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Towards the synthesis of new benzimidazolone derivatives with surfactant properties

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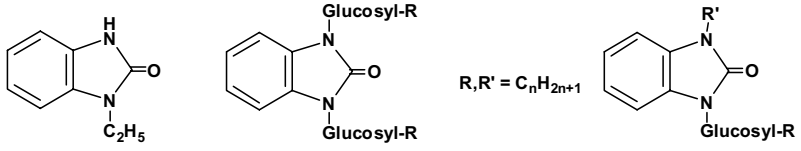
Abstract—New water-soluble benzimidazolone derivatives were synthesized. In the first approach, di-*N*-glycosyl and mono-*N*-alkyl-*N*-glycosyl compounds were obtained by grafting C-6-activated glycosides onto benzimidazolone. In the second approach, benzimidazolone derivatives bearing a glucosyl unit were synthesized using an efficient glycosylation method. Every compound structure was confirmed by means of NMR spectroscopy and elemental analysis. The preliminary surfactant properties of some compounds were evaluated.

Keywords: Benzimidazolones; N-Glycosylation; Water solubility; Surface tension

1. Introduction

Benzimidazolone is well known for its large range of biological activities[1–5] and industrial applications.[6] Thus, some benzimidazolone derivatives such as 1-ethyl-2-benzimidazolone[7] (EBIO, Scheme 1) have created a great deal of interest because of the direct activation of the potassium (K^+) cation channels.

Taking into account a number of applications of benzimidazolone derivatives, this study focuses on the synthesis of benzimidazolone bearing glucosidic units. We first dedicated ourselves to the synthesis of two



EBIO **Type I** **Type II**

Scheme 1.

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new benzimidazolones of series type I and II (Scheme 1) bearing either one or two sugar units on the nitrogen atoms. The presence of the sugar moiety should enhance the water solubility of these heterocyclic compounds, and the alkyl chain should modulate the hydrophilic–lipophilic balance (HLB). Functionalization of glucose to create glucobenzimidazolones was performed on the primary alcohol. So we used a method previously developed in our laboratory by using anhydroglucose.[8] Moreover, the anomeric position could be considered as another possibility to be functionalized considering that this method could be generalized for all carbohydrates. In the second part of this work, we present an efficient glycosylation method.

2. Results and discussion

2.1. Synthesis of 1,3-*N*,*N*′-bis-(6-deoxy-D-glucopyranos-6-yl)benzimidazol-2-one derivatives

The starting benzimidazolones **1**–**3** (Scheme 2) were prepared according to the method described by Townsend et al.[9] *o*-Phenylenediamine was reacted with 1 equiv of urea in dry *n*-butanol at 120 °C. After 10 h, benzimidazolones derivatives **1**–**3** were obtained by the filtration of the crude product in 80–94% yield.

The glucopyranosyl benzimidazolone derivatives **5**–**7** (type I) were obtained by the regiospecific condensation of benzimidazolones **1**–**3** on the anhydroglucosyl substrates **4a**–**g**[8] in the presence of K_2CO_3 at 110 °C, and by using 4:1 toluene–DMSO as solvent. Under these conditions we obtained the desired products **5**–**7** with 70–93% yield. Taking advantage of the convergent synthesis and with the aim of modulating hydrophilic–lipophilic balance, we replaced **4a** by homologues 5,6-anhydro-3-*O*-alkyl-1,2-*O*-isopropylidene-α-D-glucofuranose **4b**–**g** (R^2 = *n*-C_nH_{2n+1}; *n* = 1, 4, 6, 8, 10 and 12). Deprotection of the isopropylidene groups with 9:1 CF_3CO_2H–H_2O[10] afforded the expected glucopyranosyl benzimidazolone derivatives **8**–**10** (type I) in good yields (70–95%). All these structures were confirmed by NMR spectroscopic analyses. The ^{13}C NMR spectra of these compounds showed two anomeric carbons at 96 ppm (C-1β) and 92 ppm (C-1α), which confirmed that the glucosidic parts were in pyranose forms.

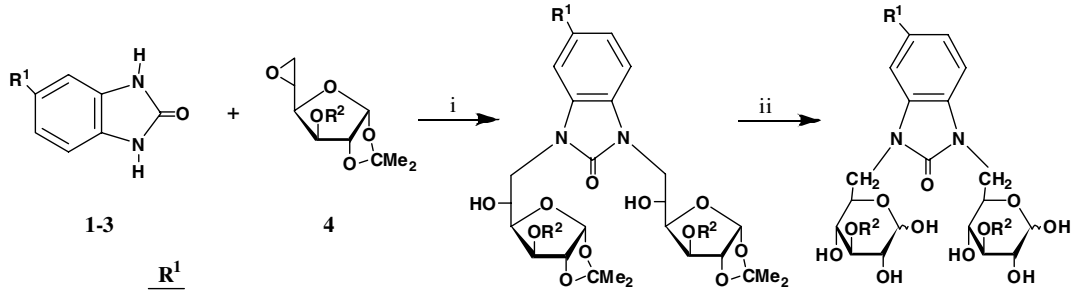
2.2. Synthesis of 3-*N*-alkyl-1-*N*-(6-deoxy-3-*O*-methyl-D-glucopyranos-6-yl)benzimidazol-2-one derivatives

A second glucobenzimidazolone series (type II) was then investigated, and its synthesis is shown in Scheme 3.

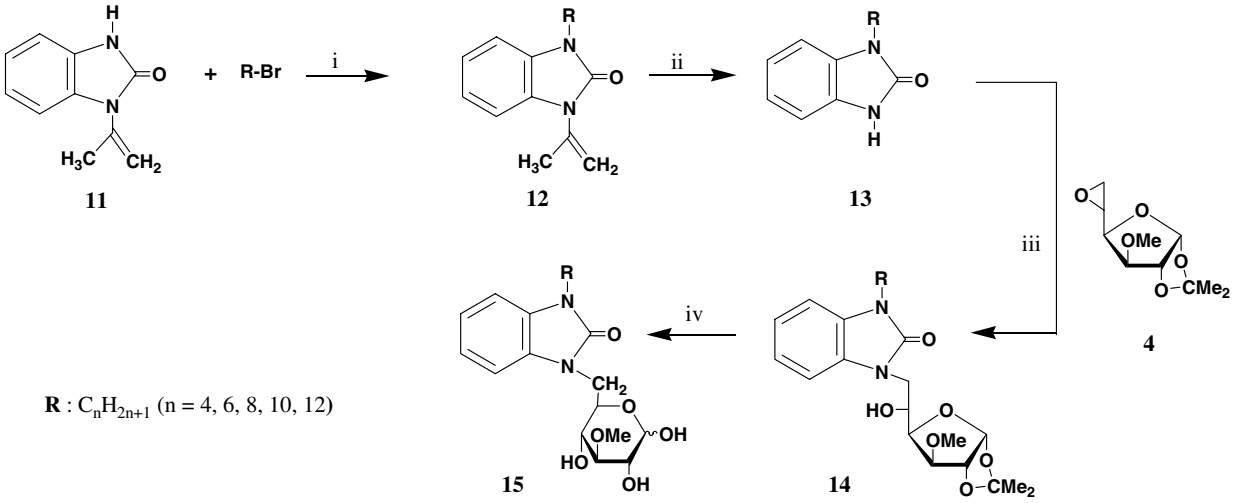
The strategy followed in this part was to partially protect the benzimidazolone unit leaving only one NH group available for an alkylation reaction with an alkyl bromide (step ii). For this purpose, the first step was performed by using the method of Meth-Cohen and Smith.[11] The condensation of *o*-phenylenediamine with ethyl acetoacetate afforded the expected benzimidazolone derivative **11** in 72% yield. To modulate the HLB, an alkyl chain (R = *n*-C_nH_{2n+1}; *n* = 1, 4, 6, 8, 10 and 12) was introduced (step i, 90–95% yield), and the protecting isopropenyl group was then removed by using 1:1 water–H_2SO_4 at room temperature. Addition of the glucose derivative **4b** to benzimidazolones **13a**–**e** using the same procedure as previously reported[8] for **5**–**7** mainly provided the desired 3-*N*-alkyl-1-*N*-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)-benzimidazol-2-one derivatives **14a**–**e** (step iii, 93–97% yield). Subsequent deprotection of **14a**–**e** was performed by using Amberlyst-15 (H^+) in 4:1 dioxane–water to lead benzimidazolone derivatives **15a**–**e** in 72–89% yield (step iv).

2.3. Glycosylation of benzimidazolone

Efficient glycosylation methods are of particular interest in the synthesis of biologically important glycomolecules.[12] For example, the benzimidazolone bearing a glucose moiety on the aromatic nitrogen strongly



Scheme 2. Reagents and conditions: (i) K_2CO_3, 4:1 toluene–DMSO, 110 °C, 2 h; (ii) 9:1 CF_3COOH–H_2O, rt, 30 min.



Scheme 3. Reagents and conditions: (i) K_2CO_3, DMF, 110 °C, 12 h; (ii) H_2SO_4 (50%), DMF, rt, 12 h; (iii) K_2CO_3, DMSO, 110 °C, 4–12 h; (iv) Amberlyst 15 (H^+), 4:1 dioxane–H_2O, 80 °C, 1–2 h.

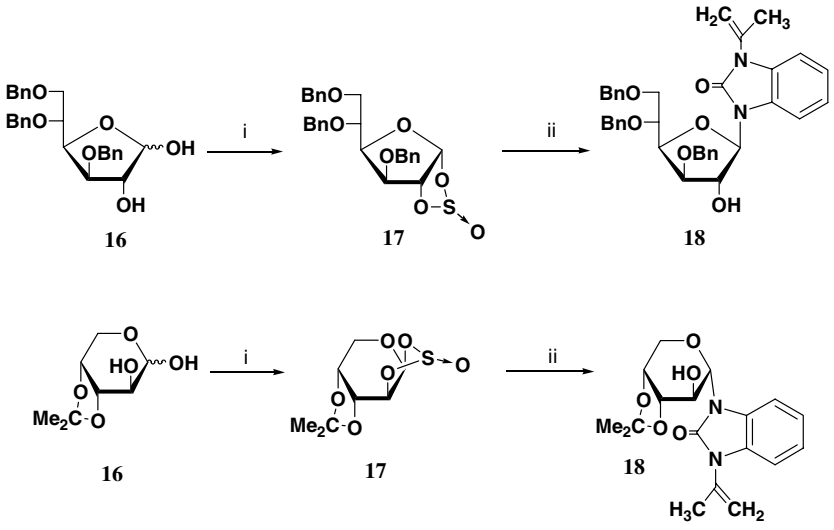
inhibits the growth of bacteria such as *Bacillus cereus*, *Streptomyces chartreusis* and *Escherichia coli*.[13] Glycosylation of benzimidazolone has been described from glycosyl bromide donors,[13,14] with mercuric acetate in the presence of pyridine. These conditions used very toxic reagents. In the previous work we had shown that *o*-sulfinyl monosaccharides are useful substrates for stereoselective N-glycosylation reactions to form glycosyl azides and 1,2-cyclic carbamates.[15] The nucleophilic opening of cyclic sulfites has also proven to be a useful method for the synthesis of chiral molecules and natural products.[16] We chose this alternative glycosylation using cyclic sulfite derivatives as glycosyl donors.

