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Cite this: *RSC Adv.*, 2014, **4**, 10856

Facile preparation of indoxyl- and nitrophenyl glycosides of lactosamine and isolactosamine†

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Received 28th November 2013
Accepted 24th January 2014

DOI: 10.1039/c3ra47128d

www.rsc.org/advances

The synthesis of the novel indoxyl glycosides of *N*-acetyl-lactosamine (X-LacNAc) and *N*-acetyl-isolactosamine (X-LNB) is reported employing glycosyl chlorides in a facile phase transfer glycosylation, followed by mild decarboxylation and finally deacetylation. Correspondingly the *ortho*-nitrophenol and *para*-nitrophenol glycosides of LacNAc and LNB could be obtained.

Introduction

N-Acetyl-lactosamine (LacNAc, Galβ1-4GlcNAc) and *N*-acetyl-isolactosamine (LNB, Galβ1-3GlcNAc) are integral parts of biologically very important glycostructures. Both represent essential subunits of complex milk oligosaccharides[1,2] as well as of antigens[3–5] and glycoconjugates.[6,7]

Access to samples or intermediates of complex glycostructures is still rather difficult. The chemical synthesis of complex saccharide structures is loaded with barriers, regarding protecting group chemistry as well as control of stereo- and regio-chemistry. Enzymatic syntheses need fewer steps, are often highly stereo- and regio-selective and are therefore superior if available. Thus, these approaches complement the array of methods, however, often enzymes are not available or difficult to isolate, purify or handle.

A convenient method for screening of glycosidases as well as transglycosidases is to use indoxyl glycosides (Fig. 1). Indoxyl is released by enzymatic cleavage of the glycosidic linkage and then rapidly oxidized, *e.g.* by atmospheric oxygen, to an indigo type dye. Common substrates are halogenated, as the substitution pattern determines colour and physical properties of the resulting indigo dye. The most common pattern of indoxyls are 5-bromo-4-chloro, 5-bromo and 5-bromo-6-chloro derivatives.[8] Nitrophenol glycosides in turn are widely utilised compounds for activity measurements and are employed as convenient donor substrates in enzymatic syntheses.[9–12]

Here we wish to report convenient syntheses of novel indoxyl glycosides of *N*-acetyl-lactosamine (X-LacNAc) and *N*-acetyl-isolactosamine (X-LNB), as well as the synthesis of *para*-nitrophenyl and *ortho*-nitrophenyl glycosides of both disaccharides.

The peracetates of LacNAc and LNB were converted into the corresponding glycosyl chlorides. The crude products could be used after washing directly without further workup for phase transfer glycosylation with the respective nitrophenol acceptor. The *o*NP and *p*NP glycosides were obtained after Zemplén deacetylation[13] in good overall yields. Preparation of the indoxyl glycosides followed our recently developed approach. In a phase transfer glycosylation indoxylic acid allyl esters were used as acceptors, followed by selective mild silver mediated decarboxylation and finally Zemplén deacetylation.[14,15]

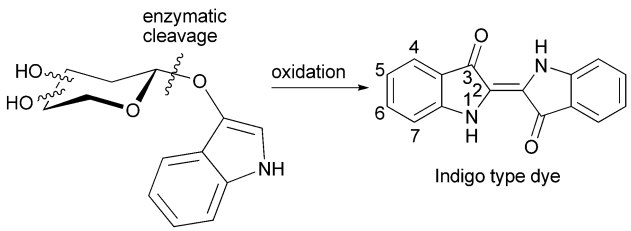

Fig. 1 Monitoring of glycosidase activity employing indoxyl glycosides.

Results and discussion

The synthetic route for the preparation of LNB-*o*NP/*p*NP (**5a**/**b**) and LacNAc-*o*NP/*p*NP (**5c**/**d**) is summarized in Scheme 1.

The peracetates **2a**/**b** were treated with acetyl chloride and methanol under argon atmosphere to give the glycosyl chlorides **3a**/**b**. These donors were dried and washed to remove acetyl chloride, and were then subjected to phase transfer glycosylation without further workup to yield peracetylated LNB-*p*NP (**4a**, 40%), LNB-*o*NP (**4b**, 34%), LacNAc-*p*NP (**4c**, 45%), LNB-*o*NP (**4d**, 44%) *via* two steps. Finally, the acetyl protecting groups were removed by Zemplén deacetylation.[13] In case of **5d** the reaction mixture needed to be kept at 45 °C overnight to achieve complete deacetylation. All glycosides crystallised during deacetylation and were washed after filtration with a small amount of cold methanol to give very pure **5a–d** in good yields.

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† Electronic supplementary information (ESI) available: NMR data for all new compounds. See DOI: 10.1039/c3ra47128d

