C-Glycosyl Amino-Substituted Hydro- and Benzoquinones: Synthesis and Preliminary Biological Evaluation

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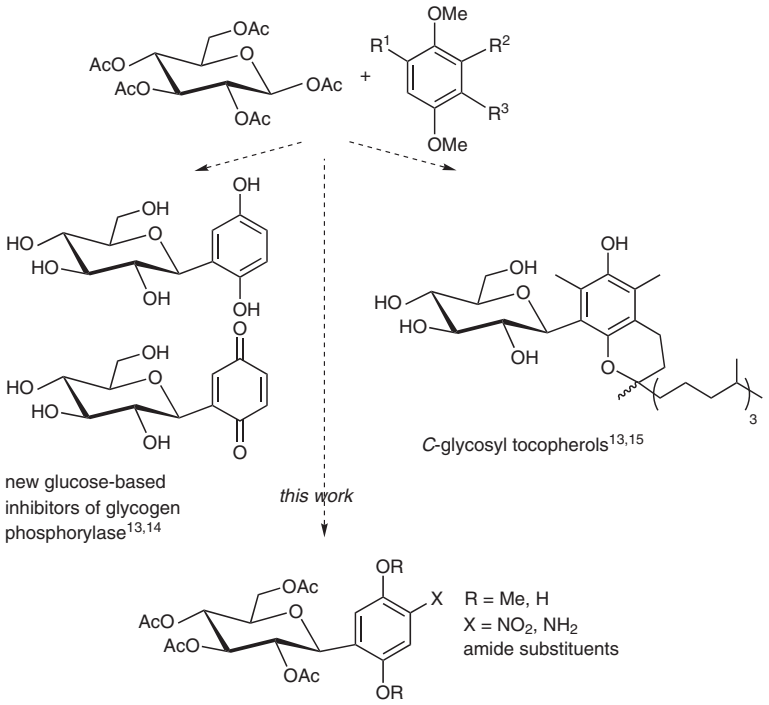
Abstract: Reaction of *C*-β-D-glycopyranosyl-1,4-dimethoxybenzenes with acetyl nitrate afforded 2-(β-D-glycopyranosyl)-1,4-dimethoxy-5-nitrobenzenes in high yields. These were converted smoothly (reduction to amines, N-acylation, oxidation, and reduction) into the corresponding *C*-glycosyl-hydro(benzo)quinone derivatives, with different amide-based substituents at C-5. Reduction of the nitro compounds to amines proceeded smoothly by catalytic hydrogen transfer with HCO_2NH_4.

Key words: glycosides, electrophilic aromatic substitution, hydrogen transfer, reduction, amines, amides

Even though *C*-glycosyl flavonoids constitute a specific class of natural products,[1] carbohydrates directly bound to an aromatic moiety through a C–C bond are rare, as compared to common sugars. However, glycosyl arenes (also termed *C*-aryl glycosides)[2] are currently attracting increasing interest, as regard to their synthesis[3] and because of bioactivities[2,4] anticipated for such glycomimics, based on possible interactions with sugar-processing enzymes and on their resistance to both acid-, and enzyme-catalyzed hydrolysis.[5]

Our interest in this field stems from earlier studies devoted to the synthesis of 5-thio-β-D-xylopyranosides[6] and *C*-5-thio-β-D-xylopyranosyl compounds[7] as orally active venous antithrombotics. *C*-5-Thio-β-D-xylopyranosyl derivatives of phenol, resorcinol, phloroglucinol were obtained by aromatic electrophilic substitution, or by *O* → *C*-glycoside rearrangement, showing the reactivity of electron-rich aryls, in agreement with studies aiming at preparing *C*-glycosyl flavonoids,[8,9] or D-glycosyl derivatives (furanose[10] or pyranose[11] type) of dimethylhydroquinone. By such a coupling and subsequent oxidation and reduction, Kalvoda first obtained various glycofura-



Scheme 1 Recent synthetic developments with 2-*C*-β-D-glycopyranosyl-1,4-dimethoxybenzenes

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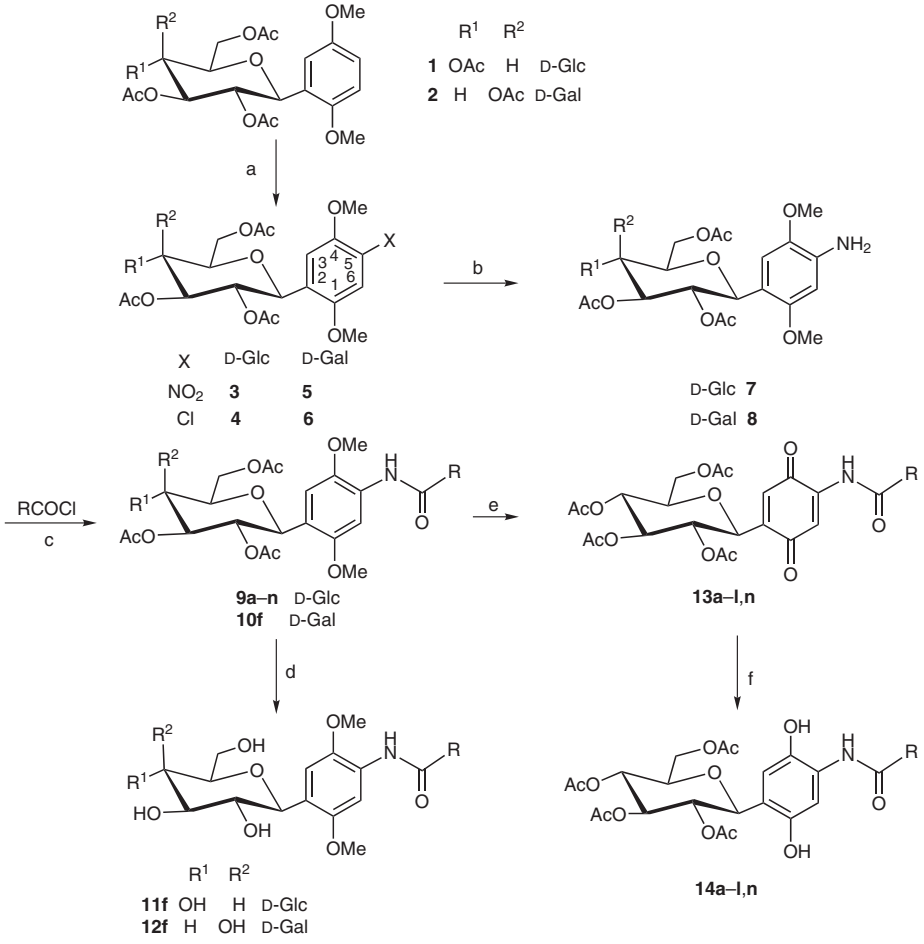
nosyl-hydro(1,4-benzo)quinones,[10] a class of simple compounds with only few synthetic[12] representatives.

Because glycosyl-hydro(benzo)quinones correspond to a stable scaffold amenable to various functionalizations or modifications, resulting in possible bioactivities,[12b] the synthesis of glycopyranosyl derivatives was carried out, using 1,4-dimethoxybenzene, and its 2,3-, and 2,6-dimethyl derivatives.[13] While enzymatic and crystallographic studies showed that the glucosyl-hydro(benzo)quinones were weak inhibitors of glycogen phosphorylase (GP) due to binding at the active site,[14] the *o*- and *m*-dimethyl analogues opened the first access to *C*-glycosyl-tocopherols,[13] as unprecedented antioxidants.[15] This encouraged us to further investigate the potential of such glycosyl-arenes, in particular by electrophilic substitution (halogenation, formylation, nitration; Scheme 1). We herein report on the synthesis of 2-glycosyl-1,4-dimethoxy-5-nitrobenzenes. After reduction, they gave access to a library of sugar-based amide-linked aromatics, which have been tested against A375 human melanoma cell lines.

Because of the lability of acetyl protecting groups, nitration of 2-(2,3,4,6-tetra-*O*-acetyl-β-D-glycopyranosyl)-1,4-dimethoxybenzenes (**1**,**2**)[13,14] was envisaged under mild conditions and in particular with acyl nitrates,[16] because such nitrating agents are accessible by simple methods avoiding harsh acidic conditions.[17] Acetyl nitrate [ca. 2.1 equiv prepared in situ in anhyd MeCN from NH_4NO_3 (2.4 equiv) and AcCl (2.1 equiv)] was found effective to achieve the regioselective nitration of **1** and **2** within 2 hours, to afford **3** and **5** in 81% and 75% yield, respectively (Scheme 2). The substrates were reactive enough for



R = **a**: vinyl; **b**: (*E*)-styryl; **c**: *p*-tolyl; **d**: 4-methoxyphenyl; **e**: 3,5-dimethoxyphenyl; **f**: 4-nitrophenyl; **g**: 4-biphenyl; **h**: 1-naphthyl; **i**: 2-naphthyl; **j**: 2-furyl; **k**: 2-thienyl; **l**: 3-pyridyl; **m**: 2-(pyridinyl-6-formate ethyl ester)

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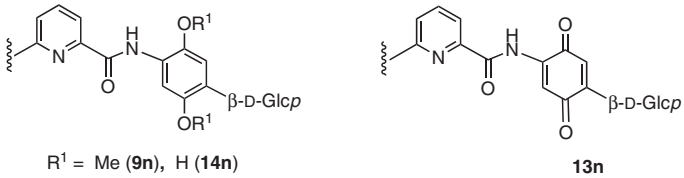


R^1 = Me (**9n**), H (**14n**)

13n

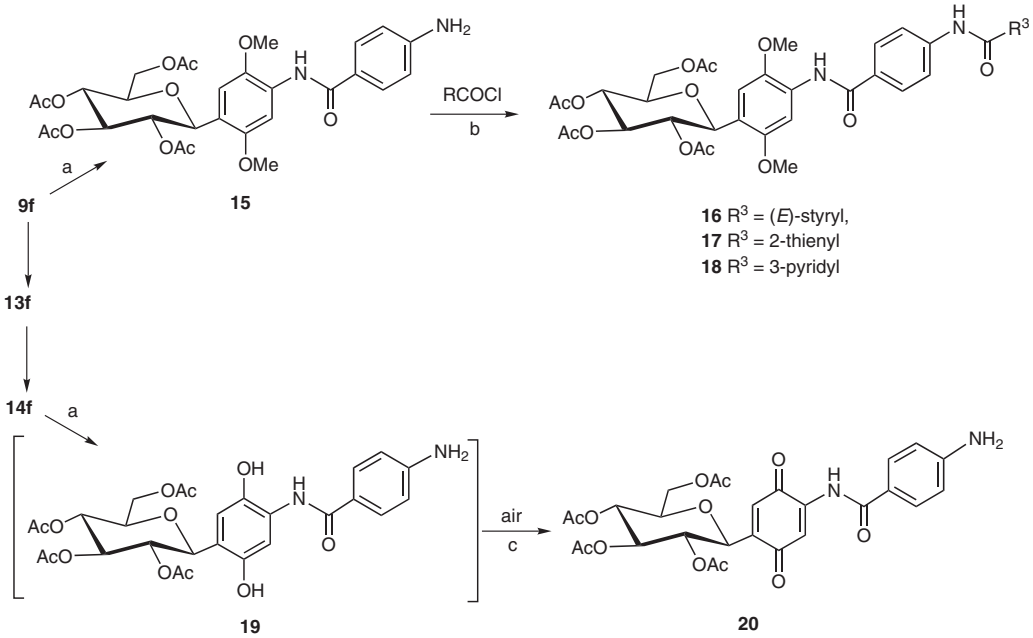
Scheme 2 *Reagents and conditions*: (a) NH_4NO_3, AcCl, MeCN, 0 °C to r.t., 2 h; (b) $Na_2S_2O_4$ (H_2O–MeOH) or HCO_2NH_4 (MeOH), 10% Pd/C, r.t.; (c) RCOCl, pyridine, CH_2Cl_2, (d) BaO, MeOH; (e) CAN, MeCN–H_2O; (f) $Na_2S_2O_4$, $CHCl_3/H_2O$.

the nitration to proceed with limited amounts of an hazardous reagent (caution: $AcONO_2$ may explode upon heating).[18] The grade of NH_4NO_3 appeared to be critical since limited drying led to incomplete nitration of **1**, while extensive drying in the presence of P_2O_5 favored dinitration (see experimental section). Minor side-products, to be fully described in a forthcoming paper, were separated by column chromatography and identified as chlorinated regioisomers (see Scheme 2 for numbering). Not surprisingly, the C-5 chloro isomers were more abundant [**4** (5-Cl): 11%, **6** (5-Cl): 13%] as compared to the C-6 analogues (D-Glc: 3%, D-Gal: 2%). Regarding their formation, we assumed that, because NO_2^+ ions or acetyl nitrate are oxidizing agents,[19] chloride anions, still present in the medium even after filtration of precipitated NH_4Cl (see experimental) may undergo oxidation, thus forming reactive species (e.g., chlorine atom, chloronium ion) capable of aromatic substitution with activated substrates. This is reminiscent of reported halogenations, occurring together with nitration,[20a] or favored by the electrophilic fluorination agent Selectfluor,[20b] or dimethyldioxirane.[20c] While more complete removal of precipitated NH_4Cl appeared difficult, few attempts to minimize chlorination by reducing the quantity of AcCl (NH_4NO_3/AcCl ratio changed from 2.4/2.1 to 2.7/1.8) were not encouraging, since the reaction was slower (3.5 h) while the chloro isomers were again detected. Probably, use of silver nitrate would allow a more efficient elimination of chloride anions, as insoluble silver chloride. Moreover, attempts to achieve nitrosation or nitration of glycosyl hydroquinone failed, mainly due to oxidation to glycosyl-benzoquinone under the conditions applied ($NaNO_2$/AcCl, NH_4NO_3/AcCl in varying amounts ~1.1 equiv, 1.5 equiv, 2.1 equiv, CAN–$NaHCO_3$).[21]

In order to prepare the corresponding amino derivatives, reduction of compounds **3** and **5** was attempted in the presence of Raney nickel in EtOH,[22] but not surprisingly this led to deacetylation and other unwanted transformations. Other reductive conditions applicable to nitro compounds were not tried because of limited efficiency ($NaBH_4$) or possible side reactions ($LiAlH_4$, NH_2NH_2), but catalytic hydrogen transfer was considered. Sodium dithionite/hydrosulfite ($Na_2S_2O_4$),[23] currently used in our group for reducing glycosyl benzoquinones **13**[13,14] was envisaged, although it usually requires heating under basic conditions. Compound **3** was reduced within 13 minutes in the presence of $Na_2S_2O_4$ and Pd/C 10% in H_2O–MeOH to afford **7** in 60% yield, together with a polar by-product. Another experiment with $HCO_2^-NH_4^+$ as the hydrogen donor in MeOH with Pd/C 10% afforded within 75 minutes **7** as the sole product in 82% yield. Use of a combination of $Na_2S_2O_4$ and HCO_2NH_4 with Pd/C in H_2O–MeOH led within 15 minutes to **7** in 54% yield, in addition to a polar by-product, assumed to be a salt of **7**.

