Supporting Information

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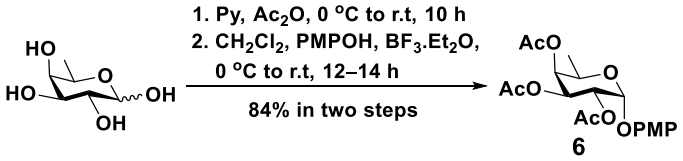
General methods

Chemicals were purchased and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz Brucker Avance III and 800 MHz Bruker Avance III spectrometers. High resolution electrospray ionization (ESI) mass spectra were obtained using Thermo Electron LTQ-Orbitrap Hybrid MS at the Mass Spectrometry Facility in the University of California, Davis. Silica gel 60 Å (230–400 mesh, Sorbent Technologies) was used for flash column chromatography. Thin-layer chromatography (TLC, Sorbent Technologies) was performed on silica gel plates using anisaldehyde sugar staining or 5% sulfuric acid in ethanol staining for detection. Gel filtration chromatography was performed with a column (100 cm × 2.5 cm) packed with Bio-Gel P-2 Fine resins (Bio-Rad). Sodium pyruvate was from Sigma, CTP was from Chemfun Medical Technology Co. *Arthrobacter ureafaciens* sialidase, *Vibrio cholerae* sialidase, and *Clostridium perfringens* sialidase (CpNanH) were purchased from Prozyme (Hayward, CA, USA). Recombinant *Pasteurella multocida* sialic acid aldolase (PmAldolase),[1] *Escherichia coli* sialic acid aldolase,[2] *Neisseria meningitidis* CMP-sialic acid synthetase (NmCSS),[2] *Pasteurella multocida* sialyltransferase 1 (PmST1),[3] PmST1 M144D mutant,[4] *Photobacterium sp*. JH-ISH-224 α2–6-sialyltransferase (Psp2,6ST),[5] *Photobacterium damselae* α2–6-sialyltransferase (Pd2,6ST),[6] human cytosolic sialidase hNEU2,[7] *Bifidobacterium infantis* sialidase BiNanH2,[8] *Streptococcus pneumoniae* sialidases SpNanA,[9] SpNanB,[9] and SpNanC[10] were expressed and purified as described previously. Neu5Acα2–3Galβ*p*NP and Neu5Acα2–6Galβ*p*NP were synthesized as described previously.[11]

Chemical synthesis of 6deoxyMan2,4diN_3 (9) and 6deoxyManNAc4NAc (4)

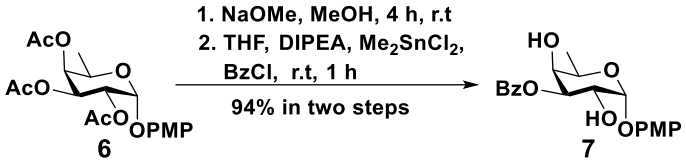
***p*-Methoxy phenyl-2,3,4-tri-*O*-acetyl-α-D-fucopyranoside (6)[12]**



To a solution of D-fucose (5 g, 30.48 mmol) in 30 mL pyridine at 0 °C, 25 mL acetic anhydride was added dropwise. After stirring at 0 °C for 1 h, the mixture was allowed to warm to room temperature and stirred for total 10 h. The solvent was removed in vacuo and co-evaporated with 30 mL of toluene 4 times. The peracetylated D-fucose was dried in vacuo for 5–6 h and directly used for next step without further purification.

To a solution of peracetate (9.34 g, 28.10 mmol) and *p*-methoxyphenol (5.23 g, 42.15 mmol) in anhydrous CH_2Cl_2 (75 mL) under nitrogen at 0 °C, $BF_3{\cdot}OEt_2$ (6.9 mL, 56.2 mmol) was added drop-wisely. After stirring at 0 °C for 2 h, the mixture was allowed to warm to room temperature, stirred for 12 h and diluted with another 50 mL of CH_2Cl_2. The organic layer was washed with water, saturated $NaHCO_3$ and brine, dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the product was purified by silica gel chromatography using hexane:EtOAc = 8:1 (by volume) as an eluent to produce compound **6** (9.3 g, yield 84% in 2 steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H), 5.62 (d, *J* = 3.7 Hz, 1H), 5.59 (dd, *J* = 10.8, 3.6 Hz, 1H), 5.36 (dd, *J* = 3.4, 1.3 Hz, 1H), 5.28 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.31 (dd, *J* = 13.2, 7.0 Hz, 1H), 3.77 (s, 3H), 2.18 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.13 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.70, 170.59, 170.24, 155.33, 150.76, 117.90, 114.81, 95.80, 71.17, 68.11, 68.07, 65.34, 55.78, 20.91, 20.86, 20.78, 16.01.

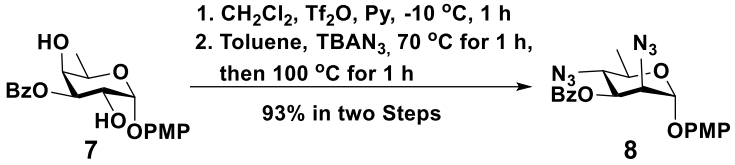
***p*-Methoxy phenyl-3-*O*-benzoyl-α-D-fucopyranoside (7)**



To a solution of 4-methoxy phenyl-2,3,4-tri-*O*-acetyl-α-D-fucopyranoside **6** (9 g, 22.7 mmol) in methanol (50 mL) was added sodium methoxide (0.5 g) at room temperature. After 4 h, the reaction mixture was neutralized with Dowex 50W (H^+), filtered and concentrated under reduced pressure. This intermediate was dried in vacuo for 5–6 h used in the next step without further purification.

To a stirred solution of intermediate (6.1 g, 22.7 mmol) in a mixture of THF (30mL) and water (6mL) and Me_2SnCl_2 (273 mg, 1.13 mmol) and DIPEA (15.8 mL, 2.37 mmol) were added and stirred for 15 min. To this BzCl (2.7 mL, 23.4 mmol) was added dropwise, after 1 h the reaction mixture was quenched with 1N HCl (50 mL) and extracted with EtOAc, dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the product was purified by silica gel chromatography using hexane:EtOAc = 4:1 (by volume) as an eluent to produce compound **7** (7.9 g, yield 94% in 2 steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.1 Hz, 2H), 5.54–5.46 (m, 2H), 4.34–4.20 (m, 2H), 4.05 (s, 1H), 3.78 (s, 3H), 2.35–2.11 (m, 2H), 1.29 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 155.41, 150.76, 133.58, 130.02, 129.75, 128.63, 118.13, 114.85, 98.77, 74.51, 70.95, 67.25, 66.86, 55.80, 16.17. HRMS (ESI) *m/z* calculated for $C_{20}H_{22}O_7$ (M+Na) 397.1258 found 397.1243.

***p*-Methoxy phenyl-2,4-di-azido-3-*O*-benzoyl-6-deoxy-α-D-mannopyranoside (8)**

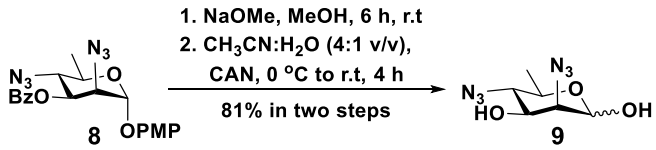


To a solution of compound **7** (3 g, 8.01 mmol) in anhydrous CH_2Cl_2 (30 mL) and anhydrous pyridine (6.48 mL) at -10 °C triflouromethanesulfonic anhydride (10.8 mL, 64.08 mmol) was added. Temperature was slowly increased to 0 °C over a period of 1 h. The reaction was diluted with addition of 70 mL of CH_2Cl_2. The organic layer was washed with 1 N HCl, saturated $NaHCO_3$, and brine solution, dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure at room temperature, was dried in vacuo for 2 h and directly used for next step without further purification.

To a solution of the 2,4-bistriflate in anhydrous toluene (50 mL) at 70 °C, tetrabutylammonium azide (6.8 g, 24.03 mmol) was added and the mixture was stirred for 1 h. The temperature was then increased to 100 °C and the mixture was stirred for another 1 h. Then the solvent was removed and the condensed mixture was diluted with 75 mL of CH_2Cl_2. The organic layer was washed with brine solution, dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the product was purified by silica gel chromatography using toluene:hexane = 25:1 (by volume) as an eluent to produce compound **8** (3.1 g, yield 93% over 2 steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.72 (dd, *J* = 10.0, 4.4 Hz, 1H), 5.40 (s, 1H), 4.50–4.27 (m, 1H), 3.85 (dq, *J* = 11.9, 5.9, 5.4 Hz, 1H), 3.78 (s, 3H), 3.75 (d, *J* = 10.0 Hz, 1H), 1.38 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 165.71, 155.54, 149.98, 134.04, 130.25, 128.88, 117.77, 114.94, 97.20, 72.67, 68.01, 63.22, 61.48, 55.87, 18.62. HRMS (ESI) *m/z* calculated for $C_{20}H_{20}N_6O_5$ (M-H) 423.1422 found 423.1434.

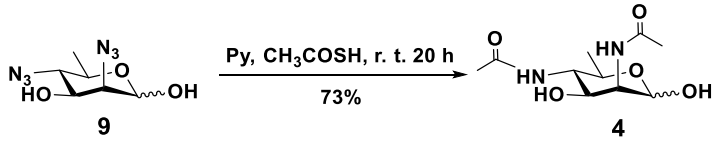
2,4-Diazido-2,4,6-trideox-D-mannose (9)



To a solution of compound **8** (3 g, 7.06 mmol) in anhydrous methanol (30 mL) was added sodium methoxide (0.3 g) at room temperature. After 6 h, the reaction mixture was neutralized with Dowex 50W (H+), filtered and concentrated under reduced pressure. This intermediate was dried in vacuo and used in the next step without further purification.

To a solution of the 2,4-diazido intermediate in 40 mL of acetonitrile:water = 4:1 (by volume) at 0 °C, ceric ammonium nitrate (12.32 g, 21.09 mmol) was added and the reaction mixture was stirred for 1 h. The reaction was warmed up to room temperature and was stirred for another 3 h. The acetonitrile was then removed under reduced pressure at room temperature and diluted with 100 mL of ethylacetate. The organic layer was washed with water saturated $NaHCO_3$, and brine solution, dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the product was purified by silica gel chromatography using hexane: EtOAc = 2:1 (by volume) as an eluent to produce compound **9** (1.2 g, yield 81% over 2 steps) as a reddish solid. ^{1}H NMR (400 MHz, D_2O) δ 5.24 (d, *J* = 1.3 Hz, 1H), 4.98 (d, *J* = 1.2 Hz, 1H), 4.14 (dd, *J* = 10.0, 3.8 Hz, 1H), 4.07 (dd, *J* = 3.7, 1.4 Hz, 1H), 4.02 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.94 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.89–3.79 (m, 1H), 3.44–3.26 (m, 3H), 1.33 (dd, *J* = 7.8, 6.1 Hz, 6H). ^{13}C NMR (100 MHz, D_2O) δ 92.79, 92.09, 71.80, 70.99, 69.21, 66.94, 65.66, 64.99, 64.47, 64.02, 17.40, 17.36. HRMS (ESI) *m/z* calculated for $C_6H_{10}N_6O_3$ (M+Na) 269.1108 found 269.1098.

6deoxyManNAc4NAc (4)[13]



To a solution of compound **9** (200 mg, 0.93 mmol) in pyridine (10 mL) was added thioacetic acid (0.530 mL, 7.44 mmol) under argon at room temperature and stir for 20 h and the product was purified by silica gel chromatography using a mixed solvent (EtOAc:methanol = 10:1, by volume) as an eluent to produce compound **4** (167 mg, yield 73%) as a reddish solid. ^{1}H NMR (400 MHz, D_2O) δ 5.03 (d, *J* = 1.6 Hz, 1H), 4.88 (d, *J* = 1.7 Hz, 1H), 4.39 (dd, *J* = 4.4, 1.7 Hz, 1H), 4.22 (dd, *J* = 4.6, 1.7 Hz, 1H), 3.99 (dd, *J* = 10.7, 4.6 Hz, 2H), 3.94–3.84 (m, *J* = 10.2, 6.3 Hz, 1H), 3.80–3.65 (m, 2H), 3.59 (t, *J* = 10.4 Hz, 1H), 3.43 (m, 1H), 2.04 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.13 (dd, *J* = 10.8, 6.2 Hz, 6H). ^{13}C NMR (100 MHz, D_2O) δ 175.85, 174.92, 174.75, 174.68, 92.77, 92.74, 71.58, 69.97, 67.00, 66.53, 53.57, 53.54, 53.18, 52.72, 22.12, 22.10, 22.08, 21.92, 16.81, 16.77. HRMS (ESI) *m/z* calculated for $C_{10}H_{18}N_2O_5$ (M+Cl^-) 281.0910, found 281.0917.

Enzymatic synthesis of 5,7-di-*N*-acetyllegionaminic acid (Leg5,7Ac$_2$) (1)[14]

The 6deoxyManNAc4NAc (**4**, 150 mg, 0.69 mmol) and sodium pyruvate (385 mg, 3.5 mmol) were dissolved in water in a 50 mL centrifuge tube containing Tris-HCl buffer (100 mM, pH 7.5) and $MgCl_2$ (20 mM). After the addition of appropriate amount of *PmAldolase* (7 mg), water was added to bring the

final volume of the reaction mixture to 30 mL. The reaction was carried out by incubating the solution at 37 °C with agitation at 125 rpm in an incubator for 72 h. The product formation was monitored by thin layer chromatography (TLC) developed with EtOAc:MeOH:H_2O:HOAc = 4:2:1:0.1 (by volume) and stained with *p*-anisaldehyde sugar stain. Upon the completion of the reaction, the mixture was centrifuged. The supernatant was concentrated and passed through a BioGel P-2 gel filtration (water was used as an eluent). The product was purified further using silica gel chromatograph to produce **1** (144 mg, yield 71%). ^{1}H NMR (800 MHz, D_2O) δ 4.28 (dd, *J* = 10.5, 1.6 Hz, 1H), 3.97–3.92 (m, 1H), 3.89–3.85 (m, 1H), 3.85–3.80 (m, 1H), 3.70 (t, *J* = 10.3 Hz each, 1H), 2.29 (dd, *J* = 13.1, 4.8 Hz, 1H), 1.85 (t, *J* = 12.3 Hz, 1H), 1.13 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (200 MHz, D_2O) δ 173.44, 173.27, 172.80, 94.87, 69.14, 66.66, 65.70, 52.68, 52.13, 38.60, 21.62, 21.30, 18.65. HRMS (ESI) *m/z* calculated for $C_{13}H_{22}N_2O_8$ (M-H) 333.1303, found 333.1289.

One-pot three-enzyme (OP3E) preparative-scale synthesis of α2–3-linked Leg5,7diN_3-glycosides

Leg5,7diN_3α2–3Galβ*p*NP (13)

Galβ*p*NP (15 mg, 0.050 mmol), 2,4-di-azido-6-deoxy-mannose (16 mg, 0.075 mmol), sodium pyruvate (38 mg, 0.35 mmol), CTP (39 mg, 0.075 mmol) were dissolved in water in a 15 mL centrifuge tube containing Tris-HCl buffer (100 mM, pH 8.5) and $MgCl_2$ (20 mM). After adding PmAldolase (0.5 mg), NmCSS (0.5 mg), and a sialyltransferase PmST1_M144D (1.5 mg) water was added to bring the final volume to 5 mL. The reaction mixture was incubated at 30 °C for 48 h. The reaction progress was monitored using TLC (EtOAc:MeOH:H_2O = 6:1:1, by volume) and mass spectrometry. The reaction mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. Upon the completion of the reaction, the mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. The mixture was then centrifuged. The supernatant was concentrated and purified using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water. The fractions containing the desired product were collected and dried to produce **15** (22 mg, yield 73%) as a white powder. ^{1}H NMR (800 MHz, D_2O) δ 8.28 (d, *J* = 9.2 Hz, 2H), 7.25 (d, *J* = 9.2 Hz, 2H), 5.28 (d, *J* = 7.8 Hz, 1H), 4.18–4.13 (m, 2H), 4.05–3.99 (m, 1H), 3.89 (q, *J* = 8.4, 6.9 Hz, 2H), 3.79–3.72 (m, 3H), 3.70 (d, *J* = 10.3 Hz, 1H), 3.61–3.55 (m, 1H), 3.42 (d, *J* = 8.7 Hz, 1H), 2.75 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.91 (t, *J* = 12.3 Hz, 1H), 1.37 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 172.87, 161.19, 142.04, 125.60, 115.93, 100.08, 99.08, 75.07, 74.91, 71.76, 68.94, 68.20, 67.12, 66.05, 64.80, 62.86, 60.14, 38.46, 18.33. HRMS (ESI) *m/z* calculated for $C_{21}H_{27}N_7O_{13}$ (M-H) 585.1594, found 585.1583.

Leg5,7diN_3α2–3GalβSTol (15)

GalβSTol (20 mg, 0.070 mmol), 2,4-di-azido-6-deoxy-mannose (22 mg, 0.10 mmol), sodium pyruvate (58 mg, 0.52 mmol), CTP (54 mg, 0.10 mmol) were dissolved in water in a 15 mL centrifuge tube containing Tris-HCl buffer (100 mM, pH 8.5) and $MgCl_2$ (20 mM). After adding PmAldolase (0.5 mg), NmCSS (0.5 mg), and a sialyltransferase PmST1_M144D (1.5 mg) water was added to bring the final volume to 5 mL. The reaction mixture was incubated at 30 °C for 48 h. The reaction progress was monitored using TLC (EtOAc:MeOH:H_2O = 6:1:1, by volume) and mass spectrometry. Upon the completion of the reaction, the mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. The mixture was then centrifuged. The supernatant was concentrated and purified using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water. The fractions containing the desired product were collected and dried to produce **13** (39 mg, yield 98%) as a white powder. ^{1}H NMR (800 MHz, D_2O) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.71 (d, *J* = 9.9 Hz, 1H), 4.18–4.10 (m, 1H), 4.05 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.97–3.94 (m, 1H), 3.79–3.73 (m, 1H), 3.73–3.67 (m, 2H), 3.67–3.61 (m, 2H), 3.60–3.48 (m, 2H), 3.43 (dd, *J* = 8.5, 2.2 Hz, 1H), 2.70 (dd,

J = 12.8, 4.7 Hz, 1H), 2.33 (s, 3H), 1.92 (t, *J* = 12.4 Hz, 1H), 1.37 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 172.07, 138.37, 131.85, 129.41, 127.59, 99.74, 87.03, 78.20, 76.57, 71.91, 68.70, 67.68, 66.75, 66.04, 64.72, 62.83, 60.36, 38.11, 19.66, 18.51. HRMS (ESI) *m/z* calculated for $C_{22}H_{30}N_6O_{10}S$ (M-H) 569.1671, found 569.1666.

Leg5,7diN$_3$α2–3LacβProCl (17)

LacβProCl (20 mg, 0.048 mmol), 2,4-di-azido-6-deoxy-mannose (15 mg, 0.070 mmol), sodium pyruvate (37 mg, 0.34 mmol), CTP (38 mg, 0.073 mmol) were dissolved in water in a 15 mL centrifuge tube containing Tris-HCl buffer (100 mM, pH 8.5) and $MgCl_2$ (20 mM). After adding PmAldolase (0.5 mg), NmCSS (0.5 mg), and a sialyltransferase PmST1_M144D (1.5 mg) water was added to bring the final volume to 5 mL. The reaction mixture was incubated at 30 °C for 48 h. The reaction progress was monitored using TLC (EtOAc:MeOH:H_2O = 5:2:1, by volume) and mass spectrometry. Upon the completion of the reaction, the mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. The mixture was then centrifuged. The supernatant was concentrated and purified using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water. The fractions containing the desired product were collected and dried to produce **17** (32 mg, yield 91%) as a white powder. ^{1}H NMR (800 MHz, D_2O) δ 4.51 (d, *J* = 7.9 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 4.17 (p, *J* = 6.4 Hz, 1H), 4.08–4.01 (m, 2H), 3.99 (d, *J* = 12.2 Hz, 1H), 3.92 (d, *J* = 2.7 Hz, 1H), 3.83 (dq, *J* = 11.3, 5.5, 4.9 Hz, 2H), 3.78–3.62 (m, 9H), 3.61–3.57 (m, 1H), 3.55 (t, *J* = 9.6 Hz, 1H), 3.46–3.40 (m, 1H), 3.31 (t, *J* = 8.2 Hz, 1H), 2.71 (dd, *J* = 12.6, 4.6 Hz, 1H), 2.09 (p, *J* = 6.2 Hz, 2H), 1.88 (t, *J* = 12.3 Hz, 1H), 1.39 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 172.92, 102.13, 101.70, 100.13, 77.85, 75.18, 74.63, 74.26, 73.88, 72.30, 71.74, 68.96, 68.85, 67.37, 66.65, 66.08, 64.80, 62.85, 60.49, 59.55, 41.26, 38.35, 31.29, 18.32. HRMS (ESI) *m/z* calculated for $C_{24}H_{39}ClN_6O_{16}$ (M-H) 701.2038, found 701.2028.

One-pot three-enzyme (OP3E) gram-scale synthesis of Leg5,7diN$_3$α2–3GalβSTol (15)

GalβSTol (1 g, 3.49 mmol), 2,4-di-azido-6-deoxy-mannose (970 mg, 4.53 mmol), sodium pyruvate (2.87 g, 26.17 mmol), and CTP (2.38 g, 4.53 mmol) were dissolved in water in a 500 mL plastic container containing Tris-HCl buffer (100 mM, pH 8.5) and $MgCl_2$ (20 mM). After adding PmAldolase (66 mg), NmCSS (60 mg), and a sialyltransferase PmST1 (40 mg), water was added to bring the final volume to 175 mL. The reaction mixture was incubated at 30 °C for 30 h. The reaction progress was monitored using TLC (EtOAc:MeOH:H_2O = 6:1:1, by volume) and mass spectrometry. Upon the completion of the reaction, the mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. The mixture was then centrifuged. The supernatant was concentrated and purified using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water. The fractions containing the desired product were collected and dried to produce **15** (1.85 g, yield 93%) as a white powder.

