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Efficient synthesis of jusbetonin, an indolo[3,2-*b*]quinoline glycoside, and its derivatives

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ABSTRACT

Jusbetonin, an indolo[3,2-*b*]quinoline alkaloid glycoside originally isolated from *Justicia betonica*, and its derivatives were synthesized. The key steps in the synthetic strategy were the construction of indolo[3,2-*b*]quinoline skeleton and efficient coupling with the saccharides, in which the α-D-glycopyranosyl bromides were shown to be effective donors. Primary screening showed that all synthesized compounds possessed moderate proliferation inhibitory activity.

1. Introduction

Cryptolepis sanguinolenta, a plant with a rich content of indoloquinoline alkaloids, is traditionally used in Central and West Africa for the treatment of rheumatism, urinary and respiratory infections. It is also used in folk medicine as an antimalarial agent.[1] Cryptolepine **1** (Fig. 1), the major indoloquinoline alkaloid isolated from *C. sanguinolenta*, is well known for its anti-tumour, anti-bacterial, anti-thrombotic and anti-malarial activities.[2–4] It was also found that Cryptolepine can interact with DNA and Topoisomerase II.[5–7] In addition, some indoloquinoline alkaloid glycoside analogues have shown high anti-tumour activities.[8]

Jusbetonin **2a**, the first natural indolo[3,2-*b*]quinoline alkaloid glycoside isolated from *Justicia betonica*,[9] has a unique structure containing β-D-glucose. However, to our best knowledge, jusbetonin has not been synthesized. Because of the small quantity isolated from plants, its bioactivities have not been studied systematically.

Most indolo[3,2-*b*]quinoline alkaloids are difficult to be dissolved in organic solvent or water, which has led to considerable difficulty in developing formulations for clinical use. However, solubility can be improved when they are glycosylated.[10] On the other hand, the sugar moiety of indoloquinoline derivatives can improve their interaction with DNA. For example, some of the DNA interacting agents, such as anthracycline antibiotics and bleomycins, are well known to possess sugar moieties that stabilize the molecular interactions with DNA. The sugar structure in these compounds plays a critical role in their anti-cancer activity.[11] To improve the bioavailability of indoloquinoline alkaloids and search for potential anti-tumour compounds, we became interested in studying the synthesis and bioactivity of indoloquinolines derivatives.[12] We report here the efficient synthesis of jusbetonin and its glycoside analogues with different sugar moieties.

2. Results and discussion

Our retrosynthetic analysis of jusbetonin suggested that **9** would be a promising intermediate for the total synthesis (Scheme 1). Moreover, the efficient coupling of compound **9** with the saccharide would be the key step in the synthesis.

Several synthetic methods have been developed to construct the indoloquinoline skeleton.[13–15] A facile strategy for the synthesis of cryptolepine analogues is polyphosphorous-catalyzed cyclic condensation.[16] We have started our synthesis from commercially available 2-aminobenzoic acid **3** and substituted anilines. Acyla-

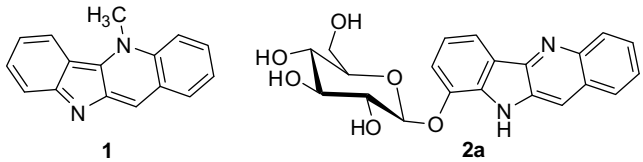

Figure 1. Structures of cryptolepine **1** and jusbetonin **2a**.

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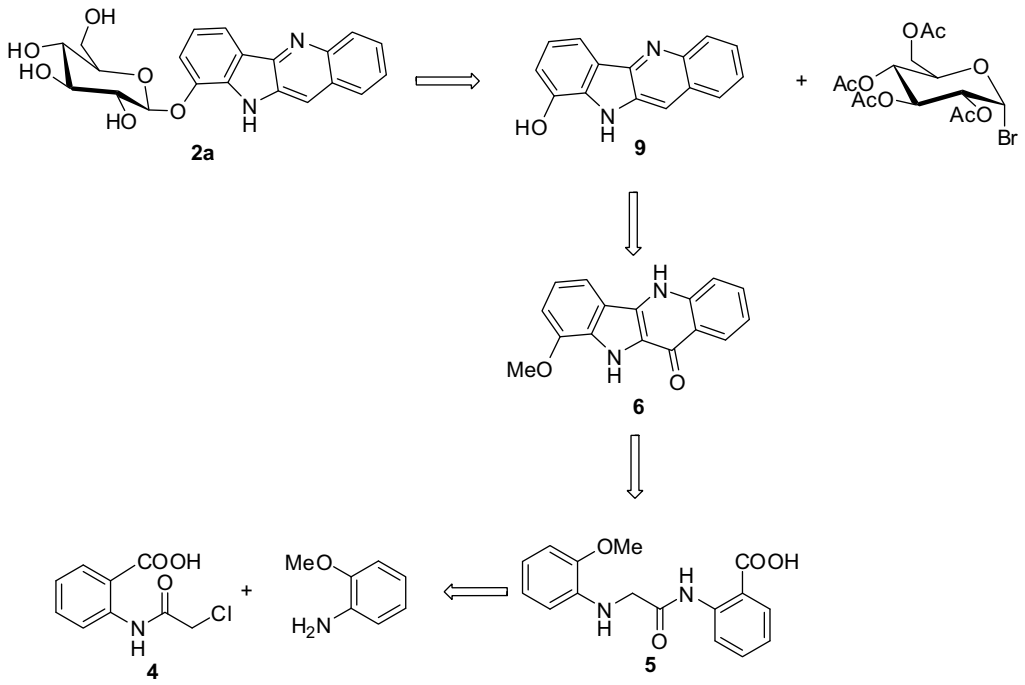


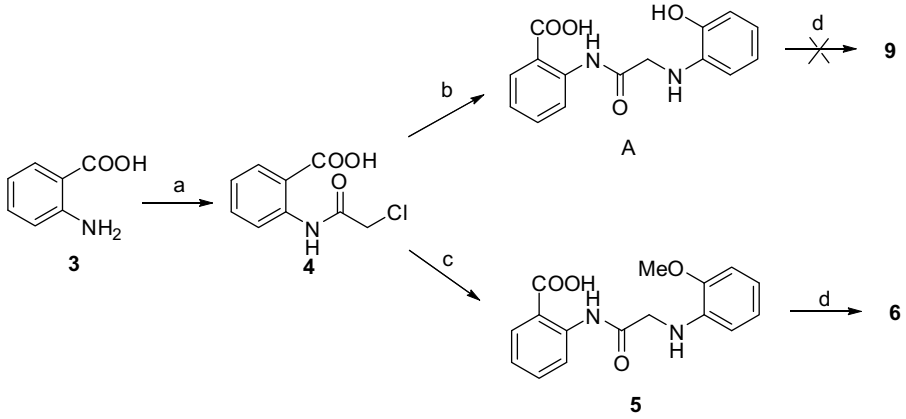
Scheme 1. Retrosynthetic analysis of jusbetonin.

