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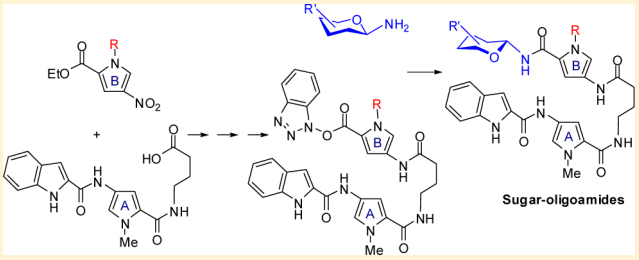
Sugar–Oligoamides: Synthesis of DNA Minor Groove Binders

Concepción Badía, Florence Souard, and Cristina Vicent*

Departamento de Síntesis, Estructura y Propiedades de los Compuestos Orgánicos, Instituto de Química Orgánica General, CSIC, c/Juan de la Cierva 3, 28006 Madrid, Spain

Supporting Information

ABSTRACT: Sugar-oligoamides have been designed and synthesized as structurally simple carbohydrate-based ligands to study carbohydrate–minor groove DNA interactions. Here we report an efficient solution-phase synthetic strategy to obtain two broad families of sugar–oligoamides. The first type, structure vector A (-Py[Me]-γ-Py-Ind), has a methyl group present as a substituent on the nitrogen of pyrrole B, connected to the C terminal of the oligoamide fragment. The second type, structure vector B (-Py[$(CH_2)_{11}$OH]-γ-Py-Ind), has an alkyl chain present on the nitrogen of pyrrole B connected to the C terminal of the oligoamide fragment and has been designed to access to di- and multivalent sugar–oligoamides. By using sequential DIPC/HOBt coupling reactions, the oligoamide fragment -Py[R]-γ-Py-Ind has been constructed. The last coupling reaction between the anomeric amino sugar and the oligoamide fragment was carried out by activating the acid derivative as a BtO- ester, which has been performed by using TFFH. The isolated esters (BtO-Py[R]-γ-Py-Ind) were coupled with selected amino sugars using DIEA in DMF. The synthesis of two different selective model vectors (vector A (**1**) and vector B (**2**)) and two types of water-soluble sugar–oligoamide ligands, with vector A structure (compounds **3**–**7**) and with vector B structure (compound **8**), was carried out.



INTRODUCTION

Over the past few decades, a number of small molecules, peptides, and proteins have been identified that target both the major and the minor grooves of B-DNA and have been shown to interfere with transcription processes.[1−6] Although there has been extensive progress in the design of small molecules capable of recognizing the minor groove of B-DNA,[4,5,7−9] a more relevant goal is the design of compounds that bind preferentially to a specific DNA sequence at a particular site.[1,10−28] For instance, a successful rational design of selective groove binders has been achieved by employing aromatic polyamides[1,3,22] and PNAs.[4,29−31] Studies of the interaction of natural glycoconjugates[7,32−34] or nuclear glycoproteins[35−38] with DNA have suggested that the glyco portion of the conjugate is responsible for sequence selectivity and that the sugar moiety of glycoproteins might act as a switch for its function.

Consequently, the study of the molecular basis of carbohydrate–DNA interactions shows great promise for the design of new carbohydrate-base selective ligands and additionally may also shed light on the molecular mechanism of action of some nuclear glycoproteins that act as transcription factors.

We have designed sugar–oligoamides as types of small molecules that bind to the minor groove of DNA. They are monosaccharide ligands designed to study carbohydrate–minor groove DNA interactions.[39−42]

The general strategy that we are carrying out to study carbohydrate–DNA interactions is to join the carbohydrate to a residue that is able to bind to the minor groove (selective vector) in order to bring monosaccharides to a selective sequence of DNA. We have chosen Py-γ-Py-Ind as the selective vector structure, which resembles the structures of the naturally occurring antibiotics distamycin A and netropsin (two minor groove binders).[43−45] We have shown that this vector can be used as a sugar carrier to target the DNA. Thus, a series of sugar–oligoamides were synthesized (R-Py-γ-Py-Ind, where R = β-Gal-, β-Glc, β-Xyl-, α-Xyl-, β-L-Fuc-),[46] and subsequent NMR studies[39,40,42] suggested that they presented a noticeable percentage of hairpin conformations in the free state, which was retained upon binding to DNA polymers.[39,40] Furthermore, competition NMR experiments suggested that the designed glycoconjugates bind to the DNA minor groove.[39] In addition, the complex formed by β-Gal-Py-γ-Py-Ind (**5**) and the Dikerson dodecamer has been elucidated, showing that β-Gal-Py-γ-Py-Ind (**5**) binds to $d(CGCGAATTCGCG)_2$ through the minor groove at the central -AATT- region of the oligonucleotide.[42]

We report a common and efficient synthetic strategy for the solution-phase synthesis of two different selective vectors (vectors A and B). As a model of vector A, Cycl-Py-γ-Py-Ind (**1**) has been synthesized; a methyl group as a substituent on the nitrogen of pyrrole B and a cyclohexyl group as the C-terminal structure are present. This general structure (-Py-γ-Py-Ind) has been used to bring simple carbohydrates to the

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selective sequence of the DNA.[39−42] As a model of vector B, Cycl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**2**) has also been synthesized. It contains an alkyl chain on the nitrogen of pyrrole B and a cyclohexyl group at the C terminus and has been designed to enable access to di- and multivalent sugar−oligoamides by modifying the extreme of the alkyl chain (Figure 1)

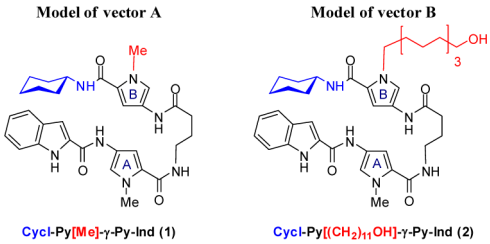

Figure 1. Models of vectors A and B: Cycl-Py-γ-Py-Ind (**1**) and Cycl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**2**).

This substitution was designed on the basis of the bound state conformation of the sugar−oligoamides (with vector A structure)[40] in the complex with *ct*DNA polymers. These data suggest that the methyl groups of the pyrroles are close to the outer region of the DNA groove; thus, its substitution would not modify the interaction properties of the ligands.

The synthetic strategy (Figure 2) we describe here allows us to obtain the two different oligoamide fragments (**II**) on a large

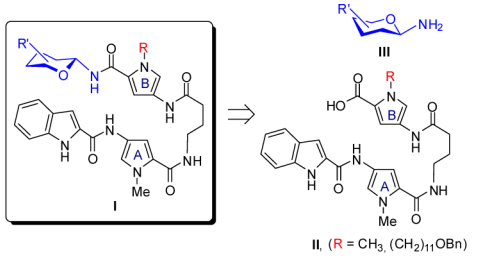

Figure 2. Retrosynthetic strategy for the solution-phase synthesis of sugar−oligoamides (**I**).

scale. The last chemical step to obtain the sugar−oligoamides (**I**) is based on the coupling of the amine with the carboxylic acid residue at the C terminal of the oligoamide. In the case of the vector models (**1** and **2**) the coupling of the oligoamide occurs with cyclohexylamine (Figure 1). Additionally, we report the synthesis of sugar−oligoamides with the vector A structure (**3**−**7**) and with the vector B structure (**8**) (Figure 3)

In previous studies regarding the solution-phase synthesis of polyamides, as well as analogues of netropsin and distamycin, the amide bonds have been constructed by preactivation of the acid (conversion to the acid chloride,[47−51] trichloroacetyl condensation reactions,[52−54] or activated esters[55]) or by in situ activation (either cyanophosphonates as DECP[56] or carbodiimide derivates[54,57−59]). Also, advances in the solid-phase synthesis of polyamides have been reported, including Boc- and Fmoc-based approaches.[60−63] Solid-phase methodologies offer many advantages for milligram-scale polyamide syntheses, including rapid and reliable amino acid couplings and facile purifications, owing to immobilization of the polyamide oligomer on a solid support. However, these techniques intrinsically limit the scale of synthesis and usually expensive reactants are needed. Conversely, efficient gram-scale solution-phase methods for polyamide synthesis are less well developed due mainly to the problem of solubility and difficult purification. Recently, Dervan et al. have developed a general solution-phase polyamide synthesis method that would allow access to gram quantities of material in high yield with minimal chromatography.[55]

Here we report a convenient solution-phase method for the synthesis of two broad families of sugar−oligoamides. The common strategy allows DNA ligands with structural diversity to be obtained, both at the C terminal and at the nitrogen of the pyrrole connected to the carbohydrate, on a convenient scale.

RESULTS AND DISCUSSION

The retrosynthetic approach for the preparation of the precursor (**II**) of the two different selective vector models (**1** and **2**) and the glyco-oligoamide type vectors A (**3**−**7**) and B (**8**) is shown in Figure 4. The common fragment for each family is compound **16**. This will be coupled with pyrrole B (**V**) to give **II**. We start with the reaction between the trichloroacetyl pyrrole **11** and the amine hydrochloride **12**, following on to a sequential method that involves the reduction of the nitro group to the corresponding amine and a subsequent coupling reaction with the corresponding carboxylic acid using DIPC/HOBt. The quantitative reduction of the nitro compound to an amine is a crucial step in utilizing the building

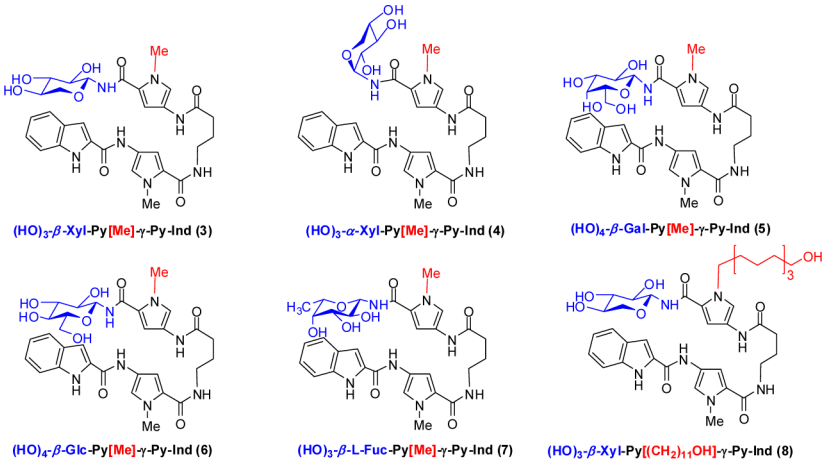

Figure 3. Sugar−oligoamides with vector A structure (**3**−**7**) and with vector B structure (**8**).

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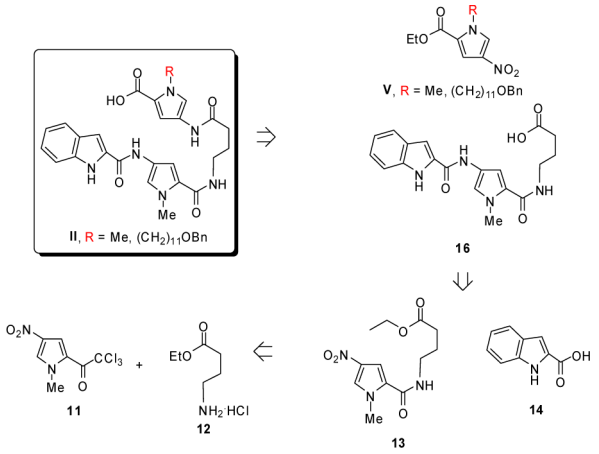

Figure 4. Retrosynthetic scheme for the synthesis of the oligoamide fragment **II**.

blocks for the construction of the oligoamide fragment by the DIPC/HOBt activation and coupling reaction.

The large-scale synthesis of HO-γ-Py-Ind (**16**), which is the common oligoamide fragment of the ligands described, is shown in Figure 5. The first two steps consist of the synthesis

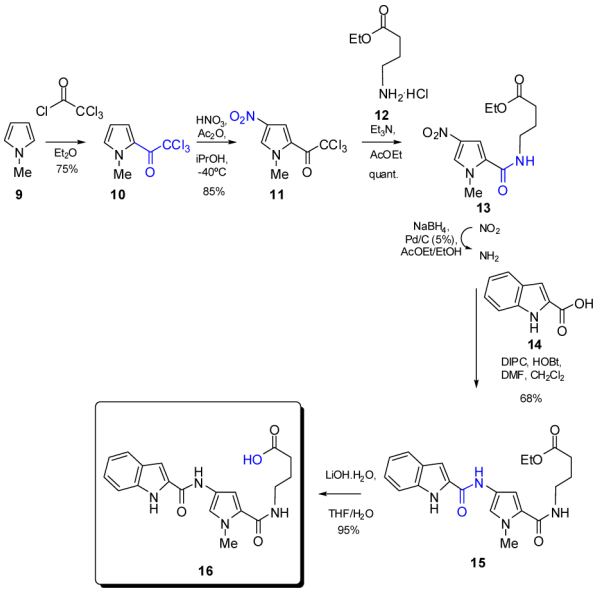

Figure 5. Scheme for the synthesis of HO-γ-Py-Ind (**16**).

of the preactivated trichloroacetyl pyrrole **11** following the procedure described in the literature.[60] Thus, **11** was coupled with *N*-(*tert*-butoxycarbonyl)-γ-aminobutyric acid **12** in the presence of triethylamine using ethyl acetate as the solvent to afford the desired compound EtO-γ-Py-NO_2 (**13**) in a quantitative yield. The main advantage of using reactants with C termini containing trichloroacetyl groups is that they are easily dissolved in $CHCl_3$, EtOAc, and EtOH. However, polyamides containing two or three heterocycles are largely insoluble in ordinary organic solvents except DMF and DMSO. This feature greatly facilitated the purification of the product, because common organic solvents could be used to wash away the reactants, leaving only product after filtration.

Afterward, by using in situ activation with DIPC/HOBt[54] in DMF, the building blocks have been effectively connected to construct the oligoamide fragment -Py[R]-γ-Py-Ind. There are two crucial elements in utilizing the building blocks for the construction of the oligoamide fragment -Py[R]-γ-Py-Ind using the DCC/HOBT coupling reaction. One is the quantitative reduction of the nitro compound to an amine, and the other is the preparation of the activated ester. The solubility of the sample is an important factor for the preparation of high-quality activated esters. Higher yields are usually associated with higher solubility of the starting materials. The reactions are carried out in DMF to be sure that all the reactants are dissolved.

The nitro group of compound **13** was reduced with $NaBH_4$ in the presence of a Pd/C catalyst to give the corresponding amino compound. The amine was obtained in 1 h and used without purification in the coupling reaction with 2-indole carboxylic acid **14** using HOBt/DIPC. This afforded the product EtO-γ-Py-Ind (**15**) in a yield of 68%. The hydrolysis of **15** with LiOH·H_2O in THF/H_2O at room temperature for 12 h gave the corresponding acid HO-γ-Py-Ind (**16**). Therefore, 8 g of the common fragment **16** for the two selective vectors was obtained with a global yield of 41% in six synthetic steps (Figure 5).

The next step in the synthetic route, as shown in the retrosynthetic scheme in Figure 4, was the introduction of the pyrrole ring B (Figure 6), in which substitution at the nitrogen atom would render diversity in the preparation of the glycooligoamides, allowing the synthesis of both families of ligands with vector A and vector B structures.

Thus, activation of the acid **16** in the presence of DIPC/HOBt in DMF followed by a coupling reaction with N-substituted amino pyrroles, which had been obtained by the reduction of N-substituted nitro pyrroles **17** and **18**, gave the oligoamides MeO-Py-γ-Py-Ind (**19**) and EtO-Py-[$(CH_2)_{11}$OBn]-γ-Py-Ind (**20**). Hydrolysis of these esters in the presence of LiOH·H_2O in dioxane/H_2O afforded the correspondencing acids HO-Py-γ-Py-Ind (**21**) and HO-Py-[$(CH_2)_{11}$OBn]-γ-Py-Ind (**22**) in yields of 91% and 90%, respectively.

