

## 10. Experimental Section

### 10.1. General remarks

All chemical were purchased from Aldrich, Acros, Fluka and used without further purification. The solvents were dried and purified according to standard procedures.

Schlenk technique were used in the experiments with protective atmosphere.

All reactions were monitored with thin lay chromatography (TLC) on silica gel on an aluminium foil (Merck). For column chromatography silica gel from Merck (230-400 mesh) was used.

All  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR-spectra were recorded with a Bruker spectrometer AC 259 (250 MHz), AM 270 (270 MHz) or AC 500 (500 MHz). For the description of the signals, the following abbreviations were used: s-singlett, d-dublett, dd-dublett of a dublett, t-triplett, q-quartett, m-multipllett, br-broad signal.

Mass spectra were recorded on a Varian spectrometer CH5 DF 7711 and 112 S.

Ionisation by Electron Bombardement was used (EI, ionisation energy 70 eV) or for substances with higher mass Fast Atom Bombardement (FAB).

GPC measurements were carried out with a Waters 150-C ALC/GPC (UV detection at 254 nm) with a toluene standard (calibration: polystyrene)

Elemental analysis were carried out with a Perkin-Elmer EA 240. For several acids and substances with free amines it was impossible to remove all traces of water and no correctdata was obtained.

## 10.2. Synthesis of unpolar dendronized polystyrene

### 10.2.1. General procedure for the hydroboration of allylic compound

To a Schlenk flask was added allyl compound, 9-BBN and dry THF. The mixture was stirred under nitrogen for 24 h. the mixture in THF was used without further purification. The conversion was determined to be 96% (NMR).

### 10.2.2. General procedure for the cross-coupling reaction

A 500-mL flask was charged with Pd(PPh<sub>3</sub>)<sub>4</sub>, THF, aqueous NaOH, aryl halides and adduct of allyl compound and 9-BBN. The mixture was degased with nitrogen. After refluxing for 48 h, The reaction mixture was cooled down to room temperature. The organic layer was separated, washed with brine and dried with magnesium sulfate. Colum chromatography on silica gel with hexane/THF gave the corresponding product.

### 10.2.3. Synthesis of unpolar G1 and G2 dendrons

#### *Allyl 3,5-dibromobenzene (3):*

To a flask was added Tetrakis(triphenylphosphine) Palladium (0) (0.84 g, 0.72 mmol), 30 mL of CHCl<sub>3</sub>, 27 g (215 mmol, in excess) of allylbromide and 29 g (72 mmol) of (3,5-dibromophenyl)trimethyl tin in that order, and then the flask was placed in an oil bath maintained at 70 °C for 48 h. The reaction mixture was cooled, partitioned between 100 mL of ether and 100 ml of one-third saturated potassium fluoride and vigorously stirred for 30 minutes. The resulting precipitate of trimethylstannyl fluoride was removed by gravity filtration, and the organic layer was separated, washed with brine, and dried (MgSO<sub>4</sub>). The crude product was purified by high vacuum distillation (1.0×10<sup>-2</sup> mbar, 55°C), followed by silica gel column chromatography using hexane as eluting solvent to give **3** as a colourless oil (52 %).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.28 (d, 2H), 5.10 (m, 2H), 5.86 (m, 1H), 7.25 (s, 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 39.4 ( $\text{CH}_2$ ), 117.3 ( $\text{CH}=\text{CH}_2$ ), 122.8, 130.4, 131.7, 135.5 ( $\text{CH}=\text{CH}_2$ ), 143.9 (Ar).

MS (70 ev),  $m/z$  (%): 278 (14.0), 276 (27.9), 274 (14.3) ( $\text{M}^+$ ), 197 (13.5), 195 (14.3), 116 (100).

Calcd. for ( $\text{C}_9\text{H}_8\text{Br}_2$ ): C, 39.17; H, 2.92; Found: C, 38.83; H, 2.38.

***Allyl-3,5-bis(3-phenylpropyl)benzene (6):***

To 30 mL of dry THF, was added allyl benzene (5.0 g, 42 mmol), 9-BBN (5.9 g, 47 mmol) and stirred for 24 h. Subsequently, to the mixture was added aqueous NaOH (3M, 16 ml),  $\text{Pd}(\text{PPh}_3)_4$  (0.50 g) and stirred for 48 h under reflux. Chromatographic separation yielded 3.5 g (47%) of **6**.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.05 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.71(m, 8H, Ar $\text{CH}_2$ ), 3.41 (d, 2H, Ar $\text{CH}_2\text{CH}_2$ ), 5.12 (m, 2H,  $\text{CH}_2\text{CH}$ ), 6.05 (m, 1H,  $\text{CH}_2\text{CH}$ ), 6.90 (s, 3H, ArH), 7.30 (m, 6H, ArH), 7.34 (d, 4H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  33.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 35.4(Ar $\text{CH}_2$ ), 40.2 (Ar $\text{CH}_2\text{CH}_2$ ), 115.6 ( $\text{CHCH}_2$ ), 125.7, 126.2, 126.4, 128.2, 128.5 (Ar), 137.7 ( $\text{CHCH}_2$ ), 139.9, 142.4 (Ar).

MS (80 ev);  $m/z$  (%): 354 (31.0) [ $\text{M}$ ] $^+$ .

Anal. calcd for  $\text{C}_{27}\text{H}_{30}$  (354.5): C, 91.48; H, 8.52. Found: C, 91.08; H, 8.34.

***Allyl{3, 5-bis{3-{3, 5-bis[3-phenylpropyl]benzylpropyl}benzylpropyl}benzene (8):***

Compound **8** was obtained by the same procedure as **6**. 1.4 g of **6** (3.3 mmol), 0.58 g of 9-BBN and 8 mL of THF. Subsequently, to the mixture was added aqueous NaOH (3M, 2.5 ml),  $\text{Pd}(\text{PPh}_3)_4$  (0.02 g) and **3** (1.5 mmol, 0.4 g) and stirred for 48 h under reflux. Chromatographic separation yielded 0.78 g (48%) of **8**.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.00 (m, 12H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.72 (m, 24H,  $\text{ArCH}_2$ ), 3.40 (d, 2H,  $\text{ArCH}_2\text{CH}$ ), 5.10 (m, 2H,  $\text{CH}_2\text{CH}$ ), 6.05 (m, 1H,  $\text{CH}_2\text{CH}$ ), 6.86 (s, 9H,  $\text{ArH}$ ), 7.30 (m, 12H,  $\text{ArH}$ ), 7.36 (m, 8H,  $\text{ArH}$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  32.9, 33.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 35.4, 35.5 ( $\text{ArCH}_2$ ), 40.2 ( $\text{ArCH}_2\text{CH}_2$ ), 115.5 ( $\text{CHCH}_2$ ), 126.0, 126.1, 126.4, 127.5, 128.1, 128.2, 128.4 ( $\text{Ar}$ ), 137.7 ( $\text{CH}=\text{CH}_2$ ), 139.9, 142.1, 142.2 ( $\text{Ar}$ ).

MS (80 eV);  $m/z$  (%): 826 (33.9)  $[\text{M}-\text{H}]^+$ .

Anal. calcd for  $\text{C}_{63}\text{H}_{70}$  (827.3): C, 91.47; H, 8.53. Found: C, 90.58; H, 8.18.

***4-Vinyl{3, 5-bis[3-phenylpropyl]benzyl}propyl benzene (9a):***

To 10 mL dry THF solution, was added 1.16 g of **6** (3.3 mmol), 0.48 g of 9-BBN (3.9 mmol). Subsequently, to the mixture was added aqueous NaOH (3M, 3 ml),  $\text{Pd}(\text{PPh}_3)_4$  (0.02 g) and stirred for 48 h under reflux. Chromatographic separation yielded 0.60 g (39%) of **9a**.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.95 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.62 (m, 12H,  $\text{ArCH}_2$ ), 5.26 (d, 1H,  $\text{CH}=\text{CH}_2$ ), 5.75 (d, 1H,  $\text{CH}=\text{CH}_2$ ), 6.74 (dd, 1H,  $\text{CH}=\text{CH}_2$ ), 6.84 (s, 3H,  $\text{ArH}$ ), 7.0-7.40 (m, 14H,  $\text{ArH}$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  32.9, 33.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 35.2, 35.4, 35.6 ( $\text{ArCH}_2$ ), 112.8 ( $\text{CH}=\text{CH}_2$ ), 125.6, 126.0, 126.1, 128.2, 128.4, 128.6, 136.7 ( $\text{CH}=\text{CH}_2$ ), 142.1, 142.2, 142.4 ( $\text{Ar}$ ).

MS (80 eV);  $m/z$  (%): 458 (63.7)  $[\text{M}]^+$ .

Anal. calcd for  $\text{C}_{35}\text{H}_{38}$  (458.7): C, 91.65; H, 8.35. Found: C, 89.92; H, 7.31.

***4-Vinyl-{3, 5-bis {3-[3, 5-bis (3-phenylpropyl) benzylpropyl]benzyl}propyl } benzene (9b):***

To 15 mL dry THF solution, was added 3.3 g of **8** (4 mmol), 0.54 g of 9-BBN (4.4 mmol). Subsequently, to the mixture was added aqueous NaOH (3M, 3 ml), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 g) and stirred for 48 h under reflux. Chromatographic separation yielded 2.0 g (49%) of **9b**.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.03 (m, 14H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.72 (m, 28H, ArCH<sub>2</sub>), 5.27 (d, 1H, CH=CH<sub>2</sub>), 5.74 (d, 1H, CH=CH<sub>2</sub>), 6.72 (dd, 1H, CH=CH<sub>2</sub>), 6.86 (s, 9H, ArH), 7.00-7.40 (m, 24H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 31.9, 33.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 35.4, 35.5 (ArCH<sub>2</sub>), 112.8 (CH=CH<sub>2</sub>), 125.6, 126.0, 126.1, 128.1, 128.2, 128.4, 128.6(Ar), 136.7 (CH=CH<sub>2</sub>), 142.1, 142.2, 142.3(Ar).

MS (80 ev); m/z (%): 930.0 (2.2) M]<sup>+</sup>.

Anal. calcd for C<sub>71</sub>H<sub>78</sub> (931.4): C, 91.56; H, 8.44. Found: C, 90.90; H, 8.20.

#### 10.2.4. Polymerisation of unpolar monomers

Polymerization was carried out in a sealed Schlenck tube under nitrogen atmosphere.

##### *Poly{4-Vinyl[3, 5-bis(3-phenylpropyl)benzyl]propyl benzene} (10a):*

For the polymerisation of G-1 monomer **9a**: 82 mg of **9a**, 107 μL of a 0.05 M solution of BPB in toluene, and 72 μL of toluene, and stirred under nitrogen at 90 °C for 48 h. The raw polymer was dissolved in 1 mL of THF, and precipitated with methanol / water (4:1/v:v) for 3 times and lyophilized from benzene.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.95 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.62 (m, 12H, ArCH<sub>2</sub>), 5.26 (d, 1H, CH=CH<sub>2</sub>), 5.75 (d, 1H, CH=CH<sub>2</sub>), 6.74 (dd, 1H, CH=CH<sub>2</sub>), 6.84 (s, 3H, ArH), 7.0-7.40 (m, 14H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  32.9, 33.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 35.2, 35.4, 35.6 ( $\text{ArCH}_2$ ), 112.8 ( $\text{CH}=\text{CH}_2$ ), 125.6, 126.0, 126.1, 128.2, 128.4, 128.6, 136.7 ( $\text{CH}=\text{CH}_2$ ), 142.1, 142.2, 142.4 (Ar).

