Bioscience, Biotechnology, and Biochemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tbbb20

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Published online: 22 May 2014.

To cite this article: Toshio NISHIKAWA, Kyoko WADA & Minoru ISOBE (2002) Synthesis of Novel α-C-Glycosylamino Acids and Reverse Regioselectivity in Larock's Heteroannulation for the Synthesis of the Indole Nucleus, Bioscience, Biotechnology, and Biochemistry, 66:10, 2273-2278, DOI: 10.1271/bbb.66.2273

To link to this article: http://dx.doi.org/10.1271/bbb.66.2273

Biosci. Biotechnol. Biochem., **66** (10), 2273–2278, 2002

Synthesis of Novel α-*C*-Glycosylamino Acids and Reverse Regioselectivity in Larock's Heteroannulation for the Synthesis of the Indole Nucleus

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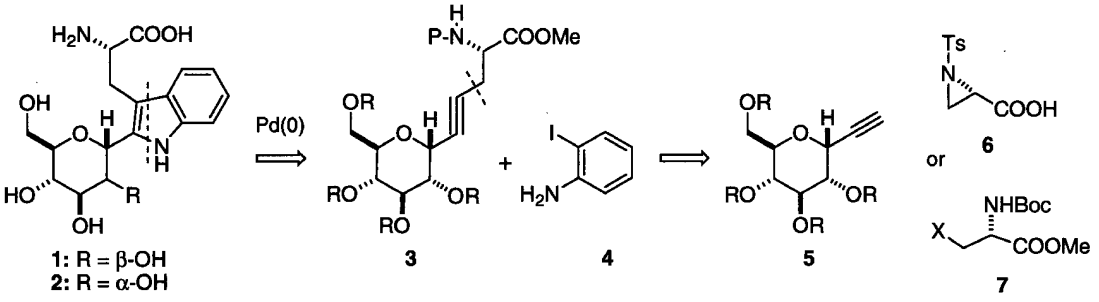
Received April 24, 2002; Accepted May 31, 2002

An α-*C*-iodoethynylglucose derivative was coupled with an L-serine-derived zinc-copper reagent to give α-*C*-glucosylpropargyl glycine, which underwent palladium catalyzed-heteroannulation with *o*-iodoaniline to give not α-*C*-glucosyl-tryptophan but α-*C*-glucosyl-*iso*-tryptophan. This is the first observation of complete reverse regioselectivity to Larock's proposal.

Key words: *C*-glycosylamino acid; propargyl glycine; indole; *iso*-tryptophan; palladium catalyst

C-Glycosylamino acids have attracted considerable interest for their stable mimic of *N*- and *O*-linked glycosylamino acids and glycosidase inhibitors to elucidate the biological roles of the carbohydrate moiety of glycopeptide and glycoprotein.[1] In the course of our synthetic studies on α-*C*-mannosyltryptophan (**1**),[2–4] a novel *C*-glycosylamino acid found in proteins,[5,6] we aimed to establish a general synthetic method for the glucose and galactose analogs of **1** for a trace analysis of the carbohydrate moiety of this sugar chain. Our initial synthetic plan for glucose analog **2** is shown in Scheme 1, which exploits the palladium-catalyzed heteroannulation developed by Larock[7,8] between *o*-iodoaniline **4** and *C*-glucosylpropargyl glycine **3** as the key reaction. The synthesis of acetylene counterpart **3** was envisaged by coupling between sugar acetylene **5**[9,10] and an L-serine derivative such as **6** or **7**. Dondoni[11] and van Boom[12] have independently reported the recent syntheses of α and β-*C*-glycosylpropargyl glycine derivatives in different ways. These reports prompted us to disclose our unreported results of a new convergent synthesis for α-*C*-glucosylpropargyl glycine **3**, and the unexpected regioselectivity observed in the palladium-catalyzed heteroannulation between **3** and **4**.

