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Synthesis of GalNAcβ1-4GlcNAcβ (LacdiNAc) *O*-sulfates

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*Spectral characteristics for oligosaccharides***.** ^{1}H NMR spectra were recorded on a Bruker AVANCE 700 and 800 MHz spectrometer at 303K. Chemical shifts δ for characteristic protons are given in ppm and coupling constants J, in Hz. The signals in ^{1}H NMR spectra were assigned using a technique of spin–spin decoupling (double resonance) and 2D-^{1}H,^{1}H- COSY experiments. The values of optical rotation were measured on a digital polarimeter Jasco DIP-360 at 25°C. Mass spectra were recorded on a MALDI-TOF Vision-2000 spectrometer using dihydroxybenzoic acid as a matrix.

3: ^{1}H NMR (800 MHz, $CDCl_3$: CD_3OD, 3:1), δ: 1.959 (m, 2H, CH_2 sp); 2.000, 2.090, 2.119, 2.201, 2.211, and 2.276 (6s, 6 x 3H, COMe); 3.397 (m, 1H, NCH sp); 3.609 (m, 1H, NCH sp); 3.656 (m, 1H, OCH sp); 3.681 (ddd, 1H, H-5', $J_{5,6a}$ 4.1, $J_{5,6b}$ 2.2, $J_{4,5}$ 9.3); 3.842 (dd, 1H, H-6'a, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 11.3); 3.892 (dd, 1H, H-6'b, $J_{5,6b}$ 2.2, $J_{6a,6b}$ 11.3); 3.921 (ddd, 1H, H-5'', $J_{5,6a}$ 7.4, $J_{5,6b}$ 6.3, $J_{4,5}$ 0.9); 4.012 (dd, 1H, H-2'', $J_{1,2}$ 8.2, $J_{2,3}$ 11.3); 4.043 (dd ≈ t, 1H, H-4', J 8.9); 4.045 (m, 1H, OCH sp); 4.082 (dd, 1H, H-2', $J_{1,2}$ 8.2, $J_{2,3}$ 10.2); 4.221 (dd, 1H, H-6''a, $J_{5,6a}$ 7.4, $J_{6a,6b}$ 11.3); 4.250 (dd, 1H, H-6''b, $J_{5,6b}$ 6.3, $J_{6a,6b}$ 11.3); 4.555 (d, 1H, H-1', $J_{1,2}$ 8.2); 4.683 and 4.855 (2d, 2 x 1H, CH_2Ph, $J_{A,B}$ 11.7); 4.748 (d, 1H, H-1'', $J_{1,2}$ 8.2); 5.168 (dd, 1H, H-3'', $J_{3,4}$ 3.5, $J_{2,3}$ 11.3); 5.184 (dd, 1H, H-3', $J_{2,3}$ 10.2, $J_{3,4}$ 8.7); 5.422 (dd, 1H, H-4'', $J_{3,4}$ 3.5, $J_{4,5} \leq 1$); 7.469–7.555 (m, 5H, Ph).

4: ^{1}H NMR (700 MHz, $CDCl_3$: CD_3OD, 3:1), δ: 1.965 (m, 2H, CH_2 sp); 2.089, 2.096, 2.128, 2.211 (2), and 2.290 (5s, 6 x 3H, COMe); 3.410 (m, 1H, NCH sp); 3.529 (ddd, 1H, H-5'); 3.609 (m, 1H, NCH sp); 3.683 (m, 1H, OCH sp); 3.812 (dd, 1H, H-6'a, $J_{5,6a}$ 3.6, $J_{6a,6b}$ 12.2); 3.950 – 4.090 (m, 5H, OCH sp, H-6'b, H-4', H-2', H-5''); 4.166 (dd, 1H, H-2'', $J_{1,2}$ 8.3, $J_{2,3}$ 11.2); 4.254 (m, 2H, H-6''a, H-6''b); 4.553 (d, 1H, H-1', $J_{1,2}$ 8.6); 4.781 (d, 1H, H-1'', $J_{1,2}$ 8.3); 5.189 (dd≈t, 1H, H-3', J 9.7); 5.198 (dd, 1H, H-3'' $J_{3,4}$ 3.4, $J_{2,3}$ 11.2); 5.455 (dd≈d, 1H, H-4'', J 3.2).

