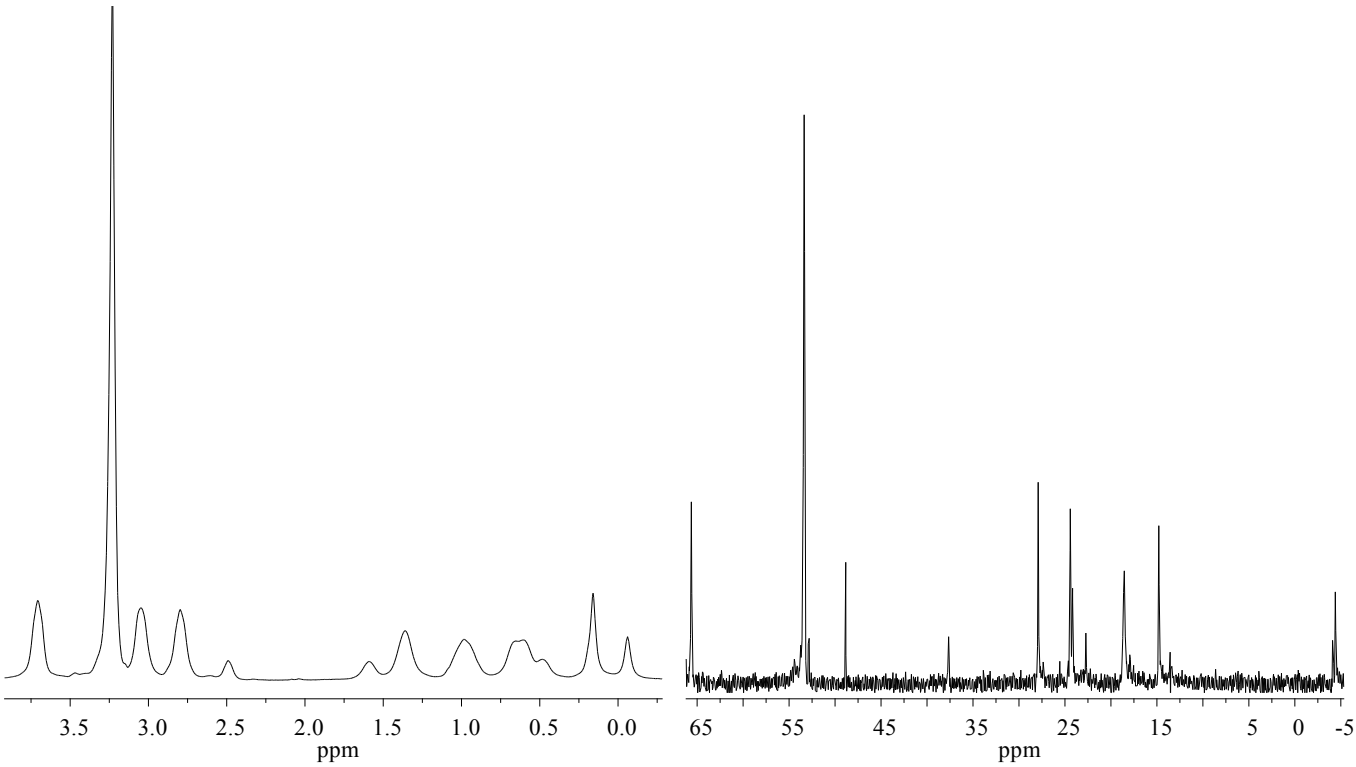


Figure S10. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **8I**.

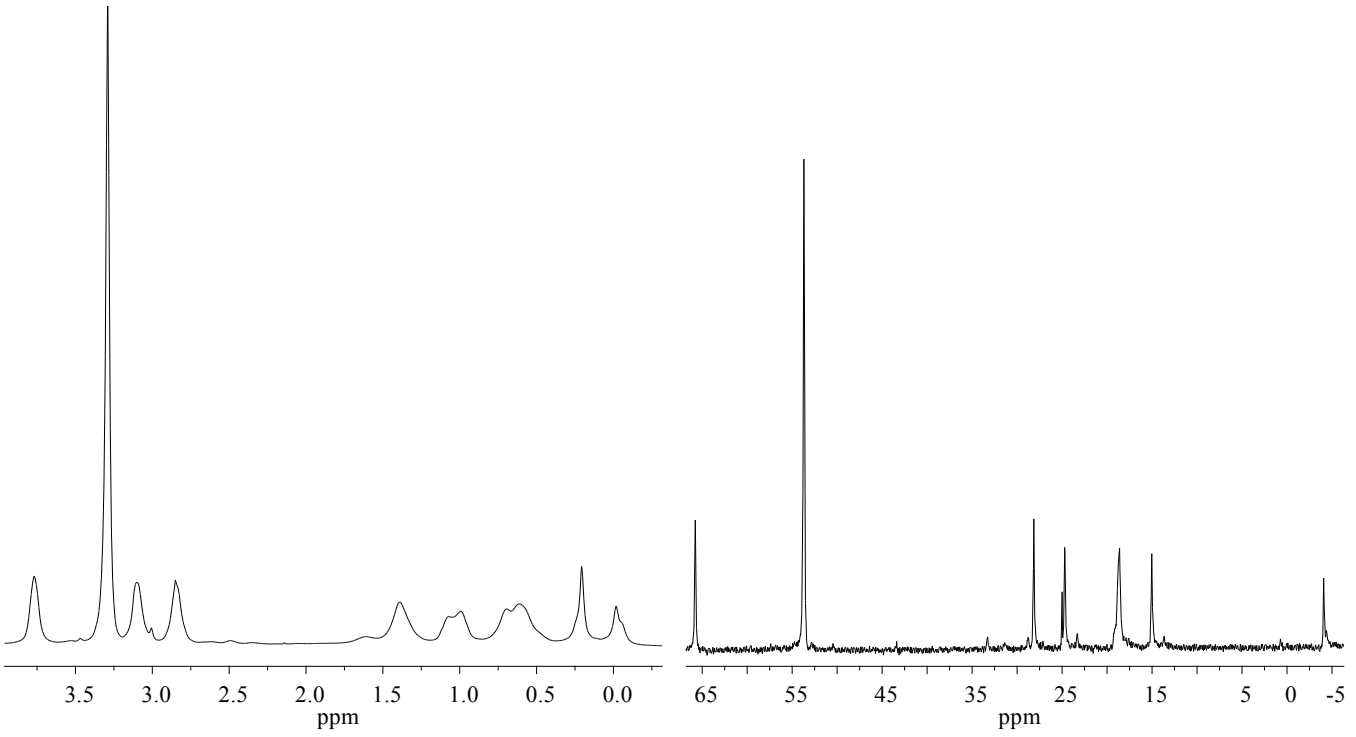


Figure S11. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **9I**.

