Supporting Information

for

Peptide-Dendron Hybrids that Adopt Sequence-Encoded β-Sheet Conformations

Deborah A. Barkley,[†] Sang Uk Han,[†] Tadanori Koga,[†,‡] and Jonathan G. Rudick[†,*]

[†]Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, United States
[‡]Department of Materials Science and Engineering, Stony Brook University, Stony Brook, New York 11794, United States

Low-resolution MALDI-TOF Mass Spectra of Hybrids 1–4

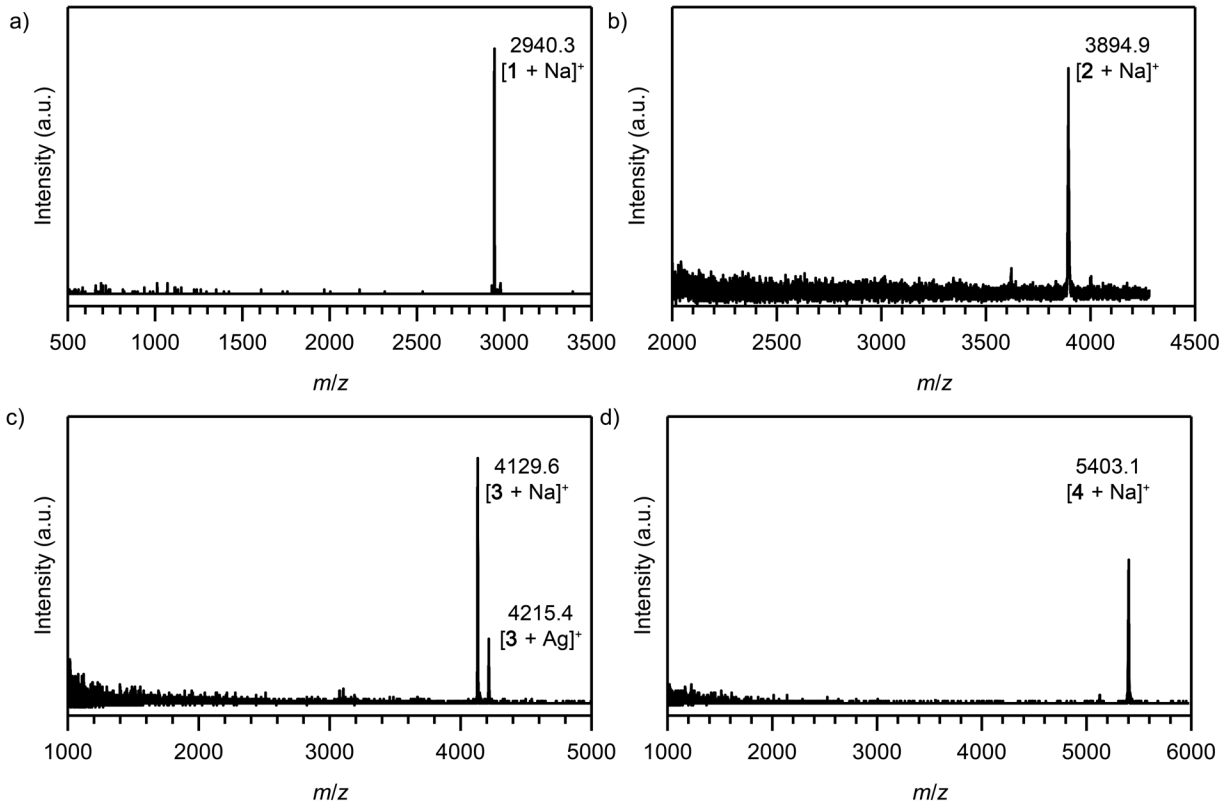


Fig. S1. MALDI-TOF mass spectra of peptide-dendron hybrids (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

Characterization of Peptide 5

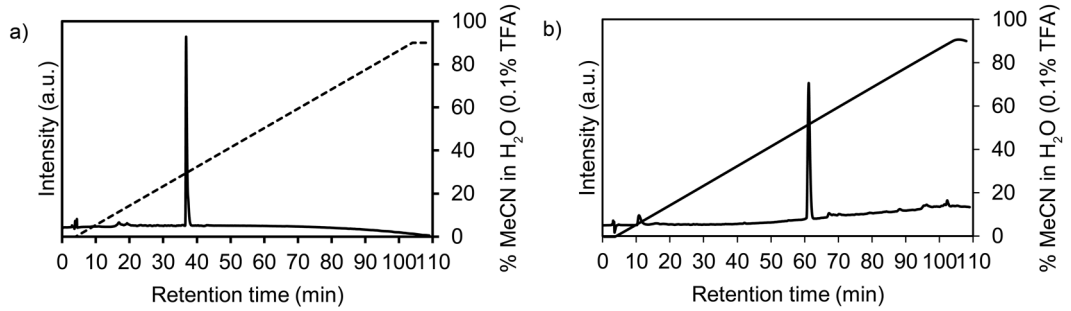


Fig. S2. Chromatograms of peptide **5** (solid line) eluted with solvent A = H_2O + 0.1% TFA and (a) solvent B = MeCN/H_2O (9:1 v/v) + 0.1% TFA and (b) solvent B = MeOH/H_2O (9:1 v/v) + 0.1% TFA. The dashed line indicates the solvent composition during elution of the peptide at 1 mL/min from a C18 column.

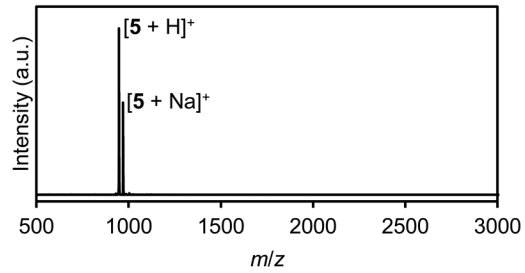


Fig. S3. MALDI-TOF mass spectrum of **5**.

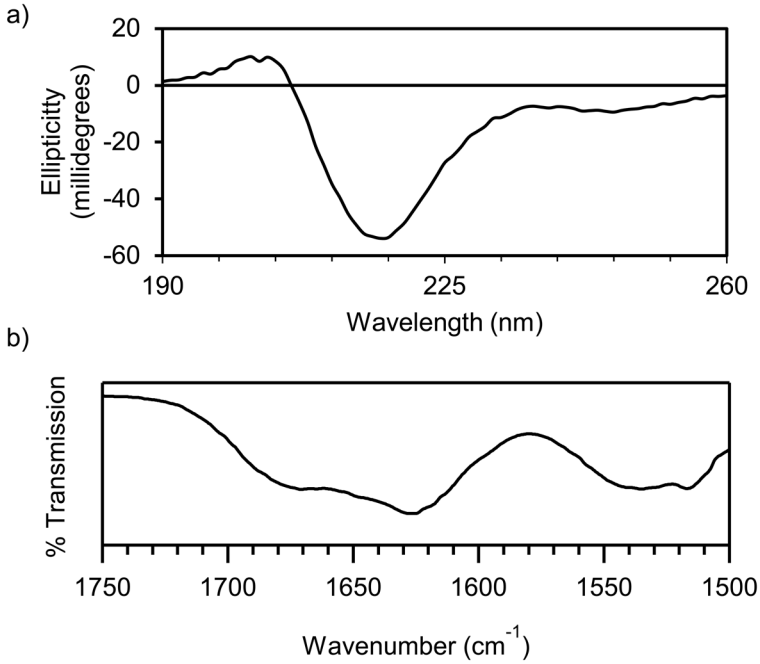


Fig. S4. (a) Circular dichroism and (b) infrared spectra of peptide **5** in a film.

Additional Experiments Related to Circular Dichroism of the Hybrids

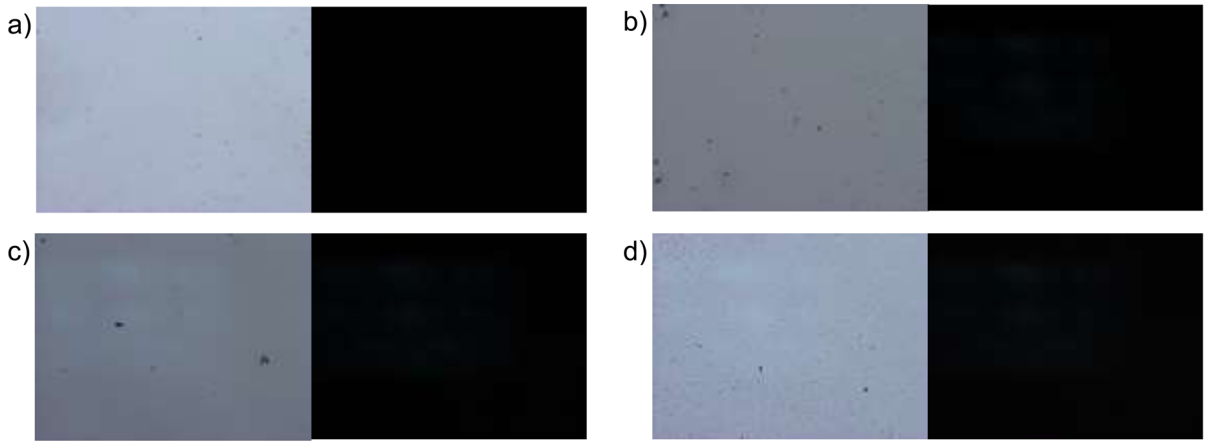


Fig. S5. Unpolarized (left) and polarized (right) optical micrographs of films of (a) **1** (98 nm thick), (b) **2** (92 nm thick), (c) **3** (74 nm thick), and (d) **4** (99 nm thick) on quartz. All micrographs are at 10x magnification. Film thicknesses are from ellipsometry.

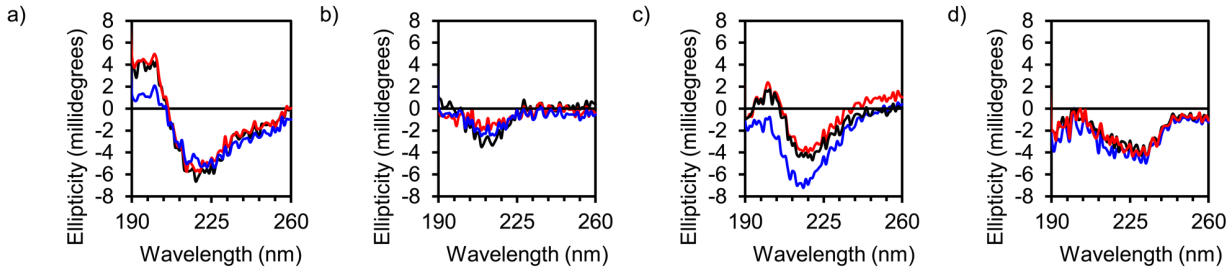
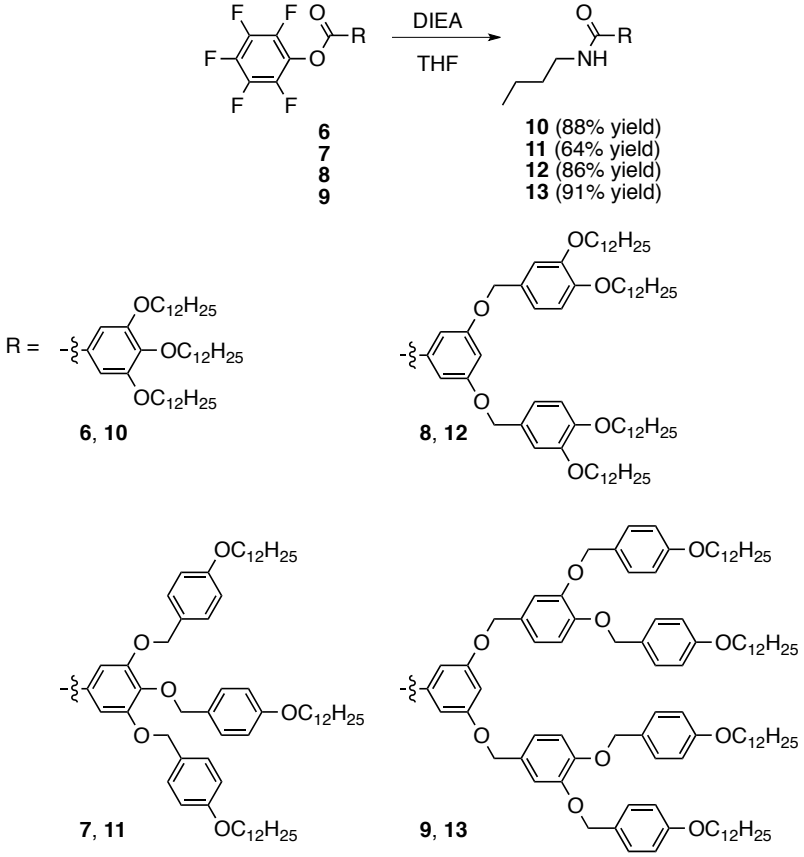


Fig. S6. CD spectra of films of (a) **1**, (b) **2**, (c) **3**, and (d) **4** at 0º (black), 90º (red), and 180º (blue).

Dendritic Butyl Amides

Scheme S1. Synthesis of the dendritic butyl amides 10–13



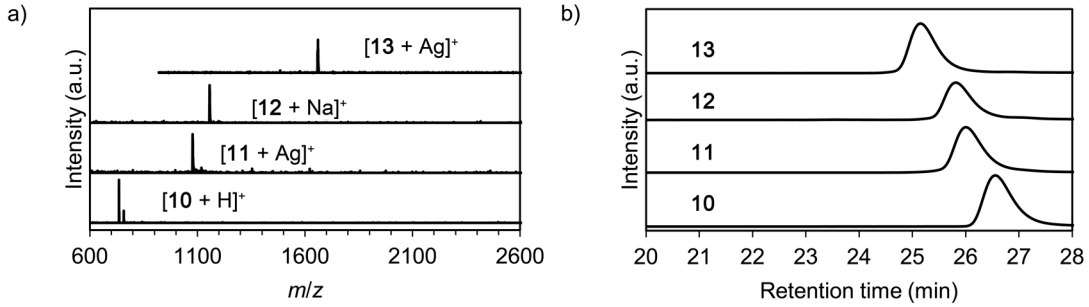


Fig. S7. (a) MALDI-TOF mass spectra of dendrons **10**–**13**. (b) Elution profiles of dendrons **10**–**13** from GPC in THF (1 mL/min; 40 ºC).

