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Supporting Information

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Fiber formation by Highly CO_2-Soluble Bis-Ureas Containing Peracetylated Carbohydrate Groups

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General Information

All reactions were run in flame-dried glassware under an atmosphere of nitrogen. Dichloromethane was dried on an Innovative Technology SPS-400 dry solvent system. All other compounds were purchased from Aldrich Chemical Company and used without further purification unless otherwise noted. Column chromatography was performed using silica gel (particle size 230-400 mesh). Analytical thin-layer chromatography (TLC) was performed with Silica Gel 60 F_{254} plate (250 μm thickness, Merck). Nuclear Magnetic Resonance (NMR) spectra were recorded either on a Bruker Avance DPX-500 or DPX-400 spectrometer at 500 and 125 MHz or 400 and 100 MHz respectively. Chemical shifts are reported in part per million (ppm, δ) chemical shift of residual solvent peak as a reference. Melting point was measured using an *Electrothermal* Melting Point Apparatus and are uncorrected. All high-resolution mass data were obtained from the Mass Spectroscopy Laboratory at the University of Illinois at Urbana-Champaign using Micromass 70-VSE-A instrument with 8 kV acceleration potential, 70eV electron energy, 100 μA emission current and 200 ^{o}C ion source temperature. Specific rotation values were measured on Perkin Elmer Polarimeter 341 using the wavelength of Na/Hal (589 nm) at 20.0 ^{o}C.

Synthesis of pentaacetylated glucamine hydrogen chloride salt (4)

To a solution of D-glucamine (**3**) (2.5 g, 13.8 mmol, 1.0 equiv) in glacial acetic acid (10.0 mL) was added acetyl chloride (22.6 mL, 318 mmol) slowly dropwise at 0 ^{o}C. The reaction mixture was stirred for 18 hours, then, the reaction mixture was concentrated under a reduced pressure and completely dried under a high vacuum. Then the reaction mixture was re-dissolved in methanol (8.0 mL) and ethanol (5.0 mL), then re-crystalized at -20 ^{o}C to afford a white crystalline solid as a HCl salt (4.24g, 9.91 mmol, 71.8 %). m.p. = 195 – 196 ^{o}C. ^{1}H NMR (DMSO, 400 MHz) δ 8.34 (s, 3H), 5.33 – 5.27 (m, 2H), 5.21 (m, 1H), 5.01 (m, 1H), 4.23 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.07 (dd, *J* = 12.5, 6.5 Hz, 1H), 3.07 – 2.93 (m, 2H), 2.11 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H). 1.99 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (DMSO, 100 MHz) δ 169.97, 169.93, 169.64, 169.48, 169.44, 68.76, 68.28, 68.16, 68.02, 61.23, 20.94, 20.59, 20.53, 20.43, 20.34.

Synthesis of bis-pentaacetylated glucamine bis-urea with butane spacer 1a

To a solution of pentaacetylated glucamine hydrogen chloride salt **(4)** (0.50 g, 1.17 mmol, 2.0 equiv) in anhydrous dichloromethane (20.0 mL) was added diisopropylethyl amine (0.22 mL, 1.28 mmol, 2.2 equiv) dropwise at room temperature. Upon addition, the glucamine salt was completely dissolved in the solution. Then, the reaction mixture was treated with 1,4-bisisocyanatobutane (0.074 mL, 0.58 mmol, 1.0 equiv) slowly dropwise at room temperature. The reaction mixture was stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. Then, the reaction mixture was concentrated under a reduced pressure and completely dried under a high vacuum. Flash column chromatography on silica eluting with 2 ~ 4 % methanol/dichloromethane isolated bis-urea **1a** as a colorless sticky solid (0.43 g, 0.47 mmol, 81%). The resulting sticky solid was dissolved into acetonitrile (4 mL) and diluted with distilled water (3 mL), then frozen in the dry ice/acetone bath and freeze dried under the lyophilizer for 24 hours. Resulting white powdery solid was collected. ^{1}H NMR (DMSO, 500 MHz) δ 5.94 (t, *J* = 5.5 Hz 2H), 5.86 (t, *J* = 6.0 Hz 2H), 5.42 (dd, *J* = 6.5, 4.0 Hz, 2H), 5.25 (dd, *J* = 6.0, 4.0 Hz, 2H), 4.98 – 4.96 (m, 4H), 4.22 (dd, *J* = 12.5, 3.5 Hz, 2H), 4.06 (dd, *J* = 12.5, 6.5 Hz, 2H), 3.25 – 3.22 (m, 4H), 2.98 – 2.90 (m, 4H), 2.08 (s, 6H), 2.01 (s, 12H), 1.99 (s, 6H), 1.97 (s, 6H), 1.34 – 1.28 (m, 4H); ^{13}C NMR (DMSO, 125 MHz) δ 169.96, 169.54, 169.48, 169.39, 169.38, 157.72, 70.90, 68.65, 68.60, 68.39, 61.19, 38.99, 38.94, 27.25, 20.55, 20.38, 20.34, 20.78, 20.77 ; $[\alpha]_D^{20.0}$ = + 16.0 ($CHCl_3$, c = 0.18) ; HRMS (ESI, *m/z*) for $[M+1]^+$ $C_{38}H_{59}N_4O_{22}$ calcd 923.3621, found 923.3599.

Synthesis of bis-pentaacetylated glucamine bis-urea with hexane spacer 1b

To a solution of pentaacetylated glucamine hydrogen chloride salt **(4)** (1.0 g, 2.33 mmol, 2.0 equiv) in anhydrous dichloromethane (40.0 mL) was added diisopropylethyl amine (0.45 mL, 2.57 mmol, 2.2 equiv) dropwise at room temperature. Upon addition, the glucamine salt was completely dissolved in the solution. Then, the reaction mixture was treated with 1,4-bis-isocyanatohexane (0.188 mL, 1.17 mmol, 1.0 equiv) slowly dropwise at room temperature. The reaction mixture was stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. Then, the reaction mixture was concentrated under a reduced pressure and completely dried under a high vacuum. Flash column chromatography on silica eluting with 2 ~ 4 % methanol/dichloromethane isolated bis-urea **1b** as a colorless sticky solid (0.86 g, 0.90 mmol, 77%). The resulting sticky solid was dissolved into acetonitrile (4 mL) and diluted with distilled water (3 mL), then frozen in the dry ice/acetone bath and freeze dried under the lyophilizer for 24 hours. Resulting white powdery solid was collected. ^{1}H NMR (DMSO, 400 MHz) δ 5.92 (t, *J* = 5.6 Hz 2H), 5.85 (t, *J* = 6.0 Hz 2H), 5.41 (dd, *J* = 6.4, 4.0 Hz, 2H), 5.25 (dd, *J* = 6.4, 4.0 Hz, 2H), 4.99 – 4.96 (m, 4H), 4.23 (dd, *J* = 12.4, 3.6 Hz, 2H), 4.05 (dd, *J* = 12.0, 6.4 Hz, 2H), 3.26 – 3.11 (m, 4H), 2.97 – 2.90 (m, 4H), 2.08 (s, 6H), 2.01 (s, 12H), 1.99 (s, 6H), 1.97 (s, 6H), 1.34 – 1.31 (m, 4H), 1.23 – 1.20 (m, 4H); ^{13}C NMR (DMSO, 125 MHz) δ 169.96, 169.55, 169.48, 169.39, 169.38, 157.80, 70.92, 68.65, 68.60, 68.40, 61.20, 39.24, 39.06, 29.88, 26.11, 20.63, 20.45, 20.41, 20.36, 20.35 ; $[\alpha]_D^{20.0}$ = + 14.4 ($CHCl_3$, c = 0.09) ; HRMS (ESI, *m/z*) for $[M+1]^+$ $C_{40}H_{63}N_4O_{22}$ calcd 951.3934, found 951.3903.

Synthesis of *N*-Boc ethylenediamine amide 8a

A solution of pentaacetylated gluconic acid **7**[1] (2.50 g, 6.15 mmol, 1.0 equiv) in anhydrous dichloromethane (25.0 mL) was treated with 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (1.18 g, 6.15 mmol, 1.0 equiv) and pyridine (0.75 mL, 9.2 mmol, 1.5 equiv). Then, *N*-Boc ethylenediamine (0.97 mL, 6.15 mmol, 1.0 equiv) was added into the reaction mixture followed by the addition of *N*,*N*-dimethylamino pyridine (catalytic amount). The reaction mixture was stirred for 24 hours, at which time TLC analysis showed full consumption of starting material. The reaction mixture was poured into the saturated ammonium chloride aqueous solution (30 mL). Organics were separated and extracted with dichloromethane (2 x 30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a sticky solid. Flash column chromatography on silica eluting with 3.5 – 4.0 % methanol/dichloromethane isolated bis-acetylated ester **8a** as a white solid (2.64 g, 4.81 mmol, 78%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.03 (br, 1H), 5.67 (t, *J* = 5.0 Hz, 1H), 5.47 (t, *J* = 5.0 Hz, 1H), 5.30 (m, 1H), 5.07 – 5.01 (m, 2H), 4.30 (dd, *J* = 12.0, 3.5 Hz, 1H), 4.12 (dd, *J* = 12.0, 5.5 Hz, 1H), 3.42 – 3.36 (m, 1H), 3.29 – 3.20 (m, 3H), 2.23 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H). 2.05 (s, 3H), 2.03

(s, 3H), 1.44 (s, 9H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 170.61, 169.87, 169.86, 169.83, 169.32, 166.65, 79.88, 71.40, 69.55, 69.13, 68.68, 61.53, 41.46, 39.71, 28.33, 20.75, 20.69, 20.68, 20.65, 20.41.

