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In Search of Glycogen Phosphorylase Inhibitors: 5-Substituted 3-*C*-Glucopyranosyl-1,2,4-oxadiazoles from β-D-Glucopyranosyl Cyanides upon Cyclization of *O*-Acylamidoxime Intermediates

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Upon treatment with hydroxylamine-, benzyl- and benzoyl-protected β-D-glucopyranosyl cyanides efficiently afforded the corresponding amidoximes. They reacted by *O*-acylation in the presence of carboxylic acids or acyl chlorides to provide benzyl- and benzoyl-protected *O*-acylamidoximes. The latter were isolated and fully characterized. Thermal cyclization of *O*-acylamidoximes yielded the corresponding 5-substituted 3-*C*-β-D-glucopyranosyl-1,2,4-oxadiazoles, either in a "one-pot" procedure (benzylated series), or in two steps (benzoylated series). The twelve 5-substituted 1,2,4-oxadiazoles obtained upon debenzoylation were assayed against glycogen phosphorylase (GP). 3-*C*-(β-D-Glucopyranosyl)-5-(2-naphthyl)-1,2,4-oxadiazole was the best inhibitor of rabbit muscle glycogen phosphorylase *b* (K_i = 38.4 ±3.0 μM).

Introduction

The increasing world-wide prevalence of both metabolic disorders and diabetes[1] (mostly the non-insulin-dependent type-2 *diabetes mellitus*) calls for better insight into the origin(s) of glucose metabolic disorders and for more effective therapeutic approaches.[2] For example, α-glucosidase inhibitors[3] have attracted much attention since they were found to be effective in lowering the post-prandial glycaemic rise after carbohydrate ingestion, as shown in particular for salacinol, a sulfur-containing natural compound isolated from an antidiabetic traditional medicine.[3a] Based on information at the molecular level, gained by studying insulin signal transduction, regulation of glucose uptake and other insulin signalling effects, in particular on glycogen metabolism, several potential therapeutic approaches to diabetes are currently receiving much attention.[4]

Being responsible for glycogenolysis with the release of glucose-1-phosphate (Glc-1-P) from glycogen, glycogen phosphorylase (GP) intervenes by providing glucose for the glycolytic pathway in muscles and to the bloodstream in the liver. In an advanced stage of type-2 diabetes, hepatic glucose production is excessive,[4,5] due to changes in insulin signalling and in particular, insulin's inability to inhibit hepatic gluconeogenesis. Hepatic glucose production represents the net contribution of gluconeogenesis, glycogenesis and glycogenolysis, three interrelated processes sharing Glc-1-P as a common intermediate. It is therefore reasonable to assume that inhibiting hepatic GP would reduce hepatic glucose production, as indicated by experiments based on the administration of potent GP inhibitors (e.g. glucose analogs, azasugars) to animals.[6,7] Another recent work concluded that GP inhibition, aimed at attenuating hyperglycaemia, is unlikely to negatively impact the metabolic and functional muscle capacity.[8] These data support the idea that GP inhibition[9] might offer opportunities for an intervention in the treatment of glucose metabolic disorders.

We have contributed to such investigations by preparing β-D-glucopyranosyl-hydroquinone derivatives[10] found to be weak inhibitors of GP[11] and *N*-acyl-*N*′-β-D-glucosyl-ureas which were studied enzymatically and crystallographically and mainly found to bind at the active site of GP.[12] This result, as well as the fact that glucopyranosyl–spiro(thio)hydantoins,[9] glucopyranosyl–benzimidazole, –benzothiazole, –1,3,4-oxadiazoles[13] and glucopyranosyl–

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spirooxathiazoles[12a,14] were GP inhibitors, encouraged further developments towards 5-substituted 3-*C*-β-D-glucopyranosyl-1,2,4-oxadiazoles. 1,2,4-Oxadiazoles[15] are considered as bioisosteres of esters and amides[16] and have various biological activities such as muscarinic agonists,[17] benzodiazepine receptor antagonists,[18] antirhinovirals,[19] anthelmintics,[20] inhibitors of tyrosine kinase,[21] angiotensin-II receptor antagonists[22] and histamine H3 receptor antagonists.[23] We now disclose a general access to novel, hydrolytically stable 5-substituted 3-*C*-β-D-glucopyranosyl-1,2,4-oxadiazoles and their evaluation from enzymatic studies as potential inhibitors of GP.

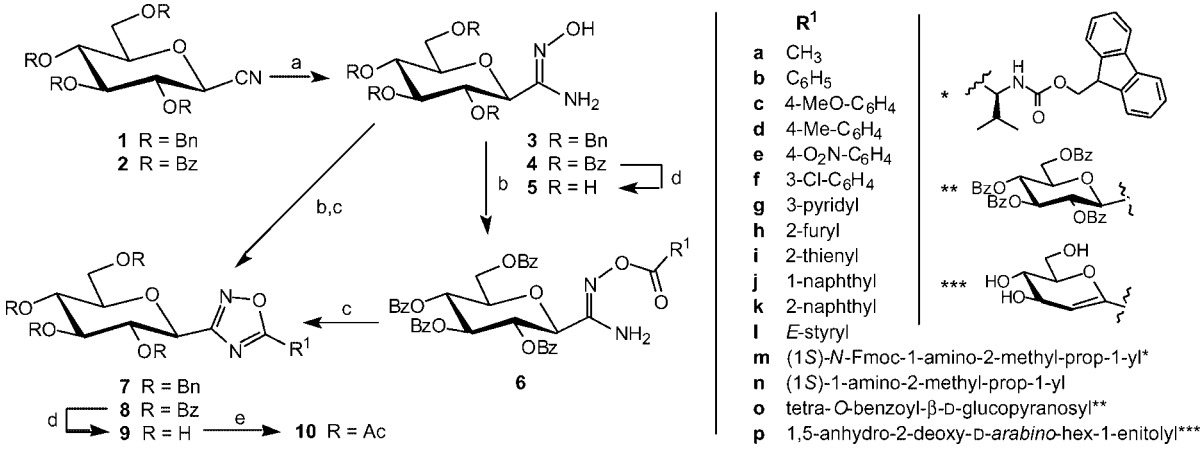
Results and Discussion

A possible route to 3-*C*-glycosyl-1,2,4-oxadiazoles involves dehydrative cyclization of *O*-acyl-amidoxime intermediates. Developing such an approach from benzyl- or benzoyl-protected D-glucopyranosyl cyanides **1**[24] and **2**[25] required the synthesis of the amidoxime precursors **3** and **4**, respectively, to be subsequently subjected to acylation, followed by cyclization. Recently improved methodologies such as solid-phase synthesis,[26] microwave irradiation[27] and applications to amino acids[28] have demonstrated the feasibility of this approach. A literature survey revealed examples of sugar derivatives displaying an amidoxime group in furanose (positions 1[29] and 3[30]) and pyranose rings (positions 1,[31] 2,[32] and 6[33]), prepared typically from cyanosugars upon reaction with hydroxylamine.

Use of benzyl ether protection on the carbohydrate moiety was presumed to be advantageous since hydrogenolysis of these ethers should provide the desired 3-*C*-glycosyl-1,2,4-oxadiazoles after a simple purification step. The benzylated amidoxime **3** was prepared from β-D-glucopyranosyl cyanide **1**[24] in MeOH by reaction with hydroxylamine, freshly prepared from its hydrochloride in the presence of sodium methoxide[34] (Scheme 1).

Treatment of amidoxime **3** with carboxylic acids or acyl chlorides with subsequent heating at 100 °C in 1,4-dioxane afforded the 1,2,4-oxadiazoles **7** as stable materials in good yields. The reaction was achieved in a one-pot two-step procedure (Scheme 1) presumably via *O*-acylamidoxime intermediates. *O*-Acylamidoximes can be obtained by using either an acid in the presence of an activating agent, an acyl chloride, or an anhydride.[15b] We did not use anhydrides due to the limited number of commercially available reagents and we observed that acyl chlorides were more efficient than carboxylic acids for preparing the oxadiazoles **7** (Table 1). Unfortunately, the attempted hydrogenolysis of the benzyl protecting groups of **7** under various conditions [EtOH, H_2 (5 atm); MeOH with cat. HCO_2H, H_2 (3 atm); cyclohexene/EtOH] with $Pd(OH)_2/C$ (20%) as the catalyst were not encouraging as judged by TLC (complex mixture of UV-active spots) and spectroscopy (NMR, MS). Hydrogenolysis [EtOH, H_2 (3 atm), $Pd(OH)_2/C$ (20%), 3 d] of benzylated amidoxime **3** afforded in low yield (22%) a mixture of partially deprotected amidoxime isomers.

Therefore, we turned our attention to the benzoylated series where final deprotections were presumed uneventful, the readily prepared D-glucopyranosyl cyanide **2**[25] was treated with hydroxylamine, liberated from its hydrochloride with sodium methoxide in MeOH, as reported.[34] We observed partial debenzoylation of the products, resulting in a complex mixture, presumably because of the presence of nucleophilic species and/or use of NaOMe in slight excess. However, when pyridine was used both as solvent and base to liberate hydroxylamine from its hydrochloride salt, **2** was efficiently converted into the benzoylated amidoxime **4** (90% yield) without cleavage of the benzoate esters (Scheme 1). Acylation of amidoxime **4** was achieved using either an acyl chloride or an acid in conjunction with an activating system (EDCI, HOBt) to afford the *O*-acylamidoximes **6** in good yields (Table 1). Acylation occurred chemoselectively at the OH group of amidoxime **4** since the NH_2 nitrogen atom has a decreased nucleophilicity, com-



Scheme 1. a) NH_2OH, MeOH (R = Bn) or NH_2OH/HCl, C_5H_5N (R = Bz), 50 °C; b) R^1COCl or R^1CO_2H, EDCI, HOBt, 1,4-dioxane; c) 1,4-dioxane, 100 °C; d) NaOMe, MeOH; e) Ac_2O, C_5H_5N.

Table 1. Isolated yields for the preparations of *O*-acylamidoximes **6** and 1,2,4-oxadiazoles **7**–**9**.

	R^1 Reagents/conditions	**3→7** (1) R^1CO_2H (2) 100 °C	**3→7** (1) R^1COCl (2) 100 °C	**4→6** R^1COCl	**4→6** R^1CO_2H	**6→8** 100 °C	**8→9** NaOMe
a	CH_3			61		50	89
b	C_6H_5	31	57	88		64	80
c	4-MeO-C_6H_4			87		87	85
d	4-Me-C_6H_4			67		60	85
e	4-O_2N-C_6H_4	69	76	100		87	95
f	3-Cl-C_6H_4			93		88	94
g	3-pyridyl		97	93		60	60
h	2-furyl			72		58	93
i	2-thienyl			79		68	70
j	1-naphthyl			90		78	89
k	2-naphthyl		55	62		98	98
l	(*E*)-styryl		47				
m	(1*S*)-*N*-Fmoc-1-amino-2-methylprop-1-yl				75	51	
n	(1*S*)-1-amino-2-methylprop-1-yl					88[a]	25
o	tetra-*O*-benzoyl-β-D-glucopyranosyl				50	95	
p	1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitolyl						45[b]

[a] **8n** was obtained upon treatment of the Fmoc-protected precursor **8m** with piperidine in CH_2Cl_2. [b] **9p** was obtained upon treatment of the benzoyl-protected precursor **8o** with NaOMe in MeOH.

pared to a typical NH_2 amino group, due to the possibility of mesomerism to form an iminium cation (C–NH_2 to C=NH_2^+).[30b,35] Such a mesomerism would increase the electron density of the OH group, thereby enhancing its nucleophilicity. Refluxing the *O*-acylamidoximes **6** in 1,4-dioxane afforded the desired benzoylated 1,2,4-oxadiazoles **8** by dehydration in 50–98% yields (Table 1). Interestingly, condensation with more elaborate acid derivatives [FmocVal-OH (Entry **8m**) or glycoheptonic acid[36] (Entry **8o**)] were also high-yielding.

Deprotection of the benzoylated oxadiazoles **8** under Zemplén conditions was generally achieved in good yields (60–98%) to afford the fully deprotected oxadiazoles **9**. All oxadiazoles **8** and **9**, as well as the acetylated 1-naphthyl derivative **10j**, were obtained as stable white crystalline materials. It is worth mentioning that, upon piperidine-catalyzed cleavage of the Fmoc group, amino acid based oxadiazole **8m** afforded deprotected oxadiazole **8n** in 88% yield, but with partial racemization of the 1-amino-2-methylprop-1-yl residue. ^{1}H NMR spectroscopy clearly indicated the presence of a 87:13 mixture of diastereoisomers as calculated from the integrals of the α-H doublets at δ = 3.91 and 3.84 ppm, respectively. The 3,5-bis(*C*-glycosyl)-1,2,4-oxadiazole **8o** underwent, under Zemplén conditions, regioselective 1,2-elimination of benzoic acid in the pyranosyl ring attached at the 5-position of the oxadiazole ring to afford **9p**. Base-induced elimination has been previously reported for a similar compound.[37] The electron-withdrawing effects exerted by the 1,2,4-oxadiazole ring and a possible tautomeric form involving an exocyclic double bond at C-5*oxa* and an H–N-4 group might explain the acidity of the proton linked to the carbon atom vicinal to C-5*oxa* and therefore the racemization of **8n**, or 1,2-elimination in **8o** to yield **9p**.

The structures of the products obtained were deduced from 1D NMR and 2D NMR spectroscopy which allowed, in most cases, complete signal assignments based on COSY, HSQC and HMBC correlations. For molecules **6h**–**i**, **8h**–**i** and **9h**–**i**, assignment of proton and carbon resonances was achieved by careful analysis of the spectra in order to distinguish 3-H, 4-H and 5-H in furan and thiophene rings, based on literature data for 2-substituted furans[38] (deshielding of nuclei at α-positions to the oxygen atom; $^3J_{3,4} \approx 3.5$ Hz > $^3J_{4,5} \approx 1.9$ Hz) and thiophenes[39] ($^3J_{4,5} \approx 5.0$–5.8 Hz > $^3J_{3,4} \approx 3.6$–4.0 Hz > $^4J_{2,5} \approx 2.5$–4.0 Hz). These assignments were supported by the HMBC correlations observed for the C-5 atoms of the oxadiazole ring with the furan and thiophene 3-H and 5-H protons, by the respective ^3J and ^4J couplings. In connection with the larger magnitude of ^3J, correlations involving the 3-H protons appeared stronger.