To the best of our knowledge, catalytic hydrogen transfer with $Na_2S_2O_4$ has not been reported previously,[24] although nitroarenes have been reduced with $Na_2S_2O_4$ in aqueous or biphasic medium in the presence of an electron transfer catalyst.[25] Interestingly, a bacterial cellulose with a palladium deposit was recently shown to catalyze the generation of hydrogen when incubated with sodium dithionite.[26]

Compounds **7**,**8** were acylated in high yields with 13 acyl chlorides to afford **9a–n** and **10f** (D-Gal) which display various substituents bound by a fairly stable amide linkage (Scheme 3). 2,6-Bis(chloroformyl)pyridine (0.53 equiv) was used to prepare compounds **9n** (87%) and **9m** (6%, an ethyl ester formed most probably during extrac-



Scheme 3 *Reagents and conditions*: (a) $Na_2S_2O_4$ (H_2O–MeOH) or HCO_2NH_4 (MeOH), 10% Pd/C, r.t.; (b) acyl chloride, pyridine, CH_2Cl_2; (c) oxidation by air.

tion with CH_2Cl_2 containing EtOH as stabilizer). Compounds **9f** and **10f** were deacetylated cleanly by BaO in anhydrous MeOH[27] at 0–4 °C to afford **11f** and **12f**. Meanwhile **9a–l** and **9n** were oxidized to the benzoquinone analogues **13a–l** and **13n** with ceric ammonium nitrate (CAN) in aqueous acetonitrile solution in good to excellent yields.[13,14] Then hydroquinone analogues **14a–l** and **14n** were obtained upon reduction with $Na_2S_2O_4$ in good to excellent yields.

Further work (Scheme 3) demonstrated the efficiency and the mildness of the reduction of nitro compounds by catalytic hydrogen transfer. For example, **9f** was reduced to afford **15** in high yield (86%) which was then converted by acylation into **16–18**. Interestingly, upon treatment with $Na_2S_2O_4$, benzoquinone **13f** was reduced as mentioned before to hydroquinone **14f**, without modification of the nitro group. However, the aniline derivative **19** was formed upon reduction with $Na_2S_2O_4$, HCO_2NH_4, 10% Pd/C in H_2O–MeOH. This compound proved to be highly sensitive to oxidation, since it was converted during work-up and chromatography into the benzoquinone **20** (71%), probably because of air oxidation. The smooth and selective reduction of both polyfunctional nitro compounds **9f** and **14f** to the corresponding anilines showed again the interest of catalytic hydrogen transfer conditions.

While assays showed no inhibition of GP by deacetylated compound **11f**, the antitumor activities *in vitro* of some of the compounds synthesized were evaluated by MTT tetrazolium dye assay[28] against A375 cell line (human melanoma cell), on consideration of structural similarities (benzoquinone, amido moieties) with anticancer agents as anthracyclines or naphthalimides.[29] Each compound was tested at five different concentrations to determine IC_{50} (μ/mL) required to inhibit cell growth by 50%. The results revealed that compounds derived from 1,4-dimethoxybenzene had low activities, as **17**, **18** were found to be inactive, while **10f** and **16** had IC_{50} = 260, 160 μg/mL respectively. The benzoquinones tested have IC_{50} (μg/mL) values as follows: **13b**: 74; **13c**: 110; **13e**: 57; **13f**: 20; **13g**: 23; **13i**: 40 (mean value for 2 assays); **13l**: 146; **13n**: no activity. The hydroquinones tested showed the following IC_{50} (μg/mL): **14b**: 20; **14c**: 87; **14g**: 107.

CH_2Cl_2 was washed three times with H_2O, dried ($CaCl_2$), and distilled over CaH_2 before use. Other organic solvents were distilled. Petroleum ether (PE) used had bp 45–60 °C. TLC was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck, Darmstadt, Germany). TLC plates were inspected under 254 and 312 nm UV light (except for **9m** and **9n**, all compounds in the 1,4-dimethoxyhydroquinone, 1,4-benzoquinone series were visible on TLC plates as either red-violet spots/312 nm UV light or black spots/254 nm UV light), and/or developed by treatment with a mixture of 5% H_2SO_4 in EtOH followed by heating. Silica gel column chromatography was performed with Geduran® silica gel Si 60 (40–63 μm) purchased from Merck. ^1H and ^{13}C NMR spectra were recorded at 23 °C using Bruker AC200, DRX300 or DRX500 spectrometers with the residual solvent as the internal standard. In the ^1H NMR spectra, the coupling constants for pyranosyl rings have been assigned and listed without duplication. NMR solvents were purchased from Euriso-Top (Saint Aubin, France). HRMS (LSIMS) mass spectra were recorded in the positive mode (unless stated otherwise) using a Thermo Finnigan Mat 95 XL spectrometer. MS (ESI) mass spectra were recorded in the positive mode using a Thermo Finnigan LCQ spectrometer. Optical rotations were measured using a PerkinElmer polarimeter. Elemental analyses were performed at the Service Central d'Analyses du CNRS (Vernaison, France).

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-nitrobenzene (3)

A mixture of NH_4NO_3 (previously dried under vacuum for 2–3 days) (175 mg, 2.18 mmol, 2.4 equiv) and AcCl (140 μL, 1.97 mmol, 2.1 equiv) in anhyd MeCN (5 mL) was stirred at 0 °C for 40 min. Due to the limited solubility of NH_4Cl, a precipitate appeared meanwhile in the turbid solution. After removal of the insoluble materials by filtration, 1,4-dimethoxy-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)benzene (**1**; 450 mg, 0.96 mmol) was added to the filtrate obtained. Upon stirring at r.t. for 2 h, TLC showed that compound **1** was converted into three compounds (R_f = 0.53, 0.49, 0.40, PE–EtOAc, 1:1). The more polar spot was easily visible under daylight. H_2O (10 mL) was added to the mixture, which was extracted with CH_2Cl_2 (3 × 15 mL). The extracts were combined and washed with brine (15 mL), H_2O (15 mL), dried ($MgSO_4$), and evaporated. The residue was purified by chromatography (PE–EtOAc, 3:1) on silica gel to afford successively the C-6 chlorinated compound (13 mg, 3%), its C-5 isomer (53 mg, 11%) (found to be identical to analytical samples obtained by other routes), and the nitro compound **3** (400 mg, 81%).

Other experiments suggested that the content of H_2O in NH_4NO_3 was critical as regard to the nitration outcome. An assay similarly carried out with **1** (20 mg), NH_4NO_3 (previously dried under vacuum for 1 day, 2.4 equiv) and AcCl (2.1 equiv) led, after 5 days, to incomplete conversion of **1**, with formation of **3** and chloro isomers (TLC). Use of NH_4NO_3 (7.2 equiv) dried for 24 h in the presence of P_2O_5 and AcCl (6.3 equiv) resulted in complete conversion of **1** after 40 min and afforded **3** (39%), the chloro isomer **4** (6.5%), and a 5,6-dichloro product (23%) (MS, NOE 1D). If the nitration was carried out with NH_4NO_3 dried for one week under vacuum in the presence of P_2O_5, **1** was not completely transformed but a dinitro compound (MS) was found predominantly among the products. Attempted nitration of **1** (60 mg) in MeCN at r.t. with NH_4NO_3, dried for one week under vacuum in the presence of P_2O_5 (2.0, 2.4 and 3.0 equiv) and trifluoroacetic anhydride[17] (6 equiv) led, even after 3–4 days, to partial conversion of **1** (ca 60%) and formation of separable dinitro isomers (MS). They were identified by NMR spectroscopy based on NOE 1D as the 3,6-dinitro (minor isomer) and the 5,6-dinitro (major isomer) derivatives.

Yellow-green solid; mp 142.5–143 °C (CH_2Cl_2–PE); R_f = 0.40 (PE–EtOAc, 1:1); $[\alpha]_D^{18}$ –25.0 (*c* 0.75 CH_2Cl_2).

^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.38 (s, 1 H, Ar), 7.17 (s, 1 H, Ar), 5.37 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.25 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.23 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.97 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.14 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.94 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 3.86 (ddd, 1 H, H-5), 2.07, 2.06, 2.01, 1.82 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 170.6, 170.0, 169.5 (4 C=O, acetyl), 150.8 (*C*OMe), 148.0 (*C*OMe), 139.5 (C_q, Ar), 131.9 (C_q, Ar), 114.5 (CH_{Ar}), 108.4 (CH_{Ar}), 76.8, 74.5, 73.1, 72.4, 69.0 (C-1/C-5), 62.7 (C-6), 57.5 (OCH_3), 56.8 (OCH_3), 21.2, 21.0, 21.0, 20.8 (4 CH_3, acetyl).

MS (ESI+): *m*/*z* (%) = 513.8 (10, $[M + H]^+$), 536.0 (15, $[M + Na]^+$), 1048.6 (100, $[2 M + Na]^+$).

HRMS (LSIMS): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{27}NO_{13}$ + Na: 536.1380; found: 536.1385.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-1,4-dimethoxy-5-nitrobenzene (5)

Treatment of **2** (350 mg, 0.75 mmol), according to the above procedure for the synthesis of **3**, afforded **5** (288 mg, 75%), as well as minor products chlorinated at C-6 (10 mg, 3%) and at C-5 (51 mg, 13%) [R_f = 0.55, 0.52 (PE–EtOAc, 1:1)]; yellow-green crystals (PE–CH_2Cl_2–Et_2O); mp 156–157 °C; R_f = 0.41 (PE–EtOAc, 1:1); $[\alpha]_D^{17}$ –10.2 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (s, 1 H, Ar), 7.23 (s, 1 H, Ar), 5.54 (br d, $J_{3,4}$ = 3.3 Hz, 1 H, H-4), 5.43 (t, $J_{2,3}$ = 9.9 Hz, 1 H, H-2), 5.24 (dd, 1 H, H-3), 4.96 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.18–4.08 (m, 3 H, H-5, H-6, H-6′), 3.97 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 2.22, 2.04, 2.00, 1.84 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.8, 170.6, 170.5, 169.6 (4 C=O, acetyl), 150.8 (*C*OMe), 148.1 (*C*OMe), 139.5, 132.3 (2 C_q, Ar), 114.8 (CH_{Ar}), 108.4 (CH_{Ar}), 75.4 (C-5), 73.6 (C-1), 72.5 (C-3), 69.7 (C-2), 68.1 (C-4), 62.0 (C-6), 57.6 (OCH_3), 56.9 (OCH_3), 21.2, 21.1, 21.0, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m*/*z* (%) = 514 (13, $[M + H]^+$), 531 (33, $[M + NH_4]^+$), 536 (15, $[M + Na]^+$), 1048 (100, $[2 M + Na]^+$).

Anal. Calcd for $C_{22}H_{27}NO_{13}$: C, 51.46; H, 5.30; N, 2.73; O, 40.51. Found: C, 51.13; H, 5.35; N, 2.70; O, 41.18.

4-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,5-dimethoxyaniline (7)

Reduction with $Na_2S_2O_4$ as the Hydrogen Donor: Compound **3** (20 mg, 0.038 mmol) was dissolved in MeOH (1 mL). $Na_2S_2O_4$ (160 mg, 0.92 mmol), H_2O (0.15 mL) and 10% Pd/C (ca 5 mg) were added to the above solution contained in a well-stoppered flask filled with argon. After 13 min, TLC showed completion of the reduction, the starting material [R_f = 0.40 (PE–EtOAc, 1:1)] being changed into two new polar compounds [R_f = 0.28 and 0 (PE–EtOAc, 1:1)]. The mixture was filtered through a Celite pad and the filtrate was extracted with $CHCl_3$ (3 × 10 mL). The extracts were combined, washed with brine (10 mL), dried ($MgSO_4$), and concentrated. The residue was purified by chromatography (PE–EtOAc, 1:1) on silica gel to afford compound **7** (11 mg, 60%).

Reduction with HCO_2NH_4 as the Hydrogen Donor: Compound **3** (22 mg, 0.042 mmol) was dissolved in MeOH (1.5 mL). HCO_2NH_4 (40 mg, 0.63 mmol) and 10% Pd/C (ca 5 mg) were added to the above solution contained in a well-stoppered flask filled with argon. After 75 min, TLC showed completion of the reduction. The mixture was filtered through a Celite pad and the filtrate was concentrated under vacuum. The residue was purified by chromatography (PE–EtOAc, 1:1) on silica gel to afford compound **7** (17 mg, 82%).

Reduction with $Na_2S_2O_4$/HCO_2NH_4 as the Hydrogen Donor: Compound **3** (20 mg, 0.038 mmol) was dissolved in MeOH (1 mL). $Na_2S_2O_4$ (85% tech.) (160 mg, 0.92 mmol, ca. 20 equiv), H_2O (0.2 mL), HCO_2NH_4 (40 mg, 0.63 mmol) and 10% Pd/C (5 mg) were added to the above solution and stirred at r.t. under argon. After 15 min, TLC showed that the starting material changed into new polar compounds (R_f = 0.28 and 0). The mixture was filtered through a Celite pad and the filtrate was extracted with $CHCl_3$ (3 × 10 mL). The extracts were combined, washed with brine (10 mL), dried ($MgSO_4$), and concentrated. The residue was purified by chromatography (PE–EtOAc, 1:1) on silica gel to afford **7** (10 mg, 54%); pale-yellow oil; $[\alpha]_D^{29}$ –16.7 (*c* 1, $CHCl_3$).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 6.75 (s, 1 H, Ar), 6.27 (s, 1 H, Ar), 5.34 (t, $J_{3,4}$ = 9.0 Hz, 1 H, H-3), 5.22 (t, $J_{2,3}$ = 9.9 Hz, 1 H, H-2), 5.20 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.85 (d, $J_{1,2}$ = 9.3 Hz, 1 H, H-1), 4.25 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.10 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.82 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 4.10–3.75 (overlapping signals, 3 H, H-5 and NH_2, exch. D_2O), 2.05, 2.03, 1.99, 1.77 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 170.8, 170.4, 169.7, 169.3 (4 C=O, acetyl), 152.5 (*C*OMe), 141.5 (*C*OMe), 137.7 (C_q, Ar), 113.0 (C_q, Ar), 110.4 (CH_{Ar}), 99.6 (CH_{Ar}), 76.0, 74.9, 73.7, 71.6, 69.0 (C-1/C-5), 62.6 (C-6), 56.6 (OCH_3), 56.1 (OCH_3), 20.8, 20.7, 20.7, 20.5 (4 CH_3, acetyl).

MS (EI, 70 eV): *m*/*z* (%) = 290 (100), 483 (85, $[M]^+$).

MS (ESI+): *m*/*z* (%) = 483.9 (100, $[M + H]^+$), 966.5 (40, $[2 M + H]^+$).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{22}H_{29}NO_{11}$: 483.1741; found: 483.1735.

The other polar compound formed with $Na_2S_2O_4$ as the hydrogen donor was poorly soluble in $CHCl_3$, but was soluble in DMSO and MeOH; R_f = 0 (PE–EtOAc, 1:1); R_f = 0.26 (MeOH–EtOAc, 1:6); $[\alpha]_D^{21}$ –12.8 (*c* 0.75, MeOH). NMR data as for **7**.