Afterward, the activated esters BtO-Py-γ-Py-Ind (**23**) and BtO-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**24**) were obtained as pure solids by treatment of the corresponding acids **21** and **22** with *N*-hydroxybenzotriazole hydrate (HOBt) and fluoro-*N*,*N*,*N*′,*N*′-tetramethylformamidinium hexafluorophosphate (TFFH)[64−66] using DMF as solvent (Figure 6). This preactivation allowed us to obtain a variety of sugar oligoamide ligands with a number of different sugars attached to the C terminus.[67]

At this point, the common core of vectors A and B had been synthesized and was ready to be coupled with cyclohexylamine and the β-glycosyl amines **25**−**28**.

The synthesis of the β-glycosyl amines **25**−**28** was needed. All of them were synthesized using the synthetic sequence (i) acetylation of the free sugar using AcONa/$(AcO)_2O$ (if needed) and (ii) formation of the azide using $SnCl_4$ and trimethylsilyl azide[68] (iii) followed by catalytic hydrogenation (5% Pd−C, MeOH)[69] of the azide to obtain the amine. After purification, pure β-glycosyl amines were obtained. (Figure 7)

The next step in the synthesis of the sugar−oligoamides was the formation of the amidoglycosidic bond. The most widely employed method for the synthesis of glycosyl amides is the condensation of protected or unprotected glycosylamines with carboxylic acid derivatives. Our methodological efforts have shown that the best results are obtained by using the ester

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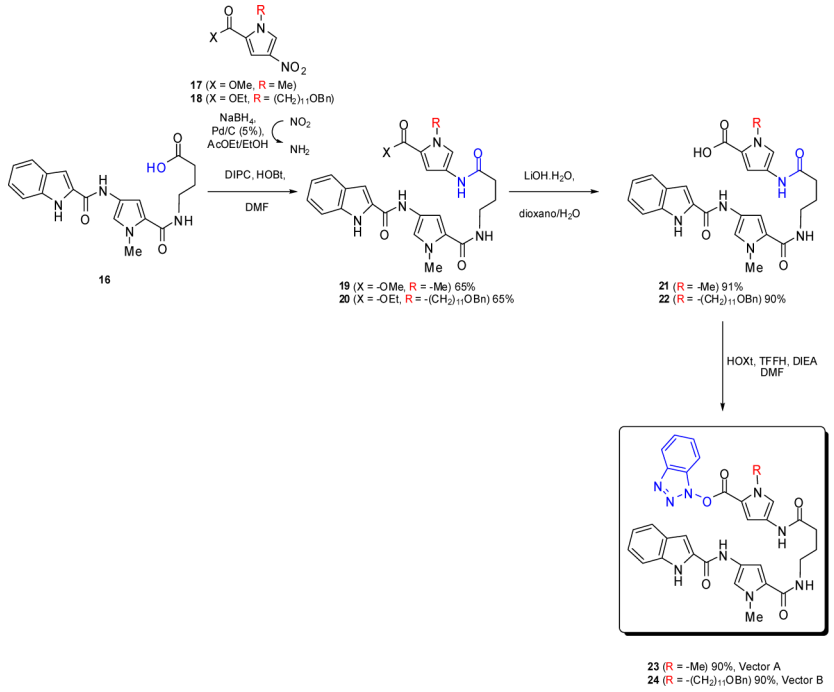

Figure 6. Scheme for the synthesis of BtO-Py[R]-γ-Py-Ind esters **23** and **24**.

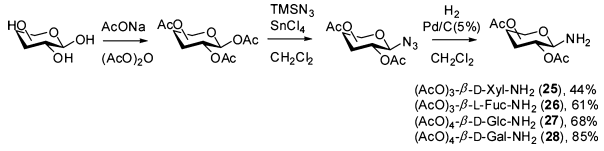

Figure 7. Scheme for the synthesis of the β-glycosyl amines **25**–**28**.

previously prepared and isolated as mentioned above, instead of the more widely used in situ activation[70−72] (Figure 8).

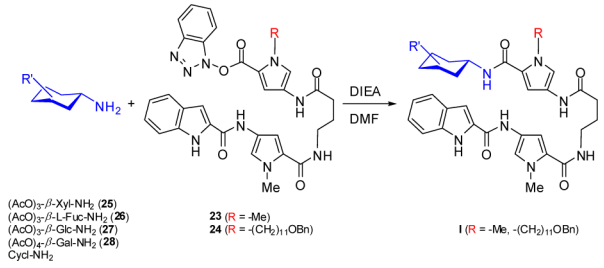

Figure 8. General scheme for the synthesis of the cyclohexyl models **1** and **29** and the protected sugar−oligoamides **30a,b**−**34a,b**).

As a result, after coupling the activated esters **23** and **24** with the corresponding β-glycosyl amines **25**−**28** the protected glyco-oligoamides **30a,b**−**34a,b** and the cyclohexyl models and **29** were obtained (Table 1). Anomerization occurred during the coupling reaction,[73] and the anomers were separated by chromatography at this step. Table 1 shows the yields of the coupling reactions as well as the differences in the α:β ratio, which were calculated using ^{1}H NMR.

For the deprotection steps of the two families of sugar−oligoamides, in the case of ligands with the vector B structure (**29** and **34**), the first step was to remove the benzyl group from the alkyl chain. Thus, the benzyl group of **29** and **34b** was removed by catalytic hydrogenolysis (Pd/C (5%), MeOH) to give Cycl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**2**) and $(AcO)_3$-β-Xyl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**35**) in yields of 90% and 85%, respectively. Then, the common and last step in the synthesis of both families of sugar−oligoamides (vector types A and B) was the deprotection of the acetylated sugar residues. Subsequently, the acetylated sugar−oligoamides **30a,b**−**33a,b** with the vector A structure and **35** with vector B structure were deprotected using MeONa/MeOH[74] to afford the target sugar−oligoamides **3**−**8** in yields between 65% and 80%.

Table 1. Results of the Coupling Reaction

amine	ester	product	α:β[a]	yield, %
Cycl-NH_2	BtO-Py[Me]-γ-Py-Ind (**23**)	Cycl-Py[Me]-γ-Py-Ind (**1**)		95
Cycl-NH_2	BtO-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**24**)	Cycl-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**29**)		70
$(AcO)_3$-β-Xyl-NH_2 (**25**)	BtO-Py[Me]-γ-Py-Ind (**23**)	$(AcO)_3$-α-/β-Xyl-Py[Me]-γ-Py-Ind (**30a,b**)	1:1	95
$(AcO)_3$-β-L-Fuc-NH_2 (**26**)	BtO-Py[Me]-γ-Py-Ind (**23**)	$(AcO)_3$-α-/β-L-Fuc-Py[Me]-γ-Py-Ind (**31a,b**)	1:3	75
$(AcO)_4$-β-Glc-NH_2 (**27**)	BtO-Py[Me]-γ-Py-Ind (**23**)	$(AcO)_4$-α-/β-Glc-Py[Me]-γ-Py-Ind (**32a,b**)	1:5	82
$(AcO)_4$-β-Gal-NH_2 (**28**)	BtO-Py[Me]-γ-Py-Ind (**23**)	$(AcO)_4$-α/β-Gal-Py[Me]-γ-Py-Ind (**33a,b**)	1:5	80
$(AcO)_3$-β-Xyl-NH_2 (**25**)	BtO-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**24**)	$(AcO)_3$-α-/β-Xyl-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**34a,b**)	1:1	60

[a]The anomer population (α:β) was measured by integration of the anomeric proton resonance in the ^{1}H NMR spectra.

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CONCLUSION

A convenient synthetic route using solution-phase methods has been developed to obtain sugar−oligoamides, DNA minor groove binders, on a convenient scale for interaction studies. Using this method, two different selective models of vectors A and B (Cycl-Py-γ-Py-Ind (**1**) and Cycl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**2**)) (Figure 1) have been obtained. Additionally, glyco-oligoamides containing β-xylose (β-Xyl-Py-γ-Py-Ind (**3**) and β-Xyl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**8**)), α-sylose (α-Xyl-Py-γ-Py-Ind (**4**)), β-galactose (β-Gal-Py-γ-Py-Ind (**5**)), β-glucose (β-Glc-Py-γ-Py-Ind (**6**)), and β-L-fucose (β-L-Fuc-Py-γ-Py-Ind (**7**)) have been reached by the same synthetic route (Figure 3). This efficient synthetic method described has been proved to be general for the synthesis of sugar−oligoamides with structural diversity both at the C terminus of the oligoamide fragment and at the pyrrole amino acid connected to the carbohydrate. This last modification allows us to assess the synthesis of divalent and multivalent DNA ligands which incorporated other sugars, amino acids, or phosphate groups.

EXPERIMENTAL SECTION

General Procedures. Flash chromatography was carried out with silica gel 60 (230−400 ASTM mesh). Silica gel 60 F254 aluminum TLC plates of 0.2 mm thickness were used to monitor the reactions. NMR spectra were obtained on 300, 400, and 500 MHz spectrometers. COSY, HSQC, and HMBC 2D-NMR experiments were performed for further assignment of the structures when required. Chemical shifts were referenced on residual solvent peaks: $CDCl_3$ (δ 7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR), DMSO-d_6 (δ 2.50 ppm for ^{1}H NMR and 39.43 ppm for ^{13}C NMR), methanol-d_4 (δ 3.31 ppm for ^{1}H NMR and 49.00 ppm for ^{13}C NMR), and acetone-d_6 (δ 2.06 ppm for ^{1}H NMR and 30.84/206.7 ppm for ^{13}C NMR). Optical rotations were measured at room temperature in a 1.0 dm cell. Mass spectra were acquired by electrospray ionization.

EtO-γ-Py-NO_2[54] (13). Et_3N (30 mL, 0.221 mol) was added dropwise to a solution of 1-methyl-4-nitro-2-trichloroacetylpyrrole (**11**;[53] 20.0 g, 0.074 mol) and ethyl-4-aminobutyrate hydrochloride (**12**; 15.0 g, 0.088 mol) in AcOEt (200 mL). After 4 h at room temperature the Et_3N hydrochloride was removed by filtration and the solvent was removed under reduced pressure to afford the title compound as a white solid (22.0 g, quantitative). Mp: 68−70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (t, J = 7.2 Hz, CH_3, 3H), 1.94 (t, J = 6.6 Hz, $CH_2\gamma_b$, 2H), 2.44 (t, J = 6.6 Hz, $CH_2\gamma_c$, 2H), 3.43 (c, J = 6.6 Hz, $CH_2\gamma_a$, 2H), 3.98 (s, CH_3, 3H), 4.16 (c, J = 7.2 Hz, CH_2, 2H), 6.59 (sa, NH, 1H), 7.09 (d, J = 1.8 Hz, CH Py, 1H), 7.55 (d, J = 1.8 Hz, CH Py, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0 (CH_3), 24.2 (CH_2), 31.8 (CH_2), 37.8 (CH_3), 39.1 (CH_2), 60.7 (CH_2), 106.9 (CH), 126.4 (C), 126.6 (CH), 134.7 (C), 160.4 (CO), 173.7 (CO). MS (ES+; m/z (%)): 284 $[M + H]^+$, 306 $[M + Na]^+$. Anal. Calcd for $C_{12}H_{17}N_3O_5$ (283.28): C, 50.88; H, 6.05; N, 14.83. Found: C, 51.02; H, 6.05; N, 15.10.

EtO-γ-Py-Ind (15). To a mixture of EtO-γ-Py-NO_2 (**13**; 22.0 g, 0.077 mol) and Pd/C (5.5 g, 5%) in AcOEt/ethanol (200 mL/200 mL) at 0 °C was added $NaBH_4$ (8.7 g, 0.231 mol) in H_2O (80 mL). After 3 h at room temperature the crude mixture was filtered through Celite to remove the Pd/C and the solvent was removed under reduced pressure to afford a brown oil. This mixture was added in CH_2Cl_2 (100 mL) to a mixture of the 2-indole carboxylic acid **14** (16.0 g, 0.098 mol) previously activated over 7 h with DMAP (12.0 g, 0.098 mol), HOBt (13.2 g, 0.098 mol), and DIPC (15.0 mL, 0.098 mol) in anhydrous CH_2Cl_2 (200 mL). After addition of the amine, the reaction mixture was stirred for 24 h. The residue was washed with HCl (1 M) and then with aqueous sodium hydrogen carbonate, dried over Na_2SO_4, and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, hexane/acetone (2/1 to 1/1)) afforded the title compound as an off-white amorphous solid (21.4 g, 68%). Mp: 165−166 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.18 (t, J = 7.0 Hz, CH_3, 3H), 1.74−1.76 (m, $CH_2\gamma_b$, 2H), 2.33 (t, J = 7.4 Hz, $CH_2\gamma_c$, 2H), 3.21 (c, J = 6.0 Hz, $CH_2\gamma_a$, 2H), 3.83 (s, CH_3, 3H), 4.05 (c, J = 7.0 Hz, CH_2, 2H), 6.88 (d, J = 1.8 Hz, CH Py, 1H), 7.05 (t, J = 7.5 Hz, CH Ind, 1H), 7.19 (t, J = 8.0 Hz, CH Ind, 1H), 7.28−7.30 (m, CH x 2, 2H), 7.46 (d, J = 7.8 Hz, CH Ind, 1H), 7.65 (d, J = 7.8 Hz, CH Ind, 1H), 8.11 (t, J = 5.8 Hz, NH, 1H), 10.31 (s, NH, 1H), 11.31 (s, NH, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.1 (CH_3), 24.8 (CH_2), 31.1 (CH_2), 36.1 (CH_3), 37.8 (CH_2), 59.8 (CH_2), 102.8 (CH), 104.1 (CH), 112.3 (CH), 118.2 (CH), 119.8 (CH), 121.6 (CH), 121.7 (C), 123.2 (C), 123.4 (CH), 127.2 (C), 131.7 (C), 136.6 (C), 158.3 (CO), 161.3 (CO), 172.8 (CO). MS (ES+; m/z (%)): 397 $[M + 1]^+$, 419 $[M + Na]^+$, 816 $[2 M + Na]^+$. IR (KBr) (cm^{-1}): 1717, 1653, 1640. Anal. Calcd for $C_{21}H_{24}N_4O_4$ (396.44): C, 63.62; H, 6.10; N, 14.13. Found: C, 63.50; H, 6.10; N, 14.00.

HO-γ-Py-Ind (16). To a solution of EtO-γ-Py-Ind (**15**; 9.0 g, 22.7 mmol) in THF (120 mL) was added LiOH·H_2O (6.3 g, 154 mmol) in a THF/H_2O mixture (70 mL/70 mL). After 12 h, the residue was washed with HCl (1 M) and extracted with AcOEt and the organic layer was dried over Na_2SO_4 and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, AcOEt (100%) to AcOEt/MeOH (4/1)) afforded the title compound as an off-white amorphous solid (8.00 g, 95%), Mp: 196−199 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.70−1.74 (m, $CH_2\gamma_b$, 2H), 2.23 (t, J = 7.3 Hz, $CH_2\gamma_c$, 2H), 3.19 (dd, J = 6.6 Hz, J = 12.6 Hz, $CH_2\gamma_a$, 2H), 3.83 (s, CH_3, 3H), 6.90 (d, J = 1.9 Hz, H-3 Py, 1H), 7.04 (ddd, J = 0.8 Hz, J = 7.1 Hz, J = 7.9 Hz, H-5 Ind, 1H), 7.19 (ddd, J = 1.0 Hz, J = 7.1 Hz, J = 8.1 Hz, H-6 Ind, 1H), 7.30 (m, H-3 Ind y H-5 Py, 2H), 7.46 (d, J = 8.3 Hz, H-7 Ind, 1H), 7.64 (d, J = 8.0 Hz, H-4 Ind, 1H), 8.20 (t, J = 5.0 Hz, NH-3, 1H), 10.42 (s, NH-2, 1H), 11.74 (s, NH-1, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.9 ($CH_2\gamma_b$), 32.0 ($CH_2\gamma_c$), 36.0 (CH_3), 38.1 ($CH_2\gamma_a$), 102.9 (C-3 Ind), 104.0 (C-3 Py), 112.2 (C-7 Ind), 118.0 (C-5 Py), 119.7 (C-5 Ind), 121.4 (C-4 Ind), 121.6 (C), 123.2 (C), 123.3 (C-6 Ind), 127.1 (C), 131.7 (C), 136.6 (C), 158.1 (CO), 161.1 (CO), 175.0 (CO). MS (ES+; m/z (%)): 369 $[M + 1]^+$, 391 $[M + Na]^+$, 759 $[2 M + Na]^+$. IR (KBr) (cm^{-1}): 3137, 2928, 1718, 1511, 1317, 1100, 847. Anal. Calcd for $C_{19}H_{20}N_4O_4$ (368.39): C, 61.95; H, 5.47; N, 15.21. Found: C, 61.67; H, 5.31; N, 15.40.