tion of **3** with chloroacetyl chloride gave intermediate **4** in 86% yield (Scheme 2). Condensation of **4** with 2-hydroxyaniline at 80 °C in DMF overnight afforded compound **A** in 49% yield. Subsequent cyclization of this anthranilic acid derivative catalyzed by PPA failed to produce the 9-hydroxy analogue of compound **6**. Possibly, the 9-hydroxy analogue of compound **6** was phosphorylated in the presence of PPA. Therefore, a methyl ether was chosen as the protecting group of the hydroxyl group and condensation of **4** with 2-methoxybenzenamine afforded the desired compound **5** in 79% yield. It has been reported that cyclization of anthranilic acid derivative can be catalyzed by polyphosphorous acid (PPA) at a fixed temperature in the range of 100–150 °C. However, this method was not satisfactory to prepare cyclized product **6** due to the low yield (9%) at 130 °C. Keeping in mind the mechanism of the cyclization, the temperature was gradually elevated from 100 to 130 °C and the key intermediate **6** was obtained in 49% yield (Scheme 2).

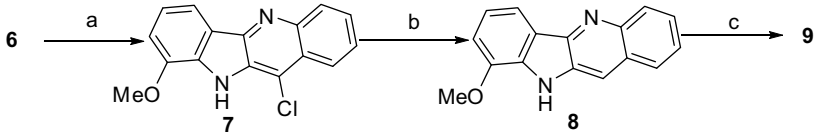
The desired 9-hydroxy-10*H*-indolo[3,2-*b*]quinoline **9** was synthesized according to the route depicted in Scheme 3. Compound **6** was chlorinated with phosphorous oxychloride ($POCl_3$), and the resulting chloride was dechlorinated with hydrogen over a palladium catalyst in the presence of triethylamine to obtain product **8**. The compound **9** was prepared from **8** through a demethylation reaction in the presence of boron tribromide.

To synthesize the target product jusbetonin, efficient and stereospecific coupling of compound **9** with the glucosyl donor is required. 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide is commonly used as a β-selective donor.[17,18] To find appropriate reaction conditions, including the proper promoter and solvent, we first explored the glycosylation of **9** with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (Table 1). The phase transfer catalysis method was used to ensure the efficient coupling of **9** with the glycosylating agent. Under the optimal conditions, compound **10a** was synthesized in 68% yield (Scheme 4). After deacetylation with sodium methoxide, jusbetonin **2a** was obtained in 93% yield.

Using this method, the jusbetonin analogues, **2b–c** and **13a–c,** were also prepared (Fig. 2). Compound **9** reacted with different su-



Scheme 2. Reagents and conditions: (a) $ClCH_2COCl$, DMF, ice bath, overnight, 86%; (b) 2-hydroxyaniline, DMF, 80 °C, overnight, 49%; (c) 2-methoxybenzenamine, DMF, 80 °C, overnight, 79%; (d) PPA, 100–130 °C, 49%.

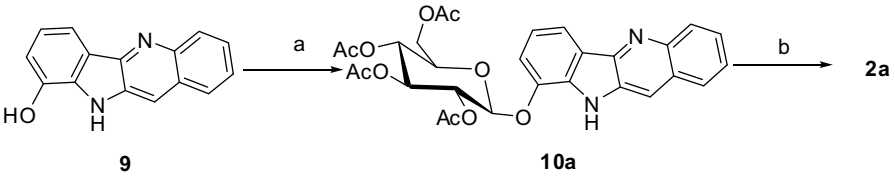


Scheme 3. Reagents and conditions: (a) $POCl_3$, reflux, 4 h, 83%; (b) H_2, Pd–C, Et_3N, CH_3OH, 92%; (c) BBr_3, CH_2Cl_2, 92%.

Table 1
Glycosylation of glucosyl donor glucopyranosyl bromide with **9**

Entry	Donor	Promotor	Solvent	Product	Yield (%)
1	Glucopyranosyl bromide (1 equiv)	Ag_2O (3 equiv)	THF	—	—
2	Glucopyranosyl bromide (1 equiv)	LiOH (1 equiv)	DMF	10a	<10
3	Glucopyranosyl bromide (5 equiv)	LiOH (1 equiv)	DMF	10a	15.8
4	Glucopyranosyl bromide (10 equiv)	LiOH (1 equiv)	DMF	10a	22.6
5[a]	Glucopyranosyl bromide (1.5 equiv)	K_2CO_3 (3 equiv)/TBAB	$H_2O/CHCl_3$	10a	68.3

[a] Phase transfer catalysis method.



Scheme 4. Reagents and conditions: (a) 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide, K_2CO_3, H_2O, $CHCl_3$, TBAB, 40 °C, 6 h, 68%; (b) CH_3ONa, CH_3OH, 0 °C, 1 h, 93%.

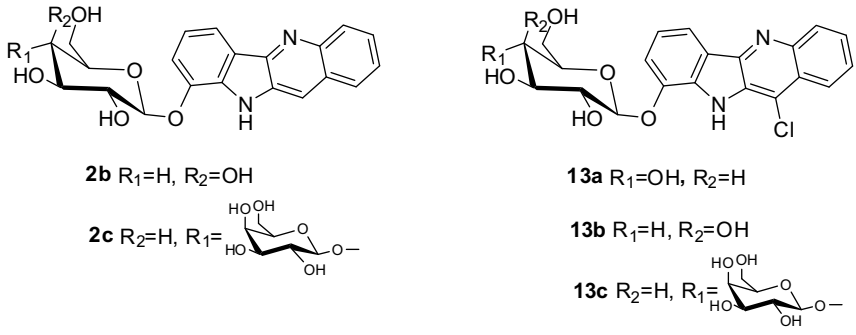
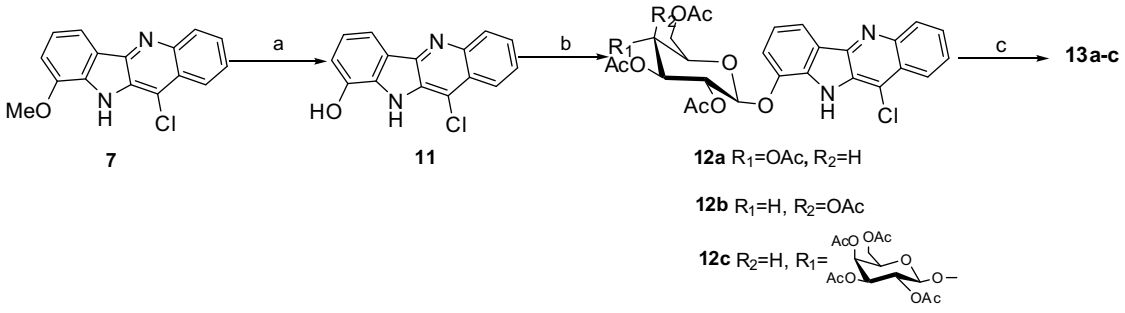


Figure 2. Structures of compounds **2b–c** and **13a–c**.