MS (80 ev); m/z (%): 458 (63.7)[M] $^+$ .

Anal. calcd for  $\text{C}_{35}\text{H}_{38}$  (458.7): C, 91.65; H, 8.35. Found: C, 89.92; H, 7.31.

***Poly{4-Vinyl{3, 5-bis {3-{3, 5-bis [3-phenylpropyl] benzylpropyl}benzylpropyl} benzene} (10b):***

For the polymerisation of G2 monomer **9b**: 99 mg of **9a**, 63  $\mu\text{L}$  of a 0.05 M solution of BPB in toluene, and 43  $\mu\text{L}$  of toluene, and stirred under nitrogen at 90  $^\circ\text{C}$  for 48 h. The raw polymer was dissolved in 1 mL of THF, and precipitated with methanol / water (4:1/v:v) for 3 times and lyophilized from benzene.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.03 (m, 14H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.72 (m, 28H,  $\text{ArCH}_2$ ), 5.27 (d, 1H,  $\text{CH}=\text{CH}_2$ ), 5.74 (d, 1H,  $\text{CH}=\text{CH}_2$ ), 6.72 (dd, 1H,  $\text{CH}=\text{CH}_2$ ), 6.86 (s, 9H, ArH), 7.00-7.40 (m, 24H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  31.9, 33.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 35.4, 35.5 ( $\text{ArCH}_2$ ), 112.8 ( $\text{CH}=\text{CH}_2$ ), 125.6, 126.0, 126.1, 128.1, 128.2, 128.4, 128.6(Ar), 136.7 ( $\text{CH}=\text{CH}_2$ ), 142.1, 142.2, 142.3(Ar)

### 10.3. Synthese of unpolar dendronized polystyrene with protected amine groups

#### 10.3.1. Synthese of G1 and G2 dendrons with protected amino functional groups

##### *Triphenylmethylaminopropene (11b):*

To a mixture of Allylamine (5.7 g, 0.1 mol) and triethylamine (10.1 g, 0.1 mol) in 100 mL methylene chloride at 0 °C, was added dropwise the solution of triphenylmethyl chloride (27.8 g, 0.1 mol) in 100 mL methylene chloride over 30 minutes, and stirred over night at room temperature. The reaction mixture was added 50 mL H<sub>2</sub>O dropwise, the organic layer was separated and dried over MgSO<sub>4</sub>. The crude product was recrystallised in acetone to give a colorless solid in 91% yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.60 (s, 2H), 2.71 (d, 2H), 5.06 (d, 1H), 5.28 (d, 1H), 5.90 (m, 1H), 7.10-7.60 (m, 15H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 46.4 (CPh<sub>3</sub>), 70.7 (CH<sub>2</sub>), 114.7 (CH=CH<sub>2</sub>), 126.2, 127.4, 128.5 (Ph), 137.2 (CH=CH<sub>2</sub>), 146.0 (Ph).

Ms (80 ev) m/z (%): 299.1 (2.26), 222.1 (100) (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>).

Calcd for C<sub>22</sub>H<sub>21</sub>N (299.4): C, 88.26; H, 7.07; N, 4.68. Found: C, 88.08; H, 7.05; N, 4.56.

##### *3-[2-(Trimethylsilyl)ethoxycarbonylamino]propene (11c):*

To a solution of 24 g (203 mmol) of 2-trimethylsilylethanol and 56 g (406 mmol) of anhydrous potassium carbonate in 200 mL of toluene was added 130 mL of a 20% solution of phosgene (225 mmol) in toluene and stirred for 1 h at 0 °C. After removing the ice bath, the solution was stirred for another hour. The solvent was removed in vacuum at a bath temperature less than 40°C in a well-ventilated hood. A mixture of the raw oil, 6.84 g (120 mmol) of allylamine dissolved in 150 mL THF and 8.5 g (152 mmol) of potassium hydroxide dissolved in 85 ml of water, was stirred at 20 °C for 24.

The organic layer was separated and washed with water (3(100 mL) and dried with magnesium sulfate. Distillation (65 °C, 10<sup>-2</sup> mbar) gave 14.0 g of **11c** (58%) as colourless oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): - 0.04 (s, 9H, TMS), 0.94 (t, 2H, TMSCH<sub>2</sub>), 3.72 (t, 2H, NHCH<sub>2</sub>), 4.13 (t, 2H, OCH<sub>2</sub>), 4.70 (br, 1H, NH), 5.10 (m, 2H, CH<sub>2</sub>=CH), 5.74 (m, 1H, CH<sub>2</sub>=CH).  
<sup>13</sup>C NMR (CDCl<sub>3</sub>): -1.5 (TMS), 17.7 (TMSCH<sub>2</sub>), 43.3 (NHCH<sub>2</sub>), 63.0 (OCH<sub>2</sub>), 115.8 (CH=CH<sub>2</sub>), 134.7 (CH=CH<sub>2</sub>), 156.6 (NHCOO).

MS (80 ev), m/z (%): 201.0 (1.1) (M)<sup>+</sup>.

HRMS: Clcd: 201.11851; Found: 201.11633, deviation: 2.2 (mmu).

Clcd. for C<sub>9</sub>H<sub>19</sub>SiO<sub>2</sub>N (201.3): C, 53.69; H, 9.51; N, 6.96. Found: C, 52.42; H, 9.20; N, 6.60

***Allyl-3,5-bis{3-{2-(trimethylsilyl)ethoxycarbonylamino}propyl} benzene (12a):***

To a dry 250 mL Schlenck flask was added 7.5 g of **11c** (37.5 mmol), 5.0 g (41.2 mmol) of 9-BBN and 80 mL of dry THF. The mixture was stirred under nitrogen for 24 h. The resulting mixture in THF was used without further purification. The conversion was determined to be 96% (NMR).

To the above solution of THF, was added 18 mL of aqueous 3 M NaOH, 0.63 g (0.55 mmol) of tetrakis(triphenylphosphine)palladium (0) and 4.0 g (14.4 mmol) of allyl -3,5-dibromobenzene. The mixture was stirred for 48 h at 77 °C. The organic layer was separated, washed with brine, and dried (MgSO<sub>4</sub>). Chromatographic separation (silica gel, hexane/ethyl acetate (4:1/v:v) yielded 6.0 g (79 %) of **12a** as colourless oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.00 (s, 18H, TMS), 0.95 (t, 4H, TMSCH<sub>2</sub>), 1.77 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.55 (t, 4H, ArCH<sub>2</sub>), 3.18 (m, 4H, NHCH<sub>2</sub>), 3.30 (d, 2H, ArCH<sub>2</sub>CH), 4.14 (t, 4H, OCH<sub>2</sub>), 4.70 (br, 2H, NH), 5.06 (m, 2H, CH<sub>2</sub>=CH), 5.92 (m, 1H, CH<sub>2</sub>=CH), 6.81 (s, 3H, ArH).



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): -1.5 (TMS), 17.7 ( $\text{TMSCH}_2$ ), 31.6 ( $\text{CH}_2$ ), 32.8, 40.0, 40.4, 62.8 ( $\text{OCH}_2$ ), 115.7, 126.2, 126.3, 137.4, 140.2, 141.6 (Ar), 156.7 ( $\text{NHCOO}$ ).

MS (80 ev), m/z (%): 520.2 (8.73) ( $\text{M}^+$ ).

Clcd. for  $\text{C}_{27}\text{H}_{48}\text{N}_2\text{O}_4\text{Si}_2$  (520.8): C, 62.26; H, 9.29; N, 5.38. Found: C, 61.62; H, 9.01; N, 5.15.

***Allyl 3,5-Ditriphenylmethylaminopropyl benzene (12b):***

A 500-mL flask was charged with  $\text{Pd}(\text{PPh}_3)_4$  (1.1 g, 1 mmol), THF (140 mL), aqueous 3 M NaOH (25 mL), Allyl 3,5-dibromobenzene (7.0 g, 25 mmol) and B-triphenylmethylaminopropyl-9-BBN (60 mmol). After refluxing for 48 h, The reaction mixture was cooled down to room temperature. The organic layer was separated, washed with brine and dried with magnesium sulfate. Column chromatography on silica gel with hexane/THF (100:4) gave **12b** as a white solid in 67 % yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.62 (s, 2H, NH), 1.9 (m, 4H,  $\text{CH}_2$ ), 2.38 (t, 4H,  $\text{CH}_2\text{NH}$ ), 2.72 (t, 4H,  $\text{CH}_2\text{Ar}$ ), 3.41 (t, 2H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.20 (m, 2H,  $\text{CH}_2=\text{CH}$ ), 6.09 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 6.94 (s, 3H, ArH), 7.10-7.80 (br, 30H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  32.5, 33.7, 40.2, 43.4, 70.8, 115.5, 118.5, 126.0.

MS (EI) m/z (%): 716.3 (0.35) [ $\text{M}^+$ ], 243.1 (100) ( $\text{CPh}^+_3$ ).

Calcd. for  $\text{C}_{53}\text{H}_{52}\text{N}_2$  (717.0): C, 88.78; H, 7.31; N, 3.91. Found: C, 88.33; H, 7.61; N, 3.66.

***Allyl 3,5-Bis(3-aminopropyl)benzene 2 • Trifluoroacetic acid (12c):***

To a solution of **12b** (4.0 g, 5.6 mmol) in  $\text{CHCl}_3$  (6 mL) and absolute MeOH (5ml, used as scavenger of Trityl group), was added Trifluoroacetic acid (10 mL) dropwise with stirring at  $0^\circ\text{C}$ , and the solution was stirred for 2 h. The crude product was separated and washed with  $\text{CHCl}_3$  (3 $\times$ 2 mL) and dried in vacuum to give an oily product.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  1.9 (q, 4H,  $\text{CH}_2\text{CH}_2\text{NH}_3^{\oplus}$ ), 2.6 (t, 4H,  $\text{CH}_2\text{Ar}$ ), 2.9 (t, 4H,  $\text{CH}_2\text{NH}_3^{\oplus}$ ), 3.3 (d, 2H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.0 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 5.3 (s, 6H,  $\text{NH}_3^{\oplus}$ ), 5.9 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 6.9 (s, 3H, ArH).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  30.3, 33.3, 40.3, 41.0, 115.9 ( $\text{CH}=\text{CH}_2$ ), 127.2, 127.7 (Ar), 138.8 ( $\text{CH}=\text{CH}_2$ ), 142.1, 142.3 (Ar), 161.0 (q,  $\text{CF}_3\text{COO}$ ). FAB, m/z (%): 465 [233+diamino] (cluster); 233 (100) [ $\text{M}-\text{CF}_3\text{COOH}-\text{CF}_3\text{COO}^-$ ]. Calcd. for  $\text{C}_{19}\text{H}_{26}\text{O}_4\text{F}_6\text{N}_2$  (460.1): C, 49.57; H, 5.65; N, 6.09. Found: C, 49.49; H, 5.32; N, 6.30.

