Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

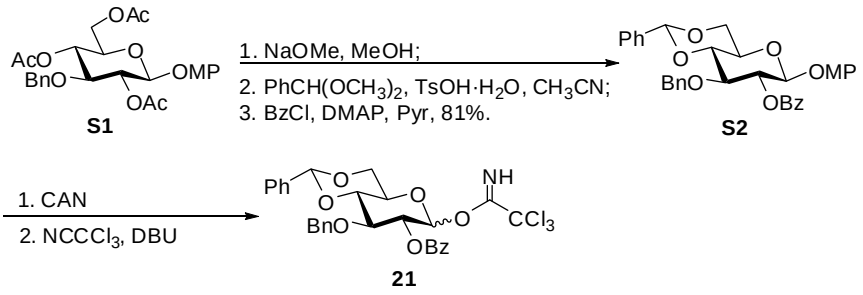
Efficient Synthesis of a Library of Heparin Tri- and Tetrasaccharides Relevant to the Substrates of Heparanase

Peng Xu, Weichang Xu, Yuanwei Dai, You Yang, and Biao Yu*

State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling road, Shanghai 200032, China. E-mail: byu@mail.sioc.ac.cn

General experimental procedures. All reactions were carried out under nitrogen or argon with anhydrous solvents in flame-dried glassware, unless otherwise noted. All glycosylation reactions were performed in the presence of 4Å or 5Å molecular sieves, which were flame-dried immediately before use in the reaction under high vacuum. Glycosylation solvents were dried using a solvent purification system and used directly without further drying. The chemicals used were reagent grade as supplied, except where noted. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compound spots were visualized by UV light (254 nm) or by heating with a solution with 10% H_2SO_4 in ethanol. Flash column chromatography was performed on silica gel H. NMR spectra were referenced using Me_4Si (0 ppm), residual $CHCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm), CD_3OD (^{1}H NMR δ = 3.31 ppm, ^{13}C NMR δ = 49.00 ppm), D_2O (^{1}H NMR δ = 4.79 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HMQC experiments. All optical rotations were measured at room temperature using the sodium D line. Splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and brs (broad singlet) for ^{1}H NMR data. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument using HP5989A or VG Quattro MS. Optical rotations were measured using a Perkin-Elmer 241 polarimeter.

2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl trichloroacetimidate (21)



4-Methoxyphenyl
2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (S2)

4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-*β*-D-glucopyranoside (**S1**)[S5] (20.0 g, 40 mmol) was dissolved in methanol (100 mL), NaOMe was added until pH = 12. After the TLC indication of complete consumption of the starting material, acidic resin was added and the mixture was stirred until pH = 7. The resin was filtered off and the solution was removed in vacuo. The residue was co-evaporated twice with toluene and dissolved in acetonitrile (100 mL). Benzaldehyde dimethyl acetal (7.5 mL, 48 mmol) and *p*-toluenesulfonic acid monohydrate (100 mg) were added, stirring was continued until TLC indicated disappearance of the raw material. Triethylamine was added and the solvent was evaporated. Crystallization from methanol afforded 4-methoxyphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside.

Benzoyl chloride (9.5 mL, 82 mmol) was added to a solution of the above product in CH_2Cl_2 (160 mL) and pyridine (80 mL) at 0 °C. Stirring was continued at 0 °C until TLC indicated disappearance of the starting material. The reaction mixture was quenched by the addition of methanol. The mixture was poured into CH_2Cl_2, and washed with brine twice. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. Crystallization from petroleum ether/EtOAc afforded **S2** (18.4 g, 81%) as a white crystal: $[\alpha]_D^{24} = 40.6$ (*c* 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–7.93 (m, 2 H), 7.67–7.33 (m, 8 H), 7.21–7.03 (m, 5 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 6.74 (d, *J* = 9.0 Hz, 2 H), 5.62 (s, 1 H), 5.59–5.46 (m, 1 H), 5.07 (d, *J* = 7.8 Hz, 1 H), 4.85 (d, *J* = 12.0 Hz, 1 H), 4.72 (d, *J* = 12.1 Hz, 1 H), 4.41 (dd, *J* = 10.5, 4.9 Hz, 1 H), 4.02–3.83 (m, 3 H), 3.71 (s, 3 H), 3.66–3.53 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 155.8, 151.3, 137.9, 137.3, 133.3, 130.0, 129.9, 129.2, 128.5, 128.4, 128.3, 128.2, 127.7, 126.2, 119.0, 114.6, 101.6, 101.5, 81.6, 78.1, 74.2, 73.5, 68.8, 66.6, 55.7; ESI-MS *m/z* 591.2 [M+Na$^+$]; ESI-MS *m/z* calcd for $C_{34}H_{32}O_8Na$ [M+Na]$^+$ 591.1985, found 591.1989.

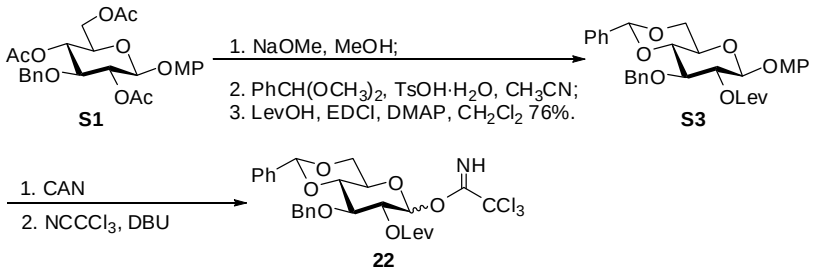
2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl trichloroacetimidate (21)

Compound **S2** (4.0 g, 7.0 mmol) was dissolved in a mixed solvent of acetonitrile, toluene, and water (70 mL, v/v/v = 1:1.5:1). Cerous ammonium nitrate (11.5 g, 21 mmol) was added at room temperature. Stirring was continued until TLC indicated disappearance of the raw material. The solvent was removed in vacuo. The residue

was dissolve in CH_2Cl_2, and washed with water, saturated sodium bicarbonate, and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to give the hemiacetal (2.9 g, 91%) as a light red solid.

The hemiacetal (2.1 g, 4.5 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C. Trichloroacetonitrile (2.3 mL, 23 mmol) and DBU (67 μL, 0.45 mmol) were added successively. After stirring at this temperature for about 2 h, the reaction mixture was concentrated in vacuo. The residue was chromatographed over silica gel (petroleum ether/EtOAc = 5:1, containing 1% Et_3N) to yield **21** (2.7 g, 98%) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1 H), 7.97 (d, J = 7.8 Hz, 2 H), 7.67–7.49 (m, 3 H), 7.49–7.34 (m, 6 H), 7.31–7.11 (m, 6 H), 6.62 (d, J = 3.2 Hz, 1 H), 5.66 (s, 1 H), 5.38 (dd, J = 9.3, 3.2 Hz, 1 H), 4.92 (d, J = 11.8 Hz, 1 H), 4.79 (d, J = 11.8 Hz, 1 H), 4.39 (dd, J = 10.4, 4.8 Hz, 1 H), 4.31 (t, J = 9.5 Hz, 1 H), 4.13 (td, J = 10.2, 5.2 Hz, 1 H), 3.92 (t, J = 9.5 Hz, 1 H), 3.84 (t, J = 10.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 160.8, 138.0, 137.1, 133.6, 130.0, 129.2, 128.5, 128.5, 128.4, 128.3, 127.8, 126.1, 101.6, 94.2, 81.7, 77.5, 77.2, 76.8, 75.3, 74.9, 72.1, 68.8, 65.4. ESI-MS m/z 628.0 $[M+Na]^+$.

2-*O*-Levulinic-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl trichloroacetimidate (22)



4-Methoxyphenyl 2-*O*-levulinic-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (S3)

Compound **S1** (2.0 g, 4.0 mmol) was dissolved in methanol (10 mL), and NaOMe was added until pH = 12. After the TLC indication of complete consumption of the starting material, acidic resin was added and the mixture was stirred until pH = 7. The resin was filtered off and the solvent was removed in vacuo. The residue was co-evaporated twice with toluene and dissolved in acetonitrile (10 mL). Benzaldehyde dimethyl acetal (0.75 mL, 4.8 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg) was added, stirring was continued until TLC indicated disappearance of the raw material. Triethylamine was added and the solvents evaporated. Crystallization from methanol afforded 4-methoxyphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside.

The above product was dissolved in CH_2Cl_2 (10 mL) under nitrogen. EDCI (1.5 g, 8.0 mmol), DMAP (50 mg, 0.4 mmol), levulinic acid (0.6 mL, 6 mmol) were added.

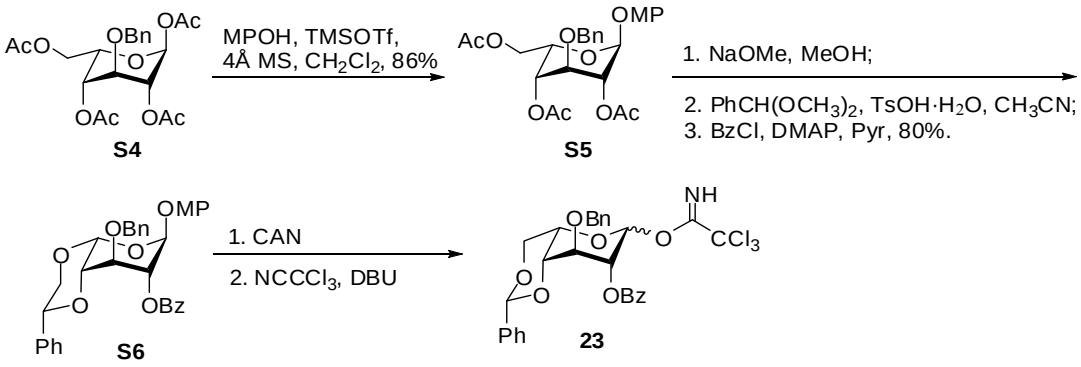
The stirring was continued until TLC indicated disappearance of the starting material. The mixture was poured into CH_2Cl_2, and washed with brine twice. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. Crystallization from petroleum ether/EtOAc afforded **S3** (1.5 g, 76%) as a white solid: $[\alpha]_D^{24} = 3.7$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.26 (m, 10 H), 6.96 (d, *J* = 9.0 Hz, 2 H), 6.82 (d, *J* = 9.3 Hz, 2 H), 5.61 (s, 1 H), 5.25 (t, *J* = 8.7 Hz, 1 H), 4.94-4.87 (m, 2 H), 4.72 (d, *J* = 11.7 Hz, 1 H), 4.39 (dd, *J* = 10.8, 5.4 Hz, 1 H), 3.90-3.75 (m, 6 H), 3.58-3.50 (m, 1 H), 2.75-2.71 (m, 2 H), 2.57-2.51 (m, 2 H), 2.17 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 171.4, 155.7, 151.2, 138.2, 137.2, 129.1, 128.4, 128.0, 127.8, 126.1, 118.8, 114.6, 101.3, 101.3, 81.3, 78.3, 74.21, 73.1, 68.7, 66.4, 55.7, 37.8, 29.9, 27.9; ESI-MS *m/z* calcd for $C_{32}H_{34}O_9Na$ $[M+Na]^+$ 585.2095, found 585.2083.

2-*O*-Levulinic-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl trichloroacetimidate (22)

Compound **S3** (1.4 g, 2.5 mmol) was dissolved in a mixed solvent of acetonitrile, toluene, and water (21 mL, v/v/v = 1:1.5:1). Cerous ammonium nitrate (4.1 g, 7.5 mmol) was added at room temperature. Stirring was continued until TLC indicated disappearance of the raw material. The solution was removed in vacuo and the residue was dissolve in CH_2Cl_2, and washed with water, saturated sodium bicarbonate, and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to give the hemiacetal (1.1 g, 83%) as light red solid: ESI-MS (*m/z*): 479.4 $[M+Na]^+$.

The above product (0.9 g, 2.0 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 ^{o}C. Trichloroacetonitrile (0.2 mL, 1.0 mmol) and DBU (cat.) were added successively. After stirring at this temperature for about 2 h, the reaction mixture was concentrated in vacuo. The residue was chromatographed over silica gel (petroleum ether/EtOAc = 4:1, containing 1% Et_3N) to yield **22** (1.13 g, 94 %) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.50–7.15 (m, 14 H), 6.42 (d, *J* = 3.7 Hz, 1 H), 5.55 (s, 1 H), 5.03 (dd, *J* = 9.6, 3.8 Hz, 1 H), 4.86 (d, *J* = 11.8 Hz, 1 H), 4.69 (d, *J* = 11.7 Hz, 1 H), 4.28 (dd, *J* = 10.4, 4.9 Hz, 1 H), 4.12–3.93 (m, 2 H), 3.79–3.67 (m, 2 H), 2.62 (td, *J* = 6.7, 2.9 Hz, 2 H), 2.52–2.35 (m, 3 H), 2.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 172.0, 161.0, 138.3, 137.1, 129.2, 128.4, 128.1, 127.9, 126.1, 101.5, 94.0, 81.5, 75.6, 75.0, 72.0, 68.7, 65.3, 37.8, 30.0, 27.7.

2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*α*-L-iduropyranosyl trichloroacetimidate (23)



4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-α-L-iduropyranoside (S5)

p-Methoxylphenol (1.86 g, 15 mmol) and 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-α-L-iduropyranoside (**S4**)[S4] (4.4 g, 10 mmol) were dissolved in CH_2Cl_2 at rt. Powdered freshly activated 4Å molecular sieves (6 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to 0 ^oC. TMSOTf (0.64 mL, 5 mmol) was added, and the stirring was continued until TLC indicated the disappearance of the starting material (about 12 h). The reaction was quenched by the addition of Et_3N. The mixture was filtered, the filtrate was concentrated in vacuo. Crystallization from petroleum ether/EtOAc afforded **S5** (4.3 g, 86%) as a white solid: $[\alpha]_D^{25}$ = -81.5 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.28 (m, 5 H), 7.11–6.91 (m, 2 H), 6.92–6.70 (m, 2 H), 5.44 (s, 1 H), 5.16 (d, *J* = 1.1 Hz, 1 H), 4.94 (s, 1 H), 4.86 (d, *J* = 11.9 Hz, 1 H), 4.73 (d, *J* = 11.9 Hz, 1 H), 4.65 (t, *J* = 6.4 Hz, 1 H), 4.26–4.07 (m, 2 H), 3.81 (s, 1 H), 3.77 (s, 3 H), 2.11 (d, *J* = 4.4 Hz, 6 H), 1.93 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.58, 170.16, 169.61, 155.30, 150.49, 137.68, 128.54, 127.98, 127.73, 118.40, 114.63, 97.32, 72.57, 72.27, 67.33, 67.14, 64.62, 62.62, 55.77; ESI-MS *m/z* calcd for $C_{26}H_{30}O_{10}Na$ $[M+Na]^+$ 525.1731, found 525.1746.

4-Methoxyphenyl
2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*a*-L-iduropyranoside (S6)

Compound **S5** (4.0 g, 4.0 mmol) was dissolved in methanol (20 mL), and NaOMe was added until pH = 12. After the TLC indication of complete consumption of the starting material, acidic resin was added and the mixture was stirred until pH = 7. The resin was filtered off and the solvent was removed in vacuo. The residue was co-evaporated twice with toluene and then dissolved in benzaldehyde (12 mL). Trifluoroacetic acid (0.8 mL) was added, stirring was continued until TLC indicated disappearance of the raw material. Triethylamine was added and the solvent was evaporated to afford the crude 4-methoxyphenyl 3-*O*-benzyl-4,6-*O*-benzylidene -β-L-iduropyranoside as a yellow solid.

Benzoyl chloride (1.4 mL, 12 mmol) was added to a solution of the above product in CH_2Cl_2 (40 mL) and pyridine (20 mL) under nitrogen at 0 ^oC. Stirring was continued at 0 ^oC until TLC indicated disappearance of the starting material. The reaction mixture was quenched by the addition of methanol. The mixture was poured into

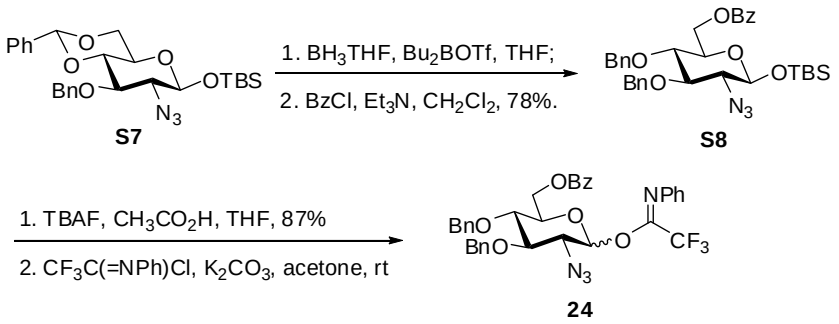
CH_2Cl_2, and washed with brine twice. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. Crystallization from petroleum ether/EtOAc afforded **S6** (3.6 g, 80%) as a white solid: $[\alpha]_D^{24}$ = -23.6 (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.06 (m, 1H), 8.01 (d, *J* = 6.7 Hz, 2H), 7.63–7.21 (m, 17H), 7.08 (dd, *J* = 9.0, 3.6 Hz, 2H), 6.91–6.74 (m, 2H), 5.76 (s, 1H), 5.58 (s, 1H), 5.50 (s, 1H), 4.99 (dd, *J* = 11.7, 2.0 Hz, 1H), 4.80–4.66 (m, 1H), 4.31 (d, *J* = 12.7 Hz, 1H), 4.16 (s, 2H), 4.10 (d, *J* = 12.5 Hz, 1H), 3.97 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 155.0, 150.7, 138.0, 137.91 133.8, 133.3, 130.3, 130.3, 129.6, 129.0, 128.6, 128.4, 128.2, 128.0, 127.9, 126.5, 117.6, 114.8, 101.1, 97.2, 74.4, 73.6, 72.0, 69.9, 66.0, 60.6, 55.8; ESI-MS *m/z* calcd for $C_{34}H_{32}O_8Na$ $[M+Na]^+$ 591.1989, found 591.1985.

2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*a*-L-iduropyranosyl trichloroacetimidate (23)

Compound **S6** (1.0 g, 1.8 mmol) was dissolved in a mixed solvent of acetonitrile, toluene, and water (14 mL, v/v/v = 1:1.5:1). Cerous ammonium nitrate (3.0 g, 5.4 mmol) was added at room temperature. Stirring was continued until TLC indicated disappearance of the raw material. The solvent was removed in vacuo and the residue was dissolve in CH_2Cl_2, and washed with water, saturated sodium bicarbonate, and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to give the hemiacetal (0.7 g, 85%) as a light red solid.

The hemiacetal (0.42 g, 0.9 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 ^{o}C. Trichloroacetonitrile (0.45 mL, 4.5 mmol) and DBU (cat.) was added successively. After stirring at this temperature for about 2 h, the reaction mixture was concentrated in vacuo. The residue was chromatographed over silica gel (petroleum ether/EtOAc = 5:1, containing 1% Et_3N) to yield **23** (0.52 g, 93%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1 H), 8.13–7.90 (m, 2 H), 7.62–7.09 (m, 14 H), 6.53 (s, 1 H), 5.58 (s, 1 H), 5.49 (s, 1 H), 4.92 (d, *J* = 11.6 Hz, 1 H), 4.70 (d, *J* = 11.6 Hz, 1 H), 4.40 (d, *J* = 12.6 Hz, 1 H), 4.24 (s, 1 H), 4.20–4.05 (m, 2 H), 3.94 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.7, 138.0, 137.5, 133.4, 130.3, 129.5, 129.1, 128.5, 128.4, 128.2, 128.0, 128.0, 126.6, 101.3, 95.9, 91.3, 73.3, 72.9, 72.2, 69.6, 64.4, 61.9.

2-Azido-6-*O*-benzoyl-3,4-di-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl *N*-phenyltrifluoroacetimidate (24)



tert-Butyldimethylsilyl 2-azido-3,4-*O*-benzyl-2-deoxy-6-*O*-benzoyl-*β*-D-glucopyranoside (S8)

tert-Butyldimethylsilyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*β*-D-glucopyranoside (**S7**)[S1] (1.0 g, 2.0 mmol) was dissolved in BH_3·THF (1 M, 20 mL, 20 mmol) under nitrogen and cooled to 0 °C. After 15 min, Bu_2B·OTf (1 M, 2 mL, 2 mmol) was added dropwise and stirring was continued at 0 °C for 2 h. The reaction mixture was quenched by the addition of Et_3N and the excess BH_3·THF was consumed by slowly adding methanol. The solvent was removed in vacuo, co-evaporated with methanol twice.

Benzoyl chloride (0.4 mL, 3.4 mmol) was added to a solution of the above product in CH_2Cl_2 (10 mL) and triethylamine (1.0 mL, 6.8 mmol) under nitrogen at 0 °C. Stirring was continued at 0 °C until TLC indicated disappearance of the starting material. The reaction mixture was quenched by the addition of methanol. The mixture was poured into CH_2Cl_2, and washed with brine twice. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 25:1) to give **S8** (0.95 g, 78%) as a colorless oil: $[\alpha]_D^{24} = 11.8$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 6.8 Hz, 2 H), 7.56 (t, J = 7.2 Hz, 1H), 7.45–7.25 (m, 12 H), 4.94–4.79 (m, 3 H), 4.63–4.56 (m, 3 H), 4.37 (dd, J = 11.6, 5.6 Hz, 1 H), 3.65–3.54 (m, 2 H), 3.47–3.35 (m, 2 H), 0.89 (s, 9 H), 0.12 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.18, 137.89, 137.50, 133.13, 129.86, 129.73, 128.57, 128.37, 128.16, 128.10, 128.01, 97.21, 83.00, 77.72, 75.65, 75.15, 73.35, 68.76, 63.55, 29.73, 25.58, 17.97, -4.30, -5.20; ESI-MS *m/z* calcd for $C_{33}H_{41}N_3O_6SiNa$ $[M+Na]^+$ 626.2657, found 626.2648.

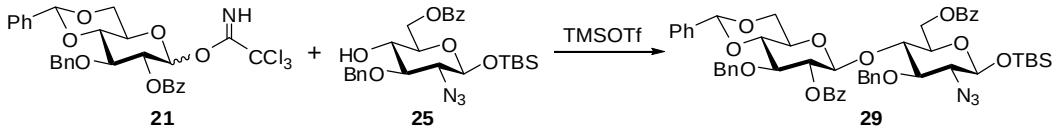
2-Azido-6-*O*-benzoyl-3,4-di-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl *N*-phenyltrifluoroacetimidate (24)

Compound **S8** (0.95 g, 1.57 mmol) was dissolved in THF (10 mL) followed by the addition of AcOH (0.27 mL, 4.7 mmol) and TBAF in THF (1 M, 2.35 mL, 2.35 mmol). Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous sodium bicarbonate and brine. The organic phase was dried with Na_2SO_4 and filtered, and the filtrate was concentrated in vacuo. The residue was chromatographed over silica gel (petroleum ether/EtOAc = 4:1) to give the hemiacetal (0.67 g, 87%) as

a colorless oil: ESI-MS (*m/z*) 512.5 $[M+Na]^+$.

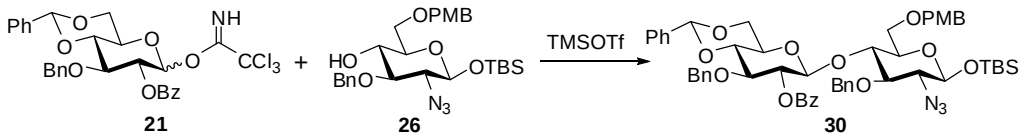
The above hemiacetal (115 mg, 0.24 mmol) was dissolved in acetone (2 mL). *N*-Phenyl-trifluoroacetimidoyl chloride (40 μL, 0.36 mmol) and K_2CO_3 (85 mg, 0.6 mmol) was added successively. Stirring was continued until TLC indicated disappearance of the starting material (about 2 h). The mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1, containing 1% Et_3N) to give **24** (160 mg, 99%) as a white solid: ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.0, 5.2 Hz, 4 H), 7.58 (dd, J = 16.3, 7.7 Hz, 3 H), 7.50–7.29 (m, 22 H), 7.11 (m, 2 H), 6.78 (t, J = 7.2 Hz, 4 H), 5.05–4.82 (m, 6 H), 4.74–4.47 (m, 5 H), 4.45–4.35 (m, 1 H), 4.11 (m, 1 H), 3.85–3.64 (m, 5 H), 3.58 (brs, 1 H); ESI-MS *m/z* 683.6 $[M+Na]^+$, 699.7 $[M+K]^+$.

tert-Butyldimethylsilyl
(2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)
-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (29)



Trichloroacetimidate **21** (2.4g, 4.0 mmol) and acceptor **25** [S1] (2.0 g, 3.8 mmol) were dissolved in CH_2Cl_2 (50 mL) under nitrogen. Powdered freshly activated 4 Å molecular sieves (4.0 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (39 μL, 0.2 mmol) was added to the mixture, and stirring was continued until TLC indicated disappearance of the imidate (about 30 min). The reaction mixture was quenched by the addition of Et_3N. The mixture was filtered, the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2 = 10:1:1) to give disaccharide **29** (3.6 g, 95%) as a white solid: $[\alpha]_D^{27} = 41.3$ (*c* 1.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.2 Hz, 2 H), 7.86 (d, J = 7.6 Hz, 2 H), 7.56 (t, J = 7.6 Hz, 1 H), 7.50–7.04 (m, 20 H), 5.54 (s, 1 H), 5.34 (t, J = 8.4 Hz, 1 H), 4.95 (d, J = 10.4 Hz, 1 H), 4.83–4.79 (m, 2 H), 4.73 (d, J = 8.0 Hz, 1 H), 4.65 (d, J = 12.0 Hz, 1 H), 4.47 (d, J = 7.2 Hz, 1 H), 4.42–4.36 (m, 2 H), 4.18–4.14 (dd, J = 4.8, 10.4 Hz, 1 H), 3.86–3.79 (m, 3 H), 3.52 (t, J = 10.4 Hz, 1 H), 3.47–3.29 (m, 4 H), 0.84 (s, 9 H), 0.06 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.1, 138.5, 137.8, 137.2, 133.4, 133.3, 130.0, 129.7, 129.2, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 126.2, 101.8, 101.4, 97.0, 81.8, 80.9, 78.1, 75.7, 74.3, 73.9, 73.2, 68.6, 68.4, 66.5, 62.9, 25.7, 18.1, -4.3, -5.1; ESI-MS *m/z* calcd for $C_{53}H_{59}N_3O_{12}SiNa$ $[M+Na]^+$ 980.3767, found 980.3760.

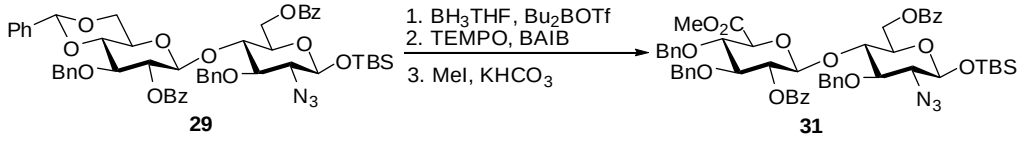
***tert*-Butyldimethylsilyl**
(2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (30)



21 **26** **30**

Trichloroacetimidate **21** (1.2 g, 2.0 mmol) and acceptor **26**[S2] (1.0 g, 1.9 mmol) were dissolved in CH_2Cl_2 (20 mL) under nitrogen. Powdered freshly activated 4 Å molecular sieves (2.0 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (20 μL, 0.1 mmol) was added to the mixture, and stirring was continued until TLC indicated disappearance of imidate (about 30 min). The reaction mixture was quenched by the addition of Et_3N. The mixture was filtered, the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2 = 10:1:1) to give disaccharide **30** (1.8 g, 91%) as a white solid: $[\alpha]_D^{24}$ = 12.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 2 H), 7.64–7.07 (m, 20 H), 6.89 (d, *J* = 8.1 Hz, 2 H), 5.53 (s, 1 H), 5.23 (t, *J* = 8.7 Hz, 1 H), 4.92 (d, *J* = 7.5 Hz, 1 H), 4.83–4.56 (m, 5 H), 4.38–4.35 (m, 1 H), 4.24–3.94 (m, 3 H), 3.74–3.09 (m, 9 H), 3.73 (s, 3 H), 0.89 (s, 9 H), 0.09, 0.08 (s, each 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.05, 159.6, 138.8, 138.1, 137.5, 133.6, 130.3, 130.1, 129.8, 129.3, 128.7, 128.49, 128.47, 128.4, 128.1, 128.0, 127.80, 127.77, 126.3, 114.1, 101.4, 101.0, 97.2, 82.0, 81.0, 78.6, 75.4, 74.9, 74.4, 74.1, 73.3, 68.8, 68.5, 67.5, 66.3, 55.5, 25.8, 18.2, -4.3, -5.1; ESI-MS *m/z* calcd for $C_{54}H_{63}N_3O_{12}SiNa[M+Na]^+$ 996.4073, found 996.4081.

tert-Butyldimethylsilyl (methyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (31)



29 **31**

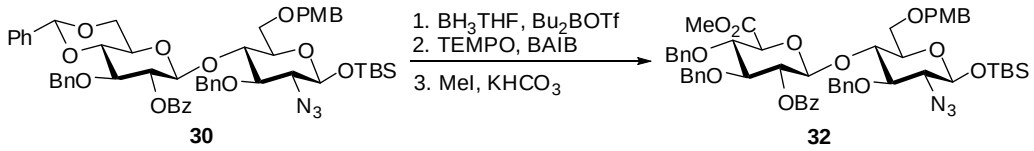
Disaccharide **29** (3.6 g, 3.8 mmol) was dissolved in BH_3·THF (1M, 38 mL, 38 mmol) under nitrogen and cooled to 0 °C. After 15 min, Bu_2B·OTf (1 M, 7.6 mL, 7.6 mmol) was added dropwise and stirring was continued at 0 °C for 2 h. The reaction mixture was quenched by the addition of Et_3N and the excess BH_3·THF was consumed by slowly adding methanol. The solvent was co-evaporated with methanol twice. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 6:1) to give the corresponding 6'-ol (3.4 g, 95%) as a white solid: ^{1}H NMR 400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2 H), 7.92 (d, *J* = 7.2 Hz, 2 H), 7.58 (t, *J* = 11.6 Hz, 1 H), 7.45–7.10 (m, 20 H), 5.32–5.27 (dd, *J* = 8.0, 9.2 Hz, 1 H), 4.96 (d, *J* = 11.2 Hz, 1 H), 4.84–4.78 (m, 2 H), 4.72 (d, *J* = 11.6 Hz, 1 H), 4.63–4.59 (m, 3 H), 4.48–4.34 (m, 3 H), 3.81–3.23 (m, 9 H), 0.85 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H);

ESI-MS *m/z* calcd for $C_{53}H_{61}N_3O_{13}SiNa$ $[M+Na]^+$ 982.3917, found 982.3942.

To a vigorously stirring solution of the above product (3.4 g, 3.4 mmol) in a mixture of CH_2Cl_2/H_2O (60 mL, v/v = 2/1), were added TEMPO (53 mg, 0.34 mmol) and BAIB (4.4 g, 13.6 mmol). Stirring was continued until TLC indicated complete conversion of the starting material (about 3 h). The reaction mixture was quenched by the addition of aqueous Na_2SO_3 (60 mL). The mixture was acidized with 5% HCl, then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine (50 mL), and then dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was co-evaporated with toluene twice.

The resulting oily residue was dissolved in DMF (60 mL) at 0 °C, then K_2CO_3 (1.4 g, 13.6) and an excess of methyl iodide (1.7 mL, 27.3 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The excess methyl iodide was quenched by the addition of AcOH. The mixture was concentrated in vacuo. The oily residue was diluted with CH_2Cl_2 and washed with saturated sodium bicarbonate and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to yield **31** (2.8 g, 81% for 2 steps) as a white solid: $[\alpha]_D^{24}$ = +30.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2 H), 7.90 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.44–7.09 (m, 15 H), 5.35 (t, *J* = 8.4 Hz, 1 H), 5.04 (d, *J* = 10.8 Hz, 1 H), 4.80–4.70 (m, 4 H), 4.62 (d, *J* = 5.6 Hz, 1 H), 4.60 (d, *J* = 5.6 Hz, 1 H), 4.47–4.43 (m, 2 H), 4.36–4.32 (dd, *J* = 5.6, 12.0 Hz, 1 H), 4.00 (t, *J* = 9.2 Hz, 1 H), 3.90 (d, *J* = 9.6 Hz, 1 H), 3.83–3.56 (m, 2 H), 3.45 (s, 3 H), 3.45–3.27 (m, 3 H), 0.83 (s, 9 H), 0.47 (s, 3 H), 0.18 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 165.9, 165.0, 138.5, 137.6, 137.5, 137.4, 133.2, 129.8, 129.7, 129.6, 129.1, 128.6, 128.4, 128.3, 128.3, 128.0, 127.99, 127.96, 127.8, 127.6, 101.4, 96.9, 81.7, 80.8, 79.4, 78.1, 77.4, 77.1, 76.7, 75.4, 75.2, 75.1, 74.7, 73.7, 73.0, 68.4, 62.8, 52.5, 25.5, 17.9, -4.4, -5.2; ESI-MS *m/z* calcd for $C_{54}H_{61}N_3O_{13}SiNa$ $[M+Na]^+$1010.3866, found 1010.3897.

tert-Butyldimethylsilyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido -3-*O*-benzyl-2-deoxy-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (32)



30 **32**

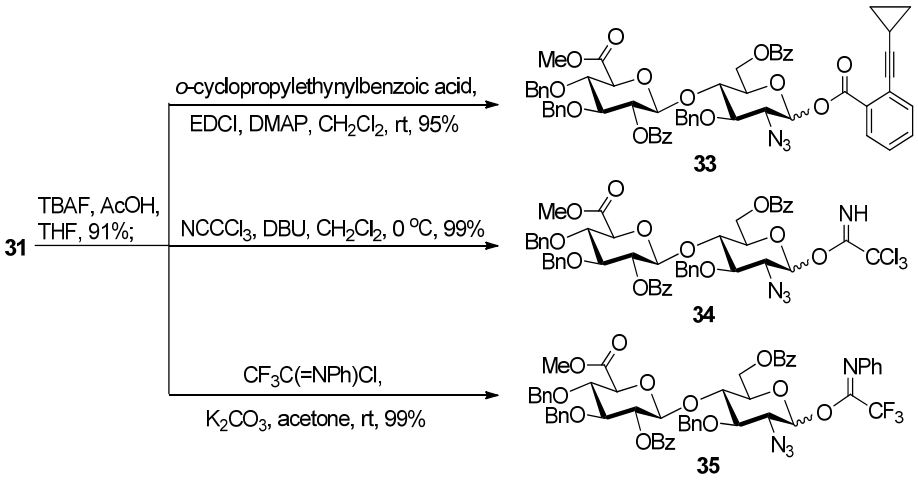
Disaccharide **30** (1.0 g, 1.0 mmol) was dissolved in BH_3·THF (1 M, 10 mL, 10 mmol) under nitrogen and cooled to 0 °C. After 15 min, Bu_2B·OTf (1 M, 2.1 mL, 2.1 mmol) was added dropwise and stirring was continued at 0 °C for 2 h. The reaction mixture was quenched by the addition of Et_3N and the excess BH_3·THF was consumed by slowly adding methanol. The solvent was removed in vacuo, and the residue was co-evaporated with methanol twice. The residue was purified by silica gel column

chromatography (petroleum ether/EtOAc = 6:1) to give the 6'-ol (1.0 g, 99%) as a white solid: ^{1}H NMR 400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2 H), 7.60 (t, J = 7.2 Hz, 1 H), 7.47–7.11 (m, 19 H), 5.19 (t, J = 8.8 Hz, 1 H), 4.94 (d, J = 10.8 Hz, 1 H), 4.80-4.56 (m, 7 H), 4.40–4.37 (m, 2 H), 4.28 (d, J = 11.6 Hz, 1 H), 3.96–3.91 (m, 1 H), 3.74 (s, 3 H), 3.67–3.25 (m, 9 H), 3.11 (d, J = 9.2 Hz, 1 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H); ESI-MS *m/z* calcd for $C_{54}H_{65}N_3O_{12}SiNa$ $[M+Na]^+$ 998.4230, found 998.4235.

To a vigorously stirring solution of the above product (0.93 g, 0.96 mmol) in a mixture of CH_2Cl_2/H_2O (24 mL, v/v = 2/1), were added TEMPO (15 mg, 0.1 mmol) and BAIB (1.2 g, 3.8 mmol). Stirring was continued until TLC indicated complete conversion of the starting material (about 3 h). The reaction was quenched by the addition of aqueous Na_2SO_3 (20 mL). The mixture was acidized with 5% HCl, then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in vacuo, the residue was co-evaporated with toluene twice.

The above oily residue was dissolved in DMF (10 mL) at 0 ^{o}C, then K_2CO_3 (0.4 g, 3.8) and an excess of methyl iodide (0.5 mL, 7.7 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The excess methyl iodide was quenched by the addition of AcOH. The mixture was concentrated in vacuo, the oily residue was diluted by CH_2Cl_2 and washed with saturated sodium bicarbonate and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to yield **32** (0.75 g, 75% for 2 steps) as a white solid: $[\alpha]_D^{24}$ = +1.8 (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2 H), 7.59 (t, J = 6.0 Hz, 1 H), 7.46–7.09 (m, 14 H), 6.93 (d, J = 8.8 Hz, 2 H), 5.24 (t, J = 8.4 Hz, 1 H), 5.00 (d, J = 10.4 Hz, 1 H), 4.76–4.54 (m, 7 H), 4.36 (d, J = 7.2 Hz, 1 H), 4.22 (d, J = 12.0 Hz, 1 H), 3.98–3.93 (m, 2 H), 3.84 (d, J = 9.2 Hz, 1 H), 3.73 (s, 3 H), 3.62–3.53 (m, 2 H), 3.59 (s, 3 H), 3.37 (d, J = 9.2 Hz, 1 H), 3.27–3.25 (m, 2 H), 3.08 (d, J = 10.0 Hz, 2 H), 0.88 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 164.8, 159.4, 138.6, 137.8, 137.7, 133.4, 130.1, 129.8, 129.7, 129.6, 128.5, 128.4, 128.3, 128, 2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.4, 114.0, 100.5, 97.0, 82.1, 80.7, 79.6, 77.4, 77.2, 77.0, 76.7, 76.5, 75.2, 75.1, 74.5, 73.7, 73.2, 68.3, 67.2, 55.2, 52.4, 25.6, 18.0, -4.3, -5.2; ESI-MS *m/z* calcd for $C_{55}H_{65}N_3O_{13}SiNa$ $[M+Na]^+$ 1026.4179, found 1026.4218.

Disaccharide donors 33-35



(Methyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl 2-(cyclopropylethynyl)-benzoate (33)

Disaccharide **31** (2.9 g, 2.9 mmol) was dissolved in THF (25 mL) followed by the addition of AcOH (0.5 mL, 8.7 mmol) and TBAF in THF (1 M, 5.8 mL, 5.8 mmol). Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with saturated aqueous sodium bicarbonate (50 mL) and brine (50 mL). The organic phase was dried with Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was chromatographed over silica gel (petroleum ether ether/EtOAc = 3:1) to give the hemiacetal (2.3 g, 91%) as a white solid: ESI-MS (*m/z*) 891.8 $[M+NH_4]^+$, 896.7 $[M+Na]^+$.

A solution of the above hemiacetal (282 mg, 0.32 mmol), *ortho*-alkynylbenzate (72 mg, 0.35 mmol), 4-dimethylaminopyridine (DMAP) (4 mg, 0.03 mmol), and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (124 mg, 0.65 mmol) in dry CH_2Cl_2 was stirred at room temperature. Stirring was continued until TLC indicated disappearance of the starting material (about 5 h). The mixture was diluted with CH_2Cl_2, and washed with saturated Sodium bicarbonate and brine, respectively. The filtrates were concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1) to give **33** (319 mg, 95%) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–7.82 (m, 5H), 7.68–6.98 (m, 25H), 6.44 (d, J = 3.8 Hz, 1H), 5.61 (d, J = 8.4 Hz, 1H), 5.44–5.32 (m, 1H), 5.24 (d, J = 10.5 Hz, 1H), 5.15 (d, J = 10.6 Hz, 1H), 4.85–4.37 (m, 8H), 4.18–3.94 (m, 2H), 3.89–3.47 (m, 8H), 1.51–1.38 (m, 1H), 0.81 (d, J = 6.6 Hz, 4H); ESI-MS *m/z* calcd for $C_{60}H_{55}N_3O_{14}Na$ $[M+Na]^+$ 1064.3576, found 1064.3570.

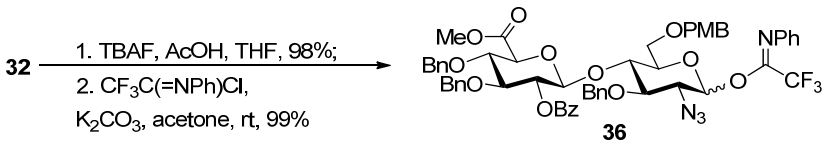
(Methyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl trichloracetimidate (34)

The hemiacetal (100 mg, 0.11 mmol) was dissolved in dry CH_2Cl_2 (2 mL) and cooled to 0 °C. Trichloroacetonitrile (60 μL, 0.6 mmol) and DBU (cat.) were added successively. Stirring was continued until TLC indicated disappearance of the starting material (about 2 h). The mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1, containing 1% Et_3N) to give **34** (115 mg, 99%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.95 (dd, J = 24.1, 7.3 Hz, 4H), 7.59 (t, J = 7.4 Hz, 1H), 7.52–6.96 (m, 22H), 6.28 (d, J = 3.5 Hz, 1H), 5.45–5.33 (m, 1H), 5.21 (d, J = 10.5 Hz, 1H), 4.86–4.54 (m, 6H), 4.52–4.30 (m, 2H), 4.15–3.93 (m, 3H), 3.93–3.74 (m, 3H), 3.63 (dd, J = 10.1, 3.6 Hz, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.22, 165.96, 165.05, 160.62, 137.93, 137.58, 137.53, 133.61, 133.55, 129.78, 129.75, 129.49, 129.13, 128.75, 128.66, 128.58, 128.50, 128.45, 128.15, 128.05, 127.92, 127.87, 101.35, 94.26, 90.81, 81.70, 79.47, 78.04, 77.31, 75.93, 75.32, 75.26, 74.99, 73.78, 71.55, 62.41, 62.10, 52.64; ESI-MS m/z 1039.7 $[M+Na]^+$.

(Methyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl *N*-phenyltrifluoroacetimidate (35)

The hemiacetal (240 mg, 0.27 mmol) was dissolved in acetone (3 mL). *N*-Phenyltrifluoroacetimidoyl chloride (45 μL, 0.41 mmol) and K_2CO_3 (95 mg, 0.7 mmol) were added successively. Stirring was continued until TLC indicated disappearance of starting material (about 2 h). The mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1, containing 1% Et_3N) to give **35** (284 mg, 99%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 30.1, 7.7 Hz, 4H), 7.57 (t, J = 7.4 Hz, 1H), 7.51–6.91 (m, 22H), 6.70 (d, J = 7.4 Hz, 2H), 5.35 (t, J = 8.5 Hz, 1H), 5.11 (d, J = 10.8 Hz, 1H), 4.84–4.52 (m, 6H), 4.49–4.27 (m, 2H), 4.09–3.69 (m, 4H), 3.67–3.41 (m, 5H), 3.09 (q, J = 7.2 Hz, 1H); ESI-MS m/z 1067.9 $[M+Na]^+$.

(Methyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-(4-methoxybenzyl)-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl *N*-phenyltrifluoroacetimidate (36)

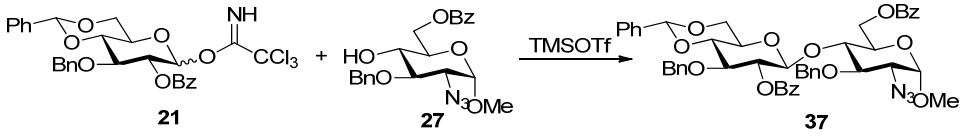


Disaccharide **32** (0.75 g, 0.75 mmol) was dissolved in THF (5 mL) followed by the addition of AcOH (0.13 mL, 2.24 mmol) and TBAF in THF (1 M, 1.5 mL, 1.5 mmol). Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous sodium bicarbonate and brine. The organic phase was dried with Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was chromatographed over

silica gel (petroleum ether ether/EtOAc = 4:1) to give the hemiacetal (0.66 g, 98%) as a white solid: ESI-MS *m/z* 907.8 $[M+NH_4]^+$, 912.8 $[M+Na]^+$.

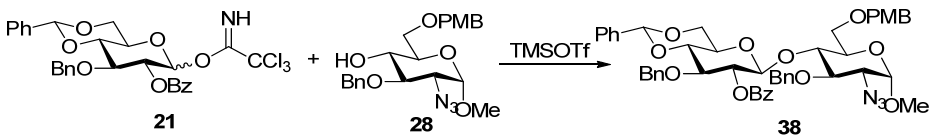
The above hemiacetal (400 mg, 0.45 mmol) was dissolved in acetone (5 mL). *N*-Phenyltrifluoroacetimidoyl chloride (74 μL, 0.67 mmol) and K_2CO_3 (155 mg, 1.1 mmol) were added successively. Stirring was continued until TLC indicated disappearance of the starting material (about 2 h). The mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1, containing 1% Et_3N) to give **36** (477 mg, 99%) as a white solid.

Methyl
(2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (37)



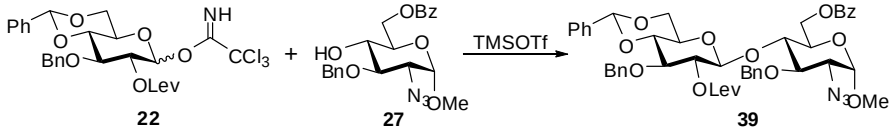
Trichloroacetimidate **21** (1.7 g, 2.87 mmol) and acceptor **27**[S3] (1.1 g, 2.61 mmol) were dissolved in CH_2Cl_2 (20 mL) under nitrogen. Powdered freshly activated 4 Å molecular sieves (4.0 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (39 μL, 0.2 mmol) was added to the mixture, and stirring was continued until TLC indicated disappearance of the imidate (about 30 min). The reaction was quenched by the addition of Et_3N. The mixture was filtered, the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2 = 10:1:1) to give disaccharide **37** (2.38 g, 97%) as a white solid: $[\alpha]_D^{27}$ = 93.9 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2 H), 7.92 (d, *J* = 7.2 Hz, 2 H), 7.59–7.32 (m, 16 H), 7.13–7.06 (m, 5 H) , 5.52 (s, 1 H), 5.37 (t, *J* = 8.4 Hz, 1 H), 5.05 (d, *J* = 10.4 Hz, 1 H), 4.82–4.71 (m, 4 H), 4.64 (d, *J* = 11.6 Hz, 1 H), 4.41 (s, 2 H), 4.14–4.10 (dd, *J* = 4.8, 10.8 Hz, 1 H), 3.94–3.76 (m, 5 H), 3.46–3.30 (m, 3 H), 3.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.1, 138.4, 137.8, 137.2, 133.5, 133.5, 130.0, 129.9, 129.7, 129.6, 129.3, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 126.1, 101.7, 101.4, 98.5, 81.8, 78.3, 78.2, 78.1, 75.6, 74.3, 73.91, 69.0, 68.5, 66.5, 63.2, 62.6, 55.6; ESI-MS *m/z* calcd for $C_{48}H_{47}N_3O_{12}Na$ $[M+Na]^+$ 880.3070, found 880.3052.

***tert*-Butyldimethylsilyl**
(2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (38)



Trichloroacetimidate **21** (0.8 g, 1.33 mmol) and acceptor **28**[S2] (0.52 g, 1.21 mmol) were dissolved in CH_2Cl_2 (10 mL) under nitrogen. Powdered freshly activated 4 Å molecular sieves (2.0 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (19 μL, 0.1 mmol) was added to the mixture, and stirring was continued until TLC indicated disappearance of the imidate (about 30 min). The reaction was quenched by the addition of Et_3N. The mixture was filtered, the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2 = 10:1:1) to give **38** (1.05 g, 90%) as a white solid: $[\alpha]_D^{24}$ = 48.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR 300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2 H), 7.64–7.09 (m, 20 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 5.51 (s, 1 H), 5.21 (t, *J* = 8.4 Hz, 1 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.83-4.59 (m, 5 H), 4.41 (d, *J* = 7.8 Hz, 1 H), 4.22–4.15 (m, 2 H), 3.99 (t, *J* = 9.3 Hz, 1 H), 3.82 (t, *J* = 9.6 Hz, 1 H), 3.69–3.15 (m, 8 H), 3.68 (s, 3 H), 3.29 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 159.9, 138.7, 137.5, 133.6, 130.3, 130.0, 129.8, 129.3, 128.7, 128.5, 128.45, 128.40, 128.2, 128.0, 127.8, 126.3, 114.3, 101.4, 100.8, 98.9, 81.9, 78.7, 78.3, 77.0, 75.4, 74.5, 74.0, 73.4, 70.3, 68.7, 67.0, 66.3, 63.1, 55.6, 55.5; ESI-MS *m/z* calcd for $C_{49}H_{51}N_3O_{12}Na$ $[M+Na]^+$ 896.3365, found 896.3366.

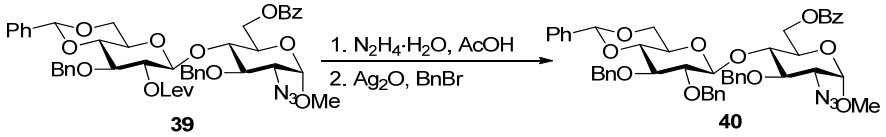
Methyl
(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (39)



Trichloroacetimidate **22** (1.9 g, 3.7 mmol) and acceptor **27** (1.82 g, 4.4 mmol) were dissolved in CH_2Cl_2 (30 mL) under nitrogen. Powdered freshly activated 4 Å molecular sieves (4.0 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (66 μL, 0.3 mmol) was added to the mixture, and stirring was continued until TLC indicated disappearance of the imidate (about 30 min). The reaction was quenched by the addition of Et_3N. The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1) to give **39** (2.7 g, 86%) as a white solid: $[\alpha]_D^{23}$ = 64.1 (*c* 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.47–7.28 (m, 17 H), 5.47 (s, 1 H), 5.07 (t, *J* = 9.6 Hz, 1 H), 4.99 (d, *J* = 10.4 Hz, 1 H), 4.84 (d, *J* = 11.6 Hz, 1 H), 4.79–4.53 (m, 6 H), 4.13–4.08 (m, 2 H), 3.99–3.93 (m, 2 H), 3.71–3.65 (m, 2 H), 3.46–3.37 (m, 5 H) , 3.26–3.20 (m, 1 H), 2.87–2.79 (m, 1 H), 2.69–2.57 (m, 2 H), 2.41–2.33 (m, 1 H), 2.14 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 171.5, 166.2, 138.3, 138.2, 137.1, 133.5, 129.8, 129.6, 129.1, 128.7, 128.4, 128.3, 128.0, 127.8, 127.7, 126.0, 101.4, 101.2, 98.4, 81.5, 78.9, 78.4, 78.0, 75.6, 74.5, 73.6, 68.8, 68.4, 66.3, 63.2, 62.9, 55.3, 37.7, 29.8, 27.8; ESI-MS *m/z* calcd for $C_{46}H_{49}N_3O_{13}Na$

[M+Na]$^+$ 874.3158, found 874.3140.

Methyl
(2,3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (40)

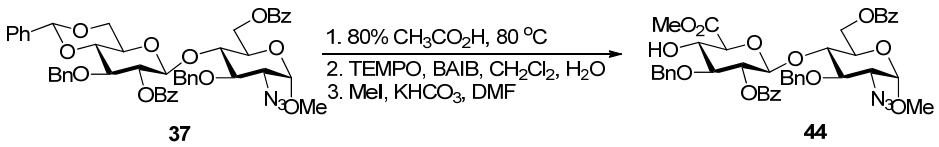


39 **40**

Disaccharide **39** (2.6 g, 3.0 mmol) was dissolved in CH_2Cl_2 (20 mL), acetic acid (0.86 mL, 15.0 mmol) and hydrazine hydrate (0.72 mL, 15.0) were added. Stirring was continued until TLC indicated disappearance of the raw material. The reaction was quenched by the addition of acetone. The solvent was removed in vacuo, the residue was dissolve in CH_2Cl_2 and washed with water and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1) to give the 2'-ol (2.1 g, 93%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 2 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.48–7.28 (m, 17 H), 5.48 (s, 1 H), 5.01–4.94 (m, 2 H), 4.85–4.70 (m, 4 H), 4.63–4.57 (m, 2 H), 4.06-3.95 (m, 4 H), 3.64–3.57 (m, 3 H), 3.50-3.45 (m, 2 H), 3.42 (s, 3 H), 3.28–3.22 (m, 1 H); ESI-MS *m/z* 776.3 [M+Na]$^+$.

The above product (1.0 g, 1.3 mmol) was dissolved in DMF (6 mL). Benzyl bromide (0.32 mL, 2.64 mmol) was added and the mixture was stirred for 30 min. Silver(I)oxide (800 mg, 3.4 mmol) was added and the reaction vessel was covered in aluminum foil to exclude light. After 8 h, the reaction mixture was filtered through Celite. The filtrate was concentrated in vacuo. Flash chromatography on silica gel (petroleum ether/EtOAc = 4: 1) gave **40** (684 mg, 60%) as a white solid: $[\alpha]_D^{23}$ = 54.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 2 H), 7.57 (t, J = 7.6 Hz, 1 H), 7.46–7.24 (m, 22 H), 5.50 (s, 1 H), 5.00 (d, J = 10.4 Hz, 1 H), 4.92–4.73 (m, 6 H), 4.65 (dd, J = 12.4 Hz, 1.6 Hz, 1 H), 4.58 (d, J = 7.6 Hz, 1 H), 4.47 (dd, J = 12.0 Hz, 4.4 Hz, 1 H), 4.17 (dd, J = 10.4, 4.4 Hz, 1 H), 3.98 (t, J = 9.2 Hz, 1 H), 3.87 (t, J = 10.0 Hz, 1 H), 3.79–3.73 (m, 2 H), 3.64 (t, J = 8.8 Hz, 1 H), 3.51–3.44 (m, 6 H), 3.29–3.23 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 138.4, 138.1, 137.2, 133.3, 129.8, 129.5, 129.0, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 126.0, 103.2, 101.1, 98.2, 82.7, 81.6, 81.2, 78.4, 76.6, 76.0, 75.5, 75.2, 69.1, 68.6, 66.1, 62.9, 62.4, 55.4; ESI-MS *m/z* calcd for $C_{48}H_{49}N_3O_{11}Na$ [M+Na]$^+$ 866.3259, found 866.3244.

Methyl (benzyl
2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (44)



37 **44**

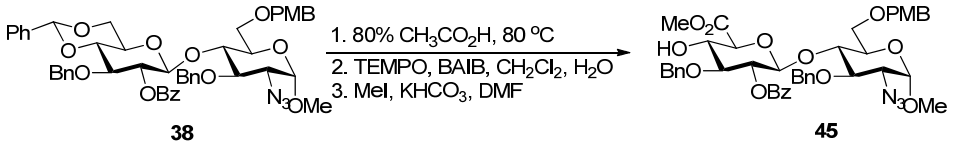
Disaccharide **37** (2.22 g, 2.58 mmol) was dissolved in CH_3CO_2H/H_2O (25 mL, v/v = 8:2). The mixture was heated at 80 °C until TLC indicated disappearance of the starting material. The mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1) to give 4',6'-diol **41** (1.9 g, 96%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 6.8 Hz, 2 H), 7.95 (d, J = 6.8 Hz, 2 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.49–7.15 (m, 15 H), 5.31 (t, J = 8.8 Hz, 1 H), 5.04 (d, J = 10.8 Hz, 1 H), 4.82 (d, J = 10.8 Hz, 1 H), 4.71–4.38 (m, 6 H), 3.94–3.61 (m, 6 H), 3.44–3.41 (dd, J = 3.6, 9.6 Hz, 1 H), 3.34 (s, 3 H), 3.34–3.16 (m, 2 H), 2.54–2.52 (m, 1 H), 1.87–1.83 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.0, 138.2, 137.7, 133.4, 129.8, 129.5, 129.2, 128.7, 128.6, 128.5, 128.0, 127.93, 127.90, 127.4, 101.0, 98.4, 82.7, 78.1, 77.7, 75.7, 75.3, 74.8, 73.9, 70.6, 68.9, 63.2, 62.6, 62.0, 55.4; ESI-MS *m/z* calcd for $C_{41}H_{43}N_3O_{12}Na$ $[M+Na]^+$ 792.2739, found 792.2745.

To a vigorously stirring solution of **41** in CH_2Cl_2/H_2O (24 mL, v/v = 2:1) were added TEMPO (7 mg, 0.04 mmol) and BAIB (1.6 g, 5.0 mmol). Stirring was continued until TLC indicated complete conversion of the starting material to a spot of lower Rf (about 3 h). The reaction was quenched by the addition of aqueous Na_2SO_3 (20 mL). The mixture was acidized with 5% HCl, then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine (25 mL), and then dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, the residue was co-evaporated with toluene twice.

The above oily residue was dissolved in DMF (15 mL) at 0 °C, then K_2CO_3 (0.8 g, 8.0 mmol) and an excess of methyl iodide (1.0 mL, 16.0 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The excess methyl iodide was quenched by the addition of AcOH. The mixture was concentrated in vacuo. The oily residue was diluted with CH_2Cl_2 and washed with saturated sodium bicarbonate and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to yield **44** (1.73 g, 84% for 2 steps) as a white solid: $[\alpha]_D^{26} = 95.0$ (c 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 6.8 Hz, 2 H), 7.93 (d, J = 6.8 Hz, 2 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.46–7.27 (m, 10 H), 7.13 (s, 5 H), 5.35–5.33 (dd, J = 8.0, 9.2 Hz, 1 H), 5.15 (d, J = 10.8 Hz, 1 H), 4.78-4.67 (m, 5 H), 4.45–4.43 (m, 2 H), 4.03-3.93 (m, 3 H), 3.78–3.76 (m, 1 H), 3.72 (d, J = 9.6 Hz, 1 H), 3.65 (t, J = 9.2 Hz, 1 H), 3.57 (s, 3 H), 3.40–3.36 (m, 1 H), 3.33 (s, 3 H), 3.01 (d, J = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 166.0, 165.0, 138.4, 137.7, 133.4, 133.3, 129.8, 129.6, 129.1, 128.6, 128.5, 128.3, 128.0, 127.81, 127.76, 127.5, 101.3, 98.5, 81.0, 78.20, 78.16, 81.0, 75.3, 74.7, 74.4, 73.1, 72.2, 68.7, 63.1, 62.5, 55.4, 52.7; ESI-MS

m/z calcd for $C_{42}H_{43}N_3O_{13}Na$ $[M+Na]^+$ 820.2688, found 820.2676.

Methyl (methyl 2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-(4-methoxybenzyl)-*α*-D-glucopyranoside (45)



38 **45**

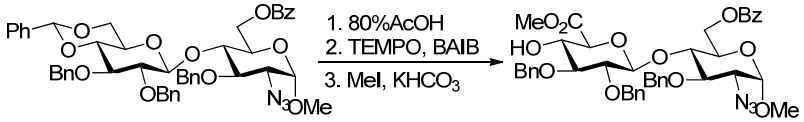
Disaccharide **38** (1.05 g, 1.2 mmol) was dissolved in CH_3CO_2H/H_2O (15 mL, v/v = 8:2). The mixture was heated at 80 °C until TLC indicated disappearance of the starting material. The mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1) to give the 4'6'-diol **42** (0.95 g, 99%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2 H, J = 8.8 Hz), 7.62 (t, J = 7.2 Hz, 1 H), 7.48 (t, J = 8.0 Hz, 1 H), 7.40–7.16 (m, 12 H), 6.99 (d, J = 8.4 Hz, 2 H), 5.17–5.13 (dd, J = 8.4, 9.6 Hz, 1 H), 4.99 (d, J = 10.8 Hz, 1 H), 4.78–4.72 (m, 3 H), 4.63–4.55 (dd, J = 11.2, 21.2 Hz, 2 H), 4.40 (d, J = 8.4 Hz, 1 H), 4.25 (d, J = 8.4 Hz, 1 H), 3.95 (t, J = 9.6 Hz, 1 H), 3.80 (s, 3 H), 3.84–3.17 (m, 10 H), 3.30 (s, 3 H), 2.37 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 159.6, 138.5, 138.0, 133.3, 130.2, 129.9, 129.7, 128.51, 128.47, 128.4, 127.9, 127.8, 127.7, 127.6, 127.4, 114.2, 100.1, 98.7, 83.1, 78.1, 77.7, 76.4, 75.3, 74.8, 74.0, 73.3, 70.9, 70.2, 66.9, 63.2, 63.1, 62.2, 55.4, 55.3; ESI-MS *m/z* calcd for $C_{42}H_{47}N_3O_{12}Na$ $[M+Na]^+$ 808.3052, found 808.3080.

To a vigorously stirring solution of the above product **42** (0.46 g, 0.6 mmol) in CH_2Cl_2/H_2O (24 mL, v/v = 2:1), were added TEMPO (2 mg, 0.01 mmol) and BAIB (0.48 g, 1.5 mmol). Stirring was continued until TLC indicated complete conversion of the starting material to a spot of lower R*f* (about 3 h). The reaction was quenched by the addition of aqueous Na_2SO_3 (20 mL). The mixture was acidized with 5% HCl, then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine (25 mL), and then dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, the residue was co-evaporated with toluene twice.

The above oily residue was dissolved in DMF (5 mL) at 0 °C, then K_2CO_3 (0.24 g, 2.4 mmol) and an excess of methyl iodide (0.3 mL, 4.8 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The excess methyl iodide was quenched by the addition of AcOH. The mixture was concentrated in vacuo. The oily residue was diluted with CH_2Cl_2 and washed with saturated sodium bicarbonate and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to yield **45** (0.38 g, 78% for 2 steps) as a white solid: $[\alpha]_D^{27}$ = 85.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2 H), 7.93–7.24 (m, 15 H), 6.98 (d, J = 8.4 Hz, 2 H), 5.17 (t, J = 9.2 Hz, 1 H), 5.10 (d, J = 7.2 Hz, 1 H), 4.77–4.70 (m, 3

H), 4.63 (t, J = 12.0 Hz, 2 H), 4.45 (d, J = 7.6 Hz, 1 H), 2.22 (d, J = 8.0 Hz, 1 H), 4.02 (t, J = 9.6 Hz, 1 H), 3.97–3.93 (m, 1 H), 3.81 (s, 3 H), 3.83–3.79 (m, 1 H), 3.70–3.67 (dd, J = 2.0, 10.8 Hz, 1 H), 3.65 (d, J = 9.6 Hz, 1 H), 3.56 (s, 3 H), 3.44–3.32 (m, 4 H), 3.28 (s, 3 H), 3.04 (d, J = 2.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 164.7, 159.7, 138.6, 138.0, 133.4, 130.2, 129.83, 129.75, 129.6, 129.5, 128.5, 128.3, 128.2, 128.0, 127.7, 127.6, 127.3, 114.2, 100.4, 98.8, 81.3, 80.0, 77.4, 75.1, 74.7, 74.1, 73.3, 73.1, 72.3, 70.0, 66.8, 62.9, 55.4, 55.3, 52.6; ESI-MS *m/z* calcd for $C_{43}H_{47}N_3O_{13}Na$ $[M+Na]^+$ 836.3001, found 836.3002.

Methyl (methyl 2,3-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-benzoyl-*α*-D-glucopyranoside (46)



40 **46**

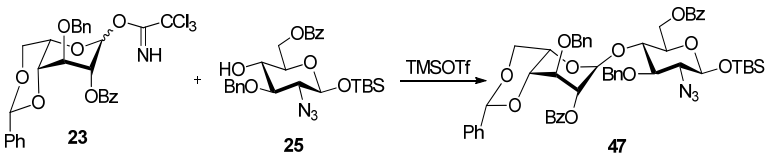
Disaccharide **40** (0.84 g, 1.0 mmol) was dissolved in CH_3CO_2H/H_2O (10 mL, v/v = 8:2). The mixture was heated at 80 ^oC until TLC indicated disappearance of the starting material. The mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 1:1) to give the 4'6'-diol **43** (0.71 g, 91%) as a white solid: ESI-MS (*m/z*) 773.5 $[M+NH_4]^+$, 778.3 $[M+Na]^+$.

To a vigorously stirring solution of the above product (0.62 g, 0.82 mmol) in CH_2Cl_2/H_2O (24 mL, v/v = 2:1) were added TEMPO (3 mg, 0.02 mmol) and BAIB (0.66 g, 2.05 mmol). Stirring was continued until TLC indicated complete conversion of the starting material to a spot of lower Rf (about 3 h). The reaction was quenched by the addition of aqueous Na_2SO_3 (20 mL). The mixture was acidized with 5% HCl, then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine (25 mL), and then were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, the residue was co-evaporated with toluene twice.

The above oily residue was dissolved in DMF (10 mL) at 0 ^oC, then K_2CO_3 (0.33 g, 3.3 mmol) and an excess of methyl iodide (0.4 mL, 6.4 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The excess methyl iodide was quenched by the addition of AcOH. The mixture was concentrated in vacuo. The oily residue was diluted with CH_2Cl_2 and washed with saturated sodium bicarbonate and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1) to yield **46** (0.54 g, 84% for 2 steps) as a white solid: $[\alpha]_D^{25}$ = 67.3 (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.6 Hz, 2 H), 7.58 (t, J = 7.4 Hz, 1 H), 7.44 (dd, J = 14.1, 7.2 Hz, 4 H), 7.38–7.13 (m, 13 H), 5.11 (d, J = 10.6 Hz, 1 H), 4.92–4.77 (m, 4 H), 4.73 (d, J = 3.6 Hz, 1 H), 4.72–4.63 (m, 2 H), 4.57 (d, J = 7.3 Hz, 1 H), 4.47

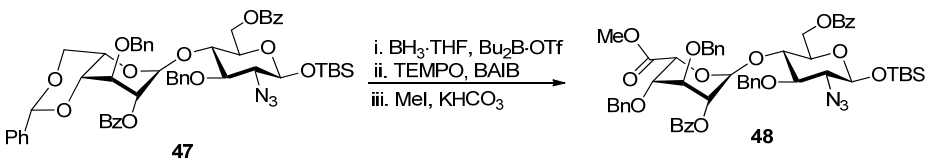
(dd, J = 12.2, 4.4 Hz, 1 H), 4.01 (t, J = 9.3 Hz, 1 H), 3.88 (t, J = 9.4 Hz, 2 H), 3.78 (dd, J = 9.4, 3.2 Hz, 1 H), 3.67 (d, J = 9.8 Hz, 1 H), 3.59 (s, 3 H), 3.54–3.34 (m, 6 H), 2.74 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 166.0, 138.5, 138.3, 138.2, 133.4, 129.7, 128.7, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 103.1, 98.6, 83.6, 82.0, 78.4, 77.9, 75.7, 75.6, 74.5, 72.1, 69.1, 63.0, 62.6, 55.6, 52.7; ESI-MS *m/z* 806.5 [M+Na$^+$]; HRMS (MALDI/DHB) calcd for $C_{42}H_{45}N_3O_{12}Na$ 806.2896, found 806.2930.

tert-Butyldimethylsilyl (2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*α*-L-iduropyranosyl) -(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (47)



Trichloroacetimidate **23** (0.5 g, 0.82 mmol) and acceptor **25** (0.39 g, 0.75 mmol) were dissolved in CH_2Cl_2 (10 mL) under nitrogen. Powdered freshly activated 4 Å molecular sieves (1.0 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 ^{o}C. TMSOTf (8 μL, 0.08 mmol) was added to the mixture, and stirring was continued until TLC indicated disappearance of the imidate (about 30 min). The reaction was quenched by the addition of Et_3N. The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2 = 8:1:1) to give **47** (0.78 g, 97%) as a white solid: $[\alpha]_D^{26}$ = -1.8 (*c* 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.54–7.15 (m, 21H), 5.37 (s, 1H), 5.25 (d, J = 7.8 Hz, 2H), 4.92–4.77 (m, 3H), 4.68 (d, J = 11.5 Hz, 1H), 4.60 (t, J = 8.4 Hz, 2H), 4.39 (dd, J = 11.6, 5.9 Hz, 1H), 4.06 (s, 1H), 3.97–3.87 (m, 3H), 3.85 (s, 1H), 3.73–3.63 (m, 1H), 3.42 (t, J = 8.7 Hz, 1H), 3.31 (dd, J = 20.3, 11.1 Hz, 2H), 0.88 (s, 9H), 0.10 (d, J = 8.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 138.3, 138.1, 137.8, 133.2, 133.1, 130.2, 129.9, 129.5, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.7, 126.5, 100.8, 98.2, 97.4, 81.3, 75.1, 74.8, 74.4, 74.1, 73.6, 72.3, 69.4, 69.2, 66.7, 63.3, 60.3, 25.7, 18.1, -4.2, -5.2; ESI-MS *m/z* $C_{53}H_{59}N_3O_{12}SiNa$ [M+Na]$^+$ 980.3760, found 980.3767.

tert-Butyldimethylsilyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*α*-L-iduropyranosyluronate)-(1→4)-2-azido-6-*O*-ben zoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (48)

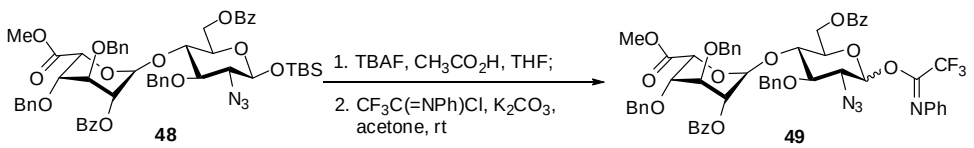


Disaccharide **47** (0.6 g, 0.63 mmol) was dissolved in BH_3·THF (1 M, 6.3 mL, 6.3 mmol) under nitrogen and cooled to 0 °C. After 15 min, Bu_2B·OEt_2 (1 M, 1.2 mL, 1.2 mmol) was added dropwise and stirring was continued at 0 °C for 2 h. The reaction was quenched by the addition of Et_3N and the excess BH_3 was consumed by slowly adding methanol. The solvent was removed in vacuo, the residue was co-evaporated with methanol twice. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1) to give the 6'-ol (0.55 g, 95%) as a white solid.

