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Chemical synthesis of variously sulfated biotinylated oligosaccharides as probes for the study of the polymerization mechanism of chondroitin sulfates chains

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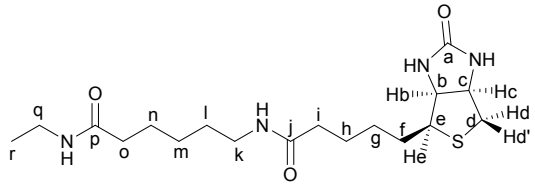
I) Experimental procedures and analytical data for new intermediates and final compounds

For biotinylated molecules **1-10**, the following numbering was adopted in the ^{1}H and ^{13}C NMR data for the attribution of protons and carbons on the biotin moiety:



2-Benzyloxycarbonylaminoethyl *O*-(Methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (16): ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.93, 166.41, 165.90, 165.59, 164.64, 164.33, 164.13, 156.29 (8 C, GlcA C-6, C=O), 136.65, 133.40, 133.25, 133.15, 132.61, 132.57, 130.05, 129.75, 129.63, 129.57, 129.42, 129.38, 129.28, 129.25, 129.06, 128.71, 128.68, 128.49, 128.40, 128.32, 128.21, 128.08, 127.96, 127.91, 127.79, 127.75 (42 C, arom. C), 102.33 (1 C, Gal^{II} C-1), 101.52 (1 C, Gal^{I} C-1), 100.67 (1 C, GlcA C-1), 80.29 (1 C, Gal^{I} C-3), 75.81 (1 C, Gal^{II} C-3), 74.83 (1C, GlcA C-2), 74.35 (1 C, GlcA C-5), 72.69 (1 C, Gal^{I} C-4), 71.95, 71.56 (2 C, Gal^{II} C-2, C-5), 71.52 (1 C, GlcA C-3), 71.14 (1 C, Gal^{I} C-5), 70.50 (1 C, Gal^{I} C-2), 69.80, 69.77 (2 C, Gal^{II} C-4, GlcA C-4), 68.65 (1 C, OCH_2), 66.70 (1 C, Gal^{I} C-6), 66.29 (1 C, CH_2-Ar), 62.85 (1C, Gal^{II} C-6), 52.83 (1 C, $COOCH_3$), 40.82 (1 C, NCH_2), 27.39, 27.56 (6 C, $C(CH_3)_3$), 23.19, 20.60 (2 C, $C(CH_3)_3$).

2-Benzyloxycarbonylaminoethyl *O*-(Methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2-*O*-benzoyl-4,6-di-*O*-chloroacetyl-β-D-galactopyranosyl)-(1→3)- 2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (17) : Trisaccharide **15**[7f] (234 mg, 0.15 mmol) was submitted to the same procedure as described for the preparation of trisaccharide **16**. Flash silica chromatography (CH_2Cl_2/acetone 12:1) afforded the alcohol **17** (133 mg, 61 %) as a white foam. M.p. 165 °C (from EtOAc/petroleum ether); $[\alpha]_D^{20}$ = + 46 (*c* =1.04 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-6.96 (m, 35 H, arom. H), 5.76 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 5.46 (dd, $J_{3,4}$ = 2.5, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.43 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^{I} H-2), 5.21-5.09 (m, 3 H, Gal^{II} H-2, GlcA H-2, H-3), 4.99-4.96 (m, 1 H, N*H*), 4.88 (ABq, 2 H, CH_2-Ar), 4.75 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.63 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA H-1), 4.57 (dd, $J_{5,6a}$ = 4.5, $J_{6a,6b}$ = 12.0 Hz, 1 H, Gal^{I} H-6a), 4.52 (d, 1 H, Gal^{I} H-1), 4.37 (dd, $J_{5,6b}$ = 7.0 Hz, 1 H, Gal^{I} H-6b), 4.23-3.98 (m, 9 H, Gal^{I} H-3, H-5, Gal^{II} H-3, H-6a, H-6b, GlcA H-4, H-5, CH_2Cl), 3.92 (m, 1 H, Gal^{II} H-5), 3.89-3.84 (m, 5 H, CH_2Cl, $COOCH_3$), 3.82-3.75 (m, 1 H, OCH_2), 3.55-3.49 (m, 1 H, OCH_2), 3.25-3.19 (m, 3 H, *H*O-4, NCH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.48, 166.92, 166.89, 166.20, 166.15, 165.90, 164.55, 163.55, 156.16 (10 C, GlcA C-6, C=O), 133.45, 133.28, 133.14, 133.08, 132.88, 132.69, 132.56, 130.07, 129.65, 129.59, 129.53, 129.44, 129.39, 129.28, 128.97, 128.62, 128.53, 128.37, 128.34, 128.29, 128.21, 128.18, 127.92, 127.83, 127.81 (42 C, arom. *C*), 101.30 (1 C, Gal^{I} C-1), 101.04 (1 C, Gal^{II} C-1), 100.74 (1C, GlcA C-1), 77.14 (1 C, Gal^{I} C-3), 75.54 (1C, Gal^{II} C-3), 74.44 (1 C, Gal^{II} C-5), 74.37, 71.99, 71.20, 70.96, 70.72, 70.70, 70.61, 70.09, 69.84 (9 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-2, C-4, GlcA C-2, C-3, C-4, C-5), 68.85 (1 C, OCH_2), 66.31(1 C, CH_2-Ar), 63.40 (1 C, Gal^{II} C-6), 63.17 (1 C, Gal^{I} C-6), 52.95 (1 C, $COOCH_3$), 40.68, 40.62, 40.49 (3 C, CH_2Cl, NCH_2); HRMS: *m/z*: calcd for $C_{75}H_{74}Cl_2N_2O_{27}$ $[M+H]^+$: 1486.35146; found: 1486.35068; elemental analysis calcd (%) for $C_{75}H_{69}Cl_2NO_{27}$: C 60.57, H 4.68, N 0.94; found C 60.02, H 4.90, N 0.85.

2-Benzyloxycarbonylaminoethyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (20) : ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.18, 169.86, 168.19, 165.88, 165.72, 165.01, 164.64, 164.34, 164.16, 163.32, 161.65, 156.27 (12 C, GlcA C-6, C=O), 136.62, 133.48, 133.35, 133.11, 132.62, 132.57, 132.49, 130.06, 129.53, 129.42, 129.36, 129.31, 129.24, 129.18, 129.02, 128.57, 128.54, 128.50, 128.30, 128.09, 128.07, 127.92, 127.91, 127.78, 127.72, 127.67 (42 C, arom. C), 102.31 (1 C, Gal^{II} C-1), 101.47, 100.95 (2 C, GlcA C-1, GalN C-1), 100.02 (1 C, Gal^{I} C-1), 92.40 (1 C, CCl_3), 80.25 (1 C, Gal^{I} C-3), 76.58 (1 C, Gal^{II} C-3), 75.74 (1 C, GlcA C-4), 73.38 (1 C, GlcA C-5), 72.69 (1 C, Gal^{I} C-4), 72.13, 71.52, 71.47, 71.29, 70.69, 70.49, 70.11, 69.74 (8 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-4, C-5, GlcA C-2, C-3, GalN C-5), 68.64 (1 C, OCH_2), 66.67, 66.27 (2 C, Gal^{I} C-6, CH_2-Ar), 66.03 (1 C, GalN H-3), 62.86 (1 C, Gal^{II} C-6), 60.08 (1 C, GalN C-6), 53.08 (1 C, $COOCH_3$), 52.62 (1 C, GalN C-2), 40.80 (1 C, NCH_2), 27.38, 27.22 (6 C, $C(CH_3)_3$), 23.18 (2 C, $C(CH_3)_3$), 20.58, 20.39, 20.38 (3 C, $OC(O)CH_3$).

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (21) : A mixture of imidate **19**[13] (200 mg, 0.23 mmol) and alcohol **16** (230 mg, 0.15 mmol) was submitted to the same procedure as described for the preparation of compound **20**. Flash silica chromatography (CH_2Cl_2/Acetone 9:1, containing 0.1 % of NEt_3) afforded the pentasaccharide **21** (258 mg, 76 %) as a white powder. M.p. 180 °C (from EtOAc/petroleum ether); $[\alpha]_D^{20}$ = +28 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-6.87 (m, 35 H, arom. H), 6.71 (d, $J_{2,NH}$ = 7.5 Hz, 1 H, GalN N*H*), 5.80 (dd, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.49 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.37 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^{I} H-2), 5.30 (m, 1 H, GalN H-4), 5.17-5.09 (m, 4 H, GlcA^{I} H-2, H-3, GlcA^{II} H-3, H-4), 5.04 (m, 1 H, N*H*), 4.92 (d, 1 H, Gal^{II} H-1), 4.91 (ABq, 2 H, CH_2-Ar), 4.84-4.81 (m, 2 H, GalN H-1, GlcA^{II} H-2), 4.77 (d, $J_{1,2}$= 7.0 Hz, 1 H, GlcA^{I} H-1), 4.69 (dd, $J_{3,4}$ = 2.5, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 4.57 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^{II} H-1), 4.42-4.40 (m, 2 H, Gal^{II} H-6a, H-6b), 4.32 (d, 1 H, Gal^{I} H-1), 4.27-4.19 (m, 3 H, Gal^{II} H-3, GlcA^{I} H-4, GalN H-3), 4.15-4.08 (m, 2 H, Gal^{I} H-6a, Gal^{II} H-5), 3.98 (dd, $J_{5,6b}$ = 2.0, $J_{6a,6b}$ = 12.0 Hz, 1 H, Gal^{I} H-6b), 3.93 (d, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA^{I} H-5), 3.92 (d, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA^{II} H-5), 3.78 (m, 1 H, Gal^{I} H-3), 3.74, 3.71 (2 s, 6 H, COOCH_3), 3.71 (m, 1 H, OCH_2), 3.61-3.58 (m, 1 H, GalN H-5), 3.56 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$= 3.0 Hz, 1 H, GalN H-2), 3.53-3.47 (m, 1 H, OCH_2), 3.35 (dd, $J_{5,6a}$ = 7.0, $J_{6a,6b}$ = 11.5 Hz, 1 H, GalN H-6a), 3.19 (m, 3 H, Gal^{I} H-5, NCH_2), 3.03 (dd, $J_{5,6b}$ = 7.0 Hz, 1 H, GalN H-6b), 2.17, 2.01, 2.00, 1.98, 1.96 (5 s, 15 H, OC(O)CH_3), 1.01, 0.95 (2 s, 18 H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.13, 169.89, 169.36, 169.15, 169.10, 168.19, 166.63, 165.79, 165.56, 164.55, 164.24, 164.06, 161.33, 156.21 (15 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 136.53, 133.36, 133.17, 133.05, 132.49, 132.43, 129.97, 129.49, 129.44, 129.38, 129.28, 129.24, 129.16, 129.12, 128.92, 128.49, 128.42, 128.37, 128.22, 128.12, 128.06, 127.98, 127.96, 127.81, 127.70, 127.62 (42 C, arom. C), 102.16 (1 C, Gal^{II} C-1), 101.39 (1 C, Gal^{I} C-1), 101.07 (1 C, GlcA^{I} C-1), 99.57 (1 C, GlcA^{II} C-1), 98.22 (1 C, GalN C-1), 92.48 (1 C, *C*Cl$_3$), 80.08 (1 C, Gal^{I} C-3), 75.56, 74.61, 73.68, 73.55, 72.62, 72.19, 71.8, 71.84, 71.53, 71.47, 71.39, 70.97, 70.68, 70.42 (17 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-2, C-3, C-5, GlcA^{I} C-2, C-3, C-4, C-5, GalN C-3, C-4, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 69.62 (1 C, Gal^{II} C-4), 68.51 (1 C, O*C*H$_2$), 66.58 (1 C, Gal^{I} C-6), 66.19 (1 C, *C*H$_2$-Ar), 62.83 (1 C, Gal^{II} C-6), 60.97 (1 C, GalN C-6), 54.74 (1 C, GalN C-2), 53.03, 52.70 (2 C, COO*C*H$_3$), 40.73 (1 C, N*C*H$_2$), 27.29, 27.14 (6 C, C(*C*H$_3$)$_3$), 23.08, 20.49 (2 C, *C*(CH$_3$)$_3$), 20.61, 20.40, 20.31, 20.12 (5 C, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{104}H_{114}Cl_3N_2O_{41}Si$ $[M+H]^+$: 2179.572637; found: 2179.573263; elemental analysis calcd (%) for $C_{104}H_{113}Cl_3N_2O_{41}Si$: C 57.26, H 5.22, N 1.28; found C 56.16, H 5.20, N 1.28.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (22) : ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.40, 170.33, 170.00, 169.76, 168.97, 166.27, 165.80, 164.67, 164.61, 164.22, 163.92, 156.92 (12 C, GlcA C-6, C=O), 136.61, 133.70, 133.43, 133.12, 132.80, 132.55, 132.45, 130.13, 129.51, 129.45, 129.32, 129.26, 129.23, 129.13, 128.98, 128.95, 128.82, 128.62, 128.56, 128.45, 128.28, 128.20, 128.05, 127.97, 127.86, 127.75, 127.70 (42 C, arom. C), 102.50 (1 C, Gal^{II} C-1), 101.47 (1 C, Gal^{I} C-1), 101.25 (1 C, GalN C-1), 99.74 (1 C, GlcA C-1), 80.42 (1 C, Gal^{I} C-3), 75.82 (1 C, GalN C-4), 75.39 (1C, Gal^{II} C-3), 73.59 (1 C, GlcA C-3), 73.14 (1 C, GlcA C-5), 72.70 (1 C, Gal^{I} C-4), 71.95, 71.69, 71.64, 71.46, 70.69, 70.53 (6 C, Gal^{I} C-2, C-5, Gal^{II} C-5, GlcA C-2, GalN C-4, C-5), 70.43 (1 C, Gal^{II} C-2), 70.24 (1 C, Gal^{II} C-4), 68.60 (1 C, O*C*H$_2$), 66.64 (1 C, Gal^{I} C-6), 66.24 (1 C, *C*H$_2$-Ar), 65.90 (1 C, GalN H-3), 62.94 (1 C, Gal^{II} C-6), 60.13 (1 C, GalN C-6), 52.87 (1 C, COO*C*H$_3$), 50.73 (1 C, GalN C-2), 40.79 (1 C, N*C*H$_2$), 27.38, 27.22 (6 C, C(*C*H$_3$)$_3$), 23.30, 23.17 (2 C, *C*(CH$_3$)$_3$), 21.50, 20.54, 20.49, 20.46 (4 C, NHC(O)*C*H$_3$, OC(O)*C*H$_3$).

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (23) : Pentasaccharide **21** (197 mg, 0.09 mmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **22**. Flash silica chromatography (CH_2Cl_2/methanol 19:1) afforded the acetamide **23** (162 mg, 86 %) as a white foam. M.p. 155 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +35.8 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-6.87 (m, 35 H, arom. H), 5.84 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.69 (d, $J_{2,NH}$ = 7.0 Hz, 1 H, GalN N*H*), 5.53 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.37 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{I} H-2), 5.26 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{I} H-3), 5.14-5.10 (m, 3 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4), 5.08 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 5.06 (m, 1 H, N*H*), 4.94 (ABq, 2 H, CH_2-Ar), 4.92 (d, 1 H, Gal^{II} H-1), 4.85 (m, 1 H, GlcA^{II} H-2), 4.77 (d, $J_{1,2}$ = 7.0 Hz, 1 H, GlcA^{I} H-1), 4.69 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.69 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 4.59 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^{II} H-1), 4.45-4.39 (m, 3 H, Gal^{II} H-6a, H-6b, GalN H-3), 4.32 (d, 1 H, Gal^{I} H-1), 4.29-4.24 (m, 2 H, Gal^{II} H-3, GlcA^{I} H-4), 4.15-4.06 (m, 2 H, Gal^{I} H-6a, Gal^{II} H-5), 3.98 (d, $J_{4,5}$ = 10.0 Hz, 1 H, GlcA^{I} H-5), 3.94-3.92 (m, 2 H, Gal^{I} H-6b, GlcA^{II} H-5), 3.78, 3.68 (2 s, 6 H, COOCH_3), 3.74-3.69 (m, 2 H, Gal^{I} H-3, OCH_2), 3.51-3.40 (m, 2 H, GalN H-5, OCH_2), 3.36 (dd, $J_{5,6a}$ = 7.0, $J_{6a,6b}$ = 11.0 Hz, 1 H, GalN H-6a), 3.23-3.17 (m, 4 H, Gal^{I} H-5, GalN H-2, NCH_2), 3.02 (dd, $J_{5,6b}$ = 6.0 Hz, 1 H, GalN H-6b), 1.98, 1.97, 1.96, 1.92, 1.82, 1.77 (6 s, 18 H, NHC(O)CH_3, OC(O)CH_3), 1.00, 0.94 (2 s, 18 H, (CCH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.88, 170.14, 169.99, 169.51, 169.25, 169.21, 167.65, 166.84, 165.87, 165.78, 165.09, 164.63, 164.17, 156.29 (15 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 136.65, 133.42, 133.32, 132.60, 132.50, 130.10, 129.80, 129.63, 129.55, 129.41, 129.28, 129.21, 129.08, 128.64, 128.49, 128.43, 128.32, 128.10, 127.90, 127.79, 127.75, 127.72, 127.68, 127.64 (42 C, arom. C), 102.26 (1 C, Gal^{II} C-1), 101.51 (1 C, Gal^{I} C-1), 100.81 (1 C, GlcA^{I} C-1), 99.34 (1 C, GlcA^{II} C-1), 98.74 (1 C, GalN C-1), 80.14 (1 C, Gal^{I} C-3), 77.20-68,98 (14 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-2, C-3, C-5, GlcA^{I} C-2, C-3, C-4, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 74,43 (1 C, GlcA^{I} C-5), 74,01 (1 C, GalN C-3), 69,78 (1 C, Gal^{II} C-4), 68.64 (1 C, O*C*H$_2$), 67.36 (1 C, GalN C-4), 66.68 (1 C, Gal^{I} C-6), 66.28 (1 C, *C*H$_2$-Ar), 63.00 (1 C, Gal^{II} C-6), 61.11 (1 C, GalN C-6), 54.20 (1 C, GalN C-

2), 53.11, 52.73 (2 C, COO*C*H$_3$), 40.82 (1 C, N*C*H$_2$), 27.38, 27.24 (6 C, C(*C*H$_3$)$_3$), 23.54 (1 C, NHC(O)*C*H$_3$), 23.17, 20.59 (2 C, *C*(CH$_3$)$_3$), 20.68, 20.52, 20.43, 20.31 (5 C, CO(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{104}H_{121}N_3O_{41}Si$ $[M+H+NH4]^{2+}$: 1047.861690; found: 1047.862464; elemental analysis calcd (%) for $C_{104}H_{116}N_2O_{41}Si$: C 6011, H 5.63, N 1.35; found C 59.27, H 5.44, N 1.32.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-*O*-benzoyl-β-D-galactopyranoside (24) : ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.47, 170.02, 129.80, 168.82, 166.55, 166.08, 164.74, 164.26, 164.03 (12 C, GlcA C-6, C=O), 136.49, 133.85, 133.60, 133.18, 132.85, 132.70, 132.64, 130.21, 129.64, 129.44, 129.33, 129.27, 129.18, 129.14, 128.98, 128.94, 128.88, 128.57, 128.50, 128.36, 128.23, 128.08, 128.01, 127.88, 127.82 (42 C, arom. *C*), 101.81 (1 C Gal^{II} C-1), 101.47 (1 C, GlcA C-1), 101.27 (1 C, Gal^{I} C-1), 99.96 (1C, GalN C-1), 80.97 (1 C, Gal^{I} C-3), 75.85 (1 C, GlcA C-4), 75.36 (1 C, Gal^{II} C-3), 74.42, 73.42, 73.40, 72.22, 71.87, 71.05, 70.55, 70.52, 70.26 (9 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-5, GalN C-4, C-5), 68.84 (1 C, Gal^{II} C-4), 68.80 (1 C, O*C*H$_2$), 68.65 (1 C, Gal^{I} C-4), 66.39 (1 C, *C*H$_2$-Ar), 65.90 (1 C, GalN C-3), 62.82 (1 C, Gal^{II} C-6), 62.04 (1 C, GalN C-6), 60.15 (1 C, Gal^{I} C-6), 53.00 (1 C, COO*C*H$_3$), 50.78 (1 C, GalN C-2), 40.85 (1 C, N*C*H$_2$), 25.28, 23.33, 20.55, 20.48 (4 C, NHC(O)*C*H$_3$, OC(O)*C*H$_3$).

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-*O*-benzoyl-β-D-galactopyranoside (25) : Pentasaccharide **23** (280 mg, 0.13 mmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **24**. Flash silica chromatography (CH_2Cl_2/methanol 18:1) afforded the diol **25** (217 mg, 83 %) as a white foam. M.p. 150 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +41.4 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-6.94 (m, 35 H, arom. H), 5.82 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1H, Gal^{II} H-4), 5.70 (d, $J_{2,NH}$ = 7.0 Hz, 1 H, GalN N*H*), 5.53 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.34-5.25 (m, 2 H, Gal^{I} H-2, GlcA^{I} H-3), 5.18-5.10 (m, 4 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4, N*H*), 5.08 (dd, $J_{3,4}$= 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 4.93 (ABq, 2 H, C*H*$_2$-Ar), 4.85 (m, 1 H, GlcA^{II} H-2), 4.80 (d, $J_{1,2}$ = 7.0 Hz, 1 H, GlcA^{I} H-1), 4.76 (d, 1 H, Gal^{II} H-1), 4.69 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.65 (dd, $J_{5,6a}$ = 4.0, $J_{6a,6b}$ = 12.0 Hz, 1 H, Gal^{II} H-6a), 4.59 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^{II} H-1), 4.43 (dd, $J_{2,3}$ = 11.0 Hz, 1 H, GalN H-3), 4.38 (m, 1 H, Gal^{II} H-6b), 4.33 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{I} H-1), 4.25-4.16 (m, 3 H, Gal^{II} H-3, H-5, GlcA^{I} H-4), 4.05 (m, 1 H, Gal^{I} H-4), 4.01 (d, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA^{I} H-5), 3.93 (m, 1 H, GlcA^{II} H-5), 3.80, 3.69 (2 s, 6 H, COOC*H*$_3$), 3.79-3.69 (m, 2 H, Gal^{I} H-3, H-6a), 3.70 (m, 1 H, OC*H*$_2$), 3.54 (m, 1 H, OC*H*$_2$), 3.50-3.33 (m, 4 H, Gal^{I} H-5, H-6b, GalN H-5, H-6a), 3.24-3.17 (m, 3 H, GalN H-2, NC*H*$_2$), 3.02 (dd, $J_{5,6b}$ = 6.5, $J_{6a,6b}$ = 11.0 Hz, 1 H, GalN H-6b), 2.01, 1.98, 1.97, 1.95, 1.93, 1.77 (6 s, 18 H, NHC(O)C*H*$_3$, OC(O)C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.16, 170,20, 170,02, 169.58, 169.36, 167.65, 166.98, 166.23, 166.17, 165.15, 164.92, 164.27, 156.39 (15 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 136.60, 133.63, 133.48, 133.21, 132.68, 13021, 129.74, 129.44, 129.39, 129.31, 129.28, 129.21, 129.09, 128.65, 128.61, 128.44, 128.38, 128.16, 128.13, 128.04, 127.98, 127.94 (42 C, arom. C), 101.70 (1 C, Gal^{II} C-1), 101.44 (1 C, Gal^{I} C-1), 100.90 (1 C, GlcA^{I} C-1), 99.40 (1 C, GlcA^{II} C-1), 98.98 (1 C, GalN C-1), 81.11 (1 C, Gal^{I} C-3), 77.36 (1 C, GlcA^{I} C-4), 75.53, 74.60, 74.50, 72.44, 72.26, 72.19, 72.15, 71.29, 70.91, 70.83, 70.78, 70.59, 69.05, 67.49 (14 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-2, C-3, C-5, GlcA^{I} C-2, C-3, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 74.05 (1 C, GalN C-3), 69.88 (1 C, Gal^{II} C-4), 68.85 (1 C, O*C*H$_2$), 68.59 (1 C, GalN C-4), 66.43 (1 C, *C*H$_2$-Ar), 63.12 (1 C, Gal^{II} C-6), 62.02 (1 C, Gal^{I} C-6), 61.17 (1 C, GalN C-6), 54.08 (1 C, GalN C-2), 53.53, 53.16 (2 C, COO*C*H$_3$), 40.66 (1 C, N*C*H$_2$), 23.40 (1 C, NHC(O)*C*H$_3$), 20.54, 20.40, 20.31, 20.22 (5C, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{96}H_{101}N_2O_{41}$ $[M+H]^+$: 1937.587427; found: 1937.587800; elemental analysis calcd (%) for $C_{96}H_{100}N_2O_{41}$: C 59.50, H 5.20, N 1.45; found C 58.79, H 5.34, N 1.43.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-4-*O*-acetyl-2-*O*-benzoyl-6-*O*-sodium sulfonato-β-D-galactopyranoside (26) : ^{13}C NMR (100 MHz, CD_3OD): δ = 173.68, 171.83, 171.73, 171.66, 171.62, 169.17, 167.71, 167.26, 166.54, 166.33, 166.14, 158.57 (13 C, GlcA C-6, C=O), 138.22, 134.52, 134.45, 134.37, 134.24, 134.03, 133.94, 131.28, 131.19, 131.05, 130.89, 130.77, 130.63, 130.55, 130.38, 130.24, 129.91, 129.83, 129.80, 129.59, 129.50, 129.44, 129.18, 128.90, 128.68 (42 C, arom. C), 102.67, 102.35, 102.27, 102.21 (4 C, Gal^{I} C-1, Gal^{II} C-1, GlcA C-1, GalN C-1), 79.44 (1 C, Gal^{II} C-3), 78.17 (1 C, Gal^{I} C-3), 77.51 (1 C, GlcA C-3), 75.20 (1 C, GlcA C-5), 74.28 (1 C, GlcA C-4), 73.40 (1 C, Gal^{II} C-5), 73.01, 72.70, 72.58, 72.36, 71.71, 71.60, 71.47, 71.30 (8 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-2, C-4, GlcA C-2, GalN C-4, C-5), 69.40 (1 C, O*C*H$_2$), 67.68 (1 C, Gal^{II} C-6), 67.36 (1 C, GalN C-3), 67.30 (1 C, *C*H$_2$-Ar), 63.85 (1 C, Gal^{I} C-6), 61.64 (1 C, GalN C-6), 53.69 (1 C, COO*C*H$_3$), 51.80 (1 C, GalN C-2), 45.49 (1C, N*C*H$_2$), 23.15, 20.87, 20.54, 20.53, 20.42 (5 C, NHC(O)*C*H$_3$, OC(O)CO*C*H$_3$).

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-4-*O*-acetyl-2-*O*-benzoyl-6-*O*-sodium sulfonato-β-D-galactopyranoside (27) : A mixture of diol **25** (141 mg, 0.07 mmol) and sulfur trioxide/trimethylamine complex (25 mg, 0.18 mmol) in anhydrous DMF (2.8 mL) was stirred for 6 h at 40 °C. More reagent (10 mg, 0.07 mmol) was then added and the mixture was stirred for 3 h then was cooled. Methanol (1 mL) was added and the mixture was concentrated and purified by flash chromatography (CH_2Cl_2/MeOH, 9:1). A mixture of the residue, pyridine (3 mL), and Ac_2O (1.5 mL) was stirred overnight at rt, then was concentrated and coevaporated with toluene. Flash silica chromatography (CH_2Cl_2/MeOH, 9:1), followed by ion exchange on a column of Sephadex SP C-25 [Na^+] (CH_2Cl_2/MeOH/water, 9:5:1) afforded the 6-sulfate **27** (86 mg, 57%) as a white powder. $[\alpha]_D^{20}$ = +7.0 (*c* = 1.01 in MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ = 8.11-6.80 (m, 35 H, arom. H), 5.86 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1H, Gal^{II} H-4), 5.60 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1H, Gal^{I} H-4), 5.45 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H,

Gal^{II} H-2), 5.40 (dd, $J_{2,3} = J_{3,4} = 10.0$ Hz, 1 H, GlcA^{I} H-3), 5.24 (m, 1 H, GlcA^{II} H-3), 5.19 (dd, $J_{1,2} = 8.5$, $J_{2,3} = 10.0$ Hz, Gal^{I} H-2), 5.09 (dd, $J_{3,4} = 3.0$, $J_{4,5} < 1$ Hz, 1 H, GalN H-4), 5.05-5.00 (m, 3 H, GlcA^{I} H-1, H-2, GlcA^{II} H-4), 4.93 (d, 1 H, Gal^{II} H-1), 4.86 (d, $J_{1,2} = 7.5$ Hz, 1 H, GlcA^{II} H-1), 4.85 (ABq, 2 H, CH_2-Ar), 4.82 (m, 1 H, GlcA^{II} H-2), 4.53 (d, 1 H, Gal^{I} H-1), 4.46 (m, 2 H, Gal^{II} H-6a, H-6b), 4.42 (d, $J_{1,2} = 8.5$ Hz, 1 H, GalN H-1), 4.34 (dd, 1 H, Gal^{II} H-3), 4.28 (m, 1 H, Gal^{II} H-5), 4.21-4.10 (m, 5 H, Gal^{I} H-3, H-5, H-6a, GlcA^{I} H-4, GlcA^{II} H-5), 4.05-3.96 (m, 3 H, Gal^{I} H-6b, GlcA^{I} H-5, GalN H-3), 3.77, 3.69 (2 s, 6 H, COOCH_3), 3.75 (m, 1 H, OCH_2), 3.69 (m, 1 H, GalN H-2), 3.54-3.52 (m, 2 H, GalN H-5, OCH_2), 3.45 (dd, $J_{5,6a} = 6.5$, $J_{6a,6b} = 11.0$ Hz, 1 H, GalN H-6a), 3.14 (m, 2 H, NCH_2), 3.02 (dd, $J_{5,6b} = 6.5$ Hz, 1 H, GalN H-6b), 2.07, 2.01, 1.97, 1.96, 1.95, 1.90, 1.78 (7 s, 21 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, CD_3OD): δ = 173.40, 172.00, 171.71, 171.64, 171.39, 171.11, 170.98, 169.13, 168.97, 167.63, 167.25, 166.62, 166.52, 166.23, 166.09, 158.54 (16 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 138.24, 134.53, 134.38, 134.21, 134.00, 133.93, 131.26, 131.20, 131.08, 130.88, 130.79, 130.61, 130.51, 130.37, 130.26, 129.97, 129.87, 129.83, 129.60, 129.50, 129.45, 129.38, 129.18, 128.91, 128.69 (42 C, arom. C), 102.68 (1 C, Gal^{II} C-1), 102.38, 102.32 (2 C, Gal^{I} C-1, GlcA^{I} C-1), 102.02 (1 C, GalN C-1), 101.27 (1 C, GlcA^{II} C-1), 79.43 (1 C, Gal^{II} C-3), 78.17, 77.23, 76.74, 75.37, 73.50, 73.35, 73.11, 73.00, 72.69, 72.58, 72.35, 72.24, 71.88, 71.71, 71.57, 70.89 (16 C, Gal^{I} C-2, C-3, C-4, C-5, Gal^{II} C-2, C-4, C-5, GlcA^{I} C-2, C-4, C-5, GalN C-3, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 74.14 (1 C, GlcA^{I} C-3), 69.57 (1 C, GalN C-4), 69.36 (1 C, OCH$_2$), 67.92 (1 C, Gal^{I} C-6), 67.31 (1 C, CH$_2$-Ar), 63.83 (1 C, Gal^{II} C-6), 62.76 (1 C, GalN C-6), 53.75, 53.32 (3 C, GalN C-2, COOCH$_3$), 41.65 (1 C, NCH$_2$), 23.54 (1 C, NHC(O)CH$_3$), 20.90, 20.82, 20.74, 20.63, 20.52, 20.45 (6 C, OC(O)CH$_3$); HRMS: *m/z*: calcd for $C_{98}H_{104}N_2O_{45}S$ $[M\text{-}Na+3H]^{2+}$: 1030.281042; found: 1030.281512.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,6-di-*O*-benzoyl-β-D-galactopyranoside (28) : ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.46, 170.37, 170.02, 169.79, 168.90, 166.57, 166.16, 166.06, 164.72, 164.69, 164.27, 164.02, 156.24 (13 C, GlcA C-6, C=O), 136.58, 133.89, 133.50, 133.19, 133.13, 132.89, 132.73, 130.23, 129.74, 129.66, 129.56, 129.47, 129.33, 129.29, 129.25, 129.16, 128.99, 128.95, 128.93, 128.57, 128.54, 128.39, 128.33, 128.25, 128.13, 128.10, 128.04, 127.83 (48 C, arom. C), 101.69 (1 C, Gal^{II} C-1), 101.30 (1 C, GlcA C-1), 101.17 (1 C, GalN C-1), 101.13(1 C, Gal^{I} C-1), 80.52 (1 C, Gal^{I} C-3), 75.85 (1 C, GlcA C-4), 75.23 (1 C, Gal^{II} C-3), 73.50, 73.31, 72.31, 72.20, 72.13, 71.96, 71.12, 70.65, 70.57, 70.23 (10 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-4, C-5, GlcA C-2, C-3, C-5, GalN C-3, C-5), 68.62 (1 C, OCH$_2$), 68.30 (1 C, Gal^{I} C-4), 66.30 (1 C, CH$_2$-Ar), 65.92 (1 C, GalN C-4), 63.72, 62.76 (2 C, Gal^{I} C-6, Gal^{II} C-6), 60.16 (1 C, GalN C-6), 53.00 (1 C, COOCH$_3$), 50.81 (1 C, GalN C-2), 40.75 (1 C, NCH$_2$), 23.37, 20.58, 20.52, 20.50 (4 C, NHC(O)CH$_3$, OC(O)CH$_3$).

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,6-di-*O*-benzoyl-β-D-galactopyranoside (29) : Pentasaccharide **25** (217 mg, 0.11 mmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **28**. Flash silica chromatography (CH_2Cl_2/MeOH, 19:1) afforded the 6-benzoate **29** (199 mg, 87 %) as a white foam. M.p. 139°C (from hot 2-propanol); $[\alpha]_D^{20}$ = +39.5 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19-6.95 (m, 40 H, arom. H), 5.82 (dd, $J_{3,4} = 3.0$, $J_{4,5} < 1$ Hz, 1 H, Gal^{II} H-4), 5.63 (d, $J_{2,NH} = 7.0$ Hz, 1 H, GalN NH), 5.54 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 10.0$ Hz, 1 H, Gal^{II} H-2), 5.33 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 9.5$ Hz, 1 H, Gal^{I} H-2), 5.27 (dd, $J_{2,3} = J_{3,4} = 9.0$ Hz, 1 H, GlcA^{I} H-3), 5.14-5.11 (m, 3 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4), 5.09 (dd, $J_{3,4} = 3.0$, $J_{4,5} < 1$ Hz, 1H, GalN H-4), 4.98 (m, 1 H, NH), 4.87 (m, 1 H, GlcA^{II} H-2), 4.85 (ABq, 2 H, CH_2-Ar), 4.79 (d, $J_{1,2} = 7.0$ Hz, 1 H, GlcA^{I} H-1), 4.76 (d, 1 H, Gal^{II} H-1), 4.70 (d, $J_{1,2} = 8.0$ Hz, 1 H, GalN H-1), 4.61 (dd, $J_{5,6a} = 4.0$, $J_{6a,6b} = 12.0$ Hz, 1 H, Gal^{II} H-6a), 4.58 (d, $J_{1,2} = 7.5$ Hz, 1 H, GlcA^{II} H-1), 4.45 (m, 1 H, Gal^{I} H-6a), 4.39 (dd, $J_{2,3} = 11.0$ Hz, 1 H, GalN H-3), 4.37-4.35 (m, 2 H, Gal^{I} H-6b, Gal^{II} H-6b), 4.36 (d, 1 H, Gal^{I} H-1), 4.32-4.16 (m, 3 H, Gal^{II} H-3, H-5, GlcA^{I} H-4), 4.12 (dd, $J_{3,4} = 3.0$, $J_{4,5} < 1$ Hz, 1H, Gal^{I} H-4), 4.00 (d, $J_{4,5} = 10.0$ Hz, 1 H, GlcA^{I} H-5), 3.93 (d, $J_{4,5} = 9.5$ Hz, 1 H, GlcA^{II} H-5), 3.84 (dd, 1 H, Gal^{I} H-3), 3.81, 3.69 (2 s, 6 H, COOCH_3), 3.77-3.67 (m, 2 H, Gal^{I} H-5, OCH_2), 3.49 (m, 1 H, OCH_2), 3.46 (m, 1 H, GalN H-5), 3.36 (dd, $J_{5,6a} = 6.5$, $J_{6a,6b} = 12.0$ Hz, 1 H, GalN H-6a), 3.21-3.17 (m, 3 H, GalN H-2, NCH_2), 3.03 (dd, $J_{5,6b} = 6.5$ Hz, 1 H, GalN H-6b), 2.90 (bs, 1 H, Gal^{I} HO-4), 2.02, 1.99, 1.98, 1.96, 1.93, 1.77 (6 s, 18 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.82, 170.01, 169.85, 169.39, 169.16, 169.12, 167.40, 166.75, 166.02, 165.97, 164.93, 164.59, 164.09, 164.02, 156.14 (16 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 136.49, 133.36, 133.04, 132.61, 132.56, 130.07, 129.61, 129.54, 129.45, 129.30, 129.26, 129.21, 129.13, 129.10, 129.07, 129.00, 128.47, 128.39, 128.30, 128.23, 128.05, 128.00, 127.95, 127.84, 127.73 (48 C, arom. C), 101.42 (1 C, Gal^{II} C-1), 101.08 (1 C, Gal^{I} C-1), 100.73 (1 C, GlcA^{I} C-1), 99.24 (1 C, GlcA^{II} C-1), 98.75 (1 C, GalN C-1), 80.27 (1 C, Gal^{I} C-3), 76.12, 75.25, 72.23, 72.18, 72.09, 72.01, 71.15, 70.87, 70.83, 70.69, 68.87 (11 C, Gal^{II} C-2, C-3, C-5, GlcA^{I} C-2, C-3, C-4, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 74.42 (1 C, GlcA^{I} C-5), 73.93 (1 C, GalN C-3), 70.44 (1 C, Gal^{I} C-2), 69.64 (1 C, Gal^{II} C-4), 68.47 (1 C, OCH$_2$), 68.16 (1 C, Gal^{I} C-4), 67.25 (1 C, GalN C-4), 66.18 (1 C, CH$_2$-Ar), 63.57 (1 C, Gal^{I} C-6), 62.78 (1 C, Gal^{II} C-6), 61.02 (1 C, GalN C-6), 54.03 (1 C, GalN C-2), 53.02, 52.62 (2 C, COOCH$_3$), 40.61 (1 C, NCH$_2$), 23.43 (1 C, NHC(O)CH$_3$), 20.56, 20.41, 20.33, 20.21 (5 C, OC(O)CH$_3$); HRMS: *m/z*: calcd for $C_{103}H_{106}N_2O_{42}$ $[M+2H]^{2+}$: 1021.310459; found: 1021.310213; elemental analysis calcd (%) for $C_{103}H_{104}N_2O_{42}$: C 60.59, H 5.13, N 1.37; found C 59.47, H 5.28, N 1.43.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,6-di-*O*-benzoyl-4-*O*-sodium sulfonato-β-D-galactopyranoside (30) : ^{13}C NMR (100 MHz, CD_3OD): δ = 173.69, 171.86, 171.64, 169.22, 167.66, 167.61, 167.53, 166.84, 166.72, 166.49, 166.20 158.56 (13 C, GlcA C-6, C=O), 138.26, 134.45, 134.36, 134.26, 134.21, 134.03, 131.61, 131.41, 131.22, 131.20, 130.85, 130.81, 130.73, 130.68, 130.64, 130.56, 130.52, 130.38, 130.02, 129.83, 129.72, 129.65, 129.55, 129.52, 129.45, 129.24, 129.19, 128.92, 128.70 (42 C, arom. *C*), 103.22, 102.48, 102.37 (4 C, Gal^{I} C-1, Gal^{II} C-1, GlcA C-1, GalN C-1), 79.83 (1 C, Gal^{II} C-3), 78.33 (1 C, Gal^{I} C-4), 77.62, 75.24, 74.36, 74.09, 73.13,

72.85, 72.32, 71.58, 71.33 (11 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-4, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 69.27 (1 C, O*C*H$_2$), 67.36 (1 C, *C*H$_2$-Ar), 67.32 (1 C, GalN C-4), 65.47 (1 C, Gal^{I} C-6), 64.18 (1 C, Gal^{II} C-6), 61.63 (1 C, GalN C-6), 53.69 (1 C, COO*C*H$_3$), 51.77 (1 C, GalN C-2), 41.69 (1 C, N*C*H$_2$), 23.16, 20.54, 20.52, 20.43 (4 C, NHC(O)*C*H$_3$, OC(O)*C*H$_3$).

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,6-di-*O*-benzoyl-4-*O*-sodium sulfonato-β-D-galactopyranoside (31) : A mixture of pentasaccharide **29** (170 mg, 0.08 mmol) and sulfur trioxide/trimethylamine complex (117 mg, 0.83 mmol) in anhydrous DMF (1.7 mL) was stirred for 20 h at 60 °C. More reagent (60 mg, 0.40 mmol) was then added and the mixture was stirred for 20 h then was cooled. Methanol (2.5 mL) was added and the mixture was directly eluted from a column of Sephadex LH-20 with 1:1 CH_2Cl_2/MeOH. Fractions containing the product were submitted to a flash silica chromatography (CH_2Cl_2/MeOH, 19:1), followed by ion exchange on a column of Sephadex SP C-25 [Na^+] (CH_2Cl_2/MeOH/water, 9:5:1) to give the 4-sulfate **31** (145 mg, 81%) as a white powder. $[\alpha]_D^{20}$ = +19.3 (*c* = 1.05 in MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ = 8.21-6.80 (m, 35 H, arom. H), 5.92 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.60 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.48 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{I} H-3), 5.32-5.25 (m, 2 H, Gal^{I} H-2, GlcA^{II} H-3), 5.15-5.12 (m, 3 H, Gal^{I} H-4, GlcA^{I} H-1, GalN H-4), 5.09-5.03 (m, 3 H, Gal^{II} H-1, GlcA^{I} H-2, GlcA^{II} H-4), 4.93 (d, $J_{1,2}$ = 7.5, 1 H, GlcA^{II} H-1), 4.86-4.81 (m, 3 H, GlcA^{II} H-2, C*H*$_2$-Ar),4.63 (2 dd, $J_{5,6a}$ = 4.0, $J_{6a,6b}$ = 12.0 Hz, 2 H, Gal^{I} H-6a, Gal^{II} H-6a), 4.59 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{I} H-1), 4.51-4.43 (m, 4 H, Gal^{I} H-6b, Gal^{II} H-3, H-6b, GalN H-1), 4.43 (m, 1 H, Gal^{II} H-5), 4.27-4.20 (m, 3 H, Gal^{I} H-3, GlcA^{I} H-4, H-5), 4.19 (d, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA^{II} H-5), 4.08 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.0 Hz, 1 H, GalN H-3), 3.88, 3.69 (2 s, 6 H, COOC*H*$_3$), 3.87 (m, 1 H, Gal^{I} H-5), 3.83-3.68 (m, 2 H, GalN H-2, OC*H*$_2$), 3.59 (m, 1 H, GalN H-5), 3.55-3.47 (m, 2 H, GalN H-6a, OC*H*$_2$), 3.14-3.12 (m, 2 H, NC*H*$_2$), 3.05 (dd, $J_{5,6b}$ = 6.0, $J_{6a,6b}$ = 12.0 Hz, 1 H, GalN H-6b), 2.05, 2.03, 1.98, 1.96, 1.92, 1.81 (6 s, 18 H, NHC(O)C*H*$_3$, OC(O)C*H*$_3$); ^{13}C NMR (100 MHz, CD_3OD): δ = 173.45, 171.99, 171.86, 171.34, 171.20, 171.11, 169.20, 167.68, 167.62, 167.52, 167.29, 166.91, 166.56, 166.22, 158.48 (16 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 138.16, 134.40, 134.34, 134.28, 134.25, 134.04, 131.60, 131.24, 131.18, 131.10, 130.82, 130.72, 130.67, 130.60, 130.55, 130.51, 130.36, 130.30, 129.73, 129.63, 129.57, 129.51, 129.43, 129.36, 129.29, 129.20, 128.91, 128.66 (48 C, arom. C), 103.37 (1 C, Gal^{II} C-1), 102.42 (2 C, Gal^{I} C-1, GlcA^{I} C-1), 102.20 (1 C, GalN C-1), 101.30 (1 C, GlcA^{II} C-1), 79.59 (1 C, Gal^{II} C-3), 78.49, 77.80, 75.39, 74.15, 73.93, 73.32, 73.17, 73.11, 71.04, 72.95, 72.25, 72.19, 70.93 (13 C, Gal^{I} C-2, C-3, C-5, Gal^{II} C-2, C-5, GlcA^{I} C-2, C-3, C-4, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 77.27 (1 C, Gal^{I} C-4), 76.87 (1 C, GalN C-3), 71.85 (1 C, GalN C-5), 71.52 (1 C, Gal^{II} C-4), 69.64 (1 C, GalN C-4), 69.40 (1 C, O*C*H$_2$), 67.28 (1 C, *C*H$_2$-Ar), 65.41 (1 C, Gal^{I} C-6), 64.17 (1 C,Gal^{II} C-6), 62.79 (1 C, GalN C-6), 53.93, 53.35 (2 C, COO*C*H$_3$), 53.20 (1 C, GalN C-2), 41.61 (1 C, N*C*H$_2$), 23.58 (1 C, NHC(O)*C*H$_3$), 20.87, 20.75, 20.67, 20.52, 20.46 (5 C, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{103}H_{109}N_3O_{45}S$ $[M+H+NH_4]^{2+}$: 1069.802141; found: 1069.802017.

2-Benzyloxycarbonylaminoethyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2-*O*-benzoyl-4,6-di-*O*-chloroacteyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (32) : A mixture of imidate **18**[11] (75 mg, 0.13 mmol) and alcohol **17** (117 mg, 0.08 mmol) was submitted to the same procedure as described for the preparation of compound **20**. Flash silica chromatography (CH_2Cl_2/Acetone 12:1, containing 0.1 % of NEt_3) afforded the tetrasaccharide **32** (102 mg, 68 %) as a white powder. M.p. 143-145 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +20.5 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-6.93 (m, 35 H, arom. H), 6.71 (d, $J_{2,NH}$ = 9.0 Hz, 1H, GalN N*H*), 5.77 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 5.46 (dd, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.43 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^{I} H-2), 5.35 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, 1 H, GlcA H-4), 5.14-5.08 (m, 4 H, Gal^{II} H-2, GlcA H-2, H-3, GalN H-4), 5.05 (dd, $J_{2,3}$ = 11.0, $J_{3,4}$ = 3.0 Hz, 1 H, GalN H-3), 4.95 (m, 1 H, N*H*), 4.88 (ABq, 2 H, C*H*$_2$-Ar), 4.82 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.75 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.65 (d, $J_{1,2}$ = 7.0 Hz, 1 H, GlcA H-1), 4.58 (dd, $J_{5,6a}$ = 4.0, $J_{6a,6b}$ = 12.0 Hz, 1 H, Gal^{I} H-6a), 4.52 (d, 1 H, Gal^{I} H-1), 4.37 (dd, $J_{5,6b}$ = 7.0 Hz, 1 H, Gal^{I} H-6b), 4.25-4.20 (m, 2 H, Gal^{II} H-6a, GlcA H-5), 4.16-4.05 (m, 5 H, Gal^{I} H-3, H-5, Gal^{II} H-6b, C*H*$_2$Cl), 3.98-3.88 (m, 5 H, Gal^{II} H-3, H-5, GalN H-2, C*H*$_2$Cl), 3.85 (s, 3 H, COOC*H*$_3$), 3.79 (m, 1 H, OCH$_2$), 3.63 (dd, $J_{5,6a}$ = 6.5, $J_{5,6b}$ = 7.0 Hz, 1 H, GalN H-5), 3.52 (m, 1 H, OC*H*$_2$), 3.30-3.15 (m, 4 H, GalN H-6a, H-6b, NC*H*$_2$), 1.95, 1.92, 1.91 (3 s, 9 H, OC(O)C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.14, 169.90, 169.80, 168.34, 167.00, 166.95, 166.18, 165.89, 164.98, 164.57, 164.49, 163.62, 161.63, 156.18 (14 C, GlcA C-6, C=O), 136.49, 133.21, 133.16, 132.91, 132.69, 132.55, 130.10, 129.63, 129.56, 129.44, 129.40, 129.31, 128.99, 128.42, 128.37, 128.32, 128.20, 128.15, 127.95, 127.9993, 127.86, 127.84 (42 C, arom.C), 101.33 (1 C, Gal^{I} C-1), 101.10, 101.04 (1 C, Gal^{II} C-1, GlcA C-1), 99.91 (1 C, GalN C-1), 92.38 (1 C, *C*Cl$_3$), 77.32 (1 C, Gal^{I} C-3), 76.10 (1 C, Gal^{II} C-3), 75.55 (1 C, GlcA C-5), 73.43, 72.00, 71.86, 71.23, 70.96, 70.88, 70.78, 70.45, 70.06, 69.90 (10 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-2, C-4, C-5, GlcA C-2, C-3, C-4, GalN C-3, C-5), 68.91 (1 C, O*C*H$_2$), 66.34 (1 C, *C*H$_2$-Ar), 66.06 (1 C, GalN C-4), 63.54 (1 C, Gal^{II} C-6), 63.16 (1 C, Gal^{I} C-6), 60.19 (1 C, GalN C-6), 53.31 (1 C, COO*C*H$_3$), 52.68 (1 C, GalN C-2), 40.66, 40.55, 40.48 (3 C, *C*H$_2$Cl, N*C*H$_2$), 20.58, 20.52, 20.36 (3 C, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{89}H_{90}Cl_5N_3O_{35}$ $[M+H+NH_4]^{2+}$: 967.689326; found: 967.689346; elemental analysis calcd (%) for $C_{89}H_{85}Cl_5N_2O_{35}$: C 55.68, H 4.46, N 1.46; found C 54.94, H 4.70, N 1.41.

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2-*O*-benzoyl-4,6-di-*O*-chloroacetyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (33) : A mixture of imidate **19**[14] (272 mg, 0.31 mmol) and alcohol **17** (310 mg, 0.21 mmol) was submitted to the same procedure as described for the preparation of compound **20**. Flash silica chromatography (CH_2Cl_2/Acetone 9:1, containing 0.1 % of NEt_3) afforded the pentasaccharide **33** (250 mg, 55 %) as a white powder. M.p. 133 °C (from hot 2-propanol); [α]

$[\alpha]_D^{20}$ = +28.9 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-6.93 (m, 35 H, arom. H), 6.75 (d, $J_{2,NH}$ = 9.0 Hz, 1H, GalN N*H*), 5.79 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.46 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.44 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^I H-2), 5.35 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^I H-3), 5.21 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 5.18-5.08 (m, 4 H, Gal^{II} H-2, GlcA^I H-2, GlcA^{II} H-3, H-4), 4.98 (m, 1 H, N*H*), 4.90 (ABq, 2 H, CH_2-Ar), 4.88 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.86 (m, 1 H, GlcA^{II} H-2), 4.77 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.65 (d, $J_{1,2}$ = 7.0 Hz, 1 H, GlcA^I H-1), 4.60 (dd, $J_{5,6a}$ = 4.0, $J_{6a,6b}$ = 12.0 Hz, 1 H, Gal^I H-6a), 4.58 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^{II} H-1), 4.54 (d, 1 H, Gal^I H-1), 4.40 (dd, $J_{5,6b}$ = 6.5 Hz, 1 H, Gal^I H-6b), 4.26-4.21 (m, 3 H, Gal^{II} H-6a, GlcA^I H-4, GalN H-3), 4.17-4.10 (m, 4 H, Gal^I H-3, Gal^{II} H-6b, CH_2Cl), 4.08 (m, 1 H, Gal^I H-5), 3.98 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-3), 3.96-3.85 (m, 5 H, Gal^{II} H-5, GlcA^I H-5, GlcA^{II} H-5, CH_2Cl), 3.85, 3.73 (2 s, 6 H, COOCH_3), 3.79 (m, 1 H, OCH_2), 3.65 (m, 1 H, GalN H-5), 3.58 (m, 1 H, GalN H-2), 3.53 (m, 1 H, OCH_2), 3.43 (dd, $J_{5,6a}$ = 5.0, $J_{6a,6b}$ = 12.0 Hz, 1 H, GalN H-6a), 3.23 (m, 1 H, NCH_2), 3.15 (dd, $J_{5,6b}$ = 6.5 Hz, 1 H, GalN H-6b), 2.02, 2.01, 1.97, 1.95, 1.78 (5 s, 15 H, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.27, 170.00, 169.42, 169.24, 169.21, 168.01, 167.00, 166.69, 166.21, 165.96, 165.20, 164.63, 164.57, 156.25 (17 C, GlcA C-6, C=O), 136.57, 133.29, 133.25, 133.21, 132.98, 132.76, 132.63, 130.15, 129.69, 129.54, 129.45, 129.38, 129.35, 129.06, 128.58, 128.49, 128.44, 128.40, 128.28, 128.17, 128.03, 127.99, 127.94, 127.89, 126.69 (42 C, arom.C), 101.40 (1 C, Gal^I C-1), 101.17 (1 C, GlcA^I C-1) 101.12 (1 C, Gal^{II} C-1), 99.69 (1 C, GlcA^{II} C-1), 98.30 (1 C, GalN C-1), 92.59 (1 C, *C*Cl$_3$), 77.36 (1 C, Gal^I C-3), 76.20 (1 C, Gal^{II} C-3), 74.63, 73.88, 73.73, 72.33, 72.08, 71.99, 71.77, 71.31, 71.22, 71.00, 70.85, 70.57, 69.16, 67.93 (16 C, Gal^I C-2, C-4, C-5, Gal^{II} C-2, C-4, C-5, GlcA^I C-2, C-3, C-4, C-5, GalN C-4, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 70.17 (1 C, GalN C-3), 68.93 (1 C, O*C*H$_2$), 66.39 (1 C, *C*H$_2$-Ar), 63.59 (1 C, Gal^{II} C-6), 63.24 (1 C, Gal^I C-6), 61.17 (1 C, GalN C-6), 54.93 (1 C, GalN C-2), 53.39, 52.82 (2 C, COO*C*H$_3$), 40.74, 40.59 (3 C, *C*H$_2$Cl, N*C*H$_2$), 20.76, 20.53, 20.45, 20.25 (5 C, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{100}H_{101}Cl_5N_2O_{43}$ $[M+2H]^{2+}$: 1096.210486; found: 1096.210310; elemental analysis calcd (%) for $C_{100}H_{99}Cl_5N_2O_{43}$: C 54.74, H 4.55, N 1.28; found C 54.34, H 4.59, N 1.35.

2-Benzyloxycarbonylaminoethyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (34) : ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.73, 170.11, 169.92, 169.84, 168.83, 167.21, 166.11, 164.89, 164.63, 163.98, 161.80, 156.15 (12 C, GlcA C-6, C=O), 136.46, 133.56, 133.15, 132.73, 132.66, 132.19, 130.17, 129.58, 129.46, 129.42, 129.40, 129.19, 129.17, 128.98, 128.92, 128.75, 128.49, 128.42, 128.34, 128.28, 128.12, 128.03, 127.98, 127.81, 127.68 (42 C, arom.C), 101.91 (1 C, GlcA C-1), 101.49 (1 C, Gal^I C-1), 100.97 (1 C, Gal^{II} C-1), 100.09 (1 C, GalN C-1), 92.42 (1 C, *C*Cl$_3$), 81.03 (1 C, Gal^{II} C-3), 78.35 (1 C, Gal^I C-3), 75.59 (1 C, GlcA C-4), 75.49 (1 C, Gal^I C-5), 73.24, 72.21, 71.69, 71.19, 70.87, 70.57, 70.28, 70.20, 69.96 (9 C, Gal^I C-2, C-4, Gal^{II} C-2, C-4, C-5, GlcA C-2, C-3, GalN C-3, C-5), 68.94 (1 C, O*C*H$_2$), 68.67 (1 C, GlcA C-5), 66.28 (1 C, *C*H$_2$-Ar), 65.95 (1 C, GalN C-4), 62.89 (1 C, Gal^I C-6), 62.59 (1 C, GalN C-6), 60.15 (1, Gal^{II} C-6), 53.26 (1 C, COO*C*H$_3$), 52.52 (1 C, GalN C-2), 40.62 (1 C, N*C*H$_2$), 21.48, 20.47, 20.34 (3 C, OC(O)*C*H$_3$).