Our glycosylation conditions were applied to benzimidazolone **11** and studied with 3,4,6-tri-*O*-benzyl-1,2-*O*-sulfinyl-α-D-glucofuranose **17a** and 3,4-*O*-isopropylidene-1,2-*O*-sulfinyl-β-D-arabinopyranose **17b** (Scheme 4).[17] These latter compounds were obtained from 1,2-diols **16a** and **16b**, respectively, by sulfinylation reaction with *N*,*N*′-sulfinyldiimidazole.[15a,17]

The nucleophilic opening of the cyclic sulfites was realized by the potassium form of the benzimidazolinone anion, preliminary formed with K_2CO_3 in DMF. The 1,2-trans compounds **18a** and **18b** were obtained in 61% and 62% yields, respectively. The latter compounds were characterized by NMR spectroscopy showing the anomeric protons at 5.82 ppm with a coupling constant $J_{1,2}$ 0 Hz for the glucofuranosyl compound **18a** and 5.25 ppm with $J_{1,2}$ 9.8 Hz for the arabinopyranoside **18b**.

2.4. Surfactant properties

Preliminary study on surfactant properties was performed to determine water solubility and surface tension of this new range of benzimidazolones. The purpose was



Scheme 4. Reagents and conditions: (i) $SOIm_2$, THF, rt; (ii) K_2CO_3, DMF, **11**, 90 °C, 3 h.

Table 1. Water solubility (10^{-3} mol L^{-1}) and surface tension (γ, mN m^{-1}) of benzimidazolone derivatives (type I) at 25 °C

	Product									
	1	**2**	**3**	**8a**	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**
$R^2 = C_nH_{2n+1}$	—	—	—	H	CH_3	$n = 4$	$n = 6$	$n = 8$	$n = 10$	$n = 12$
Water solubility	<0.075	<0.067	<0.059	>200	>200	3.5	0.48	<0.015	<0.014	<0.013
γ	—	—	—	52.2[a]	46.6[a]	41.5[b]	44.9[b]	—	—	—
	9a	**9b**	**9e**	**9f**	**9g**	**10a**	**10b**	**10e**	**10f**	**10g**
$R = C_nH_{2n+1}$	$n = 4$	$n = 6$	$n = 8$	$n = 10$	$n = 12$	$n = 4$	$n = 6$	$n = 8$	$n = 10$	$n = 12$
Water solubility	>200	>200	<0.014	<0.013	<0.012	>200	>200	<0.014	<0.013	<0.012
γ	54.0[a]	55.1[a]	—	—	—	55.8[a]	56.0[a]	—	—	—

[a] 1 g L^{-1} solution.
[b] At water solubility value.

Table 2. Water solubility (10^{-3} mol L^{-1}) and surface tension (γ, mN m^{-1}) of benzimidazolone derivatives **13** and **15** at 25 °C

	Product									
	13a	**13b**	**13c**	**13d**	**13e**	**15a**	**15b**	**15c**	**15d**	**15e**
$R = C_nH_{2n+1}$	$n = 4$	$n = 6$	$n = 8$	$n = 10$	$n = 12$	$n = 4$	$n = 6$	$n = 8$	$n = 10$	$n = 12$
Water solubility	<0.053	<0.046	<0.041	<0.036	<0.033	13.1	2.69	0.47	0.02	0.006
γ	—	—	—	—	—	39.6[a]	35.2[a]	43.8[a]	43.0[a]	—

[a] 1 g L^{-1} solution.

also to evaluate the influence of substituents on these properties. The compounds (type I and II) were evaluated for their amphiphilic characteristics and were compared to native benzimidazolones **1**–**3**. The results are summarized in Tables 1 and 2.

Data provided in Table 1 indicate that benzimidazolones **1**–**3** have water solubility (S_w) lower than 10^{-4} mol L^{-1} at 25 °C. On one hand, benzimidazolone derivatives **8**–**10a**,**b** (type I) have a water solubility higher than 200×10^{-3} mol L^{-1}, while on the other hand, the water solubility of analogues **8**–**10c**,**d** bearing an alkyl chain ($R^2 = C_4H_9$ to C_6H_{13}) decreases abruptly for analogues **8**–**10c**,**d** ($R^2 = C_8H_{17}$ to $C_{16}H_{33}$) until becoming close to the values of benzimidazolones **1**–**3**. Moreover no critical micelle concentration (cmc) was observed.

As shown in Table 2, *N*-alkylbenzimidazolones **13a**–**e** have water solubility lower than 10^{-4} mol L^{-1}, whereas the graft of 6-deoxy-3-*O*-methyl-D-glucopyranos-6-yl **15a**–**e** allows a partial water solubility that decreases with the alkyl chain length. As previously observed with the first series of benzimidazolone derivatives **8**–**10**, we observed a strong reduction of water solubility when $n > 6$ (**15b**, C_nH_{2n+1}). Moreover, compounds **15a**–**d** have shown a lower surface tension than water ($\gamma = 35$–44 mN m^{-1} vs 72 mN m^{-1} for pure water), but these compounds have not shown any cmc.

In summary, two new series of benzimidazolone derivatives were synthesized. Grafting of one or two monosaccharides on benzimidazolone led to new compounds with a strongly increased water solubility. Therefore, the addition of an alkyl chain on the sugar moiety has a strong influence on the amphiphilic characteristics. We have also shown that glycosylated benzimidazolone derivatives could be obtained by cyclic sulfite derivatives as glycosyl donors. Biological evaluations (blood–brain barrier delivery) of the glycosyl benzimidazolone derivatives are currently underway.

3. Experimental

3.1. General methods

All chemicals were purchased from Aldrich or Acros (France). All solvents were distilled before use. THF was distilled from $LiAlH_4$, and thionyl chloride from triphenylphosphite (10% v/v). Thin-layer chromatography (TLC) was performed on Silica Gel 60 F_{254} (E. Merck) plates with visualization by UV light (254 nm) and/or charring with the vanillin–H_2SO_4 reagent. Column chromatography was performed using 230–400 mesh E. Merck silica gel. Melting points were determined on an automatic electrothermal apparatus and are uncorrected. Optical rotations were determined with a Jasco Dip 370 electronic micropolarimeter (10-cm cell). ^{1}H NMR spectra were recorded on a Bruker 300 WB spectrometer at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz. Chemical shifts are given as δ values with reference to tetramethylsilane (TMS) as internal standard. Low-resolution electrospray-ionization mass spectra (ESIMS) in the positive-ion mode were obtained on a Waters-Micromass ZQ quadrupole instrument, equipped with an electrospray (Z-spray)

ion source (Waters-Micromass, Manchester, UK). High-resolution electrospray-ionization experiments (HRE-SIMS) were performed on a Waters-Micromass Q-TOF *Ultima Global* hybrid quadrupole time-of-flight instrument, equipped with an electrospray (Z-spray) ion source (Waters-Micromass, Manchester, UK). Elemental analyses were performed by the IUT de Béthune, Département de Chimie (Béthune, France). The water solubility was determined for each sample at 25 °C. For cmc studies, an initial aqueous solution (C_0) of each compound was prepared at 25 °C. Several samples were obtained by diluting S_0 in the concentration range C_0: $C_0/2$, $C_0/4$, $C_0/8$, $C_0/16$, $C_0/32$, $C_0/64$, $C_0/128$ and $C_0/256$. The surface tension (γ) of each sample was measured by the Wilhelmy plate method (Prolabo TD 2000 tensiometer) after a period of more than 6 h in the thermostated cell (25 °C).

3.2. General procedure for condensation step (i)

To a solution of benzimidazolone **1**–**3**, K_2CO_3 (2.0 equiv) in 4:1 toluene–DMSO (100 g L^{-1}) at 100 °C were added activated carbohydrate derivatives **4a**–**g** (2 equiv). When the starting material was no longer detected by TLC or HPLC, the mixture was concentrated under reduced pressure. The residue was extracted with toluene–water, the organic layer was removed, washed with satd aq NaCl, dried (Na_2SO_4) and concentrated. The crude product was purified by silica gel chromatography (hexane–acetone gradient).

3.2.1. 1,3-*N*,*N*′-Bis-(6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (5a). White solid (97%): mp 121–123 °C; $[\alpha]_D^{27}$ −66.7 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta_{glucose}$ 5.88 (d, 2H, $J_{1,2}$ 3.5 Hz, H-1), 4.45 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.05 (d, 2H, $J_{3,4}$ 2.2 Hz, H-3), 3.95 (m, 2H, $J_{5,6a}$ 3.1 Hz, $J_{5,6b}$ 5.6 Hz, H-5), 3.85 (dd, 2H, $J_{4,5}$ 8.5 Hz, H-4), 3.81 (m, 2H, $J_{6a,6b}$ 12.0 Hz, H-6a), 3.75 (dd, 2H, H-6b), 1.45–1.15 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.41–7.05 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 110.5 (C_{iso}), 104.6 (C-1), 84.6 (C-2), 81.5 (C-4), 73.0 (C-3), 65.8 (C-5), 45.1 (C-6), 26.9–26.5 (CH_{3iso}) $\delta_{benzimidazolone}$ 154.1 (CO), 130.0 (C-8, C-9), 120.3 (C-5, C-6), 108.3 (C-4, C-7); Anal. Calcd for $C_{25}H_{34}N_2O_{11}$: C, 55.75; H, 6.36; N, 5.20. Found: C, 55.63; H, 6.29; N, 5.23.

3.2.2. 1,3-*N*,*N*′-Bis-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)benzimidazol-2-one (5b). White solid (78%): mp 159–161 °C; $[\alpha]_D^{27}$ −93.1 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.51 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.27, 4.05 (m, 4H, $J_{6a,6b}$ 14.4 Hz, H-6), 4.19 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.8 Hz, H-5), 3.96 (dd, 2H, $J_{4,5}$ 8.5 Hz, H-4), 3.84 (d, 2H, $J_{3,4}$ 3.0 Hz, H-3), 3.45 (s, 6H, OCH_3), 1.42–1.29 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.47–7.05 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.6 (C_{iso}), 104.9 (C-1), 83.0 (C-3), 82.1 (C-2), 81.5 (C-4), 68.9 (C-5), 58.4 (OCH_3), 45.4 (C-6), 26.8–26.5 (CH_{3iso}) $\delta_{benzimidazolone}$ 157.3 (CO), 129.7 (C-8, C-9), 121.8 (C-5, C-6), 108.6 (C-4, C-7); Anal. Calcd for $C_{27}H_{38}N_2O_{11}$: C, 57.23; H, 6.75; N, 4.94. Found: C, 57.21; H, 6.72; N, 4.87.

3.2.3. 1,3-*N*,*N*′-Bis-(3-*O*-butyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (5c). White solid (93%): mp 114–116 °C; $[\alpha]_D^{27}$ −75.2 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta_{glucose}$ 5.85 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.50 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.27, 4.05 (m, 4H, $J_{6a,6b}$ 14.4 Hz, H-6), 4.20 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 3.95 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.85 (d, 2H, $J_{3,4}$ 3.0 Hz, H-3), 3.54, 3.42, (2dt, 4H, O–CH_2^{α}), 1.49 (m, 4H, CH_2^{β}), 1.40–1.10 (4s, 12H, CH_{3iso}), 1.23 (m, 4H, CH_2^{γ}), 0.80 (t, 6H, CH_3^{ω}) $\delta_{benzimidazolone}$ 7.28–7.05 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.1 (C-1), 82.5 (C-3), 82.1 (C-2), 80.1 (C-4), 70.5 (O–CH_2^{α}), 68.7 (C-5), 45.5 (C-6), 31.7 (CH_2^{β}), 26.6–26.3 (CH_{3iso}), 19.2 (CH_2^{γ}), 13.8 (CH_3^{ω}) $\delta_{benzimidazolone}$ 157.4 (CO), 129.7 (C-8, C-9), 121.8 (C-5, C-6), 108.8 (C-4, C-7); Anal. Calcd for $C_{33}H_{50}N_2O_{11}$: C, 60.91; H, 7.75; N, 4.30. Found: C, 60.87; H, 7.72; N, 4.33.