To a vigorously stirring solution of the above product in CH_2Cl_2/H_2O (60 mL, v/v = 2:1) were added TEMPO (10 mg, 0.06 mmol) and BAIB (0.78 g, 2.4 mmol). Stirring was continued until TLC indicated complete conversion of the starting material to a spot of lower R*f* (about 3 h). The reaction was quenched by the addition of aqueous Na_2SO_3 (60 mL). The mixture was acidized with 5% HCl, then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine (50 mL), and then dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, the residue was co-evaporated with toluene twice.

The above oily residue was dissolved in DMF (6 mL) at 0 °C, then K_2CO_3 (0.25 g, 2.4 mmol) and an excess of methyl iodide (0.3 mL, 4.8 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The excess methyl iodide was quenched by the addition of AcOH. The mixture was concentrated in vacuo. The oily residue was diluted with CH_2Cl_2 and washed with saturated sodium bicarbonate and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1) to yield **48** (0.48 g, 77% for 2 steps) as a white solid: $[\alpha]_D^{24}$ = -8.1 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.59–7.06 (m, 21H), 5.47 (d, *J* = 4.0 Hz, 1H), 5.18 (t, *J* = 3.9 Hz, 1H), 4.88–4.60 (m, 7H), 4.54–4.36 (m, 4H), 4.06–3.82 (m, 3H), 3.58 (dd, *J* = 7.8, 5.6 Hz, 1H), 3.49 (s, 3H), 3.39–3.28 (m, 2H), 0.86 (s, 9H), 0.07 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 166.1, 165.6, 138.3, 137.7, 137.4, 133.4, 133.0, 130.1, 130.0, 129.4, 129.2, 128.5, 128.5, 128.4, 128.34, 128.30, 128.1, 128.1, 128.0, 127.6, 98.2, 97.3, 80.9, 75.9, 75.2, 75.1, 74.3, 73.7, 73.1, 72.9, 70.5, 70.2, 68.7, 63.1, 51.9, 25.7, 18.0, -4.2, -5.1; ESI-MS *m/z* calcd for $C_{54}H_{61}N_3O_{13}SiNa$ $[M+Na]^+$ 1010.3866, found 1010.3816.

(Methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*a*-L-iduropyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl *N*-phenyltrifluoroacetimidate (49)

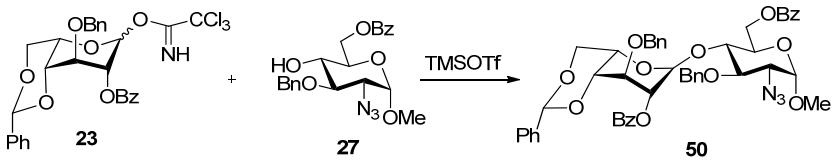


Disaccharide **48** (0.68 g, 0.69 mmol) was dissolved in THF (7 mL) followed by the

addition of AcOH (0.12 mL, 2.1 mmol) and TBAF in THF (1 M, 1.4 mL, 1.4 mmol). Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The mixture was diluted with CH_2Cl_2 and washed with saturated aqueous sodium bicarbonate and brine. The organic phase was dried with Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was chromatographed over silica gel (petroleum ether ether/EtOAc = 4:1) to give the hemiacetal (0.55 g, 92%) as a colorless oil: ESI-MS *m/z* 891.8 $[M+NH_4]^+$, 896.7 $[M+Na]^+$.

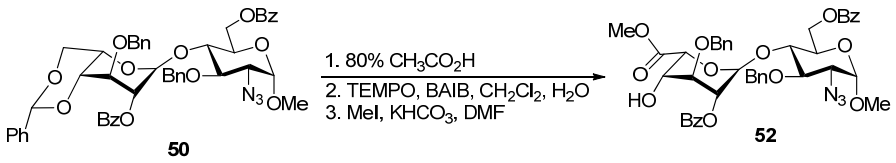
The above hemiacetal (420 mg, 0.48 mmol) was dissolved in acetone (5 mL). *N*-Phenyl-trifluoroacetimidoyl chloride (80 μL, 0.72 mmol) and K_2CO_3 (170 mg, 1.2 mmol) were added successively. Stirring was continued until TLC indicated disappearance of the starting material (about 2 h). The mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1, containing 1% Et_3N) to give **49** (491 mg, 98%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–7.88 (m, 4 H), 7.72–6.98 (m, 27 H), 6.74 (s, 2 H), 5.51 (dd, *J* = 16.6, 4.8 Hz, 1 H), 5.20 (d, *J* = 20.1 Hz, 1 H), 4.96 (dd, *J* = 25.0, 10.6 Hz, 1 H), 4.86–4.58 (m, 5 H), 4.57–4.36 (m, 3 H), 4.18 (dt, *J* = 18.7, 9.6 Hz, 1 H), 4.04 (s, 1 H), 3.99–3.84 (m, 2 H), 3.69 (brs, 1 H), 3.46 (d, *J* = 7.5 Hz, 3 H); ESI-MS *m/z* 1068.1 $[M+Na]^+$, 1083.8 $[M+K]^+$.

Methyl (2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*α*-L-iduropyranosyl)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (50)



Trichloroacetimidate **23** (0.5 g, 0.82 mmol) and acceptor **27** (0.31 g, 0.75 mmol) were dissolved in CH_2Cl_2 (20 mL) under nitrogen. Powdered freshly activated 4 Å molecular sieves (1.5 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (15 μL, 0.08 mmol) was added to the mixture, and stirring was continued until TLC indicated disappearance of the imidate (about 30 min). The reaction was quenched by the addition of Et_3N. The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2 = 10:1:1) to give **50** (0.64 g, 91%) as a white solid: $[\alpha]_D^{26}$ = 51.0 (*c* 3.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 7.9 Hz, 2 H), 7.62–7.14 (m, 21 H), 5.36 (s, 1 H), 5.27 (s, 2 H), 4.88–4.77 (m, 4 H), 4.75–4.64 (m, 2 H), 4.44 (d, *J* = 12.9 Hz, 1 H), 4.08–3.95 (m, 3 H), 3.94–3.78 (m, 4 H), 3.50 (dd, *J* = 10.1, 3.5 Hz, 1 H), 3.46 (s, 3 H), 3.21 (d, *J* = 12.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 138.2, 137.7, 133.2, 133.1, 130.2, 129.9, 129.5, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.24, 128.15, 127.8, 127.6, 126.5, 100.8, 98.6, 98.1, 79.1, 75.0, 74.8, 74.6, 73.5, 72.4, 69.8, 69.3, 66.7, 64.2, 63.0, 60.5, 60.3, 55.5; ESI-MS *m/z* calcd for $C_{48}H_{47}N_3O_{12}Na$ $[M+Na^+]$ 880.3052, found 880.3070.

Methyl (benzyl 2-*O*-benzoyl-3-*O*-benzyl-*α*-L-iduropyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (52)

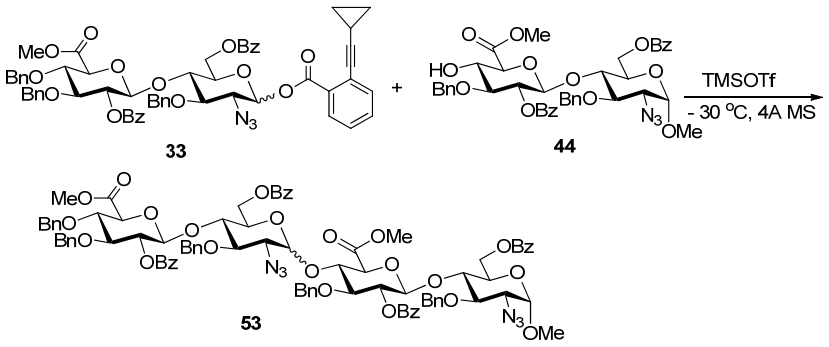


Disaccharide **50** (0.6 g, 0.71 mmol) was dissolved in CH_3CO_2H/H_2O (15 mL, v/v = 8:2). The mixture was heated at 80 ^oC until TLC indicated disappearance of the starting material. The mixture was concentrated in vacuo.

To a vigorously stirring solution of the above product **51** in CH_2Cl_2/H_2O (18 mL, v/v = 2/1) were added TEMPO (6 mg, 0.03 mmol) and BAIB (0.54 g, 1.7 mmol). Stirring was continued until TLC indicated complete conversion of the starting material to a spot of lower R*f* (~ 3 h). The reaction was quenched by the addition of aqueous Na_2SO_3 (20 mL). The mixture was acidized with 5% HCl, then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine (25 mL), and then were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, the residue was co-evaporated with toluene twice.

The above oily residue was dissolved in DMF (10 mL) at 0 ^oC, then K_2CO_3 (0.28 g, 2.8 mmol) and an excess of methyl iodide (0.35 mL, 5.6 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (about 3 h). The excess methyl iodide was quenched by the addition of AcOH. The mixture was concentrated in vacuo. The oily residue was diluted with CH_2Cl_2 and washed with saturated sodium bicarbonate and brine. The organic layers were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1) to yield **52** (0.46 g, 80% for 3 steps) as a white solid: $[\alpha]_D^{26} = 44.0$ (*c* 1.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 2 H), 7.92 (d, *J* = 7.4 Hz, 2 H), 7.60–7.15 (m, 16 H), 5.38 (s, 1 H), 5.22 (s, 1 H), 4.97 (d, *J* = 2.1 Hz, 1 H), 4.92–4.64 (m, 6 H), 4.49 (dd, *J* = 12.2, 4.0 Hz, 1 H), 4.09–3.83 (m, 5 H), 3.50–3.36 (m, 6 H), 2.66 (d, *J* = 10.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.01, 169.70, 166.08, 165.14, 160.52, 137.80, 137.34, 133.64, 133.11, 129.94, 129.85, 129.80, 129.76, 128.87, 128.69, 128.55, 128.52, 128.43, 128.20, 128.12, 128.01, 127.71, 127.47, 98.50, 98.13, 78.74, 75.48, 75.37, 74.90, 72.76, 69.31, 69.22, 68.47, 67.99, 63.81, 62.75, 55.42, 52.04; ESI-MS *m/z* calcd for $C_{42}H_{43}N_3O_{13}Na$ $[M+Na^+]$ 820.2659, found 820.2688.

Methyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*β*-D-glucopyranosyluronate)-(1→4)-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyransyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (53)



33 44

53

General Procedure for the Preparation of Tetrasaccharides with *ortho*-alkynylbenzoate Donors. Disaccharide *ortho*-alkynylbenzoate **33** (1.2 equiv) and disaccharide acceptor **44** (1.0 equiv) were dissolved in a solvent to maintain a concentration of 0.04~0.05 M. Powdered freshly activated 4Å molecular sieves (the weight of the sieves is equal to the combined weight of the donor and acceptor) were added, and the mixture was stirred for 1 hour at room temperature. A freshly prepared gold(I)-catalyst (0.1 equiv) was added, and stirring was continued until TLC indicated the disappearance of the donor. The reaction was quenched by the addition of Et_3N (0.5 mL). The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography using a gradient of toluene and EtOAc to give α-tetrasaccharide and β-tetrasaccharide respectively.

General Procedure for the Preparation of Tetrasaccharides with Trichloroacetimidate Donors. Disaccharide trichloroacetimidate donor (1.2 equiv) and disaccharide acceptor (1.0 equiv) were combined in a flask and co-evaporated with toluene (3 × 3 mL), and were then dissolved in a solvent to maintain a concentration of 0.04~0.05 M. Powdered freshly activated 4Å molecular sieves (the weight of the sieves is equal to the combined weight of the donor and acceptor) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (0.1 equiv) was added, and stirring was continued until TLC indicated the disappearance of the donor (2 hour). The reaction was quenched by the addition of Et_3N (0.5 mL). The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography using a gradient of toluene and EtOAc to give α-tetrasaccharide and β-tetrasaccharide respectively.

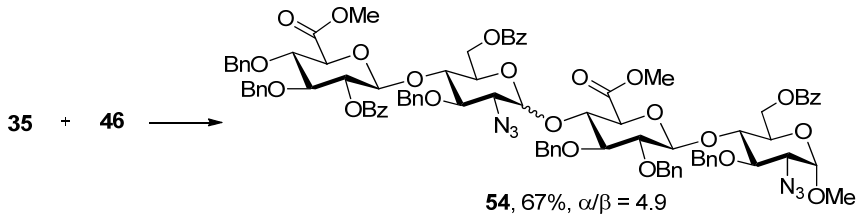
General Procedure for the Preparation of Tetrasaccharides with *N*-phenyl Trifluoroacetimidate Donors. Disaccharide *N*-phenyltrifloroacetimidate donor (1.2 equiv) and disaccharide acceptor (1.0 equiv) were combined in a flask and co-evaporated with toluene (3 × 3 mL), and were then dissolved in a solvent to maintain a concentration of 0.04~0.05 M. Powdered freshly activated 4Å molecular sieves (its weight is equal to the combined weight of the donor and acceptor) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 °C. TMSOTf (0.1 equiv) was added, and stirring was continued until TLC

indicated the disappearance of the donor (2 hour). The reaction was quenched by the addition of Et_3N (0.5 mL). The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography using a gradient of toluene and EtOAc to give the α-tetrasaccharide and β-tetrasaccharide, respectively.

53α: $[\alpha]_D^{28}$ = +50.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–7.91 (m, 8 H), 7.61–7.02 (m, 37 H), 5.40–5.34 (m, 3 H), 5.17 (d, *J* = 10.4 Hz, 1 H), 5.03 (d, *J* = 10.8 Hz, 1 H), 4.75–4.55 (m, 11 H), 4.43 (d, *J* = 10.0 Hz, 4 H), 4.18 (t, *J* = 9.2 Hz, 1 H), 3.97–3.90 (dd, *J* = 9.2, 19.6 Hz, 2 H), 3.88–3.84 (m, 3 H), 3.79–3.68 (m, 5 H), 3.50 (s, 3 H), 3.42 (d, *J* = 10.0 Hz, 1 H), 3.31 (s, 3 H), 3.26–3.23 (dd, *J* = 4.4, 10.4 Hz, 2 H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.6, 166.0, 165.9, 164.8, 164.7, 138.0, 137.9, 137.4, 137.3, 137.1, 133.5, 133.4, 129.8, 129.7, 129.6, 129.54, 129.48, 129.0, 129.0, 128.9, 128.7, 128.64, 128.59, 128.5, 128.4, 128.3, 128.2, 127.94, 127.89, 127.7, 127.61, 127.55, 101.4, 101.0, 98.6, 97.2, 82.6, 81.9, 79.4, 78.2, 78.0, 77.6, 77.2, 76.8, 75.6, 75.3, 75.0, 74.8, 74.7, 74.4, 74.2, 73.7, 73.4, 69.1, 68.7, 63.0, 62.6, 62.3, 61.9, 55.4, 52.4, 51.9; ESI-MS *m/z* calcd for $C_{90}H_{88}N_6O_{25}Na$ $[M+Na]^+$ 1675.5691, found 1675.5698.

53β: $[\alpha]_D^{28}$ = +24.6 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.90–7.84 (m, 6H), 7.56–6.74 (m, 37H), 5.32 (t, *J* = 8.4 Hz, 1H), 5.22 (t, *J* = 8.4 Hz, 1H), 5.07 (d, *J* = 7.6 Hz, 1H), 5.05 (d, *J* = 8.0 Hz, 1H), 4.75–4.54 (m, 10H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.44–4.41 (m, 1H), 4.32–4.26 (m, 4H), 4.19 (t, *J* = 8.8 Hz, 1H), 3.96–3.67 (m, 9H), 3.61 (s, 3H), 3.51 (s, 3H), 3.36–3.27 (m, 4H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 165.9, 165.8, 164.9, 164.7, 138.11, 138.06, 137.7, 137.52, 137.45, 133.5, 133.31, 133.26, 133.2, 129.9, 129.8, 129.5, 129.3, 129.1, 129.0, 128.7, 128.51, 128.48, 128.42, 128.37, 128.33, 128.3, 128.00, 127.95, 127.90, 127.82, 127.74, 127.66, 127.60, 127.53, 127. 2, 101.9, 101.4, 101.1, 98.6, 81.7, 80.8, 79.38, 79.32, 79.25, 78.1, 78.0, 77.3, 77.2, 77.0, 76.7, 75.8, 75.6, 75.2, 75.1, 74.7, 74.5, 74.3, 73.5, 72.96, 72.94, 68.7, 66.2, 63.0, 62.4, 62.3, 55.4, 52.8, 52.4; ESI-MS *m/z* calcd for $C_{90}H_{88}N_6O_{25}Na$ $[M+Na]^+$ 1675.5691, found 1675.5698.

Methyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*β*-D-glucopyranosyluronate)-(1→4)-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl 2,3-*O*-dibenzyl-*β*-D-glucopyran syluronate)-(1→4)-2-azido-6-*O*-benzoyl -3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (54)



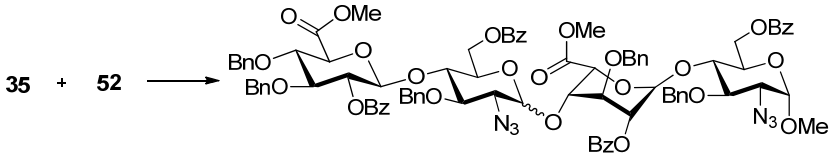
54, 67%, α/β = 4.9

54α (99.7 mg, 55.6%; a white solid): $[\alpha]_D^{28}$ = +82.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.15 (d, J = 7.8 Hz, 2 H), 8.09 (d, J = 7.9 Hz, 2 H), 8.04 (d, J = 7.9 Hz, 2 H), 7.76–7.06 (m, 39 H), 5.55 (d, J = 3.5 Hz, 1 H), 5.43 (t, J = 8.5 Hz, 1 H), 5.24 (d, J = 10.5 Hz, 1 H), 5.09 (d, J = 10.2 Hz, 1 H), 5.02 (d, J = 10.7 Hz, 1 H), 4.91–4.42 (m, 16 H), 4.18–3.93 (m, 4 H), 3.93–3.68 (m, 7 H), 3.63–3.44 (m, 8 H), 3.41 (dd, J = 10.0, 3.2 Hz, 1 H), 3.31 (dd, J = 10.2, 3.5 Hz, 1 H), 3.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.1, 165.9, 164.9, 138.1, 137.8, 137.8, 137.5, 137.4, 133.6, 133.5, 129.9, 129.7, 129.6, 129.1, 128.9, 128.8, 128.71, 128.65, 128.51, 128.47, 128.44, 128.40, 128.35, 128.1, 128.0, 127.9, 127.84, 127.79, 127.7, 127.4, 103.0, 100.9, 98.4, 97.2, 84.1, 82.7, 82.0, 79.5, 78.2, 77.9, 77.7, 75.9, 75.8, 75.6, 75.4, 75.1, 74.8, 74.6, 74.2, 73.5, 69.1, 69.0, 63.0, 62.7, 62.3, 62.1, 55.5, 52.5, 51.9; ESI-MS *m/z* calcd for $C_{90}H_{90}N_6O_{24}Na$ $[M+Na]^+$ 1661.5899, found 1661.5904.

54β (20.3 mg, 11.4%; a white solid): $[\alpha]_D^{28}$ = +49.3 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 2 H), 7.89 (d, J = 7.5 Hz, 2 H), 7.81 (d, J = 7.6 Hz, 2 H), 7.56–6.77 (m, 39 H), 5.25 (t, J = 8.6 Hz, 1 H), 5.00 (d, J = 10.6 Hz, 1 H), 4.94 (d, J = 10.1 Hz, 1 H), 4.82 (d, J = 11.3 Hz, 1 H), 4.70–4.42 (m, 14 H), 4.30 (dd, J = 12.2, 4.0 Hz, 1 H), 4.23 (d, J = 8.2 Hz, 2 H), 4.12 (d, J = 11.7 Hz, 1 H), 3.98 (d, J = 9.2 Hz, 1 H), 3.93–3.80 (m, 3 H), 3.78–3.55 (m, 9 H), 3.52–3.42 (m, 4 H), 3.37–3.23 (m, 6 H), 3.19 (t, J = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.2, 165.9, 165.9, 165.0, 138.5, 138.2, 138.1, 137.9, 137.6, 137.5, 133.6, 133.4, 123.0, 129.8, 129.68, 129.65, 129.5, 129.1, 128.8, 128.8, 128.6, 128.53, 128.45, 128.42, 128.39, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.2, 103.0, 101.8, 101.0, 98.8, 98.4, 82.2, 81.9, 81.8, 81.0, 79.6, 79.4, 78.3, 77.8, 75.9, 75.8, 75.7, 75.3, 75.2, 74.8, 74.4, 73.6, 73.0, 69.1, 66.3, 62.9, 62.5, 62.3, 55.6, 52.9, 52.5; ESI-MS *m/z* calcd for $C_{90}H_{90}N_6O_{24}Na$ $[M+Na]^+$ 1661.5899, found 1661.5904.

Methyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*β*-D-glucopyranosyluronate)-(1→4)-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-dibenzyl-2-O-benzoyl-*α*-L-iduropyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (55)



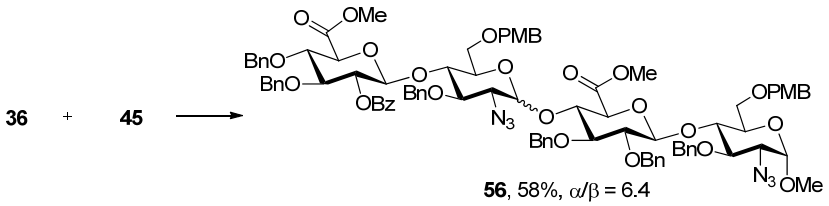
55, 66%, α/β = 3.2

55α (58.7 mg, 50.3%; a white solid): $[\alpha]_D^{30}$ = +57.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–7.91 (m, 8 H), 7.67–6.93 (m, 37 H), 5.55 (d, J = 4.8 Hz, 1 H), 5.37 (t, J = 8.5 Hz, 1 H), 5.18 (t, J = 5.1 Hz, 1 H), 4.94 (d, J = 10.5 Hz, 1 H), 4.86 (d, J = 10.6 Hz, 1 H), 4.81 (d, J = 3.4 Hz, 1 H), 4.78–4.66 (m, 8 H), 4.64–4.53 (m, 4 H), 4.51–4.31 (m, 5 H), 4.19 (d, J = 10.6 Hz, 1 H), 4.07 (t, J = 5.5 Hz, 1 H), 4.04–3.64 (m, 11 H), 3.58–3.44 (m, 4 H), 3.41 (dd, J = 10.1, 3.6 Hz, 1 H), 3.37 (s, 3 H), 3.30–3.17 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.1, 166.1, 166.0, 165.4, 165.0,

138.0, 137.9, 137.6, 137.5, 133.8, 133.7, 133.6, 133.2, 123.0, 129.9, 129.7, 129.6, 129.3, 129.1, 128.9, 128.8, 128.6, 128.42, 128.35, 128.3, 128.1, 128.0, 128.0, 127.9, 127.7, 127.7, 101.0, 98.5, 98.3, 82.1, 79.5, 78.6, 78.0, 76.5, 75.6, 75.4, 75.3, 75.2, 74.9, 74.7, 73.9, 73.6, 71.0, 70.6, 69.7, 69.3, 63.6, 62.9, 62.7, 62.0, 55.5, 52.6, 51.8; ESI-MS *m/z* calcd for $C_{90}H_{88}N_6O_{25}Na$ $[M+Na]^+$ 1675.5691, found 1675.5697.

55β (18.3 mg, 15.7%; a white solid): $[\alpha]_D^{30}$ = +24.1 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 4 H), 7.85 (d, *J* = 7.9 Hz, 2 H), 7.72 (d, *J* = 7.8 Hz, 2 H), 7.56–7.01 (m, 37 H), 5.39–5.23 (m, 2 H), 5.03 (t, *J* = 14.5 Hz, 2 H), 4.88 (s, 1 H), 4.82–4.50 (m, 13 H), 4.50–4.31 (m, 3 H), 4.20 (d, *J* = 11.9 Hz, 1 H), 4.11–3.68 (m, 12 H), 3.59–3.46 (m, 7 H), 3.46–3.34 (m, 4 H), 3.30 (t, *J* = 9.0 Hz, 1 H), 3.23–3.15 (m, 1 H), 3.10 (t, *J* = 8.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.2, 166.1, 165.8, 165.3, 164.9, 138.2, 137.9, 137.7, 137.6, 137.5, 133.6, 133.3, 133.2, 133.1, 130.0, 129.9, 129.5, 129.4, 129.1, 128.7, 128.6, 128.5, 128.4, 128.33, 128.26, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.5, 103.3, 101.3, 98.5, 98.0, 81.8, 81.0, 79.4, 78.9, 77.5, 77.4, 77.2, 76.8, 75.9, 75.7, 75.3, 74.8, 73.9, 73.6, 73.0, 72.5, 69.5, 68.1, 67.5, 66.3, 63.9, 62.9, 62.2, 55.5, 52.6, 52.1; ESI-MS *m/z* calcd for $C_{90}H_{88}N_6O_{25}Na$ $[M+Na]^+$ 1675.5691, found 1675.5697.

Methyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*β*-D-glucopyranosyluronate)-(1→4)-(2-azido-6-*O*-(4-methoxybenzyl)-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-(4-methoxybenzyl) -3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (56)

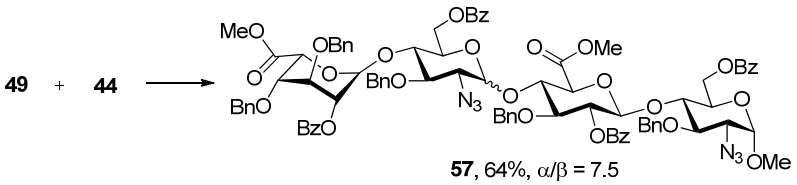


56α (75.2 mg, 50.2%; a white solid): $[\alpha]_D^{26}$ = +39.0 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.85 (m, 4 H), 7.66–6.97 (m, 39 H), 5.45 (d, *J* = 4.0 Hz, 1 H), 5.27–5.21 (m, 2 H), 5.18 (d, *J* = 10.5 Hz, 1 H), 5.01 (d, *J* = 10.7 Hz, 1 H), 4.87–4.41 (m, 12 H), 4.27 (dd, *J* = 12.1, 4.6 Hz, 2 H), 4.15–4.06 (m, 2 H), 4.05–3.99 (m, 1 H), 3.99–3.91 (m, 2 H), 3.86–3.54 (m, 13 H), 3.46–3.34 (m, 3 H), 3.34–3.23 (m, 5 H), 3.17 (d, *J* = 10.1 Hz, 1 H), 2.88 (s, 3 H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 168.4, 167.9, 164.7, 164.6, 159.9, 159.8, 138.3, 137.9, 137.8, 137.3, 133.6, 130.6, 130.4, 129.9, 129.8, 129.8, 129.7, 129.5, 129.4, 129.2, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 125.4, 114.4, 100.3, 100.1, 98.9, 97.3, 83.0, 82.5, 79.7, 77.8, 77.7, 77.4, 76.1, 75.6, 75.5, 75.2, 74.6, 74.2, 73.9, 73.6, 73.5, 73.5, 70.5, 70.0, 66.8, 66.3, 62.9, 62.6, 55.5, 55.4, 55.2, 52.6, 51.7; ESI-MS *m/z* calcd for $C_{92}H_{96}N_6O_{25}Na$ $[M+Na]^+$ 1707.6317, found 1707.6323.

56β (11.8 mg, 7.8%; a white solid): $[\alpha]_D^{25}$ = -2.60 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90–7.77 (m, 4 H), 7.58 (dd, *J* = 14.9, 7.4 Hz, 2 H), 7.50–6.84 (m, 37 H),

5.20 (dd, *J* = 9.4, 8.3 Hz, 1 H), 5.15–4.91 (m, 4 H), 4.74 (d, *J* = 10.8 Hz, 2 H), 4.71–4.34 (m, 8 H), 4.30–3.88 (m, 8 H), 3.88–3.56 (m, 14 H), 3.56–3.50 (m, 1 H), 3.44 (t, *J* = 9.2 Hz, 1 H), 3.36 (d, *J* = 9.9 Hz, 1 H), 3.34–3.23 (m, 8 H), 2.99 (d, *J* = 9.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.4, 164.8, 164.7, 159.8, 159.6, 138.7, 138.4, 138.3, 137.9, 137.8, 133.6, 133.3, 130.6, 130.2, 129.9, 129.80, 129.76, 129.71, 129.66, 129.4, 128.7, 128.6, 128.5, 128.38, 128.36, 128.2, 128.0, 127.8, 127.8, 127.7, 127.6, 127.3, 127.1, 114.3, 114.2, 101.9, 100.5, 100.3, 98.8, 82.2, 80.9, 80.6, 79.6, 79.5, 77.9, 76.7, 75.9, 75.7, 75.5, 75.3, 75.2, 75.1, 74.6, 74.5, 74.2, 73.5, 73.4, 73.03, 72.97, 70.1, 66.8, 66.6, 66.4, 62.9, 55.5, 55.4, 55.2, 52.9, 52.6; ESI-MS *m/z* calcd for $C_{92}H_{96}N_6O_{25}Na$ $[M+Na]^+$ 1707.6317, found 1707.6323.

Methyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*a*-L-iduropyranosyluronate)-(1→4)-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzyol-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (57)



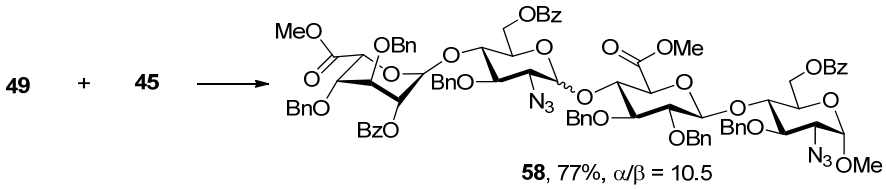
57, 64%, α/β = 7.5

57α (65.3 mg, 56.5%; a white solid): $[\alpha]_D^{27}$ = +36.4 (*c* 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 6 H), 7.95 (d, *J* = 7.3 Hz, 2 H), 7.65–7.02 (m, 37 H), 5.54 (d, *J* = 5.8 Hz, 1 H), 5.40 (t, *J* = 8.4 Hz, 2 H), 5.20 (t, *J* = 5.4 Hz, 1 H), 5.07 (d, *J* = 10.6 Hz, 1 H), 4.99 (d, *J* = 10.3 Hz, 1 H), 4.83–4.34 (m, 16 H), 4.24 (t, *J* = 9.0 Hz, 1 H), 4.17–4.03 (m, 1 H), 3.98–3.65 (m, 8 H), 3.52 (d, *J* = 10.0 Hz, 1 H), 3.41–3.25 (m, 8 H), 3.19 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 167.8, 166.2, 166.1, 165.4, 164.8, 138.1, 138.0, 137.7, 137.3, 133.61, 133.55, 133.0, 130.1, 130.0, 129.9, 129.7, 129.6, 129.3, 129.0, 128.8, 128.7, 128.43, 128.36, 128.34, 128.30, 128.27, 128.0, 127.9, 127.8, 127.7, 101.3, 98.6, 98.0, 97.3, 82.5, 78.3, 78.2, 78.1, 75.9, 75.8, 75.4, 74.93, 74.88, 74.7, 73.7, 73.0, 72.0, 71.7, 69.8, 68.8, 63.2, 63.0, 62.5, 62.0, 55.5, 52.3, 51.7; ESI-MS *m/z* calcd for $C_{90}H_{88}N_6O_{25}Na$ $[M+Na]^+$ 1675.5691, found 1675.5659.

57β (8.7 mg, 7.5%; a white solid): $[\alpha]_D^{27}$ = +32.9 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.85 (m, 8 H), 7.61–6.75 (m, 37 H), 5.40 (d, *J* = 4.5 Hz, 1 H), 5.27 (t, *J* = 8.4 Hz, 1 H), 5.15 (d, *J* = 4.2 Hz, 1 H), 5.08 (d, *J* = 10.5 Hz, 1 H), 4.88 (d, *J* = 10.5 Hz, 1 H), 4.81–4.60 (m, 7 H), 4.53 (d, *J* = 11.8 Hz, 2 H), 4.49–4.19 (m, 7 H), 4.04 (brs, 1 H), 3.97–3.81 (m, 5 H), 3.72 (t, *J* = 8.6 Hz, 2 H), 3.63 (s, 3 H), 3.46 (d, *J* = 11.3 Hz, 1 H), 3.41–3.24 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 168.3, 166.0, 165.6, 164.9, 138.2, 138.1, 137.83, 137.75, 137.4, 133.4, 133.3, 132.9, 130.2, 123.0, 129.90, 129.85, 129.7, 129.33, 129.27, 128.64, 128.57, 128.52, 128.45, 128.4, 128.31, 128.30, 128.2, 128.1, 128.02, 127.98, 127.8, 127.71, 127.68, 127.3, 102.1,

101.5, 98.6, 98.1, 81.1, 79.49, 79.45, 78.3, 78.2, 77.4, 77.2, 76.9, 75.7, 75.5, 75.4, 75.3, 74.7, 74.61, 74.57, 73.5, 73.21, 73.15, 72.9, 70.9, 70.7, 68.9, 66.7, 63.2, 62.6, 62.5, 55.5, 52.9, 51.8; ESI-MS *m/z* calcd for $C_{90}H_{88}N_6O_{25}Na$ $[M+Na]^+$ 1675.5691, found 1675.5672.

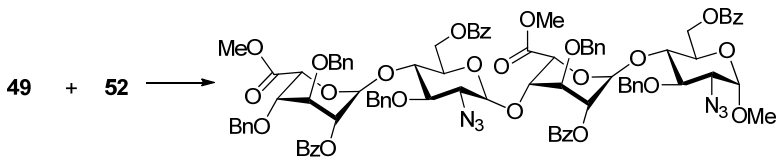
Methyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*a*-L-iduropyranosyluronate)-(1→4)-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl 2,3-*O*-dibenzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (58)



58α (87.7 mg, 70.3%; a white solid): $[\alpha]_D^{28}$ = +55.1 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.13–8.02 (m, 4 H), 7.98 (d, *J* = 7.5 Hz, 2 H), 7.67–7.05 (m, 39 H), 5.54 (d, *J* = 5.6 Hz, 1 H), 5.46 (d, *J* = 3.2 Hz, 1 H), 5.19 (t, *J* = 5.2 Hz, 1 H), 5.04 (d, *J* = 10.2 Hz, 1 H), 5.01–4.90 (m, 2 H), 4.88–4.34 (m, 18 H), 4.10 (t, *J* = 9.3 Hz, 2 H), 4.01–3.61 (m, 8 H), 3.56–3.27 (m, 10 H), 3.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.8, 168.6, 166.0, 165.9, 165.5, 138.6, 138.13, 138.08, 138.0, 137.8, 137.3, 133.43, 133.39, 132.9, 130.1, 130.0, 129.9, 129.8, 129.7, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.03, 127.98, 127.9, 127.8, 127.7, 127.4, 127.3, 103.0, 102.0, 98.5, 98.0, 82.2, 82.0, 81.2, 79.5, 78.3, 77.9, 75.8, 75.7, 75.4, 75.3, 74.7, 74.5, 73.5, 73.3, 72.9, 70.8, 70.7, 69.1, 66.6, 63.0, 62.7, 62.4, 55.6, 52.8, 51.8; ESI-MS *m/z* calcd for $C_{90}H_{90}N_6O_{24}Na$ $[M+Na]^+$ 1661.5899, found 1661.5756.
58β (8.3 mg, 6.7%; a white solid): $[\alpha]_D^{28}$ = +26.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.03–7.89 (m, 6 H), 7.62–6.93 (m, 39 H), 5.40 (d, *J* = 4.7 Hz, 1 H), 5.14 (t, *J* = 4.5 Hz, 1 H), 5.05 (d, *J* = 10.1 Hz, 1 H), 4.94 (d, *J* = 11.5 Hz, 1 H), 4.88 (d, *J* = 10.6 Hz, 1 H), 4.79–4.55 (m, 10 H), 4.47–4.32 (m, 6 H), 4.17–4.02 (m, 3 H), 4.00–3.78 (m, 6 H), 3.74–3.66 (m, 4 H), 3.60 (t, *J* = 8.9 Hz, 1 H), 3.45–3.29 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.8, 168.6, 166.0, 165.9, 165.5, 138.6, 138.1, 138.1, 138.0, 137.8, 137.3, 133.43, 133.39, 132.9, 130.1, 130.0, 129.9, 129.8, 129.7, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.03, 127.98, 127.9, 127.8, 127.7, 127.4, 127.3, 103.0, 102.0, 98.5, 98.0, 82.2, 82.0, 81.2, 79.5, 78.3, 77.9, 75.8, 75.7, 75.4, 75.3, 74.7, 74.5, 73.5, 73.3, 72.9, 70.8, 70.7, 69.1, 66.6, 63.0, 62.7, 62.4, 55.6, 52.8, 51.8; ESI-MS *m/z* calcd for $C_{90}H_{90}N_6O_{24}Na$ $[M+Na]^+$ 1661.5899, found 1661.5889.

Methyl (methyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-*a*-L-iduropyranosyluronate)-(1→4)-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl

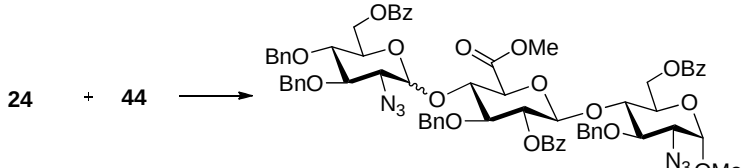
3-*O*-benzyl-2-*O*-benzyol-*α*-L-iduropyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl -3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (59)



59, 74%, α only

Compound **59** (69 mg, 74%, *α* only; a white solid): $[\alpha]_D^{27}$ = +20.0 (*c* 2.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.14–7.96 (m, 8 H), 7.63–7.05 (m, 37 H), 5.60–5.49 (m, 2 H), 5.22–5.12 (m, 2 H), 4.88 (d, *J* = 10.5 Hz, 2 H), 4.81 (d, *J* = 3.5 Hz, 2 H), 4.79–4.33 (m, 14 H), 4.19 (d, *J* = 10.2 Hz, 2 H), 4.15–3.76 (m, 9 H), 3.51 (t, *J* = 9.6 Hz, 2 H), 3.43 (dd, *J* = 10.2, 3.5 Hz, 2 H), 3.41–3.25 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.9, 169.3, 166.1, 165.5, 165.4, 137.9, 137.7, 137.5, 137.3, 133.6, 133.6, 133.2, 133.0, 130.1, 130.0, 129.91, 129.86, 129.32, 129.27, 128.8, 128.7, 128.43, 128.36, 128.3, 128.2, 128.04, 127.96, 127.7, 127.6, 98.5, 98.3, 98.2, 78.7, 78.4, 76.3, 75.9, 75.8, 75.2, 75.1, 74.6, 74.5, 73.71, 73.67, 73.0, 72.0, 71.7, 70.6, 70.2, 70.1, 69.3, 63.6, 63.2, 62.8, 61.9, 55.5, 51.9, 51.7; ESI-MS *m/z* calcd for $C_{90}H_{88}N_6O_{25}Na$ $[M+Na]^+$ 1675.5691, found 1675.5672.

Methyl
(2-azido-6-*O*-benzoyl-3,4-*O*-dibenzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(met hyl
3-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl -3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (60)



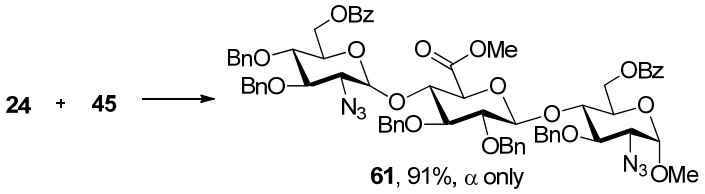
60, 83%, α/β = 5.7

60α (57.9 mg, 70.6%; a white solid): $[\alpha]_D^{31}$ = +93.2 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.08–7.82 (m, 6 H), 7.58–6.95 (m, 29 H), 5.46–5.27 (m, 2 H), 5.07 (d, *J* = 10.7 Hz, 1 H), 4.86–4.70 (m, 5 H), 4.70–4.46 (m, 5 H), 4.48–4.32 (m, 4 H), 4.27 (t, *J* = 8.8 Hz, 1 H), 4.00–3.73 (m, 5 H), 3.73–3.46 (m, 6 H), 3.41–3.16 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.9, 166.2, 166.1, 164.9, 138.2, 137.54, 137.51, 137.4, 133.6, 133.5, 133.3, 129.9, 129.8, 129.7, 129.6, 129.0, 128.8, 128.7, 128.6, 128.51, 128.46, 128.4, 128.32, 128.28, 128.2, 128.1, 128.0, 127.8, 127.7, 101.3, 98.6, 97.8, 82.1, 80.3, 78.33, 75.8, 75.6, 75.3, 75.0, 74.8, 73.7, 70.0, 68.8, 63.6, 63.2, 62.7, 62.5, 55.5, 52.8; ESI-MS *m/z* calcd for $C_{69}H_{68}N_6O_{18}Na$ $[M+Na]^+$ 1291.4482, found 1291.4535.

60β (10.1 mg, 12.4%; a white solid): $[\alpha]_D^{27}$ = +55.7 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.12–7.79 (m, 6 H), 7.66–6.89 (m, 29 H), 5.40 (d, *J* = 4.6 Hz, 1 H),

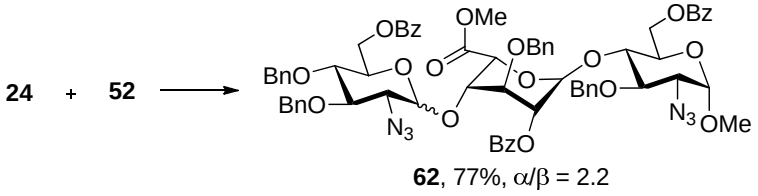
5.14 (t, *J* = 4.4 Hz, 1 H), 5.05 (d, *J* = 10.2 Hz, 1 H), 4.94 (d, *J* = 11.4 Hz, 1 H), 4.89 (d, *J* = 10.5 Hz, 1 H), 4.81–4.52 (m, 11 H), 4.50–4.29 (m, 5 H), 4.10 (dt, *J* = 25.3, 9.1 Hz, 2 H), 4.02–3.76 (m, 6 H), 3.76–3.65 (m, 4 H), 3.60 (t, *J* = 8.9 Hz, 1 H), 3.52–3.23 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 166.1, 164.9, 138.2, 137.8, 137.7, 137.4, 133.5, 133.3, 133.2, 129.9, 129.74, 129.68, 129.2, 128.69, 128.65, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.72, 127.69, 127.4, 102.2, 101.4, 98.5, 83.2, 79.5, 78.3, 78.2, 77.4, 75.9, 75.7, 75.2, 74.8, 74.6, 73.3, 73.1, 68.9, 66.9, 63.2, 63.1, 62.5, 55.5, 52.9; ESI-MS *m/z* calcd for $C_{69}H_{68}N_6O_{18}Na$ $[M+Na]^+$ 1291.4482, found 1291.4524.

Methyl
(2-azido-6-*O*-benzoyl-3,4-*O*-dibenzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 2,3-*O*-dibenzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (61)



Compound **61** (72 mg, 91% yield, *α* only; a white solid): $[\alpha]_D^{31}$ = +77.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, 4 H), 7.56–7.03 (m, 31 H), 5.41 (d, *J* = 3.3 Hz, 1 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.91 (d, *J* = 10.5 Hz, 1 H), 4.85–4.71 (m, 5 H), 4.52 (m, 9 H), 4.10 (t, *J* = 8.5 Hz, 1 H), 3.91 (t, *J* = 9.3 Hz, 1 H), 3.84–3.56 (m, 8 H), 3.53 (s, 3 H), 3.45 (t, *J* = 8.3 Hz, 1 H), 3.40–3.17 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 166.2, 165.9, 138.3, 138.0, 137.9, 137.6, 133.5, 133.2, 129.9, 129.8, 129.7, 128.74, 128.69, 128.65, 128.59, 128.51, 128.47, 128.4, 128.30, 128.23, 128.17, 128.1, 128.0, 127.94, 127.89, 127.8, 127.6, 127.4, 127.3, 103.0, 98.5, 97.8, 83.9, 82.6, 80.3, 78.3, 78.0, 77.8, 77.4, 75.9, 75.8, 75.8, 75.6, 75.4, 75.2, 74.8, 69.9, 69.1, 63.6, 63.0, 62.7, 62.4, 55.6, 52.8; ESI-MS *m/z* calcd for $C_{69}H_{70}N_6O_{17}Na$ $[M+Na]^+$ 1277.4690, found 1277.4634.

Methyl
(2-azido-6-*O*-benzoyl-3,4-*O*-dibenzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-(methyl
3-*O*-benzyl-2-*O*-benzoyl-*α*-L-iduropyranosyluronate)-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (62)

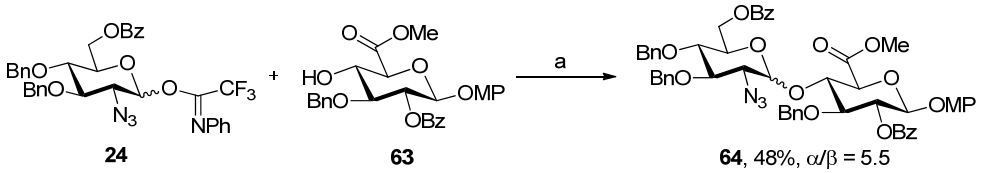


62α (37.8 mg, 52.9%; a white solid): $[\alpha]_D^{25}$ = +25.0 (*c* 2.9, $CHCl_3$); ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.19–7.99 (m, 6 H), 7.66–7.54 (m, 2 H), 7.54–7.19 (m, 27 H), 5.63 (d, J = 2.6 Hz, 1 H), 5.26 (s, 1 H), 5.03 (d, J = 10.4 Hz, 1 H), 4.99–4.78 (m, 7 H), 4.73 (d, J = 11.9 Hz, 1 H), 4.65 (d, J = 10.8 Hz, 2 H), 4.55 (dd, J = 12.1, 4.2 Hz, 1 H), 4.52–4.44 (m, 1 H), 4.32 (d, J = 10.5 Hz, 1 H), 4.26–4.07 (m, 6 H), 4.06–3.92 (m, 2 H), 3.74–3.63 (m, 2 H), 3.60 (s, 3 H), 3.53 (dd, J = 10.1, 3.7 Hz, 1 H), 3.49 (s, 3 H), 3.31 (dd, J = 9.7, 3.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 166.2, 166.1, 165.5, 138.0, 137.8, 137.6, 137.4, 133.4, 133.2, 130.1, 130.0, 129.9, 129.8, 129.7, 129.4, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 99.2, 98.61, 98.60, 80.2, 78.9, 77.7, 75.8, 75.2, 75.1, 74.4, 73.3, 70.3, 69.6, 69.3, 69.2, 63.8, 63.0, 62.6, 60.5, 55.5, 52.2; ESI-MS *m/z* calcd for $C_{69}H_{68}N_6O_{18}Na$ $[M+Na]^+$ 1291.4482, found 1291.4463.

62β (17.2 mg, 24.1%; a white solid): $[\alpha]_D^{27}$ = +1.3 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.83 (m, 6 H), 7.60–7.13 (m, 31 H), 5.38 (s, 1 H), 5.11 (s, 1 H), 4.96 (d, J = 2.3 Hz, 1 H), 4.90–4.63 (m, 8 H), 4.47 (m, 4 H), 4.26 (d, J = 8.0 Hz, 1 H), 4.21 (brs, 1 H), 4.08–3.94 (m, 4 H), 3.91–3.82 (m, 1 H), 3.60 (s, 3 H), 3.56–3.33 (m, 6 H), 3.28–3.11 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 166.2, 166.1, 165.3, 137.9, 137.7, 137.7, 137.4, 133.3, 133.2, 133.1, 130.1, 129.92, 129.88, 129.73, 129.71, 129.6, 128.7, 128.50, 128.46, 128.4, 128.34, 128.28, 128.21, 128.17, 128.15, 128.06, 127.8, 127.5, 103.5, 98.5, 98.1, 83.2, 78.9, 75.8, 75.8, 75.3, 75.2, 74.8, 74.1, 73.3, 72.6, 69.5, 68.2, 67.5, 66.9, 63.9, 63.0, 55.5, 52.1; ESI-MS *m/z* calcd for $C_{69}H_{68}N_6O_{18}Na$ $[M+Na]^+$ 1291.4482, found 1291.4457.

Methyl (2-azido-6-*O*-benzoyl-3,4-*O*-dibenzyl-2-deoxy-*α/β*-D-glucopyranosyl)-(1→4)-4-Methoxyphenyl (methyl 3-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate) (64)

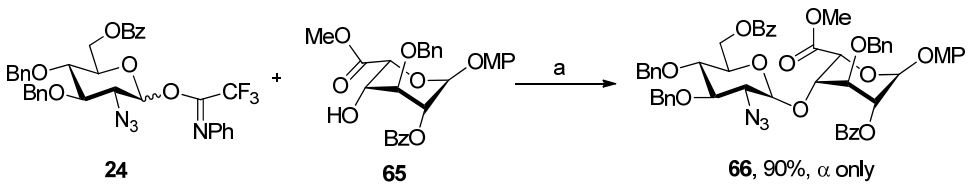


Compound **63** was prepared following a similar procedure as that for the preparation of **44**: $[\alpha]_D^{27}$ = +8.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.97 (m, 2 H), 7.59 (t, J = 7.4 Hz, 1 H), 7.45 (t, J = 7.7 Hz, 2 H), 7.24–7.11 (m, 5 H), 6.94–6.86 (m, 2 H), 6.80–6.70 (m, 2 H), 5.48 (dd, J = 9.3, 7.7 Hz, 1 H), 5.02 (d, J = 7.7 Hz, 1 H), 4.86–4.73 (m, 2 H), 4.17 (td, J = 9.4, 2.7 Hz, 1 H), 4.02 (d, J = 9.7 Hz, 1 H), 3.83 (s, 3 H), 3.78 (t, J = 9.1 Hz, 1 H), 3.73 (s, 3 H), 3.12 (d, J = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.3, 155.9, 151.4, 137.9, 133.4, 123.0, 128.6, 128.5, 128.2, 127.9, 119.0, 114.4, 101.4, 80.8, 74.6, 74.4, 73.1, 72.0, 55.7, 53.0; ESI-MS *m/z* calcd for $C_{28}H_{28}O_9Na$ $[M+Na]^+$ 531.1626, found 531.1616.

64α (37.2 mg, 40.6%; a white solid): $[\alpha]_D^{26}$ = +48.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–7.95 (m, 4 H), 7.62–7.51 (m, 2 H), 7.48–7.13 (m, 21 H),

6.95–6.85 (m, 2 H), 6.81–6.70 (m, 2 H), 5.54 (dd, *J* = 8.0, 6.5 Hz, 1 H), 5.50 (d, *J* = 3.7 Hz, 1 H), 5.17 (d, *J* = 6.4 Hz, 1 H), 4.90–4.80 (m, 4 H), 4.76 (d, *J* = 10.7 Hz, 1 H), 4.64–4.44 (m, 4 H), 4.24 (d, *J* = 8.7 Hz, 1 H), 4.08 (t, *J* = 8.3 Hz, 1 H), 4.01–3.90 (m, 1 H), 3.85 (d, *J* = 9.9 Hz, 1 H), 3.74 (s, 3 H), 3.72–3.60 (m, 4 H), 3.38 (dd, *J* = 10.3, 3.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 166.3, 165.2, 155.8, 151.1, 137.7, 137.6, 137.5, 133.5, 133.3, 129.9, 129.8, 129.6, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 118.7, 114.7, 100.7, 98.1, 81.6, 80.3, 78.1, 75.8, 75.4, 75.0, 74.7, 74.3, 73.8, 70.2, 63.7, 62.9, 55.8, 52.9; ESI-MS *m/z* calcd for $C_{55}H_{53}N_3O_{14}Na$ $[M+Na]^+$ 1002.3420, found 1002.3419.

Methyl (2-azido-6-*O*-benzoyl-3,4-*O*-dibenzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-4-methoxyphenyl (methyl 3-*O*-benzyl-2-*O*-benzoyl-*a*-L-iduropyranosyluronate) (66)



24 **65** **66**, 90%, α only

Compound **65** was prepared following a similar procedure as that for the preparation of **44**: $[\alpha]_D^{29}$ = -55.5 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.3 Hz, 2 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.50–7.23 (m, 7 H), 7.06 (d, *J* = 9.1 Hz, 2 H), 6.83 (d, *J* = 9.1 Hz, 2 H), 5.70 (s, 1 H), 5.43 (s, 1 H), 5.07 (d, *J* = 1.2 Hz, 1 H), 4.94 (d, *J* = 11.7 Hz, 1 H), 4.74 (d, *J* = 11.7 Hz, 1 H), 4.18 (d, *J* = 11.3 Hz, 1 H), 3.98 (s, 1 H), 3.78 (d, *J* = 13.5 Hz, 6 H), 2.82 (d, *J* = 11.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 165.1, 155.4, 150.5, 137.6, 134.0, 129.9, 129.0, 128.8, 128.6, 128.1, 127.8, 118.0, 114.8, 97.7, 74.5, 72.1, 68.5, 68.3, 67.4, 55.8, 52.5; ESI-MS *m/z* calcd for $C_{28}H_{28}O_9Na$ $[M+Na]^+$ 531.1626, found 531.1616.

Compound **66** (56 mg, 90%, *α* only; a white solid): $[\alpha]_D^{27}$ = +1.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39–8.13 (m, 2 H), 8.13–7.93 (m, 2 H), 7.71–7.03 (m, 25 H), 6.89 (d, *J* = 9.1 Hz, 2 H), 5.82 (s, 1 H), 5.42 (s, 1 H), 5.07 (d, *J* = 11.2 Hz, 2 H), 4.94–4.84 (m, 2 H), 4.82 (d, *J* = 10.8 Hz, 1 H), 4.74 (d, *J* = 12.3 Hz, 1 H), 4.66 (d, *J* = 10.8 Hz, 1 H), 4.56 (dd, *J* = 12.3, 2.5 Hz, 1 H), 4.32 (s, 1 H), 4.28–4.07 (m, 4 H), 3.83 (d, *J* = 5.1 Hz, 6 H), 3.68 (d, *J* = 9.8 Hz, 2 H), 3.39–3.21 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.2, 165.6, 155.4, 150.7, 137.8, 137.7, 133.5, 133.2, 130.1, 129.7, 129.6, 128.9, 128.6, 128.1, 128.0, 118.2, 114.8, 99.7, 98.5, 80.4, 77.8, 76.1, 75.2, 75.1, 73.2, 72.5, 70.5, 68.1, 64.0, 62.8, 55.78, 52.5; ESI-MS *m/z* calcd for $C_{55}H_{53}N_3O_{14}Na$ $[M+Na]^+$, 1002.3420, found 1002.3422.

General Procedure for the Saponification of the Esters. A premixed solution of 30% solution of H_2O_2 in water (100 equiv per CO_2Me) and 1 M LiOH (50 equiv per CO_2Me) were added to a solution of the starting material in THF (0.02 M). The reaction mixture was stirred at room temperature for 24 h. MeOH (0.02 M) and 3 M

KOH was added until pH = 14. The reaction mixture was left stirring for 24 h at room temperature. The mixture was then brought to pH = 8~8.5 by addition of acidic resins. The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was dissolved with CH_2Cl_2/MeOH (v/v = 1/1). The resulting solution was layered on the top of a Sephadex LH-20 chromatography column that was eluted with CH_2Cl_2/MeOH (v/v = 1/1). The appropriate fractions were concentrated in vacuo to provide the pure product.

General Procedure for the Oxidative Cleavage of the *p*-Methoxybenzyl Group. Compound was dissolved in CH_2Cl_2 and Buffer H_2O (0.3 M, v/v = 10: 1). DDQ (2.0 equiv per PMB) was added at room temperature. Stirring was continued until TLC indicated disappearance of the raw material. The solution was quenched with saturated sodium thiosulfate. The organic layers were washed with water, saturated sodium bicarbonate, and brine, and then were dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography using a gradient of petroleum ether and EtOAc to give the pure product.

General Procedure for the *O*-Sulfation. Sulfur trioxide pyridine complex (5 equiv per OH) was added to a solution of the starting material in DMF (1.0 mL for 0.05 mmol). The mixture was stirred at ambient temperature for 4 h until TLC (RP-18 silica gel, H_2O/CH_3OH, v/v = 1/2) indicated completion of the reaction. After the addition of CH_3OH (0.5 mL) stirring was continued for 15 min. The mixture was concentrated in vacuo. The residue was applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH_3OH (from v/v = 1/0 to 2/1). The fractions containing the product were concentrated in vacuo. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using CH_3OH as eluent. The fractions containing the product were concentrated in vacuo to provide the product as sodium salt.

General Procedure for the Reduction of the Azide Group. A 1 M solution of PMe_3 in THF (4 equiv per azide group) was added to the solution of the starting material in THF (1.0 mL for 0.04 mmol). A 0.1 M NaOH solution (5 equiv per azido group) was added, and the mixture was stirred at room temperature for 5 h. The progress of the reaction was monitored by TLC (RP-18 silica gel, H_2O/CH_3OH, v/v = 1/2). The pH was then adjusted to 7~8 by careful addition of 1.0 M HCl. The mixture was then concentrated in vacuo.

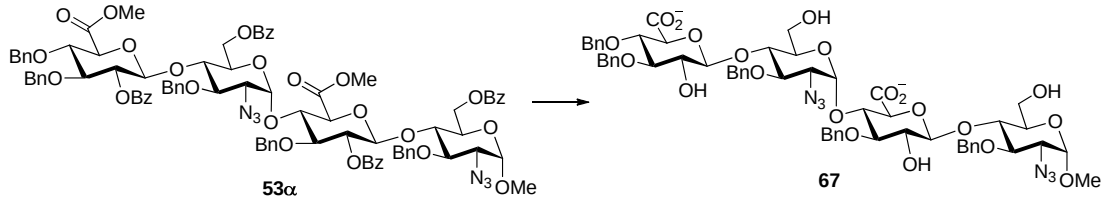
General Procedure for the Selective *N*-Acetylation. Acetic anhydride (10 equiv per NH_2) was added to a solution of the starting material in a mixture of anhydrous CH_3OH (0.02 mmol) and Et_3N (20 equiv per NH_2) at 0 ^oC. The progress of the reaction was monitored by TLC (RP-18 silica gel, H_2O/CH_3OH, v/v = 1/1). After stirring for 4 h at room temperature, the mixture was concentrated in vacuo. The

residue was vortexed with water and applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH_3OH (from v/v = 1/0 to 1/1). The fractions containing product were concentrated in vacuo, and the residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using a mixture of CH_3OH and H_2O (v/v = 9/1) as eluent. The fractions containing product were concentrated in vacuo to provide the *N*-acetylated product as sodium salt.

General Procedure for the Selective *N*-Sulfation. Sulfur trioxide pyridine complex (5 equiv per NH_2) was added to the starting material in CH_3OH (1 mL for 0.01 mmol) in a mixture of triethylamine (0.3 mL) and 0.1 M NaOH (2 equiv per NH_2) at 0 ^oC. The progress of the reaction was monitored by TLC (RP-18 silica gel, H_2O/CH_3OH, v/v = 1/1). Two additional portions of sulfur trioxide pyridine complex were added at 0 ^oC after 30 min and 1 h, respectively. After stirring for an additional 8 h at 0 ^oC, the mixture was concentrated in vacuo. The residue was vortexed with water and applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH3OH (from 1/0 to 1/1, v/v). The fractions containing product were concentrated in vacuo, and the residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using a mixture of CH_3OH and H_2O (v/v = 9/1) as eluent. The fractions containing product were concentrated in vacuo to provide the *N*-sulfated product.

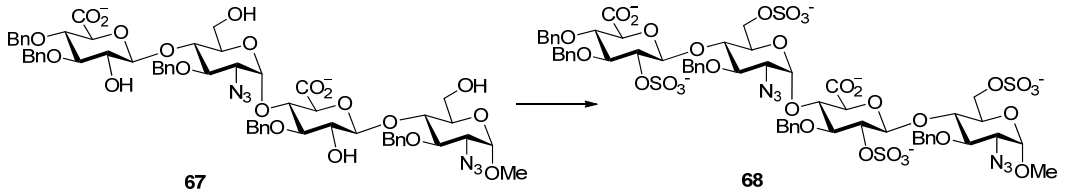
General Procedure for the Final Debenzylation. Palladium hydroxide on carbon (Degussa type, 20%, 1.0-2.0 times the weight of the starting material) was added to a solution of the starting material in CH_3OH and pH =7 buffer H_2O (v/v = 1/1, 1 mL for 10~20 mg). The mixture was placed under an atmosphere of hydrogen for 24 h. The mixture was filtered, and the residue was diluted with H_2O. The solution was layered on the top of a Sephadex G-10 chromatography column that was eluted with H_2O. The fractions containing product were concentrated in vacuo, and the residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using H_2O as eluent. The appropriate fractions were freeze dried to provide the final product as a white solid.

Methyl
(3,4-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-(2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (67)



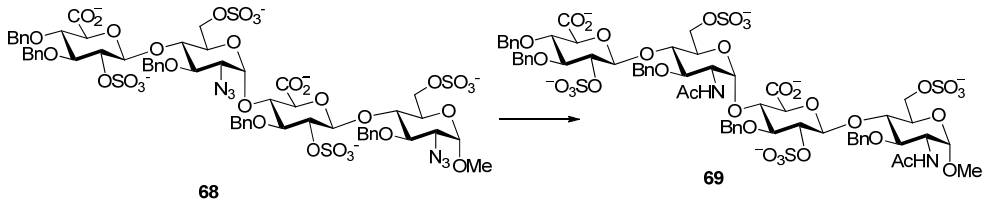
The general procedures for saponification was applied to provide **67** (85 mg, 96%) as a white solid: $[\alpha]_D^{24}$ = 46.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 7.47–7.21 (m, 25 H), 5.52 (d, *J* = 2.8 Hz, 1 H), 5.13–5.07 (m, 3 H), 4.91–4.63 (m, 10 H), 4.06–3.48 (m, 18 H), 3.31 (s, 3 H), 3.20 (dd, *J* = 9.6, 2.8 Hz, 1 H), 3.10–3.08 (m, 1 H); ^{13}C NMR (100 MHz, CD_3OD) δ 140.2, 140.1, 139.8, 139.7,139.6, 130.0, 130.0, 129.39, 129.36, 129.3, 129.1, 129.04, 129.01, 128.8, 128.73, 128.71, 128.67, 128.6, 104.7, 104.6, 100.1, 99.2, 86.1, 85.5, 81.0, 79.6, 79.2, 78.7, 77.9, 76.7, 76.40, 76.36, 76.1, 76.0, 73.1, 72.8, 64.3, 64.2, 61.1, 60.6, 55.6; ESI-MS *m/z* calcd for $C_{60}H_{68}N_6O_{21}Na$ $[M+Na]^+$ 1231.4330, found 1231.4300.

Methyl
(3,4-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyranosyluronate)-(1→4)-(2-azido-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-azido-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (68)



The general procedure for *O*-sulfation was applied to provide **68** (107 mg, 99%) as a white solid: $[\alpha]_D^{27}$ = 24.8 (*c* 0.2, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.55–7.23 (m, 25 H), 5.49 (d, *J* = 3.6 Hz, 1 H), 5.37 (d, *J* = 9.6 Hz, 1 H), 5.27–5.18 (m, 3 H), 5.07–5.02 (m, 2 H), 4.79–4.67 (m, 9 H), 4.50 (m, 2 H), 4.32–4.23 (m, 2 H), 4.07–3.87 (m, 12 H), 3.41 (s, 3 H), 3.26–3.20 (m, 2 H); ESI-MS *m/z* calcd for $C_{60}H_{65}N_6O_{33}S_4$ $[M-3H]^{3-}$ 508.4, found 509.1.

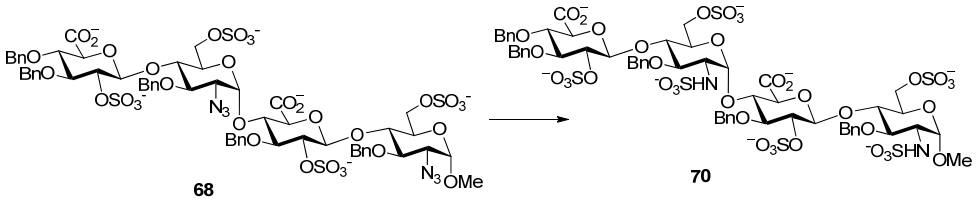
Methyl
(3,4-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyranosyluronate)-(1→4)-(2-*N*-acetyl-3-*O*-benzyl-
6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (69)



The general procedures for reduction of the azide group and selective *N*-acetylation were applied to provide **69** (53 mg, 91%) as a white solid: $[\alpha]_D^{29}$ = +8.0 (*c* 0.1, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.53–7.12 (m, 25 H), 5.34 (d, *J* = 3.2 Hz, 1 H), 5.14

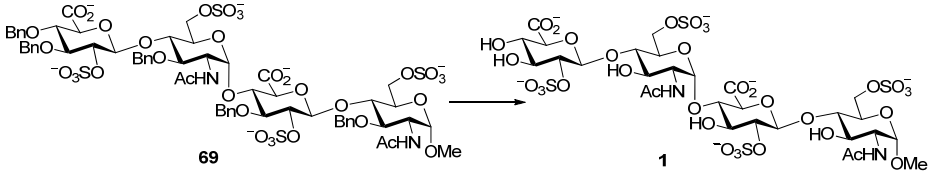
(m, 6 H), 4.78–4.38 (m, 12 H), 4.36–4.13 (m, 5 H), 4.13–3.95 (m, 7 H), 3.95–3.75 (m, 4 H), 3.37 (s, 3 H), 1.91 (s, 3 H), 1.88 (s, 3 H); ^{13}C NMR (100 MHz, CD_3OD) δ 173.5, 140.5, 140.2, 140.0, 139.5, 129.8, 129.7, 129.5, 129.3, 129.2, 129.0, 128.9, 128.5, 128.4, 128.31, 128.27, 102.1, 101.6, 99.8, 97.8, 83.9, 82.9, 81.4, 80.0, 79.9, 77.7, 77.3, 76.1, 75.8, 75.4, 75.3, 74.8, 71.3, 70.6, 67.0, 55.6, 53.7, 53.2, 23.0, 22.7; ESI-MS *m/z* calcd for $C_{64}H_{73}N_2O_{35}S_4$ $[M-3H]^{3-}$ 519.1, found 519.6.

Methyl (3,4-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyranosyluronate)-(1→4)-(2-*N*-sulfo-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(3-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (70)



The general procedures for reduction of the azide and selective *N*-sulfation were applied to provide **70** (48 mg, 86%) as a white solid: $[\alpha]_D^{27}$ = 9.3 (*c* 0.4, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.63–7.14 (m, 25 H), 5.35 (s, 1 H), 5.14–4.98 (m, 5 H), 4.94–4.83 (m, 3 H), 4.72–4.59 (m, 7 H), 4.51–4.47 (m, 2 H), 4.31–4.19 (m, 5 H), 4.09–3.95 (m, 6 H), 3.89–3.74 (m, 3 H), 3.67–3.66 (m, 1 H), 3.50–3.41 (m, 4 H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.3, 139.9, 139.8, 139.63, 139.58, 139.0, 130.4, 130.0, 129.7, 129.6, 129.3, 129.12, 129.08, 129.0, 128.9, 128.7, 128.4, 128.3, 101.7, 101.5, 100.2, 97.9, 82.9, 81.2, 81.1, 81.0, 79.0, 78.2, 75.9, 75.6, 74.9, 74.5, 74.2, 70.8, 67.2, 58.4, 55.8; ESI-MS *m/z* calcd for $C_{60}H_{69}N_2O_{39}S_6$ $[M-3H]^{3-}$ 544.4, found 544.8.