*Allyl-3,5-bis{3-[3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino] propyl]benzyl} propyl]benzene (13a):*

Compound **13a** was obtained according to the same procedure as compound **12a**. For the hydroboration, 1.08 g (8.8 mmol) of 9-BBN and 3.8 g (7.4 mmol) of **12** in 20 ml of THF, the mixture was stirred for 24 h. To the solution of THF, was added 4 ml of aqueous 3 M NaOH, 0.14 g (0.12 mmol) of tetrakis(triphenylphosphine) palladium (0), and 0.94 g (3.4 mmol) of **3**. The mixture was stirred for 48 h at 77 °C. After work-up, Chromatographic separation (silica gel, hexane/ethyl acetate (3:2/v:v) yielded 2.8 g of **13a** (70%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz): 0.00 (s, 36H, TMS), 0.97 (t, 8H,  $\text{TMSCH}_2$ ), 1.78 (m, 8H,  $\text{NHCH}_2\text{CH}_2\text{CH}_2$ ), 1.88 (m, 4H,  $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{Ar}$ ), 2.54 (t, 16H,  $\text{ArCH}_2$ ), 3.18 (m, 8H,  $\text{NHCH}_2$ ), 3.30 (d, 2H,  $\text{ArCH}_2\text{CH}$ ), 4.12 (t, 8H,  $\text{OCH}_2$ ), 4.74 (br, 4H, NH), 5.06 (m, 2H,  $\text{CH}_2=\text{CH}$ ), 5.93 (m, 1H,  $\text{CH}_2=\text{CH}$ ), 6.80 (s, 9H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62 MHz): -1.5 (TMS), 17.7 ( $\text{TMSCH}_2$ ), 31.6 ( $\text{CH}_2$ ), 32.8, 33.0, 35.5, 40.1, 40.5, 62.7 ( $\text{OCH}_2$ ), 115.5, 125.1, 125.8, 126.1, 126.3, 137.6, 139.8, 141.4, 142.3, 142.5, 156.7 (NHCOO).

MS (EI, 80 ev), m/z (%): 1158.8 (2.20) ( $\text{M}-\text{H}$ ) $^+$ .

Clcd for  $\text{C}_{63}\text{H}_{106}\text{N}_4\text{O}_8\text{Si}_4$  (1159.7): C, 65.24; H, 9.21; N, 4.83. Found: C, 64.38; H, 8.80; N, 4.60.

***Allyl-3,5-bis{3-[3,5-bis(3-triphenylmethylamino)propyl]benzylpropyl}benzene (13b):***

By the method for **12a**. 6.4 g (9.0 mmol) of **12b**, 1.32 g (10.8 mmol) of 9-BBN, 28 mL of dry THF. Subsequently, 1.0 g (3.6 mmol) of **3**, 20 mL of 1 M NaOH, 0.08 g of Pd(PPh<sub>3</sub>)<sub>4</sub>. Chromatographic separation (silic gel, hexane/ethyl acetate (2:1/v:v) gave 3.4 g (61%) of **13b**.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.55 (s, 4H, NH), 1.87 (dt, 8H, CH<sub>2</sub>CH<sub>2</sub>NH), 1.95 (dt, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.25 (t, 8H, CH<sub>2</sub>NH), 2.60 (m, 16 H, ArCH<sub>2</sub>), 3.41 (d, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.19 (m, 2H, CH=CH<sub>2</sub>), 6.03 (m, 1H, CH=CH<sub>2</sub>), 6.83 (s, 6H, ArH), 6.90 (s, 3H, ArH), 7.24 (m, 36H, ArH), 7.48 (d, 24H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 32.5, 33.0, 33.7, 35.6, 40.2, 43.5, 70.8, 115.5, 125.7, 125.8, 126.1, 126.4, 127.7, 128.6, 137.7, 139.8, 142.3, 146.2.

FAB; m/z (%): 1552.9 (3.9) (M<sup>+</sup>).

Clcd. for C<sub>115</sub>H<sub>114</sub>N<sub>4</sub> (1553.2): C, 89.03; H, 7.35; N, 3.61. Found: C, 88.13; H, 7.25; N, 3.76.

***Allyl-3,5-bis{3-[3,5-bis(3-aminopropyl)benzyl]propyl}benzene 4 (CF<sub>3</sub>CO<sub>2</sub>H) (13c):***

To a solution of 4.5 g (2.9 mmol) of **13b** in 8 mL of methanol and 8 mL of dichloromethane, was added dropwise 5 mL of trifluoroacetic acid with stirring at 0 °C. Then, the solution was stirred for 24 h at r.t.. After removal of the solvents, 10 mL of diethylether and 5 mL of water was added. The aqueous layer was separated and the extraction was repeated for 3 times. The combined aqueous layer were dried after removal of water in vacuum to give 2.3 g (76%) of **13c** as white solid.

<sup>1</sup>H NMR (CD<sub>3</sub>OD): 1.95 (m, 12H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.65 (m, 16H, CH<sub>2</sub>Ar), 2.92 (t, 8H, CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>), 3.32 (d, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.05 (m, 2H, CH=CH<sub>2</sub>), 5.93 (m, 1H, CH=CH<sub>2</sub>), 6.92 (s, 3H, ArH), 6.94(s, 6H, ArH).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ ): 30.2, 33.4, 34.6, 36.4, 36.5, 40.3, 41.1, 115.7, 118.2 (q,  $\text{CF}_3\text{CO}_2$ ), 126.9, 127.3, 127.5, 139.1, 141.2, 143.6, 144.4, 161.7 (q,  $\text{CF}_3\text{COO}$ ).

FAB;  $m/z$  (%): 583 (27) [cluster of tetraamine] [ $\text{M}+3(\text{CF}_3\text{COOH}-\text{CF}_3\text{COO}-)$ ].

Clcd. for  $\text{C}_{47}\text{H}_{62}\text{N}_4\text{O}_8\text{F}_{12}$  (1038.0): C, 54.33; H, 6.01; N, 5.39. Found: C, 52.91; H, 5.83; N, 5.99.

### 10.3.2. Synthese of G1 and G2 monomers with protected amino functional groups

#### *4-Vinyl-{3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl}benzyl}propyl benzene (14a):*

To a solution of **12a** (7.4 mmol) in THF was added 20 ml of aqueous 1 M NaOH, 0.2 g (0.18 mmol) of tetrakis(triphenylphosphine)palladium (0) and 1.9 g (10.4 mmol) of 4-bromostyrene. The mixture was stirred for 40 h at 77 °C. The organic layer was separated, washed with brine, and dried ( $\text{MgSO}_4$ ). Chromatographic separation (silica gel, hexane/ethyl acetate (3.5:1/v:v) gave 3.0 g (67 %) of **14a** as colourless oil.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 0.03 (s, 18H, TMS), 0.95 (t, 4H,  $\text{TMSCH}_2$ ), 1.77 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.90 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.57 (t, 6H, Ar $\text{CH}_2$ ), 2.61 (t, 2H, Ar $\text{CH}_2$ ), 3.15 (m, 4H,  $\text{NHCH}_2$ ), 4.14 (t, 4H,  $\text{OCH}_2$ ), 4.75 (br, 2H, NH), 5.19 (d, 1H,  $\text{CH}=\text{CH}_2$ ), 5.70 (d, 1H,  $\text{CH}=\text{CH}_2$ ), 6.69 (dd, 1H,  $\text{CH}_2=\text{CH}$ ), 6.81 (s, 3H, ArH), 7.23 (AA', BB', 4H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): -1.5 (TMS), 17.7 ( $\text{TMSCH}_2$ ), 31.6, 32.8, 32.9, 35.2, 40.4 ( $\text{CH}_2$ ), 62.8 ( $\text{OCH}_2$ ), 112.8, 126.1, 126.2, 128.5, 135.1, 136.6, 141.5, 142.0, 142.4 (Ar), 156.7 (NHCOO).

MS (80 ev),  $m/z$  (%): 624.0 (3.26) ( $\text{M}-\text{H}$ ) $^+$ .

Clcd. for  $\text{C}_{35}\text{H}_{56}\text{N}_2\text{O}_4\text{Si}_2$  (625.0): C, 67.26; H, 9.03; N, 4.48. Found: C, 66.59; H, 8.79; N, 4.27.

***4-Vinyl-[3,5-bis(3-triphenylmethylaminopropyl)benzyl]propyl benzene (14b):***

Compound **14b** was prepared according to the same procedure as compound **14a**. **12b** (7.5 mmol) in 50 mL of THF, 16 mL of 1 M NaOH, 2.1 g (11 mmol) of p-bromostyrene. Chromatographic separation (silica gel, hexane/THF (30:1/v:v)) furnished 4.2 g (69%) of **14b** as a viscous oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.60 (s, 2H, NH), 1.82 (q, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.96 (q, 2H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.27 (t, 4H, NHCH<sub>2</sub>), 2.65 (m, 8H, ArCH<sub>2</sub>), 5.26 (d, 1H, CH=CH<sub>2</sub>), 5.75 (d, 1H, CH=CH<sub>2</sub>), 6.74 (dd, 1H, CH=CH<sub>2</sub>), 6.83 (s, 3H, ArH), 7.15-7.60 (m, 34H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 32.6, 32.9, 33.7, 35.3, 43.4, 70.8, 112.8, 125.8, 126.1, 127.7, 128.6, 136.6, 142.1, 142.3, 146.2.

MS (EI, 80 ev), m/z (%) 820.1 (1,64) (M<sup>+</sup>).

Clcd. for C<sub>61</sub>H<sub>60</sub>N<sub>2</sub> (820.1 ): C, 89.27; H, 7.32; N, 3.41. Found: C, 87.93; H, 7.32; N, 3.04.

***4-Vinyl-{3,5-bis{3-[3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl}benzyl}propyl}benzylpropyl}benzene (15a):***

G-2 monomer **15a** was prepared according to the same procedure as **14a**. 2.6 g of **13a** (2.2 mmol), 0.32 g of 9-BBN (2.6 mmol), 10 mL of dry THF. Subsequently, 6 mL of 1M NaOH, 0.05 g of Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.6 g (3.3 mmol) of p-bromostyrene. Chromatographic separation (silica gel, hexane/ethyl acetate (1.7:1/v:v)) yielded 1.25 g (45 %) of **15a**.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 0.00 (s, 36H, TMS), 0.97 (t, 8H, TMSCH<sub>2</sub>), 1.78 (m, 8H, NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.88 (m, 6H, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ar), 2.55 (m, 20H, ArCH<sub>2</sub>), 3.18 (m, 8H, NHCH<sub>2</sub>), 4.12 (t, 8H, OCH<sub>2</sub>), 4.74 (br, 4H, NH), 5.18 (d, 1H, CH=CH<sub>2</sub>), 5.70 (d, 1H, CH=CH<sub>2</sub>), 6.69 (dd, 1H, CH=CH<sub>2</sub>), 6.80 (s, 9H, ArH), 7.25 (AA', BB', 4H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): -1.5 (TMS), 17.7, 31.6, 32.9, 33.0, 35.2, 35.4, 40.5, 62.8, 112.8, 125.8, 126.0, 126.1, 128.2, 128.6, 136.6, 141.5, 142.0, 142.1, 142.6, 156.8.

FAB; m/z (%): 1287.0 (9.27) (M<sup>++</sup>Na).

Clcd. for  $C_{71}H_{114}N_4O_8Si_4$  (1264.0): C, 67.46; H, 9.09; N, 4.43. Found: C, 66.86; H, 8.84; N, 4.30.

***4-Vinyl-{3,5-bis{3-[3,5-bis(3-triphenylmethylaminopropyl)benzyl]propyl} benzyl propyl} benzene (15b):***

By the method for **14a**. 3.2 g (2.0 mmol) of **13b**, 0.30 g (2.5 mmol) of 9-BBN, 16 mL of dry THF. Subsequently, 6 mL of 1 M NaOH, 0.04 g of  $Pd(PPh_3)_4$ , 0.51 g (2.8 mmol) of p-bromostyrene, Chromatographic separation (silica gel, hexane/ethyl acetate (4:1/ v:v)) gave 1.0 g (30%) of **15b**.

