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Supporting Information

Chemoenzymatic Assembly of Mammalian O-Mannose Glycans

Caicai Meng, Aniruddha Sasmal, Yan Zhang, Tian Gao, Chang-Cheng Liu, Naazneen Khan, Ajit Varki, Fengshan Wang, and Hongzhi Cao**

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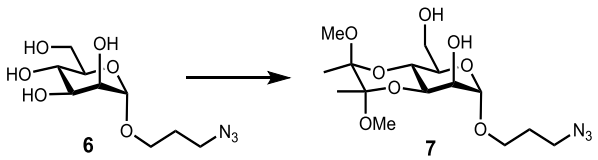
1. Chemical Synthesis

1.1 General method:

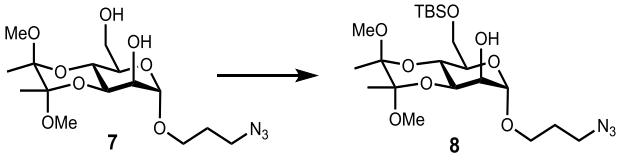
All chemicals were obtained from commercial suppliers and used without further purification unless noted. Thin layer chromatography (TLC) was performed on silica gel plates 60 F_{254} (Merck, Billerica MA). Plates were visualized under UV light and/or by treatment with 5% sulfuric acid in ethanol or *p*-anisaldehyde sugar stain followed by heating. Silica gel 60 (300-400 mesh, Haiyang, Qingdao, China) was used for flash column chromatography. Gel filtration chromatography was performed using a column (100×2.5 cm) packed with BioGel P-2 Fine resins (Bio-Rad, Hercules, CA). ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on Bruker AVANCE-600 spectrometer or Agilent VNMRS-600 spectrometer at 25 ℃. NMR spectra were calibrated using solvent signals (^{1}H: δ 7.26 for CD_3Cl_3, ^{13}C: δ 77.0 for $CDCl_3$). High resolution electrospray ionization (ESI) mass spectra were obtained at the National Glycoengineering Research Center and Drug Testing and Analysis Center in Shandong University.

1.2 Experimental Procedures



3-Azidopropyl 3,4-*O*-(2′,3′-dimethoxybutan-2′,3′-diyl)-α-D-mannopyranoside (7)

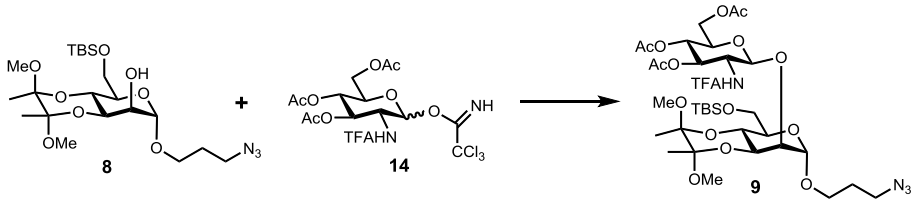
Camphorsulfonic acid (1.62 g, 6.98 mmol) was added to a solution of 3-azidopropyl α-D-mannopyranoside **6**[1] (16.7 g, 63 mmol), 2,3-butanedione (6.0 mL, 70 mmol) and trimethyl orthoformate (23 mL, 0.21 mol) in dry methanol (150 mL) under an argon atmosphere. The mixture was heated under reflux for 12 hours. The reaction was neutralized with triethylamine (1.5 mL) and the solvents was removed under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate, 1:2, v/v) to give mannoside **7** as a yellowish oil (13.9 g, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.83 (d, *J* = 1.5 Hz, 1H), 4.09 (t, *J* = 10.0 Hz, 1H), 3.97 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.91 (dd, *J* = 3.2, 1.5 Hz, 1H), 3.88 – 3.66 (m, 4H), 3.57 – 3.44 (m, 1H), 3.37 (p, *J* = 6.2 Hz, 2H), 3.27 (s, 3H), 3.25 (s, 3H), 2.37 (broad s, 2H), 1.84 (p, *J* = 6.5 Hz, 2H), 1.32 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 100.19, 100.13, 99.75, 70.84, 69.49, 68.07, 64.47, 62.61, 60.94, 48.28, 48.00, 47.79, 28.68, 17.67, 17.57; HRMS (ESI) m/z calcd for $C_{15}H_{31}N_4O_8$ $[M+NH_4]^+$ 395.2142, found 395.2129.



3-Azidopropyl 6-*O*-*tert*-butyldimethylsilyl-3,4-*O*-(2′,3′-dimethoxybutan-2′,3′-diyl)-α-D-mannopyranoside (8)

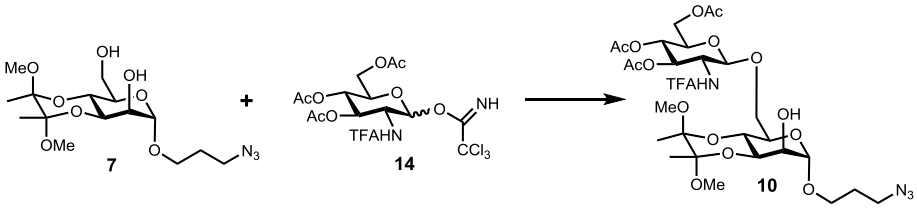
To the solution of mannoside **7** (5.0 g, 13.3 mmol) in DMF (15 mL), TBSCl (2.2 g, 14.6 mmol) and imidazole (1.36 g, 20 mmol) was added at 0 ℃. The solution was

stirred at room temperature for 1 h, and then diluted with 6.0 mL of 0.5 M HCl. The resulting mixture was extracted with Et_2O, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (hexane/ethyl acetate, 8:1, v/v) to give compound **8** as a syrup (5.5 g, 84%).^{1}H NMR (600 MHz, $CDCl_3$) δ 4.79 (d, *J* = 1.6 Hz, 1H), 4.01 – 3.93 (m, 2H), 3.91 – 3.86 (m, 1H), 3.84 (dd, *J* = 11.3, 1.9 Hz, 1H), 3.81 – 3.74 (m, 2H), 3.69 – 3.67 (m, 1H), 3.50 – 3.46 (m, 1H), 3.36 (m, 2H), 3.27 (s, 3H), 3.23 (s, 3H), 2.27 (broad s, 1H), 1.84 (p, *J* = 6.5 Hz, 2H), 1.31 (s, 3H), 1.28 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 100.23, 99.86, 99.75, 71.73, 69.71, 68.40, 64.24, 62.83, 61.63, 48.49, 48.06, 47.88, 28.79, 25.81, 18.27, 17.77, 17.68, 0.99, -5.20, -5.40; HRMS (ESI) m/z calcd for $C_{21}H_{45}N_4O_8Si$ $[M+NH_4]^+$ 509.3007, found 509.2998.



3-Azidopropyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl-(1→2)-6-*O*-*tert*-butyldimethylsilyl-3,4-*O*-(2′,3′-dimethoxybutan-2′,3′-diyl)-α-D-mannopyranoside (9)

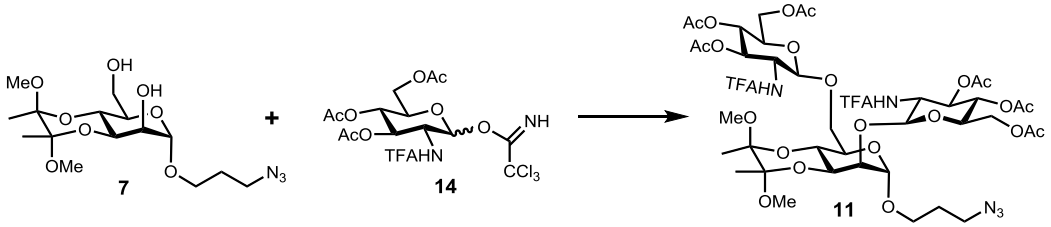
A solution of glycosyl donor **14**[2] (5.45 g, 10 mmol), glycosyl acceptor **8** (3.27 g, 6.66 mmol) and activated 4 Å molecular sieves (18.0 g) in anhydrous CH_2Cl_2 (100 mL) was stirred under argon at room temperature for 30 min. The reaction mixture was then cooled to -30 ℃, followed by adding of TMSOTf (271 μL, 1.5 mmol). The reaction mixture was quenched after 1 h with Et_3N (5 mL), filtered, concentrated, and purified by silica gel flash chromatography (hexane/ethyl acetate, 10:1, v/v) to afford disaccharide **9** (4.83 g, 83%) as a yellowish syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (d, *J* = 7.0 Hz, 1H), 5.84 (t, *J* = 9.8 Hz, 1H), 5.16 (d, *J* = 8.5 Hz, 1H), 5.07 (t, *J* = 9.6 Hz, 1H), 4.69 (d, *J* = 1.6 Hz, 1H), 4.29 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.20 (dd, *J* = 12.3, 2.4 Hz, 1H), 4.04 (dd, *J* = 10.3, 2.8 Hz, 1H), 4.00 (t, *J* = 2.1 Hz, 1H), 3.91 (t, *J* = 10.2 Hz, 1H), 3.83 (d, *J* = 11.3 Hz, 1H), 3.79 – 3.63 (m, 5H), 3.49 (dt, *J* = 10.2, 6.3 Hz, 1H), 3.39 – 3.32 (m, 2H), 3.31 (s, 3H), 3.19 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.85 (p, *J* = 6.5 Hz, 2H), 1.30 (s, 3H), 1.27 (s, 3H), 0.86 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.52, 169.98, 169.70, 100.18, 99.38, 99.36, 96.41, 72.42, 72.08, 71.46, 70.13, 68.55, 67.56, 64.41, 63.13, 61.72, 55.82, 48.47, 48.30, 47.79, 28.74, 25.74, 20.69, 20.63, 20.46, 18.19, 17.75, 17.59, 0.99, -5.32, -5.41; HRMS (ESI) m/z calcd for $C_{35}H_{61}F_3N_5O_{16}Si$ $[M+NH_4]^+$ 892.3835, found 892.3844.



3-Azidopropyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D

-glucopyranosyl-(1→6)-3,4-*O*-(2′,3′-dimethoxybutan-2′,3′-diyl)-α-D -mannopyranoside (10)

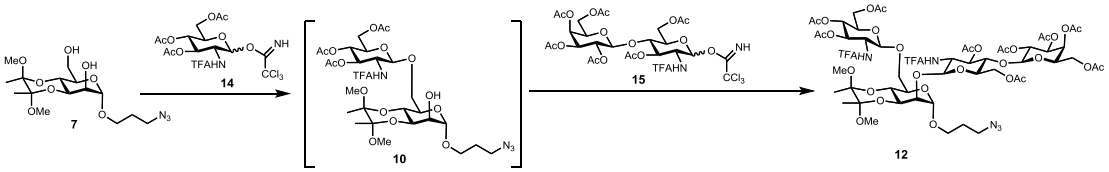
A solution of glycosyl donor **14** (2.9 g, 5.3 mmol), glycosyl acceptor **7** (2.0 g, 5.3 mmol) and activated 4 Å molecular sieves (10.0 g) in anhydrous CH_2Cl_2 (40 mL) was stirred under argon at room temperature for 30 min. The reaction mixture was then cooled to -50 ℃, followed by adding of TMSOTf (96 μL, 0.53 mmol). The reaction mixture was quenched after 1 h with Et_3N (2.5 mL), filtered, concentrated, and purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1, v/v) to afford disaccharide **10** (3.44 g, 86%) as a yellowish syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 1H), 5.18 (t, *J* = 9.3 Hz, 1H), 5.13 (t, *J* = 9.5 Hz, 1H), 4.76 (d, *J* = 8.4 Hz, 1H), 4.73 (d, *J* = 1.4 Hz, 1H), 4.30 – 4.25 (m, 2H), 4.16 (dd, *J* = 12.3, 2.5 Hz, 1H), 4.13 – 4.10 (m, 1H), 3.96 (dd, *J* = 10.0, 3.1 Hz, 1H), 3.94 – 3.90 (m, 1H), 3.89 (dd, *J* = 3.1, 1.5 Hz, 1H), 3.79 (t, *J* = 2.9 Hz, 1H), 3.78 (t, *J* = 3.5 Hz, 1H), 3.68 (dt, *J* = 9.9, 5.8 Hz, 1H), 3.47 – 3.31 (m, 4H), 3.26 (s, 3H), 3.17 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.83 (p, *J* = 6.4 Hz, 2H), 1.33 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.88, 170.67, 169.25, 157.28 (d, *J* = 37.5 Hz), 122.74 (q, *J* = 288.2 Hz), 100.51, 100.24, 100.09, 99.97, 72.48, 71.79, 69.63, 69.36, 68.95, 68.12, 67.80, 64.80, 64.11, 61.88, 54.10, 48.32, 48.17, 47.63, 28.48, 20.68, 20.52, 20.40, 17.87, 17.66; HRMS (ESI) m/z calcd for $C_{29}H_{47}F_3N_5O_{16}$ $[M+NH_4]^+$ 778.2970, found 778.2976.



3-Azidopropyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D -glucopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D -glucopyranosyl-(1→6)]-3,4-*O*-(2′,3′-dimethoxybutan-2′,3′-diyl)-α-D -mannopyranoside (11)

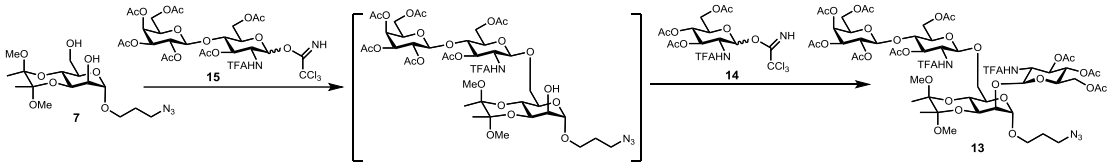
A solution of glycosyl donor **14** (4.9 g, 9.0 mmol), glycosyl acceptor **7** (1.36 g, 3.6 mmol) and activated 4 Å molecular sieves (12 g) in anhydrous CH_2Cl_2 (40 mL) was stirred under argon at room temperature for 30 min. The reaction mixture was then cooled to -30 ℃, followed by adding of TMSOTf (130 μL, 0.72 mmol). The reaction mixture was quenched after 1 h with Et_3N (1.5 mL), filtered, concentrated, and purified by silica gel flash chromatography (hexane/ethyl acetate, 3:2, v/v) to afford trisaccharide **11** (3.5 g, 85%) as a white amorphous powder. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 5.67 (t, *J* = 10.6 Hz, 1H), 5.24 (dd, *J* = 10.7, 9.3 Hz, 1H), 5.09 (t, *J* = 9.7 Hz, 1H), 5.07 (t, *J* = 9.6 Hz, 1H), 5.04 (d, *J* = 8.5 Hz, 1H), 4.62 (d, *J* = 1.5 Hz, 1H), 4.59 (d, *J* = 8.2 Hz, 1H), 4.32 – 4.23 (m, 2H), 4.17 (dd, *J* = 12.3, 2.5 Hz, 1H), 4.14 – 4.08 (m, 2H), 4.05 (dt, *J* = 10.5, 8.7 Hz, 1H), 3.99 (dd, *J* = 10.2, 2.9 Hz, 1H), 3.94 (dd, *J* = 3.0, 1.6 Hz, 1H), 3.82 (ddd, *J* = 10.0, 8.0, 1.8 Hz, 1H), 3.76 – 3.62 (m, 5H), 3.47 (dd, *J* = 10.6, 8.3 Hz, 1H), 3.43 – 3.29 (m, 3H), 3.25 (s, 3H), 3.12 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.01

(s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.82 (p, *J* = 6.5 Hz, 2H), 1.26 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.09, 170.72, 170.62, 170.44, 169.57, 169.30, 157.52 (d, *J* = 37.6 Hz), 157.18 (d, *J* = 37.3 Hz), 115.57 (d, *J* = 288.2 Hz), 115.42 (d, *J* = 288.6 Hz), 100.30, 100.13, 99.53, 98.65, 97.15, 72.73, 72.05, 71.79, 71.67, 70.49, 70.22, 68.52, 68.32, 68.18, 67.06, 64.68, 63.67, 61.88, 61.76, 55.47, 54.53, 48.44, 48.19, 47.65, 28.52, 20.66, 20.65, 20.58, 20.56, 20.44, 20.36, 17.68, 17.59; HRMS (ESI) m/z calcd for $C_{43}H_{63}F_6N_6O_{24}$ $[M+NH_4]^+$ 1161.3798, found 1161.3811.



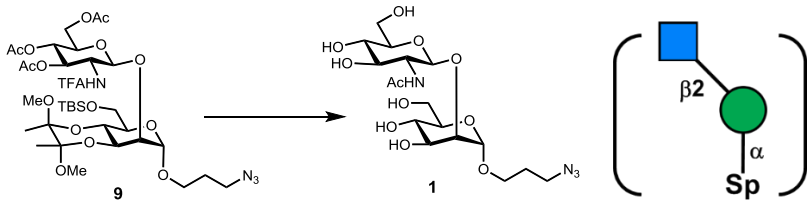
3-Azidopropyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl-(1→2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl-(1→6)]-3,4-*O*-(2′,3′-dimethoxybutan-2′,3′-diyl)-α-D-mannopyranoside (12)

A solution of glycosyl donor **14** (2.0 g, 3.7 mmol), glycosyl acceptor **7** (1.4 g, 3.7 mmol) and activated 4 Å molecular sieves (10.0 g) in anhydrous CH_2Cl_2 (40 mL) was stirred under argon at room temperature for 30 min. The reaction mixture was then cooled to -50 ℃, followed by adding of TMSOTf (67 μL, 0.37 mmol). Upon the reaction was completed as indicated by TLC, the disaccharide donor **15** (4.7 g, 5.6 mmol) and another portion of TMSOTf (100 μL, 0.56 mmol) were added, and the reaction temperature was allowed warm to -20 ℃. The reaction mixture was quenched after 1 h with Et_3N (2.5 mL), filtered, concentrated, and purified by silica gel flash chromatography (hexane/ethyl acetate, 1:1, v/v) to afford tetrasaccharide **12** (3.46 g, 65% for 2 steps) as a yellowish syrup.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 9.1 Hz, 1H), 5.36 (d, *J* = 3.3 Hz, 1H), 5.33 (t, *J* = 8.6 Hz, 1H), 5.23 (dd, *J* = 10.6, 9.3 Hz, 1H), 5.16 – 5.08 (m, 3H), 4.97 (dd, *J* = 10.5, 3.4 Hz, 1H), 4.87 (d, *J* = 7.2 Hz, 1H), 4.67 (d, *J* = 1.5 Hz, 1H), 4.64 (d, *J* = 8.2 Hz, 1H), 4.56 (dd, *J* = 12.0, 3.1 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.29 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.21 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.17 – 3.79 (m, 15H), 3.75 – 3.62 (m, 5H), 3.48 (dd, *J* = 10.6, 8.0 Hz, 1H), 3.44 – 3.30 (m, 4H), 3.24 (s, 3H), 3.14 (s, 3H), 2.15 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.83 (p, *J* = 6.5 Hz, 2H), 1.25 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.92, 170.71, 170.42, 170.35, 170.09, 170.06, 169.29, 169.21, 157.31 (d, *J* = 37.5 Hz), 157.19 (d, *J* = 37.4 Hz), 115.57 (d, *J* = 289.2 Hz), 101.14, 100.33, 100.06, 99.60, 97.68, 97.33, 75.28, 73.56, 73.14, 71.79, 71.77, 70.80, 70.73, 70.51, 70.14, 68.99, 68.32, 68.13, 66.88, 66.56, 64.77, 63.64, 62.08, 61.81, 60.80, 60.40, 54.69, 53.79, 48.47, 48.05, 47.70, 29.68, 28.53, 21.05, 20.87, 20.68, 20.64, 20.62, 20.59, 20.51, 20.39, 17.72, 17.61; HRMS (ESI) m/z calcd for $C_{55}H_{75}F_6N_5O_{32}Na$ $[M+Na]^+$ 1454.4197, found 1454.4327.



3-Azidopropyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl-(1→6)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl-(1→2)]-3,4-*O*-(2′,3′-dimethoxybutan-2′,3′-diyl)-α-D-mannopyranoside (13)

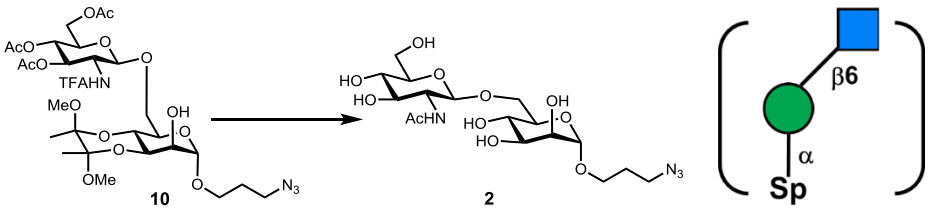
The mixture of glycosyl acceptor **7** (1.0 g, 2.65 mmol), disaccharide trichloroacetimidate donor **15** (2.2 g, 2.65 mmol) and 4 Å molecular sieves powder (2.0 g) in dry CH_2Cl_2 (20 mL) was stirred at room temperature for 30 min. The mixture was then cooled to -50 ℃ and treated with TMSOTf (48 μL, 0.26 mmol) in CH_2Cl_2. After 1 hour, as the reaction was completed, the trichloroacetimidate donor **14** (2.16 g, 3.98 mmol) and another portion of TMSOTF (74 μL, 0.4 mmol) were added, and the reaction temperature was allowed warm to -20 ℃, After 1 h, the reaction mixture was neutralized with Et_3N (1.5 mL) and then filtered and concentrated. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate, 1:1, v/v) to afford tetrasaccharide **13** (2.8 g, 74% for 2 steps) as a yellowish syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 9.5 Hz, 1H), 5.70 (t, *J* = 10.8 Hz, 1H), 5.35 (d, *J* = 3.4 Hz, 1H), 5.16 – 5.03 (m, 4H), 4.96 (ddd, *J* = 10.4, 3.7, 1.5 Hz, 1H), 4.64 (d, *J* = 1.9 Hz, 1H), 4.53 (dd, *J* = 7.1, 1.5 Hz, 1H), 4.51 – 4.43 (m, 2H), 4.30 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.18 – 4.03 (m, 6H), 4.00 (dd, *J* = 10.1, 3.0 Hz, 1H), 3.95 (dd, *J* = 3.1, 1.7 Hz, 1H), 3.88 (t, *J* = 6.8 Hz, 1H), 3.81 (q, *J* = 8.2 Hz, 2H), 3.78 – 3.60 (m, 4H), 3.48 (dd, *J* = 10.6, 7.5 Hz, 1H), 3.44 – 3.29 (m, 2H), 3.27 (s, 3H), 3.14 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.83 (q, *J* = 6.8 Hz, 2H), 1.27 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.61, 170.59, 170.37, 170.35, 170.30, 170.09, 170.03, 169.55, 169.22, 157.55 (d, *J* = 37.7 Hz), 157.21 (d, *J* = 37.5 Hz), 115.62 (d, *J* = 288.0 Hz), 115.40 115.62 (d, *J* = 288.4 Hz), 101.18, 100.15, 100.13, 99.54, 98.54, 96.93, 75.59, 72.69, 72.68, 72.07, 71.41, 70.78, 70.73, 70.37, 70.23, 68.97, 68.39, 67.80, 67.06, 66.55, 64.68, 63.55, 62.13, 61.66, 60.80, 55.60, 53.46, 48.43, 48.21, 47.70, 28.53, 20.78, 20.66, 20.58, 20.55, 20.53, 20.48, 20.43, 17.68, 17.57; HRMS (ESI) m/z calcd for $C_{55}H_{79}F_6N_6O_{32}$ $[M+NH_4]^+$ 1449.4643, found 1449.4670.



3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (1)

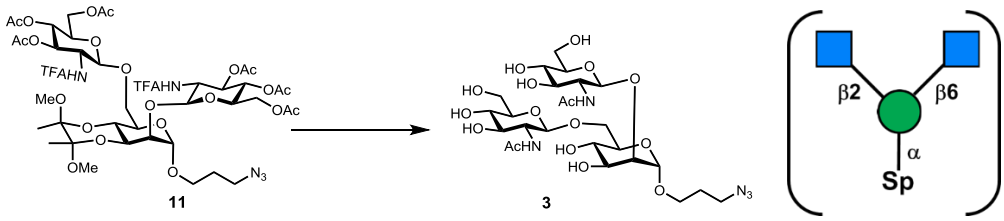
Disaccharide **9** (3.9 g, 4.34 mmol) was dissolved in TFA/H_2O (9:1, v/v, 20 mL). After stirring for 5 h at room temperature, the reaction mixture was concentrated and coevaporated with toluene (3×5 mL). The residue was then dissolved in dry MeOH

(30 mL) and sodium methoxide was added to the solution to adjust the pH to 11. The resulting mixture was stirred at room temperature and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, v/v). After complete consumption of the starting material, 1 M LiOH (30 mL) was added, the reaction mixture was stirred for another 1h at room temperature. The mixture was then neutralized with 1 M HCl and concentrated. The crude *N*-deacetyled disaccharide was then dissolved in MeOH (50 mL), and acetic anhydride (0.84 mL, 8.92 mmol) was added. The mixture was stirred at room temperature for 1 h. After completion of the reaction, the mixture was concentrated and purified by Bio-Gel P2 gel filtration chromatography to afford the disaccharide **1** (1.8 g, 87% for 3 steps) as a white solid. ^{1}H NMR (600 MHz, D_2O) δ 4.86 (d, *J* = 1.6 Hz, 1H), 4.55 (d, *J* = 8.4 Hz, 1H), 4.07 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.90 – 3.88 (m, 2H), 3.86 – 3.80 (m, 2H), 3.75 (dd, *J* = 12.4, 5.6 Hz, 1H), 3.70 (dd, *J* = 10.4, 8.4 Hz, 1H), 3.65 – 3.37 (m, 9H), 2.05 (s, 2H), 1.95 – 1.85 (m, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.70, 99.44, 96.83, 76.30, 75.73, 73.23, 72.83, 69.81, 69.54, 67.19, 64.88, 61.45, 60.52, 55.26, 48.16, 27.81, 22.21; HRMS (ESI) m/z calcd for $C_{17}H_{31}N_4O_{11}$ $[M+H]^+$ 467.1989, found 467.1983.



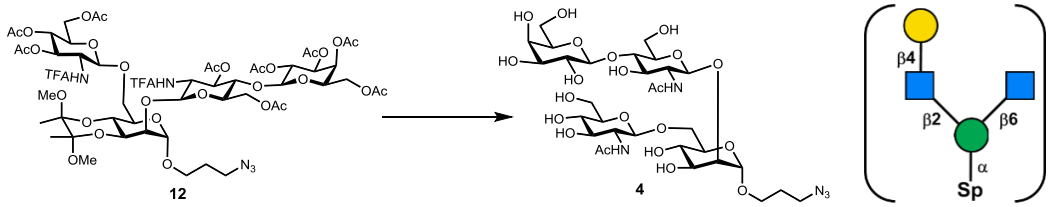
3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-α-D -mannopyranoside (2)

To a solution of disaccharide **10** (3.4 g, 4.47 mmol), TFA/H_2O (9:1, v/v, 30 mL) was added, after stirring for 30 min at room temperature, the reaction mixture was concentrated and coevaporated with toluene (3×5 mL) in vacuo. The residue was dissolved in dry MeOH (30 mL) and sodium methoxide was added to the solution to adjust the pH to 11. The resulting mixture was stirred at room temperature and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, v/v). After complete consumption of the starting material, 1 M LiOH (30 mL) was added, the reaction mixture was stirred for 1h at room temperature. The mixture was then neutralized with 1 M HCl and concentrated to give the crude *N*-deacetyled disaccharide. The crude *N*-deacetyled disaccharide was then dissolved in MeOH (30 mL), and acetic anhydride (840 μL, 8.94 mmol) was added. The mixture was stirred at room temperature for 1 h. After completion of the reaction, the mixture was concentrated and purified by Bio-Gel P2 gel filtration chromatography to afford the disaccharide **2** (1.88 g, 90% for 3 steps) as a white solid. ^{1}H NMR (600 MHz, D_2O) δ 4.80 (d, *J* = 1.7 Hz, 1H), 4.53 (d, *J* = 8.5 Hz, 1H), 4.16 (dt, *J* = 10.3 Hz, 1H), 3.92 (dd, *J* = 5.0, 1.9 Hz, 1H), 3.91 (dd, *J* = 4.1, 2.0 Hz, 1H), 3.77 – 3.69 (m, 6H), 3.63 – 3.49 (m, 3H), 3.46 – 3.38 (m, 4H), 2.02 (s, 3H), 1.88 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.31, 101.40, 99.63, 75.76, 73.77, 71.37, 70.52, 68.94, 66.67, 64.55, 62.35, 60.65, 55.41, 48.74, 48.11, 27.71, 22.11; HRMS (ESI) m/z calcd for $C_{17}H_{31}N_4O_{11}$ $[M+H]^+$ 467.1989, found 467.1981.



3-Azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-α-D-mannopyranoside (3)

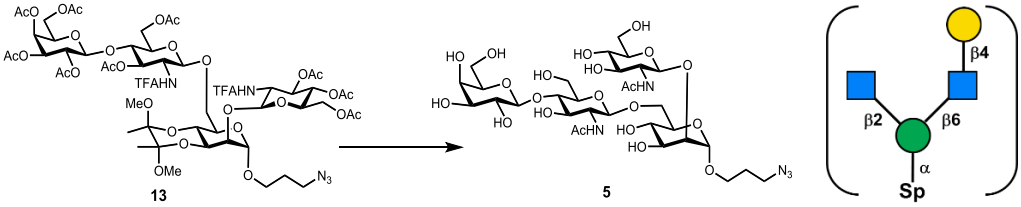
To a solution of trisaccharide **11** (2.3 g, 2.0 mmol), TFA/H_2O (9:1, v/v, 10 mL) was added, after stirring for 30 min at room temperature, the reaction mixture was concentrated and coevaporated with toluene (3×5 mL) in vacuo. The residue was dissolved in dry MeOH (30 mL) and sodium methoxide was added to the solution to adjust the pH to 11. The resulting mixture was stirred at room temperature and monitored by TLC (EtOAc/MeOH/H_2O, 8:4:1, v/v). After complete consumption of the starting material, 1 M LiOH (30 mL) was added, the reaction mixture was stirred for 1 h at room temperature. The mixture was then neutralized with 1 M HCl and concentrated. The crude *N*-deacetyled trisaccharide was then dissolved in MeOH (30 mL), and acetic anhydride (750 μL, 8.0 mmol) was added. The mixture was stirred at room temperature for 1 h. After completion of the reaction, the mixture was concentrated and purified by Bio-Gel P2 gel filtration chromatography to afford the trisaccharide **3** (1.13 g, 84% for 3 steps) as a white solid. ^{1}H NMR (600 MHz, D_2O) δ 4.52 (d, *J* = 8.3 Hz, 1H), 4.50 (d, *J* = 8.5 Hz, 1H), 4.17 (dd, *J* = 10.9, 1.7 Hz, 1H), 4.03 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.89 (td, *J* = 12.7, 1.8 Hz, 2H), 3.81 – 3.62 (m, 7H), 3.57 – 3.50 (m, 4H), 3.45 – 3.38 (m, 8H), 2.02 (s, 3H), 1.99 (s, 3H), 1.87 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.49, 174.12, 101.44, 99.56, 96.81, 76.46, 75.73, 75.71, 73.64, 73.10, 71.60, 69.89, 69.85, 69.79, 69.49, 67.34, 64.72, 60.67, 60.49, 55.41, 55.33, 48.19, 27.73, 22.31, 22.11; HRMS (ESI) m/z calcd for $C_{25}H_{43}N_5O_{16}Na$ $[M+Na]^+$ 692.2603, found 692.2595.



3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-α-D-mannopyranoside (4)

To a solution of tetrasaccharide **12** (3.0 g, 2.1 mmol), TFA/H_2O (9:1, v/v, 10 mL) was added, after stirring for 30 min at room temperature, the reaction mixture was concentrated and coevaporated with toluene (3×5 mL) in vacuo. The residue was dissolved in dry MeOH (30 mL) and sodium methoxide was added to the solution to adjust the pH to 11. The resulting mixture was stirred at room temperature and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 6:2:1:0.2, v/v). After complete consumption of the starting material, 1 M LiOH (30 mL) was added, the reaction mixture was stirred for 1h at room temperature. The mixture was then neutralized

with 1 M HCl and concentrated. The crude *N*-deacetyled tetrasaccharide was then dissolved in MeOH (30 mL), and acetic anhydride (788 μL, 8.4 mmol) was added. The mixture was stirred at room temperature for 1 h. After completion of the reaction, the mixture was concentrated and purified by Bio-Gel P2 gel filtration chromatography to afford the tetrasaccharide **4** (1.58 g, 91% for 3 steps) as a white solid. ^{1}H NMR (600 MHz, D_2O) δ 4.55 (d, *J* = 7.6 Hz, 1H), 4.51 (d, *J* = 8.4 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.17 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.04 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.99 – 3.89 (m, 4H), 3.82 – 3.67 (m, 11H), 3.64 (dd, *J* = 10.0, 3.4 Hz, 1H), 3.57 – 3.50 (m, 5H), 3.45 – 3.38 (m, 5H), 2.03 (s, 3H), 2.00 (s, 3H), 1.94 – 1.83 (m, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.45, 174.13, 102.81, 101.45, 99.41, 96.77, 78.34, 76.42, 75.74, 75.24, 74.64, 73.66, 72.38, 71.80, 71.61, 70.85, 69.92, 69.88, 69.51, 68.43, 67.36, 64.74, 60.92, 60.69, 59.86, 55.43, 54.87, 48.22, 27.75, 22.36, 22.14; HRMS (ESI) m/z calcd for $C_{31}H_{53}N_5O_{21}Na$ $[M+Na]^+$ 854.3131, found 854.3087.



3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)]-α-D-mannopyranoside (5)

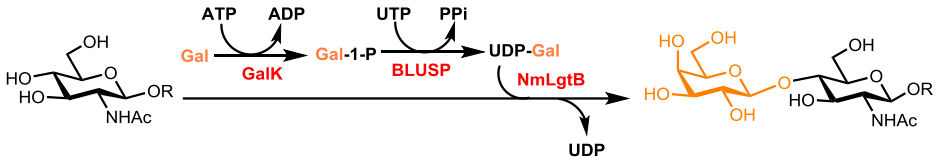
To a solution of tetrasaccharide **13** (2.7 g, 1.88 mmol), TFA/H_2O (9:1, v/v, 10 mL) was added, after stirring for 30 min at room temperature, the reaction mixture was concentrated and coevaporated with toluene (3×5 mL) in vacuo. The residue was dissolved in dry MeOH (30 mL) and sodium methoxide was added to the solution to adjust the pH to 11. The resulting mixture was stirred at room temperature and monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 6:2:1:0.2, v/v). After complete consumption of the starting material, 1 M LiOH (30 mL) was added, the reaction mixture was stirred for 1h at room temperature. The mixture was then neutralized with 1 M HCl and concentrated. The crude *N*-deacetyled tetrasaccharide was then dissolved in MeOH (30 mL), and acetic anhydride (709 μL, 7.5 mmol) was added. The mixture was stirred at room temperature for 1 h. After completion of the reaction, the mixture was concentrated and purified by Bio-Gel P2 gel filtration chromatography to afford the tetrasaccharide **5** (1.41 g, 90% for 3 steps) as a white solid.^{1}H NMR (600 MHz, D_2O) δ 4.74 (s, 1H), 4.47 (d, *J* = 8.3 Hz, 2H), 4.39 (d, *J* = 7.8 Hz, 1H), 4.12 (d, *J* = 10.8 Hz, 1H), 4.00 – 3.96 (m, 1H), 3.91 (d, *J* = 11.9 Hz, 1H), 3.85 – 3.82 (m, 2H), 3.79 – 3.32 (m, 23H), 1.97 (s, 3H), 1.94 (s, 3H), 1.82 (m, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.45, 174.04, 102.70, 101.35, 99.54, 96.73, 78.24, 76.41, 75.65, 75.19, 74.56, 73.03, 72.31, 72.19, 71.53, 70.79, 69.94, 69.73, 69.43, 68.38, 67.29, 64.65, 60.87, 60.42, 59.89, 55.27, 54.89, 48.15, 27.69, 22.28, 22.09; HRMS (ESI) m/z calcd for $C_{31}H_{53}N_5O_{21}Na$ $[M+Na]^+$ 854.3131, found 854.3105.

2. Enzymatic Synthesis

2.1 General Methods

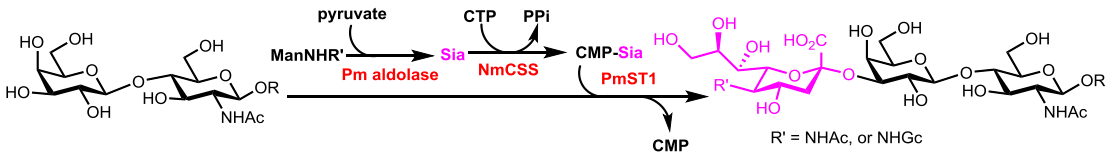
Recombinant *Escherichia coli* K-12 galactokinase (EcGalK)[3], *Bifidobacterium longum* UDP-sugar pyrophosphorylase (BLUSP)[4], *Neisseria meningitides* β1–4-galactosyltransferase (NmLgtB)[5], *Pasteurella multocida* aldolase (Pm aldolase)[6], *Neisseria meningitidis* CMP-sialic acid synthetase (NmCSS)[7], *Pasteurella multocida* α2–3-sialyltransferase 1 (PmST1)[8], *Bacteroides fragilis* bifunctional L-fucokinase/GDP-fucose pyrophosphorylase (BfFKP)[9], and *Helicobacter pylori* α1–3-fucosyltransferase (Hpα1,3FT)[10] were expressed and purified as described previously. All enzymatic reaction were monitored by thin layer chromatography (TLC), which was performed on silica gel plates 60 F_{254} (Merck, Billerica MA). Plates were visualized by treatment with 5% sulfuric acid in ethanol or *p*-anisaldehyde sugar stain followed by heating. Gel filtration chromatography was performed using a column (2.5×100 cm) packed with BioGel P-2 Fine resins (Bio-Rad, Hercules, CA). ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on Bruker AVANCE-600 spectrometer or Agilent VNMRS-600 spectrometer at 25 ℃. NMR spectra were calibrated using solvent signals (^{1}H: δ 4.79 for D_2O, ^{13}C: δ 77.0 for $CDCl_3$). High resolution electrospray ionization (ESI) mass spectra were obtained at the National Glycoengineering Research Center and Drug Testing and Analysis Center in Shandong University.

General procedure of β1–4-galactosylation with Enzyme Module 1:



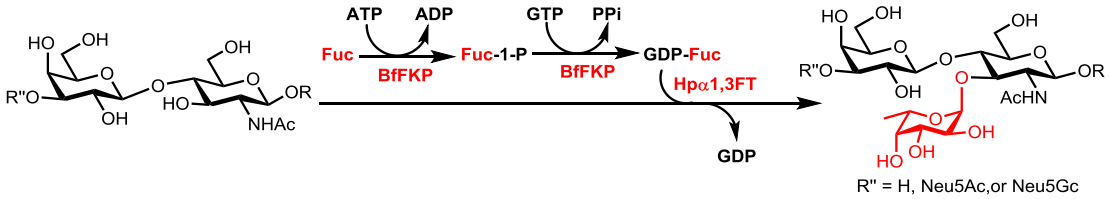
Acceptor (GlcNAcOR, 1.0 equiv.), galactose (Gal, 1.5 equiv.) adenosine 5'-triphosphate (ATP, 1.5 equiv.) and uridine 5'-triphosphate (UTP, 1.5 equiv.) were dissolved in water in a 50 mL centrifuge tube containing Tris-HCl buffer (100 mmol, pH 7.5) and $MgCl_2$ (20 mmol). After the addition of appropriate amount of EcGalK, BLUSP and NmLgtB, the reaction mixture was incubated at 37 ℃ with agitation at 140 rpm in an isotherm incubator. The product formation was monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, v/v) and stained with *p*-anisaldehyde sugar stain. The reaction was stopped by adding the same volume of cold EtOH and incubation at 4 ℃ for 30 min. The mixture was then centrifuged and the precipitates were removed. The supernatant containing the product was concentrated, purified by BioGel P-2 column (eluted with H_2O) to provide purified product.

General procedure of α2–3-sialylation with Enzyme Module 2:



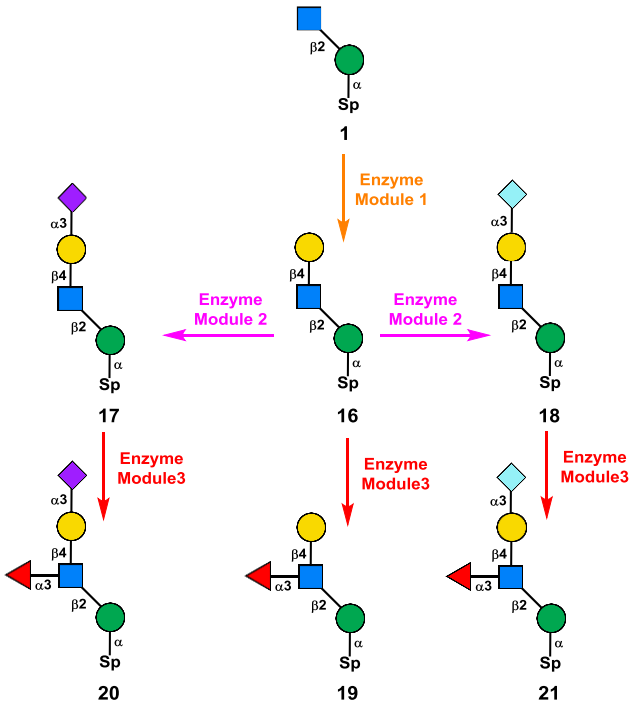
Acceptor (LacNAcOR, 1.0 equiv.), a sialic acid precursor (ManNAc or ManNGc, 1.5 equiv.), sodium pyruvate (5.0 equiv.), and cytidine 5'-triphosphate (CTP, 1.5 equiv.) were dissolved in Tris-HCl buffer (100 mmol, pH 8.0) containing $MgCl_2$ (20 mmol) and appropriate amounts of Pm aldolase, NmCSS, and PmST1. The reaction mixture was incubated at 37 ℃ with agitation at 140 rpm in an isotherm incubator. The product formation was monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, v/v) and stained with *p*-anisaldehyde sugar stain. The reaction was stopped by adding the same volume of cold EtOH and incubation at 4 ℃ for 30 min. The mixture was then centrifuged and the precipitates were removed. The supernatant containing the product was concentrated, purified by BioGel P-2 column (eluted with H_2O) to provide purified product.

General procedure of α1–3-fucosylation with Enzyme Module 3:



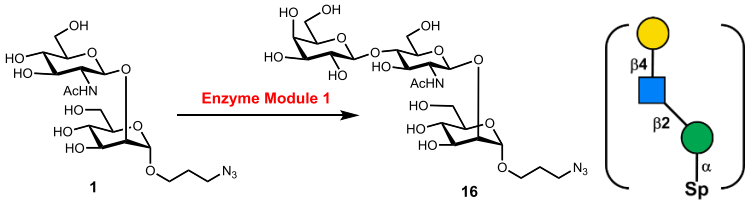
Acceptor (LacNAcOR or α2–3-sialylated LacNAcOR, 1.0 equiv.), L-fucose (Fuc, 1.5 equiv.), ATP (1.5 equiv.), GTP (1.5 equiv.) were dissolved in Tris-HCl buffer (100 mmol, pH 7.5) containing $MnCl_2$ (20 mmol) and appropriate amounts of BfFKP and Hpα1,3FT. The reaction mixture was incubated at 37 ℃ with agitation at 140 rpm in an isotherm incubator. The product formation was monitored by TLC (EtOAc/MeOH/H_2O/HOAc, 4:2:1:0.2, v/v) and stained with *p*-anisaldehyde sugar stain. The reaction was stopped by adding the same volume of cold EtOH and incubation at 4 ℃ for 30 min. The mixture was then centrifuged and the precipitates were removed. The supernatant containing the product was concentrated, purified successively by BioGel P-2 column (eluted with H_2O) to provide purified product. In case of purification of fucosylated complex asymmetrical structures, the repeat BioGel P-2 purification may required for the overlapped fractions.

2.2. Experimental Procedures



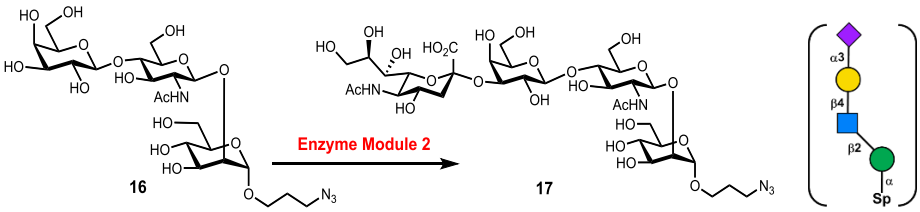
Scheme S1. Enzymatic assembly of Core M1 O-mannose glycans **16-21** from **1**

[a]**Reagents and conditions:** Enzyme module 1, Galactose (1.5 equiv), ATP (1.5 equiv), UTP (1.5 equiv), $MgCl_2$ (20 mM), EcGalK, BLUSP, NmLgtB, Tris-HCl (100 mM, pH 7.5), 37 ℃; Enzyme Module 2, ManNAc (1.5 equiv), or ManNGc (1.5 equiv), sodium pyruvate (5.0 equiv), CTP (1.5 equiv), $MgCl_2$ (20 mM), Pm aldolase, NmCSS, PmST1, Tris-HCl (100 mM, pH 8.0), 37 ℃; Enzyme Module 3, L-fucose (1.5 equiv), ATP (1.5 equiv), GTP (1.5 equiv), $MnCl_2$ (20 mM), BfFKP, Hp 1,3FT, Tris-HCl (100 mM, pH 7.5), 37 ℃, **16** (200 mg, 90%), **17** (69 mg, 95%), **18** (71 mg, 96%), **19** (45 mg, 89%), **20** (31 mg, 80%), **21** (52 mg, 75%).



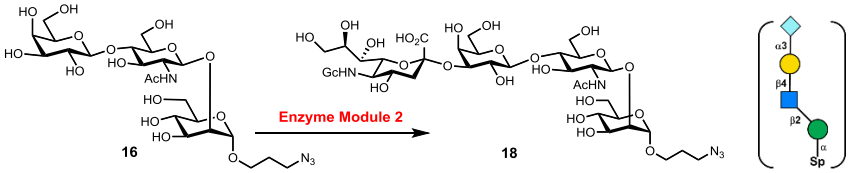
3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (16)

Trisaccharide **16** (200 mg, 90%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.86 (d, *J* = 1.7 Hz, 1H), 4.57 (d, *J* = 7.6 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.06 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.96 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.91 (d, *J* = 3.4 Hz, 1H), 3.88 (d, *J* = 10.1 Hz, 1H), 3.85 – 3.69 (m, 9H), 3.65 (dd, *J* = 10.0, 3.4 Hz, 1H), 3.62 – 3.39 (m, 8H), 2.03 (s, 3H), 1.85 (m, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.64, 102.81, 99.26, 96.77, 78.35, 76.24, 75.24, 74.63, 72.80, 72.38, 71.89, 70.85, 69.52, 68.43, 67.17, 64.88, 61.44, 60.92, 59.85, 54.78, 48.15, 27.80, 22.22; HRMS (ESI) m/z calcd for $C_{23}H_{41}N_4O_{16}$ $[M+H]^+$ 629.2518, found 629.2516.



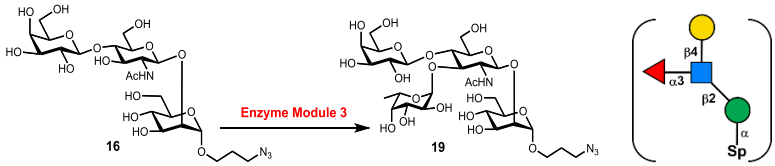
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (17)

Tetrasaccharide **17** (69 mg, 95%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.84 (d, *J* = 1.6 Hz, 1H), 4.54 (d, *J* = 7.9 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.08 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.06 – 4.03 (m, 1H), 3.95 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.92 (d, *J* = 3.1 Hz, 1H), 3.89 – 3.34 (m, 26H), 2.72 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.86 (p, *J* = 7.0 Hz, 2H), 1.76 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 174.87, 174.60, 173.76, 102.46, 99.68, 99.28, 96.75, 78.13, 76.21, 75.33, 75.04, 74.63, 72.79, 72.76, 71.93, 71.84, 71.65, 69.51, 69.26, 68.25, 67.96, 67.34, 67.15, 64.85, 62.44, 62.35, 61.44, 60.91, 59.81, 54.75, 51.55, 48.12, 39.50, 27.78, 22.19, 21.91; HRMS (ESI) m/z calcd for $C_{34}H_{56}N_5O_{24}$ $[M-H]^-$ 918.3321, found 918.3274.



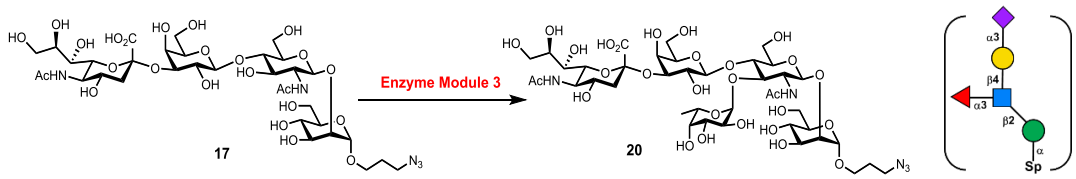
3-Azidopropyl 3,5-dideoxy-5-hydoxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (18)

Tetrasaccharide **18** (71 mg, 96%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.85 (d, *J* = 1.6 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.10 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.09 (s, 2H), 4.06 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.97 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.94 – 3.39 (m, 26H), 2.75 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.02 (s, 3H), 1.88 (p, *J* = 6.9 Hz, 2H), 1.79 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.64, 174.60, 173.79, 102.46, 99.68, 99.28, 96.74, 78.12, 78.10, 76.20, 75.32, 75.04, 74.62, 72.78, 72.47, 71.93, 71.84, 71.70, 69.51, 69.26, 67.98, 67.87, 67.32, 67.15, 64.84, 62.40, 62.34, 61.44, 60.91, 60.84, 59.81, 54.75, 51.26, 48.12, 39.56, 27.78, 22.19; HRMS (ESI) m/z calcd for $C_{34}H_{56}N_5O_{25}$ $[M-H]^-$ 934.3270, found 934.3215.



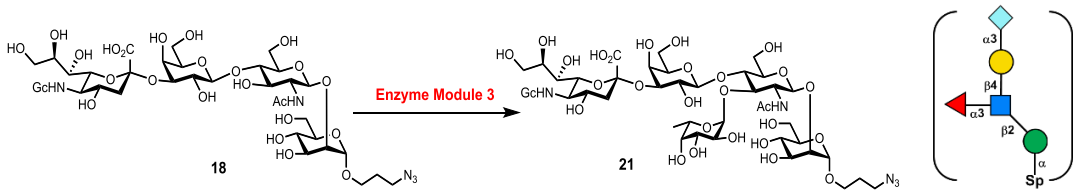
3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (19)

Tetrasaccharide **19** (45 mg, 89%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 4.0 Hz, 1H), 4.87 (d, *J* = 1.6 Hz, 1H), 4.83 (q, *J* = 6.7 Hz, 1H), 4.59 (d, *J* = 8.3 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.07 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.98 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.94 (t, *J* = 9.4 Hz, 1H), 3.91 – 3.81 (m, 8H), 3.78 (d, *J* = 3.4 Hz, 1H), 3.75 – 3.42 (m, 13H), 2.04 (s, 3H), 1.95 – 1.85 (m, 2H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.44, 101.71, 99.02, 98.49, 96.75, 76.18, 75.15, 74.82, 74.54, 73.17, 72.79, 72.34, 71.82, 70.96, 69.51, 69.08, 68.24, 67.59, 67.20, 66.60, 64.91, 61.47, 61.42, 59.61, 59.23, 48.17, 27.82, 22.35, 15.23; HRMS (ESI) m/z calcd for $C_{29}H_{50}N_4O_{20}Na$ $[M+Na]^+$ 797.2916, found 797.2911.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (20)

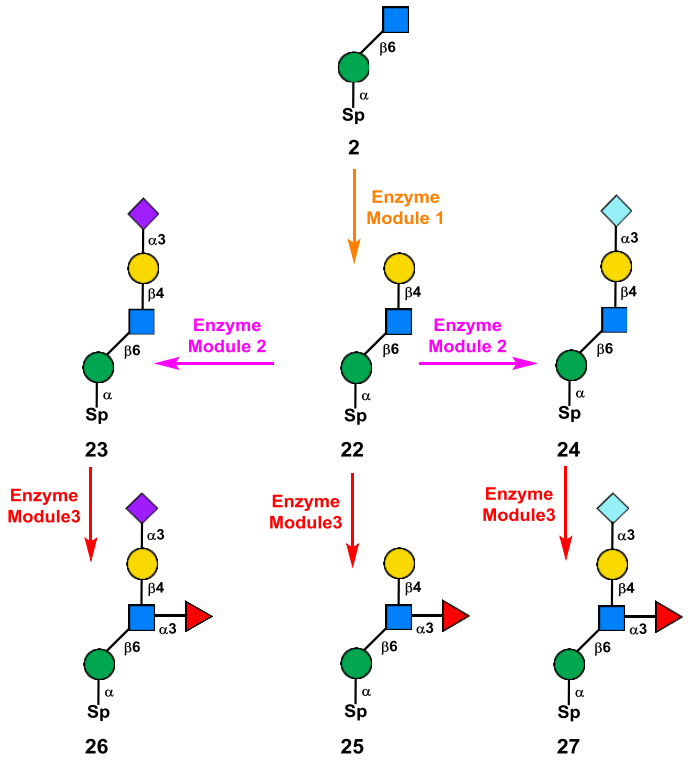
Pentasaccharide **20** (31 mg , 80%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.08 (d, *J* = 4.0 Hz, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 4.54 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 7.9 Hz, 1H), 4.04 (dd, *J* = 8.9, 3.2 Hz, 1H), 4.03 (d, *J* = 2.8 Hz, 1H), 3.96 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.93 (t, *J* = 9.4 Hz, 1H),, 3.89 – 3.77 (m, 11H), 3.74 (d, *J* = 3.4 Hz, 1H), 3.67 – 3.37 (m, 17H), 2.72 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.91 – 1.83 (m, 2H), 1.76 (t, *J* = 12.2 Hz, 1H), 1.13 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.88, 174.38, 173.77, 101.46, 99.52, 98.99, 98.44, 96.71, 76.09, 75.50, 75.04, 74.78, 74.40, 73.11, 72.77, 71.78, 71.73, 69.49, 69.16, 69.03, 68.19, 67.96, 67.58, 67.16, 66.54, 64.84, 62.45, 61.44, 61.36, 61.19, 59.46, 51.57, 48.12, 39.64, 27.78, 22.28, 21.92, 15.15; HRMS (ESI) m/z calcd for $C_{40}H_{66}N_5O_{28}$ $[M-H]^-$ 1064.3900, found 1064.3837.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (21)

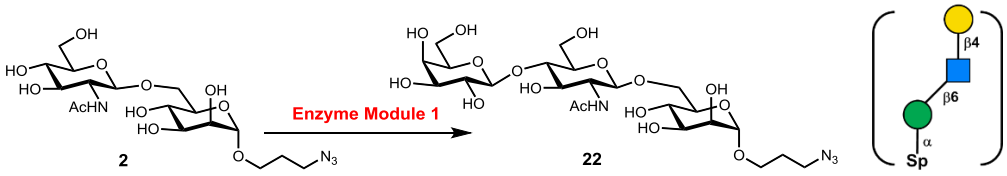
Pentasaccharide **21** (52 mg, 75%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.0 Hz, 1H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.10 (s, 2H), 4.07 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.05 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.99 – 3.39 (m, 31H), 2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.02 (s, 3H), 1.93 – 1.84 (m, 2H), 1.79 (t, *J* = 12.2 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.67, 174.39, 173.80, 101.48, 99.56, 99.02, 98.45, 96.73, 76.12, 75.52, 75.07, 74.80, 74.42, 73.14, 72.78, 72.52, 71.80, 69.51, 69.18, 69.05, 67.95,

67.91, 67.60, 67.18, 66.56, 64.86, 62.44, 61.46, 61.38, 60.86, 59.48, 59.21, 55.58, 51.28, 48.14, 39.72, 27.80, 22.30, 15.17; HRMS (ESI) m/z calcd for $C_{40}H_{66}N_5O_{29}$ $[M-H]^-$ 1080.3849, found 1080.3784.



Scheme S2. Enzymatic assembly of C6-branched Core M1 O-mannose glycans issomers **22-27** from **2**

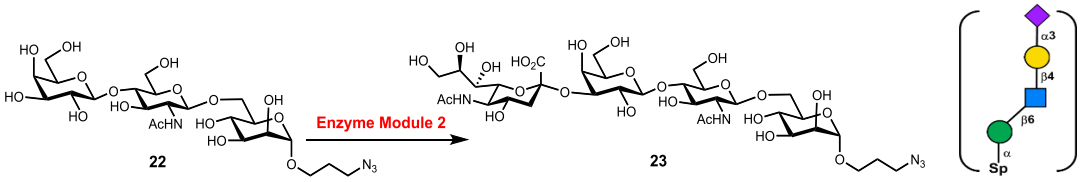
[a]**Reagents and conditions:** Enzyme module 1, Galactose (1.5 equiv), ATP (1.5 equiv), UTP (1.5 equiv), $MgCl_2$ (20 mM), EcGalK, BLUSP, NmLgtB, Tris-HCl (100 mM, pH 7.5), 37 ℃; Enzyme Module 2, ManNAc (1.5 equiv), or ManNGc (1.5 equiv), sodium pyruvate (5.0 equiv), CTP (1.5 equiv), $MgCl_2$ (20 mM), Pm aldolase, NmCSS, PmST1, Tris-HCl (100 mM, pH 8.0), 37 ℃; Enzyme Module 3, L-fucose (1.5 equiv), ATP (1.5 equiv), GTP (1.5 equiv), $MnCl_2$ (20 mM), BfFKP, Hpα1,3FT, Tris-HCl (100 mM, pH 7.5), 37 ℃, **22** (210 mg, 98%), **23** (104 mg, 97%), **24** (141 mg, 94%), **25** (36 mg, 93%), **26** (39 mg, 86%), **27** (64 mg, 82%).



3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-α-D-mannopyranoside (22)

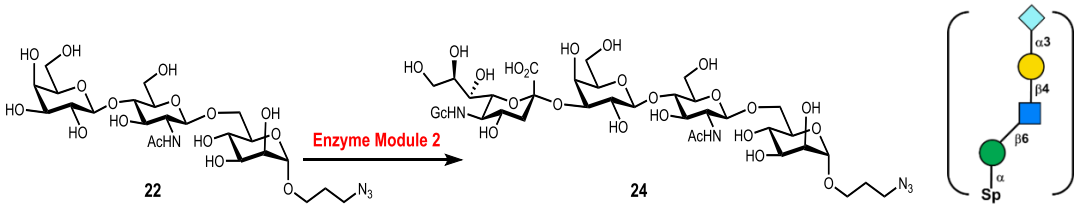
Trisaccharide **22** (210 mg, 98%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.81 (d, *J* = 1.8 Hz, 1H), 4.55 (d, *J* = 8.4 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.21 – 4.14 (m, 1H), 3.98 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.91 (dd, *J* = 3.4, 1.7 Hz, 1H),

3.90 (d, *J* = 3.4 Hz, 1H), 3.82 (dd, *J* = 12.3, 5.2 Hz, 1H), 3.79 – 3.68 (m, 10H), 3.65 (dd, *J* = 10.0, 3.4 Hz, 1H), 3.61 – 3.50 (m, 4H), 3.43 (m, 2H), 2.02 (s, 3H), 1.88 (pt, *J* = 7.4, 3.6 Hz, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.28, 102.76, 101.30, 99.63, 78.34, 75.24, 74.65, 72.37, 71.37, 70.84, 70.51, 69.83, 68.96, 68.43, 66.66, 64.56, 60.91, 59.95, 54.94, 48.11, 27.71, 22.12; HRMS (ESI) m/z calcd for $C_{23}H_{40}ClN_4O_{16}$ $[M+Cl]^-$ 663.2128, found 663.2139.



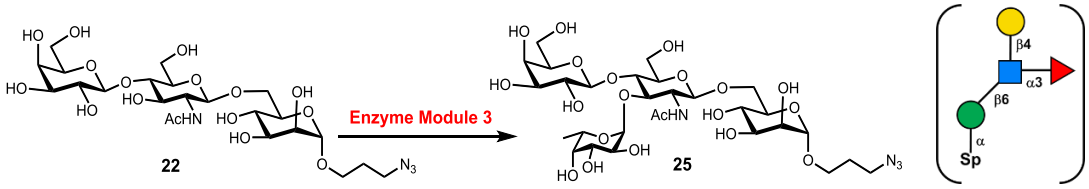
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-α-D-mannopyranoside (23)

Tetrasaccharide **23** (104 mg , 97%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.83 (d, *J* = 1.9 Hz, 1H), 4.57 (d, *J* = 8.1 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.19 (d, *J* = 10.0 Hz, 1H), 4.12 (dd, *J* = 9.9, 3.2 Hz, 1H), 4.02 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.96 (d, *J* = 3.2 Hz, 1H), 3.94 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.92 – 3.40 (m, 24H), 2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 1.91 (m, 2H), 1.80 (t, *J* = 12.2 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 174.97, 174.35, 173.85, 102.57, 101.47, 99.79, 99.71, 78.32, 75.45, 75.14, 74.73, 72.86, 72.41, 71.75, 71.47, 70.63, 69.95, 69.35, 69.07, 68.31, 68.08, 67.47, 66.78, 64.66, 62.58, 61.03, 60.05, 55.03, 51.68, 48.24, 39.61, 27.83, 22.28, 22.09; HRMS (ESI) m/z calcd for $C_{34}H_{56}N_5O_{24}$ $[M-H]^-$ 918.3321, found 918.3275.



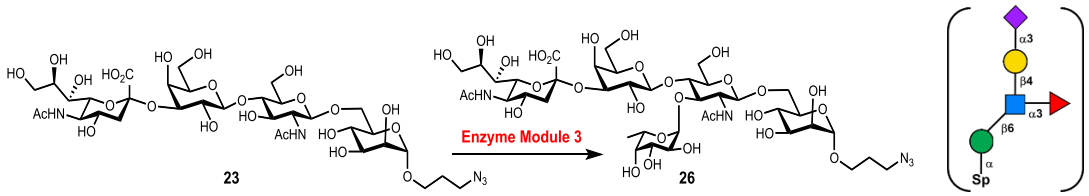
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-α-D-mannopyranoside (24)

Tetrasaccharide **24** (141 mg, 94%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.83 (d, *J* = 1.9 Hz, 1H), 4.58 (d, *J* = 8.1 Hz, 1H), 4.56 (d, *J* = 7.7 Hz, 1H), 4.19 (d, *J* = 9.9 Hz, 1H), 4.12 (s, 2H), 4.02 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.99 – 3.38 (m, 27H), 2.78 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.05 (s, 3H), 1.92 (p, *J* = 6.4 Hz, 2H), 1.82 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.74, 174.37, 173.89, 102.56, 101.46, 99.80, 99.71, 78.30, 75.43, 75.14, 74.74, 72.57, 72.42, 71.80, 71.46, 70.61, 69.94, 69.36, 69.07, 68.07, 67.99, 67.45, 66.76, 64.66, 62.52, 61.01, 60.96, 60.04, 55.03, 51.36, 48.22, 39.67, 27.81, 22.24; HRMS (ESI) m/z calcd for $C_{34}H_{56}N_5O_{25}$ $[M-H]^-$ 934.3270, found 934.3258.



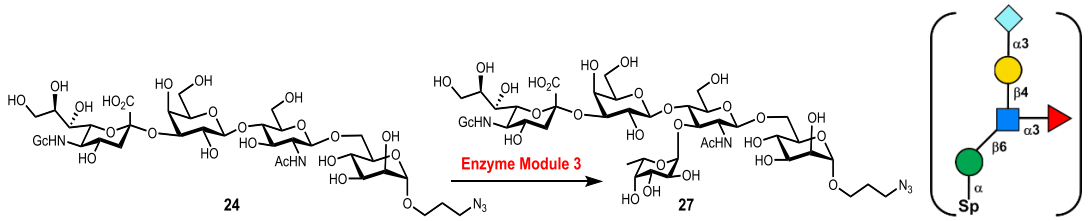
3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-α-D-mannopyranoside (25)

Tetrasaccharide **25** (36 mg, 93%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, *J* = 4.0 Hz, 1H), 4.81 (d, *J* = 1.8 Hz, 1H), 4.55 (d, *J* = 8.3 Hz, 1H), 4.42 (d, *J* = 7.9 Hz, 1H), 4.16 (d, *J* = 9.4 Hz, 1H), 3.99 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.96 – 3.34 (m, 24H), 2.00 (s, 3H), 1.88 (m, 2H), 1.15 (d, *J* = 5.8 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.07, 101.74, 101.15, 99.63, 98.58, 75.25, 74.86, 74.79, 73.32, 72.33, 71.79, 71.29, 70.91, 70.52, 69.83, 69.09, 68.99, 68.22, 67.57, 66.65, 66.60, 64.56, 61.39, 59.67, 55.62, 48.12, 27.70, 22.20, 15.19; HRMS (ESI) m/z calcd for $C_{29}H_{54}N_5O_{20}$ $[M+NH_4]^+$ 792.3362, found 792.3358.



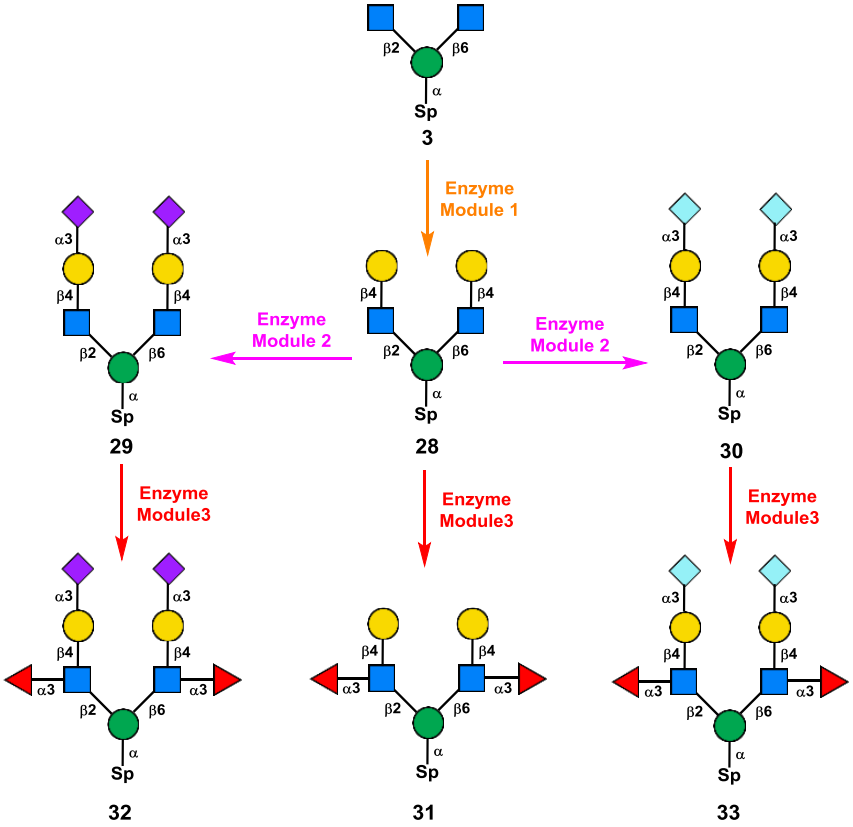
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-α-D-mannopyranoside (26)

Pentasaccharide **26** (39 mg, 86%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.0 Hz, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 4.57 (d, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 10.0 Hz, 1H), 4.09 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.02 (d, *J* = 9.9 Hz, 1H), 3.96 – 3.33 (m, 30H), 2.76 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 1.90 (m, 2H), 1.79 (t, *J* = 12.1, 3.1 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.99, 174.14, 173.86, 101.61, 101.26, 99.70, 99.62, 98.61, 75.61, 75.26, 74.86, 73.39, 72.87, 71.87, 71.82, 71.55, 71.38, 70.61, 69.92, 69.22, 69.16, 69.09, 68.28, 68.07, 67.67, 67.27, 66.75, 66.64, 64.65, 62.55, 61.45, 60.40, 59.65, 51.67, 48.21, 39.74, 27.78, 23.24, 22.28, 22.01, 15.24; HRMS (ESI) m/z calcd for $C_{40}H_{66}N_5O_{28}$ $[M-H]^-$ 1064.3900, found 1064.3856.



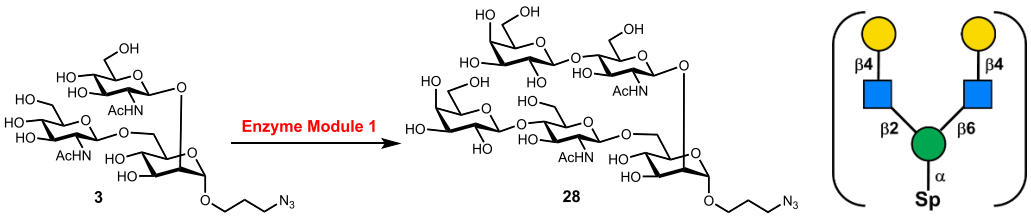
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-α-D-mannopyranoside (27)

Pentasaccharide **27** (64 mg, 82%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 4.0 Hz, 1H), 4.83 (d, *J* = 1.9 Hz, 1H), 4.58 (d, *J* = 8.4 Hz, 1H), 4.53 (d, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 9.4 Hz, 1H), 4.13 (s, 2H), 4.10 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.03 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.98 – 3.37 (m, 30H), 2.79 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.03 (s, 3H), 1.90 (m, 2H), 1.82 (t, *J* = 12.2 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.75, 174.14, 173.89, 101.62, 101.27, 99.71, 99.64, 98.62, 75.60, 75.26, 74.86, 74.85, 73.39, 72.60, 71.88, 71.38, 70.61, 69.93, 69.23, 69.17, 69.10, 68.02, 68.00, 67.67, 67.25, 66.75, 66.65, 64.66, 62.52, 61.45, 60.95, 59.65, 55.70, 51.37, 48.21, 39.81, 27.79, 22.29, 15.25; HRMS (ESI) m/z calcd for $C_{40}H_{66}N_5O_{29}$ $[M-H]^-$ 1080.3849, found 1080.3858.



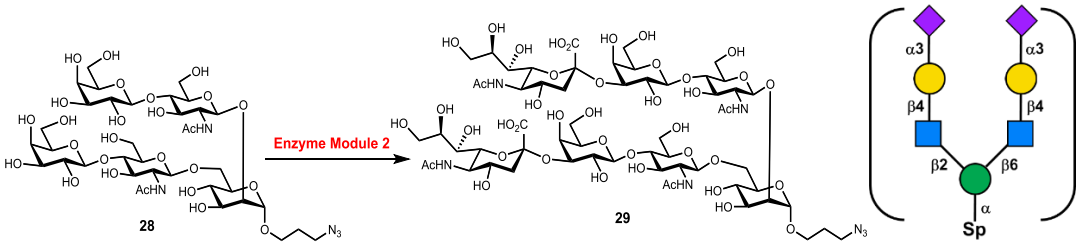
Scheme S3. Enzymatic assembly of symmetrical Core M2 O-mannose glycans issomers **28-33** from **3**

[a]**Reagents and conditions**: Enzyme module 1, Galactose (3.0 equiv), ATP (3.0 equiv), UTP (3.0 equiv), $MgCl_2$ (20 mM), EcGalK, BLUSP, NmLgtB, Tris-HCl (100 mM, pH 7.5), 37 ℃; Enzyme Module 2, ManNAc (3.0 equiv), or ManNGc (3.0 equiv), sodium pyruvate (10.0 equiv), CTP (3.0 equiv), $MgCl_2$ (20 mM), Pm aldolase, NmCSS, PmST1, Tris-HCl (100 mM, pH 8.0), 37 ℃; Enzyme Module 3, L-fucose (3.0 equiv), ATP (3.0 equiv), GTP (3.0 equiv), $MnCl_2$ (20 mM), BfFKP, Hpα1,3FT, Tris-HCl (100 mM, pH 7.5), 37 ℃, **28** (189 mg, 85%), **29** (100 mg, 94%), **30** (145 mg, 90%), **31** (23 mg, 89%), **32** (41 mg, 44%, the reaction was run twice), **33** (40 mg, 42%, the reaction was run twice).



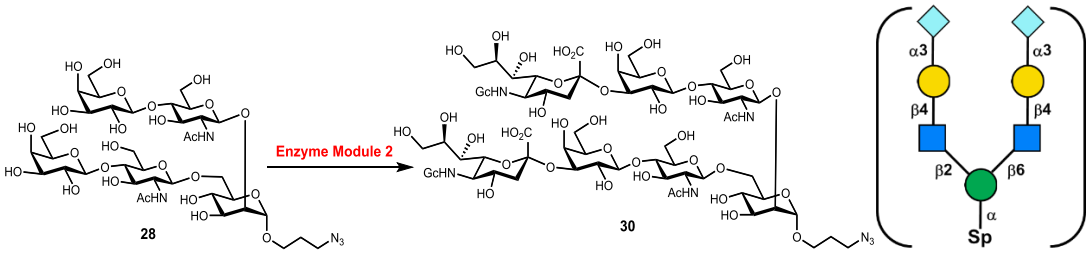
3-Azidopropyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-α-D-mannopyranoside (28)

Pentasaccharide **28** (189 mg, 85%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.81 (d, *J* = 1.7 Hz, 1H), 4.56 (d, *J* = 7.5 Hz, 1H), 4.54 (d, *J* = 8.3 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.7 Hz, 1H), 4.18 (d, *J* = 10.2 Hz, 1H), 4.04 (dd, *J* = 3.4, 1.6 Hz, 1H), 3.97 (td, *J* = 12.6 Hz, 2H), 3.90 (d, *J* = 3.4 Hz, 2H), 3.85 – 3.32 (m, 28H), 2.04 (s, 3H), 2.00 (s, 3H), 1.89 (m, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.45, 174.10, 102.81, 102.78, 101.39, 99.42, 96.77, 78.40, 78.35, 76.43, 75.25, 74.64, 72.39, 72.27, 71.80, 71.60, 70.86, 70.00, 69.49, 68.44, 67.37, 64.75, 62.37, 60.92, 60.01, 59.86, 54.96, 54.87, 48.23, 27.75, 22.36, 22.16; HRMS (ESI) m/z calcd for $C_{37}H_{63}N_5O_{26}Na$ $[M+Na]^+$ 1016.3659, found 1016.3665.



