# Parallel Combinatorial Synthesis of Glycodendrimers and Their Hydrogelation Properties

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A series of glycodendrons has been assembled using a parallel combinatorial approach, and it has been shown that subtle structural variations between dendrons give rise to significant differences in their hydrogelation behavior.

## Introduction

Recent advances in dendrimer research have focussed on the discovery of specific properties and functions that are a direct consequence of the dendritic architecture.[1] It has been proposed that the pronounced branching of higher generation dendrimers may result in three-dimensional structures possessing cavities with distinct microenvironments. Such cavities may function as specific hosts for particular guest molecules.[2−5] Dendritic architectures can modulate physical properties such as the reduction potential of encapsulated redox-active metal centers[6,7] and UV/Vis absorption of central chromophores.[8,9] These unique properties of dendrimers may be exploited for chromatography additives,[10] new materials, unimolecular micelles, catalysts, therapeutics, liquid crystals, and electrically conducting materials.[5]

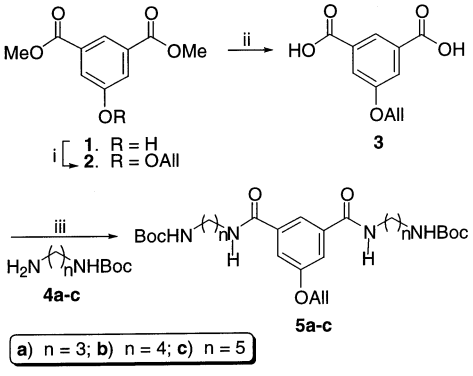
The iterative approach fundamental to dendrimer construction has traditionally involved the manipulation of building blocks derived from a single monomer unit.[1] Hence, the only structural variations possible by this procedure stem from the rudimentary differences between one generation and the next. On the other hand, the use of a small number of structurally related building blocks, which could be assembled in a parallel manner, would give access to a multitude of structurally related dendrimers.[11−14] Such libraries would provide an ideal opportunity for the systematic study of biological or physical characteristics under scrutiny, and would lay the foundation for rational optimization of any given targeted feature.

A few examples of such macromolecular "fine-tuning" have been reported. Newkome and co-workers described the synthesis and characterization of two-directional arborols in which branched domains were connected by alkyl spacer units of differing lengths.[15] It was observed that several of these arborols formed thermally reversible aqueous gels, one of which was able to gelate at concentrations as low as 1.0 wt%. This early work illustrated the physical variations possible between structurally related but constitutionally different branched macromolecules.

Recently, Hirsch and co-workers reported the construction of a series of "depsipeptide" dendrimers up to the third generation.[16] Their synthetic strategy involved the assembly of a sample of dendrons from enantiomerically pure peptide-tartaric acid conjugate building blocks, by parallel synthetic methodology. The potential for the generation of an enormous number of compounds stemmed from the variety of peptides and tartaric acid isomers available.

Concurrently, a similar strategy, the "parallel monomer combination approach", was being developed by Fréchet and co-workers.[17] Their methodology combined the synthetic power of double-exponential dendrimer growth with the efficiency of classical parallel synthesis, generating a diverse series of dendrons, all of which were derivable from two common building blocks.

Given these precedents, we report here the synthesis of a series of novel third generation glycodendrons **14a−f** (Scheme 3), obtained by the parallel combination of the three universal building blocks **5a−c** (Scheme 1). Our strategy illustrates the suitability of the parallel monomer combination approach for the investigation and optimization of structure-property relationships of interest. Monomers **5a−c** represent homologous compounds differing from each other only in the length of their alkyl chains ($n$ = 3, 4 or 5). A key aspect of the synthetic approach is that the tier length ($n$) of each dendritic layer may be tuned in such a




Scheme 1. Reagents and conditions: i) AllBr, $Cs_2CO_3$, DMF; ii) NaOH, $MeOH/H_2O$; iii) EDC, HOBT, $iPr_2NEt$, $DMF/CH_2Cl_2$

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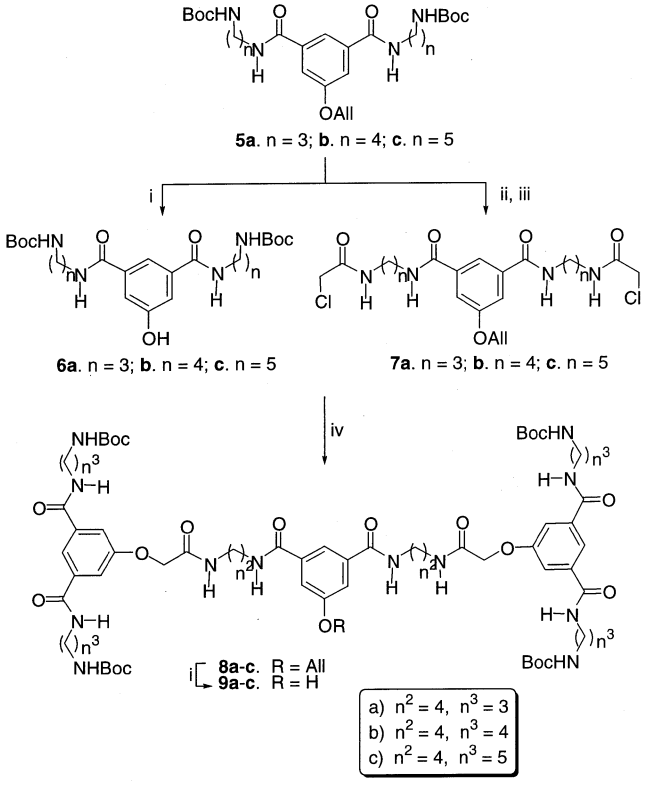
way that any combination is readily accessible. Moreover, the synthesized materials were shown to exhibit gelation properties, revealing that subtle structural variations between glycodendrons may give rise to significant differences in their physical behavior. A striking feature of these low molecular weight dendrons[18,19] is that they are monodisperse and it is evident that the rational synthesis and study of structurally related molecules will enhance efforts towards the design of improved hydrogelators, compounds that have already proven useful in a variety of medical applications ranging from drug delivery[20–22] to tissue engineering.[23]

## Results and Discussion

The synthesis of the dendrimers is based on the activation of **5a**–**c** either at the focal point, by removal of the allyl protecting group to give a phenol, or at the surface, by cleavage of the Boc groups and subsequent reaction with pentafluorophenyl chloroacetate to give a chloroacetamide derivative (Scheme 2). Dendrimer growth can be achieved by the efficient nucleophilic substitution of the chloroacetyl groups with the phenol moiety to give ether linkages. Higher generation dendrimers can be obtained by repetition of the activation and condensation reaction sequence. In the final stage of the synthesis, different groups can be attached to the exterior to give functionalized dendrimers.

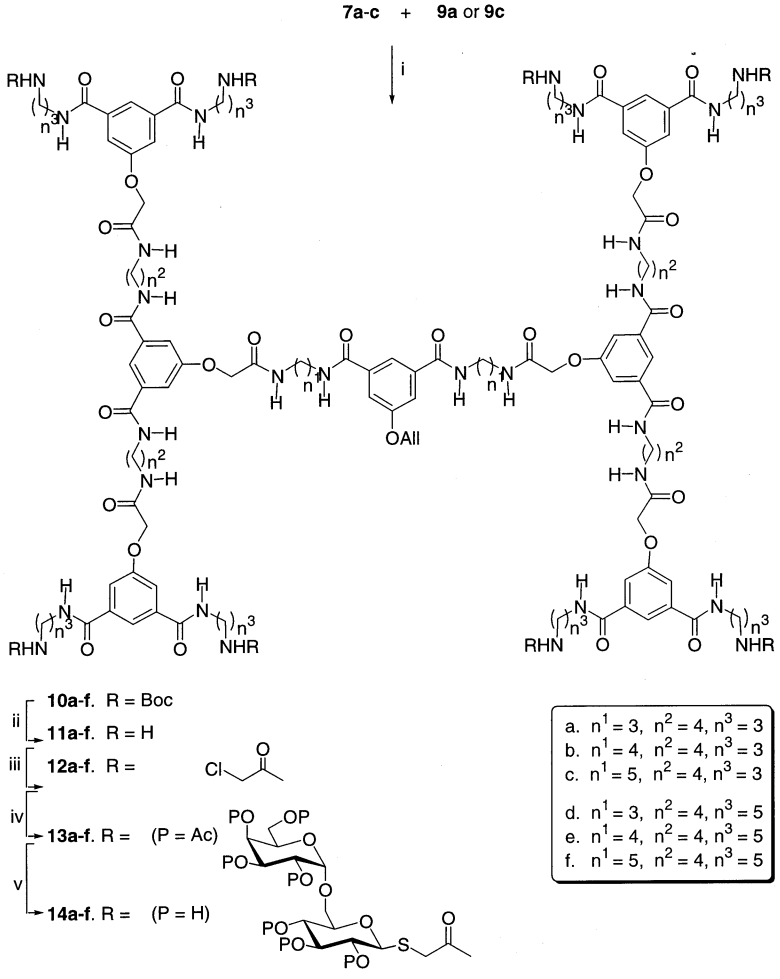



Scheme 2. Reagents and conditions: i) $Pd(PPh_3)_4$, EtOH, 80 °C; ii) $TFA/CH_2Cl_2$; iii) pentafluorophenyl chloroacetate, $Et_3N$, DMF; iv) $K_2CO_3$, acetone, $\Delta T$

Thus, treatment of phenol **1** with allyl bromide in the presence of $Cs_2CO_3$ gave dimethyl diester **2**, which upon saponification afforded diacid **3** in 90% overall yield (Scheme 1). Building blocks **5a**–**c** were obtained in excellent yields, using standard peptide coupling conditions,[24] by treatment of diacid **3** with amines **4a**–**c**, respectively.

Orthogonally protected dendrons **5a**–**c** were converted in 90–100% yields either into the corresponding phenols **6a**–**c** by palladium-catalyzed deallylation,[25] or into their corresponding chloroacetamides **7a**–**c** by removal of Boc protecting groups with TFA in $CH_2Cl_2$, followed by treatment with pentafluorophenyl chloroacetate (Scheme 2).[26] The homologous sets **6a**–**c** and **7a**–**c** represent focally and peripherally activated first generation dendrons from which $3^2 = 9$ fully protected second generation molecules can be assembled. Thus, second generation building blocks **8a**–**c** were prepared in ca. 90% yield by base-mediated condensation of chloroacetamide **7b** with phenols **6a**–**c**, respectively. Mass-spectrometric analysis of the crude reaction products showed that they were free both of starting material **7b** and of any partially substituted derivatives. The compounds were purified by silica gel or LH-20 size exclusion column chromatography.

The same synthetic strategy was employed for the efficient construction of model third generation dendrons **10a**–**c**. Thus, focally activated phenol **9a**, obtained quantitatively from second generation building block **8a**, was condensed with chloroacetamides **7a**–**c** to give the corresponding third generation subset **10a**–**c** in excellent yields (ca. 90%) (Scheme 3). The process of activation and condensation can in principle be repeated to produce higher generation dendrimers. However, the exteriors of the dendrimers can also be modified with other functionalities. In this case, saccharides were attached in a divergent manner, to produce water-soluble glycodendrimers.[27,28] Thus, the Boc protecting groups of the wedges **10a**–**c** were cleaved with TFA in dichloromethane and the resulting amino functionalities of **11a**–**c** activated by treatment with pentafluorophenyl chloroacetate to give dendrons **12a**–**c**, each bearing eight reactive chloroacetyl functionalities at the exterior. Termini of other dendrimers have been *N*-chloroacetylated by using chloroacetic anhydride;[26] however, it was found that pentafluorophenyl chloroacetate yielded equally good results without the necessity for aqueous extraction of chloroacetic acid. Fully protected melibiose hemithioacetal, conveniently generated in situ from peracetylated thioglycoside in ammoniacal DMF (−60 °C), was coupled with key precursors **12a**–**c** to afford the protected glycodendron family **13a**–**c**. It was found that deprotection in situ and condensation at ambient temperature yielded dendrimers containing α/β-mixed S-linkages (ca. 1:9). The same reagents, when combined at −60 °C and brought slowly to room temperature, gave β-S-linked products only. The compounds were isolated in yields of ca. 85% for three steps starting from **10a**–**c**. The structural homogeneity of these new materials was established by high-resolution NMR spectroscopy and MALDI-TOF mass spectrometry after purification by size-exclusion chromatography on Sephadex




Scheme 3. Reagents and conditions: i) $K_2CO_3$, acetone, $\Delta T$; ii) TFA, $CH_2Cl_2$; iii) pentafluorophenyl chloroacetate, $Et_3N$, DMF; iv) acetyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-1-thio-β-D-glucopyranose, DMF saturated with $NH_3$, −60 °C to 0 °C; v) 0.5 M NaOMe in methanol

LH-20. In particular, it was established that eight disaccharide moieties had indeed been incorporated. Removal of the acetyl protecting groups of **13a**−**c** was easily accomplished by treatment with NaOMe in methanol to afford the target molecules **14a**−**c** in quantitative yields.

