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Antiproliferative activity of new 2-glyco-3-nitro-1,2-dihydroquinolines and quinolines synthesed in solventless conditions promoted by neutral alumina

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Experimental Section

Materials and methods

All chemicals were purchased from commercial sources and used directly, without further purification. Preparative TLC was performed using silica gel (Merck 60 GF_{254}). TLC was performed on precoated Merck Kieselgel 60 GF_{254} aluminum backed plates; TLC spots were visualized by UV light. NMR spectra were recorded either on a Bruker AC/PC instrument (500 MHz for ^{1}H and 125 MHz for ^{13}C) with tetramethylsilane as internal reference and deuterated chloroform or dimethylsulfoxide as solvents. Coupling constants were recorded in Hz. Characterization of NMR signals was based on homonuclear double-resonance and DEPT experiments. High resolution mass spectra were recorded on a Micromass Autoespec spectrometer, at the Centro de Investigación Tecnológica e Innovación (CITIUS) from the Universidad de Sevilla. Infrared spectra were recorded on an IR3000 Thermo Electron Corporation spectrophotometer in the range between 4000 and 600 cm^{-1}.

Evaluation of the antiproliferative activity was accomplished following the protocol of the NCI of the United States.[30,31] For each compound, the cells were exposed to serial decimal dilutions in the range of 0.001-100 µM for a period of 48 h. After exposure, the SRB method was applied to determine the optical density of each well at 530 nm (main) and 620 nm (secondary). For each product concentration, the percentage of growth (PG) according to the NCI formulas was calculated.

General procedure for 2-glyco-3-nitro-1,2-dihydroquinolines 9a-c and **10a-c** + **11a-c.** To a heterogeneous mixture of nitroalkenes **6**-**7**[32] (1 g, 2.31 mmol) and the appropriate aminobenzaldehyde **8a-c** (2.31 mmol), neutral alumina (2.31 g) and dichloromethane (3.12% mol) (to initially homogenize the mixture) were added. The mixture was stirred at 60 °C until reaction completion (monitored by TLC, 1:5 hexane-diethyl ether). The crude product was extracted with methanol, filtered and washed with the same solvent until alumina became white. If necessary, diastereoisomers were purified by PTLC (1:5 hexane-diethyl ether).

General procedure for 2-glyco-3-nitroquinolines 12a-c and **13a-c.** Quinolines were synthesized using protocol reported in literature.[24]

General procedure for deacetylated products 14a-c and **15a-c.** To a solution of **12a-c** and **13a-c** (1 mmol) in MeOH:H_2O 9:1 (15 mL), potassium carbonate (0.57 g) was added. The suspension was stirred at room temperature for 1 hour (TLC, 3:1, benzene-methanol). Crude reaction was acidified to pH ~ 6 with diluted HCl (if a solid appears) or Amberlite IR-120 (H^+), which was then filtered. Pure products crystallized from methanol.

General procedure for *N*-formyl-1,2-dihydroquinolines 16a-c. A mixture of **9a-c** (1 mmol), formic acid (4.7 mmol) and acetic anhydride (4.8 mmol) was stirred at room temperature for 1-2 hours (TLC, 1:5 hexane-diethyl ether). After evaporation, the residue was dissolved in dichloromethane (10 mL), washed with 5% sodium bicarbonate solution and dried with magnesium sulfate. The extract was evaporated to yield pure compounds **16a-c**.

General procedure for addition of indole or pyrrole to *N*-formyl-1,2-dihydroquinolines. To a mixture of *N*-formyl-1,2-dihydroquinolines **16a-c** (1 mmol) and indole or pyrrole (1 mmol), activated basic alumina (1 g) and dichloromethane (3.12% mol) (to initially homogenize the mixture) were added, and stirred at 60-70 °C for two days. The crude reaction was extracted with methanol and filtered. Compounds were purified by PTLC (1:1 hexane-ethyl acetate, 2 elutions).

Spectroscopic data

3-Nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)-1,2-dihydroquinoline **9a**. Red solid. IR ν_{max} (KBr) 3391 (-NH), 3062 (-CH_3), 2962 (-CH_2-), 1747 (C=O), 1634, 1372 (NO_2), 1609, 1511 (C=C_{arom}), 1217 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.86 (s, 1H, H4), 7.29 (td, 1H, $J_{7,8}$ ≈ 7.0 Hz, H7), 7.26 (dd, 1H, H5), 6.81 (td, 1H, $J_{5,6}$ ≈ 7.5 Hz, H6), 6.75 (d, 1H, H8), 5.38 (d, 1H, $J_{1,2}$ ≈ 5.0 Hz, H1), 5.35 (m, 1H, H4´), 5.34 (dd, 1H, $J_{1',2'}$ ≈ 1.5 Hz, $J_{2',3'}$ ≈ 10.0 Hz, H2´), 5.25 (dd, 1H, $J_{3',4'}$ ≈ 2.0 Hz, H3´), 5,20 (dd, 1H, $J_{1',2}$ ≈ 9.5 Hz, H1´), 4.93 (ddd, 1H, H2), 4.25 (dd, 1H, $J_{4',5'a}$ ≈ 4.5 Hz, $J_{5'a,5'b}$ ≈ 12.0 Hz, H5´a), 3.80 (dd, 1H, $J_{4',5'b}$ ≈ 7.5 Hz, H5´b), 2.27, 2.12, 2.01, 1.95, 1.92 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm) 172.3, 170.4, 170.1, 169.9, 169.7 (-O*C*OCH_3), 143.1 (C3), 136.3 (C8a), 133.8, 132.1, 131.8 (C4, C5, C7), 119.3 (C6), 116.0 (C4a), 114.2 (C8), 68.9 (C1´), 68.0, 67.2, 67.0 (C2´, C3´, C4´), 62.3 (C5´), 48.5 (C2), 20.9, 20.7, 20.6, 20.5, 20.3 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 559.1528. Calculated $C_{24}H_{28}N_2O_{12}Na$ 559.1534.

6-chloro-3-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)-1,2-dihydroquinoline **9b**. Red solid. IR ν_{max} (KBr) 3391 (-NH), 3059 (-CH_3), 2962 (-CH_2-), 1747 (C=O), 1643, 1372 (NO_2), 1607, 1505 (C=C_{arom}), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.77 (s, 1H, H4), 7.24 (t, 1H, H7), 7.23 (dd, 1H, H5), 6.71 (d, 1H, $J_{7,8}$ ≈ 9.5 Hz, H8), 5.40 (d, 1H, $J_{1,2}$ ≈ 4.0 Hz, H1), 5.35 (m, 1H, H4´), 5.34 (dd, 1H, $J_{1',2'}$ ≈ 1.5 Hz, $J_{2',3'}$ ≈ 10.0 Hz, H2´), 5.25 (dd, 1H, $J_{3',4'}$ ≈ 2.0 Hz, H3´), 5.20 (dd, 1H, $J_{1',2}$ ≈ 9.5 Hz, H1´), 4.93 (ddd, 1H, H2), 4.25 (dd, 1H, $J_{4',5'a}$ ≈ 4.5 Hz, $J_{5'a,5'b}$ ≈ 12.0 Hz, H5´a), 3.80 (dd, 1H, $J_{4',5'b}$ ≈ 7.5 Hz, H5´b), 2.27, 2.12, 2.01, 1.95, 1.92 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm) 172.4, 170.3, 170.1, 169.8, 169.7 (-O*C*OCH_3), 141.5 (C3), 137.3 (C8a), 133.5, 130.6, 130.5 (C4, C5, C7), 124.0 (C6), 117.0 (C4a), 115.5 (C8), 68.8 (C1´), 68.0, 67.1, 67.0 (C2´, C3´, C4´), 62.3 (C5´), 48.5 (C2), 20.9, 20.7, 20.6, 20.5, 20.2 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 593.1148. Calculated $C_{24}H_{27}ClN_2O_{12}Na$ 593.1145.