Synthesis of Vector A Glyco-Oligoamides. *MeO-Py-NO_2 (17).* A solution of Cl_3CO-Py(*B*)-NO_2[60] (**11**; 10 g, 0.037 mol) in anhydrous methanol (100 mL) was treated with MeONa (0.384 g, 0.007 mol). After the reaction mixture was stirred for 30 min, it was quenched with HCl (50 mL, 1 M); after filtration, the title compound was afforded as a white amorphous solid (6 g, 88%). ^{1}H NMR (200 MHz, $CDCl_3$):[60] δ 3.86 (s, CH_3, 3H), 3.98 (s, CH_3, 3H), 7.41 (d, J = 1.8 Hz, CH Py, 1H), 7.60 (d, J = 1.0 Hz, CH Py, 1H).

MeO-Py-γ-Py-Ind (19). A mixture of $NaBH_4$ (0.35 g, 9.2 mmol) in water (5 mL) was added dropwise to a mixture of MeO-Py-NO_2 (**17**; 0.72 g, 3.0 mmol) and Pd/C (5%) (0.70 g) in EtOAc/MeOH (10/10) at 0 °C. After the mixture was stirred for 30 min and filtered through Celite to remove the Pd/C and the solvent was evaporated, a brown oil was afforded. This mixture was added in DMF (10 mL) to the acid HO-γ-Py-Ind (**16**; 1.45 g, 3.9 mmol) previously activated during 7 h with HOBt (0.54 g, 3.9 mmol) and DIPC (0.62 mL, 3.9 mmol) in anhydrous DMF. After the addition of the amine, the reaction was stirred 24 h. The residue was washed with saturated solution of $CuSO_4$, dried over Na_2SO_4, and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, hexane/acetone (2/1 to 1/1)), affording the title compound as an off-white amorphous solid (1.2 g, 65%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.80 (t, J = 7.2 Hz, $CH_2\gamma_b$, 2H), 2.28 (t, J = 7.2 Hz, $CH_2\gamma_c$, 2H), 3.23 (c, J = 6.6 Hz, $CH_2\gamma_a$, 2H), 3.7 (s, CH_3, 3H), 3.8 (s, CH_3, 3H), 3.8 (s, CH_3, 3H), 6.7 (d, J = 1.9 Hz, CH Py, 1H), 6.9 (d, J = 1.8 Hz, CH Py, 1H), 7.05 (dt, J = 0.7 Hz, J = 7.9 Hz, CH Ind, 1H), 7.2 (dt, J = 1.0 Hz, J = 8.2 Hz, CH Ind, 1H), 7.29 (d, J = 1.7 Hz, 2H), 7.36 (d, J = 1.9 Hz, CH Py, 1H), 7.46 (dd, J = 0.6 Hz, J = 8.2 Hz, CH Ind, 1H), 7.65 (d, J = 8.0 Hz, CH Ind, 1H), 8.10 (t, J = 5.6 Hz, NH, 1H), 9.91 (sa, NH, 1H), 10.33 (sa, NH, 1H), 11.63 (d, J = 1.4 Hz, NH, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.6 (CH_2), 33.3 (CH_2), 36.1 (CH_3), 36.2 (CH_3), 38.2, (CH_2) 51.0 (OCH_3), 102.9 (CH Ind), 104.2 (CH Py), 107.7 (CH Py), 112.4 (CH Ind), 118.1 (C), 118.6 (CH Py), 119.9

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(CH Ind), 120.5 (CH Py), 121.6 (CH Ind), 121.7 (C), 122.8 (C), 123.3 (C), 123.5 (CH Ind), 127.2 (C), 131.6 (C), 136.6 (C), 158.2 (CO), 160.7 (CO), 161.2 (CO), 169.4 (CO). MS (ES+; *m*/*z* (%)): 505 $[M + H]^+$, 528 $[M + Na]^+$. IR (KBr; cm^{-1}): 3434, 3289, 1691, 1648, 1577, 1555, 1447, 1254. Anal. Calcd for $C_{26}H_{28}N_6O_5$ (504.54): C, 61.89; H, 5.59; N, 16.66. Found: C, 61.74; H, 5.60; N, 16.85.

HO-Py-γ-Py-Ind (**21**). To a solution of MeO-Py-γ-Py-Ind (**19**; 0.700 g, 1.387 mmol) in dioxane (20 mL) was added LiOH·H_2O (0.398 g, 9.709 mmol) in H_2O (20 mL). After 1 week, the residue was washed with HCl (1 M) and extracted with EtOAc and the organic layer was dried over Na_2SO_4 and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, EtOAc (100%) to EtOAc/MeOH (4/1)), affording the title compound as an off-white amorphous solid (0.620 g, 91%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.76−1.78 (m, $CH_2\gamma_b$, 2H), 2.27−2.29 (m, $CH_2\gamma_c$, 2H), 3.17−3.19 (m, $CH_2\gamma_a$, 2H), 3.78 (s, CH_3, 3H), 3.81 (s, CH_3, 3H), 6.64 (d, *J* = 2.0 Hz, CH Py, 1H), 6.90 (d, *J* = 1.8 Hz, CH, 1H), 7.05 (ddd, *J* = 0.9 Hz, *J* = 7.0 Hz, *J* = 7.9 Hz, CH Ind 5, 1H), 7.2 (ddd, *J* = 1.1 Hz, *J* = 7.0 Hz, *J* = 8.1 Hz, CH Ind, 1H), 7.28 (sa, CH × 3, 3H), 7.46 (d, *J* = 8.2 Hz, CH Ind, 1H), 7.64 (d, *J* = 8.0 Hz, CH Ind, 1H), 8.24 (t, *J* = 5.3 Hz, NH, 1H), 10.26 (s, NH, 1H), 10.81 (s, NH, 1H), 11.99 (s, NH, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 25.7 (CH_2), 33.3 (CH_2), 36.1 (2 × CH_3), 38.2 (CH_2), 104.0 (CH), 104.3 (CH), 105.5 (CH), 112.3 (CH), 118.1 (CH), 119.4 (CH), 119.7 (CH), 121.5 (CH), 121.8 (2 × C), 122.5 (C), 123.2 (C), 123.3 (CH), 127.1 (C), 131.9 (C), 136.6 (C), 158.0 (CO), 161.3 (CO), 169.3 (CO), 170.4 (CO). MS (ES+; *m*/*z* (%)): 491 $[M + H]^+$, 513 $[M + Na]^+$, 981 $[2 M + H]^+$, 1003 $[2 M + Na]^+$. IR (KBr; cm^{-1}): 3440, 3280, 1699, 1650, 1560, 1556, 1437, 1250. Anal. Calcd for $C_{25}H_{26}N_6O_5$ (490.51): C, 61.22; H, 5.34; N, 17.13. Found: C, 61.28; H, 5.30; N, 17.15.

BtO-Py-γ-Py-Ind (**23**). A mixture of HO-Py-γ-Py-Ind (**21**; 120.00 mg, 0.244 mmol), HOBt (66.33 mg, 0.488 mmol), TFFH (142.00 mg, 0.538 mmol), and DIEA (0.17 mL, 0.976 mmol) in anhydrous DMF (2.4 mL) was stirred at room temperature. After 24 h the residue was washed with saturated aqueous $CuSO_4$ and extracted with EtOAc and the organic layer was dried over Na_2SO_4 and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, hexane/EtOAc (1/40)), affording the title compound as an off-white amorphous solid (133 mg, 90%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.82−1.86 (m, $CH_2\gamma_b$, 2H), 2.34 (t, *J* = 7.4 Hz, $CH_2\gamma_c$, 2H), 3.29−3.21 (m, $CH_2\gamma_a$, 2H), 3.85 (s, CH_3, 3H), 3.87 (s, CH_3, 3H), 6.91 (d, *J* = 1.7 Hz, CH-3 Py, 1H), 7.05 (t, *J* = 7.5 Hz, CH-5 Ind, 1H), 7.19 (t, *J* = 7.6 Hz, CH-6 Ind, 1H), 7.27−7.31 (m, CH-5 Py, CH-3 Py, CH-3 Ind, 3H), 7.46 (d, *J* = 8.2 Hz, CH-7 Ind, 1H), 7.53 (t, *J* = 7.6 Hz, CH-5 BtO, 1H), 7.62−7.68 (m, CH-6 BtO, CH-4 Ind, 2H), 7.75 (d, *J* = 1.7 Hz, CH-5 Py-B, 1H), 7.83 (d, *J* = 8.3 Hz, CH-7 BtO, 1H), 8.10−8.18 (m, H-4 BtO, NH-3, 2H), 10.14 (s, NH-4, 1H), 10.30 (s, NH-2, 1H), 11.61 (s, NH-1, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.5 ($CH_2\gamma_b$), 33.2 ($CH_2\gamma_c$), 36.0 (CH_3), 36.3 (CH_3), 38.1 ($CH_2\gamma_a$), 102.7 (CH-3 Ind), 104.0 (CH-3 Py), 109.3 (CH-7 BtO), 110.3 (CH-3 Py), 112.2 (CH-7 Ind, C-2 Py B), 118.0 (CH-5 Py A), 119.7 (2 × CH-5 Ind, CH-4 BtO), 121.5 (CH-4 Ind, C-4 Py A), 123.2 (C-2 Py A), 123.3 (CH-6 Ind), 124.2 (C-4 Py B), 125.1 (CH-5 Py-B y CH-5 BtO), 127.1 (C-3a Ind), 128.6 (C-7a BtO), 129.1 (CH-6 BtO), 131.6 (C-2 Ind), 136.5 (C-7a Ind), 142.7 (C-3a BtO), 156.0 (CO-4), 158.1 (CO), 161.1 (CO), 169.7 (CO). MS (ES+; *m*/*z* (%)): 608 $[M + H]^+$, 630 $[M + Na]^+$, 1215 $[2 M + H]^+$. IR (KBr; cm^{-1}): 3354, 3105, 2926, 2856, 2477, 2353, 1764, 1649, 1577, 1523, 1496, 1461, 1408, 1190, 1153, 1101, 1001, 982, 742. Anal. Calcd for $C_{31}H_{29}N_9O_5$ (607.62): C, 61.28; H, 4.81; N, 20.75. Found: 61.35; H, 4.90; N, 20.68.

(AcO)$_3$-β-Xyl-N$_3$. A mixture of D-xylose (20.0 g, 133.2 mmol), EtOAc (5.0 g, 60.9 mmol), and anhydrous acetic acid (80.9 mL, 847.9 mmol) was refluxed. The solution was cooled, and a mixture of ice and water (200 mL) was added. The mixture was stirred for 3 h at room temperature. The mixture was filtered, and the white solid was washed with water and recrystallized in 95% ethanol (150 mL) to afford $(AcO)_4$-β-Xyl as a white solid (21 g, 80%). After that, a solution of $SnCl_4$ (221.00 μL, 1.88 mmol) in toluene (6.0 mL) was added to a suspension of $AgClO_4$ (390.00 mg, 1.88 mmol) in CH_2Cl_2 (65 mL) at room temperature. The mixture was stirred at room temperature for 1 h in the absence of light. The mixture was added to a solution of $(AcO)_4$-β-Xyl[75] (6.00 g, 18.85 mmol) and trimethylsilyl azide ($TMSN_3$; 3.07 mL, 37.70 mmol) in CH_2Cl_2. The mixture was stirred at room temperature. After 3 h the residue was washed with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2, and the organic layer was dried over Na_2SO_4 and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, hexane/AcOEt (7/3)), affording the title compound $(AcO)_3$-β-Xyl-N_3[68] as an off-white amorphous solid (5.18 g, 91.3%). Mp: 84−85 °C. $[\alpha]_D = -79.8°$ (*c* = 1 in $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.04 (s, CH_3, 3H), 2.05 (s, CH_3, 3H), 2.08 (s, CH_3, 3H), 3.43 (dd, *J* = 9.6 Hz, *J* = 11.7 Hz, CH, 1H), 4.21 (dd, *J* = 5.0 Hz, *J* = 11.7 Hz, CH, 1H), 4.63 (d, *J* = 8.0 Hz, CH-1, 1H), 4.87 (dd, *J* = 8.0 Hz, *J* = 8.8 Hz, CH, 1H), 4.97−5.01 (m, CH, 1H), 5.19 (t, *J* = 8.8 Hz, CH, 1H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 20.6 (CH_3 × 2), 20.7 (CH_3), 64.2 (CH), 68.3 (CH), 70.3 (CH), 71.4 (CH), 88.3 (CH-1), 169.3 (CO), 169.7 (CO), 170.0 (CO). MS (ES+; *m*/*z* (%)): 319 $[M + NH_4]^+$, 324 $[M + Na]^+$, 625 $[2 M + Na]^+$. Anal. Calcd for $C_{11}H_{15}O_7N_3$ (301.25): C, 43.86; H, 5.02; N, 13.95. Found: C, 43.80; H, 4.98; N, 13.89.

(AcO)$_3$-β-Xyl-NH$_2$ (**25**). To a solution of $(AcO)_3$-β-Xyl-N_3 (1.0 g, 3.32 mmol) in anhydrous CH_2Cl_2 was added Pd/C (5%) (1.0 g). The mixture was stirred under H_2 at atmospheric pressure for 2 h. The Pd/C (5%) was removed by filtration through Celite, and the filtrate was concentrated in vacuo to remove the CH_2Cl_2. Purification of the residue by column chromatography (SiO_2, hexane/AcOEt (3/2)) afforded the title compound $(AcO)_3$-β-Xyl-NH_2 (**25**)[76] as an off-white amorphous solid (0.550 g, 60%). Mp: 101−102 °C. $[\alpha]_D = -22.4°$ (*c* = 1 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, CH_3CO, 3H), 2.01 (s, CH_3CO, 3H), 2.05 (s, CH_3CO, 3H), 3.29 (t, *J* = 11.3 Hz, CH-5, 1H), 4.01 (dd, *J* = 5.7 Hz, *J* = 11.4 Hz, CH-5′, 1H), 4.08 (d, *J* = 8.9 Hz, CH-1, 1H), 4.74 (t, *J* = 9.3 Hz, CH-2, 1H), 4.95 (dc, *J* = 5.7 Hz, *J* = 9.6 Hz, CH-4, 1H), 5.21 (t, *J* = 9.5 Hz, CH-3, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.1 (CH_3CO × 2), 21.2 (CH_3CO), 63.8 (CH-5), 69.5 (CH-4), 72.3 (CH-2), 72.7 (CH-3), 85.4 (CH-1), 169.9 (CO), 169.9 (CO), 170.3 (CO). MS (ES+; *m*/*z* (%)): 276 $[M + H]^+$, 298 $[M + Na]^+$. Anal. Calcd for $C_{11}H_{17}O_7N$ (275.14): C, 47.97; H, 6.23; N, 5.17. Found: C, 48.51; H, 6.31; N:, 5.09.

(AcO)$_3$-β-L-Fuc-N$_3$. This compound was prepared as mentioned above for $(AcO)_3$-β-Xyl-N_3 from L-fucose (10.0 g, 60.9 mmol). After solvent evaporation, the residue was purified by column chromatography (SiO_2, hexane/AcOEt (7/3)), affording the title compound as an off-white amorphous solid (14.8 g, 85%). $[\alpha]_D = 10.8°$ (*c* = 0.25 in methanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (d, *J* = 6.6 Hz, CH_3, 3H), 1.98 (s, CH_3CO, 3H), 2.08 (s, CH_3CO, 3H), 2.19 (s, CH_3CO, 3H), 3.90 (dc, *J* = 6.3 Hz, *J* = 1.2 Hz, CH-5, 1H), 4.58 (d, *J* = 8.4 Hz, CH-1, 1H), 5.02 (dd, *J* = 10.2 Hz, *J* = 3.6 Hz, CH-3, 1H), 5.13 (dd, *J* = 10.2 Hz, *J* = 8.7 Hz, CH-2, 1H), 5.26 (dd, *J* = 3.3 Hz, *J* = 1.2 Hz, CH-4, 1H).

