

Supporting Information belonging to the paper:

Synthesis of Periphery Functionalized Dendritic Molecules using Polylithiated Dendrimers as Starting Material

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General:

All syntheses were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using a Varian Inova 300 MHz spectrometer. GCMS analyses were performed on a Unicam Automass instrument (EI, 70 eV). MALDI-TOF MS spectra were acquired using a Voyager-DE Biospectrometry Workstation (PerSeptive Biosystems Inc. Framingham, MA) equipped with a nitrogen laser emitting at 337 nm. Microanalyses were performed by Kolbe Microanalytical Laboratories, Mühlheim a/d Ruhr, Germany.

Synthesis of 2a and 2b:

6 equivalents or 20 equivalents of the Grignard reagent, derived from 4-bromophenoxy-*t*-butyldimethylsilane, in THF were added to neat **1a** or neat **1b**, respectively. The reaction mixture was stirred overnight and subsequently heated at reflux during two hours. After addition of water (heat evolution!) the THF was removed by evaporation and aqueous HCl (1.0 molar) was added. The acid water layer was extracted four times with diethyl ether and the combined ether extracts were washed two times with water and dried over MgSO_4 . After filtration and concentration all volatiles (hydrolyzed Grignard reagent) were removed by Kugelrohr distillation (two hours at 120 °C / p = 0.1 mm Hg). The product was purified by column chromatography over silicagel with hexane ---> hexane 5% diethyl ether.

2a: Yield: 77% of pale yellow oil.

^1H NMR (acetone- d_6): δ 7.42 (d, 8H, $^3J_{\text{H-H}} = 8.2$ Hz, Ar-H), 6.90 (d, 8H, $^3J_{\text{H-H}} = 8.5$ Hz, Ar-H), 1.5 - 1.3 (m, 8H, C- CH_2 -C-), 1.04 (s, 36 H, Si-*t*-Bu), 0.9 - 0.7 (m, 8H, CH_2 -Si-Ar), 0.7 - 0.5 (m, 8H, CH_2 -Si- CH_2 -), 0.27 and 0.25 (2 x s, 48H, Si-Me).

^{13}C NMR (acetone- d_6): δ 156.6, 135.2, 131.2, 119.8 (4 x Ar-C); 25.6 (*t*-Bu, primary C); 20.9 (*t*-Bu, quarternary C); 18.8, 18.2, 17.5 (3 x CH_2); -2.8, -4.6 (2 x Si-Me). FAB MS: $m/z = 1242.6$, calc for $(\text{M} - \text{CH}_3)^+ = 1243.5$. MALDI-TOF MS: $m/z = 1364.8$, calc for $(\text{M} + \text{Ag})^+ = 1366.4$. Anal. Calc for $\text{C}_{68}\text{H}_{124}\text{O}_4\text{Si}_9$: C 64.90, H 9.93, Si 20.09. Found: C 64.79, H 9.98, Si 19.83.

2b: Yield: 76 % of a pale yellow oil.

^1H NMR (acetone- d_6): δ 7.43 (d, 24H, $^3J_{\text{H-H}} = 7.3$ Hz, Ar-H), 6.90 (d, 24H, $^3J_{\text{H-H}} = 7.3$ Hz, Ar-H), 1.6 - 1.2 (m, 32H, C- CH_2 -C), 1.05 (s, 108H, Si-*t*-Bu), 1.0 - 0.8 (m, 32H, CH_2 -Si-Ar), 0.8 - 0.5 (m, 32H, CH_2 -C- CH_2), 0.28 and 0.26 (2 x s, 144H, Si-Me).

^{13}C NMR (acetone- d_6): δ 156.6, 135.2, 131.2, 119.9 (4 x Ar-C); 25.7 (*t*-Bu, primary C); 21.1 (*t*-Bu, quarternary C); 18.9, 18.3, 17.6 (internal and external CH_2); -2.6, -4.5 (2 x Si-Me).