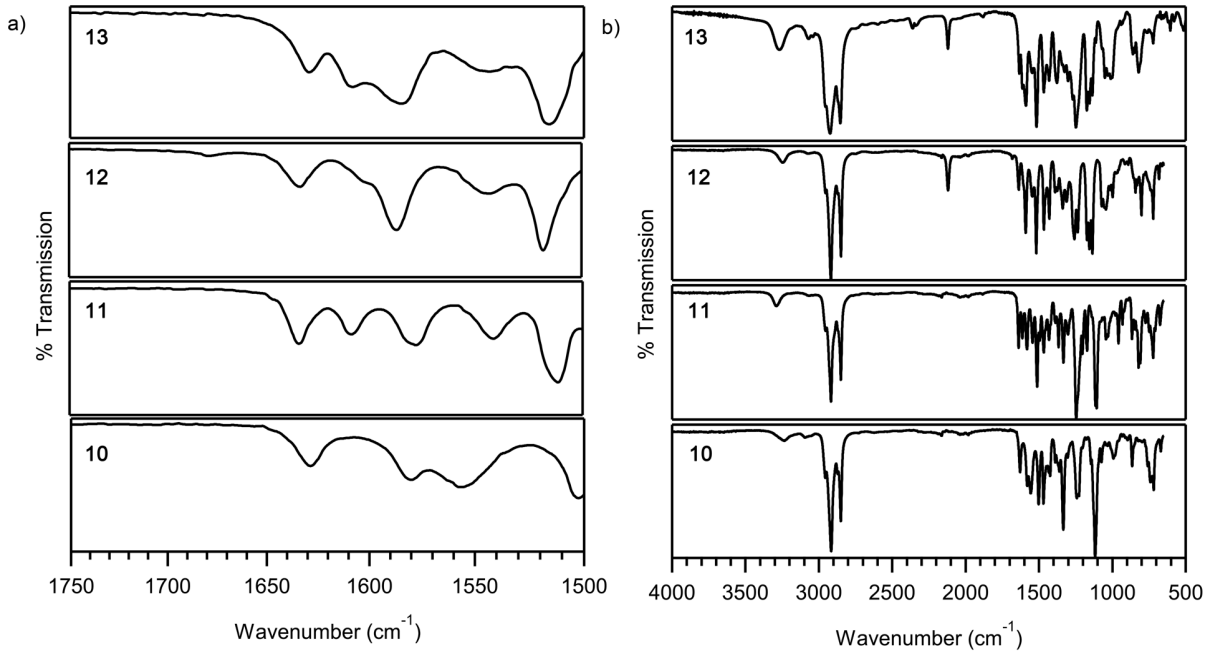


Fig. S8. Infrared spectra of dendritic monobenzamides **10**–**13** acquired at room temperature from as-cast films showing (a) the region of containing the amide I and amide II bands, and (b) the full spectrum.

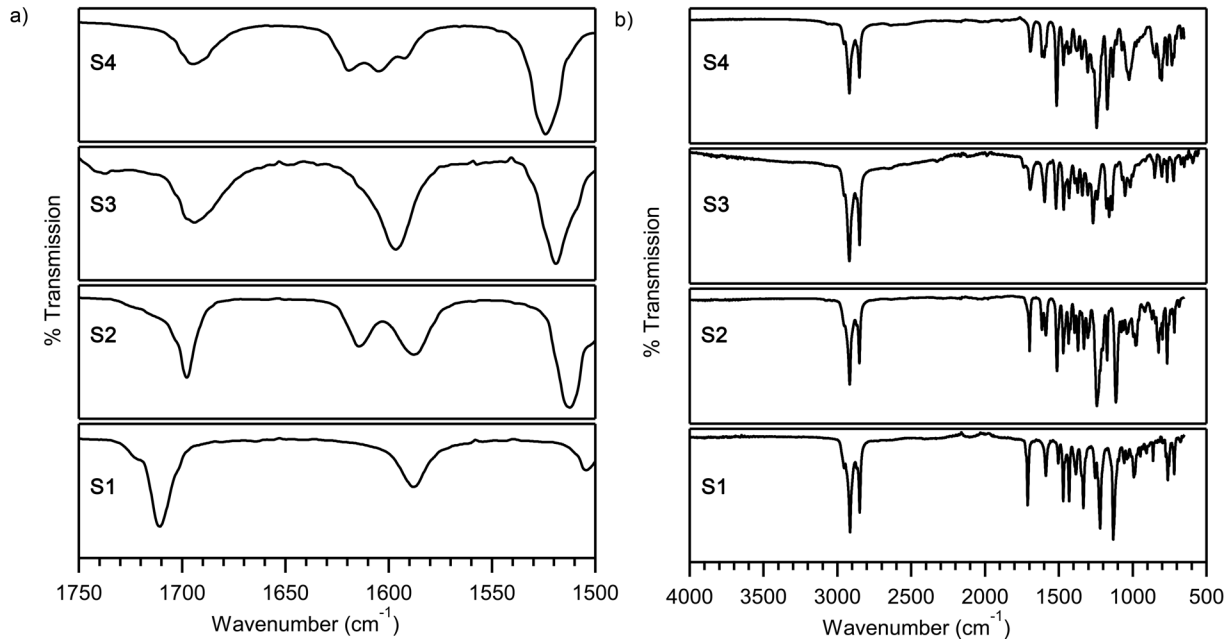


Fig. S9. Infrared spectra acquired at room temperature from as-cast films showing (a) the region of containing the amide I and amide II bands, and (b) the full spectrum for propyl 3,4,5-tridodecyloxybenzoate (**S1**), methyl 3,4,5-tri[4'-(*n*-dodecan-1-yloxy)benzyloxy]benzoate (**S2**), methyl 3,5-bis[3',4'-bis(*n*-dodecan-1-yloxy)benzyloxyl]benzamide (**S3**), and methyl 3,5-bis(3',4'-bis[4"-(*n*-dodecan-1-yloxy)benzyloxy]benzyloxy)benzoate (**S4**).

Experimental Section

Materials. Anhydrous tetrahydrofuran (THF, 99.9%), anhydrous CH_2Cl_2 (98%), 2,5-dihydroxybenzoic acid (DHB, 99%), silver trifluoroacetate (99.99% trace metals basis), trifluoroacetic acid (TFA), pentafluorophenol (99%), hexafluorobenzene (99.5%), *N*,*N*-diisopropylethylamine (DIEA), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 99%), methyl gallate (98%), methyl 3,5-dihydroxybenzoate (97%), and butylamine (99.5%) were used as received from Aldrich. *n*-Propyl gallate was used as received from AlfaAesar. α-Cyano-4-hydroxycinnamic acid (CHCA) was used as received from Fluka. A.C.S. Reagent-grade CH_2Cl_2 and $CHCl_3$ were used as received from EMD. Acetonitrile (MeCN), 2,2,2-trifluoroethanol (TFE, 99%), and acetone (A.C.S. reagent) were used as received from Fisher. Methanol (MeOH, A.C.S. reagent) and tetrahydrofuran (THF, A.C.S. reagent) were used as received from BDH. Anhydrous $MgSO_4$ (99.9%) and K_2CO_3 (A.C.S. reagent) were used as received from J. T. Baker. Dithranol (1,8-dihydroxy-9-anthrone, ≥99%) was used as received from MP Biomedicals. Chloroform-*d* with 0.03% v/v tetramethylsilane ($CDCl_3$, 99.8% D) and methylene chloride-d_2 (CD_2Cl_2, 99.8% D) were used as received

from Cambridge Isotope Laboratories. Anhydrous *N*,*N*-dimethylformamide (DMF) and Fmoc-Tyr(*t*Bu)-OH were used as received from EMD. Fmoc-Lys(Boc)-OH, Fmoc-Leu-OH, *N*-methylmorpholine (NMM), and *O*-(benzotriazol-1-yl)-*N*,*N*,*N*',*N*'-tetramethyluroniumhexafluorophosphate (HBTU) were used as received from Chem-Impex International. H-Rink amide-ChemMatrix resin (0.45 mmol/g or 0.51 mmol/g) was used as received from PCAS BioMatrix Inc. 2,3,4,5,6-Pentafluorophenyl 3,4,5-tris(*n*-dodecan-1-yloxy)benzoate (**6**), 2,3,4,5,6-pentafluorophenyl 3,4,5-tri[4'-(*n*-dodecan-1-yloxy)benzyloxy]benzoate (**7**), 2,3,4,5,6-pentafluorophenyl 3,5-bis[3',4'-bis(*n*-dodecan-1-yloxy)benzyloxyl]benzoate (**8**), and 2,3,4,5,6-pentafluorophenyl 3,5-bis(3',4'-bis[4"-(*n*-dodecan-1-yloxy)benzyloxy]benzyloxy)benzoate (**9**) were synthesized according to literature procedures.[1]

Techniques. Thin layer chromatography (TLC) was performed on 60 Å silica gel plates (250 μm, Whatman) and observed using a UV lamp (254 nm). Flash column chromatography was performed on a Teledyne Isco CombiFlash Rf with RediSep Rf Normal Phase disposable silica cartridges. NMR spectra were recorded on a Bruker NanoBay (^{1}H, 400 MHz; ^{13}C, 100 MHz) instrument or a Bruker AVANCE III instrument equipped with a Prodigy cold probe (^{1}H, 500 MHz; ^{13}C, 125 MHz). Peak multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Chemical shift values are referenced to the residual proton solvent peaks (^{1}H: $CDCl_3$, δ 7.24; CD_2Cl_2, δ 5.32; CD_3OD, δ 3.31), and solvent ^{13}C signal ($CDCl_3$, δ 77.23; CD_3OD, δ 49.15). Coupling constants are reported as absolute values.

The MALDI-TOF mass spectra were recorded on a Bruker Autoflex II TOF/TOF workstation. Dendron and dendron-peptide hybrid samples for MALDI-TOF mass spectrometry were prepared using DHB as the matrix. Silver trifluoroacetate solution in THF (10 mg/mL) was added in equal volume as the matrix as specified in the experimental data. Equal volumes of solutions (10 mg/mL) of matrix and analyte in THF were mixed. The mixture of matrix and analyte (1 μL) was deposited on the target plate and allowed to dry before measurements were taken.

Gel permeation chromatography (GPC) in THF (1 mL/min, 40 °C) 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).

Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer at ambient temperature. Interferograms were recorded between 4000–500 cm^{-1} at a resolution of 4 cm^{-1} and a total of 16 scans were averaged. Peptide-dendron hybrids **1–3** were measured as dried films cast onto a Pike Technologies KBr disk 32 x 3 mm from solution in CH_2Cl_2 (10 mM); peptide-dendron hybrid **4** was measured as a dried film cast from solution in CH_2Cl_2 (5 mM). Peptide **5** was measured as a dried film cast from solution in MeOH (10 mM).

Circular dichroism (CD) spectra were recorded of films on quartz substrates on an Applied Photophysics Chirascan instrument. The quartz slides were first cleaned by heating, uncovered, without stirring, for 20 min at 90 °C in aqueous hydrogen peroxide and ammonium hydroxide, followed by rinsing with deionized water. Thin films of the peptide-dendron hybrids were spincastfrom 5 mM solutions in THF onto the quartz substrates at a spin rate of 2000 rpm for 30 s, and then dried overnight. A thin film of the peptide **5** was spin-cast from 2 mM solution in TFE onto the quartz substrate at a spin rate of 2000 rpm for 30 s, and then dried overnight. Uniformity of each thin film was confirmed by equivalent UV/Vis absorption intensities from three different regions of the film.

UV/Vis absorption spectra were measured at room temperature on an Evolution 201 spectrophotometer. POM of the spin-cast films confirmed that the spin-cast films appeared dark under polarized light. Film thicknesses were measured by spectroscopic ellipsometry on a Horiba UVISEL FUV instrument at the Thermomechanical & Imaging Nanoscale Characterization (ThINC) core facility of the Advanced Energy Research and Technology Center at Stony Brook University.

General Solid-Phase Peptide Synthesis Procedures. Single Coupling Protocol. The resin was washed three times with DMF (15 mL/g) for 30 s each time. The resin was treated twice with a solution of piperidine (20 vol%) in DMF (15 mL/g) for 5 min each time. The resin was washed six times using DMF (15 mL/g) for 30 s each time. A solution of Fmoc-protected amino acid (0.50 M), HBTU (0.48 M), and

NMM (0.2 M) was transferred to the peptide reaction vessel and diluted with DMF to a final concentration of 0.22 M in Fmoc-protected amino acid. The coupling reaction was allowed to proceed for 20 min. The resin was washed three times with DMF for 30 s each time.

***N*$^{\alpha}$-Fmoc Deprotection Protocol.** The resin was washed three times for 30 s with DMF (15 mL/g). The resin was treated twice with a solution of piperidine (20 vol%) in DMF (15 mL/g) for 5 min each time. The resin was then washed six times with DMF for 30 s each time.

Protocol for Capping and Acetylation of the *N*-Terminus. The resin was washed six times with DMF (15 mL/g) for 30 s each time. A vial containing Ac_2O (2 mL) was diluted with a 0.2 M solution of NMM in DMF (2 mL). The Ac_2O solution solution was transferred to the reaction vessel and diluted with DMF (2.5 mL). The solution in the reaction vessel was mixed for 5 min. The resin was washed three times with DMF (15 mL/g) for 30 s each time.

