Total Synthesis of Mannosyl Tryptophan and Its Derivatives

Shino Manabe, Yoshihiko Marui, and Yukishige Ito*[a]

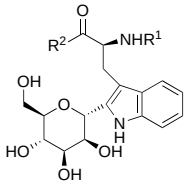
Abstract: Glycosylation is one of the most important post- or co-translational modifications of proteins, which affects the biological activities of the parent proteins by influencing the higher-order structure. Recently, a highly novel variant of glycoproteins that incorporate a C-glycosylated amino acid was identified in various proteins. The total synthesis of one such C-glycosyl amino acid, namely, C^2-α-D-*C*-mannosylpyranosyl-L-tryptophan and related peptides were successfully achieved. The mannose and tryptophan moieties were connected via ring opening of benzyl-protected 1,2-anhydro-mannose by a lithiated indole derivative. After the functional group conversion and deprotection steps, the glyco-amino acid was synthesized in a concise and stereoselective manner, in high overall yields. The stereoisomer, C^2-α-D-*C*-glycosylpyranosyl-L-tryptophan was synthesized in a similar way. Furthermore, it was revealed that the intermediate azido acid can serve as a useful building block for peptide elongation. A synthetic route for the peptide bond formation of a glycopeptide, without protection of the hydroxyl groups, using the triazine salt derivative as a coupling reagent is also reported.

Keywords: C-glycosides · carbohydrates · glycopeptides · total synthesis

Introduction

Post- or co-translational modifications of proteins, such as phosphorylation, ubiquitination, and disulfide bond formation, are involved in many important biological events.[1] One of the most common and widespread post-translational modifications of proteins is glycosylation.[2] The carbohydrate moiety of glycoproteins have been known to exert influence upon the properties of the parent proteins in various ways, such as enhancing their thermal stability, protecting against proteolysis, influencing the protein conformation, and modifying the physiochemical properties, which include solubility, electrical charge, mass, and viscosity of the solution. Characteristic carbohydrate entities, which are present in cell adhesion molecules, tumor-associated antigens, viral or bacterial invasion targets, and blood group determinants, are most typically involved in the binding process of molecular recognition systems in the form of glycoproteins.

Although other linkages have been reported,[3] in most cases, protein glycosylation can be classified into two major groups: i) O-glycosylation, where an *N*-acetylgalactosamine residue is covalently attached to the hydroxyl group of either serine or threonine of the protein, and ii) N-glycosylation, where a glycan chain is linked via a glycosylamido linkage to an asparagine side chain. The latter is further classified into subtypes as high mannose-type, complex-type, and hybrid-type. However, in 1994, a novel structural class of glycoproteins (Figure 1) was identified in human RNase Us, where a mannose residue is connected to tryptophan via a C-glycosidic linkage.[4] The primary structure of glycosylated peptide **2** was determined by Edman degradation, and by mass and NMR spectroscopy. Subsequent studies have revealed that C-mannosylation involves the attachment of a mannose residue to the indole moiety of *Trp*-Xaa-Xaa-Trp (Xaa is any amino acid; glycosylated tryptophan is italicized) as a consensus recognition site.[5] The activated donor, dolichyl-phosphate mannose, is the precursor in the biosynthetic pathway; the necessary C-mannosyltransferase activity is found in most mammalian organism.[6] Although the function of C-glycosylated tryptophan remains unclear, additional examples of C-mannosylated proteins are continually discovered from



1: $R^1 = H$, $R^2 = OH$
2: R^1 = Phe-Thr, R^2 = Ala-Gln-Trp
3: R^1 = Ala-Gln-Trp-NH_2

Figure 1. Structures of mannosylated tryptophan **1** and related peptides **2** and **3**.

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  0947-6539/03/0906-1435 $ 20.00+.50/0

several sources, including recombinant human IL-12 expressed in Chinese hamster ovary cells, thrombospondin type 1 repeat, and terminal components of complement (C6, C7, C8 and C9).[7–9] Most strikingly, properdin, a positive regulator of complement, contains 20 tryptophan residues, in which as many as 17 are mannosylated.[10] Moreover, mannosyl-tryptophan **1** was found, not only in higher vertebra, but also in marine ascidians.[11]

Rapidly growing interest to understand the molecular mechanisms of biological events involving glycoproteins has resulted in intense attention to protein glycosylation in the last decade. Since glycosylated proteins are not readily available in a homogenous form by gene technological methods, chemical syntheses of precisely defined model glycopeptides are especially important as a valuable tool.[12]

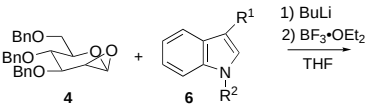
We have recently succeeded in the first total synthesis of C-mannosyl tryptophan in a concise stereocontrolled manner.[13] Isobe et al. have also reported on the synthesis of C-mannosyl-tryptophan **1** through their alkyne C-glycosylation method and indole construction by use of palladium chemistry.[14] Furthermore, an alternate synthesis of **1** was carried out through the nucleophilic addition of metalloindole derivatives to a lactone that was derived from mannose.[15] Herein, we describe the novel synthesis of C-mannosyl-tryptophan **1**, its related peptides **2** and **3**, and C-glucosyl-tryptophan, which is a stereoisomer of **1**.

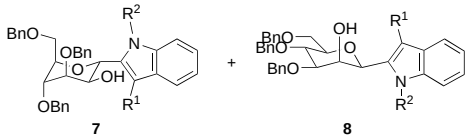
Results and Discussion

Strategy 1—Epoxide ring opening and aziridine for the amino acid precursor: Important points for the successful synthesis of **1** are: i) construction of a C–C bond between the 2-position of the indole ring of tryptophan and the anomeric carbon of mannose, and ii) installation of the asymmetric carbon of amino acid (Scheme 1). Although there are several well-established methods for the synthesis of C-glycosides,[16] our plan was to directly incorporate the indole ring at the anomeric carbon of mannose. *N*-Arylsulfonated indoles **6** (see Table 1) have been known to be amenable to direct metallation at the 2-position. Subsequent quenching with an electrophile provides an easy access to 2-substituted indole derivatives.[17] We expected that the coupling between C-2 lithiated indole derivatives and 1,2-anhydro-mannose[18] **4** would result in the direct incorporation of the C-1 linked mannose onto the 2-position of indole. Furthermore, because epoxide ring openings by organometallic reagents are known to proceed via an S_N2 pathway, the product was expected have α-configuration. In fact, some studies have demonstrated that nucleophilic attacks on 1,2-anhydro-β-D-mannopyranoses by organometallic reagents gave α-C-glycosides.[19]

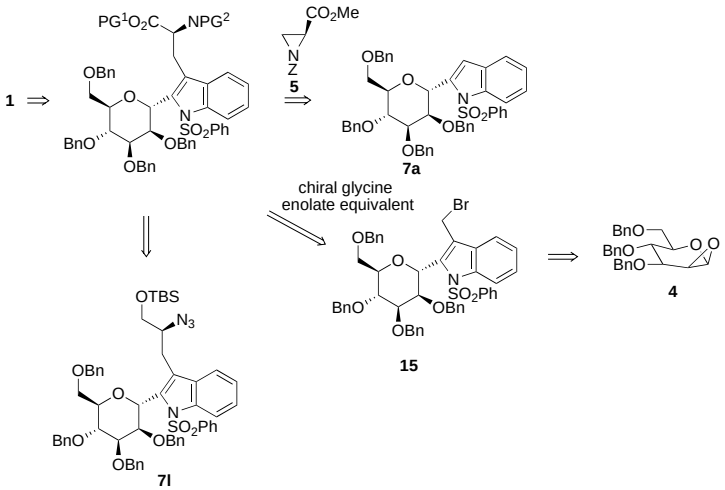
Initially, lithionated **6a** was tested as a model substrate (Table 1). Contrary to our expectation, the reaction resulted in a mixture of two compounds, which were difficult to separate by silica gel column chromatography. However, after removal of the benzyl group and subsequent acetylation (Scheme 2), compounds **9** and **10** were readily separated using silica gel column chromatography. Compound **9**, which was derived from **7a**, was confirmed as the α-linked product with $^1C_4$ conformation of the mannopyranoside ring; conversely, **8a** corresponded to **10**, which was assigned as the β-isomer with $^4C_1$ conformation (Figure 2). The stereochemistry at the anomeric carbon and conformation analyses were based on

Table 1. Sterochemistry of the reactions between epoxide **4** and lithiated indole **6**.

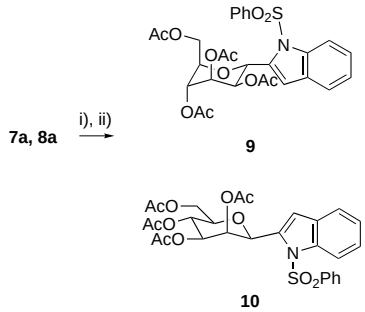




Entry	6	R^1	R^2	Yield [%]	Products	α:β
1	**a**	H	SO_2Ph	39	**7a**/**8a**	69:31
2	**b**	H	Boc	49	**7b**/**8b**	34:66
3	**c**	CH_3	SO_2Ph	39	**7c**/**8c**	87:13
4	**d**	CH_3	Boc	56	**7d**/**8d**	17:83
5	**e**	CH_2CH_3	SO_2Ph	38	**7e**/**8e**	> 95:5
6	**f**	CH_2OTBS	SO_2Ph	50	**7f**/**8f**	> 95:5
7	**g**	CH_2OTBS	Boc	17	**7g**/**8g**	77:23
8	**h**	CH_2CH_2OTBS	SO_2Ph	50	**7h**/**8h**	> 95:5



Scheme 1. Synthetic strategies for **1**. PG = protecting group.



Scheme 2. i) H_2, 20% $Pd(OH)_2$/C; ii) Ac_2O, pyridine, **9** (50%), **10** (45%).

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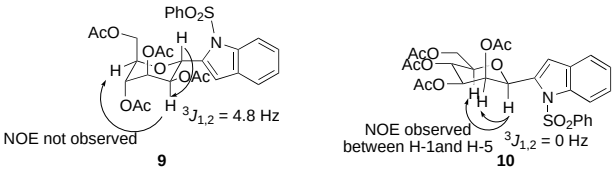
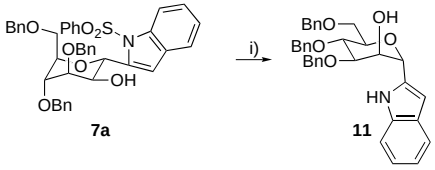


Figure 2. Conformation analyses of **9** and **10** using ^{1}H NMR spectroscopy.

^{1}H NMR studies (coupling constants between H-1 and H-2 of **9** and **10** were 4.8 Hz and ≈0 Hz, respectively; NOE between H-1 and H-5 was observed only for **10**).

Using NMR studies, Vliegenthardt et al. has also reported that the mannnopyranosyl ring of glycopeptide **2** adopted $^1C_4$ conformation.[3c, 4a] This unusual conformation can be attributed to two reasons: i) the absence of the anomeric effect in C-glycosides, which is a dominant stereoelectronic factor in O-glycosides, and 2) the bulkiness of the indole moiety, which prefers the equatorial conformation. Accordingly, following the removal of the sulfonamide moiety using basic conditions, the conformation of compound **11** flipped back to the $^4C_1$ conformation ($^3J_{1,2}$ ≈0 Hz) due to the reduced steric hindrance of the indole ring (Scheme 3).

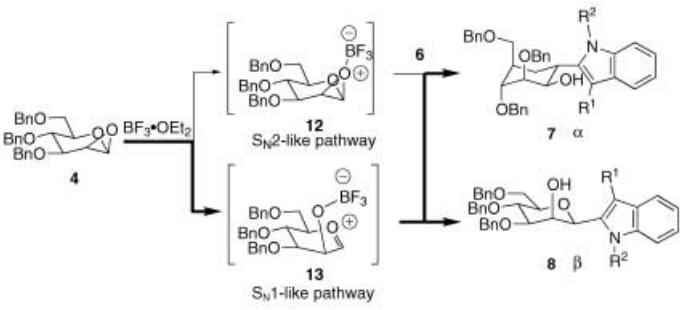


Scheme 3. i) 10% NaOH, EtOH, reflux overnight (84%).

Further systematic investigations have revealed that the stereoselectivity of epoxide opening is strongly dependent on the nature of the substituents on the nitrogen, as well as the 3-position of the indole ring. Representative results are shown in Table 1.[20] When sulfonamide was used as a nitrogen protecting group and the substituent at the 3-position of indole was larger than methyl, the reactions were highly stereoselective, in favor of the β products (Table 1, entries 1, 3, 5, 6, and 8). On the other hand, when Boc was used as a protecting group for the amine groups, the β product was obtained as a major product (Table 1, entries 2, 4, and 7). In the presence of weaker Lewis acids, such as $ZnCl_2$, $MgBr_2$, or absence of Lewis acids, the reaction did not proceed, and the unreacted epoxide was recovered.

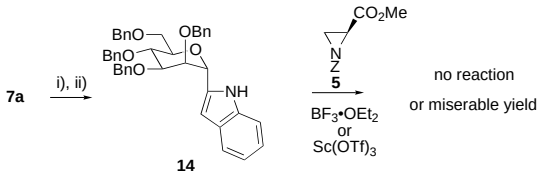
From these results, this epoxide ring opening appears to proceed through a mixed S_N1/S_N2 mechanism (Scheme 4). The significant lack of stereospecificity can be explained as the Lewis acid pre-activating epoxide **4** into oxocarbenium-type intermediate **13**, which is subsequently captured by an electrophile in a non-stereospecific manner. However, at this time, we were unable to rationalize the substituent effects on stereoselectivity.

In attempt to complete the synthesis of **1**, we undertook the seemingly straightforward reaction between aziridine **5**[21] and indole **14** to introduce the asymmetric center of amino acid (Scheme 5). However, in the presence of $BF_3 \cdot OEt_2$,[22] the



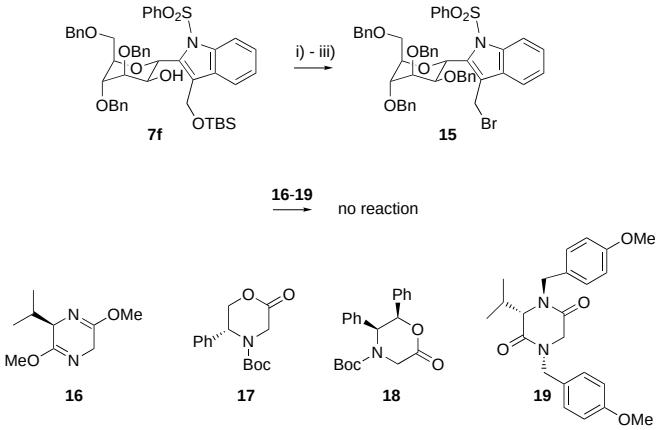
Scheme 4. Mechanisms to explain the stereochemistry of the reaction between 1,2-anhydromannose and lithiated indole derivatives.

reaction did not proceed at all, and unreacted **14** was recovered. Although the use of $Sc(OTf)_3$ as an efficient catalyst for this type of reaction was recently reported by Bennani,[23] our yields were extremely low when applied to substrate **14** (Scheme 5).[24]



Scheme 5. i) BnBr, Bu_4NI, NaH, DMF, RT, overnight (87%); ii) 10% NaOH aq, EtOH, reflux, overnight (80%).

Strategy 2—Chiral glycine enolate: Since the formation of the C–C bond between mannose and tryptophan was successful with **6 f**, we turned our attention to the synthesis of the amino acid through one-carbon homologation. Since various chiral glycine enolates have been developed,[25] our strategy involved the reaction between enolates **16**–**19**[26–29] and bromide **15**, as illustrated in Scheme 6. Following the protection of the 2-hydroxy group as a benzyl ether, the TBS group was removed under acidic conditions, and the resulting alcohol was converted to compound **15** using NBS/PPh_3 (Scheme 6).



