**Figure S1.** Differential scanning calorimetry traces for one-component gelators in toluene: a) G1-C12-G1, b) G2-C12-G2, c) G3-C12-G3.
Figure S2: Circular Dichroism Spectra

Figure S2. Circular dichroism spectra for one-component gelators: a) G1-C12-G1, b) G2-C12-G2, c) G3-C12-G3. Concentration, 3 mM; solvent, cyclohexane.
Experimental Data

Methods of Compound Characterisation

Silica column chromatography was carried out using silica gel provided by Fluorochem Ltd. (35-70µ). Thin layer chromatography was performed on commercially available Merck aluminium backed silica plates. Preparative gel permeation chromatography was carried out using a 2 m glass column packed with Biobeads SX-1 supplied by Biorad. Proton and carbon NMR spectra were recorded on a Jeol 400 spectrometer (1H 400 MHz, 13C 100 MHz). Samples were recorded as solutions in CDCl3 and chemical shifts (δ) are quoted in parts per million, referenced to residual solvent. Coupling constant values (J) are given in Hz. DEPT experiments were used to assist in the assignment of 13C NMR spectra. Melting points were measured on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected. Positive ion electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer. Positive ion fast atom bombardment mass spectra were recorded on a Fisons Instruments Autospec mass spectrometer, with 3-nitrobenzyl alcohol as matrix. Polyethylene glycols and or polyethylene glycol mono-methyl ethers were used as calibrants for HRMS determinations. The isotope distribution observed for mass spectral ions of the larger molecules is consistent with data calculated from isotopic abundances. Infra-red spectra were recorded using an ATI Mattson Genesis Series FTIR spectrometer.
Methods of Gel Characterisation

Gelation Experiments

The experiment was performed by solubilisation of a weighed amount of dendritic gelator in a measured volume of selected pure solvent. The mixture was sonicated at ambient temperature for 30 min before heating and cooling produced a gel. The gel sample was left to stand overnight. Gelation was considered to have occurred when a homogenous ‘solid-like’ material was obtained that exhibited no gravitational flow. The thermally reversible gel-sol transition temperature \( T_{\text{gel}} \) was determined using a tube inversion methodology – the gel-sol transition temperature represents the point at which the stress exerted by the gel exceeds its yield strength, and a single drop of solvent begins to run from the immobilised gel. All gel samples were prepared with a total volume of 1 mL in tubes with a diameter of 10 mm – this ensures that the stress generated by the gel on tube inversion is approximately constant in each case.

Differential Scanning Calorimetry

The thermograms were recorded on a SEIKO DSC 6200 instrument using closed stainless steel cups. The gelator was placed in the stainless steel cups and the run was recorded (in triplicate). The scan speed for the heating cycle was 5 °C/min.
**Scanning Electron Microscopy**

Gel samples were applied to stainless steel stubs and allowed to dry. Prior to examination, the gels were coated with a thin layer of Pd/Pt. Scanning electron micrographs were recorded using a LEO 1530 FEGSEM instrument. Pd/Pt deposition was performed using a Denton vacuum LLC.

**Circular Dichroism Measurements**

Circular dichroism (CD) spectra were recorded in the far – ultraviolet region (200 – 350 nm) using a JASCO 810 spectrometer and a 1.0 mm quartz cuvette. A sample interval of 1 nm and an averaging time of 3 s were used in all experiments. [Dendritic branch] = 3mM.

**¹H NMR Measurements**

¹H NMR spectra were recorded on a JEOL 400 spectrometer. Chemical shifts are denoted in δ units (ppm) relative to toluene-d₈ (¹H: δ = 7.10 ppm). All experiments were carried out with the following parameters: scan rate = 1000, relaxation time = 2 s).