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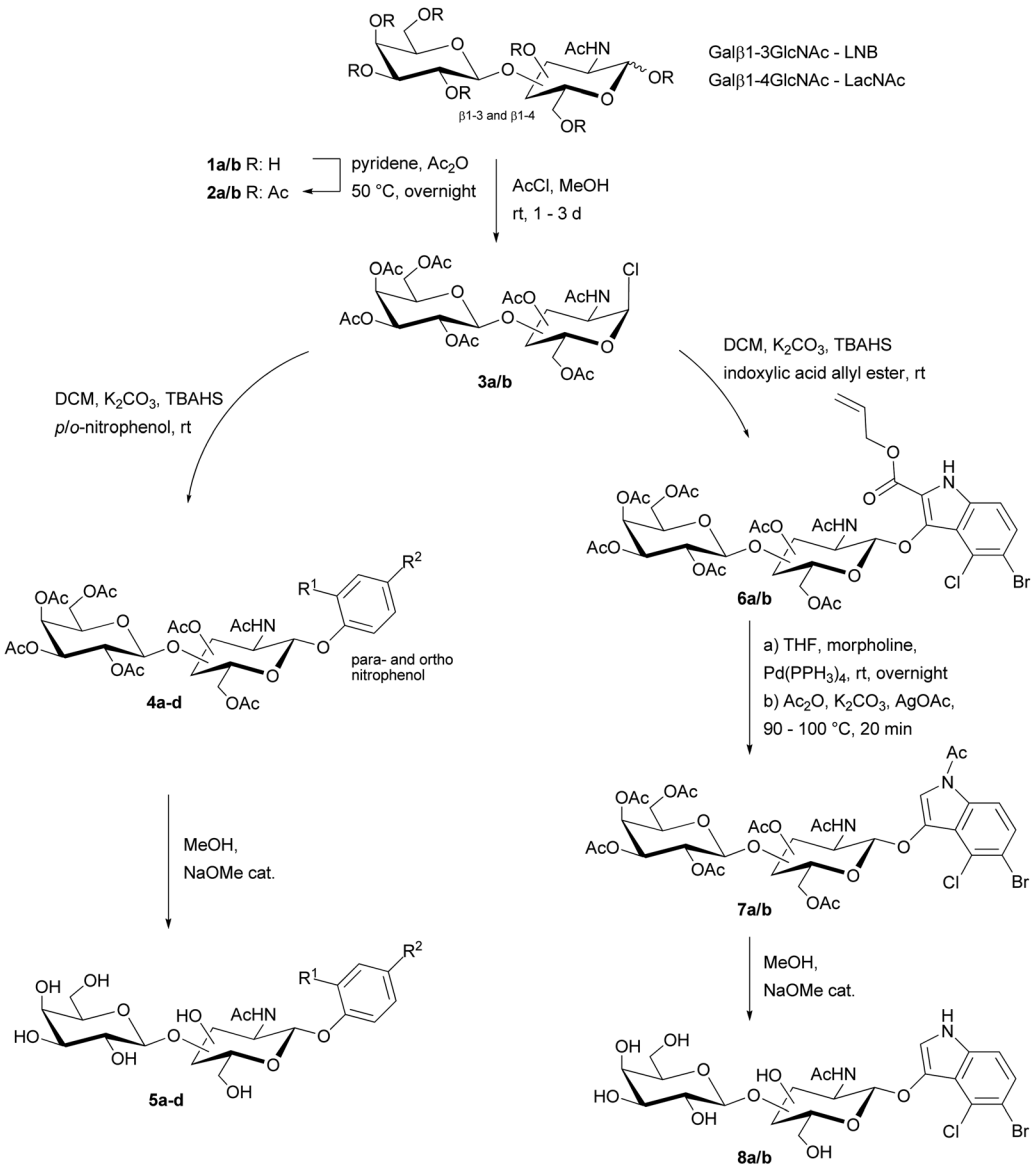

	2a	2b	4a	4b	4c	4d	5a	5b	5c	5d	6a	6b	7a	7b	8a	8b
Glycoside	β1-3	β1-4	β1-3	β1-3	β1-4	β1-4	β1-3	β1-3	β1-4	β1-4	β1-3	β1-4	β1-3	β1-4	β1-3	β1-4
Yield [%]	95	97	40*	34*	45*	44*	87	80	71	80	46*	45*	85	62	75	73
R^1	-	-	H	NO_2	H	NO_2	H	NO_2	H	NO_2	-	-	-	-	-	-
R^2	-	-	NO_2	H	NO_2	H	NO_2	H	NO_2	H	-	-	-	-	-	-

Scheme 1 Synthesis of *p*/*o*-nitrophenol glycosides of isolactosamine (**5a/b**) and lactosamine (**5c/d**) as well as indoxyl glycosides of isolactosamine (**8a**) and lactosamine (**8b**). *Yield *via* two steps.

The synthesis of the indoxyl glycosides **8a/b** was again based on the conversion of the respective peracetate **2a** or **2b** to the crude glycosyl chlorides **3a/b**. Phase transfer glycosylation under common phase transfer conditions gave **6a** (46%) and **6b** (45%). Then selective allyl ester deprotection with $Pd(PPh_3)_4$ and morpholine in THF[16] followed by mild silver mediated decarboxylation[14,15] gave the acetylated glycosides **7a** (85%) ad **7b** (62%). Finally Zemplén deacetylation[13] was used to give the novel indoxyl glycosides X-LNB in 75% and X-LacNAc in 73% yield.

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Conclusions

Within this work we could elaborate facile syntheses of novel indoxyl glycosides X-LAcNAc and X-LNB as well as the corresponding *ortho*- and *para*-nitrophenyl glycosides of LacNAc and LNB. Both reaction pathways could be carried out in good yields, employing facile phase transfer glycosylation of the crude glycosyl chloride donors, straight forward workup and crystallization.

Experimental section

General remarks

All reagents were purchased from commercial sources and used as received. TLC was performed on Merck silica gel 60 F_{254} plates. Compounds were detected by UV and/or by treatment with EtOH/H_2SO_4 (9 : 1) and subsequent heating. Column chromatography was performed with Merck/Fluka silica gel 60 (230–400 mesh). Solvents for column chromatography were distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AMX-400 or Bruker AV-400 spectrometers (400 MHz for ^{1}H, 101 MHz for ^{13}C) and calibrated using the solvent residual peak. In $CDCl_3$ TMS was used for calibration. Melting points were measured with an Büchi melting point M-565. Optical rotations were obtained using a Krüss Optronic P8000 polarimeter (589 nm). HRMS (ESI) were recorded with a Thermo Finnigan MAT 95XL mass spectrometer.

General procedures

General procedure 1. Glycosyl chlorides. A solution of the peracetylated disaccharide (1.0 mmol) in acetyl chloride (7.0 mL) was kept at 0 °C under argon atmosphere. Dry methanol (1.0 mL) was added dropwise over a period of 3 hours. After final addition, the solution was allowed to warm slowly to room temperature and stirred until TLC (heptane/acetone 3 : 7) indicated no further reaction. The solvent was removed under reduced pressure and the crude product was dissolved in DCM, concentrated again and washed with of diisopropyl ether (25 mL). The product was used directly according to general procedure 2 without further workup.

General procedure 2. Phase transfer glycosylation. The crude glycosyl chloride (1.0 mmol), TBAHS (1.0 equiv.) and the respective acceptor (1.0–1.1 equiv.) were mixed in DCM (10–15 mL) and an aqueous solution of K_2CO_3 (12.5 mL, 1 M) was added. The reaction mixture was stirred at room temperature until TLC indicated complete consumption of the donor. The organic phase was separated, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography in the solvent stated.

General procedure 3. Zemplén deacetylation. The starting material (1.0 mmol) was dissolved in MeOH (15–20 mL) and was treated with a catalytic amount of sodium methoxide. The solution was stirred until TLC indicated complete consumption of the starting material. If the product has precipitated during this time it was filtered off, otherwise the solution was neutralised with Amberlite IR-120 (H^+) resin and concentrated. The product was dried at 40 °C under high vacuum.

