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Supporting Information

for

Enhanced Reactivity of Dendrons in the Passerini Three-Component Reaction

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Passerini Reaction of Second-Generation Dendrons



^{1c} Figure S1. Chemical structures of the second-generation dendritic components in the experiments described in Figure 1 of the text.



4e (R = C₁₀H₂₁)

Figure S2. Chemical Structures of the second-generation dendrimers in the experiments described in Figure 1 of the text.



Figure S3. GPC Chromatograms (top) and MALDI-TOF spectra (bottom) for the second-generation Passerini three-component dendrimers a) **4b**, b) **4d**, and c) **4e**.

Passerini Reaction of First-Generation Dendrons

The difference in reactivity of the two linkers in the aldehyde component was also evident in Passerini reactions of first-generation dendrons. Dendrons **7**, **9**, **S1**, and **S3** are first-generation analogs of **1b**, **1c**, **2b**, and **3b**. While the reaction of **7**, **9**, and **S1** reached completion in 6 h to yield dendrimer **S2**, the reaction of **S3** with **9** and **S1** required 48 h to reach completion (Figure S4). Both of the first-generation dendrimers were isolated and purified by flash column chromatography. Dendrimers **S2** and **S4** were characterized by a combination of ¹H and ¹³C NMR spectroscopy, MALDI-TOF mass spectrometry, and gel permeation chromatography (Figure S5).

m/zFigure S5. GPC Chromatograms (top) and MALDI-TOF spectra (bottom) for the first-generation Passerini three-component dendrimers a) **S2**, and b) **S4**.

Three Generations of Dendrimers Synthesized via the Passerini Reaction

Figure S6. Chemical structures of the second-go described in Figure 3 of the text.

14 (R = C₁₀H₂₁)

Figure S7. Chemical structures of the second-generation dendritic components in the experiments described in Figure 3 of the text.

Kinetic Experiments for Passerini Reactions in CH₂Cl₂

To better understand the role that solvent plays in the enhanced rate of the Passerini reaction, we monitored the progress of reactions involving small-molecule reactants in both THF and CH_2CI_2 . Ugi reported anecdotally that the Passerini reaction is accelerated in less polar solvents.¹ Radha Krishna and Lopinti reported a study of reaction solvents for Passerini reactions with tosylmethylisocyanide (TosMIC) in which the isolated yield of product after a fixed reaction time increased with decreasing solvent polarity.² Passerini reactions of isovaleric acid and *t*-butylisocyanide with oxo-compounds **5a–5d** were performed in THF and CH_2CI_2 , and the reaction progress was determined from ¹H NMR spectra of aliquots taken at different times. The reactions of aldehyde **5a** and ketone **5d**, there is a clear increase of the reaction rate in CH_2CI_2 compared to THF (Figures S6a and S6c). A similar enhancement is also noticeable in the reaction of **5b** (Figure S6b), the aldehyde with an ether substituent on the α -carbon. While **5a**, **5b**, and **5d** reacted cleanly with isovaleric acid and *t*-butylisocyanide in CH_2CI_2 , we observed a significant amount of an undesired product in the reaction of acetone (**5c**) in CH_2CI_2 that prevented us from quantifying the progress of this reaction.

Figure S8. Plot of reaction conversion for Passerini reactions of isovaleric acid and *t*-butylisocyanide in with oxo-compounds **5a–5d** in THF (\bigcirc) and CH₂Cl₂ (\triangle). a) Isovaleraldehyde (**5a**); b) α -butoxyacetaldehyde (**5b**); and c) methoxyacetone (**5d**) ([**5**]₀:[CO₂H]₀:[N=C]₀ = 1:1.1:1.1, [**5**]₀ = 0.7 M).

Figure S9. Plot of reaction conversion for Passerini reactions of isovaleric acid and *t*-butylisocyanide in CH_2CI_2 with isovaleraldehyde (**5a**) (\bigcirc) and α -butoxyacetaldehyde (**5b**) ([**5**]₀:[CO₂H]₀:[N=C]₀ = 1:1.1:1.1, [**5**]₀ = 0.7 M).

Isovaleric and and *t*-butylisocyanide were subjected to Passerini reactions with isovaleraldehyde (**5a**) and α -butoxyacetaldehyde (**5b**) in CH₂Cl₂. The reactions were performed at room temperature in THF, and the reaction progress was determined from ¹H NMR spectra of aliquots taken at different times. Figure S7 compares the progress of these two reactions as an illustration of the effect of weakly electron withdrawing groups in a solvent promotes fast Passerini reactions. The results are nearly

indistinguishable. By extension of the results in Figures S6 and S7, we expect that the rate acceleration due to weakly electron withdrawing groups like ethers would also be indistinguishable under solvent-free reaction conditions.

Schemes Describing the Synthesis of the Component Dendrons

Figure S10. Synthesis of third-generation poly(alkyl ether) dendrons with peripheral decyl or benzyl groups.

Figure S11. Synthesis of aldehydes 7, 1b, and 8.

Figure S15. Synthesis of dendritic aldehydes S3 and 1c.

Experimental Section

Materials. Ethyl acetate (EtOAc, A.C.S. grade), hexanes (hex, A.C.S. grade), acetone (A.C.S. grade), hydrochloric acid, anhydrous tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and dichloromethane (CH₂Cl₂) were purchased from EMD. Ammonium hydroxide (NH₄OH, 28-30%) and methanol (MeOH, A.C.S. grade) were purchased from BDH. 3-Chloro-2-chloromethyl-1-propene (methallyl dichloride, 99%), dry NaH (95%), 0.5 M solution of 9-borabicyclo-[3.3.1]-nonane (9-BBN) in THF, silver trifluoroacetate (99.99%), succinic anhydride, N.N'-dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), Boc- β -alanine (Boc- β -Ala-OH), sodium chloride (NaCl), pentenoic acid, benzene, 9-nitroanthracene (93%), allyl butyl ether (98%), isovaleric acid (99%), and tert-butyl isocyanide (98%) were purchased from Aldrich. Allyl bromide (99%), propyl formate (96%), 15-crown-5 (98%), and trifluoroacetic acid (TFA, 99.5%) were purchased from Acros Organics. Triphenylphosphine (PPh₃, 99+%), triethylamine (NEt₃), potassium carbonate, p-toluenesulfonic acid (pTsOH), methanesulfonyl chloride (MsCl), 30% w/w H₂O₂ (aq.), isovaleraldehyde (98%), anhydrous dichloromethane (99.7+%, CH₂Cl₂), and pyridine (99%) were purchased from Alfa Aesar. Drierite (anhydrous calcium sulfate, 4-mesh) was purchased from VWR. Sodium sulfate (Na₂SO₄) and anhydrous magnesium sulfate (MgSO₄) were purchased from J. T. Baker. Carbon tetrachloride (CCl₄) was purchased from MP Biomedicals. Silica gel (60 Å) and sodium azide were purchased from Macron Fine Chemicals. Sodium hydroxide (NaOH) was purchased from Amresco. THF-d₈ and CDCl₃ were purchased from Cambridge Isotope Laboratories. All reagents and solvents were used as received. 4-Dimethylaminopyridinium p-toluenesulfonate (DPTS) was prepared by repeated azeotropic distillations of water from a mixture of DMAP and p-toluenesulfonic acid monohydrate in benzene.³ Anhydrous acetone was prepared by shaken with drierite (anhydrous CaSO₄) (25g/L) overnight and then decanted and distilled from fresh drierite and was used immediately. Compounds S6-S8.4 S9.5

S11,⁵ **1a**,⁴ **2a**,⁴ **3a**,⁴ **4a**,⁴ **6-G2**,⁴ **S24**,⁵ and **S25**⁵ were prepared according to literature procedures or modified literature procedures.

Techniques. ¹H NMR (400 MHz, 500 MHz, 700 MHz) and ¹³C NMR (100 MHz, 125 MHz, 175 MHz) spectra were recorded on a Bruker Avance III (400, 500, and 700) NMR spectrometer. Peak multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, pent = pentet, hept = heptet, sept = septet, and m = multiplet. Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer. The MALDI-TOF data were recorded on a Bruker Autoflex II TOF/TOF workstation. MALDI-TOF samples (10 mg/mL) were prepared in THF with 9-nitroanthracene as the matrix and silver triflate as the ionizing species. Equal volumes of the matrix and dendrimer solutions were mixed and 1 µL of the mixture was dried on the target plate. The solution of matrix and dendrimer was diluted by 10-folds with matrix solution and 1 µL of the mixture was dried on the target plate. Gel permeation chromatography (GPC) in THF (1 mL/min) was performed using a Shimadzu LC-20AD liquid chromatography pump equipped with a DGU-20A5 degasser, CBM-20A controller, RID-10A RI detector, CTO-20A column oven (all from Shimadzu), and three American Polymer Standards AM GPC gel columns of 100 Å (5 μm), 500 Å (5 μm), and 10,000 Å (5 μm). Relative molecular weights and molecular weight distributions were determined according to a calibration with narrow polydispersity polystyrene standards (American Polymer Standards). Thin layer chromatography (TLC) was performed using Whatman silica gel 60 Å plates (250 µm) with fluorescent indicator and visualized using a UV lamp (254 nm) or KMnO₄ stain. Flash chromatography was performed on a Teledyne Isco CombiFlash Rf with RedSep Rf Normal Phase disposable silica columns. Low-resolution electrospray ionization mass spectra (ESI-MS) were acquired on an Agilent LC-MSD that consists of an 1100 HPLC and a G1956A mass spectrometer. High-resolution electrospray ionization mass spectra (HRMS-ESI) were acquired by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign on a Micromass Q-Tof Ultima. M-H-W Laboratories (Phoenix, AZ) performed elemental analysis. Ozone was produced using using an Ozone Services GE 60/FM 500 from Yanco Industries Ltd.

α-Butoxyacetaldehyde (5b).⁶⁻⁷ To a 100-mL one-neck flask, allyl butyl ether (7.67 mL, 52.6 mmol) was dissolved in anhydrous CH₂Cl₂ (26.0 mL) and the reaction mixture was treated with O₃ for 7 h at -78 °C. Then a solution of PPh₃ (13.86 g, 52.84 mmol) in anhydrous CH₂Cl₂ (26.0 mL) was added dropwise while the reaction was stirred under N₂ in ice-water bath. Then the reaction was stirred at room temperature under N₂ for 44 h. The product was distilled under reduced pressure to give **5b** as a colorless oil (1.75 g, 29%). ¹H NMR (500 MHz, CDCl₃, δ): 9.74 (t, *J* = 0.92 Hz, 1H; CHO), 4.06 (d, *J* = 0.96 Hz, 2H; CH₂CHO), 3.54 (t, *J* = 6.6 Hz, 2H; C₃H₇CH₂OCH₂CHO), 1.62 (m, 2H; C₂H₅CH₂CH₂O), 1.41 (m, 2H; CH₃CH₂C₂H₄O), 0.94 (t, *J* =7.4 Hz, 3H, CH₃C₃H₆O). ¹³C NMR (125 MHz, CDCl₃, δ): 201.4 (CHO), 76.5 (CH₂CHO), 72.2 (OCH₂C₃H₇), 31.8 (OCH₂CH₂C₂H₅), 19.4 (OC₂H₄CH₂CH₃), 14.1 (OC₂H₄CH₂CH₃). 1H NMR Spectral data agree with literature.⁷

General Procedure for Kinetics Study. Each experiment was performed under an N_2 atmosphere in a 25-mL one-neck flask equipped with a magnetic stir bar and capped with a rubber septum. The amounts of reagents and reaction solvent were measured by mass, and were added to the reaction vessel in the following order: solvent, oxo-component (**5a-d**), isovaleric acid, and *t*-butyl isocyanide. The reactions were stirred at ambient temperature, and aliquots (50 µL) were taken at the times indicated in the plots. The aliquots were diluted with CDCl₃ and the ¹H NMR spectrum of the diluted aliquot was recorded within 10 min. The conversion for each reaction was calculated from the integration of the resonances corresponding to the *t*-butyl group in *t*-butyl isocyanide and the product (**6a-d**). Exact quantities from a representative kinetic experiment are provided in the synthesis of **6b** reported below.

1-(*t***-Butylaminocarbonyl)-3-methylbutyl 3-methylbutanoate (6a).** To a 25-mL one-neck flask, isovaleraldehyde (0.660 mL, 6.02 mmol), *t*-butyl isocyanide (0.680 mL, 6.01 mmol) isovaleric acid (0.670 mL, 6.07 mmol), anhydrous THF (6.1 mL) were added and stirred under N₂ at room temperature for 32 h. Excess reagents and solvent of the reaction mixture was removed by rotary evaporation. The product was purified by flash column chromatography (SiO₂, hex to hex/EtOAc 4:1) to give product **6a** as a colorless solid (1.31 g, 80%). TLC (SiO₂, 4:1 hex/EtOAc): R_f = 0.49. ¹H NMR (500 MHz, CDCl₃, δ): 5.77 (s, 1H; N*H*), 5.08 (dd, J₁ = 8.2 Hz, J₂ = 4.4 Hz, 1H; CO₂CHCO), 2.27 (d, J = 7.1 Hz, 2H;

 $O_2CCH_2CH(CH_3)_2)$, 2.13 (m, 1H; $O_2CCH_2CH(CH_3)_2)$, 1.68 (overlapped m, 3H; $CO_2CHCH_2CH(CH_3)_2$, $CO_2CHCH_2CH(CH_3)_2)$, 1.34 (s, 9H; NHC(CH_3)_3), 0.99 (d, J = 6.6 Hz, 6H; $O_2CCH_2CH(CH_3)_2)$, 0.93 (d, J = 6.3 Hz, 3H; $CO_2CHCH_2CH(CH_3)_2)$, 0.91 (d, J = 6.1 Hz, 3H; $CO_2CHCH_2CH(CH_3)_2)$. ¹³C NMR (125 MHz, CDCl₃, δ): 172.1 (NHCO), 169.7 (OCO), 73.1 (NHCOC), 51.4 ((CH_3)_3C), 43.7 (OCOCH_2), 41.0 (NHCOCHCH_2CH(CH_3)_2), 28.9 (((CH_3)_3C), 26.1 (OCOCH_2CH(CH_3)_2), 24.8 (NHCOCHCH_2CH(CH_3)_2), 23.4 (OCOCH_2CH(CH_3)_2), 22.5 (NHCOCHCH_2CH(CH_3)_2), 22.0 (NHCOCHCH_2CH(CH_3)_2).