GalNAcβ1-4GlcNAcβ-O(CH$_2$)$_3$NH$_2$ 5: ^{1}H NMR (800 MHz, D_2O), δ: 1.930 (m, 2H, CH_2 sp); 2.028 and 2.055 (2s, 2 x 3H, NCOMe); 3.064 (m ≈ t, 2H, NCH_2 sp, J 6.9); 3.513 (ddd, 1H, H-5',

$J_{4,5}$ 9.6, $J_{5,6a}$ 1.8, $J_{5,6b}$ 5.6); 3.606 (dd, 1H, H-4', $J_{4,5}$ 9.6, $J_{3,4}$ 8.0); 3.652 (dd, 1H, H-6b', $J_{5,6b}$ 5.6, $J_{6a.6b}$ 12.0); 3.665 – 3.735 (m, 4H, OCH sp, H-2', H-3', H-5''); 3.739 (dd, 1H, H-3'', $J_{2,3}$ 10.8, $J_{3,4}$ 3.5); 3.754 (dd, 1H, H-6a'', $J_{5,6a}$ 4.0, $J_{6a,6b}$ 11.7); 3.785 (dd, 1H, H-6b'', $J_{5,6b}$ 8.3, $J_{6a,6b}$ 11.7); 3.845 (dd, 1H, H-6a', $J_{5,6a}$ 1.8, $J_{6a,6b}$ 12.0); 3.915 (dd, 1H, H-2'', $J_{1,2}$ 8.4, $J_{2,3}$ 10.7); 3.929 (dd ≈ d, 1H, H-4'', J 2.0); 4.000 (m, 1H, OCH sp); 4.480 (d, 1H, H-1', $J_{1,2}$ 7.9); 4.507 (d, 1H, H-1'', $J_{1,2}$ 8.4). $[\alpha]_D$ -3.2 (c 0.5, MeCN : H_2O = 1:1). MS, m/z: 482 [M].

6-O-Su-GalNAcβ1-4GlcNAcβ-O$(CH_2)_3NH_2$ 6:^{1}H NMR (700 MHz, D_2O), δ: 1.976 (m, 2H, CH_2 sp); 2.063 and 2.115 (2s, 2 x 3H, NCOMe); 3.127 (m ≈ t, 2H, NCH_2 sp, J 6.8); 3.717 – 3.840 (m, 9H); 3.973 (dd ≈ d, 1H, H-4'', J 3.5); 3.983 (dd, 1H, H-2'', $J_{1,2}$ 8.4, $J_{2,3}$ 11.0); 4.007 (m, 1H, OCH sp); 4.164 (dd, 1H, H-6a', $J_{5,6a}$ 2.4, $J_{6a,6b}$ 11.2); 4.314 (dd ≈ d, 1H, H-6b', J 10.9); 4.550 (d, 1H, H-1' $J_{1,2}$ 8.4); 4.582 (d, 1H, H-1'', $J_{1,2}$ 8.4). $[\alpha]_D$ -7.1 (c 0.5, MeCN : H_2O = 1:1). MS, m/z: 561 [M].