3.2.4. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-hexyl-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (5d). White solid (80%): mp 92–95 °C; $[\alpha]_D^{27}$ −68.1 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta_{glucose}$ 5.85 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.51 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.27, 4.05 (m, 4H, $J_{6a,6b}$ 14.4 Hz, H-6), 4.20 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 3.95 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.85 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.53, 3.42, (2dt, 4H, O–CH_2^{α}), 1.48 (m, 4H, CH_2^{β}), 1.40–1.10 (4s, 12H, CH_{3iso}), 1.30–1.24 (m, 12H, CH_2), 0.82 (t, 6H, CH_3) $\delta_{benzimidazolone}$ 7.30–7.05 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.1 (C-1), 82.4 (C-3), 82.0 (C-2), 80.1 (C-4), 70.8 (O–CH_2^{α}), 68.7 (C-5), 45.5 (C-6), 31.4 (CH_2^{β}), 29.6, 25.6, 22.4 (CH_2), 26.6–26.2 (CH_{3iso}), 13.9 (CH_3) $\delta_{benzimidazolone}$ 157.4 (CO), 129.7 (C-8, C-9), 121.8 (C-5, C-6), 108.8 (C-4, C-7); Anal. Calcd for $C_{37}H_{58}N_2O_{11}$: C, 62.87; H, 8.27; N, 3.96. Found: C, 62.82; H, 8.25; N, 4.01.

3.2.5. 1,3-*N*,*N*′-Bis-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranos-6-yl)benzimidazol-2-one (5e). White solid (93%): mp 73–75 °C; $[\alpha]_D^{27}$ −80.3 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta_{glucose}$ 5.85 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.51 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.27, 4.05 (m, 4H, $J_{6a,6b}$ 14.4 Hz, H-6), 4.20 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 3.95 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.85 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.54, 3.42 (2dt, 4H, O–CH_2^{α}), 1.54 (m, 4H, CH_2^{β}), 1.32–1.18 (m, 20H, CH_2), 1.40–1.10 (4s, 12H, CH_{3iso}), 0.80 (t, 6H, CH_3) $\delta_{benzimidazolone}$ 7.32–7.05 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$

111.7 (C_{iso}), 105.1 (C-1), 82.5 (C-3), 82.1 (C-2), 80.1 (C-4), 70.9 (O–CH_2^{α}), 68.8 (C-5), 45.5 (C-6), 31.7–29.1, 25.9, 22.5 (CH_2), 26.6–26.2 (CH_{3iso}), 14.0 (CH_3) $\delta_{benzimidazolone}$ 157.4 (CO), 129.7 (C-8, C-9), 121.7 (C-5, C-6), 108.7 (C-4, C-7); Anal. Calcd for $C_{41}H_{66}N_2O_{11}$: C, 64.54; H, 8.72; N, 3.67. Found: C, 64.50; H, 8.69; N, 3.70.

3.2.6. 1,3-*N*,*N*′-Bis-(3-*O*-decyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (5f). Colourless syrup (79%): $[\alpha]_D^{27}$ −76.4 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.50 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.25, 4.05 (m, 4H, $J_{6a,6b}$ 14.4 Hz, H-6), 4.20 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 3.95 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.85 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.54, 3.42 (2dt, 4H, O–CH_2^{α}), 1.49 (m, 4H, CH_2^{β}), 1.32–1.22 (m, 28H, CH_2), 1.40–1.10 (4s, 12H, CH_{3iso}), 0.82 (t, 6H, CH_3) $\delta_{benzimidazolone}$ 7.28–7.02 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.1 (C-1), 82.4 (C-3), 82.1 (C-2), 80.2 (C-4), 70.8 (O–CH_2^{α}), 68.7 (C-5), 45.5 (C-6), 31.6–29.1, 26.0, 22.5 (CH_2), 26.6–26.2 (CH_{3iso}), 13.9 (CH_3) $\delta_{benzimidazolone}$ 157.4 (CO), 129.9 (C-8, C-9), 121.8 (C-5, C-6), 108.7 (C-4, C-7); Anal. Calcd for $C_{45}H_{74}N_2O_{11}$: C, 65.99; H, 9.10; N, 3.42. Found: C, 65.85; H, 8.99; N, 3.45.

3.2.7. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (5g). White solid (90%): mp 61–62 °C; $[\alpha]_D^{27}$ −69.7 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.50 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.25, 4.05 (m, 4H, $J_{6a,6b}$ 14.4 Hz, H-6), 4.20 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 3.95 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.85 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.58, 3.52 (2dt, 4H, O–CH_2^{α}), 1.54 (m, 4H, CH_2^{β}), 1.40–1.10 (4s, 12H, CH_{3iso}), 1.32–1.23 (m, 36H, CH_2), 0.84 (t, 6H, CH_3) $\delta_{benzimidazolone}$ 7.28–7.02 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.2 (C-1), 82.4 (C-3), 82.1 (C-2), 80.0 (C-4), 70.7 (O–CH_2^{α}), 68.7 (C-5), 45.6 (C-6), 31.8–29.2, 25.9, 22.6 (CH_2), 26.6–26.3 (CH_{3iso}), 14.0 (CH_3) $\delta_{benzimidazolone}$ 157.4 (CO), 129.7 (C-8, C-9), 121.6 (C-5, C-6), 108.7 (C-4, C-7); Anal. Calcd for $C_{49}H_{82}N_2O_{11}$: C, 67.25; H, 9.44; N, 3.20. Found: C, 67.21; H, 9.43; N, 3.18.

3.2.8. 1,3-*N*,*N*′-Bis-(6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)-5-methylbenzimidazol-2-one (6a). White solid (90%): mp 120–122 °C; $[\alpha]_D^{27}$ −60.6 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.88, 5.84 (2d, 2H, $J_{1,2}$ 3.5 Hz, H-1), 4.50 (2d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.22 (d, 2H, $J_{3,4}$ 2.7 Hz, H-3), 4.13 (m, 2H, H-5), 4.05 (dd, 2H, $J_{4,5}$ 6.8 Hz, H-4), 3.80–3.74 (m, 2H, $J_{6a,6b}$ 12.4 Hz, H-6), 1.42–1.26 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.00 (s, 1H, H-4), 6.94 (d, 1H, H-7), 6.83 (d, 1H, H-6), 2.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.6, 111.5 (C_{iso}), 105.3, 105.2 (C-1), 84.8 (C-2), 80.6 (C-4), 74.2 (C-3), 67.7 (C-5), 45.9, 45.1 (C-6), 26.7–26.1 (CH_{3iso}) $\delta_{benzimidazolone}$ 156.6 (CO), 131.7 (C-5), 129.5, 127.2 (C-8, C-9), 122.5 (C-6), 109.2, 109.1 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{26}H_{36}N_2O_{11}$: C, 56.51; H, 6.57; N, 5.07. Found: C, 56.45; H, 6.56; N, 5.12.

3.2.9. 1,3-*N*,*N*′-Bis-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)-5-methylbenzimidazol-2-one (6b). White solid (70%): mp 190–192 °C; $[\alpha]_D^{27}$ −104.0 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, 2H, $J_{1,2}$ 3.7 Hz, H-1), 4.52 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.25 (dd, 2H, $J_{6a,6b}$ 14.6 Hz, H-6a), 4.20 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 4.05 (dd, 2H, H-6b), 3.96 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.75 (d, 2H, $J_{3,4}$ 2.5 Hz, H-3), 3.45 (2s, 6H, OCH_3), 1.40–1.30 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.50–6.91 (m, 3H, H_{arom}), 2.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.2 (C-1), 83.9 (C-3), 81.8 (C-2), 80.0 (C-4), 68.7 (C-5), 58.2 (OCH_3), 45.7 (C-6), 26.6–26.2 (CH_{3iso}) $\delta_{benzimidazolone}$ 157.7 (CO), 131.7 (C-5), 129.5, 127.5 (C-8, C-9), 122.5 (C-6), 109.2, 108.4 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{28}H_{40}N_2O_{11}$: C, 57.92; H, 6.94; N, 4.82. Found: C, 57.86; H, 6.89; N, 4.93.

3.2.10. 1,3-*N*,*N*′-Bis-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranos-6-yl)-5-methylbenzimidazol-2-one (6e). Colourless syrup (80%): $[\alpha]_D^{27}$ −80.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.94 (d, 2H, $J_{1,2}$ 3.5 Hz, H-1), 4.54 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.31 (dd, 2H, $J_{6a,6b}$ 14.2 Hz, H-6a), 4.25 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.2 Hz, H-5), 4.08 (dd, 2H, H-6b), 4.02 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.98 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.58–3.52 (2dt, 4H, O–CH_2^{α}), 1.54 (m, 4H, CH_2^{β}), 1.32–1.24 (m, 20H, CH_2), 0.82 (s, 6H, CH_3), 1.40–1.15 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.12–6.88 (m, 3H, H_{arom}), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.1 (C-1), 82.5 (C-3), 82.1 (C-2), 80.1 (C-4), 70.9 (O–CH_2^{α}), 69.1 (C-5), 45.5 (C-6), 31.5–29.3, 25.9, 22.6 (CH_2), 26.6–26.3 (CH_{3iso}), 14.0 (CH_3) $\delta_{benzimidazolone}$ 157.6 (CO), 131.6 (C-5), 129.7, 127.5 (C-8, C-9), 122.4 (C-6), 109.3, 108.4 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{42}H_{68}N_2O_{11}$: C, 64.92; H, 8.82; N, 3.60. Found: C, 64.90; H, 8.81; N, 3.61.

3.2.11. 1,3-*N*,*N*′-Bis-(3-*O*-decyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)-5-methylbenzimidazol-2-one (6f). Colourless syrup (75%): $[\alpha]_D^{27}$ −80.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, 2H, $J_{1,2}$ 3.5 Hz, H-1), 4.50 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.25 (dd, 2H, $J_{6a,6b}$ 14.4 Hz, H-6a), 4.20 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.4 Hz, H-5), 4.05 (dd, 2H, H-6b), 4.02 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.98 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.57–3.51 (2dt, 4H, O–CH_2^{α}), 1.50 (m, 4H, CH_2^{β}), 1.32–1.23 (m, 28H, CH_2), 0.84 (s, 6H, CH_3), 1.40–1.15 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.12–6.88 (m, 3H, H_{arom}), 2.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta_{glucose}$ 111.7 (C_{iso}),

105.1 (C-1), 82.5 (C-3), 82.2 (C-2), 80.1 (C-4), 70.8 (O–CH_2^{α}), 69.8 (C-5), 45.6 (C-6), 31.8–29.3, 25.9, 22.6 (CH_2), 26.6–26.3 (CH_{3iso}), 14.0 (CH_3) $\delta_{benzimidazolone}$ 157.6 (CO), 131.7 (C-5), 129.8, 127.5 (C-8, C-9), 122.4 (C-6), 109.3, 108.4 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{46}H_{76}N_2O_{11}$: C, 66.32; H, 9.19; N, 3.36. Found: C, 66.21; H, 8.99; N, 3.43.