Synthesis of *N*-Boc aminoethyl gluconate 8b

A solution of pentaacetylated gluconic acid **7**[1] (4.07 g, 10.02 mmol, 1.0 equiv) in anhydrous dichloromethane (50.0 mL) was treated with 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (2.3 g, 11.99 mmol, 1.2 equiv) and pyridine (1.2 mL, 14.8 mmol, 1.5 equiv). Then, *N*-Boc ethanolamine (1.6 g, 9.92 mmol, 1.0 equiv in dichloromethane solution 10.0 mL) was added into the reaction mixture followed by the addition of *N,N*-dimethylamino pyridine (catalytic amount). The reaction mixture was stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. The reaction mixture was poured into the saturated ammonium chloride aqueous solution (30 mL). Organics were separated and extracted with dichloromethane (2 x 30 mL), dried (MgSO$_4$) and concentrated *in vacuo* to give a sticky solid. Flash column chromatography on silica eluting with 2 % methanol/dichloromethane isolated bis-acetylated ester **8a** as a colorless dense oil (3.79 g, 6.89 mmol, 69%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 5.62 (t, *J* = 4.5 Hz, 1H), 5.48 (dd, *J* = 6.5, 5.0 Hz, 1H), 5.22 (d, *J* = 3.5 Hz, 1H), 5.15 (m, 1H), 5.05 (m, 1H), 4.31 – 4.27 (m, 2H), 4.14 – 4.07 (m, 2H), 3.42 – 3.26 (m, 2H), 2.17 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 170.37, 169.93, 169.82, 169.62, 169.53, 166.48, 149.41, 79.85, 70.78, 69.34, 68.45, 68.37, 65.44, 61.39, 39.70, 28.33, 20.68, 20.58, 20.57, 20.34, 20.28.

Synthesis of bis-acetylated gluconate bis-urea with butane spacer 2a

To a solution of *N*-Boc ethylenediamine amide **8a** (2.51 g, 4.57 mmol, 2.0 equiv) in anhydrous dichloromethane (20.0 mL) was added trifluoroacetic acid (5.0 mL) slowly dropwise at room temperature. The reaction mixture was stirred for 3 hours, at which time TLC analysis showed full consumption of starting material. Then, the reaction mixture was concentrated under a reduced pressure and completely dried under a high vacuum. Then the reaction mixture was re-dissolved in anhydrous dichloromethane (20.0 mL) and cooled to 0 °C, then treated with *N,N*-diisopropylethyl amine (0.95 mL, 5.48 mmol, 2.4 equiv). Then, the reaction mixture was treated with 1,4-bis-isocyanatobutane (0.29 mL, 2.28 mmol, 1 equiv) at 0 °C and slowly warmed to room temperature and stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. Brine (10 mL) and dichloromethane (20 mL) were added and organics were extracted with dichloromethane (2 x 30 mL), dried (MgSO$_4$) and concentrated *in vacuo* to give a sticky solid. Flash column chromatography on silica eluting with 4 ~ 5 % methanol/dichloromethane isolated bis-acetylated gluconate bis-urea **2a** as a colorless sticky solid (1.26 g, 1.21 mmol, 53%). The resulting sticky solid was dissolved into acetonitrile (4 mL) and diluted with distilled water (3 mL), then frozen in the dry ice/acetone bath and freeze dried under the lyophilizer for 24 hours. Resulting white powdery solid was collected. ^{1}H NMR (CD$_3$OD, 500 MHz) δ 5.75 (t, *J* = 4.5 Hz, 2H), 5.58 (t, *J* = 6.0 Hz, 2H), 5.36 (d, *J* = 3.5 Hz, 2H), 5.20 (ddd, *J* = 9.5, 6.0, 4.0, 2H), 4.49 (dd, *J* = 12.5, 4.0 Hz, 2H), 4.29 (dd, *J* = 12.0, 6.0 Hz, 2H), 3.44 – 3.42 (m, 2H), 3.38 – 3.32 (m, 6H), 3.28 – 3.24 (m, 4H), 2.33 (s, 6H), 2.23 (s, 6H), 2.18 (s, 12H), 2.15 (s, 6H), 1.65 – 1.61 (m, 4H); ^{13}C NMR (CD$_3$OD, 125 MHz) δ 172.25, 171.54, 171.52, 171.51, 171.21, 161.39, 73.67, 71.03, 70.55, 70.38, 62.64, 41.63, 40.90, 40.29, 28.63, 20.77, 20.71, 20.70, 20.62, 20.48 ; $[\alpha]_D^{20.0}$ = + 36.0 (CHCl$_3$, c = 0.18) ; HRMS (ESI, *m/z*) for $[M+1]^+$ $C_{42}H_{65}N_6O_{24}$ calcd 1037.4050, found 1037.4032.

Synthesis of bis-acetylated gluconate bis-urea with butane spacer 2b

To a solution of *N-Boc*-protected 2-aminoethyl pentaacetylated gluconate **8b** (863 mg, 1.57 mmol, 2.2 equiv) in anhydrous dichloromethane (7.0 mL) was added trifluoroacetic acid (3.0 mL) slowly dropwise at room temperature. The reaction mixture was stirred for 3 hours, at which time TLC analysis showed full consumption of starting material. Then, the reaction mixture was concentrated under a reduced pressure and completely dried under a high vacuum. Then the reaction mixture was re-dissolved in anhydrous dichloromethane (8.0 mL) and cooled to 0 °C, then treated with *N*,*N*-diisopropylethyl amine (0.55 mL, 3.14 mmol, 4.4 equiv). Then, the reaction mixture was treated with 1,4-bis-isocyanatobutane (0.090 mL, 0.71 mmol, 1 equiv) at 0 °C and slowly warmed to room temperature and stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. Brine (10 mL) and dichloromethane (20 mL) were added and organics were extracted with dichloromethane (2 x 30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a sticky solid. Flash column chromatography on silica eluting with 2 ~ 4 % methanol/dichloromethane isolated bis-acetylated gluconate bis-urea **2b** as a colorless sticky solid (398 mg, 0.38 mmol, 54%). The resulting sticky solid was dissolved into acetonitrile (4 mL) and diluted with distilled water (3 mL), then frozen in the dry ice/acetone bath and freeze dried under the lyophilizer for 24 hours. Resulting white powdery solid was collected. ^{1}H NMR (DMSO, 500 MHz) δ 5.98 (t, *J* = 5.5 Hz, 2H), 5.84 (t, *J* = 6.0 Hz, 2H), 5.54 (t, *J* = 4.0 Hz, 2H), 5.42 (t, *J* = 5.5 Hz, 2H), 5.23 (d, *J* = 3.5 Hz, 2H), 5.02 – 4.99 (m, 2H), 4.26 (dd, *J* = 12.0, 3.5 Hz, 2H), 4.12 (dd, *J* = 12.0, 6.0 Hz, 2H), 4.02 – 3.97 (m, 4H), 3.26 – 3.12 (m, 4H), 3.02 – 3.2.94 (m, 4H), 2.12 (s, 6H), 2.07 (s, 6H), 2.02 (s, 6H), 2.01 (s, 6H), 1.99 (s, 6H), 1.35 – 1.31 (m, 4H); ^{13}C NMR (DMSO, 125 MHz) δ 169.87, 169.38, 169.32, 169.30, 169.10, 166.28, 157.73, 70.56, 68.86, 68.20, 67.82, 64.92, 60.96, 38.97, 37.87, 27.34, 20.37, 20.30, 20.27, 20.02, 20.00 ; $[\alpha]_D^{20.0}$ = + 24.7 ($CHCl_3$, c = 0.38) ; HRMS (ESI, *m/z*) for $[M+1]^+$ $C_{42}H_{63}N_4O_{26}$ calcd 1039.3731, found 1039.3735.

Synthesis of bis-acetylated gluconate bis-urea with hexane spacer 2c

To a solution of *N-Boc*-protected 2-aminoethyl pentaacetylated gluconate **8b** (924 mg, 1.69 mmol, 2.05 equiv) in anhydrous dichloromethane (10.0 mL) was added trifluoroacetic acid (3.0 mL) slowly dropwise at room temperature. The reaction mixture was stirred for 3 hours, at which time TLC analysis showed full consumption of starting material. Then, the reaction mixture was concentrated under a reduced pressure and completely dried under a high vacuum. Then, the reaction mixture was re-dissolved in anhydrous dichloromethane (10.0 mL) and cooled to 0 °C, then treated with *N*,*N*-diisopropylethyl amine (0.57 mL, 3.31 mmol, 4.0 equiv). Then, the reaction mixture was treated with 1,4-bis-isocyanatohexane (0.133 mL, 0.83 mmol, 1 equiv) at 0 °C and slowly warmed to room temperature and stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. Brine (10 mL) and dichloromethane (20 mL) were added and organics were extracted with dichloromethane (2 x 30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a sticky solid. Flash column chromatography on silica eluting with 2 ~ 4 % methanol/dichloromethane isolated bis-acetylated gluconate bis-urea **2c** as a colorless sticky solid (637 mg, 0.597 mmol, 72%). The resulting sticky solid was dissolved into acetonitrile (4 mL) and diluted with distilled water (3 mL), then frozen in the dry ice/acetone bath and freeze dried under the lyophilizer for 24 hours. Resulting white powdery solid was collected. ^{1}H NMR (CD_3OD, 500 MHz) δ 5.64 (dd, *J* = 5.0, 3.5 Hz, 2H), 5.50 (dd, *J* = 6.3, 5.0 Hz, 2H), 5.31 (d, *J* = 3.4 Hz, 2H), 5.09 (ddd, *J* = 10.0, 5.5, 3.5, 2H), 4.35 (dd, *J* = 12.3, 3.9 Hz, 2H), 4.20 – 4.10 (m, 6H), 3.42 – 3.36 (m, 4H), 3.13 – 3.09 (m, 4H), 2.16 (s, 6H), 2.10 (s, 6H), 2.06 (s, 6H), 2.05 (s, 6H), 2.03 (s, 6H), 1.51 – 1.45 (m, 4H), 1.37 – 1.33 (m, 4H); ^{13}C NMR (CD_3OD, 125 MHz) δ 172.22, 171.47, 171.44, 171.36, 168.42, 160.94, 72.34, 70.85, 70.14, 70.00, 66.53, 62.64, 40.97, 39.85, 31.23, 27.60, 20.77, 20.69, 20.66, 20.45, 20.40 ; $[\alpha]_D^{20.0}$ = + 27.8 ($CHCl_3$, c = 0.23) ; HRMS (ESI, *m/z*) for $[M+1]^+$ $C_{44}H_{67}N_4O_{26}$ calcd 1067.4044, found 1067.4073.