Assignment of the stereochemistry for the C=N double bond in the benzoylated amidoxime **4** was examined. Various reports based on dipole moments[40] concluded that primary amidoximes [R^1–C(=NOH)NH_2] exist predominantly in the (*Z*) configuration, whereas tertiary amidoximes [R^1–C(=NOH)NR^2R^3] exist only in the (*E*) configuration. Not surprisingly, secondary amidoximes [R^1–C(=NOH)NHR^2] are found as (*E*) and/or (*Z*) isomers. Other studies reported changes in chemical shifts for the hydroxy group of tertiary amidoximes from $\delta \approx 9.05$ ppm for the (*E*) isomer to $\delta \approx 9.70$ ppm for the (*Z*) isomer mainly due to intramolecular hydrogen bonding.[40c,41] Furthermore, the crystal structure of a primary amidoxime at the 3-position of an α-D-glucofuranose ring[30b] unambiguously displayed a (*Z*)-configured C=N bond. These data suggest a (*Z*) configuration for **4**, which was confirmed by NMR spectroscopy at 500 MHz. A solution of **4** in CD_3COCD_3 was subjected to a 1D gradient ROESY experiment. Low temperature (193 K) was required in order to obtain a sharp signal for the OH proton resonating at δ = 9.39 ppm. When this signal was selected, a ROESY effect was observed for NH_2 (0.74%). A false peak was also observed for 1-H (0.89%) due to a transfer of magnetization during the spin lock (200 ms) due to the scalar coupling between 1-H and the NH_2 group. Of par-

ticular interest is the fact that no significant interaction was observed between the 2-H and the OH proton of amidoxime **4**, as expected for a (*Z*)-configured C=N double bond. Analysis of the same solution of **4** by 2D NOESY at 298 K displayed interactions between the NH_2 and both the 2-H (strong) and 1-H (weak) protons. This was interpreted as a consequence of the free rotation about the *C*-glycosidic bond under these conditions. A positive exchange crosspeak was also observed between the OH and NH_2 protons indicative of a fast exchange rate of protons in these groups. No interaction could be evidenced between either the OH and 1-H or the OH and 2-H protons, therefore indicating a distal disposition of these groups and a (*Z*)-configured C=N double bond in **4**.

Deprotected β-D-glucosyl formamidoxime **5** and twelve 3-β-D-glucopyranosyl-1,2,4-oxadiazoles with different R^1 substituents at the 5-position of the oxadiazole ring were evaluated as inhibitors of rabbit muscle glycogen phosphorylase *b* (RMGP*b*). Amidoxime **5** and oxadiazoles **9a**, **9e**–**j** and **9p** (R^1 = Me, *p*-nitrophenyl, *m*-chlorophenyl, 3-pyridyl, 2-furyl, 2-thienyl, 1-naphthyl and 1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitolyl) showed no inhibition at a maximum concentration of 625 μM. This threshold was selected in relation to the IC_{50} values determined for a series of glucose-based inhibitors.[9] The IC_{50} and K_i values obtained for **9b**–**d** and **9k** are listed in Table 2.

Table 2. Inhibition of RMGP*b* by some 5-aryl-3-(β-D-glucopyranosyl)-1,2,4-oxadiazoles.

	9b	**9c**	**9d**	**9k**
R^1	phenyl	*p*-methoxyphenyl	*p*-tolyl	2-naphthyl
IC_{50} [μM]	625[a]	550 ± 15	350 ± 11	<300
K_i [μM][b]	–	–	–	38.4 ± 3.0

[a] 10% Inhibition was observed at this concentration. [b] K_i values were determined when IC_{50} values were <300 μM.

These data show that the presence of a heteroatom or a polar group in R^1 is not favourable in terms of inhibition of GP, leading to inactive or less active (compare **9c** and **9d**) molecules. For the active oxadiazoles, the inhibition increased according to the sequence R^1 = phenyl < *p*-methoxyphenyl < *p*-tolyl < 2-naphthyl, the 2-naphthyl derivative **9k** being the most potent inhibitor of RMGP*b* in this series with a K_i value of 38.4 μM. This again shows[9,12a] that the 2-naphthyl group is quite favourable for the inhibition of GP, in sharp contrast with the isomeric 1-naphthyl group which confers no inhibitory activity.

Conclusions

Inhibition of hepatic glycogen phosphorylase has been proposed as a new therapeutic approach for the treatment of type-2 diabetes with inhibitors usually based on glucosidic or heterocyclic scaffolds. *C*-Glucosyl-1,2,4-oxadiazoles, with such features, appeared to deserve attention and synthetic efforts. To this end, benzyl- and benzoyl-protected β-D-glucopyranosyl cyanides were converted into the corresponding *C*-glycosylformamidoximes. Subsequent *O*-acylation and dehydrative cyclization of the *O*-acylamidoximes afforded, by one-pot or stepwise processes, the corresponding 3-*C*-β-D-glucopyranosyl-1,2,4-oxadiazoles with various groups at the 5-position of the 1,2,4-oxadiazole ring (alkyl, aryl, aminoalkyl and glycosyl). Deprotected 5-substituted 3-*C*-β-D-glucopyranosyl-1,2,4-oxadiazoles were obtained by cleavage of the benzoyl protecting groups. Compound **9k** displaying a 2-naphthyl residue was the best inhibitor of RMGP*b* with a K_i value of 38.4 ± 3.0 μM. We are currently preparing, by another route, the regioisomeric 3-substituted 5-*C*-β-D-glucopyranosyl-1,2,4-oxadiazoles for comparative evaluation of the inhibition of glycogen phosphorylase.

Experimental Section

General Methods: Thin-layer chromatography (TLC) was carried out using aluminium sheets coated with silica gel 60 F_{254} (Merck). TLC plates were inspected with UV light and 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 (Darmstadt, Germany). Preparative reversed-phase chromatography (RP-18) was performed using a 15 × 150 mm column of fully endcapped silica gel 100 C_{18} (>400 mesh, Fluka). ^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. The following abbreviations are used to explain the observed multiplicities: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; t, triplet; td, triplet of doublets; q, quadruplet; m, multiplet; br, broad; p, pseudo. 1D ROESY experiments (200 ms) were performed using the Bruker *selrogp* sequence and the 2D NOESY experiments (800 ms) with the *noesygpph* sequence. NMR solvents were purchased from Euriso-Top (Saint Aubin, France). HRMS (LSIMS) data were recorded in the positive mode (unless stated otherwise) using a Thermo Finnigan Mat 95 XL spectrometer. MS (ESI) data were recorded in the positive mode using a Thermo Finnigan LCQ spectrometer. Optical rotations were measured using a Perkin–Elmer polarimeter. Elemental analyses were performed at the Service Central d'Analyses du CNRS (Vernaison, France). EDCI stands for 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride. HOBt stands for 1-hydroxybenzotriazole. Carbon atoms in the D-*gluco*-pyranosyl ring and the R^1 substituent are numbered by simple figures and primed figures, respectively, while those of the oxadiazole ring have the *oxa* suffix.

Preparation of Benzylated 1,2,4-Oxadiazoles 7 using Carboxylic Acids (Procedure A): A solution of carboxylic acid (1 equiv.), amidoxime **3** (0.08 mmol, 1.2 equiv.) and EDCI (2 equiv.) in 1,4-dioxane (2 mL) was stirred at 50 °C for 16 h. The mixture was then heated to reflux (100 °C) for an additional 3 h. The crude mixture was concentrated to afford, after silica gel column chromatography, the desired 1,2,4-oxadiazoles **7** (yield calculated based on the acid used).

Preparation of Benzylated 1,2,4-Oxadiazoles 7 using Acyl Chlorides (Procedure B): A solution of acyl chloride (1 equiv.) and amidoxime **3** (0.08 mmol, 1 equiv.) in 1,4-dioxane (2 mL) was stirred at room temperature for 16 h. The mixture was heated to reflux for 3 h and processed as indicated for procedure A.

Preparation of *O*-Acylamidoximes 6 using Acyl Chlorides (Procedure C): Acyl chloride (1.1 equiv.) was added to a suspension of amidoxime **4** (0.2 mmol, 1 equiv.) in 1,4-dioxane (3 mL). After the mix-

ture was stirred at room temperature for 16 h, the solvent was evaporated. The desired *O*-acylamidoximes **6** were purified from the crude mixture by silica gel column chromatography.

Preparation of *O*-Acylamidoximes 6 using Carboxylic Acids (Procedure D): HOBt (1.2 equiv.) and EDCI (1.2 equiv.) were added at –10 °C to a solution of carboxylic acid (1 equiv.) and amidoxime **4** (0.25 mmol, 1.2 equiv.) in CH_2Cl_2/DMF (9:1, 2 mL). The solution, stirred at –10 °C for 20 min and at room temperature for an additional 8 h, was processed as indicated for procedure C (yield calculated based on the acid used).

Preparation of Benzoylated 1,2,4-Oxadiazoles 8 (Procedure E): A solution of *O*-acylamidoxime **6** (0.08 mmol) in 1,4-dioxane (2 mL) was heated to reflux (100 °C). The reaction was monitored by TLC and the crude mixture separated by silica gel column chromatography to provide the desired 1,2,4-oxadiazoles **8**.

Zemplén Deprotection of Benzoylated *C*-Glycosides (Procedure F): NaOMe (1 M in MeOH, 50 μL) was added to a solution of benzoylated *C*-glycosides (0.15 mmol) in MeOH (2 mL). The mixture was stirred at room temperature for 3 h and then neutralized with a cation exchange resin (Dowex 50WX2, H^+ form). The resin was filtered off and washed with MeOH (3 × 10 mL). The filtrate was concentrated and the crude mixture separated by silica gel column chromatography (PE/EtOAc, 3:2, then EtOAc, then EtOAc/MeOH, 95:5 to 9:1) to provide the deprotected 1,2,4-oxadiazoles.

***C*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)formamidoxime (3):** Hydroxylamine hydrochloride (103 mg, 1.48 mmol) was dissolved in the minimum amount of MeOH with gentle heating; then the mixture was allowed to reach room temperature. A drop of phenolphthalein was added and the solution was treated with NaOMe (1 M in MeOH) until a pink colour persisted. The precipitated NaCl was eliminated by filtration to afford a solution of free hydroxylamine. The freshly prepared solution of free hydroxylamine (1.48 mmol) was added to a solution of 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl cyanide (**1**)[24] (215 mg, 0.39 mmol) in MeOH (30 mL). The mixture was heated (50 °C) and TLC monitoring (PE/EtOAc, 3:2) indicated completion of the reaction after 12 h. The solvent was evaporated; then silica gel column chromatography (PE/EtOAc, 3:2) afforded the benzylated amidoxime **3** (212 mg, 93%) as a white solid. R_f = 0.63 (PE/EtOAc, 1:1). M.p. 47–48 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = +29 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 3.40–3.48 (m, 1 H, H-5), 3.54–3.68 (m, 4 H), 3.75–3.82 (m, 2 H), 4.40–4.86 (m, 8 H, 4 CH_2Ph), 5.26 (br. s, 2 H, NH_2), 7.10–7.32 (m, 20 H, 4 CH_2*Ph*), 8.95 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 70.3 (C-6), 74.3, 75.4, 75.8, 76.4 (4 *C*H_2Ph), 79.1, 79.6, 81.4, 87.5 (C-1 to C-4), 80.2 (C-5), 128.62, 128.66, 128.8, 128.9, 129.1, 129.2, 129.4, 129.5, 129.6, 129.7 (CH*arom*), 139.9, 140.1, 140.2, 140.6 (C^{IV}*arom*), 152.4 (H_2N*C*=NOH) ppm. $C_{35}H_{38}N_2O_6$ (582.69): calcd. C 72.14, H 6.57, N 4.81, O 16.47; found C 71.65, H 6.52, N 4.87, O 16.36. MS (LSIMS, glycerol): *m*/*z* = 583 $[M+H]^+$. HRMS (LSIMS, glycerol): *m*/*z* = $C_{35}H_{39}N_2O_6$ $[M+H]^+$ calcd. 583.2808, found 583.2801.

***C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (4):** A solution of 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl cyanide (**2**)[25] (4.32 g, 7.13 mmol) and hydroxylamine hydrochloride (1.24 g, 17.83 mmol, 2.5 equiv.) in pyridine (10 mL) was heated at 50 °C for 8 h. The solvent was evaporated; then the mixture was separated by silica gel column chromatography (PE/EtOAc, 1:1) to obtain **4** (4.13 g, 90%) as a white solid. R_f = 0.48 (PE/EtOAc, 1:1). M.p. 99–100 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = +17 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.21 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.31 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.47 (dd, 1 H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.62 (dd, 1 H, $J_{5,6b}$ = 2.6 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 4.76 (s, 2 H, NH_2), 5.69 (t, 1 H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.7 Hz, H-2), 5.73 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 5.96 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{2,3}$ = 9.7 Hz, H-3), 7.24–7.43 (m, 10 H, H*arom*), 7.47–7.57 (m, 2 H, H*arom*), 7.81–8.04 (m, 8 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.4 (C-6), 69.6 (C-4), 70.2 (C-2), 74.3 (C-3), 76.7 (C-1), 76.8 (C-5), 128.7, 128.7, 128.9, 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.4 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.1, 130.2, 130.3, 133.6, 133.7, 133.7, 134.0, 149.9 (H_2N*C*=NOH), 165.6, 165.7, 166.2, 166.6 (4 O*C*OPh) ppm. $C_{35}H_{30}N_2O_{10}$ (638.62): calcd. C 65.83, H 4.73, N 4.39, O 25.05; found C 65.05, H 4.79, N 4.37, O 24.60.

***C*-(β-D-Glucopyranosyl)formamidoxime (5):** A solution of amidoxime **4** (135 mg, 0.21 mmol) was treated according to method F to obtain **5** (14 mg, 30%) as a colourless gum. R_f = 0.50 (EtOAc/MeOH, 4:1). $[\alpha]_D^{20}$ = +15 (*c* = 1, MeOH). ^{1}H NMR (300 MHz, D_2O): δ = 3.45 (m, 2 H, H-4, H-5), 3.49 (br. t, 1 H, *J* ≈ 9.0 Hz, H-3), 3.59 (dd, 1 H, $J_{1,2}$ = 9.5 Hz, $J_{2,3}$ ≈ 9 Hz, H-2), 3.70 (d, 1 H, $J_{1,2}$ = 9.5 Hz, H-1), 3.71 (dd, 1 H, $J_{5,6a}$ = 3.5 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 3.84 (dd, 1 H, $J_{6a,6b}$ = 11.8 Hz, $J_{5,6b}$ ≈ 1 Hz, H-6b) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 61.0 (C-6), 69.6 (C-4), 71.3 (C-2), 77.2 (C-3), 77.9 (C-1), 80.1 (C-5), 154.0 (H_2N*C*=NOH) ppm. MS (LSIMS, glycerol): *m*/*z* = 223.0 $[M+H]^+$. HRMS (LSIMS, glycerol): *m*/*z* = $C_7H_{15}N_2O_6$ $[M+H]^+$ calcd. 223.0930, found 223.0929.

