Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of 6*H*-Indolo-[2,3-*b*]quinoxaline-*N*-glycosides and their Cytotoxic Activity against Human Ceratinocytes (HaCaT)

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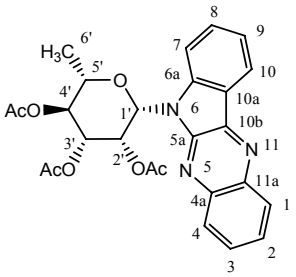
Supporting Information

Experimental procedures and compound characterization

General Comments. All solvents were dried by standard methods. ^{1}H NMR spectra (250.13 MHz, 300.13 MHz and 500.13 MHz) and ^{13}C NMR spectra (62.9 MHz, 75.5 MHz and 125.8 MHz) were recorded on Bruker spectrometers AV 250, AV 300 and AV 500 in $CDCl_3$ and DMSO-d_6 as solvents. The calibration of spectra was carried out on solvent signals ($CDCl_3$: δ (^{1}H) = 7.25, δ (^{13}C) = 77.0; DMSO-d_6: δ (^{1}H) = 2.50, δ (^{13}C) = 39.7).Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). Melting points are uncorrected. Analytical thinlayer chromatography was performed on 0.20 mm 60A silica gel plates. Column chromatography was performed on 60A silica gel (60–200 mesh).

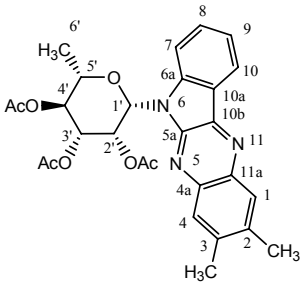
General procedure for the synthesis of 6*H*-indolo-[2,3-*b*]quinoxaline-*N*-glycosides 3a-j. A solution of isatine-*N*-glycoside **β-2a** (1.0 equiv.) and of diamine **1** (1.1 equiv.) in glacial acetic acid (10 mL) was stirred at 80 °C for 1-3 h until no educts could be detected anymore by tlc (heptanes/EtOAc = 3:1). The solution was allowed to cool to 20 °C and the solvent was removed in vacuo. To the residue was added dry benzene (10 mL) and a catalytic amount of toluenesulfonic acid. The solution was stirred at 80 °C for 1-3 h until the reaction was complete (tlc-control). The solution was allowed to cool to 20 °C and NEt_3 (for neutralisation) and toluene (4 mL) were added. The solvent was

concentrated in vacuo and the residue was purified by chromatography (heptane/EtOAc = 9:1 → 6:1→ 2:1).



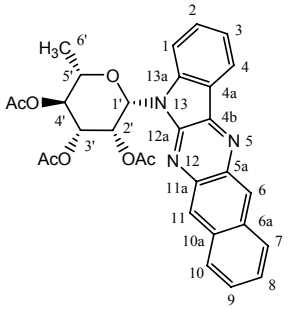
Rhamno, **β-3a**

6-(2',3',4'-Tri-*O*-acetyl-β-L-rhamnopyranosyl)-indolo[2,3-*b*]quinoxaline (β-3a). Stirring of **β-2a** (300 mg, 0.71 mmol) and **1a** (85 mg, 0.79 mmol) for 3 h at 80 °C in HOAc and for 45 min at 80 °C in benzene afforded **β-3a** (253 mg, 72%) as a slightly yellow solid. Mp. 241-243 °C (heptane/EtOAc); $[\alpha]_D = -44.95$ (c = 0.81; T = 22.1 °C; $CHCl_3$); R_f = 0.74 (heptane/EtOAc = 1:3). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.40 (ddd, $^5J_{7,10}$ = 0.7 Hz, $^4J_{8,10}$ = 1.4 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-10); 8.28, 8.13 (2 ddd, $^5J_{1,4}$ = 0.6 Hz, $^4J_{1,3} = {}^4J_{2,4}$ = 1.7 Hz, $^3J_{1,2} = {}^3J_{3,4}$ = 8.1 Hz, 2H, H-1, H-4); 8.08 (d't', $^3J_{7,8}$ = 8.5 Hz, 1H, H-7); 7.77, 7.70 (2 ddd, $^4J_{1,3} = {}^4J_{2,4}$ = 1.7 Hz, $^3J_{2,3}$ = 7.0 Hz, $^3J_{1,2} = {}^3J_{3,4}$ = 8.1 Hz, 2H, H-2, H-3); 7.62 (ddd, $^4J_{8,10}$ = 1.4 Hz, $^3J_{8,9}$ = 7.5 Hz, $^3J_{7,8}$ = 8.5 Hz, 1H, H-8); 7.36 (ddd, $^4J_{7,9}$ = 1.0 Hz, $^3J_{8,9}$ = 7.5 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-9); 6.75 (d, $^3J_{1',2'}$ = 1.6 Hz, 1H, H-1'); 5.73 (dd, $^3J_{1',2'}$ = 1.6 Hz, $^3J_{2',3'}$ = 3.5 Hz, 1H, H-2'); 5.50 (dd, $^3J_{2',3'}$ = 3.5 Hz, $^3J_{3',4'}$ = 10.2 Hz, 1H, H-3'); 5.37 ('t', $^3J_{3',4'}$ = 10.2 Hz, $^3J_{4',5'}$ = 9.7 Hz, 1H, H-4'); 3.95 (dq, $^3J_{4',5'}$ = 9.7 Hz, $^3J_{5',6'}$ = 6.2 Hz, 1H, H-5'); 2.14, 1.99, 1.77 (3s, 9H, 3 $COCH_3$); 1.44 (d, $^3J_{5',6'}$ = 6.2 Hz, 3H, H-6'). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 170.1, 169.9, 169.6 (3 CO); 144.2 (C_q); 143.1 (C-6a); 140.1 139.9, 139.9 (3 C_q); 130.4 (C-8); 129.3, 127.8 (C-1, C-4); 129.0, 126.6 (C-2, C-3); 122.2 (C-10); 121.6 (C-9); 120.3 (C-10a); 115.1 (C-7); 81.4 (C-1'); 74.1 (C-5'); 70.8 (C-3'); 70.6 (C-2'); 70.4 (C-4'); 20.8, 20.7, 20.6 (3 CO*C*H_3); 17.8 (C-6'). MS (EI, 70 eV): m/z (%) = 491 (43) [M^+]; 219 (100) [Aglykon+H]; 153 (96) [M^+-Aglykon-2HOAc]; 111 (81). HRMS (EI): calcd. for $C_{26}H_{25}N_3O_7$ ([M^+]) 491.16918. Found: 491.16870.