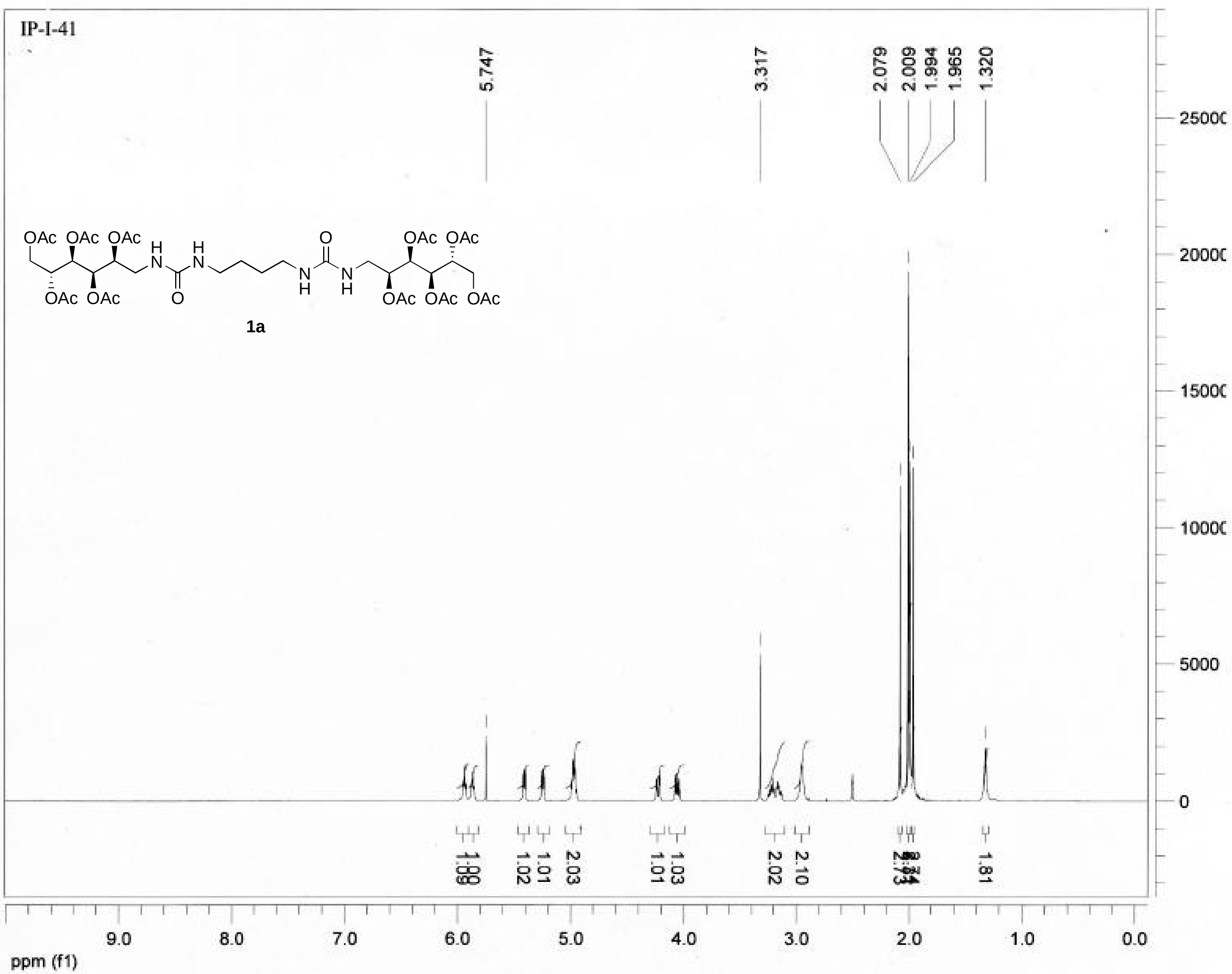
Synthesis of bis-pentaacetylatedgluconate 9

A solution of pentaacetylated gluconic acid **7**[1] (1.84 g, 4.52 mmol, 2.08 equiv) in anhydrous dichloromethane (30.0 mL) was treated with 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (0.92 g, 4.8 mmol, 2.2 equiv) and pyridine (0.60 mL, 7.4 mmol, 3.4 equiv). Then, *N*-Boc-serinol (0.41 g, 2.17 mmol, 1.0 equiv) was added into the reaction mixture followed by the addition of *N*,*N*-dimethylamino pyridine (catalytic amount). The reaction mixture was stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. The reaction mixture was poured into the saturated ammonium chloride aqueous solution (30 mL). Organics were separated and extracted with dichloromethane (2 x 30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a sticky solid. Flash column chromatography on silica eluting with 2 % methanol/dichloromethane isolated bis-acetylatedgluconate ester **9** as a colorless dense oil (1.68 g, 1.73 mmol, 80%). ^{1}H NMR (CD_3OD, 500 MHz) δ 5.65 – 5.61 (m, 2H), 5.52 – 5.49 (m, 2H), 5.32 (apparent dd, *J* = 11.7, 2.9 Hz, 2H), 5.11 – 5.07 (m, 2H), 4.36 – 4.32 (m, 2H), 4.25 – 4.15 (m, 6H), 4.12 – 4.06 (m, 1H), 2.16 (s, 3H), 2.16 (s, 3H), 2.11 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (CD_3OD, 125 MHz) δ 172.25, 172.20, 171.46, 171.43, 171.40, 171.37, 171.33, 168.27, 168.20, 157.50, 80.79, 72.29, 70.79, 70.75, 70.12, 70.05, 69.77, 65.65, 65.37, 62.67, 49.72, 28.79, 20.86, 20.75, 20.72, 20.55, 20.51, 20.41.

Synthesis of bis-urea 10

To a solution of *N-Boc*-protected bis-acetylatedgluconate ester **9** (1.29 g, 1.69 mmol, 1.33, 2.1 equiv) in anhydrous dichloromethane (5.0 mL) was added trifluoroacetic acid (1.5 mL) slowly dropwise at room temperature. The reaction mixture was stirred for 3 hours, at which time TLC analysis showed full consumption of starting material. Then, the reaction mixture was concentrated under a reduced pressure and completely dried under a high vacuum. Then, the reaction mixture was re-dissolved in anhydrous dichloromethane (6.0 mL) and cooled to 0 ^{o}C, then treated with *N*,*N*-diisopropylethyl amine (0.27 mL, 1.52 mmol, 2.4 equiv). Then, the reaction mixture was treated with 1,4-bis-isocyanatohexane (0.080 mL, 0.63 mmol, 1 equiv) at 0 ^{o}C and slowly warmed to room temperature and stirred for 12 hours, at which time TLC analysis showed full consumption of starting material. Brine (10 mL) and dichloromethane (20 mL) were added and organics were extracted with dichloromethane (2 x 30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a sticky solid. Flash column chromatography on silica eluting with 2 ~ 4 % methanol/dichloromethane isolated bis-acetylated gluconate bis-urea **10** as a colorless sticky solid (605 mg, 0.322 mmol, 51%). The resulting sticky solid was dissolved into acetonitrile (4 mL) and diluted with distilled water (3 mL), then frozen in the dry ice/acetone bath and freeze dried under the lyophilizer for 24 hours. Resulting white powdery solid was collected. ^{1}H NMR (CD_3OD, 500 MHz) δ 5.64 (dd, *J* = 4.7, 3.5 Hz, 2H), 5.62 (dd, *J* = 4.7, 3.4 Hz, 2H), 5.30 (apparent dd, *J* = 6.0, 5.2 Hz, 4H), 5.33 (apparent d, *J* = 3.4 Hz, 4H), 4.97 (apparent ddd, *J* = 9.6, 6.0, 3.7 Hz, 4H), 4.36 (apparent ddd, *J* = 12.2, 3.4, 0.7 Hz, 4H), 4.31 – 4.10 (m, 14H), 3.38 – 3.12 (m, 4H), 2.16 (s, 6H), 2.16 (s, 6H), 2.11 (apparent, 12H), 2.08 (apparent, 12H), 2.06 (apparent, 12H), 2.04 (apparent, 12H), 1.53 – 1.49 (m, 4H); ^{13}C NMR (CD_3OD, 125 MHz) δ 172.30, 171.52, 171.50, 171.49, 171.45, 171.39, 168.30, 168.26, 160.03, 72.33, 72.30, 70.87, 70.23, 70.18, 69.93, 69.85, 65.87, 62.71, 40.84, 28.61, 20.85, 20.76, 20.73, 20.54, 20.52, 20.43 ; $[\alpha]_D^{20.0}$ = + 23.4 ($CHCl_3$, c = 0.15) ; HRMS (ESI, *m/z*) for $[M+1]^+$ $C_{76}H_{107}N_4O_{50}$ calcd 1875.5953, found 1875.6506.