General procedure 4. Allyl ester deprotection and subsequent decarboxylation. The starting material (1.0 mmol) dissolved in THF (15 mL) was treated morpholine (10 equiv.) and $Pd(PPh_3)4$ (0.1 equiv.). The solution was stirred overnight at room temperature. After removal of the solvent silver acetate (3 equiv.), potassium carbonate (6–7 equiv.) and acetic anhydride (10 mL) were added. The resulting mixture was heated to 90–95 °C for 15–20 min. After cooling to room temperature, the mixture was diluted with water and DCM. The organic phase was washed twice with water and once with a diluted aqueous $NaHCO_3$ solution. After drying (Na_2SO_4) the solvent was removed under reduced pressure and the crude product was subjected to column chromatography in the solvent stated.

4-Nitrophenyl 2-acetamido-4,6-di-*O*-acetyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (4a). Prepared according to general procedures 1 and 2. (1) **2a** (3.00 g, 4.43 mmol), acetyl chloride (30 mL), methanol (4.2 mL). TLC (heptane/acetone 3 : 7, R_F: 0.45; starting material 0.40). (2) DCM (60 mL), aqueous K_2CO_3 solution (60 mL, 1 M), TBAHS (1.50 g, 4.42 mmol), *p*-nitrophenol (620 mg, 4.46 mmol). Yield 40% (1.35 g, 1.78 mmol); colorless solid; mp 129 °C; $[\alpha]_D^{25}$ -27.8 (*c* 0.50 in $CHCl_3$); R_F 0.69 (heptane/acetone 3 : 7); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21–8.16 (2H, m, H_{arom}), 7.10–7.04 (2H, m, H_{arom}), 5.93 (1H, d, $J = 7.5$ Hz, NH), 5.71 (1H, d, $J_{1,2} = 7.0$ Hz, H-1), 5.37–5.35 (1H, m, H-4′), 5.12 (1H, dd, $J_{1',2'} = 7.8$ Hz, $J_{2',3'} = 10.4$ Hz, H-2′), 5.06 (1H, dd∼vt, H-4), 4.99 (1H, dd, $J_{2',3'} = 10.4$ Hz, $J_{3',4'} = 3.4$ Hz, H-3′), 4.64 (1H, d, $J_{1',2'} = 7.8$ Hz, H-1′), 4.57 (1H, dd∼vt, H-3), 4.24 (1H, dd, $J_{5,6a} = 6.1$ Hz, $J_{6a/b} = 12.3$ Hz, H-6a), 4.19–4.07 (3H, m, H-6b, H-6′a/b), 3.98–3.88 (2H, m, H-5, H-5′), 3.67 (1H, ddd∼vdd, H-2), 2.16, 2.09, 20.8, 2.07, 2.00, 1.98 (each 3H, s, C(O)CH_3), 2.02 (3H, s, NHC(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 170.4, 170.1, 170.1, 169.1, 169.1 (*C*(O)CH_3), 161.4 (NH*C*(O)CH_3), 143.0 ($C_{quaternary}$), 125.7, 116.5 (*C*H_{arom}), 100.7 (C-1′), 96.3 (C-1), 76.0 (C-3), 72.4 (C-5), 70.9, 70.8 (C-3′, C-5′), 69.4 (C-2′), 68.5 (C-4), 66.8 (C-4′), 62.5 (C-6), 61.0 (C-6′), 56.1 (C-2), 23.5 (NHC(O)*C*H_3), 20.8, 20.8, 20.6, 20.6, 20.5 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{32}H_{40}N_2O_{19}$: $[M + Na]^+$ calcd 779.2123 found 779.2134.

2-Nitrophenyl 2-acetamido-4,6-di-*O*-acetyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (4b). Prepared according to general procedures 1 and 2. (1) **2a** (3.00 g, 4.43 mmol), acetyl chloride (30 mL), methanol (4.2 mL). TLC (heptane/acetone 3 : 7, R_F: 0.45; starting material 0.40). (2) DCM (60 mL), aqueous K_2CO_3 solution (60 mL, 1 M), TBAHS (1.50 g, 4.42 mmol), *o*-nitrophenol (620 mg, 4.46 mmol). Yield 34% (1.15 g, 1.52 mmol); colorless solid; mp 182–184 °C; $[\alpha]_D^{25}$ -49.6 (*c* 0.50 in $CHCl_3$); R_F 0.69 (heptane/acetone 3 : 7); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80–7.76 (1H, m, H_{arom}), 7.54–7.49 (1H, m, H_{arom}), 7.35–7.32 (1H, m, H_{arom}), 7.21–7.26 (1H, m, H_{arom}), 5.99 (1H, bs, NH), 5.62 (1H, d, $J_{1,2} = 8.2$ Hz, H-1), 5.37–5.34 (1H, m, H-4′), 5.08 (1H, dd, $J_{1',2'} = 7.8$ Hz, $J_{2',3'} = 10.4$ Hz, H-2′), 5.03–4.97 (1H, m, H-4), 4.98 (1H, dd, $J_{2',3'} = 10.4$ Hz, $J_{3',4'} = 3.8$ Hz, H-3′), 4.75 (1H, dd∼vt, H-3), 4.58 (1H, d, $J_{1',2'} = 7.8$ Hz, H-1′), 4.25 (1H, dd, $J_{5,6a} = 5.7$ Hz, $J_{6a/b} = 12.3$ Hz, H-6a), 4.19 (1H, dd, $J_{5,6b} = 2.5$ Hz, $J_{6a/b} = 12.3$ Hz, H-6b), 4.14–4.09 (2H, m, H-6′a/b), 3.92–3.85 (2H, m,

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H-5, H-5′), 3.45–3.37 (1H, m, H-2), 2.15, 2.10, 2.08, 2.07, 2.06, 1.98 (each 3H, s, C(O)CH_3), 2.05 (3H, s, NHC(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.9 (NH*C*(O)CH_3), 170.5, 170.4, 170.2, 170.1, 169.3, 169.1 (*C*(O)CH_3), 149.7, 141.1 ($C_{quaternary}$), 134.0, 125.1, 123.4, 119.4 (CH_{arom}), 100.8 (C-1′), 98.4 (C-1), 76.1 (C-3), 72.4 (C-5), 71.0 (C-3′), 70.7 (C-5′), 69.4 (C-2′), 68.9 (C-4), 66.9 (C-4′), 62.3 (C-6), 61.0 (C-6′), 58.2 (C-2), 23.6 (NHC(O)*C*H_3), 20.9, 20.8, 20.7, 20.6, 20.6, 20.5 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{32}H_{40}N_2O_{19}$: $[M + Na]^+$ calcd 779.2123 found 779.2139.