**Small Angle X-ray Scattering (SAXS)**

Experiments were performed on station 16.1 at the Synchrotron Radiation Source, Daresbury Lab, UK. The wavelength was λ= 1.41 Å. Data were collected on a two-dimensional gas-filled area detector (RAPID). The wave vector scale $q = 4\pi \sin \theta / \lambda$, where $2\theta$ is the scattering angle) was calibrated using a specimen of wet collagen (rat-tail
tendon). Samples were put in brass cells with mica windows and an inner spacer to hold liquids. The temperature was controlled with a water bath. The SAXS data were corrected to allow for sample transmission and background scattering (using a toluene sample as a reference).

**Simulations**

Simulations of G2-C12-G2 were performed using the MM2 function in Spartan Pro. Minima were not exhaustively searched, but the typical molecular dimensions were found to be roughly in agreement with the data generated by SAXS.

**Materials for synthesis**

The L-lysine based dendritic branches\(^{16}\) (dendrons) were synthesized in optically pure form, and in high yields, using a solution phase approach previously reported by us.\(^{17}\) The aliphatic diamines were purchased from Aldrich (C7, C8, C10, C12), Lancaster (C6, C9) and TCI-EP (C11).

**Synthesis of Novel Gelators**

**G1-C12-G1.**

1,12-Diaminododecane (0.50 g, 2.5 mmol) was suspended in ethyl acetate (EtOAc, 100 ml), triethylamine (NEt\(_3\), 1.00 ml, 0.72 g, 7.1 mmol) was added, followed by
Boc-protected L-lysine (1.90 g, 5.50 mmol). The mixture was stirred under N₂ for 5 min. The reaction was cooled to 0°C, then 1-hydroxybenzotriazole (HOBt, 1.98 g, 14.54 mmol) and 1,3-dicyclohexylcarbodiimide (DCC, 3.00 g, 14.54 mmol) were added simultaneously as a mixture of solids. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The precipitate was removed by filtration and washed with EtOAc then discarded. The filtrate was then washed first with an aqueous saturated solution of sodium hydrogen carbonate, then with aqueous sodium hydrogen sulfate (8 g in 50 ml), before being washed again with NaHCO₃aq then finally water. The solution was dried over MgSO₄ then rotary evaporated to produce a white solid. This crude product was purified by column chromatography (silica, CH₂Cl₂: MeOH 98:2) to give a white solid with the yield of 1.90 g (2.22 mmol, 88%). Mp 104-105°C; R₆ 0.55 (CH₂Cl₂: MeOH, 90:10); αD₂93 -8.9 (c =1.0, CH₃OH); δₜ (400 MHz, CDCl₃) 6.38 (2H, br, CONH), 5.25 (2H, br, NHBoc), 4.69 (2H, br, NHBoc), 4.01 (2H, br, COCH(R)NH), 3.23-3.17 (4H, m, CH₂NHOCH(R)), 3.10 (4H, m, CH₂NHBoc), 2.07-1.20 (68H, m, CH₂, CH₃); δC (400 MHz, CDCl₃) 172.1 (CONH x 2), 156.2 (NHOCH(R)NH x 2), 80.5 (OC(CH₃)₃ x 2), 79.5 (OC(CH₃)₃ x 2), 54.5 (COCH(R)NH x 2), 40.9 (CH₂NHOCH(R) x 2), 39.5 (CH₂NHOCH(R) x 2), 32.2 (CH₂), 29.4 (CCH₃ x 6), 29.2 (CCH₃ x 6), 26.9 (CH₂), 22.7 (CH₂); νmax (KBr disc) 3326m (NH), 2930w (CH₂, CH₃), 2856w (CH), 1697s (C=O), 1527s (CONH), 1456w, 1392m, 1366m, 1250m, 1172s; m/z (Electrospray) C₄₄H₆₄N₆O₁₀Na [M+Na]⁺ requires: 879.0; found 879.4 (100%), 880.5 (40%), 881.5 (10%); HR FAB-MS calculated for C₄₄H₆₄N₆O₁₀Na 879.6147, found 879.6144.
Analogous methods were applied for the following first generation gelators:

**G1-C6-G1**

Mp 52-55 °C; R_f 0.5 (CH₂Cl₂: MeOH, 90:10); α_D²⁹³ –7.1 (c =1.0, CH₃OH); δ_H (400 MHz, CDCl₃) 6.83 (2H, br, CONH), 5.50 (2H, br, NHBoc), 4.77 (2H, br, NHBoc), 4.10 (2H, br, COCH(R)NH), 3.29 (4H, m, CH₂NHOCH(R)), 3.08 (4H, m, CH₂NHBoc), 2.21-1.20 (56H, m, CH₂, CH₃); δ_C (400 MHz, CDCl₃) 172.7 (CONH x 2), 156.3 (NHOBoc x 4), 79.9 (OC(CH₃)₃ x 2), 79.2 (OC(CH₃)₃ x 2), 54.6 (COCH(R)NH x 2), 40.2 (CH₂NHOCH(R) x 2), 38.6 (CH₂NHOBoc x 2), 32.3 (CH₂), 29.7 (CCH₃ x 6), 29.0 (CCH₃ x 6), 26.9 (CH₂), 25.5 (CH₂), 22.9 (CH₂); ν_max (KBr disc) 3331m (NH), 2978m (CH₂, CH₃), 2935w (CH₂, CH₃), 2865w (CH), 1699s (C=O), 1525s (CONH), 1456w, 1392m, 1366m, 1250m, 1170s; m/z (Electrospray) C₃₈H₇₂N₆O₁₀Na [M+Na]⁺ requires: 795; found 795 (100%), 796 (40%). HR FAB-MS calculated for C₃₈H₇₂N₆O₁₀Na 795.5203, found 795.5204.

**G1-C7-G1**

Mp 57-60 °C; R_f 0.5 (CH₂Cl₂: MeOH, 90:10); α_D²⁹³ –9.9 (c =1.0, CH₃OH); δ_H (400 MHz, CDCl₃) 6.46 (2H, br, CONH), 5.30-5.28 (2H, br d, NHBoc), 4.72 (2H, br, NHBoc), 4.02 (2H, br, COCH(R)NH), 3.21 (4H, m, CH₂NHOCH(R)), 3.08 (4H, m, CH₂NHBoc), 1.77-1.23 (58H, m, CH₂, CH₃); δ_C (400 MHz, CDCl₃) 172.9 (CONH x 2), 156.5 (NHOBoc x 2), 156.1 (NHOBoc x 2), 79.9 (OC(CH₃)₃ x 2), 79.2 (OC(CH₃)₃ x 2), 54.6 (COCH(R)NH x 2), 40.1 (CH₂NHOCH(R) x 2), 39.4 (CH₂NHOBoc x 2), 32.3
(CH₂), 29.6 (CCH₃ x 6), 29.0 (CCH₃ x 6), 28.4 (CH₂), 26.9 (CH₂), 25.5 (CH₂), 22.8 (CH₂); νₘₐₓ (KBr disc) 3327m (NH), 2978m (CH₂, CH₃), 2934w (CH₂, CH₃), 2862w (CH), 1700s (C=O), 1522s (CONH), 1456w, 1392m, 1366m, 1249m, 1168s; m/z (Electrospray) C₃₀H₇₄N₆O₁₀Na [M+Na]⁺ requires: 809; found 809 (100%), 810 (40%), 811 (10%); HR FAB-MS calculated for C₃₀H₇₄N₆O₁₀Na 809.5370, found 809.5367.