6-bromo-3-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)-1,2-dihydroquinoline **9c**. Red solid. IR ν_{max} (KBr) 3360 (-NH), 3059 (-CH_3), 2962 (-CH_2-), 1747 (C=O), 1641, 1372 (NO_2), 1615, 1506 (C=C_{arom}), 1214 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.76 (s, 1H, H4), 7.36 (m, 2H, H7, H5), 6.66 (d, 1H, $J_{7,8}$ ≈ 8.5 Hz, H8), 5.42 (d, 1H, $J_{1,2}$ ≈ 4.5 Hz, H1), 5.36 (m, 1H, H4´), 5.30 (dd, 1H, $J_{1',2'}$ ≈ 1.5 Hz, $J_{2',3'}$ ≈ 10.0

Hz, H2´), 5.26 (dd, 1H, $J_{3',4'}$ ≈ 2.0 Hz, H3´), 5.16 (dd, 1H, $J_{1',2}$ ≈ 9.5 Hz, H1´), 4.91 (c, 1H, H2), 4.25 (dd, 1H, $J_{4',5'a}$ ≈ 4.5 Hz, $J_{5'a,5'b}$ ≈ 12.0 Hz, H5´a), 3.80 (dd, 1H, $J_{4',5'b}$ ≈ 7.5 Hz, H5´b), 2.27, 2.11, 2.01, 1.95 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 172.4, 170.4, 170.1, 169.8, 169.7 (-O*C*OCH$_3$), 141.9 (C3), 136.2 (C8a), 133.5, 130.5, 118.0 (C4, C5, C7), 117.5 (C4a), 115.9 (C8), 110.8 (C6), 68.9 (C1´), 68.0, 67.5, 67.1 (C2´, C3´, C4´), 62.3 (C5´), 48.5 (C2), 20.9, 20.7, 20.6, 20.5, 20.2 (-OCO*C*H$_3$). EISM Found (M+Na)$^+$ 637.0635. Calculated $C_{24}H_{27}BrN_2O_{12}Na$ 637.0640.

3-Nitro-(2*R*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)-1,2-dihydroquinoline **11a**. Red solid. IR ν_{max} (NaCl) 3367 (-NH), 2981 (-CH$_3$), 2938 (-CH$_2$-), 1742 (C=O), 1649, 1372 (NO_2), 1606, 1511 (C=C$_{arom}$), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.84 (s, 1H, H4), 7.21 (t, 1H, $J_{7,8}$ ≈ 7.0 Hz, H7), 7.16 (d, 1H, $J_{5,6}$ ≈ 7.5 Hz, H5), 6.74 (t, 1H, H6), 6.66 (d, 1H, H8), 5.50 (dd, 1H, $J_{2',3'}$ ≈ 4.0 Hz, H2´), 5.48 (dd, 1H, H2), 5.43 (dd, 1H, $J_{3',4'}$ ≈ 7.0 Hz, H3´), 5.21 (t, 1H, $J_{1',2'} = J_{1',2}$ ≈ 6.0 Hz, H1´), 5.06 (d, 1H, $J_{1,2}$ ≈ 3.0 Hz, H1), 4.97 (m, 1H, H4´), 4.23 (dd, 1H, $J_{4',5'a}$ ≈ 3.0 Hz, $J_{5'a,5'b}$ ≈ 12.5 Hz, H5´a), 4.07 (dd, 1H, $J_{4',5'b}$ ≈ 5.5 Hz, H5´b), 2.09, 2.07, 2.02, 1.98, 1.92 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.4, 170.0, 169.9, 169.7, 169.3 (-O*C*OCH$_3$), 143.7 (C3), 136.8 (C8a), 133.9, 132.0, 131.3 (C4, C5, C7), 119,2 (C6), 115.6 (C4a), 113.8 (C8), 71.4 (C1´), 69.0, 68.9, 68.3 (C2´, C3´, C4´), 61.4 (C5´), 51.3 (C2), 20.7, 20.6, 20.5 (-OCO*C*H$_3$). EISM Found (M+Na)$^+$ 559.1532. Calculated $C_{24}H_{28}N_2O_{12}Na$ 559.1534.

3-Nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)-1,2-dihydroquinoline **10a**. Red solid. IR ν_{max} (NaCl) 3401 (-NH), 2983 (-CH$_3$), 1751 (C=O), 1645, 1372 (NO_2), 1609, 1510 (C=C$_{arom}$), 1216 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.86 (s, 1H, H4), 7.23 (t, 1H, $J_{7,8}$ ≈ 9.0 Hz, H7), 7.07 (d, 1H, $J_{5,6}$ ≈ 7.0 Hz, H5), 6.65 (t, 1H, H6), 6.64 (d, 1H, H8), 5.44 (dd, 1H, $J_{1',2'}$ ≈ 10.5 Hz, $J_{2',3'}$ ≈ 2.0 Hz, H2´), 5.38 (dd, 1H, $J_{3',4'}$ ≈ 9.5 Hz, H3´), 5.27 (d, 1H, $J_{1,2}$ ≈ 3.5 Hz, H1), 5.18 (m, 1H, H4´), 5.09 (d, 1H, H1´), 4.91 (dd, 1H, $J_{2,1'}$< 1.0 Hz, H2), 4.19 (dd, 1H, $J_{4',5'a}$ ≈ 2.5 Hz, H5´a), 4.02 (dd, 1H, $J_{5'b,4'}$ ≈ 5.0 Hz, H5´b), 2.25, 2.12, 2.03, 1.67 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 172.4, 170.5, 169.9, 169.8, 169.7 (-O*C*OCH$_3$), 145.5 (C3), 136.1 (C8a), 134.1, 133.4, 130.8 (C4, C5, C7), 118.4 (C6), 115.3 (C4a), 113.4 (C8), 69.7 (C1´), 68.0, 67.1, 66.5 (C2´, C3´, C4´), 62.0 (C5´), 50.7 (C2), 20.9, 20.8, 20.6, 20.5, 20.3 (-OCO*C*H$_3$). EISM Found (M+Na)$^+$ 559.1537. Calculated $C_{24}H_{28}N_2O_{12}Na$ 559.1534.