Scheme 6. i) BnBr, Bu_4NI, NaH, DMF, RT, overnight (85%); ii) TsOH•H_2O, MeOH, RT, 5 h (90%); iii) NBS, PPh_3, CH_2CH_2, quant.

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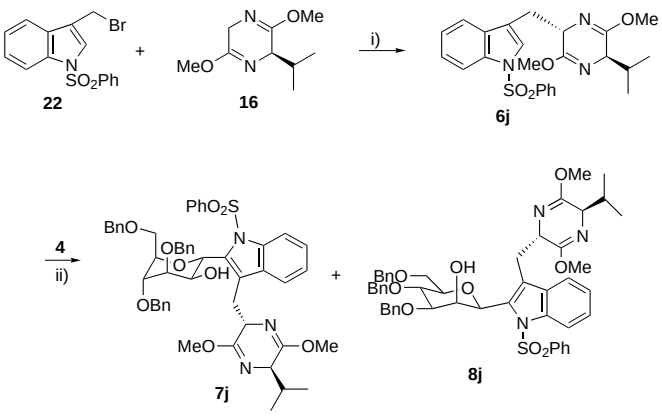
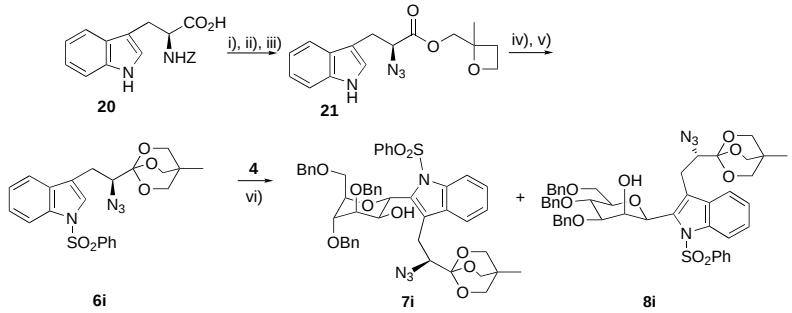
However, all four chiral glycine enolates **16**–**19** did not result in the desired products, presumably because of the steric hindrance of substrate **15**.

Strategy 3—Pre-introduction of the amino acid moiety: Since following the indole-mannose coupling with the introduction of the amino acid moiety proved to be highly challenging, our third approach involved a coupling reaction between mannose and a fully constructed and masked tryptophan, that is, **6i** (Scheme 7) and **6j** (Scheme 8). In the case of **6i**, cyclic 2,6,7-trioxabicyclo[2.2.2]octane orthoester[30] was employed as the protecting group for the carboxylic acid because of its stability under strongly basic conditions, such as BuLi, and facile deprotection under mild Brönsted acidic conditions. Following the procedures of Corey,[31] orthoester **6i** was prepared from 3-methyl-3-oxetanmethanol ester **21**, however the yield was moderate because of the acid sensitivity of the indole. Subsequently, the azide, which is stable under strongly basic conditions, was chosen as the latent amino group. After deprotection of the benzyloxycarbonyl group under catalytic hydrogenation conditions, the amino group was transformed to the azide through a diazo transfer, using TfN_3, with retention of configuration of the chiral carbon (Scheme 7).[32] Alternately, in the case of compound **6j**, the amino and the



Scheme 8. i) BuLi, THF, −78 °C (78 %); ii) BuLi, $BF_3 \cdot OEt_2$, THF, −78 °C, **7j** (10 %) and **8j** (8 %).



Scheme 7. i) 3-Methyl-3-oxetanmethanol, EDC·HCl, DMAP, DMF, RT, overnight, quant.; ii) H_2, 10 % Pd/C, MeOH, 2 h; iii) TfN_3, DMAP, CH_3CN, RT, overnight (79 %, two steps); iv) $BF_3 \cdot OEt_2$ (0.25 equiv), CH_2Cl_2 (34 %); v) $PhSO_2Cl$, BuLi, THF, −78 °C → RT, overnight (90 %); vi) BuLi, $BF_3 \cdot OEt_2$, THF, −78 °C (18 %), **7i**/**8i** 55:45 (from ^1H NMR analysis).

acid groups were protected as the bis-lactim ether ring. As shown in Scheme 8, compound **6j** was prepared from sulfonamide-protected indolyl bromide **22** and Schöllkopf's chiral bis-lactim ether[26] **16**. Although the coupling between protected tryptophan derivatives **6i** and **6j** and mannose epoxide **4** afforded the desired properly functionalized precursors of the target molecule, the yields and stereoselectivities were unsatisfactory.

The total synthesis of mannosyl tryptophan: The successful strategy involved indole derivative **6k** as a latent tryptophan moiety, in which the bulky acyclic substituent at the 3-position of the indole ring and sulfonamide as the protection group of the indole nitrogen would enhance α-selectivity. As shown in Scheme 9, the straightforward synthesis of **6k** from commercially available L-tryptophanol **23** resulted in high yields. After the amino group was converted to an azide using TfN_3, the hydroxyl group was protected as *tert*-butyldimethylsilyl (TBS) ether. The indole ring was protected as the benzenesulfomamide using benzenesulfonyl choloride and BuLi to give **6k** in 61 % yield (from **23**). Subsequent coupling with 1,2-anhydro-mannose **4** proceeded with high selectivity (95:5) and satisfactory efficiency (63 % yield) to afford **7k**, along with a small amount of stereoisomer **8k**. Benzylation and subsequent removal of the TBS ether under acidic conditions afforded **24** in 91 % yield. With expectations that the strong electron withdrawing nature of the sulfonamide group would protect the indole group from oxidation, attempts to directly oxidize alcohol **24** to carboxylic acid **25** were carried out using typical oxidizing reagents. However, under various oxidizing conditions that included Jones reagent, PCC, $RuCl_3$, and Fetizon reagent,[33] compound **24** either decomposed or was almost inert. Likewise, partial oxidation to the aldehyde using IBX,[34] Dess–Martin reagent,[35] TPAP,[36] or ADD[37] was unsuccessful. As a note, the aldehyde was obtained in a small-scale using a combination of DMSO/DCC,[38] and can be subsequently oxidized using sodium hypochlorite[39] to the carboxylic acid; unfortunately, the transformation was difficult to reproduce, especially on a larger scale. In the end, a combination of TEMPO and iodosobenzene diacetate[40] was found to afford carboxylic acid **25** directly from **24** in excellent yields.

We have previously described the final deprotection step in the synthesis of **1** as an indirect route by way of Boc-protected intermediate **27**.[13b] However, a two-step deprotection via **26** was accomplished with concurrent reduction of the azido group. Final purification was performed using reverse-phase silica gel column chromatography (H_2O/MeOH 4:1) or size-exclusion column chromatography (Bio-Gel P-2 gel, extra fine, H_2O/MeOH 9:1). ^1H NMR data of synthetically derived

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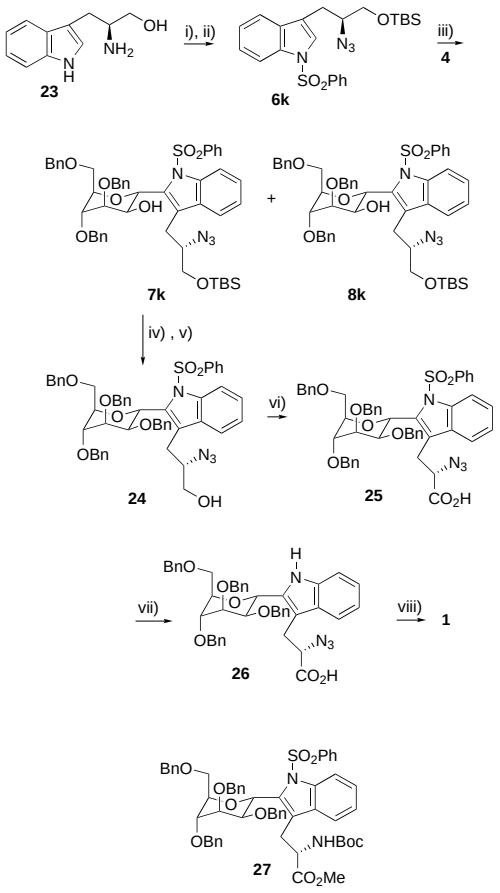
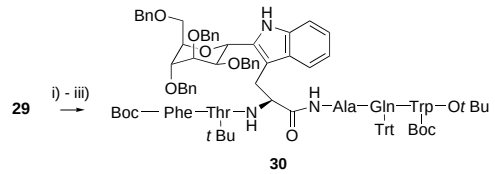


Scheme 9. i) TfN_3, DMAP, CH_3CN, RT, overnight, then TBSCl, imidazole, DMF, RT, overnight (82%, two steps); ii) $PhSO_2Cl$, BuLi, THF, $-78\,^{\circ}C \rightarrow$ RT, overnight (75%); iii) BuLi, $BF_3 \cdot OEt_2$, THF (63%), **7k**/**8k** 95:5; iv) BnBr, Bu_4NI, NaH, THF, $0\,^{\circ}C \rightarrow$ RT, overnight (92%); v) $TsOH \cdot H_2O$, MeOH, RT, overnight (91%); vi) iodosobenzene diacetate, TEMPO, CH_3CN, H_2O, RT, 3 h (97%); vii) 10% NaOH, EtOH, reflux, overnight (68%); viii) H_2, 20% $Pd(OH)_2/C$, EtOH, dioxane, H_2O (67%).

1 (in D_2O; $^3J_{1,2} = 8.1$ Hz) clearly showed that the mannose ring generally adopts the $^1C_4$ conformation, with the tryptophan moiety in the equatorial position; the NMR data is in good agreement with those reported for mannosyl-tryptophan containing peptides.[4b]

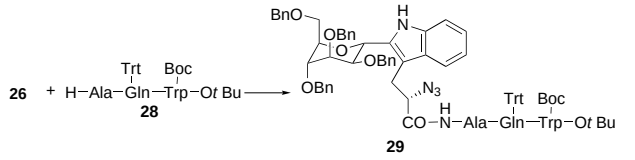
Peptide elongation: With attainment of homogeneous synthetic **1**, we consequently undertook the synthesis of hexapeptide **2**, which corresponds to residues 5–10 of human RNase Us. As shown in Scheme 10, intermediate **26** was proposed as the building block for C-mannosyl tryptophan.



Scheme 10. i) PMe_3, THF, H_2O, Fmoc-Thr-OH, EDC·HCl, HOBt, CH_2Cl_2; ii) piperidine, DMF; iii) Boc-Phe-OH, EDC·HCl, HOBt, CH_2Cl_2 (76%) (three steps).

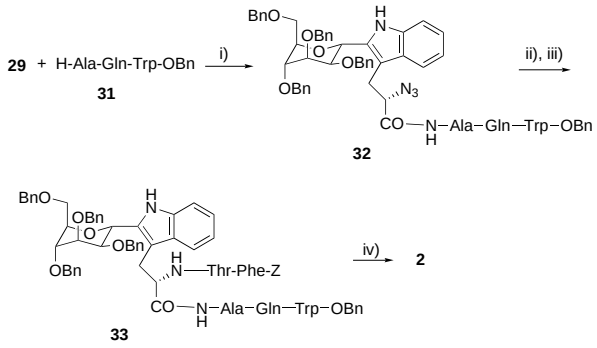
Azido acids, which do not form oxazolones, can be used for peptide synthesis without likelihood of racemization.[41] The peptide bond formation between azido acid **26** and tripeptide **28** was performed using the tetramethylfluoroformidium hexafluorophosphate (TFFH) mediated in situ acid fluoride formation protocol to provide tetrapeptide **29** in 90% yield (Table 2, entry 2),[42] which did not exhibit any epimerization, within the detection limits of 500 MHz ^{1}H NMR spectroscopy. Bromo-tris-pyrrolidino-phosphonium hexafluoroborate (PyBrop)[43] was equally effective (Table 2, entry 3), whereas a combination of carbodiimide/HOBt was less satisfactory (Table 2, entry 1).

Table 2. The peptide bond formation under various conditions.



Entry	Conditions	Yield [%]
1	EDC·HCl, HOBt, DMF	57
2	PyBrop, iPr$_2$NEt, CH_2Cl_2	90
3	TFFH, Na_2CO_3, CH_2Cl_2, H_2O	90

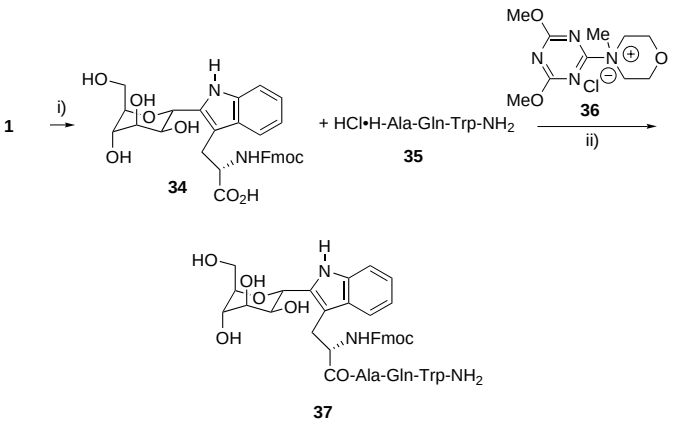
After selective reduction of the azido group using PMe_3, subsequent coupling reactions with Fmoc-Thr(tBu)-OH and Boc-Phe-OH were successfully carried out to afford **30** in good yields. However, under strongly acidic conditions, deprotection of protected hexapeptide **30** proved to be somewhat troublesome. Treatment of **30** with trifluoromethanesulfonic acid/trifluoroacetic acid/dimethyl sulfide or trimethylsilyltrifluoromethanesulfonate/dimethylsulfide,[44] or HF[45] resulted in the decomposition of the mannosyl tryptophan moiety, as evidenced by the complete disappearance of the characteristic ^{1}H NMR signal from the anomeric proton (δ 5.2). Thus, in order to avoid acidic deprotection conditions, the protection/deprotection strategy of the peptide was modified by employing benzyl groups to protect the C- and N-termini (Scheme 11). The final deprotection of compound **33** was



Scheme 11. i) TFFH, $Na_2CO_3 \cdot 10H_2O$, CH_2Cl_2, H_2O (90%); ii) PMe_3, THF, H_2O, Fmoc-Thr-OH, EDC·HCl, HOBt, CH_2Cl_2, HOBt, CH_2Cl_2 (84%); iii) piperidine, DMF, Z-Phe-OH, EDC·HCl, HOBt, CH_2Cl_2 (72%); iv) H_2, 20% $Pd(OH)_2/C$, MeOH, H_2O, THF, AcOH (57%).

performed under mild catalytic hydrogenation conditions using $Pd(OH)_2/C$ to yield product **2**, which was purified by gel filtration column chromatography (Sephadex LH-20, MeOH).