Cleavage and Side-Chain Deprotection. To the resin, a mixture of TFA/$^{i}Pr_3SiH/H_2O$ (95:2.5:2.5 v/v/v; 10 mL) was added. The reaction mixture was agitated for 1 h. The liquids were separated from the resin and collected by forcing the liquid phase through the peptide reaction vessel frit by positive pressure displacement with N_2. The resin was washed with TFA/$^{i}Pr_3SiH/H_2O$ (95:2.5:2.5 v/v/v; 2 mL) and the liquids were separated from the resin and collected by positive pressure displacement with N_2. The volume of the collected liquids was reduced under a stream of N_2. The mixture was precipitated into cold Et_2O. The solids were separated from the liquids by centrifugation (Thermo Scientific CL10) at 3500 rpm for 5 min, and the solids were isolated by decanting the supernatant liquid. The crude peptide was precipitated from TFA into cold Et_2O two more times. The solid pellet was dissolved in H_2O and lyophilized. The peptide was purified by preparative HPLC on a C18 reversed-phase column.

Assembly of AcNH-YKLKLKL-CONH$_2$. Peptide was assembled on ChemMatrix Rink amide resin (0.25 mmol, 0.5243 g) in a glass-fritted peptide reaction vessel and cleaved from the resin to yield the product. The sequence of operations is detailed in the table below:

Table S1. Protocol for the synthesis of AcNH-YKLKLKL-$CONH_2$ (**5**)

		Mass of Reagents (g)	
Cycle		Fmoc-AA-OH	HBTU
1	Single Coupling: Fmoc-Leu-OH	0.3757	0.3796
	Capping		
	N^a-Fmoc Deprotection		
2	Single Coupling: Fmoc-Lys(Boc)-OH	0.4729	0.3766
	Capping		
	N^a-Fmoc Deprotection		
3	Single Coupling: Fmoc-Leu-OH	0.3651	0.3768
	Capping		
	N^a-Fmoc Deprotection		
4	Single Coupling: Fmoc-Lys(Boc)-OH	0.4765	0.3812
	Capping		
	N^a-Fmoc Deprotection		
5	Single Coupling: Fmoc-Leu-OH	0.3533	0.3878
	Capping		
	N^a-Fmoc Deprotection		
6	Single Coupling: Fmoc-Lys(Boc)-OH	0.4899	0.3736
	Capping		
	N^a-Fmoc Deprotection		
7	Single Coupling: Fmoc-Tyr(tBu)-OH	0.5043	0.3678
	N^a-Fmoc Deprotection		
	Acetylation of the *N*-terminus		
	Cleavage and Side-Chain Deprotection		

Hybrid 1

To a round-bottom flask containing **6** (0.0402 g, 0.0478 mmol), DIEA (0.02 mL, 0.1 mmol), and THF (0.5 mL), **5** (0.0098 g, 0.010 mmol) in DMF (0.5 mL) was added. The reaction was heated at 50 °C for 2 d under a N_2 atmosphere. The volatiles were removed by rotary evaporation and the solid was purified by column chromatography (SiO_2, CH_2Cl_2 to 9:1 CH_2Cl_2/MeOH) to give **1** (0.0295 g, 78%). TLC (SiO_2, 95:5 CH_2Cl_2/MeOH) R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.03, 6.99, 6.95, 6.94 (m, 10 H, Ar*H*, Ar*H* (Y)), 4.21, 4.20, 4.12 (m, 7 H, C*H* (Y), C*H* (L), C*H* (K)), 3.97 (m, 18 H, OCH_2), 3.77 (m, 2 H, CH_2 (Y)), 3.41 (m, 6H, CH_2NH (K)), 2.05 (s, 3 H, Ac CH_3), 1.79 (m, 24 H, OCH_2CH_2, CH_2 (K)), 1.60 (m, 21 H, $(CH_2)_2$ (K), CH_2 (L), C*H* (L)), 1.46 (m, 18 H, $CH_2CH_2CH_2OAr$), 1.26 (m, 144 H, $(CH_2)_8$), 0.88 (m, 45 H, CH_3 (L), CH_3). MALDI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{176}H_{311}N_{11}NaO_{21}$ 2938.3504; found, 2938.3646; $[M + K]^+$ calcd for $C_{176}H_{311}N_{11}KO_{21}$ 2954.3243; found, 2954.3011.

Hybrid 2

To a round-bottom flask containing **7** (0.0556 g, 0.0478 mmol), DIEA (0.02 mL, 0.1 mmol), and THF (0.5 mL), **5** (0.0102 g, 0.0108 mmol) in DMF (0.5 mL) was added. The reaction was heated at 50 °C for 2d under a N_2 atmosphere. Then, the volatiles were removed by rotary evaporation and the solid was purified by column chromatography (SiO_2, CH_2Cl_2 to 9:1 CH_2Cl_2/MeOH) to give **2** (0.0295 g, 71%) as a solid. TLC (SiO_2, 95:5 CH_2Cl_2/MeOH) R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.14, 7.08, 7.05, 6.98, 6.91, 6.89, 6.87, 6.77, 6.74 (m, 46 H, Ar*H*, Ar*H* (Y)), 5.04 , 4.99, 4.95 (m, 18 H, $ArCH_2OAr$), 4.43, 4.26, 4.03 (m, 7 H, C*H* (Y), C*H* (L), C*H* (K)), 3.96, 3.95, 3.93 (m, 18 H, OCH_2), 3.77 (m, 2 H, CH_2 (Y)), 3.44 (m, 6H, CH_2NH (K)), 2.02 (s, 3 H, Ac CH_3), 1.78 (m, 24 H, OCH_2CH_2, CH_2 (K)), 1.59 (m, 21 H, $(CH_2)_2$ (K), CH_2 (L), C*H* (L)), 1.46 (m, 18 H, $CH_2CH_2CH_2OAr$), 1.28 (m, 144 H, $(CH_2)_8$), 0.90 (m, 45 H, CH_3 (L), CH_3). MALDI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{239}H_{365}N_{11}NaO_{30}$ 3892.7272; found, 3892.9287; $[M + K]^+$ calcd for $C_{239}H_{365}N_{11}KO_{30}$ 3908.7011; found, 3908.9287.

Hybrid 3

To a round-bottom flask containing **8** (0.0748 g, 0.0604 mmol), DIEA (0.04 mL, 0.2 mmol), and THF (1.0 mL), **5** (0.0190 g, 0.0201 mmol) in DMF (1.0 mL) was added. The reaction was heated at 50 °C for 6 d under a N_2 atmosphere. Then, the volatiles were removed by rotary evaporation and the solid was purified by column chromatography (SiO_2, CH_2Cl_2 to 95:5 CH_2Cl_2/MeOH) to give **3** (0.0762 g, 92%) as a solid. TLC (SiO_2, 95:5 CH_2Cl_2/MeOH) R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.06, 7.01, 6.97, 6.93, 6.91, 6.86, 6.84, 6.70, 6.67 (m, 28 H, Ar*H*, Ar*H* (Y)), 4.92, 4.88 (m, 12 H, $ArCH_2OAr$), 3.96, 3.97 (m, 7 H, C*H* (Y), C*H* (L), C*H* (K)), 3.70, 3.68, 3.67 (m, 24 H, OCH_2), 3.35 (m, 2 H, CH_2 (Y)), 3.10 (m, 6H, CH_2NH (K)), 1.90 (s, 3 H, Ac CH_3), 1.78 (m, 30 H, OCH_2CH_2, CH_2 (K)), 1.56, 1.45, 1.44, 1.42, 1.39, 1.37, 1.26 (m, 237 H, $(CH_2)_2$ (K), CH_2 (L), C*H* (L), $CH_2CH_2CH_2OAr$, $(CH_2)_8$), 0.88 (m, 54 H, CH_3 (L), CH_3). MALDI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{254}H_{419}N_{11}NaO_{30}$ 4127.1497; found, 4127.3669; $[M + K]^+$ calcd for $C_{254}H_{419}N_{11}KO_{30}$ 4143.1236; found, 4143.3208.

Hybrid 4

To a round-bottom flask containing **9** (0.0818 g, 0.0492 mmol), DIEA (0.02 mL, 0.1 mmol), and THF (0.5 mL), **5** (10.0 mg, 0.0110 mmol) in DMF (0.5 mL) was added. The reaction was heated at 50 °C for 2 d under a N_2 atmosphere. Then, the volatiles were removed by rotary evaporation and the solid was purified by column chromatography (SiO_2, CH_2Cl_2 to 9:1 CH_2Cl_2/MeOH) to give **4** (0.0500 g, 82%). TLC (SiO_2, 95:5 CH_2Cl_2/MeOH) R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34, 7.32, 7.28 (m, 32 H, Ar*H*), 7.10, 7.01, 6.91 (m, 44 H, Ar*H*, Ar*H* (Y)), 5.08, 5.02, 4.91 (m, 24 H, ArC*H*$_2$OAr), 4.53 (m, 7 H, C*H* (Y), C*H* (L), C*H* (K)), 3.98 (m, 24 H, OC*H*$_2$), 3.68 (m, 2 H, C*H*$_2$ (Y)), 3.38 (m, 6 H, C*H*$_2$NH (K)), 2.45 (s, 3 H, Ac C*H*$_3$), 1.80, 1.78 (m, 30 H, OCH$_2$C*H*$_2$, C*H*$_2$ (K)), 1.30, 1.48 (m, 237 H, (C*H*$_2$)$_9$, (C*H*$_2$)$_2$ (K), C*H*$_2$ (L), C*H*$_3$ (L)), 0.91 (m, 54 H, C*H*$_3$ (L), C*H*$_3$). MALDI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{338}H_{491}N_{11}NaO_{42}$ 5399.6521; found, 5401.1574.

Butyl 3,4,5-tri(*n*-dodecan-1-yloxy)benzamide (10)

To a round-bottom flask, **6** (0.1063 g, 0.1264 mmol), butyl amine (0.0330 g, 0.4514 mmol), DIEA (500 μL, 3 mmol), and THF (10 mL) were added. The solution was stirred at room temperature for 6 h under a N_2 atmosphere. The volatiles were removed by rotary evaporation. The solid was purified by column chromatography (SiO_2, CH_2Cl_2) to give **10** (0.0808 g, 88%) as a solid. TLC (SiO_2, CH_2Cl_2): R_f = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.97 (s, 2H, Ar*H*), 4.01 (t, *J* = 6.5 Hz, 2H, *para* C*H*$_2$OAr), 3.99 (t, *J* = 6.5 Hz, 4H, *meta* C*H*$_2$OAr), 3.44 (d, *J* = 5.4 Hz, t, *J* = 7.0 Hz, 2H, NHC*H*$_2$), 1.81 (m, 6H, *CH*$_2$CH$_2$OAr), 1.59 (m, 2H, NHCH$_2$C*H*$_2$), 1.47 (m, 6H, *CH*$_2$CH$_2$CH$_2$OAr), 1.32 (m, 2H, NHCH$_2$CH$_2$C*H*$_2$), 1.29 (m, 48H, (C*H*$_2$)$_8$), 0.98 (t, *J* = 7.3 Hz, 3H, NH(CH$_2$)$_3$C*H*$_3$), 0.90 (t, *J* = 6.8 Hz, 9H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.4 (*C*ONH), 153.1 (aromatic *C*(3) and *C*(5)), 141.1 (aromatic *C*(4)), 129.9 (aromatic *C*(1)), 105.7 (aromatic *C*(2) and *C*(6)), 73.5 (*C*H$_2$OAr *para* position), 69.4 (*C*H$_2$OAr *meta* positions), 39.9 (NH*C*H$_2$), 31.9 (*C*H$_2$CH$_2$CH$_3$), 31.8 (NHCH$_2$*C*H$_2$), 29.74 ((*C*H$_2$)$_8$), 29.72 ((*C*H$_2$)$_8$), 29.67 ((*C*H$_2$)$_8$), 29.66 ((*C*H$_2$)$_8$), 29.60 ((*C*H$_2$)$_8$), 29.42 ((*C*H$_2$)$_8$), 29.38 ((*C*H$_2$)$_8$), 26.09 ((*C*H$_2$)$_8$), 22.7 (*C*H$_2$CH$_3$), 20.2 (NH(CH$_2$)$_2$*C*H$_2$), 14.1 (*C*H$_3$), 13.8 (NH(CH$_2$)$_3$*C*H$_3$). IR (solid): 1629 cm^{-1} (amide I), 1580 cm^{-1} (Ar C=C), 1555 cm^{-1} (amide II),

1503 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m/z*): $[M + H]^+$ calcd for $C_{47}H_{88}NO_4$ 730.7; found, 731.0; $[M + Na]^+$ calcd for $C_{47}H_{87}NO_4Na$ 752.6; found, 753.1. GPC: M_n = 760, M_w/M_n = 1.05.