G1-C8-G1
Mp 105-108 °C; Rf 0.55 (CH₂Cl₂: MeOH, 90:10); δ₀ 293 –7.3 (c =1.0, CH₃OH); δ (400 MHz, CDCl₃) 6.77 (2H, br, CONH), 5.42-5.40 (2H, br d, NHBoc), 4.78 (2H, br, NHBoc), 4.07 (2H, br, COCH(R)NH), 3.28 (4H, m, CH₂NHOCH(R)), 3.07 (4H, m, CH₂NHBOc), 1.75-1.25 (60H, m, CH₂, CH₃); δ (400 MHz, CDCl₃) 172.6 (CONH x 2), 156.1 (NHCOBOc x 4), 80.1 (OC(CH₃)₃ x 2), 79.3 (OC(CH₃)₃ x 2), 54.6 (COCH(R)NH x 2), 40.1 (CH₂NHOCH(R) x 2), 39.5 (CH₂NHCOBOc x 2), 32.2 (CH₂), 28.5 (CCH₃ x 6), 28.4 (CCH₃ x 6), 28.0 (CH₂), 26.9 (CH₂), 25.5 (CH₂), 22.8 (CH₂); νₘₐₓ (KBr disc) 3327m (NH), 2978m (CH₂, CH₃), 2933w (CH₂, CH₃), 2861w (CH), 1700s (C=O), 1521s (CONH), 1456w, 1392m, 1366m, 1249m, 1169s; m/z (Electrospray) C₄₀H₇₆N₆O₁₀Na [M+Na]⁺ requires: 823; found 823 (100%), 824 (40%), 825 (7%); HR FAB-MS calculated for C₄₀H₇₆N₆O₁₀Na 823.5516, found 823.5518.

G1-C9-G1
Mp 110-113 °C; Rf 0.55 (CH₂Cl₂: MeOH, 90:10); δ₀ 293 –6.9 (c =1.0, CH₃OH); δ (400 MHz, CDCl₃) 6.68 (2H, br, CONH), 5.54-5.42 (2H, br d, NHBoc), 4.80 (2H, br, NHBoc),
4.03 (2H, br, COCH(R)NH), 3.20 (4H, d, CH$_2$NHOCH(R)), 3.05 (4H, d, CH$_2$NHBoc), 1.85-1.25 (62H, m, CH$_2$, CH$_3$); $\delta_C$ (400 MHz, CD$_3$Cl) 172.6 (CONH x 2), 156.4 (NHOBCOoc x 4), 80.1 (OC(CH$_3$)$_3$ x 2), 79.3 (OC(CH$_3$)$_3$ x 2), 54.6 (COCH(R)NH x 2), 40.1 (CH$_2$NHOCH(R) x 2), 39.5 (CH$_2$NHOCH(R) x 2), 32.2 (CH$_2$), 28.5 (CCH$_3$ x 6), 28.4 (CCH$_3$ x 6), 26.6 (CH$_2$), 25.6 (CH$_2$), 22.8 (CH$_2$), 22.6 (CH$_2$); $\nu_{\text{max}}$ (KBr disc) 3327m (NH), 2978m (CH$_2$, CH$_3$), 2932w (CH$_2$, CH$_3$), 2857w (CH), 1703s (C=O), 1528s (CONH), 1451w, 1366m, 1164s; m/z (Electrospray) C$_{41}$H$_{78}$N$_6$O$_{10}$Na $[\text{M+Na}]^+$ requires: 837; found 837.4 (100%), 838.4 (40%), 837.4 (10%); HR FAB-MS calculated for C$_{41}$H$_{78}$N$_6$O$_{10}$Na 837.5672, found 837.5674.