3.2.12. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)-5-methylbenzimidazol-2-one (6g). White solid (82%): mp 56–57 °C; $[\alpha]_D^{27}$ −72.0 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, 2H, $J_{1,2}$ 3.5 Hz, H-1), 4.50 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.28 (dd, 2H, $J_{6a,6b}$ 14.2 Hz, H-6a), 4.21 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.2 Hz, H-5), 4.06 (dd, 2H, H-6b), 4.02 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.98 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.58–3.52 (2dt, 4H, O–CH_2^{α}), 1.54 (m, 4H, CH_2^{β}), 1.40–1.15 (4s, 12H, CH_{3iso}), 1.32–1.23 (m, 36H, CH_2), 0.84 (s, 6H, CH_3) $\delta_{benzimidazolone}$ 7.12–6.88 (m, 3H, H_{arom}), 2.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.1 (C-1), 82.5 (C-3), 82.2 (C-2), 80.0 (C-4), 70.8 (O–CH_2^{α}), 69.8 (C-5), 45.6 (C-6), 31.8–29.5, 25.9, 22.6 (CH_2), 26.6–26.2 (CH_{3iso}), 14.0 (CH_3) $\delta_{benzimidazolone}$ 157.6 (CO), 131.7 (C-5), 129.8, 127.5 (C-8, C-9), 122.4 (C-6), 109.2, 108.4 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{50}H_{84}N_2O_{11}$ C, 67.54; H, 9.52; N, 3.15. Found: C, 67.49; H, 9.48; N, 3.20.

3.2.13. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (7a). White solid (88%): mp 114–116 °C; $[\alpha]_D^{27}$ −67.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (2d, 2H, $J_{1,2}$ 3.2 Hz, H-1), 4.41 (2d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.22 (d, 2H, $J_{3,4}$ 2.8 Hz, H-3), 4.13 (m, 2H, H-5), 4.05 (2dd, 2H, $J_{4,5}$ 7.6 Hz, H-4), 3.90–3.74 (m, 2H, $J_{6a,6b}$ 11.5 Hz, H-6), 1.40–1.29 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.25–7.00 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.8 (C_{iso}), 105.2 (C-1), 84.7 (C-2), 80.5 (C-4), 74.2 (C-3), 67.6 (C-5), 45.3 (C-6), 26.6–26.0 (CH_{3iso}) $\delta_{benzimidazolone}$ 156.1 (CO), 130.3 (C-5), 129.0, 127.6 (C-8, C-9), 121.0 (C-6), 109.2, 109.1 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{25}H_{33}ClN_2O_{11}$: C, 52.40; H, 5.80; N, 4.89; Cl, 6.19. Found: C, 52.19; H, 5.75; N, 4.94; Cl, 6.23.

3.2.14. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)benzimidazol-2-one (7b). White solid (76%): mp 191–193 °C; $[\alpha]_D^{27}$ −119.9 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.87 (d, 2H, $J_{1,2}$ 3.7 Hz, H-1), 4.51 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.27 (dd, 2H, $J_{5,6a}$ 2.7 Hz, $J_{6a,6b}$ 14.4 Hz, H-6a), 4.20 (m, 2H, $J_{4,5}$ 8.5 Hz, $J_{5,6b}$ 5.8 Hz, H-5), 4.05 (dd, 2H, H-6b), 3.96 (dd, 2H, $J_{3,4}$ 2.9 Hz, H-4), 3.82 (d, 2H, H-3), 3.45 (2s, 6H, OCH_3), 1.40–1.30 (4s, 12H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.30–7.00 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.8 (C_{iso}), 105.1 (C-1), 83.6 (C-3), 81.7 (C-2), 79.9 (C-4), 68.6 (C-5), 58.1 (OCH_3), 45.6 (C-6), 26.6–26.2 (CH_{3iso}) $\delta_{benzimidazolone}$ 157.7 (CO), 130.5 (C-5), 129.3, 127.5 (C-8, C-9), 121.8 (C-6), 109.6, 109.2 (C-4, C-7); Anal. Calcd for $C_{27}H_{37}ClN_2O_{11}$: C, 53.96; H, 6.20; N, 4.66; Cl, 5.90. Found: C, 53.95; H, 6.18; N, 4.73; Cl, 5.79.

3.2.15. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-octyl-α-D-glucofuranos-6-yl)benzimidazol-2-one (7e). Colourless syrup (80%): $[\alpha]_D^{27}$ −99.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.92 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.52 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.30 (dd, 2H, $J_{6a,6b}$ 14.4 Hz, H-6a), 4.24 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.2 Hz, H-5), 4.05 (dd, 2H, H-6b), 4.02 (dd, 2H, $J_{4,5}$ 8.2 Hz, H-4), 3.98 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.58, 3.51 (2dt, 4H, O–CH_2^{α}), 1.54 (m, 4H, CH_2^{β}), 1.40–1.15 (4s, 12H, CH_{3iso}), 1.32–1.23 (m, 20H, CH_2), 0.85 (s, 6H, CH_3) $\delta_{benzimidazolone}$ 7.27–7.02 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.6 (C_{iso}), 105.2 (C-1), 82.4 (C-3), 82.2 (C-2), 80.0 (C-4), 70.8 (O–CH_2^{α}), 68.7 (C-5), 45.5 (C-6), 31.8–29.2, 26.0, 22.6 (CH_2), 26.6–26.2 (CH_{3iso}), 14.1 (CH_3) $\delta_{benzimidazolone}$ 157.4 (CO), 130.6 (C-5), 128.4, 127.4 (C-8, C-9), 121.8 (C-6), 109.6, 109.3 (C-4, C-7); Anal. Calcd for $C_{41}H_{65}ClN_2O_{11}$: C, 61.75; H, 8.21; N, 3.51; Cl, 4.44. Found: C, 61.54; H, 8.06; N, 3.58; Cl, 4.41.

3.2.16. 5-Chloro-1,3-*N*,*N*′-bis-(3-*O*-decyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (7f). Colourless syrup (79%): $[\alpha]_D^{27}$ −89.9 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.92 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.52 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.30 (dd, 2H, $J_{6a,6b}$ 14.4 Hz, H-6a), 4.24 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.2 Hz, H-5), 4.05–4.00 (m, 4H, H-6b, H-4), 3.96 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.58, 3.51 (2dt, 4H, O–CH_2^{α}), 1.54 (m, 4H, CH_2^{β}), 1.40–1.15 (4s, 12H, CH_{3iso}), 1.32–1.24 (m, 28H, CH_2), 0.85 (s, 6H, CH_3) $\delta_{benzimidazolone}$ 7.35–7.00 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.8 (C_{iso}), 105.1 (C-1), 82.4 (C-3), 82.1 (C-2), 79.9 (C-4), 70.9 (O–CH_2^{α}), 68.7 (C-5), 45.6 (C-6), 31.8–29.5, 25.9, 22.6 (CH_2), 26.6–26.3 (CH_{3iso}), 14.0 (CH_3) $\delta_{benzimidazolone}$ 157.4 (CO), 130.6 (C-5), 128.4, 127.5 (C-8, C-9), 121.8 (C-6), 109.6, 109.2 (C-4, C-7); Anal. Calcd for $C_{45}H_{73}ClN_2O_{11}$: C, 63.32; H, 8.62; N, 3.28; Cl, 4.15. Found: C, 63.24; H, 8.58; N, 3.30; Cl, 4.16.

3.2.17. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-3-*O*-dodecyl-1,2-*O*-isopropylidene-α-D-glucofuranos-6-yl)benzimidazol-2-one (7g). Colourless syrup (88%): $[\alpha]_D^{27}$ −82.3 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.92 (d, 2H, $J_{1,2}$ 3.6 Hz, H-1), 4.52 (d, 2H, $J_{2,3}$ 0 Hz, H-2), 4.30 (dd, 2H, $J_{6a,6b}$ 14.4 Hz, H-6a), 4.24 (m, 2H, $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5.2 Hz, H-5), 4.07–4.00 (m, 4H, H-6b, H-4), 3.98 (d, 2H, $J_{3,4}$ 3.2 Hz, H-3), 3.58, 3.52 (2dt, 4H, O–CH_2^{α}), 1.54 (m, 4H, CH_2^{β}), 1.40–1.15 (4s, 12H, CH_{3iso}), 1.32–1.23 (m, 36H, CH_2), 0.85 (s, 6H, CH_3) $\delta_{benzimidazolone}$ 7.35–7.00 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$

111.8 (C_{iso}), 105.1 (C-1), 82.4 (C-3), 82.1 (C-2), 79.9 (C-4), 70.8 (O–CH_2^{α}), 68.7 (C-5), 45.6 (C-6), 31.8–29.3, 25.8, 22.6 (CH_2), 26.6–26.2 (CH_{3iso}), 14.0 (CH_3) $\delta_{benzimidazolone}$ 157.4 (CO), 130.6 (C-5), 128.4, 127.4 (C-8, C-9), 121.8 (C-6), 109.6, 109.3 (C-4, C-7); Anal. Calcd for $C_{49}H_{81}ClN_2O_{11}$: C, 64.70; H, 8.97; N, 3.07; Cl, 3.90. Found: C, 64.56; H, 8.92; N, 3.16; Cl, 3.86.

3.3. General procedure for deprotection step (ii)

The protected derivatives **5**–**7** were added to a stirred solution of 9:1 CF_3COOH–water (100 g L^{-1}) at room temperature. When the starting material was no longer detected by TLC or HPLC, the solution was concentrated to dryness under reduced pressure. The crude product was purified by silica gel chromatography (hexane–acetone gradient).

3.3.1. 1,3-*N*,*N*′-Bis-(6-deoxy-D-glucopyranos-6-yl)benzimidazol-2-one (8a). White solid (95%, α/β, 3:2): mp 202–204 °C; $[\alpha]_D^{27}$ 31.5–36.8 (*c* 0.6, MeOH); ^{13}C NMR (DMSO-d_6) $\delta_{glucose}$ 96.7 (C-1β), 92.1 (C-1α), 76.0, 74.5 (C-3), 73.9–69.3 (C-2, C-4, C-5), 42.9 (C-6) $\delta_{benzimidazolone}$ 153.8 (CO), 129.6 (C-8, C-9), 120.6 (C-5, C-6), 108.5 (C-4, C-7); Anal. Calcd for $C_{49}H_{81}N_2O_{11}$: C, 49.78; H, 5.72; N, 6.11. Found: C, 49.74; H, 5.69; N, 6.15.

3.3.2. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-methyl-D-glucopyranos-6-yl)benzimidazol-2-one (8b). White solid (81%, α/β, 4:3): mp 124–126 °C; $[\alpha]_D^{27}$ 48.5–50.2 (*c* 0.6, MeOH); ^{13}C NMR (DMSO-d_6) $\delta_{glucose}$ 96.6 (C-1β), 92.2 (C-1α), 85.6, 82.8 (C-3), 74.1–69.5 (C-2, C-4, C-5), 59.8 (OCH_3), 42.7 (C-6) $\delta_{benzimidazolone}$ 153.8 (CO), 129.6 (C-8, C-9), 120.7 (C-5, C-6), 108.7, 108.4 (C-4, C-7); Anal. Calcd for $C_{20}H_{28}N_2O_{11}$: C, 50.84; H, 5.97; N, 5.93. Found: C, 50.80; H, 5.94; N, 5.97.