1-(t-Butylaminocarbonyl)-2-butoxyethyl 3-methylbutanoate (6b). Compound 6b was isolated in low yield from a reaction mixture used for the kinetics experiments. To a 25-mL one-neck flask, anhydrous THF (3.8071 g), α-butoxyacetaldehyde 5b (0.4722 g, 4.065 mmol), isovaleric acid (0.4568 g, 4.473 mmol), and t-butyl isocyanide (0.3555 g, 4.276 mmol) were added in the sequence of listed above and stirred under N₂ at room temperature. After 76 h, volatiles were removed by rotary evaporation. The product was purified by flash column chromatography (SiO₂, hex to hex/EtOAc 4:1). Slight isovaleric acid impurity was removed under reduced pressure. Product 6b was obtained as colorless oil (0.55 a. 45%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.41$. ¹H NMR (500 MHz, CDCl₃, δ): 6.00 (s, 1H; NH), 5.08 (dd, $J_1 = 4.8$ Hz, $J_2 = 3.7$ Hz, 1H; CO₂CHCO), 3.78 (dd, ³J = 4.9 Hz, ²J = 10.8 Hz, 1H; CHCH₂OC₄H₉), 3.72 (dd, ³J = 3.8 Hz, ²J = 10.8 Hz, 1H; CHCH₂OC₄H₉), 3.72 (dd, ³J = 3.8 Hz, ²J = 10.8 Hz, 1H; CHCH₂OC₄H₉), 3.48 (dt, ³J = 6.5 Hz, ²J = 9.5 Hz, 1H; CH₂OCH₂C₃H₇), 3.48 (dt, ³J = 6.6 Hz, ²J = 9.5 Hz, 1H; CHCH₂OCH₂C₃H₇), 2.31 (d, J = 7.2 Hz, 2H; OCOCH₂CH(CH₃)₂), 2.13 (m, 1H; $OCOCH_2CH(CH_3)_2$, 1.52 (m, 2H; $CH_2OCH_2CH_2C_2H_5$), 1.35 (overlapping s, 9H; $NHC(CH_3)_3$; overlapped m, 2H; $CH_2OC_2H_4CH_2CH_3$), 0.994 (d, J = 6.7 Hz, 3H; $OCOCH_2CH(CH_3)_2$), 0.991 (d, J = 6.7 Hz, 3H; OCOCH₂CH(CH₃)₂), 0.90 (t, J = 7.4 Hz, 3H; CH₂OC₃H₆CH₃); ¹³C NMR (125 MHz, CDCl₃, δ): 171.7 (NHCO), 167.3 (OCO), 73.2 (NHCOCHOCO), 71.5 $(NHCOCHCH_2OCH_2C_3H_7),$ 70.2 (NHCOCHCH₂OC₄H₉), 51.5 (CH₃)₃CNH), 43.5 (OCOCH₂), 31.8 (OCH₂CH₂C₂H₅), 28.9 ((CH₃)₃CNH), 26.1 (OCOCH₂CH(CH₃)₂), 22.5 (OC₂H₄CH₂CH₃), 19.4 (OCOCH₂CH(CH₃)₂), 14.1 (OC₃H₆CH₃).

2-(*t***-Butylaminocarbonyl)-prop-2-yl 3-methylbutanoate (6c).** To a 25-mL one-neck flask, acetone (0.3014 g, 5.189 mmol), isovaleric acid (0.3414 g, 3.343 mmol), and *t*-butyl isocyanide (0.2888 g, 3.474 mmol) were added in the sequence of listed above and stirred under N₂ at room temperature for 68 h. Excess reagents were removed under reduced pressure. The product was purified by flash column chromatography (SiO₂, hex/EtOAc 95:5) to give product **6c** as colorless oil (0.32 g, 39 %). TLC (SiO₂, 9:1 hex/EtOAc): R_f = 0.19. ¹H NMR (500 MHz, CDCl₃, δ): 5.83 (s, 1H; NH), 2.19 (d, *J* = 7.1 Hz, 2H; OCOCH₂CH(CH₃)₂), 2.10 (m, 1H; OCOCH₂CH(CH₃)₂), 1.59 (s, 6H; NHCOC(CH₃)₂O), 1.35 (s, 9H; NHC(CH₃)₃), 0.98 (d, *J* = 6.6 Hz, 6H; OCOCH₂CH(CH₃)₂); ¹³C NMR (125 MHz, CDCl₃, δ): 172.4 (NHCO), 171.4 (OCO), 81.8 (NHCOC(CH₃)₂), 51.1 (NHC(CH₃)₃), 44.4 (OCOCH₂), 28.8 (C(CH₃)₃), 26.0 (OCOCH₂CH(CH₃)₂), 24.5 (NHCOC(CH₃)₂), 22.6 (OCOCH₂CH(CH₃)₂).

1-Methoxy-2-(*t***-butylaminocarbonyl)-prop-2-yl 3-methylbutanoate (6d).** To a 25-mL one-neck flask, methoxyacetone (0.3877 g, 4.400 mmol), isovaleric acid (0.3616 g, 3.225 mmol), and *t*-butyl isocyanide (0.2972 g, 3.5751 mmol) were added in the sequence of listed above and stirred under N₂ at room temperature for 20 h. Excess reagents were removed under reduced pressure. The product was purified by flash column chromatography (SiO₂, hex to hex/EtOAc 4:1) to give product **6d** as colorless oil (0.43 g, 44%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.29$. ¹H NMR (500 MHz, CDCl₃, δ): 6.21 (s, 1H; NH), 4.02 (d, ²J = 9.9 Hz, 1H; NHCOCCH₂OCH₃), 3.61 (d, ²J = 9.9 Hz, 1H; NHCOCCH₂OCH₃), 3.34 (s, 3H; OCH₃), 2.24 (d, J = 3.8 Hz, 1H; OCOCH₂CH(CH₃)₂), 2.23 (d, J = 3.3 Hz, 1H; OCOCH₂CH(CH₃)₂), 2.11 (m, 1H; OCOCH₂CH(CH₃)₂), 1.55 (s, 3H; NHCOCCH₃), 1.35 (s, 1H; C(CH₃)₃), 0.99 (d, J = 6.6 Hz , 6H; OCOCH₂CH(CH₃)₂); ¹³C NMR (125 MHz, CDCl₃, δ): 171.4 (NHCO), 170.5 (OCO), 82.9 (NHCOC), 74.5 (NHCOCCH₂OCH₃), 59.5 (OCH₃), 51.2 (NHC(CH₃)₃), 44.3 (OCOCH₂), 28.8 (C(CH₃)₃), 26.0 (OCOCH₂CH(CH₃)₂), 22.6 (OCOCH₂CH(CH₃)₂), 20.2 (NHCOCCH₃).

2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethene (S10).⁸ Dry NaH (0.80 g, 33 mmol), methallyl dichloride (1.00 mL, 8.64 mmol), and 15-Crown-5 (0.6 mL, 3 mmol) was added to an ice-water bath cooled suspension of dendron **S8** (16.84 g, 26.20 mmol) in anhydrous THF (34.0 mL). At 28 h, the reaction was not complete. Additional dry NaH (0.20 g, 8.3 mmol) was added to the cooled reaction mixture. The mixture was stirred at reflux for an additional 18 h to completion. The mixture was cooled in an ice-water bath, quenched with water and extracted three times with EtOAc and once with saturated NaCl (aq). The organic layers were combined and dried over anhydrous Na₂SO₄ and the

solvent was removed in vacuo. The product was purified by flash column chromatography (SiO₂; 9:1 hexEtOAc to 3:2) and yielded **S10** as a colorless oil (10.5 g, 90%). TLC (SiO₂, 4:1 hex/EtOAc): $R_{\rm f}$ = 0.15. ¹H NMR (400 MHz, CDCl₃, δ): 7.27 (m, 40H; Ar-*H*), 5.09 (s, 2H; H_2 C=C), 4.46 (s, 16H; OCH₂Ph), 3.87 (s, 4H; H₂C=C(CH₂O)₂), 3.52 (d, *J* = 5.9 Hz, 16H; CH₂OBn), 3.46 (d, *J* = 6.0 Hz, 16H; CH₂OCH₂), 3.38 (m, 8H; CH₂OCH₂), 2.23 (sept, *J* = 5.9 Hz, 2H; CH(CH₂OBn)₂), 2.11 (sept, *J* = 5.9 Hz, 3H; CH(CH₂O)₂). ¹³C NMR (100 MHz, CDCl₃, δ): 143.2 (H₂C=C(CH₂O)₂), 138.8 (OCH₂C=(CH)(CH)), 128.5 (Ar-CH), 127.70 (Ar-CH), 127.65 (Ar-CH), 113.2 (H₂C=C), 73.3 (OCH₂Ar), 72.0 (CH₂OCH₂), 69.7 (CH₂OCH₂), 69.1 (CH₂OCH₂), 69.0 (CH₂OCH₂), 40.7 (CH). HRMS-ESI (*m*/*z*): [M + H]⁺ calcd for C₅₂H₁₀₄O₆, 825.7911, found 825.7903. GPC: $M_{\rm n}$ = 1,130, $M_{\rm w}/M_{\rm n}$ = 1.08.

2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethanol (S12).⁸ A solution of S10 (6.75 g, 5.05 mmol) in anhydrous THF (96.0 mL) was stirred for ~5 min in an ice-water bath. To this mixture, 0.5 M 9-BBN (30.0 mL, 15.1 mmol) was added dropwise. The reaction mixture was stirred for 22 h while heating at 35 °C. The ice-water bath-cooled reaction mixture was guenched with agueous 3 M NaOH (aq) (13.5 mL, 40.4 mmol) while stirring followed by the slow addition of 30 wt% H₂O₂ (aq) solution (13.5 mL). The reaction mixture was left to stir in the ice-water bath for 26 h. The reaction mixture was saturated with K₂CO₃ and the organic layer was collected. The aqueous layer was washed three times with EtOAc. The organic layers were combined, washed with saturated NaCl (aq), and dried over anhydrous MgSO₄. The solids were removed by filtration, and the solvent was removed from the filtrate in vacuo. The product was purified by flash column chromatography (SiO2; hex/EtOAc 4:1 to 6:4) and yielded **S12** as a colorless oil (5.06 g, 74%). TLC (SiO₂, 6:4 hex/EtOAc): $R_f = 0.45$. ¹H NMR (500MHz, CDCl₃, δ): 7.29 (m, 40H; Ar-H), 4.47 (s, 16H, OCH₂Ar), 3.66 (t, J = 5.3 Hz, 2H; HOCH₂), 3.44 (m, 40H; CH₂OCH₂), 2.73 (t, J = 5.3 Hz, 1H; HOCH₂), 2.23 (sept, J = 5.9 Hz, 4H; CH₂CH(CH₂OBn)₂), 2.07 (sept, J = 6.0 Hz, 3H; CH₂CHCH₂). ¹³C NMR (125 MHz, CDCl₃, δ): 138.8 (OCH₂C=(CH)(CH)), 128.5 (Ar-CH), 127.7 (Ar-CH), 126.67 (Ar-CH), 77.4 (Ar-CH), 73.3 (OCH₂Ar), 71.4 (CH₂OCH₂), 70.1 (CH₂OCH₂), 69.8 (CH₂OCH₂), 69.7 (CH₂OCH₂), 69.0 (CH₂OCH₂), 64.3 (HOCH₂), 41.5 (HOCH₂CH), 40.6 (CH₂CH(CH₂)₂), 40.4 (CH₂CH(CH₂)₂). MALDI-TOF (m/z): [M + Ag]^{*} calcd for C₈₄H₁₀₆O₁₅Ag, 1461.658, found 1462.212. GPC: $M_{\rm n}$ = 1,134, $M_{\rm w}/M_{\rm n}$ = 1.07.

2,2-Bis(decyloxymethyl)ethyl allyl ether (S13). Dry NaH (0.0866 g, 3.60 mmol) and allyl bromide (0.13 mL, 1.5 mmol) was added to an ice-water bath cooled solution of S5 (0.48 g, 1.2 mmol) in anhydrous THF (2.6 mL). The reaction mixture was stirred at reflux for 21 h. The mixture was cooled in an ice-water bath and guenched with water until two layers formed. The organic layer was collected and the agueous layer was washed three times with EtOAc. The combined organic layers were washed once with saturated NaCl (ag) and dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate in vacuo. The product was purified by flash column chromatography (SiO₂; 1:0 hex/EtOAc to 4:1) and yielded **S13** as a colorless oil (0.47 g, 89%). TLC (SiO₂, 9:1 hex/EtOAc): $R_f = 0.59$. ¹H NMR (400MHz, CDCl₃, δ): 5.88 (pentet, J = 5.5 Hz, 1H; HC=CH₂), 5.18 (dd, J₁ = J₂ = 6.7 Hz, 2H; H₂C=CH), 3.93 (d, J = 5.2 Hz, 2H; H₂C=CHCH₂O), 3.41 (m, 10H; OCH₂CH(CH₂O)₂), 2.14 (m, 1H; CH₂CH(CH₂O)₂), 1.52 (tt, J₁ = 6.8 Hz, J₂ = 7.1 Hz, 4H; OCH₂CH₂(CH₂)₈H), 1.26 (m, overlapped), 1.24 (overlapping s, 28H; (CH₂)₇CH₃), 0.86 (t, J = 6.7 Hz, 6H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 135.3 (H₂C=CHCH₂), 116.7 (H₂C=C), 72.3 (H₂C=CHCH₂O), 71.5 (CH₂OCH₂), 69.4 (CH₂OCH₂), 69.1 40.6 $(CH_2CHCH_2),$ $(OCH_2CH_2(CH_2)_7),$ (CH_2OCH_2) , 32.1 29.91 $(OCH_2CH_2(CH_2)_7),$ 29.98 (OCH₂CH₂(CH₂)₇), 29.8 (OCH₂CH₂(CH₂)₇), 29.7 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 26.4 $(OCH_2CH_2(CH_2)_7)$, 22.9 $(OCH_2CH_2(CH_2)_7)$, 14.3 $(O(CH_2)_9CH_3)$. ESI-MS (m/z): $[M + H]^+$ calcd for $C_{27}H_{55}O_3$, 427.4; found 427.4. GPC: $M_p = 453$, $M_w/M_p = 1.04$.