MS (ESI+): *m*/*z* (%) = 484.0 (95, $[M + H]^+$), 506.1 (100, $[M + Na]^+$), 586.1 (10, $[M' + H]^+$), 608.2 (52, $[M' + Na]^+$), 966.6 (30, $[2 M + H]^+$), 989.0 (35, $[2 M + Na]^+$), 1091.0 (72, $[M + M' + Na]^+$), 1193.1 (75, $[2 M' + Na]^+$).

4-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2,5-dimethoxyaniline (8)

Treatment of **5** (205 mg, 0.4 mmol) with HCO_2NH_4 according to the previous procedure, afforded **8** (158 mg, 82%) as a pale-yellow syrup; $[\alpha]_D^{29}$ –0.9 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 6.82 (s, 1 H, Ar), 6.28 (s, 1 H, Ar), 5.55–5.48 (m, 2 H, H-2, H-4), 5.19 (dd, *J* = 3.3, 9.9 Hz, 1 H, H-3), 4.85 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.20–4.03 (m, 3 H, H-5, H-6, H-6′), 3.93–3.82 (br s, 2 H, NH_2, exch. D_2O), 3.82 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 2.20, 2.01, 1.98, 1.79 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.8, 170.8, 170.5, 169.7 (4 C=O, acetyl), 152.9, 141.7, 138.2, 113.4 (4 C_q, Ar), 111.1, 99.8 (CH_{Ar}), 74.9 (C-5), 74.5 (C-1), 73.1(C-3), 69.3, 68.4 (C-2 and C-4), 62.1 (C-6), 56.9 (OCH_3), 56.5 (OCH_3), 21.2, 21.1, 21.0, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m*/*z* (%) = 483.9 (100, $[M + H]^+$), 966.5 (40, $[2 M + H]^+$).

MS (EI, 70 eV): *m*/*z* (%) = 483 (85, $[M]^+$).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{22}H_{29}NO_{11}$: 483.1741; found: 483.1740.

Acylation of 7 and 8 to 9a–n and 10f; General Procedure A

4-*C*-Glycosyl-2,5-dimethoxyaniline **7** or **8** (1 equiv) was dissolved in anhyd CH_2Cl_2 (3 mL), and anhyd pyridine (20.3 μL, 1.2 equiv) was added. Acyl chloride (0.218 mmol, 1.05 equiv) was then added. After the above mixture had been stirred at r.t. for ~2 h, TLC showed the complete conversion of the starting material into a new more mobile compound. Then the mixture was concentrated under vacuum and purified using PE–EtOAc (1:1) as eluent to yield the desired compound.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(acrylamido)benzene (9a)

Treatment of **7** (100 mg) according to procedure A afforded **9a** (104 mg, 94%) as a colorless syrup; R_f = 0.37 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ +0.6 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.27 (s, 1 H, Ar), 8.01 (s, 1 H, CONH), 6.92 (s, 1 H, Ar), 6.43 (dd, *J* = 1.2 Hz, J_{trans} = 16.8 Hz, 1 H_{alkene}), 6.31 (dd, J_{cis} = 9.6 Hz, J_{trans} = 16.8 Hz, 1 H_{alkene}), 5.77 (dd, *J* = 1.5, 9.9 Hz, 1 H_{alkene}), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.28 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.99 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.29 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.13 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.87 (s, 3 H, OCH_3), 3.87–

3.83 (hidden, 1 H, H-5), 3.83 (s, 3 H, OCH_3), 2.07, 2.06, 2.01, 1.79 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.6, 170.0, 169.7 (4 C=O, acetyl), 163.8 (CONH), 151.9, 142.3 (2 C_q, Ar), 131.7 (CH_{alkene}), 129.0 (C_q, Ar), 128.26 ($CH_{2alkene}$), 119.0 (C_q, Ar), 109.7, 104.1 (2 CH_{Ar}), 76.5 (C-5), 74.8 (C-3), 73.3 (C-1), 72.4 (C-2), 69.2 (C-4), 63.1 (C-6), 56.7, 56.6 (2 OCH_3), 21.2, 21.1, 21.1, 20.8 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 538 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{25}H_{32}NO_{12}$: 538.1924; found: 538.1925.

(*E*)-2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(cinnamamido)benzene (9b)

Treatment of **7** (119 mg) according to procedure A afforded **9b** (151 mg, 93%); pale yellow green syrup; R_f = 0.36 (PE–EtOAc, 1:1); $[\alpha]_D^{17}$ –13.7 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.33 (s, 1 H, Ar), 8.09 (s, 1 H, CONH), 7.73 (d, *J* = 15.6 Hz, 1 H_{alkene}), 7.55 (m, 2 H, Ar), 7.38 (m, 3 H, Ar), 6.94 (s, 1 H, Ar), 6.62 (d, *J* = 15.6 Hz, 1 H_{alkene}), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.30 (t, $J_{2,3}$ = 9.0 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.00 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.29 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.5 Hz, 1 H, H-6′), 3.89 (s, 3 H, OCH_3), 3.89–3.84 (hidden, 1 H, H-5), 3.84 (s, 3 H, OCH_3), 2.06, 2.06, 2.01, 1.80 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.6, 170.1, 169.7 (4 C=O, acetyl), 164.4 (CONH), 152.0 (C_q, Ar), 142.7 (C_{alkene}), 142.4 (C_q, Ar), 135.0 (C_q, Ar), 130.4, 129.4, 129.3, 129.3, 128.4, 128.4 (6 CH_{Ar}), 121.4 (C_{alkene}), 118.9 (C_q, Ar), 109.8, 104.2 (2 CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.4 (C-1), 72.4 (C-2), 69.2 (C-4), 62.9 (C-6), 56.7, 56.6 (2 OCH_3), 21.2, 21.0, 21.0, 20.8 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 614 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{31}H_{36}NO_{12}$: 614.2237; found: 614.2240.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(4-methylbenzamido)benzene (9c)

Treatment of **7** (111 mg) according to procedure A afforded **9c** (129 mg, 93%); colorless syrup; R_f = 0.39 (EtOAc–PE, 1:1); $[\alpha]_D^{23}$ –14.0 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.60 (s, 1 H, CONH), 8.32 (s, 1 H, Ar), 7.76 (d, *J* = 8.1 Hz, 2 H, Ar), 7.29 (d, *J* = 8.1 Hz, 2 H, Ar), 6.83 (s, 1 H, Ar), 5.37 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.28 (t, $J_{2,3}$ = 9.9 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.99 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.13 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.90 (s, 3 H, OCH_3), 3.90–3.85 (hidden, 1 H, H-5), 3.85 (s, 3 H, OCH_3), 2.41 (s, 3 H, Ar*C*H_3), 2.06, 2.05, 2.00, 1.79 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.1, 169.8 (4 C=O, acetyl), 165.8 (CONH), 152.1, 142.9, 142.6, 132.5 (4 C_q, Ar), 129.9 (2 CH_{Ar}), 129.5 (C_q, Ar), 127.4 (2 CH_{Ar}), 118.8 (C_q, Ar), 109.8 (CH_{Ar}), 103.9 (CH_{Ar}), 76.5, 74.9, 73.4, 72.4, 69.3 (C-1/C-5), 62.9 (C-6), 56.8, 56.8 (2 OCH_3), 21.9, 21.2, 21.1, 21.1, 20.9 (5 CH_3, Ar*C*H_3 and 4 acetyl).

MS (CI, isobutane): *m/z* (%) = 602 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{30}H_{36}NO_{12}$: 602.2237; found: 602.2239.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(4-methoxybenzamido)benzene (9d)

Treatment of **7** (85 mg) according to procedure A afforded **9d** (103 mg, 95%) as a pale yellow syrup; R_f = 0.34 (PE–EtOAc, 1:1); $[\alpha]_D^{17}$ –16.7 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.58 (s, 1 H, CONH), 8.33 (s, 1 H, Ar), 7.85 (d, *J* = 8.7 Hz, 2 H, Ar), 6.99 (d, *J* = 8.7 Hz, 2 H, Ar), 6.95 (s, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.30 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 5.01 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.92 (s, 3 H, OCH_3), 3.90–3.83 (hidden, 1 H, H-5), 3.87 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 2.08, 2.07, 2.02, 1.81 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.0, 170.1, 169.7 (4 C=O, acetyl), 165.3 (CONH), 162.9, 152.1, 142.5, 129.5 (4 C_q, Ar), 129.3 (2 CH_{Ar}), 127.5, 118.7 (2 C_q, Ar), 114.4 (2 CH_{Ar}), 109.8, 103.9 (2 CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.4 (C-1), 72.4 (C-2), 69.3 (C-4), 63.1 (C-6), 56.8, 56.7, 55.8 (3 OCH_3), 21.2, 21.1, 21.1, 20.8 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 618 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{30}H_{36}NO_{13}$: 618.2187; found: 618.2187.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(3,5-dimethoxybenzamido)benzene (9e)

Treatment of **7** (102 mg) according to procedure A afforded **9e** (122 mg, 89%); white crystals; mp 181–182 °C; R_f = 0.36 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –12.8 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.58 (s, 1 H, CONH), 8.31 (s, 1 H, Ar), 7.00 (m, 2 H, Ar), 6.96 (s, 1 H, Ar), 6.63 (t, *J* = 2.1 Hz, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.30 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.01 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.5 Hz, 1 H, H-6′), 3.91 (s, 3 H, OCH_3), 3.91–3.85 (hidden, 1 H, H-5), 3.87 (s, 3 H, OCH_3), 3.85 (s, 6 H, OCH_3), 2.08, 2.07, 2.02, 1.81 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.6, 170.0, 169.7 (4 C=O, acetyl), 165.5 (CONH), 161.4, 161.4, 152.0, 142.6, 137.5, 129.2, 119.1 (7 C_q, Ar), 109.8, 105.4, 105.4, 104.2, 104.0 (5 CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.4 (C-1), 72.4 (C-2), 69.3 (C-4), 63.1 (C-6), 56.7, 56.7, 56.0, 56.0 (4 OCH_3), 21.2, 21.0, 21.0, 20.8 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 647.9 (48, $[M + H]^+$), 670.1 (5, $[M + Na]^+$), 1294.7 (100, $[2 M + H]^+$), 1316.7 $[2 M + Na]^+$.

Anal. Calcd for $C_{31}H_{37}NO_{14}$: C, 57.49; H, 5.76; N, 2.16; O, 34.59. Found: C, 56.82; H, 5.74; N, 1.96; O, 35.35.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(4-nitrobenzamido)benzene (9f)

Treatment of **7** (94 mg) according to procedure A afforded **9f** (118 mg, 96%); yellow-green crystals; mp 98–99 °C (CH_2Cl_2–PE–Et_2O); R_f = 0.42 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –15.3 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, CONH), 8.34 (d, *J* = 8.7 Hz, 2 H, Ar), 8.25 (s, 1 H, Ar), 8.02 (d, *J* = 8.7 Hz, 2 H, Ar), 6.97 (s, 1 H, Ar), 5.37 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.27 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.99 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.14 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.92 (s, 3 H, OCH_3), 3.87 (dq, 1 H, H-5), 3.86 (s, 3 H, OCH_3), 2.07, 2.05, 2.00, 1.79 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.7, 170.1, 169.7 (4 C=O, acetyl), 163.6 (CONH), 152.0, 150.2, 142.7, 140.8 (4 C_q, Ar), 128.6 (2 CH_{Ar}), 128.6 (C_q, Ar), 124.5 (2 CH_{Ar}), 121.1 (C_q, Ar), 110.0 (CH_{Ar}), 104.1 (CH_{Ar}), 76.6, 74.8, 73.4, 72.5, 69.3 (C-1/C-5), 63.1 (C-6), 56.8, 56.8 (2 OCH_3), 21.2, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 633 (10, $[M + H]^+$).

MS (ESI–): *m/z* (%) = 631.2 (41, $[M – H]^–$), 666.8 (100, $[M + Cl]^–$), 668.8 (100, $[M + Cl]^–$).

HRMS (CI, isobutane): $[M + H]^+$ calcd for $C_{29}H_{33}N_2O_{14}$: 633.1932; found: 633.1933.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(4-biphenylcarboxamido)benzene (9g)

Treatment of **7** (114 mg) according to procedure A, afforded **9g** (148 mg, 95%); R_f = 0.42 (PE–EtOAc, 1:1); $[\alpha]_D^{17}$ –20.3 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.69 (s, 1 H, CONH), 8.36 (s, 1 H, Ar), 7.95 (d, *J* = 8.4 Hz, 2 H, Ar), 7.71 (d, *J* = 8.1 Hz, 2 H, Ar), 7.62 (d, *J* = 8.4 Hz, 2 H, Ar), 7.44 (m, 3 H, Ar), 6.98 (s, 1 H, Ar), 5.40 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.32 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.25 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 5.03 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.31 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.92 (s, 3 H, OCH_3), 3.92–3.88 (hidden, 1 H, H-5), 3.88 (s, 3 H, OCH_3), 2.07, 2.06, 2.02, 1.82 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.7, 170.1, 169.7 (4 C=O, acetyl), 165.4 (CONH), 152.1, 152.1, 145.1, 142.6, 140.2, 133.9 (6 C_q, Ar), 129.4, 129.4, 128.5, 128.0, 128.0, 127.9, 127.9, 127.6, 127.6 (9 CH_{Ar}), 119.1 (C_q, Ar), 109.9, 104.0 (2 CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.5 (C-1), 72.5 (C-2), 69.3 (C-4), 63.1 (C-6), 56.8, 56.8 (2 OCH_3), 21.2, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 664 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{35}H_{38}NO_{12}$: 664.2394; found: 664.23910.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(1-naphthamido)benzene (9h)

Treatment of **7** (111 mg) according to procedure A afforded **9h** (148 mg, 95%); colorless syrup; $[\alpha]_D^{23}$ –8.4 (*c* 1.05, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 8.41 (br d, *J* = 4.2 Hz, 3 H, CONH and 2 Ar), 7.98 (d, *J* = 8.1 Hz, 1 H, Ar), 7.91 (d, *J* = 6.9 Hz, 1 H, Ar), 7.75 (d, *J* = 6.9 Hz, 1 H, Ar), 7.55 (m, 3 H, Ar), 6.95 (s, 1 H, Ar), 5.40 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.31 (t, $J_{2,3}$ = 9.9 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 5,03 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.15 (br d, *J* = 12.3 Hz, 1 H, H-6′), 3.91 (s, 3 H, OCH_3), 3.91–3.83 (hidden, 1 H, H-5), 3.83 (s, 3 H, OCH_3), 2.07, 2.07, 2.02, 1.84 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.1, 169.8 (4 C=O, acetyl), 167.9 (CONH), 152.1, 142.6, 134.9, 134.2 (4 C_q, Ar), 131.6 (CH_{Ar}), 130.5, 129.5 (2 C_q, Ar), 128.8, 127.8, 127.0, 125.7, 125.7, 125.2 (6 CH_{Ar}), 119.3 (C_q, Ar), 109.8, 104.1 (2 CH_{Ar}), 76.5 (C-5), 75.0 (C-3), 73.4 (C-1), 72.5 (C-2), 69.3 (C-4), 63.0 (C-6), 56.9, 56.6 (2 OCH_3), 21.2, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 638 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{33}H_{36}NO_{12}$: 638.2237; found: 638.2237.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(2-naphthamido)benzene (9i)