Compounds **14a**−**c** formed thermally reversible aqueous gels. Dissolution in water at 80 °C followed by rapid cooling to 4 °C induced hydrogelation (Table 1). Gel transition ($T_{gel}$) experiments revealed that an increase in thermal stability was concomitant with a decrease in the internal tier length, $n^1$ (Scheme 3). This implies that the observed variations in $T_{gel}$ were the result of differences in innermost tier length ($n^1$), which is the only structural element distinguishing glycodendrons **14a** from **14b**, and **14b** from **14c**. This motivated us to examine the influence on hydrogelation of the external tier length, $n^3$, in greater detail. For this purpose we required the new subset **14d**−**f** ($n^3 = 5$), differing from subset **14a**−**c** ($n^3 = 3$) only with respect to the additional methylene units in their outermost tiers. Thus, in an application of our established route, phenol **9c**, prepared quantitatively from **8c**, was treated with building blocks **7a**−**c** to give precursors **10d**−**f**. The target molecules **14d**−**f** were obtained from these in excellent yields (Scheme 3). Gel transition behavior of the extended analogs **14d**−**f** paralleled the trends observed earlier for the original subset **14a**−**c**, relating thermal stability ($T_{gel}$) with internal tier length ($n^1$), (Table 1). Moreover, comparison of **14a** with **14d**, **14b** with **14e**, and **14c** with **14f** reveals that an increase in external tier length ($n^3$) also produces an elevation of transition temperatures. However, it is clear that the dimensions of the innermost tiers ($n^1$) have the most pronounced impact on the gel transition behavior of these three-tier dendrons (Table 1). The relative water solubility of the hydrogelators is noteworthy. For example, when heated solutions (80 °C) of **14a**−**f** were each allowed to come to ambient temperature, solutions of **14a**, **14b**, **14d**, and **14e** formed hydrogels, whereas those of **14c** and **14f** formed precipitates, which could only be redissolved by heating. Furthermore, replacement of peripheral melibiose moieties with galactoside units resulted in water-insoluble glycodendrons, highlighting the dramatic influence of the bulk structural topology of these materials on their solution properties. It

should also be noted that critical hydrogel concentrations occurred at 0.33 wt%, with the notable exception of **14d**, which formed a viscous liquid below 0.5 wt%. The concentration of glycodendrons had little effect on gel solution transitions above these critical values (Figure 1).

Table 1. Gel transition data for glycodendrons **14a−f** at 1.0 wt% concentration; the matrix displays compound identity and associated $T_{gel}$

| Tier length, $n$ | $n^1 = 3$ | $n^1 = 4$ | $n^1 = 5$ |
|---|---|---|---|
| $n^3 = 3$ | **14a** (34 °C) | **14b** (17 °C) | **14c** (15 °C) |
| $n^3 = 5$ | **14d** (37 °C) | **14e** (24 °C) | **14f** (19 °C) |

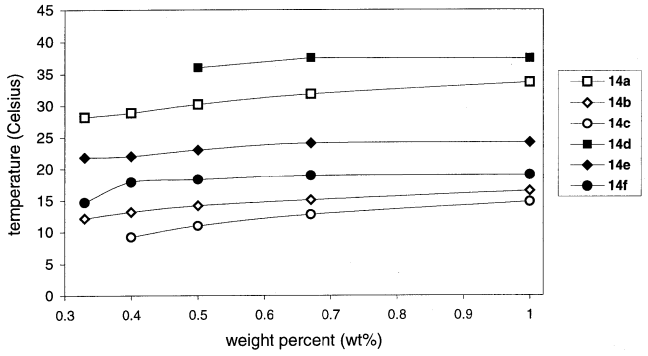



Figure 1. $T_{gel}$ values of glycodendrimers **14a−f**

## Conclusion

In summary, we have demonstrated that a series of glycodendrons can be assembled in a parallel combinatorial manner from a relatively small number of mutually compatible building blocks. An important aspect of the methodology is that the process of material discovery is accelerated by the reiterative use of first- and second-generation building blocks. A key step in the assembly is the condensation of chloroacetamides with phenols, which has proven to be an efficient method for generation growth, and to the best of our knowledge has not been reported for dendrimer synthesis. The range of dendrons obtained has allowed a systematic study to be made of their hydrogelation behavior, and has for the first time revealed that subtle structural variations have a profound influence on bulk physical properties. A wide range of small organic molecules has been found to gel a variety of organic solvents.[29−35] On the other hand, there are only a few examples of nonpolymeric molecules that form hydrogels.[36,37] Only one other report deals with dendritic hydrogelators; however, these arborols were unable to gelate below concentrations of 1.0 wt%.[15] It is to be expected that the parallel combinatorial synthesis of dendrimers will accelerate the design and evaluation of dendrimers targeted for other applications, and could underpin rational attempts to modulate desired features.

## Experimental Section

**General Procedures:** Chemicals were purchased from Aldrich and Fluka and used without further purification. Molecular sieves were activated at 350 °C in vacuo for 3 h. All solvents were distilled from the appropriate drying agents; dichloromethane and toluene were distilled from $P_2O_5$ and stored over 4 Å molecular sieves. Diethyl ether and THF were distilled from $CaH_2$, redistilled from $LiAlH_4$, and stored over sodium wire. Pyridine and acetonitrile were distilled from $CaH_2$ and stored over 4 Å molecular sieves. Methanol was distilled from sodium and stored over 4 Å molecular sieves. All reactions were performed under anhydrous conditions and monitored by TLC on 60 $F_{254}$ Kieselgel (Merck). Detection was by examination under UV light (254 nm) and by charring with 10% sulfuric acid in methanol. Column chromatography was performed on silica gel (Merck, mesh 70−230). Extracts were concentrated under reduced pressure at < 40 °C (bath). − $^1$H NMR and $^{13}$C NMR spectra were recorded with a Varian Merc300 spectrometer and a Varian Inova500 spectrometer equipped with Sun workstations. $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$, chemical shifts (δ) are given in ppm relative to solvent peaks ($^1$H: δ = 7.26; $^{13}$C: δ = 77.3) as internal standard. − Positive-ion matrix-assisted laser-desorption ionization−time of flight (MALDI−TOF) mass spectra were recorded using an HP-MALDI instrument, using gentisic acid as a matrix. − Optical rotations were measured with a Jasco P-1020 polarimeter, and $[\alpha]_D$ values are given in units of deg cm$^3$ g$^{-1}$.

**Synthesis of 2:** Allyl bromide (8.2 mL, 95 mmol) was added to a stirred solution of cesium carbonate (39.0 g, 119 mmol) and dimethyl 5-hydroxyisophthalate (**1**) (10.0 g, 48 mmol) in *N*,*N*-dimethylformamide (150 mL). After stirring for 1 h, the reaction mixture was poured into ice-cold water (200 mL) and extracted with ethyl acetate (500 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The yellow residue was redissolved in ethyl acetate, preabsorbed onto silica gel under reduced pressure, and purified by silica gel column chromatography (ethyl acetate/hexane, 0:1 → 1:5, v/v). Crystallization from ethyl acetate and hexane (1:3, v/v) afforded **2** as a white crystalline solid (11.9 g, 99%): $R_f$ = 0.45 (ethyl acetate/hexane, 1:5, v/v); m.p. 68.4−69.2 °C. − $^1$H NMR ($CDCl_3$, 300 MHz): δ = 8.28 (s, 1 H, CH Ar), 7.76 (s, 2 H, 2 CH Ar), 6.12−5.97 (m, 1 H, $OCH_2CHCH_2$), 5.47−5.30 (m, 2 H, $OCH_2CHCH_2$), 4.63−4.62 (m, 2 H, $OCH_2CHCH_2$), 3.94 (s, 6 H, 2 $CH_3$). − $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 166.1 (2 CO-OMe), 158.6 ($C_q$, Ar), 132.4 ($OCH_2CHCH_2$), 131.7 (2 $C_q$, Ar), 123.1 (CH Ar), 120.1 (2 CH Ar), 118.2 ($OCH_2CHCH_2$), 69.2 ($OCH_2CHCH_2$), 52.5 (2 $CH_3$). − FAB MS; *m*/*z* = 251 $[M + H]^+$.

**Synthesis of 3:** Compound **2** (11.9 g, 48 mmol) was added to a saturated solution of sodium hydroxide in water (10 mL) and methanol (80 mL) and refluxed for 18 h. The resultant white slurry was neutralized with Dowex-50 ($H^+$) resin until the precipitate disappeared, and was then concentrated to dryness under reduced pressure. Subsequent redissolution in methanol was only partial and the remaining precipitate was stirred a second time with Dowex-50 ($H^+$) resin until all the material had dissolved. Compound **3** was precipitated from acetone, collected by filtration, and isolated as a white solid (9.6 g, 90%): $R_f$ = 0.33 (methanol/dichloromethane, 1:9, v/v and 1 drop of acetic acid). − $^1$H NMR ($CD_3OD$, 300 MHz): δ = 8.23 (s, 1 H, CH Ar), 7.75 (s, 2 H, 2 CH Ar), 6.15−6.00 (m, 1 H, $OCH_2CHCH_2$), 5.46−5.27 (m, 2 H, $OCH_2CHCH_2$), 4.67−4.65 (m, 2 H, $OCH_2CHCH_2$). − $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 169.7 (COOH), 160.7 ($C_q$, Err), 134.9 ($OCH_2CHCH_2$), 134.8 ($C_q$, Ar), 124.9 (CH Ar), 121.4 (2 CH Ar),

118.7 ($OCH_2CHCH_2$), 70.8 ($OCH_2CHCH_2$). – CI MS; *m/z* = 240 $[M + NH_4]^+$.

**Synthesis of 4a:** A solution of Boc-ON (20.0 g, 82 mmol) in tetrahydrofuran (250 mL) was added dropwise to a stirred solution of 1,3-diaminopropane (6.8 mL, 82 mmol) in tetrahydrofuran (250 mL) at 0 °C. After stirring for 10 min, the reaction mixture was concentrated in vacuo and preabsorbed onto silica gel under reduced pressure. The dry powder was applied to a silica gel column (triethylamine/methanol/dichloromethane, 1:5:94 → 1:50:49, v/v/v) and **4a** was isolated as a viscous yellow oil (7.7 g, 54%): $R_f = 0 \rightarrow 0.1$ (methanol/dichloromethane, 13:87, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 3.22–3.11, 3.00–2.91 (2 m, 4 H, 2 $NHCH_2$), 1.91–1.77 (m, 2 H, $CH_2CH_2CH_2$), 1.45 (s, 9 H, 3 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 158.9 (NHCO), 80.4 [$C(CH_3)_3$], 38.5, 38.1 (2 $NHCH_2$), 29.3 ($CH_2CH_2CH_2$), 28.9 ($CH_3$). – FAB MS; *m/z* = 175 $[M + H]^+$.

**Compound 4b:** This compound was synthesized under the same conditions as described for the preparation of **4a**, employing 1,4-diaminobutane in place of 1,3-diaminopropane to yield a viscous yellow oil (8.0 g, 52%): $R_f = 0 \rightarrow 0.1$ (methanol/dichloromethane, 13:87, v/v). – $^1$H NMR ($CDCl_3$, 300 MHz): δ = 3.19–3.08, 2.78–2.70 (2 m, 4 H, 2 $NHCH_2$), 1.59–1.50 [m, 4 H, $CH_2(CH_2)_2CH_2$], 1.47 (s, 9 H, 3 $CH_3$). – $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 156.3 (NHCO), 79.2 [$C(CH_3)_3$], 39.9, 39.7 (2 $NHCH_2$), 28.5 ($CH_3$), 27.0, 24.8 [$CH_2(CH_2)_2CH_2$]. – FAB MS; *m/z* = 189 $[M + H]^+$.

