OL990406K

Supplementary Material

Ready Access to Sialylated Oligosaccharide Donors

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2-Naphthyl 1-thio-β-D-galactopyranoside 3b

1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (5 g; 12.8 mmol) was dissolved in dry CH_2Cl_2 (50 mL) and cooled to 0 °C under an atmosphere of argon. To this solution was added 2-naphthalene thiol (2.1 g; 13.0 mmol) followed by boron trifluoride etherate (2.3 mL; 19.0 mmol). The mixture was left to stir and warm to R.T. for 4 h. The mixture was cooled in an ice bath and quenched with triethylamine. After concentration the mixture was purified by chromatography to give **2b** (6.1 g; 98% yield): $[a]_D^{22}$ 6.0° (*c*, 0.7, $CHCl_3$); Anal. Calcd. for $C_{24}H_{26}O_9S$: C, 58.77; H, 5.41. Found C, 59.10; H, 5.41. Then **2b** (3.0 g; 6.1 mmol) was dissolved in methanol (150 mL) and freshly prepared sodium methoxide was added until pH = 10. After 4 h the reaction was neutralized with Rexyn 101(H) resin; filtered and evaporated. The residue was crystalized from absolute ethanol to give **3b**[1] (1.9 g; 97% yield): $[a]_D^{22}$ -21.3° (*c*, 1.0, CH_3OH); ^{13}C NMR (CD_3OD): δ 62.9 (C-6), 70.6 (C-4), 71.2 (C-2), 76.5 (C-3), 80.9 (C-5), 90.3 (C-1), 127.2, 127.6 (Ar-6, Ar-7), 128.6, 128.8 (Ar-5, Ar-8), 129.4 (Ar-4), 129.8 (Ar-3), 130.6 (Ar-1), 133.7, 133.8 (Ar-10, Ar-9), 135.3 (Ar-2); ^1H NMR (CD_3OD): δ 3.55 (1H, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.7 Hz, H-3), 3.65 (1H, brt, H-5), 3.69 (1H, brt, H-2), 3.76 (1H, dd, $J_{5,6b}$ = 5.1 Hz, $J_{6a,6b}$ = 11.7 Hz, H-6b) 3.83 (1H, dd, $J_{5,6a}$ = 7.3 Hz, $J_{6a,6b}$ = 11.7 Hz, H-6a), 3.94 (1H, brd, $J_{3,4}$ 2.9 Hz, H-4), 4.72 (1H, d, $J_{1,2}$ = 9.5 Hz, H-1); 7.46 (2H, m, Ar-6, Ar-7), 7.63 (1H, dd, $J_{3,4}$ = 8.6 Hz, $J_{1,3}$ = 1.8 Hz, Ar-3), 7.79 (3H, m, Ar-4, Ar-5, Ar-8), 8.08 (1H, d, $J_{1,3}$ = 1.8 Hz, Ar-1); Anal. Calcd. for $C_{16}H_{18}O_5S$: C, 59.61; H, 5.63. Found C, 59.25; H, 5.74.

Phenylthioglycosides **2a**, **13** and **3a** were prepared as described for **2b** and **3b** above, see Ref. [2].

Polymer bound acceptor **10** was prepared by glycosylation of MPEGDOXOH[3] using 3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalimido-β-D-glucopyranosyl trichloroacetimidate[4] as donor. After deacetylation using 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU, in methanol the primary hydroxyl was silylated according to Ref. [5].

Phenyl (5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)-(2→3)-1-thio-β-D-galactopyranoside 4a

Phenyl 1-thio-β-D-galactopyranoside **3a** (100 mg; 0.38 mmol) was sialylated with an α-2,3-sialyltransferase (CST-06) from *Campylobacter jejuni* (CST-06 is a *Campylobacter jejuni* α-2,3-sialyltransferase (CST-I) with *Escherichia coli* maltose-binding protein fused at the N-terminus). The reaction was performed in a total volume of 10 mL. The reaction contained **3a** (100 mg; 0.38 mmol), CTP (250 mg; 0.44 mmol), sialic acid (150 mg; 0.49 mmol), HEPES pH 7.5 (50 mM; 1.0 mL of 0.5 M HEPES), $MgCl_2$ (10 mM; 0.1 mL of 1 M $MgCl_2$), DTT (0.2 mM; 20 mL of 100 mM DTT), inorganic pyrophosphatase (10 mL; 10 U), CMP-NANA synthetase from *Neisseria meningitidis* NSY-04 (0.1 mL; 46 U) and CST-06 (2.6 mL; 0.56 U). The reaction was incubated at 32 °C overnight. The reaction was 40 % complete as determined by TLC on silica with isopropanol/

butanol/ 0.1 M HCl (2:1:1) as the developing solvent. Additional $MgCl_2$ (0.2 mL of 1 M $MgCl_2$), CST-06 (4.0 mL, 1.16 U) were added and the reaction was incubated at 32 °C overnight. The reaction was 80 % complete. Additional CTP (60 mg), sialic acid (40 mg), $MgCl_2$ (0.2 mL of 1 M $MgCl_2$), NSY-04 (0.1 mL, 46 U), inorganic pyrophosphatase (5 mL, 5 U), CST 06 (4 mL, 1.16 U) were added. The reaction was incubated at 32 °C overnight and was 95% complete. The reaction mixture was centrifuged and the supernatant was concentrated. The residue was placed on a Bio-Gel P2 column and eluted with water. Partially pure **5** was obtained (680 mg). A portion of this mixture (60 mg) was rechromatographed to obtain an analytically pure sample. The remaining amount (620 mg) was acetylated below: $[a]_D^{22}$ 1.3° (*c*, 0.2, H_2O); ^{13}C NMR (D_2O): δ 21.7 ($COCH_3$), 39.3 (C-3^{II}), 51.3 (C-5^{II}), 60.6 (C-6^{I}), 62.3 (C-9^{II}), 67.1 (C-2^{I}), 67.4 (C-4^{I}), 67.8 (C-7^{II}), 68.0 (C-4^{II}), 71.4 (C-8^{II}), 72.6 (C-6^{II}), 76.7 (C-3^{I}), 78.4 (C-5^{I}), 86.9 (C-1^{I}), 99.6 (C-2^{II}), 127.6-131.9 (Ar), 173.5 (C-1^{II}), 174.7 ($COCH_3$); ^1H NMR (D_2O): δ 1.63 (1H, t, $J_{3a,3e+3a,4}$ = 24.2 Hz, H-$3a^{II}$), 1.86 (1H, s, $COCH_3$), 2.58 (1H, dd, $J_{3e,3a}$ = 12.5 Hz, $J_{3e,4}$ = 4.4 Hz, H-$3e^{II}$), 3.42 (H-7^{II}), 3.45 (H-$9a^{II}$, H-6^{II}), 3.47 (H-2), 3.51 (H-4^{II}), 3.54 (H-$6a^{I}$, H-$6b^{I}$), 3.56 (H-5^{I}), 3.68 (H-5^{II}), 3.69 (H-$9b^{II}$), 3.70 (H-8^{II}), 3.83 (1H, d, *J*= 2.7 Hz, H-4^{I}), 3.96 (1H, dd, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 3.1 Hz, H-3^{I}), 4.68 (1H, H-1^{I}), 7.18-7.43 (5H, m, Ar); HRMS (FAB) Calcd. for $C_{23}H_{33}NO_{13}SNa$: 586.1586; found m/z: 586.1401 ($M+Na^+$).