G1-C10-G1

Mp 115-117 °C; R$_f$ 0.55 (CH$_2$Cl$_2$; MeOH, 90:10); $\alpha_D^{293}$ –9.6 (c =1.0, CH$_3$OH); $\delta_h$ (400 MHz, CDCl$_3$) 6.51 (2H, br, CONH), 5.33 (2H, s, NHBoc), 4.74 (2H, br, NHBoc), 4.03 (2H, br, COCH(R)NH), 3.20 (4H, d, CH$_2$NHOCH(R)), 3.05 (4H, d, CH$_2$NHBoc), 1.89-1.08 (64H, m, CH$_2$, CH$_3$); $\delta_C$ (400 MHz, CDCl$_3$) 172.3 (CONH x 2), 156.4 (NHOBCOoc x 4), 80.0 (OC(CH$_3$)$_3$ x 2), 79.3 (OC(CH$_3$)$_3$ x 2), 54.6 (COCH(R)NH x 2), 40.1 (CH$_2$NHOCH(R) x 2), 39.6 (CH$_2$NHOCH(R) x 2), 32.2 (CH$_2$), 29.7 (CCH$_3$ x 6), 29.4 (CCH$_3$ x 6), 26.8 (CH$_2$), 25.6 (CH$_2$), 25.0 (CH$_2$), 22.8 (CH$_2$); $\nu_{\text{max}}$ (KBr disc) 3325m (NH), 2976m (CH$_2$, CH$_3$), 2930w (CH$_2$, CH$_3$), 2853w (CH), 1700s (C=O), 1539s (CONH), 1457w, 1366m, 1247m, 1169s; m/z (Electrospray) C$_{42}$H$_{80}$N$_6$O$_{10}$Na $[\text{M+Na}]^+$ requires: 851; found 851 (100%), 852 (40%), 854 (10%); HR FAB-MS calculated for C$_{42}$H$_{80}$N$_6$O$_{10}$Na 851.5829, found 851.5827.
G1-C11-G1

Mp 117-120°C; Rf 0.55 (CH$_2$Cl$_2$: MeOH, 90:10); $\alpha_D^{293} -10.8$ (c =1.0, CH$_3$OH); $\delta_H$ (400 MHz, CDCl$_3$) 6.46 (2H, br, CONH), 5.30 (2H, br, NHBoc), 4.72 (2H, br, NHBoc), 4.02 (2H, br, COCH(R)NH), 3.20-3.19 (4H, m, CH$_2$NHOCH(R)), 3.08-3.06 (4H, d, CH$_2$NBoc), 1.80-1.23 (66H, m, CH$_2$, CH$_3$); $\delta_C$ (400 MHz, CDCl$_3$) 172.3 (CONH x 2), 156.4 (NHOBoc x 2), 156.0 (NHOBoc x 2), 80.0 (OC(CH$_3$)$_3$ x 2), 79.3 (OC(CH$_3$)$_3$ x 2), 54.6 (COCH(R)NH x 2), 40.9 (CH$_2$NHOCH(R) x 2), 39.6 (CH$_2$NHOBoc x 2), 32.2 (CH$_2$), 28.5 (CCH$_3$ x 6), 28.4 (CCH$_3$ x 6), 26.9 (CH$_2$), 22.8 (CH$_2$); $\nu_{\text{max}}$ (KBr disc) 3331m (NH), 2930w (CH$_2$, CH$_3$), 2856w (CH), 1683s (C=O), 1525s (CONH), 1456w, 1392m, 1365m, 1250m, 1177s; $m/z$ (Electrospray) C$_{43}$H$_{82}$N$_6$O$_{10}$Na $[\text{M+Na}]^+$ requires: 865; found 865 (100%), 866 (40%), 867 (10%); HR FAB-MS calculated for C$_{43}$H$_{82}$N$_6$O$_{10}$Na 865.5990, found 865.5991.

G2-C12-G2.