Scheme 5. Reagents and conditions: (a) BBr_3, CH_2Cl_2, 86%; (b) glycopyranosyl bromides, K_2CO_3, H_2O, $CHCl_3$, TBAB, 40 °C, 6 h, 63% (**12a**), 60% (**12b**), 57% (**12c**); (c) CH_3ONa, CH_3OH, 0 °C, 1 h, 91% (**13a**), 91% (**13b**), 89% (**13c**).

gar donors, 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide and 2,3,4,2′,3′,4′,6′-hepta-*O*-acetyl-α-D-lactopyranosyl bromide, to give the corresponding glycoside products. After deacetylation with sodium methoxide, the target compounds, **2b–c,** were obtained successfully.

The compounds, **13a–c**, were obtained from intermediate **7** (Scheme 5). After demethylation in the presence of boron tribromide, the desired compound **11** was obtained. The corresponding glycoside products, **12a–c**, were synthesized through phase transfer catalysis, in which the α-D-glycopyranosyl bromides were used

as donors. After deacetylation with sodium methoxide, jusbetonin analogues **13a–c** were synthesized successfully. The acetylated indolo[3,2-*b*]quinoline glycoside derivatives, **10a–c** and **12a–c**, have better solubility in common solvents such as methanol, chloroform and THF. Once deacetylated, they are more soluble in water compared to the parent indolo[3,2-*b*]quinoline compounds, **7**, **8** and **9**.

The proliferation inhibition activities of these compounds against the MDA-231 breast cancer cell line at a concentration of 1 μM were measured using a 3-(4,5-dimethylthioazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) cell viability assay. The data showed that all prepared compounds possessed moderate proliferation inhibitory activity, and compound **2c** was the most potent (Table 2).

In conclusion, we have developed an efficient and stereoselective method for the total synthesis of jusbetonin and its analogues. The gradient temperature-elevating method in the construction of indolo[3,2-*b*]quinoline skeleton **6** is critical. The prepared compounds had moderate proliferation inhibitory activity against the MDA-231 breast cancer cell line at a concentration of 1 μM. Compound **2c**, 9-(β-D-lactosyl)-10*H*-indolo[3,2-*b*]quinoline, showed the most potent inhibitory activity.

3. Experimental

3.1. General methods

Solvents were purified in a conventional manner. Thin layer chromatography (TLC) was performed on precoated E. Merck Silica Gel 60 F_{254} plates. Flash column chromatography was performed on silica gel (200–300 mesh, Qingdao, China). Melting points were determined on a Mitamura–Riken micro hot stage without correction. Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter. IR spectra were recorded by KBr pellets for solid samples on a Nicolet Nexus 470 FTIR spectrophotometer. UV–vis (UV–vis) spectra were obtained on Varian Cary-300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Jeol JNM-ECP 600 spectrometer with tetramethylsilane (Me_4Si) as the internal standard, and chemical shifts are recorded in δ values. Mass spectra were recorded on a Q-TOF Global mass spectrometer. The primary screening for proliferation inhibition activities of compounds was tested in vitro against the human breast cancer cell line (MDA-231) using an MTT cell viability assay.

3.2. 2-(*N*-(2-methoxyphenylamino)acetamido)benzoic acid (5)

To a solution of **4** (3.20 g, 15 mmol) in DMF (10 mL) was added dropwise 2-methoxybenzenamine (6 mL, 50 mmol) at rt. The reaction mixture was stirred at 80 °C for 10 h under nitrogen atmosphere. Then the mixture was poured into ice water (100 mL), and basified to pH 9 with sodium hydroxide aqueous solution. After being washed with chloroform (3 × 30 mL), the water layer was acidified to pH 4 with an aq acetic acid soln (30%, v/v) and filtered. The solid was washed with water (3 × 30 mL) to afford acid **5** (3.57 g, 79%); R_f = 0.60 ($CHCl_3$–CH_3OH 3:1); mp 182–184 °C; IR (KBr) 3403, 3325, 1683, 1582, 1522, 1413, 1270, 761, 726 cm^{-1}; UV (DMSO) 297, 257 nm; ^{1}H NMR (DMSO-d_6, 600 MHz): δ 13.45 (br s, 1H, COOH), 11.90 (s, 1H, N–H), 8.71 (dd, 1H, *J* = 8.6, 1.1 Hz, Ar-H), 7.93 (dd, 1H, *J* = 7.8, 1.6 Hz, Ar-H), 7.59 (td, 1H, *J* = 7.8, 1.6 Hz, Ar-H), 7.13 (td, 1H, *J* = 7.6, 1.1 Hz, Ar-H), 6.86 (dd, 1H, *J* = 8.6, 1.1 Hz, Ar-H), 6.74 (td, 1H, *J* = 7.6, 1.1 Hz, Ar-H), 6.61 (td, 1H, *J* = 7.6, 1.6 Hz, Ar-H), 6.36 (dd, 1H, *J* = 7.8, 1.3 Hz, Ar-H), 5.83 (t, 1H, *J* = 5.7 Hz, N–H), 3.86 (d, 2H, *J* = 6.0 Hz, CH_2), 3.83 (s, 3H, O–CH_3); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 170.8, 168.9, 146.8, 140.5, 137.7, 134.1, 131.1, 122.6, 121.1, 119.5, 116.9, 116.1, 110.2, 109.5, 55.5, 49.1. ESIMS *m/z*: ES$^+$ 301.1 [M+H]$^+$; HRESIMS: calcd for $C_{16}H_{17}N_2O_4^+$ 301.1188; found 301.1192.

3.3. 9-methoxy-5*H*-indolo[3,2-b]quinolin-11(10*H*)-one (6)

PPA (10 g) was added to **5** (300 mg, 1 mmol) and the syrup was stirred at 100 °C for 0.5 h, then 110 °C for 0.5 h, 120 °C for 0.5 h, 130 °C for 0.5 h. The mixture was poured into ice water (100 mL). The resulting precipitate was collected, washed with water and air-dried to provide the crude product. Purification by column chromatography afforded **6** as a light yellow solid (130 mg, 49%); R_f = 0.45 (EtOAc); mp >300 °C; IR (KBr) 3224, 2995, 1639, 1582, 1493, 1260, 755 cm^{-1}; UV (DMSO) 395, 305, 270 nm; ^{1}H NMR (DMSO-d_6, 600 MHz): δ 12.33 (s, 1H, N–H), 11.63 (s, 1H, N–H), 8.35 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.75 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.66–7.72 (m, 2H, Ar-H), 7.27 (t, 1H, *J* = 7.3 Hz, Ar-H), 7.13 (t, 1H, *J* = 7.8 Hz, Ar-H), 7.01 (d, 1H, *J* = 7.7 Hz, Ar-H), 3.95 (s, 3H, O–CH_3); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 167.3, 146.7, 139.0, 130.6, 129.4, 129.3, 125.2, 122.9, 120.3, 119.5, 117.5, 117.1, 112.6, 107.2, 55.5. HRESIMS: calcd for $C_{16}H_{13}N_2O_2^+$ 265.0977; found 265.0921.

