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Facile Synthesis of Aldehyde-focal Fréchet Type Dendrons and Dendrimers *via* Staudinger/*Aza*-Wittig Reactions

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Fréchet-type dendritic benzaldehydes were efficiently synthesized using 3,5-dihydroxybenzaldehyde as an aldehyde focal point functionalized unit by adding a generation to the existing dendron or direct oxidation of Fréchet-type dendritic benzyl alcohols. These dendritic benzaldehydes were applied for the construction of dendrimers containing secondary amines as connectors *via* Staudinger/*aza*-Wittig Reactions with α,α'-diazido-*p*-xylene core.

Key Words : Aldehyde, Azide, Dendrimer, Staudinger/*aza*-Wittig reaction

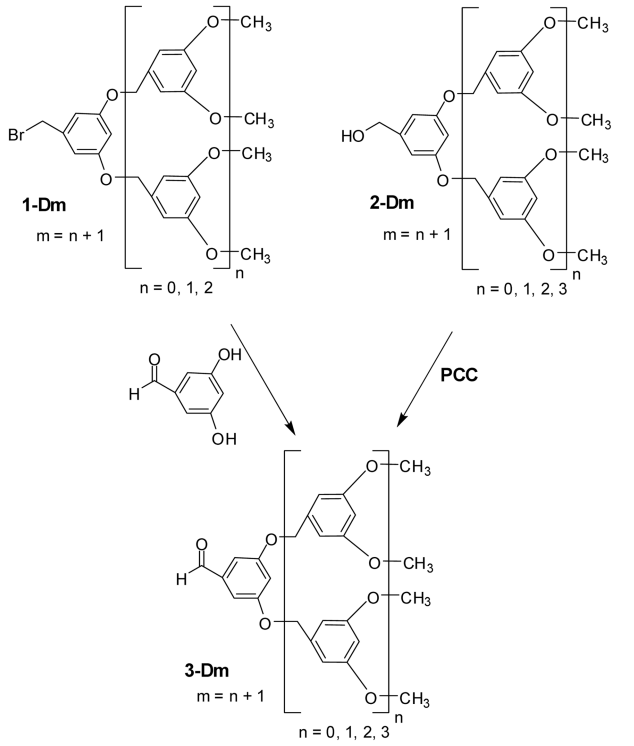
Introduction

Dendrons and dendrimers are the most intensely investigated subset of dendritic polymers. Dendrimers, which are prepared by repetition of a given set of reactions using either divergent or convergent strategies, are highly branched and regular macromolecules with well-defined structures and have served as functional objects in nanotechnology and nanoscience.[1] An effective convergent synthesis of dendrons and dendrimers requires a monomer that can undergo the activation and coupling steps in high yield and whose products can be readily isolated from excess starting material and byproducts.[2] In addition, the coupling step must be very efficient to enable complete reaction even when involving sterically demanding high generation dendrons. Recent solid chemistry is the click chemistry which is the copper-catalyzed 1,3-dipolar cycloaddition reaction between alkyne and azide developed by Sharpless and Tornøe.[3] This reaction is clearly a breakthrough in the synthesis of dendrimers[4,5] and dendritic and polymer materials.[6,7] We have developed the fusion and stitching methods for the synthesis of dendrimers using click chemistry between an alkyne and an azide.[5] In continuation with our research on the synthesis of dendrimers *via* click chemistry using azide derivatives, we have communicated for the construction of dendrimers using Staudinger/*aza*-Wittig reactions of benzene-1,4-dicarbaldehyde and azide-dendron.[8] We are still intrigued to apply this methodology for the convergent synthesis of dendrimers. Therefore, the effective synthesis of the aldehyde-focal dendrons is necessary to solve our curiosity. The poly(benzyl ether) dendrons, now frequently referred to as Fréchet-type dendrons, was selected because they are relatively readily accessed and exhibit the chemical stability associated with ether linkages.[9] Here we present a rapid synthesis of aldehyde-functionalized Fréchet-type dendrons **3-Dm** by adding one generation to the existing dendron using an aldehyde focal point functionalized unit or direct oxidation of the corresponding Fréchet-type dendritic benzyl alcohols and their application to the convergent synthesis of dendrimer **5-Gm** using sequential Staudinger/*aza*-Wittig reaction with α,α'-diazido-*p*-xylene **4** as a dendrimer core.