Synthesis of 2c:

To a solution of 7.2 g (24.0 mmol) of 4-bromo-*N-t*-butyldimethylsilyl-*N*-methylaminobenzene in 40 ml of diethyl ether was added at -70 °C 30 ml (45.0 mmol) of a solution of 1.5 molar *t*-BuLi in pentane. The reaction mixture was stirred during 30 minutes and the temperature was allowed to rise to -40 °C. To the in situ prepared organo lithium reagent 2.85 g (5.0 mmol) of **1a** dissolved in 15 ml of diethyl ether was added. The reaction mixture was stirred overnight at room temperature. Water was added and the ether layer was washed four times with water and dried over MgSO_4 . After filtration and

concentration all volatiles (hydrolyzed organolithium reagent) were removed by Kugelrohr distillation (two hours at 120 °C / p = 0.1 mm Hg). The product was purified by column chromatography (silicagel / hexane 4% Et₃N). Yield, 73% of a colorless viscous liquid.

¹H NMR (acetone-d₆) δ 7.35 (d, 8H, ³J_{H-H} = 8.5 Hz, Ar-H), 6.96 (d, 8H, ³J_{H-H} = 8.5 Hz, Ar-H), 2.96 (s, 12H, N-CH₃), 1.6 - 1.3 (m, 8H, C-CH₂-C), 1.01 (s, 36H, Si-*t*-Bu), 0.9 - 0.7 (m, 8H, CH₂-Si-Ar), 0.7 - 0.5 m, 8H, CH₂-Si-CH₂), 0.30 (s, 24H, Si-Me), 0.24 (s, 24H, Si-Me).

¹³C NMR (acetone-d₆) δ 152.2, 134.1, 127.6, 118.6 (4 x Ar-C); 36.8 (N-Me); 27.2 (Si-*t*-Bu, primary C); 21.1 (CH₂); 20.7 (Si-*t*-Bu, quarternary C); 18.9, 17.5 (2 x CH₂); -2.7, -3.2 (2 x Si-Me). MALDI-TOF MS: *m/z* = 1286.6, calc for (M + Ag - CH₃ -SiMe₂-*t*-Bu)⁺ = 1288.3. Anal. Calc for C₇₂H₁₃₆N₄Si₉: C 65.98, H 10.46, N 4.27. Found: 66.67, H 10.34, N 4.62.

Synthesis of 2d and 2e:

To a solution containing 4.5 or 15 equivalents of 4-lithio-bromobenzene in diethyl ether was added at 0 °C **1a** or **1b**, respectively. After stirring overnight water was added and the organic layer was washed three times with water and dried over MgSO₄. After filtration and concentration all volatiles (hydrolyzed organolithium reagent) were removed by Kugelrohr distillation (two hours at 120 °C / p = 0.1 mm Hg). The product was purified by column chromatography over silicagel with hexane ---> hexane 10 % diethyl ether.

2d: Yield 75 %.

¹H NMR (acetone-d₆): δ 7.53 (d, 8H, ³J_{H-H} = 8.4 Hz, Ar-H), 7.45 (d, 8H, ³J_{H-H} = 8.4 Hz, Ar-H), 1.5 - 1.2 (m, 8H, C-CH₂-C), 0.9 - 0.7 (m, 8H, CH₂-Si-Ar), 0.7 - 0.4 (m, 8H, CH₂-Si-CH₂), 0.28 (s, 24H, Si-Me).

¹³C NMR (acetone-d₆): δ 138.8, 135.7, 131.2, 123.6 (4 x Ar-C); 20.6, 18.8, 17.5 (3 x CH₂); -2.9 (Si-Me). MALDI-TOF MS: *m/z* = 1159.7, calc for (M + Ag)⁺ = 1161.0. Anal. Calc for C₄₄H₆₄Br₄Si₅: C 50.18, H 6.13, Br 30.35, Si 13.34. Found: C 50.32, H 6.25, Br 30.45, Si 13.31.

2e: yield 60 %.