$^1H$  NMR ( $CDCl_3$ ): 1.56 (s, 4H, NH), 1.86 (dt, 8H,  $CH_2CH_2NH$ ), 1.95 (dt, 6H,  $CH_2CH_2CH_2$ ), 2.25 (t, 8H,  $CH_2NH$ ), 2.63 (m, 20H, Ar $CH_2$ ), 5.25 (d, 1H,  $CH=CH_2$ ), 5.75 (d, 1H,  $CH=CH_2$ ), 6.72 (dd, 1H,  $CH=CH_2$ ), 6.83 (s, 6H, ArH), 6.92 (s, 3H, ArH), 7.24 (m, 40H, ArH), 7.50 (d, 24H, ArH).

$^{13}C$  NMR ( $CDCl_3$ ): 32.5, 33.0, 33.7, 35.2, 35.6, 43.4, 70.8, 112.8, 125.7, 125.8, 126.1, 127.7, 128.3, 128.5, 136.6, 142.0, 142.2, 146.2.

FAB; m/z (%): 1657 (0.06)  $[M+H]^+$ .

Clcd. for  $C_{123}H_{122}N_4$  (1656.3): C, 89.20; H, 7.42; N, 3.38. Found: C, 88.75; H, 7.35; N, 3.48.

### 10.3.3. Polymerisation of G1 and G2 macromonomer

Polymerization was carried out in a sealed Schlenk tube under nitrogen atmosphere.

***Poly{vinyl-{3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl} benzylpropyl}benzene} (16a):***

For G1 monomer **14a**. 80 mg of **7a**, 74  $\mu\text{L}$  of a 0.05 M solution of AIBN in toluene, and 50  $\mu\text{L}$  of toluene, and stirred under nitrogen at 55  $^{\circ}\text{C}$  for 48 h. The raw polymer was dissolved in 1 mL of THF, and precipitated with methanol/water (4:1/v:v) for 3 times and lyophilized from benzene.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): -0.15-0.15 (br, 18H, TMS), 0.86-1.05 (br, 4H, TMSCH<sub>2</sub>), 1.05-1.50 (br, 2H, CH<sub>2</sub>), 1.50-1.92 (br, 6H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.15-2.65 (br, 9H, ArCH<sub>2</sub>, CH), 2.97-3.22 (br, 4H, NHCH<sub>2</sub>), 4.00-4.24 (br, 4H, OCH<sub>2</sub>), 5.02-5.30 (br, 2H, NH), 6.02-6.48 (br, 2H, ArH), 6.50-7.00 (br, 5H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): -1.50 (TMS), 17.7, 31.5, 32.8, 35.6, 40.4, 62.6, 125.7, 125.9, 126.2, 127.6, 141.4, 142.4, 156.9.

Clcd. for  $(\text{C}_{35}\text{H}_{56}\text{N}_2\text{O}_4\text{Si}_2)_n$  (625.0)n: C, 67.26, H, 9.03; N, 4.48. Found: C, 66.56; H, 8.58; N, 4.25.

***Poly{4-Vinyl-[3,5-bis(3-triphenylmethylamino)propyl]benzylpropyl}benzene} (16b):***

From G-1 monomer **14b**. By the same method for **16a**. 83 mg of **14b**, 60  $\mu\text{L}$  of a 0.05 M solution of tBPB in toluene, 65  $\mu\text{L}$  of toluene. The mixture was stirred for 48 h. The raw polymer was dissolved in 1 mL of THF, and precipitated with methanol/water (4:1/v:v) for 3 times and lyophilized from benzene.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 1.30-1.55 (br, 4H, CH<sub>2</sub>, NH); 1.55-1.90 (br, 6H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.00-2.21 (br, 4H, NHCH<sub>2</sub>), 2.21-2.67 (br, 9H, ArCH<sub>2</sub>, ArCH), 6.03-6.49 (br, 2H, ArH), 6.49-6.90 (br, 5H, ArH), 6.90-7.30 (br, 18H, ArH), 7.32-7.51 (br, 12H, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 32.5, 33.6, 35.3, 35.6, 43.4, 70.7, 125.8, 126.0, 127.8, 128.5, 142.1, 146.2.

Clcd. for  $(\text{C}_{61}\text{H}_{60}\text{N}_2)_n$  (820.1): C, 89.27; H, 7.32; N, 3.41. Found: C, 88.19; H, 7.40; N, 2.91.

***Poly{4-vinyl- $\{3,5\}$ -[bis(3-aminopropyl)benzyl]propyl}benzene} 2 Trifluoroacetic acid (16c):***

A mixture of 0.5 g of **16b** and 0.3 ml of trifluoroacetic acid in 1 mL of methanol was stirred at 20 °C for 40 h. Subsequently, 2 mL of diethyl ether was added with stirring, and the mixture was centrifuged. After removal of the supernatant, the residue was dried. The above procedure was repeated for one or two times. The residue was lyophilized from water under high vacuum.

$^1\text{H}$  NMR (D<sub>4</sub>(MeOH): 1.00-1.55 (br, 2H, CH<sub>2</sub>), 1.55-2.02 (br, 6H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.20-2.72 (br, 9H, ArCH<sub>2</sub>, CH), 2.72-2.95 (br, 4H, NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>), 6.02-6.48 (br, 2H, ArH), 6.50-7.00 (br, 5H, ArH).

$^{13}\text{C}$  NMR (D<sub>4</sub>(MeOH): 30.3, 31.4, 33.5, 34.5, 36.5, 40.3, 41.3, 118.2 (q, CF<sub>3</sub>), 126.9, 127.7, 128.8, 142.0, 144.3, 163.0 (q, CF<sub>3</sub>COO).

Clcd. for (C<sub>27</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>F<sub>6</sub>)<sub>n</sub> (564.6)<sub>n</sub>: C: 57.44; H, 6.07; N, 4.94. Found: C, 56.63; H, 5.82; N, 4.57.

***Poly{4-vinyl- $\{3,5\}$ -bis{3- $\{3,5\}$ -bis[3-(2-(trimethylsilyl)ethoxycarbonylamino]propyl}benzyl}propyl}benzene} (17a):***

From G-2 monomer (**15a**): By the same method for **16a**. 98 mg of **15a**, 42  $\mu\text{L}$  of tBPB solution of toluene, 35  $\mu\text{L}$  of toluene. The mixture was stirred for 48 h. The raw polymer was dissolved in 1 mL of THF, and precipitated with methanol/water (4:1/v:v) for 3 times and lyophilized from benzene.

$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz): -0.15-0.15 (br, 36H, TMS), 0.86-1.04 (br, 8H, TMSCH<sub>2</sub>), 1.35-1.74 (br, 10H, ArCH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>), 1.74-2.05 (br, 6H, ArCH<sub>2</sub>CH<sub>2</sub>), 2.20-2.71 (br, 21H, ArCH<sub>2</sub>, ArCH), 2.90-3.22 (br, 8H, NHCH<sub>2</sub>), 4.00-4.21 (br, 8H, OCH<sub>2</sub>), 5.02-5.45 (br, 4H, NH), 6.00-6.48 (br, 2H, ArH), 6.50-6.96 (br, 11H, ArH).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz): -1.5 (TMS), 17.7, 31.4, 32.8, 33.1, 35.6, 40.3, 62.6, 125.8, 126.0, 127.4, 141.4, 141.9, 142.3, 156.9.



Clcd. for  $(C_{71}H_{114}N_4O_8Si_4)_n$  (1264.0) $_n$ : C, 67.46; H, 9.09; N, 4.43. Found: C, 66.67; H, 8.82; N, 4.28.

***Poly{4-Vinyl-{3,5-bis{3-[3,5-bis(3-triphenylmethylaminopropyl) benzylpropyl} benzene} (17b):***

From G-2 monomer **15b**. By the same method for **16a**. 102 mg of **15b**, 36  $\mu$ L of <sup>1</sup>BPB solution in diethyl ketone, 41  $\mu$ L of diethyl ketone. The mixture was stirred for 48 h. The raw polymer was dissolved in 1 mL of THF, and precipitated with methanol/water (4:1/v:v) for 3 times and lyophilized from benzene.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): 1.30-1.60 (br, 6H, NH, CH<sub>2</sub>), 1.60-1.92 (br, 14H, CH<sub>2</sub>), 1.92-2.26 (br, 8H, NHCH<sub>2</sub>), 2.26-2.82 (br, 21H, ArCH<sub>2</sub>, ArCH), 6.38-6.78 (br, 13H, ArH), 6.78-7.20 (br, 36H, ArH), 7.20-7.62 (br, 24H, ArH).

<sup>13</sup>C NMR: 32.5, 33.1, 33.7, 35.7, 43.5, 70.8, 126.1, 127.7, 128.6, 142.1, 146.2.

Clcd. for  $C_{123}H_{122}N_4$  (1656.3) $_n$ : C, 89.20; H, 7.42; N, 3.38. Found: C, 88.81, H, 7.51; N, 3.55.

***Poly{4-vinyl-{3,5-bis[3,5-bis(3-aminopropyl) benzyl propyl] benzyl propyl}benzene} 4 (Trifluoroacetic acid) (17c)***

From G2 Polymer **17a**. A mixture of 0.5 g of **16b** and 0.3 ml of trifluoroacetic acid was stirred at 20 °C for 40 h. Subsequently, 2 mL of diethyl ether was added with stirring, and the mixture was centrifuged. After removal of the supracant, The residue was lyophilized from water under high vacuum.

<sup>1</sup>H NMR D<sub>4</sub>(CH<sub>3</sub>OH): 1.35-2.10 (br, 16H, ArCH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>), 2.10-2.70 (br, 21H, ArCH<sub>2</sub>, ArCH), 2.71-3.05 (br, 8H, NH<sub>3</sub>(CH<sub>2</sub>), 5.70-6.50 (br, 2H, ArH), 6.50-7.10 (br, 11H, ArH).

$^{13}\text{C}$  NMR  $\text{D}_4(\text{CH}_3\text{OH})$ : 30.2, 33.4, 34.7, 36.7, 40.2, 118.0 (q,  $\text{CF}_3$ ), 126.9, 127.6, 142.0, 143.4, 144.3, 162.2 (q,  $\text{CF}_3\text{COO}$ ).

Clcd. for  $\text{C}_{63}\text{H}_{70}\text{N}_4\text{O}_8\text{F}_{12}$ : C, 61.06; H, 5.69; N, 4.52. Found: C, 57.01; H, 5.96; N, 4.44.

## 10.4. Synthesis of polystyrenes with higher generation dendritic wedges by the macromonomer route

### 10.4.1. Synthese of G2 and G3 and G4 dendrons

#### *Allyl-3,5-Bis{3-[3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoylamino]propyl}benzene (18):*

To a solution of **19a** (5.10 g, 9.2 mmol) in 75 mL of dry methylene chloride was added 1.35 g (9.2 mmol) of 1-hydroxybenzotriazole (HOBT) at 0 °C and stirred for an hour. 2.0 g (10.3 mmol) of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) was added and stirred for another hour. A solution of 2.1 g of **12c** and 3.5 mL (23.5 mmol) of 1, 8-diazobicyclo[5, 4, 0] undec-7-ene (DBU) in 10 mL of dry methylene chloride was dropped to the later solution at 0 °C. The mixture was stirred for 20 h at 25 °C. Chromatographic separation (silica gel, hexane/ethyl acetate(1.5:1/v:v) gave 3.6 g (63%) of **18** as colorless oil.