Compound G1-C12-G1 (1.10 g, 1.25 mmol) was dissolved in CH$_2$Cl$_2$ (5 ml). Trifluoroacetic acid (TFA, 3 ml) was then added and the solution stirred under N$_2$ for 30 minutes. The solution was rotary evaporated to remove the excess TFA and the solvent. The sample was then dried under high vacuum for 10 minutes. EtOAc (40 ml) was added to dissolve the deprotected intermediate and NEt$_3$ (2.7 ml, 1.86 g, 18.4 mmol) added to produce the free amine. Boc-protected L-lysine (2.73 g, 7.89 mmol, 6.3 eq.) was then added and the solution stirred under nitrogen for 2 min, before being cooled to 0°C. HOBt (2.14 g, 15.6 mmol) and DCC (3.26 g, 15.6 mmol) were then added simultaneously.
as a mixture of solids. The reaction mixture was allowed to warm to room temperature and stirred for 3 d. The precipitate (containing the product) was filtered and washed with EtOAc. The product was extracted from this solid with an excess of MeOH (using an ultra-sonic bath to break up the large solid particles). This crude product was purified by silica chromatography (CH$_2$Cl$_2$: MeOH 98:2) to get rid of excess dicyclohexylurea (DCU), then the column was eluted at higher polarity (CH$_2$Cl$_2$: MeOH 90:10) to collect all the unreacted Boc-protected L-lysine and also the product. The product was dissolved in the minimum of MeOH, Et$_2$O (100 ml) was added and the flask was placed in the freezer. The product crystallized from the solution for a period of an hour. The product was then filtered and washed with cold Et$_2$O to produce a white crystalline solid with a yield of 1.40 g (0.78 mmol, 62.5%). Mp 110-113°C; R$_f$ 0.4 (CH$_2$Cl$_2$: MeOH, 90:10); $\alpha_0^{293}$ -19.7 (c=1.0, CH$_3$OH); $\delta_H$ (400 MHz, CDCl$_3$) 7.43 (2H, br, CONH), 7.26 (2H, br, CONH), 6.83 (2H, br, CONH), 5.93 (2H, br, NHBoc), 5.61 (2H, br, NHBoc), 5.03 (2H, br, NHBoc), 4.84 (2H, br, NHBoc), 4.29 (6H, s, COCH(R)NH), 4.19 (4H, s, CH$_2$NHCOC(R)), 3.17-3.06 (12H, m, CH$_2$NHCOC(R)), 1.72-1.19 (128H, m, CH$_2$, CH$_3$); $\delta_C$ (400 MHz, CDCl$_3$) 173.5 (CONH x 2), 171.7 (CONH x 4), 156.4-156.2 (NHCOboc x 8), 80.1 (OC(CH$_3$)$_3$ x 4), 80.0 (OC(CH$_3$)$_3$ x 4), 54.4 (COCH(R)NH x 2), 54.2 (COCH(R)NH x 2), 53.5 (COCH(R)NH x 2), 40.3 (CH$_2$CH$_2$NH x 2), 40.0 (CH$_2$CH$_2$NH x 2), 39.6 (CH$_2$CH$_2$NH x 4), 32.7 (CH$_2$ x 2), 32.4 (CH$_2$ x 6), 29.6 (CH$_2$ x 6), 29.4 (CH$_2$ x 3), 29.2 (CH$_2$ x 3), 28.6 (CCH$_3$ x 24), 26.8 (CH$_2$), 22.9 (CH$_2$), 22.7 (CH$_2$ x6); $\nu_{max}$ (KBr disc) 3337m (CONH), 3094w (NH), 2978m (CH$_2$, CH$_3$), 2932m (CH$_2$, CH$_3$), 2860w (CH), 1692s (C=O), 1523s (CONH), 1456w, 1392m, 1366m, 1249m, 1173s; $m/z$
(Electrospray) \( \text{C}_{88}\text{H}_{164}\text{N}_{14}\text{O}_{22}\text{Na} \) \([\text{M+Na}]^+\) requires 1792; found 1791.9 (100%), 1792.9 (85%), 1793.5 (45%), 1794.5 (15%).