5-Phenyl-3-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (7b). a): A solution of benzoic acid (16 mg, 0.13 mmol), benzylated amidoxime **3** (89.3 mg, 0.15 mmol, 1.2 equiv.) and EDCI (49 mg, 0.25 mmol, 2 equiv.) was treated according to procedure A, to afford **7b** (26 mg, 31%), purified by silica gel column chromatography (PE/EtOAc, 4:1). **b)** A solution of benzoyl chloride (11 μL, 0.09 mmol) and benzylated amidoxime **3** (54 mg, 0.09 mmol, 1 equiv.) was treated according to procedure B. Silica gel column chromatography (PE/EtOAc, 4:1) afforded **7b** (35 mg, 57%) as a white solid. R_f = 0.75 (PE/EtOAc, 4:1). M.p. 78–79 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –32 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (m, 1 H, H-5), 3.75 (m, 2 H, H-6a, H-6b), 3.79–3.88 (m, 2 H, H-3, H-4), 4.10 (dd, 1 H, $J_{1,2}$ = 9.5 Hz, $J_{2,3}$ = 9.0 Hz, H-2), 4.45 (d, 1 H, *J* = 10.9 Hz, CH_2Ph), 4.51 (d, 1 H, *J* = 12.4 Hz, CH_2Ph), 4.59 (d, 1 H, *J* = 12.4 Hz, CH_2Ph), 4.60 (d, 1 H, *J* = 10.7 Hz, CH_2Ph), 4.61 (d, 1 H, $J_{1,2}$ = 9.5 Hz, H-1), 4.70 (d, 1 H, *J* = 10.9 Hz, CH_2Ph), 4.85 (d, 1 H, *J* = 10.7 Hz, CH_2Ph), 4.94 (s, 2 H, CH_2Ph), 7.01–7.18 (m, 7 H, H*arom*), 7.27–7.54 (m, 13 H, H*arom*), 7.57–8.09 (m, 3 H, H*arom*), 8.11 (d, 2 H, *J* = 7.0 Hz, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.2 (C-6), 73.6 (C-1), 73.9, 75.3, 75.6, 76.1 (4×*C*H_2Ph), 78.3 (C-4), 80.2 (C-2), 80.3 (C-5), 87.3 (C-3), 124.5 (C^{IV}*arom*), 128.0, 128.1, 128.1, 128.2, 128.3, 128.37, 128.45, 128.6, 128.7, 128.8, 128.9, 129.4, 133.3, 138.1 (C^{IV}*arom*), 138.3 (C^{IV}*arom*), 138.4 (C^{IV}*arom*), 138.9 (C^{IV}*arom*), 168.7 (C-3*oxa*), 176.4 (C-5*oxa*) ppm. MS (LSIMS, NBA/AcONa): *m*/*z* = 669.2 $[M+H]^+$, 691.1 $[M+Na]^+$. HRMS (LSIMS, NBA/AcONa): *m*/*z* = $C_{42}H_{40}N_2O_6$ $[M+Na]^+$ calcd. 691.2784, found 691.2782.

5-(*p*-Nitrophenyl)-3-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (7e). a) A solution of *p*-nitrobenzoic acid (11 mg, 0.065 mmol), benzylated amidoxime **3** (46 mg, 0.08 mmol, 1.2 equiv.) and EDCI (30 mg, 0.16 mmol, 2 equiv.) was treated according to procedure A, to afford **7e** (32 mg, 69%) after silica gel column chromatography (PE/EtOAc, 7:3). **b)** A solution of *p*-nitrobenzoyl chloride (15 mg, 0.08 mmol) and benzylated amidoxime **3** (48 mg, 0.08 mmol, 1 equiv.) was treated according to procedure B. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **7e** (45 mg, 76%) as a pale yellow solid. R_f = 0.73 (PE/EtOAc, 7:3). M.p. 88–89 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –42 (*c* = 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.70 (m, 1 H, H-5), 3.76 (m, 2 H,

H-6a, H-6b), 3.81 (dd, 1 H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 3.87 (dd, 1 H, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 8.9 Hz, H-3), 4.07 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.7 Hz, H-2), 4.46 (d, 1 H, J = 11.5 Hz, CH_2Ph), 4.50 (d, 1 H, J = 12.2 Hz, CH_2Ph), 4.58 (d, 1 H, J = 12.2 Hz, CH_2Ph), 4.61 (d, 1 H, J = 10.7 Hz, CH_2Ph), 4.63 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 4.74 (d, 1 H, J = 11.5 Hz, CH_2Ph), 4.87 (d, 1 H, J = 10.7 Hz, CH_2Ph), 4.96 (s, 2 H, CH_2Ph), 6.93–7.37 (m, 20 H, 4 CH$_2$*Ph*), 8.24 (dt, 2 H, ^4J_m = 2.0 Hz, ^3J_o = 9.0 Hz, *Ph*NO$_2$), 8.36 (dt, 2 H, ^4J_m = 2.0 Hz, ^3J_o = 9.0 Hz, *Ph*NO$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.2 (C-6), 73.4 (C-1), 73.9, 75.2, 75.6, 76.2 (4 *C*H$_2$Ph), 78.2 (C-4), 79.9 (C-2), 80.3 (C-5), 87.4 (C-3), 124.7 (*Ph*NO$_2$), 128.10, 128.14, 128.2, 128.32, 128.37, 128.41, 128.6, 128.8, 128.91, 128.92 (C^{IV}*arom*), 129.7 (*Ph*NO$_2$), 138.1, 138.3, 138.4, 138.8 (C^{IV}*arom*), 150.6 (C-NO$_2$), 169.2 (C-3*oxa*), 174.3 (C-5*oxa*) ppm. MS (ESI): m/z = 714.0 [M + H]$^+$. HRMS (LSIMS, NBA/AcONa): m/z = $C_{42}H_{39}N_3O_8Na$ [M + Na]$^+$ calcd. 736.2635, found 736.2637.

5-(3-Pyridyl)-3-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (7g): A solution of nicotinoyl chloride hydrochloride (15 mg, 0.08 mmol) and benzylated amidoxime **3** (50 mg, 0.08 mmol, 1 equiv.) was treated according to procedure B. Silica gel column chromatography (PE/EtOAc, 2:3) afforded **7 g** (58 mg, 97%) as a pale yellow solid. R_f = 0.63 (PE/EtOAc, 2:3). M.p. 98–99 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –41 (c = 0.67, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (m, 1 H, H-5), 3.75 (m, 2 H, H-6a, H-6b), 3.80 (dd, 1 H, $J_{3,4}$ = 8.7 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 3.87 (dd, 1 H, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.7 Hz, H-3), 4.08 (dd, 1 H, $J_{1,2}$ = 9.4 Hz, $J_{2,3}$ = 9.0 Hz, H-2), 4.47 (d, 1 H, J = 11.0 Hz, CH_2Ph), 4.54 (d, 1 H, J = 12.1 Hz, CH_2Ph), 4.57 (d, 1 H, J = 12.1 Hz, CH_2Ph), 4.60 (d, 1 H, J = 10.7 Hz, CH_2Ph), 4.63 (d, 1 H, $J_{1,2}$ = 9.4 Hz, H-1), 4.74 (d, 1 H, J = 11.0 Hz, CH_2Ph), 4.86 (d, 1 H, J = 10.7 Hz, CH_2Ph), 4.95 (s, 2 H, CH_2Ph), 6.96–7.35 (m, 20 H, CH$_2$*Ph*), 7.46 (br. s, 1 H, H*pyr*), 8.32 (d, 1 H, J = 7,8 Hz, H*pyr*), 8.82 (br. s, 1 H, H*pyr*), 9.30 (br. s, 1 H, H*pyr*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.2 (C-6), 73.4 (C-1), 73.9, 75.2, 75.6, 76.2 (4 *C*H$_2$Ph), 78.3 (C-4), 80.0 (C-2), 80.3 (C-5), 87.4 (C-3), 128.1, 128.2, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9 (*CH*arom, *CH*pyr), 135.7 (*CH*pyr), 138.1, 138.3, 138.4, 138.8 (C^{IV}*arom*), 149.6 (*CH*pyr), 153.7 (*CH*pyr), 168.9 (C-3*oxa*), 174.3 (C-5*oxa*) ppm. MS (ESI): m/z = 670.1 [M + H]$^+$, 1360.8 [2 M + Na]$^+$. HRMS (LSIMS, NBA/AcONa): m/z = $C_{41}H_{39}N_3O_6Na$ [M + Na]$^+$ calcd. 692.2737, found 692.2730.

5-(2-Naphthyl)-3-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (7k): A solution of 2-naphthoyl chloride (17 mg, 0.09 mmol) and benzylated amidoxime **3** (52 mg, 0.09 mmol, 1 equiv.) was treated according to procedure B. Silica gel column chromatography (PE/EtOAc, 4:1) afforded **7k** (35 mg, 55%) as a white solid. R_f = 0.71 (PE/EtOAc, 4:1). M.p. 112–113 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –44 (c = 0.88, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (m, 1 H, H-5), 3.77 (m, 2 H, H-6a, H-6b), 3.82 (dd, 1 H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 9.0 Hz, H-4), 3.88 (dd, 1 H, $J_{2,3}$ = 8.8 Hz, $J_{3,4}$ = 8.9 Hz, H-3), 4.13 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.8 Hz, H-2), 4.49 (d, 1 H, J = 10.9 Hz, CH_2Ph), 4.56 (d, 1 H, J = 12.2 Hz, CH_2Ph), 4.60 (d, 1 H, J = 12.2 Hz, CH_2Ph), 4.61 (d, 1 H, J = 10.7 Hz, CH_2Ph), 4.65 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 4.73 (d, 1 H, J = 10.9 Hz, CH_2Ph), 4.87 (d, 1 H, J = 10.7 Hz, CH_2Ph), 4.95 (s, 2 H, CH_2Ph), 6.96–7.12 (m, 5 H, H*arom*), 7.15–7.18 (m, 2 H, H*arom*), 7.27–7.36 (m, 13 H, H*arom*), 7.55–7.56 (m, 2 H, H-6′, H-7′), 7.87–7.99 (m, 3 H, H-4′, H-5′, H-8′), 8.12 (dd, 1 H, $J_{1',3'}$ = 1.7 Hz, $J_{3',4'}$ = 8.7 Hz, H-3′), 8.67 (pd, 1 H, $J_{1',3'}$ = 1,7 Hz, H-1′) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.2 (C-6), 73.6 (C-1), 73.9, 75.3, 75.6, 76.1 (4 *C*H$_2$Ph), 78.2 (C-4), 80.2, 80.3 (C-2, C-5), 87.3 (C-3), 121.7, 133.1 (C-4′a, C-8′a), 124.3 (C-3′), 127.6, 128.1, 128.1, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9, 128.9, 129.4, 129.6, 129.8 (C-1′), 135.7 (C-2′), 138.1 (C^{IV}*arom*), 138.3 (C^{IV}*arom*), 138.4 (C^{IV}*arom*), 138.9 (C^{IV}*arom*), 168.8 (C-3*oxa*), 176.6 (C-5*oxa*) ppm. MS (ESI): m/z = 719.2 [M + H]$^+$, 741.3 [M + Na]$^+$, 1436.7 [2 M + H]$^+$, 1459.9 [2 M + Na]$^+$. HRMS (LSIMS, NBA/AcONa): m/z = $C_{46}H_{42}N_2O_6Na$ [M + Na]$^+$ calcd. 741.2941, found 741.2945.

5-[(*E*)-Styryl]-3-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (7l): A solution of cinnamoyl chloride (13 mg, 0.076 mmol) and benzylated amidoxime **3** (45 mg, 0.076 mmol, 1 equiv.) was treated according to procedure B. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **7l** (25 mg, 47%) as a white solid. R_f = 0.83 (PE/EtOAc, 7:3). M.p. 106–107 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –42 (c = 0.76, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.65–3.78 (m, 4 H, H-4, H-5, H-6a, H-6b), 3.84 (dd, 1 H, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 8.7 Hz, H-3), 4.04 (dd, 1 H, $J_{1,2}$ = 9.6 Hz, $J_{2,3}$ = 9.0 Hz, H-2), 4.43 (d, 1 H, J = 10.9 Hz, CH_2Ph), 4.51 (d, 1 H, J = 12.1 Hz, CH_2Ph), 4.56–4.59 (m, 3 H, H-1, CH_2Ph), 4.70 (d, 1 H, J = 10.9 Hz, CH_2Ph), 4.85 (d, 1 H, J = 10,9 Hz, CH_2Ph), 4.93 (s, 2 H, CH_2Ph), 6.96 (d, 1 H, J = 16.5 Hz, C*H* = CHPh), 7.00–7.10 (m, 2 H, H*arom*), 7.12–7.23 (m, 5 H, H*arom*), 7.27–7.35 (m, 13 H, H*arom*), 7.41–7.44 (m, 3 H, H*arom*), 7.56–7.61 (m, 2 H, H*arom*), 7.80 (d, 1 H, J = 16.5 Hz, CH=C*H*Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.3 (C-6), 73.5 (C-1), 73.9, 75.3, 75.6, 76.1 (4 *C*H$_2$Ph), 78.3 (C-4), 80.2, 80.3 (C-2, C-5), 87.2 (C-3), 110.5 (CH = *C*HPh), 128.0, 128.1, 128.1, 128.2, 128.3, 128.4, 128.4, 128.7, 128.8, 128.9, 129.5, 131.0, 134.7 (C^{IV}*arom*), 138.1 (C^{IV}*arom*), 138.3 (C^{IV}*arom*), 138.4 (C^{IV}*arom*), 138.8 (C^{IV}*arom*), 143.4 (*C*H = CHPh), 168.4 (C-3*oxa*), 175.9 (C-5*oxa*) ppm. MS (ESI): m/z = 695.2 [M + H]$^+$, 717.3 [M + Na]$^+$, 1388.6 [2 M + H]$^+$, 1410.8 [2 M + Na]$^+$. HRMS (LSIMS, NBA/AcONa): m/z = $C_{44}H_{42}N_2O_6Na$ [M + Na]$^+$ calcd. 717.2941, found 717.2938.

***O*-Acetyl-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6a):** A solution of acetyl chloride (40 μL, 0.56 mmol) and benzoylated amidoxime **4** (300 mg, 0.47 mmol) was treated according to procedure C. Silica gel column chromatography (CH_2Cl_2/EtOAc, 95:5) afforded **6a** (193 mg, 61%) as a white solid. R_f = 0.38 (CH_2Cl_2/EtOAc, 95:5). M.p. 96–98 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = +0.3 (c = 0.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (s, 3 H, CH_3), 4.27 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 5.3 Hz, $J_{5,6b}$ = 2.7 Hz, H-5), 4.49 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.54 (dd, 1 H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ 12.4 Hz, H-6a), 4.65 (dd, 1 H, $J_{5,6b}$ = 2.7 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.22 (s, 2 H, NH_2), 5.73 (t, 1 H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.7 Hz, H-2), 5.77 (t, 1 H, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 5.98 (t, 1 H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 7.22–7.83 (m, 11 H, H*arom*), 7.92–8.05 (m, 9 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.8 (CH_3), 63.4 (C-6), 69.6 (C-4), 70.3 (C-2), 74.1 (C-3), 76.1 (C-1), 77.0 (C-5), 128.7, 128.8, 128.9, 128.9, 128.9 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.8 (C^{IV}*arom*), 130.1, 130.2, 130.3, 130.4, 133.7, 133.8, 134.0, 153.6 (H$_2$N*C* = NOH), 165.7, 165.9, 166.0, 166.6 (4 O*CO*Ph), 168.7 (NO*CO*) ppm. MS (LSIMS, NBA): m/z = 681 [M + H]$^+$. HRMS (LSIMS, NBA): m/z = $C_{37}H_{33}N_2O_{11}$ [M + H]$^+$ calcd. 681.2084, found 681.2089.

***O*-Benzoyl-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6b):** A solution of benzoyl chloride (39 μL, 0.34 mmol) and benzoylated amidoxime **4** (200 mg, 0.31 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6b** (204 mg, 88%) as a white solid. R_f = 0.47 (PE/EtOAc, 3:2). M.p. 98–100 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –47 (c = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.29 (ddd, 1 H, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 2.7 Hz, H-5), 4.53 (dd, 1 H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.60 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 4.65 (dd, 1 H, $J_{5,6b}$ = 2.7 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 5.24 (s, 2 H, NH_2), 5.75 (t, 1 H, $J_{1,2}$ = 9.9 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.78 (t, 1 H,

$J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 5.99 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 7.23–7.58 (m, 15 H, H*arom*), 7.82 (dd, 2 H, *J* = 1.4 Hz, *J* = 8.5 Hz, H*arom*), 7.90–7.96 (m, 6 H, H*arom*), 8.04 (dd, 2 H, *J* = 1.4 Hz, *J* = 8.5 Hz, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.4 (C-6), 69.6 (C-4), 70.4 (C-2), 74.1 (C-3), 76.3 (C-1), 77.1 (C-5), 128.7, 128.8, 128.9, 128.9, 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.5 (C^{IV}*arom*), 129.8 (C^{IV}*arom*), 129.9, 130.1, 130.2, 130.3, 130.4, 133.4, 133.7, 133.8, 154.6 (H_2NC=NO), 163.7 (NO*C*O), 165.7, 166.0, 166.1, 166.6 (4 O*C*OPh) ppm. $C_{42}H_{34}N_2O_{11}$ (742.73): calcd. C 67.92, H 4.61, N 3.77, O 23.70; found C 67.66, H 4.92, N 3.79, O 23.41. MS (LSIMS, NBA): *m*/*z* = 743.6 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{42}H_{35}N_2O_{11}$ $[M+H]^+$ calcd. 743.2241, found 743.2243.