**Compound 4c:** This compound was synthesized under the same conditions as described for the preparation of **4a**, employing 1,5-diaminopentane in place of 1,3-diaminopropane to yield a viscous yellow oil (4.2 g, 52%): $R_f = 0 \rightarrow 0.1$ (methanol/dichloromethane, 13:87, v/v). – $^1$H NMR ($CDCl_3$, 300 MHz): δ = 3.19–3.07, 2.77–2.68 (2 m, 4 H, 2 $NHCH_2$), 1.58–1.32 [m, 6 H, $CH_2(CH_2)_3CH_2$], 1.48 (s, 9 H, 3 $CH_3$). – $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 156.0 (NHCO), 79.0 [$C(CH_3)_3$], 41.9, 40.6 (2 $NHCH_2$), 33.0, 30.1, 24.2 [$CH_2(CH_2)_3CH_2$], 28.6 ($CH_3$). – FAB MS; *m/z* = 203 $[M + H]^+$.

**Synthesis of 5a:** 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (11.9 g, 62 mmol) and *N*,*N*-diisopropylethylamine (7.7 mL, 44 mmol) were added to an ice-cold solution of **4a** (7.7 g, 44 mmol), diacid **3** (3.9 g, 18 mmol), and 1-hydroxybenzotriazole (6.0 g, 44 mmol) in *N*,*N*-dimethylformamide/dichloromethane (100 mL, 3:1, v/v). The mixture was stirred for 18 h at room temperature. The dichloromethane present in the solvents was evaporated under reduced pressure, and the remaining slurry was diluted with ethyl acetate (500 mL). The resultant organic solution was washed with ice-cold water (1 × 100 mL), aqueous ammonium chloride (saturated, 1 × 100 mL), and aqueous sodium bicarbonate (saturated, 1 × 100 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo, and the residue was purified by silica gel chromatography (acetone/hexane, 1:9 → 3:7, v/v) to afford **5a** as a white foam (9.3 g, 99%): $R_f = 0.39$ (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.84 (s, 1 H, CH Ar), 7.53 (s, 2 H, 2 CH Ar), 6.19–6.00 (m, 1 H, $OCH_2CHCH_2$), 5.48–5.24 (m, 2 H, $OCH_2CHCH_2$), 4.69–4.61 (m, 2 H, $OCH_2CHCH_2$), 3.47–3.34, 3.19–3.07 (2 m, 8 H, 4 $NHCH_2$), 1.83–1.69 (m, 4 H, 2 $CH_2CH_2CH_2$), 1.43 (s, 18 H, 6 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 169.1, 160.3, 137.5 (4 NHCO, 3 $C_q$ Ar), 134.3 ($OCH_2CHCH_2$), 119.4 (CH Ar), 118.0 ($OCH_2CHCH_2$), 117.6 (2 CH Ar), 80.0 [2 $C(CH_3)_3$], 70.3 ($OCH_2CHCH_2$), 39.0, 38.6 (4 $NHCH_2$), 30.9 (2 $CH_2CH_2CH_2$), 29.0 (6 $CH_3$). – FAB MS; *m/z* = 535 $[M + H]^+$. – $C_{27}H_{43}N_4O_7$: *m/z* calcd. 535.3132, found 535.3116.

**Compound 5b:** This compound was synthesized under the same conditions as described for the preparation of **5a**, employing **4b** in place of **4a** to yield a white foam (8.7 g, 91%): $R_f = 0.39$ (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.82 (s, 1 H, CH Ar), 7.51 (s, 2 H, 2 CH Ar), 6.12–5.99 (m, 1 H, $OCH_2CHCH_2$), 5.47–5.23 (m, 2 H, $OCH_2CHCH_2$), 4.67–4.60 (m, 2 H, $OCH_2CHCH_2$), 3.44–3.33, 3.12–2.99 (2 m, 8 H, 4 $NHCH_2$), 1.69–1.46 (m, 8 H, 2 $CH_2(CH_2)_2CH_2$), 1.42 (s, 18 H, 6 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 169.1, 160.2, 137.6 (4 NHCO, 3 $C_q$ Ar), 134.3 ($OCH_2CHCH_2$), 119.4 (CH Ar), 118.0 ($OCH_2CHCH_2$), 117.5 (2 CH Ar), 80.0 [2 $C(CH_3)_3$], 70.3 ($OCH_2CHCH_2$), 41.2, 40.9 (4 $NHCH_2$), 29.0 (6 $CH_3$), 28.7, 27.9 [$CH_2(CH_2)_2CH_2$]. – FAB MS; *m/z* = 585 $[M + Na]^+$. – $C_{29}H_{47}N_4O_7$: *m/z* calcd. 563.3445, found 563.3458.

**Compound 5c:** This compound was synthesized under the same conditions as described for the preparation of **5a**, employing **4c** in place of **4a** to yield a white foam (4.9 g, 98%): $R_f = 0.39$ (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.83 (s, 1 H, CH Ar), 7.51 (s, 2 H, 2 CH Ar), 6.16–5.99 (m, 1 H, $OCH_2CHCH_2$), 5.47–5.23 (m, 2 H, $OCH_2CHCH_2$), 4.67–4.61 (m, 2 H, $OCH_2CHCH_2$), 3.42–3.32, 3.08–2.99 (2 m, 8 H, 4 $NHCH_2$), 1.70–1.40 [m, 12 H, 2 $CH_2(CH_2)_3CH_2$], 1.40 (s, 18 H, 6 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 169.1, 160.2, 137.6 (4 NHCO, 3 $C_q$ Ar), 134.3 ($OCH_2CHCH_2$), 119.4 (CH Ar), 118.0 ($OCH_2CHCH_2$), 117.5 (2 CH Ar), 80.0 [2 $C(CH_3)_3$], 70.3 ($OCH_2CHCH_2$), 41.4, 41.2 (4 $NHCH_2$), 29.0 (6 $CH_3$), 30.9, 30.3, 25.4 [2 $CH_2(CH_2)_3CH_2$]. – FAB MS; *m/z* = 591 $[M + H]^+$.

**Synthesis of 6a:** A solution of **5a** (8.5 g, 16 mmol) and tetrakis(triphenylphosphane)palladium(0) (900 mg, 0.8 mmol) in deoxygenated ethanol (50 mL) was refluxed for 1 h. The resultant black slurry was filtered through Celite and washed with hot methanol (200 mL). The filtrate was repeatedly boiled (3 times) and filtered to reduce and remove black palladium metal. The precipitate formed on cooling was collected by filtration (6.0 g). The filtrate was concentrated under reduced pressure, purified by silica gel column chromatography (methanol/dichloromethane, 1:49 → 1:19, v/v), and combined with the precipitate to afford **6a** as a white foam (7.1 g, 90%): $R_f = 0.31$ (acetone/hexane, 1:1, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.71 (s, 1 H, CH Ar), 7.38 (s, 2 H, 2 CH Ar), 3.45–3.38, 3.18–3.08 (2 m, 8 H, 4 $NHCH_2$), 1.82–1.72 (m, 4 H, 2 $CH_2CH_2CH_2$), 1.46 (s, 18 H, 6 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 169.6, 159.1, 158.6, 137.6 (4 NHCO, 3 $C_q$ Ar), 118.2, 117.8 (3 CH Ar), 80.2 [2 $C(CH_3)_3$], 39.0, 38.6 (4 $NHCH_2$), 31.0 (2 $CH_2CH_2CH_2$), 29.0 (6 $CH_3$). – FAB MS; *m/z* = 495 $[M + H]^+$. – $C_{24}H_{39}N_4O_7$: *m/z* calcd. 495.2819, found 495.2807.

**Compound 6b:** This compound was synthesized under the same conditions as described for the preparation of **6a**, employing **5b** in place of **5a** to yield a white foam (1.4 g, 98%): $R_f = 0.31$ (acetone/hexane, 1:1, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.68 (s, 1 H, CH Ar), 7.37 (s, 2 H, 2 CH Ar), 3.42–3.35, 3.12–3.03 (2 m, 8 H, 4 $NHCH_2$), 1.70–1.48 [m, 8 H, 2 $CH_2(CH_2)_2CH_2$], 1.42 (s, 18 H, 6 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 168.3, 157.9, 157.3, 136.5 (4 NHCO, 3 $C_q$ Ar), 116.9, 116.5 (3 CH Ar), 78.7 [2 $C(CH_3)_3$], 40.0, 39.7 (4 $NHCH_2$), 27.8 (6 $CH_3$), 27.4, 26.7 [2 $CH_2(CH_2)_2CH_2$]. – FAB MS; *m/z* = 523 $[M + H]^+$. – $C_{26}H_{43}N_4O_7$: *m/z* calcd. 523.3132, found 523.3083.

**Compound 6c:** This compound was synthesized under the same conditions as described for the preparation of **6a**, employing **5c** in place of **5a** to yield a white foam (330 mg, 100%): $R_f = 0.31$ (acetone/hexane, 1:1, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.67 (s, 1 H, CH Ar), 7.36 (s, 2 H, 2 CH Ar), 3.42–3.34, 3.08–3.00 (2

m, 8 H, 4 $NHCH_2$), 1.68−1.40 [m, 12 H, 2 $CH_2(CH_2)_3CH_2$], 1.42 (s, 18 H, 6 $CH_3$). − $^{13}C$ NMR ($CD_3OD$, 75 MHz): δ = 167.7, 157.4, 156.7, 135.9 (4 NHCO, 3 $C_q$ Ar), 116.4, 116.0 (3 CH Ar), 78.1 [2 $C(CH_3)_3$], 39.6, 39.3 (4 $NHCH_2$), 29.1, 28.5, 23.6 [2 $CH_2(CH_2)_3CH_2$], 27.2 (6 $CH_3$). − FAB MS; *m/z* = 551 $[M + H]^+$. − $C_{28}H_{47}N_4O_7$:*m/z* calcd. 551.3445, found 551.3434.

**Synthesis of 7a:** Trifluoroacetic acid (4 mL) was added dropwise to a suspension of **5a** (267 mg, 0.5 mmol) in dichloromethane (2 mL). The solution was stirred for 30 min, coevaporated under reduced pressure with 1,2 dichloroethane/toluene (3 × 10 mL, 1:1, v/v), and stored under vacuum (1.5 mbar) for 3 h. The crude residue was dissolved in *N*,*N*-dimethylformamide (4 mL) and triethylamine was added dropwise (ca. 20 drops) until basic conditions were reached (pH ≈ 8). A solution of pentafluorophenyl chloroacetate (287 mg, 1.1 mmol) in *N*,*N*-dimethylformamide (0.5 mL) was rapidly added, followed by a further 15 drops of triethylamine. The reaction mixture was stirred for 5 min, concentrated to dryness, coevaporated with toluene (5 × 10 mL), dissolved in methanol (20 mL), and preabsorbed onto silica gel under reduced pressure. The immobilized solid was purified by silica gel chromatography (acetone/dichloromethane, 0 → 2:3, v/v) to yield **7a** as a white powder (203 mg, 84%): $R_f$ = 0.32 (acetone/dichloromethane, 1:1, v/v). − $^1H$ NMR ($CDCl_3$, 300 MHz): δ = 7.78 (s, 1 H, CH Ar), 7.46 (s, 2 H, 2 CH Ar), 6.02−5.87 (m, 1 H, $OCH_2CHCH_2$), 5.39−5.18 (m, 2 H, $OCH_2CHCH_2$), 4.55−4.50 (m, 2 H, $OCH_2CHCH_2$), 3.98 (s, 4 H, 2 $CH_2Cl$), 3.42−3.28 (m, 8 H, 4 $NHCH_2$), 1.77−1.65 (m, 4 H, 2 $CH_2CH_2CH_2$). − $^{13}C$ NMR ($CDCl_3$, 75 MHz): δ = 167.2, 167.1, 159.2, 136.1 (4 NHCO, 3 $C_q$ Ar), 132.7 ($OCH_2CHCH_2$), 118.3 (CH Ar), 117.5 ($OCH_2CHCH_2$), 116.9 (2 CH Ar), 69.4 ($OCH_2CHCH_2$), 42.9 (2 $CH_2Cl$), 36.9, 36.8 (4 $NHCH_2$), 29.6 (2 $CH_2CH_2CH_2$). − FAB MS; *m/z* = 487 $[M + H]^+$. − $C_{21}H_{29}{}^{35}Cl_2N_4O_5$: *m/z* calcd. 487.1515, found 487.1528.