(AcO)$_3$-β-L-Fuc-NH$_2$ (**26**).[77] This compound was prepared as mentioned above for $(AcO)_3$-β-Xyl-NH_2 (**25**) from $(AcO)_3$-β-L-Fuc-N_3 (1.0 g, 3.17 mmol) to afford the title compound as an off-white amorphous solid (0.734 g, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.14 (d, CH_3, *J* = 6.5 Hz, 3H), 1.95 (s, CH_3CO, 3H), 2.04 (s, CH_3CO, 3H), 2.14 (s, CH_3CO, 3H), 3.76 (dc, *J* = 6.5 Hz, *J* = 1.0 Hz, H-5, 1H), 4.09 (d, *J* = 8.0 Hz, CH-1, 1H), 4.96 (dd, *J* = 8.0 Hz, *J* = 10.5 Hz, CH-2, 1H), 5.02 (dd, *J* = 3.0 Hz, *J* = 10.5 Hz, CH-3, 1H), 5.21 (dd, *J* = 1.0 Hz, *J* = 3.0 Hz, CH-4, 1H).

(AcO)$_4$-β-Glc-N$_3$. A solution of $(AcO)_5$-β-Glc (10.00 g, 25.6 mmol), trimethylsilyl azide ($TMSN_3$; 3.85 mL, 29.0 mmol), and fuming $SnCl_4$ (2.58 mL, 22.0 mmol) in anhydrous CH_2Cl_2 (200 mL) was stirred at room temperature. After 2 h the residue was washed with saturated aqueous $NaHCO_3$ and H_2O and extracted with EtOAc and the organic layer was dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure to afford the title compound as an off-white amorphous solid (9.5 g, 99%). Mp: 124−126 °C. $[\alpha]_D = -33.0°$ (*c* = 2.485, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.00 (s, CH_3CO, 3H), 2.02 (s, CH_3CO, 3H), 2.07 (s, CH_3CO, 3H), 2.09 (s, CH_3CO, 3H), 3.78 (ddd, *J* = 2.4 Hz, *J* = 4.6 Hz, *J* = 9.8 Hz, CH-5, 1H), 4.15 (dd, *J* = 2.4 Hz, *J* = 12.4 Hz, CH-6′), 4.27 (dd, *J* = 4.6 Hz, *J* = 12.4 Hz, CH-6), 4.64 (d, *J* = 8.8 Hz, CH-1, 1H), 4.95 (dd, *J* = 8.8 Hz, *J* = 9.2 Hz, CH-2,

1H), 5.09 (dd, J = 9.4 Hz, J = 9.5 Hz, CH-4, 1H), 5.22 (dd, J = 9.2 Hz, J = 9.4 Hz, H-3, 1H). MS (ES+; m/z): 331 [M − N_3] $^+$, 391 [M + NH_4]$^+$, 396 [M + Na]$^+$. IR (KBr; cm^{-1}): 2118, 1756, 1733, 1371, 1242, 1213, 1059, 1039.

*(AcO)$_4$-β-Glc-NH$_2$ (**27**).*[78,79] This compound was prepared as mentioned above for (AcO)$_3$-β-Xyl-NH$_2$ (**25**) from (AcO)$_4$-β-Glc-N_3 (1.0 g, 0.26 mmol) to afford the title compound as an off-white amorphous solid (0.791 g, 85%). Mp: 120−122 °C. [α]$_D$ = +11.1° (c = 0.543 in $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.00 (s, CH_3CO, 3H), 2.01 (s, CH_3CO, 3H), 2.06 (s, CH_3CO, 3H), 2.08 (s, CH_3CO, 3H), 3.70 (ddd, J = 2.4 Hz, J = 4.8 Hz, J = 9.90 Hz, CH-5, 1H), 4.12 (dd, J = 2.4 Hz, J = 12.3 Hz, CH-6′, 1H), 4.16−4.26 (m, CH-6 y CH-1, 2H), 4.82 (dd, J = 9.0 Hz, J = 9.9 Hz, CH-2, 1H), 5.03 (dd, J = 9.3 Hz, J = 9.9 Hz, CH-4, 1H), 5.28 (dd, J = 9.3 Hz, J = 9.5 Hz, CH-3, 1H). MS (ES+; m/z): 331 [M − NH_2]$^+$, 348 [M + H]$^+$, 370 [M + Na]$^+$, 694 [2 M + H]$^+$, 717 [2 M + Na]$^+$. IR (KBr; cm^{-1}): 1755, 1732, 1378, 1244, 1226, 1038.

(AcO)$_4$-β-Gal-N$_3$. This compound was prepared as mentioned above for (AcO)$_4$-β-Glc-N_3 from (AcO)$_5$-β-Gal (2.60 g, 6.66 mmol). After solvent evaporation, the residue was purified by column chromatography (SiO_2, hexane/AcOEt (7/3)), affording the title compound as an off-white amorphous solid (2.04 g, 85%). Mp: 93−95 °C. [α]$_D$ = −16.2° (c = 2.886 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, CH_3CO, 3H), 2.06 (s, CH_3CO, 3H), 2.09 (s, CH_3CO, 3H), 2.17 (s, CH_3CO, 3H), 4.01 (td, J = 1.0 Hz, J = 6.2 Hz, CH-5, 1H), 4.16 (m, CH_2-6, 2H), 4.60 (d, J = 8.6 Hz, CH-1, 1H), 5.02 (dd, J = 3.3 Hz, J = 10.3 Hz, CH-3, 1H), 5.16 (dd, J = 8.8 Hz, J = 10.3 Hz, CH-2, 1H), 5.42 (dd, J = 1.2 Hz, J = 3.3 Hz, CH-4, 1H). MS (ES+; m/z): 391 [M + NH_4]$^+$, 396 [M + Na]$^+$. IR (KBr; cm^{-1}): 2120, 1760, 1777, 1365, 1250, 128, 1067, 1029.

*(AcO)$_4$-β-Gal-NH$_2$ (**28**).*[80] This compound was prepared as mentioned above for (AcO)$_3$-β-Xyl-NH$_2$ (**25**) from (AcO)$_4$-β-Gal-N_3 (1.0 g, 0.26 mmol) to afford the title compound as an off-white amorphous solid (0.722 g, 80%). Mp: 134−136 °C. [α]$_D$ = +26.7° (c = 1.004 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.90 (s, CH_3CO, 3H), 1.97 (s, CH_3CO, 3H), 2.00 (s, CH_3CO, 3H), 2.07 (s, CH_3CO, 3H), 3.82 (dt, J = 1.0 Hz, J = 6.6 Hz, CH-5, 1H), 4.01−4.03 (m, CH_2-6, 2H), 4.08 (d, J = 8.1 Hz, CH-1, 1H), 4.94 (dd, J = 8.1 Hz, J = 10.4 Hz, CH-2, 1H), 4.97 (dd, J = 3.0 Hz, J = 10.4 Hz, CH-3, 1H), 5.32 (dd, J = 1.0 Hz, J = 3.3 Hz, CH-4, 1H). MS (ES+; m/z): 331 [M − NH_2]$^+$, 348 [M + H]$^+$, 370 [M + Na]$^+$. IR (KBr; cm^{-1}): 1760, 1738, 1384, 1248, 1230, 1040.

*(AcO)$_3$-α-/β-Xyl-Py-γ-Py-Ind (**30a,b**).* A solution of BtO-Py-γ-Py-Ind (**23**; 100 mg, 0.16 mmol), (AcO)$_3$-β-Xyl-NH_2 (**25**; 90.46 mg, 0.329 mmol), and DIEA (103.4 μL, 0.64 mmol) in anhydrous DMF was stirred at room temperature. After 72 h, the residue was washed with saturated aqueous $CuSO_4$, and extracted with AcOEt and the organic layer was dried over Na_2SO_4 and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, AcOEt (100%)), affording the title compound (AcO)$_3$-Xyl-Py-γ-Py-Ind (**30a,b**) as a mixture of α/β anomers (1/1) (92 mg, 95%). An analytical sample of the β isomer was separated and characterized. Data for (AcO)$_3$-β-Xyl-Py-γ-Py-Ind (**30b**) are as follows. [α]$_D$ = −12.88° (c = 0.1 in $CHCl_3$). ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.78−1.80 (m, $CH_2\gamma_b$, 2H), 1.91 (s, CH_3, 3H), 1.97 (s, CH_3, 3H), 2.00 (s, CH_3, 3H), 2.25−2.29 (m, $CH_2\gamma$, 2H), 3.19−3.23 (m, $CH_2\gamma$, 2H), 3.54−3.58 (m, CH, 1H), 3.77 (s, CH_3, 3H), 3.83 (s, CH_3, 3H), 3.87−3.91 (m, CH, 1H), 4.79−4.83 (m, CH, 1H), 5.06 (dd, J = 9.2 Hz, J = 9.4 Hz, CH-1, 1H), 5.28−5.32 (m, CH × 2, 2H), 6.72 (d, J = 1.4 Hz, CH, 1H), 6.89 (d, J = 1.8 Hz, CH, 1H), 7.04 (dd, J = 7.8 Hz, J = 7.2 Hz, CH, 1H), 7.18−7.22 (m, CH × 2, 2H), 7.27 (s, CH × 2, 2H), 7.45 (d, J = 8.0 Hz, CH, 1H), 7.64 (d, J = 7.8 Hz, CH, 1H), 8.10 (m, NH-3, 1H), 8.58 (d, J = 9.2 Hz, NH-5, 1H), 9.85 (s, NH-4, 1H), 10.28 (s, NH-2, 1H), 11.60 (s, NH-1, 1H). ^{13}C NMR (200 MHz, DMSO-d_6): δ 20.2 (3 × CH_3), 25.5 (CH_2), 33.2 (CH_2), 35.8 (2 × CH_3), 38.1 (CH_2), 63.2 (CH_2-5), 68.6 (CH), 70.6 (CH), 72.7 (CH), 77.6 (CH), 102.7 (CH), 104.1 (CH), 104.8 (CH),112.1 (CH), 118.0 (CH), 118.9 (CH), 119.6 (CH), 121.5 (CH), 121.9 (3 × C), 122.0 (C), 123.2 (CH), 127.0 (C), 131.6 (C), 136.5 (C), 158.1(HNCO), 160.9 (HNCO), 161.1 (HNCO), 168.9 ($COCH_3$), 169.2 ($COCH_3$), 169.4 ($COCH_3$). MS (ES+; m/z (%)): 748 [M + H]$^+$, 770 [M + Na]$^+$, 1495 [2 M + H]$^+$, 1517 [2 M + Na]$^+$. IR (KBr; cm^{-1}): 3412, 2931, 1754, 1648, 1527, 1439, 1403, 1370, 1229, 1146, 1058, 748, 604. Anal. Calcd for $C_{36}H_{41}N_7O_{11}$ (747.75): C, 57.82; H, 5.53; N, 13.11. Found: C, 57.85; H, 5.57; N, 13.16.

*(AcO)$_3$-α-/β-L-Fuc-Py-γ-Py-Ind (**31a,b**).* This compound was prepared as mentioned above for (AcO)$_3$-β-Xyl-Py-γ-Py-Ind (**30a,b**) from BtO-Py-γ-Py-Ind (**23**; 206 mg, 0.340 mmol) and (AcO)$_4$-β-Fuc-NH_2 (**26**; 200 mg, 0.68 mmol). The residue was purified by column chromatography (SiO_2, EtOAc (100%)), affording the title compound (AcO)$_3$-α-/β-L-Fuc-Py-γ-Py-Ind (**31a,b**) as mixture of α/β anomers (1/3) (195 mg, 75%). An analytical sample of the β isomer was separated and characterized. Data for (AcO)$_3$-β-L-Fuc-Py-γ-Py-Ind (**31b**) are as follows. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.17 (d, J = 6.4 Hz, CH_3, 3H), 1.93−1.97 (m, CH_2, 2H), 1.99 (s, CH_3, 3H), 2.00 (s, CH_3, 3H), 2.05 (s, CH_3, 3H), 2.30 (m, CH_2, 2H), 3.32−3.36 (m, CH_2, 2H), 3.79 (s, CH_3, 3H), 3.82 (s, CH_3, 3H), 3.92−3.96 (m, CH, 1H), 5.05−5.35 (m, 4 × CH, 4H), 6.43−6.47 (m, NH, 1H), 6.48 (d, J = 1.8 Hz, CH, 1H), 6.69 (d, J = 1.6 Hz, CH, 1H), 7.08−7.35 (m, NH + CH × 6, 7H), 7.42 (d, J = 8.2 Hz, CH, 1H), 7.63 (d, J = 7.6 Hz, CH, 1H), 8.52 (s, NH, 1H), 8.65 (s, NH, 1H), 9.87 (s, NH, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.1 (CH_3), 20.3 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 25.7 (CH_2), 33.7 (CH_2), 36.3 (CH_3), 36.6 (CH_3), 38.5 (CH_2), 68.5 (CH), 70.4 (CH), 70.7 (CH), 71.5 (CH), 78.4 (CH), 103.7 (CH), 104.6 (CH), 104.7 (CH), 112.0 (CH), 119.8 (CH), 120.5 (CH), 120.6 (CH), 121.1 (C), 121.6 (C), 121.7 (C), 121.9 (CH), 123.1 (C), 124.5 (CH), 127.5 (C), 130.7 (C), 136.7 (C), 159.5 (CO), 161.5 (CO), 162.3 (CO), 170.0 (CO), 170.4 (CO), 170.7 (CO), 171.6 (CO). MS (ES+; m/z (%)): 762 [M + H]$^+$, 1523 [2 M + H]$^+$, 1545 [2 M + Na]$^+$. IR (KBr; cm^{-1}): 3376, 2928, 1750, 1710, 1531, 1443, 1371, 1227, 1078, 912, 824, 749, 602.

*(AcO)$_4$-β-Glc-Py-γ-Py-Ind (**32b**).* This compound was prepared as mentioned above for (AcO)$_3$-β-Xyl-Py-γ-Py-Ind (**30b**) from BtO-Py-γ-Py-Ind (**23**) (330 mg, 0.540 mmol) and (AcO)$_4$-β-Glc-NH_2 (**27**; 360 mg, 1.08 mmol). (AcO)$_4$-α/β-Glc-Py-γ-Py-Ind (**32a,b**) was obtained as a mixture of anomers (α/β = 1/5). The residue was purified by column chromatography (SiO_2, AcOEt (100%)), affording the β anomer (AcO)$_4$-β-Glc-Py-γ-Py-Ind (**32b**) as a white solid (301 mg, 68%). Mp: 160−161 °C. [α]$_D$ = +10.6° (c = 1.56 in DMSO-d_6). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78−1.82 (m, $CH_2\gamma$, 2H), 1.90 (s, CH_3 (AcO), 3H), 1.94 (s, CH_3 (AcO), 3H), 1.99 (s, CH_3 (AcO), 3H), 2.00 (s, CH_3 (AcO), 3H), 2.28 (t, J = 7.4 Hz, $CH_2\gamma$, 2H), 3.21−3.25 (m, $CH_2\gamma$, 2H), 3.79 (s, CH_3, 3H), 3.84 (s, CH_3, 3H), 4.00 (dd, J = 1.9 Hz, J = 12.3 Hz, CH, 1H), 4.10 (ddd, J = 2.1 Hz, J = 4.3 Hz, J = 10.0 Hz, CH, 1H), 4.19 (dd, J = 4.5 Hz, J = 12.4 Hz, CH, 1H), 4.91 (dd, J = 9.7 Hz, J = 9.9 Hz, CH, 1H), 5.09 (dd, J = 9.3 Hz, J = 9.5 Hz, CH, 1H), 5.36 (dd, J = 9.5 Hz, J = 9.7 Hz, CH, 1H), 5.50 (dd, J = 9.3 Hz, J = 9.5 Hz, CH, 1H), 6.77 (d, J = 2.0 Hz, CH Py, 1H), 6.90 (d, J = 1.8 Hz, CH Py, 1H), 7.05−7.07 (m, CH, 1H), 7.17−7.23 (m, 2 × CH, 2H), 7.27−7.29 (m, 2 × CH, 2H), 7.46 (dd, J = 0.9 Hz, J = 8.2 Hz, CH, 1H), 7.65 (d, J = 7.9 Hz, CH, 1H), 8.09 (dd, J = 5.5 Hz, J = 5.9 Hz, CH, 1H), 8.66 (d, J = 9.5 Hz, NH, 1H), 9.84 (s, NH, 1H), 10.27 (s, NH, 1H), 11.59 (d, J = 1.8 Hz, NH, 1H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 20.3 (CH_3 (AcO)), 20.3 (CH_3 (AcO)), 20.4 (CH_3 (AcO)), 20.5 (CH_3 (AcO)), 25.6 ($CH_2\gamma$), 33.2 ($CH_2\gamma$), 36.0 (CH_3), 36.1 (CH_3), 38.2 ($CH_2\gamma$), 61.7 (CH_2-6), 67.9 (CH), 70.6 (CH), 72.0 (CH), 73.1 (CH), 77.7 (C-1), 102.8 (CH), 104.1 (CH), 104.9 (CH), 112.3 (CH), 118.1 (CH), 119.2 (CH), 119.8 (CH), 121.4 (CH), 121.5 (C), 121.6 (C), 122.2 (C), 123.3 (C), 123.4 (CH), 127.1 (C), 127.1 (C), 136.6 (C), 158.2 (CO), 160.9 (CO), 161.2 (CO), 169.0 (CO), 169.3 (CO), 169.3 (CO), 169.5 (CO), 170.0 (CO). MS (ES+; m/z (%)): 820 [M + H]$^+$, 842 [M + Na]$^+$. IR (KBr; cm^{-1}): 1749, 1645, 1234. Anal. Calcd for $C_{39}H_{45}N_7O_{13}\cdot 1.2H_2O$: C, 55.67; H, 5.68; N, 11.65. Found: C, 55.42; H, 5.49; N, 11.44.