3.4. 11-chloro-9-methoxy-10*H*-indolo[3,2-*b*]quinoline (7)

Phosphorous oxychloride (20 mL) was added to **6** (530 mg, 2 mmol) and the mixture was stirred under reflux for 4 h. The excess $POCl_3$ was removed under reduced pressure and water (20 mL) was added. The solution was adjusted to pH 7 with an aq sodium hydroxide soln (20%) and extracted with CH_2Cl_2 (3 × 100 mL). The organic phase was washed with brine (3 × 50 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, a yellow solid was obtained. Purification by column chromatography afforded **7** as a light yellow solid (470 mg, 83%); R_f = 0.3 (EtOAc–*n*-hexane 1:3); mp 190–192 °C; IR (KBr) 3413, 3206, 1591, 1440, 1392, 1245, 735 cm^{-1}; UV (DMSO) 400, 343, 276 nm; ^{1}H NMR (DMSO-d_6, 600 MHz): δ 11.86 (s, 1H, N–H); 8.31 (dd, 1H, *J* = 7.8, 0.9 Hz, Ar-H), 8.27 (dd, 1H, *J* = 8.28, 0.96 Hz, Ar-H), 7.9 (m, 2H, Ar-H), 7.7 (m, 2H, Ar-H), 4.05 (s, 3H, O–CH_3); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 146.2, 146.1, 143.9, 134.2, 130.2, 129.2, 129.1, 127.0, 126.9, 126.3, 123.7, 122.3, 121.0, 113.6, 111.1, 55.7. ESIMS *m/z*: ES$^+$ 283.1 [M+H]$^+$. HRESIMS: calcd for $C_{16}H_{12}N_2OCl^+$ 283.0638; found 283.0625.

3.5. 9-methoxy-10*H*-indolo[3,2-*b*]quinoline (8)

Pd/C (10%) was added to a solution of **7** (560 mg, 2 mmol) and triethylamine (0.28 mL, 2 mmol) in CH_3OH (30 mL) and the reaction mixture was stirred under hydrogen at rt for 10 h. The mixture was filtered through diatomite and was concentrated to give a yellow solid. Purification of this solid by column chromatography afforded **8** as a yellow solid (460 mg, 92%); R_f = 0.25 (EtOAc–*n*-hex-

Table 2
Proliferation inhibition activities of compounds (1 μm) against tumour cell MDA-231

Compound (1 μm)	Proliferation inhibition (%)
6	30.3
7	26.8
8	27.1
9	25.8
11	25.8
10a	28.4
10c	26.9
2c	37.9
12a	28.8
13a	30.6
12c	21.1
13c	27.1

ane 1:3); mp 170–172 °C; IR (KBr) 3423, 2926, 1586, 1507, 1396, 1260, 738 cm^{-1}; UV (DMSO) 390, 342, 276 nm; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.33 (d, 1H, J = 9.7 Hz, H-4), 8.27 (s, 1H, N–H), 8.13 (d, 1H, J = 7.8 Hz, H-1), 8.07 (s, 1H, H-11), 7.93 (d, 1H, J = 7.8 Hz, H-6), 7.65 (m, 1H, H-3), 7.52 (m, 1H, H-2), 7.26 (t, 1H, J = 7.8 Hz, H-7), 7.08 (d, 1H, J = 7.8 Hz, H-8), 4.04 (s, 3H, O–CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 146.7, 145.6, 144.4, 133.9, 132.1, 129.2, 127.2, 126.9, 126.6, 125.2, 122.9, 120.6, 114.3, 113.6, 109.7, 55.6. ESIMS m/z ES^+ 249.1 $[M+H]^+$; HRESIMS: calcd for $C_{16}H_{13}N_2O^+$ 249.1028; found 249.1039.

3.6. 9-hydroxy-10*H*-indolo[3,2-*b*]quinoline (9)

Boron tribromide (0.3 mL, 3 mmol) was added to a solution of **8** (250 mg, 1 mmol) in absolute CH_2Cl_2 (20 mL) at 0 °C under a nitrogen atmosphere. After stirring for 4 h, ice water (20 mL) was added dropwise. The mixture was adjusted to pH 7 with aq sodium hydroxide soln (20%). The resulting precipitate was collected, washed with water and dried to obtain compound **9** (210 mg, 92%) as a yellow solid; R_f = 0.35 (EtOAc–*n*-hexane 1:1); mp 195–198 °C; IR (KBr) 3430, 3209, 3055, 1588, 1504, 1398, 1268, 775, 738 cm^{-1}; UV (DMSO) 397, 344, 278 nm; ^1H NMR (CD_3OD, 600 MHz): δ 8.25 (s, 1H, H-11), 8.18 (d, 1H, J = 8.7 Hz, H-4), 8.01 (dd, 1H, J = 8.2, 1.4 Hz, H-1), 7.96 (dd, 1H, J = 7.8, 0.9 Hz, H-6), 7.64 (m, 1H, H-3), 7.52 (m, 1H, H-2), 7.10 (t, 1H, J = 7.8 Hz, H-7), 7.03 (dd, 1H, J = 7.8, 0.9 Hz, H-8); ^{13}C NMR (CD_3OD, 150 MHz): δ 147.5, 144.8, 144.5, 135.8, 134.4, 128.6, 128.5, 128.4, 127.7, 126.1, 123.2, 121.4, 115.6, 115.3, 113.9. ESIMS m/z ES^+ 235.1 $[M+H]^+$; HRESIMS: calcd for $C_{15}H_{11}N_2O^+$ 235.0871; found 235.0867.

3.7. 9-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-10*H*-indolo[3,2-*b*]quinoline (10a)