2-Naphthyl (5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)-(2→3)-1-thio-β-D-galactopyranoside (4b)

2-Naphthyl 1-thio-β-D-galactopyranoside **3b** was sialylated with an α-2,3-sialyltransferase (CST-04) from *Campylobacter jejuni* (CST-04 is a *Campylobacter jejuni* α-2,3-sialyltransferase (CST-I) with CMP-Neu5Ac synthetase from *Neisseria meningitidis* fused at the N-terminus). The reaction was performed in a total volume of 500 mL. The reaction contained **3b** (1.0 g; 3.1 mmol), CTP (2.0 g; 3.5 mmol), sialic acid (1.25 g, 4.0 mmol), HEPES pH 7.5 (50 mM; 25 mL of 1 M HEPES), $MgCl_2$ (30 mM; 15 mL of 1 M $MgCl_2$), DTT (0.2 mM; 0.1 mL of 1M DTT) and CST-04 (50 mL; 75 U). The reaction was incubated at 32 °C and at 100 rpm overnight. The product formation was followed by TLC on silica with isopropanol/ butanol/ 0.1 M HCl (2:1:1) as the developing solvent. The reaction was 89 % complete as determined by capillary electrophoresis. The pH of the reaction was adjusted from 6.7 to 7.5 with 10 N NaOH. Additional $MgCl_2$ (15 mL of 1 M $MgCl_2$), CTP (0.3 g, 0.5 mmol), sialic acid (0.2 g; 0.65 mmol) and CST-04 were added. After 90 min at 37 °C the reaction was 97 % complete. The reaction mixture was centrifuged for 30 min at 10 K. The pellet was washed with water (100 mL) and recentrifuged. The supernatants were combined and recentrifuged for 30 min at 14 K. The final volume of the reaction mixture was 680 mL. The product was purified by reverse phase column chromatography on C-18 silica gel (35-70 micron particles). The reaction mixture was divided into 4 parts, each part was diluted to 800 mL and loaded on a column of 100 g of C-18 silica gel, at the rate of 4 mL/min. The column was washed with water (150 mL), 10 % MeOH (150 mL) and 50% MeOH (400 mL), 100% MeOH (100 mL). The product **4b** was obtained in the 50% MeOH fraction (1.7 g; 90% yield). $[\alpha]_D^{22}$ 6.4° (*c*, 1.0, H_2O); ^{13}C NMR (D_2O): δ 21.8 ($COCH_3$), 39.4 (C-3^{II}), 51.4 (C-5^{II}), 60.8 (C-6^{I}), 62.4 (C-9^{II}), 67.3 (C-2^{I}), 67.5 (C-4^{I}), 67.8 (C-7^{II}), 68.1 (C-4^{II}), 71.5 (C-8^{II}), 72.7 (C-6^{II}), 76.8 (C-3^{I}), 78.7 (C-5^{I}), 87.0 (C-1^{I}), 99.7 (C-2^{II}), 126.6-133.0 (Ar), 173.6 (C-1^{II}), 174.8 ($COCH_3$); ^1H NMR (D_2O): δ 1.63 (1H, t, $J_{3a,3e+3a,4}$ = 24.4 Hz, H-$3a^{II}$), 1.86 (1H, s, $COCH_3$), 2.59 (1H, dd, $J_{3e,3a}$ = 12.7 Hz, $J_{3e,4}$ = 4.9 Hz, H-$3e^{II}$), 3.41 (H-7^{II}), 3.45 (H-$9a^{II}$), 3.46 (H-6^{II}), 3.51 (H-4^{II}), 3.53 (H-2), 3.56 (H-$6a^{I}$, H-$6b^{I}$), 3.60 (H-5^{I}), 3.68 (H-5^{II}), 3.67 (H-$9b^{II}$), 3.70 (H-8^{II}), 3.85 (1H, d, *J* = 2.4 Hz, H-4^{I}), 3.99 (1H, dd, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 3.2 Hz, H-3^{I}), 4.78 (1H, $J_{2,3}$ = 9.8 Hz, H-1^{I}), 7.39-

7.94 (7H, Ar). Anal. Calcd. for $C_{27}H_{35}NO_{13}S$: C, 52.76; H, 5.74; N, 2.28. Found C, 52.56; H, 5.76; N, 2.09.

Phenyl [(5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl-1'→ 2-lactone)]-(2→3)-*O*-4,6-di-*O*-acetyl-1-thio-β-D-galactopyranoside (5a)
Partially pure phenyl thioglycoside **4a** (620 mg) was dissolved in pyridine (16 mL). Acetic anhydride (8 mL) was added at 0 °C. After 24 h at room temperature, additional pyridine (4 mL) and acetic anhydride (2 mL) were added. The reaction mixture was stirred for another 20 h and concentrated. It was dissolved in dichloromethane and washed with water. The organic extracts were dried over magnesium sulfate and concentrated. The residue was column chromatographed with hexane/ ethyl acetate/ methanol (3:3:0.5) as eluant. The title compound **5a** was obtained as a solid (193 mg; 75% yield from **3a**): $[\alpha]_D^{22}$ -31.3° (*c*, 0.3, CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.7, 20.8, 20.9, 20.94, 23.1 (7CO*C*H_3), 37.8 (C-3^{II}), 49.4 (C-5^{II}), 61.7 (C-6^{I}), 62.3 (C-9^{II}), 66.4 (C-4^{I}), 67.4 (C-7^{II}), 69.3 (C-4^{II}), 69.8 (C-8^{II}), 72.2 (C-2^{I}), 73.1 (C-6^{II}), 74.5 (C-5^{I}), 75.7 (C-3^{I}), 86.9 (C-1^{I}), 97.1 (C-2^{II}), 128.4, 129.1, 132.7, 133.2, (Ar), 163.6 (C-1^{II}), 169.7, 169.8, 170.2, 170.3, 170.4, 170.8, 170.9 (*C*OCH$_3$); ^1H NMR ($CDCl_3$): δ 1.91, 2.03, 2.06, 2.12, 2.13, 2.25, 2.63 (21H, 7s, 7COC*H*$_3$), 1.94 (1H, t, H-3a^{II}), 2.50 (1H, dd, $J_{3e,3a}$ = 13.2 Hz, $J_{3e,4}$ = 5.4 Hz, H-3e^{II}), 3.77 (1H, dd, H-6^{II}), 3.93 (1H, t, $J_{4,5+5,6}$ = 13.2 Hz, H-5), 4.03 (1H, dd, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 2.9 Hz, H-3^{I}), 4.12 (H-9^{II}), 4.15 (H-6a^{I}), 4.19 (2H, H-6b^{I}, H-5^{II}), 4.34 (1H, dd, $J_{8,9}$ = 2.9 Hz, $J_{9,9}$ = 12.7 Hz, H-9b^{II}), 4.68 (1H, d, $J_{1,2}$ = 9.8 Hz, H-1^{I}), 4.95 (1H, t, $J_{1,2+2,3}$ = 20.0 Hz, H-2^{I}), 5.19 (1H, m, H-8^{II}), 5.34 (1H, dd, H-7^{II}), 5.42 (1H, d, $J_{NH,5}$ = 5.9 Hz, N*H*Ac), 5.47 (1H, m, H-4^{II}), 5.53 (1H, d, *J*= 2.0 Hz, H-4^{I}), 7.33-7.58 (5H, m, Ar). MS(MALDI-TOF) Calcd. for $C_{35}H_{44}NO_{18}SNa$: 797.2200, found m/z: 798.3 ($M+H^+$); 820.3 ($M+Na^+$); 836.3 ($M+K^+$); HRMS (FAB) found m/z: 797.2133 ($M+Na^+$). Anal. Calcd. for $C_{35}H_{43}NO_{18}S$: C, 52.69; H, 5.43; N, 1.76. Found C, 53.12; H, 5.43; N, 1.64.