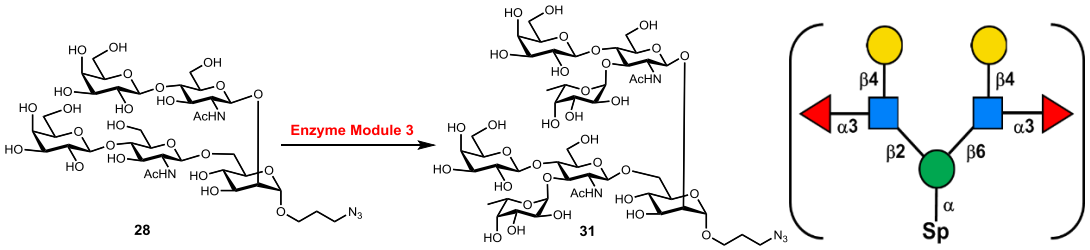
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-[5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-α-D-mannopyranoside (29)

Heptasaccharide **29** (100 mg, 94%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.57 – 4.46 (m, 3H), 4.16 (d, *J* = 10.6 Hz, 1H), 4.07 (dd, *J* = 9.9, 3.1 Hz, 2H), 4.02 (d, *J* = 3.7 Hz, 1H), 3.95 (t, *J* = 10.1 Hz, 2H), 3.90 (d, *J* = 3.1 Hz, 2H), 3.86 – 3.31 (m, 41H), 2.71 (dd, *J* = 12.5, 4.6 Hz, 2H), 2.01 (s, 3H), 1.99 (s, 6H), 1.97 (s, 3H), 1.91 – 1.81 (m, 2H), 1.76 (t, *J* = 12.1 Hz, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.87, 174.43, 174.07, 173.76, 102.46, 101.45, 99.68, 99.42, 96.71, 78.22, 78.13, 76.36, 75.33, 75.05, 74.62, 72.76, 72.22, 71.75, 71.65, 71.60, 70.05, 69.48, 69.26, 68.25, 67.96, 67.36, 64.73, 62.45, 60.92, 59.97, 59.82, 59.20, 54.94, 54.83, 51.56, 48.22, 39.50, 27.74, 22.35, 22.14, 21.94; HRMS (ESI) m/z calcd for $C_{59}H_{95}N_7O_{42}$ $[M-2H]^{2-}$ 786.7762, found 786.7726.



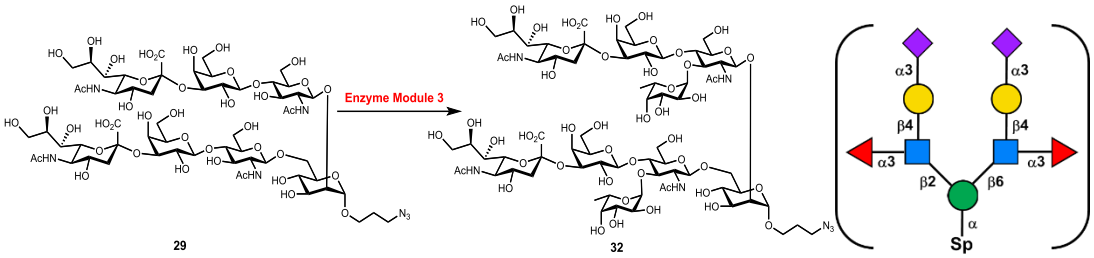
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-[3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-α-D-mannopyranoside (30)

Heptasaccharide **30** (145 mg, 90%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 7.82 (d, *J* = 1.7 Hz, 1H), 4.57 (d, *J* = 7.2 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 2H), 4.54 (d, *J* = 7.9 Hz, 1H), 4.20 (d, *J* = 10.5 Hz, 2H), 4.15 – 4.10 (m, 6H), 4.06 (d, *J* = 3.7 Hz, 1H), 4.04 – 3.34 (m, 43H), 2.77 (dd, *J* = 12.5, 4.6 Hz, 2H), 2.05 (s, 3H), 2.02 (s, 3H), 1.96-1.87 (m, 2H), 1.82 (t, *J* = 12.1 Hz, 2H); ^{13}C NMR (151 MHz, D_2O) δ 175.67, 174.45, 174.09, 173.82, 102.51, 101.46, 99.74, 99.47, 96.76, 78.28, 78.19, 76.46, 75.36, 75.08, 74.66, 72.51, 72.24, 71.75, 71.63, 70.03, 69.51, 69.30, 68.00, 67.93, 67.40, 64.77, 62.47, 60.95, 60.91, 60.02, 59.86, 54.98, 54.88, 51.31, 48.26, 39.60, 27.78, 26.40, 22.41, 22.21; HRMS (ESI) m/z calcd for $C_{59}H_{96}N_7O_{44}$ $[M-H]^-$ 1606.5495, found 1606.5430.



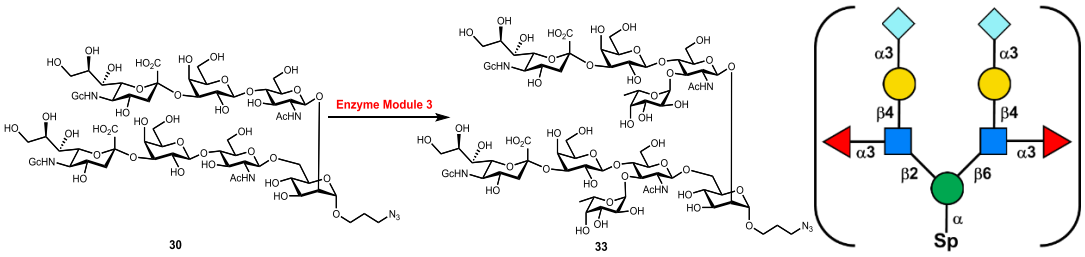
3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (31)

Heptasaccharide **31** (23 mg, 89%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.1 Hz, 1H), 5.09 (d, *J* = 4.0 Hz, 1H), 4.83 – 4.80 (m, 2H), 4.58 (m, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.42 (t, *J* = 7.5 Hz, 2H), 4.16 (d, *J* = 9.8 Hz, 1H), 4.04 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.98 (td, *J* = 12.2 Hz, 2H), 3.94 – 3.38 (m, 37H), 2.03 (s, 3H), 1.99 (s, 3H), 1.94 – 1.82 (m, 2H), 1.15 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, D_2O) δ 174.26, 173.87, 101.71, 101.15, 99.12, 98.53, 98.44, 96.78, 76.36, 75.21, 75.16, 74.80, 74.39, 73.32, 73.18, 72.33, 71.94, 71.80, 71.54, 70.93, 69.84, 69.50, 69.08, 68.23, 67.60, 67.31, 66.60, 64.76, 62.36, 61.40, 59.70, 59.60, 59.20, 55.71, 48.22, 27.73, 22.48, 22.24, 15.20; HRMS (ESI) m/z calcd for $C_{49}H_{83}N_5O_{34}Na$ $[M+Na]^+$ 1308.4817, found 1308.4799.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (32)

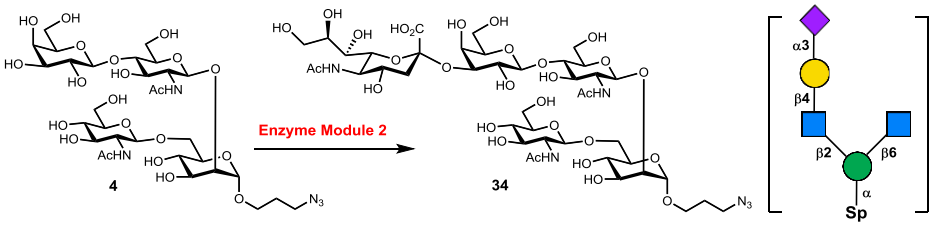
Nonasaccharide **32** (41 mg, 44%), white solid after lyophilization. The reaction was run twice to achieve better yields. ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 5.10 (d, *J* = 4.0 Hz, 1H), 4.84 – 4.82 (m, 2H) 4.60 (d, *J* = 6.9 Hz, 1H), 4.56 (d, *J* = 8.3 Hz, 1H), 4.52 (t, *J* = 7.3 Hz, 2H), 4.18 (d, *J* = 10.8 Hz, 1H), 4.09 (dd, *J* = 9.8, 3.1 Hz, 2H), 4.06 (dd, *J* = 3.5, 1.5 Hz, 1H), 4.01 (t, *J* = 10.9 Hz, 2H), 3.98 – 3.36 (m, 50H), 2.77 (dd, *J* = 12.4, 4.6 Hz, 2H), 2.05 (s, 3H), 2.03 (s, 6H), 2.01 (s, 3H), 1.95 – 1.86 (m, 2H), 1.80 (t, *J* = 12.1 Hz, 2H), 1.17 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (151 MHz, D_2O) δ 174.97, 174.31, 173.92, 173.85, 101.59, 101.57, 101.28, 99.62, 99.18, 98.56, 98.49, 96.83, 76.40, 75.60, 75.20, 75.16, 74.87, 74.75, 74.38, 73.39, 73.24, 72.87, 71.88, 71.83, 71.64, 69.99, 69.57, 69.25, 69.22, 69.15, 69.13, 68.28, 68.07, 67.68, 67.41, 67.27, 66.64, 64.84, 62.55, 61.45, 59.68, 59.57, 59.39, 55.79, 51.67, 48.30, 39.74, 27.81, 22.55, 22.31, 22.02, 15.25; HRMS (ESI) m/z calcd for $C_{71}H_{115}N_7O_{50}$ $[M-2H]^{2-}$ 932.8341, found 932.8353.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (33)

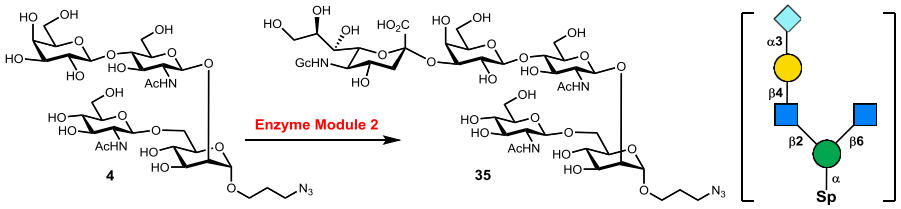
Nonasaccharide **33** (40 mg, 42%), white solid after lyophilization. The reaction was run twice to achieve better yields. ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 4.1 Hz, 1H), 5.10 (d, *J* = 3.9 Hz, 1H), 4.83 (m, 2H), 4.60 (d, *J* = 6.9 Hz, 1H), 4.56 (d, *J* = 8.3 Hz, 1H), 4.52 (t, *J* = 7.3 Hz, 2H), 4.18 (d, *J* = 10.0 Hz, 1H), 4.12 (s, 4H), 4.10 (dd, *J* =

9.8, 3.1 Hz, 2H), 4.06 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.01 (t, *J* = 10.7 Hz, 2H), 3.98 – 3.34 (m, 49H), 2.78 (dd, *J* = 12.4, 4.6 Hz, 2H), 2.05 (s, 3H), 2.01 (s, 3H), 1.90 (m, 2H), 1.81 (t, *J* = 12.2 Hz, 2H), 1.17 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, D_2O) δ 175.75, 174.32, 173.92, 173.89, 101.59, 101.57, 101.28, 99.63, 99.19, 98.56, 98.49, 96.83, 76.40, 75.59, 75.21, 75.16, 74.87, 74.75, 74.37, 73.38, 73.24, 72.59, 71.88, 71.64, 69.99, 69.58, 69.25, 69.23, 69.15, 68.04, 68.00, 67.69, 67.41, 67.25, 66.64, 64.84, 62.52, 61.46, 60.95, 59.69, 59.58, 55.79, 51.37, 48.30, 39.81, 27.81, 22.55, 22.31, 15.25; HRMS (ESI) m/z calcd for $C_{71}H_{115}N_7O_{52}$ $[M-2H]^{2-}$ 948.8290, found 948.8262.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2 –nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D -glucopyranosyl-(1→2)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D -mannopyranoside (34)

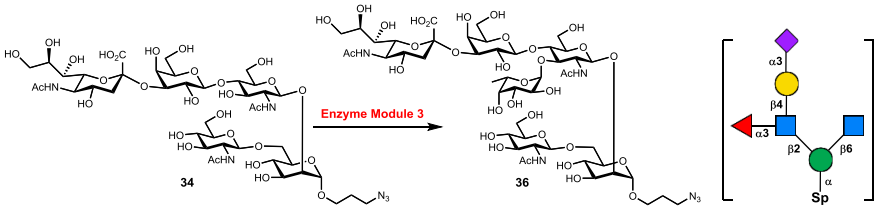
Pentasaccharide **34** (400 mg, 94%) white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.83 (s, 1H), 4.58 (d, *J* = 7.2 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.54 (d, *J* = 8.2 Hz, 1H), 4.20 (d, *J* = 10.6 Hz, 1H), 4.12 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.07 (d, *J* = 3.5 Hz, 1H), 4.00 (d, *J* = 12.6 Hz, 1H), 3.96 (d, *J* = 3.1 Hz, 1H), 3.94 (d, *J* = 11.9 Hz, 1H), 3.91 – 3.43 (m, 29H), 2.77 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.91 (m, 2H), 1.81 (t, *J* = 12.2 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 174.97, 174.51, 174.21, 173.85, 102.57, 101.52, 99.78, 99.54, 96.84, 78.25, 76.53, 75.81, 75.43, 75.13, 74.73, 73.73, 72.85, 71.85, 71.74, 71.69, 70.00, 69.96, 69.59, 69.35, 68.32, 68.06, 67.45, 64.82, 62.55, 61.00, 60.77, 59.92, 55.51, 54.93, 51.66, 48.30, 48.28, 39.60, 27.83, 22.45, 22.28, 22.23, 22.04; HRMS (ESI) m/z calcd for $C_{42}H_{69}N_6O_{29}$ $[M-H]^-$ 1121.4114, found 1121.4139.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2 -nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D -glucopyranosyl-(1→2)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D -mannopyranoside (35)

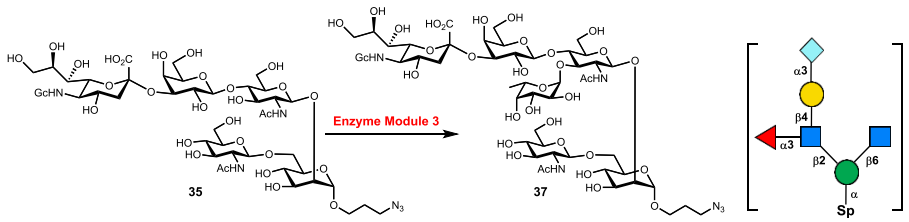
Pentasaccharide **35** (435 mg, 90%) white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.83 (s, 1H), 4.57 (d, *J* = 7.1 Hz, 1H), 4.54 (d, *J* = 7.7 Hz, 1H), 4.53 (d, *J* = 8.5 Hz, 1H), 4.20 (d, *J* = 10.7 Hz, 1H), 4.13 (m, 1H), 4.12 (s, 2H), 4.07 (d, *J* = 3.5 Hz, 1H), 4.00 – 3.41 (m, 32H), 2.78 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.06 (s, 3H), 2.03 (s,

3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.74, 174.50, 174.21, 173.88, 102.56, 101.51, 99.78, 99.54, 96.84, 78.25, 76.52, 75.81, 75.42, 75.14, 74.73, 73.73, 72.57, 71.85, 71.79, 71.69, 70.00, 69.95, 69.59, 69.35, 68.07, 67.98, 67.44, 67.41, 64.81, 62.50, 61.00, 60.94, 60.76, 59.92, 55.51, 54.92, 51.35, 48.29, 39.66, 27.82, 22.43, 22.20; HRMS (ESI) m/z calcd for $C_{42}H_{69}N_6O_{30}$ $[M-H]^-$ 1137.4064, found 1137.4097.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (36)

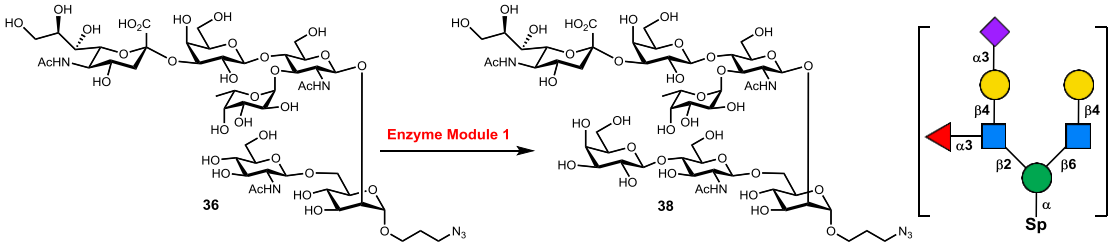
Hexasaccharide **36** (170 mg, 50%), white solid after lyophilization. The reaction was run twice to achieve better yields. ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 4.81 (m, 2H), 4.58 (d, *J* = 6.4 Hz, 1H), 4.53 (d, *J* = 8.2 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 4.08 (dd, *J* = 9.7, 3.1 Hz, 1H), 4.05 (d, *J* = 3.7 Hz, 1H), 4.01 – 3.40 (m, 35H), 2.76 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.79 (t, *J* = 12.1 Hz, 1H), 1.17 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.98, 174.30, 174.20, 173.85, 101.57, 101.52, 99.63, 99.27, 98.49, 96.83, 76.46, 75.81, 75.61, 75.17, 74.88, 74.39, 73.72, 73.24, 72.88, 71.88, 71.84, 71.68, 69.96, 69.58, 69.26, 69.14, 68.28, 68.08, 67.71, 67.44, 67.27, 66.64, 64.83, 62.57, 61.45, 60.77, 59.58, 55.51, 51.68, 48.30, 39.75, 27.83, 22.54, 22.23, 22.03, 15.25; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{33}$ $[M-H]^-$ 1267.4694, found 1267.4677.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (37)

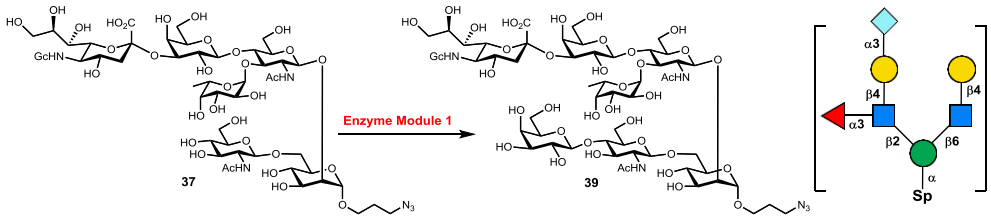
Hexasaccharide **37** (166 mg, 49%), white solid after lyophilization. The reaction was run twice to achieve better yields. ^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, *J* = 4.0 Hz, 1H), 4.81 (m, 2H), 4.49 (d, *J* = 9.1 Hz, 1H), 4.48 (d, *J* = 8.5 Hz, 1H), 4.17 (d, *J* = 10.5 Hz, 1H), 4.07 (s, 2H), 4.06 (dd, *J* = 9.9, 3.2 Hz, 1H), 4.03 (m, 1H), 3.98 – 3.37 (m, 36H), 2.75 (dd, *J* = 12.5, 4.7 Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.87 (m, 2H), 1.78 (t, *J* = 12.1 Hz, 1H), 1.14 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.68,

174.23, 174.14, 173.82, 101.51, 101.45, 99.58, 99.20, 98.42, 96.77, 76.40, 75.74, 75.53, 75.10, 74.32, 73.65, 73.18, 72.53, 71.83, 71.61, 69.89, 69.51, 69.20, 69.08, 67.96, 67.94, 67.63, 67.37, 67.19, 66.57, 64.76, 62.46, 61.39, 60.89, 60.69, 59.51, 55.44, 51.31, 48.24, 39.74, 27.76, 22.47, 22.17, 15.19; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{34}$ $[M-H]^-$ 1283.4643, found 1283.4622.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (38)

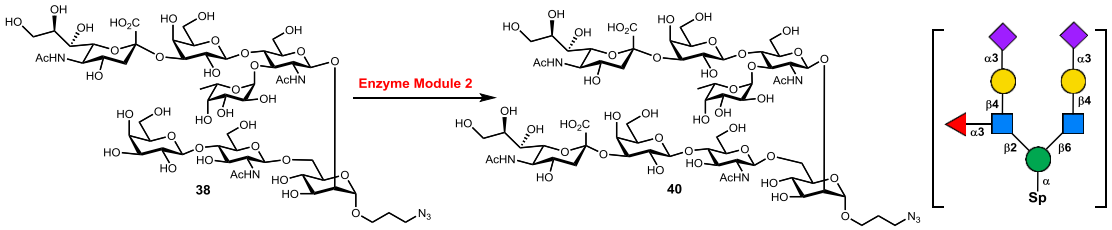
Heptasaccharide **38** (123 mg, 80%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.08 (d, *J* = 4.0 Hz, 1H), 4.55 (m, 1H), 4.51 (d, *J* = 6.3 Hz, 1H), 4.47 (d, *J* = 8.2 Hz, 1H), 4.43 (d, *J* = 7.8 Hz, 1H), 4.16 (d, *J* = 10.6 Hz, 1H), 4.05 (dd, *J* = 9.9, 3.2 Hz, 1H), 4.02 (dd, *J* = 3.9, 0.9 Hz, 1H), 3.98 – 3.35 (m, 35H), 2.73 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.87 (m, 2H), 1.76 (t, *J* = 12.2 Hz, 1H), 1.13 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.88, 174.19, 174.06, 173.75, 102.76, 101.48, 101.37, 99.53, 99.19, 98.40, 96.73, 78.38, 76.37, 75.52, 75.24, 75.07, 74.79, 74.61, 73.15, 72.79, 72.39, 72.24, 71.80, 71.75, 71.57, 70.86, 69.95, 69.48, 69.17, 69.06, 68.44, 68.19, 67.99, 67.62, 67.36, 67.19, 66.55, 64.73, 62.48, 61.37, 60.92, 60.00, 59.49, 54.94, 51.58, 48.22, 39.66, 27.75, 22.45, 22.16, 21.95, 15.17; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{38}$ $[M-H]^-$ 1429.5222, found 1429.5219.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (39)

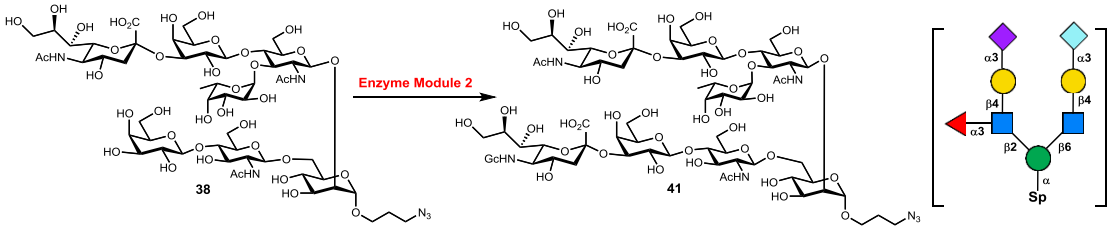
Heptasaccharide **39** (103 mg, 66%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, *J* = 4.0 Hz, 1H), 4.81 (m, 2H), 4.56 (m, 1H), 4.52 (d, *J* = 8.2 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 9.9 Hz, 1H), 4.09 (s, 2H), 4.07 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.03 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.01 – 3.33 (m, 35H), 2.75 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.88 (m, 2H), 1.79 (t, *J* = 12.2 Hz, 1H), 1.14 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.68, 174.21, 174.08, 173.81, 102.78, 101.49, 101.38, 99.56, 99.19, 98.42, 96.75, 78.39,

76.38, 75.52, 75.25, 75.09, 74.80, 74.62, 73.16, 72.52, 72.39, 72.26, 71.81, 71.58, 70.86, 69.97, 69.49, 69.19, 69.06, 68.44, 67.95, 67.92, 67.63, 67.36, 67.18, 66.57, 64.74, 62.45, 61.38, 60.92, 60.87, 60.00, 59.50, 54.95, 51.29, 48.23, 39.73, 27.75, 22.45, 22.16, 15.17; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{39}$ $[M-H]^-$ 1445.5171, found 1445.5146.



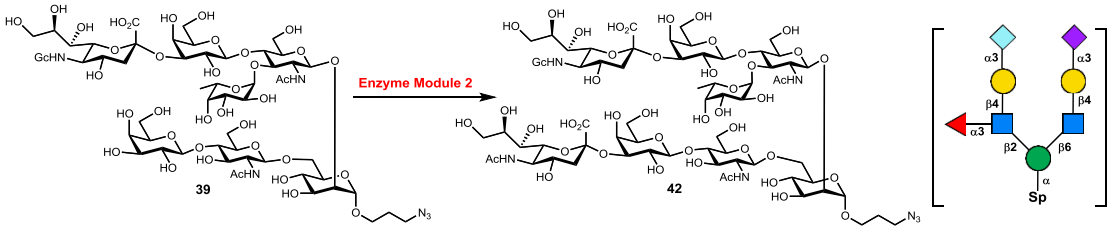
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (40)

Octasaccharide **40** (32 mg, 93%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 2H), 4.61 (d, *J* = 7.8 Hz ,1H), 4.56 (d, *J* = 8.0 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.20 (d, *J* = 10.5 Hz, 1H), 4.12 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.09 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.07 (dd, *J* = 3.7, 0.9 Hz, 1H), 4.03 – 3.40 (m, 47H), 2.77 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.76 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 6H), 2.03 (s, 3H), 1.91 (m, 2H), 1.81 (t, *J* = 12.0 Hz, 1H), 1.80 (t, *J* = 12.0 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.98, 174.31, 174.16, 173.86, 102.55, 101.58, 101.51, 99.79, 99.63, 98.50, 96.80, 96.37, 78.31, 76.46, 75.58, 75.42, 75.14, 75.13, 74.86, 74.68, 73.24, 72.87, 72.84, 72.28, 71.90, 71.86, 71.76, 71.66, 70.32, 70.18, 69.56, 69.36, 69.26, 69.15, 68.49, 68.31, 68.27, 68.08, 67.68, 67.47, 67.28, 67.23, 66.63, 64.83, 63.26, 62.57, 61.46, 61.01, 60.06, 59.58, 55.04, 52.25, 51.69, 48.33, 39.74, 39.58, 39.36, 27.83, 22.58, 22.29, 22.14, 22.08, 15.27; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{46}$ $[M-2H]^{2-}$ 859.8052, found 859.8071.



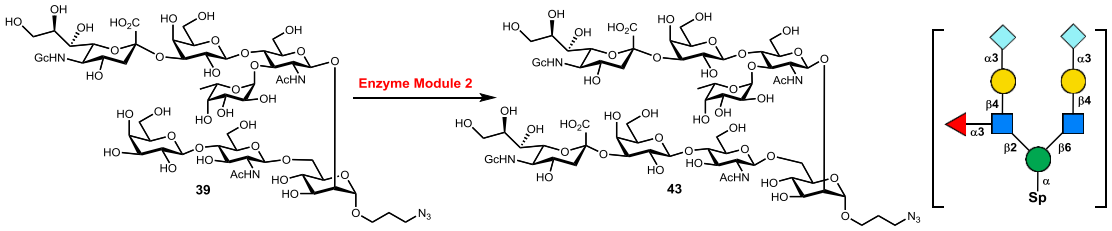
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (41)

Octasaccharide **41** (31 mg, 89%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 2H), 4.59 (m, 1H), 4.55 (d, *J* = 8.0 Hz, 2H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.19 (d, *J* = 10.5 Hz, 1H), 4.13 (dd, *J* = 9.8, 3.0 Hz, 1H), 4.12 (s, 2H), 4.08 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.06 (dd, *J* = 3.8, 0.9 Hz, 1H), 4.04 – 3.32 (m, 47H), 2.77 (dd, *J* = 12.2, 4.7 Hz, 1H), 2.75 (dd, *J* = 12.2, 4.7 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.7 Hz, 1H), 1.80 (t, *J* = 12.6 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.72, 174.97, 174.30, 174.15, 173.87, 173.84, 102.55, 101.57, 101.51, 99.78, 99.62, 99.25, 98.49, 96.79, 78.32, 76.44, 75.58, 75.42, 75.15, 75.13, 74.86, 74.68, 74.39, 73.24, 72.87, 72.56, 72.28, 71.89, 71.84, 71.80, 71.65, 70.04, 69.55, 69.36, 69.25, 69.14, 68.26, 68.07, 68.05, 67.98, 67.68, 67.45, 67.27, 66.62, 64.83, 62.57, 62.52, 61.45, 61.00, 60.96, 60.06, 59.57, 55.03, 51.68, 51.37, 48.31, 39.73, 39.64, 27.83, 26.44, 22.56, 22.27, 22.06, 15.26; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{47}$ $[M-2H]^{2-}$ 867.8025, found 867.8015.



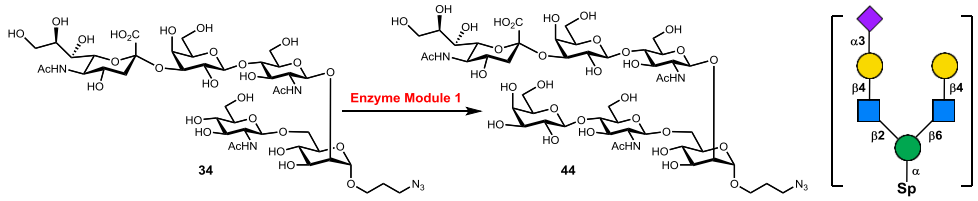
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (42)

Octasaccharide **42** (28 mg, 95%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 2H), 4.59 (m, 1H), 4.55 (d, *J* = 8.0 Hz, 2H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.20 (d, *J* = 10.5 Hz, 1H), 4.13 (s, 2H), 4.12 – 4.11 (m, 1H), 4.10 (dd, *J* = 9.7, 3.2 Hz, 1H), 4.07 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.05 – 3.36 (m, 47H), 2.77 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.2 Hz, 1H), 1.81 (t, *J* = 12.2 Hz, 1H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.75, 174.97, 174.31, 174.16, 173.89, 173.86, 102.55, 101.57, 101.52, 99.78, 99.64, 99.22, 98.49, 96.79, 78.33, 76.41, 75.60, 75.43, 75.14, 74.87, 74.70, 73.24, 72.85, 72.60, 72.30, 71.89, 71.74, 71.67, 70.29, 70.17, 69.55, 69.35, 69.27, 69.14, 68.51, 68.33, 68.06, 68.03, 68.00, 67.69, 67.45, 67.26, 66.64, 64.83, 63.25, 62.55, 62.53, 61.46, 61.00, 60.95, 60.07, 59.58, 59.31, 55.03, 51.66, 51.37, 48.31, 39.81, 39.59, 27.83, 22.54, 22.24, 22.09, 22.03, 15.25; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{47}$ $[M-2H]^{2-}$ 867.8025, found 867.7985.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (43)

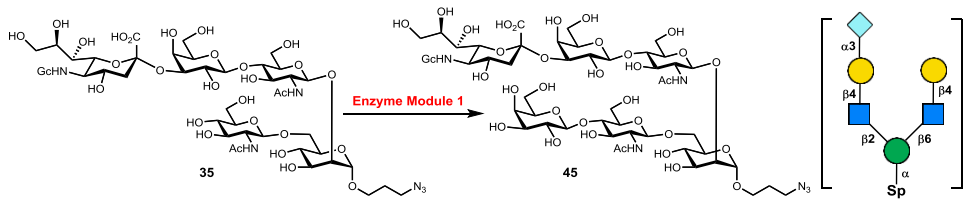
Octasaccharide **43** (27 mg, 91%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.0 Hz, 1H), 4.80 (m, 2H), 4.57 (m, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.53 (d, *J* = 8.2 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 10.5 Hz, 1H), 4.12 – 4.09 (m, 4H), 4.07 (dd, *J* = 9.9, 3.2 Hz, 1H), 4.04 (dd, *J* = 3.4, 1.6 Hz, 1H), 4.01 – 3.34 (m, 44H), 2.77 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.75 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.03 (s, 3H), 2.00 (s, 3H), 1.89 (m, 2H), 1.80 (t, *J* = 12.2 Hz, 1H), 1.79 (t, *J* = 12.1 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.66, 174.23, 174.08, 173.82, 102.46, 101.48, 101.44, 99.70, 99.55, 99.16, 98.42, 96.71, 96.70, 78.22, 78.21, 76.32, 75.49, 75.32, 75.05, 74.79, 74.60, 74.32, 73.14, 72.50, 72.49, 72.21, 71.80, 71.71, 71.57, 69.46, 69.27, 69.18, 69.04, 67.99, 67.95, 67.89, 67.89, 67.59, 67.35, 67.16, 66.55, 64.74, 62.41, 61.38, 60.92, 60.86, 59.97, 59.49, 54.94, 51.27, 48.22, 39.71, 39.57, 27.74, 22.46, 22.16, 15.17; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{48}$ $[M-2H]^{2-}$ 875.8001, found 875.8006.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (44)

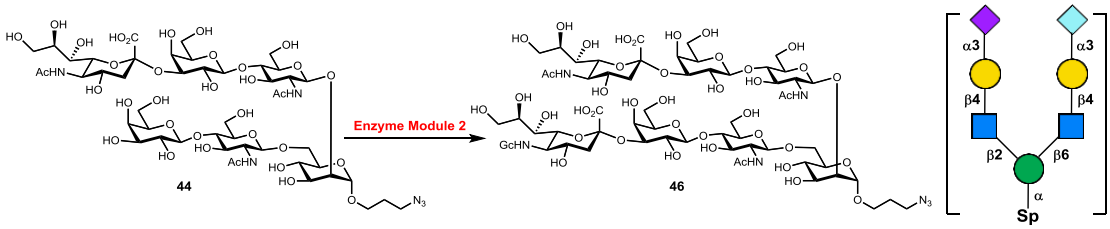
Hexasaccharide **44** (241 mg, 86%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.82 (m, 1H), 4.54 (d, *J* = 7.7 Hz, 1H), 4.52 (d, *J* = 8.3 Hz, 1H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 9.6 Hz, 1H), 4.08 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.04 (dd, *J* = 3.4, 1.6 Hz, 1H), 3.98 – 3.95 (m, 2H), 3.93 (d, *J* = 3.2 Hz, 1H), 3.89 (d, *J* = 3.5 Hz, 1H), 3.88 – 3.38 (m, 34H), 2.73 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.88 (m, 2H), 1.77 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 174.89, 174.43, 174.08, 173.77, 102.78, 102.48, 101.39, 99.70, 99.47, 96.75, 78.39, 78.16, 76.44, 75.35, 75.25, 75.06, 74.65, 74.62, 72.77, 72.39, 72.26, 71.77, 71.66, 71.60, 70.86, 70.02, 69.50, 69.27, 68.45, 68.25, 67.97, 67.36, 64.73, 62.47, 60.92, 60.00, 59.83, 54.95, 54.84, 51.57, 48.23, 48.20, 39.52,

27.75, 22.37, 22.16, 21.95; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{34}$ $[M-H]^-$ 1283.4643, found 1283.4587.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (45)

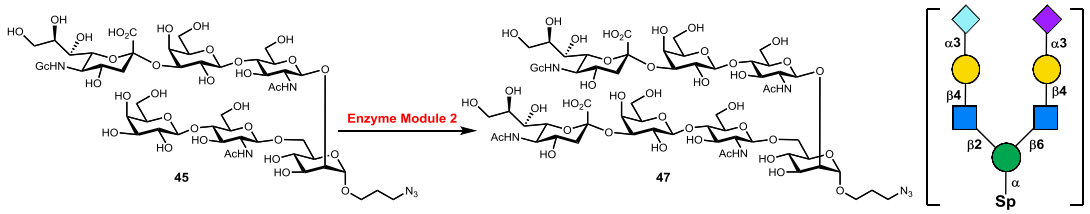
Hexasaccharide **45** (202 mg, 85%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.82 (m, 1H), 4.54 (d, *J* = 7.0 Hz, 1H), 4.52 (d, *J* = 8.2 Hz, 1H), 4.51 (d, *J* = 8.1 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 10.4 Hz, 1H), 4.11 – 4.09 (m, 3H), 4.04 (d, *J* = 3.6 Hz, 1H), 3.98 – 3.37 (m, 38H), 2.74 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.87 (m, 2H), 1.79 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.65, 174.43, 174.08, 173.81, 102.77, 102.49, 101.39, 99.72, 99.47, 96.75, 78.37, 78.14, 76.46, 75.33, 75.24, 75.05, 74.64, 74.62, 72.49, 72.39, 72.24, 71.75, 71.72, 71.60, 70.86, 69.99, 69.49, 69.27, 68.45, 67.98, 67.89, 67.36, 64.73, 62.43, 60.92, 60.87, 59.98, 59.82, 54.95, 54.86, 51.29, 48.23, 39.57, 27.75, 22.38, 22.18; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{35}$ $[M-H]^-$ 1299.4592, found 1299.4534.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (46)

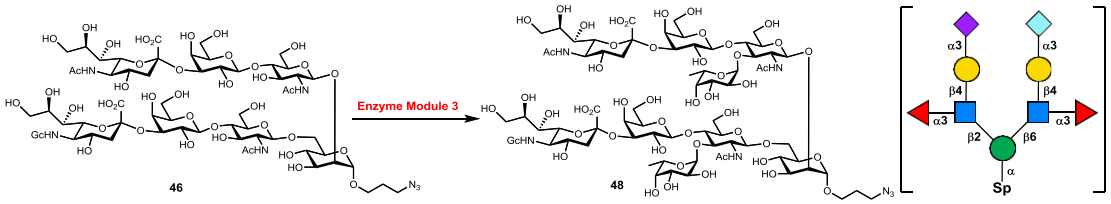
Heptasaccharide **46** (198 mg, 92%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.81 (s, 1H), 4.56 (d, *J* = 8.9 Hz, 1H), 4.54 (d, *J* = 7.9 Hz, 1H), 4.53 (d, *J* = 8.2 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.18 (d, *J* = 10.6 Hz, 1H), 4.14 – 4.08 (m, 4H), 4.05 (dd, *J* = 3.4, 1.6 Hz, 1H), 4.02 – 3.36 (m, 44H), 2.76 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.73 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.04 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.89 (m, 2H), 1.80 (t, *J* = 11.7 Hz, 1H), 1.78 (t, *J* = 11.7 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.66, 174.89, 174.44, 174.08, 173.82, 173.78, 102.48, 101.46, 99.70, 99.70, 99.43, 96.72, 78.25, 78.16, 76.38, 75.35, 75.06, 74.65, 74.63, 72.77, 72.49, 72.23, 71.76, 71.72, 71.66, 71.61, 70.05, 69.49, 69.27, 68.25, 68.00, 67.98, 67.90, 67.37, 64.74, 62.47, 62.43, 60.93, 60.88, 59.99, 59.84, 54.95, 54.85, 51.58, 51.28, 48.23, 39.59,

39.52, 27.75, 22.36, 22.16, 21.96; HRMS (ESI) m/z calcd for $C_{59}H_{95}N_7O_{43}$ $[M-2H]^{2-}$ 794.7737, found 794.7773.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (47)

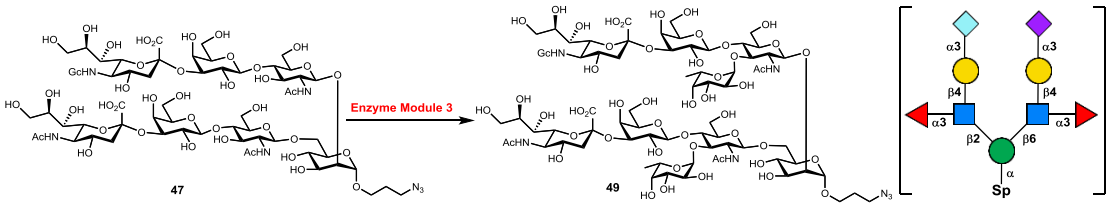
Heptasaccharide **47** (128 mg, 95%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.54 – 4.512 (m, 4H), 4.17 (d, *J* = 9.3 Hz, 1H), 4.10 – 4.07 (m, 4H), 4.03 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.99 – 3.36 (m, 44H), 2.74 (dd, *J* = 12.3, 4.7 Hz, 1H), 2.72 (dd, *J* = 12.3, 4.7 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.87 (m, 2H), 1.78 (t, *J* = 12.2 Hz, 1H), 1.77 (t, *J* = 12.3 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.65, 174.87, 174.43, 174.07, 173.78, 173.75, 102.48, 102.46, 101.45, 99.69, 99.68, 99.42, 96.72, 78.23, 78.15, 76.37, 75.34, 75.05, 74.64, 74.62, 72.77, 72.49, 72.22, 71.76, 71.70, 71.65, 71.61, 70.05, 69.48, 69.27, 68.24, 67.98, 67.90, 67.37, 64.74, 62.46, 62.42, 60.92, 60.86, 59.98, 59.83, 54.94, 54.84, 51.57, 51.27, 48.23, 39.57, 39.50, 27.74, 22.35, 22.15, 21.94; HRMS (ESI) m/z calcd for $C_{59}H_{95}N_7O_{43}$ $[M-2H]^{2-}$ 794.7737, found 794.7771.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (48)

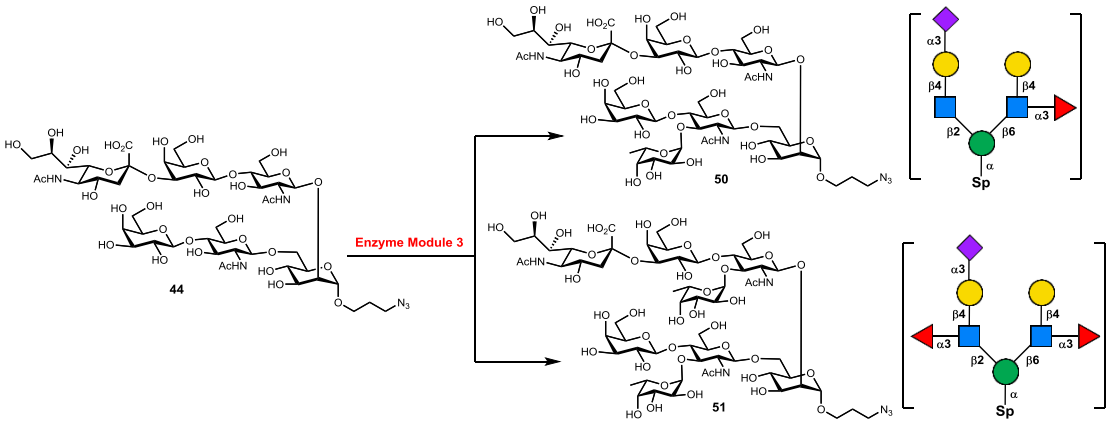
Nonasaccharide **48** (25 mg, 45%, the reaction was run twice), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.0 Hz, 1H), 5.09 (d, *J* = 3.9 Hz, 1H), 4.82 (m, 3H), 4.58 (m, 1H), 4.54 (d, *J* = 8.3 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 4.49 (d, *J* = 7.7 Hz, 1H), 4.16 (d, *J* = 10.7 Hz, 1H), 4.11 (s, 2H), 4.08 (dd, *J* = 6.8, 3.1 Hz, 1H), 4.07 (dd, *J* = 6.9, 3.2 Hz, 1H), 4.04 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.99 (t, *J* = 12.0 Hz, 2H), 3.94 – 3.32 (m, 48H), 2.77 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.75 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.89 (m, 2H), 1.80 (t, *J* = 11.8 Hz, 1H), 1.78 (t, *J* = 11.8 Hz, 1H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C

NMR (151 MHz, D_2O) δ 175.68, 174.91, 174.25, 173.86, 173.83, 173.78, 101.52, 101.51, 101.22, 99.57, 99.14, 98.51, 98.42, 96.77, 76.35, 75.54, 75.14, 75.10, 74.81, 74.69, 73.33, 73.18, 72.81, 72.53, 71.82, 71.77, 71.57, 69.51, 69.18, 69.09, 69.07, 68.21, 68.01, 67.96, 67.93, 67.62, 67.35, 67.20, 66.57, 64.78, 62.49, 62.46, 61.39, 60.88, 59.62, 59.50, 55.71, 51.61, 51.31, 48.24, 39.75, 39.68, 27.75, 22.49, 22.25, 21.96, 15.19; HRMS (ESI) m/z calcd for $C_{71}H_{115}N_7O_{51}$ $[M-2H]^{2-}$ 940.8316, found 940.8322.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (49)

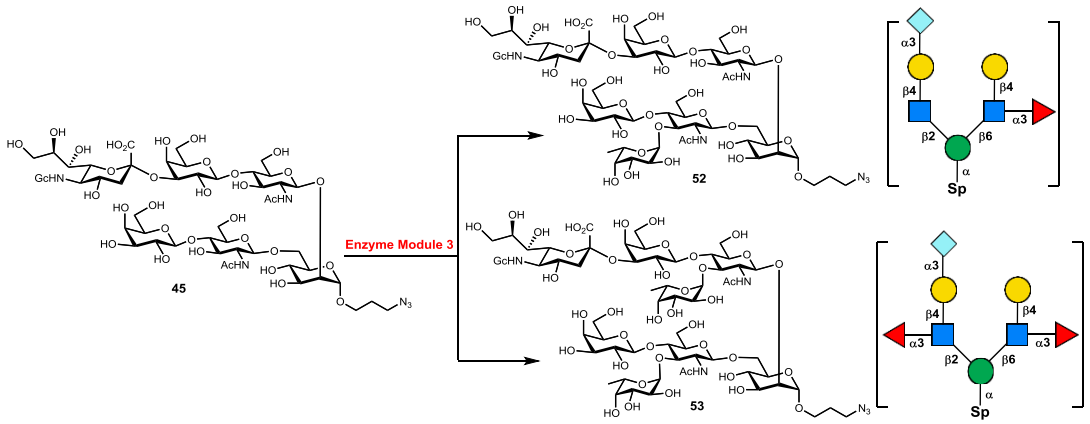
Nonasaccharide **49** (74 mg, 50%, the reaction was run twice), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 5.11 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 3H), 4.59 (m, 1H), 4.57 (d, *J* = 7.9 Hz, 1H), 4.53 (d, *J* = 7.8 Hz, 1H), 4.52 (d, *J* = 7.7 Hz, 1H), 4.18 (d, *J* = 10.6 Hz, 1H), 4.13 (s, 2H), 4.10 (dd, *J* = 5.9, 3.1 Hz, 1H), 4.08 (dd, *J* = 5.9, 3.1 Hz, 1H), 4.06 (dd, *J* = 3.5, 1.5 Hz, 1H), 4.02 (t, *J* = 10.1 Hz, 2H), 3.96 – 3.41 (m, 48H), 2.78 (dd, *J* = 12.3, 4.6 Hz, 1H), 2.78 (dd, *J* = 12.3, 4.6 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.2 Hz, 1H), 1.80 (t, *J* = 12.2 Hz, 1H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.65, 174.88, 174.24, 173.82, 173.78, 101.48, 101.47, 101.19, 99.54, 99.52, 99.13, 98.49, 98.41, 96.74, 76.32, 75.49, 75.08, 74.78, 74.28, 73.28, 73.13, 72.77, 72.49, 71.79, 71.53, 69.47, 69.16, 69.05, 68.19, 67.94, 67.57, 67.31, 67.16, 66.55, 64.74, 62.44, 61.37, 60.86, 59.47, 55.68, 51.58, 51.27, 48.21, 39.71, 27.73, 22.47, 22.24, 21.97, 15.18; HRMS (ESI) m/z calcd for $C_{71}H_{115}N_7O_{51}$ $[M-2H]^{2-}$ 940.8316, found 940.8338.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (50) and 3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (51)

The compound **50** and **51** were derived from compound **44** (90 mg, 0.07 mmol), the reaction was run twice to achieve better yields. Heptasaccharide **50** (73 mg, 73%) , white solid after lyophilization, and octasaccharide **51** (26 mg, 24%) as a white solid after lyophilization. For heptasaccharide **50:** ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 4.84 (m, 2H), 4.58 (d, *J* = 7.4 Hz, 1H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.54 (d, *J* = 7.9 Hz, 1H), 4.46 (d, *J* = 7.7 Hz, 1H), 4.19 (dd, *J* = 10.4, 2.3 Hz, 1H), 4.12 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.07 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.01 (td, *J* = 13.0 Hz, 2H), 3.96 (d, *J* = 3.2 Hz, 1H), 3.95 – 3.41 (m, 38H), 2.76 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.80 (t, *J* = 12.1 Hz, 1H), 1.18 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.97, 174.51, 173.94, 173.85, 102.56, 101.80, 101.22, 99.77, 99.53, 98.60, 96.87, 78.24, 76.52, 75.42, 75.30, 75.13, 74.88, 74.72, 73.41, 72.85, 72.42, 71.88, 71.84, 71.74, 71.65, 71.00, 70.01, 69.60, 69.34, 69.18, 68.32, 68.06, 67.68, 67.43, 66.67, 64.82, 62.55, 61.47, 61.00, 59.91, 59.79, 59.39, 55.77, 54.94, 51.65, 48.30, 39.59, 27.82, 22.46, 22.31, 22.02, 15.29; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{38}$ $[M-H]^-$ 1429.5222, found 1429.5177.

For octasaccharide **51:** ^{1}H NMR (600 MHz, D_2O) δ 5.08 (d, *J* = 4.0 Hz, 1H), 5.07 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 3H), 4.55 (m, 1H), 4.54 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 8.1 Hz, 1H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.14 (d, *J* = 10.6 Hz, 1H), 4.04 (dd, *J* = 9.9, 3.2 Hz, 1H), 4.02 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.97 (d, *J* = 5.4 Hz, 1H), 3.95 (d, *J* = 5.5 Hz, 1H), 3.94 – 3.35 (m, 42H), 2.72 (dd, *J* = 12.5, 4.7 Hz, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.87 (m, 2H), 1.76 (t, *J* = 12.2 Hz, 1H), 1.14 (d, *J* = 5.3 Hz, 3H), 1.13 (d, *J* = 5.3 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.87, 174.23, 173.84, 173.75, 101.70, 101.47, 101.13, 99.51, 99.15, 98.51, 98.40, 96.75, 76.37, 75.48, 75.18, 75.05, 74.77, 74.28, 73.29, 73.13, 72.77, 72.32, 71.79, 71.74, 71.52, 70.90, 69.83, 69.49, 69.15, 69.08, 69.04, 68.23, 68.18, 67.97, 67.57, 67.30, 67.17, 66.58, 66.54, 64.73, 62.46, 61.40, 61.36, 59.68, 59.46, 55.68, 51.58, 48.20, 39.63, 27.73, 22.48, 22.25, 21.96, 15.21, 15.16; HRMS (ESI) m/z calcd for $C_{60}H_{99}N_6O_{42}$ $[M-H]^-$ 1575.5801, found 1575.5790.

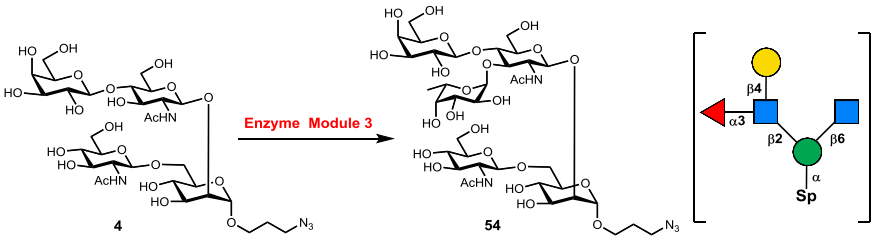


3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (52) and 3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2–deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (53)

The compound **52** and **53** were derived from compound **45** (90 mg, 0.07 mmol), the reaction was run twice to achieve better yields. Heptasaccharide **52** (69 mg, 69%), white solid after lyophilization, and octasaccharide **53** (31 mg, 28%) as a white solid after lyophilization. For heptasaccharide **52:** ^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 2H), 4.55 (d, *J* = 7.3 Hz, 1H), 4.54 (d, *J* = 7.0 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.43 (d, *J* = 7.7 Hz, 1H), 4.16 (d, *J* = 10.6 Hz, 1H), 4.12-4.07 (m, 3H), 4.04 (dd, *J* = 3.2, 1.9 Hz, 1H), 4.00 – 3.38 (m, 41H), 2.75 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.03 (s, 3H), 1.99 (s, 3H), 1.87 (m, 2H), 1.79 (t, *J* = 12.1 Hz, 1H), 1.15 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.64, 174.42, 173.85, 173.80, 102.45, 101.71, 101.14, 99.68, 99.44, 98.51, 96.77, 78.11, 76.41, 75.31, 75.20, 75.04, 74.78, 74.63, 73.29, 72.47, 72.31, 71.78, 71.76, 71.70, 71.55, 70.90, 69.93, 69.92, 69.50, 69.25, 69.08, 68.22, 67.98, 67.87, 67.58, 67.32, 66.58, 64.72, 62.40, 61.38, 60.91, 60.84, 59.81, 59.68, 55.68, 54.83, 51.25, 48.20, 39.56, 27.72, 22.35, 22.20, 15.18; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{39}$ $[M-H]^-$ 1445.5171, found 1445.5128.

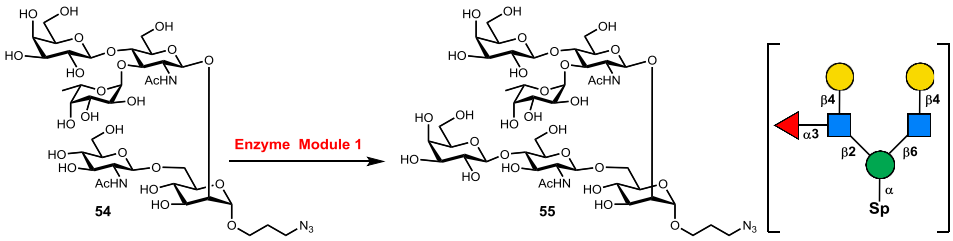
For octasaccharide **53:** ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 4.4 Hz, 1H), 5.10 (d, *J* = 4.3 Hz, 1H), 4.83 (m, 3H), 4.59 (m, 1H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 10.5 Hz, 1H), 4.12 (s, 2H), 4.09 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.05 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.03 – 3.34 (m, 44H), 2.77 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.04 (s, 3H), 2.01 (s, 3H), 1.90 (m, 2H), 1.81 (t, *J* = 12.2 Hz, 1H), 1.17 (d, *J* = 6.6, Hz, 3H), 1.16 (d, *J* = 6.6, Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.69, 174.26, 173.89, 173.82, 101.74, 101.52, 101.16, 99.59, 99.19, 98.54, 98.44, 96.81, 76.42, 75.54, 75.23, 75.11, 74.81, 74.33, 73.36, 73.20, 72.54, 72.37, 71.84, 71.58, 70.95, 69.88, 69.54, 69.21, 69.13, 69.09, 68.27, 67.97, 67.95, 67.63, 67.35,

67.20, 66.62, 66.58, 64.79, 62.48, 61.42, 60.90, 59.75, 59.52, 55.73, 51.32, 48.25, 39.75, 27.77, 22.52, 22.29, 15.24, 15.20; HRMS (ESI) m/z calcd for $C_{60}H_{99}N_6O_{43}$ $[M-H]^-$ 1591.5750, found 1591.5766.



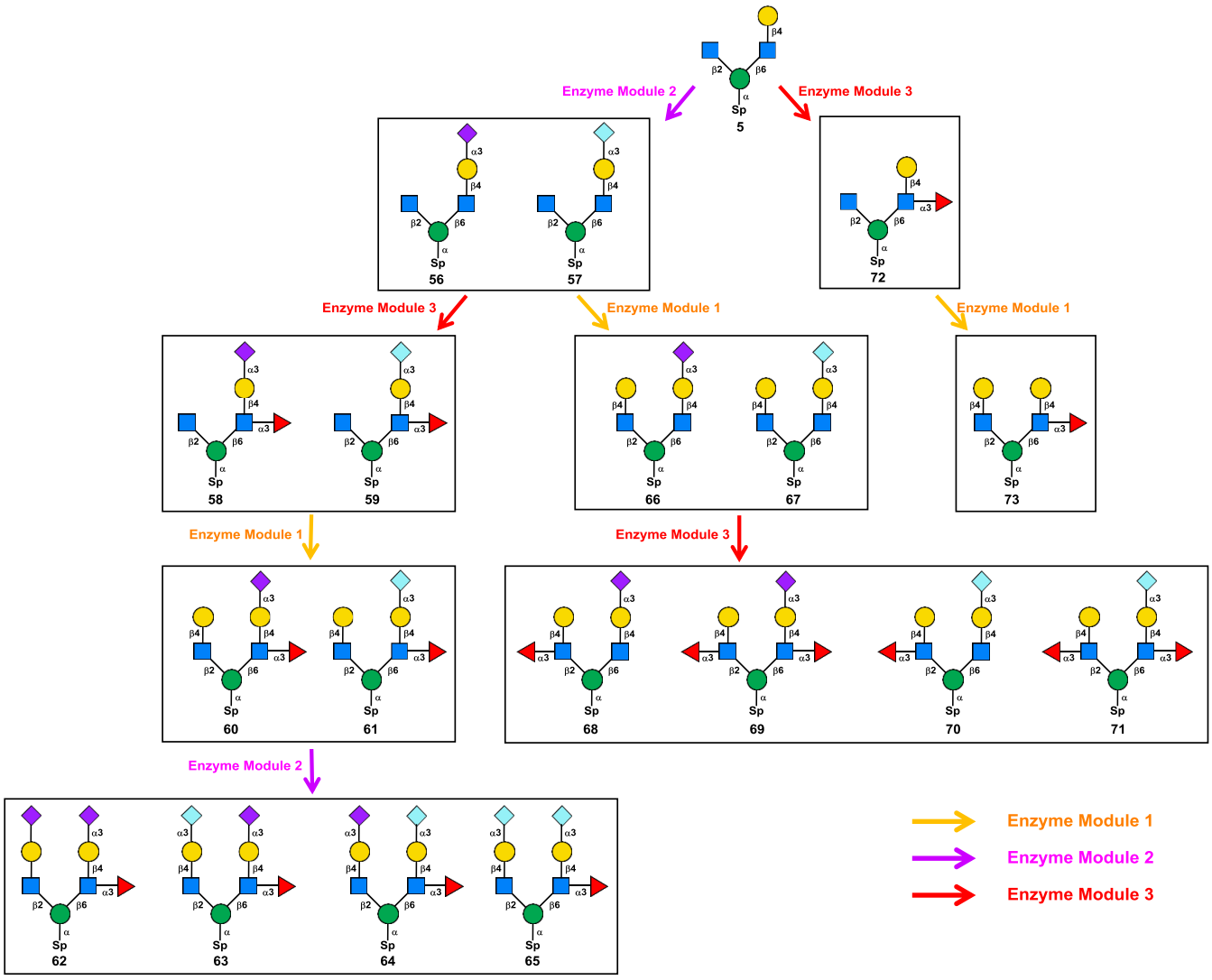
3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (54)

Pentasaccharide **54** (67 mg, 95%) white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 4.0 Hz, 1H), 4.83 (m, 2H), 4.60 (d, *J* = 7.2 Hz, 1H), 4.53 (d, *J* = 8.4 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.20 (d, *J* = 10.6 Hz, 1H), 4.06 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.99 (dd, *J* = 12.6, 2.3 Hz, 1H), 3.94 – 3.41 (m, 27H), 2.07 (s, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.91 (m, 2H), 1.18 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 173.46, 173.34, 100.93, 100.66, 98.37, 97.66, 95.98, 75.59, 74.95, 74.39, 74.02, 72.87, 72.41, 71.57, 71.03, 70.81, 70.18, 69.10, 69.08, 68.71, 68.30, 67.45, 66.84, 66.57, 65.81, 63.98, 60.61, 59.91, 59.58, 58.83, 54.65, 47.44, 26.97, 21.68, 21.42, 21.37, 14.42; HRMS (ESI) m/z calcd for $C_{37}H_{63}N_5O_{25}Na$ $[M+Na]^+$ 1000.3710, found 1000.3751.



3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)}-α-D-mannopyranoside (55)

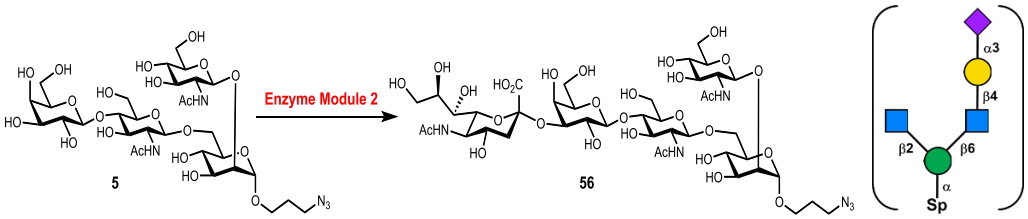
Hexasaccharide **55** (30 mg, 89%) white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 2H), 4.58 (m, 1H), 4.54 (d, *J* = 5.8 Hz, 1H), 4.56 (d, *J* = 8.3 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.19 (dd, *J* = 11.2, 1.9 Hz, 1H), 4.05 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.00 – 3.40 (m, 34H), 2.05 (s, 3H), 2.02 (s, 3H), 1.90 (m, 2H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.31, 174.15, 102.85, 101.78, 101.46, 99.24, 98.51, 96.82, 78.48, 76.44, 75.31, 75.24, 74.87, 74.69, 74.48, 73.25, 72.46, 72.41, 72.33, 71.88, 71.65, 71.03, 70.93, 70.02, 69.55, 69.15, 68.51, 68.30, 67.69, 67.43, 66.66, 64.82, 61.46, 60.99, 60.08, 59.68, 55.02, 48.29, 27.81, 22.52, 22.23, 15.26; HRMS (ESI) m/z calcd for $C_{43}H_{73}N_5O_{30}Na_2$ $[M+2Na]^{2+}$ 592.7068, found 592.7050.



Scheme S4. Enzymatic assembly of asymmetrical Core M2 O-mannose glycans issomers **56-73** from **5**

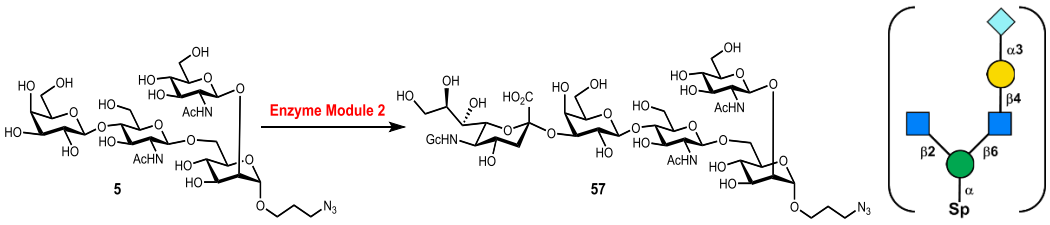
[a]**Reagents and conditions:** Enzyme module 1, Galactose (1.5 equiv), ATP (1.5 equiv), UTP (1.5 equiv), $MgCl_2$ (20 mM), EcGalK, BLUSP, NmLgtB, Tris-HCl (100 mM, pH 7.5), 37 ℃; Enzyme Module 2, ManNAc (1.5 equiv), or ManNGc (1.5 equiv), sodium pyruvate (5.0 equiv), CTP (1.5 equiv), $MgCl_2$ (20 mM), Pm aldolase, NmCSS, PmST1, Tris-HCl (100 mM, pH 8.0), 37 ℃; Enzyme Module 3, L-fucose (1.5 equiv), ATP (1.5 equiv), GTP (1.5 equiv), $MnCl_2$ (20 mM), BfFKP, Hpα1,3FT, Tris-HCl (100 mM, pH 7.5), 37 ℃, **56** (300 mg, 95%), **57** (250 mg, 92%), **58** (90 mg, 68%, the reaction was run twice), **59** (90 mg, 78%, the reaction was run twice), **60** (61 mg, 61%), **61** (49 mg, 48%), **62** (17 mg, 94%), **63** (16 mg, 88%), **64** (11 mg, 92%), **65** (10 mg, 85%), **66** (90 mg, 52%), **67** (70 mg, 52%), **68** (60 mg, 60%, **68** and **69** were derived from **66** in one-pot, the reaction was run twice with 3.0 equiv L-Fuc, 3.0 equiv ATP and 3.0 equiv GTP), **69** (40 mg, 36%, **68** and **69** were derived from **66** in one-pot, the reaction was run twice with 3.0 equiv L-Fuc, 3.0 equiv ATP and 3.0 equiv GTP), **70** (40 mg, 51%, **70** and **71** were derived from **67** in one-pot, the reaction was

run twice with 3.0 equiv L-Fuc, 3.0 equiv ATP and 3.0 equiv. GTP),**71** (38 mg, 45%, **70** and **71** were derived from **67** in one-pot, the reaction was run twice with 3.0 equiv L-Fuc, 3.0 equiv ATP and 3.0 equiv GTP), **72** (95 mg, 93%), **73** (59 mg, 74%).



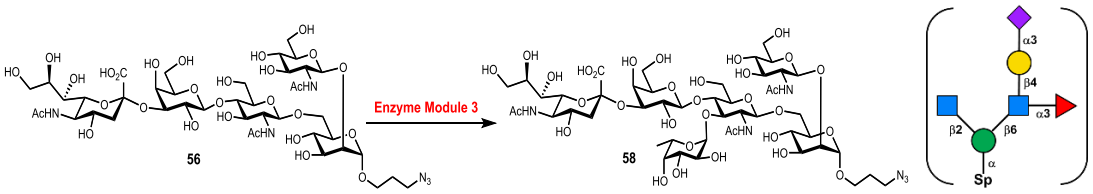
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (56)

Pentasaccharide **56** (300 mg, 95%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.74 (s, 1H), 4.47 (d, *J* = 8.2 Hz, 3H), 4.12 (d, *J* = 10.5 Hz, 1H), 4.04 (dd, *J* = 9.9, 3.1 Hz, 1H), 3.98 (d, *J* = 3.6 Hz, 1H), 3.93 (d, *J* = 11.9 Hz, 1H), 3.87 (d, *J* = 3.1 Hz, 1H), 3.84 – 3.20 (m, 30H), 2.68 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.98 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.82 (m, 2H), 1.72 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 174.85, 174.50, 174.07, 173.81, 102.43, 101.47, 99.66, 99.53, 96.74, 78.13, 76.38, 75.70, 75.32, 75.05, 74.61, 73.08, 72.75, 72.21, 71.66, 71.57, 70.03, 69.79, 69.46, 69.26, 68.26, 67.93, 67.34, 64.73, 64.70, 62.43, 60.94, 60.49, 59.92, 55.31, 54.92, 51.55, 48.20, 39.48, 27.75, 22.35, 22.16, 21.96; HRMS (ESI) m/z calcd for $C_{42}H_{69}N_6O_{29}$ $[M-H]^-$ 1121.4114, found 1121.4146.



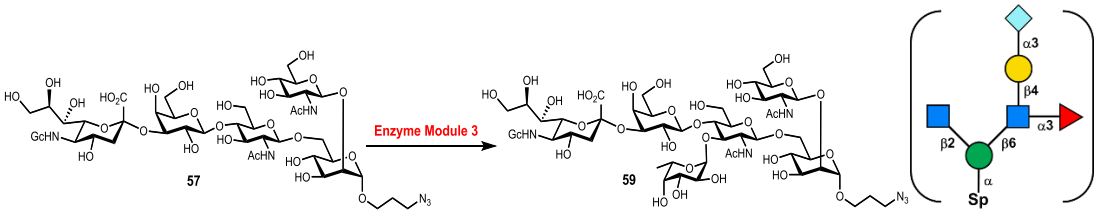
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (57)

Pentasaccharide **57** (250 mg, 92%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.52 (d, *J* = 7.9 Hz, 3H), 4.16 (d, *J* = 10.9 Hz, 1H), 4.10 (m, 1H), 4.09 (s, 2H), 4.03 (dd, *J* = 3.6, 2.0 Hz, 1H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.93 – 3.37 (m, 32H), 2.74 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.87 (m, 2H), 1.78 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.65, 174.50, 174.07, 173.80, 102.45, 101.46, 99.68, 99.51, 96.75, 78.23, 76.38, 75.71, 75.33, 75.06, 74.62, 73.08, 72.48, 72.23, 71.70, 71.61, 70.01, 69.80, 69.48, 69.27, 67.99, 67.88, 67.35, 64.73, 64.70, 62.40, 60.92, 60.85, 60.50, 59.97, 55.33, 54.94, 51.26, 48.21, 39.57, 27.73, 22.32, 22.13; HRMS (ESI) m/z calcd for $C_{42}H_{69}N_6O_{30}$ $[M-H]^-$ 1137.4064, found 1137.4118.



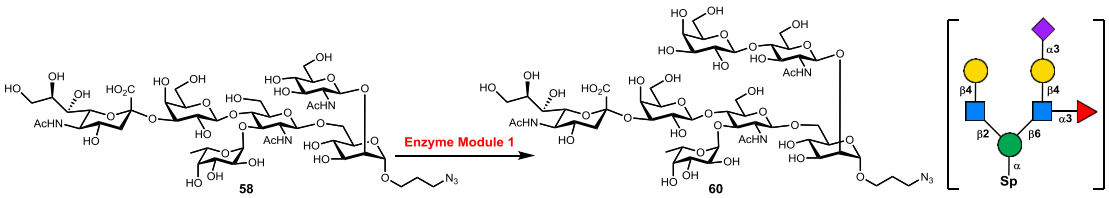
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (58)

Hexasaccharide **58** (90 mg, 68%) white solid after lyophilization. The reaction was run twice to achieve better yields. ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 4.0 Hz, 1H), 4.83 (m, 2H), 4.56 (d, *J* = 8.4 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.18 (d, *J* = 9.8 Hz, 1H), 4.08 (dd, *J* = 9.8, 3.1 Hz, 1H), 4.06 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.02 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.96 – 3.41 (m, 34H), 2.76 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 1.91 (m, 2H), 1.80 (t, *J* = 12.2 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.97, 174.58, 173.92, 173.84, 101.59, 101.30, 99.62, 99.59, 98.57, 96.89, 76.52, 75.80, 75.61, 75.22, 74.87, 74.76, 73.39, 73.18, 72.88, 71.88, 71.83, 71.66, 70.03, 69.90, 69.60, 69.22, 69.16, 68.28, 68.07, 67.69, 67.43, 67.28, 66.64, 64.84, 62.56, 61.46, 60.59, 59.68, 55.78, 55.45, 51.67, 48.30, 39.76, 27.82, 22.44, 22.31, 22.03, 15.26; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{33}$ $[M-H]^-$ 1267.4694, found 1267.4728.



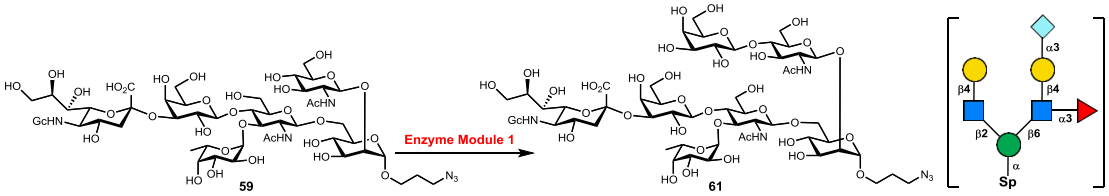
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (59)

Hexasaccharide **59** (90 mg, 78%) white solid after lyophilization. The reaction was run twice to achieve better yields. ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 3.9 Hz, 1H), 4.83 (m, 1H), 4.82 (d, *J* = 1.5 Hz, 1H), 4.56 (d, *J* = 8.4 Hz, 1H), 4.55 (d, *J* = 8.3 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.17 (dd, *J* = 11.1, 1.8 Hz, 1H), 4.12 (s, 2H), 4.09 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.06 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.02 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.96 – 3.41 (m, 34H), 2.78 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.81 (t, *J* = 12.2 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.75, 174.59, 173.93, 173.88, 101.59, 101.30, 99.63, 99.58, 98.57, 96.88, 76.50, 75.80, 75.61, 75.23, 74.87, 74.77, 73.39, 73.17, 72.60, 71.88, 71.66, 70.03, 69.90, 69.59, 69.23, 69.16, 68.01, 67.69, 67.43, 67.26, 66.65, 64.84, 62.52, 61.46, 60.95, 60.59, 59.69, 59.56, 55.78, 55.45, 51.37, 48.30, 39.81, 27.81, 22.43, 22.30, 15.25; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{34}$ $[M-H]^-$ 1283.4643, found 1283.4664.



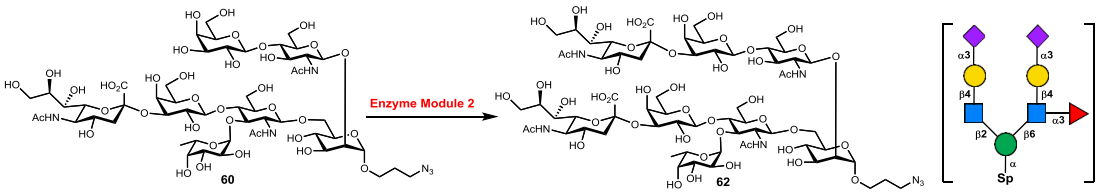
3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (60)

Heptasaccharide **60** (61 mg, 61%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.10 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 2H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 10.7 Hz, 1H), 4.08 (dd, *J* = 9.7, 3.1 Hz, 1H), 4.07 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.03 – 3.29 (m, 41H), 2.77 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.90 (m, 2H), 1.80 (t, *J* = 12.1 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.98, 174.54, 173.94, 173.86, 102.89, 101.60, 101.30, 99.63, 99.44, 98.57, 96.85, 78.43, 76.48, 75.62, 75.32, 75.23, 74.88, 74.77, 74.72, 73.40, 72.88, 72.47, 71.89, 71.86, 71.84, 71.66, 70.93, 70.05, 69.59, 69.23, 69.17, 68.52, 68.28, 68.08, 67.69, 67.44, 67.28, 66.65, 64.85, 62.57, 61.46, 61.00, 59.94, 59.69, 54.97, 51.68, 48.32, 39.76, 27.82, 22.46, 22.32, 22.03, 15.27; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{38}$ $[M-H]^-$ 1429.5222, found 1429.5183.