*(AcO)$_4$-β-Gal-Py-γ-Py-Ind (**33b**).* This compound was prepared as mentioned above for (AcO)$_3$-β-Xyl-Py-γ-Py-Ind (**30b**) from BtO-Py-γ-Py-Ind (**23**; 320 mg, 0.525 mmol) and (AcO)$_4$-β-Gal-NH_2 (**28**; 364 mg, 1.05 mmol). (AcO)$_4$-α-/β-Gal-Py-γ-Py-Ind (**33a,b**) (α/β = 1/5) was obtained as a mixture of anomers (α/β = 1/5). The residue was purified by column chromatography (SiO_2, AcOEt (100%)), affording

the β anomer $(AcO)_4$-β-Gal-Py-γ-Py-Ind (**33b**) as a white solid (280 mg, 66%). Mp: 165−167 °C. $[\alpha]_D$ = +0.925° (c = 3.09 in acetone). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.80 (t, J = 7.5 Hz, $CH_2\gamma_b$, 2H), 1.91 (s, CH_3 (AcO), 3H), 1.92 (s, CH_3 (AcO), 3H), 1.99 (s, CH_3 (AcO), 3H), 2.12 (s, CH_3 (AcO), 3H), 2.29 (t, J = 7.5 Hz, $CH_2\gamma$, 2H), 3.22−3.34 (m, $CH_2\gamma$, 2H), 3.78 (s, CH_3, 3H), 3.84 (s, CH_3, 3H), 4.02 (m, 2H), 4.32 (t, J = 6.0 Hz, CH, 1H), 5.22 (t, J = 9.3 Hz, CH, 1H), 5.30 (m, 2H), 5.45 (t, J = 9.3 Hz, CH, 1H), 6.78 (s, CH Py, 1H), 6.90 (s, CH Py, 1H), 7.05 (t, J = 7.5 Hz, CH Ind, 1H), 7.20 (t, J = 7.8 Hz, CH Ind, 1H), 7.24 (s, CH, 1H), 7.28 (s, 2 × CH, 2H), 7.46 (d, J = 8.0 Hz, CH Ind, 1H), 7.65 (d, J = 8.0 Hz, CH Ind, 1H), 8.07 (m, NH, 1H), 8.74 (d, J = 9.5 Hz, NH, 1H), 9.82 (s, NH, 1H), 10.30 (s, NH, 1H), 11.58 (s, NH, 1H). ^{13}C NMR (500 MHz, DMSO-d_6): δ 20.3 (CH_3 (AcO)), 20.4 (CH_3 (AcO)), 20.4 (CH_3 (AcO)), 20.4 (CH_3 (AcO)), 25.6 ($CH_2\gamma$), 33.2 ($CH_2\gamma$), 36.0 (CH_3), 36.1 (CH_3), 38.2 ($CH_2\gamma$), 61.4 (CH_2), 67.6 (CH), 68.3 (CH), 71.1 (CH), 71.3 (CH), 77.5 (C-1), 102.8 (CH), 104.1 (CH), 104.9 (CH), 112.2 (CH), 118.0 (CH), 119.2 (CH), 119.7 (CH), 121.5 (CH), 121.5 (C), 121.6 (C), 122.1 (C), 123.3 (C), 123.3 (CH), 127.1 (C), 131.6 (C), 136.5 (C), 158.2 (CO), 160.9 (CO), 161.2 (CO), 169.0 (CO), 169.3 (CO), 169.4 (CO), 169.8 (CO), 169.9 (CO). MS (ES+; m/z (%)): 821 $[M + H]^+$, 843 $[M + Na]^+$, 1641 $[2 M + H]^+$, 1663 $[2 M + Na]^+$. IR (KBr; cm^{-1}): 1748, 1646, 1531, 1248, 1232. Anal. Calcd for $C_{39}H_{45}N_7O_{13}$ (819.81): C, 57.14; H, 5.53; N, 11.96. Found: C, 56.78; H, 5.60; N, 11.69.

Cycl-Py-γ-Py-Ind (1). This compound was prepared as mentioned above for $(AcO)_3$-β-Xyl-Py-γ-Py-Ind (**30b**) from BtO-Py-γ-Py-Ind (**23**; 305 mg, 0.50 mmol) and Cycl-NH_2 (100 mg, 1.01 mmol). The residue was purified by column chromatography (SiO_2, AcOEt (100%)), affording the title compound (550 mg, 95%). Mp: 224−226 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.25−1.27 (m, CH_2 × 2, 4H), 1.59 (d, J = 11.8 Hz, CH_2, 2H), 1.73−1.91 (m, CH_2 × 3, 6H), 2.28 (t, J = 7.5 Hz, $CH_2\gamma$, 2H), 3.20−3.22 (m, $CH_2\gamma$, 2H), 3.65 (sa, CH-1 cHx, 1H), 3.76 (s, CH_3, 3H,), 3.84 (s, CH_3, 3H), 6.69 (d, J = 1.8 Hz, CH Py, 1H), 6.89 (d, J = 1.8 Hz, CH Py, 1H), 7.02−7.07 (m, 2 × CH, 2H), 7.19 (dd, J = 7.2 Hz, J = 8.1 Hz, 1H), 7.28 (s, 2H), 7.46 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 8.08 (t, J = 5.5 Hz 1H), 9.71 (s, NH, 1H), 10.26 (s, NH, 1H), 11.58 (s, NH, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 24.9 (CH_2), 25.2 (CH_2), 25.6 (CH_2), 32.4 (CH_2), 33.2 (CH_2), 35.7 (CH_3), 35.8 (CH_3), 38.3 ($CH_2\gamma$), 47.4 (CH-1 cHx), 102.8 (CH), 103.6 (CH), 104.1 (CH), 112.2 (CH), 117.3 (CH), 118.0 (CH), 119.6 (CH), 121.4 (CH), 121.6 (C), 121.7 (C), 123.2 (C + CH), 127.1 (C), 131.6 (C), 136.5(C), 158.1 (CO), 160.2 (CO), 161.1 (CO), 169.1 (CO). MS (ES+; m/z (%)): 571 $[M + H]^+$; 594 $[M + Na]^+$. IR (KBr; cm^{-1}): 3400, 1632, 1577, 1532, 1461, 1439, 1403, 1306, 1241, 1147. Anal. Calcd for $C_{31}H_{37}N_7O_4$ (571.67): C, 65.13; H, 6.52; N, 17.15. Found: C, 64.95; H, 6.52%: N, 16.90.

$(HO)_3$-β-Xyl-Py-γ-Py-Ind (3) and $(HO)_3$-α-Xyl-Py-γ-Py-Ind (4). A solution of $(AcO)_3$-α-/β-Xyl-Py-γ-Py-Ind (**30a,b**; 100 mg, 0.133 mmol) in MeOH (10 mL) was treated with sodium methoxide (100 mg, 4.34 mmol) in MeOH (10 mL) in one portion to immediately produce a deeper yellow color, indicative of completion of the reaction. After solvent evaporation, the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH (5/1)) to afford $(HO)_3$-α/β-Xyl-Py-γ-Py-Ind (**3**/**4**) (66 mg, 81%). Both anomers are separable by column chromatography. Data for $(HO)_3$-β-Xyl-Py-γ-Py-Ind (**3**) are as follows. $[\alpha]_D$ = +5.5° (c = 1 in DMSO). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78−1.80 (m, $CH_2\gamma$, 2H), 2.28 (t, J = 7.6 Hz, $CH_2\gamma$, 2H), 3.04 (t, J = 10.8 Hz, $CH_2\gamma$, 2H), 3.10−3.36 (m, CH 4, 4H), 3.65 (m, CH, 1H), 3.77 (s, CH_3, 3H), 3.83 (s, CH_3, 3H), 4.77 (t, J = 8.8 Hz, CH-1, 1H), 4.86 (d, J = 5.6 Hz, OH), 4.95 (d, J = 5.2 Hz, OH), 5.04 (d, J = 4.8 Hz, OH), 6.83 (d, J = 1.6 Hz, CH Py, 1H), 6.89 (d, J = 2.0 Hz, CH Py, 1H), 7.05 (dd, J = 6.8 Hz, J = 8.0 Hz, CH, 1H), 7.17−7.21 (m, CH × 2, 2H), 7.28 (sa, CH Py + CH Ind, 2H), 7.45 (d, J = 8.4 Hz, CH, 1H), 7.64 (d, J = 8.0 Hz, CH, 1H), 8.12 (t, J = 5.6 Hz, NH-3, 1H), 8.35 (d, J = 8.8 Hz, NH-5, 1H), 9.83 (s, NH-4, 1H), 10.31 (s, NH-2, 1H), 11.62 (s, NH-1, 1H). ^{13}C NMR (500 MHz, DMSO-d_6): δ 26.6 (CH_2), 33.2 (CH_2), 35.9 (CH_3), 36.1 (CH_3), 38.2 (CH_2), 67.3 (CH_2), 69.7 (CH), 71.6 (CH), 77.6 (CH), 80.5 (CH-1), 102.8 (CH), 104.1 (CH), 104.6 (CH), 112.3 (CH), 118.1 (CH), 118.5 (CH), 119.7 (CH), 121.5 (CH), 121.6 (C), 121.9 (C), 122.2 (C), 123.2 (C), 123.3 (CH), 127.1 (C), 131.6 (C), 136.5 (C), 158.2 (C), 161.2 (C), 161.3 (C), 169.2 (C). MS (ES+; m/z (%)): 622 $[M + H]^+$, 644 $[M + Na]^+$. IR (KBr; cm^{-1}): 3401, 3269, 2930, 1630, 1576, 1530, 1463, 1440, 1402, 1319, 1263, 1233, 1207, 1151, 1053, 1007, 819, 747, 617. Anal. Calcd for $C_{30}H_{35}N_7O_8$ (621.64): C, 57.96; H, 5.67; N, 15.77. Found: C, 57.89; H, 5.68; N, 15.69. Data for $(HO)_3$-α-Xyl-Py-γ-Py-Ind (**4**) are as follows. $[\alpha]_D$ = −7.8° (c = 0.11 in methanol). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78−1.80 (m, $CH_2\gamma_b$, 2H), 2.28 (t, J = 7.4 Hz, $CH_2\gamma_c$, 2H), 3.21 (m, $CH_2\gamma_a$, 2H), 3.30−3.76 (m, CH × 5, 5H), 3.77 (s, CH_3, 3H), 3.83 (s, CH_3, 3H), 4.98 (s, OH, 1H), 5.04 (s, OH, 1H), 5.17 (s, OH, 1H), 5.36 (dd, J = 8.4 Hz, J = 3.2 Hz, CH-1 Xyl, 1H), 6.80 (d, J = 1.6 Hz, CH Py, 1H), 6.89 (d, J = 1.6 Hz, CH Py, 1H), 7.05 (dd, J = 7.2 Hz, J = 8.0 Hz, CH Ind, 1H), 7.17−7.21 (m, CH × 2, 2H), 7.28 (sa, CH Ind + CH Py, 2H), 7.45 (d, J = 8.4 Hz, CH Ind, 1H), 7.64 (d, J = 8.0 Hz, CH Ind, 1H), 7.70 (d, J = 8.8 Hz, NH-5, 1H), 8.11 (t, J = 5.6 Hz, NH-3, 1H), 9.81 (s, NH-4, 1H), 10.32 (s, NH-2, 1H), 11.65 (s, NH-1, 1H). ^{13}C NMR (300 MHz, DMSO-d_6): δ 21.7 ($CH_2\gamma$), 33.3 ($CH_2\gamma$), 36.1 (2 × CH_3), 38.2 ($CH_2\gamma$), 64.9 (CH_2), 68.8 (CH), 70.5 (CH), 70.6 (CH), 75.8 (CH), 102.9 (CH), 104.1 (CH), 104.6 (CH), 112.3 (CH), 118.1 (CH), 118.6 (C), 119.8 (CH), 121.5 (CH), 121.6 (CH), 122.0 (C), 122.1 (C), 123.2 (C), 123.4 (CH), 127.1 (C), 131.7 (C), 136.6 (C), 158.2 (CO), 161.1 (CO), 161.2 (CO), 169.3 (CO). MS (ES+; m/z (%)): 622 $[M + H]^+$, 644 $[M + Na]^+$. IR (KBr; cm^{-1}): 3338, 3020, 2926, 2855, 1717, 1666, 1530, 1464, 1215, 1051, 756, 668. Anal. Calcd for $C_{30}H_{35}N_7O_8$ (621.64): C, 57.96; H, 5.67; N, 15.77. Found: C, 57.99; H, 5.75; N, 15.81.