[1] X. Fan, V. K. Potluri, M. C. McLeod, Y. Wang, J. Liu, R. M. Enick, A. D. Hamilton, C. B. Roberts, J. K. Johnson, E. J. Beckman, *J. Am. Chem. Soc.* **2005**, *127*, 11754 - 11762.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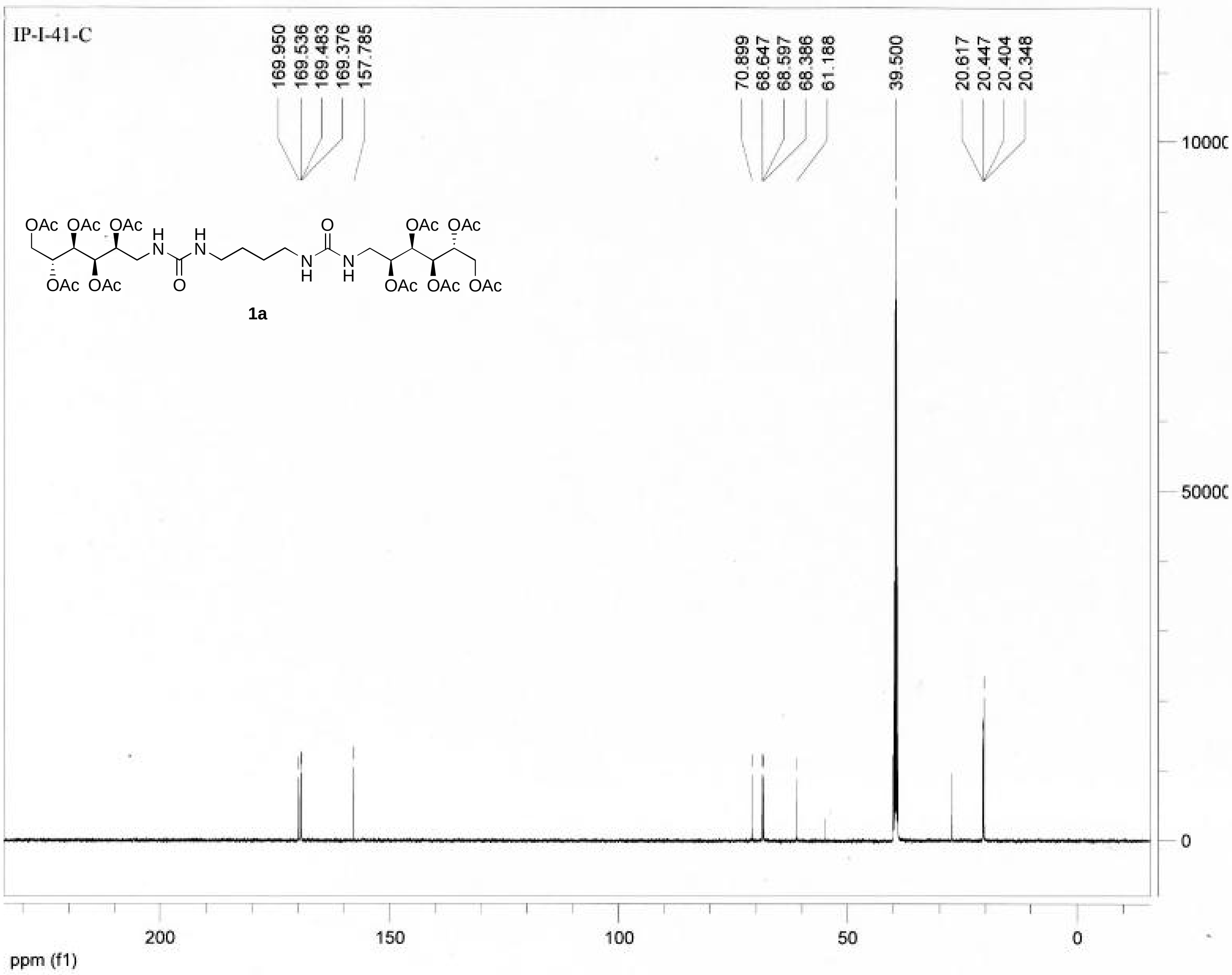