3.3.3. 1,3-*N*,*N*′-Bis-(3-*O*-butyl-6-deoxy-D-glucopyranos-6-yl)benzimidazol-2-one (8c). White solid (90%, α/β, 9:5): mp 104–106 °C; $[\alpha]_D^{27}$ 103.3 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.7 (C-1β), 92.2 (C-1α), 84.3, 81.2 (C-3), 74.3–69.6 (C-2, C-4, C-5), 71.9 (O–CH_2^{α}), 42.8 (C-6), 31.9 (CH_2^{β}), 18.6 (CH_2^{γ}), 13.8 (CH_3) $\delta_{benzimidazolone}$ 156.1 (CO), 129.6 (C-8, C-9), 120.6 (C-5, C-6), 108.7, 108.4 (C-4, C-7); Anal. Calcd for $C_{20}H_{28}N_2O_{11}$: C, 56.83; H, 7.42; N, 4.91. Found: C, 56.79; H, 7.28; N, 4.97.

3.3.4. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-hexyl-D-glucopyranos-6-yl)benzimidazol-2-one (8d). White solid (88%, α/β, 9:5): mp 92–94 °C; $[\alpha]_D^{27}$ 102.1 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.7 (C-1β), 92.3 (C-1α), 83.6, 81.1 (C-3), 74.5–69.9 (C-2, C-4, C-5), 72.0 (O–CH_2^{α}), 42.4 (C-6), 31.8–29.1, 26.0, 22.6 (CH_2), 13.9 (CH_3) $\delta_{benzimidazolone}$ 155.8 (CO), 129.6 (C-8, C-9), 120.6 (C-5, C-6), 109.2 (C-4, C-7); Anal. Calcd for $C_{31}H_{50}N_2O_{11}$: C, 59.41; H, 8.04; N, 4.47. Found: C, 59.34; H, 7.97; N, 4.56.

3.3.5. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-octyl-D-glucopyranos-6-yl)benzimidazol-2-one (8e). White solid (80%, α/β, 7:4): mp 86–88 °C; $[\alpha]_D^{27}$ 92.7 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.9 (C-1β), 92.3 (C-1α), 83.3, 81.0 (C-3), 74.7–70.3 (C-2, C-4, C-5), 72.0 (O–CH_2^{α}), 42.3 (C-6), 31.8–29.1, 25.9, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 156.0 (CO), 129.8, 129.5 (C-8, C-9), 121.8 (C-5, C-6), 109.5 (C-4, C-7); Anal. Calcd for $C_{35}H_{58}N_2O_{11}$: C, 61.56; H, 8.56; N, 4.10. Found: C, 61.54; H, 8.53; N, 4.16.

3.3.6. 1,3-*N*,*N*′-Bis-(3-*O*-decyl-6-deoxy-D-glucopyranos-6-yl)benzimidazol-2-one (8f). White solid (83% yield, α/β, 2:0): mp 84–86 °C; $[\alpha]_D^{27}$ 103.2 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.9 (C-1β), 92.2 (C-1α), 83.4, 81.0 (C-3), 74.8–70.7 (C-2, C-4, C-5), 72.1 (O–CH_2^{α}), 42.3 (C-6), 31.8–29.2, 26.0, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 159.9 (CO), 129.8, 129.6 (C-8, C-9), 121.8 (C-5, C-6), 109.5 (C-4, C-7); Anal. Calcd for $C_{39}H_{66}N_2O_{11}$: C, 63.39; H, 9.00; N, 3.79. Found: C, 63.30; H, 8.94; N, 3.86.

3.3.7. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-dodecyl-D-glucopyranos-6-yl)benzimidazol-2-one (8g). White solid (84%, α/β, 7:4): mp 84–86 °C; $[\alpha]_D^{27}$ 80.1 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.9 (C-1β), 92.2 (C-1α), 83.3, 80.9 (C-3), 74.8–70.7 (C-2, C-4, C-5), 72.0 (O–CH_2^{α}), 42.3 (C-6), 31.8–29.1, 26.1, 25.9, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 156.1 (CO), 129.8, 129.5 (C-8, C-9), 121.8 (C-5, C-6), 109.5 (C-4, C-7); Anal. Calcd for $C_{43}H_{74}N_2O_{11}$: C, 64.96; H, 9.38; N, 3.52. Found: C, 64.92; H, 9.40; N, 3.54.

3.3.8. 1,3-*N*,*N*′-Bis-(6-deoxy-D-glucopyranos-6-yl)-5-methylbenzimidazol-2-one (9a). White solid (80%, α/β, 5:3): mp 196–198 °C; $[\alpha]_D^{27}$ 57.7–51.6 (*c* 0.6, MeOH); ^{13}C NMR (DMSO-d_6) $\delta_{glucose}$ 96.7 (C-1β), 92.1 (C-1α), 76.0, 74.5 (C-3), 73.8–69.4 (C-2, C-4, C-5), 42.9 (C-6) $\delta_{benzimidazolone}$ 153.8 (CO), 129.6 (C-8, C-9), 120.7 (C-5, C-6), 108.7, 108.4 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{20}H_{28}N_2O_{11}$: C, 50.84; H, 5.97; N, 5.93. Found: C, 50.81; H, 5.96; N, 5.97.

3.3.9. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-methyl-D-glucopyranos-6-yl)-5-methylbenzimidazol-2-one (9b). White solid (80%, α/β, 9:5): mp 128–130 °C; $[\alpha]_D^{27}$ 52.3–53.8 (*c* 0.6, MeOH); ^{13}C NMR (DMSO-d_6) $\delta_{glucose}$ 96.6 (C-1β), 92.2 (C-1α), 83.9, 82.8 (C-3), 74.1–69.5 (C-2, C-4, C-5), 59.8 (OCH_3), 42.7 (C-6) $\delta_{benzimidazolone}$ 154.0 (CO), 130.8 (C-5), 129.7, 127.5 (C-8, C-9), 121.1 (C-6), 109.09, 108.7 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for

$C_{21}H_{30}N_2O_{11}$: C, 51.85; H, 6.21; N, 5.76. Found: C, 51.81; H, 6.18; N, 5.86.

3.3.10. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-octyl-D-glucopyranos-6-yl)-5-methylbenzimidazol-2-one (9e). White solid (84%, α/β, 5:3): mp 87–89 °C; $[\alpha]_D^{27}$ 106.2 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.9 (C-1β), 92.3 (C-1α), 83.5, 81.0 (C-3), 74.7–70.7 (C-2, C-4, C-5), 72.0 ($O–CH_2^{\alpha}$), 42.3 (C-6), 31.8–29.2, 25.9, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 156.2 (CO), 131.6 (C-5), 129.9, 129.5 (C-8, C-9), 122.7 (C-6), 109.8, 109.2 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{36}H_{60}N_2O_{11}$: C, 62.05; H, 8.68; N, 4.02. Found: C, 62.00; H, 8.64; N, 4.04.

3.3.11. 1,3-*N*,*N*′-Bis-(3-*O*-decyl-6-deoxy-D-glucopyranos-6-yl)-5-methylbenzimidazol-2-one (9f). White solid (70%, α/β, 2): mp 90–92 °C; $[\alpha]_D^{27}$ 99.4 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.9 (C-1β), 92.3 (C-1α), 83.5, 80.9 (C-3), 74.8–70.8 (C-2, C-4, C-5), 72.1 ($O–CH_2^{\alpha}$), 42.3 (C-6), 31.8–29.3, 25.0, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 156.3 (CO), 131.6 (C-5), 129.9, 129.6 (C-8, C-9), 122.6 (C-6), 109.8, 109.2 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{40}H_{68}N_2O_{11}$: C, 63.80; H, 9.10; N, 3.72. Found: C, 63.76; H, 9.04; N, 3.78.

3.3.12. 1,3-*N*,*N*′-Bis-(6-deoxy-3-*O*-dodecyl-D-glucopyranos-6-yl)-5-methylbenzimidazol-2-one (9g). White solid (87%, α/β, 7:4): mp 85–87 °C; $[\alpha]_D^{27}$ 87.4 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 97.0 (C-1β), 92.3 (C-1α), 83.4, 81.1 (C-3), 74.9–70.7 (C-2, C-4, C-5), 72.0 ($O–CH_2^{\alpha}$), 42.3 (C-6), 31.9–29.1, 25.1, 22.6 (CH_2), 14.1 (CH_3) $\delta_{benzimidazolone}$ 156.3 (CO), 131.6 (C-5), 130.0, 129.6 (C-8, C-9), 122.6 (C-6), 109.8, 109.0 (C-4, C-7), 21.4 (CH_3); Anal. Calcd for $C_{44}H_{76}N_2O_{11}$: C, 65.32; H, 9.47; N, 3.46. Found: C, 65.25; H, 9.42; N, 3.50.

3.3.13. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-D-glucopyranos-6-yl)benzimidazol-2-one (10a). The White solid (84%, α/β, 3:2): mp 170–172 °C; $[\alpha]_D^{27}$ 38.4–33.5 (*c* 0.6, MeOH); ^{13}C NMR (DMSO-d_6) $\delta_{glucose}$ 96.6 (C-1β), 92.1 (C-1α), 76.0, 74.5 (C-3), 73.8–69.4 (C-2, C-4, C-5), 43.1 (C-6) $\delta_{benzimidazolone}$ 153.7 (CO), 128.6 (C-8, C-9), 120.3 (C-5, C-6), 108.8, 108.5 (C-4, C-7); Anal. Calcd for $C_{19}H_{25}ClN_2O_{11}$: C, 46.30; H, 5.11; N, 5.68; Cl, 7.19. Found: C, 47.23; H, 5.33; N, 5.60; Cl, 7.05.

3.3.14. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-3-*O*-methyl-D-glucopyranos-6-yl)benzimidazol-2-one (10b). White solid (70%, α/β, 5:3): mp 143–146 °C; $[\alpha]_D^{27}$ 44.8–45.8 (*c* 0.6, MeOH); ^{13}C NMR (DMSO-d_6) $\delta_{glucose}$ 96.6 (C-1β), 92.2 (C-1α), 85.9, 82.8 (C-3), 74.1–69.4 (C-2, C-4, C-5), 59.8 (OCH_3), 42.9 (C-6) $\delta_{benzimidazolone}$ 153.7 (CO), 130.8 (C-5), 128.6, 124.9 (C-8, C-9), 120.3 (C-6), 109.9, 108.5 (C-4, C-7); Anal. Calcd for $C_{20}H_{27}ClN_2O_{11}$: C, 47.39; H, 5.37; N, 5.53; Cl, 6.99. Found: C, 47.23; H, 5.33; N, 5.60; Cl, 7.05.

3.3.15. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-3-*O*-octyl-D-glucopyranos-6-yl)benzimidazol-2-one (10e). White solid (83%, α/β, 5:3): mp 88–90 °C; $[\alpha]_D^{27}$ 109.2 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.8 (C-1β), 92.2 (C-1α), 83.4, 81.0 (C-3), 74.7–70.3 (C-2, C-4, C-5), 72.1 ($O–CH_2^{\alpha}$), 42.5 (C-6), 31.8–29.3, 25.9, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 156.0 (CO), 130.6 (C-5), 128.2, 127.3 (C-8, C-9), 121.3 (C-6), 110.2, 109.8 (C-4, C-7); Anal. Calcd for $C_{35}H_{57}ClN_2O_{11}$: C, 58.60; H, 8.01; N, 3.90; Cl, 4.94. Found: C, 58.56; H, 7.93; N, 3.97; Cl, 4.97.

