

## Experiment Part

Compounds G1-Br,<sup>11</sup> G2-Br,<sup>11</sup> **5**,<sup>4</sup> **6**,<sup>4</sup> and **10**<sup>4</sup> were prepared according to literature procedures. All the chemicals were purchased from Aldrich or Acros and used without further purification except for Pd(PPh<sub>3</sub>)<sub>4</sub> which was recrystallized before use. Solvents were worked up according to the standard procedure. All reactions were carried out under nitrogen. The <sup>1</sup>H-NMR spectra were recorded on Bruker 270 or 500 MHz spectrometers. The molecular weight determinations were done using a Thermo Separation Products set up with three DVB-mixed (DVB = divinylbenzene) bead columns, a H520B viscometer detector, and a Wyatt Dawn DSP laser Photometer, coupled with an Optilab 903 interferometric refractometer. Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) was used with trans-3-indoleacrylic acid (20 mg/ml in THF) as matrix.

### General Procedure for Ether Synthesis Using Phenol and Benzylic

**Bromide.** A mixture of phenol, benzylic bromide, K<sub>2</sub>CO<sub>3</sub>, and acetone was refluxed for 24h. The solvent was evaporated to dryness, the residue partitioned between water and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, the aqueous one extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic layer dried over MgSO<sub>4</sub>, and evaporated to dryness. The crude product was purified by silica gel chromatography. Some lower molar mass compounds were recrystallized, and the higher molar mass compounds were freeze-dried after column separation.

**General Procedure for Conversion of the Benzylic Alcohol into the Corresponding Bromide.** To a stirred solution of the alcohol and  $\text{CBr}_4$  in minimal THF, was added a solution of  $\text{PPh}_3$  in THF at  $0\text{ }^\circ\text{C}$ . After addition, the mixture was allowed to reach room temperature and stirred for 2 h. Then water was added, and the mixture extracted 3 times with  $\text{CH}_2\text{Cl}_2$ . The combined organic layer was dried over  $\text{MgSO}_4$ , and evaporated to dryness. The crude product was purified by silica gel column chromatography.

**General Procedure for the Reduction of Carboxylic Ester to Alcohol with  $\text{LiBH}_4$ .**

A solution of  $\text{LiBH}_4$  in THF was refluxed for 1 h, then cooled to room temperature, and a solution of dendritic ester (**2a**, **3a**, and **4a**) in THF was added dropwise. After addition the mixture was refluxed for further 6 h. Solvent was removed with rotary evaporator, the residue was acidified with dilute HCl, and the resulting solid extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 100 ml). The combined organic layer was dried over  $\text{MgSO}_4$  and evaporated to dryness. The crude product was purified by silica gel column chromatography.

**General Procedure for Suzuki Cross-Coupling Reaction.** A mixture of the respective dendrimer (**11a**, **11b**, and **11c**), *p*-*tert*-butylbenzeneboronic acid,  $\text{NaHCO}_3$ ,  $\text{H}_2\text{O}$ , and THF was carefully de-aired before  $\text{Pd}(\text{PPh}_3)_4$  was added. The mixture was then refluxed for 5 d with stirring.  $\text{CH}_2\text{Cl}_2$  (200 ml) was then added, the organic layer separated, and dried over  $\text{MgSO}_4$ . After removal of the solvent, the residue was purified by silica gel chromatography, and then freeze-dried from benzene.

**Methyl-4-bromo-3,5-dihydroxybenzoate (1)** A mixture of 4-bromo-3,5-dihydroxybenzoic acid (18.9 g, 81.1 mmol), methanol (200 ml), and H<sub>2</sub>SO<sub>4</sub> (5 ml) was refluxed for 16 h. The methanol was removed under reduced pressure, and the residue partitioned between water (200 ml) and diethylether (400 ml). The organic layer was washed with water (200 ml), saturated NaHCO<sub>3</sub> solution (30 ml), water (2 x 200 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The crude product was recrystallized from methanol. Yield 15.0 g (75%). Calc. for C<sub>8</sub>H<sub>7</sub>BrO<sub>4</sub>: C, 38.90; H, 2.86. Found C, 38.81; H, 2.77. <sup>1</sup>H NMR (270 MHz, DMSO-[d<sub>6</sub>]) 10.47 (s, 2H), 7.00 (s, 2H), 3.79 (s, 3H). <sup>13</sup>C NMR (68 MHz, DMSO-[d<sub>6</sub>]) 165.8, 155.5, 129.2, 107.0, 103.4, 52.2.