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (35) : Pentasaccharide **33** (310 mg, 0.14 mmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **34**. Flash silica chromatography (CH_2Cl_2/methanol 19:1) afforded the diol **35** (260 mg, 90 %) as a white foam. M.p. 144 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +21 (*c* = 1.04 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15-6.75 (m, 35 H, arom. H), 6.87 (d, $J_{2,NH}$ = 8.5 Hz, 1H, GalN N*H*), 5.90 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.51 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^I H-2), 5.38 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^I H-3), 5.23 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^{II} H-2), 5.20 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 5.19-5.08 (m, 3 H, GlcA^I H-2, GlcA^{II} H-3, H-4), 4.99 (m, 1 H, N*H*), 4.90 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.85 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.0 Hz, 1 H, GlcA^{II} H-2), 4.84 (ABq, 2 H, CH_2-Ar), 4.79 (d, $J_{1,2}$ = 7.0 Hz, 1 H, GlcA^I H-1), 4.73 (d, Gal^{II} H-1), 4.61 (d, 1 H, GlcA^{II} H-1), 4.54 (d, 1 H, Gal^I H-1), 4.53 (m, 1 H, Gal^I H-6a), 4.40 (dd, $J_{6a,6b}$ = 12.0, $J_{5,6b}$ = 6.5 Hz, 1 H, Gal^I H-6b), 4.27-4.23 (m, 2 H, GlcA^I H-4, GalN H-3), 4.10 (dd, 1 H, Gal^I H-3), 4.07 (m, 1 H, Gal^I H-5), 4.03 (d, $J_{4,5}$ = 10.0 Hz, 1 H, GlcA^I H-5), 4.01 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 3.93 (d, $J_{4,5}$ = 10.0 Hz, 1 H, GlcA^{II} H-5), 3.83 (dd, 1 H, Gal^{II} H-3), 3.80-3.72 (m, 2 H, GalN H-6a, OCH_2), 3.72, 3.66 (2 s, 6 H, COOCH_3), 3.66-3.58 (m, 4 H, Gal^{II} H-5, GalN H-2, H-5, H-6b), 3.52 (m, 1 H, OCH_2), 3.41 (dd, $J_{5,6a}$ = 6.5, $J_{6a,6b}$ = 12.0 Hz, 1 H, Gal^{II} H-6a), 3.22 (m, 1 H, NCH_2), 3.15 (dd, $J_{5,6b}$ = 6.5 Hz, 1 H, Gal^{II} H-6b), 2.04, 1.99, 1.97, 1.96, 1.80 (5 s, 15 H, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.25, 169.92, 169.45, 169.26, 169.20, 168.41, 167.34, 166.66, 166.17, 165.17, 164.85, 164.60, 163.94, 161.46, 156.23 (15 C, GlcA C-6, C=O), 136.54, 133.68, 133.23, 132.72, 132.69, 132.26, 130.29, 129.67, 129.56, 129.52, 129.44, 129.25, 129.02, 128.99, 128.81, 128.61, 128.55, 128.43, 128.37, 128.14, 128.11, 128.02, 127.91, 127.76 (42 C, arom.C), 102.06 (1 C, Gal^{II} C-1), 101.59 (1 C, Gal^I C-1) 101.29 (1 C, GlcA^I C-1), 99.75 (1 C, GlcA^{II} C-1), 98.48 (1 C, GalN C-1), 92.58 (1 C, *C*Cl$_3$), 80.95 (1 C, Gal^{II} C-3), 78.73 (1 C, Gal^I C-3), 75.65, 74.63, 73.83, 73.73, 71.97, 71.81, 71.78, 71.17, 71.10, 70.93, 70.81, 70.33, 70.28 (13 C, Gal^I C-2, C-5, Gal^{II} C-2, C-5, GlcA^I C-2, C-3, C-4, C-5, GalN C-3, C-5, GlcA^{II} C-2, C-3, C-4), 72.37 (1 C, GlcA^{II} C-5), 69.17 (1 C, Gal^I C-4), 69.04 (1 C, O*C*H$_2$), 68.83 (1 C, Gal^{II} C-4), 67.85 (1 C, GalN C-4), 66.37 (1 C, *C*H$_2$-Ar), 62.94 (1 C, Gal^I C-6), 62.80 (1 C, GalN C-6), 61.11 (1 C, Gal^{II} C-6), 54.89 (1 C, GalN C-2), 53.31, 52.76 (2 C, COO*C*H$_3$), 40.72 (1 C, N*C*H$_2$), 20.74, 20.66, 20.52, 20.43, 20.25 (5 C, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{96}H_{99}Cl_3N_2O_{41}$ $[M+2H]^{2+}$: 1020.238893; found: 1020.238390; elemental analysis calcd (%) for $C_{96}H_{97}Cl_3N_2O_{41}$: C 56.49, H 4.79, N 1.37; found C 55.07, H 5.12, N 1.42.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (36) : Tetrasaccharide **34** (267 mg, 0.15 mmol) was submitted to the same procedure as described

for the preparation of tetrasaccharide **22**. Flash silica chromatography (CH_2Cl_2/methanol 19:1) afforded the acetamide **36** (163 mg, 65 %) as a white foam. M.p. 145-148 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +23 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14-6.70 (m, 35 H, arom. H), 5.90 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.51 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^I H-2), 5.50-5.47 (m, 1 H, GalN N*H*), 5.35 (dd, $J_{2,3}$ = 7.5, $J_{3,4}$ = 8.5 Hz, 1 H, GlcA H-3), 5.26 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.09-5.04 (m, 2 H, GlcA H-2, GalN H-4), 4.97-4.92 (m, 3 H, GalN H-3, N*H,* CH_2-Ar), 4.84-4.80 (m, 2 H, GlcA H-1, CH_2-Ar), 4.71 (d, 1 H, Gal^{II} H-1), 4.60 (d, $J_{1,2}$ = 8.0, 1 H, GalN H-1), 4.52 (d, 1 H, Gal^I H-1), 4.50 (m, 1 H, Gal^I H-6a), 4.41-4.32 (m, 2 H, Gal^I H-6b, GlcA H-4), 4.13 (d, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA H-5), 4.09-4.04 (m, 2 H, Gal^I H-3, H-5), 4.00 (m, 1 H, Gal^{II} H-4), 3.91-3.78 (m, 8 H, Gal^{II} H-3, H-5, GalN H-2, H-6a, OCH_2, COOCH_3), 3.65 (m, 1 H, GalN H-6b), 3.59-3.49 (m, 2 H, GalN H-5, OCH_2), 3.40 (m, 1 H, Gal^{II} H-6a), 3.25-3.18 (m, 4 H, Gal^{II} H-6b, OH-4, NCH_2), 1.92, 1.89, 1.88 (3 s, 12 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.37, 170.01, 169.84, 169.11, 167.25, 166.15, 164.79, 164.75, 164.71, 164.13, 156.19 (12 C, GlcA C-6, C=O), 1363.50, 133.62, 133.20, 132.90, 132.69, 132.24, 130.27, 129.63, 129.52, 129.47, 129.23, 129.02, 128.95, 128.89, 128.80, 128.55, 128.48, 128.41, 128.38, 128.33, 128.27, 128.22, 128.17, 128.08, 127.87, 127.71 (42 C, arom. C), 102.09 (1C, Gal^{II} C-1), 101.57 (1 C, Gal^I C-1), 101.11 (1 C, GalN C-1), 100.70 (1 C, GlcA C-1), 81.26 (1 C, Gal^{II} C-3), 78.63 (1 C, Gal^I C-3), 76.08 (1 C, GlcA C-4), 75.68 (1 C, Gal^{II} C-5), 73.32 (1 C, GlcA C-5), 72.95 (1 C, GlcA C-3), 71.74, 71.67, 70.92, 70.87, 70.41, 70.30, 69.03 (7 C, Gal^I C-2, C-4, C-5, Gal^{II} C-2, GlcA C-2,GalN C-3, C-5), 68.66 (1 C, O*C*H$_2$), 67.04 (1 C, Gal^{II} C-4), 66.34 (1 C, *C*H$_2$-Ar), 65.88 (1 C, GalN C-4), 62.90, 62.73 (2 C, Gal^I C-6, GalN C-6), 60.17 (1 C, Gal^{II} C-6), 53.27 (1 C, COO*C*H$_3$), 50.79 (1 C, GalN C-2), 40.68 (1 C, N*C*H$_2$), 23.31, 20.55, 20.47 (4 C, NHC(O)*C*H$_3$, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{85}H_{88}N_2O_{33}$ $[M+2H]^{2+}$: 832.262918; found: 832.263206; elemental analysis calcd (%) for $C_{85}H_{86}N_2O_{33}$: C 61.37, H 5.21, N 1.68; found C 59.52, H 5.32, N 1.80.

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (37) : Pentasaccharide **35** (260 mg, 0.13 mmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **22**. Flash silica chromatography (CH_2Cl_2/methanol 19:1) afforded the acetamide **37** (210 mg, 85 %) as a white foam. M.p. 140 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +25.7 (*c* = 1.1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15-6.73 (m, 35 H, arom. H), 5.91 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.70 (d, $J_{2,NH}$ = 7.5 Hz, 1H, GalN N*H*), 5.50 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^I H-2), 5.33 (dd, $J_{2,3}$ = $J_{3,4}$ = 8.5 Hz, 1 H, GlcA^I H-3), 5.24 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.17-5.13 (m, 3 H, GlcA^I H-2, GlcA^{II} H-3, H-4), 5.10 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 4.98 (m, 1 H, N*H*), 4.89 (ABq, 2 H, CH_2-Ar), 4.88 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.0 Hz, 1 H, GlcA^{II} H-2), 4.81 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^I H-1), 4.78 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.72 (d, Gal^{II} H-1), 4.60 (d, 1 H, GlcA^{II} H-1), 4.53 (d, 1 H, Gal^I H-1), 4.52 (m, 1 H, Gal^I H-6a), 4.43 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, GalN H-3), 4.40 (dd, $J_{6a,6b}$ = 12.0, $J_{5,6b}$ = 7.0 Hz, 1 H, Gal^I H-6b), 4.29 (dd, $J_{4,5}$ = 10.0 Hz, 1 H, GlcA^I H-4), 4.10 (dd, 1 H, Gal^I H-3), 4.10-4.07 (m, 2 H, Gal^I H-5, GlcA^I H-5), 3.99 (m, 1 H, Gal^{II} H-4), 3.94 (d, $J_{4,5}$ = 10.0 Hz, 1 H, GlcA^{II} H-5), 3.84-3.80 (m, 3 H, Gal^{II} H-3, GalN H-6a, OCH_2), 3.79, 3.69 (2 s, 6 H, COOCH_3), 3.67 (m, 1 H, GalN H-6b), 3.59 (m, 1 H, GalN H-5), 3.52-3.46 (m, 3 H, Gal^{II} H-5, H-6a, OCH_2), 3.24-3.20 (m, 2 H, GalN H-2, NCH_2), 3.11 (dd, $J_{6a,6b}$ = 12.0, $J_{5,6b}$ = 5.0 Hz, 1 H, Gal^{II} H-6b), 2.02, 1.99, 1.98, 1.97, 1.92, 1.78 (6 s, 18 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.84, 170.23, 169.98, 169.55, 169.28, 169.26, 168.13, 167.34, 166.85, 166.17, 165.05, 164.80, 164.67, 163.96 (15 C, GlcA C-6, C=O), 136.57, 133.64, 133.25, 133.22, 132.79, 132.68, 132.30, 130.30, 129.68, 129.57, 129.53, 129.27, 129.12, 129.06, 129.04, 128.89, 128.64, 128.60, 128.57, 128.42, 128.37, 128.20, 128.09, 128.05, 127.91, 127.78 (42 C, arom.C), 102.11 (1 C, Gal^{II} C-1), 101.61 (1 C, Gal^I C-1) 101.04 (1 C, GlcA^I C-1), 99.28 (1 C, GlcA^{II} C-1), 98.82 (1 C, GalN C-1), 80.51 (1 C, Gal^{II} C-3), 78.75 (1 C, Gal^I C-3), 75.67 (1 C, GalN C-5), 75.15, 74.22, 74.04, 72.21, 72.16, 72.12, 71.79, 71.34, 69.02 (9 C, Gal^I C-5, Gal^{II} C-4, GlcA^I C-2, C-3, C-4, C-5, GalN C-3, GlcA^{II} C-3, C-4, C-5), 70.95, 70.93 (3 C, Gal^I C-2, Gal^{II} C-5, GlcA^{II} C-2), 70.42 (1 C, Gal^{II} C-2), 70.21 (1 C, Gal^I C-4), 68.99 (1 C, O*C*H$_2$), 67.34 (1 C, GalN C-4), 66.37 (1 C, *C*H$_2$-Ar), 62.93 (1 C, Gal^I C-6), 62.79 (1 C, GalN C-6), 61.23 (1 C, Gal^{II} C-6), 54.20 (1 C, GalN C-2), 53.32, 52.75 (2 C, COO*C*H$_3$), 40.72 (1 C, N*C*H$_2$), 23.50, 20.68, 20.64, 20.53, 20.44, 20.32 (6 C, NHC(O)*C*H$_3$, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{96}H_{102}N_2O_{41}$ $[M+2H]^{2+}$: 969.297352; found: 969.298502; elemental analysis calcd (%) for $C_{96}H_{100}N_2O_{41}$: C 59.50, H 5.20, N 1.45; found C 59.08, H 5.17, N 1.54.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(4-*O*-acetyl-2-*O*-benzoyl-6-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (38) : A mixture of diol **36** (45 mg, 0.03 mmol) and sulfur trioxide/trimethylamine complex (15 mg, 0.12 mmol) in anhydrous DMF (0.9 mL) was stirred for 60 h at 40 °C then was cooled. Methanol (1 mL) was added and the mixture was concentrated and purified by flash chromatography (CH_2Cl_2/MeOH, 19:1 then 9:1). A mixture of the residue, pyridine (3 mL), and Ac_2O (1.5 mL) was stirred overnight at rt, then was concentrated and coevaporated with toluene. Flash silica chromatography (CH_2Cl_2/MeOH, 9:1), followed by ion exchange on a column of Sephadex SP C-25 [Na^+] (CH_2Cl_2/MeOH/water, 9:5:1) afforded the 6-sulfate **38** (41 mg, 84%) as a white powder. $[\alpha]_D^{20}$ = +10.5 (*c* = 1 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 1/1): δ = 8.01-6.87 (m, 35 H, arom. H), 5.87 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.43 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.40-5.35 (m, 2 H, Gal^I H-2, GlcA H-2), 5.10 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.06-5.02 (m, 2 H, GalN H-4, CH_2-Ar), 4.94 (dd, $J_{2,3}$ = 11.0, $J_{3,4}$ = 3.0 Hz, 1 H, GalN H-3), 4.86-4.80 (m, 2 H, Gal^{II} H-1, CH_2-Ar), 4.72 (d, $J_{1,2}$ = 7.5 Hz, 1 H, Gal^I H-1), 4.56 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.50 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^I H-3), 4.47-4.35 (m, 3 H, Gal^{II} H-6a, H-6b, GlcA H-1), 4.32-4.28 (m, 1 H, Gal^{II} H-5), 4.21 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 4.11-4.04 (m, 5 H, Gal^I H-5, H-6a, H-6b, GlcA H-4, H-5), 4.01 (dd, 1 H, Gal^{II} H-3), 3.87 (s, 3 H, COOCH_3), 3.79-3.74 (m, 2 H, GalN H-2, OCH_2), 3.58-3.54 (m, 2 H, GalN H-5, OCH_2), 3.38 (dd, 1 H, $J_{5,6a}$ = 7.0, $J_{6a,6b}$ = 11.0, GalN H-6a), 3.22 (dd, $J_{5,6b}$ = 6.0 Hz, 1 H, GalN H-6b), 3.16-3.12 (m, 2 H,

NCH_2), 1.95, 1.91, 1.89, 1.88, 1.87 (5 s, 15 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD 1/1): δ = 173.45, 171.78, 171.66, 171.50, 169.23, 167.61, 167.49, 166.33, 166.01, 165.76, 160.56, 158.26, 157.58 (13 C, GlcA C-6, C=O), 137.83, 134.33, 134.18, 134.15, 134.07, 133.82, 133.59, 131.03, 130.93, 130.68, 130.54, 130.53, 130.39, 130.29, 130.24, 130.10, 129.73, 129.61, 129.42, 129.37, 129.30, 129.24, 128.98, 1283.91, 128.75, 128.51 (42 C, arom. C), 102.43 (4 C, Gal^{I} C-1), 102.26, 101.93 (2 C, Gal^{II} C-1, GlcA C-1), 101.88 (1 C, GalN C-1), 78.73 (1 C, Gal^{II} C-3), 77.27, 77.12 (2 C, Gal^{I} C-3, GlcA C-3), 74.86, 74.03, 73.32, 72.90, 72.73, 71.98, 71.24, 71.12 (12 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-2, C-4, C-5, GlcA C-2, C-4, C-5, GalN C-3, C-4, C-5), 70.65 (1 C, OCH_2), 69.53 (1 C, Gal^{I} C-6), 67.28 (1 C, CH_2-Ar), 64.40 (1 C, Gal^{II} C-6), 61.49 (1 C, GalN C-6), 53.74 (1 C, COOCH_3), 51.62 (1 C, GalN C-2), 41.52 (1 C, NCH_2), 23.13, 20.70, 203.61, 20.59, 20.48 (5 C, NHC(O)CH_3, OC(O)CH_3); HRMS: *m/z*: calcd for $C_{87}H_{87}N_2O_{37}S$ [M-Na]$^{-}$: 1783.471389; found: 1783.470989.

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(4-*O*-acetyl-2-*O*-benzoyl-6-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (39) : A mixture of diol **37** (128 mg, 0.066 mmol) and sulfur trioxide/trimethylamine complex (23 mg, 0.17 mmol) in anhydrous DMF (2.4 mL) was stirred for 4 h at 40 °C. More reagent (14 mg, 0.10 mmol) was then added and the mixture was stirred for 15 h then was cooled. Methanol (1 mL) was added and the mixture was concentrated and purified by flash chromatography (CH_2Cl_2/MeOH, 9:1). A mixture of the residue, pyridine (3 mL), and Ac_2O (1.5 mL) was stirred overnight at rt, then was concentrated and coevaporated with toluene. Flash silica chromatography (CH_2Cl_2/MeOH, 9:1), followed by ion exchange on a column of Sephadex SP C-25 [Na^+] (CH_2Cl_2/MeOH/water, 9:5:1) afforded the 6-sulfate **39** (76 mg, 55%) as a white powder. $[\alpha]_D^{20}$ = +23.3 (*c* = 1.0 in MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ = 8.15-6.80 (m, 35 H, arom. H), 5.93 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 5.50 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.45 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^{I} H-2), 5.43 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1 H, GlcA^{II} H-4), 5.30 (dd, $J_{2,3}$ = $J_{3,4}$ = 10.0 Hz, 1 H, GlcA^{I} H-3), 5.18-5.14 (m, 2 H, Gal^{II} H-2, GalN H-4), 5.09 (dd, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{I} H-2), 5.07 (dd, $J_{2,3}$ = 9.5 Hz, 1 H, GlcA^{II} H-3), 4.96 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^{II} H-1), 4.92 (d, $J_{1,2}$ = 8.0 Hz, Gal^{II} H-1), 4.87 (ABq, 2 H, CH_2-Ar), 4.88 (m, 1 H, GlcA^{II} H-2), 4.84 (d, 1 H, GlcA^{I} H-1), 4.80 (d, 1 H, Gal^{I} H-1), 4.57 (dd, 1 H, Gal^{I} H-3), 4.53 (m, 1 H, Gal^{II} H-6a), 4.52 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.42 (dd, $J_{6a,6b}$ = 12.0, $J_{5,6b}$ = 7.0 Hz, 1 H, Gal^{II} H-6b), 4.39 (m, 1 H, Gal^{II} H-5), 4.25-4.22 (m, 2 H, GlcA^{I} H-4, GlcA^{II} H-5), 4.20-4.07 (m, 5 H, Gal^{I} H-5, H-6a, H-6b, Gal^{II} H-3, GlcA^{I} H-5), 4.08 (dd, $J_{2,3}$ = 3.0, $J_{3,4}$ = 10.0 Hz, 1 H, GalN H-3), 3.95, 3.71 (2 s, 6 H, COOCH_3), 3.80 (m, 1 H, OCH_2), 3.75 (m, 1 H, GalN H-2), 3.64-3.58 (m, 2 H, GalN H-5, OCH_2), 3.53 (dd, $J_{6a,6b}$ = 12.0, $J_{5,6b}$ = 4.0 Hz, 1 H, GalN H-6a), 3.18 (m, 2 H, NCH_2), 3.11 (dd, $J_{5,6b}$ = 6.5 Hz, 1 H, GalN H-6b), 2.03, 2.01, 2.00, 1.99, 1.98, 1.83 (6 s, 21 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, CD_3OD): δ = 173.38, 171.96, 171.90, 171.74, 171.34, 171.10, 170.99, 169.39, 169.01, 167.66, 167.57, 166.51, 166.14, 165.97 (15 C, GlcA C-6, C=O), 131.30, 131.02, 130.94, 130.70, 130.66, 130.49, 130.34, 130.27, 129.59, 129.53, 129.37, 129.14, 129.06, 128.62 (42 C, arom.C), 102.58 (1 C, Gal^{I} C-1), 102.41 (1 C, Gal^{II} C-1) 102.05 (1 C, GlcA^{I} C-1), 101.97 (1 C, GalN C-1), 101.31 (1 C, GlcA^{II} C-1), 79.05, 76.74, 75.19, 74.10, 73.56, 73.31, 73.07, 73.03, 72.96, 72.91 (11 C, Gal^{I} C-2, C-4, C-5, Gal^{II} C-3, C-5, GlcA^{I} C-2, C-3, C-4, C-5, GlcA^{II} C-4, C-5), 77.28 (1 C, Gal^{I} C-3), 77.21 (1 C, GalN C-3), 72.21, 72.15 (2 C, Gal^{II} C-2, GlcA^{II} C-2), 71.89 (1 C, GalN C-5), 70.87, 70.84 (2 C, Gal^{II} C-4, GlcA^{II} C-3), 69.64 (1 C, GalN C-4), 69.55 (1 C, OCH_2), 67.50 (1 C, Gal^{I} C-6), 67.24 (1 C, CH_2-Ar), 64.47 (1 C, Gal^{II} C-6), 62.79 (1 C, GalN C-6), 53.96, 53.27 (2 C, COOCH_3), 53.50 (1 C, GalN C-2), 41.66 (1 C, NCH_2), 23.48, 20.77, 20.69, 20.58, 20.46, 20.40 (7 C, NHC(O)CH_3, OC(O)CH_3); HRMS: *m/z*: calcd for $C_{98}H_{103}N_2NaO_{45}S$ [M+H+Na]$^{2+}$: 1041.272014; found: 1041.273033.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,6-di-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (40) : Tetrasaccharide **36** (148 mg, 0.09 mmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **28**. Flash silica chromatography (CH_2Cl_2/2-propanol 16:1) afforded the 6-benzoate **40** (135 mg, 86 %) as a white foam. M.p. 130-133 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +23 (*c* = 1.02 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-6.86 (m, 40 H, arom. H), 5.85 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 5.75 (d, $J_{NH,2}$ =9.0 Hz, 1 H, GalN N*H*), 5.44 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^{I} H-2), 5.36 (dd, $J_{2,3}$ = 6.5, $J_{3,4}$ = 8.5 Hz, 1 H, GlcA H-3), 5.27 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^{II} H-2), 5.07-5.00 (m, 3 H, GlcA H-2, GalN H-4, N*H*), 4.96-4.91 (m, 2 H, GalN H-3, CH_2-Ar), 4.85 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA H-1), 4.85-4.81 (m, 1 H, CH_2-Ar), 4.69 (d, 1 H, Gal^{II} H-1), 4.64-4.61 (m, 3 H, Gal^{I} H-6a, H-6b, GalN H-1), 4.50 (d, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA H-5), 4.47-4.44 (m, 3 H, Gal^{I} H-1, Gal^{II} H-6a, GlcA H-4), 4.20-4.16 (m, 3 H, Gal^{I} H-3, Gal^{II} H-4, H-6b), 4.00-3.95 (m, 2 H, Gal^{II} H-5, GalN H-2), 3.93-3.90 (m, 1 H, *H*O-6), 3.86-3.77 (m, 2 H, Gal^{I} H-5, OCH_2), 3.73-3.68 (m, 4 H, Gal^{II} H-3, COOCH_3), 3.56-3.48 (m, 1 H, OCH_2), 3.46 (dd, $J_{5,6a}$ = 7.0, $J_{6a,6b}$ = 10.5 Hz, 1 H, GalN H-6a), 3.33 (m, 1 H, GalN H-5), 3.29-3.19 (m, 3 H, GalN H-6b, NCH_2), 1.95, 1.93, 1.92, 1.87 (4 s, 12 H, NHCOCH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.53, 170.37, 170.01, 169.85, 169.70, 166.18, 166.03, 165.69, 164.77, 164.61, 164.57, 164.13, 156.20 (13C, GlcA C-6; C=O), 136.47, 133.22, 133.12, 133.10, 133.00, 132.94, 132.84, 132.15, 130.07, 129.98, 129.81, 129.61, 129.56, 129.53, 129.50, 129.47, 129.40, 129.37, 129.03, 128.95, 128.74, 128.68, 128.45, 128.42, 128.34, 128.30, 128.27, 128.23, 128.13, 128.10, 127.82, 127.70, 126.97 (48 C, arom. C), 101.41 (1 C, Gal^{I} C-1), 101.12, 101.07 (2 C, Gal^{II} C-1, GalN C-1), 100.35 (1 C, GlcA C-1), 81.31 (1 C, Gal^{II} C-3), 76.08 (1 C, Gal^{I} C-3), 76.04 (1 C, GlcA C-5), 75.68 (1 C, GlcA C-3), 73.31, 73.00, 72.17, 71.90, 71.67 (5 C, Gal^{I} C-2, C-5, Gal^{II} C-5, GlcA C-2, C-4), 71.47, 70.42, 70.38, 70.07 (4 C, Gal^{I} C-4, Gal^{II} C-2, GalN C-3, C-5), 68.87 (1 C, OCH_2), 67.72 (1 C, Gal^{II} C-4), 66.31 (1 C, CH_2-Ar), 65.87 (1 C, GalN C-4), 63.12 (1 C, Gal^{I} C-6), 62.79 (1 C, Gal^{II} C-6), 60.21 (1 C, GalN C-6), 53.25 (1 C, COOCH_3), 50.67 (1 C, GalN C-2), 40.64 (1 C, NCH_2), 23.24, 20.51, 20.45, 20.43 (4 C, NHCOCH_3, OC(O)CH_3); HRMS: *m/z*: calcd for $C_{92}H_{92}N_2O_{34}$ [M+2H]$^{2+}$: 884.276025; found: 884.275481; elemental analysis calcd (%) for $C_{92}H_{90}N_2O_{34}$: C 62.51, H 5.13, N 1.58; found C 61.55, H 5.23, N 1.46.

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,6-di-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (41) : Pentasaccharide **37** (157 mg, 0.08 mmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **28**. Flash silica chromatography (CH_2Cl_2/MeOH, 19:1) afforded the 6-benzoate **41** (148 mg, 78 %) as a white foam. M.p. 135 °C (from hot 2-propanol); $[\alpha]_D^{20}$ = +27.7 (*c* = 1 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15-6.80 (m, 40 H, arom. H), 5.84 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.68 (d, $J_{2,NH}$ = 7.5 Hz, 1H, GalN N*H*), 5.43 (dd, $J_{1,2}$ = 7.5, $J_{2,3}$ = 9.5 Hz, 1 H, Gal^I H-2), 5.33 (dd, $J_{2,3}$ = $J_{3,4}$ = 8.5 Hz, 1 H, GlcA^I H-3), 5.24 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.19-5.14 (m, 3 H, GlcA^I H-2, GlcA^{II} H-3, H-4), 5.10 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 5.02 (m, 1 H, N*H*), 4.94 (ABq, 2 H, CH_2-Ar), 4.88 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.0 Hz, 1 H, GlcA^{II} H-2), 4.81 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^I H-1), 4.78 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.70 (d, Gal^{II} H-1), 4.63-4.60 (m, 3 H, Gal^I H-6a, H-6b, GlcA^{II} H-1), 4.46-4.44 (m, 3 H, Gal^I H-1, Gal^{II} H-6a, H-6b), 4.43 (dd, $J_{2,3}$ = 8.5 Hz, 1 H, GalN H-3), 4.35 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA^I H-4), 4.18 (dd, 1 H, Gal^I H-3), 4.13 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 4.08 (d, 1 H, GlcA^I H-5), 3.98 (m, 1 H, Gal^{II} H-5), 3.95 (d, $J_{4,5}$ = 10.0 Hz, 1 H, GlcA^{II} H-5), 3.86 (m, 1 H, Gal^I H-5), 3.78 (dd, 1 H, Gal^{II} H-3), 3.74 (m, 1 H, OCH_2), 3.74, 3.71 (2 s, 6 H, COOCH_3), 3.52-3.49 (m, 3 H, GalN H-5, H-6a, OCH_2), 3.29-3.22 (m, 3 H, GalN H-2, NCH_2), 3.14 (dd, $J_{6a,6b}$ = 12.0, $J_{5,6b}$ = 9.0 Hz, 1 H, GalN H-6b), 2.03, 2.00, 1.99, 1.97, 1.95, 1.81 (6 s, 18 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.44, 170.79, 170.37, 170.11, 169.71, 169.46, 169.41, 168.65, 167.03, 166.34, 166.16, 165.77, 165.18, 164.72, 164.11, 156.40 (16 C, GlcA C-6, C=O), 136.59, 133.56, 133.34, 133.21, 133.12, 133.03, 132.93, 132.30, 130.18, 130.14, 129.93, 129.74, 129.71, 129.68, 129.65, 129.61, 129.56, 129.52, 129.49, 129.47, 129.20, 129.12, 129.08, 128.88, 128.59, 128.50, 128.46, 128.43, 128.40, 128.34, 128.27, 128.11, 128.07, 127.96, 127.86 (48 C, arom.C), 101.54 (1 C, Gal^I C-1), 101.16 (1 C, GlcA^I C-1) 101.03 (1 C, Gal^{II} C-1), 99.47 (1 C, GlcA^{II} C-1), 99.23 (1 C, GalN C-1), 80.79 (1 C, Gal^{II} C-3), 75.77 (1 C, Gal^I C-3), 75.35, 72.23, 72.19, 72.03, 71.65, 71.42, 71.00, 70.95, 69.12, 69.09, 68.14, 67.58 (12 C, Gal^I C-2, C-5, Gal^{II} C-4, GlcA^I C-2, C-4, GalN C-3, C-4, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 74.30 (1 C, GlcA^I C-5), 73.94 (1 C, Gal^{II} C-5), 72.62 (1 C, GlcA^I C-3), 70.36 (1 C, Gal^{II} C-2), 70.15 (1 C, Gal^I C-4), 68.96 (1 C, O*C*H$_2$), 66.48 (1 C, *C*H$_2$-Ar), 63.17 (1 C, Gal^I C-6), 62.93 (1 C, Gal^{II} C-6), 61.33 (1 C, GalN C-6), 53.88 (1 C, GalN C-2), 53.35, 52.81 (2 C, COO*C*H$_3$), 40.78 (1 C, N*C*H$_2$), 23.44, 20.74, 20.71, 20.49, 20.40, 20.36 (6 C, NHC(O)*C*H$_3$, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{103}H_{106}N_2O_{42}$ $[M+2H]^{2+}$: 1021.310459; found: 1021.311743; elemental analysis calcd (%) for $C_{103}H_{104}N_2O_{42}$: C 60.59, H 5.13, N 1.37; found C 59.45, H 5.16, N 1.38.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,6-di-*O*-benzoyl-4-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (42) : A mixture of tetrasaccharide **40** (123 mg, 0.07 mmol) and sulfur trioxide/trimethylamine complex (97 mg, 0.70 mmol) in anhydrous DMF (2 mL) was stirred for 62 h at 60 °C then was cooled. Methanol (2.5 mL) was added and the mixture was directly eluted from a column of Sephadex LH-20 with 1:1 CH_2Cl_2/MeOH. Fractions containing the product were submitted to a flash silica chromatography (CH_2Cl_2/2-propanol, 16:1), followed by ion exchange on a column of Sephadex SP C-25 [Na^+] (CH_2Cl_2/MeOH/water, 9:5:1) to give the 4-sulfate **42** (116 mg, 89%) as a white powder. $[\alpha]_D^{20}$ = +27.5 (*c* = 1.03 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 1/1): δ = 8.16-6.91 (m, 40 H, arom. H), 5.78 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.41-5.33 (m, 2 H, Gal^I H-2, GlcA H-3), 5.23 (dd, $J_{1,2}$ = 7.5, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.19 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.13 (dd, $J_{1,2}$ = 7.0, $J_{2,3}$ = 9.5 Hz, 1 H, GlcA H-2), 5.03 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 4.94 (dd, $J_{3,4}$ = 9.5, $J_{4,5}$ = 10.0 Hz, 1 H, GlcA H-4), 4.86-4.69 (m, 8 H, Gal^{II} H-1, Gal^{II} H-6a, H-6b, GlcA H-1, GalN H-1, H-3, CH_2-Ar), 4.50 (d, $J_{1,2}$ = 7.5 Hz, 1 H, Gal^I H-1), 4.32-4.22 (m, 3 H, Gal^I H-6a, H-6b, Gal^I H-3), 4.18 (d, 1 H, GlcA H-5), 4.09-4.07 (m, 2 H, Gal^{II} H-3, Gal^{II} H-5), 3.94-3.89 (m, 2 H, Gal^I H-5, GalN H-2), 3.76 (s, 3 H, COOCH_3), 3.75-3.71 (m, 1 H, OCH_2), 3.54-3.49 (m, 2 H, GalN H-5, H-6a), 3.40-3.34 (m, 1 H, OCH_2), 3.26 (dd, $J_{5,6a}$ = 6.0, $J_{6a,6b}$ = 11.0 Hz, 1 H, GalN H-6b), 3.14-3.11 (m, 2 H, NCH_2), 1.93, 1.87, 1.85 (4 s, 12 H, NHCOCH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD 1/1): 172.96, 172.93, 171.32, 171.10, 170.98, 167.25, 167.00, 166.49, 166.15, 165.86, 165.79, 165.71 157.55 (13 C, GlcA C-6, C=O), 137.10, 134.15, 133.96, 133.90, 133.80, 133.78, 133.24, 130.72, 130.49, 130.30, 130.24, 130.20, 130.15, 130.06, 129.94, 129.67, 129.54, 129.19, 129.08, 129.02, 128.92, 128.85, 128.69, 128.55, 128.49, 128.26 (48 C, arom. C), 102.47, 102.23, 101.93, 101.78 (4 C, Gal^I C-1, Gal^{II} C-1, GlcA C-1, GalN C-1), 77.70 (1 C, Gal^{II} C-3), 77.33 (1 C, Gal^I C-3), 76.50, 76.32, 74.56, 74.27, 73.75, 73.58, 72.70, 72.39, 71.96, 71.78 (10 C, Gal^I C-2, C-4, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3), 71.00 (1 C, Gal^I C-4), 69.43 (1 C, GalN C-5), 69.38 (1 C, O*C*H$_2$), 67.09 (1 C, *C*H$_2$-Ar), 66.91 (1 C, GalN C-4), 64.77 (1 C, Gal^{II} C-6), 63.85 (1 C, Gal^I C-6), 62.00 (1 C, GalN C-6), 53.41 (1 C, COO*C*H$_3$), 51.22 (1 C, GalN C-2), 41.26 (1 C, N*C*H$_2$), 23.30, 20.63, 20.56 (4 C, NHC(O)*C*H$_3$, OC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{92}H_{92}N_2O_{37}S$ $[M+3H-Na]^{2+}$: 924.254433; found: 924.254057.

2-Benzyloxycarbonylaminoethyl *O*-(methyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-(2,6-di-*O*-benzoyl-4-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (43) : A mixture of pentasaccharide **41** (132 mg, 0.065 mmol) and sulfur trioxide/trimethylamine complex (90 mg, 0.65 mmol) in anhydrous DMF (1.3 mL) was stirred for 20 h at 60 °C. More reagent (90 mg, 0.65 mmol) was then added and the mixture was stirred for 48 h then was cooled. Methanol (2.0 mL) was added and the mixture was directly eluted from a column of Sephadex LH-20 with 1:1 CH_2Cl_2/MeOH. Fractions containing the product were submitted to a flash silica chromatography (CH_2Cl_2/MeOH, 19:1), followed by ion exchange on a column of Sephadex SP C-25 [Na^+] (CH_2Cl_2/MeOH/water, 9:5:1) to give the 4-sulfate **43** (84 mg, 62%) as a white powder. $[\alpha]_D^{20}$ = +20.0 (*c* = 1.05 in MeOH); ^{1}H NMR (400 MHz, CD_3OD): δ = 8.10-6.90 (m, 40 H, arom. H), 5.88 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 5.50 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^I H-3), 5.43 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^I H-2), 5.36 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{II} H-3), 5.34 (dd, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^I H-2), 5.23 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^{II} H-2), 5.20 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 5.15 (dd, $J_{3,4}$

= 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 5.08 (dd, $J_{4,5}$ = 9.5 Hz, 1 H, GlcA^{II} H-4), 4.99 (d, 1 H, GlcA^{I} H-1), 4.97 (d, 1 H, Gal^{II} H-1), 4.96 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.88-4.83 (m, 4 H, Gal^{I} H-6a, GlcA^{II} H-2, CH_2-Ar), 4.70-4.66 (m, 3 H, Gal^{I} H-1, H-6b, GalN H-1), 4.56 (dd, $J_{4,5}$ = 9.0 Hz, 1 H, GlcA^{I} H-4), 4.43 (dd, 1 H, Gal^{I} H-3), 4.30-4.22 (m, 5 H, Gal^{I} H-5, Gal^{II} H-6a, H-6b, GlcA^{I} H-5, GlcA^{II} H-5), 4.18 (dd, 1 H, Gal^{II} H-3), 4.06-4.03 (m, 2 H, Gal^{II} H-5, GalN H-3), 3.89, 3.68 (2 s, 6 H, COOCH_3), 3.87 (m, 1 H, GalN H-2), 3.78 (m, 1 H, OCH_2), 3.59-3.54 (m, 3 H, GalN H-6a, H-5, OCH_2), 3.19-3.14 (m, 3 H, GalN H-6b, NCH_2), 2.07, 2.04, 2.00, 1.98, 1.87 (6 s, 18 H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, CD_3OD): δ = 173.50, 171.90, 171.85, 171.34, 171.17, 171.08, 170.19, 169.14, 167.80, 167.46, 167.14, 167.00, 166.68, 166.56, 166.48, 158.48 (16 C, GlcA C-6, C=O), 138.50, 134.46, 134.34, 134.31, 134.22, 131.53, 130.99, 130.88, 130.71, 130.61, 130.48, 130.36, 129.78, 129.76, 129.70, 129.54, 129.44, 129.37, 129.21, 129.19, 128.85, 128.61 (48 C, arom.C), 103.11, 102.95 (2 C, Gal^{II} C-1, GlcA^{I} C-1), 102.56, 102.03 (2 C, Gal^{I} C-1, GalN C-1), 101.33 (1 C, GlcA^{II} C-1), 78.95, 77.05, 75.07, 73.86, 73.69, 73.32, 73.08, 73.00 (8 C, Gal^{I} C-5, Gal^{II} C-3, C-5, GlcA^{I} C-2, C-5, GalN C-3, GlcA^{II} C-3, C-5), 78.48 (1 C, Gal^{I} C-3), 75.35 (1 C, Gal^{II} C-4), 76.96 (1 C, GlcA^{I} C-4), 74.40 (1 C, GlcA^{I} C-3), 72.68 (1 C, Gal^{I} C-2), 72.50 (1 C, Gal^{I} C-4), 72.25, 72.16 (2 C, Gal^{II} C-2, GlcA^{II} C-2), 71.86 (1 C, GalN C-5), 70.93 (1 C, GlcA^{II} C-4), 69.70 (1 C, GalN C-4), 69.52 (1 C, OCH_2), 67.24 (1 C, CH_2-Ar), 65.21 (1 C, Gal^{I} C-6), 64.38 (1 C, Gal^{II} C-6), 62.55 (1 C, GalN C-6), 53.89, 53.25 (2 C, COOCH_3), 53.15 (1 C, GalN C-2), 41.57 (1 C, NCH_2), 23.59, 20.81, 20.69, 20.60, 20.46, 20.40 (6 C, NHC(O)CH_3, OC(O)CH_3); HRMS: *m/z*: calcd for $C_{103}H_{106}N_2O_{45}S$ $[M+3H-Na]^{2+}$: 1061.288867; found: 1061.289528.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (44) : ^{13}C NMR (100 MHz, D_2O): δ = 175.63, 175.23, 159.02 (3 C, GlcA C-6, C=O), 137.10, 137.08, 129.38, 128.97, 128.32, 128.27 (6 C, arom. C), 104.54, 104.42, 103.27 (3 C, Gal^{I} C-1, Gal^{II} C-1, GlcA C-1), 101.59 (1 C, GalN C-1), 83.14, 82.84 (2 C, Gal^{I} C-3, Gal^{II} C-3), 80.10, 77.02, 75.84, 75.38, 75.34, 74.28, 73.52, 71.68, 70.66, 70.47 (10 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 69.47 (1 C, OCH_2), 68.99, 68.69, 68.39 (3 C, Gal^{I} C-4, Gal^{II} C-4, GalN C-4), 67.53 (CH_2-Ar), 61.66, 61.54, 61.47 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 52.93 (1 C, GalN C-2), 41.12 (1 C, CH_2N), 23.07 (1 C, NHC(O)CH_3).

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-6-*O*-sodium sulfonato-β-D-galactopyranoside (45) : Tetrasaccharide **26** (117 mg, 0.065 mmol) was submitted to the same procedure as described for the preparation of **44** to give disodium salt **45** (46 mg, 69%) as a white powder. R_f = 0.30 (EtOAc/MeOH/water, 4:2:1); $[\alpha]_D^{20}$ = +8.5 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 7.46-7.44 (m, 5 H, arom. H), 5.14 (s, 2 H, CH_2-Ar), 4.69 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA H-1), 4.67, 4.44 (2 d, $J_{1,2}$ = 8.5 Hz, 2 H, Gal^{I} H-1, Gal^{II} H-1), 4.49 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.24 (d, $J_{3,4}$ = 2.5, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 4.20-4.18 (m, 2 H, Gal^{II} H-6a, H-6b), 4.16 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1Hz, 1 H, Gal^{II} H-4), 3.98 (m, 1 H, OCH_2), 3.93 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1Hz, 1 H, GalN H-4), 3.90-3.86 (m, 2 H, Gal^{II} H-3, GalN H-2), 3.84-3.68 (m, 14 H, Gal^{I} H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-5, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b, OCH_2), 3.64 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.47 (dd, 1 H, GlcA H-2), 3.42-3.36 (m, 2 H, CH_2N), 2.06 (s, 3 H, NHC(O)CH_3); ^{13}C NMR (100 MHz, D_2O): δ = 175.62, 175.10, 158.97 (3 C, GlcA C-6, C=O), 137.12, 129.38, 128.95, 128.34, 128.33 (6 C, arom. C), 104.59, 104.42, 103.20 (3 C, Gal^{I} C-1, Gal^{II} C-1, GlcA C-1), 101.59 (1 C, GalN C-1), 83.13, 82.68 (2 C, Gal^{I} C-3, Gal^{II} C-3), 80.11, 76.90, 75.84, 75.35, 74.27, 73.52, 72.96, 71.69, 70.67, 70.35 (10 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-5, GalN C-3, C-5), 69.51 (1 C, OCH_2), 68.73, 68.68, 68.39 (3 C, Gal^{I} C-4, Gal^{II} C-4, GalN C-4), 67.71 (1 C, Gal^{I} C-6), 67.48 (CH_2-Ar), 61.65, 61.49 (2 C, Gal^{II} C-6, GalN C-6), 52.94 (1 C, GalN C-2), 41.15 (1 C, CH_2N), 23.07 (1C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{36}H_{55}N_2O_{27}S$ $[M+3H-2Na]^+$ 979.270742; found: 979.270970.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-4-*O*-sodium sulfonato-β-D-galactopyranoside (46) : Tetrasaccharide **30** (100 mg, 53 μmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **44** to give the disodium salt **46** (39 mg, 72%) as a white powder. R_f = 0.37 (EtOAc/MeOH/water, 4:2:1); $[\alpha]_D^{20}$ = +8 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 7.49-7.40 (m, 5 H, arom. H), 5.14 (s, 2 H, CH_2-Ar), 4.85 (d, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1Hz, 1 H, Gal^{I} H-4), 4.70, 4.46 (2 d, $J_{1,2}$ = 8.0 Hz, 2 H, Gal^{I} H-1, Gal^{II} H-1), 4.68 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA H-1), 4.49 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.14 (dd, $J_{3,4}$ = 2.5, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 3.98-3.94 (m, 2 H, Gal^{I} H-3, OCH_2), 3.92-3.83 (m, 2 H, GalN H-2, H-4), 3.82-3.66 (m, 16 H, Gal^{I} H-2, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b, OCH_2), 3.63 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.47 (dd, 1 H, GlcA H-2), 3.39-3.34 (m, 2 H, CH_2N), 2.06 (s, 3 H, NHC(O)CH_3); ^{13}C NMR (100 MHz, D_2O): δ = 175.62, 175.14, 159.01 (3 C, GlcA C-6, C=O), 137.10, 129.38, 128.95, 128.28 (6 C, arom. C), 104.53, 103.34 (3 C, Gal^{I} C-1, Gal^{II} C-1, GlcA C-1), 101.59 (1 C, GalN C-1), 83.10 (1 C, Gal^{II} C-3), 80.14 (1 C, Gal^{I} C-3), 77.98 (1 C, Gal^{I} C-4), 79.05, 76.98, 75.83, 75.50, 75.09, 74.26, 73.51, 71.71, 70.95, 70.64 (10 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 69.63 (1 C, OCH_2), 69.04, 68.39 (2C, Gal^{II} C-4, GalN C-4), 67.50 (CH_2-Ar), 61.64, 61.52 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 52.93 (1 C, GalN C-2), 41.09 (1 C, CH_2N), 23.06 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{36}H_{56}N_2O_{24}$ $[M+4H-SO_3Na-Na]^{2+}$ 450.160602; found: 450.160612.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(6-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (47) : Tetrasaccharide **38** (116 mg, 0.064 mmol) was submitted to the same procedure as described for the preparation of **44** to give disodium salt **47** (46 mg, 70%) as a white powder. R_f = 0.30 (EtOAc/MeOH/water, 4:2:1); $[\alpha]_D^{20}$ = +6.5 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 7.47-7.42 (m, 5 H, arom. H), 5.14 (s, 2 H, CH_2-Ar), 4.69 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA H-1), 4.66,

4.42 (2 d, $J_{1,2}$ = 7.5 Hz, 2 H, Gal^{I} H-1, Gal^{II} H-1), 4.49 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.26 (d, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 4.22-4.19 (m, 3 H, Gal^{I} H-4, Gal^{II} H-6a, H-6b), 3.99-3.82 (m, 5 H, Gal^{I} H-3, Gal^{II} H-3, GalN H-2, H-4, OCH_2), 3.80-3.67 (m, 13 H, Gal^{I} H-2, H-5, H-6a, H-6b, Gal^{II} H-2, H-5, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b, OCH_2), 3.64 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.48 (dd, 1 H, GlcA H-2), 3.40-3.37 (m, 2 H, CH_2N), 2.07 (s, 3 H, NHC(O)CH_3); ^{13}C NMR (100 MHz, D_2O): δ = 175.63, 175.22 (2 C, GlcA C-6, C=O), 158.99 (1 C, NHC(O)O), 137.08, 129.39, 128.98, 128.34 (6 C, arom. C), 104.44, 104.36, 103.24 (3 C, Gal^{I} C-1, Gal^{II} C-1, GlcA C-1), 101.54 (1 C, GalN C-1), 83.33, 82.93 (2 C, Gal^{I} C-3, Gal^{II} C-3), 80.06, 77.01, 75.83, 75.55, 74.25, 73.53, 73.07, 71.70, 70.51, 70.29 (10 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 69.41 (1 C, OCH_2), 69.01, 68.59 (3 C, Gal^{I} C-4, Gal^{II} C-4, GalN C-4), 68.39 (1 C, Gal^{II} C-6), 67.50 (CH_2-Ar), 61.79, 61.64 (2 C, Gal^{I} C-6, GalN C-6), 52.92 (1 C, GalN C-2), 41.16 (1 C, CH_2N), 23.06 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{36}H_{53}N_2O_{27}S$ [M+H-2Na]$^-$: 977.256189; found: 977.256222.

2-Benzyloxycarbonylaminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(4-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (48) : Tetrasaccharide **42** (115 mg, 0.061 mmol) was submitted to the same procedure as described for the preparation of **44** to give disodium salt **48** (45 mg, 71%) as a white powder. R_f = 0.27 (EtOAc/MeOH/water, 4:2:1); $[\alpha]_D^{20}$ = +6.5 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 7.48-7.44 (m, 5 H, arom. H), 5.14 (s, 2 H, CH_2-Ar), 4.77-4.75 (m, 2 H, Gal^{II} H-4, GlcA H-1), 4.70 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.51 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.45 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{I} H-1), 4.18 (d, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 4.02 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$= 3.0 Hz, 1 H, Gal^{II} H-3), 3.99-3.84 (m, 3 H, GalN H-2, H-4, OCH_2), 3.82-3.67 (m, 16 H, Gal^{I} H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-5, H-6a, H-6b, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b, OCH_2), 3.62 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.47 (dd, $J_{1,2}$= 8.0 Hz, 1 H, GlcA H-2), 3.41-3.37 (m, 2 H, NCH_2), 2.07 (s, 3 H, NHC(O)CH_3); ^{13}C NMR (100 MHz, D_2O): δ = 175.60, 175.18 (2 C, GlcA C-6, C=O), 158.99 (1 C, NHC(O)O), 137.07, 129.38, 128.96, 128.32 (6 C, arom. C), 104.65 (1 C, Gal^{II} C-1), 103.79 (1 C, GlcA C-1), 103.28 (1 C, Gal^{I} C-1), 101.67 (1 C, GalN C-1), 83.00, 80.45 (2 C, Gal^{I} C-3, GlcA C-4), 77.82 (1 C, Gal^{II} C-4), 77.64 (1 C, Gal^{II} C-3), 77.22, 75.80, 75.34, 75.03, 74.36, 73.51, 71.74, 71.41, 70.48 (9 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-5, GalN C-3, C-5), 69.46 (1 C, OCH_2), 68.89 (1 C, Gal^{I} C-4), 68.39 (1 C, GalN C-4), 67.50 (CH_2-Ar), 61.59, 61.51, 61.47 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 52.91 (1 C, GalN C-2), 41.13 (1 C, CH_2N), 23.07 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{36}H_{52}N_2NaO_{27}S$ [M-Na]$^-$: 999.238133; found: 999.238162.

2-Benzyloxycarbonylaminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (49) : Pentasaccharide **25** (115 mg, 0.060 mmol) was submitted to the same procedure as described for the preparation of **44** to give disodium salt **49** (47 mg, 71%) as a white powder. R_f = 0.30 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$ = -8.5 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 7.48-7.40 (m, 5 H, arom. H), 5.13 (s, 2 H, CH_2-Ar), 4.68 (d, $J_{1,2}$= 8.0 Hz, 1 H, GlcA^{I} H-1), 4.66 (d, $J_{1,2}$ = 7.0 Hz, 1 H, Gal^{II} H-1), 4.53 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.50 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^{II} H-1), 4.42 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{I} H-1), 4.19-4.16 (m, 3 H, Gal^{I} H-4, Gal^{II} H-4, GalN H-4), 4.03 (dd, $J_{2,3}$ = 11.0 Hz, 1 H, GalN H-2), 3.96 (m, 1 H, OCH_2), 3.84-3.62 (m, 19 H, Gal^{I} H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA^{I} H-3, H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OCH_2), 3.53-3.45 (m, 3 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4), 3.38 (m, 2 H, NCH_2), 3.34 (m, 1 H, GlcA^{II} H-2), 2.05 (s, 3 H, NHC(O)CH_3); ^{13}C NMR (100 MHz, D_2O): δ = 176.45, 175.48, 175.08, 158.92 (4 C, GlcAI C-6, GlcAII C-6, C=O), 137.00, 129.31, 128.89, 128.25 (6 C, arom. C), 104.62, 104.44, 104.32 (3 C, Gal^{II} C-1, GlcA^{I} C-1, GlcA^{II} C-1), 103.19 (1 C, Gal^{I} C-1), 101.35 (1 C, GalN C-1), 83.04, 82.76, 80.80, 80.15, 76.95, 76.62, 75.82, 75.51, 75.28, 75.25, 74.22, 73.42, 73.24, 72.32, 70.58, 70.39 (16 C, Gal^{I} C-2, C-3, C-5, Gal^{II} C-2, C-3, C-5, GlcA^{I} C-2, C-3, C-4, C-5, GalN C-3, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 69.38 (1 C, OCH_2), 68.90, 68.61, 68.20 (3 C, Gal^{I} C-4, Gal^{II} C-4, GalN C-4), 67.43 (1 C, CH_2-Ar), 61.62, 61.46, 61.38 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 51.56 (1 C, GalN C-2), 41.04 (1 C, NCH_2), 23.04 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{42}H_{61}N_2O_{30}$ [M+H-2Na]$^-$: 1073.331462; found: 1073.331015.

2-Benzyloxycarbonylaminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-6-*O*-sodium sulfonato-β-D-galactopyranoside (50) : Pentasaccharide **27** (74 mg, 0.035 mmol) was submitted to the same procedure as described for the preparation of **44** to give disodium salt **50** (29 mg, 67%) as a white powder. R_f = 0.35 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$ = -9.8 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = ^{1}H NMR (400 MHz, D_2O): δ = 7.48-7.40 (m, 5 H, arom. H), 5.13 (s, 2 H, CH_2-Ar), 4.68 (d, $J_{1,2}$= 7.5 Hz, 1 H, GlcA^{I} H-1), 4.66 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.53 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.50 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.43 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{I} H-1), 4.23, 4.20 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 2 H, Gal^{I} H-4, Gal^{II} H-4), 4.18-4.16 (m, 2 H, Gal^{I} H-6a, H-6b), 4.15 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 2 H, GalN H-4), 4.01 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, GalN H-2), 3.94 (m, 1 H, OCH_2), 3.88 (m, 1 H, Gal^{I} H-5), 3.83-3.67 (m, 15 H, Gal^{I} H-2, H-3, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA^{I} H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OCH_2), 3.63 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{I} H-3), 3.50-3.45 (m, 3 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4), 3.37 (m, 2 H, NCH_2), 3.33 (dd, $J_{2,3}$ = 9.5 Hz, 1 H, GlcA^{II} H-2), 2.03 (s, 3 H, NHC(O)CH_3); ^{13}C NMR (100 MHz, D_2O): δ = 175.56, 174.57, 174.19, 158.00 (4 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 136.13, 128.39, 127.95, 127.34 (6 C, arom. C), 103.71 (1 C, GlcA^{II} C-1), 103.59 (1 C, Gal^{II} C-1), 103.42 (1 C, GlcA^{I} C-1), 102.21 (1 C, Gal^{I} C-1), 100.41 (1 C, GalN C-1), 82.14, 81.66, 79.89, 79.21 (4 C, Gal^{I} C-3, Gal^{II} C-3, GlcA^{I} C-4, GalN C-3), 76.02, 75.70, 74.90, 74.59, 74.35, 73.29, 72.51, 71.40, 69.66, 69.35 (10 C, Gal^{I} C-2, Gal^{II} C-2, C-5, GlcA^{I} C-2, C-3, C-5, GalN C-5, GlcA^{II} C-3, C-4, C-5), 72.32 (1 C, GlcA^{II} C-2), 71.96 (1 C, Gal^{I} C-5), 68.53 (1 C, OCH_2), 67.74, 67.29 (2 C, Gal^{I} C-4, Gal^{II} C-4), 67.69 (1 C, GalN C-4), 66.74 (1 C, Gal^{I} C-6), 66.50 (1 C, CH_2-Ar), 60.70, 60.50 (2 C, Gal^{II} C-6, GalN

C-6), 50.67 (1 C, GalN C-2), 40.15 (1 C, N*C*H$_2$), 22.12 (1 C, NHC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{42}H_{61}N_2O_{33}S$ [M+2H-3Na]$^-$: 1153.288277; found: 1153.288424.

2-Benzyloxycarbonylaminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-4-*O*-sodium sulfonato-β-D-galactopyranoside (51) : Pentasaccharide **31** (140 mg, 0.065 mmol) was submitted to the same procedure as described for the preparation of **44** to give trisodium salt **51** (50 mg, 63%) as a white powder. *R*f = 0.35 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$ = -8.3 (*c* = 1 in water); ^{1}H NMR (400 MHz, D$_2$O): δ = ^{1}H NMR (400 MHz, D$_2$O): δ = 7.48-7.40 (m, 5 H, arom. H), 5.14 (s, 2 H, C*H*$_2$-Ar), 4.86 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 4.70 (d, $J_{1,2}$= 7.5 Hz, 1 H, Gal^{II} H-1), 4.68 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^I H-1), 4.53 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.50 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.46 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^I H-1), 4.18, 4.14 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 2 H, Gal^{II} H-4, GalN H-4), 4.05-3.99 (m, 2 H, Gal^I H-3, GalN H-2), 3.95 (m, 1 H, OC*H*$_2$), 3.84-3.68 (m, 17 H, Gal^I H-2, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA^I H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OC*H*$_2$), 3.65 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^I H-3), 3.51-3.45 (m, 3 H, GlcA^I H-2, GlcA^{II} H-3, H-4), 3.39 (m, 2 H, NC*H*$_2$), 3.33 (dd, $J_{2,3}$ = 9.5 Hz, 1 H, GlcA^{II} H-2), 2.05 (s, 3 H, NHC(O)C*H*$_3$); ^{13}C NMR (100 MHz, D$_2$O): δ = 176.48, 175.60, 175.11, 159.03 (4 C, GlcA^I C-6, GlcA^{II} C-6, C=O), 137.14, 129.43, 129.06, 129.01, 128.33 (6 C, arom. C), 104.75, 104.56 (3 C, Gal^{II} C-1, GlcA^I C-1, GlcA^{II} C-1), 103.38 (1 C, Gal^I C-1), 101.47 (1 C, GalN C-1), 83.15, 80.93, 80.29 (3 C, Gal^{II} C-3, GlcA^I C-4, GalN C-3), 79.09 (1 C, Gal^I C-3), 78.04 (1 C, Gal^I C-4), 77.02, 76.72, 75.93, 75.62, 75.52, 75.11, 74.31, 73.52, 73.35, 72.42 (12 C, Gal^I C-2, C-5, Gal^{II} C-2, C-5, GlcA^I C-2, C-3, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 66.68 (1 C, O*C*H$_2$), 69.08, 68.32 (2 C, Gal^{II} C-4, GalN C-4), 67.55 (1 C, *C*H$_2$-Ar), 61.72, 61.68, 61.54 (3 C, Gal^I C-6, Gal^{II} C-6, GalN C-6), 51.67 (1 C, GalN C-2), 41.11 (1 C, N*C*H$_2$), 23.04 (1 C, NHC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{42}H_{63}N_2O_{33}S$ [M+4H-3Na]$^+$: 1155.302830; found: 1155.302200.

2-Benzyloxycarbonylaminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(6-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (52) : Pentasaccharide **39** (58 mg, 0.027 mmol) was submitted to the same procedure as described for the preparation of **44** to give trisodium salt **52** (23 mg, 68%) as a white powder. R_f = 0.35 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$ = -6.8 (*c* = 1 in water); ^{1}H NMR (400 MHz, D$_2$O): δ = 7.48 (m, 5 H, arom. H), 5.16 (s, 2 H, C*H*$_2$-Ar), 4.72 (d, $J_{1,2}$= 8.0 Hz, 1 H, GlcA^I H-1), 4.68, 4.44 (2 d, $J_{1,2}$ = 8.0 Hz, 2 H, Gal^I H-1, Gal^{II} H-1), 4.55 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.52 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.28 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 4.22, 4.20 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 2 H, Gal^I H-4, Gal^{II} H-4), 4.04 (dd, $J_{2,3}$ = 9.0 Hz, 1 H, GalN H-2), 3.97-3.95 (m, 2 H, Gal^{II} H-5, OC*H*$_2$), 3.87-3.62 (m, 16 H, Gal^I H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, GlcA^I H-3, H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OC*H*$_2$), 3.52-3.48 (m, 3 H, GlcA^I H-2, GlcA^{II} H-3, H-4), 3.40 (m, 2 H, NC*H*$_2$), 3.35 (dd, $J_{2,3}$ = 9.5 Hz, 1 H, GlcA^{II} H-2), 2.06 (s, 3 H, NHC(O)C*H*$_3$); ^{13}C NMR (100 MHz, D$_2$O): δ = 176.60, 175.63, 175.22, 159.07 (4 C, GlcA^I C-6, GlcA^{II} C-6, C=O), 137.04, 129.45, 129.05, 128.41 (6 C, arom. C), 104.77 (1 C, GlcA^{II} C-1), 104.51, 104.42, 103.31 (3 C, Gal^I C-1, Gal^{II} C-1, GlcA^I C-1), 101.47 (1 C, GalN C-1), 83.18, 82.99, 80.99, 80.26 (4 C, Gal^I C-3, Gal^{II} C-3, GlcA^I C-4, GalN C-3), 77.05, 76.76, 75.95, 75.64, 75.62, 74.34, 73.57, 73.38, 73.15, 72.45, 70.57, 70.35, 69.47, 68.66, 68.50, 67.57 (16 C, Gal^I C-2, C-4, C-5, Gal^{II} C-2, C-4, C-5, GlcA^I C-2, C-3, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 66.68 (1 C, O*C*H$_2$), 69.08, 68.32 (2 C, Gal^{II} C-2, C-3, C-4, C-5, GalN C-4, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 69.68 (1 C, Gal^{II} C-6), 68.34 (1 C, *C*H$_2$-Ar), 61.86, 61.74 (2 C, Gal^I C-6, GalN C-6), 51.68 (1 C, GalN C-2), 41.22 (1 C, N*C*H$_2$), 23.17 (1 C, NHC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{42}H_{61}N_2O_{33}S$ [M+2H-3Na]$^-$: 1153.288277; found: 1153.289834.

2-Benzyloxycarbonylaminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(4-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (53) : Pentasaccharide **43** (82 mg, 0.038 mmol) was submitted to the same procedure as described for the preparation of **44** to give trisodium salt **53** (26 mg, 57%) as a white powder. R_f = 0.35 (EtOAc/MeOH/water, 4:2:1); $[\alpha]_D^{20}$ = -11.2 (*c* = 1 in water); ^{1}H NMR (400 MHz, D$_2$O): δ = 7.48 (m, 5 H, arom. H), 5.16 (s, 2 H, C*H*$_2$-Ar), 4.79 (d, $J_{1,2}$= 8.0 Hz, 1 H, GlcA^I H-1), 4.76 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 4.71 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.56 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.52 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.44 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^I H-1), 4.21, 4.20 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 2 H, Gal^I H-4, GalN H-4), 4.07-4.02 (m, 2 H, Gal^{II} H-3, GalN H-2), 3.97 (m, 1 H, OC*H*$_2$), 3.87-3.64 (m, 18 H, Gal^I H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA^I H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OC*H*$_2$), 3.64 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^I H-3), 3.52-3.46 (m, 3 H, GlcA^I H-2, GlcA^{II} H-3, H-4), 3.40 (m, 2 H, NC*H*$_2$), 3.35 (dd, $J_{2,3}$ = 9.5 Hz, 1 H, GlcA^{II} H-2), 2.06 (s, 3 H, NHC(O)C*H*$_3$); ^{13}C NMR (100 MHz, D$_2$O): δ = 175.94, 174.96, 174.50, 158.42 (4 C, GlcA^I C-6, GlcA^{II} C-6, C=O), 137.04, 128.79, 128.67, 128.38, 127.73 (6 C, arom. C), 104.12 (1 C, GlcA^{II} C-1), 104.05 (1 C, Gal^{II} C-1), 103.21 (1 C, GlcA^I C-1), 102.70 (1 C, Gal^I C-1), 100.92 (1 C, GalN C-1), 82.40, 80.39, 79.98 (3 C, Gal^I C-3, GlcA^I C-4, GalN C-3), 77.23 (1 C, Gal^{II} C-4), 77.08 (1 C, Gal^{II} C-3), 76.66, 76.10, 75.31, 74.96, 74.75, 74.45, 73.80, 72.89, 72.74, 71.81, 70.82, 69.89 (12 C, Gal^I C-2, C-5, Gal^{II} C-2, C-5, GlcA^I C-2, C-3, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 68.87 (1 C, O*C*H$_2$), 68.31, 67.68 (2 C, Gal^I C-4, GalN C-4), 66.92 (1 C, *C*H$_2$-Ar), 61.05, 60.91, 60.88 (3 C, Gal^I C-6, Gal^{II} C-6, GalN C-6), 51.02 (1 C, GalN C-2), 40.54 (1 C, N*C*H$_2$), 22.53 (1 C, NHC(O)*C*H$_3$); HRMS: *m/z*: calcd for $C_{42}H_{60}N_2NaO_{33}S$ [M+H-2Na]$^-$: 1175.270221; found: 1175.270850.

2-(6-Biotinylamidohexanoyl)aminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-6-*O*-sodium sulfonato-β-D-galactopyranoside (2) : Tetrasaccharide **45** (21 mg, 20 μmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **1**. Lyophilization afforded the sodium salt **2** (16 mg, 64%) as a white powder. R_f = 0.42 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$

= +16 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.69 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA H-1), 4.67, 4.49 (2 d, $J_{1,2}$ = 7.5 Hz, Gal^I H-1, Gal^{II} H-1), 4.63 (ddd, $J_{c,d}$ <1.0, $J_{c,d'}$ = 4.5, $J_{b,c}$ = 8.0 Hz, 1 H, H-c), 4.50 (d, $J_{1,2}$ = 8.5 Hz; 1 H, GalN H-1), 4.45 (dd, $J_{b,e}$ = 4.5 Hz, 1 H, H-b), 4.27 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1.0 Hz, 1 H, Gal^I H-4), 4.23-4.21 (m, 2 H, Gal^I H-6a, H-6b), 4.17 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1.0 Hz, Gal^{II} H-4), 4.00-3.87 (m, 4 H, Gal^I H-3, GalN H-2, H-4, OCH_2), 3.86-3.69 (m, 14 H, Gal^I H-2, H-5, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b, OCH_2), 3.64 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.49-3.44 (m, 3 H, GlcA H-2, NCH_2), 3.39-3.30 (m, 1 H, H-e), 3.22-3.18 (m, 2 H, CH_2-k), 3.02 (dd, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.80 (dd, 1 H, H-d), 2.36-2.25 (m, 4 H, CH_2-i, CH_2-o), 2.07 (s, 3 H, NHC(O)CH_3), 1.79-1.30 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m and CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.68, 177.20, 175.63, 175.21 (4 C, GlcA C-6, C=O), 165.90 (1 C, C-a), 104.57, 104.41, 103.14, 101.57 (4 C, Gal^I C-1, Gal^{II} C-1, GlcA C-1, GalN C-1), 83.15, 82.71 (2 C, Gal^I C-3, Gal^{II} C-3), 80.09, 77.01, 75.83, 75.35, 74.27, 73.53, 73.05, 71.70, 70.67, 70.35 (10 C, Gal^I C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 69.27 (1 , OCH_2), 68.79, 68.67, 68.39 (3 C, Gal^I C-4, Gal^{II} C-4, GalN C-4), 67.91 (1 C, Gal^I C-6), 62.67 (1 C, C-b), 61.65, 61.49 (2 C, Gal^{II} C-6, GalN C-6), 60.84 (1 C, C-c), 55.97 (1 C, C-e), 52.93 (1 C, GalN C-2), 40.30 (1 C, C-d), 39.95, 39.69 (2 C, C-k, NCH_2), 36.21, 36.13 (2 C, C-i, C-o), 28.59, 28.44, 28.27, 26.13, 25.82, 25.55 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.06 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{44}H_{71}N_5NaO_{28}S_2$ [M-Na]$^-$ 1204.363017; found: 1204.362693.

2-(6-Biotinylamidohexanoyl)aminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-4-*O*-sodium sulfonato-β-D-galactopyranoside (3) : Tetrasaccharide **46** (19 mg, 19 μmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **1**. Lyophilization afforded the sodium salt **3** (17 mg, 74%) as a white powder. R_f = 0.33 (EtOAc/MeOH/water, 2:1:1); $[\alpha]_D^{20}$ = +20 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.87 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 4.71 (d, $J_{1,2}$ = 7.5 Hz, 1 H, Gal^{II} H-1), 4.68 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA H-1), 4.63 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = $J_{b,c}$ = 5.0 Hz, 1H, H-c), 4.50 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^I H-1), 4.49 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.44 (dd, $J_{b,e}$ = 4.5 Hz, 1 H, H-b), 4.14 (dd, $J_{3,4}$ = 2.5, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 4.04 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, Gal^I H-3), 3.99 (m, 1 H, OCH_2), 3.94 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 3.89 (m, 1 H, GalN H-2), 3.80-3.70 (m, 17 H, Gal^I H-2, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b, OCH_2), 3.63 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.49-3.43 (m, 3 H, GlcA H-2, NCH_2), 3.35 (m, 1 H, H-e), 3.22-3.16 (m, 2 H, CH_2-k), 3.02 (dd, $J_{d',c}$ = 5.0, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.81 (dd, 1 H, H-d), 2.31-2.25 (m, 4 H, CH_2-i, CH_2-o), 2.06 (s, 3 H, NHC(O)CH_3), 1.79-1.25 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m and CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.69, 177.18, 175.61, 175.20 (4 C, GlcA C-6, C=O), 165.90 (1 C, C-a), 104.54 (2 C, Gal^{II} C-1, GlcA C-1), 103.21 (1 C, Gal^I C-1), 101.58 (1 C, GalN C-1), 83.12 (1 C, Gal^{II} C-3), 79.13 (1 C, Gal^I C-3), 78.01 (1 C, Gal^I C-4), 80.13, 77.03, 75.83, 75.51, 75.12, 74.26, 73.52, 71.72, 70.97, 70.65 (10 C, Gal^I C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 69.11 (1 C, OCH_2), 69.04 (1 C, Gal^{II} C-4), 68.40 (1 C, GalN C-4), 62.68 (1 C, C-b), 61.64, 61.59 (3 C, Gal^I C-6, Gal^{II} C-6, GalN C-6), 60.84 (1 C, C-c), 55.99 (1 C, C-e), 52.93 (1 C, GalN C-2), 40.30 (1 C, C-d), 39.87, 39.68 (2 C, C-k, NCH_2), 36.21, 36.12 (2 C, C-i, C-o), 28.61, 28.44, 28.27, 26.13, 25.81, 25.55 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.06 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{44}H_{71}N_5NaO_{28}S_2$ [M-Na]$^-$ 1204.363017; found: 1204.363307.

2-(6-Biotinylamidohexanoyl)aminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(6-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (4) : Tetrasaccharide **47** (25.5 mg, 25 μmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **1**. Lyophilization afforded the sodium salt **4** (21 mg, 69%) as a white powder; *R*f = 0.20 (EtOAc/MeOH/water, 2:1:1); $[\alpha]_D^{20}$ = +17.5 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.69 (d, $J_{1,2}$= 8.0 Hz, 1 H, GlcA H-1), 4.67, 4.48 (2 d, $J_{1,2}$ = 7.5 Hz, 2 H, Gal^I H-1, Gal^{II} H-1), 4.63 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = 4.5, $J_{b,c}$ = 8.0, H-c), 4.49 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.44 (dd, $J_{b,e}$ = 4.5 Hz, 1 H, H-b), 4.29 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 4.22-4.19 (m, 3 H, Gal^I H-4, Gal^{II} H-6a, H-6b), 4.03-3.97 (m, 1 H, OCH_2), 3.94-3.86 (m, 3 H, Gal^I H-3, GalN H-2, H-4), 3.84-3.68 (m, 14 H, Gal^I H-2, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b, OCH_2), 3.64 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.49-3.44 (m, 3 H, GlcA H-2, NCH_2), 3.39-3.27 (m, 1 H, H-e), 3.22-3.18 (m, 2 H, CH_2-k), 3.02 (dd, $J_{d',c}$ = 5.0, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.81 (dd, 1 H, H-d), 2.31-2.25 (m, 4 H, CH_2-i, CH_2-o), 2.07 (s, 3 H, NHC(O)CH_3), 1.93-1.30 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m et CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.68, 177.18, 175.63, 175.21 (4 C, GlcA C-6, C=O), 165.89 (1 C, C-a), 104.45, 107.34, 103.15 (3 C, Gal^I C-1, Gal^{II} C-1, GlcA C-1), 101.54 (1 C, GalN C-1), 83.37, 82.96 (2 C, Gal^I C-3, Gal^{II} C-3), 80.05, 77.01, 75.83, 75.61, 74.26, 73.54, 73.08, 71.71, 70.52, 70.32 (10 C, Gal^I C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 69.03, 68.99 (2 C, Gal^{II} C-6, OCH_2), 68.58, 68.39 (3 C, Gal^I C-4, Gal^{II} C-4, GalN C-4), 62.68 (1 C, C-b), 61.87, 61.64 (2 C, Gal^I C-6, GalN C-6), 60.84 (1 C, C-c), 55.98 (1 C, C-e), 52.92 (1 C, GalN C-2), 40.29 (1 C, C-d), 39.90, 39.68 (2 C, C-k, NCH_2), 36.20, 36.12 (2 C, C-i, C-o), 28.61, 28.45, 28.27, 26.14, 25.81, 25.55 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.06 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{44}H_{75}N_5O_{28}S_2$ $[M+4H-2Na]^{2+}$: 592.701451; found: 592.701469.

2-(6-Biotinylamidohexanoyl)aminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(4-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (5) : Tetrasaccharide **48** (24 mg, 23 μmol) was submitted to the same procedure as described for the preparation of tetrasaccharide **1**. Lyophilization afforded the sodium salt **5** (25 mg, 86%) as a white powder. R_f = 0.37 (EtOAc/MeOH/water, 2:1:1); $[\alpha]_D^{20}$ = +19.5 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.77 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 4.76 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA H-1), 4.71 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.63 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = 5.0, $J_{b,c}$ = 8.0 Hz, 1 H, H-c), 4.51 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.48 (d, $J_{1,2}$= 8.0 Hz, 1 H, Gal^I H-1), 4.44 (dd, $J_{b,e}$ = 4.5 Hz, 1 H, H-b), 4.20 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^I H-4), 4.02 (dd, $J_{2,3}$ = 10.5 Hz, 1 H, Gal^{II} H-3), 4.00-3.97 (m, 2 H, OCH_2), 3.94 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H,

GalN H-4), 3.91-3.86 (m, 1 H, GalN H-2), 3.85-3.60 (m, 15 H, Gal^{I} H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-5, H-6a, H-6b, GlcA H-4, H-5, GalN H-3, H-5, H-6a, H-6b), 3.62 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz, 1 H, GlcA H-3), 3.48-3.44 (m, 3 H, GlcA H-2, NCH_2), 3.38-3.33 (m, 1 H, H-e), 3.22-3.18 (m, 2 H, CH_2-k), 3.02 (dd, $J_{d',c}$ = 5.0, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.80 (dd, 1 H, H-d), 2.31-2.25 (m, 4 H, CH_2-i, CH_2-o), 2.07 (s, 3 H, NHC(O)CH_3), 1.83-1.30 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m et CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.68, 177.17, 175.60, 175.17 (4 C, GlcA C-6, C=O), 165.89 (1 C, C-a), 104.64 (1 C, Gal^{II} C-1), 103.79 (1 C, GlcA C-1), 103.18 (1 C, Gal^{I} C-1), 101.67 (1 C, GalN C-1), 83.06 (1 C, Gal^{II} C-3), 80.45 (1 C, Gal^{I} C-3), 77.81 (1 C, Gal^{II} C-4), 77.64, 77.22, 75.79, 75.38, 75.03, 74.36, 73.50, 71.73, 71.41, 70.48 (10 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA C-2, C-3, C-4, C-5, GalN C-3, C-5), 68.99 (1 C, OCH_2), 68.90, 68.38 (2 C, Gal^{I} C-4, GalN C-4), 62.67 (1 C, C-b), 61.58, 61.53, 61.50 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 60.83 (1 C, C-c), 55.98 (1 C, C-e), 52.89 (1 C, GalN C-2), 40.29 (1 C, C-d), 39.88, 39.67 (2 C, C-k, NCH_2), 36.20, 36.11 (2 C, C-i, C-o), 28.61, 28.44, 28.27, 26.14, 25.81, 25.55 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.07 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{44}H_{71}NaN_5O_{28}S_2$ [M-Na]$^-$: 1204.363017; found: 1204.363307.

2-(6-Biotinylamidohexanoyl)aminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (6) : Pentasaccharide **49** (25 mg, 0.022 mmol) was submitted to the same procedure as described for the preparation of **1**. Lyophilization afforded disodium salt **6** (14 mg, 48%) as a white powder. R_f = 0.30 (EtOAc/MeOH/water, 3:2:2); $[\alpha]_D^{20}$ = +6.6 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.68 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{I} H-1), 4.68 (d, $J_{1,2}$ = 7.5 Hz, 1 H, Gal^{II} H-1), 4.63 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = 5.0, $J_{b,c}$ = 8.0 Hz, 1 H, H-c), 4.53 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.50 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.47 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{I} H-1), 4.44 (dd, $J_{b,e}$ = 5.0 Hz, 1 H, H-b), 4.19-4.16 (m, 3 H, Gal^{I} H-4, Gal^{II} H-4, GalN H-4), 4.05-3.96 (m, 2 H, GalN H-2, OCH_2), 3.86-3.62 (m, 19 H, Gal^{I} H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA^{I} H-3, H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OCH_2), 3.52-3.42 (m, 5 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4, NCH_2), 3.38-3.31 (m, 2 H, GlcA^{II} H-2, H-e), 3.21-3.17 (m, 2 H, CH_2-k), 3.01 (dd, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.80 (dd, 1 H, H-d), 2.30-2.24 (m, 4 H, CH_2-i, CH_2-o), 2.04 (s, 3 H, NHC(O)CH_3), 1.79-1.30 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m, CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 178.08, 177.56, 177.06 (5 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 166.02 (1 C, C-a), 104.58, 104.39, 104.27 (3 C, Gal^{II} C-1, GlcA^{I} C-1, GlcA^{II} C-1), 103.06 (1 C, Gal^{I} C-1), 101.30 (1 C, GalN C-1), 82.99, 82.76, 80.75, 80.11, 76.91, 76.55, 75.77, 75.46, 75.25, 74.18, 73.37, 73.19, 72.26, 70.53, 70.34 (16 C, Gal^{I} C-2, C-3, C-5, Gal^{II} C-2, C-3, C-5, GlcA^{I} C-2, C-3, C-4, C-5, GalN C-3, C-5, GlcA^{II} C-2, C-3, C-4, C-5), 68.87 (1 C, OCH_2), 68.85, 68.55, 68.16 (3 C, Gal^{I} C-4, Gal^{II} C-4, GalN C-4), 62.55 (1 C, C-b), 61.55, 61.41 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 60.71 (1 C, C-c), 55.85 (1 C, C-e), 51.50 (1 C, GalN C-2), 40.16 (1 C, C-d), 39.75 (1C, NCH_2), 39.55 (1C, C-k), 36.08, 35.99 (2 C, C-i, C-o), 28.48, 28.30, 28.13, 26.01, 25.67, 25.41 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 22.98 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{50}H_{80}N_5O_{31}S$ [M+H-2Na]$^-$: 1278.456345; found: 1278.456253.

2-(6-Biotinylamidohexanoyl)aminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-6-*O*-sodium sulfonato β-D-galactopyranoside (7) : Pentasaccharide **50** (29 mg, 0.024 mmol) was submitted to the same procedure as described for the preparation of **1**. Lyophilization afforded trisodium salt **7** (21 mg, 62%) as a white powder. *R*f = 0.40 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$ = +8.0 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.74 (d, $J_{1,2}$ = 7.5 Hz, 1 H, GlcA^{I} H-1), 4.73, 4.52 (2 d, $J_{1,2}$ = 8.0 Hz, 2 H, Gal^{I} H-1, Gal^{II} H-1), 4.68 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = 5.0, $J_{b,c}$ = 8.0 Hz, 1 H, H-c), 4.59 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.55 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.48 (dd, $J_{b,e}$ = 5.0 Hz, 1 H, H-b), 4.30, 4.23 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4, Gal^{II} H-4), 4.28-4.26 (m, 2 H, Gal^{I} H-6a, H-6b), 4.21 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 4.07 (dd, $J_{2,3}$ = 9.0 Hz, 1 H, GalN H-2), 4.03-3.99 (m, 2 H, Gal^{I} H-5, OCH_2), 3.92-3.73 (m, 14 H, Gal^{I} H-2, H-3, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA^{I} H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OCH_2), 3.69 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{I} H-3), 3.56-3.48 (m, 5 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4, NCH_2), 3.42-3.37 (m, 2 H, GlcA^{II} H-2, H-e), 3.27-3.22 (m, 2 H, CH_2-k), 3.05 (dd, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.83 (dd, 1 H, H-d), 2.32-2.25 (m, 4 H, CH_2-i, CH_2-o), 2.09 (s, 3 H, NHC(O)CH_3), 1.80-1.32 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m, CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.72, 177.23, 176.20, 175.6, 175.00 (5 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 165.95 (1 C, C-a), 104.76, 104.62, 104.46, 103.21 (4 C, Gal^{I} C-1, Gal^{II} C-1, GlcA^{I} C-1, GlcA^{II} C-1), 101.50 (1 C, GalN C-1), 83.18, 82.75, 80.95, 80.32 (4 C, Gal^{I} C-3, Gal^{II} C-3, GlcA^{I} C-4, GalN C-3), 77.01, 76.67, 75.95, 75.64, 75.41, 74.37, 73.56, 73.38, 73.11, 72.43, 70.74 (11 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA^{I} C-2, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 70.41 (1 C, GlcA^{I} C-3), 69.32 (1 C, OCH_2), 68.85, 68.74, 68.34 (3 C, Gal^{I} C-4, Gal^{II} C-4, GalN C-4), 67.97 (1 C, Gal^{I} C-6), 62.73 (1 C, C-b), 61.74, 61.56 (2 C, Gal^{II} C-6, GalN C-6), 60.90 (1 C, C-c), 56.01 (1 C, C-e), 51.69 (1 C, GalN C-2), 40.34 (1 C, C-d), 40.00 (1C, NCH_2), 39.74 (1C, C-k), 36.27, 36.19 (2 C, C-i, C-o), 28.64, 28.49, 28.32, 26.19, 25.86, 25.59 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.16 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{50}H_{83}N_5O_{34}S_2$ [M+5H-3Na]$^{2+}$: 680.717495; found: 680.718187.

2-(6-Biotinylamidohexanoyl)aminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(β-D-galactopyranosyl)-(1→3)-4-*O*-sodium sulfonato β-D-galactopyranoside (8) : Pentasaccharide **51** (30 mg, 0.024 mmol) was submitted to the same procedure as described for the preparation of **1**. Lyophilization gave trisodium salt **8** (14 mg, 57%) as a white powder. R_f = 0.40 (EtOAc/MeOH/water, 2:1:1); $[\alpha]_D^{20}$ = +5.8 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.89 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4), 4.72 (d, $J_{1,2}$ = 7.5 Hz, 1 H, Gal^{II} H-1), 4.69 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{I} H-1), 4.64 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = 5.0, $J_{b,c}$ = 8.0 Hz, 1 H, H-c), 4.55 (d, $J_{1,2}$ = 8.5 Hz, 1 H, GalN H-1), 4.52 (2 d, $J_{1,2}$ = 8.0 Hz, 2 H, Gal^{I} H-1, GlcA^{II} H-1), 4.45 (dd, $J_{b,e}$ = 5.0 Hz, 1 H, H-b), 4.20, 4.15 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4, GalN H-4), 4.06-3.98 (m, 3 H, Gal^{I} H-3, GalN H-2, OCH_2), 3.88-3.67 (m, 17 H, Gal^{I} H-2, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, H-5, H-6a, H-6b, GlcA^{I} H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OCH_2), 3.64 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{I} H-3), 3.52-3.42 (m, 5 H, GlcA^{I} H-2, GlcA^{II} H-3,

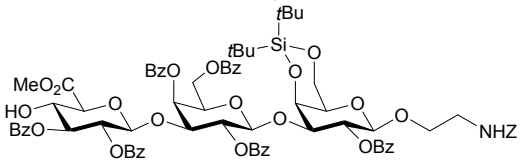
H-4, NCH_2), 3.39-3.31 (m, 2 H, GlcA^{II} H-2, H-e), 3.23-3.17 (m, 2 H, CH_2-k), 3.03 (dd, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.82 (dd, 1 H, H-d), 2.32-2.25 (m, 4 H, CH_2-i, CH_2-o), 2.06 (s, 3 H, NHC(O)CH_3), 1.79-1.30 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m, CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.78, 177.27, 176.59, 175.61, 175.21 (5 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 165.98 (1 C, C-a), 104.79, 104.61, 103.28 (4 C, Gal^{I} C-1, Gal^{II} C-1, GlcA^{I} C-1, GlcA^{II} C-1), 101.50 (1 C, GalN C-1), 83.18, 80.99, 80.34 (3 C, Gal^{II} C-3, GlcA^{I} C-4, GalN C-3), 79.20 (1 C, Gal^{I} C-3), 78.08 (1 C, Gal^{I} C-4), 77.12, 76.76, 75.96, 75.65, 75.59, 75.19, 73.56, 73.39, 72.46, 71.04, 70.71 (11 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA^{I} C-2, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 74.36 (1 C, GlcA^{I} C-3), 69.18 (1 C, OCH_2), 69.11, 68.35 (2 C, Gal^{II} C-4, GalN C-4), 62.74 (1 C, C-b), 61.74, 61.66 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 60.91 (1 C, C-c), 56.04 (1 C, C-e), 51.69 (1 C, GalN C-2), 40.36 (1 C, C-d), 39.93 (1C, NCH_2), 39.74 (1C, C-k), 36.27, 36.18 (2 C, C-i, C-o), 28.66, 28.49, 28.32, 26.18, 25.86, 25.61 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.17 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{50}H_{83}N_5O_{34}S_2$ $[M+5H-3Na]^{2+}$: 680.717495; found: 680.717529.

2-(6-Biotinylamidohexanoyl)aminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(6-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (9) : Pentasaccharide **52** (23 mg, 0.019 mmol) was submitted to the same procedure as described for the preparation of **1**. Lyophilization afforded trisodium salt **9** (15 mg, 58%) as a white powder. R_f = 0.35 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$ = +6.7 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.70 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{I} H-1), 4.68, 4.49 (2 d, $J_{1,2}$ = 8.0 Hz, 2 H, Gal^{I} H-1, Gal^{II} H-1), 4.66 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = 5.0, $J_{b,c}$ = 8.0 Hz, 1 H, H-c), 4.54 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.51 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.45 (dd, $J_{b,e}$ = 5.0 Hz, 1 H, H-b), 4.30 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, GalN H-4), 4.22, 4.20 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4, Gal^{II} H-4), 4.22-4.20 (m, 2 H, Gal^{II} H-6a, H-6b), 4.04 (dd, $J_{2,3}$ = 9.5 Hz, 1 H, GalN H-2), 4.02 (m, 1 H, OCH_2), 3.9 (m, 1 H, Gal^{II} H-5), 3.86-3.69 (m, 15 H, Gal^{I} H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-3, GlcA^{I} H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OCH_2), 3.66 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{I} H-3), 3.54-3.44 (m, 5 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4, NCH_2), 3.39-3.32 (m, 2 H, GlcA^{II} H-2, H-e), 3.23-3.18 (m, 2 H, CH_2-k), 3.03 (dd, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.82 (dd, 1 H, H-d), 2.32-2.25 (m, 4 H, CH_2-i, CH_2-o), 2.06 (s, 3 H, NHC(O)CH_3), 1.77-1.33 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m, CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.72, 177.23, 176.20, 175.6, 175.00 (5 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 165.95 (1 C, C-a), 104.78 (1 C, GlcA^{II} C-1), 104.51, 104.39, 103.22 (3 C, Gal^{I} C-1, Gal^{II} C-1, GlcA^{I} C-1), 101.47 (1 C, GalN C-1), 83.45, 83.01, 81.00, 80.27 (4 C, Gal^{I} C-3, Gal^{II} C-3, GlcA^{I} C-4, GalN C-3), 77.01, 76.76, 75.96, 75.66, 75.65, 74.36, 73.58, 73.39, 73.16, 72.45, 70.59 (11 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA^{I} C-2, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 70.38 (1 C, GlcA^{I} C-3), 69.08 (1 C, OCH_2), 69.07 (1 C, Gal^{II} C-4), 68.65, 68.34 (2 C, Gal^{I} C-4, GalN C-4), 68.50 (1 C, Gal^{II} C-6), 62.74 (1 C, C-b), 61.94, 61.76 (2 C, Gal^{I} C-6, GalN C-6), 60.91 (1 C, C-c), 56.03 (1 C, C-e), 51.69 (1 C, GalN C-2), 40.35 (1 C, C-d), 39.97 (1C, NCH_2), 39.74 (1C, C-k), 36.26, 36.18 (2 C, C-i, C-o), 28.67, 28.50, 28.33, 26.20, 25.87, 25.61 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.17 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{50}H_{78}N_5O_{34}S_2$ $[M-3Na]^{3-}$: 452.132869; found: 452.132593.

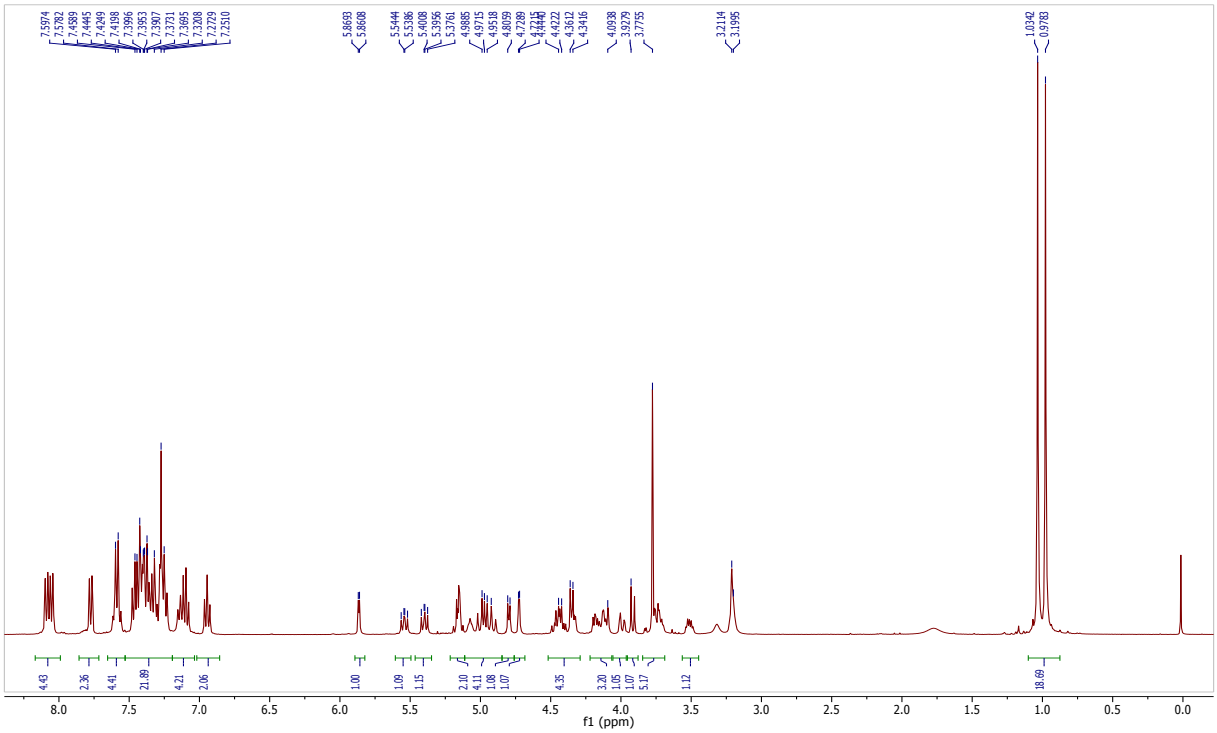
2-(6-Biotinylamidohexanoyl)aminoethyl-*O*-(sodium-β-D-glucopyranosyluronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(sodium-β-D-glucopyranosyluronate)-(1→3)-(4-*O*-sodium sulfonato-β-D-galactopyranosyl)-(1→3)-β-D-galactopyranoside (10) : Pentasaccharide **53** (25 mg, 0.020 mmol) was submitted to the same procedure as described for the preparation of **1**. Lyophilization afforded trisodium salt **10** (15 mg, 51%) as a white powder. R_f = 0.35 (EtOAc/MeOH/water, 3:2:1); $[\alpha]_D^{20}$ = -1.5 (*c* = 1 in water); ^{1}H NMR (400 MHz, D_2O): δ = 4.73 (dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{II} H-4), 4.72 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{I} H-1), 4.66 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{II} H-1), 4.58 (ddd, $J_{c,d}$ < 1.0, $J_{c,d'}$ = 5.0, $J_{b,c}$ = 8.0 Hz, 1 H, H-c), 4.49 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GalN H-1), 4.46 (d, $J_{1,2}$ = 8.0 Hz, 1 H, GlcA^{II} H-1), 4.41 (d, $J_{1,2}$ = 8.0 Hz, 1 H, Gal^{I} H-1), 4.38 (dd, $J_{b,e}$ = 5.0 Hz, 1 H, H-b), 4.15, 4.13 (2 dd, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, Gal^{I} H-4, GalN H-4), 4.00-3.95 (m, 2 H, Gal^{II} H-3, GalN H-2), 3.92 (m, 1 H, OCH_2), 3.80-3.64 (m, 17 H, Gal^{I} H-2, H-3, H-5, H-6a, H-6b, Gal^{II} H-2, H-5, H-6a, H-6b, GlcA^{I} H-4, H-5, GalN H-3, H-5, H-6a, H-6b, GlcA^{II} H-5, OCH_2), 3.57 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, GlcA^{I} H-3), 3.47-3.37 (m, 5 H, GlcA^{I} H-2, GlcA^{II} H-3, H-4, NCH_2), 3.32-3.26 (m, 2 H, GlcA^{II} H-2, H-e), 3.16-3.13 (m, 2 H, CH_2-k), 2.97 (dd, $J_{d,d'}$ = 13.0 Hz, 1 H, H-d'), 2.75 (dd, 1 H, H-d), 2.23-2.18 (m, 4 H, CH_2-i, CH_2-o), 1.99 (s, 3 H, NHC(O)CH_3), 1.70-1.27 (m, 12 H, CH_2-f, CH_2-g, CH_2-h, CH_2-l, CH_2-m, CH_2-n); ^{13}C NMR (100 MHz, D_2O): δ = 177.74, 177.25, 176.57, 175.59, 174.80 (5 C, GlcA^{I} C-6, GlcA^{II} C-6, C=O), 165.97 (1 C, C-a), 104.77 (1 C, GlcA^{II} C-1), 104.69 (1 C, Gal^{II} C-1), 103.83 (1 C, GlcA^{I} C-1), 103.26 (1 C, Gal^{I} C-1), 101.58 (1 C, GalN C-1), 83.11, 81.05, 80.67 (3 C, Gal^{I} C-3, GlcA^{I} C-4, GalN C-3), 77.88 (1 C, Gal^{II} C-4), 77.69 (1 C, Gal^{II} C-3), 77.32, 76.73, 75.97, 75.61, 75.45, 75.11, 73.54, 73.40, 72.46, 71.50, 70.55 (11 C, Gal^{I} C-2, C-5, Gal^{II} C-2, C-5, GlcA^{I} C-2, C-5, GalN C-5, GlcA^{II} C-2, C-3, C-4, C-5), 74.47 (1 C, GlcA^{I} C-3), 69.06 (1 C, OCH_2), 68.96, 68.33 (2 C, Gal^{I} C-4, GalN C-4), 62.74 (1 C, C-b), 61.70, 61.61 (3 C, Gal^{I} C-6, Gal^{II} C-6, GalN C-6), 60.90 (1 C, C-c), 56.03 (1 C, C-e), 51.68 (1 C, GalN C-2), 40.35 (1 C, C-d), 39.95 (1C, NCH_2), 39.74 (1C, C-k), 36.27, 36.18 (2 C, C-i, C-o), 28.67, 28.49, 28.32, 26.20, 25.86, 25.60 (6 C, C-f, C-g, C-h, C-l, C-m, C-n), 23.18 (1 C, NHC(O)CH_3); HRMS: *m/z*: calcd for $C_{50}H_{79}N_5O_{34}S_2$ $[M+H-3Na]^{2-}$: 678.702942; found: 678.704088.

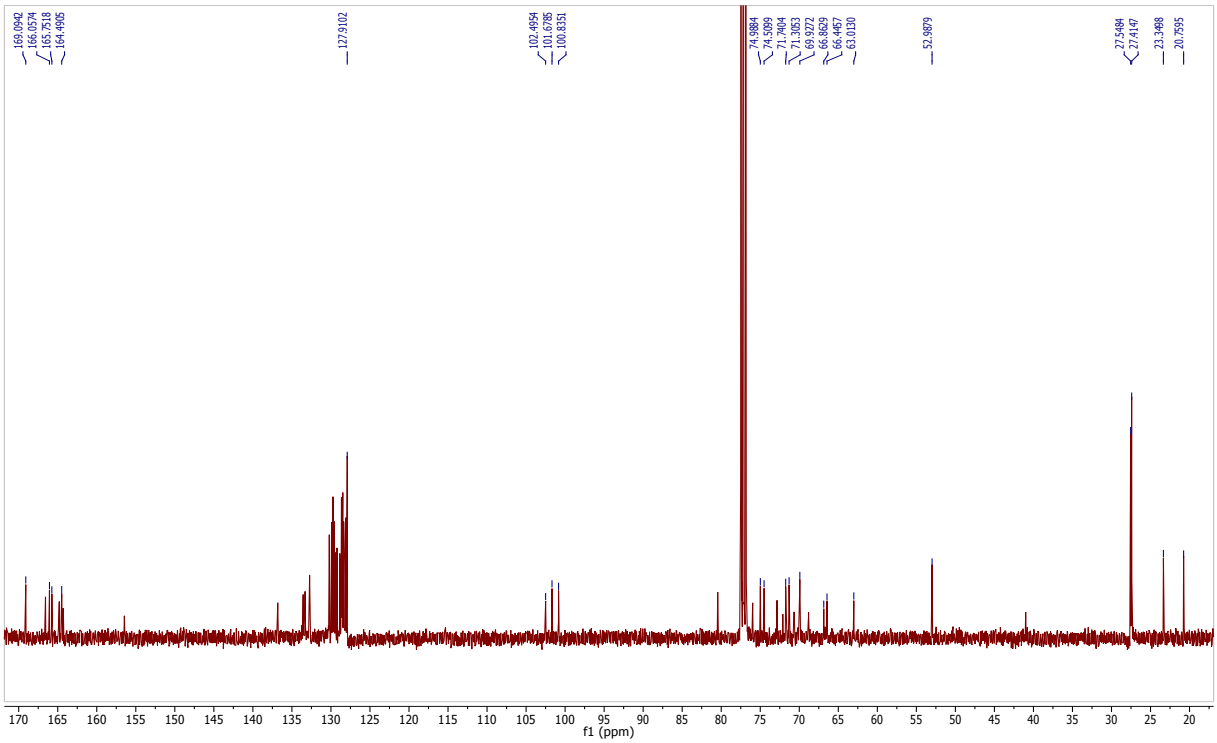
II) ^{1}H and ^{13}C NMR for new intermediates and final compounds

^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **16**

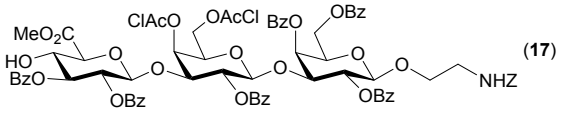


(**16**)





^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **17**



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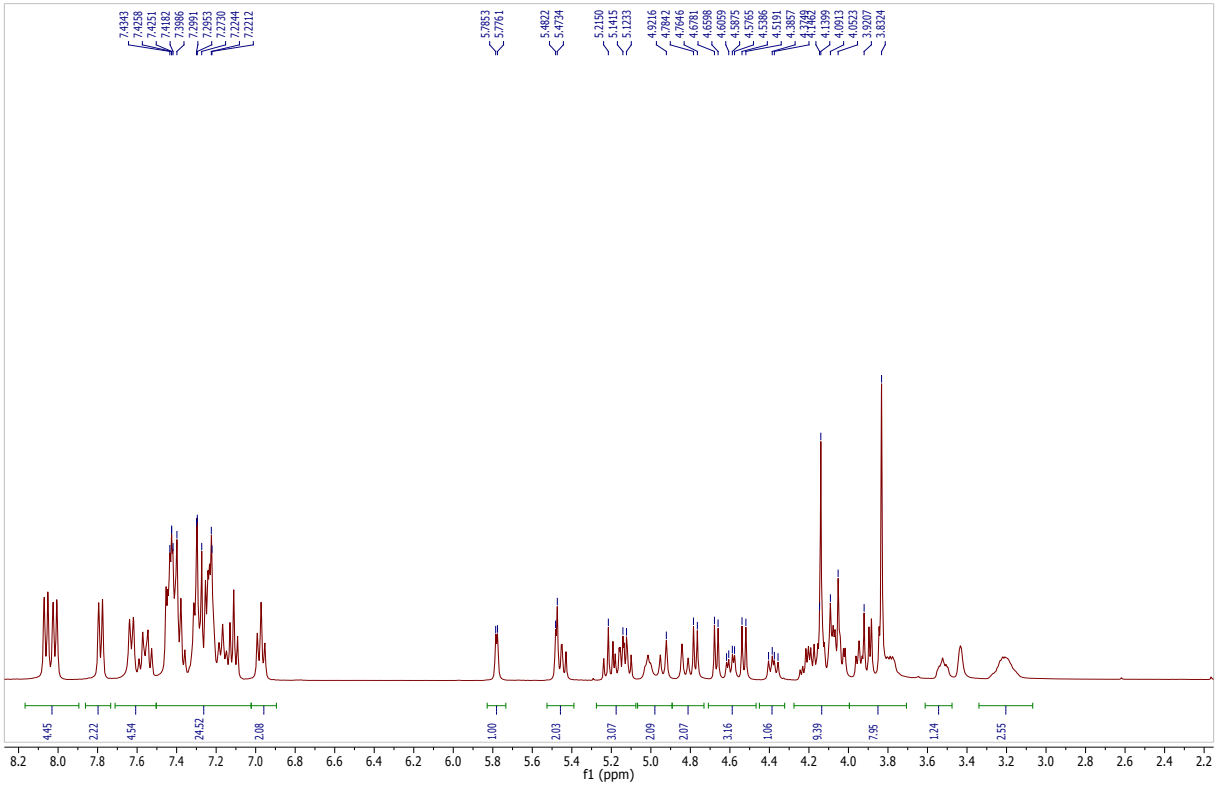
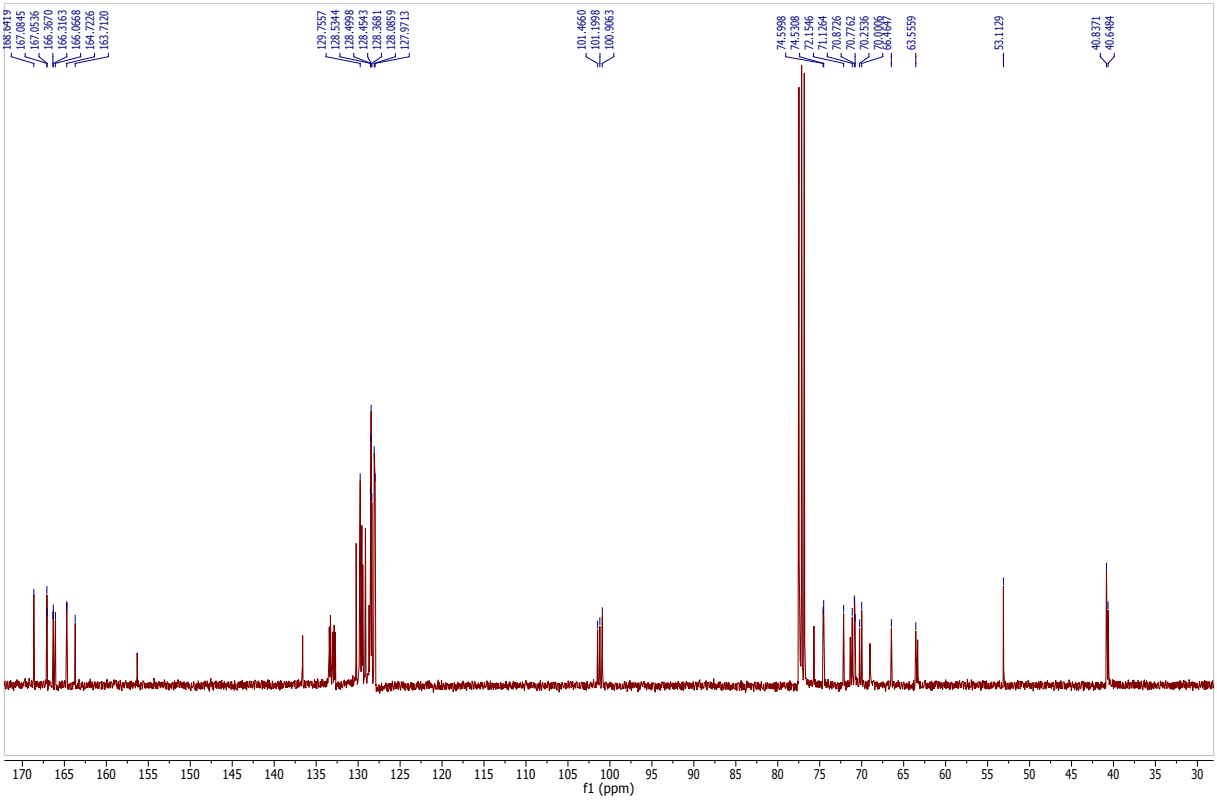
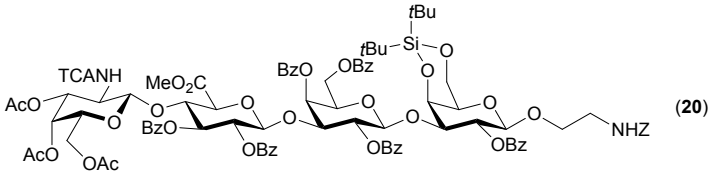
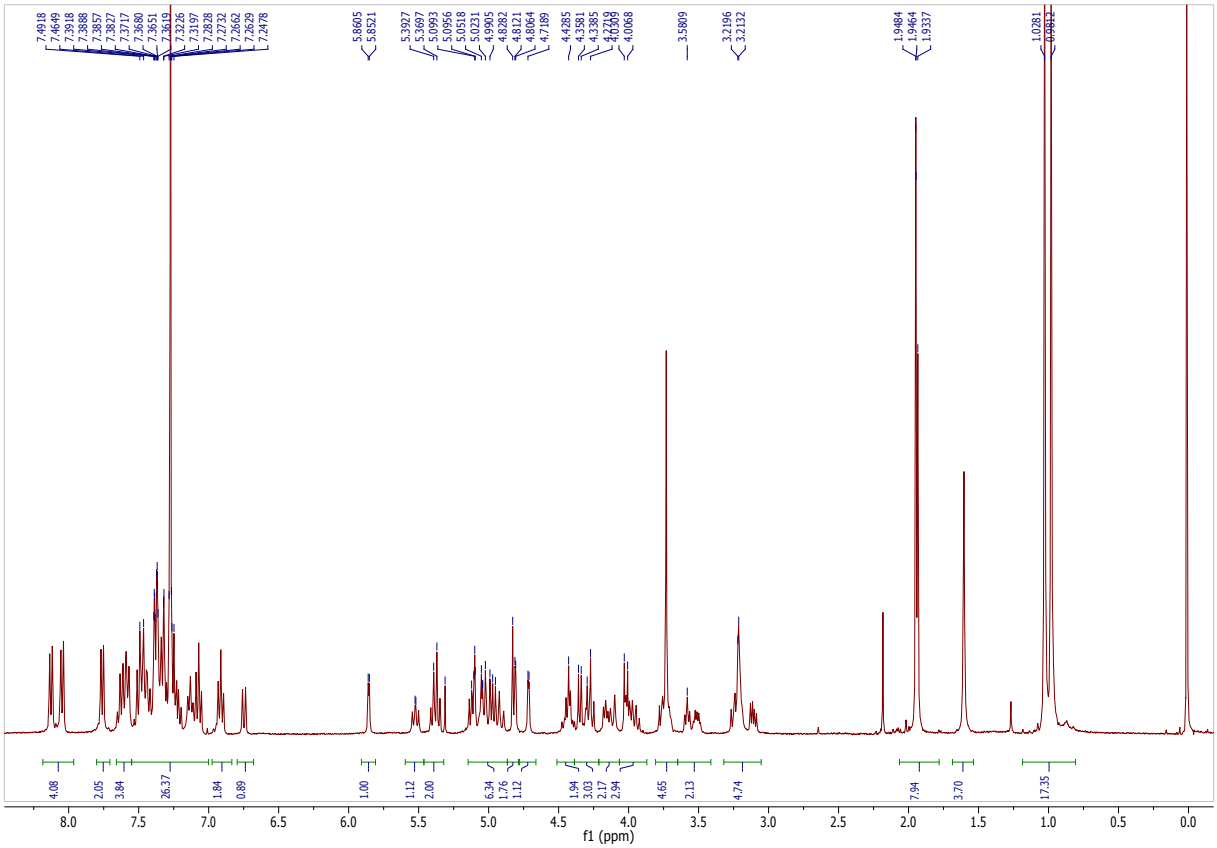


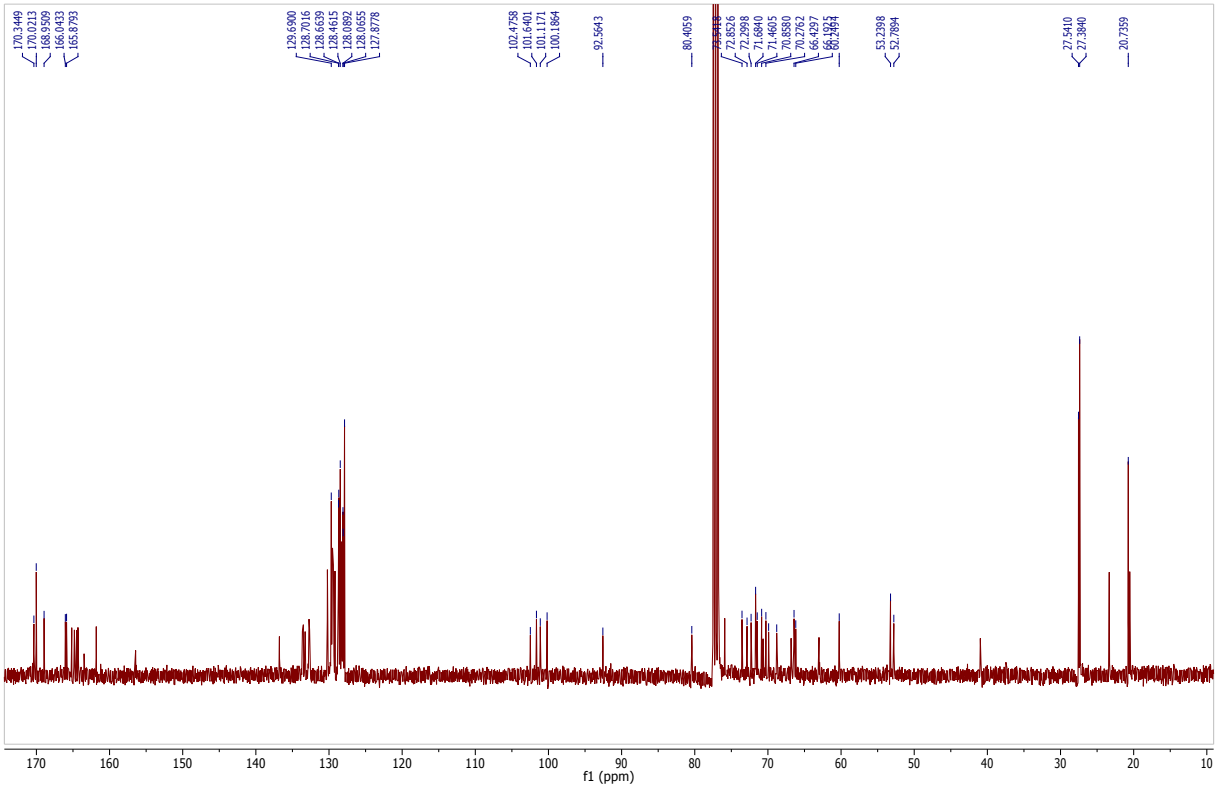


^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **20**

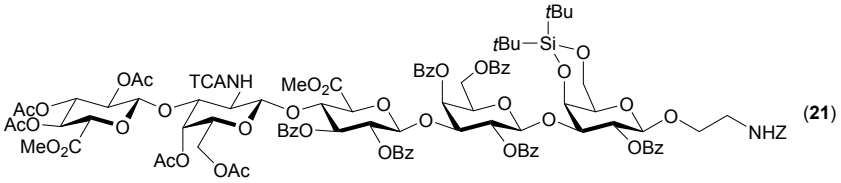


(**20**)