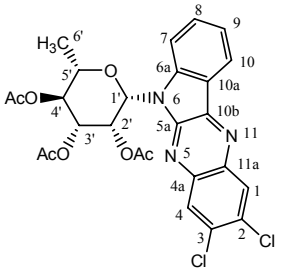
Rhamno, **β-3b**

2,3-Dimethyl-6-(2',3',4'-tri-*O*-acetyl-β-L-rhamno-pyranosyl)indolo[2,3-*b*]quinoxaline (β-3b). Stirring of **β-2a** (300 mg, 0.71 mmol) and of **1b** (107 mg, 0.79 mmol) for 1.5 h at 80 °C in HOAc and for 2 h at 80 °C in benzene afforded **β-3b** (231 mg; 63%) as a slightly yellow solid. Mp. 251-252 °C (heptane/EtOAc); $[\alpha]_D = -75.09$ ($c = 0.99$; $T = 22.3$ °C; $CHCl_3$); $R_f = 0.73$ (heptane/EtOAc = 1:3). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 8.63$ (ddd, $^5J_{7,10} = 0.7$ Hz, $^4J_{8,10} = 1.4$ Hz, $^3J_{9,10} = 7.8$ Hz, 1H, H-10); 8.06 (d't', $^3J_{7,8} = 8.5$ Hz, 1H, H-7); 8.02, 7.87 (2 br s, 2H, H-1, H-4); 7.58 (ddd, $^4J_{8,10} = 1.3$ Hz, $^3J_{8,9} = 7.4$ Hz, $^3J_{7,8} = 8.5$, 1H, H-8); 7.32 (ddd, $^4J_{7,9} = 0.9$ Hz, $^3J_{8,9} = 7.4$ Hz, $^3J_{9,10} = 7.8$ Hz, 1H, H-9); 6.72 (d, $^3J_{1',2'} = 1.5$ Hz, 1H, H-1'); 5.71 (dd, $^3J_{1',2'} = 1.5$ Hz, $^3J_{2',3'} = 3.5$ Hz, 1H, H-2'); 5.49 (dd, $^3J_{2',3'} = 3.5$ Hz, $^3J_{3',4'} = 10.2$ Hz, 1H, H-3'); 5.36 ('t', $^3J_{3',4'} = 10.2$ Hz, $^3J_{4',5'} = 9.7$ Hz, 1H, H-4'); 3.95 (dq, $^3J_{4',5'} = 9.7$ Hz, $^3J_{5',6'} = 6.2$ Hz, 1H, H-5'); 2.53, 2.51 (2 br s, 6H, 2 CH_3); 2.13, 1.98, 1.76 (3s, 9H, 3 $COCH_3$); 1.44 (d, $^3J_{5',6'} = 6.2$ Hz, 3H, H-6'). ^{13}C-NMR (75.5 MHz, $CDCl_3$): $\delta = 170.1$, 169.9, 169.6 (3 CO); 144.0 (C_q); 142.7 (C-6a); 139.5, 138.9, 138.9, 138.8, 136.7 (5 C_q); 129.9 (C-8); 128.4, 127.0 (C-1, C-4); 121.8 (C-10); 121.4 (C-9); 120.6 (C-10a); 115.0 (C-7); 81.4 (C-1'); 74.1 (C-5'); 70.9 (C-3'); 70.6 (C-2'); 70.5 (C-4'); 20.8, 20.7, 20.6 (3 CO*C*H_3); 20.4, 20.2 (2 CH_3); 17.8 (C-6'). MS (EI, 70 eV): m/z (%) = 519 (42) [M^+]; 247 (100) [Aglykon+H]; 153 (77) [M^+-Aglykon-2HOAc]; 111 (53). HRMS (EI): calcd. for $C_{28}H_{29}N_3O_7$ ([M^+]) 519.20113. Found: 519.20000. Anal.: calcd. for $C_{28}H_{29}N_3O_7$ (519.55): C, 64.73; H, 5.63; N, 8.09. Found: C, 64.22; H, 5.67; N, 7.90.



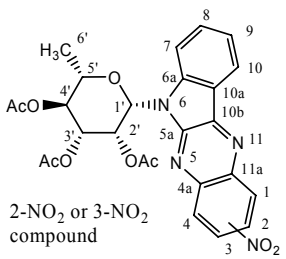
Rhamno, **β-3c**

13-(2',3',4'-Tri-*O*-acetyl-β-L-rhamnopyranosyl)-5,12,13-triazaindeno[1,2-*b*]anthracene (β-3c). Stirring of **β-2a** (300 mg, 0.71 mmol) and **1c** (124 mg, 0.79 mmol) for 1.5 h at 80 °C in HOAc and for 1.5 h at 80 °C in benzene afforded **β-3c** (197 mg, 61%) as a yellow solid. Mp 296-298°C (heptane/EtOAc); $[\alpha]_D = -147.13$ ($c = 0.85$; $T = 21.9$ °C; $CHCl_3$); $R_f = 0.74$ (heptane/EtOAc = 1:3). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 8.86$, 8.65 (2s, 2H, H-6, H-11); 8.40 (ddd, $^5J_{1,4} = 0.8$ Hz, $^4J_{2,4} = 1.2$ Hz, $^3J_{3,4} = 7.7$ Hz, 1H, H-4); 8.14 ('t', 2H, H-7, H-10); 8.04 ('d', $^3J_{1,2} = 8.2$ Hz, 1H, H-1); 7.63 (ddd, $^4J_{2,4} = 1.2$ Hz, $^3J_{2,3} = 7.3$ Hz, $^3J_{1,2} = 8.2$ Hz, 1H, H-2); 7.58-7.52 (2 m, 2H, H-8, H-9); 7.35 (ddd, $^4J_{1,3} = 0.8$ Hz, $^3J_{2,3} = 7.3$ Hz, $^3J_{3,4} = 7.7$ Hz, 1H, H-3); 6.73 (d, $^3J_{1',2'} = 1.7$ Hz, 1H, H-1'); 5.79 (dd, $^3J_{1',2'} = 1.7$ Hz, $^3J_{2',3'} = 3.5$ Hz, 1H, H-2'); 5.52 (dd, $^3J_{2',3'} = 3.5$ Hz, $^3J_{3',4'} = 10.2$ Hz, 1H, H-3'); 5.37 ('t', $^3J_{3',4'} = 10.2$ Hz, $^3J_{4',5'} = 9.6$ Hz, 1H, H-4'); 3.98 (dq, $^3J_{5',6'} = 6.1$ Hz, $^3J_{4',5'} = 9.6$ Hz, 1H, H-5'); 2.14, 2.00, 1.80 (3 s, 9H, 3 $COCH_3$); 1.45 (d, $^3J_{5',6'} = 6.1$ Hz, 3H, H-6'). ^{13}C-NMR (125.5 MHz, $CDCl_3$): $\delta = 170.1$, 169.9, 169.6 (3 CO); 144.9, 144.2 (2 C_q); 142.4 (C-13a); 137.7, 137.3, 133.5, 131.8 (4 C_q); 131.3 (C-2); 128.4, 127.9 (C-7, C-10); 127.7, 125.0 (C-6, C-11); 126.4, 125.4 (C-8, C-9); 122.6 (C-4); 121.8 (C-3); 120.4 (C-4a); 115.1 (C-1); 81.4 (C-1'); 74.2 (C-5'); 70.8 (C-3'); 70.6 (C-2'); 70.5 (C-4'); 20.8, 20.7, 20.6 (3 CO*C*H_3); 17.8 (C-6'). MS (EI, 70 eV): m/z (%) = 541 (41) [M^+]; 269 (100) [Aglykon+H]; 168 (35); 153 (32) [M^+-Aglykon-2HOAc]; 111 (27). HRMS (EI): calcd. for $C_{30}H_{27}N_3O_7$ ([M^+]) 541.18431. Found: 541.18435. Anal.: calcd. for $C_{30}H_{27}N_3O_7$ (541.55): C, 66.53; H, 5.03; N, 7.76. Found: C, 66.45; H, 5.07; N, 7.30.