6-chloro-3-nitro-(2*R*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)-1,2-dihydroquinoline **11b**. Red solid. IR ν_{max} (NaCl) 3390 (-NH), 3064 (-CH_3), 2954, 2922 (-CH_2-), 1748 (C=O), 1647, 1371 (NO_2), 1606, 1510 (C=C_{arom}), 1218 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.76 (s, 1H, H4), 7.16 (t, 1H, $J_{7,8}$ ≈ 7.0 Hz, H7), 7.15 (d, 1H, $J_{5,6}$ ≈ 7.5 Hz, H5), 6.64 (d, 1H, H8), 5.50 (dd, 1H, $J_{2',3'}$ ≈ 5.0 Hz, H2´), 5.48 (dd, 1H, H2), 5.41 (dd, 1H, $J_{3',4'}$ ≈ 6.5 Hz, H3´), 5.18 (t, 1H, $J_{1',2'} = J_{1',2}$ ≈ 5.5 Hz, H1´), 5.13 (d, 1H, $J_{1,2}$ ≈ 3.0 Hz, H1), 4.99 (m, 1H, H4´), 4.25 (dd, 1H, $J_{4',5'a}$ ≈ 3.5 Hz, $J_{5'a,5'b}$ ≈ 12.5 Hz, H5´a), 4.10 (dd, 1H, $J_{4',5'b}$ ≈ 5.5 Hz, H5´b), 2.11, 2.08, 2.03, 2.01, 1.94 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 170.5, 170.2, 170.0, 169.7, 169.3 (-O*C*OCH_3), 142.1 (C3), 138.0 (C8a), 133.5, 130.5, 130.2 (C4, C5, C7), 123.9 (C6), 116.8 (C4a), 115.1 (C8), 71.3 (C1´), 69.1, 69.0, 68.4 (C2´, C3´, C4´), 61.3 (C5´), 51.0 (C2), 20.7, 20.6, 20.5 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 593.1146. Calculated $C_{24}H_{27}ClN_2O_{12}Na$ 593.1145.

6-chloro-3-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)-1,2-dihydroquinoline **10b**. Red solid. IR ν_{max} (NaCl) 3399 (-NH), 2926 (-CH_2-), 1752 (C=O), 1647, 1371 (NO_2), 1606, 1513 (C=C_{arom}), 1218 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.77 (s, 1H, H4), 7.15 (dd, 1H, $J_{5,7}$ ≈ 2.0 Hz, $J_{7,8}$ ≈ 9.0 Hz, H7), 7.05 (d, 1H, H5), 6.60 (d, 1H, H8), 5.40 (dd, 1H, $J_{1',2'}$ ≈ 10.5 Hz, $J_{2',3'}$ ≈ 2.0 Hz, H2´), 5.38 (dd, 1H, $J_{3',4'}$ ≈ 9.5 Hz, H3´), 5.31 (d, 1H, $J_{1,2}$ ≈ 3.5 Hz, H1), 5.19 (m, 1H, H4´), 5.07 (dd, 1H, $J_{1',2}$ ≈ 1.5 Hz, H1´), 4.92 (dd, 1H, H2), 4.20 (dd, 1H, $J_{4',5'a}$ ≈ 2.5 Hz, $J_{5'a,5'b}$ ≈ 12.5 Hz, H5´a), 4.02 (dd, 1H, $J_{4',5'b}$ ≈ 5.5 Hz, H5´b), 2.25, 2.11, 2.04, 1.73 (s, 3H, -OCOCH_3). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ (ppm) 172.5, 170.5, 169.9, 169.8, 169.7 (-O*C*OCH_3), 143.9 (C3), 137.1 (C8a), 133.7, 132.0, 129.5 (C4, C5, C7), 122.8 (C6), 116.3 (C4a), 114.7 (C8), 69.7 (C1´), 68.0, 67.1, 66.5 (C2´, C3´, C4´), 62.0 (C5´), 50.9 (C2), 21.0, 20.9, 20.7, 20.6, 20.4 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 593.1145. Calculated $C_{24}H_{27}ClN_2O_{12}Na$ 593.1145.

6-bromo-3-nitro-(2*R*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)-1,2-dihydroquinoline **11c**. Red solid. IR ν_{max} (NaCl) 3378 (-NH), 2963 (-CH_2-), 1752 (C=O), 1643, 1371 (NO_2), 1603, 1509 (C=C_{arom}), 1261 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.75 (s, 1H, H4), 7.28 (d, 2H, H5, H7), 6.59 (d, 1H, $J_{7,8}$ ≈ 8.5 Hz, H8), 5.49 (dd, 1H, $J_{1',2'}$ ≈ 3.5 Hz, $J_{2',3'}$ ≈ 5.5 Hz, H2´), 5.48 (dd, 1H, $J_{1,2}$ ≈ 3.5 Hz, $J_{1',2}$ ≈ 5.0 Hz, H2), 5.42 (dd, 1H, $J_{3',4'}$ ≈ 6.5 Hz, H3´), 5.28 (d, 1H, H1), 5.18 (t, 1H, H1´), 4.99 (m, 1H, H4´), 4.25 (dd, 1H, $J_{4',5'a}$ ≈ 3.0 Hz, $J_{5'a,5'b}$ ≈ 12.5 Hz, H5´a), 4.09 (dd, 1H, $J_{4',5'b}$ ≈ 6.0 Hz, H5´b), 2.10,

2.08, 2.04, 2.02, 1.93 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 170.6, 170.3, 170.1, 169.8, 169.4 (-O*C*OCH$_3$), 142.6 (C3), 137.6 (C8a), 136.2, 133.1, 130.4 (C4, C5, C7), 117.3 (C4a), 115.5 (C8), 110.5 (C6), 71.4 (C1´), 69.1, 68.9, 68.3 (C2´, C3´, C4´), 61.3 (C5´), 51.0 (C2), 20.7, 20.6, 20.5 (-OCO*C*H$_3$). EISM Found $(M+Na)^+$ 637.0638. Calculated $C_{24}H_{27}BrN_2O_{12}Na$ 637.0640.

6-bromo-3-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)-1,2-dihydroquinoline **10c**. Red solid. IR ν_{max} (NaCl) 3400 (-NH), 2922 (-CH_2-), 1749 (C=O), 1645, 1371 (NO_2), 1601, 1512 (C=C_{arom}), 1218 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.76 (s, 1H, H4), 7.27 (dd, 1H, $J_{5,7}$ ≈ 2.5 Hz, $J_{7,8}$ ≈ 8.5 Hz, H7), 7.18 (d, 1H, H5), 6.55 (d, 1H, H8), 5.39 (dd, 1H, $J_{1´,2´}$ ≈ 10.5 Hz, $J_{2´,3´}$ ≈ 2.5 Hz, H2´), 5.37 (dd, 1H, $J_{3´,4´}$ ≈ 11.0 Hz, H3´), 5.32 (d, 1H, $J_{1,2}$ ≈ 3.5 Hz, H1), 5.18 (m, 1H, H4´), 5.06 (dd, 1H, $J_{1´,2}$ ≈ 1.0 Hz, H1´), 4.91 (dd, 1H, H2), 4.18 (dd, 1H, $J_{4´,5´a}$ ≈ 2.5 Hz, $J_{5´a,5´b}$ ≈ 12.5 Hz, H5´a), 4.01 (dd, 1H, $J_{4´,5´b}$ ≈ 5.5 Hz; H5´b), 2.24, 2.10, 2.03, 2.02, 1.72 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 172.5, 170.5, 169.9, 169.8, 169.7 (-O*C*OCH$_3$), 144.2 (C3), 136.9 (C8a), 136.4, 132.4, 131,9 (C4, C5, C7), 116.8 (C4a), 115.1 (C8), 109.4 (C6), 69.6 (C1´), 69.9, 67.0, 66.5 (C2´, C3´, C4´), 61.9 (C5´), 50.8 (C2), 20.9, 20.8, 20.6, 20.5, 20.4 (-OCO*C*H$_3$). EISM Found $(M+Na)^+$ 637.0644. Calculated $C_{24}H_{27}BrN_2O_{12}Na$ 637.0640.