Treatment of **7** (92 mg) according to procedure A afforded **9i** (120 mg, 99%); colorless syrup; R_f = 0.42 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –19.5 (*c* 0.7, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.78 (s, 1 H, CONH), 8.40 (s, 1 H, Ar), 8.39 (s, 1 H, Ar), 7.93 (m, 4 H, Ar), 7.58 (m, 2 H, Ar), 6.97 (s, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.31 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 5.25 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.02 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.2 Hz, 1 H, H-6′), 3.94 (s, 3 H, OCH_3), 3.94–3.89 (hidden, 1 H, H-5), 3.89 (s, 3 H, OCH_3), 2.08, 2.07, 2.01, 1.81 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.1, 169.8 (4 C=O, acetyl), 165.9 (CONH), 152.1, 142.7, 135.3, 133.1, 132.6 (5 C_q, Ar), 129.5 (CH_{Ar}), 129.4 (C_q, Ar), 129.2 (CH_{Ar}), 128.4, 128.2, 128.1, 127.4, 123.8 (5 CH_{Ar}), 119.1 (C_q, Ar), 109.9 (CH_{Ar}), 104.1 (CH_{Ar}), 76.6, 74.9, 73.4, 72.5, 69.3 (C-1/C-5), 62.9 (C-6), 56.8, 56.8 (2 OCH_3), 21.2, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 638 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{33}H_{36}NO_{14}$: 638.2237; found: 638.2237.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(2-furylcarboxamido)benzene (9j)

Treatment of **7** (81 mg) according to procedure A afforded **9j** (94 mg, 97%); pale yellow syrup; R_f = 0.29 (PE–EtOAc, 1:1); $[\alpha]_D^{23}$ –13.8 (*c* 1.05, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 8.82 (s, 1 H, CONH), 8.28 (s, 1 H, Ar), 7.55 (br s, 1 H_{furyl}), 7.22 (d, *J* = 4.2 Hz, 1 H_{furyl}), 6.95 (s, 1 H, Ar), 6.56 (q, J_m = 1.8 Hz, J_o = 3.0 Hz, 1 H_{furyl}), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.30 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.00 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.29 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.93 (s, 3 H, OCH_3), 3.89 (dq, 1 H, H-5), 3.86 (s, 3 H, OCH_3), 2.08, 2.07, 2.01, 1.80 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.7, 170.1, 169.7 (4 C=O, acetyl), 156.5 (CONH), 152.0, 148.3 (2 C_q, Ar), 144.9 (CH_{Ar}), 142.6, 128.8, 119.1 (3 C_q, Ar), 115.6, 113.0, 109.9, 104.0 (4 CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.5 (C-1), 72.4 (C-2), 69.2 (C-4), 62.9 (C-6), 56.8, 56.7 (2 OCH_3), 21.2, 21.1, 21.1, 20.8 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 578 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{27}H_{32}NO_{13}$: 578.1874; found: 578.1874.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(2-thienylcarboxamido)benzene (9k)

Treatment of **7** (52 mg) according to procedure A afforded **9k** (61 mg, 96%); pale yellow syrup; R_f = 0.41 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –12.6 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.47 (s, 1 H, CONH), 8.23 (s, 1 H, Ar), 7.59 (dd, J_o = 3.9 Hz, J_m = 0.9 Hz, 1 $H_{thienyl}$), 7.54 (dd, J_o = 4.8 Hz, J_m = 0.9 Hz, 1 $H_{thienyl}$), 7.11 (dd, J_o = 3.9 Hz, J_o = 4.8 Hz, 1 $H_{thienyl}$), 6.93 (s, 1 H, Ar), 5.37 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.27 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.98 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.14 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.90 (s, 3 H, OCH_3), 3.85 (dq, 1 H, H-5), 3.83 (s, 3 H, OCH_3), 2.06, 2.05, 2.00, 1.78 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.8, 170.3, 169.7, 169.3 (4 C=O, acetyl), 159.8 (CONH), 151.7, 142.0, 139.6 (3 C_q, Ar), 131.1 (CH_{Ar}), 128.7 (C_q, Ar), 128.2, 127.9 (2 CH_{Ar}), 118.7 (C_q, Ar), 109.5, 103.6 (2 CH_{Ar}), 76.2, 74.5, 73.1, 72.1, 68.9 (C-1/C-5), 63.0 (C-6), 56.5, 56.4 (2 OCH_3), 20.9, 20.7, 20.7, 20.5 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 594 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{27}H_{32}NO_{12}S$: 594.1645; found: 594.1647.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-nicotinamidobenzene (9l)

Treatment of **7** (85 mg) according to procedure A (note: 2.2 equiv of pyridine was added) afforded **9l** (61 mg, 91%); pale yellow syrup; R_f = 0.21 (PE–EtOAc, 1:2); $[\alpha]_D^{17}$ –8.9 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 9.13 (br s, 1 H_{py}), 8.79 (d, *J* = 3.9 Hz, 1 H, Ar), 8.65 (s, 1 H, CONH), 8.28 (s, 1 H, Ar), 8.21 (dt, *J* = 7.8, 1.8, 1.8 Hz, 1 H_{py}), 7.47 (dd, *J* = 7.8, 4.8 Hz, 1 H_{py}),

6.98 (s, 1 H, Ar), 5.40 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.30 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 5.25 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 5.02 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.93 (s, 3 H, OCH_3), 3.93–3.87 (hidden, 1 H, H-5), 3.87 (s, 3 H, OCH_3), 2.08, 2.07, 2.02, 1.81 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.0, 170.6, 170.0, 169.7 (4 C=O, acetyl), 163.8 (CONH), 153.0 (CH_{py}), 152.0 (C_q, Ar), 148.4 (CH_{py}), 142.6 (C_q, Ar), 135.4 (CH_{py}), 131.0, 128.8 (2 C_q, Ar), 124.1 (CH_{py}), 119.7 (C_q, Ar), 109.9, 104.1 (2 CH_{Ar}), 76.5 (C-5), 74.8 (C-3), 73.4 (C-1), 72.4 (C-2), 68.2 (C-4), 62.9 (C-6), 56.8, 56.7 (2 OCH_3), 21.2, 21.0, 21.0, 20.8 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 589 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{33}N_2O_{12}$: 589.2033; found: 589.2031.

N-Carbonyl-(6-ethoxycarbonyl-2-pyridyl)-4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,5-dimethoxyaniline (9m) and 2,6-[Bis-2,5-dimethoxy-4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)anilino-*N*-carbonyl]pyridine (9n)

Treatment of **7** (102 mg) according to procedure A (note: 0.53 equiv of pyridine-2,6-dicarbonyl chloride was added) afforded **9m** (8 mg, 6%) and **9n** (101 mg, 87%).

9m

Yellow-green syrup; R_f = 0.55 (PE–EtOAc, 1:1, UV 312 nm orange, 254 nm black).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 10.75 (s, 1 H, CONH), 8.43 (dd, J_m = 1.2 Hz, J_o = 7.8 Hz, 1 H, pyridine H-3′ or H-5′), 8.37 (s, 1 H, Ar), 8.29 (dd, *J* = 1.2, 7.8 Hz, 1 H, pyridine H-3′ or H-5′), 8.06 (t, *J* = 7.8 Hz, 1 H, H-4′), 6.97 (s, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.32 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 5.25 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 5.01 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.51 (q, *J* = 7.0, 2 H, OCH_2), 4.30 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.98 (s, 3 H, OCH_3), 3.89 (m, 1 H, H-5), 3.89 (s, 3 H, OCH_3), 2.09, 2.07, 2.01, 1.79 (4 s, 12 H, $OCOCH_3$), 1.52 (t, *J* = 7.0 Hz, 3 H, CH_3CH_2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.1, 169.7 (4 C=O, acetyl), 164.8 (CO_2Et), 161.8 (CONH), 152.1, 150.4, 147.3, 143.4 (4 C_q, Ar), 139.3 (CH, pyridine, C-4′), 127.8, 125.5 (CH, pyridine, C-3′ and C-5′), 119.3 (C_q, Ar), 110.2 (CH_{Ar}), 103.9 (CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.6 (C-1), 72.4 (C-2), 69.3 (C-4), 62.9 (C-6), 56.9, 56.8 (2 OCH_3), 21.2, 21.1, 21.1, 20.8 (4 CH_3, acetyl), 14.7 (CH_3CH_2O).

MS (CI, isobutane): *m*/*z* (%) = 661 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{31}H_{37}N_2O_{14}$: 661.2245; found: 661.2248.

9n

Yellow-green syrup; $[\alpha]_D^{17}$ –72.7 (*c* 1.0, CH_2Cl_2); R_f = 0.34 (PE–EtOAc, 1:1, UV 312 nm orange, 254 nm black).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 10.37 (s, 2 H, CONH), 8.48 (d, *J* = 7.8 Hz, 2 H_{py}), 8.38 (s, 2 H, Ar), 8.17 (t, *J* = 7.8 Hz, 1 H_{py}), 7.06 (s, 2 H, Ar), 5.41 (t, $J_{3,4}$ = 9.0 Hz, 2 H, H-3), 5.33 (t, $J_{2,3}$ = 9.6 Hz, 2 H, H-2), 5.27 (t, $J_{4,5}$ = 9.3 Hz, 2 H, H-4), 5.05 (d, $J_{1,2}$ = 9.6 Hz, 2 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 2 H, H-6), 4.14 (dd, $J_{5,6'}$ = 1.8 Hz, 2 H, H-6′), 3.95 (s, 6 H, 2 OCH_3), 3.87 (hidden, 2 H, H-5), 3.92 (s, 6 H, 2 OCH_3), 2.11, 2.08, 2.03, 1.82 (4 s, 24 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.1, 170.7, 170.0, 169.7 (8 C=O, acetyl), 161.5 (2 CONH), 152.1, 149.5, 143.4 (6 C_q, Ar), 140.0 (CH_{Ar}), 128.7 (2 C_q, Ar), 125.7 (2 CH_{Ar}), 119.8 (2 C_q, Ar), 110.5 (2 CH_{Ar}), 104.1 (2 CH_{Ar}), 76.6 (2 C-5), 74.9 (2 C-3), 73.4 (2 C-1), 72.4 (2 C-2), 69.2 (2 C-4), 68.2 (2 C-6), 57.1, 56.8 (4 OCH_3), 21.2, 21.1, 21.1, 20.9 (8 CH_3, acetyl).

MS (ESI+): *m*/*z* (%) = 1120.3 (95, $[M + Na]^+$), 1098.1 (100, $[M + H]^+$).

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-1,4-dimethoxy-5-(4-nitrobenzamido)benzene (10f)

Treatment of **8** (157 mg) according to procedure A afforded **10f** (205 mg, 99%); yellow-green crystals; mp 84–85 °C (CH_2Cl_2–PE–Et_2O); R_f = 0.40 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –1.2 (*c* 0.93, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, CONH), 8.34 (d, *J* = 9.0 Hz, 2 H, Ar), 8.26 (s, 1 H, Ar), 8.04 (d, *J* = 9.0 Hz, 2 H, Ar), 7.06 (s, 1 H, Ar), 5.56 (d, $J_{3,4}$ = 3.3 Hz, 1 H, H-4), 5.48 (t, $J_{2,3}$ = 9.9 Hz, 1 H, H-2), 5.26 (dd, 1 H, H-3), 5.00 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.23–4.11 (m, 3 H, H-5, H-6, H-6′), 3.97 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 2.24, 2.04, 2.00, 1.84 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 170.6, 170.4, 169.8 (4 C=O, acetyl), 163.5 (CONH), 151.9, 150.1, 142.6, 140.7 (4 C_q, Ar), 128.6 (2 CH_{Ar}), 128.5 (C_q, Ar), 124.4 (2 CH_{Ar}), 120.5 (C_q, Ar), 110.3 (CH_{Ar}), 104.1 (CH_{Ar}), 75.1 (C-5), 73.9 (C-1), 72.7 (C-3), 69.8 (C-2), 68.3 (C-4), 62.1 (C-6), 56.8 (2 OCH_3), 21.1, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m*/*z* (%) = 632.8 (100, $[M + H]^+$), 655.1 (8, $[M + Na]^+$), 710.5 (15, $[M + H + DMSO]^+$), 1286.6 (97, $[2 M + Na]^+$).

MS (ESI–): *m*/*z* (%) = 631.2 (45, $[M – H]^-$), 666.7 (100, $[M + Cl]^-$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{33}N_2O_{14}$: 633.1932; found: 633.1929.

2-(β-D-Glucopyranosyl)-1,4-dimethoxy-5-(4-nitrobenzamido)benzene (11f)

Compound **9f** (59 mg, 0.187 mmol) was dissolved in anhyd MeOH (5 mL) and cooled in an ice-water mixture. After the addition of $Ba(OMe)_2$ solution [1.25 mL of 0.02 M/L of $Ba(OMe)_2$, prepared by dissolving BaO (153 mg) in anhyd MeOH (50 mL)], the mixture was allowed to stand, with occasional shaking, in the refrigerator for 20 h. TLC showed that the starting material **9f** (R_f = 0.92, MeOH–CH_2Cl_2, 1:5) had completely changed into a more polar compound **11f** (R_f = 0.45 (MeOH–CH_2Cl_2, 1:5). BaO was removed by stirring with a slight excess of Dowex 50wX2 (H^+) ion-exchange resin. The solution was filtered and evaporated to a syrup under reduced pressure and purified using 12:1 MeOH–CH_2Cl_2 as eluent to yield pure **11f** (42 mg, 97%); orange-red solid; mp 202–204 °C; $[\alpha]_D^{21}$ –10.6 (*c* 0.62, DMSO).

^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 9.88 (s, 1 H, CONH), 8.36 (d, *J* = 8.7 Hz, 2 H, Ar), 8.18 (d, *J* = 8.7 Hz, 2 H, Ar), 7.45 (s, 1 H, Ar), 7.02 (s, 1 H, Ar), 4.97 (d, *J* = 4.2 Hz, 1 H, OH exch. D_2O), 4.93 (d, *J* = 4.2 Hz, 1 H, OH exch. D_2O), 4.71 (d, *J* = 5.4 Hz, 1 H, OH exch. D_2O), 4.50 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.45 (t, *J* = 5.7 Hz, 1 H, OH exch. D_2O), 3.80 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.68 (m, 1 H, H-6), 3.48–3.40 (m, 2 H, H-2 and H-6′), 3.30 (m, 1 H, H-5), 3.21 (br s, 2 H, H-3 and H-4).

^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 151.2, 149.1, 145.8, 140.1 (CONH and 3 C_q, Ar), 129.1, 129.1 (2 CH_{Ar}), 126.1, 125.9 (2 C_q, Ar), 123.5, 123.5 (2 CH_{Ar}), 114.1 (C_q, Ar), 111.6, 109.0 (2 CH_{Ar}), 81.5 (C-3 or C-4), 78.5 (C-5), 74.1 (C-1), 73.6 (C-2), 70.4 (C-4 or C-3), 61.4 (C-6), 56.6, 52.2 (2 OCH_3).