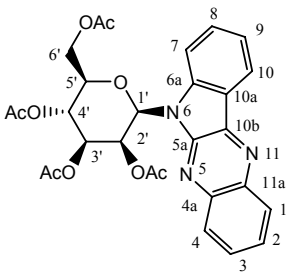
Rhamno, **β-3d**

2,3-Dichloro-6-(2',3',4'-tri-*O*-acetyl-β-L-rhamnopyranosyl)-indolo[2,3-*b*]quinoxaline (β-3d). Stirring of **β-2a** (300 mg, 0.71 mmol) and **1d** (139 mg, 0.79 mmol) for 1.5 h at 80 °C in HOAc and for 45 min at 80 °C in benzene afforded **β-3d** (40 mg; 10%) as a yellow to green solid. Mp. 235-237 °C (heptane/EtOAc); R_f = 0.77 (heptane/EtOAc = 1:3). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.37, 8.23 (2 s, 2H, H-1, H-4); 8.35 (ddd, $^5J_{7,10}$ = 0.7 Hz, $^4J_{8,10}$ = 1.3 Hz, $^3J_{9,10}$ = 7.7 Hz, 1H, H-10); 8.07 (d't', $^3J_{7,8}$ = 8.4, 1H, H-7); 7.65 (ddd, $^4J_{8,10}$ = 1.3 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{7,8}$ = 8.4, 1H, H-8); 7.37 (ddd, $^4J_{7,9}$ = 0.9 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{9,10}$ = 7.7 Hz, 1H, H-9); 6.66 (d, $^3J_{1',2'}$ = 1.5 Hz, 1H, H-1'); 5.71 (dd, $^3J_{1',2'}$ = 1.5 Hz, $^3J_{2',3'}$ = 3.5 Hz, 1H, H-2'); 5.47 (dd, $^3J_{2',3'}$ = 3.5 Hz, $^3J_{3',4'}$ = 10.2 Hz, 1H, H-3'); 5.36 ('t', $^3J_{3',4'}$ = 10.2 Hz, $^3J_{4',5'}$ = 9.6 Hz, 1H, H-4'); 3.95 (dq, $^3J_{4',5'}$ = 9.6 Hz, $^3J_{5',6'}$ = 6.2 Hz, 1H, H-5'); 2.14, 1.99, 1.75 (3 s, 9H, 3 $COCH_3$); 1.44 (d, $^3J_{5',6'}$ = 6.2 Hz, 3H, H-6'). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 170.0, 169.9, 169.6 (3 CO); 144.4 (C_q); 143.5 (C-6a); 140.9, 138.8, 138.5, 133.2 (4 C_q); 131.1 (C-8); 130.6 (C_q); 129.8, 128.4 (C-1, C-4); 122.5 (C-10); 122.0 (C-9); 119.9 (C-10a); 115.3 (C-7); 81.5 (C-1'); 74.3 (C-5'); 70.7 (C-3'); 70.4 (C-2'); 70.3 (C-4'); 20.8, 20.7, 20.7 (3 CO*C*H_3); 17.8 (C-6'). MS (EI, 70 eV): *m/z* (%) = 559 (16) [M^+]; 287 (47) [Aglykon+H]; 153 (100) [M^+-Aglykon-2HOAc]; 111 (79). HRMS (ESI): calcd. for $C_{26}H_{23}Cl_2N_3O_7$ ([M+H]$^+$) 560.09858. Found: 560.09860.



Rhamno, **β-3e**

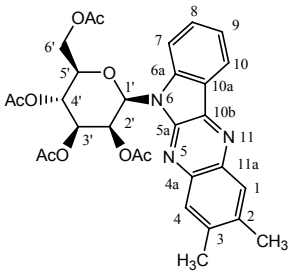
2/3-Nitro-6-(2',3',4'-tri-*O*-acetyl-β-L-rhamnopyra-nosyl)-indolo[2,3-*b*]quinoxaline (β-3e). Stirring of **β-2a** (300 mg, 0.71 mmol) and **1e** (120 mg, 0.79 mmol) for 1.5 h at 80 °C in HOAc and for 45 min at 80 °C in benzene afforded **β-3e** (33 mg, 9%) as a slightly yellow solid. Mp. 241-243 °C (heptane/EtOAc); R_f = 0.68 (heptane/EtOAc = 1:3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.15 (d, ^4J = 2.5 Hz, 1H), 8.17 (d, ^3J = 9.2 Hz, 1H), (H-1, H-4); 8.51 (dd, ^4J = 2.5 Hz, ^3J = 9.2 Hz, 1H, H-2 or H-3); 8.39 (ddd, $^5J_{7,10}$ = 0.6 Hz, $^4J_{8,10}$ = 1.3 Hz, $^3J_{9,10}$ = 7.9 Hz, 1H, H-10); 8.10 (br d, $^3J_{7,8}$ = 8.5 Hz, 1H, H-7); 7.69 (ddd, $^4J_{8,10}$ = 1.3 Hz, $^3J_{8,9}$ = 7.4 Hz, $^3J_{7,8}$ = 8.5 Hz, 1H, H-8); 7.42 (d't', $^4J_{7,9}$ = 0.8 Hz, $^3J_{8,9}$ = 7.4 Hz, $^3J_{9,10}$ = 7.9 Hz 1H, H-9); 6.71 (d, $^3J_{1',2'}$ = 1.5 Hz, 1H, H-1'); 5.73 (dd, $^3J_{1',2'}$ = 1.5 Hz, $^3J_{2',3'}$ = 3.5 Hz, 1H, H-2'); 5.48 (dd, $^3J_{2',3'}$ = 3.5 Hz, $^3J_{3',4'}$ = 10.0 Hz, 1H, H-3'); 5.37 ('t', $^3J_{4',5'}$ = 9.7 Hz, $^3J_{3',4'}$ = 10.0 Hz, 1H, H-4'); 3.97 (dq, $^3J_{4',5'}$ = 9.7 Hz, $^3J_{5',6'}$ = 6.2 Hz, 1H, H-5'); 2.14, 1.99, 1.76 (3 s, 9H, 3 $COCH_3$); 1.46 (d, $^3J_{5',6'}$ = 6.2 Hz, 3H, H-6'). ^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 170.0, 169.9, 169.5 (3 CO); 145.3, 145.2, 143.7, 143.1, 142.3, 138.1 (6 C_q); 131.7 (C-8); 128.9, 125.9 (C-1, C-4); 122.8 (C-10); 122.5 (C-9); 122.4 (CH, C-2 or C-3); 119.6 (C-10a); 115.5 (C-7); 81.6 (C-1'); 74.3 (C-5'); 70.7 (C-3'); 70.3 (C-2'); 70.2 (C-4'); 20.8, 20.6, 20.5 (3 $COCH_3$); 17.8 (C-6'). MS (EI, 70 eV): m/z (%) = 536 (7) [M^+]; 506 (23); 273 (22) [M^+-Aglykon]; 235 (16); 234 (79); 153 (68) [M^+-Aglykon-2HOAc]; 111 (51). HRMS (EI): calcd. for $C_{26}H_{24}N_4O_9$ ([M^+]) 536.154434. Found: 536.15378.



Manno, **β-3f**

6-(2',3',4',6'-Tetra-*O*-acetyl-β-D-mannopyranosyl)-indolo[2,3-*b*]quinoxaline (β-3f). Stirring of **β-2b** (300 mg, 0.63 mmol) and **1a** (75 mg, 0.69 mmol) for 2 h at 80 °C in HOAc and for 2 h at 80 °C in benzene afforded **β-3f** (230 mg, 69%) as a slightly yellow solid. Mp. 159-161 °C (heptane/EtOAc); $[\alpha]_D$ = –1.82 (c = 0.96; T = 21.8 °C; $CHCl_3$); R_f = 0.54 (heptane/EtOAc = 1:3). ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.41 (ddd, $^5J_{7,10}$ = 0.8 Hz, $^4J_{8,10}$ = 1.3 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-10); 8.28, 8.12 (2 m, 2H, H-1, H-4); 8.05 (d't', $^3J_{7,8}$ = 8.5 Hz, 1H, H-7); 7.80-