7: ^{1}H NMR (700 MHz, $CDCl_3$: CD_3OD, 3:1), δ: 1,969 (m, 2H, CH_2 sp); 2.098 and 2.152 (2s, 2 x 3H, COMe); 3.410 (m, 1H, NCH sp); 3.596–3.682 (m, 3H, NCH and OCH sp, H-5'); 3.699 (m ≈ s, 1H, H-5''); 3.743 (dd ≈ t, 1H, H-4', $J_{3,4}$ 8.5, $J_{4,5}$ 9.5); 3.813 (dd, 1H, H-3'', $J_{2,3}$ 10.8, $J_{3,4}$ 3.7); 3.822 (dd, 1H, H-3', $J_{2,3}$ 10.4, $J_{3,4}$ 8.5); 3.871 (dd, 1H, H-6'a, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 11.5); 3.907 (dd, 1H, H-6'b, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 11.5); 3.936 (dd, 1H, H-2', $J_{1,2}$ 8.2, $J_{2,3}$ 10.4); 4.044 (m, 1H, OCH sp); 4.143 (dd, 1H, H-2'', $J_{1,2}$ 8.5, $J_{2,3}$ 10.8); 4.246 (dd, 1H, H-6''a, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 12.7); 4.404 (dd, 1H, H-6'b, $J_{5,6a}$ 1.3, $J_{6a,6b}$ 12,6); 4.509 (d, 1H, H-1', $J_{1,2}$ 8.2); 4.632 (d, 1H, H-1', $J_{1,2}$ 8.5); 4.692 and 4.862 (2d, 2 x 1H, CH_2Ph, $J_{A,B}$ 11.7); 5.735 (s, 1H, CHPh); 7.469 – 7.539 (m, 10H, 2 x Ph).

3,3'-O-Su_2-GalNAcβ1-4GlcNAcβ-O$(CH_2)_3NH_2$ 8: ^{1}H NMR (700 MHz, D_2O), δ: 1.978 (m, 2H, CH_2 sp); 2.040 and 2.081 (2s, 2 x 3H, NCOMe); 3.117 (m ≈ t, 2H, NCH_2 sp, J 6.9); 3.671 (ddd, 1H, H-5', $J_{5,6a}$ 2.8, $J_{5,6b}$ 5.9, $J_{4,5}$ 8.7); 3.712 – 3.768 (m, 3H, OCH sp, H-5', H-6b''); 3.772 (dd, 1H, H-6b', $J_{5,6b}$ 5.9, $J_{6a,6b}$ 11.9); 3.891 (dd, 1H, H-6a'', $J_{5,6a}$ 7.6, $J_{6a,6b}$ 11.7); 3.907 (dd ≈ t, 1H, H-4', J 8.5); 3.952 (dd, 1H, H-6'a, $J_{5,6a}$ 2.8, $J_{6a,6b}$ 11.9); 3.980 (dd ≈ t, 1H, H-2', J 8.5); 4.041 (m, 1H, OCH sp); 4.078 (dd, 1H, H-2'', $J_{1,2}$ 8.3, $J_{2,3}$ 10.5); 4.242 (dd ≈ d, 1H, H-4'', J 3.2); 4.436 (dd, 1H, H-3'', $J_{3,4}$ 3.2, $J_{2,3}$ 11.0); 4.572 (dd, 1H, H-3', $J_{3,4}$ 8.2, $J_{2,3}$ 8.9); 4.608 (d, 1H, H-1', $J_{1,2}$ 8.0); 4.707 (d, 1H, H-1'', $J_{1,2}$ 8.4). $[\alpha]_D$ -18.0 (c 0.15, MeCN: H_2O = 1:1). MS, m/z: 663 [M].

3'-O-Su-GalNAcβ1-4GlcNAcβ-O$(CH_2)_3NH_2$ 9: ^{1}H NMR (700 MHz, D_2O), δ: 1.969 (m, 2H, CH_2 sp); 2.067 and 2.084 (2s, 2 x 3H, NCOMe); 3.106 (m ≈ t, 2H, NCH_2 sp, J 7.0); 3.565 (ddd,