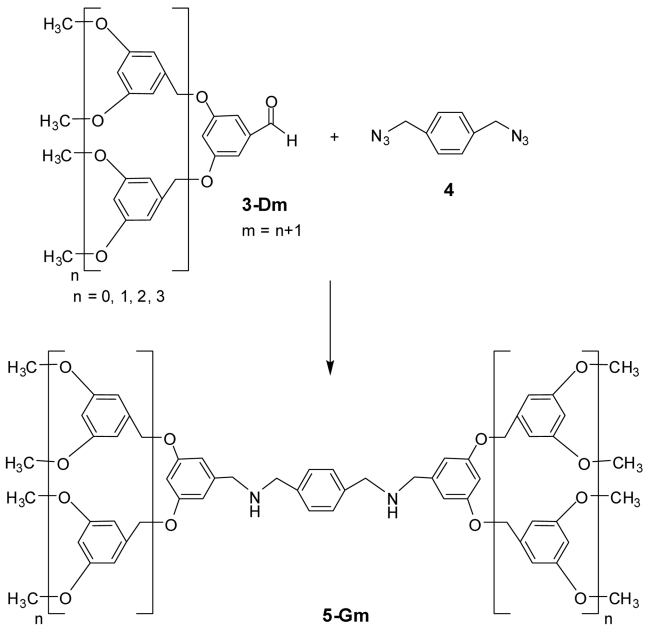
Results and Discussion

In response to the tedious purification in intensive iterative dendrimer syntheses, many researchers have combined the convergent and divergent strategies to reduce the number of linear synthetic steps required to access larger dendritic materials.[9a] These procedures generally maintain the versatility and product monodispersity offered by the traditional convergent method, but reduce the number of linear synthetic steps required to access larger dendritic materials. For the effective synthesis of the Fréchet-type dendron aldehydes, we have designed and utilized 3,5-dihydroxybenzaldehyde as an aldehyde focal point functionalized unit for the efficient synthesis of aldehyde-functionalized Fréchet-type dendrons.

To probe the effectiveness for the synthesis of the aldehyde focal point functionalized Fréchet-type dendrons **3-Dm** (*m* = 1, 2, 3, and 4: generation of dendron), we have reacted 3,5-dihydroxybenzaldehyde with the dendritic benzyl bromide **1-Dm** (Scheme 1). The dendritic benzyl bromide **1-Dm** (*m* = 1, 2, and 3: generation of dendron) was prepared according to the reported procedure.[10] The reaction of 3,5-dihydroxybenzaldehyde with first generation dendritic benzyl bromide **1-D1** in DMF in the presence of K_2CO_3 for 1.5 h at 50 °C provided the second generation dendritic benzaldehyde **3-D2** in 99% yield. Next, we conducted the reaction for the preparation of higher generation dendrons. The reactions of 3,5-dihydroxybenzaldehyde with **1-D2** and **1-D3** under the same condition gave the dendritic benzaldehydes **3-D3** and **3-D4** in yields of 98% and 95%, respectively, after 2.5 and 3.5 h. It was proven that the reaction using an aldehyde focal point functionalized unit added



Scheme 1. Structures of dendrons and synthesis of aldehyde focal point functionalized Fréchet-type dendrons **3-Dm**.