Butyl 3,4,5-tri[4'-(*n*-dodecan-1-yloxy)benzyloxy]benzamide (11)

To a round-bottom flask, **7** (0.0485 g, 0.0417 mmol), butyl amine (0.0222 g, 0.3035 mmol), DIEA (200 μL, 1 mmol), and THF (5 mL) were added. The solution was stirred at room temperature for 6 h under a N_2 atmosphere. The volatiles were removed by rotary evaporation. The solid was purified by column chromatography (SiO_2, CH_2Cl_2) to give **11** (0.0279 g, 64%) as a solid. TLC (SiO_2, CH_2Cl_2): R_f = 0.74. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33 (d, *J* = 8.6 Hz, 4H, aromatic C(3')*H* and C(5')*H*), 7.27 (d, *J* = 8.4 Hz, 2H, aromatic C(3')*H* and C(5')*H*), 7.04 (s, 2H, aromatic C(2)*H* and C(6)*H*), 6.91 (d, *J* = 8.6 Hz, 4H, aromatic C(2')*H* and C(6')*H*), 6.78 (d, *J* = 8.6 Hz, 2H, aromatic C(2')*H* and C(6')*H*), 5.05 (s, 4H, ArCH_2OAr), 5.00 (s, 2H, ArCH_2OAr), 3.96 (t, *J* = 6.6 Hz, 4H, CH_2OAr), 3.92 (t, *J* = 6.6 Hz, 2H, CH_2OAr), 3.43 (d, *J* = 5.4 Hz, t, *J* = 7.0 Hz, 2H, NHCH_2), 1.83 (m, 6H, CH_2CH_2OAr), 1.60 (m, 2H, $NHCH_2CH_2$), 1.47 (m, 6H, $CH_2CH_2CH_2$OAr), 1.32 (m, 2H, $NHCH_2CH_2CH_2$), 1.29 (m, 48H, $(CH_2)_8$), 0.98 (t, *J* = 7.3 Hz, 3H, $NH(CH_2)_3CH_3$), 0.90 (t, *J* = 6.8 Hz, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.2 (*C*ONH), 159.1 (aromatic *C*(5)), 159.0 (aromatic *C*(3), 152.8 (aromatic *C*(4')), 130.3 (aromatic *C*(1)), 129.5 (aromatic *C*(2') and (6')), 129.3 (aromatic *C*(1')), 128.7 (aromatic *C*O(1)), 114.5 (aromatic *C*(3') and (5')), 114.1 (aromatic *C*(2) and (6)), 107.1 (aromatic *C*(4)), 74.8 (CH_2OAr *para* position) 71.4 (CH_2OAr *meta* position), 68.1 (CH_2O), 68.0 (CH_2O), 39.9 ($NHCH_2$), 31.9 ($CH_2CH_2CH_3$), 31.7 ($NHCH_2CH_2$), 29.70 ($(CH_2)_8$), 29.66 ($(CH_2)_8$), 29.64 ($(CH_2)_8$), 29.46 ($(CH_2)_8$), 29.37 ($(CH_2)_8$), 29.32 ($(CH_2)_8$), 26.09 ($(CH_2)_8$), 22.7 (CH_2CH_3), 20.2 ($NH(CH_2)_2CH_2$), 14.1 (CH_3), 13.8 ($NH(CH_2)_3CH_3$). IR (solid): 1638 cm^{-1} (amide I), 1613 cm^{-1} (Ar C=C), 1582 cm^{-1} (Ar C=C), 1544 cm^{-1} (amide II), 1513 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m/z*): $[M + Na]^+$ calcd for $C_{68}H_{105}NNaO_7$ 1,070.8; found, 1,071.4. GPC: M_n = 1,130, M_w/M_n = 1.08.

Butyl 3,5-bis[3',4'-bis(*n*-dodecan-1-yloxy)benzyloxyl]benzamide (12)

To a round-bottom flask, **8** (0.1044 g, 0.0844 mmol), butyl amine (0.0211 g, 0.2885 mmol), DIEA (500 μL, 3 mmol), and THF (10 mL) were added. The solution was stirred at room temperature for 6 h under a N_2 atmosphere. The volatiles were removed by rotary evaporation. The solid was purified by column chromatography (SiO_2, CH_2Cl_2) to give **12** (0.0814 g, 86%) as a solid. TLC (SiO_2, CH_2Cl_2): R_f = 0.79. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.00 (d, ^4J = 2.2 Hz, 2H, aromatic C(2)*H*, C(6)*H*), 6.97 (d, ^3J = 8.2 Hz, 2H, aromatic C(6')*H*), 6.94 (d, ^3J = 8.2 Hz, 2H, aromatic C(5')*H*), 6.90 (s, 2H, aromatic C(2')*H*), 6.74 (t, ^4J = 2.4 Hz, 1H, aromatic C(4)*H*), 4.97 (s, 4H, ArCH_2OAr), 4.02 (t, J = 6.5 Hz, 4H, CH_2OAr), 4.01 (t, J = 6.5 Hz, 4H, CH_2OAr), 3.45 (d, J = 5.4 Hz, t, J = 7.0 Hz, 2H, NHCH_2), 1.83 (m, 8H, CH_2CH$_2$OAr), 1.60 (m, 2H, NHCH$_2$CH_2), 1.49 (m, 8H, CH_2CH$_2$CH$_2$OAr), 1.32 (m, 2H, NHCH$_2$CH$_2$CH_2), 1.29 (m, 64H, (CH_2)$_8$), 0.98 (t, J = 7.4 Hz, 3H, NH(CH$_2$)$_3$CH_3), 0.90 (t, J = 6.2 Hz, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.2 (CONH), 160.1 (aromatic *C*(3) and (5)), 149.4 (aromatic *C*(3')), 149.2 (aromatic *C*(4')), 137.1 (aromatic *C*(1)), 129.0 (aromatic *C*(1')), 120.6 (aromatic *C*(6')), 113.8 (aromatic *C*(5')), 113.7 (aromatic *C*(2')), 106.6 (aromatic *C*(2) and C(6)), 104.8 (aromatic *C*(4)), 70.5 (Ar*C*H$_2$OAr), 69.4 (CH$_2$*C*H$_2$O), 69.3 (CH$_2$*C*H$_2$O), 39.8 (NH*C*H$_2$), 31.9 (CH$_3$CH$_2$*C*H$_2$), 31.7 ((NHCH$_2$*C*H$_2$), 29.73 ((*C*H$_2$)$_8$), 29.68 ((*C*H$_2$)$_8$), 29.48 ((*C*H$_2$)$_8$), 29.46 ((*C*H$_2$)$_8$), 29.39 ((*C*H$_2$)$_8$), 29.35 ((*C*H$_2$)$_8$), 29.32 ((*C*H$_2$)$_8$), 26.09 ((*C*H$_2$)$_8$), 26.07 ((*C*H$_2$)$_8$), 25.5 ((*C*H$_2$)$_8$), 24.7 ((*C*H$_2$)$_8$), 22.7 (CH$_3$*C*H$_2$), 20.2 (NHCH$_2$CH$_2$*C*H$_2$), 14.1 (*C*H$_3$), 13.8 (NH(CH$_2$)$_3$*C*H$_3$). IR (solid): 1638 cm^{-1} (amide I), 1590 cm^{-1} (Ar C=C), 1547 cm^{-1} (amide II), 1519 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m*/*z*): [M + Na]$^+$ calcd for $C_{73}H_{123}NNaO_7$ 1,148.9; found, 1,149.7. GPC: M_n = 1,250, M_w/M_n = 1.10.

Butyl 3,5-bis(3',4'-bis[4''-(*n*-dodecan-1-yloxy)benzyloxy]benzyloxy)benzamide (13)

To a round-bottom flask, **9** (0.0445 g, 0.0267 mmol), butyl amine (0.0027 g, 0.037 mmol), DIEA (90 μL, 0.5 mmol), and THF (2.7 mL) were added. The solution was stirred at room temperature for 5 h under a N_2 atmosphere. The volatiles were removed by rotary evaporation. The solid was purified by column chromatography (SiO_2, CH_2Cl_2) to give **13** (0.0376 g, 91%) as a solid. TLC (SiO_2, 95:5 CH_2Cl_2/MeOH):

R_f = 0.29. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.35 (dd, ^3J = 7.9 Hz, ^4J = 3.3 Hz, 8H, aromatic C(2")*H* and C(6")*H*), 7.05 (s, 2H, aromatic C(2)*H* and C(6)*H*), 6.96 (s, 2H, aromatic C(6')*H*), 6.94 (s, 4H, aromatic C(2')*H* and C(5')*H*), 6.88 (dd, ^3J = 7.9 Hz, ^4J = 3.3 Hz, 8H, aromatic C(3")*H* and C(5")*H*), 6.70 (s, 1H, aromatic C(4)*H*), 6.04 (t, *J* = 5.4 Hz, 1H, N*H*), 5.08 (s, 8H, ArCH_2O), 4.95 (s, 4H, ArCH_2O), 3.96 (t, *J* = 6.2 Hz, 4H, CH_2OAr), 3.95 (t, *J* = 6.2 Hz, 4H, CH_2OAr), 3.45 (d, *J* = 5.4 Hz, t, *J* = 7.0 Hz, 2H, NHCH_2), 1.80 (m, 8H, CH_2CH_2OAr), 1.60 (m, 2H, $NHCH_2CH_2$), 1.47 (m, 8H, $CH_2CH_2CH_2$OAr), 1.32 (m, 2H, $NHCH_2CH_2CH_2$), 1.28 (m, 64H, $(CH_2)_8$), 0.98 (t, *J* = 7.4 Hz, 3H, $NH(CH_2)_3CH_3$), 0.90 (t, *J* = 6.2 Hz, 12H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 167.2 (*C*ONH), 160.0 (aromatic *C*(3) and *C*(5)), 158.9 (aromatic *C*(4")), 149.3 (aromatic *C*(3')), 149.1 (aromatic *C*(4')), 129.6 (aromatic *C*(1)), 129.1 (aromatic *C*(1')), 129.1 (aromatic C(1"), 129.0 (aromatic *C*(2"), and *C*(6")), 121.0 (aromatic *C*(6')), 115.3 (aromatic *C*(5')), 115.0 (aromatic *C*(2')), 114.5 (aromatic *C*(3") and *C*(5")), 106.0 (aromatic *C*(2) and *C*(6)), 104.8 (aromatic *C*(4)), 71.3 (Ar*C*H_2OAr 3,5-(3',4') positions), 70.3 (Ar*C*H_2OAr 3,5 positions), 68.1 (CH_2OAr), 39.8 (NH*C*H_2), 31.9 ($CH_3CH_2CH_2$), 31.7 ((NHCH$_2$*C*H_2), 29.69 (*C*H_2CH_2O), 29.66 ((*C*H_2)$_5$), 29.63 ((*C*H_2)$_5$), 29.61 ((*C*H_2)$_5$), 29.45 ((*C*H_2)$_5$), 29.37 ((*C*H_2)$_5$), 29.32 ($CH_3(CH_2)_2CH_2$), 26.1 (*C*$H_2CH_2CH_2$O), 22.7 (CH_3CH_2), 20.2 ((NHCH$_2$CH$_2$*C*H_2), 14.2 (*C*H_3), 13.8 ($NH(CH_2)_3CH_3$). IR (solid): 1633 cm^{-1} (amide I), 1612 cm^{-1} (Ar C=C), 1589 cm^{-1} (Ar C=C), 1547 cm^{-1} (amide II), 1517 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m*/*z*): $[M + Ag]^+$ calcd for $C_{101}H_{147}NO_{11}Na$ 1,574.1; found, 1,574.1. GPC: M_n = 2,510, M_w/M_n = 1.05.

Propyl 3,4,5-tris(*n*-dodecan-1-yloxy)benzoate (S1)[2]

A suspension of K_2CO_3 (17.67 g, 127.9 mmol) in 1-bromodecane (10.1 mL, 41.8 mmol) and DMF (200 mL) was sparged with N_2 for 15 min. A solution of propyl gallate (2.96 g, 13.9 mmol) in DMF (50 mL) was sparged with N_2 for 15 min, and then added dropwise to the solution. The solution was stirred at 80 °C for 24 h under a N_2 atmosphere. The product was precipitated by diluting the reaction mixture in ice-water (400 mL). The precipitate was collected by filtration, and dried under vacuum. The resulting solid was purified by column chromatography (SiO_2, hex to 95:5 hex/EtOAc). Recrystallization of the

crude solid from acetone (100 mL), by cooling to 10 °C, produced **S1** (8.51 g, 85%) as a colorless solid. TLC (SiO_2, 95:5 hex/EtOAc): R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.25 (s, 2H, Ar*H*), 4.25 (t, *J* = 6.7 Hz, 2H, CO_2CH_2), 4.01 (t, *J* = 6.5 Hz, 4H, CH_2OAr), 4.01 (t, *J* = 6.5 Hz, 2H, CH_2OAr), 1.81 (m, 6H, CH_2CH_2OAr), 1.76 (m, 2H, $CO_2CH_2CH_2$), 1.47 (m, 6H, $CH_2CH_2CH_2OAr$), 1.28 (overlapped m, 54H, $(CH_2)_9$), 1.04 (t, *J* = 7.5 Hz, 3H $CO_2CH_2CH_2CH_3$), 0.90 (t, *J* = 6.8 Hz, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.5 (CO_2), 152.7 (aromatic *C*(3) and *C*(5)), 142.3 (aromatic *C*(4)), 124.9 (aromatic *C*(1)), 107.9 (aromatic *C*(2) and *C*(6)), 73.4 (CH_2OAr), 69.1 (CH_2OAr), 66.4 (CO_2CH_2), 31.9 ($(CH_2)_9$), 30.4 ($(CH_2)_9$), 29.7 ($(CH_2)_9$), 29.6 ($(CH_2)_9$), 29.5 ($(CH_2)_9$), 29.4 ($(CH_2)_9$), 29.3 ($(CH_2)_9$), 29.2 ($(CH_2)_9$), 26.0 ($(CH_2)_9$), 22.6 (CH_2CH_3), 22.1 ($OCH_2CH_2CH_3$), 14.1 (CH_3), 10.5 ($OCH_2CH_2CH_3$). IR (solid): 1711 cm^{-1} (C=O), 1588 cm^{-1} (Ar C=C), 1505 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m*/*z*): $[M + Na]^+$ calcd for $C_{46}H_{84}NaO_5$ 739.6; found, 740.3. GPC: M_n = 945, M_w/M_n = 1.06. Spectral data agree with those previously reported.[3]

Methyl 3,4,5-tri[4'-(*n*-dodecan-1-yloxy)benzyloxy]benzoate (S2)[4]