**Methyl-3,5-bis(benzyloxy)-4-bromobenzoate (2a).** Benzylbromide (18.2 g, 0.106 mol), **1** (11.1 g, 0.045 mol), K<sub>2</sub>CO<sub>3</sub> (15 g, 0.11 mol), and acetone (300 ml) were used. Crude product was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/hexane (1 : 1) increasing to CH<sub>2</sub>Cl<sub>2</sub> as eluent. Yield 16.8 g (87%). Calc. for C<sub>22</sub>H<sub>19</sub>BrO<sub>4</sub>: C, 61.84; H, 4.48. Found: C, 61.64; H, 4.33. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) 7.51-7.31 (m, 12H), 5.20 (s, 4H), 3.90 (s, 3H); <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) 166.3, 156.3, 136.1, 130.0, 128.6, 128.0, 127.1, 108.4, 107.3, 71.1, 52.4.

**Methyl-3,5-bis[3,5-bis(benzyloxy)benzyloxy]-4-bromobenzoate (3a).** Fréchet G1 bromide (1.95 g, 5.09 mmol), **1** (0.62 g, 2.554 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 g, 7.3 mmol), and acetone (150 ml) were used. Crude product was purified by chromatography on silica gel column using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Yield 1.6 g (74%). Calc. for C<sub>50</sub>H<sub>43</sub>BrO<sub>8</sub>: C, 70.50; H, 5.09. Found: C,

70.22; H, 4.91.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ) 7.42-7.27 (m, 22H), 6.75 (d, 4H), 6.56 (t, 2H), 5.13 (s, 4H), 5.04 (s, 8H), 3.89 (s, 3H);  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ) 166.2, 160.2, 156.1, 138.6, 136.8, 130.1, 128.6, 128.0, 127.5, 107.3, 105.8, 101.8, 70.8, 70.1, 52.4.

**Methyl 3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}-4-**

**bromobenzoate (4a).** Fréchet G2 bromide (4.00 g, 4.96 mmol), **1** (0.60 g, 2.42 mmol),  $\text{K}_2\text{CO}_3$  (1.4 g, 10.1 mmol), and acetone (200 ml) were used.

Crude product was purified by chromatography on silica gel column using

$\text{CH}_2\text{Cl}_2$  as eluent. Yield 3.8 g (92%). Calc. for  $\text{C}_{106}\text{H}_{91}\text{BrO}_{16}$ : C, 74.86; H,

5.39. Found: C, 74.53; H 5.38.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ) 7.41-7.27 (m,

42H), 6.74 (d, 2H), 6.68 (d, 4H), 6.56 (two sets of sigals incorporated into

two peaks, 6H), 5.11 (s, 4H), 5.01 (s, 16H), 4.98 (s, 8H), 2.73 (s, 3H);  $^{13}\text{C}$

NMR (68 MHz,  $\text{CDCl}_3$ ) 166.2, 160.1, 160.0, 156.1, 139.2, 138.6, 136.8,

130.1, 128.5, 127.9, 127.5, 108.3, 107.3, 106.3, 105.9, 101.8, 101.6, 70.8,

70.1, 70.0, 52.4.

**3,5-Bis(benzyloxy)-4-bromobenzylalcohol (2b).** **2a** (8.0 g, 18.7 mmol),

$\text{LiBH}_4$  (1.8 g, 84.2 mmol), and THF (150 ml) were used.  $\text{CH}_2\text{Cl}_2$ /methanol

(10:1) was used as eluent. Yield 7.0 g (94%).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )

7.49-7.27 (m, 10H), 6.60 (s, 2H), 5.13 (s, 2H), 4.55 (s, 2H);  $^{13}\text{C}$  NMR (68

MHz,  $\text{CDCl}_3$ ) 156.3, 141.6, 136.5, 128.5, 127.9, 126.9, 104.8, 70.8, 64.9.