1H, H-5', $J_{5,6a}$ 2.0, $J_{5,6b}$ 5.6, $J_{4,5}$ 9.8); 3.666 (dd, 1H, H-4', $J_{4,5}$ 9.8, $J_{3,4}$ 8.0); 3.701 (dd, 1H, H-6b', $J_{5,6b}$ 5.6, $J_{6a,6b}$ 12.1); 3.712–3.850 (m 6H, OCH sp, H-2', H-3', H-5'', H-6a'', H-6b''); 3.893 (dd, 1H, H-6a', $J_{5,6a}$ 2.0, $J_{6a,6b}$ 12.1); 4.037 (m, 1H, OCH sp); 4.085 (dd ≈ t, 1H, H-2'', J 9.5); 4.280 (dd ≈ d, 1H, H-4'', J 3.1); 4.461 (dd, 1H, H-3'', $J_{3,4}$ 2.9, $J_{2,3}$ 11.0); 4.522 (d, 1H, H-1', $J_{1,2}$ 8.0); 4.701 (d, 1H, H-1'', $J_{1,2}$ 8.5). $[\alpha]_D$ -10.5 (c 0.5, MeCN:H_2O = 1:1). MS, m/z: 561 [M].

10: ^{1}H NMR (700 MHz, $CDCl_3$: CD_3OD, 3:1), δ: 1.970 (m, 2H, CH_2 sp); 2.011, 2.076, 2.179, and 2.201 (4s, 4 x 3H, COMe); 3.403 (m, 1H, NCH sp); 3.479 (m ≈ s, 1H, H-5''); 3.610 (m, 1H, NCH sp); 3.663 (m, 1H, OCH sp); 3.678 (ddd, 1H, H-5', $J_{5,6a}$ 2.0, $J_{5,6b}$ 3.9, $J_{4,5}$ 9.3); 3.854 (dd, 1H, H-6'b, $J_{5,6b}$ 3.9, $J_{6a,6b}$ 11.1); 3.901 (dd, 1H, H-6'a, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 11.1); 4.004 (dd, 1H, H-2'', $J_{1,2}$ 8.4, $J_{2,3}$ 11.3); 4.046 (m, 1H, OCH sp); 4.082 (dd ≈ t, 1H, H-4', J 9.1); 4.106 (dd, 1H, H-2', $J_{1,2}$ 8.4, $J_{2,3}$ 10.4); 4.175 (dd, 1H, H-6''a, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 12.4); 4.394 (dd, 1H, H-6''b, $J_{5,6b}$ 1.5, $J_{6a,6b}$ 12.4); 4.425 (dd ≈ d, 1H, H-4'', J 3.5); 4.563 (d, 1H, H-1', $J_{1,2}$ 8.4); 4.699 and 4.852 (2d, 2 x 1H, CH_2Ph, $J_{A,B}$ 11.7); 4.842 (d, 1H, H-1'', $J_{1,2}$ 8.3); 5.194 (dd, 1H, H-3', $J_{2,3}$ 10.4, $J_{3,4}$ 8.9); 5.280 (dd, 1H, H-3'', $J_{3,4}$ 3.7, $J_{2,3}$ 11.3); 5.651 (d, 1H, CHPh); 7.468–7.601 (m, 10H, 2 x Ph).

11: ^{1}H NMR (700 MHz, $CDCl_3$: CD_3OD, 3:1), δ: 1.969 (m, 2H, CH_2 sp); 1.991, 2.090, 2.210, and 2.218 (4s, 4 x 3H, COMe); 3.388 (m, 1H, NCH sp); 3.576 (ddd, 1H, H-5'', $J_{5,6a}$ 5.6, $J_{5,6b}$ 6.1, $J_{4,5} \leq 1$); 3.606 (m, 1H, NCH sp); 3.660 (m, 1H, OCH sp); 3.699 (ddd, 1H, H-5', $J_{5,6a}$ 2.4, $J_{5,6b}$ 4.5, $J_{4,5}$ 8.9); 3.825 (dd, 1H, H-6'b, $J_{5,6b}$ 4.5, $J_{6a,6b}$ 11.1); 3.872 (dd, 1H, H-6''a, $J_{5,6a}$ 5.6, $J_{6a,6b}$ 11.3); 3.891 (dd, 1H, H-6'a, $J_{5,6a}$ 2.4, $J_{6a,6b}$ 11.1); 3.918 (dd, 1H, H-6''b, $J_{5,6b}$ 6.1, $J_{6a,6b}$ 11.3); 4.034 (dd, 1H, H-4', $J_{4,5}$ 8.9, $J_{3,4}$ 8.7); 4.021 – 4.053 (m, 1H, OCH sp); 4.082 (dd, 1H, H-2', $J_{1,2}$ 8.2, $J_{2,3}$ 9.8); 4.126 (dd ≈ d, 1H, H-4'', J 3.0); 4.163 (dd, 1H, H-2'', $J_{1,2}$ 8.5, $J_{2,3}$ 11.1); 4.556 (d, 1H, H-1', $J_{1,2}$ 8.2); 4.628 (d, 1H, H-1'', $J_{1,2}$ 8.5); 4.676 and 4.849 (2d, 2 x 1H, CH_2Ph, $J_{A,B}$ 11.8); 4.967 (dd, 1H, H-3'', $J_{2,3}$ 11.1, $J_{3,4}$ 3.3); 5.177 (dd, 1H, H-3'. $J_{2,3}$ 9.8, $J_{3,4}$ 8.7); 7.475 – 7.563 (m, 5H, Ph).

