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Carbohydrates

# Exploration of the Chiral Recognition of Sugar-Based Diindolylmethane Receptors: Anion and Receptor Structures

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**Abstract:** In this study, we have conducted a systematic investigation of the chiral recognition of carboxylic anions by D-glucuronic acid/diindolylmethane receptors. We investigate the influence of the anion structure on chiral recognition in the diindolylmethane/glucuronic acid-based receptor **1a**. We found that presence of an additional hydrogen-bond donor at the α position to the carboxylic function is essential for effective chiral differentiation in these systems. Furthermore, we present a synthetic procedure that allows for the synthesis of sugar-decorated receptors that possess a modified substituent at the anomeric position. Four new receptors **1b–e** have been synthesized, and their chiral-discrimination ability toward model carboxylates is studied. The obtained results show that the chiral recognition of these receptors can be fine-tuned by incorporation of a proper substituent into the receptor structure.

## Introduction

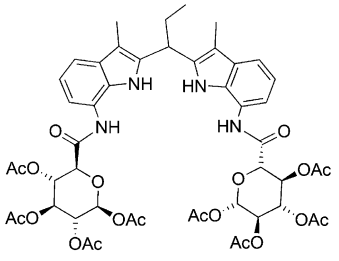
Chiral recognition is one of the most subtle processes found in nature. This type of recognition requires a capacity to differentiate between enantiomers that differ from one another solely in terms of the spatial arrangement of the substituents that belong to their stereogenic center.[1] For different enantiomers to be distinguishable, at least three interactions need to exist between a host and guest (the three-point-attachment rule).[2] By implementing this concept in various ways, many varied sources of chirality, such as carbohydrates,[3] α-amino acids,[4] steroids,[5] chiral amines,[6] and other chiral motifs,[7] have been used to modify artificial receptors. However, the factors that underlie the general phenomenon of chiral discrimination and affect the design of receptors enantioselective for a given guest still remain poorly understood.

Sugars offer an attractive source of chirality[8] because they are cheap renewable materials, and the configuration of their stereogenic centers can easily be modified by using diastereomeric sugars derived from the D-series. However, sugars have to date rarely been used in artificial receptors, especially in anion-receptor chemistry, owing to their structural complexity.

We previously demonstrated that a hybrid anion receptor containing diindolomethane and D-glucuronic acid is effective in chiral-anion recognition.[9] Another important aspect of this approach was also enantiomer recognition based on receptor **1a** with different patterns of guest-binding-induced chemical-shift changes.[10] There have been no systematic investigations of chiral recognition in these systems to date, a fact that prompted us to further explore such a hybrid design. This present study consists of two parts: In the first, we investigate the influence of anion structure on the chiral-recognition ability of receptor **1a** and present our findings that the presence of an additional hydrogen-bond donor at the α position to the carboxylate group is essential for the recognition process. In the second part, we modified the glucuronic acid part of the receptor by changing its acyl substituent at the anomeric position. It is well known that the substituent present at the anomeric position plays an important role in carbohydrate chemistry;[11] therefore, we expected that the chiral recognition of these receptors may be improved through such a modification.

## Results and Discussion

To gain insight into the role played by anion structure in the chiral recognition process, we explored the ability of receptor **1a** to discriminate various chiral anions that possess different substituents (Figure 1). Table 1 shows the results obtained from titrations under $^1$H NMR spectroscopic control in [D$_6$]DMSO + 0.5% H$_2$O.[12]




**1a**

**Figure 1.** Structure of investigated anion receptor **1a**.

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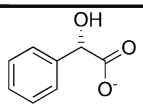
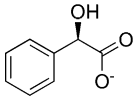
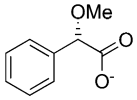
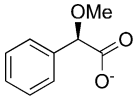
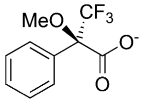
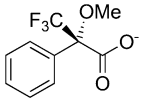
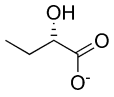
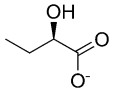
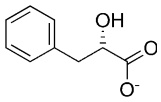
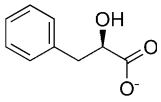
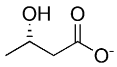
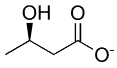
**Table 1.** Exploring the influence of anion structure on the chiral recognition ability of receptor **1a**.

| Entry | Anion[a] | Binding constant [$M^{-1}$][b] | $K_R/K_S$ |
|---|---|---|---|
| 1 |  | 119 | 1.95:1 |
| 2 |  | 233 | |
| 3 |  | 2236 | 1.02:1 |
| 4 |  | 2284 | |
| 5 |  | 35.6 | 1.31:1 |
| 6 |  | 27.0 | |
| 7 |  | 607 | 2.55:1 |
| 8 |  | 1542 | |
| 9 |  | 259 | 3.68:1 |
| 10 |  | 952 | |
| 11 |  | 737 | 1.22:1 |
| 12 |  | 902 | |

[a] Used as tetrabutylammonium salts. [b] Binding constants were recorded in [$D_6$]DMSO + 0.5% $H_2O$ and obtained by $^1$H NMR spectroscopic analysis; the titration errors are less than 10%.

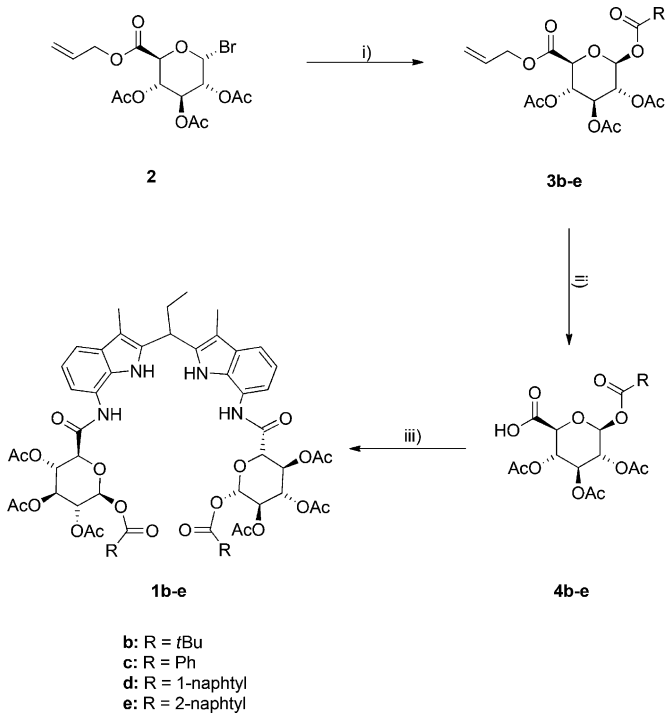
When comparing the recognition of anions derived from mandelic acid with its *O*-methyl derivative (Table 1, entries 1 and 2 versus 3 and 4), one can clearly see that protection of the hydroxy group causes decreased chiral recognition. Moreover, the binding constants are at least ten times higher than those for anions derived from mandelic acid itself.