**3,5-Bis[3,5-bis(benzyloxy)benzyloxy]-4-bromobenzylalcohol (3b).** **3a**

(1.5 g, 1.76 mmol),  $\text{LiBH}_4$  (0.17 g, 7.92 mmol), THF (100 ml) were used.

$\text{CH}_2\text{Cl}_2$ /methanol (10:1) was used as eluent. Yield 1.05 g (73%). Calc. for

$\text{C}_{49}\text{H}_{43}\text{BrO}_7$ : C, 71.44; H, 5.26. Found: C, 70.03; H, 5.27.  $^1\text{H}$  NMR (270

MHz, CDCl<sub>3</sub>) 7.43-7.29 (m, 20H), 6.73 (d, 4H), 6.57 (s, 2H), 6.55 (t, 2H), 5.07 (s, 4H), 5.03 (s, 8H), 4.54 (d, 2H); <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) 160.1, 156.2, 141.6, 139.0, 136.8, 128.5, 127.9, 127.5, 105.7, 104.8, 101.6, 70.6, 70.0, 64.9.

**3,5-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}-4-**

**bromobenzylalcohol (4b).** **4a** (3.66 g, 2.15 mmol), LiBH<sub>4</sub> (0.35 g, 15.9 mmol), THF (150 mmol) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 2.5 g (70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.40-7.26 (m, 40H), 6.70 (s, 4H), 6.65 (s, 8H), 6.54-6.50 (three sets of signals incorporated together, 8H), 5.04 (s, 4H), 4.99 (s, 16H), 4.95 (s, 8H), 4.50 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 160.1, 159.9, 156.1, 141.7, 139.2, 139.0, 136.7, 128.5, 128.0, 127.6, 106.2, 105.6, 104.8, 101.6, 101.5, 101.1, 70.6, 70.0, 69.9, 62.8, 52.4.

**3,5-Bis(benzyloxy)-4-bromobenzylbromide (2c) 2b** (6.01 g, 15.0 mmol), CBr<sub>4</sub> (7.48 g, 22.54 mmol), PPh<sub>3</sub> (5.91 g, 22.54 mmol) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Hexane (1:4). Yield 5.1 g (73%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.50-7.31 (m, 10H), 6.65 (s, 2H), 5.15 (s, 4H), 4.38 (s, 2H). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) 156.4, 138.0, 136.3, 128.6, 128.0, 127.0, 107.3, 71.0, 33.3.

**3,5-Bis[3,5-bis(benzyloxy)benzyloxy]-4-bromobenzylbromide (3c). 3b**

(1.00 g, 1.22 mmol), CBr<sub>4</sub> (0.65 g, 1.95 mmol), PPh<sub>3</sub> (0.51 g, 1.95 mmol) were used. CH<sub>2</sub>Cl<sub>2</sub>/Hexane (1:2) increasing to CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 0.78 g (72%). Calc. for C<sub>49</sub>H<sub>43</sub>BrO<sub>7</sub>: C, 66.38; H 4.77. Found: C, 66.38; H, 4.89. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.43-7.30 (m, 20H), 6.73 (d, 4H), 6.59 (s, 2H), 6.57 (t, 2H), 5.08 (s, 4H), 5.04 (s, 8H), 4.35 (s, 2H). <sup>13</sup>C

NMR (68 MHz, CDCl<sub>3</sub>) 160.1, 156.2, 138.7, 138.0, 136.8, 128.6, 128.0, 127.5, 107.3, 105.8, 101.7, 70.8, 70.0. 33.3.

**3,5-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}-4-**

**bromobenzylbromide (4c). 4b** (2.2 g, 1.32 mmol), CBr<sub>4</sub> (0.88 g, 2.65 mmol), PPh<sub>3</sub> (0.70 g, 2.65 mmol) were used. CH<sub>2</sub>Cl<sub>2</sub>/Hexane (1:2) increasing to CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 1.6 g (70%). Calc. for C<sub>105</sub>H<sub>90</sub>Br<sub>2</sub>O<sub>14</sub>: C, 72.66; H 5.23. Found: C, 72.30; H, 5.09. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.42 -7.30 (m, 40H), 6.73 (d, 4H), 6.69 (d, 8H), 6.60 (s, 2H), 6.57 (two sets of signals incorporated together, 6H), 5.05 (s, 4H), 5.01 (s, 16H), 4.98 (s, 8H), 4.35 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 160.1, 159.9, 156.1, 139.2, 138.7, 138.0, 136.6, 128.5, 127.9, 127.7, 127.5, 127.3, 107.2, 106.2, 105.7, 102.6, 101.6, 101.4, 70.7, 70.0, 69.9, 33.3.