¹H NMR (chloroform-d₁): δ 7.54 (d, 24H, ³J_{H-H} = 8.2 Hz, Ar-H), 7.42 (d, 24H, ³J_{H-H} = 8.2 Hz, Ar-H), 1.5 - 1.2 (m, 32H, C-CH₂-C), 0.9 - 0.7 (m, 32H, CH₂-Si-Ar), 0.7 - 0.4 (m, 32H, -CH₂-Si-CH₂-), 0.32 (s, 72H, Si-Me).

¹³C NMR (acetone-d₆): δ 138.7, 135.5, 131.2, 123.9 (4 x Ar-C); 20.8, 19.0, 18.9, 18.4, 18.2, 17.7 (internal and external CH₂); -2.5 (Si-Me). MALDI-TOF MS: *m/z* = 3497.3, calc for (M + Ag)⁺ = 3491.6. Anal. Calc for C₁₄₄H₂₁₆Br₁₂Si₁₇: C 51.11, H 6.43. Found: C 51.34, H 6.35.

Synthesis of 2f:

1.85 mmol of **5a** in 25 ml of diethyl ether was quenched with water. The organic layer was washed three times with water and dried over MgSO₄. After filtration and concentration all volatiles were removed by Kugelrohr distillation (two hours at 120 °C / p = 0.1 mm Hg). The product was purified by column chromatography over silicagel with hexane ---> hexane 5 % diethyl ether.

Yield: 73% of a colorless viscous liquid.

^1H NMR (acetone- d_6): δ 7.7 - 7.5 (m, 8H, Ar-H), 7.5 - 7.3 (m, 12H, Ar-H), 1.6 - 1.3 (m, 8H, C- CH_2 -C), 1.0 - 0.8 (m, 8H, CH_2 -Si-Ar), 0.8 - 0.5 (m, 8H, CH_2 -Si- CH_2 -), 0.35 (s, 24H, Si-Me).

^{13}C NMR (acetone- d_6): δ 139.6, 133.8, 129.1, 128.1 (4x Ar-C); 20.8, 19.0, 17.7 (3x - CH_2); -2.8 (Si-Me). MALDI-TOF MS: m/z = 845.0 and 767.9, calc for $(\text{M} + \text{Ag})^+ = 845.4$ and $(\text{M} + \text{Ag} - \text{C}_6\text{H}_5)^+ = 768.3$. Anal. Calc for $\text{C}_{44}\text{H}_{68}\text{Si}_5$: C 71.66, H 9.29, Si 19.04. Found: C 71.77, H 9.35, Si 19.06.

Synthesis of 3a, 3b and 4

The corresponding *t*-butyldimethylsilyl protected derivative was stirred overnight with 2 equivalents of $\text{Et}_3\text{N}\cdot\text{HF}$ in THF. The solvents were evaporated and the residue was washed five times with pentane and subsequently dissolved in CH_2Cl_2 . The solution was washed five times with water and dried over MgSO_4 . After filtration and evaporation of the solvents all volatiles were removed by Kugelrohr distillation during two hours at 80 $^\circ\text{C}$ / $p = 0.1$ mm Hg.

3a: Yield 84 %.

^1H NMR (acetone- d_6): 8.38 (s, 4H, Ar-OH), 7.40 (d, 8H, $^3J_{\text{H-H}} = 8.2$ Hz, Ar-H), 6.93 (d, 8H, $^3J_{\text{H-H}} = 8.2$ Hz, Ar-H), 1.6 - 1.3 (m, 8H, C- CH_2 -C), 0.9 - 0.7 (m, 8H, CH_2 -Si-Ar), 0.7 - 0.5 (m, 8H, CH_2 -Si- CH_2), 0.27 (s, 24H, Si-Me).

^{13}C NMR (acetone- d_6): δ 158.3, 135.3, 128.9, 115.4 (4 x Ar-C); 21.0, 18.9, 17.6 (3 x CH_2); -2.6 (Si-Me). FAB MS: m/z = 823.3, calc for $(\text{M} + \text{Na})^+ = 824.4$. MALDI-TOF MS: m/z = 909.5, calc for $(\text{M} + \text{Ag})^+ = 909.4$. Anal. Calc. for $\text{C}_{44}\text{H}_{68}\text{O}_4\text{Si}_5$: C 65.94, H 8.55, Si 17.52. Found: C 65.76, H 8.64, Si 17.32.