3-Nitro-2-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)quinoline **12a**. Yellow solid. IR ν_{max} (KBr) 3066 (-CH-), 2961 (-CH_2-), 1752 (C=O), 1667, 1370 (NO_2), 1606, 1534 (C=C_{arom}), 1212 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.95 (s, 1H, H4), 8.11 (d, 1H, $J_{7,8}$ ≈ 8.5 Hz, H8), 7.97 (d, 1H, $J_{5,6}$ ≈ 8.0 Hz, H5), 7.90 (ddd, 1H, $J_{6,7}$ ≈ 7.0 Hz, H7), 7.68 (ddd, 1H, H6), 6.55 (s, 1H, H1´), 5.78 (s, 2H, H2´, H3´), 5.47 (m, 1H, H4´), 4.34 (dd, 1H, $J_{4´,5´a}$ ≈ 5.0 Hz, $J_{5´a,5´b}$ ≈ 11.5 Hz, H5´a), 3.97 (dd, 1H, $J_{4´,5´b}$ ≈ 7.5 Hz, H5´b), 2.23, 2.20, 2.04, 2.00, 1.77 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.5, 170.4, 170.2, 169.9, 169.8 (-O*C*OCH$_3$), 149.0 (C2), 148.3 (C8a), 141.9 (C3), 134.6, 133.5, 129.3, 129.2, 128.9 (C4, C5, C6, C7, C8), 125.8 (C4a), 69.7 (C1´), 68.6, 68.4, 67.9 (C2´, C3´, C4´), 62.1 (C5´), 20.7, 20.6, 20.6, 20.5, 20.3 (-OCO*C*H$_3$). EISM Found $(M+H)^+$ 535.1561. Calculated $C_{24}H_{27}N_2O_{12}$ 535.1564.

6-chloro-3-nitro-2-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)quinoline **12b**. Yellow solid. IR ν_{max} (KBr) 3063 (=CH-), 2962 (-CH_2-), 1746 (C=O), 1667, 1372 (NO_2),

1603, 1537 (C=C_{arom}), 1219 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.86 (s, 1H, H4), 8.05 (d, 1H, $J_{7,8}$ ≈ 9.0 Hz, H8), 7.95 (d, 1H, $J_{5,7}$ ≈ 2.5 Hz, H5), 7.82 (dd, 1H, H7), 6.50 (d, 1H, $J_{1',2'}$ ≈ 1.5 Hz, H1´), 5.77 (dd, 1H, $J_{2',3'}$ ≈ 10.0 Hz, H2´), 5.73 (dd, 1H, $J_{3',4'}$ ≈ 1.5 Hz, H3´), 5.47 (ddd, 1H, H4´), 4.34 (dd, 1H, $J_{4',5'a}$ ≈ 5.5 Hz, $J_{5'a,5'b}$ ≈ 12.0 Hz, H5´a), 3.97 (dd, 1H, $J_{4',5'b}$ ≈ 7.5 Hz, H5´b), 2.23, 2.22, 2.05, 2.00, 1.77 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.5, 170.4, 170.2, 169.9, 169.7 (-O*C*OCH_3), 149.4 (C2), 146.7 (C8a), 142.5 (C3), 135.0 (C6), 134.4, 133.6, 130.8, 127.6 (C4, C5, C7, C8), 126.5 (C4a), 69.6 (C1´), 68.6, 68.3, 67.9 (C2´, C3´, C4´), 62.1 (C5´), 20.7, 20.6, 20.6, 20.5, 20.5 (-OCO*C*H_3). EISM Found $(M+H)^+$ 569.1174. Calculated $C_{24}H_{26}N_2O_{12}$ 569.1174.

6-bromo-3-nitro-2-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)quinoline **12c**. Yellow solid. IR ν_{max} (KBr) 3063 (-CH-), 2963 (-CH_2-), 1747 (C=O), 1673, 1372 (NO_2), 1614, 1537 (C=C_{arom}), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.86 (s, 1H, H4), 8.13 (s, 1H, H8), 7.97 (s, 2H, H5, H7), 6.50 (s, 1H, H1´), 5.73 (dd, 2H, H2´, H3´), 5.47 (m, 1H, H4´), 4.33 (dd, 1H, $J_{4',5'a}$ ≈ 7.0 Hz, $J_{5'a,5'b}$ ≈ 9.5 Hz, H5´a), 3.97 (dd, 1H, $J_{4',5'b}$ ≈ 8.0 Hz, H5´b), 2.23, 2.05, 2.00, 1.77 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 171.1, 170.4, 170.2, 169.9, 169.8 (-O*C*OCH_3), 149.5 (C2), 146.9 (C8a), 142.4 (C3), 137.0, 133.5, 131.0, 130.8 (C4, C5, C7, C8), 127.0 (C4a), 123.1 (C6), 69.6 (C1´), 68.5, 68.3, 67.8 (C2´, C3´, C4´), 62.1 (C5´), 20.7, 20.6, 20.5, 20.4 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 635.0471. Calculated $C_{24}H_{25}BrN_2O_{12}Na$ 635.0483.

3-Nitro-2-(D-*galacto*-pentitol-1'-yl)quinoline **14a**. White solid. IR ν_{max} (KBr) 3428 (-OH), 3085 (-CH-), 1620, 1338 (NO_2), 1606 , 1523 (C=C_{arom}), 1095 (C-OH) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 9.16 (s, 1H, H4), 8.24 (d, 1H, $J_{5,6}$ ≈ 8.5 Hz, H5), 8.17 (d, 1H, $J_{7,8}$ ≈ 8.5 Hz, H8), 7.98 (dd, 1H, $J_{6,7}$ ≈ 7.5 Hz, H7), 7.78 (t, 1H, H6), 5.70 (d, 1H, $J_{1',OH}$ ≈ 6.0 Hz, H1´), 5.19 (d, 1H exchangeable, OH), 4.45 (s, 1H exchangeable, OH), 4.40 (d, 1H exchangeable, OH), 4.23 (d, 1H exchangeable, OH), 4.19 (d, 1H exchangeable, OH), 3.98-3.34 (5H, H2´, H3´, H4´, H5´a, H5´b). ^{13}C-NMR (DMSO-d_6, 125M Hz): δ (ppm) 154.5 (C2), 146.3 (C8a), 142.7 (C3), 133.7, 133.0, 129.3, 128.4, 128.1 (C4, C5, C6, C7, C8), 125.4 (C4a), 71.3 (C1´), 69.7, 69.6, 69.3 (C2´, C3´, C4´), 63.0 (C5´). EISM Found $(M+H)^+$ 325.1037. Calculated $C_{14}H_{17}N_2O_7$ 325.1036.

