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Reagent controlled stereoselective synthesis of teichoic acid α-(1,2)-glucans†

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The stereoselective construction of 1,2-*cis*-glycosidic linkages is key in the assembly of biologically relevant glycans, but remains a synthetic challenge. Reagent-controlled glycosylation methodologies, in which external nucleophiles are employed to modulate the reactivity of the glycosylation system, have become powerful means for the construction of 1,2-*cis*-glycosidic linkages. Here we establish that nucleophilic additives can support the construction of α-1,2-glucans, and apply our findings in the construction of a D-alanine kojibiose functionalized glycerol phosphate teichoic acid fragment. This latter molecule can be found in the cell wall of the opportunistic Gram-positive bacterium, *Enterococcus faecalis* and represents a structural element that can possibly be used in the development of therapeutic vaccines and diagnostic tools.

Introduction

α-Glucans, polysaccharides composed of glucose monosaccharides connected through α-glycosidic linkages, are widely found in nature.[1] The most abundant α-glucans are the α-1,4-glucans, that occur as starch and glycogen, and can be found as extracellular polysaccharides surrounding bacteria, such as *Mycobacterium tuberculosis*.[2] α-1,3-Glucans are prominent components of fungal cell walls and play a role in the interaction between the pathogenic fungus *Aspergillus fumigatus* and the host immune system.[3] α-1,2-Glucans, also referred to as koji-oligosaccharides, have been found in koji extract, sake, beer and honey and they have also been encountered in bacterial cell walls.[4] Kojibiose, kojitriose and kojitetraose have been found as part of the lipoteichoic acid (LTA) of *Enterococcus faecalis*, which is a commensal Gram-positive bacterium.[5] Although this bacterium is generally of low virulence, it is the causative agent of life-threatening infections in immunocompromised patients and one of the most prominent hospital bacteria.[6] LTA is an anionic polymer featuring a glycolipid tail, through which it is anchored in the cell wall of the bacteria. The polyanionic part is composed of glycerol phosphate repeating units, which can be functionalised with glycans and D-alanine esters at C2 of the glycerol moieties (Fig. 1).[7] Kojibiose is a prominent appendage of *E. faecalis* LTA, and it can be decorated with D-alanyl esters at both C6-hydroxyl groups of the disaccharide.[7] D-Alanylation plays a critical role in the virulence of the bacteria and it renders the bacteria less susceptible to (cationic) antimicrobial peptides. *E. faecalis* LTA fragments, containing a single α-glucosyl substituent have previously been explored as components in synthetic vaccine conjugates,[8] and antibodies raised by these conjugates have been shown to be opsonophagocytic and capable of inducing killing of the bacteria in both active and passive immunization strategies.[9]

The microheterogeneity of naturally occurring LTA makes it challenging if not impossible- to establish clear structure–activity relationships for these molecules, and therefore organic synthesis is the method of choice to generate well-defined single LTA molecules.[9,10] Only a few chemical syntheses of α-(1,2)-glucans have been reported. Takeo and Suzuki reported a procedure to assemble kojitriose, kojitetraose and kojipentaose based on Koenings-Knorr-type glycosylations, using anomeric chlorides under the activation of silver per-

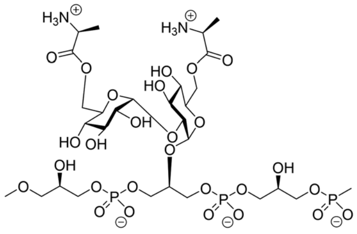

Fig. 1 The structure of *E. faecalis* D-alanine kojibiose functionalized LTA.

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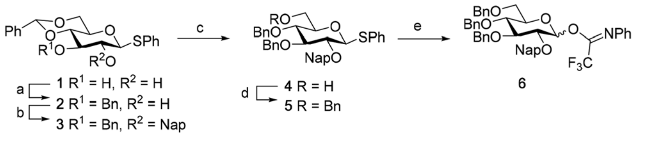
chlorate.[11] Hogendorf *et al.* relied on Crich's α-glucosylation protocol, which involves the use of benzylidene glucose donors for the synthesis of a kojibiose glycerol building block.[9] We have previously shown that additive-controlled glycosylations[12] of per-benzylated glucosyl imidate donors can be used effectively for the introduction of α-(1,4)- and α-(1,3)-glucosyl linkages, which we used to assemble a set of *M. tuberculosis* α-(1,4)-glucans and *A. fumigatus* α-(1,3)-glucans.[13] In this strategy we exploited a suite of orthogonal benzyl ethers to discriminate between different hydroxyl functionalities that had to be protected permanently (using a benzyl (Bn) group), and hydroxyl groups that were used for chain elongation (protected with 2-methylnaphthyl (Nap) ethers) and hydroxyl groups from which branching occurred (using *para*-methoxybenzyl (PMB) ethers). The use of solely benzylic ethers to protect the hydroxyls ensured that the nature of the protecting groups does not induce variation in the reactivity of the building blocks and that we could rely on reactivity tuning by the used external nucleophile to control the stereoselective construction of the α-glucan linkages. This strategy could provide an effective entry to construct α-(1,2)-linkages and generate (substituted) kojioligosaccharides such as encountered in *E. faecalis* LTA. We here describe the use of additive-controlled glycosylation methodology for the construction of α-(1,2)-glucans and we show the application of the methodology in the preparation of a D-alanine-kojibiose functionalized LTA fragment.

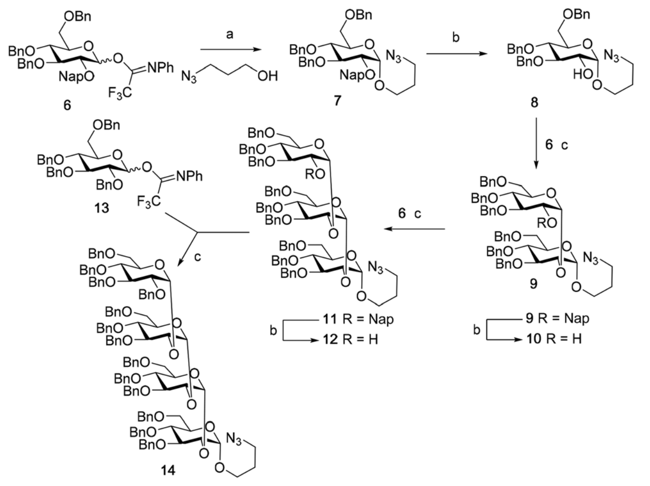
Results and discussion

We first explored the assembly of spacer-functionalized kojioligosaccharides. To achieve this aim, donor **6** (Scheme 1) was designed and assembled. The building block bears three permanent Bn-ethers to mask the C3, C4 and C6 hydroxyls and a Nap-ether as a temporary protecting group at the C2-OH. The synthesis of this building block used benzylidene protected glucose building block **1** as starting compound. Selective protection of the C3-OH as the benzyl ether was achieved through the formation of an intermediate tin ketal which was treated with benzyl bromide and cesium fluoride to give compound **2**. Protection of the remaining C2-OH with a Nap ether then provided compound **3**. Selective opening of the benzylidene and protection of the liberated primary alcohol provided the fully benzylated thiodonor **5**. The anomeric thioacetal in this building block was hydrolyzed using *N*-iodosuccinimide (NIS) in acetone/water to liberate the anomeric hydroxyl group, which could then be turned into the required *N*-phenyltrifluoroacetimidate **6**.



Scheme 1 Synthesis of donor **6**. (a) (i) Bu_2SnO, toluene, 120 °C; (ii) CsF, BnBr, 76%. (b) NapBr, NaH, DMF, 91%. (c) $BF_3{\cdot}Et_2O$, TES, DCM. (d) BnBr, NaH, DMF, 88%. (e) (i) NIS, acetone/H_2O (10 : 1, v : v); (ii) 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride, Cs_2CO_3, acetone, 81% (over two steps).

With donor **6** in hand, the assembly of kojioligosaccharides was explored as depicted in Scheme 2. Firstly, donor **6** was glycosylated with azidopropanol, a primary and relatively reactive alcohol, using the TMSI-$Ph_3P{=}O$ activation couple. TMSI transforms the anomeric imidate into the α-glucosyl iodide, which under the agency of $Ph_3P{=}O$ is isomerized into its less stable but more reactive β-counterpart. These conditions formed azidopropyl glucoside **7** in good yield and stereoselectivity (α : β = 10 : 1), in line with results previously described.[13a,14] Deprotection of the C2-O-Nap ether under oxidative conditions (dichlorodicyanobenzoquinone (DDQ) in DCM/H_2O, 10 : 1 v/v) provided alcohol **8** which was purified by silica gel column chromatography to deliver the pure α-anomer. Next the secondary and less reactive alcohol acceptor **8** was glycosylated with donor **6** under the agency of TfOH and DMF. This latter additive generates a mixture α/β-glucosyl imidinium ions, which are in rapid equilibrium. Substitution of the more reactive β-ion then leads to the stereoselective formation of α-glucosyl linkages. This additive has found wide application in the construction of various 1,2-*cis*-linked oligosaccharides.[15] The condensation of **8** and **6** provided disaccharide **9** in 95% yield and a 15 : 1 α : β-ratio. Deprotection of the C2-O-Nap ether by DDQ provided disaccharide acceptor **10** and the third glycosylation, again performed under DMF mediated glycosylation conditions, then provided trisaccharide **11**. The stereoselectivity of this glycosylation diminished slightly and **11** was formed as a 10 : 1 α : β-mixture. The erosion of stereoselectivity developed further upon elongation of the trisaccharide, as the DMF-mediated glycosylation of acceptor **12**, obtained after DDQ treatment of **11**, with per-benzyl donor

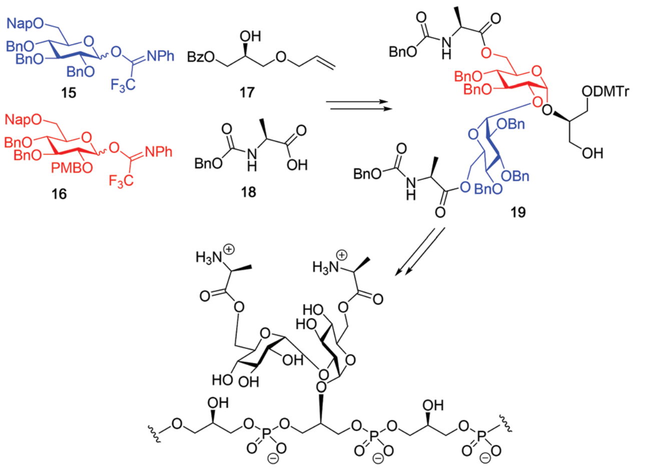


Scheme 2 The assembly of kojioligosaccharides. (a) TMSI, $Ph_3P{=}O$, DCM, 36 h, 75%, α : β = 10 : 1. (b) DDQ, DCM : H_2O = 10 : 1 (v : v), **8**: 75%; **10**: 49%; **12**: 47%. (c) DMF, TfOH, DCM, **9**: 95%, α : β = 15 : 1; **11**: 67%, α : β = 10 : 1; **14**: 67%, α : β = 2 : 1.