MS (ESI+): *m*/*z* (%) = 950.8 (100, $[2 M + Na]^+$).

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{24}N_2O_{10}$ + Na: 487.1329; found: 487.1331.

2-(β-D-Galactopyranosyl)-1,4-dimethoxy-5-(4-nitrobenzamido)benzene (12f)

Treatment of **10f** (88 mg) according to the above procedure afforded **12f** (61 mg, 94); orange-red solid; mp 214–216 °C; R_f = 0.44 (MeOH–CH_2Cl_2, 1:5); $[\alpha]_D^{21}$ –2.6 (*c* 0.53, DMSO).

^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 9.90 (s, 1 H, CONH), 8.36 (d, *J* = 8.7 Hz, 2 H, Ar), 8.19 (d, *J* = 8.7 Hz, 2 H, Ar), 7.44 (s, 1 H, Ar), 7.10 (s, 1 H, Ar), 4.73 (br s, 1 H, OH exch. D_2O), 4.58 (br s, 2 H, OH exch. D_2O), 4.46 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.37 (br s, 1 H, OH exch. D_2O), 3.80 (s, 3 H, OCH_3), 3.80–3.73 (hidden, 2 H, H-2 and H-3), 3.73 (s, 3 H, OCH_3), 3.51–3.41 (m, 4 H, H-4, H-5, H-6, H-6′).

^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 163.6 (CONH), 151.1, 149.1, 145.8 (3 C_q, Ar), 129.5, 129.5 (2 CH_{Ar}), 126.3, 126.0 (2 C_q, Ar), 123.5, 123.5 (2 CH_{Ar}), 114.1 (C_q, Ar), 111.8, 108.9 (2 CH_{Ar}), 79.8, 75.1, 74.4 (C-1), 70.6, 69.0 (C-2 to C-5), 60.8 (C-6), 56.5, 52.2 (2 OCH_3).

MS (ESI+): *m*/*z* (%) = 950.8 (100, [2 M + Na]$^+$).

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{24}N_2O_{10}$ + Na: 487.1329; found: 487.1330.

Oxidation of 9a–9l and 9n to 13a–13l and 13n; General Procedure B

The *C*-glycosyl amido benzene (1 equiv) dissolved in MeCN (2 mL) was reacted with ceric ammonium nitrate (400 mg, 0.73 mmol, 4 equiv) dissolved in H_2O (5 mL) at r.t. After ~2 h, TLC (PE–EtOAc, 1:1 or similar) showed that the starting material had been consumed, to afford a more mobile compound. H_2O (10 mL) was poured into the mixture which was extracted with CH_2Cl_2 (3 × 15 mL). The extracts were combined and washed with brine (15 mL), H_2O (15 mL), dried ($MgSO_4$), and concentrated. The residue was chromatographed (PE–EtOAc, 3:2 or similar) on silica gel. Concentration of the homogeneous fractions led to the desired benzoquinone.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(acrylamido)-1,4-benzoquinone (13a)

Treatment of compound **9a** (98 mg) according to procedure B afforded **13a** (62 mg, 67%) as a yellow-green syrup; R_f = 0.44 (PE–EtOAc, 1:1); $[\alpha]_D^{19}$ –19.0 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.21 (s, 1 H, CONH), 7.64 (s, 1 H, Ar), 6.93 (s, 1 H, Ar), 6.47 (d, *J* = 16.2 Hz, 1 H_{alkene}), 6.32 (dd, *J* = 16.2, 10.2 Hz, 1 H_{alkene}), 5.90 (d, *J* = 10.2, 16.2 Hz, 1 H_{alkene}), 5.37 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.14 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.93 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 4.72 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.26 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.82 (dq, 1 H, H-5), 2.10, 2.06, 2.01, 1.91 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.4, 182.9 (2 C=O, benzoquinone), 171.0, 170.3, 170.3, 170.0 (4 C=O, acetyl), 164.6 (CONH), 146.4, 138.7 (2 C_q, Ar), 130.7 ($CH_{2alkene}$), 130.7 (CH_{alkene}), 115.1, 104.6 (2 CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.0 (C-1), 68.7 (C-4), 62.5 (C-6), 21.1, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 510 (100, [phenol + H]$^+$), 508 (20, [M + H]$^+$).

MS (ESI+): *m*/*z* (%) = 1036.6 (100, [2 M + Na]$^+$), 530.1 (55, [M + Na]$^+$), 507.9 (40, [M + H]$^+$).

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{25}NO_{12}$ + Na: 530.1274; found: 530.12761.

(*E*)-2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(cinnamamido)-1,4-benzoquinone (13b)

Treatment of compound **9b** (148 mg) according to procedure B afforded **13b** (134 mg, 95%) as a orange-red solid; mp 194–196 °C; R_f = 0.63 (PE–EtOAc, 1:1); $[\alpha]_D^{17}$ –26.7 (*c* 1.1, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.34 (s, 1 H, CONH), 7.76 (d, *J* = 15.6 Hz, 1 H_{alkene}) 7.69 (s, 1 H, Ar), 7.58 (m, 2 H, Ar), 7.42 (m, 3 H, Ar), 6.93 (s, 1 H, Ar), 6.69 (d, *J* = 15.6 Hz, 1 H_{alkene}), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.16 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.94 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 4.74 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.27 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.83 (dq, 1 H, H-5), 2.10, 2.06, 2.01, 1.92 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.4, 183.0 (2 C=O, benzoquinone), 171.0, 170.4, 170.3, 170.0 (4 C=O, acetyl), 165.1 (CONH), 146.4 (C_q, Ar), 145.2 (CH_{alkene}), 139.0, 134.4 (2 C_q, Ar), 131.2, 130.7, 129.4, 129.4, 128.7, 128.7 (6 CH_{Ar}), 119.8 (CH_{alkene}), 114.8 (CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.2 (C-2), 71.9 (C-1), 68.7 (C-4), 62.5 (C-6), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 586 (100, [phenol + H]$^+$), 584 (45, [M + H]$^+$).

HRMS (CI, isobutane): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{30}NO_{12}$: 584.1768; found: 584.1767.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-methylbenzamido)-1,4-benzoquinone (13c)

Treatment of compound **9c** (85 mg) according to procedure B afforded **13c** (74 mg, 91%); yellow-green crystals; mp 103–104 °C (CH_2Cl_2–PE–Et_2O); R_f = 0.52 (EtOAc–PE, 1:1); $[\alpha]_D^{17}$ –21.0 (*c* 0.6, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.82 (s, 1 H, CONH), 7.78 (d, *J* = 8.1 Hz, 2 H, Ar), 7.72 (s, 1 H, Ar), 7.33 (d, *J* = 8.1 Hz, 2 H, Ar), 6.96 (s, 1 H, Ar), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.14 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.94 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.74 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.26 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.82 (dq, 1 H, H-5), 2.45 (s, 3 H, CH_3), 2.10, 2.06, 2.01, 1.92 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.5, 183.2 (2 C=O, benzoquinone), 171.1, 170.4, 170.4, 170.0 (4 C=O, acetyl), 166.1 (CONH), 146.5, 144.4, 138.9 (3 C_q, Ar), 130.7 (CH_{Ar}), 130.6 (C_q, Ar), 130.2, 127.8 (4 CH_{Ar}), 114.5 (CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.4 (C-6), 22.1 (Ar*C*H_3), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 572 (100, [M + H]$^+$).

HRMS (CI, isobutane): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{30}NO_{12}$: 572.1768; found: 572.17675.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-methoxybenzamido)-1,4-benzoquinone (13d)

Treatment of compound **9d** (100 mg) according to procedure B afforded **13d** (81 mg, 85%); yellow crystals; mp 141–142 °C (CH_2Cl_2–PE–Et_2O); R_f = 0.48 (EtOAc–PE, 1:1); $[\alpha]_D^{23}$ –20.5 (*c* 0.88, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.78 (s, 1 H, CONH), 7.85 (d, *J* = 8.7 Hz, 2 H, Ar), 7.69 (s, 1 H, Ar), 7.00 (d, *J* = 8.7 Hz, 2 H, Ar), 6.96 (s, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.6 Hz, 1 H, H-3), 5.15 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.95 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 4.75 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.89 (s, 3 H, OCH_3), 3.84 (dq, 1 H, H-5), 2.11, 2.06, 2.02, 1.92 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.5, 183.2 (2 C=O, benzoquinone), 171.0, 170.4, 170.3, 170.0 (4 C=O, acetyl), 165.6 (CONH), 163.8, 146.5, 138.9 (3 C_q, Ar), 130.6 129.8, 129.8 (3

CH_{Ar}), 125.6 (C_q, Ar), 114.7, 114.7, 114.3 (CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.0 (C-1), 68.7 (C-4), 62.4 (C-6), 56.0 (OCH_3), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 590 (100, [phenol + H]$^+$).

MS (ESI+): *m/z* (%) = 588.0 (20, [M + H]$^+$), 610.1 (25, [M + Na]$^+$), 1196.6 (100, [2 M + Na]$^+$).

HRMS (ESI+): *m/z* [M + H]$^+$ calcd for $C_{28}H_{30}NO_{13}$: 588.1717; found: 588.1718.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(3,5-dimethoxybenzamido)-1,4-benzoquinone (13e)

Treatment of compound **9e** (105 mg) according to procedure B afforded **13e** (97 mg, 97%) as yellow-green crystals; mp 207–208 °C (CH_2Cl_2–PE–Et_2O); R_f = 0.40 (EtOAc–PE, 1:1); $[\alpha]_D^{19}$ –16.2 (*c* 0.82, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.77 (s, 1 H, CONH), 7.68 (s, 1 H, Ar), 6.96 (m, 3 H, Ar), 6.66 (t, *J* = 2.1, 2.1 Hz, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.15 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.91 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.74 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.26 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.91–3.82 (m, 1 H, H-5), 3.86 (s, 6 H, OCH_3), 2.10, 2.06, 2.01, 1.92 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.4, 183.0 (2 C=O, benzoquinone), 171.0, 170.3, 170.3, 169.9 (4 C=O, acetyl), 166.0 (CONH), 161.6, 161.6, 146.5, 138.7, 135.5 (5 C_q, Ar), 130.7, 114.8, 105.6, 105.6, 105.3 (5 CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.4 (C-6), 56.1, 56.1 (2 OCH_3), 21.1, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1256.7 (100, [2 M + Na]$^+$), 1234.5 (45, [2 M + H]$^+$), 617.9 (100, [M + H]$^+$).

HRMS (ESI+): *m/z* [M + H]$^+$ calcd for $C_{29}H_{32}NO_{14}$: 618.1823; found: 618.18234.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-nitrobenzamido)-1,4-benzoquinone (13f)

Treatment of compound **9f** (81 mg) according to procedure B afforded **13f** (72 mg, 93%) as yellow-green crystals; mp 111–113 °C (CH_2Cl_2–PE– Et_2O); R_f = 0.48 (PE–EtOAc, 1:1); $[\alpha]_D^{19}$ –26.8 (*c* 1.11, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.86 (s, 1 H, CONH), 8.37 (d, *J* = 8.7 Hz, 2 H, Ar), 8.05 (d, *J* = 8.7 Hz, 2 H, Ar), 7.69 (s, 1 H, Ar), 6.98 (s, 1 H, Ar), 5.37 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.12 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.91 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 4.71 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.26 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.14 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.82 (dq, 1 H, H-5), 2.08, 2.04, 2.00, 1.90 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.3, 182.8 (2 C=O, benzoquinone), 171.0, 170.4, 170.3, 170.0 (4 C=O, acetyl), 164.2 (CONH), 150.8, 146.9, 138.7, 138.3 (4 C_q, Ar), 130.6 (CH_{Ar}), 129.0 (2 CH_{Ar}), 124.7 (2 CH_{Ar}), 115.6 (CH_{Ar}), 76.7 (C-5), 73.8 (C-3), 73.3 (C-2), 72.1 (C-1), 68.7 (C-4), 62.5 (C-6), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 603 (55, [M + H]$^+$).

HRMS (CI, isobutane): *m/z* [M + H]$^+$ calcd for $C_{27}H_{27}N_2O_{14}$: 603.1462; found: 603.1463.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-biphenylcarboxamido)-1,4-benzoquinone (13g)

Treatment of compound **9g** (146 mg) according to procedure B afforded **13g** (131 mg, 94%) as yellow crystals; mp 199–200 °C (CH_2Cl_2–PE–Et_2O); R_f = 0.48 (PE–EtOAc, 1:1); $[\alpha]_D^{19}$ –26.2 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.89 (s, 1 H, CONH), 7.94 (d, *J* = 8.1 Hz, 2 H, Ar), 7.73 (d, *J* = 8.4 Hz, 3 H, Ar), 7.73 (s, 1 H, Ar), 7.44 (m, 3 H, Ar), 6.99 (s, 1 H, Ar), 5.40 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.16 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.96 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 4.75 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.26 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.84 (dq, 1 H, H-5), 2.11, 2.06, 2.02, 1.93 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.5, 183.1 (2 C=O, benzoquinone), 171.0, 170.4, 170.4, 170.0 (4 C=O, acetyl), 165.9 (CONH), 146.6, 146.2, 139.8, 138.8, 131.9 (5 C_q, Ar), 130.7, 129.5, 129.5, 128.9, 128.3, 128.3, 128.0, 128.0, 127.7, 127.7, 114.7 (11 CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.5 (C-6), 21.2, 21.0, 21.0, 21.0 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 636 (100, [phenol + H]$^+$), 634 (60, [M + H]$^+$).

HRMS (CI, isobutane): *m/z* [M + H]$^+$ calcd for $C_{33}H_{32}N_1O_{14}$: 634.1924; found: 634.19245.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(1-naphthamido)-1,4-benzoquinone (13h)

Treatment of compound **9h** (43 mg) according to procedure B afforded **13h** (36 mg, 88%); yellow-green syrup; R_f = 0.54 (PE–EtOAc, 1:1); $[\alpha]_D^{23}$ –18.9 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.65 (s, 1 H, CONH), 8.36 (dd, J_o = 7.5 Hz, J_m = 1.5 Hz, 1 H, Ar), 8.04 (d, *J* = 8.4 Hz, 1 H, Ar), 7.93 (dd, J_o = 7.5 Hz, J_m = 1.5 Hz, 1 H, Ar), 7.83 (s, 1 H, Ar), 7.76 (dd, *J* = 0.9 Hz, 7.2 Hz, 1 H, Ar), 7.65–7.52 (m, 3 H, Ar), 6.96 (d, *J* = 0.9 Hz, 1 H, Ar), 5.40 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.15 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.96 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.75 (dd, $J_{1,2}$ = 9.6 Hz, *J* = 0.9 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.83 (dq, 1 H, H-5), 2.10, 2.06, 2.02, 1.96 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.6, 182.9 (2 C=O, benzoquinone), 171.0, 170.4, 170.4, 170.0 (4 C=O, acetyl), 168.3 (CONH), 146.5, 138.9, 134.2 (3 C_q, Ar), 133.0 (CH_{Ar}), 132.5 (C_q, Ar), 130.7 (CH_{Ar}), 130.4 (C_q, Ar), 129.0, 128.4, 127.3, 126.3, 125.3, 125.0, 115.0 (7 CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.5 (C-6), 21.2, 21.0, 21.0, 21.0 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 610 (50), 608 (100, [M + H]$^+$).