One-pot three-enzyme (OP3E) preparative-scale synthesis of α2–6-linked Leg5,7diN$_3$-glycosides

Leg5,7diN$_3$α2–6Galβ*p*NP (14)

Galβ*p*NP (15 mg, 0.050 mmol), 2,4-di-azido-6-deoxy-mannose (16 mg, 0.075 mmol), sodium pyruvate (38 mg, 0.35 mmol), CTP (39 mg, 0.075 mmol) were dissolved in water in a 15 mL centrifuge tube containing Tris-HCl buffer (100 mM, pH 8.5) and $MgCl_2$ (20 mM). After adding PmAldolase (0.5 mg), NmCSS (0.5 mg), and Psp2,6ST (1.5 mg) water was added to bring the final volume to 5 mL. The reaction mixture was incubated at 30 °C for 48 h. The reaction progress was monitored using TLC (EtOAc:MeOH:H_2O = 6:1:1, by volume) and mass spectrometry. The reaction mixture was diluted with

the same volume of ethanol and incubated at 4 °C for 30 min. Upon the completion of the reaction, the mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. The mixture was then centrifuged. The supernatant was concentrated and purified using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water. The fractions containing the desired product were collected and dried to produce **16** (21 mg, yield 70%) as a white powder. ^{1}H NMR (800 MHz, D_2O) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 9.6 Hz, 2H), 5.18 (d, *J* = 7.2 Hz, 1H), 4.09–4.04 (m, 1H), 4.01 (d, *J* = 3.3 Hz, 1H), 3.97 (dd, *J* = 7.6, 4.5 Hz, 1H), 3.88 (dd, *J* = 10.5, 7.8 Hz, 1H), 3.86–3.83 (m, 1H), 3.78 (dd, *J* = 10.0, 3.4 Hz, 1H), 3.75–3.69 (m, 2H), 3.67 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.48 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.43 (t, *J* = 9.8 Hz, 1H), 2.74–2.71 (m, 1H), 1.71 (t, *J* = 12.3 Hz, 1H), 1.34 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 172.62, 161.33, 142.01, 125.58, 116.04, 100.08, 99.26, 73.56, 71.85, 71.37, 69.78, 68.82, 67.89, 66.25, 65.35, 63.13, 62.77, 39.50, 18.29. HRMS (ESI) *m/z* calculated for $C_{21}H_{27}N_7O_{13}$ (M-H) 585.1594, found 585.1589.

Leg5,7diN$_3$α2–6GalβSTol (16)

GalβSTol (15 mg, 0.052 mmol), 2,4-diazido-6-deoxy-mannose (16 mg, 0.075 mmol), sodium pyruvate (41 mg, 0.37 mmol), CTP (42 mg, 0.080 mmol) were dissolved in water in a 15 mL centrifuge tube containing Tris-HCl buffer (100 mM, pH 8.5) and $MgCl_2$ (20 mM). After adding PmAldolase (0.5 mg), NmCSS (0.5 mg), and Psp2,6ST (1.5 mg) water was added to bring the final volume to 5 mL. The reaction mixture was incubated at 30 °C for 48 h. The reaction progress was monitored using TLC (EtOAc:MeOH:H_2O = 6:1:1, by volume) and mass spectrometry. Upon the completion of the reaction, the mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. The mixture was then centrifuged. The supernatant was concentrated and purified using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water. The fractions containing the desired product were collected and dried to produce **14** (29 mg, yield 93%) as a white powder. ^{1}H NMR (800 MHz, D_2O) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.63 (d, *J* = 9.8 Hz, 1H), 4.10 (p, *J* = 6.4 Hz, 1H), 3.96 (d, *J* = 3.3 Hz, 1H), 3.86 (dd, *J* = 10.1, 7.6 Hz, 1H), 3.80–3.77 (m, 1H), 3.75–3.69 (m, 2H), 3.64 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.59–3.53 (m, 2H), 3.51–3.47 (m, 2H), 2.69 (dd, *J* = 12.8, 4.8Hz, 1H), 2.34 (s, 3H), 1.70 (t, *J* = 12.3 Hz, 1H), 1.36 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 172.30, 138.22, 131.51, 129.43, 128.14, 99.99, 87.65, 76.79, 73.33, 71.54, 68.76, 68.61, 68.14, 66.21, 65.29, 63.09, 62.99, 58.81, 39.41, 19.67, 18.40. HRMS (ESI) *m/z* calculated for $C_{22}H_{30}N_6O_{10}S$ (M-H) 569.1671, found 569.1662.

Leg5,7diN$_3$α2–6LacβProCl (18)

LacβProCl (25 mg, 0.060 mmol), 2,4-di-azido-6-deoxy-mannose (20 mg, 0.093 mmol), sodium pyruvate (51 mg, 0.47 mmol), CTP (49 mg, 0.093 mmol) were dissolved in water in a 15 mL centrifuge tube containing Tris-HCl buffer (100 mM, pH 8.5) and $MgCl_2$ (20 mM). After adding PmAldolase (0.5 mg), NmCSS (0.5 mg), and Psp2,6ST (1.5 mg) water was added to bring the final volume to 5 mL. The reaction mixture was incubated at 30 °C for 48 h. The reaction progress was monitored using TLC (EtOAc:MeOH:H_2O = 5:2:1, by volume) and mass spectrometry. Upon the completion of the reaction, the mixture was diluted with the same volume of ethanol and incubated at 4 °C for 30 min. The mixture was then centrifuged. The supernatant was concentrated and purified using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water. The fractions containing the desired product were collected and dried to produce **18** (42 mg, yield 97%) as a white powder. ^{1}H NMR (800 MHz, D_2O) δ 4.50 (d, *J* = 8.0 Hz, 1H), 4.41 (d, *J* = 7.9 Hz, 1H), 4.18–4.13 (m, 1H), 4.06 (dt, *J* = 11.0, 6.1 Hz, 1H), 3.97 (d, *J* = 12.3 Hz, 1H), 3.93–3.88 (m, 2H), 3.84 (dt, *J* = 11.0, 6.2 Hz, 1H), 3.82–3.75 (m, 3H), 3.71 (ddd, *J* = 24.5, 10.4, 4.2 Hz, 4H), 3.64 (dd, *J* = 10.0, 3.3 Hz, 1H), 3.61–3.54 (m, 4H), 3.53–3.50 (m, 1H), 3.46 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.32 (t, *J* = 8.7 Hz, 1H), 2.69 (dd,

J = 12.8, 4.8 Hz, 1H), 2.09 (p, *J* = 6.4 Hz, 2H), 1.79 (t, *J* = 12.3 Hz, 1H), 1.38 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 172.71, 102.80, 101.60, 100.04, 79.41, 74.13, 74.11, 73.07, 72.13, 71.94, 71.53, 70.33, 68.93, 67.85, 66.62, 66.04, 65.27, 63.02, 62.86, 59.81, 41.29, 39.39, 31.30, 18.38. HRMS (ESI) *m/z* calculated for $C_{24}H_{39}ClN_6O_{16}$ (M-H) 701.2038, found 701.2031.

General procedures for converting Leg5,7diN_3-glycosides to Leg5,7Ac_2-glycosides

To a stirred solution of azido glycoside (6–30 mg) in saturated sodium bicarbonate solution at 65 °C, thioacetic acid (10 eq) was added drop-wisely under an inert atmosphere. After 12 h, another portion of thioacetic acid (15 eq) was added and the reaction mixture was stirred for another 24 h. Upon the completion of the reaction, the mixture was passed through a BioGel P-2 gel filtration column (water was used as an eluent). The fractions containing the product were concentrated and purified further using a C18 column on a CombiFlash Rf 200i system eluted with a gradient of 0–100% acetonitrile in water to obtain the pure compound.

Leg5,7Ac_2α2–3Galβ*p*NP (19)

Yield 81%, 8.5 mg, white solid. ^{1}H NMR (800 MHz, D_2O) δ 8.28 (d, *J* = 9.6 Hz, 1H), 7.26 (d, *J* = 9.6 Hz, 1H), 5.29 (d, *J* = 7.8 Hz, 1H), 4.25–4.21 (m, 1H), 4.03 (d, *J* = 2.8 Hz, 1H), 3.99–3.94 (m, 1H), 3.94–3.88 (m, 2H), 3.85–3.80 (m, 3H), 3.76 (d, *J* = 6.1 Hz, 2H), 3.73 (s, 0H), 3.58 (td, *J* = 11.2, 5.0 Hz, 1H), 2.81 (dd, *J* = 12.8, 4.8 Hz, 1H), 1.96 (s, 2H), 1.94 (s, 2H), 1.77 (t, *J* = 12.0 Hz, 1H), 1.13 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.49, 173.35, 173.24, 161.18, 142.05, 125.61, 115.93, 99.14, 99.13, 74.97, 74.94, 71.29, 68.31, 68.22, 66.84, 66.29, 60.17, 53.39, 51.50, 39.62, 21.62, 21.45, 17.56. HRMS (ESI) *m/z* calculated for $C_{25}H_{35}N_3O_{15}$ (M-H) 616.1995, found 616. 1991.

Leg5,7Ac_2α2–6Galβ*p*NP (20)

Yield 78%, 6.5 mg, white solid. ^{1}H NMR (800 MHz, D_2O) δ 8.31 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 9.6 Hz, 2H), 5.19 (d, *J* = 7.2 Hz, 1H), 4.04–3.97 (m, 3H), 3.96–3.91 (m, 1H), 3.89–3.83 (m, 2H), 3.81–3.74 (m, 2H), 3.64 (dd, *J* = 10.0, 2.2 Hz, 1H), 3.60–3.54 (m, 2H), 2.80 (dd, *J* = 12.8, 4.8 Hz, 1H), 1.92 (s, 3H), 1.85 (s, 3H), 1.62 (t, *J* = 11.2 Hz, 1H), 1.12 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.43, 173.06, 173.02, 161.45, 142.06, 125.63, 115.96, 99.67, 99.44, 73.61, 71.88, 71.10, 69.79, 68.10, 68.04, 66.63, 62.89, 53.46, 51.65, 39.92, 21.60, 21.34, 17.57. HRMS (ESI) *m/z* calculated for $C_{25}H_{35}N_3O_{15}$ (M-H) 616.1995, found 616. 1984.

Leg5,7Ac_2α2–3GalβSTol (21)

Yield 88%, 27.8 mg, white solid**.** ^{1}H NMR (800 MHz, D_2O) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.73 (d, *J* = 9.8 Hz, 1H), 4.11 (dd, *J* = 9.3, 3.1 Hz, 1H), 3.96 (dd, *J* = 12.9, 6.5 Hz, 2H), 3.82 (ddd, *J* = 20.2, 9.8, 3.1 Hz, 2H), 3.71 (dd, *J* = 12.7, 3.8 Hz, 2H), 3.69–3.65 (m, 2H), 3.61 (t, *J* = 9.6 Hz, 1H), 3.58–3.54 (m, 1H), 2.76 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.33 (s, 3H), 1.98 (s, 3H), 1.93 (s, 3H), 1.74 (t, *J* = 12.0 Hz, 1H), 1.14 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.48, 173.38, 173.28, 138.37, 131.82, 129.42, 127.63, 99.25, 87.12, 78.28, 76.63, 71.29, 68.23, 66.91, 66.81, 66.78, 60.44, 53.40, 51.49, 39.56, 21.62, 21.48, 19.65, 17.58. HRMS (ESI) *m/z* calculated for $C_{26}H_{38}N_2O_{12}S$ (M-H) 601.2072, found 601.2078.

Leg5,7Ac_2α2-6GalβSTol (22)

Yield 84%, 5.2 mg, white solid. ^{1}H NMR (800 MHz, D_2O) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.68 (d, *J* = 9.6 Hz, 1H), 4.01–3.94 (m, 3H), 3.89 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.84–3.80 (m, 1H), 3.78 (dd, *J* = 8.3, 3.1 Hz, 1H), 3.71–3.64 (m, 2H), 3.61 (t, *J* = 9.6 Hz, 1H), 3.59–3.53 (m, 2H), 2.75 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.34 (s, 3H), 1.93 (s, 3H), 1.87 (s, 3H), 1.64 (t, *J* = 12.0 Hz, 2H), 1.13 (d, *J* = 6.3

Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.43, 173.11, 173.00, 138.09, 130.87, 129.51, 128.64, 99.72, 87.52, 76.94, 73.36, 71.09, 68.66, 68.42, 68.15, 66.62, 63.53, 53.51, 51.64, 39.94, 21.63, 21.36, 19.62, 17.61. HRMS (ESI) *m/z* calculated for $C_{26}H_{38}N_2O_{12}S$ (M-H) 601.2072, found 601.2063.

Leg5,7Ac$_2$α2–3LacβProCl (23)
Yield 72%, 5.6 mg, white solid. ^{1}H NMR (800 MHz, D_2O) δ 4.50 (t, *J* = 8.0 Hz, 2H), 4.11 (dd, *J* = 9.9, 2.9 Hz, 1H), 4.05 (dt, *J* = 11.2, 6.0 Hz, 1H), 3.99 (dt, *J* = 8.2, 4.7 Hz, 2H), 3.94 (d, *J* = 2.8 Hz, 1H), 3.86–3.79 (m, 4H), 3.78–3.69 (m, 5H), 3.69–3.63 (m, 3H), 3.57 (ddt, *J* = 20.3, 10.5, 5.8 Hz, 3H), 3.31 (t, *J* = 8.2 Hz, 1H), 2.78 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.08 (p, *J* = 6.2 Hz, 2H), 1.98 (s, 3H), 1.94 (s, 3H), 1.74 (t, *J* = 12.0 Hz, 1H), 1.16 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.48, 173.47, 173.22, 102.15, 101.69, 99.00, 77.82, 74.88, 74.64, 74.26, 73.87, 72.30, 71.31, 68.90, 68.24, 66.74, 66.65, 66.39, 60.52, 59.59, 53.39, 51.53, 41.25, 39.62, 31.28, 21.63, 21.44, 17.58. HRMS (ESI) *m/z* calculated for $C_{28}H_{47}ClN_2O_{18}$ (M-H) 733.2439, found 734.2425.

Leg5,7Ac$_2$α2–6LacβProCl (24)
Yield 69%, 7.1 mg, white solid. ^{1}H NMR (800 MHz, D_2O) δ 4.51 (d, *J* = 8.0 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 1H), 4.06 (dt, *J* = 10.9, 6.0 Hz, 1H), 4.02–3.96 (m, 3H), 3.94–3.87 (m, 2H), 3.86–3.78 (m, 4H), 3.75–3.69 (m, 3H), 3.69–3.60 (m, 4H), 3.59–3.52 (m, 3H), 3.36 (t, *J* = 8.4 Hz, 1H), 2.72 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.09 (p, *J* = 6.2 Hz, 2H), 2.00 (s, 3H), 1.94 (s, 3H), 1.73 (t, *J* = 12.0 Hz, 1H), 1.15 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.43, 173.27, 172.92, 102.70, 101.57, 99.83, 78.93, 74.17, 74.12, 73.13, 72.37, 71.91, 71.12, 70.21, 68.26, 67.93, 66.62, 62.91, 59.72, 53.51, 51.57, 41.28, 39.63, 31.31, 21.64, 21.62, 17.57. HRMS (ESI) *m/z* calculated for $C_{28}H_{47}ClN_2O_{18}$ (M-H) 733.2439, found 734.2431.

General procedure for producing Leg5,7Ac$_2$-terminated propylazido-β-glycosides from propyl chloro-β-glycosides
To a stirred solution of Leg5,7Ac$_2$α2–3LacβProCl (5.0 mg) or Leg5,7Ac$_2$α2–6LacβProCl (5.2 mg) in DMF, NaN_3 (10 eq) and NaI (1 eq) were added and the reaction was left under 60 °C for 12 h. After completion of the reaction the solvent was concentrated in vaccuo. The crude product was purified by automated flash chromatograph using C18 column (CH_3CN in H_2O gradient was used as running solvents) to give the pure compounds.

Leg5,7Ac$_2$α2–3LacβProN$_3$ (25)
Yield 85%, 4.3 mg, white solid. ^{1}H NMR (800 MHz, D_2O) δ 4.51 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 8.0 Hz, 1H), 4.11 (dd, *J* = 9.9, 3.0 Hz, 1H), 4.02–3.96 (m, 3H), 3.95 (d, *J* = 2.9 Hz, 1H), 3.86–3.79 (m, 3H), 3.78–3.73 (m, 2H), 3.73–3.69 (m, 2H), 3.69–3.63 (m, 3H), 3.62–3.54 (m, 3H), 3.46 (t, *J* = 6.7 Hz, 2H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.78 (dd, *J* = 12.8, 4.8 Hz, 1H), 1.98 (s, 3H), 1.94 (s, 3H), 1.91 (q, *J* = 6.6 Hz, 2H), 1.74 (t, *J* = 12.0 Hz, 1H), 1.16 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.48, 173.47, 173.22, 102.15, 101.63, 99.00, 77.83, 74.88, 74.64, 74.26, 73.88, 72.29, 71.31, 68.90, 68.23, 66.87, 66.73, 66.39, 60.51, 59.59, 53.39, 51.53, 47.37, 39.61, 27.74, 21.63, 21.43, 17.57. HRMS (ESI) *m/z* calculated for $C_{28}H_{47}N_5O_{18}$ (M-H) 740.2843, found 740.2840.

Leg5,7Ac$_2$α2–6LacβProN$_3$ (26)
Yield 92%, 4.8 mg, white solid. ^{1}H NMR (800 MHz, D_2O) δ 4.50 (d, *J* = 8.0 Hz, 1H), 4.43 (d, *J* = 8.0 Hz, 1H), 4.03–3.96 (m, 4H), 3.92–3.88 (m, 2H), 3.86–3.79 (m, 3H), 3.79–3.74 (m, 1H), 3.71 (t, *J* = 10.0 Hz, 1H), 3.69–3.64 (m, 4H), 3.64–3.60 (m, 3H), 3.59–3.53 (m, 2H), 3.46 (t, *J* = 6.4 Hz, 1H), 3.36 (t, *J* = 8.8 Hz, 1H), 2.72 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.00 (s, 3H), 1.94 (s, 3H), 1.91 (q, *J* = 6.3 Hz, 1H), 1.73 (t,

J = 12.0 Hz, 1H), 1.15 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (200 MHz, D_2O) δ 173.43, 173.27, 172.93, 102.71, 101.51, 99.83, 78.97, 74.17, 74.13, 73.13, 72.36, 71.91, 71.12, 70.22, 68.26, 67.93, 66.84, 66.62, 62.91, 59.73, 53.51, 51.57, 47.39, 39.63, 27.75, 21.64, 21.62, 17.57. HRMS (ESI) *m/z* calculated for $C_{28}H_{47}N_5O_{18}$ (M-H) 740.2843, found 740.2807.

Sialidase substrate specificity studies

Assays were carried out in duplicates. For each reaction in a final volume of 20 μL, a sialoside was incubated with an appropriate amount of a sialidase in a buffer solution in a 0.5 mL microcentrifuge tube at 37 °C for 16 hs. The sialidase amounts and buffers used were: *A. ureafaciens* sialidase (0.5 mU), NaOAc buffer (100 mM, pH 5.5); *C. perfringens* sialidase (0.75 mU), MES buffer (100 mM, pH 5.0); *V. cholerae* sialidase (1.5 mU), NaCl (150 mM), $CaCl_2$ (10 mM), NaOAc buffer (100 mM, pH 5.5); SpNanA (1.5 ng), NaOAc buffer (100 mM, pH 6.0); SpNanB (3 ng), NaOAc buffer (100 mM, pH 6.0); SpNanC (20 ng), MES buffer (100 mM, pH 6.5); PmST1 (0.4 μg), NaOAc buffer (100 mM, pH 5.5), CMP (0.4 mM); hNEU2 (1.3 μg), MES buffer (100 mM, pH 5.0); BiNanH2 (4 ng), NaOAc buffer (100 mM, pH 5.0). The reactions were stopped by adding 20 μL of pre-chilled ethanol. The mixtures were then centrifuged and the supernatants were analyzed by Agilent 1290 Infinity HPLC system at 315 nm or P/ACE^{TM} MDQ Capillary Electrophoresis at 315 nm. A C14 reverse phase Rapid Resolution High Definition column (BONUS RP RRHD 1.8 μm, 2.1 × 150 mm, Agilent) was used for analyzing samples with Neu5Acα2−3Galβ*p*NP and Neu5Acα2–6Galβ*p*NP, which are used as control. A C18 reverse phase Rapid Resolution High Definition column (EclipsePlusC18 RRHD 1.8 μm, 2.1 × 50 mm, Agilent) was used for analyzing samples with Leg5,7Ac$_2$α2–3Galβ*p*NP (**19**) and Leg5,7Ac$_2$α2–6Galβ*p*NP (**20**). The mobile phases used were acetonitrile in H_2O mixed solvent with varied percentages of acetonitrile: 12% for Neu5Acα2–3Galβ*p*NP; 4.5% for Neu5Acα2–6Galβ*p*NP; 6% for Leg5,7Ac$_2$α2–3Galβ*p*NP (**19**) and Leg5,7Ac$_2$α2−6Galβ*p*NP (**20**). P/ACE^{TM} MDQ Capillary Electrophoresis was used for analyzing Leg5,7diN$_3$α2−3Galβ*p*NP (**13**) and Leg5,7diN$_3$α2−6Galβ*p*NP (**14**).

Kinetic studies for PmST1

The kinetic studies for PmST1 were performed in duplicates at 37 °C for 10 min. Each reaction in a total volume of 20 μL contained NaOAc buffer (100 mM, pH 5.5), CMP (0.4 mM), a sialidase substrate Neu5Acα2–3Galβ*p*NP or Leg5,7Ac$_2$α2–3Galβ*p*NP (**19**), and PmST1 (0.2 μg when Neu5Acα2–3Galβ*p*NP was used as the substrate and 4 μg when Leg5,7Ac$_2$α2–3Galβ*p*NP (**19**) was used as the substrate). The reactions were stopped by adding 20 μL of pre-chilled ethanol. The mixtures were then centrifuged and the supernatants were analyzed by the HPLC system described above for sialidase substrate specificity studies assays. Apparent kinetic parameters were obtained by varying substrate concentrations from 0.1–40 mM (0.1, 0.2, 0.4, 1, 2, 4, 10, 20, and 40 mM) and fitting the data (the average values of duplicate assay results) into the Michaelis–Menten equation using Grafit 5.0.