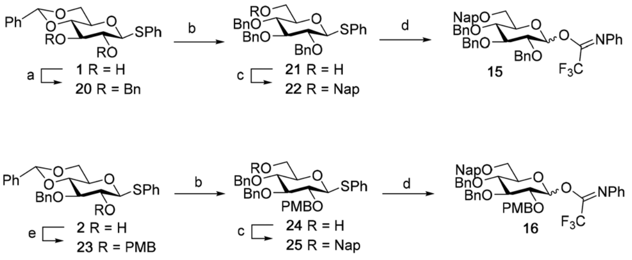
13 delivered tetrasaccharide **14** as a 2 : 1 α : β-mixture. Possibly the overall structure of the twisted α-(1,2)-oligosaccharide is at the root of the erosion of stereoselectivity, with increasing steric demands leading to lower yields and poorer selectivity.

Although a limitation of the DMF-mediated glycosylation protocol come forward in the above described kojitetraose assembly, the synthesis also showed that the additive controlled glycosylation approach can provide a rapid entry into the assembly of smaller kojibiose derivatives. Therefore, the assembly of an *E. faecalis* D-Ala-kojibiose LTA fragment was next explored. The synthesis of D-Ala-kojibiose LTA requires the availability of compound **19** featuring the kojibiose, decorated with two D-alanine esters at both primary alcohols, attached to the glycerol through an α-bond (Scheme 3). Compound **19** can be assembled from four building blocks: two benzyl type protected glucosyl donors, **15** and **16**, glycerol **17** protected with a benzoyl ester (Bz) and allyl ether and *N*-benzyloxycarbonyl protected D-alanine **18** (Scheme 3). The glucosyl donors are protected with the triad of Bn, PMB and Nap-ethers to discriminate the alcohol groups that required permanent protection or needed to be removed to introduce the next glucose residue or introduce the D-alanine esters.

The synthesis of the used building blocks is depicted in Scheme 4. Firstly, donor **15** was synthesized from compound **1** by benzylation of the C2 and C3-hydroxyls, regioselective opening of the benzylidene acetal and protection of the liberated primary alcohol with a Nap-ether, to give thio donor **22**. Hydrolysis of the thioacetal and introduction of the 2,2,2-trifluoro-*N*-phenylacetimidate formed donor **15**. Donor **16** was obtained from compound **2** following a similar sequence of reactions: protection of the C2-OH with a PMB-ether, regioselective opening of the benzylidene acetal and installation of the C6-*O*-Nap ether provided thioacetal **25**, which was transformed into the corresponding imidate donor **16**.

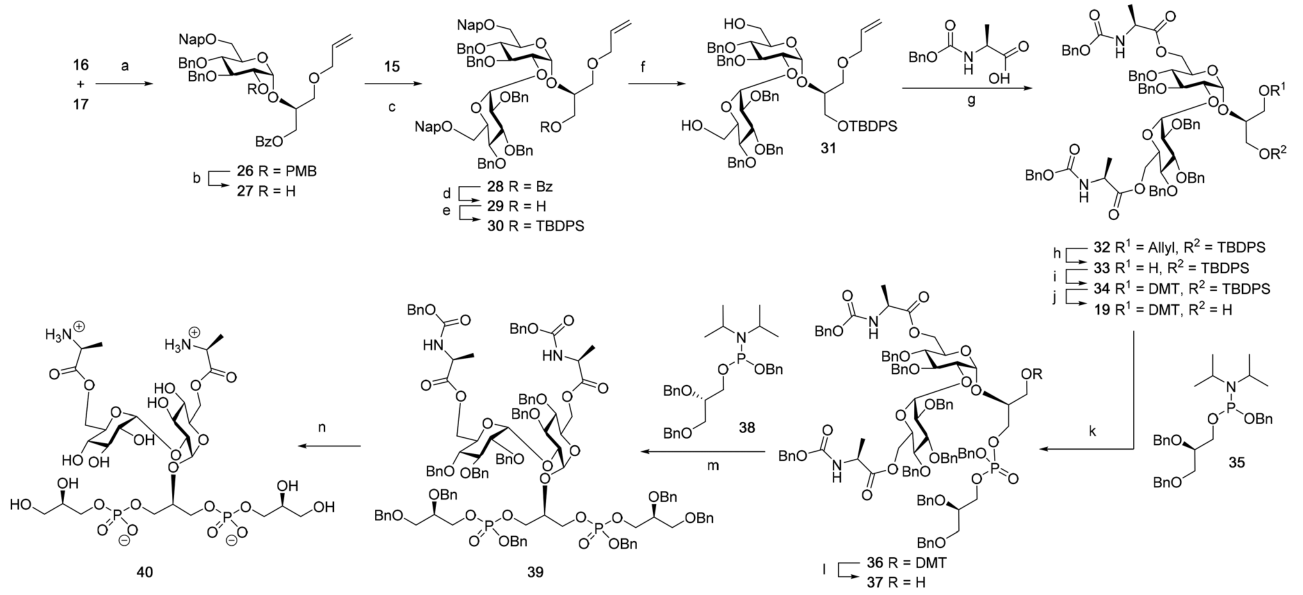


Scheme 3 Building blocks applied in the here-presented studies in the synthesis of D-alanine kojibiose functionalized LTA-fragments of *Enterococcus faecalis*.



Scheme 4 Synthesis of donor **15** and **16**. (a) BnBr, NaH, DMF, **20**: 96%. (b) BH_3.THF, $Cu(OTf)_2$, **21**: 80%; **24**: 76%. (c) NapBr, NaH, DMF, **22**: 91%; **25**: 93%. (d) 1) NIS, acetone : H_2O = 10 : 1 (v : v); (2) 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride, Cs_2CO_3, acetone, yield **15**: 86%; **16**: 84%. (e) PMBCl, NaH, DMF, 94%.

With all the required building blocks available, we explored the assembly of a kojibiose LTA fragment as depicted in Scheme 5. First, glycerol building block **19** was assembled. To this end glycerol **17** was glycosylated with donor **16**, of which the primary alcohol groups were protected by a benzoate ester and an allyl ether, using the TMSI-$Ph_3P{=}O$ activation conditions to give the compound **26** in good yield and excellent selectivity. Next, the C2-O-PMB was selectively removed using a catalytic amount of HCl in a mixture of hexafluoro-iso-propanol (HFIP) and DCM to give C2-OH acceptor **27** in 95% yield.[16] All other benzyl ethers remained unaffected under these conditions. Acceptor **27** was then glycosylated with donor **15** using the DMF-mediated glycosylation conditions to form the disaccharide **28** with good selectivity and excellent yield. To set the stage for the introduction of the D-alanyl esters, first the glycerol benzoate was replaced by a TBDPS ether, after which the two C-6-O-Nap ethers were removed to give diol **31**. The introduction of the two D-alanine esters was accomplished using PyBOP as a condensing agent to form 6,6-di-alanyl-α-kojibiose **32** in 90% yield. To transform this building block into a synthon suitable for the assembly of TA-fragments, the allyl ether was replaced by a 4,4′-dimethoxytrityl (DMTr) group. Therefore, the allyl group was isomerized to the corresponding enol ether using an iridium catalyst, which was subsequently hydrolyzed using I_2 in combination with sodium bicarbonate. The liberated primary alcohol was treated with DMTrCl in DCM to give compound **34**, which was treated with HF-pyridine to give the 6,6-di-alanyl-α-kojibiose **19** in 86% yield. For the construction of the kojibiobiosyl glycerol trimer **40**, we chose to use benzyl phosphoramidites, as opposed to the more commonly employed cyanoethyl reagents.[10] The latter group however requires basic conditions for its removal, that may jeopardize the labile D-alanine esters in the target compound.[17] Thus, compound **19** and phosporamidite **35** were coupled under the agency of dicyanoimidazole (DCI), to provide the intermediate phosphite triester, which was immediately oxidized to the phosphate using (1*S*)-(+)-(10-camphorsulfonyl)-oxaziridine (CSO), and the resulting dimer **36** was treated with a catalytic amount of *p*-toluenesulfonic acid (TsOH) in DCM/MeOH to provide compound **37** in 93% over three steps. A similar coupling of phophoramidite **38** and alcohol **37** then provided



Scheme 5 Synthesis of a di-alanyl-α-kojibiose containing LTA fragment. (a) TMSI, $Ph_3P{=}O$, DCM, 36 h, 76%, α : β > 20 : 1. (b) TES, HCl/HFIP, DCM : HFIP = 1 : 1 (v : v), 93%. (c) DMF, TfOH, 24 h, 95%, α : β > 10 : 1. (d) CH_3ONa, DCM : CH_3OH = 1 : 1 (v : v), 92%. (e) TBDPSCl, imidazole, DMF, 99%. (f) DDQ, DCM : H_2O = 10 : 1 (v : v), 77%. (g) PyBOP, NMI, DCM, 90%. (h) (1) $Ir(COD)(Ph_2MeP)_2PF_6$; (2) I_2, $NaHCO_3$, H_2, THF, 85%. (i) DMTrCl, DIPEA, DCM, 95%. (j) HF-pyridine, THF/pyridine, 86%. (k) 1) DCI, CH_3CN; (2) CSO. (l) TsOH, DCM/CH_3OH = 1 : 1 (v : v), 93%. (m) DCI, CH_3CN; (2) CSO, 88%. (n) H_2, Pd/C, dioxane/H_2O = 2 : 1 (v : v), 3 day, 95%.

trimer **39** in 88% yield. Removal of all benzyl ethers, benzyl carbamates and benzyl phosphotriesters in **39** in a single hydrogenolysis event delivered **40**.

Conclusion

In conclusion, we have here explored additive controlled glycosylations for the construction of α-1,2-glucosyl linkages. After the successful construction of α-1,3-glucosyl and α-1,4-glucosyl linkages, described previously, we have shown that conditions, involving the activation of per-benzylated glucosyl imidate donors with stoichiometric TfOH in the presence of an excess DMF, can be profitably used for the construction of α-1,2-glucosyl linkages. The assembly of a linear kojitetraose however has brought to light that the stereoselectivity of the glycosylation reactions decrease with growing chain length. A kojibiose was assembled with excellent stereoselectivity (α : β = 15 : 1) and elongation of this disaccharide proceeded with good selectivity (α : β = 10 : 1), but extension of the trisaccharide with a fourth residue led to an anomeric mixture (α : β = 2 : 1). Using the methodology and building on a triad of benzyl-type protecting groups, a D-alanine-kojibiose functionalized LTA from the *E. faecalis* cell wall was synthesized. Through the use of mild global deprotection conditions the labile D-alanine esters were maintained in the final product. The generation of this structure will enable binding studies with antibodies, which may pave the way to the generation of a synthetic vaccine, based on this structure, directed at this important nosocomial pathogen.