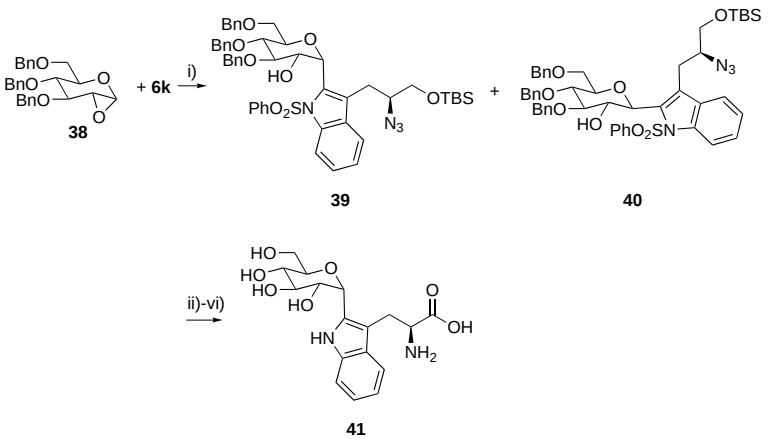
A more concise approach to glycopeptide synthesis is based upon minimal protection strategy, in which only the side chain carboxylic acid and amino groups are protected. Because of the large differences in reactivities between amino and hydroxyl groups, protection of the hydroxyl groups of the sugar moiety may be omitted. Accordingly, synthesis of glycopeptides using non-protected sugar moieties has been reported,[46] in which a pentafluorophenyl ester was employed as the activated amino acid. In contrast, we turned our attention to a novel amide formation protocol that is compatible with hydroxyl groups, which features 4-(4,6-dimethoxyl-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride (**36**). Compound **36** was reported to be effective for amide bond formation in protic solvents (MeOH, H_2O).[47] The amino group of mannosyl tryptophan was protected with Fmoc in a usual manner in 68% yield (Scheme 12). The



Scheme 12. i) Fmoc-OSu, $NaHCO_3$, DME, H_2O (67%); ii) **35**, **36**, MeOH (94%).

peptide bond formation between **34** and **35** in MeOH proceeded smoothly, and was complete within 30 min. Racemization of **37** was not observed within the detection limits of 400 MHz ^1H NMR spectroscopy. The advantage of this procedure is that the carboxylic acid can be used directly without previous activation.

Synthesis of glucosyl tryptophan: Using similar procedures as described above, glucosyl tryptophan, which is a steroisomer of mannosyl tryptophan, was synthesized (Scheme 13). Reaction between 1,2-anhydro-glucose **38**[48] and indole derivative **6k** afforded a mixture of α-isomer **39** and β-isomer **40** in a ratio of 82:18;[49] following similar procedures as described for the synthesis of **1**, glycosylated tryptophan **41** was obtained, and purified by reverse-phase column chromatography. From the ^1H NMR coupling constants, the glycosyl pyranose ring seemed to adopt the non-chair conformation ($^3J_{1,2} = 5.6$ Hz, in D_2O).



Scheme 13. i) BuLi, $BF_3 \cdot OEt_2$, THF, **39** (10%) and **40** (2%); ii) BnBr, Bu_4NI, NaH, THF, 0 °C, RT, overnight (77%); iii) $TsOH \cdot H_2O$, MeOH, RT, overnight (99%); iv) iodosobenzene diacetate, TEMPO, CH_3CN, H_2O, RT, 3 h (85%); v) 10% NaOH, EtOH, reflux, overnight (56%); v) H_2, 20% $Pd(OH)_2/C$, EtOH, dioxane, H_2O (65%).

Conclusion

In summary, the total synthesis of C-linked glyco amino acid **1** was achieved in a concise and stereoselective manner. Furthermore, our strategy proved to be useful for peptide elongation reactions, with or without protection of the hydroxyl groups. Investigations on conformational analysis of peptides containing **1** are currently underway.

Experimental Section

General procedures: ^1H and ^{13}C NMR spectra were taken by JEOL EX-270 or AL-400 apparatus as solutions in $CDCl_3$. Chemical shifts are expressed in ppm relative to the signal of either $CHCl_3$ or Me_4Si, adjusted to 7.24 or 0.00 ppm, respectively unless otherwise mentioned. $CHCl_3$ (δ_C 77.0 ppm) was used as an internal standard. Melting points were uncorrected. Optical rotations were measured by JASCO DIP-310 as solutions in $CHCl_3$ at ambient temperature. THF was distilled from Na/benzophenon just before use. Kanto silica gel (spherical, neutral, 100–210 μm) was used for column chromatography. TLC analysis was performed on Merck TLC plates (silica gel $60F_{254}$). Reverse phase silica gel was purchased from Senshu Kagaku. Bio-Gel P-2 gel and Bio-Beads S-X4 are available from BIO-RAD. Sephadex LH-20 was purchased from Amersham Pharmacia Biotech AB.

1,2-Anhydro-3,4,6-tri-*O*-benzyl-*β*-D-mannose (4): KO*t*Bu (3.05 g, 27.14 mmol) was added in small portions to a solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannosyl chloride (12.61 g, 24.67 mmol) in THF (300 mL). The mixture was heated under reflux under exclusion of moisture with $CaCl_2$ tube for 1 h. After cooling, the mixture was partitioned between $CHCl_3$ and brine. The aqueous layer was extracted with $CHCl_3$. The combined layers were washed with brine and dried over Na_2SO_4. After

0947-6539/03/0906-1440 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 6

filtration through Celite, the solvent was evaporated. The residue was washed with Et_2O/hexane to give 1,2-anhydride **4** as a white powder (9.98 g, 94%). The physical data was identical with those reported in ref. [17].

1-(Phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7a): BuLi (1.2 mL, 1.59 M in hexane, 1.95 mmol) was added dropwise at −78 °C to a solution of indole **6a** (537.0 mg, 2.09 mmol) in THF (8 mL). The mixture was stirred at 0 °C for 30 min. To a solution of epoxide **4** (611 mg, 1.39 mmol) in THF (20 mL), the solution of lithiated indole was transferred through a cannula. Then $BF_3 \cdot OEt_2$ (0.25 mL, 1.95 mmol) was added at −78 °C. The whole mixture was stirred at −78 °C for 10 h. The mixture was neutralized with Et_3N (0.5 mL), then partitioned between sat. NH_4Cl and EtOAc. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (toluene/EtOAc 9:1 → 4:1) to give **7a** (258 mg, 27%) and **8a** (115 mg, 12%). $[\alpha]_D^{24} = +102$ ($c = 1.90$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.10$ (d, $J = 8.3$ Hz, 1H), 7.87 (d, $J = 8.3$ Hz, 2H), 7.5–7.2 (m, 21H), 6.74 (s, 1H), 5.73 (d, $J = 7.3$ Hz, 1H), 4.66 (d, $J = 11.5$ Hz, 1H), 4.6–4.5 (m, 6H), 4.3 (m, 1H), 3.84 (dd, $J = 5.9$ Hz, $J = 10.2$ Hz, 1H), 3.57 (dd, $J = 5.6$, 10.2 Hz, 1H), 2.52 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR: $\delta = 138.7$ (C), 138.5 (C), 138.2 (C), 137.9 (C), 137.4 (C), 137.2 (C), 133.5 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 126.8 (CH), 125.0 (CH), 123.7 (CH), 121.2 (CH), 115.0 (CH), 111.6 (CH), 77.8 (CH), 74.9 (CH), 73.3 (CH), 73.2 (CH_2), 72.7 (CH_2), 68.9 (CH), 68.1 (CH_2), 68.0 (CH); elemental analysis calcd (%) for $C_{41}H_{39}NO_7S$: C 71.39, H 5.70, N 1.97; found C 71.44, H 5.74, N 1.97.

1-(Phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-1*H*-indole (8a): $[\alpha]_D^{24} = 92$ ($c = 0.45$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.02$ (d, $J = 8.2$ Hz, 1H), 7.82 (d, $J = 8.6$ Hz, 2H), 7.5–7.2 (m, 21H), 5.23 (s, 1H), 4.92 (d, $J = 10.9$ Hz, 1H), 4.82 (d, $J = 11.6$ Hz, 1H), 4.72 (d, $J = 11.6$ Hz, 1H), 4.61 (d, $J = 11.9$ Hz, 1H), 4.6 (m, 1H), 4.49 (d, $J = 11.9$ Hz, 1H), 4.0–3.7 (m, 5H), 2.39 (d, $J = 3.4$ Hz, 1H); ^{13}C NMR: $\delta = 138.4$ (C), 138.3 (C), 138.2 (C), 137.6 (C), 137.2 (C), 137.0 (C), 133.6 (CH), 129.5 (CH), 129.0 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 126.6 (CH), 124.9 (CH), 123.8 (CH), 121.3 (CH), 114.8 (CH), 112.6 (CH), 83.2 (CH), 79.4 (CH), 76.5 (CH), 75.2 (CH_2), 74.3 (CH), 73.5 (CH), 73.3 (CH_2), 71.5 (CH_2), 69.3 (CH_2), 68.4 (CH); elemental analysis calcd (%) for $C_{41}H_{39}NO_7S$: C 71.39, H 5.70, N 1.97; found C 72.09, H 5.70, N 1.99.

2-(3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole-1-carboxy *tert*-butyl ester (7b): *t*BuLi (0.31 mL, 1.59 M in pentane, 0.49 mmol) was added dropwise at −78 °C to a solution of indole **6b** (115 mg, 0.529 mmol) in THF (10 mL). The mixture was stirred at −78 °C for 30 min. Then the epoxide **4** (152 mg, 0.353 mmol) in THF (5 mL) was added to the lithiated indole. The flask was rinsed with THF (1 mL). Then $BF_3 \cdot OEt_2$ (63 μL, 0.49 mmol) was added dropwise. After the mixture was stirred at −78 °C for 10 h, Et_3N (0.2 mL) was added to neutralize the mixture. The mixture was partitioned between EtOAc and sat. $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc 7:3) to give β-product **8b** (80 mg, 32%) and α-product **7b** (41 mg, 17%). $[\alpha]_D^{24} = +92.2$ ($c = 1.08$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.01$ (d, $J = 8.4$ Hz, 1H), 7.4–7.1 (m, 23H), 6.27 (s, 1H), 5.70 (d, $J = 3.2$ Hz, 1H), 4.79 (d, $J = 11.6$ Hz, 1H), 4.73 (d, $J = 11.2$ Hz, 1H), 4.71 (d, $J = 11.9$ Hz, 1H), 4.57 (d, $J = 11.1$ Hz, 1H), 4.54 (d, $J = 12.2$ Hz, 1H), 4.47 (d, $J = 12.2$ Hz, 1H), 4.35 (m, 1H), 3.95 (m, 2H), 3.73 (dd, $J = 10.5$, 4.6 Hz, 1H), 3.62 (dd, $J = 10.5$, 3.2 Hz, 1H), 3.50 (m, 1H), 1.63 (s, 9H); ^{13}C NMR: $\delta = 150.3$ (C), 138.1 (C), 137.8 (C), 136.9 (C), 136.3 (C), 128.6 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 124.5 (CH), 122.6 (CH), 120.5 (CH), 114.8 (CH), 109.1 (CH), 84.4 (C), 79.2 (CH), 74.5 (CH), 74.2 (CH_2), 73.9 (CH), 73.3 (CH_2), 72.6 (CH_2), 71.7 (CH_2), 69.4 (CH), 68.8 (CH_2), 27.9 (CH_3); elemental analysis calcd (%) for $C_{40}H_{43}NO_7$: C 73.94, H 6.67, N 2.16; found: C 73.86, H 6.78, N 2.09.

2-(3,4,6-Tri-*O*-benzyl-β-D-mannopyranosyl)-1*H*-indole-1-carboxy *tert*-butyl ester (8b): $[\alpha]_D^{24} = +30.5$ ($c = 0.59$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.01$ (d, $J = 8.2$ Hz, 1H), 7.51 (d, $J = 7.4$ Hz, 1H), 7.4–7.2 (m, 17H), 6.88 (s, 1H), 5.31 (s, 1H), 4.92 (d, $J = 10.5$ Hz, 1H), 4.79 (d, $J = 11.6$ Hz, 1H), 4.72 (d, $J = 11.6$ Hz, 1H), 4.64 (d, $J = 11.3$ Hz, 1H), 4.58 (d, $J = 11.3$ Hz, 1H), 4.44 (m, 1H), 3.95 (dd, $J = 9.7$ Hz, 1H), 3.9–3.7 (m, 3H), 3.7–3.6 (m, 1H), 2.14 (br s, 1H), 1.62 (s, 9H); ^{13}C NMR: $\delta = 150.3$ (C), 138.3 (C), 138.3 (C), 137.9 (C), 136.9 (C), 136.4 (C), 129.1 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 124.0 (CH), 122.8 (CH), 120.6 (CH), 115.7 (CH), 110.0 (CH), 84.3 (CH), 82.9 (CH), 79.6 (C), 75.1 (CH_2), 75.0 (CH), 74.4 (CH), 73.4 (CH_2), 71.3 (CH_2), 69.3 (CH_2), 67.4 (CH_2), 28.2 (CH_3); elemental analysis calcd (%) for $C_{40}H_{43}NO_7$: C 73.94, H 6.67, N 2.16; found: C 73.81, H 6.67, N 2.16.

3-Methyl-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7c): *t*BuLi (1.53 M pentane solution, 0.13 mL, 0.20 mmol) was added at −78 °C to a solution of indole **6c** (82.8 mg, 0.215 mmol) in THF (6 mL). The mixture was stirred at −78 °C for 1 h. To the solution of lithiated indole, a solution of epoxide **4** (62 mg, 0.14 mmol) in THF (1 mL) was added. The flask was rinsed with THF (0.5 mL). Then $BF_3 \cdot OEt_2$ (25 μL, 0.20 mmol) was added. The mixture was stirred at −78 °C for 10 h. Then Et_3N (0.5 mL) was added to neutralize the mixture. The mixture was partitioned between EtOAc and sat. $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc 9:1 → 4:1). Further purification was achieved by preparative TLC (toluene/EtOAc 9:1) to give α-product **7c** (38.4 mg, 33%) and β-product **8c** (5.9 mg, 5.0%). $[\alpha]_D^{25} = +63$ ($c = 1.05$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.14$ (dd, $J = 0.99$, 7.2 Hz, 1H), 7.72 (dd, $J = 0.99$, 8.4 Hz, 2H), 7.4–7.2 (m, 21H), 5.77 (d, $J = 10.0$ Hz, 1H), 4.67 (d, $J = 11.9$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 4.54 (d, $J = 11.6$ Hz, 1H), 4.54 (d, $J = 11.9$ Hz, 1H), 4.48 (d, $J = 12.2$ Hz, 1H), 4.40 (d, $J = 12.2$ Hz, 1H), 4.4–4.3 (m, 2H), 3.98 (dd, $J = 3.2$ Hz, 3.2 Hz, 1H), 3.9–3.7 (m, 3H), 2.41 (s, 3H); ^{13}C NMR: $\delta = 138.7$ (C), 138.1 (C), 137.9 (C), 137.6 (C), 134.1 (CH), 133.3 (C), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 127.6 (CH), 126.5 (CH), 124.9 (CH), 123.5 (C), 121.2 (CH), 118.9 (CH), 115.3 (CH), 77.3 (CH), 74.6 (CH), 73.2 (CH_2, CH, CH_2), 71.5 (CH_2), 68.0 (CH), 67.8 (CH_2), 65.9 (CH), 9.8 (CH_3); elemental analysis calcd (%) for $C_{42}H_{41}NO_7S$: C 71.67, H 5.87, N 1.99; found: C 71.56, H 5.81, N 1.96.

3-Methyl-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-1*H*-indole (8c): $[\alpha]_D^{25} = -75$ ($c = 0.39$, in $CHCl_3$); ^{1}H NMR (500 MHz): $\delta = 8.12$ (dd, $J = 7.6$, 1.6 Hz, 1H), 7.54 (d, $J = 7.3$ Hz, 1H), 7.4–7.2 (m, 22H), 5.45 (s, 1H), 4.93 (d, $J = 11.1$ Hz, 1H), 4.78 (d, $J = 11.6$ Hz, 1H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.60 (d, $J = 11.1$ Hz, 1H), 4.60 (d, $J = 12.1$ Hz, 1H), 4.55 (m, 1H), 4.53 (d, $J = 12.1$ Hz, 1H), 3.97 (t, $J = 9.1$ Hz, 1H), 3.87 (dd, $J = 2.9$, 8.9 Hz, 1H), 3.77 (m, 2H), 3.55 (m, 1H), 2.46 (s, 3H), 2.23 (br s, 1H, D_2O exchangeable); ^{13}C NMR (125 MHz): $\delta = 138.4$ (C), 137.8 (C), 136.6 (C), 133.6 (CH), 132.2 (C), 130.9 (C), 130.5 (C), 129.2 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 128.0 (CH), 127.6 (CH), 126.0 (C), 124.9 (CH), 123.7 (CH), 122.4 (CH), 119.0 (CH), 115.2 (CH), 82.9 (CH), 79.9 (CH), 75.9 (CH), 75.2 (CH_2), 74.0 (CH), 73.3 (CH_2), 71.4 (CH_2), 69.5 (CH_2), 69.3 (CH_2), 10.4 (CH_3); elemental analysis calcd (%) for $C_{42}H_{41}NO_7S$: C 71.67, H 5.87, N 1.99; found: C 71.58, H 5.80 N 1.87.