^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **21**



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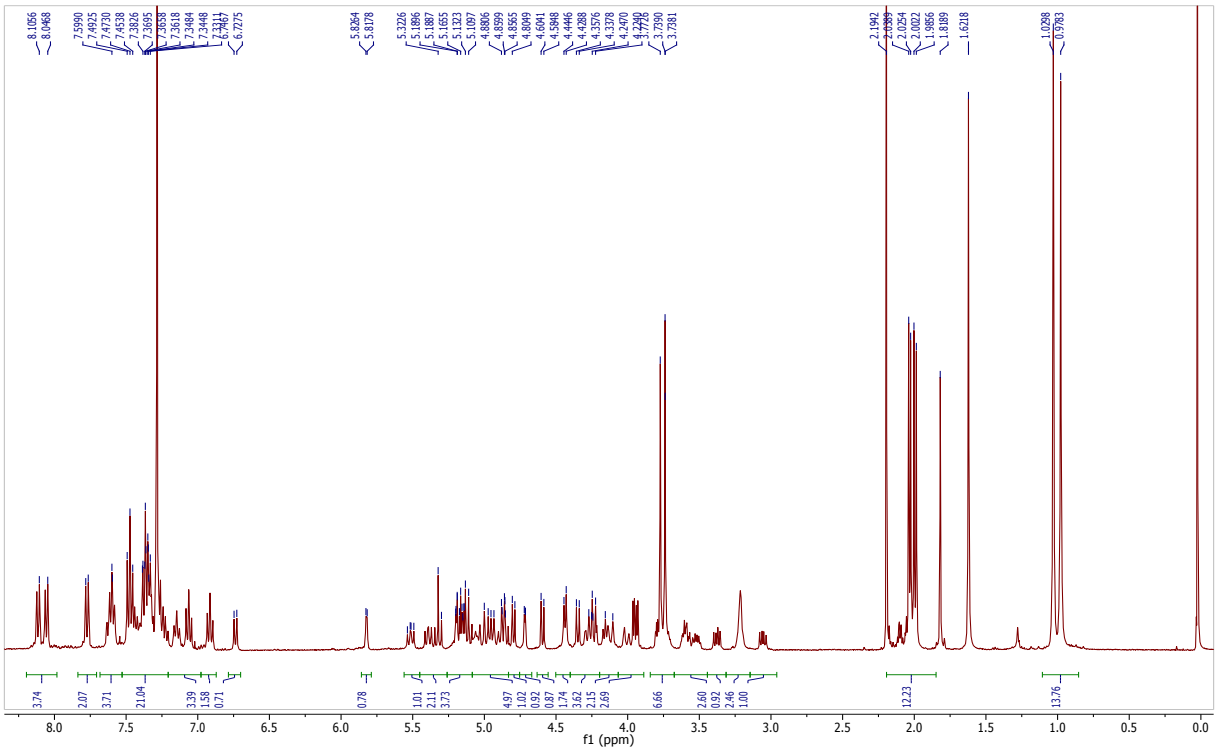
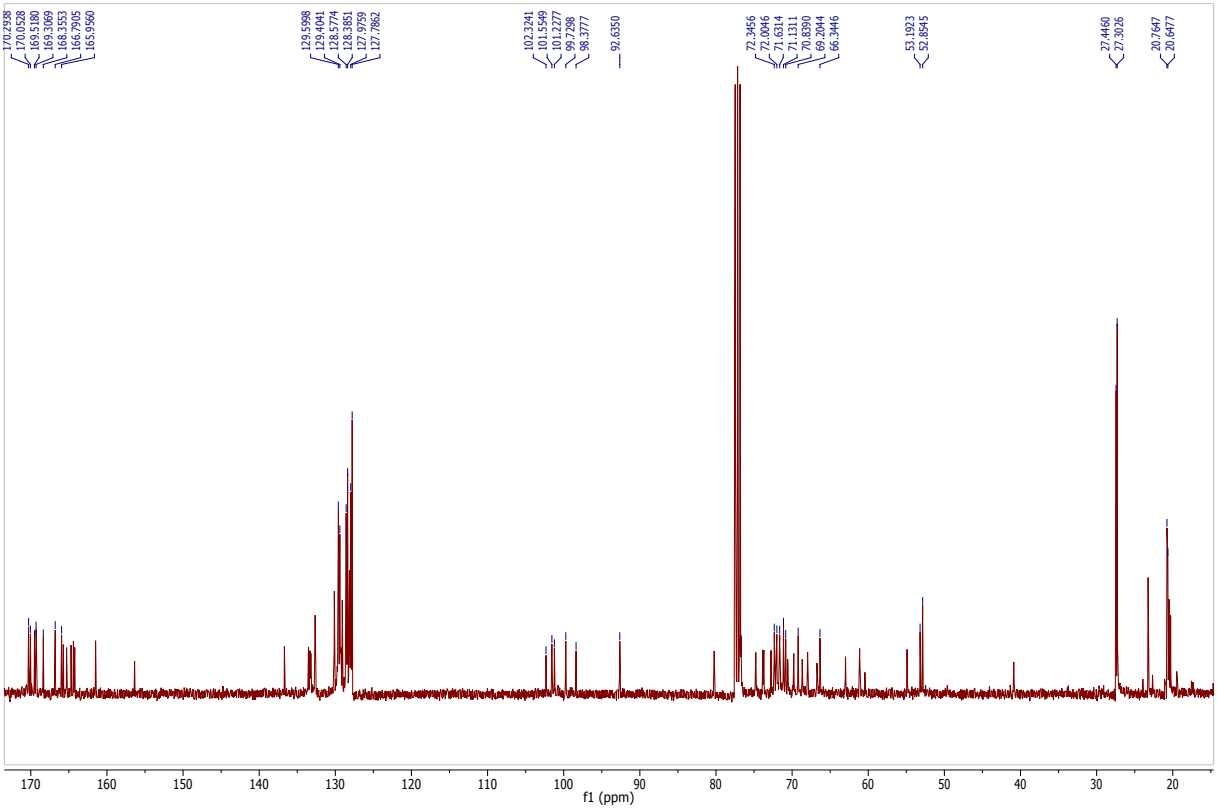
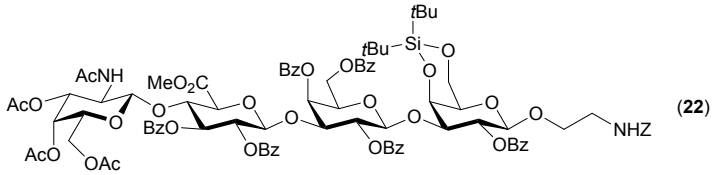




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **22**



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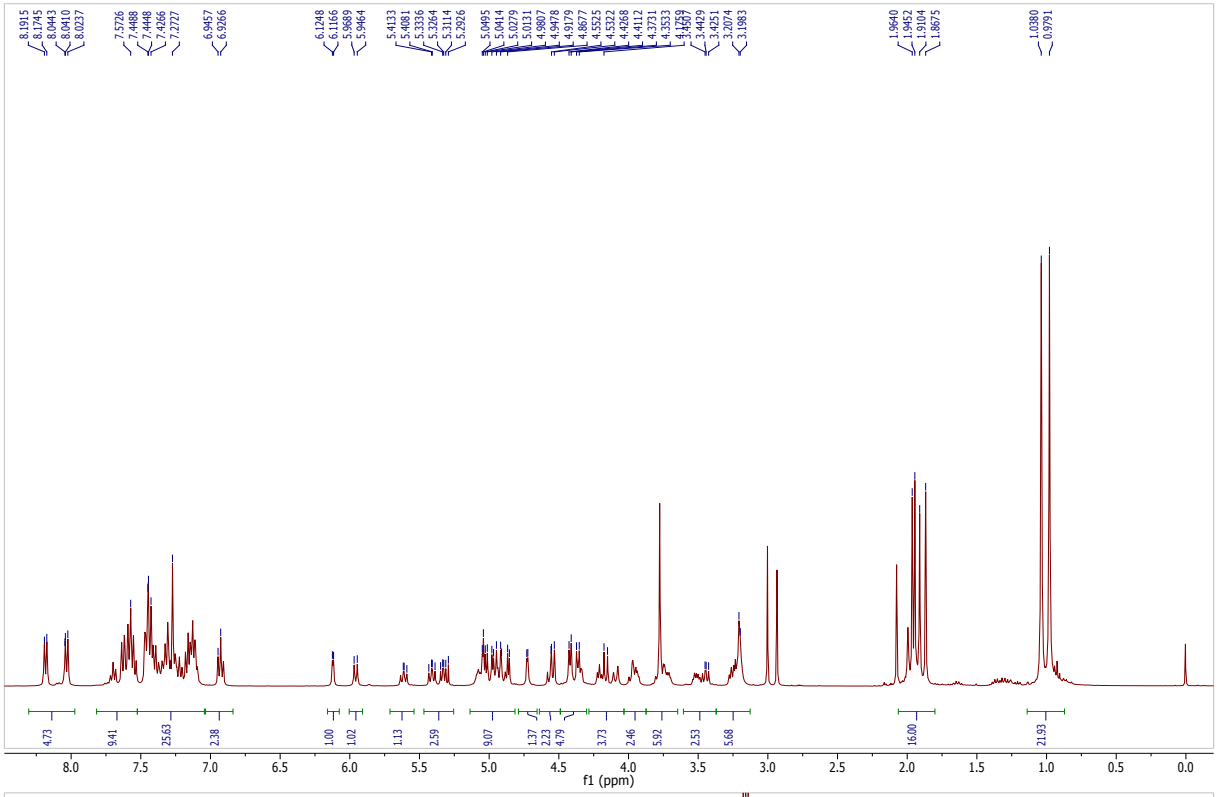
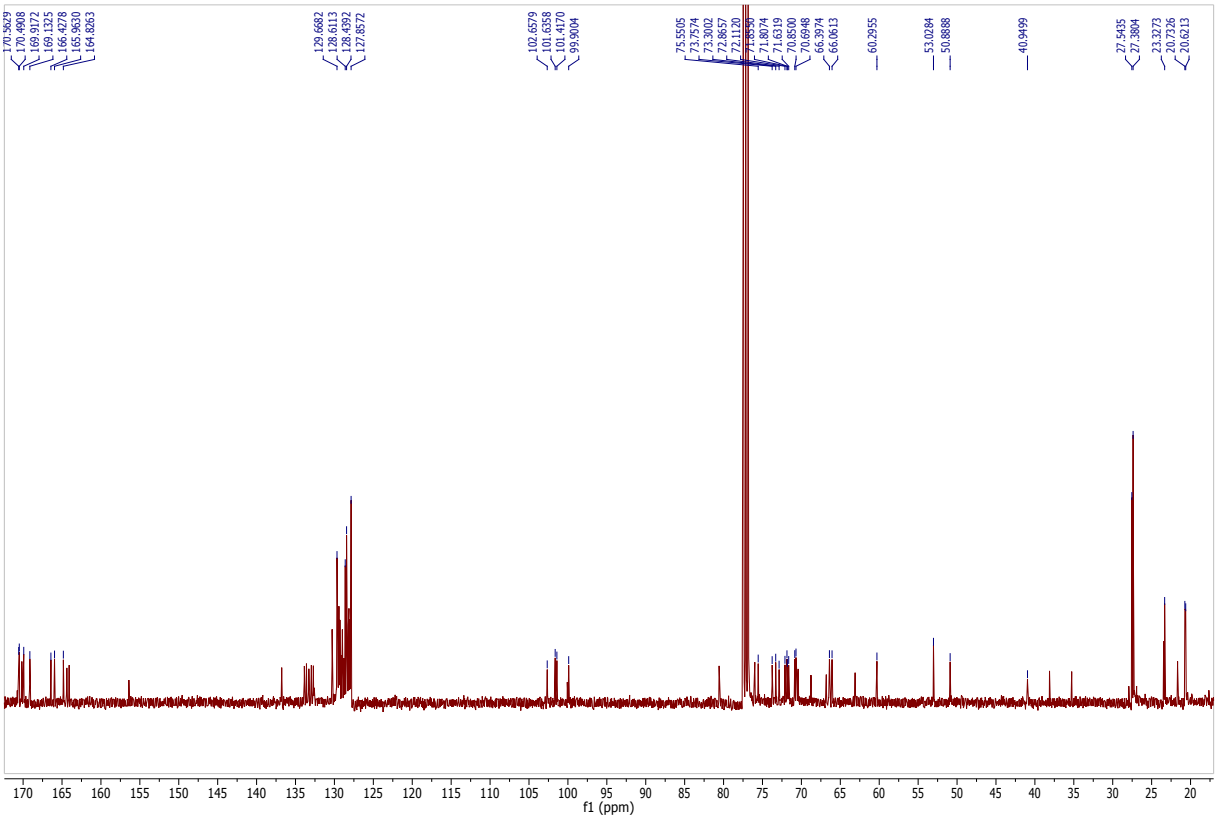
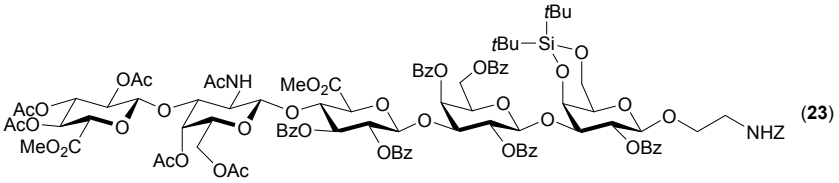
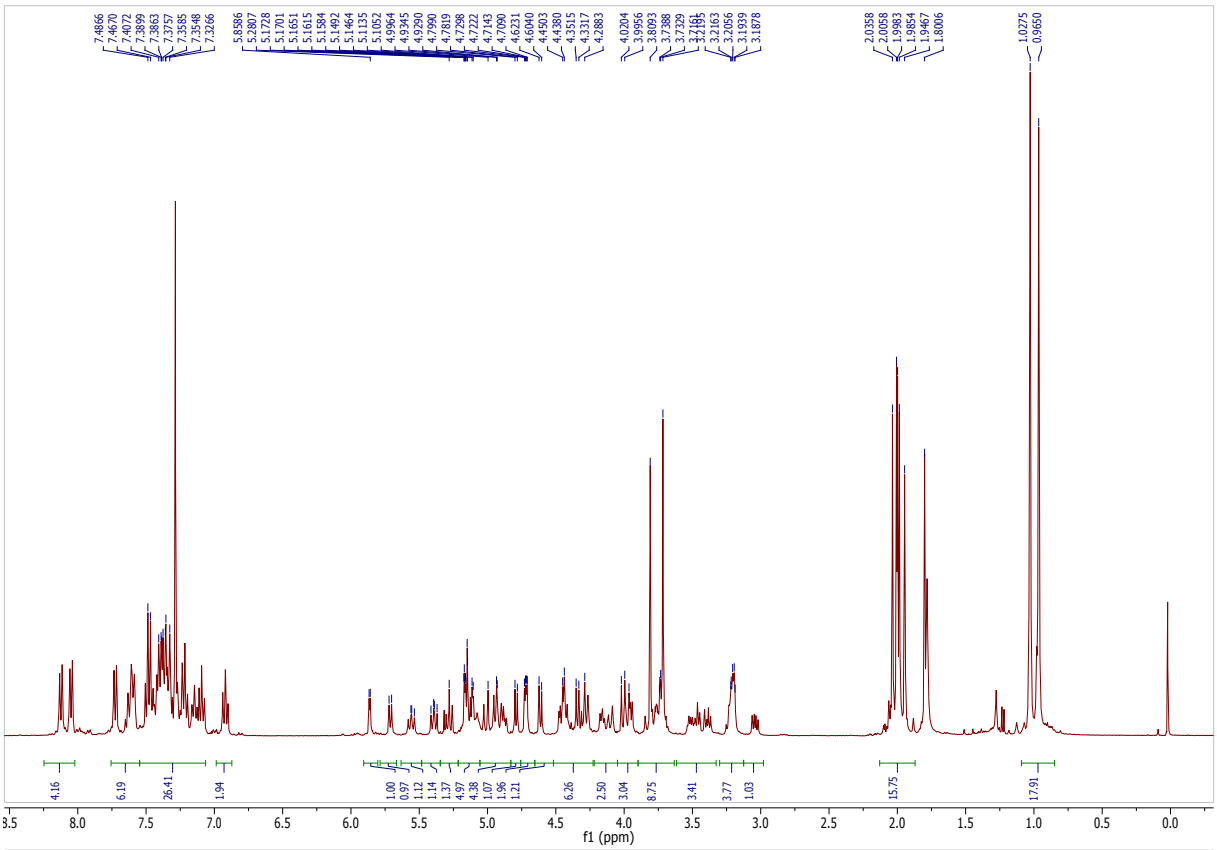


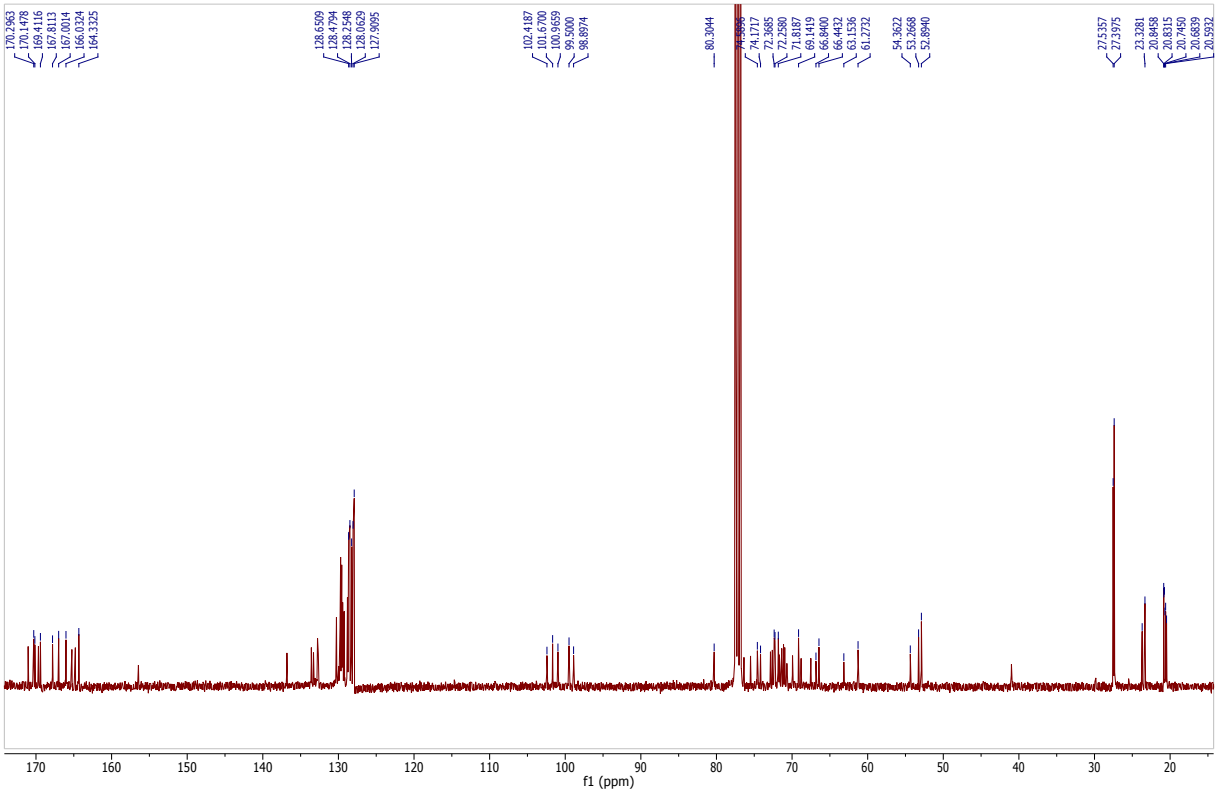


^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **23**

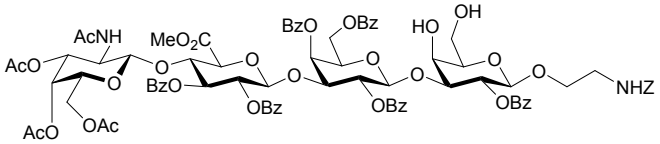


(**23**)





^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **24**



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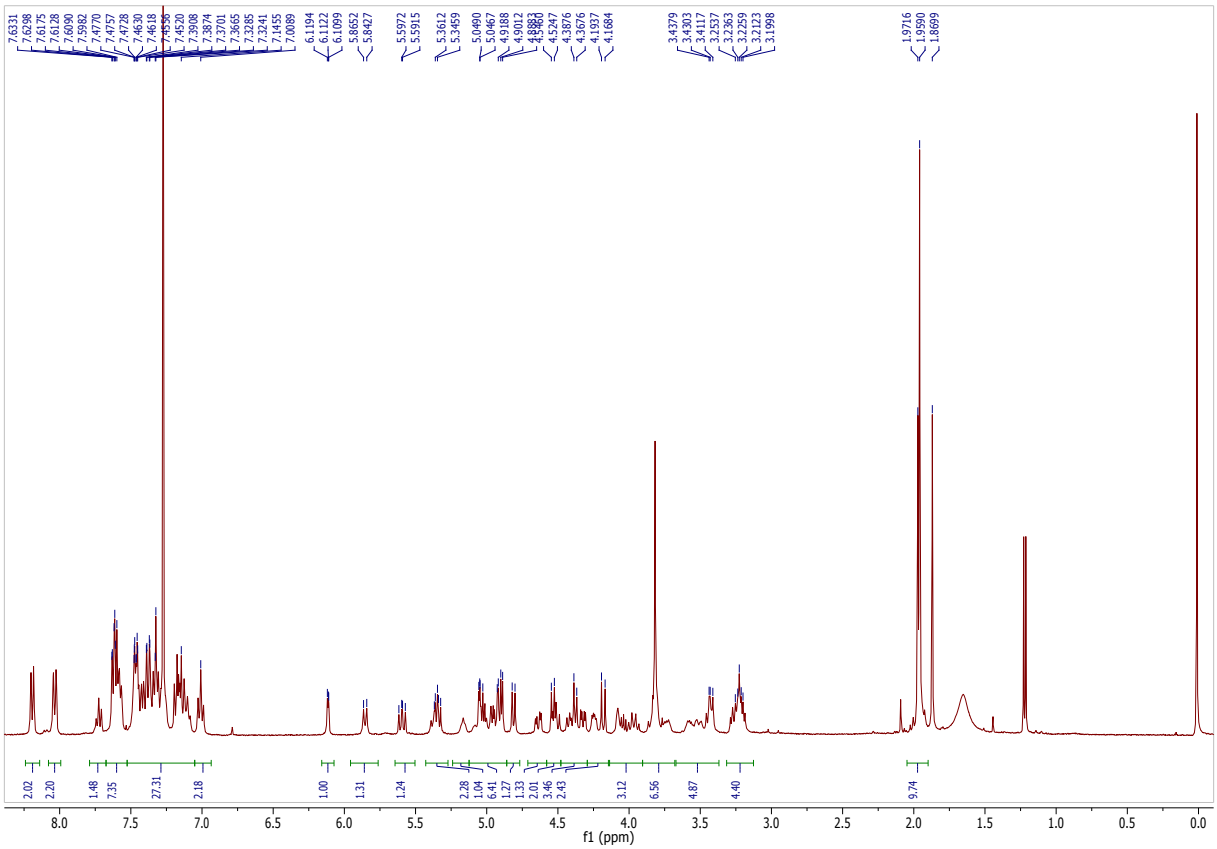
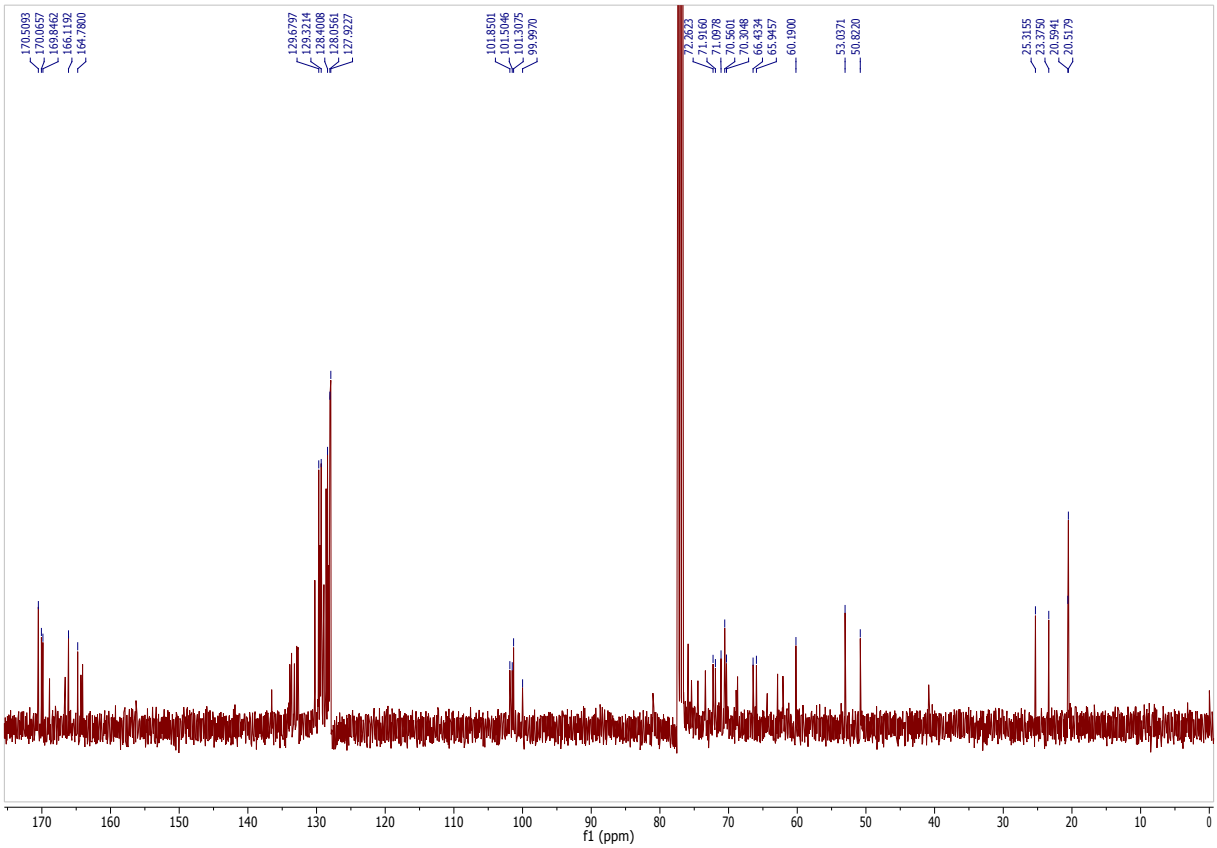
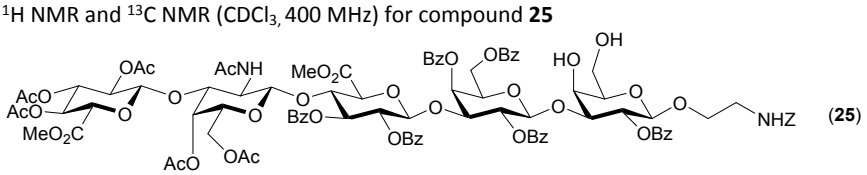




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **25**



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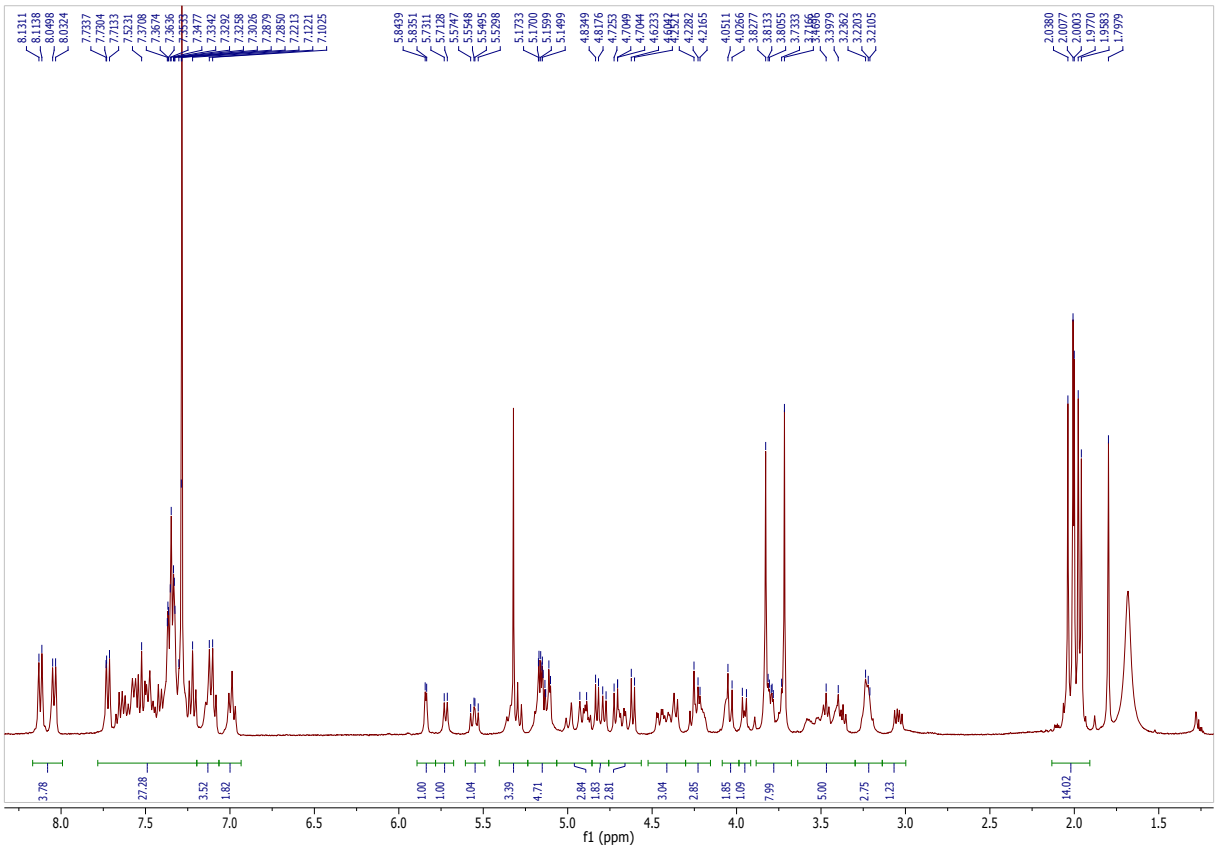
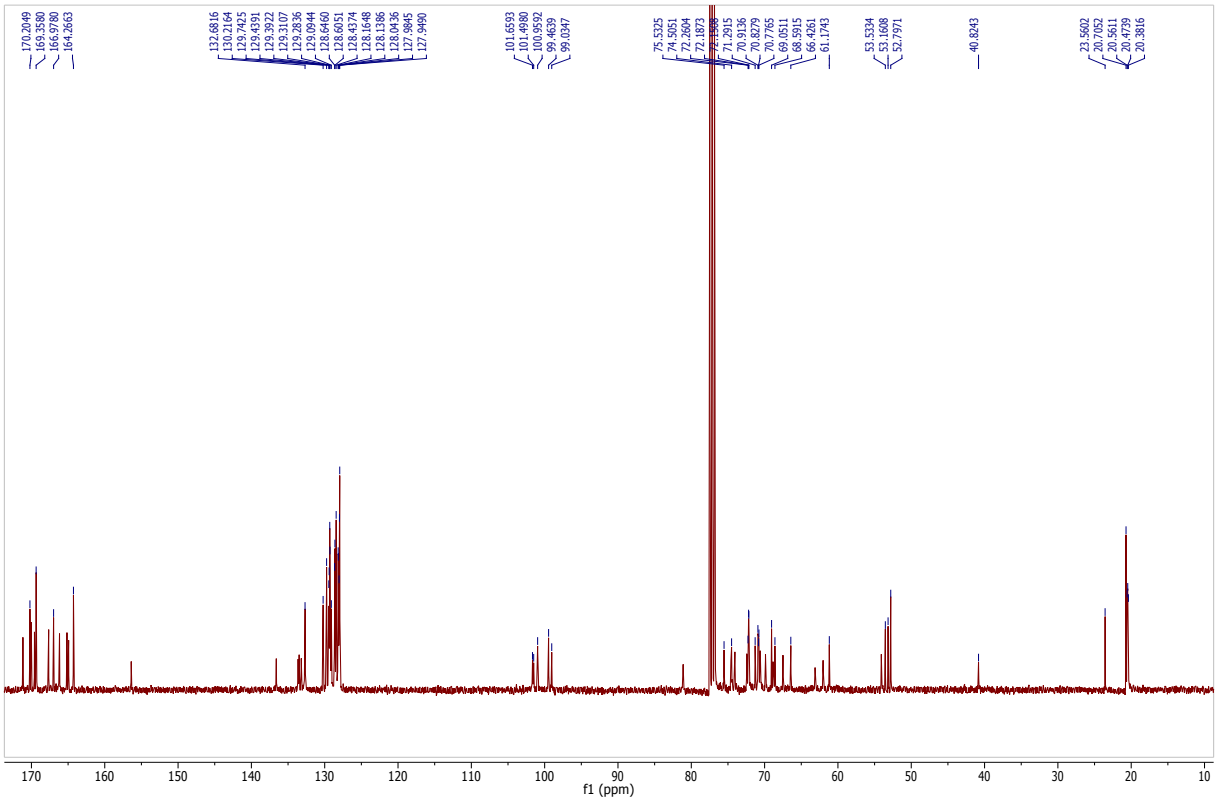
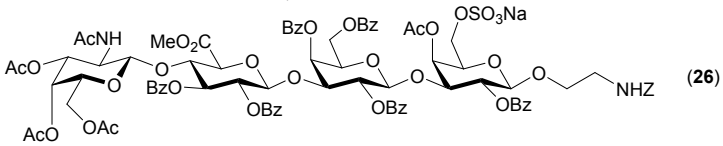




^{1}H NMR and ^{13}C NMR (CD_3OD, 400 MHz) for compound **26**



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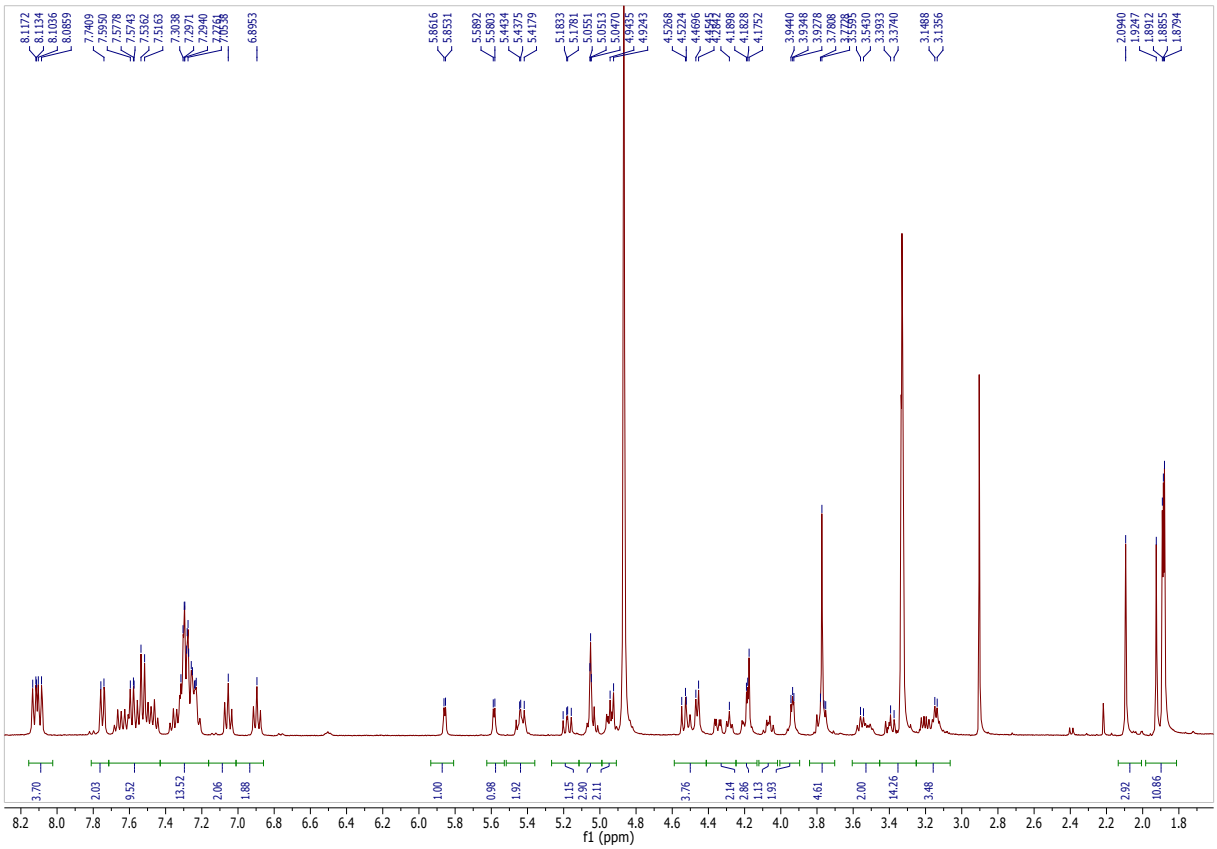
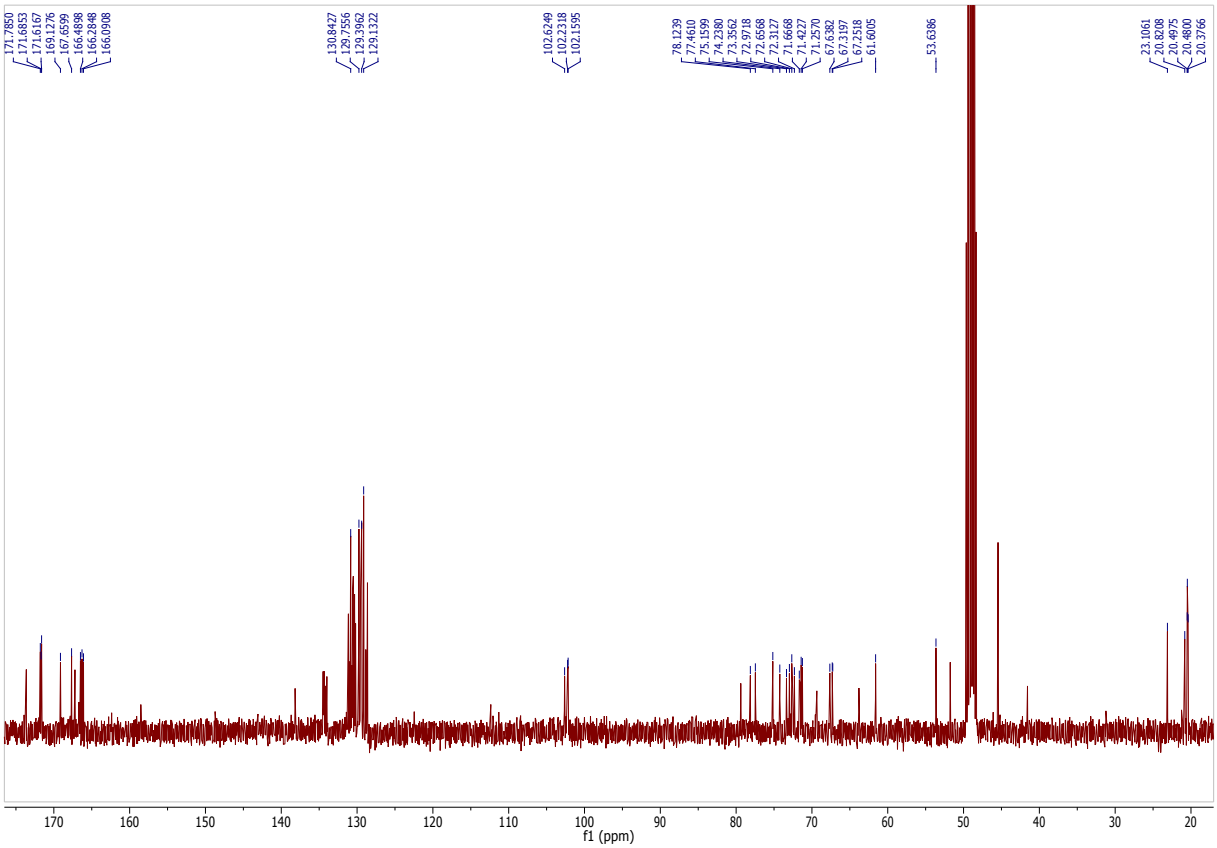
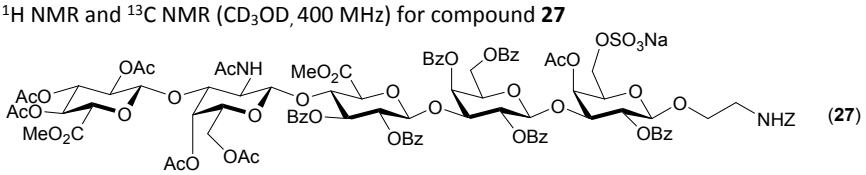




^{1}H NMR and ^{13}C NMR (CD_3OD, 400 MHz) for compound **27**



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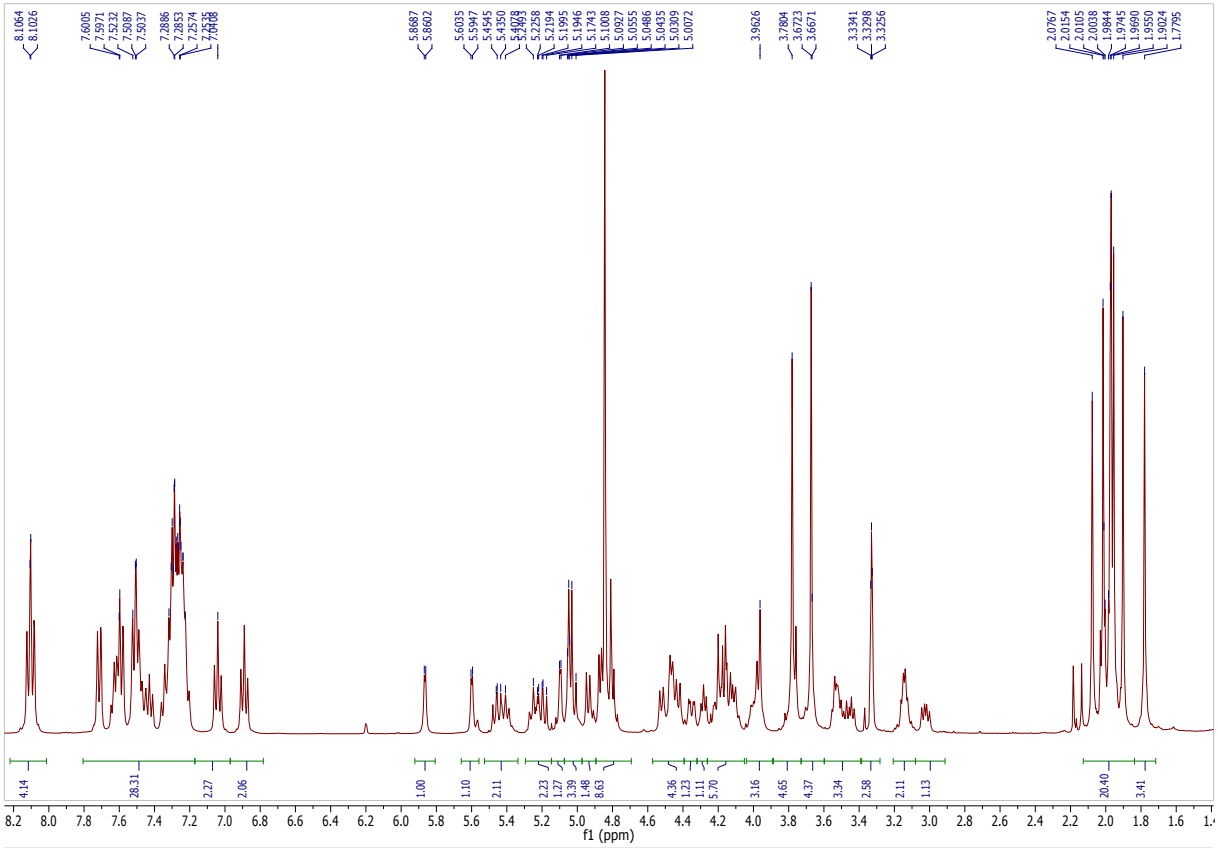
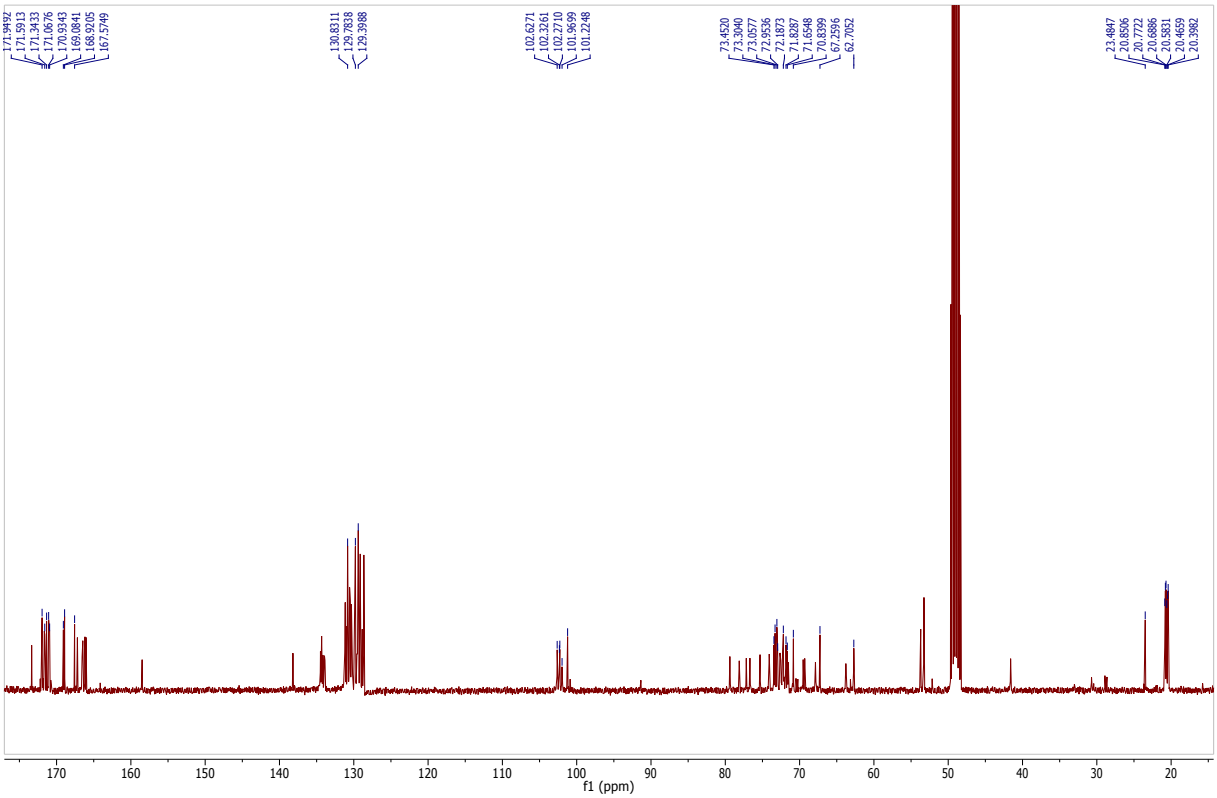
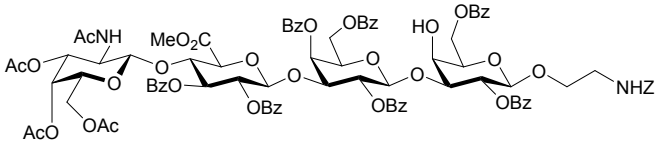




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **28**



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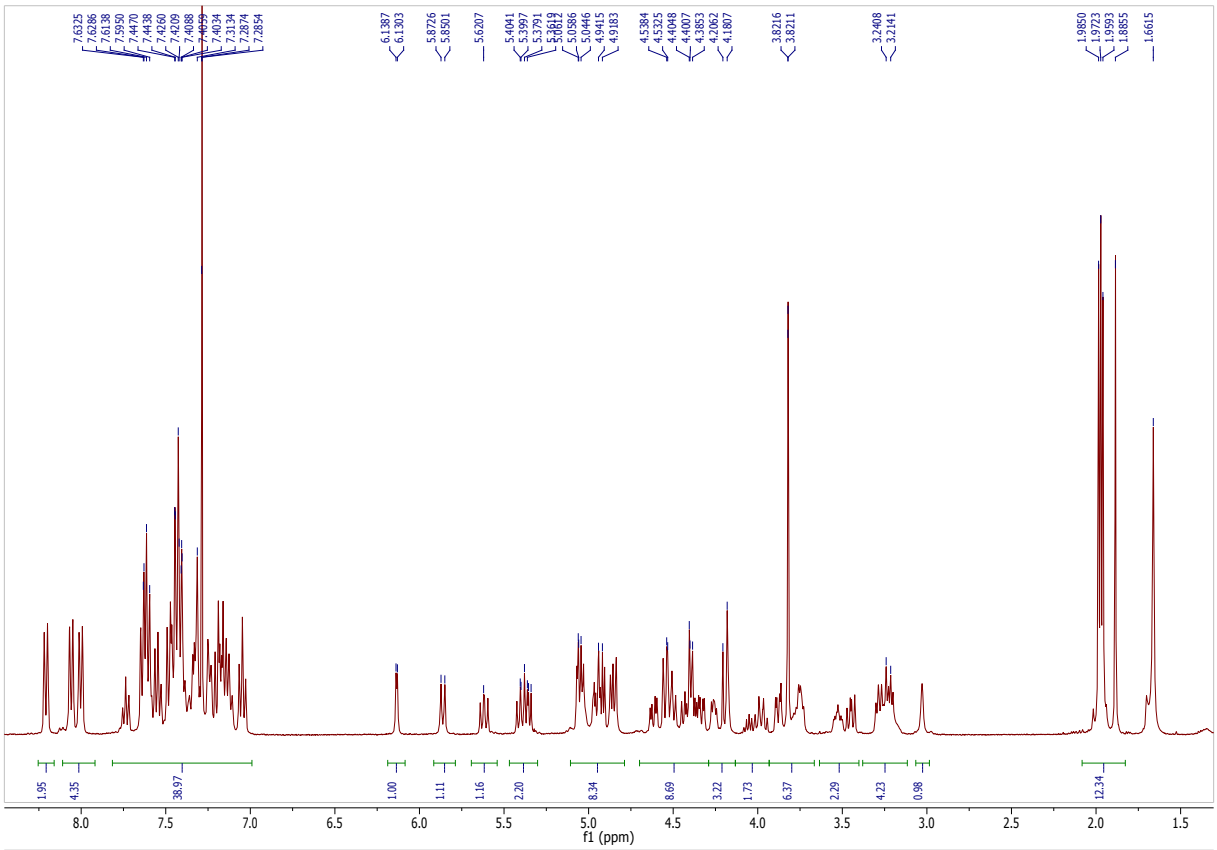
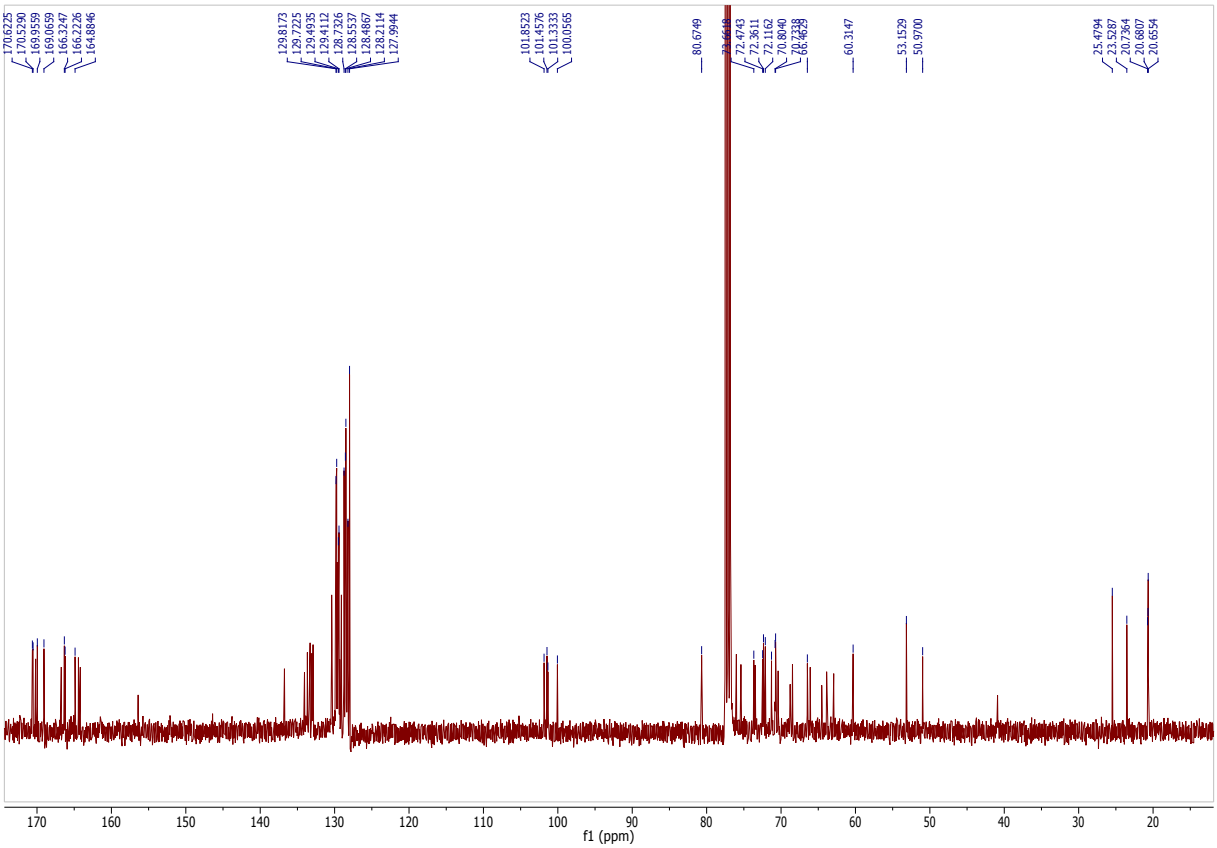
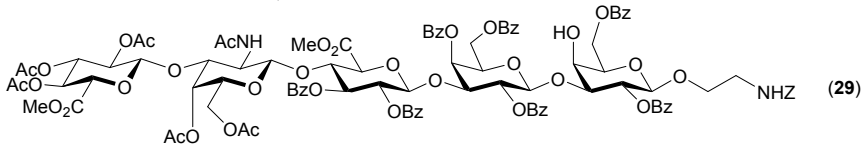




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **29**



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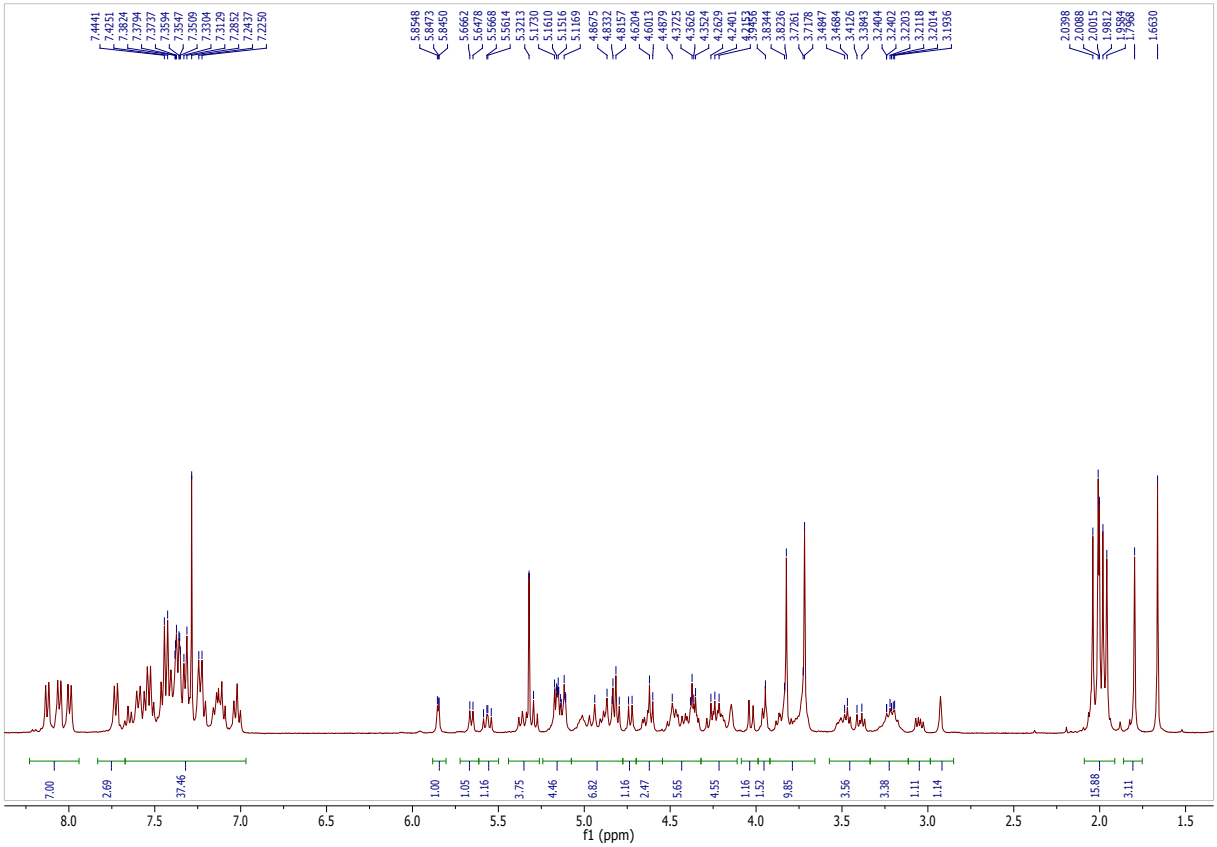
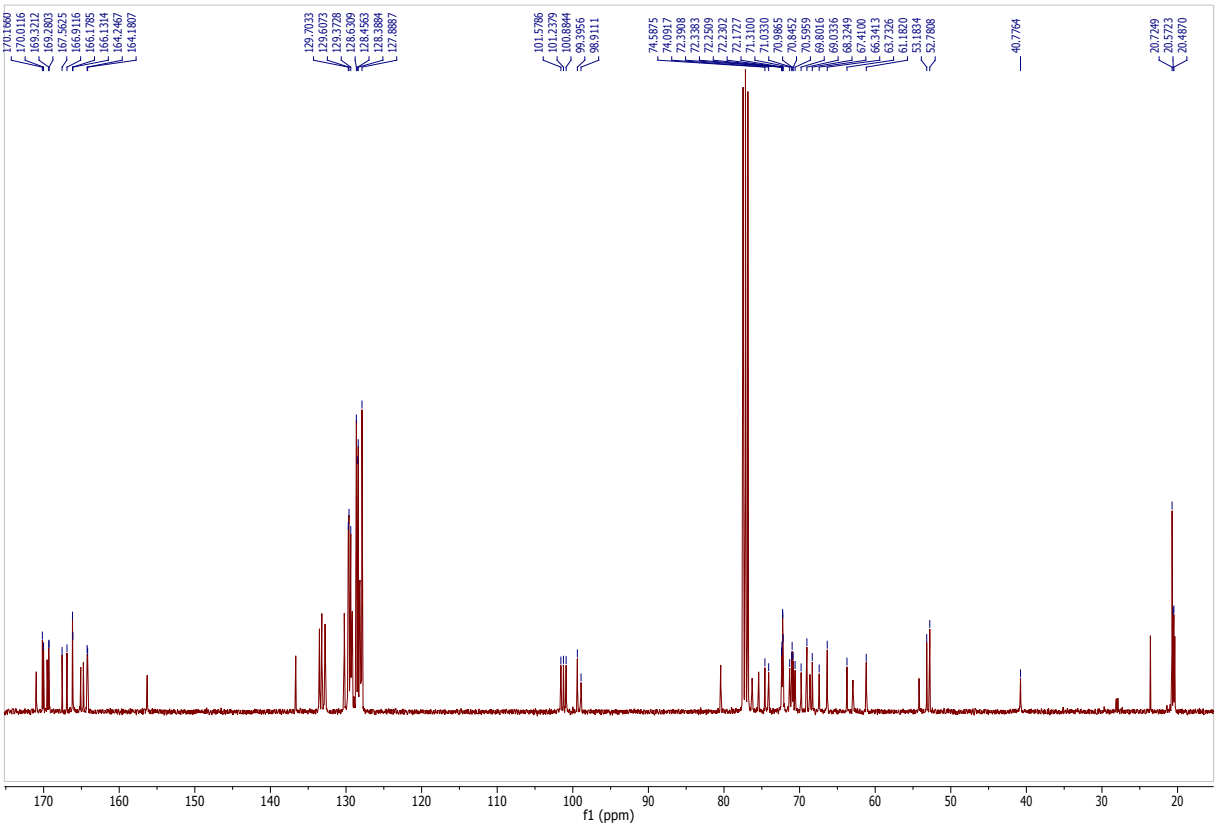
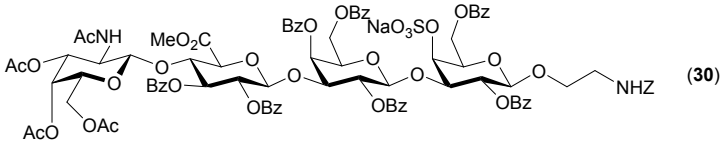