To a solution of water (5 mL) and chloroform (5 mL) was added tetrabutylammonium bromide (320 mg, 1 mmol). After heating to 40 °C, a mixture of **9** (230 mg, 1 mmol) and K_2CO_3 (414 mg, 3 mmol) in water (20 mL) was added. Then, a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (615 mg, 1.5 mmol) in chloroform (20 mL) was added dropwise. After stirring for 6 h, the organic layer was separated and washed successively with water, aq $NaHCO_3$ soln and water, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude reaction product by column chromatography afforded compound **10a** (385 mg, 68%) as a yellow powder; R_f = 0.3 (EtOAc–*n*-hexane 1:1); mp 101–104 °C. IR (KBr) 3206, 1756, 1501, 1436, 1228, 1039, 780, 743 cm^{-1}; UV (DMSO) 385, 341, 276 nm; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.72 (s, 1H, N–H), 8.31 (m, 2H, H-1, H-4), 8.21 (s, 1H, H-11), 7.96 (d, 1H, J = 7.8 Hz, H-6), 7.66 (m, 1H, H-3), 7.54 (m, 1H, H-2), 7.23 (t, 1H, J = 7.8 Hz, H-7), 7.18 (dd, 1H, J = 7.8, 0.9 Hz, H-8), 5.39 (dd, 1H, J = 7.6, 9.6 Hz, H-2′), 5.33 (dd, 1H, J = 9.2, 9.6 Hz, H-4′), 5.24 (t, 1H, J = 9.6 Hz, H-3′), 5.13 (d, 1H, J = 7.8 Hz, H-1′), 4.48 (dd, 1H, J = 1.9, 12.4 Hz, H-6′a), 4.18 (dd, 1H, J = 4.6, 12.4 Hz, H-6′b), 3.84 (m, 1H, H-5'), 2.16–2.08 (4s, 12H, Ac-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 171.0, 170.2, 169.8, 169.4, 146.2, 144.5, 142.3, 135.8, 132.6, 129.3, 127.3, 127.2, 126.7, 125.4, 124.3, 120.2, 118.2, 117.5, 114.2, 101.7, 72.5, 72.4, 71.3, 68.1, 61.3, 20.9, 20.8, 20.6. ESIMS m/z ES^+ 565.2 $[M+H]^+$; HRESIMS: calcd for $C_{29}H_{29}N_2O_{10}^+$ 565.1822; found 565.1816.

3.8. 9-(β-D-glucopyranosyl)-10*H*-indolo[3,2-*b*]quinoline (2a)

To a solution of **10a** (140 mg, 0.25 mmol) in CH_3OH–CH_3Cl (1:1) was added CH_3ONa in CH_3OH (0.63 M, 1 mL) at 0 °C. After stirring at rt for 1 h, the resulting precipitate was collected and washed with CH_3OH to obtain compound **2a** (92 mg, 93%) as a yellow powder; R_f = 0.4 (EtOAc–CH_3OH, 2:1); mp >300 °C; $[\alpha]_D^{26}$ −46.5 (*c* 0.1, CH_3OH); IR (KBr) 3562, 3224, 1502, 1399, 1062, 778, 739 cm^{-1}; UV (DMSO) 387, 342, 277 nm; ^1H NMR (DMSO-d_6, 600 MHz): δ 11.22 (s, 1H, N–H), 8.30 (s, 1H, H-11), 8.18 (d, 1H, J = 8.3 Hz, H-4), 8.11 (d, 1H, J = 7.3 Hz, H-1), 8.02 (d, 1H, J = 7.8 Hz, H-6), 7.64 (m, 1H, H-3), 7.56 (m, 1H, H-2), 7.43 (d, 1H, J = 7.7 Hz, H-8), 7.20 (t, 1H, J = 7.8 Hz, H-7), 5.42 (br s, 1H, –OH), 5.20 (br s, 1H, –OH), 5.14 (br s, 1H, –OH), 5.00 (d, 1H, J = 7.8 Hz, H-1′), 4.85 (br s, 1H, –OH), 3.81–3.78 (m, 1H, H-6′a), 3.53 (m, 1H, H-6′b), 3.47–3.34 (m, 3H, H-2′, H-3′, H-5′), 3.26–3.23 (m, 1H, H-4′); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 145.8 (C-5a), 143.7 (C-9), 143.5 (C-4a), 134.8 (C-9a), 132.4 (C-10a), 128.7 (C-4), 127.5 (C-1), 126.7 (C-11a), 126.2 (C-3), 124.9 (C-2), 122.6 (C-5b), 119.8 (C-7), 115.7 (C-8), 115.3 (C-6), 113.6 (C-11), 102.5 (C-1′), 77.3 (C-5′), 76.2 (C-3′), 73.6 (C-2′), 70.0 (C-4′), 60.9 (C-6′). ESIMS m/z ES^+ 397.1 $[M+H]^+$; HRESIMS: calcd for $C_{21}H_{21}N_2O_6^+$ 397.1400; found 397.1404.

3.9. 9-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-10*H*-indolo[3,2-*b*] quinoline (10b)

This compound was prepared from **9** (230 mg, 1 mmol) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (615 mg, 1.5 mmol) using the same procedure as described for **10a**. Purification of the residue resulted in **10b** (398 mg, 71%) as a yellow powder; R_f = 0.4 (EtOAc–*n*-hexane 2:1); mp 106–108 °C; IR (KBr) 3209, 1755, 1501, 1435, 1229, 1039, 780, 743 cm^{-1}; UV (DMSO) 386, 341, 276 nm; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.45 (s, 1H, N–H), 8.32 (d, 1H, J = 8.3 Hz, H-4), 8.28 (d, 1H, J = 7.8 Hz, H-1), 8.15 (s, 1H, H-11), 7.95 (d, 1H, J = 8.2 Hz, H-6), 7.66 (m, 1H, H-3), 7.55 (m, 1H, H-2), 7.25 (m, 1H, H-7), 7.20 (dd, 1H, J = 7.7, 0.9 Hz, H-8), 5.60 (dd, 1H, J = 7.8, 10.05 Hz, H-4′), 5.52 (d, 1H, J = 8.8 Hz, H-1′), 5.17 (m, 2H, H-3′, H-2′), 4.33 (dd, 1H, J = 7.3, 11.9 Hz, H-6′a), 4.21 (dd, 1H, J = 5.5, 11.5 Hz, H-6′b), 4.11 (m, 1H, H-5′), 2.24–1.97 (4s, 12H, Ac-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.4, 170.2, 170.1, 170.0, 146.1, 144.2, 142.3, 135.0, 132.3, 128.9, 127.2, 126.9, 126.7, 125.3, 123.7, 120.2, 117.5, 115.6, 114.1, 101.1, 71.4, 70.5, 68.9, 66.9, 61.4, 20.9, 20.6, 20.5. ESIMS m/z ES^+ 565.1 $[M+H]^+$; HRESIMS: calcd for $C_{29}H_{29}N_2O_{10}^+$ 565.1822; found 565.1812.