3-Methyl-2-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-1*H*-indole-carboxy *tert*-butyl ester (8d): BuLi (2.9 mL, 1.59 M in hexane, 4.44 mmol) was added dropwise at −78 °C under Ar atmosphere to a solution of indole **6d** (1.37 g, 4.76 mmol) in THF (50 mL). After stirring the mixture for 30 min at −78 °C, the mixture was warmed to 0 °C. Then the mixture was stirred at 0 °C for 10 min. To a solution of epoxide **4** (1.37 g, 3.17 mmol) in THF (20 mL), the solution of lithium reagent was transferred through a cannula at −78 °C. Then $BF_3 \cdot OEt_2$ (0.40 mL, 3.17 mmol) was added dropwise. The whole mixture was stirred at −78 °C for 10 h. After neutralize the mixture with Et_3N (1 mL), the mixture was partitioned between sat. NH_4Cl and EtOAc. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried over Na_2SO_4. The residue was purified by silica gel column chromatography (hexane/EtOAc 4:1) to give **8d** (1.01 g, 48%). ^{1}H NMR ($CDCl_3$): $\delta = 7.97$ (d, $J = 7.3$ Hz, 1H), 7.5–7.1 (m, 24H), 5.52 (s, 1H), 4.94 (d, $J = 10.9$ Hz, 1H), 4.79 (d, $J = 11.5$ Hz, 1H), 4.72 (d, $J = 11.5$ Hz, 1H), 4.7–4.4 (m, 3H), 4.0–3.7 (m, 5H), 3.78 (m, 1H), 2.51 (s, 3H), 2.24 (d, $J = 3.3$ Hz, 1H); ^{13}C NMR: $\delta = 150.6$ (C), 138.5 (C), 138.4 (C), 138.0 (C), 135.3 (C), 131.3 (C), 130.9 (C), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 124.2 (CH), 122.4 (CH), 119.3 (C), 118.5 (CH), 115.5 (CH), 83.9 (C), 82.7 (CH), 79.5 (CH), 76.1 (CH), 75.1 (CH_2), 74.4 (CH), 73.4 (CH_2), 73.1 (CH_2), 71.3 (CH_2), 69.6 (CH_2), 68.8 (CH), 28.3 (CH_3), 10.3 (CH_3); elemental analysis calcd (%) for $C_{41}H_{45}NO_7$: C 74.19, H 6.83, N 2.11; found: C 73.98, H 6.87, N 2.00.

3-Ethyl-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7e): BuLi (0.15 mL, 1.53 M hexane solution, 0.23 mmol) was

added at −78 °C under Ar atmosphere to a solution of indole **6e** (70.0 mg, 0.245 mmol) in THF (6 mL). After stirring the mixture at −78 °C for 1.5 h, a solution of epoxide **4** (70.0 mg, 0.164 mmol) in THF (3 mL) was added. Then $BF_3 \cdot OEt_2$ (29 μL, 0.23 mmol) was added, and the whole mixture was stirred at −78 °C overnight. After addition of triethylamine (0.05 mL), sat. $NaHCO_3$ was added. The aqueous layer was extracted with EtOAc, then the combined layers were washed with brine. After the organic layer was dried over Na_2SO_4, the solvent was evaporated. The crude was purified by silica gel column chromatography (hexane/EtOAc 4:1) to give the adduct **8e** (44.2 mg, 38%). $[\alpha]_D^{24} = +54.3$ ($c = 1.02$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.03$ (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.6–7.0 (m, 21H), 5.66 (d, $J = 10.1$ Hz, 1H), 4.56 (d, $J = 11.9$ Hz, 1H), 4.52 (d, $J = 12.1$ Hz, 1H), 4.52 (d, $J = 12.1$ Hz, 1H), 4.43 (d, $J = 11.9$ Hz, 1H), 4.32 (q, $J = 7.6$ Hz, 1H), 4.19 (m, 1H), 3.98 (m, 1H), 3.76 (d, $J = 3.5$ Hz, 1H), 3.65 (m, 2H), 2.92 (m, 1H), 2.77 (m, 1H), 1.09 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR: $\delta = 138.7$ (C), 138.1 (C), 137.6 (C), 134.0 (C), 133.3 (CH), 130.9 (C), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 126.5 (CH), 124.7 (CH), 123.4 (CH), 119.2 (CH), 115.6 (CH), 74.6 (CH), 73.4 (CH), 73.2 (CH_2), 71.5 (CH_2), 68.7 (CH), 67.9 (CH_2), 66.1 (CH), 14.5 (CH_3); elemental analysis calcd (%) for $C_{43}H_{43}NO_7S$: C 71.94, H 6.04, N 1.95; found: C 71.88, H 5.97, N 1.77.

3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7f): BuLi (1.53 M hexane, 0.14 mL, 0.209 mmol) was added dropwise at −78 °C to a solution of indole **6f** (86.4 mg, 0.224 mmol) in THF (4 mL). After stirring the mixture for 1 h at −78 °C, a solution of epoxide **4** (64 mg, 0.149 mmol) in THF (3 mL) was added at −78 °C. Then $BF_3 \cdot OEt_2$ (26 μL, 0.209 mmol) was added. After stirring the mixture for 10 h at −78 °C, Et_3N (0.1 mL) was added to neutralize the mixture. After the mixture was partitioned between EtOAc and sat. $NaHCO_3$, the aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the mixture over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc 9:1) to give the adduct **8f** (61.4 mg, 50%). ^{1}H NMR: $\delta = 8.11$ (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.3$ Hz, 1H), 7.66 (d, $J = 7.3$ Hz, 1H), 7.3–7.1 (m, 21H), 5.86 (d, $J = 10.3$ Hz, 1H), 5.07 (d, $J = 12.4$ Hz, 1H), 5.00 (d, $J = 12.4$ Hz, 1H), 4.63 (d, $J = 11.6$ Hz, 1H), 4.62 (d, $J = 12.2$ Hz, 1H), 4.61 (d, $J = 12.2$ Hz, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 4.50 (d, $J = 12.2$ Hz, 1H), 4.45 (d, $J = 11.9$ Hz, 1H), 4.37 (d, $J = 11.9$ Hz, 1H), 4.3–4.2 (m, 2H), 3.95 (d, $J = 3.2$, 3.2 Hz, 1H), 3.9–3.6 (m, 3H), 2.64 (d, $J = 10.3$ Hz, 1H), 0.82 (s, 9H), 0.00 (s, 3H), −0.08 (s, 3H); ^{13}C NMR: $\delta = 138.51$ (C), 138.03 (C), 127.66 (C), 137.63 (C), 136.76 (C), 134.98 (C), 133.20 (CH), 130.38 (C), 128.75 (CH), 128.36 (CH), 128.30 (CH), 128.19 (CH), 128.14 (CH), 128.02 (CH), 127.86 (CH), 127.73 (CH), 127.66 (CH), 127.54 (CH), 127.46 (CH), 127.38 (CH), 126.50 (CH), 125.76 (CH), 124.16 (C), 123.38 (CH), 120.56 (CH), 115.16 (CH), 77.32 (CH), 75.18 (CH), 73.56 (CH), 73.29 (CH_2), 73.12 (CH_2), 71.65 (CH_2), 69.43 (CH), 67.96 (CH_2), 65.71 (CH), 56.70 (CH_2), 26.11 (CH_3), 18.42 (C), −5.14 (CH_3), −5.28 (CH_3); elemental analysis calcd (%) for $C_{48}H_{55}NO_8SSi$: C 69.12, H 6.65, N 1.68; found: C 68.82, H 6.35, N 1.65.

3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole-carboxy *tert*-butyl ester (7g and 8g): BuLi (1.53 M hexane, 0.15 mL, 0.23 mmol) was dropped at −78 °C to a solution of indole **6g** (90 mg, 0.25 mmol) in THF (6 mL). After 1 h at −78 °C, a solution of epoxide **4** (72 mg, 0.17 mmol) in THF (2 mL) was transferred through a cannula. Then, $BF_3 \cdot OEt_2$ (29 μL, 0.23 mmol) was added. The whole mixture was stirred at −78 °C for 6 h. After the mixture was neutralized with Et_3N (0.1 mL), the mixture was partitioned between EtOAc and sat. $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the mixture over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc 9:1 → 4:1) to give the adduct (22.0 mg, 17%) as a mixture of α-product **7g** and β-product **8g** (α-**7g**:β-**8g** = 1:0.3 from ^{1}H NMR analysis). ***α* product 7g**: ^{1}H NMR: $\delta = 7.94$ (d, $J = 6.6$ Hz, 1H), 7.84 (d, $J = 7.1$ Hz, 1H), 7.3–7.0 (m, 17H), 5.87 (d, $J = 10.0$ Hz, 1H), 5.07 (s, 2H), 4.40 (d, $J = 12.2$ Hz, 1H), 4.33 (d, $J = 12.2$ Hz, 1H), 4.22 (t, $J = 6.2$ Hz, 1H), 3.93 (t, $J = 3.0$ Hz, 1H), 1.60 (s, 9H), 0.84 (s, 9H), 0.00 (s, 3H); ***β* product 8g**: $\delta = 5.52$ (s, 1H), 5.27 (d, $J = 11.3$ Hz, 1H), 4.88 (t, $J = 11.9$ Hz, 1H), 4.76 (d, $J = 11.6$ Hz, 1H), 3.57 (d, $J = 8.4$ Hz, 1H), 0.09 (s, 3H), 0.06 (s, 3H).

3-[2-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7h): BuLi (0.19 mL, 1.53 M hexane solution, 0.28 mmol) was dropped at −78 °C under Ar atmosphere to a solution of indole **6h** (126.0 mg, 0.303 mmol) in THF (5 mL). After 1 h at −78 °C, a solution of epoxide **4** (87.0 mg, 0.202 mmol) in THF (2 mL) was transferred via cannula. Then, $BF_3 \cdot OEt_2$ (36 μL, 0.28 mmol) was added, and the mixture was stirred at −78 °C for 13 h. After addition of triethylamine (0.1 mL), sat. $NaHCO_3$ was added. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried over Na_2SO_4. After evaporation, the reside was purified by silica gel column chromatography (hexane/EtOAc 4:1) to give **7h** (85.1 mg, 50%) of adduct as a colorless oil. $[\alpha]_D^{26} = +35.3$ ($c = 1.2$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.22$ (d, $J = 7.4$ Hz, 1H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 7.1$ Hz, 1H), 7.4–7.2 (m, 15H), 5.88 (d, $J = 10.1$ Hz, 1H), 4.73 (d, $J = 12.2$ Hz, 1H), 4.68 (s, 2H), 4.61 (d, $J = 12.2$ Hz, 1H), 4.53 (d, $J = 11.9$ Hz, 1H), 4.46 (d, $J = 11.9$ Hz, 1H), 4.5–4.3 (m, 2H), 4.1 (m, 1H). 4.0–3.7 (m, 5H), 3.4–3.2 (m, 2H), 0.88 (s, 9H), −0.11 (s, 6H); ^{13}C NMR: $\delta = 138.7$ (C), 138.2 (C), 138.0 (C), 137.7 (C), 136.9 (C), 135.3 (C), 133.3 (C), 131.3 (CH), 128.8 (C), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 126.5 (CH), 124.8 (CH), 123.4 (CH), 122.4 (C), 119.8 (CH), 115.4 (CH), 77.5 (CH), 74.8 (CH), 73.3 (CH), 73.2 (CH_2), 71.5 (CH_2), 68.8 (CH), 68.0 (CH_2), 66.1 (CH), 63.4 (CH_2), 28.7 (CH_2), 26.0 (CH_3), 18.4 (C), −5.4 (CH_3); elemental analysis calcd (%) for $C_{49}H_{57}NO_8SSi$: C 69.39, H 6.77, N 1.65; found: C 69.30, H 6.86, N 1.67.

2-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl)-1*H*-indole (9): A suspension of benzyl ether **7a** (94.0 mg, 0.136 mmol) and 20% $Pd(OH)_2$/C (20 mg) in EtOH (20 mL) and THF (5 mL) was stirred at room temperature vigorously under H_2 atmosphere. The catalyst was filtered through celite and washed with $CHCl_3$ and MeOH. After evaporation, the material was dried in vacuo, and dissolved in pyridine (1 mL) and acetic anhydride (0.5 mL). The mixture was stirred overnight, and subsequently the solvent was evaporated and purified by preparative TLC (hexane/EtOAc 3:2) to give **9** (40 mg, 50%). $[\alpha]_D^{24} = +107$ ($c = 1.22$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.12$ (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 2H), 7.54 (m, 2H), 7.43–7.25 (m, 4H), 7.02 (s, 1H), 5.96 (d, $J = 4.8$ Hz, 1H), 5.85 (dd, $J = 3.6$, 4.8 Hz, 1H), 5.47 (dd, $J = 3.2$, 7.6 Hz, 1H), 5.26 (t, $J = 7.2$ Hz, 1H), 4.31 (dd, $J = 5.6$, 12.0 Hz, 1H), 3.74 (m, 1H), 3.63 (dd, $J = 12.4$, 3.6 Hz, 1H), 2.13 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H); ^{13}C NMR: $\delta = 170.57$ (C), 170.11 (C), 169.95 (C), 169.31 (C), 138.76 (C), 137.44 (C), 134.76 (C), 133.77 (CH), 128.99 (CH), 128.28 (C), 126.56 (CH), 125.76 (CH), 123.93 (CH), 121.54 (CH), 115.05 (CH), 112.74 (CH), 100.50 (CH), 72.31 (CH), 69.44 (CH), 68.40 (CH), 68.24 (CH), 67.14 (CH), 61.16 (CH_2), 20.94 (CH_3), 20.85 (CH_3), 20.80 (CH_3); elemental analysis calcd (%) for $C_{28}H_{29}NO_{11}S$: C 57.23, H 4.97, N 2.38; found: C 57.14, H 4.99, N 2.22.

2-(3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (11): 10% NaOH (0.12 mL) was added to a solution of sulfonamide **7a** (13.6 mg, 0.0197 mmol) in EtOH (1.5 mL), and the mixture was heated under reflux for 3 h. After cooling to room temperature, the mixture was partitioned between brine and $CHCl_3$. The aqueous layer was partitioned with $CHCl_3$ and dried over Na_2SO_4. After evaporation, the crude material was purified by preparative TLC (toluene/EtOAc 1:1) to give **11** (8.4 mg, 84%) of the desired product. $[\alpha]_D^{24} = +84.4$ ($c = 1.20$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.50$ (br s, 1H), 7.67–7.0 (m, 20H), 6.03 (s, 1H), 5.25 (s, 1H), 4.80 (d, $J = 11.5$ Hz, 1H), 4.79 (d, $J = 11.2$ Hz, 1H), 4.72 (d, $J = 11.5$ Hz, 1H), 4.59 (d, $J = 11.9$ Hz, 1H), 4.53 (d, $J = 11.9$ Hz, 1H), 4.50 (d, $J = 11.2$ Hz, 1H), 4.45 (m, 1H), 3.90 (dd, $J = 3.3$, 8.6 Hz, 1H), 3.80 (t, $J = 8.9$ Hz, 1H), 3.8–3.7 (m, 2H), 3.53 (m, 1H), 2.78 (br s, 1H); ^{13}C NMR: $\delta = 137.85$ (C), 137.48 (C), 135.78 (C), 133.82 (C), 128.53 (CH), 128.26 (CH), 128.17 (CH), 128.10 (CH), 127.90 (C), 127.63 (CH), 127.56 (CH), 127.51 (CH), 122.08 (CH), 120.16 (CH), 119.68 (CH), 110.85 (CH), 100.42 (CH), 79.88 (CH), 74.69 (CH_2), 74.62 (CH), 74.11 (CH), 73.35 (CH_2), 72.65 (CH), 69.42 (CH_2), 68.43 (CH); elemental analysis calcd (%) for $C_{35}H_{35}NO_5$: C 76.48, H 6.42, N 2.55; found: C 76.50, H 6.55, N 2.45.