^{1}H NMR and ^{13}C NMR (CD_3OD, 400 MHz) for compound **30**



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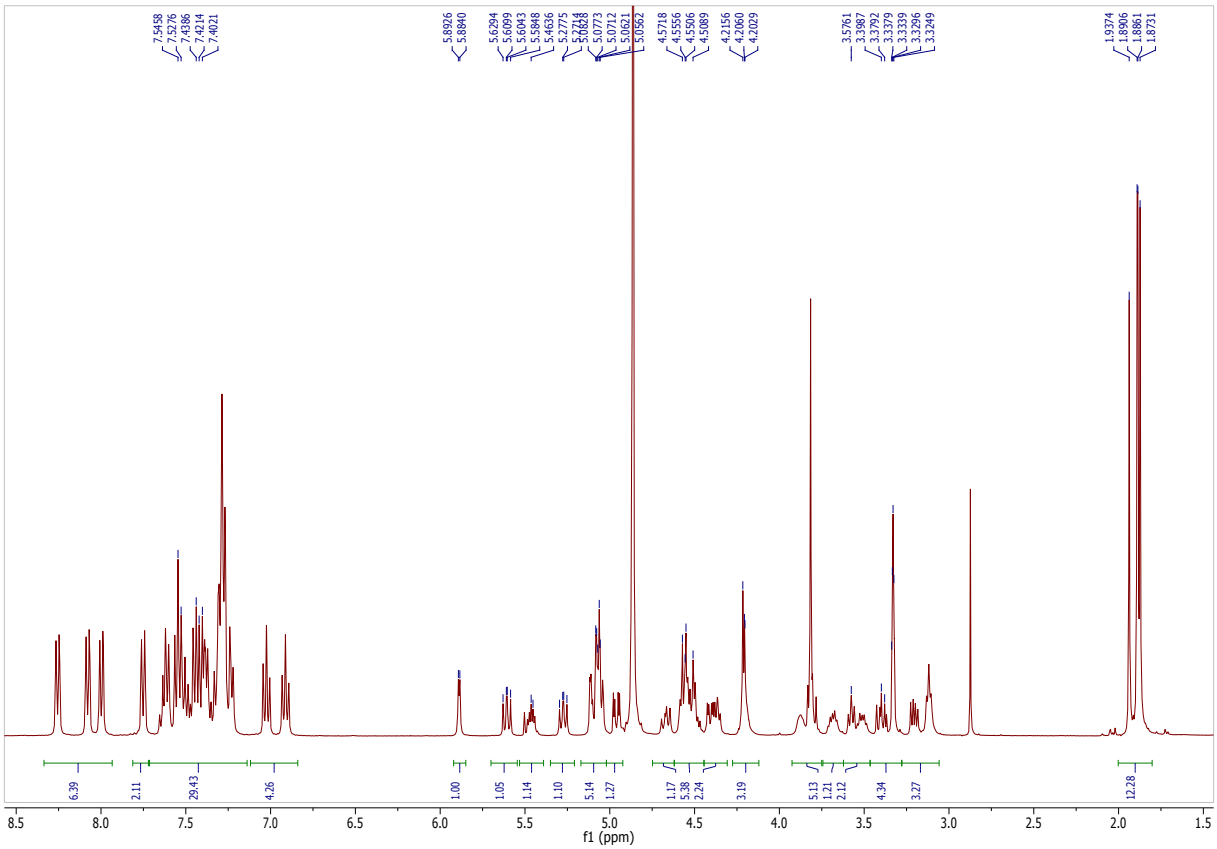
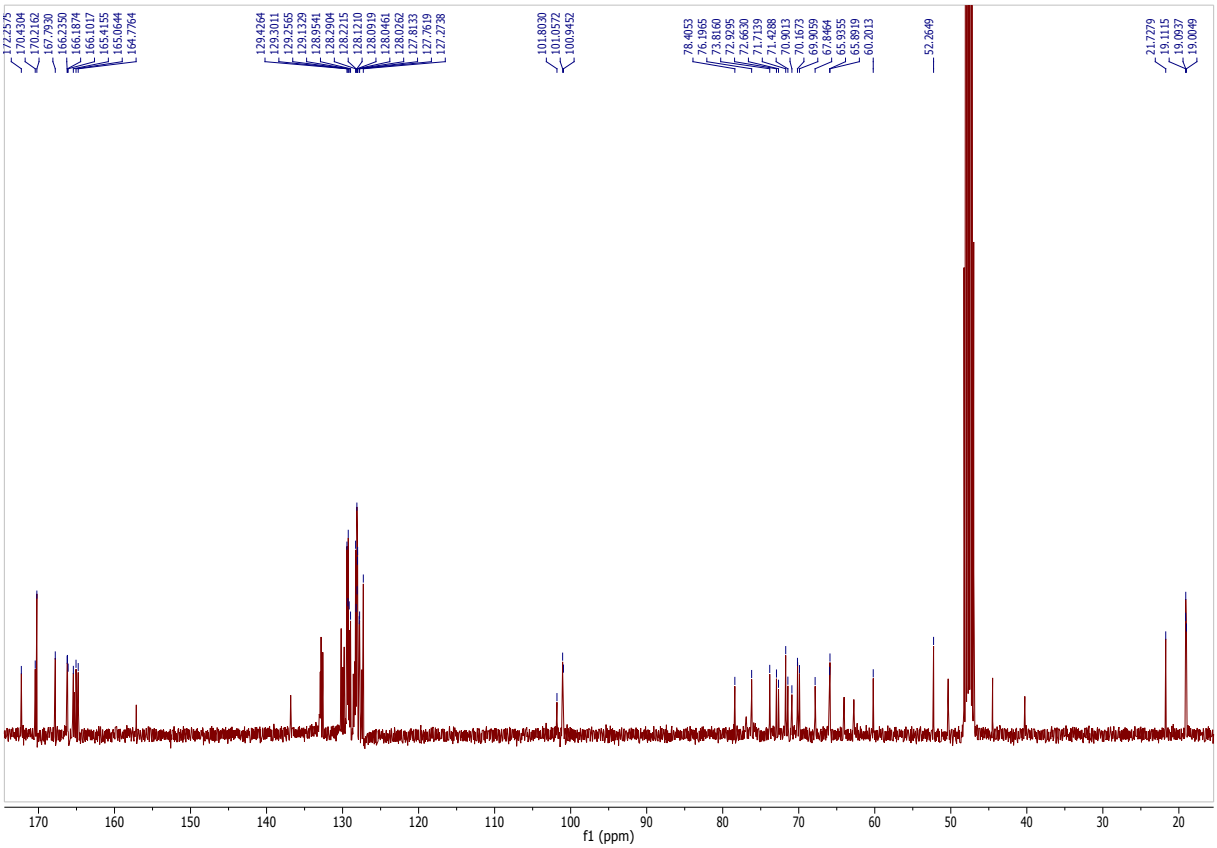
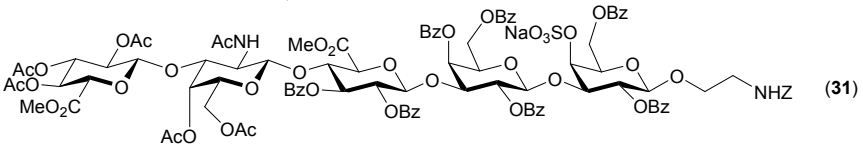




^{1}H NMR and ^{13}C NMR (CD_3OD, 400 MHz) for compound **31**



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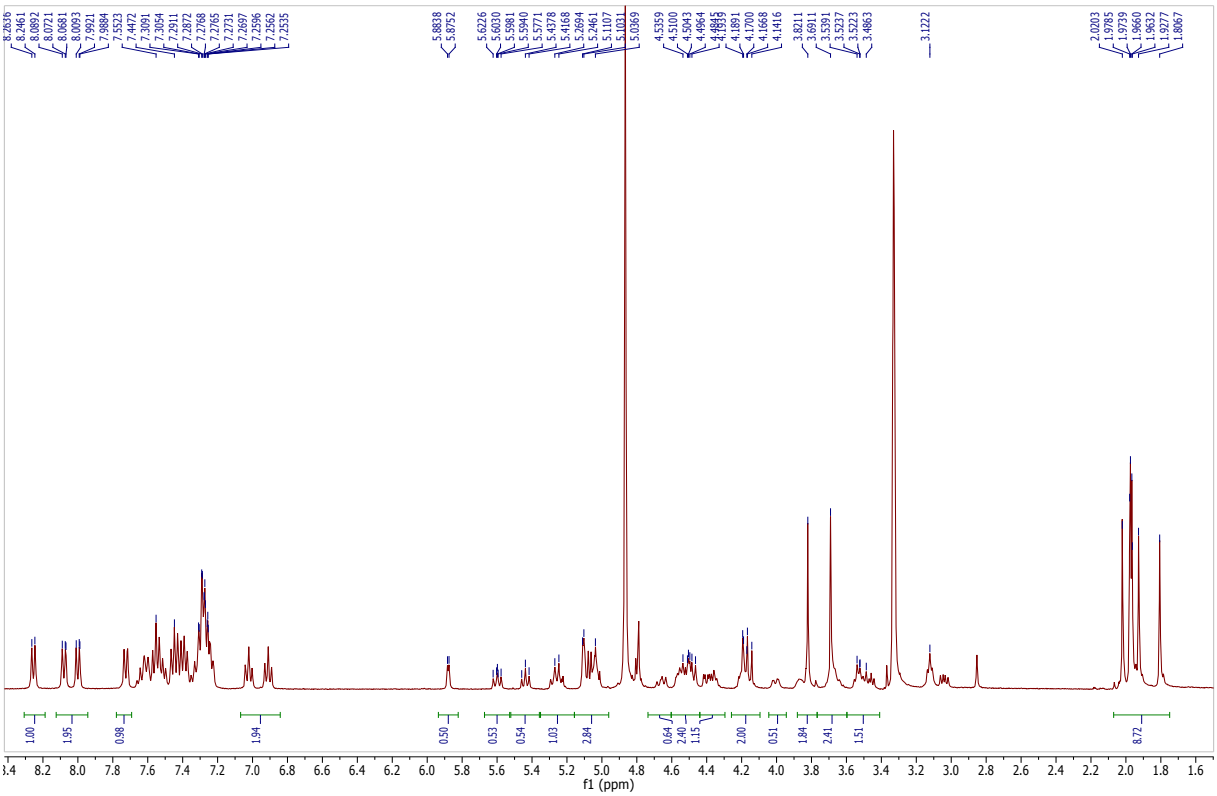
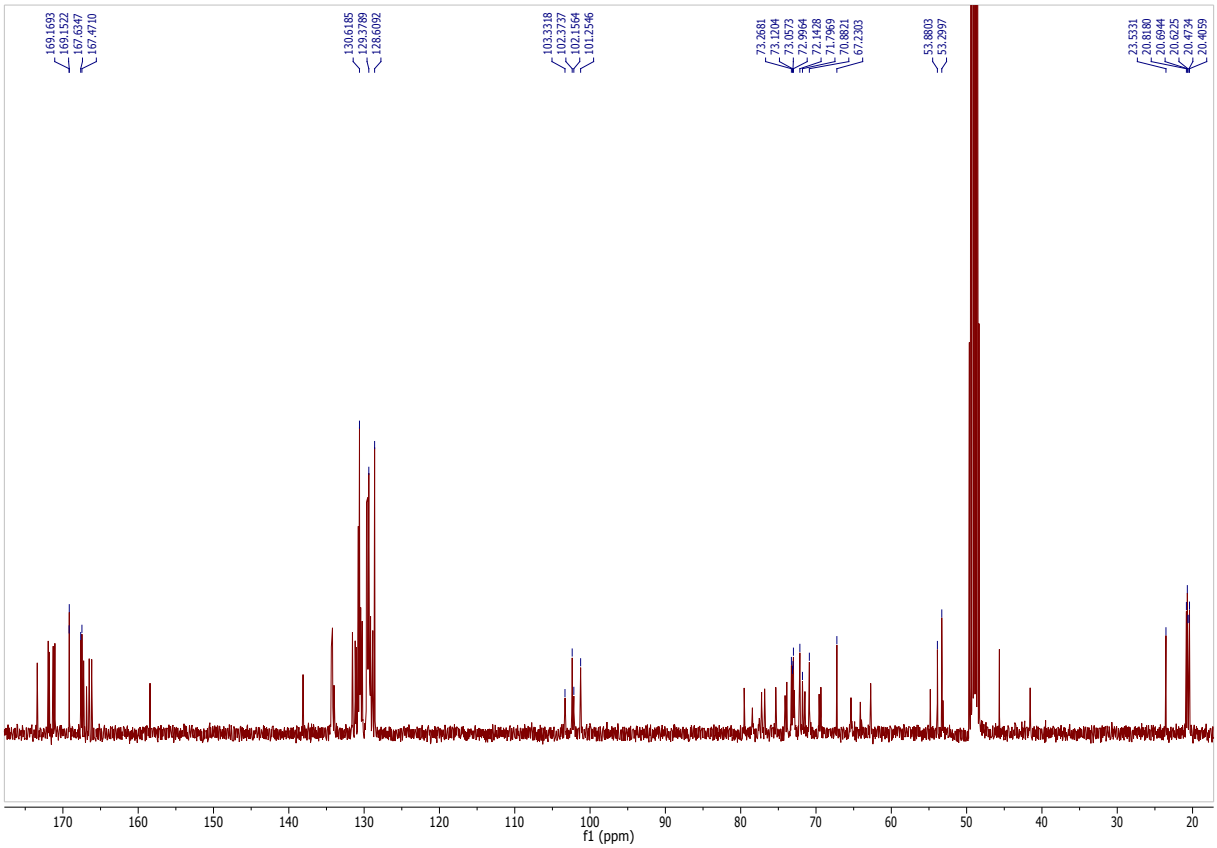
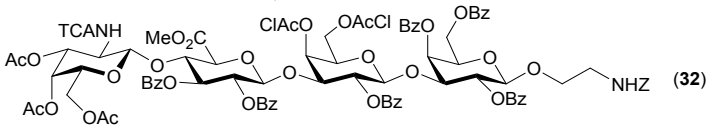




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **32**



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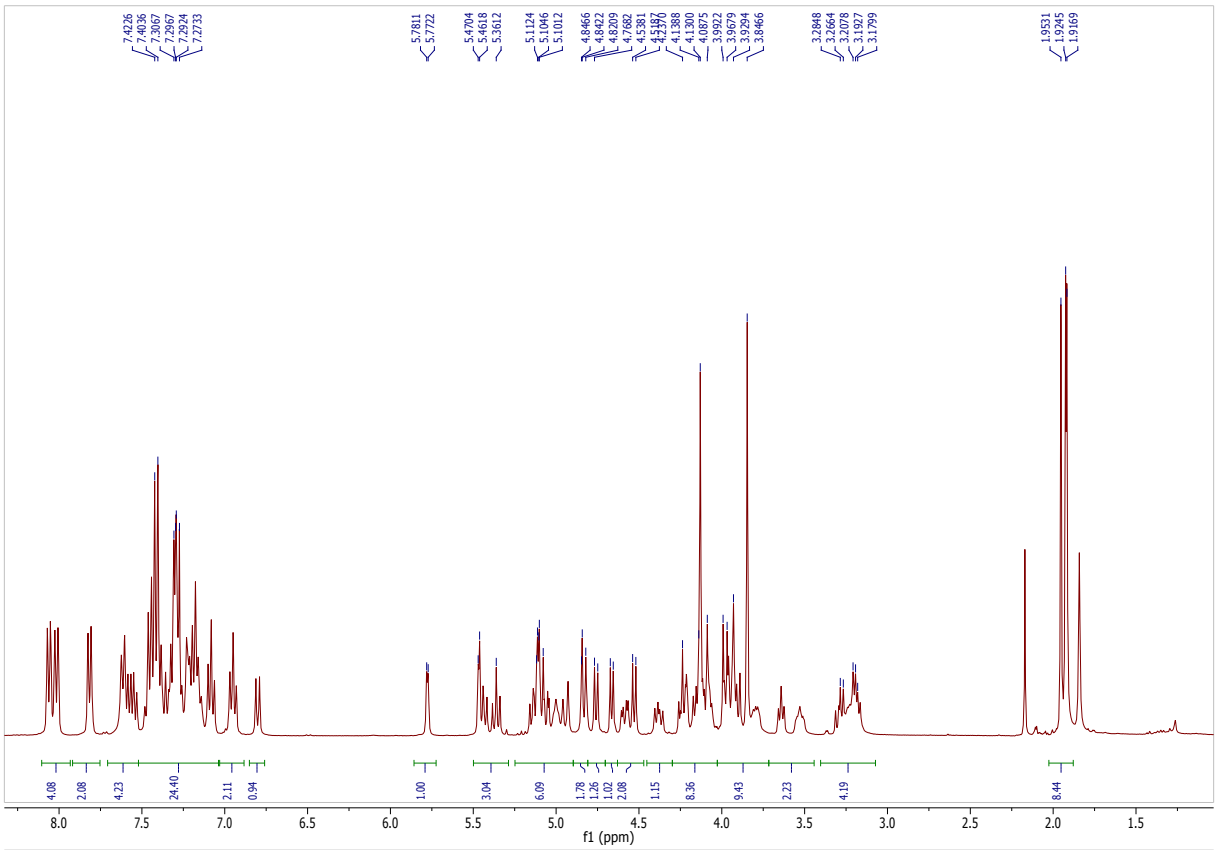
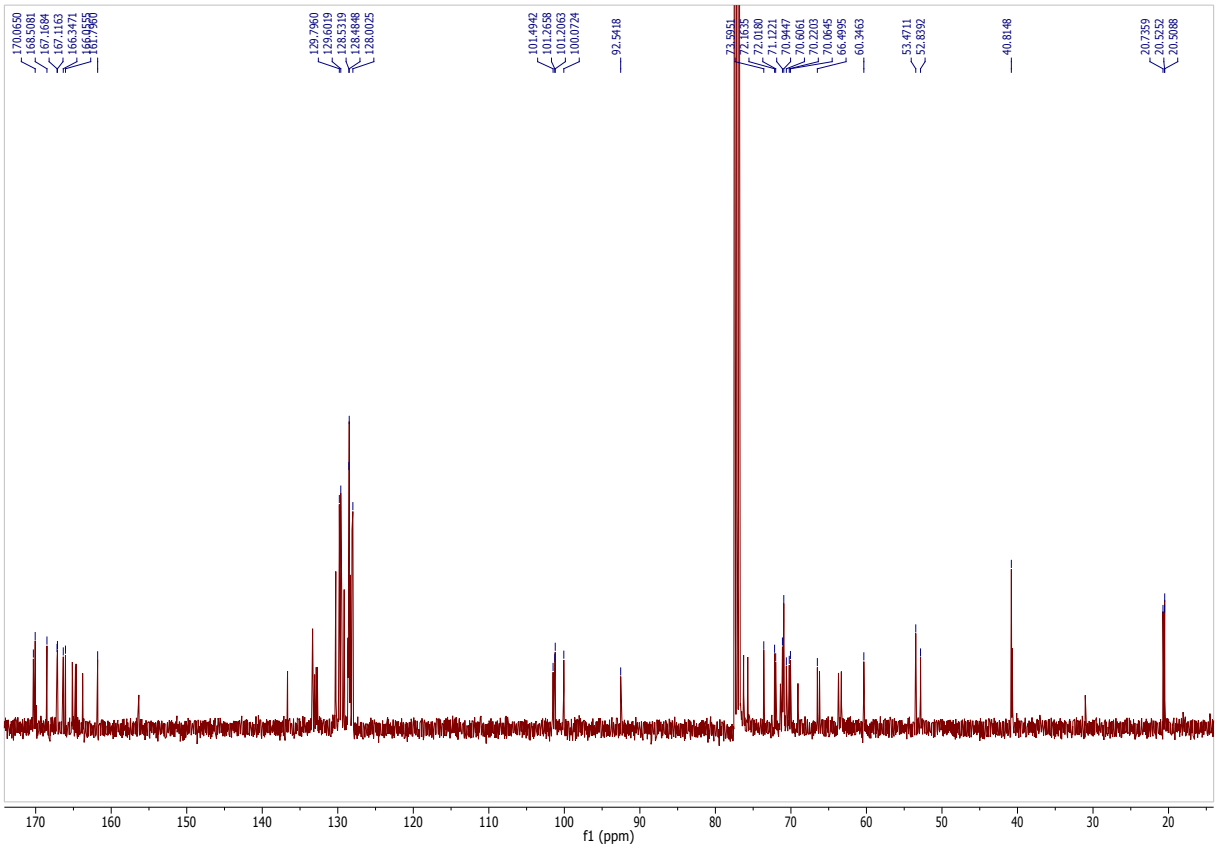
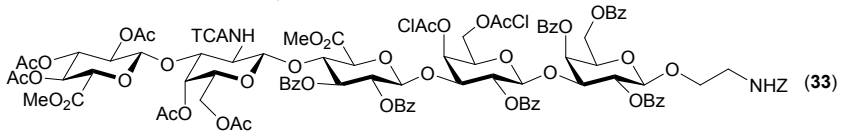




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **33**



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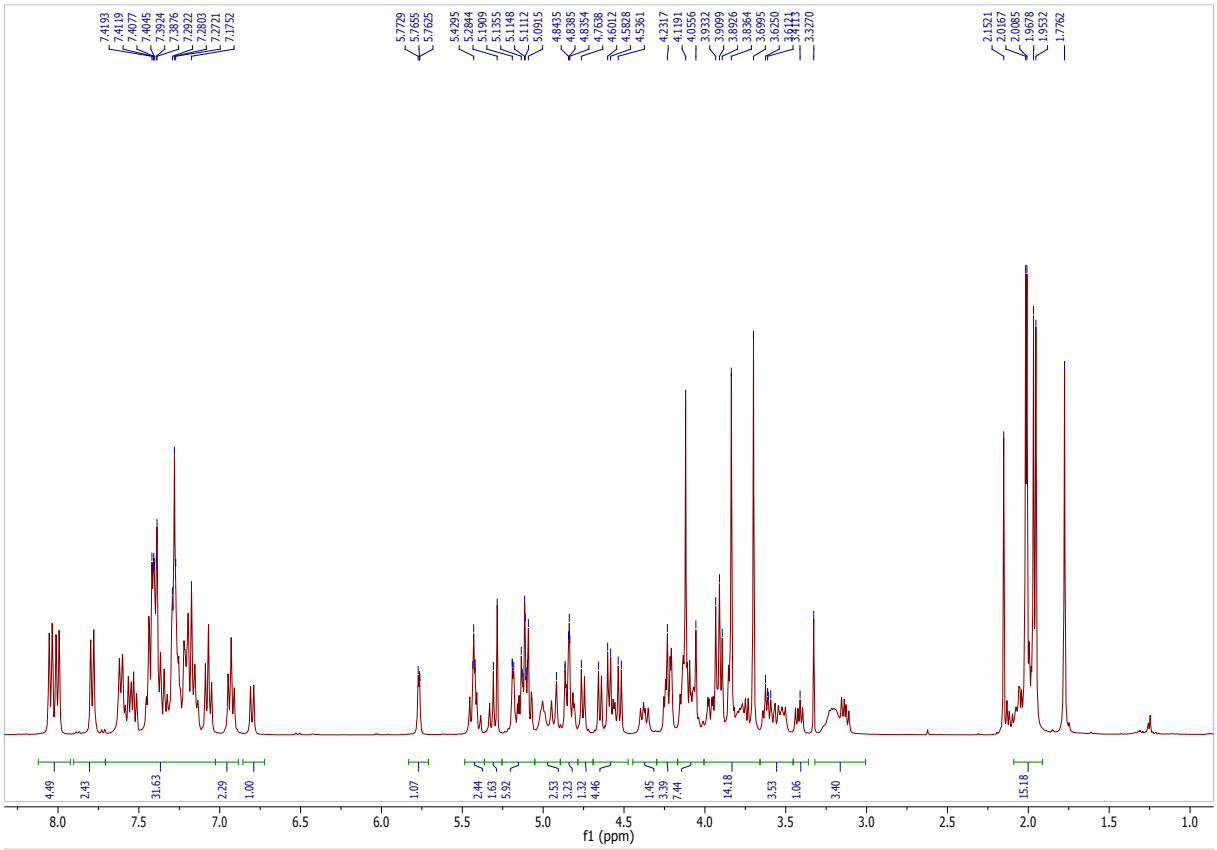
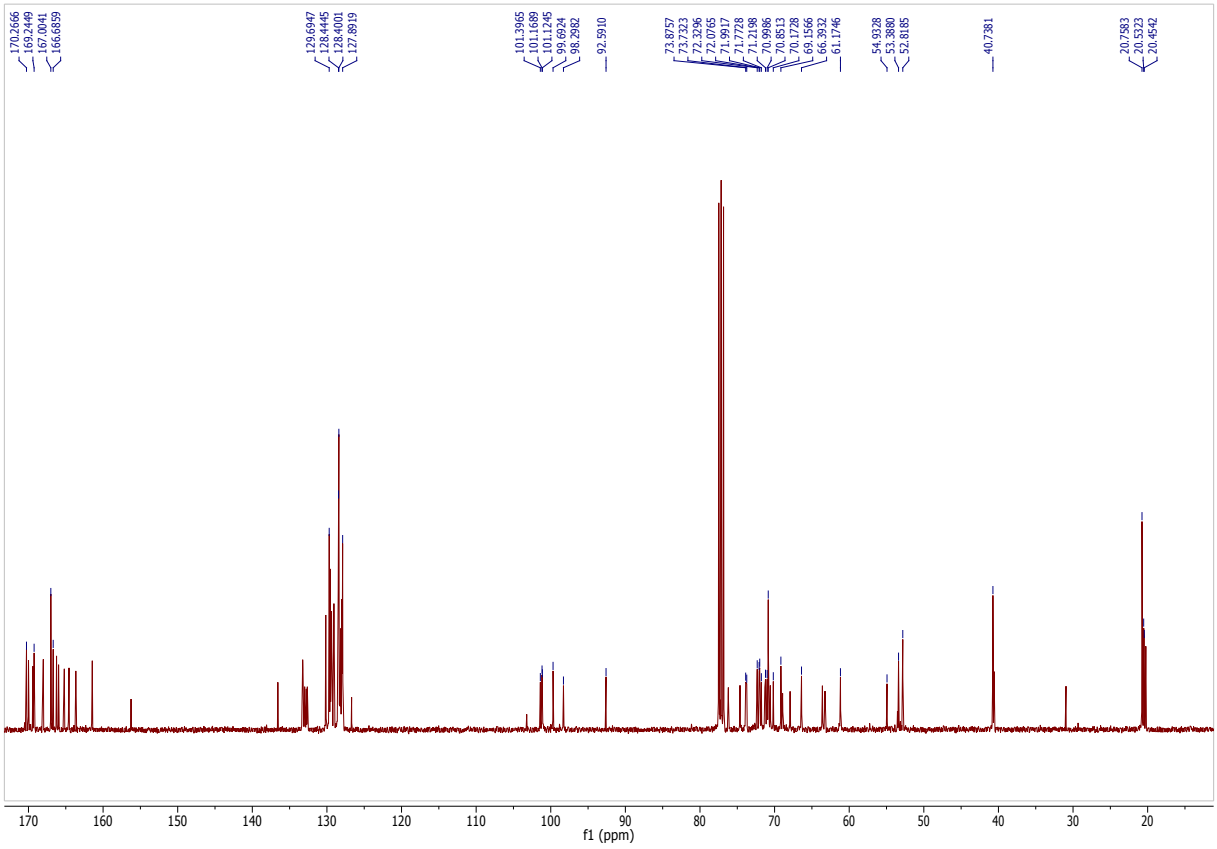
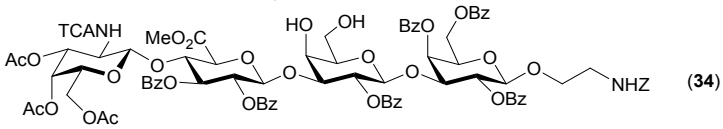




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **34**



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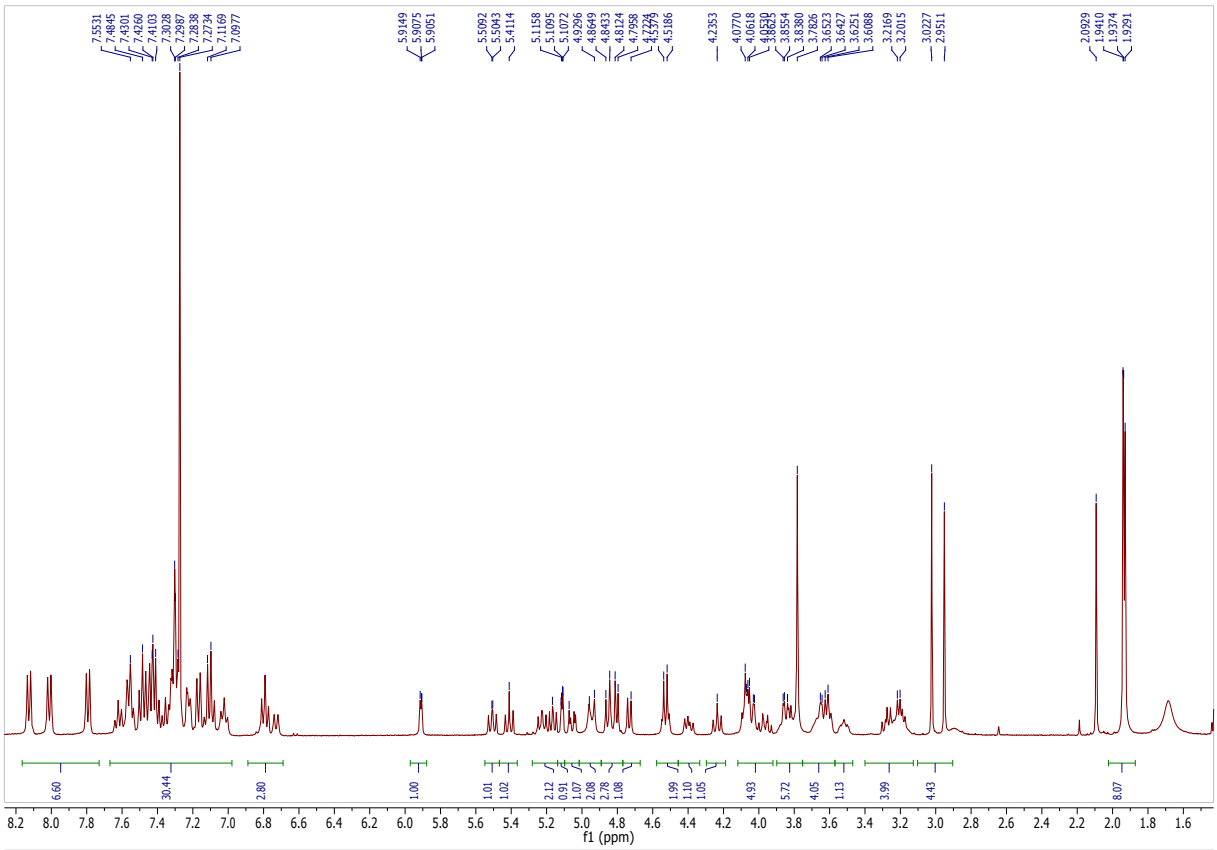
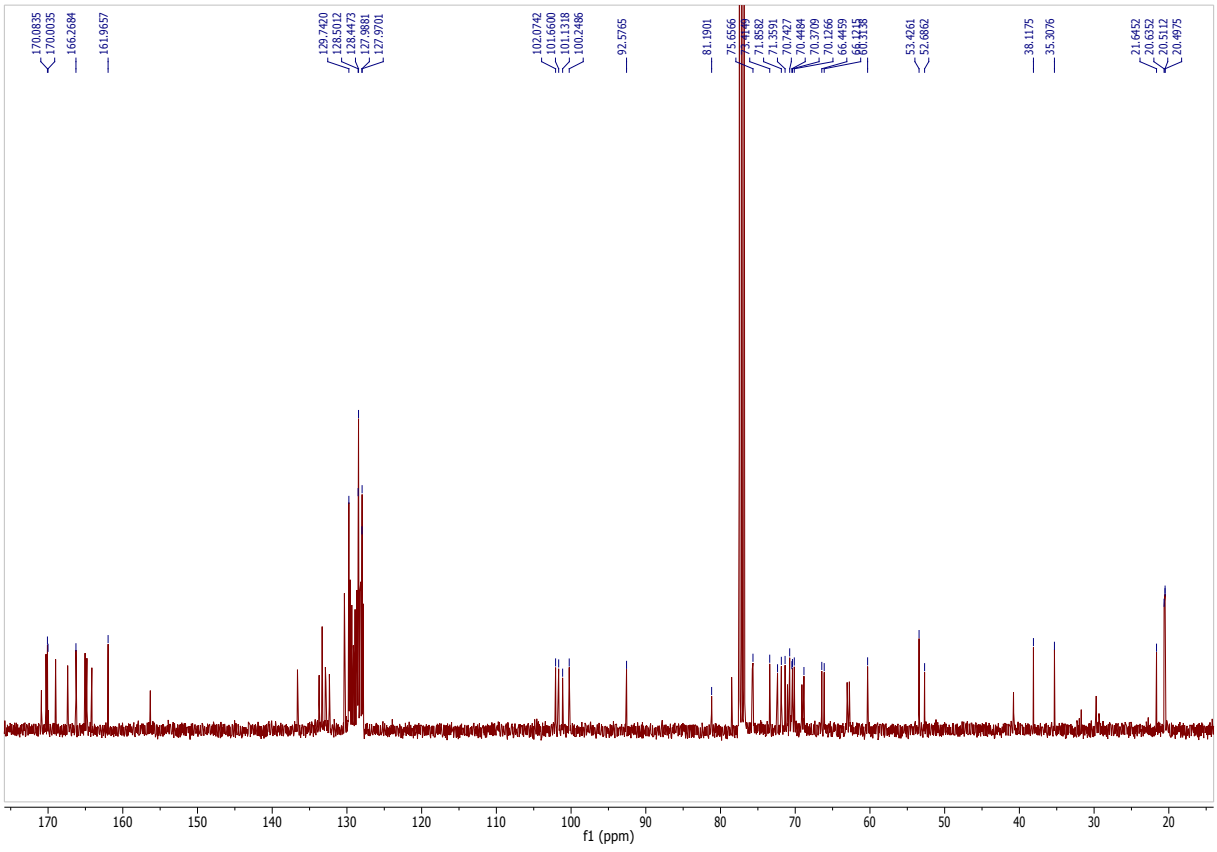
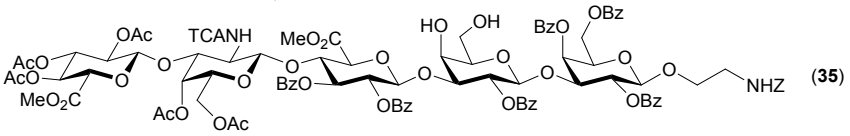




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **35**



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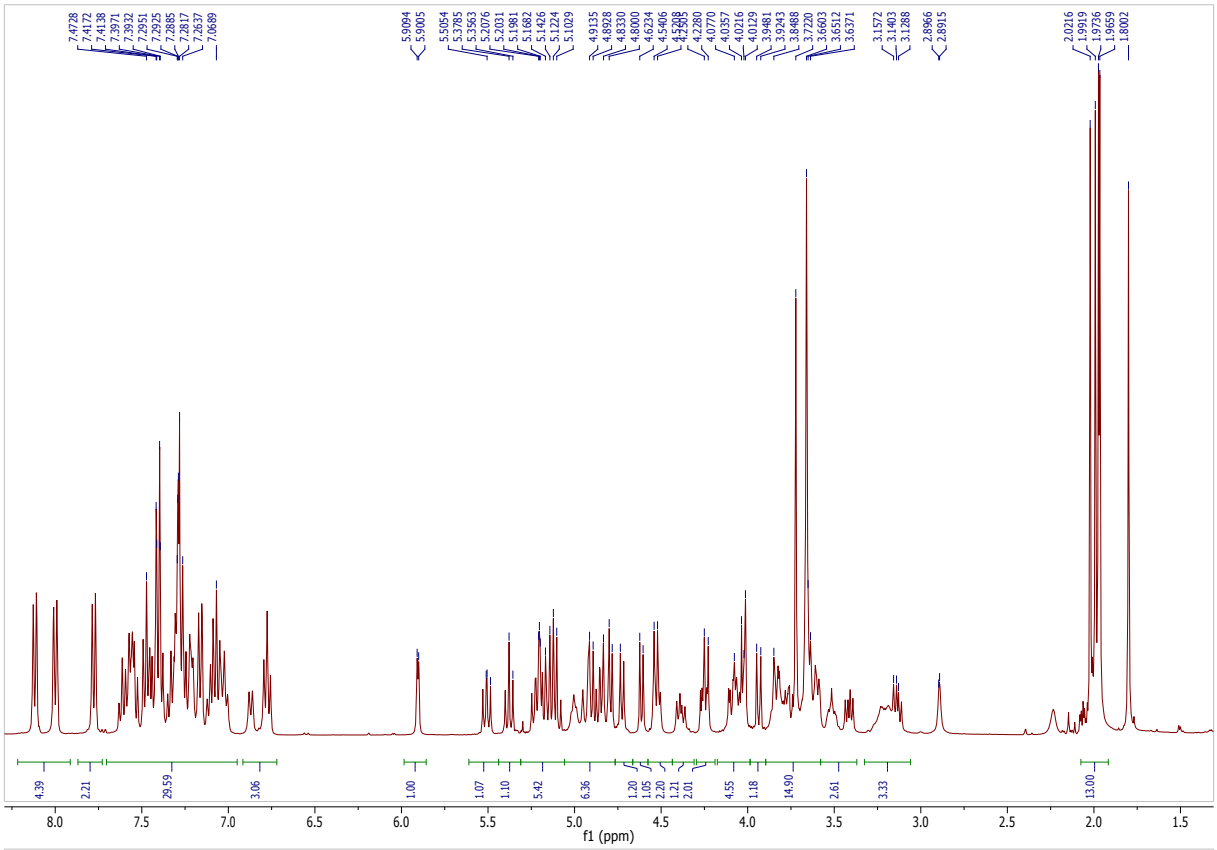
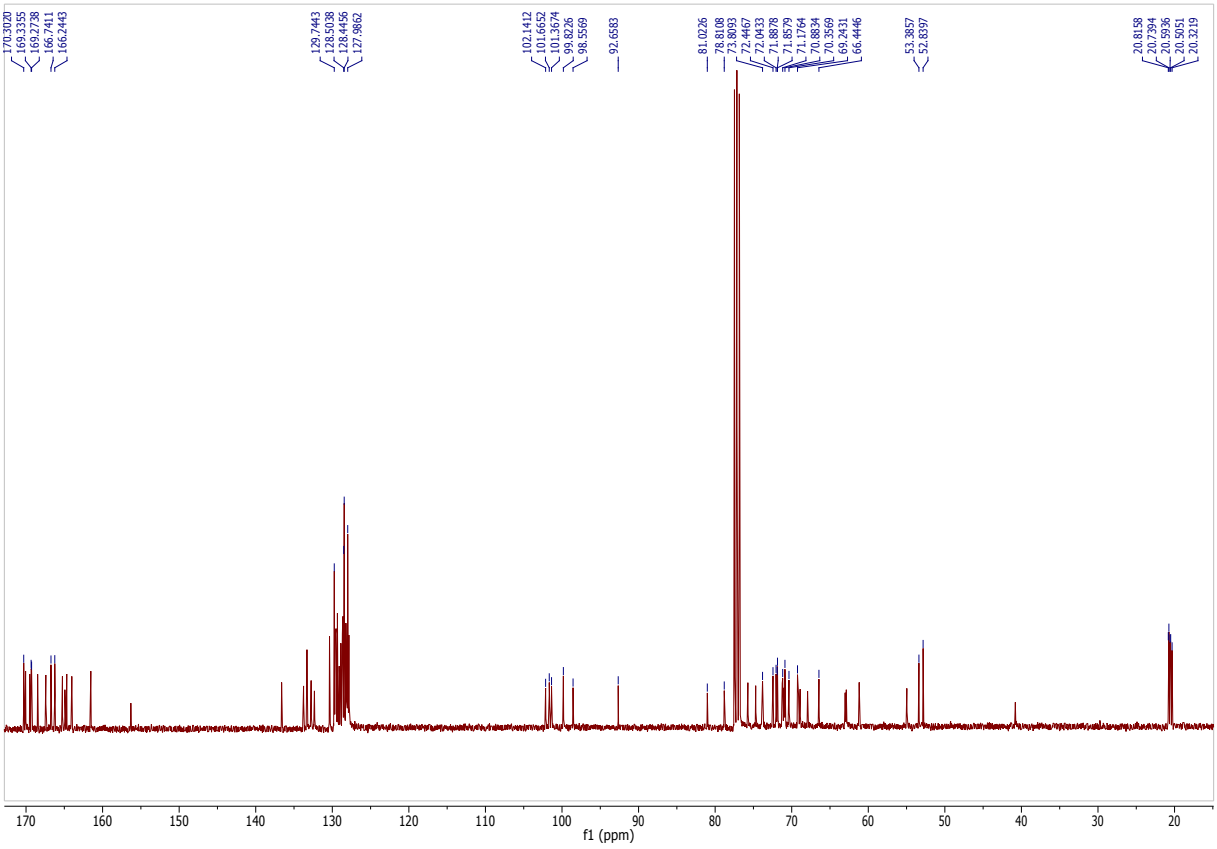
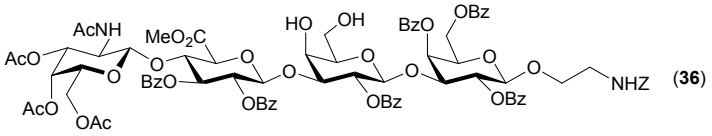




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **36**



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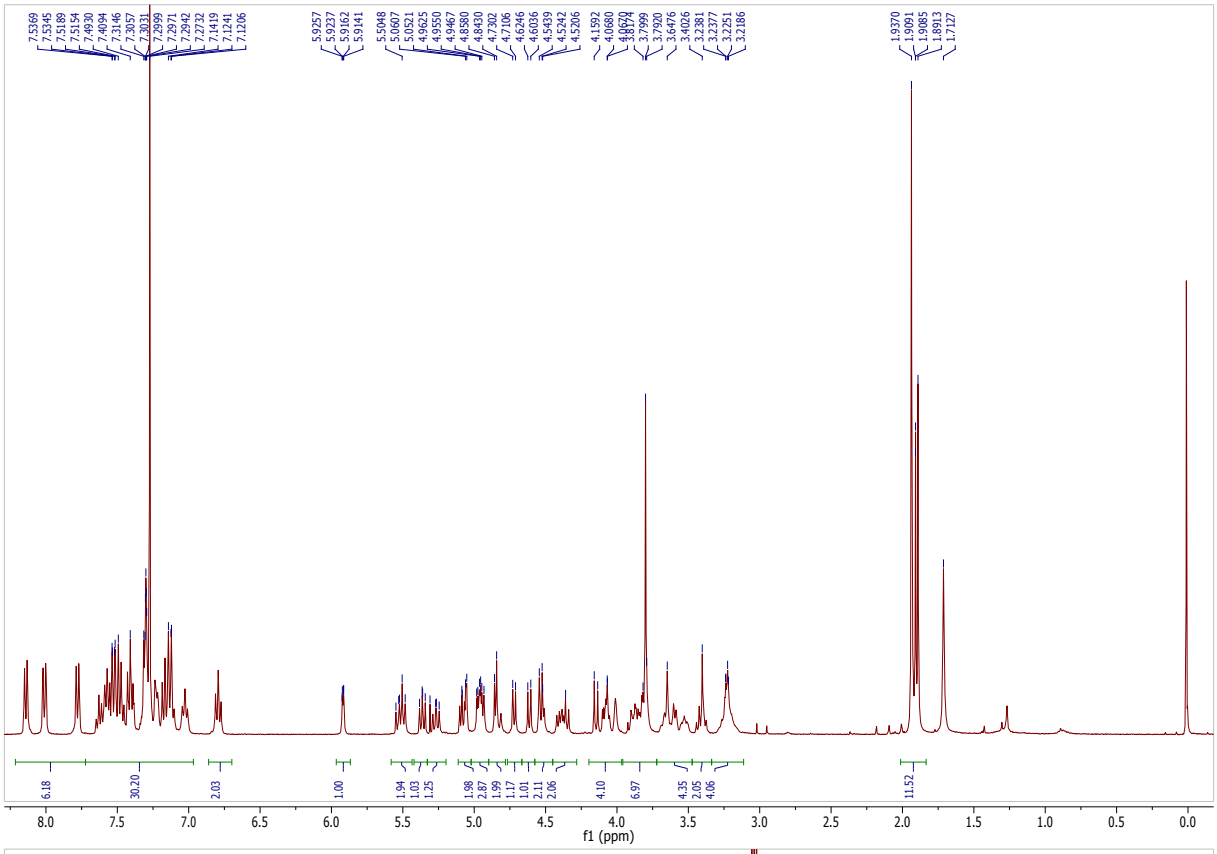
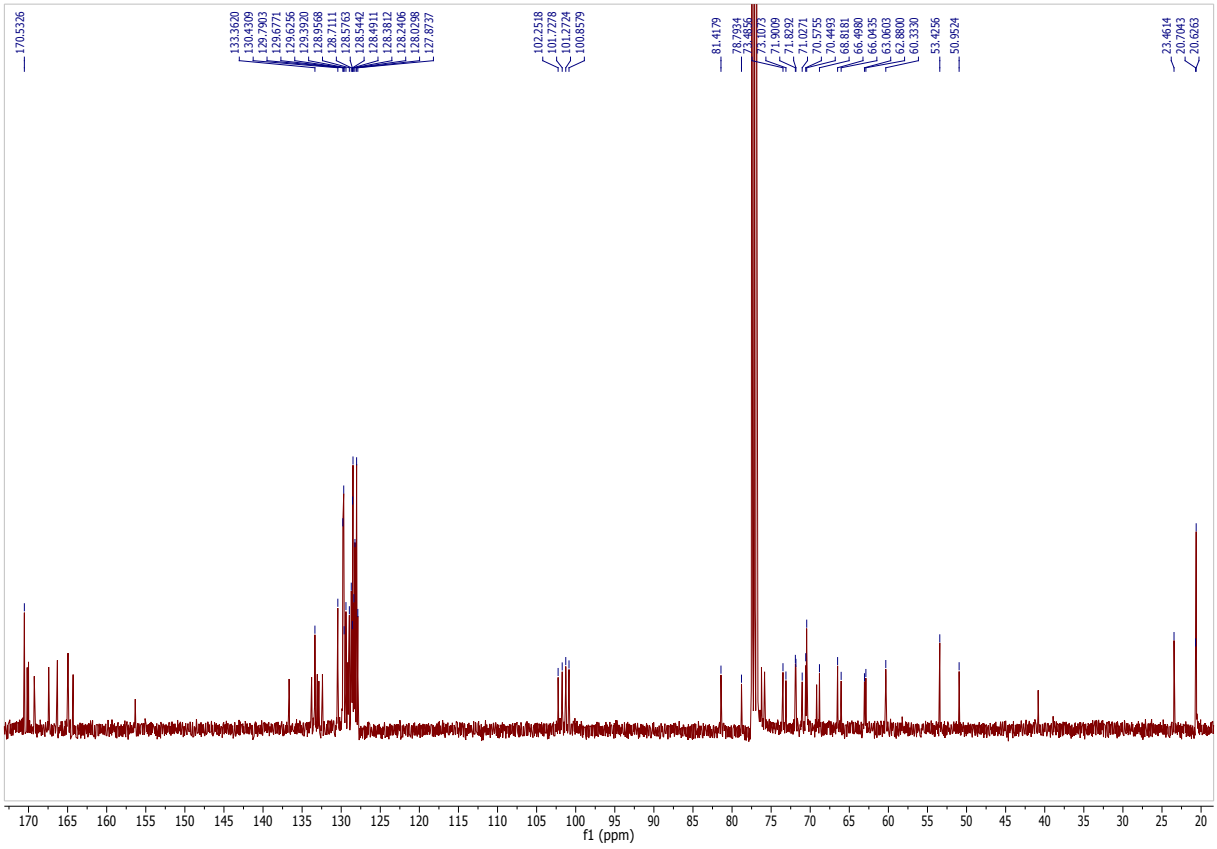
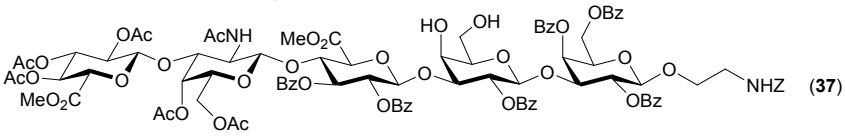




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **37**



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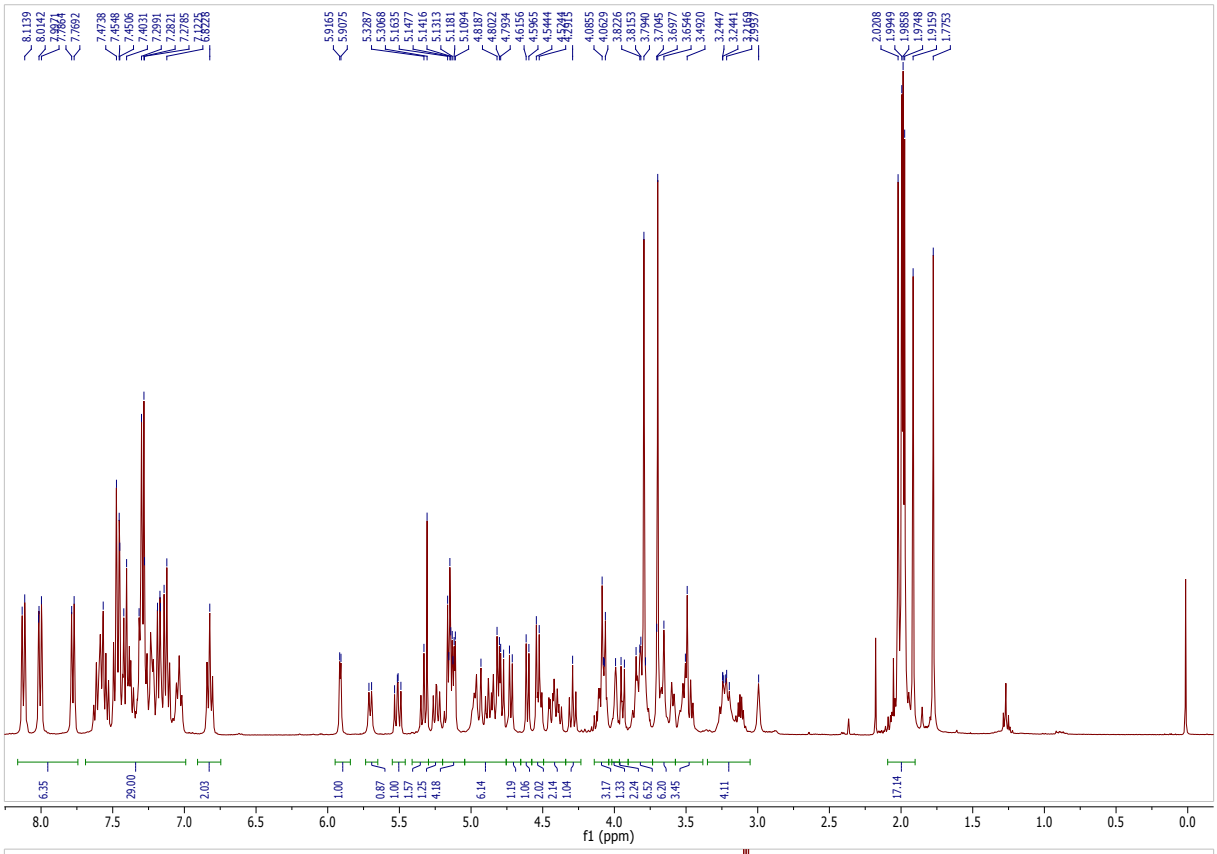
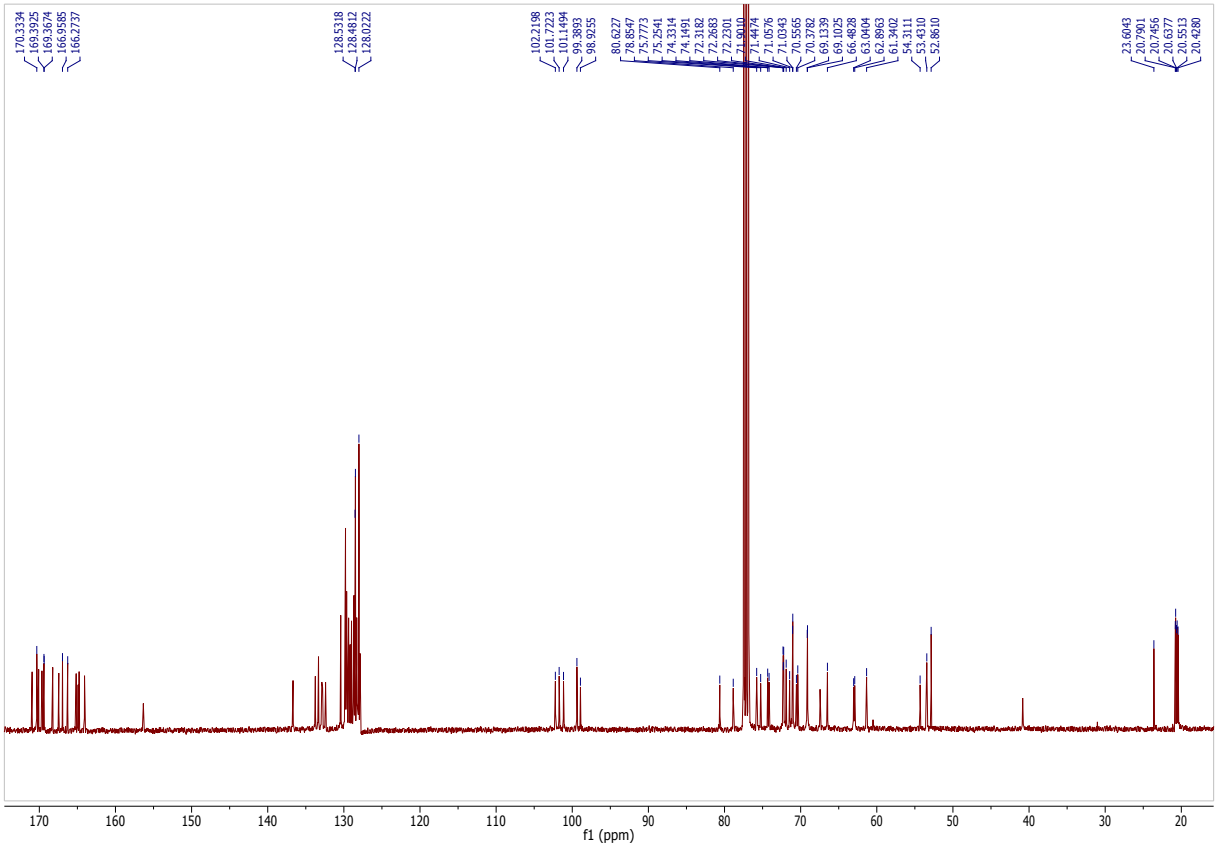
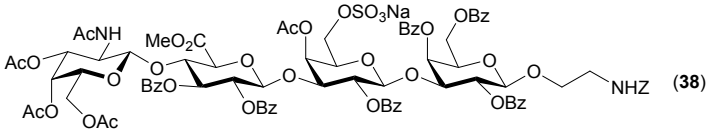