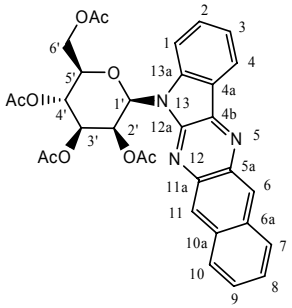
7.66 (m, 2H, H-2, H-3); 7.61 (ddd, $^4J_{8,10}$ = 1.3 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{7,8}$ = 8.5, 1H, H-8); 7.37 (ddd, $^4J_{7,9}$ = 0.9 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-9); 6.78 (d, $^3J_{1',2'}$ = 1.5 Hz, 1H, H-1'); 5.75 (dd, $^3J_{1',2'}$ = 1.5 Hz, $^3J_{2',3'}$ = 3.0 Hz, 1H, H-2'); 5.61-5.51 (m, 2H, H-3', H-4'); 4.41 (dd, $^3J_{5',6'a}$ = 5.2 Hz, $^2J_{6'a,6'b}$ = 12.4 Hz, 1H, H-6'a); 4.30 (dd, $^3J_{5',6'b}$ = 2.5 Hz, $^2J_{6'a,6'b}$ = 12.4 Hz, 1H, H-6'b); 4.15-4.05 (m, 1H, H-5'); 2.13, 2.12, 1.99, 1.75 (4s, 12H, 4 $COCH_3$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 170.5, 169.9, 169.8, 169.5 (4 CO); 144.2, 143.0, 140.1, 139.9, 139.9 (5 C_q); 130.4 (C-8); 129.4, 127.8 (C-1, C-4); 129.1, 126.7 (C-2, C-3); 122.2 (C-10); 121.7 (C-9); 120.4 (C-10a); 115.1 (C-7); 81.6 (C-1'); 75.7 (C-5'); 70.8 (C-3'); 70.2 (C-2'); 65.6 (C-4'); 62.4 (C-6'); 20.8, 20.7, 20.7, 20.5 (4 CO*C*H_3). MS (EI, 70 eV): *m/z* (%) = 549 (12) [M^+]; 219 (100) [Aglykon+H]; 169 (72) [M^+-Aglykon-HOAc-Ac_2O]; 109 (34). HRMS (EI): calcd. for $C_{28}H_{27}N_3O_9$ ([M^+]) 549.17483. Found: 549.17418. Anal.: calcd. for $C_{28}H_{27}N_3O_9$ (549.53): C, 61.20; H, 4.95; N, 7.65. Found: C, 61.25; H, 5.15; N, 7.10.



Manno, **β-3g**

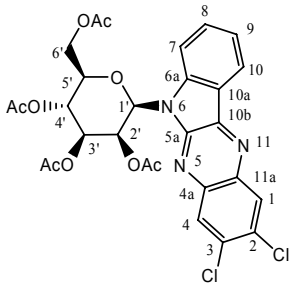
2,3-Dimethyl-6-(2',3',4',6'-tetra-*O*-acetyl-β-D-mannopyranosyl)indolo[2,3-*b*]quinoxaline (β-3g). Stirring of **β-2b** (300 mg, 0.63 mmol) and **1b** (94 mg, 0.69 mmol) for 1 h at 80 °C in HOAc and for 1.5 h at 80 °C in benzene and recrystallization from EtOAc and heptane afforded **β-3g** (260 mg, 72%) as yellow to orange needles. Mp. 240-242°C (heptane/EtOAc); $[\alpha]_D$ = +16.56 (c = 1.08; T = 22.0 °C; $CHCl_3$); R_f = 0.68 (heptane/EtOAc = 1:3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.36 (ddd, $^5J_{7,10}$ = 0.6 Hz, $^4J_{8,10}$ = 1.3 Hz, $^3J_{9,10}$ = 7.9 Hz, 1H, H-10); 8.02 (d't', $^3J_{7,8}$ = 8.4 Hz, 1H, H-7); 7.99, 7.84 (2 br s, 2H, H-1, H-4); 7.56 (ddd, $^4J_{8,10}$ = 1.4 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{7,8}$ = 8.4 Hz, 1H, H-8); 7.34 (ddd, $^4J_{7,9}$ = 0.9 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{9,10}$ = 7.9 Hz, 1H, H-9); 6.74 (d, $^3J_{1',2'}$ = 1.6 Hz, 1H, H-1'); 5.73 (dd, $^3J_{1',2'}$ = 1.6 Hz, $^3J_{2',3'}$ = 3.0 Hz, 1H, H-2'); 5.58-5.52 (m, 2H, H-3', H-4'); 4.39 (dd, $^3J_{5',6'a}$ = 5.3 Hz, $^2J_{6'a,6'b}$ = 12.4 Hz, 1H, H-6'a); 4.30 (2dd, $^3J_{5',6'b}$ = 2.4 Hz, $^2J_{6'a,6'b}$ = 12.4 Hz, 1H, H-6'b); 4.09 (m, 1H, H-5'); 2.50, 2.49 (2 br s, 6H, 2 CH_3); 2.12, 2.12, 1.98, 1.74 (4s, 12H, 4 $COCH_3$). ^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 170.6, 169.8,

169.8, 169.5 (4 CO); 143.9 (Cq); 142.6 (C-6a); 139.7, 138.9, 138.9, 138.7, 136.9 (5 C_q); 129.8 (C-8); 128.5, 127.0 (C-1, C-4); 121.9 (C-10); 121.5 (C-9); 120.6 (C-10a); 115.0 (C-7); 81.5 (C-1'); 75.7 (C-5'); 70.9 (C-3'); 70.3 (C-2'); 65.7 (C-4'); 62.5 (C-6'), 20.8, 20.7, 20.7, 20.6 (4 CO*C*H_3); 20.4, 20.2 (2 CH_3). MS (EI, 70 eV): *m/z* (%) = 577 (39) [M^+]; 247 (100) [Aglykon+H]; 169 (50) [M^+-Aglykon-HOAc-AC_2O]; 111 (13). HRMS (EI): calcd. for $C_{30}H_{31}N_3O_9$ ([M^+]) 577.206457. Found: 577.10548. Anal.: calcd. for $C_{30}H_{31}N_3O_9$ (577.58): C, 62.38; H, 5.41; N, 7.28. Found: C, 62.24; H, 5.50; N, 6.80.