Scheme 2. Synthetic strategies of dendrimers **5-Gm** by *in-situ* Staudinger/*aza*-Wittig reactions followed by the reduction of imine intermediates. *Reagents and conditions:* (a) PPh_3, toluene, reflux. (b) $NaBH_4$, MeOH, rt.

efficiently a generation to the existing dendron. Also the reaction of 3,5-dihydroxybenzaldehyde with iodomethane provided the first generation dendritic benzaldehyde **3-D1** in 99% yield. All dendrons **3-Dm** were compared with the authentic compounds which was obtained by direct oxidation of the corresponding Fréchet-type dendritic benzyl alcohols **2-Dm** using PCC and confirmed by ^{1}H and ^{13}C NMR spectroscopy and their FAB mass spectra.

Staudinger/*aza*-Wittig reactions are a powerful tool in organic synthetic strategies directed towards the preparation of nitrogen-containing compounds.[11] We decided to apply this methodology for the synthesis of dendrimer. The synthetic strategy for Fréchet-type dendrimers, linked by the secondary amines, utilized a convergent method using the aldehyde-functionalized Fréchet-type dendrons **3-Dm** and the di-azides compound (Scheme 2). The α,α'-diazido-*p*-xylene **4** was chosen to present azide functionalities available for dendrimer growth *via* new click reaction with the dendrons. Our strategies in the synthesis of dendrimers are *in-situ* Staudinger/*aza*-Wittig reactions using an aldehyde-dendron and azides in the presence of triphenylphosphine and followed by the reduction of imine intermediates. To demonstrate the effectiveness of Staudinger/*aza*-Wittig reactions of **4** and aldehyde-dendron **3-D1** (Scheme 2), we have screened with several conditions in different solvents and/or temperature. We have found that the reaction conducted from toluene in the presence of triphenylphosphine for 24 h under reflux afforded the imine intermediate. The disappearance of α,α'-diazido-*p*-xylene **4**, aldehyde-dendron **3-D1**, and triphenylphosphine and the appearance of triphenylphosphine oxide and new spot were observed from TLC analysis. The resultant imine product was identified by ^{1}H-NMR spectroscopy which showed the characteristic imine peak at 8.25 ppm (Ar-C*H*=N-). This process can be achieved by the conversion of the azide into an imonophosphorane (the Staudinger reaction) followed by *in-situ aza*-Wittig reaction with aldehyde. The reduction of the imine intermediate with $NaBH_4$ in MeOH gave the desired secondary amine product.

With this basic result, we began our study by establishing the validity of the chemistry in the synthesis of dendrimers. The reaction of α,α'-diazido-*p*-xylene **4** and 2 equiv of aldehyde-dendron **3-D1** in the presence of PPh_3 (2.2 equiv) in toluene (0.1 M) for 24 h under reflux followed by reduction with $NaBH_4$ afforded the desired product **5-G1** in yield of 96%. The dendrimer **5-G1** was purified by column chromatography and the structure of dendrimer was confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and FAB mass spectra. Given the success in the synthesis of first generation dendrimer, we expanded this reaction to get higher generation dendrimers. Reactions of α,α'-diazido-*p*-xylene **4** with dendron **3-D2** and **3-D3** afforded the dendrimers **5-G2** and **5-G3** in yields of 97 and 94%, respectively, which were separated by column chromatography. In case of **3-D4**, the dendrimer **5-G4** was obtained in 92% yield. This comparative efficiency of the new click methodology is emphasized by the synthesis of the dendrimers with the tailor made core unit. Therefore this approach may provide new methodological insight into introduction of various functional cores and would greatly contribute to researches on the application side. We are now investigating for self-emissive dendrimer with a fluorescent probe in core

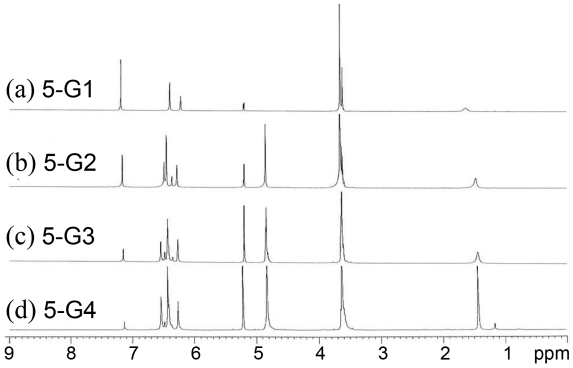


Figure 1. ^{1}H-NMR spectra for (a) **5-G1**, (b) **5-G2**, (c) **5-G3**, and (d) **5-G4**.

region.