3-Methyloxy-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole: NaH (68 mg, 1.70 mmol) was added at room temperature to a solution of **7f** (852 mg, 1.02 mmol), BnBr (0.5 mL, 2.04 mmol) and Bu_4NI (377 mg, 1.02 mmol) in DMF (2 mL). After the mixture was stirred overnight, the excess benzyl bromide was quenched with triethylamine. The mixture was partitioned between EtOAc and brine. The aqueous layer was extracted with EtOAc. After drying the extract over Na_2SO_4, the solvent was evaporated. To a solution of silyl ether (802 mg, 85%) in MeOH (5 mL), $TsOH \cdot H_2O$ (3 mg) was added. The mixture was stirred

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overnight and subsequently concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 7:3) to give alcohol (631 mg, 90%). $[\alpha]_D^{27} = +41$ ($c = 1.26$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.12$ (d, $J =$ 7.3 Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 9.1$ Hz, 1H), 7.5–7.2 (m, 25H), 5.87 (d, $J = 10.1$ Hz, 1H), 4.95 (d, $J = 12.7$ Hz, 1H), 4.80 (d, $J =$ 12.7 Hz, 1H), 4.66 (d, $J = 11.9$ Hz, 1H), 4.61 (s, 2H), 4.53 (d, $J = 11.9$ Hz, 1H), 4.44 (d, $J = 11.9$ Hz, 1H), 4.38 (d, $J = 11.9$ Hz, 1H), 4.3 (m, 2H), 3.98 (dd, $J = 3.2$, 3.2 Hz, 1H), 3.83 (m, 1H), 3.80 (dd, $J = 10.0$, 7.3 Hz, 1H), 3.65 (dd, $J = 10.0$, 3.7 Hz, 1H); elemental analysis calcd (%) for $C_{42}H_{41}NO_8S$: C 70.08, H 5.74, N 1.95; found: C 69.78, H 5.87, N 1.90.

3-Bromomethyl-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (15): PPh_3 (12 mg, 0.066 mmol) and NBS (17 mg, 0.066 mmol) were added at 0 °C to a solution of alcohol (38.7 mg, 0.0551 mmol) in CH_2Cl_2 (0.5 mL). After 1 h, the mixture was purified by silica gel column chromatography directly (hexane/EtOAc 7:3) to give bromide **15** (40.2 mg, 96%). ^{1}H NMR: $\delta = 8.14$ (dd, $J = 1.8$, 6.1 Hz, 1H), 7.73 (d, $J = 7.4$ Hz, 2H), 7.61 (d, $J = 1.0$, 6.4 Hz, 1H), 7.5–7.1 (m, 25H), 5.90 (d, $J = 10.3$ Hz, 1H), 5.17 (d, $J = 10.5$ Hz, 1H), 4.75 (d, $J = 10.5$ Hz, 1H), 4.65 (d, $J = 11.6$ Hz, 1H), 4.57 (d, $J = 11.6$ Hz, 1H), 4.50 (d, $J = 11.9$ Hz, 1H), 4.41 (d, $J = 11.9$ Hz, 1H), 4.32 (dd, $J = 3.2$ Hz, 1H), 4.04 (d, $J = 3.2$ Hz, 1H), 3.87 (dd, $J = 10.0$ Hz, 7.8 Hz, 1H), 3.8 (m, 1H), 3.66 (dd, $J = 10.0$, 6.2 Hz, 1H), 2.50 (d, $J = 11.4$ Hz, 1H).

***N*-(Benzyloxycarbonyl)-(2-methyl-2-oxetanyl)-L-tryptophan methyl ester**: EDC·HCl (2.64 g, 13.8 mmol) was added at 0 °C to a solution of Z-Trp-OH (4.66 g, 13.8 mmol), 3-methyl-3-oxetanemethanol (1.1 mL) and DMAP (90 mg, 0.74 mmol) in CH_2Cl_2 (30 mL). After the mixture was stirred at 0 °C to room temperature overnight, 1M HCl was added to the mixture. The aqueous layer was extracted with EtOAc. The combined layer was washed with brine. After the extract was dried over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc 7:3) to give ester (4.85 g, quant). ^{1}H NMR: $\delta = 8.12$ (br s, 1H), 7.52 (d, $J = 11.6$ Hz, 1H), 7.3–6.99 (m, 9H), 5.32 (m, 1H), 5.10 (s, 2H), 4.74 (m, 1H), 4.3–4.0 (m, 7H), 3.2 (m, 2H), 0.88 (s, 3H); elemental analysis calcd (%) for $C_{24}H_{26}N_2O_5$: C 68.23, H 6.20, N 6.63; found: C 68.09, H 6.20, N 6.40.

(α*S*)-α-Azido-1*H*-indole-3-propanoic acid (2-methyl-2-oxetanyl) methyl ester (21): The suspension of benzyloxycarbonyl compound (0.42 g, 1.00 mmol) and 10% Pd/C (50 mg) in MeOH was stirred vigorously under H_2 atmosphere. After consuming the starting material from TLC analysis, the catalyst was filtered through Celite. The catalyst was washed with MeOH. The mixture was concentrated in vacuo. To a solution of the above prepared amine (0.29 g, 1.01 mmol) and DMAP (488 mg, 4.00 mmol) in CH_3CN (20 mL), TfN_3 (0.20M, CH_2Cl_2 solution) was added at 0 °C. After the mixture was stirred at room temperature overnight, the solvent was evaporated. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc 7:3) to give azido compound **21** (0.23 g, 72%). ^{13}C NMR: $\delta = 170.51$ (C), 136.13 (C), 127.00 (C), 123.14 (CH), 122.37 (CH), 119.76 (CH), 118.40 (CH), 111.31 (CH), 79.26 (CH_2), 70.00 (CH_2), 62.39 (CH), 38.90 (C), 27.72 (CH_2), 20.85 (CH_3); elemental analysis calcd (%) for $C_{16}H_{18}N_4O_3$: C 61.13, H 5.77, N 17.82; found: C 59.97, H 5.70, N 17.50.

3-[(2*S*)-2-Azido-2-(4-methyl-2,6,7-trioxabicyclo[2.2.2]oct-1-yl)ethyl]-1*H*-indole: $BF_3 \cdot OEt_2$ (58 μL, 0.46 mmol) was added dropwise at −10 °C to a solution of ester **21** (640.7 mg, 1.82 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred at −10 °C for 21 h, then at 0 °C for 6 h. After neutralized the reaction mixture by adding triethylamine (0.1 mL), sat. NH_4Cl was added. The aqueous layer was extracted with ethyl acetate. The combined layers were washed with sat. $NaHCO_3$ and brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The crude material was purified by silica gel column chromatography (hexane/EtOAc 3:2) to give orthoester as a colorless oil (218.8 mg, 34%). ^{1}H NMR: $\delta = 8.02$ (br s, 1H), 7.64 (d, $J =$ 7.6 Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.2–7.0 (m, 3H), 4.02 (s, 6H), 3.64 (dd, $J = 2.4$, 11.3 Hz, 1H), 3.25 (dd, $J = 2.4$, 14.6 Hz, 1H), 2.85 (dd, $J = 14.6$, 11.3 Hz, 1H), 0.87 (s, 3H); ^{13}C NMR: $\delta = 136.17$ (C), 127.31 (C), 122.85 (CH), 121.93 (CH), 119.30 (CH), 118.71 (CH), 112.03 (C), 111.13 (CH), 108.69 (CH), 72.76 (CH_2), 64.98 (CH), 30.68 (C), 24.61 (CH_2), 14.26 (CH_3); elemental analysis calcd (%) for $C_{15}H_{16}N_4O_3$: C 59.99, H 5.37, N 18.66; found: C 59.70, H 5.32, N 18.46.

3-[(2*S*)-2-Azido-2-(4-methyl-2,6,7-trioxabicyclo[2.2.2]oct-1-yl)ethyl]-1-(phenylsulfonyl)-1*H*-indole (6i): BuLi (1.53M hexane, 0.59 mL, 0.91 mmol) was added at −78 °C to a solution of the above indole (259.0 mg, 0.824 mmol) in THF (8 mL). After addition, the mixture was warmed to 0 °C then stirred for 1 h. The mixture was cooled to −78 °C again, and $PhSO_2Cl$ (126 μL, 0.989 mmol) was added dropwise. The mixture was warmed gradually to room temperature and the mixture was stirred at room temperature for 1 d. The mixture was quenched with sat. NH_4Cl, and the aqueous layer was extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After evaporation, the crude material was purified by silica gel column chromatography (hexane/EtOAc 7:3) to give **23** (256.7 mg, 68%) of sulfonamide **6i**. $[\alpha]_D^{28} = -9.0$ ($c = 1.00$, in $CHCl_3$); ^{1}H NMR: $\delta = 7.98$ (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 7.0$ Hz, 1H), 7.52–7.20 (m, 8H), 3.98 (s, 6H), 3.54 (dd, $J = 2.2$, 10.8 Hz, 1H), 3.12 (dd, $J = 2.4$ Hz, 15.1 Hz, 1H), 2.75 (dd, $J = 15.1$, 10.8 Hz, 1H), 0.85 (s, 3H); ^{13}C NMR: $\delta = 138.13$ (C), 135.32 (C), 133.66 (CH), 130.78 (C), 129.16 (CH), 126.67 (CH), 124.77 (CH), 124.50 (CH), 123.23 (CH), 119.45 (CH), 113.84 (CH), 108. 58 (C), 72.82 (CH_2), 64.02 (CH), 30.77 (CH), 24.51 (CH), 21.46 (CH_2), 14.30 (CH_3); elemental analysis calcd (%) for $C_{21}H_{20}N_4O_5S$: C 57.26, H 4.58, N 12.72; found: C 57.03, H 4.50, N 12.59.

3-[(2*S*)-2-Azido-2-(4-methyl-2,6,7-trioxabicyclo[2.2.2]oct-1-yl)ethyl]-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7i): BuLi (0.15 mL, 1.53M hexane solution, 0.23 mmol) was added at −78 °C under Ar atmosphere to a solution of indole **6i** (112.0 mg, 0.246 mmol) in THF (6 mL). After 1 h at −78 °C, a solution of epoxide **4** (71 mg, 0.16 mmol) in THF (3 mL) was transferred through a cannula. Then $BF_3 \cdot OEt_2$ (29 μL, 0.23 mmol) was added. The mixture was stirred at −78 °C for 5 h. After addition of triethylamine (0.1 mL), then sat. $NaHCO_3$ was added. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried over Na_2SO_4. After evaporation, the indole derivative **6i** was removed by silica gel column chromatography (hexane/EtOAc 7:3) and purified by preparative TLC (toluene/EtOAc 9:1) to give α-adduct **7i** (14.3 mg, 9.8%) and β-adduct **8i** (23.1 mg, 15%). $[\alpha]_D^{28} = -2.0$ ($c = 0.70$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.13$ (d, $J = 7.8$ Hz, 1H), 7.67 (dd, $J = 7.4$, $J = 1.2$ Hz, 1H), 7.55 (dd, $J = 6.6$, 1.7 Hz, 1H), 7.2–7.0 (m, 21H), 5.78 (d, $J = 10.1$ Hz, 1H), 4.72 (d, $J = 12.2$ Hz, 1H), 4.64 (d, $J =$ 11.9 Hz, 1H), 4.58 (d, $J = 11.9$ Hz, 1H), 4.51 (d, $J = 12.2$ Hz, 1H), 4.4–4.3 (m, 4H), 3.98 (m, 1H), 3.88 (m, 1H), 3.75 (s, 6H), 3.84 (dd, $J = 4.3$, 9.7 Hz, 1H), 3.35 (dd, $J = 4.3$, 14.6 Hz, 1H), 3.20 (dd, $J = 14.6$, 9.7 Hz, 1H), 0.71 (s, 3H); ^{13}C NMR: $\delta = 138.41$ (C), 138.33 (C), 138.29 (C), 137.67 (C), 137.28 (C), 135.89 (C), 133.27 (CH), 131.39 (CH), 128.76 (CH), 128.55 (CH), 128.36 (CH), 128.29 (CH), 127.96 (CH), 127.75 (CH), 127.64 (CH), 127.58 (CH), 127.49 (CH), 126.46 (CH), 124.83 (CH), 123.59 (CH), 122.63 (C), 120.07 (CH), 115.72 (CH), 108.59 (C), 77.93 (CH), 74.13 (CH), 73.26 (CH), 73.06 (CH_2), 72.53 (CH_2), 71.36 (CH_2), 68.62 (CH), 67.93 (CH_2), 66.36 (CH),. 64.38 (CH), 30.50 (CH_2), 24.84 (C), 14.26 (CH_3); elemental analysis calcd (%) for $C_{49}H_{50}N_4O_{10}S$: C 66.35, H 5.68, N 6.32; found: C 66.21, H 5.60, N 6.01.

[3-[[(2*S*,5*R*)-2,5-Dihydro-3,6-dimethoxy-5-(1-methylethyl)pyrazinyl]-methyl]-1-(phenylsulfonyl)-indole (6j): BuLi (1.53M hexane, 0.74 mL, 1.13 mmol) was added dropwise within 10 min at −78 °C under Ar atmosphere to a solution of pyrazine **16** (207 mg, 1.13 mmol) in THF (10 mL). After 30 min, the bromide **22** (358 mg, 1.02 mmol) was added as a solution of THF (13 mL) to the resulting yellow solution at −78 °C. The mixture was stirred at −78 °C for 14 h. The mixture was partitioned between sat. NH_4Cl and EtOAc. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the mixture over Na_2SO_4, the solvent was evaporated. The crude material was purified by silica gel column chromatography (hexane/EtOAc 9:1 → 4:1) to give the desired compound **6j** (358 mg, 78%). $[\alpha]_D^{27} = +6.8$ ($c = 0.89$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.02$ (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 8.6$ Hz, 1H), 7.6–7.2 (m, 6H), 4.41 (dd, $J = 4.5$ Hz, 8.2 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.3–3.2 (m, 3H), 2.17 (d, sesq, $J = 3.5$ Hz, $J = 6.9$ Hz, 1H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.68 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR: $\delta =$ 163.88 (C), 162.03 (C), 138.24 (C), 133.52 (CH), 131.53 (C), 129.12 (CH), 126.48 (CH), 124.44 (CH), 124.41 (CH), 122.79 (CH), 120.00 (CH), 118.61 (C), 113.33 (CH), 60.33 (CH), 55.54 (CH), 52.25 (CH_3), 31.33 (CH), 29.07 (CH_2), 18.89 (CH_3), 16.39 (CH_3); elemental analysis calcd (%) for $C_{24}H_{27}N_3O_4S$: C 63.56, H 6.00, N 9.26; found: C 62.53, H 5.88, N 9.07.