Table S1. Apparent kinetics parameters for PmST1

Sialidase	Substrate	k_{cat} (min^{-1})	K_M (mM)	k_{cat}/K_M (min^{-1} mM^{-1})
PmST1	Neu5Acα2–3Galβ*p*NP	555.4 ± 11.1	4.73 ± 0.31	117
	Leg5,7Ac$_2$α2–3Galβ*p*NP (**19**)	69.3 ± 1.3	17.38 ± 0.70	4

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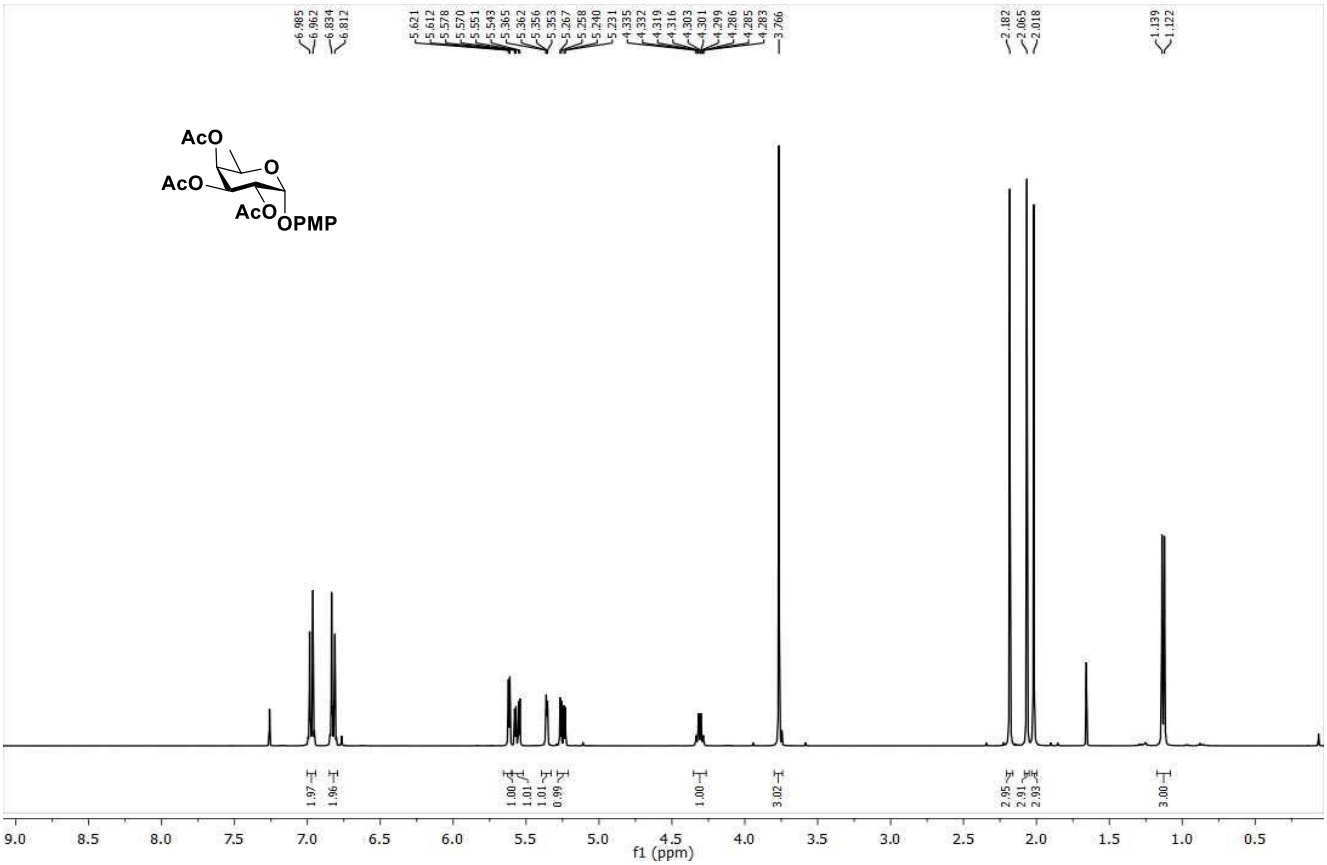
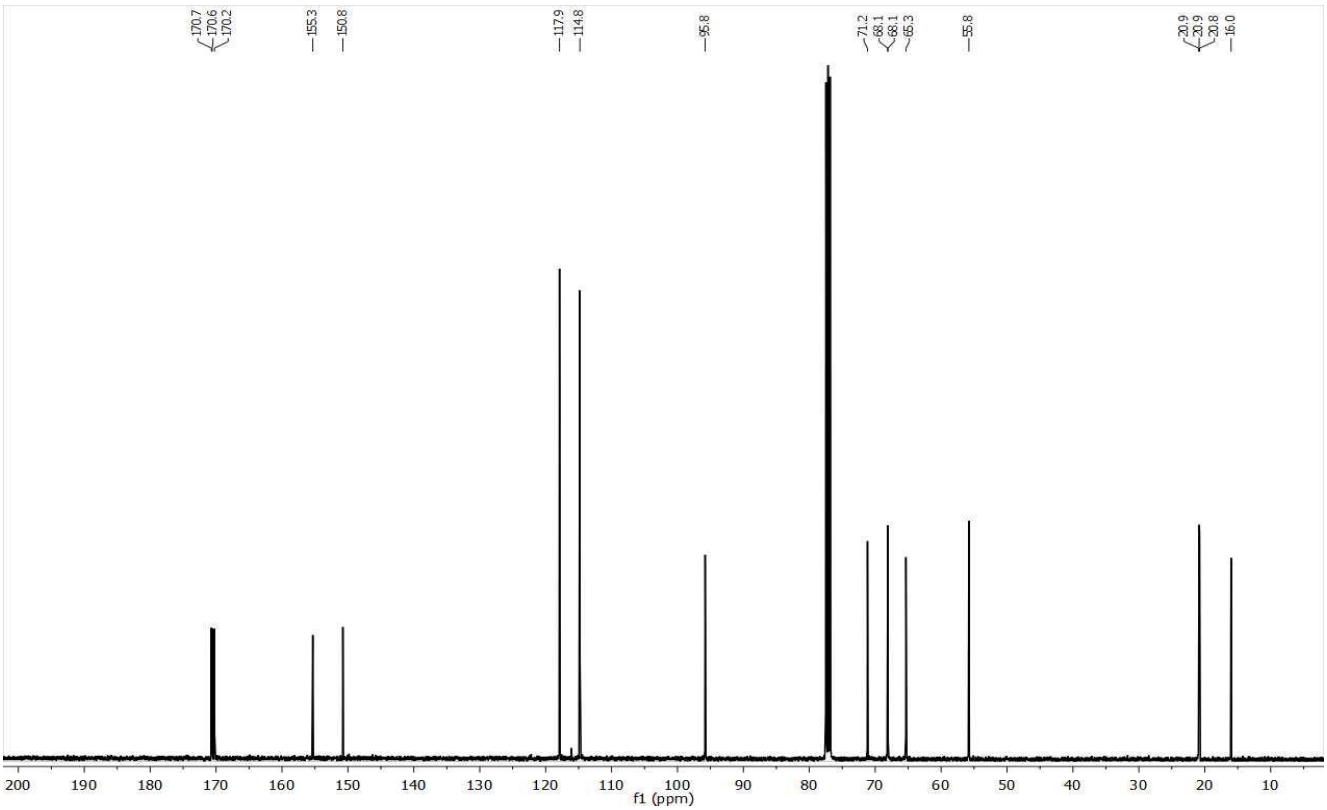
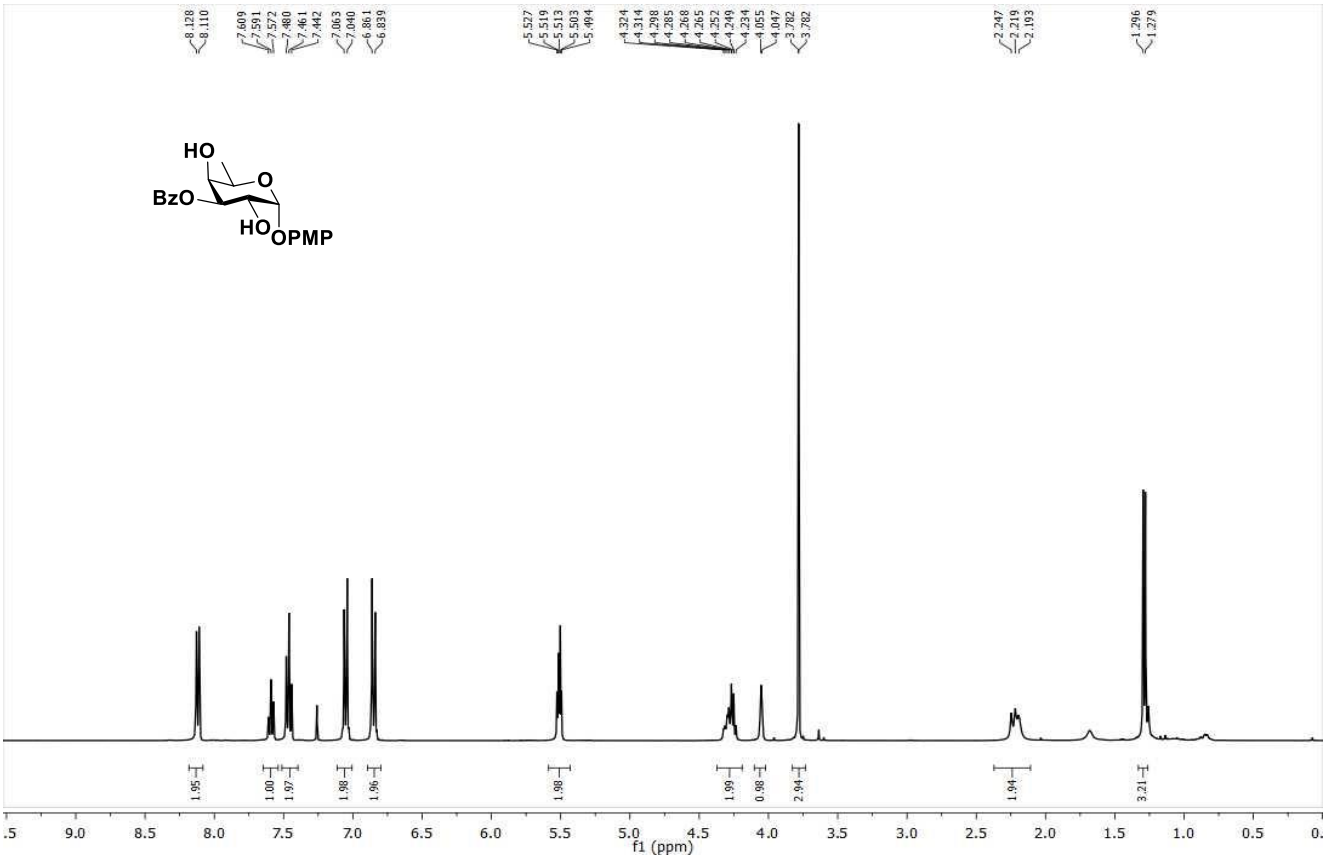
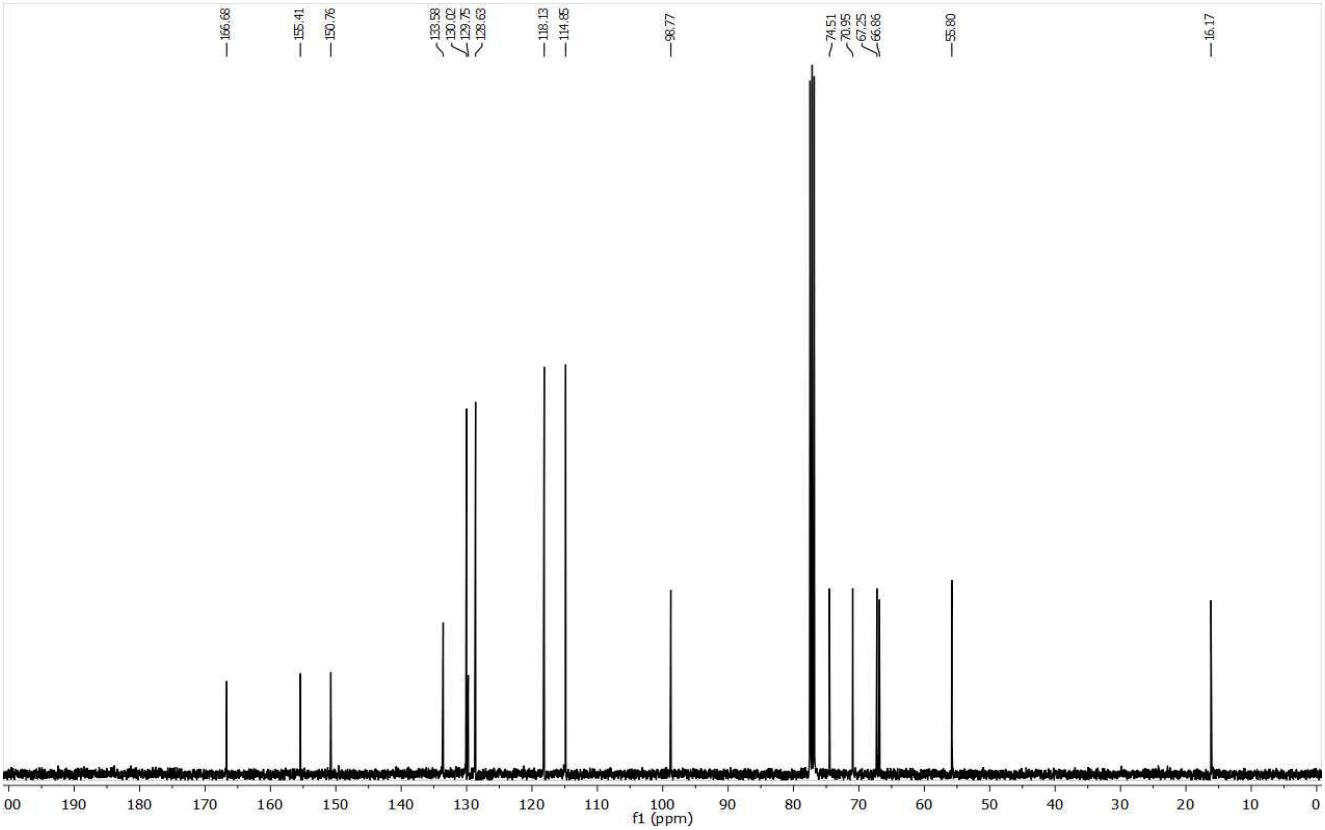
^{1}H and ^{13}C NMR spectra of *p*-methoxy phenyl-2,3,4-tri-*O*-acetyl-α-D-fucopyranoside (**6**)



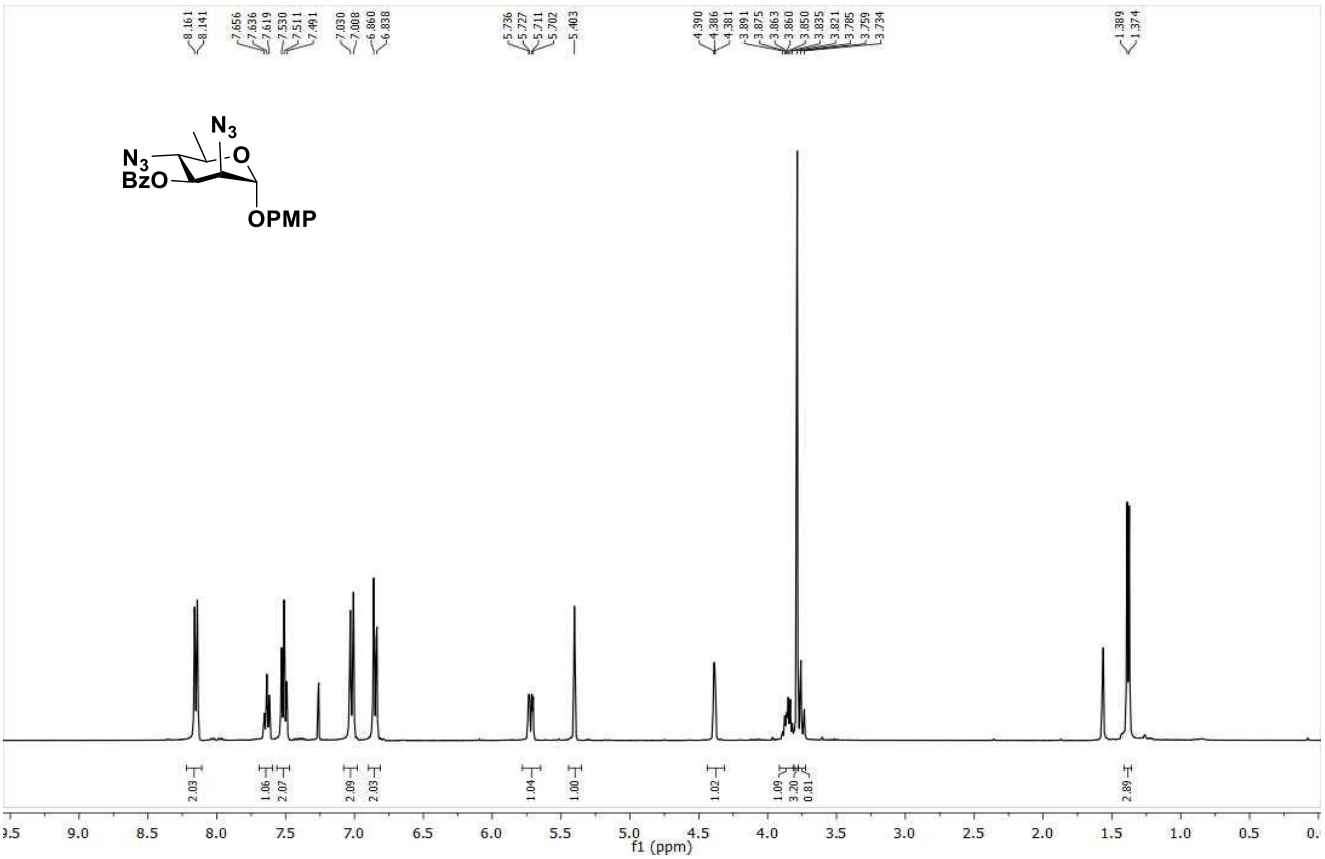


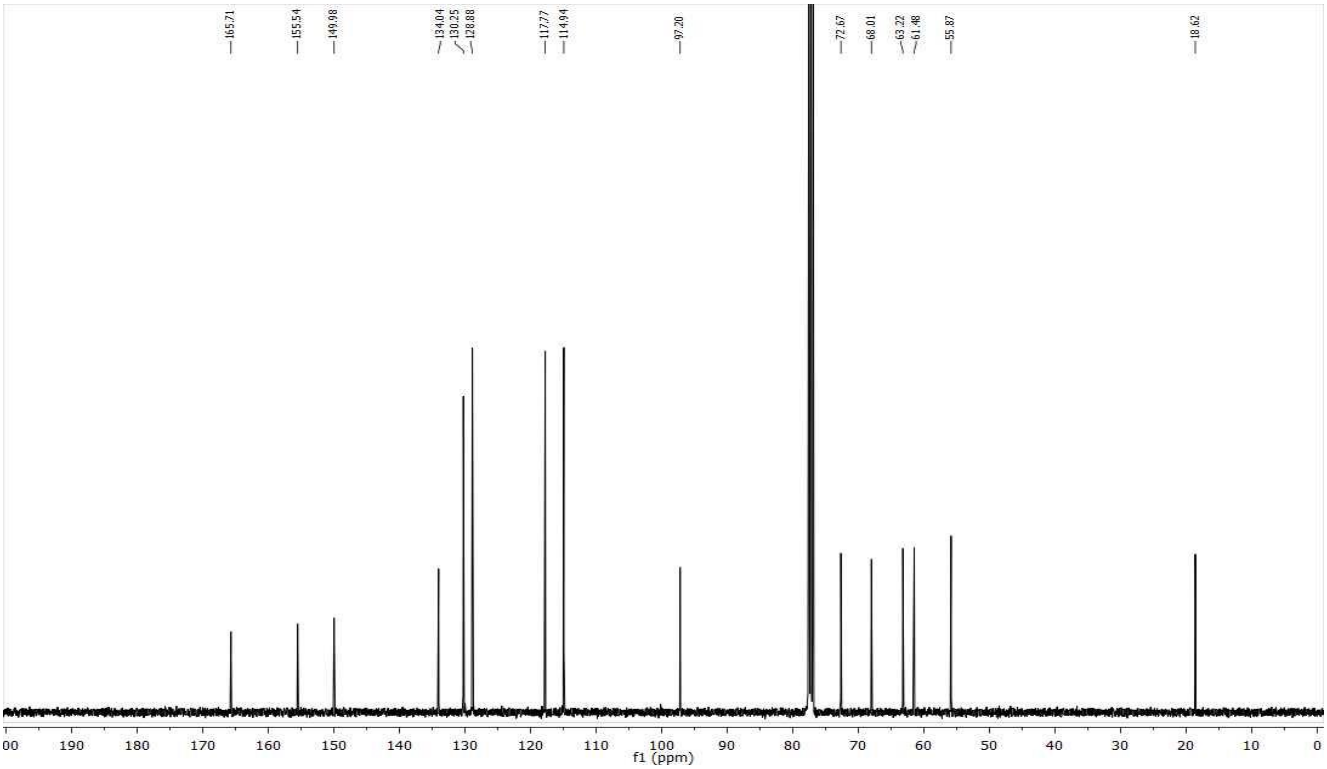
^{1}H and ^{13}C NMR spectra of *p*-methoxy phenyl-3-*O*-benzoyl-α-D-fucopyranoside (**7**)