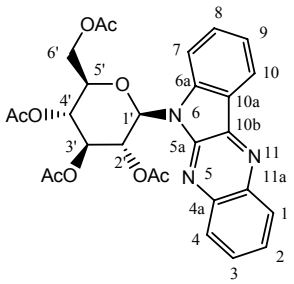
Manno, **β-3h**

13-(2',3',4',6'-Tetra-*O*-acetyl-β-D-mannopyranosyl)-5,12,13-triaza-indeno[1,2-*b*]anthracene (β-3h). Stirring of **β-2b** (300 mg, 0.63 mmol) and **1c** (110 mg, 0.69 mmol) for 1 h at 80 °C in HOAc and for 1 h at 80 °C in benzene and recrystallization from EtOAc and heptane afforded **β-3h** (245 mg; 65%) as a yellow to orange solid. Mp. 238-240 °C (heptane/EtOAc); R_f = 0.68 (heptane/EtOAc = 1:3). ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.86, 8.65 (2 br s, 2H, H-6, H-11); 8.40 (ddd, $^5J_{1,4}$ = 0.8 Hz, $^4J_{2,4}$ = 1.4 Hz, $^3J_{3,4}$ = 7.8 Hz, 1H, H-4); 8.17-8.10 (m, 2H, H-7, H-10); 8.01 (d't', $^3J_{1,2}$ = 8.4 Hz, 1H, H-1); 7.66-7.50 (m, 3H, H-2, H-8, H-9); 7.36 (ddd, $^4J_{1,3}$ = 1.0 Hz, $^3J_{2,3}$ = 7.3 Hz, $^3J_{3,4}$ = 7.8 Hz, 1H, H-3); 6.77 (d, $^3J_{1',2'}$ = 1.5 Hz, 1H, H-1'); 5.80 (dd, $^3J_{1',2'}$ = 1.5 Hz, $^3J_{2',3'}$ = 2.5 Hz, 1H, H-2'); 5.62-5.51 (m, 2H, H-3', H4'); 4.41 (dd, $^3J_{5',6'a}$ = 5.3 Hz, $^2J_{6'a,6'b}$ = 12.4 Hz, 1H, H-6'a); 4.30 (dd, $^3J_{5',6'b}$ = 2.5 Hz, $^2J_{6'a,6'b}$ = 12.4 Hz, 1H, H-6'b); 4.17-4.04 (m, 1H, H-5'); 2.14, 2.12, 2.00, 1.80 (4s, 12H, 4 $COCH_3$). ^{13}C-NMR (125.5 MHz, $CDCl_3$): δ = 170.6, 169.8, 169.8, 169.5 (4 CO); 144.8, 144.2 (2 Cq); 142.4 (C-13a); 137.7, 137.2, 133.5, 131.9 (4 C_q); 131.3 (C-2); 128.5, 127.9 (C-7, C-10); 127.7, 125.0 (C-6, C-11); 126.5, 125.5 (C-8, C-9); 122.6 (C-4); 121.9 (C-3); 120.4 (C-4a); 115.1 (C-1); 81.5 (C-1'); 75.7 (C-5'); 70.8 (C-3'); 70.2 (C-2'); 65.6 (C-4'); 62.4 (C-6'); 20.8, 20.7, 20.7, 20.6 (4s, 4xC(O)*C*H_3). HRMS (ESI): calcd. for $C_{32}H_{29}N_3O_9$ ([M+H]$^+$) 600.19766. Found: 600.19739.



Manno, **β-3i**

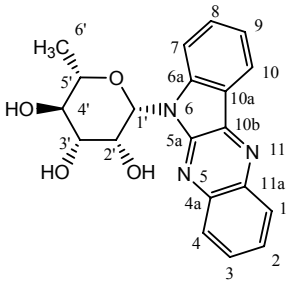
2,3-Dichloro-6-(2',3',4',6'-tetra-*O*-acetyl-β-D-mannopyranosyl)indolo[2,3-*b*]quinoxaline (β-3i). Stirring of **β-2b** (300 mg, 0.63 mmol) and **1d** (123 mg, 0.69 mmol) for 1 h at 80 °C in HOAc and for 1 h at 80 °C in benzene and recrystallization from EtOAc and heptane afforded **β-3i** (170 mg; 44%) as yellow to orange crystals. Mp. 251-253 °C (heptane/EtOAc); $[\alpha]_D$ = (c = 1.06; T = 22.9 °C; $CHCl_3$); R_f = 0.75 (heptane/EtOAc = 1:3). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.37, 8.22 (2 br s, 2H, H-1, H-4); 8.36 (ddd, $^5J_{7,10}$ = 0.6 Hz, $^4J_{8,10}$ = 1.3 Hz, $^3J_{9,10}$ = 7.9 Hz, 1H, H-10); 8.04 (d't', $^3J_{7,8}$ = 8.4 Hz, 1H, H-7); 7.64 (ddd, $^4J_{8,10}$ = 1.3 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{7,8}$ = 8.4 Hz, 1H, H-8); 7.38 (ddd, $^4J_{7,9}$ = 0.9 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{9,10}$ = 7.9 Hz, 1H, H-9); 6.70 (d, $^3J_{1',2'}$ = 1.5 Hz, 1H, H-1'); 5.73 (dd, $^3J_{1',2'}$ = 1.5 Hz, $^3J_{2',3'}$ = 3.0 Hz, 1H, H-2'); 5.60 - 5.49 (m, 2H, H-3', H-4'); 4.41 (dd, $^3J_{5',6'a}$ = 5.2 Hz, $^2J_{6'a,6'b}$ = 12.5 Hz, 1H, H-6'a); 4.30 (dd, $^3J_{5',6'b}$ = 2.2 Hz, $^2J_{6'a,6'b}$ = 12.5 Hz, 1H, H-6'b); 4.15-4.06 (m, 1H, H-5'); 2.13, 2.13, 1.99, 1.75 (4s, 12H, 4 $COCH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.5, 169.8, 169.7, 169.5 (4 CO); 144.4 (Cq); 143.4 (C-6a); 140.9, 138.8, 138.6, 133.3 (4 C_q); 131.1 (C-8); 130.8 (C_q); 129.8, 128.3 (C-1, C-4); 122.5 (C-10); 122.2 (C-9); 120.0 (C-10a); 115.2 (C-7); 81.6 (C-1'); 75.7 (C-5'); 70.7 (C-3'); 70.1 (C-2'); 65.6 (C-4'); 62.4 (C-6'); 20.8, 20.7, 20.6, 20.5 (4 COCH_3). MS (EI, 70 eV): m/z (%) = 618 (4) [M^+]; 287 (38) [Aglykon+H]; 169 (100) [M^+-Aglykon-HOAc-Ac_2O]; 109 (38). HRMS (EI): calcd. for $C_{28}H_{25}Cl_2N_3O_9$ ([M^+]) 617.096917. Found: 617.09624. Anal.: calcd. for $C_{28}H_{25}Cl_2N_3O_9$ (618.42): C, 54.38; H, 4.07; N, 6.79. Found: C, 54.30; H, 4.09; N, 6.55.



Gluco, **β-3j**

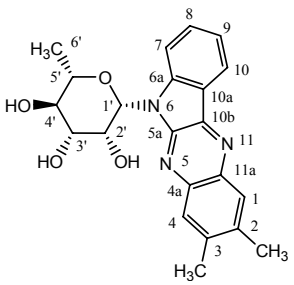
6-(2',3',4',6'-Tetra-*O*-acetyl-β-D-glucopyranosyl)indolo[2,3-*b*]quinoxaline (β-3j). Stirring of **β-2c** (200 mg, 0.42 mmol) **1a** (50 mg, 0.46 mmol) for 1 h at 80 °C in HOAc and for 1 h at 80 °C in benzene afforded **β-3j** (171 mg, 75%) as a slightly yellow solid. Mp 226-228 °C (heptane/EtOAc); $[\alpha]_D$ = +32.93 (c = 1.05; T = 23.5 °C; $CHCl_3$); R_f = 0.68 (heptane/EtOAc = 1:3). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.44 (ddd, $^5J_{7,10}$ = 0.7 Hz, $^4J_{8,10}$ = 1.4 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-10); 8.29, 8.14 (2 m, 2H, H-1, H-4); 7.81-7.67 (m, 4H, H-2, H-3, H-7, H-8); 7.44 (ddd, $^4J_{7,9}$ = 1.0 Hz, $^3J_{8,9}$ = 7.5 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-9); 6.55 (d, $^3J_{1',2'}$ = 9.5 Hz, 1H, H-1'); 6.00 (br 't', 1H, H-2'); 5.59 ('t', $^3J_{2',3'} = {}^3J_{3',4'}$ = 9.5 Hz, 1H, H-3'); 5.44 ('t', $^3J_{3',4'}$ = 9.5 Hz, $^3J_{4',5'}$ = 10.0 Hz, 1H, H-4'); 4.33 (dd, $^3J_{5',6'a}$ = 4.5 Hz, $^2J_{6'a,6'b}$ = 12.5 Hz, 1H, H-6'a); 4.24 (dd, $^3J_{5',6'b}$ = 2.5 Hz, $^2J_{6'a,6'b}$ = 12.5 Hz, 1H, H-6'b); 4.14 (ddd, $^3J_{5',6'b}$ = 2.5 Hz, $^3J_{5',6'a}$ = 4.5 Hz, $^3J_{4',5'}$ = 10.0 Hz, 1H, H-5'); 2.12, 2.09, 2.02, 1.44 (4 s, 12H, 4 $COCH_3$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 170.5, 170.1, 169.6, 168.7 (4 CO); 145.3 (C_q); 142.0 (C-6a); 140.0, 140.0, 139.9 (3 C_q); 131.3 (C-8); 129.2, 126.9 (C-2, C-3); 129.4, 127.9 (C-1, C-4); 122.7 (C-10); 122.4 (C-9); 120.5 (C-10a); 112.7 (C-7); 81.0 (C-1'); 74.5 (C-5'); 73.5 (C-3'); 68.7 (C-2'); 68.1 (C-4'); 61.9 (C-6'), 20.7, 20.6, 20.6, 19.9 (4 CO*C*H_3). HRMS (ESI): calcd. for $C_{28}H_{27}N_3O_9$ ($[M+H]^+$) 550.18201. Found: 550.18198. Anal.: calcd. for $C_{28}H_{27}N_3O_9$ (549.53): C, 61.20; H, 4.95; N, 7.65. Found: C, 60.84; H, 5.01; N, 7.42.