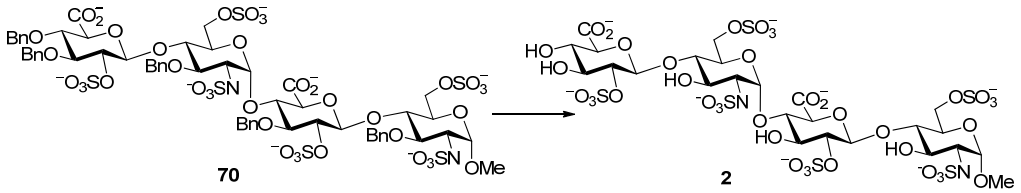
Methyl (2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (1)



The general procedure for global debenzylation was applied to provide **1** (41 mg, 99%) as a white solid: $[\alpha]_D^{28}$ = +39.0 (*c* 0.2, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.35 (d, *J* = 3.5 Hz, 1 H), 4.58 (t, *J* = 9.2 Hz, 2 H), 4.36–3.66 (m, 15 H), 3.60 (t, *J* = 9.5 Hz, 1 H), 3.39 (s, 2 H), 2.05 (d, *J* = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz, D_2O) δ 175.4, 174.5, 174.3, 99.7, 97.8, 97.4, 80.1, 79.5, 77.9, 77.6, 77.5, 76.3, 75.6, 74.9, 74.3, 71.6, 69.1,

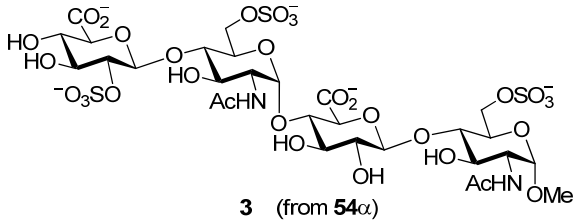
68.9, 68.8, 68.1, 65.7, 55.2, 53.2, 53.0, 21.9, 21.8; ESI-MS *m/z* calcd for $C_{29}H_{43}N_2O_{35}S_4$ $[M-3H]^{3-}$ 369.0, found 369.3; *m/z* calcd for $C_{29}H_{44}N_2O_{35}S_4$ $[M-2H]^{2-}$ 554.0, found 554.1.

Methyl (2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (2)



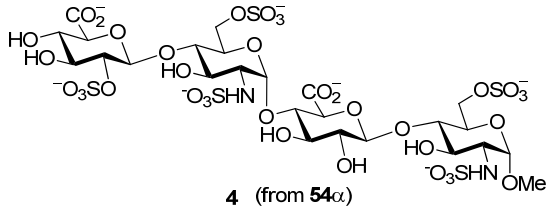
The general procedure for global debenzylation was applied to provide compound **2** (35 mg, 99%) as a white solid: $[\alpha]_D^{28}$ = +12.3 (*c* 0.6, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.51 (d, *J* = 3.6 Hz, 1 H), 5.03 (d, *J* = 3.2 Hz, 1 H), 4.79 (d, 1 H), 4.59–4.54 (m, 2 H), 4.27-4.09 (m, 4 H), 4.04–3.95 (m, 3 H), 3.85–3.69 (m, 9 H) , 3.59 (t, *J* = 9.6 Hz, 1 H), 3.42 (s, 3 H), 3.31–3.28 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 100.1, 99.8, 98.6, 98.2, 79.8, 79.7, 78.8, 78.1, 77.6, 76.6, 75.7, 74.53, 74.46, 71.7, 69.4, 69.1, 68.0, 65.9, 65.8, 57.9, 57.2, 55.5, 55.4; ESI-MS (*m/z*) 394.8 $[M-8Na^+ + 5H^+]/3$, 367.8 $[M-8Na^+ + 5H^+ - SO_3]/3$. ESI-MS *m/z* calcd for $C_{25}H_{39}N_2O_{39}S_6$ $[M-3H]^{3-}$ 394.3, found 394.8; *m/z* calcd for $C_{25}H_{39}N_2O_{36}S_5$ $[M-SO_3-3H]^{3-}$ 367.7, found 367.8.

Methyl (2-*O*-sulfo-*β*-D-glucopyranosyluronate)-(1→4)-(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (3)



Similar procedures as that for **53α→2** were applied for **54α→3** (26 mg, 67%; a white solid): $[\alpha]_D^{28}$ = +23.9 (*c* 0.6, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.34 (s, 1 H), 4.64–4.50 (m, 2 H), 4.46–4.30 (m, 2 H), 4.20 (d, *J* = 11.1 Hz, 1 H), 4.11 (t, *J* = 8.3 Hz, 1 H), 4.07–3.66 (m, 12 H), 3.60 (t, *J* = 9.6 Hz, 1 H), 3.47–3.28 (m, 4 H), 2.05 (s, 2 H), 2.04 (s, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 174.4, 102.3, 99.8, 97.7, 97.3, 79.6, 79.0, 77.8, 77.7, 76.6, 76.1, 75.7, 74.4, 73.6, 71.7, 69.5, 69.0, 68.9, 68.4, 66.5, 65.8, 55.3, 53.3, 53.1, 22.0, 21.9; ESI-MS *m/z* calcd for $C_{29}H_{43}N_2O_{32}S_3Na$ $[M+Na-3H^+]^{2-}$ 525.1, found 525.3.

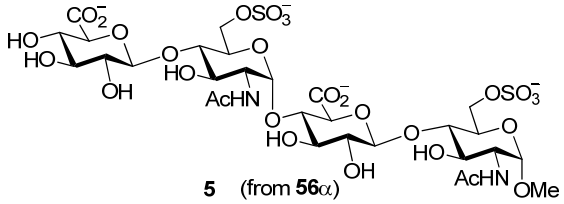
Methyl (2-*O*-sulfo-*β*-D-glucopyranosyluronate)-(1→4)-(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (4)



4 (from **54**α)

Similar procedures as that for **53α→2** were applied for **54α→4** (32 mg, 64%; a white solid): $[\alpha]_D^{28}$ = +21.4 (*c* 0.2, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.52 (d, *J* = 3.6 Hz, 1 H), 5.05 (d, *J* = 3.2 Hz, 1 H), 4.79 (d, 1 H), 4.60 (d, *J* = 8.0 Hz, 1 H), 4.56 (d, *J* = 10.8 Hz, 1 H), 4.42 (d, *J* = 10.8 Hz, 1 H), 4.33 (dd, *J* = 11.2 Hz, 3.6 Hz, 1 H) , 4.20 (d, *J* = 10.8 Hz, 1 H), 4.12 (t, *J* = 8.8 Hz, 1 H), 4.03-4.01 (m, 2 H), 3.88–3.68 (m, 9 H), 3.60 (t, *J* = 9.6 Hz, 1 H), 3.44 (s, 3 H), 3.42–3.31 (m, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 181.5, 175.6, 102.2, 100.8, 99.8, 98.2, 79.7, 78.8, 78.7, 77.6, 76.6, 75.7, 75.7, 74.5, 73.0, 71.7, 69.7, 69.4, 69.0, 68.3, 66.6, 65.9, 57.9, 57.2, 55.5; ESI-MS *m/z* calcd for $C_{25}H_{39}N_2O_{36}S_5$ $[M\text{-}3H^+]^{3-}$ 367.7, found 367.5.

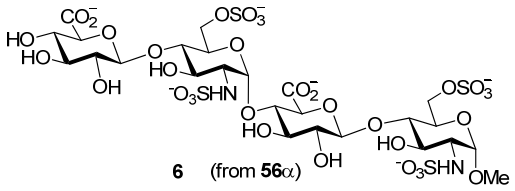
Methyl (*β*-D-glucopyranosyluronate)-(1→4)-(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (5)



5 (from **56**α)

Similar procedures as that for **53α→2** were applied for **56α→5** (15 mg, 52%; a white solid): $[\alpha]_D^{27}$ = +17.0 (*c* 0.4, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.42 (d, *J* = 3.6 Hz, 1 H), 4.58 (dd, *J* = 7.8, 2.1 Hz, 2 H), 4.46 (d, *J* = 9.7 Hz, 1 H), 4.43–4.27 (m, 2 H), 4.19 (d, *J* = 9.7 Hz, 1 H), 4.11–3.64 (m, 13 H), 3.60–3.46 (m, 2 H), 3.44–3.28 (m, 5 H), 2.05 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 175.7, 174.8, 174.4, 102.2, 101.9, 97.7, 96.7, 78.8, 77.4, 76.5, 76.3, 75.7, 75.0, 73.6, 73.0, 71.9, 69.5, 69.1, 68.8, 68.3, 66.4, 65.8, 55.3, 53.1, 21.91, 21.86; ESI-MS *m/z* calcd for $C_{29}H_{44}N_2O_{29}S_2$ $[M\text{-}2H]^{2-}$ 474.1, found 474.2.

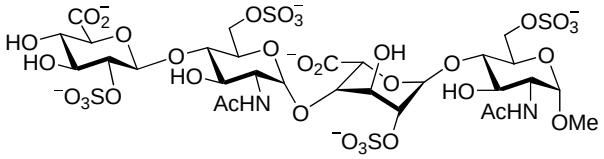
Methyl (*β*-D-glucopyranosyluronate)-(1→4)-(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (6)



6 (from **56**α)

Similar procedures as that for **53α→2** were applied for **56α→6** (18 mg, 35%; a white solid): $[\alpha]_D^{28}$ = +21.0 (*c* 0.1, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.66 (d, *J* = 3.5 Hz, 1 H), 5.05 (d, *J* = 3.5 Hz, 2 H), 4.60 (d, *J* = 7.8 Hz, 3 H), 4.48 (d, *J* = 10.0 Hz, 1 H), 4.41 (d, *J* = 10.0 Hz, 1 H), 4.33 (dd, *J* = 11.1, 4.9 Hz, 1 H), 4.19 (d, *J* = 10.8 Hz, 1 H), 4.03 (d, *J* = 9.7 Hz, 2 H), 3.91–3.63 (m, 9 H), 3.60–3.25 (m, 10 H); ^{13}C NMR (100 MHz, D_2O) δ 175.7, 174.9, 101.9, 101.7, 98.1, 97.0, 78.1, 76.9, 76.3, 76.2, 76.0, 75.7, 75.0, 72.9, 72.8, 71.8, 69.5, 69.3, 68.6, 68.1, 66.3, 65.7, 57.5, 57.1, 55.5; ESI-MS *m/z* calcd for $C_{25}H_{39}N_2O_{33}S_4Na$ $[M+Na-3H]^{2-}$ 523.1, found 523.6.

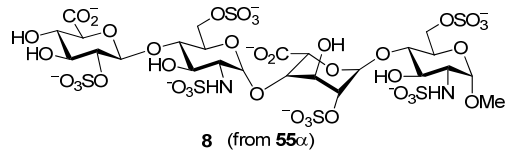
Methyl
(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (7)



7 (from **55**α)

Similar procedures as that for **53α→2** were applied for **55α→7** (9 mg, 64%; a white solid): $[\alpha]_D^{28}$ = +21.0 (*c* 0.9, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.21 (s, 1 H), 5.17 (d, *J* = 3.7 Hz, 1 H), 4.83 (d, *J* = 2.1 Hz, 2 H), 4.60 (d, *J* = 10.4 Hz, 1 H), 4.44–4.19 (m, 5 H), 4.19–4.11 (m, 1 H), 4.10–4.00 (m, 4 H), 3.98 (dd, *J* = 10.2, 3.6 Hz, 1 H), 3.89–3.56 (m, 8 H), 3.41 (s, 3 H), 2.09 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 174.7, 174.5, 100.0, 99.3, 97.8, 94.2, 79.7, 78.1, 77.3, 75.7, 74.7, 74.5, 72.6, 71.7, 69.9, 69.3, 69.1, 68.7, 68.4, 66.9, 65.8, 65.6, 55.2, 53.7, 53.0, 22.2, 21.9; ESI-MS *m/z* calcd for $C_{29}H_{42}N_2O_{35}S_4Na_2$, $[M+2Na-4H]^{2-}$, 576.1, found 576.2.

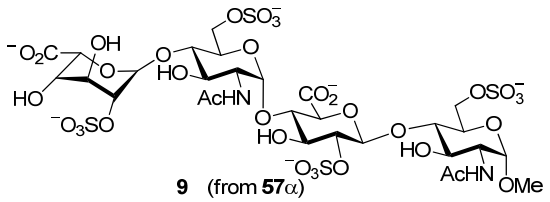
Methyl
(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (8)



8 (from **55**α)

Similar procedures as that for **53α→2** were applied for **55α→8** (27 mg, 58%; a white solid): $[\alpha]_D^{28}$ = +25.6 (*c* 0.6, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.42 (s, 1 H), 5.28 (s, 1 H), 5.04 (d, *J* = 2.4 Hz, 1 H), 4.59 (d, *J* = 10.3 Hz, 1 H), 4.45–3.94 (m, 8 H), 3.89–3.51 (m, 7 H), 3.44 (s, 3 H), 3.39–3.14 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 100.4, 98.6, 97.7, 80.2, 78.4, 77.7, 77.2, 76.4, 74.9, 72.2, 70.4, 69.5, 69.3, 69.0, 67.4, 66.3, 58.2, 55.9; ESI-MS *m/z* calcd for $C_{25}H_{39}N_2O_{39}S_6$ $[M-3H]^{3-}$ 394.3, found 394.2; *m/z* calcd for $C_{25}H_{38}N_2O_{39}S_6Na$ $[M+Na-4H]^{3-}$ 401.7, found 401.9.

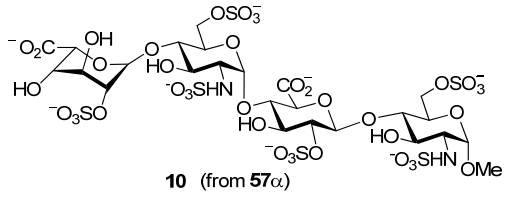
Methyl
(2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl -6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (9)



9 (from **57**α)

Similar procedures as that for **53α→2** were applied for **57α→9** (18 mg, 55%; a white solid): $[\alpha]_D^{28}$ = +40.9 (*c* 0.3, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.36 (d, *J* = 3.8 Hz, 1 H), 5.15 (s, 1 H), 4.75–4.66 (m, 3 H), 4.64–4.50 (m, 1 H), 4.37–4.14 (m, 5 H), 4.12–3.67 (m, 15 H), 3.35 (s, 3 H), 2.02 (s, 3 H), 2.00 (s, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 176.2, 174.7, 174.5, 174.5, 100.0, 99.2, 97.8, 97.1, 80.3, 78.1, 76.5, 76.4, 75.3, 74.3, 69.5, 69.3, 69.0, 69.0, 68.3, 66.3, 66.0, 55.4, 53.7, 53.2, 22.02, 21.99; ESI-MS *m/z* calcd for $C_{29}H_{42}N_2O_{35}S_4Na_2$ $[M+2Na-3H]^{2-}$ 576.1, found 576.2.

Methyl
(2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (10)

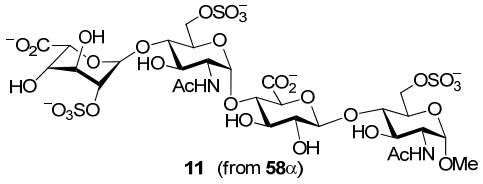


10 (from **57**α)

Similar procedures as that for **53α→2** were applied for **57α→10** (21 mg, 54%; a white solid): $[\alpha]_D^{28}$ = +13.8 (*c* 0.8, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.60 (d, *J* = 3.7 Hz, 1 H), 5.46 (s, 1 H), 5.17 (s, 1 H), 5.03 (d, *J* = 3.6 Hz, 1 H), 4.84 (d, *J* = 2.2 Hz, 2 H), 4.58 (dd, *J* = 11.2, 2.2 Hz, 1 H), 4.36–4.19 (m, 4 H), 4.16-4.10 (m, 2 H), 4.04–3.92 (m, 4 H), 3.89–3.68 (m, 6 H), 3.41 (s, 3 H), 3.33–3.20 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 176.4, 174.8, 100.1, 99.1, 98.4, 97.9, 79.9, 78.0, 77.1, 76.5, 75.0, 74.2, 69.9, 69.6, 69.2, 69.0, 68.2, 66.4, 66.0, 58.1, 57.3, 55.6; ESI-MS *m/z* calcd for

$C_{25}H_{38}N_2O_{39}S_6Na_2$ [M+2Na-4H]$^{2-}$ 614.0, found 614.4; *m/z* calcd for $C_{25}H_{39}N_2O_{39}S_6$ [M-3H]$^{3-}$ 394.3, found 394.1.

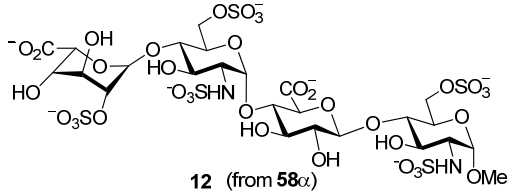
Methyl (2-*O*-sulfo-*α*-L-iduropyranosyluronate)-(1→4)-(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-actyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (11)



11 (from **58**α)

Similar procedures as that for **53α→2** were applied for **58α→11** (16 mg, 77%; a white solid): $[\alpha]_D^{28}$ = +48.1 (*c* 0.3, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 8.46 (s, 1 H), 5.40 (d, *J* = 3.5 Hz, 1 H), 5.18 (s, 1 H), 4.58 (d, *J* = 7.9 Hz, 1 H), 4.51–4.19 (m, 5 H), 4.16–3.61 (m, 13 H), 3.40 (s, 3 H), 3.36 (t, *J* = 8.4 Hz, 2 H), 2.05 (d, 3 H), 2.04 (d, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 176.3, 174.8, 174.5, 102.3, 99.2, 97.9, 97.0, 78.8, 76.6, 76.5, 76.4, 74.3, 73.7, 69.6, 69.5, 69.3, 69.0, 68.5, 66.6, 66.4, 55.5, 53.8, 53.3, 22.10, 22.05; ESI-MS *m/z* calcd for $C_{29}H_{43}N_2O_{32}S_3$ [M-3H]$^{3-}$ 342.4, found 342.7.

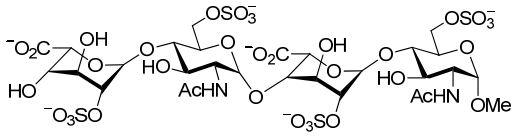
Methyl (2-*O*-sulfo-*α*-L-iduropyranosyluronate)-(1→4)-(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (12)



12 (from **58**α)

Similar procedures as that for **53α→2** were applied for **58α→12** (30 mg, 77%; a white solid): $[\alpha]_D^{27}$ = +36.6 (*c* 0.4, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.61 (d, *J* = 2.7 Hz, 1 H), 5.22 (s, 1 H), 5.05 (d, *J* = 3.3 Hz, 2 H), 4.60 (d, *J* = 7.9 Hz, 1 H), 4.48–4.18 (m, 5 H), 4.13 (s, 1 H), 4.01 (s, 3 H), 3.93–3.60 (m, 7 H), 3.52–3.18 (m, 6 H); ^{13}C NMR (100 MHz, D_2O) δ 102.2, 98.2, 97.4, 78.6, 76.9, 76.4, 76.0, 74.0, 73.0, 69.7, 69.1, 68.9, 68.2, 66.5, 66.3, 58.0, 57.2, 55.5; ESI-MS *m/z* calcd for $C_{25}H_{39}N_2O_{36}S_5$ [M-3H]$^{3-}$ 367.7, found 367.7.

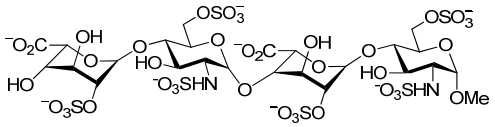
Methyl (2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (13)



13 (from **59**α)

Similar procedures as that for **53α→2** were applied for **59α→13** (10 mg, 71%; a white solid): $[\alpha]_D^{28}$ = +19.2 (*c* 0.7, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.18 (s, 1 H), 5.14 (d, *J* = 3.3 Hz, 2 H), 4.82 (dd, *J* = 6.8, 2.3 Hz, 3 H), 4.75 (d, *J* = 3.5 Hz, 1 H), 4.46–4.21 (m, 7 H), 4.10 (t, *J* = 3.4 Hz, 1 H), 4.08–3.96 (m, 5 H), 3.94 (d, *J* = 3.6 Hz, 1 H), 3.85–3.66 (m, 4 H), 3.39 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 176.3, 175.0, 174.7, 174.4, 99.3, 99.3, 97.7, 93.5, 77.4, 76.7, 74.4, 73.9, 71.4, 69.9, 69.9, 69.3, 69.0, 68.8, 68.7, 68.2, 66.9, 66.4, 64.8, 55.2, 53.7, 53.4, 22.2, 21.9; ESI-MS *m/z* calcd for $C_{29}H_{43}N_2O_{35}S_4Na$ $[M+Na-3H]^{2-}$ 565.1, found 565.1.

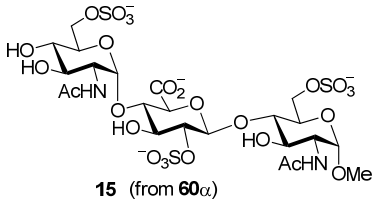
Methyl
(2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*α*-L-iduropyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (14)



14 (from **59**α)

Similar procedures as that for **53α→2** were applied for **59α→14** (14 mg, 73%; a white solid): $[\alpha]_D^{28}$ = +27.8 (*c* 0.6, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.44 (d, *J* = 3.5 Hz, 1 H), 5.23 (d, *J* = 3.2 Hz, 1 H), 5.19 (s, 1 H), 5.04 (d, *J* = 3.6 Hz, 1 H), 4.87 (d, *J* = 2.3 Hz, 1 H), 4.41–4.24 (m, 7 H), 4.20 (dd, *J* = 6.3, 3.8 Hz, 1 H), 4.13 (d, *J* = 3.7 Hz, 2 H), 4.07 (d, *J* = 9.7 Hz, 1 H), 4.03–3.95 (m, 2 H), 3.83–3.62 (m, 4 H), 3.44 (s, 3 H), 3.29 (dt, *J* = 10.2, 3.7 Hz, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 176.4, 174.5, 99.5, 99.2, 98.3, 96.5, 77.1, 76.5, 76.0, 74.2, 70.0, 69.7, 69.2, 69.0, 68.6, 67.0, 58.1, 57.8, 55.5; ESI-MS *m/z* calcd for $C_{25}H_{42}N_2O_{39}S_6$ $[M-3H]^{3-}$ 394.3, found 394.6.

Methyl
(2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (15)

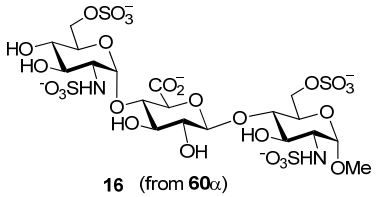


15 (from **60**α)

Similar procedures as that for **53α→2** were applied for **60α→15** (20 mg, 66%; a white solid): $[\alpha]_D^{28}$ = +58.3 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.44 (d, *J* = 3.8

Hz, 1 H), 4.61 (dd, *J* = 11.2, 2.0 Hz, 1 H), 4.39 (dd, *J* = 11.1, 2.1 Hz, 1 H), 4.26 (d, *J* = 9.5 Hz, 1 H), 4.21–4.08 (m, 1 H), 4.05–3.82 (m, 3 H), 3.80–3.70 (m, 1 H), 3.60 (t, *J* = 9.6 Hz, 1 H), 3.40 (s, 1 H), 2.07 (s, 1 H), 2.04 (s, 1 H); ^{13}C NMR (100 MHz, D_2O) δ 174.8, 100.0, 97.8, 97.2, 80.3, 77.9, 76.4, 76.0, 70.6, 70.1, 69.1, 68.3, 55.3, 53.2, 22.0; ESI-MS *m/z* calcd for $C_{23}H_{36}N_2O_{26}S_3$ $[M\text{-}2H]^{2-}$ 426.0, found 426.2; *m/z* calcd for $C_{23}H_{35}N_2O_{26}S_3Na$ $[M+Na\text{-}3H]^{3-}$ 437.0, found 437.4, *m/z* calcd for $C_{51}H_{60}N_2O_{23}S_2$ $[M\text{-}SO_3\text{-}2H]^{2-}$ 386.0, found 386.4; *m/z* calcd for $C_{23}H_{36}N_2O_{26}S_3$ $[M\text{-}3H]^{2-}$ 283.7, found 283.9.

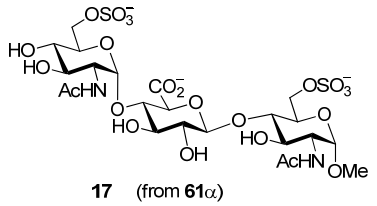
Methyl (2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (16)



16 (from **60**α)

Similar procedures as that for **53α→2** were applied for **60α→16** (14 mg, 70%; a white solid): $[\alpha]_D^{28}$ = +42.8 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.69 (d, *J* = 2.4 Hz, 1 H), 5.07 (d, *J* = 2.8 Hz, 1 H), 4.79 (d, *J* = 3.6 Hz, 1 H), 4.62 (d, *J* = 10.0 Hz, 1 H), 4.40 (d, *J* = 10.4 Hz, 1 H), 4.29 (d, *J* = 11.2 Hz, 1 H), 4.23–4.15 (m, 2 H), 4.04–3.60 (m, 9 H), 3.46 (s, 3 H), 3.33–3.27 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 100.1, 98.3, 97.8, 79.9, 77.9, 76.5, 75.1, 71.3, 70.0, 69.5, 69.1, 68.1, 66.4, 66.0, 58.0, 57.3, 55.5; ESI-MS *m/z* calcd for $C_{19}H_{31}N_2O_{30}S_5$ $[M\text{-}3H]^{3-}$ 309.0, found 309.2; *m/z* calcd for $C_{19}H_{32}N_2O_{30}S_5$ $[M\text{-}2H]^{2-}$ 464.0, found 464.2.

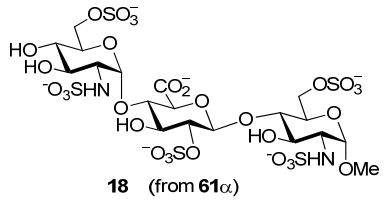
Methyl (2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (17)



17 (from **61**α)

Similar procedures as that for **53α→2** were applied for **61α→17** (8 mg, 78%; a white solid): $[\alpha]_D^{28}$ = +42.6 (*c* 0.3, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.42 (d, *J* = 3.0 Hz, 1 H), 4.58 (d, *J* = 7.8 Hz, 1 H), 4.35 (d, *J* = 9.9 Hz, 3 H), 4.17 (d, *J* = 10.5 Hz, 1 H), 4.07–3.64 (m, 11H), 3.58 (d, *J* = 9.6 Hz, 1 H), 3.45–3.23 (m, 5 H), 2.03 (d, *J* = 10.2 Hz, 6 H); ^{13}C NMR (100 MHz, D_2O) δ 174.9, 174.6, 102.3, 97.9, 97.0, 78.7, 76.6, 76.5, 75.9, 73.7, 70.7, 70.2, 69.6, 69.3, 68.5, 66.5, 55.5, 53.6, 53.3, 22.1, 22.0; ESI-MS *m/z* calcd for $C_{23}H_{36}N_2O_{23}S_2Na$ $[M+Na\text{-}2H]^-$ 795.1, found 795.4.

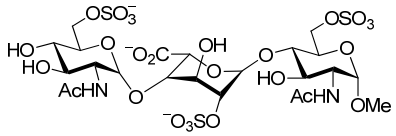
Methyl
(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyanosyluronate)-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (18)



18 (from **61**α)

Similar procedures as that for **53α→2** were applied for **61α→18** (21 mg, 75%; a white solid): $[\alpha]_D^{28}$ = +23.9 (*c* 0.3, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.67 (d, *J* = 3.6 Hz, 2 H), 5.07 (d, *J* = 3.6 Hz, 1 H), 4.63 (d, *J* = 8.0 Hz, 1 H), 4.43–4.35 (m, 3 H), 4.19 (d, *J* = 10.8 Hz, 1 H), 4.03–4.01 (m, 1 H), 3.92–3.80 (m, 4 H), 3.77–3.70 (m, 2 H), 3.67–3.58 (m, 2 H), 3.46 (s, 3 H), 3.41 (t, *J* = 8.4 Hz, 1 H), 3.34–3.28 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 102.1, 98.2, 97.4, 78.5, 76.4, 76.3, 76.2, 73.0, 71.1, 69.8, 69.7, 69.0, 69.2, 66.5, 66.4, 57.9, 57.3, 55.5; ESI-MS *m/z* calcd for $C_{19}H_{31}N_2O_{27}S_4$ $[M-3H]^{3-}$ 283.3, found 282.3; *m/z* calcd for $C_{19}H_{32}N_2O_{27}S_4$ $[M-2H]^{2-}$ 424.0, found 424.2.

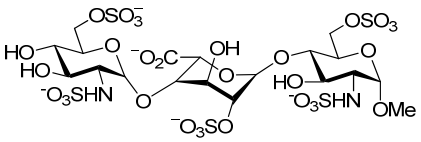
Methyl
(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-L-idurop yanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (19)



19 (from **62**α)

Similar procedures as that for **53α→2** were applied for **62α→19** (8 mg, 46%; a white solid): $[\alpha]_D^{28}$ = +33.6 (*c* 0.4, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.19 (s, 1 H), 5.15 (d, *J* = 3.5 Hz, 1 H), 4.84 (d, *J* = 2.2 Hz, 1 H), 4.75 (d, *J* = 3.6 Hz, 1 H), 4.30 (m, 6 H), 4.06 (br s, 1 H), 4.05–3.90 (m, 4H), 3.85–3.68 (m, 3 H), 3.54 (t, *J* = 9.6 Hz, 1 H), 3.38 (s, 3 H), 2.05 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (100 MHz, D_2O) δ 175.2, 174.9, 174.5, 99.3, 97.9, 94.0, 77.5, 74.6, 71.6, 71.3, 70.2, 70.0, 69.4, 68.8, 68.3, 67.0, 66.7, 65.0, 55.3, 53.8, 53.4, 22.4, 22.0; ESI-MS *m/z* calcd for $C_{23}H_{35}N_2O_{26}S_3$ $[M-2H]^{2-}$ 283.7, found 283.9; *m/z* calcd for $C_{23}H_{36}N_2O_{26}S_3$ $[M-3H]^{3-}$ 426.0, found 426.9.

Methyl
(2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(2-*O*-sulfo-*β*-L-idurop yanosyluronate)-(1→4)-2-*N*-acetyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (20)



20 (from **62**α)

Similar procedures as that for **53α→2** were applied for **62α→20** (10 mg, 42%; a white solid): $[\alpha]_D^{28}$ = +8.0 (*c* 0.2, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.43 (d, *J* = 3.4 Hz, 1 H), 5.22 (d, *J* = 3.1 Hz, 1 H), 5.03 (d, *J* = 3.5 Hz, 1 H), 4.46–4.28 (m, 4 H), 4.28–4.14 (m, 2 H), 4.11 (t, *J* = 3.3 Hz, 1 H), 4.05–3.86 (m, 2 H), 3.76 (t, *J* = 9.4 Hz, 1 H), 3.71–3.50 (m, 3 H), 3.42 (s, 3 H), 3.34–3.20 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 174.6, 99.4, 98.3, 96.7, 77.0, 76.4, 75.9, 71.1, 70.04, 69.96, 69.6, 69.4, 68.6, 67.0, 66.6, 58.0, 57.8, 55.5; ESI-MS *m/z* calcd for $C_{19}H_{31}N_2O_{30}S_5$ $[M-3H]^{3-}$ 309.0, found 309.0; *m/z* calcd for $C_{19}H_{31}N_2O_{30}S_5Na$ $[M+Na-3H]^{2-}$ 475.0, found 475.0.

Reference:

(S1) Orgueira, H.; Bartolozzi, A.; Schell, P.; Litjens, R.; Palmacci, E.; Seeberger, P. H. *Chem. Eur. J.* **2003**, *9*, 140-169.

(S2) Chen, J.; Zhou, Y.; Chen, C.; Xu, W.; Yu, B. *Carbohydr. Res.* **2008**, *343*, 2853-2862.

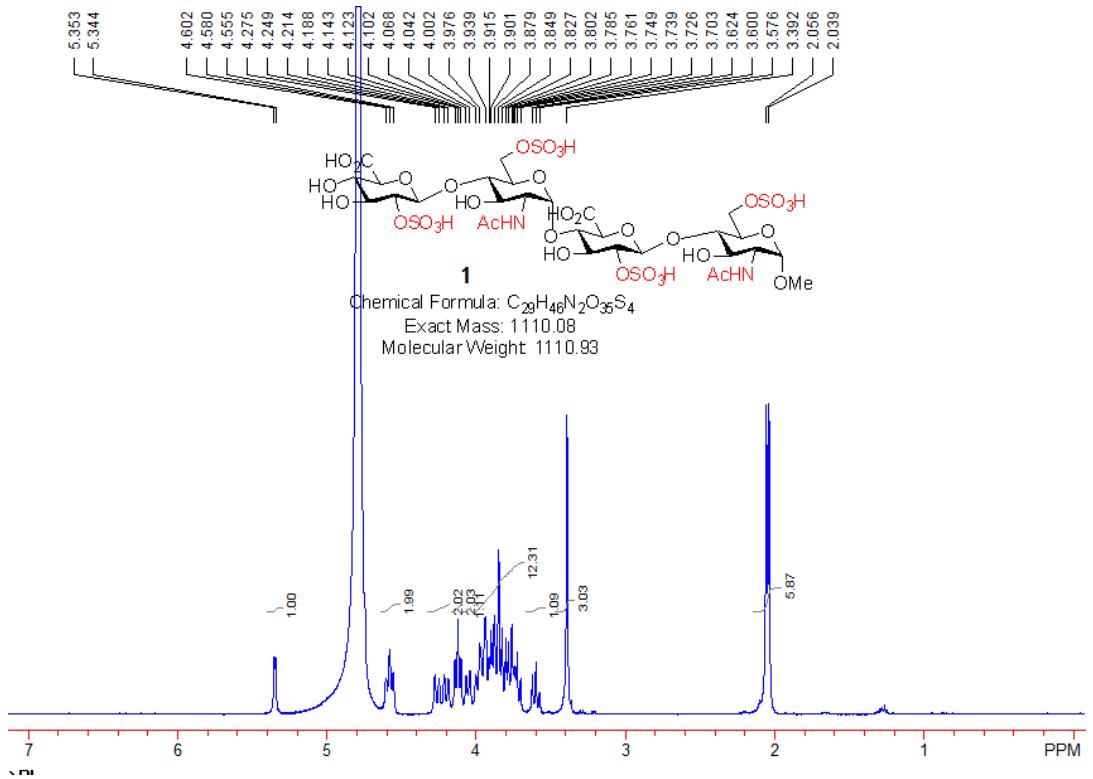
(S3) Zhou, Y.; Lin, F.; Chen, J.; Yu, B. *Carbohydr. Res.* **2006**, *341*, 1619-1629.

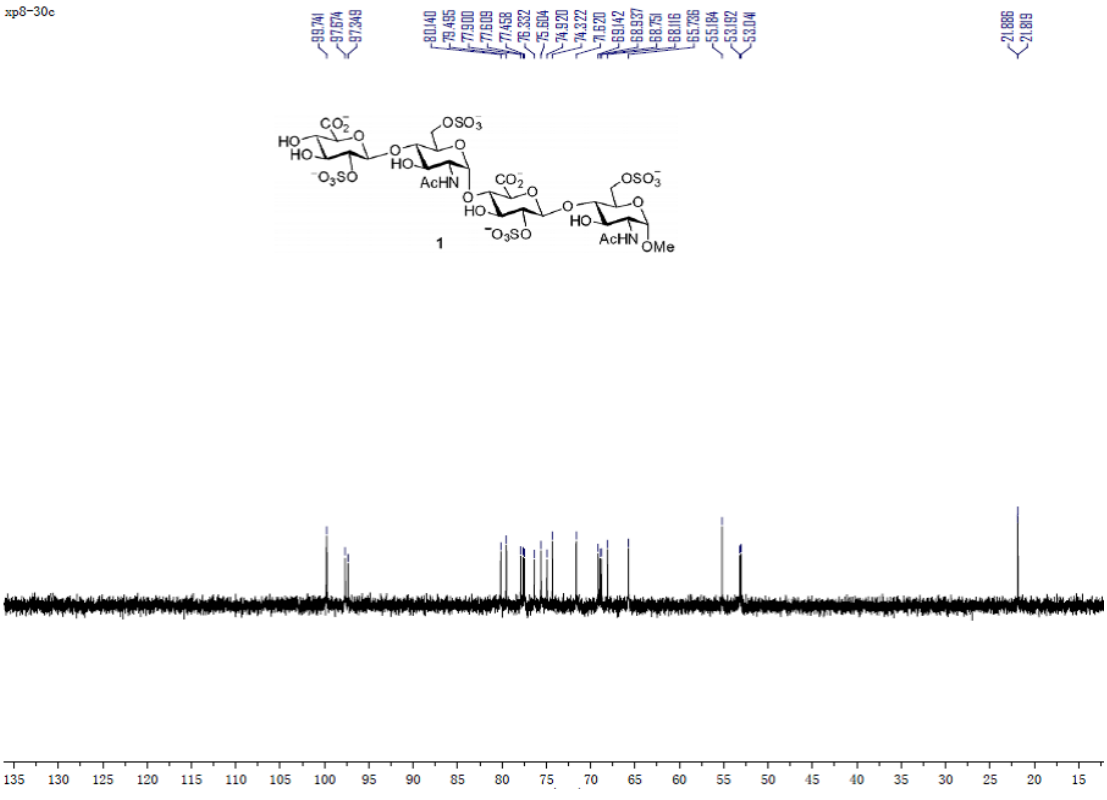
(S4) Polat T.; Wong, C.-H. *J. Am. Chem. Soc.* **2007**, *129*, 12795-12800.

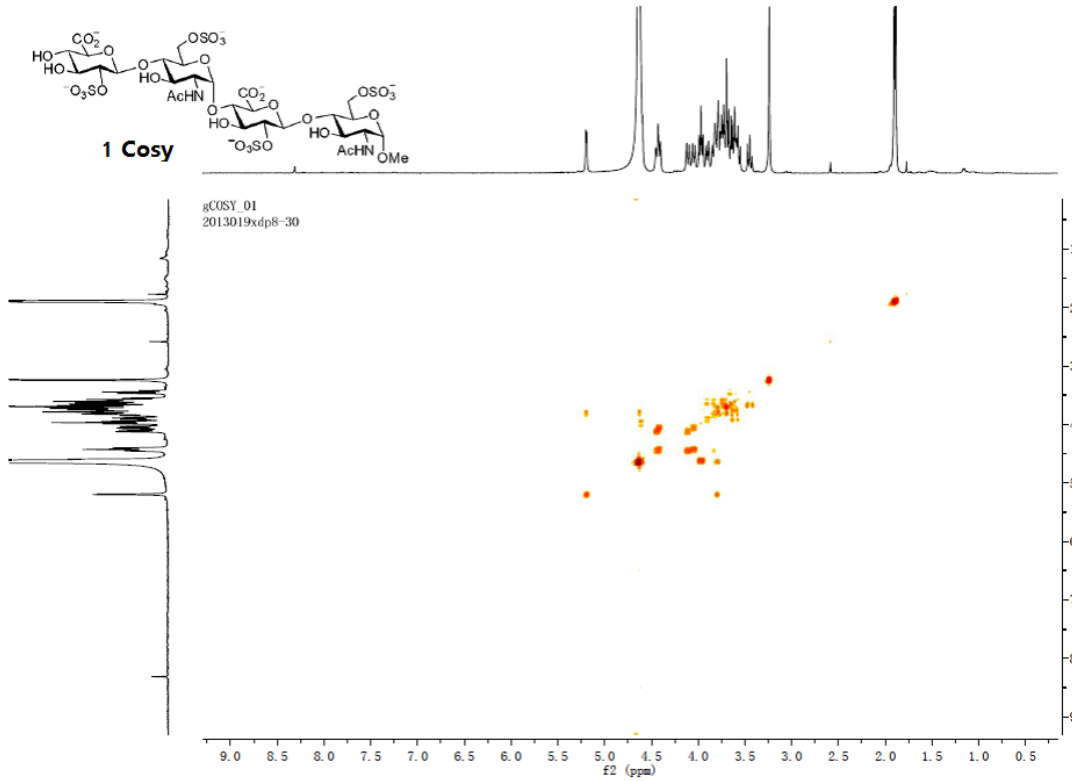
(S5) Nathalie, K.; Jean-Claude J. *J. Chem. Soc., Perkin Trans. 1* **2000**, *16*, 2709-2718.

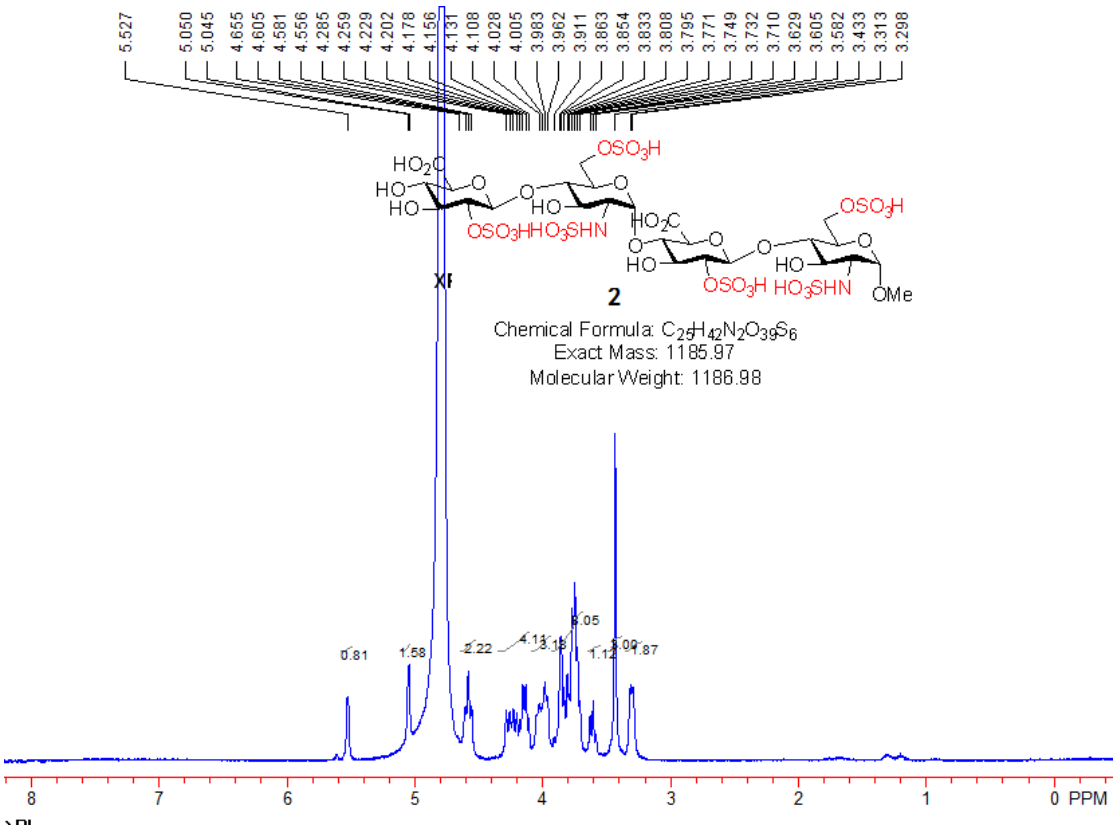
(S6) Masato, O.; Tatsushi, T.; Naohiro, F.; Shoichi, K. *Tetrahedron Lett.* **2004**, *45*, 4039-4042.

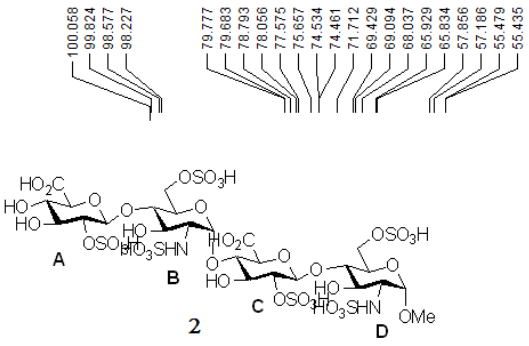
(S7) Nadine, B.; Jean-Claude, J. *Carbohydr. Res.* **2002**, *337*, 673-690.

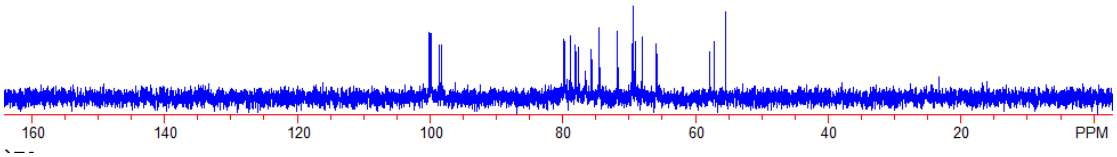

1
Chemical Formula: C29H46N2O35S4
Exact Mass: 1110.08
Molecular Weight: 1110.93
PPM

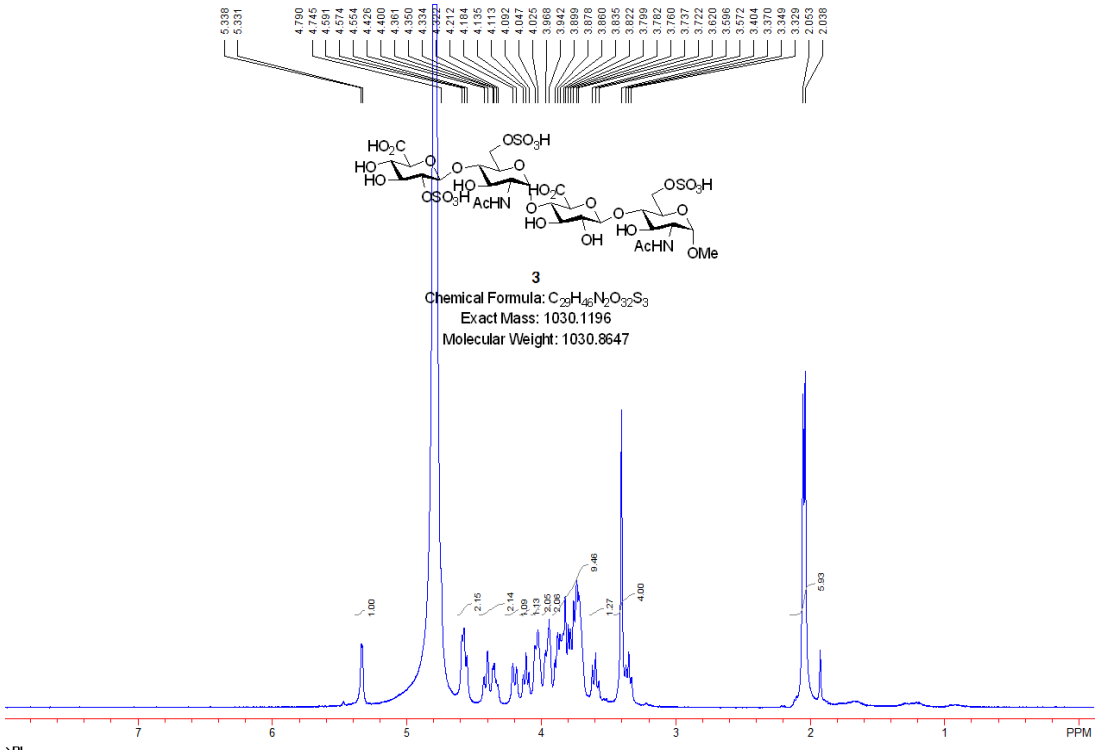

xp8-30c
1

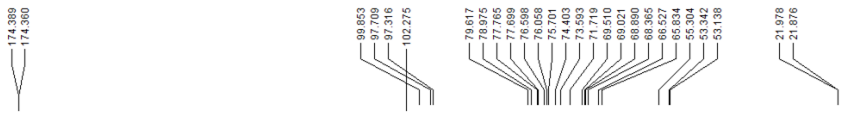

1 Cosy
gCOSY_01
2013019xdp8-30
f2 (ppm)

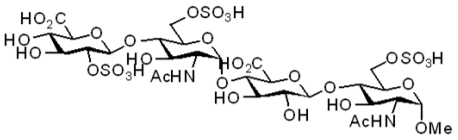

2
Chemical Formula: C25H42N2O39S6
Exact Mass: 1185.97
Molecular Weight: 1186.98
PPM


100.058
99.824
98.577
98.227
79.777
79.683
78.793
78.056
77.575
75.657
74.534
74.461
71.712
69.429
69.094
68.037
65.929
65.834
57.856
57.186
55.479
55.435
A
B
C
D
2


160
140
120
100
80
60
40
20
PPM

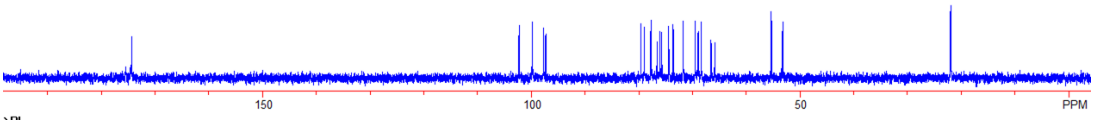

5.338
5.331
4.790
4.745
4.591
4.574
4.554
4.426
4.400
4.361
4.350
4.334
4.322
4.212
4.184
4.135
4.113
4.092
4.047
4.025
3.968
3.942
3.899
3.878
3.860
3.835
3.822
3.799
3.782
3.760
3.737
3.722
3.620
3.596
3.572
3.404
3.370
3.349
3.329
2.053
2.038
3
Chemical Formula: C29H46N2O32S3
Exact Mass: 1030.1196
Molecular Weight: 1030.8647
1.00
2.15
2.14
1.09
1.13
2.05
2.06
9.46
1.27
4.00
5.93
7
6
5
4
3
2
1
PPM

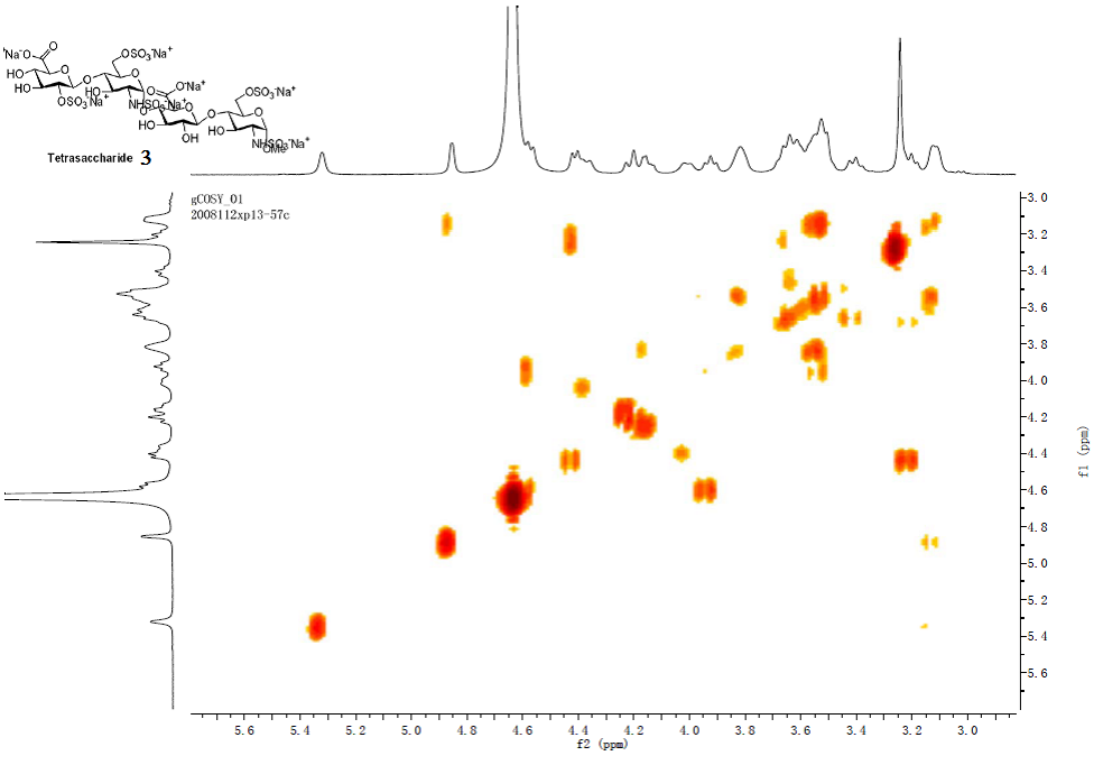


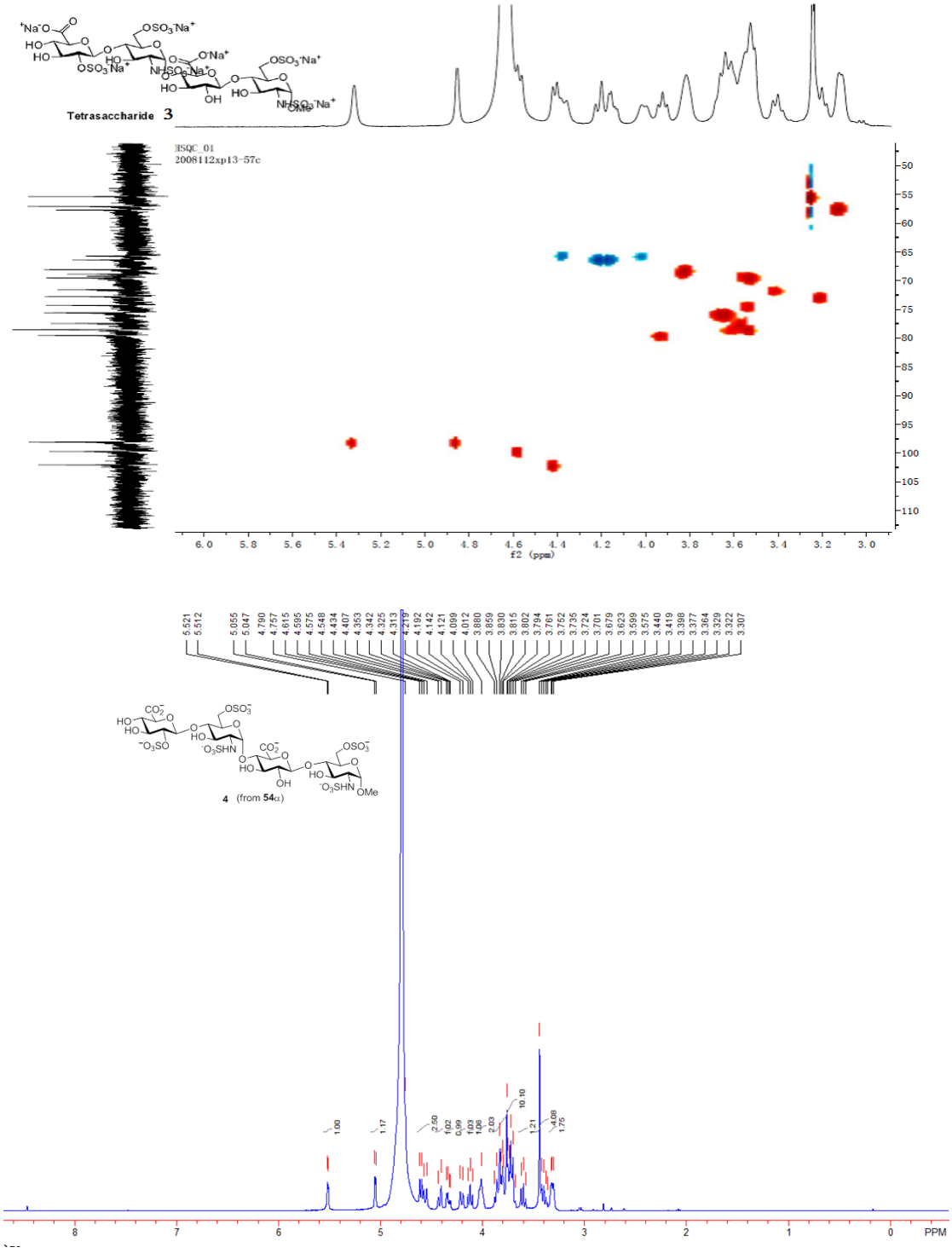


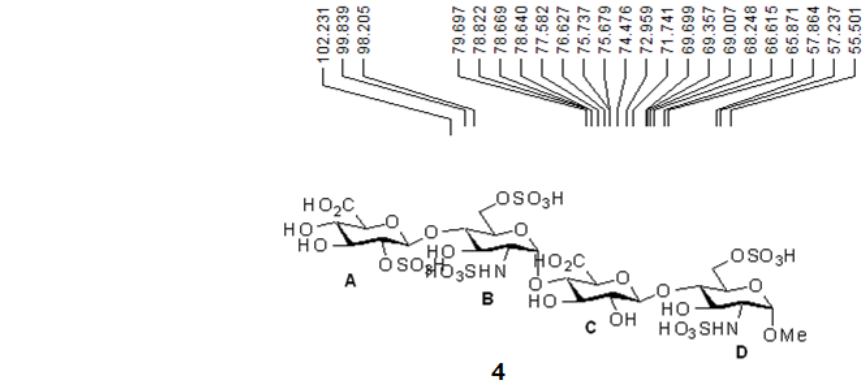
3

Chemical Formula: $C_{29}H_{46}N_2O_{32}S_3$
Exact Mass: 1030.1196
Molecular Weight: 1030.8647

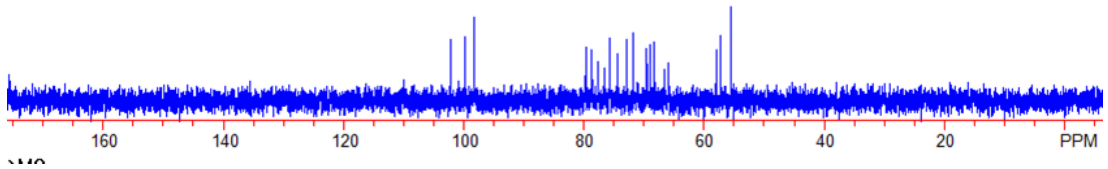


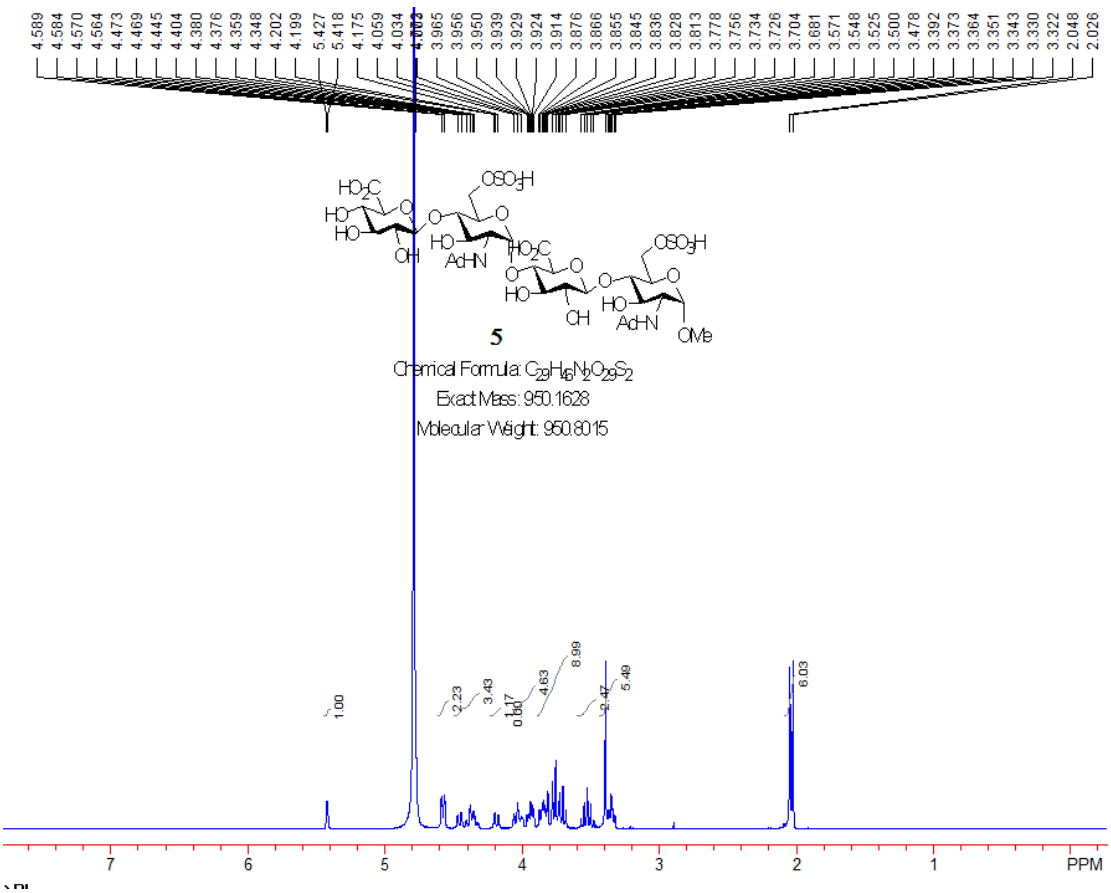



Tetrasaccharide 3
HSQC_01
2008112xp13-57c
f2 (ppm)
4 (from 54α)
PPM



4



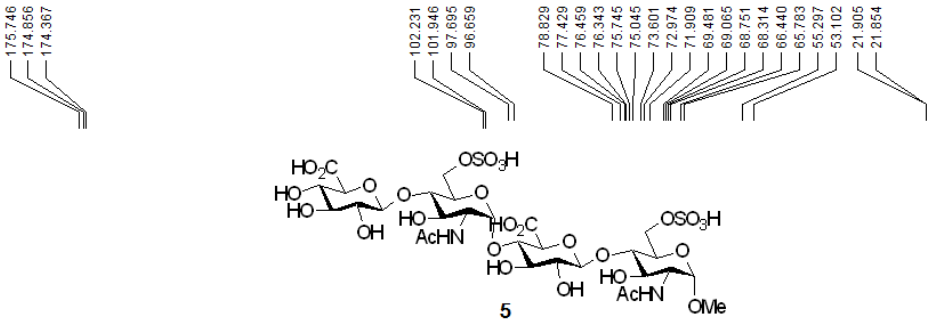


5

Chemical Formula: $C_{29}H_{46}N_2O_{29}S_2$

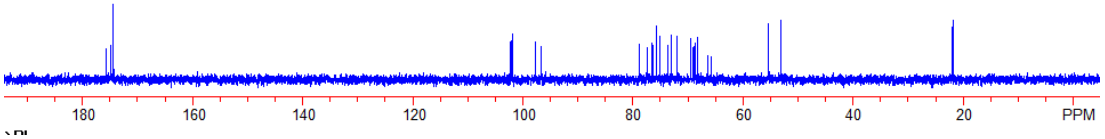
Exact Mass: 950.1628

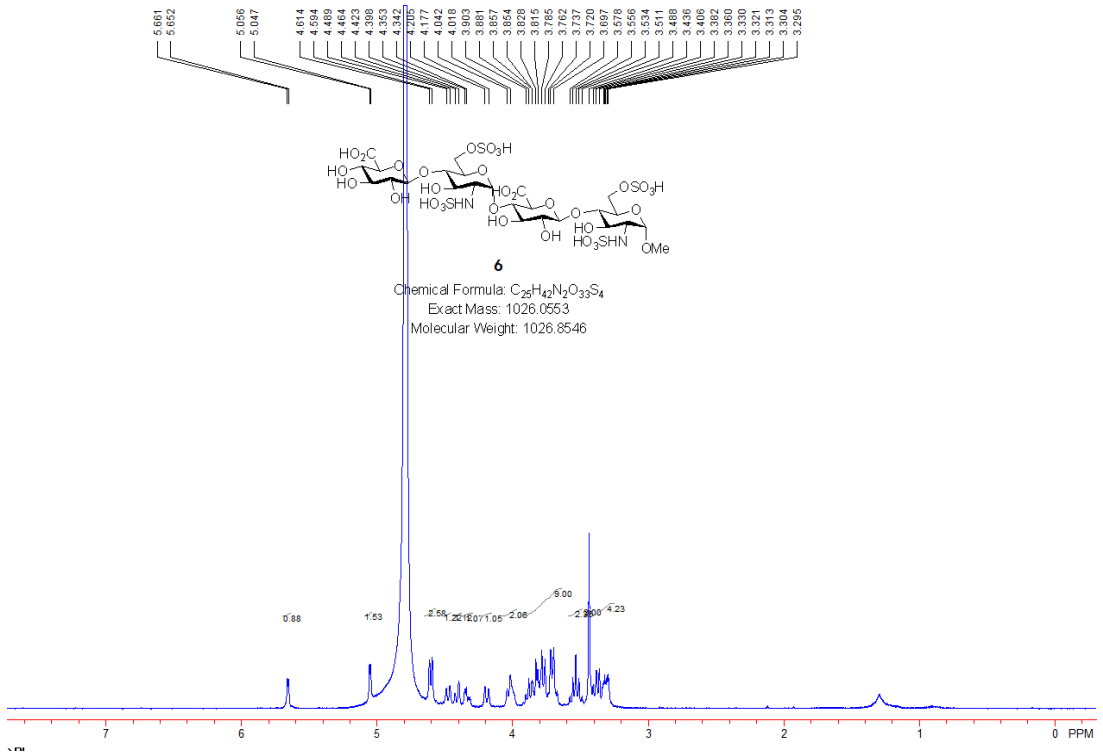
Molecular Weight: 950.8015



5

Chemical Formula: $C_{29}H_{46}N_2O_{29}S_2$
Exact Mass: 950.1628
Molecular Weight: 950.8015

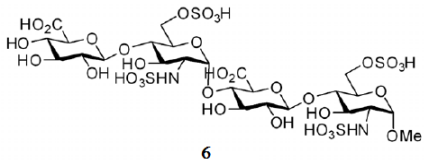




6

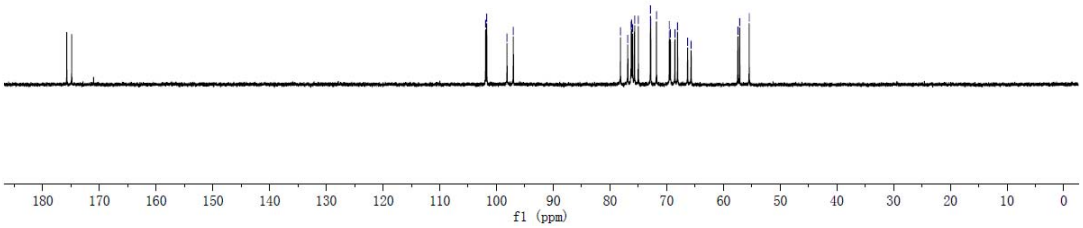
Chemical Formula: $C_{25}H_{42}N_2O_{33}S_4$
Exact Mass: 1026.0553
Molecular Weight: 1026.8546