Structural characterization of the dendrimers **5-Gm** with ^{1}H NMR, ^{13}C NMR, and IR spectroscopy showed no defects due to incomplete reaction. From their ^{1}H NMR spectra (CD_2Cl_2), the peaks of the benzene protons of core and the secondary amine protons in dendrimers **5-Gm** were found at 7.19 and 1.63 ppm for **5-G1**, 7.16 and 1.47 ppm for **5-G2**, 7.15 and 1.44 ppm for **5-G3**, and 7.12 and 1.41 ppm for **5-G4**, respectively (Figure 1). As the dendrimer generation increased, the peaks of the benzene protons of core and the secondary amine protons showed up-field shift which may be influenced by the dendritic microenvironment effect.[12] The IR spectra show the disappearance of the aldehyde peak and the azide peak in the final dendrimer (Figure 2). Analysis of the dendrimers by mass spectrometry as well as by gel-permeation chromatography (GPC) provides no signs of products with defects that would arise from incomplete coupling (Figure 3). As expected, the obtained dendrimer possessed a very well-defined molecular structure with very low polydispersity values (PDI = 1.01-1.02).

In summary, we have demonstrated that an efficient route to aldehyde-functionalized Fréchet-type dendrons is available by adding a generation to the existing dendron using an aldehyde focal point functionalized unit and that Staudinger/*aza*-Wittig reactions between aldehyde-dendrons and diazido-central linker lead to the formation of first through fourth generation dendrimers containing secondary amines

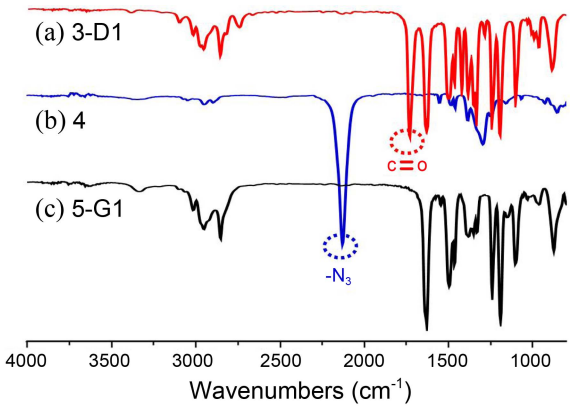


Figure 2. IR spectra for (a) **3-D1**, (b) **4**, and (c) **5-G1**.

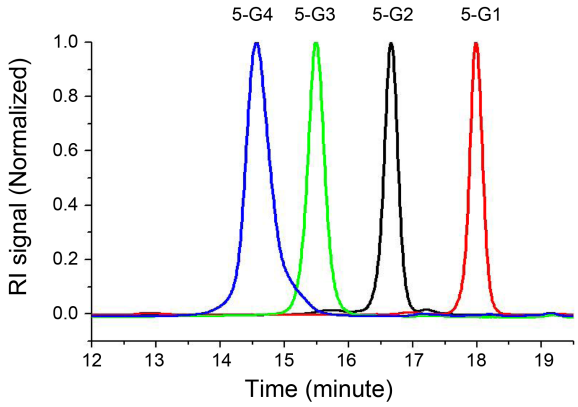


Figure 3. GPC diagrams of dendrimers **5-Gm** obtained from THF eluent.

as connectors in high yields. This method may provide an insight into designing various functional symmetrical dendrimers. We are currently working towards the synthesis of fluorophore-encapsulated dendrimers using this strategy for various applications.