Experimental

General experimental procedures

All reagents were of commercial grade and used as received. All moisture sensitive reactions were performed under an argon atmosphere. DCM used in the glycosylation reactions was dried with flamed 4 Å molecular sieves before being used. Reactions were monitored by TLC analysis with detection by UV (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH or with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (25 g L^{-1}) and $(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$ (10 g L^{-1}) in 10% sulfuric acid (aq.) followed by charring at ∼150 °C. Column chromatography was carried out using silica gel (0.040–0.063 mm). Size-exclusion chromatography was carried out using Sephadex LH-20.^{1}H and ^{13}C spectra were recorded on a Bruker AV 400 and Bruker AV 500 in $CDCl_3$ or D_2O. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard (^{1}H NMR in $CDCl_3$) or the residual signal of the deuterated solvent. Coupling constants (J) are given in Hz. All ^{13}C spectra are proton decoupled. NMR peak assignments were made using COSY and HSQC experiments, where applicable Clean TOCSY, HMBC and GATED experiments were used to further elucidate the structure. The anomeric product ratios were analysed through integration of proton NMR signals.

Experimental procedures and characterization data of products

For the synthesis procedure and data of known compounds **13**,[13] **17**,[18] **22**,[19] **23** [20] see references. We used "a", "b", "c" and "d" to specify the H-1 and C-13 NMR signals of sugar rings from the "reducing" to the "non-reducing" end and "°" to specify the H-1 and C-13 NMR signals of the spacer.

Standard procedures

Procedure A for the glycosylation of secondary alcohols. A mixture of donor (1.0 eq.), acceptor (0.7 eq.) (donors and acceptors co-evaporated with toluene three times), DMF (16 eq.) in dry DCM were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to −78 °C, after which TfOH (1.0 eq.) was added. After 30 min, the reaction was stirred at 0 or −10 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The products were purified by size exclusion and silica gel column chromatography.

Procedure B for the glycosylation of primary alcohols. A mixture of donor (1.0 eq.), acceptor (0.7 eq.) (donor and acceptor co-evaporated with toluene three times), $Ph_3P{=}O$ (6 eq.) in dry DCM were stirred over fresh flame-dried molecular sieves 3A under nitrogen. Then TMSI (1.0 eq.) was added slowly in the mixture. The reaction was stirred at room temperature until TLC-analysis indicated the reaction to be complete. The solution was diluted and the reaction quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The products were purified by size exclusion and silica gel column chromatography.

Procedure C for deprotection of the PMB protecting group. The starting material (1 eq.) was dissolved in DCM : HFIP (1 : 1, 0.1 M). TES (1.0 eq.) and 0.1 M HCl/HFIP (0.1 eq.) were added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (15 min–2 h). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography.

Procedure D for deprotection of the Nap protecting group. The starting material (1 eq.) was dissolved in DCM : H_2O (10 : 1, 0.1 M). DDQ (1.1 eq.) was added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (±2 h). Then the mixture was diluted with DCM and the reaction quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography.

Phenyl 4,6-*O*-benzelidine-2-*O*-(naphthalen-2-ylmethyl)-3-*O*-benzyl-1-thio-β-D-glucopyranoside 3. Compound **1** (7.7 g, 21.4 mmol) and Bu_2SnO (5.9 g, 23.7 mmol) was dissolved in dry toluene. The mixture was refluxed at 120 °C for 3 h. Then CsF (3.6 g, 23.7 mmol) and BnBr (2.8 mL, 23.7 mmol) were added in the mixture. The mixture was refluxed at 120 °C until the reaction was completed by TLC monitoring. Then the mixture was dilutted with EtOAc and washed with 1 mol L^{-1} KF and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography. Compound **2** was obtained with 76% yield. Then compound **2** (7.3 g, 16.2 mmol) was dissolved in DMF at 0 °C. Then NaH (1.95 g, 48.6 mmol) and NapBr (5 g, 20.6 mmol) were added the mixture under N_2. The reaction was stirring at 0 °C untill the reaction was completed by TLC monitoring. Then the mixture was dilutted with EtOAc and washed with H_2O and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography. Compound **3** was obtained with 91% yield. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.80–7.77 (m, 4 H, aromatic *H*), 7.55–7.22 (m, 18 H, aromatic *H*), 5.54 (s, 1 H), 5.02–4.94 (m, 3 H, 3 CH*H*), 4.79–4.76 (m, 2 H, H-1, 1 CH*H*), 4.35 (dd, J_1 = 4.8 Hz, J_2 = 10.4 Hz, 1 H, H-6$_a$), 3.86–3.66 (m, 3 H, H-6, H-4, H-3), 3.56 (t, *J* = 8.4 Hz, 1 H, H-2), 3.47–3.41 (m, 1 H, H-5).^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.34, 137.29, 135.56, 133.29, 133.18, 133.08 (aromatic *C*), 132.31, 129.05, 128.99, 128.41, 128.28, 128.12, 128.99, 128.87, 127.78, 127.73, 126.90, 126.26, 126.07, 126.03, 125.94 (aromatic *C*H), 101.08 (Ph*C*H), 88.27 (C-1), 82.99 (C-3), 81.45 (C-4), 80.48 (C-2), 75.92, 75.28 (*C*H_2), 70.22 (C-5), 68.67 (C-6).

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(naphthalen-2-ylmethyl)-1-thio-β-D-glucopyranoside 5. Compound **3** (8.7 g, 14.7 mmol) was dissolved in dry DCM under N_2 at 0 °C. Then TES (23 mL, 144 mmol) and $BF_3\cdot Et_2O$ (3.7 mL, 29 mmol) were added in the solution. The reaction was stirring at *t* 0 °C untill the reaction was completed by TLC monitoring. Then the mixture was dilutted with EtOAc and washed with H_2O and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Crude compound **4** was dissolved in DMF at 0 °C. Then NaH (1.8 g, 45 mmol) and BnBr (2.6 mL, 21.9 mmol) were added the mixture under N_2. The reaction was stirring at 0 °C untill the reaction was completed by TLC monitoring. Then the mixture was dilutted with EtOAc and washed with H_2O and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography. Compound **5** was obtained with 88% yield. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.81–7.75 (m, 4 H, aromatic *H*), 7.62–7.18 (m, 23 H, aromatic *H*), 5.04 (d, *J* = 10.4 Hz, 1 H, 1 CH*H*), 4.93–4.82 (m, 4 H, 4 CH*H*), 4.71 (d, *J* = 9.6 Hz, 1 H, H-1), 4.62–4.52 (m, 3 H, 3 CH*H*), 3.81–3.65 (m, 4 H, H-6, H-4, H-3), 3.60–3.50 (m, 2 H, H-2, H-5).^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.49, 138.37, 138.11, 135.62, 133.94, 133.37, 133.16 (aromatic *C*), 132.01, 129.02, 128.55, 128.45, 128.25, 128.07, 128.04, 127.92, 127.85, 127.79, 127.76, 127.67, 127.54, 127.00, 126.34, 126.12, 126.00 (aromatic *C*H), 87.57 (C-1), 86.86 (C-3), 80.92 (C-2), 79.18 (C-4), 77.89 (C-5), 75.93, 75.59, 75.16, 73.50 (*C*H_2), 69.08 (C-6).

3,4,6-Tri-*O*-benzyl-2-*O*-(naphthalen-2-ylmethyl)-α/β-D-glucopyranosyl *N*-phenyltrifluoroacetimidate 6. Compound **5** (11.5 g, 16.8 mmol) was dissolved in acetone (200 mL). *N*-Iodosuccinimide (NIS, 7.5 g, 33.6 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$. Then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography. The lactol (8.7 g, 90% yield) was obtained as a white solid. Next, the lactol (8.7 g, 15.1 mmol) was dissolved in acetone (150 mL). Cs_2CO_3 (7.4 g, 22.6 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (3.5 mL, 25.1 mmol) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography (pentane : EA = 40 : 1–20 : 1). Compound **6** (9.6 g, 92% yield, α : β = 1 : 1) was obtained as yellow syrup. ^{1}H-NMR ($CDCl_3$, 500 MHz, 60 °C) δ 7.79–7.74 (m, aromatic *H*), 7.49–7.01 (m, aromatic *H*), 6.83–6.73 (m, aromatic *H*), 6.40 (bs, 1 H, H-1α), 5.58 (bs, 1 H, H-1β), 4.96–4.53 (m), 4.02–3.95 (m), 3.79–3.59 (m), 3.40 (bs, 1 H).^{13}C-APT ($CDCl_3$, 125 MHz, 60 °C) δ 159.77, 159.73, 143.96, 143.73, 143.42, 138.99, 138.77, 138.38, 138.31, 135.81, 135.70, 133.57, 133.32, 130.33, 130.26 (aromatic *C*), 129.86, 129.43, 128.80, 128.46, 128.43, 128.33, 128.28, 128.06, 127.98, 127.94, 127.91, 127.84, 127.78, 127.69, 127.65, 127.60, 126.78, 126.72, 126.22, 126.20, 126.01, 125.97, 124.41, 124.28, 119.69, 119.58, 114.20, 114.17 (aromatic *C*H), 117.62 (q, *C*F_3), 97.71, 94.00, 84.78, 81.75, 80.86, 79.41, 77.61, 77.36, 76.06, 75.31, 75.63, 75.55, 75.27, 75.02, 74.72, 73.82, 73.73, 73.48, 73.24, 68.73, 68.66, 55.83, 55.36. HR-MS: calculated for $C_{46}H_{42}F_3NO_6$ $[M - [O(C{=}NPh)CF_3] + OH + NH_4]^+$: 608.30066, found: 608.29853.