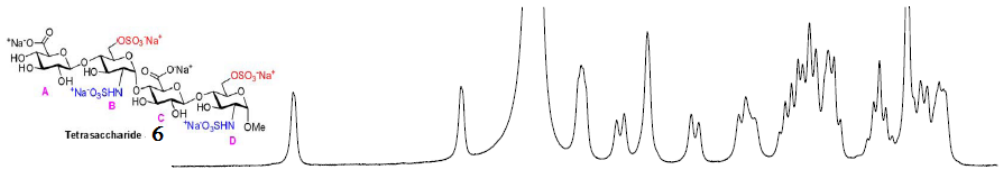
xp15-12C

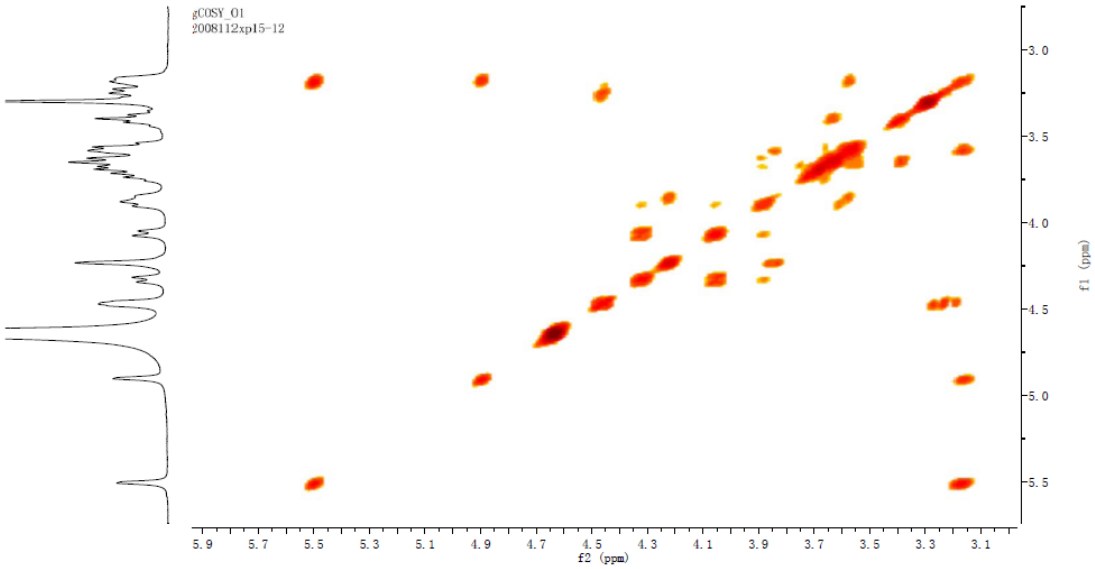


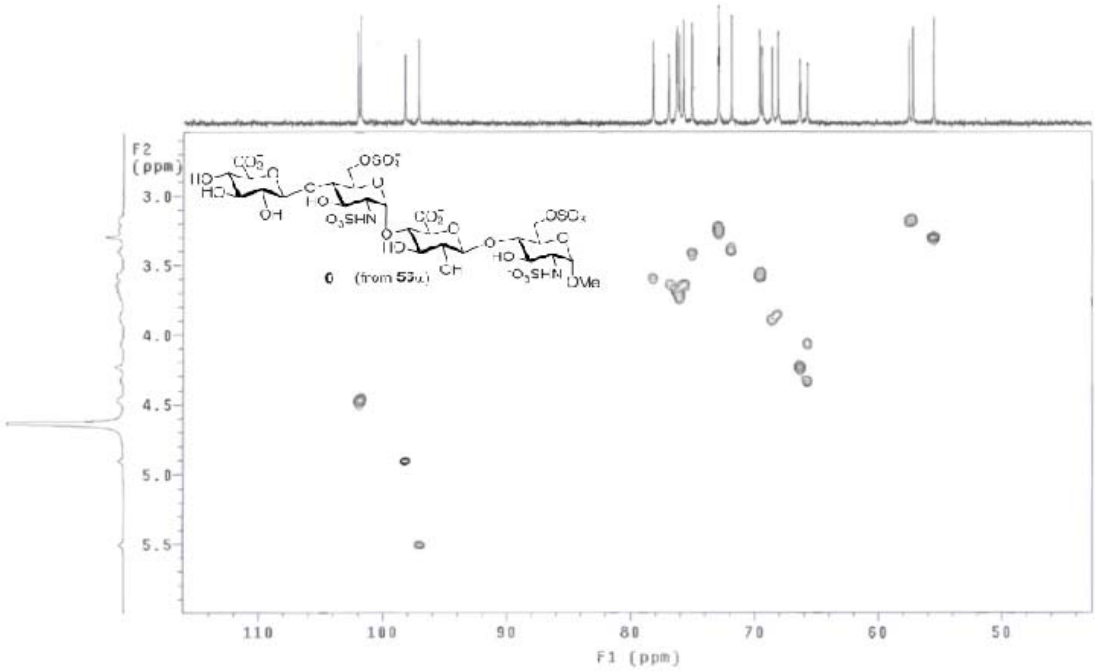
6

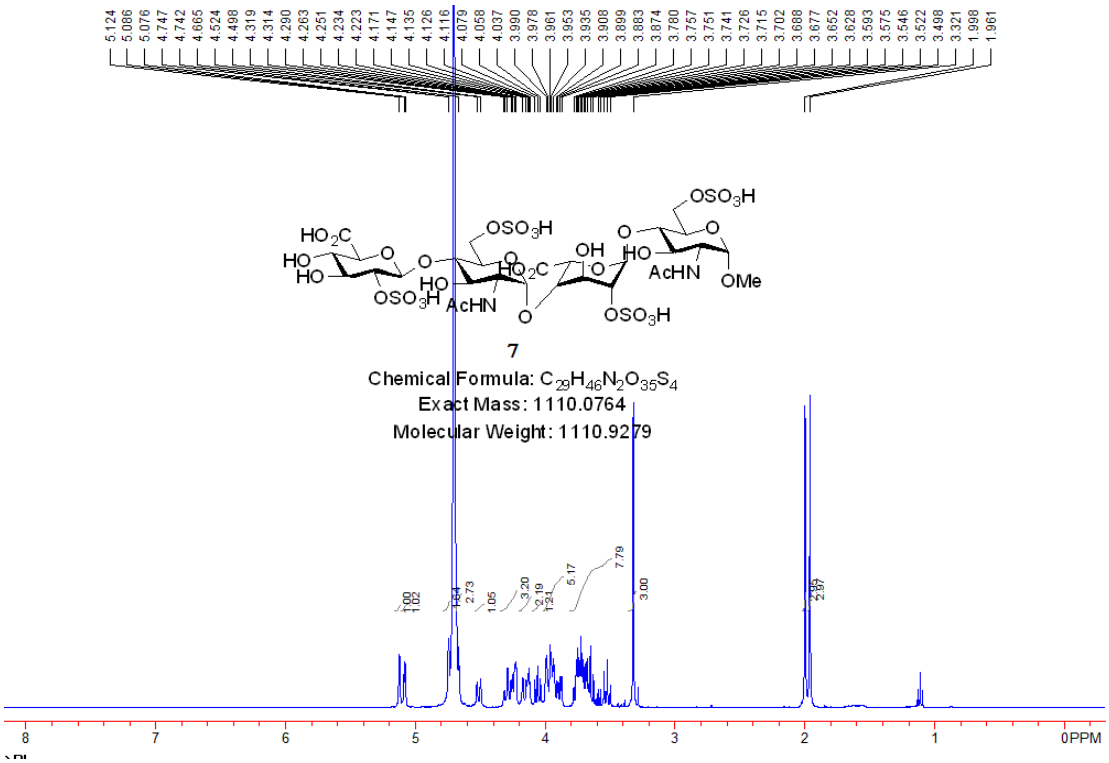
Chemical Formula: $C_{25}H_{42}N_2O_{33}S_4$
Exact Mass: 1026.0553
Molecular Weight: 1026.8546

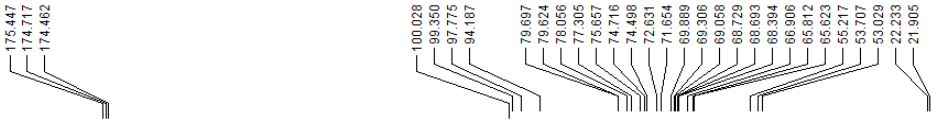


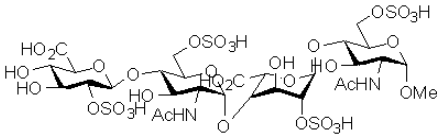





F2 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
110
100
90
80
70
60
50
F1 (ppm)

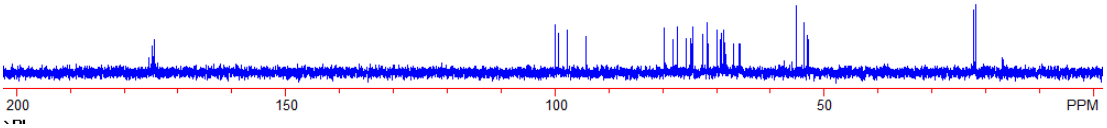

7
Chemical Formula: C29H46N2O35S4
Exact Mass: 1110.0764
Molecular Weight: 1110.9279
8
7
6
5
4
3
2
1
0PPM

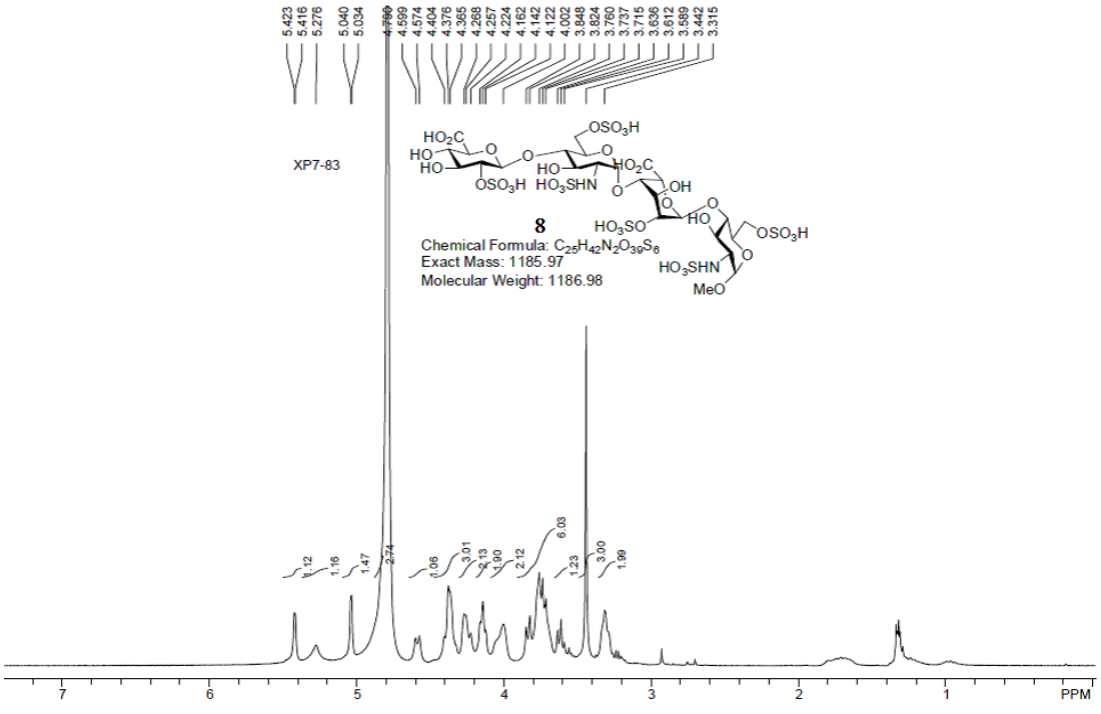


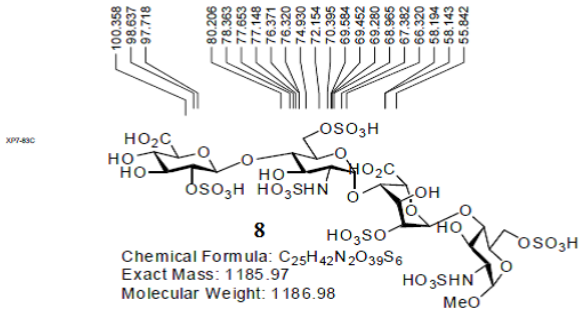


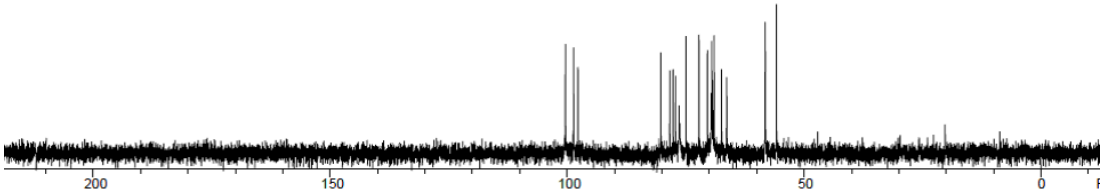
7

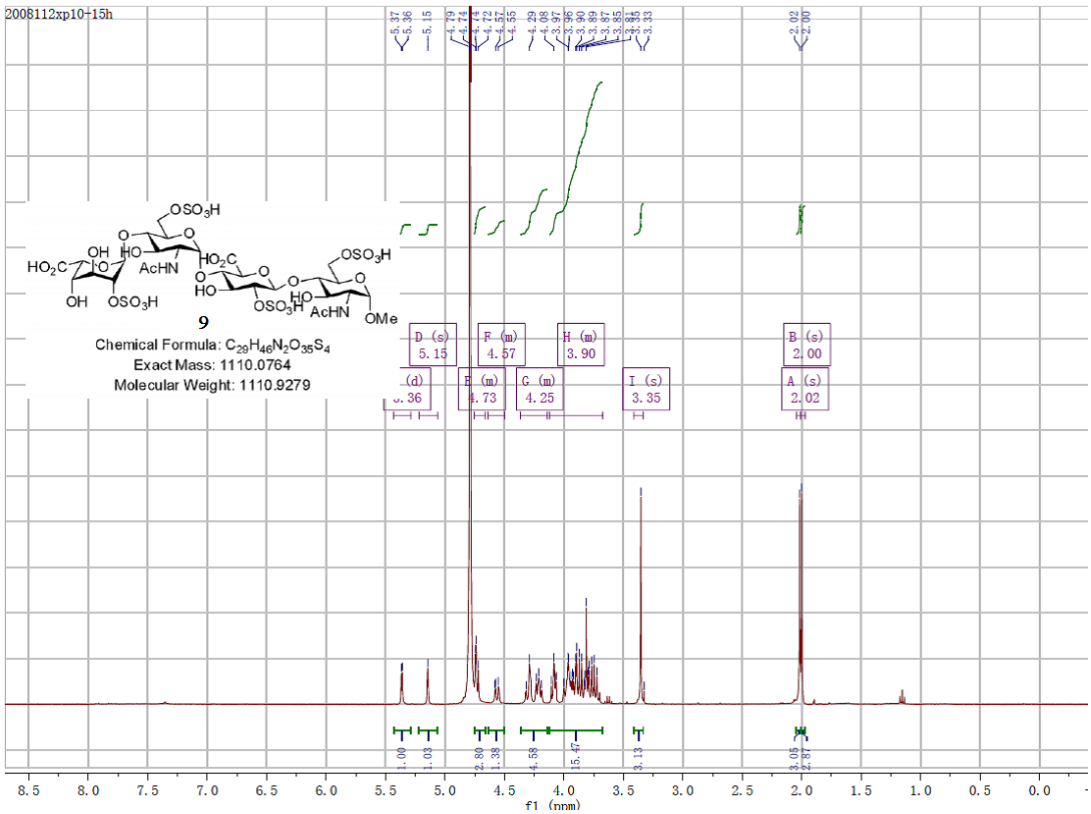
Chemical Formula: $C_{29}H_{46}N_2O_{35}S_4$
Exact Mass: 1110.0764
Molecular Weight: 1110.9279

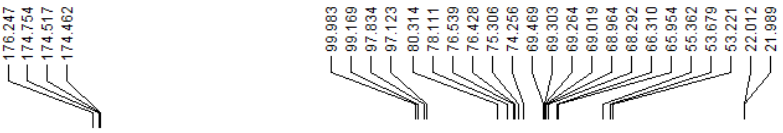


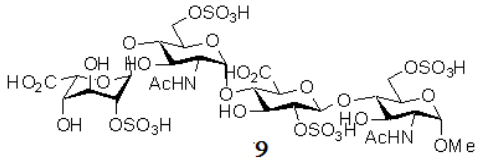



100.358
98.637
97.718
80.206
78.363
77.653
77.148
76.371
76.320
74.930
72.154
70.395
69.584
69.452
69.280
68.965
67.382
66.320
58.194
58.143
55.842
8
Chemical Formula: C25H42N2O39S6
Exact Mass: 1185.97
Molecular Weight: 1186.98


200
150
100
50
0

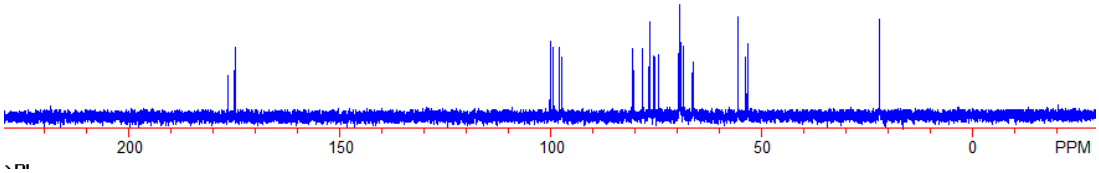

20080112xp10-15h
9
Chemical Formula: C29H46N2O35S4
Exact Mass: 1110.0764
Molecular Weight: 1110.9279
D (s) 5.15
F (m) 4.57
H (m) 3.90
B (s) 2.00
I (s) 3.35
A (s) 2.02
f1 (ppm)

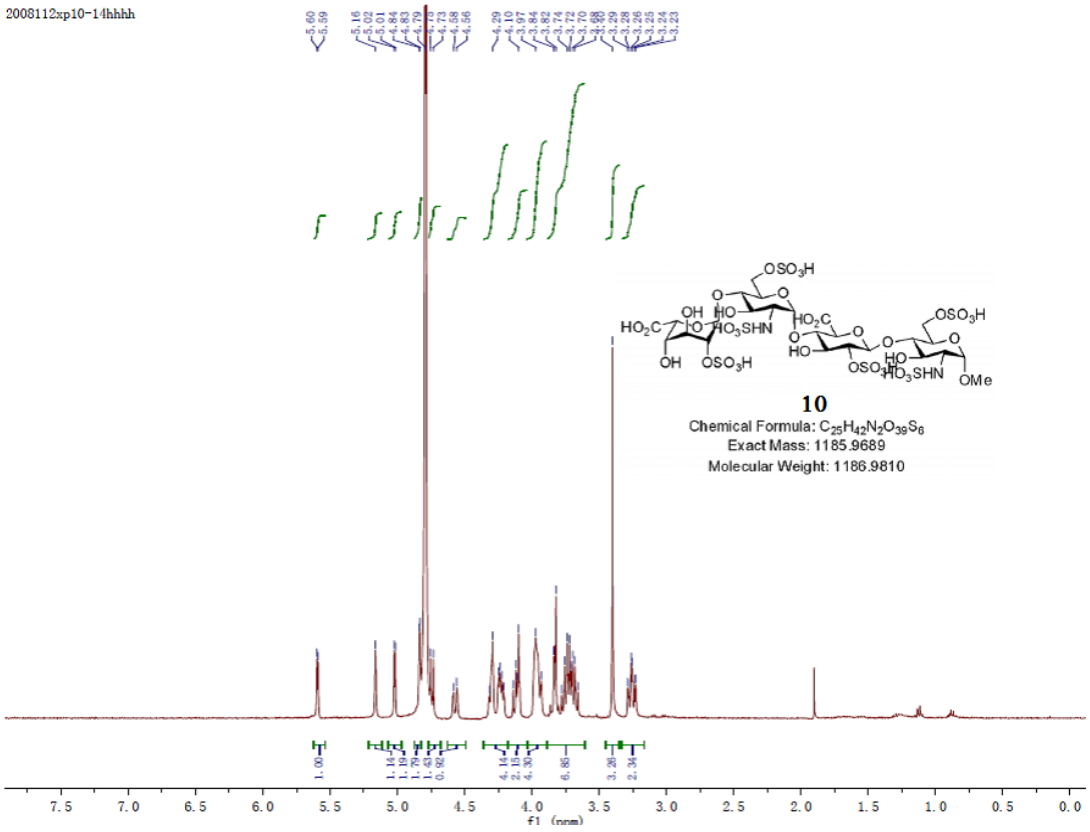




9

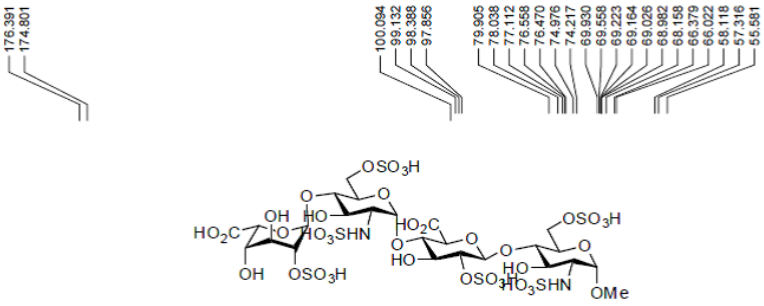
Chemical Formula: $C_{29}H_{46}N_2O_{35}S_4$
Exact Mass: 1110.0764
Molecular Weight: 1110.9279





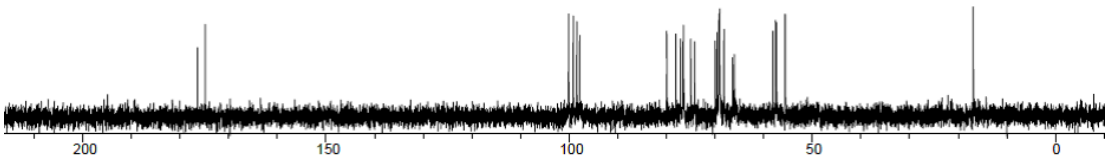
10

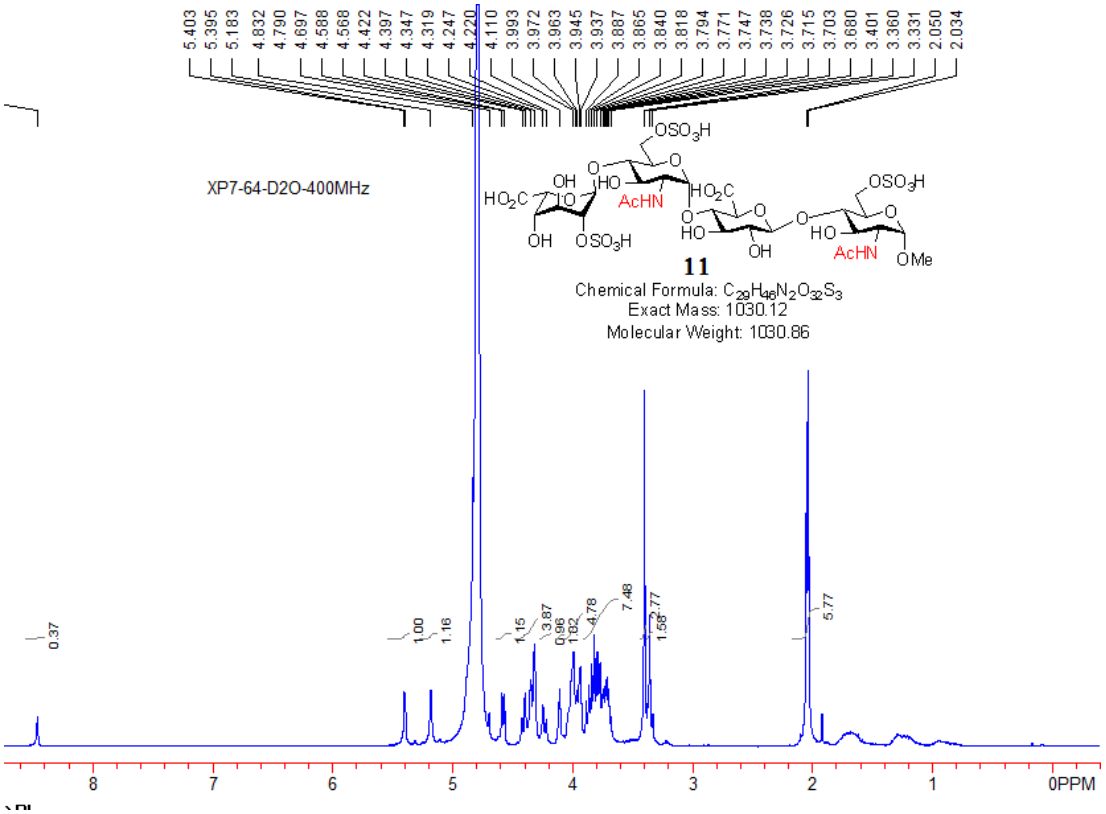
Chemical Formula: $C_{25}H_{42}N_2O_{39}S_6$
Exact Mass: 1185.9689
Molecular Weight: 1186.9810



10

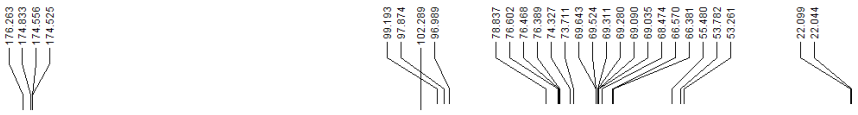
Chemical Formula: $C_{25}H_{42}N_2O_{39}S_6$
Exact Mass: 1185.9689
Molecular Weight: 1186.9810

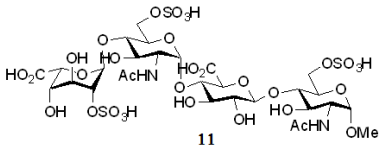




11

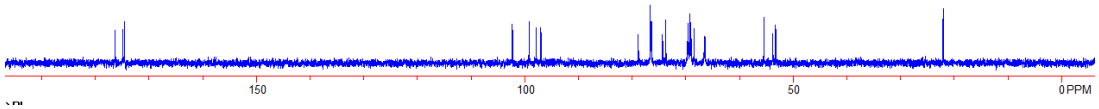
Chemical Formula: $C_{29}H_{46}N_2O_{32}S_3$
Exact Mass: 1030.12
Molecular Weight: 1030.86

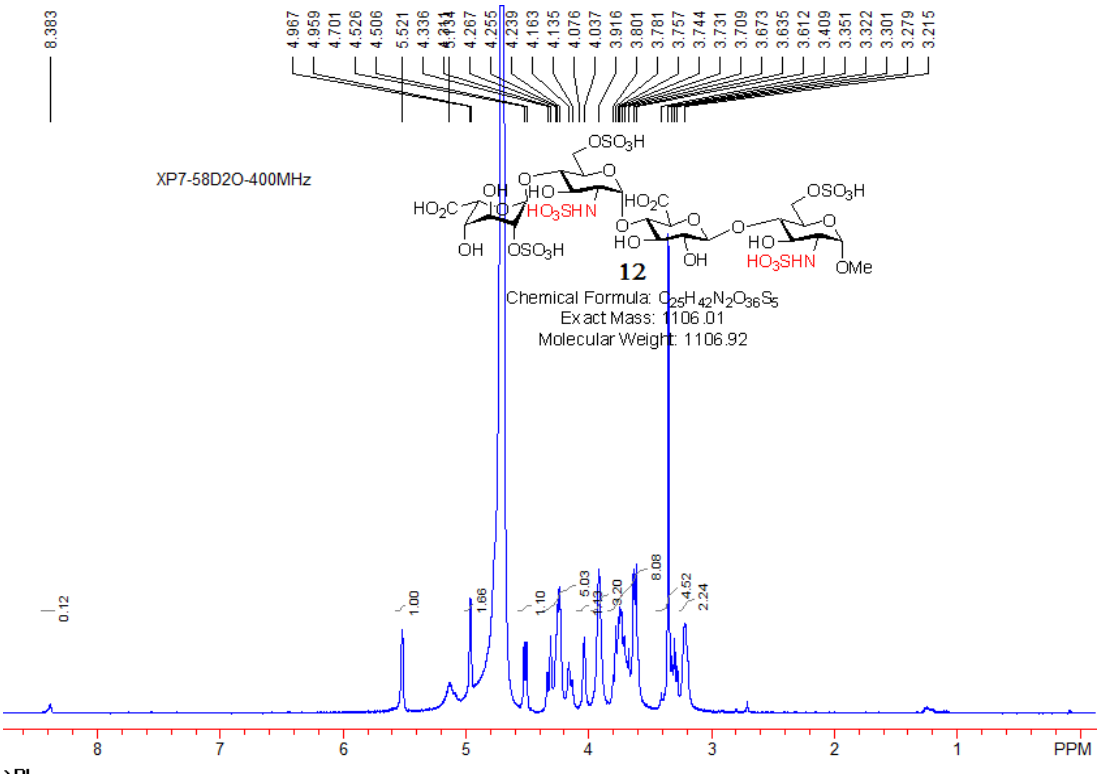




11

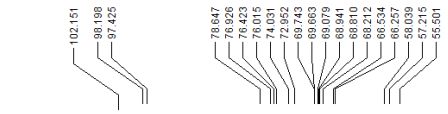
Chemical Formula: $C_{29}H_{46}N_2O_{32}S_3$
Exact Mass: 1030.1196
Molecular Weight: 1030.8647

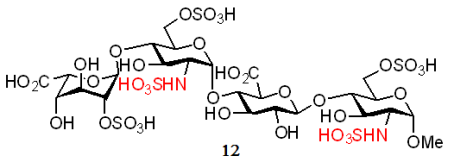




12

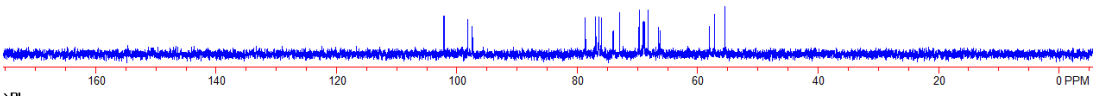
Chemical Formula: $C_{25}H_{42}N_2O_{36}S_5$
Exact Mass: 1106.01
Molecular Weight: 1106.92

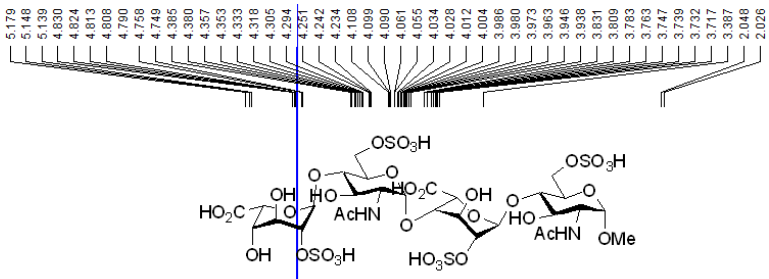




12

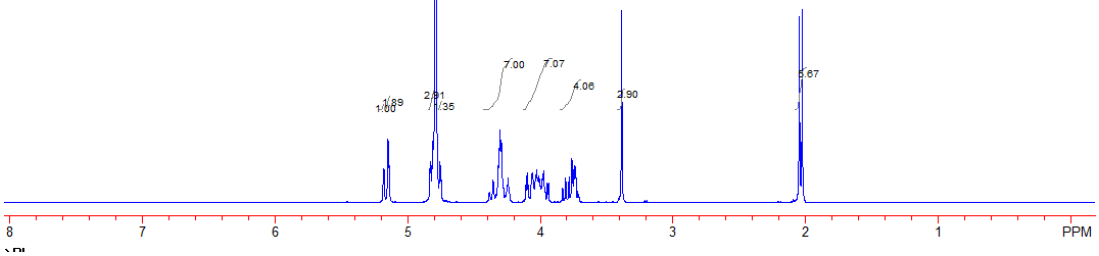
Chemical Formula: $C_{25}H_{42}N_2O_{36}S_5$
Exact Mass: 1106.01
Molecular Weight: 1106.92

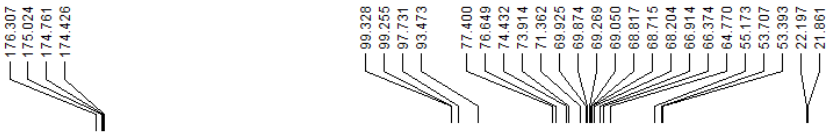


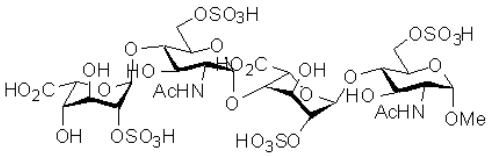


13

Chemical Formula: $C_{29}H_{46}N_2O_{35}S_4$
Exact Mass: 1110.0764
Molecular Weight: 1110.9279

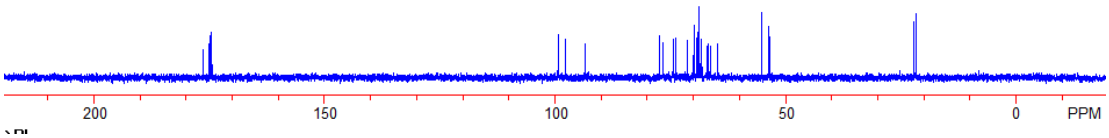


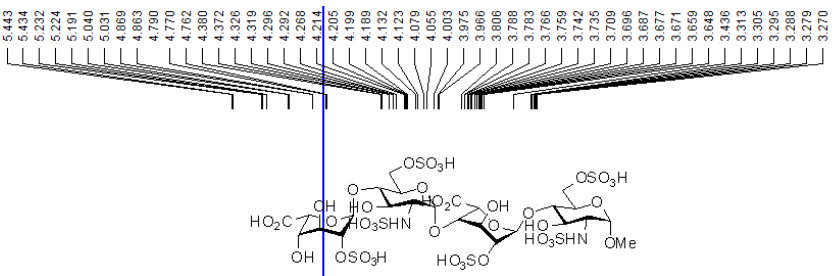




13

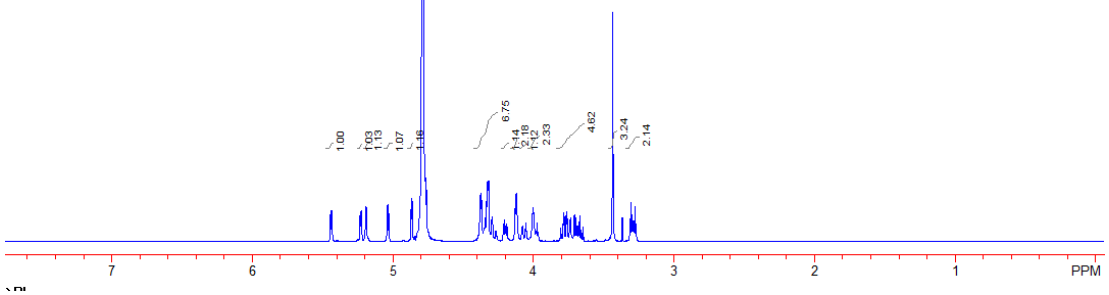
Chemical Formula: $C_{29}H_{46}N_2O_{35}S_4$
Exact Mass: 1110.0764
Molecular Weight: 1110.9279

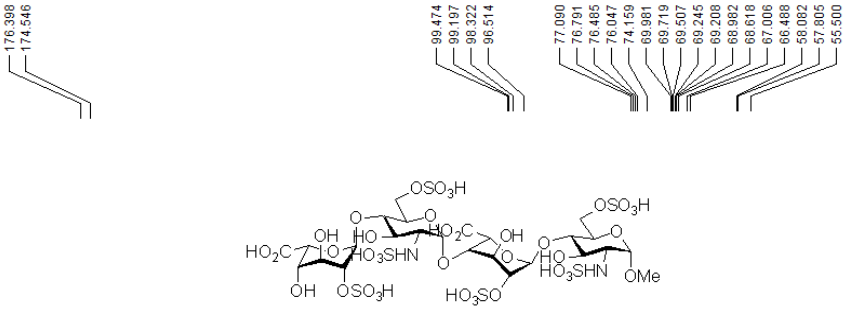




14

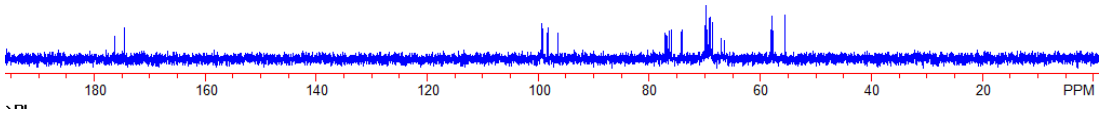
Chemical Formula: $C_{25}H_{42}N_2O_{39}S_6$
Exact Mass: 1185.9689
Molecular Weight: 1186.9810

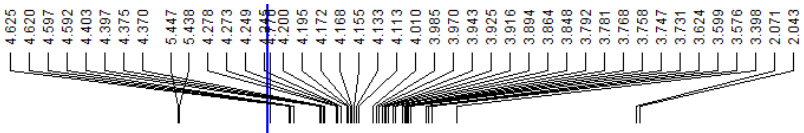


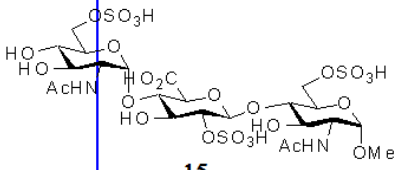


14

Chemical Formula: $C_{25}H_{42}N_2O_{39}S_6$
Exact Mass: 1185.9689
Molecular Weight: 1186.9810

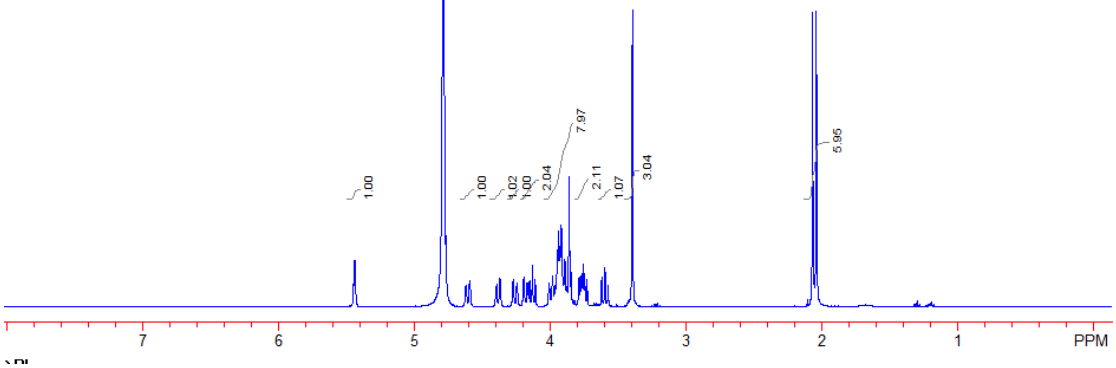


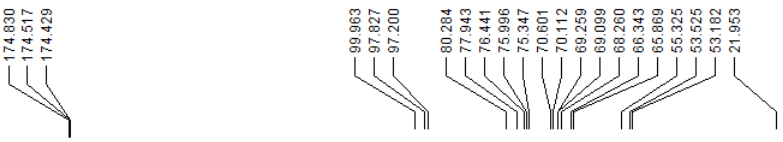


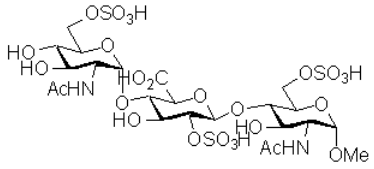


15

Chemical Formula: $C_{23}H_{38}N_2O_{26}S_3$
Exact Mass: 854.0875
Molecular Weight: 854.7406

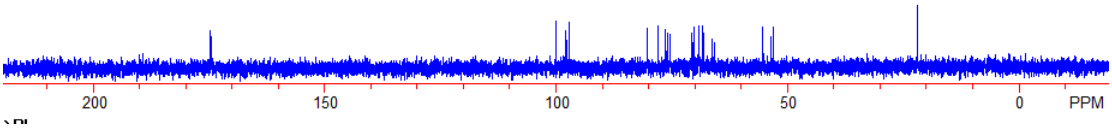


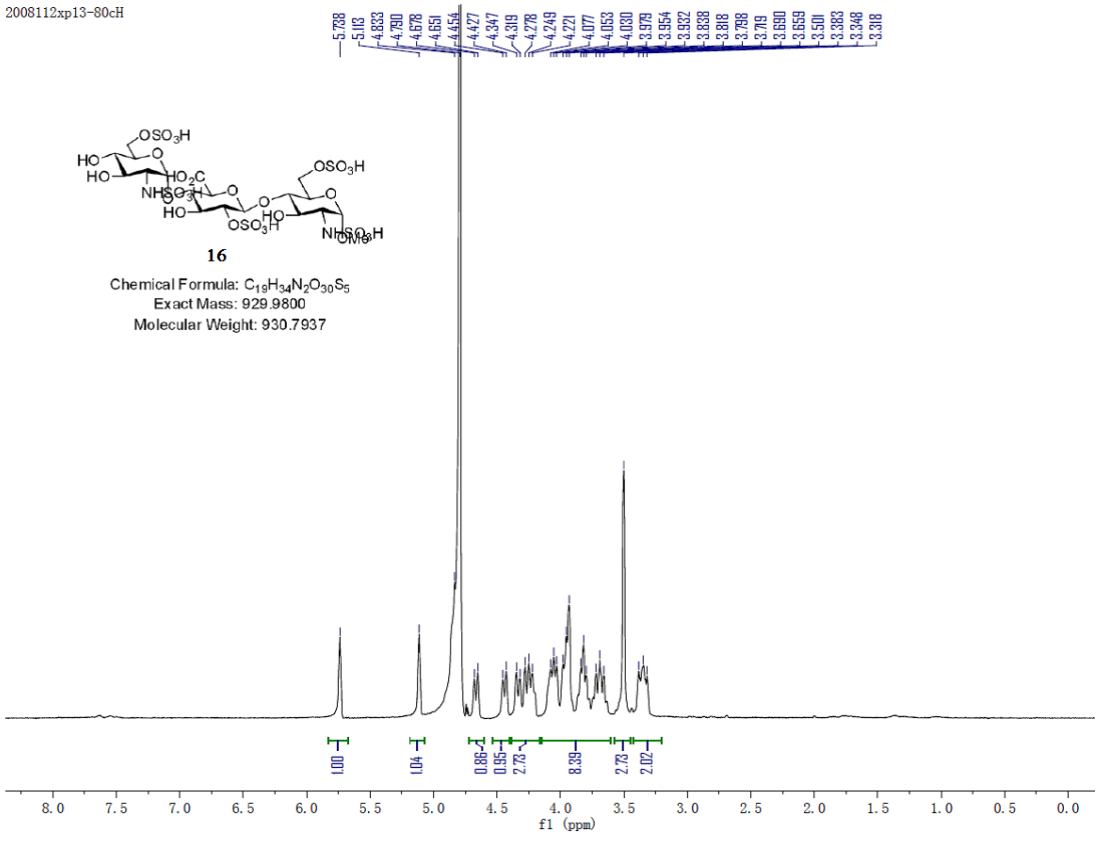




15

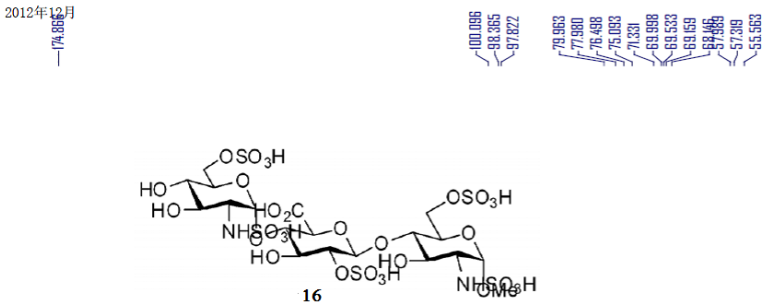
Chemical Formula: $C_{23}H_{38}N_2O_{26}S_3$
Exact Mass: 854.0875
Molecular Weight: 854.7406





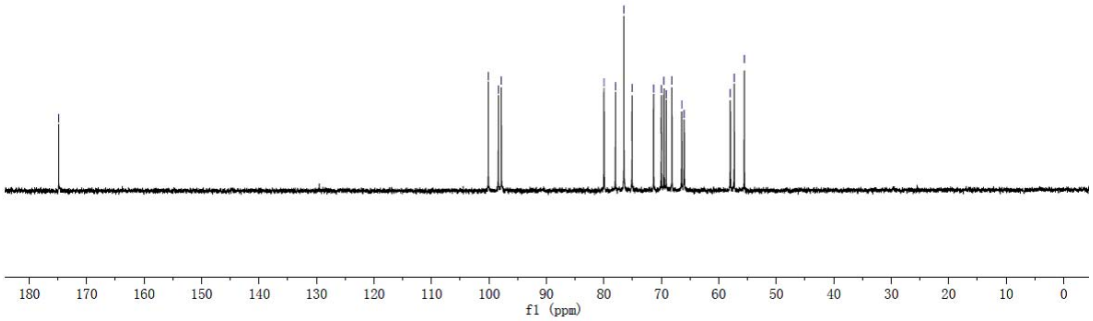
16

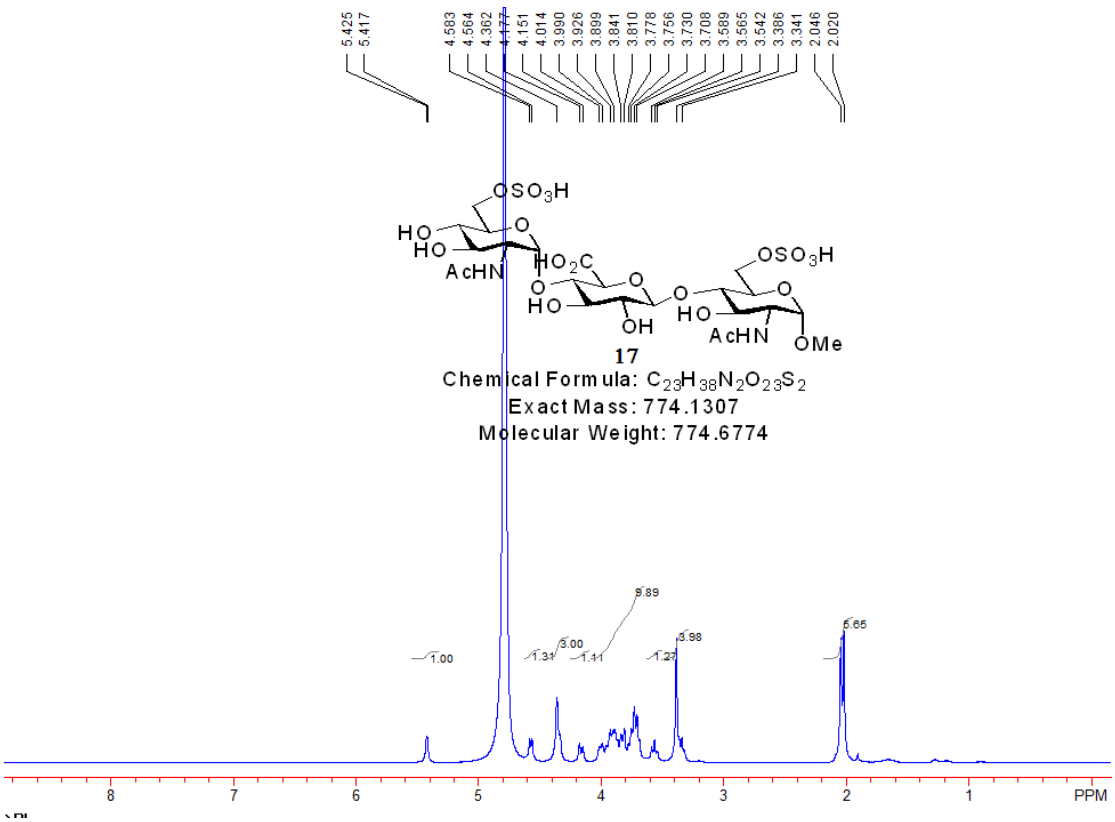
Chemical Formula: $C_{19}H_{34}N_2O_{30}S_5$
Exact Mass: 929.9800
Molecular Weight: 930.7937



16

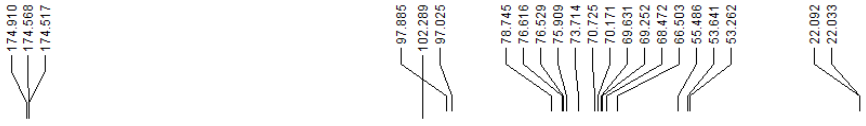
Chemical Formula: $C_{19}H_{34}N_2O_{30}S_5$
Exact Mass: 929.9800
Molecular Weight: 930.7937

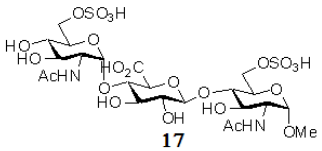




17

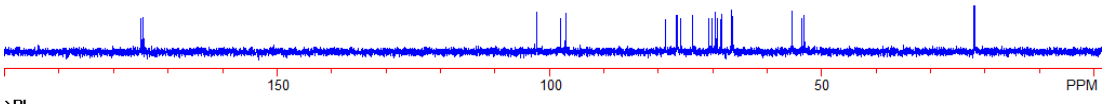
Chemical Formula: $C_{23}H_{38}N_2O_{23}S_2$
Exact Mass: 774.1307
Molecular Weight: 774.6774

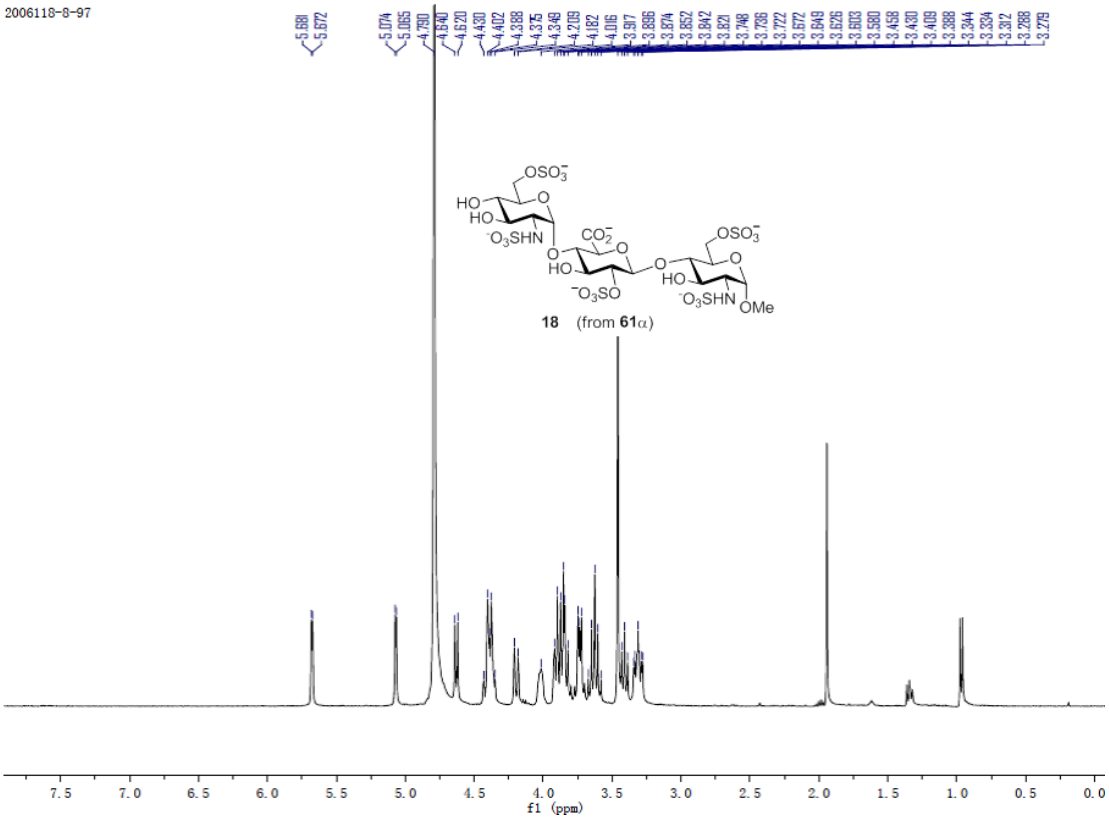




17

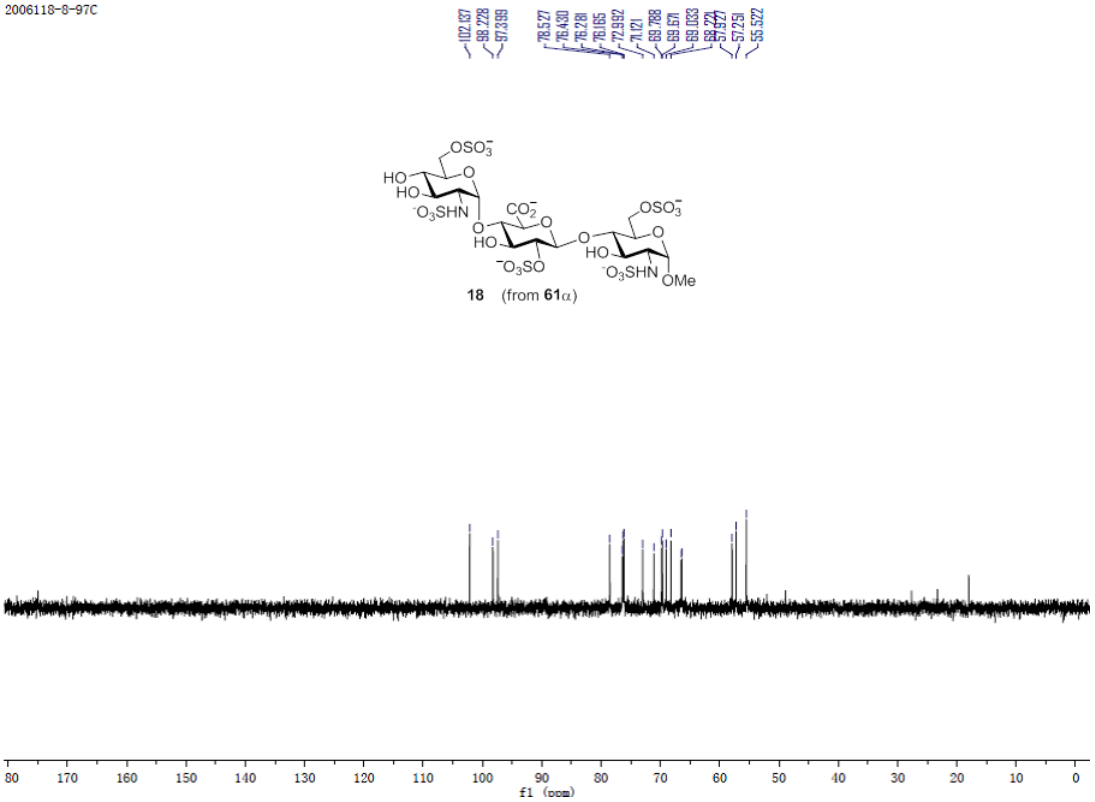
Chemical Formula: $C_{23}H_{38}N_2O_{23}S_2$
Exact Mass: 774.1307
Molecular Weight: 774.6774



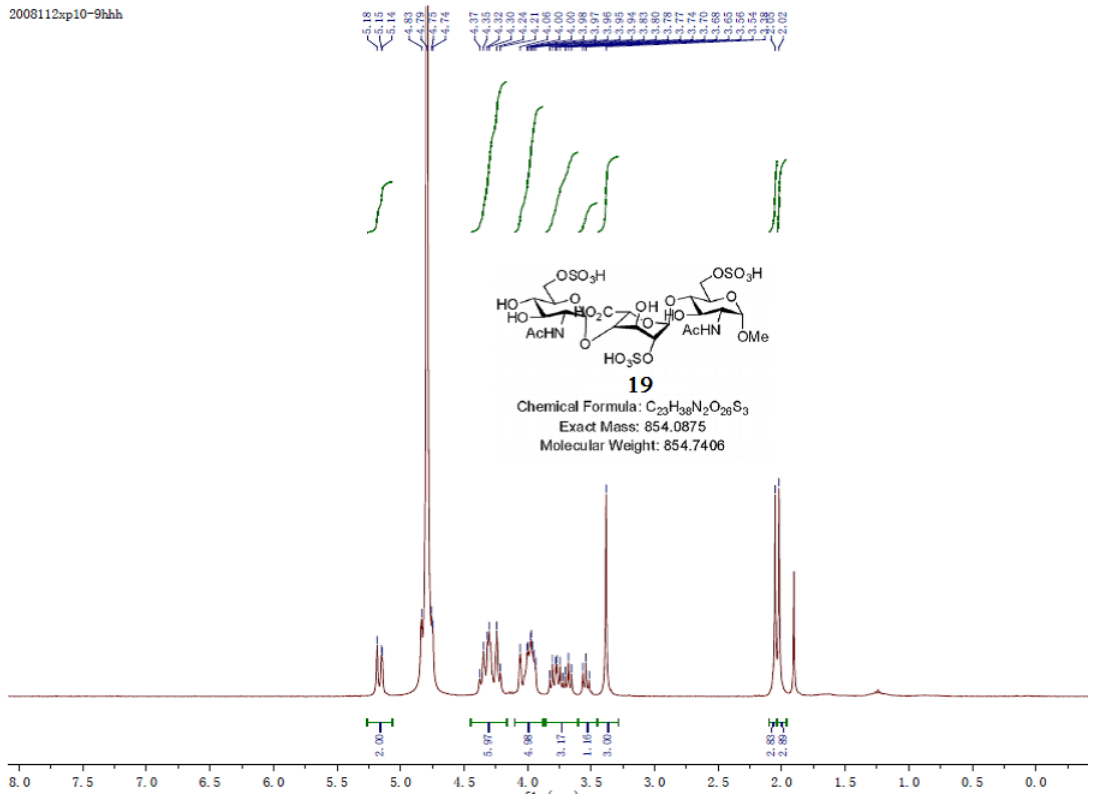


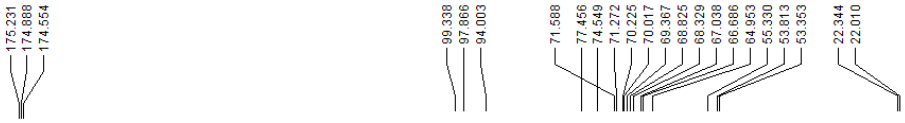
18 (from **61**α)

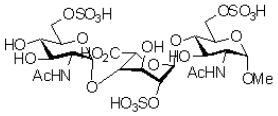
2006118-8-97C



2008112xp10-9hhh

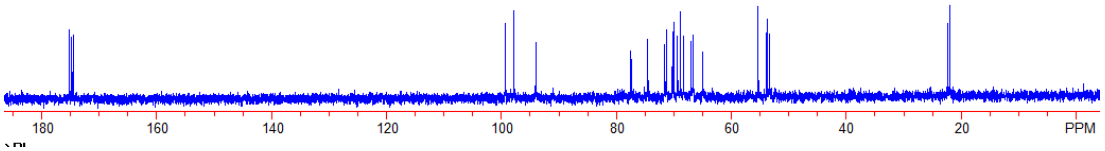


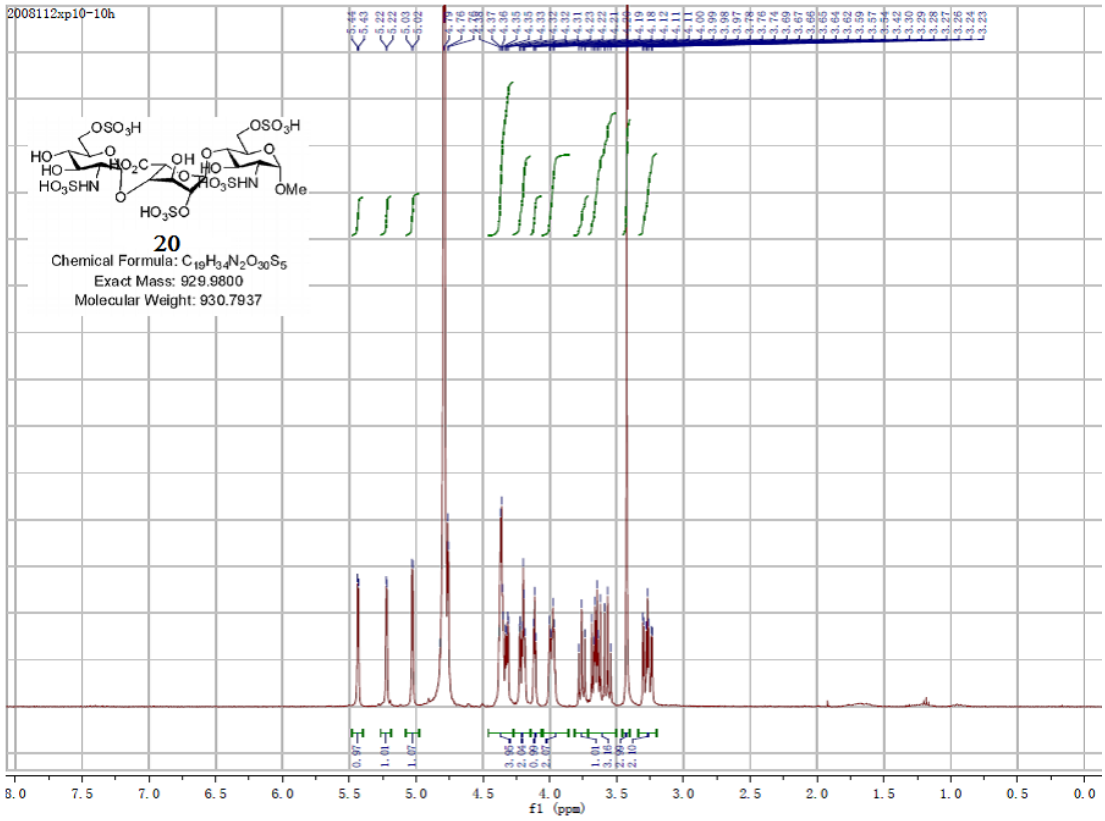




19

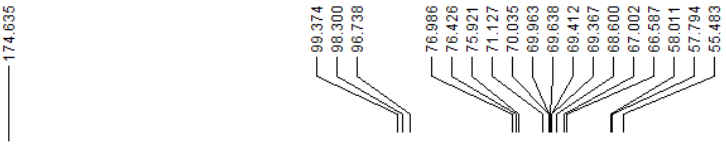
Chemical Formula: $C_{23}H_{38}N_2O_{26}S_3$
Exact Mass: 854.0875
Molecular Weight: 854.7406

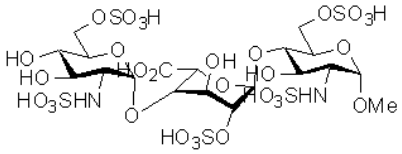




20

Chemical Formula: $C_{19}H_{34}N_2O_{30}S_5$
Exact Mass: 929.9800
Molecular Weight: 930.7937



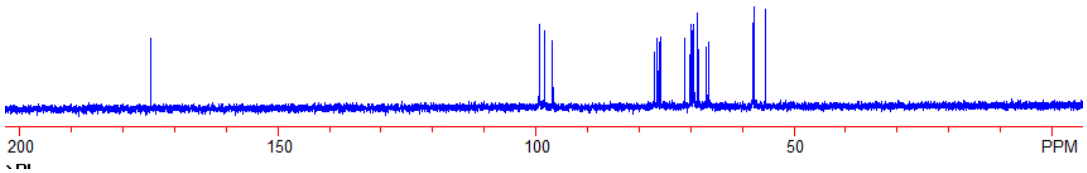


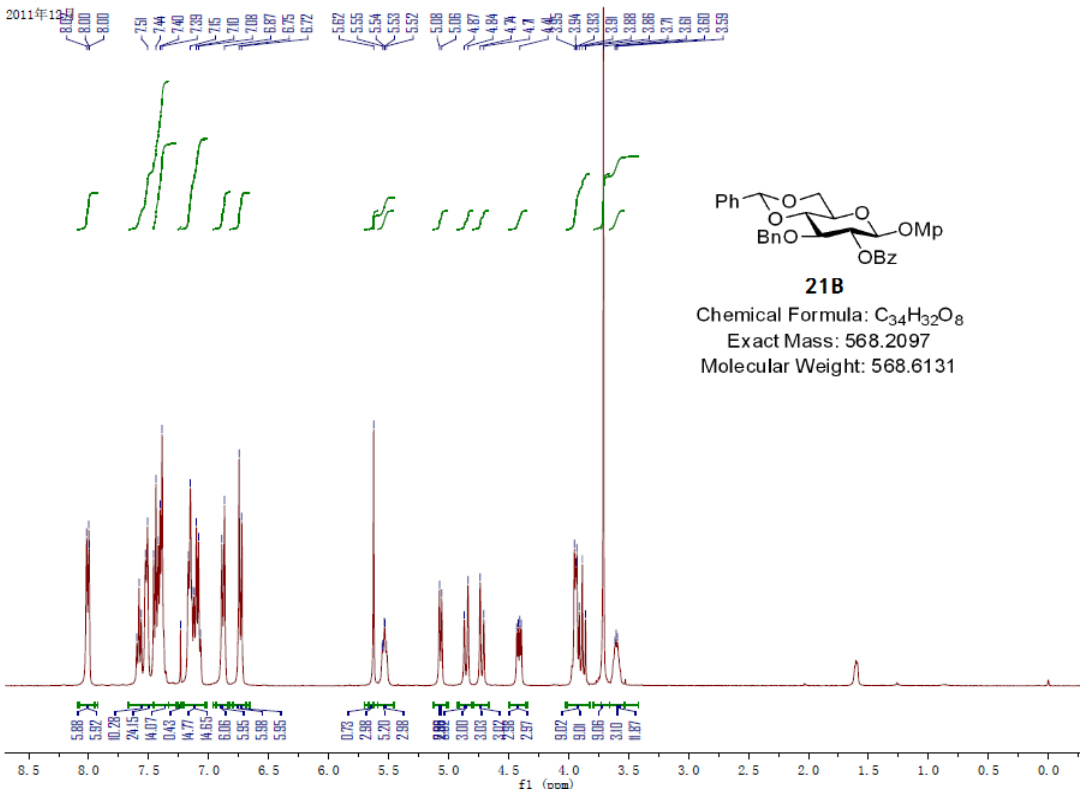
20

Chemical Formula: $C_{19}H_{34}N_2O_{30}S_5$

Exact Mass: 929.9800

Molecular Weight: 930.7937



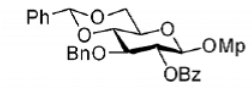


21B

Chemical Formula: $C_{34}H_{32}O_8$

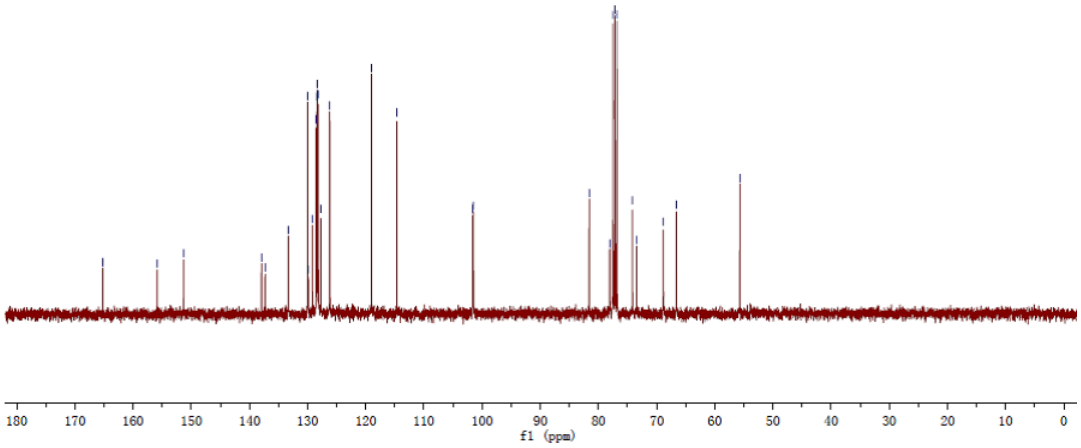
Exact Mass: 568.2097

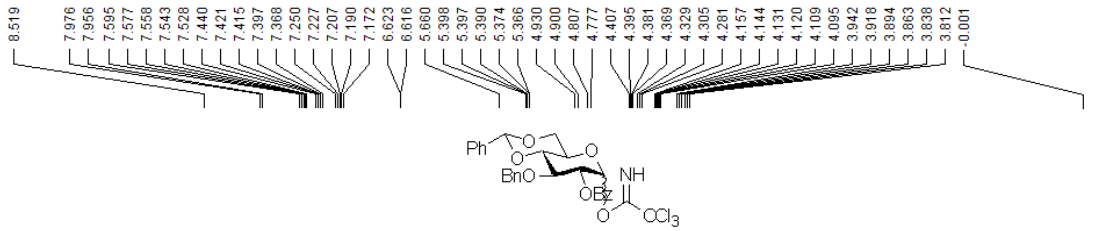
Molecular Weight: 568.6131



21B

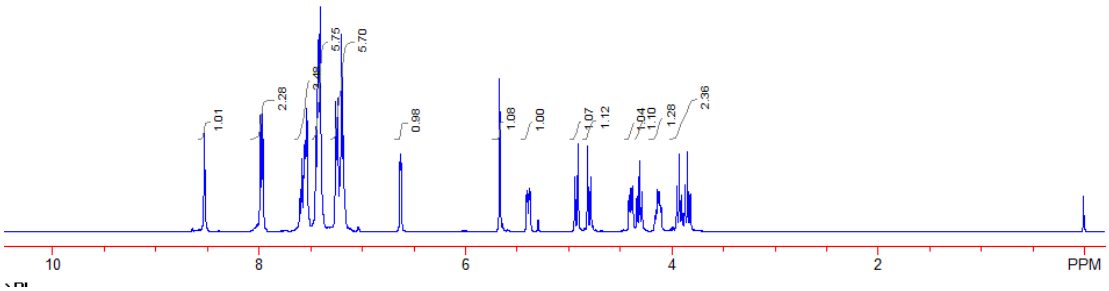
Chemical Formula: $C_{34}H_{32}O_8$
Exact Mass: 568.2097
Molecular Weight: 568.6131