**3-[3,5-Bis(benzyloxy)-4-bromobenzyloxy]-5-[3,5-**

**bis(benzyloxy)benzyloxy]benzyl**

**alcohol (7a). 5** (3.90 g, 8.81 mmol), **2c** (4.07 g, 8.81 mmol), K<sub>2</sub>CO<sub>3</sub> (1.82 g, 13.2 mmol), and acetone (250 ml) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 7.0 g (96%). Calc. for C<sub>49</sub>H<sub>43</sub>BrO<sub>7</sub>: C, 71.44; H, 5.26. Found: C, 71.21; H, 5.37. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.49-7.30 (m, 20H), 6.68 (two sets of signals overlapping, 4H), 6.60-6.49 (three sets of signals overlapping, 4H), 5.13 (s, 4H), 5.01 (s, 4H), 4.95 (s, 2H), 4.90 (s, 2H), 4.59 (s, 2H). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) 160.1, 159.9, 159.7, 156.3, 143.5, 139.1, 137.4, 136.6, 136.4, 128.5, 128.0, 127.8, 127.5, 126.9, 106.3, 105.7, 105.4, 101.4, 101.2, 70.8, 70.0, 69.8, 69.6, 65.0.

**3-{3,5-Bis[3,5-bis(benzyloxy)benzyloxy]-4-bromobenzyloxy}-5-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}benzylalcohol (8a). 3c**

(0.68 g, 0.77 mmol), **6** (0.67 g, 0.77 mmol), K<sub>2</sub>CO<sub>3</sub> (0.91 g, 6.50 mmol), and acetone (200 ml) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 1.03 g (80%). Calc. for C<sub>105</sub>H<sub>91</sub>BrO<sub>15</sub>: C, 75.39; H, 5.48. Found: C, 75.32; H, 5.74. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.41-7.29 (m, 40H), 6.72 (d, 4H), 6.65 (d, 4H), 6.64-6.62 (two sets of signals overlapping, 4H), 6.56-6.53 (four sets of signals overlapping, 7H), 5.52 (t, 1H), 5.06 (s, 4H), 5.01 (s, 8H), 4.99 (s, 8H), 4.83 (s, 6H), 4.87 (s, 2H), 4.53 (s, 2H). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) 160.1, 160.0, 159.7, 156.2, 143.6, 139.2, 139.0, 137.5, 136.7, 128.5, 127.9, 127.5, 106.3, 105.7, 105.5, 101.6, 101.5, 101.2, 70.7, 70.0, 69.9, 69.7, 65.0.

**3-[3,5-Bis(benzyloxy)-4-bromobenzyloxy]-5-[3,5-bis(benzyloxy)benzyloxy]benzyl**

**bromide (7b). 7a** (4.33 g, 5.26 mmol), CBr<sub>4</sub> (2.61 g, 7.88 mmol), PPh<sub>3</sub> (2.07 g, 7.88 mmol) were used. CH<sub>2</sub>Cl<sub>2</sub>/Hexane (1:2) increasing to CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 4.6 g (99%). Calc. for C<sub>49</sub>H<sub>42</sub>Br<sub>2</sub>O<sub>6</sub>: C, 66.38; H, 4.77. Found: C, 66.29; H, 4.84. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) 7.49-7.30 (m, 20H), 6.66 (two sets of signals overlapping, 4H), 6.62 (t, 1H), 6.58 (d, 2H), 6.47 (t, 1H), 5.15 (s, 4H), 5.02 (s, 4H), 4.95(s, 2H), 4.91 (s, 2H), 4.39 (s, 2H). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) 160.2, 159.9, 159.7, 156.4, 139.8, 138.9, 137.2, 136.7, 136.4, 128.5, 128.0, 127.9, 127.5, 127.0, 108.3, 108.2, 106.4, 105.5, 102.2, 101.5, 70.9, 70.1, 70.0, 69.8, 33.5.