6-chloro-3-nitro-2-(D-*galacto*-pentitol-1'-yl)quinoline **14b**. White solid. IR ν_{max} (KBr) 3403 (-OH), 1651, 1368 (NO_2), 1630, 1569 ($C=C_{arom}$), 1087 (C-OH) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 9.10 (s, 1H, H4), 8.36 (s, 1H, H5), 8.17 (d, 1H, $J_{7,8}$ ≈ 7.0 Hz, H7), 8.00 (t, 1H, H8), 5.65 (s, 1H, H1´), 5.19 (bs, 1H exchangeable, OH), 4.43 (bs, 1H exchangeable, OH), 4.41 (bs, 1H exchangeable, OH), 4.21 (bs, 1H exchangeable, OH), 4.18 (bs, 1H exchangeable, OH), 3.98-3.34 (5H, H2´, H3´, H4´, H5´a, H5´b). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 155.2 (C2), 144.9 (C8a), 143.5 (C3), 133.3, 132.9, 130.5, 127.7 (C4, C5, C7, C8), 132.4 (C6), 126.3 (C4a), 71.3 (C1´), 69.8, 69.7, 69.3 (C2´, C3´, C4´), 63.0 (C5´). EISM Found $(M+Na)^+$ 381.0445. Calculated $C_{14}H_{15}ClN_2O_7Na$ 381.0460.

6-bromo-3-nitro-2-(D-*galacto*-pentitol-1'-yl)quinoline **14c**. White solid. IR ν_{max} (KBr) 3385 (-OH), 1667, 1372 (NO_2), 1599 ($C=C_{arom}$), 1082 m (C-OH) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 9.10 (s, 1H, H4), 8.52 (s, 1H, H5), 8.11 (s, 2H, H7, H8), 5.64 (d, 1H, $J_{1´,2´}$ ≈ 8.5 Hz, H1´), 5.19 (d, 1H exchangeable, OH), 4.46 (t, 1H exchangeable, OH), 4.41 (d, 1H exchangeable, OH), 4.22 (d, 1H exchangeable, OH), 4.19 (d, 1H exchangeable, OH), 3.98, 3.73, 3.61, 3.36 (5H, H2´, H3´, H4´, H5´a, H5´b). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 155.3 (C2), 145.1 (C8a), 143.4 (C3), 135.8, 132.8, 131.0, 130.6 (C4, C5, C7, C8), 126.9 (C4a), 121.1 (C6), 71.3 (C1´), 69.9, 69.7, 69.3 (C2´, C3´, C4´), 63.0 (C5´). EISM Found $(M+Na)^+$ 424.9944. Calculated $C_{14}H_{15}BrN_2O_7Na$ 424.9955.

3-Nitro-2-(D-*manno*-pentitol-1'-yl)quinoline **15a**. White solid. IR ν_{max} (KBr) 3450 (-OH), 3245 (-CH-), 1620, 1335 (NO_2), 1605, 1528 ($C=C_{arom}$), 1057 (C-OH) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 9.04 (s, 1H, H4), 8.21 (d, 1H, $J_{5,6}$ ≈ 8.0 Hz, H5), 8.16 (d, 1H, $J_{7,8}$ ≈ 8.5 Hz, H8), 7.98 (ddd, 1H, H7), 7.77 (t, 1H, H6), 5.44 (bs, 1H exchangeable, OH), 5.36 (d, 1H, $J_{1´,OH}$ ≈ 9.0 Hz, H1´), 4.33 (m, 4H exchangeables, 4 OH), 3.92, 3.73 (each one d, 1H, $J_{1´,2´}$ ≈ 9.0 Hz, H2´, H3´), 3.64 (dd, 1H, $J_{4´,5´}$ ≈ 3.0 Hz, $J_{3´,4´}$ ≈ 10.5 Hz, H4´), 3.44 (m, 2H, H5a´, H5b´). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 155.7 (C2), 146.9 (C8a), 144.3 (C3), 132.7, 132.4, 129.2, 128.4, 128.1 (C4, C5, C6, C7, C8), 125.5 (C4a), 72.7 (C1´), 71.1, 69.5, 68.7 (C2´, C3´, C4´), 64.0 (C5´). EISM Found $(M+H)^+$ 325.1037. Calculated $C_{14}H_{17}N_2O_7$ 325.1036.

6-chloro-3-nitro-2-(D-*manno*-pentitol-1'-yl)quinoline **15b**. White solid. IR ν_{max} (KBr) 3570 (-OH), 3204 (-CH-), 1534, 1361 (NO_2), 1605 ($C=C_{arom}$), 1066 (C-OH) cm^{-1}. ^{1}H-NMR

(DMSO-d_6, 500 MHz): δ (ppm) 9.00 (s, 1H, H4), 8.34 (s, 1H, H5), 8.17 (d, 1H, $J_{7,8}$ ≈ 9.0 Hz, H8), 7.99 (d, 1H, H7), 5.52 (bs, 1H exchangeable, OH), 5.33 (d, 1H, $J_{1',OH}$ ≈ 8.0 Hz, H1´), 4.47-4.37 (m, 4H exchangeables, 4 OH), 3.92, 3.72, 3.64, 3.44 (d, 1H, H2´, H3´, H4´, H5a´, H5b´). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 156.4 (C2), 145.4 (C8a), 144.8 (C3), 132.4 (C6), 133.1, 131.6, 130.5, 127.6 (C4, C5, C7, C8), 126.3 (C4a), 72.6 (C1´), 71.0, 69.5, 68.8 (C2´, C3´, C4´); 63.8 (C5´). EISM Found $(M+H)^+$ 325.1037. Calculated $C_{14}H_{17}N_2O_7$ 325.1036.

6-bromo-3-nitro-2-(D-*manno*-pentitol-1'-yl)quinoline **15c**. White solid. IR ν_{max} (KBr) 3285 (-CH-, -OH), 1531, 1359 (NO_2), 1613, (C=C_{arom}), 1021 (C-OH) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 8.97 (s, 1H, H4), 8.47 (s, 1H, H5), 8.09 (s, 2H, H7, H8), 5.52 (bs, 1H exchangeable, OH), 5.33 (d, 1H, $J_{1',OH}$ ≈ 8.0 Hz, H1´), 4.47-4.37 (m, 4H exchangeables, 4 OH), 3.92, 3.72, 3.64, 3.44 (d, 1H, H2´, H3´, H4´, H5a´, H5b´). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 156.6 (C2), 145.8 (C8a), 145.0 (C3), 127.0 (C6), 135.9, 131.7, 131.1, 130.8 (C4, C5, C7, C8), 121.3 (C4a), 72.9 (C1´), 71.2, 69.7, 69.0 (C2´, C3´, C4´), 64.0 (C5´). EISM Found $(M+Na)^+$ 424.9949. Calculated $C_{14}H_{15}BrN_2O_7Na$ 424.9955.