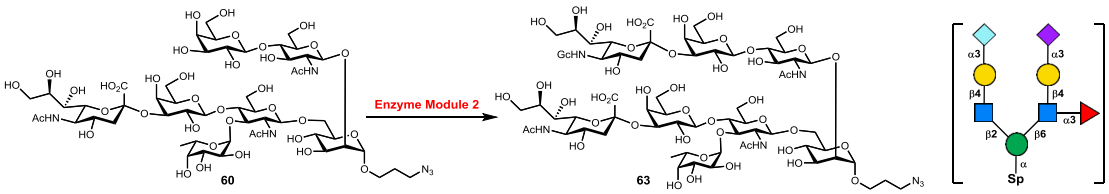
3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (61)

Heptasaccharide **61** (49 mg, 48%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 3.9 Hz, 1H), 4.83 (m, 2H), 4.58 (d, *J* = 7.9 Hz, 1H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 10.7 Hz, 1H), 4.12 (s, 2H), 4.10 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.07 (d, *J* = 3.5 Hz, 1H), 4.04 – 3.41 (m, 41H), 2.78 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.81 (t, *J* = 12.2 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.78, 174.57, 173.97, 173.92, 102.91, 101.63, 101.33, 99.67, 99.47, 98.60, 96.88, 78.46, 76.50, 75.64, 75.35, 75.26, 74.91, 74.81, 74.75, 73.42, 72.63, 72.50, 71.92, 71.89, 71.69, 70.96, 70.08, 69.62, 69.27, 69.19, 68.54, 68.06, 68.03, 67.72, 67.46, 67.30, 66.68, 64.88, 62.56, 61.49, 61.02, 60.98, 59.97, 59.72, 55.00, 51.41, 48.34, 39.85, 27.85, 22.49, 22.34, 15.29; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{39}$ $[M-H]^-$ 1445.5171, found 1445.5179.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (62)

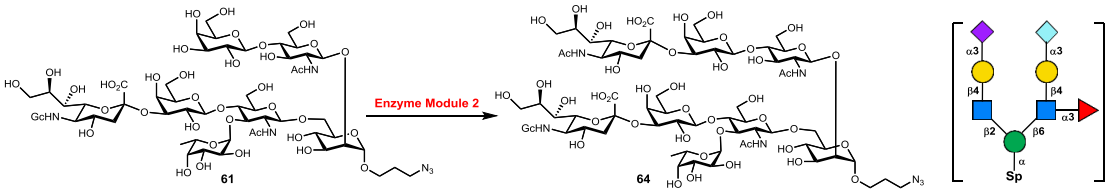
Octasaccharide **62** (17 mg, 94%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 4.0 Hz, 1H), 4.83 (m, 2H), 4.58 (d, *J* = 8.2 Hz, 1H), 4.57 (d, *J* = 10.1 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.53 (d, *J* = 7.7 Hz, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 4.12 (dd, *J* = 9.8, 3.1 Hz, 1H), 4.09 (dd, *J* = 9.6, 3.1 Hz, 1H), 4.07 (d, *J* = 3.5 Hz, 1H), 4.04 – 3.41 (m, 47H), 2.77 (dt, *J* = 12.4, 4.6 Hz, 2H), 2.06 (s, 3H), 2.04 (s, 6H), 2.02 (s, 3H), 1.91 (m, 2H), 1.81 (t, *J* = 12.4 Hz, 2H), 1.17 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.98, 174.72, 174.54, 173.94, 173.86, 102.56, 101.60, 99.78, 99.62, 99.49, 98.57, 96.84, 96.37, 78.24, 76.47, 75.61, 75.43, 75.22, 75.13, 74.88, 74.73, 73.39, 72.87, 71.84, 71.74, 71.66, 70.29, 70.17, 69.59, 69.35, 69.23, 69.16, 68.51, 68.33, 68.07, 67.68, 67.44, 67.27, 66.65, 64.84, 63.25, 62.56, 61.46, 61.00, 59.91, 59.69, 54.94, 52.23, 51.67, 48.31, 39.75, 39.59, 39.35, 27.82, 22.46, 22.32, 22.09, 22.03, 15.26; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{46}$ $[M-2H]^{2-}$ 860.3068, found 860.3096.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (63)

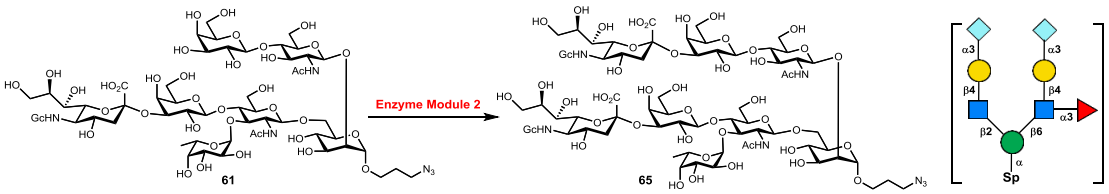
Octasaccharide **63** (16 mg, 88%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.11 (d, *J* = 4.0 Hz, 1H), 4.84 (m, 2H), 4.58 (d, *J* = 8.3 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.55 (d, *J* = 8.4 Hz, 1H), 4.58 (d, *J* = 7.7 Hz, 1H), 4.19 (d, *J* = 10.8 Hz, 1H), 4.14 (d, *J* = 4.5 Hz, 1H), 4.13 (s, 2H), 4.10 – 3.41 (m, 49H), 2.77 (dt, *J* = 12.0, 5.2 Hz, 2H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.1 Hz, 1H), 1.80 (t, *J* = 12.1 Hz, 1H), 1.17 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.74, 174.98, 174.53, 173.94, 173.89, 173.86, 102.57, 101.60, 101.30, 99.79, 99.62, 99.49, 98.57, 96.84, 78.25, 76.47, 75.60, 75.42, 75.22, 75.13, 74.87, 74.76, 74.73, 73.39, 72.87, 72.57, 71.83, 71.80 71.66, 70.08, 69.95, 69.59, 69.35, 69.23, 69.16, 68.29, 68.07, 67.98, 67.68, 67.43, 67.28, 66.64, 64.84, 62.56, 62.51, 61.46, 61.00,

60.95, 59.91, 59.68, 55.77, 54.94, 51.67, 51.35, 48.31, 39.75, 39.66, 27.82, 22.46, 22.31, 22.03, 15.26; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{47}$ $[M-2H]^{2-}$ 867.8026, found 867.8017.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (64)

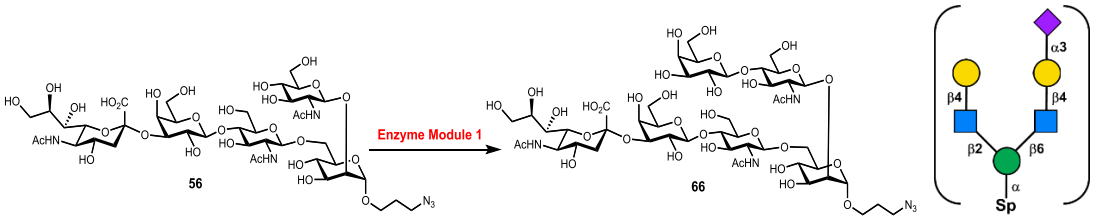
Octasaccharide **64** (11 mg, 92%) white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 4.83 (m, 2H), 4.59 (d, *J* = 7.5 Hz, 1H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.55 (d, *J* = 7.8 Hz, 1H), 4.53 (d, *J* = 7.7 Hz, 1H), 4.20 (d, *J* = 10.8 Hz, 1H), 4.13 (s, 2H), 4.12 – 4.10 (m, 2H), 4.07 (m, 1H), 4.04 – 3.41 (m, 47H), 2.78 (dd, *J* = 12.6, 4.7 Hz, 1H), 2.76 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.2 Hz, 1H), 1.81 (t, *J* = 12.1 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.75, 174.98, 174.54,173.95, 173.90, 173.86, 102.56, 101.60, 101.29, 99.78, 99.64, 99.49, 98.57, 96.84, 78.23, 76.48, 75.59, 75.42, 75.22, 75.13, 74.87, 74.76, 74.72, 73.39, 72.85, 72.60, 71.89, 71.84, 71.74, 71.66, 70.08, 69.58, 69.35, 69.24, 69.16, 68.33, 68.06, 68.04, 68.00, 67.68, 67.44, 67.26, 66.65, 64.84, 62.54, 62.52, 61.46, 61.00, 60.95, 59.91, 59.69, 59.29, 54.94, 51.65, 51.37, 48.31, 39.81, 39.58, 27.82, 22.47, 22.32, 22.03, 15.26; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{47}$ $[M-2H]^{2-}$ 867.8026, found 867.8008.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (65)

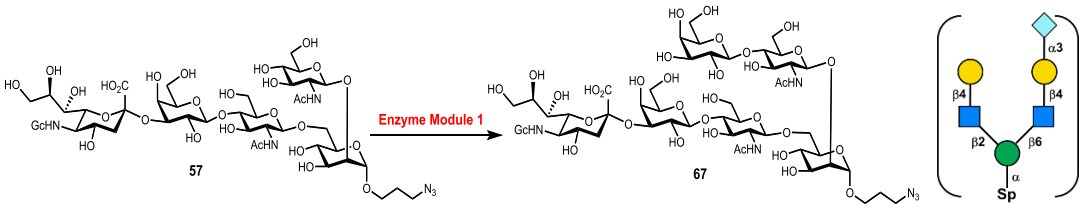
Octasaccharide **65** (10 mg, 85%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 3.9 Hz, 1H), 4.84 (m, 2H), 4.60 (d, *J* = 7.4 Hz, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.53 (d, *J* = 7.7 Hz, 1H), 4.20 (d, *J* = 10.7 Hz, 1H), 4.15 – 4.10 (m, 5H), 4.08 (d, *J* = 3.6 Hz, 1H), 4.04 – 3.42 (m, 48H), 2.79 (dt, *J* = 12.4, 4.6 Hz, 2H), 2.06 (s, 3H), 2.03 (s, 3H), 1.91 (m, 2H), 1.83 (t, *J* = 12.2 Hz, 1H), 1.82 (t, *J* = 12.2 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ

175.74, 174.54, 173.95, 173.90, 102.57, 101.60, 101.29, 99.80, 99.64, 99.50, 98.57, 96.84, 78.24, 76.50, 75.59, 75.41, 75.22, 75.13, 74.87, 74.75, 74.72, 73.39, 72.60, 72.57, 71.90, 71.83, 71.81, 71.66, 70.07, 69.59, 69.36, 69.24, 69.17, 68.07, 68.03, 67.99, 67.67, 67.44, 67.27, 66.65, 64.84, 62.52, 61.47, 61.01, 60.96, 59.92, 59.69, 55.78, 54.95, 51.37, 48.32, 39.81, 39.65, 27.82, 26.44, 22.48, 22.33, 15.27; HRMS (ESI) m/z calcd for $C_{65}H_{105}N_7O_{48}$ $[M-2H]^{2-}$ 875.8001, found 875.8000.



3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (66)

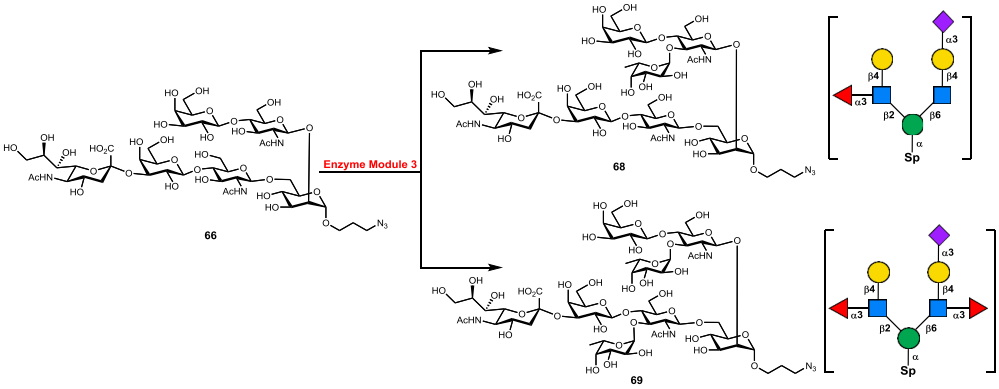
Hexasaccharide **66** (90 mg, 52%) white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.82 (m, 1H), 4.57 (d, *J* = 7.7 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 2H), 4.46 (d, *J* = 7.9 Hz, 1H), 4.19 (d, *J* = 10.2 Hz, 1H), 4.11 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.06 (dd, *J* = 3.4, 1.6 Hz, 1H), 4.02 – 3.40 (m, 38H), 2.75 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.90 (m, 2H), 1.80 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 174.95, 174.51, 174.14, 173.83, 102.88, 102.54, 101.52, 99.77, 99.44, 96.80, 78.43, 78.33, 76.45, 75.43, 75.30, 75.13, 74.70, 72.84, 72.46, 72.30, 71.85, 71.73, 71.68, 70.92, 70.08, 69.56, 69.34, 68.50, 68.31, 68.05, 67.44, 64.82, 62.54, 60.99, 60.06, 59.94, 55.02, 54.94, 51.65, 48.31, 39.59, 27.82, 22.43, 22.23, 22.03; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{34}$ $[M-H]^-$ 1283.4643, found 1283.4653.



3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (67)

Hexasaccharide **67** (70 mg, 52%) white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 4.83 (d, *J* = 1.5 Hz, 1H), 4.58 (d, *J* = 7.7 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 2H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.20 (dd, *J* = 11.2, 1.9 Hz, 1H), 4.14 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.13 (s, 2H), 4.07 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.03 – 3.41 (m, 38H), 2.78 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.1 Hz, 1H); ^{13}C NMR (151 MHz, D_2O) δ 175.74, 174.53, 174.16, 173.89, 102.89, 102.56, 101.54, 99.79, 99.45, 96.81, 78.44, 78.35, 76.46, 75.43, 75.31, 75.14, 74.71, 72.57, 72.46, 72.31, 71.86, 71.79, 71.69, 70.93, 70.10, 69.56, 69.36, 68.51, 68.07, 67.98, 67.44,

64.84, 62.51, 61.00, 60.95, 60.08, 59.95, 59.31, 55.03, 54.95, 51.36, 48.32, 39.66, 27.82, 22.44, 22.24; HRMS (ESI) m/z calcd for $C_{48}H_{79}N_6O_{35}$ $[M-H]^-$ 1299.4592, found 1299.4625.

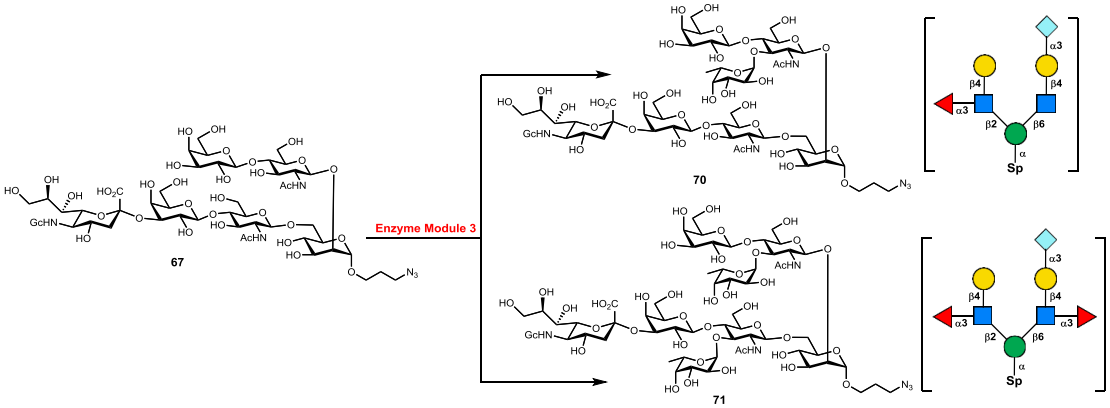


3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (68) and 3-Azidopropyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (69)

The compound **68** and **69** were derived from compound **66** (90 mg, 0.07 mmol), the reaction was run twice to achieve better yields. Heptasaccharide **68** (60 mg, 60%), white solid after lyophilization, and octasaccharide **69** (40 mg, 36%), white solid after lyophilization. For heptasaccharide **68:** ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 3.9 Hz, 1H), 4.83 (m, 2H), 4.59 (d, *J* = 6.9 Hz, 1H), 4.55 (d, *J* = 8.1 Hz, 2H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 4.11 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.06 (d, *J* = 3.5 Hz, 1H), 4.00 (t, *J* = 11.0 Hz, 2H), 3.96 – 3.40 (m, 39H), 2.76 (dd, *J* = 12.5, 4.5 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.90 (m, 2H), 1.80 (t, *J* = 12.1 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.97, 174.32, 174.15, 173.85, 102.55, 101.79, 101.53, 99.78, 99.20, 98.52, 96.80, 78.35, 76.40, 75.44, 75.25, 75.14, 74.88, 74.70, 74.48, 73.27, 72.85, 72.43, 72.30, 71.89, 71.74, 71.67, 71.04, 70.04, 69.55, 69.35, 69.16, 68.32, 68.06, 67.69, 67.45, 66.67, 64.84, 62.55, 61.47, 61.01, 60.08, 59.69, 55.02, 51.66, 48.32, 39.60, 27.83, 22.54, 22.25, 22.04, 15.29; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{38}$ $[M-H]^-$ 1429.5222, found 1429.5275.

For octasaccharide **69:** ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.1 Hz, 1H), 5.10 (d, *J* = 4.0 Hz, 1H), 4.81 (m, 3H), 4.60 (d, *J* = 7.7 Hz, 1H), 4.56 (d, *J* = 7.7 Hz, 1H), 4.52 (d, *J* = 7.6 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 9.8 Hz, 1H), 4.10 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.06 (dd, *J* = 3.6, 1.5 Hz, 1H), 4.03 – 3.40 (m, 44H), 2.77 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.80 (t, *J* = 12.2 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.99, 174.35, 173.94, 173.86, 101.79, 101.60, 101.29, 99.63, 99.17, 98.57,

98.52, 96.85, 76.41, 75.62, 75.25, 75.22, 74.89, 73.40, 73.28, 72.88, 72.43, 71.89, 71.84, 71.65, 71.04, 69.58, 69.23, 69.16, 68.31, 68.29, 68.08, 67.69, 67.41, 67.28, 66.66, 64.86, 62.57, 61.47, 60.64, 59.69, 55.80, 51.68, 48.31, 39.76, 27.82, 22.56, 22.33, 22.25, 22.03, 15.28, 15.26; HRMS (ESI) m/z calcd for $C_{60}H_{99}N_6O_{42}$ $[M-H]^-$ 1575.5801, found 1575.5798.

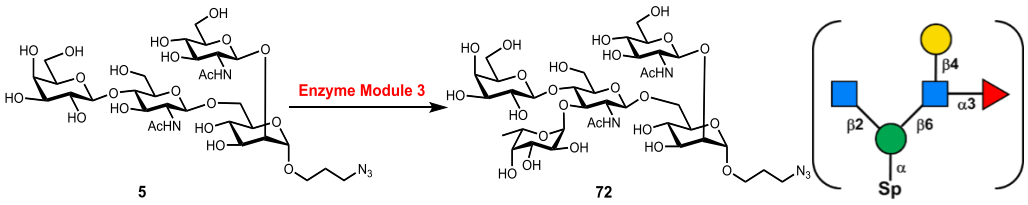


3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (70) and 3-Azidopropyl 3,5-dideoxy-5-hydroxyacetamido-D-glycero-α-D-*galacto*-2-nonulopyranosyl-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (71)

The compound **70** and **71** were derived from compound **67** (70 mg, 0.05 mmol), the reaction was run twice to achieve better yields. Heptasaccharide **70** (40 mg, 51%), white solid after lyophilization, and octasaccharide **71** (38 mg, 45%) as a white solid after lyophilization. For hepetasaccharide **70:** ^{1}H NMR (600 MHz, D_2O) δ 5.13 (d, *J* = 4.0 Hz, 1H), 4.83 (m, 2H), 4.60 (d, *J* = 7.3 Hz, 1H), 4.55 (dd, *J* = 8.1, 2.3 Hz, 2H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 4.13 (m, 1H), 4.12 (s, 2H), 4.06 (d, *J* = 3.6 Hz, 1H), 4.02 – 3.40 (m, 41H), 2.78 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.05 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.82 (t, *J* = 12.1 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.74, 174.32, 174.16, 173.88, 102.55, 101.78, 101.53, 99.79, 99.19, 98.51, 96.80, 78.35, 76.39, 75.43, 75.25, 75.14, 74.88, 74.70, 74.47, 73.27, 72.57, 72.42, 72.30, 71.89, 71.79, 71.67, 71.03, 70.04, 69.55, 69.35, 69.15, 68.31, 68.07, 67.98, 67.68, 67.43, 66.66, 64.84, 62.50, 61.46, 61.00, 60.95, 60.08, 59.69, 55.79, 55.02, 51.35, 48.31, 39.66, 27.82, 22.53, 22.23, 15.27; HRMS (ESI) m/z calcd for $C_{54}H_{89}N_6O_{39}$ $[M-H]^-$ 1445.5171, found 1445.5142.

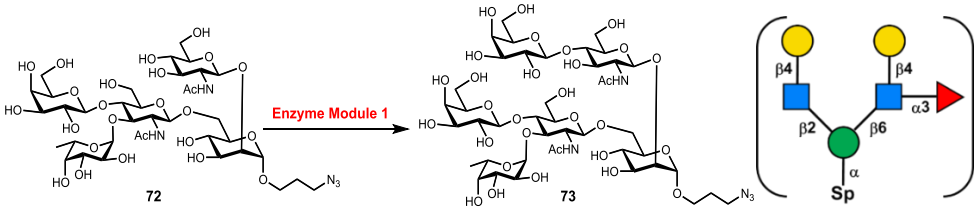
For octasaccharide **71:** ^{1}H NMR (600 MHz, D_2O) δ 5.12 (d, *J* = 4.0 Hz, 1H), 5.11 (d, *J* = 4.0 Hz, 1H), 4.82 (m, 3H), 4.60 (d, *J* = 7.1 Hz, 1H), 4.56 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.44 (d, *J* = 7.6 Hz, 1H), 4.18 (d, *J* = 10.8 Hz, 1H), 4.12 (s, 2H), 4.10 (dd, *J* = 9.8, 3.0 Hz, 1H), 4.06 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.03 – 3.40 (m, 44H), 2.78 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.05 (s, 3H), 2.02 (s, 3H), 1.91 (m, 2H), 1.81 (t, *J* =

12.2 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 175.75, 174.34, 173.93, 173.89, 101.79, 101.60, 101.29, 99.64, 99.17, 98.57, 98.52, 96.85, 76.41, 75.61, 75.25, 75.22, 74.88, 74.77, 74.47, 73.40, 73.28, 72.60, 72.42, 71.89, 71.64, 71.04, 69.97, 69.58, 69.24, 69.16, 68.31, 68.03, 68.00, 67.69, 67.41, 67.26, 66.66, 64.86, 62.52, 61.46, 60.95, 59.69, 59.46, 55.82, 55.79, 51.38, 48.31, 39.82, 27.82, 22.56, 22.32, 15.27, 15.26; HRMS (ESI) m/z calcd for $C_{60}H_{99}N_6O_{43}$ $[M-H]^-$ 1591.5750, found 1591.5719.



3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (72)

Pentasaccharide **72** (95 mg, 93%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.08 (d, *J* = 4.0 Hz, 1H), 4.83 – 4.80 (m, 1H), 4.54 (d, *J* = 8.6 Hz, 1H), 4.53 (d, *J* = 8.3 Hz, 1H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.15 (d, *J* = 10.7 Hz, 1H), 4.03 (m, 1H), 3.98 (d, *J* = 11.2 Hz, 1H), 3.91 – 3.39 (m, 29H), 2.03 (s, 3H), 1.99 (s, 3H), 1.87 (m, 2H), 1.14 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.50, 173.86, 101.71, 101.16, 99.56, 98.52, 96.83, 76.48, 75.71, 75.21, 74.80, 74.77, 73.30, 73.09, 72.33, 71.79, 71.56, 70.91, 69.90, 69.79, 69.51, 69.08, 68.23, 67.58, 67.33, 66.59, 64.74, 61.39, 60.48, 59.69, 55.35, 48.20, 27.73, 22.35, 22.22, 15.20; HRMS (ESI) m/z calcd for $C_{37}H_{63}N_5O_{25}Na$ $[M+Na]^+$ 1000.3710, found 1000.3765.

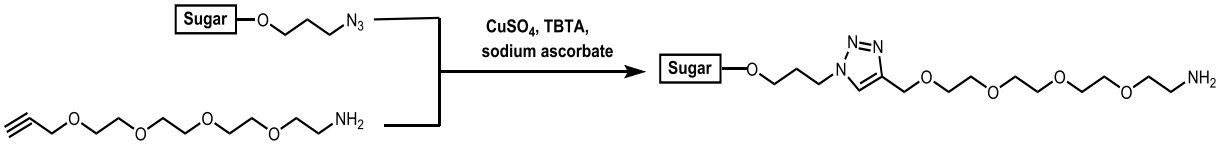


3-Azidopropyl β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-{β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)}-α-D-mannopyranoside (73)

Hexasaccharide **73** (59 mg, 74%), white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O) δ 5.06 (d, *J* = 4.0 Hz, 1H), 4.52 (d, *J* = 8.3 Hz, 1H), 4.51 (d, *J* = 9.7 Hz, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 7.9 Hz, 1H), 4.14 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.01 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.96 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.92 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.89 – 3.32 (m, 33H), 2.00 (s, 3H), 1.96 (s, 3H), 1.85 (m, 2H), 1.12 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, D_2O) δ 174.48, 173.89, 102.81, 101.73, 101.18, 99.40, 98.57, 96.79, 78.29, 76.40, 75.25, 75.23, 74.82, 74.64, 73.30, 72.37, 72.33, 71.80, 71.57, 70.92, 70.85, 69.96, 69.51, 69.09, 68.43, 68.25, 67.60, 67.33, 66.62, 64.75, 61.42, 60.93, 59.84, 59.70, 54.87, 48.21, 27.74, 22.37, 22.22, 15.21; HRMS (ESI) m/z calcd for $C_{43}H_{77}N_6O_{30}$ $[M+NH_4]^+$ 1157.4684, found 1157.4691.

3. General methods of glycan microarray

General procedure for converting 3-azidopropyl linker of synthetic O-mannose glycans to ready-for-print amine-terminated spacer via click chemistry:



The synthetic 3-azidopropyl O-mannose glycan (10 mg) and a commercially available triethylene glycol 2-aminoethyl propargyl ether (H_2N-PEG4-ALK, 1.0 equiv., Sigma) were added to a stirred solution of $CuSO_4$ (0.2 equiv.), sodium ascorbate (0.5 equiv.) and *tris*-benzyltriazolylmethyl amine (TBTA, 0.2 equiv.) in *tert*-butyl alcohol/water (2.0 mL, 2:1, v/v). The reaction mixture was stirred at room temperature. Upon completion (about 1 h), the solvent was removed under reduced pressure and the residue was purified by Bio-Gel P2 gel filtration chromatography to afford the product as a white solid. All the resulted sialyl O-mannose glycans were quantitated using DMB-HPLC[11] method before the slide printing.

General procedure for glycan microarray analysis:

Each O-mannose glycan with amine-terminated spacer was dissolved in 300 mM sodium phosphate buffer (pH 8.4) to obtain a 100 μM glycan solution. Glycan printing as replicates of four spots was performed in ArrayIt SpotBot® Extreme instrument. Glycan microarrays were fabricated using PolyAn 3-D NHS-functionalized glass slides purchased from Automate Scientific. Printed glycan microarray slides were left to dry at 20 ℃ for 10 hours and then unreacted NHS esters on slides were blocked by prewarmed ethanolamine solution (50 mM in 100 mM Tris-HCl, pH 9.0), washed with warm Milli-Q water, dried, and then fitted in a multi-well microarray hybridization cassette (ArrayIt, CA) to divide into subarrays. The subarrays were blocked with Ovalbumin (1% w/v) in PBS (pH 7.4) for 1 hour at room temperature in a humid chamber with gentle shaking. Subsequently, the blocking solution was discarded, and properly diluted primary antibodies (antibodies/lectins were diluted as described in figure legends) were added to each subarray. After incubating for 2 hours at room temperature with gentle shaking, the slides were extensively washed (first with PBS with 0.1% Tween and then only PBS, pH 7.4) to remove non-specifically bound proteins. The corresponding secondary antibodies were then added and after 1 hour of incubation followed the same washing cycle. The developed glycan microarray slides were then washed, dried and subjected to scanning by a Genepix 4000B microarray scanner (Molecular Devices Corp., Union City, CA). Data analysis was done using the Genepix Pro 7.3 analysis software (Molecular Devices Corp., Union City, CA). Plant lectins of *Maackia amurensis* lectin I (MAL-I), MAL-II and *Sambucus nigra* agglutinin (SNA) were purchased from Vector Laboratories (Burlingame, CA, USA). Chicken polyclonal anti-Neu5Gc

antibody IgY (pChGc) was purchased from BioLeagend (San Diegeo, USA). Human L1 cell adhesion molecule (L1CAM/CD171) and human myelin-associated glycoprotein (MAG/Siglec-4a) were purchased from R&D Systems (Minneapolis, MN, USA). Human sialic acid-binding lectin Siglec-9 (hSiglec-9-Fc)[12], human anti-Neu5Gc antibody rich serum[12b], His-tagged typhoid toxin (PltB-His)[13] and the recombinant human Fc-fusion CD33 (hSiglec-3)[14] were prepared as described previously.

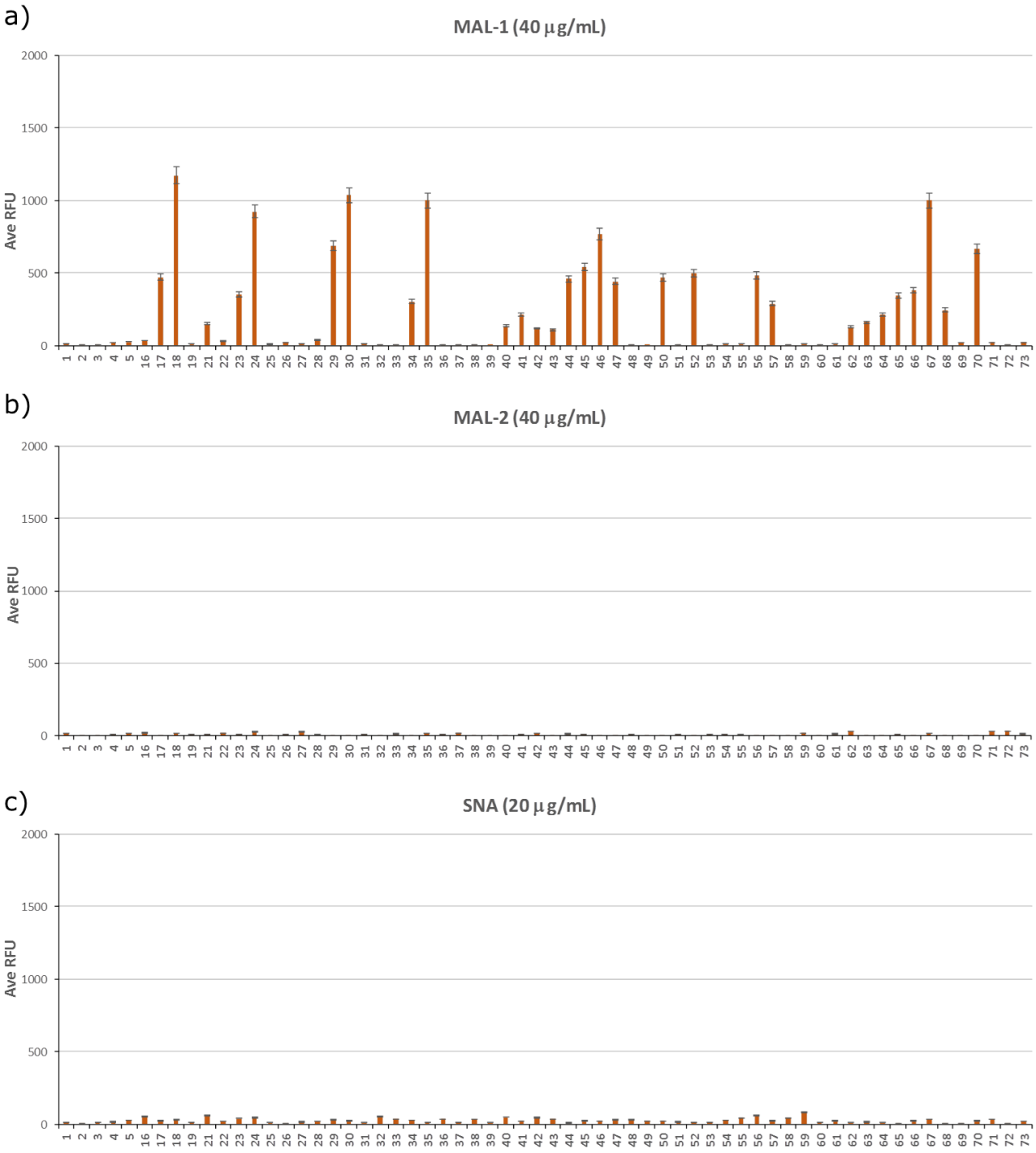


Figure S1. Binding profiles of O-mannose glycans with plant lectins of MAL-I, MAL-II and SNA

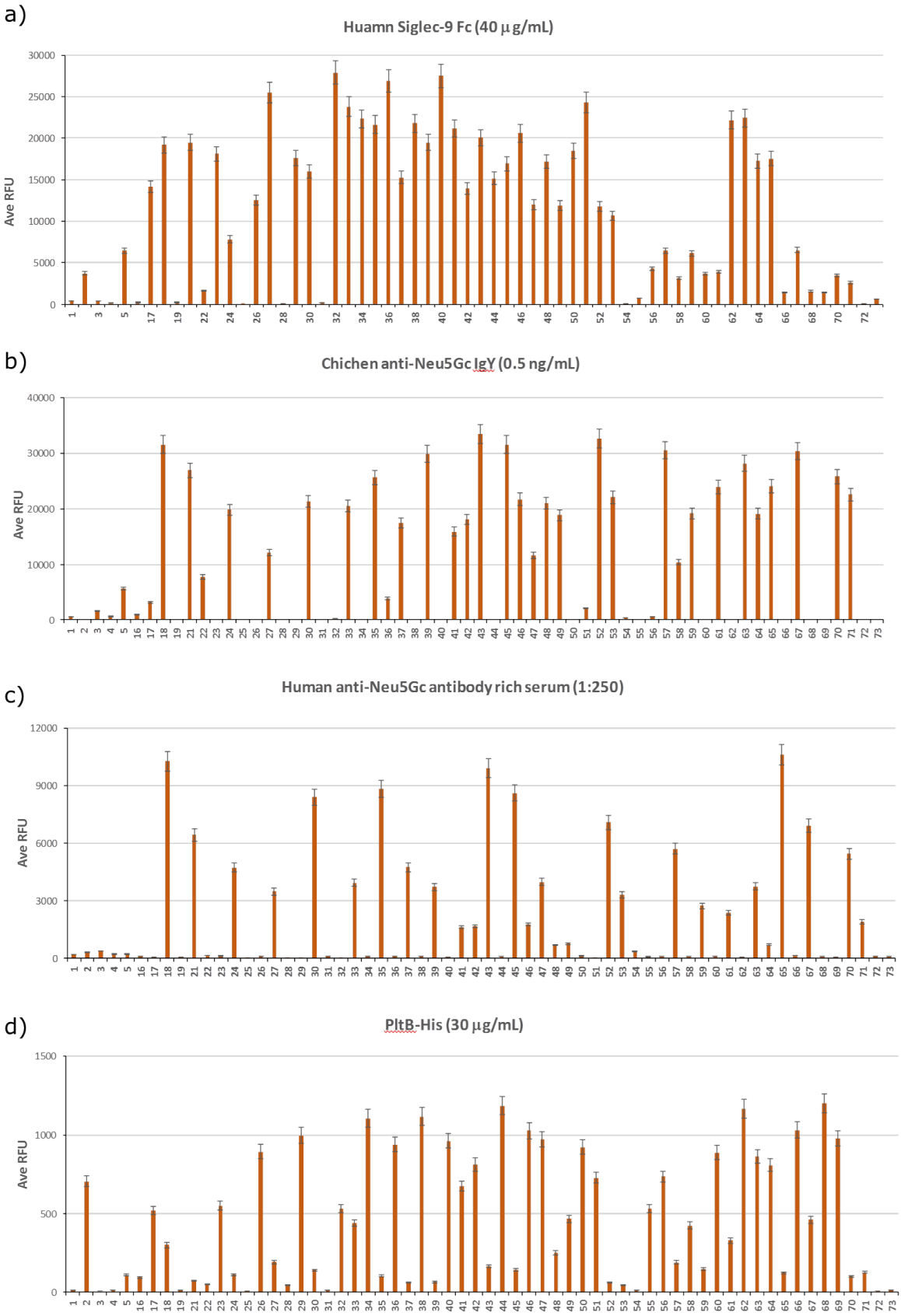


Figure S2. Binding profiles of O-mannose glycans with Siglec-9-Fc, pChGc, human anti-Neu5Gc antibody rich serum and PltB-His

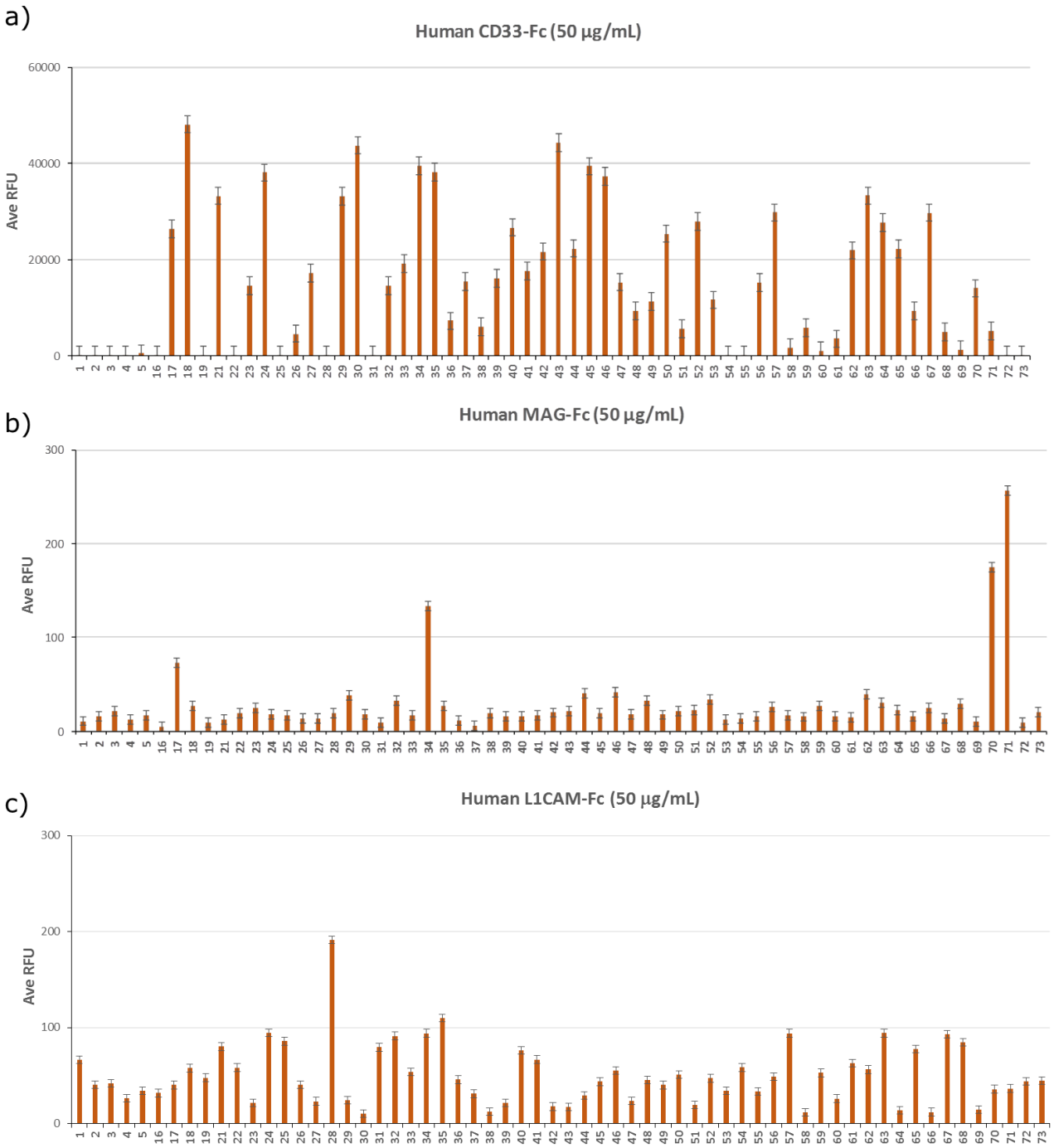


Figure S3. Binding profiles of O-mannose glycans with human brain proteins of CD33-Fc, MAG-Fc and L1CAM-Fc

Reference

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12. (a) Angata, T.; Varki, A. *J. Biol. Chem.* **2000**, 275, 22127–22135; (b) Padler-Karavani, V.; Song, X.; Yu, H.; Hurtado-Ziola, N.; Huang, S.; Muthana, S.; Chokhawala, H. A.; Cheng, J.; Verhagen, A.; Langereis, M. A.; Kleene, R.; Schachner, M.; de Groot, R. J.; Lasanajak, Y.; Matsuda, H.; Schwab, R.; Chen, X.; Smith, D. F.; Cummings, R. D.; Varki, A. *J. Biol. Chem.* **2012**, 287, 22593-22608; (c) Song, X.; Yu, H.; Chen, X.; Lasanajak, Y.; Tappert, M. M.; Air, G. M.; Tiwari, V. K.; Cao, H.; Chokhawala, H. A.; Zheng, H.; Cummings, R. D.; Smith, D. F. *J. Biol. Chem.* **2011**, 286, 31610–31622.
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3. NMR Spectra

CHZ-614

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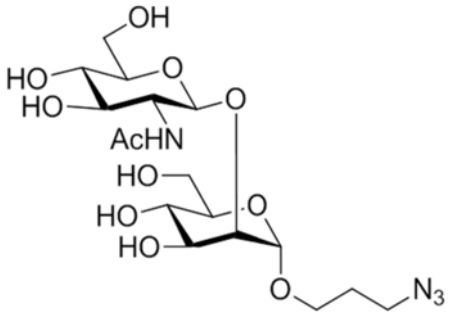
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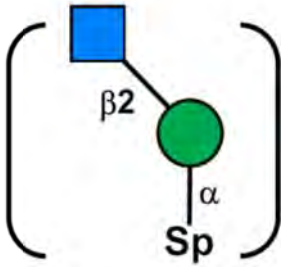
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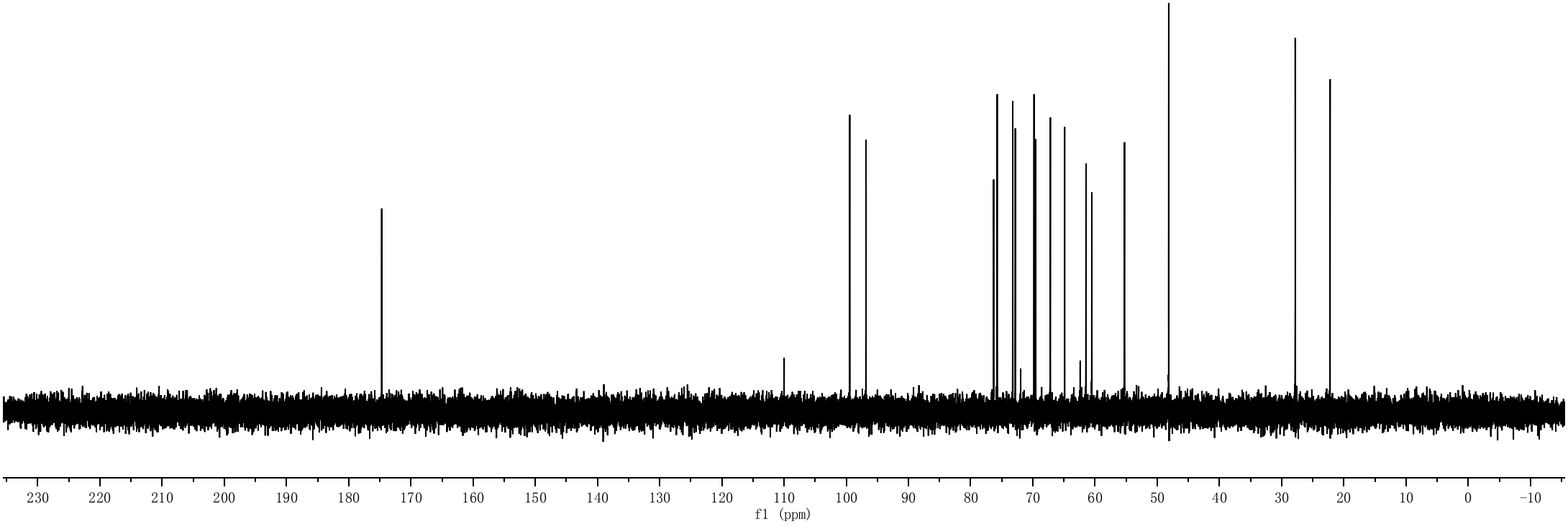
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f1 (ppm)

CHZ-614

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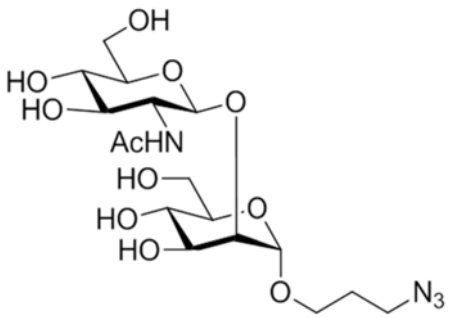
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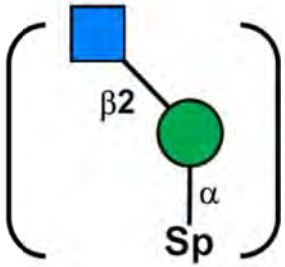
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Sp

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f1 (ppm)

CHZ-589

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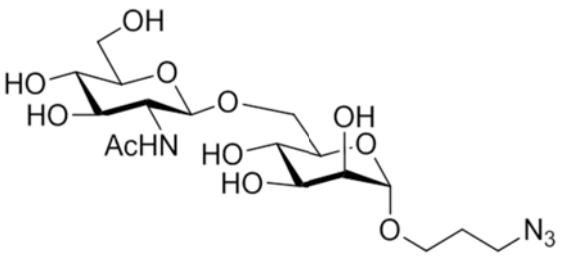
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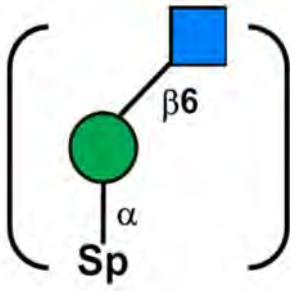
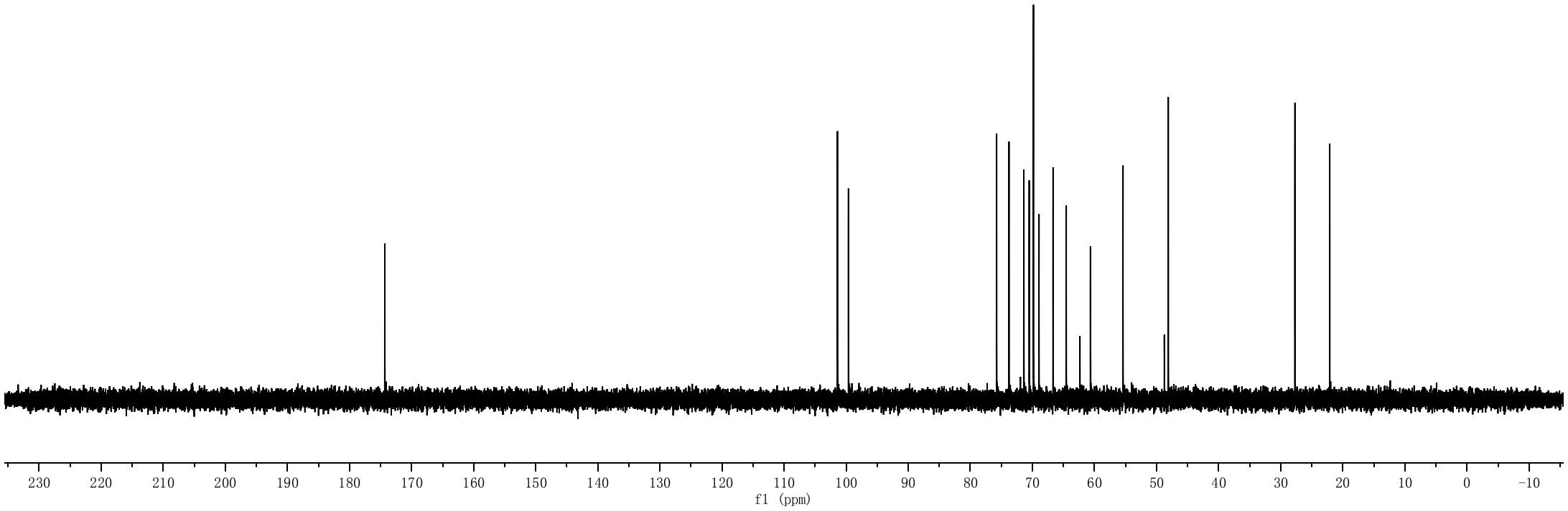

β6
α
Sp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f1 (ppm)

CHZ-589

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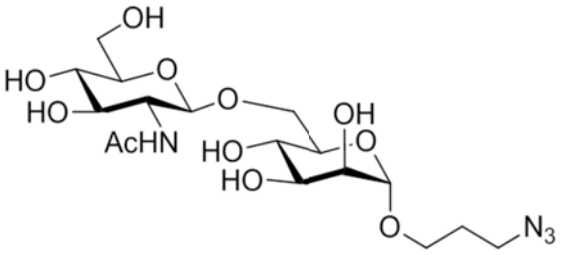
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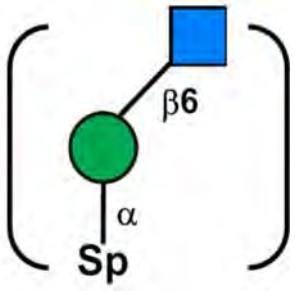
β6
α
Sp

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f1 (ppm)

S55

CHZ-656

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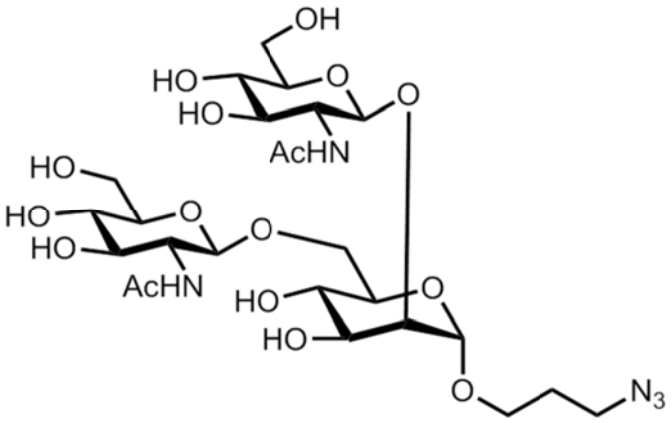
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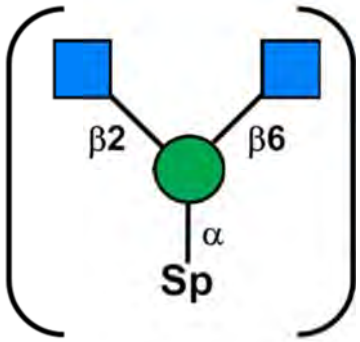
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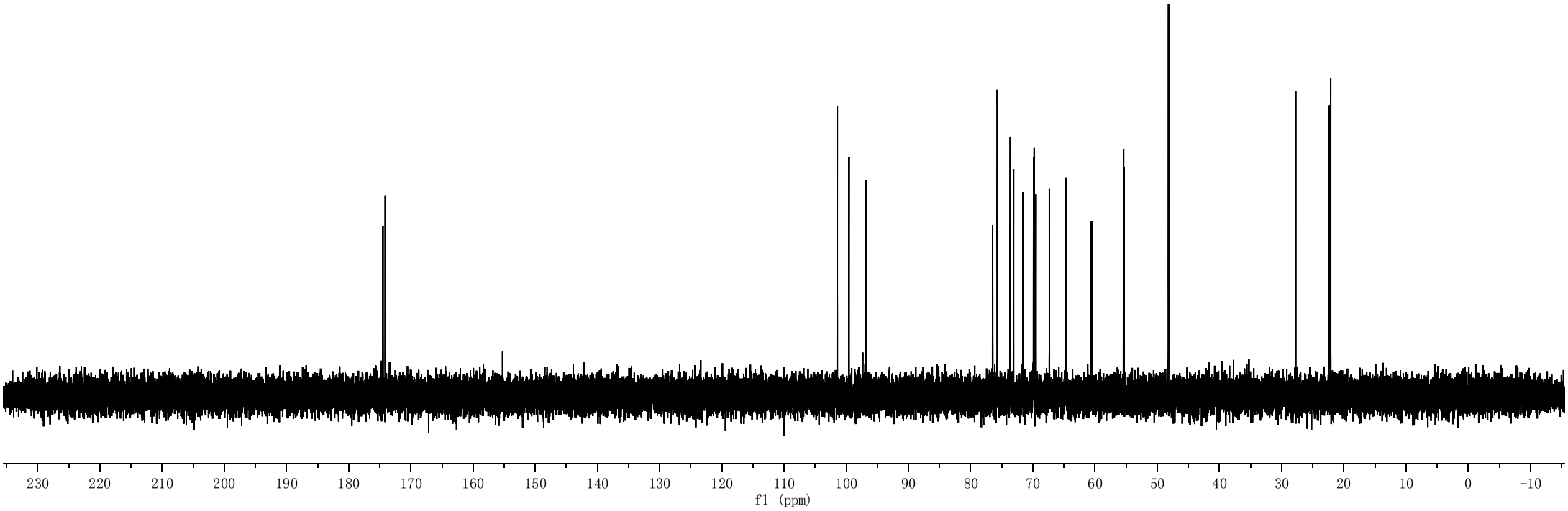
β6
α
Sp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0
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f1 (ppm)

CHZ-656

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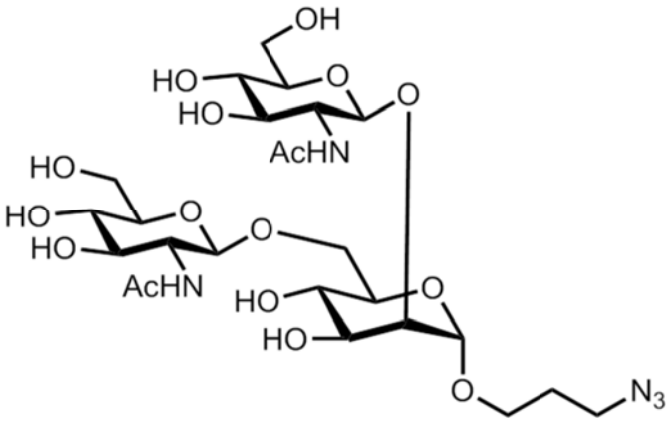
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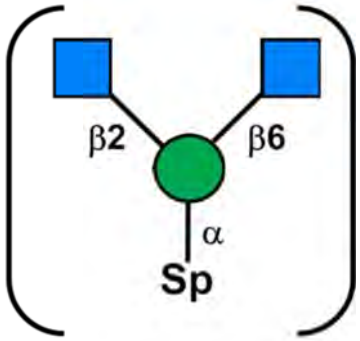
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β6
α
Sp

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0.0
f1 (ppm)

CHZ-864

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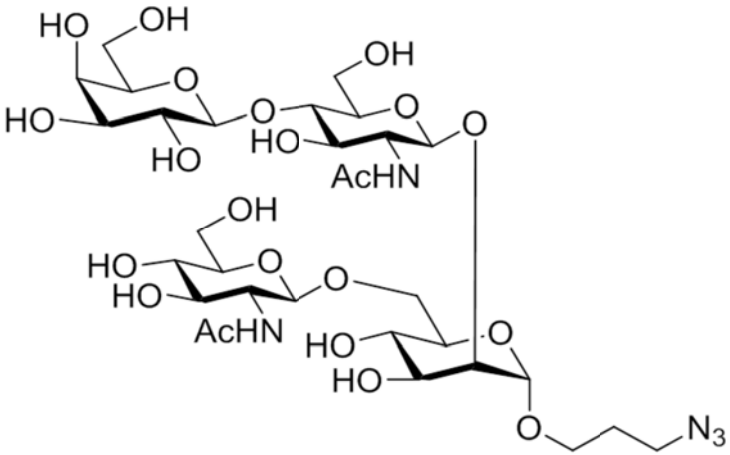
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AcHN
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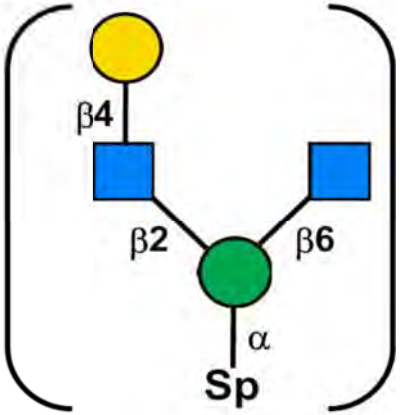
HO
O
O
N3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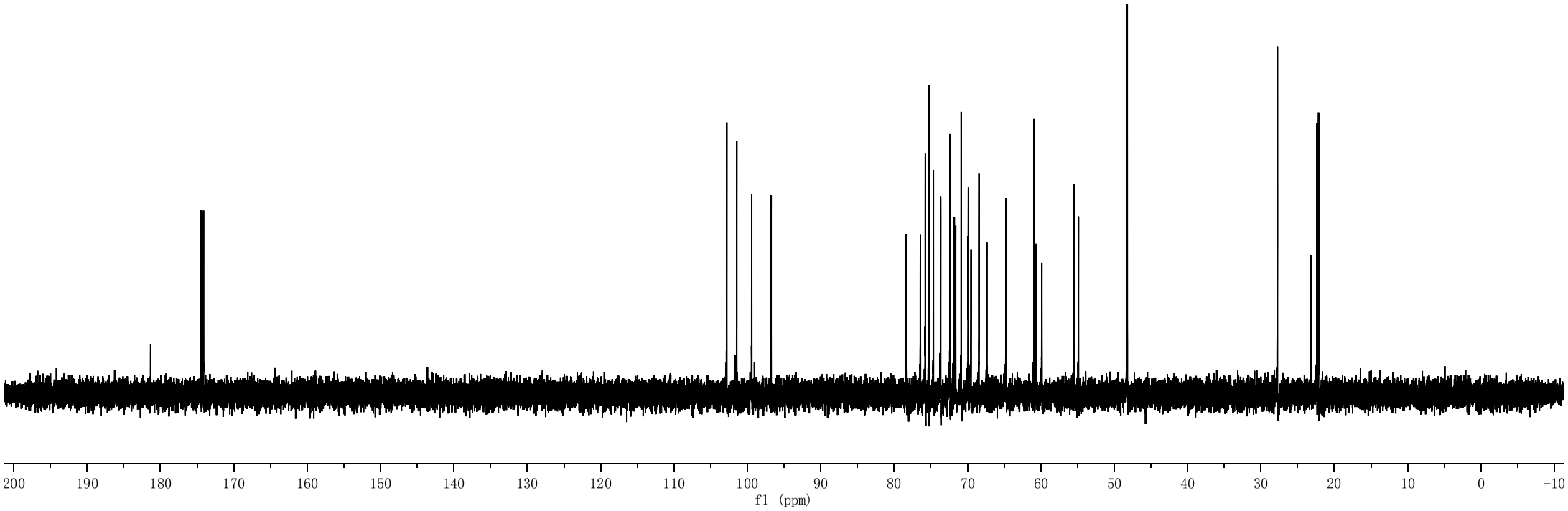
β2
β6
α
Sp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0
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f1 (ppm)

CHZ-864

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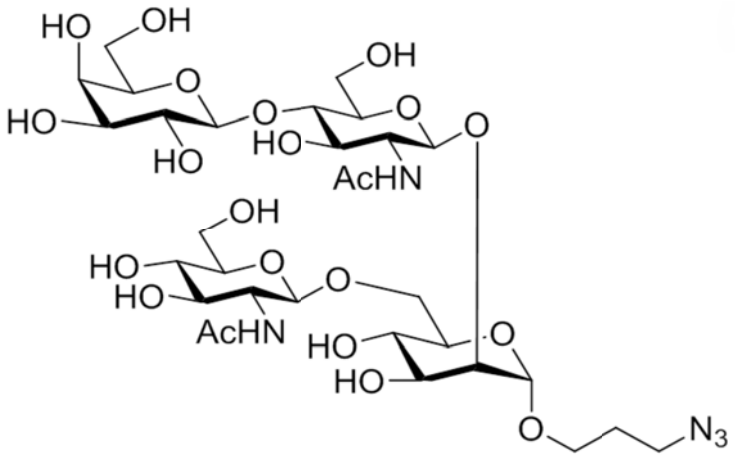
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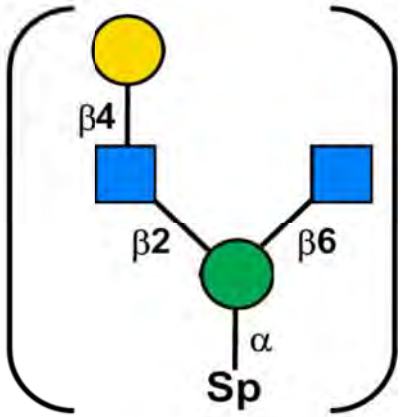
O
N3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β2
β6
α
Sp

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0.5
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f1 (ppm)

CHZ-775

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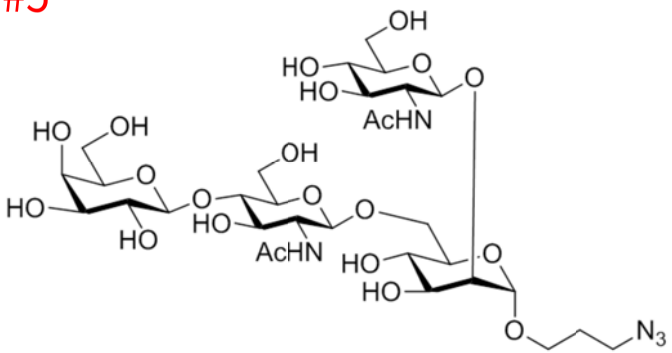
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AcHN
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HO
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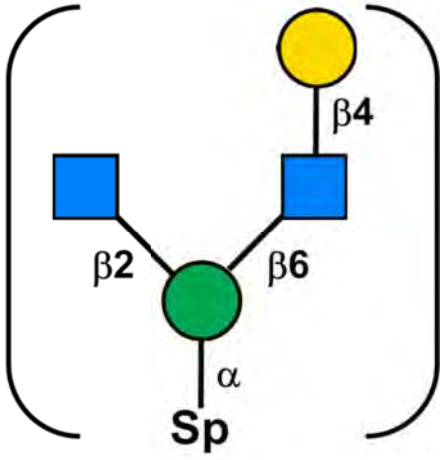
O
N3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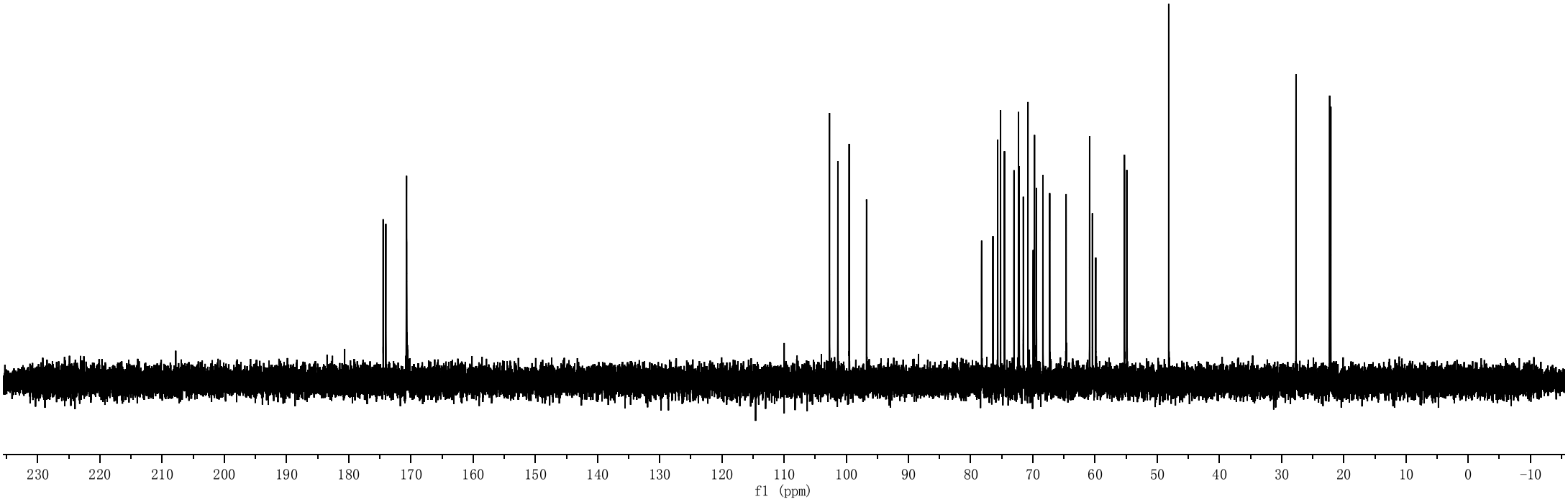
β2
β6
α
Sp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f1 (ppm)

CHZ-775

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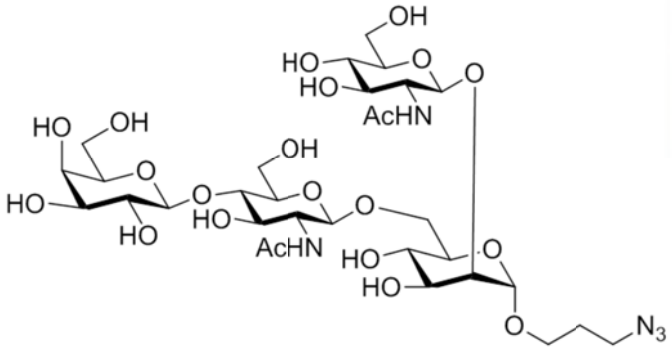
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AcHN
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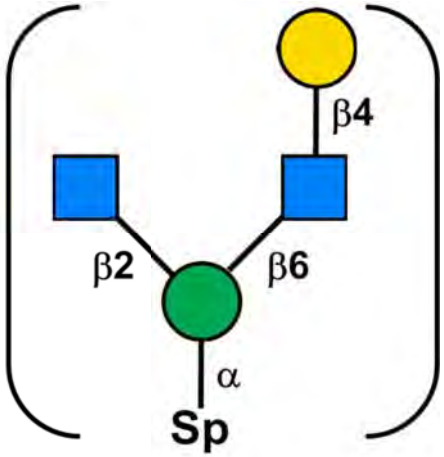
O
N3


β4
β2
β6
α
Sp

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CHZ-512

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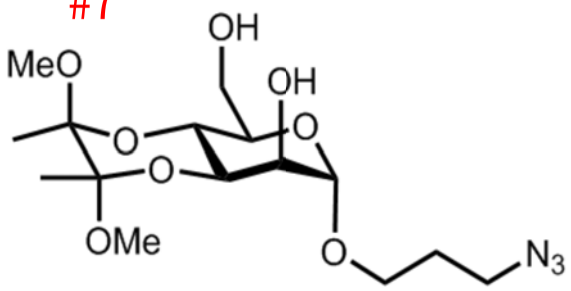
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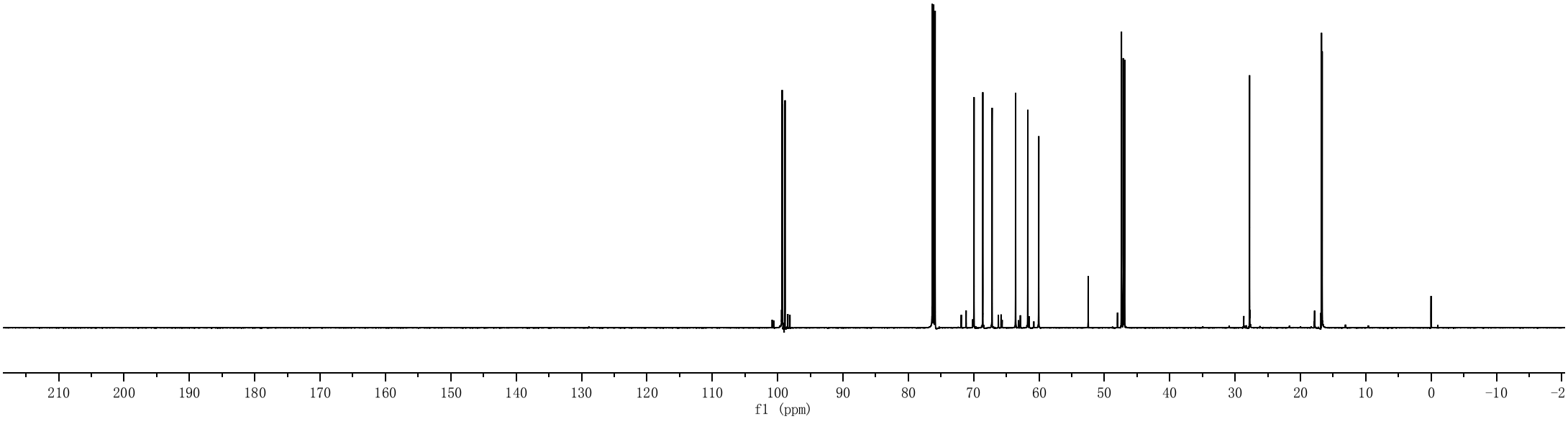
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−10
−2
f1 (ppm)

CHZ-512

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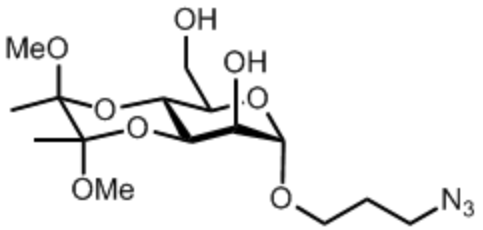
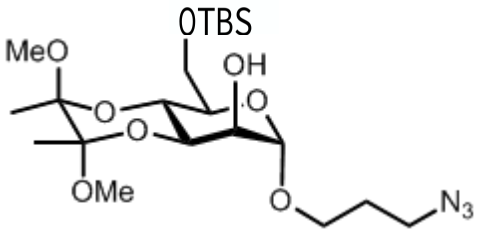