4-Nitrophenyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (4c). Prepared according to general procedures 1 and 2. (1) **2b** (3.00 g, 4.43 mmol), acetyl chloride (30 mL), methanol (4.2 mL). TLC (heptane/acetone 3:7, R_F: 0.52; starting material 0.43). (2) DCM (60 mL), aqueous K_2CO_3 solution (60 mL, 1 M), TBAHS (1.50 g, 4.42 mmol), *p*-nitrophenol (620 mg, 4.46 mmol). Yield 45% (1.59 g, 2.10 mmol); colorless solid; mp 156–157 °C (lit.,[17] 155–156 °C); $[\alpha]_D^{25}$ -36.2 (*c* 0.5 in $CHCl_3$) (lit.,[17] $[\alpha]_D$ −36.7 (*c* 1.3 in $CHCl_3$)); R_F 0.47 (heptane/acetone 3 : 7); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21–8.17 (2H, m, H_{arom}), 7.10–7.05 (2H, m, H_{arom}), 6.19 (1H, d, J = 8.8 Hz, NH), 5.40–5.38 (1H, m, H-4′), 5.30 (1H, d, $J_{1,2}$ = 6.0 Hz, H-1), 5.21 (1H, dd∼vt, H-3), 5.14 (1H, dd, $J_{1',2'}$ = 7.9 Hz, $J_{2',3'}$ = 10.4 Hz, H-2′), 5.02 (1H, dd, $J_{2',3'}$ = 10.4 Hz, $J_{3',4'}$ = 3.5 Hz, H-3′), 4.51 (1H, d, $J_{1',2'}$ = 7.9 Hz, H-1′), 4.47 (1H, dd, $J_{5,6a}$ = 4.1 Hz, $J_{6a/b}$ = 12.0 Hz, H-6a), 4.43–4.37 (1H, m, H-2), 4.20–4.08 (3H, m, H-6b, H-6′a/b), 3.97–3.90 (2H, m, H-5, H-5′), 3.89–3.85 (1H, m, H-4), 2.14, 2.13, 2.10, 2.06, 2.01, 1.99 (each 3H, s, C(O)CH_3), 2.02 (NC(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.3, 170.3, 170.2, 170.1, 170.0, 169.9, 169.8 (C(O)CH_3), 161.3, 142.8 ($C_{quaternary}$), 125.7, 116.4 (CH_{arom}), 100.7 (C-1′), 97.8 (C-1), 74.0 (C-4), 72.9 (C-5), 71.0 (C-5′), 70.4 (C-3, C-3′), 69.0 (C-2′), 66.6 (C-4′), 62.5 (C-6), 60.8 (C-6′), 51.1 (C-2), 23.1 (NC(O)*C*H_3), 20.9, 20.7, 20.6, 20.6, 20.5, 20.5 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{32}H_{40}N_2O_{19}$: $[M + Na]^+$ calcd 779.2123 found 779.2133.

2-Nitrophenyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (4d). Prepared according to general procedures 1 and 2. (1) **2b** (3.00 g, 4.43 mmol), acetyl chloride (30 mL), methanol (4.2 mL). TLC (heptane/acetone 3 : 7, R_F: 0.52; starting material 0.43). (2) DCM (60 mL), aqueous K_2CO_3 solution (60 mL, 1 M), TBAHS (1.50 g, 4.42 mmol), *o*-nitrophenol (620 mg, 4.46 mmol). Yield 44% (1.49 g, 1.97 mmol); colorless solid; mp 118 °C; $[\alpha]_D^{25}$ -12.0 (*c* 0.55 in $CHCl_3$); R_F 0.40 (heptane/acetone 3 : 7); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78 (1H, dd, H_{arom}), 7.54–7.48 (1H, m, H_{arom}), 7.36–7.32 (1H, m, H_{arom}), 7.17–7.12 (1H, m, H_{arom}), 6.22 (1H, d, J = 8.8 Hz, NH), 5.40–5.35 (2H, m, H-1, H-4′), 5.25 (1H, dd∼vt, H-3), 5.16 (1H, dd, $J_{1',2'}$ = 7.8 Hz, $J_{2',3'}$ = 10.4 Hz, H-2′), 5.03 (1H, dd, $J_{2',3'}$ = 10.4 Hz, $J_{3',4'}$ = 3.5 Hz, H-3′), 4.54 (1H, dd, $J_{5',6a'}$ = 3.8 Hz, $J_{6a/b'}$ = 11.6 Hz, H-6a), 4.52 (1H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.32–4.22 (2H, m, H-2, H-6b), 4.20–4.28 (2H, m, H-6′a/b), 3.96–3.88 (3H, m, H-4, H-5, H-5′), 2.16, 2.16, 2.08, 2.04, 1.98, 1.98 (each 3H, s, C(O)CH_3), 2.05 (3H, s, NC(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 170.0, 169.9, 169.7 (*C*(O)CH_3), 149.2, 141.2 ($C_{quaternary}$), 133.7, 125.1, 122.9, 119.0 (*C*H_{arom}), 100.6 (C-1′), 98.4 (C-1), 73.7 (C-4), 72.9 (C-5), 71.0 (C-5′), 70.5 (C-3′), 69.4 (C-3), 69.0 (C-2′), 66.6 (C-4′), 62.4 (C-6), 60.8 (C-6′), 50.9 (C-2) 23.1 (NC(O)*C*H_3), 20.8, 20.7, 20.6, 20.6, 20.6, 20.5 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{32}H_{40}N_2O_{19}$: $[M + Na]^+$ calcd 779.2123 found 779.2122.