$(HO)_3$-β-L-Fuc-Py-γ-Py-Ind (7). This compound was prepared as mentioned above for $(HO)_3$-α/β-Xyl-Py-γ-Py-Ind (**3**/**4**) from $(AcO)_3$-α-/β-L-Fuc-Py-γ-Py-Ind (**31a,b**) (1/3; 100 mg, 0.131 mmol). The residue was purified by column chromatography (SiO_2, EtOAc 100% to EtOAc/MeOH 7/3), affording the title compound $(HO)_3$-α-/β-L-Fuc-Py-γ-Py-Ind (28 mg, 59%) (1:3) as a white solid. The β isomer was separated and characterized. Data for $(HO)_3$-β-L-Fuc-Py-γ-Py-Ind (**7**) are as follows. $[\alpha]_D$ = −21.43° (c = 0.1 in DMSO). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.10 (d, J = 6.3 Hz, CH_3, 3H), 1.78−1.80 (m, $CH_2\gamma_b$, CH_2, 2H), 2.27−2.29 (m, $CH_2\gamma_c$, 2H), 3.20−3.24 (m, $CH_2\gamma_a$, 2H), 3.15−3.60 (m, CH × 4, 4H), 3.79 (s, CH_3, 3H), 3.84 (s, CH_3, 3H), 4.37 (d, J = 4.2 Hz, OH, 1H), 4.58 (d, J = 5.1 Hz, OH, 1H), 4.67 (d, J = 5.7 Hz, OH, 1H), 4.80 (dd, J = 8.7 Hz, J = 9.0 Hz, CH, 1H), 6.84 (d, J = 1.8 Hz, CH Py, 1H), 6.89 (d, J = 1.8 Hz, CH Py, 1H), 7.05 (t, J = 7.4 Hz, CH Ind, 1H), 7.16−7.22 (m, CH × 2, 2H), 7.27 (s, CH × 2, 2H), 7.45 (d, J = 8.4 Hz, CH Ind, 1H), 7.64 (d, J = 7.5 Hz, CH Ind, 1H), 8.08 (t, J = 5.4 Hz, NH, 1H), 8.29 (d, J = 8.7 Hz, NH, 1H), 9.79 (s, NH, 1H), 10.27 (s, NH, 1H), 11.59 (s, NH, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 16.7 (CH_3), 25.6 (CH_2), 33.2 (CH_2), 36.1 (CH_3), 36.2 (CH_3), 38.2 (CH_2), 68.8 (CH), 71.2 (CH), 71.4 (CH), 74.5 (CH), 80.0 (CH), 102.9 (CH), 104.1 (CH), 104.5 (CH), 112.3 (CH), 118.1 (CH), 118.5 (CH), 119.7 (CH), 121.5 (CH), 121.6 (C), 121.9 (C), 122.2 (C), 123.2 (C), 123.3 (CH), 127.1 (C), 131.7 (C), 136.6 (C), 158.2 (CO), 161.2 (CO), 161.3 (CO), 169.2 (CO). MS (ES+; m/z (%)): 636 $[M + H]^+$, 658 $[M + Na]^+$, 1272 $[2 M + 2H]^+$, 1293 $[2 M + Na]^+$. IR (KBr; cm^{-1}): 3401, 2932, 2461, 2390, 1643, 1581, 1530, 1462, 1403, 1307, 1251, 1146, 1073, 746, 579. Anal. Calcd for $C_{31}H_{37}N_7O_8$ (635.67): C, 58.57; H, 5.87; N, 15.42. Found: C, 58.55; H, 5.99; N, 15.50.

$(HO)_4$-β-Gal-Py-γ-Py-Ind (5). This compound was prepared as mentioned above for $(HO)_3$-α-/β-Xyl-Py-γ-Py-Ind (**3**/**4**) from $(AcO)_4$-β-Gal-Py-γ-Py-Ind (**33b**; 92 mg, 0.112 mmol). The residue was purified by column chromatography (SiO_2, CH_2Cl_2: MeOH (5/1)), affording the title compound as a white solid (50 mg, 65%). Mp: 200 °C. $[\alpha]_D$ = +23.7° (c = 1.35 in DMSO-d_6). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78−1.80 (m, $CH_2\gamma_b$, 2H), 2.26−2.30 (m, $CH_2\gamma_a$, 2H), 3.22 (m, $CH_2\gamma_c$, 2H), 3.30−3.54 (m, 3H), 3.57−3.64 (m, 2H), 3.70 (d, J = 2.7 Hz, CH, 1H), 3,79 (s, CH_3, 3H), 3.84 (s, CH_3, 3H), 4.83 (t, J = 8.9 Hz, CH, 1H), 6.85 (d, J = 1.7 Hz, CH Py, 1H), 6.89 (d, J = 1.7 Hz, CH Py, 1H), 7.05 (t, J = 8.0 Hz, CH Ind, 1H), 7.19−7.21 (m, CH × 2, 2H), 7.28 (s, CH × 2, 2H), 7.53 (d, J = 8.2 Hz, CH Ind, 1H), 7.64 (d, J = 8.2 Hz, CH Ind, 1H), 8.12 (t, J = 5.7 Hz, NH-3), 8.36 (d, J = 8.8

Hz, NH-5, 1H), 9.83 (s, NH, 1H), 10.30 (s, NH, 1H), 11.61 (d, J = 1.5 Hz, NH, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): 25.6 ($CH_2\gamma$), 33.3 ($CH_2\gamma$), 36.0 (CH_3), 36.1 (CH_3), 38.2 ($CH_2\gamma$), 60.4 (CH_2), 66.3 (CH), 69.1 (CH), 74.3 (CH), 76.6 (CH), 80.1 (CH-1), 102.8 (CH), 104.1 (CH), 104.5 (CH), 112.2 (CH), 118.0 (CH), 118.4 (CH), 119.6 (CH), 121.4 (CH), 121.5 (C), 121.8 (C), 122.2 (C), 123.2 (CH), 127.0 (C), 131.5 (C), 136.5 (C), 141.3 (C), 158.1 (CO), 161.1 (CO), 161.1 (CO), 169.2 (CO). MS (ES+; m/z (%)): 653 [M + H]$^+$, 675 [M + Na]$^+$, 1304 [2 M + H]$^+$. IR (KBr; cm^{-1}): 3600−2500, 1643, 1584, 1530. Anal. Calcd for $C_{31}H_{37}N_7O_9$ (651.67) + 2H_2O: C, 54.14; H, 6.01; N, 14.26. Found: C, 54.14; H, 6.02; N, 14.35.

*(HO)$_4$-β-Glc-Py-γ-Py-Ind (**6**).* This compound was prepared as mentioned above for (HO)$_3$-α-/β-Xyl-Py-γ-Py-Ind (**3**/**4**) from (AcO)$_4$-β-Glc-Py-γ-Py-Ind (**32b**; 100 mg, 0.122 mmol). The residue was purified by column chromatography (SiO_2, CH_2Cl_2: MeOH (5/1)), affording the title compound as a white solid (50 mg, 65%). Mp: 196−197 °C. $[\alpha]_D$ = +12.9° (c = 0.760 in DMSO-d_6). ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.78−1.80 (m, $CH_2\gamma_b$, 2H), 2.28−2.30 (m, $CH_2\gamma_c$, 2H), 3.19−3.21 (m, $CH_2\gamma_a$, 2H), 3.63−3.65 (m, CH, 1H), 3.79 (s, CH_3, 3H), 3.84 (s, CH_3, 3H), 4.51 (t, J = 5.7 Hz, CH, 1H), 4.81 (d, J = 5.3 Hz, CH, 1H), 4.87 (d, J = 4.4 Hz, CH, 1H), 4.96 (d, J = 4.0 Hz, CH, 1H), 6.85 (d, J = 1.7 Hz, CH Py, 1H), 6.90 (d, J = 1.7 Hz, CH Py, 1H), 7.05−7.07 (m, CH, 1H), 7.18−7.20 (m, CH × 2, 2H), 7.28 (s, CH × 2, 2H), 7.46 (d, J = 8.2 Hz, CH, 1H), 7.65 (d, J = 7.9 Hz, CH Ind, 1H), 8.13 (t, J = 4.9 Hz, NH, 1H), 8.36 (d, J = 8.8 Hz, CH Ind, 1H), 9.82 (s, NH, 1H), 10.29 (s, NH, 1H), 11.60 (s, NH, 1H). ^{13}C NMR (200 MHz, DMSO-d_6): δ 25.6 ($CH_2\gamma$), 33.3 ($CH_2\gamma$), 35.8 (CH_3), 36.0 (CH_3), 38.2($CH_2\gamma$), 61.0 (CH_2^6), 70.1 (CH), 71.8 (CH), 77.6 (CH), 78.4 (CH), 79.6 (C-1), 103.2 (CH Ind), 104.1 (CH Py), 104.5 (CH Py), 112.5 (CH Ind), 118.2 (CH Py), 119.6 (CH Py), 121.5 (CH Ind), 121.8 (CH Ind), 121.8 (C), 122.2 (C), 123.2 (C), 123.2 (CH), 127.0 (C), 131.6 (C), 136.5 (C), 141.3 (C), 158.1 (CO), 161.1 (CO), 161.1 (CO), 169.6 (CO). MS (ES+; m/z (%)): 652 [M + H]$^+$, 674 [M + Na]$^+$, 1304 [2 M + H]$^+$. IR (KBr; cm^{-1}): 3600−2800, 1638, 1584, 1532. Anal. Calcd for $C_{31}H_{37}N_7O_9$ (651.67): C, 57.14; H, 5.72; N, 15.05. Found: C, 57.19; H, 5.68; N, 15.1.

Synthesis of Vector B Type Glyco-Oligoamides. *EtO-Py-[(CH$_2$)$_{11}$OBn]-NO$_2$ (**18**).* A suspension of EtO-Py-NO_2[81,82] (975 mg, 5.3 mmol), K_2CO_3 (21.970 g, 159 mmol), and $Bu_4N^+Br^-$ (1.7 mg, 0.0053 mmol) in acetonitrile (15 mL) was added dropwise to a solution of Br(CH$_2$)$_{11}$OBn[83] (2.184 mg, 6.4 mmol) in acetonitrile (15 mL). After 96 h the residue was washed with HCl (1 M) and then with aqueous sodium hydrogen carbonate, dried over Na_2SO_4, and filtered. After solvent evaporation, the residue was purified by column chromatography (SiO_2, hexane/EtOAc (20/1 to 3/1)), affording the title compound as an off-white amorphous solid (1.5 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22−1.42 (m, CH_2 × 7, 14H), 1.36 (t, J = 7.1 Hz, CH_3, 3H), 1.53−1.67 (m, CH_2CH_2O, 2H), 1.71−1.86 (m, CH_2CH_2N, 2H), 3.46 (t, J = 6.6 Hz, CH_2O, 2H), 4.32 (c, J = 7.1 Hz, J = 7.1 Hz, CH_2, 2H), 4.27−4.37 (m, CH_2N, 2H), 4.50 (s, CH_2 Bn, 2H), 7.24−7.39 (m, CH × 5 Bn, 5H), 7.43 (d, J = 2.0 Hz, CH Py), 7.61 (d, J = 2.0 Hz, CH Py). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3 EtO), 26.1 (CH_2), 26.4 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 29.4 (CH_2 × 2), 29.4 (CH_2), 29.7 (CH_2), 31.1 (CH_2), 50.4 (CH_2), 60.8 (CH_2), 70.5 (CH_2), 72.8 (CH_2), 113.0 (CH Py), 122.4 (CH Py), 126.6 (C), 127.4 (C), 127.5 (CH × 2 Bn), 127.6 (C), 128.3 (CH × 2 Bn), 138.7 (C), 159.9 (CO). MS (ES+; m/z (%)): 445.3 [M + H]$^+$, 467.1 [M + Na]$^+$, 483.1 [M + K]$^+$. IR (KBr; cm^{-1}): 3137, 2928 (CH_2), 1718 (CO), 1511 (NO_2), 1317, 1100, 847. Anal. Calcd for $C_{25}H_{36}N_2O_5$ (444.56): C, 67.54; H, 8.16; N, 6.30. Found: C, 67.29; H, 7.93; N, 6.32.

*EtO-Py[(CH$_2$)$_{11}$OBn]-γ-Py-Ind (**20**).* This compound was prepared as mentioned above for MeO-Py-γ-Py-Ind (**19**) from HO-γ-Py-Ind (**16**; 1.450 g, 3.9 mmol) and EtO-Py[(CH$_2$)$_{11}$OBn]-NO_2 (**18**; 1.4 g, 3.0 mmol). Purification of the residue by column chromatography (SiO_2, hexane/acetone (2/1; 1/1)) afforded the title compound as an off-white amorphous solid (1.9 g, 65%). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.20−1.42 (m, CH_2 × 7, 14H), 1.29 (t, J = 7.1 Hz, CH_3 EtO, 3H), 1.52−1.64 (m, CH_2CH_2O, 2H), 1.66−1.79 (m, CH_2CH_2N, 2H), 1.88−1.95 (m, CH_2 γ, 2H), 2.40 (t, J = 7.0 Hz, CH_2 γ, 2H), 3.35−3.42 (m, CH_2 γ, 2H), 3.46 (t, J = 6.5 Hz, CH_2O, 2H), 3.93 (s, CH_3, 3H), 4.22 (c, J = 7.1 Hz, J = 7.1 Hz, CH_2, 2H), 4.28−4.35 (m, CH_2N, 2H), 4.48 (s, CH_2 Bn, 2H), 6.79 (d, J = 2.0 Hz, CH Py, 1H), 6.91 (d, J = 1.9 Hz, CH Py, 1H), 7.08 (ddd, J = 8.0 Hz, J = 7.1 Hz, J = 0.9 Hz, H-5 Ind, 1H), 7.19 (d, J = 1.5 Hz, H-3 Ind, 1H), 7.24 (ddd, J = 8.2 Hz, J = 7.0 Hz, J = 1.1 Hz, H-6 Ind, 1H), 7.31 (d, J = 1.9 Hz, CH Py, 1H), 7.32−7.36 (m, CH × 5 Bn, 5H), 7.51 (d, J = 2.0 Hz, CH Py, 1H), 7.57 (d, J = 7.5 Hz, H-7 Ind, 1H), 7.64 (d, J = 8.1 Hz, H-4 Ind, 1H), 7.93 (d, J = 8.4 Hz, NH-3, 1H), 9.30 (s, NH-4, 1H), 9.67 (s, NH-2, 1H), 10.82 (s, NH-1, 1H). ^{13}C NMR (400 MHz, acetone-d_6): δ 15.4 (CH_3), 27.6 ($CH_2\gamma_b$), 27.9 (CH_2), 29.9 (CH_2), 30.12−31.17 (CH_2 × 6), 33.1 (CH_2CH_2O), 35.2 ($CH_2\gamma_c$), 37.3 (CH_3), 40.1 ($CH_2\gamma_a$), 50.1 (CH_2N), 60.8 (CH_2), 71.6 (CH_2O), 73.8 (CH_2 Bn), 103.7 (CH Ind), 105.0 (CH Py), 109.4 (CH Py), 113.7 (CH Ind), 119.6 (CH Py), 120.3 (C), 121.1 (CH Py), 121.6 (CH Ind), 123.2 (CH Ind), 123.8 (C), 124.6 (C), 124.7 (C), 125.2 (CH Ind), 128.69 (CH Bn), 128.9 (CH × 2 Bn), 129.5 (C), 129.7 (CH × 2 Bn), 133.3 (C), 138.5 (C), 140.7 (C), 159.9 (CO), 162.0 (CO), 163.2 (CO), 171.1 (CO). MS (ES+; m/z (%)): 765.3 [M + H]$^+$, 788.3 [M + Na]$^+$; IR (KBr; cm^{-1}): 3286, 2925, 1700, 1577, 1530, 1258, 1091, 811, 747. Anal. Calcd for $C_{44}H_{56}N_6O_6$ (764.95): C, 69.09; H, 7.38; N, 10.99; O, 12.55. Found: C, 68.79; H, 7.27; N, 11.01.

*HO-Py[(CH$_2$)$_{11}$OBn]-γ-Py-Ind (**22**).* This compound was prepared as mentioned above for HO-Py-γ-Py-Ind (**21**) from EtO-Py-[(CH$_2$)$_{11}$OBn]-γ-Py-Ind (**20**; 1.9 g, 2.4 mmol). The title compound was afforded as an off-white amorphous solid (1.5 g, 90%). Mp: 115−117 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 1.29−1.43 (m, CH_2 × 7, 14H), 1.54−1.64 (m, CH_2CH_2O, 2H), 1.65−1.79 (CH_2CH_2N, 2H), 1.91−1.93 (m, $CH_2\gamma_b$, 2H), 2.41 (t, J = 7.0 Hz, $CH_2\gamma_c$, 2H), 3.39 (dd, J = 6.3 Hz, J = 12.5 Hz, $CH_2\gamma_a$, 2H), 3.46 (t, J = 6.4 Hz, CH_2O, 2H), 3.93 (s, CH_3, 3H), 4.32 (t, J = 7.3 Hz, CH_2N, 2H), 4.48 (s, CH_2 Bn, 2H), 6.81 (d, J = 1.8 Hz, CH-3 Py(B), 1H), 6.92 (d, J = 1.6 Hz, CH-3 Py(A), 1H), 7.08 (t, J = 7.8 Hz, CH-5 Ind, 1H), 7.20 (d, J = 1.1 Hz, CH-3 Ind, 1H), 7.24 (t, J = 7.3 Hz, CH-6 Ind, 1H), 7.31 (d, J = 1.2 Hz, CH-5 Py(A), 1H), (7.32−7.34) (m, CH × 5 Bn, 5H), 7.56 (d, J = 1.7 Hz, CH-5 Py(B), 1H), 7.56−7.57 (m, NH-3, 1H), 7.57 (d, J = 8.1 Hz CH-7 Ind, 1H), 7.63 (d, J = 8.1 Hz, CH-4 Ind, 1H), 9.32 (s, NH-4, 1H), 9.68 (s, NH-2, 1H), 10.85 (s, NH-1, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ 27.6 (CH_2), 28.1 (CH_2), 28.6 (CH_2), 30.0−31.0 (CH_2 γ + CH_2 × 5), 33.6 (CH_2CH_2O), 35.7 ($CH_2\gamma$), 37.8 (CH_3), 40.5 ($CH_2\gamma$), 50.5 (CH_2N), 72.1 (CH_2O), 74.3 (CH_2 Bn), 104.1 (CH Ind), 105.4 (CH Py), 110.2 (CH Py), 114.1 (CH Ind), 120.1 (CH Ind), 120.2 (C), 121.7 (CH Ind), 122.1 (CH Ind), 123.7 (C), 124.2 (C), 124.3 (C), 125.0 (C), 125.1 (C), 125.8 (CH Py), 129.2 (CH Bn), 129.4 (CH × 2 Bn), 129.9 (C), 130.2 (CH × 2 Bn), 133.7 (C), 138.8 (C), 141.3 (C), 163.2 (CO), 171.5 (CO), 171.6 (CO); MS (ES−; m/z): 735.3 [M − H]$^-$, 736.3 [M]$^-$. IR (KBr; cm^{-1}): 3434, 2927, 2252, 2126, 1703, 1663, 1537, 1234, 1053, 1027, 1006, 823, 761. Anal. Calcd for $C_{42}H_{52}N_6O_6$ (736.90): C, 68.46; H, 7.11; N, 11.40; O, 13.03. Found: C, 68.15; H, 7.26; N, 11.54.