3b: yield 82 %.

^1H NMR (acetone- d_6) δ 8.45 (s, 12H, Ar-OH), 7.38 (d, 24H, $^3J_{\text{H-H}} = 8.2$ Hz, Ar-H), 6.89 (d, 24H, $^3J_{\text{H-H}} = 8.2$ Hz, Ar-H), 1.6 - 1.2 (m, 32H, C- CH_2 -C), 0.9 - 0.7 (m, 32H, CH_2 -Si-Ar), 0.7 - 0.4 (m, 32H, CH_2 -Si- CH_2), 0.25 (s, 72H, Si-Me).

^{13}C NMR (acetone- d_6) δ 158.4, 135.2, 128.8, 115.4 (4 x Ar-H); 21.1, 19.0, 18.9, 18.0, 17.7 (internal and external CH_2); -2.7 (Si-Me). MALDI-TOF MS: m/z = 2736.8, calc for $(\text{M} + \text{Ag})^+ = 2736.8$.

4 Yield 64 % after chromatography (silicagel / hexane : diethyl ether = 1 : 1).

^1H NMR (acetone- d_6): δ 7.29 (d, 8H, $^3J_{\text{H-H}} = 8.5$ Hz, Ar-H), 6.61 (d, 8H, $^3J_{\text{H-H}} = 8.5$ Hz, Ar-H), 4.92 (s (broad), 4H, N-H), 2.79 (s, 12H, N- CH_3), 1.6 - 1.3 (m, 8H, C- CH_2 -C), 0.9 - 0.7 (m, 8H, CH_2 -Si-Ar), 0.7 - 0.5 (m, 8H, CH_2 -Si- CH_2), 0.22 (s, 24H, Si-Me).

^{13}C NMR (acetone- d_6): δ 150.9, 134.7, 124.1, 111.9 (4 x Ar-C); 29.7 (N- CH_3); 21.2, 18.9, 17.6 (3 x CH_2); -2.7 (Si-Me). Anal. Calc for $\text{C}_{48}\text{H}_{80}\text{N}_4\text{Si}_5$: C 67.54, H 9.45, N 6.56. Found: C 67.59, H 9.49, N 6.48.

General Procedure for the Lithiation of 2d and 2e: Synthesis of 5a and 5b.

To 1.5 -3.0 g (0.8 equivalents) of **2d** or **2e** in 20 to 40 ml of diethyl ether was added at ambient temperature 0.9 x 4 equivalents *n*-BuLi (1.6 molar in hexane) for **2d** or 0.9 x 12 equivalents *n*-BuLi (1.6 molar in hexane) for **2e**. A sticky precipitate was formed. The flask was occasionally shaken during one hour with the help of a whirlmixer. As an

alternative the lithiation reaction can be performed with two molar equivalents of *t*-BuLi at $-70\text{ }^{\circ}\text{C}$.

Due to its air and moisture sensitivity the obtained materials were not further analyzed and used as such in further reactions with the appropriate electrophile. However, the quantitative formation of **2f** from reaction of **5a** with H_2O indicated that a quantitative Br-Li exchange had occurred.

Synthesis of **6a**, **6b** and **6c**:

To a suspension of the appropriate organolithium derivative in diethyl ether a slight excess of chlorodiphenylphosphine or chlorodicyclohexylphosphine was added. The reaction mixture was stirred overnight, centrifuged and the solvent was decanted. After evaporation of the solvents the last volatiles from the residue were removed by Kugelrohr distillation during two hours at $130\text{ }^{\circ}\text{C}$ / $p = 0.1\text{ mm Hg}$. The residue was an off white sticky material.

6a: Yield: 97%.