^{1}H NMR and ^{13}C NMR ($CD_3OD/CDCl_3$ 1/1, 400 MHz) for compound **38**



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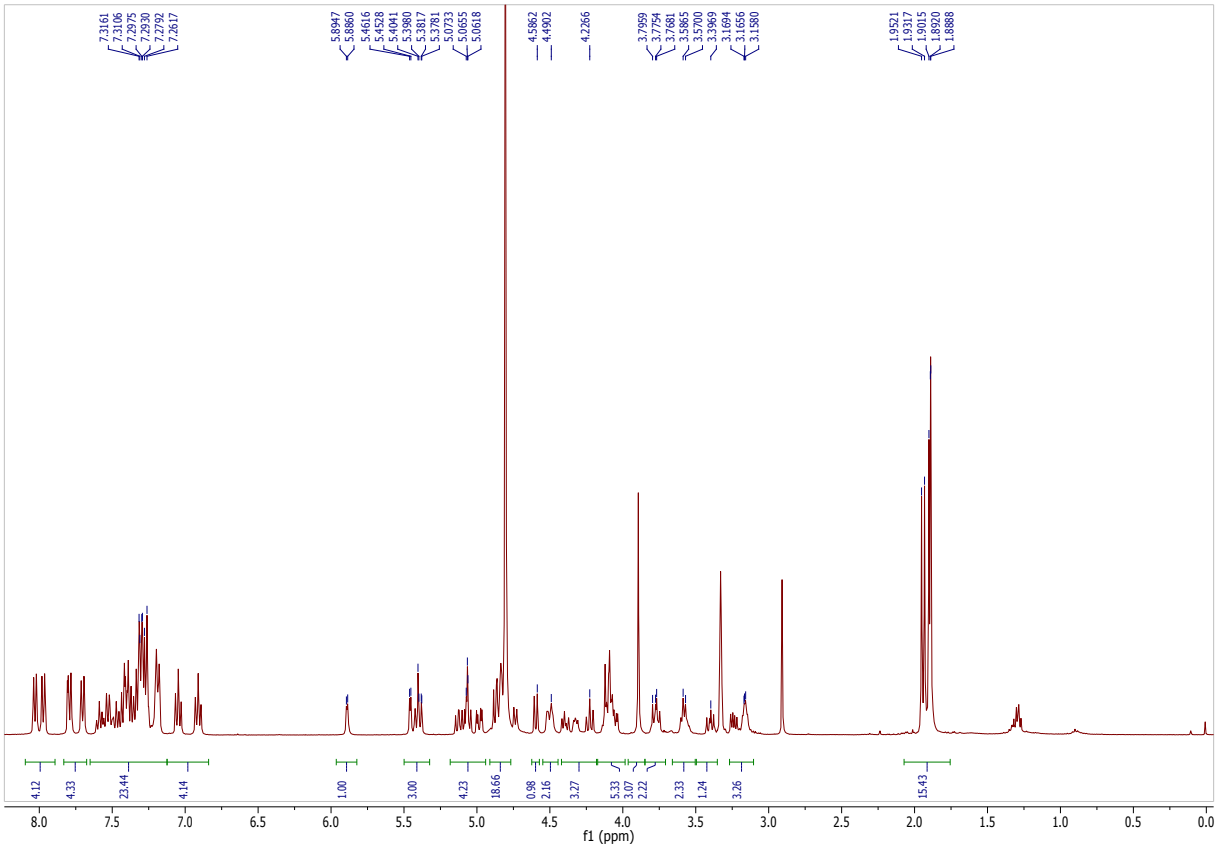
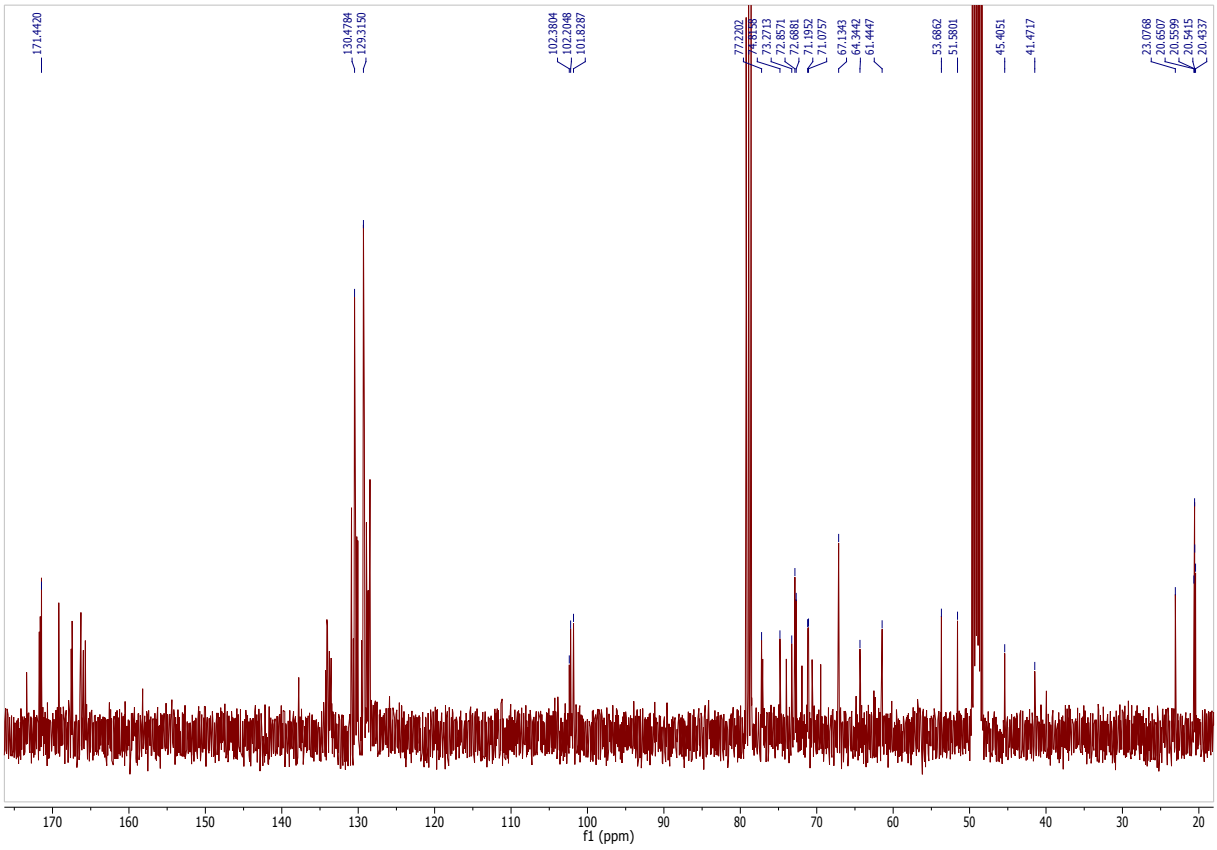
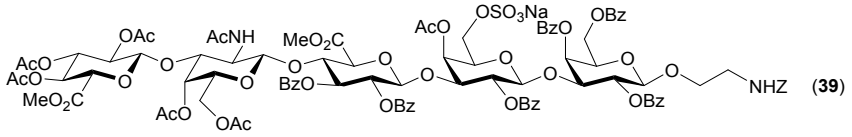




^{1}H NMR and ^{13}C NMR (CD_3OD, 400 MHz) for compound **39**



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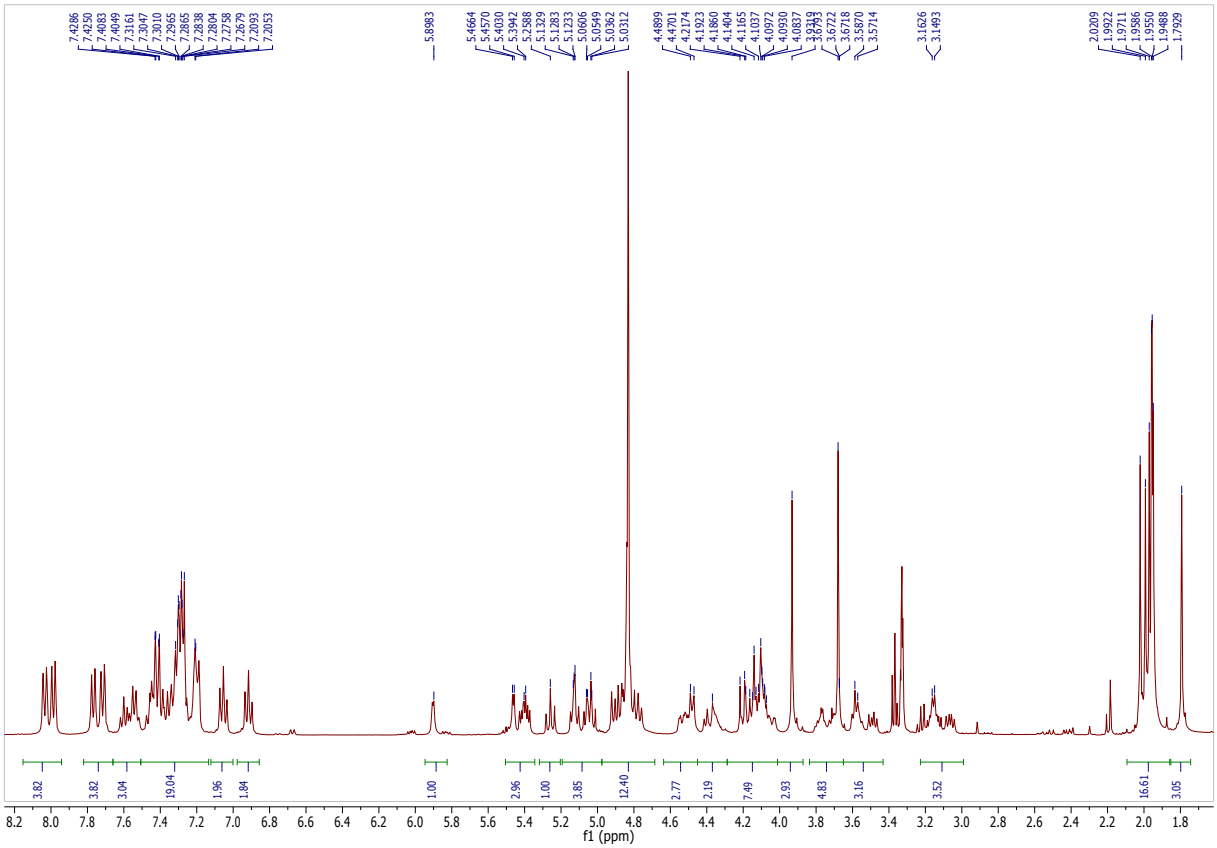
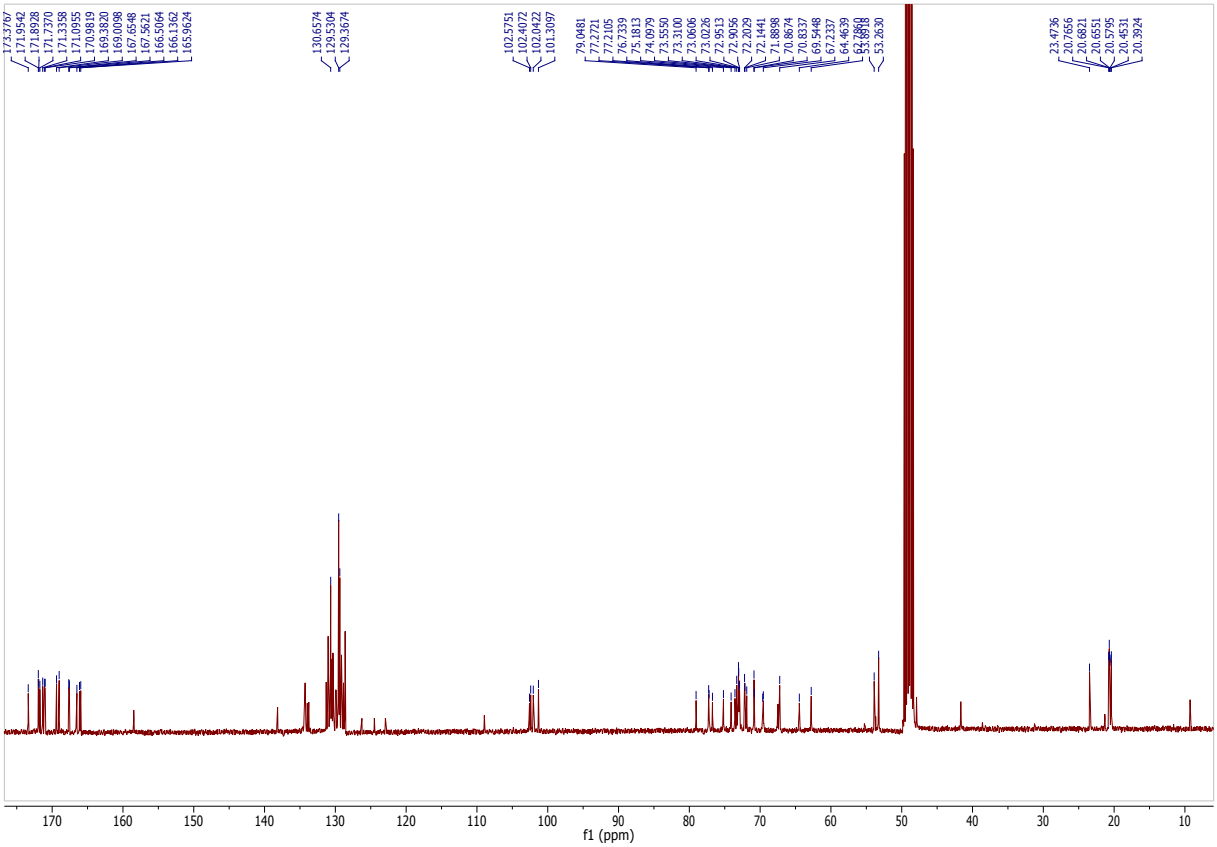
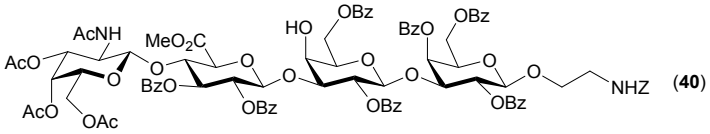




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **40**



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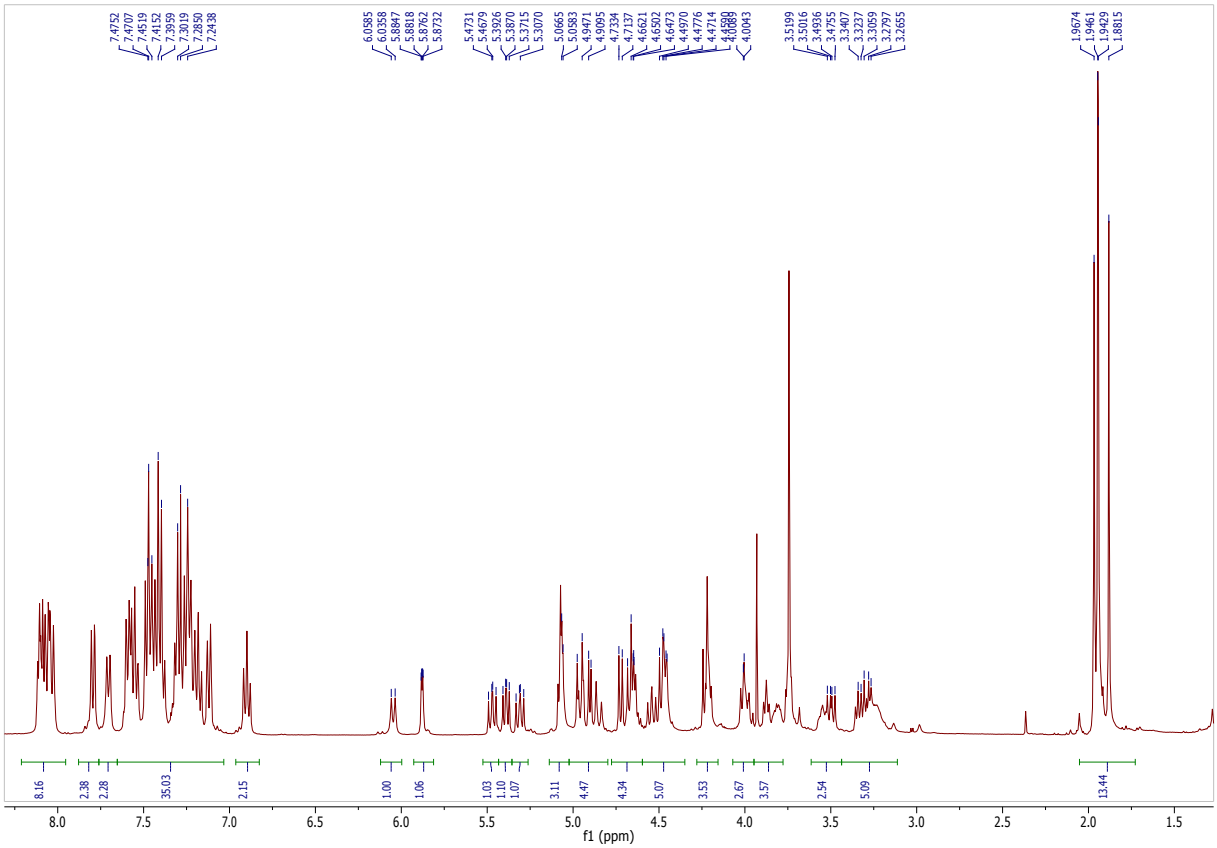
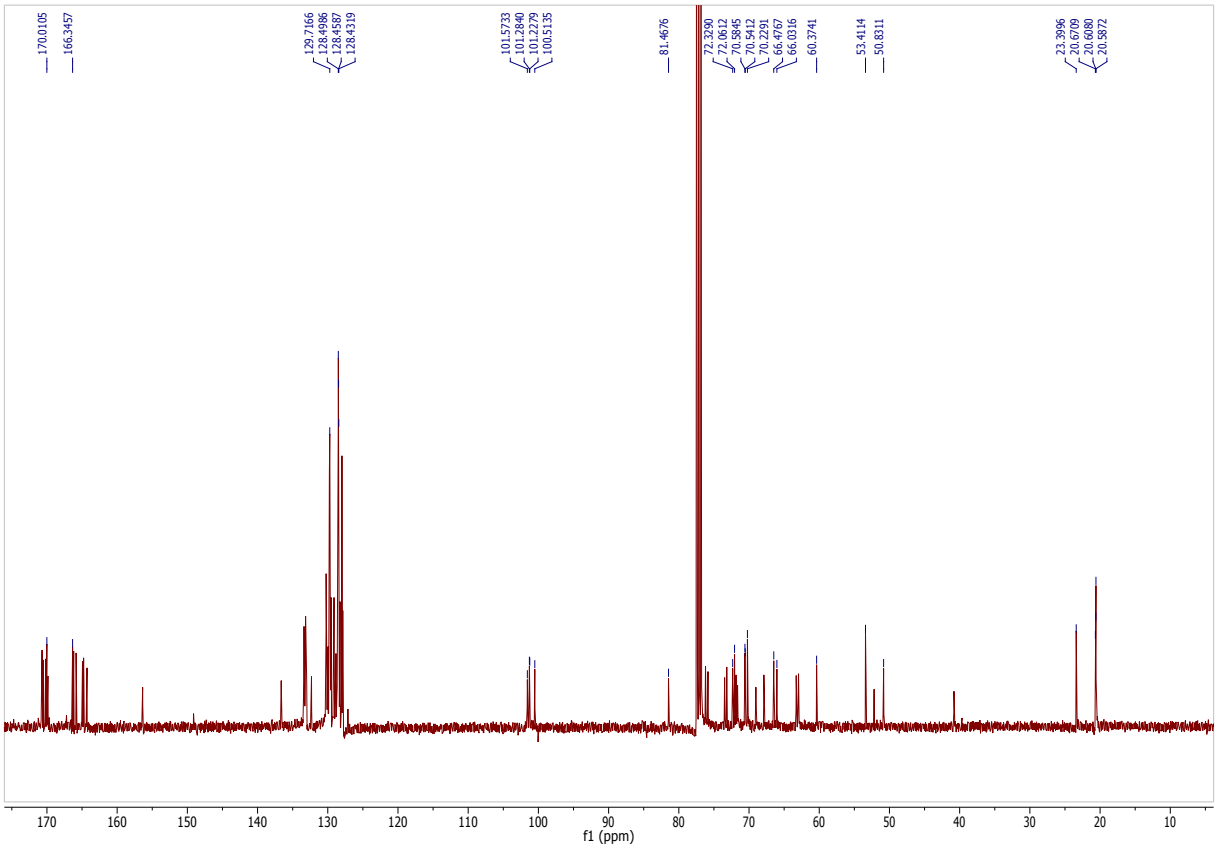
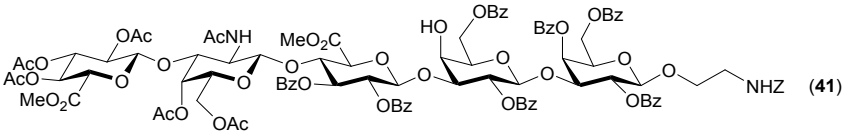




^{1}H NMR and ^{13}C NMR ($CDCl_3$, 400 MHz) for compound **41**



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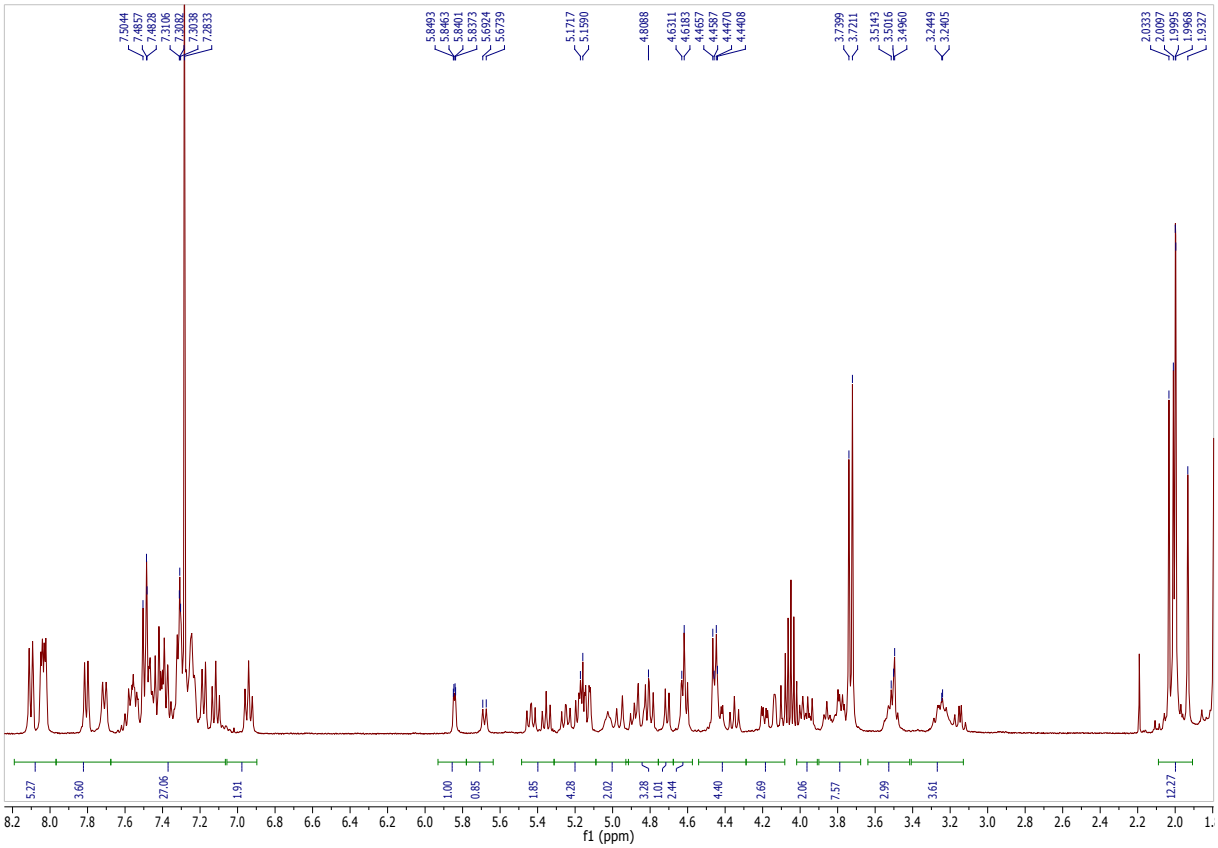
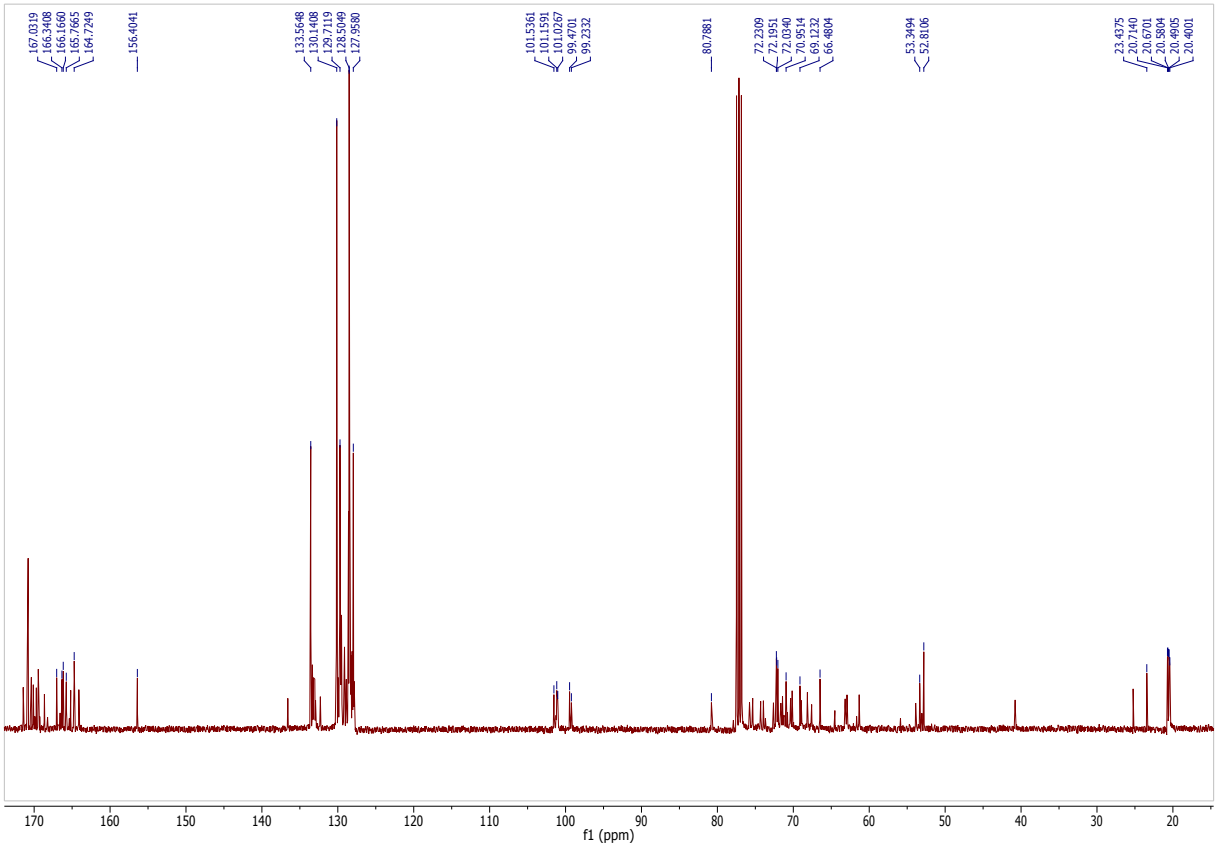
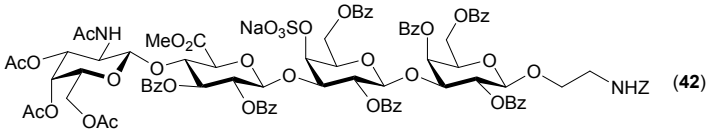




^{1}H NMR and ^{13}C NMR ($CD_3OD/CDCl_3$ 1/1, 400 MHz) for compound **42**



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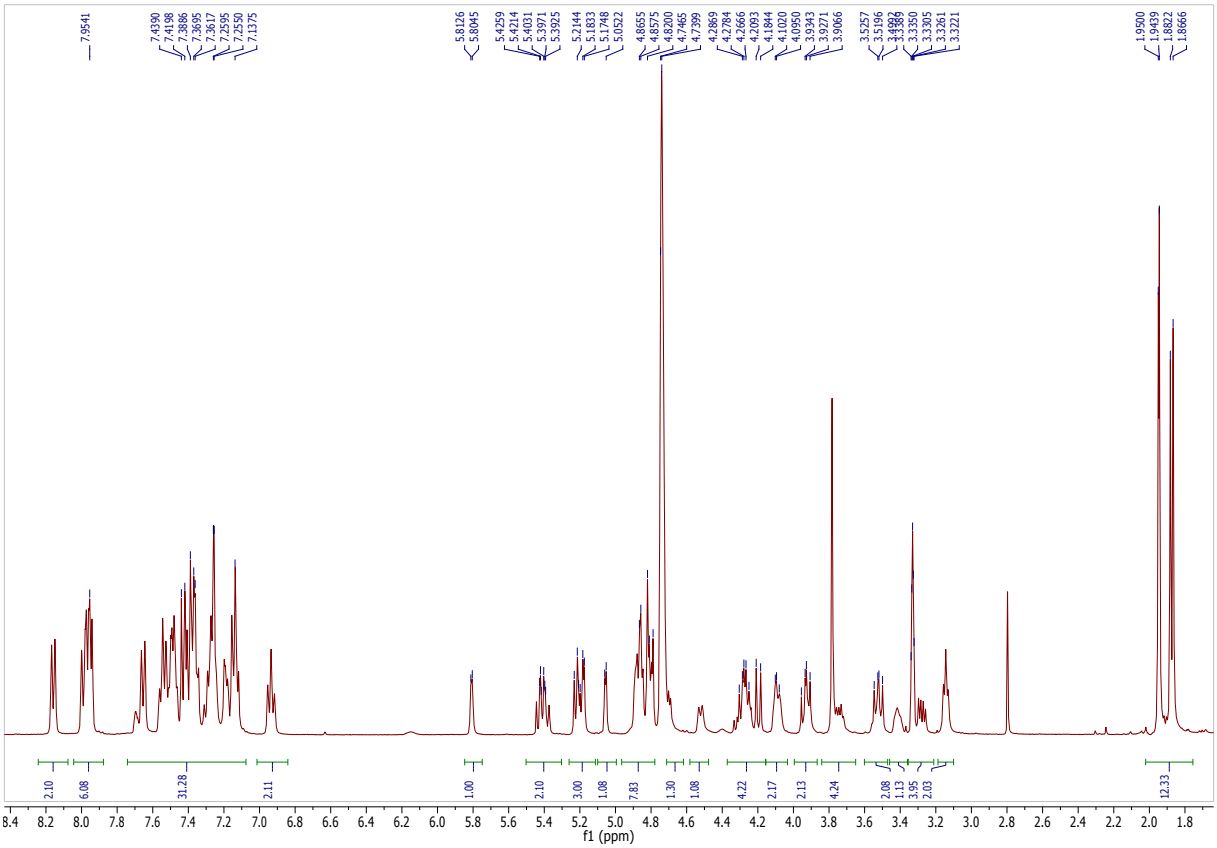
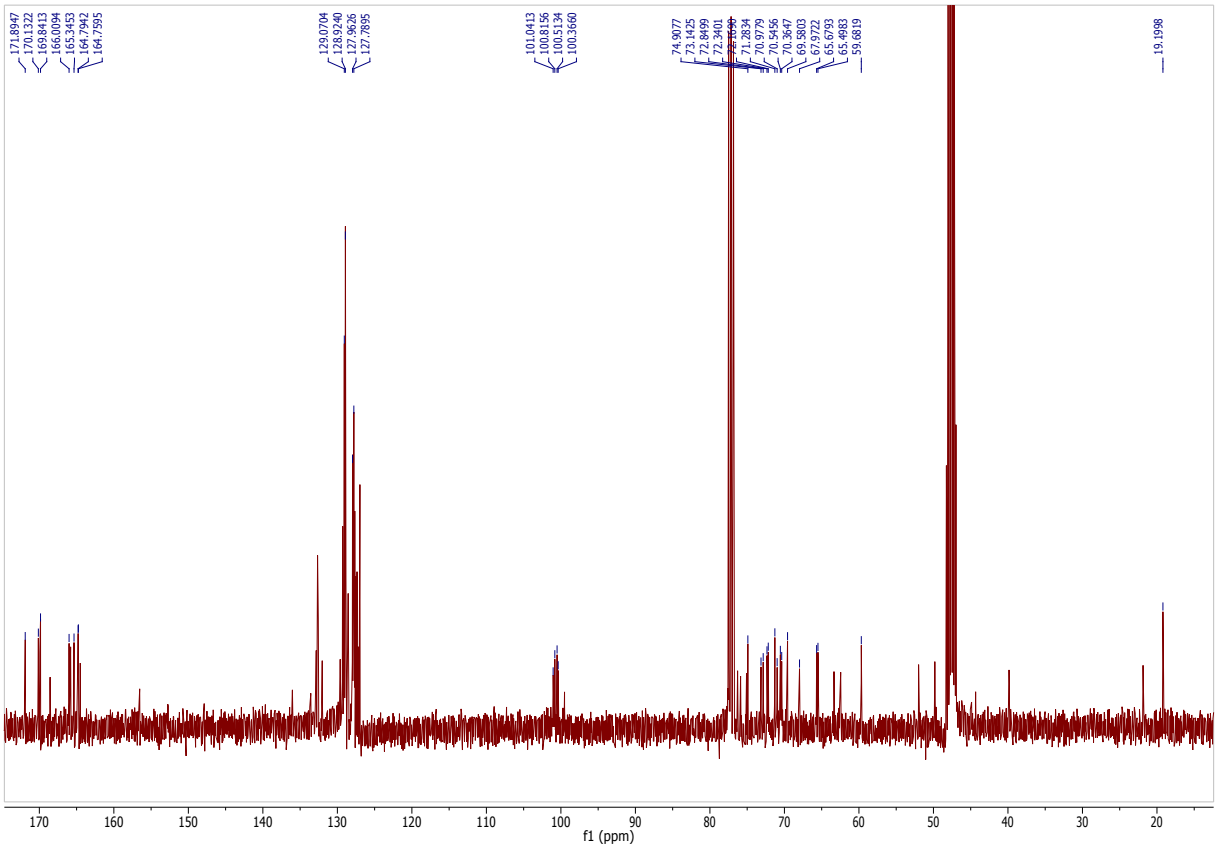
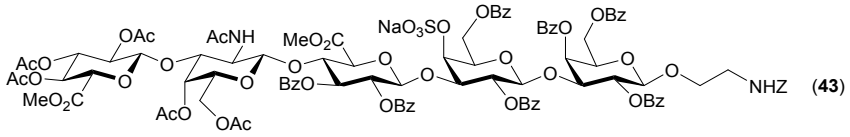




^{1}H NMR and ^{13}C NMR (CD_3OD, 400 MHz) for compound **43**



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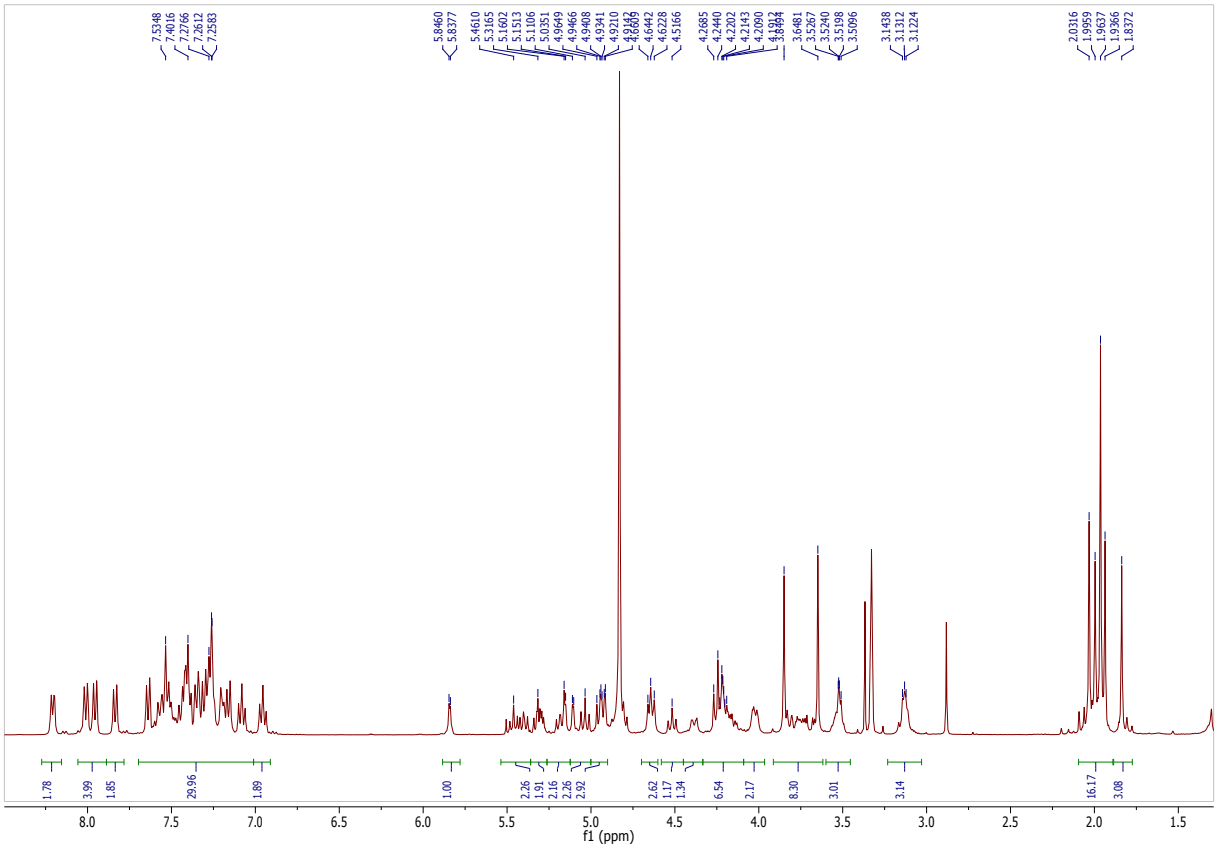
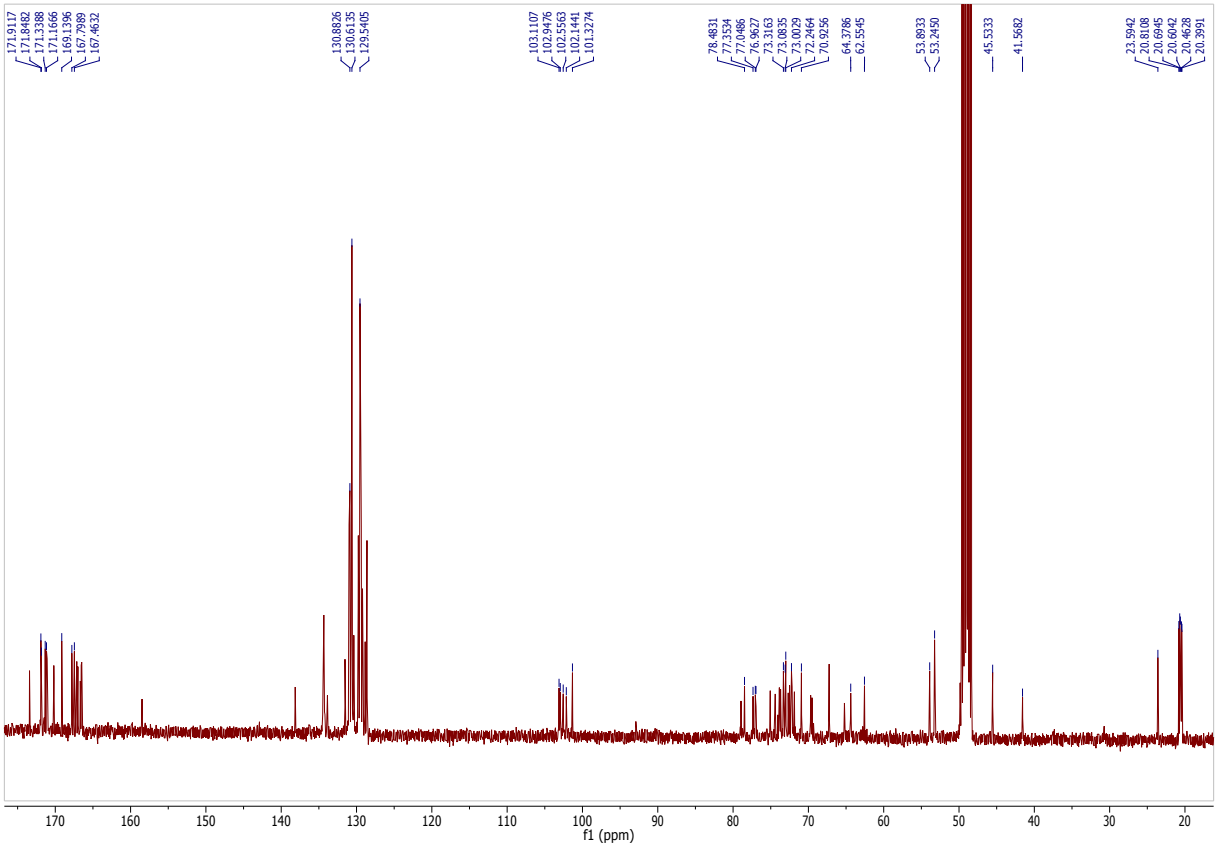
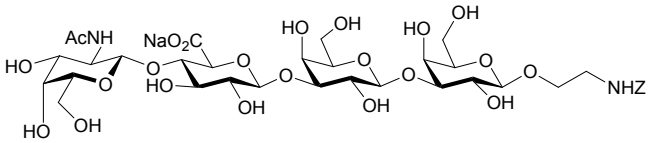




^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **44**



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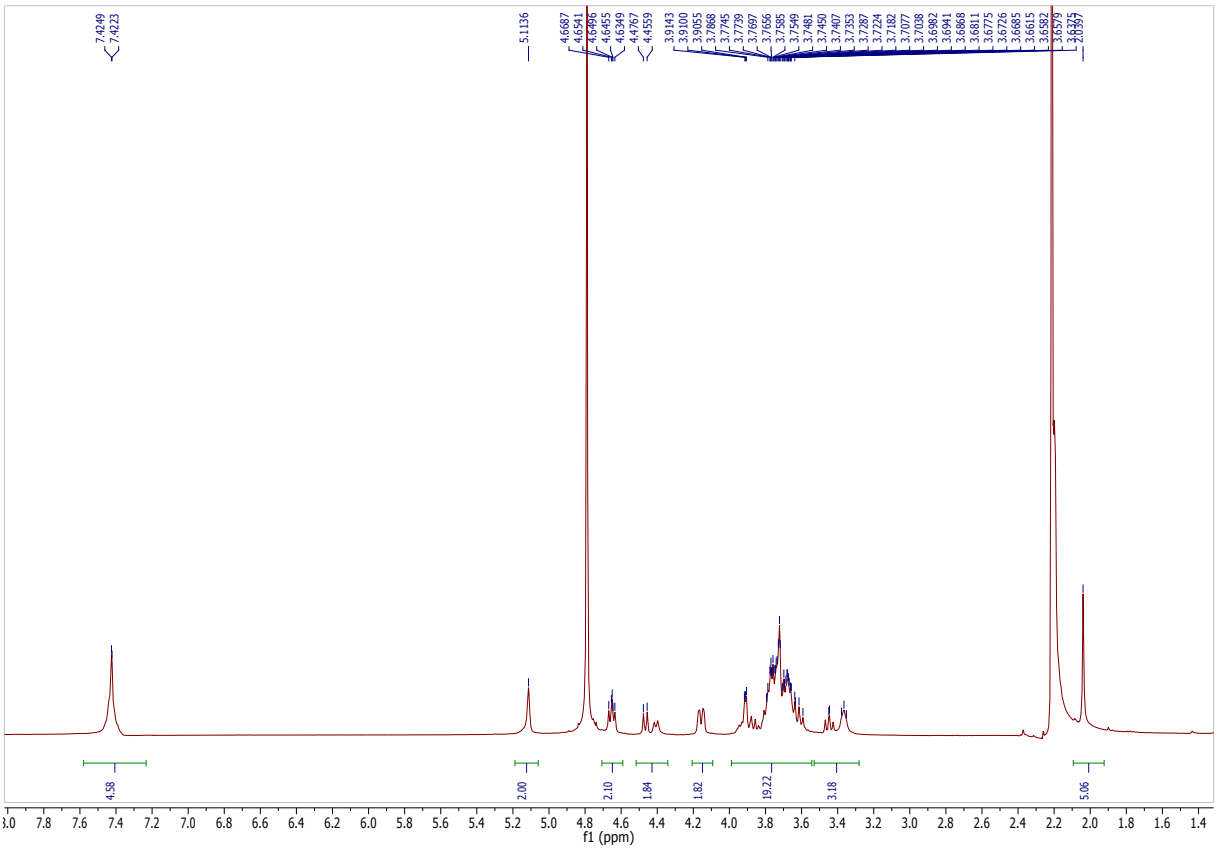
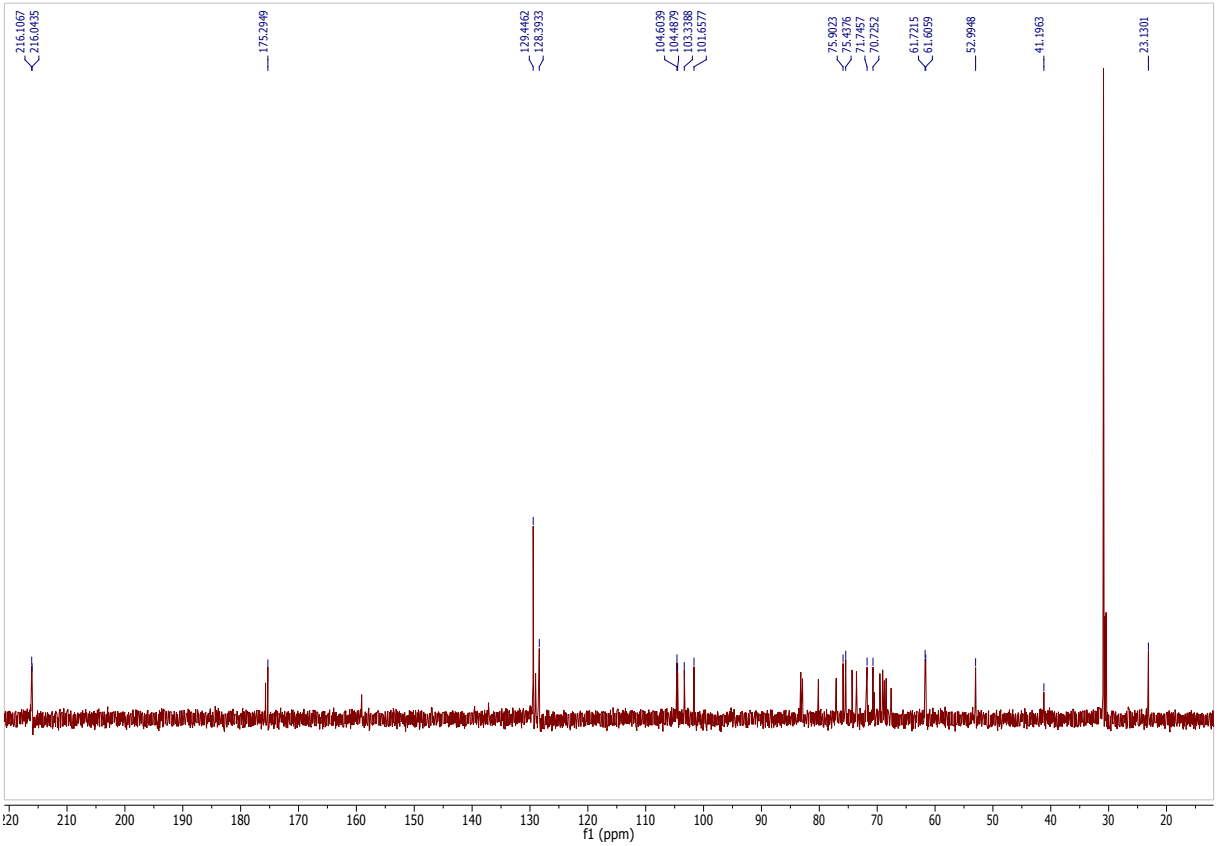
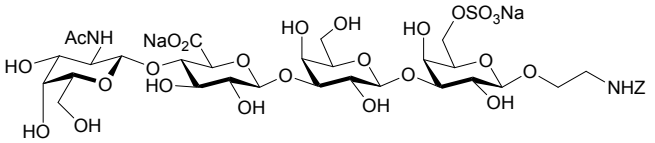




^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **45**



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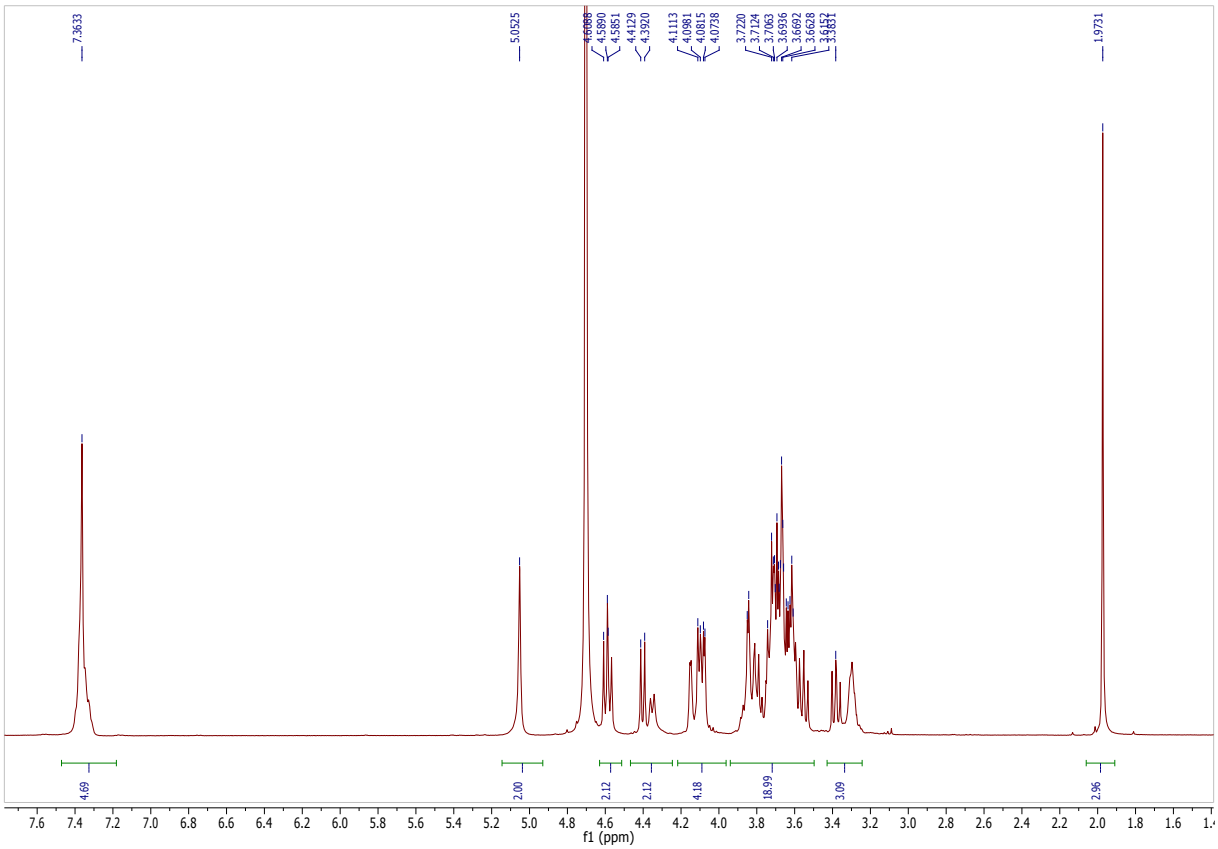
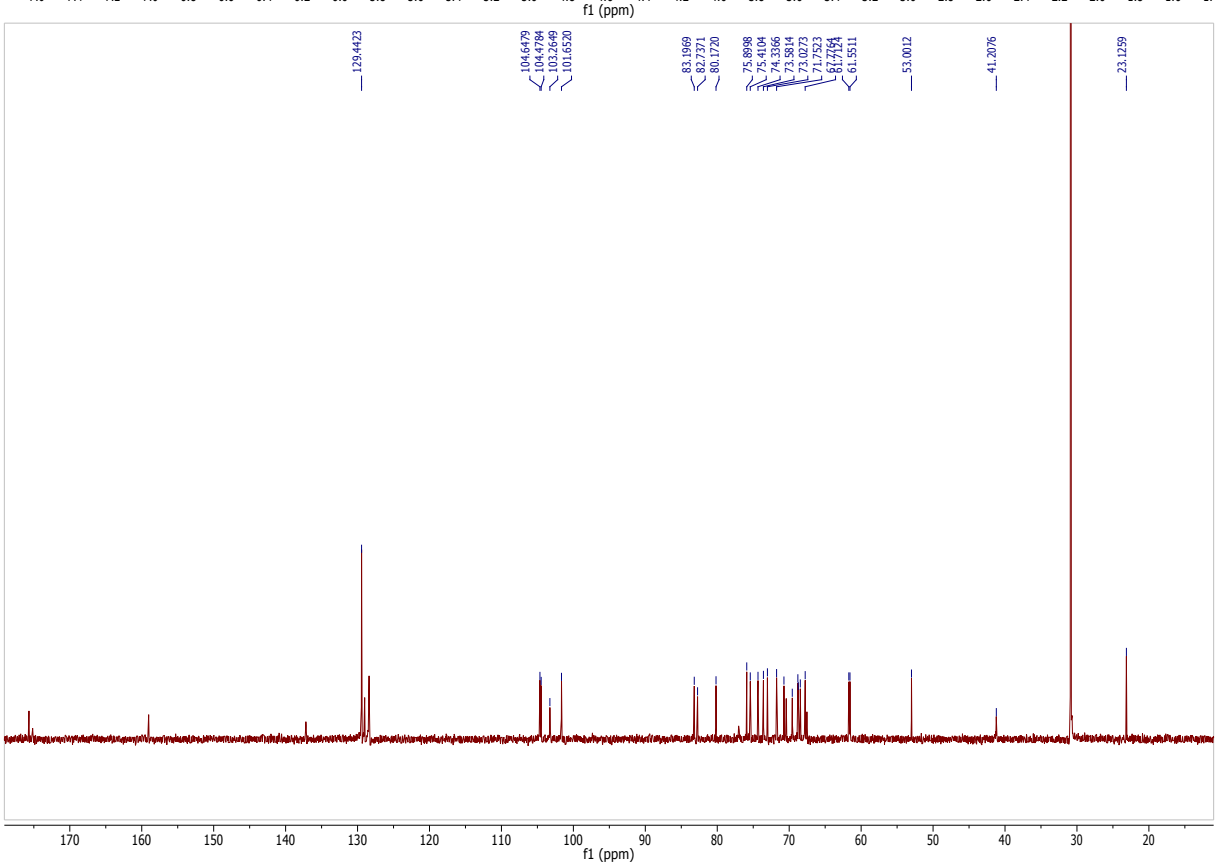
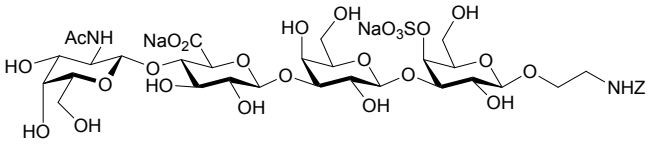
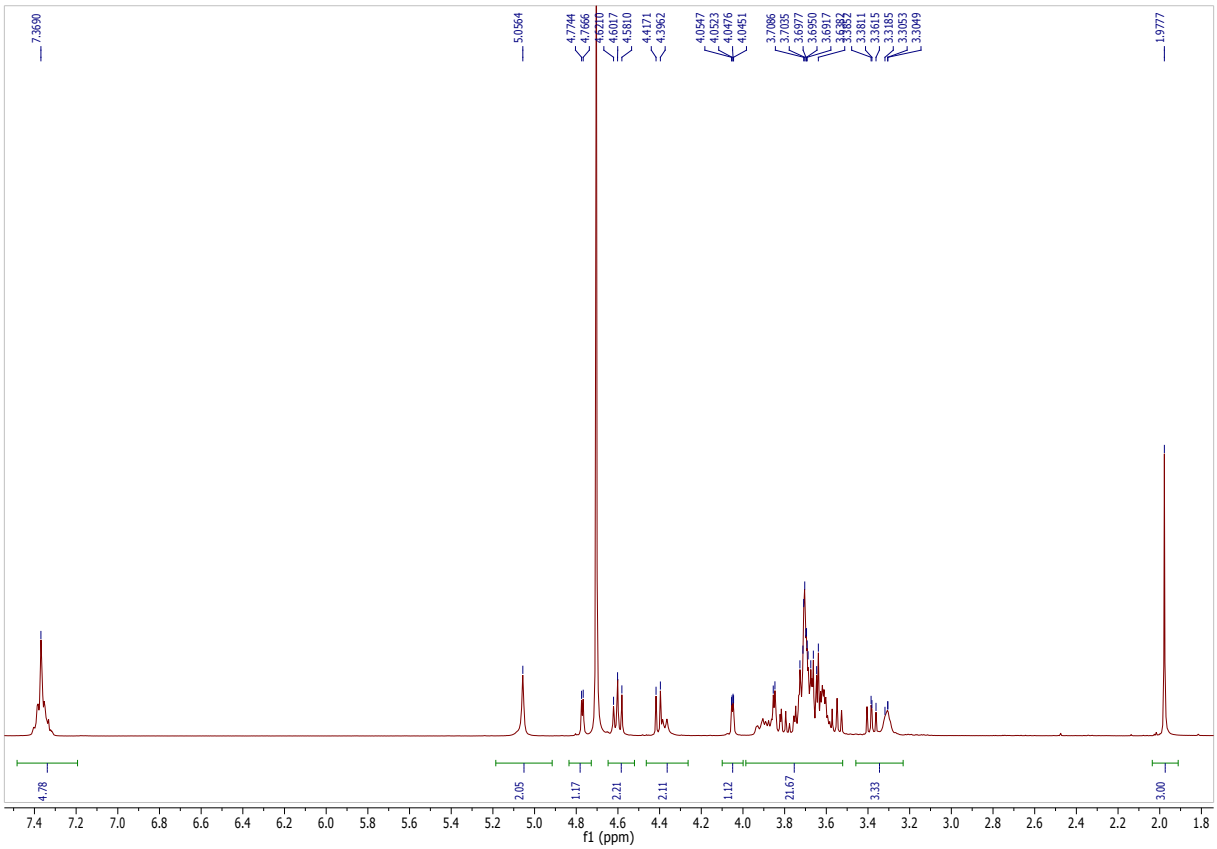