*BtO-Py[(CH$_2$)$_{11}$OBn]-γ-Py-Ind (**24**).* This compound was prepared as mentioned above for BtO-Py-γ-Py-Ind (**23**) from HO-Py-[(CH$_2$)$_{11}$OBn]-γ-Py-Ind (**22**; 1.51 g, 2.04 mmol). The title compound was afforded as an off-white amorphous solid (1.6 g, 90%). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.14−1.40 (m, CH_2 × 7, 14H), 1.52−1.60 (m, CH_2CH_2O, 2H), 1.68−1.80 (m, CH_2CH_2N, 2H), 1.93−2.00 (m, $CH_2\gamma_b$, 2H), 2.47 (t, J = 7.0 Hz, CH_2 γ, 2H), 3.40−3.46 (m, CH_2 γ, 2H), 3.44 (t, J = 6.5 Hz, CH_2O, 2H), 3.93 (s, CH_3, 3H), 4.28−4.34 (m, CH_2N, 2H), 4.47 (s, CH_2 Bn, 2H), 6.69 (d, J = 1.7 Hz, CH Py, 1H), 7.08 (ddd, J = 1.0 Hz, J = 7.0 Hz, J = 8.0 Hz, CH-5 Ind, 1H), 7.19 (dd, J = 0.7 Hz, J = 2.0 Hz, CH-3 Ind, 1H), 7.23 (ddd, J = 1.2 Hz, J = 7.0 Hz, J = 8.2 Hz, CH-6 Ind, 1H), 7.31 (d, J = 1.8 Hz, CH Py, 1H), 7.31−7.36 (m, CH × 5 Bn, 5H), 7.37 (d, J = 1.2 Hz, CH Py, 1H), 7.48−7.53 (m, CH BtO, 1H), 7.55−7.58 (m, NH-3, 1H), 7.56 (dd, J = 0.9 Hz, J = 8.3 Hz, CH-7 Ind, 1H), 7.62 (dd, J = 0.8 Hz, J = 8.0 Hz, CH-4 Ind, 1H), 7.62−7.67 (m, CH BtO, 1H), 7.75 (td, J = 0.9 Hz, J = 8.4 Hz, CH BtO, 1H), 7.91 (d, J = 1.9 Hz, CH Py, 1H), 8.09 (td, J = 0.9 Hz, J = 8.4 Hz, CH BtO, 1H), 9.63 (s, NH-4, 1H), 9.74 (s, NH-2, 1H), 10.86 (s, NH-1, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 27.5 ($CH_2\gamma$), 28.0 (CH_2), 28.1 (CH_2), 30.3 (CH_2), 30.8 (CH_2), 31.2

(CH_2), 31.3 (CH_2), 31.4 (CH_2), 31.5 (CH_2CH_2O), 33.1, (CH_2CH_2N), 35.6 ($CH_2\gamma$), 37.7 (CH_3), 40.4 ($CH_2\gamma$), 50.9 (CH_2N), 71.9 (CH_2O), 74.1 (CH_2 Bn), 104.1 (C-3 Ind), 105.5 (CH Py), 110.8 (CH HOBt), 112.6 (CH Py), 114.1 (C-7 Ind), 120.0 (CH Py), 121.9 (CH BtO), 122.0 (C-6 Ind), 123.6 (CH BtO), 124.2 (C), 125.5 (C), 125.6 (C-4 Ind), 126.0 (C), 126.3 (CH Ind), 126.6 (CH Py), 126.7 (CH BtO), 129.1 (CH), 129.2 (CH × 2 Bn), 129.8 (C), 130.0 (CH × 2 Bn), 130.7 (CH), 131.1 (C), 133.6 (C), 141.2 (C), 145.3 (C), 158.15 (CO), 160.3 (CO), 163.7 (CO), H172.0 (CO). MS (ES+; *m*/*z*): 855 $[M + 1]^+$, 877 $[M + Na]^+$. IR (KBr; cm^{-1}): 3417, 3286, 3132, 2929, 2855, 1774, 1641, 1581, 1407, 1308, 1252, 1147, 1096, 965, 851, 781, 744, 558. Anal. Calcd for $C_{48}H_{55}N_9O_6$ (854.01): C, 67.51; H, 6.49; N, 14.76; O, 11.24. Found: C, 67.58; H, 6.55; N, 14.82.

Cycl-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**29**). This compound was prepared as mentioned above for $(AcO)_3$-α-/β-Xyl-Py-γ-Py-Ind (**30a,b**) from BtO-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**24**; 1.20 g, 1.4 mmol) and cHx-NH_2 (277 mg, 2.8 mmol). Purification of the residue by column chromatography (SiO_2, AcOEt (100%)) afforded the title compound as an off-white amorphous solid (800 mg, 70%). Mp: 122−125 °C; ^{1}H NMR (acetone-d_6, 400 MHz): δ 1.00−1.40 (m, CH_2 × 7 + CH_2 × 2 cHx, 18H), 1.40−1.60 (m, CH_2CH_2O, + CH_2 cHx, 4H), 1.6−1−75 (m, CH_2CH_2N + CH_2 cHx, 4H), 1.75−1.95 (m, $CH_2\gamma_b$ + CH_2 cHx, 4H), 2.35 (t, *J* = 7.1 Hz, $CH_2\gamma_c$, 2H), 3.30−3.40 (m, $CH_2\gamma_a$, 2H), 3.42 (t, *J* = 6.5 Hz, CH_2O, 2H), 3.70−3.90 (m, CH-1 cHx, 1H), 3.98 (s, CH_3, 3H), 4.28 (t, *J* = 7.2 Hz, CH_2N, 2H), 4.47 (s, CH_2 Bn, 2H), 6.65 (d, *J* = 1.9 Hz, CH Py, 1H), 6.91 (d, *J* = 1.9 Hz, CH Py, 1H), 7.05 (ddd, *J* = 8.0 Hz, *J* = 7.0 Hz, *J* = 1.0 Hz, CH Ind, 1H), 7.05 (d, *J* = 8.1 Hz, NH-5), 7.20−7.22 (m, CH Ind, 1H), 7.22−7.24 (m, CH Py + CH Ind, 2H), 7.29−7.32 (m, CH × 5 Bn + CH Py, 6H), 7.50 (m, CH Ind + NH-3, 2H), 7.60 (d, *J* = 8.0 Hz, CH Ind, 1H), 9.27 (s, NH-4, 1H), 9.77 (s, NH-2, 1H), 10.93 (s, NH-1, 1H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 26.5 (CH_2), 27.0 (CH_2 × 2), 27.3 (CH_2), 27.6 (CH_2), 27.9 (CH_2 × 2), 28.3 (CH_2), 31.0 (CH_2), 31.2 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 31.3 (CH_2), 31.5 (CH_2), 33.7 (CH_2), 34.7 ($CH_2\gamma$), 37.7 (CH_3), 40.4, ($CH_2\gamma$), 49.9 (CH-1 cHx), 50.0 (CH_2N), 71.9 (CH_2O), 74.9 (CH_2 Bn), 104.2 (CH Ind), 105.1 (CH Py), 105.5 (CH Py), 114.0 (CH Ind), 118.5 (CH Py), 120.2 (CH Py), 121.9 (CH Ind), 123.5 (C), 124.1 (C), 124.2 (CH Ind), 125.1 (C), 125.4 (C), 125.6 (CH Ind), 129.0 (CH Bn), 129.2 (CH × 2 Bn), 129.8 (C), 130.0 (CH × 2 Bn), 133.6 (C), 138.8 (C), 141.1 (C Bn), 160.4 (C), 162.7 (CO), 171.4 (CO), 171.4 (CO), 171.5 (CO). MS (ES+; *m*/*z* (%)): 818.3 $[M + H]^+$, 819.3 $[M + 3]^+$. IR (KBr; cm^{-1}): 3428, 3302, 2928, 2853, 1635, 1578, 1524, 1451, 1401, 1307, 1251, 1145, 1101, 773, 745, 698. Anal. Calcd for $C_{48}H_{63}N_7O_5$: C, 70.47; H, 7.76; N, 11.99; O, 9.78. Found: C, 70.18; H, 7.48; N, 11.98.

$(AcO)_3$-α-/β-Xyl-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**34a,b**). This compound was prepared as mentioned above for $(AcO)_3$-α-/β-Xyl-Py-γ-Py-Ind (**30a,b**) from BtO-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**24**; 1.22 g, 1.4 mmol) and $(AcO)_3$-β-Xyl-NH_2 (**25**; 790 mg, 2.8 mmol). The residue was purified by column chromatography (SiO_2, EtOAc (100%)), affording the title compound as a mixture of anomers (α/β = 1/1) (840 mg, *R* = 60%). The anomers were separated by column chromatography. Data for $(AcO)_3$-β-Xyl-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**34b**) are as follows. Mp: 95−97 °C. $[\alpha]_D$ = −35.33° (*c* = 0.15 in acetone). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.18−1.42 (m, CH_2 × 7, 14H), 1.54−1.64 (m, CH_2CH_2O, 2H), 1.64−1.75 (m, CH_2CH_2N, 2H), 1.91 (t, *J* = 6.8 Hz, $CH_2\gamma$, 2H), 1.95 (s, CH_3 (AcO), 3H), 1.99 (s, CH_3 (AcO), 3H), 2.00 (s, CH_3 (AcO), 3H), 2.39 (t, *J* = 7.0 Hz, CH_2 γ, 2H), 3.35−3.43 (m, CH_2 γ, 2H), 3.46 (t, *J* = 6.5 Hz, CH_2O, 2H), 3.57 (t, *J* = 11.0 Hz, CH-5ec Xyl, 1H), 3.92 (s, CH_3), 4.00 (dd, *J* = 11.3 Hz, *J* = 5.9 Hz, CH-5ax Xyl, 1H), 4.23−4.38 (m, CH_2N, 2H), 4.48 (s, CH_2 Bn, 2H), 4.90−4.96 (m, CH-4 Xyl, 1H), 5.05 (t, *J* = 9.4 Hz, CH-2 Xyl, 1H), 5.35 (t, *J* = 9.6 Hz, CH-3 Xyl, 1H), 5.40 (t, *J* = 9.5 Hz, CH-1 Xyl, 1H), 6.65 (d, *J* = 1.8 Hz, CH-3 Py B, 1H), 6.92 (d, *J* = 1.8 Hz, CH-3 Py A, 1H), 7.08 (t, *J* = 7.1 Hz, CH-6 Ind, 1H), 7.20 (d, *J* = 1.5 Hz, CH-3 Ind, 1H), 7.24 (ddd, *J* = 1.0 Hz, *J* = 7.1 Hz, *J* = 8.2 Hz, CH-5 Ind, 1H), 7.31 (d, *J* = 1.8 Hz, CH Py, 1H), 7.32−7.35 (m, CH × 5 Bn, 5H), 7.44 (d, *J* = 1.8 Hz, CH Py, 1H), 7.52 (t, *J* = 5.6 Hz, NH-3, 1H), 7.56 (d, *J* = 8.3 Hz, CH-4 Ind, 1H), 7.63 (d, *J* = 8.7 Hz, NH-5, 1H), 7.77 (d, *J* = 10.2 Hz, CH-7 Ind, 1H), 9.32 (s, NH-4, 1H), 9.68 (s, NH-2, 1H), 10.88 (s, NH-1, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 21.7 (CH_3 (AcO)), 21.8 (CH_3 (AcO)), 21.9 (CH_3 (AcO)), 27.6 ($CH_2\gamma$), 28.0 (CH_2), 28.4 (CH_2), 30.0 (CH_2CH_2O + CH_2 × 4), 33.7 (CH_2CH_2N), 35.6 ($CH_2\gamma$), 37.7 (CH_3), 40.5 ($CH_2\gamma$), 50.4 (CH_2N), 65.8 (CH_2-5 Xyl), 71.0 (CH-4 Xyl), 72.9 (CH_2O), 74.2 (CH-2 Xyl), 74.6 (CH_2 Bn), 74.8 (CH-3 Xyl), 80.5 (CH-1 Xyl), 104.1 (CH-3 Ind), 105.1 (CH Py), 106.2 (CH Py), 114.2 (CH-4 Ind), 120.1 (CH Py), 120.5 (CH Py), 122.0 (CH-6 Ind), 123.3 (CH-7 Ind), 123.6 (CH-5 Ind), 124.2 (C), 125.6 (C), 125.7 (C), 129.1 (CH Bn), 129.3 (CH × 2 Bn), 129.9 (C), 130.1 (CH × 2 Bn), 133.7 (C), 138.9 (C), 141.2 (C Bn), 160.4 (CO), 162.9 (CO), 163.7 (CO), 171.2 (CO), 171.4 (CO AcO), 171.5 (CO AcO), 171.7 (CO AcO); MS (ES+; *m*/*z* (%)):994.5 $[M + H]^+$, 995.5 $[M + 2]^+$, 1016.5 $[M + Na]^+$, 1017.5 $[M + Na + 1]^+$; IR (KBr; cm^{-1}): 3379, 2928, 2855, 1755, 1654, 1579, 1526, 1441, 1403, 1369, 1307, 1227, 1145, 1064, 1036, 937, 903, 812, 747, 698, 605; Anal. Calcd for $C_{53}H_{67}N_7O_{12}$ (994.14): C, 64.03; H, 6.79; N, 9.86; O, 19.31. Found: C, 63.79; H, 6.58; N, 9.81. Data for $(AcO)_3$-α-Xyl-Py-[$(CH_2)_{11}$OBn]-γ-Py-Ind (**34a**) are as follows. Mp: 90−95 °C. $[\alpha]_D$ = 12.74° (*c* = 1 in acetone). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.18−1.41 (m, CH_2 × 7, 14H), 1.53−1.64 (m, CH_2CH_2O, 2H), 1.64−1.76 (m, CH_2CH_2N, 2H), 1.89−1.94 (m, CH_2 γ, 2H), 2.02 (s, CH_3 (AcO), 3H), 2.04 (s, CH_3 (AcO), 3H), 2.06 (s, CH_3 (AcO), 3H), 2.39 (t, *J* = 7.0 Hz, CH_2 γ, 2H), 3.36−3.41 (m, CH_2 γ, 2H), 3.46 (t, *J* = 6.5 Hz, CH_2O, 2H), 3.87 (dd, *J* = 5.6 Hz, *J* = 12.6 Hz, CH_2-5 Xyl, 2H), 3.93 (s, CH_3, 3H), 4.27−4.32 (m, CH_2N, 2H), 4.48 (s, CH_2 Bn, 2H), 4.83 (dt, *J* = 4.4 Hz, *J* = 6.8 Hz, CH-4 Xyl, 1H), 4.95 (dd, *J* = 4.2 Hz, *J* = 7.4 Hz, CH-2 Xyl, 1H), 5.46 (t, *J* = 7.1 Hz, CH-3 Xyl, 1H), 5.92 (dt, *J* = 3.8 Hz, *J* = 7.5 Hz, CH-1 Xyl, 1H), 6.85 (d, *J* = 1.8 Hz, CH Py, 1H), 6.93 (d, *J* = 1.9 Hz, CH Py, 1H), 7.08 (ddd, *J* = 1.0 Hz, *J* = 7.0 Hz, *J* = 8.0 Hz, CH-6 Ind, 1H), 7.20 (d, *J* = 0.6 Hz, CH-3 Ind, 1H), 7.24 (ddd, *J* = 1.1 Hz, *J* = 7.0 Hz, *J* = 8.2 Hz, CH-5 Ind, 1H), 7.32 (d, *J* = 1.8 Hz, CH Py, 1H), 7.32−7.35 (m, CH × 5 Bn), 7.38 (d, *J* = 1.9 Hz, CH Py), 7.56 (dd, *J* = 8.3 Hz, *J* = 0.7 Hz CH-4 Ind, 1H), 7.50−7.60 (sa, NH-3, 1H), 7.63 (d, *J* = 8.0 Hz, CH-7 Ind, 1H), 8.03 (d, *J* = 9.4 Hz, NH-5, 1H), 9.33 (s, NH-4, 1H), 9.73 (s, NH-2, 1H), 10.87 (s, NH-1, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 21.7 (CH_3 (AcO)), 21.7 (CH_3 (AcO)), 21.7 (CH_3 (AcO)), 27.6 ($CH_2\gamma_b$), 27.9 (CH_2), 28.3 (CH_2), 30.9 (CH_2), 31.1 (CH_2), 31.1 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 31.5 (CH_2), 33.6 (CH_2CH_2N), 35.4 ($CH_2\gamma$), 37.6 (CH_3), 39.7, ($CH_2\gamma$), 50.2 (CH_2N), 63.5 (CH_2-5 Xyl), 69.8 (CH-4 Xyl), 70.2 (CH-2 Xyl), 70.9 (CH-3 Xyl), 71.9 (CH_2O), 74.1 (CH_2 Bn), 80.5 (CH-1 Xyl), 104.1 (CH Ind), 105.3 (CH Py), 106.9 (CH Py), 114.0 (CH Ind), 119.9 (CH Py), 120.1 (CH Ind), 121.9 (CH Ind), 123.3 (C), 123.3 (C), 123.5 (CH Ind), 124.0 (C), 124.4 (C), 125.6 (CH Py), 129.0 (CH Bn), 129.2 (CH × 2 Bn), 129.7 (C), 130.0 (CH × 2 Bn), 138.7 (C), 138.8 (C), 141.1 (C Bn), 163.1 (CO), 163.6 (CO), 163.6 (CO), 170.9 (CO), 171.2 (CO (AcO)), 171.3 (CO (AcO)), 171.4 (CO (AcO)). MS (ES+; *m*/*z*): 994.5 $[M + H]^+$, 995.5 $[M + 2H]^+$, 1016.5 $[M + Na]^+$, 1017.5 $[M + Na + H]^+$. IR (KBr; cm^{-1}): 3377, 2928, 2854, 1753, 1646, 1579, 1523, 1440, 1403, 1369, 1307, 1223, 1145, 1044, 874, 804, 746, 698, 638, 604. Anal. Calcd for $C_{53}H_{67}N_7O_{12}$: C, 64.03; H, 6.79; N, 9.86; O, 19.31. Found: C, 64.07; H, 6.82; N, 9.89.