^1H NMR (benzene- d_6): δ 7.6 - 7.2 (m, 32H, Ar-ortho, para H), 7.2 - 6.8 (m, 24H, Ar-meta H), 1.6 - 1.3 (m, 8H, C- CH_2 -C), 0.9 - 0.7 (m, 8H, CH_2 -Si-Ar), 0.7 - 0.5 (m, 8H, CH_2 -Si- CH_2), 0.21 (s, 24H, Si-Me).

^{13}C NMR (benzene- d_6): δ 140.1 (s, Ar-para C, Si- C_6H_4 -P); 138.7 (d, $^1\text{J}_{\text{P-C}} = 12.1\text{ Hz}$, Ar-*ipso* C, Si- C_6H_4 -P); 137.8 (d, $^1\text{J}_{\text{P-C}} = 12.2\text{ Hz}$, Ar-*ipso* C, C_6H_5); 134.2 (d, $^2\text{J}_{\text{P-C}} = 20.0\text{ Hz}$, Ar-ortho C, C_6H_5); 133.9 (d, $^3\text{J}_{\text{P-C}} = 6.7\text{ Hz}$, Ar-meta C, Si- C_6H_4 -P); 133.3 (d, $^2\text{J}_{\text{P-C}} = 18.8\text{ Hz}$, Ar-ortho C, Si- C_6H_4 -P); 128.8 (s, Ar-para C, C_6H_5); 128.7 (d, $^3\text{J}_{\text{P-C}} = 6.7\text{ Hz}$, Ar-meta C, C_6H_5); 20.7, 19.0, 17.7 (3 x CH_2); -2.8 (Si-Me). ^{31}P NMR (benzene- d_6): δ -4.6.

6b: Yield 98 %

^1H NMR (benzene- d_6): δ 7.6 - 7.2 (m, 96H, Ar-ortho, para H), 7.2 - 6.7 (m, 72H, Ar-meta H), 1.8 - 1.4 (m, 32H, C- CH_2 -C), 1.0 - 0.6 (m, 64H, 2x - CH_2), 0.25 (Si-Me).

^{13}C NMR (benzene- d_6): δ 140.1 (s, Ar-para C, Si- C_6H_4 -P); 138.8 (d, $^1\text{J}_{\text{P-C}} = 12.8\text{ Hz}$, Ar-*ipso* C, Si- C_6H_4 -P); 137.8 (d, $^1\text{J}_{\text{P-C}} = 12.1\text{ Hz}$, Ar-*ipso* C, C_6H_5); 134.2 (d, $^2\text{J}_{\text{P-C}} = 20.0\text{ Hz}$, Ar-ortho C, C_6H_5); 134.0 (d, $^3\text{J}_{\text{P-C}} = 6.1\text{ Hz}$, Ar-meta C, Si- C_6H_4 -P); 133.4 (d, $^2\text{J}_{\text{P-C}} = 18.8\text{ Hz}$, Ar-ortho C, Si- C_6H_4 -P); 128.8 (s, Ar-para C, C_6H_5); 128.7 (d, $^3\text{J}_{\text{P-C}} = 6.7\text{ Hz}$, Ar-meta C, C_6H_5); 20.8, 19.1, 17.8 (3 x CH_2 external); 19.3, 18.7, 18.4 (3 x CH_2 internal); -2.6 (Si-Me). ^{31}P NMR (benzene- d_6): δ -4.9.

6c: Yield

^1H NMR (benzene- d_6): δ 7.64 - 7.55 (m, 8H, Ar-ortho H, Si- C_6H_4 -P), 7.51 (d, 8H, $J = 7.0\text{ Hz}$, Ar-meta H, Si- C_6H_4 -P), 2.2 - 0.9 (several m, 96H, Cy-H and C- CH_2 -C), 0.9 - 0.7 (m, 8H, CH_2 -Si-Ar), 0.7 - 0.5 (m, 8H, CH_2 -Si- CH_2), 0.25 (s, 24H, Si-Me).