HRMS (CI, isobutane): *m/z* [M + H]$^+$ calcd for $C_{31}H_{30}N_1O_{12}$: 608.1768; found: 608.1767.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(2-naphthamido)-1,4-benzoquinone (13i)

Treatment of compound **9i** (56 mg) according to procedure B afforded **13i** (46 mg, 86%); yellow-green crystals; mp 165–166 °C (CH_2Cl_2–PE–Et_2O); R_f = 0.54 (PE–EtOAc, 1:1); $[\alpha]_D^{23}$ –28.3 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 9.01 (s, 1 H, CONH), 8.41 (s, 1 H, Ar), 7.95 (m, 4 H, Ar), 7.78 (s, 1 H, Ar), 7.63 (m, 2 H, Ar), 7.00 (s, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.15 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.96 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.76 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.84 (dq, 1 H, H-5), 2.11, 2.06, 2.02, 1.93 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.5, 183.2 (2 C=O, benzoquinone), 171.0, 170.4, 170.3, 170.0 (4 C=O, acetyl), 166.3 (CONH), 146.6, 138.9, 135.8, 132.9 (4 C_q, Ar), 130.7 (CH_{Ar}), 130.6 (C_q, Ar), 129.7, 129.6, 129.1, 128.8, 128.3, 127.7, 123.6, 114.8 (8 CH_{Ar}), 76.7 (C-5), 74.0 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.5 (C-6), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1236.6 (75, [2 M + Na]$^+$), 607.9 (100, [M + H]$^+$).

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(2-furylcarboxamido)-1,4-benzoquinone (13j)

Treatment of compound **9j** (62 mg) according to procedure B afforded **13j** (52 mg, 89%); golden-yellow needles; mp 89–91 °C (CH_2Cl_2–PE– Et_2O); R_f = 0.42 (PE–EtOAc, 1:1); $[\alpha]_D^{23}$ –21.7 (*c* 0.78, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 8.98 (s, 1 H, CONH), 7.65 (s, 1 $H_{quinone}$), 7.61 (dd, J_o = 1.8 Hz, J_m = 0.6 Hz, 1 H_{furyl}), 7.31 (dd, J_m = 0.6 Hz, J_o = 3.6 Hz, 1 H_{furyl}), 6.96 (d, *J* = 0.9 Hz, 1 $H_{quinone}$), 6.61 (dd, J_o = 1.8 Hz, J_o = 3.6 Hz, 1 H_{furyl}), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.14 (t, $J_{4,5}$ = 10.2 Hz, 1 H, H-4), 4.94 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.73 (dd, $J_{1,2}$ = 9.6, 0.9 Hz, 1 H, H-1), 4.27 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.83 (dq, 1 H, H-5), 2.10, 2.06, 2.01, 1.92 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.3, 182.7 (2 C=O, benzoquinone), 171.0, 170.4, 170.3, 170.0 (4 C=O, acetyl), 156.7 (CONH), 147.0, 146.4 (2 C_q, Ar), 146.0 (CH_{Ar}), 138.5 (C_q, Ar), 130.7 (CH_{Ar}), 117.7, 114.7, 113.5 (3 CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.4 (C-6), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 548 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{26}N_1O_{13}$: 548.1404; found: 548.1406.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(2-thienylcarboxamido)-1,4-benzoquinone (13k)

Treatment of compound **9k** (60 mg) according to procedure B afforded **13k** (54 mg, 95%) as golden-yellow crystals; mp 168–169 °C (CH_2Cl_2–Et_2O–PE); R_f = 0.44 (EtOAc–PE, 1:1); $[\alpha]_D^{20}$ –20.1 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.64 (s, 1 H, CONH), 7.68 (dd, J_o = 3.9 Hz, J_m = 0.9 Hz, 1 $H_{thienyl}$), 7.65 (dd, J_o = 5.1 Hz, J_m = 0.9 Hz, 1 $H_{thienyl}$), 7.61 (s, 1 H, Ar), 7.16 (dd, J_o = 3.9 Hz, J_o = 5.1 Hz, 1 $H_{thienyl}$), 6.94 (d, *J* = 0.9 Hz, 1 H, Ar), 5.36 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.12 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.92 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 4.98 (dd, $J_{1,2}$ = 9.6 Hz, *J* = 0.9 Hz, 1 H, H-1), 4.25 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.13 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.81 (dq, 1 H, H-5), 2.09, 2.04, 1.99, 1.90 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.3, 182.9 (2 C=O, benzoquinone), 171.0, 170.3, 170.3, 170.0 (4 C=O, acetyl), 160.5 (CONH), 146.6, 138.6, 138.0 (3 C_q, Ar), 133.4, 130.6, 130.3, 128.7, 114.7 (5 CH_{Ar}), 76.6 (C-5), 73.9 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.4 (C-6), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 564 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{26}NO_{12}S$: 564.1176; found: 564.1175.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-nicotinamido-1,4-benzoquinone (13l)

Treatment of compound **9l** (92 mg) according to procedure B afforded **13l** (67 mg, 77%); yellow-green syrup; R_f = 0.24 (PE–EtOAc, 1:3); $[\alpha]_D^{23}$ –29.0 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 9.14 (s, 1 H_{py}), 8.86 (s, 1 H, CONH) 8.84 (br s, 1 H_{py}), 8.20 (dt, *J* = 7.8, 2.1, 1.8 Hz, 1 H_{py}), 7.71 (s, 1 H, Ar), 7.50 (dd, *J* = 8.1, 4.8 Hz, 1 H_{py}), 6.99 (s, 1 H, Ar), 5.39 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.15 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.94 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.74 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.84 (dq, 1 H, H-5), 2.10, 2.06, 2.01, 1.92 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.0, 182.4 (2 C=O, benzoquinone), 170.6, 170.0, 170.0, 169.6 (4 C=O, acetyl), 164.2 (CONH), 154.0, 148.7 (2 CH_{py}), 146.4, 138.1 (2 C_q, Ar), 135.2 (CH_{py}), 130.3 (CH_{Ar}), 128.9 ($C_{q\ py}$), 124.8 (CH_{py}), 115.1 (CH_{Ar}), 76.3 (C-5), 73.5 (C-3), 72.9 (C-2), 71.7 (C-1), 68.3 (C-4), 62.1 (C-6), 20.8, 20.6, 20.6, 20.5 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 561 (100, $[phenol + H]^+$).

MS (ESI+): *m*/*z* (%) = 1116.7 (80, $[2 M + H]^+$), 559.0 (100, $[M + H]^+$).

HRMS (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{27}N_2O_{12}$: 559.1564; found: 559.15591.

2,6-Bis[2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-benzoquinone-5-amino-*N*-carbonyl]pyridine (13n)

Treatment of compound **9n** (98 mg) according to procedure B (note: 8 equiv CAN was added) afforded **13n** (76 mg, 80%); golden yellow crystals; mp 202–204 °C (CH_2Cl_2–Et_2O–PE); R_f = 0.55 (PE–EtOAc, 1:2); $[\alpha]_D^{19}$ –40.7 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 10.53 (s, 2 H, CONH), 8.52 (d, *J* = 7.5 Hz, 2 H_{py}), 8.24 (t, *J* = 7.2 Hz, 1 H_{py}), 7.78 (s, 2 H, Ar), 7.14 (s, 2 H, Ar), 5.41 (t, $J_{3,4}$ = 9.3 Hz, 2 H, H-3), 5.17 (t, $J_{4,5}$ = 9.3 Hz, 2 H, H-4), 4.95 (t, $J_{2,3}$ = 9.0 Hz, 2 H, H-2), 4.76 (d, $J_{1,2}$ = 9.3 Hz, 2 H, H-1), 4.30 (dd, $J_{5,6}$ = 3.6 Hz, $J_{6,6'}$ = 12.0 Hz, 2 H, H-6), 4.17 (d, 2 H, H-6′), 3.86 (dd, 2 H, H-5), 2.13, 2.07, 2.03, 1.94 (4 s, 24 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.6, 186.6, 182.9, 182.9 (4 C=O, benzoquinone), 171.1, 171.1, 170.4, 170.4, 170.3, 170.3, 170.0, 170.0 (8 C=O, acetyl), 162.2, 162.2 (2 CONH), 148.3, 148.3, 146.5, 146.5 (4 C_q, Ar), 140.6 (CH_{py}), 138.3, 138.3 (2 C_q, Ar), 131.0, 131.0, 127.2, 127.2, 115.5, 115.5 (6 CH_{Ar}), 76.5, 76.5 (2 C-5), 73.9, 73.9 (2 C-3), 73.3 (2 C-2), 72.2 (2 C-1), 68.6 (2 C-4), 62.3 (2 C-6), 21.2, 21.2, 21.0, 21.0, 21.0, 21.0, 20.9, 20.9 (8 CH_3, acetyl).

MS (ESI+): *m*/*z* (%) = 1060.2 (35, $[M + Na]^+$), 1037.9 (100, $[M + H]^+$).

Reduction of 13a–l and 13n to 14a–l and 14n; General Procedure C

The *C*-glycosyl benzoquinone (1 equiv) was dissolved in $CHCl_3$ (3 mL). A solution of $Na_2S_2O_4$ (85% tech., 400 mg, 0.978 mmol, 6 equiv) in H_2O (3 mL) was added to the solution. After stirring the mixture vigorously for 45 min at r.t., TLC showed the starting material was still present while a new more polar compound appeared. Another portion of $Na_2S_2O_4$ (132 mg, 2 equiv) was added to the mixture and after 1 h, TLC showed the complete conversion of the starting material. After extracting the mixture with $CHCl_3$ (3 × 15 mL), the combined organic phases were washed with brine (15 mL), H_2O (15 mL), and dried ($MgSO_4$). After filtration and concentration, the residue was chromatographed (PE–EtOAc, 1:1) on silica gel to afford the desired hydroquinone.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(acrylamido)hydroquinone (14a)

Treatment of compound **13a** (45 mg) according to procedure C afforded **14a** (29 mg, 65%); yellow syrup; R_f = 0.17 (PE–EtOAc, 1:1); $[\alpha]_D^{22}$ +14.6 (*c* 0.57, $CHCl_3$).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.34, 8.07 (2 s, 2 H, CONH and OH, exch. D_2O), 6.93 (s, 1 H, Ar), 6.65 (s, 1 H, Ar), 6.40 (d, *J* = 17.1 Hz, 1 H_{alkene}), 6.23 (dd, *J* = 10.8, 17.1 Hz, 1 H_{alkene}), 5.76 (d, *J* = 10.8 Hz, 1 H_{alkene}), 5.29 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.22 (t, $J_{2,3}$ = 9.0 Hz, 1 H, H-2), 5.18 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.57 (d, $J_{1,2}$ = 9.3 Hz, 1 H, H-1), 4.26 (dd, $J_{5,6}$ = 4.2 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.09 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.81 (dq, 1 H, H-5), 2.03, 2.00, 1.94, 1.80 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.0, 170.0, 169.7 (4 C=O, acetyl), 165.3 (CONH), 150.8, 148.9, 141.5, 129.0 (4 C_q, Ar), 127.5 ($CH_{2\ alkene}$), 127.4 (CH_{alkene}), 110.4, 110.3 (2 CH_{Ar}), 76.5, 74.5, 74.2,

71.4, 68.6 (C-1/C-5), 62.2 (C-6), 21.2, 21.1, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 510 (100, $[M + H]^+$).

(*E*)-2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(cinnamamido)hydroquinone (14b)

Treatment of compound **13b** (95 mg) according to procedure C afforded **14b** (89 mg, 93%); pale yellow foam; R_f = 0.11 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –29.9 (*c* 0.7, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.54 (s, 1 H, OH exch. D_2O), 8.45 (s, 1 H, CONH, exch. D_2O), 7.72 (d, *J* = 15.6 Hz, 1 H_{alkene}), 7.69 (s, 1 H, OH exch. D_2O), 7.51–7.48 (m, 2 H, Ar), 7.35 (s, 1 H, Ar), 7.33–7.29 (m, 3 H, Ar), 6.79 (s, 1 H, Ar), 6.61 (d, *J* = 15.6 Hz, 1 H_{alkene}), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.31 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.74 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (br d, $J_{5,6'}$ = 1.5 Hz, 1 H, H-6′), 3.86 (dq or ddd, 1 H, H-5), 2.06, 2.03, 2.00, 1.84 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.4, 170.8, 170.3, 170.1 (4 C=O, acetyl), 165.9 (CONH), 148.8 (C_q, Ar), 143.8 (CH_{alkene}), 141.1, 134.8 (2 C_q, Ar), 130.7, 129.4, 129.0, 128.5, 128.1 (5 CH_{Ar}), 127.8 (C_q, Ar), 127.5 (CH_{Ar}), 120.1 (*C*H_{alkene}), 119.2 (C_q, Ar), 110.0 (CH_{Ar}), 77.2 (C-1), 76.5 (C-5), 74.5 (C-3), 72.0 (C-2), 68.9 (C-4), 62.6 (C-6), 21.1, 21.1, 21.1, 21.0 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1778.6 (25, $[3 M + Na]^+$), 1192.9 (50, $[2 M + Na]^+$), 1170.9 (100, $[2 M + H]^+$), 608.1 (15, $[M + Na]^+$), 586.0 (90, $[M + H]^+$).

HRMS (ESI+): *m/z* $[M + H]^+$ calcd for $C_{29}H_{32}NO_{12}$: 586.1924; found: 586.1924.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-methylbenzamido)hydroquinone (14c)

Treatment of compound **13c** (57 mg) according to procedure C afforded **14c** (54 mg, 94%); colorless syrup; R_f = 0.13, (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –25.0 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, CONH), 8.08 (s, 1 H, OH exch. D_2O), 7.75 (d, *J* = 8.4 Hz, 2 H, Ar), 7.56 (br s, 1 H, exch. D_2O, OH), 7.44 (s, 1 H, Ar), 7.26 (d, *J* = 8.4 Hz, 2 H, Ar), 6.79 (s, 1 H, Ar), 5.36 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.28 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.73 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.29 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.13 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.86 (dq, 1 H, H-5), 2.40 (s, 3 H, CH_3), 2.06, 2.06, 2.00, 1.83 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.3, 170.8, 170.2, 170.1 (4 C=O, acetyl), 167.4 (CONH), 149.1, 143.5, 140.9, 131.2 (4 C_q, Ar), 129.9, 129.0 (2 CH_{Ar}), 128.1 (C_q, Ar), 127.8, 127.5 (2 CH_{Ar}), 118.8 (C_q, Ar), 117.3, 110.0 (2 CH_{Ar}), 77.1 (C-1), 76.4 (C-5), 74.4 (C-3), 71.8 (C-2), 68.9 (C-4), 62.5 (C-6), 21.9 (Ar*C*H_3), 21.1, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1741.5 (40, $[3 M + Na]^+$), 1720.4 (20, $[3 M + H]^+$), 1168.9 (55, $[2 M + Na]^+$), 1146.8 (100, $[2 M + H]^+$), 596.1 (15, $[M + Na]^+$), 573.9 (90, $[M + H]^+$).