The synthesis of α-*C*-glucosylpropargyl glycine was first examined. Initial attempts to couple lithium or magnesium acetylide generated from ethynylglucose **10** (**5**: R = Bn) with aziridine carboxylic acid **6**[13] or 3-iodo-L-serine derivative **7**[14] failed, because of β-elimination and preferential attack by acetylide to the carbonyl groups of the carbamate and ester.[15,16] We next turned our attention to an alternative coupling method with reverse polarity (Scheme 2); that is, iodoacetylene **11** as an electrophile and L-serine derived organozinc-copper reagent **9** as a nucleophile according to the Knochel[17,18] and Jackson[19,20] reports. Iodoethynylglucose **11** was prepared by iodination[21] of α-ethynylglucose **10**,[11,22] which had been synthesized by highly α-selective *C*-glycosidation of glucose derivative with tinacetylene under our established conditions,[2] while L-serine derived Zn-Cu reagent **9** had been prepared from iodoalanine **8** according to the literature.[23,24] These reagents were coupled together in THF to give α-*C*-glucosylpropargyl glycine **12** in a moderate yield along with ethynylglucose **10** as a by-product.[25] The method described here should be efficient and flexible for the synthesis of a wide variety of *C*-glycosylpropargyl glycines.[26]



Scheme 1. Retrosynthetic Plan for α-*C*-Glycosyltryptophan.

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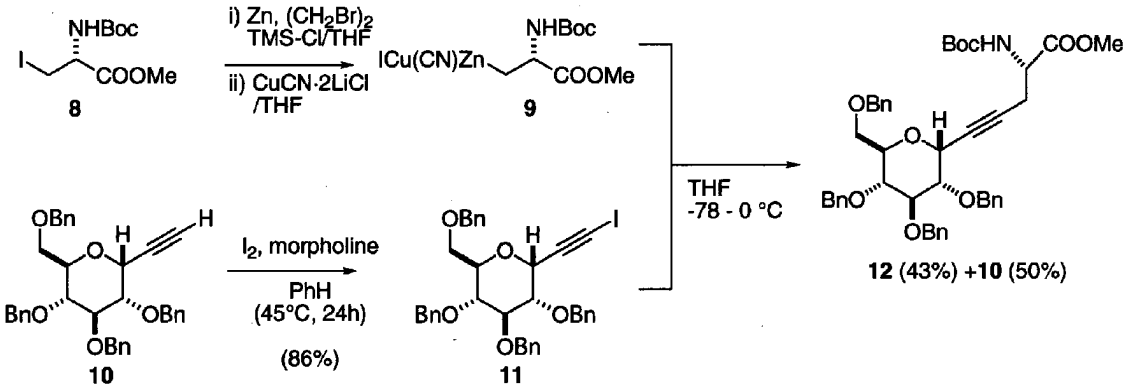
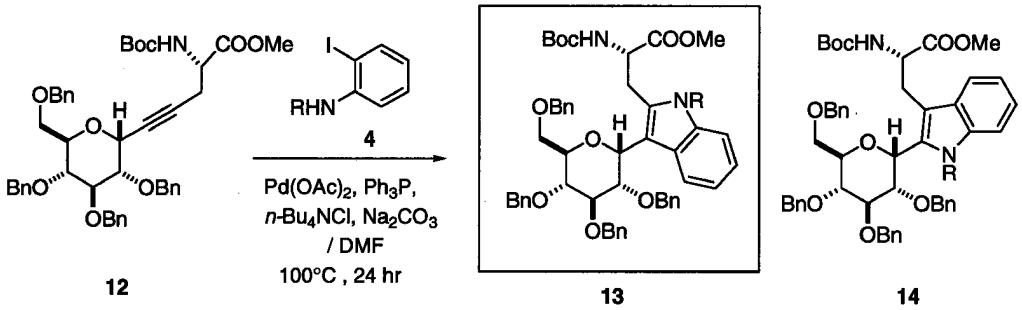


Scheme 2. Synthesis of *C*-Glucosylpropargyl Glycine **12**.



Scheme 3.

With the precursor for the heteroannulation in hand, we examined palladium-catalyzed indole synthesis under the conditions reported by Larock[7,8] (Scheme 3 and Table). When unprotected *o*-iodoaniline **4a** was employed as a coupling partner, a complex mixture was obtained (entry 1). In sharp contrast, the reactions with *N*-acetyl and *N*-Boc-protected *o*-iodoaniline **4b** and **4c** respectively gave **13b** (30% yield) and **13c** (30% yield) as single products, but in low yields (entries 2 and 3). We finally found that *o*-iodo-tosylanilide **4d** was the best coupling partner to afford product **13d** in about a 90% yield (entry 4). To our surprise, the structures of these products were determined to be not desired tryptophan **14**, but *iso*-tryptophan **13**[27,28] from an analysis of the NOESY spectra,[29] in which correlation between aromatic protons of the Ts group and the α-proton of the amino acid moiety was observed. Larock *et al.* have suggested that the regiochemistry of this annulation was controlled by steric balance between two substituents of acetylene to afford a product having a sterically hindered substituent at the 2-position of indole in high selectivity.[7,8,30] As the carbohydrate moiety of **12** seemed to be larger, a tryptophan type of product (**14**) was expected. However, only *iso*-tryptophan adducts **13b**, **13c** and **13d** were obtained in these specific cases. To our knowledge, this is the first example of complete reverse regioselectivity in Larock's heteroannulation.