^{13}C NMR (benzene- d_6): δ 140.0 (Ar-para C, Si- C_6H_4 -P), 136.4 (d, $^1\text{J}_{\text{P-C}} = 20.7\text{ Hz}$, Ar-*ipso* C, Si- C_6H_4 -P), 134.5 (d, $^3\text{J}_{\text{P-C}} = 18.9\text{ Hz}$, Ar-meta C, Si- C_6H_4 -P), 133.4 (d, $^2\text{J}_{\text{P-C}} = 6.7\text{ Hz}$, Ar-ortho C, Si- C_6H_4 -P); 32.9 and 30.4 (d, $^2\text{J}_{\text{P-C}} = 14.0\text{ Hz}$ and 17.1 Hz , 2 x Cy- C_2); 29.2 and 27.3 (d, $^3\text{J}_{\text{P-C}} = 7.9\text{ Hz}$ and 7.3 Hz , 2 x Cy- C_3); 27.5 (d, $^1\text{J}_{\text{P-C}} = 12.2\text{ Hz}$, Cy- C_1); 26.6 (s, Cy- C_4); 20.8, 19.0, 17.6 (3 x CH_2); -2.8 (Si-Me). ^{31}P NMR (benzene- d_6): δ 2.2.

Synthesis of **6a'** and **6b'**:

Because **6a** and **6b** are sensitive towards air oxidation (and always contain some phosphine oxide derivative) for analytical purposes these compounds were fully oxidized to the phosphine oxide derivatives. A solution of **6a** or **6b** in THF was stirred with an

excess of H₂O₂. The reaction mixture was extracted three times with diethyl ether and the combined organic layers were washed with aqueous FeSO₄ (removal of excess peroxide). The ether extract was dried over MgSO₄, filtrated and concentrated. The residue was purified over silicagel (**6a'** EtOAc ----> EtOAc : MeOH = 1 : 1, **6b'** acetone 2% MeOH -> acetone 10% MeOH). All the volatiles were removed by Kugelrohr distillation (two hours at 120 °C / p = 0.1 mm Hg).

For assignment COSY, DEPT, HETCOR and Long Range H-C Correlation techniques were used.

6a': Yield 72 %.

¹H NMR (benzene-d₆): δ 7.9 - 7.5 (m, 24H, Ar-ortho H), 7.5 - 7.3 (m, 8H, Ar-para H), 7.2 - 6.9 (m, 24H, Ar-meta H), 1.6 - 1.3 (m, 8H, C-CH₂-C), 0.9 - 0.7 (m, 8H, CH₂-Si-Ar), 0.7 - 0.5 (m, 8H, CH₂-Si-CH₂), 0.19 (s, 24H, Si-Me).

¹³C NMR (benzene-d₆): δ 145.2 (d, ⁴J_{p-c} = 2.4 Hz, Ar-para C, Si-C₆H₄-P); 134.7 (d, ¹J_{p-c} = 102.0 Hz, Ar-ipso C, Si-C₆H₄-P); 134.2 (d, ¹J_{p-c} = 102.6 Hz, Ar-ipso C, C₆H₅); 133.7 (d, ³J_{p-c} = 11.6 Hz, Ar-meta C, Si-C₆H₄-P); 132.3 (d, ²J_{p-c} = 9.7 Hz, Ar-ortho C, Si-C₆H₄-P); 131.6 (s, Ar-para C, C₆H₅); 131.5 (d, ²J_{p-c} = 9.8 Hz, Ar-ortho C, C₆H₅); 128.5 (d, ³J_{p-c} = 11.6 Hz, Ar-meta C, C₆H₅); 20.4, 19.0, 17.7 (3 x CH₂); -2.8 (Si-Me). ³¹P NMR (benzene-d₆): δ 25.7. MALDI-TOF MS: *m/z* = 1539.5, calc for M⁺ = 1538.2. Anal. Calc for C₉₂H₁₀₄O₄P₄Si₅: C 71.84, H 6.82, P 8.05. Found: C 71.75, H 6.80, P 8.09.

6b': Yield 66 %.