Similarly, we found that anions derived from the Mosher acid (Table 1, entries 5 and 6) are not recognized by receptor **1a**, and the binding constants are substantially lower relative to mandelates (compare with entries 1 and 2 in Table 1). It seems that the quaternary center present in these anions causes many unfavorable steric interactions. This observation (Table 1, entries 1–6) suggests that receptor **1a** prefers anions that possess a hydrogen-bond donor at the $\alpha$ position to be more effective in chiral recognition. To support this notion, we carried out titrations of anions derived from 3-hydroxybutyric acid (Table 1, entries 11 and 12), and the results obtained confirmed this requirement. Prompted by this finding, we measured the binding affinities of anions derived from two other $\alpha$-hydroxy acids, namely, 2-hydroxybutyric and 3-phehnyllactic acid (Table 1, entries 7–10). In both cases, we found that receptor **1a** can discriminate these anions with excellent $K_R/K_S$ ratios of up to 3.68:1. Ratios are given relative to 1.

Armed with this knowledge of the crucial factors important for receptor **1a** to be effective in chiral recognition, we decided to synthesize four new receptors **1b**–**e** that differ in terms of the acyl group at the anomeric position. We assumed that the introduction of aromatic substituents at this position should allow for improved chiral recognition; for example, the introduction of the aromatic substituent present in receptors **1c**–**e** might allow for an additional $\pi$–$\pi$ interaction.[13] In contrast, chiral recognition can also be tailored by increasing the steric bulkiness of the receptor; therefore, we also decided to introduce a *t*Bu substituent at this position to yield receptor **1b**. The synthesis of modified receptors **1b**–**e** started with the reaction of a protected bromide of D-glucuronic acid **2** with anions of the proper carboxylic acid[14] to give derivatives **3b**–**e** (Scheme 1). In the next step, the glucuronic esters were deprotected by using $[Pd(PPh_3)_4]$[15] to yield free acids **4b**–**e**, which were treated with oxalyl chloride in the last step followed by treatment with 1,1-bis-(3-methyl-7-amino-1*H*-indol-2-yl)propane in situ to give the desired receptors **1b**–**e** in satisfactory yields (66–93%).

We conducted $^1$H NMR spectroscopic titrations of chiral anions derived from three representative acids to validate how successful our receptors are. We investigated anions derived from 3-phenyllactic acid, mandelic acid, and Boc-*N*-tryphtophane. These four new receptors **1b**–**e** allowed for direct comparison with the parent receptor **1a** (Table 2).

In the case of mandelates, receptors **1b**–**e** can discriminate the enantiomers of mandelic acid on the same level as receptor **1a** and showed virtually no dependence of chiral recognition on the substituent present at the anomeric position. Nevertheless, receptor **1d** showed a pronounced increase in the $K_R/K_S$ value to 4.14:1 for anions derived from 3-phenyllactic acid, whereas the introduction of a large bulky *t*Bu substituent in receptor **1b** caused a decreased chiral recognition of these anions of $K_R/K_S = 2.41$:1 (compare with entries 9 and 10 in Table 1). It seems that the methylene spacer in 3-phenyllactates allows additional interactions between the anion and receptor, that is, favorable interactions for receptor **1d** (i.e., $\pi$–$\pi$ interactions between the aromatic rings)[13] or unfavorable (steric) interactions for **1b**. Figure 2 shows the possible structure of receptor **1c** with D-phenyllactate, thus illustrating the interactions between the receptor and anion.



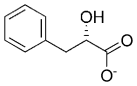
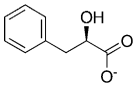
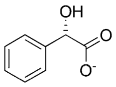
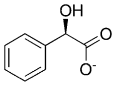
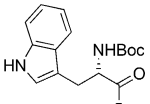
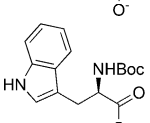

**Scheme 1.** Synthetic route to receptors **1 b**–**e** that possess a modified anomeric position. i) RCOOH, $Cs_2CO_3$, DMSO 40–67%; ii) $[Pd(PPh_3)_4]$, pyrrolidine, MeCN, 0 °C, 71–90%; iii) a) $(COCl)_2$, DMF, DCM, 0 °C; b) 1,1-bis-(3-methyl-7-amino-1*H*-indol-2-yl)-propane, pyridine, DCM, 66–93%. DCM = dichloromethane.

The third chiral guest investigated was an anion derived from Boc-*N*-tryphtophane, which contains a more spatial aromatic system and the bulky Boc protecting group, thus allowing for some additional interactions. Modification of the substituent at the anomeric position led to improved chiral recognition for all receptors **1 b**–**e**.

A significant increase in chiral recognition was noted for receptors **1 c**–**e**, which possess aromatic substituents. Receptor **1 b**, with a *t*Bu group, exhibited a reduced $K_R/K_S$ value of 3.03:1. The obtained results demonstrate that chiral recognition by diindolylmethane/glucuronic acid receptors depends on the structure and can be fine-tuned through modification of the glucuronic acid unit. On the other hand, the proper anion geometry is also an important factor, which may allow for additional interactions with glucopyranose rings that possess modified anomeric positions. In this regard, anions derived from mandelic acid are geometrically unfit for this purpose. Figure 3 shows a graphical representation of the chiral recognition of receptors **1 a**–**e** with model anions.

Figure 4, in turn, shows representative chemical-shift changes during the titration of receptors **1 d** with anions derived from phenyllactic acid. Receptors **1 b**–**e** showed similar binding characteristics relative to **1 a**, as described in detail in our previous report.[9] Notably, the enantiomer with the greatest stability constant out of most of the anions investigated also exhibited the greatest $\Delta\delta_{max}$ value (see the Supporting Information for binding isotherms of the other anions).

**Table 2.** Recognition of chiral anions by receptors **1 a**–**e**.

| Anion[a] | Receptor | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **1 a** | $K_R/K_S$ [b] | **1 b** | $K_R/K_S$ [b] | **1 c** | $K_R/K_S$ [b] | **1 d** | $K_R/K_S$ [b] | **1 e** | $K_R/K_S$ [b] |
|  | 259 | 3.68:1 | 328 | 2.41:1 | 250 | 3.44:1 | 317 | 4.14:1 | 304 | 3.46:1 |
|  | 952 | | 790 | | 859 | | 1312 | | 1053 | |
|  | 119 | 1.95:1 | 105 | 1.96:1 | 97 | 1.92:1 | 115 | 2.12:1 | 107 | 1.95:1 |
|  | 233 | | 206 | | 187 | | 245 | | 209 | |
|  | 88 | 2.57:1 | 89 | 3.03:1 | 77.7 | 3.61:1 | 104 | 3.85:1 | 100 | 3.53:1 |
|  | 227 | | 270 | | 281 | | 401 | | 353 | |

[a] Used as tetrabutylammonium salts. [b] Binding constants were recorded in $[D_6]$DMSO + 0.5% $H_2O$ and obtained by $^1$H NMR spectroscopic analysis; the titration errors are less than 10%.