To a three-neck, round-bottom flask, methyl gallate (0.0576 g, 0.313 mmol), K_2CO_3 (0.4046 g, 2.927 mmol), and DMF (5 mL) were added and sparged with N_2. An addition funnel was charged with 4-(*n*-dodecan-1-yloxy)benzyl chloride[4] (0.3100 g, 0.9971 mmol) and DMF (5 mL). The solution was sparged with N_2 then added dropwise to the reaction. The reaction mixture was heated at 80 °C and stirred for 15 h under a N_2 atmosphere. The product was precipitated from solution by pouring over ice-water (150 mL). The mixture was filtered. The solid was purified by column chromatography (SiO_2, 95:5 hex/EtOAc) to produce **S2** (0.1341g, 43%) as a colorless solid. TLC (SiO_2, CH_2Cl_2): R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 (s, 2H, aromatic C(2)*H* and C(6)*H*), 7.34 (d, *J* = 8.6 Hz, 2H, aromatic C(3')*H* and C(5')*H*), 7.24 (d, *J* = 8.6 Hz, 4H aromatic C(3')*H* and C(5')*H*),), 6.90 (d, *J* = 8.7 Hz, 4H, aromatic C(2')*H* and C(6')*H*), 6.76 (d, *J* = 8.6 Hz, 2H, aromatic C(2')*H* and C(6')*H*), 5.06 (s, 4H, C(3)OCH_2 and C(5)OCH_2), 5.02 (s, 2H, C(4)OCH_2), 3.96 (t, *J* = 6.6 Hz, 4H, CH_2OAr), 3.92 (t, *J* = 6.6 Hz, 2H, CH_2OAr), 3.90 (s, 3H, CO_2CH_3), 1.79 (m, 6H, CH_2CH_2OAr), 1.48 (m, 6H, $CH_2CH_2CH_2OAr$), 1.28 (overlapped m,

48H, $(CH_2)_8$), 0.90 (t, J = 6.7 Hz, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.8 (*C*=O), 159.02 (aromatic *C*(3) and *C*(5)), 158.97 (aromatic *C*(3) and *C*(5)), 152.7 (aromatic *C*(4')), 130.3 (aromatic *C*(1)), 129.5 (aromatic *C*(2') and *C*(6')), 129.3 (aromatic *C*(2') and *C*(6')), 128.6 (aromatic *C*(1')), 114.5 (aromatic *C*(3') and *C*(5')), 114.1 (aromatic *C*(2) and *C*(6)), 109.2 (aromatic *C*(4)), 74.7 (Ar*C*H_2OAr), 71.1 (Ar*C*H_2OAr), 68.1 (*C*H_2O), 68.0 (*C*H_2O), 52.2 (CO_2*C*H_3) 32.0 (*C*H_2CH$_2$CH$_3$), 29.7 ((*C*H_2)$_8$), 29.7 ((*C*H_2)$_8$), 29.7 ((*C*H_2)$_8$), 29.6 ((*C*H_2)$_8$), 29.5 ((*C*H_2)$_8$), 29.5 ((*C*H_2)$_8$), 29.4 ((*C*H_2)$_8$), 29.3 ((*C*H_2)$_8$), 26.1 ((*C*H_2)$_8$), 22.7 (*C*H_2CH$_3$), 14.2 (*C*H_3). IR (solid): 1698 cm^{-1} (C=O), 1614 cm^{-1} (Ar C=C), 1588 cm^{-1} (Ar C=C), 1512 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m*/*z*): $[M + Na]^+$ calcd for $C_{65}H_{98}NaO_8$ 1029.7; found, 1030.6. GPC: M_n = 1383, M_w/M_n = 1.09. NMR spectral data agree with those previously reported.[4]

Methyl 3,5-bis[3',4'-bis(*n*-dodecan-1-yloxy)benzyloxyl]benzoate (S3)[5]

A suspension of K_2CO_3 (2.72 g, 5.50 mmol), methyl 3,5 dihydroxybenzoate (0.33 g, 1.9 mmol) and DMF (20 mL) was sparged with N_2 for 15 min. A solution of 3,4-bis(*n*-dodecan-1-yloxy)benzyl chloride[5] (2.06 g, 4.16 mmol) and DMF (20 mL) was sparged with N_2 for 15 min, then added dropwise to the solution. The reaction was heated at 80 °C under N_2 atmosphere for 17 h. The product was precipitated by pouring the reaction mixture over ice (300 mL). After the ice melted, the precipitate was collected by filtration. The product was purified by column chromatography (SiO_2, 9:1 hex/EtOAc). Recrystallization of the crude solid from acetone/CH_2Cl_2 (30 mL), by cooling to 10 °C, produced **S3** (1.20 g, 57 %) as a colorless crystals. TLC (SiO_2, 9:1 hex/EtOAc): R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 (d, ^4J = 2.4 Hz, 2H, aromatic C(2)*H*, C(6)*H*), 6.95 (s, 2H, aromatic C(2')*H*), 6.92 (d, ^3J = 8.2 Hz, 2H, aromatic C(6')*H*), 6.90 (d, ^3J = 8.2 Hz, 2H, aromatic C(5')*H*), 6.82 (t, ^4J = 2.4 Hz, 1H, aromatic C(4)*H*), 5.00 (s, 4H, ArCH_2OAr), 4.04 (t, J = 6.5 Hz, 8H, CH_2OAr), 4.03 (t, J = 6.5 Hz, 8H, CH_2OAr), 3.94 (s, 3H, CO_2CH_3), 1.85 (m, 8H, CH_2CH$_2$OAr), 1.50 (m, 8H, CH_2CH$_2$CH$_2$OAr), 1.29 (m, 64H, CH$_3$(CH_2)$_8$), 0.88 (t, J = 6.8 Hz, 6H, CH_3), 0.88 (t, J = 6.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.9 (CO_2CH_3), 159.9 (aromatic *C*(3) and (5)), 149.4 (aromatic *C*(3')), 149.2 (aromatic *C*(4')), 132.0 (aromatic *C*(1)), 128.9 (aromatic *C*(1')), 120.6 (aromatic *C*(6')), 113.8 (aromatic *C*(5')), 113.7 (aromatic *C*(2')), 108.3 (aromatic *C*(2) and C(6)), 107.3

(aromatic *C*(4)), 70.4 (Ar*C*H_2OAr), 69.3 (CH_2*C*H_2OAr), 52.3 (CO_2*C*H_3), 32.0 (*C*$H_2CH_2CH_3$), 29.7 ((*C*H_2)$_9$), 29.7 ((*C*H_2)$_9$), 29.7 ((*C*H_2)$_9$), 29.5 ((*C*H_2)$_9$), 29.5 ((*C*H_2)$_9$), 29.4 ((*C*H_2)$_9$), 29.3 ((*C*H_2)$_9$), 29.3 ((*C*H_2)$_9$), 26.1 ((*C*H_2)$_9$), 26.1 ((*C*H_2)$_9$), 22.7 (*C*H_2CH_3), 14.1 (*C*H_3). IR (solid): 1695 cm^{-1} (C=O), 1596 cm^{-1} (Ar C=C), 1519 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m*/*z*): $[M + Na]^+$ calcd for $C_{70}H_{116}NaO_8$ 1107.9; found, 1108.8. GPC: M_n = 1560, M_w/M_n = 1.09. Spectral data agree with those previously reported.[5]

Methyl 3,5-Bis(3',4'-bis[4"-(*n*-dodecan-1-yloxy)benzyloxy]benzyloxy)benzoate (S4)[6]

To a three-neck round-bottom flask, 3,4-bis[4-(*n*-dodecan-1-yloxy)benzyloxy]benzyl chloride[7] (2.2736 g, 3.2161 mmol), K_2CO_3 (1.3307 g, 9.6281 mmol), and DMF (5 mL) were added. To an addition funnel, methyl 3,5-dihydroxybenzoate (0.2396 g, 1.425 mmol) and DMF (20 mL) were added. Both mixtures were sparged with N_2 for 15 min to degas. The flask was heated to 80 °C under a N_2 atmosphere and the methyl 3,5-dihydroxybenzoate solution was added dropwise from the addition funnel. The reaction was heated at 80 °C for 16 h under a N_2 atmosphere, and then cooled to room temperature. The reaction mixture was poured over ice (400 mL). The precipitate that formed was collected by filtration. The solid was purified by column chromatography (SiO_2, CH_2Cl_2). Recrystallization of the crude solid from acetone (10 mL), by cooling to 10 °C, produced **S4** (0.9348 g, 43%) as a colorless solid. TLC (SiO_2, CH_2Cl_2): R_f = 0.26. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.35 (d, *J* = 7.9 Hz, 8H, aromatic C(2")*H* and C(6")*H*), 7.33 (d, ^4J = 2.2 Hz, 2H, aromatic C(2)*H* and C(6)*H*), 7.07 (s, 2H, aromatic C(6')*H*), 6.96 (s, 4H, aromatic C(2')*H* and C(5')*H*), 6.89 (d, *J* = 7.9 Hz, 8H, aromatic C(3")*H* and C(5")*H*), 6.82 (t, ^4J = 2.2 Hz, 1H, aromatic C(4)*H*), 5.09 (s, 8H, ArCH_2O), 4.98 (s, 4H, ArCH_2O), 3.94 (t, *J* = 6.2 Hz, 4H, CH_2OAr), 3.93 (t, *J* = 6.2 Hz, 4H, CH_2OAr), 3.93 (s, 3H, CO_2CH_3), 1.80 (m, 8H, CH_2CH_2OAr), 1.47 (m, 8H, $CH_2CH_2CH_2$OAr), 1.28 (m, 68H, (CH_2)$_8$), 0.90 (t, *J* = 6.2 Hz, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 166.8 (CO_2), 159.9 (aromatic *C*(3) and *C*(5)), 158.9 (aromatic *C*(4")), 149.3 (aromatic *C*(3')), 149.1 (aromatic *C*(4')), 132.0 (aromatic *C*(1)), 129.6 (aromatic *C*(1')), 129.1 (aromatic *C*(1"), *C*(2"), and *C*(6")), 129.0 (aromatic *C*(1"), *C*(2"), and *C*(6")), 121.0 (aromatic *C*(6')), 115.4 (aromatic *C*(5')), 114.9 (aromatic *C*(2')), 114.5 (aromatic *C*(3") and *C*(5")), 108.4 (aromatic *C*(2) and *C*(6)), 107.2 (aromatic *C*(4)), 71.3 (Ar*C*H_2OAr 3,5-

(3',4') positions), 70.2 (Ar*C*H_2OAr 3,5 positions), 68.0 (*C*H_2OAr), 52.3 (CO_2CH_3), 31.9 ($CH_3CH_2CH_2$), 29.7 (*C*H_2CH_2O), 29.7 ((CH_2)$_6$), 29.6 ((CH_2)$_6$), 29.6 ((CH_2)$_6$), 29.5 ((CH_2)$_6$), 29.4 ((CH_2)$_6$), 29.3 ((CH_2)$_6$), 26.1 (*C*$H_2CH_2CH_2O$), 22.7 (CH_3CH_2), 14.2 (*C*H_3). IR (solid): 1692 cm^{-1} (C=O), 1614 cm^{-1} (Ar C=C), 1599 cm^{-1} (Ar C=C), 1586 cm^{-1} (Ar C=C), 1515 cm^{-1} (Ar C=C). MALDI-TOF (DHB, *m*/*z*): $[M + Na]^+$ calcd for $C_{98}H_{140}NaO_{12}$ 1533.0; found, 1533.1. GPC: M_n = 2430, M_w/M_n = 1.08. Spectral data agree with those previously reported.[6]

References

1. D. A. Barkley, Y. Rokhlenko, J. E. Marine, R. David, D. Sahoo, M. D. Watson, T. Koga, C. O. Osuji and J. G. Rudick, *J. Am. Chem. Soc.*, 2017, **139**, 15977-15983.

2. V. Percec, D. Schlueter, J. C. Ronda, G. Johansson, G. Ungar and J. P. Zhou, *Macromolecules*, 1996, **29**, 1464-1472.

3. D. A. Barkley, T. Koga and J. G. Rudick, *Macromolecules*, 2015, **48**, 2849-2854.

4. V. Percec and J. Heck, *J. Polym. Sci., Part A: Polym. Chem.*, 1991, **29**, 591-597.

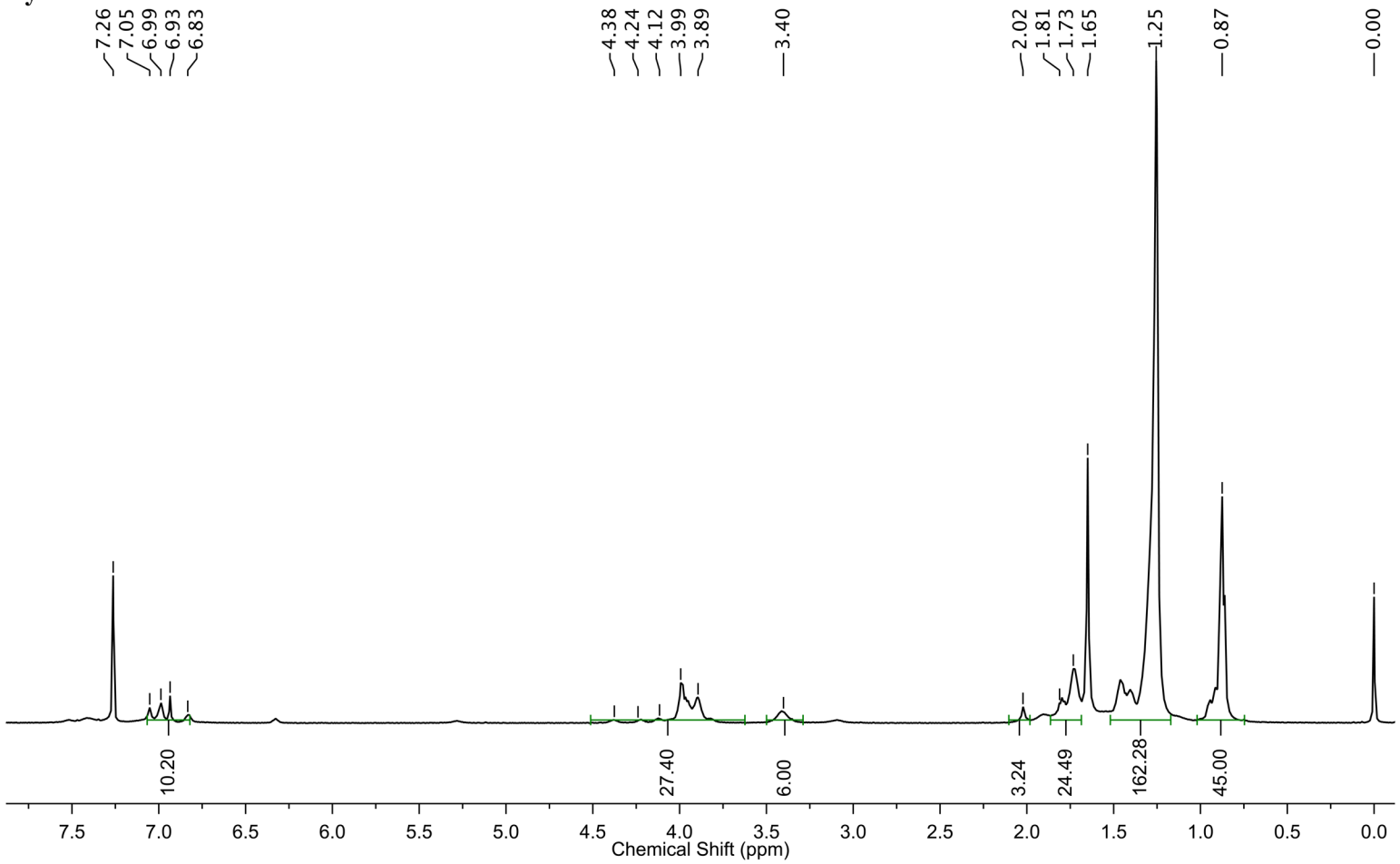
5. V. Percec, C.-H. Ahn, W.-D. Cho, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. D. Cheng, A. Zhang, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 1998, **120**, 8619-8631.