Phenyl [Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate)]-(2→3)-*O*-4,6-di-*O*-acetyl-1-thio-β-D-galactopyranoside (6)
The lactone **5a** (170 mg; 0.22 mmol) was dissolved in methanol (4.5 mL). 4-(Dimethylamino)pyridine (0.5 mL of a 10% solution; 0.05 mmol) was added at 0 °C. The reaction was stirred for 24 h at room temperature and concentrated under reduced pressure. The residue was column chromatographed with hexane/ ethyl acetate/ methanol (3:3:0.5) as eluant. The title compound **6a** was obtained as a solid (145 mg; 81% yield); $[\alpha]_D^{22}$ -6.5° (*c*, 0.46, CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 20.6, 20.7, 21.4, 23.2 (CO*C*H_3), 37.7 (C-3^{II}), 49.4 (C-5^{II}), 53.2 (OC*H*$_3$), 62.2 (C-9^{II}), 62.4 (C-6^{I}), 66.7 (C-7^{II}), 67.8 (C-2^{I}), 67.9 (C-4^{I}, C-8^{II}), 68.7 (H-4^{II}), 72.4 (H-6^{II}), 74.4 (C-5^{I}), 75.1 (C-3^{I}), 87.1 (C-1^{I}), 96.9, (C-2^{II}), 109.7 (C-1^{II}), 127.4-132.9 (Ar), 167.6 (C-1^{II}), 170.2, 170.4, 170.6, 170.7 (*C*OCH$_3$); ^1H NMR ($CDCl_3$): δ 1.71 (1H, t, $J_{3a,3e+3a,4}$ = 24.4 Hz, H-3a^{II}), 1.86, 1.98, 2.02, 2.05, 2.07, 2.09, 2.18, 2.26 (24H, 8s, 8COC*H*$_3$), 2.59 (1H, dd, $J_{3e,3a}$ = 12.7 Hz, $J_{3e,4}$ = 4.9 Hz, H-3e^{II}), 3.66 (1H, dd, $J_{5,6}$ = 10.8 Hz, $J_{6,7}$ = 2.2 Hz, H-6^{II}), 3.86 (3H, s, OC*H*$_3$), 3.94 (1H, t, $J_{4,5+5,6}$ = 12.1 Hz, H-5^{I}), 3.99 (1H, dd, $J_{8,9}$ = 5.4 Hz, $J_{9,9}$ = 12.3 Hz, H-9a^{II}), 4.07 (3H, m, H-6a^{I}, H-6b^{I}, H-5^{II}), 4.37 (1H, dd, $J_{8,9}$ = 2.1 Hz, $J_{9,9}$ = 12.3 Hz, H-9b^{II}), 4.66 (1H, dd, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{I}), 4.88 (1H, m, H-4^{II}), 4.90 (1H, d, $J_{1,2}$ = 9.8 Hz, H-1^{I}), 4.96 (1H, d, *J*= 2.9 Hz, H-4^{I}), 5.04 (1H, d, $J_{NH,5}$ = 10.3 Hz, N*H*Ac), 5.08 (1H, t, $J_{1,2+2,3}$ = 19.5 Hz, H-2^{I}), 5.38 (1H, dd, $J_{6,7}$ = 2.2 Hz, $J_{7,8}$ = 8.8 Hz, H-7^{II}), 5.56 (1H, m, H-8^{II}), 7.29 (3H, m, Ar), 7.54 (2H, m, Ar); HRMS (FAB) Calcd. for $C_{36}H_{47}NO_{19}SNa$: 852.2360, found m/z: 852.2418 ($M+Na^+$); Anal. Calcd. for $C_{36}H_{47}NO_{19}S$: C, 52.11; H, 5.71; N, 1.69. Found C, 51.96; H, 5.64; N, 1.52.