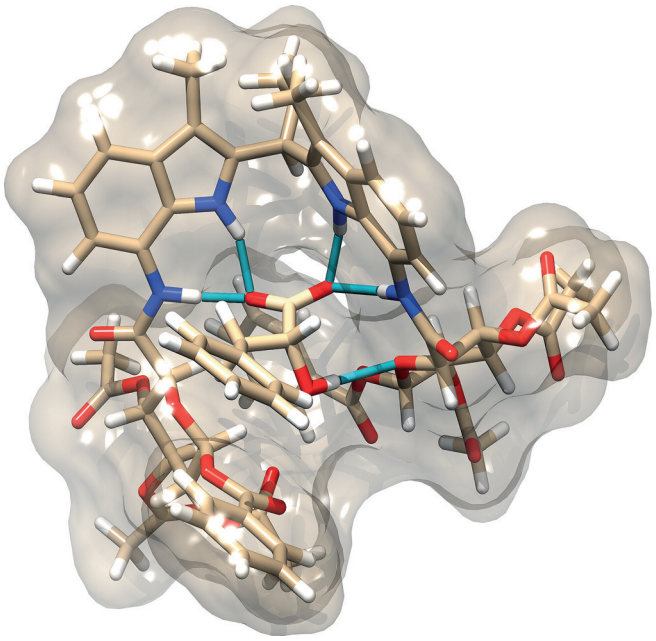


**Figure 2.** Model of the structure that shows possible interactions between receptor **1 c** and D-3-phenyllactate. Hydrogen bonds between the carboxylate anion and binding pocket of the receptor and an additional hydrogen bond between the hydroxy group of the anion and the anomeric oxygen atom of the receptor are depicted in blue. The π–π interaction between the aromatic rings of the host and guest is also visible.

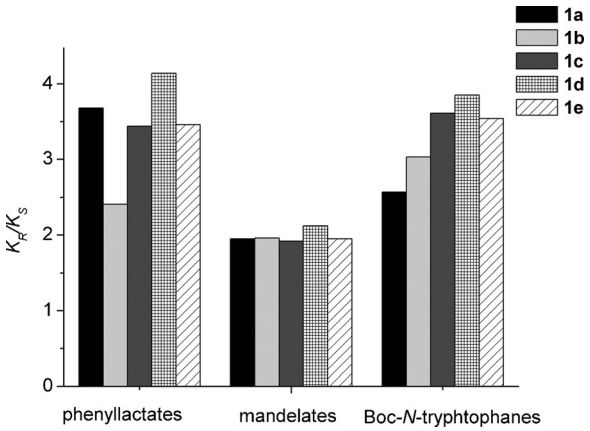



**Figure 3.** Bar graph that shows chiral recognition of the investigated anions by receptors **1 a**–**e**.

## Conclusion

We have investigated the structural factors that are important for chiral anions to be effectively recognized by receptors of type **1**. We found that the main prerequisite is the presence of an additional hydrogen-bond donor at the α position. We have also developed a simple synthetic procedure that allows the introduction of a variety of substituents into this receptor class. The modified receptors **1 b**–**e** also exhibited improved chiral recognition relative to receptor **1 a**, with an enantioselectivity of up to 4.14. These findings pave the way for further exploration of chiral-anion recognition through the synthesis of various receptors that may be incorporated into more complicated systems.

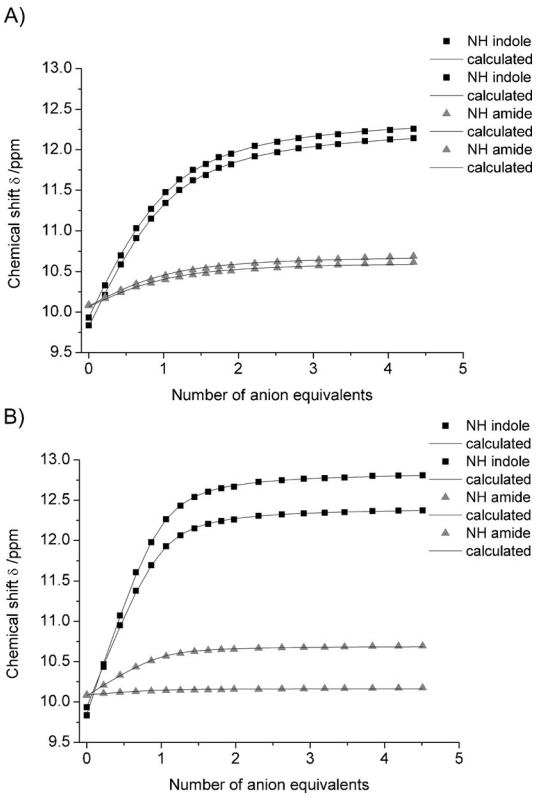



**Figure 4.** Comparison of binding isotherms for titrations of receptor **1 d** with anions derived from 3-phenyllactic acid: A) L-phenyllactate and B) D-3-phenyllacate. Squares represent chemical-shift changes for the indole NH group and triangles represent the amide groups. Lines show fitted data.

## Experimental Section

All the solvents were of reagent-grade quality. Dichloromethane was dried over calcium hydride and THF was dried over sodium benzophenone ketyl. All the reagents were purchased from Sigma-Aldrich and used without further purification. *N*-Boc-protected amino acids were obtained from Iris Biotech GMBH. Column chromatography was carried out by using Merck Kieselgel 60 (230–400 mesh) and TLC analysis was carried out on Merck Kieselgel F254 plates. Melting points were determined on a Boëtius M HMK hot-stage apparatus and were uncorrected. The $^{1}H$ and $^{13}C$ NMR spectra were recorded on VarianMercury 400 and Varian S600 instruments. Chemical shifts are reported in ppm. The splitting pattern of multiplets is described by abbreviations (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, dd = doublet of doublets, m = complex multiplicity, c = covered signal).The *J* coupling constants values are reported in Hz. Mass-spectrometric analysis was performed by using ESI-TOF on a Mariner mass spectrometer from PerSeptive Biosystem. 1,1-Bis-(3-methyl-7-nitro-1*H*-indol-2-yl)propane[16] and 1,2,3,4-tetra-*O*-acetyl-β-glucopyranuronic acid allyl ester[15] were prepared as described previously. The synthesis of receptor **1 a** is described in our previous report.[9]

**Allyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyluronate bromide (2)**: 1,2,3,4-Tetra-*O*-acetyl-β-glucopyranuronic acid allyl ester (8.45 g, 21.0 mmol) was dissolved in dichloromethane (21 mL) and cooled

to 0 °C in an ice/water bath. A solution of hydrobromic acid in acetic acid (33%, 31.6 mL) was added to this solution. The reaction mixture was allowed to reach room temperature over 4 h. After this time, the reaction mixture was diluted with diethyl ether (200 mL), transferred into a separatory funnel, washed with water (3×100 mL) and aqueous saturated sodium hydrogen carbonate (100 mL), and dried over $Na_2SO_4$. The solvent was removed under reduced pressure and the product was purified by column chromatography with a gradient of dichloromethane→dichloromethane/AcOEt (9:1, v/v) as the eluent to give colorless crystals (5.51 g, 62%). M.p. 57–58 °C; $[\alpha]_D^{20} = +187.8$ ($c = 1.118$ in dichloromethane); $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 6.94$ (d, $J = 3.8$ Hz, 1H), 5.89 (ddt, $J = 17.2$, 10.4, 5.8 Hz, 1H), 5.46–5.24 (m, 4H), 5.14 (dd, $J = 9.8$, 3.9 Hz, 1H), 4.67–4.52 (m, 2H), 4.51 (dd, $J = 10.1$, 0.5 Hz, 1H), 2.05 (s, 3H), 2.01 (s, 3H), 1.99 ppm (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$]DMSO): $\delta = 169.54$, 169.10, 169.04, 165.45, 131.46, 119.25, 88.04, 71.98, 69.14, 69.06, 67.58, 66.26, 20.37, 20.32, 20.29 ppm; HRMS: $m/z$ calcd for $C_{15}H_{19}O_9Br$: 445.0110 $[M+Na]^+$; found: 445.0110.

### General procedure for the synthesis of allyl esters 3b–e

Carboxylic acid (1.0 equiv) and caesium carbonate (1.0 equiv) were suspended in methanol (50 mL) and stirred for complete dissolution. Methanol was removed from the reaction mixture under reduced pressure. The obtained cesium salt was dissolved in DMSO (10 mL) and bromide **2** (0.83 equiv) in DMSO (10 mL) was added to this solution. The reaction mixture was further stirred in an argon atmosphere for 3 h, diluted with ethyl acetate (150 mL), and washed with water (150 mL), aqueous conc. sodium hydrogen carbonate (3×100 mL), and brine (100 mL). The solution was dried over anhydrous $Na_2SO_4$, the solvent was removed under reduced pressure, and the product was purified by column chromatography.

**Allyl 2,3,4-tri-*O*-acetyl-1-*O*-(pivaloyl)-β-D-glucopyranuronate (3b)**: This product was obtained by starting from pivalic acid (491.14 mg, 4.8 mmol) and caesium carbonate (781 mg, 2.4 mmol). Compound **3b** was purified by column chromatography with dichloromethane/AcOEt (10:1, v/v) as the eluent to obtain a white solid (707 mg, 40%). M.p. 113–114 °C; $[\alpha]_D^{20} = +10.6$ ($c = 0.956$ in dichloromethane); $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 5.99$ (d, $J = 8.2$ Hz, 1H), 5.88 (ddt, $J = 16.1$, 10.5, 5.7 Hz, 1H), 5.54 (t, $J = 9.6$ Hz, 1H), 5.33 (ddd, $J = 17.2$, 3.0, 1.5 Hz, 1H), 5.26 (dd, $J = 10.4$, 1.5 Hz, 1H), 5.11–4.98 (m, 2H), 4.73 (d, $J = 9.9$ Hz, 1H), 4.56 (dddt, $J = 36.6$, 13.3, 5.9, 1.3 Hz, 2H), 1.99 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.11 ppm (s, 9H); $^{13}$C NMR (101 MHz, [D$_6$]DMSO): $\delta = 175.58$, 169.43, 169.17, 168.96, 166.17, 131.64, 119.02, 90.84, 71.53, 70.71, 69.66, 68.95, 65.94, 38.23, 26.32 (s, 3C), 20.31 (s, 2C), 20.21 ppm; HRMS: $m/z$ calcd for $C_{20}H_{28}O_{11}$: 467.1529 $[M+Na]^+$; found: 467.1531.

**Allyl 2,3,4-tri-*O*-acetyl-1-*O*-benzoyl-β-D-glucopyranuronate (3c)**: This product was obtained by starting from benzoic acid (586 mg, 4.8 mmol) and cesium carbonate (781 mg, 2.4 mmol). Compound **3c** was purified by column chromatography with dichloromethane/AcOEt (10:1, v/v) as the eluent to obtain a white solid (1.16 g, 63%). M.p. 98–99 °C; $[\alpha]_D^{20} = -11.6$ ($c = 1.117$ in dichloromethane); $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 7.97$–$7.90$ (m, 2H), 7.77–7.69 (m, 1H), 7.62–7.54 (m, 2H), 6.27 (d, $J = 7.9$ Hz, 1H), 5.86 (ddt, $J = 22.1$, 10.4, 5.8 Hz, 1H), 5.62 (t, $J = 9.4$ Hz, 1H), 5.35–5.16 (m, 3H), 5.13 (t, $J = 9.5$ Hz, 1H), 4.82 (d, $J = 9.7$ Hz, 1H), 4.62–4.45 (m, 2H), 2.01 (s, 3H), 1.99 (s, 3H), 1.98 ppm (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$]DMSO): $\delta = 169.45$, 169.23, 169.22, 166.22, 163.78, 134.46, 131.59, 129.55 (s, 2C), 129.11 (s, 2C), 127.92, 119.16, 91.41, 71.52, 70.53, 69.69, 68.79, 66.00, 20.35 (s, 2C), 20.27 ppm; HRMS: $m/z$ calcd for $C_{22}H_{24}O_{11}$: 487.1216 $[M+Na]^+$; found: 487.1217.