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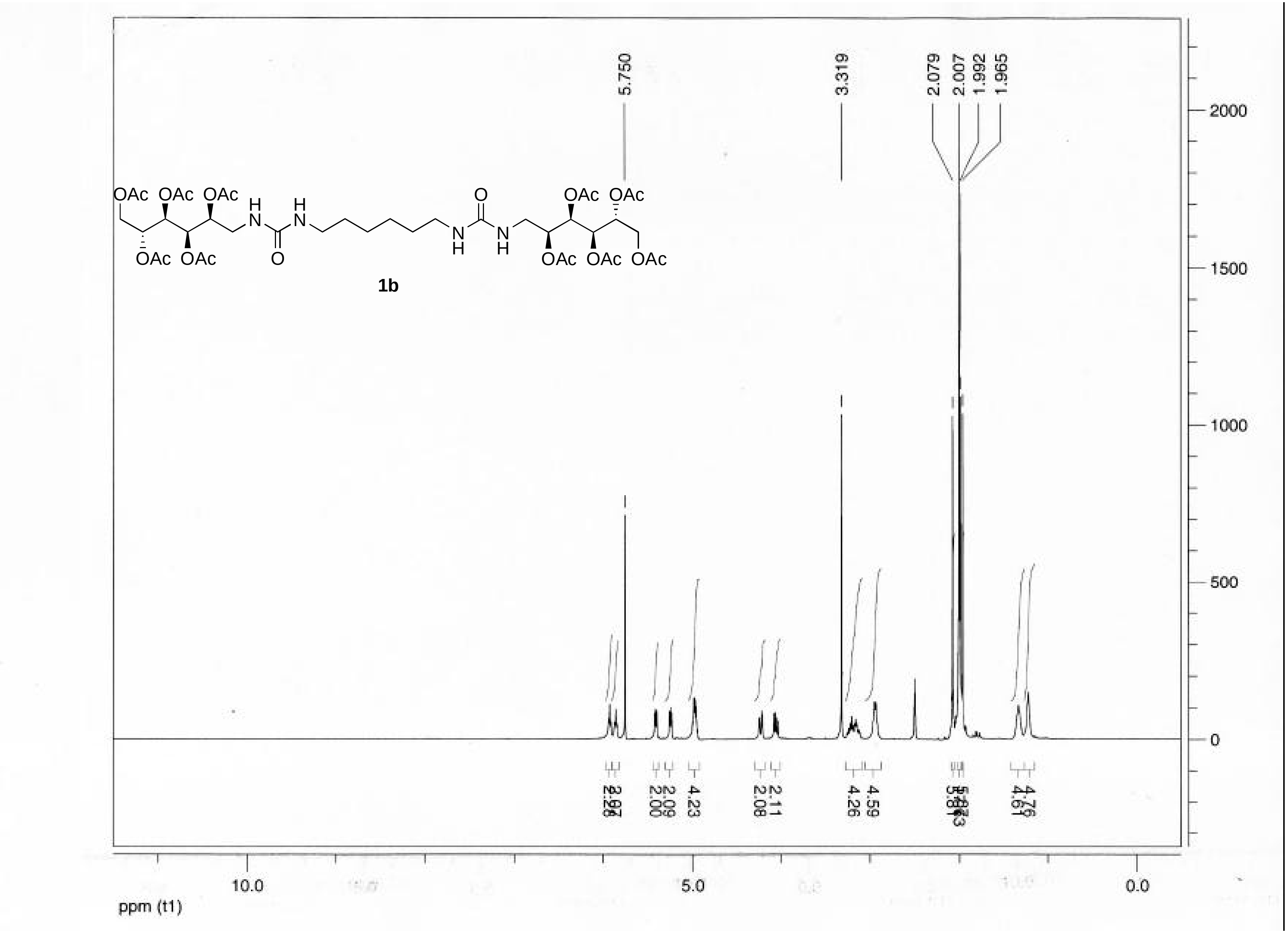
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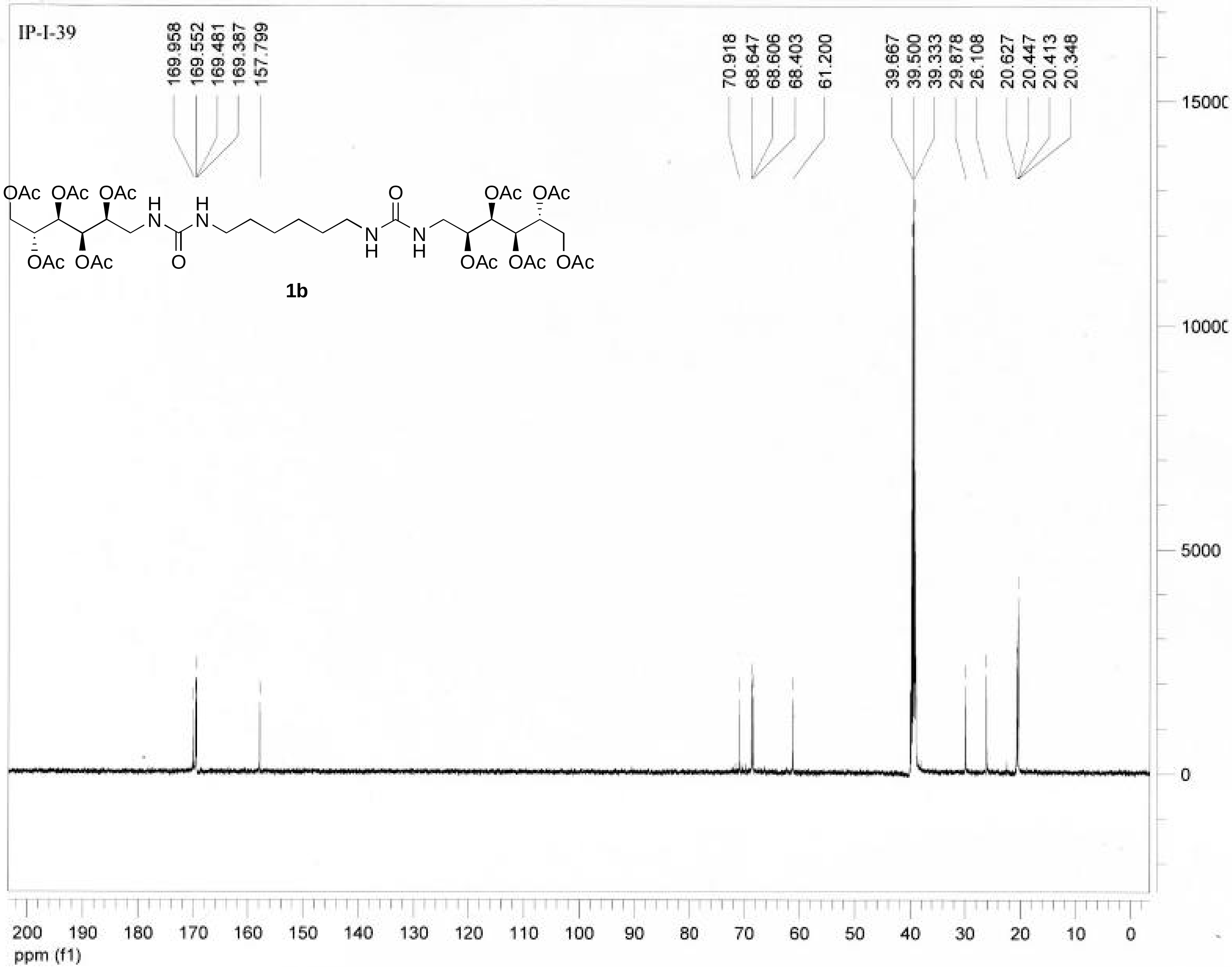
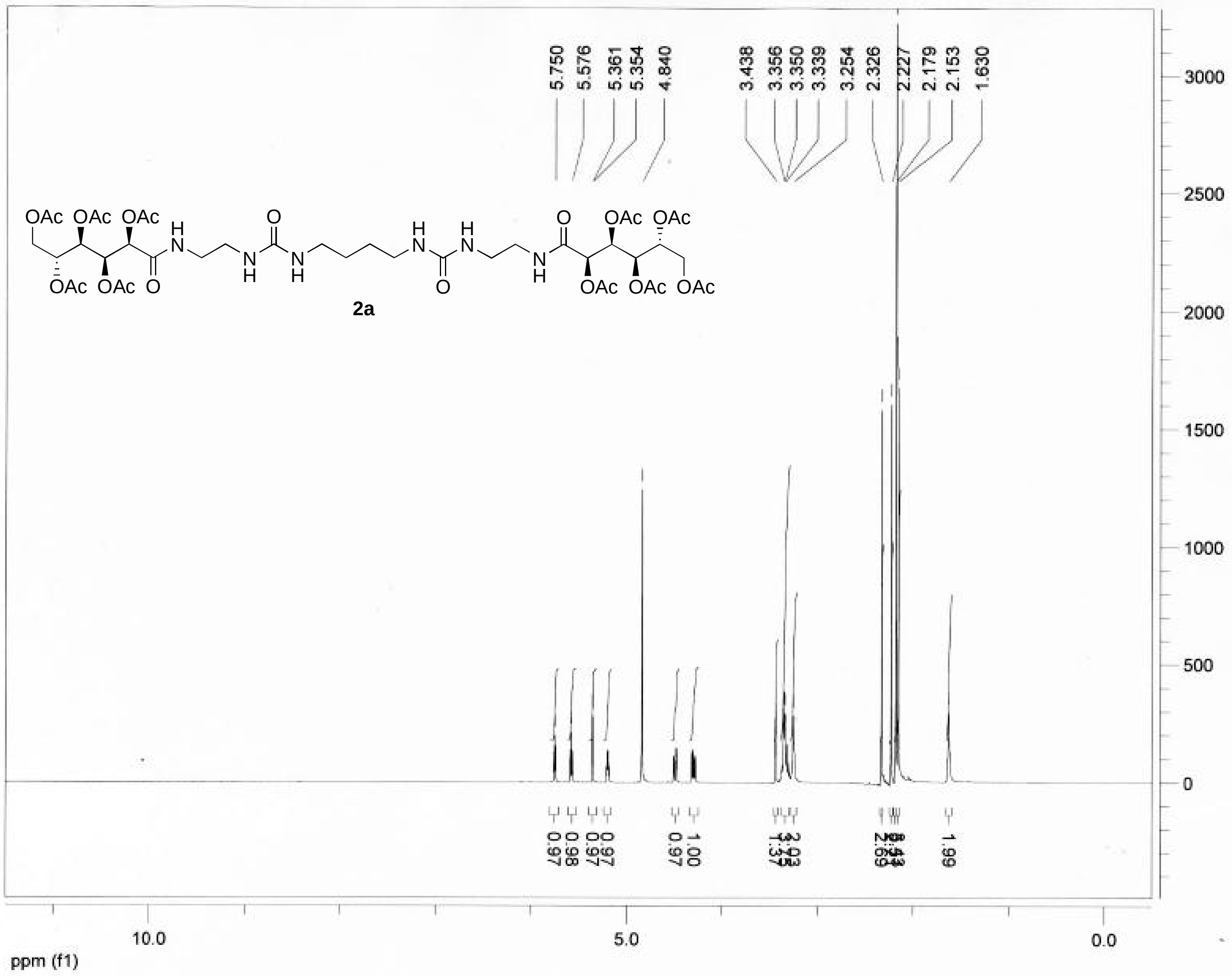
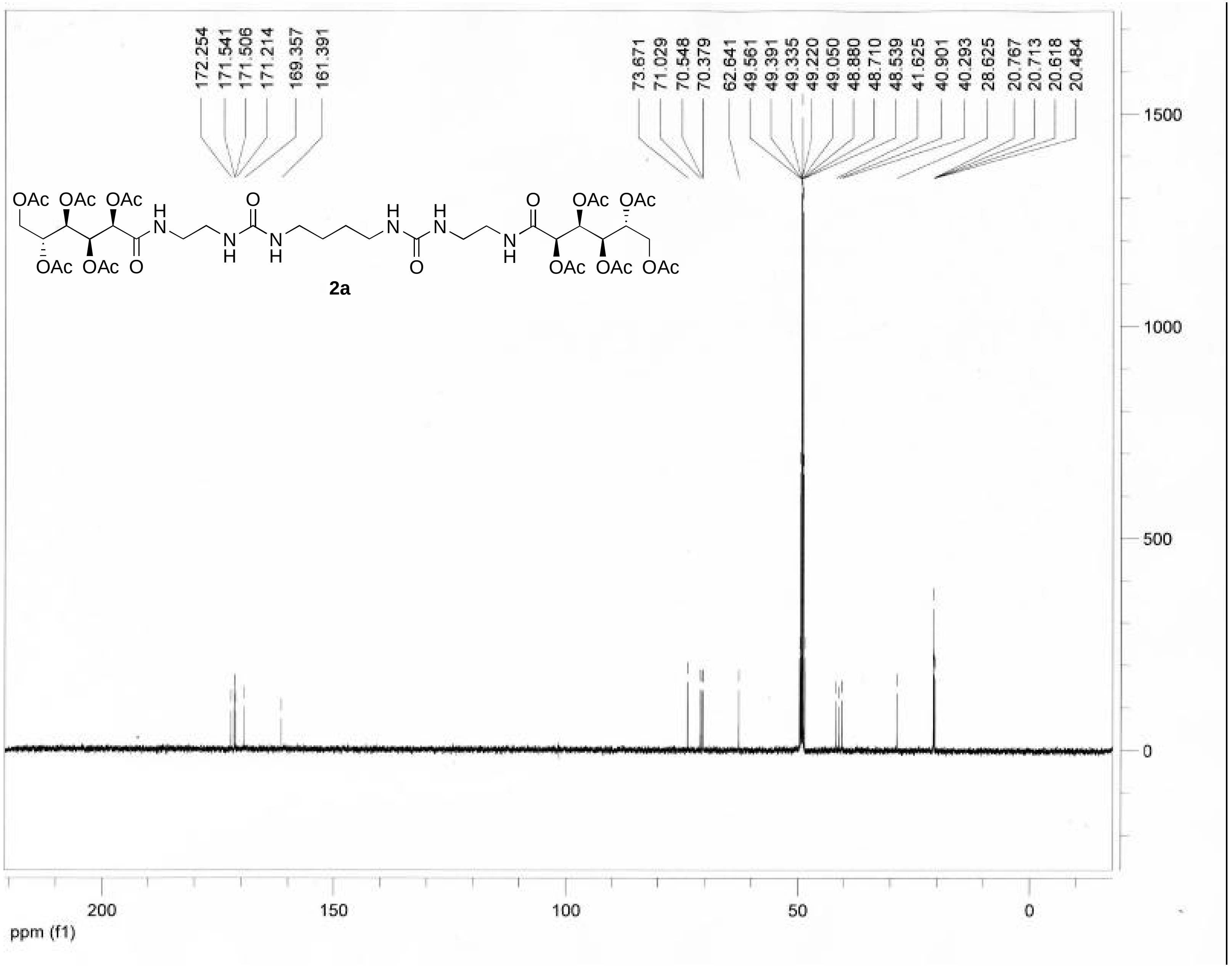
OAc
2000
1500
1000
500
0
2.00
2.09
4.23
2.08
2.11
4.26
4.59
5.81
4.61
4.76
10.0
5.0
0.0
ppm (t1)