Synthesis of 7. The reaction was carried out according to the standard procedure B, using **6** (2000 mg, 2.6 mmol, 0.1 M in DCM), 3-aminopropanol (370 μL, 3.9 mmol), $Ph_3P{=}O$ (4.4 g, 15.8 mmol) and TMSI (371 μL, 2.6 mmol). The product was purified by silica gel column chromatography (pentane : EA = 10 : 1). Compound **7** (1300 mg, 75% yield, α : β = 10 : 1) was obtained as a colourless syrup. IR (neat, cm^{-1}) ν 697, 735, 818, 1027, 1155, 1358, 1454, 2095, 2866, 2922. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.83–7.74 (m, 4 H, aromatic *H*), 7.49–7.12 (m, 18 H, aromatic *H*), 5.02 (d, *J* = 11.2 Hz, 1 H, 1 CH*H*), 4.92 (d, *J* = 12.4 Hz, 1 H, 1 CH*H*), 4.86–4.77 (m, 3 H, 3 CH*H*), 4.74 (d, *J* = 3.6 Hz, 1 H, H-1), 4.59 (d, *J* = 11.6 Hz, 1 H, 1 CH*H*), 4.48–4.41 (m, 2 H, 2 CH*H*), 3.99 (t, *J* = 9.2 Hz, 1 H, H-2), 3.75–3.59 (m, 6 H, H-6, H-5, H-4, H-2, H-1$_a$°), 3.48–3.35 (m, 3 H, H-3°, H-1$_b$°), 1.97–1.81 (m, 2 H, H-2°).^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.93, 138.25, 138.14, 127.98, 135.72, 133.29, 133.17 (aromatic *C*), 128.52, 128.49, 128.46, 128.40, 128.06, 128.00, 127.84, 127.79, 127.70, 127.03, 126.29, 126.13, 126.06 (aromatic *C*H), 97.31 (C-1), 82.10 (C-3), 80.10 (C-2), 77.75 (C-4), 75.81, 75.24, 73.57, 73.53 (*C*H_2), 70.43 (C-5), 68.50 (C-6), 64.83 (C-1°), 48.41 (C-3°), 28.96 (C-2°). HR-MS: calculated for $C_{41}H_{43}N_3O_6$ $[M + NH_4]^+$: 691.34901, found: 691.34807.

Synthesis of 8. The reaction was carried out according to the general procedure D, using **7** (1.3 g, 1.93 mmol, 0.1 M in DCM : H_2O) and DDQ (482 mg, 2.1 mmol). The product was purified by silica gel column chromatography. Compound **8** (770 mg, 75% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +90.5 (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 735, 1027, 1066, 1038, 1359, 1454, 1497, 2095, 2870, 2923. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.39–7.13 (m, 15 H, aromatic *H*), 4.94–4.80 (m, 4 H, H-1, 3 CH*H*), 4.63 (d, *J* = 12.4 Hz, 1 H, 1 CH*H*), 4.52–4.48 (m, 2 H, 2 CH*H*), 3.85–3.61 (m, 7 H, H-6, H-5, H-4, H-3, H-2, H-3$_a$°), 3.56–3.51 (m, 1 H, H-3$_b$°), 3.43–3.32 (m, 2 H, H-1°), 2.18 (d, *J* = 7.6 Hz, 1 H, O*H*), 1.94–1.82 (m, 2 H, H-2°).^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.69, 138.11, 137.93 (aromatic *C*), 128.50, 128.47, 128.02, 127.97, 127.96, 127.84, 127.80, 127.77 (aromatic *C*H), 98.66 (C-1), 83.31 (C-3), 77.46 (C-4), 75.43, 75.11, 73.59 (*C*H_2), 72.94 (C-2), 70.82 (C-5), 68.47 (C-6), 65.15 (C-1°), 48.53 (C-3°), 28.86 (C-2°). HR-MS: calculated for $C_{30}H_{35}N_3O_6$ $[M + NH_4]^+$: 551.28641, found: 551.28604.

Synthesis of 9. The reaction was carried out according to the standard procedure B, using **6** (845 mg, 1.11 mmol), **8** (455 mg, 0.85 mmol, 0.05 M in DCM), DMF (1.4 mL, 17.7 mmol) and TfOH (98 μL, 1.11 mmol). The reaction was stirred at −78–0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion chromatography (DCM : MeOH = 1 : 1). Compound **9** (1160 mg, 95% yield, α : β = 15 : 1) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +75.4 (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 736, 1029, 1069, 1359, 1454, 1497, 2098, 2866, 2922. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.83–7.71 (m, 4 H, aromatic *H*), 7.49–7.45 (m, 3 H, aromatic *H*), 7.34–7.21 (m, 23 H, aromatic *H*), 7.16–7.03 (m, 7 H, aromatic *H*), 5.07 (d, *J* = 3.2 Hz, 1 H, H-1b), 5.05 (d, *J* = 3.2 Hz, 1 H, H-1a), 5.01–4.79 (m, 8 H, 8 CH*H*), 4.63–4.39 (m, 5 H, 5 CH*H*), 4.31 (d, *J* = 12.4 Hz, 1 H, 1 CH*H*), 4.11 (t, *J* = 91.6 Hz, 1 H, H-3b), 4.06–3.99 (m, 2 H, H-3a, H-5a), 3.83 (dd, J_1 = 3.2 Hz, J_2 = 9.6 Hz, 1 H, H-2a), 3.78–3.61 (m, 7 H, H-6, H-5b, H-4b, H-4a, H-2b, H-3$_a$°), 3.55–3.39 (m, 3 H, H-6, H-3$_b$°), 3.29–3.19 (m, 2 H, H-1°), 1.84–1.70 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.81, 138.72, 138.32, 138.25, 138.00, 137.98, 135.69, 133.29, 133.11 (aromatic *C*), 128.49, 128.43, 128.42, 128.39, 128.29, 128.09, 128.03, 128.01, 127.97, 127.90, 127.81, 127.80, 127.71, 127.66, 127.62, 127.52, 126.87, 126.33, 126.12, 125.89 (aromatic *C*H), 96.06 (C-1a), 94.72 (C-1b), 82.17 (C-3b), 80.79 (C-3a), 79.14 (C-2b), 78.07 (C-4), 77.68 (C-4), 76.18, 75.71 (*C*H_2), 75.45 (C-2a), 75.20, 74.95, 73.60, 73.45, 72.99 (*C*H_2), 70.61 (C-5b), 70.44 (C-5a), 68.52 (C-6), 68.04 (C-6), 65.15 (C-1°), 48.36 (C-3°), 28.02 (C-2°). HR-MS: calculated for $C_{68}H_{71}N_3O_6$ $[M + NH_4]^+$: 1123.54269, found: 1123.54104.

Synthesis of 10. The reaction was carried out according to the general procedure D, using **9** (970 mg, 0.88 mmol, 0.1 M in DCM : H_2O) and DDQ (217 mg, 0.96 mmol). The product was purified by silica gel column chromatography. Compound **10** (416 mg, 49% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +90.8 (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 735, 1027, 1050, 1132, 1361, 1454, 2098, 2866, 2929.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.38–7.06 (m, 30 H, aromatic *H*), 5.02–4.97 (m, 3 H, H-1a, H-1b, 1 CH*H*), 4.87–4.75 (m, 5 H, 5 CH*H*), 4.63–4.44 (m, 5 H, 5 CH*H*), 4.32 (d, *J* = 12.0 Hz, 1 H, 1 CH*H*), 3.94–3.65 (m, 11 H), 3.53–3.33 (m, 5 H, H-6), 1.91–1.84 (m, 2 H, H-2°).^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.69, 138.61, 137.97, 137.86, 737.83 (aromatic *C*), 128.41, 128.39, 128.34, 128.30, 128.28, 128.16, 128.08, 127.97, 127.95, 127.87, 127.82, 127.78, 127.72, 127.65, 127.60, 127.55, 127.41 (aromatic *C*H), 96.21 (C-1b), 85.58 (C-1a), 83.28 (C-3b), 80.50 (C-3a), 77.79 (C-4), 76.94 (C-4), 76.00 (*C*H$_2$), 75.37 (C-2a), 75.12, 74.75, 73.48, 73.29 (*C*H$_2$), 72.79 (C-2b), 70.62 (C-5), 70.58 (C-5), 68.28 (C-6), 67.86 (C-6), 64.83 (C-1°), 48.33 (C-3°), 28.62 (C-2°). HR-MS: calculated for $C_{68}H_{71}N_3O_{11}$ $[M + NH_4]^+$: 983.48003, found: 983.47815.

Synthesis of 11. The reaction was carried out according to the standard procedure B, using **6** (547 mg, 0.72 mmol), **10** (347 mg, 0.36 mmol, 0.05 M in DCM), DMF (900 μL, 11.4 mmol) and TfOH (64 μL, 0.72 mmol). The reaction was stirred at −78–0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion chromatography (DCM : MeOH = 1 : 1). Compound **11** (372 mg, 67% yield, α : β = 10 : 1) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +96.5 (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}) *ν* 697, 735, 1029, 1069, 1359, 1454, 1497, 2098, 2845, 2921. ^{1}H-NMR ($CDCl_3$, 400 MHz) *δ* 7.82 (s, 1 H, aromatic *H*), 7.71–7.62 (m, 3 H, aromatic *H*), 7.52–7.50 (m, 1 H, aromatic *H*), 7.41–7.37 (m, 1H, aromatic *H*), 7.32–6.96 (m, 46 H, aromatic *H*), 5.49 (d, *J* = 3.6 Hz, 1 H, H-1c), 5.41 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.23 (d, *J* = 2.0 Hz, 1 H, H-1a), 5.16 (d, *J* = 12.0 Hz, 1 H, 1 CH*H*), 4.99–4.34 (m, 18 H, 18 CH*H*), 44.18–3.52 (m, 21 H), 3.31–3.22 (m, 2 H, H-3°), 1.93–1.82 (m, 2 H, H-2°). ^{13}C-APT ($CDCl_3$, 100 MHz) *δ* 138.78, 138.76, 138.74, 138.45, 138.26, 138.16, 138.09, 137.98, 137.90, 136.09, 133.35, 132.94 (aromatic *C*), 128.72, 128.45, 128.44, 128.40, 128.38, 128.29, 128.26, 128.13, 128.06, 128.04, 127.93, 127.79, 127.72, 127.65, 127.60, 127.56, 127.51, 127.46, 126.11, 125.84, 125.77, 125.55 (aromatic *C*H), 95.84 (C-1c), 92.77 (C-1b), 92.09 (C-1a), 81.96 (C-3c), 81.45 (C-3a), 80.99 (C-3b), 79.97 (C-2c), 77.37 (2 C-4), 77.05 (C-4), 76.08, 75.99, 75.65, 74.94, 74.84 (*C*H$_2$), 74.71 (C-2), 74.60 (C-2), 73.58, 73.50, 71.60 (*C*H$_2$), 70.94 (C-5), 70.80 (C-5), 70.61 (C-5), 68.61 (C-6), 68.34 (C-6), 68.07 (C-6), 65.16 (C-1°), 48.31 (C-3°), 29.20 (C-2°). HR-MS: calculated for $C_{95}H_{99}N_3O_{16}$ $[M + NH_4]^+$: 1555.73636, found: 1555.73599.