3-Nitro-2-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)quinoline **13a**. IR $\nu_{max.}$ (NaCl) 3064 (-CH_3), 2954 (-CH_2-), 1747 (C=O), 1664, 1372 (NO_2), 1606, 1537 (C=C_{arom}), 1218 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.71 (s, 1H, H4), 8.20 (d, 1H, $J_{7,8}$ ≈ 8.5 Hz, H8), 7.95 (d, 1H, $J_{5,6}$ ≈ 8.0 Hz, H5), 7.91 (ddd, 1H, $J_{5,7}$ ≈ 1.0 Hz, H7), 7,70 (ddd, 1H, H6), 6.54 (d, 1H, $J_{1',2'}$ ≈ 10.0 Hz, H1´), 5.96 (dd, 1H, $J_{2',3'}$ ≈ 2.0 Hz, H2´), 5.76 (dd, 1H, $J_{3',4'}$ ≈ 9.5 Hz, H3´), 5.15 (m, 1H, H4´), 4.28 (dd, 1H, $J_{4'5'a}$ ≈ 2.5 Hz, $J_{5'a,5'b}$ ≈ 12.5 Hz, H5´a), 4.16 (dd, 1H, $J_{4',5'b}$ ≈ 5.0 Hz, H5´b), 2.23, 2.14, 2.07, 2.05, 1.77 (s, 3H, -$OCOCH_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.6, 169.9, 169.8, 169.7, 169.1 (-O*C*OCH_3), 148.6 (C2), 148.2 (C8a), 143.5 (C3), 133.2, 133.1, 129.7, 129.1, 128.8 (C4, C5, C6, C7, C8), 126.0 (C4a), 70.6 (C1´), 68.7, 67.9, 67.8 (C2´, C3´, C4´), 62.0 (C5´), 20.8, 20.7, 20.6, 20.5, 20.1 (-OCO*C*H_3). EISM Found $(M+H)^+$ 535.1563. Calculated $C_{24}H_{27}N_2O_{12}$ 535.1564.

6-chloro-3-nitro-2-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)quinoline **13b**. IR $\nu_{max.}$ (NaCl) 3068 (-CH_3), 2980 (-CH_2-), 1751 (C=O), 1556, 1371 (NO_2), 1602, 1538 (C=C_{arom}), 1219 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.61 (s, 1H, H4), 8.13 (d, 1H, $J_{7,8}$ ≈ 9.0 Hz, H8), 7.93 (d, 1H, $J_{5,7}$ ≈ 2.5 Hz, H5), 7.83 (dd, 1H, H7), 6.47 (d, 1H,

$J_{1',2'}$ ≈ 9.5 Hz, H1′), 5.92 (dd, 1H, $J_{2',3'}$ ≈ 1.5 Hz, H2′), 5.75 (dd, 1H, $J_{3',4'}$ ≈ 9.0 Hz, H3′), 5.16 (m, 1H, H4′), 4.28 (dd, 1H, $J_{4',5'a}$ ≈ 2.5 Hz, $J_{5'a,5'b}$ ≈ 12.5 Hz, H5′a), 4.16 (dd, 1H, $J_{4',5'b}$ ≈ 5.0 Hz, H5′b), 2.22, 2.14, 2.07, 2.05, 1.78 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.6, 169.1, 169.8, 169.7, 169.1 (-O*C*OCH$_3$), 149.0 (C2), 146.5 (C8a), 144.1 (C3), 135.4 (C6), 134.2, 132.1, 131.2 (C7, C4, C8), 127.2 (C5), 126.7 (C4a), 70.5 (C1′), 68.6, 67.9, 67.7 (C2′, C3′, C4′), 62.0 (C5′), 20.8, 20.7, 20.6, 20.5, 20.1 (-OCO*C*H$_3$). EISM Found $(M+H)^+$ 569.1188. Calculated $C_{24}H_{26}ClN_2O_{12}$ 569.1174.

6-bromo-3-nitro-2-(1',2',3',4',5'-penta-*O*-acetyl-D-*manno*-pentitol-1'-yl)quinoline **13c**. IR $\nu_{max.}$ (NaCl) 2963 (-CH_2-), 1748 (C=O), 1537, 1371 (NO_2), 1599 (C=C_{arom}), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.53 (s, 1H, H4), 8.04 (d, 1H, $J_{5,7}$ ≈ 1.2 Hz, H5), 7.99 (d, 1H, $J_{7,8}$ ≈ 8.8 Hz, H8), 7.89 (dd, 1H, H7), 6.40 (d, 1H, $J_{1',2'}$ ≈ 9.6 Hz, H1′), 5.84 (dd, 1H, $J_{2',3'}$ ≈ 1.2 Hz, H2′), 5.67 (dd, 1H, $J_{3',4'}$ ≈ 9.6 Hz, H3′), 5.08 (m, 1H, H4′), 4.20 (dd, 1H, $J_{4',5'a}$ ≈ 2.0 Hz, $J_{5'a,5'b}$ ≈ 12.4 Hz, H5′a), 4.09 (dd, 1H, $J_{4',5'b}$ ≈ 4.8 Hz, H5′b), 2.15, 2.07, 2.00, 1.97, 1.70 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.6, 169.9, 169.8, 169.7, 169.1 (-O*C*OCH$_3$), 149.1 (C2), 146.7 (C8a), 144.0 (C3), 136.7, 132.0, 131.1, 130.5 (C4, C5, C7, C8), 127.0 (C6), 123.5 (C4a), 70.5 (C1′), 68.5, 67.9, 67.6 (C2′, C3′, C4′), 62.0 (C5′), 20.8, 20.7, 20.6, 20.5, 20.1 (-OCO*C*H$_3$). EISM Found $(M+Na)^+$ 635.0476. Calculated $C_{24}H_{25}BrN_2O_{12}Na$ 635.0483.

(1*Z*)-Formyl-(4*S*)-(indol-3''-yl)-(3*R*)-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)tetrahydroquinoline **19a**. IR $\nu_{max.}$ (NaCl) 3379 (-NH), 3059 (-CH_3), 2964 (-CH_2-), 1752 (C=O, ester), 1686 (C=O, amide), 1622, 1372 (NO_2), 1584, 1556 (C=C_{arom}), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.65 (s, 1H, -NCHO), 8.48 (bs, 1H, NH), 7.35-6.65 (9H, arom.), 5.80 (dd, 1H, $J_{1',2}$ ≈ 10.5 Hz, $J_{2,3}$ ≈ 4.0 Hz, H2), 5.58 (dd, 1H, $J_{1',2'}$ ≈ 1.5 Hz, H1′), 5.25 (d, 1H, $J_{3,4}$ ≈ 11.5 Hz, H4), 5.17 (dd, 1H, $J_{2',3'}$ ≈ 8.0 Hz, H2′), 5.07 (m, 3H, H3, H3′, H4′), 4.14 (dd, 1H, $J_{4',5'a}$ ≈ 4.5 Hz, $J_{5'a,5'b}$ ≈ 12.5 Hz, H5′a), 3.58 (dd, 1H, $J_{4',5'b}$ ≈ 6.5 Hz, H5′b), 2.16, 2.05, 2.04, 2.01, 1.92 (s, 3H, -OCOCH$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.4, 170.4, 170.2, 170.0, 169.8 (-O*C*OCH$_3$), 161.5 (-N*C*HO), 136.6, 133.0, 131.1, 129.7, 128.7, 127.2, 125.3, 124.7, 122.3, 119.9, 119.7, 119.3, 118.1, 112.7, 111.8 (C8a, C4a, C5, C6, C7, C8, C2′′, C3′′a, C7′′a, C5′′, C6′′, C7′′), 84.3 (C3), 68.1, 68.0, 66.9, 66.0 (C1′, C2′, C3′, C4′), 62.0 (C5′), 49.0 (C2), 35.6 (C4), 20.9, 20.8,

20.7, 20.6 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 704.2043. Calculated $C_{33}H_{35}N_3O_{13}Na$ 704.2062.