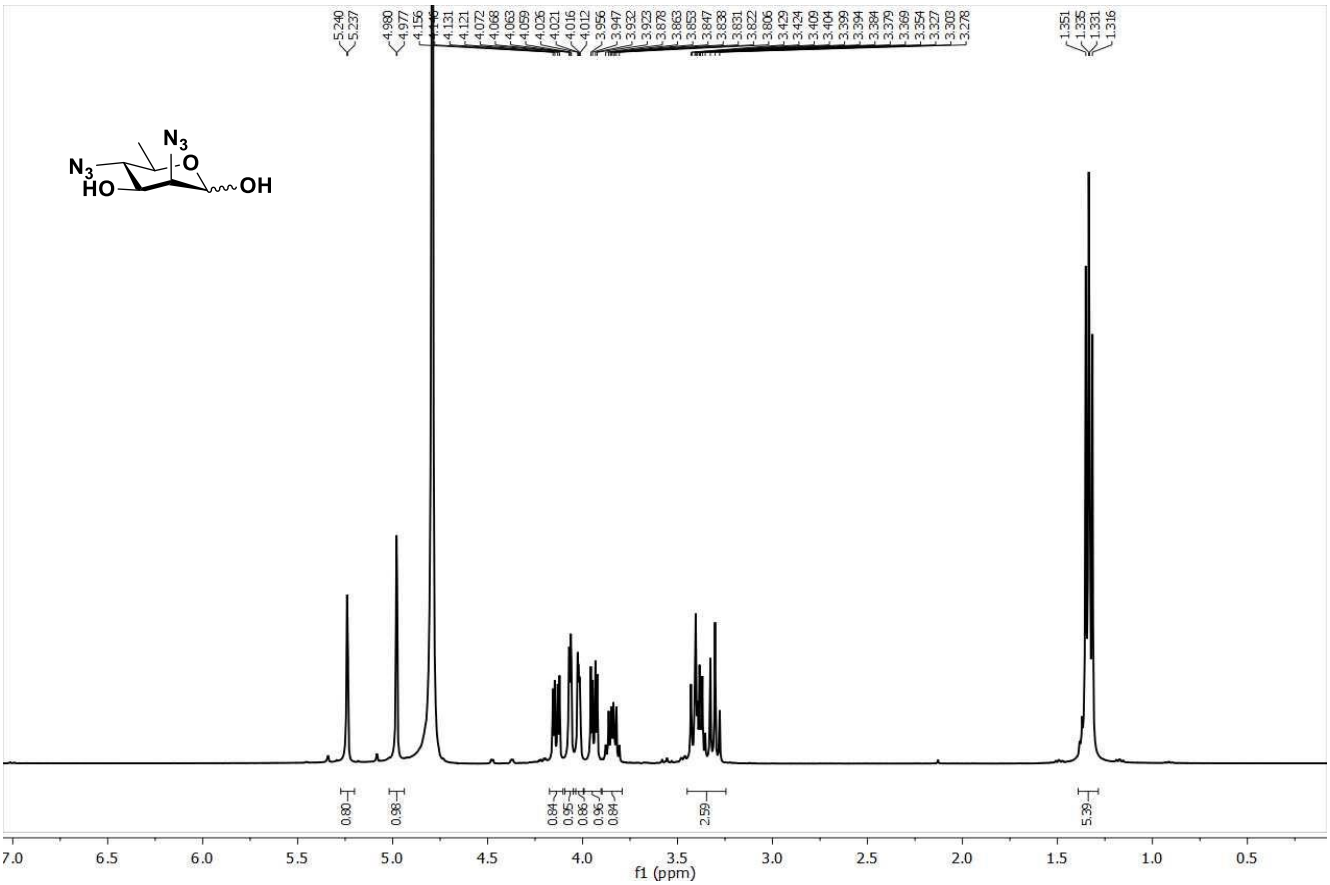


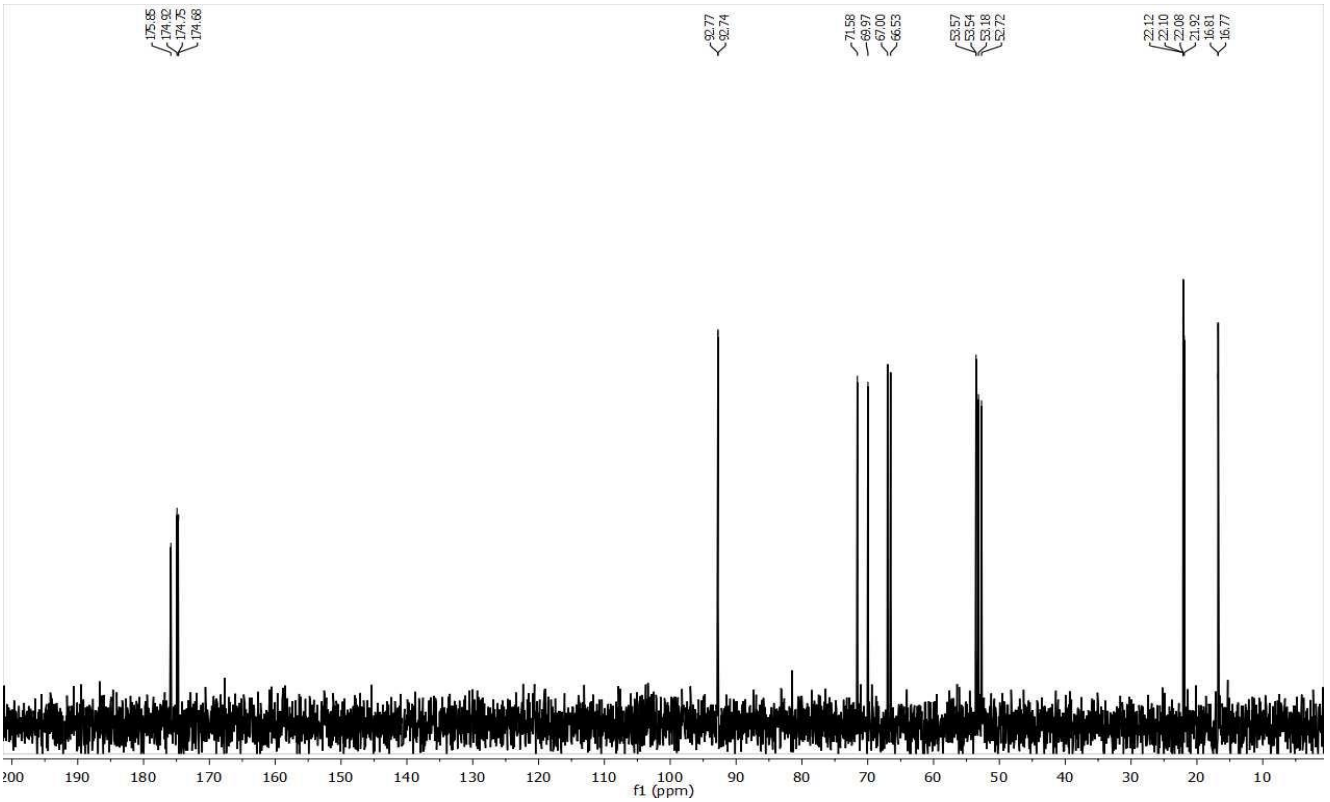
^{1}H and ^{13}C NMR spectra of *p*-methoxy phenyl-2,4-di-azido-3-*O*-benzoyl-6-deoxy-α-D-mannopyranoside (**8**)



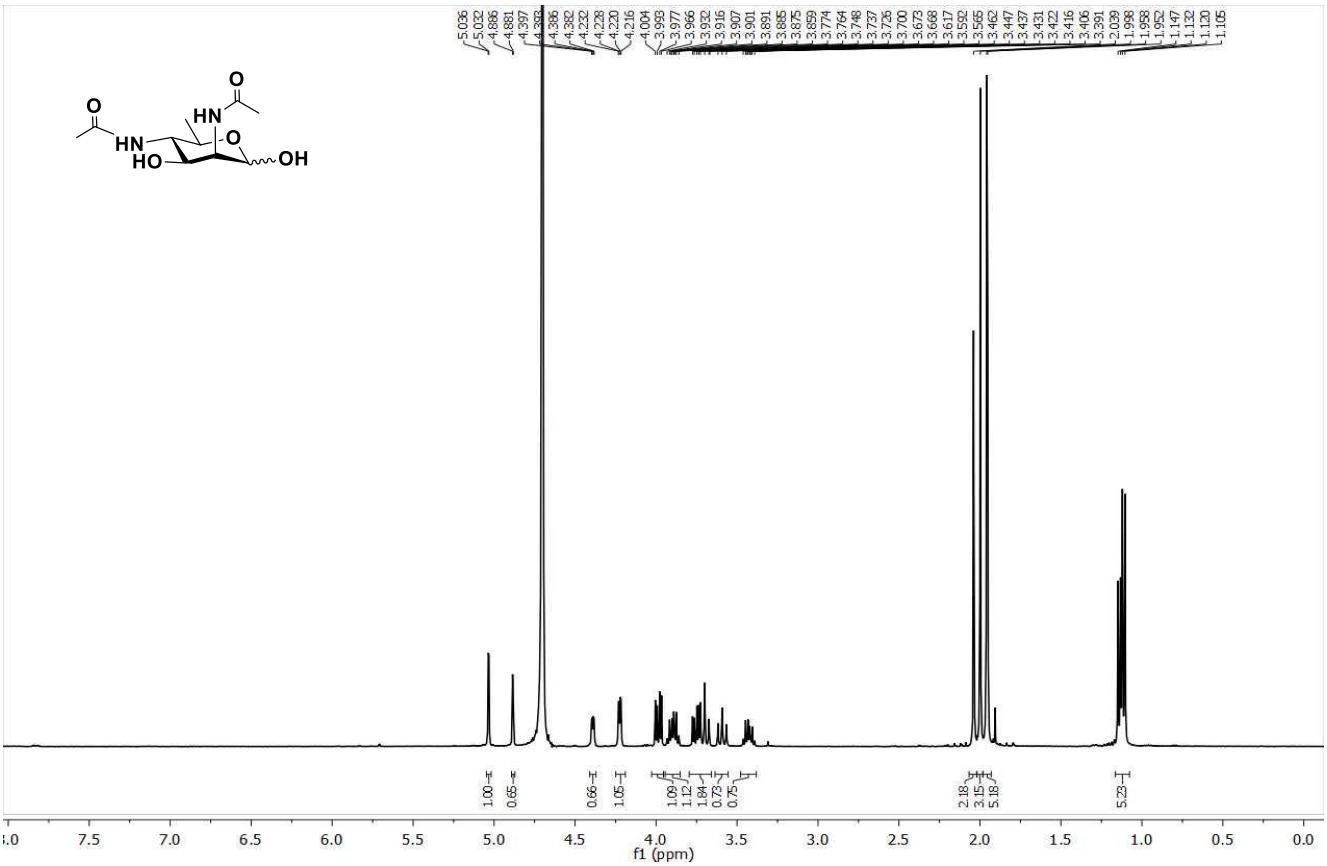


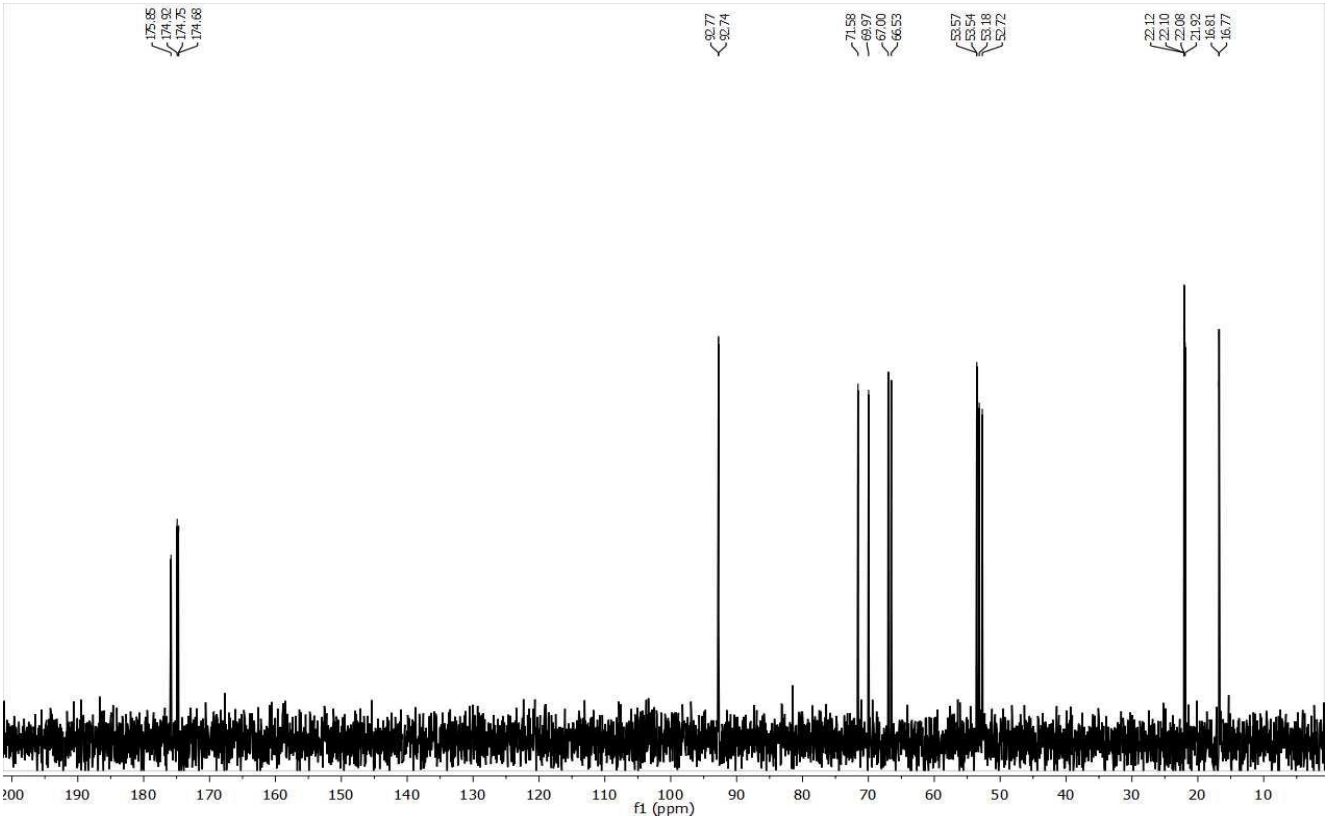
^{1}H and ^{13}C NMR spectra of 2,4-diazido-2,4,6-trideoxy-D-mannose (**9**)



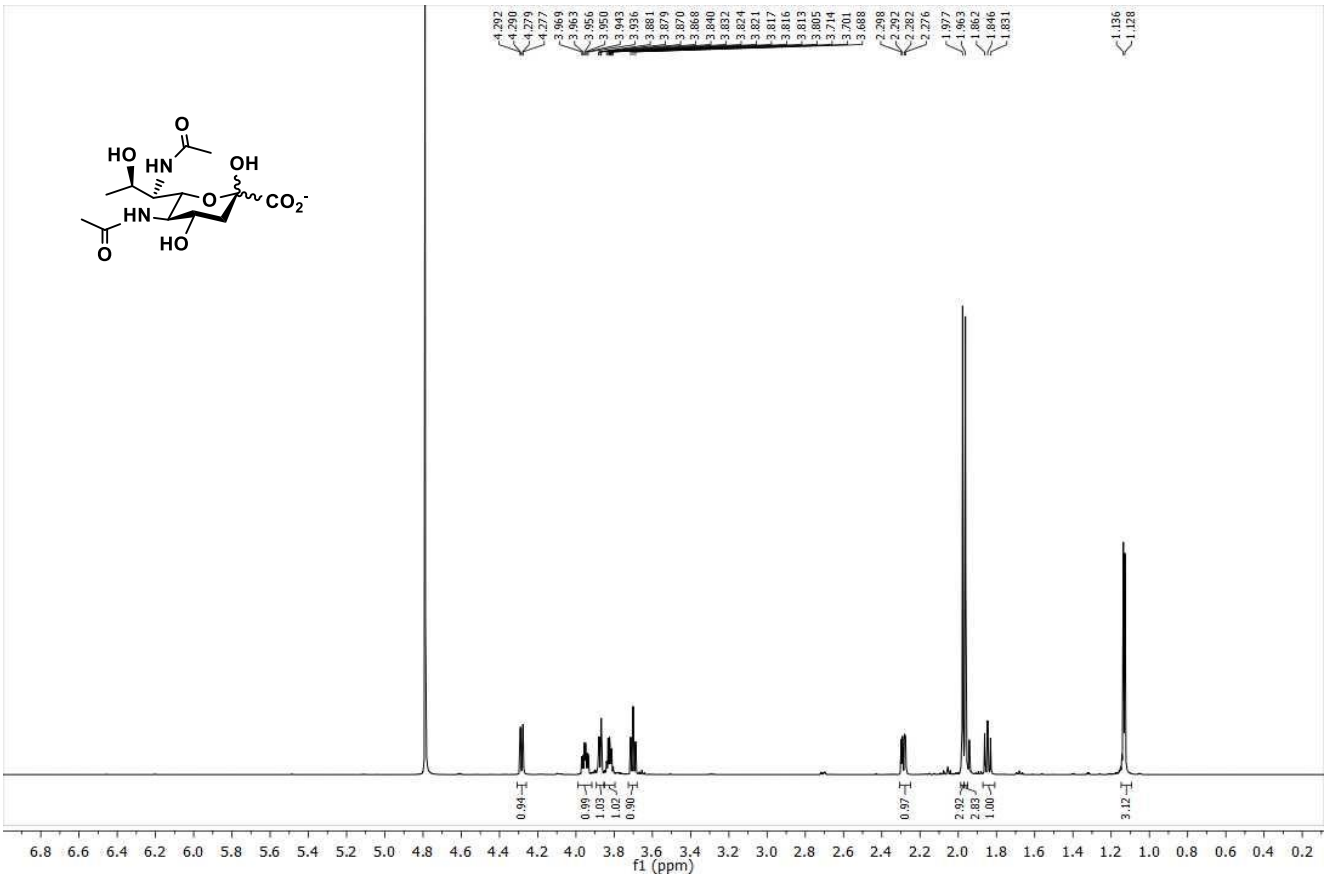


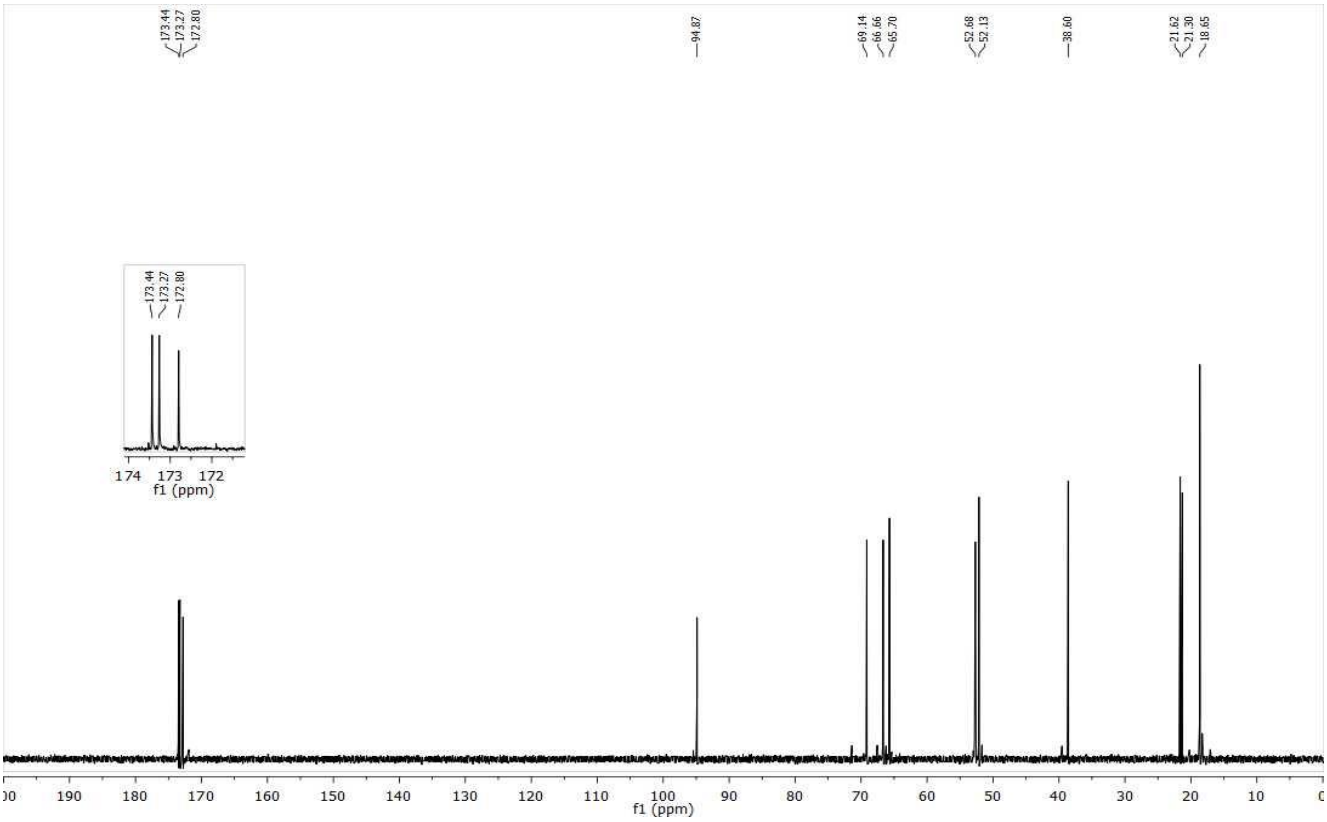
^{1}H and ^{13}C NMR spectra of 6deoxyManNAc4NAc (**4**)