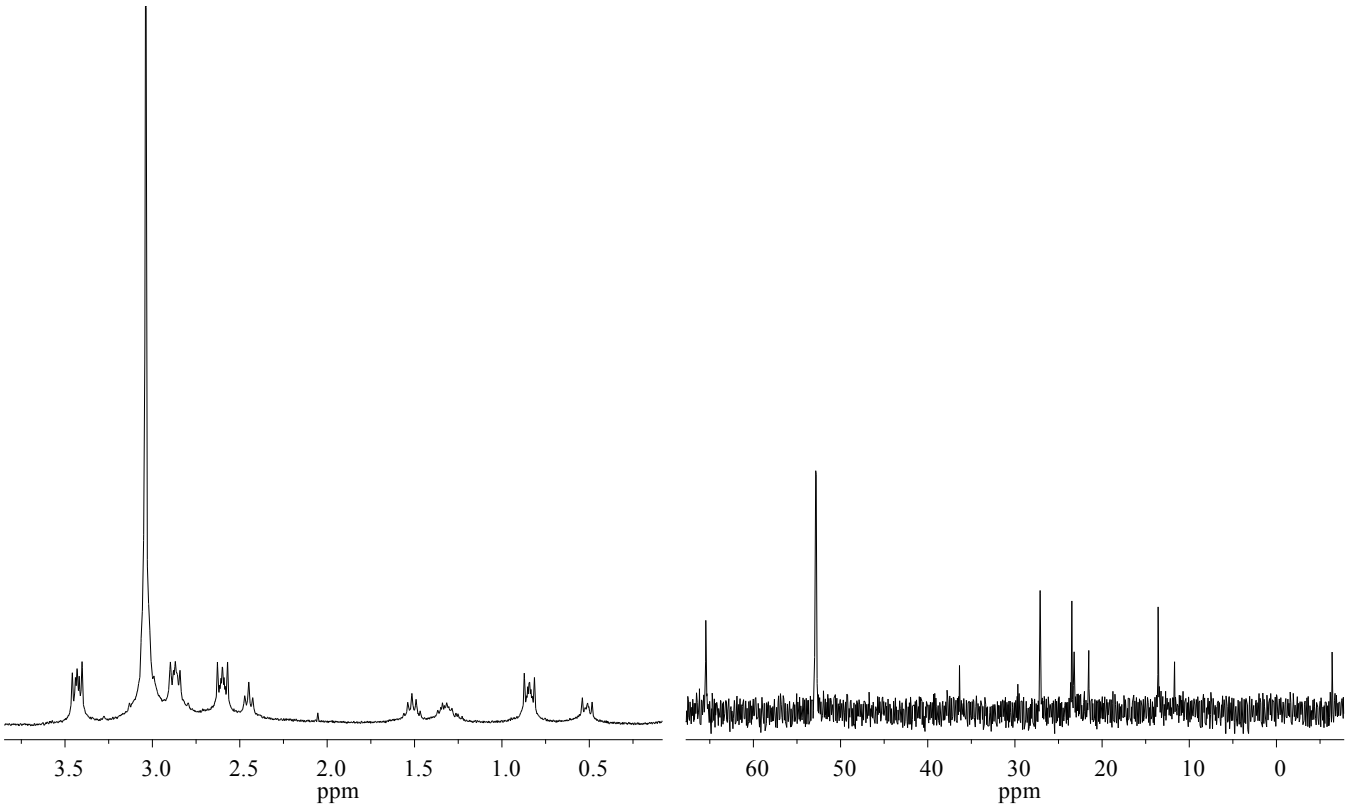


Figure S12. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **7Cl**.

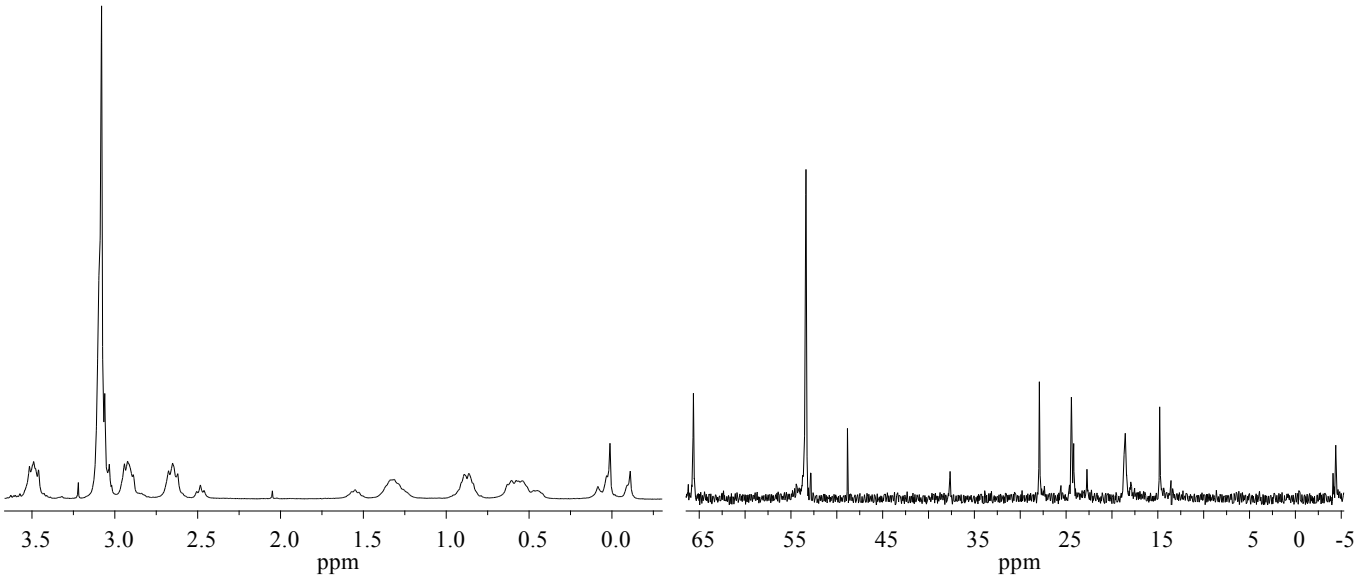


Figure S13. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **8Cl**.