Phenyl [Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate)]-(2→3)-*O*-2,4,6-tri-*O*-acetyl-1-thio-β-D-galactopyranoside (7)
Alcohol **6** (110 mg; 0.13 mmol) was treated with pyridine (5 mL) and acetic anhydride (2.5 mL) at 10 °C. The reaction was stirred for 16 h at room temperature and concentrated under reduced pressure. The residue was column chromatographed with hexane/ ethyl acetate/ methanol (3:3:0.5) as eluant. The title compound **7** was obtained as a solid (114 mg; 88% yield): $[\alpha]_D^{22}$ 1.3° (*c*, 0.54, CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 20.7, 20.75, 20.78, 20.9, 21.5, 23.2 ($COCH_3$), 37.6 (C-3^{II}), 49.1 (C-5^{II}), 53.2 (OCH_3), 62.3 (C-6^{I}), 62.4 (C-9^{II}), 67.1 (C-7^{II}), 67.8 (C-4^{I}), 67.8 (C-8^{II}), 67.9(H-2^{I}), 69.3 (C-4^{II}), 72.1 (C-6^{II}), 72.3 (C-3^{I}), 74.3 (C-5^{I}), 85.6 (C-1^{I}), 96.8, (C-2^{II}), 127.6, 128.7, 132.0, 133.0 (Ar), 167.9 (C-1^{II}), 169.6, 169.7, 170.27, 170.33, 170.5, 170.9 ($COCH_3$); ^1H NMR ($CDCl_3$): δ 1.71 (1H, t, $J_{3a,3e+3a,4}$ = 24.4 Hz, H-3a^{II}), 1.86, 1.98, 2.02, 2.05, 2.07, 2.09, 2.18, 2.26 (24H, 8s, 8$COCH_3$), 2.59 (1H, dd, $J_{3e,3a}$ = 12.7 Hz, $J_{3e,4}$ = 4.9 Hz, H-3e^{II}), 3.66 (1H, dd, $J_{5,6}$ = 10.8 Hz, $J_{6,7}$ = 2.2 Hz, H-6^{II}), 3.86 (3H, s, OCH_3), 3.94 (1H, t, $J_{4,5+5,6}$ = 12.1 Hz, H-5^{I}), 3.99 (1H, dd, $J_{8,9}$ = 5.4 Hz, $J_{9,9}$ = 12.3 Hz, H-9a^{II}), 4.07 (3H, m, H-6a^{I}, H-6b^{I}, H-5^{II}), 4.37 (1H, dd, $J_{8,9}$ = 2.1 Hz, $J_{9,9}$ = 12.3 Hz, H-9b^{II}), 4.66 (1H, dd, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 3.4 Hz, H-3^{I}), 4.88 (1H, m, H-4^{II}), 4.90 (1H, d, $J_{1,2}$ = 9.8 Hz, H-1^{I}), 4.96 (1H, d, J= 2.9 Hz, H-4^{I}), 5.04 (1H, d, $J_{NH,5}$ = 10.3 Hz, N*H*Ac), 5.08 (1H, t, $J_{1,2+2,3}$ = 19.5 Hz, H-2^{I}), 5.38 (1H, dd, $J_{6,7}$ = 2.2 Hz, $J_{7,8}$ = 8.8 Hz, H-7^{II}), 5.56 (1H, m, H-8^{II}), 7.29 (3H, m, Ar), 7.54 (2H, m, Ar); HRMS (FAB) Calcd. for $C_{38}H_{49}NO_{20}SNa$: 894.2465, found m/z: 894.2424 ($M+Na^+$); Anal. Calcd. for $C_{38}H_{49}NO_{20}S$: C, 52.35; H, 5.66; N, 1.61. Found C, 52.12; H, 5.37; N, 1.57.

2-Naphthyl [(5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl-1'→ 2-lactone)]-(2→3)-*O*-4,6-di-*O*-acetyl-1-thio-β-D-galactopyranoside (5b)
Naphthyl thioglycoside **4b** (100 mg; 0.16 mmol) was treated with pyridine (7 mL) and acetic anhydride (4 mL) at 0 °C. The reaction was stirred for 24 h at room temperature and concentrated under reduced pressure. The residue was column chromatographed with hexane/ ethyl acetate/ methanol (3:3:0.5) as eluant. The title compound **5b** was obtained as a solid (126 mg; 90% yield). $[\alpha]_D^{22}$ -20.6° (*c*, 0.54, CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.65, 20.8, 20.9, 21.0, 23.2 (7$COCH_3$), 37.7 (C-3^{II}), 49.3 (C-5^{II}), 61.8 (C-6^{I}), 62.9 (C-9^{II}), 66.5 (C-4^{I}), 67.4 (C-7^{II}), 69.3 (C-4^{II}), 69.9 (C-8^{II}), 72.3 (C-2^{I}), 73.1 (C-6^{II}), 74.6 (C-5^{I}), 75.6 (C-3^{I}), 86.9 (C-1^{I}), 97.1 (C-2^{II}), 126.8, 127.6, 127.7, 128.7, 129.7, 130.4, 132.1, 132.8, 133.5 (Ar), 163.6 (C-1^{II}), 169.7, 169.9, 170.3, 170.4, 170.44, 170.8, 171.0 ($COCH_3$); ^1H NMR ($CDCl_3$): δ 1.92, 2.02, 2.03, 2.13, 2.14, 2.28 (21H, 6s, 7$COCH_3$), 1.97 (1H, t, $J_{3a,3e+3a,4}$ = 17.6 Hz, H-3a^{II}), 2.52 (1H, dd, $J_{3e,3a}$ = 13.7 Hz, $J_{3e,4}$ = 5.4 Hz, H-3e^{II}), 3.80 (1H, d, $J_{5,6}$ = 10.7 Hz, H-6^{II}), 3.93 (1H, t, $J_{4,5+5,6}$ = 12.7 Hz, H-5^{I}), 4.05 (1H, dd, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 2.9 Hz, H-3^{I}), 4.13 (H-9^{II}), 4.17 (H-6a^{I}), 4.21 (H-5^{II}), 4.24 (H-6b^{I}), 4.36 (1H, dd, $J_{8',9'}$= 2.9 Hz, $J_{9',9'}$ = 12.7 Hz, H-9b^{II}), 4.76 (1H, d, $J_{1,2}$ = 9.7 Hz, H-1^{I}), 5.0 (1H, t, $J_{1,2+2,3}$ = 20.0 Hz, H-2^{I}), 5.23 (1H, m, H-8^{II}), 5.35 (1H, dd, $J_{6,7}$ = 1.5 Hz, $J_{7,8}$ = 6.4 Hz, H-7^{II}), 5.47 (1H, m, H-4^{II}), 5.48 (1H, d, N*H*Ac), 5.53 (1H, d, J= 2.9 Hz, H-4^{I}), 7.50-7.53 (2H, m, Ar), 7.61-7.63 (1H, dd, Ar), 7.78-7.84 (3H, m, Ar), 8.06 (1H, x, Ar). HRMS (FAB) Calcd. for $C_{39}H_{45}NO_{18}SNa$: 870.2254, found m/z: 870.2252 ($M+Na^+$). Anal. Calcd. for $C_{39}H_{45}NO_{18}S$: C, 55.25; H, 5.35; N, 1.65. Found C, 55.18; H, 5.45; N, 1.48.