PROTON_01

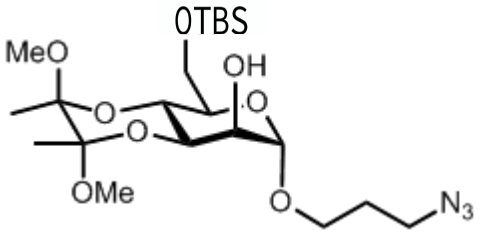
CHZ-518

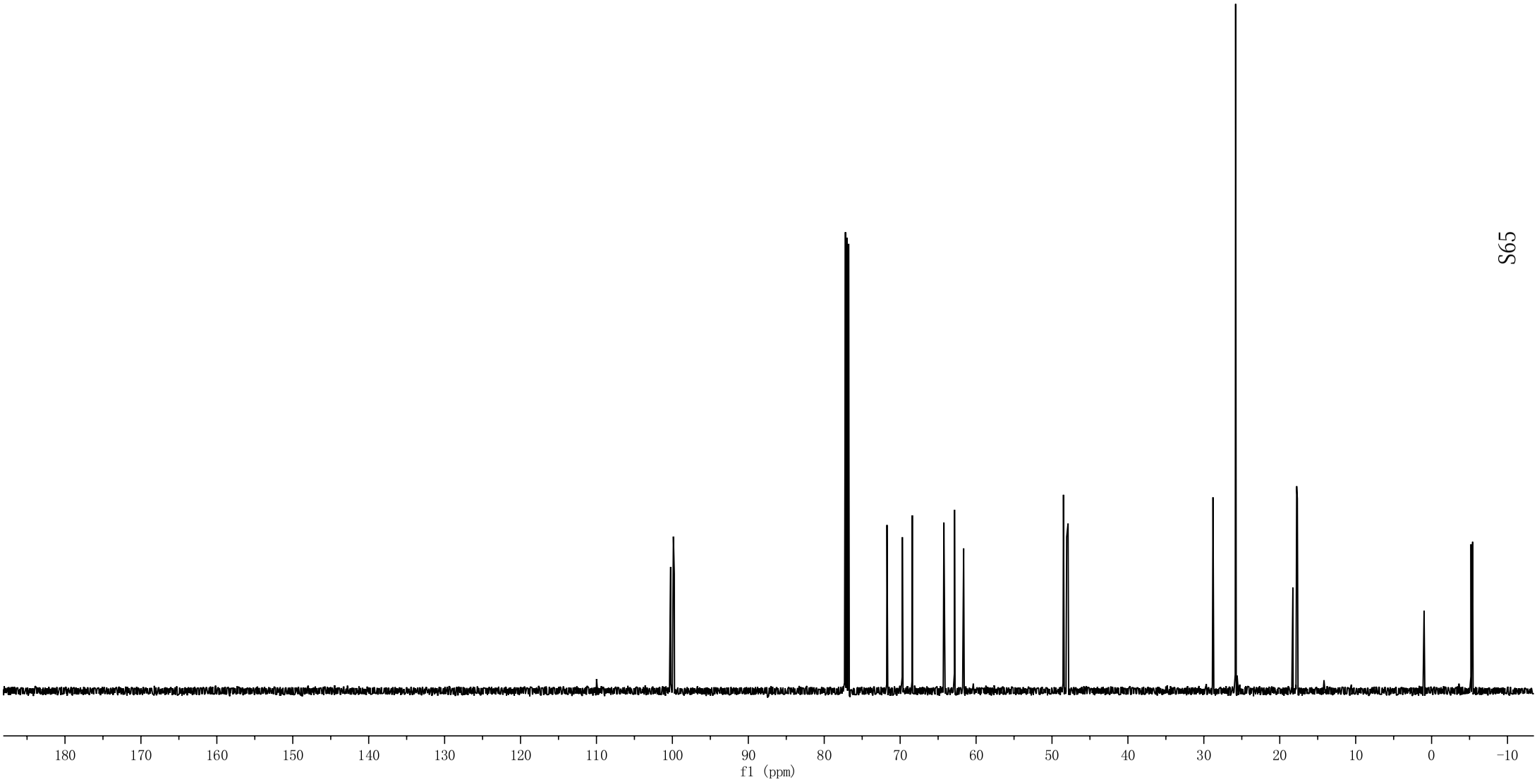
#8



CHZ-518

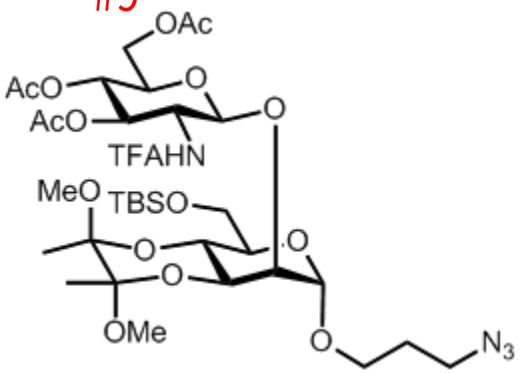
#8


OTBS
MeO
OH
O
O
O
OMe
O
N_3


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-546

#9

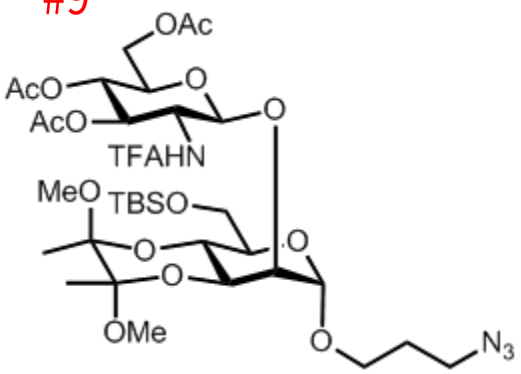


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

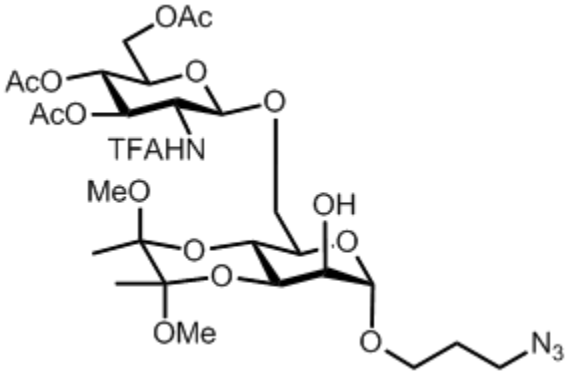
CHZ-546

#9



CHZ-570

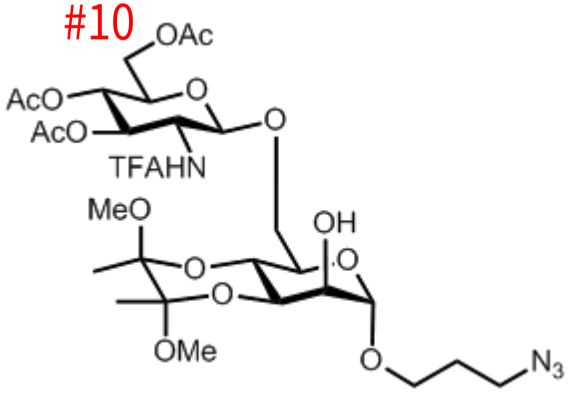
#10


OAc
AcO
AcO
O
O
TFAHN
MeO
OH
O
O
O
OMe
O
N_3

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

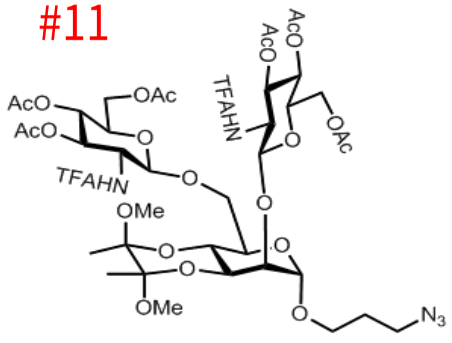
CHZ-570

#10



CHZ-571

#11



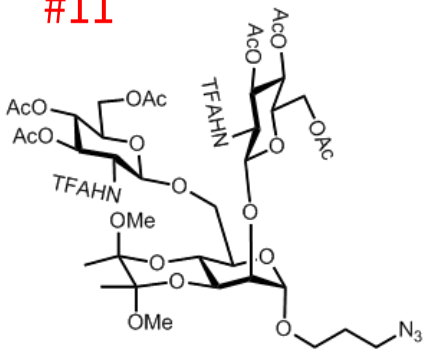
S70

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

CHZ-571

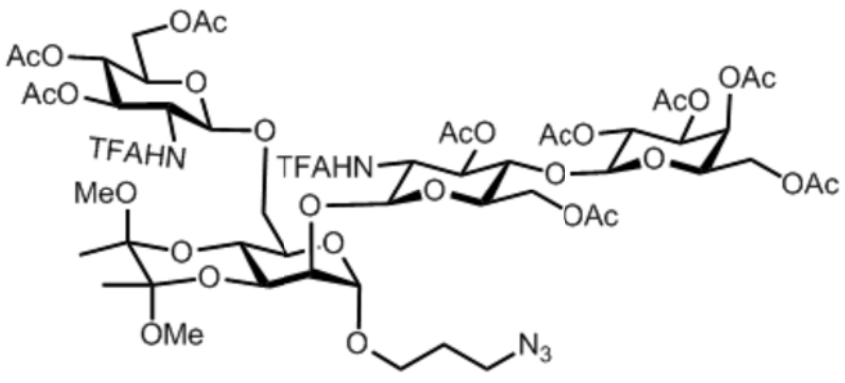
#11



f1 (ppm)

CHZ-874

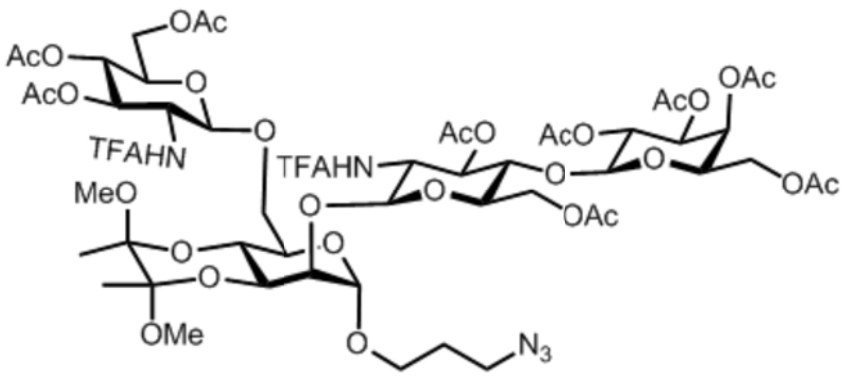
#12


OAc
AcO
AcO
O
TFAHN
O
MeO
O
O
O
OMe
TFAHN
AcO
AcO
O
O
OAc
AcO
OAc
O
OAc
O
N3

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

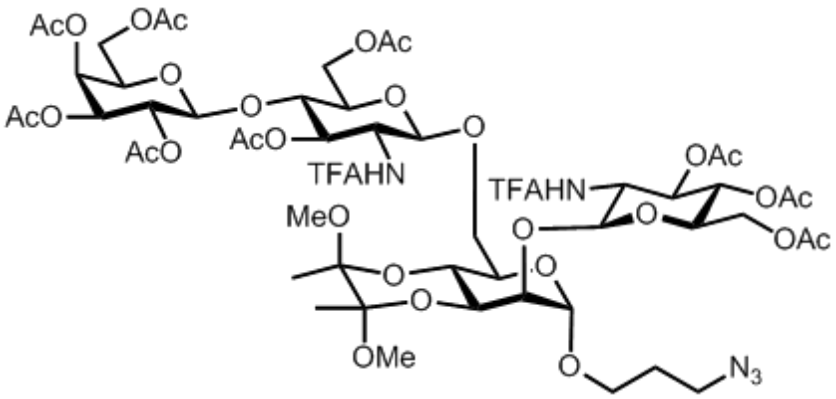
CHZ-874

#12


OAc
AcO
AcO
O
TFAHN
O
MeO
O
O
O
OMe
AcO
AcO
TFAHN
O
O
OAc
AcO
OAc
O
OAc
O
N3

10.5
10.0
9.5
9.0
8.5
8.0
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
-0.5
f1 (ppm)

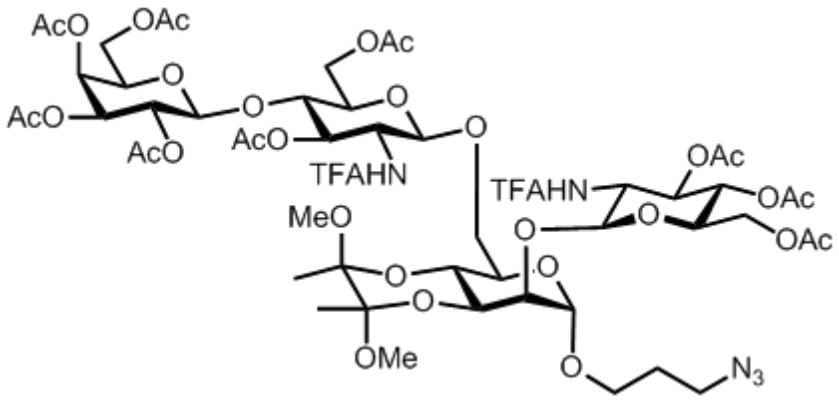
CHZ-750 #13



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

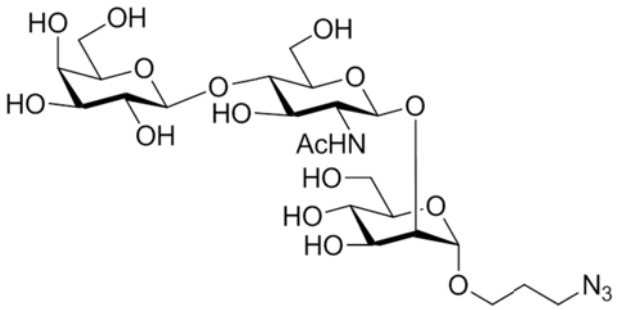
CHZ-750 #13

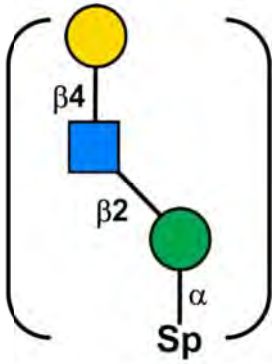

AcO
OAc
AcO
AcO
TFAHN
OAc
AcO
TFAHN
OAc
OAc
MeO
OMe
N3

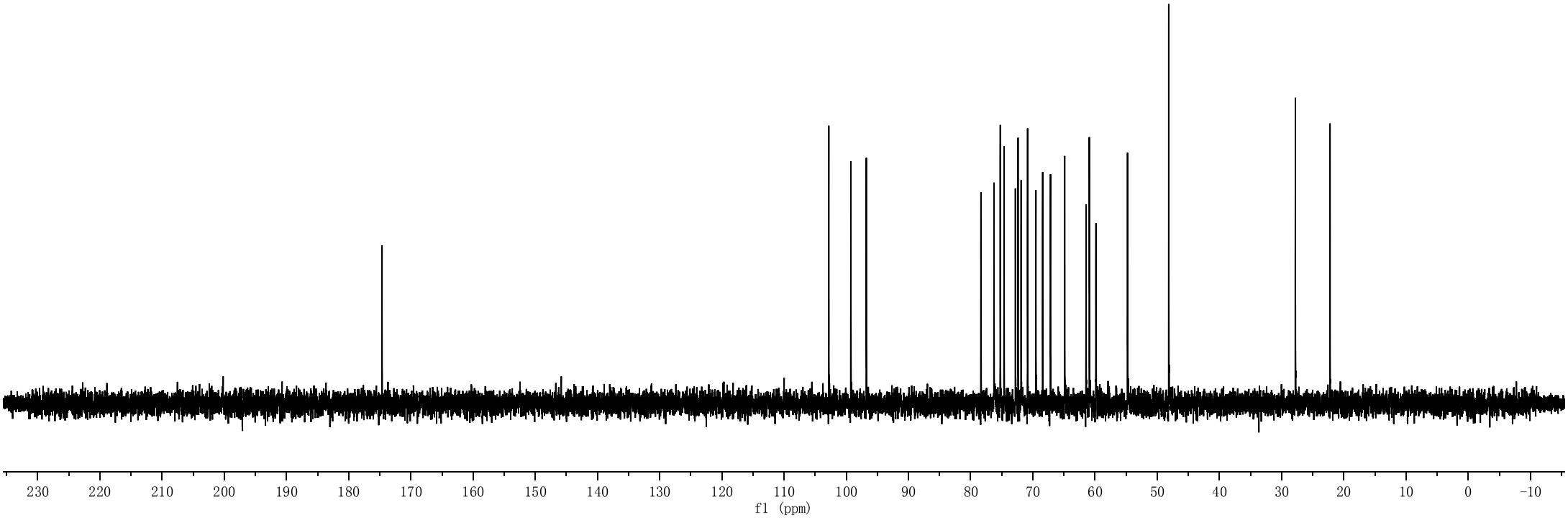
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

CHZ-696

#16

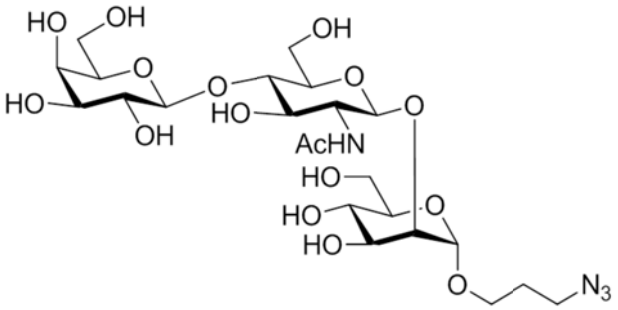

HO
OH
O
HO
OH
O
O
HO
OH
O
O
AcHN
HO
HO
HO
O
O
N3

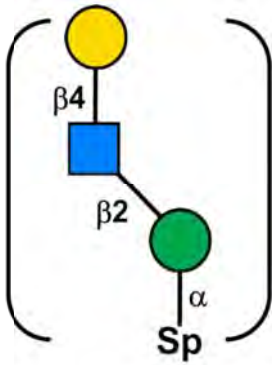

β4
β2
α
Sp


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-696

#16

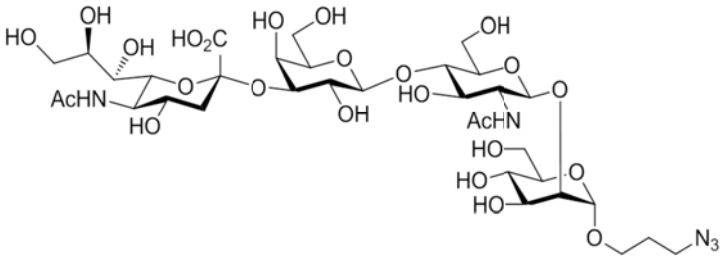

HO
OH
O
HO
OH
O
HO
OH
AcHN
O
HO
HO
HO
O
O
N3

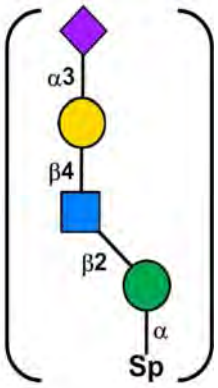

β4
β2
α
Sp

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
f1 (ppm)

CHZ-701

#17

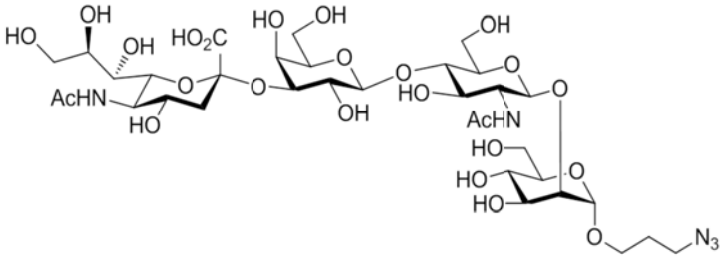

HO
OH
OH
HO2C
HO
OH
OH
AcHN
HO
O
HO
AcHN
HO
HO
HO
N3

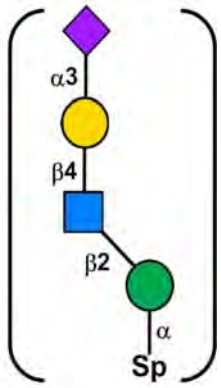

α3
β4
β2
α
Sp

8.0
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
f1 (ppm)

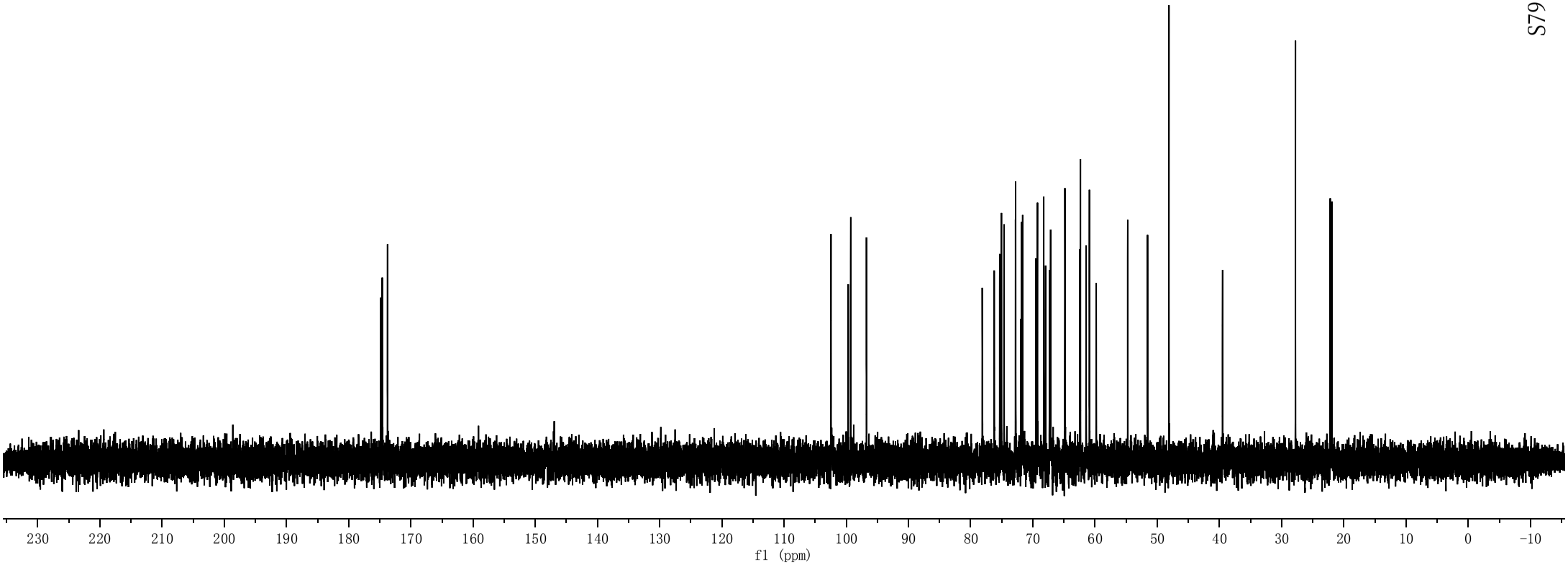
CHZ-701

#17



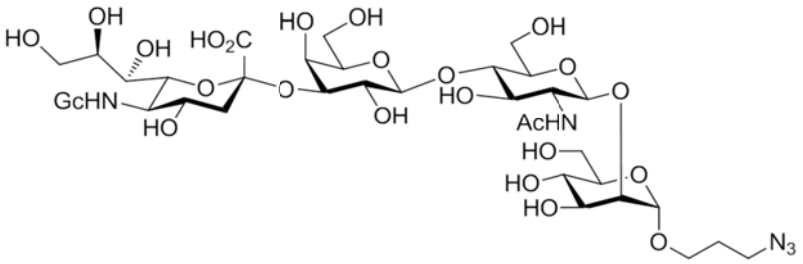


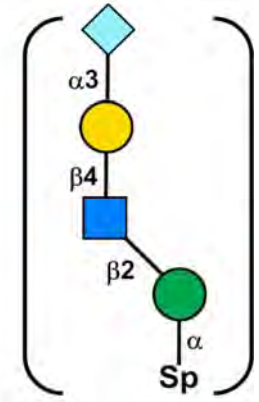
S79



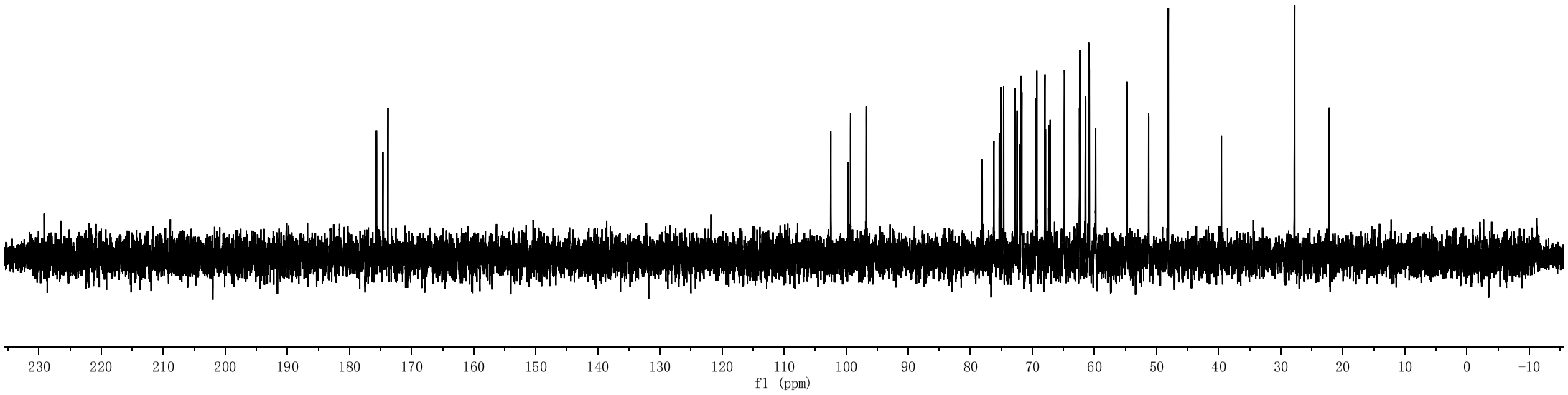
CHZ-705

#18



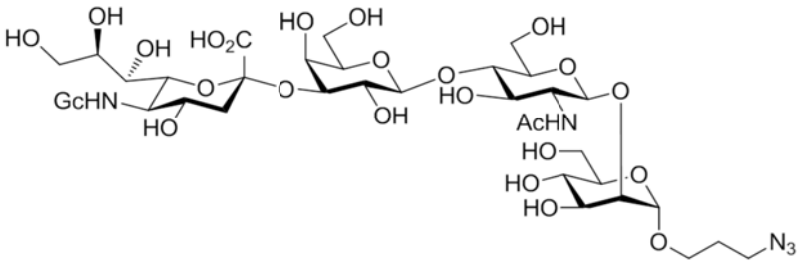


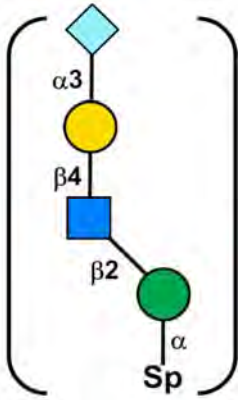
S80



CHZ-705

#18

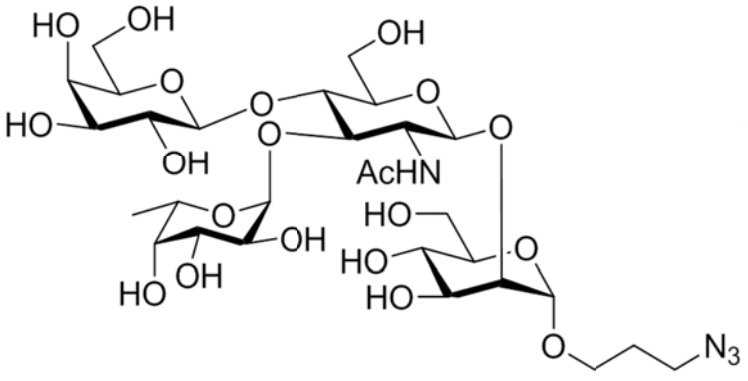

HO
OH
OH
HO2C
GcHN
HO
O
HO
OH
O
HO
OH
O
HO
AcHN
O
HO
HO
HO
O
O
N3

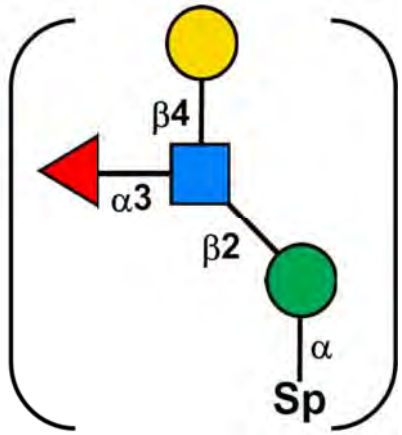

α3
β4
β2
α
Sp

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
f1 (ppm)

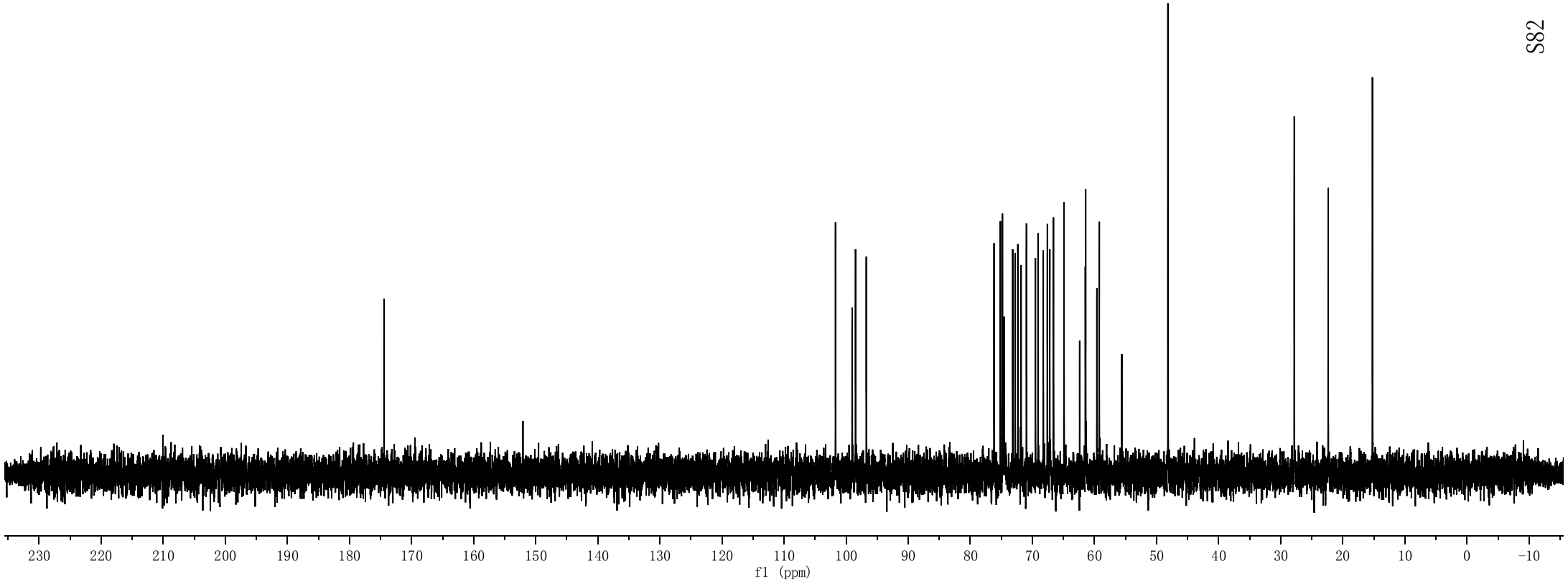
CHZ-706

#19



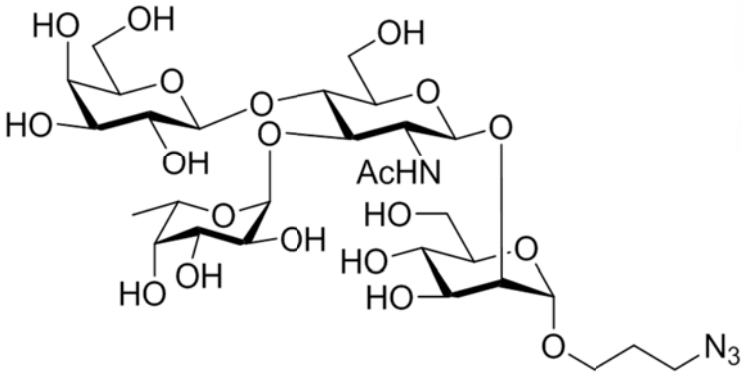


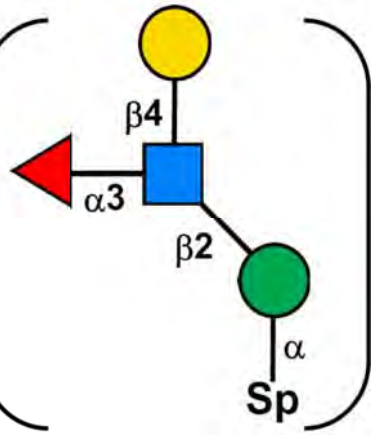
S82



CHZ-706

#19





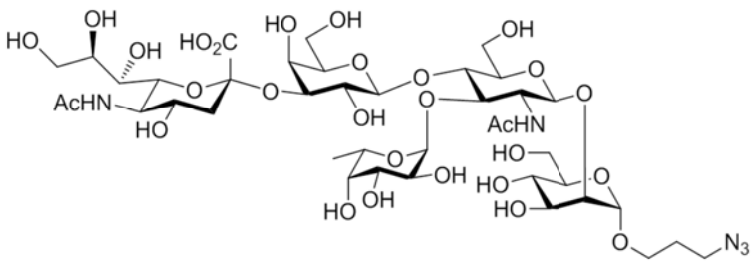
S83

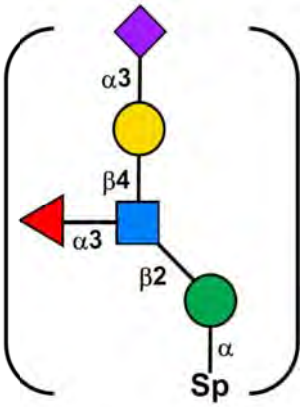
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

CHZ-716

#20

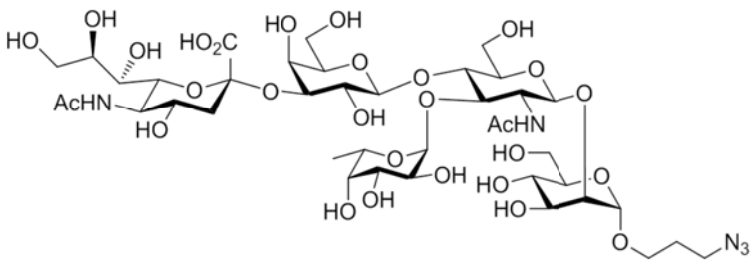


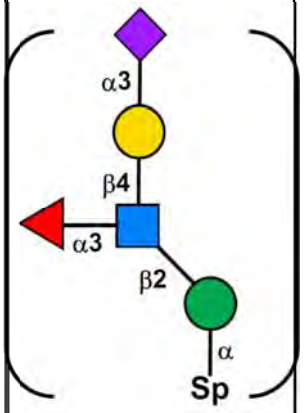


S84

CHZ-716

#20

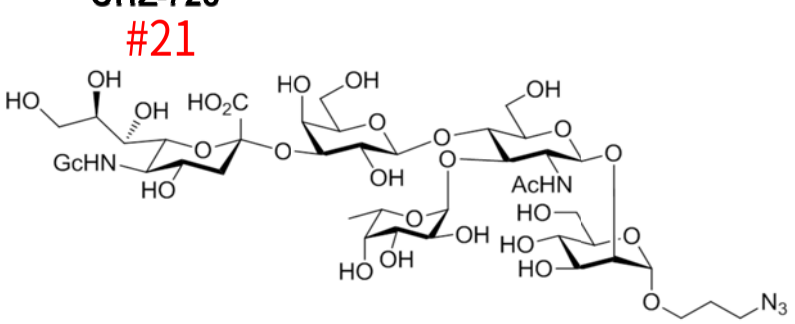


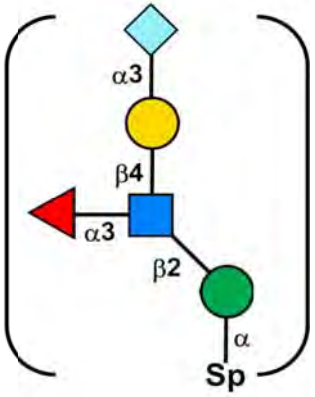


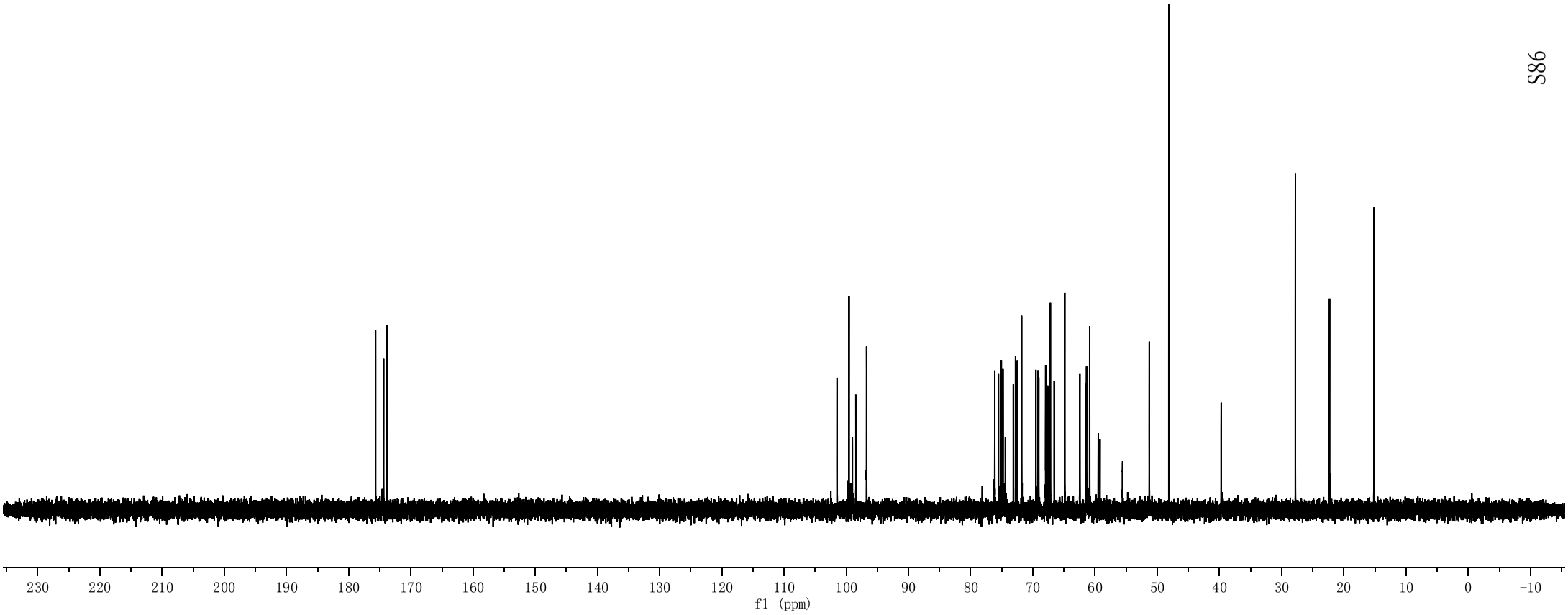
S85

CHZ-725

#21

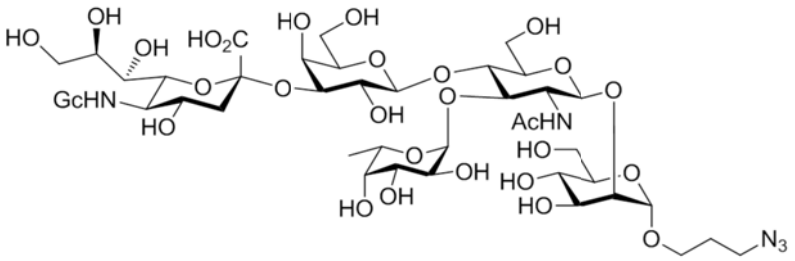

HO
OH
OH
HO2C
GcHN
HO
O
HO
OH
OH
O
O
O
AcHN
OH
HO
HO
OH
HO
OH
HO
HO
O
O
N3

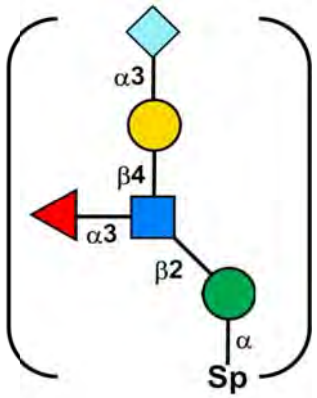

α3
β4
α3
β2
α
Sp


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-725

#21

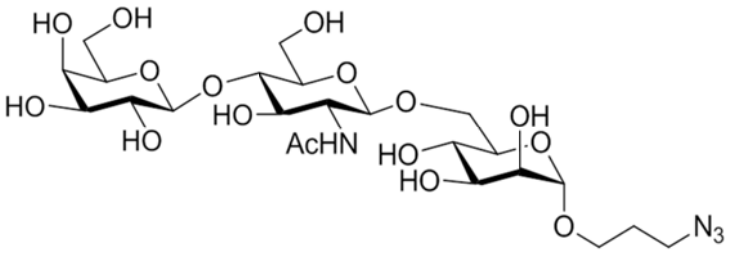

HO
OH
OH
HO2C
GcHN
HO
O
HO
OH
OH
O
O
AcHN
HO
HO
HO
OH
HO
OH
HO
HO
O
O
N3

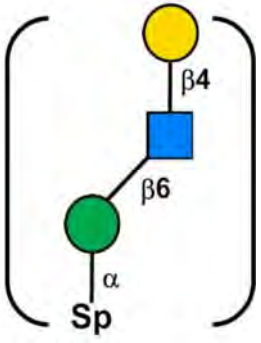

α3
β4
α3
β2
α
Sp

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
f1 (ppm)

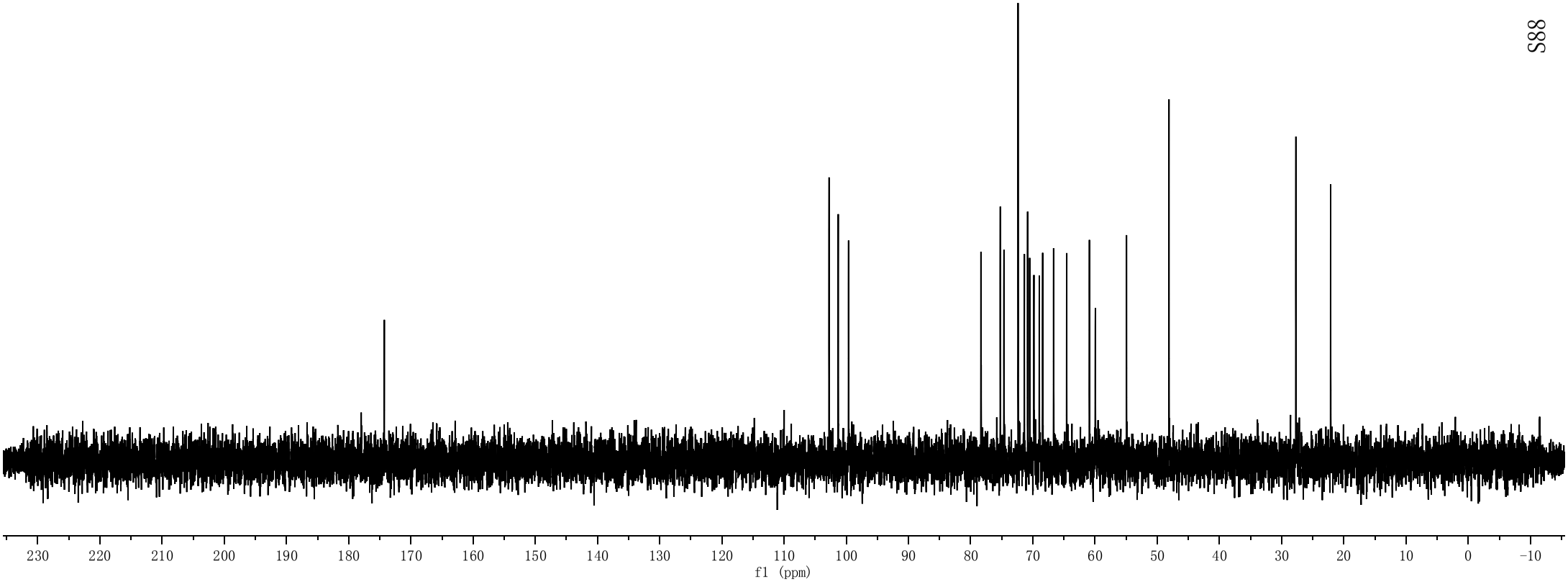
CHZ-660

#22



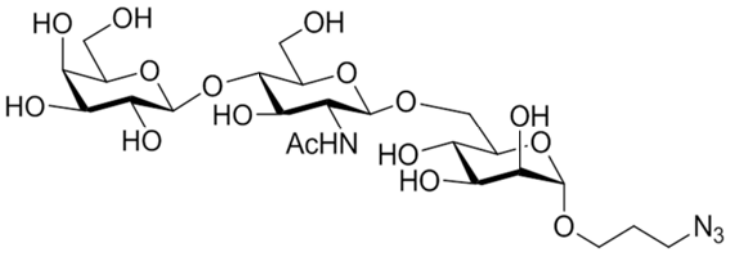


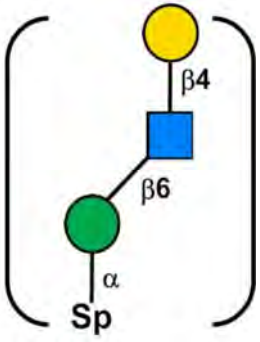
S88



CHZ-660

#22

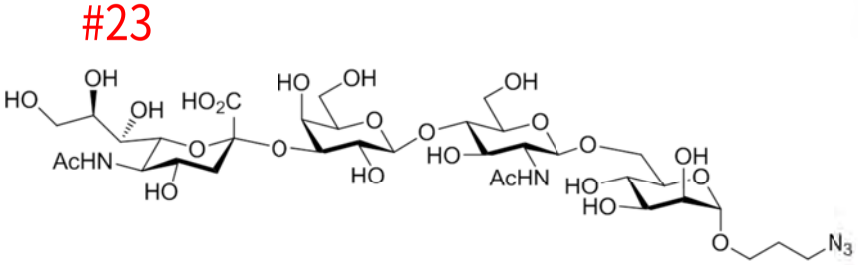

HO
OH
O
HO
HO
O
HO
OH
O
AcHN
O
HO
HO
OH
O
O
N_3

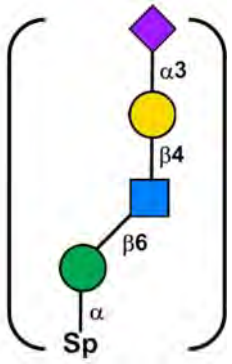

β4
β6
α
Sp

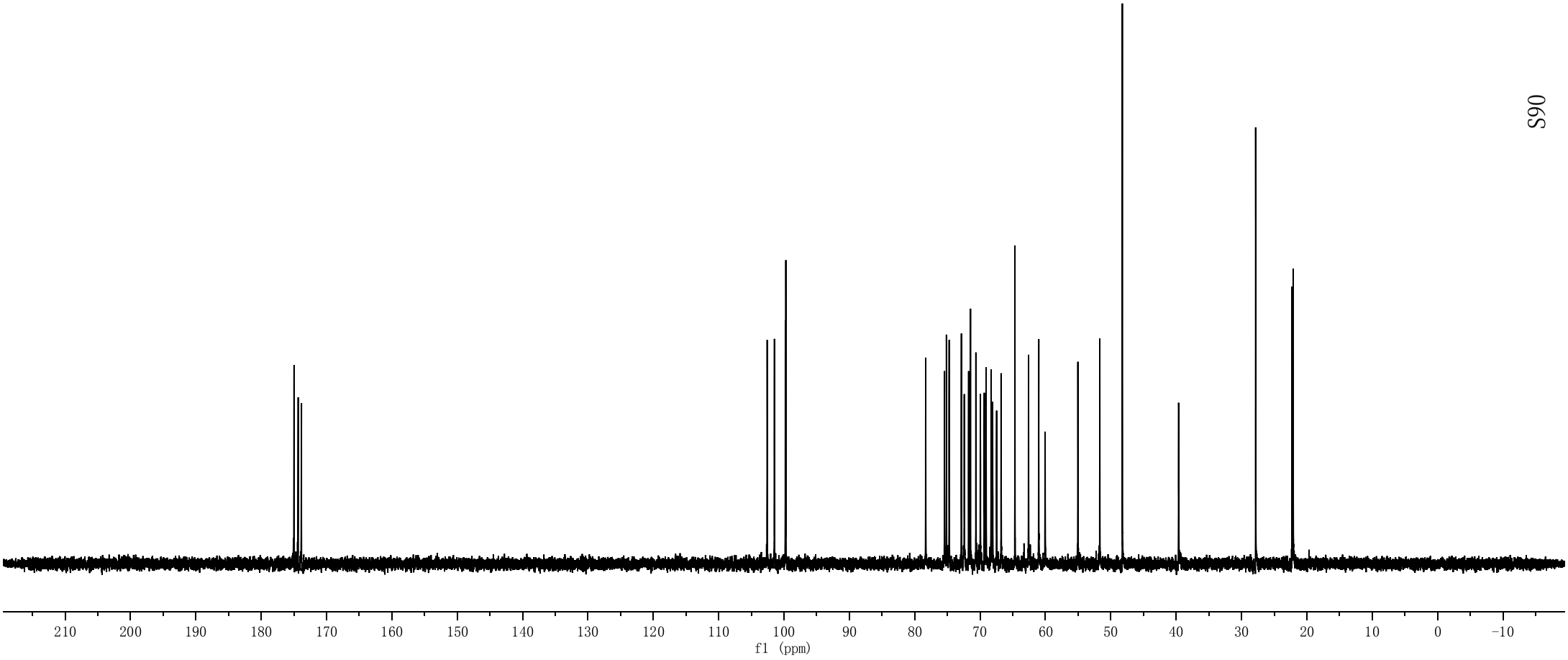
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1511

#23

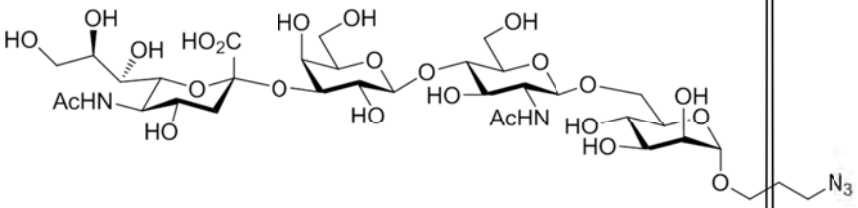


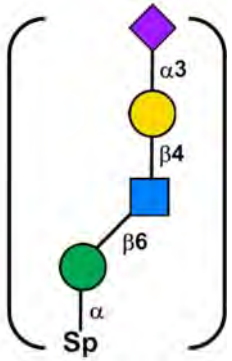

α3
β4
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-1511

#23

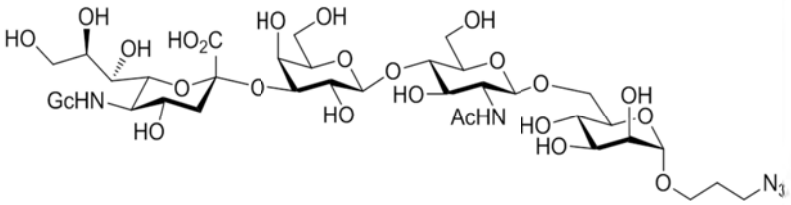

HO
OH
OH
HO2C
AcHN
HO
O
HO
OH
HO
O
HO
OH
AcHN
O
HO
HO
OH
O
O
N3

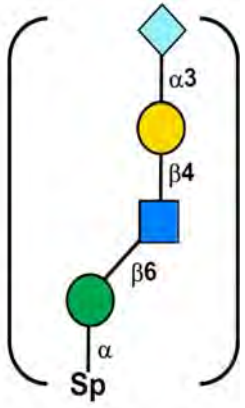

α3
β4
β6
α
Sp

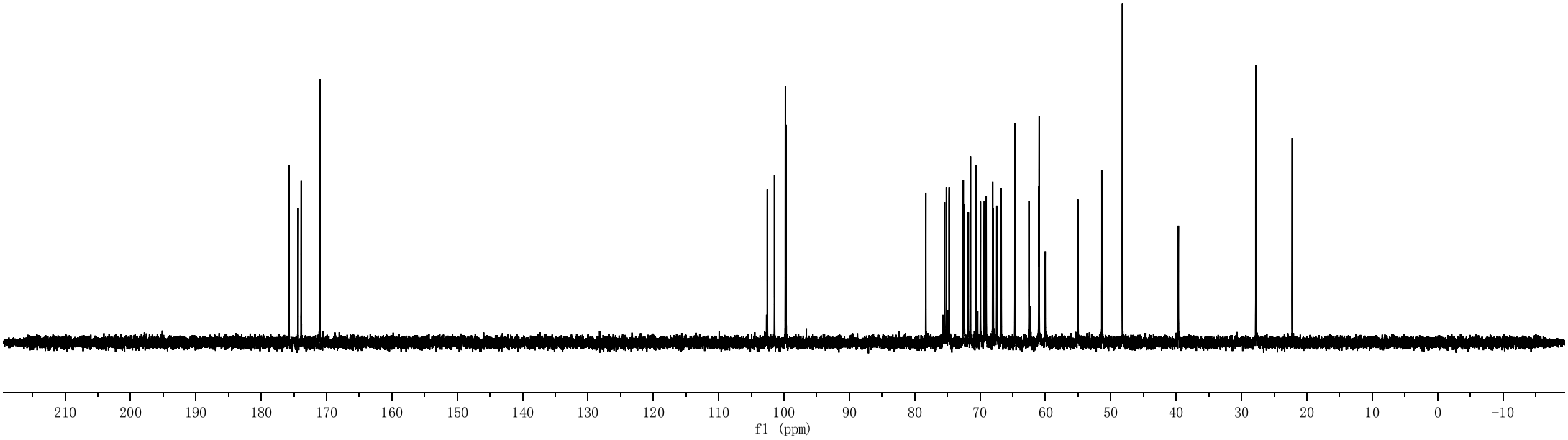
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1398

#24

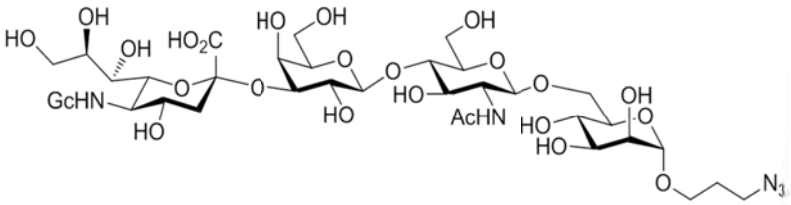

OH
HO
OH
HO2C
HO
OH
OH
O
O
O
O
O
GcHN
HO
HO
HO
AcHN
HO
HO
OH
O
O
N3

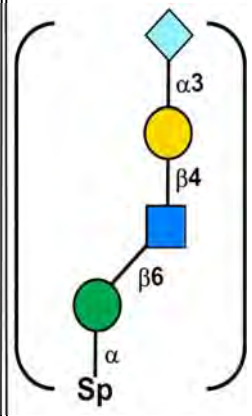

α3
β4
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1398

#24

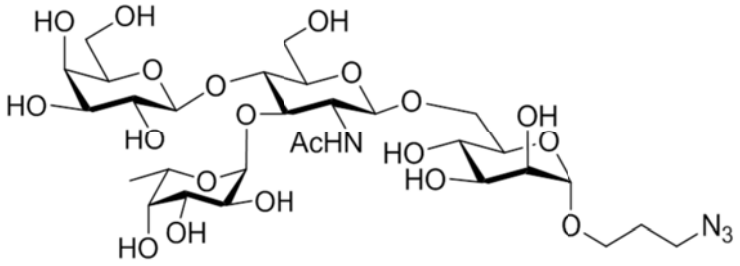

HO
OH
OH
HO2C
GcHN
HO
O
HO
OH
HO
O
HO
OH
O
HO
AcHN
O
HO
HO
OH
O
O
N3

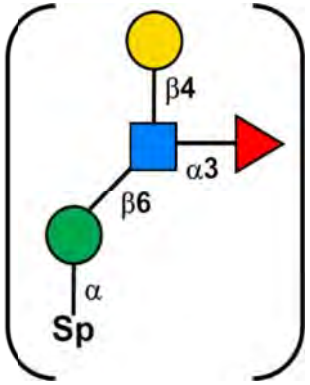

α3
β4
β6
α
Sp

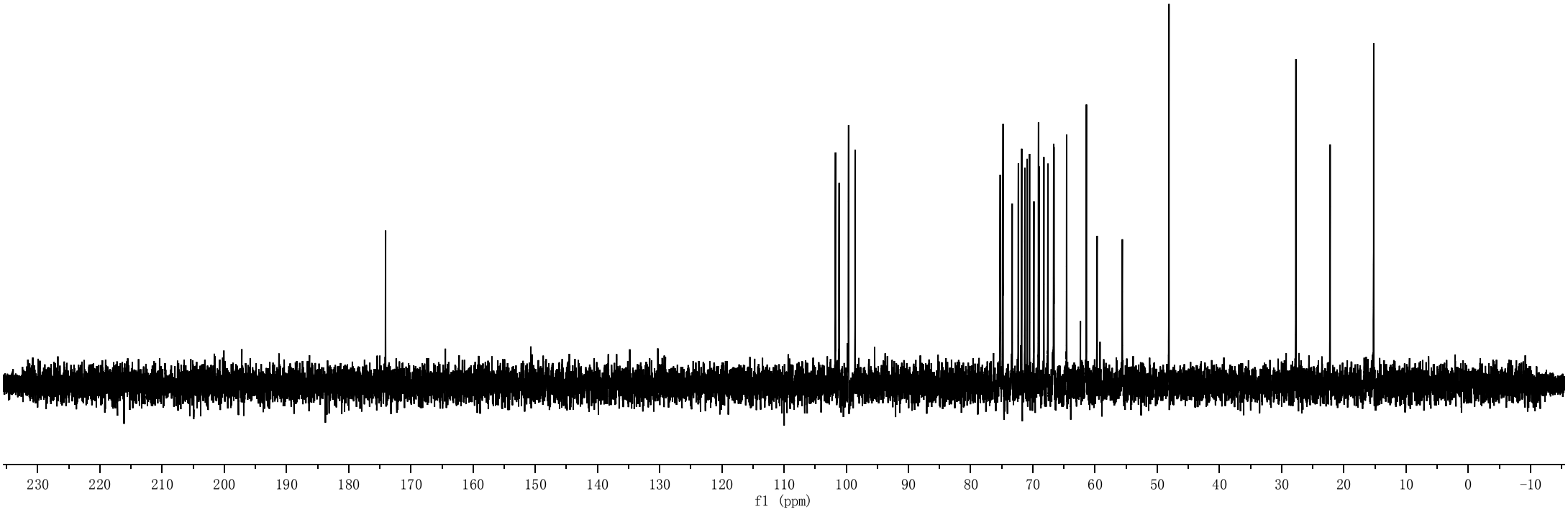
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-663

#25

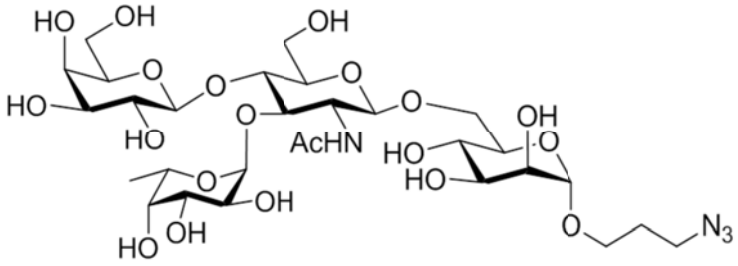

HO
OH
O
HO
HO
O
OH
O
AcHN
O
HO
HO
OH
O
O
N3
O
OH
HO
OH

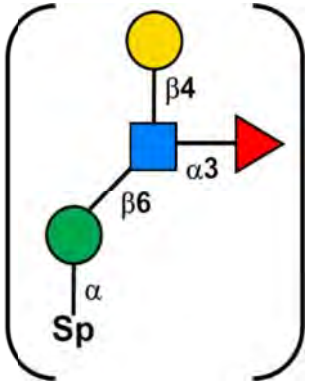

β4
α3
β6
α
Sp


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-663

#25

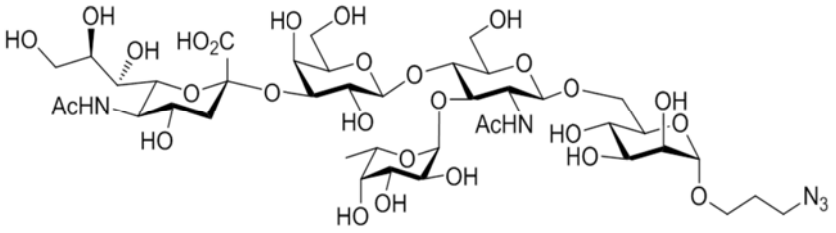

HO
OH
O
HO
HO
O
O
OH
AcHN
O
HO
HO
OH
O
O
OH
HO
OH
O
N3

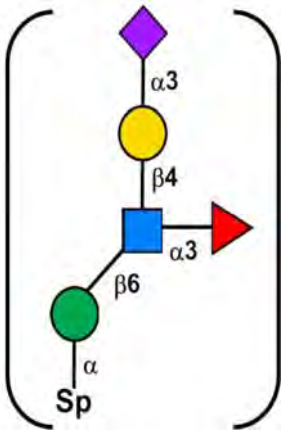

β4
α3
β6
α
Sp

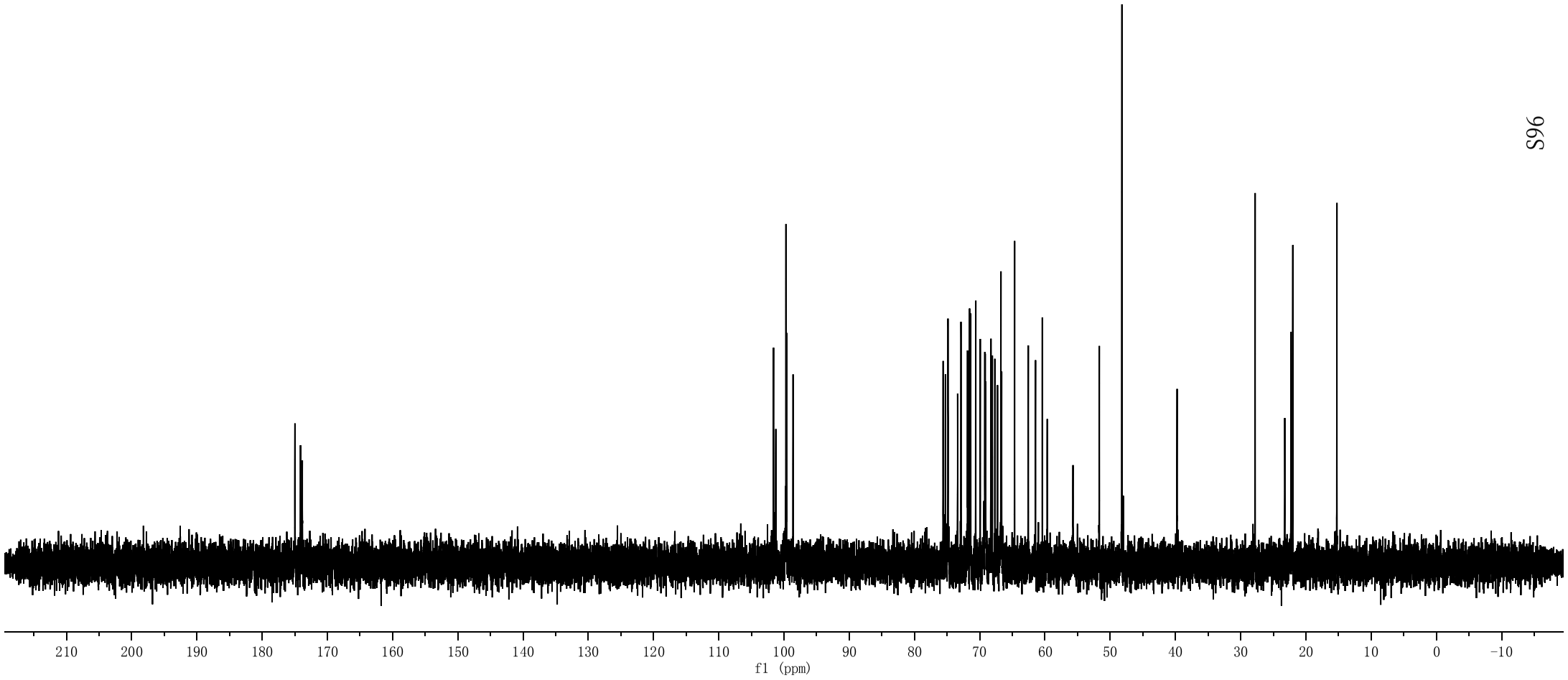
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1459

#26

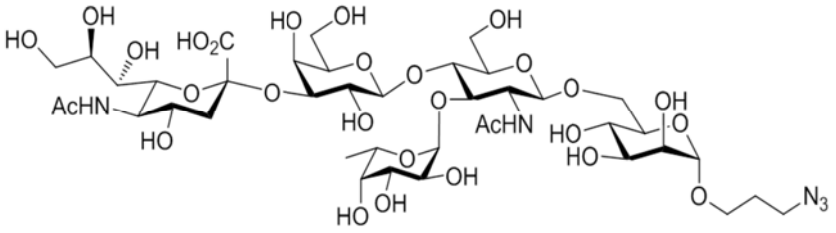

HO
OH
OH
HO2C
AcHN
HO
O
HO
OH
HO
OH
O
AcHN
HO
HO
OH
O
HO
OH
O
N3

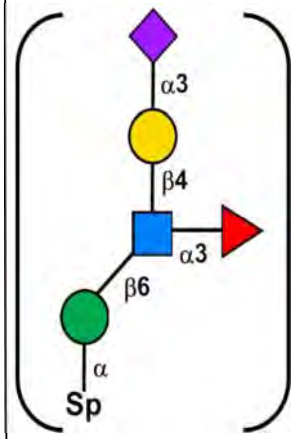

α3
β4
α3
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-1459

#26

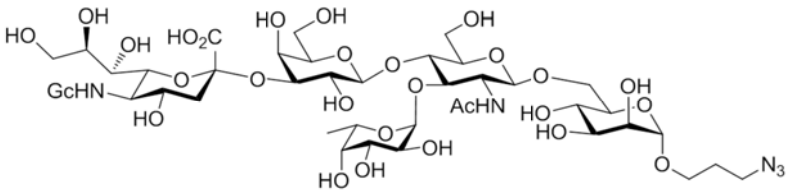

HO
OH
OH
HO2C
AcHN
HO
O
HO
OH
HO
OH
O
AcHN
HO
HO
OH
O
HO
OH
O
N3

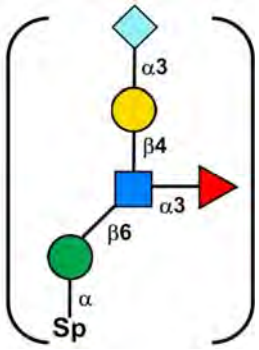

α3
β4
α3
β6
α
Sp

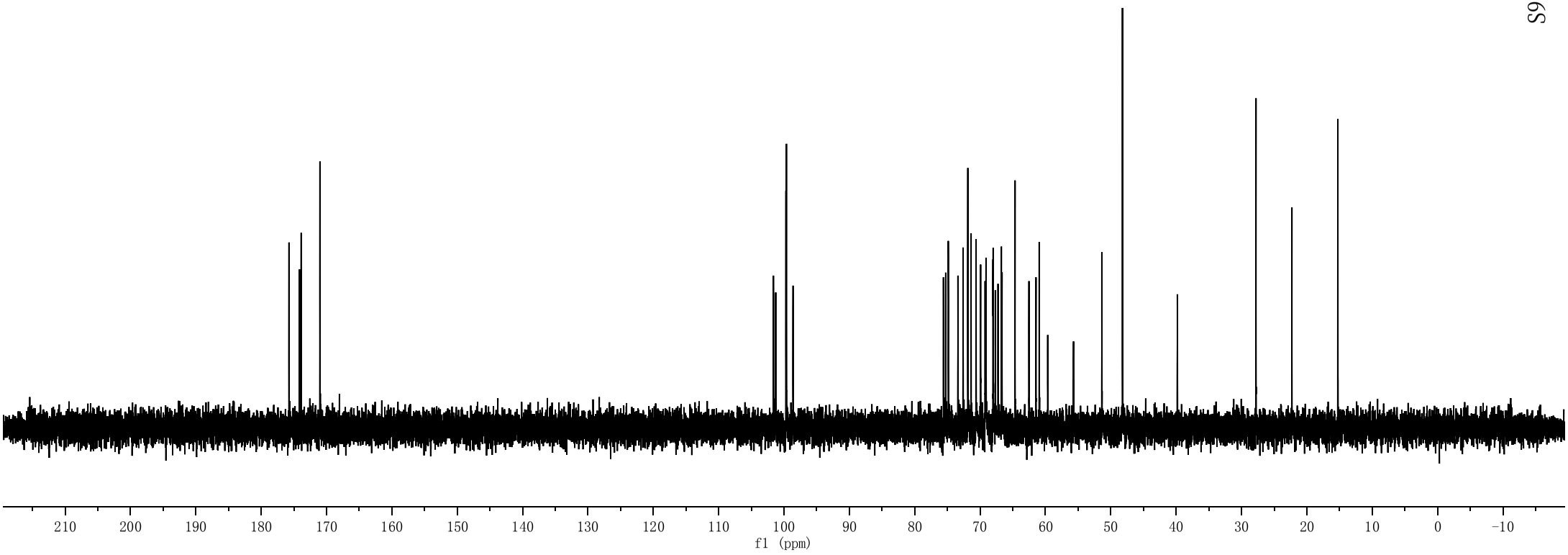
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1395

#27

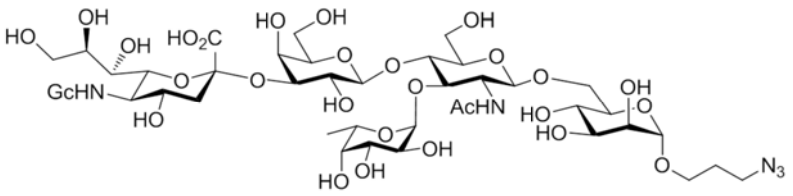

OH
HO
OH
HO2C
GcHN
HO
HO
OH
HO
OH
AcHN
HO
HO
OH
HO
OH
O
N3

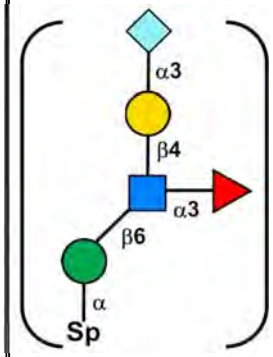

α3
β4
α3
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1395

#27





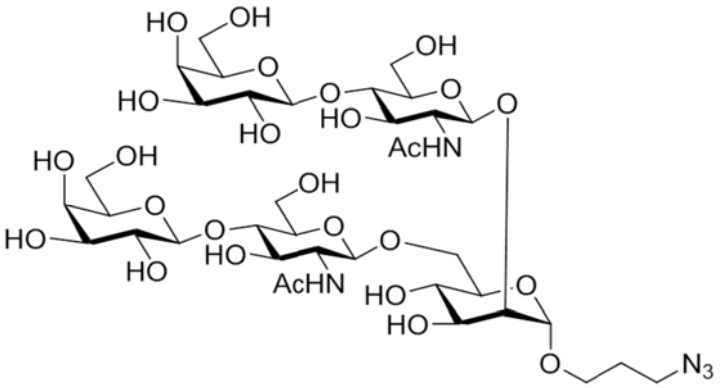
S99

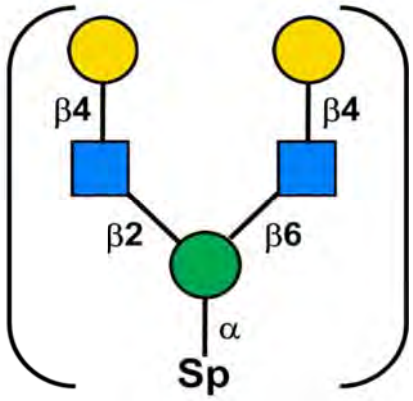
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