Synthesis of 12. The reaction was carried out according to the general procedure D, using **11** (700 mg, 0.45 mmol, 0.1 M in DCM : H_2O) and DDQ (140 mg, 0.6 mmol). The product was purified by silica gel column chromatography. Compound **12** (300 mg, 47% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +122.1 (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}) *ν* 697, 735, 1027, 1050, 1132, 1361, 1454, 2098, 2866, 2929.^{1}H-NMR ($CDCl_3$, 400 MHz) *δ* 7.37–6.98 (m, 45 H, aromatic *H*), 5.18 (d, *J* = 3.2 Hz, 1 H, H-1b), 5.06 (d, *J* = 3.2 Hz, 1 H, H-1a), 5.00–4.90 (m, 3 H, H-1a, 2 CH*H*), 4.84–4.30 (m, 16 H, 16 CH*H*), 4.01–3.34 (m, 22 H), 2.41 (s, 1 H, O*H*), 2.06–1.85 (m, 2 H, H-2°).^{13}C-APT ($CDCl_3$, 100 MHz) *δ* 138.89, 138.85, 138.56, 138.24, 138.22, 138.02, 137.96, 137.95, 137.89 (aromatic *C*), 128.56, 128.53, 128.51, 128.50, 128.42, 128.38, 128.36, 128.28, 128.08, 128.07, 127.86, 127.82, 127.79, 127.74, 127.67, 127.63, 127.60, 127.50 (aromatic *C*H), 96.03 (C-1c), 95.04 (C-1a), 91.66 (C-1b), 83.42 (C-3c), 80.90 (C-3a), 80.62 (C-3b), 77.89 (C-4), 77.73 (C-4), 76.84 (C-4), 76.30, 76.25, 75.20, 75.15, 74.94, 74.92 (*C*H$_2$), 74.67 (C-2b), 74.00 (C-2a), 73.65, 73.59, 73.45 (*C*H$_2$), 72.67 (C-2c), 70.69 (C-5), 70.64 (C-5), 70.57 (C-5), 68.38 (C-6), 68.00 (C-6), 67.97 (C-6), 64.50 (C-1°), 48.51 (C-3°), 28.77 (C-2°). HR-MS: calculated for $C_{84}H_{91}N_3O_{16}$ $[M + NH_4]^+$: 1415.67376, found: 1415.67378.

Synthesis of 14. The reaction was carried out according to the standard procedure B, using **13** (190 mg, 0.27 mmol), **12** (70 mg, 0.05 mmol, 0.05 M in DCM), DMF (78 μL, 0.99 mmol) and TfOH (23 μL, 0.27 mmol). The reaction was stirred at −78–0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion chromatography (DCM : MeOH = 1 : 1). Compound **14** (64 mg, 67% yield, α : β = 2 : 1) was obtained as a colourless syrup. IR (neat, cm^{-1}) *ν* 695, 734, 1027, 1069, 1209, 1359, 1454, 1497, 1729, 2096, 2859, 2923. HR-MS: calculated for $C_{118}H_{125}N_3O_{21}$ $[M + NH_4]^+$: 1937.91438, found: 1937.91440.

Synthesis of 15. Compound **22** (1.0 g, 1.46 mmol) was dissolved in acetone : H_2O (10 : 1, 15 mL). *N*-Iodosuccinimide (NIS) (660 mg, 2.93 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$. Then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography. The lactol was obtained as a white solid. Next, the lactol was dissolved in acetone (15 mL). Cs_2CO_3 (713 mg, 2.19 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (355 μL, 2.19 mmol) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography. Compound **15** (959 mg, 86% yield over two steps, α : β = 1 : 1) was obtained as yellow syrup. IR (neat, cm^{-1}) *ν* 695, 734, 1027, 1073, 1153, 1208, 1314, 1454, 1597, 1716, 2869, 2915. ^{1}H-NMR ($CDCl_3$, 400 MHz) *δ* 7.82–6.50 (m, aromatic *H*), 6.53 (bs, 1 H, H-1), 5.67 (bs, 1 H, H-1), 5.00–4.61 (m), 4.52–4.46 (m), 4.06–3.97 (m), 3.81–3.66 (m). ^{13}C-APT ($CDCl_3$, 125 MHz) *δ* 143.78, 143.55, 138.67, 138.64, 137.92, 137.83, 135.45, 135.28, 133.35, 133.19, 133.16 (aromatic *C*), 129.51, 128.82, 128.64, 128.61, 128.57, 128.55, 128.49, 128.43, 128.36, 128.33, 128.13, 128.05, 127.99, 127.92, 127.88, 127.84, 127.81, 127.78, 127.00, 126.88, 126.49, 126.30, 126.26, 126.10, 126.08, 126.05, 124.39, 120.57, 119.44 (aromatic *C*H), 84.64, 81.62, 81.04, 79.37, 77.27, 76.94, 75.91, 75.82, 75.74, 75.44, 75.31, 75.17, 73.76, 73.65, 73.44, 73.19, 68.12.

Synthesis of 16. Compound **23** (2.57 g, 4.5 mmol) was dissolved in dry DCM under N_2 at 0 °C. Then TES (7.2 mL, 45 mmol) and $BF_3 \cdot Et_2O$ (1.2 mL, 9 mmol) were added in the solution. The reaction was stirring at *t* 0 °C untill the reaction was completed by TLC monitoring. Then the mixture was dilutted with EtOAc and washed with H_2O and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product purified by column chromatography. Compound **24** was dissolved in DMF at 0 °C. Then NaH (540 g, 13.05 mmol) and NapBr (1.4 g, 6.7 mmol) were added the mixture under N_2. The reaction was stirring at 0 °C untill the reaction was completed by TLC monitoring. Then the mixture was dilutted with EtOAc and washed with H_2O and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography. Compound **25** was obtained with 83% yield over two steps. Compound **25** (4.8 g, 6.73 mmol) was dissolved in acetone : H_2O (10 : 1, 77 mL). *N*-Iodosuccinimide (NIS) (3.0 g, 13.3 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$. Then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*, and the product purified by column chromatography. The lactol was obtained as a white solid. Next, the lactol was dissolved in acetone (70 mL). Cs_2CO_3 (6.3 g, 19.5 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (3.2 mL, 19.5 mmol) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography. Compound **16** (4.48 g, 84% yield over two steps, α : β = 1 : 1) was obtained as yellow syrup. ^{1}H-NMR ($CDCl_3$, 500 MHz, 60 °C) δ 7.79–7.74 (m, aromatic *H*), 7.49–7.01 (m, aromatic *H*), 6.83–6.73 (m, aromatic *H*), 6.40 (bs, 1 H, H-1α), 5.58 (bs, 1 H, H-1β), 4.96–4.53 (m), 4.02–3.95 (m), 3.79–3.59 (m), 3.40 (bs, 1 H). ^{13}C-APT ($CDCl_3$, 125 MHz, 60 °C) δ 159.77, 159.73, 143.96, 143.73, 143.42, 138.99, 138.77, 138.38, 138.31, 135.81, 135.70, 133.57, 133.32, 130.33, 130.26 (aromatic *C*), 129.86, 129.43, 128.80, 128.46, 128.43, 128.33, 128.28, 128.06, 127.98, 127.94, 127.91, 127.84, 127.78, 127.69, 127.65, 127.60, 126.78, 126.72, 126.22, 126.20, 126.01, 125.97, 124.41, 124.28, 119.69, 119.58, 114.20, 114.17 (aromatic *C*H), 117.62 (q, *C*F_3), 97.71, 94.00, 84.78, 81.75, 80.86, 79.41, 77.61, 77.36, 76.06, 75.31, 75.63, 75.55, 75.27, 75.02, 74.72, 73.82, 73.73, 73.48, 73.24, 68.73, 68.66, 55.83, 55.36. HR-MS: calculated for $C_{47}H_{44}F_3NO_7$ $[M - [O(C{=}NPh)CF_3] + OH + Na]^+$: 643.26662, found: 643.26659.

(*S*)-3-(Allyloxy)-2-hydroxypropyl benzoate 17. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07–8.04 (m, 2 H, aromatic *H*), 7.58–7.53 (m, 1 H, aromatic *H*), 7.45–7.41 (m, 2 H, aromatic *H*), 5.95–5.85 (m, 1 H, H-5), 5.31–5.17 (m, 2 H, H-6), 4.45–4.36 (m, 2 H, H-1), 4.19–4.14 (m, 1 H, H-2), 4.05–4.03 (m, 2 H, H-4), 3.63–3.53 (m, 2 H, H-3), 3.01 (bs, 1 H, O*H*). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 166.69 (*C*=O), 134.30, 133.18 (aromatic *C*H), 129.87 (aromatic *C*), 129.80 (aromatic *C*H), 128.43 (C-5), 117.54 (C-6), 772.43, 71.02, 68.93 (C-2), 66.07. HR-MS: calculated for $C_{13}H_{16}O_4$ $[M + Na]^+$: 259.0941, found: 259.0948.

Synthesis of 26. The reaction was carried out according to the standard procedure B, using **15** (1.5 g, 1.9 mmol), **17** (410 mg, 1.74 mmol, 0.1 M in DCM), $Ph_3P{=}O$ (3.16 g, 11.4 mmol) and TMSI (270 μL, 1.9 mmol). The product was purified by silica gel column chromatography. Compound **26** (1100 mg, 76% yield, α : β > 20 : 1) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +38.9 (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 713, 820, 1037, 1072, 1095, 1249, 1272, 1452, 1513, 1720, 2865, 2912. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.99–7.97 (m, 2 H, aromatic *H*), 7.76–7.63 (m, 4 H, aromatic *H*), 7.46–7.08 (m, 16 H, aromatic *H*), 6.92 (bd, 2 H, aromatic *H*), 6.85–6.82 (m, 2 H, aromatic *H*), 5.93–5.84 (m, 1 H, H-5°), 5.31–5.25 (m, 1 H, H-6$_a$°), 5.19–5.16 (m, 2 H, H-1a, H-6$_b$°), 4.99 (d, *J* = 10.8 Hz, 1 H, CH*H*), 4.81–4.77 (m, 2 H, 2 CH*H*), 4.70–4.63 (m, 3 H, 3 C*H*H), 4.57 (dd, J_1 = 3.6 Hz, J_2 = 11.6 Hz, 1 H, H-1$_a$°), 4.45–4.35 (m, 3 H, 2 CH*H*, H-1$_b$°), 4.28–4.24 (m, 1 H, H-2°), 4.04–3.99 (m, 4 H, H-3a, H-5a, H-4°), 3.74 (s, 3 H, OCH_3), 3.73–3.58 (m, 4 H, H-2a, H-4a, H-3°), 3.50 (dd, 1 H, J_1 = 2.8 Hz, J_2 = 11.8 Hz, H-6a$_a$), 3.37 (dd, 1 H, J_1 = 2.0 Hz, J_2 = 10.4 Hz, H-6a$_b$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 166.19 (*C*=O), 159.30, 138.91, 138.22, 135.16 (aromatic *C*), 134.38 (C-5°), 133.11, 132.96 (aromatic *C*), 132.88 (aromatic *C*H), 130.27, 129.84 (aromatic *C*), 129.62, 129.60, 128.31, 128.28, 128.11, 127.85, 127.82, 127.67, 127.48, 127.44, 126.80, 126.03, 125.97, 125.83 (aromatic *C*H), 117.19 (C-6°), 113.78 (aromatic *C*H), 96.13 (C-1a), 81.83 (C-5a), 79.26 (C-2a), 77.47 (C-4a), 75.59, 74.83 (*C*H_2), 73.59 (C-2°), 73.52, 72.43 (*C*H_2), 72.35 (C-4°), 70.23 (C-3a), 69.59 (C-3°), 67.97 (C-6a), 65.01 (C-1°), 55.16 (O*C*H_3). HR-MS: calculated for $C_{52}H_{54}O_{10}$ $[M + Na]^+$: 861.3609, found: 861.3647.