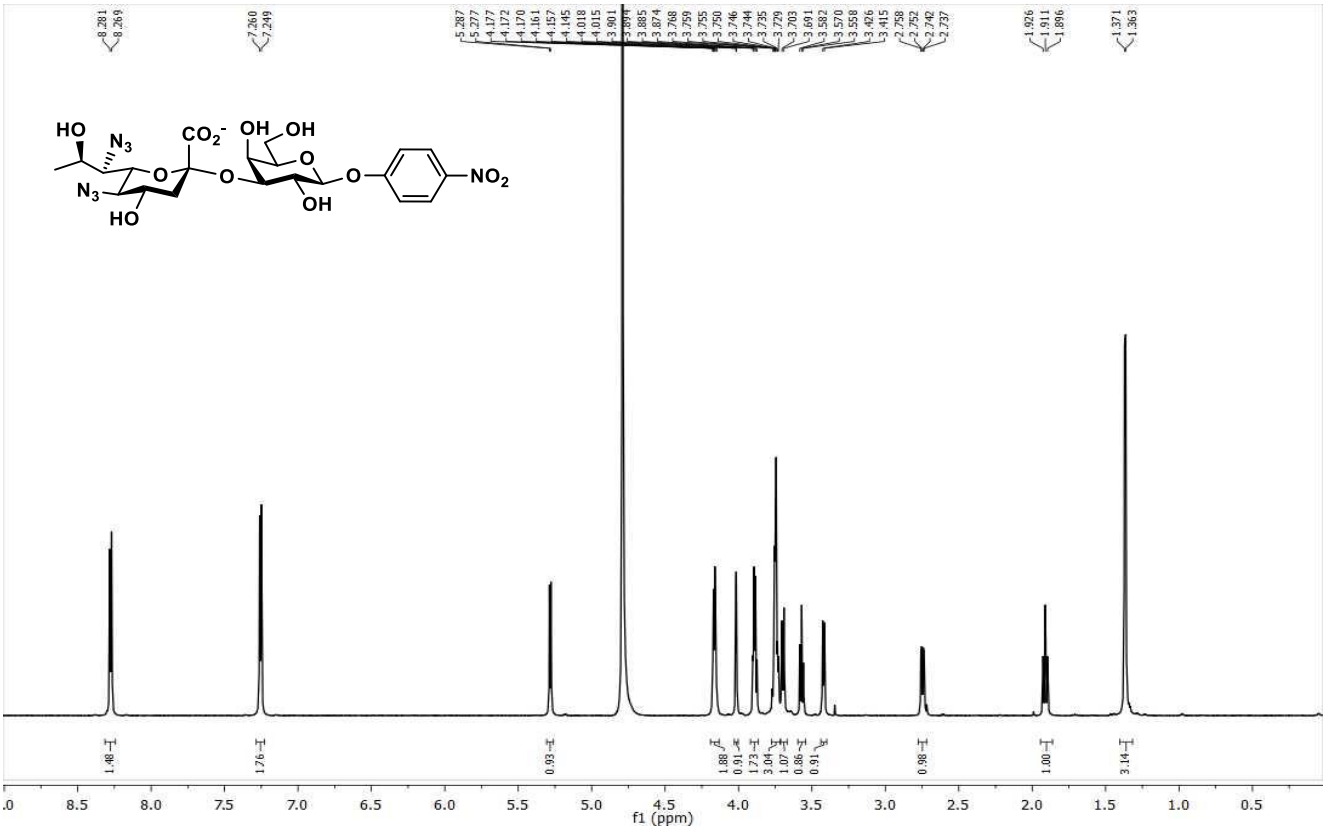


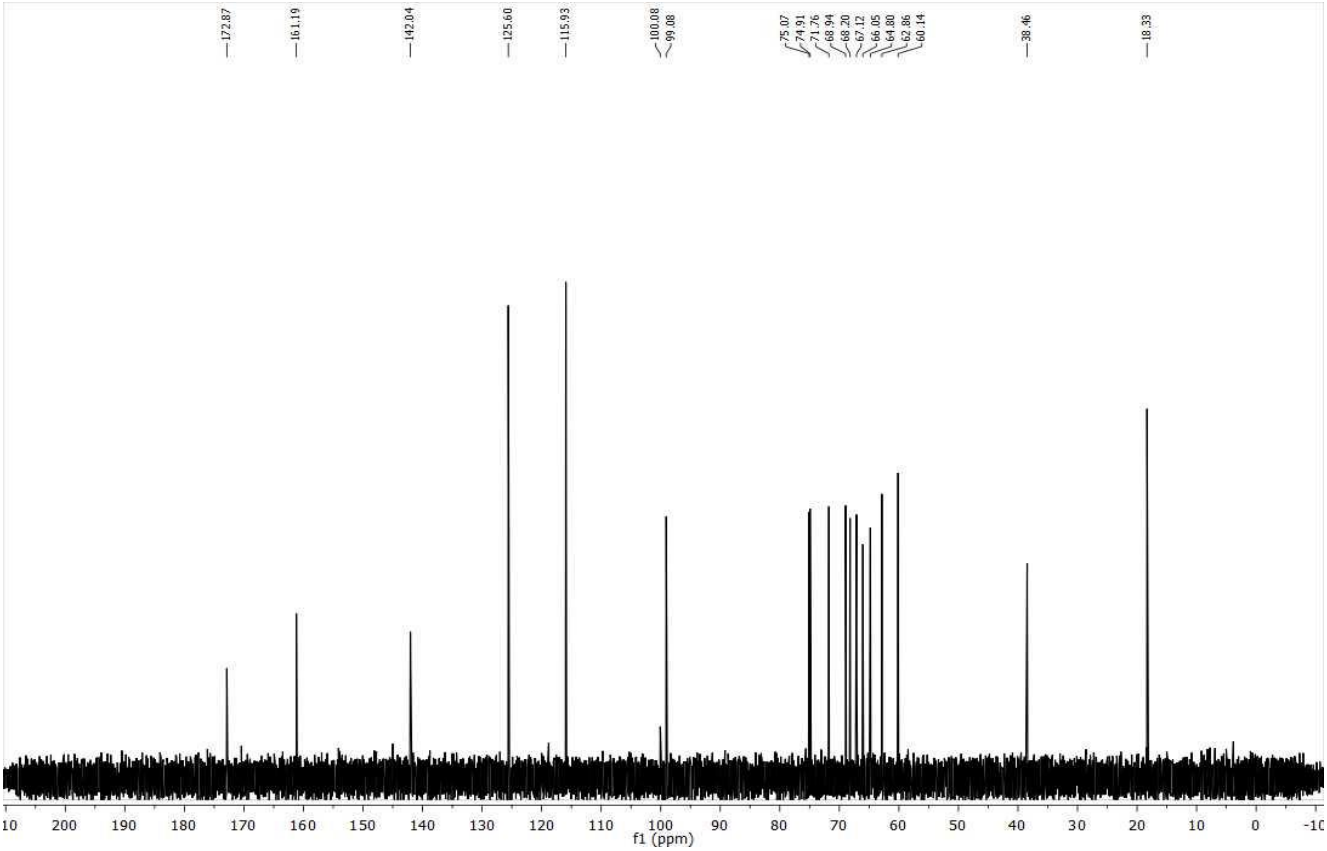
^{1}H and ^{13}C NMR spectra 5,7-di-*N*-acetyllegionaminic acid (**1**)



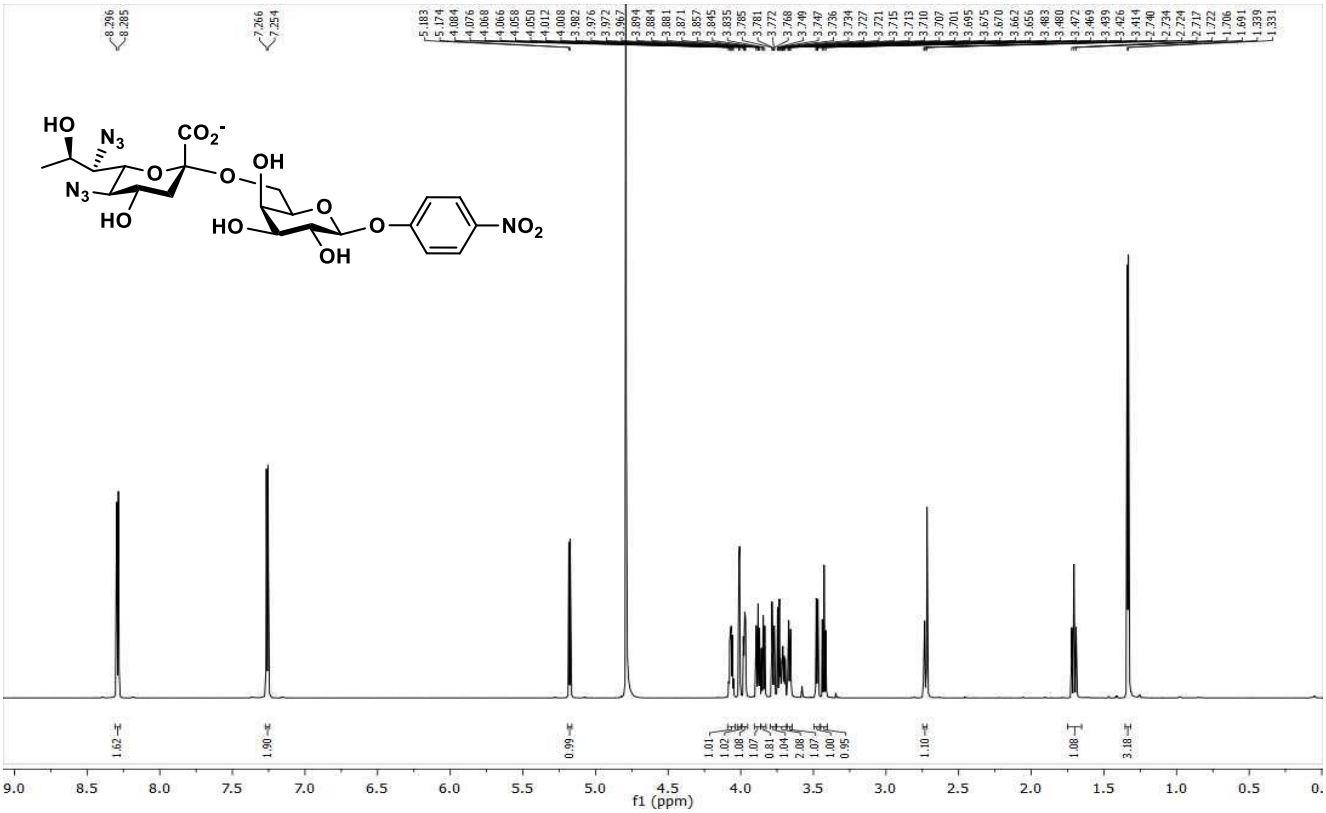


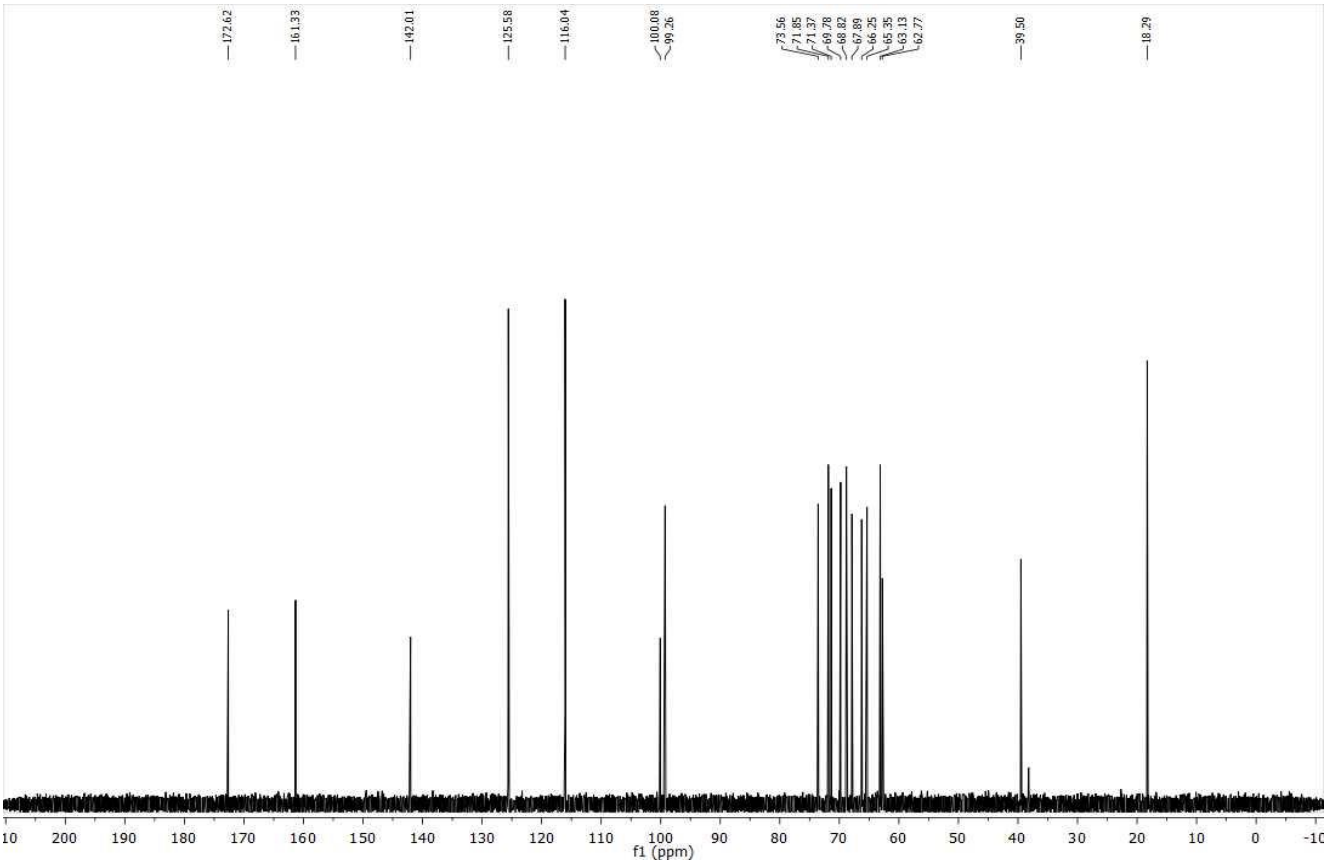
^{1}H and ^{13}C NMR spectra of Leg5,7diN_3α2–3Galβ*p*NP (**13**)



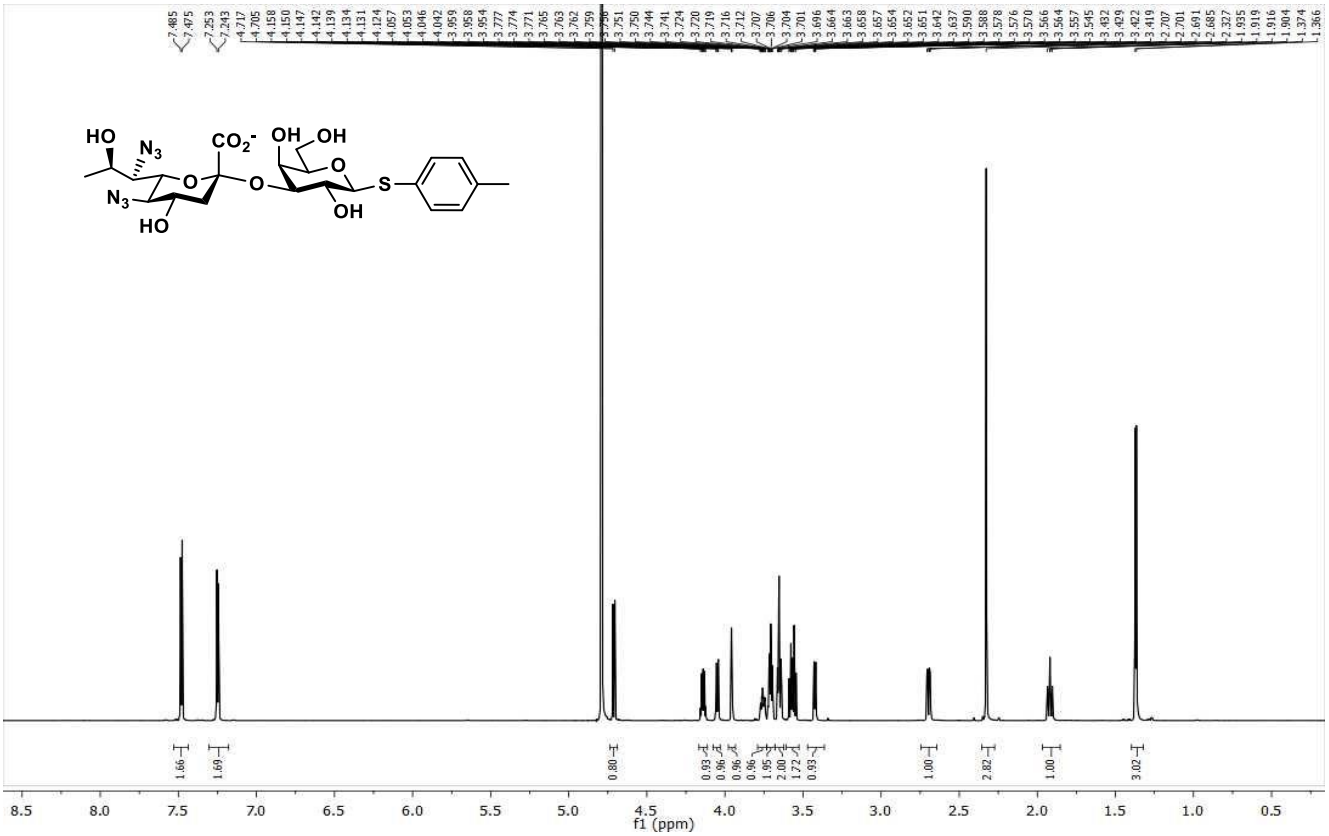


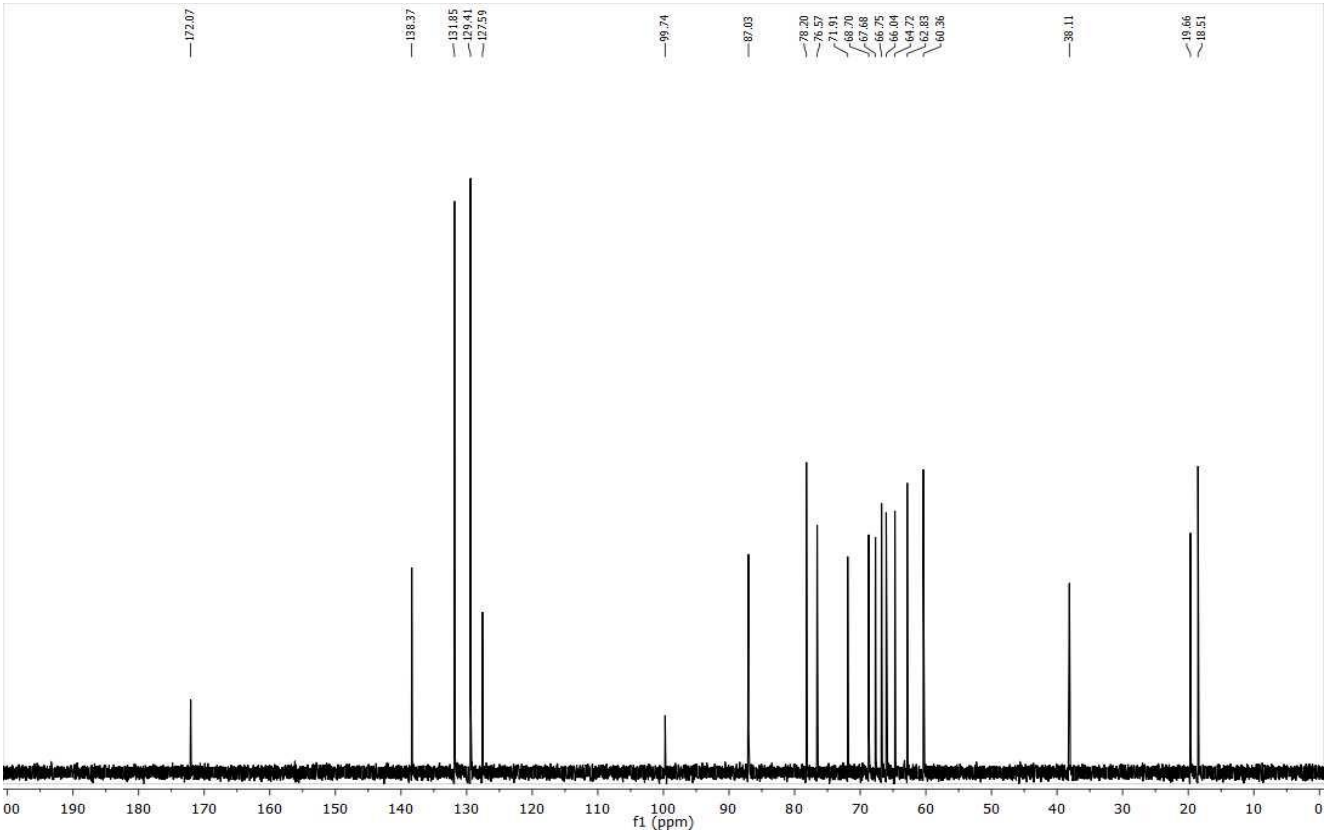
^{1}H and ^{13}C NMR spectra of Leg5,7diN$_3$α2–6Galβ*p*NP (**14**)



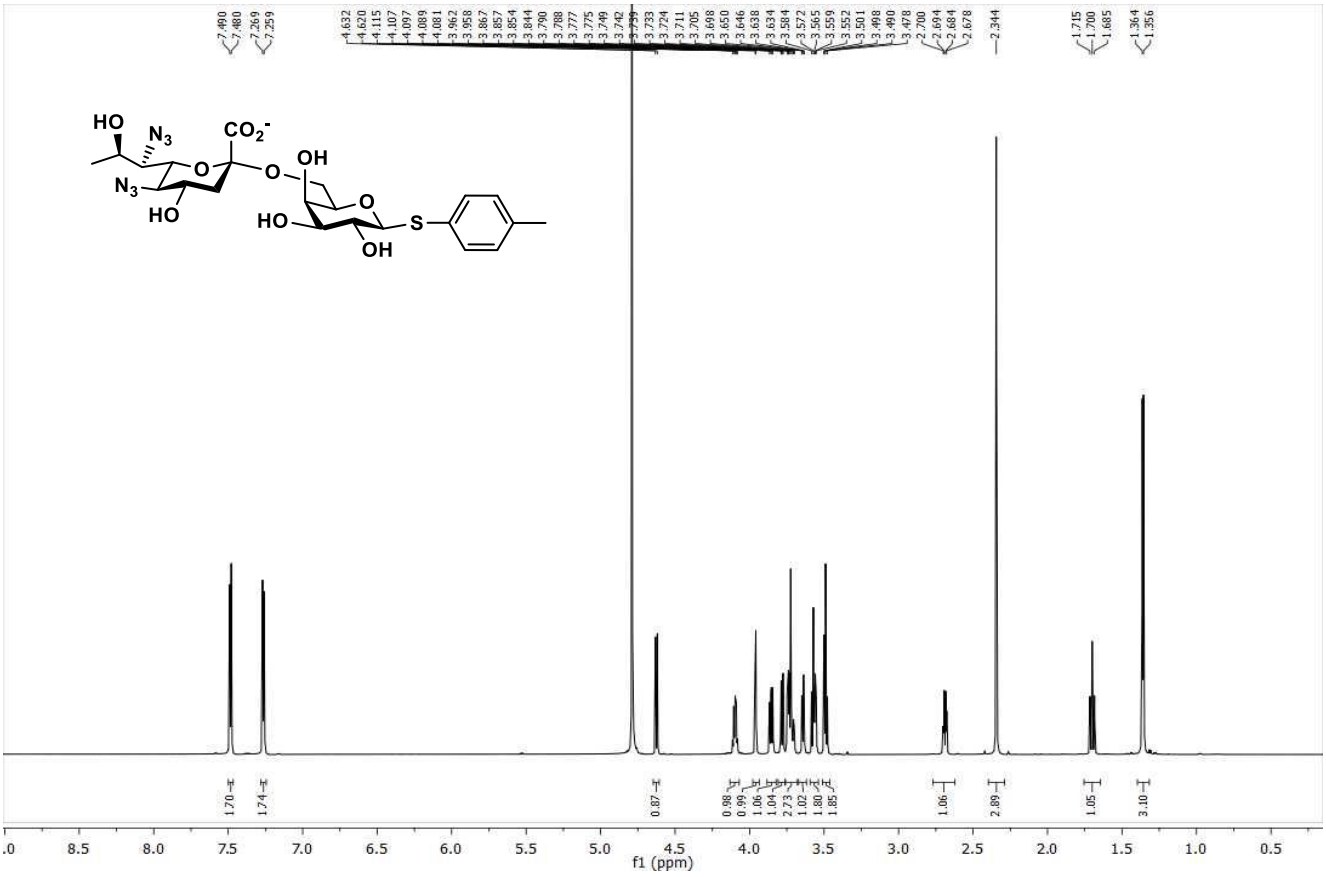


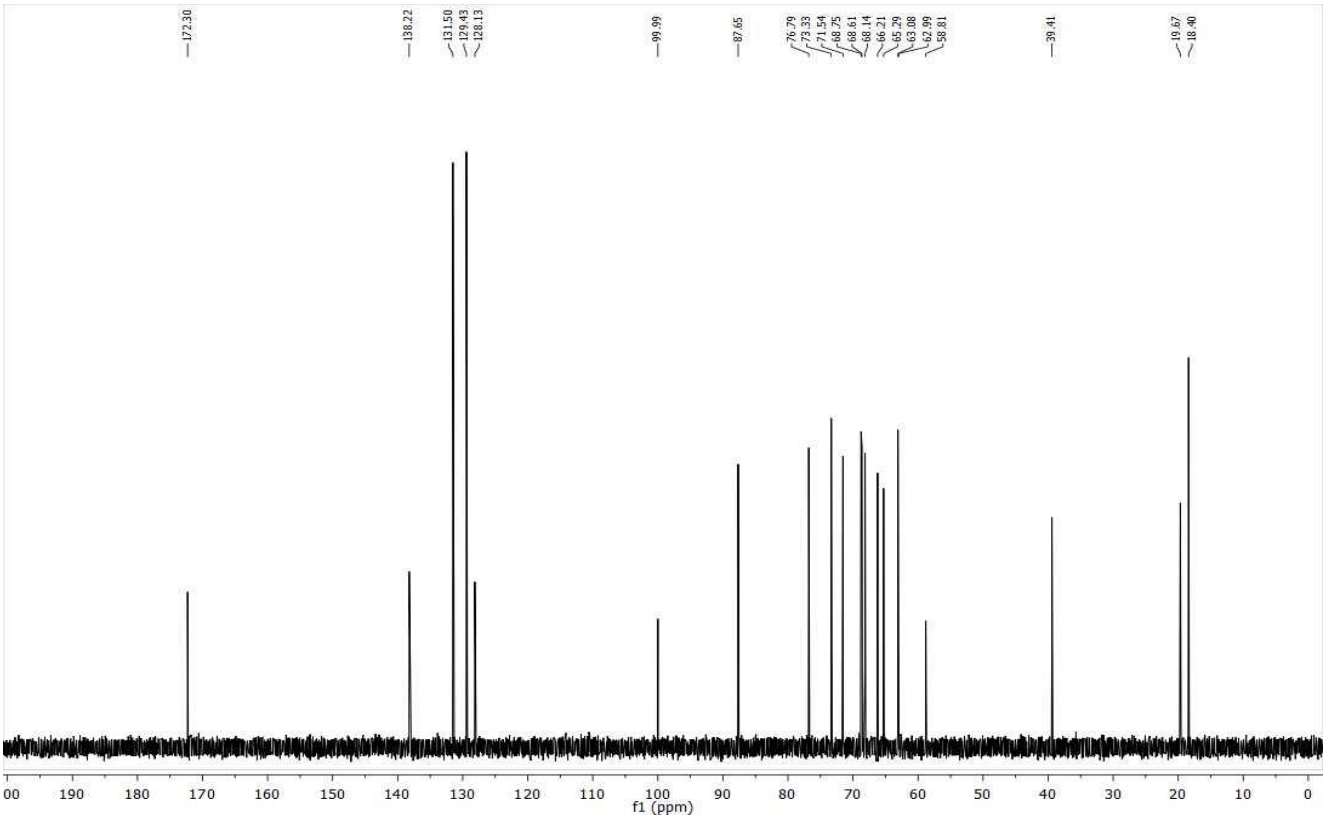
^{1}H and ^{13}C NMR spectra of Leg5,7diN$_3$α2–3GalβSTol (**15**)