3.10. 9-(β-D-galatopyranosyl)-10*H*-indolo[3,2-*b*]quinoline (2b)

This compound was prepared from **10b** (140 mg, 0.25 mmol) using the same procedure as described for **2a**. Purification of the precipitate resulted in **2b** (88 mg, 89%) as a yellow powder; R_f = 0.4 (EtOAc–CH_3OH 2:1); mp >300 °C; $[\alpha]_D^{26}$ −61.1 (*c* 0.1, CH_3OH); IR (KBr) 3555, 3350, 3213, 1500, 1427, 1076, 777, 738 cm^{-1}; UV (DMSO) 385, 342, 276 nm; ^1H NMR (DMSO-d_6, 600 MHz): δ 11.22 (s, 1H, N–H), 8.31 (s, 1H, H-11), 8.18 (d, 1H, J = 8.7 Hz, H-4), 8.11 (d, 1H, J = 8.2 Hz, H-1), 8.02 (d, 1H, J = 7.8 Hz, H-6), 7.64 (m, 1H, H-3), 7.56 (m, 1H, H-2), 7.44 (d, 1H, J = 7.8 Hz, H-8), 7.20 (t, 1H, J = 7.8 Hz, H-7), 5.25 (d, 1H, J = 4.6 Hz, –OH), 4.98 (d, 1H, J = 5.5 Hz, –OH), 4.95 (d, 1H, J = 7.8 Hz, H-1′), 4.88 (t, 1H, J = 5.5 Hz, –OH), 4.64 (d, 1H, J = 4.6 Hz, –OH), 3.78 (m, 1H, H-4′), 3.74 (m, 1H, H-6′a), 3.68 (m, 1H, H-6′b), 3.70–3.67 (m, 2H, H-2′, H-3′), 3.48(m, 1H, H-5′); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 145.8, 143.9, 143.5, 134.8, 132.4, 128.7, 127.5, 126.7, 126.2, 124.9, 122.6, 119.8, 115.7, 115.3, 113.6, 103.2, 75.9, 72.9, 70.6, 68.2, 60.6. HRESIMS: calcd for $C_{21}H_{21}N_2O_6^+$ 397.1400; found 397.1385.

3.11. 9-(2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-β-D-lactosyl)-10*H*-indolo[3,2-*b*]quinoline (10c)

This compound was prepared from **9** (230 mg, 1 mmol) and 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-α-D-lactosyl bromide (1.04 g,

1.5 mmol) using the same procedure as described for **10a**. Purification of the residue resulted in **10c** (538 mg, 63%) as a yellow powder; R_f = 0.2 (EtOAc–*n*-hexane 1:1); mp 98–102 °C; IR (KBr) 3209, 1752, 1434, 1228, 1054 cm^{-1}; UV (DMSO) 385, 341, 277 nm; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.93 (s, 1H, N–H), 8.34 (d, 1H, J = 7.8 Hz, H-4), 8.32 (d, 1H, J = 8.2 Hz, H-1), 8.28 (s, 1H, H-11), 7.97 (d, 1H, J = 8.3 Hz, H-6), 7.66 (m, 1H, H-3), 7.53 (m, 1H, H-2), 7.22 (t, 1H, J = 7.8 Hz, H-7), 7.16 (dd, 1H, J = 7.8, 0.9 Hz, H-8), 5.38 (d, 1H, J = 3.2 Hz, H-4″), 5.34–5.29 (m, 2H, H-2′, H-3′), 5.11 (m, 2H, H-2″, H-3″), 5.02 (d, 1H, J = 7.8 Hz, H-1′), 4.91 (dd, 1H, J = 1.8, 12.4 Hz, H-6′a), 4.62 (d, 1H, J = 8.3 Hz, H-1″), 4.17 (dd, 1H, J = 6.0, 11.4 Hz, H-6′b), 4.09 (m, 2H, H-6″a, H-6″b), 3.93 (m, 2H, H-5″, H-4′), 3.68 (m, 1H, H-5′), 2.20–1.98 (7s, 21H, Ac-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 171.0, 170.4, 170.1, 170.0, 169.7, 168.9, 146.2, 144.4, 142.3, 136.3, 132.7, 129.2, 127.4, 127.2, 126.6, 125.3, 124.3, 120.1, 119.0, 118.7, 114.4, 102.3, 101.0, 75.5, 73.5, 72.5, 71.5, 70.8, 70.7, 69.2, 66.6, 60.7, 21.1, 20.9, 20.8, 20.6, 20.5. ESIMS m/z ES^+ 853.2 $[M+H]^+$; HRESIMS: calcd for $C_{41}H_{45}N_2O_{18}^+$ 853.2667; found 853.2695.

3.12. 9-(β-D-lactosyl)-10*H*-indolo[3,2-*b*]quinoline (2c)

This compound was prepared from **10c** (213 mg, 0.25 mmol) using the same procedure as described for **2a**. Purification of the precipitate resulted in **2c** (130 mg, 94%) as a yellow powder; R_f = 0.3 (EtOAc–CH_3OH 1:1); mp >300 °C; $[\alpha]_D^{26}$ −65.6 (*c* 0.04, CH_3OH). IR (KBr) 3555, 3350, 1500, 1430, 1400, 1064, 777, 738 cm^{-1}; UV (DMSO) 385, 342, 276 nm; ^1H NMR (DMSO-d_6, 600 MHz): δ 11.23 (s, 1H, N–H), 8.32 (s, 1H, H-11), 8.19 (d, 1H, J = 8.7 Hz, H-4), 8.11 (d, 1H, J = 8.2 Hz, H-1), 8.03 (d, 1H, J = 7.8 Hz, H-6), 7.65 (m, 1H, H-3), 7.56 (m, 1H, H-2), 7.44 (d, 1H, J = 8.3 Hz, H-8), 7.22 (t, 1H, J = 7.8 Hz, H-7), 5.53 (d, 1H, J = 4.1 Hz, –OH), 5.16 (d, 1H, J = 4.6 Hz, –OH), 5.14 (d, 1H, J = 7.3 Hz, H-1′), 4.89 (s, 1H, –OH), 4.84 (m, 2 H, –OH), 4.72 (t, 1H, J = 5.0 Hz, –OH), 4.57 (d, 1H, J = 4.6 Hz, –OH), 4.28 (d, 1H, J = 7.3 Hz, H-1″), 3.88–3.33 (m, 11H, Lac-H); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 145.7, 143.5, 134.7, 132.4, 128.7, 127.5, 126.7, 126.2, 124.9, 122.6, 119.8, 115.5, 115.4, 113.6, 103.8, 101.7, 99.4, 80.4, 75.6, 75.2, 74.5, 73.3, 73.2, 70.5, 68.2, 60.5, 60.3. ESIMS m/z ES^+ 559.2 $[M+H]^+$; HRESIMS: calcd for $C_{27}H_{31}N_2O_{11}^+$ 559.1928; found 559.1909.

3.13. 9-hydroxy-11-chloro-10*H*-indolo[3,2-*b*]quinoline (11)

To a solution of **7** (560 mg, 2 mmol) in absolute CH_2Cl_2 (30 mL) was added BBr_3 (0.57 mL, 6 mmol) at 0 °C under nitrogen atmosphere. After 4 h of stirring, ice water (30 ml) was added dropwise. The mixture was adjusted to pH 7 with aq sodium hydroxide soln (20%). The resulting precipitate was collected, washed with water and dried to provide **11** (458 mg, 86%) as a yellow solid; R_f = 0.4 (EtOAc–*n*-hexane 1:1); mp 248–252 °C; IR (KBr) 3209, 1420, 1398, 733 cm^{-1}; UV (DMSO) 406, 345, 279 nm; ^1H NMR (CD_3OD, 600 MHz): δ 8.34 (dd, 1H, J = 8.2, 0.9 Hz, H-1), 8.21 (d, 1H, J = 8.7 Hz, H-4), 7.93 (dd, 1H, J = 7.8, 0.9 Hz, H-6), 7.73 (m, 1H, H-3), 7.66 (m, 1H, H-2), 7.15 (t, 1H, J = 7.7 Hz, H-7), 7.07 (dd, 1H, J = 7.8, 0.9 Hz, H-8); ^{13}C NMR (CD_3OD, 150 MHz): δ 145.1, 135.6, 132.1, 128.7, 128.6, 127.3, 125.4, 123.7, 122.5, 116.2, 114.0. ESIMS m/z ES^+ 269.0 $[M+H]^+$; HRESIMS: calcd for $C_{15}H_{10}N_2OCl^+$ 269.0482; found 269.0480.