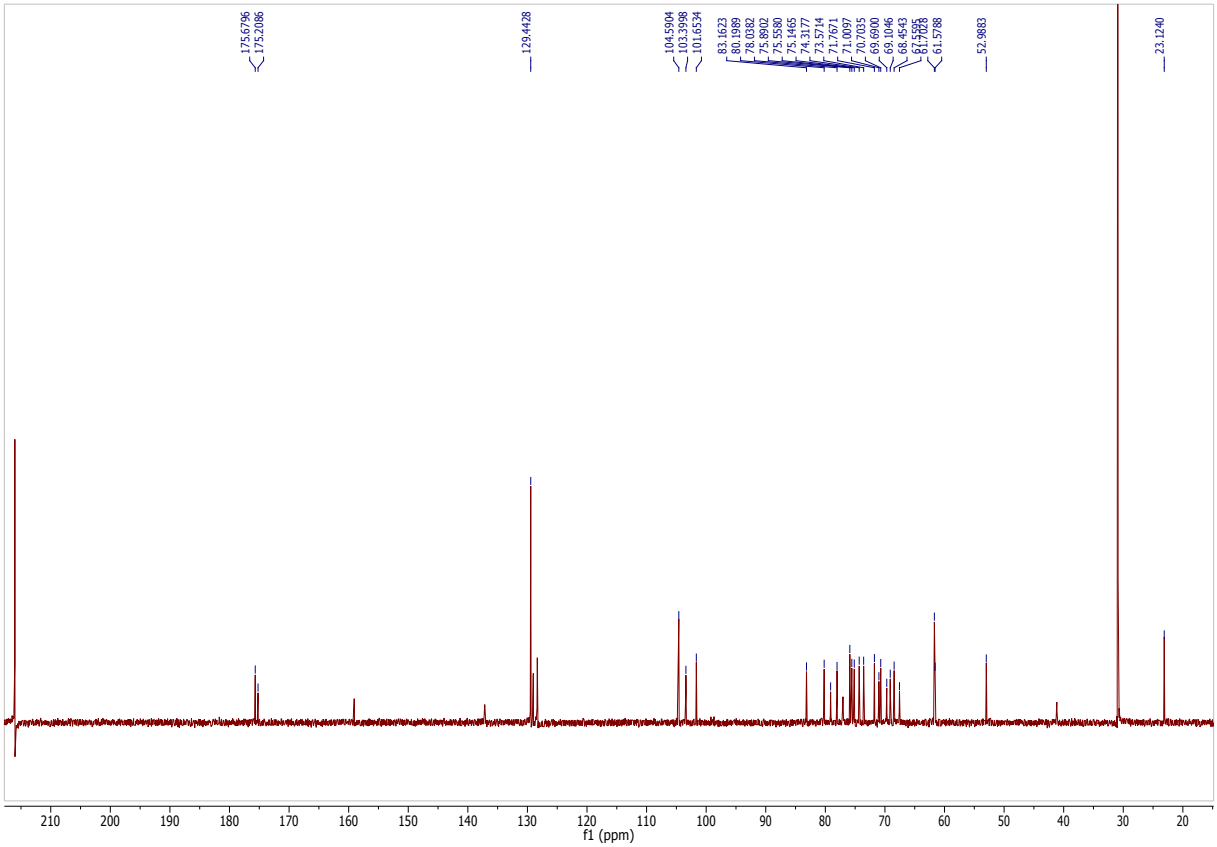


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **46**

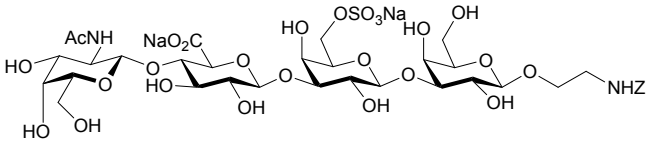


(**46**)

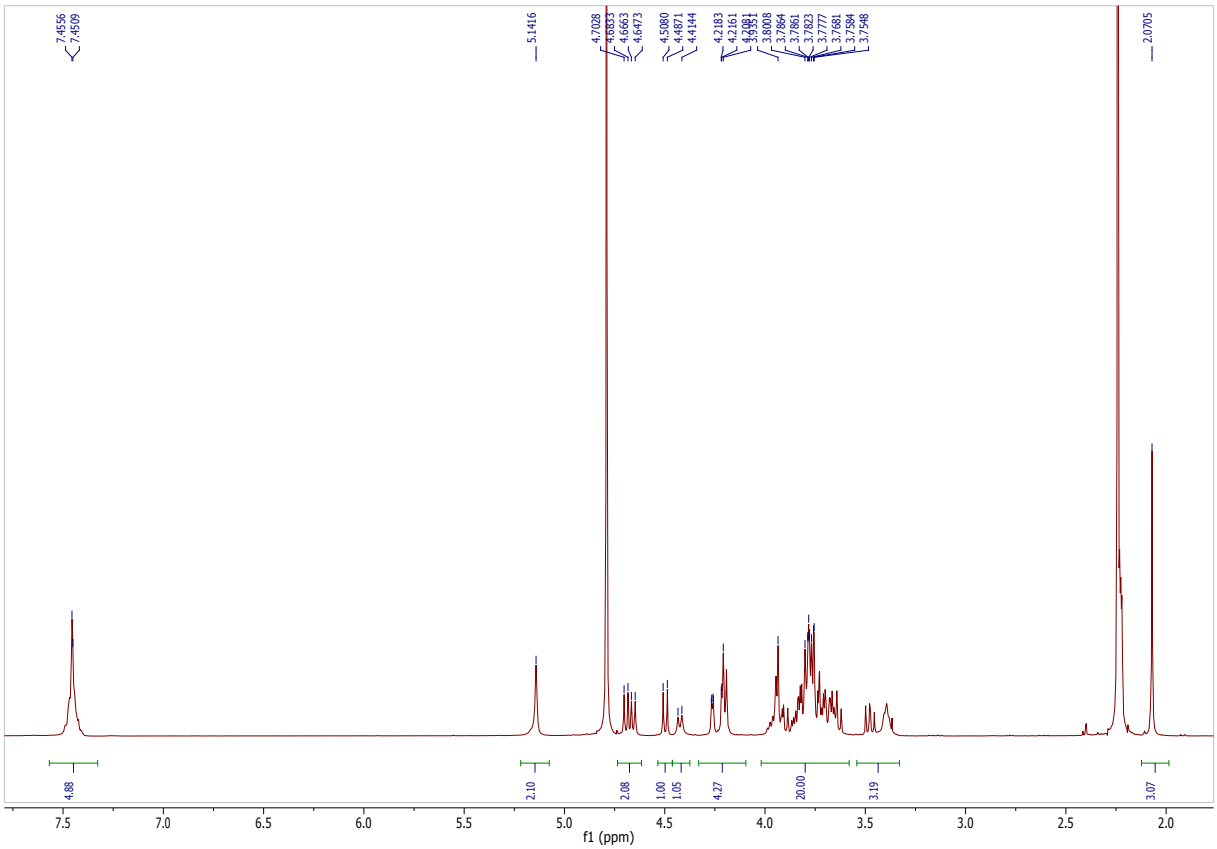


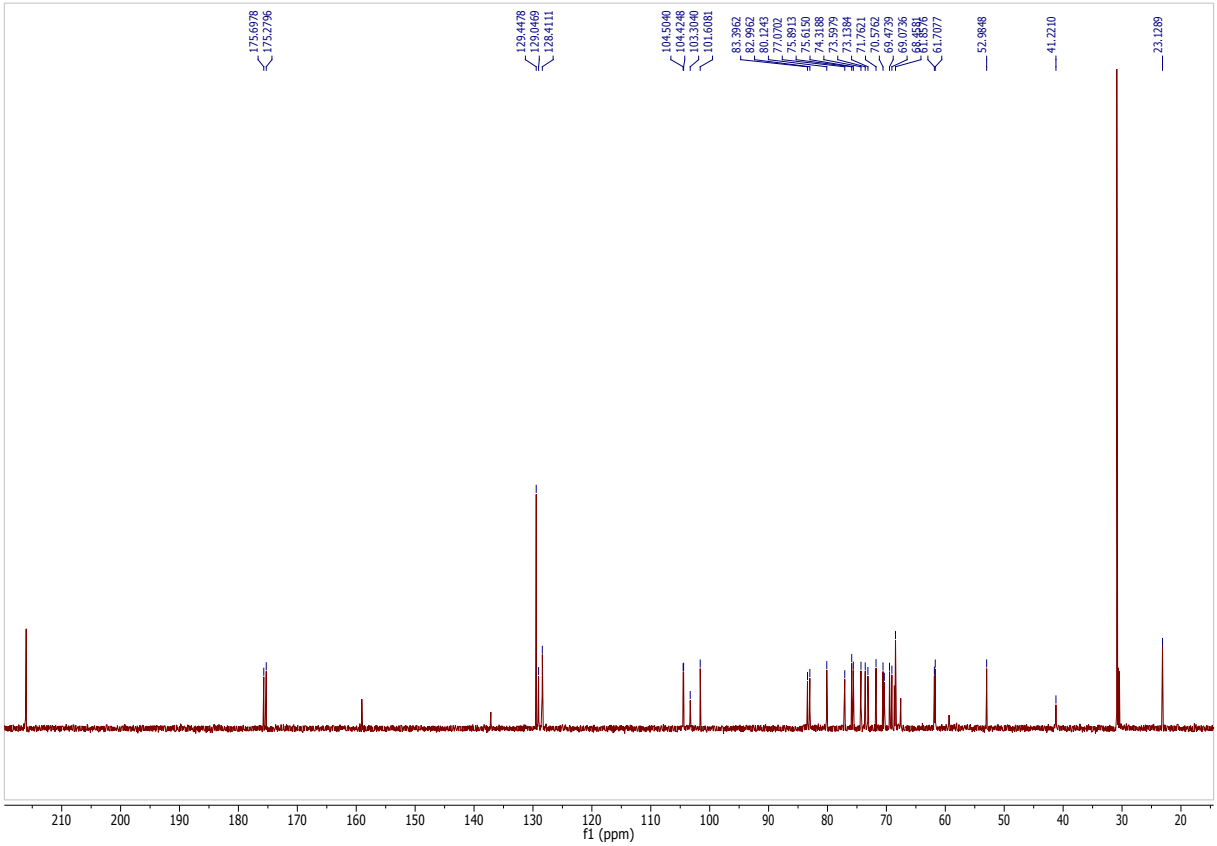


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **47**

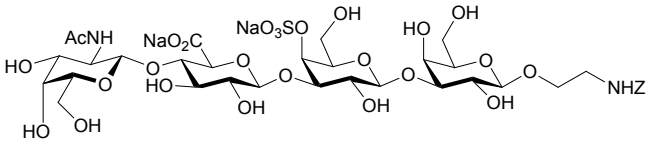


(**47**)

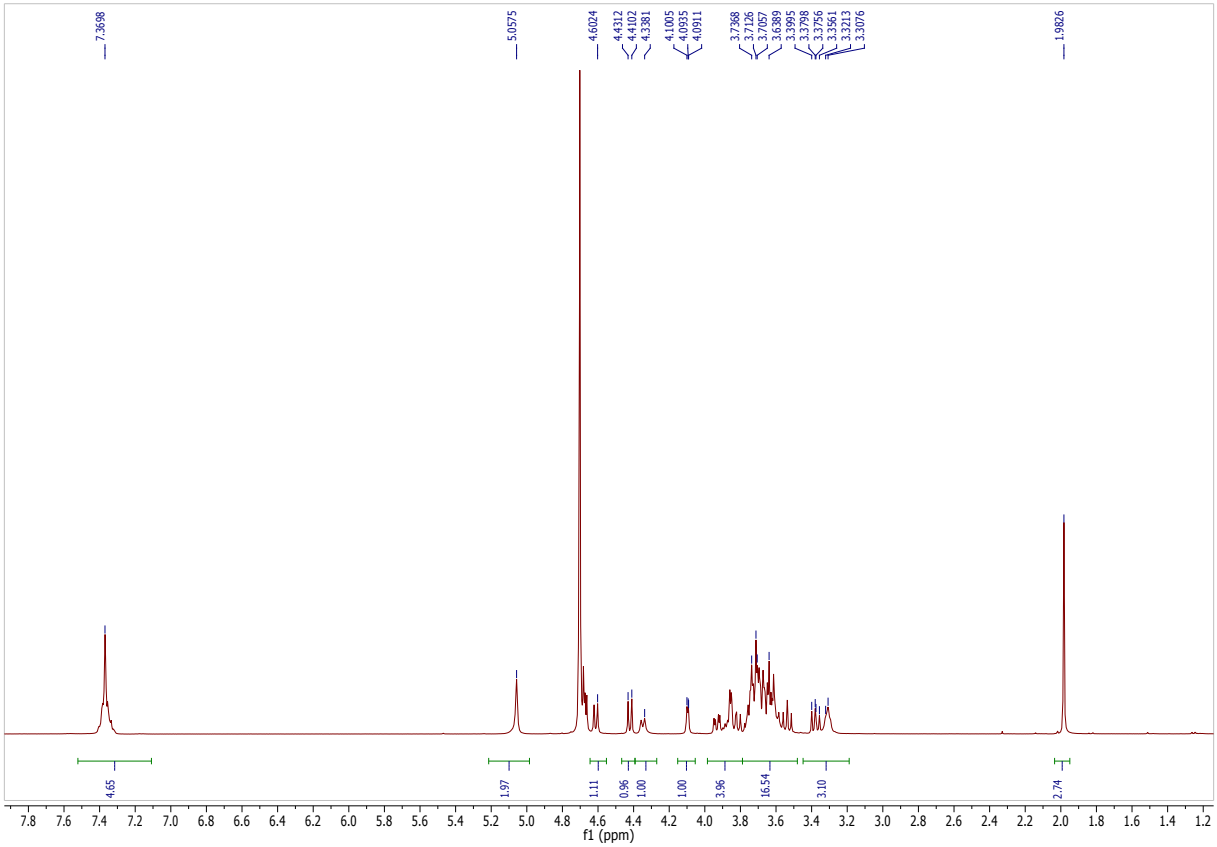


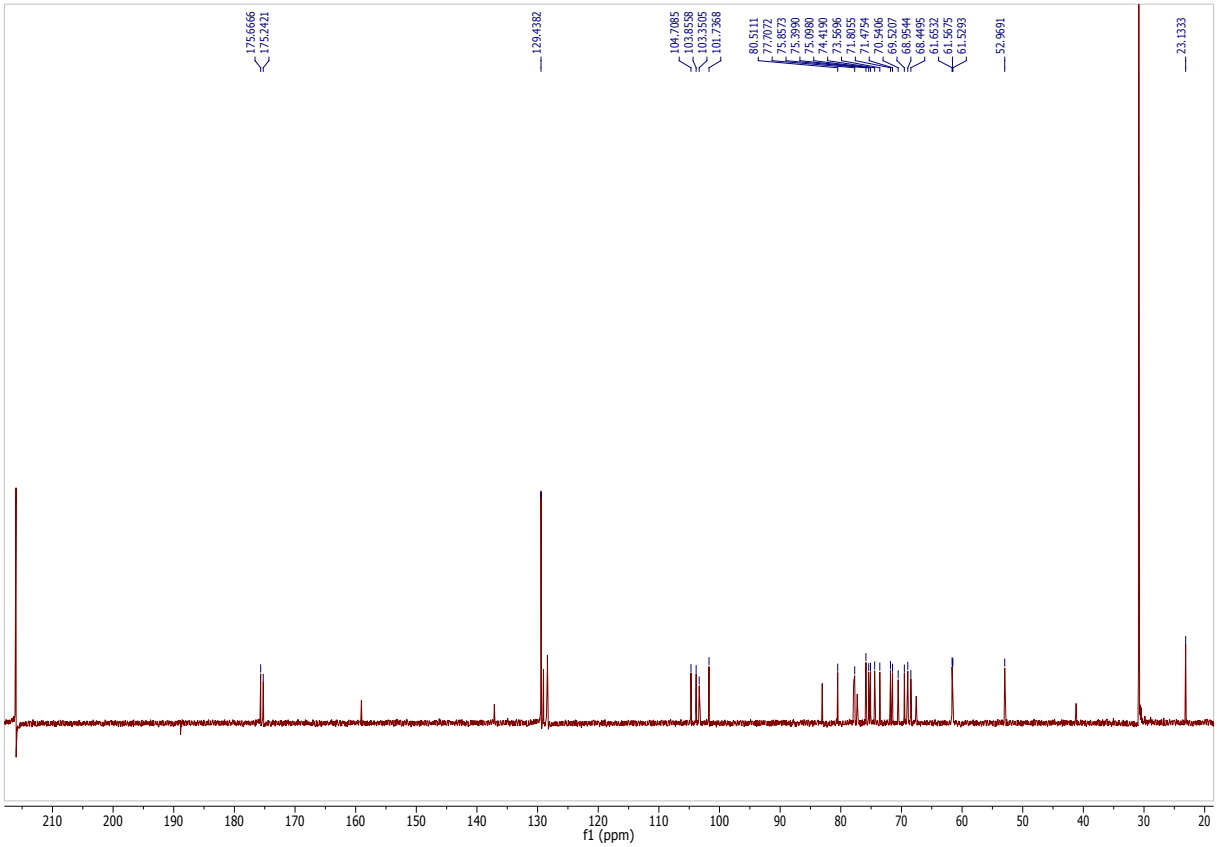


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **48**

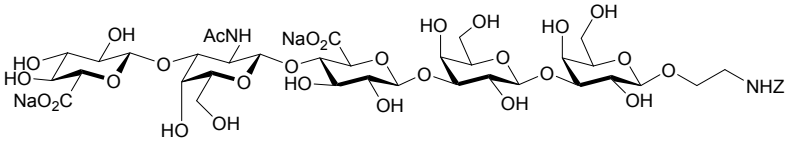


(**48**)

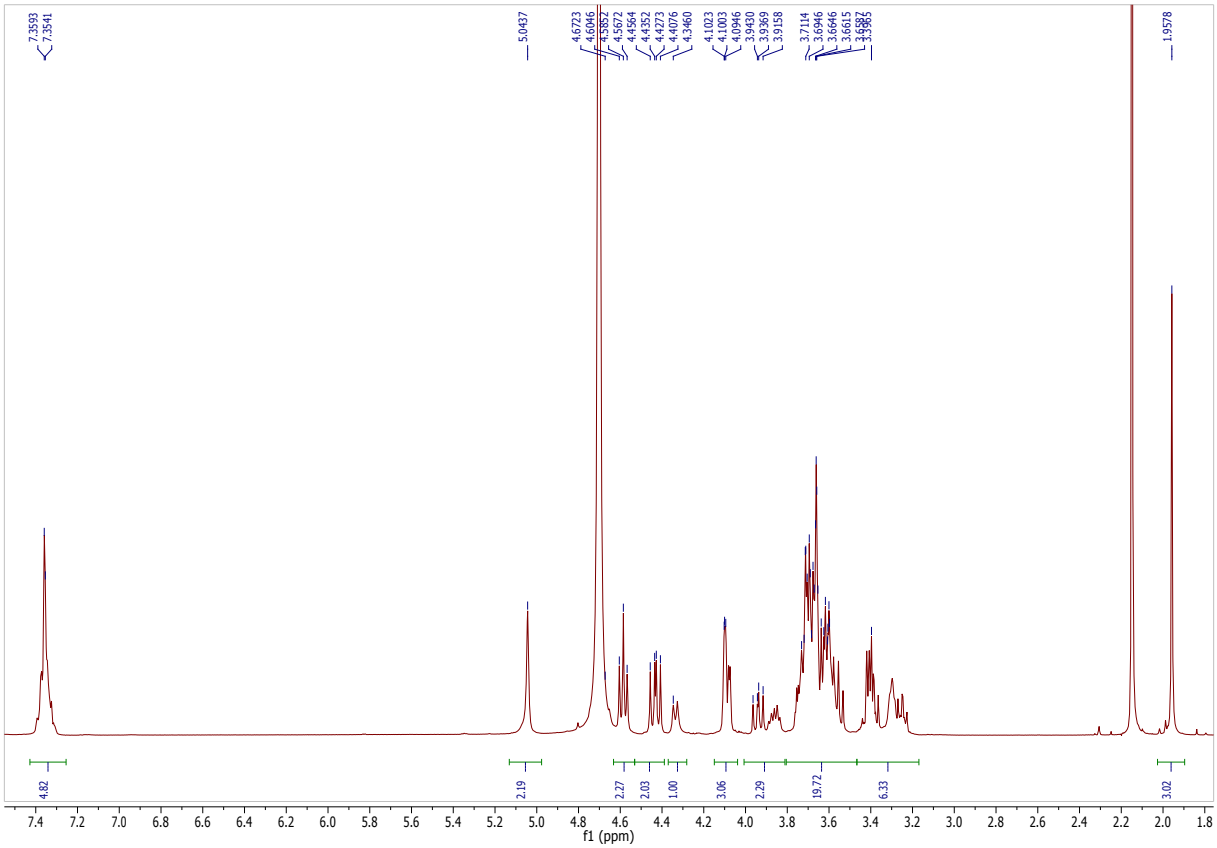


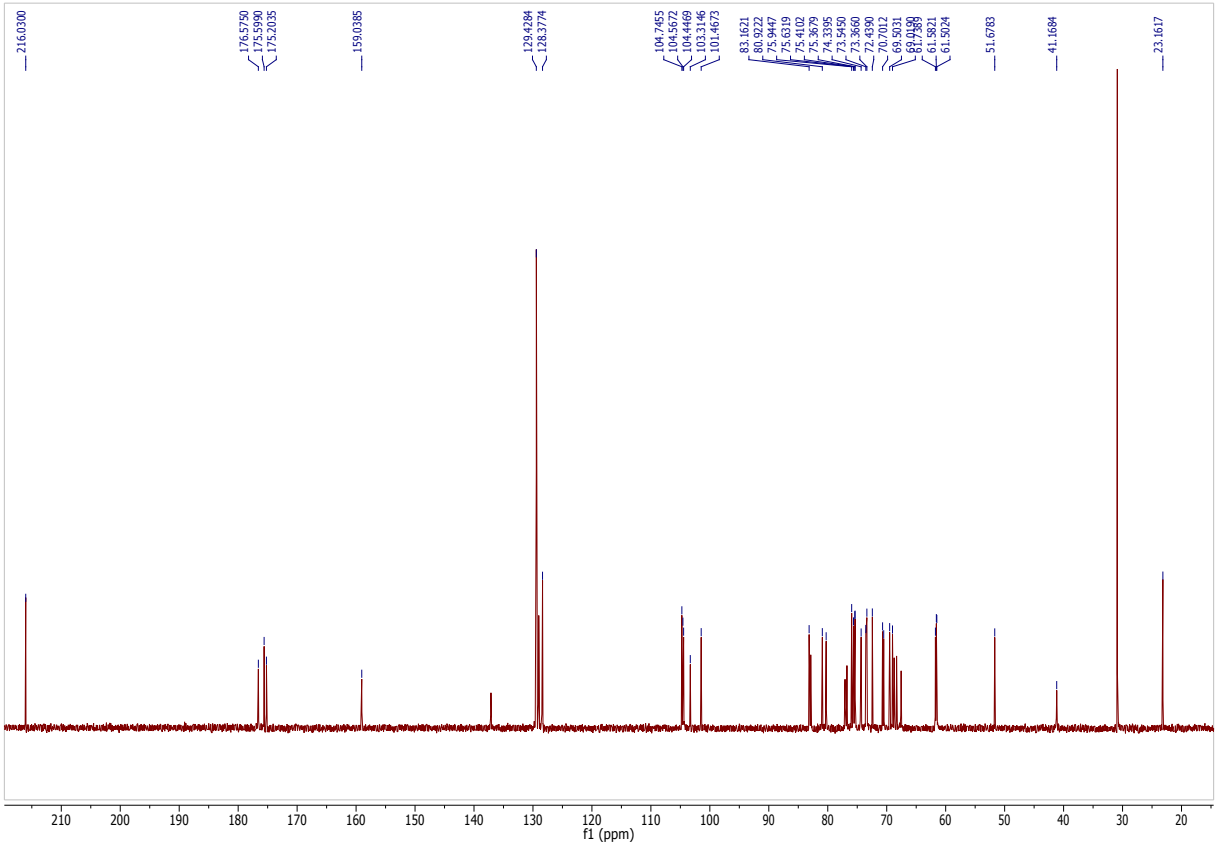


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **49**

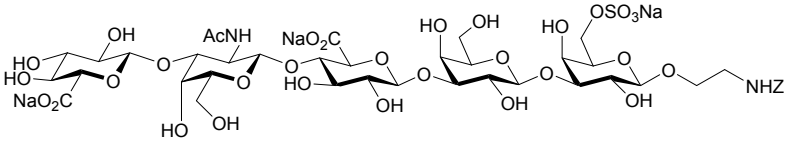


(**49**)

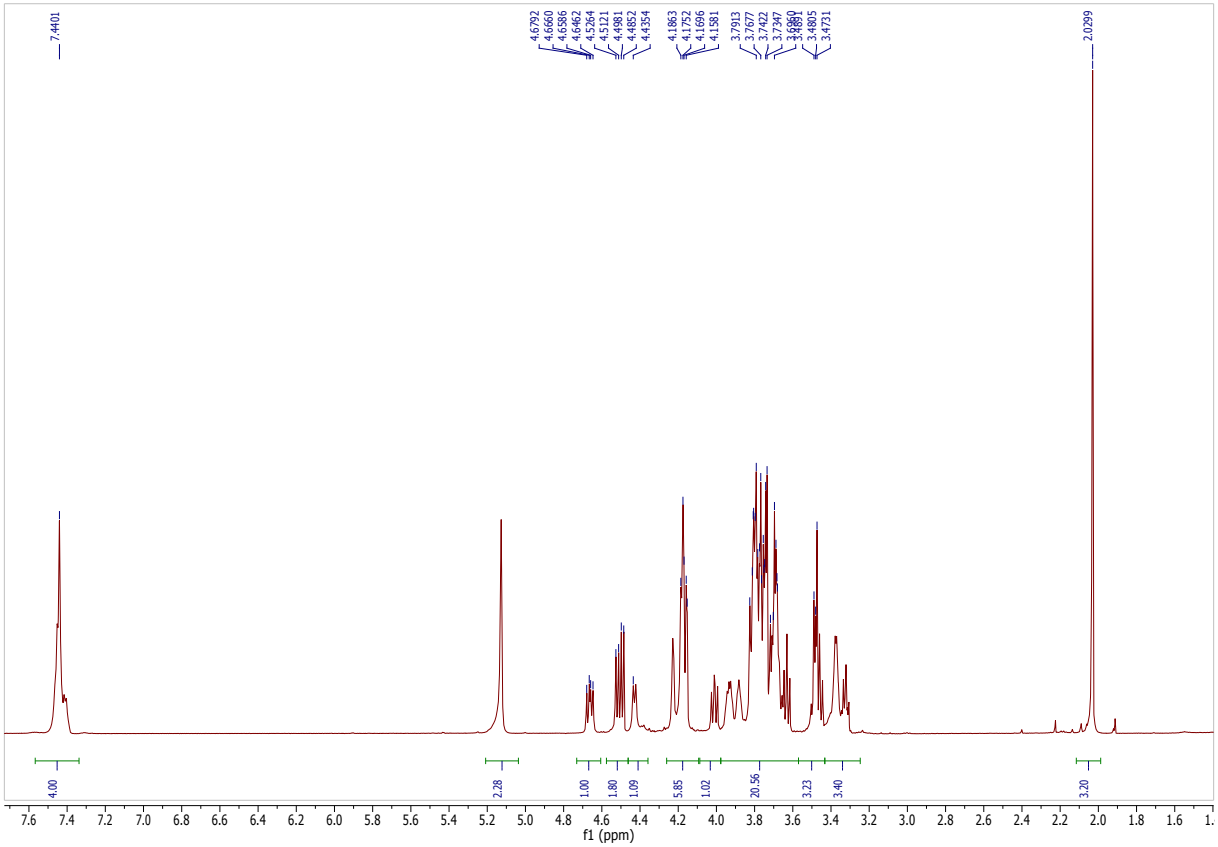


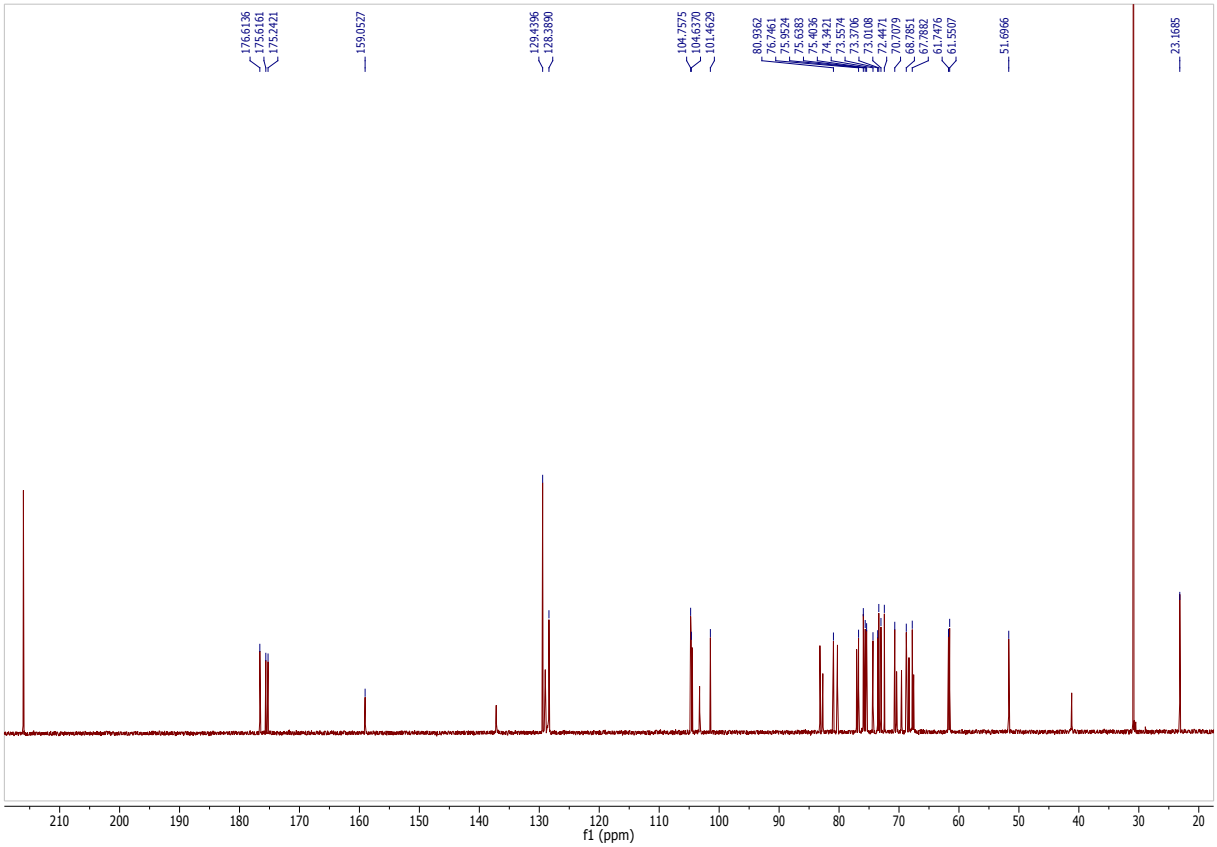


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **50**

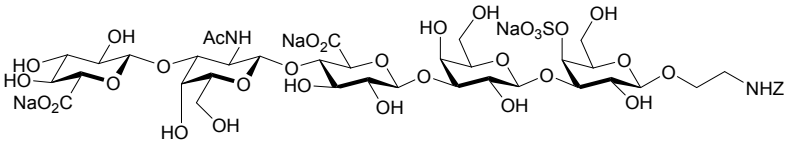


(**50**)

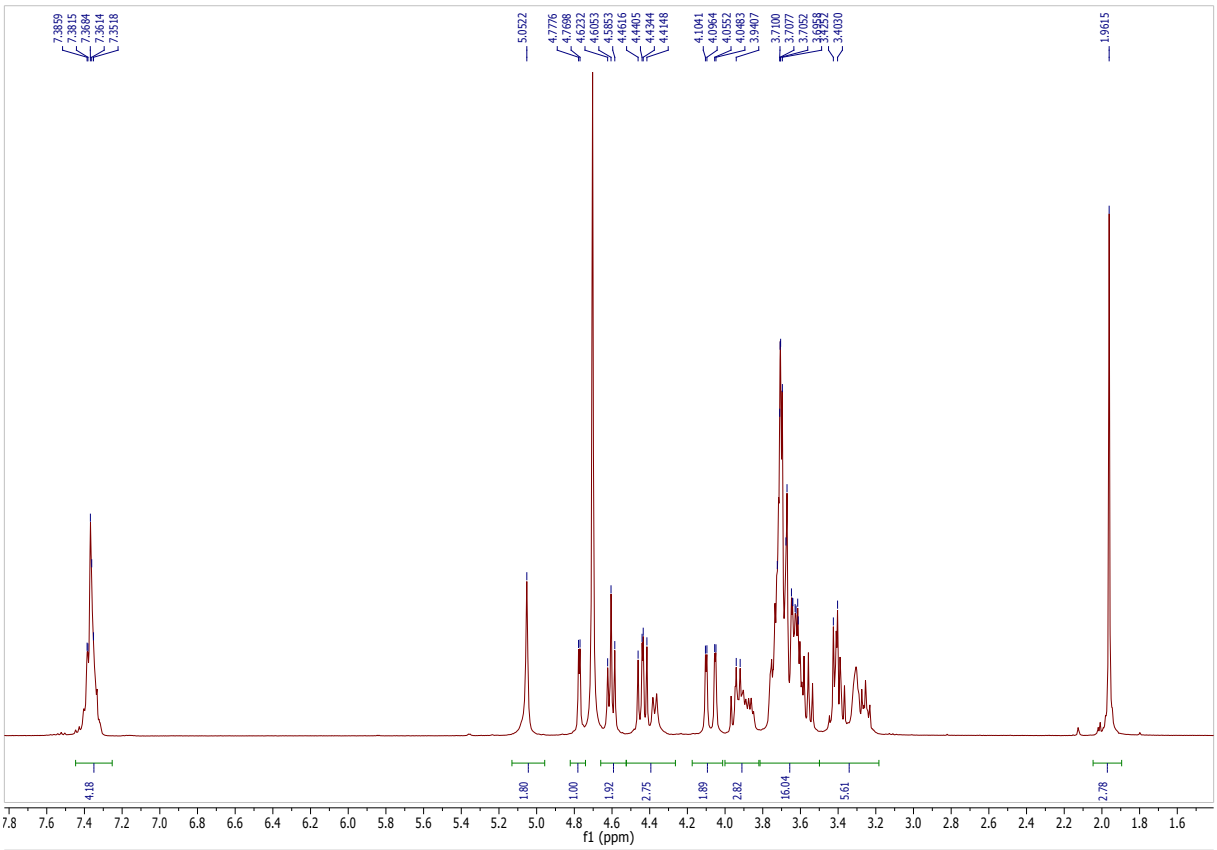


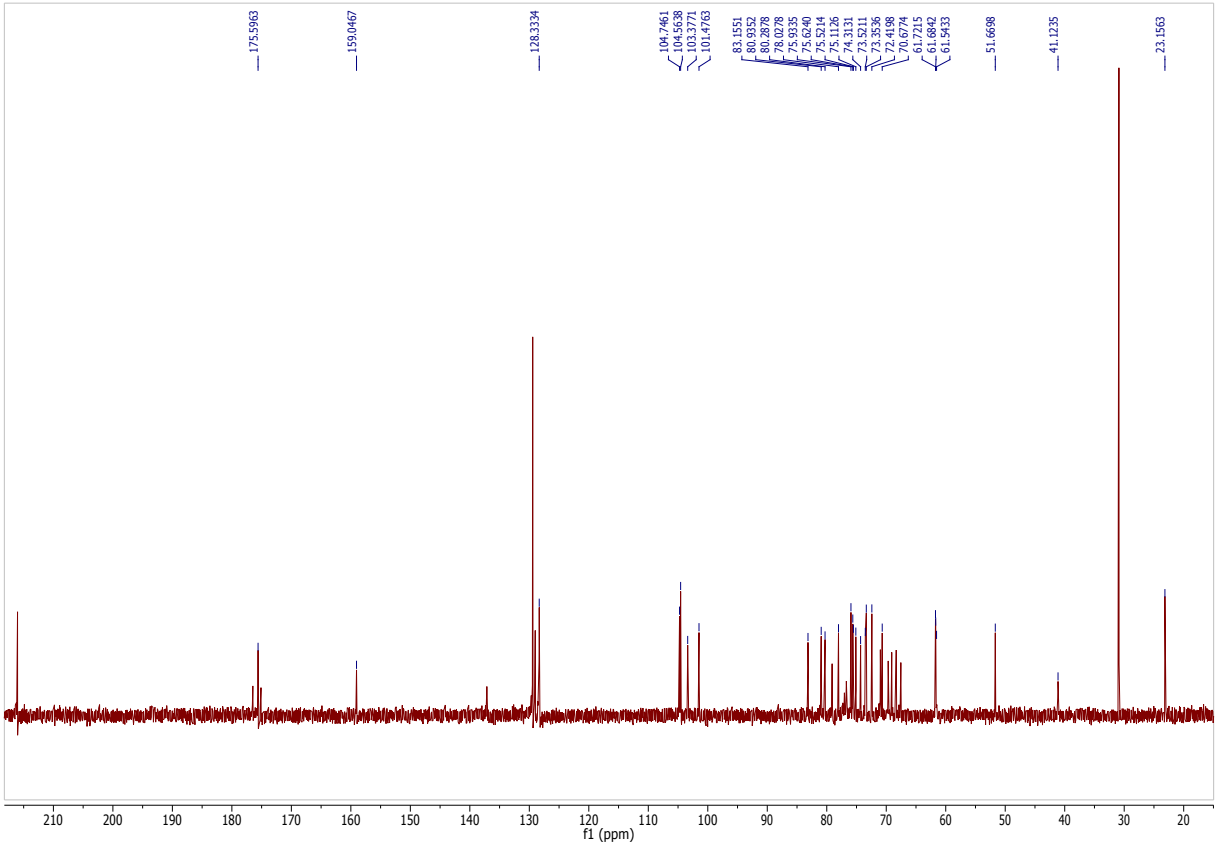


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **51**

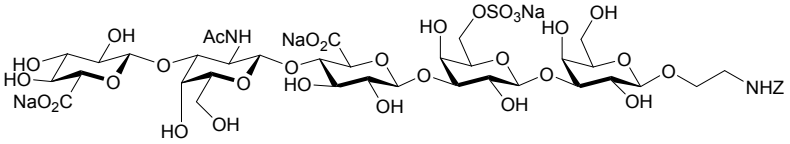


(**51**)

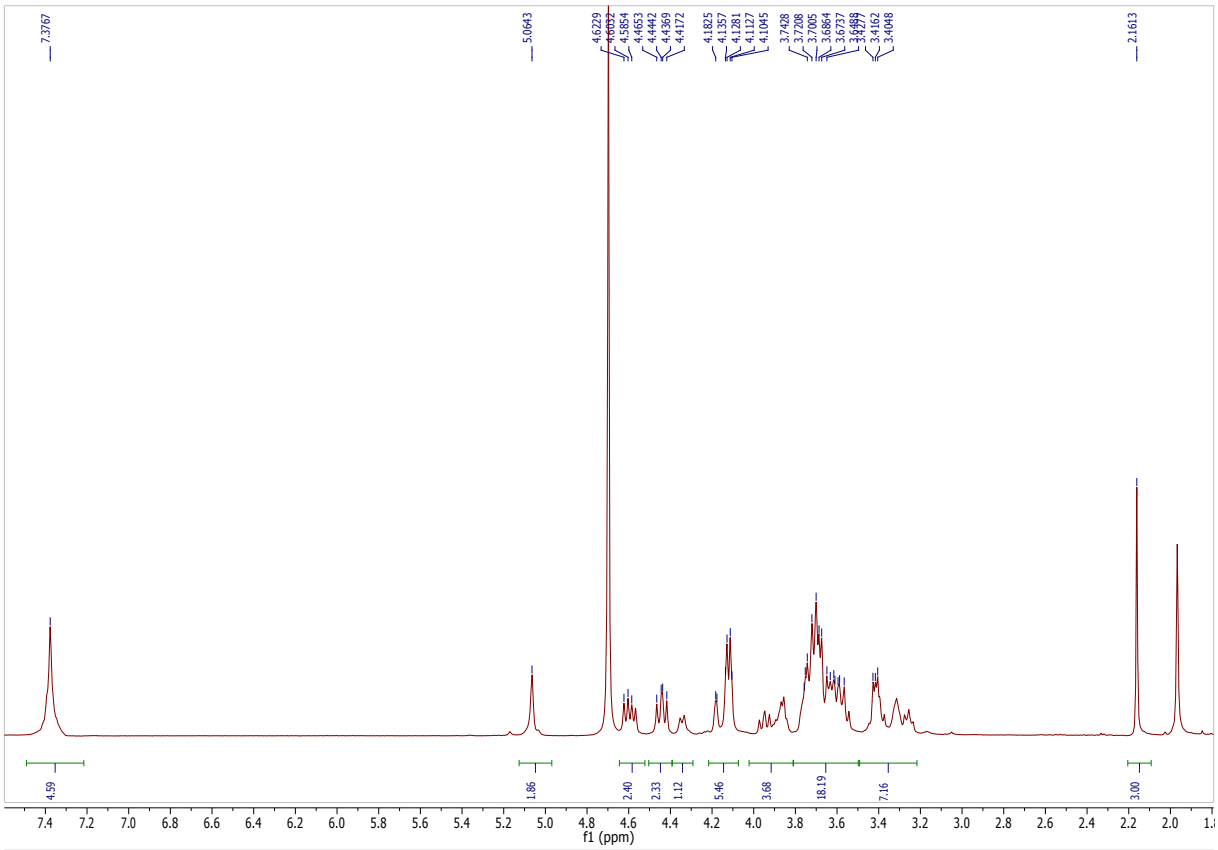


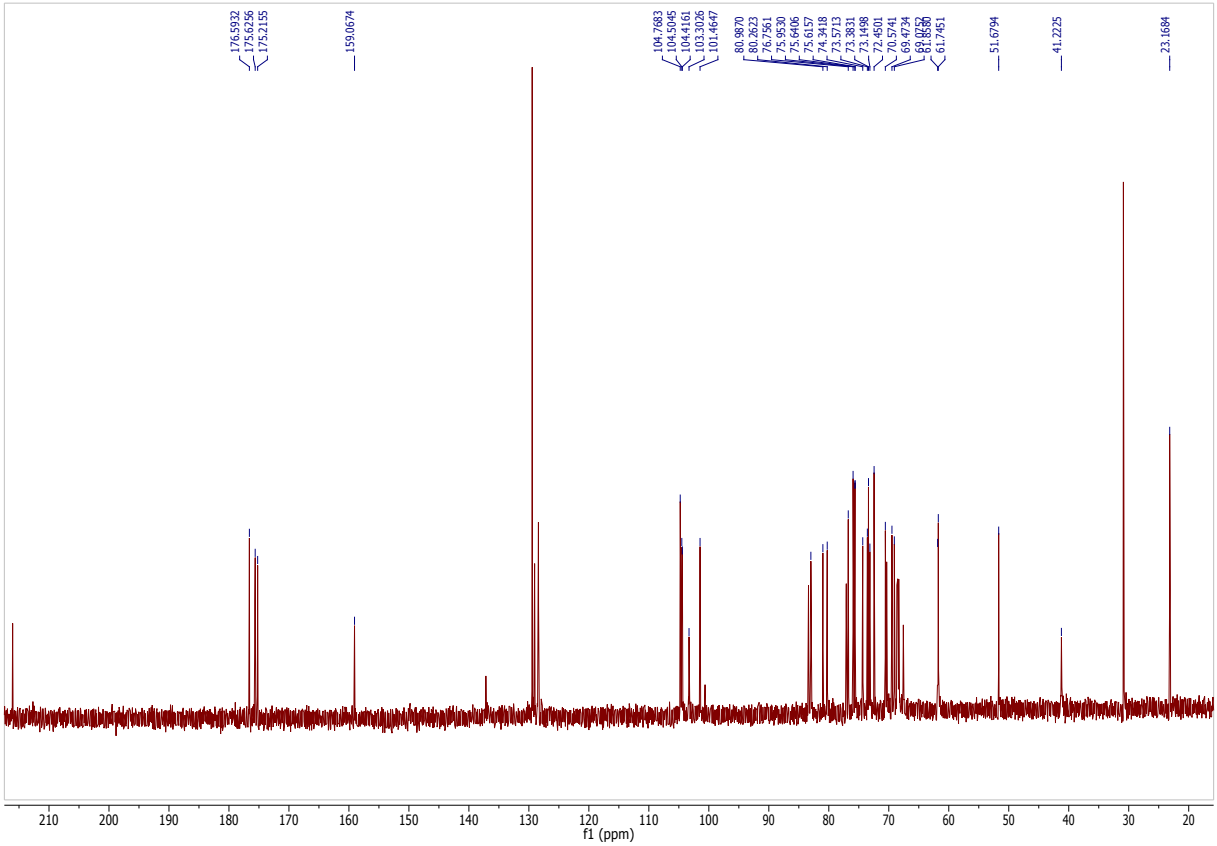


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **52**

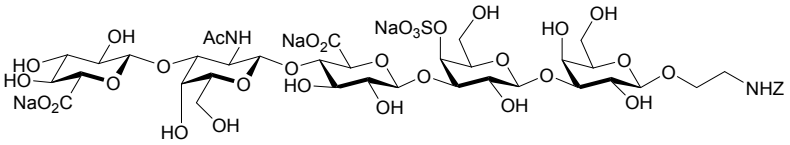


(**52**)

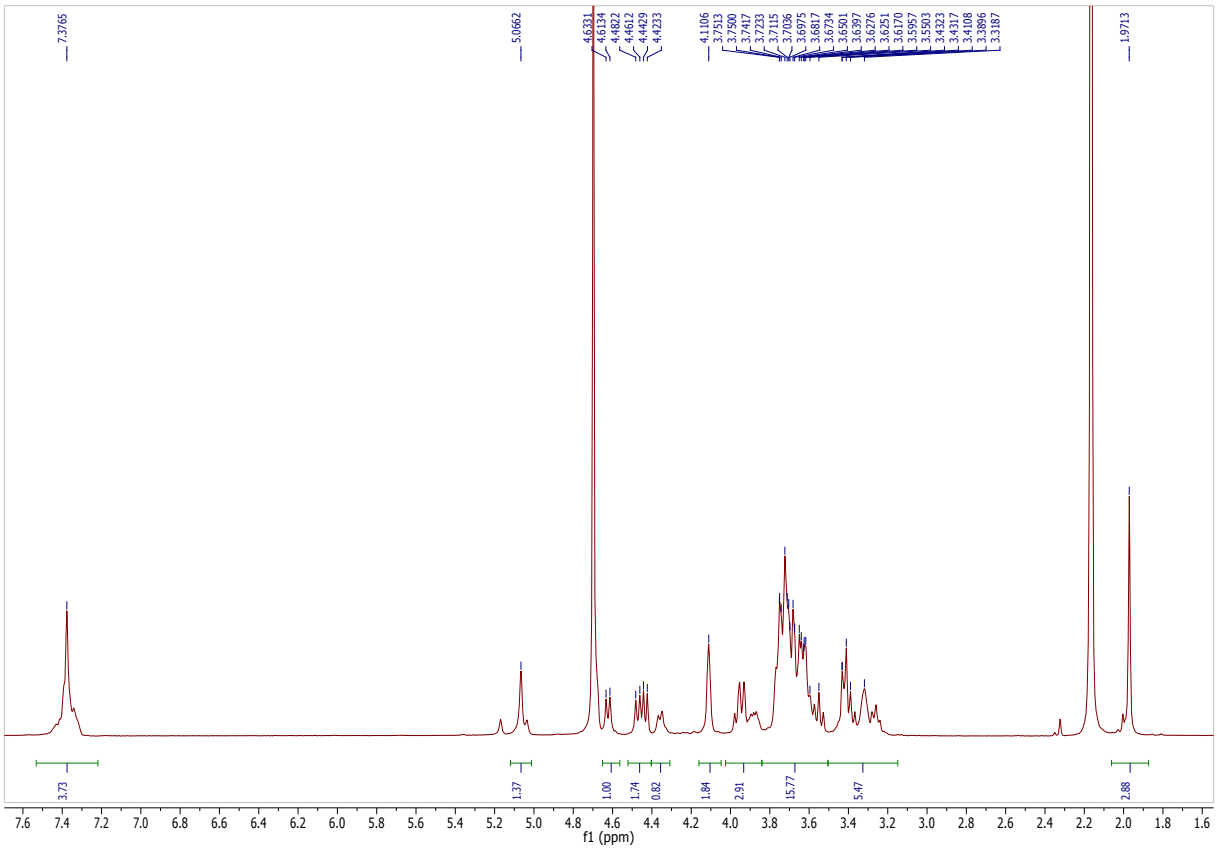


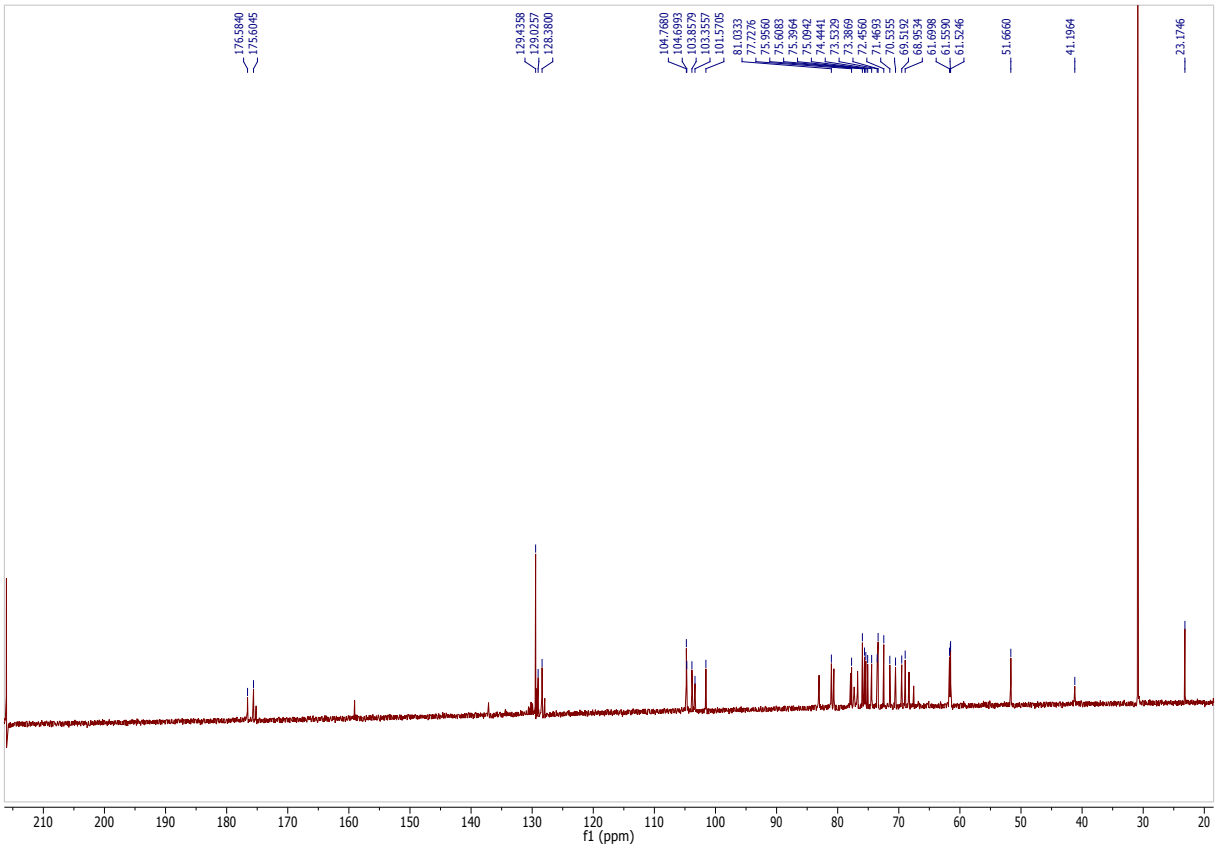


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **53**

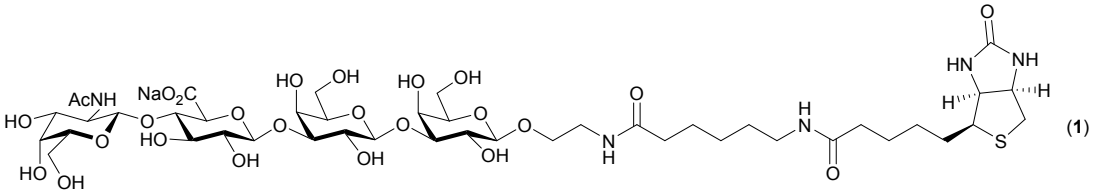


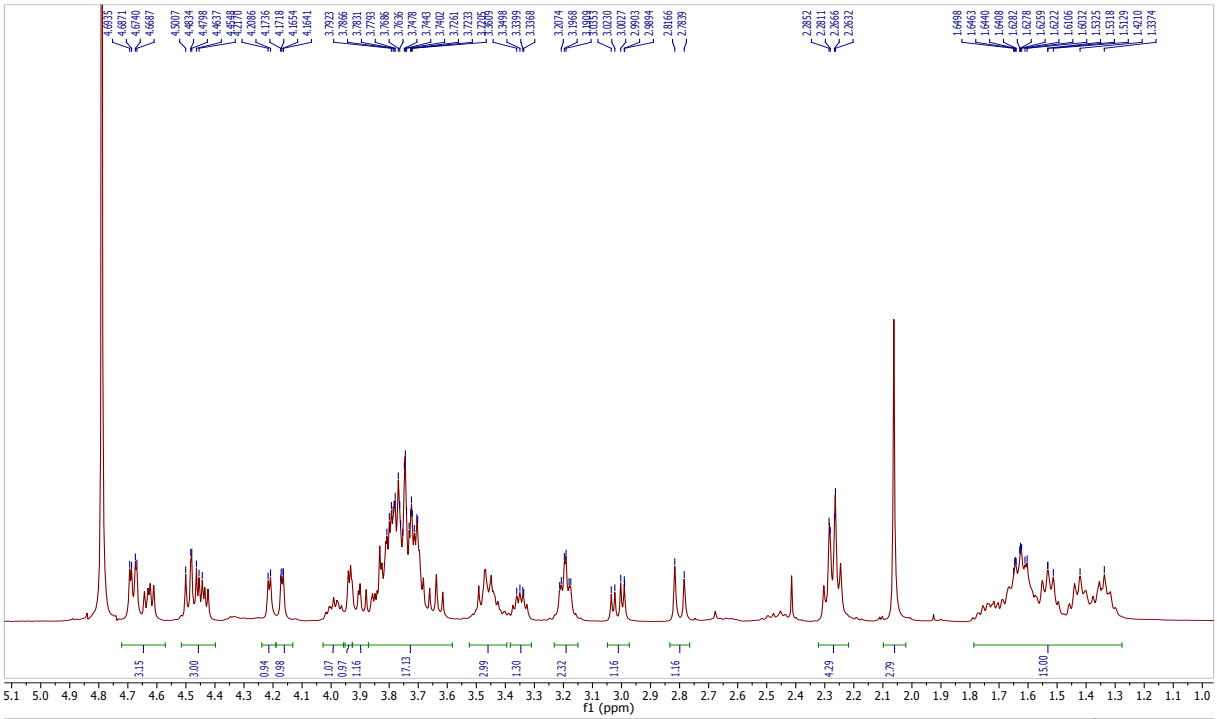
(**53**)