3-[[(2*S*,5*R*)-2,5-Dihydro-3,6-dimethoxy-5-(1-methylethyl)pyrazinyl]methyl]-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7j and 8j): BuLi (1.53M hexane, 0.24 mL, 0.370 mmol) was added to a solution of indole **6j** (193 mg, 0.401 mmol) in THF (8 mL). After stirring

the mixture for 30 min at −78 °C, a solution of epoxide **4** (115 mg, 0.267 mmol) in THF (3 mL) was added to the mixture. Then $BF_3 \cdot OEt_2$ (47 μL, 0.370 mmol) was added. The mixture was stirred at −78 °C for 10 h. After neutralization of the mixture with Et_3N (0.1 mL), the mixture was partitioned between EtOAc and sat. $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After evaporation, the residue was purified by silica gel column chromatography (hexane/EtOAc 4:1) to give the adduct (19.3 mg, 8.7 %) as a mixture of (α:β 55:45 from ^{1}H NMR analysis) isomers.

3-[(2*S*)-2-Azido-3-[(*tert*-butyldimethylsilyl]oxy]propyl]-1*H*-indole: A solution of TfN_3 (0.26 M) in CH_2Cl_2 (10 mL) was added dropwise at room temperature within 15 min to a solution of L-tryptophanol **23** (380.0 mg, 2.00 mmol) and DMAP (1.07 g, 8.80 mmol) in CH_3CN (20 mL). After stirring the mixture overnight, the solvent was removed by evaporation. The concentrated solution was directly purified by silica gel column chromatography (hexane/ethyl acetate 7:3 → 1:1). The obtained pale yellow oil (476 mg) was dissolved in DMF (20 mL), then imidazole (216 mg, 3.00 mmol) was added. TBSCl (364 mg, 2.42 mmol) was added to the solution in small portions at 0 °C. The mixture was stirred at room temperature overnight. The mixture was diluted with ethyl acetate (200 mL), then sat. aq NH_4Cl (40 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (50 mL), then brine (50 mL). After drying the mixture over Na_2SO_4, the solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (hexane/EtOAc 9:1 → 4:1) to afford the silyl ether as a colorless oil (543.2 mg, 82 %, two steps). $[\alpha]_D^{28} = -16.3$ ($c = 1.01$, in $CHCl_3$); ^{1}H NMR (270 MHz): $\delta = 7.95$ (br s, 1H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.2 – 7.0 (m, 3H), 3.7 – 3.6 (m, 3H), 2.95 (dd, $J = 9.6$, 14.8 Hz, 1H), 2.85 (dd, $J = 7.0$, 14.8 Hz, 1H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (67.8 MHz): $\delta = 136.17$ (C), 127.40 (C), 122.70 (CH), 122.14 (CH), 119.50 (CH), 118.66 (CH), 111.87 (C), 111.18 (CH), 65.58 (CH_2), 63.61 (CH), 26.26 (CH_2), 25.82 (CH_3), 18.24 (C), −5.51 (CH_3); elemental analysis calcd (%) for $C_{17}H_{26}N_4OSi$: C 61.78, H 7.93, N 16.95; found: C 61.89, H 7.93, N 16.85.

3-[(2*S*)-2-Azido-3-[(*tert*-butyldimethylsilyl)oxy]propyl]-1-(phenylsulfonyl)-1*H*-indole (6k): BuLi (1.51 M in hexane, 44.0 mL, 66.63 mmol) was added dropwise at −78 °C under Ar atmosphere to a solution of the above indole (20.0 g, 60.57 mmol) in THF (500 mL). The mixture was stirred at −78 °C for 15 min, then at 0 °C for 60 min. The mixture was cooled again to −78 °C, then benzenesulfonyl chloride (8.5 mL, 66.61 mmol) was dropped. The mixture was warmed slowly to room temperature, then stirred for 5 h. The reaction was quenched with sat. aq NH_4Cl (20 mL), then the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined layers were washed with sat. aq $NaHCO_3$ (30 mL) and brine (30 mL). After drying the extract over Na_2SO_4, the solvent was removed. The residue was purified by silica gel column chromatography (hexane/EtOAc 20:1 → 10:1) to afford **6k** as a pale yellow oil (22.27 g, 78 %). $[\alpha]_D^{24} = +4.8$ ($c = 0.91$, in $CHCl_3$); ^{1}H NMR (270 MHz): $\delta = 7.92$ (d, $J = 8.1$ Hz, 1H), 7.71 (d, $J = 8.1$ Hz, 2H), 7.59 (dd, $J = 1.2$, 6.9 Hz, 1H), 7.5 – 7.2 (m, 7H), 3.65 (dd, $J = 3.0$, 7.0 Hz, 1H), 3.6 – 3.5 (m, 2H), 2.88 (dd, $J = 10.0$, 3.8 Hz, 1H), 2.75 (dd, $J = 10.0$, 5.4 Hz, 1H), 1.48 (s, 9H), −0.01 (s, 6H); ^{13}C NMR (67.8 MHz): $\delta = 138.14$ (C), 135.23 (C), 133.74 (CH), 130.71 (CH), 129.22 (CH), 126.69 (CH), 124.92 (CH), 124.33 (CH), 123.28 (CH), 119.32 (CH), 118.73 (C), 113.83 (CH), 65.41 (CH_2), 62.56 (CH), 26.01 (CH_2), 25.78 (CH_3), 18.21 (C), −5.5 (CH_3); elemental analysis cacld (%) for $C_{23}H_{30}N_4O_3SiS$: C 58.69, H 6.24, N 11.90; found: C 58.56, H 6.45, N 11.67.

3-[(2*S*)-2-Azido-3-[(*tert*-butyldimethylsilyl)oxy]propyl]-1-(phenylsulfonyl)-2-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (7k): *n*BuLi (1.52 M hexane solution, 4.4 mL, 6.64 mmol) was added dropwise at −78 °C under Ar atmosphere to a solution of **6k** (3.32 g, 7.09 mmol) in THF (150 mL). The mixture was stirred at −78 °C for 1.5 h, then a THF solution (30 mL) of epoxide **4** (2.03 g, 4.71 mmol) in THF (30 mL) was transferred through a cannula at −78 °C. The flask was rinsed with THF (2 × 5 mL). Then $BF_3 \cdot OEt_2$ (0.84 mL, 6.6 mmol) was added dropwise. The mixture was stirred at −78 °C for 20 h, then triethylamine (5 mL) was added to neutralize the mixture. After 5 min, sat. aq $NaHCO_3$ (40 mL) was added. The aqueous layer was extracted with ethyl acetate (200 mL, 3 × 100 mL). The combined layers were washed with brine (50 mL), then dried over Na_2SO_4. After filtration, the solvent was evaporated, and the crude mixture was purified by silica gel column chromatography (hexane/ethyl acetate 20:1 → 10:1) to give **7k** as a colorless oil (2.68 g, 63 %). $[\alpha]_D^{24} = +33.6$ ($c = 0.63$, in $CHCl_3$); ^{1}H NMR (270 MHz): $\delta = 8.18$ (d, $J = 8.4$ Hz, 1H), 7.73 (dd, $J = 8.2$, 1.0 Hz, 2H), 7.69 (dd, $J = 1.0$, 6.9 Hz, 1H), 7.5 – 7.1 (m, 20H), 5.85 (d, $J = 10.1$ Hz, 1H, H-1′), 4.72 (d, $J = 12.2$ Hz, 1H, Bn), 4.65 (d, $J = 11.5$ Hz, 1H, Bn), 4.61 (d, $J = 11.5$ Hz, 1H, Bn), 4.55 (d, $J = 12.2$ Hz, 1H, Bn), 4.49 (d, $J = 11.9$ Hz, 1H, Bn), 4.43 (d, $J = 11.9$ Hz, 1H, Bn), 4.4 – 4.2 (m, 2H), 3.99 (t, $J = 3.0$ Hz, 1H), 3.9 – 3.8 (m, 2H), 3.8 – 3.7 (m, 2H), 3.55 (dd, $J = 10.5$, 3.5 Hz, 1H), 3.31 (dd, $J = 10.5$, 5.9 Hz, 1H), 3.13 (m, 2H), 2.57 (d, $J = 11.4$ Hz, 1H, *OH*), 0.89 (s, 9H, Bu), 0.00 (s, 3H, Me), −0.02 (s, 3H, Me); ^{13}C NMR (67.8 MHz): $\delta = 138.11$ (C), 137.82 (C), 137.49 (C), 136.92 (C), 136.00 (C), 133.37 (CH), 128.78 (CH), 128.58 (CH), 128.48 (CH), 128.32 (CH), 128.04 (CH), 127.93 (CH), 127.82 (CH), 127.79 (CH), 127.71 (CH), 127.62 (CH), 127.58 (CH), 126.53 (CH), 125.08 (CH), 123.73 (C), 121.89 (CH), 119.68 (CH), 115.73 (CH), 77.37 (CH), 74.49 (CH), 73.17 (CH_2), 73.13 (CH_2), 72.88 (CH), 71.54 (CH_2), 68.33 (CH), 67.70 (CH_2), 65.00 (CH_2), 63.99 (CH), 25.83 (CH_3), 25.63 (CH_2), 18.25 (C), −5.5 (CH_3), −5.6 (CH_3); elemental analysis calcd (%) for $C_{50}H_{58}N_4O_8SiS$: C 66.49, H 6.47, N 6.20; found: C 66.40, H 6.58, N 6.08.

3-[(2*S*)-2-Azido-3-[(*tert*-butyldimethylsilyl)oxy]propyl]-1-(phenylsulfonyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole: NaH (60 %, 58 mg, 1.45 mmol) was added in several portions at 0 °C to a solution of alcohol **7k** (653 mg, 0.723 mmol), BnBr (0.34 mL, 2.89 mmol), and nBu$_4$NI (773 mg, 1.45 mmol) in DMF (15 mL). The mixture was stirred at 0 °C → room temperature overnight. Triethylamine (2 mL) was added to destroy the excess of benzyl bromide. After 20 min, sat. aq NH_4Cl (30 mL) was added to the mixture, and the aqueous layer was extracted with ethyl acetate (100 mL, 3 × 50 mL). The combined layers were washed with brine (50 mL), then dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (hexane/ethyl acetate 9:1) to give the product (652 mg, 92 %). $[\alpha]_D^{24} = +36.7$ ($c = 0.55$, in $CHCl_3$); ^{1}H NMR (270 MHz): $\delta = 8.29$ (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 7.4$ Hz, 2H), 7.5 – 7.1 (m, 22H), 7.03 (t, $J = 7.3$ Hz, 2H), 6.84 (d, $J = 7.3$ Hz, 2H), 6.32 (br s, 1H, H-1′), 4.89 (d, $J = 12.2$ Hz, 1H, Bn), 4.73 (d, $J = 12.2$ Hz, 1H, Bn), 4.65 (d, $J = 12.2$ Hz, 1H, Bn), 4.55 (d, $J = 11.6$ Hz, 1H, Bn), 4.51 (d, $J = 11.9$ Hz, 1H, Bn), 4.38 (m, 1H), 4.3 – 4.2 (m, 3H), 4.2 – 4.0 (m, 3H), 3.8 (m, 2H), 3.6 (m, 1H), 3.37 (dd, $J = 3.2$, 10.8 Hz, 1H), 3.03 (dd, $J = 5.1$, 10.8 Hz, 1H), 2.94 (dd, $J = 5.1$, 13.2 Hz, 1H), 2.75 (dd, $J = 8.9$, 13.2 Hz, 1H), −0.06 (s, 9H), 0.00 (s, 3H), −0.03 (s, 3H); ^{13}C NMR (67.8 MHz): $\delta = 138.45$ (C), 138.31 (C), 138.11 (C), 137.19 (C), 133.04 (CH), 128.40 (CH), 128.34 (CH), 128.24 (CH), 128.13 (CH), 127.98 (CH), 127.95 (CH), 127.88 (CH), 127.70 (CH), 127.64 (CH), 127.59 (CH), 127.47 (CH), 127.46 (CH), 127.08 (CH), 124.99 (CH), 123.79 (CH), 123.09 (CH), 119.56 (CH), 5.17 (CH), 74.97 (CH), 73.27 (CH_2), 68.26 (CH), 64.20 (CH_2), 63.33 (CH), 25.84 (CH_3), 24.95 (CH_2), 18.23 (CH_2), −5.6 (CH_3), −5.6 (CH_3); elemental analysis calcd (%) for $C_{50}H_{58}N_4O_8SSi$:C 66.49, H 6.47, N 6.20; found: C 66.29, H 6.21, N 5.90.

3-[(2*S*)-2-Azido-3-hydroxypropyl]-1-(phenylsulfonyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole (24): $TsOH \cdot H_2O$ (100 mg) was added at room temperature to a solution of TBS ether (3.14 g, 3.16 mmol) in MeOH (150 mL). The mixture was stirred at room temperature for 11 h, then $TsOH \cdot H_2O$ was quenched by triethylamine (2 mL). After removal of MeOH, the residue was purified directly by silica gel column chromatography (hexane/ethyl acetate 7:3) to give **24** (2.77 g quant.). $[\alpha]_D^{24} = +48$ ($c = 0.59$, in $CHCl_3$); ^{1}H NMR (270 MHz): $\delta = 8.24$ (d, $J = 8.2$ Hz, 1H), 7.75 (d, $J = 7.6$ Hz, 2H), 7.43 (dd, $J = 0.7$, 7.7 Hz, 1H), 7.4 – 7.2 (m, 21H), 6.96 (t like, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 7.7$ Hz, 1H), 6.27 (br s, 1H, H-1′), 4.82 (d, $J = 12.2$ Hz, 1H, Bn), 4.62 (d, $J = 12.7$ Hz, 1H, Bn), 4.56 (d, $J = 12.4$ Hz, 1H, Bn), 4.53 (d, $J = 12.7$ Hz, 1H, Bn), 4.48 (d, $J = 11.9$ Hz, 1H, Bn), 4.43 (d, $J = 13.5$ Hz, 1H, Bn), 4.4 – 3.9 (m, 6H), 3.7 – 3.6 (m, 3H), 3.0 – 2.9 (m, 3H), 2.58 (m, 1H), 2.20 (t, $J = 6.4$ Hz, *OH*, 1H); ^{13}C NMR (67.8 MHz): $\delta = 138.32$ (C), 138.16 (C), 137.94 (C), 137.45 (C), 133.19 (CH), 128.43 (CH), 128.38 (CH), 128.32 (CH), 128.26 (CH), 128.02 (CH), 127.98 (CH), 127.93 (CH), 127.80 (CH), 127.76 (CH), 127.66 (CH), 127.53 (CH), 126.99 (CH), 125.20 (CH), 124.10 (CH), 119.75 (CH), 116.76 (CH), 76.66 (CH), 75.71 (CH_2), 74.32 (CH_2), 73.24 (CH_2), 71.60 (CH), 67.94 (CH_2), 63.69 (CH), 62.55 (CH_2), 25.37 (CH_2); HRMS: m/z: cacld for $C_{51}H_{51}N_4O_8S$: 879.3428; found: 879.3484.

α-Azido-1-(phenylsulfonyl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole-3-propanoic acid (25): TEMPO (7.0 mg, 0.045 mmol) was added at room temperature to a mixture of alcohol **24** (175.0 mg, 0.199 mmol), and iodosobenzene diacetate (153.0 mg, 0.475 mmol) in CH_3CN (4 mL) and H_2O (4 mL). The mixture was stirred vigorously at room temperature for 3 h. The reaction mixture was diluted with $CHCl_3$

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(100 mL), then 1M HCl (15 mL) solution was added. After separation, the aqueous layer was further extracted with $CHCl_3$ (2×50 mL). The combined layers were dried over Na_2SO_4. After evaporation, the crude was purified by silica gel column chromatography ($CHCl_3$/ethyl acetate 1:2) to afford acid **25** (169.5 mg, 97%); HRMS: m/z: calcd for $C_{51}H_{49}N_4O_9S$: 893.3220; found: 893.3222.