Analogous methods were applied for the following second generation gelators:

**G2-C6-G2**

Mp 90-94ºC; \( R_f \) 0.4 (CH\(_2\)Cl\(_2\): MeOH, 90:10); \( \alpha_d^{293} \) –19.7 (c=1.0, CH\(_3\)OH); \( \delta_H \) (400 MHz, CDCl\(_3\)) 7.62 (2H, br, CONH), 7.49 (2H, br, CONH), 7.17 (2H, br, CONH), 5.94 (2H, br, NH\(_{\text{Boc}}\)), 5.63 (2H, br, NH\(_{\text{Boc}}\)), 5.22 (2H, br, NH\(_{\text{Boc}}\)), 4.85 (2H, br, NH\(_{\text{Boc}}\)), 4.42-4.31 (6H, m, CO\(_2\text{H}\)NH), 3.36 (4H, s, CH\(_2\)NHCOCH(R)), 3.08 (12H, s, CH\(_2\)NHCOC\(_2\)H), 1.68-1.19 (116H, m, CH\(_2\), CH\(_3\)); \( \delta_C \) (400 MHz, CDCl\(_3\)) 172.2 (CONH x 6), 156.4 (NHCOBoc x 8), 79.9 (OC(CH\(_3\))\(_3\) x 4), 79.0 (OC(CH\(_3\))\(_3\) x 4), 54.1 (CO\(_2\text{H}\)NH x 6), 41.1 (CH\(_2\)CH\(_2\)NH x 8), 32.9 (CH\(_2\) x 8), 29.6 (CH\(_2\) x 6), 28.6 (CCH\(_3\) x 24), 25.7 (CH\(_2\) x 6), 22.9 (CH\(_2\) x 2); \( \nu_{\text{max}} \) (KBr disc) 3340m (NH), 3097w (NH), 2935m (CH\(_2\), CH\(_3\)), 2862w (CH), 1691s (C=O), 1522s (CONH), 1456w, 1392m, 1366m, 1248m, 1172s; \( m/z \) (Electrospray) \( \text{C}_{82}\text{H}_{152}\text{N}_{14}\text{O}_{22}\text{Na} \) \([\text{M+Na}]^+\) requires 1707; found 1707.7 (100%), 1708.8 (85%), 1709.8 (45%), 1710.9 (15%).

**G2-C9-G2**

Mp 105-107ºC; \( R_f \) 0.4 (CH\(_2\)Cl\(_2\): MeOH, 90:10); \( \alpha_d^{293} \) –19.7 (c=1.0, CH\(_3\)OH); \( \delta_H \) (400 MHz, CDCl\(_3\)) 7.46 (2H, br, CONH), 7.22 (2H, br, CONH), 6.94 (2H, br, CONH), 5.92 (2H, br, NH\(_{\text{Boc}}\)), 5.45 (2H, br, NH\(_{\text{Boc}}\)), 5.17 (2H, br, NH\(_{\text{Boc}}\)), 4.82 (2H, br, NH\(_{\text{Boc}}\)),
4.33 (6H, s, COCH(R)NH), 3.46 (4H, s, CH$_2$NHOCH(R)), 3.07-2.93 (12H, m, CH$_2$NHOCH*H), 1.70-1.19 (12H, m, CH$_2$, CH$_3$); $\delta$C (400 MHz, CDCl$_3$) 173.4 (CONH x 4), 171.8 (CONH x 2), 156.6-156.2 (NHCOBoc x 8), 80.0 (OC(CH$_3$)$_3$ x 4), 79.1 (OC(CH$_3$)$_3$ x 4), 54.2 (COCH(R)NH x 6), 40.4 (CH$_2$CH$_2$NH x 2), 39.8 (CH$_2$CH$_2$NH x 2), 39.4 (CH$_2$CH$_2$NH x 2), 33.1 (CH$_2$ x 2), 32.9 (CH$_2$ x 6), 29.7 (CH$_2$ x 6), 29.5 (CH$_2$ x 3), 29.2 (CH$_2$ x 3), 28.6 (CCH$_3$ x 24), 22.9 (CH$_2$ x 2), 22.3 (CH$_2$ x 3); $\nu_{\text{max}}$ (KBr disc) 3335m (NH), 3096w (NH), 2978m (CH$_2$, CH$_3$), 2934m (CH$_2$, CH$_3$), 2862w (CH), 1692s (C=O), 1523s (CONH), 1456w, 1392m, 1366m, 1249m, 1172s; m/z (Electrospray) C$_{85}$H$_{158}$N$_{14}$O$_{22}$Na [M+Na]$^+$ requires 1750; found 1750.9 (100%), 1751.9 (45%), 1752.8 (15%).