**Allyl 2,3,4-tri-*O*-acetyl-1-*O*-1-naphthoyl-β-D-glucopyranuronate (3d)**: This product was obtained by starting from 1-naphtoic acid (969.5 mg, 4.69 mmol) and cesium carbonate (781 mg, 2.4 mmol). Compound **3d** was purified by column chromatography with dichloromethane/AcOEt (20:1, v/v) as the eluent to obtain a white solid (1.64 g, 67%). M.p. 114–115 °C; $[\alpha]_D^{20} = -19.5$ ($c = 1.070$ in dichloromethane); $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.81$–$8.76$ (m, 1H), 8.29 (d, $J = 8.2$ Hz, 1H), 8.15 (dd, $J = 7.4$, 1.3 Hz, 1H), 8.08 (dd, $J = 8.3$, 1.1 Hz, 1H), 7.73–7.62 (m, 3H), 6.41 (d, $J = 8.0$ Hz, 1H), 5.95–5.79 (m, 1H), 5.66 (t, $J = 9.4$ Hz, 1H), 5.35–5.21 (m, 3H), 5.16 (t, $J = 9.5$ Hz, 1H), 4.88 (d, $J = 9.7$ Hz, 1H), 4.63–4.48 (m, 2H), 2.02 (s, 3H), 2.02 (s, 3H), 2.01 ppm (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$]DMSO): $\delta = 169.48$, 169.29, 169.25, 166.25, 164.29, 134.91, 133.48, 131.60, 131.03, 130.62, 129.02, 128.51, 126.69, 124.97, 124.65, 124.09, 119.10, 91.33, 71.58, 70.73, 69.84, 68.81, 65.99, 20.35 (s, 2C), 20.32 ppm; HRMS: $m/z$ calcd for $C_{26}H_{26}O_{11}$: 537.1373 $[M+Na]^+$; found: 537.1373.

**Allyl 2,3,4-tri-*O*-acetyl-1-*O*-2-naphthoyl-β-D-glucopyranuronate (3e)**: This product was obtained by starting from 2-naphtoic acid (826.5 mg, 4.8 mmol) and cesium carbonate (781 mg, 2.4 mmol). Compound **3e** was purified by column chromatography with dichloromethane/AcOEt (20:1, v/v) as the eluent to obtain a white solid (1.39 g, 67%). M.p. 96–97 °C; $[\alpha]_D^{20} = -23.2$ ($c = 1.080$ in dichloromethane); $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.63$ (s, 1H), 8.14 (d, $J = 7.9$ Hz, 1H), 8.09 (d, $J = 8.8$ Hz, 1H), 8.04 (d, $J = 8.2$ Hz, 1H), 7.93 (dd, $J = 8.6$, 1.7 Hz, 1H), 7.72 (ddd, $J = 8.2$, 6.9, 1.3 Hz, 1H), 7.68–7.63 (m, 1H), 6.35 (d, $J = 7.9$ Hz, 1H), 5.86 (ddt, $J = 17.2$, 10.4, 5.8 Hz, 1H), 5.64 (t, $J = 9.4$ Hz, 1H), 5.34–5.21 (m, $J = 9.5$, 3.9, 1.4 Hz, 3H), 5.16 (t, $J = 9.5$ Hz, 1H), 4.86 (d, $J = 9.7$ Hz, 1H), 4.63–4.46 (m, 2H), 2.03 (s, 3H), 2.00 (s, 3H), 1.98 ppm (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$]DMSO): $\delta = 169.48$, 169.25 (s, 2C), 166.25, 163.91, 135.49, 131.95, 131.60, 131.56, 129.52, 129.26, 128.81, 127.82, 127.34, 125.23, 124.56, 119.17, 91.52, 71.57, 70.55, 69.82, 68.77, 66.01, 20.37 (s, 2C), 20.30 ppm; HRMS: $m/z$ calcd for $C_{26}H_{26}O_{11}$: 537.1373 $[M+Na]^+$; found: 537.1373.

### General procedure for the deprotection of allyl esters 3b–e

Proper allyl ester **3** (1.0 equiv) was dissolved in dry acetonitrile (15 mL) in an argon atmosphere and cooled to 0 °C. Complex $[Pd(PPh_3)_4]$ (10 mol%) and then pyrrolidine (1.1 equiv) were added to the reaction mixture, which was stirred for 20 min. The mixture was filtered through a pad of celite, the solvent was removed under reduced pressure, and the residue was dissolved in AcOEt (100 mL) and washed with water (100 mL). The organic phase was removed and the aqueous phase was acidified with aqueous 0.1 M HCl to pH 2. The product was re-extracted with AcOEt (2×50 mL). The organic phase was separated, dried over anhydrous $Na_2SO_4$, and evaporated to give the corresponding acid.

**2,3,4-Tri-*O*-acetyl-1-*O*-pivaoyl-β-D-glucopyranuronic acid (4b)**: This product was obtained by starting from allyl ester **3b** (632 mg, 1.42 mmol) and by using $[Pd(PPh_3)_4]$ (164 mg, 0.14 mmol) and pyrrolidine (1.57 mmol, 0.13 mL, 112 mg). Compound **4b** was obtained as a white solid (401 mg, 71%). M.p. 171–172 °C; $[\alpha]_D^{20} = +8.4$ ($c = 0.967$ in dichloromethane); $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 13.42$ (s, 1H), 5.96 (d, $J = 8.1$ Hz, 1H), 5.49 (t, $J = 9.5$ Hz, 1H), 5.07 (t, $J = 9.6$ Hz, 1H), 4.99 (dd, $J = 9.6$, 8.1 Hz, 1H), 4.53 (d, $J = 9.9$ Hz, 1H), 1.99 (s, 3H), 1.97 (s, 6H), 1.12 ppm (s, 9H); $^{13}$C NMR (101 MHz, [D$_6$]DMSO): $\delta = 175.60$, 169.45, 169.05, 169.01, 167.96, 90.85, 71.73, 70.95, 69.75, 68.87, 38.24, 26.35(s, 3C), 20.35, 20.34, 20.24 ppm; HRMS: $m/z$ calcd for $C_{17}H_{24}O_{11}$: 427.1216 $[M+Na]^+$; found: 427.1213.

**2,3,4-Tri-*O*-acetyl-1-*O*-benzoyl-β-D-glucopyranuronic acid (4c)**: This product was obtained by starting from allyl ester **3c** (1.088 g, 2.34 mmol) and by using $[Pd(PPh_3)_4]$ (270 mg, 0.234 mmol) and pyrrolidine (2.57 mmol, 0.22 mL, 182 mg). Compound **4c** was obtained as a white solid (772 mg, 77%). M.p. 175–176 °C; $[\alpha]_D^{20} = -21.9$ ($c =$ 0.991 in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) $\delta = 8.05$–8.01 (m, 2H), 7.63–7.57 (m, 1H), 7.48–7.43 (m, 2H), 7.07 (s, 1H), 6.01 (d, $J = 7.3$ Hz, 1H), 5.45–5.26 (m, 3H), 4.34 (d, $J = 9.3$ Hz, 1H), 2.06 (s, 3H), 2.06 (s, 3H), 2.00 ppm (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta =$ 170.11, 169.92, 169.90, 169.48, 164.58, 134.29, 130.37(s, 2C), 128.81(s, 2C), 128.26, 92.01, 72.50, 71.67, 69.90, 68.82, 20.75, 20.69 ppm (s, 2C); HRMS: *m/z* calcd for $C_{19}H_{20}O_{11}$: 447.0903 $[M + Na]^+$; found: 447.0889.