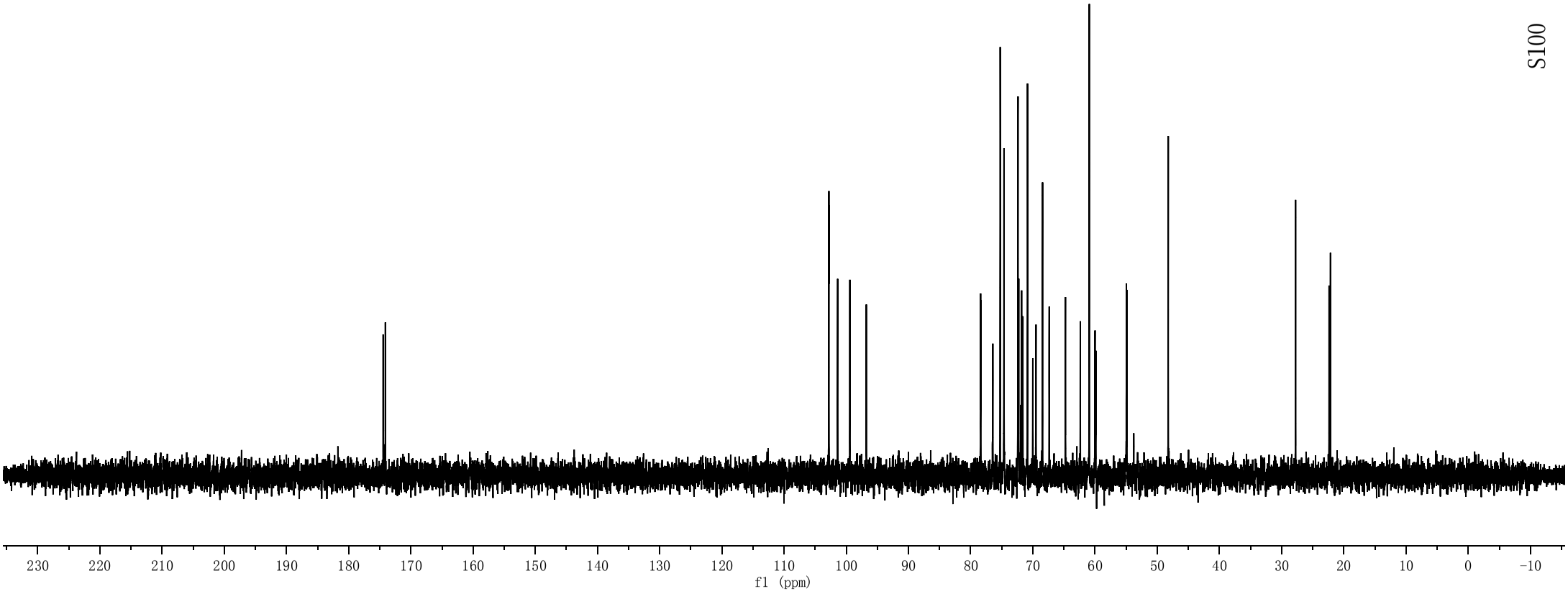
CHZ-695

#28



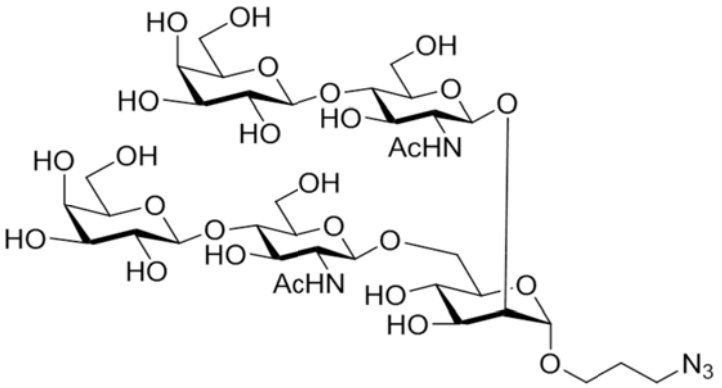


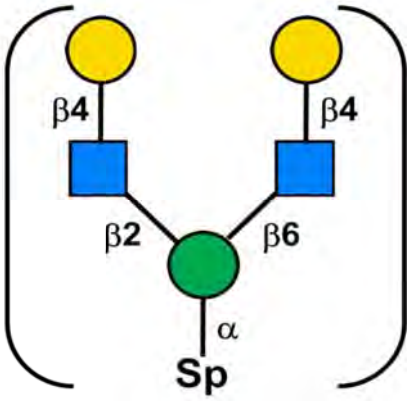
S100



CHZ-695

#28

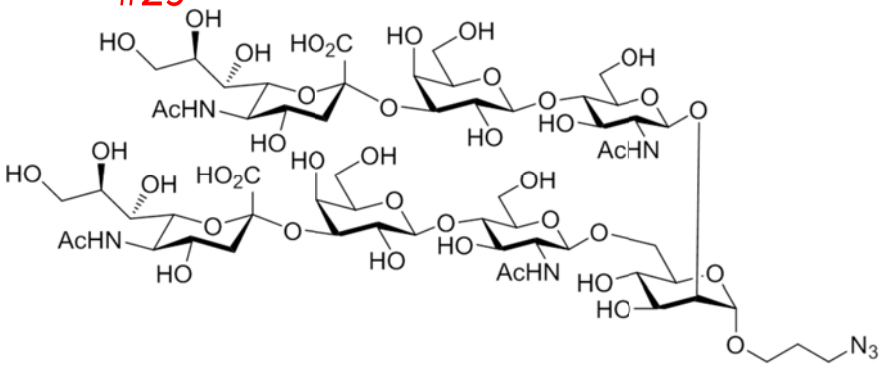

HO
OH
O
HO
HO
HO
AcHN
N3

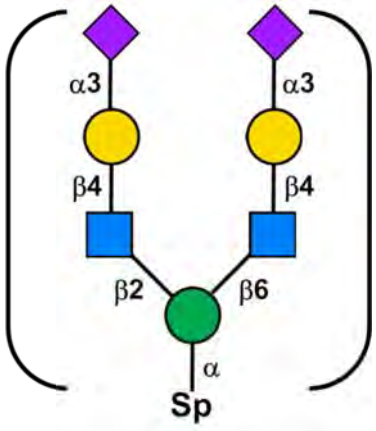

β4
β4
β2
β6
α
Sp

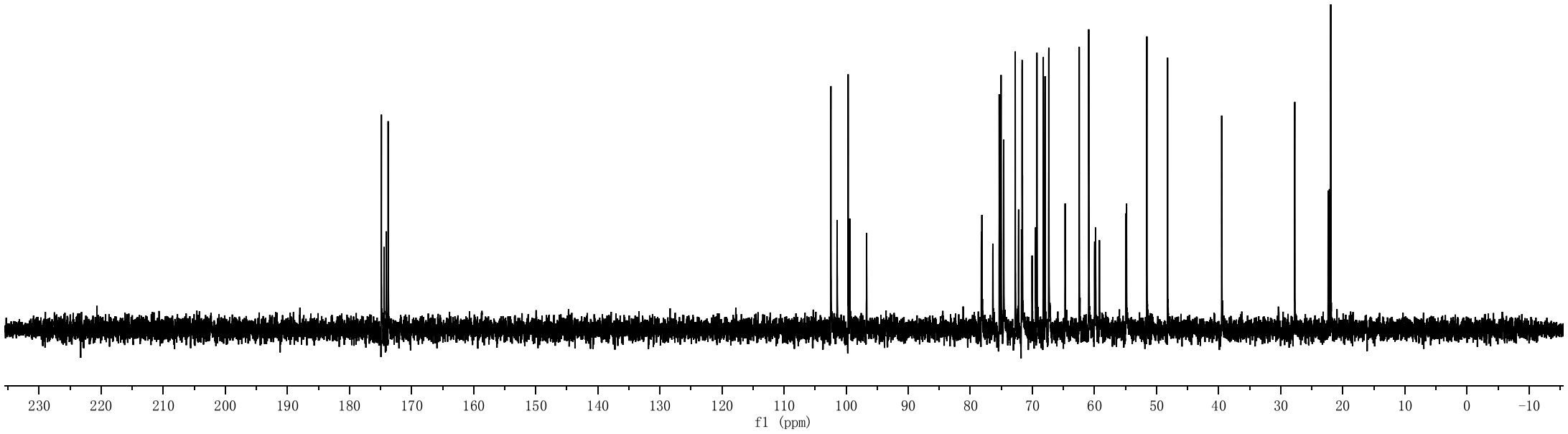
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-715

#29

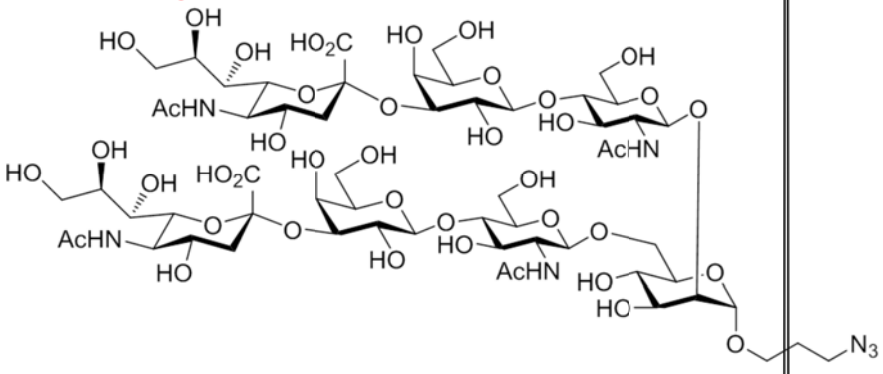


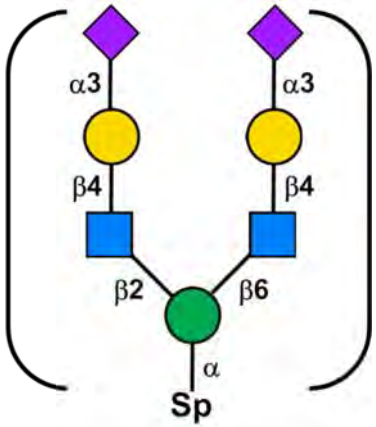

α3
α3
β4
β4
β2
β6
α
Sp


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

CHZ-715

#29



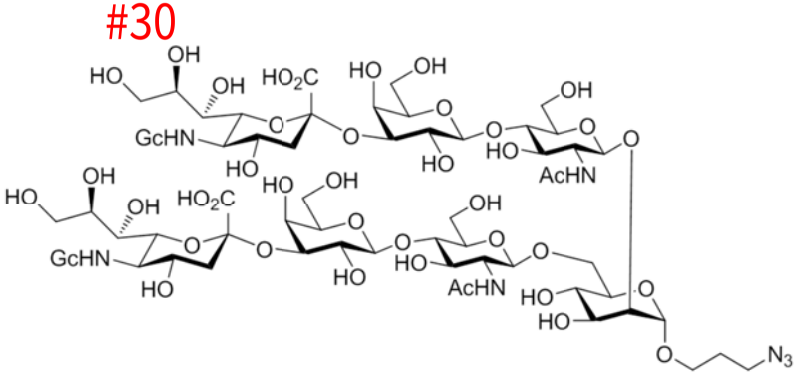


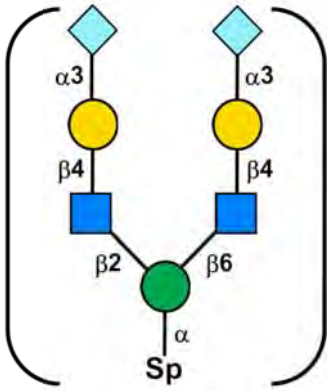
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

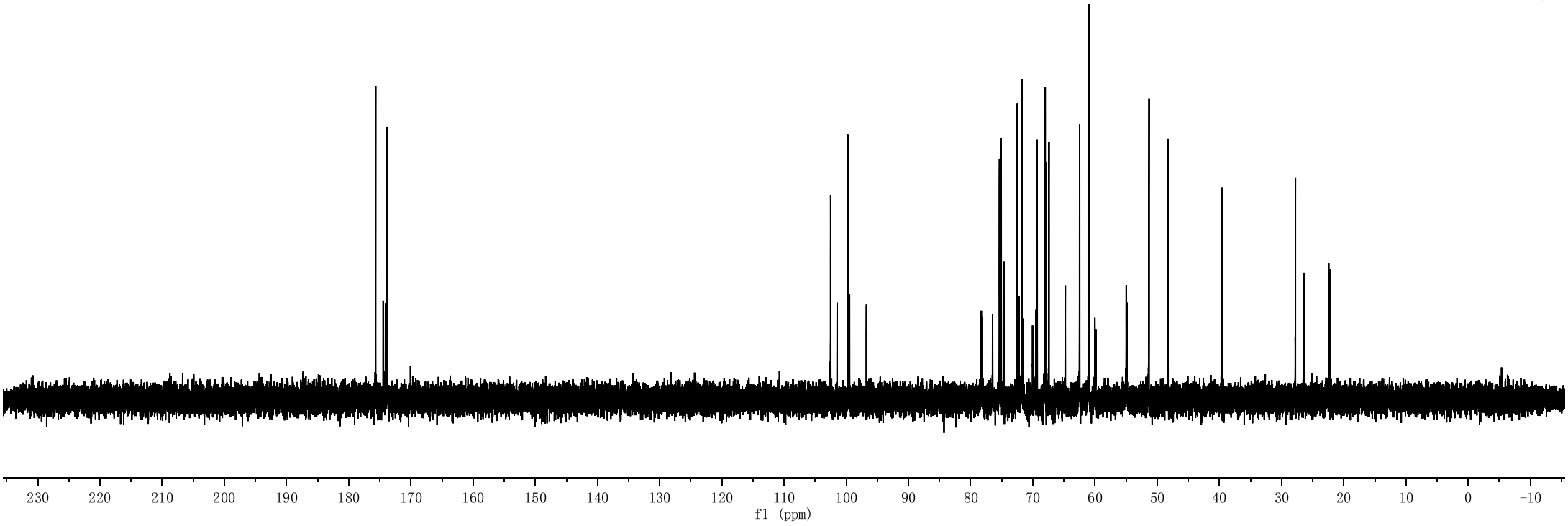
CHZ-1363

#30



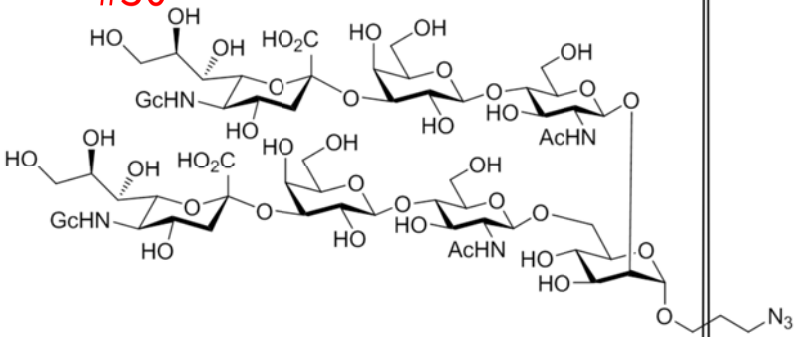


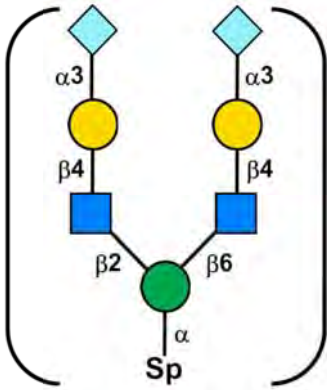
S104



CHZ-1363

#30

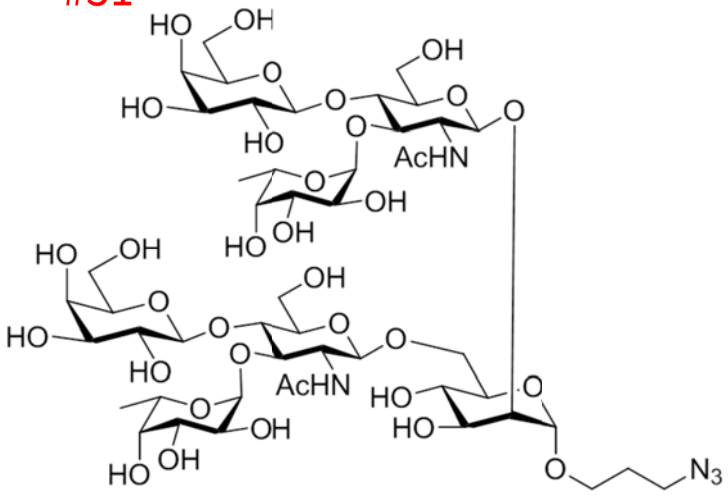

OH
HO
OH
HO2C
HO
OH
GcHN
HO
HO
O
OH
HO
AcHN
N3

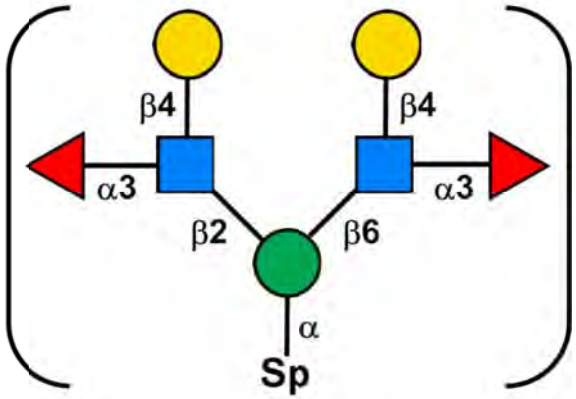

α3
α3
β4
β4
β2
β6
α
Sp

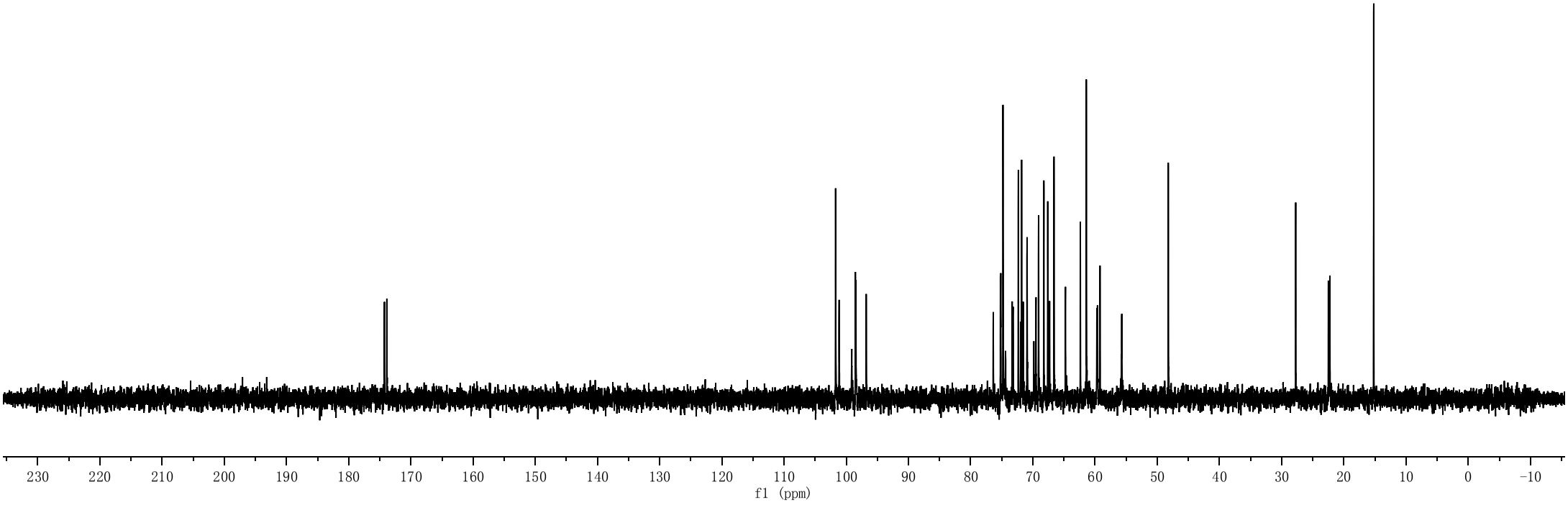
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-707

#31

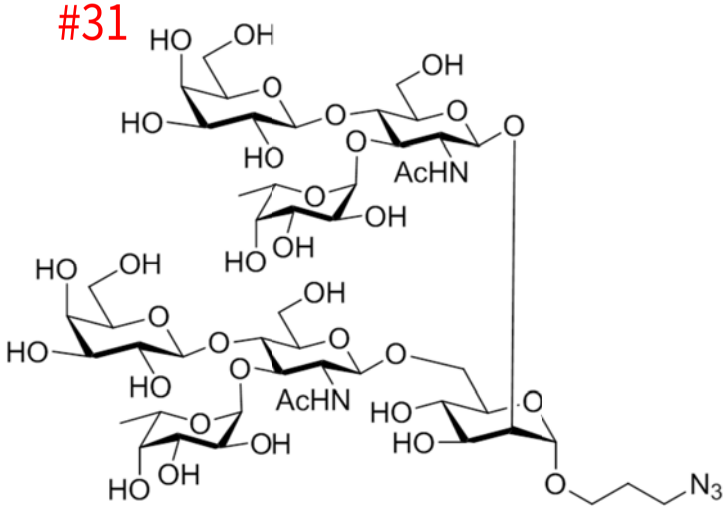

HO
OH
O
HO
HO
O
O
OH
AcHN
O
HO
OH
HO
OH
HO
OH
O
HO
O
O
OH
AcHN
O
HO
HO
O
O
HO
OH
HO
OH
O
N3

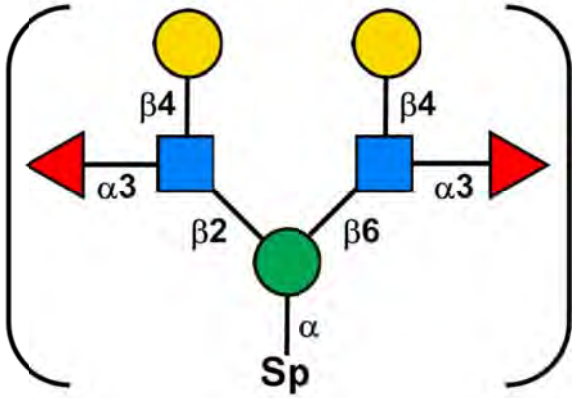

β4
β4
α3
α3
β2
β6
α
Sp


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-707

#31

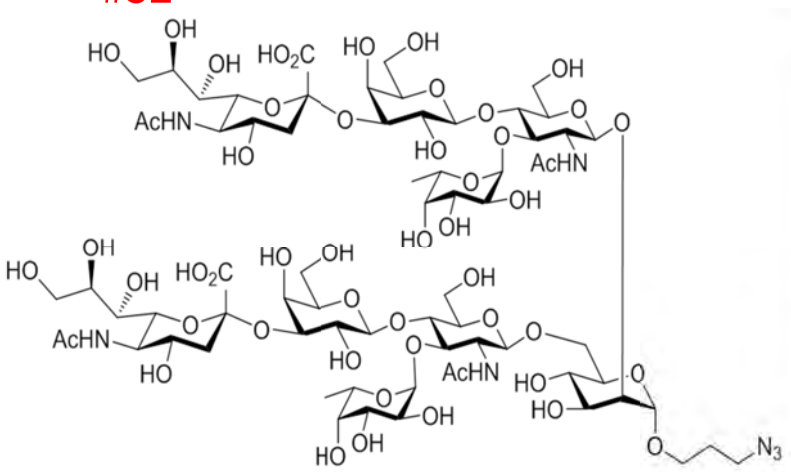


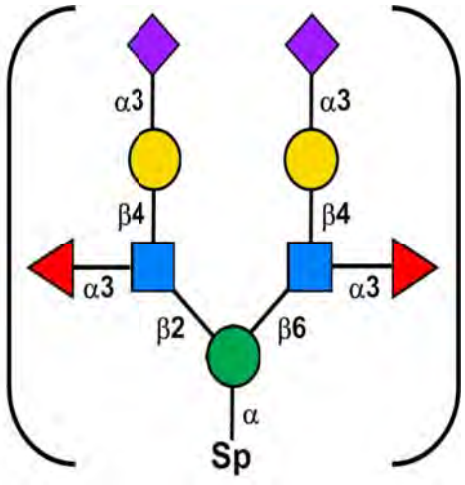


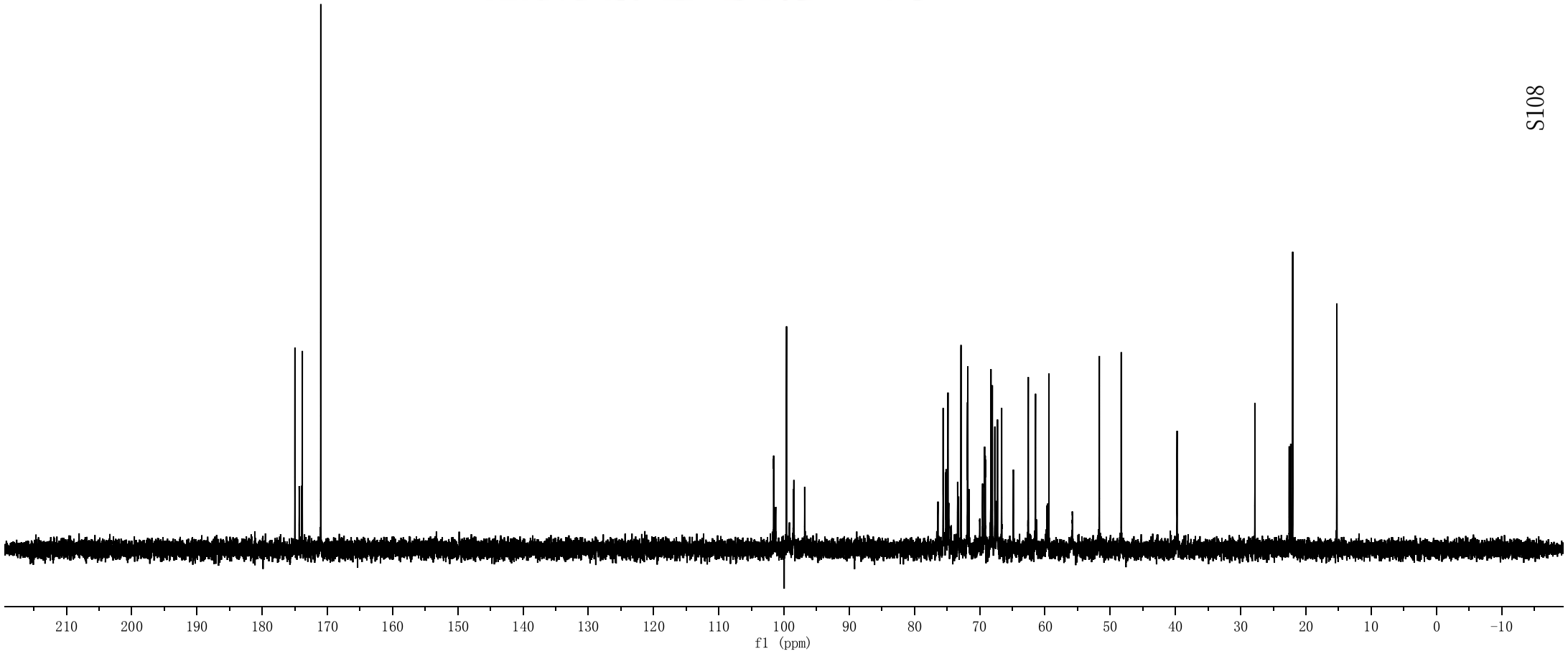
S107

CHZ-1445

#32

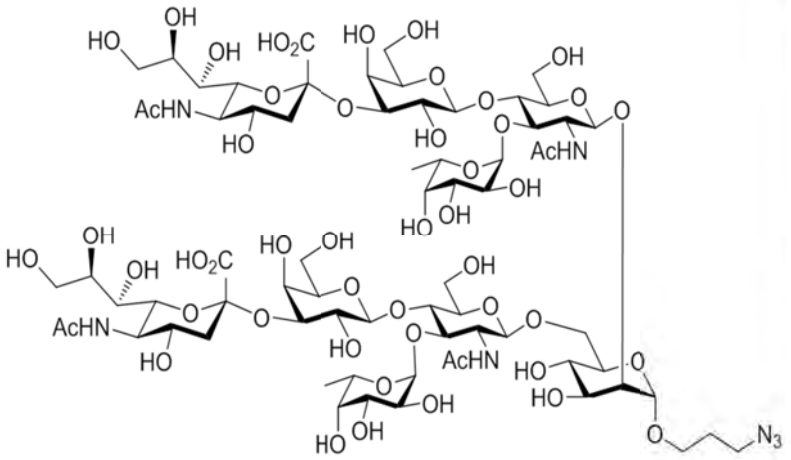


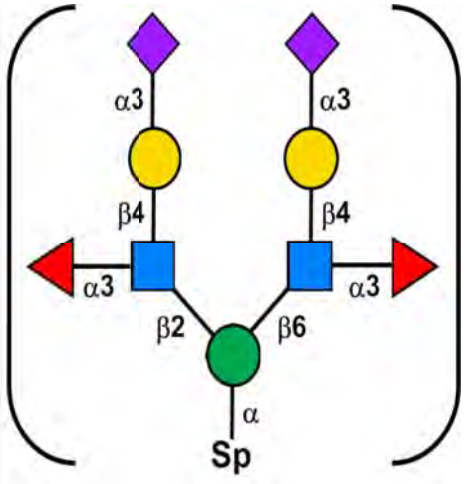

α3
α3
β4
β4
α3
α3
β2
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1445

#32



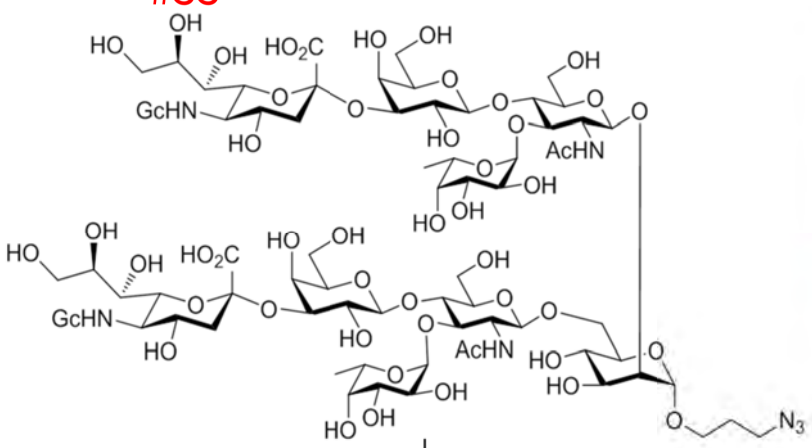


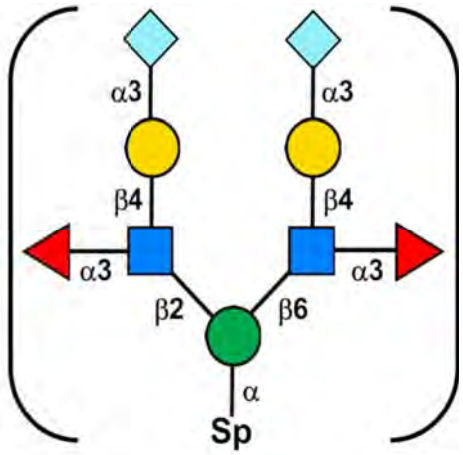
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

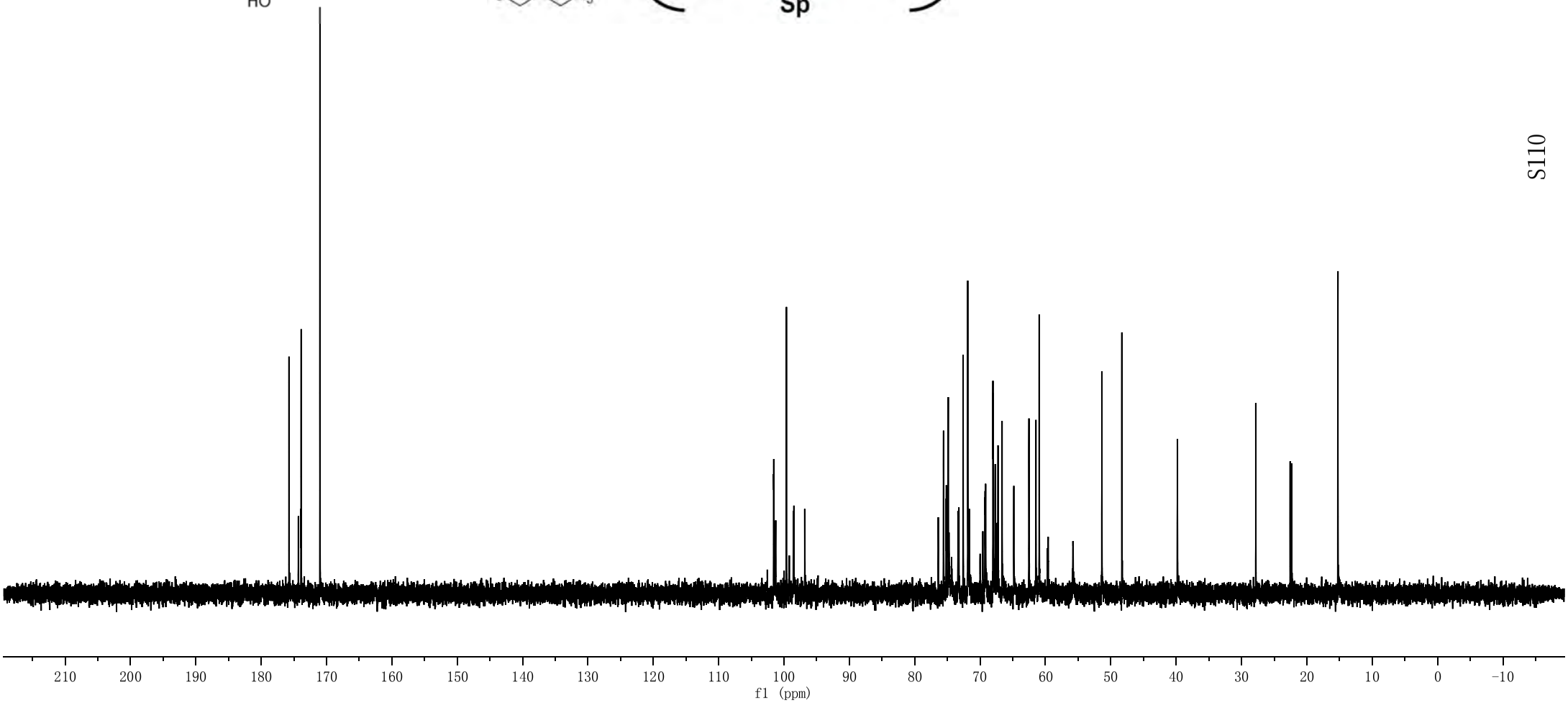
CHZ-1412

#33



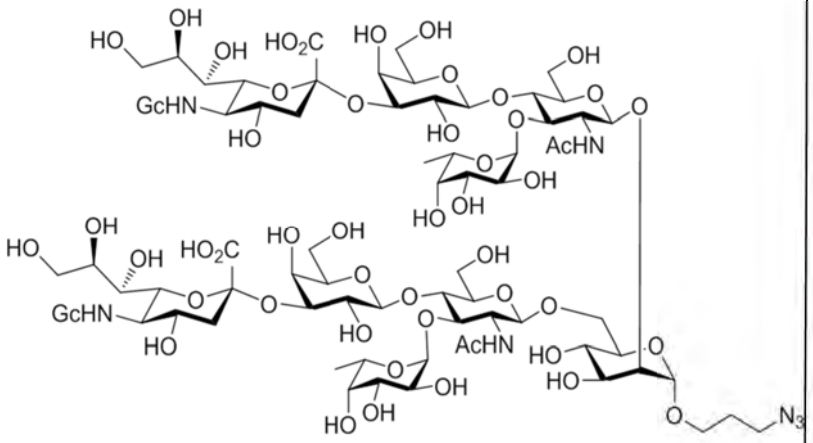


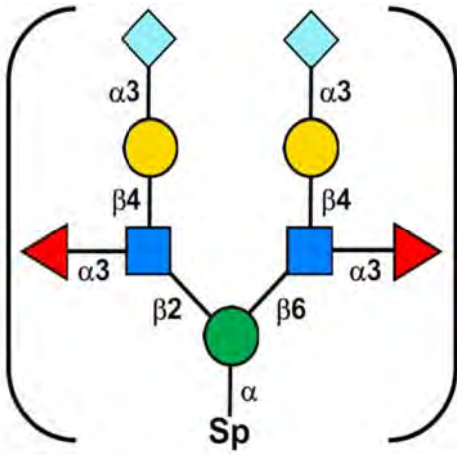
S110



CHZ-1412

#33

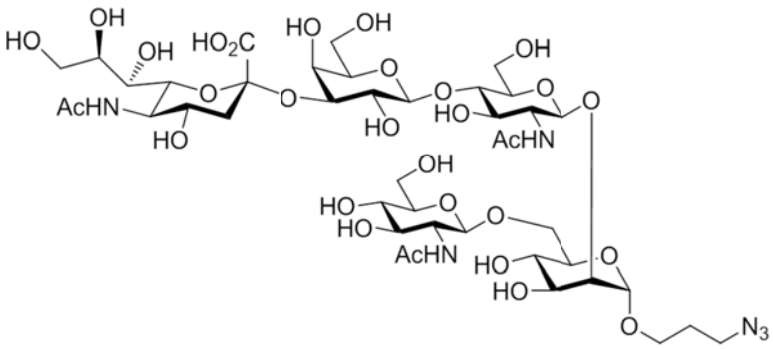

HO
OH
HO2C
GcHN
AcHN
N3

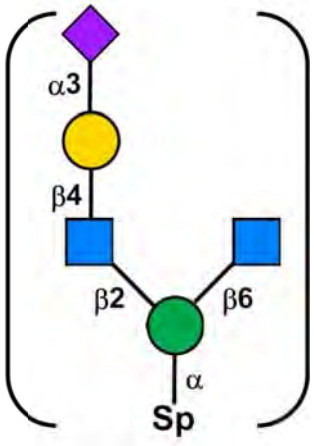

α3
α3
β4
β4
α3
α3
β2
β6
α
Sp

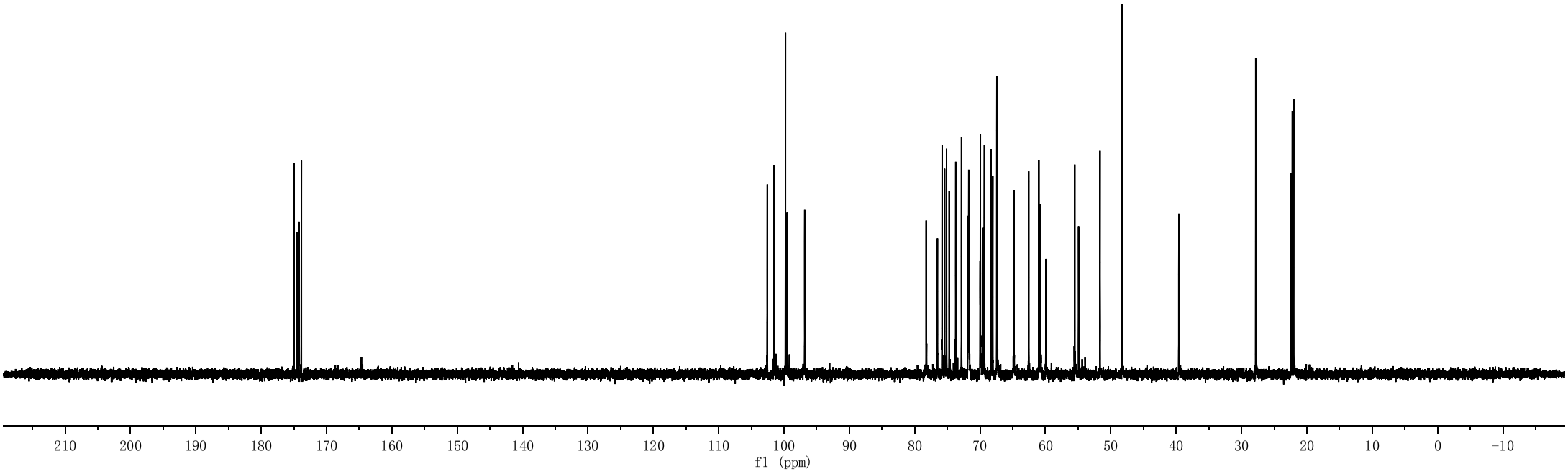
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1098

#34

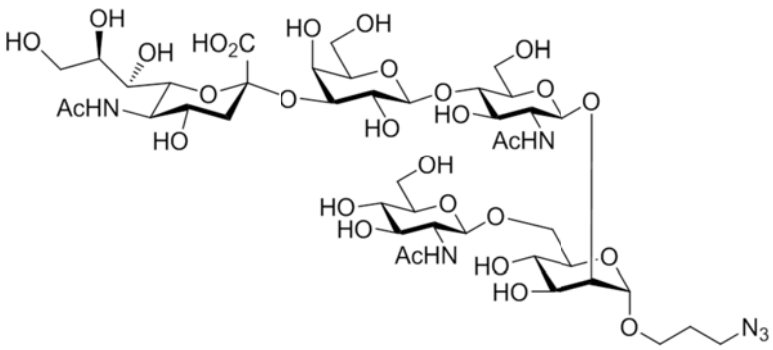

OH
HO
OH
HO2C
AcHN
HO
O
HO
OH
HO
AcHN
OH
HO
HO
AcHN
HO
HO
O
N3

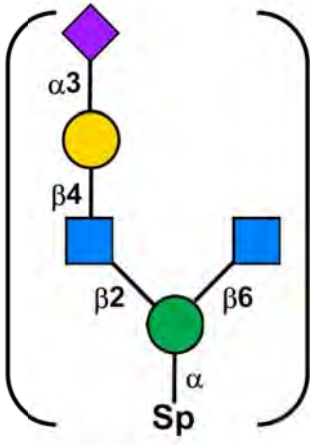

α3
β4
β2
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-1098

#34

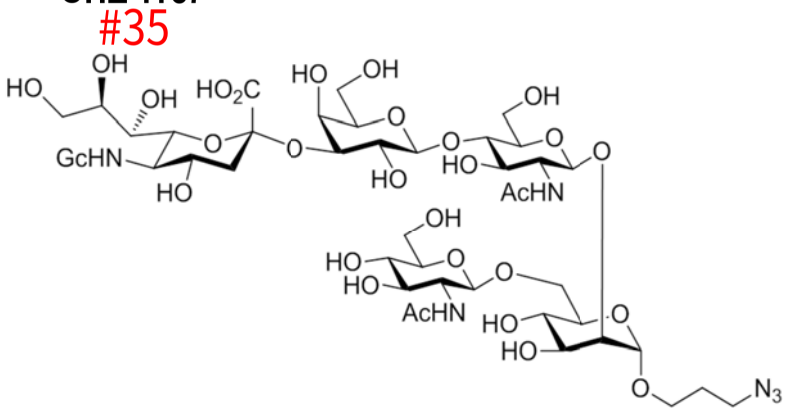

OH
HO
OH
HO2C
AcHN
HO
HO
OH
HO
AcHN
OH
HO
HO
AcHN
HO
HO
O
N3

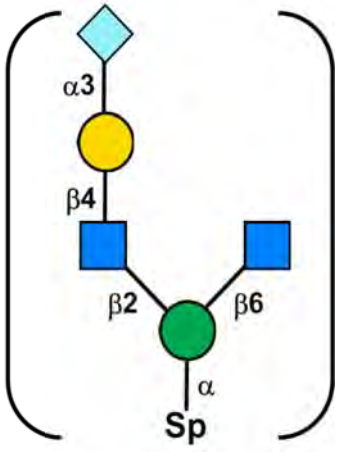

α3
β4
β2
β6
α
Sp

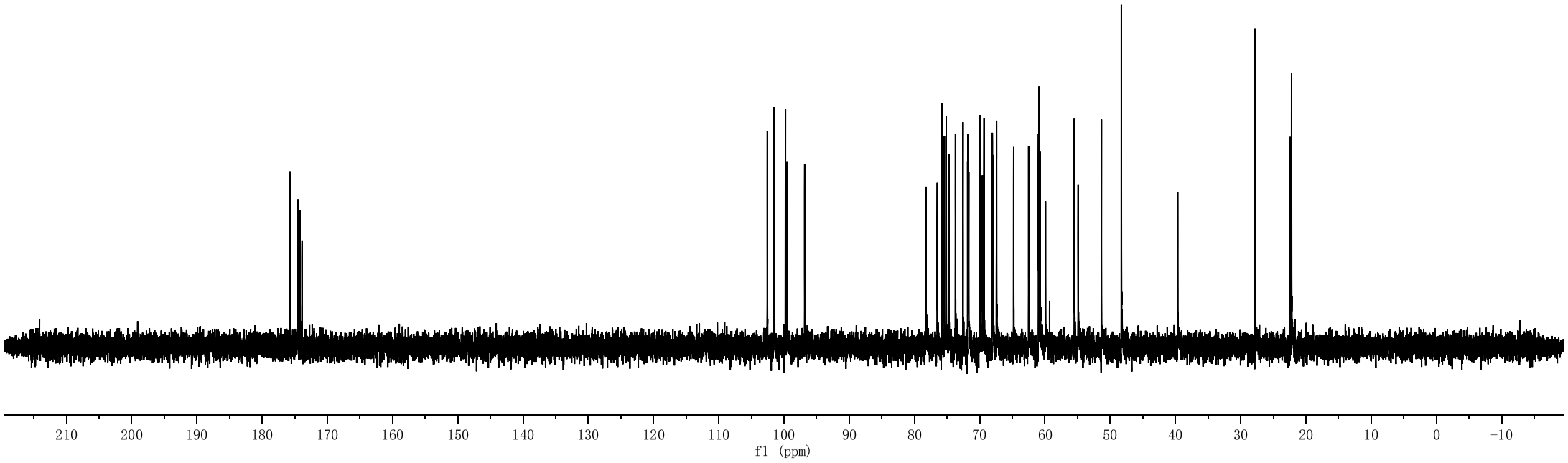
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1167

#35

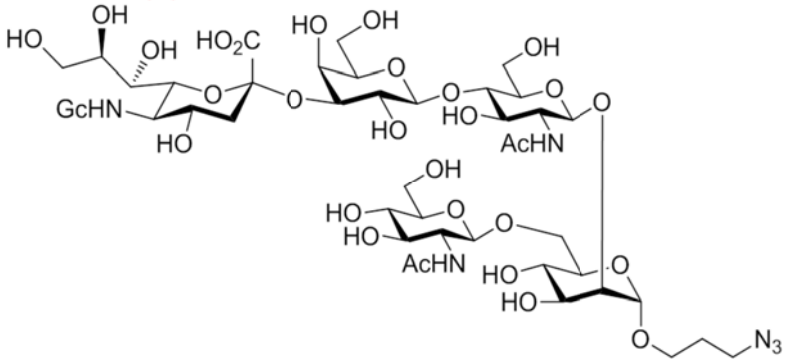

OH
HO
OH
HO2C
HO
OH
OH
GcHN
HO
HO
AcHN
OH
HO
HO
AcHN
HO
HO
O
N3

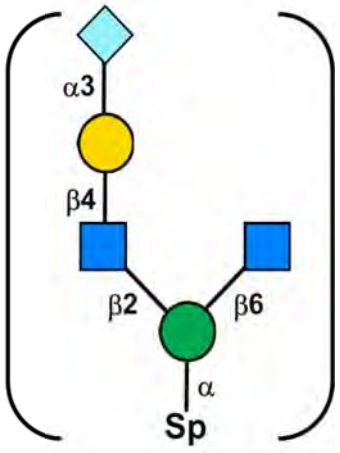

α3
β4
β2
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1167

#35

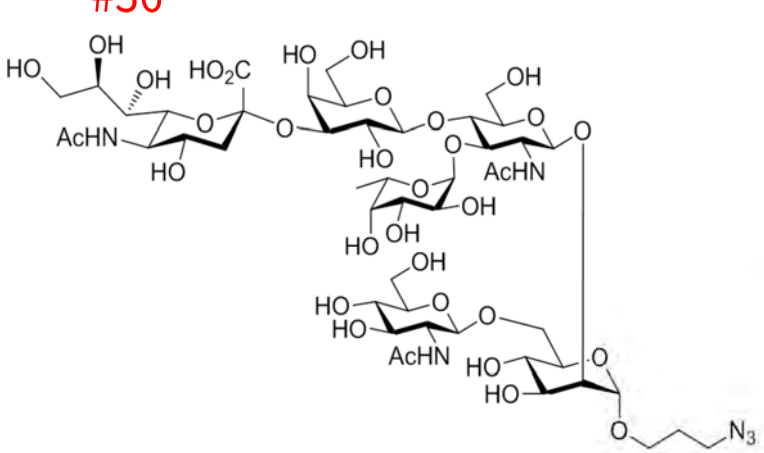

HO
OH
HO2C
GcHN
HO
HO
OH
HO
HO
OH
HO
AcHN
OH
HO
HO
AcHN
HO
HO
O
N3

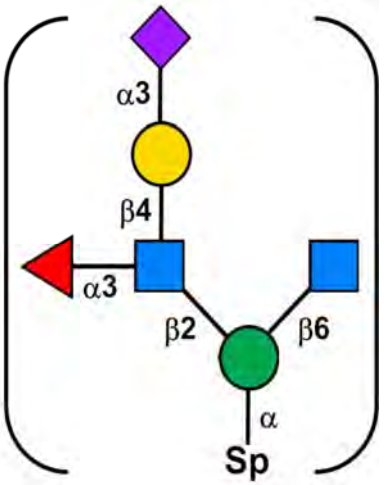

α3
β4
β2
β6
α
Sp

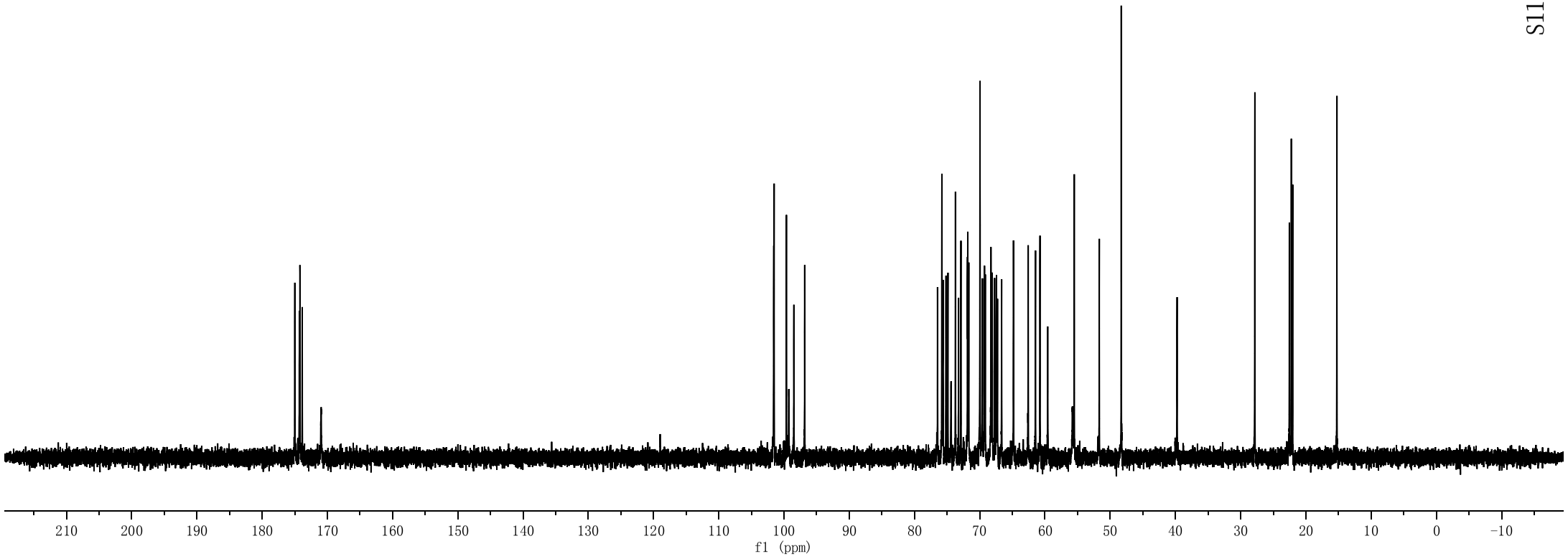
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1166

#36

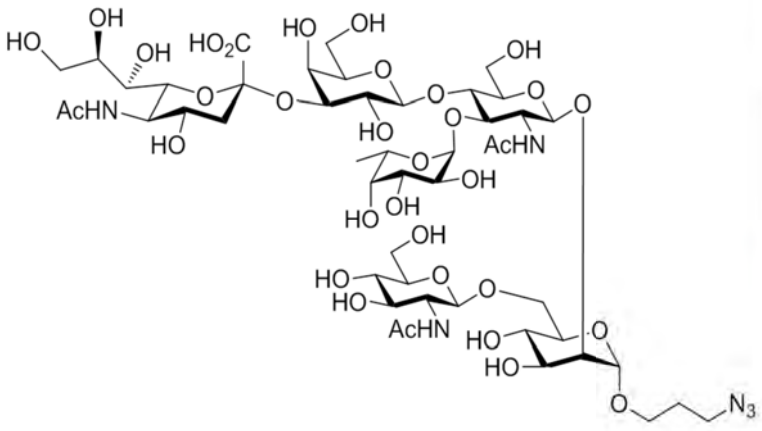


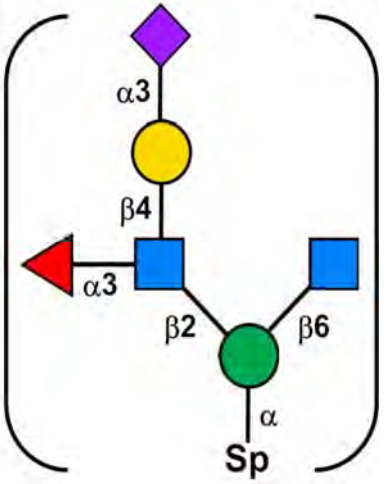

α3
β4
α3
β2
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1166

#36

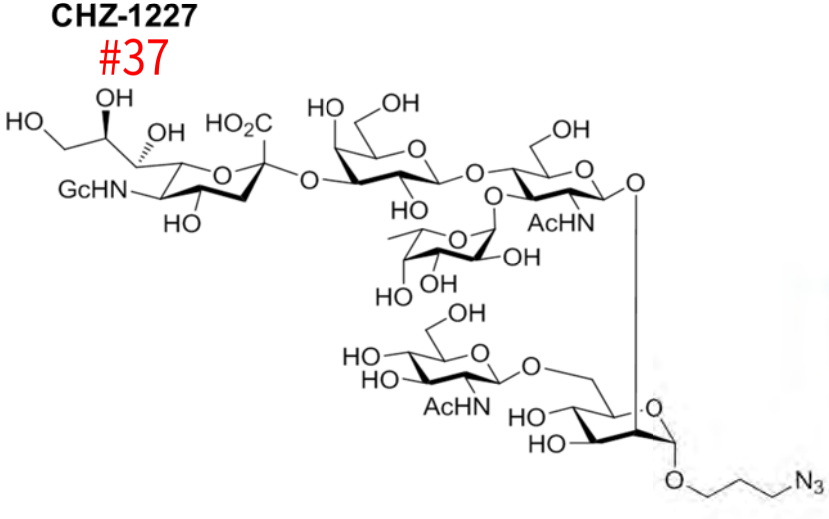


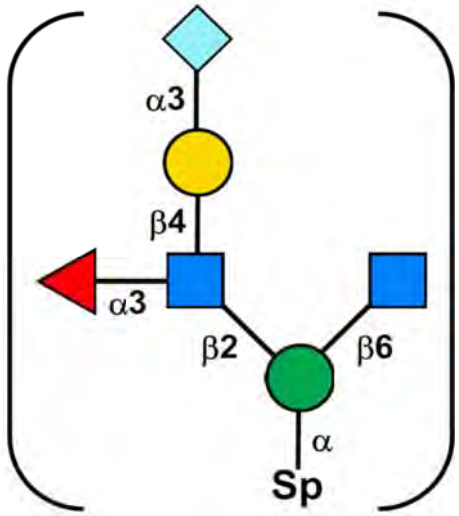


S117

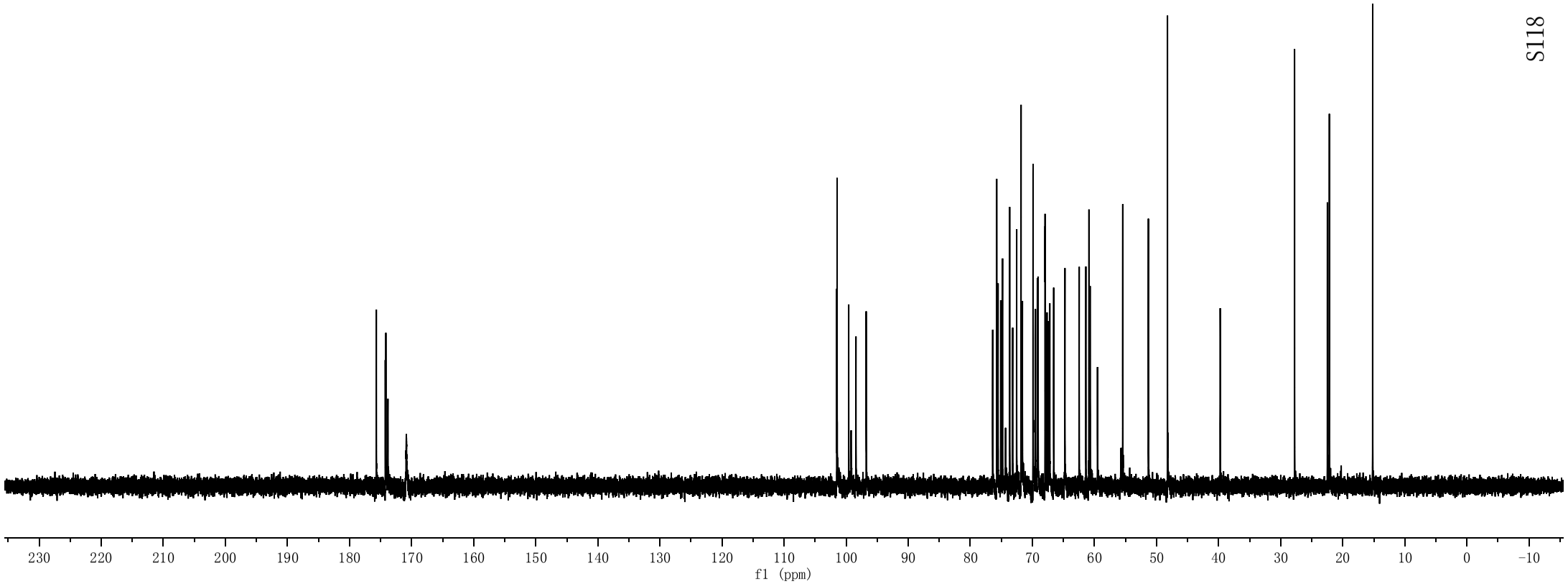
CHZ-1227

#37

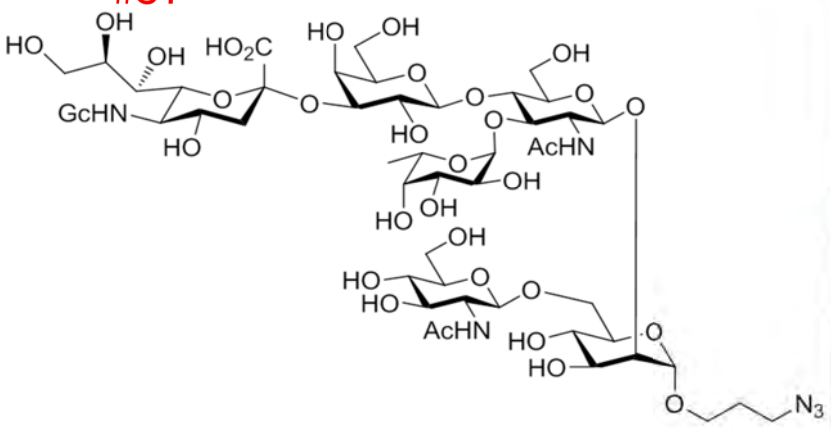


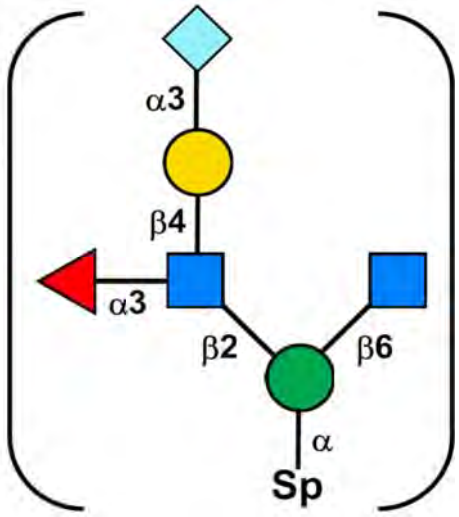


S118



CHZ-1227
#37

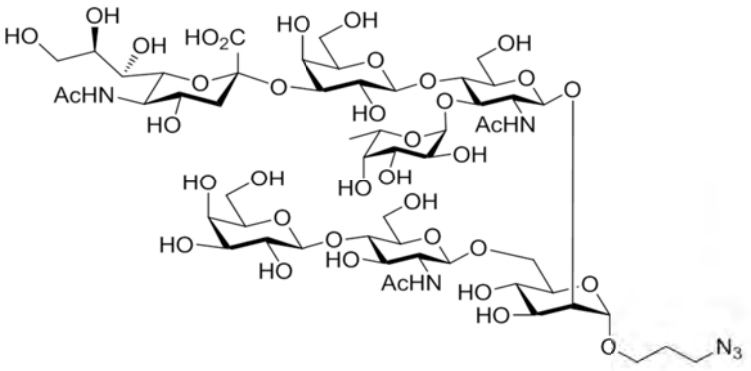

HO
OH
HO2C
GcHN
HO
HO
OH
HO
OH
AcHN
HO
OH
HO
OH
HO
HO
AcHN
HO
HO
O
N3

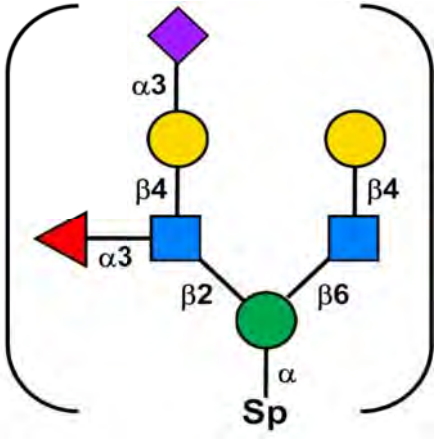

α3
β4
α3
β2
β6
α
Sp

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
f1 (ppm)

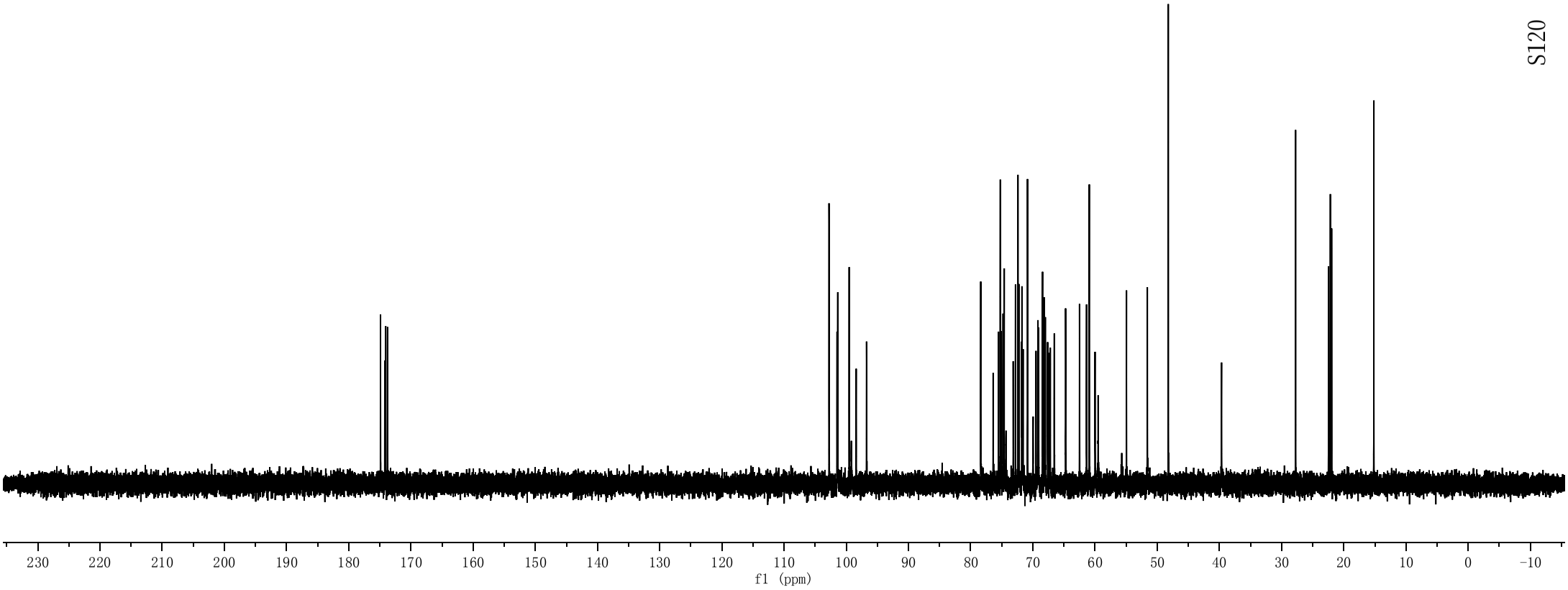
CHZ-1228

#38



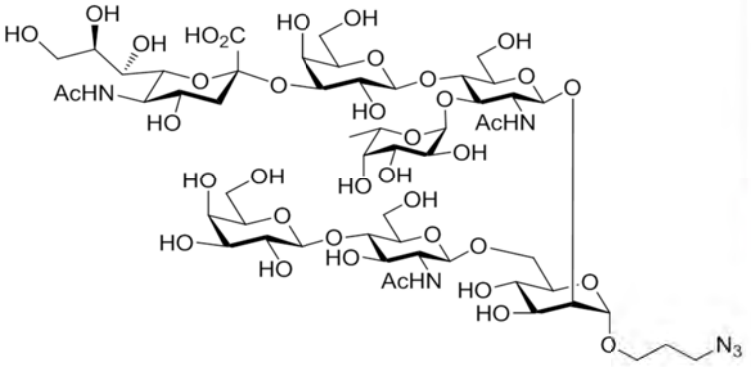


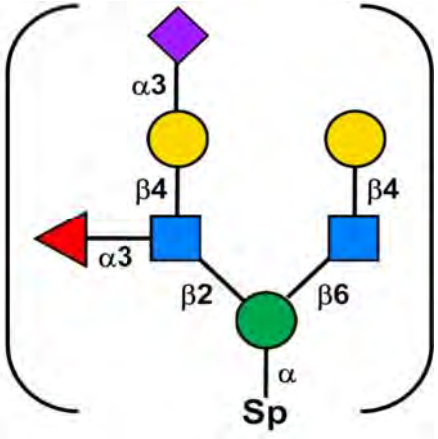
S120



CHZ-1228

#38

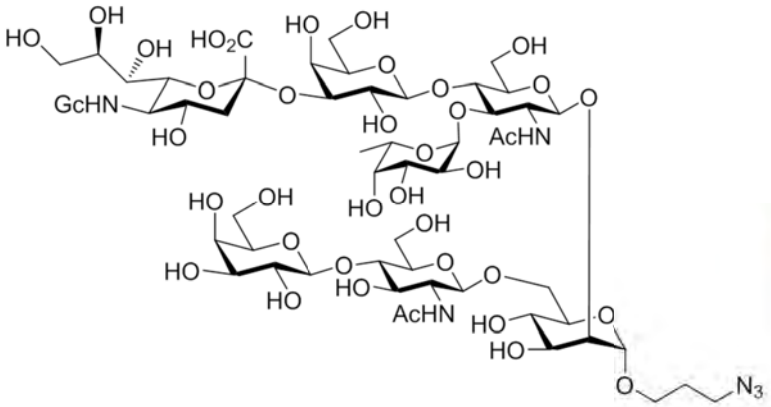


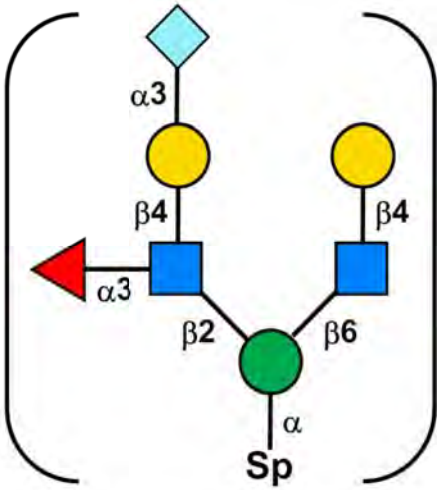


S121

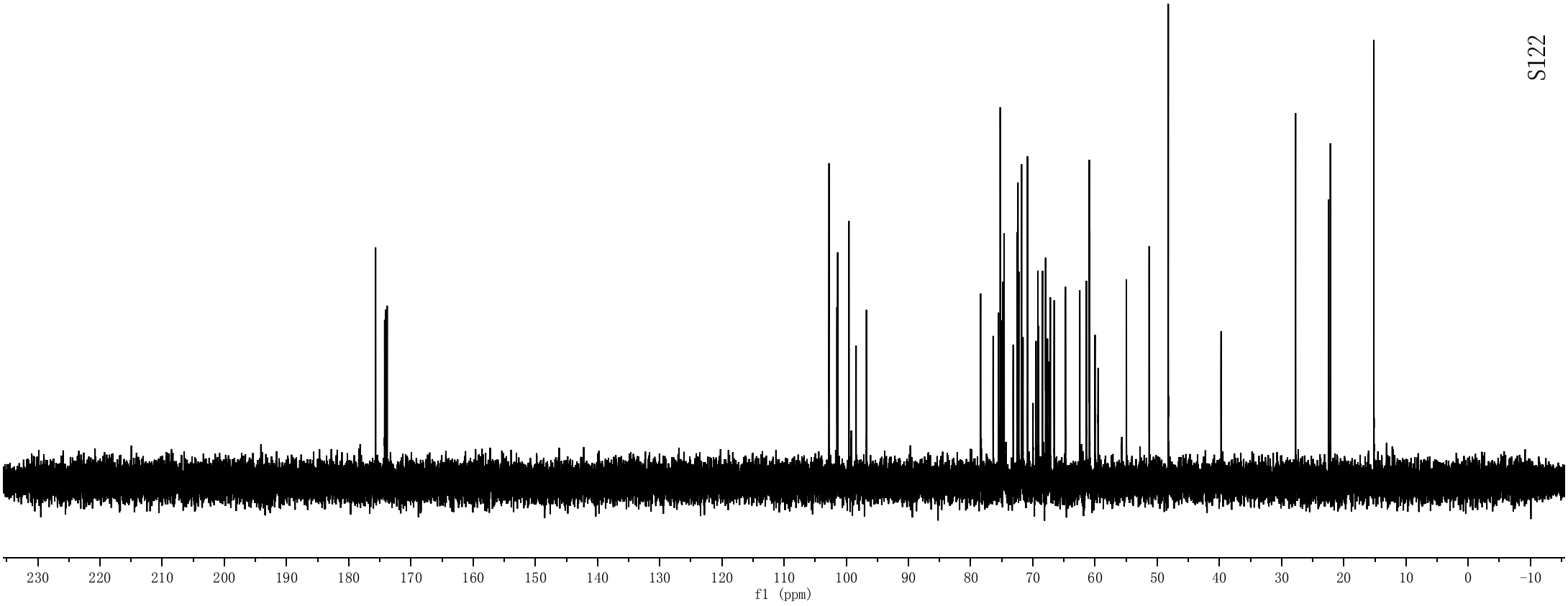
CHZ-1229

#39



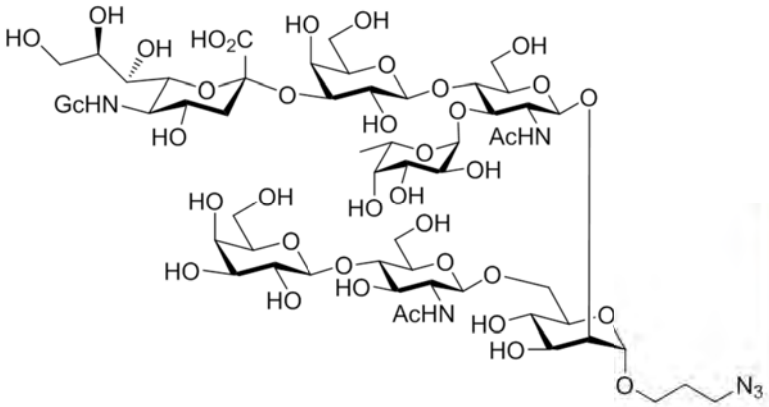


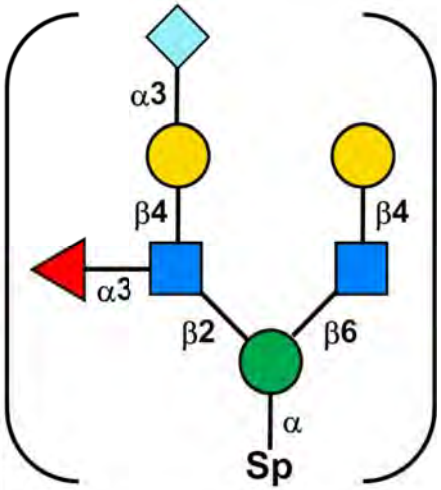
S122



CHZ-1229

#39





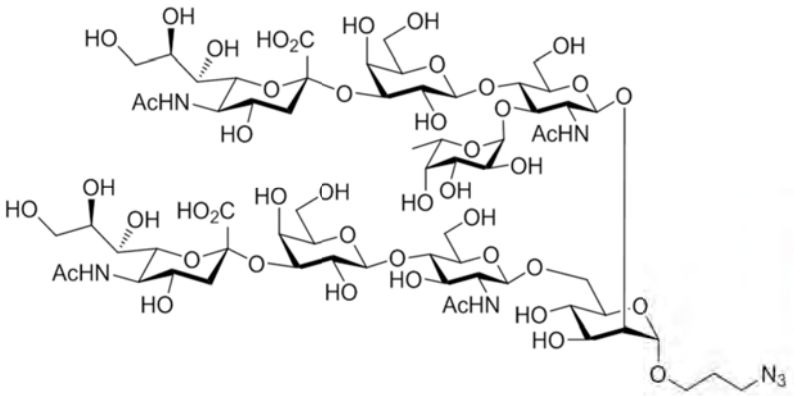
S123

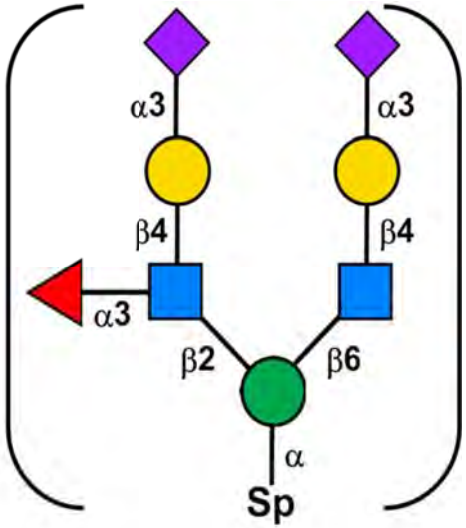
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