HRMS (ESI+): *m/z* $[M + H]^+$ calcd for $C_{28}H_{32}NO_{12}$: 574.1924; found: 574.1926.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-methoxybenzamido)hydroquinone (14d)

Treatment of compound **13d** (53 mg) according to procedure C afforded **14d** (51 mg, 89%); pale yellow foam; R_f = 0.17 (PE–EtOAc, 1:1); $[\alpha]_D$ –26.3 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.51 (s, 1 H, CONH), 7.74 (d, *J* = 8.7 Hz, 2 H, Ar), 7.34 (s, 1 H, OH, exch. D_2O), 7.26 (d, *J* = 1.2 Hz, 1 H, Ar), 6.86 (d, *J* = 8.7 Hz, 2 H, Ar), 6.70 (s, 1 H, Ar), 5.28 (t, $J_{3,4}$ = 9.0 Hz, 1 H, H-3), 5.26 (s, 1 H, OH, exch. D_2O), 5.20 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 5.14 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.71 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.22 (dd, $J_{5,6}$ = 4.2 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.06 (dd, $J_{5,6'}$ = 1.2 Hz, 1 H, H-6′), 3.80 (hidden, 1 H, H-5), 3.78 (s, 3 H, OCH_3), 1.98, 1.98, 1.92, 1.75 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.3, 170.8, 170.1, 169.9 (4 C=O, acetyl), 166.9, 163.3, 149.0, 141.2, 140.8 ($CONH_q$, 4 Ar), 129.8, 129.8 (2 CH_{Ar}), 126.1 (C_q, Ar), 118.7 (1 C_q, Ar), 117.3, 114.5, 114.5, 110.0 (4 CH_{Ar}), 77.2, 76.4, 74.5, 71.8, 68.9 (C-1/C-5), 62.6 (C-6), 55.9 (OCH_3), 21.1, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 590 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{28}H_{32}NO_{13}$: 590.1873; found: 590.1875.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(3,5-dimethoxybenzamido)hydroquinone (14e)

Treatment of compound **13e** (75 mg) according to procedure C afforded **14e** (68 mg, 90%); pale yellow foam; R_f = 0.12 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –21.1 (*c* 0.97, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.67 (s, 1 H, CONH, exch. D_2O), 7.98, 7.80 (2 s, 2 H, OH exch. D_2O), 7.35 (d, *J* = 4.2 Hz, 2 H, Ar), 6.98 (d, *J* = 1.5 Hz, 1 H, Ar), 6.78 (s, 1 H, Ar), 6.61 (br s, 1 H, Ar), 5.34 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.26 (t, $J_{2,3}$ = 9.0 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.79 (d, $J_{1,2}$ = 9.3 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 4.2 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.16 (br d, $J_{5,6'}$ = 1.2 Hz, 1 H, H-6′), 3.90 (dq, 1 H, H-5), 3.84 (s, 6 H, OCH_3), 2.08, 2.05, 2.00, 1.82 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.4, 170.8, 170.2, 170.1 (4 C=O, acetyl), 167.1 (CONH), 161.3, 149.2, 141.1, 140.3, 136.3 (5 C_q, Ar), 129.0, 128.1 (2 CH_{Ar}), 127.9 (C_q, Ar), 127.5 (CH_{Ar}), 118.6 (C_q, Ar), 105.7, 104.6 (2 CH_{Ar}), 76.5 (C-5 and C-1), 74.5 (C-3), 72.0 (C-2), 70.3 (C-4), 62.6 (C-6), 56.0, 56.0 (2 OCH_3), 21.1, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1260.9 (45, $[2 M + Na]^+$), 1238.9 (100, $[2 M + H]^+$), 620.0 (60, $[M + H]^+$).

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-nitrobenzamido)hydroquinone (14f)

Treatment of compound **13f** (63 mg) according to procedure C afforded **14f** (57 mg, 90%); yellow-green foam; R_f = 0.20 (PE–EtOAc, 1:1); $[\alpha]_D^{22}$ –26.8 (*c* 1.27, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.69 (s, 1 H, CONH), 8.29 (d, *J* = 8.7 Hz, 2 H, Ar), 8.01 (d, *J* = 8.7 Hz, 2 H, Ar), 7.59 (br s, 1 H, OH exch. D_2O), 7.38 (s, 1 H, Ar), 7.24 (br s, 1 H, OH exch. D_2O), 6.76 (s, 1 H, Ar), 5.37 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.30 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.71 (d, $J_{1,2}$ = 9.3 Hz, 1 H, H-1), 4.31 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.19 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.91 (dq, 1 H, H-5), 2.07, 2.07, 2.01, 1. 86 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.4, 170.8, 170.2, 170.2 (4 C=O, acetyl), 165.0 (CONH), 150.4, 149.1, 140.8, 139.6 (4 C_q, Ar), 129.0 (2 CH_{Ar}), 127.2 (C_q, Ar), 124.5 (2 CH_{Ar}), 119.4 (C_q, Ar), 117.4 (CH_{Ar}), 110.2 (CH_{Ar}), 77.5 (C-1), 76.6 (C-5), 74.3 (C-3), 71.7 (C-2), 68.8 (C-4), 62.5 (C-6), 21.2, 21.1, 21.1, 21.0 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 605 (10, $[M + H]^+$), 498 (100).

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{27}H_{29}N_2O_{14}$: 605.1619; found: 605.1623.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-biphenylcarboxamido)hydroquinone (14g)

Treatment of compound **13g** (70 mg) according to procedure C afforded **14g** (60 mg, 85%); pale yellow syrup; R_f = 0.12 (PE–EtOAc, 1:1); $[\alpha]_D^{22}$ –33.5 (*c* 0.95, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.70 (s, 1 H, CONH), 7.98 (s, 1 H, OH exch. D_2O), 7.91 (d, *J* = 8.4 Hz, 2 H, Ar), 7.66 (d, *J* = 8.1 Hz, 2 H, Ar), 7.59–7.51 (m, 3 H, Ar), 7.44–7.36 (m, 4 H, 3 Ar and OH, exch. D_2O), 6.82 (s, 1 H, Ar), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.32 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.25 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 4.75 (d, $J_{1,2}$ = 9.0 Hz, 1 H, H-1), 4.31 (dd, $J_{5,6}$ = 4.2 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 1.5 Hz, 1 H, H-6′), 3.89 (m, 1 H, H-5), 2.06, 2.06, 1.99, 1.84 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.3, 170.8, 170.2, 170.1 (4 C=O, acetyl), 167.2 (CONH), 149.1, 145.5, 141.0, 140.0, 132.6 (5 C_q, Ar), 129.9, 129.0, 128.7, 128.4, 128.4, 127.8, 127.8 (7 CH_{Ar}), 127.8 (C_q, Ar), 127.6, 127.6 (2 CH_{Ar}), 119.0 (C_q, Ar), 117.6, 110.2 (2 CH_{Ar}), 77.4 (C-1), 76.5 (C-5), 74.4 (C-3), 71.8 (C-2), 68.9 (C-4), 62.5 (C-6), 21.1, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (ESI+): *m*/*z* (%) = 1927.6 (25, [3 M + Na]$^+$), 1906.5 (20, [3 M + H]$^+$), 1292.9 (70, [2 M + Na]$^+$), 1270.8 (100, [2 M + H]$^+$), 658.2 (20, [M + Na]$^+$), 636.0 (85, [M + H]$^+$).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{34}NO_{12}$: 636.2081; found: 636.2079.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(1-naphthamido)hydroquinone (14h)

Treatment of compound **13h** (37 mg) according to procedure C afforded **14h** (32 mg, 86%); yellow syrup; R_f = 0.24 (EtOAc–PE, 1:1); $[\alpha]_D^{17}$ –21.6 (*c* 0.75, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 8.52 (s, 1 H, CONH, exch. D_2O), 8.29 (dd, *J* = 2.4, 9.0 Hz, 1 H, Ar), 8.22 (br s, 1 H, OH, exch. D_2O), 7.95 (d, *J* = 8.4 Hz, 1 H, Ar), 7.87 (m, 1 H, Ar), 7.69 (dd, *J* = 0.9, 6.9 Hz, 1 H, Ar), 7.54 (m, 2 H, Ar), 7.44 (dd, *J* = 8.4, 4.5 Hz, 1 H, Ar), 7.10 (br s, 2 H, Ar, and OH exch. D_2O), 6.76 (s, 1 H, Ar), 5.33 (br t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.29 (t, $J_{2,3}$ = 9.0 Hz, 1 H, H-2), 5.23 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.58 (dd, $J_{1,2}$ = 9.6 Hz, $J_{1,3}$ = 2.7 Hz, 1 H, H-1), 4.30 (dd, $J_{5,6}$ = 3.9 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.13 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.84 (dq, 1 H, H-5), 2.08, 2.05, 1.96, 1.78 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.0, 170.0 (4 C=O, acetyl), 169.6 (CONH), 148.9, 141.5, 134.1, 133.1 (4 C_q, Ar), 132.1 (CH_{Ar}), 130.3 (C_q, Ar), 128.9, 128.0 (2 CH_{Ar}), 127.7 (C_q, Ar), 127.2, 126.2, 125.5, 125.0 (4 CH_{Ar}), 119.5 (C_q, Ar), 118.9, 110.8 (2 CH_{Ar}), 78.8 (C-1), 76.5 (C-5), 74.2 (C-3), 71.3 (C-2), 68.5 (C-4), 62.2 (C-6), 21.1, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 610 (20, [M + H]$^+$).

HRMS (CI, isobutane): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{32}NO_{12}$: 610.1924; found: 610.1923.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(2-naphthamido)hydroquinone (14i)

Treatment of compound **13i** (32 mg) according to procedure C afforded **14i** (28 mg, 90%); yellow syrup; R_f = 0.20 (PE–EtOAc, 1:1); $[\alpha]_D^{17}$ –28.1 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 8.54 (s, 1 H, CONH), 8.40 (s, 1 H, Ar), 8.17 (s, 1 H, OH exch. D_2O), 7.96–7.87 (m, 4 H, Ar), 7.63–7.57 (m, 2 H, Ar), 7.06 (d, *J* = 1.8 Hz, 1 H, Ar), 6.99 (s, 1 H, OH exch. D_2O), 6.78 (s, 1 H, Ar), 5.36 (m, $J_{3,4}$ = 9.0 Hz, 1 H, H-3), 5.32 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.26 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.62 (dd, $J_{1,2}$ = 9.0 Hz, $J_{1,3}$ = 2.7 Hz, 1 H, H-1), 4.33 (dd, $J_{5,6}$ = 4.2 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.17 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 3.88 (dq, 1 H, H-5), 2.09, 2.08, 2.00, 1.87 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 169.9, 169.8 (4 C=O, acetyl), 167.5 (CONH), 149.1, 141.8, 135.5, 132.9, 130.8, (5 C_q, Ar), 129.5, 129.3, 128.9, 128.8, 128.3, 127.6 (6 CH_{Ar}), 127.6 (C_q, Ar), 123.8 (CH_{Ar}), 119.4 (C_q, Ar), 119.1, 111.1 (2 CH_{Ar}), 79.2 (C-1), 76.6 (C-5), 74.1 (C-3), 71.3 (C-2), 68.5 (C-4), 62.2 (C-6), 21.1, 21.1, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 610 (60, [M + H]$^+$).

HRMS (CI, isobutane): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{32}NO_{12}$: 610.1924; found: 610.1923.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(2-furylcarboxamido)hydroquinone (14j)

Treatment of compound **13j** (44 mg) according to procedure C afforded **14j** (37 mg, 84%); yellow-green foam; R_f = 0.13 (EtOAc–PE, 1:1); $[\alpha]_D^{17}$ –22.5 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 8.74 (s, 1 H, CONH), 8.14 (s, 1 H, OH exch. D_2O), 7.77 (s, 1 H, Ar), 7.55 (br s, 1 H_{furyl}), 7.52 (s, 1 H, OH exch. D_2O), 7.32 (d, *J* = 3.6 Hz, 1 H_{furyl}), 6.83 (s, 1 H, Ar), 6.60 (br d, *J* = 0.6 Hz, 1 H_{furyl}), 5.42 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.28 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.87 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.32 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.19 (br d, 1 H, H-6′), 3.93 (dq, 1 H, H-5), 2.08, 2.08, 2.02, 1.86 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.4, 170.9, 170.2, 170.1 (4 C=O, acetyl), 157.4 (CONH), 149.4, 147.3 (2 C_q, Ar), 145.5 (CH_{furyl}), 139.9, 127.2, 118.5 (3 C_q), 116.9 (CH_{furyl}), 116.3 (CH_{Ar}), 113.3 (CH_{furyl}), 109.3 (CH_{Ar}), 76.5 (C-5), 76.1 (C-1), 74.6 (C-3), 72.1 (C-2), 69.1 (C-4), 62.7 (C-6), 21.2, 21.1, 21.1, 21.0 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 550 (100, [M + H]$^+$).

HRMS (CI, isobutane): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{28}NO_{13}$: 550.1561; found: 550.1561.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(2-thienylcarboxamido)hydroquinone (14k)

Treatment of compound **13k** (52 mg) according to procedure C afforded **14k** (38 mg, 76%); pale yellow syrup; R_f = 0.16 (PE–EtOAc, 1:1); $[\alpha]_D^{23}$ –28.9 (*c* 0.9, CH_2Cl_2).

^{1}H NMR (300.14 MHz, $CDCl_3$): δ = 8.55 (s, 1 H, CONH), 7.90 (br s, 1 H, OH exch. D_2O), 7.69 (dd, J_m = 0.9 Hz, J_o = 3.6 Hz, 1 $H_{thienyl}$), 7.58 (dd, J_o = 4.8 Hz, J_m = 0.9 Hz, 1 $H_{thienyl}$), 7.32 (s, 2 H, Ar, and OH, exch. D_2O), 7.12 (dd, J_o = 3.6 Hz, J_o = 4.8 Hz, 1 $H_{thienyl}$), 6.78 (s, 1 H, Ar), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.28 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.23 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.72 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.31 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 1.8 Hz, H-6′), 3.89 (dq, 1 H, H-5), 2.07, 2.07, 2.01, 1.85 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.3, 170.8, 170.1, 170.1 (4 C=O, acetyl), 161.5 (CONH), 149.0, 140.9, 138.2 (3 C_q, Ar), 132.2, 130.1, 128.5 (3 CH_{Ar}), 127.5, 119.0 (2 C_q, Ar), 117.5, 110.2 (2 CH_{Ar}), 77.4 (C-1), 76.5 (C-5), 74.4 (C-3), 71.8 (C-2), 68.8 (C-4), 62.5 (C-6), 21.1, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m*/*z* (%) = 566 (100, [M + H]$^+$).