**3-{3,5-Bis[3,5-bis(benzyloxy)benzyloxy]-4-bromo-benzyloxy}-5-3-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}benzylbromide (8b). 8a**

(1.00 g, 0.60 mmol), CBr<sub>4</sub> (2.61 g, 7.88 mmol), PPh<sub>3</sub> (2.07 g, 7.88 mmol) were used. CH<sub>2</sub>Cl<sub>2</sub>/Hexane (1:2) increasing to CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 0.24 g (23%). Calc. for C<sub>105</sub>H<sub>90</sub>Br<sub>2</sub>O<sub>14</sub>: C, 72.66; H, 5.23. Found: C, 72.28; H, 5.16. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) 7.39-7.27 (m, 40H), 6.72 (d, 4H), 6.64 (d, 4H), 6.61-6.53 (six sets of signals overlapping, 11H), 6.52 (t, 1H), 5.07 (s, 4H), 5.01 (s, 8H), 4.99 (s, 8H), 4.93 (s, 4H), 4.92 (s, 2H), 4.87 (s, 2H), 4.33 (s, 2H). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) 160.2, 160.1, 160.0, 156.5, 139.8, 139.2, 139.0, 137.4, 136.5, 128.6, 128.0, 127.5, 127.0, 108.2, 106.4, 105.6, 102.2, 101.6, 71.0, 70.1, 70.0, 69.8, 33.5.

**3-{3-[3,5-Bis(benzyloxy)-4-bromobenzyloxy]-5-[3,5-bis(benzyloxy)-benzyloxy]benzyloxy}-5-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}**

**benzylbenzylalcohol (9a). 7b** (1.31 g, 1.48 mmol), **6** (1.28 g, 1.48 mmol), K<sub>2</sub>CO<sub>3</sub> (1.00 g, 7.25 mmol), and acetone (200 ml) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 1.91 g (77%). Calc. for C<sub>105</sub>H<sub>91</sub>BrO<sub>15</sub>: C, 75.39; H, 5.48. Found: C, 75.34; H 5.69. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.46-7.28 (m, 40H), 6.65-6.50 (11 sets of signals overlapping, 20H), 5.11 (s, 4H), 4.99 (two sets of signals overlapping, 12H), 4.93 (four sets of signals overlapping, 10H), 4.89 (s, 2H), 4.55 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 160.08, 159.96, 159.91, 159.76, 156.34, 139.34, 139.21, 139.11, 139.09, 137.36, 136.65, 136.41, 129.20, 128.55, 128.01, 127.63, 127.56, 127.48, 127.07, 126.90, 106.90, 106.42, 106.18, 106.04, 105.67, 105.54, 105.31,



101.99, 101.76, 101.54, 101.35, 101.18, 101.03, 70.97, 70.83, 70.70,  
70.19, 70.02, 69.89, 69.73, 65.12.

**3-{3-[3,5-Bis(benzyloxy)-4-bromobenzyloxy]-5-[3,5-bis(benzyloxy)-  
benzyloxy]benzyloxy}-5-{3,5-bis[3,5-  
bis(benzyloxy)benzyloxy]benzyloxy}**

**benzylbenzylbromide (9b). 9a** (1.20 g, 0.72 mmol), CBr<sub>4</sub> (0.38 g, 1.15 mmol), PPh<sub>3</sub> (0.30 g, 1.15 mmol) were used. CH<sub>2</sub>Cl<sub>2</sub>/Hexane (1:2) increasing to CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 0.54 g (43%). Calc. for C<sub>105</sub>H<sub>90</sub>Br<sub>2</sub>O<sub>14</sub>: C, 72.66; H, 5.23. Found: C, 72.33; H, 5.16. <sup>1</sup>H NMR (270MHz, CDCl<sub>3</sub>) 7.46-7.27 (m, 40H), 6.66-6.49 (11 sets of signals overlapping, 20H), 5.12 (s, 4H), 5.00 (two sets of signals incorporated into one peak, 12H), 4.94 (two sets of signals incorporated into one peak, 6H), 4.92 (two sets of signals incorporated into one peak, 4H), 4.90 (s, 2H), 4.36 (s, 2H). <sup>13</sup>C NMR (68MHz, CDCl<sub>3</sub>) 160.2, 160.1, 159.9, 156.4, 139.8, 139.1, 139.0, 137.4, 136.7, 136.5, 128.6, 128.0, 127.9, 127.5, 127.0, 108.2, 106.4, 105.6, 102.2, 101.6, 70.9, 70.1, 70.0, 69.8, 33.6.