4-Nitrophenyl 2-acetamido-2-deoxy-3-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (5a). Prepared according to general procedure 3. **4a** (1.20 g, 1.56 mmol), MeOH (25 mL), cat. NaOMe. Yield 88% (706 mg, 1.40 mmol); colorless solid; mp 160 °C dec (lit.,[18] 184–186); $[\alpha]_D^{25}$ -13.4 (*c* 0.35 in H_2O) (lit.,[18] $[\alpha]_D^{24}$ -14 (*c* 0.5 in H_2O)); ^{1}H-NMR (400 MHz, D_2O) δ 8.29–8.24 (2H, m, H_{arom}), 7.25–7.20 (2H, m, H_{arom}), 5.39 (1H, d, $J_{1,2}$ = 8.3 Hz, H-1), 4.52 (1H, d, $J_{1',2'}$ = 7.6 Hz, H-1′), 4.22 (1H, dd, $J_{1,2}$ = 8.3 Hz, $J_{2,3}$ = 10.4 Hz, H-2), 4.03–3.95 (3H, m, H-3, H-4′, H-6a), 3.89–3.69 (6H, m, H-4, H-5, H-5′, H-6b, H-6′a/b), 3.69 (1H, dd, $J_{2',3'}$ = 10.1 Hz, $J_{3',4'}$ = 3.5 Hz, H-3′), 3.59 (1H, dd, $J_{1',2'}$ = 7.6 Hz, $J_{2',3'}$ = 10.1 Hz, H-2′), 2.05 (3H, s, NHC(O)CH_3); ^{13}C-NMR (100 MHz, D_2O) δ 174.5 (NH*C*(O)CH_3), 161.7, 142.7 ($C_{quaternary}$), 126.1, 116.5 (CH_{arom}), 103.5 (C-1′), 98.4 (C-1), 81.8 (C-3), 75.8, 75.3 (C-5, C-5′), 72.5 (C-3′), 70.7 (C-2′), 68.6, 68.4 (C-4, C-4′), 61.0 (C-6′), 60.5 (C-6), 54.3 (C-2), 22.1 (NHC(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{20}H_{26}N_2O_{13}$: $[M + Na]^+$ calcd 527.1489 found 527.1488.

2-Nitrophenyl 2-acetamido-2-deoxy-3-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (5b). Prepared according to general procedure 3. **4b** (750 mg, 991 μmol), MeOH (15 mL), cat. NaOMe. Yield 80% (400 mg, 793 μmol); colorless solid; mp 203–204 °C; $[\alpha]_D^{25}$ -35.7 (*c* 0.41 in H_2O); ^{1}H-NMR (400 MHz, D_2O) δ 7.90–7. 86 (1H, m, H_{arom}), 7.70–7.65 (1H, m, H_{arom}), 7.49–7.45 (1H, m, H_{arom}), 7.31–7.26 (1H, m, H_{arom}), 5.25 (1H, d, $J_{1,2}$ = 8.5 Hz, H-1), 4.46 (1H, d, $J_{1',2'}$ = 7.6 Hz, H-1′), 4.18 (1H, dd∼vt, H-2), 4.02–3.97 (1H, m, H-6a), 3.94–3.88 (2H, m, H-3, H-4′), 3.85 (1H, dd, $J_{5,6b}$ = 4.7 Hz, $J_{6a/b}$ = 12.3 Hz, H-6b), 3.82–3.62 (5H, m, H-4, H-5, H-5′, H-6′a/b), 3.65 (1H, dd, $J_{2',3'}$ = 10.4 Hz, $J_{3',4'}$ = 3.8 Hz, H-3′), 3.55 (1H, dd∼vt, H-2′), 2.03 (3H, s, NHC(O)CH_3); ^{13}C-NMR (100 MHz, D_2O) δ 174.8 (NH*C*(O)CH_3), 149.3 ($C_{quaternary}$), 134.9, 125.2, 123.6, 118.2 (CH_{arom}), 103.5 (C-1′), 100.2 (C-1), 81.8 (C-3), 75.9, 75.3 (C-5, C-5′), 72.5 (C-3′), 70.7 (C-2′), 68.5, 68.4 (C-4, C-4′), 61.0 (C-6′), 60.5 (C-6), 54.1 (C-2), 22.1 (NHC(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{20}H_{26}N_2O_{13}$: $[M + Na]^+$ calcd 527.1489 found 527.1490.

4-Nitrophenyl 2-acetamido-2-deoxy-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (5c). Prepared according to general procedure 3. **4c** (1.40 g, 1.85 mmol), MeOH (35 mL), cat. NaOMe. Yield 80% (750 mg, 1.49 mmol); colorless solid; mp 213 °C (lit.,[19] 213 °C); $[\alpha]_D^{25}$ -22.2 (*c* 0.5 in H_2O) (lit.,[19] $[\alpha]_D^{25}$ -18.4 (*c* 1 in H_2O)); ^{1}H-NMR (400 MHz, D_2O) δ 8.28–8.20 (2H, m, H_{arom}), 7.23–7.18 (2H, m, H_{arom}), 5.37 (1H, d, $J_{1,2}$ = 8.6 Hz, H-1), 4.55 (1H, d, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.16–4.10 (1H, m, H-2), 4.10–4.04 (1H, m, H-6a), 3.98–3.96 (1H, m, H-4′), 3.96–3.86 (4H, m, H-3, H-4, H-5, H-6b), 3.85–3.76 (3H, m, H-5′, H-6′a/b), 3.72 (1H, dd, $J_{2',3'}$ = 9.8 Hz, $J_{3',4'}$ = 3.5 Hz, H-3′), 3.61 (1H, dd, $J_{1',2'}$ = 7.8 Hz, $J_{2',3'}$ = 9.8 Hz, H-2′), 2.06 (3H, s, NHC(O)CH_3); ^{13}C-NMR (100 MHz, D_2O) δ 174.9 (*C*(O)CH_3), 161.7, 142.6 ($C_{quaternary}$), 126.8, 116.5 (CH_{arom}), 102.9 (C-1′), 98.5 (C-1), 78.1 (C-4), 75.4, 75.1 (C-5, C-5′), 72.5 (C-3′), 72.0 (C-3), 71.0 (C-2′), 68.6 (C-4′), 61.6 (C-6′), 59.8 (C-6), 54.9 (C-2), 22.1 (NHC(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{20}H_{26}N_2O_{13}$: $[M + Na]^+$ calcd 527.1489 found 527.1496.