2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl allyl ether (S14). Dry NaH (0.0818 g, 3.41 mmol), allyl bromide (0.15 mL, 1.73 mmol), and 15-crown-5 (25 μ L, 0.13 mmol) was added to an ice-water bath cooled solution of **S7** (1.06 g, 1.26 mmol) in anhydrous THF (2.4 mL). The reaction mixture was stirred at reflux for 21 h. The mixture was cooled in an ice-water bath and quenched with water until two layers formed. The organic layer was collected and the aqueous layer was washed three times with EtOAc. The combined organic layers were washed once with saturated NaCl (aq) and dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc to 9:1) and yielded **S14** as a colorless oil (1.09 g, 98%). TLC (SiO₂, 9:1 hex/EtOAc): $R_f = 0.43$. ¹H NMR (400 MHz, CDCl₃, δ): 5.87

(pentet, 1H; *H*C=CH₂), 5.18 (dd, $J_1 = J_2 = 6.7$ Hz, 2H; $H_2C=CH$), 3.93 (d, J = 5.5 Hz, 2H; $H_2C=CHCH_2O$), 3.40 (overlapping m, 26H; CH_2OCH_2 , $OCH_2(CH_2)_9$ H), 2.11 (m, 3H; $CH_2CH(CH_2O)_2$), 1.52 (tt, $J_1 = 7.3$ Hz, $J_2 = 6.7$ Hz, 4H; $OCH_2CH_2(CH_2)_8$ H), 1.24 (m, overlapped), 1.24 (overlapping s, 56H; $(CH_2)_7CH_3$), 0.86 (t, J = 6.7 Hz, 12H; CH_3). ¹³C NMR (100 MHz, CDCl₃, δ): 135.3 ($H_2C=CHCH_2$), 116.7 ($H_2C=C$), 72.3 ($H_2C=CHCH_2O$), 71.5 (CH_2OCH_2), 69.9 (CH_2OCH_2), 69.8 (CH_2OCH_2), 69.4 (CH_2OCH_2), 69.0 (CH_2OCH_2), 40.6 (CH_2CHCH_2), 32.2 ($OCH_2CH_2(CH_2)_7$), 29.95 ($OCH_2CH_2(CH_2)_7$), 29.89 ($OCH_2CH_2(CH_2)_7$), 29.84 ($OCH_2CH_2(CH_2)_7$), 29.76 ($OCH_2CH_2(CH_2)_7$), 29.6 ($OCH_2CH_2(CH_2)_7$), 26.4 ($OCH_2CH_2(CH_2)_7$), 22.9 ($OCH_2CH_2(CH_2)_7$), 14.3 ($O(CH_2)_9CH_3$). ESI-MS (m/z): [M + NH₄]⁺ calcd for C₅₅H₁₁₄NO₇, 900.9; found 900.8. GPC: $M_n = 1,109 M_w/M_n = 1.06$.

2,2-Bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethyl allyl ether (S15). Dry NaH (0.0817 g, 3.40 mmol), allyl bromide (53 µL, 0.61 mmol), and 15-crown-5 (10 µL, 0.050 mmol) were added to a ice-water bath cooled solution of S11 (0.9043 g, 0.5147 mmol) in anhydrous THF (1.0 mL). The reaction mixture was stirred at reflux for 22 h. The mixture was cooled in an ice-water bath and quenched with water until two layers formed. The organic layer was collected and the aqueous layer was washed three times with EtOAc. The combined organic layers were washed once with saturated NaCl (aq) and dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate in vacuo. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc) and yielded **S15** as a colorless mixture (0.68 g, 74%). TLC (SiO₂, 9:1 hex/EtOAc): $R_f = 0.32$. ¹H NMR (500 MHz, CDCl₃, δ): 5.87 (pent, J = 5.5 Hz, 1H; HC=CH₂), 5.19 (dd, J₁ = 5.0, J₂ = 4.4 Hz, 2H; H₂C=CH), 3.93 (d, J = 5.5 Hz, 2H; H₂C=CHCH₂O), 3.39 (overlapping m, 56H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.10 (pent, J = 5.9 Hz, 7H; CH₂CH(CH₂O)₂), 1.52 (tt, J₁ = J₂ = 7.0 Hz, 16H; OCH₂CH₂(CH₂)₈H), 1.24 (m, overlapped), 1.24 (overlapping s, 112H; $(CH_2)_7 CH_3$), 0.86 (t, J = 7.0 Hz, 24H; CH_3). ¹³C NMR (125 MHz, CDCl₃, δ): 135.3 (H₂C=CHCH₂), 116.7 (H₂C=C), 72.3 (H₂C=CHCH₂O), 71.5 (CH₂OCH₂), 69.9 (CH₂OCH₂), 69.88 (CH₂OCH₂), 69.86 (CH₂OCH₂), 69.76 (CH₂OCH₂), 69.4 (CH₂OCH₂), 68.9 (CH₂OCH₂), 40.6 (CH₂CHCH₂), 32.2 (OCH₂CH₂(CH₂)₇), 29.96 (OCH₂CH₂(CH₂)₇), 29.90 (OCH₂CH₂(CH₂)₇), 29.85 (OCH₂CH₂(CH₂)₇), 29.78 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 26.4 (OCH₂CH₂(CH₂)₇), 22.9 $(OCH_2CH_2(CH_2)_7)$, 14.4 $(O(CH_2)_9CH_3)$. GPC: $M_n = 2,399 M_w/M_n = 1.04$.

2,2-Bis(decyloxymethyl)ethoxyacetaldehyde (7). Ozone was bubbled through a stirred solution of **S13** (0.47 g, 1.1 mmol) in anhydrous CH₂Cl₂ (18.0 mL) while cooling the reaction vessel in a dry ice-acetone bath. The reaction mixture was stirred for 40 min at which time the reaction mixture turned blue. The mixture was quenched with NEt₃ (0.48 mL, 3.5 mmol) and stirred for 14 h at room temperature. The solvent was removed *in vacuo*. The product was purified by flash column chromatography (SiO₂; 1:0 hex/EtOAc to 9:1) and yielded **7** as a colorless oil (0.20 g, 43%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.55$. ¹H NMR (400 MHz, CDCl₃, δ): 9.71 (s, 1H; CHO), 4.02 (s, 2H; CHO(CH₂O), 3.58 (d, J = 5.8 Hz, 2H; OCH₂CH(CH₂O)₂), 3.45 (d, J = 6.0 Hz, 4H; CHCH₂O), 3.37 (t, J = 6.6 Hz, 4H; CH₂OCH₂CH₂), 2.18 (m, 1H; CH₂CH(CH₂O)₂), 1.52 (tt, $J_1 = 7.1$ Hz, $J_2 = 6.9$ Hz, 4H; OCH₂CH₂(CH₂)₈H), 1.24 (m, overlapped), 1.24 (overlapping s, 28H; (CH₂)₇CH₃), 0.86 (t, J = 6.8 Hz, 6H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 201.6 (CHO), 76.8 (OCH₂CHO), 71.6 (OCH₂(CH₂)₈CH₃), 70.8 (OCH₂CH(CH₂O)₂), 69.1 (CHCH₂OC₁₀H₂₁), 40.6 (CH₂CHCH₂), 32.1 (OCH₂CH₂(CH₂)₇), 29.89 (OCH₂CH₂(CH₂)₇), 29.86 (OCH₂CH₂(CH₂)₇), 29.82 (OCH₂CH₂(CH₂)₇), 29.7 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.3 (O(CH₂)₉CH₃). HRMS-ESI (*m*/z): [M + H]⁺ calcd for C₂₆H₅₃O₄, 429.3944; found 429.3948. GPC: $M_n = 458$, $M_w/M_n = 1.05$.

2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethoxyacetaldehyde (1b). Ozone was bubbled through a chilled solution of **S14** (1.09 g, 1.23 mmol) in anhydrous CH_2CI_2 (17.0 mL) while stirring in a dry ice-acetone bath. The clear reaction mixture turned blue after 25 min. The mixture was quenched with NEt₃ (0.55 mL, 4.0 mmol) and stirred for 7 h at room temperature. The solvent was removed *in vacuo*. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc to 4:1) and yielded **1b** as a colorless oil (0.65 g, 60%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.41$. ¹H NMR (400 MHz, CDCl₃, δ): 9.71 (s, 1H; CHO), 4.00 (s, 2H; CHO(CH₂O), 3.56 (d, J = 5.8 Hz, 2H; OCH₂CH(CH₂O)₂), 3.39 (overlapping m, 24H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.11 (m, 3H; CH₂CH(CH₂O)₂), 1.52 (tt, $J_1 = J_2 = 6.7$ Hz, 8H; OCH₂CH₂(CH₂)₈H), 1.24 (m, overlapped), 1.24 (overlapping s, 56H; (CH₂)₇CH₃), 0.86 (t, J = 6.8 Hz, 24H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 201.6 (CHO), 76.9 (CHO(CH₂O)), 71.6 (CH₂OCH₂), 32.16

 $(OCH_2CH_2(CH_2)_7)$, 32.14 $(OCH_2CH_2(CH_2)_7)$, 29.88 $(OCH_2CH_2(CH_2)_7)$, 29.83 $(OCH_2CH_2(CH_2)_7)$, 29.75 $(OCH_2CH_2(CH_2)_7)$, 29.58 $(OCH_2CH_2(CH_2)_7)$, 29.57 $(OCH_2CH_2(CH_2)_7)$, 26.4 $(OCH_2CH_2(CH_2)_7)$, 22.9 $(OCH_2CH_2(CH_2)_7)$, 14.3 $(O(CH_2)_9CH_3)$. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{54}H_{109}O_8$, 885.8122; found 885.8126. GPC: $M_n = 1,234$, $M_w/M_n = 1.06$.

2,2-Bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethoxyacetaldehyde (8). Ozone was bubbled through a chilled solution of **S15** (0.68 g, 0.38 mmol) in anhydrous CH₂Cl₂ (15.0 mL) while stirring in a dry ice-acetone bath. The clear reaction mixture turned blue after 30 min. The mixture was quenched with NEt₃ (0.15 mL, 1.1 mmol) and stirred for an additional 20 h at room temperature. The solvent was removed *in vacuo*. The product was purified by flash column chromatography (SiO₂; 9:1 hex/EtOAc to 4:1) and yielded **8** as a colorless oil (0.43 g, 63%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.49$. ¹H NMR (500 MHz, CDCl₃, δ): 9.70 (s, 1H; CHO), 4.01 (s, 2H; CHO(CH₂O), 3.55 (d, J = 5.7 Hz, 2H; OCH₂CH(CH₂O)₂), 3.38 (overlapping m, 56H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.10 (m, 7H; CH₂CH(CH₂O)₂), 1.52 (tt, $J_1 = J_2 = 6.9$ Hz, 16H; OCH₂CH₂(CH₂)₈H), 1.24 (m, overlapped), 1.24 (overlapping s, 112H; (CH₂O₇CH₃), 0.86 (t, J = 6.9 Hz, 24H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ): 201.4 (CHO), 77.0 (CHO(CH₂O)), 71.5 (CH₂OCH₂), 69.94 (CHOCH₂OCH₂), 69.71 (CH₂OCH₂), 69.53 (CH₂OCH₂), 69.42 (CH₂OCH₂), 40.58 (CH₂CHCH₂), 40.51 (CH₂CH₂(CH₂)₇), 29.90 (OCH₂CH₂(CH₂)₇), 29.95 (OCH₂CH₂(CH₂)₇), 29.93 (OCH₂CH₂(CH₂)₇), 29.96 (OCH₂CH₂(CH₂)₇), 29.78 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 26.4 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.4 (O(CH₂)₉CH₃). MALDI-TOF (*m*/z): [M + H]⁺ calcd for C₁₁₀H₂₂₁O₁₆, 1799.651 found 1799.969. GPC: $M_n = 2,244, M_w/M_n = 1.08$.

Succinic acid 2,2-bis(decyloxymethyl)ethyl ester (9). Succinic anhydride (0.80 g, 8.0 mmol) and DMAP (0.32 g, 2.6 mmol) was added to a solution of **S5** (1.04 g, 2.69 mmol) in anhydrous CH₂Cl₂ (5.2 mL). The reaction mixture was left to stir for 5 h. The reaction mixture was washed with saturated NaCl (aq), and dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; hex/EtOAc 9:1 to 4:1) and yielded **9** as a colorless oil (1.21 g, 96%). TLC (SiO₂, 1:1 hex/EtOAc): $R_f = 0.34$. ¹H NMR (400 MHz, CDCl₃, $\overline{0}$): 4.16 (d, J = 6.0 Hz, 2H; COOCH₂), 3.39 (overlapping m, 8H; CH₂OCH₂), 2.64 (m, 4H; HO₂CCH₂CH₂), 2.19 (sept, J = 6.0 Hz, 1H; CH₂CH(CH₂O)₂), 1.52 (tt, $J_1 = J_2 = 7.0$ Hz, 4H; OCH₂CH₂(CH₂)₈H), 1.24 (overlapping s, 28H; (CH₂)₇CH₃), 0.86 (t, J = 6.8 Hz, 12H; CH₃). ¹³C NMR (100 MHz, CDCl₃, $\overline{0}$): 172.2 (COO), 71.6 (CH₂OCH₂), 63.9 (CH₂COCH₂), 63.9 (CH₂COCH₂), 39.6 (CH₂CH(CH₂)₂), 32.1 (OCH₂CH₂(CH₂)₇), 29.87 (HO₂CCH₂CH₂CH₂COO), 29.86 (OCH₂CH₂(CH₂)₇), 29.83 (OCH₂CH₂(CH₂)₇), 29.7 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 26.4 (OCH₂CH₂(CH₂)₇), 29.83 (OCH₂CH₂(CH₂)₇), 14.3 (O(CH₂)₉CH₃). HRMS-ESI (*m*/z): [M + H]⁺ calcd for C₂₈H₅₅O₆, 487.400, found 487.400. GPC: $M_n = 570$, $M_w/M_n = 1.04$.