Phenyl (5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)-(2→3)-β-D-galactopyranosyl-(1→4)-1-thio-β-D-glucopyranoside 14
Thioglycoside **13** (100 mg; 0.23 mmol) was sialylated as above for **4b** using CST-04. The

product was partially purified by P-2 gel permeation chromatography to yield 95% pure **14** (152 mg; 87% yield): $[a]_D^{22}$ -15.2° (*c*, 0.11, CH_3OH); ^{13}C NMR (D_2O): δ 22.9 ($COCH_3$), 40.2 (C-3^{III}), 52.5 (C-5^{III}), 60.9 (C-6^{I}), 61.9 (C-6^{II}), 63.4 (C-9^{II}), 68.3 (C-4^{II}), 69.2 (C-2^{II}), 69.4 (C-6^{III}), 70.2 (C-7^{II}), 72.3 (C-2^{I}), 72.6 (C-8^{III}), 73.7 (C-4^{III}), 76.3 (C-3^{II}), 76.6 (C-3^{I}), 78.6 (C-4^{I}), 79.6 (C-5^{I}), 88.0 (C-1^{I}), 100.6 (C-2^{III}), 103.4 (C-1^{I}), 128.9, 130.1, 132.5, 132.7 (Ar), 174.7 (C-1^{III}), 175.8 ($COCH_3$); ^1H NMR (D_2O): δ 1.69 (1H, t, $J_{3a,4}$ = 12.7 Hz, $J_{3e,3a}$ 12.2 Hz, H-$3a^{III}$), 1.92 (1H, s, $COCH_3$), 2.65 (1H, dd, $J_{3e,3a}$ = 12.2 Hz, $J_{3e,4}$ = 4.4 Hz, H-$3e^{III}$), 3.30 (1H, dd, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.3 Hz, H-2^{I}), 3.39 (1H, m, H-6^{III}), 3.44 (1H, m, H-7^{III}), 3.46 (1H, m, H-2^{II}), 3.52 (2H, m, H-5^{I}, H-4^{III}), 3.53 (1H, m, H-$9a^{III}$), 3.57 (1H, m, H-4^{I}), 3.58 (2H, m, H-3^{I}, H-5^{II}), 3.62 (2H, m, H-$6ab^{II}$), 3.71 (H-$6a^{I}$), 3.76 (1H, m, H-$9b^{III}$), 3.77 (1H, m, H-8^{III}), 3.80 (1H, m, H-5^{III}), 3.85 (1H, m, H-4^{II}), 3.86(1H, m, H-$6b^{I}$), 4.01 (1H, dd, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 3.6 Hz, H-3^{II}), 4.42 (1H, d, $J_{1,2}$ = 7.8 Hz, H-1^{II}), 4.71 (1H, d, $J_{1,2}$ = 9.8 Hz, H-1^{I}), 7.28 (3H, m, Ar), 7.48 (2H, d, *J* = 6.8 Hz, Ar); HRMS(FAB) Calcd. for $C_{29}H_{43}NO_{18}SNa$: 748.2099, found m/z: 748.2030 ($M+Na^+$).

Phenyl [(5-Acetamido-4,8,9-tri-*O*-benzoyl-l-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl-1'→2-lactone)]-(2→3)-*O*-4,6-di-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (15)

Partially pure phenyl thioglycoside **14** (130 mg; 0.18 mmol) was dissolved in pyridine (20 mL). Benzoic anhydride (1.62 g, 40 eq.) was added and the mixture heated at 40 °C. After 44 h the reaction was cooled and quenched with methanol and concentrated. The residue was column chromatographed with hexane/ ethyl acetate (6:4) as eluant. The title compound **15** was obtained as a slightly impure solid (141 mg; 50% yield). A small portion was rechromatographed with toluene/ ethyl acetate (6:4) as eluant to yield analytically pure material. $[\alpha]_D^{22}$ -23.2° (*c* 0.75 $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 22.8 ($COCH_3$), 37.6 (C-3^{III}), 51.3 (C-5^{III}), 60.5 (C-6^{II}), 61.8 (C-6^{I}), 63.0 (C-9^{III}), 66.0 (C-7^{III}), 66.1 (C-4^{II}), 69.2 (C-4^{III}), 70.1 (C-2^{I}), 70.2 (C-8^{III}), 71.3 (C-5^{II}), 72.9 (C-6^{III}),73.3 (C-3^{I}), 73.4 (C-2^{II}), 73.7 (C-3^{II}), 76.2 (C-4^{I}), 76.6 (C-5^{I}), 85.7 (C-1^{I}), 97.1 (C-2^{III}), 100.0 (C-1^{II}), 128.3, 130.0, 133.3 (Ar), 163.2 (C-1^{I}), 165.2, 165.3, 165.4, 166.1, 167.2 (*C*OPh), 172.9 (*C*ON); ^1H NMR ($CDCl_3$): δ 1.85 (3H, s, $COCH_3$), 2.00 (1H, t, $J_{3a,3e+3a,4}$ = 13.4 Hz, H-$3a^{III}$), 2.47 (1H, dd, $J_{3e,3a}$ = 12.2 Hz, $J_{3e,4}$ = 5.5 Hz, H-$3e^{III}$), 3.23 (1H, m, H-5^{I}), 3.50 (1H, m, H-6^{III}), 3.53 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, $J_{5,6b}$ = 6.1 Hz, H-$6b^{II}$), 3.66 (2H, m, H-5^{II}, H-$6a^{II}$), 3.86 (1H, m, H-7^{III}), 3.98 (1H, brt, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ 9.8 Hz, H-4^{I}), 4.08 (1H, brdd, $J_{4,5}$ = 10.4 Hz, $J_{5,NH}$ = 7.9 Hz, H-5^{III}), 4.32 (2H, m, H-$6a^{I}$, H-$9b^{III}$), 4.48 (1H, d, $J_{1,2}$ = 7.6 Hz, H-1^{II}), 4.58 (1H, brd, $J_{6a,6b}$ = 11.3 Hz, H-$6a^{I}$), 4.84 (2H, m, H-8^{III}, H-2^{II}), 4.84 (1H, d, $J_{1,2}$ = 9.8 Hz, H-1^{I}), 4.88 (1H, m, H-3^{II}), 4.99 (1H, m, H-8^{III}), 5.33 (1H, t, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{I}), 5.53 (1H, brd, $J_{3,4}$ 2.8 Hz, H-4^{II}), 5.80 (1H, t, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.8 Hz, H-3^{I}), 5.86 (1H, ddd, $J_{3a,4}$ = 5.5 Hz, $J_{3b,4}$ = 12.2 Hz, $J_{4,5}$ = 10.4 Hz, H-4^{III}), 6.14 (1H, d, $J_{NH,5}$ = 7.9 Hz, NH), 7.07 (2H, t, *J* = 7.4 Hz, Ar), 7.16 (2H, t, *J* = 7.4 Hz, Ar), 7.27 (2H, m, Ar), 7.40 (12H, m, Ar), 7.48 (6H, m, Ar), 7.55 (5H, m, Ar), 7.89, 7.93, 7.95, 7.96, 7.99, 8.01, 8.06, 8.10, 8.12 (18H, 9brd, *J* = 7.6 Hz, Ar). MS (FAB) Calcd. for $C_{85}H_{73}NO_{25}SNa$: m/z: 1562.4089, found m/z: 1563 ($M+Na^+$), 956 (M-GlcSPh$^+$). Anal. Calcd. for $C_{85}H_{73}NO_{25}S$: C, 66.27; H, 4.78; N, 0.97. Found C, 66.37; H, 4.74; N, 0.76.