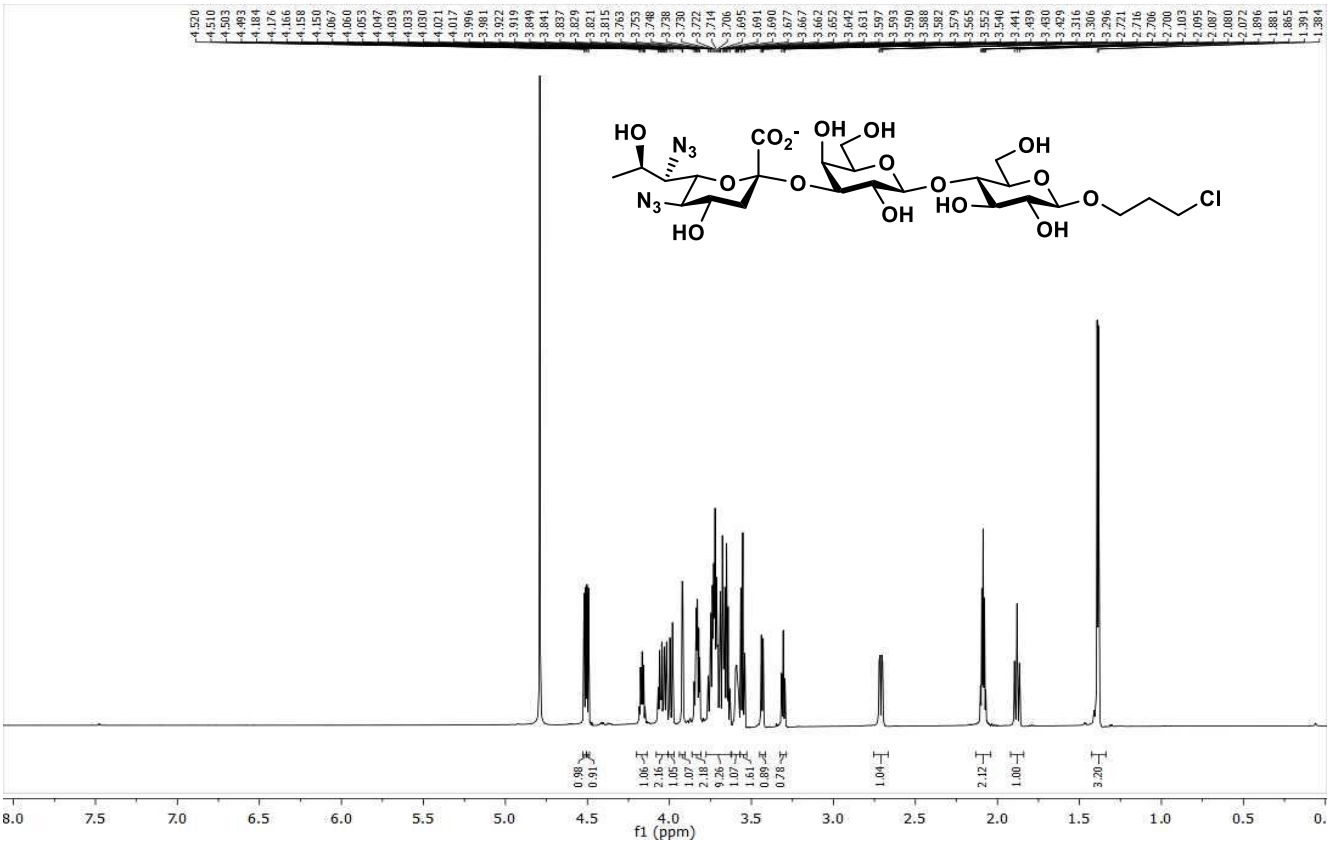


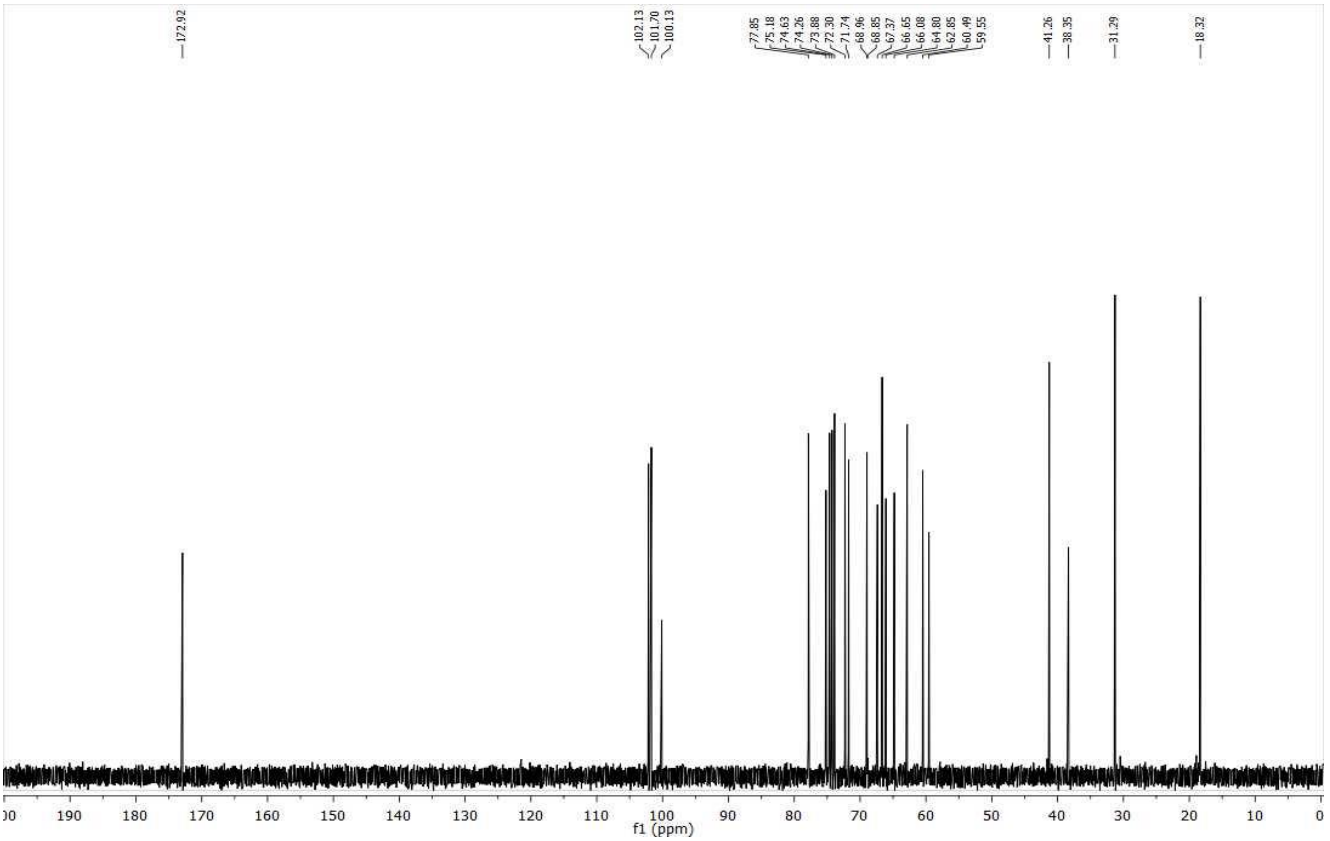
^{1}H and ^{13}C NMR spectra of Leg5,7diN$_3$α2–6GalβSTol (**16**)



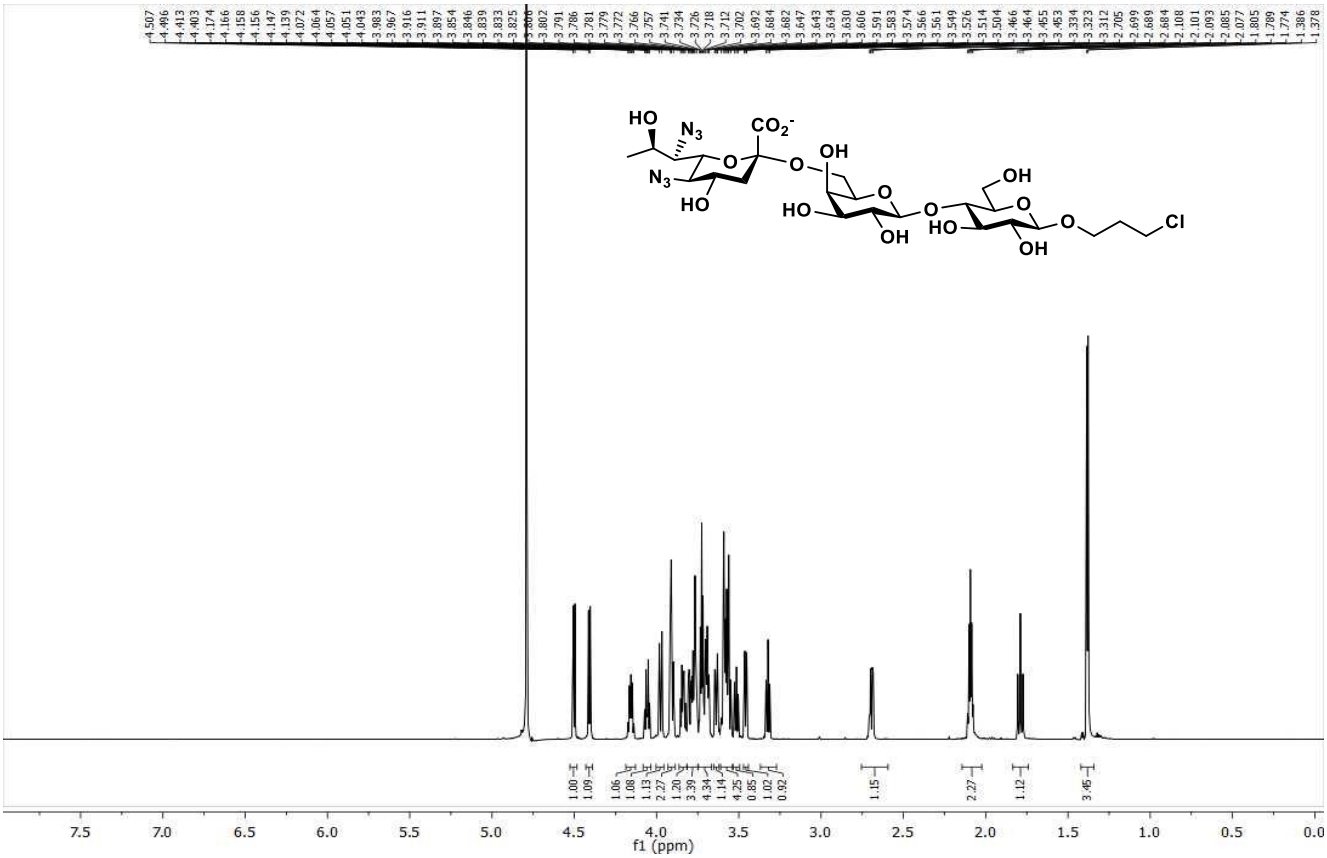


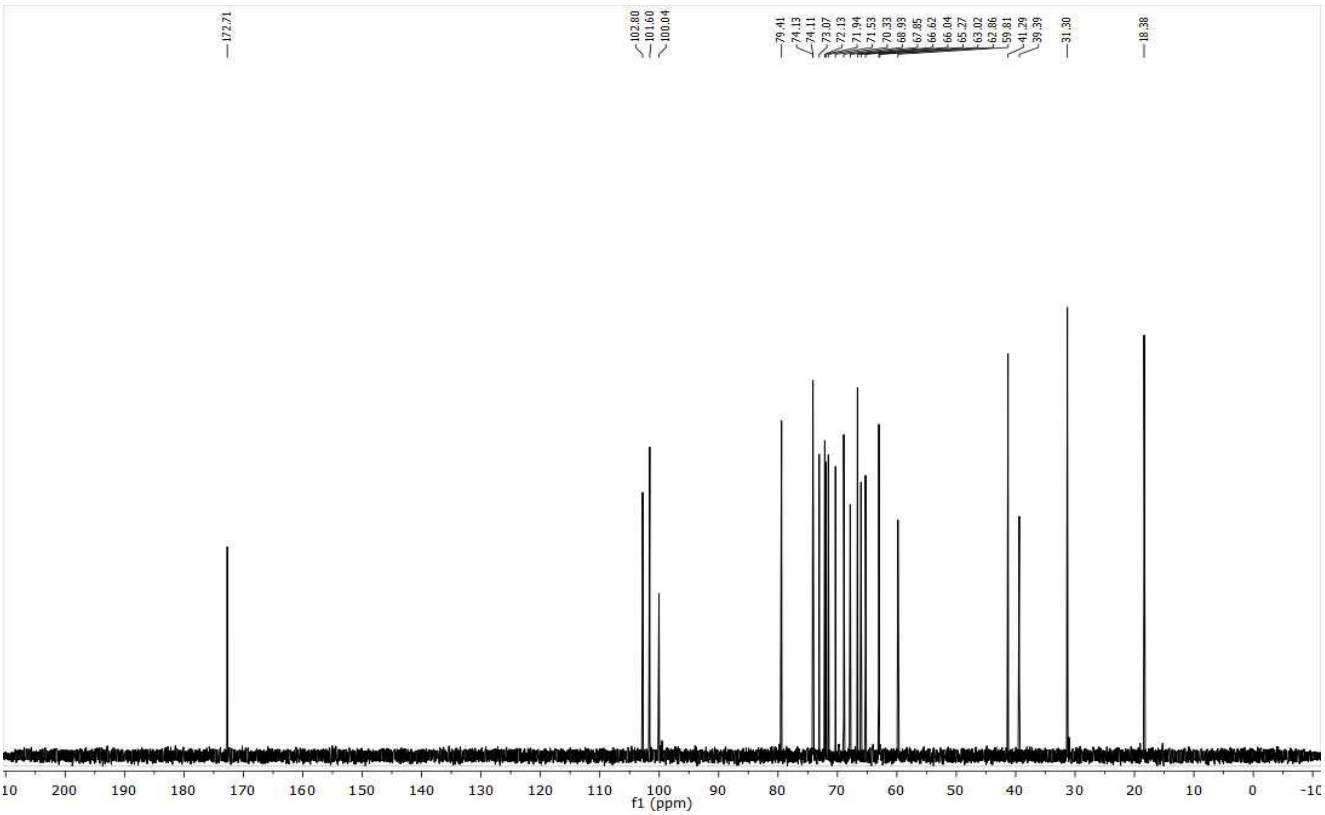
^{1}H and ^{13}C NMR spectra of Leg5,7diN$_3$α2–3LacβProCl (**17**)



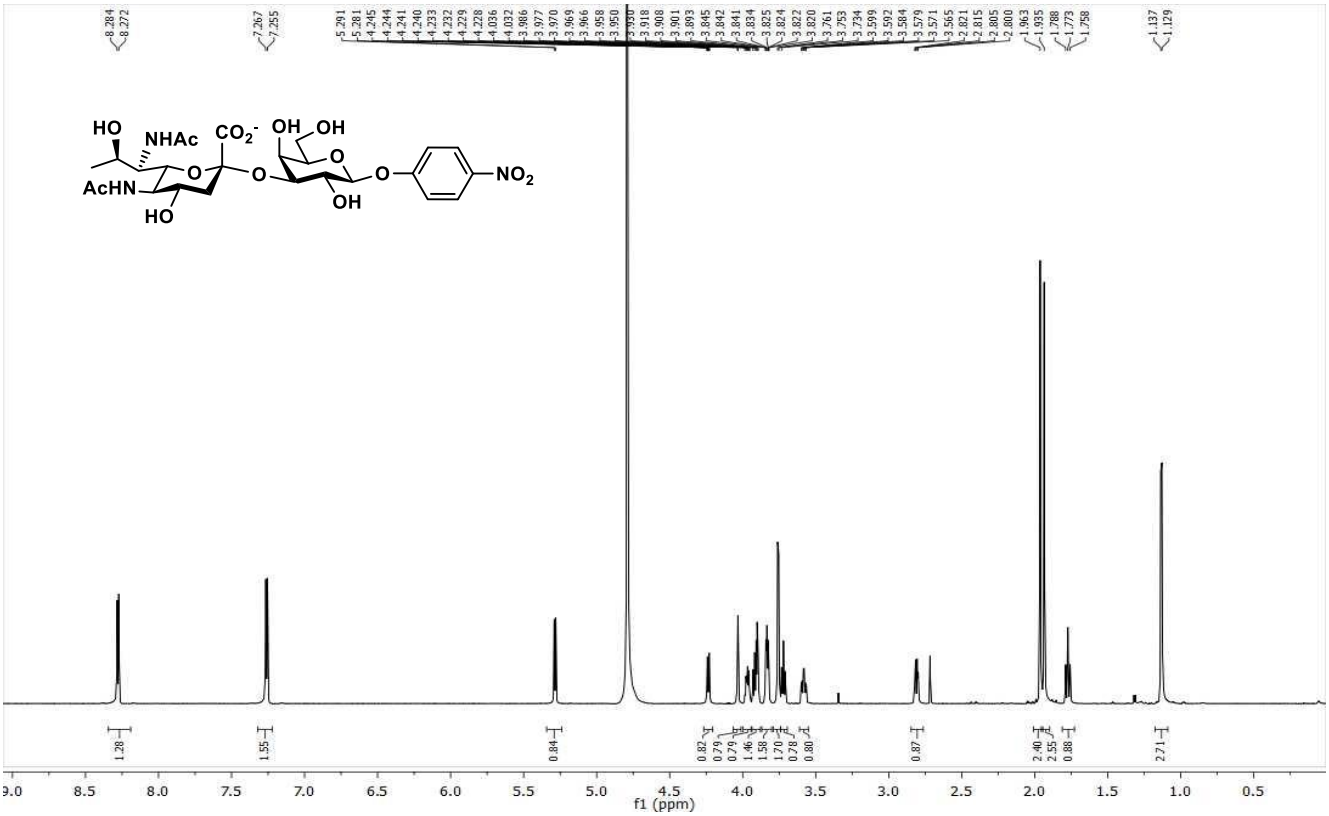


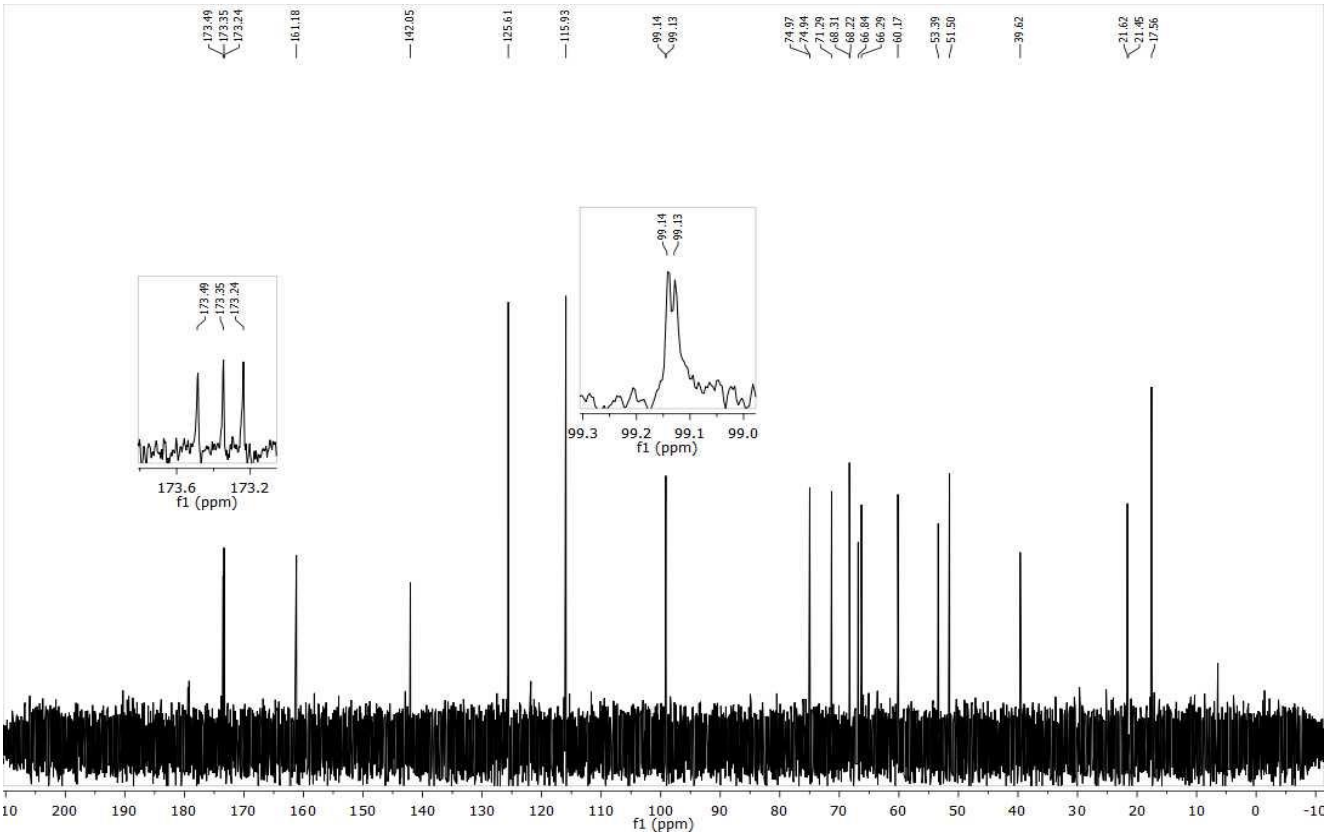
^{1}H and ^{13}C NMR spectra of Leg5,7diN$_3$α2–6LacβProCl (**18**)