**Compound 7b:** This compound was synthesized under the same conditions as described for the preparation of **7a**, employing **5b** in place of **5a** to yield a white powder (1.2 g, 85%): $R_f$ = 0.32 (acetone/dichloromethane, 1:1, v/v). − $^1H$ NMR ($CD_3OD$, 300 MHz): δ = 7.83 (s, 1 H, CH Ar), 7.51 (s, 2 H, 2 CH Ar), 6.14−5.99 (m, 1 H, $OCH_2CHCH_2$), 5.47−5.24 (m, 2 H, $OCH_2CHCH_2$), 4.65−4.60 (m, 2 H, $OCH_2CHCH_2$), 4.02 (s, 4 H, 2 $CH_2Cl$), 3.42−3.34, 3.33−3.20 (2 m, 8 H, 4 $NHCH_2$), 1.72−1.52 [m, 8 H, 2 $CH_2(CH_2)_2CH_2$]. − $^{13}C$ NMR ($CD_3OD$, 75 MHz): δ = 168.0, 167.9, 159.0, 136.4 (4 NHCO, 3 $C_q$ Ar), 133.1 ($OCH_2CHCH_2$), 118.2 (CH Ar), 116.8 ($OCH_2CHCH_2$), 116.3 (2 CH Ar), 69.1 ($OCH_2CHCH_2$), 42.2 (2 $CH_2Cl$), 39.6, 39.4 (4 $NHCH_2$), 26.7 [2 $CH_2(CH_2)_2CH_2$]. − FAB MS; *m/z* = 515 $[M + H]^+$. − $C_{23}H_{33}{}^{35}Cl_2N_4O_5$: *m/z* calcd. 515.1828, found 515.1813.

**Compound 7c:** This compound was synthesized under the same conditions as described for the preparation of **7a**, employing **5c** in place of **5a** to yield a white powder (240 mg, 88%): $R_f$ = 0.32 (acetone/dichloromethane, 1:1, v/v). − $^1H$ NMR ($CD_3OD$, 300 MHz): δ = 7.82 (s, 1 H, CH Ar), 7.51 (s, 2 H, 2 CH Ar), 6.15−6.00 (m, 1 H, $OCH_2CHCH_2$), 5.47−5.24 (m, 2 H, $OCH_2CHCH_2$), 4.67−4.62 (m, 2 H, $OCH_2CHCH_2$), 4.00 (2 $CH_2Cl$), 3.42−3.33, 3.29−3.20 (2 m, 8 H, 4 $NHCH_2$), 1.71−1.52, 1.50−1.38 [2 m, 12 H, 2 $CH_2(CH_2)_3CH_2$]. − $^{13}C$ NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 167.9, 167.8, 159.0, 136.3 (4 NHCO, 3 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 118.1 (CH Ar), 117.2 ($OCH_2CHCH_2$), 116.5 (2 CH Ar), 69.2 ($OCH_2CHCH_2$), 42.3 (2 $CH_2Cl$), 40.0, 39.7 (4 $NHCH_2$), 29.0, 28.9, 24.3 [2 $CH_2(CH_2)_3CH_2$]. − FAB MS; *m/z* = 543 $[M + H]^+$. − $C_{25}H_{37}{}^{35}Cl_2N_4O_5$: *m/z* calcd. 543.2141, found 543.2125.

**Synthesis of 8a:** A solution of **6a** (3.6 g, 7.3 mmol), **7b** (2.1 g, 3.5 mmol), and potassium carbonate (2.42 g, 17.5 mmol) in acetone (150 mL) was stirred under reflux for 18 h. The white slurry was filtered rapidly through a column of silica gel (methanol/dichloromethane, 1:1, v/v) and the eluted solution concentrated and preabsorbed onto silica gel (25 g) under reduced pressure. The immobilized crude material was purified by silica gel column chromatography (acetone/dichloromethane, 2:3 → 4:1, v/v) to afford **8a** as a white foam (4.5 g, 91%): $R_f$ = 0.15 (acetone/dichloromethane, 3:2, v/v). − $^1H$ NMR ($CD_3OD$, 300 MHz): δ = 7.87 (s, 2 H, 2 CH Ar), 7.83 (s, 1 H, CH Ar), 7.55 (s, 4 H, 4 CH Ar), 7.50 (s, 2 H, 2 CH Ar), 6.12−5.98 (m, 1 H, $OCH_2CHCH_2$), 5.46−5.22 (m, 2 H, $OCH_2CHCH_2$), 4.65−4.56 (m, 6 H, $OCH_2CHCH_2$; 2 $OCH_2CO$), 3.44−3.30, 3.18−3.06 (2 m, 24 H, 12 $NHCH_2$), 1.81−1.55 [m, 16 H, 8 $CH_2(CH_2)_nCH_2$], 1.42 (s, 36 H, 12 $CH_3$). − $^{13}C$ NMR ($CD_3OD$, 75 MHz): δ = 170.3, 169.0, 168.8, 160.2, 159.2, 137.7, 137.5 (12 NHCO, 9 $C_q$ Ar), 134.3 ($OCH_2CHCH_2$), 120.2, 119.4 (3 CH Ar), 118.1 ($OCH_2CHCH_2$), 117.7, 117.6 (6 CH Ar), 80.1 [4 $C(CH_3)_3$], 70.3 ($OCH_2CHCH_2$), 68.6 (2 $OCH_2CO$), 40.9, 40.0, 39.0, 38.6 (12 $NHCH_2$), 30.9, 28.1, 27.9 [8 $CH_2(CH_2)_nCH_2$], 29.0 (12 $CH_3$). − FAB MS; *m/z* = 1354 $[M + Na]^+$.

**Compound 8b:** This compound was synthesized under the same conditions as described for the preparation of **8a**, employing **6b** in place of **6a** to yield a white foam (930 mg, 89%): $R_f$ = 0.15 (acetone/dichloromethane, 3:2, v/v). − $^1H$ NMR ($CD_3OD$, 300 MHz): δ = 7.85 (s, 2 H, 2 CH Ar), 7.83 (s, 1 H, CH Ar), 7.53 (s, 4 H, 4 CH Ar), 7.50 (s, 2 H, 2 CH Ar), 6.13−5.98 (m, 1 H, $OCH_2CHCH_2$), 5.46−5.22 (m, 2 H, $OCH_2CHCH_2$), 4.65−4.56 (m, 6 H, $OCH_2CHCH_2$, 2 $OCH_2CO$), 3.44−3.30, 3.12−3.00 (2 m, 24 H, 12 $NHCH_2$), 1.68−1.50 [m, 24 H, 6 $CH_2(CH_2)_2CH_2$], 1.41 (s, 36 H, 12 $CH_3$). − $^{13}C$ NMR ($CD_3OD$, 75 MHz): δ = 169.1, 167.8, 167.5, 159.0, 158.0, 157.2, 136.6, 136.3 (12 NHCO, 9 $C_q$ Ar), 133.1 ($OCH_2CHCH_2$), 119.0, 118.2 (3 CH Ar), 116.9 ($OCH_2CHCH_2$), 116.5, 116.3 (6 CH Ar), 78.7 [4 $C(CH_3)_3$], 69.1 ($OCH_2CHCH_2$), 67.4 (2 $OCH_2CO$), 40.0, 39.8, 39.7, 38.7 (12 $NHCH_2$), 27.8, 27.5, 26.9, 26.7 [6 $CH_2(CH_2)_2CH_2$], 29.0 (12 $CH_3$). − FAB MS; *m/z* = 1488 $[M + H]^+$.

**Compound 8c:** This compound was synthesized under the same conditions as described for the preparation of **8a**, employing **6c** in place of **6a** to yield a white foam (220 mg, 89%): $R_f$ = 0.15 (acetone/dichloromethane, 3:2, v/v). − $^1H$ NMR ($CD_3OD$, 300 MHz): δ = 7.86 (s, 2 H, 2 CH Ar), 7.84 (s, 1 H, CH Ar), 7.53 (s, 4 H, 4 CH Ar), 7.50 (s, 2 H, 2 CH Ar), 6.12−5.99 (m, 1 H, $OCH_2CHCH_2$), 5.46−5.22 (m, 2 H, $OCH_2CHCH_2$), 4.64−4.57 (m, 6 H, $OCH_2CHCH_2$, 2 $OCH_2CO$), 3.40−3.28, 3.08−2.98 (2 m, 24 H, 12 $NHCH_2$), 1.68−1.40 [m, 32 H, 16 $CH_2(CH_2)_nCH_2$], 1.40 (s, 36 H, 12 $CH_3$). − $^{13}C$ NMR ($CD_3OD$, 75 MHz): δ = 169.1, 167.8, 167.5, 159.0, 158.0, 157.2, 136.6, 136.3 (12 NHCO, 9 $C_q$ Ar), 133.1 ($OCH_2CHCH_2$), 119.0, 118.3 (3 CH Ar), 116.9 ($OCH_2CHCH_2$), 116.5, 116.4 (6 CH Ar), 78.7 [4 $C(CH_3)_3$], 69.1 ($OCH_2CHCH_2$), 67.4 (2 $OCH_2CO$), 40.2, 40.0, 39.7, 38.7 (12 $NHCH_2$), 29.7, 29.1, 26.9, 26.7, 24.2 [12 $CH_2(CH_2)_nCH_2$], 27.8 (12 $CH_3$). − FAB MS; *m/z* = 1567 $[M + Na]^+$.

**Synthesis of 9a:** A solution of **8a** (7.5 g, 5.2 mmol) and tetrakis(triphenylphosphane)palladium(0) (303 mg, 0.26 mmol) in deoxygenated ethanol (75 mL) was refluxed for 1 h. The resultant black slurry was filtered through Celite and washed with hot methanol (200 mL). The filtrate was repeatedly boiled (3 times) and filtered to reduce and remove black palladium metal, concentrated under reduced pressure, and the residue purified by silica gel column chromatography (methanol/dichloromethane, 1:24 → 1:9, v/v) to afford **9a** as a white foam (7.0 g, 96%): $R_f$ = 0.10 (methanol/dichlo-

romethane, 2:23, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.87 (s, 2 H, 2 CH Ar), 7.67 (s, 1 H, CH Ar), 7.55 (s, 4 H, 4 CH Ar), 7.35 (s, 2 H, 2 CH Ar), 4.60 (s, 4 H, 2 $OCH_2CO$), 3.44–3.30, 3.18–3.09 (2 m, 24 H, 12 $NHCH_2$), 1.81–1.70, 1.69–1.58 [2 m, 16 H, 8 $CH_2(CH_2)_nCH_2$], 1.42 (s, 36 H, 12 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 169.1, 168.2, 167.6, 158.1, 157.8, 136.5, 136.4 (12 NHCO, 9 $C_q$ Ar), 119.0, 117.0, 116.5 (9 CH Ar), 78.9 [4 $C(CH_3)_3$], 67.4 (2 $OCH_2CO$), 39.6, 38.8, 37.8, 37.4 (12 $NHCH_2$), 29.7, 26.8, 26.7 [8 $CH_2(CH_2)_nCH_2$], 27.8 (12 $CH_3$). – FAB MS; $m/z$ = 1415 $[M + Na]^+$.

**Compound 9b:** This compound was synthesized under the same conditions as described for the preparation of **9a**, employing **8b** in place of **8a**: white foam (500 mg, 98%): $R_f$ = 0.10 (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.82 (s, 2 H, 2 CH Ar), 7.64 (s, 1 H, CH Ar), 7.51 (s, 4 H, 4 CH Ar), 7.32 (s, 2 H, 2 CH Ar), 4.58 (s, 4 H, 2 $OCH_2CO$), 3.40–3.30, 3.08–2.98 (2 m, 24 H, 12 $NHCH_2$), 1.68–1.40 [m, 24 H, 6 $CH_2(CH_2)_2CH_2$], 1.38 (s, 36 H, 12 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 171.1, 170.1, 169.5, 159.9, 159.2, 138.4, 138.3 (12 NHCO, 9 $C_q$ Ar), 120.8, 118.8, 118.4, 118.3 (9 CH Ar), 80.5 [4 $C(CH_3)_3$], 69.1 (2 $OCH_2CO$), 41.7, 41.5, 41.3, 40.4 (12 $NHCH_2$), 30.2 (12 $CH_3$), 29.5, 29.1, 28.4, 28.3 [6 $CH_2(CH_2)_2CH_2$]. – FAB MS; $m/z$ = 1470 $[M + Na]^+$.