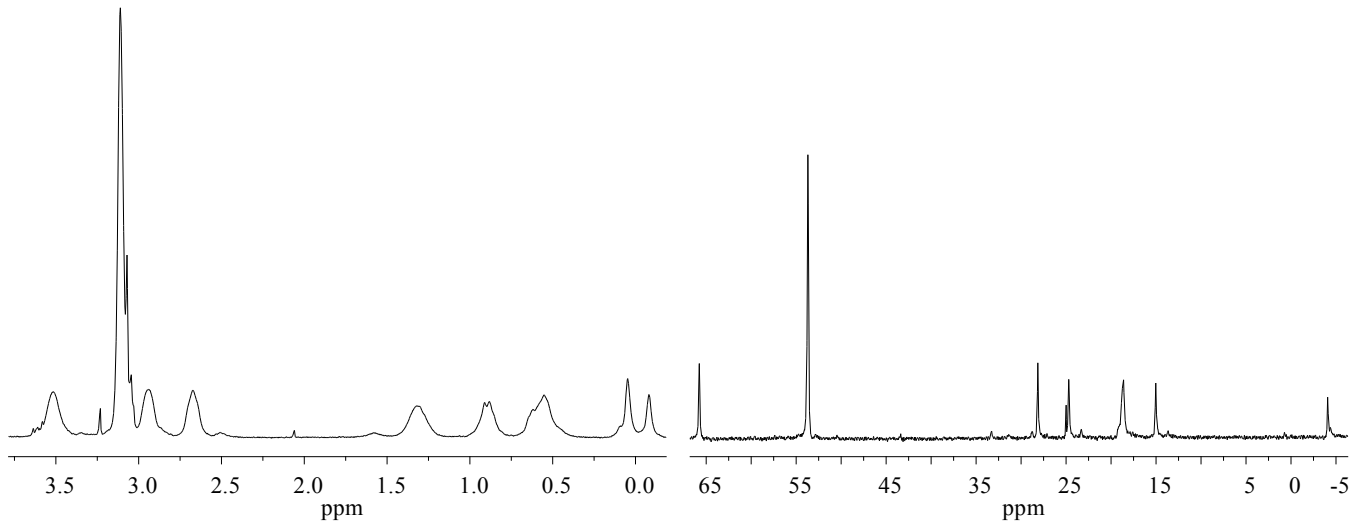


Figure S14. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) compound **9Cl**.

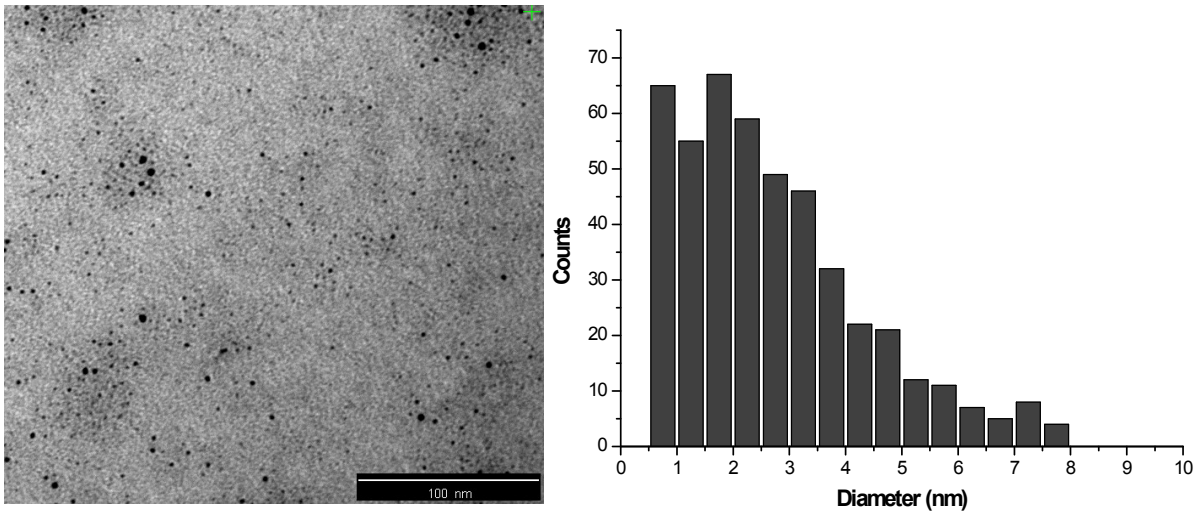


Figure S15. TEM Image and Size distribution histogram associate to **AuNP(SG_2(S-NMe_2)$_4$)** functionalized with neutral second generation dendrons (average size = 1.88 nm (469 measure nanoparticles with Image J program)).