Experimental Section

^{1}H NMR spectra were recorded on a 300 or 500 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. ^{13}C NMR spectra were proton decoupled and recorded on a 75 or 125 MHz NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. EI, FAB, and MADLI mass spectra were obtained from Korean Basic Science Institute in Daegu or Daejeon and POSTECH. Flash chromatography was performed with 37-75 μm silica gel. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by UV lamp or using an iodine chamber. Polydispersity (PDI) of dendrimers was determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Agilent 1100 series GPC, Plgel 5 μm MIXED-C, refractive index detector) in THF solution. All chemicals were obtained from commercial sources and used as received, unless otherwise mentioned. α,α'-Diazido-*p*-xylene **4** was prepared by the azidation of α,α'-dichloro-*p*-xylene.

General Procedure for the Perparation of Dendritic Benzaldehydes 3-Dm. A mixture of 3,5-dihydroxybenzaldehyde (1.0 equiv.) and dendritic benzyl bromide **1-Dm** (2.2 equiv.) in DMF (0.1 *M* solution) in the presence of potassium carbonate (3.0 equiv.) was stirred for 1.5~3.5 h at 50 °C. The resulting mixture was diluted with EtOAc and filtered and the filtrate was concentrated and purified by column chromatography (EtOAc/hexane system) to afford one generation added product. To obtain **3-D1**, iodomethane (3 equiv.) was used instead of dendritic benzyl bromide.

3-D1: 99% yield; A white solid; mp 38-40 ºC. IR 3005, 2943, 2843, 1701, 1597, 1468, 1299, 1208, 1157, 1065 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 6H), 6.71 (t, J = 2.2 Hz, 1H), 7.02 (d, J = 2.3 Hz, 2H), 9.90 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.6, 107.1, 107.2, 138.4, 161.2, 191.9; MS (EI): *m/z* 166 [M^+]; HRMS (EI) Calcd for $C_9H_{10}O_3$: 166.0630 Found: 166.0629 [M^+].

3-D2: 99% yield; A white solid; mp 100-102 ºC. IR 2997, 2931, 2835, 1694, 1593, 1454, 1292, 1200, 1153, 1049 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 12H), 5.03 (s, 4H), 6.42 (s, 2H), 6.57 (d, J = 2.0 Hz, 4H), 6.85 (s, 1H), 7.10 (d, J = 2.2 Hz, 2H), 9.89 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4, 70.3, 100.0, 105.2, 108.3, 108.7, 138.4, 138.5, 160.3, 161.1, 191.8; MS (EI): *m/z* 438 [M^+]; HRMS (EI) Calcd for $C_{25}H_{26}O_7$: 438.1679. Found: 438.1675 [M^+].

3-D3: 98% yield; A colorless oil; IR 3005, 2940, 2839, 1697, 1597, 1458, 1300, 1204, 1157, 1053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 24H), 4.98 (s, 8H), 5.02 (s, 4H), 6.41 (s, 4H), 6.57 (m, 10H), 6.66 (s, 4H), 6.82 (s, 1H), 7.07 (s, 2H), 9.87 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.2, 69.9, 99.8, 101.6, 105.1, 106.2, 108.1, 108.5, 138.3, 138.6, 139.0, 160.0, 160.9, 191.6; MS (FAB): *m/z* 982.5 [M^+]; HRMS (FAB) Calcd for $C_{57}H_{58}O_{15}$: 982.3776. Found: 982.3783 [M^+].

3-D4: 95% yield; A colorless oil; IR 3001, 2939, 2839, 1697, 1597, 1458, 1300, 1204, 1153, 1053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 48H), 4.95 (s, 24H), 5.00 (s, 4H), 6.39 (s, 8H), 6.55 (m, 22H), 6.66 (m, 12H), 6.84 (s, 1H), 7.07 (s, 2H), 9.85 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.2, 69.9, 70.1, 99.8, 101.5, 105.1, 106.3, 108.2, 108.4, 138.3, 138.6, 139.0, 160.0, 160.1, 160.9, 191.6; MS (MALDI): Calcd for $C_{121}H_{122}O_{31}$: 2070.7970. Found: 2093.7833 [M^+ + Na].