4',6'-O-Su_2-GalNAcβ1-4GlcNAcβ-O$(CH_2)_3NH_2$ 12: ^{1}H NMR (700 MHz, D_2O), δ: 1.927 (m, 2H, CH_2 sp); 2.036 and 2.064 (2s, 2 x 3H, NCOMe); 3.059 (m ≈ t, 2H, NCH sp, J 6.9); 3.561 (ddd, 1H, H-5', $J_{5,6a}$ 1.9, $J_{5,6b}$ 5.6, $J_{4,5}$ 9.8); 3.609 (dd, 1H, H-4', $J_{3,4}$ 8.1, $J_{4,5}$ 9.8); 3.663 (dd, 1H, H-6'b, $J_{5,6b}$ 5.6, $J_{6a,6b}$ 12.0); 3.703 (m, 1H, OCH sp); 3.726 (dd, 1H, H-2', $J_{1,2}$ 8.4, $J_{2,3}$ 10.4); 3.779 (dd, 1H, H-3', $J_{2,3}$ 10.4, $J_{3,4}$ 8.1); 3.846 (dd, 1H, H-6'a, $J_{5,6a}$ 1.9, $J_{6a,6b}$ 12.0); 3.914 (dd, 1H, H-3'', $J_{3,4}$ 2.9, $J_{2,3}$ 11.0); 3.944 (dd, 1H, H-2'', $J_{1,2}$ 7.8, $J_{2,3}$ 11.0); 4.005 (m, 1H, OCH sp); 4.110 (ddd, 1H, H-5'', $J_{5,6a}$ 3.0, $J_{5,6b}$ 9.0, $J_{4,5} \leq 1$); 4.232 (dd, 1H, H-6''b, $J_{5,6b}$ 9.0, $J_{6a,6b}$ 11.5); 4.314 (dd, 1H, H-6''a, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 11.5); 4.489 (d, 1H, H-1', $J_{1,2}$ 8.4); 4.639 (d, 1H, H-1'', $J_{1,2}$ 7.8);

4.720 (dd ≈ d, 1H, H-4'', $J_{3,4}$ 2.9, $J_{4,5} \leq 1$). $[\alpha]_D$ -3.4 (c 0.5, MeCN:H_2O = 1:1). MS, m/z: 663 [M].