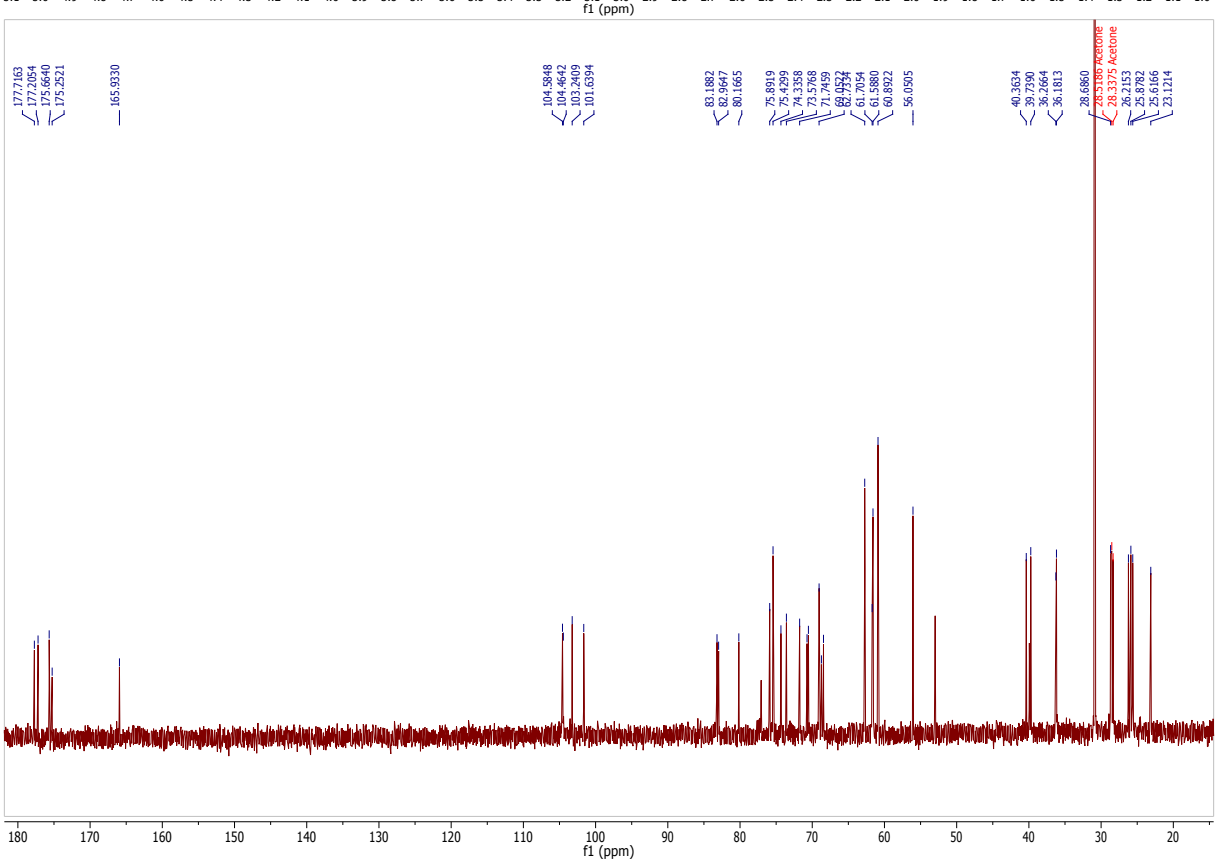




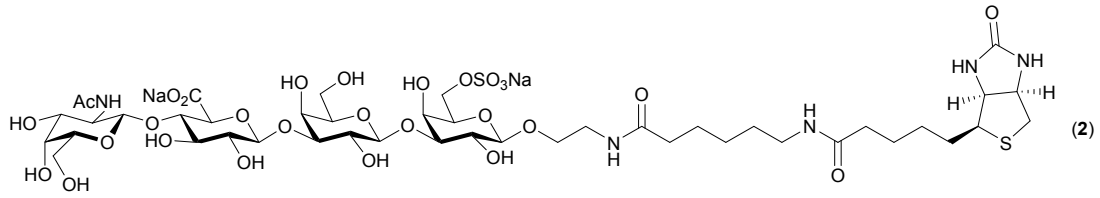
^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **1**

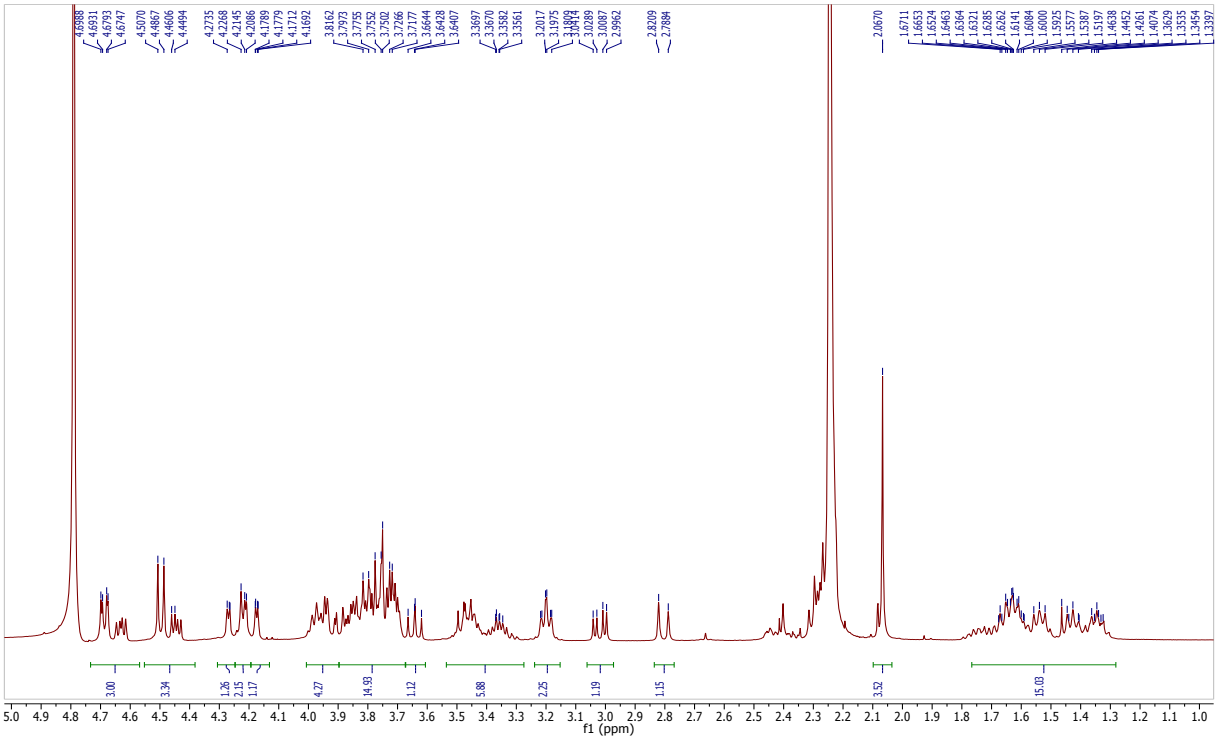


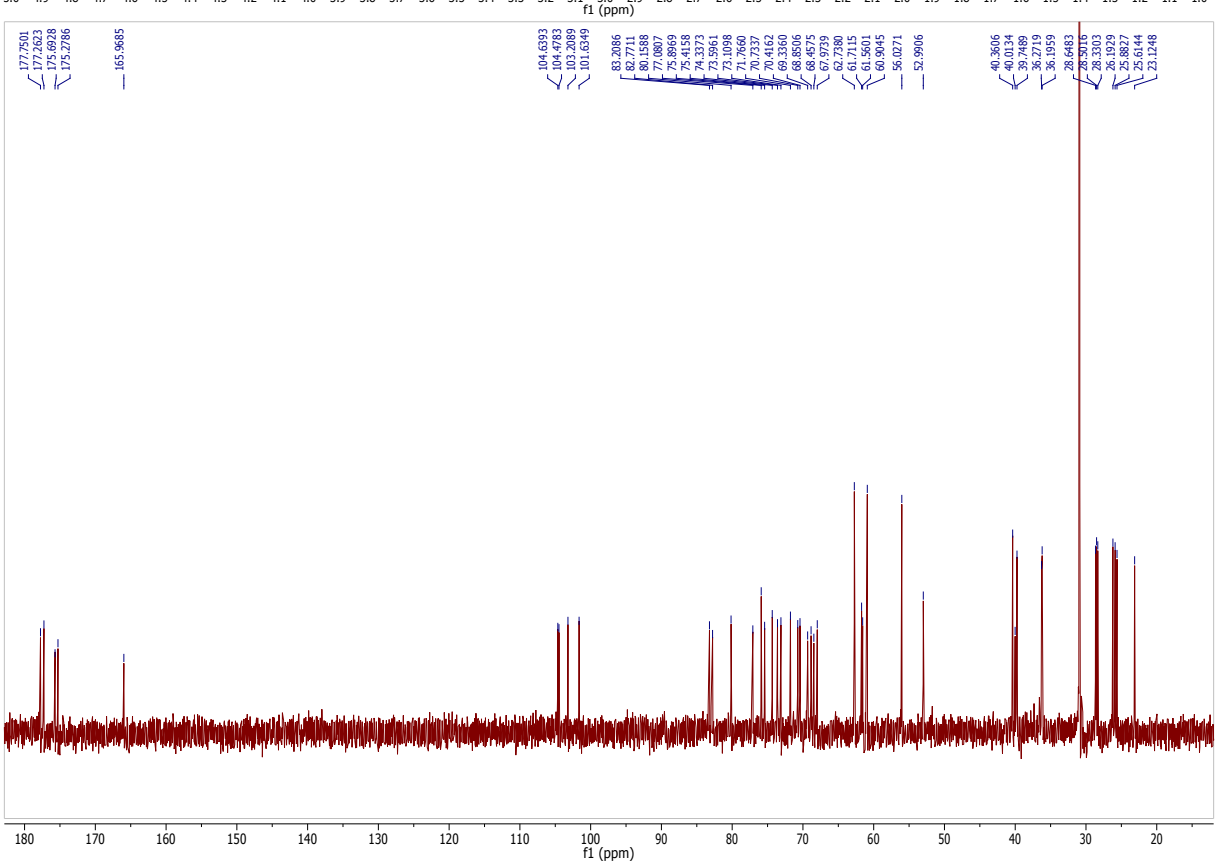




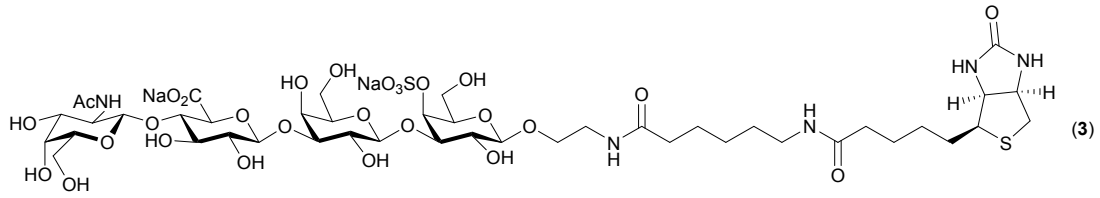
^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **2**

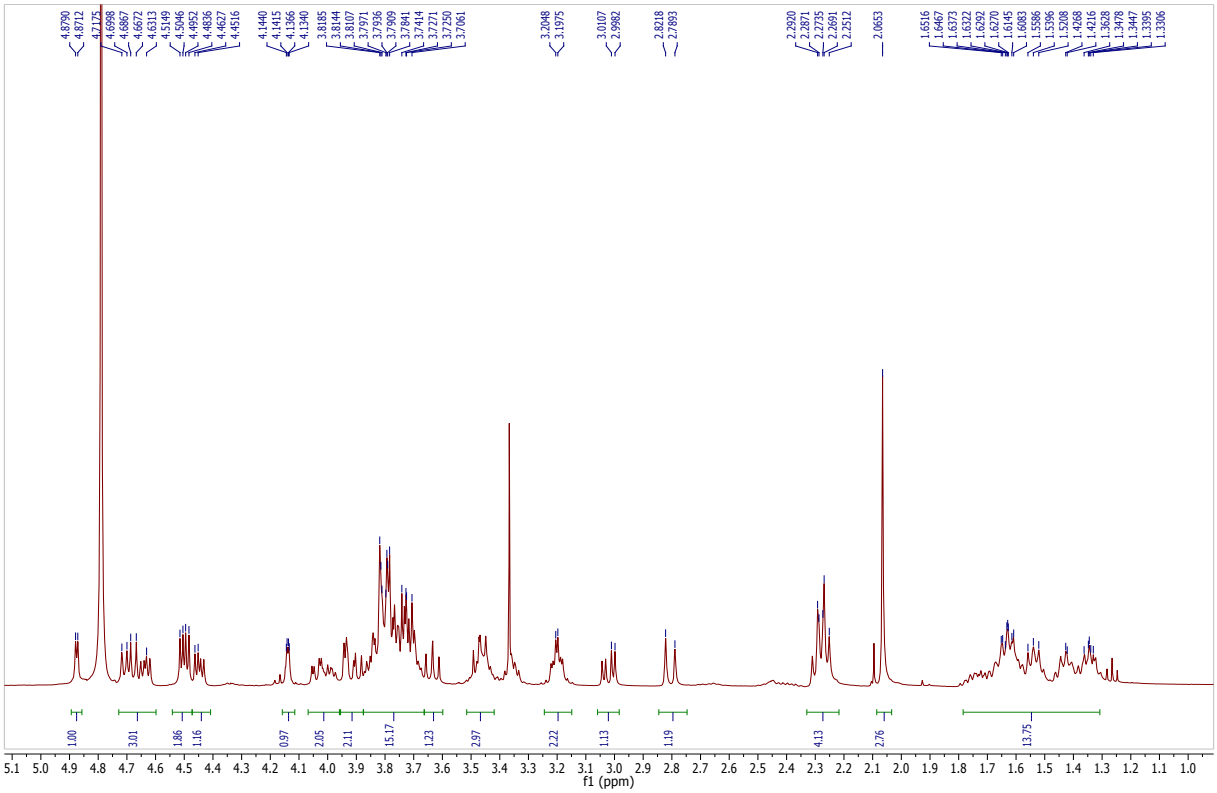


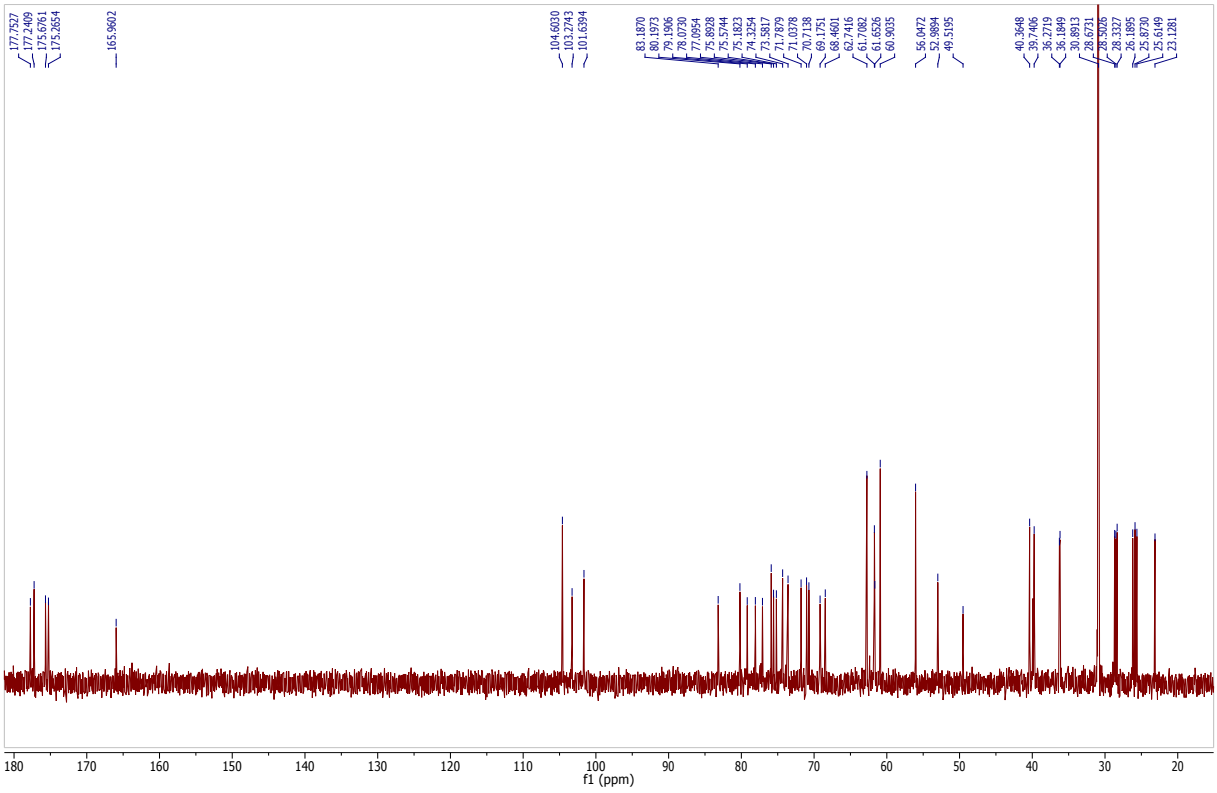




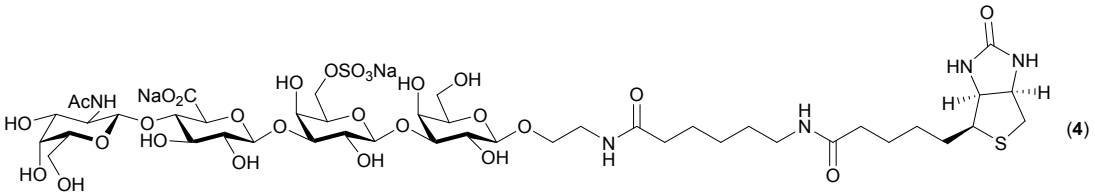
^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **3**

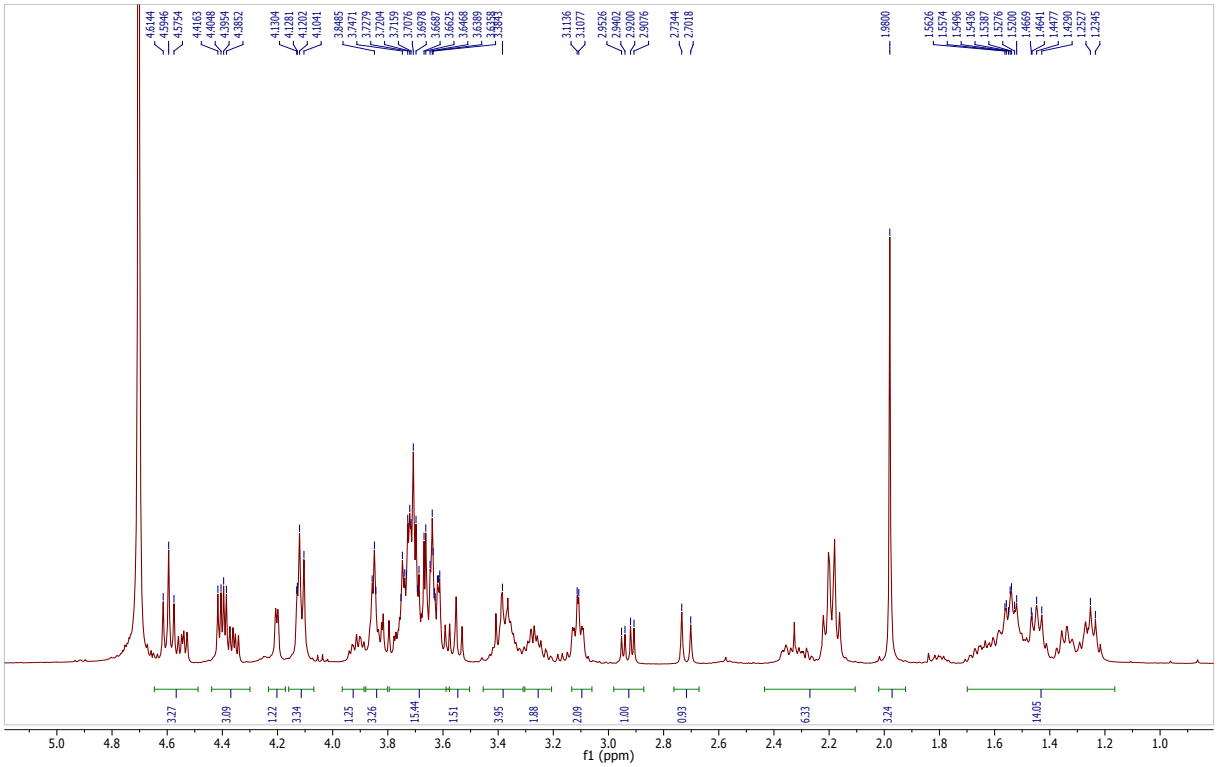


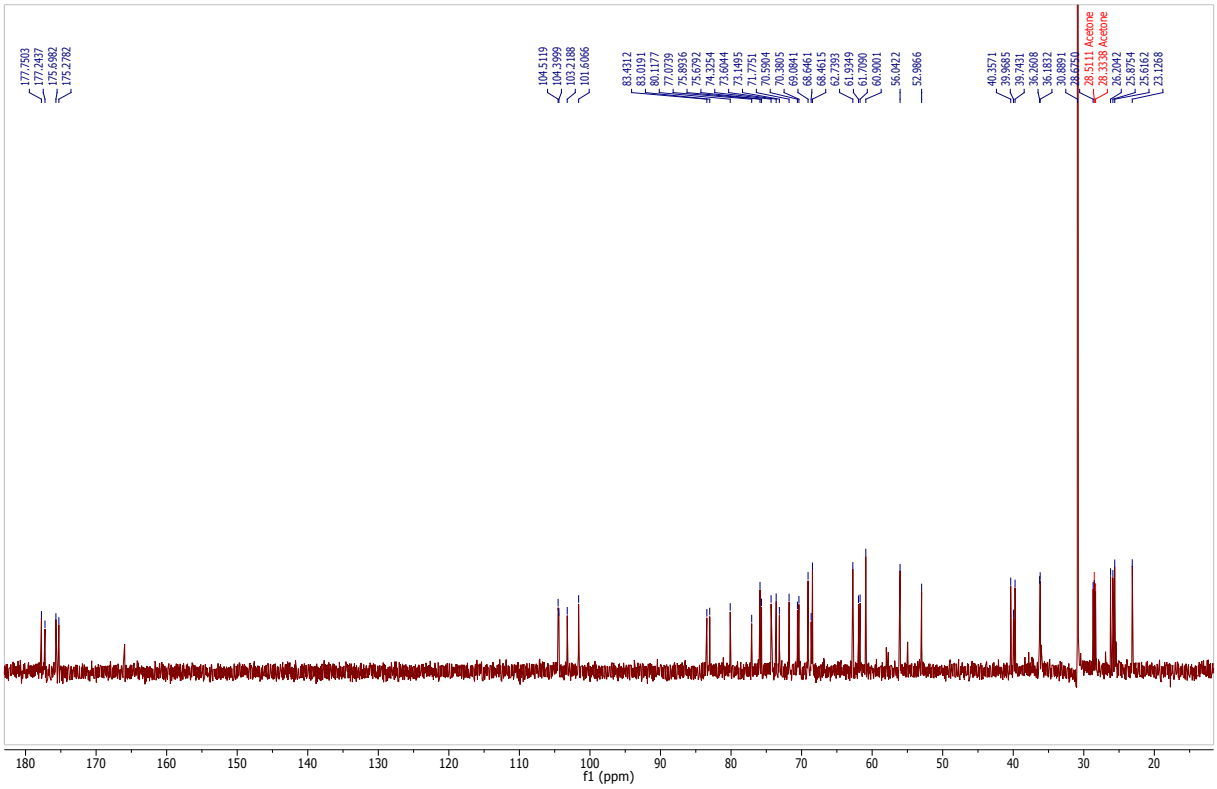




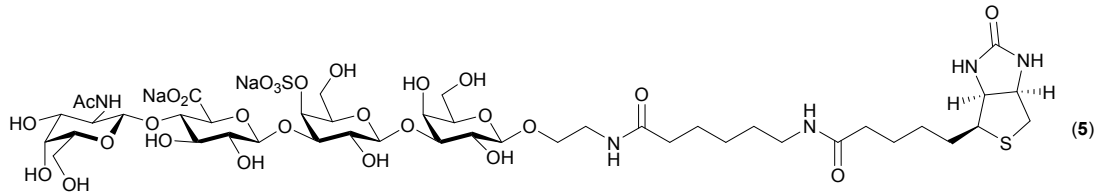
^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **4**

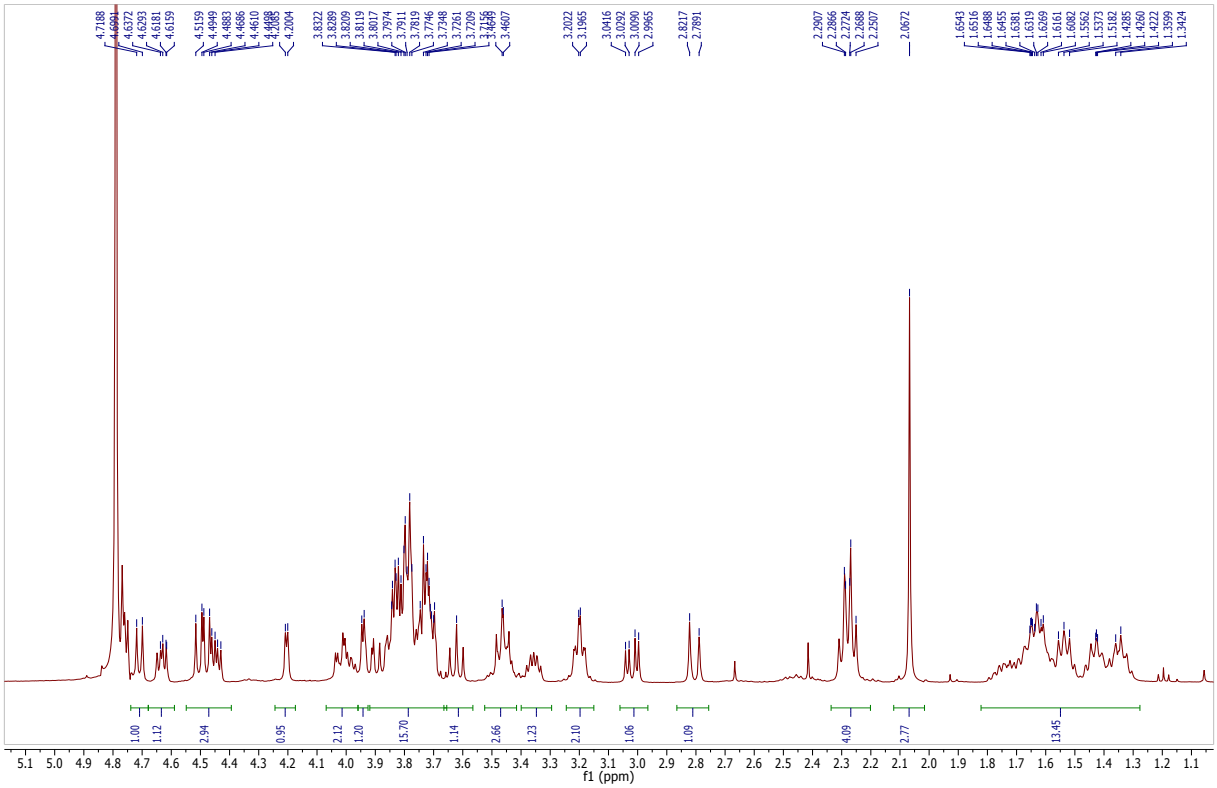


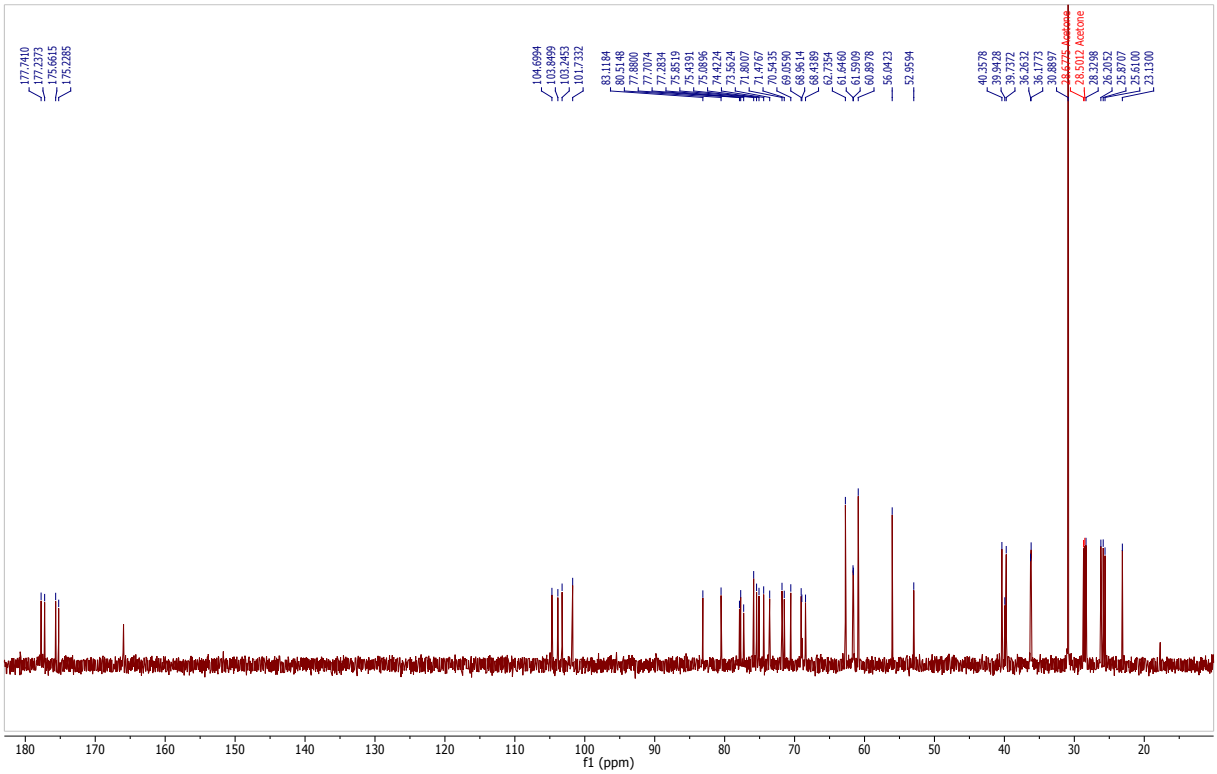




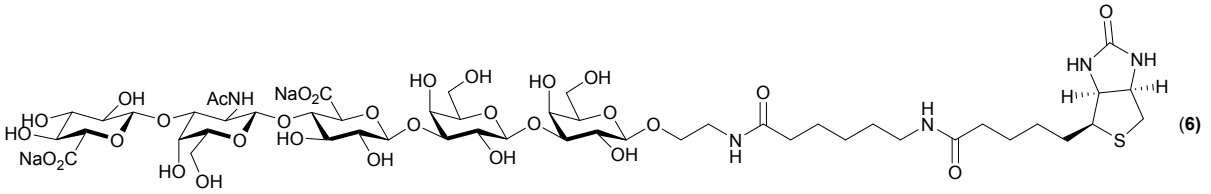
^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **5**

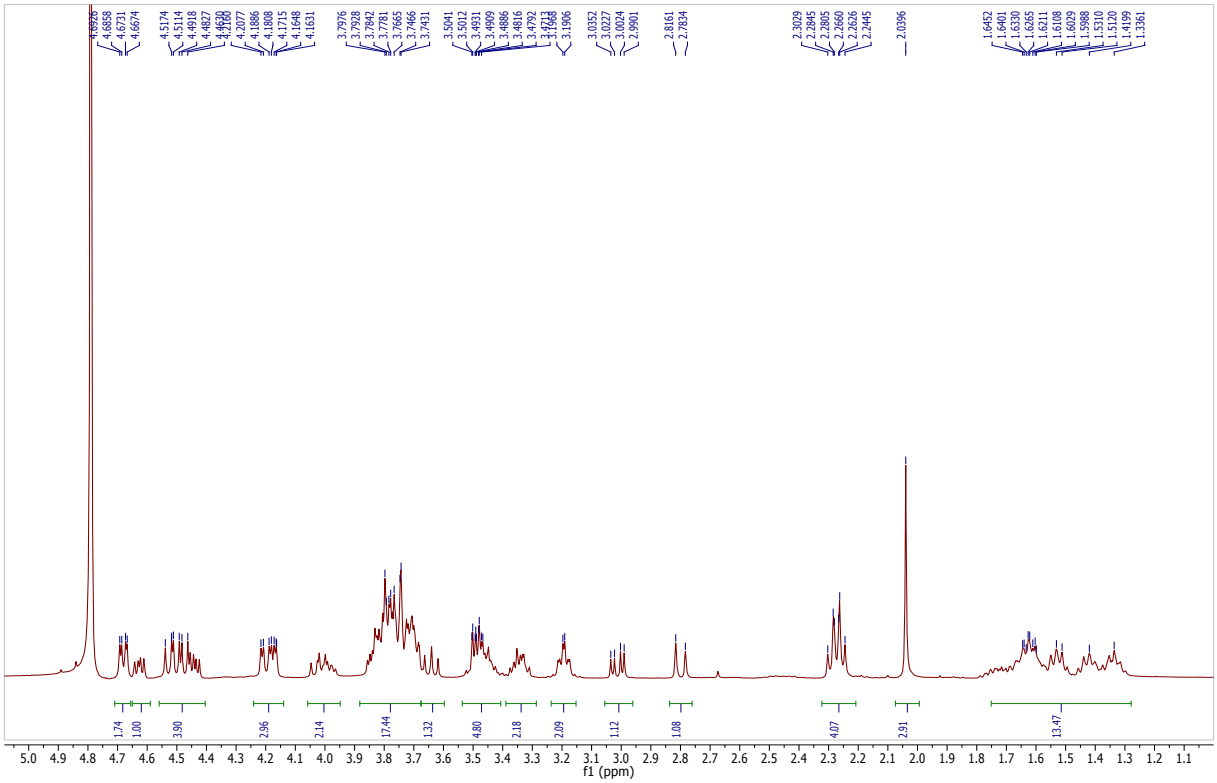


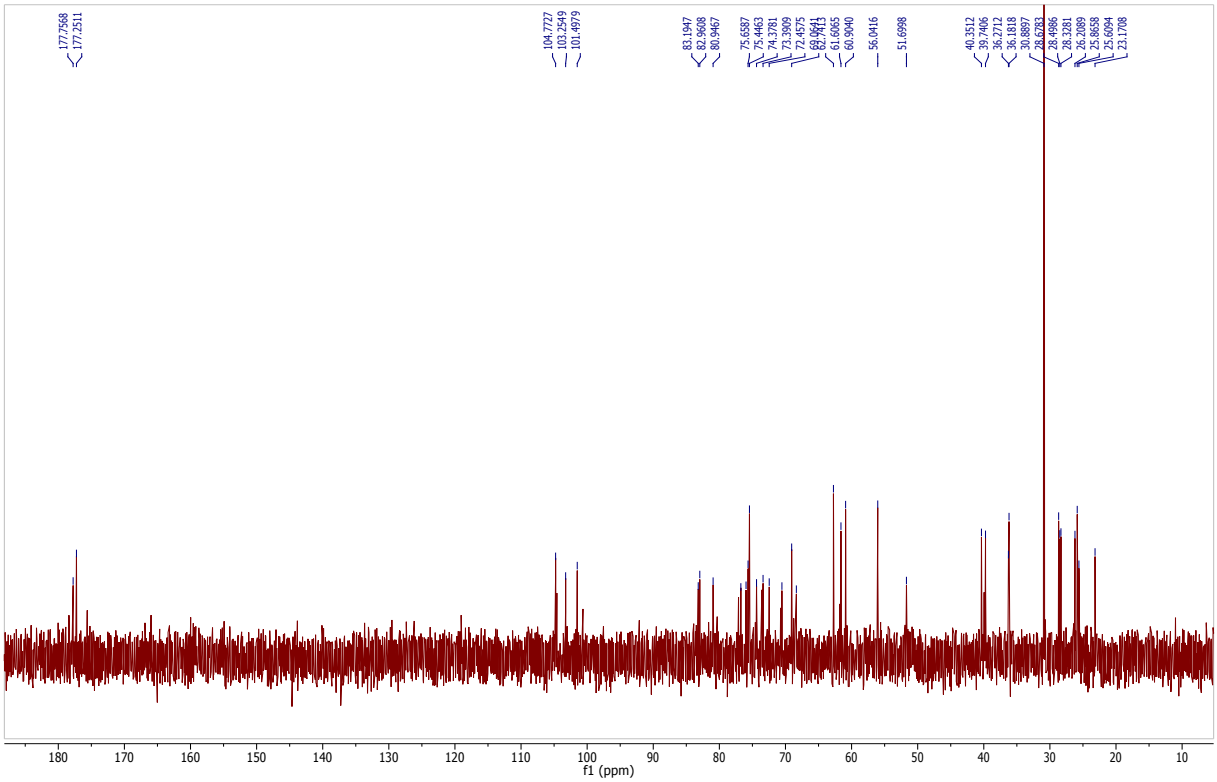




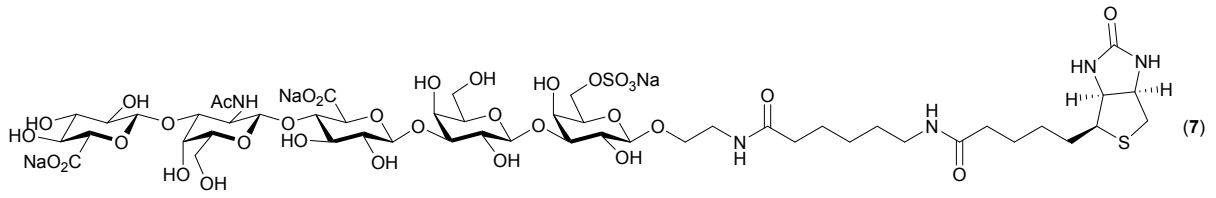
^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **6**



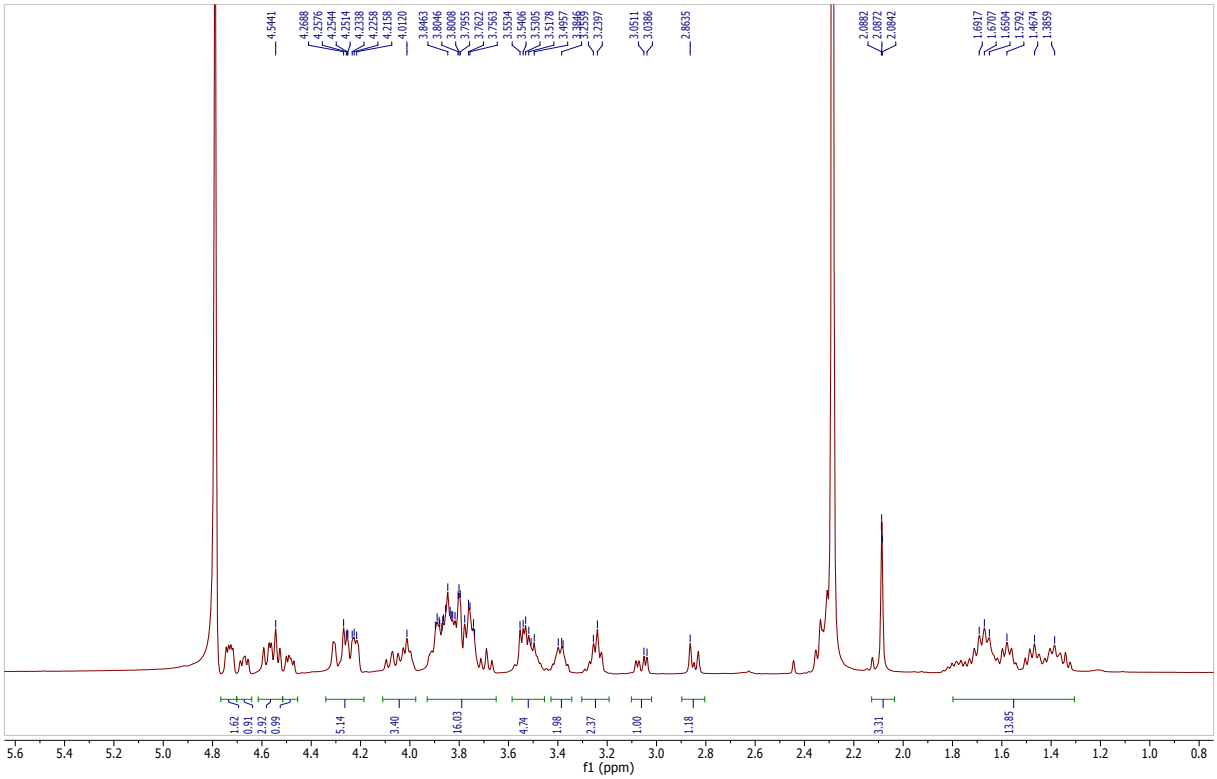


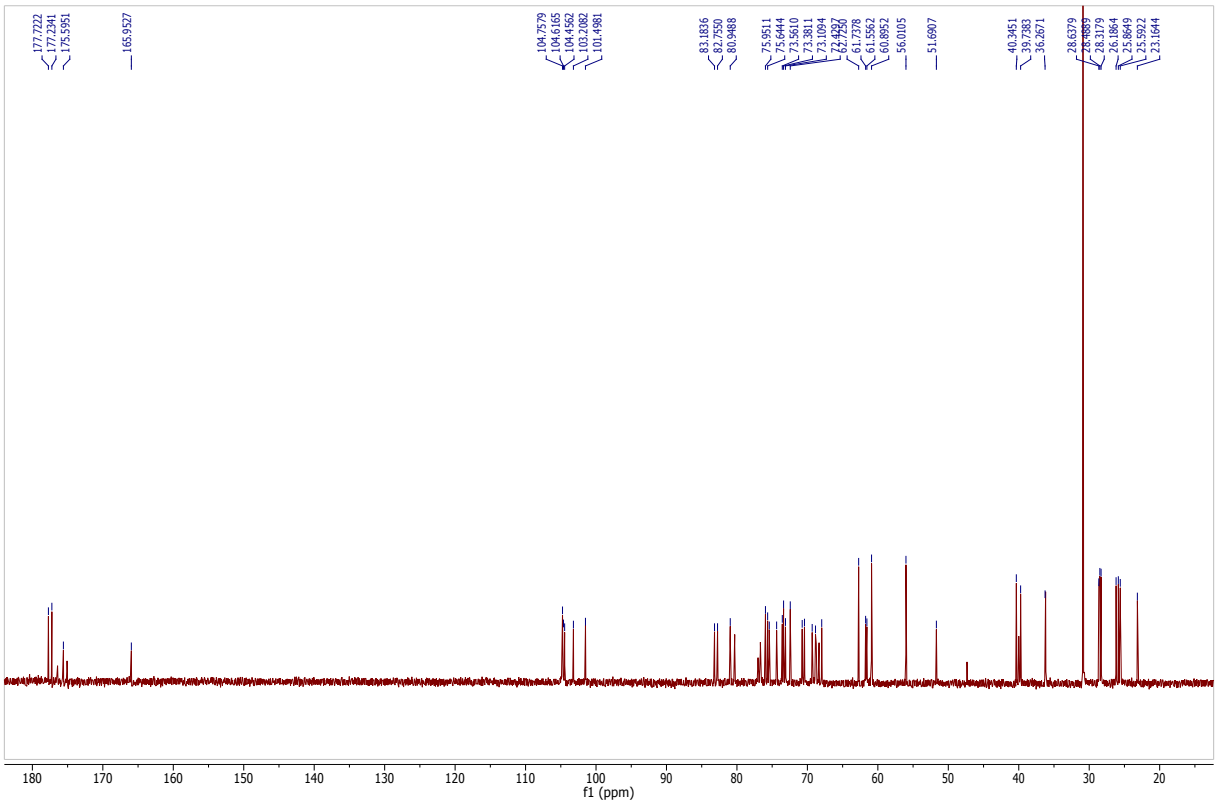


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **7**


HO
OH
AcNH
NaO2C
HO
OH
OSO3Na
O
HN
NH
H
S
N
H

(**7**)


4.5441
4.2688
4.2576
4.2544
4.2514
4.2338
4.2258
4.2158
4.0120
3.8463
3.8046
3.8008
3.7955
3.7622
3.7563
3.5534
3.5406
3.5305
3.5178
3.4957
3.3397
3.0511
3.0386
2.8635
2.0882
2.0872
2.0842
1.6917
1.6707
1.6504
1.5792
1.4674
1.3859
1.62
0.91
2.92
0.99
5.14
3.40
16.03
4.74
1.98
2.37
1.00
1.18
3.31
13.85
f1 (ppm)


177.7222
177.2341
175.5951
165.9527
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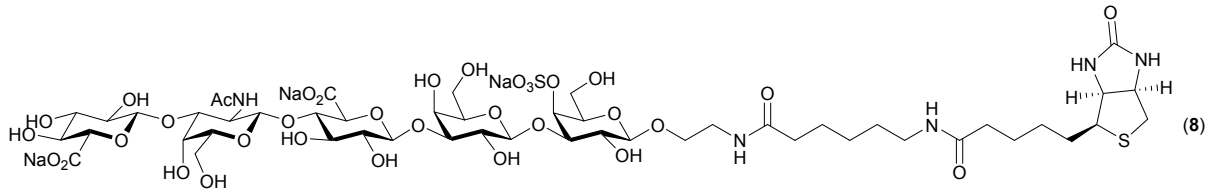
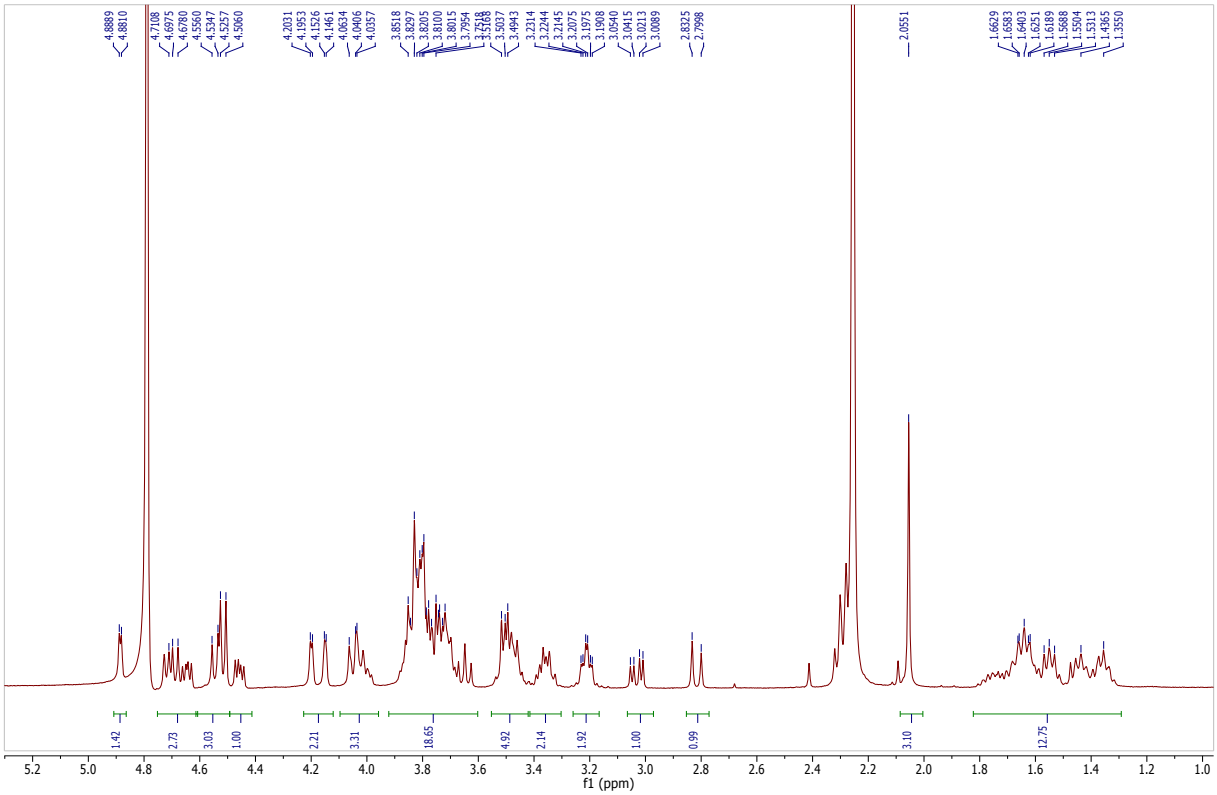
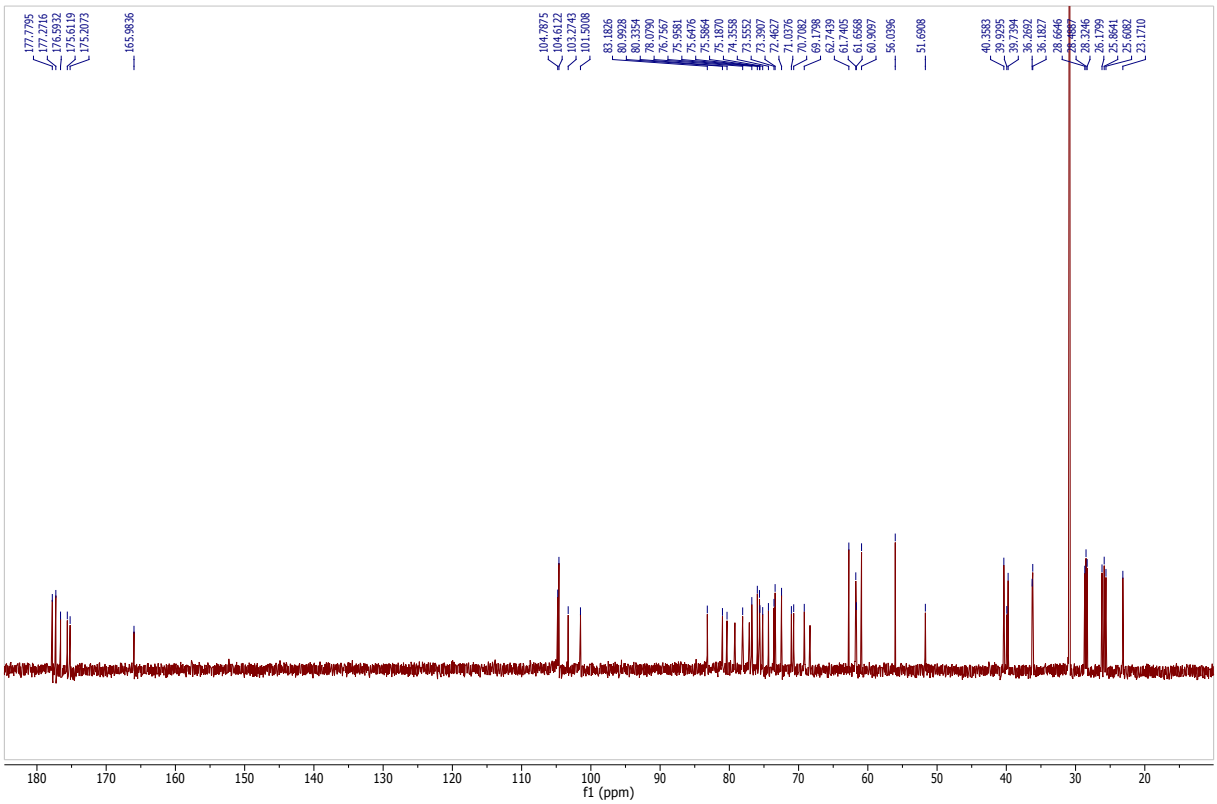
104.6165
104.4562
103.2082
101.4981
83.1836
82.7550
80.9488
75.9511
75.6444
73.5610
73.3811
73.1094
72.4282
72.2750
61.7378
61.5562
60.8952
56.0105
51.6907
40.3451
39.7383
36.2671
28.6379
28.4889
28.3179
26.1864
25.8649
25.5922
23.1644
f1 (ppm)

^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **8**

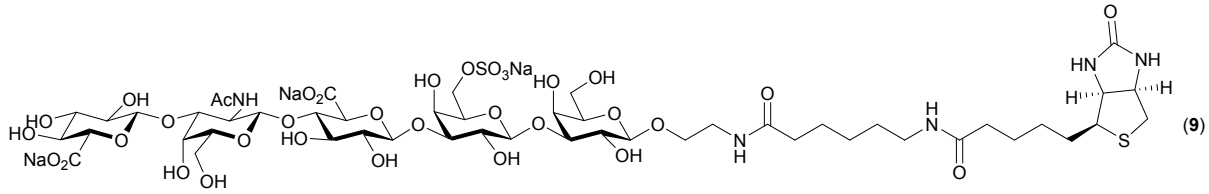


(**8**)

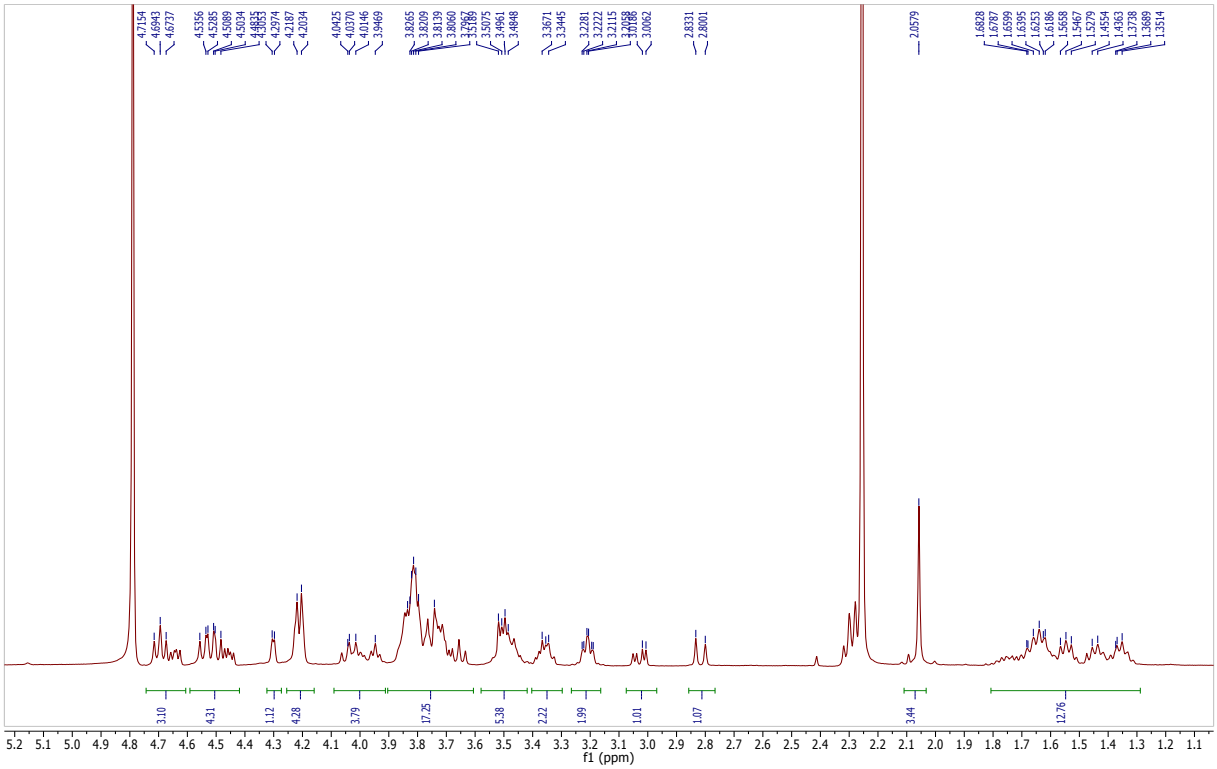


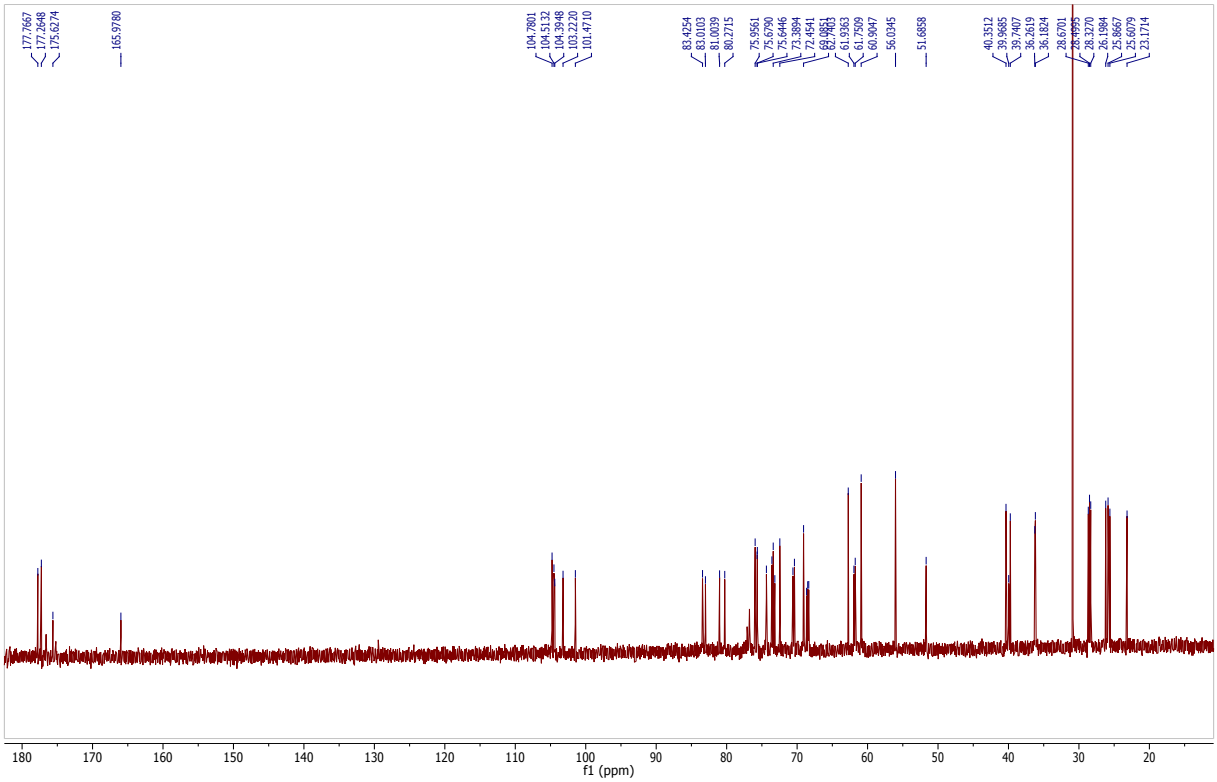


^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **9**

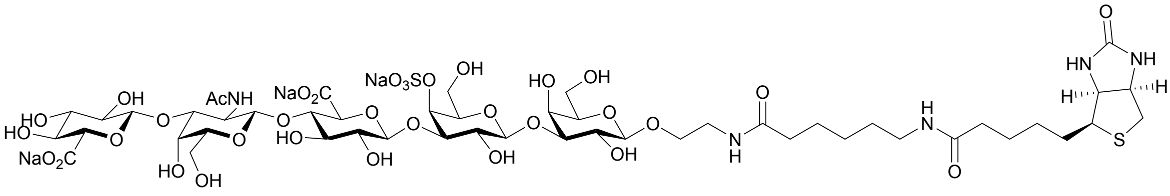


(**9**)





^{1}H NMR and ^{13}C NMR (D_2O, internal acetone, 400 MHz) for compound **10**



(**10**)