**Compound 9c:** This compound was synthesized under the same conditions as described for the preparation of **9a**, employing **8c** in place of **8a** to yield a white foam (1.4 g, 97%): $R_f$ = 0.10 (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD$, 300 MHz): δ = 7.86 (s, 2 H, 2 CH Ar), 7.69 (s, 1 H, CH Ar), 7.54 (s, 4 H, 4 CH Ar), 7.36 (s, 2 H, 2 CH Ar), 4.60 (s, 4 H, 2 $OCH_2CO$), 3.40–3.29, 3.08–2.98 (2 m, 24 H, 12 $NHCH_2$), 1.68–1.40 [m, 32 H, 16 $CH_2(CH_2)_nCH_2$], 1.40 (s, 36 H, 12 $CH_3$). – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 169.2, 168.2, 167.6, 158.0, 157.8, 157.3, 136.5, 136.3 (12 NHCO, 9 $C_q$ Ar), 119.0, 117.1, 116.7, 116.5 (9 CH Ar), 78.9 [4 $C(CH_3)_3$], 67.3 (2 $OCH_2CO$), 40.2, 40.1, 39.7, 38.8 (12 $NHCH_2$), 29.6, 29.0, 26.8, 26.7, 24.2 [16 $CH_2(CH_2)_nCH_2$], 27.8 (12 $CH_3$). – FAB MS; $m/z$ = 1504 $[M + H]^+$.

**Synthesis of 10a:** A solution of **9a** (612 mg, 0.44 mmol), **7a** (100 mg, 0.21 mmol), and potassium carbonate (3.4 g, 25 mmol) in acetone (50 mL) was stirred under reflux for 18 h. The white slurry was filtered rapidly through a column of silica gel (methanol/dichloromethane, 1:1, v/v) and the eluted solution concentrated and preabsorbed onto silica gel (25 g) under reduced pressure. The immobilized crude material was purified by silica gel column chromatography (methanol/ dichloromethane, 7:93 → 7:43, v/v) to afford **10a** as a white foam (603 mg, 92%): $R_f$ = 0.08 (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 300 MHz): δ = 7.92–7.82 (m, 7 H, 7 CH Ar), 7.58–7.46 (m, 14 H, 14 CH Ar), 6.10–5.94 (m, 1 H, $OCH_2CHCH_2$), 5.44–5.22 (m, 2 H, $OCH_2CHCH_2$), 4.64–4.54 (m, 14 H, $OCH_2CHCH_2$, 6 $OCH_2CO$), 3.43–3.04 (m, 56 H, 28 $NHCH_2$), 1.84–1.51 [m, 36 H, 18 $CH_2(CH_2)_nCH_2$], 1.40 (s, 72 H, 24 $CH_3$). – $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 169.2, 168.9, 167.9, 167.5, 157.9, 157.3, 136.4, 136.1 (28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1 (7 CH Ar), 117.3 ($OCH_2CHCH_2$), 116.7 (14 CH Ar), 79.2 [8 $C(CH_3)_3$], 69.2 ($OCH_2CHCH_2$), 67.5 (6 $OCH_2CO$), 39.8, 38.9, 37.8, 37.5 (28 $NHCH_2$), 29.7, 29.2, 26.9, 26.7 [18 $CH_2(CH_2)_nCH_2$], 28.1 (24 $CH_3$). – MALDI TOF MS; $m/z$ = 3220 $[M + Na]^+$.

**Compound 10b:** This compound was synthesized under the same conditions as described for the preparation of **10a**, employing **7b** in place of **7a** to yield a white foam (281 mg, 87%): $R_f$ = 0.08 (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 300 MHz): δ = 7.89–7.81 (m, 7 H, 7 CH Ar), 7.55–7.46 (m, 14 H, 14 CH Ar), 6.10–5.96 (m, 1 H, $OCH_2CHCH_2$), 5.44–5.22 (m, 2 H, $OCH_2CHCH_2$), 4.62–4.52 (m, 14 H, $OCH_2CHCH_2$, 6 $OCH_2CO$), 3.45–3.10 (m, 56 H, 28 $NHCH_2$), 1.82–1.53 [m, 40 H, 20 $CH_2(CH_2)_nCH_2$], 1.40 (s, 72 H, 24 $CH_3$). – $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 168.9, 167.8, 167.5, 167.4, 157.9, 157.3, 136.4, 136.2 (28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1 (7 CH Ar), 117.4 ($OCH_2CHCH_2$), 116.7 (14 CH Ar), 79.2 [8 $C(CH_3)_3$], 69.2 ($OCH_2CHCH_2$), 67.4 (6 $OCH_2CO$), 39.8, 38.9, 37.8, 37.5 (28 $NHCH_2$), 30.3, 29.7, 26.9, 26.7, 23.4 [20 $CH_2(CH_2)_nCH_2$], 28.2 (24 $CH_3$). – MALDI TOF MS; $m/z$ = 3247 $[M + Na]^+$.

**Compound 10c:** This compound was synthesized under the same conditions as described for the preparation of **10a**, employing **7c** in place of **7a** to yield a white foam (437 mg, 94%): $R_f$ = 0.08 (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 300 MHz): δ = 7.90–7.79 (m, 7 H, 7 CH Ar), 7.56–7.43 (m, 14 H, 14 CH Ar), 6.08–5.94 (m, 1 H, $OCH_2CHCH_2$), 5.43–5.21 (m, 2 H, $OCH_2CHCH_2$), 4.62–4.50 (m, 14 H, $OCH_2CHCH_2$, 6 $OCH_2CO$), 3.45–3.04 (m, 56 H, 28 $NHCH_2$), 1.84–1.51 [m, 44 H, 22 $CH_2(CH_2)_nCH_2$], 1.40 (s, 72 H, 24 $CH_3$). – $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 169.8, 168.6, 168.4, 158.8, 158.1, 137.3, 137.1 (28 NHCO, 21 $C_q$ Ar), 133.7 ($OCH_2CHCH_2$), 119.9 (7 CH Ar), 118.1 ($OCH_2CHCH_2$), 117.5 (14 CH Ar), 80.0 [8 $C(CH_3)_3$], 70.0 ($OCH_2CHCH_2$), 68.3 (6 $OCH_2CO$), 40.9, 40.6, 39.9, 39.7, 38.6, 38.3 (28 $NHCH_2$), 30.6, 30.0, 29.8, 27.8, 27.5, 25.1 [22 $CH_2(CH_2)_nCH_2$], 29.0 (24 $CH_3$). – MALDI TOF MS; $m/z$ = 3276 $[M + Na]^+$.

**Compound 10d:** This compound was synthesized under the same conditions as described for the preparation of **10a**, employing **9c** in place of **9a** to yield a white foam (109 mg, 88%): $R_f$ = 0.08 (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 300 MHz): δ = 7.90–7.81 (m, 7 H, 7 CH Ar), 7.58–7.46 (m, 14 H, 14 CH Ar), 6.10–5.94 (m, 1 H, $OCH_2CHCH_2$), 5.44–5.22 (m, 2 H, $OCH_2CHCH_2$), 4.62–4.53 (m, 14 H, $OCH_2CHCH_2$, 6 $OCH_2CO$), 3.45–2.96 (m, 56 H, 28 $NHCH_2$), 1.67–1.35 [m, 68 H, 34 $CH_2(CH_2)_nCH_2$], 1.39 (s, 72 H, 24 $CH_3$). – $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 169.0, 167.4, 157.9, 157.2, 136.5, 136.1 (28 NHCO, 21 $C_q$ Ar), 132.8 ($OCH_2CHCH_2$), 119.0 (7 CH Ar), 117.3 ($OCH_2CHCH_2$), 116.5 (14 CH Ar), 78.9 [8 $C(CH_3)_3$], 69.2 ($OCH_2CHCH_2$), 67.4 (6 $OCH_2CO$), 40.3, 40.1, 39.8, 38.9 (28 $NHCH_2$), 29.7, 29.1, 26.9, 26.7, 24.3 [34 $CH_2(CH_2)_nCH_2$], 28.1 (24 $CH_3$). – MALDI TOF MS; $m/z$ = 3443 $[M + Na]^+$.

**Compound 10e:** This compound was synthesized under the same conditions as described for the preparation of **10a**, employing **7b** in place of **7a**, and **9c** in place of **9a** to yield a white foam (105 mg, 89%): $R_f$ = 0.08 (methanol/dichloromethane, 2:23, v/v). – $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 300 MHz): δ = 7.80–7.72 (m, 7 H, 7 CH Ar), 7.47–7.40 (m, 14 H, 14 CH Ar), 6.02–5.85 (m, 1 H, $OCH_2CHCH_2$), 5.36–5.14 (m, 2 H, $OCH_2CHCH_2$), 4.54–4.43 (m, 14 H, $OCH_2CHCH_2$, 6 $OCH_2CO$), 3.35–2.91 (m, 56 H, 28 $NHCH_2$), 1.61–1.35 [m, 72 H, 36 $CH_2(CH_2)_nCH_2$], 1.32 (s, 72 H, 24 $CH_3$). – $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 169.0, 167.4, 157.9, 157.2, 136.5, 136.4 (28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1 (7 CH Ar), 117.3 ($OCH_2CHCH_2$), 116.6 (14 CH Ar), 79.0 [8 $C(CH_3)_3$], 69.2 ($OCH_2CHCH_2$), 67.4 (6 $OCH_2CO$), 40.3, 40.2, 38.9 (28 $NHCH_2$), 29.7, 29.1, 27.0, 26.7, 24.3 [36 $CH_2(CH_2)_nCH_2$], 28.1 (24 $CH_3$). – MALDI TOF MS; $m/z$ = 3472 $[M + Na]^+$.

**Compound 10f:** This compound was synthesized under the same conditions as described for the preparation of **10a**, employing **7c** in place of **7a**, and **9c** in place of **9a** to yield a white foam (100 mg, 91%): $R_f$ = 0.08 (methanol/dichloromethane, 2:23, v/v). − $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 300 MHz): δ = 7.82−7.70 (m, 7 H, 7 CH Ar), 7.47−7.38 (m, 14 H, 14 CH Ar), 6.00−5.76 (m, 1 H, $OCH_2CHCH_2$), 5.36−5.14 (m, 2 H, $OCH_2CHCH_2$), 4.54−4.42 (m, 14 H, $OCH_2CHCH_2$, 6 $OCH_2CO$), 3.35−2.91 (m, 56 H, 28 $NHCH_2$), 1.61−1.35 [m, 76 H, 38 $CH_2(CH_2)_nCH_2$], 1.32 (s, 72 H, 24 $CH_3$). − $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 169.0, 168.9, 167.4, 157.9, 157.2, 136.5, 136.3 (28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1, 118.1 (7 CH Ar), 117.3 ($OCH_2CHCH_2$), 116.6 (14 CH Ar), 79.0 [8 $C(CH_3)_3$], 69.2 ($OCH_2CHCH_2$), 67.4 (6 $OCH_2CO$), 40.3, 40.2, 39.8, 39.1, 38.9 (28 $NHCH_2$), 29.7, 29.2, 29.0, 27.0, 26.7, 24.3 [38 $CH_2(CH_2)_nCH_2$], 28.2 (24 $CH_3$). − MALDI TOF MS; *m/z* = 3501 $[M + Na]^+$.