3.3.16. 5-Chloro-1,3-*N*,*N*′-bis-(3-*O*-decyl-6-deoxy-D-glucopyranos-6-yl)benzimidazol-2-one (10f). White solid (80%, α/β, 2): mp 83–85 °C; $[\alpha]_D^{27}$ 104.3 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.9 (C-1β), 92.3 (C-1α), 83.4, 81.0 (C-3), 74.7–70.6 (C-2, C-4, C-5), 72.1 ($O–CH_2^{\alpha}$), 42.3 (C-6), 31.8–29.2, 25.9, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 156.0 (CO), 130.7 (C-5), 128.2, 127.2 (C-8, C-9), 121.4 (C-6), 110.2, 109.8 (C-4, C-7); Anal. Calcd for $C_{39}H_{65}ClN_2O_{11}$: C, 60.57; H, 8.47; N, 3.62; Cl, 4.58. Found: C, 60.56; H, 8.45; N, 3.64; Cl, 4.54.

3.3.17. 5-Chloro-1,3-*N*,*N*′-bis-(6-deoxy-3-*O*-dodecyl-D-glucopyranos-6-yl)benzimidazol-2-one (10g). White solid (88%, α/β, 7:4): mp 90–92 °C; $[\alpha]_D^{27}$ 90.6 (*c* 0.6, $CHCl_3$); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.9 (C-1β), 92.3 (C-1α), 83.4, 81.0 (C-3), 74.7–70.6 (C-2, C-4, C-5), 72.0 ($O–CH_2^{\alpha}$), 42.3 (C-6), 31.8–29.3, 25.8, 22.6 (CH_2), 14.0 (CH_3) $\delta_{benzimidazolone}$ 156.0 (CO), 130.6 (C-5), 128.5, 128.2 (C-8, C-9), 121.9 (C-6), 110.2, 109.8 (C-4, C-7); Anal. Calcd for $C_{43}H_{73}ClN_2O_{11}$: C, 62.26; H, 8.87; N, 3.38; Cl, 4.27. Found: C, 62.20; H, 8.84; N, 3.42; Cl, 4.29.

3.4. General procedure for alkylation step (i)

To a solution of 1-*N*-isopropenylbenzimidazolone **11** and K_2CO_3 (1.5 equiv) in DMF (160 g L^{-1}) at 110 °C, was added *n*-bromoalkyl benzimidazolone (1.1 equiv, C_nH_{2n+1}, $n = 4$, 6, 8, 10, 12). When starting material was no longer detected by TLC or HPLC, the mixture was extracted with toluene–aq NH_4Cl, the organic layer was recovered, washed with satd aq NaCl, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (hexane–acetone gradient).

3.4.1. 1-*N*-Butyl-3-*N*-isopropenylbenzimidazol-2-one (12a). Colourless syrup (94%): ^1H NMR ($CDCl_3$) δ 7.10–6.85 (m, 4H, H_{arom}), 5.25, 5.10 (2s, 2H, C=CH_2), 3.80 (t, 2H, N–CH_2^{α}), 2.20 (s, 3H, CH_3), 1.70 (m, 2H, CH_2^{β}), 1.35 (m, 2H, CH_2^{γ}), 0.95 (t, 3H, CH_3^{ω}); ^{13}C NMR ($CDCl_3$) δ 152.7 (CO), 138.1 (*C*=CH_2), 129.7, 128.8 (C-8, C-9), 121.3, 121.0 (C-5, C-6), 112.5 (C=*C*H_2), 108.9, 107.6 (C-4, C-7), 40.7 (N–CH_2^{α}), 30.3

(CH_2^{β}), 20.1 (CH_3), 20.0 (CH_2^{γ}), 13.7 (CH_3^{ω}); Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.16. Found: C, 72.56; H, 7.86; N, 12.25.

3.4.2. 1-*N*-Hexyl-3-*N*-isopropenylbenzimidazol-2-one (12b). Colourless syrup (92%): ^{1}H NMR ($CDCl_3$) δ 7.10–6.80 (m, 4H, H_{arom}), 5.25, 5.15 (2s, 2H, C=CH_2), 3.75 (t, 2H, N–CH_2^{α}), 2.20 (s, 3H, CH_3), 1.70 (m, 2H, CH_2^{β}), 1.40–1.10 (m, 2H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 152.7 (CO), 138.2 (*C*=CH_2), 129.6, 128.7 (C-8, C-9), 121.3, 120.9 (C-5, C-6), 112.3 (C=*C*H_2), 108.6, 107.6 (C-4, C-7), 40.7 (N–CH_2^{α}), 31.3–26.4, 22.4 (CH_2), 20.1 (CH_3), 13.7 (CH_3); Anal. Calcd for $C_{16}H_{22}N_2O$: C, 74,38; H, 8.58; N, 10.84. Found: C, 74.31; H, 8.54; N, 10.89.

3.4.3. 3-*N*-Isopropenyl-1-*N*-octylbenzimidazol-2-one (12c). Colourless syrup (95%): ^{1}H NMR ($CDCl_3$) δ 7.10–6.80 (m, 4H, H_{arom}), 5.25, 5.15 (2s, 2H, C=CH_2), 3.74 (t, 2H, N–CH_2^{α}), 2.20 (s, 3H, CH_3), 1.70 (m, 2H, CH_2^{β}), 1.40–1.12 (m, 10H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 152.7 (CO), 138.1 (*C*=CH_2), 129.6, 128.9 (C-8, C-9), 121.3, 120.9 (C-5, C-6), 112.4 (C=*C*H_2), 108.8, 107.7 (C-4, C-7), 40.7 (N–CH_2^{α}), 31.8–26.5, 22.4 (CH_2), 20.1 (CH_3), 13.8 (CH_3); Anal. Calcd for $C_{18}H_{26}N_2O$: C, 75.48; H, 9.15; N, 9.78. Found: C, 75.45; H, 9.12; N, 9.85.

3.4.4. 1-*N*-Decyl-3-*N*-isopropenylbenzimidazol-2-one (12d). Colourless syrup (90%): ^{1}H NMR ($CDCl_3$) δ 7.11–6.80 (m, 4H, H_{arom}), 5.25, 5.15 (2s, 2H, C=CH_2), 3.75 (t, 2H, N–CH_2^{α}), 2.20 (s, 3H, CH_3), 1.70 (m, 2H, CH_2^{β}), 1.40–1.10 (m, 14H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 152.7 (CO), 138.0 (*C*=CH_2), 129.7, 128.8 (C-8, C-9), 121.4, 121.0 (C-5, C-6), 112.3 (C=*C*H_2), 108.6, 107.8 (C-4, C-7), 40.9 (N–CH_2^{α}), 31.9–26.6, 22.4 (CH_2), 20.1 (CH_3), 13.9 (CH_3). Anal. Calcd for $C_{20}H_{30}N_2O$: C, 76.39; H, 9.61; N, 8.90. Found: C, 76.31; H, 9.52; N, 8.84.

3.4.5. 1-*N*-Dodecyl-3-*N*-isopropenylbenzimidazol-2-one (12e). Colourless syrup (90%): ^{1}H NMR ($CDCl_3$) δ 7.10–6.80 (m, 4H, H_{arom}), 5.25, 5.15 (2s, 2H, C=CH_2), 3.74 (t, 2H, N–CH_2^{α}), 2.20 (s, 3H, CH_3), 1.70 (m, 2H, CH_2^{β}), 1.40–1.12 (m, 18H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 152.7 (CO), 138.1 (*C*=CH_2), 129.7, 128.8 (C-8, C-9), 121.3, 120.9 (C-5, C-6), 112.5 (C=*C*H_2), 108.6, 107.6 (C-4, C-7), 41.0 (N–CH_2^{α}), 31.8–26.8, 22.6 (CH_2), 20.1 (CH_3), 14.0 (CH_3); Anal. Calcd for $C_{22}H_{34}N_2O$: C, 77.14; H, 10.01; N, 8.18. Found: C, 77.10; H, 9.89; N, 8.16.

3.5. General procedure for deprotection step (ii)

To a solution of protected derivatives **12a**–**e** in DMF (100 g L^{-1}) at room temperature was added a solution of 1:1 H_2SO_4–water. After 12 h the final products **14a**–**e** were obtained as crystals after diluting the mixture in cold water and after filtration.

3.5.1. 1-*N*-Butylbenzimidazol-2-one (13a). White solid (75%): mp 98–100 °C; ^{13}C NMR ($CDCl_3$) δ 156.3 (CO), 130.8, 128.5 (C-8, C-9), 121.8, 121.5 (C-5, C-6), 110.3, 108.3 (C-4, C-7), 41.1 (N–CH_2^{α}), 30.9–20.5 (CH_2), 14.1 (CH_3); Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42; N, 14.72. Found: C, 69.38; H, 8.35; N, 14.75.

3.5.2. 1-*N*-Hexylbenzimidazol-2-one (13b). White solid (83%): mp 56–59 °C; ^{13}C NMR ($CDCl_3$) δ 156.3 (CO), 130.8, 128.5 (C-8, C-9), 121.7, 121.5 (C-5, C-6), 110.3, 108.3 (C-4, C-7), 41.3 (N–CH_2^{α}), 31.9–22.9 (CH_2), 14.4 (CH_3); Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.52; H, 8.21; N, 12.83. Found: C, 71.49; H, 8.16; N, 12.75.

3.5.3. 1-*N*-Octylbenzimidazol-2-one (13c). White solid (94%): mp 68–70 °C; ^{13}C NMR ($CDCl_3$) δ 156.1 (CO), 130.7, 128.4 (C-8, C-9), 121.8, 121.6 (C-5, C-6), 110.1, 108.3 (C-4, C-7), 41.3 (N–CH_2^{α}), 32.2–23.0 (CH_2), 14.1 (CH_3); Anal. Calcd for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00; N, 11.37. Found: C, 73.05; H, 8.89; N, 11.48.

3.5.4. 1-*N*-Decylbenzimidazol-2-one (13d). White solid (98%): mp 64–66 °C; ^{13}C NMR ($CDCl_3$) δ 156.2 (CO), 130.7, 128.3 (C-8, C-9), 121.7, 121.4 (C-5, C-6), 110.0, 108.3 (C-4, C-7), 41.2 (N–CH_2^{α}), 32.3–23.0 (CH_2), 14.1 (CH_3); Anal. Calcd for $C_{17}H_{26}N_2O$: C, 74.41; H, 9.55; N, 10.21. Found: C, 74.39; H, 5.79; N, 10.31.

3.5.5. 1-*N*-Dodecylbenzimidazol-2-one (13e). White solid (99%): mp 74–76 °C; ^{13}C NMR ($CDCl_3$) δ 156.2 (CO), 130.8, 128.5 (C-8, C-9), 121.9, 121.7 (C-5, C-6), 110.0, 108.3 (C-4, C-7), 41.2 (N–CH_2^{α}), 32.1–22.9 (CH_2), 14.1 (CH_3); Anal. Calcd for $C_{19}H_{30}N_2O$: C, 75.45; H, 10.00; N, 9.26. Found: C, 75.42; H, 9.87; N, 9.32.

3.6. General procedure for condensation step (iii)

To a solution of benzimidazolones **13a**–**e** and K_2CO_3 (1.1 equiv) in DMSO (100 g L^{-1}) at 110 °C was added activated carbohydrate derivative **4b** (1 equiv). When the starting material was no longer detected by TLC or HPLC, the mixture was extracted with toluene–aq NH_4Cl, the organic layer was recovered, washed with satd aq NaCl, dried (Na_2SO_4) and concentrated under diminished pressure. The crude product was purified by silica gel chromatography (hexane–acetone gradient).