Phenyl [Methyl (5-acetamido-4,8,9-tri-*O*-benzoyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate)]-(2→3)-*O*-4,6-di-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (16)

Lactone **15** (78 mg; 0.051 μmol) was converted to its methyl ester as described above for **6a** (44 mg, 55%). $[\alpha]_D^{22}$ -7.7° (*c* 0.64 $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 23.0 ($COCH_3$), 37.7 (C-3^{III}), 51.7 (C-

5^{III}), 52.5 (OCH_3), 61.3 (C-6^{II}), 63.1 (C-6^{I}), 64.3 (C-9^{III}), 67.0 (C-7^{III}), 68.2 (C-4^{II}), 68.9 (C-4^{III}), 69.9 (C-8^{III}), 70.0 (C-2^{II}), 70.5 (C-2^{I}), 71.1 (C-5^{II}), 74.4 (C-6^{III}), 74.4 (C-3^{II}), 74.8 (C-3^{I}), 75.6 (C-4^{I}), 77.5 (C-5^{I}), 85.9 (C-1^{I}), 96.8 (C-2^{III}), 103.7 (C-1^{II}), 128.3, 129.7, 132.9 (Ar), 165.2, 165.3, 165.4, 165.5, 165.9, 166.0 (*C*OPh), 167.5 (C-1^{I}), 172.8 (*C*ON); ^{1}H NMR ($CDCl_3$): δ 1.92 (3H, s, $COCH_3$), 1.94 (1H, t, $J_{3a,3e+3a,4}$ = 12.8 Hz, H-$3a^{III}$), 2.59 (1H, dd, $J_{3e,3a}$ = 12.5 Hz, $J_{3e,4}$ = 4.9 Hz, H-$3e^{III}$), 3.25 (3H, s, OCH_3), 3.31 (1H, brs, OH), 3.54 (1H, dd, $J_{6a,6b}$ = 11.3 Hz, $J_{5,6b}$ = 6.4 Hz, H-$6b^{II}$), 3.57 (1H, m, H-6^{III}), 3.70 (1H, dd, $J_{6a,6b}$ = 11.3 Hz, $J_{5,6a}$ = 7.0 Hz, H-$6a^{II}$), 3.78 (1H, dd, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 10.1 Hz, H-2^{II}), 3.86 (1H, brt, H-5^{II}), 4.02 (1H, dd, $J_{6,7}$ = 4.9 Hz, $J_{7,8}$ = 8.2 Hz, H-7^{III}), 4.14 (1H, m, H-5^{III}), 4.14 (1H, m, H-5^{I}), 4.36 (1H, brt, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ 9.5 Hz, H-4^{I}), 4.62 (1H, dd, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 3.0 Hz, H-3^{II}), 4.65 (1H, dd, $J_{9a,9b}$ = 12.2 Hz, $J_{8,9b}$ = 4.9 Hz, H-$9b^{III}$), 4.78 (1H, dd, $J_{6a,6b}$ = 11.9 Hz, $J_{5,6b}$ = 5.2 Hz H-$6b^{I}$), 4.89 (1H, d, $J_{1,2}$ = 7.6 Hz, H-1^{II}), 4.97 (1H, dd, $J_{9a,9b}$ = 12.2 Hz, $J_{8,9a}$ = 3.9 Hz, H-$9a^{III}$), 5.02 (1H, d, $J_{1,2}$ = 9.8 Hz, H-1^{I}), 5.19 (1H, m, H-$6a^{I}$), 5.19 (1H, m, H-4^{II}), 5.25 (1H, ddd, $J_{3a,4}$ = 4.9 Hz, $J_{3b,4}$ = 12.5 Hz, $J_{4,5}$ = 10.7 Hz, H-4^{III}), 5.49 (1H, t, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{I}), 5.83 (1H, m, H-8^{III}), 5.86 (1H, t, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.8 Hz, H-3^{I}), 6.09 (1H, d, $J_{NH,5}$ = 7.9 Hz, NH), 7.07 (2H, t, J = 7.9 Hz, Ar), 7.13 (2H, t, J = 7.3 Hz, Ar), 7.26 (5H, m, Ar), 7.48 (20H, m, Ar), 7.74, 7.89, 7.93, 7.95, 7.99, 8.01, 8.01, 8.03 (16H, 8brd, J = 7.6 Hz, Ar). MS (FAB) Calcd. for $C_{86}H_{77}NO_{26}SNa$: m/z: 1594.4351, found m/z: 1594.3 ($M+Na^+$), 618 ($Bz_3MeNeu5Ac^+$). Anal. Calcd. for $C_{86}H_{77}NO_{26}S$: C, 65.69; H, 4.94; N, 0.89. Found C, 66.13; H, 4.91; N, 0.77.

Phenyl [Methyl (*5*-diacetamido-7-*O*-acetyl-4,8,9-tri-*O*-benzoyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate)]-(*2→3*)-*O*-2-*O*-acetyl-4,6-di-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (17)