***O*-(*p*-Anisoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6c)**: A solution of *p*-anisoyl chloride (58 μL, 0.43 mmol) and benzoylated amidoxime **4** (250 mg, 0.39 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6c** (262 mg, 87%) as a pale yellow solid. R_f = 0.52 (PE/EtOAc, 1:1). M.p. 100–101 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –62 (*c* = 0.56, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 4.28 (ddd, 1 H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 5.3 Hz, $J_{5,6b}$ = 2.7 Hz, H-5), 4.53 (dd, 1 H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.59 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 4.65 (dd, 1 H, $J_{5,6b}$ = 2.7 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6b), 5.19 (s, 2 H, NH_2), 5.76 (m, 2 H, H-2, H-4), 5.98 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 6.84 (d, 2 H, *J* = 8.9 Hz, H-2′, H-6′), 7.24–7.58 (m, 12 H, H*arom*), 7.81–7.96 (m, 6 H, H*arom*), 7.88 (d, 2 H, *J* = 8.9 Hz, H-3′, H-5′), 8.04 (m, 2 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 63.0 (C-6), 69.2 (C-4), 69.9 (C-2), 73.7 (C-3), 75.9 (C-1), 76.7 (C-5), 113.6 (C-2′, C-6′), 121.3 (C-4′), 128.3, 128.4, 128.47, 128.51 (C^{IV}*arom*), 128.7 (C^{IV}*arom*), 128.8 (C^{IV}*arom*), 129.4 (C^{IV}*arom*), 129.7, 129.8, 129.9, 130.0, 131.5 (C-3′, C-5′), 133.27 (2 C), 133.33, 133.6, 153.8 (H_2NC=NO), 163.1 (NO*C*O), 163.4 (C-1′), 165.3, 165.6, 165.7, 166.2 (4 O*C*OPh) ppm. $C_{43}H_{36}N_2O_{12}$ (772.75): calcd. C 66.83, H 4.70, N 3.63, O 24.85; found C 66.63, H 4.83, N 3.48, O 24.90.

***C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-*O*-(*p*-toluoyl)formamidoxime (6d)**: A solution of *p*-toluoyl chloride (45 μL, 0.34 mmol) and benzoylated amidoxime **4** (200 mg, 0.31 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **6d** (160 mg, 67%) as a white solid. R_f = 0.38 (PE/EtOAc, 7:3). M.p. 105–107 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –56 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 4.30 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.5 Hz, $J_{5,6b}$ = 2.7 Hz, H-5), 4.54 (dd, 1 H, $J_{5,6a}$ = 5.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.63 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.65 (dd, 1 H, $J_{5,6b}$ = 2.7 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 5.30 (s, 2 H, NH_2), 5.80 (t, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{1,2}$ = 9.8 Hz, H-2), 5.81 (t, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 6.01 (t, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 7.10 (d, 2 H, *J* = 8.0 Hz, H*tol*), 7.21–7.55 (m, 12 H, H*arom*), 7.81 (m, 4 H, *J* = 8.4 Hz, *J* = 8.1 Hz, H*tol*, H*arom*), 7.92–7.96 (m, 4 H, H*arom*), 8.03 (m, 2 H, *J* = 8.4 Hz, *J* = 1.4 Hz, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (CH_3), 63.5 (C-6), 69.7 (C-4), 70.4 (C-2), 74.2 (C-3), 76.4 (C-1), 77.1 (C-5), 126.7 (C^{IV}arom), 128.7, 128.8, 128.9, 129.0 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.5, 129.8 (C^{IV}*arom*), 129.9, 130.1, 130.2, 130.3, 130.4, 133.7, 133.8, 134.1, 144.1 (C^{IV}*tol*), 154.5 (H_2NC=NO), 163.8 (NO*C*O), 165.7, 166.1, 166.2, 166.6 (4 O*C*OPh) ppm. MS (LSIMS, glycerol): *m*/*z* = 779 $[M+Na]^+$. HRMS (LSIMS, glycerol): *m*/*z* = $C_{43}H_{36}N_2NaO_{11}$ $[M+Na]^+$ calcd. 779.2217, found 779.2220.

***O*-(*p*-Nitrobenzoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6e)**: A solution of *p*-nitrobenzoyl chloride (47 mg, 0.25 mmol) and benzoylated amidoxime **4** (135 mg, 0.21 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6e** (166 mg, 100%) as a white solid. R_f = 0.54 (PE/EtOAc, 3:2). M.p. 114–115 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –57 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.7 Hz, H-5), 4.58 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.64 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.66 (dd, 1 H, $J_{5,6b}$ = 2.7 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.47 (s, 2 H, NH_2), 5.81 (t, 1 H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.83 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 6.04 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 7.21–7.54 (m, 12 H, H*arom*), 7.80–8.13 (m, 12 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = (ppm) 63.5 (C-6), 69.6 (C-4), 70.5 (C-2), 74.0 (C-3), 76.0 (C-1), 77.1 (C-5), 123.9, 128.7, 128.8, 128.9, 128.9, 129.0 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.7 (C^{IV}*arom*), 130.1, 130.2, 130.3, 130.4, 130.9, 133.8, 133.9, 134.1, 134.9 (C^{IV}*arom*), 150.7 (C^{IV}*arom*), 155.4 (H_2NC=NO), 162.0 (NO*C*O), 165.7, 166.0, 166.2, 166.6 (4 O*C*OPh) ppm. $C_{42}H_{33}N_3O_{13}$ (787.72): calcd. C 64.04, H 4.22, N 5.33, O 26.40; found C 63.60, H 4.18, N 5.31, O 25.68.

***O*-(*m*-Chlorobenzoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6f)**: A solution of *m*-chlorobenzoyl chloride (54 μL, 0.42 mmol) and benzoylated amidoxime **4** (223 mg, 0.35 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6f** (253 mg, 93%) as a white solid. R_f = 0.55 (PE/EtOAc, 3:2). M.p. 96–97 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –48 (*c* = 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.28 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 2.6 Hz, H-5), 4.53 (dd, 1 H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.57 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.66 (dd, 1 H, $J_{5,6b}$ = 2.6 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.21 (s, 2 H, NH_2), 5.72 (t, 1 H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.77 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 5.98 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 7.25–7.60 (m, 14 H, H*arom*), 7.78–7.84 (m, 3 H, Harom), 7.88 (t, 1 H, *J* = 1.7 Hz, H*arom*), 7.92–7.96 (m, 4 H, H*arom*), 8.03–8.06 (m, 2 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.3 (C-6), 69.5 (C-4), 70.4 (C-2), 74.0 (C-3), 76.2 (C-1), 77.2 (C-5), 128.0, 128.8, 128.9, 129.1 (C^{IV}*arom*), 129.8 (C^{IV}*arom*), 129.9, 130.1, 130.2, 130.3, 130.4, 131.2 (C^{IV}*arom*), 133.5, 133.7, 133.8, 134.1, 135.0 (C^{IV}*arom*), 154.7 (H_2NC=NO), 162.5 (NO*C*O), 165.7, 166.0, 166.1, 166.6 (4 O*C*-OPh) ppm. MS (ESI): *m*/*z* = 777.0 $[M+H]^+$, 799.1 $[M+Na]^+$, 1554.7 $[2M+H]^+$, 1574.6 $[2M+Na]^+$. HRMS (LSIMS, NBA/AcONa): *m*/*z* = $C_{42}H_{33}ClN_2O_{11}Na$ $[M+Na]^+$ calcd. 799.1671, found 799.1680.

***O*-Nicotinoyl-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6g):** A solution of nicotinoyl chloride hydrochloride (58 mg, 0.33 mmol) and benzoylated amidoxime **4** (150 mg, 0.23 mmol) was treated according to procedure C. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and the aqueous layer extracted with $CHCl_3$ (3 × 20 mL). Organic layers were combined, dried (Na_2SO_4), filtered and the solvents evaporated. Silica gel column chromatography (PE/EtOAc, 3:7) afforded **6g** (156 mg, 93%) as a white solid. R_f = 0.45 (PE/EtOAc, 3:7). M.p. 115–116 °C (CH_2Cl_2:PE). $[\alpha]_D^{20}$ = –43 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.36 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.58 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.65 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 4.68 (dd, 1 H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.61 (s, 2 H, NH_2), 5.84 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 5.85 (t, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 6.05 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 7.21–7.57 (m, 13 H, H*arom*), 7.83–8.18 (m, 9 H, H*arom*), 8.68 (d, 1 H, *J* = 3.0 Hz, H*arom*), 9.13 (s, 1 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.5 (C-6), 69.6 (C-4), 70.4 (C-2), 74.1 (C-3), 76.2 (C-1), 77.1 (C-5), 123.8, 125.7 (C^{IV}*arom*), 128.7, 128.8, 128.9, 129.1 (C^{IV}*arom*),

129.2 (C^{IV}*arom*), 129.7 (C^{IV}*arom*), 130.1, 130.2, 130.3, 130.4, 133.7, 133.8, 133.9, 134.1, 137.5, 150.7, 153.7, 155.2 (H_2NC=NO), 162.5 (NO*C*O), 165.7, 166.1, 166.2, 166.6 (4 O*C*OPh) ppm. $C_{41}H_{33}N_3O_{11}$ (743.71): calcd. C 66.21, H 4.47, N 5.65, O 23.66; found C 65.54, H 4.63, N 5.71, O 23.47.

***O*-(2-Furoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6h):** A solution of 2-furoyl chloride (32 μL, 0.33 mmol) and benzoylated amidoxime **4** (200 mg, 0.31 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6h** (165 mg, 72%) as a white solid. R_f = 0.32 (PE/EtOAc, 3:2). M.p. 104–106 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –48 (*c* = 0.68, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.30 (ddd, 1 H, $J_{4,5}$ = 9.4 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.54 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.61 (d, 1 H, $J_{1,2}$ = 10.2 Hz, H-1), 4.65 (dd, 1 H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.41 (s, 2 H, NH_2), 5.81 (m, 2 H, H-2, H-4), 6.00 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 6.35 (dd, 1 H, $J_{3',4'}$ = 3.3 Hz, $J_{4',5'}$ = 1.7 Hz, H-4′), 7.11 (d, 1 H, $J_{3',4'}$ = 3.3 Hz, H-3′), 7.20–7.55 (m, 11 H, H*arom*), ≈ 7.46 (d, 1 H, $J_{4',5'}$ = 1.7 Hz, H-5′), 7.81–8.04 (m, 9 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.5 (C-6), 69.6, 70.4 (C-2, C-4), 74.2 (C-3), 76.2 (C-1), 77.1 (C-5), 112.2 (C-4′), 118.8 (C-3′), 128.7, 128.8, 128.8, 128.9, 128.9 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.8 (C^{IV}*arom*), 130.1, 130.2, 130.3, 130.4, 133.7, 133.8, 134.1, 143.5 (C-2′), 146.8 (C-5′), 154.8 (H_2NC=NO), 156.1 (NO*C*O), 165.7, 166.1, 166.2, 166.6 (4 O*C*OPh) ppm. MS (LSIMS, NBA/AcONa): *m*/*z* = 755 $[M+Na]^+$. HRMS (LSIMS, NBA/AcONa): *m*/*z* = $C_{40}H_{32}N_2O_{12}Na$ $[M+Na]^+$ calcd. 755.1853, found 755.1858.

***C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-*O*-(2-thienoyl)formamidoxime (6i):** A solution of 2-thienoyl chloride (35 μL, 0.33 mmol) and benzoylated amidoxime **4** (200 mg, 0.31 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6i** (186 mg, 79%) as a white solid. R_f = 0.37 (PE/EtOAc, 3:2). M.p. 102–103 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –44 (*c* = 0.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.31 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.55 (dd, 1 H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.61 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 4.66 (dd, 1 H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.35 (s, 2 H, NH_2), 5.81 (t, 1 H, $J_{1,2}$ = 9.9 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 5.82 (t, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 6.01 (t, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 6.95 (dd, 1 H, $J_{4',5'}$ = 4.9 Hz, $J_{3',4'}$ = 3.8 Hz, H-4′), 7.20–7.54 (m, 12 H, H*arom*), 7.43 (dd, 1 H, $J_{4',5'}$ = 4.9 Hz, $J_{3',5'}$ = 1.2 Hz, H-5′), 7.72 (dd, 1 H, $J_{3',4'}$ = 3.8 Hz, $J_{3',5'}$ = 1.2 Hz, H-3′), 7.80–8.05 (m, 8 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.5 (C-6), 69.7 (C-4), 70.4 (C-2), 74.2 (C-3), 76.2 (C-1), 77.1 (C-5), 128.1 (C-4′), 128.8, 128.9, 128.9, 129.0 (C^{IV}*arom*), 129.2, 129.2 (C^{IV}*arom*), 129.8, 130.1, 130.2, 130.3, 130.4, 132.0 (C^{IV}*arom*), 132.9 (C-5′), 133.7, 133.8, 134.1 (C-3′), 134.2, 154.5 (H_2NC=NO), 159.4 (NO*C*O), 165.7, 166.1, 166.2, 166.6 (4 O*C*OPh) ppm. MS (LSIMS, NBA): *m*/*z* = 749.9 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{40}H_{33}N_2O_{11}S$ $[M+H]^+$ calcd. 749.1805, found 749.1809.

***O*-(1-Naphthoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6j):** A solution of 1-naphthoyl chloride (225 mg, 1.18 mmol) and benzoylated amidoxime **4** (420 mg, 0.66 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6j** (465 mg, 90%) as a white solid. R_f = 0.47 (PE/EtOAc, 3:2). M.p. 90–92 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –39 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 2.6 Hz, H-5), 4.56 (dd, 1 H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.66 (dd, 1 H, $J_{5,6b}$ = 2.6 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 4.71 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 5.37 (s, 2 H, NH_2), 5.85 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 5.86 (t, 1 H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 6.09 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 7.17–7.50 (m, 15 H, H*arom*), 7.73–8.04 (m, 11 H, H*arom*), 8.44 (dd, 1 H, *J* = 1.1 Hz, *J* = 9.1 Hz, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.6 (C-6), 69.8 (C-4), 70.6 (C-2), 74.2 (C-3), 76.4 (C-1), 77.1 (C-5), 124.8, 126.0, 126.8, 127.2 (C^{IV}*arom*), 128.2, 128.8, 128.8, 128.9, 129.0, 129.2 (C^{IV}*arom*), 129.3 (C^{IV}*arom*), 129.5, 129.8 (C^{IV}*arom*), 130.1, 130.2, 130.4, 130.5, 131.6 (C^{IV}*arom*), 133.4, 133.7, 133.8, 133.9, 134.0 (C^{IV}*arom*), 134.1, 154.7 (H_2NC=NO), 165.0 (NO*C*O), 165.8, 166.2, 166.3, 166.7 (4 O*C*OPh) ppm. $C_{46}H_{36}N_2O_{11}$ (792.78): calcd. C 69.69, H 4.58, N 3.53, O 22.20; found C 69.12, H 4.62, N 3.46, O 21.55.