6-chloro-(1*Z*)-formyl-(4*S*)-(indol-3''-yl)-(3*R*)-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)tetrahydroquinoline **19b**. IR $\nu_{max.}$ (NaCl) 2924 (-CH_2-), 1749 (C=O, ester), 1690 (C=O, amide), 1558 (C=C_{arom}), 1371 (NO_2), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.61 (s, 1H, -NCHO), 8.28 (bs, 1H, NH), 7.37-6.67 (8H, arom.), 5.80 (dd, 1H, $J_{1',2} \approx 10.0$ Hz, $J_{2,3} \approx 3.5$ Hz, H2), 5.54 (d, 1H, H1´), 5.21 (d, 1H, $J_{3,4} \approx$ 11.5 Hz, H4), 5.13 (d, 1H, $J_{2',3'} \approx 8.5$ Hz, H2´), 5.03 (m, 3H, H3, H3´, H4´), 4.14 (dd, 1H, $J_{4',5'a} \approx 4.5$ Hz, $J_{5'a,5'b} \approx 12.0$ Hz, H5´a), 3.66 (dd, 1H, $J_{4',5'b} \approx 6.0$ Hz, H5´b), 2.16, 2.06, 2.04, 2.02, 1.96 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 170.4, 170.4, 170.2, 170.0, 169.9 (-O*C*OCH$_3$), 161.1 (-NCHO), 136.7, 132.9, 131.8, 131.7, 130.9, 129.2, 125.4, 124.5, 122.7, 122.6, 120.7, 120.3, 118.0, 112.2, 111.9 (C8a, C4a, C5, C6, C7, C8, C2´´, C3´´a, C7´´a, C5´´, C6´´, C7´´), 83.7 (C3), 68.0, 67.9, 66.9, 65.9 (C1´, C2´, C3´, C4´), 62.1 (C5´), 49.0 (C2), 35.6 (C4), 21.0, 20.8, 20.7, 20.6, 20.5 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 738.1658. Calculated $C_{33}H_{34}ClN_3O_{13}Na$ 738.1672.

6-chloro-(1*E*)-formyl-(4*S*)-(indol-3''-yl)-(3*R*)-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)tetrahydroquinoline **20b**. IR $\nu_{max.}$ (NaCl) 2925 (-CH_2-), 1748 (C=O, ester), 1691 (C=O, amide), 1556 (C=C_{arom}), 1371 (NO_2), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.45 (s, 1H, -NCHO), 8.39 (bs, 1H, NH), 7.70-6.94 (8H, arom.), 5.51 (dd, 1H, $J_{1',2} \approx 10.0$ Hz, $J_{2,3} \approx 2.0$ Hz, H2), 5.39 (d, 1H, $J_{3,4} \approx 5.5$ Hz, H4), 5.37 (dd, 1H, $J_{1',2'} \approx 2.0$ Hz, H1´), 5.30 (m, 2H, H2´, H3´), 5.07 (dd, 1H, H3), 5.02 (td, 1H, H4´), 4.22 (dd, 1H, $J_{4',5'a} \approx 5.5$ Hz, $J_{5'a,5'b} \approx 11.5$ Hz, H5´a), 3.80 (dd, 1H, $J_{4',5'b} \approx 6.5$ Hz, H5´b), 2.28, 2.15, 2.09, 2.07, 2.04 (s, 3H, -OCOC*H*$_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 171.4, 170.4, 170.2, 170.0, 169.9 (-O*C*OCH$_3$), 163.5 (-NCHO), 135.5, 133.4, 132.0, 130.4, 129.7, 128.7, 127.1, 124.7, 122.8, 121.0, 120,5, 117.7, 111.6, 110.2 (C8a, C4a, C5, C6, C7, C8, C2´´, C3´´a, C8´´a, C5´´, C6´´, C7´´), 82.4 (C3), 68.7, 67.8, 67.5, 66.4 (C1´, C2´, C3´, C4´), 61.6 (C5´), 50.1 (C2), 34.1 (C4), 21.1, 20.9, 20.7, 20.6 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 738.1651. Calculated $C_{33}H_{34}ClN_3O_{13}Na$ 738.1672.

6-bromo-(1*Z*)-formyl-(4*S*)-(indol-3''-yl)-(3*R*)-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)tetrahydroquinoline **19c**. IR $\nu_{max.}$ (NaCl) 3406 (NH), 2925 (-CH_2-),

1749 (C=O, ester), 1689 (C=O, amide), 1558 (C=C_{arom}), 1371 (NO_2), 1216 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.60 (s, 1H, -NC*H*O), 8.26 (bs, 1H, NH), 7.62-6.67 (8H, arom.), 5.79 (dd, 1H, $J_{1',2}$ ≈ 10.5 Hz, $J_{2,3}$ ≈ 4.0 Hz, H2), 5.54 (dd, 1H, $J_{1',2'}$ ≈ 1.5 Hz, H1´), 5.21 (d, 1H, $J_{3,4}$ ≈ 11.5 Hz, H4), 5.13 (dd, 1H, $J_{2',3'}$ ≈ 8.5 Hz, H2´), 5.09-5.02 (m, 3H, H3, H3´, H4´), 4.14 (dd, 1H, $J_{4',5'a}$ ≈ 4.5 Hz, $J_{5'a,5'b}$ ≈ 12.0 Hz, H5´a), 3.66 (dd, 1H, $J_{4',5'b}$ ≈ 6.5 Hz, H5´b), 2.16, 2.06, 2.04, 2.02, 1.97 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 171.4, 170.4, 170.3, 170.0, 169.9 (-O*C*OCH_3), 163.5 (-NCHO), 135.4, 133.9, 132.6, 131.6, 130.7, 129.1, 127.0, 124.7, 122.8, 121.2, 120.4, 119.7, 117.6, 111.6, 110.1 (C8a, C4a, C5, C6, C7, C8, C2´´, C3´´a, C7´´a, C5´´, C6´´, C7´´), 82.3 (C3), 68.6, 67.7, 67.4, 66.3 (C1´, C2´, C3´, C4´), 61.6 (C5´), 50.0 (C2), 34.0 (C4), 21.1, 20.9, 20.8, 20.6 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 782.1166. Calculated $C_{33}H_{34}BrN_3O_{13}Na$ 782.1167.