General procedure for the deacetylation. Product **3** was suspended in dry MeOH under argon atmosphere. To the suspension was added a MeOH solution of NaOMe (0.1 M, prepared from 23 mg of sodium and 10 mL of dry MeOH). The solution was stirred at 20 °C until the reaction is complete (tlc-control, $CHCl_3$/EtOH = 5:1). The precipitate was filtered off washed several times with *n*-pentane and dried in vacuo.



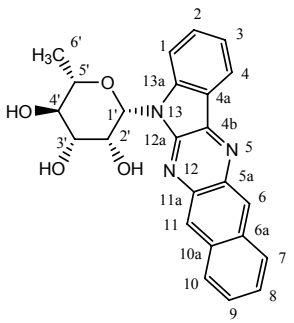
Rhamno, **β-4a**

6-(β-L-Rhamnopyranosyl)indolo[2,3-*b*]quinoxaline (β-4a): Starting with **β-3a** (200 mg, 0.41 mmol), 40 mL of MeOH and 0.5 mL of a 0.1 M MeOH solution of NaOMe, **β-4a** was isolated (146 mg, 98%) after stirring for 7 h as a slightly yellow solid. Mp. 339-341 °C (heptane/EtOAc); $[\alpha]_D$ = +9.63 (c = 0.53; T = 21.5 °C; DMSO); R_f = 0.40 ($CHCl_3$/EtOH = 5:1). ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 8.32 (ddd, $^5J_{7,10}$ = 0.6 Hz, $^4J_{8,10}$ = 1.3 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-10); 8.29, 8.13 (2 ddd, $^5J_{1,4}$ = 0.6 Hz, $^4J_{1,3}$ = $^4J_{2,4}$ = 1.7 Hz, $^3J_{1,2}$ = $^3J_{3,4}$ = 8.1 Hz, 2H, H-1, H-4); 8.19 (d't', $^3J_{7,8}$ = 8.5 Hz, 1H, H-7); 7.84, 7.76 (2 ddd, $^4J_{1,3}$ = $^4J_{2,4}$ = 1.7 Hz, $^2J_{2,3}$ = 6.8 Hz, $^3J_{1,2}$ = $^3J_{3,4}$ = 8.1 Hz, 2H, H-2, H-3); 7.67 (ddd, $^4J_{8,10}$ = 1.3 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{7,8}$ = 8.5 Hz, 1H, H-8); 7.37 (d't', $^4J_{7,9}$ = 0.8 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{9,10}$ = 7.8 Hz, 1H, H-9); 6.38 (d, $^3J_{1',2'}$ = 1.0 Hz, 1H, H-1'); 5.25 (d, $^3J_{2',OH}$ = 4.9 Hz, 1H, $OH_{(2')}$); 5.06 (d, $^3J_{4',OH}$ = 5.1 Hz, 1H, $OH_{(4')}$); 4.93 (d, $^3J_{3',OH}$ = 5.8 Hz, 1H, $OH_{(3')}$) 4.10-4.06 (m, 1H, H-2'); 3.72-3.66 (m, 1H, H-3'); 3.63-3.45 (m, 2H, H-4', H-5'); 1.34 (d, $^3J_{5',6'}$ = 5.9 Hz, 3H, H-6'). ^{13}C-NMR (75.5 MHz, DMSO-d_6): δ = 144.7, 144.1, 139.9, 139.6, 139.0 (5 C_q); 130.8 (C-8); 129.3, 127.6 (C-1, C-4); 129.2, 126.6 (C-2, C-3); 121.3 (C-10); 121.2 (C-9); 119.0 (C-10a); 117.0 (C-7); 83.6 (C-1'); 75.7 (C-5'); 73.4 (C-3'); 72.1 (C-2'); 71.6 (C-4'); 18.4 (C-6'). MS (EI, 70 eV): m/z (%) = 365 (5) [M^+]; 248 (23); 219 (100) [Aglykon+H]; 153 (2) [M^+-Aglykon-2HOAc]. HRMS (EI): calcd. for $C_{20}H_{19}N_3O_4$ ([M^+]) 365.136463. Found: 365.13701.



Rhamno, **β-4b**

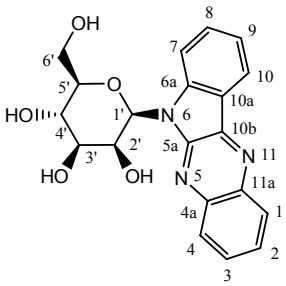
2,3-Dimethyl-6-(β-L-rhamnopyranosyl)indolo[2,3-*b*]quinoxaline (β-4b). Starting with **β-3b** (160 mg, 0.31 mmol), 20 mL of MeOH and 0.5 mL of a 0.1 M MeOH solution of NaOMe, **β-4b** was isolated (103 mg, 85%) after stirring for 24 h as a slightly yellow solid. Mp. 347-350 °C (heptane/EtOAc); $[\alpha]_D$ = +3.33 (c = 0.50; T = 21.6 °C; DMSO); R_f = 0.45 ($CHCl_3$/EtOH = 5:1). ^{1}H-NMR (250 MHz, DMSO-d_6): δ = 8.26 (ddd, $^5J_{7,10}$ = 0.6 Hz, $^4J_{8,10}$ = 1.3 Hz, $^3J_{9,10}$ = 7.7 Hz, 1H, H-10); 8.15 (d't', $^3J_{7,8}$ = 8.5 Hz, 1H, H-7); 8.03, 7.91 (2 br s, 2H, H-1, H-4); 7.63 (ddd, $^4J_{8,10}$ = 1.3 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{7,8}$ = 8.5 Hz, 1H, H-8); 7.33 (ddd, $^4J_{7,9}$ = 0.9 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{9,10}$ = 7.7 Hz, 1H, H-9); 6.33 (d, $^3J_{1',2'}$ = 1.0 Hz, 1H, H-1'); 5.31 (d, $^3J_{2',OH}$ = 4.6 Hz, 1H, $OH_{(2')}$); 5.07 (d, $^3J_{4',OH}$ = 5.0 Hz, 1H, $OH_{(4')}$); 4.94 (d, $^3J_{3',OH}$ = 5.7 Hz, 1H, $OH_{(3')}$); 4.06 (m, 1H, H-2'); 3.71-3.63 (m, 1H, H-3'); 3.61-3.46 (m, 2H, H-4', H-5'); 2.49 (2 s, 6H, 2 CH_3); 1.34 (d, $^3J_{5',6'}$ = 5.5 Hz, 3H, H-6'). ^{13}C-NMR (75.5 MHz, DMSO-d_6): δ = 144.1, 143.8, 139.5, 138.8, 138.3, 137.9, 136.4 (7 C_q); 130.2 (C-8); 128.2, 126.8 (C-1, C-4); 121.0 (C-10); 120.9 (C-9); 119.2 (C-10a); 116.7 (C-7); 83.6 (C-1'); 75.7 (C-5'); 73.4 (C-3'); 72.1 (C-2'); 71.6 (C-4'); 20.1, 19.8 (2 CH_3); 18.3 (C-6'). MS (EI, 70 eV): m/z (%) = 393 (7) [M^+]; 276 (33); 247 (100) [Aglykon+H]; 246 (36); 232 (58). HRMS (EI): calcd. for $C_{22}H_{23}N_3O_4$ ([M^+]) 393.168130. Found: 393.16831.