General Procedure for the Preparation of Dendrimers 5-Gm by Reaction between α,α'-diazido-*p*-xylene 4 and Aldehyde-dendrons 3-Dm. A solution of α,α'-diazido-*p*-xylene **4** (0.4 mmol) and aldehyde-dendron **3-Dm** (0.8 mmol) in toluene (8 mL) in the presence of triphenylphosphine (0.88 mmol) was stirred under reflux. After 24 h, the reaction solution was diluted with MeOH (8 mL) and subsequently added $NaBH_4$ (0.9 mmol). Then the reaction was stirred overnight at room temperature. After evaporation, the residue was partitioned in CH_2Cl_2 and saturated Na_2CO_3 aqueous solution and extracted two to three times with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and filtered and the filtrate was concentrated. The crude product was purified by flash chromatography to afford the dendrimer **5-Gm**.

5-G1: 96% yield; A white solid; mp 72-74 ºC. IR 3001, 2936, 2835, 1597, 1462, 1432, 1346 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 1.63 (s, 2H), 3.62 (s, 4H), 3.65 (s, 16H), 6.22 (t, J = 2.0 Hz, 2H), 6.40 (d, J = 2.0 Hz, 4H), 7.19 (s, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 53.3, 53.7, 55.8, 99.3, 106.4, 128.7, 139.7, 143.6, 161.5; MS (FAB): *m/z* 437.15 [M^+ + H]; HRMS (FAB) Calcd for $C_{26}H_{32}N_2O_4$: 436.2362. Found: 437.2438 [M^+ + H]. PDI: 1.01.

5-G2: 97% yield; A white solid; mp 60-62 ºC. IR 3001, 2936, 2839, 1597, 1459, 1431, 1323 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 3.63 (s, 4H), 3.65 (s, 28H), 4.85 (s, 8H), 6.28 (m, 4H), 6.36 (m, 2H), 6.45 (d, J = 1.0 Hz, 8H), 6.49 (m, 4H), 7.16 (s, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 53.4, 53.7, 55.9, 70.5, 100.2, 101.1, 105.8, 107.6, 128.7, 139.8, 140.1, 143.9, 160.5, 161.6; MS (FAB): *m/z* 981.3 [M^+ + H]; HRMS (FAB) Calcd for $C_{58}H_{64}N_2O_{12}$: 980.4459. Found: 981.4534 [M^+ + H]. PDI: 1.01

5-G3: 94% yield; A white solid; mp 56-58 ºC; IR 3001, 2936, 2839, 1597, 1458, 1431, 1373 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 3.64 (m, 56H), 4.84 (s, 24H), 6.27 (m, 8H), 6.35 (m, 2H), 6.43 (m, 20H), 6.48 (m, 4H), 6.55 (m, 8H), 7.15 (s, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 53.4, 53.7, 55.9, 70.4, 70.6, 100.3, 101.1, 102.0, 105.8, 106.9, 107.6, 128.7, 139.8, 139.9, 140.3, 143.9, 160.5, 160.6, 161.6; MS (MALDI): Calcd for $C_{122}H_{128}N_2O_{28}$: 2068.8654. Found: 2069.8203 [M^+ + H]. PDI: 1.01.

5-G4: 92% yield; A white oil; IR 3001, 2939, 2839, 1597, 1458, 1431, 1373 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 3.61 (m, 104H), 4.81 (s, 56H), 6.25 (m, 16H), 6.36 (m, 2H), 6.39 (m, 12H), 6.41 (m, 32H), 6.47 (m, 4H), 6.52 (m, 24H), 7.12 (s, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 53.4, 53.7, 55.8, 70.40, 70.48, 70.54, 100.3, 101.1, 102.0, 102.1, 105.8, 106.9, 107.6, 128.7, 139.8, 139.9, 140.0, 140.3, 144.0, 160.5, 160.6, 161.6; MS (MALDI): Calcd for $C_{250}H_{256}N_2O_{60}$: 4245.7042. Found: 4246.6340 [M^+ + H]. PDI: 1.02.

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