Succinic acid 2,2-bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl ester (2b). Succinic anhydride (0.36 g, 3.6 mmol) and DMAP (0.15 g, 1.2 mmol) was added to a solution of **S7** (1.00 g, 1.19 mmol) in anhydrous CH₂Cl₂ (2.4 mL). The reaction mixture was left to stir for 18 h. The reaction mixture was washed with saturated NaCl (aq), and dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; hex/EtOAc 9:1 to 4:1) and yielded **2b** as a colorless oil (0.92 g, 84%). TLC (SiO₂, 3:2 hex/EtOAc): $R_f = 0.08$. ¹H NMR (400 MHz, CDCl₃, δ): 4.13 (d, J = 5.7 Hz, 2H; COOCH₂), 3.39 (overlapping m, 24H; CH₂OCH₂), 2.60 (s, 4H; HO₂CCH₂CH₂), 2.14 (m, 3H; CH₂CH(CH₂O)₂), 1.53 (tt, $J_1 = J_2 = 6.9$ Hz, 8H; OCH₂CH₂(CH₂)₈H), 1.24 (overlapping s, 56H; (CH₂)₇CH₃), 0.87 (t, J = 6.7 Hz, 12H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 174.1 (COOH), 172.0 (COOCH₂), 71.62 (CH₂OCH₂), 71.60 (CH₂OCH₂), 32.1 (OCH₂CH₂(CH₂)₇), 30.0 (HO₂CCH₂CH₂CO), 29.86 (OCH₂CH₂(CH₂)₇), 29.82 (OCH₂CH₂(CH₂)₇), 29.79 (OCH₂CH₂(CH₂)₇), 29.71 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 26.4 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.3 (O(CH₂)₉CH₃). HRMS-ESI (*m*/z): [M + H]⁺ calcd for C₅₆H₁₁₁O₁₀, 943.8177, found 943.8148. GPC: $M_n = 1.580$, $M_w/M_n = 1.05$.

Succinic acid 2,2-Bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethyl ester (10). Succinic anhydride (0.0923 g, 0.9224 mmol) and DMAP (0.0363 g, 0.2971 mmol) was added to a solution

of **S11** (0.5012 g, 0.2853 mmol) in anhydrous CH₂Cl₂ (0.6 mL). The reaction mixture was left to stir for 22 h. The reaction mixture was washed with saturated NaCl (aq), and dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; hex/EtOAc 95:5 to 4:1) and yielded **10** as a colorless oil (0.3682 g, 69%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.36$. ¹H NMR (400 MHz, CDCl₃, δ): 4.15 (d, J = 5.4 Hz, 2H; COOCH₂), 3.39 (overlapping m, 56H; CH₂OCH₂), 2.58 (s, 4H; HO₂CCH₂CH₂), 2.13 (m, 7H; CH₂CH(CH₂O)₂), 1.53 (tt, $J_1 = J_2 = 7.0$ Hz, 16H; OCH₂CH₂(CH₂)₈H), 1.24 (overlapping s, 112H; (CH₂)₇CH₃), 0.86 (t, J = 6.8 Hz, 24H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 173.3 (COOH), 172.2 (COOCH₂), 71.5 (CH₂OCH₂), 70.0 (CH₂OCH₂), 69.7 (CH₂OCH₂), 69.4 (CH₂OCH₂), 63.1 (CH₂COOCH₂), 40.4 (CH₂CH(CH₂)₂), 40.3 (CH₂CH(CH₂)₂), 32.2 (OCH₂CH₂(CH₂)₇), 29.90 (HO₂CCH₂CH₂CH₂COO), 29.85 (OCH₂CH₂(CH₂)₇), 29.76 (OCH₂CH₂(CH₂)₇), 29.59 (OCH₂CH₂(CH₂)₇), 26.4 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.4 (O(CH₂)₉CH₃). MALDI-TOF (*m*/*z*): [M + Ag]⁺ calcd for C_{11 2}H₂₂₂ O₁₈Na, 1879.639, found 1879.852. GPC: $M_n = 2,510$, $M_w/M_n = 1.06$.

2,2-Bis(benzyloxymethyl)ethyl mesylate (S16). Pyridine (6.0 mL, 74 mmol) and methanesulfonyl chloride (5.6 mL, 72 mmol) was added to a solution of **S6** (4.18 g, 14.6 mmol) in CH₂Cl₂ (58.0 mL). The reaction mixture was stirred at room temperature for 17 h. The reaction mixture was washed twice with 0.6M HCl (aq.) and the combined organic layer was dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; 4:1 hex/EtOAc to 1:1) and yielded **S16** as a colorless oil (4.98 g, 94%). TLC (SiO₂, 3:2 hex/EtOAc): $R_f = 0.56$. ¹H NMR (500 MHz, CDCl₃, δ): 7.31 (m, 10H; Ar*H*), 4.49 (s, 4H; CH₂Ph), 4.36 (d, J = 5.6 Hz, 2H; CH₃SO₃CH₂), 3.55 (m, 4H; CHCH₂O), 2.92 (s, 3H; H₃CSO₃CH₂), 2.40 (sept, J = 6.0 Hz, 1H; CHCH₂OBn). ¹³C NMR (125 MHz, CDCl₃, δ): 138.2 (aromatic C(1)), 128.6 (aromatic C(2) and C(6)), 128.0 (aromatic C(3), C(5)), 127.9 (aromatic C(4)), 73.5 (CH₂Ph), 68.6 (SO₃CH₂), 67.6 (CH₂OCH₂), 40.08 (SO₃CH₂CH), 37.1 (H₃CSO₃). HRMS (*m*/*z*): [M+NH₄]⁺ calcd for C₁₉H₂₈NO₅S, 382.168, found 382.168. GPC: $M_n = 240$, $M_w/M_n = 1.05$.

2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethyl mesylate (S17). Pyridine (1.1 mL, 13 mmol) and methanesulfonyl chloride (1.0 mL, 13 mmol) was added to a solution of **S12** (3.7668 g, 2.7784 mmol) in CH₂Cl₂ (11.0 mL). The reaction mixture was stirred at room temperature for 5 h. The reaction mixture was washed twice with 0.6M HCl (aq.) and the combined organic layer was dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; 3:2 hex/EtOAc) and yielded **S17** as a colorless oil (3.93 g, 98%). TLC (SiO₂, 3:2 hex/EtOAc): $R_f = 0.70$. ¹H NMR (500 MHz, CDCl₃, δ): 7.29 (m, 40H; Ar*H*), 4.46 (s, 16H; CH₂Ph), 4.23 (d, J = 5.3 Hz, 2H; CH₃SO₃CH₂), 3.40 (m, overlapped, 40H; CH₂OCH₂), 2.86 (s, 3H; H₃CSO₃CH₂), 2.22 (sept, J = 5.7 Hz, 5H; SO₃CH₂CH, CHCH₂OBn), 2.07 (septet, J = 5.8 Hz, 2H; CH₂CH(CH₂O)₂). ¹³C NMR (125 MHz, CDCl₃, δ): 138.8 (aromatic C(1)), 128.5 (aromatic C(2) and C(6)), 127.7 (aromatic C(3), C(5), C(4)), 73.3 (CH₂Ph), 69.9 (CH₂OCH₂), 69.8 (CH₂OCH₂), 69.6 (CH₂OCH₂), 69.0 (CH₂OCH₂), 68.5 (SO₃CH₂), 40.76 (CHCH₂OBn), 40.5 (SO₃CH₂CH), 39.9 (CH₂CHCH₂), 37.0 (H₃CSO₃). MALDI-TOF (*m*/z): [M + Ag]⁺ calcd for C₈₅H₁₀₈O₁₇SAg, 1539.636, found 1541.861. GPC: $M_n = 1.350$, $M_w/M_n = 1.05$.

1-Azido-2,2-bis(benzyloxymethyl)ethane (S18). Sodium azide (4.39 g, 67.5 mmol) was added to a solution of dendron **S16** (4.91 g, 13.5 mmol) in DMF (50.0 mL). The reaction mixture was stirred at 125 °C for 16.5 h. The solids were removed by filtration and volatiles were removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; 4:1 hex/EtOAc to 7:3) and yielded **S18** as a colorless oil (3.70 g, 88%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.62$. ¹H NMR (500 MHz, CDCl₃, δ): 7.30 (m, 10H; Ar-*H*), 4.49 (s, 4H; *CH*₂Ph), 3.12 (overlapping m, 6H; *CH*₂OBn, N₃*CH*₂), 2.21 (sept, *J* = 6.0 Hz, 1H; *CH*CH₂OBn). ¹³C NMR (125 MHz, CDCl₃, δ): 138.5 (aromatic *C*(1)), 128.6 (aromatic *C*(2) and *C*(6)), 127.8 (aromatic *C*(3), *C*(5), *C*(4)), 73.5 (*CH*₂Ph), 68.8 (*CH*₂OBn), 50.7 (*CH*₂N₃), 40.4 (N₃CH₂C*H*). HRMS (*m/z*): [M-2N+H]⁺ calcd for C₁₈H₂₂NO₂, 284.165, found 284.165. GPC: $M_n = 170$, $M_w/M_n = 1.05$.

1-Azido-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (S19). Sodium azide (0.92 g, 14 mmol) was added to a solution of dendron **S17** (3.91 g, 2.73 mmol) in DMF (11.0 mL). The reaction mixture was stirred at 125 °C for 3 h. The solids were removed by filtration and volatiles were removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂;

4:1 hex/EtOAc) and yielded **S19** as a colorless oil (2.91 g, 77%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.26$. ¹H NMR (500 MHz, CDCl₃, δ): 7.29 (m, 40H; Ar-*H*), 4.47 (s, 16H; C*H*₂Ph), 3.53 (d, *J* = 5.9 Hz, 16H; C*H*₂OCH₂Bn), 3.46 (d, *J* = 6.0 Hz, 8H; C*H*₂CH(CH₂OCH₂Bn)₂), 3.31 (overlapping m, 18H; C*H*₂OC*H*₂, C*H*₂N₃), 2.23 (sept, *J* = 5.9 Hz, 4H; C*H*CH₂OBn), 2.07 (sept, *J* = 6.0 Hz, 3H; N₃CH₂C*H*, CH₂C*H*(CH₂O)₂). ¹³C NMR (125 MHz, CDCl₃, δ): 138.8 (aromatic C(1)), 128.5 (aromatic C(2) and C(6)), 127.7 (aromatic C(3), C(5), C(4)), 73.3 (CH₂Ph), 69.9 (CH₂OCH₂), 69.8 (CH₂OCH₂), 69.7 (CH₂OCH₂), 69.6 (CH₂OCH₂), 69.0 (CH₂OCH₂), 50.5 (CH₂N₃), 40.7 (C*H*CH₂OBn), 40.5 (N₃CH₂C*H*), 40.2 (CH₂CHCH₂). MALDI-TOF (*m*/*z*): [M-N₂ + Ag]⁺ calcd for C₈₄H₁₀₅NO₁₄Ag, 1458.659, found 1458.915. GPC: *M*_n = 1,288, *M*_w/*M*_n = 1.04.

1-Formamido-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (S23). To a solution of dendron S19 (2.87 g, 3.30 mmol) in THF/H₂O (13.0 mL/0.3 mL), PPh₃ (1.35 g, 5.15 mmol) was added. The reaction mixture was stirred at room temperature for 3.5 h. The solvent was removed in vacuo. The product was purified by flash column chromatography (SiO₂; Step-wise elution: EtOAc, followed by 95:5 CHCl₃/MeOH washed in NH₄OH) and yielded S21 as a colorless oil with trace amount of triphenylphosphine oxide (0.82 g). TLC (SiO₂, 95:5 CHCl₃ washed in NH₄OH/MeOH): R_{f} = 0.62. Propyl formate (0.20 mL, 2.1 mmol) and K₂CO₃ (0.14 g, 1.0 mmol) was added to S21 (0.82 g). The reaction mixture was stirred at reflux for 6 h. The solvent was removed in vacuo. The product was purified by flash column chromatography (SiO₂: 95:5 CH₂Cl₂/MeOH) and vielded S23 as a colorless oil (0.67 g, 15% over two-steps). TLC (SiO₂, 95:5 CH₂Cl₂/MeOH): R_f = 0.41. ¹H NMR (500 MHz, CDCl₃, δ): 8.01 (s, 1H; CHO), 7.30 (m, 40H; Ar-H), 6.39 (broad s, 1H; NH), 4.47 (s, 16H; CH₂Ph), 3.53 (d, J = 5.6 Hz, 16H; CH₂OCH₂Bn), 3.46 (d, J = 5.8 Hz, 8H; CH₂CH(CH₂OCH₂Bn)₂), 3.33 (m, 16H; CH₂OCH₂), 3.22 (t, J = 7.4 Hz, 2H; HC(=O)NHCH₂), 2.23 (sept, J = 5.6 Hz, 4H; CHCH₂OBn), 2.08 (sept, J = 5.8 Hz, 2H; $CH_2CH(CH_2O)_2$, 2.01 (sept, J = 5.9 Hz, 2H; HC(=O)NHCH₂CH). ¹³C NMR (125 MHz, CDCl₃, δ): 161.3 (NHCHO), 138.8 (aromatic C(1)), 128.5 (aromatic C(2) and C(6)), 127.7 (aromatic C(3), C(5), C(4)), 73.3 (CH₂Ph), 71.6 (HC(=O)NHCH₂O), 71.1 (CH₂OCH₂), 69.79 (CH₂OCH₂), 69.77 (CH₂OCH₂), 69.75 (CH₂OCH₂), 69.0 (CH₂OCH₂), 68.99 (CH₂OCH₂), 40.6 (CHCH₂OBn), 40.4 (CH₂CHCH₂), 39.4 (CH₂CHCH₂), 39.2 (HC(=O)NHCH₂CH). MALDI-TOF (*m*/*z*): [M + Ag]⁺ calcd for C₈₅H₁₀₇NO₁₅Ag, 1488.669, found 1488.627. GPC: $M_{\rm p}$ = 1,273, $M_{\rm w}/M_{\rm p}$ = 1.05.