***O*-(2-Naphthoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-formamidoxime (6k):** A solution of 2-naphthoyl chloride (89 mg, 0.47 mmol) and benzoylated amidoxime **4** (200 mg, 0.31 mmol) was treated according to procedure C. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6h** (154 mg, 62%) as a white solid. R_f = 0.63 (PE/EtOAc, 3:2). M.p. 105–106 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –72 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.29 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 2.6 Hz, H-5), 4.54 (dd, 1 H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.62 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 4.67 (dd, 1 H, $J_{5,6b}$ = 2.6 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.25 (s, 2 H, NH_2), 5.75 (t, 1 H, $J_{1,2}$ = 9.9 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.78 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 6.00 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 7.26–7.59 (m, 14 H, H*arom*), 7.82–7.97 (m, 10 H, H*arom*), 8.06 (m, 2 H, H*arom*), 8.49 (br. s, 1 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.4 (C-6), 69.5 (C-4), 70.4 (C-2), 74.1 (C-3), 76.3 (C-1), 77.2 (C-5), 125.4, 126.7, 127.2, 128.2, 128.6 128.7, 128.9, 128.9, 129.2 (C^{IV}*arom*), 129.7, 129.8 (C^{IV}*arom*), 130.1, 130.2, 130.3, 130.4, 131.4, 132.8 (C^{IV}*arom*), 133.7, 133.8, 134.1, (C *arom*), 135.9 (C^{IV}*arom*), 154.5 (H_2NC = NOH), 163.9 (NO*C*O), 165.7, 166.0, 166.2, 166.6 (4 O*C*OPh) ppm. $C_{46}H_{36}N_2O_{11}$ (792.78): calcd. C 69.69, H 4.58, N 3.53, O 22.20; found C 68.19, H 4.57, N 3.48, O 21.68.

***O*-[(1*S*)-*N*-{[(9*H*-Fluoren-9-yl)methoxy]carbonyl}valinoyl]-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidoxime (6m)**: HOBt (52 mg, 0.39 mmol), EDCI (75 mg, 0.39 mmol), Fmoc-Val-OH (111 mg, 0.33 mmol) and amidoxime **4** (250 g, 0.39 mmol) in CH_2Cl_2/DMF (9:1, 10 mL) were treated according to procedure D. The solvent was evaporated and the crude product dissolved in EtOAc (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL), water (50 mL), 0.5 M aqueous $KHSO_4$ (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), filtered and concentrated to dryness. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **6m** (235 mg, 75%) as a white solid. R_f = 0.26 (PE/EtOAc, 7:3). M.p. 173–175 °C (CH_2Cl_2/hexane). $[\alpha]_D^{20}$ = –8 (*c* = 0.92, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (d, 3 H, *J* = 6.7 Hz, CH_3), 0.86 (d, 3 H, *J* = 6.7 Hz, CH_3), 2.04 (m, 1 H, $J_{H\alpha,H\beta}$ = 5.1 Hz, H-β), 4.17 (t, 1 H, *J* = 6.8 Hz, *J* = 6.8 Hz, H*Fmoc*), 4.23 (ddd, 1 H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.30 (dd, 1 H, $J_{H\alpha,H\beta}$ = 5.1 Hz, $J_{H\alpha,NH}$ = 9.5 Hz, H-*α*), 4.38 (d, 2 H, *J* = 6.8 Hz, CH_2*Fmoc*), 4.46 (d, 1 H, $J_{1,2}$ = 9,7 Hz, H-1), 4.50 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.65 (dd, 1 H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6b), 5.20 (s, 2 H, NH_2), 5.23 (d, 1 H, $J_{H\alpha,NH}$ = 9.5 Hz, NH), 5.67 (t, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.76 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.9 Hz, H-4), 5.95 (t, 1 H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 7.23–7.58 (m, 18 H, H*arom*), 7.75 (d, 2 H, *J* = 9.0 Hz, H*arom*), 7.80 (m, 2 H, H*arom*), 7.88–7.95 (m, 4 H, H*arom*), 8.02–8.05 (m, 2 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9 (CH_3), 19.3 (CH_3), 31.7 (C-β), 47.6 (CH*Fmoc*), 58.5 (C-*α*), 63.3 (C-6), 67.4 (CH_2*Fmoc*), 69.4 (C-4), 70.3 (C-2), 73.9 (C-3), 76.0 (C-1), 77.2 (C-5), 120.4, 125.4, 127.5, 128.1, 128.6 128.7, 128.9, 129.0 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.8

(C^{IV}*arom*), 130.1, 130.2, 130.3, 130.4, 133.7, 134.0, 141.7 (2 C^{IV}*arom*), 144.1 (C^{IV}*arom*), 144.3 (C^{IV}*arom*), 154.6 (H_2NC=NO), 156.6 (CO*Fmoc*), 165.7, 166.0, 166.0, 166.6 (4 O*C*OPh), 169.2 (NO*C*O) ppm. MS (LSIMS, NBA): *m*/*z* = 960 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{55}H_{50}N_3O_{13}$ $[M+H]^+$ calcd. 960.3344, found 960.3350.

***C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-*O*-[(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formyl]formamidoxime (6o):** HOBt (52 mg, 0.39 mmol), EDCI (74 mg, 0.39 mmol), *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formic acid[36] (200 mg, 0.32 mmol) and amidoxime **4** (250 g, 0.39 mmol) in CH_2Cl_2/DMF (9:1, 10 mL) were treated according to procedure D. The solvent was evaporated and the crude product dissolved in EtOAc (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL), water (50 mL), 0.5 M aqueous $KHSO_4$ (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), filtered and concentrated to dryness. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **6o** (200 mg, 50%) as a white solid. R_f = 0.42 (PE/EtOAc, 3:2). M.p. 95–96 °C (CH_2Cl_2/hexane). $[\alpha]_D^{20}$ = –7 (*c* = 0.65, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.14 (m, 1 H, H-5), 4.22 (m, 1 H, H-5′), 4.42–4.56 (m, 4 H, H-1, H-1′, H-6a, H-6′a), 4.63–4.72 (m, 2 H, H-6b, H-6′b), 5.45 (br. s, 2 H, NH_2), 5.63–5.99 (m, 6 H, H-2, H-2′, H-3, H-3′, H-4, H-4′), 7.21–7.61 (m, 23 H, H*arom*), 7.82–8.09 (m, 17 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 62.7 (C-6), 62.8 (C-6′), 68.9 (2 C), 69.4, 69.7, 73.5, 73.7, 75.3, 76.5, 76.6, 76.7, 128.1–129.8 (12 signals for 40 C*arom*), 133.0–133.6 (6 signals for 8 CH*arom*), 154.9 (H_2NC=NO), 162.9 (NO*C*O), 165.0, 165.1, 165.3, 165.4, 165.5, 165.6, 166.0, 166.1 (8 O*C*OPh) ppm. MS (LSIMS, NBA): *m*/*z* = 1245.1 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{70}H_{57}N_2O_{20}$ $[M+H]^+$ calcd. 1245.3505, found 1245.3509.

5-Methyl-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8a): A solution of **6a** (192 mg, 0.28 mmol) was treated according to procedure E for 2 d. Silica gel column chromatography (CH_2Cl_2/EtOAc, 95:5) afforded **8a** (89 mg, 50%) as a white solid. R_f = 0.87 (CH_2Cl_2/EtOAc, 95:5). M.p. 60–61 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = +6 (*c* = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.55 (s, 3 H, CH_3), 4.36 (ddd, 1 H, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 3.1 Hz, H-5), 4.54 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.65 (dd, 1 H, $J_{5,6b}$ = 3.1 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.10 (d, 1 H, $J_{1,2}$ = 9.4 Hz, H-1), 5.83 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 5.98 (t, 1 H, $J_{1,2}$ = 9.4 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 6.05 (t, 1 H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 7.24–7.54 (m, 12 H, H*arom*), 7.82–8.09 (m, 8 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.9 (CH_3), 63.8 (C-6), 69.9 (C-4), 71.0 (C-2), 72.8 (C-1), 74.5 (C-3), 77.4 (C-5), 128.7, 128.8, 128.8, 128.9, 129.0 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.2, 130.2, 130.3, 133.5, 133.7, 133.8, 133.9, 165.1, 165.6, 166.2 166.6 (4 O*C*OPh), 166.8 (C-3*oxa*), 178.1 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 663 $[M + H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{37}H_{31}N_2O_{10}$ $[M+H]^+$ calcd. 663.1979, found 663.1977.

5-Phenyl-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8b): A solution of **6b** (255 mg, 0.34 mmol) was treated according to procedure E for 10 d. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **8b** (158 mg, 64%) as a white solid. R_f = 0.56 (PE/EtOAc, 3:2). M.p. 136–137 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –36 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.38 (ddd, 1 H, $J_{4,5}$ = 9.3 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.56 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.68 (dd, 1 H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.17 (d, 1 H, $J_{1,2}$ = 9.1 Hz, H-1), 5.88 (dd, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.4 Hz, H-4), 6.06 (t, 1 H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 6.11 (t, 1 H, $J_{1,2}$ = 9.1 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 7.25–7.59 (m, 15 H, H*arom*), 7.85 (m, 4 H, H*arom*), 7.93 (d, 2 H, *J* = 7.8 Hz, H*arom*), 8.01–8.08 (m, 4 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.7 (C-6), 69.8 (C-4), 71.0 (C-2), 73.0 (C-1), 74.6 (C-3), 77.5 (C-5), 124.1 (C^{IV}*arom*), 128.7, 128.8, 128.9, 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.4, 129.9 (C^{IV}*arom*), 130.2, 130.3, 133.4, 133.5, 133.7, 133.9, 165.1, 165.6, 166.3 166.6 (4 O*C*OPh), 167.3 (C-3*oxa*), 177.0 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 725.2 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{42}H_{33}N_2O_{10}$ $[M+H]^+$ calcd. 725.2135, found 725.2138.

5-(*p*-Methoxyphenyl)-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8c): A solution of **6c** (213 mg, 0.28 mmol) was treated according to procedure E for 17 d. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **8c** (180 mg, 87%) as a pale yellow solid. R_f = 0.45 (PE/EtOAc, 3:2). M.p. 88–89 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –56 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 4.37 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 3.0 Hz, H-5), 4.56 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.67 (dd, 1 H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.15 (d, 1 H, $J_{1,2}$ = 9.4 Hz, H-1), 5.87 (t, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 6.05 (t, 1 H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 6.11 (t, 1 H, $J_{1,2}$ = 9.4 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 6.95 (d, 2 H, *J* = 8.9 Hz, H-2′, H-6′), 7.26–7.55 (m, 12 H, H*arom*), 7.84 (m, 4 H, H*arom*), 7.93 (d, 2 H, *J* = 8.9 Hz, H-3′, H-5′), 8.01 (m, 4 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 63.3 (C-6), 69.4 (C-4), 70.5 (C-2), 72.6 (C-1), 74.2 (C-3), 77.0 (C-5), 114.4 (C-2′, C-6′), 116.3 (C-4′), 128.3 (2 C), 128.4, 128.7 (C^{IV}*arom*), 128.8 (C^{IV}*arom*), 128.9 (C^{IV}*arom*), 129.5 (C^{IV}*arom*), 129.79 (2 C), 129.82, 129.9, 130.3 (C-3′, C-5′), 133.1, 133.2 (2 C), 133.5, 163.3 (C-1′), 164.7, 165.2, 165.8, 166.2 (4 O*C*OPh), 166.7 (C-3*oxa*); 176.5 (C-5*oxa*) ppm. $C_{43}H_{34}N_2O_{11}$ (754.74): calcd. C 68.43, H 4.54, N 3.71, O 23.32; found C 67.15, H 4.73, N 3.29, O 21.98.

3-*C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-5-(*p*-tolyl)-1,2,4-oxadiazole (8d): A solution of **6d** (125 mg, 0.16 mmol) was treated according to procedure E for 5 d. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **8d** (73 mg, 60%) as a white solid. R_f = 0.39 (PE/EtOAc, 7:3). M.p. 74–76 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –47 (*c* = 0.51, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 4.39 (ddd, 1 H, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 3.0 Hz, H-5), 4.57 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.68 (dd, 1 H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 5.17 (d, 1 H, $J_{1,2}$ = 9.5 Hz, H-1), 5.88 (t, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 6.06 (dd, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 6.12 (dd, 1 H, $J_{1,2}$ = 9.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 7.24–7.55 (m, 14 H, H*arom*), 7.84 (m, 4 H, H*arom*), 7.93 (m, 4 H, H*arom*), 8.02 (m, 2 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1 (CH_3), 63.7 (C-6), 69.8 (C-4), 71.0 (C-2), 73.0 (C-1), 74.7 (C-3), 77.5 (C-5), 121.4 (C^{IV}*arom*), 128.7, 128.8, 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.3 (C^{IV}*arom*), 129.6 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.1, 130.2, 130.3, 133.5, 133.7 (2 C), 133.9, 144.3 (C^{IV}*arom*), 165.1, 165.6, 166.3, 166.6 (4 O*C*OPh), 167.2 (C-3*oxa*), 177.2 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 739 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{43}H_{35}N_2O_{10}$ $[M+H]^+$ calcd. 739.2292, found 739.2296.

5-(*p*-Nitrophenyl)-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8e): A solution of **6e** (244 mg, 0.31 mmol) was treated according to procedure E for 16 h. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **8e** (207 mg, 87%) as a pale yellow solid. R_f = 0.61 (PE/EtOAc, 3:2). M.p. 98–100 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –58 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.40 (ddd, 1 H, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 2.7 Hz, H-5), 4.56 (dd, 1 H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.70 (dd, 1 H, $J_{5,6b}$ = 2.7 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.23 (m, 1

H, H-1), 5.89 (m, 1 H, H-4), 6.07 (m, 2 H, H-2, H-3), 7.25–7.56 (m, 12 H, H*arom*), 7.84–8.04 (m, 8 H, H*arom*), 8.28 (m, 4 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63,2 (C-6), 69.2 (C-4), 70.6 (C-2), 72.4 (C-1), 74.0 (C-3), 77.0 (C-5), 124.2, 128.3, 128.4, 128.4, 128.6 (C^{IV}*arom*), 128.7 (C^{IV}*arom*), 128.9 (C^{IV}*arom*), 129.3, 129.5 (C^{IV}*arom*), 129.7, 129.8, 133.1, 133.3, 133.4, 133.5, 150.3 (C^{IV}*arom*), 164.7, 165.1, 165.7, 166.1 (4 O*C*OPh), 167.4 (C-3*oxa*), 174.5 (C-5*oxa*) ppm. $C_{42}H_{31}N_3O_{12}$ (769.71): calcd. C 65.54, H 4.06, N 5.46, O 24.94; found C 64.65, H 4.21, N 5.43, O 24.21.