**Synthesis of 13a:** Trifluoroacetic acid (6 mL) was added dropwise to a suspension of **10a** (202 mg, 63 μmol) in dichloromethane (3 mL). The solution was stirred for 30 min, coevaporated under reduced pressure with 1,2-dichloroethane/toluene (3 × 10 mL, 1:1, v/v), and stored under vacuum (1.5 mbar) for 3 h. The crude residue was dissolved in *N*,*N*-dimethylformamide (4 mL) and triethylamine was added dropwise (ca. 20 drops) until the solution was basic (pH ≈ 8). A solution of pentafluorophenyl chloroacetate (197 mg, 760 μmol) in *N*,*N*-dimethylformamide (0.5 mL) was rapidly added, followed by a further 15 drops of triethylamine. The reaction mixture was stirred for 5 min and concentrated under reduced pressure to a smaller volume (ca. 0.3 mL). The lower molecular weight chlorides were removed by size exclusion chromatography (LH-20, *N*,*N*-dimethylformamide). A fraction of the yellow residue **12a** (6 μmol) and peracetylated melibiose thioacetal (45 mg, 64 μmol) was dissolved in *N*,*N*-dimethylformamide (2 mL) and stirred at −60 °C. To this mixture was added dropwise a cooled (−60 °C), saturated solution of ammonia in *N*,*N*-dimethylformamide (3 mL). The mixture was allowed to come to room temperature over a period of 2 h, concentrated under reduced pressure, and purified by size exclusion chromatography (LH-60, methanol/dichloromethane, 1:1, v/v) to afford **13a** as a white foam (43 mg, 86%): $R_f$ = 0.50 (methanol/dichloromethane, 3:22, v/v); $[\alpha]_D^{25}$ = +36.4 (*c* = 1, methanol/dichloromethane, 3:1, v/v). − $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 600 MHz): δ = 7.89, 7.85, 7.81 (3 s, 7 H, 7 CH Ar), 7.56, 7.54, 7.47 (3 s, 14 H, 14 CH Ar), 6.05−5.96 (m, 1 H, $OCH_2CHCH_2$), 5.40 (d, 8 H, 8 H-4′, $J_{3',4'}$ = 2.9 Hz), 5.40−5.22 (m, 2 H, $OCH_2CHCH_2$), 5.29 (dd, 8 H, 8 H-3′, $J_{2',3'}$ = 11.0 Hz), 5.24 (t, 8 H, 8 H-3, $J_{2,3}/J_{3,4}$ = 9.5 Hz), 5.20 (d, 8 H, 8 H-1′, $J_{1',2'}$ = 3.4 Hz), 5.14 (t, 8 H, 8 H-4, $J_{4,5}$ = 9.5 Hz), 5.02 (dd, 8 H, 8 H-2′), 4.90 (t, 8 H, 8 H-2, $J_{1,2}$ = 10.3 Hz), 4.80 (d, 8 H, 8 H-1), 4.60−4.55 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 4.23−4.18 (m, 8 H, 8 H-5′), 4.10−4.02 (m, 16 H, 8 H-6a′, 8 H-6b′), 3.82−3.77 (m, 8 H, 8 H-5), 3.72 (dd, 8 H, 8 H-6a, $J_{5,6a}$ = 3.9, $J_{6a,6b}$ = 11.7 Hz), 3.69−3.65 (m, 8 H, 8 H-6b), 3.45−3.20 (m, 72 H, 8 $SCH_2$, 28 $NHCH_2$), 2.12, 2.09, 2.00, 1.99, 1.95, 1.94 (6 s, 168 H, 56 $CH_3CO$), 1.83−1.76, 1.62−1.58, [2 m, 36 H, 18 $CH_2(CH_2)_nCH_2$]. − $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 171.0, 170.9, 170.7, 170.5, 170.4, 169.9, 169.8, 169.1, 168.9, 167.9, 167.4, 167.3, 159.0, 158.0, 157.9, 136.5, 136.4, 136.2 (56 $CH_3CO$, 28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.2, 119.1 (7 CH Ar), 117.5 ($OCH_2CHCH_2$), 116.7 (14 CH Ar), 96.4 (8 C-1′), 82.9 (8 C-1), 76.9 (8 C-5), 74.2 (8 C-3), 70.4 (8 C-2), 69.2 ($OCH_2CHCH_2$), 68.7 (8 C-4), 68.5 (8 C-2′), 68.3 (8 C-4′), 67.9 (8 C-3′), 67.5 (6 $OCH_2CO$), 66.6 (8 C-5′), 65.7 (8 C-6), 61.8 (8 C-6′), 39.9, 38.9, 37.4, 37.2 (28 $NHCH_2$), 33.3 (8 $SCH_2$), 29.2, 27.0, 26.8 [18 $CH_2(CH_2)_nCH_2$], 20.5, 20.3, 20.2, 20.1 (56 $CH_3CO$). − MALDI TOF MS; *m/z* = 7967 $[M + Na]^+$.

**Compound 13b:** This compound was synthesized under the same conditions as described for the preparation of **13a**, employing **10b** in place of **10a** to yield a white foam (37 mg, 76%): $R_f$ = 0.50 (methanol/dichloromethane, 3:22, v/v); $[\alpha]_D^{25}$ = +33.1 (*c* = 1, methanol/dichloromethane, 3:1, v/v). − $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 600 MHz): δ = 7.89, 7.84, 7.79 (3 s, 7 H, 7 CH Ar), 7.56, 7.51, 7.47 (3 s, 14 H, 14 CH Ar), 6.05−5.96 (m, 1 H, $OCH_2CHCH_2$), 5.40 (d, 8 H, 8 H-4′, $J_{3',4'}$ = 3.0 Hz), 5.40−5.22 (m, 2 H, $OCH_2CHCH_2$), 5.29 (dd, 8 H, 8 H-3′, $J_{2',3'}$ = 10.7 Hz), 5.24 (t, 8 H, 8 H-3, $J_{2,3}J_{3,4}$ = 9.5 Hz), 5.20 (d, 8 H, 8 H-1′, $J_{1',2'}$ = 3.4 Hz), 5.14 (t, 8 H, 8 H-4, $J_{4,5}$ = 9.5 Hz), 5.02 (dd, 8 H, 8 H-2′), 4.90 (t, 8 H, 8 H-2, $J_{1,2}$ = 10.3 Hz), 4.80 (d, 8 H, 8 H-1), 4.60−4.55 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 4.23−4.18 (m, 8 H, 8 H-5′), 4.10−4.02 (m, 16 H, 8 H-6a′, 8 H-6b′), 3.82−3.78 (m, 8 H, 8 H-5), 3.72 (dd, 8 H, 8 H-6a, $J_{5,6a}$ = 3.9, $J_{6a,6b}$ = 12.2 Hz), 3.67 (dd, 8 H, 8 H-6b, $J_{5,6b}$ = 2.0 Hz), 3.45−3.22 (m, 72 H, 8 $SCH_2$, 28 $NHCH_2$), 2.13, 2.10, 2.00, 1.99, 1.95, 1.94 (6 s, 168 H, 56 $CH_3CO$), 1.82−1.76, 1.62−1.57 [2 m, 40 H, 20 $CH_2(CH_2)_nCH_2$]. − $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 171.0, 170.9, 170.7, 170.5, 170.4, 169.9, 168.9, 167.7, 167.4, 167.3, 158.9, 158.0, 157.9, 136.5, 136.4, 136.3 (56 $CH_3CO$, 28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1, 118.2 (7 CH Ar), 117.4 ($OCH_2CHCH_2$), 116.7 (14 CH Ar), 96.4 (8 C-1′), 82.9 (8 C-1), 76.9 (8 C-5), 74.2 (8 C-3), 70.4 (8 C-2), 69.2 ($OCH_2CHCH_2$), 68.7 (8 C-4), 68.5 (8 C-2′), 68.3 (8 C-4′), 67.9 (8 C-3′), 67.5 (6 $OCH_2CO$), 66.6 (8 C-5′), 65.6 (8 C-6), 61.8 (8 C-6′), 39.9, 38.9, 37.4, 37.2 (28 $NHCH_2$), 33.3 (8 $SCH_2$), 29.2, 27.0, 26.7 [20 $CH_2(CH_2)_nCH_2$], 20.5, 20.3, 20.2, 20.1 (56 $CH_3CO$). − MALDI TOF MS; *m/z* = 7992 $[M + Na]^+$.

**Compound 13c:** This compound was synthesized under the same conditions as described for the preparation of **13a**, employing **10c** in place of **10a** to yield a white foam (43 mg, 85%): $R_f$ = 0.50 (methanol/dichloromethane, 3:22, v/v); $[\alpha]_D^{25}$ = +29.4 (*c* = 1, methanol/dichloromethane, 3:1, v/v). − $^1$H NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 600 MHz): δ = 7.90, 7.84, 7.77 (3 s, 7 H, 7 CH Ar), 7.56, 7.51, 7.44 (3 s, 14 H, 14 CH Ar), 6.03−5.95 (m, 1 H, $OCH_2CHCH_2$), 5.40 (d, 8 H, 8 H-4′, $J_{3',4'}$ = 3.4 Hz), 5.40−5.23 (m, 2 H, $OCH_2CHCH_2$), 5.29 (dd, 8 H, 8 H-3′, $J_{2',3'}$ = 10.7 Hz), 5.24 (t, 8 H, 8 H-3, $J_{2,3}J_{3,4}$ = 9.5 Hz), 5.20 (d, 8 H, 8 H-1′, $J_{1',2'}$ = 3.4 Hz), 5.14 (t, 8 H, 8 H-4, $J_{4,5}$ = 9.5 Hz), 5.02 (dd, 8 H, 8 H-2′), 4.90 (t, 8 H, 8 H-2, $J_{1,2}$ = 9.8 Hz), 4.80 (d, 8 H, 8 H-1), 4.60−4.52 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 4.23−4.18 (m, 8 H, 8 H-5′), 4.10−4.02 (m, 16 H, 8 H-6a′, 8 H-6b′), 3.82−3.78 (m, 8 H, 8 H-5), 3.72 (dd, 8 H, 8 H-6a, $J_{5,6a}$ = 3.9, $J_{6a,6b}$ = 12.2 Hz), 3.67 (dd, 8 H, 8 H-6b, $J_{5,6b}$ = 2.0 Hz), 3.45−3.22 (m, 72 H, 8 $SCH_2$, 28 $NHCH_2$), 2.12, 2.10, 2.00, 1.99, 1.95, 1.94 (6 s, 168 H, 56 $CH_3CO$), 1.82−1.76, 1.64−1.52, 1.39−1.31 [3 m, 44 H, 22 $CH_2(CH_2)_nCH_2$]. − $^{13}$C NMR ($CD_3OD/CDCl_3$, 3:1, v/v, 75 MHz): δ = 171.0, 170.9, 170.7, 170.5, 170.4, 169.9, 169.8, 168.9, 167.7, 167.4, 167.3, 158.9, 158.0, 157.9, 136.5, 136.4, 136.3 (56 $CH_3CO$, 28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1, 118.2 (7 CH Ar), 117.4 ($OCH_2CHCH_2$), 116.7, 116.5 (14 CH Ar), 96.4 (8 C-1′), 82.9 (8 C-1), 76.9 (8 C-5), 74.2 (8 C-3), 70.4 (8 C-2), 69.2 ($OCH_2CHCH_2$), 68.7 (8 C-4), 68.5 (8 C-2′), 68.3 (8 C-4′), 67.9 (8 C-3′), 67.5 (6 $OCH_2CO$), 66.6 (8 C-5′), 65.6 (8 C-6), 61.8 (8 C-6′), 40.1, 39.9, 39.1, 38.9, 37.4, 37.2 (28 $NHCH_2$), 33.3 (8 $SCH_2$), 29.2, 29.1, 27.0, 26.8, 24.3 [22 $CH_2(CH_2)_nCH_2$], 20.5, 20.3, 20.2, 20.1 (56 $CH_3CO$). − MALDI TOF MS; *m/z* = 8019 $[M + Na]^+$.