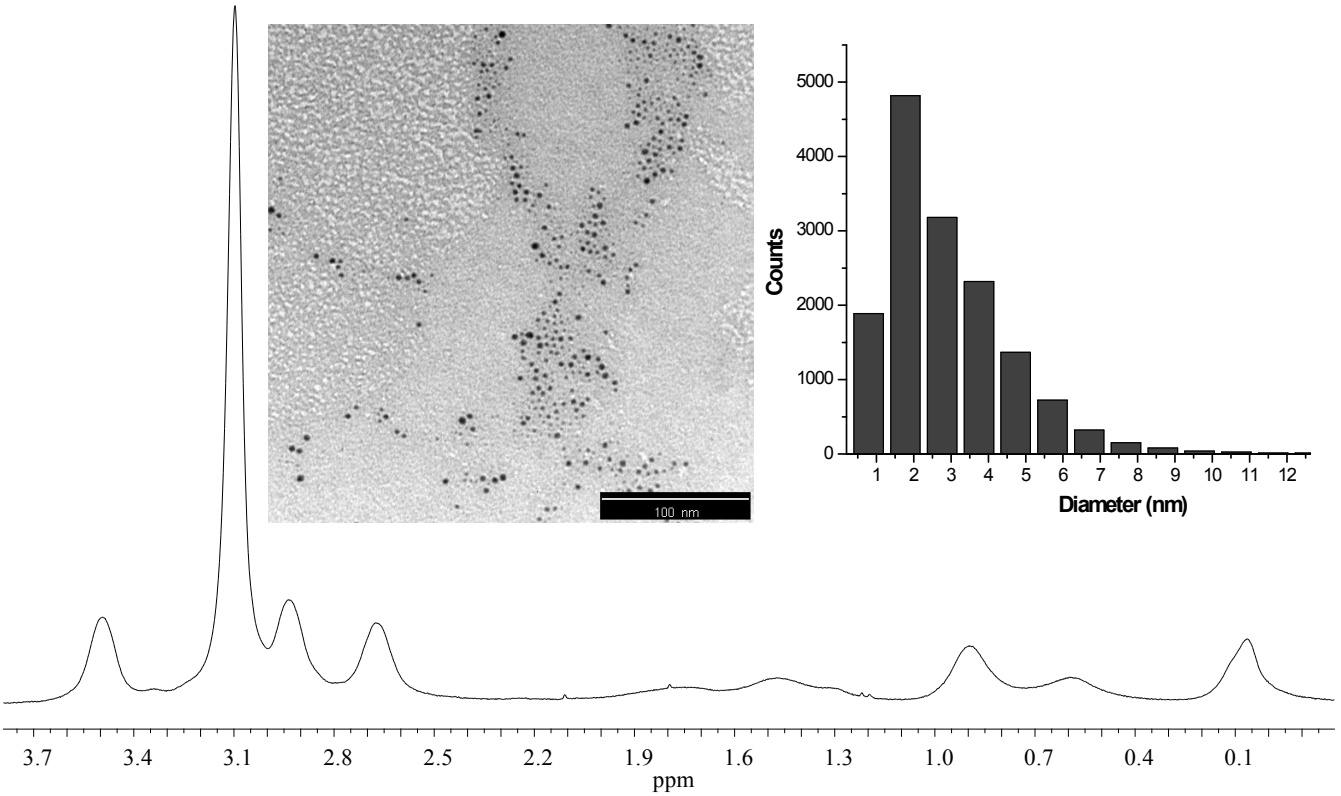


Figure S16. ^{1}H RMN, TEM Image and Size distribution histogram associate to AuNPs **13** functionalized with cationic first generation dendrons **7Cl** (average size = 1.8 nm (14975 measure nanoparticles with Image J program)).

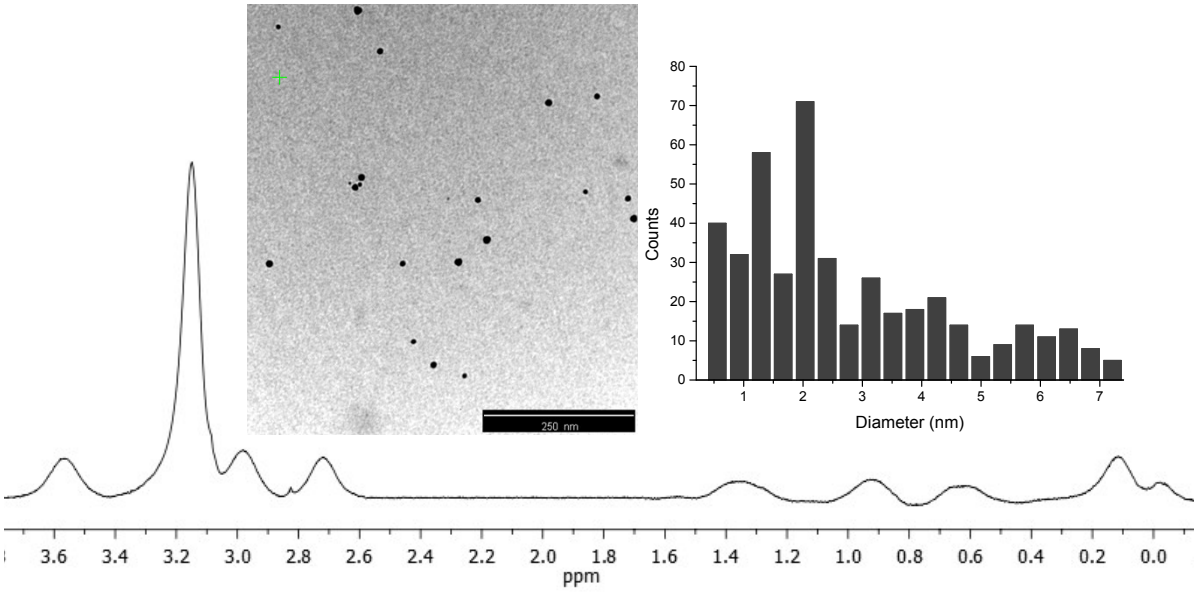


Figure S17. ^{1}H RMN, TEM Image and Size distribution histogram associate to AuNPs **14** functionalized with cationic second generation dendrons **8Cl** (average size = 2.2 nm (789 measure nanoparticles with Image J program)).

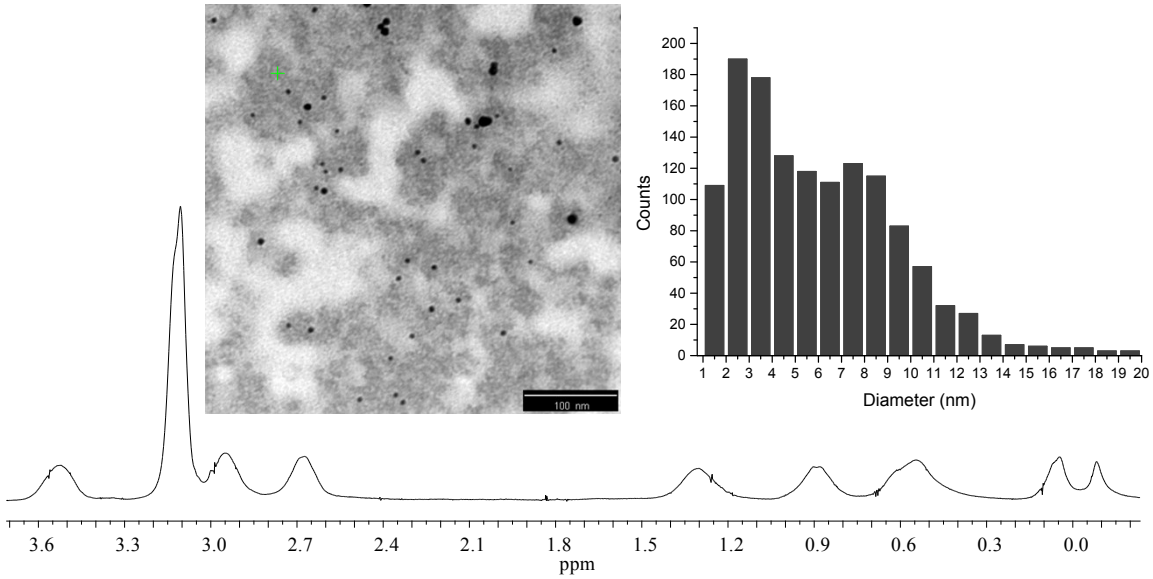


Figure S18.[1]H RMN, TEM Image and Size distribution histogram associate to AuNPs **15** functionalized with cationic thrid generation dendrons **9Cl** (average size = 2.0 nm (1360 measure nanoparticles with Image J program)).