1-Isocyano-2,2-bis(benzyloxymethyl)ethane (11). To a solution of dendron S18 (3.65 g, 11.7 mmol) in THF/H₂O (46 mL/1 mL), PPh₃ (4.61 g, 17.6 mmol) was added. The reaction mixture was stirred at room temperature for 22 h. The reaction mixture was separated and the aqueous layer was washed twice with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate in vacuo. Propyl formate (3.4 mL, 35 mmol) and K₂CO₃ (2.54 g, 18.4 mmol) was added to dendron **S20**. The reaction mixture was stirred at reflux for 22 h. The solids were removed by filtration and the solvent was removed in vacuo. The product was purified by flash column chromatography (SiO₂; 1:1 hex/EtOAc to EtOAc) and yielded S22 as a colorless oil with trace amount of triphenylphosphine oxide (6.44 g). TLC (SiO₂, 95:5 CH₂Cl₂/MeOH): R_f = 0.30. Dendron S22 was used as it is in the next step. Triethylamine (5.0 mL, 36 mmol), CCl₄ (6.0 mL, 35 mmol), and PPh₃ (9.39 g, 35.7 mmol) was added to a solution of dendron S22 in CH₂Cl₂ (24.0 mL). The reaction mixture was stirred at reflux for 21 h. The solvent was removed in vacuo. The product was purified by flash column chromatography (SiO₂; 4:1 hex/EtOAc to EtOAc) and yielded **11** as a yellow oil (0.6646 g, 19% over three-steps). TLC (SiO₂, 4:1 hex/EtOAc): $R_{\rm f}$ = 0.51. ¹H NMR (500 MHz, CDCl₃, δ): 7.31 (m, 10H; Ar-H), 4.50 (s, 4H; CH₂Ph), 3.56 (overlapping m, 6H; CH₂OBn, CNCH₂CH), 2.30 (broad sept, 1H; CHCH₂OBn). ¹³C NMR (125 MHz, CDCl₃, δ): 156.96 (CN), 138.1 (aromatic C(1)), 128.7 (aromatic C(2) and C(6)), 127.9 (aromatic C(3), C(5), C(4)), 73.6 (CH₂Ph), 67.9 (CH₂OCH₂), 40.8 (CNCH₂CH), 39.7 $(CNCH_2CH)$. HRMS (m/z): $[M]^+$ calcd for $C_{19}H_{22}NO_2$, 296.165, found 296.165. GPC: $M_n = 180$, $M_w/M_n = 180$, $M_w/M_m = 180$, 1.07.

1-Isocyano-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (12). Triethylamine (0.20 mL, 1.4 mmol), CCl₄ (0.25 mL, 1.5 mmol), and PPh₃ (0.38 g, 1.4 mmol) was added to a solution of dendron **S23** (0.66 g, 0.48 mmol) in CH₂Cl₂ (1.0 mL). The reaction mixture was stirred at reflux for 4 h. The solvent was removed *in vacuo*. The product was purified by flash column chromatography (SiO₂; 2:3 hex/EtOAc to EtOAc) and yielded **12** as a yellow oil (0.55 g, 85%). TLC (SiO₂, 3:2 hex/EtOAc): $R_f = 0.63$. ¹H NMR (400 MHz, CDCl₃, δ): 7.30 (m, 40H; Ar-H), 4.47 (s, 16H; CH₂Ph), 3.53 (d, J = 5.8 Hz, 16H; CH₂OCH₂Bn), 3.46 (d, J = 6.0 Hz, 8H; CH₂CH(CH₂OCH₂Bn)₂), 3.36 (d, J = 6.0 Hz, 8H; CH₂CH(CH₂OCH₂Bn)₂), 3.36 (d, J = 6.0 Hz, 8H; CH₂CH(CH₂OCH₂Bn)₂), 3.26 (d, J = 6.0 Hz, 8H; CH₂CH(CH₂OCH₂Bn)₂), 3.36 (d, J

16H; CH_2OCH_2), 3.27 (overlapped t, 2H; $CNCH_2$), 2.23 (sept, J = 5.6 Hz, 4H; $CHCH_2OBn$), 2.08 (sept, J = 5.8 Hz, 3H; $CH_2CH(CH_2O)_2$, $CNCH_2CH$). ¹³C NMR (100 MHz, $CDCI_3$, δ): 138.8 (aromatic C(1)), 128.5 (aromatic C(2) and C(6)), 127.7 (aromatic C(3), C(5), C(4)), 73.3 (CH_2Ph), 70.0 (CH_2OCH_2), 69.8 (CH_2OCH_2), 69.6 (CH_2OCH_2), 69.0 (CH_2OCH_2), 68.7 ($CNCH_2CHCH_2O$), 40.7 ($CHCH_2OBn$), 40.5 ($CNCH_2CH$), 39.5 ($CNCH_2CH$). MALDI-TOF (m/z): [M+Ag]⁺ calcd for $C_{85}H_{106}NO_{14}Ag$, 1471.666, found 1471.675. GPC: $M_n = 1,416$, $M_w/M_n = 1.05$.

N-Formyl-[2-(2,2-bis(decyloxymethyl)ethoxy)carbonylethyl]amine (S26). Propyl formate (0.40 mL, 4.1 mmol) and K₂CO₃ (0.32 g, 2.3 mmol) was added to **S24** (1.00 g, 2.18 mmol) and stirred at reflux for 21 h. The solids were removed by filtration and washed with CH₂Cl₂. The solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; CH₂Cl₂/MeOH 98:2 to 95:5) and yielded **S26** as a colorless oil (0.68 g, 68%). TLC (SiO₂, 95:5 CH₂Cl₂/MeOH): $R_{\rm f}$ = 0.45. ¹H NMR (400MHz, CDCl₃, δ): 8.12 (s, 1H; CHO),6.31 (broad s, 1H; NH), 4.17 (d, *J* = 5.9 Hz, 2H; COOCH₂CH), 3.55 (q, *J* = 6.0 Hz, 2H; NHCH₂CH₂), 3.82 (overlapping m, 8H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.54 (t, *J* = 5.86 Hz, 2H; NHCH₂CH₂), 2.19 (sept, *J* = 5.9 Hz, 1H; CH₂CH(CH₂O)₂), 1.52 (tt, *J*₁ = *J*₂ = 6.6 Hz, 4H; OCH₂CH₂(CH₂)₈H), 1.24 (overlapping s, 28H; (CH₂)₇CH₃), 0.86 (t, *J* = 6.9 Hz, 6H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 172.5 (COOCH₂), 161.2 (NHCHO), 71.7 (CH₂OCH₂), 69.2 (CH₂OCH₂), 64.1 (COOCH₂CH), 39.6 (CH₂CHCH₂), 34.2 (HNCH₂CH₂COO), 33.6 (HNCH₂CH₂), 32.1 (OCH₂CH₂(CH₂)₇), 29.83 (OCH₂CH₂(CH₂)₇), 29.81 (OCH₂CH₂(CH₂)₇), 29.7 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 26.4 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.3 (O(CH₂)₉CH₃). ESI-MS (*m*/z): [M + H]⁺ calcd for C₂₈H₅₉ N₂O₅, 503.4, found 503.4. GPC: M_n = 580, M_w/M_n = 1.04.

N-Formyl-[2-(2,2-bis(2,2-di(decyloxymethyl)ethoxymethyl)ethoxy)carbonylethyl]amine (S27). Propyl formate (0.16 mL, 1.7 mmol) and K₂CO₃ (0.15 g, 1.1 mmol) was added to **25** (0.84 g, 0.92 mmol. The reaction mixture was stirred at reflux for 41 h. The solids were removed by filtration and washed with CH₂Cl₂. The solvent was removed from the filtrate *in vacuo*. The product was purified by flash column chromatography (SiO₂; hex/EtOAc 9:1 to 4:1) and yielded **S27** as a colorless oil (0.56 g, 64%). TLC (SiO₂, 95:5 CH₂Cl₂/MeOH): $R_{\rm f}$ = 0.38. ¹H NMR (400MHz, CDCl₃, δ): 8.12 (s, 1H; CHO), 6.36 (broad s, 1H; NH), 4.16 (d, *J* = 5.9 Hz, 2H; COOCH₂CH), 3.55 (q, *J* = 6.0 Hz, 2H; NHCH₂CH₂), 3.38 (overlapping m, 24H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.54 (t, *J* = 5.79 Hz, 2H; NHCH₂CH₂), 2.19 (m, 1H; COOCH₂CH(CH₂O)₂), 2.09 (m, 2H; CH₂CH(CH₂O)₂), 1.52 (tt, *J*₁ = *J*₂ = 6.9 Hz, 8H; OCH₂CH₂(CH₂)₈H), 1.24 (overlapping s, 56H; (CH₂)₇CH₃), 0.86 (t, *J* = 6.8 Hz, 12H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 172.5 (COOCH₂), 161.3 (NHCHO), 71.6 (CH₂OCH₂), 70.0 (CH₂OCH₂), 69.3 (CH₂OCH₂), 69.28 (CH₂OCH₂), 63.6 (COOCH₂CH), 40.5 (CH₂CHCH₂), 39.5 (CH₂CHCH₂), 34.2 (HNCH₂CH₂COO), 33.7 (HNCH₂CH₂), 32.1 (OCH₂CH₂(CH₂)₇), 29.9 (OCH₂CH₂(CH₂)₇), 29.88 (OCH₂CH₂(CH₂)₇), 29.84 (OCH₂CH₂(CH₂)₇), 29.75 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 29.9 (OCH₂CH₂(CH₂)₇), 20.9 (OCH₂CH₂(CH₂)₇), 20.9 (S9.9 (S9.9, 959.9, found 959.8. GPC: *M*₀ = 1,260, *M*_w/*M*₀ = 1.05.

2-(2,2-Bis(decyloxymethyl)ethoxy)carbonylethylisocyanide (S1). To a solution of dendron **S26** (0.68 g, 1.4 mmol) in CH₂Cl₂ (1.8 mL), NEt₃ (0.60 mL, 4.3 mmol), CCl₄ (0.70 mL, 4.1 mmol), and PPh₃ (0.75 g, 2.9 mmol) were added. The reaction mixture was stirred at reflux for 15 h. The solvent was removed *in vacuo*. The product was purified by flash column chromatography (SiO₂; CH₂Cl₂ to 95:5 CH₂Cl₂/MeOH) and yielded **S1** as a yellow oil (0.41 g, 61%). TLC (SiO₂, CH₂Cl₂): $R_f = 0.15$. ¹H NMR (400MHz, CDCl₃, δ): 4.21 (d, J = 6.0 Hz, 2H; COOCH₂), 3.67 (t, J = 6.9 Hz, 2H; CNCH₂), 3.40 (overlapping m, 8H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.72 (t, J = 6.8 Hz, 2H; CNCH₂CH₂), 2.21 (sept, J = 5.9 Hz, 1H; COOCH₂CH(CH₂O)₂), 1.52 (m, 4H; OCH₂CH₂(CH₂)₈H), 1.24 (overlapping s, 28H; (CH₂)₇CH₃), 0.86 (t, J = 6.8 Hz, 6H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 169.8 (COOCH₂), 72.0 (CH₂OCH₂), 69.2 (CH₂OCH₂), 64.7 (CH₂OCH₂), 39.9 (CH₂CH(CH₂)₂), 37.6 (CNCH₂CH₂), 34.7 (CNCH₂CH₂), 30.2 (OCH₂CH₂(CH₂)₇), 30.0 (OCH₂CH₂(CH₂)₇), 29.9 (OCH₂CH₂(CH₂)₇), 26.7 (OCH₂CH₂(CH₂)₇), 23.2 (OCH₂CH₂(CH₂)₇), 14.7 (O(CH₂)₉CH₃). HRMS–ESI (*m*/z): [M]⁺ calcd for C₂₈H₅₄NO₄, 468.4053, found 468.4048. GPC: $M_n = 590$, $M_w/M_n = 1.04$.

2-(2,2-Bis(2,2-di(decyloxymethyl)ethoxymethyl)ethoxy)carbonylethylisocyanide (3b). To a solution of dendron **S27** (0.50 g, 0.53 mmol) in CH_2Cl_2 (1.2 mL), NEt₃ (0.33 mL, 2.4 mmol), CCl_4 (0.40 mL, 2.4 mmol), and PPh₃ (0.55 g, 2.1 mmol) were added. The reaction mixture was stirred at reflux for 47 h. The solvent was removed *in vacuo*. The product was purified by flash column chromatography (SiO₂; hex/EtOAc 95:5 to 4:1) and yielded **3b** as a yellow oil (0.41 g, 83%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f =$

0.57. ¹H NMR (500MHz, CDCl₃, δ): 4.18 (d, *J* = 6.0 Hz, 2H; COOCH₂), 3.66 (t, *J* = 7.0 Hz, 2H; CNCH₂), 3.38 (overlapping m, 24H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.71 (t, *J* = 7.0 Hz, 2H; CNCH₂CH₂), 2.20 (m, 1H; COOCH₂CH(CH₂O)₂), 2.10 (m, 1H; CH₂CH(CH₂O)₂), 1.52 (m, 8H; OCH₂CH₂(CH₂)₈H), 1.24 (overlapping s, 56H; (CH₂)₇CH₃), 0.86 (t, *J* = 6.7 Hz, 12H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ): 169.5 (COOCH₂), 71.6 (CH₂OCH₂), 70.0 (CH₂OCH₂), 69.4 (CH₂OCH₂), 64.2 (COOCH₂), 40.6 (CH₂CH(CH₂)₂), 39.5 (CH₂CH(CH₂)₂), 37.3 (CNCH₂), 34.4 (CNCH₂CH₂), 32.1 (OCH₂CH₂(CH₂)₇), 29.9 (OCH₂CH₂(CH₂)₇), 29.88 (OCH₂CH₂(CH₂)₇), 29.84 (OCH₂CH₂(CH₂)₇), 29.75 (OCH₂CH₂(CH₂)₇), 29.65 (OCH₂CH₂(CH₂)₇), 29.57 (OCH₂CH₂(CH₂)₇), 26.4 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.3 (O(CH₂)₉CH₃). HRMS-ESI (*m*/*z*): [M]⁺ calcd for C₅₆H₁₁₄ N₂O₈, 924.8231, found 942.8235. GPC: *M*_n = 1,360, *M*_w/*M*_n = 1.05.