Table. Heteroannulation between Glucosylpropargyl Glycine **12** and *o*-Iodoaniline **4**

Entry	*o*-Iodoaniline		Product		
		R		R	Yield (%)
1	**4a**	H	**13a**	H	complex mixture
2	**4b**	Ac	**13b**	Ac	30
3	**4c**	Boc	**13c**	Boc	30
4	**4d**	Ts	**13d**	Ts	89

This unexpected result implies unknown important factor(s) controlling the regioselectivity in this heteroannulation. In most of the substrates for the Larock indole synthesis so far reported, one terminus of the acetylenes was substituted by a silyl group.[31-35] As tryptophan synthesis by means of the heteroannulation has been reported,[36-38] an amino acid functional group should not interfere with the regioselectivity. Work on defining the origin and mechanism for this reverse selectivity is currently underway in our laboratory.

In summary, we developed an efficient synthetic route to *C*-glycosylpropargyl glycine and *C*-glycosyl-*iso*-tryptophan. Although the heteroannulation strategy was revealed to be unsuitable for the synthesis of α-*C*-glycosyltryptophan, the resulting novel *C*-glycosylamino acids might be possible candidates for biologically active compounds such as enzyme inhibi-

tors.[39,40]

Experimental

Infrared spectra were recorded with a Jasco FT/IR-8300 spectrophotometer and are reported in wave number (cm^{-1}). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded with a Brucker ARX-600 (600 MHz), a Brucker ARX-400 (400 MHz) or a Varian Gemini-2000 (300 MHz) spectrometers, and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded with a ARX-600 (150 MHz), a ARX-400 (100 MHz) or a Varian Gemini-2000 (75 MHz) spectrometers. Optical rotation values were measured by a Jasco DIP-370 digital polarimeter, and mass spectra (EI) were recorded by a Jeol Mstation spectrometer.

2-Iodoethynyl-2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside (11). To a solution of iodine (454 mg, 1.79 mmol) in benzene (2.4 ml) at 45°C was added morpholine (0.47 ml, 5.37 mmol) in benzene (0.57 ml). The dark orange iodo-morpholine complex formed rapidly. α-1-Ethynylglucose **10** (966 mg, 1.79 mmol) in benzene (3.3 ml) was added, and the mixture was stirred at 45°C for 24 hr. After cooling to rt, the hydroiodide salt was removed by suction filtration through filter paper, and the filtrate was diluted with ether. The organic layer was successively washed with a saturated NH_4Cl solution (×2), saturated $NaHCO_3$ solution (×2) and brine (×2), passed through a short column packed with anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel (30 g) column chromatography (CH_2Cl_2:hexane = 1:1→2:1) to afford **11** (1.02 g, 86%) as a colorless oil. $[\alpha]_D^{23}$ + 93.0 (*c* 1.11, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 3031, 2865, 2178, 1455, 1088. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.60 (1H, dd, J = 9.5, 6 Hz, H-2), 3.62 (1H, t, J = 9.5 Hz, H-4), 3.65 (1H, dd, J = 11, 2 Hz, H-6), 3.75 (1H, dd, J = 11, 3.5 Hz, H-6), 3.92 (1H, t, J = 9.5 Hz, H-3), 3.93–3.97 (1H, m, H-5), 4.47(1H, d, J = 10 Hz, CH_EH$_F$Ph), 4.47 (1H, d, J = 12 Hz, CH_AH$_B$Ph), 4.60 (1H, d, J = 12 Hz, CH$_A$$H_B$Ph), 4.67 (1H, d, J = 12.5 Hz, CH_CH$_D$Ph), 4.72 (1H, d, J = 12.5 Hz, CH$_C$$H_D$Ph), 4.82 (1H, d, J = 10 Hz, CH$_E$$H_F$Ph), 4.83 (1H, d, J = 10.5 Hz, CH_GH$_H$Ph), 4.88 (1H, d, J = 6 Hz, H-1), 4.99 (1H, d, J = 10.5 Hz, CH$_G$$H_H$Ph), 7.10–7.38 (20H, m, C$_6$$H_5$ × 4). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 6.0, 68.1, 68.4, 72.9, 73.5, 73.8, 75.3, 75.7, 77.3, 79.0, 83.0, 89.5, 127.66, 127.78, 127.87, 127.98, 128.03, 128.06, 128.14, 128.4, 128.5, 128.6, 137.9, 138.1, 138.8. MS (FAB) m/z 675 (M + H). *Anal.* Calcd. for $C_{36}H_{35}IO_5$: C, 64.10; H, 5.23%. Found: C, 64.21; H, 5.37%.