3.14. 9-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-11-chloro-10*H*-indolo[3,2-*b*] quinoline (12a)

To a solution of water (5 mL) and chloroform (5 mL) was added tetrabutylammonium bromide (320 mg, 1 mmol). After heating to 40 °C, a mixture of **11** (268 mg, 1 mmol) and K_2CO_3 (414 mg, 3 mmol) in water (20 mL) was added. Then the solution of glucose donor 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (615 mg, 1.5 mmol) in chloroform (20 mL) was added dropwise. After 6 h of stirring, the organic layer was separated and washed successively with water, aq $NaHCO_3$ soln and water, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude reaction product by column chromatography afforded compound **12a** (374 mg, 63%) as a yellow powder; R_f = 0.35 (EtOAc–*n*-hexane 1:1); mp 200–202 °C; IR (KBr) 3404, 3224, 1748, 1499, 1390, 1228, 1073 cm^{-1}; UV (DMSO) 397, 342, 277 nm; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.59 (s, 1H, N–H), 8.31 (m, 2H, H-1, H-4), 8.26 (d, 1H, J = 6.9 Hz, H-6), 7.72 (m, 1H, H-3), 7.66 (m, 1H, H-2), 7.27 (m, 1H, H-7), 7.26 (d, 1H, J = 8.2 Hz, H-8), 5.42 (dd, 1H, J = 6.9 Hz, H-2′), 5.36 (dd, 1H, J = 9.2, 9.6 Hz, H-4′), 5.24 (dd, 1H, J = 9.6 Hz, H-3′), 5.18 (d, 1H, J = 7.8 Hz, H-1′), 4.35 (dd, 1H, J = 5.5, 12.4 Hz, H-6′a), 4.23 (dd, 1H, J = 2.3, 12.4 Hz, H-6′b), 3.90 (m, 1H, H-5′), 2.16–2.03 (4s, 12H, Ac-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.5, 170.2, 169.9, 169.4, 142.5, 135.1, 130.1, 129.5, 127.4, 126.5, 124.4, 122.6, 121.2, 118.2, 117.4, 101.5, 72.3, 71.5, 68.1, 61.8, 20.9, 20.6, 20.5. ESIMS m/z ES^+ 599.5 $[M+H]^+$; HRESIMS: calcd for $C_{29}H_{28}N_2O_{10}Cl^+$ 599.1432; found 599.1444.

3.15. 9-(β-D-glucopyranosyl)-11-chloro-10*H*-indolo[3,2-b]quinoline (13a)

To a solution of **12a** (149 mg, 0.25 mmol) in CH_3OH–CH_3Cl (1:1) was added CH_3ONa in CH_3OH (0.63 M, 1 mL) at 0 °C. After stirring at rt for 1 h, the resulting precipitate was collected and washed with CH_3OH to obtain compound **13a** (97.3 mg, 91%) as a yellow powder; R_f = 0.45 (EtOAc–CH_3OH 2:1); mp >300 °C; $[\alpha]_D^{26}$ −70.3 (c 0.03, CH_3OH); IR (KBr) 3224, 1493, 1427, 1082, 738 cm^{-1}; UV (DMSO) 397, 343, 278 nm; ^1H NMR (DMSO-d_6, 600 MHz): δ 11.41 (s, 1H, N–H), 8.32 (m, 1H, H-1), 8.28 (m, 1H, H-4), 8.02 (d, 1H, J = 7.8 Hz, H-6), 7.75 (m, 2H, H-3, H-2), 7.52 (d, 1H, J = 7.3 Hz, H-8), 7.27 (t, 1H, J = 7.8 Hz, H-7), 5.62 (d, 1H, J = 3.6 Hz, –OH), 5.19 (d, 1H, J = 4.6 Hz, –OH), 5.14 (d, 1H, J = 5.4 Hz, –OH), 4.94 (d, 1H, J = 7.8 Hz, H-1′), 4.72 (t, 1H, J = 5.9 Hz, –OH), 3.80 (m, 1H, H-6′a), 3.53 (m, 1H, H-6′b), 3.51–3.32 (m, 3H, H-2′, H-3′, H-5′), 3.26–3.23 (m, 1H, H-4′); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 146.2, 144.2, 144.0, 134.6, 130.1, 129.3, 127.1, 126.5, 123.6, 122.7, 122.2, 121.1, 118.6, 115.9, 115.4, 102.9, 77.4, 75.5, 73.5, 69.9, 60.8. ESIMS m/z ES^+ 430.9 $[M+H]^+$; HRESIMS: calcd for $C_{21}H_{20}ClN_2O_6^+$ 431.1010; found 431.1008.

3.16. 9-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl))-11-chloro-10*H*-indolo [3,2-*b*]quinoline (12b)

This compound was prepared from **11** (268 mg, 1 mmol) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (615 mg, 1.5 mmol) using the same procedure as described for **12a**. Purification of the residue resulted in **12b** (359 mg, 60%) as a yellow powder; R_f = 0.3 (EtOAc–*n*-hexane 1:1); mp 198–200 °C; IR (KBr) 3404, 3210, 1748, 1499, 1368, 1229, 1073 cm^{-1}; UV (DMSO) 396, 342, 277 nm; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.60 (s, 1H, N–H), 8.34 (m, 2H, H-1, H-4), 8.26 (d, 1H, J = 9.8 Hz, H-6), 7.74 (m, 1H, H-3), 7.67 (m, 1H, H-2), 7.31–7.28 (m, 2H, H-7, H-8), 5.61 (dd, 1H, J = 8.2, 10.4 Hz, H-2′), 5.52 (d, 1H, J = 3.3 Hz, H-4′), 5.18 (dd, 1H, J = 3.3, 10.4 Hz, H-3′), 5.18 (d, 1H, J = 8.2 Hz, H-1′), 4.29 (dd, 1H, J = 6.5, 11.6 Hz, H-6′a), 4.23 (dd, 1H, J = 6.1, 11.6 Hz, H-6′b), 4.13 (m, 1H, H-5′), 2.25–1.99 (4s, 12H, Ac-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.4, 170.3, 170.2, 170.1, 142.7, 134.9, 130.1, 126.5, 124.4, 122.7, 121.2, 116.9, 101.8, 71.4, 70.5, 69.1, 66.8, 61.4, 21.1, 20.7, 20.6. ESIMS m/z ES^+ 599.1 $[M+H]^+$; HRESIMS: calcd for $C_{29}H_{28}N_2O_{10}Cl^+$ 599.1432; found 599.1423.