2-Nitrophenyl 2-acetamido-2-deoxy-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (5d). Prepared according to general procedure 3. **4d** (1.30 g, 1.72 mmol), MeOH (25 mL), cat. NaOMe,

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45 °C. Yield 80% (698 mg, 1.38 mmol); colorless solid; mp 209–212 °C; $[\alpha]_D^{22}$ -27.0 (*c* 0.35, H_2O); ^{1}H-NMR (400 MHz, D_2O) δ 7.89–7.86 (1H, m, H_{arom}), 7.69–7.64 (1H, m, H_{arom}), 7.47–7.44 (1H, m, H_{arom}), 7.30–7.25 (1H, m, H_{arom}), 5.23 (1H, d, $J_{1,2}$ = 8.5 Hz, H-1), 4.51 (1H, d, $J_{1',2'}$ = 7.9 Hz, H-1′), 4.08 (1H, dd, $J_{1,2}$ = 8.5 Hz, $J_{2,3}$ = 10.0 Hz, H-2), 4.06–4.02 (1H, m, H-6a), 3.95–3.89 (2H, m, H-4′, H-6b), 3.88–3.73 (6H, m, H-3, H-4, H-5, H-5′, H-6′a/b), 3.68 (1H, dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 3.5 Hz, H-3′), 3.56 (1H, dd, $J_{1',2'}$ = 7.9 Hz, $J_{2',3'}$ = 10.0 Hz, H-2′), 2.04 (s, 3H, NH(C(O)CH_3)); ^{13}C-NMR (100 MHz, D_2O) δ 174.7 (*C*(O)CH_3), 149.3, 140.3 ($C_{quaternary}$), 134.9, 125.1, 123.5, 118.2 (CH_{arom}), 102.9 (C-1′), 100.2 (C-1), 77.9 (C-4), 75.4, 75.2 (C-5, C-5′), 72.5 (C-3′), 72.1 (C-3), 70.9 (C-2′), 68.5 (C-4′), 61.0 (C-6′), 59.8 (C-6), 54.6 (C-2), 22.1 (NH(*C*(O)CH_3)); HRMS (ESI) *m*/*z* for $C_{20}H_{26}N_2O_{13}$: $[M + Na]^+$ calcd 527.1489 found 527.1491.

(5-Bromo-4-chloro-indox-3-ylic acid allyl ester) 2-acetamido-4,6-di-*O*-acetyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (6a). Prepared according to general procedures 1 and 2. (1) **2a** (1.00 g, 1.47 mmol), acetyl chloride (15 mL), methanol (1.5 mL). TLC (heptane/acetone 3 : 7, R_F: 0.52; starting material 0.43). (2) DCM (17 mL), aqueous K_2CO_3 solution (17 mL, 1 M), TBAHS (520 mg, 1.53 mmol), 5-bromo-4-chloro-indoxylic acid allyl ester (500 mg, 1.51 mmol). Yield 46% (635 mg, 0.670 mmol); colorless solid; mp 152–155 °C; $[\alpha]_D^{23}$ -24.2 (*c* 0.5, $CHCl_3$); R_F 0.39 (hexane/acetone 1 : 1); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.69 (1H, s, NH), 7.49 (1H, d, *J* = 8.9 Hz, H_{arom}), 7.10 (1H, d, *J* = 8.9 Hz, H_{arom}), 6.37 (1H, d, *J* = 7.6 Hz, *C*2–NH), 6.09–6.01 (1H, m, –O–CH_2–C*H*=CH_2), 5.47–5.43 (1H, m, O–CH_2–CH=CH_2a), 5.40–5.35 (3H, m, H-1, H-4′, O–CH_2–CH=CH_2b), 5.09 (1H, dd, $J_{1',2'}$ = 7.9 Hz, $J_{2',3'}$ = 10.4 Hz, H-2′), 5.03–4.98 (2H, m, H-3′, H-4), 4.70 (1H, d, $J_{1',2'}$ = 7.9 Hz, H-1′), 4.90–4.83 (2H, m, O–CH_2–CH=CH_2), 4.35 (1H, dd∼vt, H-3), 4.10 (1H, dd, $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 4.00 (1H, dd, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6b), 3.99–3.94 (1H, m, H-2), 3.92–3.88 (1H, m, H-5′), 3.62 (1H, ddd, $J_{4,5}$ = 9.4 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 3.0 Hz, H-5), 2.15, 2.13, 2.06, 2.03, 1.97, 1.95 (each 3H, s, C(O)CH_3), 1.99 (3H, s, NHC(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 170.8, 170.6, 170.4, 169.6, 169.4 (*C*(O)CH_3), 159.9 (*C*(O)O–CH_2–), 140.3, 133.5 ($C_{quaternary}$), 131.7 (O–CH_2–*C*H=CH_2), 131.7 (CH_{arom}), 127.3, 120.9 ($C_{quaternary}$), 119.9 (O–CH_2–CH=*C*H_2), 116.9, 115.7 ($C_{quaternary}$), 111.7 (CH_{arom}), 102.1 (C-1), 100.9 (C-1′), 77.6 (C-3), 72.3 (C-5), 71.4, 69.4 (C-3′, C-4), 70.6 (C-5′), 69.3 (C-2′), 67.1 (C-4′), 66.1 (O–*C*H_2–CH=CH_2), 62.1 (C-6), 61.1 (C-6′), 57.3 (C-2), 23.7 (NHC(O)*C*H_3), 21.1, 20.9, 20.8, 20.8, 20.8, 20.7 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{38}H_{44}BrClN_2O_{19}$: $[M + Na]^+$ calcd 969.1308 found 969.1293.