2,2-Bis(decyloxymethyl)ethyl 4-pentenoate (S28). A solution of S5 (1.00 g, 2.59 mmol), pentenoic acid (0.30 mL, 2.9 mmol), in anhydrous CH₂Cl₂ (5.0 mL) was stirred at room temperature for ~5 mins. To the solution, DCC (0.65 g, 3.2 mmol) and DPTS (0.0870 g, 0.278 mmol) were added as solids. The reaction mixture was stirred for 21 h at room temperature. A precipitate was observed to form during the reaction, and the solids were removed by filtration. Volatiles were removed from the filtrate in vacuo. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc to 9:1) and yielded S28 as a colorless oil (1.06 g, 88%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.77$. ¹H NMR (400MHz, CDCl₃, δ): 5.80 (pent, J = 5.6 Hz, 1H; $HC=CH_2$), 5.01 (dd, $J_1 = J_2 = 4.4$ Hz, 2H; $H_2C=CH$), 4.13 (d, J = 6.0 Hz, 2H; CO_2CH_2CH), 3.40 (m, 8H; $OCH_2CH(CH_2O)_2$), 2.37 (m, 4H; $CHCH_2CH_2CO_2$), 2.19 (sept, J = 6.0 Hz, 1H; $CH_2CH(CH_2O)_2)$, 1.52 (tt, $J_1 = J_2 = 6.9$ Hz, 4H; $OCH_2CH_2(CH_2)_8H)$, 1.24 (m, overlapped), 1.24 (overlapping s, 28H; $(CH_2)_7CH_3$), 0.86 (t, J = 6.9 Hz, 6H; CH_3). ¹³C NMR (100 MHz, CDCl₃, δ): 173.2 (CO₂CH₂), 137.0 (H₂C=CHCH₂), 115.7 (H₂C=C), 71.6 (H₂C=CHCH₂O), 69.0 (CH₂OCH₂), 63.4 (CH₂OCH₂), 39.7 (CH₂CHCH₂), 33.8 (CHCH₂CH₂CO₂), 32.1 (OCH₂CH₂(CH₂)₇), 29.88 (OCH₂CH₂(CH₂)₇), 29.86 (OCH₂CH₂(CH₂)₇), 29.82 (OCH₂CH₂(CH₂)₇), 29.7 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.3 (O(CH₂)₉CH₃). ESI-MS (*m*/*z*): [M + H]⁺ calcd for C₂₉H₅₇O₄, 469.4; found 469.4. GPC: $M_n = 532$, $M_w/M_n = 1.04$.

2,2-Bis((2,2-di[decyloxymethyl]ethoxymethyl)ethyl 4-pentenoate (S29). A solution of S7 (0.91 q. 1.1 mmol), pentenoic acid (0.15 mL, 1.5 mmol), in anhydrous CH₂Cl₂ (2.2 mL) was stirred at room temperature for ~5 mins. To the solution, DCC (0.27 g, 1.3 mmol) and DPTS (0.0401 g, 0.128 mmol) were added as solids. The reaction mixture was stirred for 48 h at room temperature. A precipitate was observed to form during the reaction, and the solids were removed by filtration. Volatiles were removed from the filtrate in vacuo. The product was purified by flash column chromatography (SiO₂; 9:1 hex/EtOAc to 4:1) and yielded **S29** as a colorless oil (0.96 g, 96%). TLC (SiO₂, 4:1 hex/EtOAc): R_f = 0.56. ¹H NMR (400MHz, CDCl₃, δ): 5.79 (pent, J = 6.3 Hz, 1H; HC=CH₂), 5.14 (dd, J₁ = J₂ = 14.0 Hz, 2H; H₂C=CH), 4.11 (d, J = 6.0 Hz, 2H; CO_2CH_2CH), 3.39 (m, 24H; CH_2OCH_2), 2.37 (m, 4H; $H_2C=CHCH_2CH_2$), 2.18 (sept, J = 5.9 Hz, 1H; CH₂CH(CH₂O)₂),), 2.10 (sept, J = 5.9 Hz, 2H; CH₂CH(CH₂O)₂), 1.52 (tt, $J_1 = J_2 =$ 6.8 Hz, 4H; OCH₂CH₂(CH₂)₈H), 1.24 (m, overlapped), 1.24 (overlapping s, 56H; (CH₂)₇CH₃), 0.86 (t, J = 6.9 Hz, 12H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 173.1 (CO₂CH₂), 136.9 (H₂C=CHCH₂), 115.7 (H₂C=C), 71.5 (H₂C=CHCH₂O), 69.9 (CH₂OCH₂), 69.4 (CH₂OCH₂), 69.3 (CH₂OCH₂), 63.2 (COOCH₂), 40.6 (CH₂CHCH₂), 39.5 (CH₂CHCH₂), 32.1 (CHCH₂CH₂CO₂), 29.9 (OCH₂CH₂(CH₂)₇), 29.88 (OCH₂CH₂(CH₂)₇), 29.84 (OCH₂CH₂(CH₂)₇), 29.75 (OCH₂CH₂(CH₂)₇), 29.6 (OCH₂CH₂(CH₂)₇), 29.1 (CHCH₂CH₂CO₂), 26.4 $(OCH_2CH_2(CH_2)_7)$, 22.9 $(OCH_2CH_2(CH_2)_7)$, 14.3 $(O(CH_2)_9CH_3)$. MALDI-TOF (m/z): $[M + Ag]^+$ calcd for $C_{57}H_{112}O_8K$, 963.799; found 964.702. GPC: $M_n = 1,330$, $M_w/M_n = 1.04$.

2,2-Bis(decyloxymethyl)ethyl 4-oxobutanoate (S3). Ozone was bubbled through a chilled solution of **S28** (0.80 g, 1.7 mmol) in anhydrous CH_2CI_2 (45.0 mL) while stirring in a dry ice-acetone bath. The clear reaction mixture turned blue after 2 h. The mixture was quenched with NEt₃ (0.52 mL, 3.7 mmol) and stirred for an additional 18 h at room temperature. The solvent was removed *in vacuo*. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc to 4:1) and yielded **S3** as a colorless oil (0.77 g, 97%). TLC (SiO₂, 4:1 hex/EtOAc): $R_f = 0.45$. ¹H NMR (400 MHz, CDCl₃, δ): 9.79 (s, 1H; CHO), 4.15 (d, J = 6.0 Hz, 2H; OCH₂CH(CH₂O)₂), 3.38 (overlapping m, 8H; CH₂OCH₂, OCH₂(CH₂)₉H), 2.77 (t, J = 6.6 Hz, 2H; CO₂CH₂CH₂CHO), 2.61 (t, J = 6.7 Hz, 2H; CO₂CH₂CH₂CHO), 2.19 (sept, J = 6.0 Hz, 1H; CH₂CH(CH₂O)₂), 1.52 (tt, $J_1 = J_2 = 6.8$ Hz, 4H; OCH₂CH₂(CH₂)₈H), 1.24 (m, overlapped), 1.24 (overlapping s, 28H; (CH₂)₇CH₃), 0.86 (t, J = 6.9 Hz, 6H; CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 200.1 (CHO), 172.4 (CO₂(CH₂)₂), 71.6 (CH₂OCH₂), 69.0 (CH₂OCH₂), 63.8 (CH₂OCH₂), 39.6 (CH₂CHCH₂), 38.9

 $(HC(=O)CH_2CH_2CO_2)$, 29.87 $(OCH_2CH_2(CH_2)_7)$, 29.85 $(OCH_2CH_2(CH_2)_7)$, 29.82 $(OCH_2CH_2(CH_2)_7)$, 29.6 $(OCH_2CH_2(CH_2)_7)$, 26.8 $(OCH_2CH_2(CH_2)_7)$, 26.4 $(OCH_2CH_2(CH_2)_7)$, 22.9 $(OCH_2CH_2(CH_2)_7)$, 14.3 $(O(CH_2)_9CH_3)$. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{28}H_{55}O_5$, 471.4049; found 471.4049. GPC: $M_n = 520$, $M_w/M_n = 1.05$.

2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl 4-oxobutanoate (1c). Ozone was bubbled through a chilled solution of **S29** (0.7116 g. 0.7689 mmol) in anhydrous CH₂Cl₂ (20.0 mL) while stirring in a dry ice-acetone bath. The clear reaction mixture turned blue after 2 h. The mixture was guenched with NEt₃ (0.22 mL, 1.6 mmol) and stirred for an additional 17 h at room temperature. The solvent was removed in vacuo. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc to 4:1) and yielded **1c** as a colorless oil (0.4950 g, 69%). TLC (SiO₂, 4:1 hex/EtOAc): $R_{f} = 0.48$. ¹H NMR (500 MHz, CDCl₃, δ): 9.79 (s, 1H; CHO), 4.12 (d, J = 6.1 Hz, 2H; OCH₂CH(CH₂O)₂), 3.38 (overlapping m, 24H; CH_2OCH_2 , $OCH_2(CH_2)_9H$), 2.77 (t, J = 6.6 Hz, 2H; $OC(=O)CH_2CH_2CHO$), 2.61 (t, J = 6.7 Hz, 2H; $OC(=O)CH_2CH_2CHO)$, 2.14 (sept, J = 6.0 Hz, 3H; $CH_2CH(CH_2O)_2$), 1.52 (tt, $J_1 = J_2 = 6.8$ Hz, 8H; OCH₂CH₂(CH₂)₈H), 1.24 (m, overlapped), 1.24 (overlapping s, 56H; (CH₂)₇CH₃), 0.86 (t, J = 6.9 Hz, 12H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ): 200.1 (CHO), 172.3 (CO₂(CH₂)₂), 71.5 (CH₂OCH₂), 70.0 (CH₂OCH₂), 69.4 (CH₂OCH₂), 69.2 (CH₂OCH₂), 63.7 (CH₂OCH₂), 40.5 (CH₂CHCH₂), 39.5 (CH₂CHCH₂), 38.8 (HC(=O)CH₂CH₂CO₂), 29.9 (OCH₂CH₂(CH₂)₇), 29.89 (OCH₂CH₂(CH₂)₇), 29.84 (OCH₂CH₂(CH₂)₇), 29.76 (OCH₂CH₂(CH₂)₇), 29.6 (HC(=O)CH₂CH₂CO₂), 26.4 (OCH₂CH₂(CH₂)₇), 22.9 (OCH₂CH₂(CH₂)₇), 14.4 (O(CH₂)₉CH₃). HRMS-ESI (m/z): [M + H]⁺ calcd for C₅₆H₁₁₁O₉, 927.8228; found 927.8193. GPC: M_n = $1,205, M_w/M_n = 1.06.$

Dendrimer 4b. A mixture of 1b (0.0502 g, 0.0567 mmol), 2a (0.0493 g, 0.0575 mmol), and 3a (0.0377 g, 0.0577 mmol) was gently agitated for 24 h at ambient temperature. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc to 1:1). The dendrimer product containing trace amounts of 2a and 3a was gently agitated with 0.2M HCl in 1:1 CH₂Cl₂/MeOH (1 mL) for 1 h at ambient temperature. The reaction mixture was separated and the aqueous layer was washed three times with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄. The solids were removed by filtration and the solvent was removed from the filtrate in vacuo. The product was purified by flash column chromatography (SiO₂; 95:5 hex/EtOAc to 1:1), then repeated with (SiO₂; CHCl₃ washed in NH₄OH) to vield **4b** as a colorless oil (0.0664 g, 49%), TLC (SiO₂, 4:1 hex:EtOAc); $R_{\rm f}$ = 0.29. ¹H NMR (500 MHz, CCl₄, δ): 7.27 (m, 20H; ArH), 6.82 (t, J = 5.9 Hz, 1H, NHC(=O)), 5.30 (t, J = 4.3 Hz, 1H; NH(O=)CCH), 4.49 (s, 8H; OCH₂Ph), 3.74 (m, 4H; OC(=O)CH(CH₂O)₂), 3.68 (m, 2H, CHCH₂OCH₂CH(O)(C=O)), 3.53-3.27 (m, 64H; CH₂OCH₂, CHCH₂OCH₂CH(O)(C=O)), 3.23 (m, 2H, (C=O)NHCH₂), 3.01 (pent, J = 6.2 Hz, 1H; OC(=O)CH(CH₂O)₂), 2.23 (sept, J = 5.9 Hz, 2H; CH₂CH(CH₂OBn)₂), 2.10 (sept, J = 5.8 Hz, 5H; $HN(O=)CCH_2CH$, $CH(CH_2OC_{10}H_{21})_2$), 1.99 (sept, J = 6.2 Hz, 1H, $HCCH_2OCH_2CH(O)(C=O)$), 1.53 (m, 16H; OCH₂CH₂(CH₂)₇CH₃), 1.26 (m, 112H; OCH₂CH₂(CH₂)₇CH₃), 0.88 (t, J = 6.9 Hz, 24H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ): 171.1 (O₂CCH), 167.9 (C(=O)NH), 138.8 (aromatic C(1)), 128.5 (aromatic C(2) and C(6)), 127.7 (aromatic C(3) and C(5), (aromatic C(4)), 73.3 (OCH₂Ph, CH₂CH(O)(C=O)), 71.6 $(CH_2OCH_2),$ (CH_2OCH_2) , 71.5 70.8 $(C(=O)NHCH_2),$ 70.5 $(CH_2OCH_2CH(O)(C=O)),$ 70.4 (CH₂OCH₂CH(O)(C=O)), 70.3 (CH₂OCH₂), 70.2 (CH₂OCH₂), 70.0 (CH₂OCH₂), 69.98 (CH₂OCH₂), 69.95 (CH₂OCH₂), 69.5 (CH₂OCH₂), 69.4 (CH₂OCH₂), 69.2 (CH₂OCH₂), 69.1 (CH₂OCH₂), 69.08 (CH₂OCH₂), 69.00 (CH2OCH2), 68.9 (CH2OCH2), 68.5 (CH2OCH2), 46.5 (O2CCH), 40.64 (CH(CH2OBN2), 40.63 (CH(CH₂OBn)₂), 40.60 (C(=O)HNCH₂CH), 40.5 (CH(CH₂OC₁₀H₂₁)₂), 40.4 (CH(CH₂OC₁₀H₂₁)₂), 40.1 (HCCH₂OCH₂CH(O)(C=O)), $(CH(CH_2OC_{10}H_{21})_2),$ 39.3 32.2 $(OCH_2CH_2(CH_2)_7CH_3)$, 30.0 (OCH₂(CH₂)₈CH₃), 29.9 (OCH₂(CH₂)₈CH₃), 29.87 (OCH₂(CH₂)₈CH₃), 29.80 (OCH₂(CH₂)₈CH₃), 29.6 (OCH₂(CH₂)₈CH₃), 26.5 (OCH₂CH₂(CH₂)₇CH₃), 22.9 (OCH₂CH₂(CH₂)₇CH₃), 14.4 (O(CH₂)₉CH₃). MALDI-TOF (m/z): $[M + Ag]^+$ calcd for C₁₄₇H₂₆₁NO₂₂Ag, 2500.842; found 2501.821. Anal. Calcd for C₁₄₇H₂₆₁NO₂₂: C, 73.73; H, 10.99; N, 0.58. Found: C, 74.00; H, 10.79; N, 0.76. GPC: M_n = 2,790, M_w/M_n = 1.04.