<sup>1</sup>H NMR(CDCl<sub>3</sub>) δ 0.0 (s, 36H,TMS), 0.9 (t, 8H, TMSCH<sub>2</sub>),1.9 (br, 12H, CH<sub>2</sub>), 2.6 (t, 4H, ArCH<sub>2</sub>), 3.2-3.5 (br. 12H, NHCH<sub>2</sub>, 2H, CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.9 (t, 8H, ArOCH<sub>2</sub>), 4.1 (t, 8H, OCH<sub>2</sub>), 5.0 (br, 4H, NH), 5.1 (br, 2H, CH=CH<sub>2</sub>), 5.9 (m, 1H, CH=CH<sub>2</sub>), 6.5 (s, 2H, ArH), 6.6 (br, 2H, NH), 6.7 (s, 4H, ArH), 6.8 (s, 2H, ArH), 6.9 (s, 1H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 1.2 (TMS), 17.6 (TMSCH<sub>2</sub>), 29.3, 30.6, 33.0 (CH<sub>2</sub>), 37.9, 39.9, 62.7, 65.6 (OCH<sub>2</sub>), 104.1, 105.5, 115.6, 126.1, 126.3, 136.6, 137.2, 140.2 (Ar), 156.8 (NHCOO), 159.7 (OAr), 167.1 (CONH).

#### *3,5-Bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy} benzoic N-hydroxysuccinimidylester (19b) :*

To a solution of **19a** (3.6 g, 6.45 mmol) in 225 ml of dry dichloromethane, was added 0.9 g (7.7 mmol) of N-hydroxysuccinimide and 1.65 g (8.0 mmol) of DCC. The mixture was stirred for 24 h at room temperature. The resulted precipitate was filtered. Chromatographic separation (silica gel, hexane/ethyl acetate (2:1/(v:v))) gave 3.8 g of **19b** (89%) as colorless solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): 0.00 (s, 18H, TMS), 0.95 (t, 4H, TMSCH<sub>2</sub>), 1.92 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 2.90 (s, 4H, NHCOCH<sub>2</sub>), 3.34 (t, 4H, NHCH<sub>2</sub>), 3.92 (t, 4H, ArOCH<sub>2</sub>), 4.10 (t, 4H, OCH<sub>2</sub>), 4.90 (br, 2H, NH), 6.70 (s, 1H, ArH), 7.20 (s, 2H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 62 MHz): -1.6 (TMS), 17.6, 25.5, 29.2, 37.9, 62.8, 65.9, 108.3, 108.6, 156.7, 159.9, 161.5, 169.1.

MS (EI, 80 ev), m/z (%): 653.3 (0.63) (M<sup>+</sup>).

Clcd. for C<sub>29</sub>H<sub>47</sub>N<sub>3</sub>O<sub>10</sub>Si<sub>2</sub> (653.8): C, 53.27; H, 7.24; N, 6.42. Found: C, 53.21; H, 7.17; N, 6.34.

*Allyl-3,5-bis{3-{3,5-bis{3-{3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propoxy}benzoylamino}propyl}benzylpropyl}benzylpropyl}benzene (20):*

To 0.8 g (0.77 mmol) of **13c** in 5 mL of methanol, was added 0.2 mL of Et<sub>3</sub>N, 2.9 g (4.4 mmol) of **19b**. The solution was stirred for 24 h at r.t.. Chromatographic separation (silica gel, hexane/ethyl acetate (1:1.6/v:v)) gave 1.2 g (57%) of **20** as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 0.00 (s, 72H, TMS), 0.92 (t, 16H, TMSCH<sub>2</sub>), 1.92 (br, 28H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.53 (br, 16H, ArCH<sub>2</sub>), 3.22 (br, 18H, OCONHCH<sub>2</sub>, CH<sub>2</sub>CH=CH<sub>2</sub>), 3.45 (t, 8H, ArCONHCH<sub>2</sub>), 3.84 (t, 16H, ArOCH<sub>2</sub>), 4.09 (t, 16 H, OCH<sub>2</sub>CH<sub>2</sub>TMS), 5.00 (m, 2H, CH=CH<sub>2</sub>), 5.32 (s, 8H, NH), 5.88(m, 1H, CH=CH<sub>2</sub>), 6.42 (s, 4H, ArH), 6.78 (br, 17H, ArH), 7.18 (s, 4H, NH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): -1.5, 17.5, 29.3, 30.5, 32.8, 35.1, 37.8, 39.5, 39.9, 62.6, 65.4, 104.0, 105.4, 115.4, 125.7, 125.9, 126.1, 136.5, 137.4, 139.6, 141.4, 142.0, 142.4, 156.8, 159.6, 167.1.

FAB; m/z (%): 2737.0 (2.5) (M-H)<sup>+</sup>.

Clcd. for C<sub>139</sub>H<sub>226</sub>N<sub>12</sub>O<sub>28</sub>Si<sub>8</sub> (2738.0): C, 60.97; H, 8.32; N, 6.13. Found: C, 60.19; H, 8.17; N, 5.91.

**3, 5-Bis {3- {3, 5-bis [3- [2-(trimethylsilyl) ethoxycarbonylamino] propyloxy] benzoylamino }propyloxy }benzoic-N-hydroxysuccinimidyl ester (21b):**

A solution of 4.2 g (3.1 mmol) of **21a**, 0.40 g (3.4 mmol) of N-hydroxysuccinimide and 0.75 g (3.6 mmol) of DCC in 70 ml of dry dichloride methylene was stirred at room temperature for 24h. The resulting precipitate was filtered off. Chromatographic separation (silica gel, hexane/ethyl acetate (2:1/v:v) gave 2.0 g of **21b** (45%) as a colorless solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.0(s, 36H, TMS), 0.9 (t, 8H, TMSCH<sub>2</sub>), 1.8 (q, 8H, CH<sub>2</sub>), 2.1 (q, 4H, CH<sub>2</sub>), 2.8 (s, 4H, CH<sub>2</sub>), 3.3 (q, 8H, NHCH<sub>2</sub>), 3.5 (q, 4H, NHCH<sub>2</sub>), 3.9 (t, 8H, ArOCH<sub>2</sub>), 4.1 (t, 4H, ArOCH<sub>2</sub>), 4.2 (t, 8H, OCH<sub>2</sub>), 5.1 (br, 4H,NH), 6.5 (t, 2H, ArH), 6.6(t, 1H, ArH), 6.9 (m, 6H, ArH), 7.1 (d, 2H, ArH), 7.4 (br, 2H, NH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -1.6, (TMS), 17.6 (TMSCH<sub>2</sub>), 25.5, 28.7, 29.3, 37.1, 37.9 (NHCH<sub>2</sub>), 62.8, 65.6, 66.1 (OCH<sub>2</sub>), 104.3, 105.5, 108.4, 126.3, 136.4, 156.8, 159.7, 159.8 (OAr), 161.5, 167.2 (CONH), 169.3.

**Allyl-3,5-bis{3- {3,5-bis {3- {3,5-bis{3- [2-(trimethylsilyl) ethoxycarbony amino] propyloxy}benzoylamino}propyl}benzylpropyl}benzylpropyl} benzylpropyl} benzene (22):**

To 0.58 g ( 0.55 mmol) of **13c** in 5 mL of methanol, was added 3.9 g (2.3 mmol) of **21b**. The solution was stirred for 24 h at r.t.. Chromatographic separation (silica gel, hexane/ethyl acetate (1:2 / v:v)) gave 2.0 g (57%) of **22** as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): -0.20 (s, 144H, TMS), 0.75 (t, 32H, TMSCH<sub>2</sub>), 1.72 (br, 60H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.43 (br, 16H, ArCH<sub>2</sub>), 3.07 (br, 34H, OCONHCH<sub>2</sub>,

CH<sub>2</sub>CH=CH<sub>2</sub>), 3.13 (s, 8H, OCONHCH<sub>2</sub>), 3.27 (t, 16H, ArCONHCH<sub>2</sub>), 3.64 (t, 16H, ArOCH<sub>2</sub>), 3.68 (t, 32H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.95 (t, 32H, OCH<sub>2</sub>CH<sub>2</sub>TMS), 4.90 (m, 2H, CH=CH<sub>2</sub>), 5.02 (s, 16H, NH), 5.78 (m, 1H, CH=CH<sub>2</sub>), 6.13 (s, 4H, ArH), 6.28 (br, 8H, ArH), 6.60 (br, 8H, ArH), 6.65 (br, 9H, ArH), 6.70 (s, 16H, ArH), 7.05 (br, 4H, NH), 7.25 (br, 8H, NH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): -1.4, 17.7, 28.9, 29.4, 30.5, 32.8, 33.1, 35.4, 37.4, 38.0, 39.6, 40.1, 62.8, 65.8, 66.0, 76.7, 76.9, 77.2, 104.2, 104.5, 105.8, 115.5, 125.8, 126.1, 126.3, 126.4, 136.6, 136.7, 137.6, 139.9, 141.5, 142.2, 142.7, 156.9, 159.7, 159.8, 167.2, 167.4.

***4-Vinyl-{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoyamino}propyl}benzylpropyl}benzene (23):***

To a solution of the adduct (1 mmol) of 9-BBN and **18** in 8 ml THF, was added aqueous 1 M NaOH (3 mL), Tetrakis(triphenylphosphine) Palladium (0) (0.06 g, 0.05 mmol), and 4-bromostyrene (0.26 g, 1.67 mmol). The mixture was stirred for 18 h at 70 °C. The organic layer was separated, washed with brine, and dried (MgSO<sub>4</sub>). Chromatographic separation (silica gel, hexane/ethyl acetate (1.5:1/v:v) gave 0.8 g (56 %) of **23** as colourless oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.0 (s, 36H, TMS), 0.9 (t, 8H, TMSCH<sub>2</sub>), 1.9 (br, 12H, CH<sub>2</sub>), 2.6 (br, 8H, ArCH<sub>2</sub>), 3.3 (m, 8H, NHCH<sub>2</sub>), 3.4 (m, 4H, NHCH<sub>2</sub>), 3.9 (t, 8H, ArOCH<sub>2</sub>), 4.1 (t, 8H, OCH<sub>3</sub>), 5.2 (m, 5H, CH=CH<sub>2</sub>, NH), 5.7 (d, 1H, CH=CH<sub>2</sub>), 6.5 (s, 2H, ArH), 6.6-6.7 (dd, 1H, CH=CH<sub>2</sub>), 6.7-6.9 (br, 9H, NH, ArH), 7.1 (d, 2H, ArH), 7.3 (d, 2H, ArH).  
<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -1.6 (TMS), 17.6 (TMSCH<sub>2</sub>), 29.3, 30.6, 32.7, 33.1, 35.2, 37.9, 39.5, 62.8, 65.6 (CH<sub>2</sub>), 104.1, 105.5 (Ar), 112.8 (CH=CH<sub>2</sub>), 125.9, 126.0, 126.3, 128.4, 135.0, 136.5, 136.7, 141.4, 141.9, 142.5, 156.8 (NHCOO), 159.7 (OAr), 167.1 (CONH).

FAB; m/z (%): 1415 (0.19) [M+H]<sup>+</sup>.