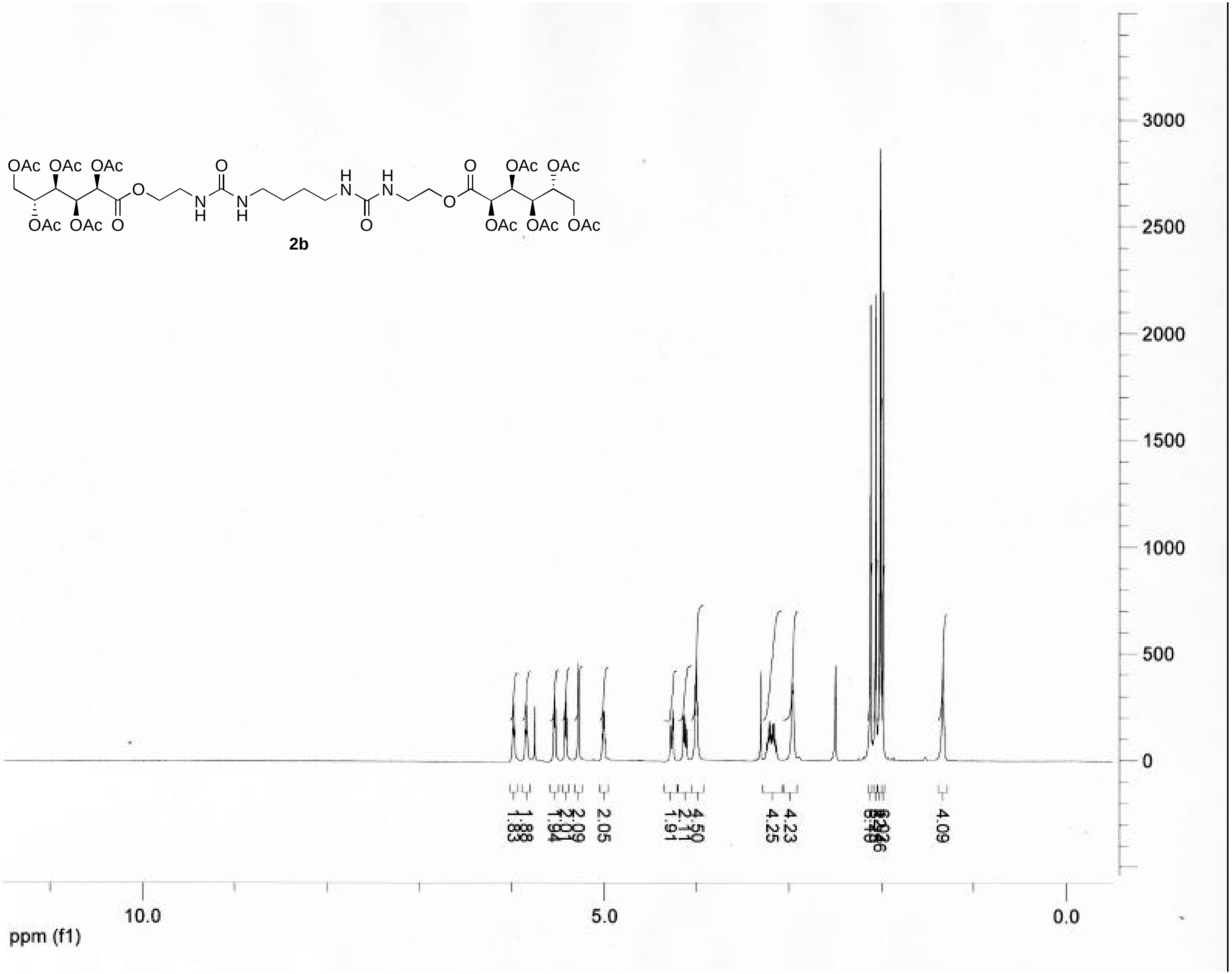
1b


IP-I-39
169.958
169.552
169.481
169.387
157.799
70.918
68.647
68.606
68.403
61.200
39.667
39.500
39.333
29.878
26.108
20.627
20.447
20.413
20.348
OAc
H
N
O
1b
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)


5.750
5.576
5.361
5.354
4.840
3.438
3.356
3.350
3.339
3.254
2.326
2.227
2.179
2.153
1.630
OAc
OAc
OAc
H
N
O
N
H
N
H
H
N
H
N
O
OAc
OAc
OAc
OAc
OAc
O
O
N
H
OAc
OAc
OAc
0.97
0.98
0.97
0.97
0.97
1.00
1.37
3.03
2.69
1.99
3000
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (f1)

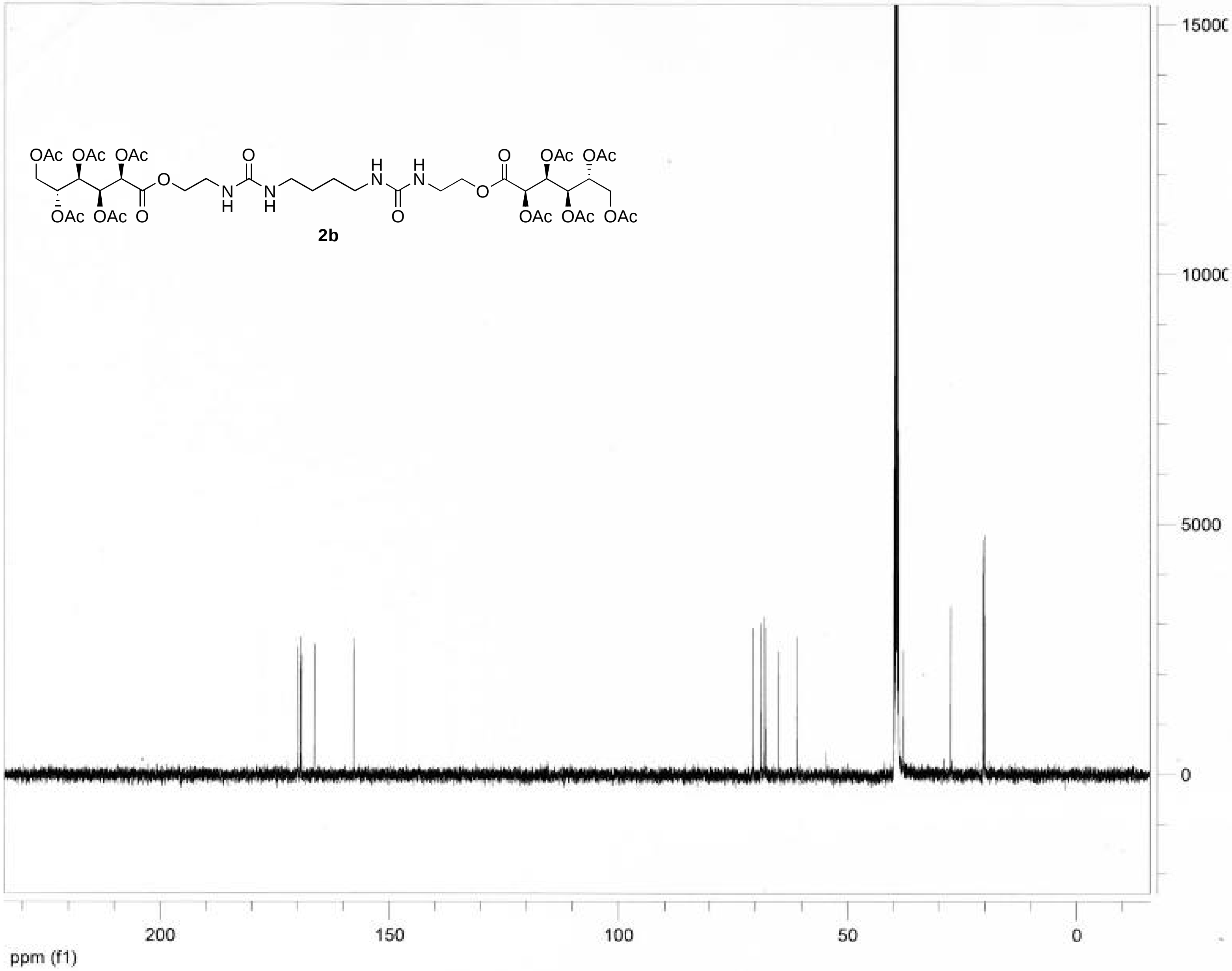
2a


2a
172.254
171.541
171.506
171.214
169.357
161.391
73.671
71.029
70.548
70.379
62.641
49.561
49.391
49.335
49.220
49.050
48.880
48.710
48.539
41.625
40.901
40.293
28.625
20.767
20.713
20.618
20.484
1500
1000
500
0
200
150
100
50
0
ppm (f1)
OAc
OAc
OAc
OAc
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
O
H
N
N
H
N
H
H
N
H
N
N
H