Dendrimer 4c. A mixture of **1b** (0.0497 g, 0.0561 mmol), **2b** (0.0537 g, 0.0569 mmol), and **3a** (0.0381 g, 0.0584 mmol) in anhydrous THF (56 μ L) was gently agitated for 24 h at ambient temperature. The product was purified by flash column chromatography (SiO₂; 95:5 hex:EtOAc to 1:1). The dendrimer product containing traces of **3a** was gently agitated with 0.2M HCl in 1:1 CH₂Cl₂/MeOH (1 mL) for 30 min at ambient temperature. The reaction mixture was separated and the aqueous layer was washed three times with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄. The solids were

removed by filtration and the solvent was removed from the filtrate in vacuo. The product was purified by flash column chromatography (SiO₂; 95:5 hex: EtOAc to 4:1) to yield **4c** as a colorless oil (0.0721 g, 52%). TLC (SiO₂, 4:1 hex:EtOAc): $R_f = 0.25$. ¹H NMR (500 MHz, CDCl₃, δ): 7.29 (m, 20H; ArH), 6.78 (t, J = 5.8 Hz, 1H, NHC(=O)), 5.27 (t, J = 4.7 Hz, 1H; NH(O=)CCH), 4.47 (s, 8H; OCH₂Ph), 4.10 (d, J = 6.1 Hz, 2H; CO₂CH₂CH), 3.74 (d, J = 4.7 Hz, 2H; CHCH₂OCH₂CH(O)(C=O)), 3.54-3.33 (m, 68H; CH₂OCH₂, $C(=O)NHCH_2$, $CHCH_2OCH_2CH(O)(C=O)$), 2.60 (m, 4H; $C(=O)CH_2CH_2(C=O)$), 2.23 (sept, J = 5.9 Hz, 2H; $CH(CH_2OBn)_2$, 2.18 (sept, J = 6.0 Hz, 1H; $HN(O=)CCH_2CH$), 2.11 (sept, J = 5.8 Hz, 5H; O_2CCH , $CH_2CH(CH_2OC_{10}H_{21})_2$, 2.04 (sept, J = 6.0 Hz, 1H; $CHCH_2OCH_2CH(O)(C=O)$), 1.53 (pent, J = 6.8 Hz, 16H; OCH₂CH₂(CH₂)₇CH₃), 1.26 (m, 112H; OCH₂CH₂(CH₂)₇CH₃), 0.88 (t, J = 7.0 Hz, 24H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 172.5 (O₂CCH), 171.4 (O₂CCH), 167.7 (C(=O)NH), 138.8 (aromatic C(1)), 128.5 (aromatic C(2) and C(6)), 127.7 (aromatic C(3), C(5), C(4)), 73.6 (CH₂CH(OC=O)(C=O)), 73.3 (OCH₂Ph), 71.5 (CH₂OCH₂), 70.9 (CH₂OCH₂CH(O)(C=O)), 70.04 (CH₂OCH₂), 70.00 (CH₂OCH₂), 69.5 (HNC(=O)CH₂), 69.4 (CH₂OCH₂), 69.36 (CH₂OCH₂), 69.14 (CH₂OCH₂CH(O)(C=O)), 69.0 (CH₂OCH₂), 63.8 (COOCH₂CH), 40.6 (CH(CH₂O)₂), 40.59 (CH(CH₂O)₂), 40.57 (CH(CH₂O)₂), 40.4 (CH(CH₂O)₂), 40.0 (CO₂CH₂CH), 39.6 (NHCH₂CH), 39.55 (CHCH₂OCH₂C(O)(C=O)), 32.2 (OCH₂CH₂(CH₂)₇CH₃), 29.96 (OCH₂(CH₂)₈CH₃), 29.95 (OCH₂(CH₂)₈CH₃), 29.93 (OCH₂(CH₂)₈CH₃), 29.90 (OCH₂(CH₂)₈CH₃), 29.86 (OCH₂(CH₂)₈CH₃), 29.79 (OCH₂(CH₂)₈CH₃), 29.77 (OCH₂(CH₂)₈CH₃), 29.6 (OCH₂(CH₂)₈CH₃), 29.1 (O₂CCH₂CH₂CO₂), 29.0 (O₂CCH₂CH₂CO₂), 26.4 (OCH₂CH₂(CH₂)₇CH₃), 22.9 (OCH₂CH₂(CH₂)₇CH₃), 14.4 $(O(CH_2)_9CH_3)$. MALDI-TOF (*m*/z): $[M + Ag]^+$ calcd for C₁₅₁H₂₆₇NO₂₄Ag, 2586.879; found 2588.353. GPC: $M_{\rm n} = 3,050, M_{\rm w}/M_{\rm n} = 1.04.$

Dendrimer 4d. A mixture of 1b (0.0500 g, 0.0565 mmol), 2b (0.0540 g, 0.0570 mmol), and 3b (0.0536 g, 0.0580 mmol) in anhydrous THF (58.5 µL) was gently agitated for 24 h at ambient temperature. The product was purified by flash column chromatography (SiO₂; 9:1 hex/EtOAc to 4:1) to yield 4d as a colorless oil (0.1145 g, 74%). TLC (SiO₂, 4:1 hex:EtOAc): R_f = 0.37. ¹H NMR (400 MHz, CCl₄, δ): 6.93 (t, J = 5.4 Hz, 1H; CONH), 5.29 (t, J = 6.0 Hz, 1H; NH(O=)CCH), 4.10 (t, J = 5.9 Hz, 4H; COOCH₂CH), 3.74 (t, J = 5.9 Hz, 2H; COONHCH₂), 3.42 (overlapping m, 76H; CH₂OCH₂), 2.68 (m, 4H; C(=O)CH₂CH₂C(=O)), 2.52 (t, J = 6.8 Hz, 2H; C(=O)NHCH₂CH₂), 2.18 (sept, J = 5.6 Hz, 3H; CH₂CH), 2.10 (sept, J = 5.8 Hz, 6H; CH₂CH), 1.52 (tt, $J_1 = J_2 = 6.8$ Hz, 12H; OCH₂CH₂(CH₂)₇CH₃), 1.24 (m, 168H; $OCH_2CH_2(CH_2)_7CH_3)$, 0.86 (t, \overline{J} = 6.8 Hz, 36H; $\overline{CH_3}$). ¹³C NMR (175 MHz, $\overline{CDCI_3}$, $\overline{\delta}$): 172.7 (CH_2CO_2), 172.1 (CH₂CO₂), 171.4 (CH₂CO₂), 167.9 (COONH), 73.4 (CH(O)(C=O)), 71.6 (CH₂OCH₂), 70.3 (C(=O)NHCH₂), 70.0 (CH₂OCH₂), 69.97 (CH₂OCH₂), 69.5 (CH₂OCH₂), 69.41 (OCH₂CH(O)(C=ONH), 69.36 (CH₂OCH₂), 69.18 (CH₂OCH₂), 69.15 (CH₂OCH₂), 63.9 (CO₂CH₂CH), 63.7 (CO₂CH₂CH), 40.6 (OCH₂CH), 40.4 (OCH₂CH), 39.6 (OCH₂CH), 35.1 (CHCH₂OCH₂CH(O)(C=O)), 33.9 (O=CNHCH₂CH₂), 32.2 (OCH₂(CH₂)₈CH₃), 29.95 (OCH₂(CH₂)₈CH₃), 29.90 (OCH₂(CH₂)₈CH₃), 29.86 (OCH₂(CH₂)₈CH₃), 29.78 (OCH₂(CH₂)₈CH₃), 29.6 (OCH₂(CH₂)₈CH₃), 29.3 (C(=O)CH₂CH₂C(=O)), 29.2 (C(=O)CH₂CH₂C(=O)), 26.4 (OCH₂(CH₂)₈CH₃), 22.9 (OCH₂(CH₂)₈CH₃), 14.4 (O(CH₂)₉CH₃). MALDI-TOF (*m/z*): [M + Ag]⁺ calcd for C166H327NO26Ag, 2859.338; found 2858.556. Anal. Calcd for C166H327NO26; C, 72.41; H, 11.97; N, 0.51. Found: C, 72.20; H, 11.70; N, 0.71. GPC: *M*_n = 3,200, *M*_w/*M*_n = 1.04.

Dendrimer 4e. A mixture of 1c (0.0793 g, 0.0855 mmol), 2b (0.0865 g, 0.0917 mmol), and 3b (0.0793 g, 0.0858 mmol) in anhydrous THF (85 µL) was gently agitated for 72 h at ambient temperature. The product was purified by flash column chromatography (SiO₂; hex:EtOAc 95:5 to 4:1) to yield 4e as a colorless oil (0.1237 g, 52%). TLC (SiO₂, 4:1 hex:EtOAc): R_f = 0.33. ¹H NMR (700 MHz, CCl₄, δ): 6.89 (t, J = 6.5 Hz, 1H; CONH), 5.16 (t, J = 4.8 Hz, 1H; NH(O=)CCH), 4.10 (overlapping m, 6H; COOCH₂CH), 3.50 (m, 2H; COONHCH₂), 3.37 (overlapping m, 72H; CH₂OCH₂), 2.65 (m, 6H; C(=O)CH₂CH₂C(=O)), 2.52 (t, J = 6.6 Hz, 2H; C(=O)NHCH₂CH₂), 2.39 (m, 2H; C(=O)CH₂CH₂CH(O)), 2.13 (m, 9H; CH₂CH), 1.52 (tt, J₁= J₂ = 6.8 Hz, 24H; OCH₂CH₂(CH₂)₇CH₃), 1.24 (m, 168H; OCH₂CH₂(CH₂)₇CH₃), 0.86 (t, J = 7.1 Hz, 18H; CH₃). ¹³C NMR (175 MHz, CDCl₃, δ): 172.7 (CH₂CO₂), 172.5 (CH₂CO₂), 172.3 (CH₂CO₂), 171.4 (CH₂CO₂), 169.3 (COONH), 73.3 (CH₂OCH₂CH(O)(C=O)), 71.6 (CH₂OCH₂), 70.0 (CH₂OCH₂), 69.4 (CH₂OCH₂), 69.19 (CH₂OCH₂), 69.15 (CH₂OCH₂), 64.0 (CO₂CH₂), 63.7 (CO₂CH₂), 63.5(CO₂CH₂), 40.6 (OCH₂CH), 39.58 (OCH₂CH), 39.54 (CH₂CH), 35.1 (C(=O)NHCH₂CH₂), 33.9 (O=CNHCH₂CH₂), 32.2 (OCH₂(CH₂)₈CH₃), 29.95 (CH2CH(O)(C=O)), 29.90 (OCH₂(CH₂)₈CH₃), 29.85 (OCH₂(CH₂)₈CH₃), 29.77 (OCH₂(CH₂)₈CH₃), 29.6 (OCH₂(CH₂)₈CH₃), 29.24 ((O=C)CH₂CH₂(C=O)), 29.17 ((O=C)CH₂CH₂(C=O), 27.3 (OCH₂(CH₂)₈CH₃), 26.4 (OCH₂(CH₂)₈CH₃), 22.9 (OCH₂(CH₂)₈CH₃), 14.4 (O(CH₂)₉CH₃), MALDI-TOF (m/z): $[M + Ag]^+$ calcd for C₁₆₈H₃₂₉NO₂₇Ag, 2901.349; found 2902.118. GPC: $M_n = 3,539$, $M_w/M_n = 1.04$.

Dendrimer 13. A mixture of 7 (0.0499 g, 0.116 mmol), 9 (0.0574 g, 0.118 mmol), and 11 (0.0428 g, 0.144 mmol) in anhydrous THF (0.11 mL) was gently agitated for 6 h at ambient temperature. The product was purified by flash column chromatography (SiO₂: 95:5 hex:EtOAc to 1:1). The dendrimer product containing traces of **9** was purified by flash column chromatography (SiO₂; CHCl₃ washed in NH₄OH) to yield **13** as a colorless oil (0.0898 g, 64%). TLC (SiO₂, 4:1 hex:EtOAc): $R_{\rm f}$ = 0.18. ¹H NMR (500 MHz, CDCl₃, δ): 7.29 (m, 10H; ArH), 6.68 (t, J = 5.6 Hz, 1H; NHC(=O)), 5.28 (t, J = 4.3 Hz, 1H; NH(O=)CCH), 4.49 (s, 4H; OCH₂Ph), 4.13 (d, J = 6.1 Hz, 2H; CO₂CH₂CH), 3.75 (m, 2H; CHCH₂OCH₂CH(O)(C=O)), 3.59-3.34 (m, 24H; CH₂OCH₂, (C=O)NHCH₂CH, CHCH₂OCH₂CH(O)(C=O)), 2.60-2.42 (m, 4H; $C(=O)CH_2CH_2(C=O))$, 2.16 (sept, J = 5.6 Hz, 7H; O_2CCH , $CH_2CH(CH_2O)_2$), 2.17 (m, 1H: $HN(O=)CCH_2CH), 2.18$ (sept, J = 6.1 Hz, 2H; $HC(CH_2O)_2$), 2.12 (sept, J = 5.7 Hz, 1H; CHCH₂OCH₂CH(O)(C=O)), 1.52 (m, 8H; OCH₂CH₂(CH₂)₇CH₃), 1.26 (m, 56H; OCH₂CH₂(CH₂)₇CH₃), 0.88 (t, J = 6.9 Hz, 12H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ , ppm): 172.4 (O₂CCH), 171.3 (O₂CCH), 167.8 (C(=O)NH), 138.5 (aromatic C(1)), 128.6 (aromatic C(2) and C(6)), 127.8 (aromatic C(3), C(5), C(4)), 73.8 (CH₂CH(OC=O)(C=O)), 73.6 (OCH₂Ph), 73.5 (OCH₂Ph), 71.63 (CH₂OCH₂), 71.55 (CH₂OCH₂), 70.6 (HNC(=O)CH₂), 70.5 ((CH₂OCH₂CH(O)(C=O)), 70.4 (CH₂OCH₂), 69.21 (CH₂OCH₂), 69.19 (CH₂OCH₂), 68.9 (CH₂OCH₂), 63.9 (COOCH₂CH), 40.5 (CH(CH₂O)₂), 40.4 (CH(CH₂O)₂), 39.62 (CH(CH₂O)₂), 32.1 (OCH₂CH₂(CH₂)₇CH₃), 29.95 (OCH₂(CH₂)₈CH₃), 29.88 (OCH₂(CH₂)₈CH₃), 29.87 (OCH₂(CH₂)₈CH₃), 29.84 (OCH₂(CH₂)₈CH₃), 29.83 (OCH₂(CH₂)₈CH₃), 29.76 (OCH₂(CH₂)₈CH₃), 29.73 (OCH₂(CH₂)₈CH₃), 29.6 (OCH₂(CH₂)₈CH₃), 29.2 (O₂CCH₂CH₂CO₂), 29.0 (O₂CCH₂CH₂CO₂), 26.4 (OCH₂CH₂(CH₂)₇CH₃), 26.38 $(OCH_2CH_2(CH_2)_7CH_3)$, 22.9 $(OCH_2CH_2(CH_2)_7CH_3)$, 14.4 $(O(CH_2)_9CH_3)$. MALDI-TOF (m/z): $[M + Ag]^+$ calcd for C₇₃H₁₂₇NO₁₂Ag, 1316.841; found 1318.069. Anal. Calcd for C₇₃H₁₂₇NO₁₂: C, 72.41; H, 10.57; N, 1.16. Found: C, 72.26; H, 10.60; N, 1.17. GPC: M_n = 1,630, M_w/M_n = 1.04.