5-(*m*-Chlorophenyl)-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8f): A solution of **6f** (222 mg, 0.28 mmol) was treated according to procedure E for 10 d. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **8f** (190 mg, 88%) as a white solid. R_f = 0.68 (PE/EtOAc, 7:3). M.p. 80–81 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –44 (*c* = 1.25, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.40 (m, 1 H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.9 Hz, H-5), 4.57 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.70 (dd, 1 H, $J_{5,6b}$ = 2.9 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 5.19 (m, 1 H, H-1), 5.90 (m, 1 H, H-4), 6.09 (m, 1 H, H-3), 6.10 (m, 1 H, H-2), 7.25–7.52 (m, 14 H, H*arom*), 7.83–7.87 (m, 4 H, H*arom*), 7.92–7.95 (m, 3 H, H*arom*), 8.02 (m, 3 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.7 (C-6), 69.7 (C-4), 71.1 (C-2), 72.9 (C-1), 74.5 (C-3), 77.5 (C-5), 125.7 (C^{IV}*arom*), 126.7, 128.7, 128.8, 128.9, 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.4 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.2, 130.3, 130.8, 133.5, 133.6, 133.7, 133.8, 133.9, 135.6 (C^{IV}*arom*), 165.2, 165.6, 166.3, 166.6 (4 O*C*OPh), 167.6 (C-3*oxa*), 175.8 (C-5*oxa*) ppm. MS (LSIMS, NBA/AcONa): *m*/*z* = 781.7 [M + Na]$^+$. HRMS (LSIMS, NBA/AcONa): *m*/*z* = $C_{42}H_{31}ClN_2O_{10}Na$ [M + Na]$^+$ calcd. 781.1565, found 781.1567.

5-(3-Pyridyl)-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8 g): A solution of **6 g** (250 mg, 0.39 mmol) was treated according to procedure E for 2 d. The crude mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and the aqueous layer extracted with $CHCl_3$ (3 × 20 mL). The organic layers were combined, dried (Na_2SO_4), filtered and the solvents were evaporated. Silica gel column chromatography (PE/EtOAc, 1:1) afforded **8 g** (73 mg, 60%) as a white solid. R_f = 0.33 (PE/EtOAc, 1:1). M.p. 88–90 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –34 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.39 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.56 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.69 (dd, 1 H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.19 (m, 1 H, H-1), 5.89 (m, 1 H, H-4), 6.08 (m, 2 H, H-2, H-3), 7.29–7.58 (m, 13 H, 12 H*arom*, H-5′), 7.84 (m, 4 H, H*arom*), 7.93 (dd, 2 H, *J* = 1.3 Hz, *J* = 7.2 Hz, H*arom*), 8.02 (dd, 2 H, *J* = 1.3 Hz, *J* = 7.2 Hz, H*arom*), 8.33 (dt, 1 H, $J_{2',4'}$ = $J_{4',6'}$ 1.9 Hz, $J_{4',5'}$ 8.0 Hz, H-4′), 8.79 (dd, 1 H, $J_{4',6'}$ = 1.9 Hz, $J_{5',6'}$ = 4.9 Hz, H-6′), 9.29 (d, 1 H, $J_{2',4'}$ = 1.9 Hz, H-2′) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.6 (C-6), 69.7 (C-4), 71.0 (C-2), 72.9 (C-1), 74.5 (C-3), 77.5 (C-5), 120.7 (C-3′), 124.2 (C-5′), 128.7, 128.8, 128.8, 128.9, 129.0 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.2, 130.3, 133.6, 133.7, 133.8, 133.9, 135.9 (C-4′), 149.6 (C-2′), 153.9 (C-6′), 165.1, 165.5, 166.2, 166.5 (4 O*C*OPh), 167.5 (C-3*oxa*), 175.0 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 726 [M + H]$^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{41}H_{32}N_3O_{10}$ [M + H]$^+$ calcd. 726.2088, found 726.2088.

5-(2-Furyl)-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8h): A solution of **6h** (143 mg, 0.19 mmol) was treated according to procedure E for 13 d. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **8h** (81 mg, 58%) as a white solid. R_f = 0.60 (PE/EtOAc, 3:2). M.p. 76–78 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –47 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4,37 (ddd, 1 H, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 5.4 Hz, $J_{5,6b}$ = 3.0 Hz, H-5), 4.56 (dd, 1 H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.67 (dd, 1 H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.17 (m, 1 H, $J_{1,2}$ ≈ 9,5 Hz,H-1), 5.86 (m, 1 H, H-4), 6.06 (m, 1 H, H-3), 6.08 (m, 1 H, H-2), 6.57 (dd, 1 H, $J_{3',4'}$ = 3.6 Hz, $J_{4',5'}$ = 1.7 Hz, H-4′), 7.28 (dd, 1 H, $J_{3',4'}$ = 3.6 Hz, $J_{3',5'}$ = 0.7 Hz, H-3′), 7.30–7.54 (m, 12 H, H*arom*), 7.64 (dd, 1 H, $J_{3',5'}$ 0.7 Hz, $J_{4',5'}$ = 1.7 Hz, H-5′), 7.82–8.02 (m 8 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63,7 (C-6), 69.8 (C-4), 71.0 (C-2), 72.8 (C-1), 74.6 (C-3), 77.4 (C-5), 113.0 (C-4′), 117.8 (C-3′), 128.7, 128.9, 129.1 (C^{IV}*arom*), 129.2 (2 C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.2, 130.3, 133.5, 133.7, 133.7, 133.9, 140.1 (C-2′), 147.4 (C-5′), 165.1, 165.6, 166.2, 166.6 (4 O*C*OPh), 167.1 (C-3*oxa*), 168.7 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 715.1 [M + H]$^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{40}H_{31}N_2O_{11}$ [M + H]$^+$ calcd. 715.1928, found 715.1933.

3-*C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-5-(2-thienyl)-1,2,4-oxadiazole (8i): A solution of **6i** (139 mg, 0.19 mmol) was treated according to procedure E for 6 d. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **8i** (92 mg, 68%) as a white solid. R_f = 0.41 (PE/EtOAc, 7:3). M.p. 79–80 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –40 (*c* = 0.54, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.37 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 3.0 Hz, H-5), 4.56 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.67 (dd, 1 H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.15 (m, 1 H, H-1), 5.86 (m, 1 H, H-4), 6.02–6.12 (m, 2 H, H-2, H-3), 7.12 (dd, 1 H, $J_{3',4'}$ = 4.0 Hz, $J_{4',5'}$ = 5.0 Hz, H-4′), 7.24–7.54 (m, 12 H, H*arom*), 7.58 (dd, 1 H, $J_{3',5'}$ ≈ 1.0 Hz, $J_{4',5'}$ = 5.0 Hz, H-5′), 7.83 (dd, 1 H, $J_{3',4'}$ = 4.0 Hz, $J_{3',5'}$ ≈ 1.0 Hz, H-3′), 7.83–7.86 (m, 4 H, H*arom*), 7.92 (m, 2 H, H*arom*), 8.01 (m, 2 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.7 (C-6), 69.7 (C-4), 71.0 (C-2), 72.9 (C-1), 74.6 (C-3), 77.5 (C-5), 125.6 (C-2′), 128.7, 128.9 (C-4′), 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.3 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.2, 130.3, 132.8, 133.0 (C-3′, C-5′), 133.5, 133.7, 133.7, 133.9, 165,1, 165.6, 166.3, 166.6 (4 O*C*OPh), 167.2 (C-3*oxa*), 172.6 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 731 [M + H]$^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{40}H_{31}N_2O_{10}S$ [M + H]$^+$ calcd. 731.1699, found 731.1698.

5-(1-Naphthyl)-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8j): A solution of **6j** (451 mg, 0.57 mmol) was treated according to procedure E for 7 d. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **8j** (339 mg, 78%) as a white solid. R_f = 0.56 (PE/EtOAc, 7:3). M.p. 66–67 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –33 (*c* = 0.78, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47 (ddd, 1 H, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.61 (dd, 1 H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.74 (dd, 1 H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 5.33 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 5.97 (t, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 6.17 (t, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 6.30 (t, 1 H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 7.22–7,59 (m, 15 H, H*arom*), 7.81–8.05 (m, 10 H, H*arom*), 8.21 (dd, 1 H, *J* = 1.0 Hz, *J* = 7.3 Hz, H-2′), 9.02 (d, 1 H, *J* = 8.4 Hz, H-8′) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.8 (C-6), 69.9 (C-4), 71.2 (C-2), 73.1 (C-1), 74.7 (C-3), 77.5 (C-5), 120.7 (C^{IV}*arom*), 125.2, 126.1, 127.2, 128.8, 128.9, 129.1, 129.2 (C^{IV}*arom*), 129.3 (C^{IV}*arom*), 129.3 (C^{IV}*arom*), 130.0 (C^{IV}*arom*), 130.2, 130.3, 130.5 (C^{IV}*arom*), 130.6, 133.6, 133.7, 133.8, 134.0, 134.1, 134.3, 165.2, 165.7, 166.4, 166.6 (4 O*C*OPh), 167.3 (C-3*oxa*), 177.2 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 775 [M + H]$^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{46}H_{35}N_2O_{10}$ [M + H]$^+$ calcd. 775.2292, found 775.2290.

5-(2-Naphthyl)-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8k): A solution of **6k** (106 mg, 0.13 mmol) was treated according to procedure E for 16 h. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **8k** (101 mg, 98%) as a

white solid. R_f = 0.52 (PE/EtOAc, 7:3). M.p. 93–95 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –40 (*c* = 0.25, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.43 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 3.0 Hz, H-5), 4.60 (dd, 1 H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.72 (dd, 1 H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.24 (d, 1 H, $J_{1,2}$ = 9.4 Hz, H-1), 5.93 (t, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 6.12 (t, 1 H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 6.18 (t, 1 H, $J_{1,2}$ = 9.4 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 7.23–7.56 (m, 14 H, H*arom*), 7.81–8.05 (m, 12 H, H*arom*), 8.60 (s, 1 H, H-1′) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.8 (C-6), 69.8 (C-4), 71.1 (C-2), 73.1 (C-1), 76.6 (C-3), 77.5 (C-5), 121.3, 124.2, 127.6, 128.4, 128.8, 128.9, 129.0, 129.1 (C^{IV}*arom*), 129.2, 129.3 (C^{IV}*arom*), 129.4, 129.6, 129.9 (C^{IV}*arom*), 130.0 (C-1′), 130.2, 130.3, 133.0 (C^{IV}*arom*), 133.6, 133.7, 133.8, 134.0, 135.7 (C^{IV}*arom*), 165.2, 165.7, 166.3, 166.6 (4 O*C*OPh), 167.5 (C-3*oxa*), 177.2 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 775.2 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{46}H_{35}N_2O_{10}$ $[M+H]^+$ calcd. 775.2292, found 775.2287.

5-[(1*S*)-1-({[(9*H*-Fluoren-9-yl)methoxy]carbonyl}amino)-2-methylpropyl]-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8m): A solution of **6m** (198 mg, 0.21 mmol) was treated according to procedure E for 6 d. Silica gel column chromatography (PE/EtOAc, 7:3) afforded **8m** (98 mg, 51%) as a white solid. R_f = 0.58 (PE/EtOAc, 7:3). M.p. 78–80 °C (CH_2Cl_2/hexane). $[\alpha]_D^{20}$ = –33 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82 (d, 6 H, $J \approx$ 6.5 Hz, 2 CH_3), 2.15 (m, 1 H, $J \approx$ 6.5 Hz, H-β), 4.20 (t, 1 H, *J* = 6.9 Hz, *J* = 6.9 Hz, H*Fmoc*), 4.34 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 5.5 Hz, $J_{5,6b}$ = 2.9 Hz, H-5), 4.41 (m, 2 H, *J* = 6.9 Hz, CH_2*Fmoc*), 4.49 (dd, 1 H, $J_{5,6a}$ = 5.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.64 (dd, 1 H, $J_{5,6b}$ = 2.9 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 4.95 (dd, 1 H, $J_{H\alpha,H\beta}$ = 6.1 Hz, $J_{H\alpha,NH}$ = 9.4 Hz, H-α), 5.08 (d, 1 H, $J_{1,2}$ = 9.3 Hz, H-1), 5.48 (d, 1 H, $J_{H\alpha,NH}$ = 9.4 Hz, NH), 5.81 (t, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 5.98 (t, 1 H, $J_{1,2}$ = 9.3 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 6.04 (t, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 7.25–7.63 (m, 18 H, H*arom*), 7.75–7.99 (m, 10 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3 (CH_3), 18.6 (CH_3), 33.3 (C-β), 47.5 (CH*Fmoc*), 54.3 (C-α), 63.7 (C-6), 67.7 (CH_2*Fmoc*), 69.8 (C-4), 71.0 (C-2), 72.7 (C-1), 74.3 (C-3), 77.5 (C-5), 120.4, 125.5, 127.5, 128.2, 128.7, 128.8, 128.8, 128.9 (C^{IV}*arom*), 129.0 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.1, 130.2, 130.3, 133.5, 133.7, 133.9, 133.9, 141.7, 143.9, 144.2 (4 C^{IV}*arom*-*Fmoc*), 156.3 (*CO*Fmoc*), 165.1, 165.6, 166.2, 166.5 (4 O*C*OPh), 166.6 (C-3*oxa*), 180.2 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 942.1 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{55}H_{48}N_3O_{12}$ $[M+H]^+$ calcd. 942.3238, found 942.3250.

5-[(1*S*)-1-amino-2-methylpropyl]-3-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (8n): A solution of **8m** (89 mg, 0.09 mmol) in CH_2Cl_2/piperidine (9:1, 3 mL) was stirred at room temp. for 45 min. Silica gel chromatography (PE/EtOAc, 7:3) afforded **8n** (59 mg, 88%) as a white solid, shown to be a 87:13 diastereoisomeric mixture (NMR). The minor diastereoisomer gave a doublet (δ = 3.84 ppm, *J* = 5.8 Hz) in the ^1H NMR spectrum. R_f = 0.27 (PE/EtOAc, 7:3). Major isomer: ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.85 (d, 3 H, *J* = 6.8 Hz, CH_3), 1.66 (br. s, 2 H, NH_2), 2.05 (m, 1 H, *J* = 6.8 Hz, H-β), 3.91 (d, 1 H, $J_{H\alpha,H\beta}$ = 5.7 Hz, H-α), 4.34 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 3.0 Hz, H-5), 4.54 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.65 (dd, 1 H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 5.08 (d, 1 H, $J_{1,2}$ = 9.5 Hz, H-1), 5.84 (t, 1 H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 5.99 (t, 1 H, $J_{1,2}$ = 9.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 6.05 (t, 1 H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 7.25–7.56 (m, 12 H, H*arom*), 7.79–8.02 (m, 8 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9 (CH_3), 18.9 (CH_3), 33.9 (C-β), 55.2 (C-α), 63.7 (C-6), 69.8 (C-4), 71.1 (C-2), 72.8 (C-1), 74.3 (C-3), 77.5 (C-5), 128.7, 128.8, 128.9, 129.0 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.1, 130.2, 130.3, 133.5, 133.7, 133.8, 133.9, 165.0, 165.6, 166.2, 166.4 (4 O*C*OPh), 166.6 (C-3*oxa*), 184.1 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 720.2 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{40}H_{38}N_3O_{10}$ $[M+H]^+$ calcd. 720.2557, found 720.2559.