(5-Bromo-4-chloro-indox-3-ylic acid allyl ester) 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (6b). Prepared according to general procedures 1 and 2. (1) **2b** (900 mg, 1.32 mmol), acetyl chloride (10 mL), methanol (1.5 mL). TLC (heptane/acetone 3 : 7, R_F: 0.52; starting material 0.43). (2) DCM (15 mL), aqueous K_2CO_3 solution (15 mL, 1 M), TBAHS (414 mg, 1.22 mmol), 5-bromo-4-chloro-indoxylic acid allyl ester (400 mg, 1.21 mmol). Yield 45% (562 mg, 0.593 mmol); colorless solid; mp 149–152 °C; $[\alpha]_D^{23}$ -7.6 (*c* 0.5 in $CHCl_3$); R_F 0.41 (hexane/acetone 1 : 1); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.64 (1H, s, NH), 7.48 (1H, d, *J* = 8.8 Hz, H_{arom}), 7.09 (1H, d, *J* = 8.8 Hz, H_{arom}), 6.58 (1H, d, *J* = 8.6 Hz, C2–NH), 6.08–6.01 (1H, m, –O–CH_2–C*H*=CH_2), 5.49–5.45 (1H, m, O–CH_2–CH = CH_2a), 5.41–5.38 (1H, m, O–CH_2–CH=CH_2b), 5.35–5.33 (1H, m, H-4′), 5.15–5.07 (3H, m, H-1, H-2′, H-3), 4.96 (1H, dd, $J_{2',3'}$ = 10.5 Hz, $J_{3',4'}$ = 10.5 Hz, H-3′), 4.89–4.81 (2H, m, O–CH_2–CH=CH_2), 4.53 (1H, d, $J_{1',2'}$ = 7.6 Hz, H-1′), 4.46–4.41 (1H, m, H-2), 4.31 (1H, dd, $J_{5,6a}$ = 2.4 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 4.15–4.09 (2H, m, H-6′a/b), 3.93 (1H, dd∼vt, H-4), 3.90–3.86 (1H, m, H-5′), 3.46–3.42 (1H, m, H-5), 2.14, 2.12, 2.06, 1.98 (each 3H, s, C(O)CH_3), 1.99 (3H, s, NHC(O)CH_3), 1.95 (6H, s, 2C(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 170.6, 170.3, 170.2, 170.1, 170.0, 169.1 (*C*(O)CH_3), 159.4 (*C*(O)O–CH_2–), 141.3, 133.2 ($C_{quaternary}$), 131.4 (O–CH_2–*C*H=CH_2), 131.0 (CH_{arom}), 127.4, 120.7 ($C_{quaternary}$), 120.1 (O–CH_2–CH=*C*H_2), 116.1, 115.7 ($C_{quaternary}$), 111.5 (CH_{arom}), 103.2 (C-1), 101.2 (C-1′), 74.1 (C-3), 73.3 (C-4), 72.8 (C-5), 70.9 (C-3′), 70.7 (C-5′), 69.2 (C-2′), 66.6 (C-4′), 66.0 (O–*C*H_2–CH=CH_2), 61.2 (C-6), 60.8 (C-6′), 54.3 (C-2), 23.3 (NHC(O)*C*H_3), 20.9, 20.6, 20.6, 20.6, 20.5 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{38}H_{44}BrClN_2O_{19}$: $[M + Na]^+$ calcd 969.1308 found 969.1288.

(*N*-Acetyl-5-bromo-4-chloro-indox-3-yl) 2-acetamido-4,6-di-*O*-acetyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (7a). Prepared according to general procedure 4. **6a** (520 mg, 0.548 mmol), THF (10 mL), morpholine (500 μL, 5.74 mmol), $Pd(PPh_3)_4$ (60 mg, 0.052 mmol), 15 min, 90–95 °C. Yield 85% (420 mg, 0.463 mmol), colorless solid; mp 157–159 °C; $[\alpha]_D^{23}$ -44.0 (*c* 0.5 in $CHCl_3$); R_F 0.36 (hexane/acetone 1 : 1); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.25 (1H, d, *J* = 8.9 Hz, H_{arom}), 7.55 (1H, d, *J* = 8.9 Hz, H_{arom}), 7.29 (1H, s, =C*H*–N), 5.87 (1H, d, *J* = 7.8 Hz, C2–NH), 5.41 (1H, d, $J_{1,2}$ = 7.9 Hz, H-1), 5.37–5.35 (1H, m, H-4′), 5.10 (1H, dd, $J_{1',2'}$ = 7.8 Hz, $J_{2',2''}$ = 10.5 Hz, H-2′), 5.03 (1H, dd∼vt, H-4), 4.99 (1H, dd, $J_{2',3'}$ = 10.5 Hz, $J_{3',4'}$ = 3.4 Hz, H-3′), 4.66–4.59 (1H, m, H-3), 4.62 (1H, d, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.37 (1H, dd, $J_{5,6a}$ = 2.7 Hz, $J_{6a/b}$ = 12.4 Hz, H-6a), 4.18 (1H, dd, $J_{5,6b}$ = 5.5 Hz, $J_{6a/b}$ = 12.4 Hz, H-6b), 4.14–4.08 (2H, m, H-6′a/b), 3.92–3.84 (2H, m, H-5, H-5′), 3.66–3.57 (1H, m, H-2), 2.60, 2.16, 2.09, 2.09, 2.08, 2.06, 2.05, 1.98 (each 3H, s, C(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 170.5, 170.4, 170.2, 170.1, 169.3, 169.1, 168.2 (*C*(O)CH_3), 140.0, 133.4 ($C_{quaternary}$), 130.5 (CH_{arom}), 124.7, 122.6, 118.4 ($C_{quaternary}$), 116.3 (CH_{arom}), 112.4 (=*C*H–N), 100.8 (C-1′), 99.4 (C-1), 76.2 (C-3), 72.6 (C-5), 71.0 (C-5′), 70.7 (C-3′), 69.4, 69.0 (C-2′, C-4), 66.9 (C-4′), 62.4 (C-6), 61.0 (C-6′), 57.4 (C-2), 23.8, 23.8, 20.9, 20.8, 20.8, 20.7, 20.6, 20.5 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{36}H_{42}BrClN_2O_{18}$: $[M + Na]^+$ calcd 927.1202 found 927.1194.

(*N*-Acetyl-5-bromo-4-chloro-indox-3-yl) 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (7b). Prepared according to general procedure 4. **6b** (390 mg, 0.411 mmol), THF (8 mL), morpholine (350 μL, 4.02 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), 15 min, 90–95 °C. Yield 62% (230 mg, 0.254 mmol); colorless solid; mp 146–148 °C; $[\alpha]_D^{23}$ -38.0 (*c* 0.25 in $CHCl_3$); R_F 0.32 (hexane/acetone 1 : 1); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (1H, d, *J* = 8.9 Hz, H_{arom}), 7.54 (1H, d, *J* = 8.9 Hz, H_{arom}), 7.44 (1H, s, =CH–N), 6.19 (1H, d, *J* = 9.1 Hz, *C*2–NH), 5.41–5.38 (1H, m, H-4′), 5.22–5.15 (2H, m, H-3, H-2′), 5.11 (1H, d, $J_{1,2}$ = 5.4 Hz, H-1), 5.05 (1H, dd, $J_{2',3'}$ = 10.4 Hz, $J_{3',4'}$ = 3.3 Hz, H-3′), 4.81 (1H, dd, $J_{5,6a}$ = 4.7 Hz, $J_{6a/b}$ = 11.8 Hz, H-6a), 4.57 (1H, d, $J_{1',2'}$ = 8.0 Hz, H-1′), 4.44–4.39 (1H, m, H-2), 4.24 (1H, dd, $J_{5,6b}$ = 5.0 Hz, $J_{6a/b}$ = 11.8 Hz, H-6b),