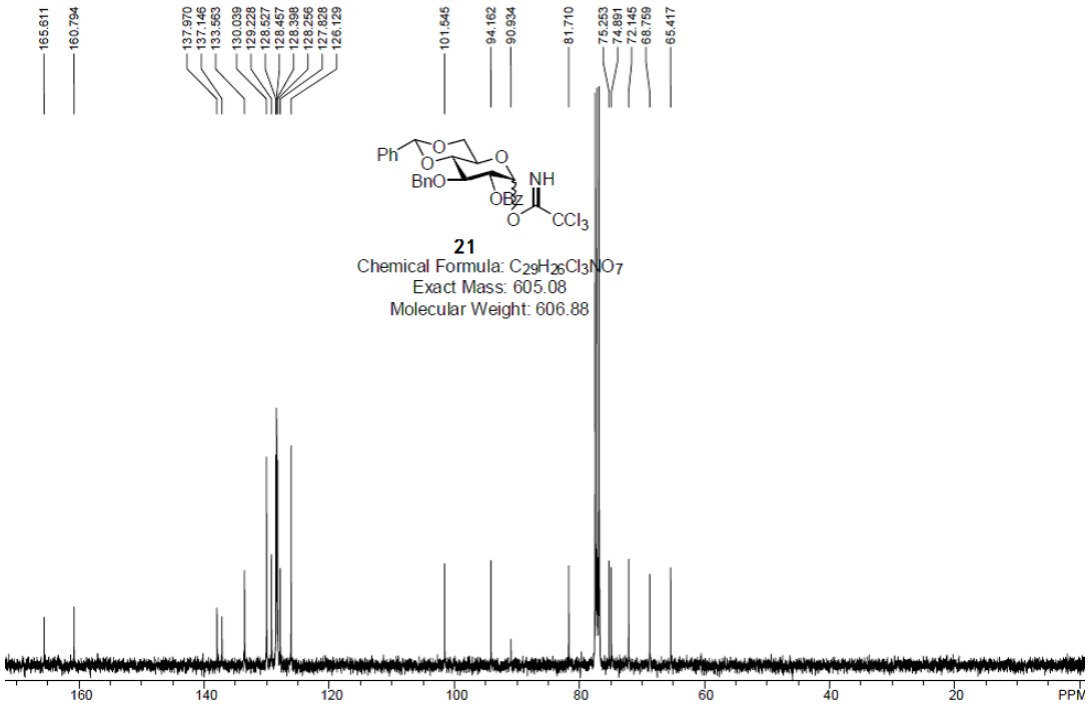


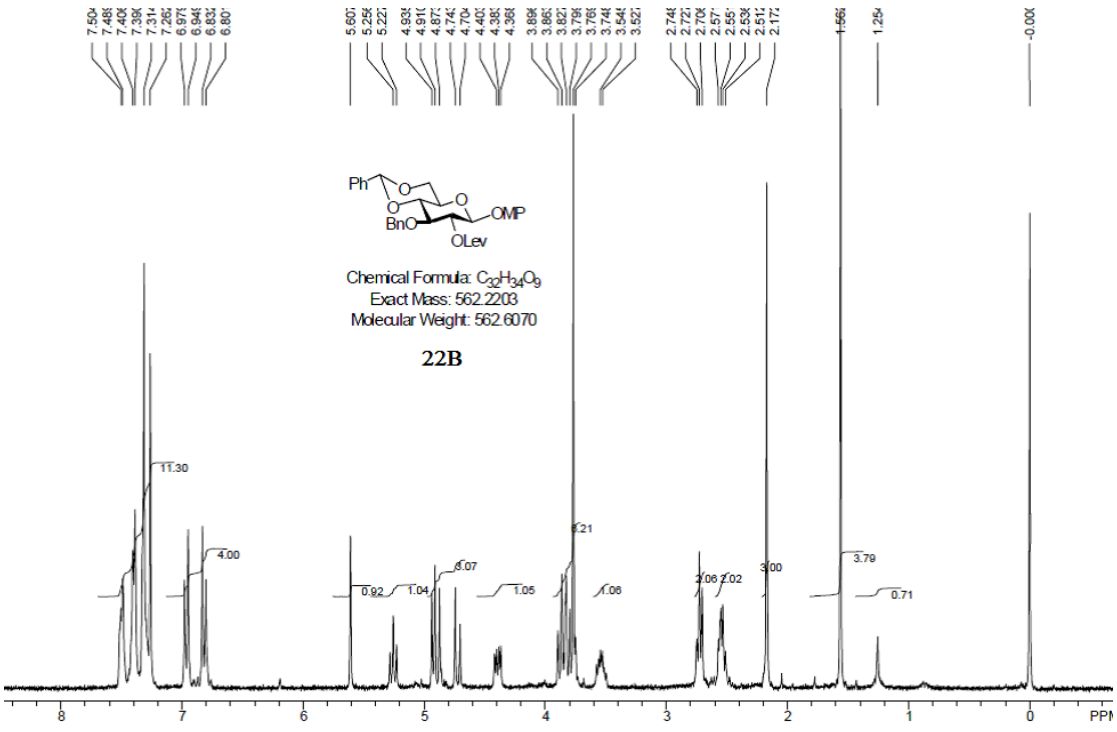


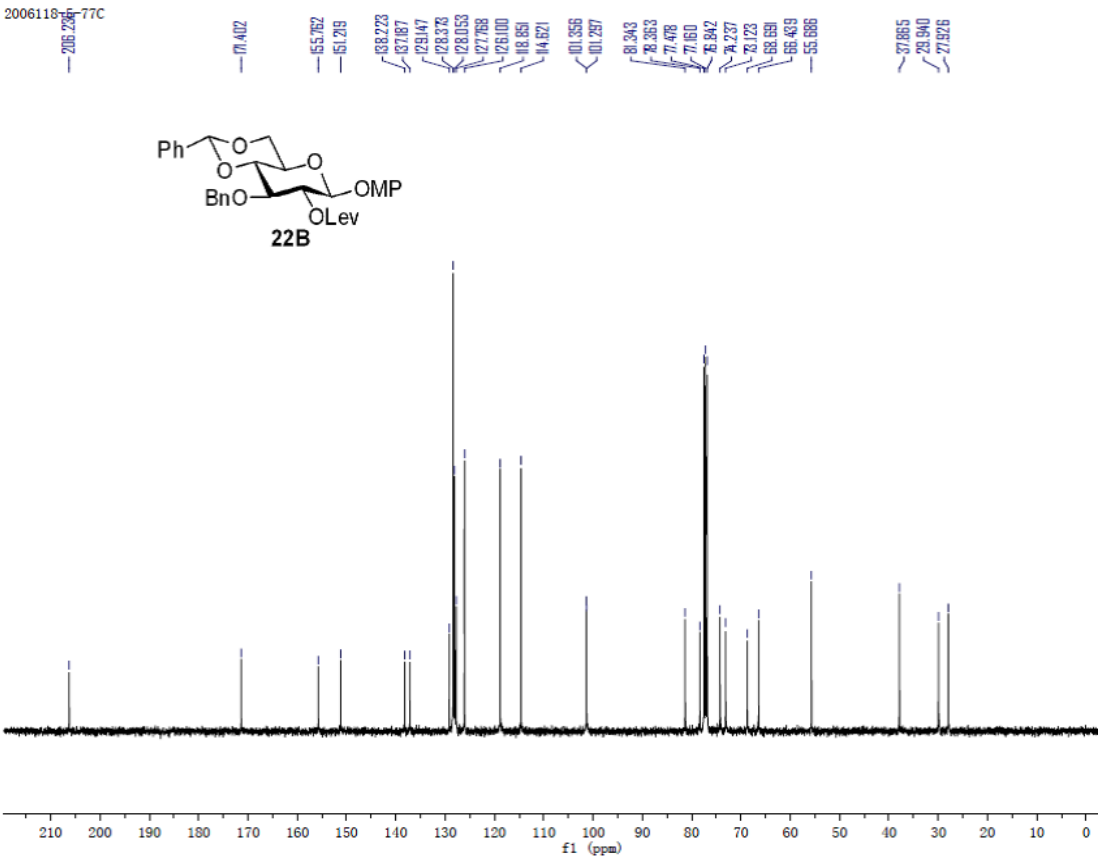
21

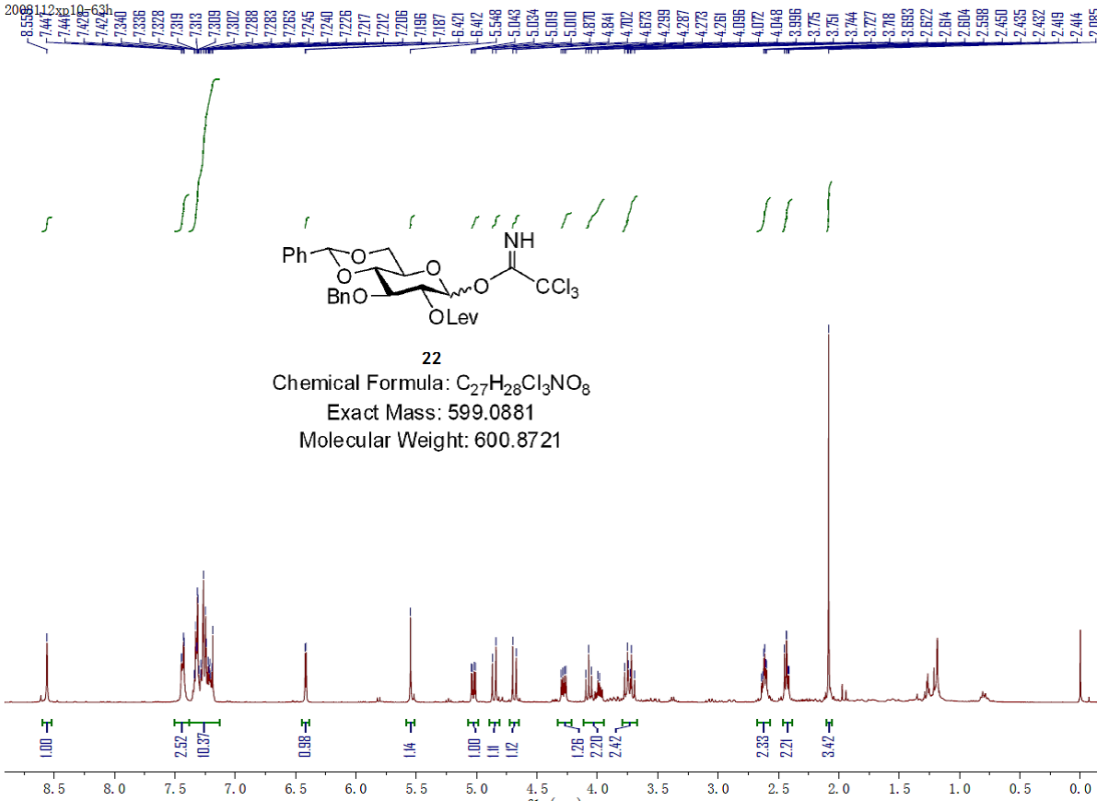
Chemical Formula: $C_{29}H_{26}Cl_3NO_7$
Exact Mass: 605.08
Molecular Weight: 606.88




165.611
160.794
137.970
137.146
133.563
130.039
129.228
128.527
128.457
128.398
128.256
127.828
126.129
101.545
94.162
90.934
81.710
75.253
74.891
72.145
68.759
65.417
Ph
BnO
OBz
NH
CCl3
21
Chemical Formula: C29H26Cl3NO7
Exact Mass: 605.08
Molecular Weight: 606.88
160
140
120
100
80
60
40
20
PPM


Ph
BnO
OMP
OLev
Chemical Formula: C32H34O9
Exact Mass: 562.2203
Molecular Weight: 562.6070
22B
11.30
4.00
0.92
1.04
3.07
1.05
6.21
1.06
2.06
2.02
3.00
3.79
0.71
8
7
6
5
4
3
2
1
0
PPM



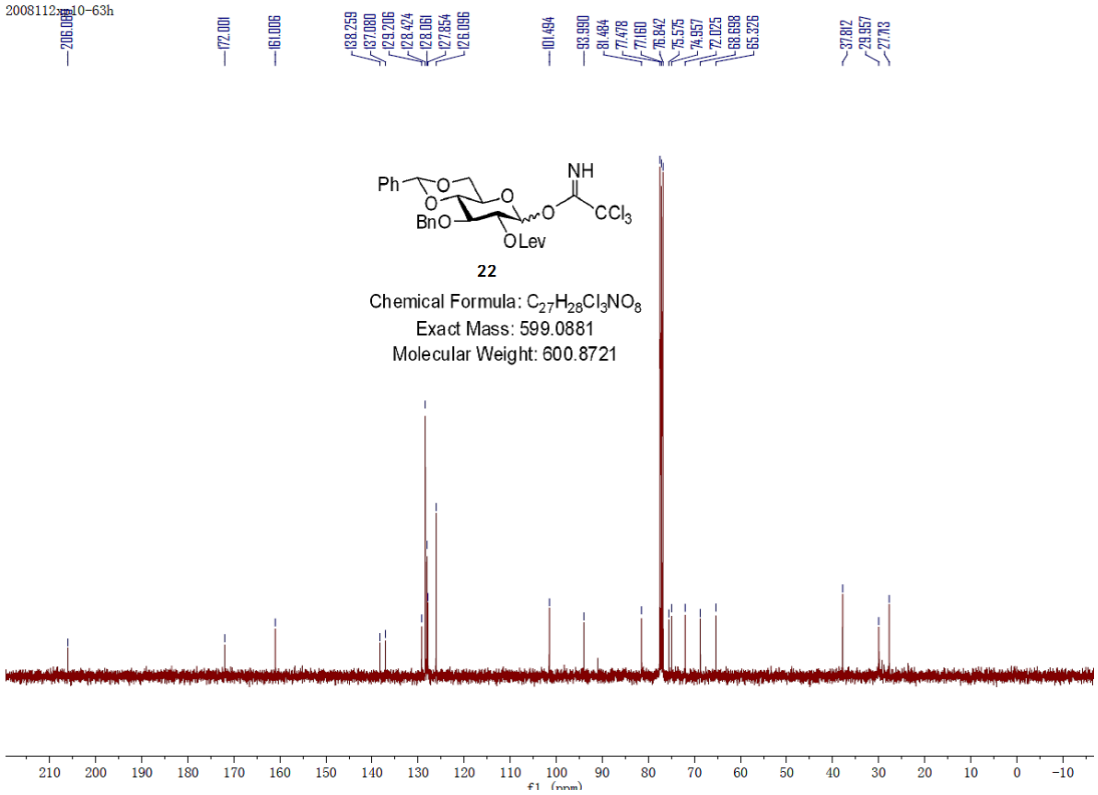


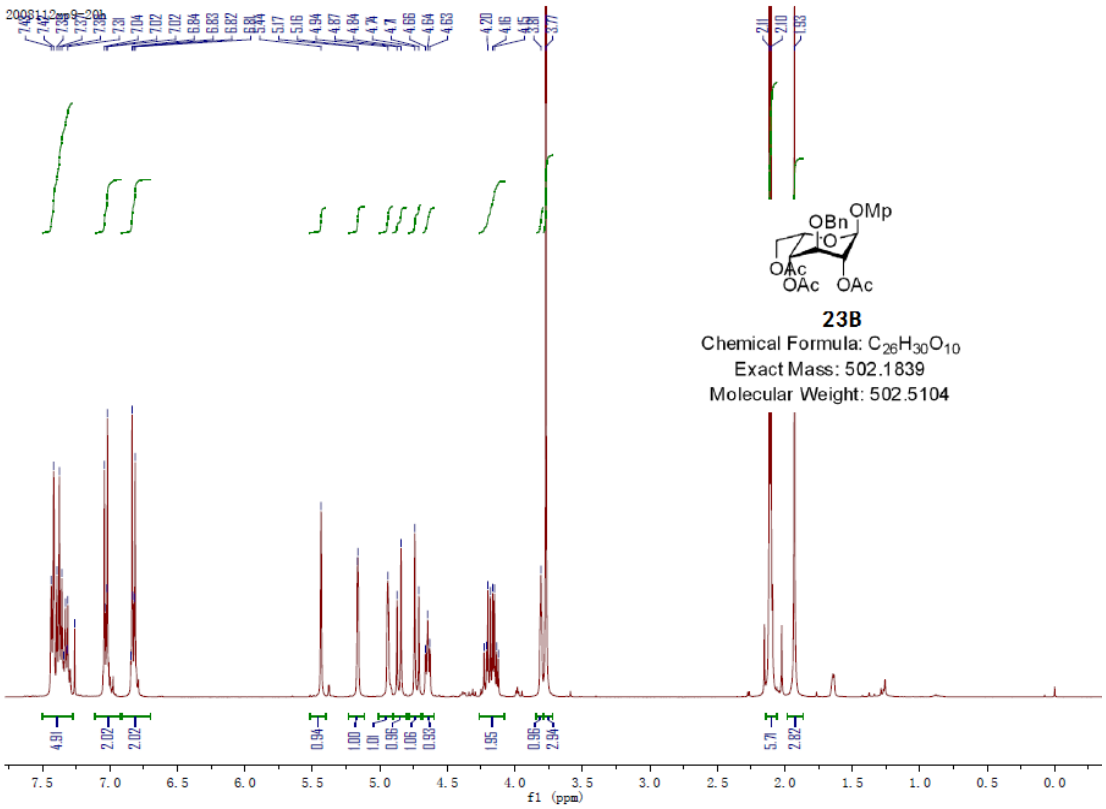
22

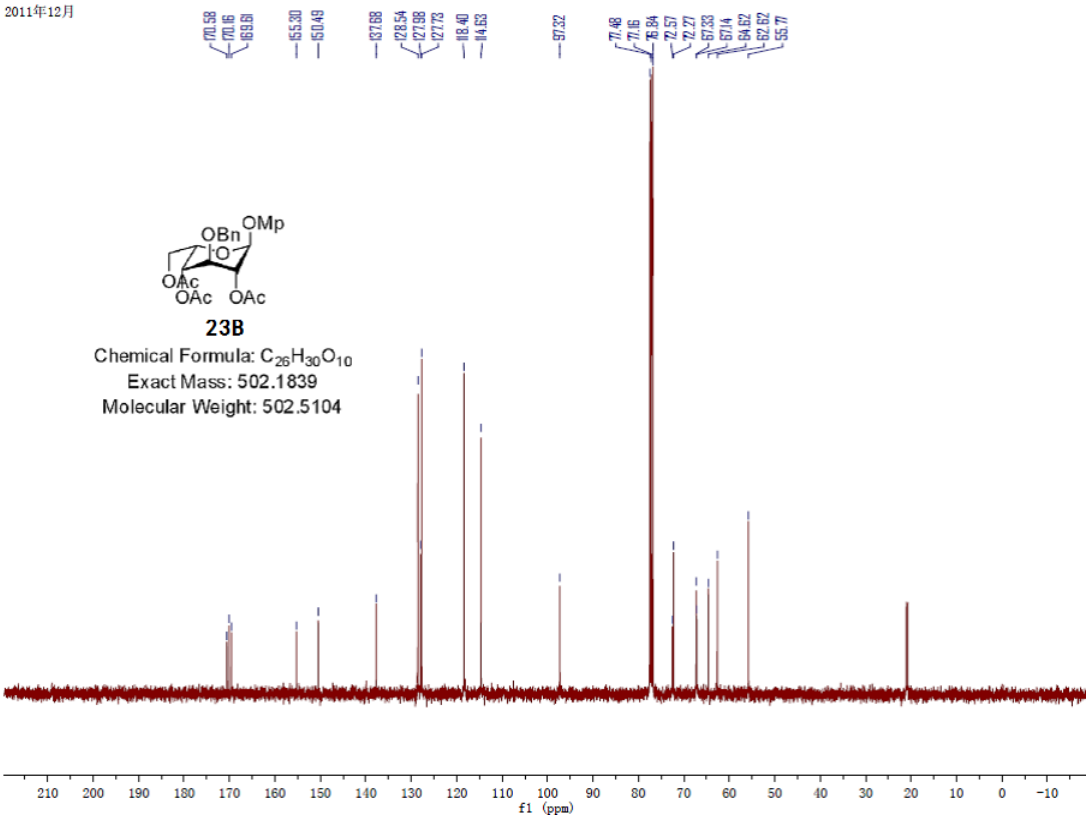
Chemical Formula: $C_{27}H_{28}Cl_3NO_8$

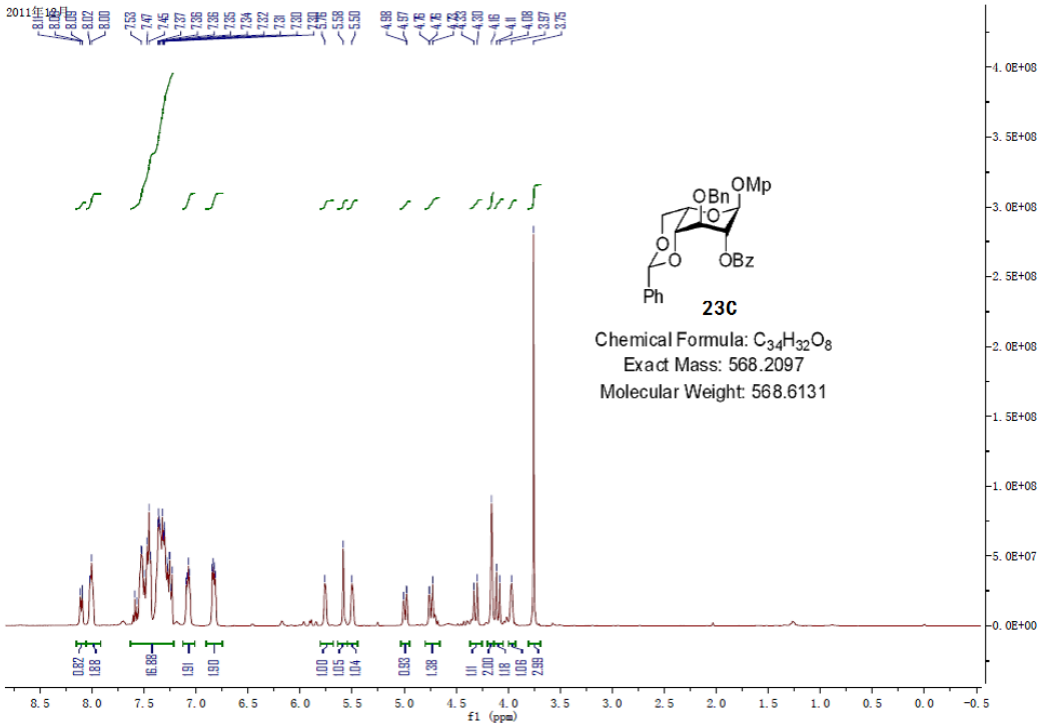
Exact Mass: 599.0881

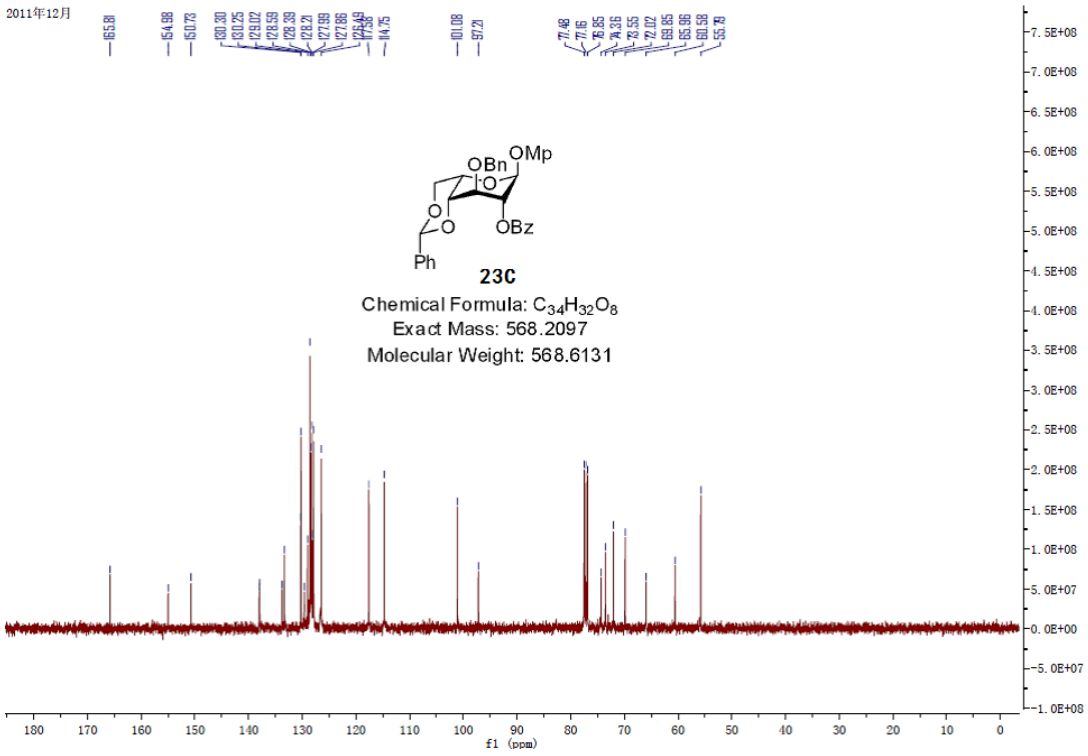
Molecular Weight: 600.8721

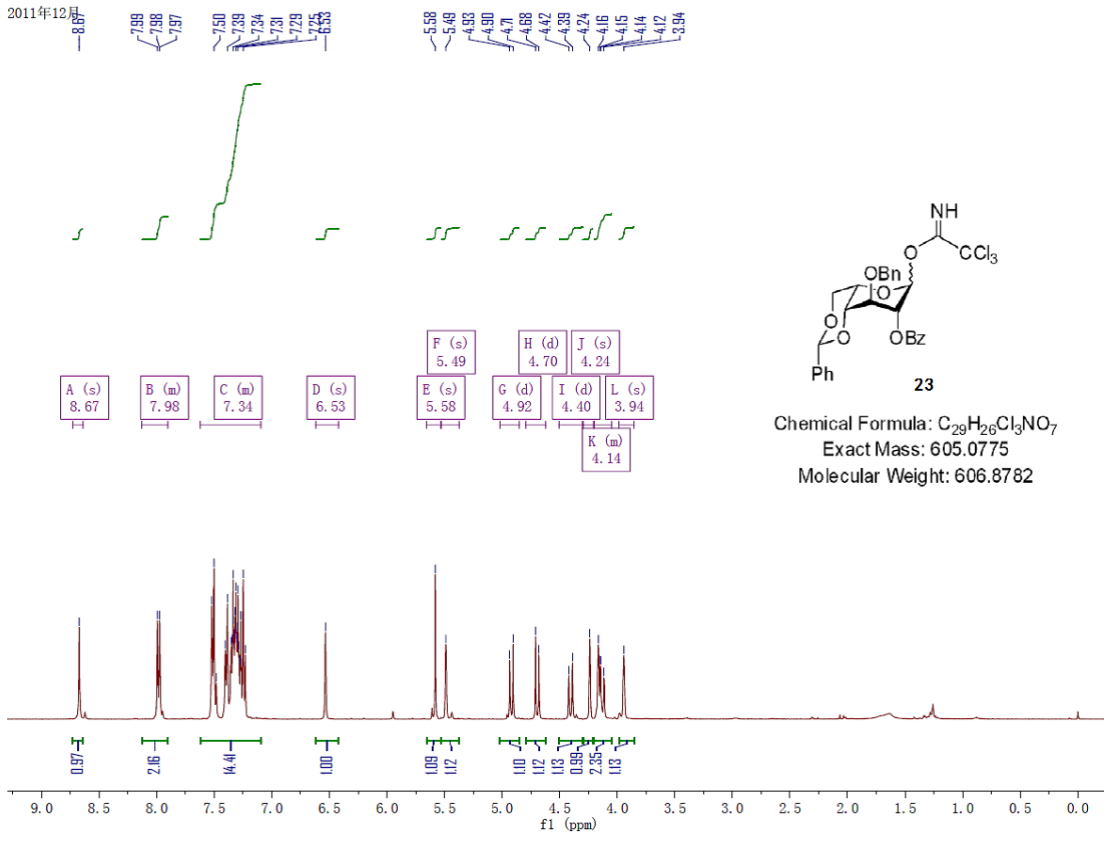

2008112xm10-63h
172.001
161.006
138.259
137.080
129.206
128.424
128.061
127.854
126.096
101.494
93.990
81.484
77.478
77.160
76.842
75.575
74.957
72.025
68.858
65.326
37.812
29.957
27.713
Ph
O
O
O
BnO
OLev
NH
O
CCl3
22
Chemical Formula: C27H28Cl3NO8
Exact Mass: 599.0881
Molecular Weight: 600.8721
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

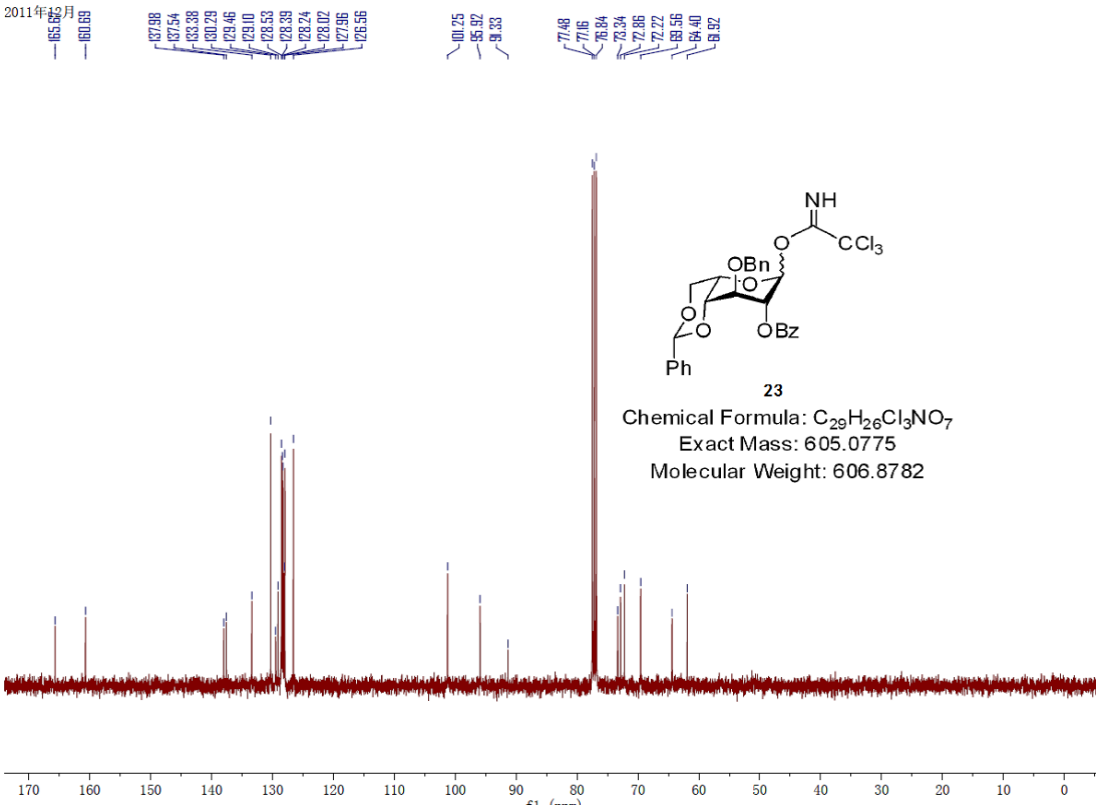

7.44
7.29
7.27
7.26
7.23
7.04
7.02
7.02
6.84
6.83
6.82
6.83
5.44
5.17
5.16
4.94
4.87
4.84
4.78
4.77
4.66
4.64
4.63
4.20
4.16
4.15
3.88
3.77
2.11
2.10
1.93
OBn
OMp
O
OAc
OAc
OAc
23B
Chemical Formula: C26H30O10
Exact Mass: 502.1839
Molecular Weight: 502.5104
4.91
2.02
2.02
0.94
1.00
1.01
0.98
1.06
0.92
1.95
0.96
2.94
5.71
2.82
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)

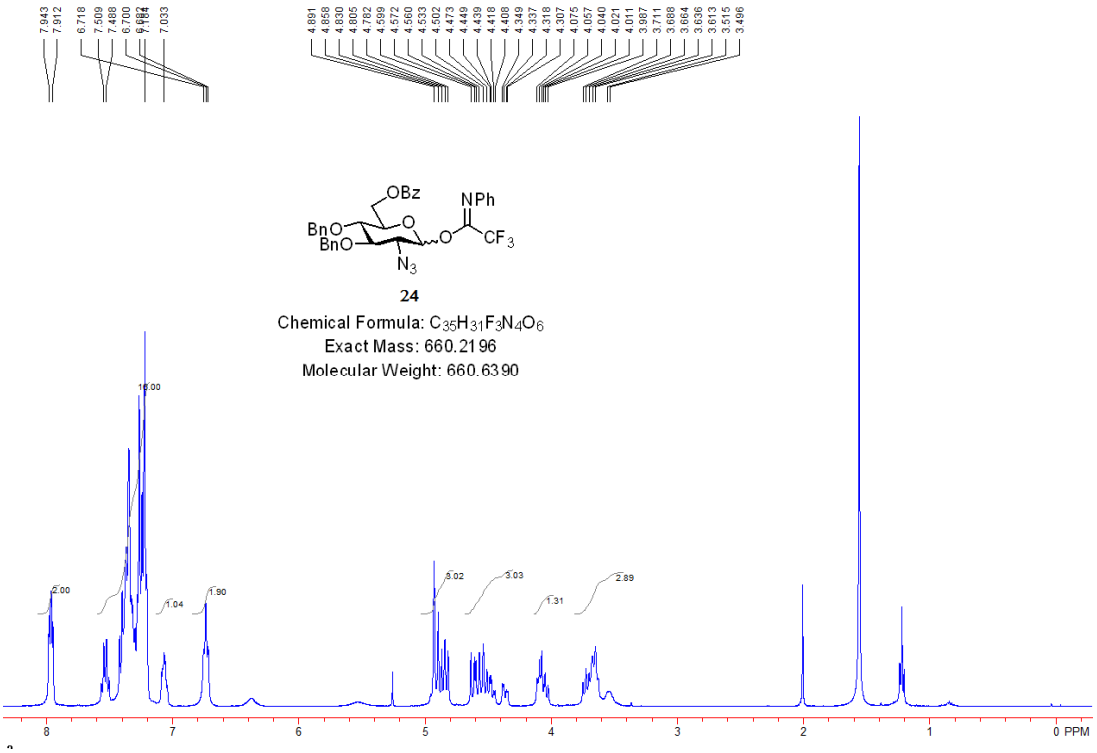

2011年12月
OBn
OMp
OAc
OAc
OAc
23B
Chemical Formula: C26H30O10
Exact Mass: 502.1839
Molecular Weight: 502.5104
f1 (ppm)

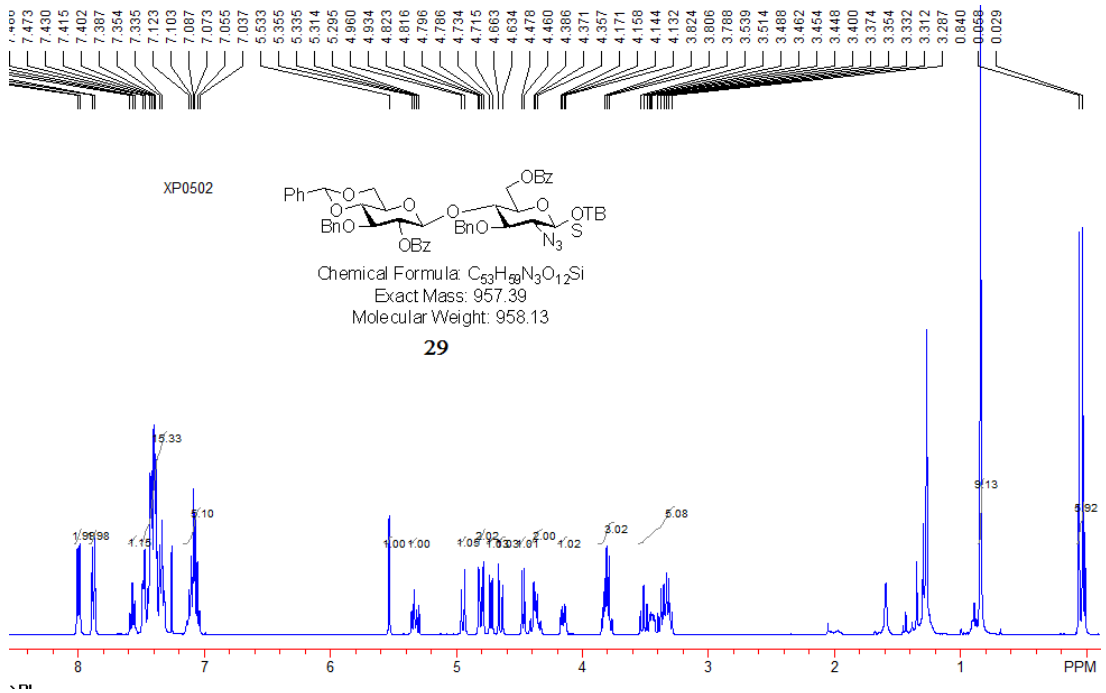

OBn
OMp
O
O
OBz
Ph
23C
Chemical Formula: C34H32O8
Exact Mass: 568.2097
Molecular Weight: 568.6131
f1 (ppm)

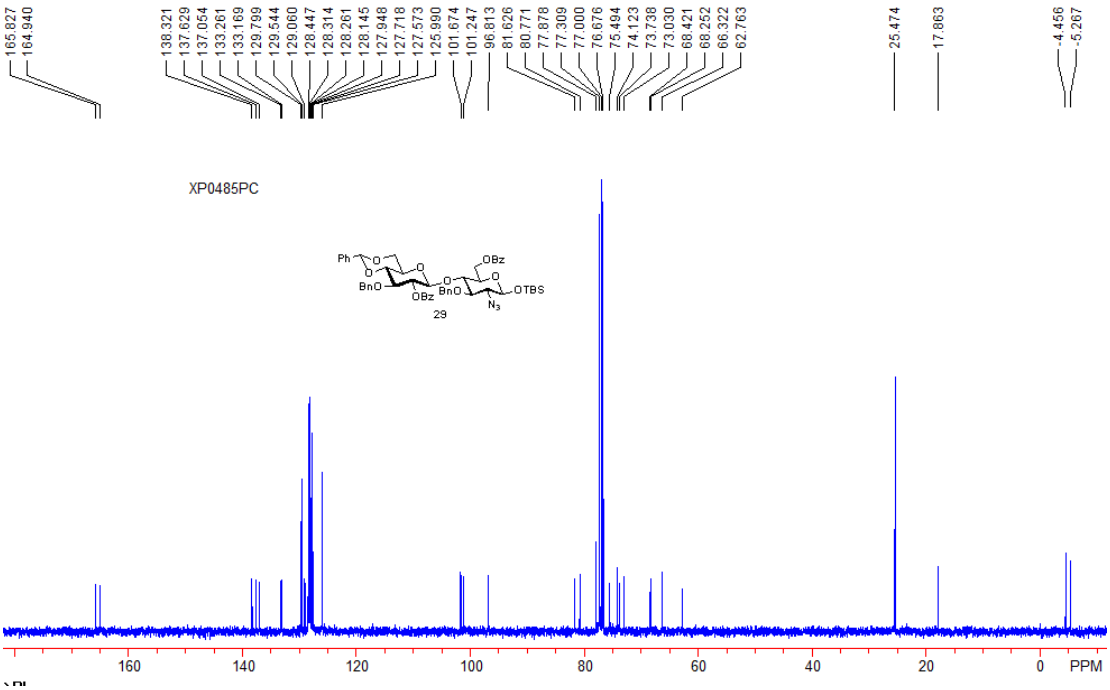

2011年12月
OBn
OMp
OBz
Ph
23C
Chemical Formula: C34H32O8
Exact Mass: 568.2097
Molecular Weight: 568.6131
f1 (ppm)

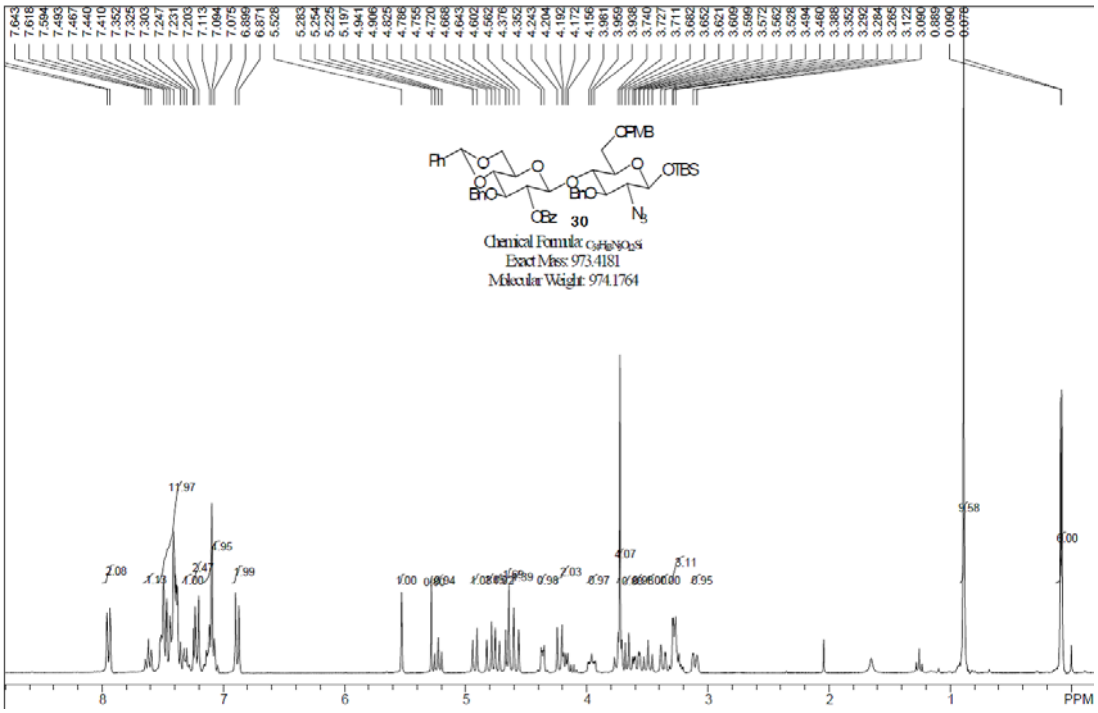

2011年12月
A (s) 8.67
B (m) 7.98
C (m) 7.34
D (s) 6.53
E (s) 5.58
F (s) 5.49
G (d) 4.92
H (d) 4.70
I (d) 4.40
J (s) 4.24
K (m) 4.14
L (s) 3.94
NH
CCl3
OBn
OBz
Ph
23
Chemical Formula: C29H26Cl3NO7
Exact Mass: 605.0775
Molecular Weight: 606.8782
f1 (ppm)


2011年12月
165.66
160.69
137.98
137.54
133.38
130.29
129.46
129.10
128.53
128.39
128.24
128.02
127.96
126.56
101.25
95.92
9.33
77.48
77.16
76.84
73.34
72.88
72.22
69.56
64.40
9.92
NH
CCl3
O
OBn
O
O
O
OBz
Ph
23
Chemical Formula: C29H26Cl3NO7
Exact Mass: 605.0775
Molecular Weight: 606.8782
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

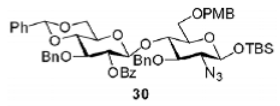

7.943
7.912
6.718
7.509
7.488
6.700
7.184
7.033
4.891
4.858
4.830
4.805
4.782
4.599
4.572
4.560
4.533
4.502
4.473
4.449
4.439
4.418
4.408
4.349
4.337
4.318
4.307
4.075
4.057
4.040
4.021
4.011
3.987
3.711
3.688
3.664
3.636
3.613
3.515
3.496
OBz
NPh
BnO
BnO
O
O
CF3
N3
24
Chemical Formula: C35H31F3N4O6
Exact Mass: 660.2196
Molecular Weight: 660.6390
16.00
2.00
1.04
1.90
3.02
3.03
1.31
2.89
8
7
6
5
4
3
2
1
0 PPM

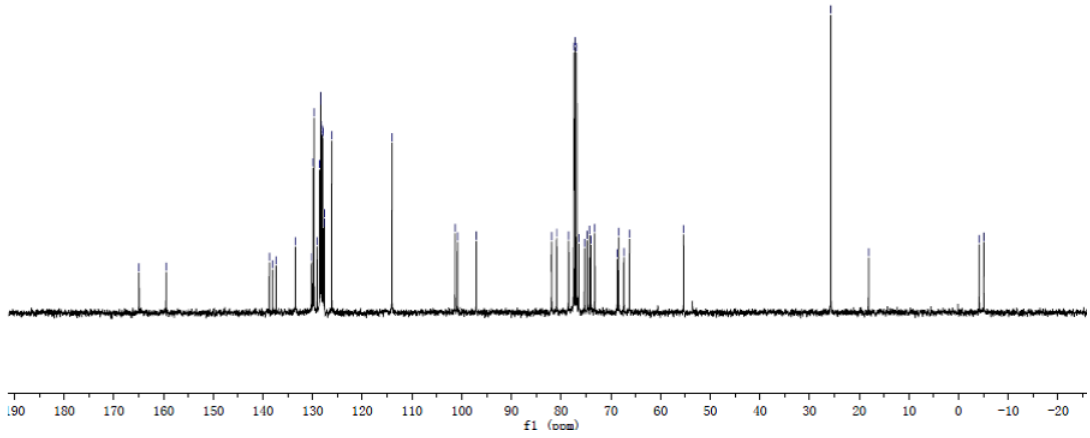

XP0502
Chemical Formula: $C_{53}H_{59}N_3O_{12}Si$
Exact Mass: 957.39
Molecular Weight: 958.13
29
PPM

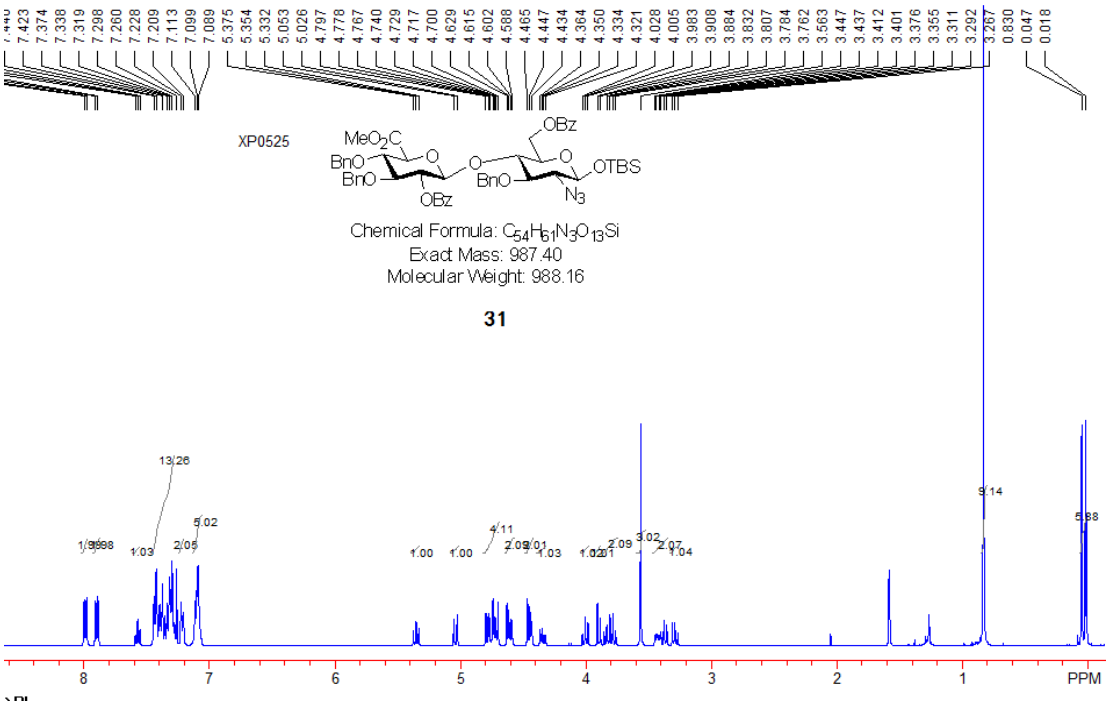

XP0485PC
29
PPM

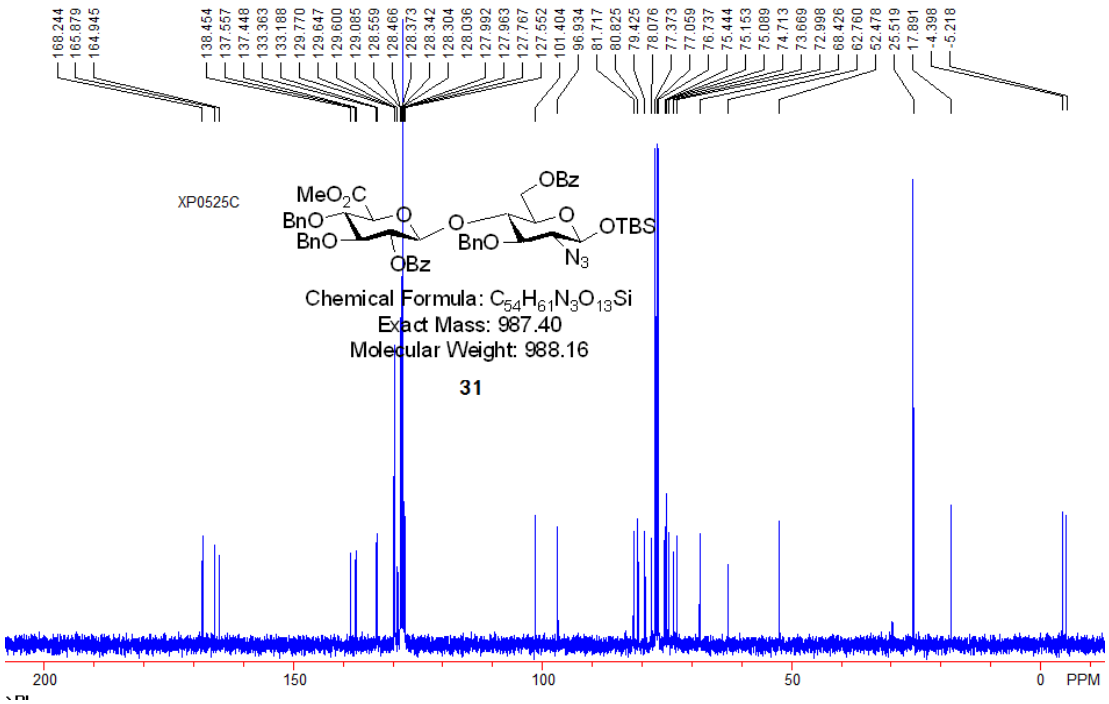

OPMB
Ph
OTBS
BnO
BnO
OBz
30
N_3
Chemical Formula: $C_{54}H_{63}N_3O_9Si$
Exact Mass: 973.4181
Molecular Weight: 974.1764
PPM

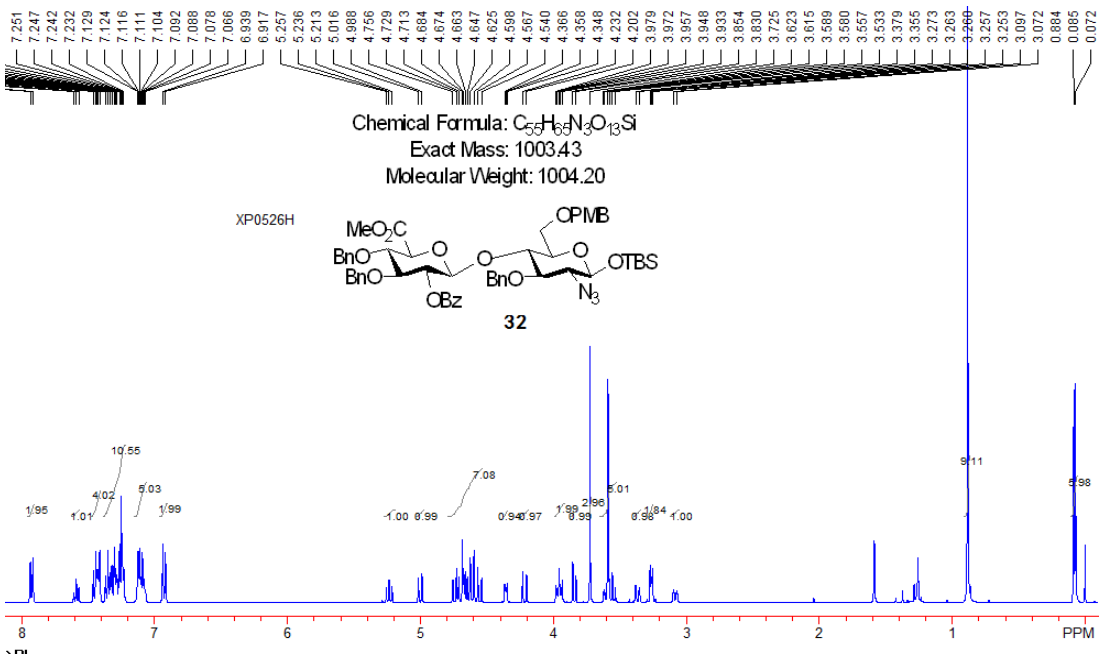

c-474[1]
Std carbon

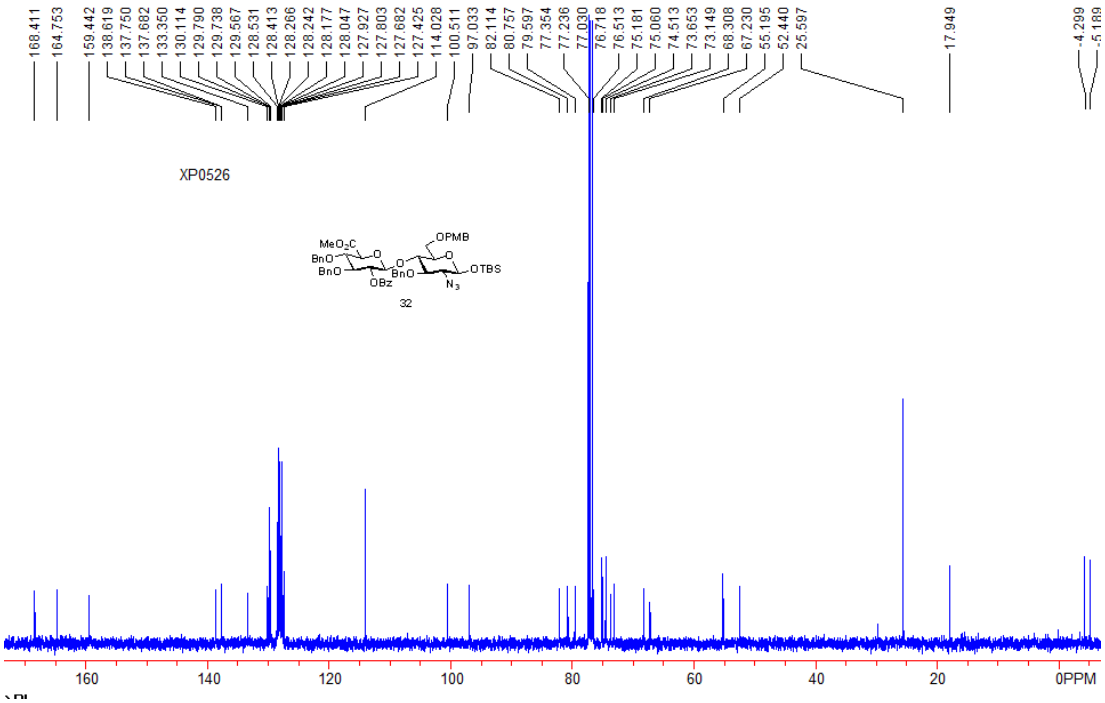

OPMB
Ph
OTBS
BnO
BnO
OBz
30
N_3

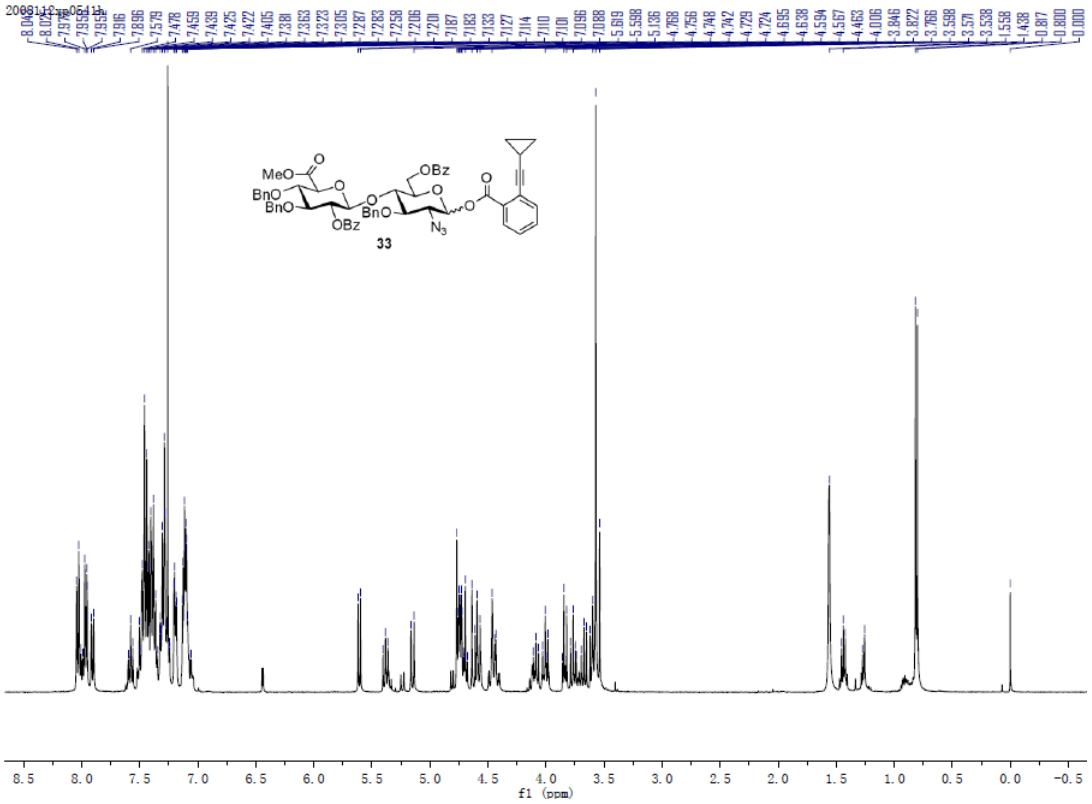

f1 (ppm)

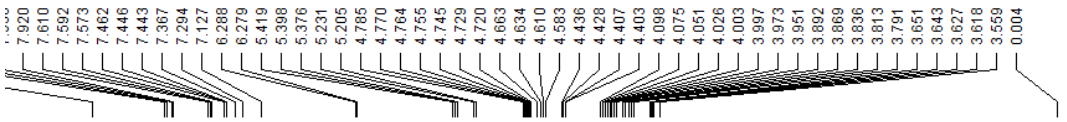

XP0525
Chemical Formula: C54H61N3O13Si
Exact Mass: 987.40
Molecular Weight: 988.16
31
PPM

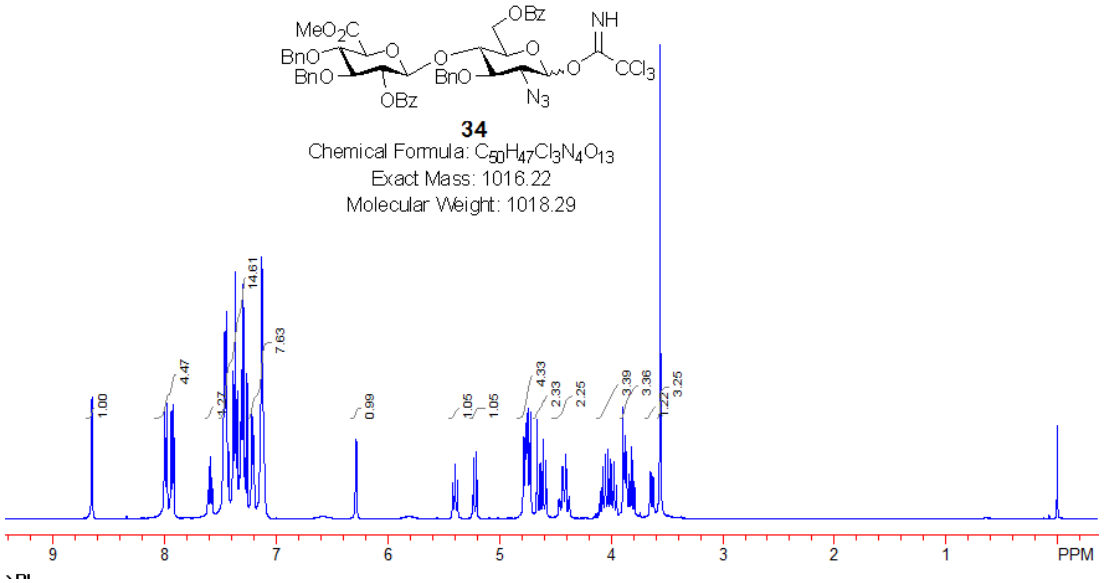

XP0525C
Chemical Formula: C54H61N3O13Si
Exact Mass: 987.40
Molecular Weight: 988.16
31
PPM

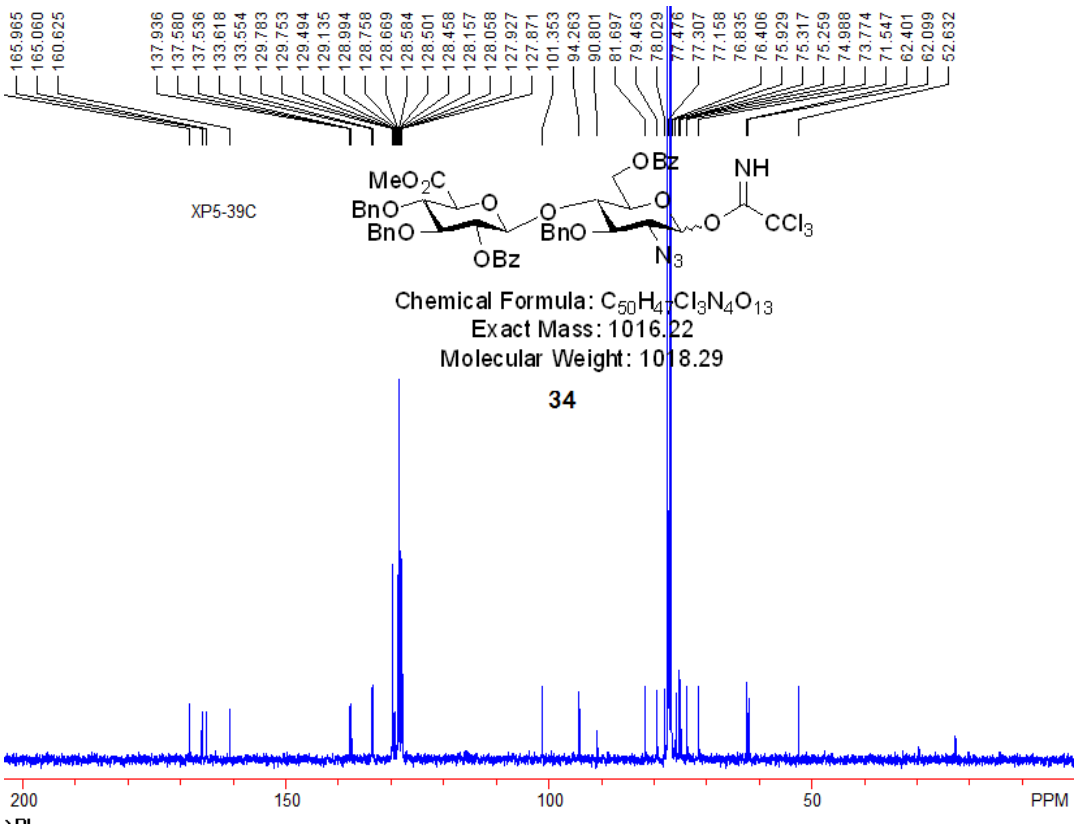

Chemical Formula: C55H65N3O13Si
Exact Mass: 1003.43
Molecular Weight: 1004.20
XP0526H
MeO2C
BnO
BnO
OBz
O
O
BnO
OPMB
O
OTBS
N3
32
PPM

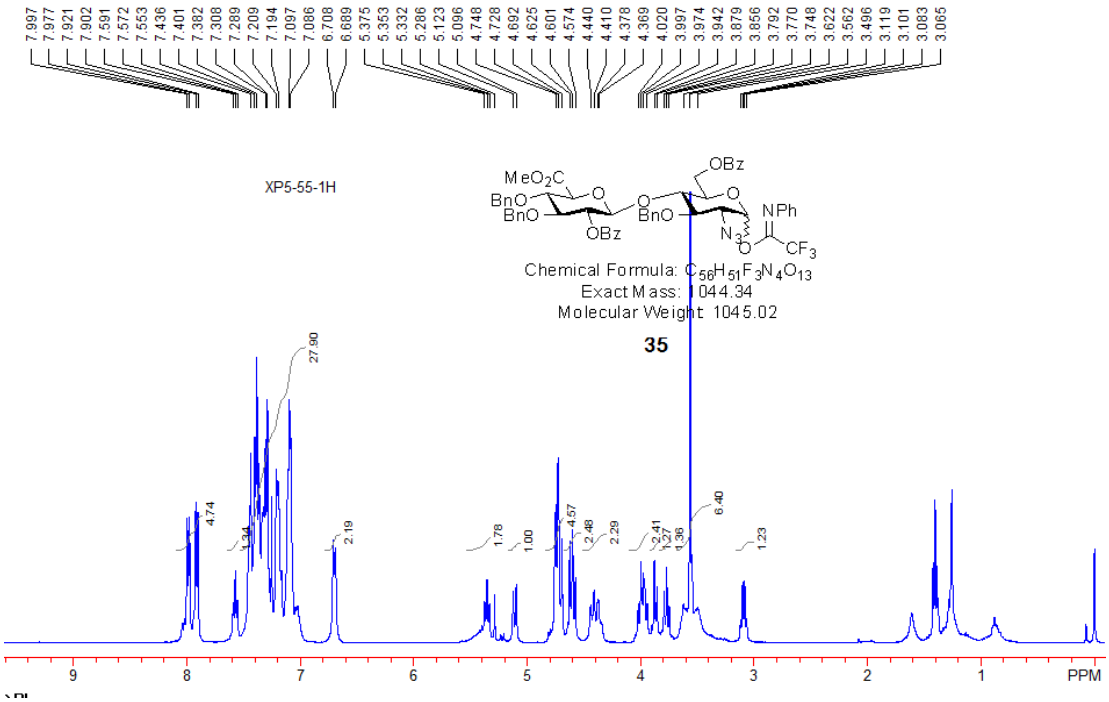

XP0526
MeO2C
BnO
BnO
OBz
O
O
BnO
OPMB
O
OTBS
N3
32
PPM

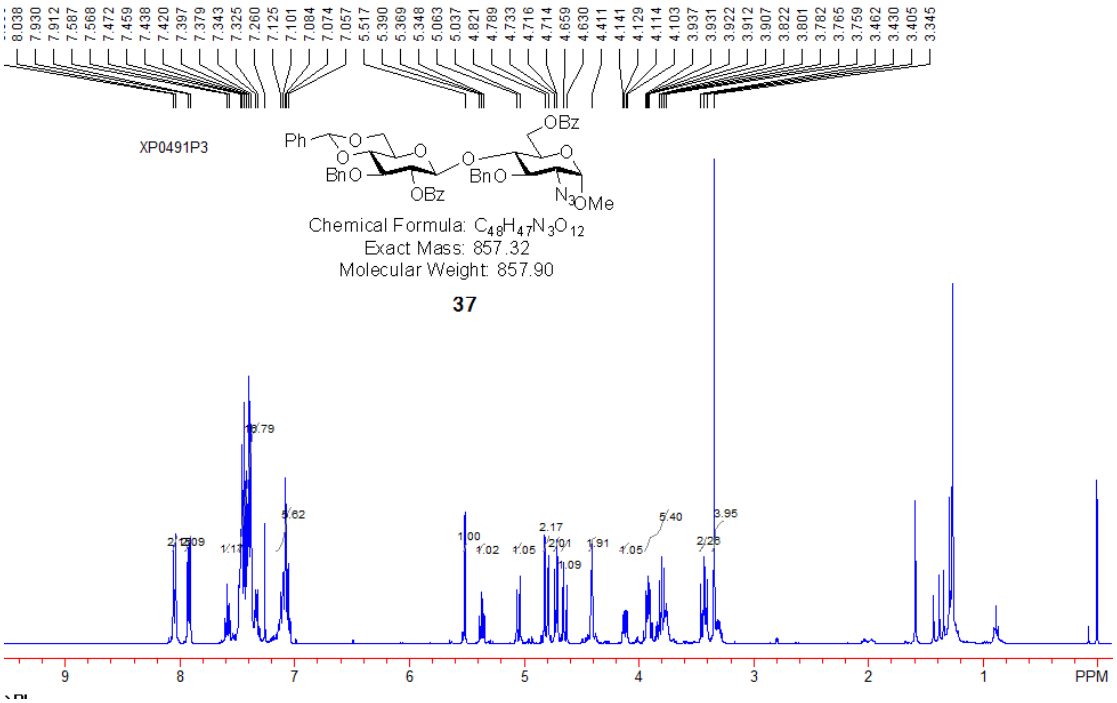

MeO
BnO
BnO
OBz
BnO
OBz
N3
33
f1 (ppm)