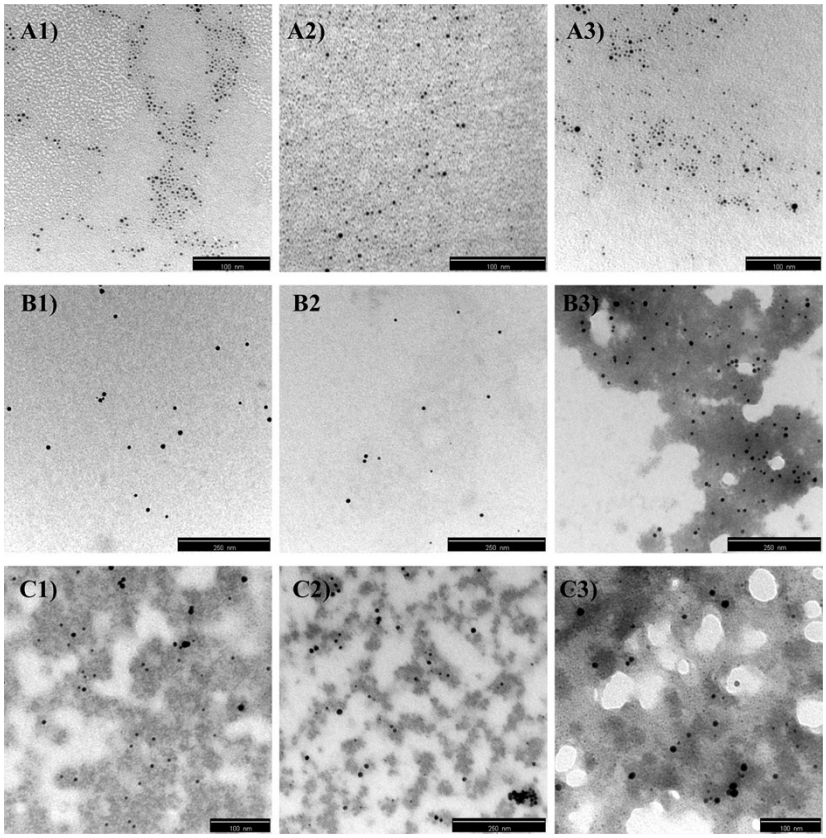


Figure S19. TEM Image of AuNPs **13** (A), **14** (B), and **15** (C) after synthesis (A-C1), 5 months (A-C2), and 10 months (A-C3).

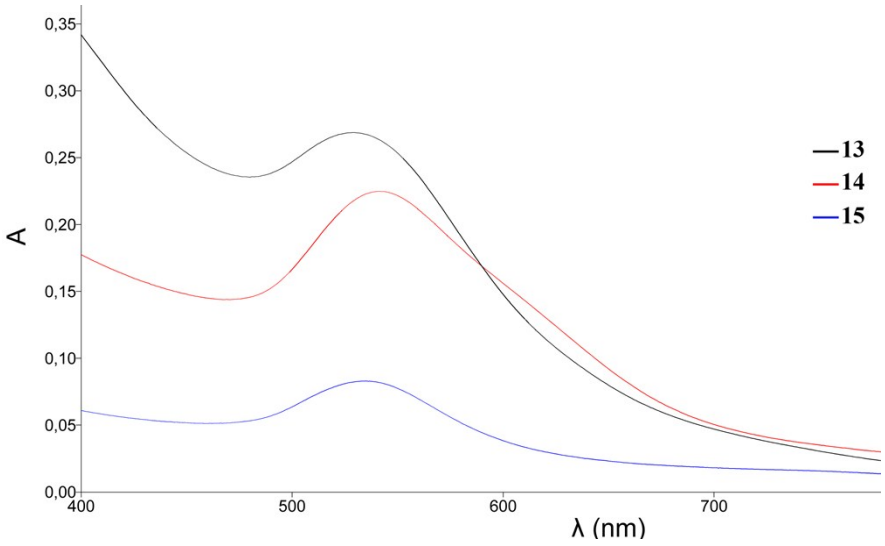


Figure S20. UV-Vis spectra of AuNPs **13-15**.

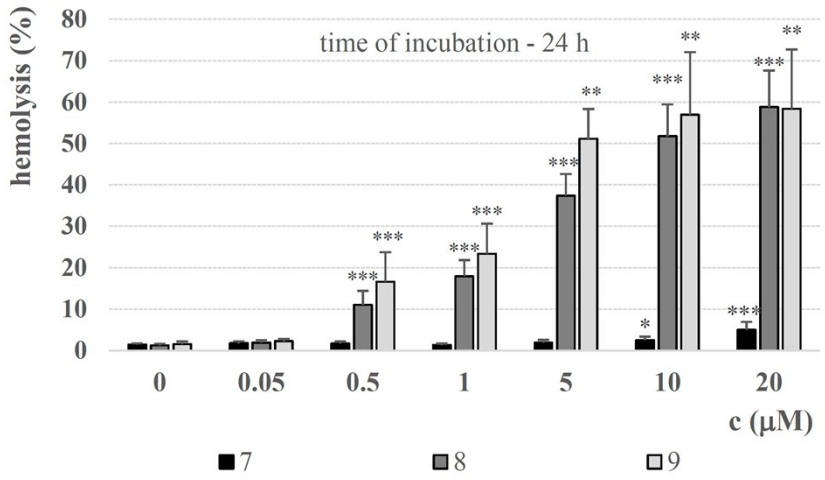


Figure S21. Extent of hemolysis induced by dendrons $HSG_n(S\text{-}NMe_3^+)_m$ (**7-9**) at various concentrations after 24 h incubation. Statistical significance of differences *vs*. control samples of blood erythrocytes alone (at *p < 0.05,**p < 0.01, and ***p < 0.001) was estimated by the *post-hoc* Student t test with the Bonferroni's correction.

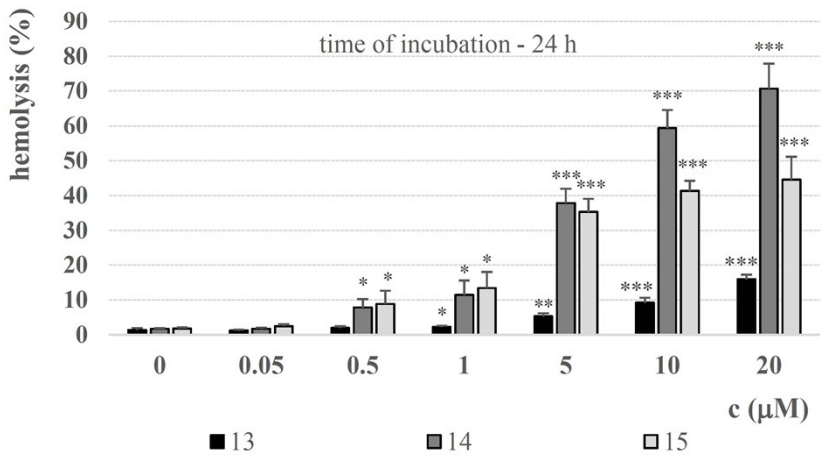


Figure S22. Extent of hemolysis induced by AuNP(SG_n(S-NMe_3^+)$_m$) (**13-15**) at various concentrations after 24h incubation (corresponding to dendron concentration in AuNP). Statistical significance of differences *vs*. control samples of blood erythrocytes alone (at *p < 0.05,**p < 0.01, and ***p < 0.001) was estimated by the *post-hoc* Student t test with the Bonferroni's correction.