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4.19 (1H, dd, $J_{5',6'a} = 6.2$ Hz, $J_{6'a/b} = 11.3$ Hz, H-6′a), 4.12 (1H, dd, $J_{5',6'b} = 7.1$ Hz, $J_{6'a/b} = 11.3$ Hz, H-6′b), 3.97–3.87 (3H, m, H-4, H-5, H-5′), 2.17, 2.09, 1.99 (each 3H, s, C(O)CH_3), 2.08, 2.06 (each 6H, s, 2C(O)CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 170.4, 170.3, 170.1, 170.0, 170.0, 169.7, 168.6 (*C*(O)CH_3), 139.4, 133.5 ($C_{quaternary}$), 130.4 (CH_{arom}), 118.3 ($C_{quaternary}$), 116.3 (CH_{arom}), 111.8 (=*C*H–N), 100.8 (C-1′), 99.7 (C-1), 73.8, 73.1 (C-4, C-5), 71.0 (C-5′), 70.5 (C-3′), 70.0 (C-3), 69.1 (C-2′), 66.6 (C-4′), 62.3 (C-6), 60.8 (C-6′), 50.3 (C-2), 23.9, 23.2, 20.8, 20.7, 20.6, 20.5 (C(O)*C*H_3); HRMS (ESI) *m*/*z* for $C_{36}H_{42}BrClN_2O_{18}$: $[M + Na]^+$ calcd 927.1202 found 927.1187.

(5-Bromo-4-chloro-indox-3-yl) 2-acetamido-2-deoxy-3-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (8a). Prepared according to general procedure 3. **7a** (100 mg, 0.110 mmol), MeOH (3 mL), cat. NaOMe, rt. Yield 75% (51 mg, 0.083 mmol); colorless solid; mp 230 °C dec; $[\alpha]_D^{25}$ -100.8 (*c* 0.25 in 50% DMF/H_2O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 11.15 (1H, bs, NH), 7.91 (1H, d, $J = 8.3$ Hz, C2–NH), 7.36–7.16 (3H, m, 2 H_{arom}, =CH–N), 4.87 (1H, d, $J_{1,2} = 8.5$ Hz, H-1), 4.83–4.70 (3H, m, 3 OH), 4.66 (1H, bs, OH), 4.50 (1H, bs, OH), 4.33 (1H, bs, OH), 4.15 (1H, d, $J_{1',2'} = 6.6$ Hz, H-1′), 3.85–3.75 (2H, m, H-2, H-6a), 3.66–3.58 (2H, m, H-3, H-4′), 3.57–3.49 (3H, m, H-6b, H-6′a/b), 3.49–3.31 (5H, m, H-2′, H-3′, H-4, H-5, H-5′), 1.82 (3H, s, NHC(O)C*H*$_3$); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 169.9 (*C*(O)CH_3), 132.9 ($C_{quaternary}$), 125.5 (CH_{arom}), 122.9, 117.6 ($C_{quaternary}$), 114.0, 112.3 (CH_{arom}, =*C*H–N), 111.7 ($C_{quaternary}$), 104.0 (C-1′), 101.7 (C-1), 84.6 (C-3), 76.8, 75.8 (C-5, C-5′), 72.9, 68.9 (C-3′, C-4), 70.6 (C-2′), 68.2 (C-4′), 60.8, 60.6 (C-6, C-6′), 54.2 (C-2), 23.1 (C(O)*C*H_3) ppm.

(5-Bromo-4-chloro-indox-3-yl) 2-acetamido-2-deoxy-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (8b). Prepared according to general procedure 3. **7b** (95 mg, 0.10 mmol), MeOH (3 mL), cat. NaOMe, rt. Yield 73% (45 mg, 0.073 mmol); colorless solid; mp 230 °C dec; $[\alpha]_D^{23}$ -43.8 (*c* 0.5 in 50% DMF/H_2O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 11.12 (1H, bs, NH), 7.88 (1H, d, $J = 9.2$ Hz, C2–NH), 7.31 (1H, d, $J = 8.8$ Hz, H_{arom}), 7.29 (s, 1H, =CH–N), 7.22 (1H, d, $J = 8.8$ Hz, H_{arom}), 5.07 (1H, bs, OH), 4.79 (1H, bs, OH), 4.75 (1H, t, OH), 4.72 (1H, bs, OH), 4.71 (1H, d, $J_{1,2} = 8.6$ Hz, H-1), 4.67 (1H, t, OH), 4.51 (1H, d, OH), 4.23 (1H, d, $J_{1',2'} = 7.4$ Hz, H-1′), 3.93–3.88 (1H, m, H-6a), 3.87–3.81 (1H, m, H-2), 3.68–3.60 (2H, m, H-4′, H-6b), 3.56 (1H, dd∼vt, H-3), 3.54–3.50 (2H, m, H-6′a/b), 3.49–3.42 (1H, m, H-5), 3.40 (1H, dd∼vt, H-4), 3.34–3.32 (2H, m, H-2′, H-3′), 1.82 (3H, s, NHC(O)CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 168.7 (*C*(O)CH_3), 136.9, 132.9 ($C_{quaternary}$), 125.5 (CH_{arom}), 123.0, 117.6 ($C_{quaternary}$), 114.0 (=*C*H–N), 112.3 (CH_{arom}), 111.6 ($C_{quaternary}$), 104.0 (C-1′), 102.0 (C-1), 81.4 (C-4), 75.6, 75.4 (C-5, C-5′), 73.2, 70.6 (C-2′, C-3′), 72.3 (C-3), 68.2 (C-4′), 60.5, 60.4 (C-6, C-6′), 54.6 (C-2), 23.1 (C(O)*C*H_3) ppm.

Acknowledgements

Support of this work by Glycom A/S, Copenhagen, Denmark, is gratefully acknowledged.

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