Rhamno, **β-4c**

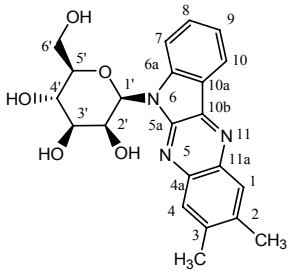
13-(β-L-Rhamnopyranosyl)-5,12,13-triaza-indeno[1,2-*b*]anthracene (β-4c). Starting with **β-3c** (100 mg, 0.19 mmol) in 15 mL of MeOH and 0.3 mL of a 0.1 M MeOH solution of NaOMe, **β-4c** was isolated (61 mg; 79%) after stirring for 24 h as a yellow to orange solid. Mp. 359-360 °C (heptane/EtOAc); $[\alpha]_D$ = –20.85 (c = 047; T = 22.3 °C; DMSO); R_f = 0.52 ($CHCl_3$/EtOH = 5:1). ^{1}H-NMR (250 MHz, DMSO-d_6): δ = 8.93, 8.72 (2s, 2H, H-6, H-11); 8.32 (br d, $^3J_{3,4}$ = 7.6 Hz, 1H, H-4); 8.27-8.19 (m, 2H, H-7, H-10); 8.14 (d, $^3J_{1,2}$ = 8.4 Hz,

1H, H-1); 7.71 - 7.56 (m, 3H, H-2, H-8, H-9); 7.36 ('t', $^3J_{2,3} = {}^3J_{3,4} = 7.6$ Hz, 1H, H-3); 6.35 (br s, 1H, H-1'); 5.32 (d, $^3J_{2',OH} = 5.0$ Hz, 1H, $OH_{(2')}$); 5.09 (d, $^3J_{4',OH} = 5.2$ Hz, 1H, $OH_{(4')}$); 4.96 (d, $^3J_{3',OH} = 5.9$ Hz, 1H, $OH_{(3')}$); 4.14 (br 't', 1H, H-2'); 3.74-3.66 (m, 1H, H-3'); 3.63-3.47 (m, 2H, H-4', H-5'); 1.36 (d, $^3J_{5',6'} = 5.7$ Hz, 3H, H-6'). ^{13}C-NMR (75.5 MHz, DMSO-d_6): $\delta = 145.9$, 144.8, 142.6, 137.0, 136.9, 133.1, 131.7 (7 C_q); 131.3 (C-2); 128.4, 127.8 (C-7, C-10); 127.4, 124.6 (C-6, C-11); 126.6, 125.6 (C-8, C-9); 121.8 (C-4); 121.4 (C-3); 119.2 (C-4a); 116.8 (C-1); 83.7 (C-1'); 75.7, 73.4, 71.6 (3s, C-3', C-4', C-5'); 71.9 (C-2'); 18.3 (C-6'). MS (EI, 70 eV): m/z (%) = 415 (7) [M^+]; 298 (10); 270 (48); 269 (100) [Aglykon+H]; 140 (10). HRMS (EI): calcd. for $C_{24}H_{21}N_3O_4$ ([M^+]) 415.151893. Found: 415.15266.



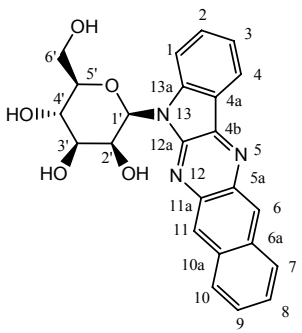
Manno, **β-4f**

6-(β-D-Mannopyranosyl)indolo[2,3-*b*]quinoxaline (β-4f). Starting with **β-3f** (50 mg, 0.10 mmol), 10 mL of MeOH and 0.5 mL of a 0.1 M solution of NaOMe, **β-4f** was isolated (25 mg, 72%) after stirring for 24 h as a slightly yellow solid. Mp. 325-327 °C (heptane/EtOAc); $[\alpha]_D = -20.52$ ($c = 0.47$; $T = 22.3$ °C; DMSO); $R_f = 0.29$ ($CHCl_3$/EtOH = 5:1). ^{1}H-NMR (250 MHz, DMSO-d_6): $\delta = 8.34$-8.23 (m, 3H), 8.14 (m, 1H) (H-1, H-4, H-7, H-10); 7.84, 7.76 (2 ddd, $^5J_{1,4} = 0.6$ Hz, $^4J_{1,3} = {}^4J_{2,4} = 1.7$ Hz; $^3J_{2,3} = 6.8$ Hz, $^3J_{1,2} = J_{3,4} = 8.1$ Hz, 2H, H-2, H-3); 7.65 (ddd, $^4J_{8,10} = 1.4$ Hz, $^3J_{8,9} = 7.5$ Hz, $^3J_{7,8} = 8.3$ Hz, 1H, H-8); 7.37 (d't', $^4J_{7,9} = 0.9$ Hz, $^3J_{8,9} = 7.5$ Hz, $^3J_{9,10} = 7.8$ Hz, 1H, H-9); 6.38 (d, $^3J_{1',2'} = 0.8$ Hz, 1H, H-1'); 5.26 (br s, 1H, $OH_{(2')}$); 5.02 (br s, 1H, $OH_{(4')}$); 4.97 (br s, 1H, $OH_{(3')}$); 4.63 (br t, 1H, $OH_{(6')}$); 4.07 (br s, 1H, H-2'); 3.88-3.47 (m, 5H, H-3', H-4'; H-5', H-6'a, H-6'b). ^{13}C-NMR (75.5 MHz, DMSO-d_6): $\delta = 144.8$, 144.1, 139.9, 139.6, 139.0 (5 C_q); 130.8 (C-8); 129.3, 127.6 (C-1, C-4); 129.2, 126.6 (C-2, C-3); 121.2, 121.2 (C-9, C-10); 119.0 (C-10a); 117.4 (C-7); 83.6 (C-1'); 81.1 (C-5'); 73.7 (C-3'); 71.9 (C-2'); 66.6 (C-4'); 61.3 (C-6'). HRMS (ESI): calcd. for $C_{20}H_{19}N_3O_5$ ([M+H]$^+$) 382.13975. Found: 382.12953.