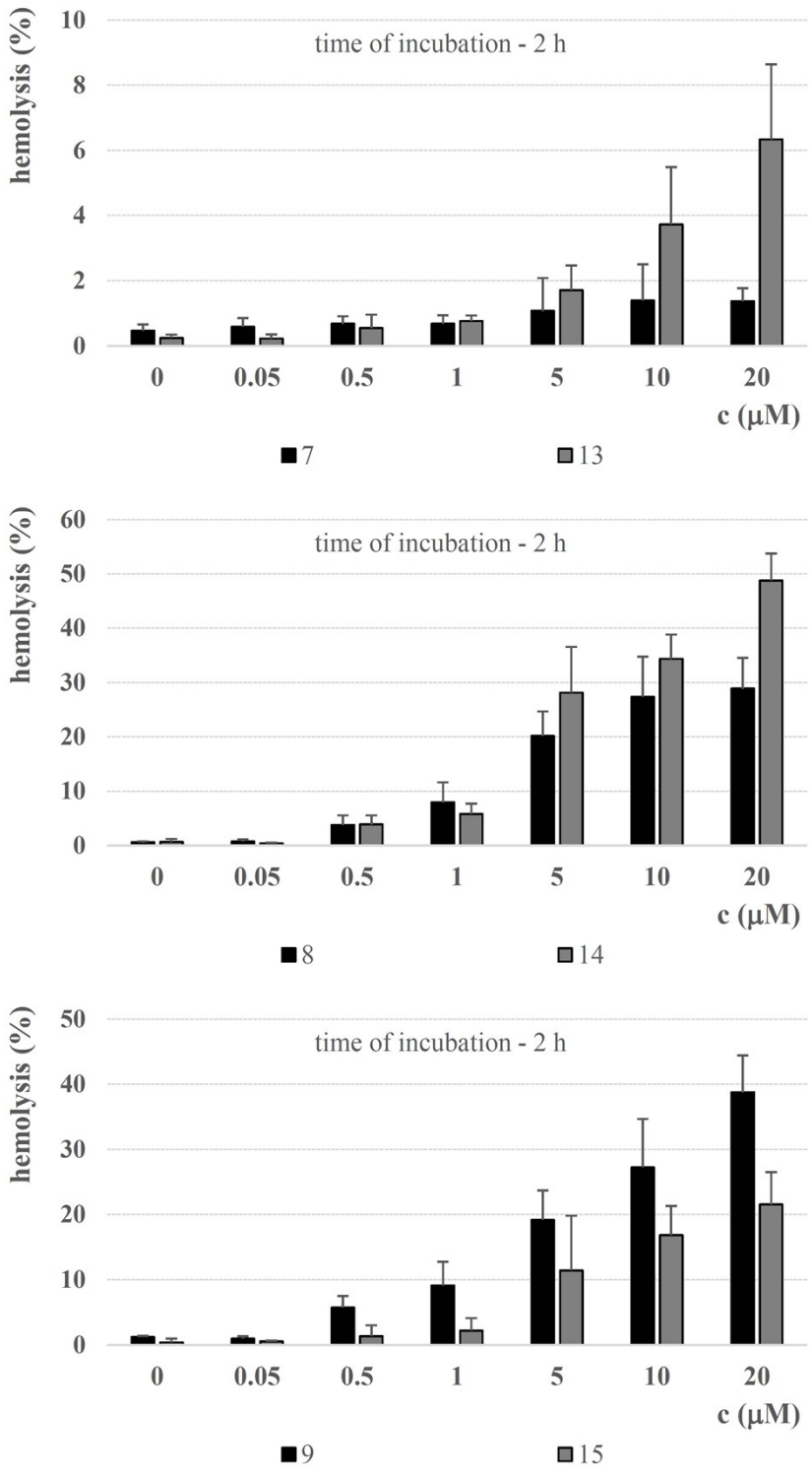


Figure S23. Comparison of hemolysis induced by AuNP($SG_n(S\text{-}NMe_3^+)_m$) (**13-15**) versus corresponding dendrons $HSG_n(S\text{-}NMe_3^+)_m$ (**7-9**) attached to surface after 2 h incubation.