6. V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 2001, **123**, 1302-1315.

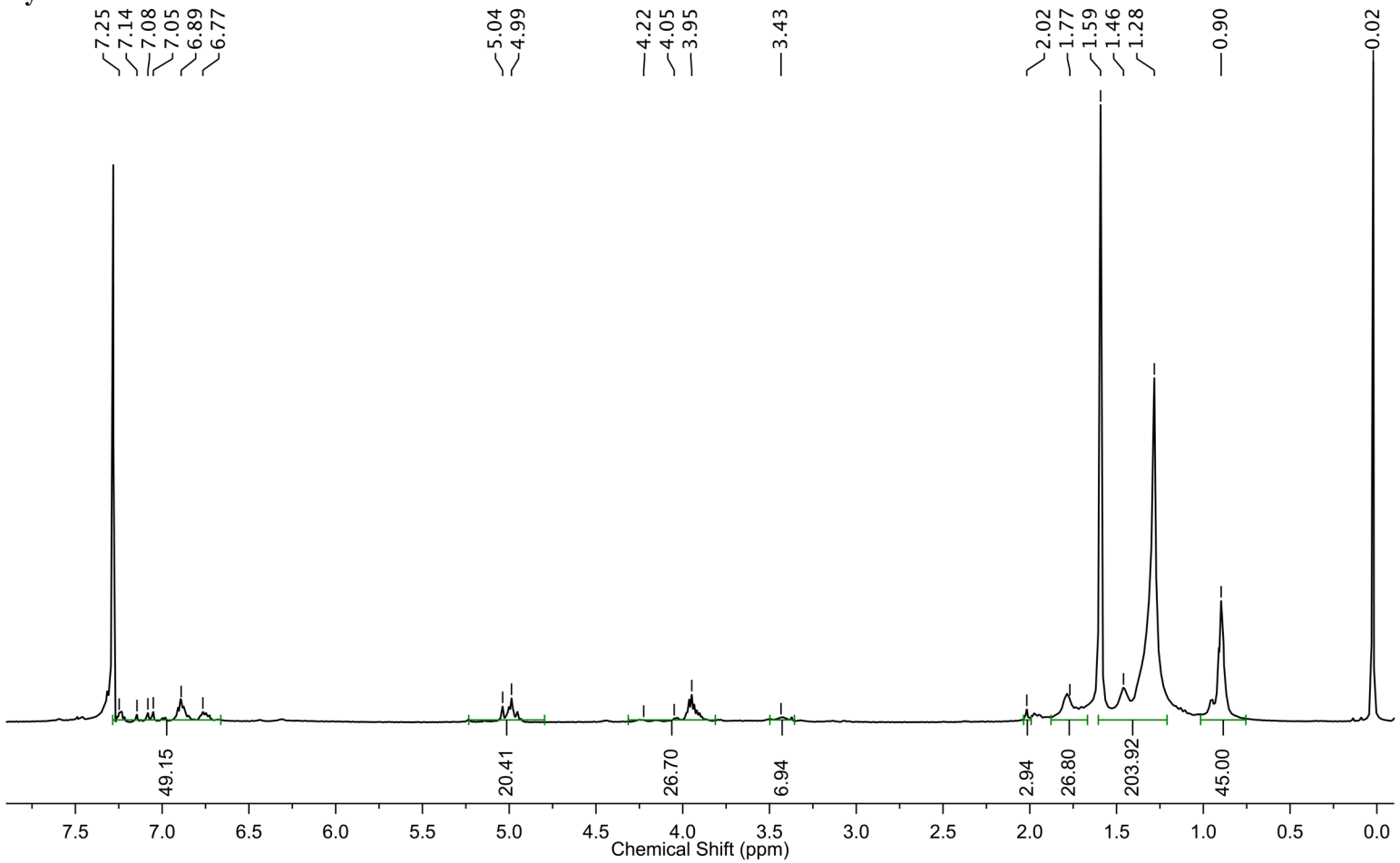
7. V. Percec, W.-D. Cho and G. Ungar, *J. Am. Chem. Soc.*, 2000, **122**, 10273-10281.

NMR Spectra

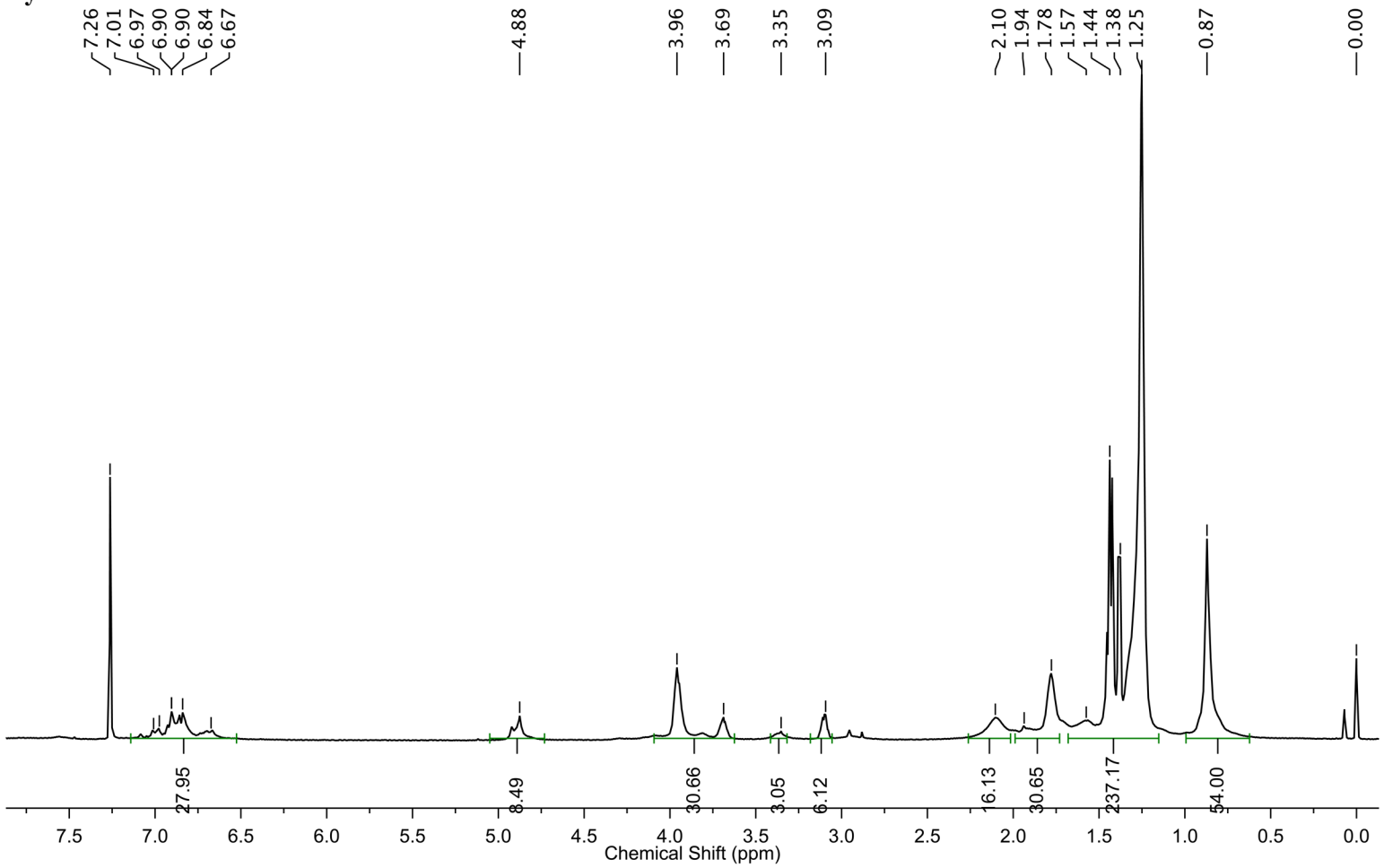
Hybrid 1



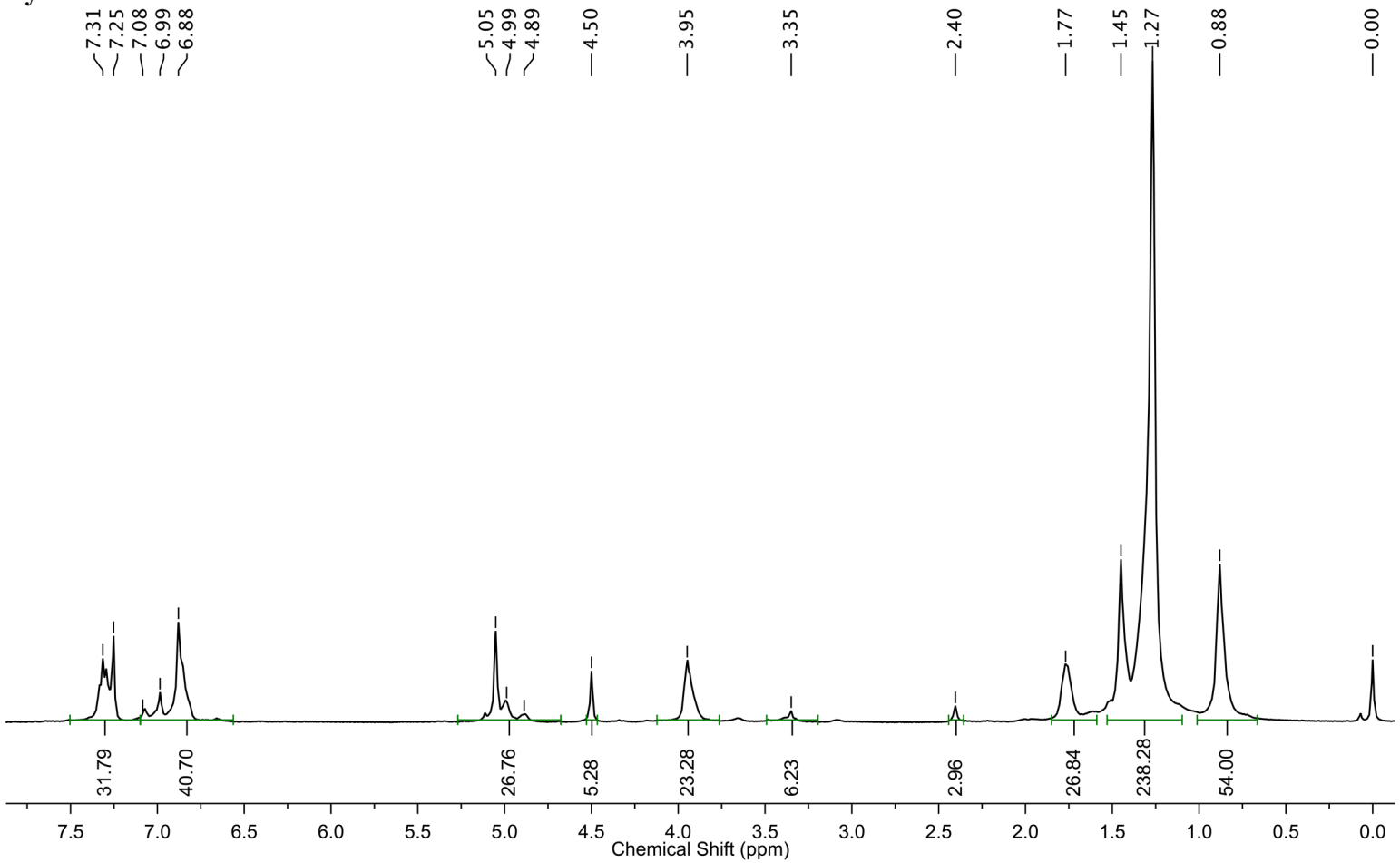
Hybrid 2


7.25
7.14
7.08
7.05
6.89
6.77
5.04
4.99
4.22
4.05
3.95
3.43
2.02
1.77
1.59
1.46
1.28
0.90
0.02
49.15
20.41
26.70
6.94
2.94
26.80
203.92
45.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