**Compound 13d:** This compound was synthesized under the same conditions as described for the preparation of **13a**, employing **10d** in place of **10a** to yield a white foam (44 mg, 85%): $R_f$ = 0.50

(methanol/dichloromethane, 3:22, v/v); $[\alpha]_D^{25} = +27.1$ ($c = 1$, methanol/dichloromethane, 3:1, v/v). – $^1$H NMR ($CD_3OD$, 600 MHz): δ = 7.86–7.81 (m, 7 H, 7 CH Ar), 7.54–7.45 (m, 14 H, 14 CH Ar), 6.07–5.96 (m, 1 H, $OCH_2CHCH_2$), 5.41 (d, 8 H, 8 H-4′, $J_{3',4'} = 3.4$ Hz), 5.40–5.22 (m, 2 H, $OCH_2CHCH_2$), 5.29 (dd, 8 H, 8 H-3′, $J_{2',3'} = 10.7$ Hz), 5.24 (t, 8 H, 8 H-3, $J_{2,3}J_{3,4} = 9.5$ Hz), 5.20 (d, 8 H, 8 H-1′, $J_{1',2'} = 3.4$ Hz), 5.14 (t, 8 H, 8 H-4, $J_{4,5} = 9.8$ Hz), 5.02 (dd, 8 H, 8 H-2′), 4.89 (t, 8 H, 8 H-2, $J_{1,2} = 9.8$ Hz), 4.80 (d, 8 H, 8 H-1), 4.62–4.56 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 4.26–4.22 (m, 8 H, 8 H-5′), 4.12–4.04 (m, 16 H, 8 H-6a′, 8 H-6b′), 3.83–3.79 (m, 8 H, 8 H-5), 3.74 (dd, 8 H, 8 H-6a, $J_{5,6a} = 3.9$, $J_{6a,6b} = 12.2$ Hz), 3.70–3.66 (m, 8 H, 8 H-6b), 3.44–3.13 (m, 72 H, 8 $SCH_2$, 28 $NHCH_2$), 2.11, 2.10, 2.01, 2.00, 1.95, 1.94 (6 s, 168 H, 56 $CH_3CO$), 1.64–1.50, 1.41–1.35 [2 m, 68 H, 34 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 171.3, 171.2, 170.8, 170.7, 170.4, 169.7, 169.6, 167.9, 158.5, 137.1 (56 $CH_3CO$, 28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.6 (7 CH Ar), 117.5 ($OCH_2CHCH_2$), 117.0 (14 CH Ar), 96.9 (8 C-1′), 83.4 (8 C-1), 77.4 (8 C-5), 74.7 (8 C-3), 70.8 (8 C-2), 69.6 ($OCH_2CHCH_2$), 69.2 (8 C-4), 68.8 (8 C-2′, 8 C-4′), 68.4 (8 C-3′), 67.9 (6 $OCH_2CO$), 67.1 (8 C-5′), 66.1 (8 C-6), 62.2 (8 C-6′), 40.5, 40.2, 39.3 (28 $NHCH_2$), 33.8 (8 $SCH_2$), 29.5, 27.4, 27.2, 24.8 [34 $CH_2(CH_2)_nCH_2$], 20.5, 20.3, 20.2, 20.1 (56 $CH_3CO$). – MALDI TOF MS; $m/z = 8185$ $[M + Na]^+$.

**Compound 13e:** This compound was synthesized under the same conditions as described for the preparation of **13a**, employing **10e** in place of **10a** to yield a white foam (50 mg, 82%): $R_f = 0.50$ (methanol/dichloromethane, 3:22, v/v); $[\alpha]_D^{25} = +39.9$ ($c = 1$, methanol/dichloromethane, 3:1, v/v). – $^1$H NMR ($CD_3OD$, 600 MHz): δ = 7.86–7.81 (m, 7 H, 7 CH Ar), 7.54–7.46 (m, 14 H, 14 CH Ar), 6.07–5.96 (m, 1 H, $OCH_2CHCH_2$), 5.41 (d, 8 H, 8 H-4′, $J_{3',4'} = 3.4$ Hz), 5.40–5.22 (m, 2 H, $OCH_2CHCH_2$), 5.29 (dd, 8 H, 8 H-3′, $J_{2',3'} = 10.7$ Hz), 5.24 (t, 8 H, 8 H-3, $J_{2,3}J_{3,4} = 9.5$ Hz), 5.20 (d, 8 H, 8 H-1′, $J_{1',2'} = 3.4$ Hz), 5.14 (t, 8 H, 8 H-4, $J_{4,5} = 9.5$ Hz), 5.02 (dd, 8 H, 8 H-2′), 4.89 (t, 8 H, 8 H-2, $J_{1,2} = 9.3$ Hz), 4.80 (d, 8 H, 8 H-1), 4.62–4.56 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 4.26–4.22 (m, 8 H, 8 H-5′), 4.12–4.04 (m, 16 H, 8 H-6a′, 8 H-6b′), 3.83–3.79 (m, 8 H, 8 H-5), 3.74 (dd, 8 H, 8 H-6a, $J_{5,6a} = 3.9$, $J_{6a,6b} = 12.2$ Hz), 3.70–3.66 (m, 8 H, 8 H-6b), 3.44–3.13 (m, 72 H, 8 $SCH_2$, 28 $NHCH_2$), 2.12, 2.10, 2.01, 2.00, 1.95, 1.94 (6 s, 168 H, 56 $CH_3CO$), 1.64–1.50, 1.41–1.35 [2 m, 72 H, 36 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 170.8, 170.7, 170.3, 170.2, 169.9, 169.1, 167.4, 158.0, 136.6 (56 $CH_3CO$, 28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1 (7 CH Ar), 117.0 ($OCH_2CHCH_2$), 116.5 (14 CH Ar), 96.5 (8 C-1′), 83.0 (8 C-1), 76.9 (8 C-5), 74.3 (8 C-3), 70.3 (8 C-2), 69.1 ($OCH_2CHCH_2$), 68.8 (8 C-4), 68.4 (8 C-2′, 8 C-4′), 68.0 (8 C-3′), 67.5 (6 $OCH_2CO$), 66.7 (8 C-5′), 65.6 (8 C-6), 61.7 (8 C-6′), 40.0, 39.7, 38.8 (28 $NHCH_2$), 33.3 (8 $SCH_2$), 29.1, 27.0, 26.7, 24.4 [36 $CH_2(CH_2)_nCH_2$], 20.0, 19.8, 19.6 (56 $CH_3CO$). – MALDI TOF MS; $m/z = 8212$ $[M + Na]^+$.

**Compound 13f:** This compound was synthesized under the same conditions as described for the preparation of **13a**, employing **10f** in place of **10a** to yield a white foam (42 mg, 82%): $R_f = 0.50$ (methanol/dichloromethane, 3:22, v/v); $[\alpha]_D^{25} = +50.0$ ($c = 1$, methanol/dichloromethane, 3:1, v/v);$^1$H NMR ($CD_3OD$, 600 MHz): δ = 7.87–7.79 (m, 7 H, 7 CH Ar), 7.53–7.43 (m, 14 H, 14 CH Ar), 6.07–5.96 (m, 1 H, $OCH_2CHCH_2$), 5.41 (d, 8 H, 8 H-4′, $J_{3',4'} = 3.4$ Hz), 5.40–5.21 (m, 2 H, $OCH_2CHCH_2$), 5.29 (dd, 8 H, 8 H-3′, $J_{2',3'} = 10.7$ Hz), 5.24 (t, 8 H, 8 H-3, $J_{2,3}J_{3,4} = 9.5$ Hz), 5.20 (d, 8 H, 8 H-1′, $J_{1',2'} = 3.9$ Hz), 5.14 (t, 8 H, 8 H-4, $J_{4,5} = 9.5$ Hz), 5.02 (dd, 8 H, 8 H-2′), 4.89 (t, 8 H, 8 H-2, $J_{1,2} = 9.8$ Hz), 4.80 (d, 8 H, 8 H-1), 4.62–4.56 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 4.26–4.22 (m, 8 H, 8 H-5′), 4.12–4.04 (m, 16 H, 8 H-6a′, 8 H-6b′), 3.83–3.79 (m, 8 H, 8 H-5), 3.74 (dd, 8 H, 8 H-6a, $J_{5,6a} = 3.9$, $J_{6a,6b} = 12.2$ Hz), 3.70–3.66 (m, 8 H, 8 H-6b), 3.44–3.13 (m, 72 H, 8 $SCH_2$, 28 $NHCH_2$), 2.12, 2.10, 2.01, 2.00, 1.95, 1.94 (6 s, 168 H, 56 $CH_3CO$), 1.64–1.50, 1.41–1.35 [2 m, 76 H, 38 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($CD_3OD$, 75 MHz): δ = 170.8, 170.7, 170.4, 170.2, 169.9, 169.1, 167.4, 158.1, 136.6 (56 $CH_3CO$, 28 NHCO, 21 $C_q$ Ar), 132.9 ($OCH_2CHCH_2$), 119.1 (7 CH Ar), 117.1 ($OCH_2CHCH_2$), 116.5 (14 CH Ar), 96.5 (8 C-1′), 83.0 (8 C-1), 76.9 (8 C-5), 74.3 (8 C-3), 70.3 (8 C-2), 69.2 ($OCH_2CHCH_2$), 68.7 (8 C-4), 68.4 (8 C-2′, 8 C-4′), 68.0 (8 C-3′), 67.5 (6 $OCH_2CO$), 66.7 (8 C-5′), 65.6 (8 C-6), 61.7 (8 C-6′), 40.0, 39.7, 38.8 (28 $NHCH_2$), 33.3 (8 $SCH_2$), 29.1, 27.0, 26.7, 24.4 [38 $CH_2(CH_2)_nCH_2$], 20.0, 19.8, 19.6 (56 $CH_3CO$). – MALDI TOF MS; $m/z = 8237$ $[M + Na]^+$.

**Synthesis of 14a:** A methanolic solution of sodium methoxide (1.0 M, 2 mL) was added to a solution of **13a** (17.4 mg, 2.1 μmol) in methanol (1 mL). The mixture was stirred for 1 h and neutralized with Dowex-50 ($H^+$) resin. The resin was extracted repeatedly with water/methanol/*N*,*N*-dimethylformamide (5 × 6 mL, 1:1:1, v/v/v). The washings were combined, concentrated under reduced pressure, and purified by size exclusion chromatography (G-25, water) to afford **13a** as a white glass (11.4 mg, 97%): $[\alpha]_D^{25} = +17.8$ ($c = 1$, water). – $^1$H NMR ($D_2O$, 600 MHz): δ = 7.46, 7.43, 7.31 (3 s, 7 H, 7 CH Ar), 7.11, 6.95, 6.84 (3 s, 14 H, 14 CH Ar), 5.79–5.70 (m, 1 H, $OCH_2CHCH_2$), 5.20–5.09 (m, 2 H, $OCH_2CHCH_2$), 4.77 (d, 8 H, 8 H-1′, $J_{1',2'} = 3.3$ Hz), 4.42 (d, 8 H, 8 H-1, $J_{1,2} = 9.9$ Hz), 4.36–4.07 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 3.84–3.74 (m, 24 H, 8 H-6a, 8 H-4′, 8 H-5′), 3.70 (dd, 8 H, 8 H-3′, $J_{2',3'} = 10.3$, $J_{3',4'} = 2.6$ Hz), 3.63 (dd, 8 H, 8 H-2′), 3.58–3.51 (m, 24 H, 8 H-6b, 8 H-6a′, 8 H-6b′), 3.45–3.37 (m, 16 H, 8 H-4, 8 H-5), 3.36–3.30 (m, 16 H, 8 H-3, 8 SCHaHb), 3.25–3.05 (m, 72 H, 8 H-2, 8 SCHaHb, 28 $NHCH_2$), 1.68–1.58, 1.44–1.32 [2 m, 36 H, 18 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($D_2O$, 125 MHz): δ = 172.2, 170.0, 168.2, 167.7, 157.4, 157.1, 135.7, 135.5, 135.2 (28 NHCO, 21 $C_q$ Ar), 132.6 ($OCH_2CHCH_2$), 119.2, 116.7, 116.2 (21 CH Ar, $OCH_2CHCH_2$), 98.4 (8 C-1′), 85.9 (8 C-1), 78.7 (8 C-5), 77.7 (8 C-3), 72.6 (8 C-2), 71.3 (8 C-5′), 69.9 (8 C-3′), 69.6 (8 C-4′), 69.5 (8 C-4), 68.8 (8 C-2′), 67.1 ($OCH_2CHCH_2$, 6 $OCH_2CO$), 65.9 (8 C-6), 61.4 (8 C-6′), 40.1, 39.1, 38.0, 37.8, (28 $NHCH_2$), 33.9 (8 $SCH_2$), 28.5, 26.5, 26.3 [18 $CH_2(CH_2)_nCH_2$].