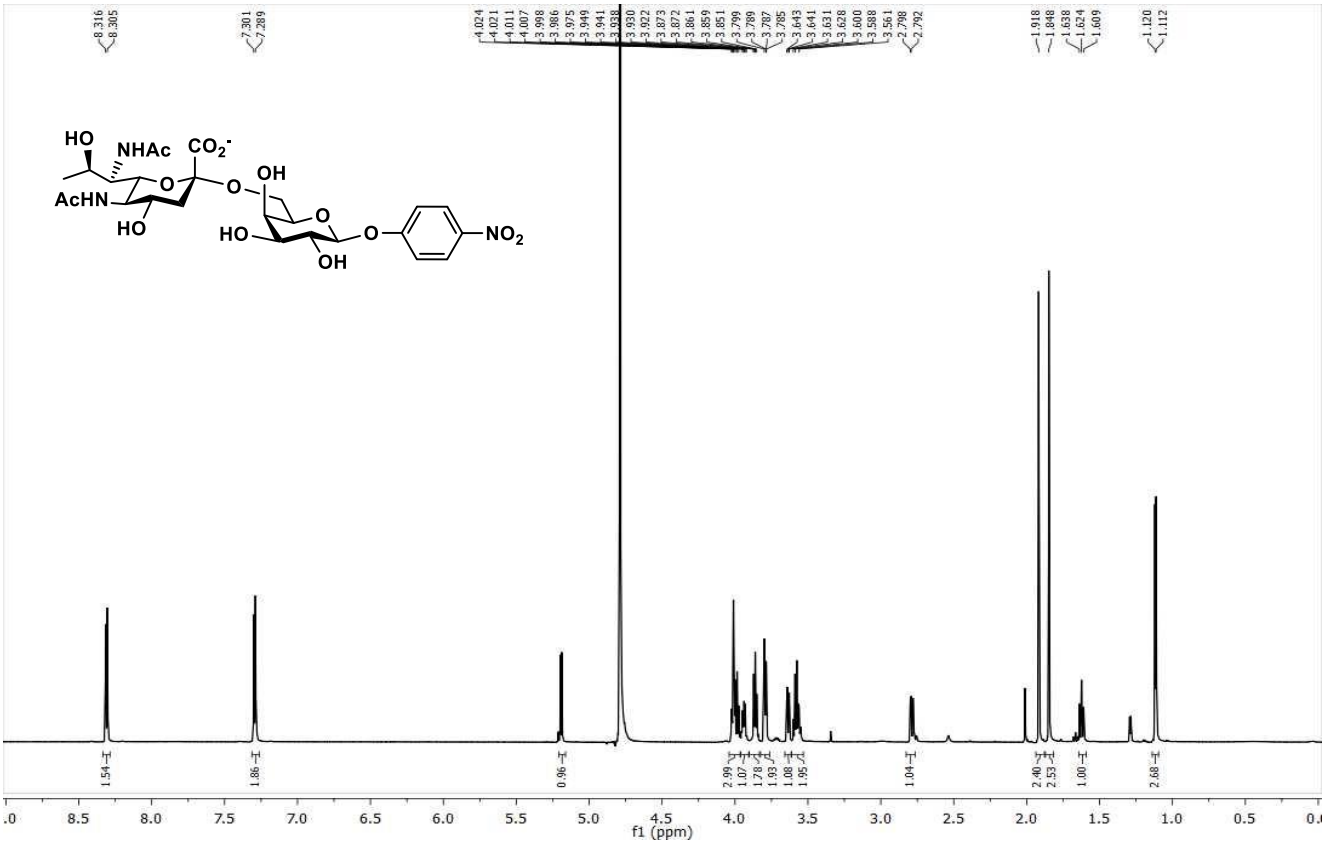


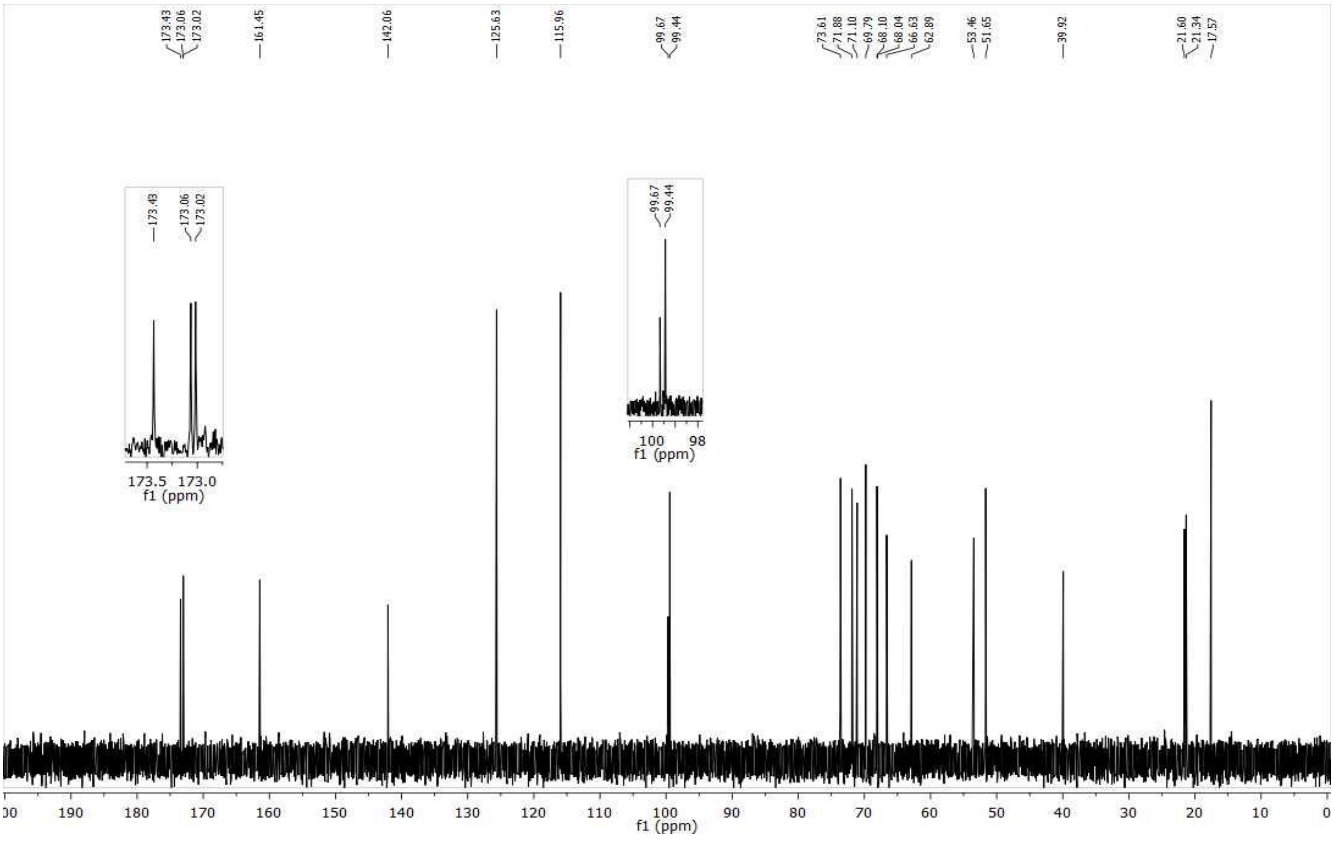
^{1}H and ^{13}C NMR spectra of Leg5,7Ac$_2$α2–3Galβ*p*NP (**19**)



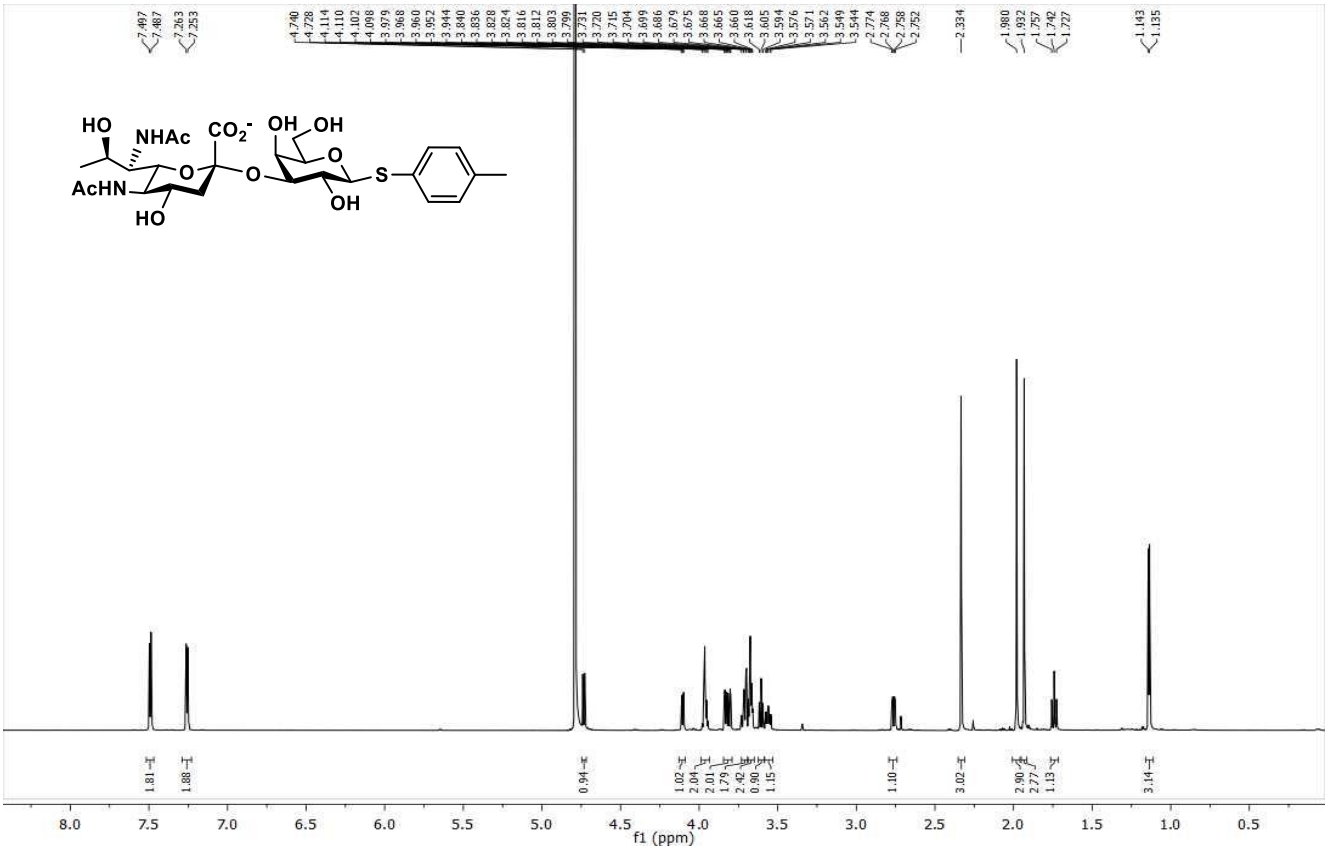


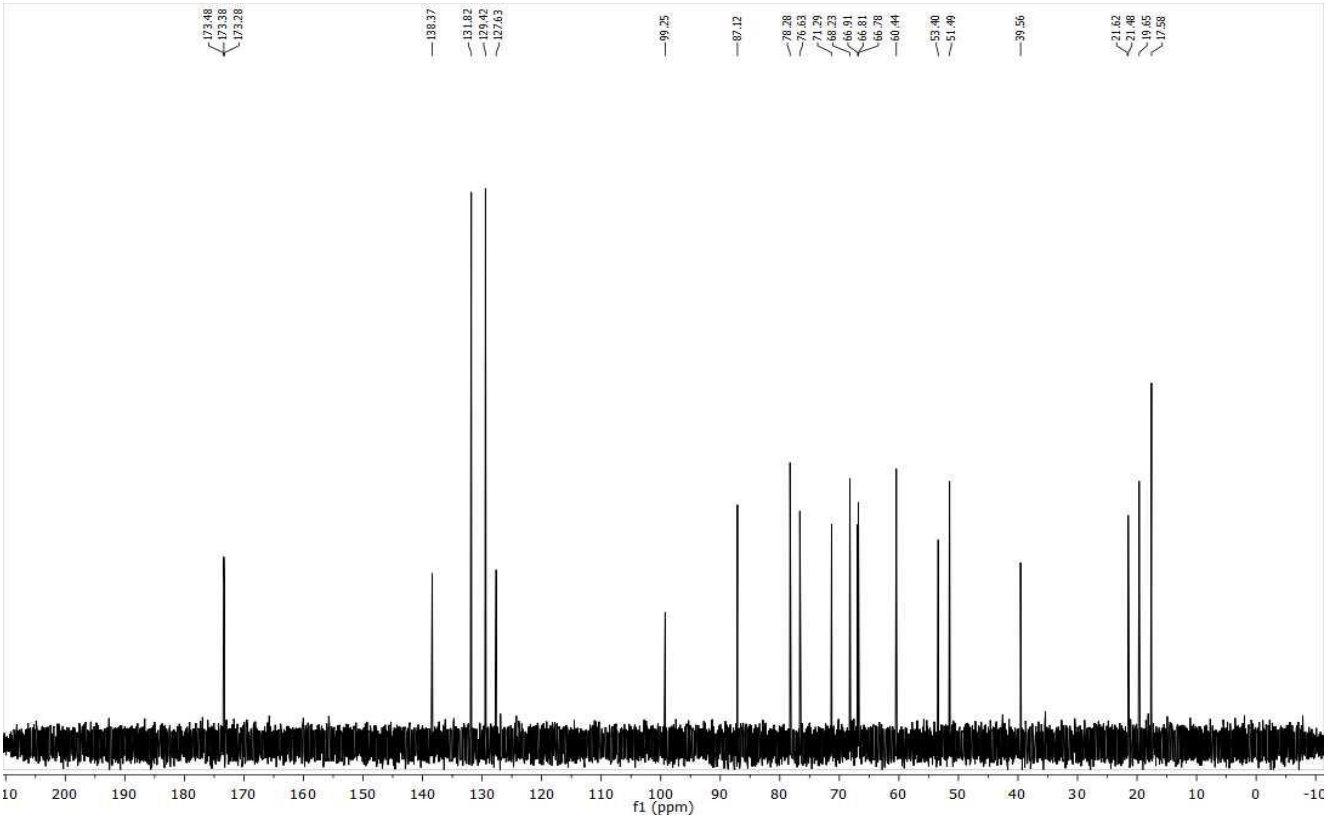
^{1}H and ^{13}C NMR spectra of Leg5,7Ac$_2$α2–6Galβ*p*NP (**20**)



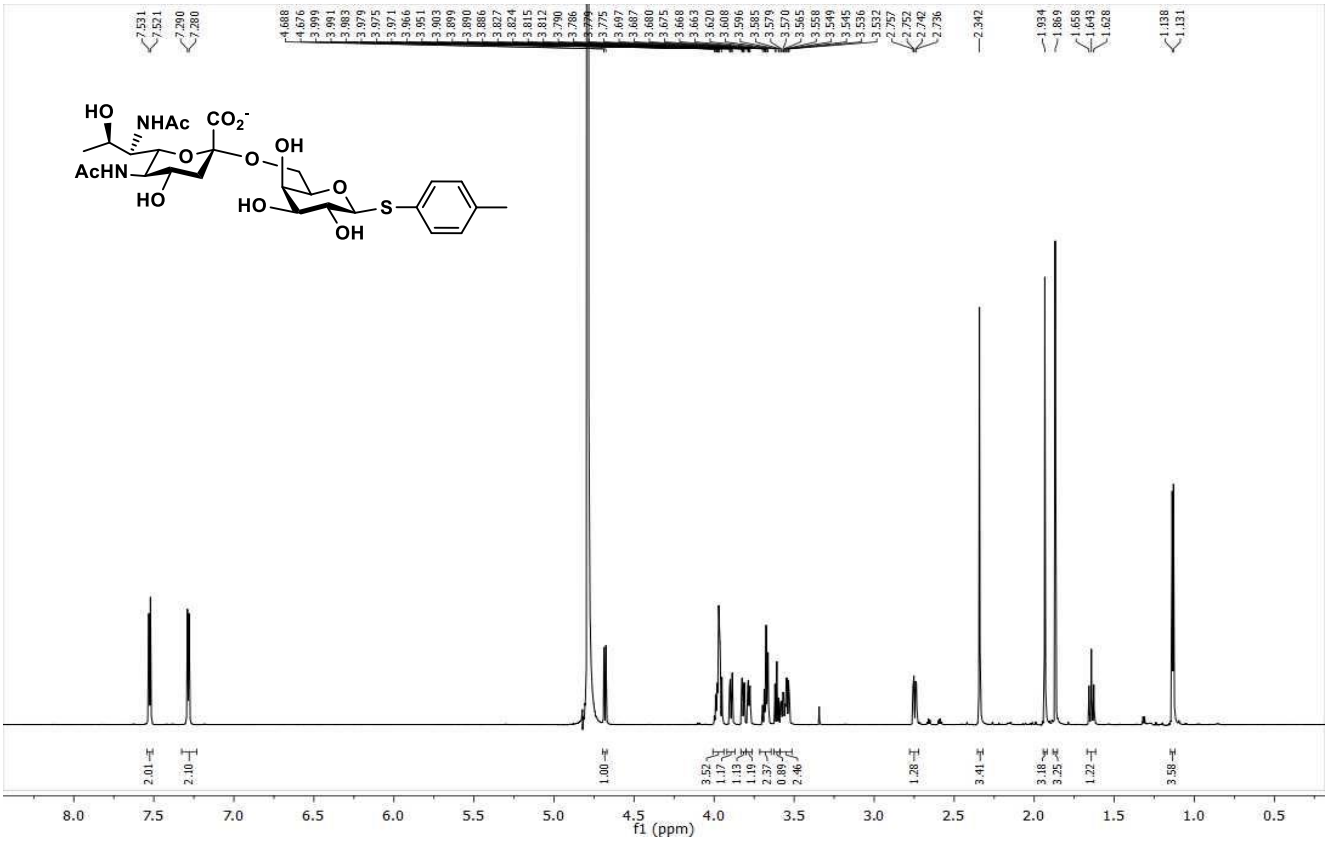


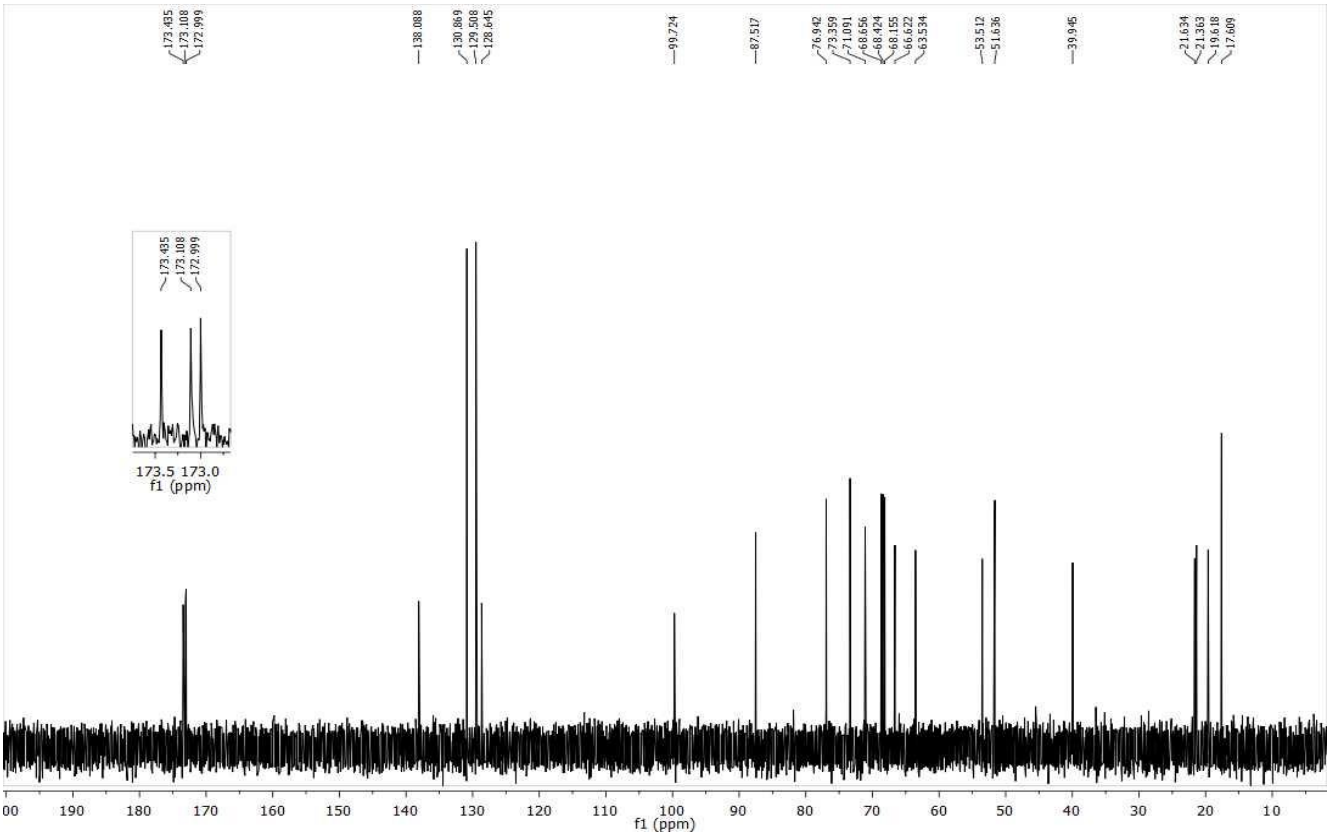
^{1}H and ^{13}C NMR spectra of Leg5,7Ac$_2$α2–3GalβSTol (**21**)