Synthesis of 27. The reaction was carried out according to the general procedure C, using **26** (1000 mg, 1.19 mmol, 0.1 M in DCM : HFIP), triethylsilane (190 μL, 1.19 mmol) and 0.1 M HCl/HFIP (1.2 ml, 0.12 mmol). The product was purified by silica gel column chromatography (PE : EA = 6 : 1). Compound **27** (800 mg, 93% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +73.0 (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 710, 713, 738, 1027, 1070, 1095, 1272, 1452, 1721, 2866, 2915. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.02–8.00 (m, 2 H, aromatic *H*), 7.78–7.66 (m, 4 H, aromatic *H*), 7.49–7.09 (m, 14 H, aromatic *H*), 6.96–6.94 (m, 4 H, aromatic *H*), 5.93–5.84 (m, 1 H, H-5°), 5.32–5.26 (m, 1 H, H-6°$_a$), 5.23–5.19 (m, 1 H, H-6°$_b$), 5.12 (d, *J* = 3.2 Hz, 1 H, H-1a), 4.99 (d, *J* = 11.2 Hz, 1 H, 1 CH*H*), 4.81 (d, *J* = 11.2 Hz, 1 H, 1 CH*H*), 4.78 (d, *J* = 11.2 Hz, 1 H, 1 CH*H*), 4.69 (d, *J* = 12.4 Hz, 1 H, 1 CH*H*), 4.49–4.38 (m, 4 H, 3 C*H*H, H-1°),4.24–4.18 (m, 1 H, H-2°), 4.07–3.98 (m, 2 H, H-4°), 3.97–3.93 (m, 1 H, H-3a), 3.80–3.73 (m, 2 H, H-2a, H-5a), 3.68–3.57 (m, 4 H, H-3°, H-4a, H-6a$_a$), 3.42 (dd, 1 H, J_1 = 2.0 Hz, J_2 = 10.4 Hz, H-6a$_b$), 2.77 (d, 1 H, *J* = 8.0 Hz, O*H*). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 166.29 (*C*=O), 138.93, 138.25, 135.30 (aromatic *C*), 134.03 (C-5°), 133.24 (aromatic *C*), 133.18 (aromatic *C*H), 133.07, 129.83 (aromatic *C*), 129.75, 128.47, 128.41, 128.26, 127.99, 127.94, 127.80, 127.77, 127.61, 127.59, 126.86, 126.16, 126.05, 125.95 (aromatic *C*H), 117.92 (C-6°), 99.40 (C-1a), 83.53 (C-5a), 77.02 (C-4a), 76.14 (C-2°), 75.33, 74.95, 73.65 (*C*H_2), 73.44 (C-2a), 72.46 (C-4°), 71.08 (C-3a), 69.23 (C-3°), 68.11 (C-6a), 64.80 (C-1°). HR-MS: calculated for $C_{44}H_{46}O_9$ $[M + Na]^+$: 741.3034, found: 741.3062.

Synthesis of 28. The reaction was carried out according to the standard procedure B, using **15** (1210 mg, 1.59 mmol), **27** (760 mg, 1.05 mmol, 0.1 M in DCM), DMF (1.3 mL, 16.8 mmol) and TfOH (140 μL, 1.59 mmol). The reaction was stirred at −78–0 °C until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion chromatography (DCM : MeOH = 1 : 1). Compound **28** (2.06 g, 95% yield, α : β > 10 : 1) was obtained as a colourless syrup. Then the compound was purified by silica gel column chromatography to get pure α product. $[\alpha]_D^{20}$ +75.1 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 713, 820, 1046, 1070, 1095, 1272, 1359, 1454, 1721, 2863, 2919.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.00–7.81 (m, 2 H, aromatic *H*), 7.78–7.63 (m, 8 H, aromatic *H*), 7.44–6.91 (m, 34 H, aromatic *H*), 5.81–5.76 (m, 1 H, H-5°), 5.46 (d, J = 3.6 Hz, 1 H, H-1a), 5.29 (d, J = 3.6 Hz, 1 H, H-1b), 5.22–5.10 (m, 2 H, H-6°), 4.98–4.67 (m, 10 H, 10 CH*H*), 4.56–4.33 (m, 6 H, 4 CH*H*, H-1°), 4.29–4.23 (m, 1 H, H-2°), 4.14–4.04 (m, 4 H, H-5a, H-5b, H-3a, H-3b), 3.91–3.88 (m, 3 H, H-3a, H-4°), 3.80–3.43 (m, 9 H, H-3°, H-2b, H-4a, H-4b, H-6a, H-6b). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 166.23 (*C*═O), 138.69, 138.46, 138.34, 138.31, 138.27, 135.33, 135.22 (aromatic *C*), 134.27 (C-5°), 133.18, 133.15, 133.01, 132.99 (aromatic *C*), 132.91 (aromatic *C*H), 129.92 (aromatic *C*), 129.62, 128.41, 128.38, 128.35, 128.31, 128.19, 128.17, 128.15, 128.09, 127.92, 127.87, 127.74, 127.69, 127.63, 127.54, 127.51, 127.46, 127.43, 127.34, 126.88, 126.80, 126.09, 126.06, 125.98, 125.85, 125.84 (aromatic *C*H), 117.41 (C-6°), 99.70 (C-1b), 94.53 (C-1a), 82.10 (C-5b), 80.73 (C-5a), 79.35 (C-2b), 77.80 (C-4), 77.56 (C-4), 76.03, 75.54 (*C*H_2), 75.39 (C-2a), 74.85, 74.82, 73.54, 73.53 (*C*H_2), 73.14 (C-2°), 72.36, 72.22 (*C*H_2), 70.46 (C-3a and 3b), 69.23 (C-3°), 68.98 (C-6a and 6b), 64.96 (C-1°). HR-MS: calculated for $C_{82}H_{82}O_{14}$ $[M + Na]^+$: 1313.5597, found: 1313.5624.

Synthesis of 29. Compound **28** (1100 mg, 0.85 mmol) was dissolved in DCM : CH_3OH (1 : 1/v : v, 8.5 mL) stirring at room temperature. Then 5 drops of solution of CH_3ONa in CH_3OH (5.4 M) was added in the mixture. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial (3 h). Then the mixture was diluted with DCM. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography. Compound **29** (930 mg, 92% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +69.4 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 737, 818, 1069, 1209, 1359, 1454, 2865, 2921.^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.83–7.69 (m, 8 H, aromatic *H*), 7.49–7.09 (m, 25 H, aromatic *H*), 7.03–6.92 (m, 6 H, aromatic *H*), 5.86–5.76 (m, 1 H, H-5°), 5.31 (d, J = 3.6 Hz, 1 H, H-1b), 5.22–5.10 (m, 3 H, H-6°, H-1a), 4.94–4.35 (m, 14 H, 14 CH*H*), 4.09–3.98 (m, 4 H, H-5a, H-5b, H-3a, H-3b), 3.89–3.45 (m, 14 H). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.73, 138.52, 138.31, 138.21, 137.98135.41, 135.20 (aromatic *C*), 134.56 (C-5°), 133.33, 133.29, 133.18, 133.12 (aromatic *C*), 128.60, 128.45, 128.42, 128.31, 128.22, 128.07, 128.04, 128.01, 127.95, 127.84, 127.81, 127.78, 127.74, 127.67, 127.64, 127.49, 126.98, 126.26, 126.19, 126.06, 126.04, 125.97 (aromatic *C*H), 117.25 (C-6°), 95.62 (C-1b), 95.08 (C-1a), 82.22 (C-5a), 80.73 (C-5b), 79.24 (C-2b), 78.89 (C-2b), 78.28 (C-4), 77.71 (C-4), 76.15 (*C*H_2), 75.73 (C-2°), 75.69, 75.16, 74.99, 73.70, 73.61, 72.86 (*C*H_2), 72.34 (C-4°), 70.86 (C-3b), 70.59 (C-3a), 69.67 (C-3°), 68.64, 68.08 (C-6a and 6b), 63.61 (C-1°). HR-MS: calculated for $C_{75}H_{78}O_{13}$ $[M + Na]^+$: 1209.5335, found: 1209.5356.

Synthesis of 30. Compound **29** (350 mg, 0.3 mmol) was dissolved in DMF (6 mL) stirring at room temperature. Then TBDPSCl (153 μL, 0.6 mmol) and imidazole (120 mg, 1.8 mmol) were added in the mixture. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial. Then the mixture was diluted with DCM. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography. Compound **29** (423 mg, 99% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +62.1 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 738, 818, 1047, 1070, 1361, 1454, 2858, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.80–7.62 (m, 12 H, aromatic *H*), 7.48–7.06 (m, 31 H, aromatic *H*), 6.97–6.94 (m, 6 H, aromatic *H*), 5.87–5.77 (m, 1 H, H-5°), 5.48 (d, J = 3.2 Hz, 1 H, H-1a), 5.34 (d, J = 3.2 Hz, 1 H, H-1b), 5.22–5.10 (m, 2 H, H-6°), 4.95–4.35 (m, 14 H, 14 CH*H*), 4.11–4.00 (m, 4 H, H-5a, H-5b, H-3a, H-2°), 3.89–3.84 (m, 4 H, H-3b, H-2a, H-4°), 3.78–3.40 (m, 11 H), 1.01 (s, 9 H, 3 C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.86, 138.70, 138.58, 138.54, 138.44 (aromatic *C*), 135.68 (aromatic *C*H), 135.52 (aromatic *C*), 134.70 (C-5°), 133.44, 133.43, 133.32, 133.13 (aromatic *C*), 129.77, 129.76, 128.68, 128.43, 128.40, 128.38, 128.31, 128.23, 128.19, 128.13, 128.05, 128.01, 127.98, 127.86, 127.84, 127.73, 127.60, 127.58, 127.45, 127.41, 126.98, 126.89, 126.23, 126.21, 126.15, 125.98, 125.93 (aromatic *C*H), 117.33 (C-6°), 94.22 (C-1a), 93.60 (C-1b), 82.16 (C-5b), 81.01 (C-5a), 79.44 (C-2b), 77.76 (C-4), 77.57 (C-4), 76.29, 75.67 (*C*H_2), 75.12 (C-2°), 74.94, 74.85 (*C*H_2), 74.79 (C-2a), 73.70, 72.28, 71.91 (*C*H_2), 70.43 (C-3b), 70.34 (C-3a), 69.29, 68.22, 63.77 (*C*H_2), 27.00 (3 *C*H_3), 19.30. HR-MS: calculated for $C_{91}H_{96}O_{13}Si$ $[M + Na]^+$: 1447.6512, found: 1447.6539.