α-Azido-2-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-1*H*-indole-3-propanoic acid (36): 10% NaOH aq (0.9 mL) was added to a solution of sulfonamide **25** (78.6 mg, 0.0881 mmol) in EtOH (9 mL). Then the mixture was heated under reflux for 20 h. The solvent was evaporated, and 1M aq HCl was added. The aqueous layer was extracted with $CHCl_3$. The combined layers were dried over Na_2SO_4. Then the solvent was evaporated. The residue was purified by silica gel column chromatography ($CHCl_3$/CH_3CN 4:1 → 1:1) to give deprotected compound **26** (45.0 mg, 68%). $[\alpha]_D^{24} = +40$ ($c = 0.46$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.29$ (s, 1H), 7.54 (d, $J =$ 7.3 Hz, 1H), 7.37–7.0 (m, 28H), 6.85 (d, $J = 6.8$ Hz, 2H), 5.16 (d, $J = 9.7$ Hz, 1H), 4.82 (d, $J = 12.2$ Hz, 1H), 4.70 (d, $J = 11.9$ Hz, 1H), 4.6–4.5 (m, 2H), 4.46 (d, $J = 11.9$ Hz, 1H), 4.39 (d, $J = 11.9$ Hz, 1H), 4.32 (d, $J = 11.6$ Hz, 1H), 4.24 (m, 1H), 4.04 (d, $J = 10.8$ Hz, 1H), 4.00 (d, $J = 10.8$ Hz, 1H), 3.9–3.8 (m, 3H), 3.5–3.2 (m, 4H); ^{13}C NMR: $\delta = 172.99$ (C), 137.98 (C), 137.64 (C), 137.29 (C), 136.70 (C), 135.52 (C), 133.78 (C), 128.47 (CH). 128.41 (CH), 128.39 (CH), 128.23 (CH), 128.11 (CH), 127.99 (CH), 127.93 (CH), 127.77 (CH), 127.69 (CH), 127.55 (CH), 127.46 (CH), 122.26 (CH), 119.55 (CH), 118.04 (CH), 111.23 (CH), 108.60 (C), 75.48 (CH), 75.38 (CH), 75.15 (CH), 73.95 (CH), 73.54 (CH_2), 72.61 (CH_2), 72.08 (CH_2), 71.86 (CH_2), 66.94 (CH_2), 64.37 (CH), 61.39 (CH), 27.50 (CH_2); elemental analysis calcd (%) for $C_{45}H_{44}N_4O_7$: C 71.79, H 5.89, N 7.44; found C 71.55, H 5.71, N 7.16.

2-α-D-*C*-Mannosylpyranosyl-L-tryptophan (1): 20% Pd(OH)$_2$/C (100 mg) was added to a solution of tetrabenzyl indole **26** (431 mg, 0.573 mmol) in dioxane (40 mL) and H_2O (20 mL). The mixture was stirred at 40 °C under H_2 atmosphere for 2 d. The catalyst was filtered through Celite. The Celite was washed with MeOH and water. The mixture was evaporated and purified by reverse-phase silica gel column chromatography (MeOH/H_2O 1:4)to give **1** (140.0 mg, 67%). ^{1}H NMR (D_2O, *t*BuOH was used as an internal standard, $\delta = 1.23$): $\delta = 7.73$ (d, $J = 7.7$ Hz, 1H, H-4), 7.52 (d, $J =$ 7.7 Hz, 1H, H-7), 7.30 (t, $J = 7.3$ Hz, 1H, H-6), 7.20 (t, $J = 7.3$ Hz, 1H, H-5), 5.16 (d, $J = 8.1$ Hz, 1H, H-1′), 4.42 (dd, $J = 8.1$, 3.3 Hz, 1H, H-2′), 4.25 (dd, $J = 12.5$, 8.8 Hz, 1H, H-6′), 4.11 (dd, $J = 3.3$, 3.3 Hz, 1H, H-3′), 4.01 (dd, $J =$ 9.2, 5.1 Hz, 1H, H-α), 3.94 (dd, $J = 4.0$, 3.3 Hz, 1H, H-4′), 3.88 (ddd, $J = 3.3$, 3.3, 8.8 Hz, 1H, H-5′), 3.72 (dd, $J = 3.3$, 12.5 Hz, 1H, H-6′), 3.55 (dd, $J = 5.1$, 15.3 Hz, 1H, H-β), 3.35 (dd, $J = 15.3$, 9.2 Hz, 1H, H-β); ^{13}C NMR: $\delta = 175.9$ (C), 137.5 (C), 134.8 (C), 128.5 (C), 124.4 (CH, C-6), 121.3 (CH, C-5), 120.2 (CH, C-4), 113.3 (CH, C-7), 109.8 (C), 80.5 (CH, C-5′), 71.9 (CH, C-3′), 70.4 (CH, C-4′), 69.1 (CH, C-2′), 67.4 (CH, C-1′), 60.4 (CH_2, C-6′), 56.6 (CH, C-α), 27.3 (CH_2, C-β).

Tetrapeptide (32): TFFH (16 mg, 0.061 mmol) was added at room temperature to a solution of HCl·H-Ala-Gln-Trp-OBn (**31**; 65 mg, 0.13 mmol), acid **29** (31.7 mg, 0.0420 mmol) and $Na_2CO_3 \cdot 10H_2O$ (48 mg, 0.17 mmol) in CH_2Cl_2 (2 mL) and H_2O (1 mL). The mixture was stirred overnight and then partitioned between CH_2Cl_2 and brine. The aqueous layer was extracted with CH_2Cl_2. After drying the extracts over Na_2SO_4, the solvent was evaporated. The crude material was purified by silica gel column chromatography ($CHCl_3$/EtOAc 1:1 → 1:4) to give tetrapeptide **32** (47 mg, 90%). ^{1}H NMR: $\delta = 9.04$ (s, 1H), 8.41 (s, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 7.6$ Hz, 1H), 7.4–6.9 (m, 30H), 6.79 (s, 1H), 6.21 (d, $J = 7.1$ Hz, 1H), 5.64 (s, 1H), 5.24 (s, 1H), 5.22 (s, 1H), 5.03 (d, $J = 12.0$ Hz, 1H), 4.98 (s, $J =$ 12.0 Hz, 1H), 4.76 (m, 1H), 4.78 (m, 1H), 4.67 (d, $J = 12.4$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.50 (d, $J = 12.4$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.38 (d, $J = 11.6$ Hz, 1H), 4.32 (d, $J = 12.0$ Hz, 1H), 4.1 (m, 6H), 3.91 (m, 1H), 3.84 (m, 1H), 3.80 (m, 1H), 3.68 (m, 1H), 2.0–1.9 (m, 4H), 0.70 (d, 7.1 Hz, 3H); ^{13}C NMR: $\delta = 175.30$ (C), 171.68 (C), 171.55 (C), 170.53 (C), 169.35 (C), 137.92 (C), 137.70 (C), 137.58 (C), 137.49 (C), 135.93 (C), 135.42 (C), 135.05 (C), 133.53 (C), 128.87 (CH), 128.39 (CH), 128.33 (CH), 128.24 (CH), 128.20 (CH), 128.15 (CH), 128.06 (CH), 127.76 (CH), 127.66 (CH), 127.61 (CH), 127.51 (CH), 127.12 (CH), 123.40 (CH), 122.01 (CH), 121.79 (CH), 119.34 (CH), 119.24 (CH), 118.24 (CH), 118.20 (CH), 111.22 (CH), 109.22 (C), 108.20 (C), 75.67 (CH), 75.42 (CH), 74.14 (CH), 73.15 (CH_2), 72.94 (CH_2), 72.17 (CH_2), 71.97 (CH_2), 68.34 (CH_2), 67.25 (CH_2), 65.72 (CH), 63.60 (CH), 52.88 (CH), 52.55 (CH), 48.82 (CH), 31.01 (CH_2), 27.60 (CH_2), 27.27 (CH_2), 27.18 (CH_2), 18.10 (CH_3).

α-D-*C*-Mannosylpyranosyl-L-tryptophan-*N*-fluorenylmethyl carbamate (34): Fmoc-OSu (18.8 mg, 0.0557 mmol) was added to a solution of *C*-mannosyl tryptophan **1** (6.8 mg, 0.0186 mmol) in 0.5% aq $NaHCO_3$ (1 mL), and DME (1 mL). The mixture was stirred at room temperature overnight. The mixture was acidified to pH 4 with 1M HCl. Then the mixture was purified directly by reverse-phase silica gel column chromatography (MeOH/H_2O 1:9 → 1:1 → MeOH only) to give Fmoc-mannosyltryptophan **34** (7.4 mg, 68%). $[\alpha]_D^{24} = +20$ ($c = 0.61$, MeOH); ^{1}H NMR (CD_3OD, 55 °C): $\delta = 7.82$ (d, $J = 7.3$ Hz, 3H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.4–7.2 (m, 5H), 6.61 (t, $J = 7.3$ Hz, 1H), 7.13 (t, $J = 7.3$ Hz, 1H), 5.34 (d, $J = 8.0$ Hz, 1H), 4.41 (dd, $J = 3.2$, 7.6 Hz, 1H), 4.30 (d, $J = 12.0$ Hz, 1H), 4.29 (d, $J = 12.0$ Hz, 1H), 4.12 (m, 3H), 4.01 (t, $J = 3.2$ Hz, 1H), 3.96 (m, 1H), 3.88 (dd, $J = 3.6$, 12.0 Hz, 1H), 3.54 (dd, $J =$ 14.4 Hz, 5.2 Hz, 1H), 3.32 (dd, $J = 9.2$ Hz, 14.4 Hz, 1H); ^{13}C NMR (CD_3OD, 55 °C): $\delta = 180.15$, 157.91, 145.18, 145.07, 142.15, 142.08, 137.32, 135.02, 129.34, 128.33, 127.90, 126.45, 126.22, 122.40, 120.48, 120.44, 119.80, 119.58, 111.72, 110.75, 80.76, 72.25, 70.86, 69.65, 68.34, 67.80, 61.27, 58.28, 28.75.

Tetrapeptide (37): Triazine compound **36** (9.0 mg) and *i*Pr$_2$NEt (10 μL) were added to a solution of tripeptide **35** (25 mg) and **34** (12.5 mg, 0.0213 mmol) in MeOH (1 mL). The mixture was stirred at room temperature for 30 min. The mixture was purified directly by size-exclusion column chromatography (Sephadex LH20; MeOH) and preparative TLC to give tetrapeptide **37** (18.9 mg, 94%). $[\alpha]_D^{24} = +4.4$ ($c = 0.29$, in MeOH); ^{1}H NMR (CD_3OD): $\delta = 7.73$ (d, $J = 7.6$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 2H), 7.35–7.3 (m, 3H), 7.25–7.22 (m, 2H), 7.0–6.9 (m, 4H), 5.12 (d, $J = 8.8$ Hz, 1H), 4.63 (dd, $J = 4.8$ Hz, 8.8 Hz, 1H), 4.47 (dd, $J = 5.6$ Hz, 9.6 Hz, 1H), 4.28–4.05 (m, 7H), 3.91 (m, 2H), 3.72 (dd, $J = 2.0$ Hz, 12.4 Hz, 1H), 3.16–3.11 (m, 2H), 2.1–2.0 (m, 2H), 2.0–1.9 (m, 2H), 1.19 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR: $\delta = 178.08$ (C), 177.59 (C), 176.80 (C), 176.76 (C), 175.93 (C), 175.45 (C), 173.55 (C), 173.45 (C), 158.83 (C), 145.17 (C), 144.96 (C), 142.44 (C), 141.40 (C), 139.30 (C), 138.04 (C), 137.97 (C), 137.59 (C), 135.73 (C), 129.86 (CH), 128.68 (CH), 128.18 (CH), 128.15 (CH), 126.46 (CH), 126.29 (CH), 124.58 (CH), 122.97 (CH), 122.42 (CH), 122.02 (CH), 120.79 (CH), 120.65 (CH), 119.88 (CH), 119.34 (CH), 112.31 (CH), 112.24 (CH), 112.14 (CH), 111.16 (C), 111.09 (C), 109.51 (C), 108.19 (C), 81.32 (CH), 81.13 (CH), 72.48 (CH), 72.23 (CH), 71.07 (CH), 69.34 (CH), 69.14 (CH), 68.16 (CH_2), 67.54 (CH), 67.06 (CH), 61.32 (CH_2), 61.06 (CH_2), 57.74 (CH), 57.26 (CH), 55.31 (CH), 55.23 (CH), 55.18 (CH), 55.07 (CH), 51.37 (CH), 51.18 (CH), 48.83 (CH), 32.35 (CH_2), 31.89 (CH_2), 30.74 (CH_2), 30.67 (CH_2), 28.70 (CH_2), 28.69 (CH_2), 27.99 (CH_2), 27.80 (CH_2), 27.44 (CH_2), 24.23 (CH), 17.27 (CH_3), 17.14 (CH_3).

3-[(2*S*)-2-Azido-3-[(*tert*-butyldimethylsilyl)oxy]propyl]-1-(phenylsulfonyl)-[3,4,6-tris-*O*-(4-methoxybenzyl)-α-D-glucopyranosyl]-1*H*-indole (39): BuLi (0.51 mL, 0.76 mmol) was added at −78 °C under Ar atmosphere to a solution of indole **6k** (386 mg, 0.82 mmol) in THF (17 mL). After stirring the mixture at −78 °C for 1.5 h, the epoxide **4** (236 mg, 0.547 mmol) in THF (4 mL) was transferred through a cannula. Then, $BF_3 \cdot OEt_2$ (95 μL, 0.075 mmol) was added. The mixture was stirred at −78 °C overnight. After triethylamine (0.2 mL) was added to neutralize the mixture, the mixture was partitioned between sat. aq NH_4Cl and EtOAc. After the aqueous layer was extracted with EtOAc, the combined layers were washed with brine. After drying the mixture over Na_2SO_4, the solvent was evaporated. The crude was purified by silica gel column chromatography (hexane/EtOAc 6:1) and size exclusion column chromatography (Biobeads S-X4, toluene) to give α-product **39** (45.0 mg, 10%) and β-product **40** (10.0 mg, 2%). $[\alpha]_D^{27} = +24.8$ ($c = 0.97$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.14$ (d, $J = 8.3$ Hz, 1H), 7.64 (d, $J = 7.3$ Hz, 2H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.29–7.13 (m, 20H), 6.90–6.82 (m, 6H), 5.80 (d, $J = 10.3$ Hz, 1H), 4.60 (d, $J =$ 11.7 Hz, 1H), 4.54 (d, $J = 11.2$ Hz, 1H), 4.49 (d, $J = 11.2$ Hz, 1H), 4.45 (s, 1H), 4.42 (s, 1H), 4.36 (d, $J = 11.7$ Hz, 1H), 4.26 (m, 1H), 4.21 (m, 1H), 3.9–3.7 (m, 6H), 3.82 (s, 6H), 3.79 (s, 3H), 3.62 (dd, $J = 6.1$, 10.0 Hz, 1H), 3.51 (dd, $J = 3.2$, 10.5 Hz, 1H), 3.25 (dd, $J = 6.1$, 10.5 Hz, 1H), 3.09 (d, $J =$ 7.3 Hz, 2H), 2.47 (d, $J = 11.5$ Hz, 1H), 0.86 (s, 9H), 0.00 (s, 6H); ^{13}C NMR: $\delta = 159.2$ (C), 159.1 (C), 158.9 (C), 137.8 (C), 136.7 (C), 136.0 (C), 133.2 (C), 131.4 (C), 130.1 (C), 129.8 (C), 129.5 (C), 129.2 (CH), 129.1 (CH), 128.6 (CH), 126.5 (CH), 124.9 (CH), 123.6 (CH), 121.8 (C), 119.6 (CH), 115.7 (CH), 113.8 (CH), 113.7 (CH), 113.6 (CH), 77.3 (CH), 77.2 (CH), 74.6 (CH), 72.8 (CH), 72.5 (CH), 71.1 (CH_2), 68.2 (CH), 67.5 (CH_2), 65.0 (CH), 64.0 (CH), 60.4 (CH), 55.3 (CH_2), 55.3 (CH_2), 26.0 (CH_3), 25.7 (CH_2), 21.7 (CH_2), 18.4 (C), 14.3 (CH_3), −5.3 (CH_3), −5.4 (CH_3); elemental analysis

calcd (%) for $C_{53}H_{64}N_4O_{11}SSi$: C 64.59, H 6.49, N 5.64: found: C 64.04, H 6.53, N 5.66.