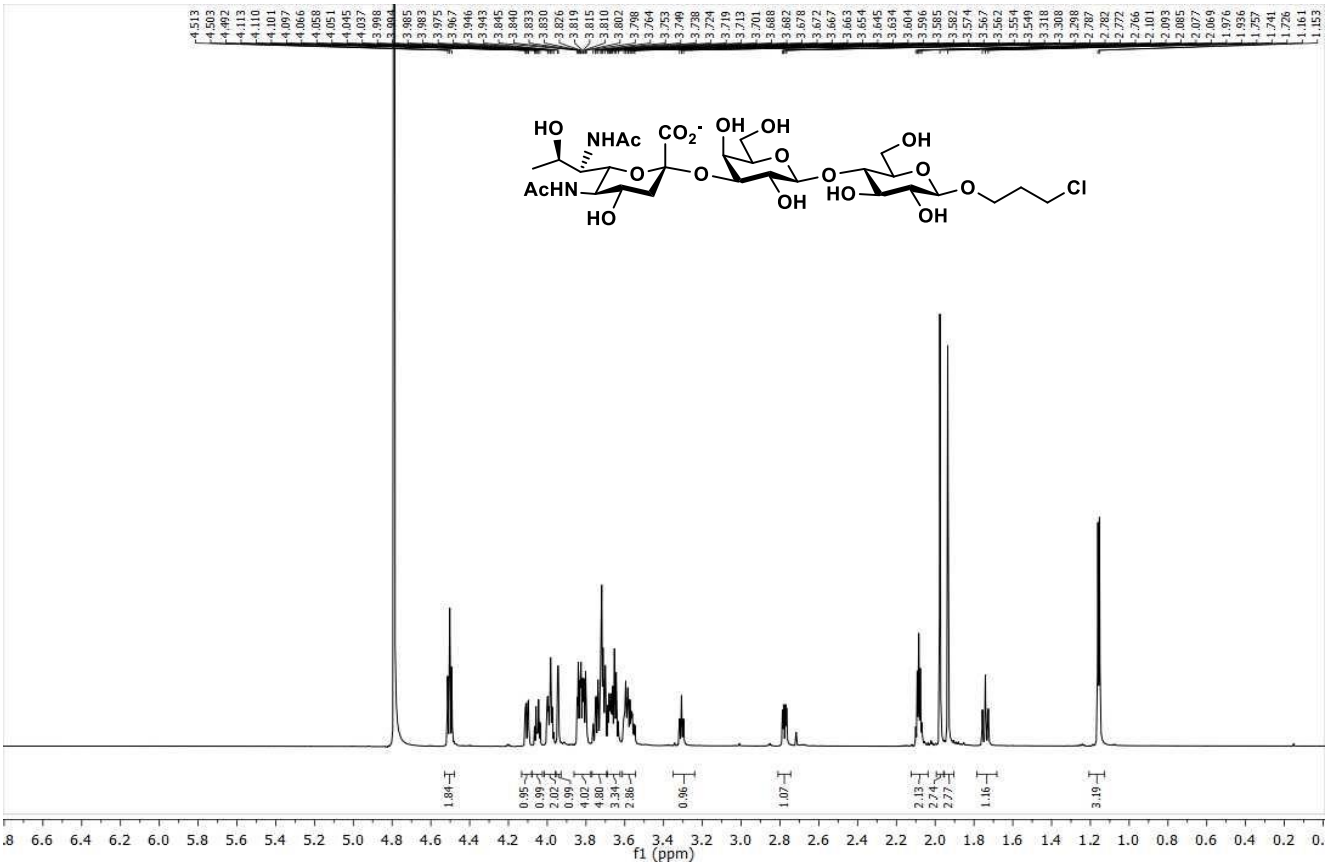


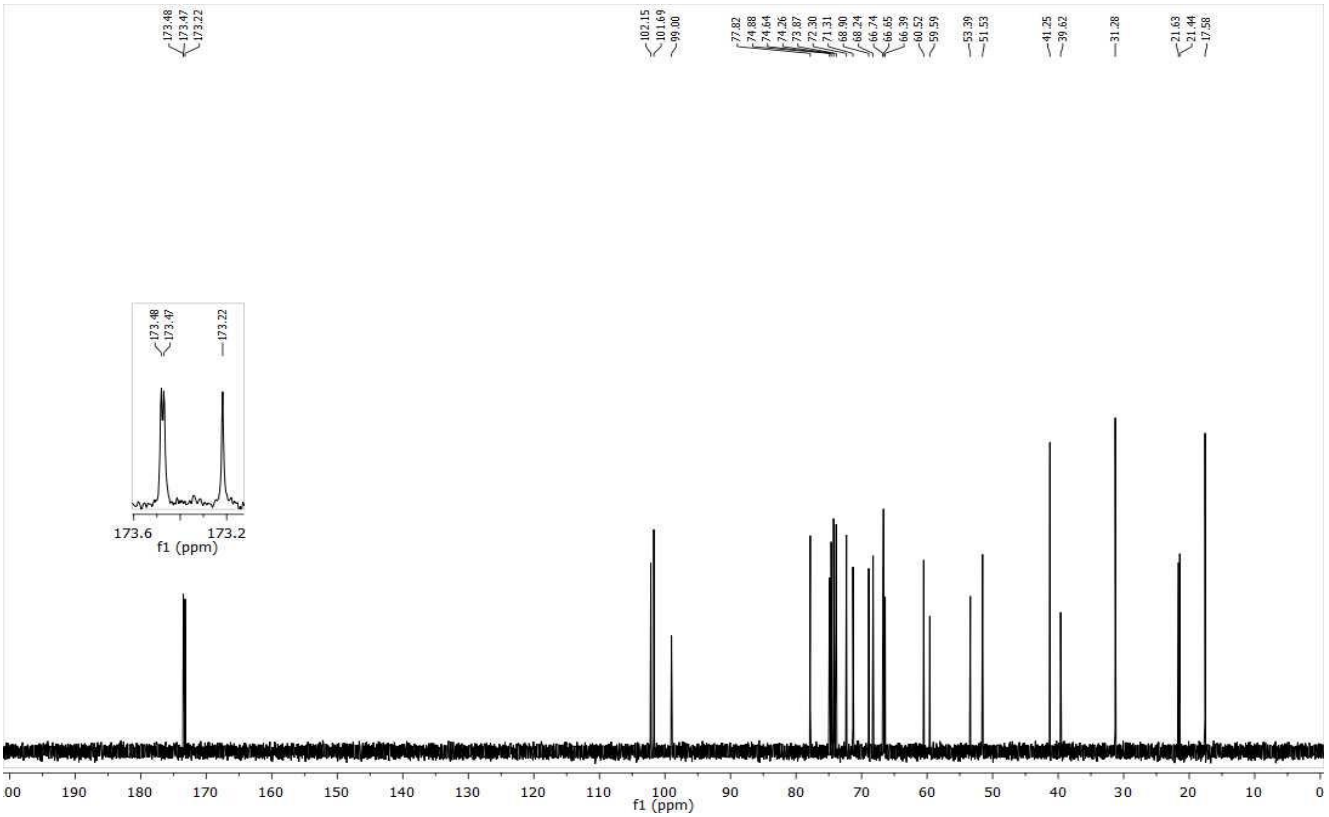
^{1}H and ^{13}C NMR spectra of Leg5,7Ac$_2$α2–6GalβSTol (**22**)



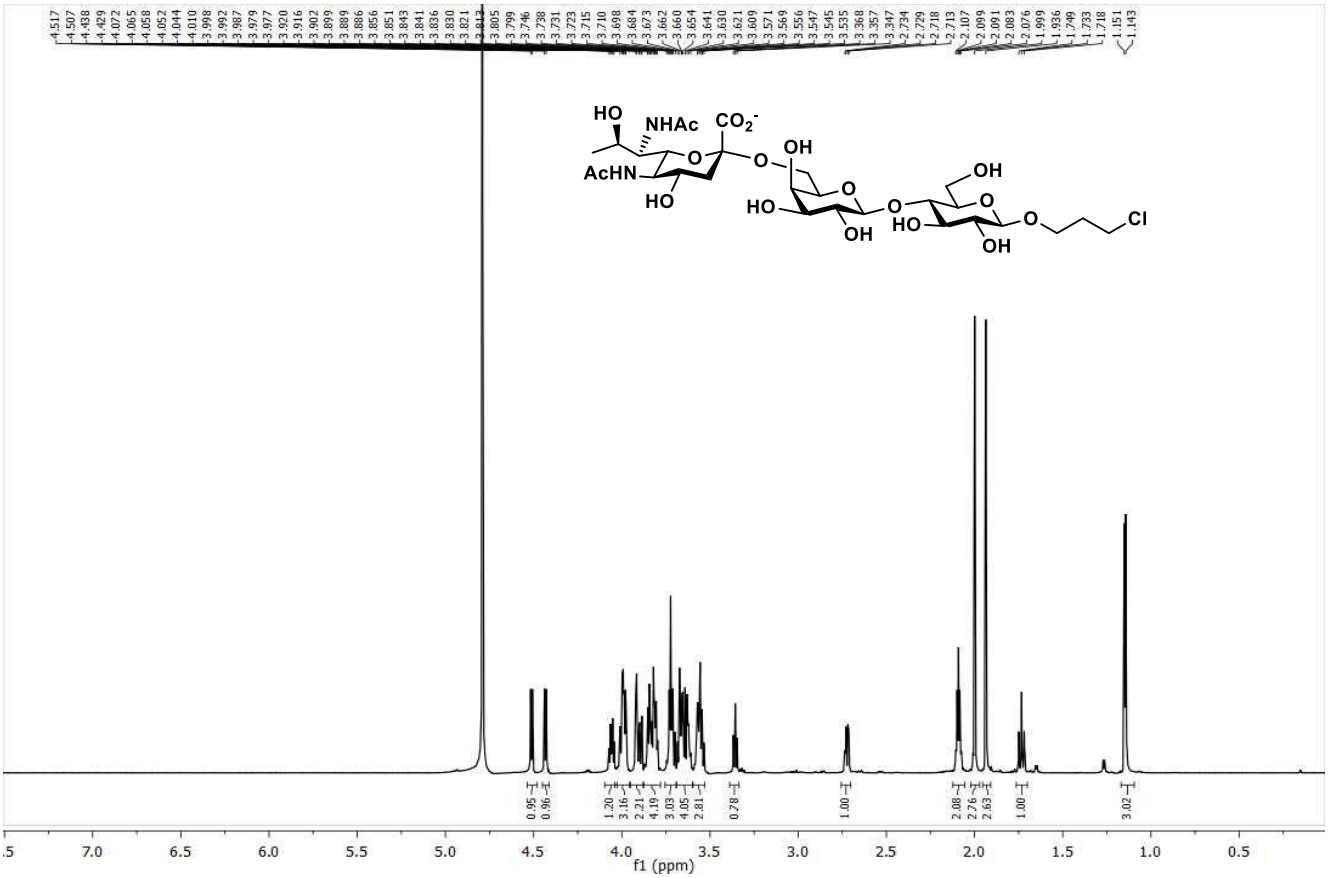


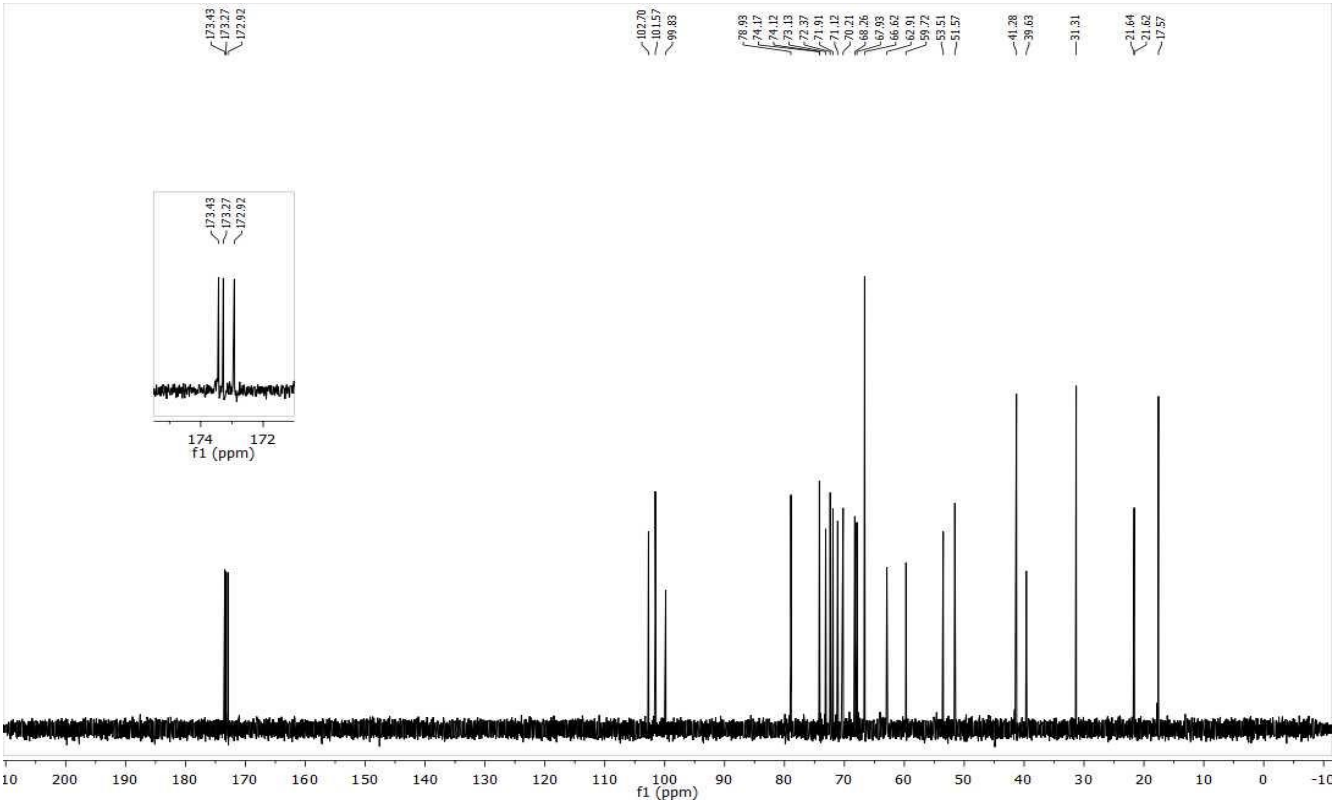
^{1}H and ^{13}C NMR spectra of Leg5,7Ac$_2$α2–3LacβProCl (**23**)



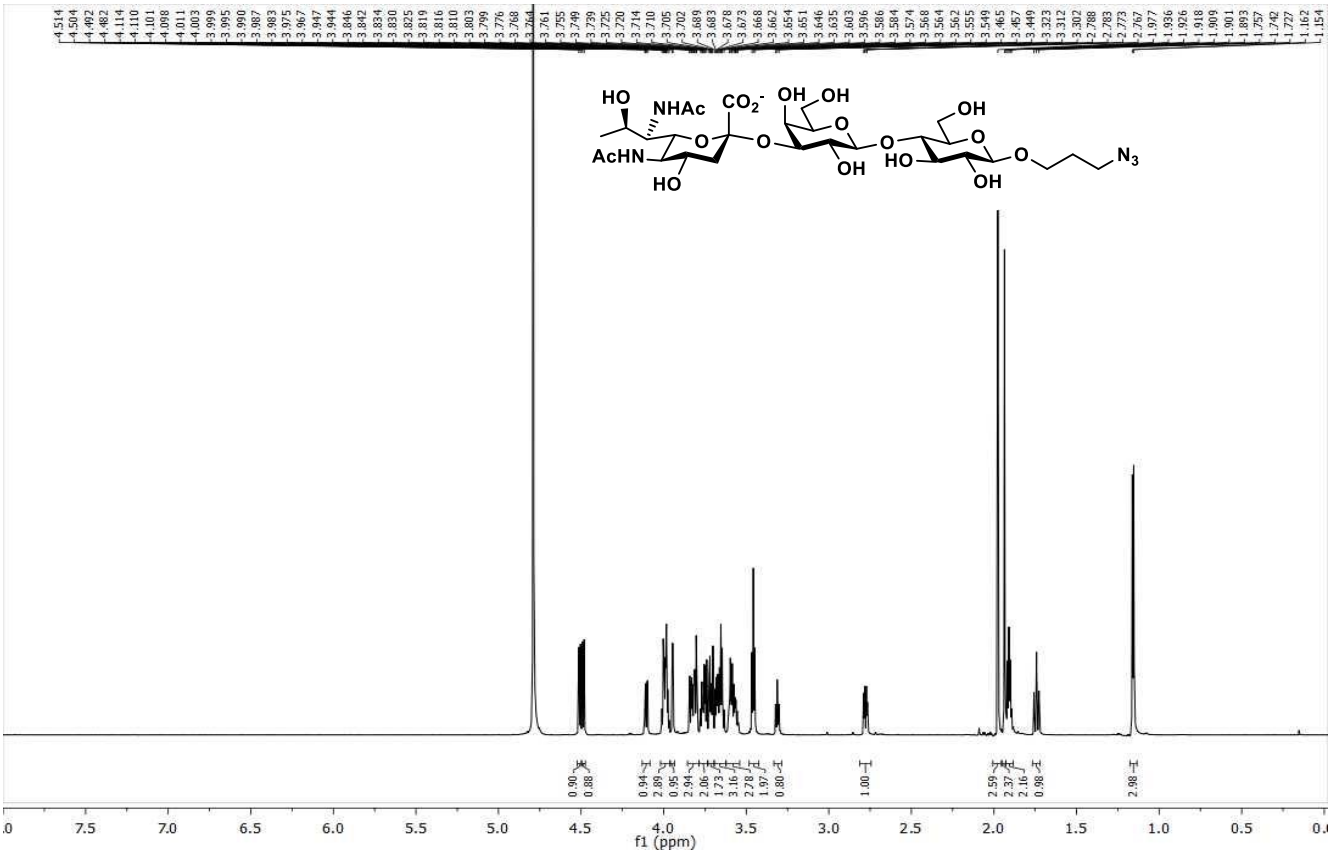


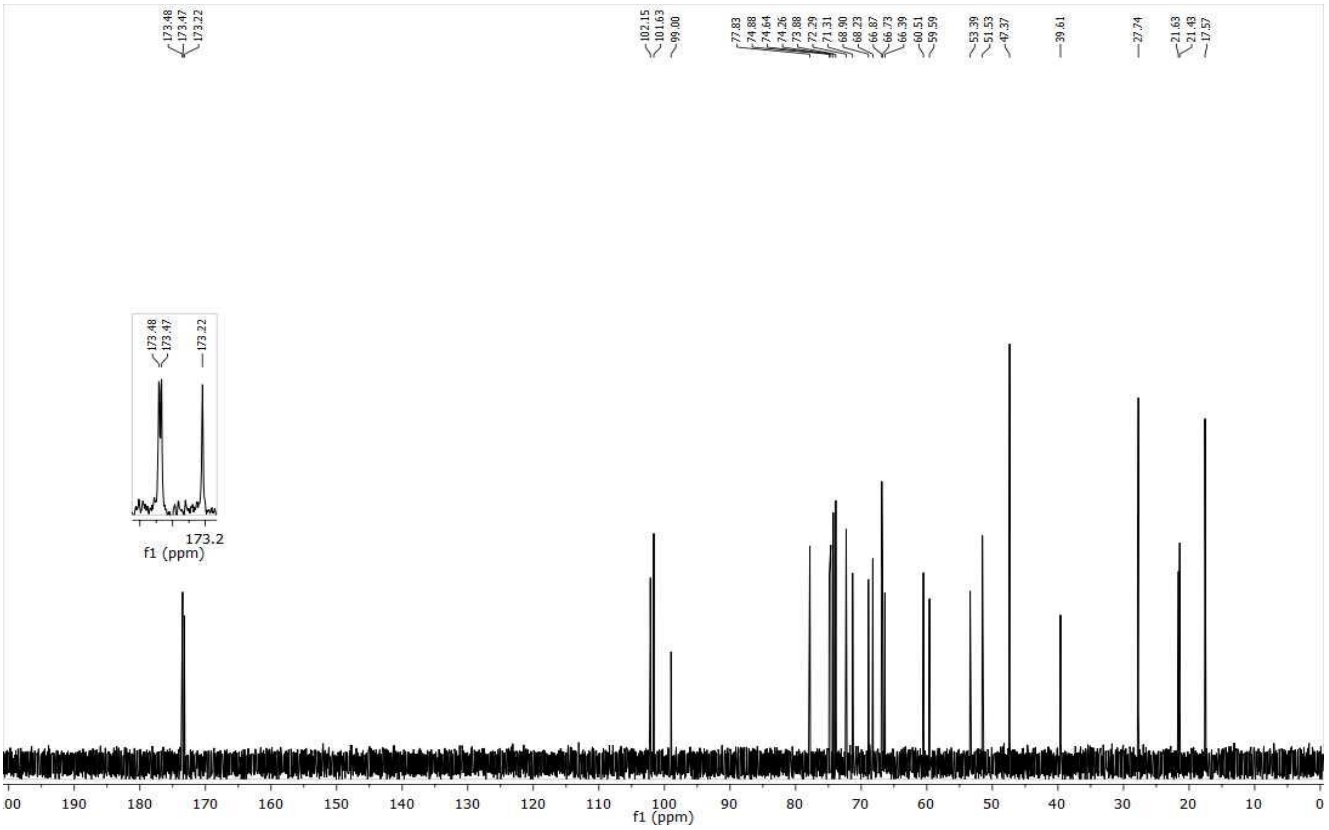
^{1}H and ^{13}C NMR spectra of Leg5,7Ac$_2$α2–6LacβProCl (**24**)





^{1}H and ^{13}C NMR spectra of Leg5,7Ac_2α2–3LacβProN_3 (**25**)





^{1}H and ^{13}C NMR spectra of Leg5,7Ac_2α2–6LacβProN_3 (**26**)