HRMS (CI, isobutane): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{28}NO_{12}S$: 566.1332; found : 566.1333.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-nicotinamidohydroquinone (14l)

Treatment of compound **13l** (52 mg) according to procedure C afforded **14l** (51 mg, 97%); pale yellow-green syrup; R_f = 0.10 (PE–EtOAc, 1:3); $[\alpha]_D^{21}$ –21.4 (*c* 0.78, $CHCl_3$).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 9.10 (s, 1 H, CONH, exch. D_2O), 9.00 (s, 1 H, Ar), 8.72 (s, 1 H, OH exch. D_2O), 8.62 (m, 1 H, Ar), 8.12 (d, *J* = 7.8 Hz, 1 H, Ar), 7.51 (m, 2 H, Ar), 6.75 (s, 1 H, Ar), 5.28 (t, $J_{3,4}$ = 9.0 Hz, 1 H, H-3), 5.22 (s, 1 H, OH exch. D_2O), 5.19 (t, $J_{2,3}$ = 9.0 Hz, 1 H, H-2), 5.13 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.74 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.29 (dd, $J_{5,6}$ = 4.2 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.14 (br d, *J* = 0.9 Hz, 1 H, H-6′), 3.88 (m, 1 H, H-5), 2.06, 2.04, 1.99, 1.83 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.3, 170.8, 170.2, 170.2 (4 C=O, acetyl), 164.7 (CONH), 152.4 (CH_{Ar}), 149.0 (C_q, Ar), 148.0 (CH_{Ar}), 141.2, 140.9,136.8 (3 C_q, Ar), 129.0, 128.0, 127.4 (3 CH_{Ar}), 119.2 (C_q, Ar), 109.8 (CH_{Ar}), 76.5, 76.2, 74.5, 71.9, 68.9 (C-1/C-5), 62.6 (C-6), 56.0 (2 OCH_3), 21.2, 21.1, 21.1, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 561 (100) $[M + H]^+$.

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{26}H_{29}N_2O_{12}$: 561.1721; found : 561.1718.

2,6-Bis[2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)hydroquinone-5-amino-*N*-carbonyl]pyridine (14n)

Treatment of compound **13n** (60 mg) according to procedure C (note: 16 equiv of $Na_2S_2O_4$ were added) afforded **14n** (51 mg, 85%); yellow green syrup; R_f = 0.15 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –33.8 (*c* 0.81, acetone).

^{1}H NMR (300.13 MHz, acetone-d_6 and $CDCl_3$): δ = 10.40 (s, 2 H, CONH, exch. D_2O), 8.60 (s, 2 H, OH, exch. D_2O), 8.44 (d, *J* = 7.8 Hz, 2 H, Ar), 8.27 (dd, *J* = 7.5 Hz, *J* = 8.1 Hz, 1 H, Ar), 8.18 (d, *J* = 7.8 Hz, 2 H, Ar), 7.88 (s, 2 H, Ar), 6.88 (s, 2 H, Ar), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 2 H, H-3), 5.20 (t, $J_{2,3}$ = 9.6 Hz, 2 H, H-2), 5.19 (t, $J_{4,5}$ = 9.3 Hz, 2 H, H-4), 4.99 (d, $J_{1,2}$ = 9.9 Hz, 2 H, H-1), 4.28 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.3 Hz, 2 H, H-6), 4.16 (dd, $J_{5,6'}$ = 2.1 Hz, H-6′), 3.90 (dq, 2 H, H-5), 1.94, 1.94, 1.86, 1.71 (4 s, 24 H, $OCOCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.4, 170.0, 169.7, 169.0 (8 C=O, acetyl), 161.3 (2 CONH), 149.5, 148.6 (4 C_q, Ar), 140.3, 128.5 (2 CH_{Ar}), 128.5 (C_q, Ar), 127.4 (2 C_q, Ar), 127.2, 127.0 (2 CH_{Ar}), 127.0 (C_q, Ar), 125.6 (CH_{Ar}), 119.1 (2 C_q, Ar), 114.8, 108.0 (2 CH_{Ar}), 76.3, 74.6, 74.4, 72.7, 69.2 (2 C-1/C-5), 62.8 (2 C-6), 20.5, 20.5, 20.4, 20.2 (8 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1064.2 (65, $[M + Na]^+$, 1042.1 (100, $[M + H]^+$).

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(4-aminobenzamido)benzene (15)

Reduction of **9f** (111 mg) according to the procedure applied for preparing compound **7** afforded **15** (91 mg, 86%); colorless syrup; R_f = 0.15 (EtOAc–PE, 1:1); $[\alpha]_D^{21}$ –19.8 (*c* 0.85, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.52 (s, 1 H, CONH), 8.33 (s, 1 H, Ar), 7.71 (d, *J* = 8.7 Hz, 2 H, Ar), 6.93 (s, 1 H, Ar), 6.70 (d, *J* = 8.7 Hz, 2 H, Ar), 5.38 (t, $J_{3,4}$ = 9.0 Hz, 1 H, H-3), 5.30 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.00 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.29 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.3 Hz, 1 H, H-6), 4.15 (dd, $J_{5,6'}$ = 2.1 Hz, 1 H, H-6′), 4.10 (br s, 2 H, NH_2), 3.90 (s, 3 H, OCH_3), 3.90–3.86 (hidden, 1 H, H-5), 3.86 (s, 3 H, OCH_3), 2.08, 2.06, 2.01, 1.80 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.1, 169.8 (4 C=O, acetyl), 165.6 (CONH), 152.1, 150.5, 142.5, 129.9 (4 C_q, Ar), 128.3 (2 CH_{Ar}), 124.6, 118.3 (2 C_q, Ar), 114.6, 114.6, 109.7, 103.8 (4 CH_{Ar}), 76.5 (C-5), 75.0 (C-3), 73.5 (C-1), 72.4 (C-2), 68.3 (C-4), 62.9 (C-6), 56.8, 56.8 (2 OCH_3), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

MS (CI, isobutane): *m/z* (%) = 603 (100, $[M + H]^+$).

HRMS (CI, isobutane): *m/z* $[M + H]^+$ calcd for $C_{29}H_{35}N_2O_{12}$: 603.2190; found: 603.2192.

(*E*)-2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(4-cinnamamidobenzamido)benzene (16)

Treatment of **15** (40 mg) according to procedure A afforded **16** (48 mg, 98%); white solid; mp 109–112 °C; R_f = 0.17 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –21.2 (*c* 0.74, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.53, 8.50 (2 s, 2 H, 2 CONH), 8.31 (s, 1 H, Ar), 7.79 (m, 5 H, 4 H_{Ar} and 1 H_{alkene}), 7.49 (m, 2 H, Ar), 7.37 (m, 3 H, Ar), 6.93 (s, 1 H, Ar), 6.66 (d, *J* = 15.6 Hz, 1 H_{alkene}), 5.41 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.29 (t, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.24 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.00 (d, $J_{1,2}$ = 9.9 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.16 (d, $J_{5,6}$ = 1.5 Hz, 1 H, H-6′), 3.89 (s, 3 H, OCH_3), 3.89–3.82 (hidden, 1 H, H-5), 3.82 (s, 3 H, OCH_3), 2.07, 2.04, 2.03, 1.83 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.7, 170.2, 170.1 (4 C=O, acetyl), 165.1, 164.9 (2 CONH), 151.9 (C_q, Ar), 143.3 (CH_{Ar}), 142.6, 142.3, 134.9 (3 C_q, Ar), 130.6 (CH_{Ar}), 130.1 (C_q, Ar), 129.4, 128.5, 128.4 (6 CH_{Ar}), 121.0 (CH_{alkene}), 119.8 (CH_{Ar}), 119.8 (CH_{alkene}), 119.0 (C_q, Ar), 109.6 (CH_{Ar}), 104.6 (C_q, Ar), 103.8 (CH_{Ar}), 76.5 (C-5), 74.8 (C-3), 73.4 (C-1), 72.9 (C-2), 69.3 (C-4), 62.9 (C-6), 56.7 (2 OCH_3), 21.2, 21.1, 21.1, 21.0 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1486.9 (20, $[2 M + Na]^+$), 1464.8 (100, $[2 M + H]^+$), 755.1 (20, $[M + Na]^+$), 733.0 (70, $[M + H]^+$).

HRMS (ESI+): *m/z* $[M + H]^+$ calcd for $C_{38}H_{41}N_2O_{13}$: 733.2609; found: 733.2609.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-[4-(2-thienylcarboxamido)benzamido]benzene (17)

Treatment of **15** (90 mg) according to procedure A afforded **17** (92 mg, 86%); white solid; mp 116–119 °C; R_f = 0.17 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –33.4 (*c* 0.73, CH_2Cl_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.71, 8.56 (2 s, 2 H, 2 CONH), 8.28 (s, 1 H, Ar), 7.84–7.74 (m, 5 H, 4 H_{Ar} + 1 $H_{thienyl}$), 7.56 (d, *J* = 5.1 Hz, 1 $H_{thienyl}$), 7.08 (t, *J* = 4.2, 4.5 Hz, 1 $H_{thienyl}$), 6.93 (s, 1 H, Ar), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.27 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.99 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.16 (dd, $J_{5,6'}$ = 1.2 Hz, 1 H, H-6′), 3.91 (s, 3 H, OCH_3), 3.86 (m, 1 H, H-5), 3.82 (s, 3 H, OCH_3), 2.06, 2.06, 2.02, 1.81 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.6, 170.1, 169.9 (4 C=O, acetyl), 165.1, 160.8 (2 CONH), 151.9, 142.6, 141.9, 139.5 (4 C_q, Ar), 131.9 (CH_{Ar}), 130.5 (C_q, Ar), 129.3, 128.4, 128.4, 128.3, 120.3 (5 CH_{Ar}), 120.3, 119.1 (2 C_q, Ar), 109.7, 104.5, 104.0 (3 CH_{Ar}), 76.5 (C-5), 74.9 (C-3), 73.5 (C-1), 72.7 (C-2), 69.3 (C-4), 62.9 (C-6), 56.7 (2 OCH_3), 21.2, 21.1, 21.1, 20.8 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1446.7 (40, $[2 M + Na]^+$), 1424.8 (100, $[2 M + H]^+$), 713.0 (50 $[M + H]^+$).

HRMS (ESI+): *m/z* $[M + H]^+$ calcd for $C_{34}H_{37}N_2O_{13}S_1$: 713.2016; found: 713.2018.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,4-dimethoxy-5-(4-nicotinamidobenzamido)benzene (18)

Treatment of **15** (90 mg) according to procedure A afforded **18** (75 mg, 71%); white syrup; R_f = 0.07 (PE–EtOAc, 1:1); $[\alpha]_D^{21}$ –18.1 (*c* 0.68, CH_2Cl_2).

^{1}H NMR (300.13MHz, $CDCl_3$): δ = 9.13 (s, 1 H, Ar), 9.06 (br s, 1 H, CONH), 8.73 (br s, 1 H, Ar), 8.60 (s, 1 H, CONH), 8.26 (s, 1 H, Ar), 8.23 (d, *J* = 7.8 Hz, 1 H, Ar), 7.85 (m, 4 H, Ar), 7.40 (br s, 1 H, Ar), 6.94 (s, 1 H, Ar), 5.38 (t, $J_{3,4}$ = 9.3 Hz, 1 H, H-3), 5.27 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 5.22 (t, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 4.99 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.28 (dd, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.16 (d, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.91 (s, 3 H, OCH_3), 3.86 (dq, 1 H, H-5), 3.82 (s, 3 H, OCH_3), 2.07, 2.07, 2.01, 1.81 (4 s, 12 H, OCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.2, 170.6, 170.1, 169.8 (4 C=O, acetyl), 165.0, 164.7 (2 CONH), 152.9 (CH_{Ar}), 152.0 (C_q, Ar), 148.6 (CH_{Ar}), 142.7 (C_q, Ar), 136.0 (CH_{Ar}), 131.1, 131.0, 130.9, 129.2 (4 C_q, Ar), 128.5, 128.5, 124.5, 120.5, 120.5 (5 CH_{Ar}), 119.2 (C_q, Ar), 109.8, 104.0 (2 CH_{Ar}), 76.5 (C-5), 74.8 (C-3), 73.4 (C-1), 72.6 (C-2), 69.3 (C-4), 62.9 (C-6), 56.7, 56.7 (2 OCH_3), 21.2, 21.1, 21.1, 20.8 (4 CH_3, acetyl).

MS (ESI+): *m/z* (%) = 1436.8 (30, [2 M + Na]$^+$), 1414.7 (70, [2 M + H]$^+$), 730.2 (10, [M + Na]$^+$), 708.1 (100, [M + H]$^+$).

HRMS (ESI+): *m/z* [M + H]$^+$ calcd for $C_{35}H_{38}N_3O_{13}$: 708.2405; found: 708.2406.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-5-(4-aminobenzamido)-1,4-benzoquinone (20)

Compound **14f** (48 mg, 0.0794 mmol) was dissolved in MeOH (3 mL). HCO_2NH_4 (40 mg, 0.62 mmol, 7.7 equiv) and 10% Pd/C (10 mg) were added to the solution, and the mixture was stirred under argon. TLC showed that compound **14f** had changed completely into a new polar compound [R_f = 0.12 (EtOAc–PE, 1:1)], assumed to be hydroquinone **19**. The mixture was filtered through a Celite pad and the filtrate was concentrated. The yellow residue was chromatographed (PE–EtOAc, 2:3) on silica gel. When the residue was added into the column, it turned dark red and a dark-red product [R_f = 0.36 (PE–EtOAc, 1:1)] eluted from the column very quickly, yielding upon concentration a dark red syrup (34 mg, 71%), identified as benzoquinone **20** by NMR spectroscopy (no OH signals, C=O of quinone in the ^{1}H and ^{13}C NMR spectra, respectively).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.72 (s, 1 H, CONH), 7.66 (d, *J* = 8.4 Hz, 2 H, Ar), 7.68 (s, 1 H, Ar), 6.94 (s, 1 H, Ar), 6.71 (d, *J* = 8.4 Hz, 2 H, Ar), 5.38 (t, $J_{3,4}$ = 9.6 Hz, 1 H, H-3), 5.14 (t, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.94 (t, $J_{2,3}$ = 9.3 Hz, 1 H, H-2), 4.74 (d, $J_{1,2}$ = 9.6 Hz, 1 H, H-1), 4.27 (dd, $J_{5,6}$ = 5.1 Hz, $J_{6,6'}$ = 12.6 Hz, 1 H, H-6), 4.20 (br s, 2 H, NH_2), 4.14 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, H-6′), 3.82 (dq, 1 H, H-5), 2.10, 2.06, 2.01, 1.92 (4 s, 12 H, $OCOCH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.5, 183.4 (2 C=O, quinone), 171.0, 170.4, 170.3, 170.0 (4 C=O, acetyl), 165.7 (CONH), 151.5, 146.4, 139.1 (3 C_q, Ar), 130.6, 129.9, 129.9 (3 CH_{Ar}), 122.6 (C_q, Ar), 114.6, 114.6, 113.9 (3 CH_{Ar}), 76.6 (C-5), 74.0 (C-3), 73.2 (C-2), 72.1 (C-1), 68.7 (C-4), 62.5 (C-6), 21.2, 21.0, 21.0, 20.9 (4 CH_3, acetyl).

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