3,5-Bis[*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)]-1,2,4-oxadiazole (8o): A solution of **6o** (162 mg, 0.13 mmol) was treated according to procedure E for 2 d. Silica gel column chromatography (PE/EtOAc, 3:2) afforded **8o** (151 mg, 95%) as a white solid. R_f = 0.60 (PE/EtOAc, 3:2). M.p. 182–184 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –3 (*c* = 0,72, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.31 (m, 2 H, H-5, H-5′), 4.51–4.67 (m, 4 H, H-6a, H-6b, H-6′a, H-6′b), 5.11 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 5.23 (d, 1 H, $J_{1',2'}$ = 9.8 Hz, H-1′), 5.75 (t, 1 H, *J* = 9.7 Hz, H-4 or H-4′), 5.79 (t, 1 H, *J* = 9.7 Hz, H-2), 5.81 (t, 1 H, *J* = 9.7 Hz, H-4 or H-4′), 5.88 (t, 1 H, *J* = 9.7 Hz, H-2′), 6.02 (t, 1 H, *J* = 9.4 Hz, H-3 or H-3′), 6.04 (t, 1 H, *J* = 9.4 Hz, H-3 or H-3′), 7.20–7.52 (m, 24 H, H*arom*), 7.68–8.02 (m, 16 H, H*arom*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.5, 63.8 (C-6, C-6′), 69.4, 69.7 (C-4, C-4′), 71.0, 71.1 (C-2, C-2′), 72.8 (C-1), 73.0 (C-1′), 74.2, 74.4 (C-3, C-3′), 77.3, 77.6 (C-5, C-5′), 128.7, 128.7, 128.8, 128.8, 128.9, 128.9, 129.0 (C^{IV}*arom*), 129.0 (C^{IV}*arom*), 129.0 (C^{IV}*arom*), 129.1 (C^{IV}*arom*), 129.2 (C^{IV}*arom*), 129.8 (C^{IV}*arom*), 129.9 (C^{IV}*arom*), 130.2, 130.2, 130.3, 133.5, 133.6 (2 C), 133.7, 133.8 (2 C), 133.9, 134.0, 164.9, 165.1, 165.5, 165.6, 166.1, 166.2, 166.6 (2 C) (8 O*C*OPh), 167.0 (C-3*oxa*), 174.8 (C-5*oxa*) ppm. MS (LSIMS, NBA): *m*/*z* = 1227.0 $[M+H]^+$. HRMS (LSIMS, NBA): *m*/*z* = $C_{70}H_{55}N_2O_{19}$ $[M+H]^+$ calcd. 1227.3399, found 1227.3386.

3-*C*-(β-D-Glucopyranosyl)-5-methyl-1,2,4-oxadiazole (9a): A solution of **8a** (77 mg, 0.12 mmol) was treated according to procedure F to obtain **9a** (25 mg, 89%) as a hygroscopic solid. R_f = 0.30 (EtOAc/MeOH, 4:1). $[\alpha]_D^{20}$ = +16 (*c* = 0,9, MeOH). ^1H NMR (300 MHz, CD_3OD): δ = 2.62 (s, 3 H, CH_3), 3.44 (m, 2 H, H-4, H-5), 3.49 (m, 1 H, H-3), 3.67 (m, 2 H, H-2, H-6a), 3.86 (dd, 1 H, $J_{5,6b}$ = 1.3 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b) 4.41 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 12.1 (CH_3), 62.9 (C-6), 71.3 (C-4), 73.4 (C-2), 74.9 (C-1), 79.2 (C-3), 82.6 (C-5), 169.3 (C-3*oxa*), 179.1 (C-5*oxa*) ppm. MS (LSIMS, glycerol): *m*/*z* = 247 $[M+H]^+$. HRMS (LSIMS, glycerol): *m*/*z* = $C_9H_{15}N_2O_6$ $[M+H]^+$ calcd. 247.0930, found 247.0931.

3-*C*-(β-D-Glucopyranosyl)-5-phenyl-1,2,4-oxadiazole (9b): A solution of **8b** (117 mg, 0.16 mmol) was treated according to procedure F to obtain **9b** (41 mg, 80%) as a pale yellow solid. R_f = 0.17 (EtOAc/MeOH, 4:1). M.p. 52–54 °C (MeOH/hexane). $[\alpha]_D^{20}$ = +9 (*c* = 1, MeOH). ^1H NMR (300 MHz, D_2O): δ = 3.56 (m, 2 H, H-4, H-5), 3.63 (t, 1 H, *J* ≈ 8.5 Hz, H-3), 3.71 (dd, 1 H, $J_{1,2}$ = 9.5 Hz, $J_{2,3}$ = 8.5 Hz, H-2), 3.75 (dd, 1 H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 3.88 (dd, 1 H, $J_{5,6b}$ = 1.6 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6b), 4.58 (d, 1 H, $J_{1,2}$ = 9.5 Hz, H-1), 7.47 (m, 2 H, H*arom*), 7.59 (m, 1 H, H*arom*), 7.93 (m, 2 H, H*arom*) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 61.1 (C-6), 69.6 (C-4), 72.2 (C-2), 73.4 (C-1), 77.2 (C-3), 80.7 (C-5), 123.0 (C^{IV}*arom*), 128.4 (2 C), 129.7 (2 C), 134.2, 168.1 (C-3*oxa*), 177.3 (C-5*oxa*) ppm. MS (LSIMS, thioglycerol): *m*/*z* = 309 $[M+H]^+$. HRMS (LSIMS, thioglycerol): *m*/*z* = $C_{14}H_{17}N_2O_6$ $[M+H]^+$ calcd. 309.1087, found 309.1088.

3-*C*-(β-D-Glucopyranosyl)-5-(*p*-methoxyphenyl)-1,2,4-oxadiazole (9c): A solution of **8c** (155 mg, 0.46 mmol) was treated according to procedure F to obtain **9c** (60 mg, 85%) as a white solid. R_f = 0.59 (EtOAc/MeOH, 4:1). M.p. 182–183 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = +10 (*c* = 0.75, MeOH). ^1H NMR (300 MHz, CD_3OD): δ = 3.46–3.55 (m, 3 H, H-3, H-4, H-5), 3.70 (dd, 1 H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 3.78 (t, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.7 Hz, H-2),

3.89 (s, 3 H, OCH_3), 3.90 (d, 1 H, $J_{6a,6b}$ = 12.1 Hz, H-6b), 4.48 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 7.11 (d, 2 H, J = 9.0 Hz, H-2′, H-6′), 8.08 (d, 2 H, J = 9.0 Hz, H-3′, H-5′) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 56.2 (OCH_3), 62.9 (C-6), 71.4 (C-4), 73.5 (C-2), 75.1 (C-1), 79.3 (C-3), 82.7 (C-5), 115.9 (C-2′, C-6′), 117.4 (C-4′), 131.1 (C-3′, C-5′), 165.2 (C-1′), 169.8 (C-3*oxa*); 177.5 (C-5*oxa*) ppm. $C_{15}H_{18}N_2O_7$ (338.31): calcd. C 53.25, H 5.36, N 8.28, O 33.10; found C 53.37, H 5.57, N 8.06, O 33.38.

3-*C*-(β-D-Glucopyranosyl)-5-(*p*-tolyl)-1,2,4-oxadiazole (9d): A solution of **8d** (60 mg, 0.08 mmol) was treated according to procedure F to obtain **9d** (22 mg, 85%) as a white solid. R_f = 0.60 (EtOAc/MeOH, 4:1). M.p. 67–69 °C (MeOH/hexane). $[\alpha]_D^{20}$ = +7 (c = 1, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 2.46 (s, 3 H, CH_3), 3.48–3.60 (m, 3 H, H-3, H-4, H-5), 3.72 (dd, 1 H, $J_{5,6a}$ = 4.2 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 3.81 (t, 1 H, $J_{1,2}$ = 9.6 Hz, $J_{2,3}$ = 8.7 Hz, H-2), 3.91 (br. d, 1 H, $J_{5,6b} < 1.0$ Hz, $J_{6a,6b}$ = 12.2 Hz, H-6b), 4.51 (d, 1 H, $J_{1,2}$ = 9.6 Hz, H-1), 7.42 (d, 2 H, J = 8.2 Hz, H*arom*), 8.04 (d, 2 H, J 8.2 Hz, H*arom*) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 20.7 (CH_3), 61.8 (C-6), 70.4 (C-4), 72.5 (C-2), 74.1 (C-1), 78.3 (C-3), 81.7 (C-5), 121.4 (C^{IV}*arom*), 128.1 (2 C), 130.1 (2 C), 144.6 (C^{IV}*arom*), 168.9 (C-3*oxa*), 176.7 (C-5*oxa*) ppm. MS (LSIMS, glycerol): m/z = 323 $[M+H]^+$. HRMS (LSIMS, glycerol): m/z = $C_{15}H_{19}N_2O_6$ $[M+H]^+$ calcd. 323.1243, found 323.1242.

3-*C*-(β-D-Glucopyranosyl)-5-(*p*-nitrophenyl)-1,2,4-oxadiazole (9e): A solution of **8e** (139 mg, 0.18 mmol) was treated according to procedure F to obtain **9e** (60 mg, 95%) as a white solid. R_f = 0.20 (EtOAc/MeOH, 4:1). M.p. 92–94 °C (MeOH/hexane). $[\alpha]_D^{20}$ = +9 (c = 0.72, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.44–3.53 (m, 2 H, H-4, H-5), 3.56 (t, 1 H, $J \approx$ 9 Hz, H-3), 3.72 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 3.84 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.7 Hz, H-2), 3.92 (dd, 1 H, $J_{5,6b}$ = 1.5 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6b), 4.56 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 8.93–8.48 (m, 4 H, $J \approx$ 9 Hz, H*arom*) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 61.9 (C-6), 70.4 (C-4), 72.5 (C-2), 74.0 (C-1), 78.2 (C-3), 81.8 (C-5), 124.6 (2 C), 129.4 (C^{IV}*arom*), 129.4 (2 C), 150.9 (C^{IV}*arom*), 169.5 (C-3*oxa*), 174.7 (C-5*oxa*) ppm. MS (LSIMS, negative mode, NBA): m/z = 352 $[M-H]^-$. HRMS (LSIMS, negative mode, NBA): m/z = $C_{14}H_{14}N_3O_8$ $[M-H]^-$ calcd. 352.0781, found 352.0785.

5-(*m*-Chlorophenyl)-3-*C*-(β-D-glucopyranosyl)-1,2,4-oxadiazole (9f): A solution of **8f** (150 mg, 0.19 mmol) was treated according to procedure F to obtain **9f** (63 mg, 94%) as a white solid. R_f = 0.47 (EtOAc/MeOH, 4:1). M.p. 99–101 °C (MeOH/hexane). $[\alpha]_D^{20}$ = +8 (c = 0.85, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.46–3.55 (m, 2 H, H-4, H-5), 3.57 (t, 1 H, $J \approx$ 9 Hz, H-3), 3.74 (dd, 1 H, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 3.83 (dd, 1 H, $J_{1,2}$ = 9.6 Hz, $J_{2,3}$ = 8.7 Hz, H-2), 3.92 (dd, 1 H, $J_{5,6b}$ = 0.8 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6b), 4.54 (d, 1 H, $J_{1,2}$ = 9.6 Hz, H-1), 7.60 (dd, 1 H, $J_{4',5'}$ = 8.0 Hz, $J_{5',6'}$ = 7.8 Hz, H-5′), 7.68 (ddd, 1 H, $J_{2',4'}$ = 2.0 Hz, $J_{4',5'}$ = 8.0 Hz, $J_{4',6'}$ = 1.2 Hz, H-4′), 8.07 (dt, 1 H, $J_{2',6'}$ = 1.5 Hz, $J_{4',6'}$ = 1.2 Hz, $J_{5',6'}$ = 7.8 Hz, H-6′), 8.13 (t, 1 H, $J_{2',4'}$ = 2.0 Hz, $J_{2',6'}$ = 1.5 Hz, H-2′) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 61.9 (C-6), 70.4 (C-4), 72.5 (C-2), 74.0 (C-1), 78.3 (C-3), 81.7 (C-5), 125.9 (C^{IV}*arom*), 126.4 (C-6′), 127.8 (C-2′), 131.2 (C-5′), 133.2 (C-4′), 135.4 (C^{IV}*arom*), 169.1 (C-3*oxa*), 175.2 (C-5*oxa*) ppm. MS (LSIMS, glycerol): m/z = 343 $[M+H]^+$. HRMS (LSIMS, glycerol): m/z = $C_{14}H_{16}ClN_2O_6$ $[M+H]^+$ calcd. 343.0697, found 343.0695.

3-*C*-(β-D-Glucopyranosyl)-5-(3-pyridyl)-1,2,4-oxadiazole (9g): A solution of **8g** (75 mg, 0.1 mmol) was treated according to procedure F to obtain **9g** (18 mg, 60%) as a white solid. R_f = 0.20 (EtOAc/MeOH, 4:1). M.p. 162–164 °C (MeOH/PE). $[\alpha]_D^{20}$ = +11 (c = 0.55, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.50 (m, 2 H, H-4, H-5), 3.55 (t, 1 H, J = 8.9 Hz, H-3), 3.71 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 3.83 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.7 Hz, H-2), 3.92 (dd, 1 H, $J_{5,6a}$ = 1.5 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6b), 4.54 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 7.70 (ddd, 1 H, $J_{2',5'} \approx$ 0.5 Hz, $J_{4',5'}$ = 8.0 Hz, $J_{5',6'}$ = 4.9 Hz, H-5′), 8.57 (dt, 1 H, $J_{2',4'} = J_{4',6'}$ = 1.9 Hz, $J_{4',5'}$ = 8.0 Hz, H-4′), 8.84 (dd, 1 H, $J_{4',6'}$ = 1.9 Hz, $J_{5',6'}$ = 4.9 Hz, H-6′), 9.33 (br. s, 1 H, H-2′) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 61.9 (C-6), 70.5 (C-4), 72.4 (C-2), 74.0 (C-1), 78.2 (C-3), 81.8 (C-5), 121.3 (C-3′), 124.8 (C-5′), 136.2 (C-4′), 148.5 (C-2′), 153.2 (C-6′), 169.2 (C-3*oxa*), 174.4 (C-5*oxa*) ppm. MS (LSIMS, glycerol): m/z = 310.1 $[M+H]^+$. HRMS (LSIMS, glycerol): m/z = $C_{13}H_{16}N_3O_6$ $[M+H]^+$ calcd. 310.1039, found 310.1037.

5-(2-Furyl)-3-*C*-(β-D-glucopyranosyl)-1,2,4-oxadiazole (9h): A solution of **8h** (68 mg, 0.09 mmol) was treated according to procedure F to obtain **9h** (26 mg, 93%) as a hygroscopic solid. R_f = 0.60 (EtOAc/MeOH, 4:1). $[\alpha]_D^{20}$ = +8 (c = 0.74, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.50 (m, 2 H, H-4, H-5), 3.54 (t, 1 H, $J \approx$ 9 Hz, H-3), 3.72 (br. dd, 1 H, $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 3.76 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3} \approx$ 9 Hz, H-2), 3.90 (dd, 1 H, $J_{5,6a}$ = 1.1 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6b), 4.51 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 6.77 (dd, 1 H, $J_{3',4'}$ = 3.6 Hz, $J_{4',5'}$ = 1.8 Hz, H-4′), 7.48 (dd, 1 H, $J_{3',4'}$ = 3.6 Hz, $J_{3',5'}$ = 0.7 Hz, H-3′), 7.93 (dd, 1 H, $J_{3',5'}$ = 0.7 Hz, $J_{4',5'}$ = 1.8 Hz, H-5′) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 61.8 (C-6), 70.3 (C-4), 72.4 (C-2), 73.8 (C-1), 78.2 (C-3), 81.7 (C-5), 112.8 (C-4′), 117.4 (C-3′), 140.1 (C-2′), 148.1 (C-5′), 168.4 (C-5*oxa*), 168.6 (C-3*oxa*) ppm. MS (LSIMS, glycerol): m/z = 299.0 $[M+H]^+$. HRMS (LSIMS, glycerol): m/z = $C_{12}H_{15}N_2O_7$ $[M+H]^+$ calcd. 299.0879, found 229.0877.