6-bromo-(1*E*)-formyl-(4*S*)-(indol-3''-yl)-(3*R*)-nitro-(2*S*)-(1',2',3',4',5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)tetrahydroquinoline **20c**. IR $\nu_{max.}$ (NaCl) 3370 (NH), 2929 (-CH_2-), 1749 (C=O, ester), 1692 (C=O, amide), 1557 (C=C_{arom}), 1371 (NO_2), 1216 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.42 (bs, 2H, -NCHO, NH), 7.70-6.92 (8H, arom.), 5.48 (dd, 1H, $J_{1',2}$ ≈ 10.0 Hz, $J_{2,3}$ ≈ 2.5 Hz, H2), 5.37 (d, 1H, $J_{3,4}$ ≈ 6.0 Hz, H4), 5.34 (dd, 1H, $J_{1',2'}$ ≈ 2.0 Hz, H1´), 5.31-5.27 (2 dd, 2H, H2´, H3´), 5.03 (dd, 1H, H3), 4.99 (td, 1H, H4´), 4.21 (dd, 1H, $J_{4',5'a}$≈ 5.0 Hz, $J_{5'a,5'b}$ ≈ 11.5 Hz, H5´a), 3.78 (dd, 1H, $J_{4',5'b}$ ≈ 6.5 Hz, H5´b), 2.26, 2.13, 2.07, 2.06, 2.02 (s, 3H, -OCOCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 171.4, 170.4, 170.2, 170.0, 169.9 (-O*C*OCH_3), 163.5 (-NCHO), 135.5, 133.9, 132.6, 130.7, 129.1, 127.0, 126.1, 124.7, 122.8, 121.3, 119.7, 117.6, 111.6, 110.1 (C8a, C4a, C5, C6, C7, C8, C2´´, C3´´, C3´´a, C7´´, C7´´a, C5´´, C6´´, C4´´), 82.3 (C3), 68.7, 67.8, 67.5, 66.4 (C1´, C2´, C3´, C4´), 61.6 (C5´), 50.1 (C2), 34.0 (C4), 21.1, 20.9, 20.8, 20.6 (-OCO*C*H_3). EISM Found $(M+Na)^+$ 782.1169. Calculated $C_{33}H_{34}BrN_3O_{13}Na$ 782.1167.

6-Chloro-(1*Z*)-formyl-(4*S*)-(pyrrol-2''-yl)-(3*R*)-(3a)-nitro-(2*S*)-(2e)- (1 ', 2', 3 ', 4', 5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)tetrahydroquinoline **21b**. IR $\nu_{max.}$ (NaCl) 3368 (-NH), 2925 (-CH_2-), 1749 (C=O, ester), 1692 (C=O, amide), 1557 (C=C_{arom}), 1371 (NO_2), 1215 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.37 (s, 1H, -NCHO), 8.28 (bs, 1H, NH), 7.39, 7.20, 7.13 (3H, H8, H5, H7), 6.74 (1H, m, H5´´), 6.23 (1H, q, H4´´), 6.16 (1H, c, H3´´), 5.45 (dd, 1H, $J_{1',2}$ ≈ 10.0 Hz, $J_{2,3}$ ≈ 2.5 Hz, H2), 5.27 (dd, 1H, $J_{2',3'}$ ≈ 9.5 Hz, $J_{1',2'}$ ≈ 2.0 Hz, H2´), 5.21 (dd, 1H, $J_{3',4'}$ ≈ 2.0 Hz, H3´), 5.16 (dd, 1H, H1´), 5.08 (d, 1H, $J_{3,4}$ ≈

5.0 Hz, H4), 4.98 (ddd, 1H, H4´), 4.90 (c, 1H, H3), 4.18 (dd, 1H, $J_{4´,5´a}$ ≈ 5.5 Hz, $J_{5´a,5´b}$ ≈ 12.0 Hz, H5´a), 3.76 (dd, 1H, $J_{4´,5´b}$ ≈ 6.5 Hz, H5´b), 2.19, 2.11, 2.05, 2.01 (s, 3H, -$OCOCH_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 171.3, 170.4, 170.2, 170.0, 169.8 (-O*C*OCH_3), 163.2 (-NCHO), 133.1 (C8a), 132.4 (C2´´), 129.2, 129.0, 120.8 (C5, C7, C8), 128.7 (C6), 123.5 (C4a), 119.8 (C5´´), 111.3 (C4´´), 108.5 (C3´´), 83.2 (C3), 68.7, 67.8, 67.4, 66.3 (C1´, C2´, C3´, C4´), 61.6 (C5´), 50.7 (C2), 36.7 (C4), 21.0, 20.8, 20.7, 20.6 (-$OCOCH_3$). EISM Found $(M+Na)^+$ 688.1512. Calculated $C_{29}H_{32}ClN_3O_{13}Na$ 688.1516.

6-Bromo-(1*Z*)-formyl-(4*S*)-(pyrrol-2''-yl)-(3*R*)-(3a)-nitro-(2*S*)-(2e)- (1 ', 2', 3 ', 4', 5'-penta-*O*-acetyl-D-*galacto*-pentitol-1'-yl)tetrahydroquinoline **21c**. IR $\nu_{max.}$ (NaCl) 3400 (-NH), 2925 (-CH_2-), 1749 (C=O, ester), 1692 (C=O, amide), 1557 (C=C_{arom}), 1372 (NO_2), 1216 (C-O-C) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.29 (s, 1H, -NCHO), 7.94 (d, 1H, $J_{NH,5´´}$ ≈ 1.5 Hz, NH), 7.46, 7.21, 7.07 (3H, H8, H5, H7), 6.67 (q, 1H, H5´´), 6.16 (m, 1H, H4´´), 6.09 (c, 1H, H3´´), 5.38 (dd, 1H, $J_{1´,2}$ ≈ 10.0 Hz, $J_{2,3}$ ≈ 2.5 Hz, H2), 5.20 (dd, 1H, $J_{2´,3´}$ ≈ 9.5 Hz, $J_{1´,2´}$ ≈ 2.0 Hz, H2´), 5.14 (dd, 1H, $J_{3´,4´}$ ≈ 2.5 Hz, H3´), 5.08 (dd, 1H, $J_{1´,2´}$ ≈ 2.0 Hz, H1´), 5.02 (d, 1H, $J_{3,4}$ ≈ 5.0 Hz, H4), 4.91 (td, 1H, H4´), 4.82 (c, 1H, H3), 4.11 (dd, 1H, $J_{4´,5´a}$ ≈ 5.5 Hz, $J_{5´a,5´b}$ ≈ 11.5 Hz, H5´a), 3.68 (dd, 1H, $J_{4´,5´b}$ ≈ 6.5 Hz, H5´b), 2.12, 2.04, 1.98, 1.95, 1.94 (s, 3H, -$OCOCH_3$). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 171.4, 170.4, 170.2, 170.0, 169.8 (-O*C*OCH_3), 163.2 (-NCHO), 133.6 (C8a), 129,0 (C2´´), 132.1, 131.9, 121.1, 120.0 (C5, C7, C8, C5´´), 123.5 (C4a), 119.8 (C6), 111.3 (C4´´), 108.4 (C3´´), 83.1 (C3), 68.7, 67.8, 67.4, 66.2 (C1´, C2´, C3´, C4´), 61.6 (C5´), 50.6 (C2), 36.5 (C4), 21.0, 20.8, 20.7, 20.6 (-$OCOCH_3$). EISM Found $(M+Na)^+$ 732.1011. Calculated $C_{29}H_{32}BrN_3O_{13}Na$ 732.1011.