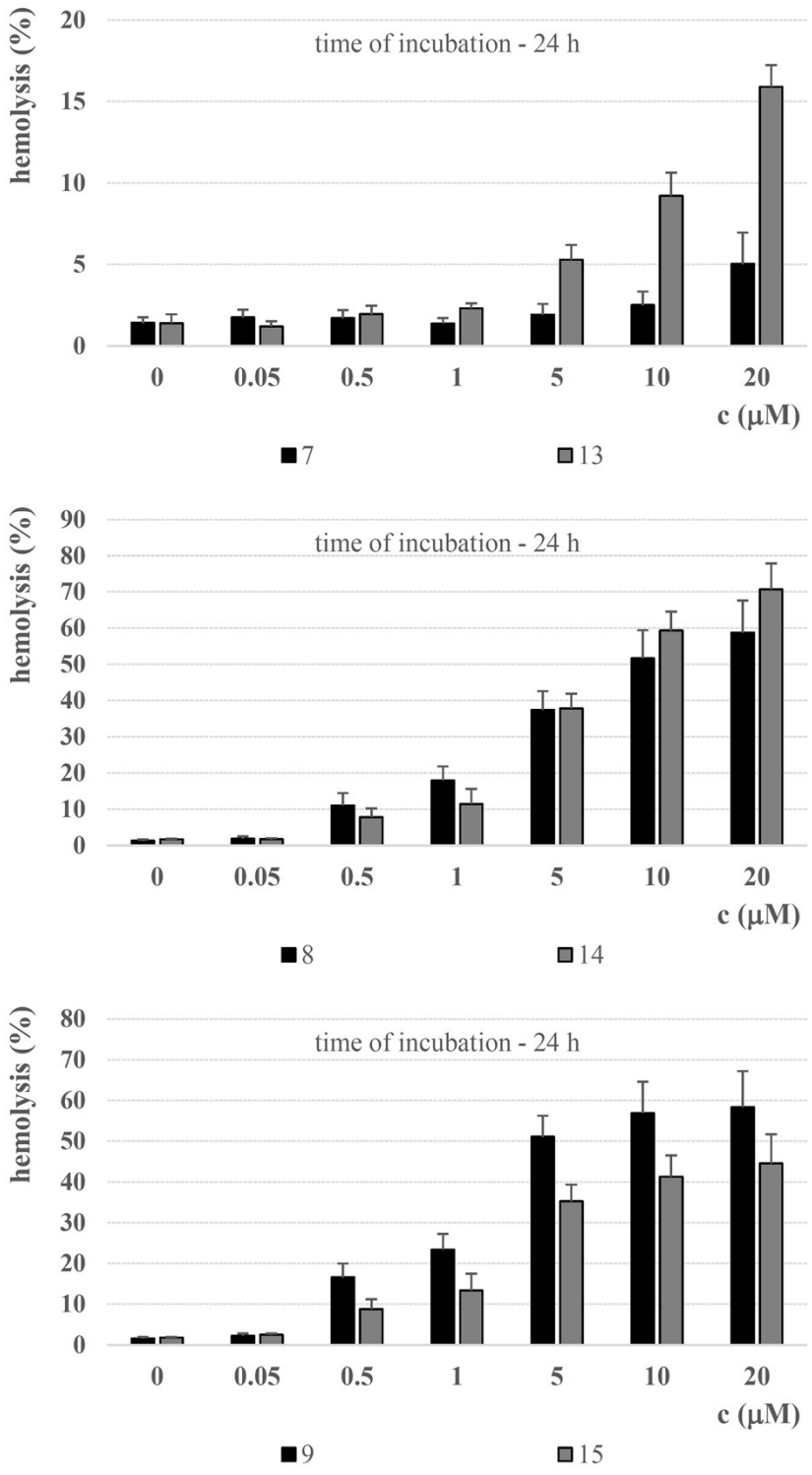


Figure S24. Comparison of hemolysis induced by AuNP($SG_n(S\text{-}NMe_3^+)_m$) (**13-15**) versus corresponding dendrons $HSG_n(S\text{-}NMe_3^+)_m$ (**7-9**) attached to surface after 24 h incubation.

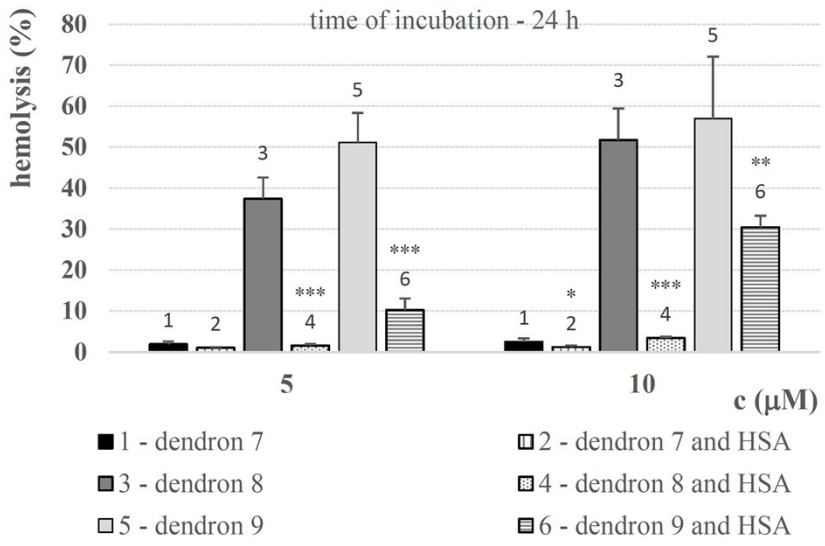


Figure S25. Extent of hemolysis induced by dendrons **7-9** at 5 μM and 10 μM concentration after 24 h incubation in the absence and presence of human serum albumin (HSA). Statistical significance of differences dendron/dendron with HSA (at *p < 0.05,**p < 0.01, and ***p < 0.001) was estimated by paired Student t-test (pSt).

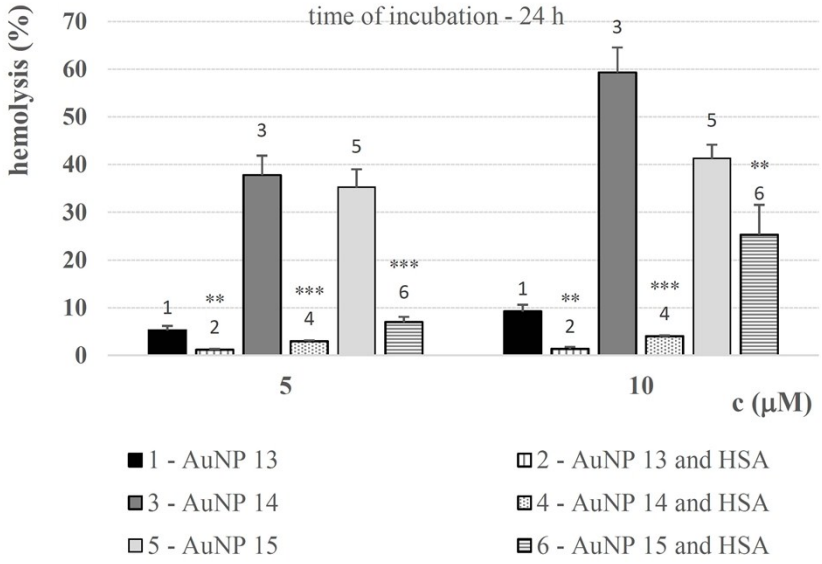


Figure S26. Extent of hemolysis induced by AuNPs **13-15** at 5 μM and 10 μM concentration after 2 h incubation in the absence and presence of human serum albumin (HSA) (corresponding to dendron concentration in AuNP). Statistical significance of differences AuNP/AuNP with HSA (at *p < 0.05,**p < 0.01, and ***p < 0.001) was estimated by paired Student t-test (pSt).

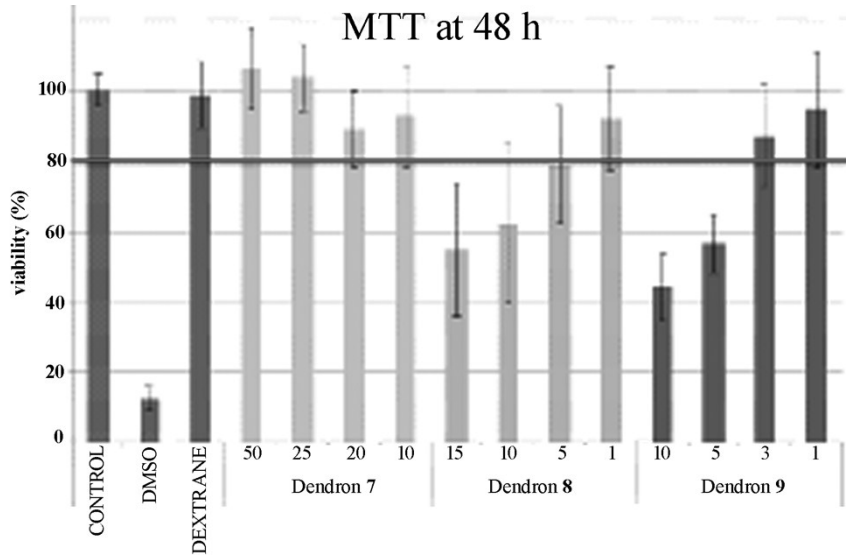


Figure S27. MTT of PBMC cells (μM) at 48 h of dendrons $HSG_n(S\text{-}NMe_3^+)_m$ (**7-9**).