3.6.1. 3-*N*-Butyl-1-*N*-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)benzimidazol-2-one (14a). White solid (97%): mp 100–102 °C; $[\alpha]_D^{26}$ −76.9 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.93 (d, H, $J_{1,2}$ 3.7 Hz, H-1), 4.52 (d, H, $J_{2,3}$ 0 Hz, H-2), 4.20 (m, H,

$J_{5,6a}$ 2.7 Hz, $J_{5,6b}$ 5.7 Hz, H-5), 4.28, 4.05 (2dd, 2H, $J_{6a,6b}$ 14.6 Hz, H-6), 3.95 (dd, H, $J_{4,5}$ 8.6 Hz, H-4), 3.89 (d, H, $J_{3,4}$ 3.9 Hz, H-3), 3.40 (s, 3H, OCH_3), 1.35, 1.23 (2s, 6H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.47–7.05 (m, 4H, H_{arom}), 3.85 (t, 2H, N–CH_2^{α}), 1.71 (m, 2H, CH_2^{β}), 1.30 (m, 2H, CH_2^{γ}), 0.95 (t, 3H, CH_3^{ω}); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.6 (C_{iso}), 105.1 (C-1), 83.6 (C-3), 81.8 (C-2), 80.1 (C-4), 68.8 (C-5), 58.2 (OCH_3), 45.6 (C-6), 26.6–26.2 (CH_{3iso}) $\delta_{benzimidazolone}$ 156.0 (CO), 129.7, 129.3 (C-8, C-9), 121.5, 121.3 (C-5, C-6), 108.7, 107.7 (C-4, C-7), 41.0 (N–CH_2^{α}), 30.4 (CH_2^{β}), 20.0 (CH_2^{γ}), 13.7 (CH_3^{ω}); Anal. Calcd for $C_{21}H_{30}N_2O_6$: C, 62.05; H, 7.44; N, 6.89. Found: C, 62.00; H, 7.39; N, 6.96.

3.6.2. 1-*N*-(6-Deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)-3-*N*-hexylbenzimidazol-2-one (14b). White solid (96%): mp 96–98 °C; $[\alpha]_D^{26}$ −68.4 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, H, $J_{1,2}$ 3.7 Hz, H-1), 4.52 (d, H, $J_{2,3}$ 0 Hz, H-2), 4.20 (m, H, $J_{5,6a}$ 2.7 Hz, $J_{5,6b}$ 5.7 Hz, H-5), 4.28, 4.06 (2dd, 2H, $J_{6a,6b}$ 14.6 Hz, H-6), 3.95 (dd, H, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 8.6 Hz, H-4), 3.85 (m, 2H, H-3), 3.40 (s, 3H, OCH_3), 1.34, 1.24 (2s, 6H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.20–6.85 (m, 4H, H_{arom}), 3.75 (t, 2H, N–CH_2^{α}), 1.70 (m, 2H, CH_2^{β}), 1.40–1.10 (m, 6H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.6 (C_{iso}), 105.0 (C-1), 83.5 (C-3), 81.8 (C-2), 80.2 (C-4), 68.3 (C-5), 58.1 (OCH_3), 45.4 (C-6), 26.5, 26.1 (CH_{3iso}) $\delta_{benzimidazolone}$ 155.8 (CO), 129.7, 129.3 (C-8, C-9), 121.3, 121.1 (C-5, C-6), 108.6, 107.5 (C-4, C-7), 41.0 (N–CH_2^{α}), 31.5, 29.3, 25.7, 22.7 (CH_2), 13.7 (CH_3); Anal. Calcd for $C_{25}H_{38}N_2O_6$: C, 63.58; H, 7.89; N, 6.44. Found: C, 63.53; H, 7.79; N, 6.40.

3.6.3. 1-*N*-(6-Deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)-3-*N*-octylbenzimidazol-2-one (14c). White solid (95%): mp 70–72 °C; $[\alpha]_D^{26}$ −68.0 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.94 (d, H, $J_{1,2}$ 3.7 Hz, H-1), 4.55 (d, H, $J_{2,3}$ 0 Hz, H-2), 4.22 (m, H, $J_{5,6a}$ 2.7 Hz, $J_{5,6b}$ 5.7 Hz, H-5), 4.30, 4.06 (2dd, 2H, $J_{6a,6b}$ 14.6 Hz, H-6), 3.95 (dd, H, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 8.6 Hz, H-4), 3.85 (m, 4H, H-3), 3.40 (s, 3H, OCH_3), 1.34, 1.24 (2s, 6H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.20–6.85 (m, 4H, H_{arom}), 3.85 (N–CH_2^{α}), 1.70 (m, 2H, CH_2^{β}), 1.40–1.10 (m, 10H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.6 (C_{iso}), 105.0 (C-1), 83.5 (C-3), 81.9 (C-2), 80.3 (C-4), 68.7 (C-5), 58.1 (OCH_3), 45.2 (C-6), 26.5, 26.1 (CH_{3iso}) $\delta_{benzimidazolone}$ 155.8 (CO), 129.7, 129.3 (C-8, C-9), 121.3, 121.1 (C-5, C-6), 108.6, 107.5 (C-4, C-7), 41.1 (N–CH_2^{α}), 31.6–29.3, 25.9, 22.3 (CH_2), 13.7 (CH_3); Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 64.91; H, 8.28; N, 6.06. Found: C, 64.86; H, 8.26; N, 6.09.

3.6.4. 3-*N*-Decyl-1-*N*-(6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos)-6-ylbenzimidazol-2-one (14d). White solid (93%): mp 53–55 °C; $[\alpha]_D^{26}$ −62.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.93 (d, H, $J_{1,2}$ 3.7 Hz, H-1), 4.57 (d, H, $J_{2,3}$ 0 Hz, H-2), 4.25 (m, H, $J_{5,6a}$ 2.7 Hz, $J_{5,6b}$ 5.7 Hz, H-5), 4.32, 4.09 (2dd, 2H, $J_{6a,6b}$ 14.6 Hz, H-6), 3.95 (dd, H, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 8.6 Hz, H-4), 3.85 (m, 4H, H-3), 3.40 (s, 3H, OCH_3), 1.35, 1.23 (2s, 6H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.23–6.89 (m, 4H, H_{arom}); 3.80 (t, 2H, N–CH_2^{α}), 1.70 (m, 2H, CH_2^{β}), 1.38–1.14 (m, 14H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.1 (C-1), 83.6 (C-3), 81.8 (C-2), 80.1 (C-4), 68.9 (C-5), 58.2 (OCH_3), 45.6 (C-6), 26.5, 26.2 (CH_{3iso}) $\delta_{benzimidazolone}$ 155.2 (CO), 129.7, 129.3 (C-8, C-9), 121.4, 121.3 (C-5, C-6), 108.7, 107.7 (C-4, C-7), 41.4 (N–CH_2^{α}), 31.8–29.4, 26.0, 22.0 (CH_2), 13.8 (CH_3); Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.09; H, 8.63; N, 5.71. Found: C, 65.96; H, 8.57; N, 5.76.

3.6.5. 1-*N*-(6-Deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-6-yl)-3-*N*-dodecylbenzimidazol-2-one (14e). White solid (91%): mp 50–52 °C; $[\alpha]_D^{26}$ −59.6 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 5.90 (d, H, $J_{1,2}$ 3.7 Hz, H-1), 4.55 (d, H, $J_{2,3}$ 0 Hz, H-2), 4.20 (m, H, $J_{5,6a}$ 2.7 Hz, $J_{5,6b}$ 5.7 Hz, H-5), 4.28, 4.05 (2dd, 2H, $J_{6a,6b}$ 14.6 Hz, H-6), 3.95 (dd, H, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 8.6 Hz, H-4), 3.85 (m, 4H, H-3), 3.35 (s, 3H, OCH_3), 1.35, 1.23 (2s, 6H, CH_{3iso}) $\delta_{benzimidazolone}$ 7.20–6.85 (m, 4H, H_{arom}); 3.80 (t, 2H, N–CH_2^{α}), 1.70 (m, 2H, CH_2^{β}), 1.40–1.10 (m, 18H, CH_2), 0.95 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 111.7 (C_{iso}), 105.1 (C-1), 83.6 (C-3), 81.9 (C-2), 80.1 (C-4), 68.8 (C-5), 58.2 (OCH_3), 45.6 (C-6), 26.5, 26.2 (CH_{3iso}) $\delta_{benzimidazolone}$ 155.8 (CO), 129.7, 129.2 (C-8, C-9), 121.4, 121.3 (C-5, C-6), 108.6 (C-4, C-7), 41.2 (N–CH_2^{α}), 31.7–29.6, 25.6, 22.5 (CH_2), 13.9 (CH_3^{ω}); Anal. Calcd for $C_{29}H_{46}N_2O_6$: C, 67.15; H, 8.94; N, 5.40. Found: C, 66.98; H, 8.86; N, 5.46.

3.7. General procedure for deprotection step (iv)

The protected derivatives **14a**–**e** and Amberlyst resin 15 (H^+) were added to a stirred solution of 4:1 dioxane–water (100 g L^{-1}) at 80 °C. When the starting material was no longer detected by TLC or HPLC, the solution was concentrated to dryness under reduced pressure. The crude product was purified by silica gel chromatography (hexane–acetone gradient).

3.7.1. 3-*N*-Butyl-1-*N*-(6-deoxy-3-*O*-methyl-D-glucopyranos-6-yl)benzimidazol-2-one (15a). White solid (83%, α/β, 4:3): mp 67–69 °C; $[\alpha]_D^{26}$ −34.9 to 40.6 (*c* 1, MeOH); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.7 (C-1β), 92.2 (C-1α), 85.9, 82.8 (C-3), 74.1–69.5 (C-2, C-4, C-5), 59.8 (OCH_3), 42.6 (C-6) $\delta_{benzimidazolone}$ 153.6 (CO), 129.7, 128.8 (C-8, C-9), 120.6 (C-5, C-6), 108.7, 107.5 (C-4, C-7), 40.5 (N–CH_2^{α}), 29.9 (CH_2^{β}), 19.3 (CH_2^{γ}), 13.5 (CH_3^{ω}); Anal. Calcd for $C_{18}H_{26}N_2O_6$: C, 59.00; H, 7.15; N, 7.64. Found: C, 58.96; H, 7.12; N, 7.63.

3.7.2. 1-*N*-(6-Deoxy-3-*O*-methyl-D-glucopyranos-6-yl)-3-*N*-hexylbenzimidazol-2-one (15b). White solid (89%, α/β, 9:7): mp 64–66 °C; $[\alpha]_D^{26}$ −35.5 to 39.2 (*c* 1, MeOH); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.7 (C-1β), 92.1 (C-1α), 86.0, 82.8 (C-3), 74.2–69.5 (C-2, C-4, C-5), 59.9 (OCH_3), 42.6 (C-6) $\delta_{benzimidazolone}$ 153.5 (CO), 129.6, 128.8 (C-8, C-9), 120.6 (C-5, C-6), 108.5, 107.5 (C-4, C-7), 40.2 (CH_2^{α}), 30.7–21.9 (CH_2) 13.7 (CH_3); Anal. Calcd for $C_{20}H_{30}N_2O_6$: C, 60.90; H, 7.66; N, 7.10. Found: C, 60.86; H, 7.64; N, 7.07.