¹H NMR (methanol-d₄): δ 7.8 - 7.2 (m, 168 H, Ar-H), 1.5 - 1.2 (m, 32H, C-CH₂-C), 0.9 - 0.7 (m, 32H, CH₂-Si-Ar), 0.7 - 0.4 (m, 32H, CH₂-Si-CH₂), 0.20 (s, 72H, Si-Me). ¹³C NMR: δ 145.5, 134.0, 133.8, 132.9, 132.6, 132.5, 132.0, 131.9, 131.5, 131.2, 131.0, 129.0, 128.8 (Ar-C); 20.2, 19.1, 18.8, 18.0, 17.5 (CH₂ external and internal); -3.4 (Si-Me). ³¹P NMR (methanol-d₄): δ 36.0. MALDI-TOF MS: *m/z* = 4945.3 and 4867.1, calc for (M + Ag)⁺ = 4946.9 and for (M + Ag - C₆H₅)⁺ = 4869.8. Anal. Calc for C₂₈₈H₃₃₆O₁₂P₁₂Si₁₇: C 71.48, H 7.00, P 7.68, Si 9.87. Found: C 71.56, H 7.06, P 7.65, Si 9.78.

Synthesis of 7, 8, 9, 10a and 10b:

To a suspension of the appropriate organolithium compound, **5a** or **5b**, a slight excess of the corresponding electrophile (DMF, N-*t*-butylphenylimine, acetone or acetylpyridine) was added. The reaction mixture was stirred overnight and subsequently quenched with water. The organic phase was washed three times with water, dried over MgSO₄, filtered and concentrated. The residue was chromatographed over silicagel and the volatiles were removed by Kugelrohr distillation (two hours at 80 °C / p = 0.1 mm Hg).

7: Yield 64 %

¹H NMR (acetone-d₆): δ 10.06 (s, 4H, -CHO), 7.90 (d, 8H, ³J_{H-H} = 7.9 Hz, Ar-H), 7.75 (d, 8H, ³J_{H-H} = 7.9 Hz, Ar-H), 1.6 - 1.3 (m, 8H, C-CH₂-C), 1.0 - 0.7 (m, 8H, CH₂-Si-Ar), 0.7 - 0.5 (m, 8H, CH₂-Si-CH₂), 0.33 (s, 24H, Si-Me).

¹³C NMR (acetone-d₆): δ 192.3 (aldehyde C); 148.2, 137.2, 134.4, 128.8 (4 x Ar-C); 20.3, 18.8, 17.4 (3 x CH₂); -3.1 (Si-Me). MALDI-TOF MS: *m/z* = 957.7, calc for (M + Ag)⁺ = 957.4. Anal. Calc for C₄₈H₆₈O₄Si₅: C 67.87, H 8.07, Si 16.53. Found: C 67.94, H 8.01, Si 16.39.

8: Yield 72 %.

Analysis by NMR showed the presence of amino functionalized terminal groups and phenyl terminal groups in a 4 : 1 ratio.

^1H NMR (acetone- d_6): δ 8.0 - 7.0 (m, Ar-H), 5.17 (s, benzylic-H), 1.6 - 1.2 (m, C- CH_2 -C), 1.16 (s, *t*-Bu), 1.0 - 0.8 (m, CH_2 -Si-Ar), 0.8 - 0.5 (m, CH_2 -Si- CH_2), 0.36 and 0.32 (2x s, Si-Me).

^{13}C NMR (acetone- d_6): δ 148.1, 147.4, 137.3, 133.9, 128.5, 127.7, 127.2, 126.7 (8 x Ar-C); 139.6, 133.8, 129.1, 128.1 (4 x Ar-C); 61.8 (benzylic-C); 51.8 (*t*-Bu, quarternary-C); 30.2 (*t*-Bu, primary-C); 20.9, 18.9, 17.6 (3 x CH_2); 20.8, 18.9, 17.6 (3 x CH_2); -2.7 (Si-Me); -2.8 (Si-Me).

9: Yield: 61%.