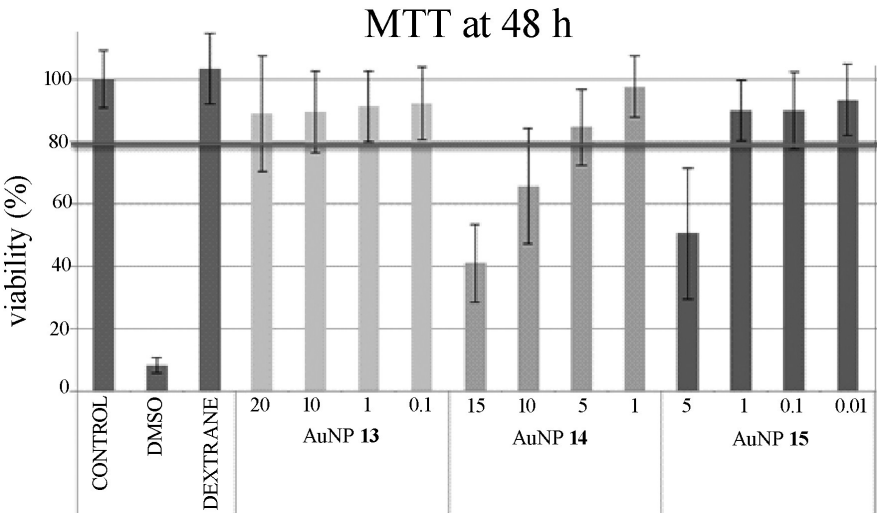


Figure S28. MTT of PBMC cells (μM with respect to dendron concentration) at 48 h of $AuNP(SG_n(S\text{-}NMe_3^+)_m)$ (**13-15**).

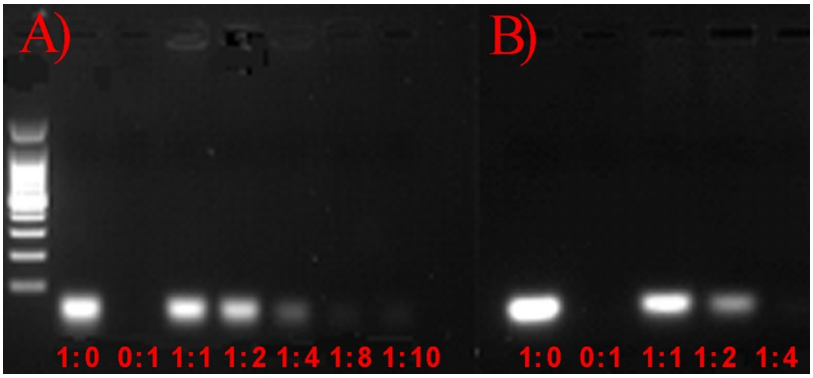


Figure S29. Electrophoresis gel in agarose of dendriplexes formed with $HSG_3(S\text{-}NMe_3^+)_8$ (**9**, A) or $AuNP(SG_1(S\text{-}NMe_3^+)_2)$ (**13**, B) at different siRNA Nef:dendrimer ratios after 48 h of incubation.

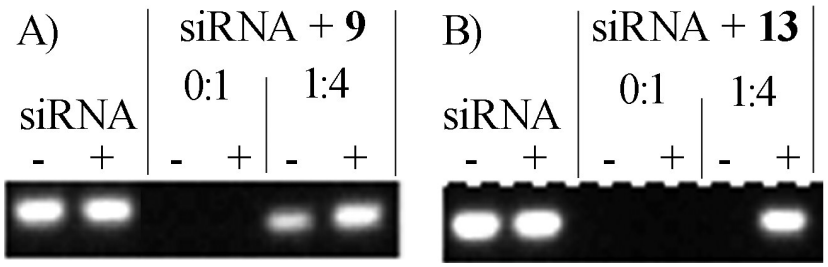


Figure S30. Polyacrylamide gel electrophoresis of dendriplexes/heparine competition (absence of heparin (-), presence of heparin (+)).

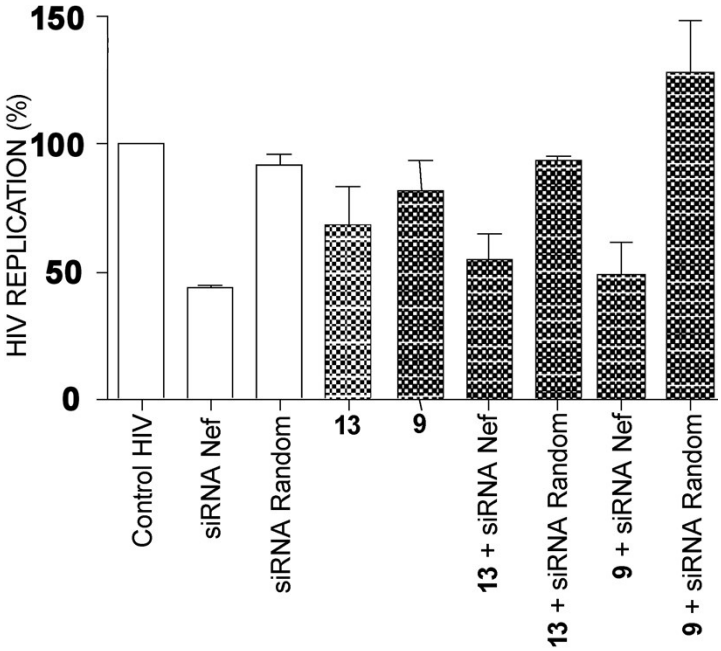


Figure S31. HIV inhibition assay (protein p24 ELISA test) of infected PBMC after 48 h of treatment at -/+ charge ratio 1/4. **9** and **13** mean inhibition in the presence of dendron and AuNP alone below their cytotoxicity levels at those ratios. Dendriplexes with random siRNA were formed at the same charge ratio than siRNA Nef. siRNA concentrations of 200 nM were used. Incubation time for dendriplex formation was 15 min and incubation time of PBMC with HIV virus was 1 h.