Calcd. for C<sub>73</sub>H<sub>116</sub>N<sub>6</sub>O<sub>14</sub>Si<sub>4</sub> (1414.1): C, 62.00; H, 8.27; N, 5.94. Found: C, 61.35; H, 8.10; N, 5.80.

***4-Vinyl-{3,5-bis{3-{3,5-bis{3-{3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy}benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene (24):***

By the same method for **23**. 1.2 g (0.44 mmol) of **20**, 0.07 g (0.57 mmol) of 9-BBN, 12 mL of dry THF. subsequently, 5 mL of 1 M NaOH, 0.01 g of Pd(PPh<sub>3</sub>)<sub>4</sub>. 0.28 g (1.5 mmol) of 4-bromostyrene. Chromatographic separation (silica gel, hexane/ethyl acetate (1:1.8/v:v)) gave 0.50 g (40%) of **24** as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 0.00 (s, 72H, TMS), 0.93 (t, 16H, TMSCH<sub>2</sub>), 1.90 (br, 30H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.58 (br, 20H, ArCH<sub>2</sub>), 3.27 (t, 16H, OCONHCH<sub>2</sub>), 3.48 (t, 8H, ArCONHCH<sub>2</sub>), 3.89 (t, 16H, ArOCH<sub>2</sub>), 4.11 (t, 16H, OCH<sub>2</sub>CH<sub>2</sub>TMS), 5.10 (br, 8H, NH), 5.13 (d, 1H, CH=CH<sub>2</sub>), 5.18 (d, 1H, CH=CH<sub>2</sub>), 6.45 (s, 4H, ArH), 6.65 (dd, 1H, CH=CH<sub>2</sub>) 6.68 (br, 17H, ArH), 6.90 (br, 4H, NH), 7.20 (AA', BB', 4H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): -1.5, 17.7, 29.3, 30.6, 32.9, 35.1, 35.3, 35.4, 37.9, 39.5, 62.8, 65.6, 104.1, 105.5, 112.8, 125.8, 126.0, 126.3, 128.5, 135.0, 136.5, 136.7, 141.4, 142.0, 142.7, 156.8, 159.7, 167.1.

FAB; m/z (%): 2842.6 (1.0) (M+H)<sup>+</sup>.

Clcd. for C<sub>147</sub>H<sub>234</sub>N<sub>12</sub>O<sub>28</sub>Si<sub>8</sub> (2841.6): C, 62.12; H, 8.30; N, 5.91. Found: C, 61.43; H, 8.12; N, 5.77.

#### **10.4.2. Polymerisation of G2 and G3 monomers**

***Poly{4-vinyl-{3,5-bis{3-{3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy}benzoylamino}propyl}benzyl}propyl}benzene} (26a):***

To a 10 mL tube was added 0.07 mmol of **23**, 42  $\mu\text{L}$  (3 mol %) of a 0.05 M initiator solution in toluene, and 65  $\mu\text{L}$  of toluene, and stirred under nitrogen at 90 °C for 48 h. The crude polymer was dissolved in THF, precipitated with methanol/water (4:1/v:v), and lyophilized from benzene .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): -0.05 (br, 36H, TMS), 0.9 (br, 11H,  $\text{TMSCH}_2$ , CH,  $\text{CH}_2$ ), 1.5-2.0 (br, 12H,  $\text{CH}_2$ ), 2.1-2.6 (br, 8H,  $\text{ArCH}_2$ ), 2.9-3.5 (br, 12H,  $\text{NHCH}_2$ ), 3.5-3.9 (br,  $\text{ArOCH}_2$ ), 3.9-4.2 (br, 8H,  $\text{OCH}_2$ ), 5.4-5.7 (br, 4H, NH), 6.3-6.5 (br, 2H, ArH), 6.5-6.8 (br, 3H, ArH, NH), 6.8-7.1 (br, 8H, ArH, NH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.5 (TMS), 17.7 ( $\text{TMSCH}_2$ ), 29.3, 30.7, 33.0, 37.9, 39.9 ( $\text{NHCH}_2$ ), 62.7, 65.5, 104.3, 105.6 (Ar), 126.1, 136.5, 141.3, 157.0 (OAr), 159.7 ( $\text{NHCOO}$ ), 167.5 (CONH).

Calcd for  $(\text{C}_{73}\text{H}_{116}\text{N}_6\text{O}_{14}\text{Si}_4)_n$  (1414.1) $_n$ : C, 62.00; H, 8.27; N, 5.94. Found: C, 60.08; H, 8.01; N, 5.39.

***Poly{4-vinyl-[3,5-bis[3-[3,5-bis(3-aminopropoxy)benzoylamino]propyl]benzylpropyl}benzene} 4•Trifluoroacetic acid (26b):***

To 0.1 g of Teoc-protected polymer **26a** was added 5 mL of trifluoroacetic acid and stirred for 20 h at room temperature. The trifluoroacetic acid was removed and the residue was lyophilized from water.

$^1\text{H}$  NMR ( $[\text{D}_4]$  MeOH):  $\delta$  1.5-2.0 (br, 3H, CH,  $\text{CH}_2$ ), 2.0-2.2 (br, 6H,  $\text{CH}_2$ ), 2.2-2.9 (br, 8H,  $\text{ArCH}_2$ ), 2.9-3.2 (br, 8H,  $\text{NH}_3^{\oplus}\text{CH}_2$ ), 3.2-3.5 (br, 4H,  $\text{NHCH}_2$ ), 3.8-4.2 (br, 8H,  $\text{ArOCH}_2$ ), 6.4-6.6 (br, 2H, ArH), 6.6-6.9 (br, 7H, ArH), 6.9-7.2 (br, 4H, ArH).

$^{13}\text{C}$  NMR:  $\delta$  28.2, 30.6, 32.1, 34.4, 36.5, 38.4, 41.1, 66.5 ( $\text{OCH}_2$ ), 105.8, 107.4 (Ar), 114.6, 117.0, 119.3, 121.6, 127.4, 129.0, 137.8, 142.9, 143.9, 161.1 (OAr), 162.5 (q,  $\text{CF}_3\text{COO}$ ), 169.5 (CONH).



Calcd for  $(C_{57}H_{72}N_6O_{14}F_{12})_n$  (1293.2)<sub>n</sub>: C, 52.94; H, 5.61; N, 6.50. Found: C, 50.94; H, 5.36; N, 5.97.

***Poly{4-Vinyl-{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene} (27a):***

From G-3 monomer **24**. By the same method for **23**. 140 mg of **24**, 33  $\mu$ L of <sup>1</sup>BPB solution of toluene, 36  $\mu$ L of toluene.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): -0.05 (br, 72H, TMS), 0.80-1.00 (br, 16H, TMSCH<sub>2</sub>), 1.20-2.00 (br, 32H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>), 2.00-2.80 (br, 21H, ArCH<sub>2</sub>, CH), 2.85-3.47 (br, 26H, OCONHCH<sub>2</sub>, ArCONHCH<sub>2</sub>), 3.48-3.90 (br, 16 H, ArOCH<sub>2</sub>), 3.90-4.25 (br, 16 H, OCH<sub>2</sub>CH<sub>2</sub>TMS), 5.00-5.87 (br, 8H, NH), 6.10-6.46 (br, 6H, ArH), 6.46-7.12 (br, 17H, ArH), 7.40-8.30 (br, 4H, NH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): - 1.5, 17.7, 29.3, 30.6, 32.9, 35.4, 37.9, 39.5, 62.7, 63.6, 65.5, 104.1, 105.7, 126.3, 126.9, 127.9, 136.5, 141.4, 142.0, 142.4, 157.0, 159.7, 167.4.

Clcd. for  $(C_{147}H_{234}N_{12}O_{28}Si_8)_n$  (2841.6)<sub>n</sub>: C, 62.12; H, 8.30; N, 5.91. Found: C, 61.40; H, 8.11; N, 5.62.

***Poly{4-Vinyl-{3,5-bis{3-{3,5-bis{3-[3,5-bis(3-aminopropoxy)benzoylamino]propyl}benzyl}propyl}benzylpropyl}benzene} 8  $\square$  Trifluoroacetic acid (27b):***

From G-3 Polymer **27a**.

<sup>1</sup>H NMR ([D<sub>4</sub>] CH<sub>3</sub>OH): 1.43-1.92 (br, 16H, ArCH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>), 1.92-2.21 (br, 16H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.21-2.80 (br, 20H, ArCH<sub>2</sub>, CH), 2.90-3.17 (br, 16H, CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>), 3.17-3.32 (br, 8H, CH<sub>2</sub>NHCO), 3.63-4.22 (br, 16H, OCH<sub>2</sub>), 6.30-6.84 (br, 14H, ArH), 6.84-7.15 (br, 11H, ArH).

$^{13}\text{C}$  NMR ( $[\text{D}_4]$   $\text{CH}_3\text{OH}$ ): 28.2, 32.0, 34.4, 36.7, 38.3, 41.0, 42.0, 66.4, 105.6, 107.2, 118.2 (q,  $\text{CF}_3$ ), 127.4, 128.6, 129.3, 137.7, 142.1, 142.9, 143.4, 143.8, 161.1, 162.6, 163.0, 163.2, 169.5.

Clcd. for  $(\text{C}_{115}\text{H}_{146}\text{N}_{12}\text{O}_{28}\text{F}_{24})_n$  (2600.4): C, 53.13; H, 5.66; N, 6.46. Found: C, 52.49; H, 6.21; N, 7.58.

## 10.5. Synthese of higher generation dendronized polystyrene by the attach-to route

### 10.5.1. Synthese of higher generation dendronized polystyrene by the attach-to route

#### *Poly{4-vinyl- $\{3,5\}$ -bis{3- $\{3,5\}$ -bis(3-(2-(trimethylsilyl)ethoxycarbonyl amino)propyloxy)benzoyl amino}propyl}benzyl propyl}benzene} (26)*

To a solution of 28 mg of **16c** in 2 ml of methanol, was added 0.20 g (2.0 mmol) of triethyl amine and 0.123 g (0.19 mmol) of **19b**. After 3 hour's stirring at room temperature, 2 ml of dichloromethylene was added. The resulting mixture was stirred for 48 h. After removing the solvents, The residue was dissolved in 2 ml of THF, and precipitated with methane/water (4:1/v:v) for 4 times and lyophilized from benzene.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): -0.05 (br, 36H, TMS), 0.80-1.02 (8H,  $\text{TMSCH}_2$ ), 1.28-2.03 (br, 16H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2$ ), 2.03-2.62 (br, 9H,  $\text{ArCH}_2$ , CH), 2.90-3.48 (br, 12H,  $\text{NHCH}_2$ ), 3.48-3.91 (br, 8H,  $\text{ArOCH}_2$ ), 3.91-4.22 (br, 8H,  $\text{OCH}_2$ ), 5.41-5.73 (br, 4H, NH), 6.30-6.50 (br, 4H, ArH), 6.50-7.12 (br, 9H, ArH), 7.60-8.32 (br, 2H, NH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): -1.5 (TMS), 17.7 ( $\text{TMSCH}_2$ ), 29.3, 30.7, 33.0, 37.9, 39.9 ( $\text{NHCH}_2$ ), 62.7, 65.5, 104.3, 105.6, 126.1, 136.5, 141.3, 157.0 (OAr), 159.7 ( $\text{NHCOO}$ ), 167.5 (CONH).

Clcd. for  $(\text{C}_{73}\text{H}_{116}\text{N}_6\text{O}_{14}\text{Si}_4)_n$  (1414.1)n: C, 62.00; H, 8.27; N, 5.94. Found: C, 61.02; H, 8.04; N, 5.70.