Synthesis of 31. The reaction was carried out according to the general procedure D, using **30** (460 mg, 0.32 mmol, 0.1 M in DCM : H_2O) and DDQ (170 mg, 0.75 mmol). The product was purified by silica gel column chromatography. Compound **31** (280 mg, 77% yield, pentane : EA = 4 : 1, R_f = 0.33) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +72.3 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 737, 1027, 1072, 1209, 1361, 1454, 2858, 2929. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.66–7.63 (m, 4 H, aromatic *H*), 7.41–7.07 (m, 31 H, aromatic *H*), 5.88–5.78 (m, 1 H, H-5°), 5.44 (d, J = 3.2 Hz, 1 H, H-1a), 5.34 (d, J = 3.6 Hz, 1 H, H-1b), 5.23–5.13 (m, 2 H, H-6°), 4.99–4.58 (m, 10 H, 10 CH*H*), 4.11–4.00 (m, 3 H, H-5a, H-5b, H-2°), 3.92–3.88 (m, 3 H, H-3b, H-4°), 3.76–3.51 (m, 14 H), 1.76 (s, 1 H, OH), 1.64 (s, 1 H, OH), 1.04 (s, 9 H, 3 C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.69, 138.58, 138.44, 138.38, 138.35 (aromatic *C*), 135.62, 135.61 (aromatic *C*H), 134.52 (C-5°), 133.27, 133.24 (aromatic *C*), 129.81, 128.46, 128.44, 128.41, 128.38, 128.36, 128.05, 127.87, 127.84, 127.77, 127.70, 127.67, 127.62, 127.58 (aromatic *C*H), 117.28 (C-6°), 94.19 (C-1a), 93.40 (C-1b), 81.80 (C-5b), 80.69 (C-5a), 79.65 (C-2b), 77.31 (C-4), 77.25 (C-4), 76.09, 75.57 (*C*H_2), 75.04 (C-2°), 74.93 (*C*H_2), 74.90 (C-2a), 72.24, 71.93 (*C*H_2), 71.25 (C-3b), 70.94 (C-3a), 69.84, 63.67, 61.68, 61.50 (*C*H_2), 26.93 (3 *C*H_3), 19.22. HR-MS: calculated for $C_{69}H_{80}O_{13}Si$ $[M + Na]^+$: 1167.5260, found: 1167.5280.

Synthesis of 32. Compound **31** (650 mg, 0.57 mmol) and **18** (633 mg, 2.83 mmol) were dissolved in DCM (6 mL) stirring at room temperature. Then TPyBOP (1.48 g, 2.85 mmol) and NMI (454 μL, 5.7 mmol) were added in the mixture. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial. Then the mixture was diluted with DCM. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography. Compound **29** (800 mg, 90% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +66.3 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 738, 1029, 1070, 1171, 1208, 1251, 1454, 1498, 1725, 2858, 2931. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.67–7.63 (m, 4 H, aromatic *H*), 7.41–7.06 (m, 41 H, aromatic *H*), 5.85–5.75 (m, 1 H, H-5°), 5.42–5.34 (m, 3 H, H-1a, H-1b, H-6°), 5.21–4.73 (m, 13 H), 4.59–4.50 (m, 3 H), 4.35–3.45 (m, 22 H), 1.36 (d, J = 6.8 Hz, 1 H, C*H*$_3$), 1.25 (d, J = 7.2 Hz, 1 H, C*H*$_3$), 1.04 (s, 9 H, 3 C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 172.78, 172.69, 155.62 (4 *C*=O), 138.54, 138.32, 138.26, 138.19, 136.33 (aromatic *C*), 135.62, 135.60 (aromatic *C*H), 134.46 (C-5°), 133.20 (aromatic *C*), 129.86, 128.57, 128.46, 128.40, 128.35, 128.19, 128.10, 128.03, 127.88, 127.76, 127.70, 127.66, 127.60 (aromatic *C*H), 117.39 (C-6°), 96.64 (C-1a), 93.00 (C-1b), 81.86 (C-5b), 80.79 (C-5a), 79.60, 77.36, 76.12, 75.63, 74.96, 74.68, 72.22, 71.84, 69.30, 69.12, 68.71, 66.95, 63.73, 63.66, 63.50, 49.69 (2 *C*HNH), 29.34 (*C*H$_3$), 26.95 (3 *C*H$_3$), 19.23, 18.73 (*C*H$_3$). HR-MS: calculated for $C_{91}H_{102}N_2O_{19}Si$ $[M + Na]^+$: 1577.67383, found: 1577.67285.

Synthesis of 33. A solution of **32** (600 mg, 0.38 mmol) and freshly activated molecular sieves 3A in freshly distilled THF (4 ml) was stirred under argon for 30 min. After the addition of $Ir(COD)(Ph_2MeP)_2PF_6$ (33 mg, 10 mol%) the solution turned red and the mixture was purged with H_2 until the solution turned colourless again (5–15 seconds). After stirring under argon for 4 h, the solution was diluted with THF and satd aq $NaHCO_3$. After the addition of I_2 (73 mg, 0.57 mmol), the mixture was allowed to stir overnight at room temperature. The mixture was diluted with EtOAc and washed with satd aq NaS_2O_3 and brine, respectively. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography afforded **33** (734 mg, 85%) as colourless syrup. $[\alpha]_D^{20}$ +55.9 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 737, 1027, 1069, 1168, 1208, 1258, 1454, 1498, 1720, 2858, 2929. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.66–7.64 (m, 4 H, aromatic *H*), 7.43–7.07 (m, 41 H, aromatic *H*), 5.33 (d, J = 7.2 Hz, 1 H, N*H*), 5.26 (d, J = 7.6 Hz, 1 H, N*H*), 5.11–4.73 (m, 14 H, 12 CH*H*, H-1a, H-1b), 4.52 (bt, 2 H, 2 CH*H*), 4.32–4.25 (m, 2 H, 2 C*H*NH), 4.17–3.99 (m, 6 H, H-5a, H-5b, H-3, 3 CH*H*), 3.91–3.74 (m, 5 H, H-3, H-2°, 3 CH*H*), 3.67–3.61 (m, 3 H, H-2a, 2 CH*H*), 3.50–3.42 (m, 3 H, H-2b, H-4a, H-4b), 1.35 (d, J = 6.8 Hz, 1 H, C*H*$_3$), 1.28 (d, J = 7.2 Hz, 1 H, C*H*$_3$), 1.06 (s, 9 H, 3 C*H*$_3$).^{13}C-APT ($CDCl_3$, 100 MHz) δ 172.82, 172.65, 155.65, 155.57 (4 *C*=O), 138.38, 138.15, 137.92, 137.83, 137.55, 136.29 (aromatic *C*), 135.65, 135.62 (aromatic *C*H), 133.17, 133.09 (aromatic *C*), 128.71, 128.58, 128.52, 128.48, 128.43, 128.39, 128.22, 128.20, 128.18, 128.16, 127.98, 127.95, 127.93, 127.90, 127.77, 127.73 (aromatic *C*H), 96.63 (C-1a), 95.90 (C-1b), 82.27 (C-5b), 80.14 (C-5a), 79.57 (C-2°), 77.97 (C-2b), 77.67 (C-4), 77.59 (C-4), 76.41 (C-2a), 75.95, 75.61, 75.08, 75.03, 73.81 (*C*H$_2$), 69.21 (C-3b), 69.06 (C-3a), 69.97, 63.84, 63.09, 63.03, 62.12 (*C*H$_2$), 49.68 (*C*HNH), 49.60 (*C*HNH), 26.94 (3 *C*H$_3$), 19.26, 18.70 (*C*H$_3$), 18.57 (*C*H$_3$). HR-MS: calculated for $C_{88}H_{98}N_2O_{19}Si$ $[M + Na]^+$: 1537.64253, found: 1537.64262.

Synthesis of 34. Compound **32** (610 mg, 0.4 mmol) and DMTrCl (273 mg, 0.8 mmol) were dissolved in DCM (4 mL) stirring at room temperature. Then DIPEA (283 μL, 1.6 mmol) was added in the mixture. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial. Then the mixture was diluted with DCM. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography. Compound **34** (691 mg, 95% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +118.8 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 738, 827, 1029, 1070, 1175, 1209, 1249, 1454, 1508, 1607, 1724, 2931. ^{1}H-NMR (d-acetone, 400 MHz) δ 7.74–7.68 (m, 4 H, aromatic *H*), 7.55–7.12 (m, 50 H, aromatic *H*), 6.89 (bd, 4 H, aromatic *H*), 6.82 (d, J = 7.6 Hz, 1 H, N*H*), 6.79 (d, J = 8.0 Hz, 1 H, N*H*), 5.58 (d, J = 2.8 Hz, 1 H, H-1a), 5.25 (d, J = 2.8 Hz, 1 H, H-1b), 5.15–5.05 (m, 5 H, 5 CH*H*), 4.97–4.71 (m, 6 H, 2 CH*H*), 4.56–4.11 (m, 13 H), 3.91 (dd, J_1 = 2.8 Hz, J_2 = 9.6 Hz, 1 H, H-2a), 3.82–3.66 (m, 10 H), 3.59–3.52 (m, 2 H, H-2b, H-6$_a$), 3.34–3.31 (m, 1 H, H-6$_b$), 1.49–1.45 (m, 6 H, 2 C*H*$_3$), 1.04 (s, 9 H, 3 C*H*$_3$). ^{13}C-APT (d-acetone, 100 MHz) δ 173.52, 173.41 (2 *C*=O), 159.55 (aromatic *C*), 156.90, 156.87 (2 *C*=O), 146.16, 139.99, 139.74, 139.68, 138.48, 139.32, 138.03, 137.98, 136.85, 136.69 (aromatic *C*), 136.40, 136.38 (aromatic *C*H), 134.06, 134.03 (aromatic *C*), 131.04, 131.00, 130.67, 130.65, 129.10, 129.07, 129.01, 128.95, 128.83, 128.67, 128.55, 128.40, 128.33, 128.26, 128.24, 128.17, 127.58, 114.08, 114.06 (aromatic *C*H), 94.97 (C-1a), 93.94 (C-1b), 87.37 (quaternary *C*), 82.55 (C-5a), 81.79 (C-5b), 80.87 (C-2b), 78.59 (C-4), 78.26 (C-4), 76.90 (C-2°), 76.58 (*C*H$_2$), 76.03 (C-2a), 75.86, 75.64, 75.53, 72.41 (*C*H$_2$), 70.29 (C-3b), 70.11 (C-3a), 66.93, 66.90, 64.59, 64.54, 63.86 (*C*H$_2$), 55.53 (2 O*C*H$_3$), 50.72 (2 *C*HNH), 27.39 (3 *C*H$_3$), 19.73 (quaternary *C*), 17.97 (*C*H$_3$), 17.93 (*C*H$_3$). HR-MS: calculated for $C_{109}H_{116}N_2O_{21}Si$ $[M + Na]^+$: 1839.77321, found: 1839.77281.