**Dendrimer 11a. 9b** (75 mg, 0.043 mmol), **10** (150 mg, 0.043 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.7 g, 2.2 mmol), and acetone (100 ml) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 0.18 g (81%). Calc. for C<sub>335</sub>H<sub>287</sub>BrO<sub>45</sub>: C, 78.70; H, 5.66. Found: C, 78.03; H, 5.63. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.42-7.27 (m, 120H), 6.88 (AB system, 12H), 6.65-6.45 (complexive shape, 62H), 5.09 (s, 4H), 4.95 (two sets of signals overlapping, 42H), 4.90-4.85 (six sets of signals overlapping, 44H), 2.03 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 160.1, 160.0, 156.7, 156.4, 142.0, 139.5, 139.2, 137.4, 136.7, 136.4, 129.6,

128.5, 128.0, 127.9, 127.5, 127.0, 113.9, 106.4, 106.3, 105.5, 101.5, 70.8, 70.0, 69.9. MALDI-TOF: Calc. for  $C_{335}H_{287}BrO_{45}$ : 5112.81; Found: 5136.1 (M + Na<sup>+</sup>), 5151.9 (M + K<sup>+</sup>).

**Dendrimer 11b. 8b** (110 mg, 0.064 mmol), **10** (220 mg, 0.64 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.8 g, 2.5 mmol), and acetone (100 ml) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 0.19 g (58%). Calc. for  $C_{335}H_{287}BrO_{45}$ : C, 78.70; H, 5.66. Found: C, 77.92; H, 5.51. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.39-7.25 (m, 120H), 6.88 (AB system, 12H), 6.79-6.51 (complex shape, 62H), 5.03 (s, 4H), 4.98-4.85 (seven sets of signals overlapping, 86H), 2.03 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 163.3, 160.1, 160.0, 159.8, 156.7, 156.2, 142.0, 139.6, 139.5, 139.1, 138.9, 137.4, 136.6, 129.6, 128.5, 128.0, 127.5, 113.9, 110.6, 106.3, 105.6, 101.5, 88.3, 82.4, 70.6, 70.0, 69.9, 50.6, 30.7. MALDI-TOF: Calc. for  $C_{335}H_{287}BrO_{45}$ : 5112.81; Found: 5136.0 (M + Na<sup>+</sup>), 5151.9 (M + K<sup>+</sup>).

**Dendrimer 11c. 4c** (275 mg, 0.159 mmol), **10** (548 mg, 0.159 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.0 g, 3.1 mmol), and acetone (150 ml) were used. CH<sub>2</sub>Cl<sub>2</sub> was used as eluent. Yield 0.68 g (81%). Calc. for  $C_{335}H_{287}BrO_{45}$ : C, 78.70; H, 5.66. Found: C, 78.20; H, 5.70. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.40-7.27 (m, 120H), 6.88 (two sets of signals overlapping, 12H), 6.72-6.51 (62H), 5.03 (s, 4H), 4.96-4.82 (seven sets of signals overlapping, 86H), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 160.05, 160.0, 156.66, 156.42, 156.19, 141.90, 139.46, 139.16, 139.09, 138.90, 136.64, 130.14, 129.45, 129.15, 128.63, 128.53, 128.43, 127.95, 127.64, 127.54, 127.43, 126.89, 114.13, 113.75, 106.89, 106.42, 106.09, 105.55, 102.02, 101.55, 101.32, 100.87, 70.62, 70.23,

70.14, 69.96, 69.86, 69.69, 50.56. MALDI-TOF: Calc. for  $C_{335}H_{287}BrO_{45}$ : 5112.81; Found: 5136.1 ( $M+Na^+$ ), 5152.1 ( $M + K^+$ ).