#### *Poly{4-Vinyl- $\{3,5\}$ -bis{3- $\{3,5\}$ -bis{3- $\{3,5\}$ -bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy]benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene} (27):*

By the same method for (**16c** +**19b**). 55 mg of **17c**, 0.1 mL of triethyl amine, 0.17 g (0.26 mmol) of **19b**, 2 mL of methanol. Subsequently, 2 mL of dichloromethane was added.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): -0.05 (br, 72H, TMS), 0.80-1.00 (br, 18H, TMSCH<sub>2</sub>, CH<sub>2</sub>), 1.20-2.00 (br, 32H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH), 2.00-2.80 (br, 21H, ArCH<sub>2</sub>, CH), 2.85-3.47 (br, 26H, OCONHCH<sub>2</sub>, ArCONHCH<sub>2</sub>), 3.48-3.90 (br, 16 H, ArOCH<sub>2</sub>), 3.90-4.25 (br, 16 H, OCH<sub>2</sub>CH<sub>2</sub>TMS), 5.00-5.87 (br, 8H, NH), 6.10-6.46 (br, 6H, ArH), 6.46-7.12 (br, 17H, ArH), 7.40-8.30 (br, 4H, NH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): -1.5, 17.7, 29.3, 30.6, 32.9, 35.4, 37.9, 39.5, 62.7, 63.6, 65.5, 104.1, 105.7, 126.3, 126.9, 127.9, 136.5, 141.4, 142.0, 142.4, 157.0, 159.7, 167.4. Calcd. for (C<sub>147</sub>H<sub>234</sub>N<sub>12</sub>O<sub>28</sub>Si<sub>8</sub>)<sub>n</sub> (2841.6)<sub>n</sub>: C, 62.12; H, 8.30; N, 5.91. Found: C, 61.94; H, 8.11; N, 6.00.

*Poly{4-Vinyl-{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-[2-(trimethylsilyl)ethoxycarbonylamino]propyloxy}benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene} (28):*

By the same method for (**16c** +**19b**). 20 mg of **17c**, 0.05 mL of triethyl amine, 30 mg of **19b** (70% of equiv.), 2 mL of methanol. Subsequently, 2 mL of dichloromethane was added. The resulting mixture was stirred for 48 h. After removing the solvents, The residue was dissolved in 2 ml of THF, and precipitated with methane/water (4:1/v:v) for 4 times and lyophilized from benzene.

Part of <sup>13</sup>C NMR spectrum, see text page 52.

*Poly{4-Vinyl{3, 5-Bis{3-{3, 5-bis[3-{3, 5-Bis{3-{3, 5-bis[3-2-(trimethylsilyl)ethoxycarbonylamino]propyloxy}benzoylamino}propyloxy}benzoylamino}propyl}benzyl}propyl}benzylpropyl}benzene} (29):*

To a solution of 90 mg of **17c** in 3 ml of methanol were added 0.30 g (3.0 mmol) of triethylamine and 225 mg (0.34 mmol) of **21b**. After the mixture was stirred for 2 h at

room temperature, 2 ml of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, 3 ml of dichloromethane, 0.20 g (2.0 mmol) of triethylamine and 90 mg (0.14 mmol) of **21b** were added to the residue. The solution was stirred for another 48 h. After removal of the solvent and base, the residue was dissolved in 3 ml of THF and precipitated four times into methanol/water (4:1/v:v) and lyophilized from benzene to give 0.19 g (91 %) of **29**.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -0.5-0.2 (br, TMS), 0.6-1.2 (br,  $\text{TMSCH}_2$ ), 1.35-2.2 (br,  $\text{CH}_2$ ), 2.2-2.7 (br,  $\text{ArCH}_2$ ), 2.7-3.5 (br,  $\text{CONHCH}_2$ ), 3.5-3.9 (br,  $\text{ArOCH}_2$ ), 3.9-4.4 (br,  $\text{COCH}_2$ ), 5.4-6.0 (br, NH), 6.1-6.6 (br, ArH), 6.6-7.2 (br, ArH).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.5 (TMS), 17.7 ( $\text{TMSCH}_2$ ), 29.4, 33.0, 37.9, 62.7 ( $\text{OCH}_2$ ), 65.6 ( $\text{OCH}_2$ ), 105.8 (Ar), 126.3, 136.4, 141.9 (Ar), 157.0 ( $\text{NHCOO}$ ), 159.8 (OAr), 167.5 (CONH).

Anal. calcd for  $\text{C}_{71}\text{H}_{78}$  (931.4): C, 91.56; H, 8.44. Found: C, 90.90; H, 8.20.

***Methyl 3,5-Bis {3-[2,4-dinitrophenylamino ]propyloxy }benzoate (31):***

To a solution of 0.1 g (0.3 mmol) of **30** in 5 ml of methanol were added 0.2 ml of triethylamine and 0.13 g (0.7 mmol) of **7**. The mixture was warmed to 65 °C for 10 minutes. After cooling to room temperature, the yellow precipitate was collected, dissolved in 5ml of methylene chloride, and precipitated by adding 8 ml of methanol to give 0.17 g (88%) of **31** as a yellow solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.3 (m, 4H,  $\text{CH}_2$ ), 3.7 (m, 4H,  $\text{NHCH}_2$ ), 3.9 (s, 3H,  $\text{CH}_3$ ), 4.2 (t, 4H,  $\text{OCH}_2$ ), 6.9 (s, 1H, ArH), 7.0 (d, 2H, ArH), 7.2 (s, 2H, ArH), 8.2 (d, 2H, ArH), 8.9 (s, 2H, NH), 9.1 (s, 2H, ArH).

MS (70 ev)  $m/z$  (%): 614.3 (3.86) [ $\text{M}^+$ ].

Calcd. for  $\text{C}_{26}\text{H}_{26}\text{N}_6\text{O}_{12}$  (614.5): C, 50.82; H, 4.26; N, 13.67. Found: C, 51.01; H, 3.94; N, 13.57.

### ***2,4-dinitrophenyl labelled G4 polymers:***

15 mg of **29** in 0.2 ml tetrachloroethane was treated with 0.1 ml of 0.1 M sodium bicarbonate and 0.1 ml of 0.5 % (weight percentage) of 1-Fluoro-2,4-dinitrobenzene in tetrachloroethane. The mixture was stirred for 1 h at 65 °C, cooled, and acidified with 0.01 ml acetic acid. 2 ml of tetrachloroethane and 2 ml of water were added to the mixture. The organic layer was separated. After removal of the solvents, the residue was dissolved in 1 ml of THF, and precipitated in methanol/water (4:1). this procedure was repeated for 4 times. The obtained polymer was lyophilized from benzene to give 13 mg of 2,4-dinitrophenyl labelled G4 polymer **29**.

### **10.5.2. Synthese of dendronized polystyrene with higher molar mass**

#### ***Poly{4-vinyl-{3,5-bis{3-[3,5-bis{3-(2-(trimethylsilyl)ethoxycarbonylamino}propyloxy)benzoylamino}propyloxy}benzoylamino}propyloxy}benzoylamino}benzene} (33a):***

To a solution of 0.82 g of **32b** in 10 ml of methanol were added 1.1 g of triethylamine and 2.1 g of **19b**. After the mixture was stirred for 2 h at room temperature, 5 ml of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, 8 ml of dichloromethane, 0.20 g (2.0 mmol) of triethylamine and 1.2 g of **19b** were added to the residue. The solution was stirred for another 48 h. After removal of the solvent and base, the residue was dissolved in 7 ml of THF and precipitated four times into methanol/water (4:1/v:v) and lyophilized from benzene to give polymer **33a**.

#### ***Poly{4-vinyl-{3,5-bis{3-[3,5-bis(3-aminopropyloxy)benzoylamino}propyloxy}benzoylamino}propyloxy}benzoylamino}benzene} 4 Trifluoroacetic acid (33b):***

To 0.2 g of Teoc-protected polymer **33a** was added 1 mL of trifluoroacetic acid and stirred for 20 h at room temperature. The trifluoroacetic acid was removed and the residue was lyophilized from water.

***Ethyl 3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl}benzoate (35a):***

To 15 ml toluene was added 1.5 g of **11c** and 1.1 g of 9-BBN. The mixture was stirred for 24 h. Subsequently, to the mixture was added 7.5 ml of aqueous 1M NaOH, 0.23 g of Pd(PPh<sub>3</sub>)<sub>4</sub> and 0.94 g of **34**. The mixture was stirred for 48 h at 74 °C. Chromatographic separation gave 0.94 g of **35a** (82%) as colorless solid.

<sup>1</sup>H NMR: 0.00 (s, 18H, TMS), 0.93 (t, 4H, CH<sub>2</sub>TMS), 1.35 (t, 3H, CH<sub>3</sub>), 1.80 (m, 4H, CH<sub>2</sub>), 2.63 (t, 4H, ArCH<sub>2</sub>), 3.15 (m, 4H, CH<sub>2</sub>NH), 4.10 (t, 4H, OCH<sub>2</sub>), 4.31 (q, 2H, COOCH<sub>2</sub>), 4.72 (br, 2H, NH), 7.13 (s, 1H, ArH), 7.61 (s, 2H, ArH).

<sup>13</sup>C NMR: -1.5 (TMS), 14.2(CH<sub>3</sub>), 17.6 (CH<sub>2</sub>TMS), 31.4 (CH<sub>2</sub>), 32.5 (ArCH<sub>2</sub>), 40.1 (CH<sub>2</sub>NH), 60.8 (NHCOOCH<sub>2</sub>), 62.8 (OCH<sub>2</sub>), 127.0 (Ar), 130.0 (Ar), 133.0 (Ar), 141.8 (Ar), 156.8 (NHCO), 166.6 (COO).

***3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl}benzoic acid (35b):***

A solution of 6.0 g of **35a** and 2.0 g of potassium hydroxide in 150 ml of methanol/water (1:1/v:v) was refluxed for 10 h. After removal of the solvent, the oily residue was dissolved in ethyl acetate, washed with a 10% citric acid solution in water and dried with magnesium sulfate. The removal of the solvent gave 5.5 g (96%) of **35b** as a viscous oil.

<sup>1</sup>H NMR: 0.00 (s, 18H, TMS), 0.98 (t, 4H, CH<sub>2</sub>TMS), 1.82 (m, 4H, CH<sub>2</sub>), 2.60 (t, 4H, ArCH<sub>2</sub>), 3.20 (m, 4H, CH<sub>2</sub>NH), 4.15 (t, 4H, OCH<sub>2</sub>), 4.80 (br, 2H, NH), 7.20 (s, 1H, ArH), 7.70 (s, 2H, ArH), 7.90 (br, 1H, COOH).

$^{13}\text{C}$  NMR: -1.5 (TMS), 17.6 ( $\text{CH}_2\text{TMS}$ ), 31.4 ( $\text{CH}_2$ ), 32.6 ( $\text{ArCH}_2$ ), 40.4 ( $\text{CH}_2\text{NH}$ ), 62.8 ( $\text{OCH}_2$ ), 127.0 (Ar), 130.4 (Ar), 133.4 (Ar), 141.8 (Ar), 156.9 (NHCO), 170.5 (COOH).  
MS (EI, 80ev), m/z (%): 524.3 (0.78).