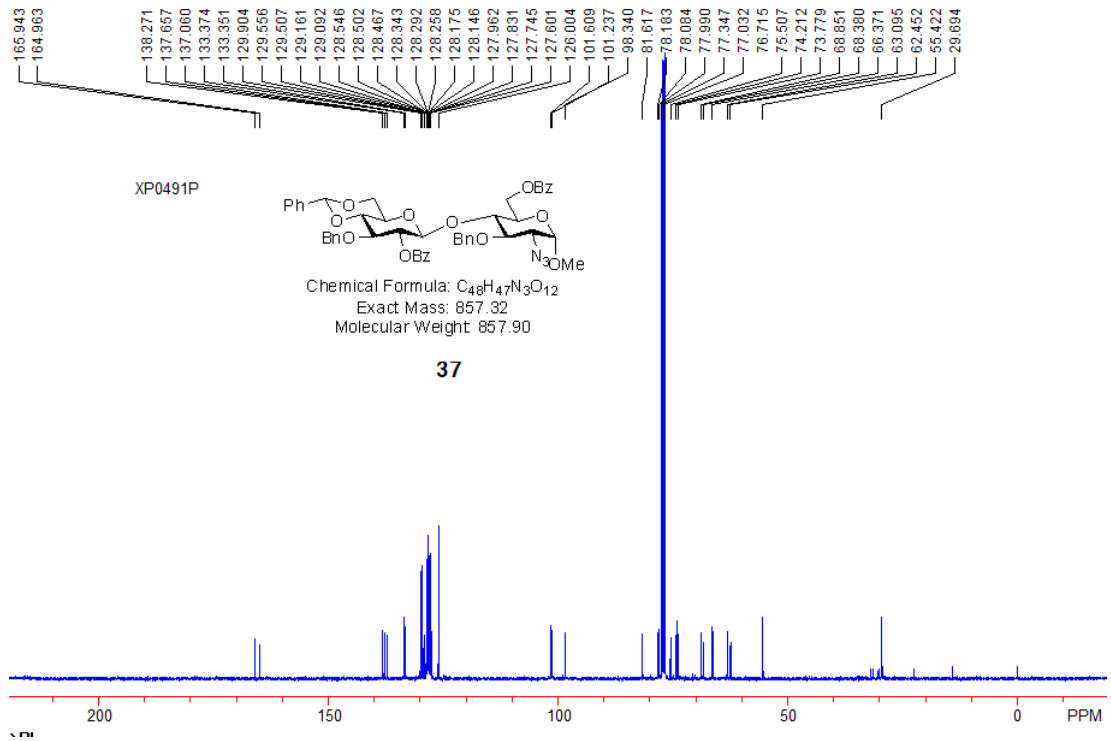


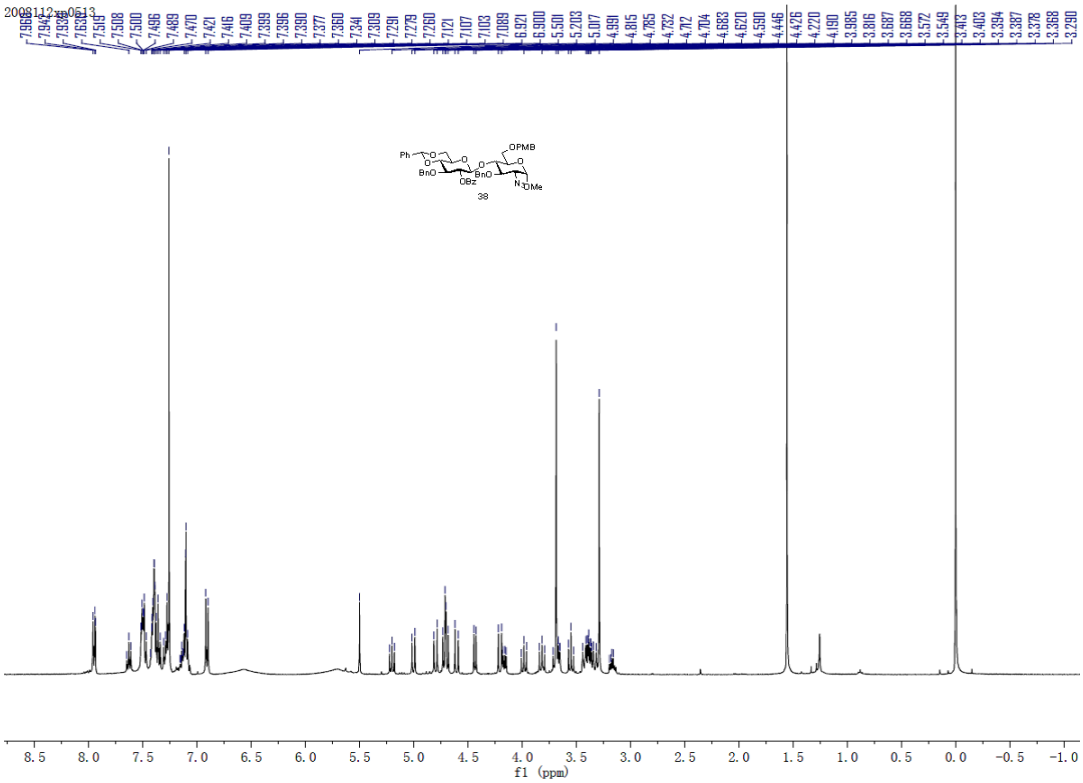

MeO2C
BnO
BnO
OBz
BnO
OBz
NH
CCl3
N3
34
Chemical Formula: C50H47Cl3N4O13
Exact Mass: 1016.22
Molecular Weight: 1018.29
PPM

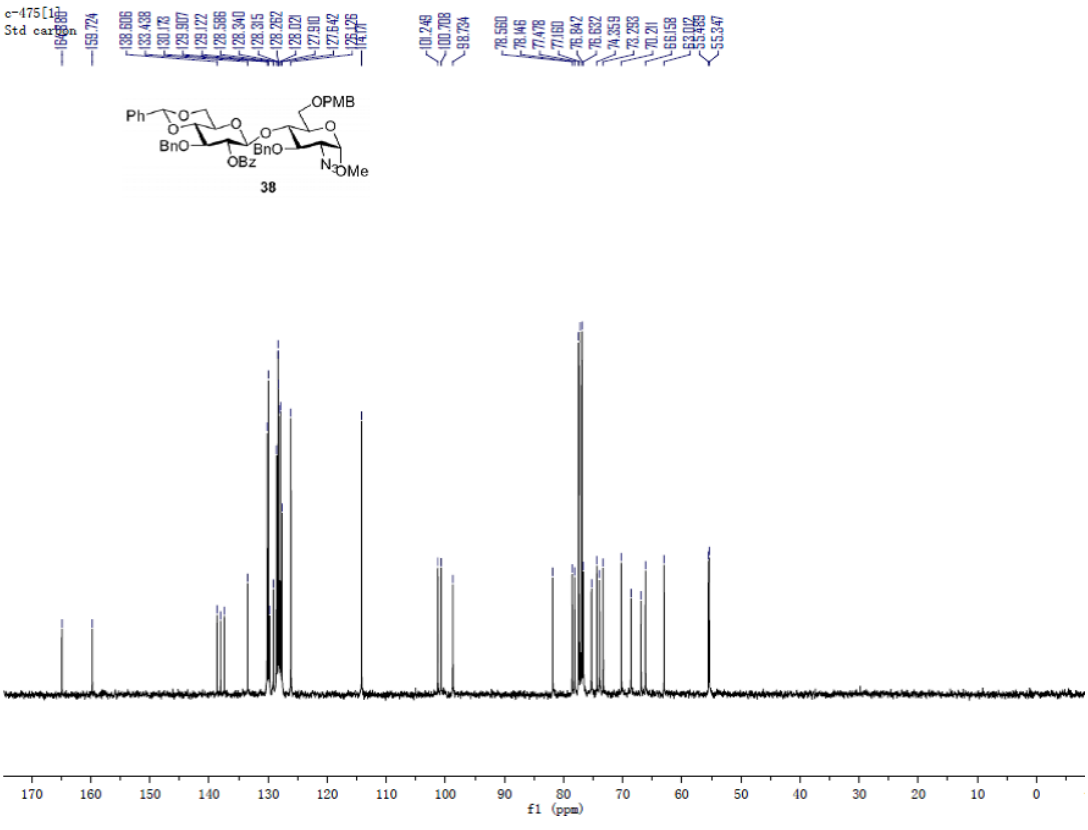

XP5-39C
Chemical Formula: C50H47Cl3N4O13
Exact Mass: 1016.22
Molecular Weight: 1018.29
34
PPM

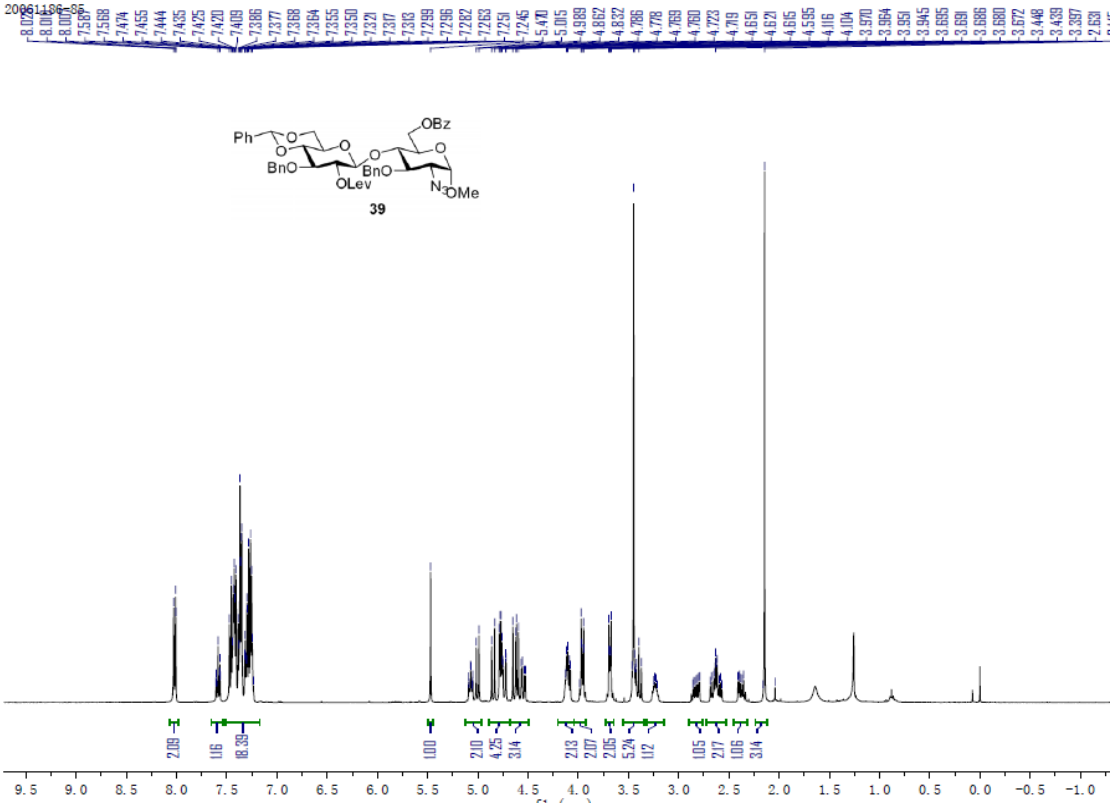

XP5-55-1H
Chemical Formula: C56H51F3N4O13
Exact Mass: 1044.34
Molecular Weight: 1045.02
35
PPM

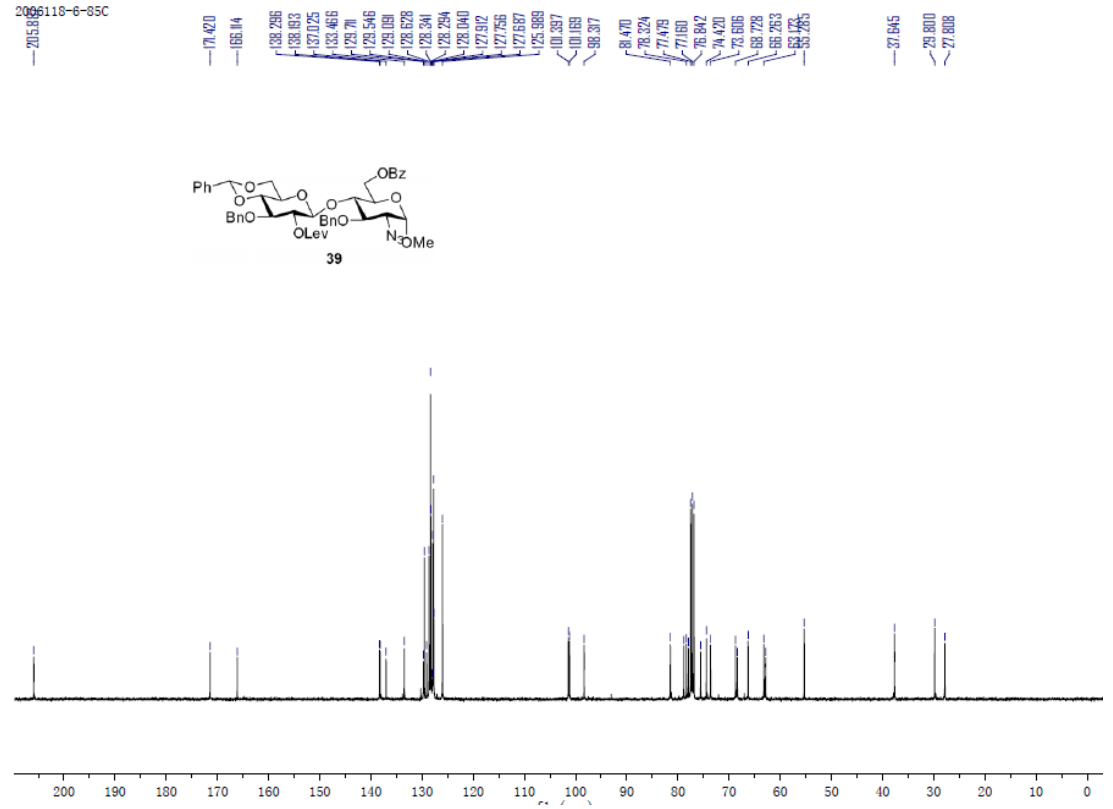

XP0491P3
Chemical Formula: C48H47N3O12
Exact Mass: 857.32
Molecular Weight: 857.90
37
PPM

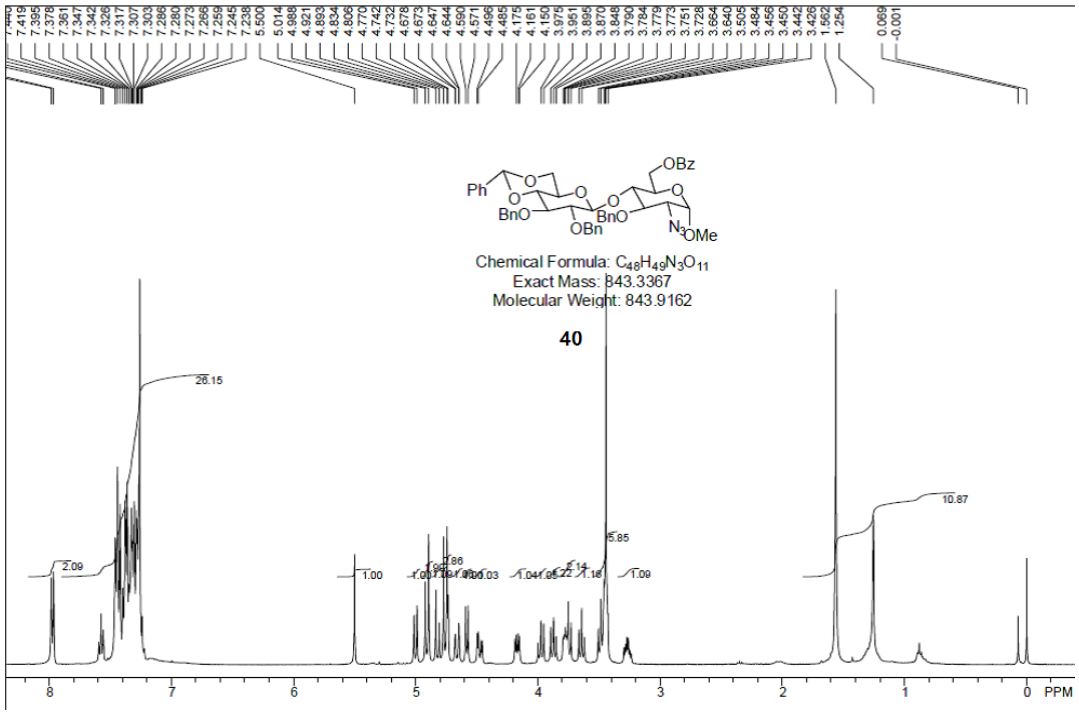

XP0491P
Chemical Formula: C48H47N3O12
Exact Mass: 857.32
Molecular Weight: 857.90
37
PPM

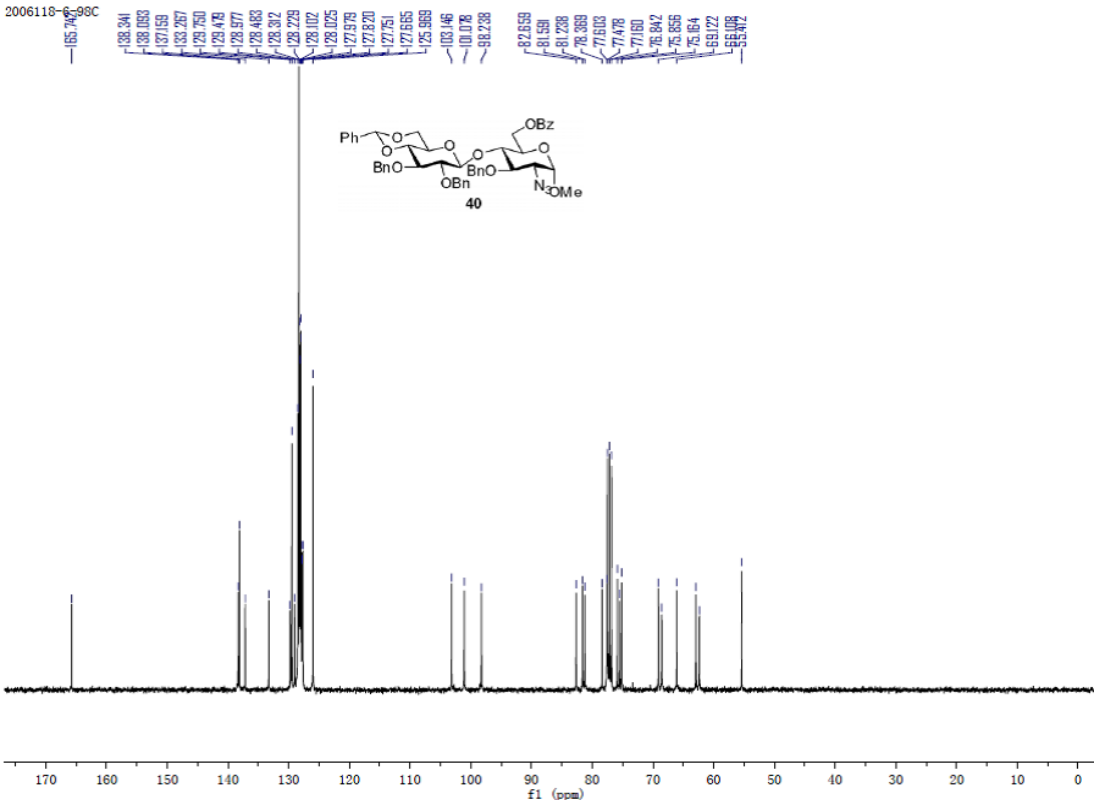

f1 (ppm)

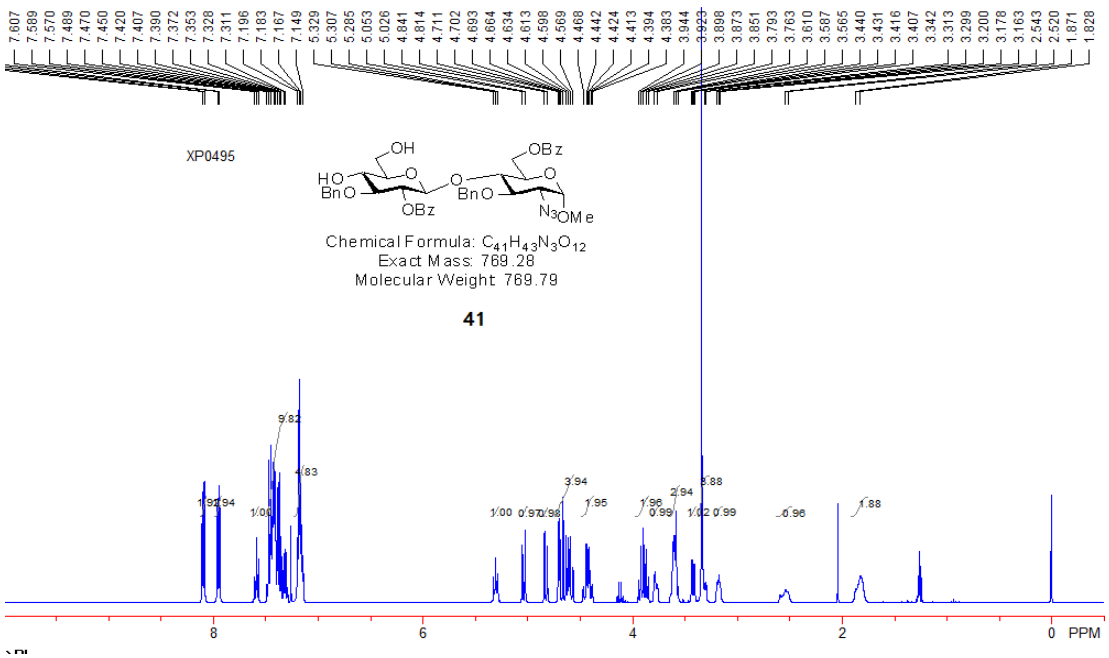

Std carbon
f1 (ppm)

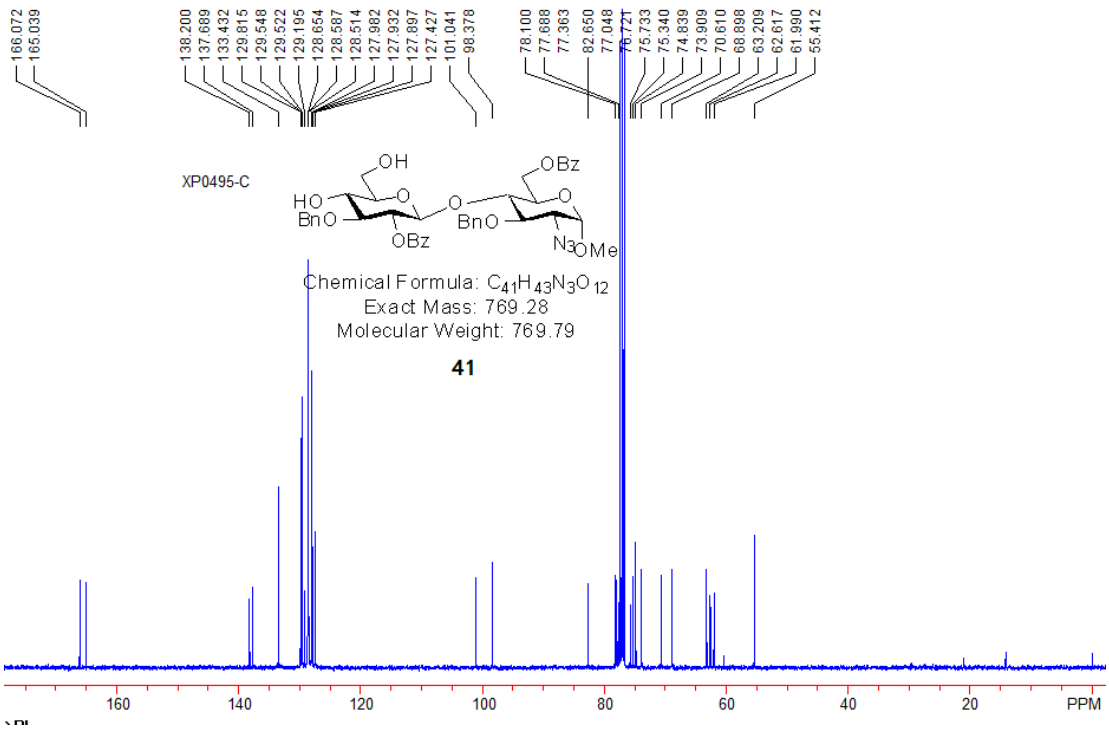

20061196-85
Ph
BnO
OLev
BnO
OBz
N3
OMe
39

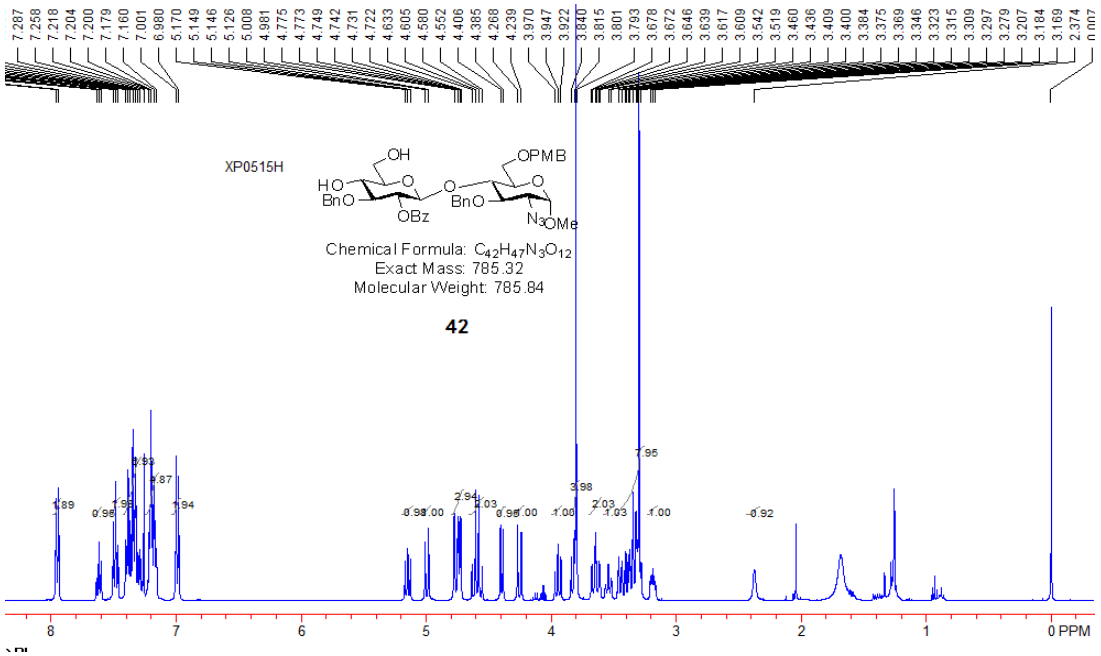

20061118-6-85C
Ph
BnO
OLev
BnO
OBz
N3
OMe
39

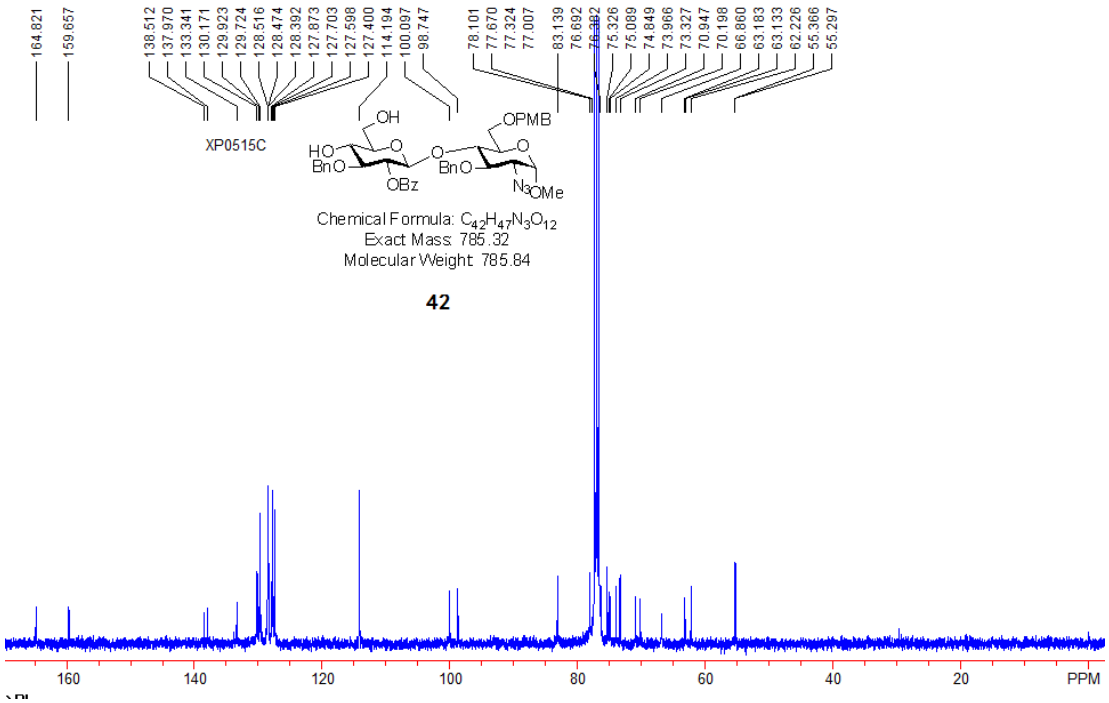

Chemical Formula: C48H49N3O11
Exact Mass: 843.3367
Molecular Weight: 843.9162
40
PPM

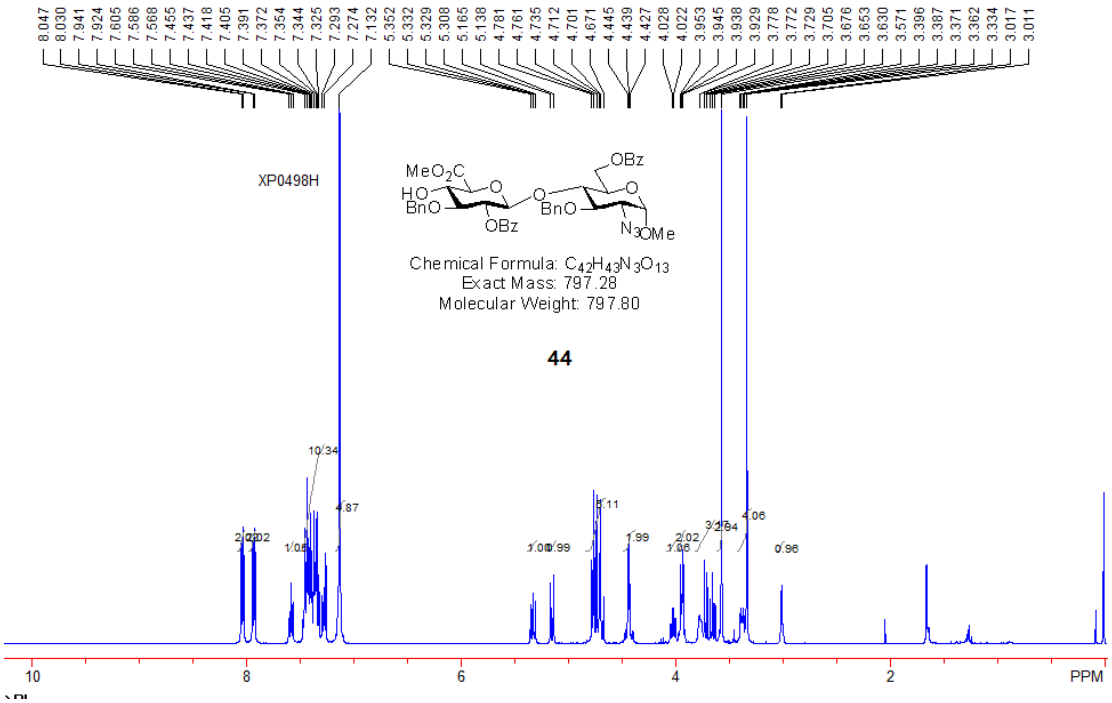

2006118-C-98C
40
f1 (ppm)

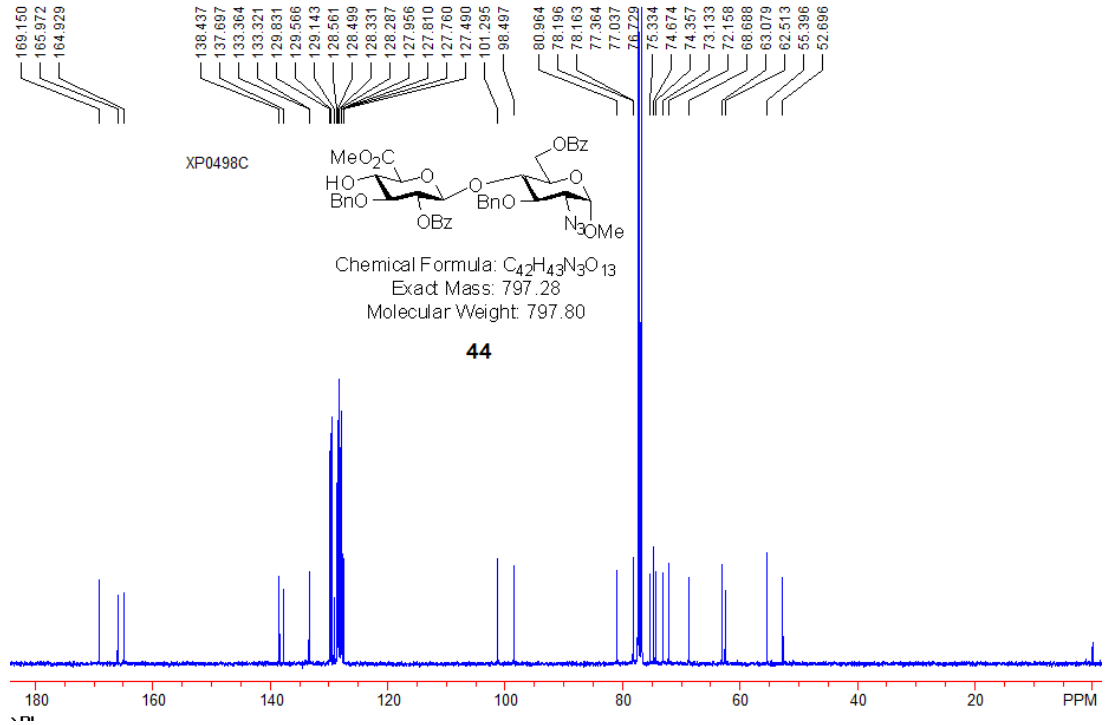

XP0495
Chemical Formula: C41H43N3O12
Exact Mass: 769.28
Molecular Weight: 769.79
41
PPM

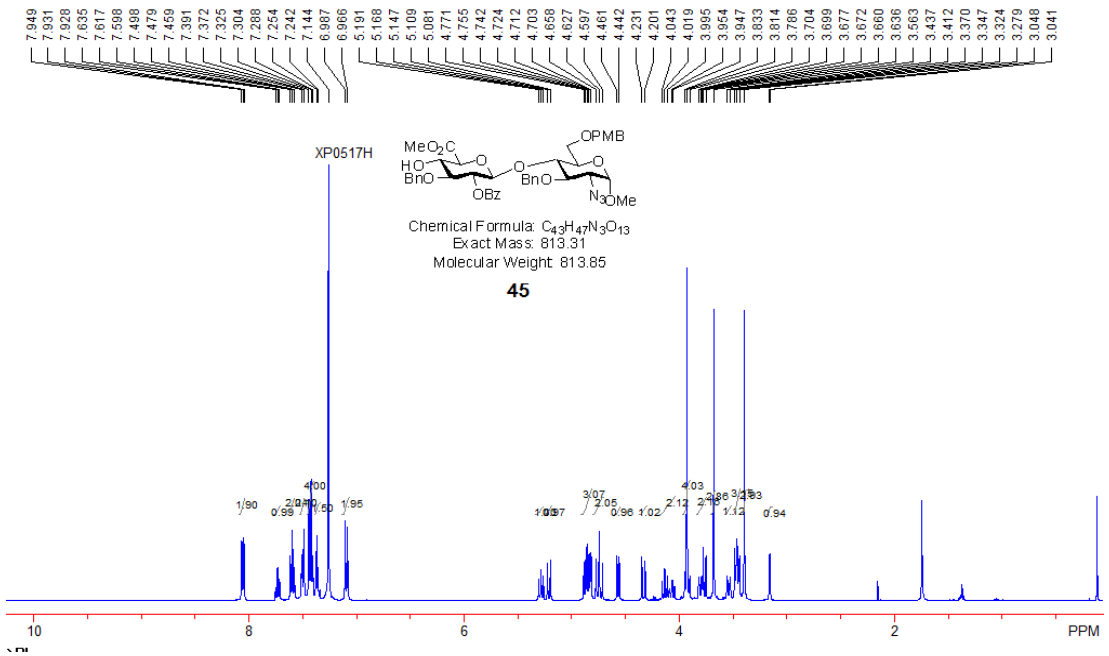

XP0495-C
Chemical Formula: C41H43N3O12
Exact Mass: 769.28
Molecular Weight: 769.79
41
PPM

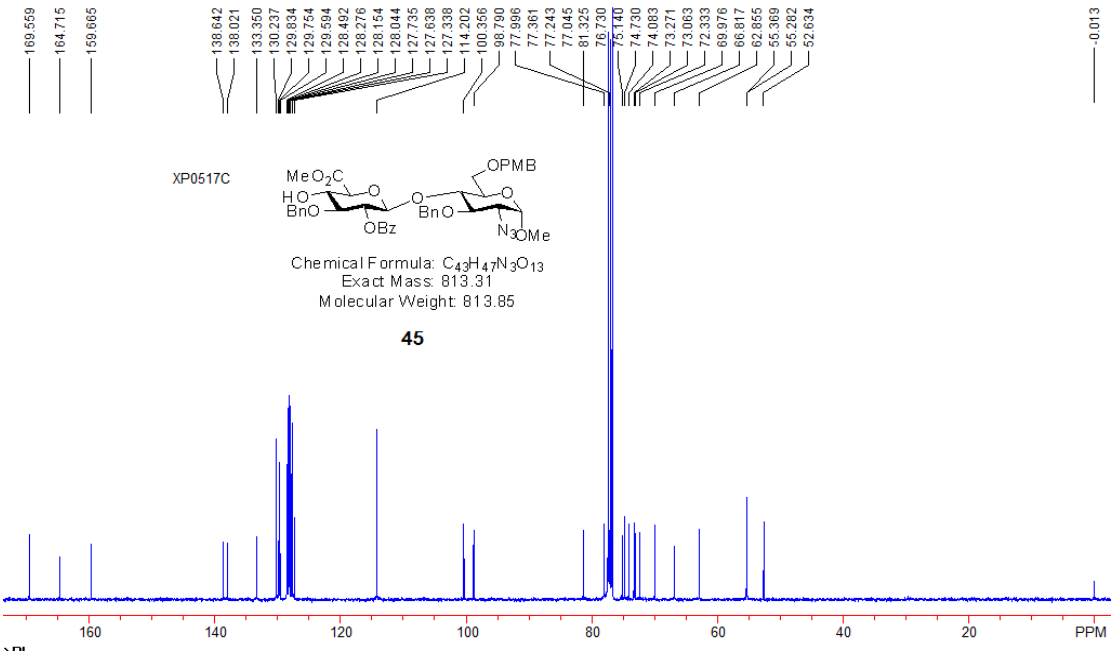

XP0515H
Chemical Formula: C42H47N3O12
Exact Mass: 785.32
Molecular Weight: 785.84
42
PPM

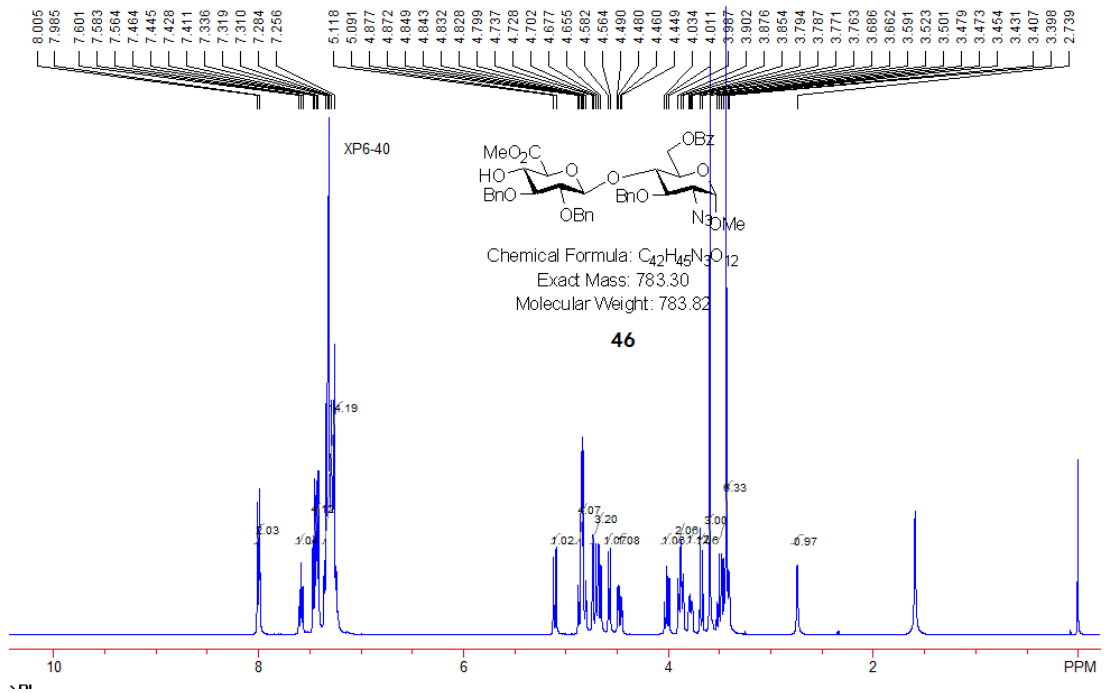

XP0515C
Chemical Formula: C42H47N3O12
Exact Mass: 785.32
Molecular Weight: 785.84
42
PPM

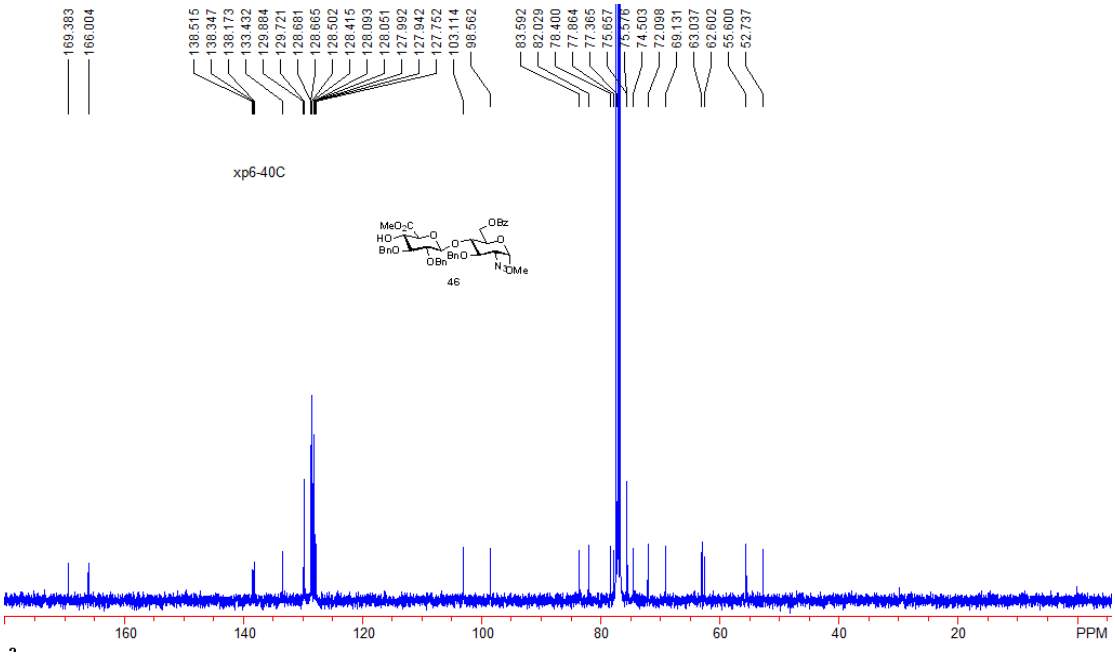

XP0498H
Chemical Formula: C42H43N3O13
Exact Mass: 797.28
Molecular Weight: 797.80
44
PPM

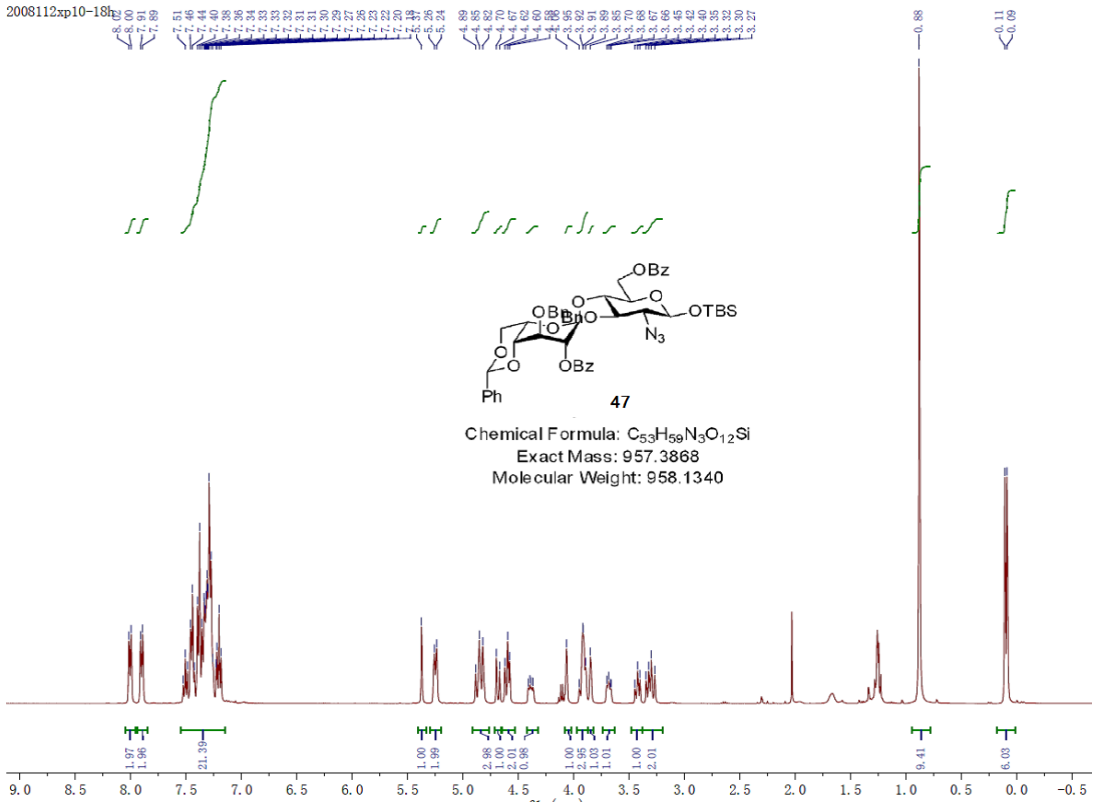

XP0498C
Chemical Formula: C42H43N3O13
Exact Mass: 797.28
Molecular Weight: 797.80
44
PPM

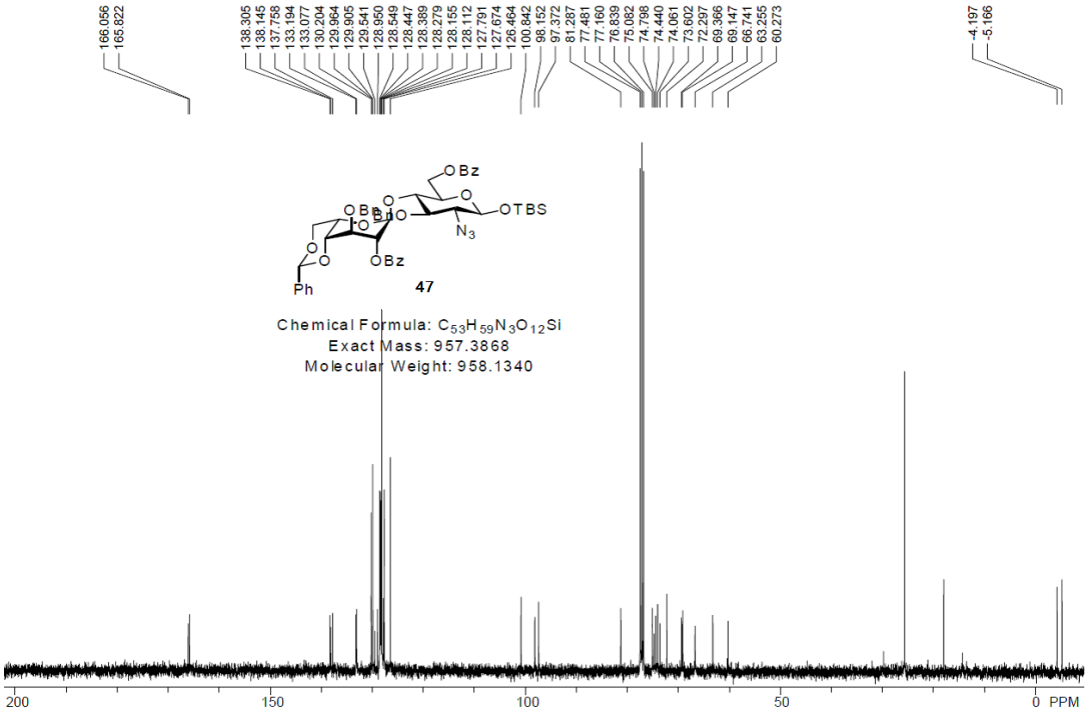

XP0517H
Chemical Formula: C43H47N3O13
Exact Mass: 813.31
Molecular Weight: 813.85
45
PPM

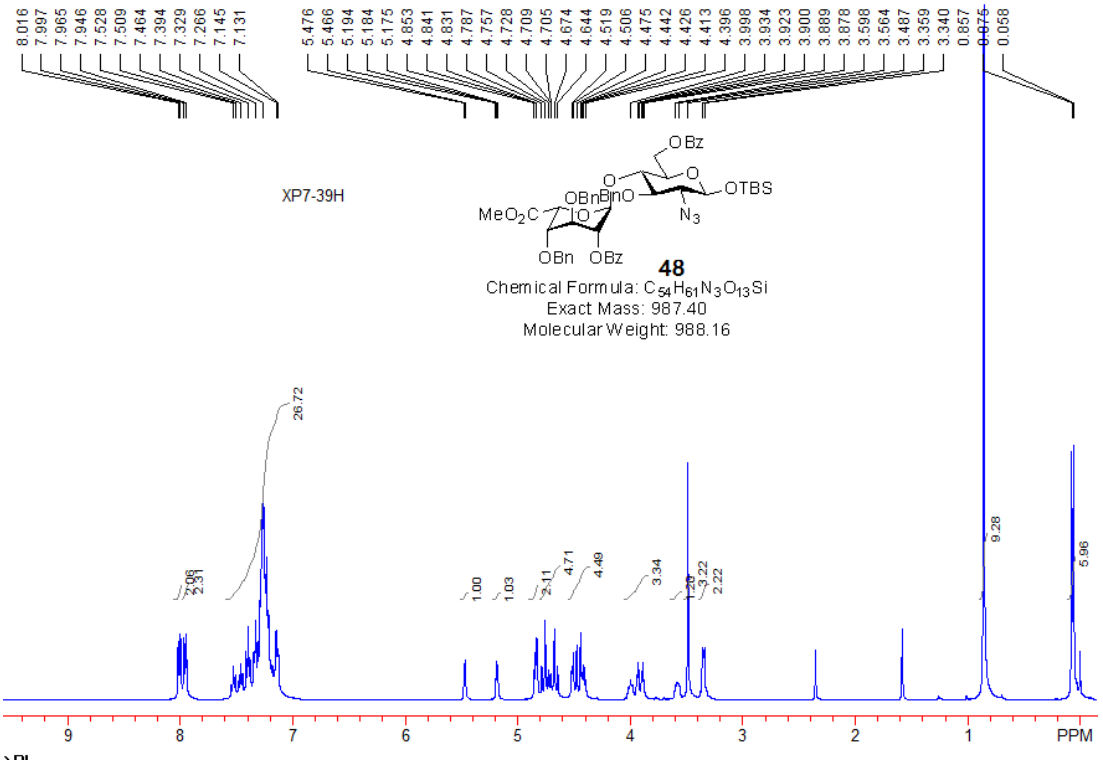

XP0517C
Chemical Formula: C43H47N3O13
Exact Mass: 813.31
Molecular Weight: 813.85
45
PPM

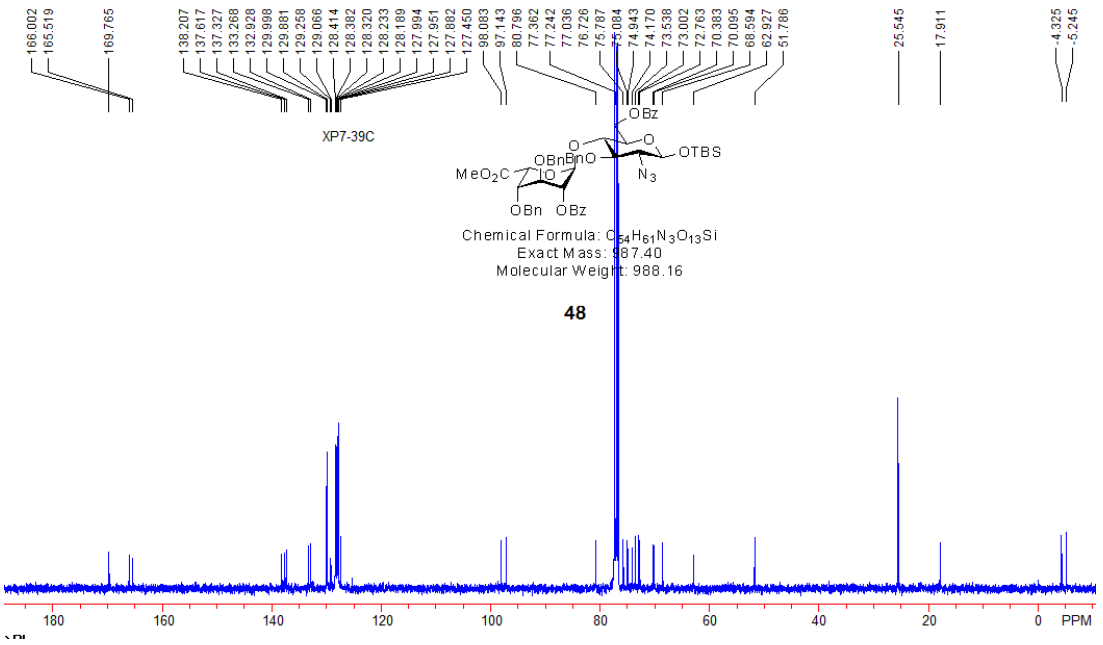

XP6-40
Chemical Formula: C42H45N3O12
Exact Mass: 783.30
Molecular Weight: 783.82
46
PPM

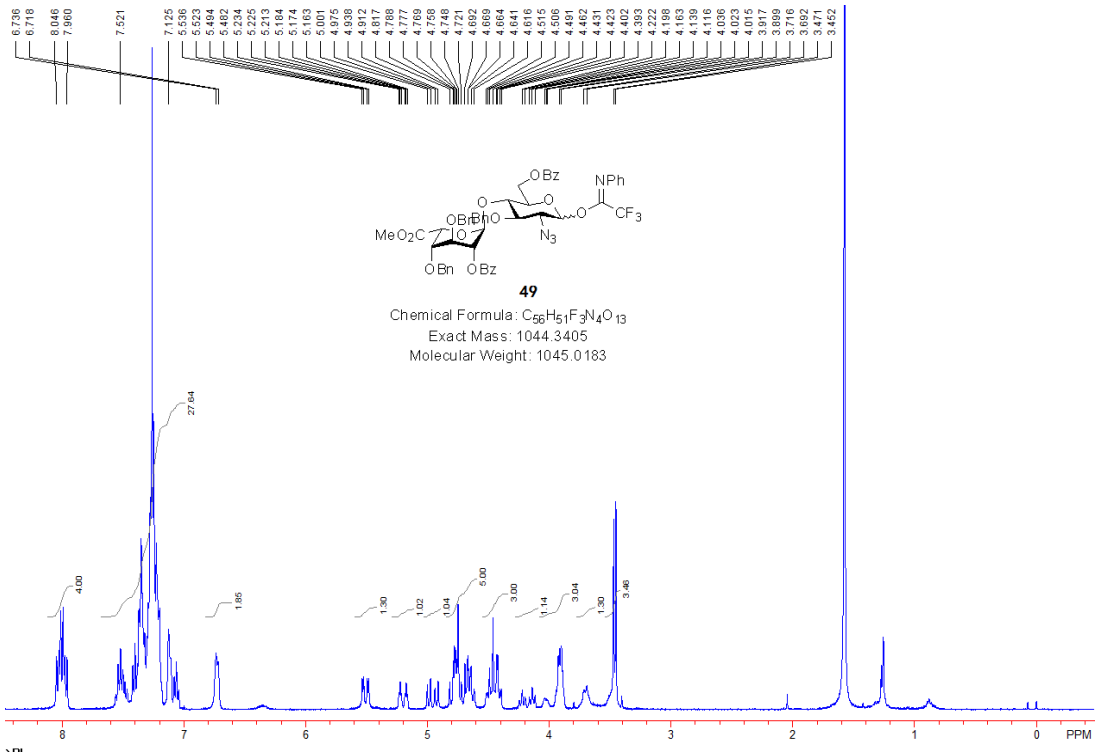

xp6-40C
46
PPM


2008112xp10-18h
OBz
OBz
OBz
OTBS
N3
Ph
47
Chemical Formula: C53H59N3O12Si
Exact Mass: 957.3868
Molecular Weight: 958.1340


OBz
OBz
OBz
OTBS
N3
Ph
47
Chemical Formula: C53H59N3O12Si
Exact Mass: 957.3868
Molecular Weight: 958.1340
PPM

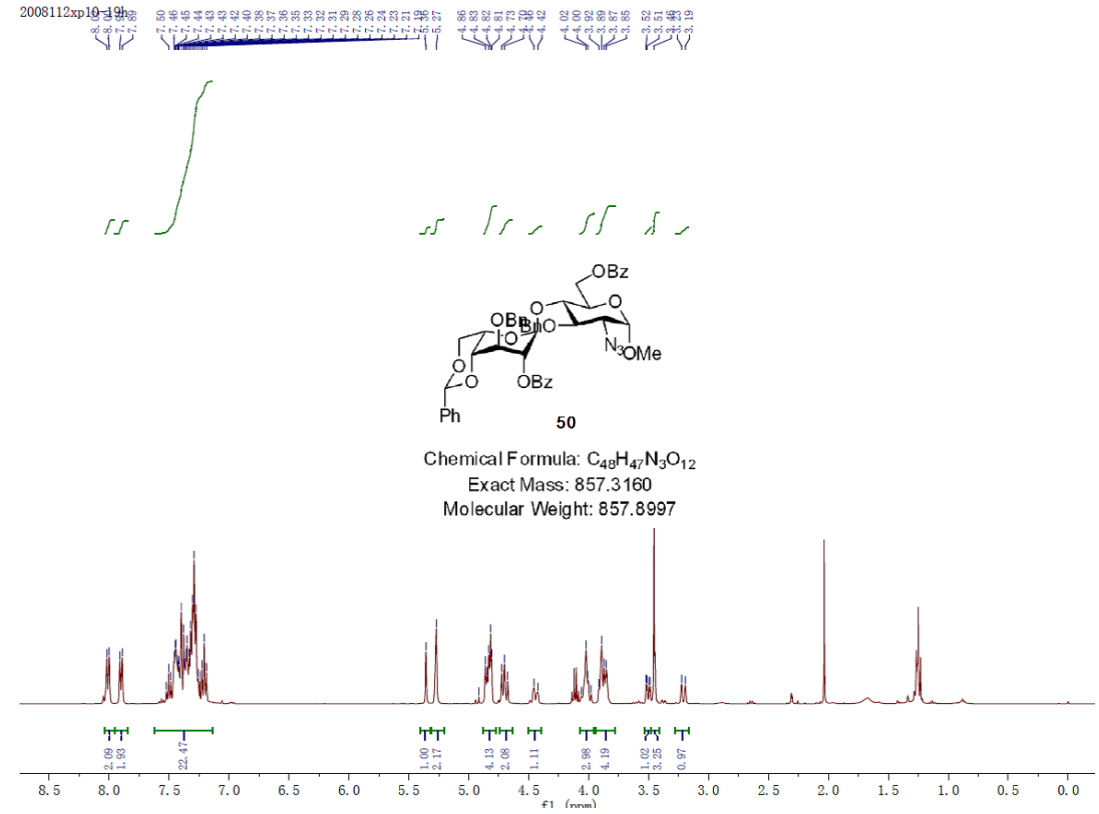

XP7-39H
48
Chemical Formula: C54H61N3O13Si
Exact Mass: 987.40
Molecular Weight: 988.16
PPM


XP7-39C
48
Chemical Formula: C54H61N3O13Si
Exact Mass: 987.40
Molecular Weight: 988.16
PPM



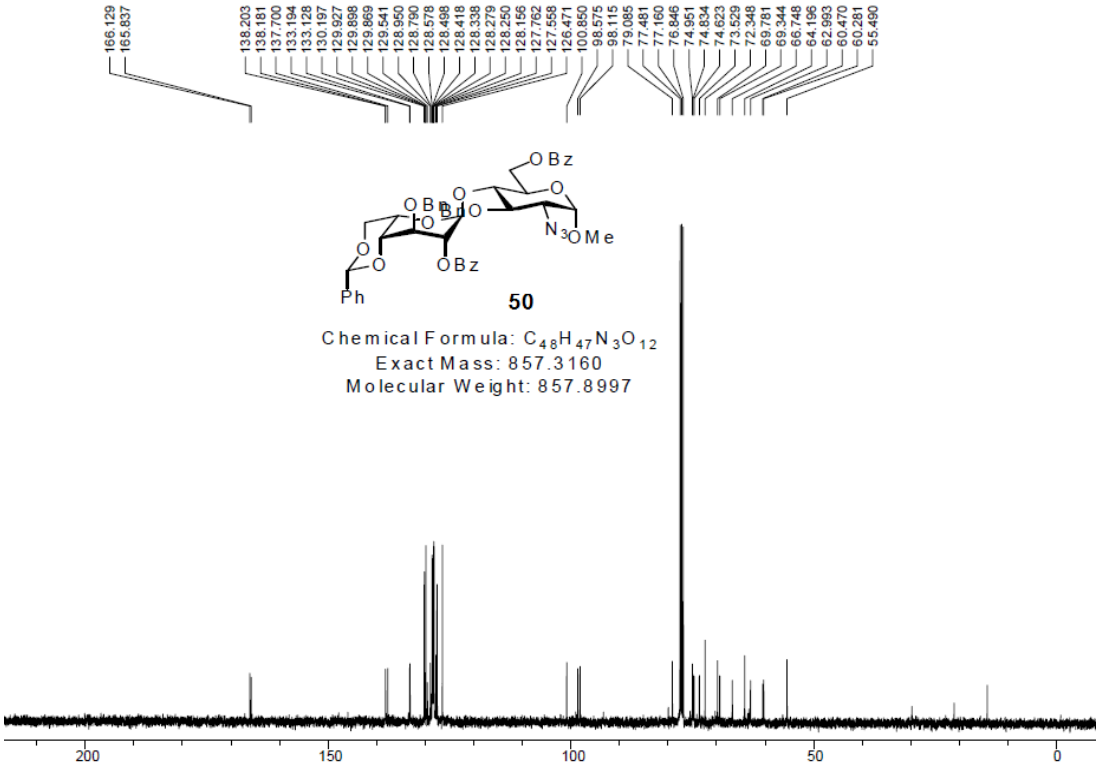
49

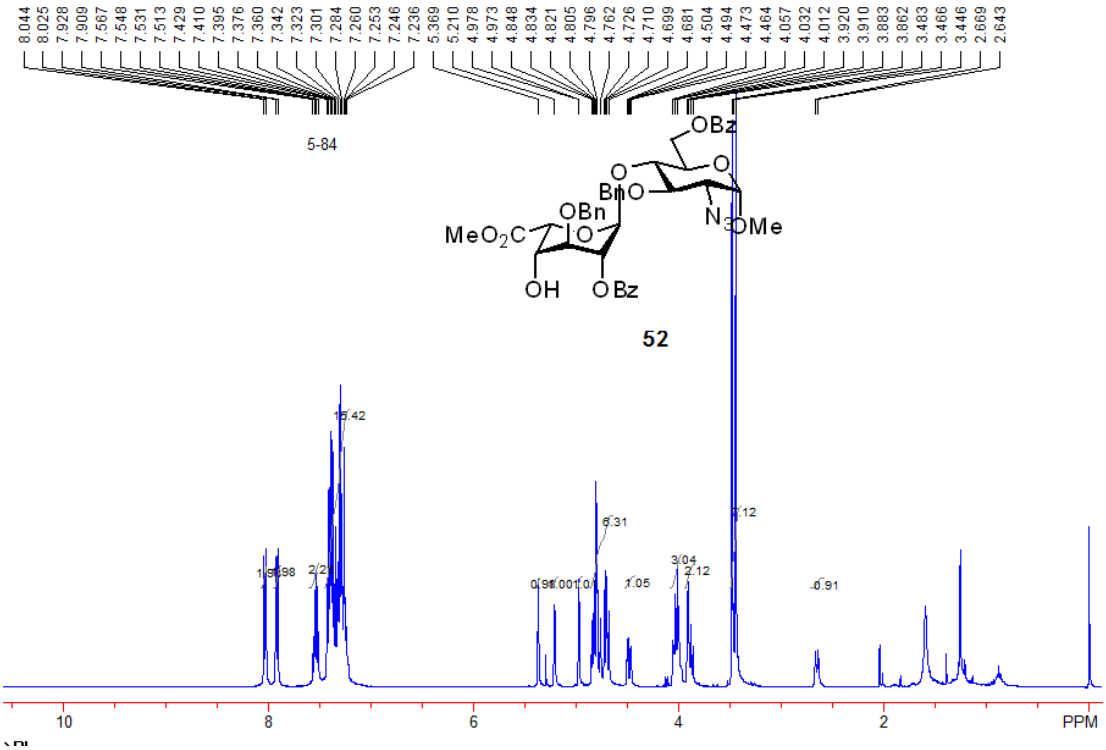
Chemical Formula: $C_{56}H_{51}F_3N_4O_{13}$
Exact Mass: 1044.3405
Molecular Weight: 1045.0183

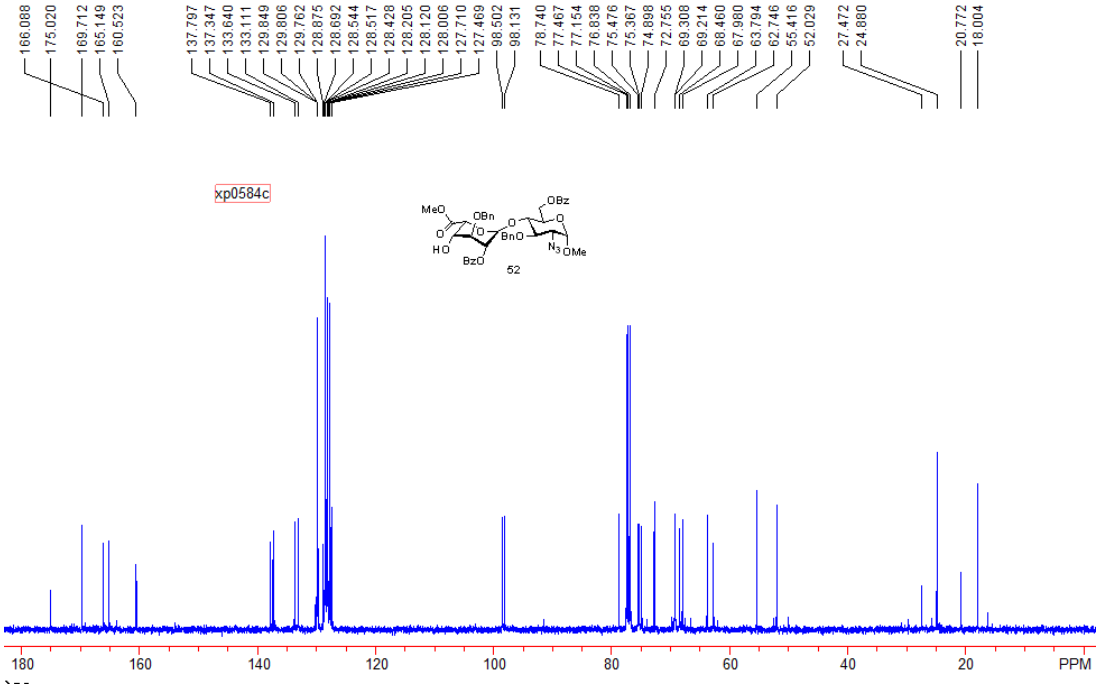


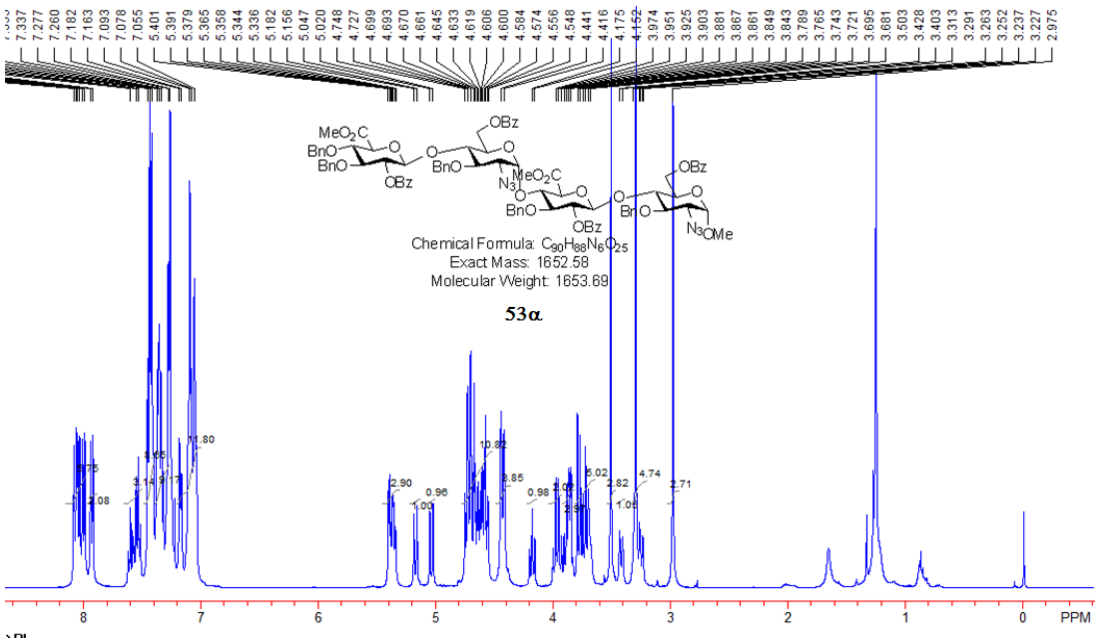
50

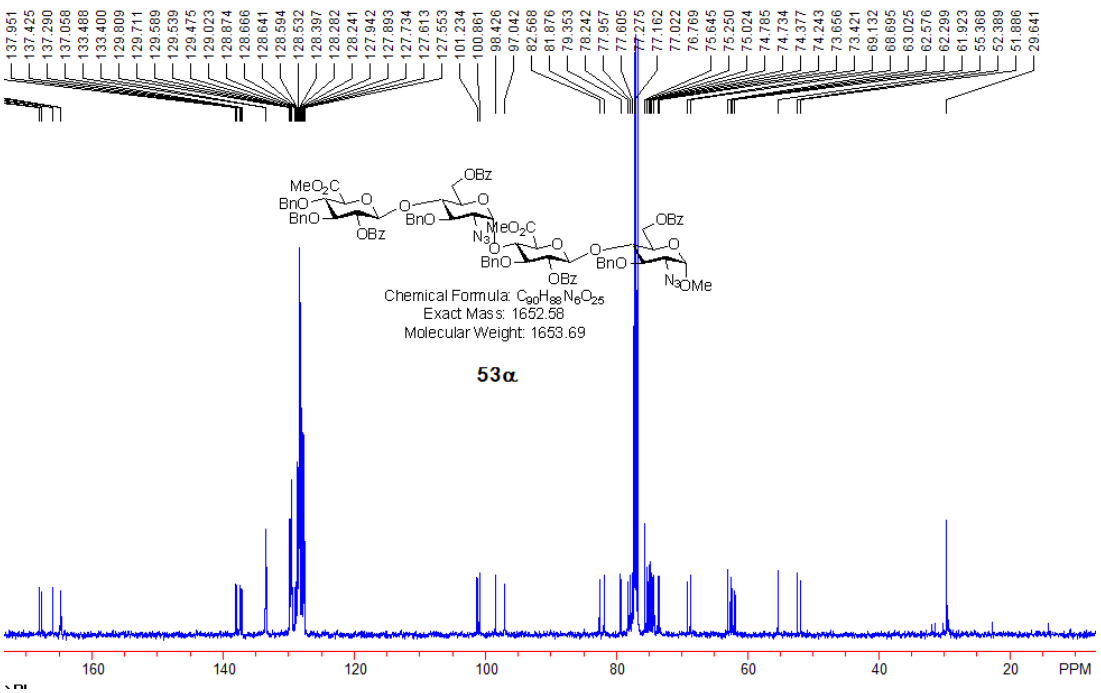
Chemical Formula: $C_{48}H_{47}N_3O_{12}$
Exact Mass: 857.3160
Molecular Weight: 857.8997