Diol **16** (29 mg; 18 μmol) was dissolved in isopropenyl acetate (4 mL) to which was added *p*-toluenesulphonic acid (2 mg) and heated at 70 °C for 16 h. The mixture was neutralized with a few drops of triethylamine and after concentration was purified by column chromatography eluting with ethyl acetate/ hexanes (6:4) to give **17** (29 mg; 92% yield); $[\alpha]_D^{22}$ 2.3° (*c* 0.26 $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 20.9, 21.3 ($OCOCH_3$), 26.8, 28.0 ($NCOCH_3$), 38.6 (C-3^{III}), 56.2 (C-5^{III}), 52.8 (OCH_3), 60.7 (C-6^{II}), 63.1 (C-6^{I}), 63.1 (C-9^{III}), 67.6 (C-7^{III}), 67.6 (C-4^{II}), 67.6 (C-4^{III}), 69.4 (C-8^{III}), 70.6 (C-2^{II}), 70.5 (C-2^{I}), 70.9 (C-5^{II}), 70.0 (C-6^{III}), 72.0 (C-3^{II}), 74.6 (C-3^{I}), 77.0 (C-4^{I}), 77.2 (C-5^{I}), 86.0 (C-1^{I}), 97.2 (C-2^{III}), 101.6 (C-1^{II}), 128.3, 129.6, 133.0 (Ar), 165.0, 165.2, 165.4, 165.8, 166.0 (*C*OPh), 167.4 (C-1^{I}), 169.8, 170.1($COCH_3$), 173.3, 174.2 (*C*ON); ^{1}H NMR ($CDCl_3$): δ 1.59 (1H, t, $J_{3a,3e+3a,4}$ = 12.8 Hz, H-$3a^{III}$), 2.04, 2.07, 2.26, 2.33 (12H, s, $COCH_3$), 2.63 (1H, dd, $J_{3e,3a}$ = 12.5 Hz, $J_{3e,4}$ = 5.2 Hz, H-$3e^{III}$), 3.46 (3H, s, OCH_3), 3.40 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, $J_{5,6b}$ = 8.2 Hz, H-$6b^{II}$), 3.48 (1H, dd, $J_{6a,6b}$ = 11.0 Hz, $J_{5,6a}$ = 5.5 Hz, H-$6a^{II}$), 3.76 (1H, brt, H-5^{II}), 3.99 (1H, m, H-5^{I}), 4.10 (1H, brt, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ 9.5 Hz, H-4^{I}), 4.27 (1H, dd, $J_{9a,9b}$ = 12.5 Hz, $J_{8,9b}$ = 6.1 Hz, H-$9b^{III}$), 4.46 (1H, dd, $J_{6a,6b}$ = 11.9 Hz, $J_{5,6b}$ = 6.1 Hz H-$6b^{I}$), 4.53 (1H, t, $J_{4,5}$ = 10.4 Hz, $J_{5,6}$ = 10.1 Hz, H-5^{III}), 4.77 (1H, dd, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 3.0 Hz, H-3^{II}), 4.77 (1H, dd, $J_{5,6}$ = 10.1 Hz, $J_{6,7}$ = 2.1 Hz, H-6^{III}), 4.91 (1H, d, $J_{1,2}$ = 7.9 Hz, H-1^{II}), 4.91 (1H, m, H-$9a^{III}$), 4.91 (1H, m, H-1^{I}), 4.91 (1H, m, H-$6a^{I}$), 5.03 (1H, brd, $J_{3,4}$ = 3.1 Hz, H-4^{II}), 5.06 (1H, dd, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.1 Hz, H-2^{II}), 5.38 (1H, t, $J_{1,2}$ = 9.2 Hz, $J_{2,3}$ = 9.5 Hz, H-2^{I}), 5.39 (1H, m, H-7^{III}), 5.66 (1H, ddd, $J_{3a,4}$ = 5.2 Hz, $J_{3b,4}$ = 12.8 Hz, $J_{4,5}$ = 10.7 Hz, H-4^{III}), 5.73 (1H, t, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.8 Hz, H-3^{I}), 5.86 (1H, m, H-8^{III}), 7.00 (2H, t, J = 7.9 Hz, Ar), 7.06 (2H, t, J = 7.3 Hz, Ar), 7.19 (3, m, Ar), 7.32 (14H, m Ar), 7.45 (8H, m Ar), 7.73, 7.78, 7.79, 7.79, 7.81, 7.89, 7.91, 7.98 (16H, 8brd, J = 7.6 Hz, Ar). MS (FAB) Calcd. for $C_{92}H_{83}NO_{29}SK$: m/z: 1720.4667, found m/z: 1720.2 ($M+Na^+$), 1588.4 ($M-SPh^+$), 1114.3 ($Bz_5Ac_4MeNeu5AcGal^+$).

Methyl [(5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl-1"→ 2'-lactone)]-(2→3)-*O*-(4,6-di-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-*O*-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9)

1. Preparation from 5a.

A mixture of compound **5a** (22 mg; 0.03 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **8** (14 mg; 0.03 mmol) and 4Å molecular sieves in anhydrous dichloromethane (0.7 mL) was stirred under argon for 1 h. The reaction mixture was cooled to 0-5 °C and treated with *N*-iodosuccinimide (17 mg; 0.08 mmol) and triflic acid (2.2 μL, 0.02 mmol). The reaction mixture was stirred at room temperature for 4 h, cooled to 0 °C, quenched with triethylamine, filtered and concentrated. The residue was column chromatographed with hexane/ ethyl acetate/ ethanol (3:3:0.5) as eluant. The title compound **9** was obtained as a foam (28 mg; 90% yield).

2. Preparation from 5b

A mixture of compound **5b** (15 mg; 0.02 mmol) and **8** (14 mg; 0.03 mmol) and 4Å molecular sieves in anhydrous dichloromethane (0.5 mL) was stirred under argon for 1 h. The reaction mixture was cooled to 0-5 °C and treated *N*-iodosuccinimide (17 mg; 0.08 mmol) and triflic acid (1.7 μL; 0.02 mmol). The reaction mixture was stirred at room temperature for 4 h, cooled to 0 °C and quenched with triethylamine, filtered and concentrated. The residue was column chromatographed with hexane/ ethyl acetate/ ethanol (3:3:0.5) as eluant. The title compound **9** was obtained as a foam (19 mg; 86% yield). $[\alpha]_D^{22}$ -5.6° (*c*, 0.54, CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 20.6, 20.61, 20.7, 20.8, 23.1 (7COCH$_3$), 37.8 (C-3^{III}), 49.4 (C-5^{III}), 55.5 (OCH$_3$), 61.1 (C-6^{I}), 62.0 (C-9^{III}), 66.1 (C-4^{II}), 67.1 (C-7^{III}), 68.9 (C-6^{II}), 69.4 (C-4^{III}, C-8^{III}), 70.0 (C-5^{I}), 70.8 (C-5^{II}), 72.8 (C-6^{III}), 73.1 (Bn), 73.3 (H-2^{II}), 74.0 (C-3^{II}), 74.9 (Bn), 75.7 (Bn), 77.4 (C-4^{I}), 79.3 (C-2^{I}), 81.9 (C-3^{I}), 97.0 (C-2^{III}), 97.9 (C-1^{I}), 100.6 (C-1^{III}), 127.5-138.8 (Ar), 163.5 (C-1^{II}), 169.5, 169.6, 169.8, 170.4, 170.43, 170.6, 170.9 (7*C*OCH$_3$); ^1H NMR ($CDCl_3$): δ 1.90, 2.02, 2.03, 2.04, 2.09, 2.19 (21H, 6s, 7COC*H*$_3$), 1.89 (1H, t, $J_{3a,3e+3a,4}$ = 24.9 Hz, H-3a^{III}), 2.44 (1H, dd, $J_{3e,3a}$ = 13.5 Hz, $J_{3e,4}$ = 5.6 Hz, H-3e^{III}), 3.42 (3H, s, OC*H*$_3$), 3.53 (1H, dd, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 9.3 Hz, H-2^{I}), 3.65-3.69 (2H, m, H-6^{III}, H-4^{I}), 3.73 (1H, dd, $J_{5,6}$ = 4.9 Hz, $J_{6,6}$ = 10.8 Hz, H-6a^{II}), 3.81 (1H,dd, $J_{4,5}$ = 10.3 Hz, $J_{5,6}$ = 4.4 Hz, H-5^{I}), 3.87 (1H, t, $J_{4,5+5,6}$ = 13.7 Hz, H-5^{II}), 3.92 (1H, dd, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 2.9 Hz, H-3^{II}), 4.01 (1H, t, $J_{2,3+3,4}$ = 18.6, Hz, H-3^{I}), 4.08-4.18 (5H, m, H-6^{I}a, H-6^{I}b, H-5^{III}, H-6^{II}, H-9^{III}), 4.24 (1H, dd, $J_{8,9}$ = 2.9 Hz, $J_{9,9}$ = 12.2 Hz, H-9b^{III}), 4.63 (1H, d, $J_{1,2}$ = 3.4 Hz, H-1^{I}), 4.69 (2H, d, 2C*H*HC$_6$H$_5$), 4.77 (1H, d, C*H*HC$_6$H$_5$), 4.77 (1H, t, $J_{1,2+2,3}$ = 20.3 Hz, H-2^{II}), 4.83 (1H, d, C*H*HC$_6$H$_5$),), 4.93 (1H, d, C*H*HC$_6$H$_5$), 5.0 (1H, d, C*H*HC$_6$H$_5$), 5.09 (1H, m, H-8^{III}), 5.32 (1H, dd, $J_{7,8}$ = 7.8 Hz, H-7^{III}), 5.40 (1H, ddd, H-4^{III}), 5.44 (1H, d, *J*= 2.5 Hz, H-4^{II}), 5.54 (1H, d, *J*=10.3, N*H*Ac), 7.20-7.30 (15H, m, Ar); MS (MALDI-TOF) Calcd. for $C_{57}H_{69}NO_{24}Na$: 1174.4105, found m/z: 1174.8 (M+Na$^+$); 1190.8 (M+K$^+$).