**2,3,4-Tri-*O*-acetyl-1-*O*-1-naphthoyl-β-D-glucopyranuronic acid (4d)**: This product was obtained by starting from allyl ester **3d** (1.53 g, 2.97 mmol) and by using $[Pd(PPh_3)_4]$ (343 mg, 0.297 mmol) and pyrrolidine (3.27 mmol, 0.27 mL, 232 mg). Compound **4d** was obtained as a white solid (1.106 g, 79%). M.p. 184–185 °C; $[\alpha]_D^{20} =$ −25.3 ($c = 1.161$ in dichloromethane); $^1$H NMR (400 MHz, $[D_6]$DMSO): $\delta = 13.47$ (s, 1H), 8.79 (d, $J = 8.6$ Hz, 1H), 8.29 (d, $J =$ 8.2 Hz, 1H), 8.15 (dd, $J = 7.3$, 1.2 Hz, 1H), 8.08 (d, $J = 8.7$ Hz, 1H), 7.76–7.58 (m, 3H), 6.37 (d, $J = 7.9$ Hz, 1H), 5.61 (t, $J = 9.4$ Hz, 1H), 5.28–5.09 (m, 2H), 4.67 (d, $J = 9.7$ Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 2.01 ppm (s, 3H); $^{13}$C NMR (101 MHz, $[D_6]$DMSO): $\delta = 169.50$, 169.34, 169.13, 168.02, 164.34, 134.85, 133.49, 130.99, 130.63, 129.02, 128.49, 126.69, 124.99, 124.69, 124.21, 91.34, 71.77, 70.97, 69.93, 68.77, 20.40, 20.37, 20.34 ppm; HRMS: *m/z* calcd for $C_{23}H_{22}O_{11}$: 497.1060 $[M + Na]^+$; found: 497.1056.

**2,3,4-Tri-*O*-acetyl-1-*O*-2-naphthoyl-β-D-glucopyranuronic acid (4e)**: This product was obtained by starting from allyl ester **3e** (1.181 g, 2.30 mmol) and by using $[Pd(PPh_3)_4]$ (265 mg, 0.230 mmol) and pyrrolidine (2.53 mmol, 0.21 mL, 180 mg). Compound **4e** was obtained as a white solid (984 mg, 90%). M.p. 183–184 °C; $[\alpha]_D^{20} = -38.3$ ($c = 1.203$ in dichloromethane); $^1$H NMR (400 MHz, $[D_6]$DMSO): $\delta = 13.46$ (s, 1H), 8.63 (s, 1H), 8.13 (d, $J =$ 8.0 Hz, 1H), 8.09 (d, $J = 8.6$ Hz, 1H), 8.04 (d, $J = 8.1$ Hz, 1H), 7.94 (dd, $J = 8.5$, 1.4 Hz, 1H), 7.72 (t, $J = 7.5$ Hz, 1H), 7.65 (t, $J = 7.5$ Hz, 1H), 6.33 (d, $J = 7.4$ Hz, 1H), 5.60 (t, $J = 9.3$ Hz, 1H), 5.26–5.14 (m, $J = 19.5$, 8.8 Hz, 2H), 4.66 (d, $J = 9.6$ Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 ppm, (s, 3H); $^{13}$C NMR (101 MHz, $[D_6]$DMSO): $\delta = 169.50$, 169.30, 169.14, 168.04, 163.96, 135.48, 131.97, 131.52, 129.53, 129.22, 128.80, 127.82, 127.32, 125.35, 124.58, 91.52, 71.73, 70.80, 69.91, 68.72, 20.40 (s, 2C), 20.31 ppm; HRMS: *m/z* calcd for $C_{23}H_{22}O_{11}$: 497.1060 $[M + Na]^+$; found: 497.1062.

### General procedure for the synthesis of receptors 1b–e

Acid **4** (1.0 equiv) was dissolved in dry dichloromethane (100 mL) and cooled to 0 °C. Oxalyl chloride (1.10 equiv) and DMF (2.0 equiv) were added to the reaction mixture, which was maintained at this temperature for 30 min. The mixture was allowed to warm to room temperature and was stirred for 1 h to yield a solution of the acid chloride. In a separate flask, 1,1-bis-(3-methyl-7-nitro-1*H*-indol-2-yl)propane (1.0 equiv) was dissolved in methanol (50 mL) and 10% palladium on charcoal (50 mg) was added. The reaction mixture was stirred in a hydrogen atmosphere. The progress of the reaction was monitored by TLC analysis. After judging the reaction to be complete, the catalyst was removed on celite, and solvent was removed, thus giving 1,1-bis-(7-amino-3-methyl-1*H*-indol-2-yl)-propane. A solution of the crude amine and pyridine (2.5 equiv) in dichloromethane (50 mL) was slowly added to the acid chloride at 0 °C. The reaction mixture was stirred at this temperature for 30 min and then 2 h at room temperature. The reaction mixture was transferred into a separatory funnel and washed with aqueous HCl (50 mL, 0.1 M) and saturated aqueous $NaHCO_3$ (50 mL). The organic layer was dried with $Na_2SO_4$ and the solvent was removed by evaporation. The crude product was purified by column chromatography.