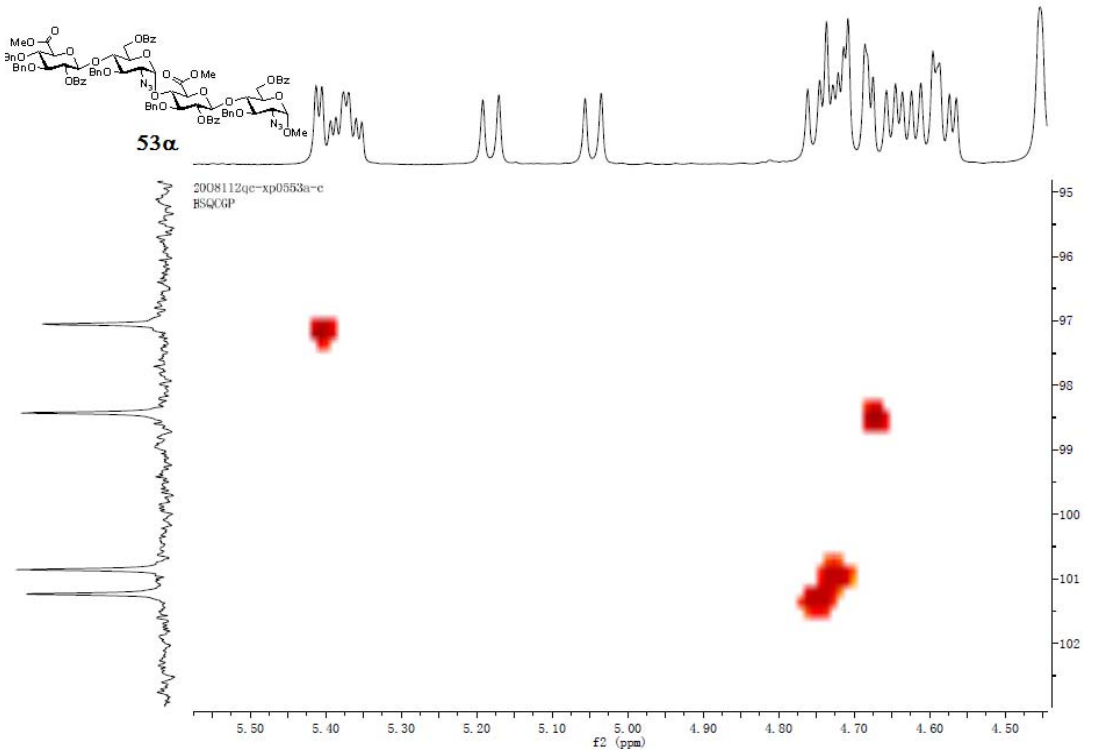

166.129
165.837
138.203
138.181
137.700
133.194
133.128
130.197
129.927
129.898
129.869
129.541
128.950
128.790
128.578
128.498
128.418
128.338
128.279
128.250
128.156
127.762
127.558
126.471
100.850
98.575
98.115
79.085
77.481
77.160
76.846
74.951
74.834
74.623
73.529
72.348
69.781
69.344
66.748
64.196
62.993
60.470
60.281
55.490
OBz
OBn
BnO
N3
OMe
OBz
Ph
50
Chemical Formula: C48H47N3O12
Exact Mass: 857.3160
Molecular Weight: 857.8997
200
150
100
50
0

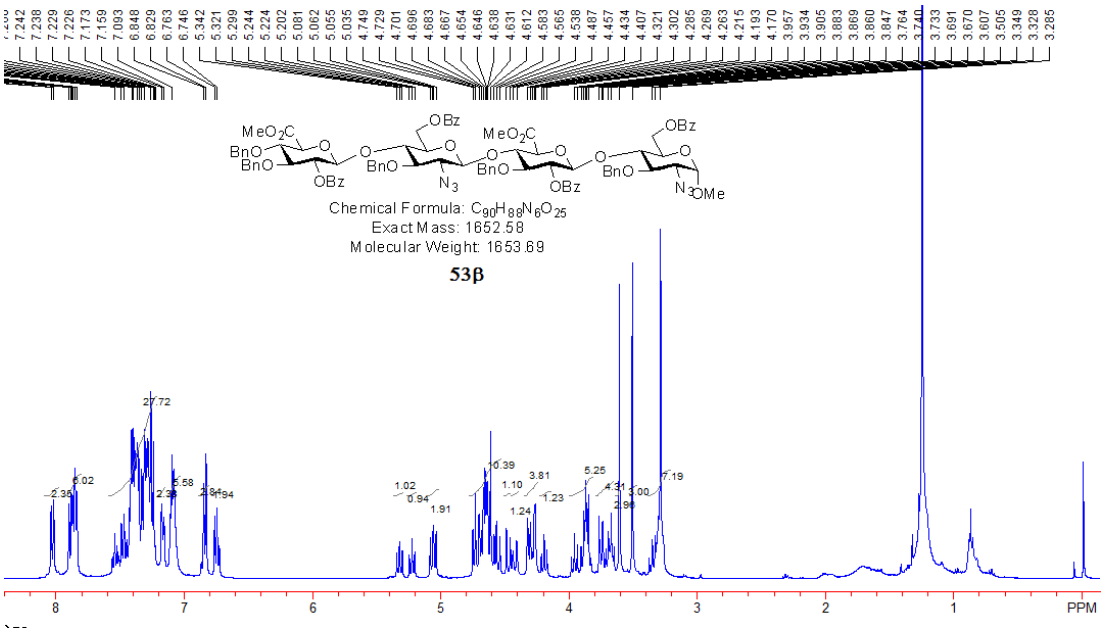

8.044
8.025
7.928
7.909
7.567
7.548
7.531
7.513
7.429
7.410
7.395
7.376
7.360
7.342
7.323
7.301
7.284
7.260
7.253
7.246
7.236
5.369
5.210
4.978
4.973
4.848
4.834
4.821
4.805
4.796
4.762
4.726
4.710
4.699
4.681
4.504
4.494
4.473
4.464
4.057
4.032
4.012
3.920
3.910
3.883
3.862
3.483
3.466
3.446
2.669
2.643
5-84
OBz
BnO
OBn
MeO2C
OH
OBz
N3
OMe
52
15.42
6.31
3.12
3.04
2.12
1.05
0.91
10
8
6
4
2
PPM

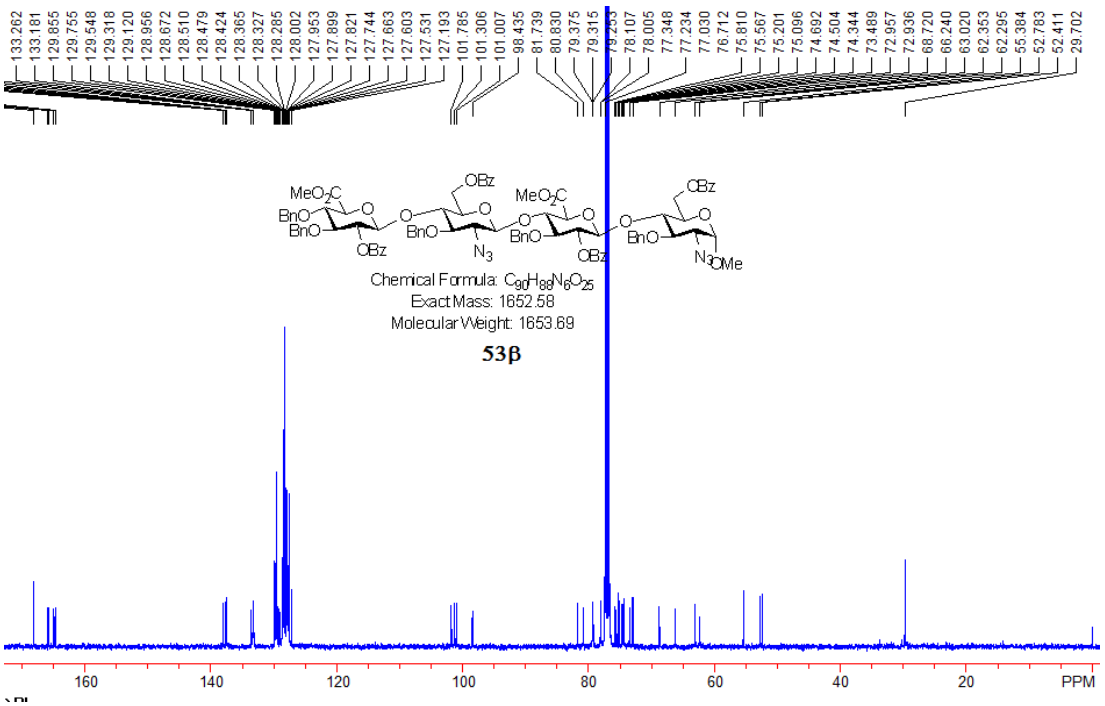

166.088
175.020
169.712
165.149
160.523
137.797
137.347
133.640
133.111
129.849
129.806
129.762
128.875
128.692
128.544
128.517
128.428
128.205
128.120
128.006
127.710
127.469
98.502
98.131
78.740
77.467
77.154
76.838
75.476
75.367
74.898
72.755
69.308
69.214
68.460
67.980
63.794
62.746
55.416
52.029
27.472
24.880
20.772
18.004
xp0584c
52
180
160
140
120
100
80
60
40
20
PPM

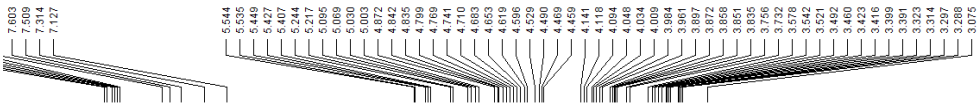

Chemical Formula: C90H88N6O25
Exact Mass: 1652.58
Molecular Weight: 1653.69
53α
8
7
6
5
4
3
2
1
0
PPM

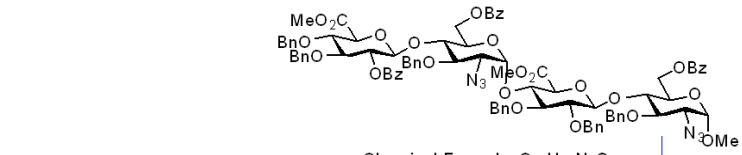

137.951
137.425
137.290
137.058
133.488
133.400
129.809
129.711
129.589
129.539
129.475
129.023
128.874
128.666
128.641
128.594
128.532
128.397
128.282
128.241
127.942
127.893
127.734
127.613
127.553
101.234
100.861
98.426
97.042
82.568
81.876
79.353
78.242
77.957
77.605
77.275
77.162
77.022
76.769
75.645
75.250
75.024
74.785
74.734
74.377
74.243
73.656
73.421
69.132
68.695
63.025
62.576
62.299
61.923
55.368
52.389
51.886
29.641
Chemical Formula: C90H88N6O25
Exact Mass: 1652.58
Molecular Weight: 1653.69
53α
160
140
120
100
80
60
40
20
PPM


53α
2008112qc-xp0553a-c
BSQCGP
95
96
97
98
99
100
101
102
5.50
5.40
5.30
5.20
5.10
5.00
4.90
4.80
4.70
4.60
4.50
f2 (ppm)


Chemical Formula: C90H88N6O25
Exact Mass: 1652.58
Molecular Weight: 1653.69
53β
PPM

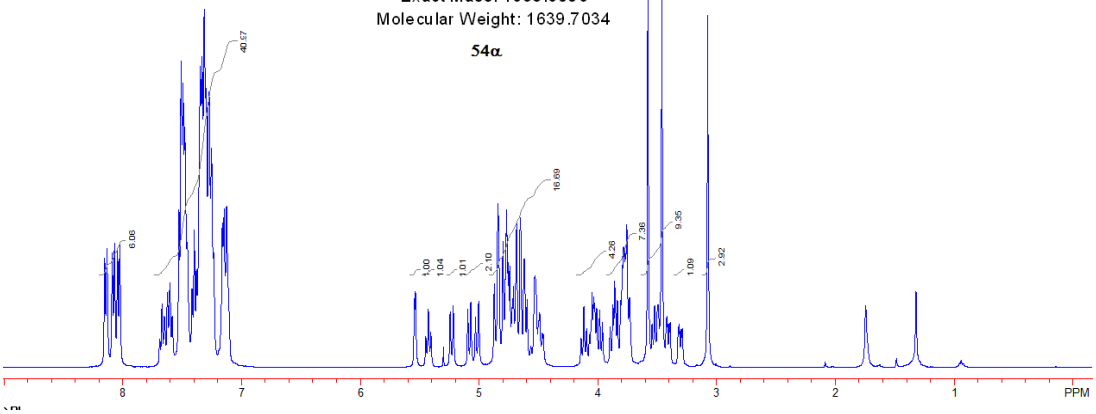

Chemical Formula: C90H88N6O25
Exact Mass: 1652.58
Molecular Weight: 1653.69
53β
PPM

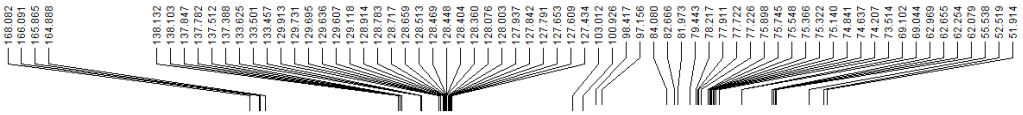


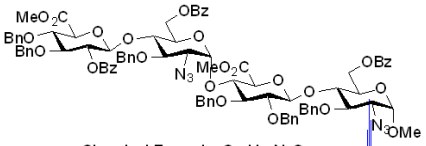


Chemical Formula: $C_{90}H_{90}N_6O_{24}$
Exact Mass: 1638.6006
Molecular Weight: 1639.7034

54α

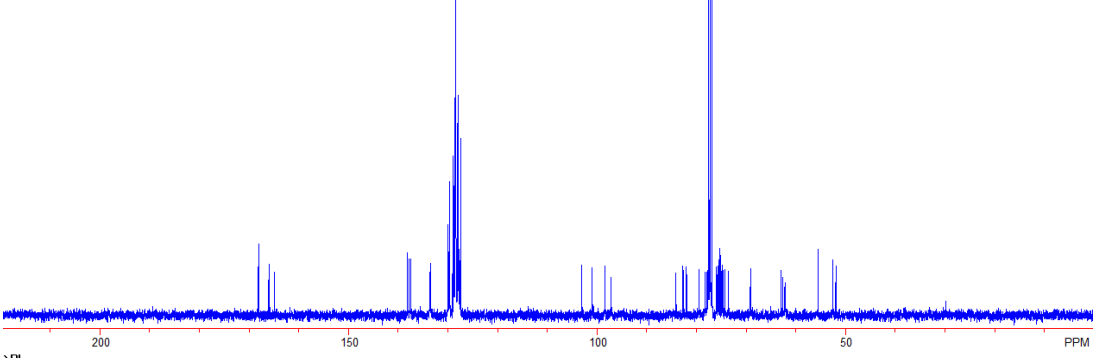


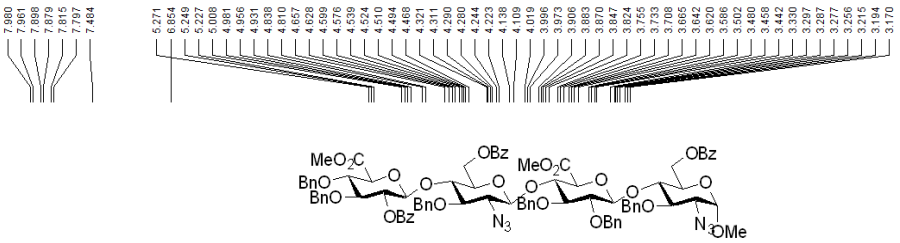




Chemical Formula: $C_{90}H_{90}N_6O_{24}$
Exact Mass: 1638.6006
Molecular Weight: 1639.7034

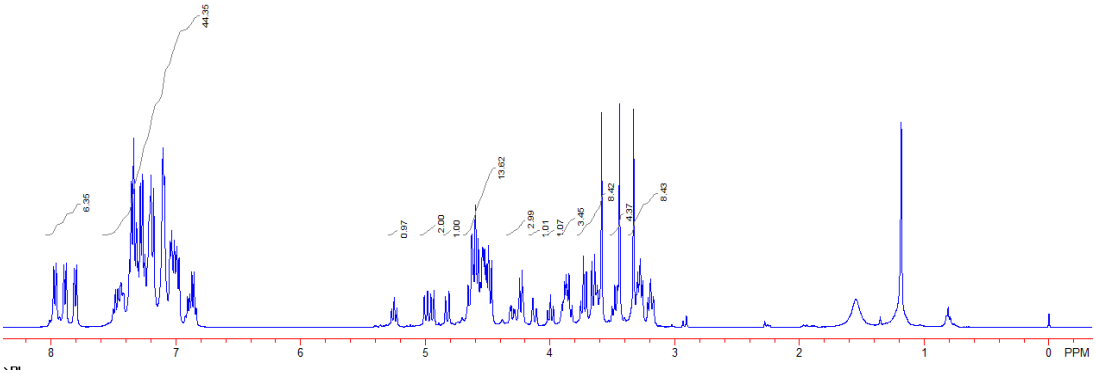
54α

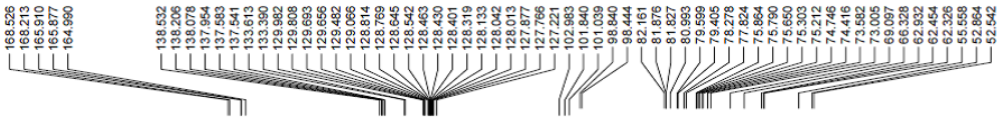


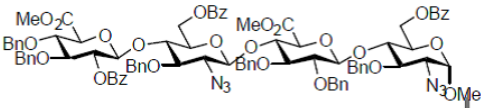


Chemical Formula: $C_{90}H_{90}N_6O_{24}$
Exact Mass: 1638.6006
Molecular Weight: 1639.7034

54β

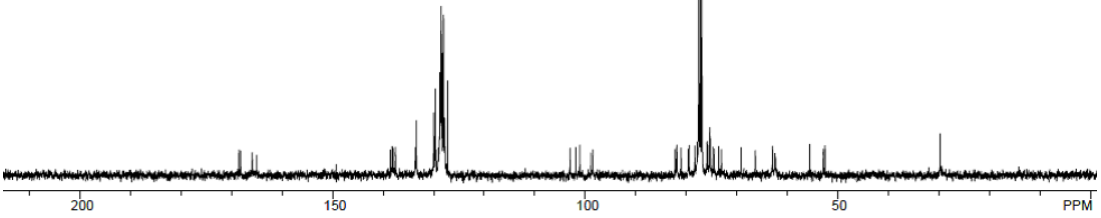


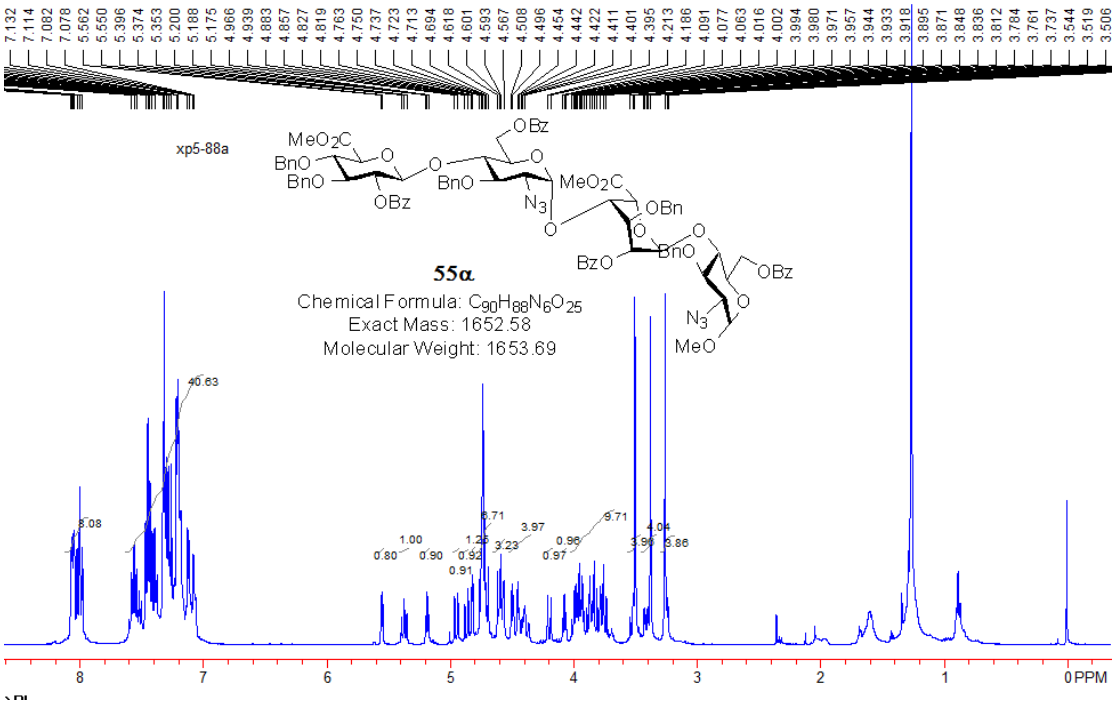


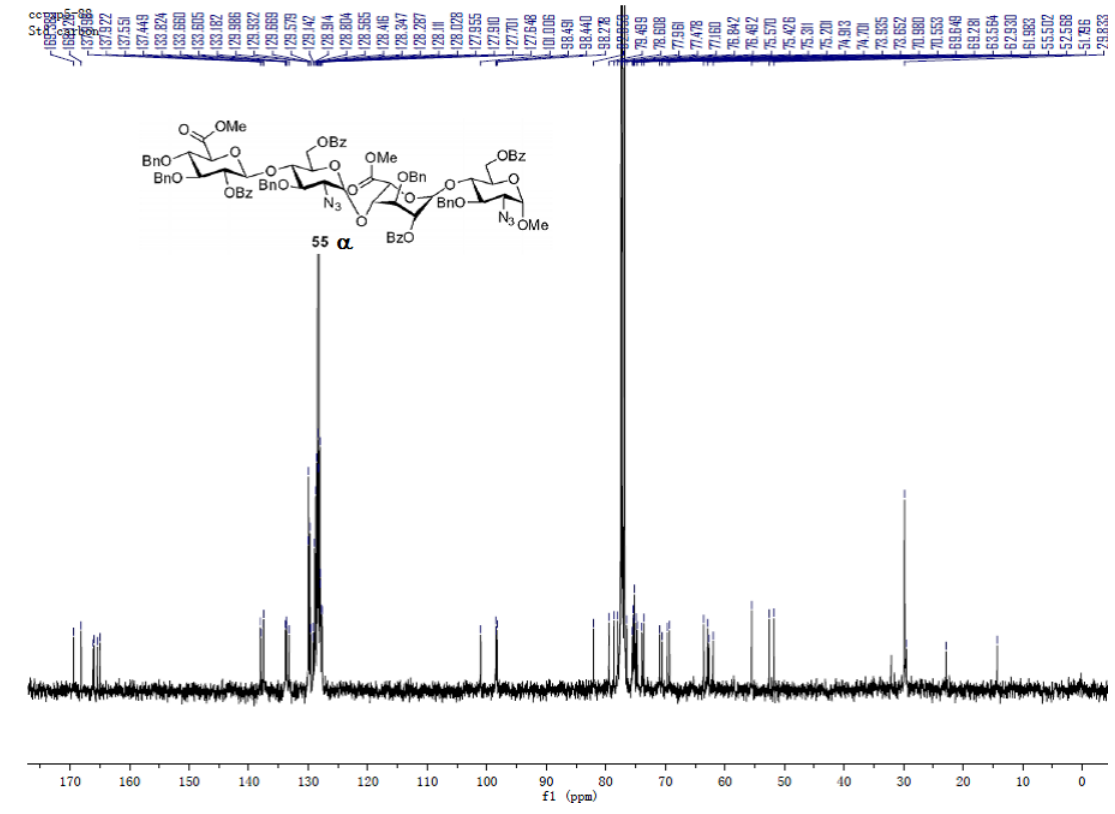


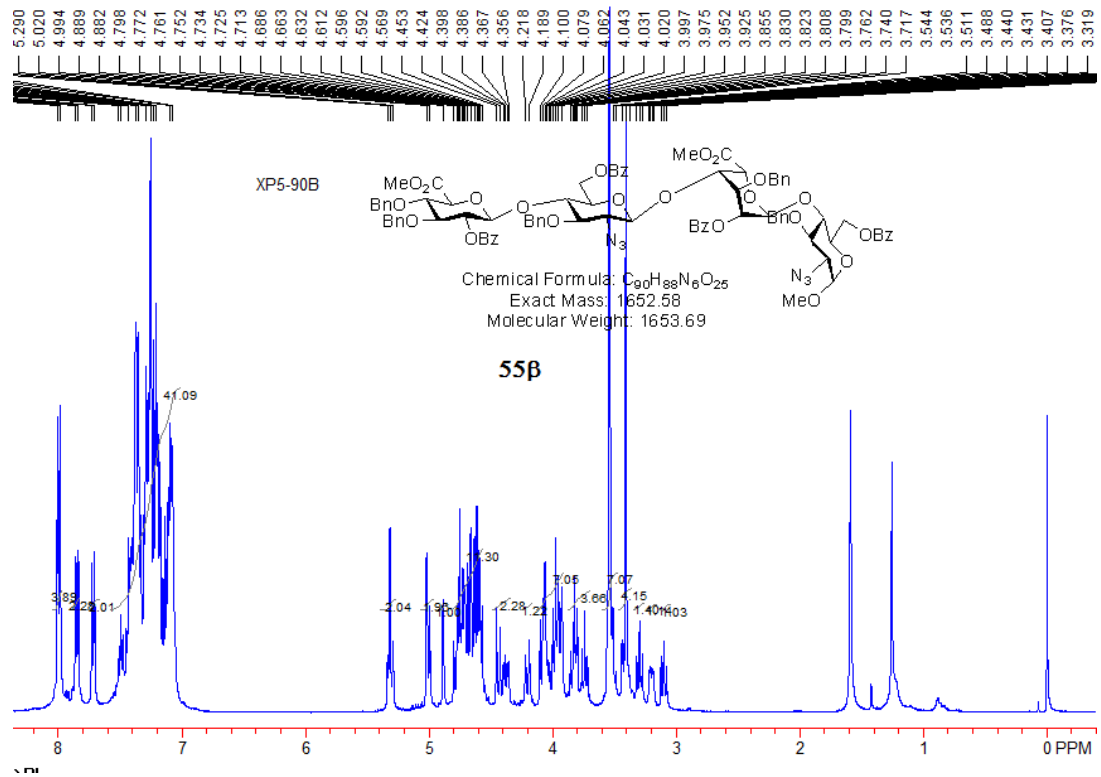
Chemical Formula: $C_{90}H_{90}N_6O_{24}$
Exact Mass: 1638.6006
Molecular Weight: 1639.7034

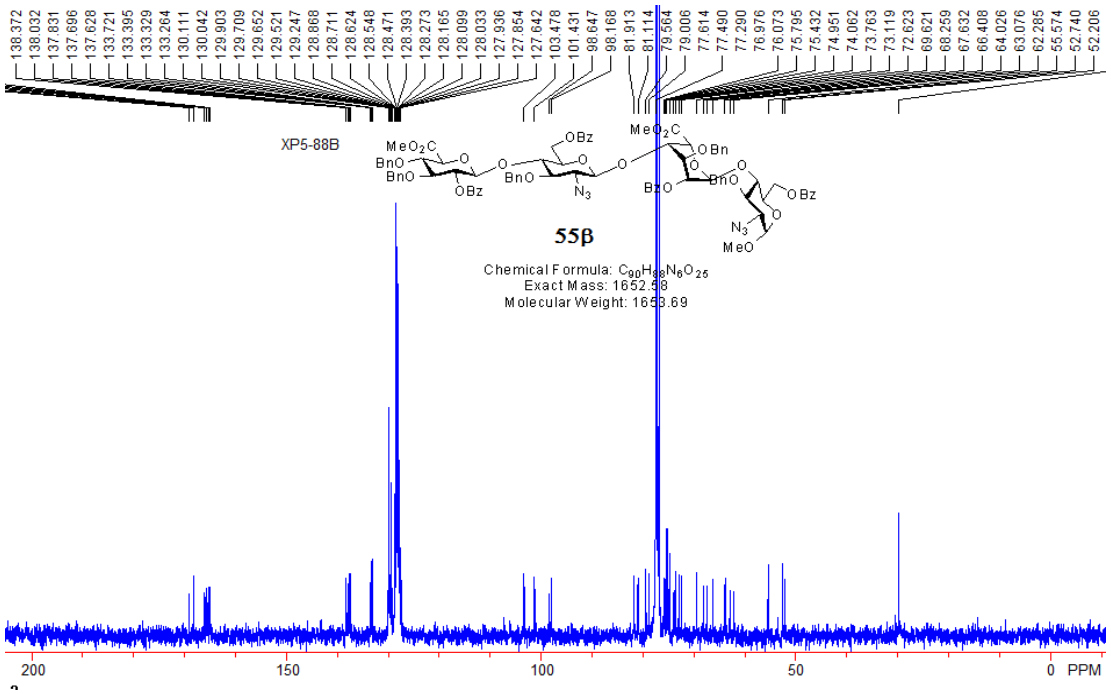
54β

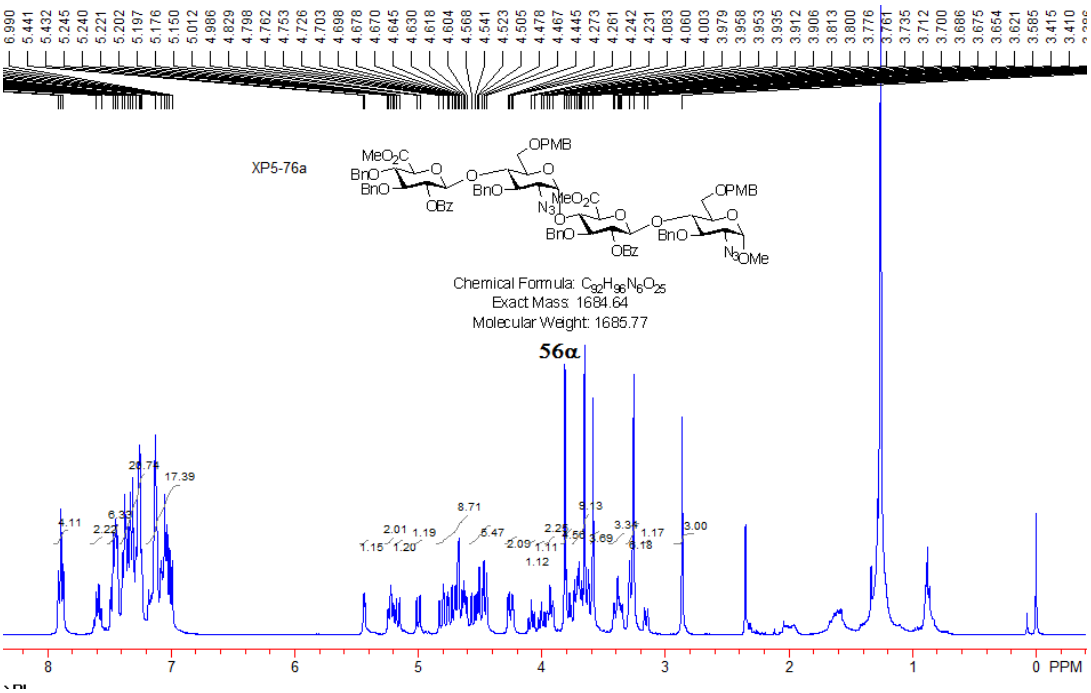


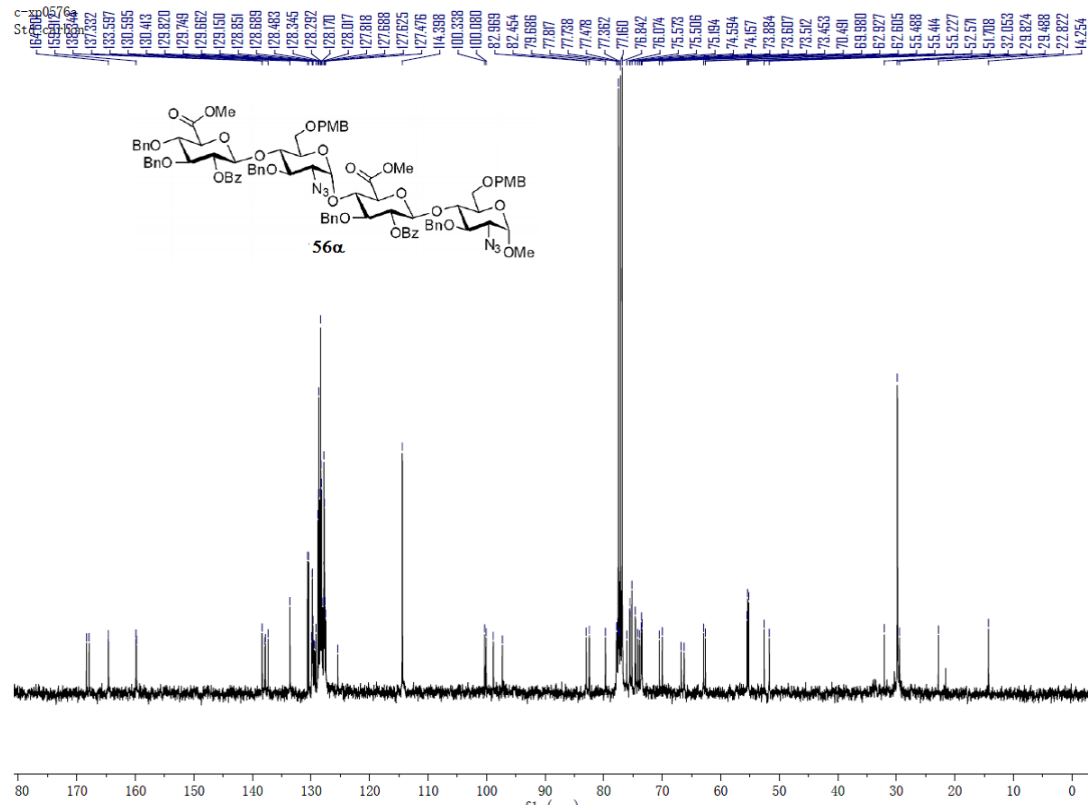

xp5-88a
55α
Chemical Formula: C90H88N6O25
Exact Mass: 1652.58
Molecular Weight: 1653.69
40.63
8.08
1.00
6.71
3.97
9.71
4.04
PPM

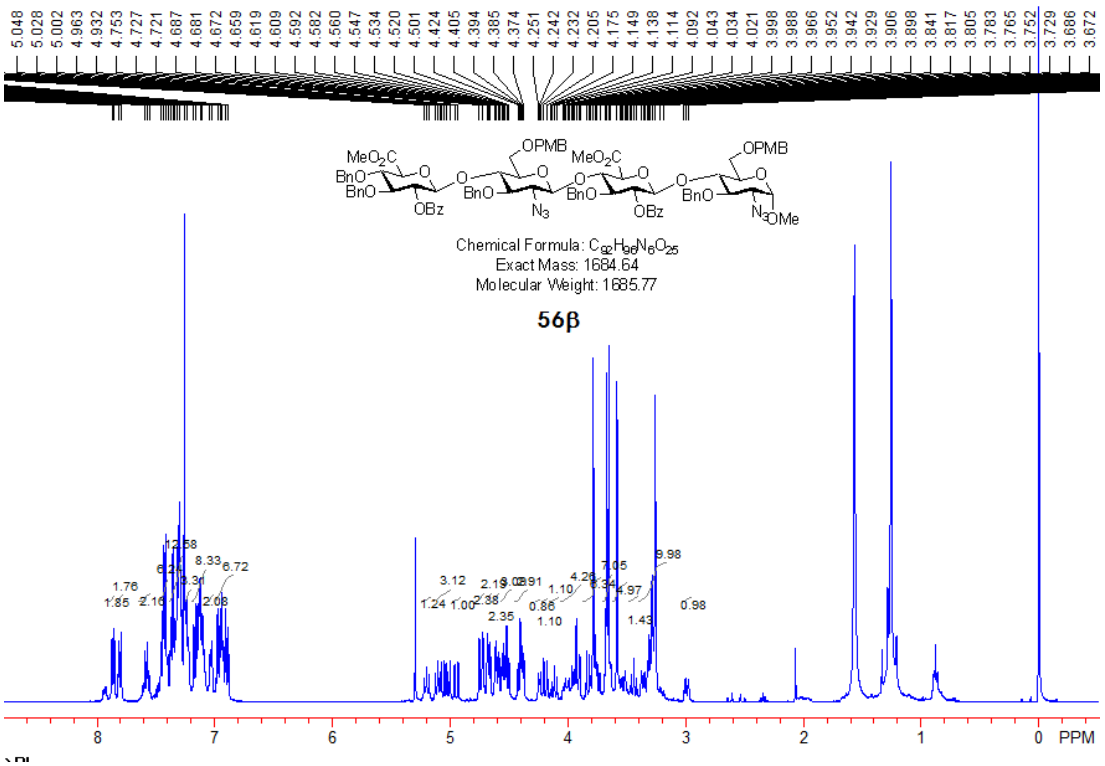

55 α
f1 (ppm)

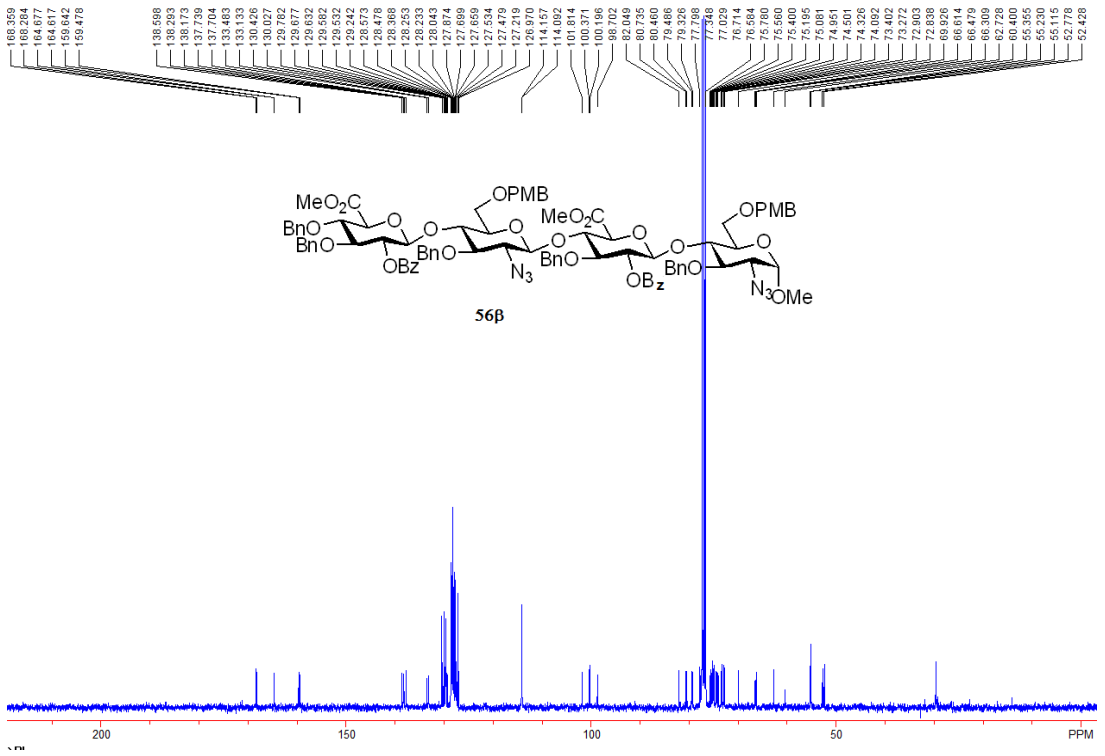

XP5-90B
Chemical Formula: C90H88N6O25
Exact Mass: 1652.58
Molecular Weight: 1653.69
55β
PPM

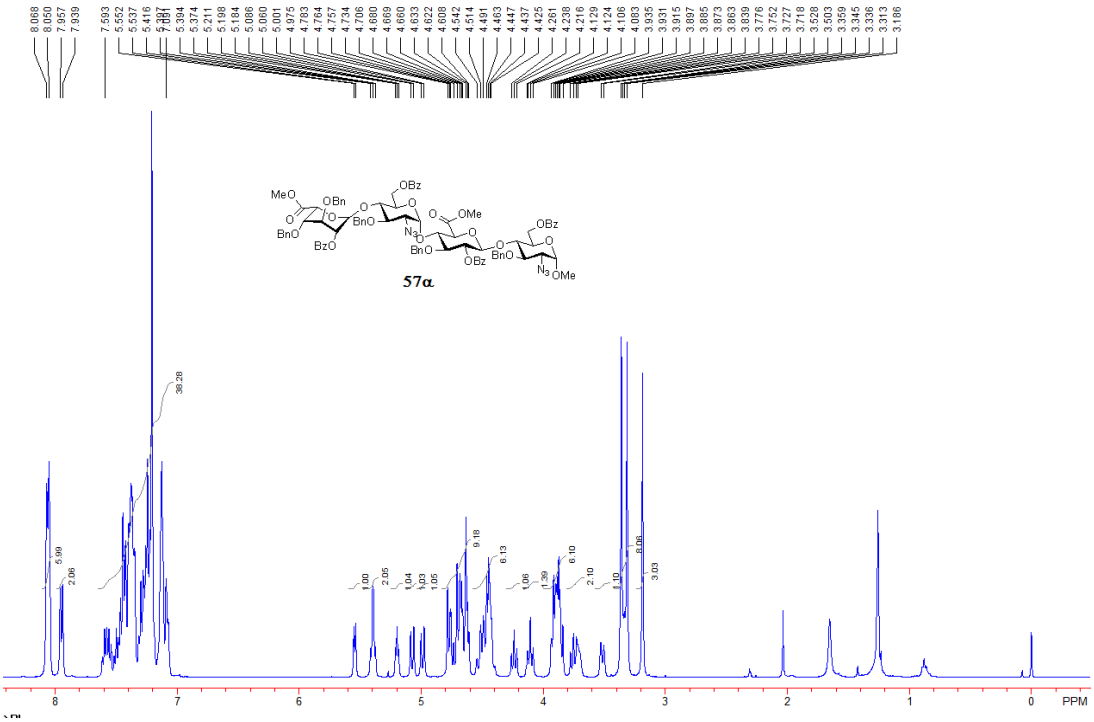

XP5-88B
55β
Chemical Formula: C90H88N6O25
Exact Mass: 1652.58
Molecular Weight: 1653.69
PPM


XP5-76a
Chemical Formula: C92H96N6O25
Exact Mass: 1684.64
Molecular Weight: 1685.77
56α
PPM

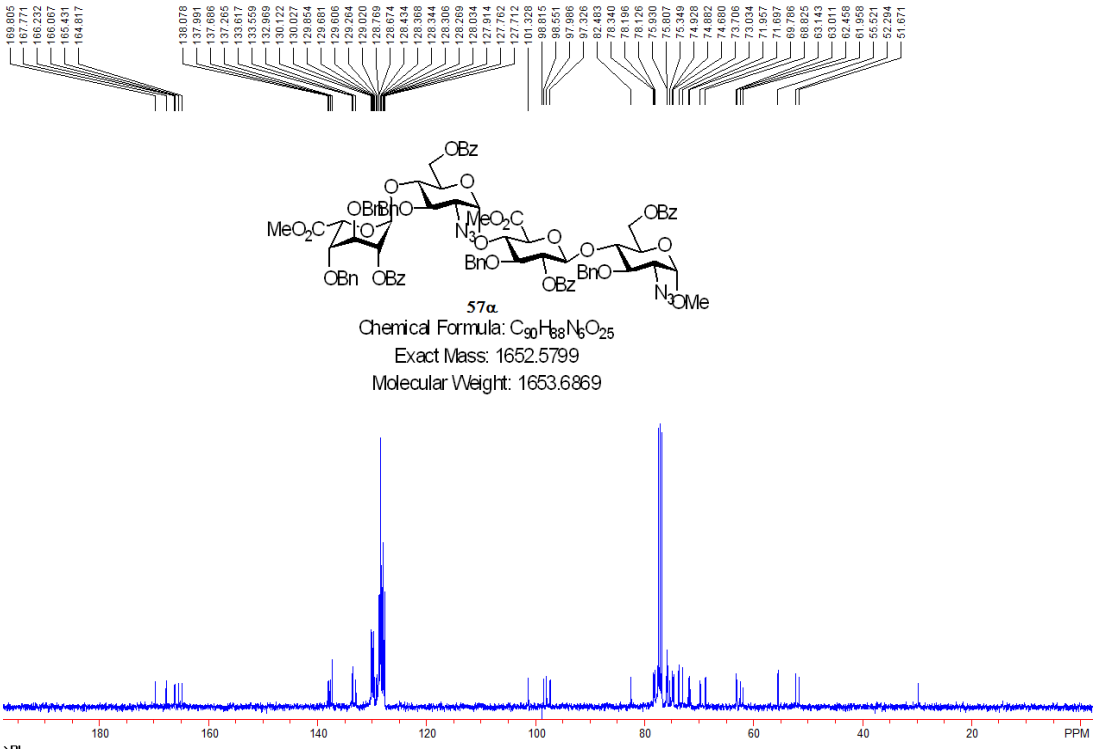

56α


Chemical Formula: C92H96N6O25
Exact Mass: 1684.64
Molecular Weight: 1685.77
56β
PPM


56β
PPM



57α

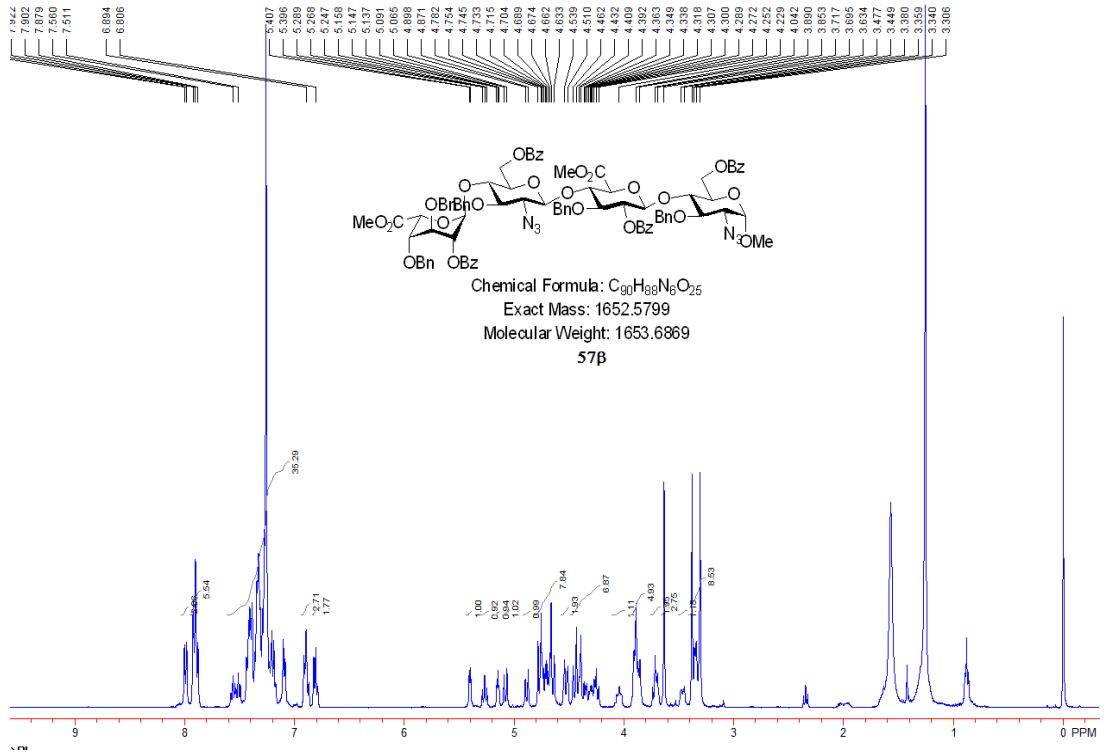


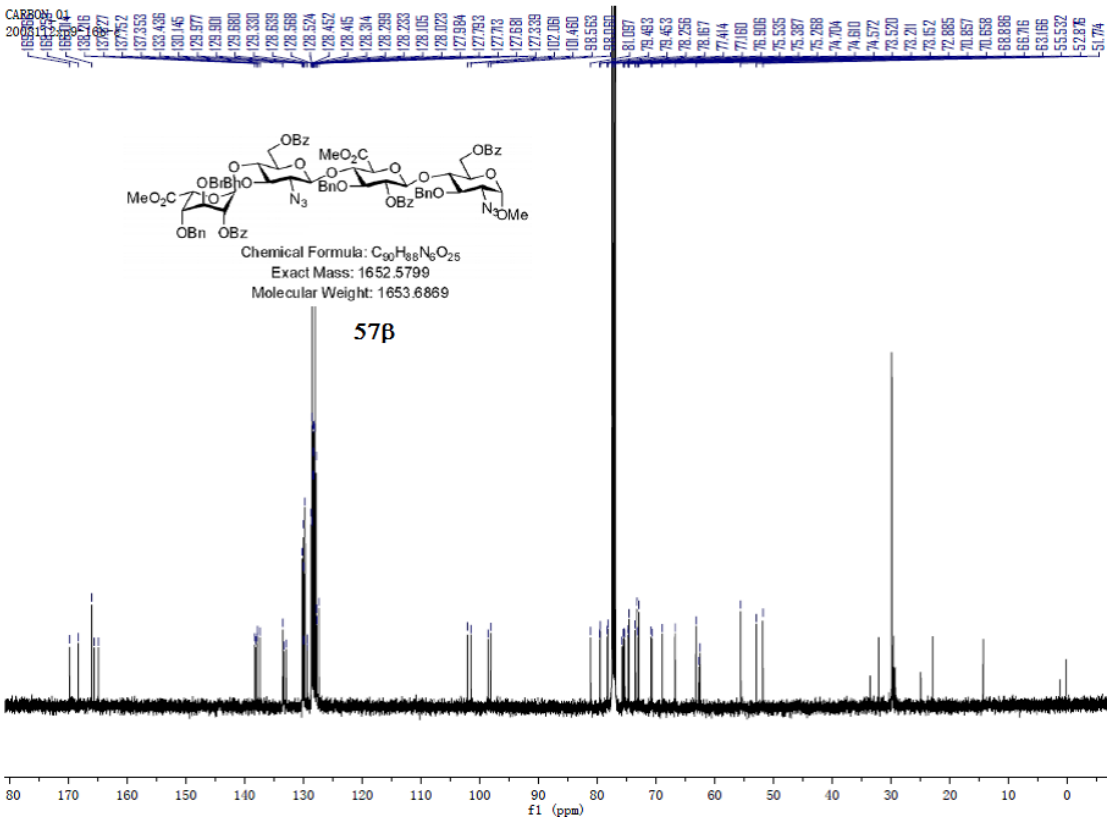
57α

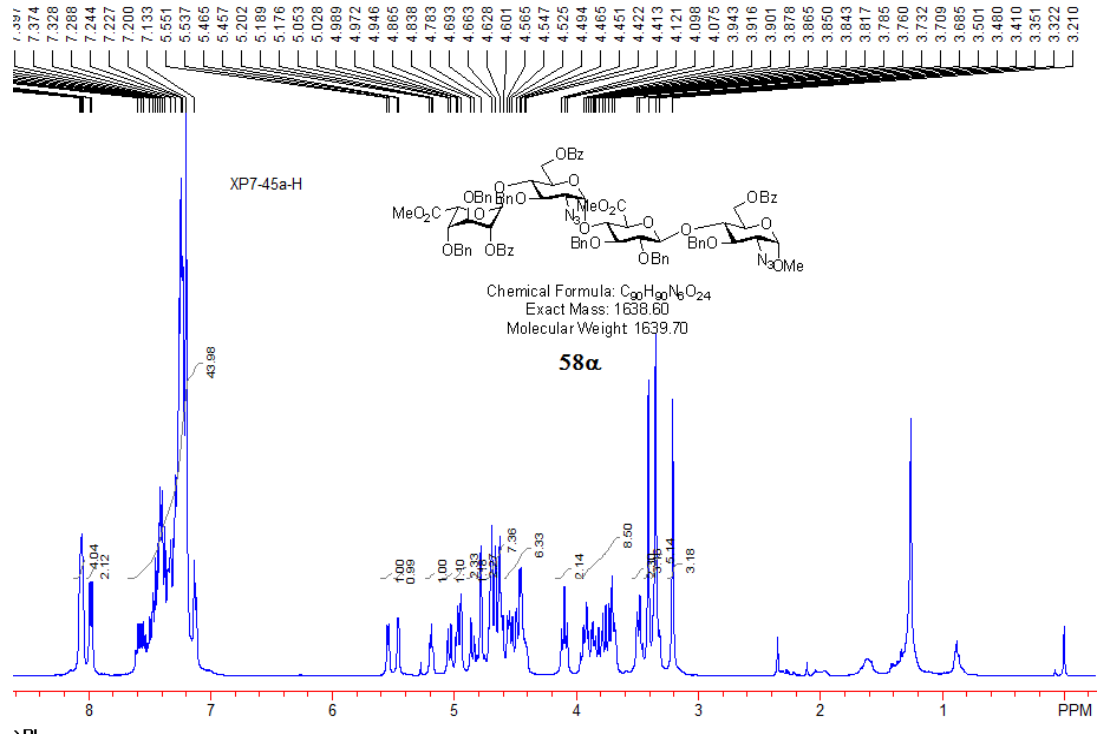
Chemical Formula: $C_{90}H_{88}N_6O_{25}$

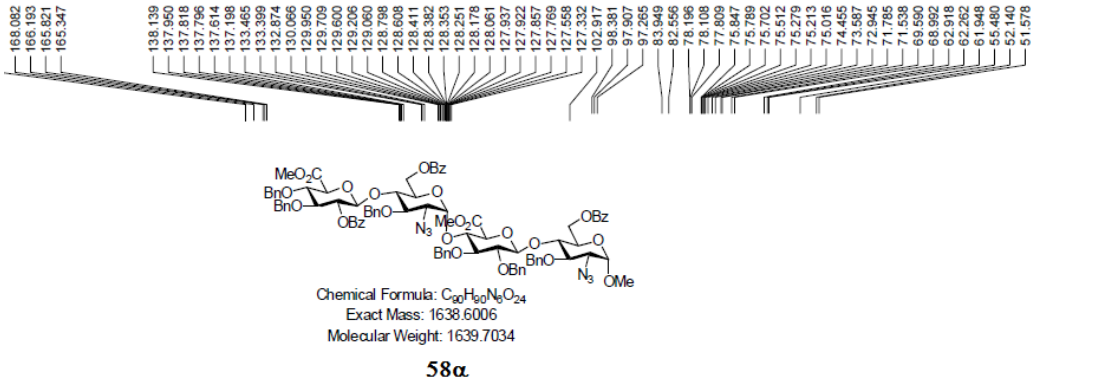
Exact Mass: 1652.5799

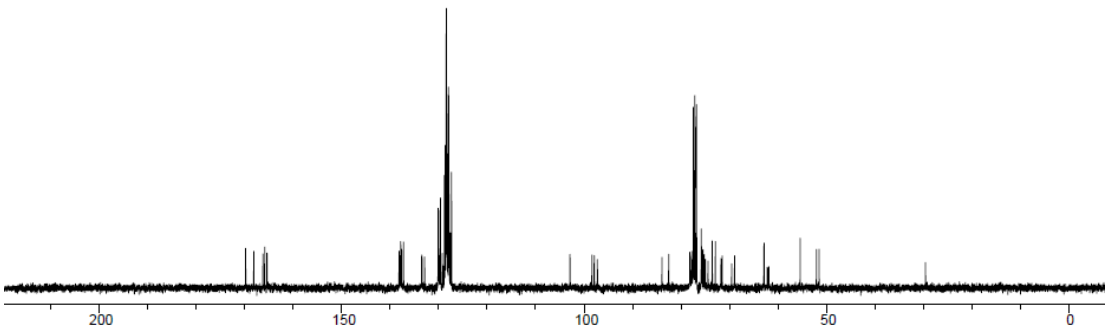
Molecular Weight: 1653.6869

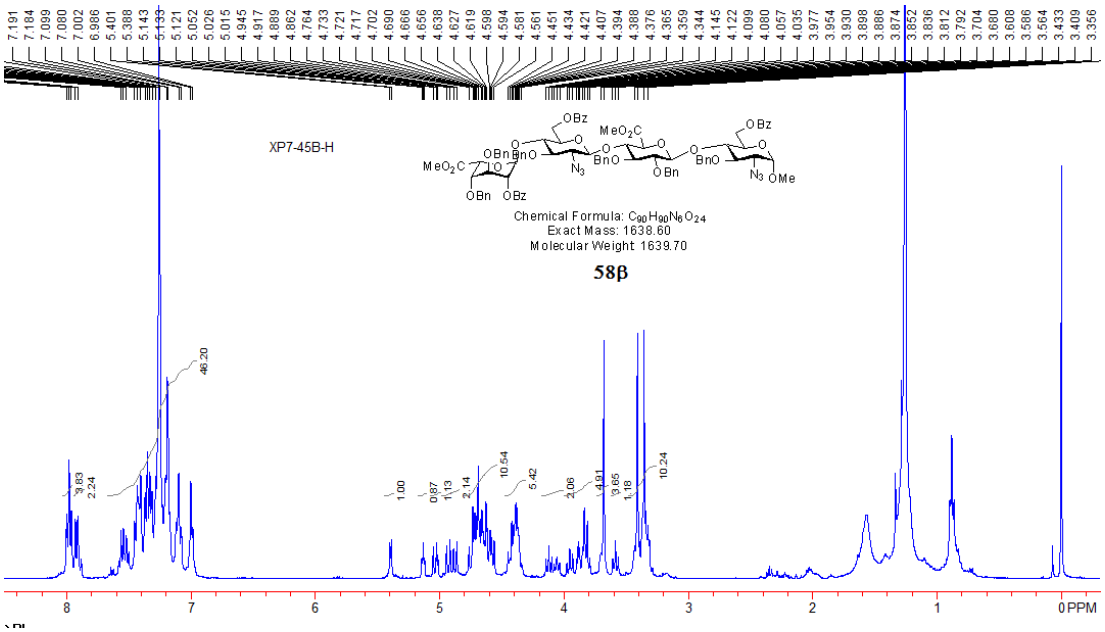

Chemical Formula: C90H88N6O25
Exact Mass: 1652.5799
Molecular Weight: 1653.6869
57β

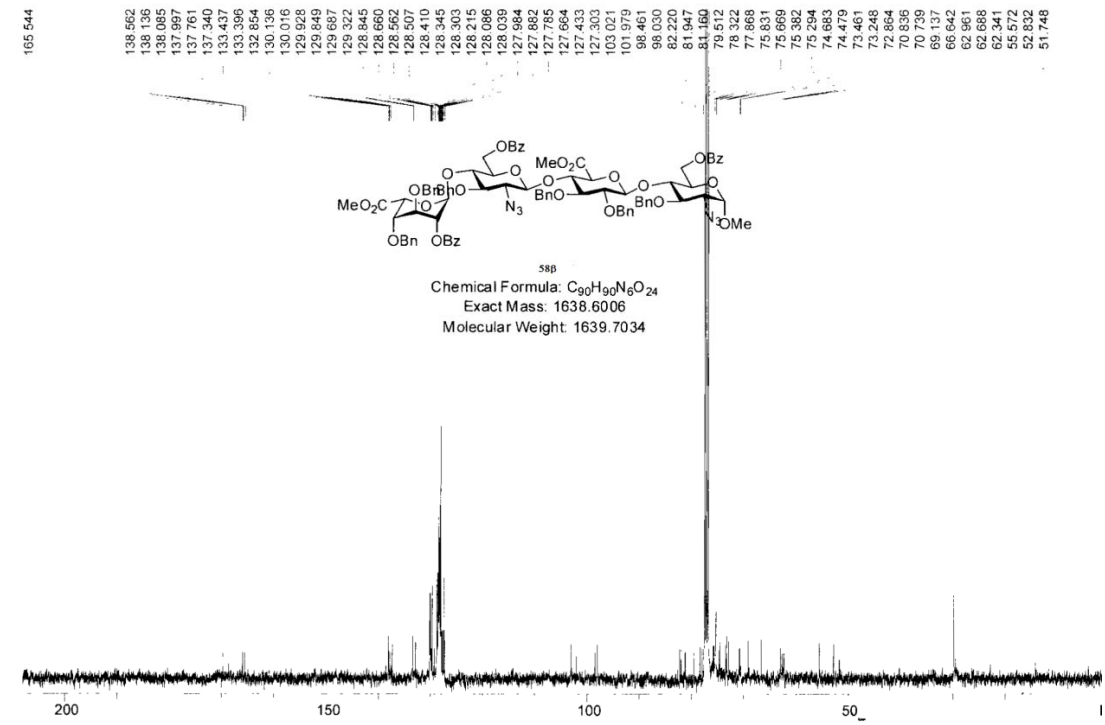

Chemical Formula: C90H88N6O25
Exact Mass: 1652.5799
Molecular Weight: 1653.6869
57β

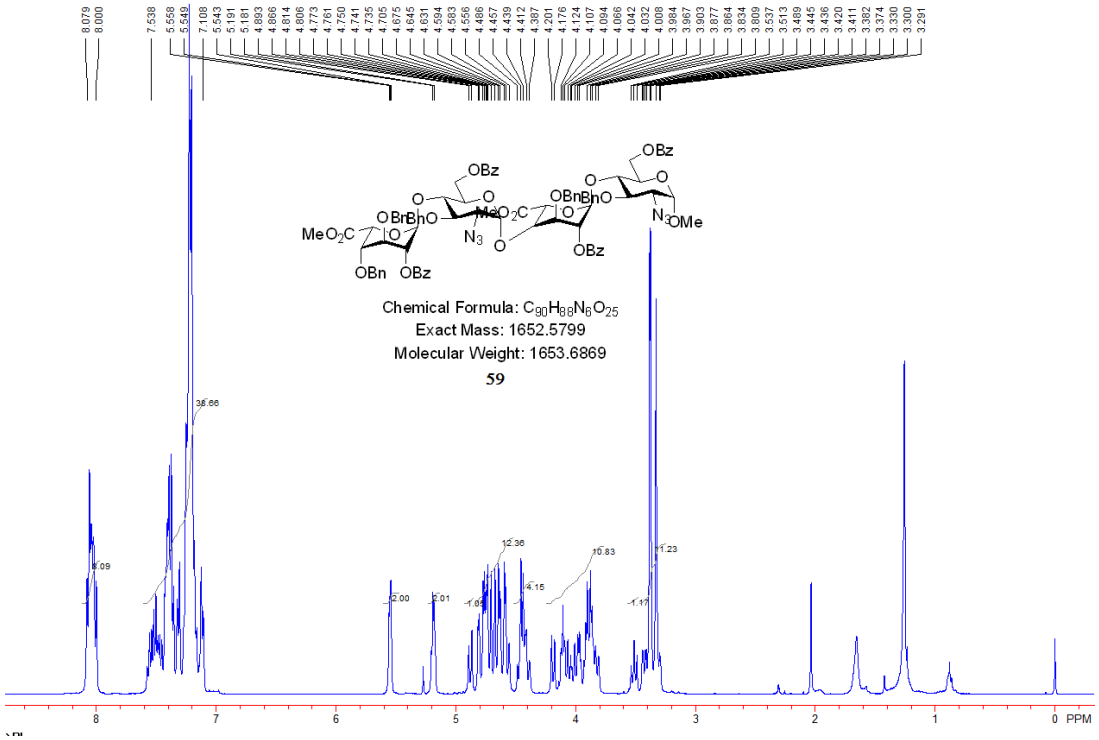

XP7-45a-H
Chemical Formula: C90H90N6O24
Exact Mass: 1638.60
Molecular Weight 1639.70
58α
PPM

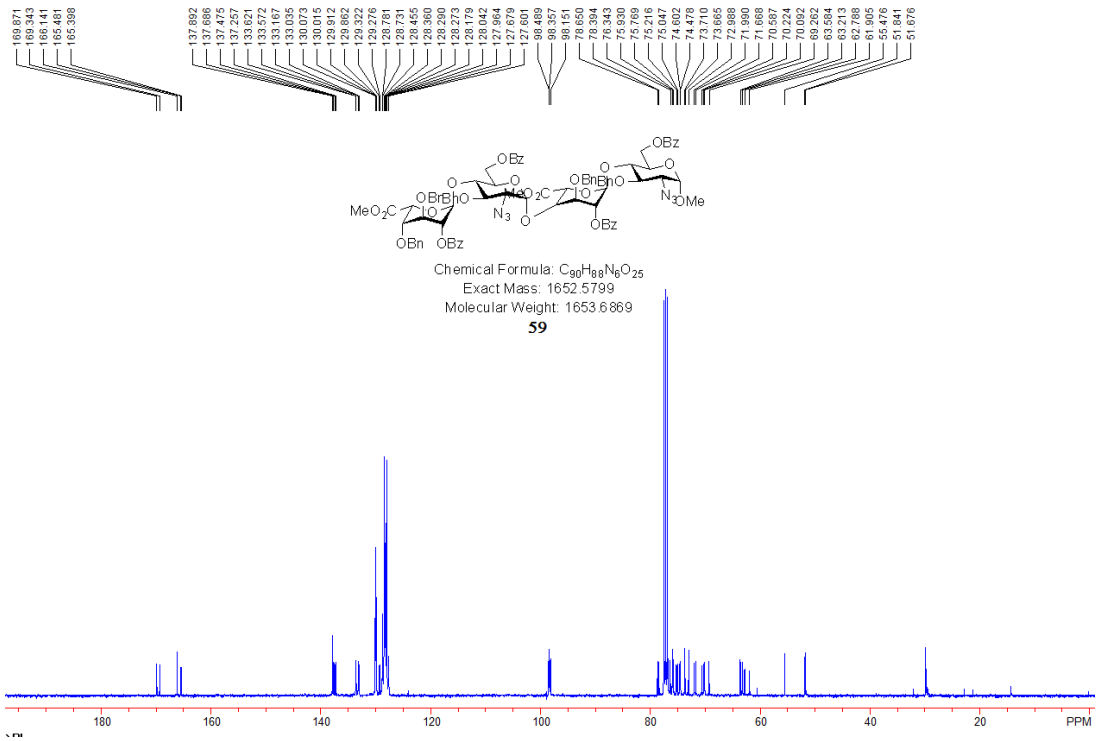

Chemical Formula: C90H90N6O24
Exact Mass: 1638.6006
Molecular Weight: 1639.7034
58α