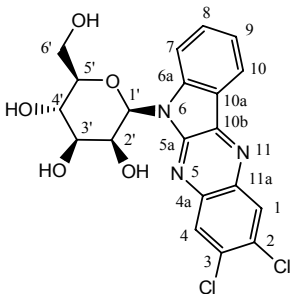
Manno, **β-4g**

2,3-Dimethyl-6-(β-D-mannopyranosyl)indolo[2,3-*b*]quinoxaline (β-4g). Starting with **β-3g** (260 mg, 0.45 mmol), 25 mL of MeOH and 0.5 mL of a 0.8 M MeOH solution of NaOMe, **β-4g** was isolated (173 mg, 94%) after stirring for 24 h as a slightly yellow solid. Mp. 352-354 °C (heptane/EtOAc); $[\alpha]_D$ = –10.09 (c = 0.49; T = 21.7 °C; DMSO); R_f = 0.24 ($CHCl_3$/EtOH = 5:1). ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 8.27 (br d, $^3J_{9,10}$ = 7.6 Hz, 1H, H-10); 8.20 (br d, $^3J_{7,8}$ = 8.5 Hz, 1H, H-7); 8.03, 7.91 (2 br s, 2H, H-1, H-4); 7.61 (ddd, $^4J_{8,10}$ = 1.0 Hz, $^3J_{8,9}$ = 7.4 Hz, $^3J_{7,8}$ = 8.5 Hz, 1H, H-8); 7.34 (d't', $^4J_{7,9}$ = 0.9 Hz, $^3J_{8,9}$ = 7.4 Hz, $^3J_{9,10}$ = 7.6 Hz, 1H, H-9); 6.33 (d, $^3J_{1',2'}$ = 1.0 Hz, 1H, H-1'); 5.30 (br s, 1H, $OH_{(2')}$); 5.00 (br s, 1H, $OH_{(4')}$); 4.95 (br s, 1H, $OH_{(3')}$); 4.61 (br t, 1H, $OH_{(6')}$); 4.06 (br s, 1H, H-2'); 3.87-3.47 (m, 5H, H-3', H-4', H-5', H-6'a, H-6'b); 2.50 (2 s, 6H, 2 CH_3). ^{13}C-NMR (75.5 MHz, DMSO-d_6): δ = 144.2, 143.8, 139.5, 138.8, 138.3, 137.9, 136.4 (7 C_q); 130.2 (C-8); 128.2, 126.7 (C-1, C-4); 121.0; 120.9 (C-9; C-10); 119.2 (C-10a); 117.1 (C-7); 83.6 (C-1'); 81.2 (C-5'); 73.7 (C-3'); 71.9 (C-2'); 66.6 (C-4'); 61.5 (C-6'); 20.1, 19.8 (2 CH_3). MS (EI, 70 eV): m/z (%) = 409 (3) [M$^+$]; 276 (13); 248 (21); 247 (100) [Aglykon+H]; 246 (21); 232 (32). HRMS (EI): calcd. for $C_{22}H_{23}N_3O_5$ ([M$^+$]) 409.163493. Found: 409.16322.



Manno, **β-4h**

13-(β-D-Mannopyranosyl)-5,12,13-triaza-indeno[1,2-*b*]anthracene (β-4h). Starting with **β-3h** (78 mg, 0.13 mmol), 10 mL of MeOH and 0.5 mL of a 0.5 M MeOH solution of NaOMe, **β-4h** was isolated (54 mg; 97%) after stirring for 24 h as a yellow to orange solid. Mp. 320-322 °C (heptane/EtOAc); R_f = 0.25 ($CHCl_3$/EtOH = 5:1). ^{1}H-NMR (250 MHz, DMSO-d_6): δ = 8.95, 8.74 (2 s, 2H, H-6, H-11); 8.35-8.10 (m, 4H, H-1, H-4, H-7, H-10); 7.71-7.57 (m, 3H, H-2, H-8, H-9); 7.37 ('t', $^3J_{2,3} = {}^3J_{3,4}$ = 7.5 Hz, 1H, H-3); 6.35 (br s, 1H, H-1'); 5.31 (d, $^3J_{2',OH}$ = 4.8 Hz, 1H, $OH_{(2')}$); 5.04 (d, $^3J_{4',OH}$ = 4.5 Hz, 1H, $OH_{(4')}$); 4.97 (d, $^3J_{3',OH}$ = 5.0 Hz, 1H, $OH_{(3')}$); 4.65 (t, $^3J_{6',OH}$ = 5.5 Hz, 1H, $OH_{(6')}$); 4.12 (br s, 1H, H-2'); 3.90-3.47 (m, 5H, H-3', H-4', H-5', H-6'a, H-6'b). ^{13}C-NMR (75.5 MHz, DMSO-d_6): δ = 145.9, 144.8, 142.6, 137.0, 136.9, 133.0, 131.7 (7 C_q); 131.2 (C-2); 128.4, 127.8 (C-7, C-10); 127.4, 124.5 (C-6, C-11); 126.6, 125.6 (C-8, C-9); 121.6 (C-4); 121.4 (C-3); 119.1 (C-4a); 117.2 (C-1); 83.7 (C-1'); 81.1 (C-5'); 73.6 (C-3'); 71.8 (C-2'); 66.5 (C-4'); 61.4 (C-6'). HRMS (ESI): calcd. for $C_{24}H_{21}N_3O_4$ ([M+H]$^+$) 432.15540. Found: 432.15519.



Manno, **β-4i**

2,3-Dichloro-6-(β-D-mannopyranosyl)indolo[2,3-*b*]quinoxaline (β-4i). Starting with **β-3i** (100 mg, 0.18 mmol), 15 mL of MeOH and 0.5 mL of a 0.5 M MeOH solution of NaOMe, **β-4i** was isolated (60 mg, 75%) after stirring for 24 h as a slightly yellow solid. Mp. 323-324 °C (heptane/EtOAc); $[\alpha]_D$ = –3.04 (c = 0.63; T = 22.6 °C; DMSO); R_f = 0.41 ($CHCl_3$/EtOH =5:1). ^{1}H-NMR (250 MHz, DMSO-d_6): δ = 8.52, 8.38 (2 s, 2H, H-1, H-4); 8.30-8.23 (m, 2H, H-7, H-10); 7.68 (ddd, $^4J_{8,10}$ = 1.1 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{7,8}$ = 8.4 Hz, 1H, H-8); 7.38 (ddd, $^4J_{7,9}$ = 0.9 Hz, $^3J_{8,9}$ = 7.3 Hz, $^3J_{9,10}$ = 7.7 Hz, 1H, H-9); 6.34 (d, $^3J_{1',2'}$ = 0.8 Hz, 1H, H-1'); 5.18 (br s, 1H, $OH_{(2')}$); 5.03 (br s, 1H, $OH_{(4')}$); 5.02 (br s, 1H, $OH_{(3')}$); 4.66 (t, 1H, $OH_{(6')}$); 4.05 (br s, 1H, H-2'); 3.90-3.45 (m, 5H, H-3', H-4', H-5', H-6'a, H-6'b). ^{13}C-NMR (75.5 MHz, DMSO-d_6): δ = 145.2, 144.4

141.1, 138.7, 137.8, 131.5 (6 C_q); 131.5 (C-8); 129.8, 128.4 (C-1, C-4); 128.8 (C_q); 121.6 (C-9); 121.6 (C-10); 118.6 (C-10a); 117.7 (C-7); 83.7 (C-1'); 81.2 (C-5'); 73.6 (C-3'); 71.9 (C-2'); 66.4 (C-4'); 61.4 (C-6'). HRMS (ESI): calcd. for $C_{20}H_{17}Cl_2N_3O_5$ ($[M+H]^+$) 450.06180. Found: 450.06229.

Biological studies:

The screeening toward antiproliferative properties was performed in accordance to the NIH protocols. The cell viability was investigated using the Neutral Red assay with subsequent measurement of the absorption at 630nm. Stock solutions of the test compounds were prepared using DMSO. All experiments were performed in 2 independend experiments with 4 parallel dilutions over aperiod of 3 days. Etoposide was used a positive control and DMSO as the negative control experiment.