**Compound 14b:** This compound was synthesized under the same conditions as described for the preparation of **14a**, employing **13b** in place of **13a** to yield a white glass (11.6 mg, 95%): $[\alpha]_D^{25} = +18.2$ ($c = 1$, water). – $^1$H NMR ($D_2O$, 600 MHz): δ = 7.47, 7.36, 7.28 (3 s, 7 H, 7 CH Ar), 7.11, 6.99, 6.92 (3 s, 14 H, 14 CH Ar), 5.83–5.73 (m, 1 H, $OCH_2CHCH_2$), 5.22–5.09 (m, 2 H, $OCH_2CHCH_2$), 4.77 (d, 8 H, 8 H-1′, $J_{1',2'} = 3.4$ Hz), 4.42 (d, 8 H, 8 H-1, $J_{1,2} = 9.8$ Hz), 4.36–4.17 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 3.84–3.74 (m, 24 H, 8 H-6a, 8 H-4′, 8 H-5′), 3.70 (dd, 8 H, 8 H-3′, $J_{2',3'} = 10.3$, $J_{3',4'} = 3.4$ Hz), 3.63 (dd, 8 H, 8 H-2′), 3.58–3.51 (m, 24 H, 8 H-6b, 8 H-6a′, 8 H-6b′), 3.45–3.37 (m, 16 H, 8 H-4, 8 H-5), 3.36–3.30 (m, 16 H, 8 H-3, 8 SCHaHb), 3.25–3.05 (m, 72 H, 8 H-2, 8 SCHaHb, 28 $NHCH_2$), 1.68–1.58, 1.44–1.32 [2 m, 40 H, 20 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($D_2O$, 125 MHz): δ = 172.2, 170.0, 168.2, 167.7, 158.3, 157.4, 135.7 (28 NHCO, 21 $C_q$ Ar), 132.6 ($OCH_2CHCH_2$), 119.2, 116.7, 116.2 (21 CH Ar, $OCH_2CHCH_2$), 98.4 (8 C-1′), 85.9 (8 C-1), 78.7 (8 C-5), 77.7 (8 C-3), 72.6 (8 C-2), 71.3 (8 C-5′), 69.9 (8 C-3′), 69.6 (8 C-4′), 69.5 (8 C-4), 68.8 (8 C-2′), 67.1 ($OCH_2CHCH_2$, 6 $OCH_2CO$), 65.9 (8 C-6), 61.4 (8 C-6′), 40.0, 39.1, 37.9, 37.8 (28 $NHCH_2$), 33.9 (8 $SCH_2$), 28.5, 26.5, 26.3 [20 $CH_2(CH_2)_nCH_2$].

**Compound 14c:** This compound was synthesized under the same conditions as described for the preparation of **14a**, employing **13c** in place of **13a** to yield a white glass (14.0 mg, 100%): $[\alpha]_D^{25} = +19.0$ ($c$ = 1, water). – $^1$H NMR ($D_2O$, 500 MHz): δ = 7.49, 7.45, 7.27 (3 s, 7 H, 7 CH Ar), 7.14, 6.99, 6.84 (3 s, 14 H, 14 CH Ar), 5.82–5.70 (m, 1 H, $OCH_2CHCH_2$), 5.20–5.08 (m, 2 H, $OCH_2CHCH_2$), 4.78 (d, 8 H, 8 H-1′, $J_{1',2'}$ = 3.4 Hz), 4.42 (d, 8 H, 8 H-1, $J_{1,2}$ = 9.8 Hz), 4.38–4.08 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 3.84–3.74 (m, 24 H, 8 H-6a, 8 H-4′, 8 H-5′), 3.71 (dd, 8 H, 8 H-3′, $J_{2',3'}$ = 10.3, $J_{3',4'}$ = 3.4 Hz), 3.64 (dd, 8 H, 8 H-2′), 3.61–3.52 (m, 24 H, 8 H-6b, 8 H-6a′, 8 H-6b′), 3.45–3.31 (m, 32 H, 8 H-3, 8 H-4, 8 H-5, 8 SCHaHb), 3.25–3.00 (m, 72 H, 8 H-2, 8 SCHaHb, 28 $NHCH_2$), 1.68–1.60, 1.45–1.28, 1.10–1.02 [3 m, 44 H, 22 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR [$(CD_3)_2SO$, 125 MHz]: δ = 171.9, 169.9, 168.3, 160.4, 138.9 (28 NHCO, 21 $C_q$ Ar), 136.1 ($OCH_2CHCH_2$), 121.7, 120.4, 118.9 (21 CH Ar, $OCH_2CHCH_2$), 101.4 (8 C-1′), 87.3 (8 C-1), 81.6 (8 C-5), 80.9 (8 C-3), 75.9 (8 C-2), 73.9 (8 C-5′), 73.1 (8 C-3′), 72.5 (8 C-4′), 71.8 (8 C-4), 71.3 (8 C-2′), 70.1 ($OCH_2CHCH_2$, 6 $OCH_2CO$), 69.6 (8 C-6), 63.5 (8 C-6′), 41.3, 41.0, 40.1, 39.8 (28 $NHCH_2$), 35.1 (8 $SCH_2$), 32.1, 31.9, 31.8, 29.7, 29.5, 26.9 [22 $CH_2(CH_2)_nCH_2$].

**Compound 14d:** This compound was synthesized under the same conditions as described for the preparation of **14a**, employing **13d** in place of **13a** to yield a white glass (11.6 mg, 100%): $[\alpha]_D^{25} = +47.0$ ($c$ = 1, water). – $^1$H NMR ($D_2O$, 600 MHz): δ = 7.46, 7.44, 7.36 (3 s, 7 H, 7 CH Ar), 7.08, 6.99, 6.91 (3 s, 14 H, 14 CH Ar), 5.79–5.70 (m, 1 H, $OCH_2CHCH_2$), 5.20–5.09 (m, 2 H, $OCH_2CHCH_2$), 4.79 (d, 8 H, 8 H-1′, $J_{1',2'}$ = 3.4 Hz), 4.39 (d, 8 H, 8 H-1, $J_{1,2}$ = 9.8 Hz), 4.36–4.12 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 3.85–3.76 (m, 24 H, 8 H-6a, 8 H-4′, 8 H-5′), 3.72 (dd, 8 H, 8 H-3′, $J_{2',3'}$ = 10.3, $J_{3',4'}$ = 2.9 Hz), 3.66 (dd, 8 H, 8 H-2′), 3.60–3.51 (m, 24 H, 8 H-6b, 8 H-6a′, 8 H-6b′), 3.44–3.37 (m, 16 H, 8 H-4, 8 H-5), 3.35–3.27 (m, 16 H, 8 H-3, 8 SCHaHb), 3.25–2.96 (m, 72 H, 8 H-2, 8 SCHaHb, 28 $NHCH_2$), 1.72–1.11 [m, 68 H, 34 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($D_2O$, 125 MHz): δ = 172.2, 170.0, 168.3, 167.7, 157.4, 135.8 (28 NHCO, 21 $C_q$ Ar), 132.6 ($OCH_2CHCH_2$), 119.2, 116.7, 116.2 (21 CH Ar, $OCH_2CHCH_2$), 98.8 (8 C-1′), 86.0 (8 C-1), 79.1 (8 C-5), 78.0 (8 C-3), 72.9 (8 C-2), 71.6 (8 C-5′), 70.0 (8 C-3′), 69.9 (8 C-4′, 8 C-4), 69.1 (8 C-2′), 67.5 ($OCH_2CHCH_2$, 6 $OCH_2CO$), 66.5 (8 C-6), 61.7 (8 C-6′), 40.3, 39.4, 38.0 (28 $NHCH_2$), 33.9 (8 $SCH_2$), 28.5, 26.5, 26.3, 24.2 [34 $CH_2(CH_2)_nCH_2$].

**Compound 14e:** This compound was synthesized under the same conditions as described for the preparation of **14a**, employing **13e** in place of **13a** to yield a white glass (14.5 mg, 100%): $[\alpha]_D^{25} = +56.9$ ($c$ = 1, water). – $^1$H NMR ($D_2O$, 600 MHz): δ = 7.44, 7.41, 7.34 (3 s, 7 H, 7 CH Ar), 7.09, 7.04, 6.97 (3 s, 14 H, 14 CH Ar), 5.79–5.71 (m, 1 H, $OCH_2CHCH_2$), 5.18–5.06 (m, 2 H, $OCH_2CHCH_2$), 4.80 (d, 8 H, 8 H-1′, $J_{1',2'}$ = 3.4 Hz), 4.40 (d, 8 H, 8 H-1, $J_{1,2}$ = 9.8 Hz), 4.38–4.14 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 3.85–3.76 (m, 24 H, 8 H-6a, 8 H-4′, 8 H-5′), 3.72 (dd, 8 H, 8 H-3′, $J_{2',3'}$ = 10.3, $J_{3',4'}$ = 2.9 Hz), 3.66 (dd, 8 H, 8 H-2′), 3.60–3.51 (m, 24 H, 8 H-6b, 8 H-6a′, 8 H-6b′), 3.44–3.37 (m, 16 H, 8 H-4, 8 H-5), 3.35–3.27 (m, 16 H, 8 H-3, 8 SCHaHb), 3.25–2.96 (m, 72 H, 8 H-2, 8 SCHaHb, 28 $NHCH_2$), 1.48–1.01 [m, 72 H, 36 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($D_2O$, 125 MHz): δ = 172.1, 170.2, 168.3, 168.0, 157.9, 136.4 (28 NHCO, 21 $C_q$ Ar), 133.1 ($OCH_2CHCH_2$), 119.5, 118.8, 117.0 (21 CH Ar, $OCH_2CHCH_2$), 98.9 (8 C-1′), 86.0 (8 C-1), 79.1 (8 C-5), 78.0 (8 C-3), 72.9 (8 C-2), 71.5 (8 C-5′), 70.3 (8 C-3′), 69.9 (8 C-4′, 8 C-4), 69.1 (8 C-2′), 67.6 ($OCH_2CHCH_2$, 6 $OCH_2CO$), 66.5 (8 C-6), 61.7 (8 C-6′), 40.5, 40.2, 39.3 (28 $NHCH_2$), 33.9 (8 $SCH_2$), 28.8, 28.6, 26.7, 26.5, 24.3 [36 $CH_2(CH_2)_nCH_2$].

**Compound 14f:** This compound was synthesized under the same conditions as described for the preparation of **14a**, employing **14f** in place of **14a** to yield a white glass (14.8 mg, 100%): $[\alpha]_D^{25} = +50.1$ ($c$ = 1, water). – $^1$H NMR ($D_2O$, 600 MHz): δ = 7.50–7.28 (m, 7 H, 7 CH Ar), 7.15–6.84 (m, 14 H, 14 CH Ar), 5.78–5.68 (m, 1 H, $OCH_2CHCH_2$), 5.17–5.05 (m, 2 H, $OCH_2CHCH_2$), 4.80 (s, 8 H, 8 H-1′), 4.40 (d, 8 H, 8 H-1, $J_{1,2}$ = 9.3 Hz), 4.36–4.08 (m, 14 H, 6 $OCH_2CO$, $OCH_2CHCH_2$), 3.86–3.76 (m, 24 H, 8 H-6a, 8 H-4′, 8 H-5′), 3.72–3.64 (m, 16 H, 8 H-3′, 8 H-2′), 3.63–3.51 (m, 24 H, 8 H-6b, 8 H-6a′, 8 H-6b′), 3.45–3.37 (m, 16 H, 8 H-4, 8 H-5), 3.35–3.27 (m, 16 H, 8 H-3, 8 SCHaHb), 3.25–2.96 (m, 72 H, 8 H-2, 8 SCHaHb, 28 $NHCH_2$), 1.48–1.00 [m, 76 H, 38 $CH_2(CH_2)_nCH_2$]. – $^{13}$C NMR ($D_2O$, 125 MHz): δ = 172.1, 170.2, 168.3, 157.8, 136.4 (28 NHCO, 21 $C_q$ Ar), 133.1 ($OCH_2CHCH_2$), 119.5, 118.8, 117.0 (21 CH Ar, $OCH_2CHCH_2$), 98.9 (8 C-1′), 86.0 (8 C-1), 79.1 (8 C-5), 78.0 (8 C-3), 72.9 (8 C-2), 71.5 (8 C-5′), 70.3 (8 C-3′), 69.9 (8 C-4′, 8 C-4), 69.1 (8 C-2′), 67.7 ($OCH_2CHCH_2$, 6 $OCH_2CO$), 66.5 (8 C-6), 61.7 (8 C-6′), 40.6, 40.2, 39.3 (28 $NHCH_2$), 33.9 (8 $SCH_2$), 28.8, 28.7, 26.7, 26.5, 24.3 [38 $CH_2(CH_2)_nCH_2$].

**Experimental Procedure for the Study of the Dependence of $T_{gel}$ Values on Hydrogelator Concentration:** See Figure 1. The appropriate amount of water was added to each freeze-dried sample, and this was heated with gentle agitation for 2 min at 80 °C. The clear solutions obtained were rapidly cooled to 4 °C and maintained at this temperature for 3.5 h. The samples were then heated from 2.0 °C at a rate of 0.2 °C $min^{-1}$. $T_{gel}$ was defined as the temperature range over which the gel phase became liquid, as determined by test tube tilting method and the ball drop method. The range in all cases was < 1.5 °C; curtailed mean values are reported for clarity.

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