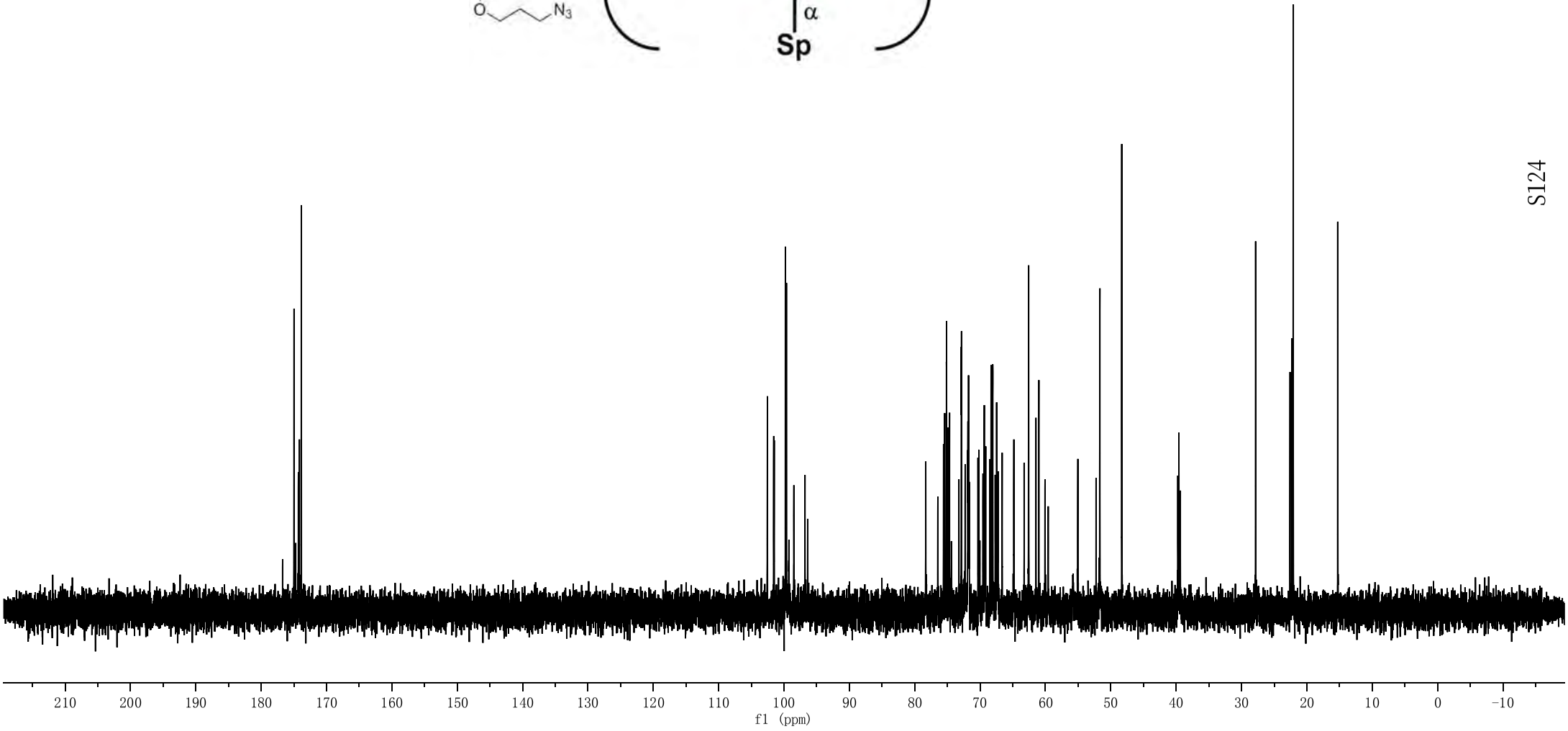
CHZ-1399

#40



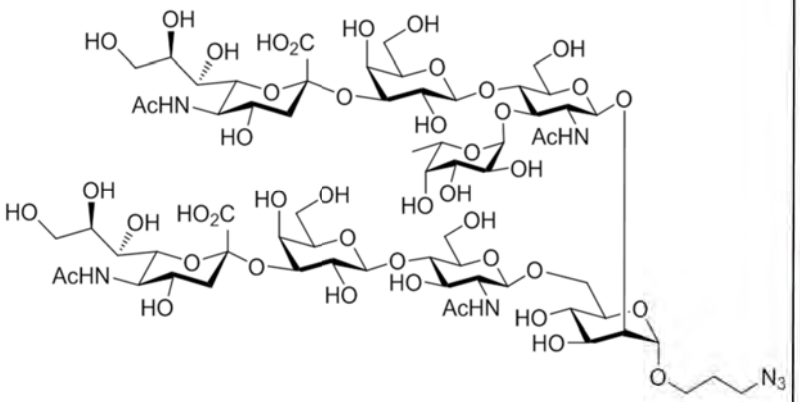


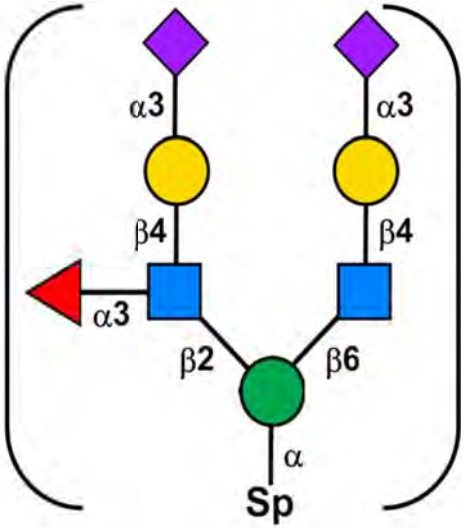
S124



CHZ-1399

#40

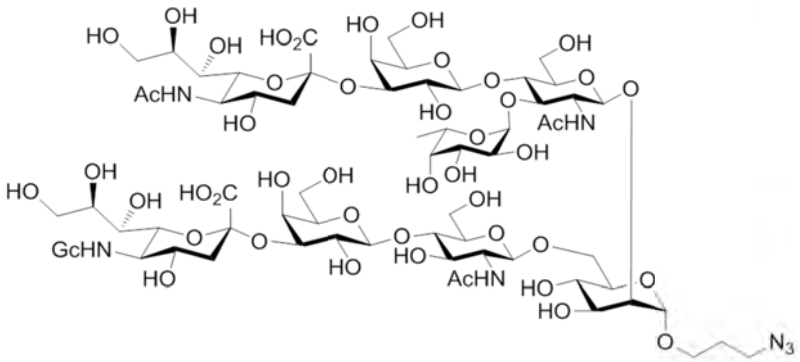

OH
HO
OH
HO2C
HO
OH
OH
AcHN
O
HO
AcHN
OH
HO
OH
N3

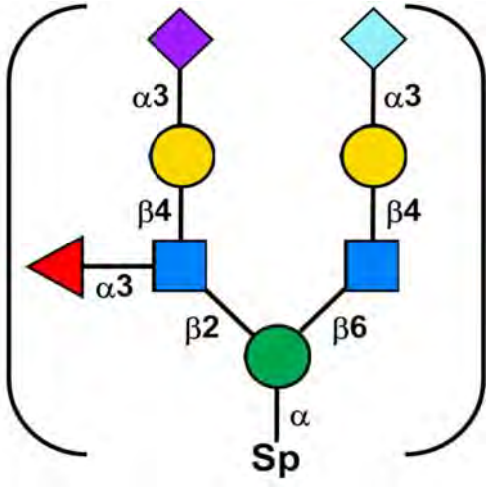

α3
α3
β4
β4
α3
β2
β6
α
Sp

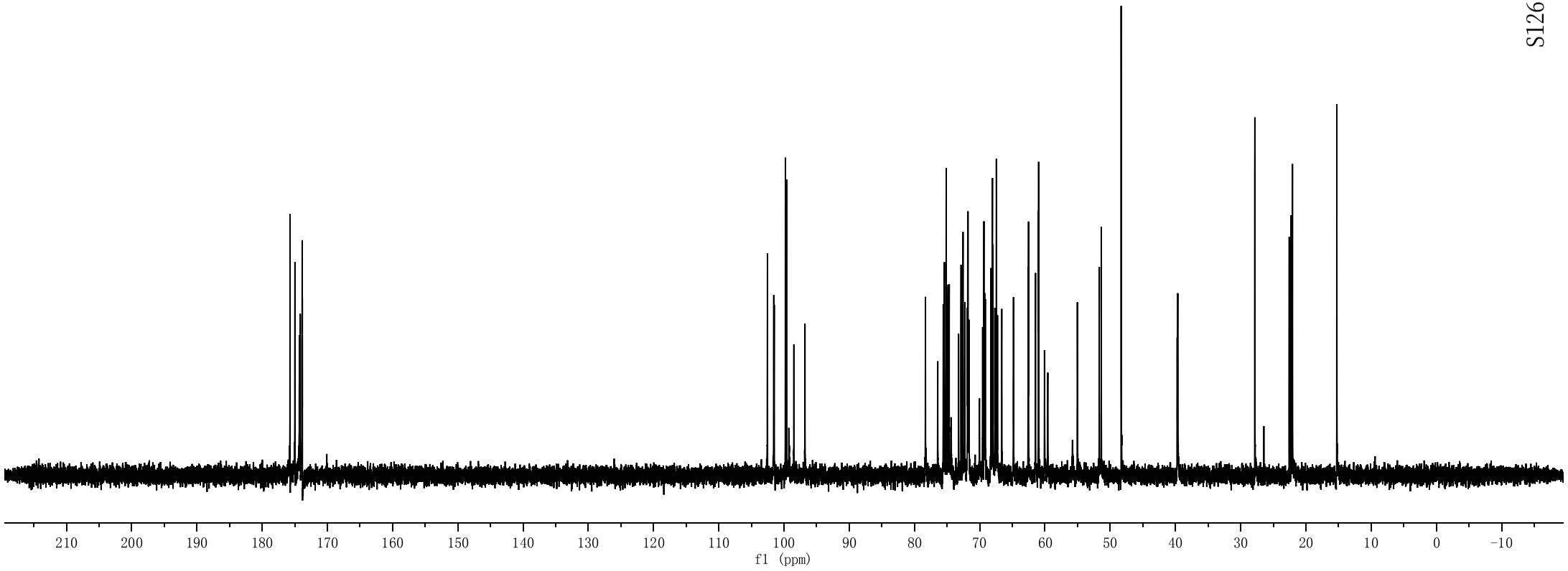
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1383

#41

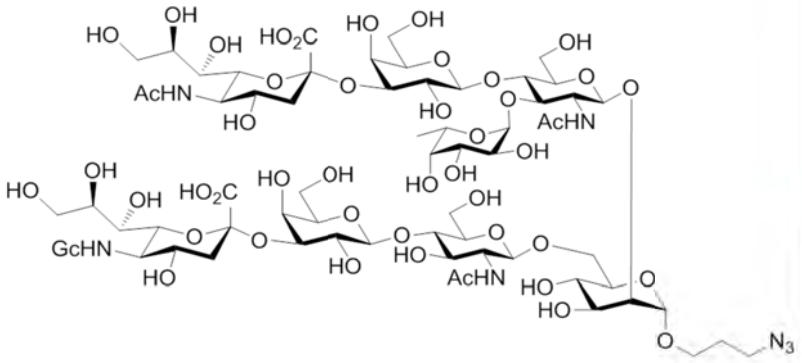


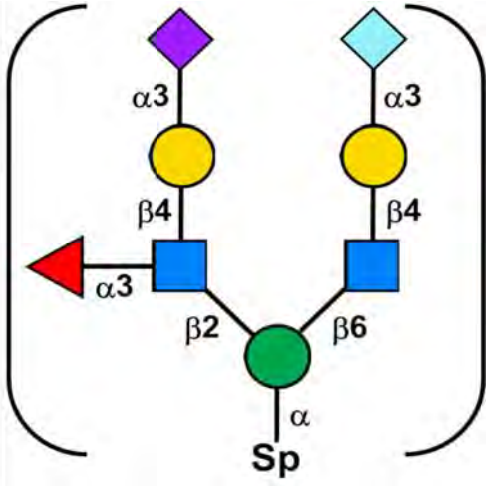

α3
α3
β4
β4
α3
β2
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1383

#41

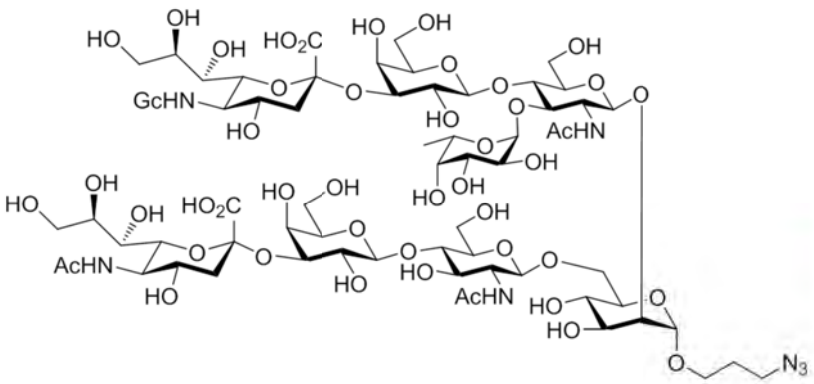


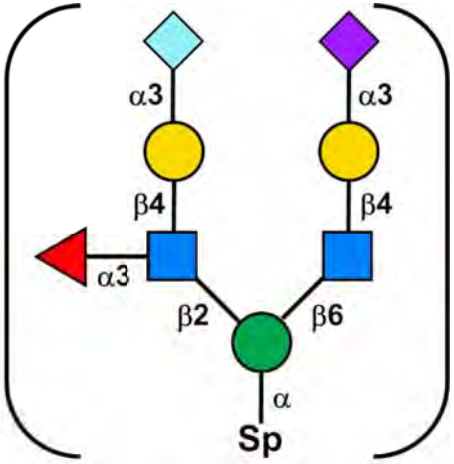


S127

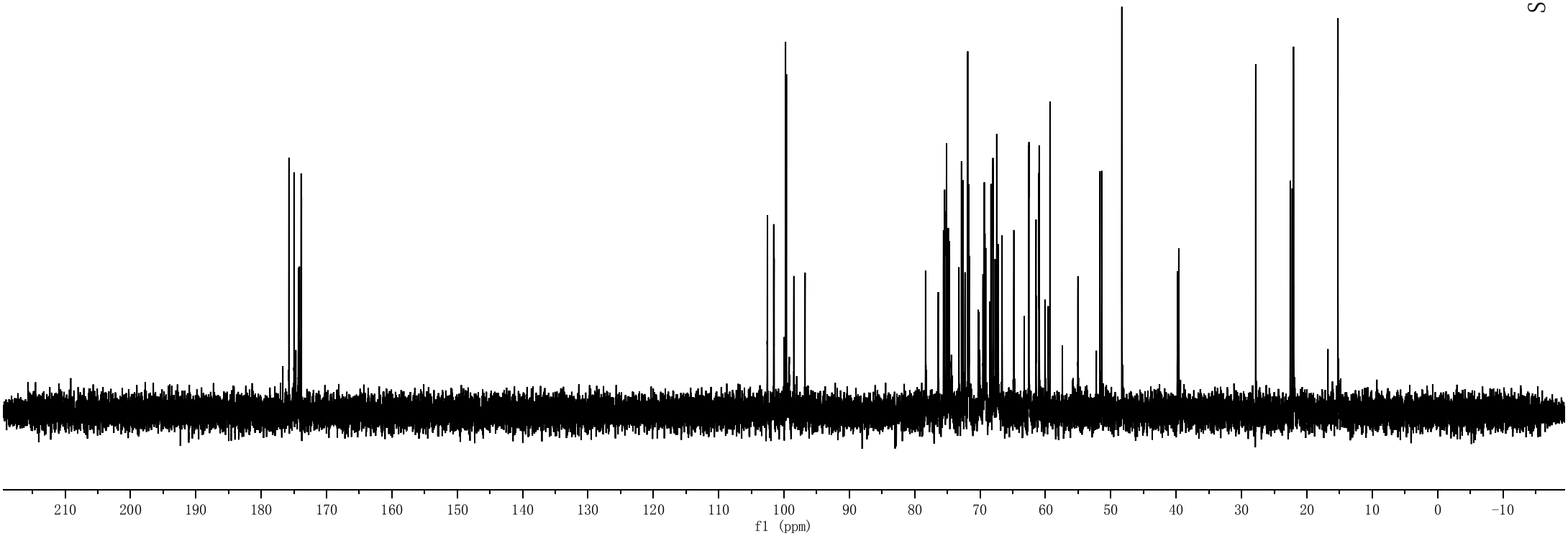
CHZ-1467

#42



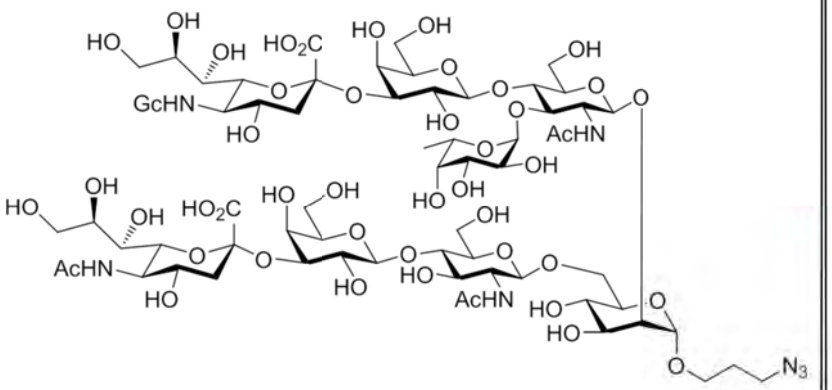


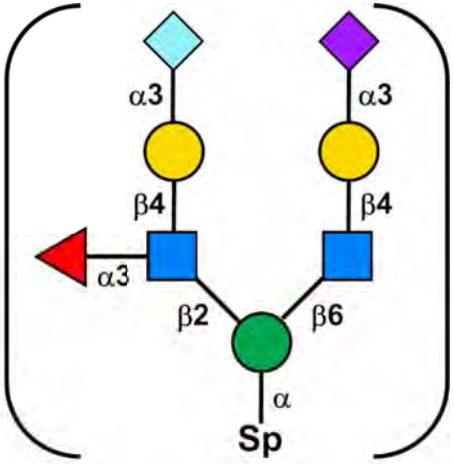
S128



CHZ-1467

#42

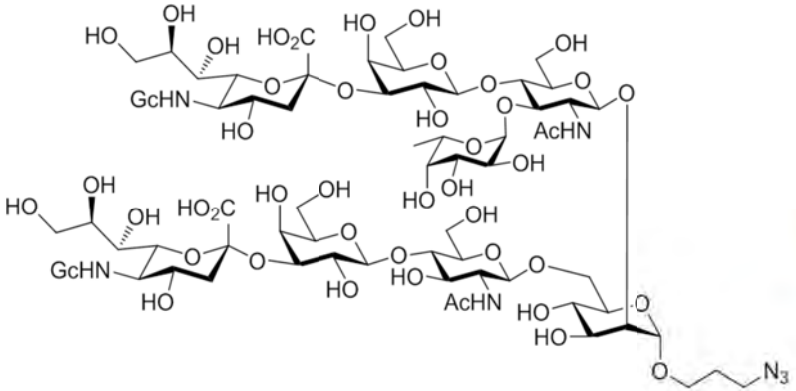

OH
HO
OH
HO2C
HO
OH
OH
GcHN
HO
O
HO
AcHN
OH
HO
OH
HO
OH
HO2C
HO
OH
OH
AcHN
HO
HO
AcHN
HO
HO
O
O
N3

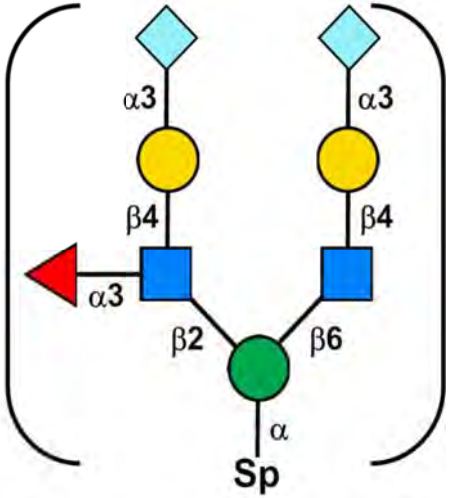

α3
α3
β4
β4
α3
β2
β6
α
Sp

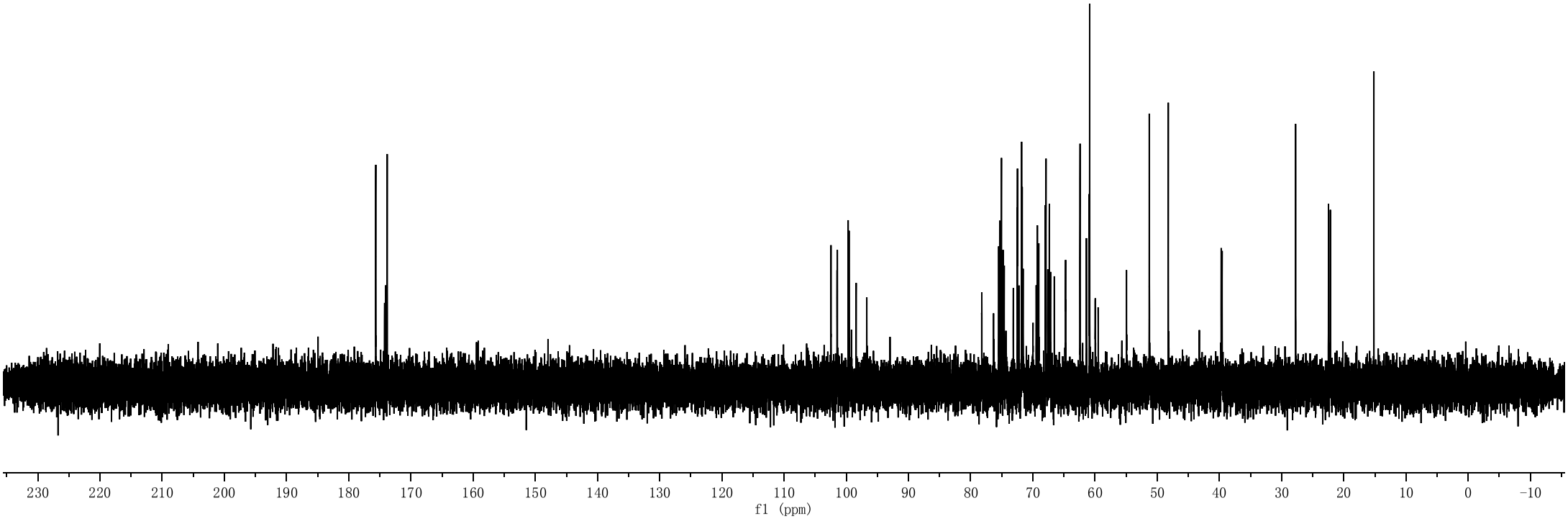
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1257

#43

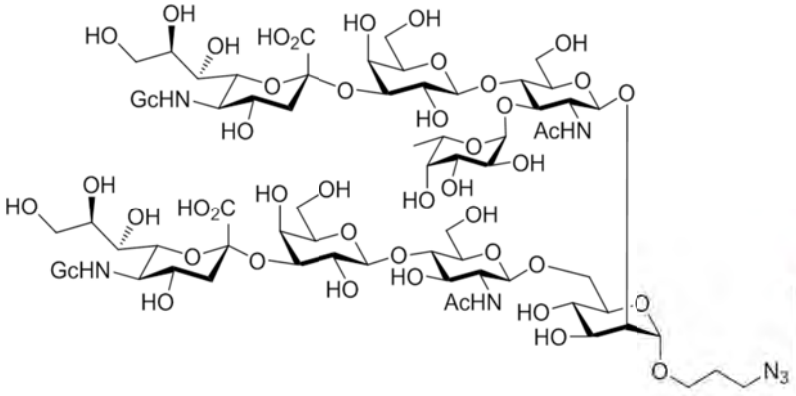

HO
OH
HO2C
GcHN
HO
AcHN
N3

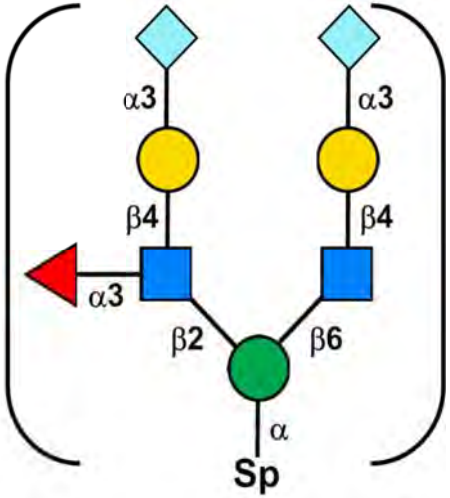

α3
α3
β4
β4
α3
β2
β6
α
Sp

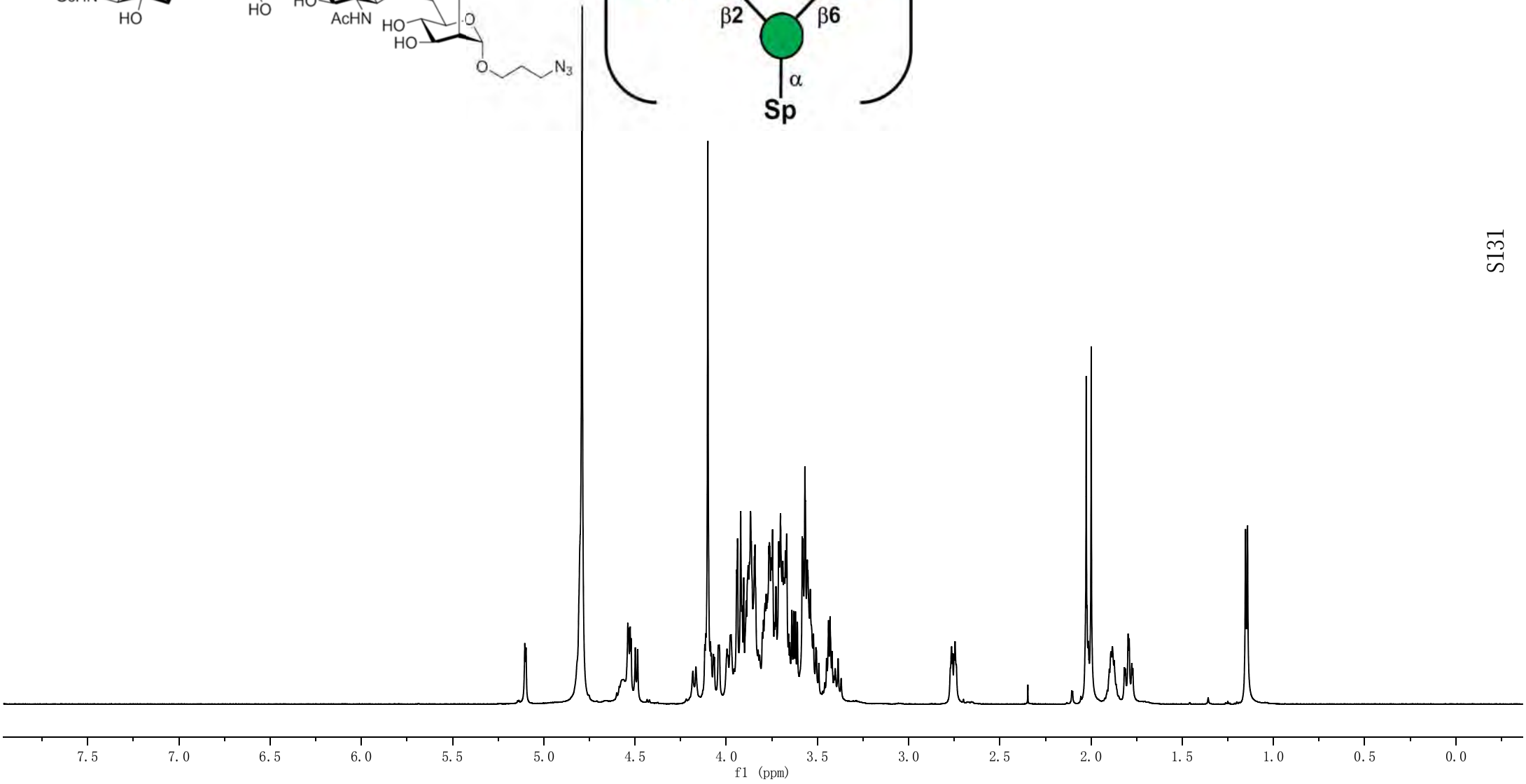

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-1257

#43



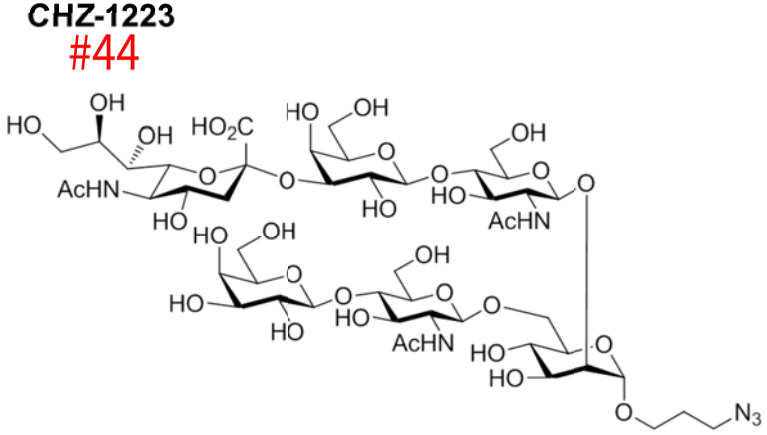


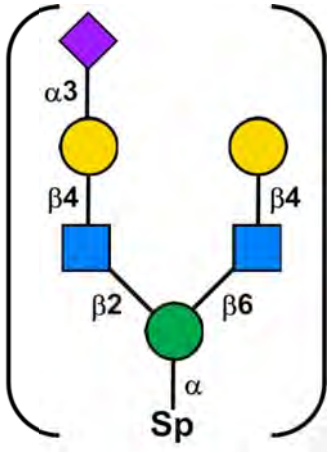


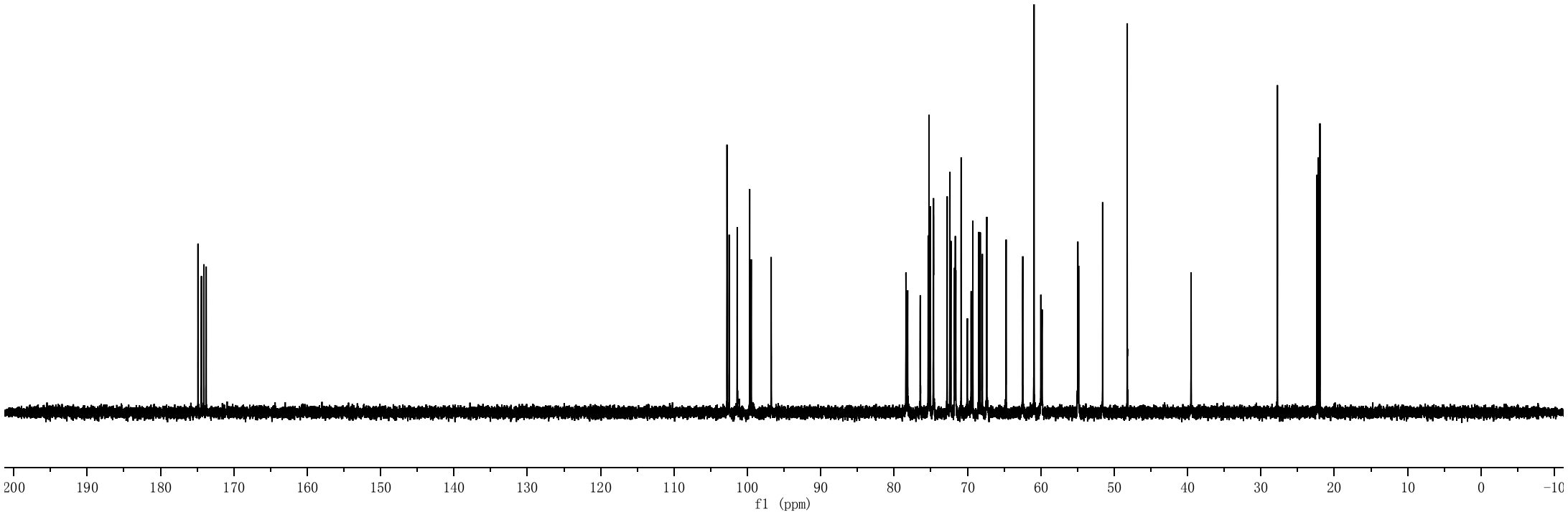
S131

CHZ-1223

#44

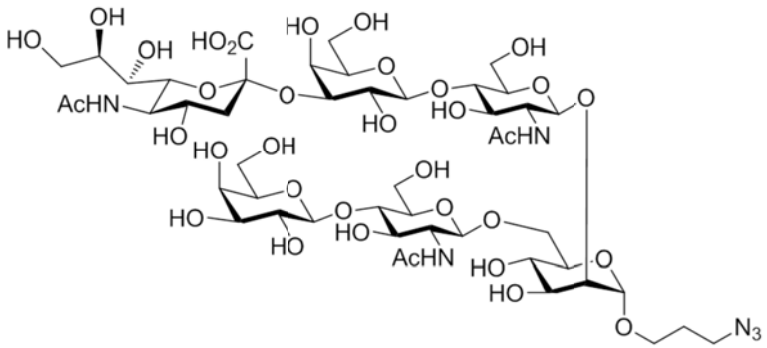


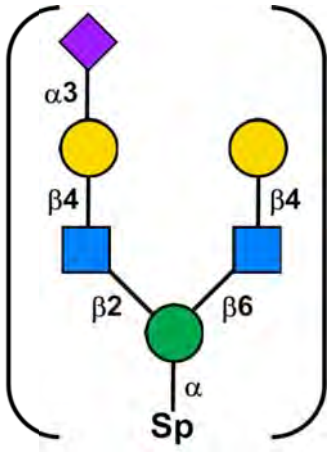

α3
β4
β4
β2
β6
α
Sp


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1223

#44

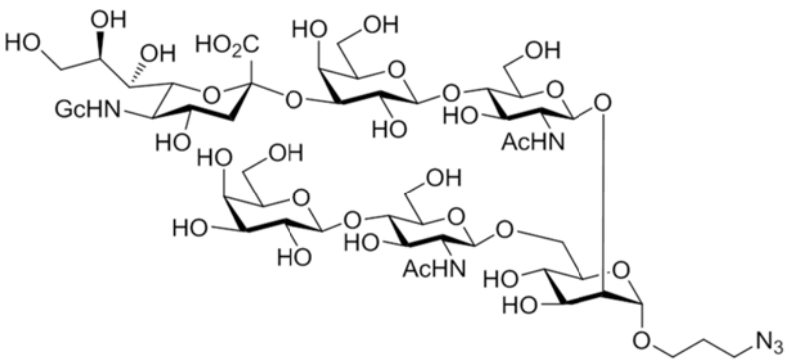

HO
OH
OH
HO2C
HO
OH
OH
AcHN
HO
HO
AcHN
HO
OH
HO
HO
OH
HO
AcHN
HO
HO
O
N3

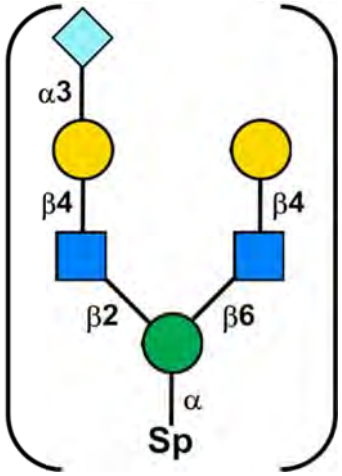

α3
β4
β4
β2
β6
α
Sp

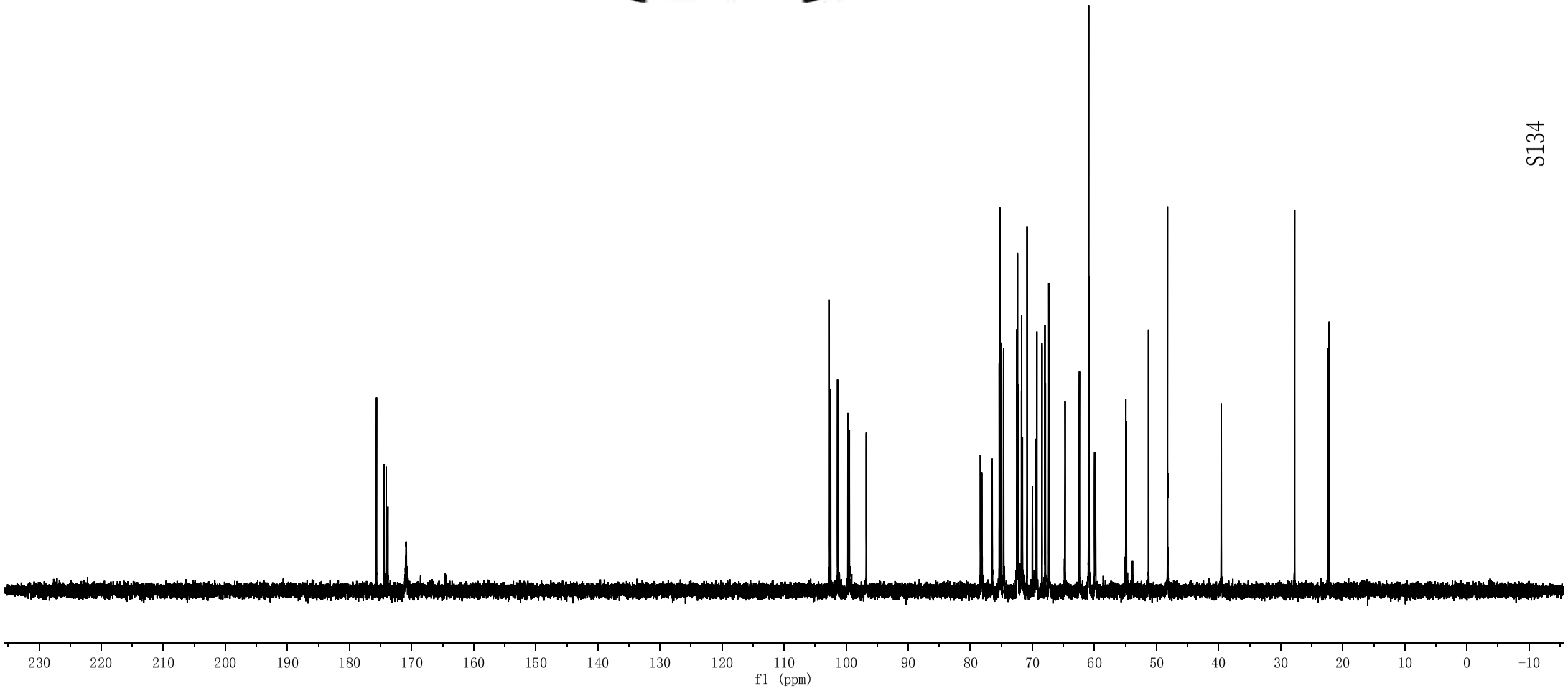
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1224

#45

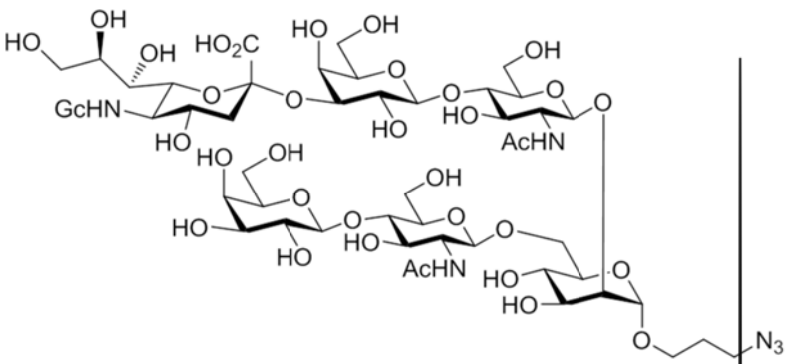

HO
OH
OH
HO2C
GcHN
HO
HO
O
HO
OH
HO
O
HO
AcHN
OH
HO
OH
HO
HO
O
HO
AcHN
OH
HO
HO
O
N3

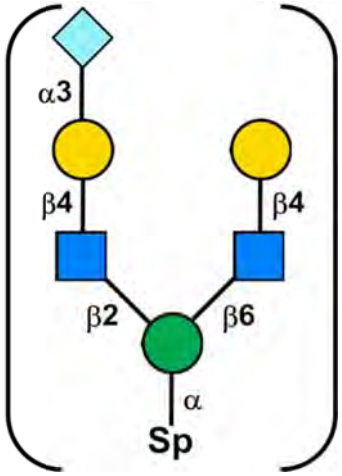

α3
β4
β4
β2
β6
α
Sp


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-1224

#45

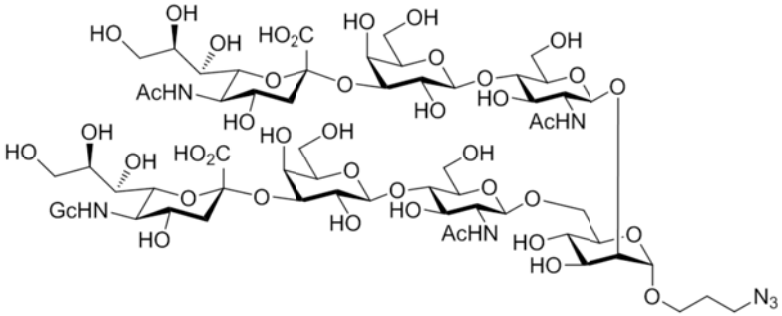

HO
OH
OH
HO2C
GcHN
HO
HO
O
HO
OH
HO
O
HO
AcHN
OH
HO
HO
O
HO
AcHN
OH
HO
HO
O
O
N3

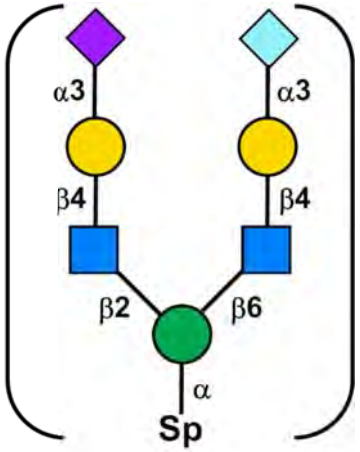

α3
β4
β4
β2
β6
α
Sp

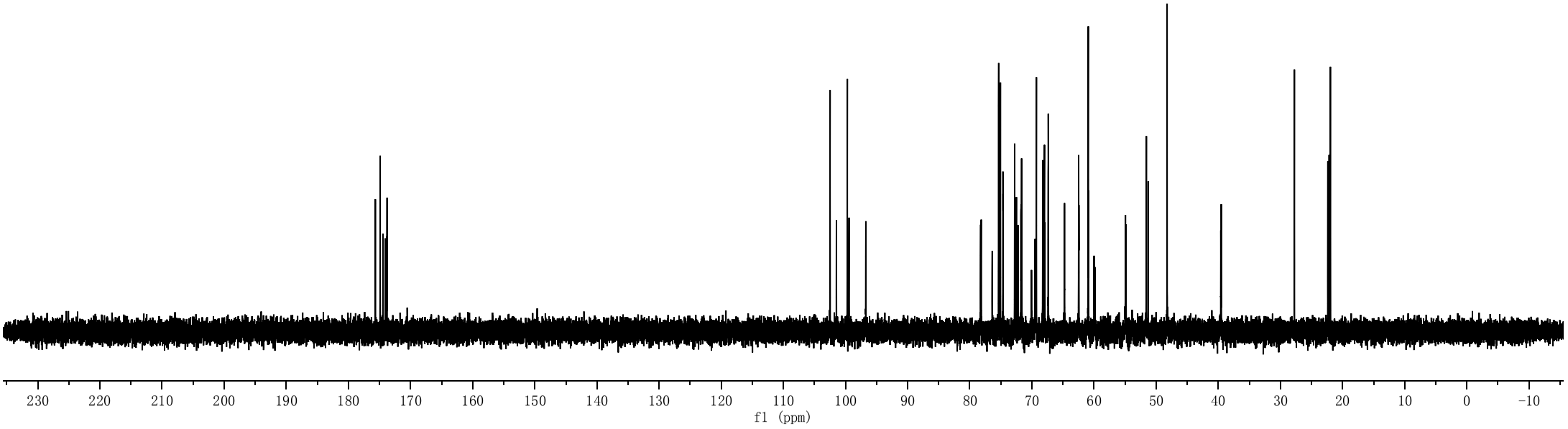
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

CHZ-1225

#46

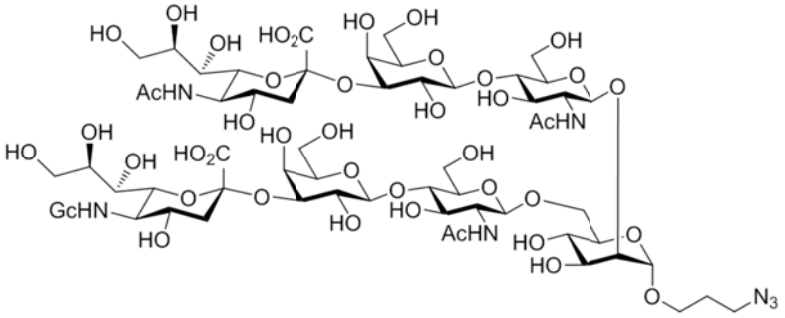


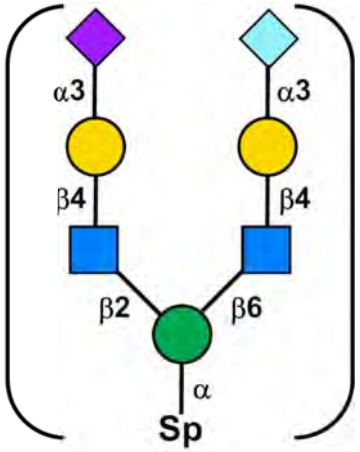

α3
α3
β4
β4
β2
β6
α
Sp


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

CHZ-1225

#46

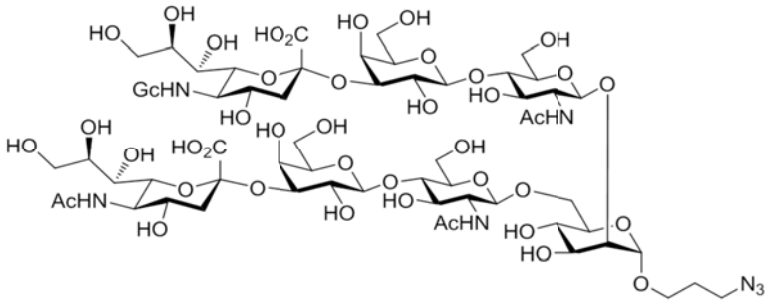

HO
OH
AcHN
HO2C
O
HO
OH
HO
AcHN
GcHN
N3

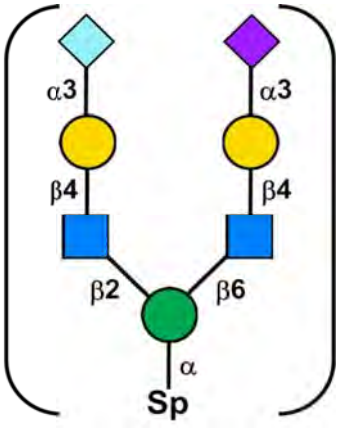

α3
α3
β4
β4
β2
β6
α
Sp

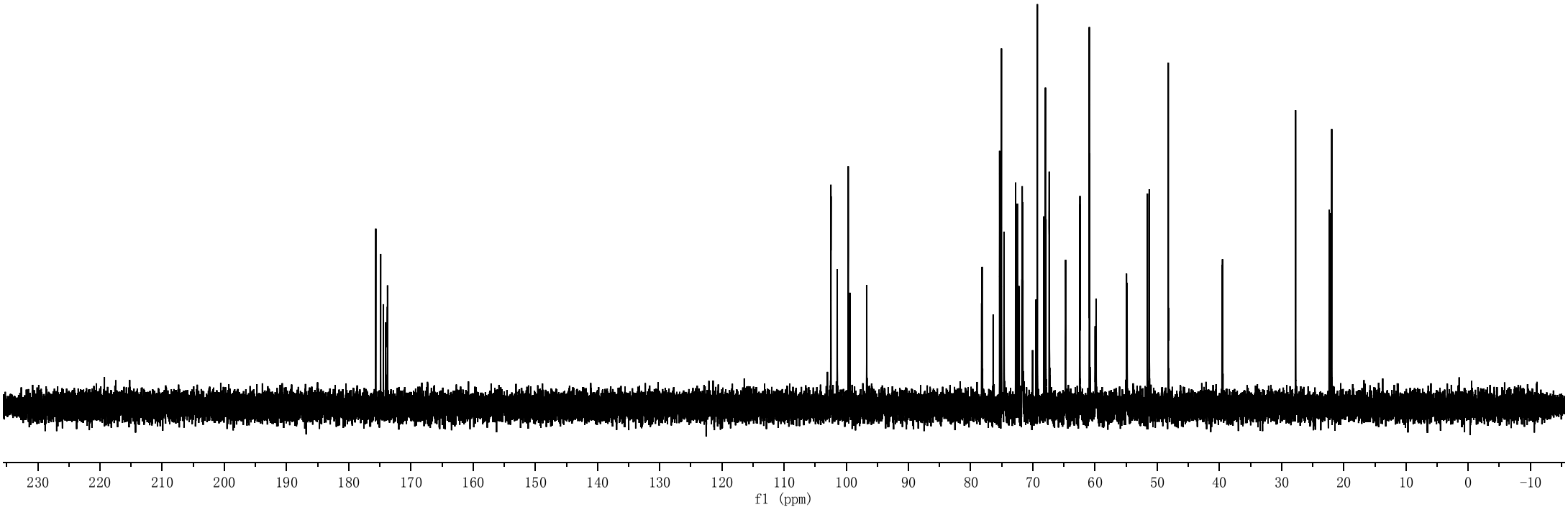
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1226

#47

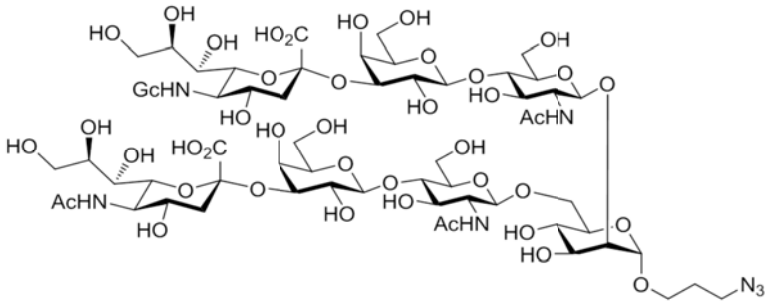

HO
OH
HO2C
GcHN
AcHN
N3

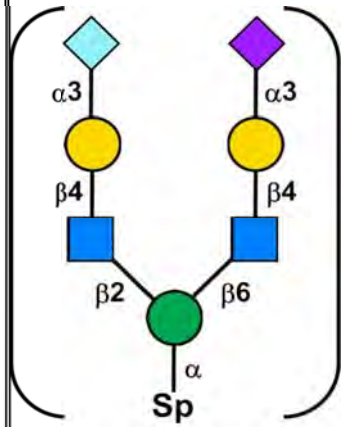

α3
α3
β4
β4
β2
β6
α
Sp


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

CHZ-1226

#47

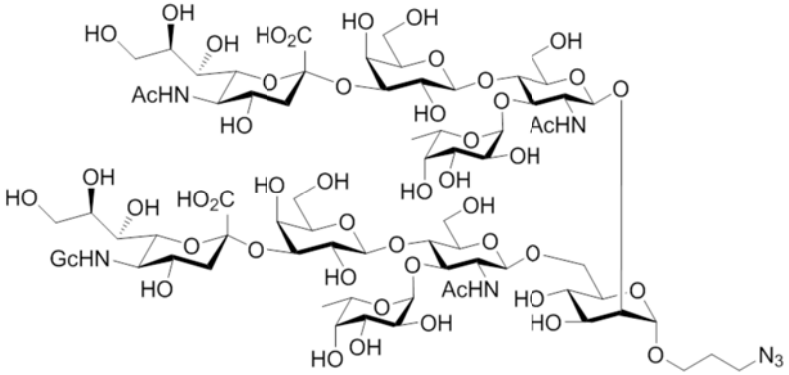

HO
OH
HO2C
GcHN
AcHN
N3

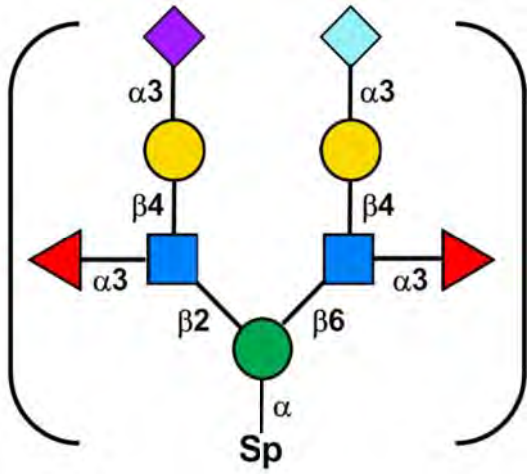

α3
α3
β4
β4
β2
β6
α
Sp

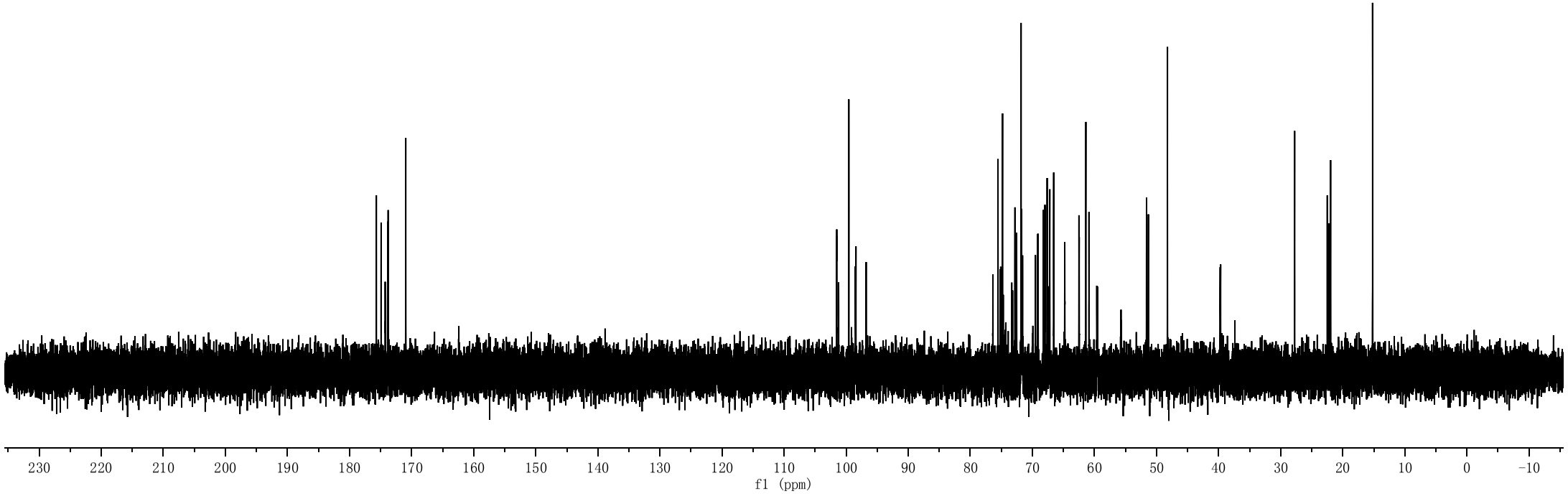
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1352

#48

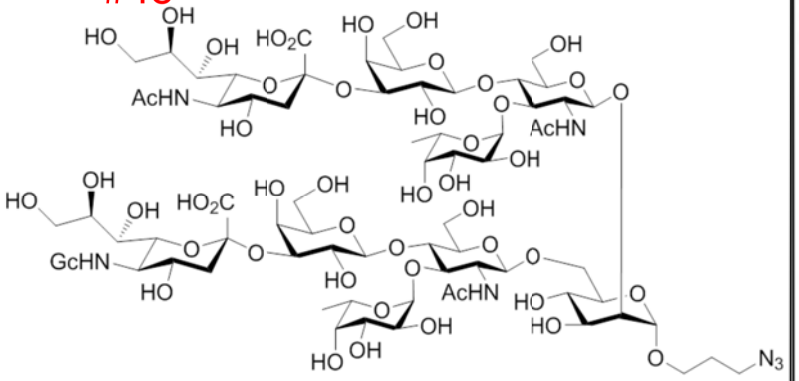


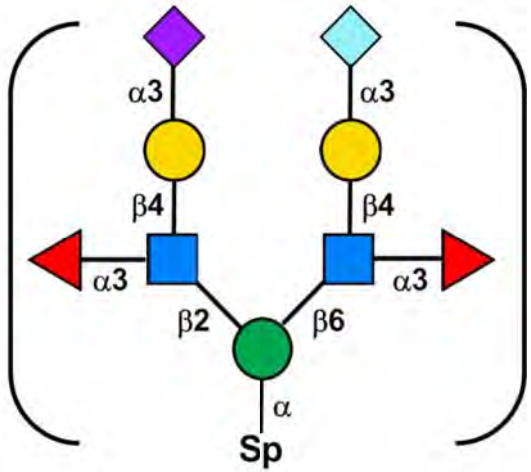

α3
α3
β4
β4
α3
α3
β2
β6
α
Sp


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

CHZ-1352

#48

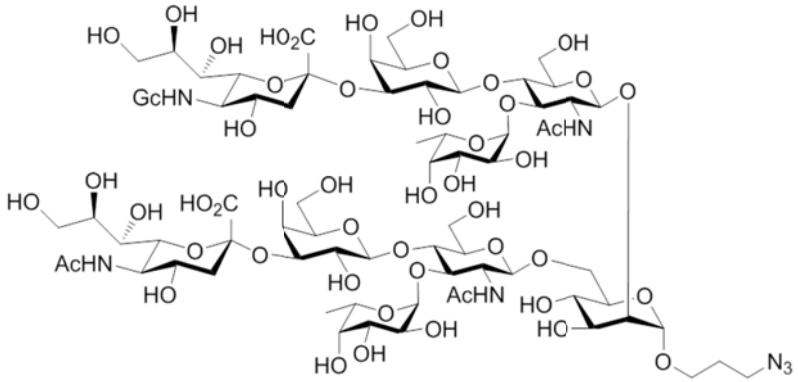

HO
OH
AcHN
HO
HO2C
O
N3

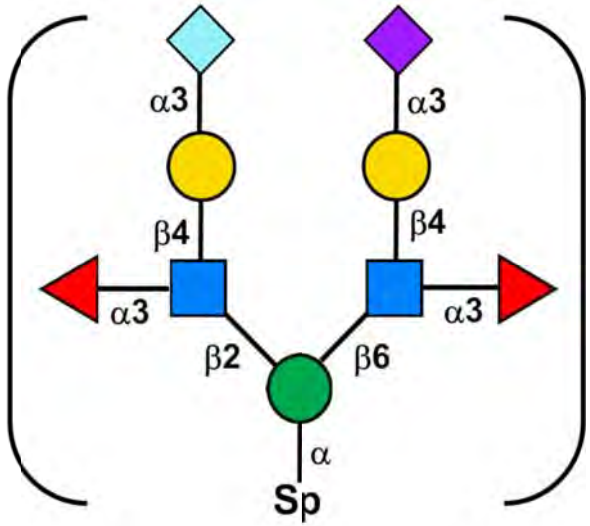

α3
α3
β4
β4
α3
α3
β2
β6
α
Sp

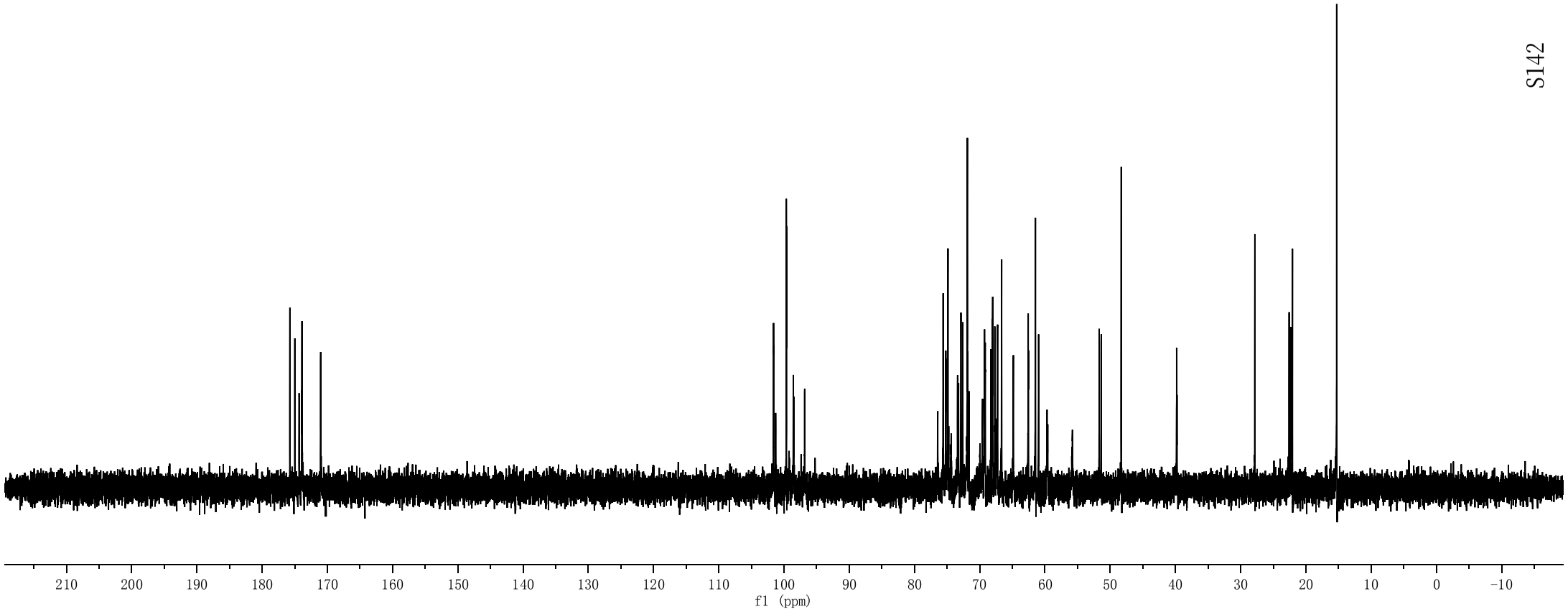
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1313

#49



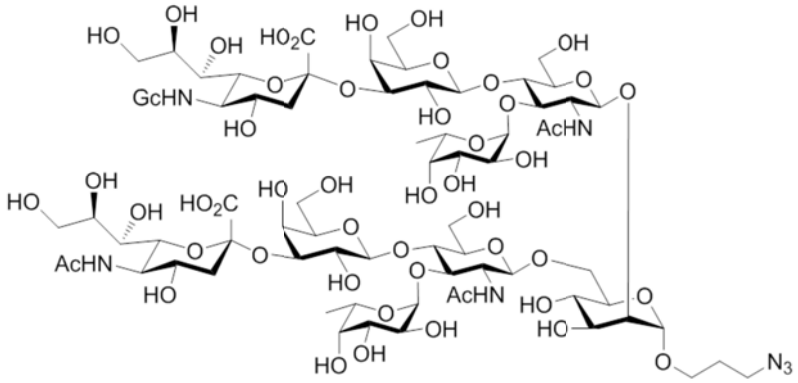


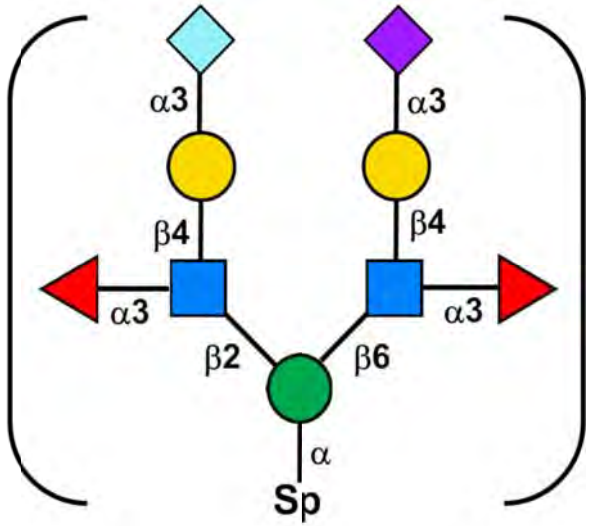


S142

CHZ-1313

#49

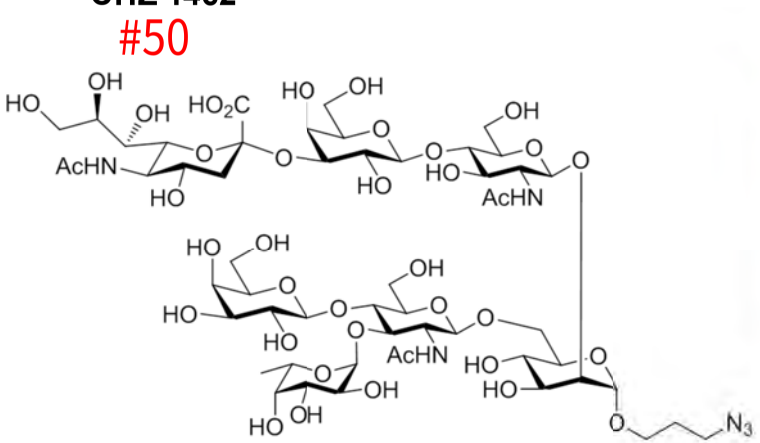

HO
OH
HO2C
GcHN
AcHN
N3

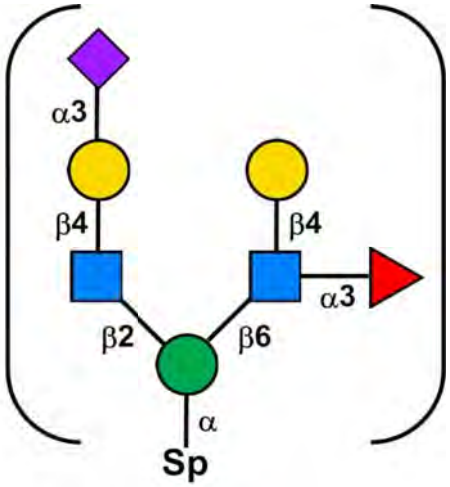

α3
α3
β4
β4
α3
α3
β2
β6
α
Sp

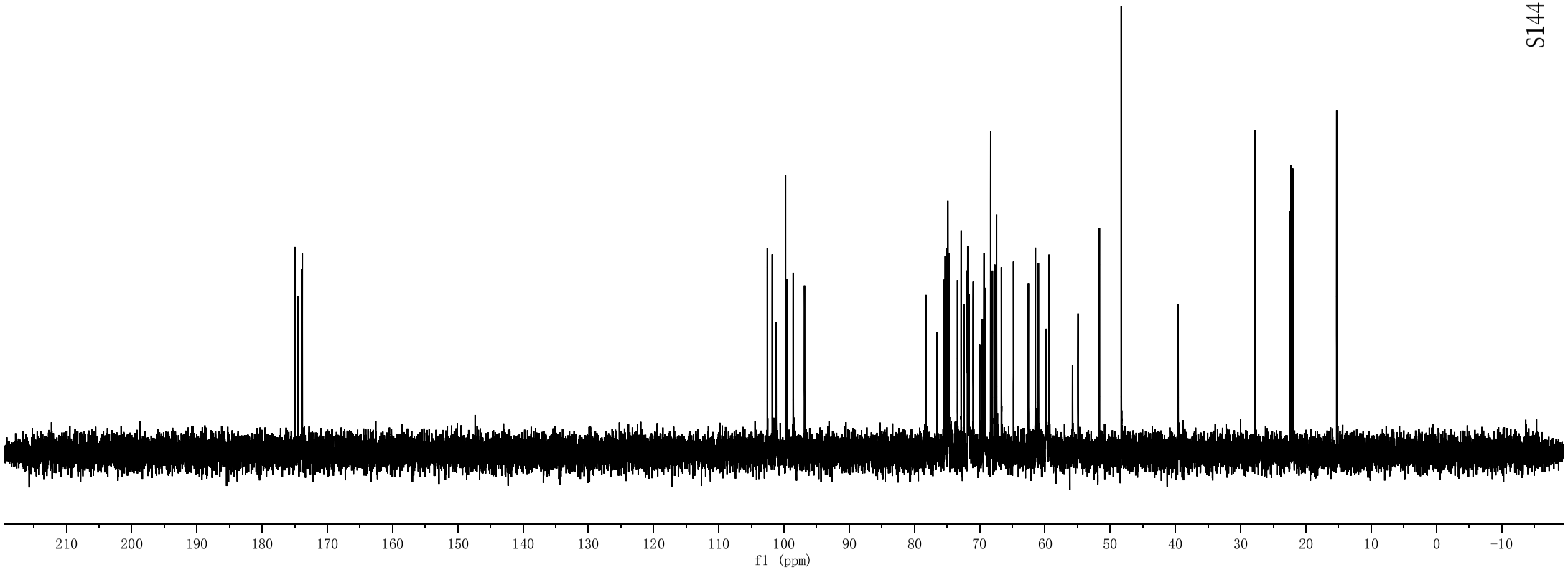
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1462

#50

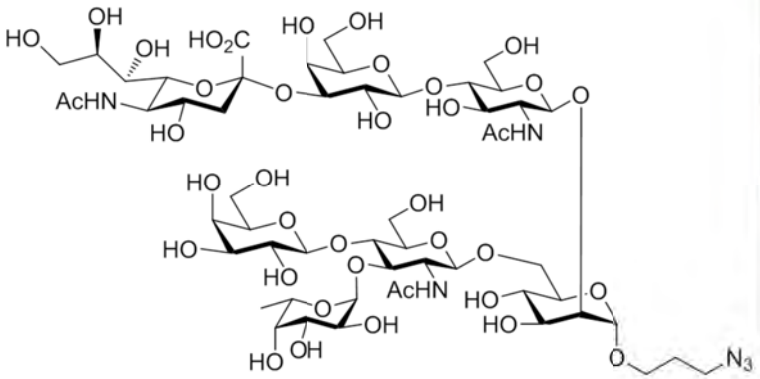


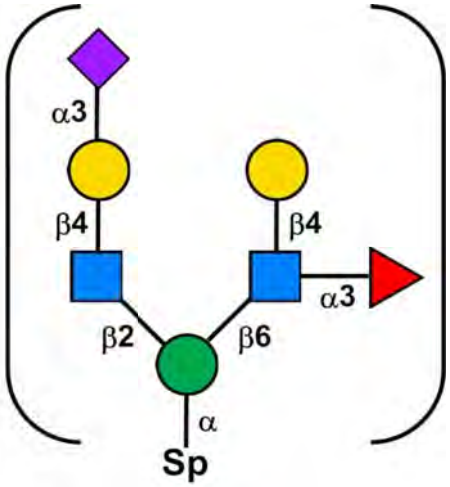

α3
β4
β4
α3
β2
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CHZ-1462

#50

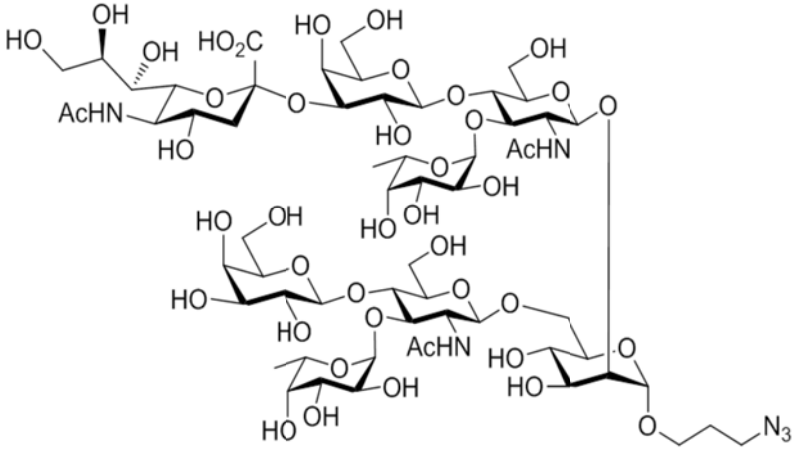


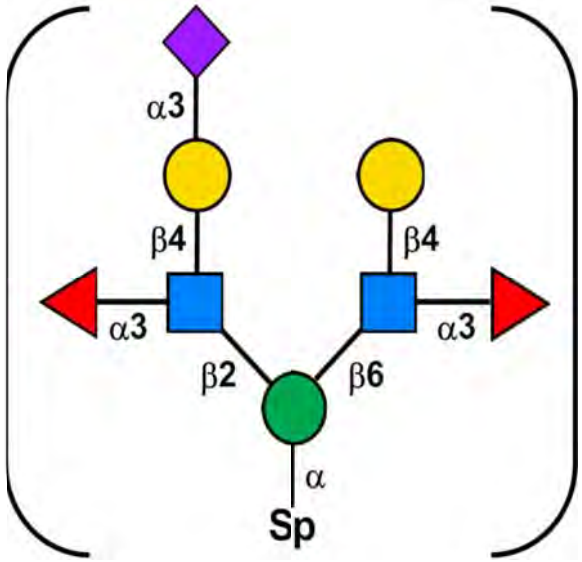

α3
β4
β4
α3
β2
β6
α
Sp

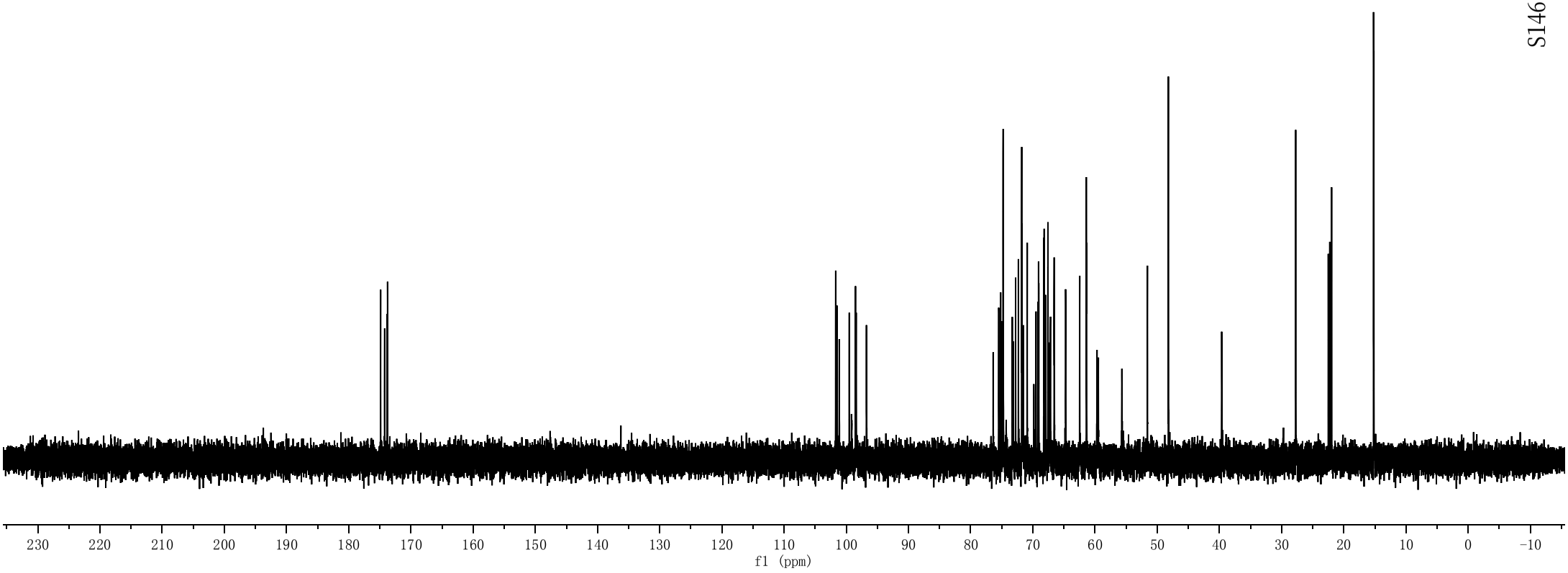
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1327