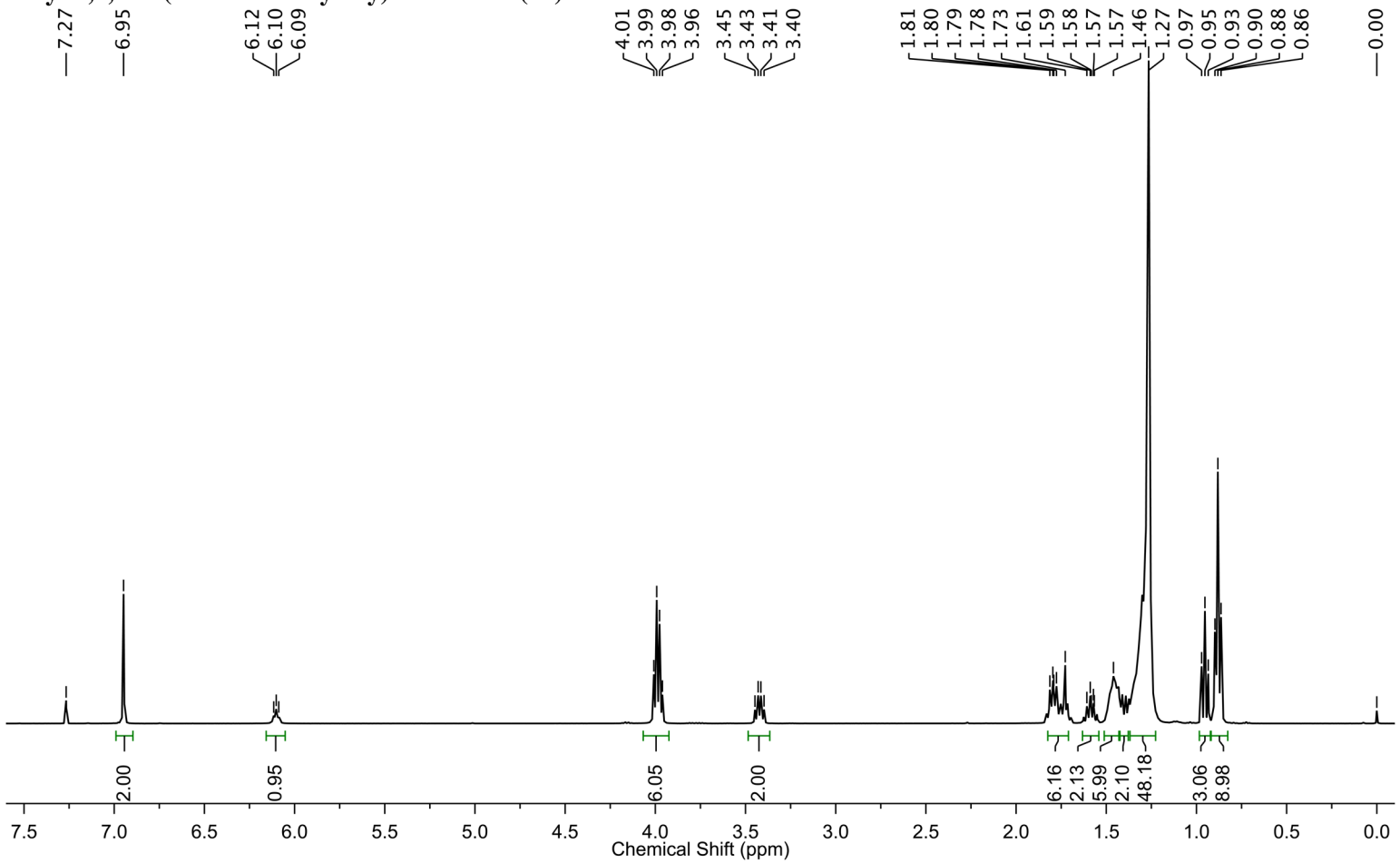
Hybrid 3


7.26
7.01
6.97
6.90
6.90
6.84
6.67
4.88
3.96
3.69
3.35
3.09
2.10
1.94
1.78
1.57
1.44
1.38
1.25
0.87
0.00
27.95
8.49
30.66
3.05
6.12
16.13
30.65
237.17
54.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

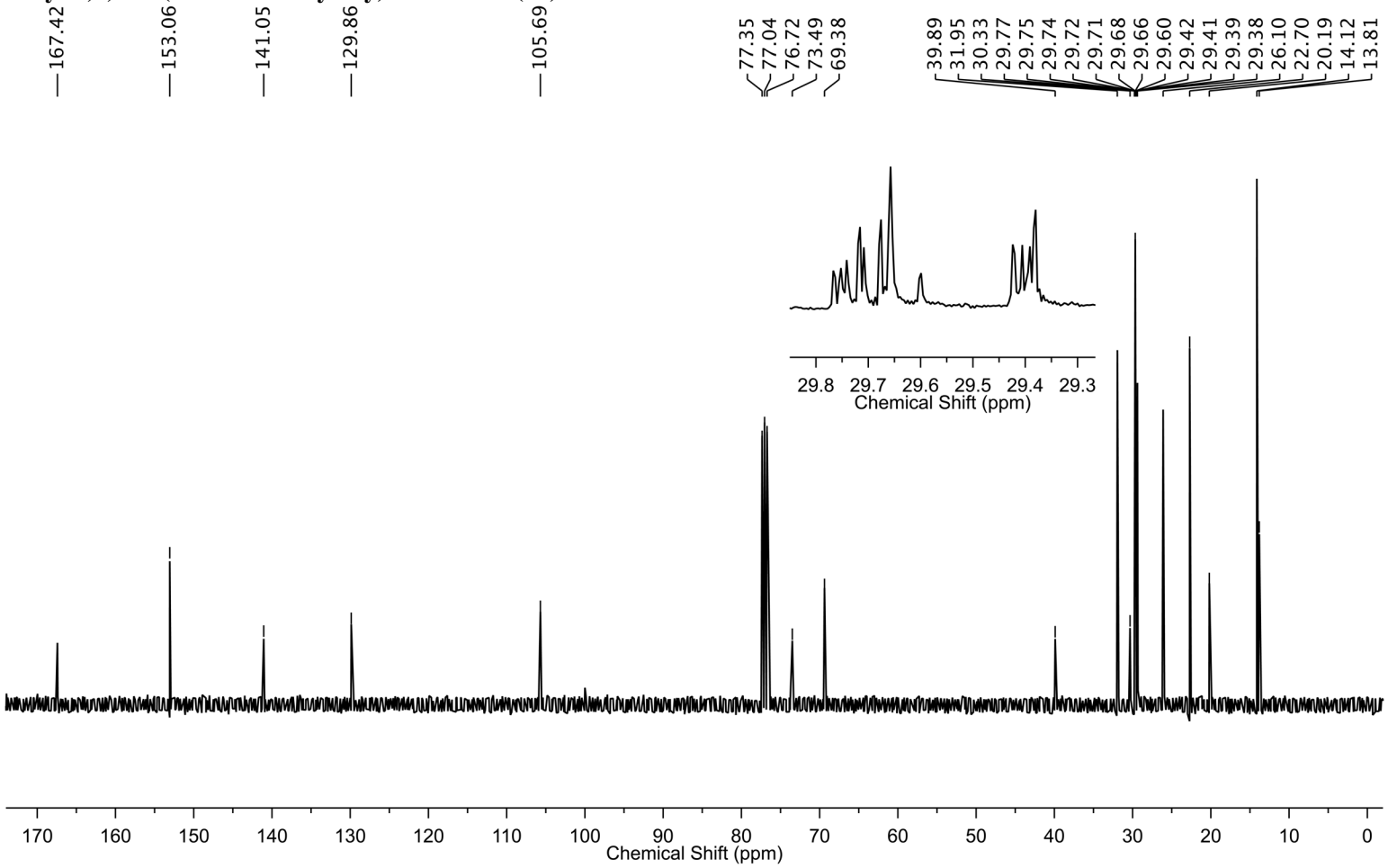
Hybrid 4


7.31
7.25
7.08
6.99
6.88
5.05
4.99
4.89
4.50
3.95
3.35
2.40
1.77
1.45
1.27
0.88
0.00
31.79
40.70
26.76
5.28
23.28
6.23
2.96
26.84
238.28
54.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

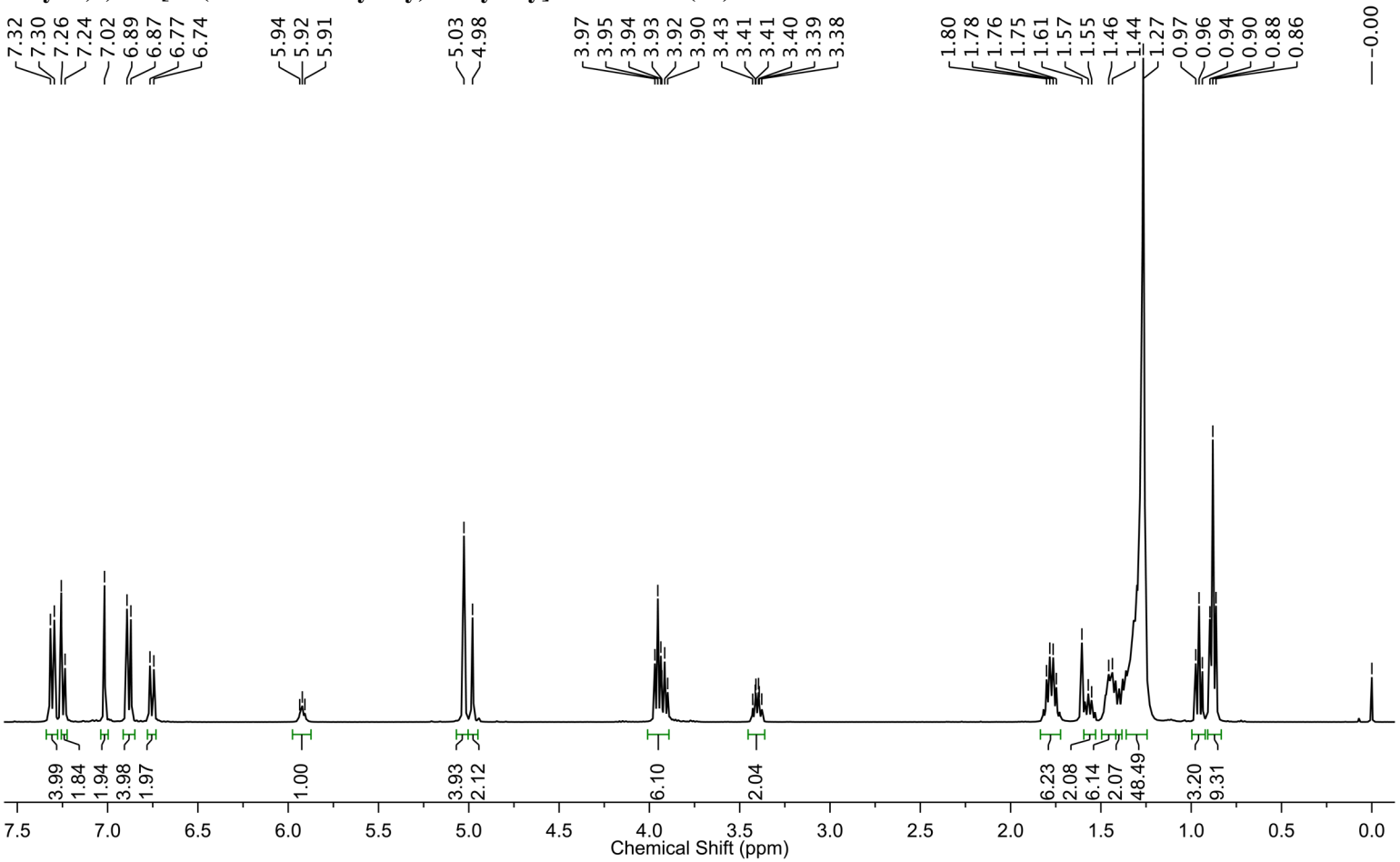
Butyl 3,4,5-tri(*n*-dodecan-1-yloxy)benzamide (10)



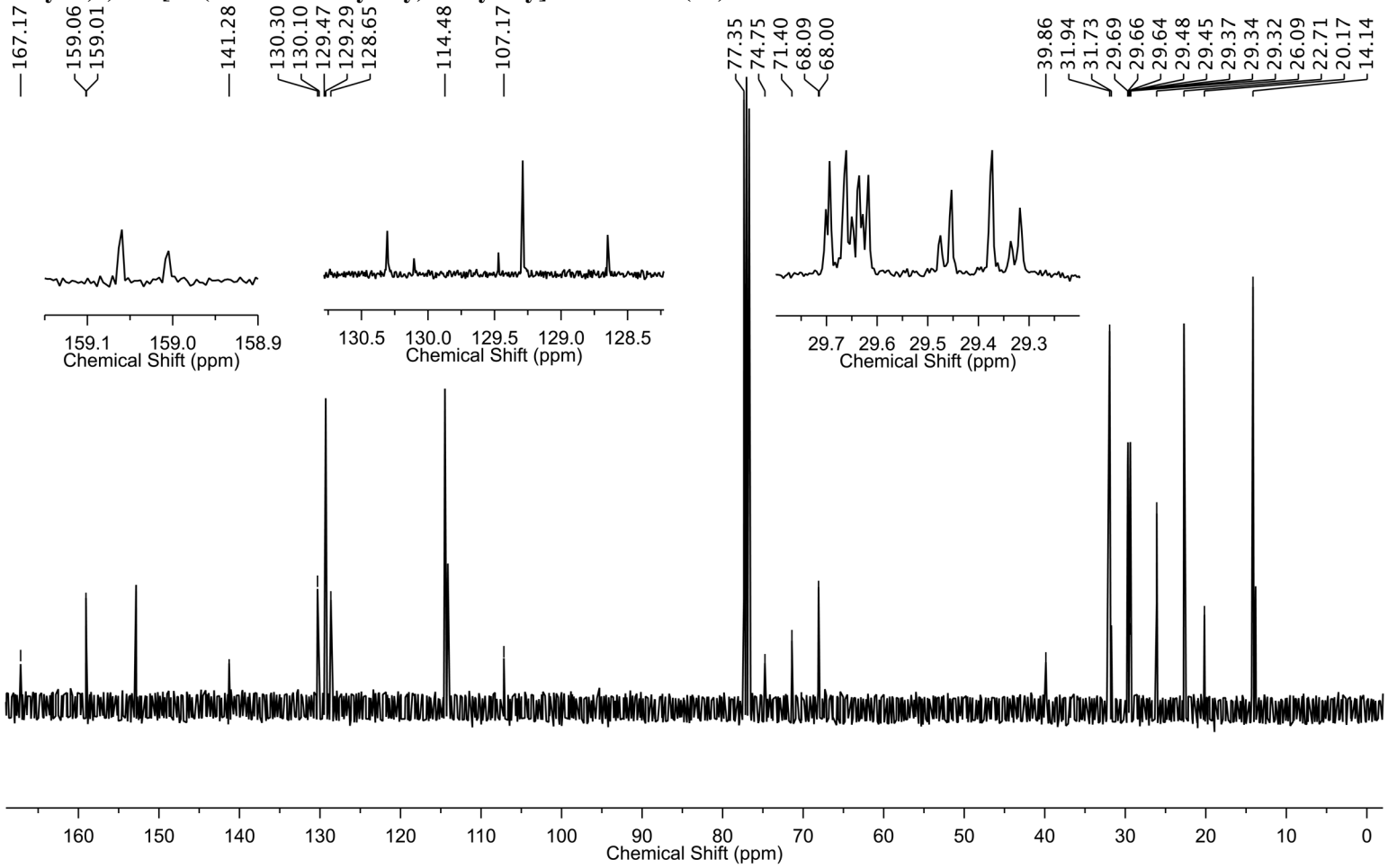
Butyl 3,4,5-tri(*n*-dodecan-1-yloxy)benzamide (10)