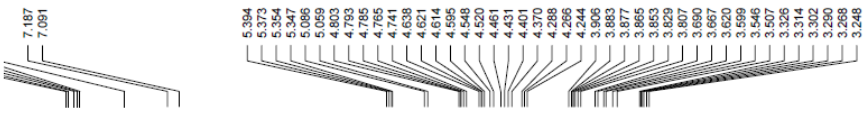


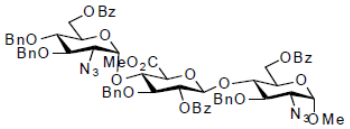

XP7-45B-H
Chemical Formula: C90H90N6O24
Exact Mass: 1638.60
Molecular Weight 1639.70
58β


58β
Chemical Formula: C90H90N6O24
Exact Mass: 1638.6006
Molecular Weight: 1639.7034


Chemical Formula: C90H88N6O25
Exact Mass: 1652.5799
Molecular Weight: 1653.6869
59
PPM

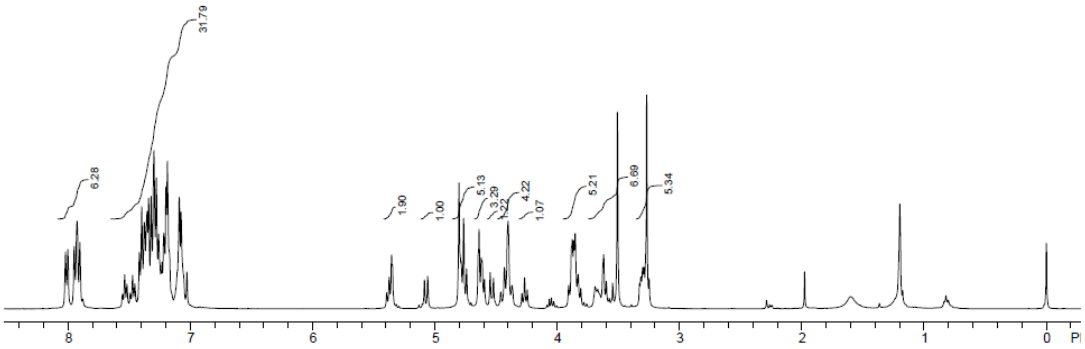

Chemical Formula: C90H88N6O25
Exact Mass: 1652.5799
Molecular Weight: 1653.6869
59
PPM

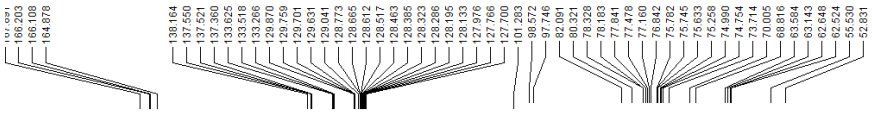


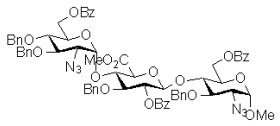


60α

Chemical Formula: $C_{69}H_{68}N_6O_{18}$
Exact Mass: 1268.4590
Molecular Weight: 1269.3076

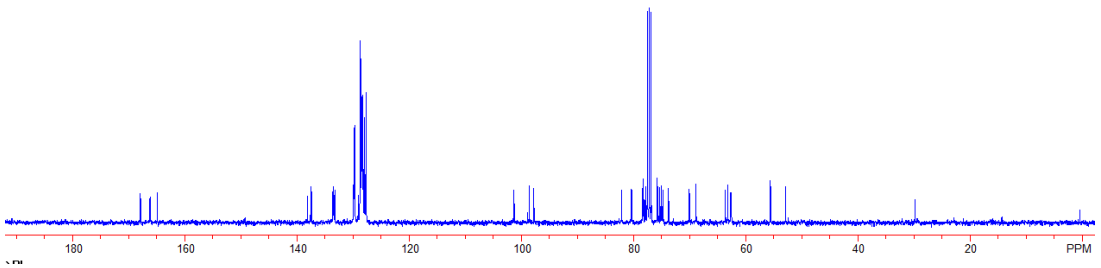


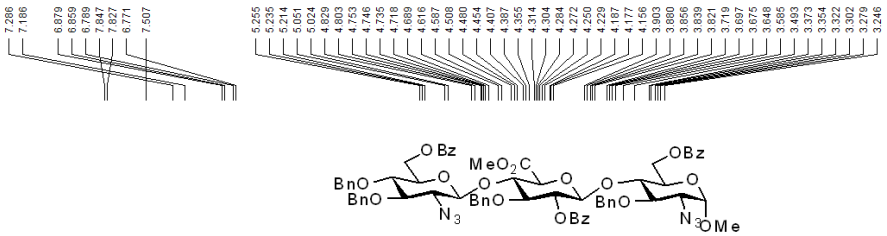




60α

Chemical Formula: $C_{69}H_{68}N_6O_{18}$
Exact Mass: 1268.4590
Molecular Weight: 1269.3076



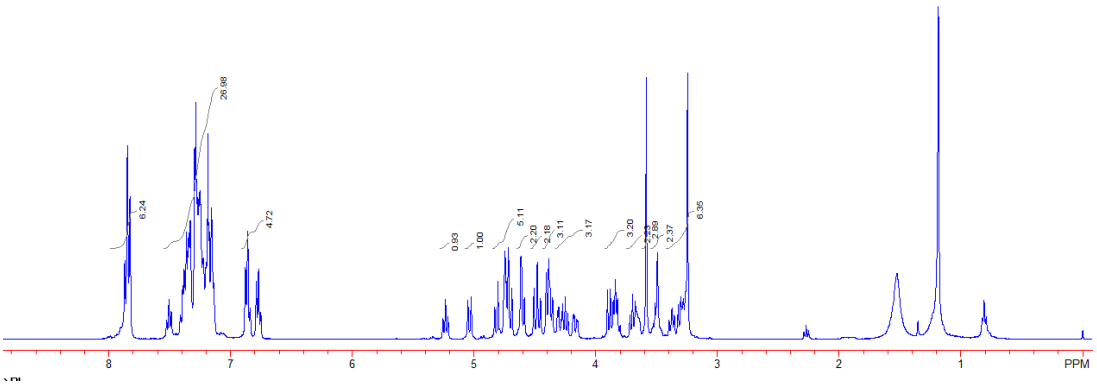


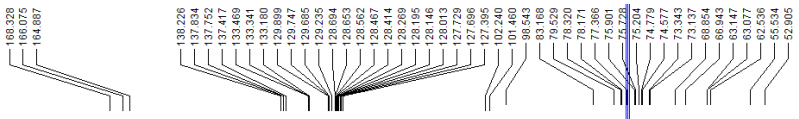
60β

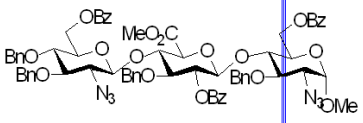
Chemical Formula: $C_{69}H_{68}N_6O_{18}$

Exact Mass: 1268.4590

Molecular Weight: 1269.3076





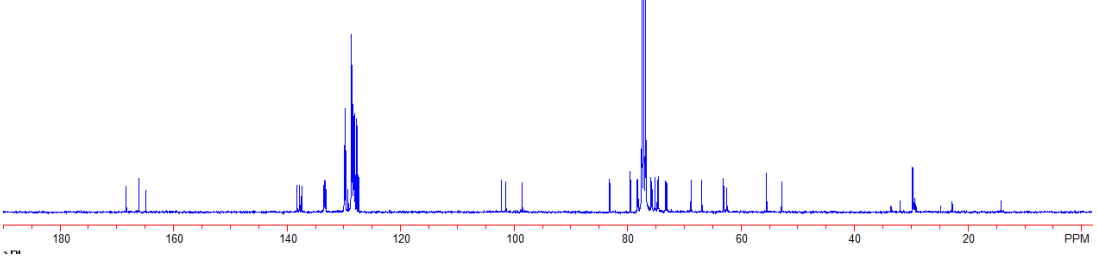


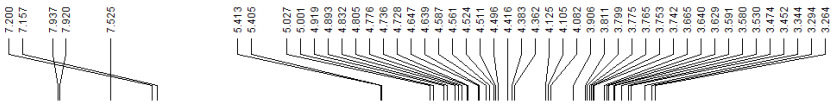
60β

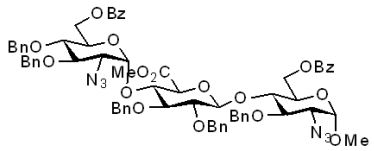
Chemical Formula: $C_{69}H_{68}N_6O_{18}$

Exact Mass: 1268.4590

Molecular Weight: 1269.3076

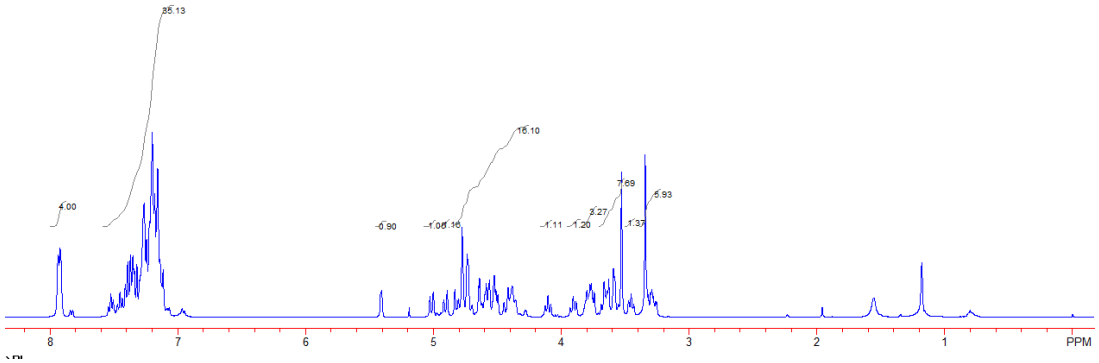


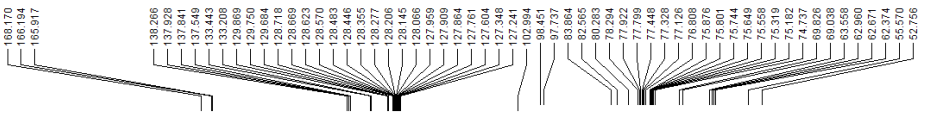


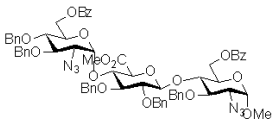


61

Chemical Formula: $C_{69}H_{70}N_6O_{17}$
Exact Mass: 1254.4797
Molecular Weight: 1255.3241

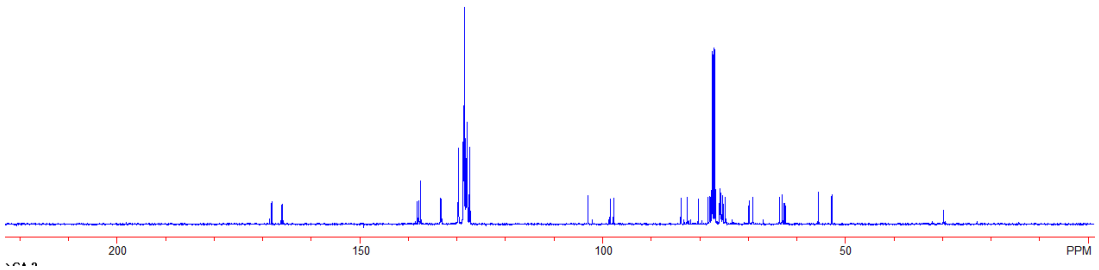


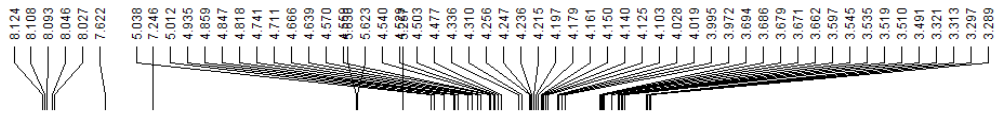


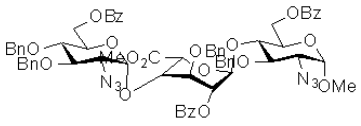


61

Chemical Formula: $C_{69}H_{70}N_6O_{17}$
Exact Mass: 1254.4797
Molecular Weight: 1255.3241





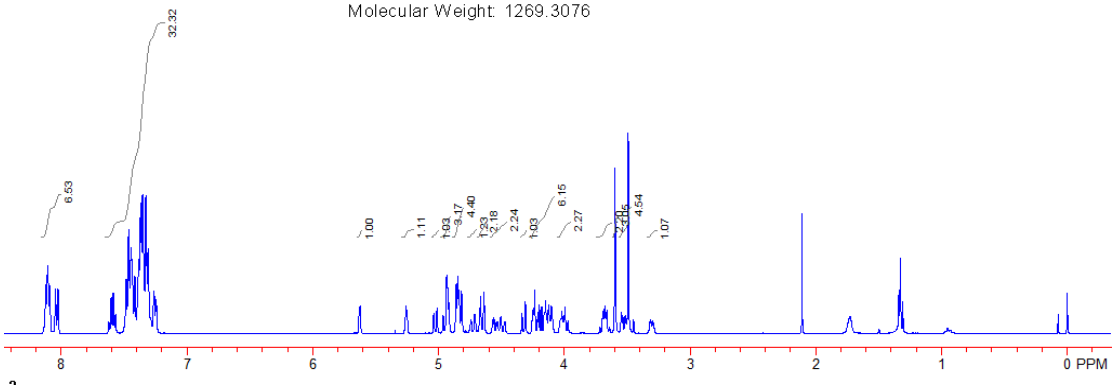


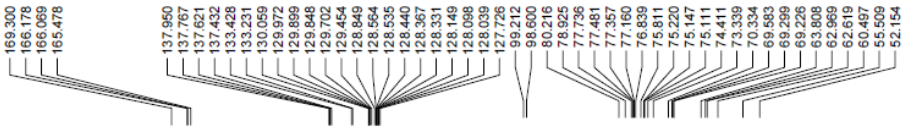
62α

Chemical Formula: $C_{69}H_{68}N_6O_{18}$

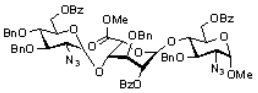
Exact Mass: 1268.4590

Molecular Weight: 1269.3076

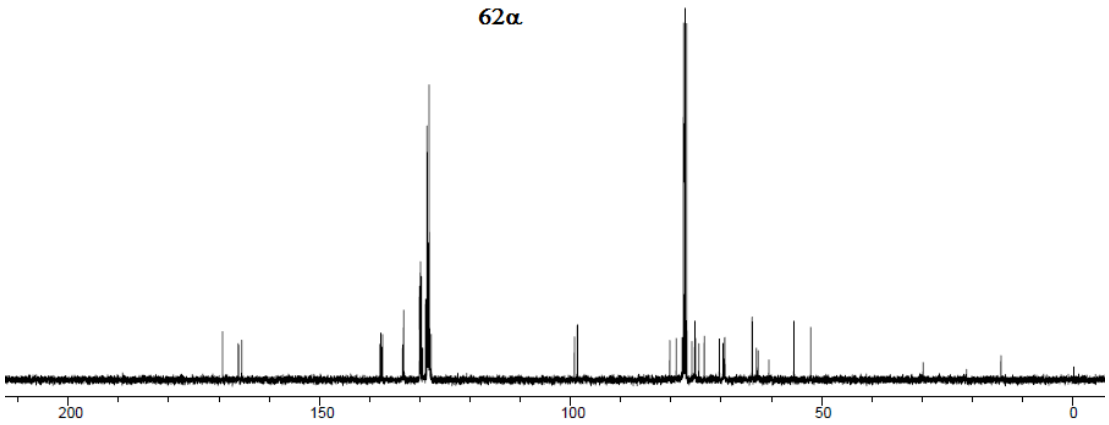


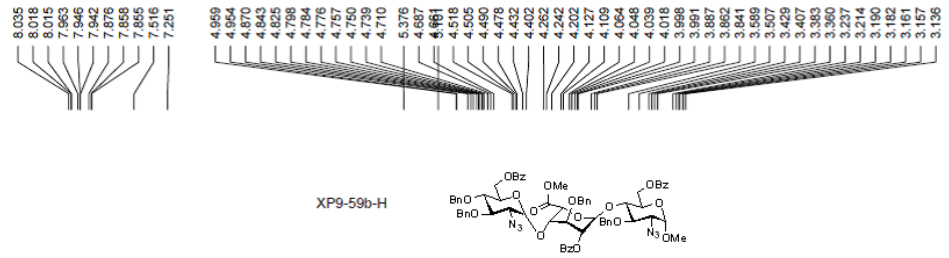


XP9-59a-C

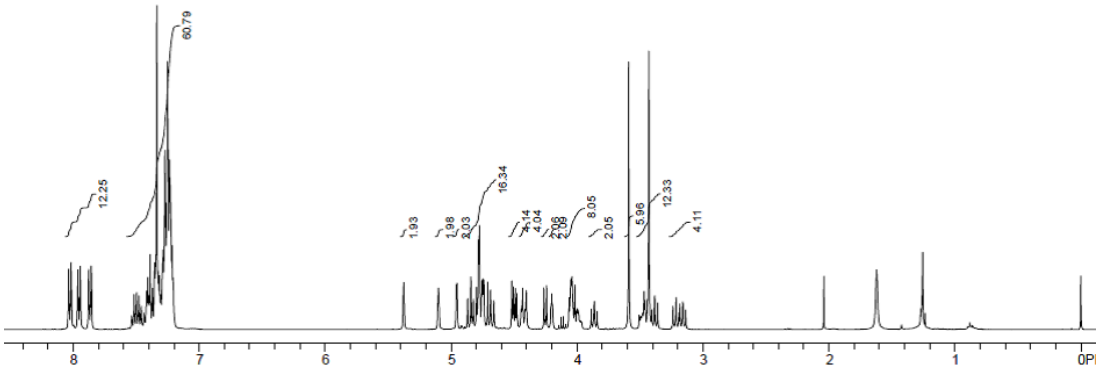


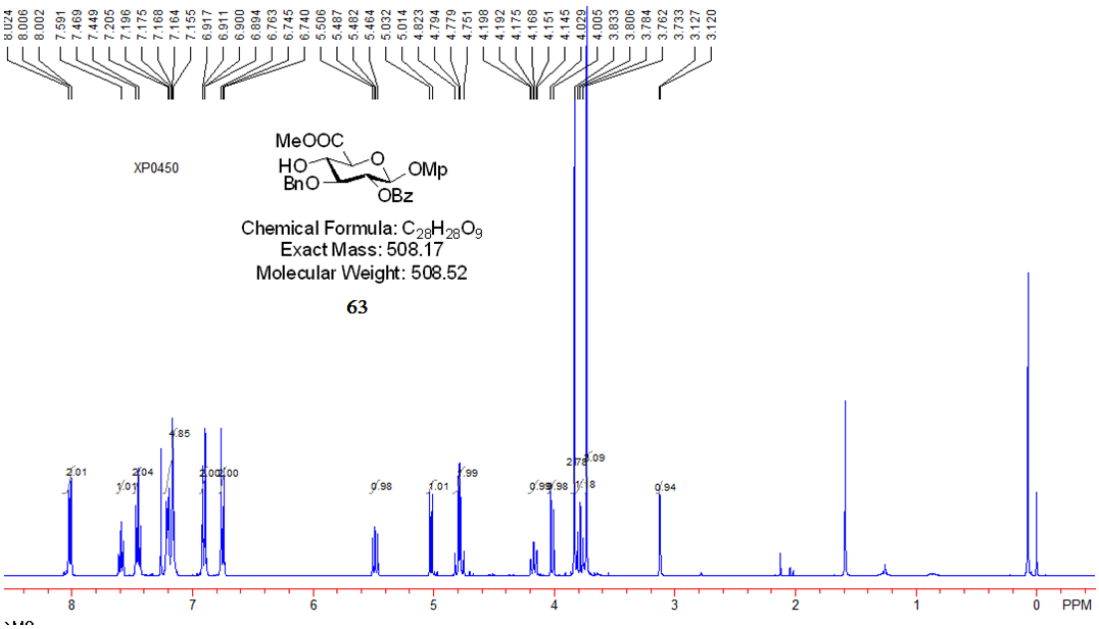
62α



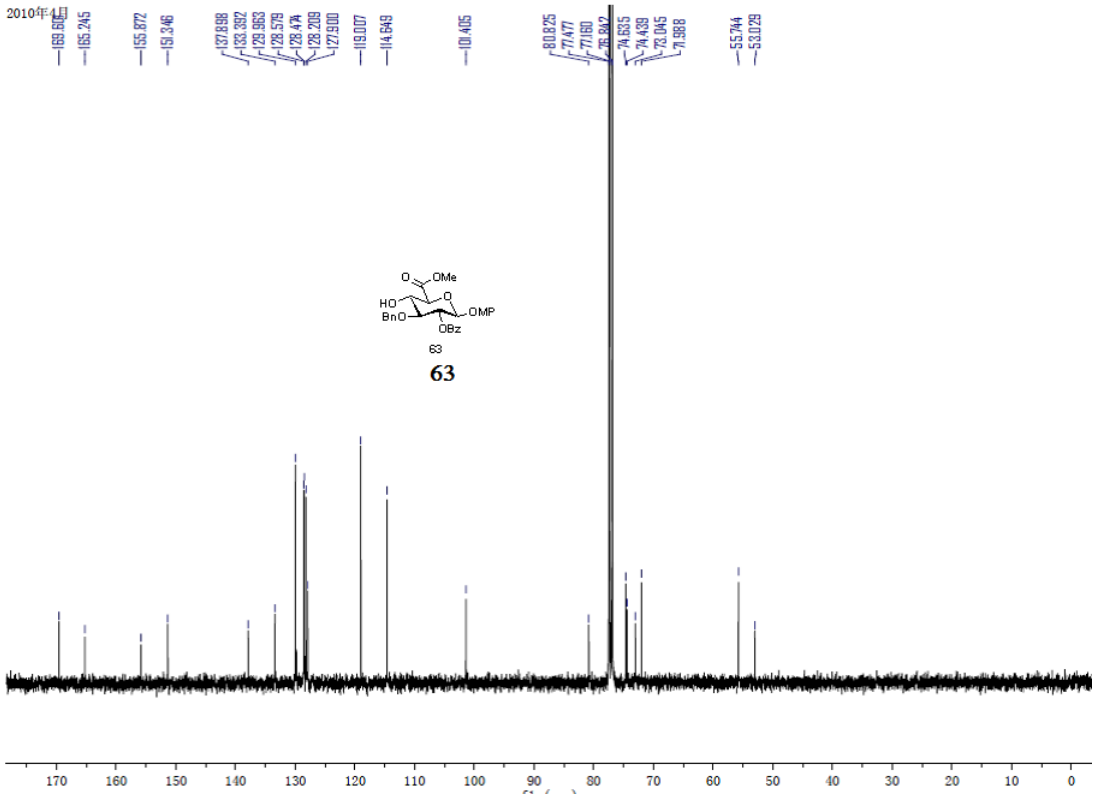

XP9-59b-H

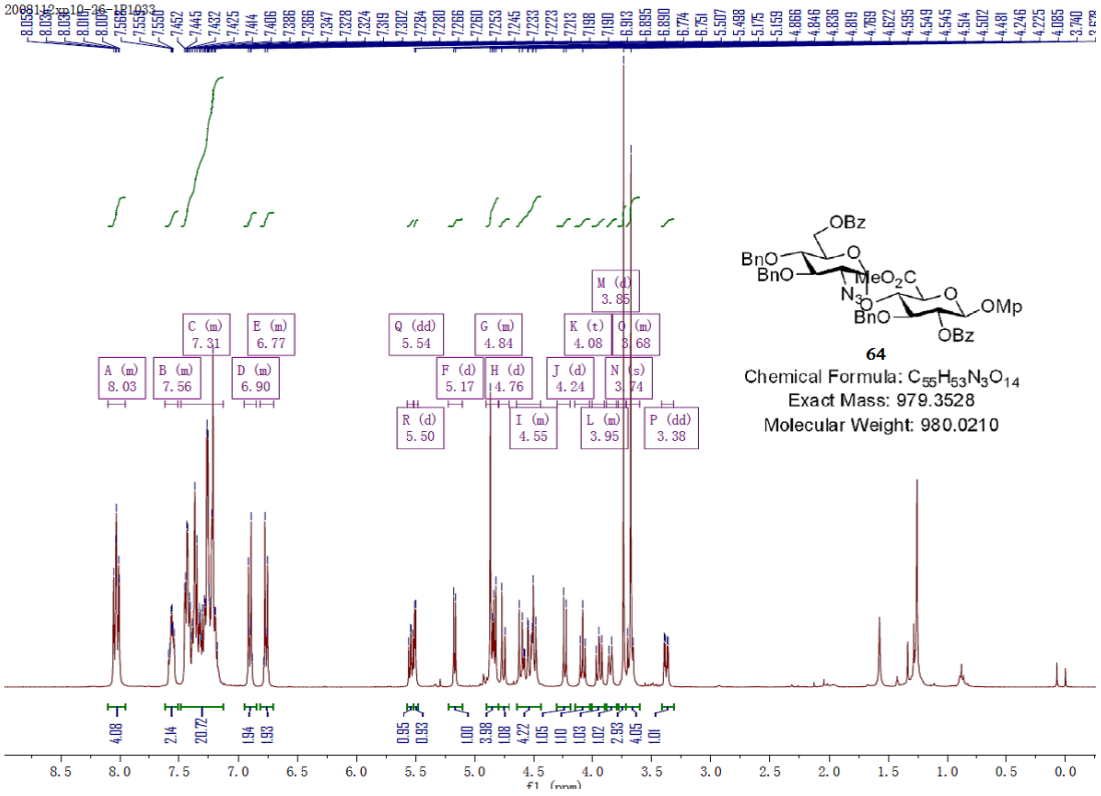
62β

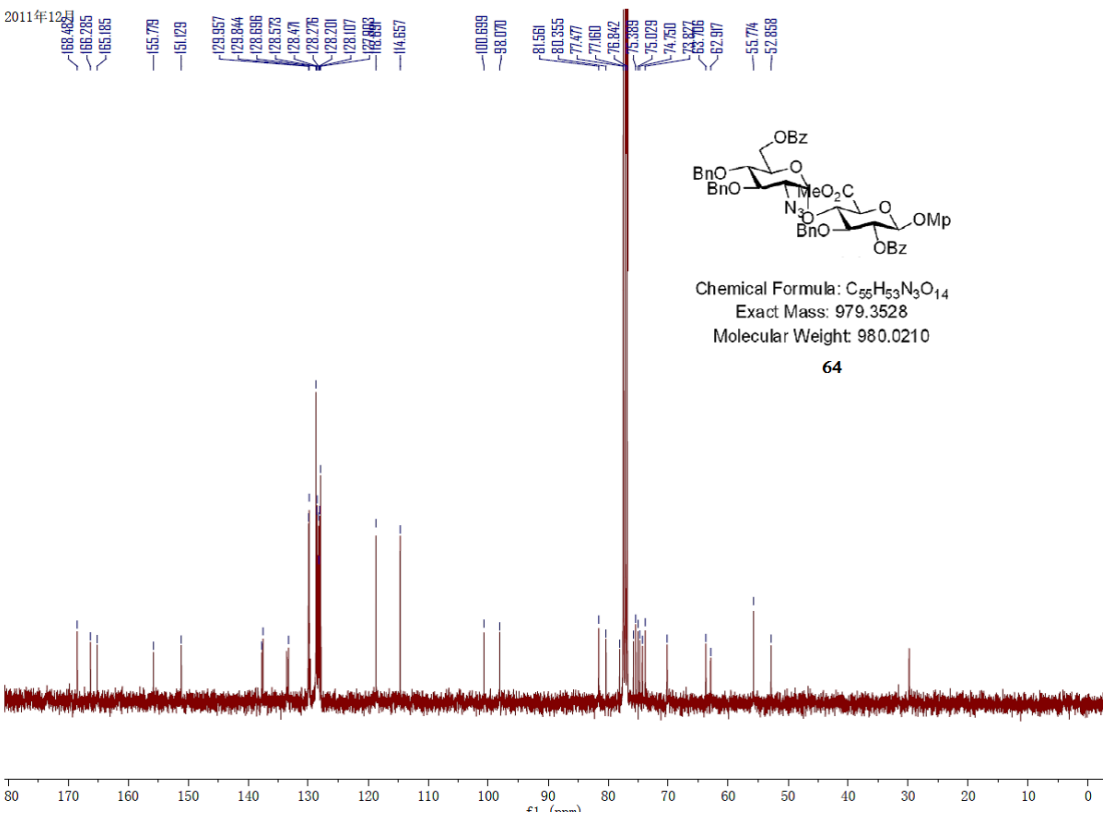


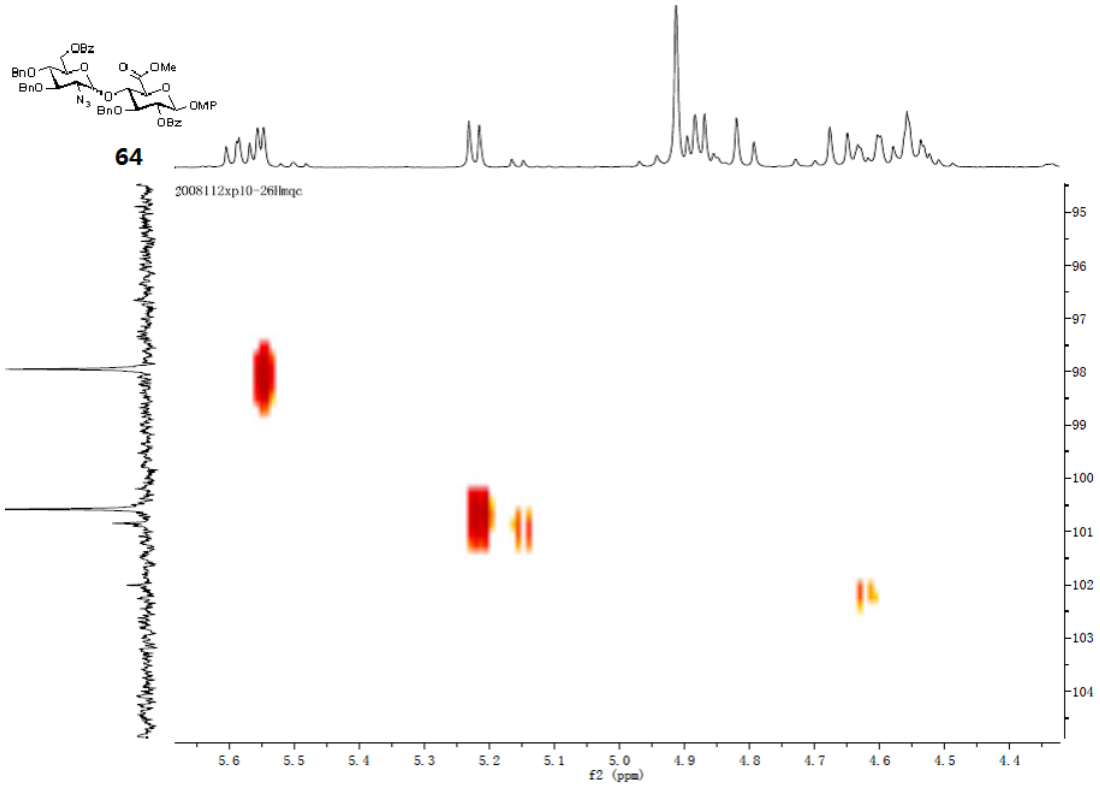

XP0450
MeOOC
HO
BnO
OMp
OBz
Chemical Formula: C28H28O9
Exact Mass: 508.17
Molecular Weight: 508.52
PPM

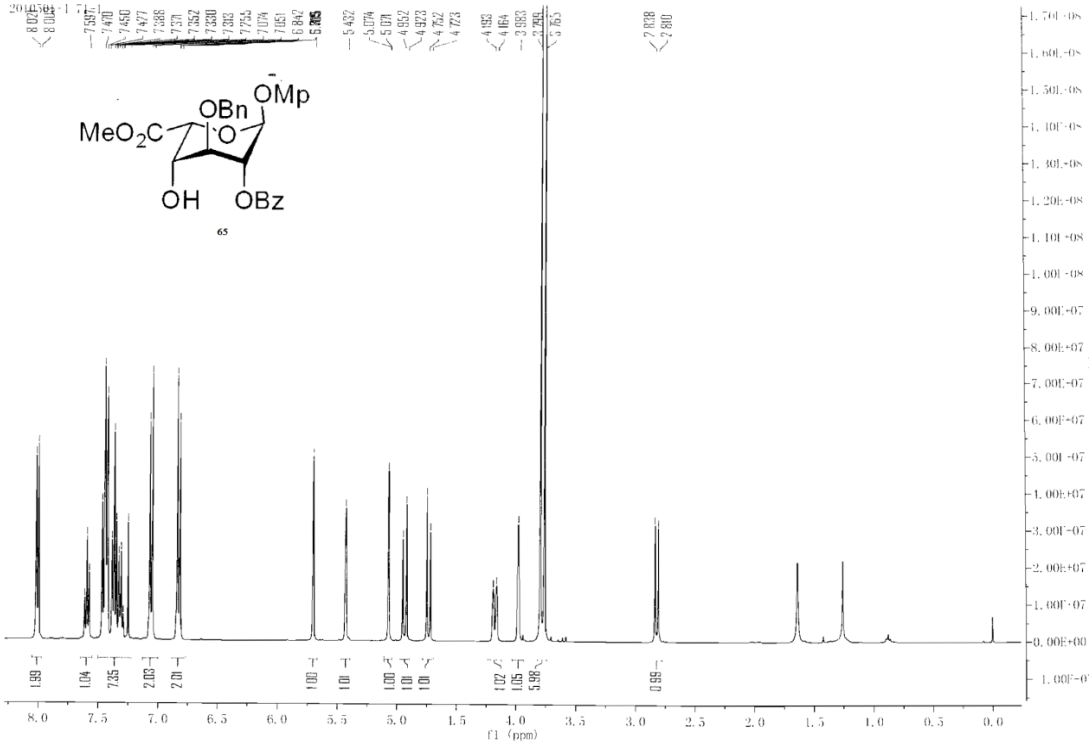
63

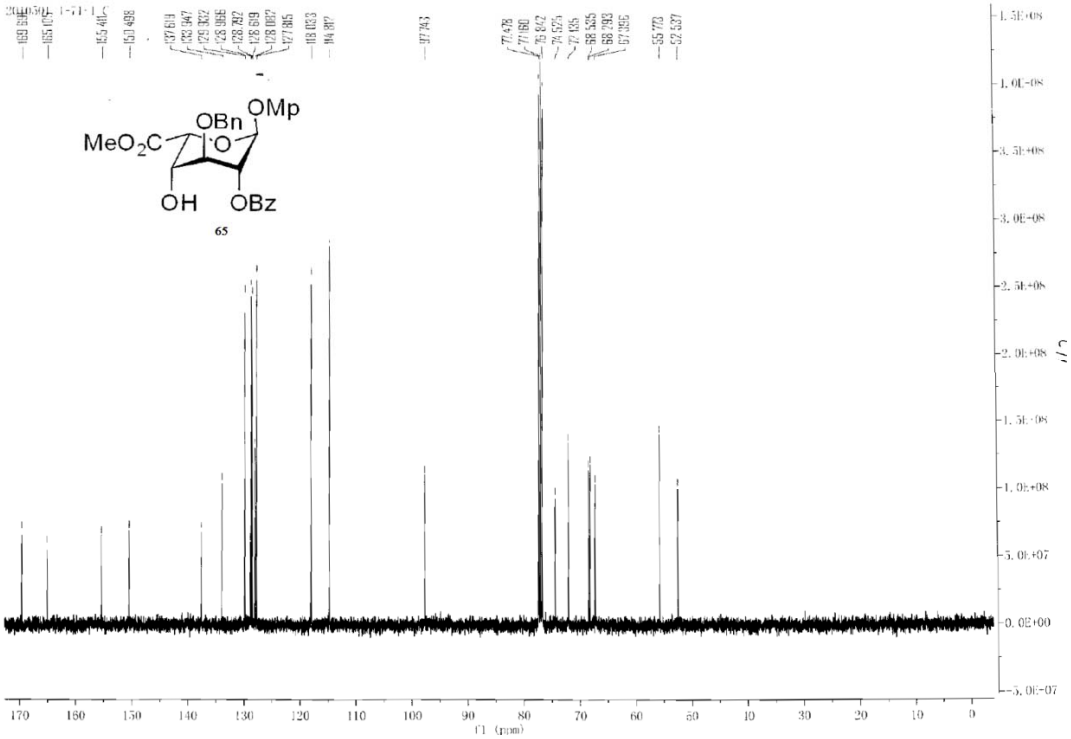

63
63

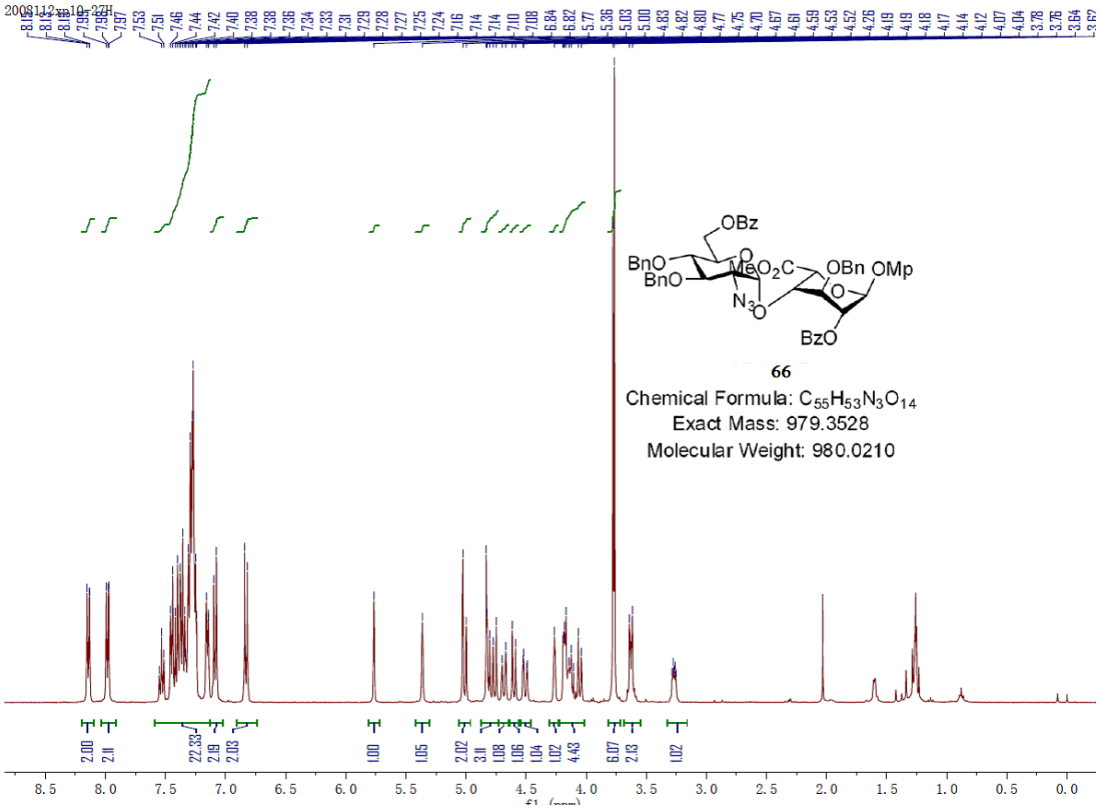

64
Chemical Formula: C55H53N3O14
Exact Mass: 979.3528
Molecular Weight: 980.0210

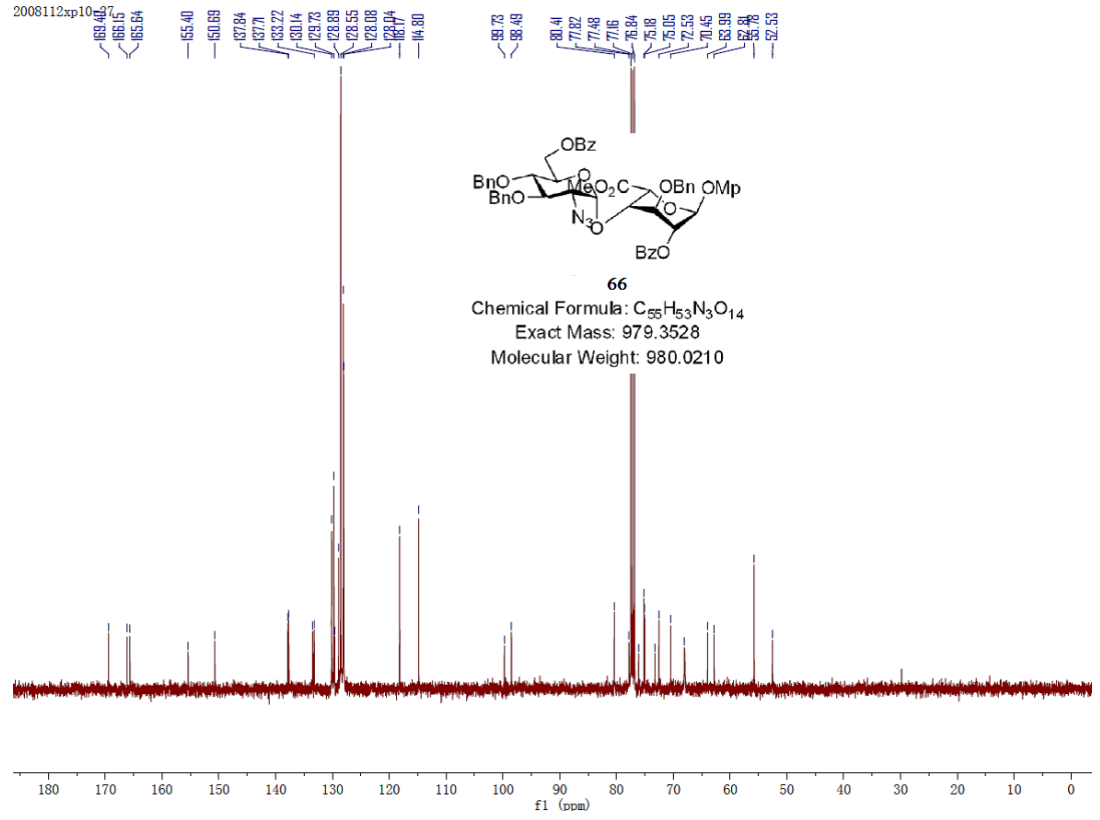

2011年12月
168.482
166.265
165.185
155.778
151.129
129.957
129.844
128.696
128.573
128.471
128.276
128.201
128.107
114.657
100.699
98.070
81.581
80.355
77.477
77.160
76.842
75.383
75.023
74.750
73.827
63.706
62.917
55.774
52.858
OBz
BnO
BnO
MeO2C
N3
O
BnO
OMp
OBz
Chemical Formula: C55H53N3O14
Exact Mass: 979.3528
Molecular Weight: 980.0210
64
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

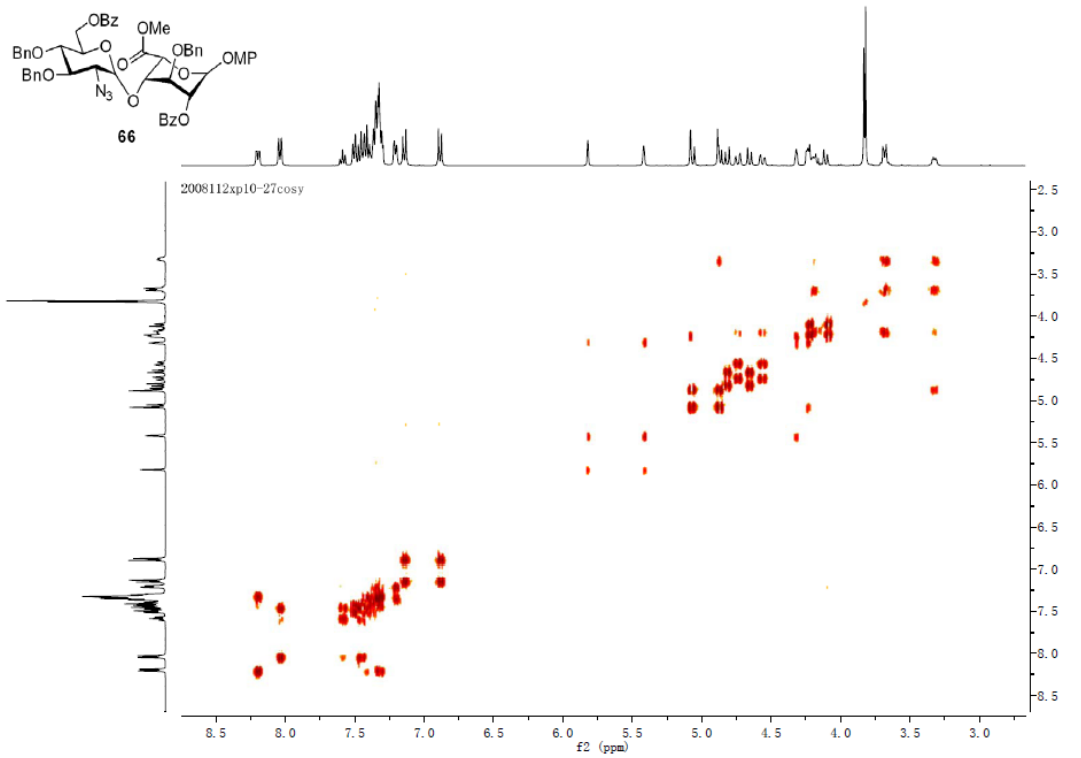

OBz
BnO
BnO
O
OMe
N3
O
BnO
OMP
OBz
64
2008112xp10-26ihmqc
95
96
97
98
99
100
101
102
103
104
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
f2 (ppm)

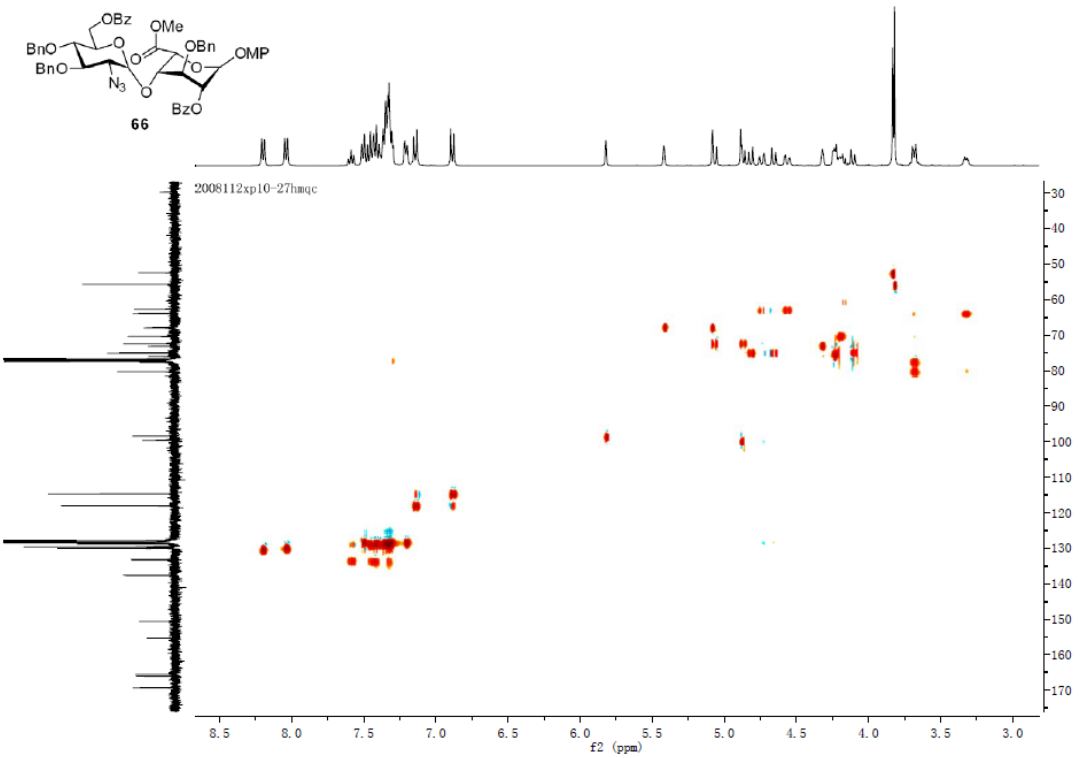

OBn
OMp
MeO2C
O
OH
OBz
65
f1 (ppm)

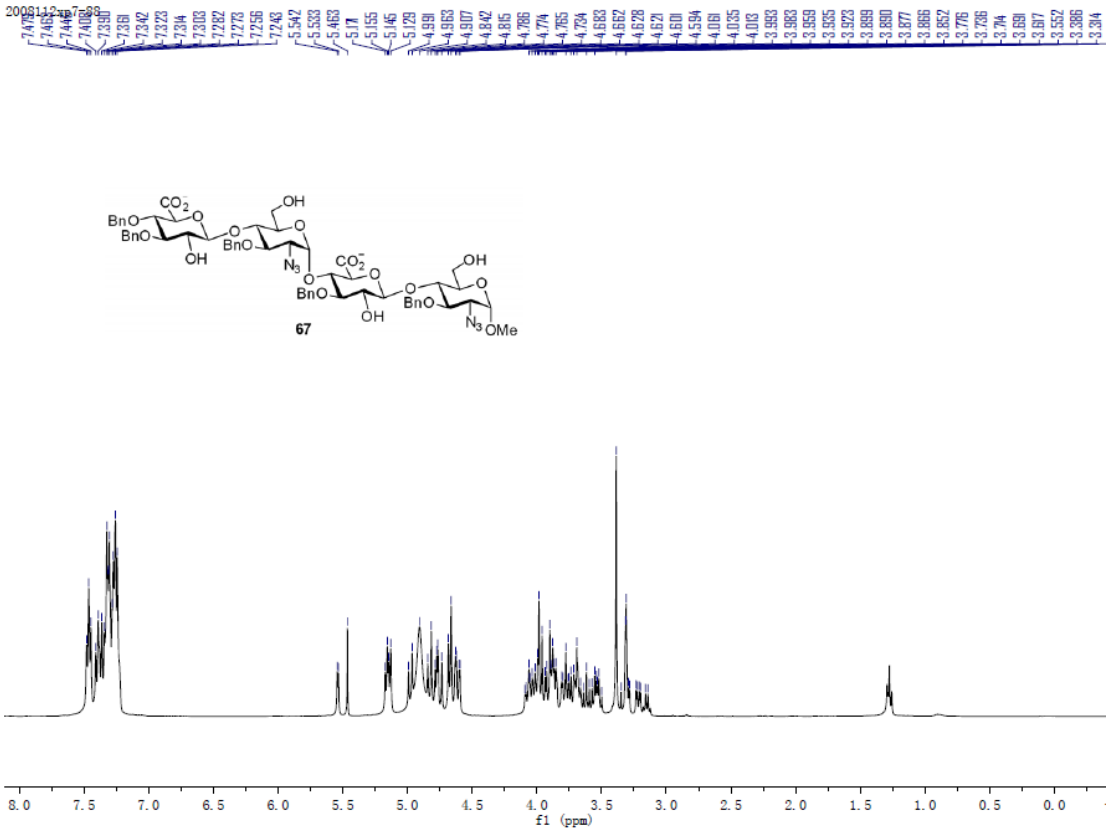

OBn
OMp
MeO2C
O
OH
OBz
65
f1 (ppm)

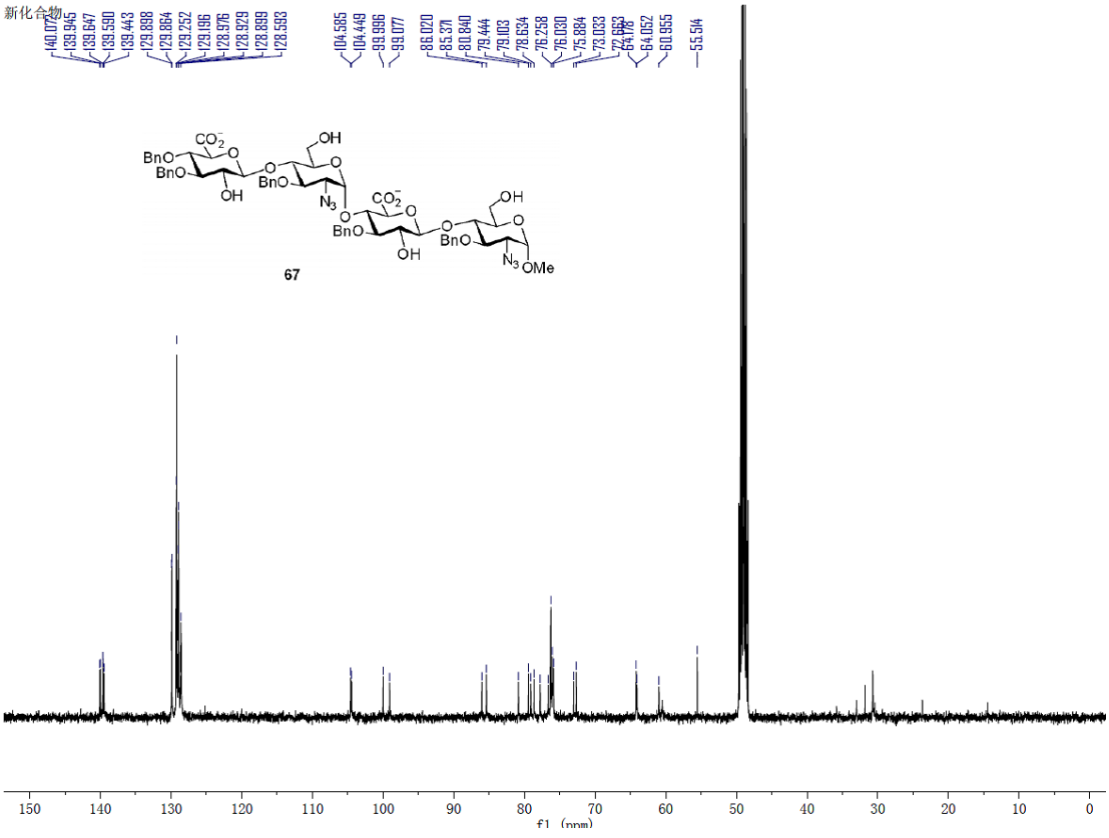

OBz
BnO
BnO
MeO2C
OBn OMp
N3
BzO
66
Chemical Formula: C55H53N3O14
Exact Mass: 979.3528
Molecular Weight: 980.0210

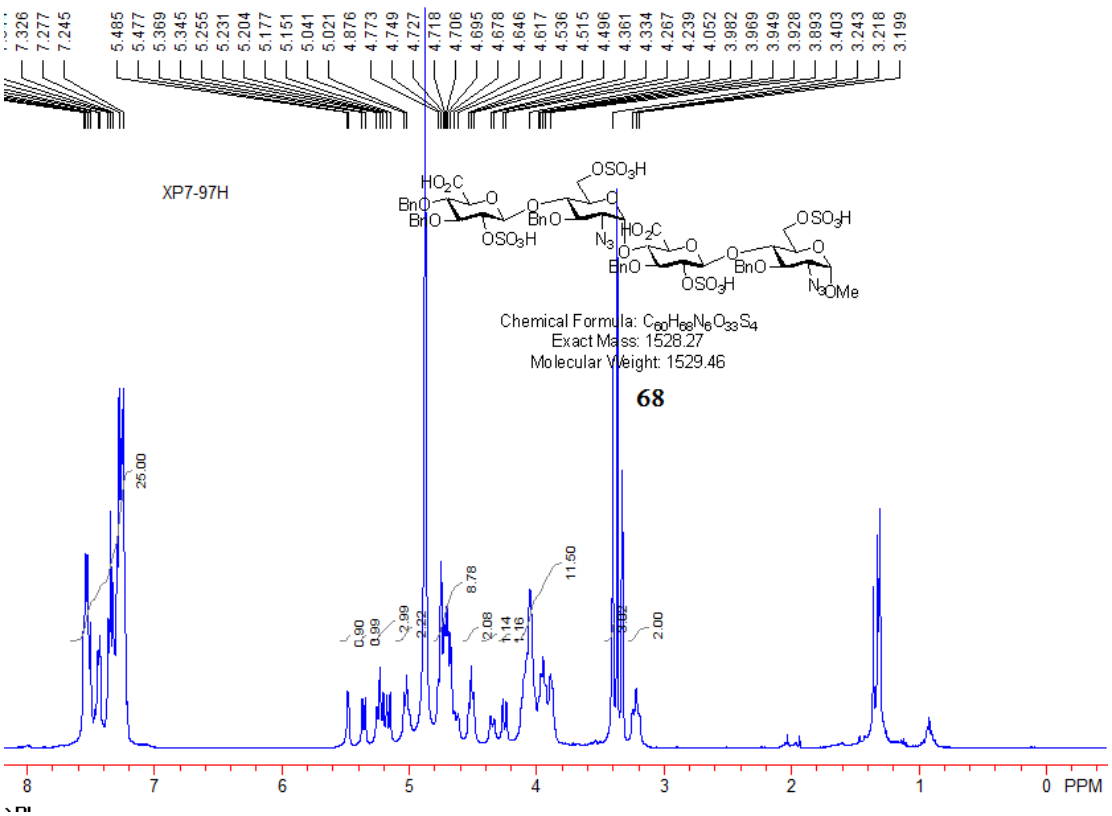

OBz
BnO
BnO
MeO2C
OBn OMp
N3
BzO
66
Chemical Formula: C55H53N3O14
Exact Mass: 979.3528
Molecular Weight: 980.0210
f1 (ppm)

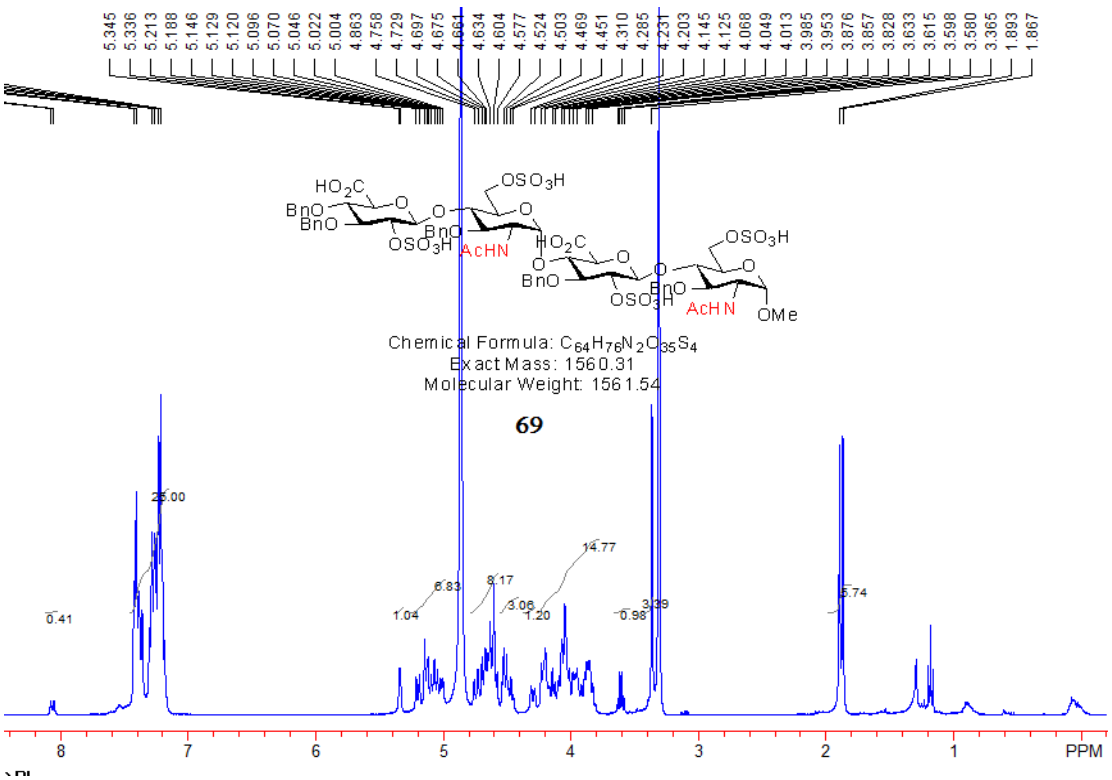

OBz
OMe
BnO
OBn
OMP
BnO
N3
O
BzO
66
2008112xp10-27cosy
f2 (ppm)

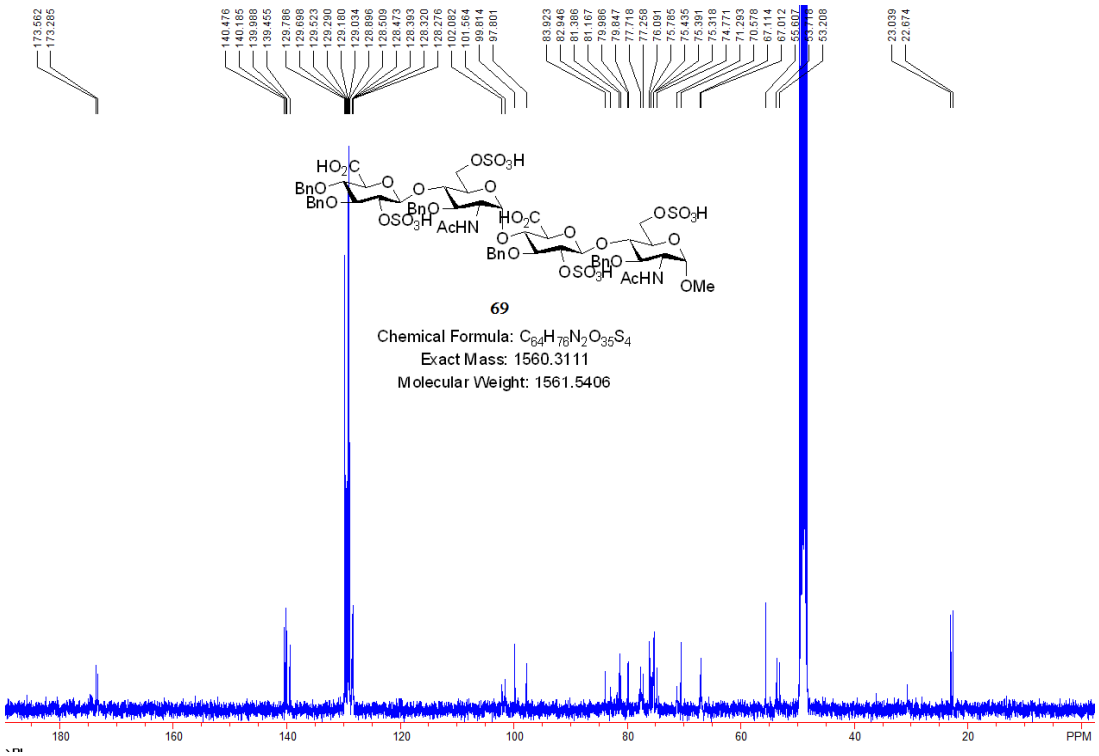

OBz
OMe
BnO
OBn
OMP
BnO
N3
O
BzO
66
2008112xp10-27hmqc
f2 (ppm)

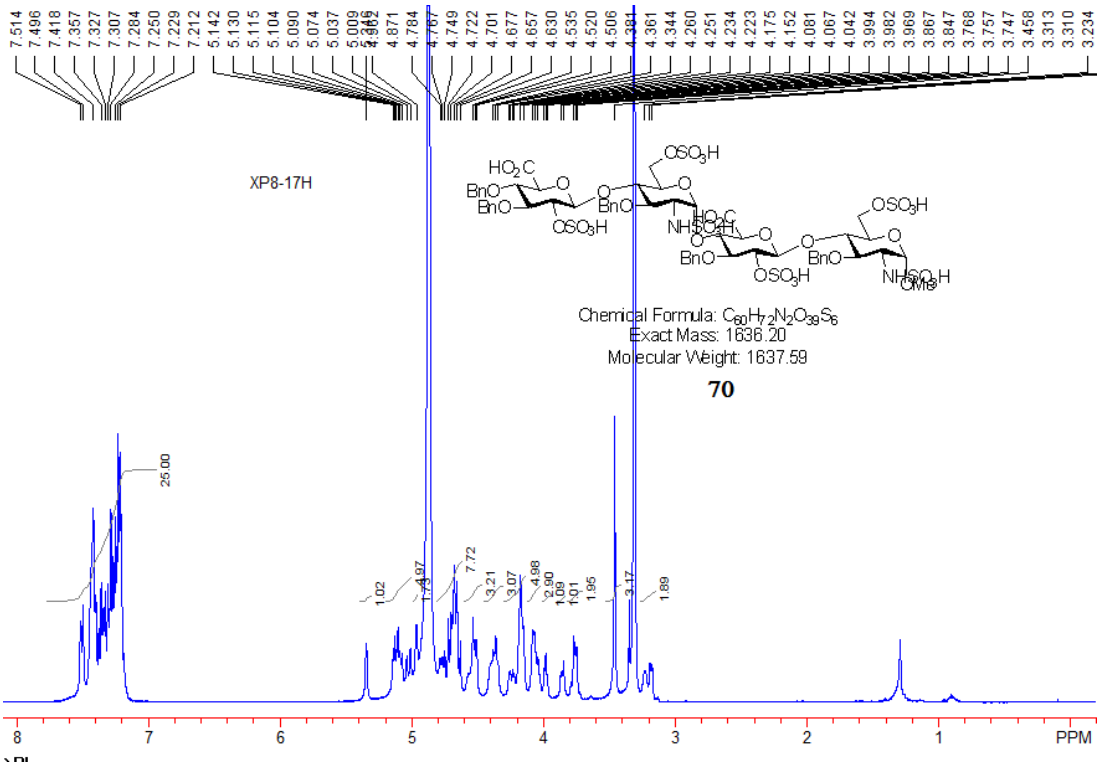

67
f1 (ppm)

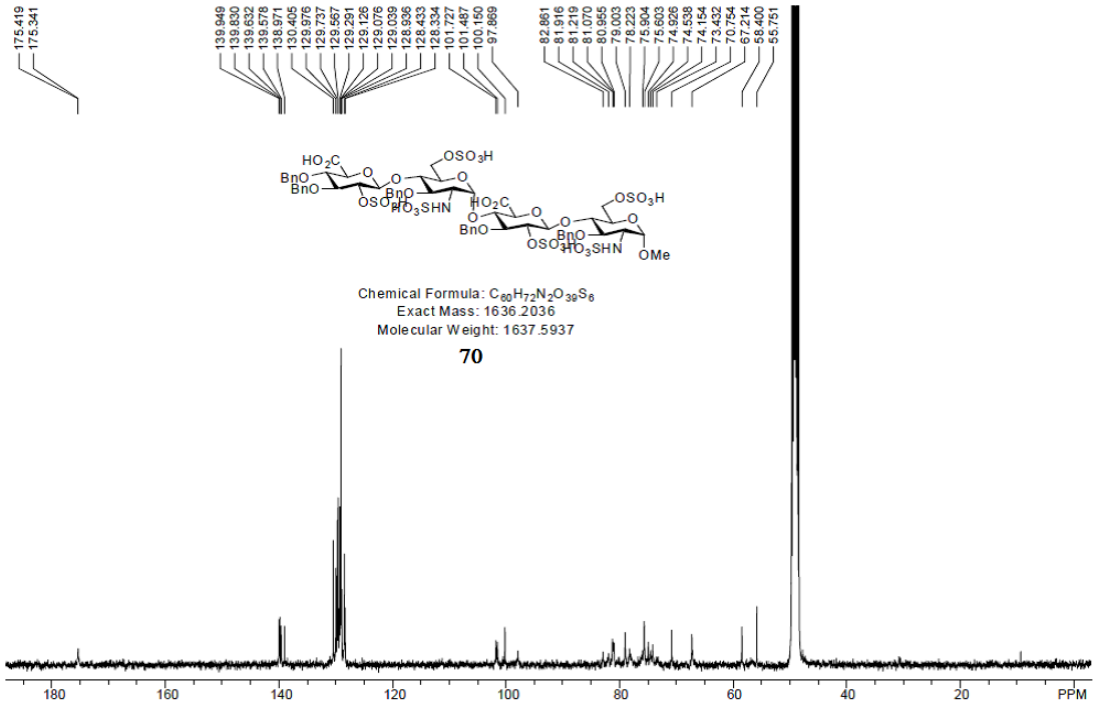

新化合物
67
f1 (ppm)


XP7-97H
Chemical Formula: C80H88N6O33S4
Exact Mass: 1528.27
Molecular Weight: 1529.46
68
PPM


Chemical Formula: C64H76N2O35S4
Exact Mass: 1560.31
Molecular Weight: 1561.54
69
PPM


69
Chemical Formula: $C_{84}H_{76}N_2O_{35}S_4$
Exact Mass: 1560.3111
Molecular Weight: 1561.5406


XP8-17H
Chemical Formula: $C_{60}H_{72}N_2O_{39}S_6$
Exact Mass: 1636.20
Molecular Weight: 1637.59
70


175.419
175.341
139.949
139.830
139.632
139.578
138.971
130.405
129.976
129.737
129.567
129.291
129.126
129.076
129.039
128.936
128.433
128.334
101.727
101.487
100.150
97.869
82.861
81.916
81.219
81.070
80.955
79.003
78.223
75.904
75.603
74.926
74.538
74.154
73.432
70.754
67.214
58.400
55.751
Chemical Formula: C60H72N2O39S6
Exact Mass: 1636.2036
Molecular Weight: 1637.5937
180
160
140
120
100
80
60
40
20
PPM

70