#51

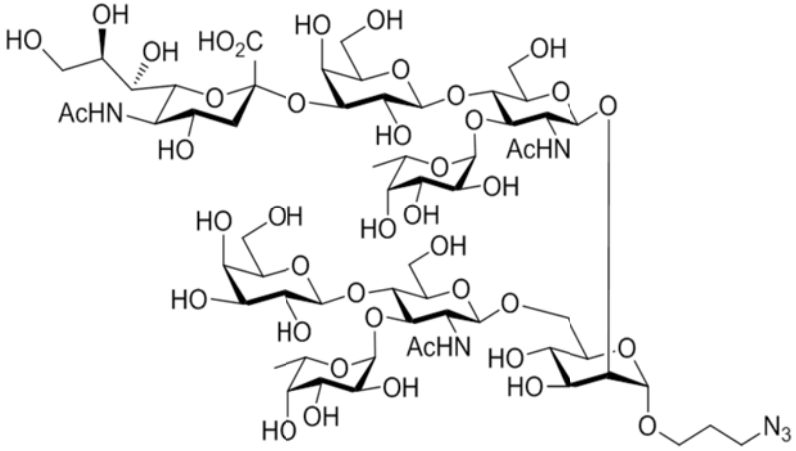


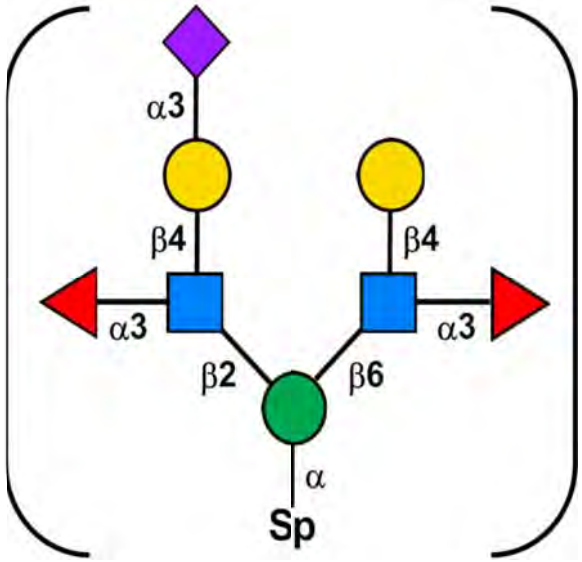

α3
β4
β4
α3
α3
β2
β6
α
Sp


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

CHZ-1327

#51

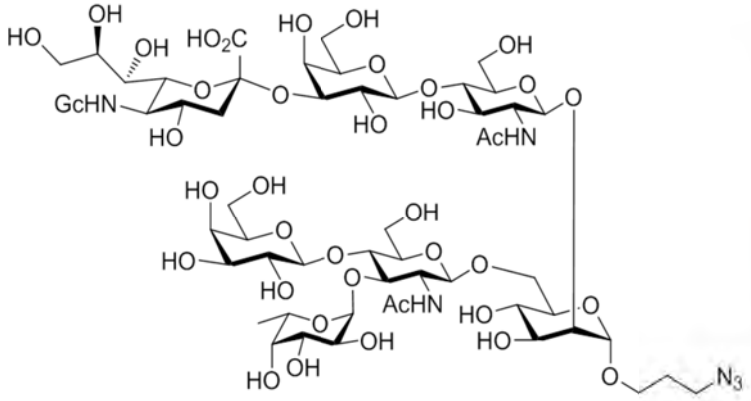


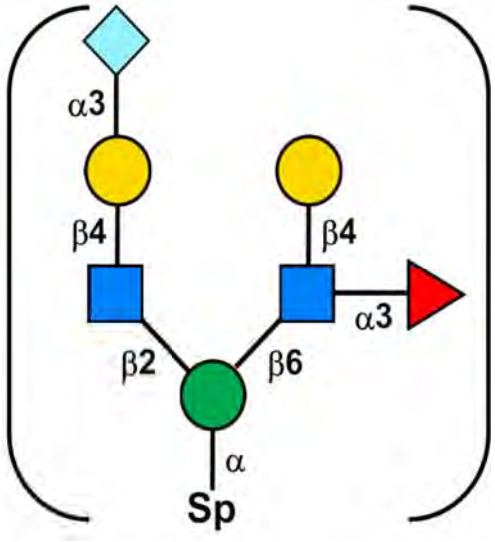

α3
β4
β4
α3
α3
β2
β6
α
Sp

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
f1 (ppm)

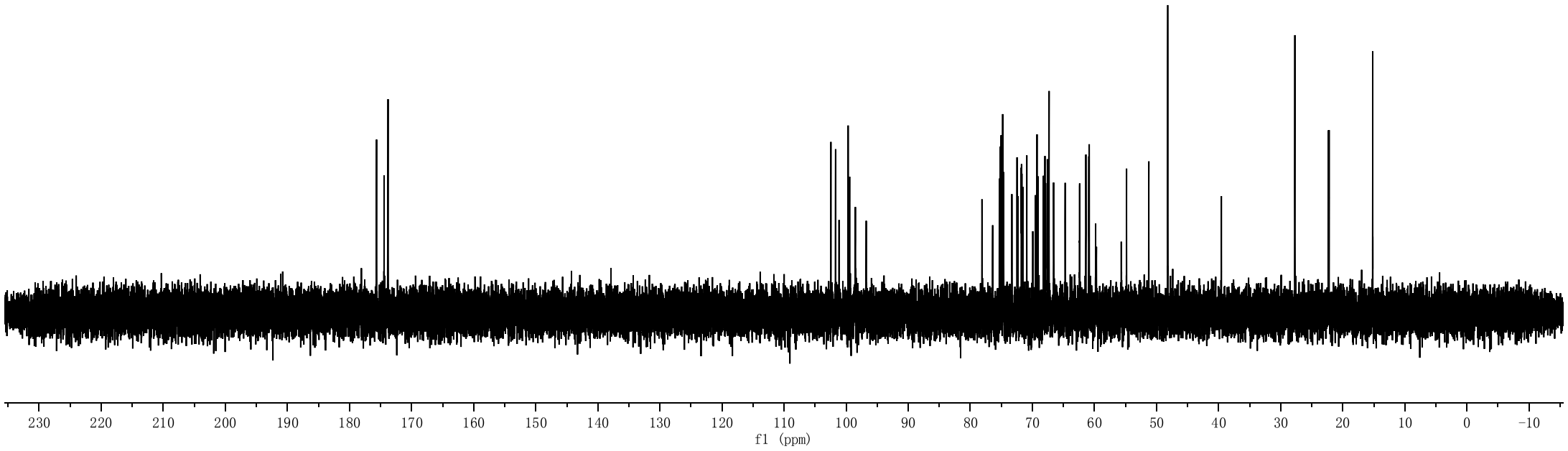
CHZ-875

#52



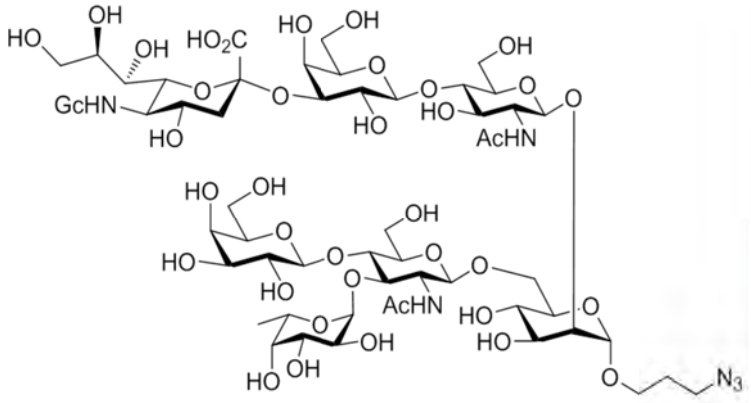


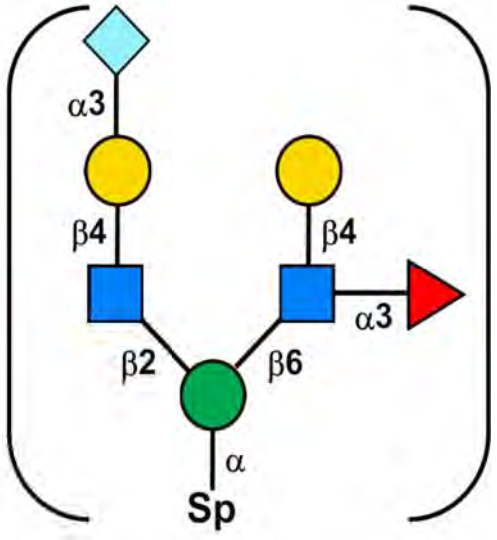
S148



CHZ-875

#52



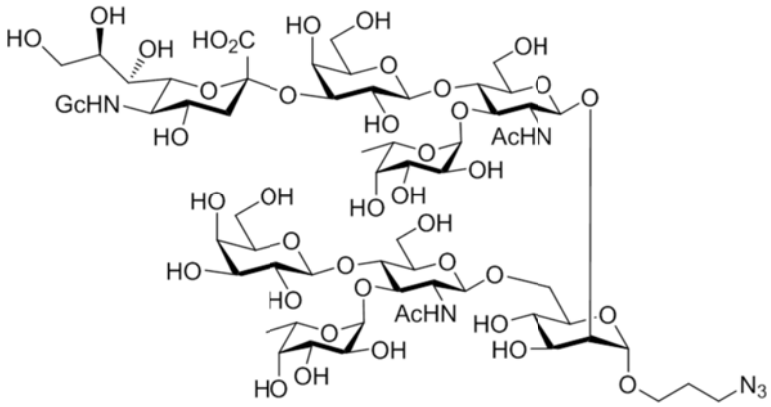


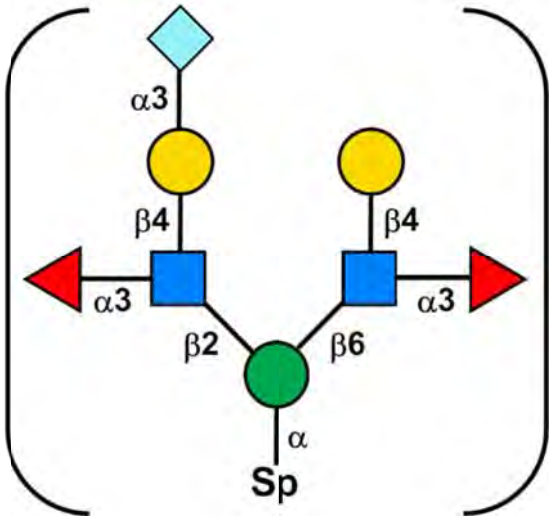
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

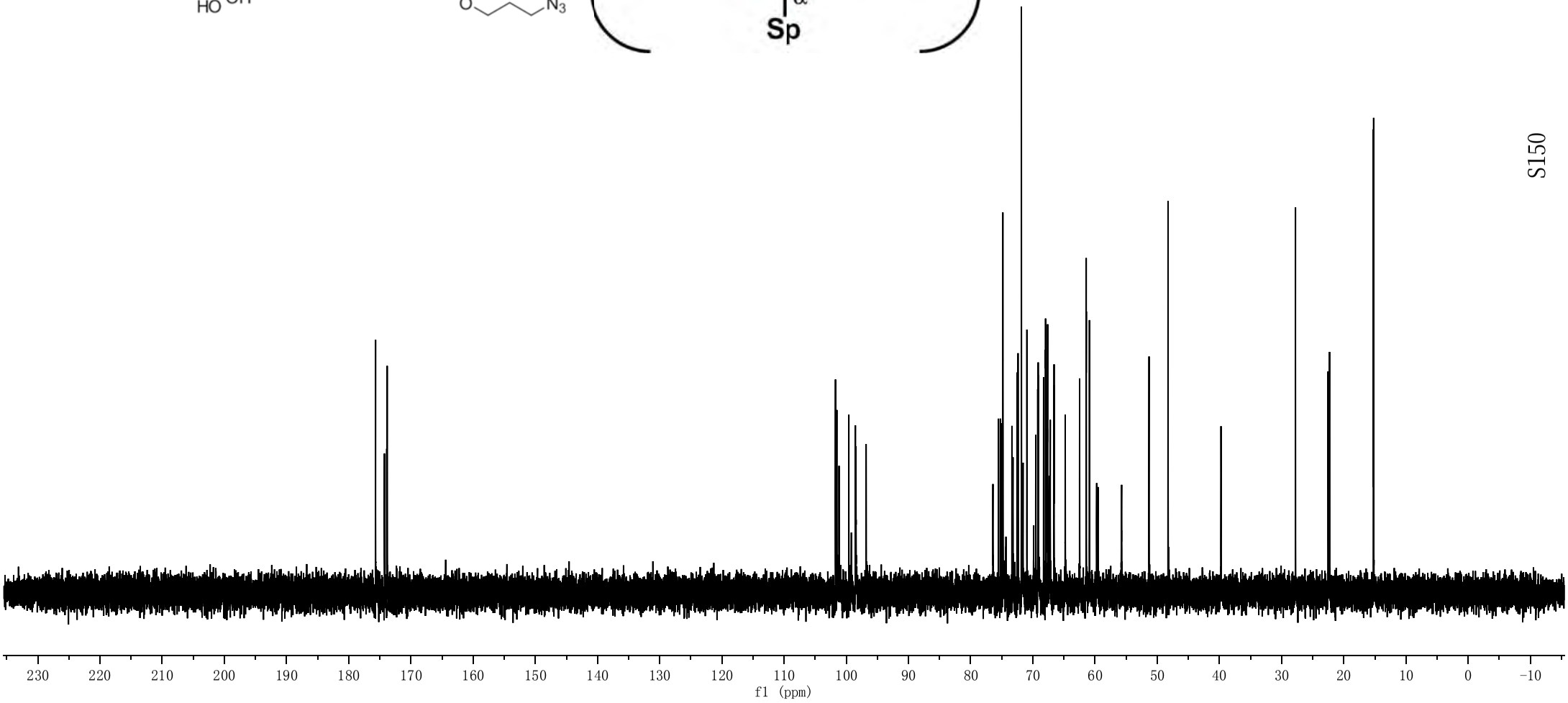
CHZ-1353

#53



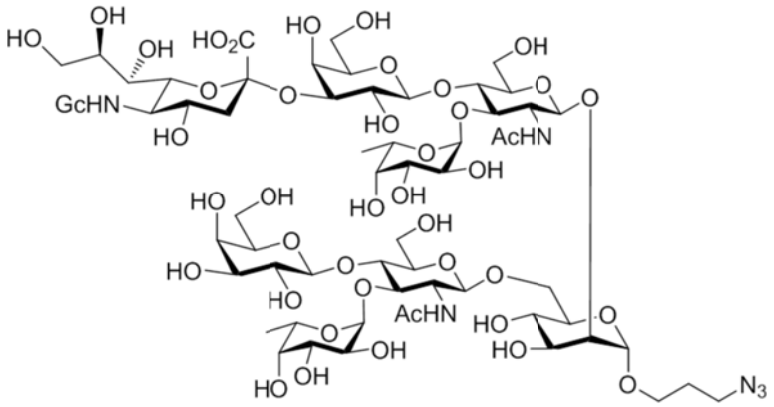


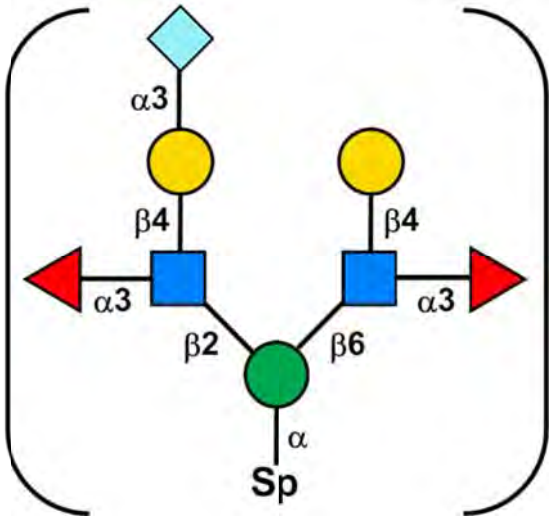
S150



CHZ-1353

#53

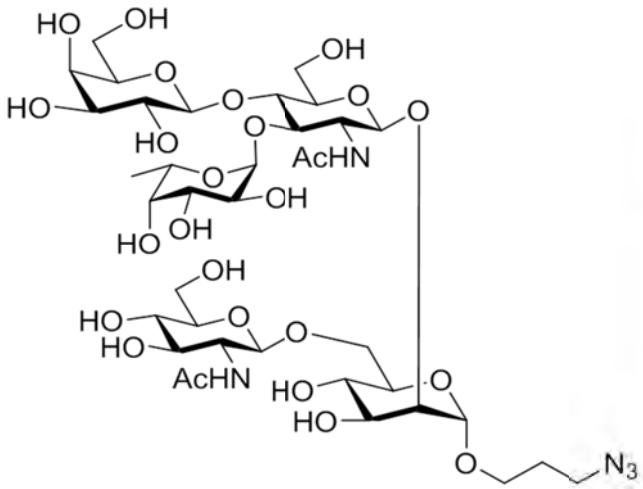


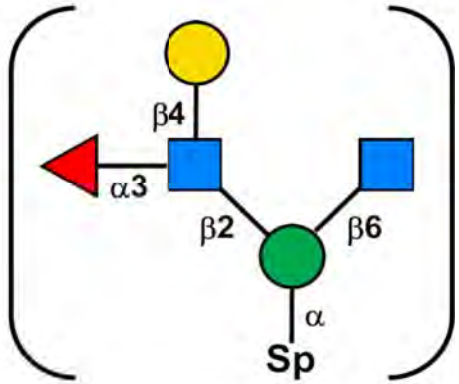


S151

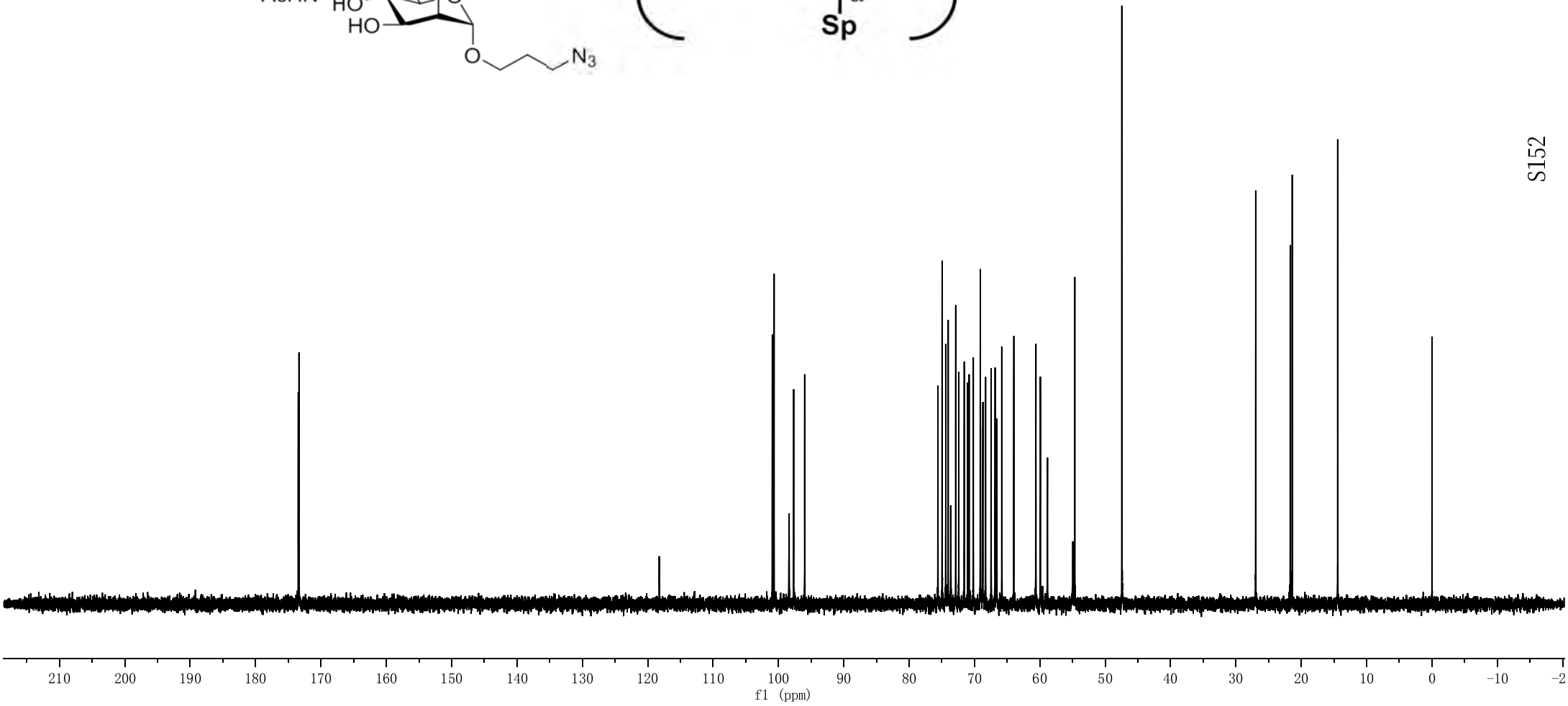
CHZ-1071

#54



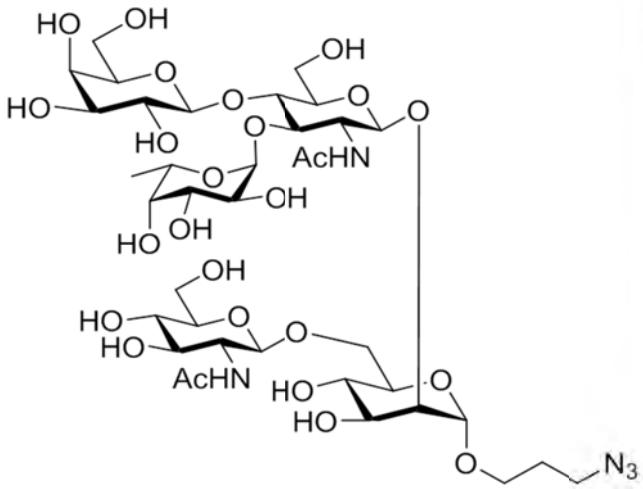


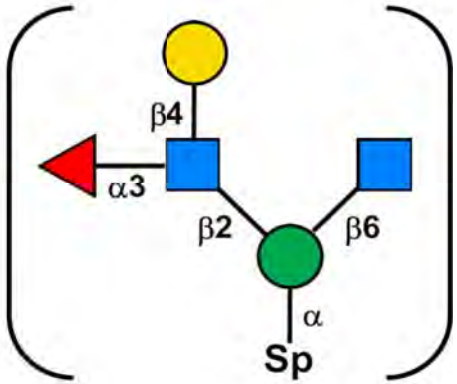
S152



CHZ-1071

#54

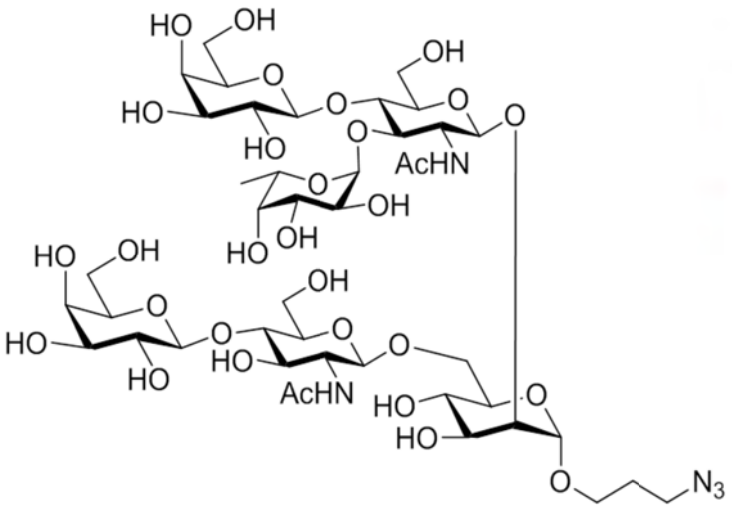

HO
OH
HO
O
O
OH
O
HO
HO
AcHN
O
OH
HO
OH
HO
OH
HO
HO
AcHN
O
HO
HO
O
O
N3

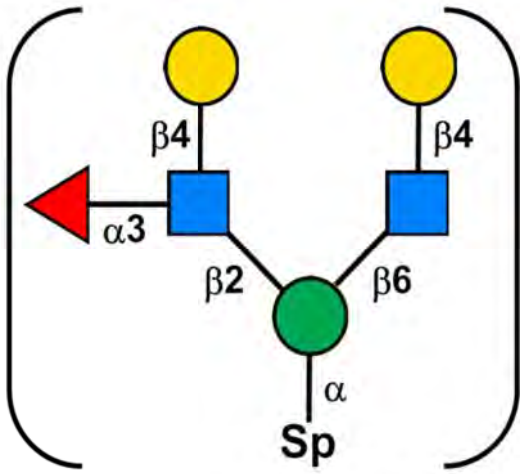

β4
α3
β2
β6
α
Sp

8.0
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
f1 (ppm)

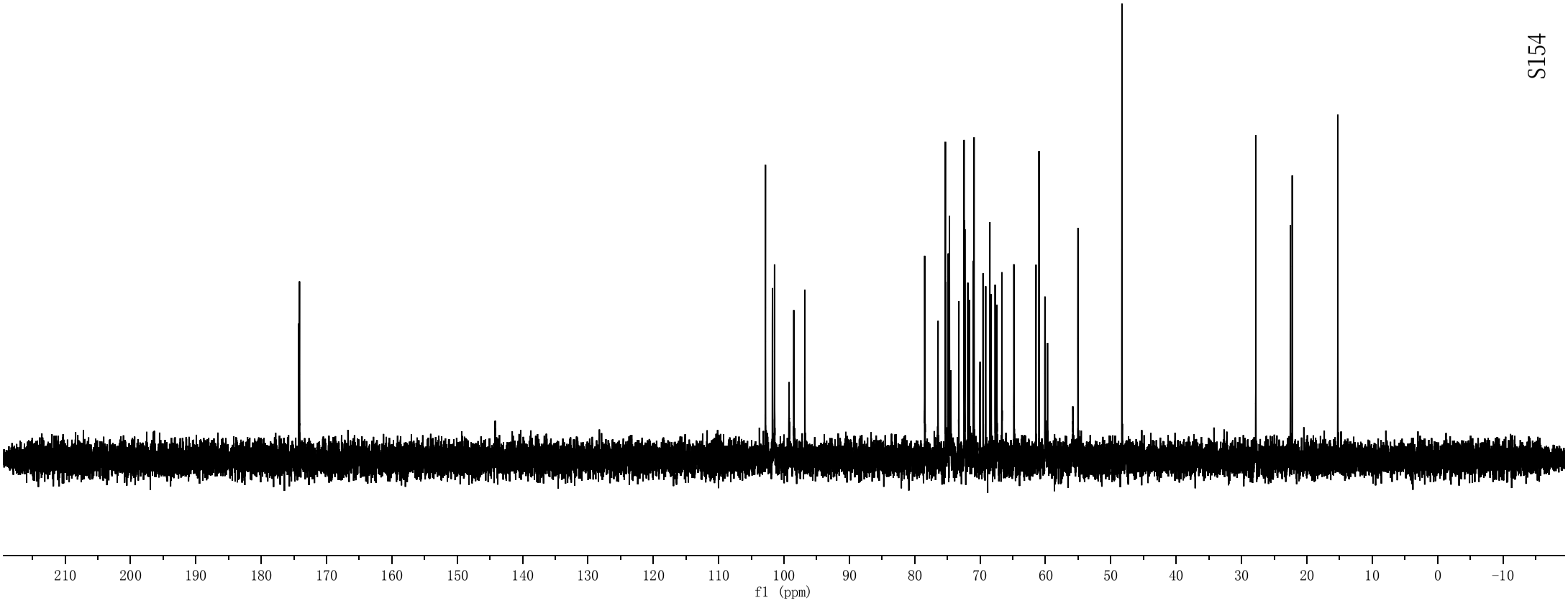
CHZ-1432

#55



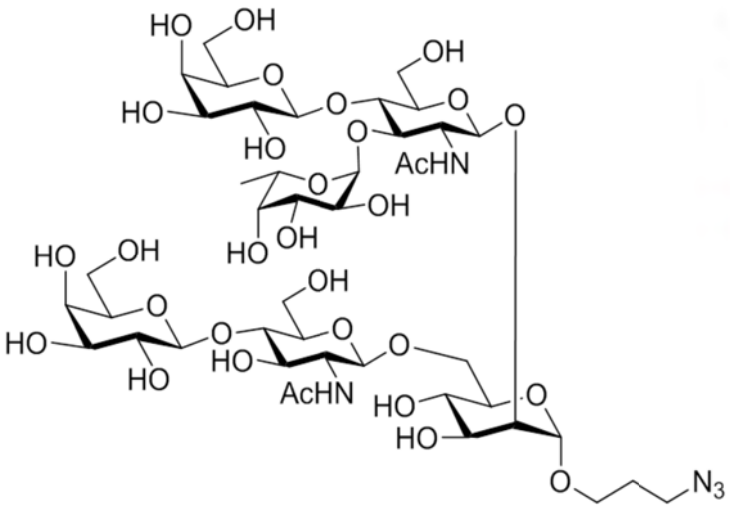


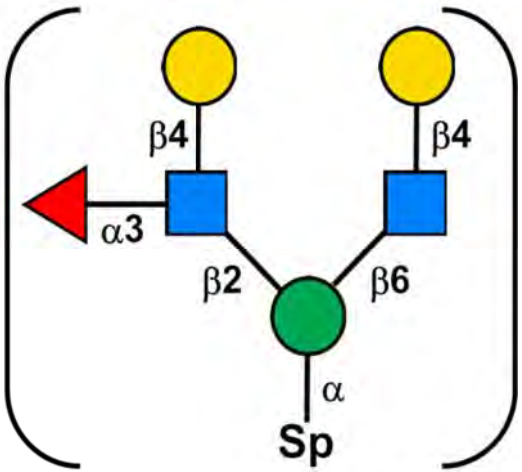
S154



CHZ-1432

#55

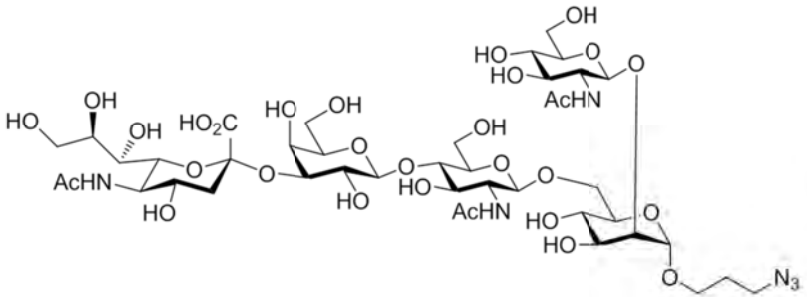


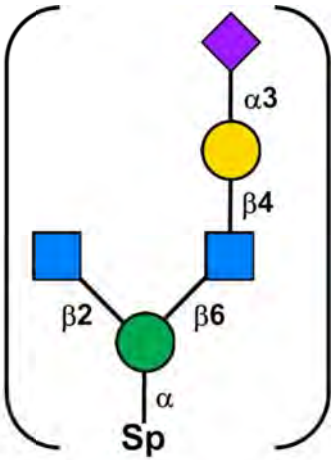


S155

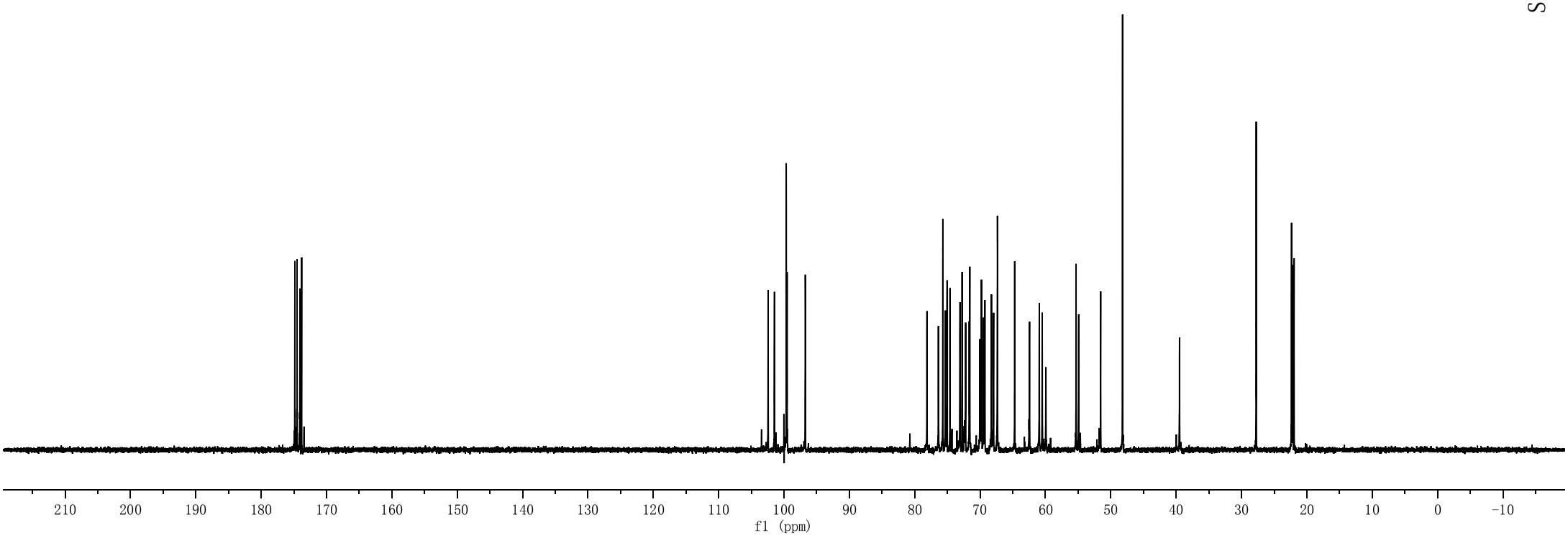
CHZ-966

#56



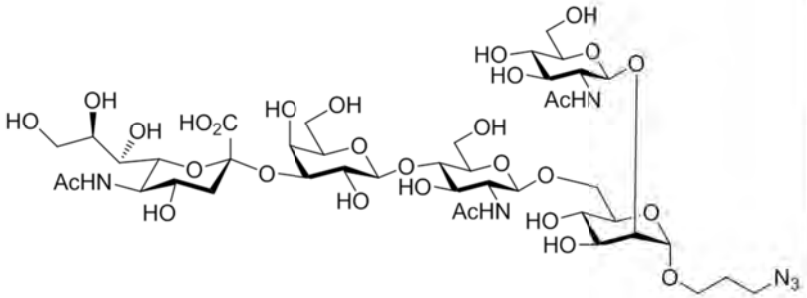


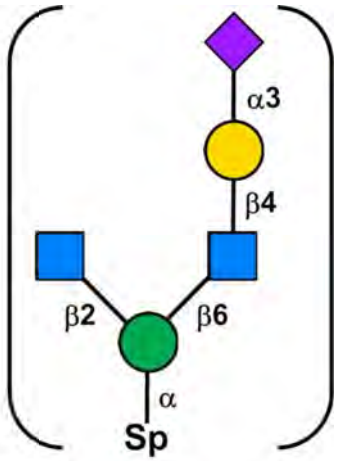
S156



CHZ-966

#56

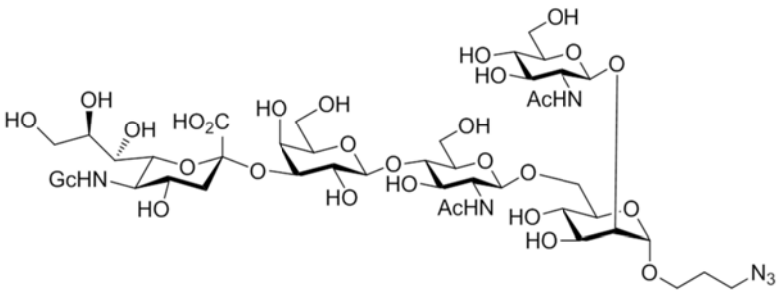

HO
OH
OH
AcHN
HO
HO2C
HO
OH
HO
O
HO
AcHN
OH
HO
HO
AcHN
HO
HO
O
O
O
O
O
O
O
N3

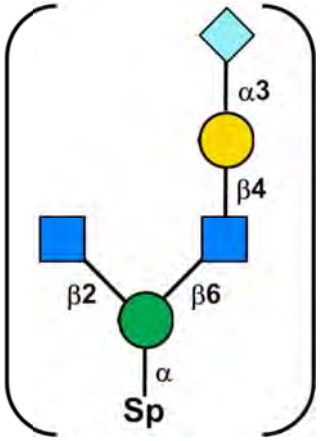

α3
β4
β2
β6
α
Sp

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
f1 (ppm)

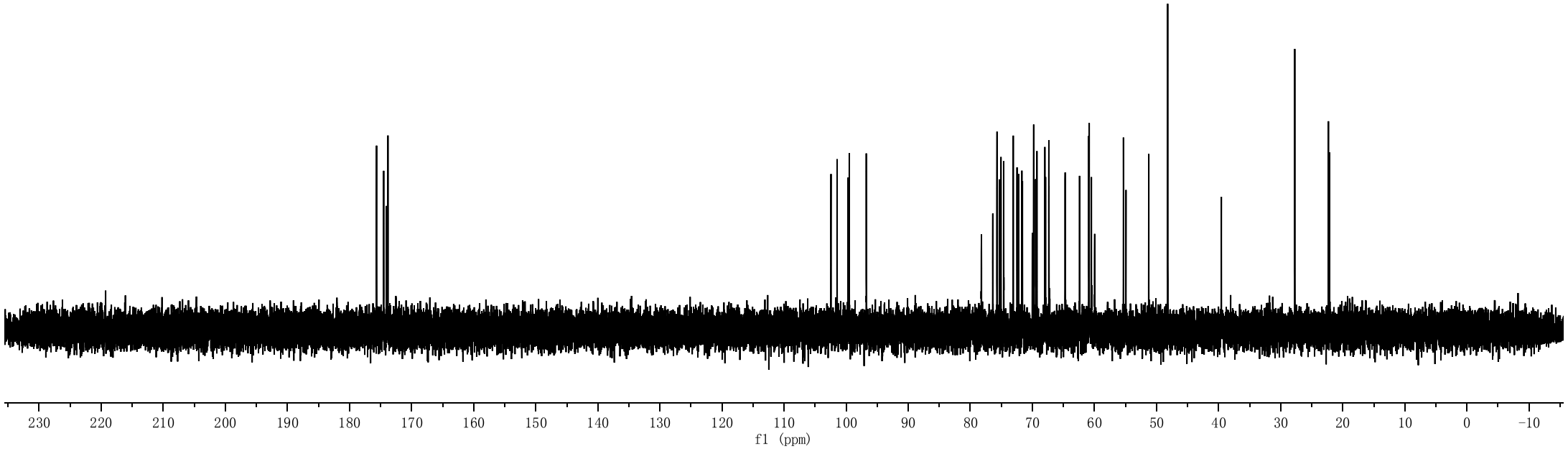
CHZ-876

#57



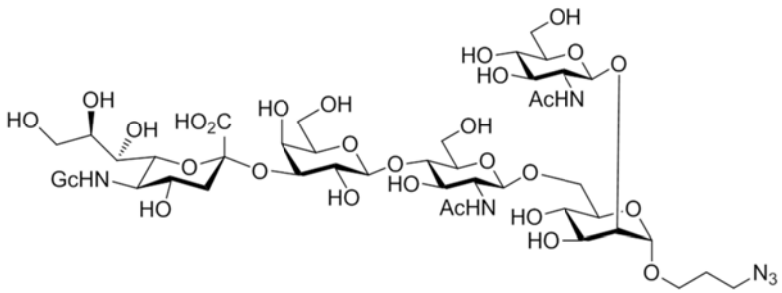


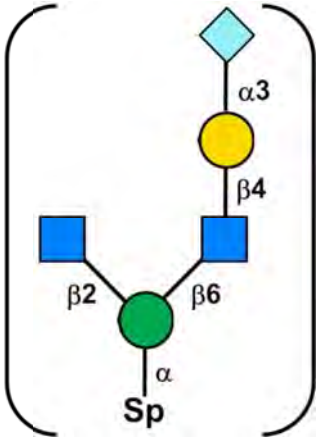
S158



CHZ-876

#57

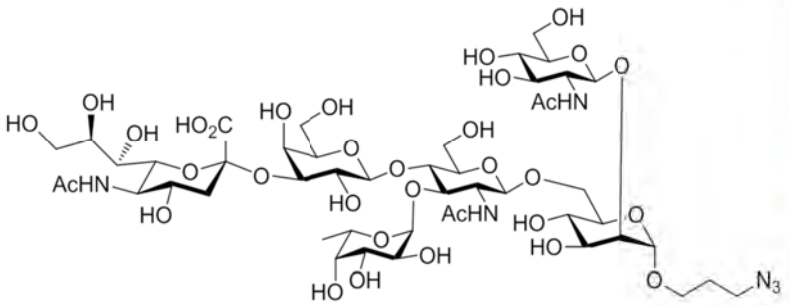

OH
HO
HO
O
O
AcHN
HO
OH
HO
HO2C
OH
HO
O
O
O
O
GcHN
HO
HO
AcHN
HO
HO
O
O
N3

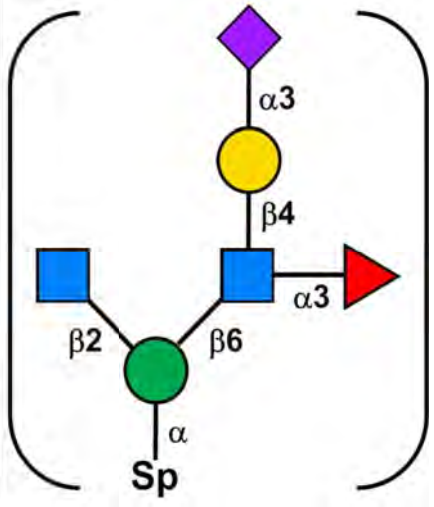

α3
β4
β2
β6
α
Sp

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
f1 (ppm)

CHz-1015

#58

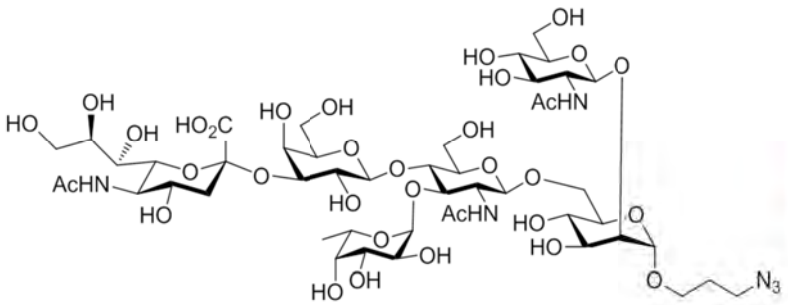


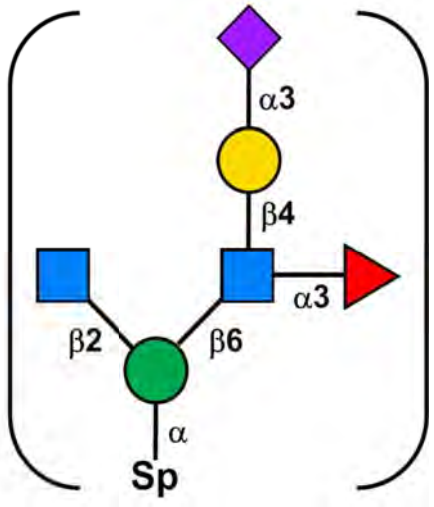


S160

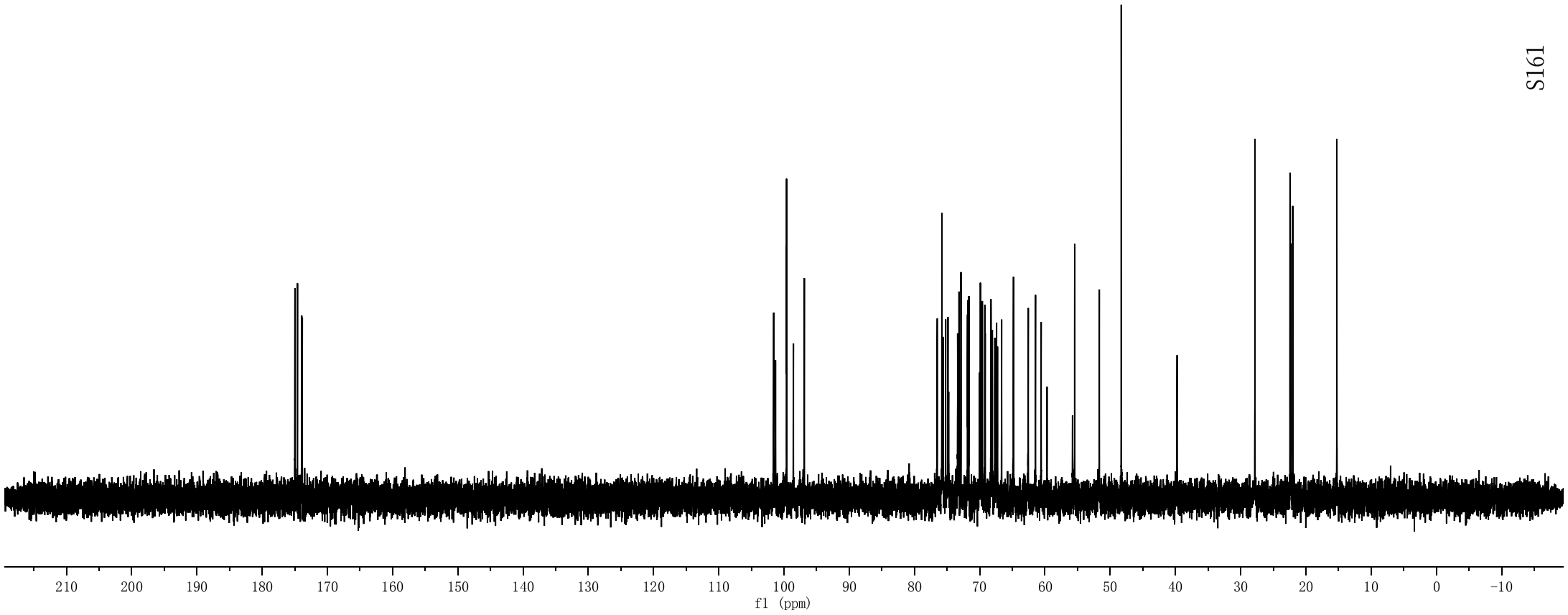
CHz-930

#58



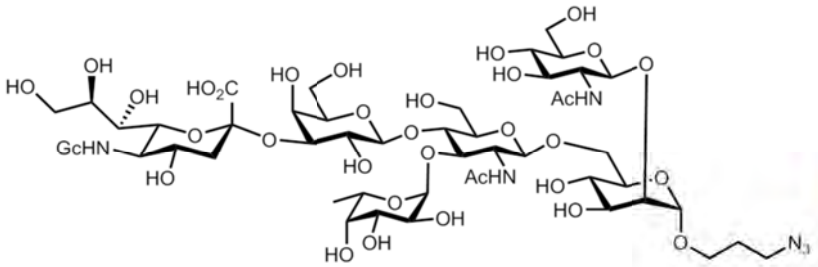


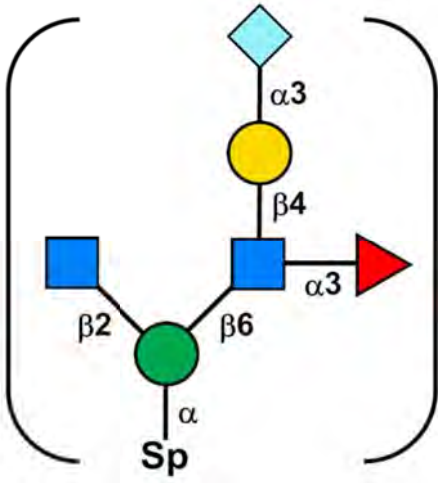
S161



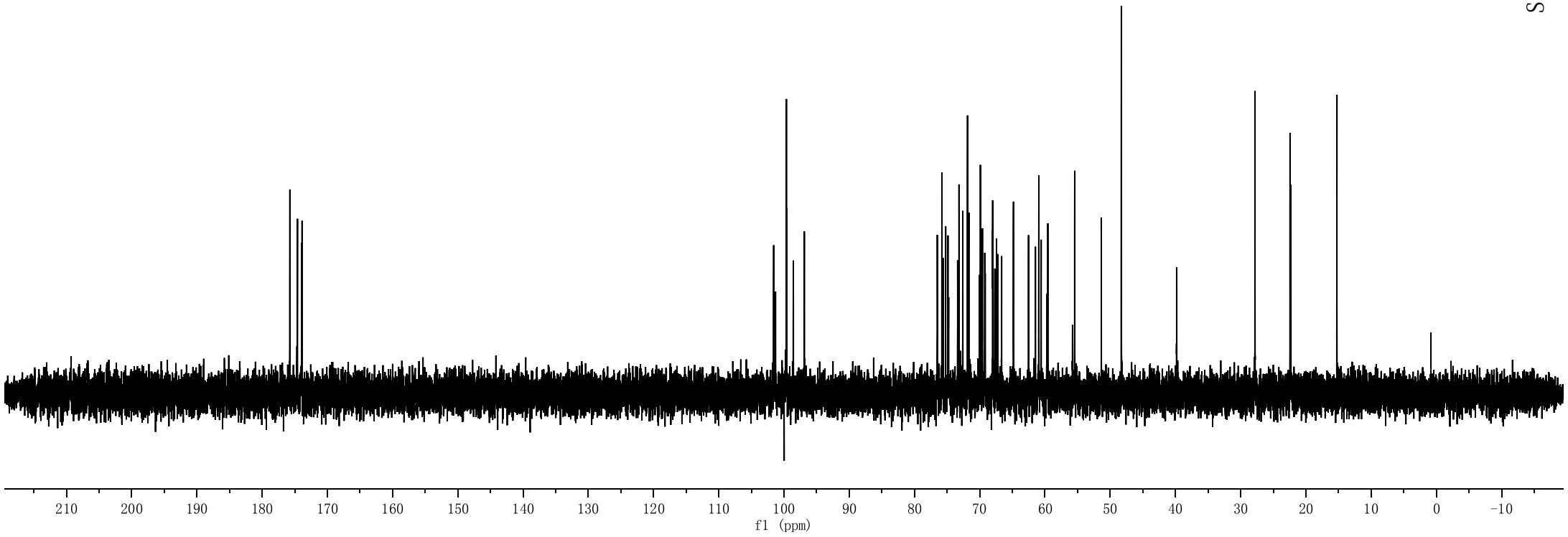
CHZ-939

#59



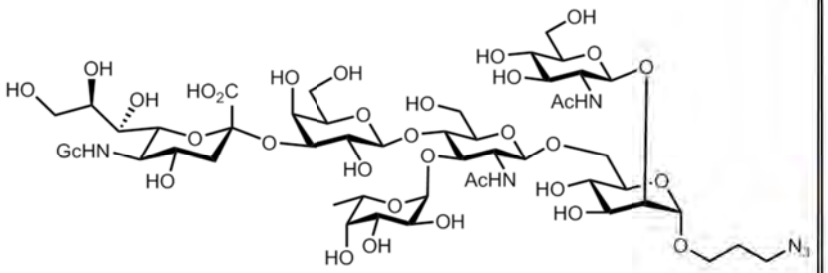


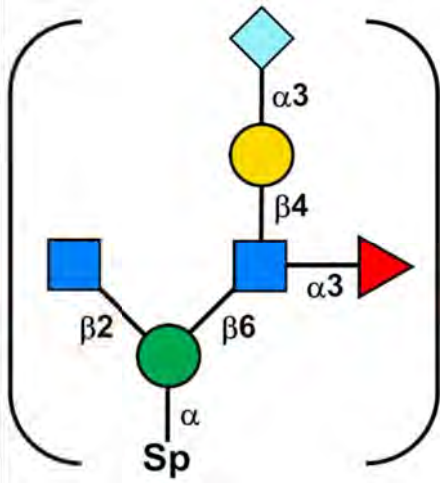
S162



CHZ-939

#59

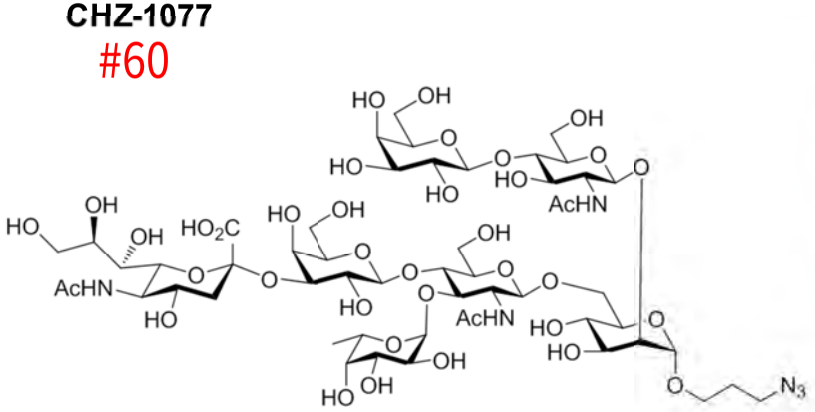


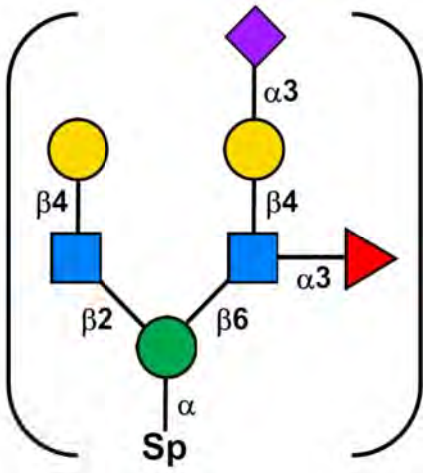


S163

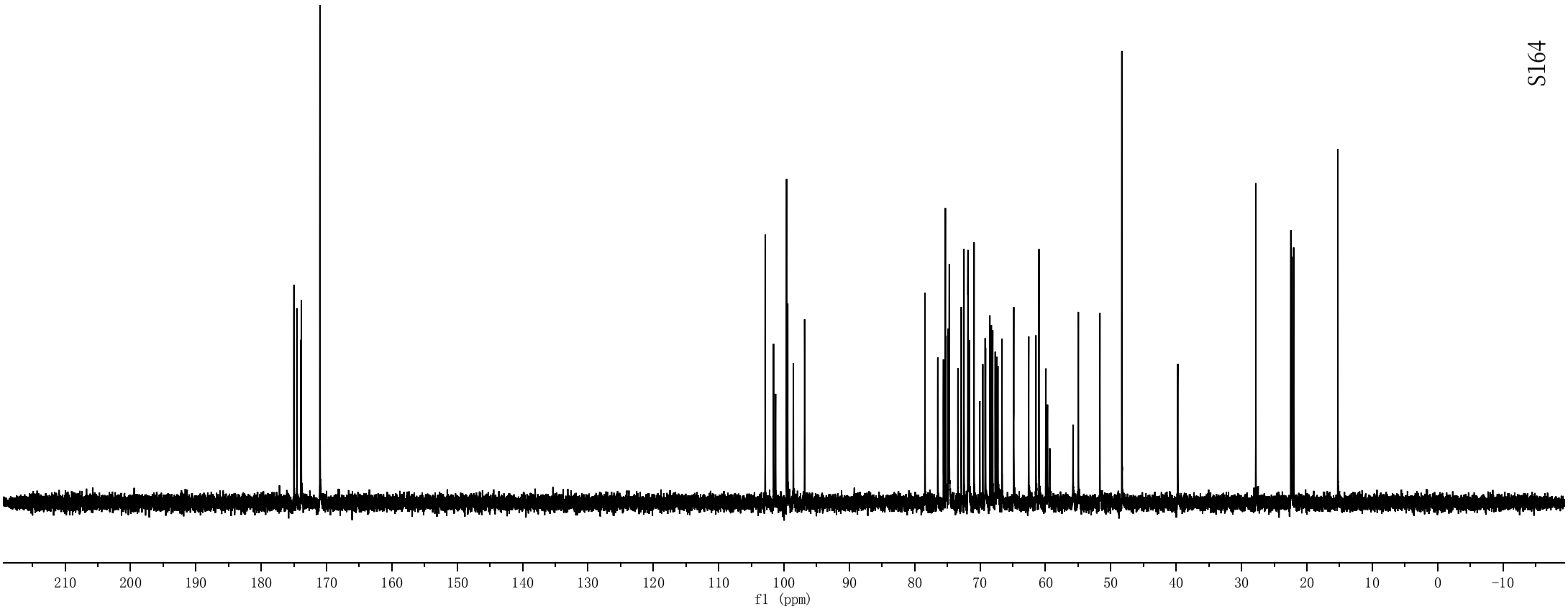
CHZ-1077

#60



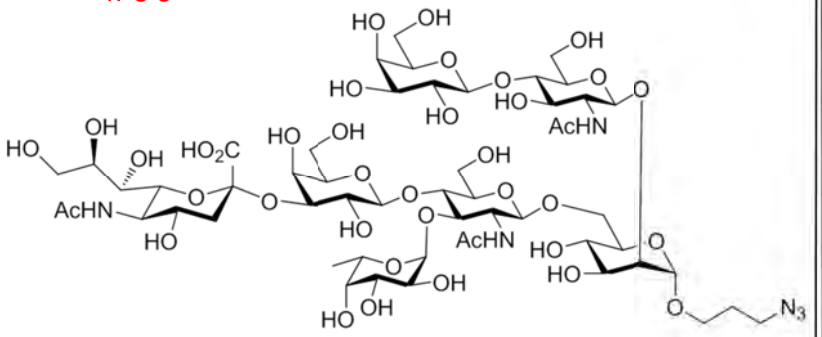


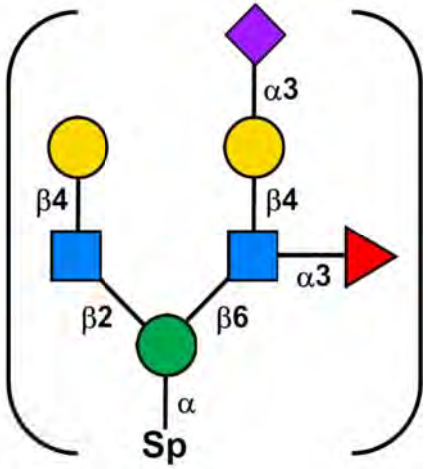
S164



CHZ-1077

#60





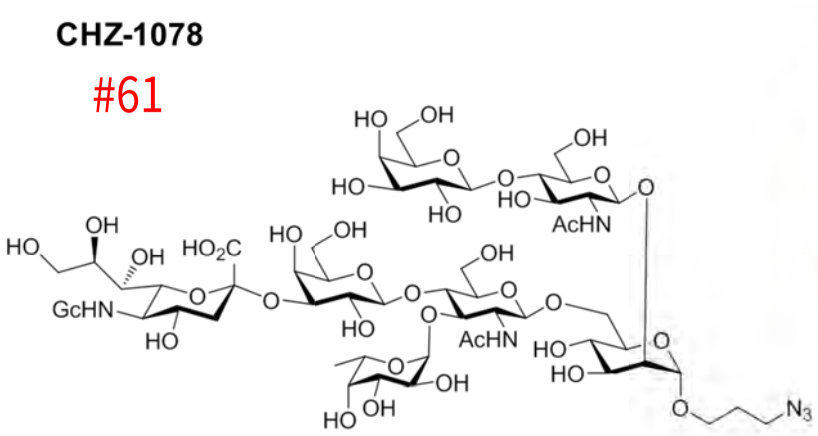
S165

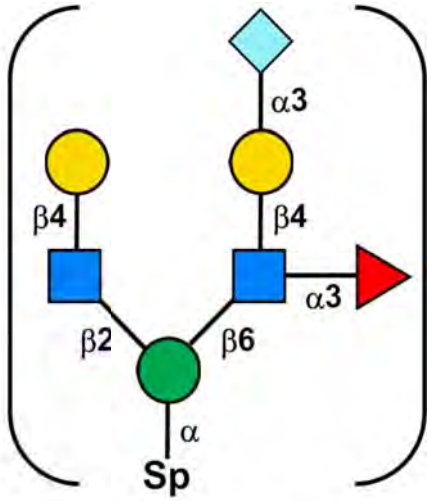
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

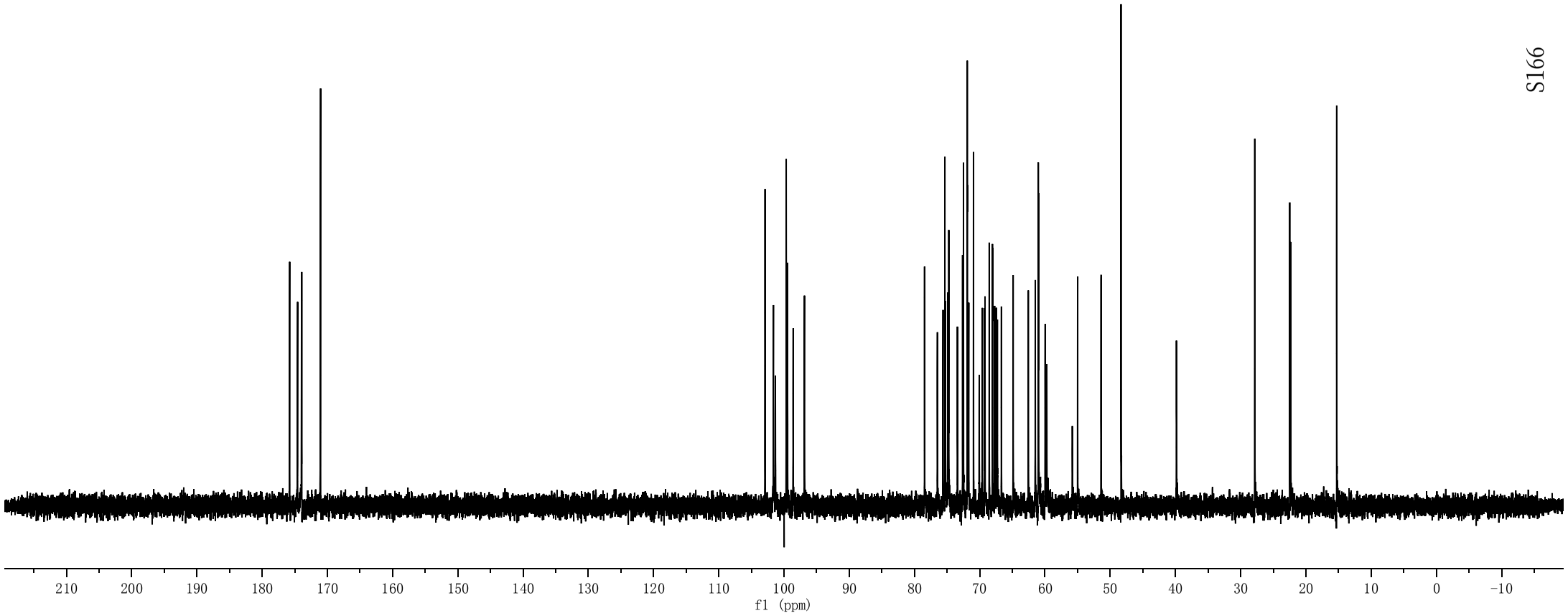
f1 (ppm)

CHZ-1078

#61



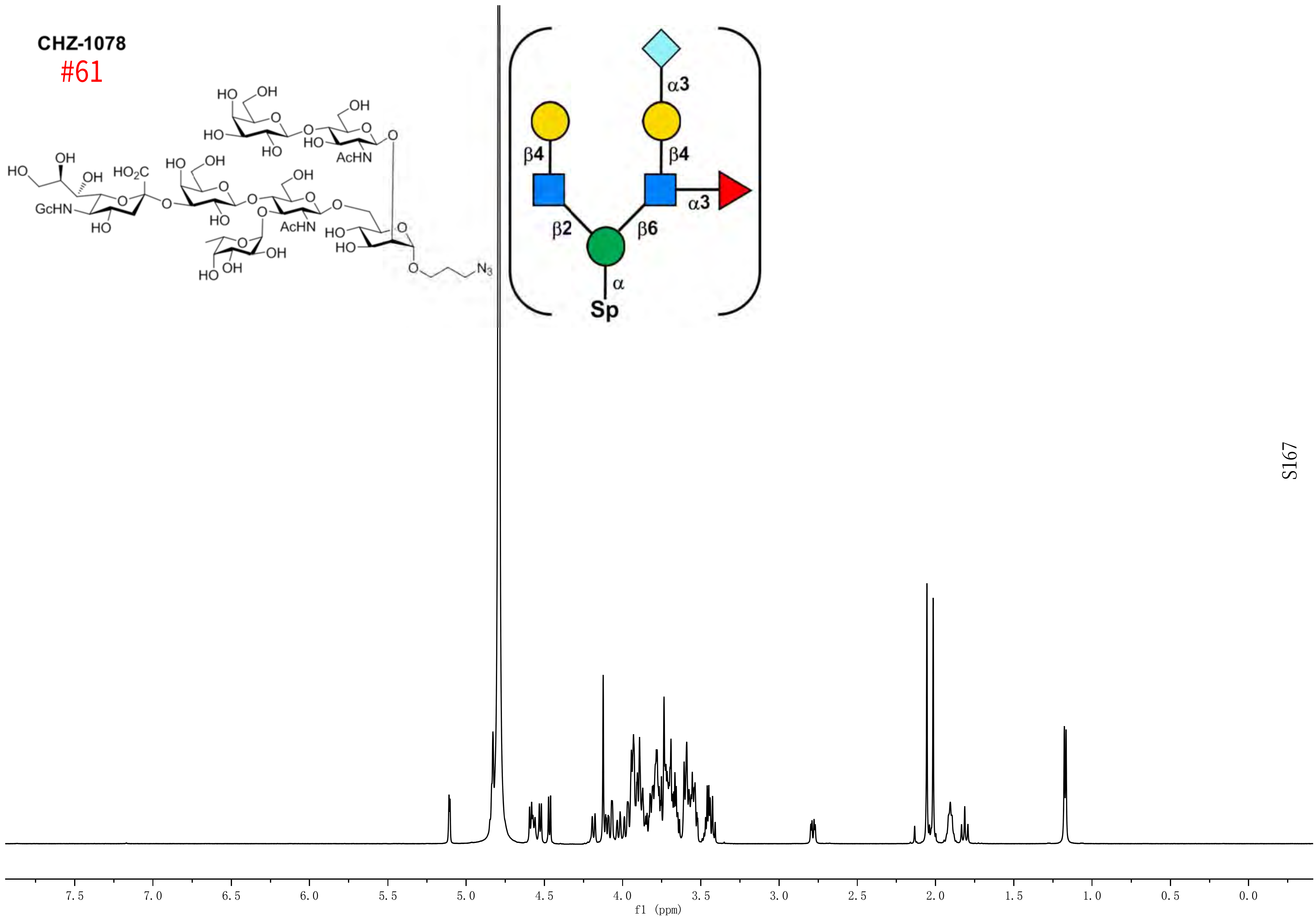




S166

CHZ-1078

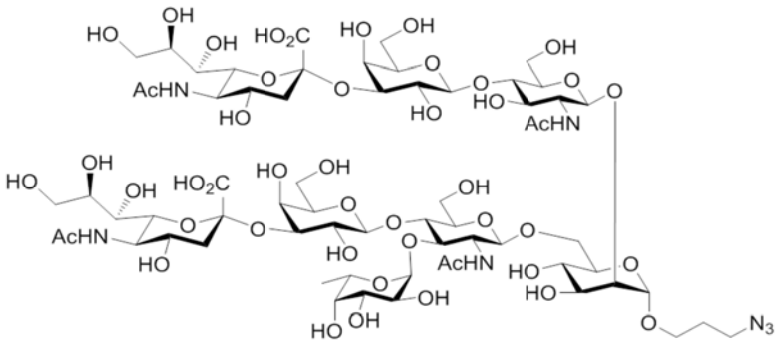
#61

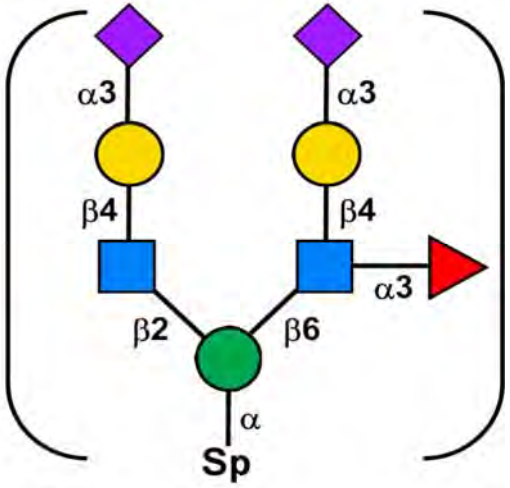


HO
OH
OH
HO2C
GcHN
HO
O
HO
OH
HO
OH
AcHN
HO
OH
HO
HO
OH
HO
OH
O
N3
β4
β2
α
Sp
β6
β4
α3
α3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

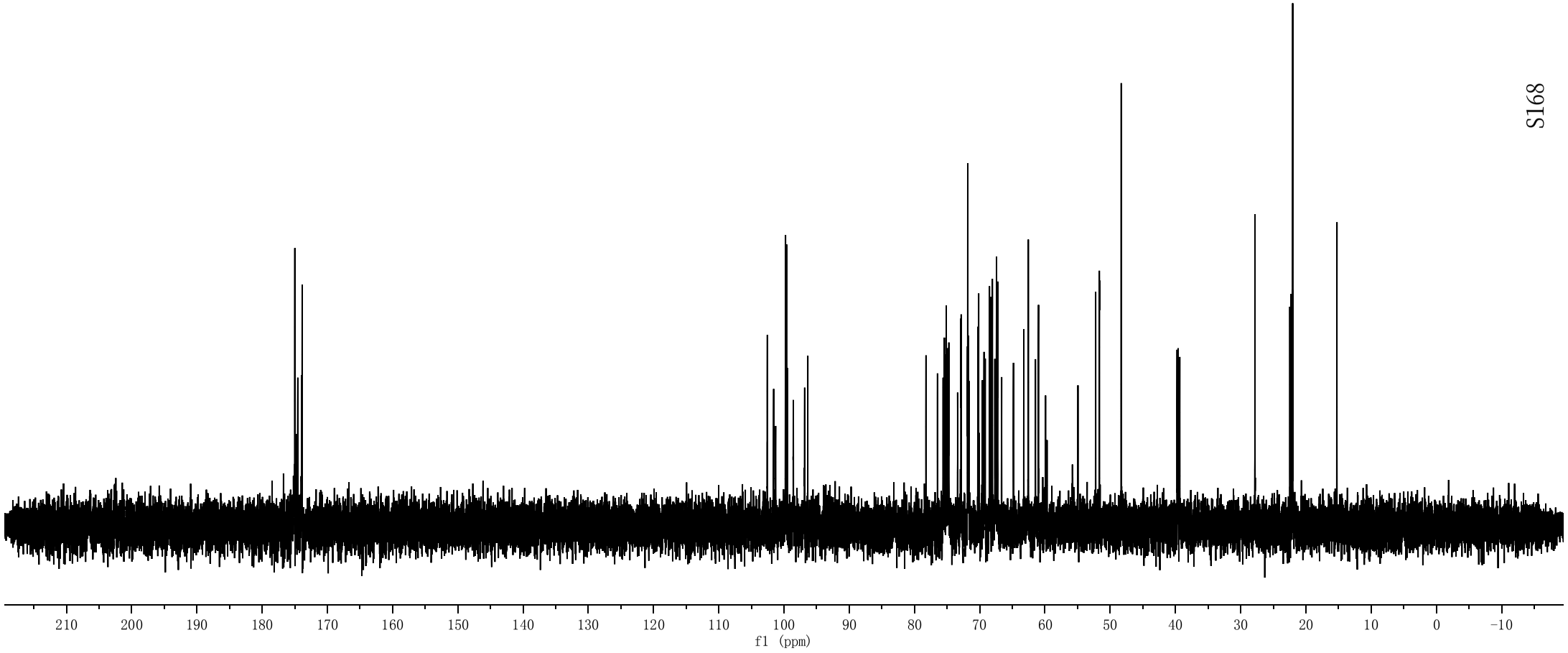
CHZ-1139

#62



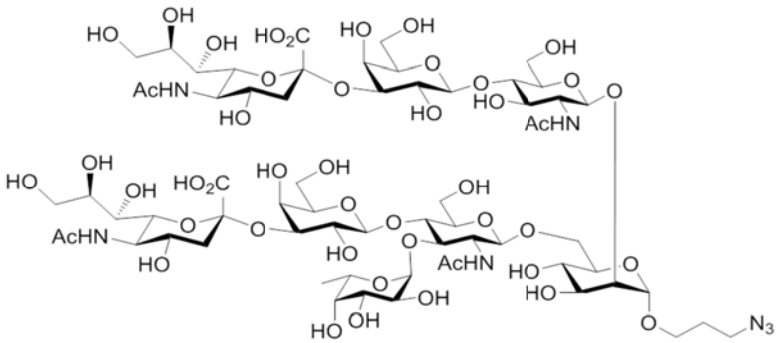


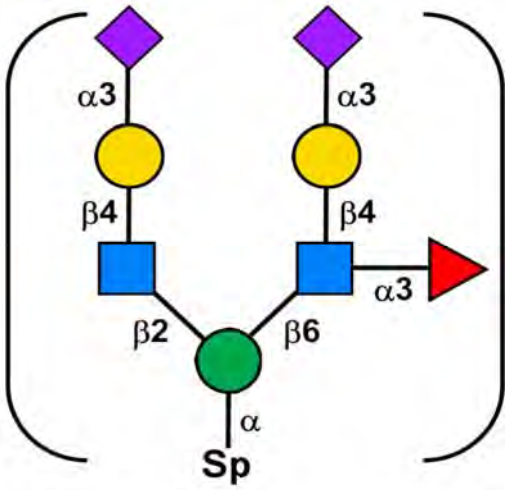
S168



CHZ-1139

#62

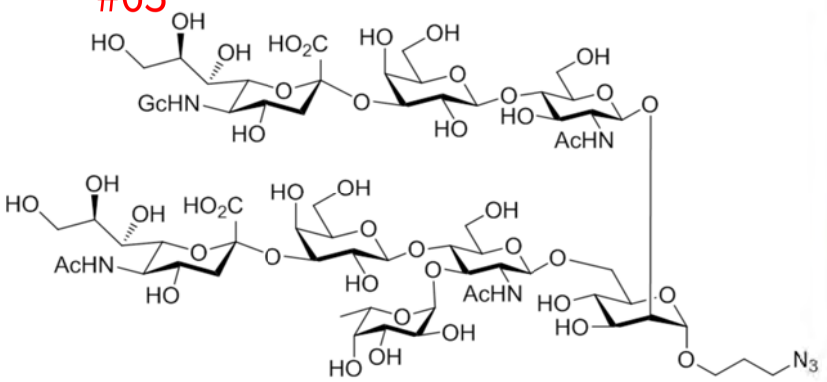


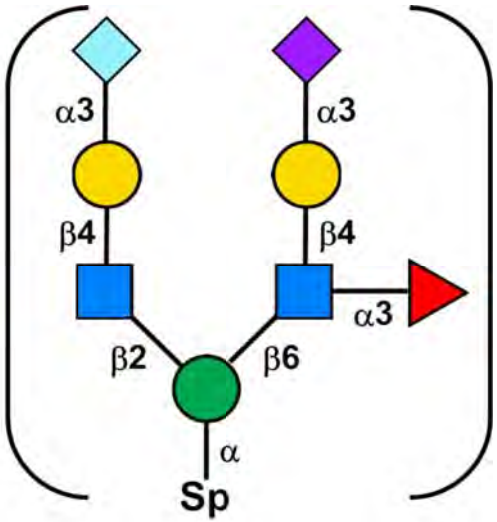

α3
α3
β4
β4
α3
β2
β6
α
Sp

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
f1 (ppm)