**1,1-Bis-[7-(2,3,4-tri-*O*-acetyl-1-*O*-pivaoyl-β-D-glucopyranuronyl)-amino-3-methyl-1*H*-indol-2-yl]propane (1b)**: The acid chloride of **4b** (829.5 mg, 2.05 mmol) obtained in the presence of oxalyl chloride (2.25 mmol, 0.19 mL) and DMF (4.1 mmol, 0.32 mL) was treated with an amine prepared by the reduction of 1,1-bis-(3-methyl-7-nitro-1*H*-indol-2-yl)propane (403 mg, 1.02 mmol) in the presence of pyridine (5.13 mmol, 0.42 mL). The crude product was purified by column chromatography with a gradient of $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt (5:1, v/v) as the eluent, thus giving **1b** (752 mg, 66%) as an off-white powder. M.p. 224–225 °C (decomp.); $[\alpha]_D^{20} = +38.0$ ($c =$ 1.002 in dichloromethane); $^1$H NMR (600 MHz, $[D_6]$DMSO): $\delta = 10.08$ (s, 1H), 10.06 (s, 1H), 10.02 (s, 1H), 9.86 (s, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.28 (d, $J = 7.6$ Hz, 1H), 7.24 (dd, $J = 7.7$, 5.2 Hz, 2H), 6.94 (td, $J = 7.8$, 1.4 Hz, 2H), 6.06 (d, $J = 8.1$ Hz, 1H), 6.03 (d, $J = 8.1$ Hz, 1H), 5.62–5.55 (m, $J = 14.3$, 9.6 Hz, 2H), 5.38–5.32 (m, $J = 9.6$, 5.4 Hz, 2H), 5.17–5.12 (m, 2H), 4.55 (d, $J = 9.8$ Hz, 1H), 4.51 (d, $J = 9.8$ Hz, 1H), 4.46 (t, $J = 8.0$ Hz, 1H), 2.28–2.22 (m, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.87 (s, 3H), 1.83 (s, 3H), 1.14 (s, 9H), 1.13 (s, 9H), 0.92 ppm (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (151 MHz, $[D_6]$DMSO): $\delta = 175.71$, 175.70, 169.48, 169.46, 169.02 (s, 2C), 169.01, 168.97, 164.20, 164.17, 135.49, 135.27, 130.74, 130.67, 127.26, 127.06, 121.61, 121.51, 118.42, 118.40, 114.98, 114.89, 114.00, 113.78, 106.96, 106.92, 91.11 (s, 2C), 73.85, 73.78, 71.06 (s, 2C), 69.66, 69.63, 69.42 (s, 2C), 38.25, 38.24, 36.91, 26.33 (s, 3C), 26.32 (s, 3C), 25.90, 20.32 (s, 2C), 20.23 (s, 2C), 20.19, 20.16, 12.09, 8.42, 8.41 ppm; HRMS: *m/z* calcd for $C_{55}H_{68}N_4O_{20}$: 1127.4325 $[M + Na]^+$; found: 1127.4310; elemental analysis (%) calcd for $C_{55}H_{68}N_4O_{20}$: C 59.77, H 6.20, N 5.07; found: C 59.76, H 6.36, N 4.85.

**1,1-Bis-[7-(2,3,4-tri-*O*-acetyl-1-*O*-benzoyl-β-D-glucopyranuronyl)-amino-3-methyl-1*H*-indol-2-yl]propane (1c)**: The acid chloride of **4c** (742 mg, 1.75 mmol) obtained in the presence of oxalyl chloride (1.92 mmol, 0.16 mL) and DMF (1.92 mmol, 0.26 mL) was treated with an amine prepared by the reduction 1,1-bis-(3-methyl-7-nitro-1*H*-indol-2-yl)propane (343 mg, 0.87 mmol) in the presence of pyridine (2.5 mmol, 0.35 mL). The crude product was purified by column chromatography with $CH_2Cl_2$/AcOEt (5:1, v/v) as the eluenet, thus giving **1c** (932 mg, 93%) as an off-white powder. M.p. 143–144 °C; $[\alpha]_D^{20} = -16.7$ ($c = 0.981$ in dichloromethane); $^1$H NMR (400 MHz, $[D_6]$DMSO): $\delta = 10.10$ (s, 1H), 10.05 (s, 1H), 9.97 (s, 1H), 9.81 (s, 1H), 7.97 (d, $J = 8.2$ Hz, 4H), 7.80–7.65 (m, 2H), 7.57 (td, $J = 7.7$, 4.7 Hz, 4H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.23–7.18 (m, 3H), 6.91 (t, $J = 7.8$ Hz, 2H), 6.34 (t, $J = 7.8$ Hz, 2H), 5.69 (q, $J = 9.8$ Hz, 2H), 5.48–5.24 (m, 4H), 4.64 (dd, $J = 15.5$, 9.7 Hz, 2H), 4.44 (t, $J =$ 8.0 Hz, 1H), 2.28–2.16 (m, 2H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (s, 6H), 1.98 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H), 1.86 (s, 3H), 0.90 ppm (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (151 MHz, $[D_6]$DMSO): $\delta = 169.52$, 169.50, 169.29, 169.27, 169.16, 169.09, 164.29, 164.26, 163.93, 163.92, 135.54, 135.29, 134.42, 134.39, 130.71, 130.65, 129.56 (s, 4C), 129.05 (s, 2C), 129.02 (s, 2C), 128.02, 127.98, 127.55, 127.31, 121.49, 121.35, 118.34 (s, 2C), 115.04, 114.93, 114.41, 114.12, 106.84, 106.78, 91.74 (s, 2C), 73.70, 73.65, 70.99, 70.97, 69.78 (s, 2C), 69.46, 69.43, 36.92, 25.97, 20.33 (s, 2C), 20.23 (s, 3C), 20.20, 12.12, 8.42 ppm (s, 2C); HRMS: *m/z* calcd for $C_{59}H_{60}N_4O_{20}$: 1167.3699 $[M + Na]^+$; found: 1167.3665; elemental analysis (%) calcd for $C_{59}H_{60}N_4O_{20}$: C 61.88, H 5.25, N 4.89; found: C 61.64, H 5.39, N 4.87.

**1,1-Bis-[7-(2,3,4-tri-*O*-acetyl-1-*O*-1-naphtoyl-β-D-glucopyranuronyl)amino-3-methyl-1*H*-indol-2-yl]propane (1d)**: The acid chlo-