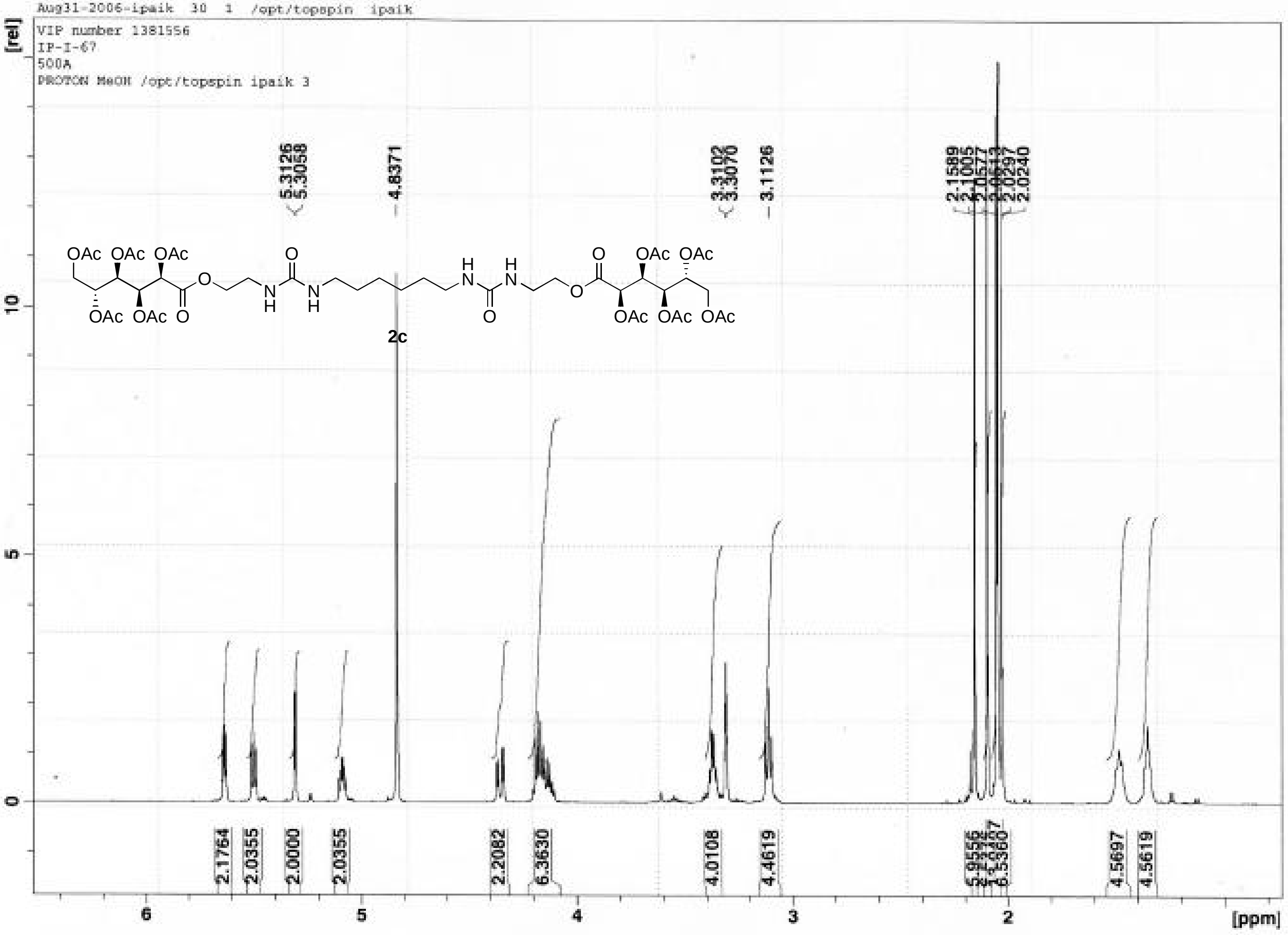


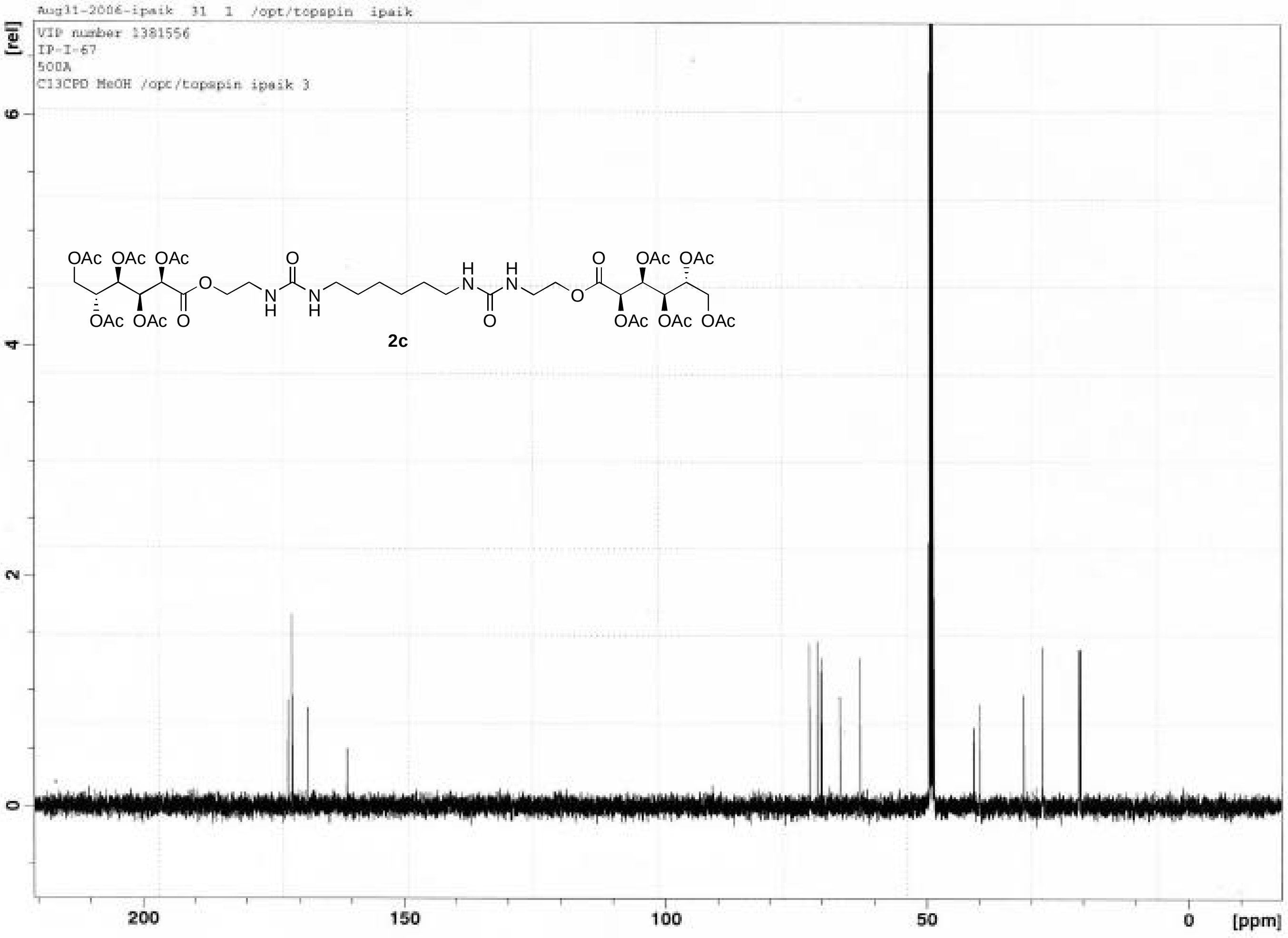
2b

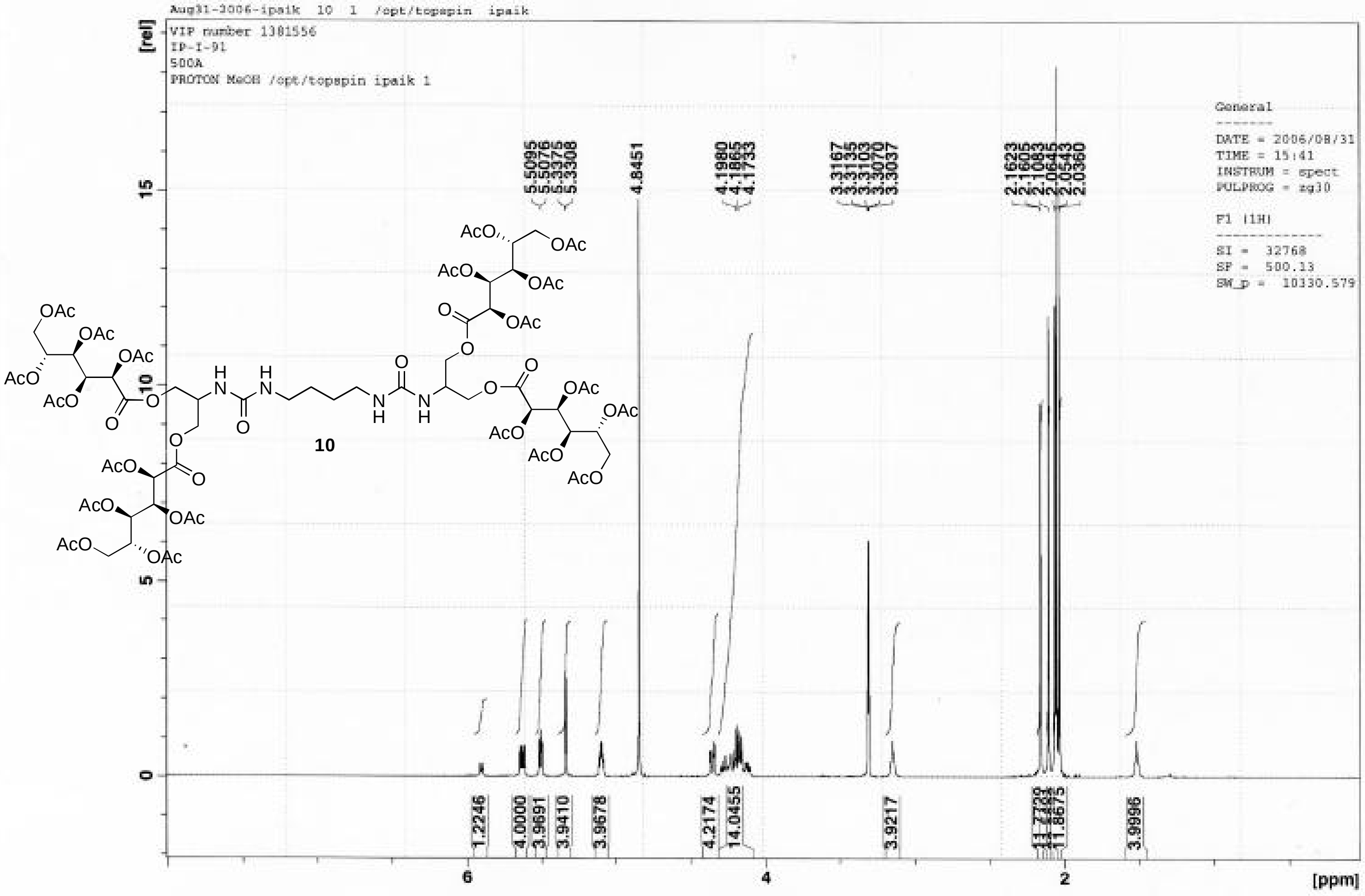
OAc OAc OAc
OAc OAc O
O
H
N
N
H
H
N
H
N
O
O
OAc OAc
OAc OAc OAc
3000
2500
2000
1500
1000
500
0
1.83
1.88
1.94
2.01
2.09
2.05
1.91
2.11
4.50
4.25
4.23
4.09
10.0
5.0
0.0
ppm (f1)


OAc
OAc
OAc
OAc
OAc
O
O
O
N
H
N
H
H
N
H
N
O
O
O
OAc
OAc
OAc
OAc
OAc
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

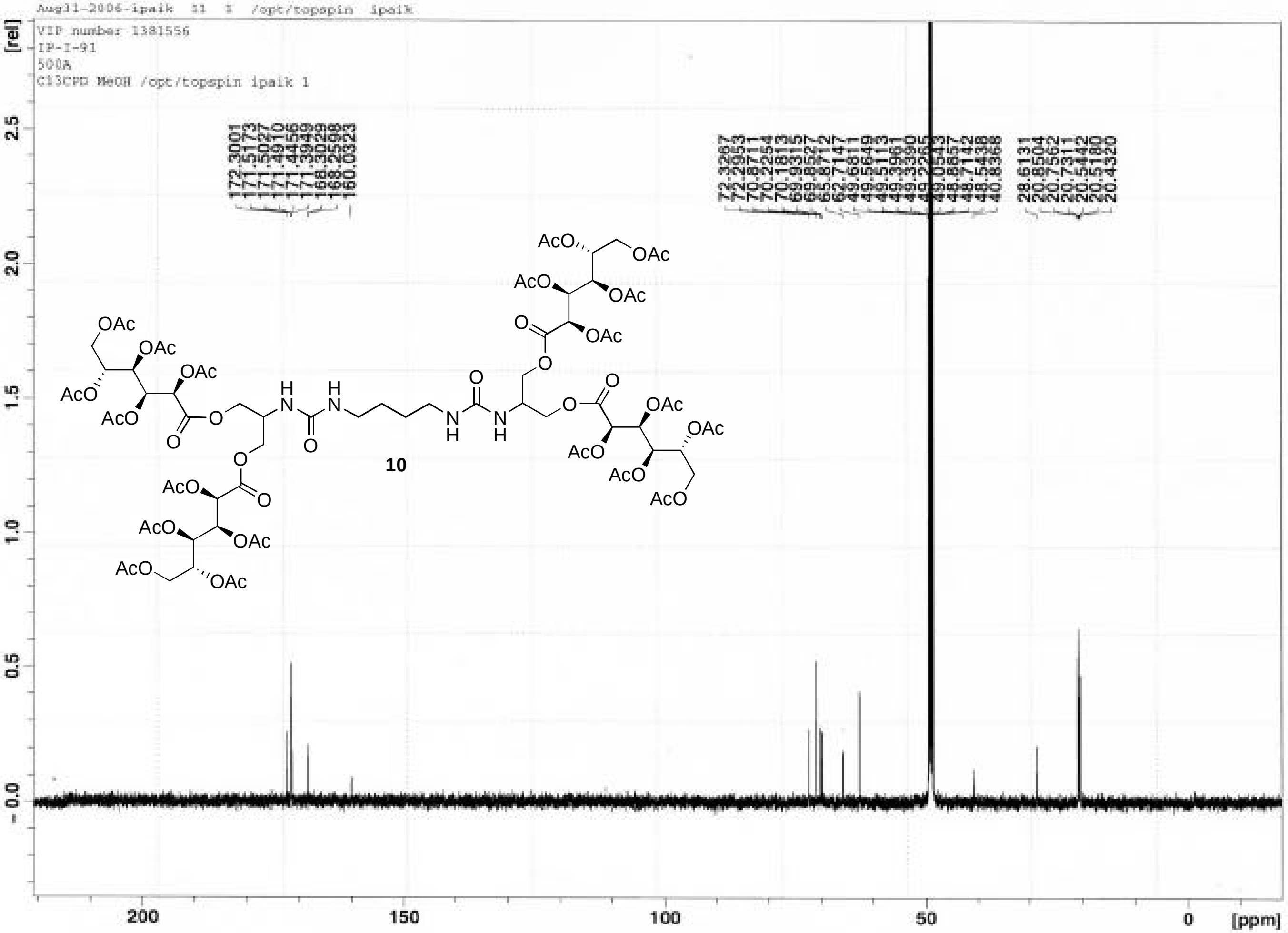
2b


2c
Aug31-2006-ipaik 30 1 /opt/topspin ipaik
VIP number 1381556
IP-I-67
500A
PROTON MeOH /opt/topspin ipaik 3
[rel]
10
5
0
5.3126
5.3058
4.8371
3.3102
3.3070
3.1126
2.1589
2.1005
2.0577
2.0613
2.0297
2.0240
OAc
OAc
OAc
O
O
N
H
N
H
N
H
N
H
O
O
O
OAc
OAc
OAc
OAc
OAc
OAc
O
O
O
2.1764
2.0355
2.0000
2.0355
2.2082
6.3630
4.0108
4.4619
6.9556
6.5360
4.5697
4.5619
6
5
4
3
2
[ppm]


Aug31-2006-ipaik 31 1 /opt/topspin ipaik
VIP number 1381556
IP-I-67
500A
C13CPD MeOH /opt/topspin ipaik 3
[rel]
6
4
2
0
200
150