6'-O-Su-GalNAcβ1-4GlcNAcβ-O(CH_2)$_3$$NH_2$ 13: ^{1}H NMR (700 MHz, D_2O), δ: 1.934 (m, 2H, CH_2 sp); 2.035 and 2.060 (2s, 2 x 3H, NCOMe); 3.072 (m ≈ t, 2H, NCH_2 sp, J 7.0); 3.549 (ddd, 1H, H-5', $J_{4,5}$ 9.8, $J_{5,6a}$ 2.0, $J_{5,6b}$ 5.6); 3.597 (dd, 1H, H-4', $J_{4,5}$ 9.8, $J_{3,4}$ 7.8;); 3.660 (dd, 1H, H-6'b, $J_{5,6b}$ 5.6, $J_{6a,6b}$ 12.0); 3.699 (m, 1H, OCH sp); 3.747 (m, 3H, H-2', H-3', H-3''); 3.843 (dd, 1H, H-6a', $J_{5,6a}$ 2.0, $J_{6a,6b}$ 12.0); 3.942 (dd, 1H, H-2'', $J_{1,2}$ 8.5, $J_{2,3}$ 10.8); 3.968 (ddd, 1H, H-5'', $J_{5,6a}$ 4.7, $J_{5.6b}$ 7.6, $J_{4,5} \leq 1$); 3.993 (dd ≈ d, 1H, H-4'', J 2.7); 4.008 (m, 1H, OCH sp); 4.207 (dd, 1H, H-6''b, $J_{5,6b}$ 7.6, $J_{6a,6b}$ 10.9); 4.228 (dd, 1H, H-6a'', $J_{5,6a}$ 4.7, $J_{6a,6b}$ 10.9); 4.486 (d, 1H, H-1', $J_{1,2}$ 8.0); 4.556 (d, 1H, H-1'', $J_{1,2}$ 8.5). $[\alpha]_D$ -4.0 (c 0.25, MeCN:H_2O = 1:1). MS, m/z: 561 [M].

14: ^{1}H NMR (600 MHz, $CDCl_3$: CD_3OD, 3:1), δ: 1.960 (m, 2H, CH_2 sp); 1.973, 2.081, 2.130, and 2.213 (4s, 4 x 3H, COMe); 3.397 (m, 1H, NCH sp); 3.594 (m, 1H, NCH sp); 3.629-3.673 (m, 2H, OCH sp, H-5'); 3.684 (ddd ≈ t, 1H, H-5'', J 6.0); 3.786 (dd, 1H, H-6''a, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 9.6); 3.823 (dd, 1H, H-6'a, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 11.1); 3.856 (dd, 1H, H-6'b, $J_{5,6b}$ 2.2, $J_{6a,6b}$ 11.0); 3.876 (dd, 1H, H-6''b, $J_{5,6b}$ 6.5, $J_{6a,6b}$ 9.6); 4.022 (dd ≈ t, 1H, H-4', J 8.8); 4.029 (m, 1H, OCH sp); 4.097 (dd, 1H, H-2', $J_{1,2}$ 8.2, $J_{2,3}$ 10.0); 4.128 (dd ≈ d, 1H, H-4'', J 3.1); 4.147 (dd, 1H, H-2'', $J_{1,2}$ 8.4, $J_{2,3}$ 11.1); 4.526 (d, 1H, H-1', $J_{1,2}$ 8.2); 4.587 (d, 1H, H-1'', $J_{1,2}$ 8.4); 4.652 and 4.852, 4.681 and 4.706 (4d, 4 x 1H, 2 x CH_2Ph, $J_{A,B}$ 11.8); 4.954 (dd, 1H, H-3'', $J_{3,4}$ 3.1, $J_{2,3}$ 11.1); 5.149 (dd, 1H, H-3', $J_{2,3}$ 10.0, $J_{3,4}$ 8.5); 7.432 – 7.538 (m, 10H, 2 x Ph).

4'-O-Su-GalNAcβ1-4GlcNAcβ-O(CH_2)$_3$$NH_2$ 15: ^{1}H NMR (700 MHz, D_2O), δ: 1.937 (m, 2H, CH_2 sp); 2.032 and 2.062 (2s, 2 x 3H, NCOMe); 3.068 (m ≈ t, NCH_2 sp, J 7.0); 3.522 (ddd, 1H, H-5', $J_{5,6a}$ 1.8, $J_{5,6b}$ 5.5, $J_{4,5}$ 9.6); 3.588 – 3.867 (m, 9H); 3.899 (dd, 1H, H-3'', $J_{2,3}$ 11.0, $J_{3,4}$ 2.7); 3.925 (dd, 1H, H-2'', $J_{2,3}$ 11.0, $J_{1,2}$ 7.7); 4.007 (m, 1H, OCH sp); 4.485 (m, 1H, H-1', $J_{1,2}$ 8.2); 4.582 (d, 1H, H-1'', $J_{1,2}$ 7.6); 4.685 (dd ≈ d, H-4'', J 2.5). $[\alpha]_D$ -16.2 (c 0.5, MeCN:H_2O = 1:1). MS, m/z: 561 [M].