ride of **4d** (895 mg, 1.89 mmol) obtained in the presence of oxalyl chloride (2.08 mmol, 0.18 mL) and DMF (3.78 mmol, 0.29 mL) was treated with an amine prepared by the reduction of 1,1-bis-(3-methyl-7-nitro-1*H*-indol-2-yl)propane (372 mg, 0.95 mmol) in the presence of pyridine (4.72 mmol, 0.35 mL). The crude product was purified by column chromatography with $CH_2Cl_2$/AcOEt (5:1, v/v) as the eluent, thus giving **1d** (1006 mg, 86%) as an off-white powder. M.p. 160–161 °C (decomp.); $[\alpha]_D^{20} = -31.8$ ($c = 1.125$ in dichloromethane); $^1$H NMR (600 MHz, [D$_6$]DMSO): $\delta = 10.11$ (s, 1H), 10.10 (s, 1H), 9.96 (s, 1H), 9.86 (s, 1H), 8.80 (d, $J = 8.8$ Hz, 1H), 8.78 (d, $J = 8.7$ Hz, 1H), 8.26 (d, $J = 8.3$ Hz, 2H), 8.17 (ddd, $J = 7.3$, 3.7, 1.0 Hz, 2H), 8.08–8.03 (m, 2H), 7.70–7.59 (m, 6H), 7.27 (d, $J = 7.7$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 7.16 (t, $J = 7.1$ Hz, 2H), 6.89 (td, $J = 7.8$, 3.9 Hz, 2H), 6.49 (t, $J = 8.5$ Hz, 2H), 5.75–5.68 (m, $J = 9.7$ Hz, 2H), 5.46–5.40 (m, $J = 9.6$, 5.4 Hz, 2H), 5.40–5.34 (m, $J = 9.6$, 8.1, 5.4 Hz, 2H), 4.71 (d, $J = 9.7$ Hz, 1H), 4.69 (d, $J = 9.7$ Hz, 1H), 4.41 (t, $J = 8.0$ Hz, 1H), 2.25–2.18 (m, 2H), 2.03 (s, 6H), 2.03 (s, 12H), 1.90 (s, 3H), 1.87 (s, 3H), 0.87 ppm (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (151 MHz, [D$_6$]DMSO): $\delta = 169.54$, 169.53, 169.37 (s, 2C), 169.20, 169.15, 164.42 (s, 2C), 164.39, 164.36, 135.47, 135.31, 134.80, 134.78, 133.47, 133.45, 130.98, 130.96, 130.77, 130.68, 130.62, 130.60, 128.96, 128.95, 128.41, 128.38, 127.39, 127.26, 126.64, 126.62, 124.90 (s, 2C), 124.70 (s, 2C), 124.31, 124.26, 121.49, 121.42, 118.32 (s, 2C), 114.97, 114.91, 114.24, 114.10, 106.86, 106.77, 91.62 (s, 2C), 73.76, 73.73, 71.13 (s, 2C), 69.95, 69.94, 69.44 (s, 2C), 37.11, 25.85, 20.34 (s, 2C), 20.31 (s, 2C), 20.25, 20.23, 12.11, 8.40, 8.37 ppm; HRMS: *m/z* calcd for $C_{67}H_{64}N_4O_{20}$: 1267.3998 $[M+Na]^+$; found: 1267.4006; elemental analysis (%) calcd for $C_{67}H_{64}N_4O_{20}$: C 64.62, H 5.18, N 4.50; found: C 64.47, H 5.48, N 4.40.

**1,1-Bis-[7-(2,3,4-tri-*O*-acetyl-1-*O*-2-naphtoyl-β-D-glucopyranuronyl)amino-3-methyl-*1H*-indol-2-yl]propane (1e)**: The acid chloride of **4e** (809 mg, 1.70 mmol) obtained in the presence of oxalyl chloride (1.87 mmol, 0.16 mL) and DMF (3.40 mmol, 0.26 mL) was treated with an amine prepared by the reduction of 1,1-bis-(3-methyl-7-nitro-1*H*-indol-2-yl)propane (333 mg, 0.95 mmol) in the presence of pyridine(4.25 mmol, 0.34 mL). The crude product was purified by column chromatography with $CH_2Cl_2$/AcOEt (5:1, v/v) as the eluent, thus giving **1e** (846 mg, 80%) as an off-white powder. M.p. 160–161 °C (decomp.); $[\alpha]_D^{20} = -23.2$ ($c = 1.019$ in dichloromethane); $^1$H NMR (600 MHz, [D$_6$]DMSO): $\delta = 10.14$ (s, 1H), 10.09 (s, 1H), 10.02 (s, 1H), 9.84 (s, 1H), 8.65 (s, 2H), 8.08 (dt, $J = 15.2$, 7.5 Hz, 4H), 8.03 (dd, $J = 8.0$, 4.7 Hz, 2H), 7.99–7.95 (m, 2H), 7.74–7.69 (m, 2H), 7.64 (dd, $J = 15.9$, 8.0 Hz, 2H), 7.29 (d, $J = 7.7$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.16 (dd, $J = 7.8$, 2.8 Hz, 2H), 6.88 (t, $J = 7.8$ Hz, 2H), 6.45 (dd, $J = 10.0$, 8.1 Hz, 2H), 5.79–5.70 (m, $J = 18.9$, 9.6 Hz, 2H), 5.48–5.36 (m, 4H), 4.71 (d, $J = 9.7$ Hz, 1H), 4.67 (d, $J = 9.6$ Hz, 1H), 4.42 (t, $J = 8.0$ Hz, 1H), 2.20 (dt, $J = 14.9$, 7.3 Hz, 2H), 2.07 (s, 3H), 2.05 (s, 6H), 2.04 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H), 1.88 (s, 3H), 0.87 ppm (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (151 MHz, [D$_6$]DMSO): $\delta = 170.00$, 169.98, 169.76, 169.74, 169.59, 169.54, 164.77, 164.71, 164.50, 164.48, 135.96, 135.91, 135.89, 135.73, 132.35 (s, 2C), 132.00 (s, 2C), 131.11, 131.05, 129.88, 129.85, 129.62 (s, 2C), 129.19, 129.15, 128.22 (s, 2C), 127.96, 127.71 (s, 3C), 125.76, 125.73, 125.02, 124.99, 121.95, 121.81, 118.76 (s, 2C), 115.44, 115.33, 114.80, 114.50, 107.24, 107.18, 92.30 (s, 2C), 74.22, 74.13, 71.47 (s, 2C), 70.34 (s, 2C), 69.91, 69.87, 37.34, 26.44, 20.80 (s, 2C), 20.69, 20.67, 20.66 (s, 2C), 12.53, 8.84 ppm (s, 2C); HRMS: *m/z* calcd for $C_{67}H_{64}N_4O_{20}$: 1267.3998 $[M+Na]^+$; found: 1267.4012; elemental analysis (%) calcd for $C_{67}H_{64}N_4O_{20}$: C 64.62, H 5.18, N 4.50; found: C 64.45, H 5.30, N 4.30.

### $^1$H NMR spectroscopic titration experiments

Tetrabutylammonium salts were used as a source of anions. Tetrabutylammonium salts of the investigated acids and amino acids were prepared by the addition of one equivalent of $Bu_4NOH$ to one equivalent of a carboxylic acid or an *N*-Boc-protected amino acid dissolved in MeOH, which was removed by evaporation in vacuo. The salts were dried under high vacuum over $P_2O_5$. Distilled water was added to commercially available [D$_6$]DMSO (99.8% isotopic purity; Euriso) to obtain the appropriate water concentration. A solution of a receptor in DMSO (ca. $1\times10^{-2}$ M) was titrated in an NMR tube with a solution of the respective tetrabutylammonium salt (ca. 0.1–0.2 M). The solution of the salt contained a certain amount of the receptor to keep a constant concentration during the titration. A total of 19 data points were recorded. The binding constants were calculated by taking into account the changes in the chemical shifts of the ligand NH protons. A nonlinear curve fitting for a 1:1 binding model was carried out by using the HypNMR program[17] to give global-association constants.

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