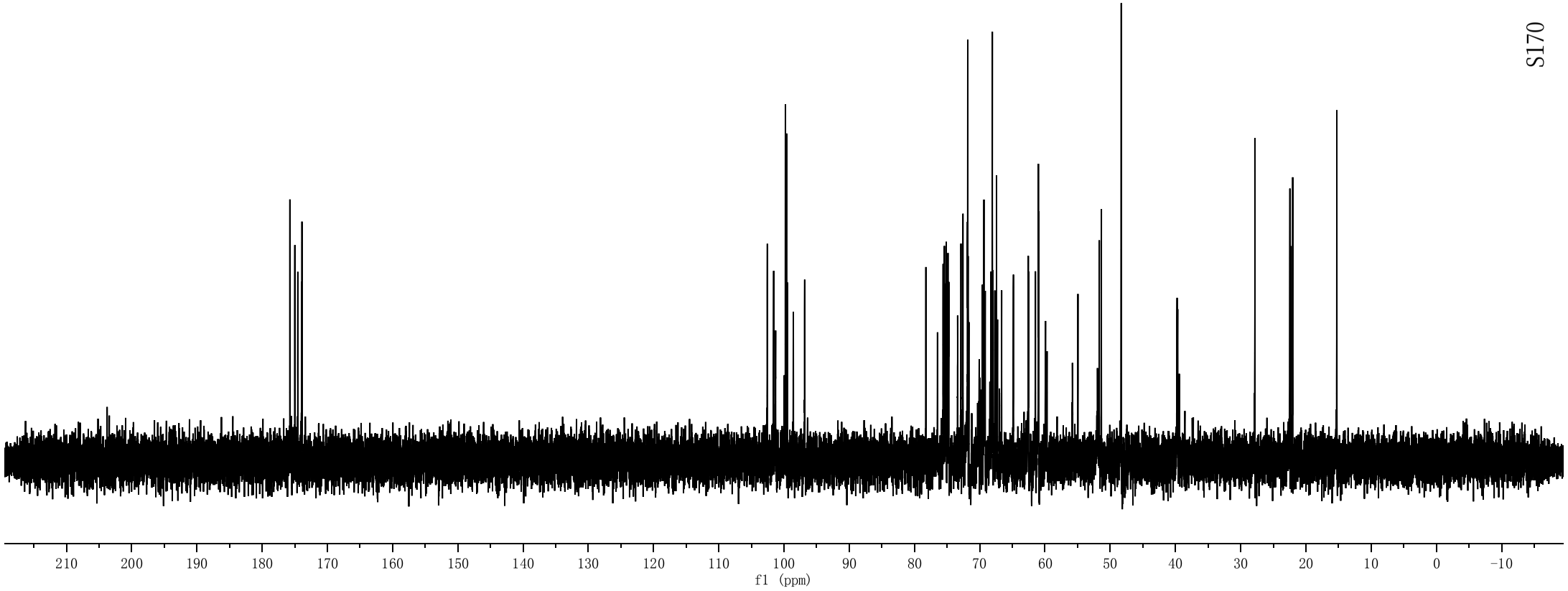
CHZ-1140

#63



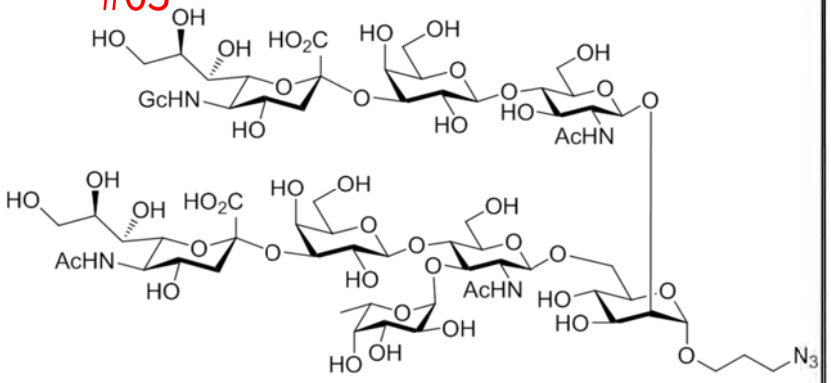


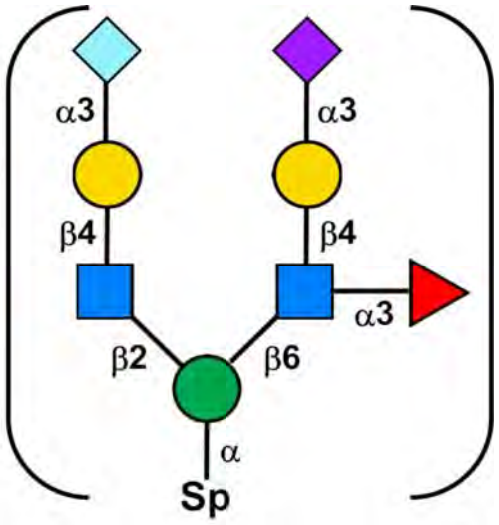
S170



CHZ-1140

#63

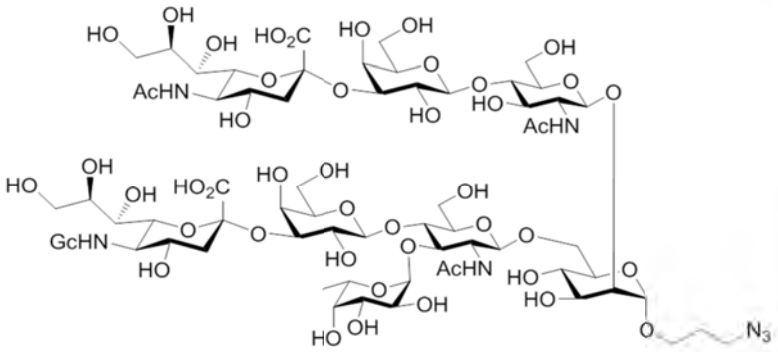


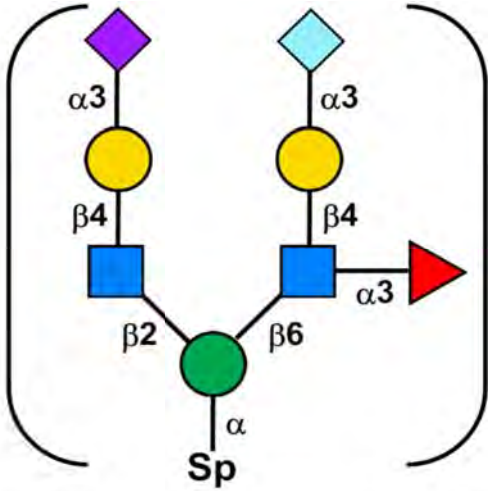


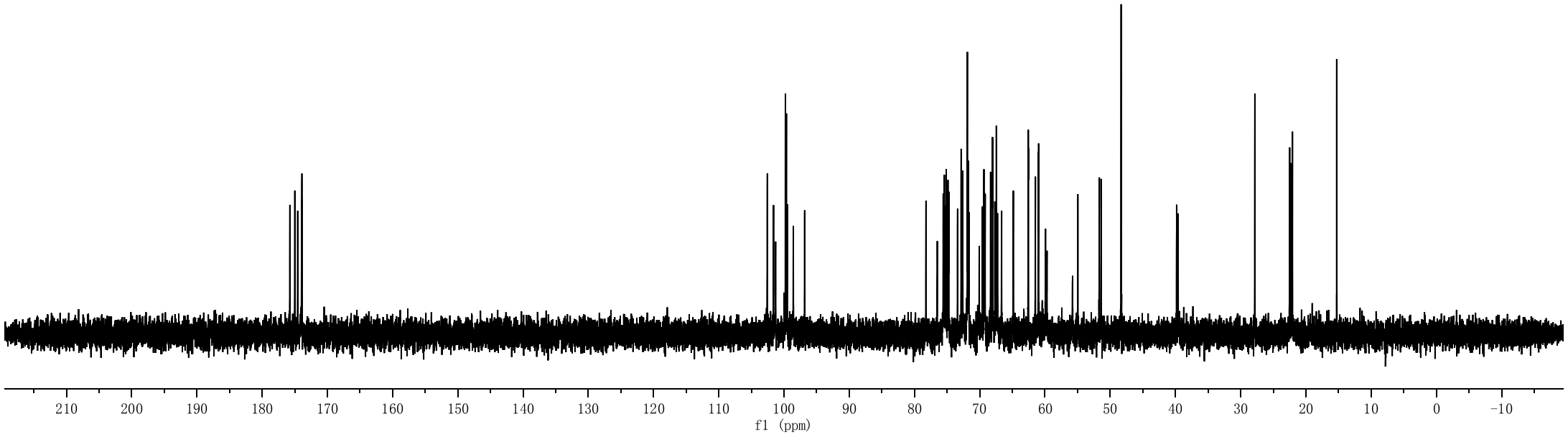
S171

CHZ-1446

#64

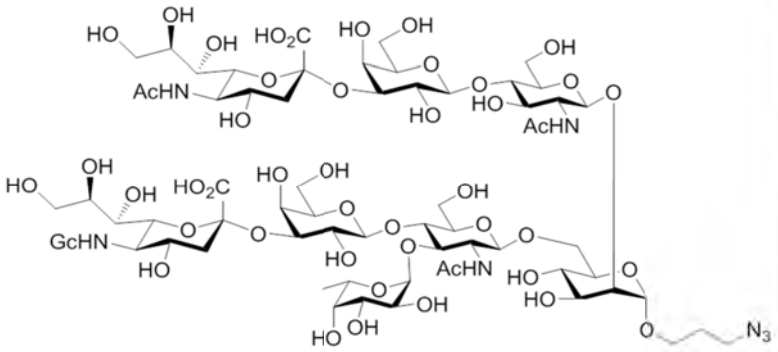

HO
OH
HO2C
AcHN
GcHN
N3

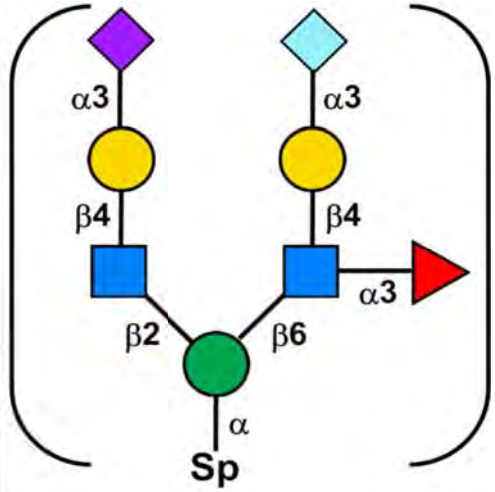

α3
α3
β4
β4
α3
β2
β6
α
Sp


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHZ-1099

#64

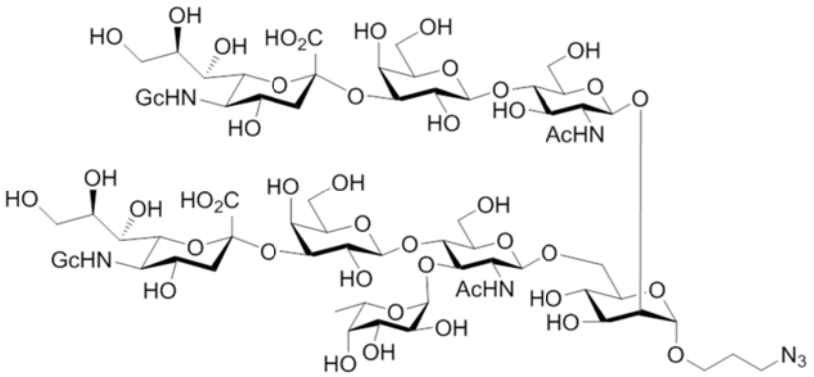


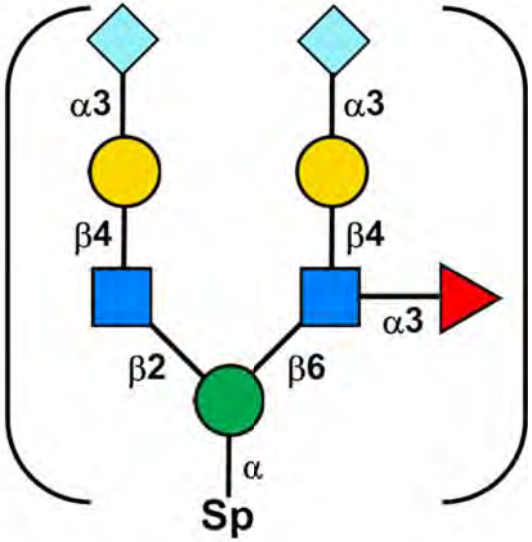


S173

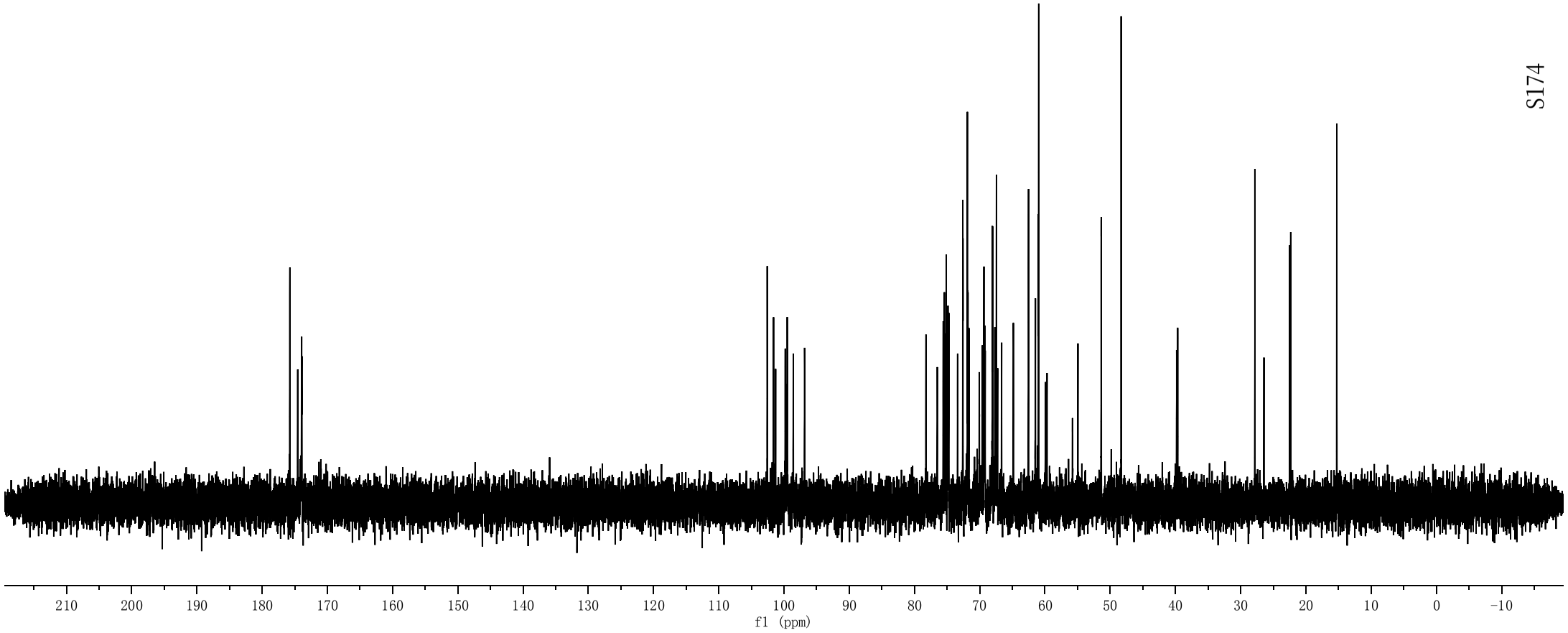
CHZ-1105

#65



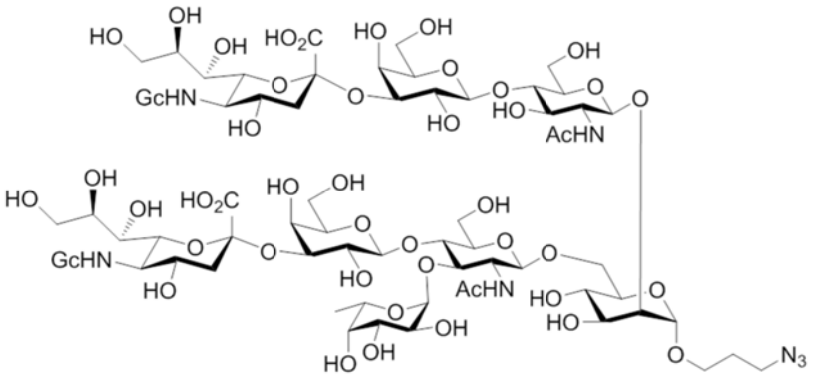


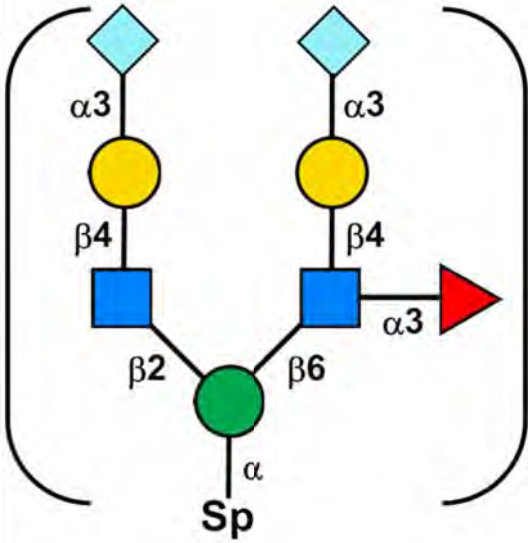
S174



CHZ-1105

#65

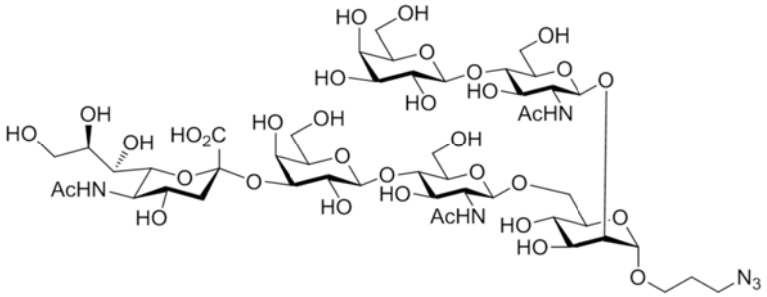


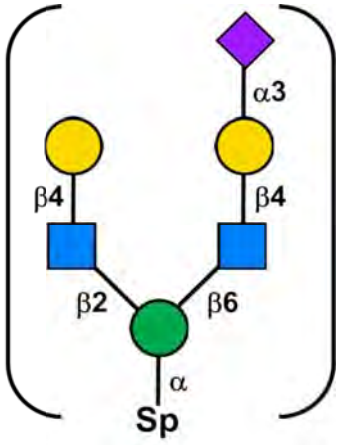


S175

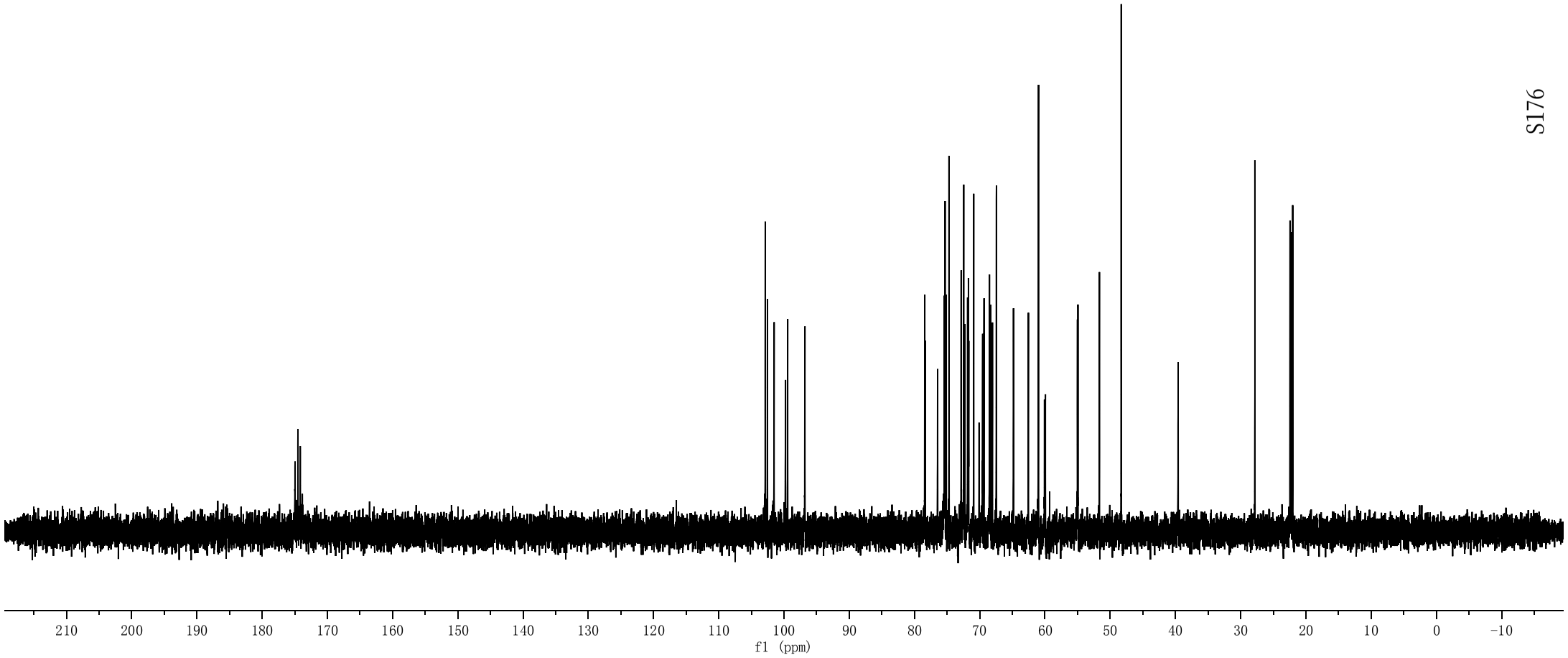
CHZ-948

#66



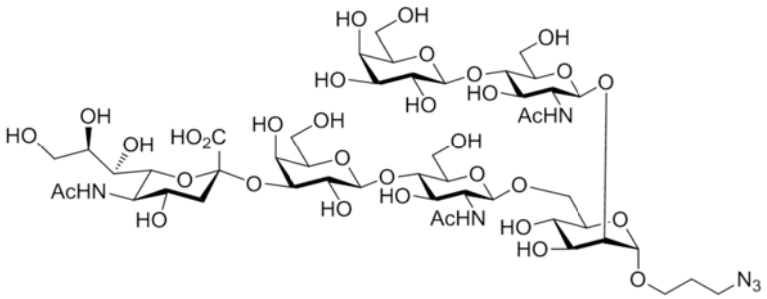


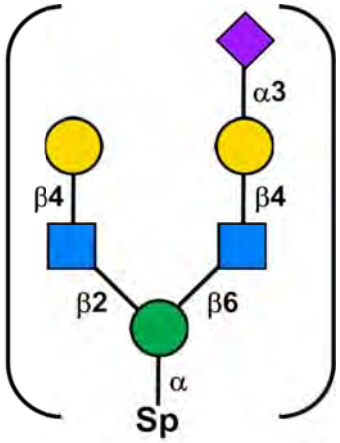
S176



CHZ-948

#66

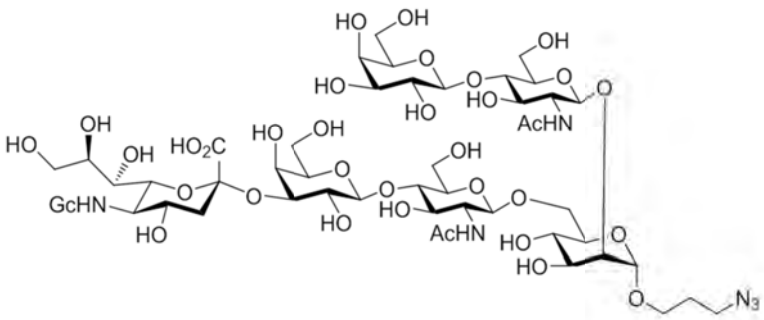


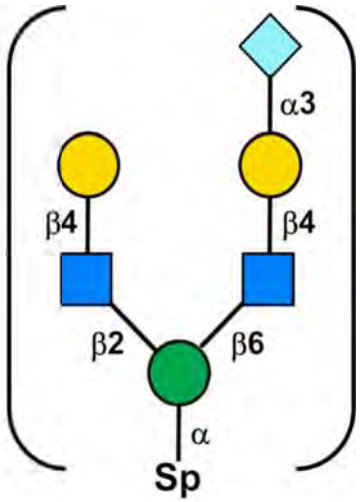


S177

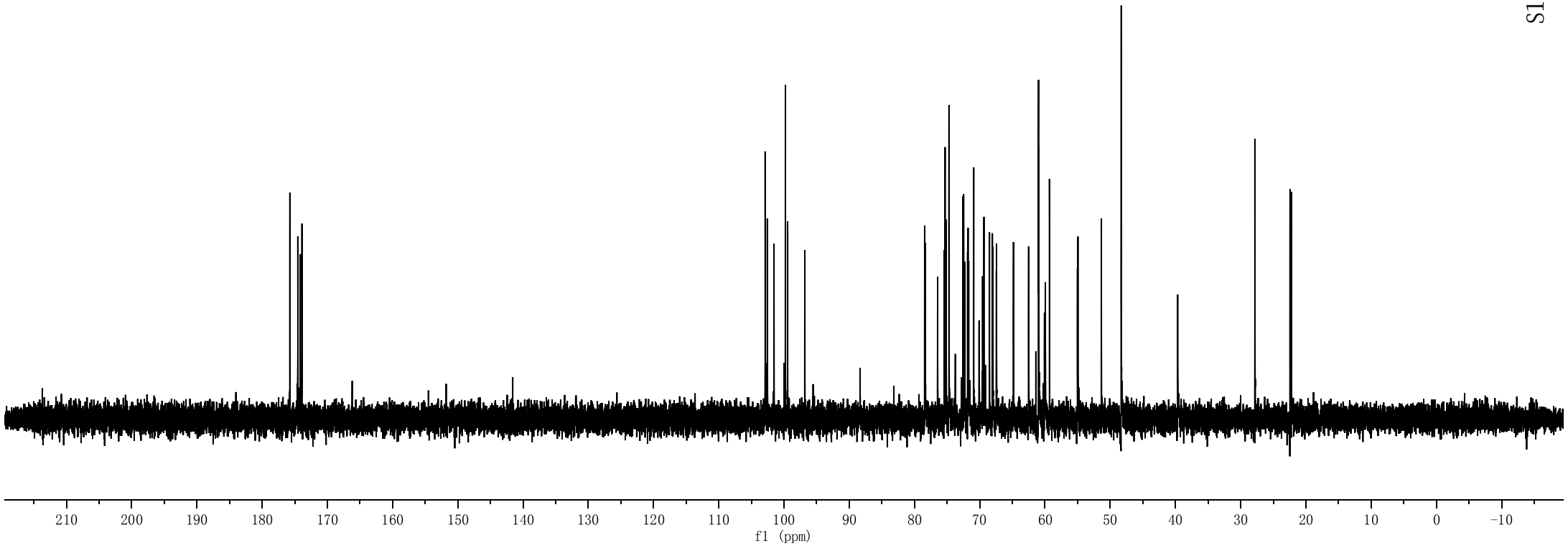
CHZ-949

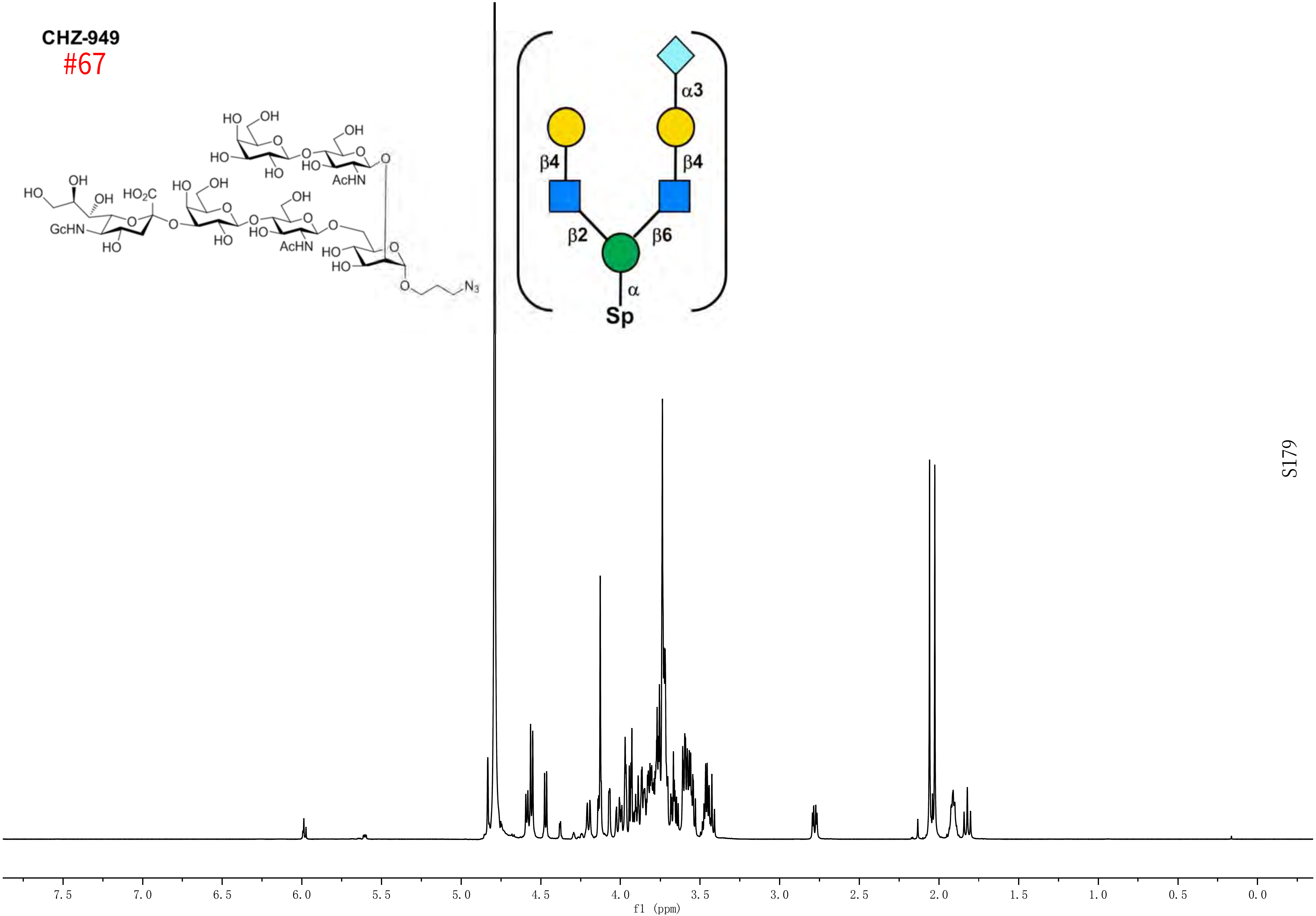
#67





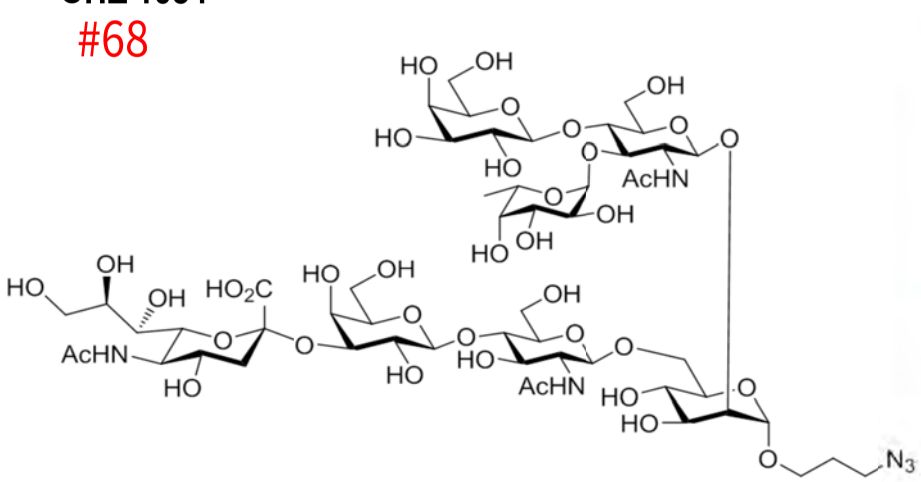
S178

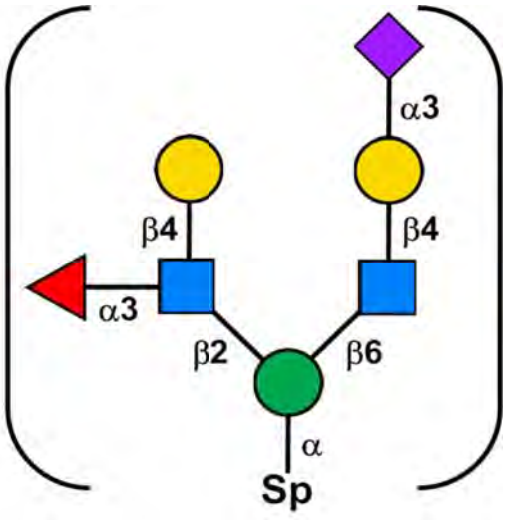



CHZ-949
#67
HO
OH
OH
HO2C
GcHN
HO
O
AcHN
N3
β4
β2
β6
α3
α
Sp
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

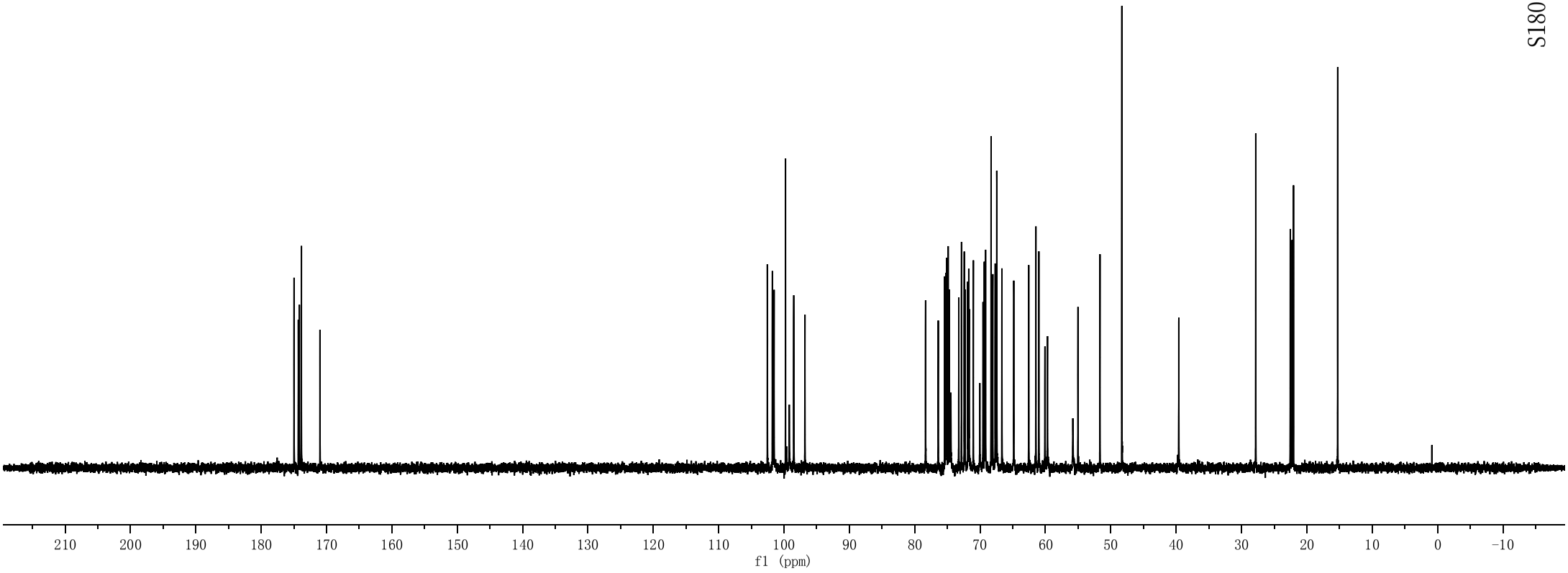
CHZ-1034

#68



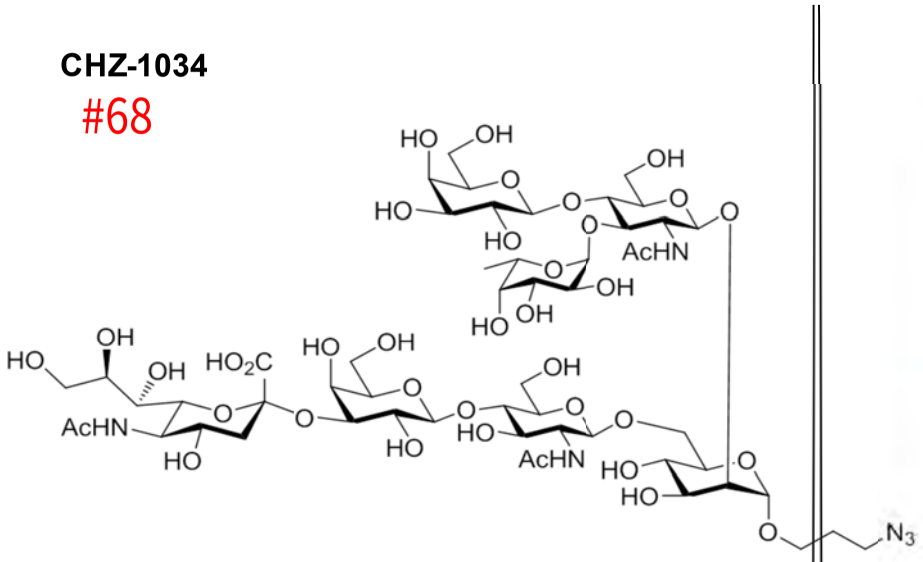


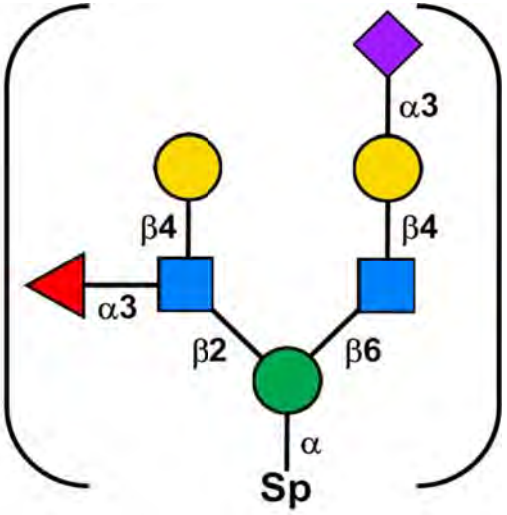
S180



CHZ-1034

#68





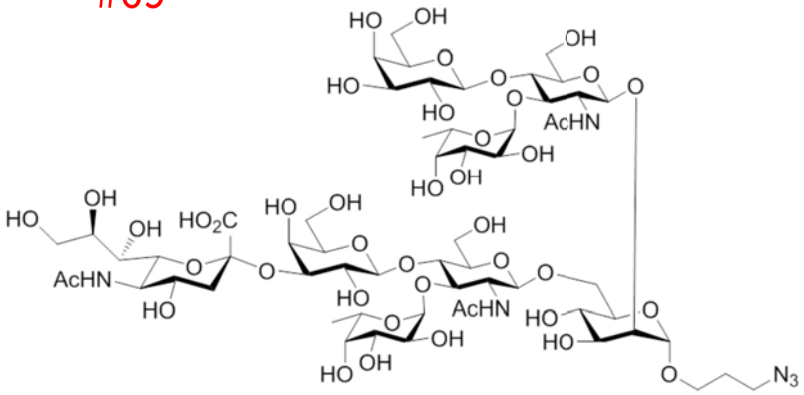
S181

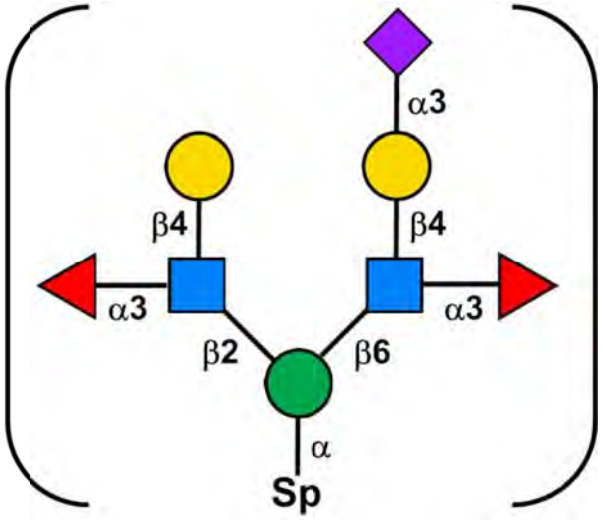
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

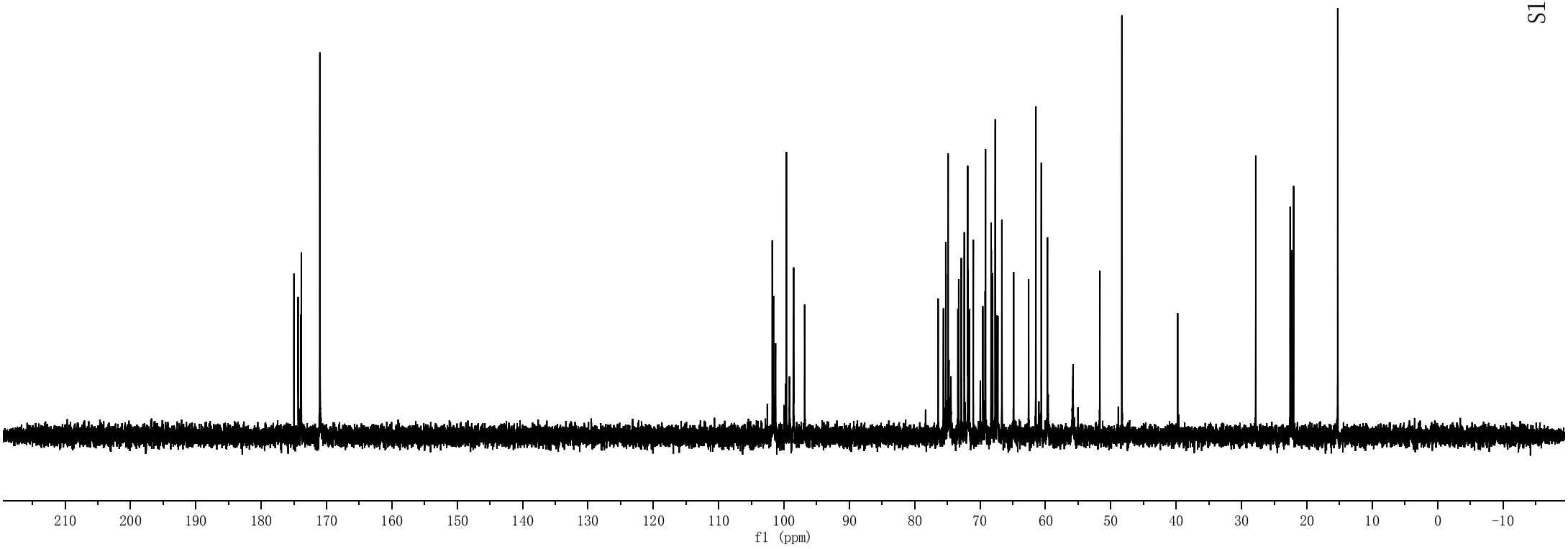
CHZ-1035

#69



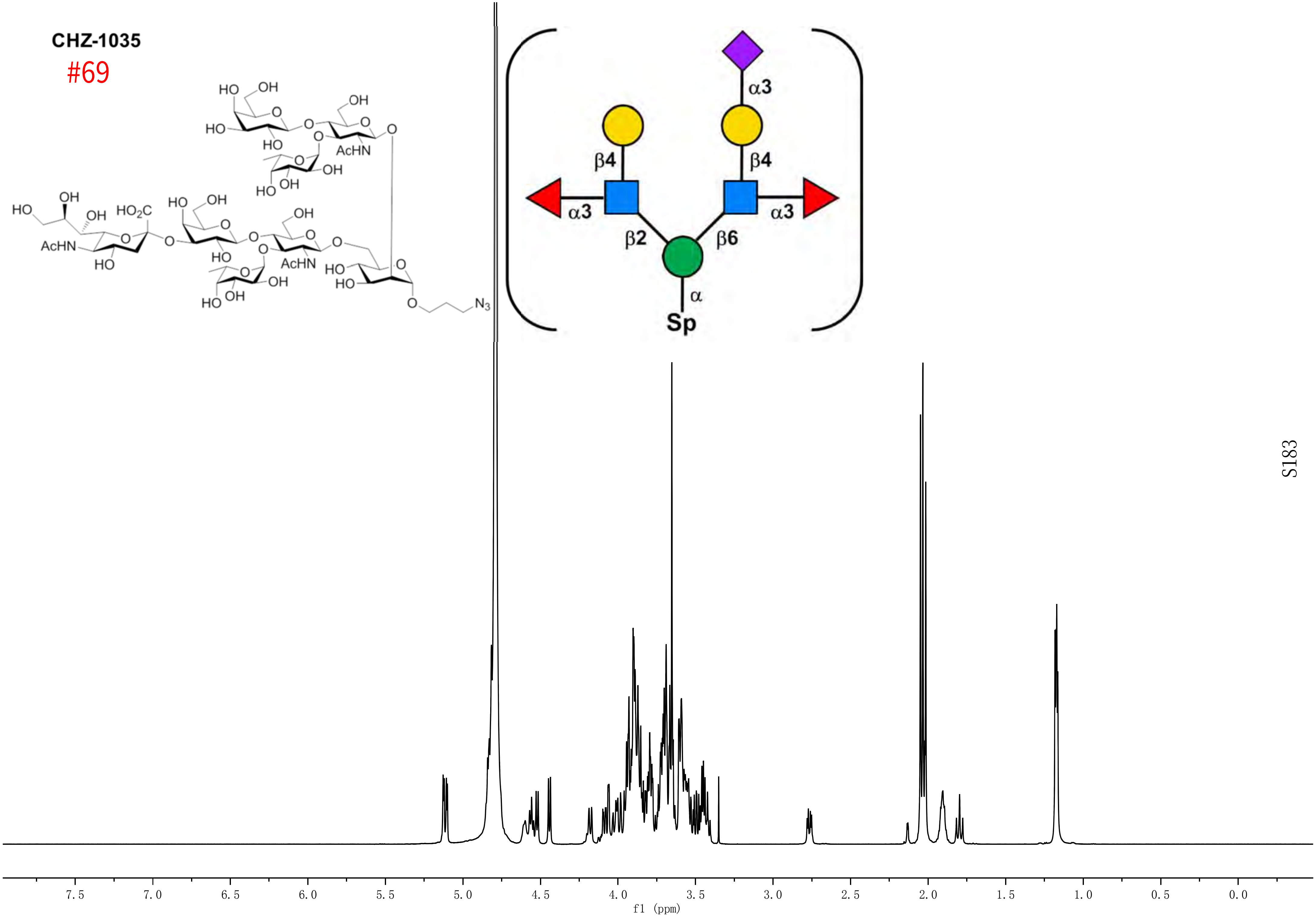


S182



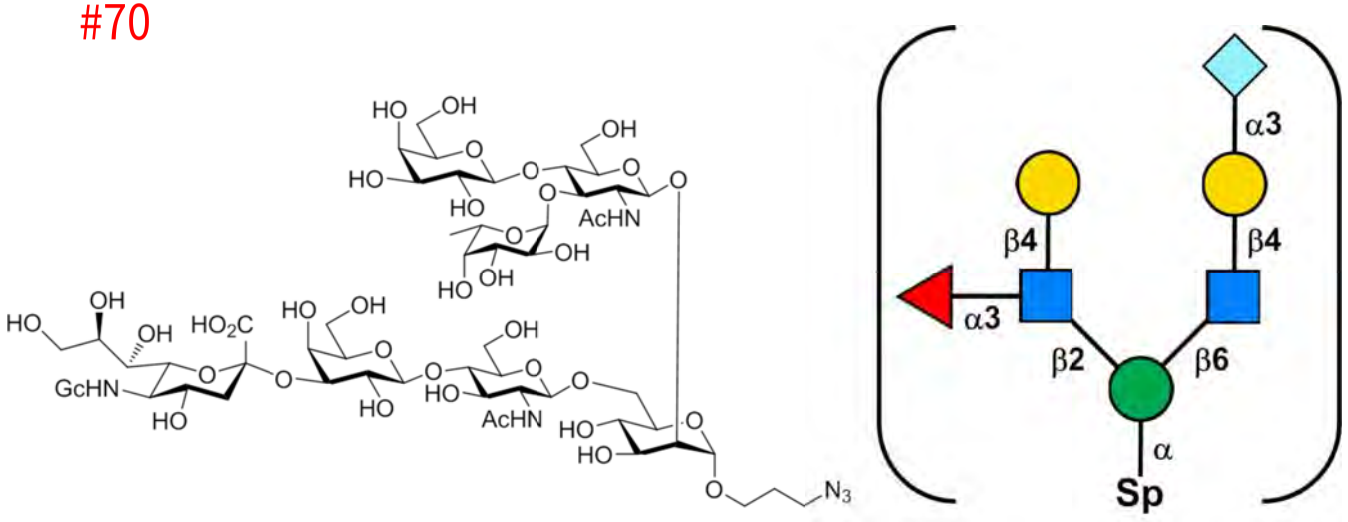
CHZ-1035

#69

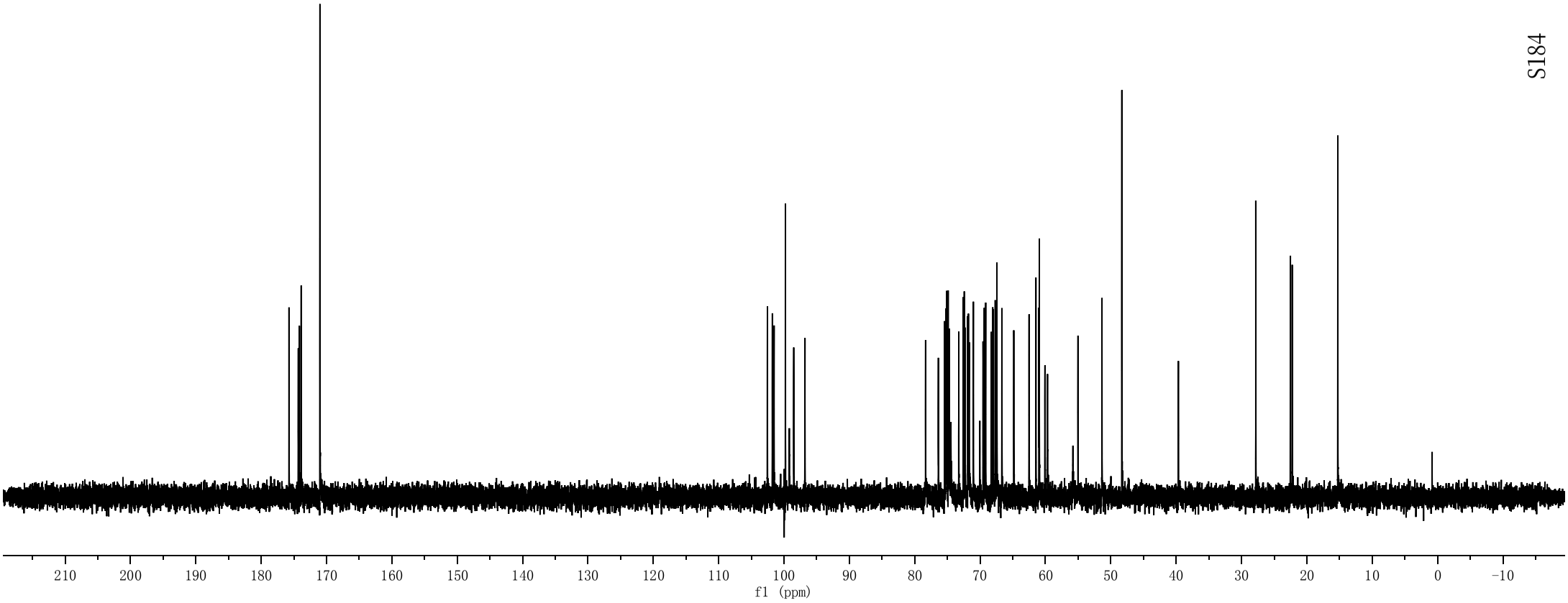

α3
β4
β4
α3
α3
β2
β6
α
Sp
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CHZ-1076

#70

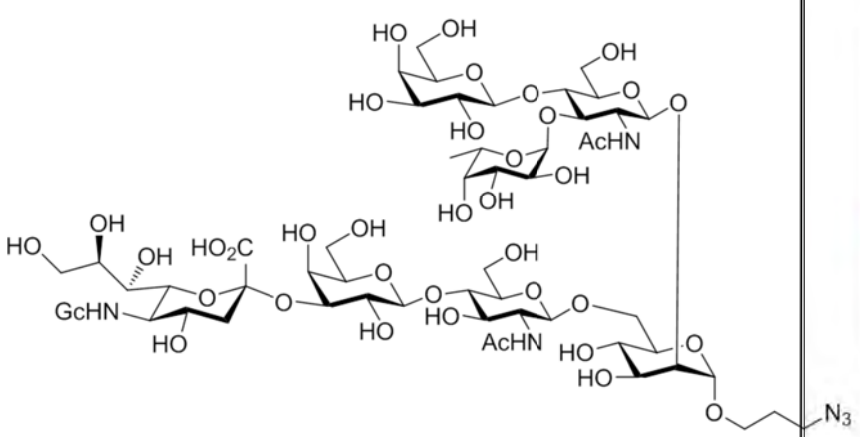


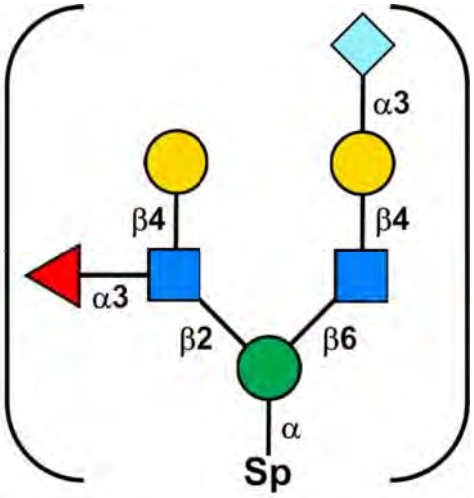
S184



CHZ-1076

#70

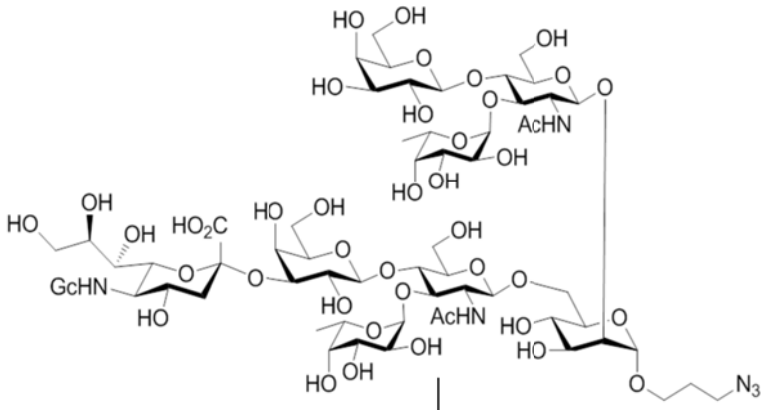

HO
OH
HO
O
OH
O
HO
HO
O
AcHN
OH
HO
OH
HO
OH
HO2C
GcHN
HO
HO
OH
HO
O
HO
AcHN
OH
HO
HO
O
O
N3

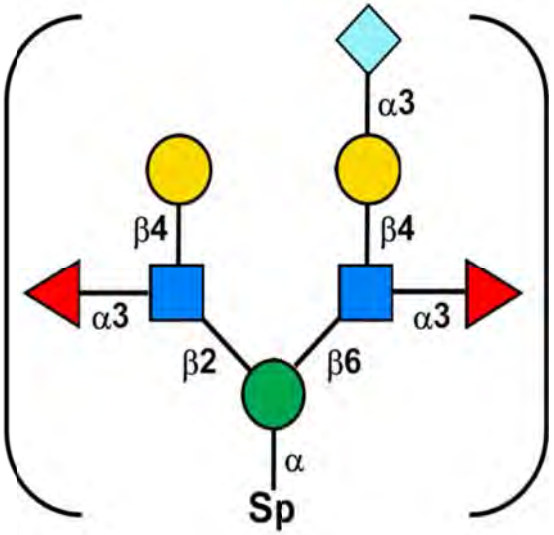

α3
β4
β4
α3
β2
β6
α
Sp

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
f1 (ppm)

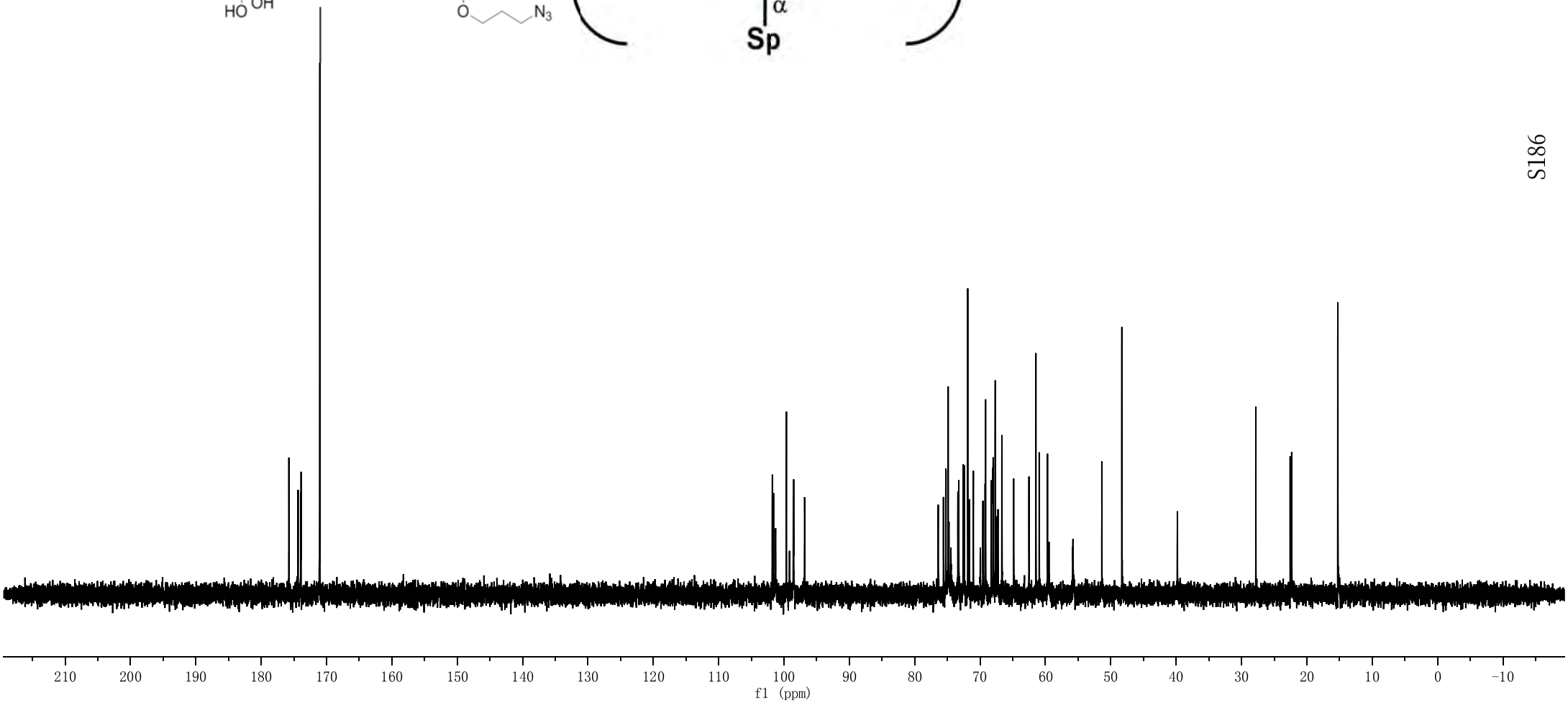
CHZ-1075

#71



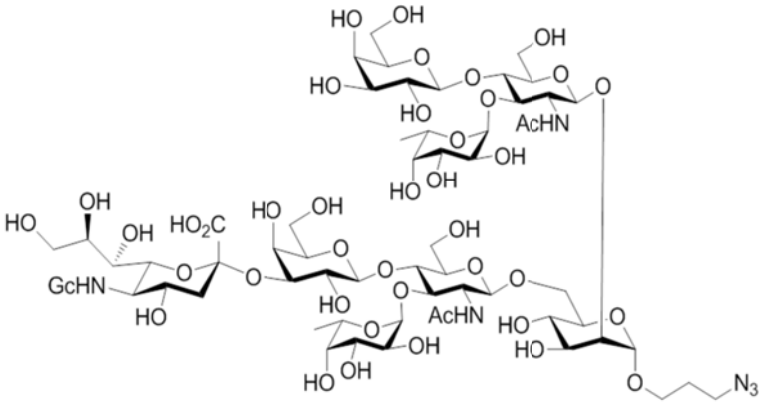


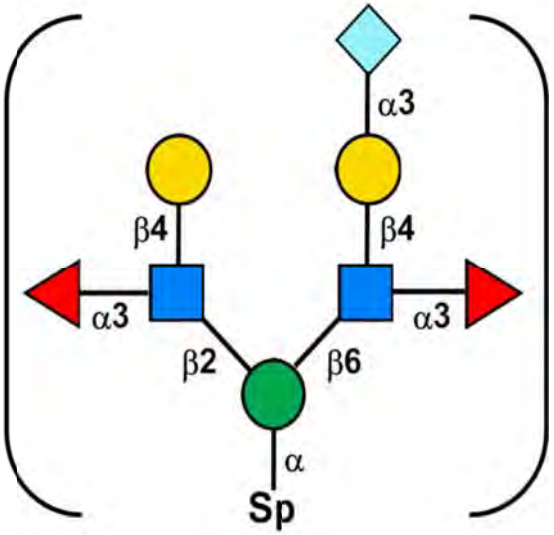
S186



CHZ-1075

#71

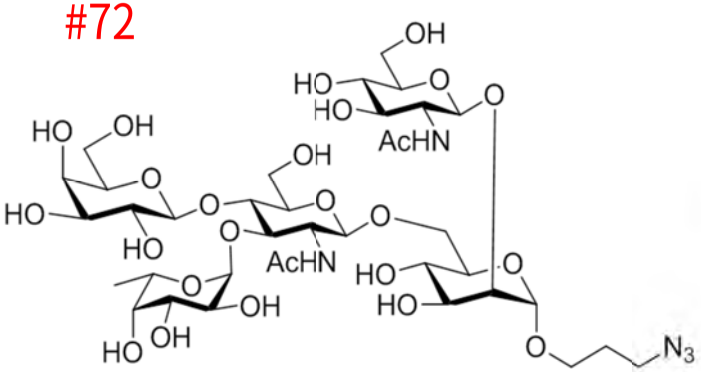


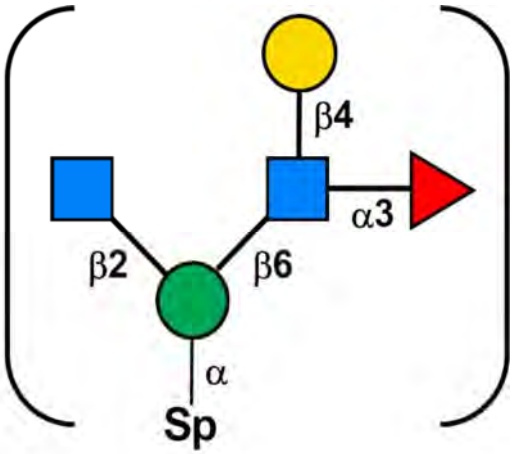


S187

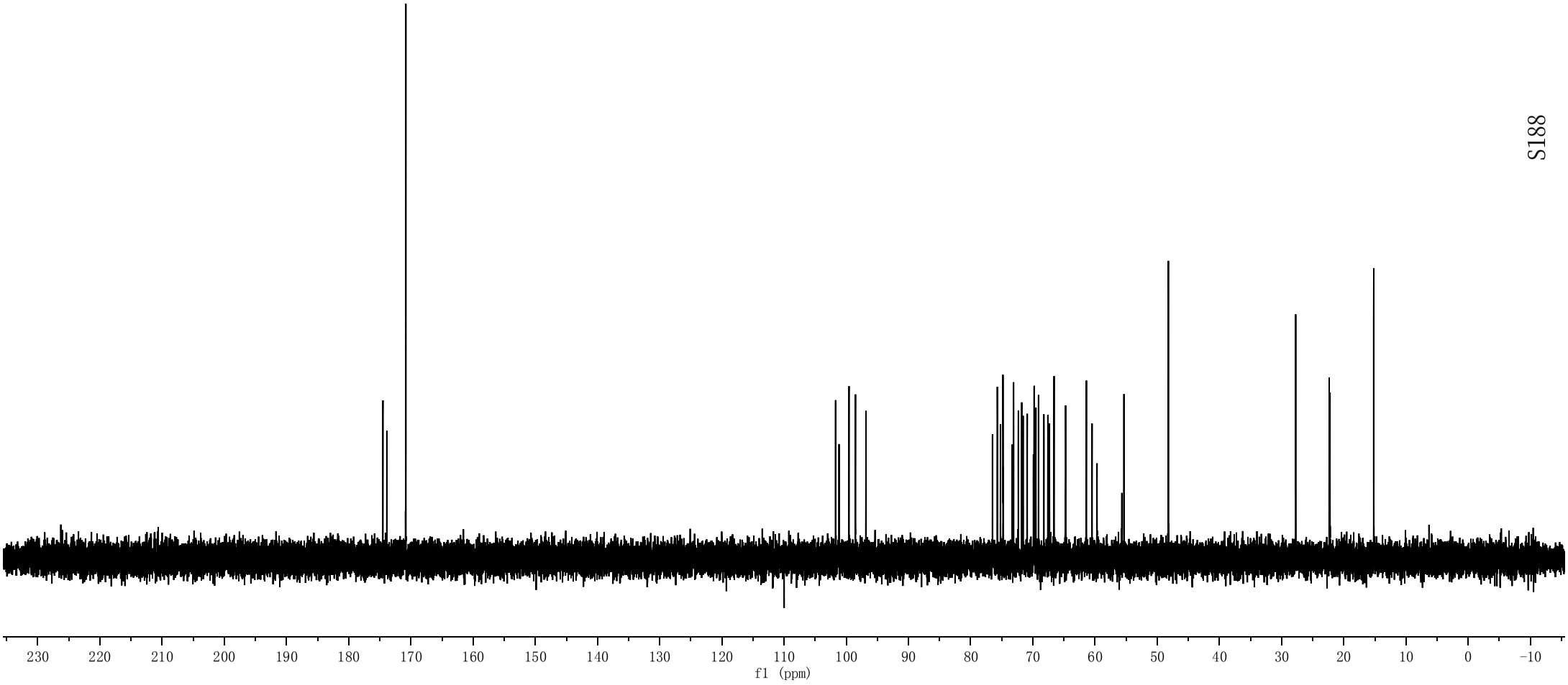
CHZ-779

#72



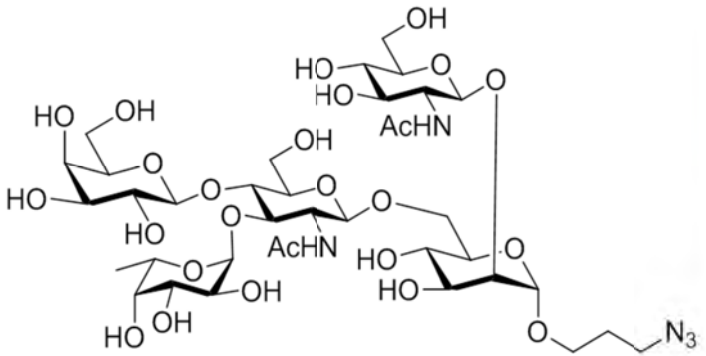


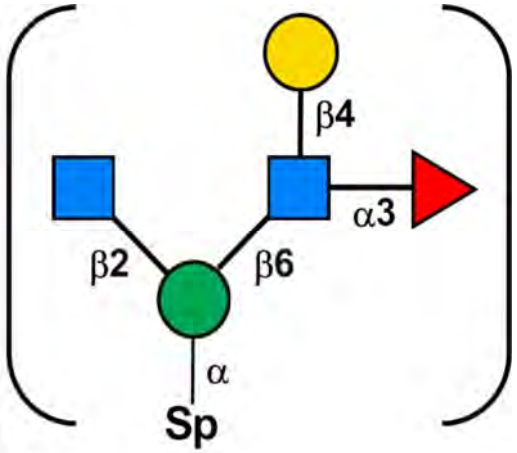
S188



CHZ-779

#72

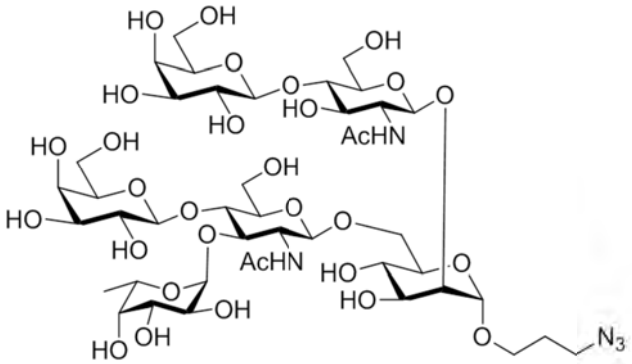


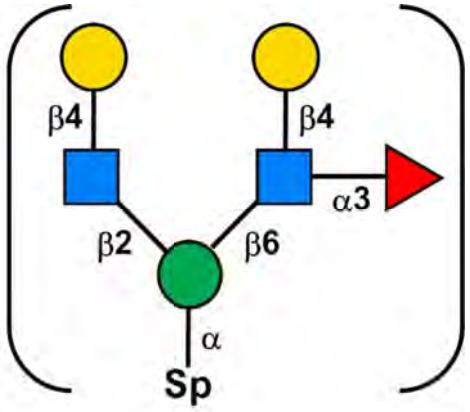


S189

CHZ-794

#73





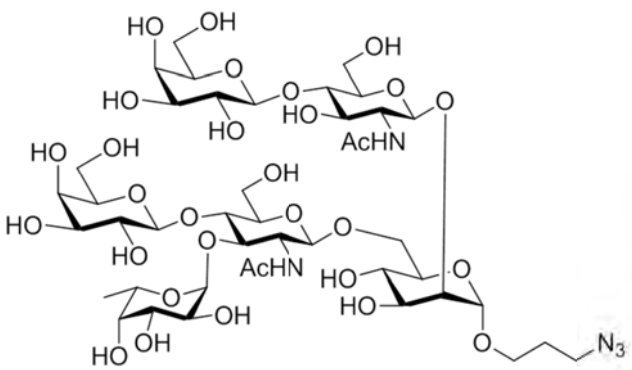
S190

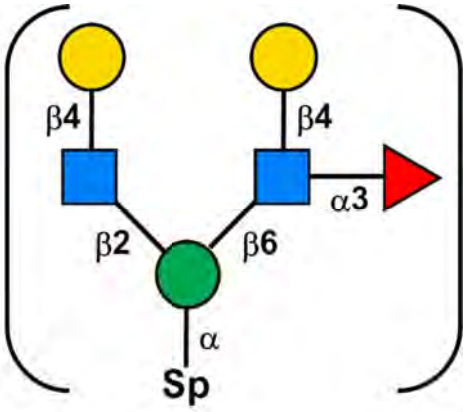
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

CHZ-794

#73





S191