16: ^{1}H NMR (800 MHz, $CDCl_3$: CD_3OD, 3:1), δ: 1.956 (m, 2H, CH_2 sp); 2.087, 2.090, 2.129, 2.210, and 2.284 (5s, 5 x 3H, COMe); 3.406 (m, 1H, NCH sp); 3.546 (ddd, 1H, H-5', $J_{5,6a}$ 4.0, $J_{5,6b}$ 2.2, $J_{4,5}$ 9.3); 3.615 (m, 1H, NCH sp); 3.641 (dd, 1H, H-6''a, $J_{6a,6b}$ 11.2, $J_{5,6a}$ 6.2); 3.677 (m, 1H, OCH sp); 3.785 (dd, 1H, H-6''b, $J_{5,6b}$ 6.8, $J_{6a,6b}$ 11.2); 3.793 (dd, 1H, H-6'a, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 12.1); 3.829 (ddd ≈ t, 1H, H-5'', J 6.5); 3.971 (dd, 1H, H-6'b, $J_{5,6b}$ 2.2, $J_{6a,6b}$ 12.1); 4.008 (m, 1H,

OCH sp); 4.013 (dd, 1H, H-4', $J_{4,5}$ 9.2, $J_{3,4}$ 8.9); 4.036 (dd, 1H, H-2', $J_{1,2}$ 8.3, $J_{2,3}$ 10.1); 4.174 (dd, 1H, H-2'', $J_{1,2}$ 8.4, $J_{2,3}$ 11.1); 4.546 (d, 1H, H-1', $J_{1,2}$ 8.3); 4.744 (d, 1H, H-1'', $J_{1,2}$ 8.4); 5.166 (dd, 1H, H-3'', $J_{3,4}$ 3.5, $J_{2,3}$ 11.1); 5.183 (dd, 1H, H-3', $J_{2,3}$ 10.0, $J_{3,4}$ 8.9); 5.498 (dd ≈ d, H-4'', J 3.2).

6,6'-O-Su$_2$-GalNAcβ1-4GlcNAcβ-O(CH$_2$)$_3$NH$_2$ 17: ^{1}H NMR (700 MHz, D_2O), δ: 1.942 (m, 2H, CH_2 sp); 2.031 and 2.089 (2s, 2 x 3H, NCOMe); 3.098 (m ≈ t, 2H, NCH_2 sp, J 6.7); 3.676 – 3.785 (m, 6H, OCH sp, H-3'', H-2', H-3', H-4', H-5'); 3.944 – 4.012 (m, 4H, OCH sp, H-2'', H-4'', H-5''); 4.124 (dd, 1H, H-6'a, $J_{6a,6b}$ 11.0, $J_{6a,5}$ 4.4); 4.204 (dd, 1H, H-6''a, $J_{6a,6b}$ 10.7, $J_{6a,5}$ 7.4); 4.226 (dd, 1H, H-6''b, $J_{6a,6b}$ 10.7, $J_{6b,5}$ 4.9); 4.270 (dd, 1H, H-6'b, $J_{6a,6b}$ 11.0, $J_{6b,5}$ 1.6); 4.520 (d, 1H, H-1', $J_{1,2}$ 7.8); 4.586 (d, 1H, H-1'', $J_{1,2}$ 8.5). $[\alpha]_D$ -2.3 (c 0.3, MeCN:H_2O = 1:1). MS, m/z: 663 [M].