3.7.3. 1-*N*-(6-Deoxy-3-*O*-methyl-D-glucopyranos-6-yl)-3-*N*-octylbenzimidazol-2-one (15c). White solid (84%, α/β, 4:3): mp 54–56 °C; $[\alpha]_D^{26}$ −33.3 to 38.8 (*c* 1, MeOH); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.8 (C-1β), 92.2 (C-1α), 85.9, 82.8 (C-3), 74.2–69.6 (C-2, C-4, C-5), 59.9 (OCH_3), 42.6 (C-6) $\delta_{benzimidazolone}$ 153.5 (CO), 129.7, 128.6 (C-8, C-9), 120.5 (C-5, C-6), 108.7, 107.4 (C-4, C-7), 40.2 (N–CH_2^{α}), 31.1–21.9 (CH_2) 13.7 (CH_3); Anal. Calcd for $C_{22}H_{34}N_2O_6$: C, 62.53; H, 8.11; N, 6.63. Found: C, 62.48; H, 8.04; N, 6.67.

3.7.4. 3-*N*-Decyl-1-*N*-(6-deoxy-3-*O*-methyl-D-glucopyranos-6-yl)benzimidazol-2-one (15d). White solid (93%, α/β, 5:3): mp 51–53 °C; $[\alpha]_D^{26}$ −29.3 to 35.5 (*c* 1, MeOH); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.7 (C-1β), 92.2 (C-1α), 85.9, 82.8 (C-3), 74.2–69.5 (C-2, C-4, C-5), 59.8 (OCH_3), 42.6 (C-6) $\delta_{benzimidazolone}$ 153.5 (CO), 129.7, 128.8 (C-8, C-9), 120.6 (C-5, C-6), 108.5, 107.5 (C-4, C-7), 40.2 (N–CH_2^{α}), 31.2–22.0 (CH_2) 13.8 (CH_3); Anal. Calcd for $C_{24}H_{38}N_2O_6$: C, 63.98; H, 8.50; N, 6.22. Found: C, 63.76; H, 8.41; N, 5.96.

3.7.5. 1-*N*-(6-Deoxy-3-*O*-methyl-D-glucopyranos-6-yl)-3-*N*-dodecylbenzimidazol-2-one (15e). White solid (72%, α/β, 1): mp 44–46 °C; $[\alpha]_D^{26}$ −25.5 to 32.1 (*c* 1, MeOH); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 96.7 (C-1β), 92.2 (C-1α), 86.0, 82.9 (C-3), 74.2–69.5 (C-2, C-4, C-5), 59.8 (OCH_3), 42.6 (C-6) $\delta_{benzimidazolone}$ 153.6 (CO), 129.7, 128.8 (C-8, C-9), 120.5 (C-5, C-6), 108.7 107.4 (C-4, C-7), 40.2 (N–CH_2^{α}), 31.2–22.0 (CH_2) 13.8 (CH_3); Anal. Calcd for $C_{26}H_{42}N_2O_6$: C, 65.25; H, 8.84; N, 5.85. Found: C, 65.19; H, 8.76; N, 5.86.

3.8. General procedure for the N-glycosylation of 1,2-*O*-cyclic sulfite derivatives

To a solution of the 1,2-*O*-cyclic sulfite derivatives **17a**,**b** (1 mmol) in anhyd DMF (10 mL) was added dropwise a solution of *N*-isopropenylbenzimidazolone (2 mmol, **11**) previously stirred at 70 °C for 2 h with K_2CO_3 (2.1 mmol) in anhyd DMF (10 mL). The mixture was stirred for 3 h at 90 °C, then filtered through a Celite pad. The filtrate was concentrated and extracted with 8:2 CH_2Cl_2–water (3 × 60 mL). The combined organic layers were successively dried, concentrated, and flash chromatographied on silica gel (4:1 hexane–EtOAc), giving the corresponding products **18a**–**b**.

3.8.1. 1-*N*-Isopropenyl-3-*N*-(3,5,6-tri-*O*-benzyl-1-deoxy-β-D-glucofuranos-1-yl)benzimidazol-2-one (18a). Colourless syrup: 370 mg (61%); $[\alpha]_D^{20}$ −23 (*c* 0.35, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) $\delta_{glucose}$ 7.34–7.25 (m, 15H, Ph), 5.98 (s, 1H, $J_{1,2}$ 0 Hz, H-1), 4.90–4.50 (m, 7H, H-4, 3CH_2), 4.33–4.24 (m, 3H, H-2, H-3, H-5), 3.87 (dd, 1H, $J_{5,6a}$ 5.2 Hz, $J_{6a,6b}$ 10.4 Hz, H-6a), 3.67 (dd, 1H, $J_{5,6b}$ 8.8 Hz, $J_{6a,6b}$ 10.4 Hz, H-6b) $\delta_{benzimidazolone}$ 7.11–7.03 (m, 4H, H_{arom}), 5.38, 5.16 (2s, 2H, C=CH_2), 2.18 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{glucose}$ 129.3–122.46 (Ph), 91.0 (C-1), 85.3 (C-2), 79.3 (C-3), 78.3 (C-4), 76.0 (C-5), 73.9, 73.4, 71.8 (CH_2 (Bn)), 71.7 (C-6) $\delta_{benzimidazolone}$ 152.6 (C=O), 137.9 (*C*=CH_2), 128.8, 127.8 (C-8, C-9), 122.4, 121.8 (C-5, C-6), 114.3 (C=*C*H_2), 110.27, 109.3 (C-4, C-7), 20.5 (CH_3); HRE-SIMS: *m*/*z* 629.2637. Calcd for $C_{37}H_{38}N_2NaO_6$, 606.2730; Anal. Calcd for $C_{37}H_{38}N_2O_6$: C, 73.25; H, 6.31; N, 4.62. Found: C, 73.52; H, 6.22; N, 4.70.

3.8.2. [1-*N*-(1-Deoxy-3,4-*O*-isopropylidene-α-D-arabinopyranos-1-yl)-3-*N*-isopropenylbenzimidazol-2-one (18b). Colourless syrup: 376 mg (62%); $[\alpha]_D^{20}$ −17 (*c* 0.43, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) $\delta_{arabinose}$ 5.25 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.45–4.40 (m, 2H, H-2, H-5a), 4.28–4.24 (m, 2H, H-3, H-4), 4.03 (dd, 1H, $J_{4,5b}$ 2.1 Hz, $J_{5a,5b}$ 13.7 Hz, H-5b), 3.88 (s, 1H, OH), 1.62, 1.41 (2s, 2 × 3H, CH_{3iso}) $\delta_{benzimidazolone}$ 7 28–7.07 (m, 4H, H_{arom}), 5.35, 5.18 (2s, 2H, C=CH_2), 2.15 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta_{arabinose}$ 110.4 (C_{iso}), 83.3 (C-1), 79.9 (C-3), 74.1 (C-4), 70.3 (C-2), 66.3 (C-5), 28.7, 26.6 (CMe_2) $\delta_{benzimidazolone}$ 152.6 (C=O), 138.0 (*C*=CH_2), 129.6, 128.0 (C-8, C-9), 122.4, 122.3 (C-5, C-6), 114.3 (C=*C*H_2), 110.7, 109.6 (C-4, C-7), 20.4 (CH_3); HRE-SIMS: *m*/*z* 369.1414. Calcd for $C_{18}H_{22}N_2NaO_5$: 369.1426; Anal. Calcd for $C_{18}H_{22}N_2O_5$: C, 62.42; H, 6.40; N, 8.09. Found: C, 62.48; H, 6.37; N, 8.13.

References

1. Yu, K. H.; Wang, X. A.; Civiello, R. L.; Trehan, A. K.; Pearce, B. C.; Yin, Z.; Combrick, K.; Gulgeze, H. B.; Zhang, Y.; Kadow, K.; Cianci, C.; Clarke, J.; Genovesi, E.; Medina, I.; Lamb, L.; Wyde, P.; Krystal, M.; Meanwell, N. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1115–1122.
2. Li, Q.; Li, T.; Woods, K. W.; Gu, W. Z.; Cohen, J.; Stoll, V.; Galicia, T.; Hutchins, C.; Frost, D.; Rosenberg, S. H.; Sham, H. L. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 2918–2922.
3. Baragatti, B.; Biagi, G.; Calderone, V.; Giorgi, I.; Livi, O.; Martinotti, E.; Scartoni, V. *Eur. J. Med. Chem.* **2000**, *35*, 949–955.
4. Zhang, P.; Terefenko, E. A.; Wrobel, J.; Zhang, Z.; Zhu, Y.; Cohen, J.; Marschke, K. B.; Mais, D. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2747–2750.

5. Biagi, G.; Calderone, V.; Giorgi, I.; Livi, O.; Scartoni, V.; Baragatti, B.; Martinotti, E. *Il Farmaco* **2001**, *56*, 841–849.
6. (a) Torres, R. A.; Sarria, V.; Torres, W.; Peringer, P.; Pulgarin, C. *Water Res.* **2003**, *37*, 3118–3124; (b) Sarri, V.; Kenfack, S.; Guillod, O.; Pulgarin, C. *J. Photochem. Photobiol.* **2003**, *159*, 89–99.
7. (a) Devor, D. C.; Singh, A. K.; Frizzell, R. A.; Bridges, R. J. *Am. J. Physiol.* **1996**, *271*, 775–784; (b) Anderson, N. J.; Watson, W. P.; Slough, S. *Eur. J. Pharm.* **2006**, *546*, 48–53.
8. (a) Goueth, P. Y.; Ronco, G.; Villa, P. *J. Carbohydr. Chem.* **1994**, *13*, 679–696; (b) Lakhrissi, B.; Essassi, E. M.; Massoui, M.; Goethals, G.; Lequart, V.; Monflier, E.; Cecchelli, R.; Martin, P. *J. Carbohydr. Chem.* **2004**, *23*, 389–401.
9. Townsend, L. B.; Devivar, R. V.; Turk, S. R.; Nassiri, R. M.; Drach, J. C. *J. Med. Chem.* **1995**, *38*, 4098–4105.
10. Christensen, J. E.; Goodman, L. *Carbohydr. Res.* **1968**, *7*, 507–509.
11. Meth-Cohen, O.; Smith, D. I. *J. Chem. Soc., Perkin Trans. 1* **1982**, 261–270.
12. For reviews, see: (a) Pellissiet, H. *Tetrahedron* **2005**, *61*, 2947–2993; (b) Toshima, H. *Carbohydr. Res.* **2006**, *341*, 1282–1287.
13. Messaoudi, S.; Sancelme, M.; Polard-Housset, V.; Aboab, B.; Moreau, P.; Prudhomme, M. *Eur. J. Med. Chem.* **2004**, *39*, 453–458.
14. Zinner, H.; Peseke, K. *J. Prakt. Chem.* **1970**, *312*, 307–313.
15. (a) El Meslouti, A.; Beaupère, D.; Demailly, G.; Uzan, R. *Tetrahedron Lett.* **1994**, *35*, 3913–3916; (b) Beaupère, D.; El Meslouti, A.; Lelièvre, P.; Uzan, R. *Tetrahedron Lett.* **1995**, *36*, 5347–5348; (c) Roussel, F.; Wadouachi, A.; Beaupère, D. *Carbohydr. Lett.* **2000**, *3*, 397–404.
16. For reviews, see: (a) Lorhay, B. B. *Synthesis* **1992**, 1035–1052; (b) Byun, H. S.; He, L.; Bittman, R. *Tetrahedron* **2000**, *56*, 7051–7091.
17. Benksim, A.; Beaupère, D.; Wadouachi, A. *Org. Lett.* **2004**, *6*, 3913–3915.