3-[(2*S*)-2-Azido-3-[(*tert*-butyldimethylsilyl)oxy]propyl]-1-(phenylsulfonyl)-(3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-1*H*-indole (40): $[\alpha]_D^{24} = -21.6$ ($c = 0.56$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.11$ (d, $J = 7.1$ Hz, 1H), 7.55 (d, $J = 7.1$ Hz, 3H), 7.49 (m, 1H), 7.35–7.23 (m, 20H), 7.08 (d, $J = 8.5$ Hz, 1H), 6.89–6.82 (m, 6H), 5.43 (s, 1H), 4.81 (d, $J = 10.5$ Hz, 1H), 4.71 (d, $J = 11.2$ Hz, 1H), 4.63 (d, $J = 11.2$ Hz, 1H), 4.55 (m, 1H), 4.54 (s, 1H), 4.43 (d, $J = 2.2$ Hz, 1H), 4.41 (s, 1H), 3.92 (m, 1H), 3.83 (m, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.75–3.69 (m, 6H), 3.55 (m, 1H), 3.24 (dd, $J = 4.9$, 13.6 Hz, 1H), 2.92 (dd, $J = 9.5$, 13.6 Hz, 1H), 2.53 (d, $J = 2.2$ Hz, 1H), 0.89 (s, 9H), 0.00 (s, 6H); ^{13}C NMR: $\delta = 170.9$ (C), 159.0 (C), 138.0 (C), 136.7 (C), 133.6 (C), 132.5 (C), 131.6 (C), 130.4 (C), 130.0 (C), 129.7 (C), 129.6 (CH), 129.4 (CH), 129.3 (CH), 129.1 (CH), 125.8 (CH), 125.0 (CH), 123.8 (CH), 122.9 (C), 119.6 (CH), 115.4 (CH), 113.8 (CH), 113.7 (CH), 113.6 (CH), 82.5 (CH), 79.7 (CH), 77.2 (CH), 76.3 (CH), 74.8 (CH_2), 73.8 (CH), 72.8 (CH_2), 71.0 (CH_2), 69.4 (CH_2), 69.0 (CH), 66.4 (CH_2), 65.4 (CH), 60.4 (CH_2), 55.3 (CH_3), 55.2 (CH_3), 26.0 (CH_3), 21.2 (CH_3), 18.4 (C), 14.4 (CH_3), −5.2 (CH_3); elemental analysis calcd (%) for $C_{53}H_{64}N_4O_{11}SSi$: C 64.59, H 6.49, N 5.64: found:C 64.34, H 6.33, N 5.56.

3-[(2*S*)-2-Azido-3-[(*tert*-butyldimethylsilyl)oxy]propyl]-1-(phenylsulfonyl)-(2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl)-1*H*-indole: NaH (29 mg, 0.73 mmol) was added at 0 °C under Ar atmosphere to a solution of alcohol **39** (308.0 mg, 0.341 mmol), Bu_4NI (365 mg, 0.988 mmol) and BnBr (0.16 mL, 1.3 mmol) in DMF (5 mL). The mixture was stirred at 0 °C → room temperature overnight. Triethylamine (0.2 mL) was added to destroy the excess of benzyl bromide. After 10 min, the mixture was partitioned between EtOAc and sat. NH_4Cl. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine, and dried over Na_2SO_4. After evaporation, the residue was purified by silica gel column chromatography (hexane/EtOAc 9:1 → 4:1) to give tetrabenzyl ether as a colorless oil (259.5 mg, 77%). $[\alpha]_D^{24} = +89.8$ ($c = 1.12$, $CHCl_3$); ^{1}H NMR: $\delta = 8.20$ (d, $J = 8.0$ Hz, 1H), 7.6–7.1 (m, 26H), 6.91 (m, 2H), 6.04 (s, 1H), 4.73 (d, $J = 11.2$ Hz, 1H), 4.72 (d, $J = 11.2$ Hz, 1H), 4.58 (d, $J = 12.8$ Hz, 1H), 4.57 (d, $J = 12.8$ Hz, 1H), 4.5–4.4 (m, 3H), 4.27 (m, 3H), 4.11 (m, 1H), 4.0–3.7 (m, 5H), 3.51 (m, 1H), 3.29 (m, 2H), 2.97 (m, 1H), 0.89 (s, 9H), −0.03 (s, 6H); ^{13}C NMR: $\delta = 138.23$ (C), 138.16 (C), 137.84 (C), 137.49 (C), 137.23 (C), 136.57 (C), 133.73 (C), 133.32 (CH), 132.13 (C), 128.74 (CH), 128.26 (CH), 128.14 (CH), 128.13 (CH), 128.02 (CH), 127.95 (CH), 127.85 (CH), 127.63 (CH), 127.45 (CH), 127.37 (CH), 127.31 (CH), 126.11 (CH), 124.70 (CH), 123.76 (CH), 123.38 (C), 119.31 (CH), 115.69 (CH), 80.16 (CH), 77.70 (CH), 75.90 (CH), 73.91 (CH), 73.21 (CH_2), 72.89 (CH_2), 72.46 (CH_2), 71.87 (CH_2), 70.44 (CH), 69.18 (CH_2), 64.97 (CH_2), 64.31 (CH), 25.99 (CH_3), 25.64 (CH_2), 18.42 (C), −5.26 (CH_3), −5.32 (CH_3); elemental analysis calcd (%) for $C_{57}H_{64}N_4O_8SSi$: C 68.92, H 6.49, N 5.64; found: C 68.62, H 6.56, N 5.35.

3-[(2*S*)-2-Azido-3-hydroxypropyl]1-(phenylsulfonyl)-2-(2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl)-1*H*-indole: $TsOH \cdot H_2O$ (1 mg) was added to a solution of TBS ether (55.9 mg, 0.0564 mmol) in MeOH (4 mL). The mixture was stirred at room temperature. One drop of triethylamine was added to neutralize the mixture. After evaporation of the solvent, the residue was purified by preparative TLC (hexane/EtOAc 7:3) to give the alcohol as a colorless oil (48.9 mg, 99%). $[\alpha]_D^{24} = +80.7$ ($c = 0.98$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.20$ (d, $J = 7.6$ Hz, 1H), 7.6–7.5 (m, 3H), 7.5–7.2 (m, 18H), 7.17 (dd, $J = 10.0$, 8.4 Hz, 3H), 7.07 (t, $J = 6.8$ Hz, 2H), 6.92 (d, $J = 6.8$ Hz, 2H), 6.04 (d, $J = 2.0$ Hz, 1H), 4.69 (d, $J = 11.2$ Hz, 1H), 4.67 (d, $J = 11.2$ Hz, 1H), 4.54 (d, $J = 11.6$ Hz, 1H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 12.0$ Hz, 1H), 4.40 (d, $J = 11.6$ Hz, 1H), 4.24 (m, 1H), 4.14 (d, $J = 12.0$ Hz, 1H), 3.9–3.8 (m, 2H), 3.8–3.7 (m, 2H), 3.71 (dd, $J = 3.6$, 10.4 Hz, 1H), 3.27–3.17 (m, 4H); ^{13}C NMR: $\delta = 138.2$ (C), 138.2 (C), 137.8 (C), 137.5 (C), 137.2 (C), 136.6 (C), 133.7 (C), 133.3 (CH), 132.1 (C), 128.7 (CH), 128.3 (CH), 128.1 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.7 (CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.0 (CH), 124.8 (CH), 124.0 (CH), 123.2 (CH), 119.2 (CH), 115.8 (CH), 77.7 (CH), 74.91 (CH), 74.27 (CH), 73.12 (CH), 72.52 (CH_2), 72.50 (CH_2), 91.95 (CH_2), 70.02 (CH), 68.81 (CH_2), 64.58 (CH), 63.61 (CH_2), 26.03 (CH_2); elemental analysis calcd (%) for $C_{51}H_{50}N_4O_8S$: C 69.68, H 5.73, N 6.37; found: C 69.45, H 5.84, N 6.21.

***α*-Azido-1-(phenylsulfonyl)-2-(2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl)-1*H*-indole-3-propanoic acid**: TEMPO (5 mg, 0.03 mmol) was added at room temperature to a solution of alcohol (47.9 mg, 0.0546 mmol) and iodosobenzene diacetate (42 mg, 0.13 mmol) in CH_3CN (1 mL), and H_2O (1 mL). After 2 h, the mixture was diluted with $CHCl_3$, then the organic layer was washed with aq 1M HCl. The aqueous layer was extracted with $CHCl_3$. After the combined layers were dried over Na_2SO_4 and filtered off, the solvent was evaporated. The crude material was purified by preparative TLC ($CHCl_3$/EtOAc 1:1) to give the acid as a colorless oil (41.3 mg, 85%). $[\alpha]_D^{24} = +50$ ($c = 0.73$, in $CHCl_3$); ^{1}H NMR: $\delta = 8.09$ (d, $J = 6.3$ Hz, 1H), 7.54 (d, $J = 6.3$ Hz, 1H), 7.49 (d, $J = 8.3$ Hz, 2H), 7.3–7.1 (m, 23H), 6.84 (d, $J = 7.6$ Hz, 2H), 5.92 (s, 1H), 4.34 (d, $J = 11.2$ Hz, 1H), 4.58 (d, $J = 11.6$ Hz, 1H), 4.46 (d, $J = 11.6$ Hz, 1H), 4.45 (d, $J = 11.2$ Hz, 1H), 4.39 (d, $J = 12.0$ Hz, 1H), 4.35 (m, 1H), 4.28 (d, $J = 11.2$ Hz, 1H), 4.25 (m, 1H), 4.19 (m, 1H), 4.03 (m, 1H), 3.78 (m, 1H), 3.74 (dd, $J = 7.6$ Hz, 10.4 Hz, 1H), 3.61 (m, 1H), 3.57 (m, 1H), 3.38 (dd, $J = 3.6$ Hz, 14.4 Hz, 1H), 3.25 (dd, $J = 8.0$, 14.4 Hz, 1H); ^{13}C NMR: $\delta = 137.7$ (C), 137.54 (C), 137.40 (C), 136.7 (C), 136.5 (C), 133.5 (CH), 131.6 (C), 129.0 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.7 (CH), 125.9 (CH), 125.0 (CH), 124.0 (CH), 121.7 (C), 119.1 (CH), 115.4 (CH), 76.1 (CH), 74.6 (CH), 73.3 (CH_2), 72.7 (CH_2), 72.4 (CH_2), 71.9 (CH_2), 69.9 (CH), 68.7 (CH_2), 62.7 (CH), 27.7 (CH_2); elemental analysis calcd (%) for $C_{51}H_{48}N_4O_9S$: C 68.59, H 5.42, N 6.27; found: C 68.25, H 5.33, N 6.20.

***α*-Azido-2-(2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl)-1*H*-indole-3-propanoic acid**: 10% NaOH (0.3 mL) was added at room temperature to a solution of the above acid (25.9 mg, 0.0290 mmol) in EtOH (3 mL). The mixture was heated under reflux overnight. The mixture was neutralized with aq 2M HCl. The aqueous layer was extracted with $CHCl_3$. After drying the combined organic layers over Na_2SO_4 and filtering, the solvent was evaporated. The crude material was purified by preparative TLC ($CHCl_3$/CH_3CN 3:2) to give deprotected indole (11.8 mg, 56%). $[\alpha]_D^{24} = 10.6$ ($c = 1.17$, MeOH); ^{1}H NMR (CD_3OD): $\delta = 8.30$ (s, 1H), 8.09 (d, $J = 7.6$ Hz, 1H), 7.7–7.5 (m, 16H), 7.48 (t, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 6.8$ Hz, 1H), 5.86 (s, 1H), 4.68 (t, $J = 11.2$ Hz, 2H), 4.56 (d, $J = 11.2$ Hz, 2H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 12.0$ Hz, 1H), 4.13 (m, 2H), 4.0–3.8 (m, 4H), 3.7–3.6 (m, 2H), 3.56 (m, 1H); ^{13}C NMR (CD_3OD): $\delta = 139.53$ (C), 139.29 (C), 139.07 (C), 136.99 (C), 134.10 (C), 129.23 (CH), 129.18 (CH), 128.98 (CH), 128.90 (CH), 128.83 (CH), 128.68 (CH), 128.59 (CH), 128.53 (CH), 128.45 (CH), 122.38 (CH), 119.64 (CH), 119.42 (CH), 112.06 (CH), 111.03 (C), 79.98 (CH), 76.54 (CH), 75.86 (CH), 74.29 (CH_2), 72.51 (CH), 69.53 (CH_2), 68.82 (CH), 67.77 (CH), 29.02 (CH_2); elemental analysis calcd (%) for $C_{45}H_{44}N_4O_7$: C 7.18, H 5.89, N 7.44; found: C 71.37, H 5.78, N 7.31.

2-*α*-D-Glucopyranosyl-L-tryptophan (41): A suspension of benzyl ether (36.3 mg, 0.0483 mmol) and 20% $Pd(OH)_2$ (15 mg) in dioxane (2 mL), and H_2O (1.2 mL) was stirred vigorously under H_2 atmosphere at 40 °C for 2 d. After filtration of the catalyst through Celite, the Celite was washed with MeOH and water. After evaporation, the crude was purified by reverse phase silica gel column chromatography (H_2O/MeOH 9:1) to give glycosyl tryptophan **41** (11 mg, 65%). ^{1}H NMR (D_2O, *t*BuOH as internal standard; *t*Bu = 1.23, 600 MHz): $\delta = 7.72$ (d, $J = 8.3$Hz, 1H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.20 (t, $J = 7.3$ Hz, 1H), 5.56 (d, $J = 5.4$ Hz, 1H), 4.09 (m, 2H), 4.01 (t, $J = 8.3$ Hz, 1H), 3.78 (s, 1H, H-6′), 3.77 (s, 1H, H-6′), 3.54 (t, $J = 8.3$ Hz, 1H), 3.49 (m, 2H, H-*β*), 3.44 (m, 1H); ^{13}C NMR (D_2O, *t*BuOH as internal standard; *t*Bu as 31.00, 150.80 MHz): $\delta = 176.42$ (C), 137.14 (C), 133.20 (C), 128.58 (C), 124.20 (CH), 121.38 (CH), 119.96 (CH), 113.52 (CH), 110.21 (C), 76.82 (CH), 75.36 (CH), 73.04 (CH), 71.18 (CH), 71.06 (CH, C-1′), 61.99 (CH_2, C-6′), 56.81 (CH), 27.30 (CH_2, C-*β*).

Acknowledgements

This work was supported by the Special Researcher's Basic Science Program at RIKEN, the Novartis Foundation (Japan), Mizutani Foundation and Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science (Grant No. 13480191). We thank Ms. A. Takahashi for technical assistance. We thank Dr. J. Uzawa, Dr. H. Koshino and Ms. T. Chijimatsu for recording NMR spectra. We thank Dr. Chihara and his staff for elemental analysis.

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Received: September 13, 2002 [F4424]