Cycl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**2**). To a solution of Cycl-Py-[$(CH_2)_{11}$OBn]-γ-Py-Ind (**29**; 60 mg, 0.085 mmol) in methanol was added Pd/C (5%) (180 mg). The mixture was stirred under H_2 at atmospheric pressure for 10 h. The Pd/C (5%) was removed by filtration through filter paper, and the filtrate was concentrated in vacuo to remove the methanol. Purification of the residue by column chromatography (SiO_2, hexane/AcOEt (1/40)) afforded the title compound as an off-white amorphous solid (40 mg, 90%). Mp: 140−144 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ 1.16−1.44 (m, CH_2 × 7 + CH_2 × 3 cHx, 20H), 1.44−1.55 (m, CH_2CH_2O, 2H), 1.62−1−80 (m, CH_2CH_2N + CH_2 cHx, 4H), 1.84−1.95 (m, $CH_2\gamma_b$ + CH_2 cHx, 4H), 2.37 (t, *J* = 7.0 Hz, $CH_2\gamma_c$, 2H), 3.33−3.41 (m, $CH_2\gamma_a$, 2H), 3.42−3.46 (m, OH), 3.48−3.56 (m, CH_2O, 2H), 3.70−3.84 (m, CH-1 cHx, 1H), 3.90 (s, CH_3, 3H), 4.28−4.36 (m, CH_2N, 2H), 6.63 (d, *J* = 1.9 Hz, CH Py, 1H), 6.90 (d, *J* = 1.9 Hz, CH Py, 1H), 7.03 (d, *J* = 7.8 Hz, NH-5 cHx, 1H), 7.08 (ddd, *J* = 1.0 Hz, *J* = 7.0 Hz, *J* = 8.0 Hz, CH Ind, 1H), 7.17−7.20 (sa, CH Ind, 1H), 7.20−7.27 (m, 2 × CH, 2H), 7.31 (d, *J* = 1.9 Hz, CH Py, 1H), 7.56 (dd, *J* = 0.8 Hz, *J* = 8.3 Hz, CH Ind, 1H),

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7.54−7.60 (sa, NH-3, 1H), 7.64 (d, J = 7.9 Hz, CH Ind, 1H), 9.66 (s, NH-4, 1H), 9.92 (s, NH-2, 1H), 10.81 (s, NH-1, 1H). ^{13}C NMR (acetone-d_6, 125 MHz): δ 27.1 (2 × CH_2), 27.4 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 28.7 (CH_2), 30.00−31.50 (7 × CH_2), 33.6 (CH_2), 33.7 (CH_2), 35.6 (CH_2), 37.6 (CH_3), 40.4 (CH_2), 49.8 (CH-1 cHx), 49.9 (CH_2N), 63.5 (CH_2O), 103.9 (CH Ind), 104.8 (CH Py), 105.3 (CH Py), 114.3 (CH Ind), 118.3 (CH Py), 119.9 (CH Py), 121.9 (CH Ind), 123.5 (CH), 124.2 (C), 124.3 (C), 125.1 (C), 125.5 (C), 125.6 (CH Ind), 128.0 (C), 131.8 (CH Ind), 134.4 (C), 138.7 (C), 162.5 (CO), 163.6 (CO), 169.9 (CO), 171.3 (CO). MS (ES+; m/z): 728.8 [M + H]$^+$, 729.8 [M + 2]$^+$, 750 [M + Na]$^+$. IR (KBr; cm^{-1}): 3000−3800, 2928, 2854, 1637, 1579, 1521, 1447, 1403, 1308, 1253, 1146, 853, 745, 559. Anal. Calcd for $C_{41}H_{57}N_7O_5$: C, 67.65; H, 7.89; N, 13.47; O, 10.99. Found: C, 67.68; H, 7.92; N, 13.50.

(AcO)$_3$-β-Xyl-Py[(CH$_2$)$_{11}$OH]-γ-Py-Ind (**35**). This compound was prepared as mentioned above for Cycl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**2**) from $(AcO)_3$-β-Xyl-Py[$(CH_2)_{11}$OBn]-γ-Py-Ind (**34b**; 185 mg, 0.186 mmol) to afford the title compound as an off-white amorphous solid (140 mg, 85%). Mp: 105−110 °C. $[\alpha]_D$ = −21° (c = 0.1, acetone). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.20−1.38 (m, CH_2 × 7, 14H), 1.46−1.54 (m, CH_2CH$_2$O, 2H), 1.66−1.74 (m, CH_2CH$_2$N, 2H), 1.91 (m, $CH_2\gamma$, 2H), 1.95 (s, CH_3, (AcO), 3H), 1.99 (s, CH_3, (AcO), 3H), 2.01 (s, CH_3, (AcO), 3H), 2.39 (t, J = 7.0 Hz, CH_2 γ, 2H), 3.38 (dd, J = 6.4 Hz, J = 12.5 Hz, CH_2 γ, 2H), 3.41−3.48 (m, OH, 1H), 3.53 (t, J = 6.5 Hz, CH_2O, 2H), 3.56 (dd, J = 19.7 Hz, J = 8.8 Hz, CH-5′ Xyl, 1H), 3.92 (s, CH_3, 3H), 4.00 (dd, J = 11.3 Hz, J = 5.6 Hz, CH-5 Xyl, 1H), 4.22−4.41 (m, CH_2N, 2H), 4.92 (dt, J = 10.2 Hz, J = 10.0 Hz, J = 5.6 Hz, CH-4 Xyl, 1H), 5.04 (t, J = 9.4 Hz, CH-2 Xyl, 1H), 5.35 (t, J = 9.6 Hz, CH-3 Xyl, 1H), 5.37 (t, J = 9.6 Hz, CH-1 Xyl, 1H), 6.64 (d, J = 1.7 Hz, CH Py, 1H), 6.91 (d, J = 1.8 Hz, CH Py, 1H), 7.08 (t, J = 7.0 Hz, CH-5 Ind, 1H), 7.18−7.20 (s, CH-3 Ind, 1H), 7.24 (ddd, J = 8.2 Hz, J = 7.0 Hz, J = 1.1 Hz, CH-6 Ind, 1H), 7.31 (d, J = 1.8 Hz, CH Py, 1H), 7.44 (d, J = 1.8 Hz, CH Py, 1H), 7.53−7.57 (sa, NH-3, 1H), 7.56 (dd, J = 8.3 Hz, J = 0.8 Hz, CH-7 Ind, 1H), 7.61−7.67 (CH-4 Ind + NH-5, 2H), 9.33 (s, NH-4, 1H), 9.69 (s, NH-2, 1H), 10.84 (s, NH-1, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 21.6 (CH_3 × 2 (AcO)), 21.7 (CH_3 (AcO)), 27.5 ($CH_2\gamma$), 27.7 (CH_2), 28.2 (CH_2), 30.9 (CH_2) 31.1 (CH_2), 31.2 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 33.6 (CH_2CH_2N), 34.8 (CH_2CH_2O), 35.5 ($CH_2\gamma$), 37.6 (CH_3), 40.4 ($CH_2\gamma$), 50.3 (CH_2N), 63.5 (CH_2O), 65.8 (CH_2-5 Xyl), 71.0 (CH Xyl), 72.8 (CH-4 Xyl), 74.6 (CH Xyl), 80.4 (CH-1 Xyl), 104.0 (CH Ind), 105.3 (CH Py), 106.1 (CH Py), 114.0 (CH Ind), 119.9 (CH Py), 120.4 (CH Py), 121.9 (CH Ind), 123.1 (C), 123.5 (CH Ind), 124.1 (C), 124.7 (C), 125.6 (CH Ind), 129.8 (C), 133.7 (C), 138.8 (C), 160.2 (C), 160.2 (CO), 162.8 (CO), 163.6 (CO), 171.2 (CO), 171.3 (CO), 171.4 (CO), 171.6 (CO). MS (ES+; m/z): 904.3 [M + H]$^+$, 905.3 [M + 2H]$^+$, 926.3 [M + Na]$^+$. IR (KBr; cm^{-1}): 3420, 2926, 2854, 1755, 1646, 1580, 1524, 1440, 1404, 1370, 1260, 1063, 804, 747. Anal. Calcd for $C_{46}H_{61}N_7O_{12}$: C, 61.12; H, 6.80; N, 10.85; O, 21.24. Found: C, 61.18; H, 6.84; N, 10.90.

(HO)$_3$-β-Xyl-Py[(CH$_2$)$_{11}$OH]-γ-Py-Ind (**8**). This compound was prepared as mentioned above for $(HO)_3$-β-Xyl-Py-γ-Py-Ind (**3**) from $(AcO)_3$-β-Xyl-Py[$(CH_2)_{11}$OH]-γ-Py-Ind (**35**; 15 mg, 0.016 mmol). The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH (5/1)), affording the title compound (10 mg, 80%). $[\alpha]_D$ = −14.13° (c = 0.1 in acetone). ^{1}H NMR (acetone-d_6, 500 MHz): δ 1.18−1.40 (m, CH_2 × 7, 14H), 1.52−1.65 (m, CH_2CH$_2$O, 2H), 1.65−1.79 (m, CH_2CH$_2$N, 2H), 1.91 (dt, J = 13.7 Hz, CH_2 γ_b, 2H), 2.38 (t, J = 7.0 Hz, CH_2 γ, 2H), 3.28 (dd, J = 9.4 Hz, J = 11.30 Hz, CH-5_{ax} Xyl, 1H), 3.38 (dd, J = 6.4 Hz, J = 12.5 Hz, $CH_2\gamma$, 2H), 3.46 (t, J = 6.5 Hz, CH_2O, 2H), 3.42−3.50 (m, CH-2, CH-3 y CH-4 Xyl, 3H), 3.82 (dd, J = 4.7 Hz, J = 11.4 Hz, CH-5_{eq} Xyl, 1H), 3.91 (s, CH_3, 3H), 4.24−4.36 (m, CH_2N, 2H), 5.07 (t, J = 8.5 Hz, CH-1 β Xyl, 1H), 6.82−6.85 (sa, J = 1.8 Hz, CH Py, 1H), 6.93 (d, J = 1.6 Hz, CH Py, 1H), 7.07 (t, J = 7.5 Hz, CH Ind, 1H), 7.20 (d, J = 1.3 Hz, CH Ind, 1H), 7.23 (dd, J = 1.0 Hz, J = 7.1 Hz, J = 8.2 Hz, CH Ind, 1H), 7.32 (d, J = 1.5 Hz, CH Py, 1H), 7.33 (d, J = 1.7 Hz, CH Py, 1H), 7.51−7.60 (sa, NH-3, 1H), 7.56 (d, J = 8.1 Hz, CH Ind, 1H), 7.64 (d, J = 8.0 Hz, CH Ind, 1H), 7.74 (d, J = 8.2 Hz, NH-5, 1H), 9.30 (s, NH-4, 1H), 9.80 (s, NH-2, 1H), 10.96 (s, NH-1, 1H). ^{13}C NMR (125 MHz, acetone-d_6): δ 27.6 ($CH_2\gamma$), 28.0 (CH_2), 28.4 (CH_2), 30.9 (CH_2), 31.1 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 31.5 (CH_2), 33.7 (**C**H$_2$CH$_2$N), 35.5 ($CH_2\gamma$), 37.6 (CH_3), 40.4 ($CH_2\gamma$), 50.3 (CH_2N), 62.8 (CH_2O), 68.1 (CH_2-5 Xyl), 71.3 (CH Xyl), 73.5 (CH Xyl), 78.2 (CH Xyl), 79.4 (CH-1 Xyl), 104.2 (CH Ind), 105.5 (CH Py), 106.1 (CH Py), 114.6 (CH Py), 119.8 (CH Py), 120.0 (CH Ind), 120.9 (CH Ind), 121.9 (C), 123.5 (CH Ind), 123.8 (C), 124.1 (C), 124.5 (C), 125.5 (C), 125.6 (CH Ind), 129.1 (C), 138.1 (C), 163.8 (CO × 2), 171.5 (CO × 2). MS (ES+; m/z): 778.3 [M + H]$^+$, 779.3 [M + 2H]$^+$, 800.3 [M + Na]$^+$. IR (KBr; cm^{-1}): 3000−3600, 2968, 2920, 2860, 1740, 1655, 1445, 1265, 1027. Anal. Calcd for $C_{47}H_{61}N_7O_9$ (777.91): C, 65.03; H, 7.08; N, 11.30; O, 16.59. Found: C, 65.13; H, 7.10; N, 11.32.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +34-91-564-48-53. E-mail: cvicent@iqog.csic.es.

Notes

The authors declare no competing financial interest.

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