Dendrimer 14. A mixture of 8 (0.1003 g, 0.05576 mmol), 10 (0.1034 g, 0.05568 mmol), and 12 (0.0764 g, 0.05594 mmol) in anhydrous THF (56 µL) was gently agitated for 44 h at ambient temperature. The product was purified by flash column chromatography (SiO₂; 97.5:2.5 hex:EtOAc to 1:1) to yield 14 as a colorless oil (0.11 g, 39%). TLC (SiO₂, 4:1 hex:EtOAc): R_{f} = 0.32. ¹H NMR (700 MHz, CDCl₃, δ): 7.27 (m, 40H; ArH), 6.62 (t, J = 6.0 Hz, 1H, NHC(=O)), 5.26 (t, J = 4.9 Hz, 1H; NH(O=)CCH), 4.45 (s, 16H; OCH_2Ph), 4.08 (d, J = 6.1 Hz, 2H; CO_2CH_2CH), 3.71 (m, 2H; $CHCH_2OCH_2CH(O)(C=O)$), 3.52-3.29 (m, 156H; CH₂OCH₂, C(=O)NHCH₂, CHCH₂OCH₂CH(O)(C=O)), 2.63 (m, 4H; C(=O)CH₂CH₂(C=O)), 2.22 (pent, J = 5.6 Hz, 7H; O₂CCH, CH₂CH(CH₂O)₂), 2.17 (m, 1H; HN(O=)CCH₂CH), 2.10 (sept, J = 5.6 Hz, 12H; $HC(CH_2O)_2$, 2.00 (sept, J = 5.6 Hz, 1H; $CH(O)(C=O)CH_2OCH_2HC$), 1.53 (m, 32H; OCH₂CH₂(CH₂)₇CH₃), 1.26 (m, 224H; OCH₂CH₂(CH₂)₇CH₃), 0.88 (t, J = 7.0 Hz, 48H; CH₃). ¹³C NMR (175 MHz, CDCl₃, δ, ppm): 172.4 (O₂CCH), 171.5 (O₂CCH), 167.7 (C(=O)NH), 138.9 (aromatic C(1)), 128.5 (aromatic C(2) and C(6)), 127.7 (aromatic C(3), C(5), C(4)), 73.7 (CH₂CH(OC=O)(C=O)), 73.3 (OCH₂Ph), 71.5 (HNC(=O)CH₂, CH₂OCH₂, CH₂OCH₂CH(O)(C=O)), 70.2 (CH₂OCH₂), 70.0 (CH₂OCH₂), 69.8 (CH₂OCH₂), 69.6 (CH₂OCH₂), 69.5 (CH₂OCH₂), 69.4 (CH₂OCH₂), 69.2 (CH₂OCH₂), 69.0 (CH₂OCH₂), 63.8 (COOCH2CH), 40.7 (O2CCH2CH, CH(CH2O)2), 40.61 (CH(CH2O)2), 40.56 (CH(CH2O)2), 39.9 $(HN(O=)CCH_2CH), 32.2 (OCH_2CH_2(CH_2)_7CH_3), 29.98 (O_2CCH_2CH_2CO_2, OCH_2(CH_2)_8CH_3), 29.92$ (OCH₂(CH₂)₈CH₃), 29.87 (OCH₂(CH₂)₈CH₃), 29.80 (OCH₂(CH₂)₈CH₃), 29.6 (OCH₂(CH₂)₈CH₃), 26.4 $(OCH_2(CH_2)_8CH_3)$, 22.9 $(OCH_2(CH_2)_8CH_3)$, 14.4 $(O(CH_2)_9CH_3)$. MALDI-TOF (m/z): $[M + Ag]^+$ calcd for $C_{307}H_{547}NO_{48}Ag$, 5126.954; found 5127.738. GPC: $M_p = 5,257$, $M_w/M_p = 1.05$.

Dendrimer S2. A mixture of **7** (0.0364 g, 0.0849 mmol), **9** (0.0435 g, 0.0894 mmol), and **S1** (0.0420 g, 0.0896 mmol) in anhydrous THF (0.0840 mL) was gently agitated for 6 h at ambient temperature. The product was purified by flash column chromatography (SiO₂; hex:EtOAc 95:5 to 4:1) to yield **S2** as a colorless oil (0.0886 g, 76%). TLC (SiO₂, 4:1 hex:EtOAc): $R_f = 0.20$. ¹H NMR (500 MHz, CCl₄, δ): 6.97 (t, J = 6.0 Hz, 1H; CONH), 5.29 (t, J = 4.5 Hz, 1H; NH(O=)CCH), 4.13 (t, J = 6.2 Hz, 4H; COOCH₂CH), 3.75 (m, 2H; COONHCH₂), 3.53-3.33 (m, 28H; CH₂OCH₂), 2.68 (m, 4H; C(=O)CH₂CH₂C(=O)), 2.54 (t, J = 6.6 Hz, 2H; C(=O)NHCH₂CH₂), 2.18 (m, 2H; CH₂CH), 2.09 (m, 1H; CH₂CH), 1.51 (tt, $J_1 = J_2 = 6.4$ Hz, 12H; OCH₂CH₂(CH₂)₇CH₃), 1.24 (m, 84H; OCH₂CH₂(CH₂)₇CH₃), 0.86 (t, J = 6.9 Hz, 24H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ): 172.7 (CH₂CO₂), 172.2 (CH₂CO₂), 171.4 (CH₂CO₂), 167.9 (COONH), 73.6 (CH₂OCH₂CH(O)(C=ONH), 69.2 (CH₂OCH₂), 68.9 (CH₂OCH₂), 68.8 (CH₂OCH₂), 64.0 (CO₂CH₂CH), 63.8

 (CO_2CH_2CH) , 40.4 (OCH_2CH) , 39.6 (OCH_2CH) , 35.1 $(CHCH_2OCH_2CH(O)(C=O))$, 34.0 $(O=CNHCH_2CH_2)$, 32.1 $(OCH_2(CH_2)_8CH_3)$, 29.9 $(OCH_2(CH_2)_8CH_3)$, 29.88 $(OCH_2(CH_2)_8CH_3)$, 29.7 $(OCH_2(CH_2)_8CH_3)$, 29.6 $(OCH_2(CH_2)_8CH_3)$, 29.4 $(OCH_2(CH_2)_8CH_3)$, 29.3 $(C(=O)CH_2CH_2C(=O))$, 26.4 $(OCH_2(CH_2)_8CH_3)$, 22.9 $(OCH_2(CH_2)_8CH_3)$, 14.4 $(O(CH_2)_9CH_3)$. MALDI-TOF (m/z): $[M + Ag]^+$ calcd for $C_{82}H_{159}NO_{14}Ag$, 1489.081; found 1491.734. Anal. Calcd for $C_{82}H_{159}NO_{14}$: C, 71.21; H, 11.59; N, 1.01. Found: C, 71.00; H, 11.40; N, 0.94. GPC: $M_n = 1,913$, $M_w/M_n = 1.04$.

Dendrimer S4. A mixture of **S3** (0.0399 g, 0.0848 mmol), **9** (0.0430 g, 0.0883 mmol), and **S1** (0.0417 g, 0.0890 mmol) in anhydrous THF (85 μ L) was gently agitated for 48 h at ambient temperature. The product was purified by flash column chromatography (SiO₂; hex:EtOAc 95:5 to 4:1) to yield **S4** as a colorless oil (0.0816 g, 68%). TLC (SiO₂, 4:1 hex:EtOAc): $R_f = 0.18$. ¹H NMR (500 MHz, CCl₄, δ): 6.96 (t, J = 6.0 Hz, 1H; CONH), 5.17 (t, J = 6.0 Hz, 1H; NH(O=)CCH), 4.13 (overlapping m, 6H; COOCH₂CH), 3.50 (m, 2H; COONHCH₂), 3.38 (overlapping m, 28H; CH₂OCH₂), 2.65 (m, 4H; C(=O)CH₂CH₂C(=O)), 2.53 (t, J = 6.5 Hz, 2H; C(=O)NHCH₂CH₂(CH₂), CH₃), 1.24 (m, 84H; OCH₂CH₂CH₂(CH₂), CH₃), 0.86 (t, J = 6.9 Hz, 18H; CH₃). ¹³C NMR (125 MHz, CDCl₃, δ): 172.85 (CH₂CO₂), 172.60 (CH₂COCH₂), 68.90 (CH₂OCH₂), 68.87 (CH₂OCH₂), 68.81 (CH₂OCH₂), 64.1 (CH₂OCH₂), 63.9(CH₂OCH₂), 63.6 (CH₂OCH₂), 39.6 (OCH₂CH), 39.58 (OCH₂CH), 32.1 (C(=O)NHCH₂CH₂), 29.89 (O=CNHCH₂CH₂), 29.87 (OCH₂(CH₂)₈CH₃), 29.84 (CH₂CH(O)(C=O)), 29.82 ((O=C)CH₂CH₂(C=O)), 29.7 (OCH₂(CH₂)₈CH₃), 29.6 (OCH₂(CH₂)₈CH₃), 29.84 (OCH₂(CH₂)₈CH₃), 22.9 (OCH₂(CH₂)₈CH₃), 14.4 (O(CH₂)₉CH₃). MALDI-TOF (*m*/z): [M + Ag]⁺ calcd for C₈₄₄H₁₆₁NO₁₅Ag, 1531.092; found 1533.087. GPC: *M*_n = 2,011, *M*_w/*M*_n = 1.04.

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¹H and ¹³C NMR Spectra

α-Butoxyacetaldehyde (5b)

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200 190 180 170 160 150 140 130 120	110 100 90 80 70 60 Chemical Shift (ppm)	50 40 30 20 10 0

1-(*t*-Butylaminocarbonyl)-3-methylbutyl 3-methylbutanoate (6a)

1-(*t*-Butylaminocarbonyl)-2-butoxyethyl 3-methylbutanoate (6b)

2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethene (S10)

2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethene (S10)

2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethanol (S12)


2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethanol (S12)



2,2-Bis(decyloxymethyl)ethyl allyl ether (S13)





2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl allyl ether (S14)





2,2-Bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethyl allyl ether (S15)



2,2-Bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethyl allyl ether (S15)











2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethoxyacetaldehyde (1b)



2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethoxyacetaldehyde (1b)



2,2-Bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethoxyacetaldehyde (8)



2,2-Bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethoxyacetaldehyde (8)







Succinic acid 2,2-bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl ester (2b)

7.5



Succinic acid 2,2-bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl ester (2b)



Succinic acid 2,2-bis(2,2-di[2,2-di(decyloxymethyl)ethoxymethyl]ethoxymethyl)ethyl ester (10)







2,2-Bis(benzyloxymethyl)ethyl mesylate (S16)











2,2-Bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethyl mesylate (S17)

1-Azido-2,2-bis(benzyloxymethyl)ethane (S18)



1-Azido-2,2-bis(benzyloxymethyl)ethane (S18)



1-Azido-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (S19)





1-Azido-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (S19)

1-Formamido-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (S23)





1-Formamido-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (S23)



1-lsocyano-2,2-bis(benzyloxymethyl)ethane (11)



1-Isocyano-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (12)





1-lsocyano-2,2-bis(2,2-di[2,2-di(benzyloxymethyl)ethoxymethyl]ethoxymethyl)ethane (12)



N-Formyl-[2-(2,2-bis(decyloxymethyl)ethoxy)carbonylethyl]amine (S26)

N-Formyl-[2-(2,2-bis(decyloxymethyl)ethoxy)carbonylethyl]amine (S26)





N-Formyl-[2-(2,2-bis(2,2-di(decyloxymethyl)ethoxymethyl)ethoxy)carbonylethyl]amine (S27)


N-Formyl-[2-(2,2-bis(2,2-di(decyloxymethyl)ethoxymethyl)ethoxy)carbonylethyl]amine (S27)

2-(2,2-Bis(decyloxymethyl)ethoxy)carbonylethylisocyanide (S1)





2-(2,2-Bis(decyloxymethyl)ethoxy)carbonylethylisocyanide (S1)



2-(2,2-Bis(2,2-di(decyloxymethyl)ethoxymethyl)ethoxy)carbonylethylisocyanide (3b)



2-(2,2-Bis(2,2-di(decyloxymethyl)ethoxymethyl)ethoxy)carbonylethylisocyanide (3b)







2,2-Bis((2,2-di[decyloxymethyl]ethoxymethyl)ethyl 4-pentenoate (S29)



2,2-Bis((2,2-di[decyloxymethyl]ethoxymethyl)ethyl 4-pentenoate (S29)



2,2-Bis(decyloxymethyl)ethyl 4-oxobutanoate (S3)

 		77.55 77.23 76.91 76.91 63.83	23.13 38.79 38.79 32.13 29.85 29.85 29.85 29.85 29.55 14.34
	30.2 30.0 29.8 29.6 29.4 29.2 Chemical Shift (ppm)		



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200	190	180	170	160	150	140	130	120	110 Chemic	100 al Shift	90 (ppm)	80	70	60	50	40	30	20	10	0



2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl 4-oxobutanoate (1c)



2,2-Bis(2,2-di[decyloxymethyl]ethoxymethyl)ethyl 4-oxobutanoate (1c)







Dendrimer 4b







Dendrimer 4c



Dendrimer 4d



Dendrimer 4e





Dendrimer 4e







Dendrimer 13





Dendrimer 14



Dendrimer S2



Dendrimer S2



Dendrimer S4