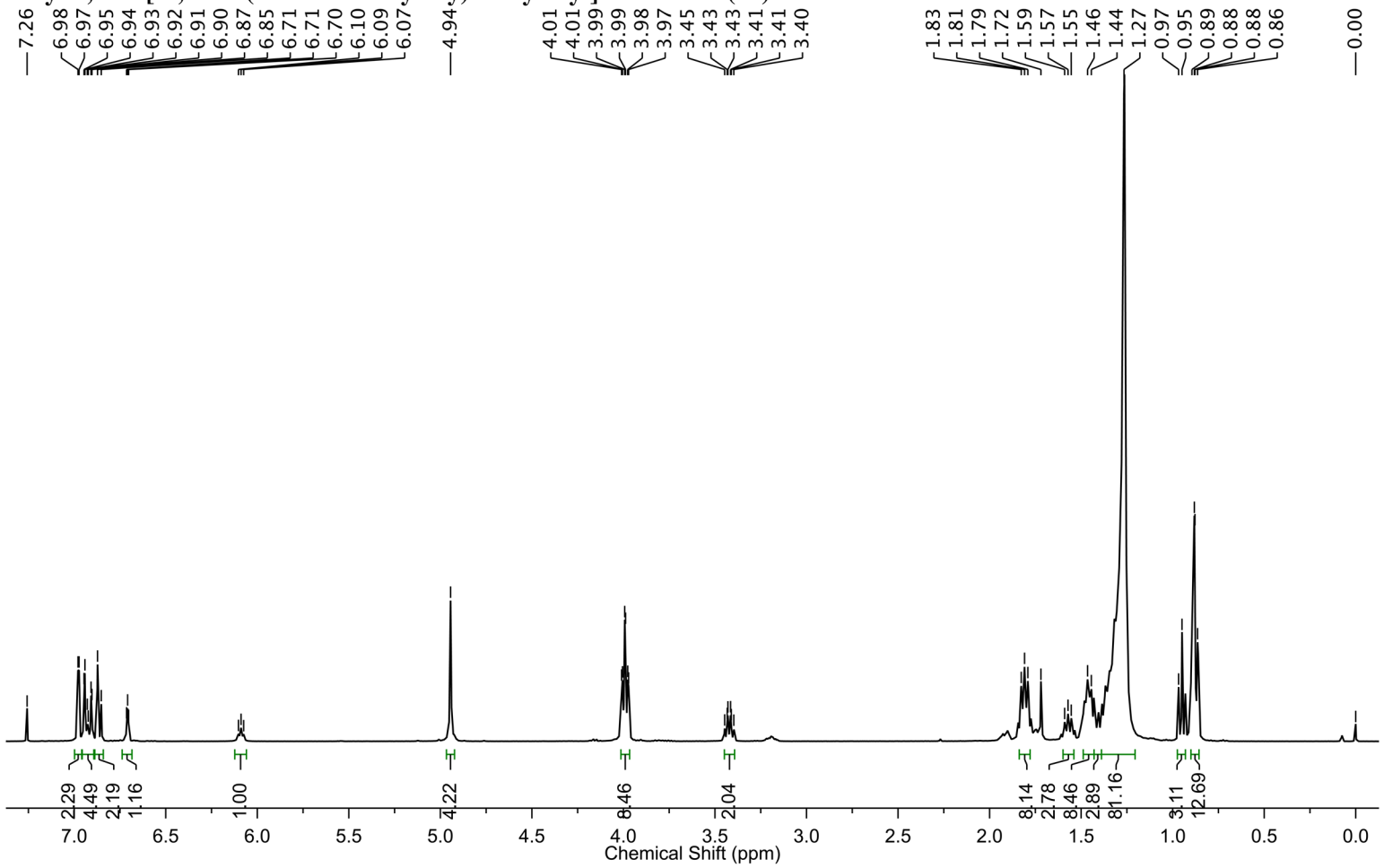
Butyl 3,4,5-tri[4'-(*n*-dodecan-1-yloxy)benzyloxy]benzamide (11)



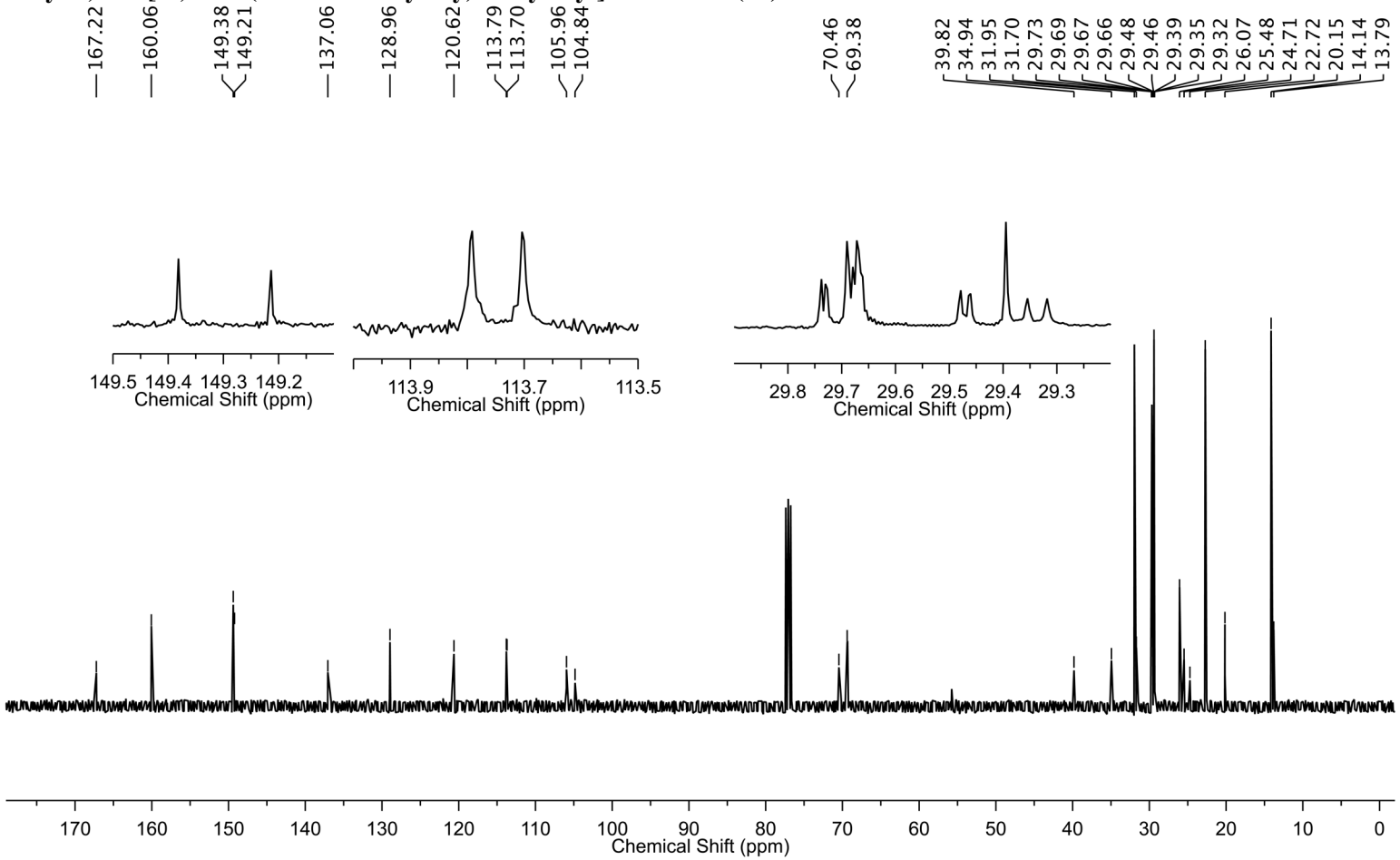
Butyl 3,4,5-tri[4'-(*n*-dodecan-1-yloxy)benzyloxy]benzamide (11)



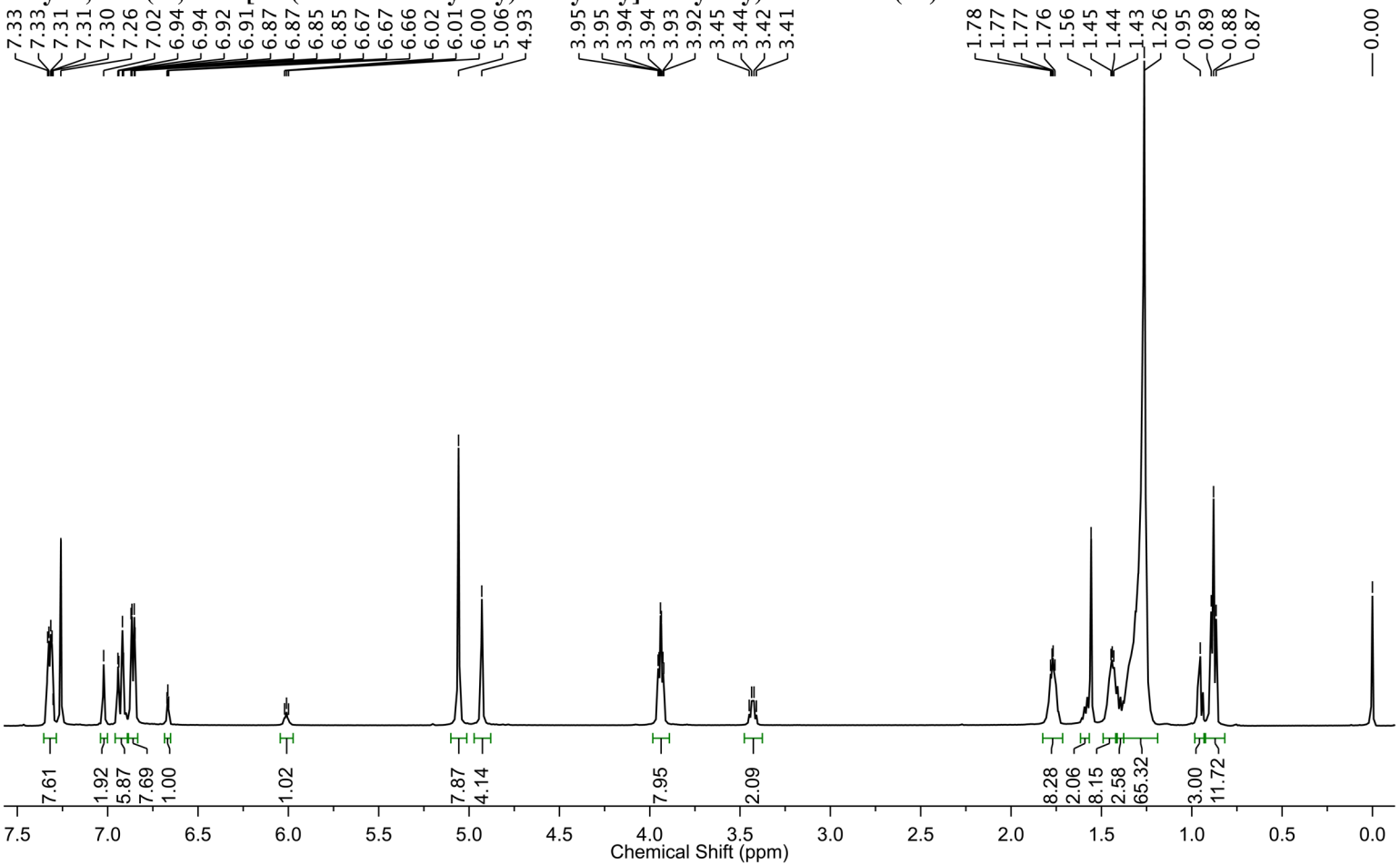
Butyl 3,5-bis[3',4'-bis(*n*-dodecan-1-yloxy)benzyloxyl]benzamide (12)



Butyl 3,5-bis[3',4'-bis(*n*-dodecan-1-yloxy)benzyloxyl]benzamide (12)



Butyl 3,5-bis(3',4'-bis[4''-(*n*-dodecan-1-yloxy)benzyloxy]benzyloxy)benzamide (13)



Butyl 3,5-bis(3',4'-bis[4''-(*n*-dodecan-1-yloxy)benzyloxy]benzyloxy)benzamide (13)