3-*C*-(β-D-Glucopyranosyl)-5-(2-thienyl)-1,2,4-oxadiazole (9i): A solution of **8i** (95 mg, 0.13 mmol) was treated according to procedure F to obtain **9i** (28 mg, 70%) as a colourless oil. R_f = 0.54 (EtOAc/MeOH, 4:1). $[\alpha]_D^{20}$ = +6 (c = 1, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.41 (m, 2 H, H-4, H-5), 3.45 (t, 1 H, $J \approx$ 9 Hz, H-3), 3.63 (dd, 1 H, $J_{5,6a}$ = 4.6 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 3.70 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3} \approx$ 9 Hz, H-2), 3.82 (br. d, 1 H, $J_{6a,6b}$ = 12.0 Hz, H-6b), 4.41 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 7.22 (dd, 1 H, $J_{3',4'}$ = 3.7 Hz, $J_{4',5'}$ = 5.0 Hz, H-4′), 7.83 (br. d, 1 H, $J_{4',5'}$ = 5.0 Hz, H5′), 7.91 (br. d, 1 H, $J_{3',4'}$ = 3.7 Hz, H-3′) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 61.8 (C-6), 70.3 (C-4), 72.4 (C-2), 73.9 (C-1), 78.2 (C-3), 81.7 (C-5), 125.3 (C-2′), 129.0 (C-4′), 132.6 (C-3′), 133.3 (C-5′), 168.8 (C-3*oxa*), 172.2 (C-5*oxa*) ppm. MS (LSIMS, glycerol): m/z = 315.1 $[M+H]^+$. HRMS (LSIMS, glycerol): m/z = $C_{12}H_{14}N_2NaO_6S$ $[M+Na]^+$ calcd. 337.0470, found 337.0470.

3-*C*-(β-D-Glucopyranosyl)-5-(1-naphthyl)-1,2,4-oxadiazole (9j): A solution of **8j** (220 mg, 0.28 mmol) was treated according to procedure F to obtain **9j** (90 mg, 89%) as a colourless oil. R_f = 0.51 (EtOAc/MeOH, 4:1). $[\alpha]_D^{20}$ = +10 (c = 0.86, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.59 (m, 2 H, H-4, H-5), 3.64 (t, 1 H, $J \approx$ 9 Hz, H-3), 3.79 (br. d, 1 H, $J \approx$ 12 Hz, $J \approx$ 5 Hz, H-6a), 3.97 (d, 1 H, $J_{6a,6b}$ = 12.5 Hz, H-6b), 3.99 (t, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.0 Hz, H-2), 4.65 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 7.54–7.66 (m, 3 H, H*naph*), 7.93 (br. d, 1 H, J = 7.9 Hz, H-5′), 8.09 (br. d, 1 H, J = 8.2 Hz, H-4′), 8.26 (dd, 1 H, J = 1.0 Hz, J = 7.3 Hz, H-2′), 8.99 (br. d, 1 H, J = 8.0 Hz, H-8′) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 60.7 (C-6), 69.2 (C-4), 71.3 (C-2), 73.0 (C-1), 77.1 (C-3), 80.5 (C-5), 119.3 (C^{IV}*naph*), 123.8, 124.2 (C-8′), 125.7, 127.1, 127.7 (C-5′), 128.8 (C-2′), 129.0 (C^{IV}*naph*), 132.7 (C-4′), 133.0 (C^{IV}*naph*), 167.6 (C-3*oxa*), 175.4 (C-5*oxa*) ppm. MS (LSIMS, glycerol): m/z = 359 $[M+H]^+$. HRMS (LSIMS, glycerol): m/z = $C_{18}H_{19}N_2O_6$ $[M+H]^+$ calcd. 359.1243, found 359.1251.

3-*C*-(β-D-Glucopyranosyl)-5-(2-naphthyl)-1,2,4-oxadiazole (9k): A solution of **8k** (89 mg, 0.11 mmol) was treated according to pro-

cedure F to obtain **9k** (40 mg, 98%) as a white solid. R_f = 0.50 (EtOAc/MeOH, 4:1). M.p. 98–100 °C (MeOH/hexane). $[\alpha]_D^{20}$ = +5 (c = 0.82, MeOH). ^{1}H NMR (500 MHz, CD_3OD, 60 °C): δ = 3.55 (m, 2 H, H-4, H-5), 3.59 (t, 1 H, $J \approx 9$ Hz, H-3), 3.77 (br. dd, 1 H, $J_{5,6a}$ = 5,1 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 3.89 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.8 Hz, H-2), 3.93 (dd, 1 H, $J_{5,6b}$ = 1.1 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6b), 4.57 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 7.60–7.67 (m, 2 H, H-6′, H-7′), 7.96 (d, 1 H, J = 8.0 Hz, H-8′), 8.03 (d, 1 H, $J_{5',6'}$ = 8.0 Hz, H-5′), 8.04 (d, 1 H, $J_{3',4'}$ = 8.6 Hz, H-4′), 8.14 (dd, 1 H, $J_{1',3'}$ = 1.5 Hz, $J_{3',4'}$ = 8.6 Hz, H-3′), 8.72 (br. s, 1 H, H-1′) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 62.1 (C-6), 70.6 (C-4), 72.6 (C-2), 74.3 (C-1), 78.5 (C-3), 81.7 (C-5), 121.4 (C-2′), 123.5 (C-3′), 127.5, 128.0 (C-8′), 128.8, 129.2 (C-1′), 129.3, 129.3, 133.2 (C-4′a), 135.8 (C-8′a), 169.2 (C-3*oxa*), 176.7 (C-5*oxa*) ppm. NMR spectra were recorded at 60 °C due to poor solubility of the compound in CD_3OD. MS (ESI): m/z = 359.0 $[M+H]^+$, 381.1 $[M+Na]^+$, 716.8 $[2\,M+H]^+$, 738.9 $[2\,M+Na]^+$. HRMS (LSIMS, NBA): m/z = $C_{18}H_{18}N_2NaO_6$ $[M+Na]^+$ calcd. 381.1063, found 381.1066.

5-[(1*S*)-1-Amino-2-methylpropyl]-3-*C*-(β-D-glucopyranosyl)-1,2,4-oxadiazole (9n): A solution of **8n** (58 mg, 0.08 mmol) was treated according to procedure F to obtain **9n** (6 mg, 25%) as a colourless oil. R_f = 0.35 (EtOAc/MeOH, 4:1). $[\alpha]_D^{20}$ = +24 (c = 0.45, H_2O). ^{1}H NMR (500 MHz, D_2O): δ = 0.93 (d, 3 H, J = 6.8 Hz, CH_3), 1.02 (d, 3 H, J = 6.8 Hz, CH_3), 2.40 (m, 1 H, H-β), 3.47 (t, 1 H, J = 9.5 Hz, H-4), 3.57 (m, 2 H, H-3, H-5), 3.67 (m, 2 H, H-2, H-6a), 3.83 (br. d, 1 H, J = 11.7 Hz, H-6b), 4.62 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.70 (m, 1 H, H-α) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 19.9 (CH_3), 20.3 (CH_3), 33.7 (C-β), 56.2 (C-α), 63.5 (C-6), 72.2 (C-4), 74.5 (C-2), 75.6 (C-1), 79.7, 83.4 (C-3, C-5), 170.4 (C-3*oxa*), 178.8 (C-5*oxa*) ppm. MS (LSIMS, glycerol): m/z = 304 $[M+H]^+$. HRMS (LSIMS, glycerol): m/z = $C_{12}H_{22}N_3O_6$ $[M+H]^+$ calcd. 304.1509, found 304.1507.

5-*C*-(2-Deoxy-D-*arabino*-hex-1-enopyranosyl)-3-*C*-(β-D-glucopyranosyl)-1,2,4-oxadiazole (9p): A solution of **8o** (138 mg, 0.11 mmol) was treated according to procedure F to obtain **9p** (19 mg, 45%) as a hygroscopic solid after RP-18 column chromatography (H_2O, then H_2O/MeOH, 4:1). R_f = 0.15 (EtOAc/MeOH, 4:1). M.p. 118–120 °C. $[\alpha]_D^{20}$ = +16 (c = 0.56, D_2O). ^{1}H NMR (300 MHz, D_2O): δ = 3.53 (t, 1 H, $J \approx 9$ Hz, H-4), 3.62 (ddd, 1 H, $J_{4,5} \approx 9$ Hz, $J_{5,6a}$ = 5.3 Hz, $J_{5,6b}$ = 1.8 Hz, H-5), 3.63 (t, 1 H, $J_{2,3} = J_{3,4} \approx 9$ Hz, H-3), 3.70 (t, 1 H, $J_{1,2}$ = 9.3 Hz, $J_{2,3} \approx$ 9 Hz, H-2), 3.74 (dd, 1 H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 3.81 (dd, 1 H, $J_{3',4'}$ = 7.4 Hz, $J_{4',5'}$ = 9.7 Hz, H-4′), 3.90 (dd, 1 H, $J_{5,6b}$ = 1.8 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6b), 3.94 (dd, 1 H, $J_{5',6'a}$ = 5.2 Hz, $J_{6'a,6'b}$ = 12.8 Hz, H-6′a), 4.02 (dd, 1 H, $J_{5',6'a}$ = 2.4 Hz, $J_{6'a,6'b}$ = 12.8 Hz, H-6′b), 4.19 (ddd, 1 H, $J_{4',5'}$ = 9.7 Hz, $J_{5',6'a}$ = 5.2 Hz, $J_{5',6'b}$ = 2.4 Hz, H-5′), 4.45 (dd, 1 H, $J_{2',3'}$ = 2.8 Hz, $J_{3',4'}$ = 7.4 Hz, H-3′), 4.64 (d, 1 H, $J_{1,2}$ = 9.3 Hz, H-1), 6.16 (d, 1 H, $J_{2',3'}$ = 2.8 Hz, H-2′) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 60.4 (C-6′), 61.2 (C-6), 68.2 (C-4′), 68.7 (C-3′), 69.7 (C-4), 72.2 (C-2), 73.2 (C-1), 77.1 (C-3), 80.3 (C-5′), 80.7 (C-5), 112.4 (C-2′), 139.6 (C-1′), 167.9 (C-3*oxa*), 172.4 (C-5*oxa*) ppm. MS (ESI): m/z = 377.0 $[M+H]^+$, 399.1 $[M+Na]^+$, 774.9 $[2\,M+Na]^+$. HRMS (LSIMS, glycerol): m/z = $C_{14}H_{21}N_2O_{10}$ $[M+H]^+$ calcd. 377.1196, found 377.1192.

5-(1-Naphthyl)-3-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1,2,4-oxadiazole (10j): A solution of **9j** (36 mg, 0.1 mmol) in pyridine/Ac_2O (9:1, 3 mL) was stirred at room temp. for 16 h. The mixture was poured into saturated aqueous $NaHCO_3$ (25 mL) and the aqueous layer was extracted with $CHCl_3$ (3 × 25 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated to afford **10j** (53 mg, 100%) as a white solid. R_f = 0.56 (PE/EtOAc, 7:3). M.p. 142–143 °C (CH_2Cl_2/PE). $[\alpha]_D^{20}$ = –32 (c = 0,94, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (CH_3), 2.06 (CH_3), 2.08 (CH_3), 2.09 (CH_3), 3.96 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 2.2 Hz, $J_{5,6b}$ = 5.0 Hz, H-5), 4.22 (dd, 1 H, $J_{5,6a}$ = 2.2 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.34 (dd, 1 H, $J_{5,6b}$ = 5.0 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6b), 4.90 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 5.32 (t, 1 H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 5.43 (t, 1 H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 5.74 (dd, 1 H, $J_{1,2}$ = 10.0 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 7.59 (dd, 1 H, $J_{3',4'}$ = 8.2 Hz, $J_{2',3'}$ = 7.3 Hz, H-3′), 7.60 (ddd, 1 H, $J_{5',6'}$ = 8.0 Hz, $J_{6',7'}$ = 6.7 Hz, $J_{6',8'}$ = 1.5 Hz, H-6′), 7.72 (ddd, 1 H, $J_{6',7'}$ = 6.7 Hz, $J_{7',8'}$ = 8.5 Hz, $J_{5',7'}$ = 1.4 Hz, H-7′), 7.93 (dm, 1 H, $J_{5',6'}$ = 8.0 Hz, $J_{5',7'}$ = 1.4 Hz, $J_{5',8'}$ = 1.0 Hz, H-5′), 8.09 (br. d, 1 H, $J_{3',4'}$ = 8.2 Hz, H-4′), 8.34 (dd, 1 H, $J_{2',3'}$ = 7.3 Hz, $J_{2',4'}$ = 1.2 Hz, H-2′), 9.11 (dm, 1 H, $J_{5',8'} \approx 1.0$ Hz, $J_{6',8'}$ = 1.5 Hz, $J_{7',8'}$ = 8.5 Hz, H-8′) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 21.0, 21.1, 21.2 (4 CH_3), 62.5 (C-6), 68.5 (C-4), 70.3 (C-2), 72.5 (C-1), 74.4 (C-3), 77.1 (C-5), 120.6 (C-8′a), 125.2 (C-3′), 126.1 (C-8′), 127.2 (C-6′), 128.9 (C-7′), 129.2 (C-5′), 130.5 (C-1′), 130.6 (C-2′), 134.2 (C-4′a), 134.4 (C-4′), 167.1 (C-3*oxa*), 169.4, 169.8, 170.8, 171.1 (4 *C*OCH$_3$), 177.2 (C-5*oxa*) ppm. MS (LSIMS, NBA): m/z = 527.1 $[M+H]^+$. HRMS (LSIMS, NBA): m/z = $C_{26}H_{27}N_2O_{10}$ $[M+H]^+$ calcd. 527.1666, found 527.1662.

Enzyme Assays: Glycogen phosphorylase *b* was prepared from rabbit skeletal muscle according to the method of Fischer and Krebs[42] using 2-mercaptoethanol instead of L-cysteine and recrystallized at least three times before use. The kinetic studies with glycogen phosphorylase were performed as described previously.[43] Kinetic data for the inhibition of rabbit skeletal muscle glycogen phosphorylase *b* by monosaccharide compounds was collected using different concentrations of α-D-glucose-1-phosphate (4, 6, 8, 10, 12, and 14 mM) and constant concentrations of glycogen (1%, w/v) and AMP (1 mM). Compounds were dissolved in DMSO in a final concentration of 250 mM then diluted in a buffer for the phosphorylase inhibition assay so that the DMSO concentration would not be higher than 0.25%. Consequently, the highest inhibitor concentration applied was 625 μM. The enzymatic activities are presented in the form of double-reciprocal plots (Lineweaver–Burk) applying a nonlinear data-analysis program. The inhibition constants (K_i) were determined whenever lower than about 300 μM, according to Dixon by replotting the slopes from the Lineweaver–Burk plots against the inhibitor concentrations. The means of standard errors for all calculated kinetic parameters averaged to less than 10%.[44] Otherwise, IC_{50} values were determined in the presence of 4 mM α-D-glucose-1-phosphate, 1 mM AMP, 1% glycogen and varying concentrations of the inhibitor.

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