^1H NMR (acetone- d_6): δ 7.59 (d, 8H, $^3J_{\text{H-H}} = 8.2$ Hz, Ar-H), 7.53 (d, 8H, $^3J_{\text{H-H}} = 8.2$ Hz, Ar-H), 4.09 (s, 4H, OH), 1.7 - 1.4 (m, 8H, C- CH_2 -C), 1.58 (s, 24H, C-Me), 1.0 - 0.8 (m, 8H, CH_2 -Si-Ar), 0.7 - 0.5 (m, 8H, CH_2 -Si- CH_2), 0.33 (s, 24H, Si-Me).

^{13}C NMR (acetone- d_6): δ 151.2, 136.7, 133.5, 124.4 (4 x Ar-C); 71.6 (benzylic C); 32.0 (C-Me); 20.8, 18.9, 17.6 (3 x CH_2); -2.8 (Si-Me). MALDI-TOF MS: $m/z = 1012.4$, calc for (M + Ag - CH_3 -C(OH)- CH_3) $^+$ = 1018.7. Anal. Calc. for $\text{C}_{56}\text{H}_{92}\text{O}_4\text{Si}_5$: C 69.36, H 9.56. Found: C 69.53, H 9.52.

10a: Yield 64 %.

For assignment APT, DEPT, COSY and HETCOR techniques were used.

^1H NMR (chloroform- d_1): δ 8.50 (d, 4H, $^3J_{\text{H-H}} = 4.6$ Hz, Py-ortho H), 7.64 (d, 8H, $^3J_{\text{H-H}} = 7.9$ Hz, Ar-H), 7.59 (d, 8H, $^3J_{\text{H-H}} = 7.9$ Hz, Ar-H), 7.53 (m, 4H, Py-para H), 7.38 (m, 4H, Py-meta H), 7.07 (m, 4H, Py-meta H), 6.03 (s, 4H, OH), 2.00 (s, 12H, C-Me), 1.6 - 1.4 (m, 8H, C- CH_2 -C), 1.0 - 0.8 (m, 8H, CH_2 -Si-Ar), 0.8 - 0.6 (m, 8H, CH_2 -Si- CH_2), 0.37 (s, 24H, Si-Me).

^{13}C NMR (chloroform- d_1): δ 165.0 (quarternary C); 148.0 (quarternary C); 147.7 (Py-ortho C); 138.5 (quarternary C); 137.2 (Py-para C); 133.8, 125.5 (2 x Ar-C); 122.3, 120.6 (Py-2x meta C); 75.6 (benzylic C); 29.7 (C-Me); 21.0, 19.0, 17.8 (3 x CH_2); -2.3 (Si-Me). MALDI-TOF MS: $m/z = 1223.2$ and 1331.1. Calc for M^+ = 1222.0 and (M + Ag) $^+$ = 1329.9. Anal. Calc. for $\text{C}_{72}\text{H}_{96}\text{N}_4\text{O}_4\text{Si}_5$: C 70.77, H 7.92, N 4.58, Si 11.49. Found: C 70.62, H 8.11, N 4.22, Si 11.50.

10b: Yield 60 %.

^1H NMR (acetone- d_6): δ 8.50 (m, 12H, Py-ortho H), 7.0 - 8.0 (several m, 84H, Ar-H and Py-H), 5.57 (s, 12H, OH), 1.96 (s, 36H, C-Me), 1.6 - 1.2 (m, 32H, C- CH_2 -C), 0.1.0 - 0.7 (m, 32H, CH_2 -Si-Ar), 0.7 - 0.4 (m, 32H, CH_2 -Si- CH_2), 0.25 (s, 72H, Si-Me).

^{13}C NMR (acetone- d_6): δ 166.0, 149.0, 147.8, 137.4, 137.0, 133.4, 125.4, 122.1, 120.4 (9 x Ar-C); 75.6 (benzylic C); 29.4 (C-Me); 20.7, 19.0, 18.9, 18.0, 17.6 (external and internal C); -3.0 (Si-Me).