**Dendrimer 11d. 11a** (125 mg, 0.0245 mmol), **12** (35 mg, 0.197 mmol),  $NaHCO_3$  (1.0 g),  $H_2O$  (10 ml), THF (15 ml), and  $Pd(PPh_3)_4$  (2.0 mg) were used.  $CH_2Cl_2/Hexane$  (1:1) increasing to  $CH_2Cl_2$  was used as eluent.

Yield: 120 mg (95%). Calc. for  $C_{345}H_{300}O_{45}$ : C, 80.21; H, 5.85. Found: C, 79.75; H, 5.89.  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 7.40-7.10 (complex peaks, 124H), 6.88 (AB system, 12H), 6.72 (s, 2H), 6.66-6.49 (20H), 4.96-4.87 (45H), 2.03 (s, 3H), 1.34 (s, 9H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ) 160.1, 160.0, 156.9, 156.7, 139.1, 137.2, 136.7, 130.6, 129.6, 128.5, 128.2, 128.0, 127.5, 127.4, 126.6, 124.4, 113.9, 106.4, 106.3, 106.1, 101.5, 70.5, 70.0, 69.9, 69.8, 31.4. MALDI-TOF: Calc. for  $C_{345}H_{300}O_{45}$ : 5166.12; Found: 5189.1 ( $M+Na^+$ ), 5205.0 ( $M + K^+$ ).

**Dendrimer 11e. 11b** (120.2 mg, 0.024 mmol), **12** (33 mg, 0.185 mmol),  $NaHCO_3$  (0.6 g),  $H_2O$  (10 ml), THF (15 ml), and  $Pd(PPh_3)_4$  (3.0 mg) were used.  $CH_2Cl_2/Hexane$  (1:1) increasing to  $CH_2Cl_2$  was used as eluent.

Yield: 0.12 g (97%). Calc. for  $C_{345}H_{300}O_{45}$ : C, 80.21; H, 5.85. Found: C, 79.62; H, 5.95.  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 7.40-7.22 (124H), 6.86 (two AB systems overlapping, 12H), 6.71 (s, 2H), 6.63-6.45 (20H), 4.95-4.86 (90H), 2.03 (s, 3H), 1.15 (s, 9H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ) 160.07, 159.98, 159.88, 156.78, 156.69, 139.67, 139.12, 136.70, 136.67, 130.69, 129.60, 128.54, 128.50, 127.97, 127.94, 127.62, 127.54, 124.43, 113.92, 106.38, 106.30, 105.69, 105.18, 101.48, 101.12, 69.99, 69.91, 31.24.

MALDI-TOF: Calc. for  $C_{345}H_{300}O_{45}$ : 5166.12; Found: 5189.6 ( $M+Na^+$ ), 5205.4 ( $M + K^+$ ).

**Dendrimer 11f. 11c** (335 mg, 0.066 mmol), **12** (66 mg, 0.185 mmol),  $NaHCO_3$  (0.6 g),  $H_2O$  (10 ml), THF (15 ml), and  $Pd(PPh_3)_4$  (1.6 mg) were used.  $CH_2Cl_2/Hexane$  (1:1) increasing to  $CH_2Cl_2$  was used as eluent. Yield: 0.30 g, (88%). Calc. for  $C_{345}H_{300}O_{45}$ : C, 80.21; H, 5.85. Found: C, 79.71; H, 6.01.  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 7.39-7.27 (m, 124H), 6.88 (two AB systems incorporated together, 12H), 6.72 (s, 2H), 6.63-6.44 (20H), 4.95-4.81 (90H), 2.05 (s, 3H), 1.15 (s, 9H).  $^{13}C$  NMR (125MHz,  $CDCl_3$ ) 160.07, 160.04, 159.97, 159.78, 156.77, 156.68, 141.98, 139.70, 139.48, 139.12, 136.67, 130.71, 129.60, 128.54, 128.53, 128.37, 127.96, 127.53, 127.51, 124.44, 113.93, 106.39, 106.28, 105.80, 105.23, 101.47, 101.17, 70.14, 69.99, 69.97, 69.89, 69.83, 50.59, 31.27. MALDI-TOF: Calc. for  $C_{345}H_{300}O_{45}$ : 5166.12; Found: 5189.1 ( $M + Na^+$ ), 5205.3 ( $M + K^+$ ).