**G3-C12-G3.**

Compound **G2-C12-G2** (1.00 g, 0.57 mmol) was dissolved in CH$_2$Cl$_2$ (5 ml). TFA (3 ml) was then added and the solution stirred under N$_2$ for 30 minutes. The solution was rotary evaporated to remove the excess TFA and the solvent. The sample was then dried under high vacuum for 10 minutes. CH$_2$Cl$_2$ (40 ml) was added to dissolve the deprotected intermediate and dimethylaminopyridine (DMAP, 2.60 g, 21.30 mmol) was added to produce the free amine. Boc-protected L-lysine(2.00 g, 5.78 mmol, 10 eq.) was then added and the solution stirred under N$_2$ for 2 min, before being cooled to 0°C. HOBT (2.56 g, 18.80 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 3.6 g, 18.8 mmol) were added simultaneously as a mixture of solids. The reaction mixture was allowed to warm to room temperature and stirred for 5 d. The precipitate
(containing the product) was filtered off and washed with CH₄Cl₂. The product was extracted from this solid with an excess of MeOH (using an ultrasonic bath to break up the large particles). The crude mixture was then purified by size-exclusion chromatography (Sephadex LH-20, MeOH) to give a white solid product with a yield of 1.10 g (0.31 mmol, 55%). Mp 113-115°C; Rf 0.35 (CH₃Cl₂: MeOH, 90:10); αD²⁹³ –35.2 (c=1.0, CH₃OH); δH (400 MHz, CDCl₃ – the NMR spectrum was very broad due to aggregation) 4.20 (2H, s, COCH(R)NH), 4.00 (2H, s, COCH(R)NH), 3.09 (16H, br, CH₂NHOCH(R)), 2.99 (16H, s, CH₂CH₂NH), 1.72- 1.16 (242H, m, CH₂, CH₃); δC (400 MHz, CDCl₃) 173.5 (CONH x 2), 171.7 (CONH x 4), 156.4-156.2 (NHCOBoc x 8), 80.1 (OC(CH₃)₃ x 4), 80.0 (OC(CH₃)₃ x 4), 54.4 (COCH(R)NH x 2), 54.2 (COCH(R)NH x 2), 53.5 (COCH(R)NH x 2), 40.3 (CH₂CH₂NH x 2), 40.0 (CH₂CH₂NH x 2), 39.6 (CH₂CH₂NH x 4), 32.7 (CH₂ x 2), 32.4 (CH₂ x 6), 29.6 (CH₂ x 6), 29.4 (CH₂ x 3), 29.2 (CH₂ x 3), 28.6 (CCH₃ x 24), 26.8 (CH₂), 22.9 (CH₂), 22.7 (CH₂ x 6); νmax (KBr disc) 3337m (CONH), 3094w (NH), 2978m (CH₂, CH₃), 2932m (CH₂, CH₃), 2860w (CH), 1692s (C=O), 1523s (CONH), 1456w, 1392m, 1366m, 1249m, 1173s; m/z (Electrospray) C₁₇₆H₃₂₄N₃₀O₄₆Na₂ [M+2Na]²⁺ requires 1821.2 (doubly charged ion); found 1819.7 (50%), 1820.2 (95%), 1820.7 (100%), 1821.2 (80%), 1821.7 (50%), 1822.2 (25%), 1822.7 (12%).