MPEG-DOXyl [Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate)]-(2→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside 11

A mixture of compound **7** (20 mg; 0.02 mmol) and MPEG-DOXyl 6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside **10** (100 mg; 0.02 mmol) was dried over drierite/$CaCl_2$ overnight under vacuum. The reaction flask was opened under argon and freshly activated 4Å molecular sieves were added. Anhydrous dichloromethane (0.8 mL) was added and the reaction mixture was stirred for 1 h. It was cooled to 0°C and treated with *N*-iodosuccinimide (18 mg; 0.08 mmol), followed by triflic acid (2.0 μl; 0.02 mmol). The reaction mixture was warmed to room temperature, stirred for 1 h. At this point TLC indicated complete

exhaustion of the glycosyl donor **7**. The reaction mixture was cooled to 0 °C and diisopropylethylamine (2 drops) was added, followed in 10 min by excess *tert*-butyl methyl ether (75 mL). The reaction was vigorously stirred for 15 min in order to precipitate the polymer. The polymer was filtered and recrystallized from absolute ethanol (75 mL). The white precipitate was collected by filtration and rinsed with diethyl ether (2x10 mL) and dried *in vacuo* to afford the polymer bound trisaccharide **11** (70 mg; 70 % yield). The product was characterized as the cleaved compound **12**.

4-*O*-Acetyl-DOXyl [Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate)]-(2→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside 12
The polymer bound trisaccharide **11** (70 mg; 0.014 mmol) was dissolved in dichloromethane (0.7 mL). Acetic anhydride (0.7 mL) was added followed by scandium (III) trifluoromethane sulfonate (7 mg; 0.014 mmol). The reaction mixture was stirred under argon for 3.5 h, cooled to 0 °C, and treated with an excess of *tert*-butyl methyl ether (75 mL). The mixture was stirred for 15 min in order to precipitate the polymer. The precipitate was filtered and the filtrate was concentrated. The residue was purified by column chromatography with hexane/ ethyl acetate/ ethanol (3:3:0.5) as eluant. The title compound **12** was obtained (11 mg; 52 % yield). $[\alpha]_D^{22}$ 6.1° (*c*, 0.31, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 20.2- 20.9 ($COCH_3$), 26.6 ($C(CH_3)_3$) 37.2 (C-3^{III}), 48.9 (C-5^{III}), 52.9 (OCH3), 55.0 (C-2^{I}), 61.2 (C-6^{II}), 62.3 (C-9^{III}), 63.1 (C-6^{I}), 65.7 ($CH_2C_6H_5$-DOX), 66.9 (C-4^{II}), 67.0 (C-7^{III}), 67.6 (C-8^{III}), 69.1 (C-4^{III}), 69.9 (C-5^{I}), 70.0 ($CH_2C_6H_5$-DOX), 70.1 (C-2^{II}), 71.2 (C-3^{II}), 71.9 (C-6^{III}), 75.4 (C-5^{II}), 76.3 (H-4^{I}), 96.7 (C-1^{I}), 100.2 (C-1^{II}), 130.0-140.0 (Ar); ^1H NMR ($CDCl_3$): δ 1.10 (9H, s, $C(CH_3)_3$), 1.67 (1H, t, $J_{3a,3e+3a,4}$ = 24.9 Hz, H-$3a^{III}$), 1.85, 1.96, 1.98, 2.01, 2.04, 2.06, 2.08, 2.09, 2.12 (30H, 9s, $10COCH_3$), 2.56 (1H, dd, $J_{3e,3a}$ = 12.7 Hz, $J_{3e,4}$ = 4.4 Hz, H-$3e^{III}$), 3.60 (1H, dd, H-6^{III}), 3.82 (OCH_3, H-5^{II}), 3.83 (H-5^{I}), 3.89 (H-$9a^{III}$), 3.90 (H-6^{I}a), 3.93 (H-$6a^{II}$), 3.96 (H-4^{I}), 3.97 (H-$6b^{II}$), 4.02 (H-5^{III}), 4.13 (H-6^{I}b),), 4.22 (1H, dd, $J_{1,2+2,3}$ = 19.1 Hz, H-2^{I}), 4.33(H-$9b^{III}$), 4.40 ($CHHC_6H_5$), 4.52 (1H, dd, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 2.9 Hz, H-3^{II}), 4.74 ($CHHC_6H_5$), 4.85 (H-4^{II}, H-4^{III}), 4.86 (H-1^{II}), 4.92 (H-2^{II}), 5.0 (2H, s, $CH_2C_6H_5$), 5.06 (1H, d, *J* = 10.8 Hz, N*H*), 5.33 (1H, m, H-7^{III}), 5.41 (1H, d, $J_{1,2}$ = 8.8 Hz, H-1^{I}), 5.51 (1H, m, H-8^{III}), 5.77 (1H, t, $J_{2,3+3,4}$ = 19.1 Hz, H-3^{I}), 7.07 (4H, dd, Ar-DOX), 7.38-7.80 (Ar). MS (MALDI-TOF) Calcd. for $C_{74}H_{88}N_2O_{30}SiNa$: 1535.5088, found m/z: 1535.7 ($M+Na^+$); 1551.7 ($M+K^+$).

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