Synthesis of 19. Compound **33** (730 mg, 0.4 mmol) was dissolved in THF/pyridine (1 : 1/v : v, 6 mL) stirring at room temperature. Then HF-pyridine (0.4 mL) was added in the mixture. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial (10 h). Then the mixture was diluted with EtOAc. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography. Compound **19** (548 mg, 86% yield) was obtained as a colourless syrup. $[\alpha]_D^{20}$ +64.0 (c = 1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 751, 830, 1029, 1070, 1176, 1213, 1251, 1302, 1454, 1508, 1608, 1724, 2928.^{1}H-NMR (d-acetone, 400 MHz) δ 7.49–7.10 (m, 44 H, aromatic *H*), 6.87–6.73 (m, 5 H, 4 aromatic *H*, 1 N*H*), 6.74 (d, J = 7.6 Hz, 1 H, N*H*), 5.52 (d, J = 2.8 Hz, 1 H, H-1a), 5.26 (d, J = 2.8 Hz, 1 H, H-1b), 5.10–5.02 (m, 5 H, 5 CH*H*), 4.93–4.80 (m, 4 H, 2 CH*H*), 4.70–4.62 (m, 3 H), 4.56–4.48 (m, 2 H), 4.42–4.21 (m, 7 H), 4.17–4.01 (m, 4 H), 3.88–3.86 (m, 2 H), 3.75–3.47 (m, 12 H), 3.19 (dd, J_1 = 5.6 Hz, J_2 = 10.0 Hz, 1 H), 1.47–1.38 (m, 6 H, 2 C*H*$_3$). ^{13}C-APT (d-acetone, 100 MHz) δ 173.50, 173.43 (2 *C*=O), 159.60, 159.58 (aromatic *C*), 156.99, 156.89 (2 *C*═O), 146.16, 140.03, 139.77, 139.58, 139.50, 138.07, 138.04, 136.93, 136.71 (aromatic *C*), 131.07, 130.99, 129.25, 129.14, 129.13, 129.09, 129.07, 129.05, 129.04, 128.99, 128.83, 128.76, 128.67, 128.64, 128.43, 128.34, 128.25, 128.19, 128.62, 114.06, 114.04 (aromatic *C*H), 95.52 (C-1a), 93.96 (C-1b), 87.35 (quaternary *C*), 82.63, 81.72, 80.85, 78.83, 78.59, 78.29, 76.48, 76.06, 75.86, 75.63, 72.42, 70.34, 70.20, 66.92, 65.28, 64.32, 63.92, 63.43, 55.54 (2 O*C*H$_3$), 50.78 (*C*HNH), 50.74 (*C*HNH), 17.98 (2 *C*H$_3$). HR-MS: calculated for $C_{93}H_{98}N_2O_{21}$ [M + NH$_4$]$^+$: 1596.70003, found: 1596.69828.

Synthesis of 36. Compound **19** (40 mg, 0.025 mmol) and DCI (1.5 eq., 0.25 M in CH$_3$CN) was dissolved in dry CH$_3$CN (1 mL) stirring at room temperature. Then compound **35** (1.1 eq.) was added in the solution. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial (2–3 h). Then CSO (0.5 M in CH$_3$CN) was added in the mixture. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial (10–30 min). Then the mixture was diluted with DCM. The organic phase was washed with water and brine, dried with anhydrous MgSO$_4$, filtered and concentrated *in vacuo*. Crude compound **36** (50 mg) was obtained as a colourless syrup.

Synthesis of 37. Crude compound **36** (50 mg, 0.025 mmol) was dissolved in CH$_3$OH/DCM = 1 : 1 (v : v, 1 mL) stirring at room temperature. Then TsOH (0.1 eq.) was added in the solution. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial (2–3 h). Then the reaction was quenched with Et$_3$N, diluted with DCM. The organic phase was washed with water and brine, dried with anhydrous MgSO$_4$, filtered and concentrated *in vacuo*. The product was purified by size exclusion chromatography (DCM : MeOH = 1 : 1). Compound **37** (40 mg, 93%) was obtained as a colourless syrup. ^{1}H-NMR (d-acetone, 400 MHz) δ 7.47–7.05 (m, 50 H, aromatic *H*), 6.95 (d, *J* = 7.6 Hz, 1 H, 1 N*H*), 6.74 (d, *J* = 7.6 Hz, 1 H, NH), 5.42–5.35 (m, 2 H, 2 H-1), 5.12–3.58 (m, 44 H), 2.89 (s, 1 H), 1.42–1.37 (m, 6 H, 2 C*H*$_3$). ^{13}C-APT (d-acetone, 100 MHz) δ 173.52, 173.33, 156.93, 156.82 (4 *C*═O), 138.91, 139.64, 139.49, 139.39, 139.33, 138.03 (aromatic *C*), 129.36, 129.17, 129.09, 129.04, 129.02, 128.87, 128.85, 128.77, 128.71, 128.68, 128.60, 128.53, 128.52, 128.46, 128.35, 128.24, 128.22, 128.17, 128.14 (aromatic *C*H), 96.03 (C-1), 85.08 (C-1), 82.74, 81.47, 79.96, 78.89, 78.53, 77.80, 77.71, 77.67, 77.60, 76.43, 76.09, 75.93, 75.56, 73.72, 73.07, 72.50, 70.22, 70.15, 69.87, 69.84, 67.89, 67.73, 66.81, 64.14, 63.64, 61.32, 61.25, 63.43, 55.54, 50.76, 50.65 (*C*HNH), 50.74 (*C*HNH), 17.85, 17.79 (2 *C*H$_3$).^{31}P (d-acetone, 400 MHz) δ 0.77, 0.66.

Synthesis of 39. Compound **37** (40 mg, 0.023 mmol) and DCI (1.5 eq., 0.25 M in CH$_3$CN) was dissolved in dry CH$_3$CN (1 mL) stirring at room temperature. Then compound **38** (1.1 eq.) was added in the solution. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial (2–3 h). Then CSO (0.5 M in CH$_3$CN) was added in the mixture. The reaction was stirred at rt until TLC-analysis showed complete conversion of the starting martial (10–30 min). Then the mixture was diluted with DCM. The organic phase was washed with water and brine, dried with anhydrous MgSO$_4$, filtered and concentrated *in vacuo*. The product was purified by size exclusion chromatography (DCM : MeOH = 1 : 1). Compound **39** (44 mg, 88%) was obtained as a colourless syrup. ^{1}H-NMR (d-acetone, 400 MHz) δ 7.45–7.06 (m, 65 H, aromatic *H*), 6.94–6.92 (m, 1 H, 1 N*H*), 6.73 (d, *J* = 7.6 Hz, 1 H, N*H*), 5.38–5.34 (m, 2 H, 2 H-1), 5.12–3.54 (m, 57 H), 1.42–1.37 (m, 6 H, 2 C*H*$_3$). ^{13}C-APT (d-acetone, 100 MHz) δ 173.39, 173.22, 156.79, 156.68 (4 *C*═O), 139.87, 139.54, 139.51, 139.49, 139.33, 139.23, 137.88, 137.19, 137.14, 137.07, 137.02 (aromatic *C*), 129.26, 129.23, 129.11, 129.06, 129.05, 129.04, 129.00, 129.96, 129.93, 128.90, 128.87, 128.85, 128.83, 128.72, 128.68, 128.62, 128.55, 128.53, 128.45, 128.38, 128.35, 128.26, 128.20, 128.11, 128.07, 127.99, 127.97 (aromatic *C*H),96.37, 96.23 (C-1), 94.95, 94.80 (C-1), 82.60, 81.25, 80.24, 78.55, 78.24, 77.53, 77.50, 77.47, 77.45, 77.38, 76.27, 76.24, 76.07, 75.95, 75.79, 75.49, 75.43, 73.57, 72.97, 72.93, 72.87, 72.37, 72.35, 72.33, 72.31, 70.38, 70.07, 69.83, 69.79, 69.76, 69.73, 69.71, 69.67, 67.85, 67.80, 67.76, 67.69, 67.65, 66.68, 65.92, 65.87, 63.91, 63.55, 50.61 (*C*HNH), 50.51 (*C*HNH), 17.71, 17.64 (2 *C*H$_3$). ^{31}P (d-acetone, 400 MHz) δ 0.53, 0.57, 0.62, 0.65, 0.68, 0.78, 0.82. HR-MS: calculated for $C_{120}H_{130}N_2O_{29}P_2$ [M + Na]$^+$: 2147.81267, found: 2147.81610.

Synthesis of 40. Crude compound **39** (11 mg, 0.005 mmol) was dissolved in dioxane/H$_2$O = 2 : 1 (v : v, 1 mL) stirring at room temperature. Then Pd/C was added in the solution. The reaction was stirred at rt for 3 days under a H$_2$ atmosphere, filtered and concentrated *in vacuo*. Compound **40** (~5 mg, 93%) was obtained as a white solid. ^{1}H-NMR (d-acetone, 400 MHz) δ 5.42 (d, 1 H, H-1), 5.11 (d, 1 H, H-1), 4.63–4.57 (m, 2 H), 4.42–4.38 (m, 2 H), 4.21–4.15 (m, 5 H), 3.98–3.56 (m, 20 H), 3.50–3.38 (m, 2 H), 1.87 (s, 1 H), 1.57–1.53 (m, 6 H, 2 C*H*$_3$). ^{13}C-APT (d-acetone, 100 MHz) δ 170.46, 170.38 (2 *C*═O), 96.00, 94.42, 75.04, 74.70, 72.37, 72.17, 71.71, 71.54, 71.04, 70.85, 70.72, 70.68, 70.64, 70.61, 69.82, 69.43, 69.20, 66.42, 66.37, 66.32, 65.22, 64.90, 64.50, 62.47, 62.04, 62.01, 60.38, 50.45, 48.72, 16.06, 15.20. ^{31}P (d-acetone, 400 MHz) δ 1.22, 1.13. HR-MS: calculated for $C_{27}H_{52}N_2O_{25}P_2$ [M + H]$^+$: 867.24071, found: 867.24106.

Conflicts of interest

There are no conflicts to declare.

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