***3,5-bis{3-[2-(trimethylsilyl)ethoxycarbonylamino]propyl}benzoic  
N-hydroxysuccinimidylester (35c):***

To 30 ml of dichloride methylene, was added 1.5 g (2.86 mmol) of **35b**, 0.36 g (3.1 mmol) of N-hydroxysuccinimidyl Ester and 0.69 g (3.3 mmol) of DCC. The mixture was stirred for 24 h. After filtration of the precipitate, Chromatographic separation gave **35c** as a viscous oil.

$^1\text{H}$  NMR: 0.00(s, 18H, TMS), 0.93 (t, 4H,  $\text{CH}_2\text{TMS}$ ), 1.90 (m, 4H,  $\text{CH}_2$ ), 2.63 (t, 4H,  $\text{ArCH}_2$ ), 2.84 (s, 4H,  $\text{CH}_2\text{CH}_2\text{CON}$ ), 3.15 (m, 4H,  $\text{CH}_2\text{NH}$ ), 4.10 (t, 4H,  $\text{OCH}_2$ ), 4.72 (br, 2H, NH), 7.30 (s, 1H, ArH), 7.71 (s, 2H, ArH).

$^{13}\text{C}$  NMR: -1.5 (TMS), 17.6 ( $\text{CH}_2\text{TMS}$ ), 25.6 ( $\text{CH}_2\text{CONOC}$ ), 31.4 ( $\text{CH}_2$ ), 32.5 ( $\text{ArCH}_2$ ), 40.1 ( $\text{CH}_2\text{NH}$ ), 62.8 ( $\text{OCH}_2$ ), 125.2 (Ar), 128.0 (Ar), 135.2 (Ar), 142.5 (Ar), 156.8 (NHCO), 161.8 (CON), 169.2 (CO).

FAB; (m/z) (%): 622 (0.37)  $[\text{M}+\text{H}]^+$

Clcd. for:  $\text{C}_{29}\text{H}_{47}\text{N}_3\text{O}_8\text{Si}_2$  (621.3): C, 56.01, H, 7.62, N, 6.76. Found: C, 56.40, H, 7.71, N, 6.46.

***Poly{4-vinyl--{3,5-bis{3-{3,5-bis{3-{3,5-bis[3-(2-(trimethylsilyl)  
ethoxycarbonylamino]propyl}benzoylamino}propyloxy}propyloxy}  
benzoylamino}methyl}benzene} (36a):***

To a solution of 0.54 g of **33b** in 10 ml of methanol were added 0.5 g of triethylamine and 1.0 g of **35c**. After the mixture was stirred for 2 h at room temperature, 5 ml of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, 8 ml of dichloromethane, 0.20 g (2.0 mmol) of triethylamine and 0.8 g



of **35c** were added to the residue. The solution was stirred for another 48 h. After removal of the solvent and base, the residue was dissolved in 6 ml of THF and precipitated four times into methanol/water (4:1/v:v) and lyophilized from benzene to give 0.80 g of polymer **36a**.

*Poly{4-vinyl--{3,5-bis{3-{3,5-bis{3-[3,5-bis(3-aminopropyl)]benzoylamino} propyloxy} propyloxy}benzoylamino}methyl}benzene} 8•Trifluoroacetic acid (36b):*

To 0.1 g of Teoc-protected polymer **36a** was added 1.2 mL of trifluoroacetic acid and stirred for 20 h at room temperature. The trifluoroacetic acid was removed and the residue was lyophilized from water.

*Poly{4-vinyl-{3,5-bis{3-{3,5-bis{3-{3,5-bis{3-(2-(trimethylsilyl)ethoxycarbonylamino]propyl]benzoylamino}propyl]benzoylamino}propyloxy} benzoylamino}propyloxy}benzoylamino}methyl}benzene} (37a):*

To a solution of 0.26 g of **36b** in 8 ml of methanol were added 0.3 g of triethylamine and 0.6 g of **35c**. After the mixture was stirred for 2 h at room temperature, 4 ml of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, 6 ml of dichloromethane, 0.10 g (2.0 mmol) of triethylamine and 0.3 g of **35c** were added to the residue. The solution was stirred for another 48 h. After removal of the solvent and base, the residue was dissolved in 4 ml of THF and precipitated four times into methanol/water (4:1/v:v) and lyophilized from benzene to give 0.80 g of polymer **37a**.

*Poly{4-vinyl-{3,5-bis{3-{3,5-bis{3-{3,5-bis{3-aminopropyl] benzoylamino}propyl]benzoylamino}propyloxy}benzoylamino}propyloxy} benzoylamino}methyl}benzene} } 16•Trifluoroacetic acid (37b):*

To 0.08 g of Teoc-protected polymer **37a** was added 0.8 mL of trifluoroacetic acid and stirred for 20 h at room temperature. The trifluoroacetic acid was removed and the residue was lyophilized from water.

## 10.6. Modification of dendronized polystyrene

### 10.6.1. Modification of dendronized polystyrene with activated alkyl chains

*Poly{4-vinyl- $\{3,5\}$ -bis[3-N-(dodecanoicaminopropyl)benzyl]propyl}benzene}* 2□  
*Trifluoroacetic acid (16d):*

To a solution of 0.06 g of **16c** in 2 ml of methanol were added 0.05 g of triethylamine and 0.11 g of N-(dodecanoyloxy)succinimide. After the mixture was stirred for 2 h at room temperature, 2 ml of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, 2 ml of dichloromethane, the solution was stirred for another 48 h. After removal of the solvent and base, the residue was dissolved in 4 ml of THF and precipitated four times into methanol/water (4:1/v:v) and lyophilized from benzene to give polymer **16d**.

*Poly{4-vinyl- $\{3,5\}$ -bis[3- $\{3,5\}$ -bis(3-dodecanoicaminopropoxy)benzylamino]propoxy]benzylaminomethyl}benzene}* (38)

To a solution of 10 mg of **32b** in 1.5 ml of methanol were added 0.05 g of triethylamine and 20 mg of N-(dodecanoyloxy)succinimic-N-hydroxysuccinimidyl ester. After the mixture was stirred for 2 h at room temperature, 1 ml of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, 2 ml of dichloromethane, the solution was stirred for another 48 h. After removal of the solvent and base, the residue was dissolved in 4 ml of THF and precipitated four times into methanol/water (4:1/v:v) and lyophilized from benzene to give polymer **38**.

*Poly{4-vinyl- $\{3,5\}$ -bis[3- $\{3,5\}$ -bis(3-dodecanoicaminopropoxy)benzylamino]propoxy} benzylaminomethyl}benzene}* (39):

According to the same procedure as polymer **38**: 61 mg of **33b**, 0.14 g of N-(dodecanoyloxy)succinimic-N-hydroxysuccinimidyl ester.

*Poly{4-vinyl-{3,5-bis[3-{3,5-bis(3-N,N-didodecylsuccinamicaminopropoxy) benzoyl amino] propoxy}benzoylaminomethyl}benzene} (41):*

To a solution of 32 mg of **32b** in 1.5 ml of methanol were added 0.05 g of triethylamine and 0.17 g of N,N-didodcyl-succinimic-N-hydroxysuccinimidyl ester. After the mixture was stirred for 2 h at room temperature, 1 ml of dichloromethane was added. The resulting mixture was stirred for 48 h. After removal of the solvents, 2 ml of dichloromethane, the solution was stirred for another 48 h. After removal of the solvent and base, the residue was dissolved in 1.5 ml of THF and precipitated four times into methanol/water (4:1/v:v) and lyophilized from benzene to give polymer **41**.

*Poly{4-vinyl-{3,5-bis{3-[3,5-bis(3-N,N-didodecylsuccinamicaminopropoxy) benzoyl amino] propoxy} benzoylaminomethyl}benzene} (42):*

According to the same procedure as polymer **41**: 72 mg of **33b**, 0.35 g of N,N-didodcyl-succinimic-N-hydroxysuccinimidyl Ester.

*Poly{4-vinyl--{3,5-bis{3-{3,5-bis{3-[3,5-bis(3-N,N-didodecylsuccinamicaminopropyl) benzoyl amino}propoxy}propoxy} benzoylaminomethyl}benzene} (43):*

According to the same procedure as polymer **41**: 40 mg of **36b**, 0.20 g of N,N-didodcyl-succinimic-N-hydroxysuccinimidyl Ester.

*Poly{4-vinyl-{3,5-bis{3-{3,5-bis{3-{3,5-bis{3-N,N-didodecylsuccinamicaminopropyl}benzoyl amino}propyl}benzoyl amino}propoxy} benzoyl amino}propoxy} benzoylaminomethyl}benzene} (44)*

According to the same procedure as polymer **41**: 41 mg of **37b**, 0.27 g of N,N-dicyclohexylsuccinimide-N-hydroxysuccinimidyl Ester.

### 10.6.2. Modification of dendronized polystyrene with other activated Esters

#### *Ferrocenecarboxylic- N-hydroxysuccinimidyl Ester (45):*

To 35 ml dry acetonitril was added Ferrocenecarboxylic acid (0.60 g, 2.6 mmol), N-hydroxysuccinimide (0.33 g, 2.8 mmol), DCC (0.64 g, 3.1 mmol). yield: 55 %, 0.48 g.

<sup>1</sup>H NMR: 2.8 (s, 4H), 4.4 (s, 5H), 4.6 (s, 3H), 4.9 (s, 2H).

<sup>13</sup>C NMR: 25.9, 70.6, 70.7, 72.7, 169.4.

MS (80 ev), m/z (%): 327 (17.7) (M-H)<sup>+</sup>.

#### *4-Carboxybenzo-18-crown-6-N-hydroxysuccinimidyl Ester (46):*

To 30 ml dry dichloride methylene was added 4-Carboxybenzo-18-crown-6 (0.60 g, 1.68 mmol), N-hydroxysuccinimide (0.21 g, 1.8 mmol), DCC (0.42 g, 2.0 mmol). yield: 72 %, 0.55 g.

<sup>1</sup>H NMR: 2.8 (s, 4H, CH<sub>2</sub>), 3.7 (m, 12H, CH<sub>2</sub>), 3.9 (m, 4H, CH<sub>2</sub>), 4.2 (m, 4H, CH<sub>2</sub>), 6.9 (d, 1H, Ar), 7.6 (s, 1H, Ar), 7.8 (d, 1H, Ar).

<sup>13</sup>C NMR: 25.6, 68.9, 69.1, 69.2, 69.3, 70.5, 70.6, 70.7, 70.8, 112.2, 114.8, 117.1, 148.5, 154.7, 161.4, 169.3.

MS (80 ev), m/z (%): 453 (3.87) (M-H)<sup>+</sup>.

#### *3, 5-Bis{(3-(2-tetrahydropyranyloxy)propyloxy)}benzoic N-hydroxysuccinimidyl Ester (47):*

3, 5-Bis{(3-(2-tetrahydropyranyloxy)propyloxy)}benzoic acid (5.0 g, 11.4 mmol), N-hydroxysuccimide (1.45 g, 12 mmol), DCC (2.70 g, 13 mmol).

<sup>1</sup>H NMR: 1.4-1.8 (m, 12H), 2.1 (t, 4H), 2.8 (s, 4H) 3.5 (m, 4H), 3.8 (m, 4H), 4.1 (m, 4H), 4.5 (t, 2H), 6.7 (s, 1H), 7.2 (s, 2H).

<sup>13</sup>C NMR: 19.4, 25.2, 25.5, 29.3, 30.5, 62.1, 63.5, 65.2, 98.7, 108.3, 108.4, 126.4, 160.1, 169.0.

MS (80 ev), m/z (%): 535.2 (2.17) (M)<sup>+</sup>.