3.17. 9-(β-D-galatopyranosyl)-11-chloro-10*H*-indolo[3,2-*b*]quinoline (13b)

This compound was prepared from **12b** (149 mg, 0.25 mmol) using the same procedure as described for **13a**. Purification of the precipitate resulted in **13b** (98 mg, 91%) as a yellow powder; R_f = 0.4 (EtOAc–CH_3OH 2:1); mp >300 °C; $[\alpha]_D^{26}$ −54.3 (c 0.1, CH_3OH); IR (KBr) 3209, 1493, 1420, 1082, 738 cm^{-1}; UV (DMSO) 399, 343, 278 nm; ^1H NMR (DMSO-d_6, 600 MHz): δ 8.32 (m, 1H, H-1), 8.28 (m, 1H, H-4), 8.03 (d, 1H, J = 7.3 Hz, H-6), 7.74 (m, 2H, H-3, H-2), 7.52 (d, 1H, J = 7.7 Hz, H-8), 7.27 (t, 1H, J = 7.8 Hz, H-7), 5.01 (br s, 1H, –OH), 4.89 (d, 1H, J = 7.8 Hz, H-1′), 4.80 (br s, 1H, –OH), 4.65 (br s, 1H, –OH), 3.83 (m, 1H, H-4′), 3.77 (m, 1H, H-6′a), 3.70 (m, 1H, H-6′b), 3.65 (m, 2H, H-2′, H-3′), 3.52 (m, 1H, H-5′); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 146.2, 144.3, 143.9, 129.3, 127.0, 126.5, 123.6, 122.8, 122.2, 121.1, 118.6, 116.2, 115.4, 103.8, 76.0, 72.3, 70.6, 68.2, 60.6. ESIMS m/z ES^+ 431.2 $[M+H]^+$. HRESIMS: calcd for $C_{21}H_{20}ClN_2O_6^+$ 431.1010; found 431.1020.

3.18. 9-(2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-β-D-lactosyl)-11-chloro-10*H*-indolo[3,2-*b*] quinoline (12c)

This compound was prepared from **11** (268 mg, 1 mmol) and 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-α-D-lactosyl bromide (1.04 g, 1.5 mmol) using the same procedure as described for **12a**. Purification of the residue resulted in **12c** (501 mg, 57%) as a yellow powder; R_f = 0.2 (EtOAc–*n*-hexane 1:1); mp 138–140 °C; IR (KBr) 3403, 3212, 1748, 1390, 1368, 1228, 1073 cm^{-1}; UV (DMSO) 401, 342, 278 nm; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.62 (s, 1H, N–H), 8.34 (d, 1H, J = 8.7 Hz, H-4), 8.32 (d, 1H, J = 8.7 Hz, H-1), 8.26 (d, 1H, J = 7.3 Hz, H-6), 7.73 (m, 1H, H-3), 7.67 (m, 1H, H-2), 7.29–7.25 (m, 2H, H-8, H-7), 5.38–5.32 (m, 3H, H-2′, H-3′, H-4″), 5.17–5.13 (m, 2H, H-1″, H-2″), 4.98 (dd, 1H, J = 3.4, 10.1 Hz, H-3″), 4.57 (dd, 1H, J = 1.8, 12.4 Hz, H-6″a), 4.54 (d, 1H, J = 8.2 Hz, H-1′), 4.21 (dd, 1H, J = 6.0, 12.4 Hz, H-6″b), 4.17 (dd, 1H, J = 6.4, 10.9 Hz, H-6′a), 4.09 (dd, 1H, J = 7.3, 10.9 Hz, H-6′b), 3.99–3.91 (m, 2H, H-5″, H-4′), 3.82 (m, 1H, H-5′), 2.17–1.98 (7s, 21H, Ac-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.4, 170.3, 170.2, 170.1, 170.0, 169.7, 169.1, 142.5, 135.1, 130.2, 129.3, 127.5, 126.5, 124.4, 122.6, 121.2, 118.2, 117.5, 101.1, 76.0, 73.2, 72.3, 71.8, 70.9, 70.8, 69.1, 66.6, 61.9, 60.8, 20.9, 20.8, 20.7, 20.6, 20.5. ESIMS m/z ES^+ 887.2 $[M+H]^+$; HRESIMS: calcd for $C_{41}H_{44}N_2O_{18}Cl^+$ 887.2278; found 887.2299.

3.19. 9-(β-D-lactosyl)-11-chloro-10*H*-indolo[3,2-*b*]quinoline (13c)

This compound was prepared from **12c** (221 mg, 0.25 mmol) using the same procedure as described for **13a**. Purification of the precipitate resulted in **13c** (131 mg, 89%) as a yellow powder; R_f = 0.2 (EtOAc/CH_3OH, 2:1); mp >300 °C; $[\alpha]_D^{26}$ −64.6 (c 0.02, DMSO). IR (KBr) 3206, 1493, 1420, 1082, 738 cm^{-1}; UV (DMSO) 403, 343, 278 nm; ^1H NMR (DMSO-d_6, 600 MHz): δ 11.44 (s, 1H, N–H), 8.32 (d, 1H, J = 7.7 Hz, H-1), 8.28 (d, 1H, J = 7.7 Hz, H-4), 8.03 (d, 1H, J = 7.7 Hz, H-6), 7.75 (m, 2H, H-3, H-2), 7.52 (d, 1H, J = 7.7 Hz, H-8), 7.28 (dd, 1H, J = 7.7, 8.2 Hz, H-7), 5.69 (s, 1H, –OH), 5.16 (d, 1H, J = 4.4 Hz, –OH), 5.07 (d, 1H, J = 6.6 Hz, H-1′), 4.88 (s, 1H, –OH), 4.84 (d, 1H, J = 5.5 Hz, –OH), 4.75 (t, 1H, J = 5.5 Hz, –OH), 4.72 (t, 1H, J = 4.9 Hz, –OH), 4.57 (d, 1H, J = 4.4 Hz, –OH), 4.28 (d, 1H, J = 7.1 Hz, H-1″), 3.89–3.50 (m, 9H, Lac-H); ^{13}C NMR (DMSO-d_6, 150 MHz): δ 146,1, 144.0, 134.6, 130.1, 129.3, 127.1, 126.6, 123.7, 122.8, 122.3, 121.1, 118.7, 115.9, 115.5, 103.9, 102.3, 80.4, 75.6, 75.3, 73.8, 73.3, 70.5, 68.2, 60.5, 60.2. ESIMS m/z ES^+ 593.2 $[M+H]^+$; HRESIMS: calcd for $C_{27}H_{30}ClN_2O_{11}^+$ 593.1538; found 593.1516.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.11.015.

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