100
50
0
[ppm]
OAc
O
N
H
2c


Aug31-2006-ipaik 10 1 /opt/topspin ipaik
VIP number 1381556
IP-I-91
500A
PROTON MeOH /opt/topspin ipaik 1
[rel]
15
10
5
0
General
DATE = 2006/08/31
TIME = 15:41
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 500.13
SW_p = 10330.579
5.5095
5.5076
5.3375
5.3308
4.8451
4.1980
4.1865
4.1733
3.3167
3.3135
3.3103
3.3070
3.3037
2.1623
2.1605
2.1083
2.0645
2.0543
2.0360
1.2246
4.0000
3.9691
3.9410
3.9678
4.2174
14.0455
3.9217
11.7729
11.8675
3.9996
6
4
2
[ppm]
AcO
OAc
O
H
N
OAc

10



Aug31-2006-ipaik 11 1 /opt/topspin ipaik
VIP number 1381556
IP-I-91
500A
C13CPD MeOH /opt/topspin ipaik 1
[rel]
2.5
2.0
1.5
1.0
0.5
0.0
172.3001
171.5173
171.5027
171.4910
171.4456
171.3949
168.3029
168.2598
160.0323
72.3267
72.2953
70.8711
70.2254
70.1813
69.9315
69.8527
65.8712
62.7147
49.6811
49.5649
49.5113
49.3961
49.3390
49.2265
48.8857
48.7142
48.5438
40.8368
28.6131
20.8504
20.7562
20.7311
20.5442
20.5180
20.4320
OAc
AcO
O
H
N
10
200
150
100
50
0
[ppm]