(S)-2-tert-Butoxycarbonylamino-5-(2′,3′,4′,6′-tetra-O-benzyl-α-D-glucopyranosyl)-pentynoic acid methyl ester (12). A 20-ml two-necked round-bottomed flask was charged with zinc-sand (349 mg, 5.34 mmol, Kanto Chemicals) and connected to a vacuum/argon line. The flask was evacuated and then filled with argon. This evacuation/filling cycle was conducted three times. Dry THF (0.39 ml) and 1,2-dibromoethane (0.019 ml, 0.223 mmol) were added, and the resulting suspension was heated at 60°C for 3 min. After cooling to room temperature, TMSCl (0.023 ml, 0.178 mmol) was added, and the mixture was sonicated for 30 min. Iodoalanine **8** (586 mg, 1.78 mmol) in dry THF (2.89 ml) was added *via* a cannula tubing, and the mixture was sonicated at 40°C for 8 hr. (Iodoalanine was converted to the zinc reagent as judged by TLC.) The solution of the zinc reagent was cooled to 0°C, and a solution prepared from CuCN (159 mg, 1.78 mmol) and LiCl (151 mg, 3.56 mmol) in dry THF (2.62 ml) was added via a cannula tubing. The mixture was stirred at 0°C for 10 min and then cooled to −78°C. The resulting zinc-copper reagent (**9**) was added to a stirred solution of the α-1-iodoethynylglucose **11** (307 mg, 0.445 mmol) in THF (2.70 ml) at −78°C in a 30-ml two-necked round-bottomed flask *via* a cannula tubing. The reaction mixture was stirred at −78°C for 3 hr, and then at 4°C for an additional 12 hr under argon. The reaction was quenched with a saturated NH_4Cl solution, then the mixture was extracted with AcOEt (×3). The combined organic extract was successively washed with H_2O (×2), a saturated NH_4Cl solution (×2) and brine (×2), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel (30 g) column chromatography (Et_2O:hexane = 1:4→1:2) to afford **12** (145 mg, 43%) and α-1-ethynylglucose **10** (125 mg, 50%) as a colorless oil. $[\alpha]_D^{24}$ + 72.0 (c 1.05, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 3353, 3031, 2876, 2240, 1749, 1718, 1455, 1089. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.38 (9H, s, OC(CH_3)$_3$), 2.79 (1H, ddd, J = 16, 5, 2 Hz, H-β), 2.87 (1H, ddd, J = 16, 4, 2 Hz, H-β), 3.58 (1H, dd, J = 10, 9 Hz, H-4′), 3.61 (1H, dd, J = 9, 5.5 Hz, H-2′), 3.64 (1H, dd, J = 11, 2 Hz, H-6′), 3.68 (3H, s, COOCH_3), 3.71 (1H, dd, J = 11, 3.5 Hz, H-6′), 3.88 (1H, t, J = 9 Hz, H-3′), 3.88 (1H, ddd, J = 10, 3.5, 2 Hz, H-5′), 4.47 (1H, d, J = 12 Hz, CH_AH$_B$Ph), 4.48 (1H, d, J = 10.5 Hz, CH_CH$_D$Ph), 4.52 (1H, br dd, J = 8.5, 4.5 Hz, H-α) 4.58 (1H, d, J = 12 Hz, CH$_A$$H_B$Ph), 4.69 (2H, s, C$H_E$$H_F$Ph), 4.70 (1H, dd, J = 5.5, 2 Hz, H-1′), 4.81 (1H, d, J = 10.5 Hz, CH$_C$$H_D$Ph), 4.81 (1H, d, J = 10.5 Hz, CH_GH$_H$Ph), 4.98 (1H, d, J = 10.5 Hz, CH$_G$$H_H$Ph), 5.54 (1H, d, J = 8.5 Hz, NH), 7.12–7.15 (2H, m, aromatic), 7.24–7.39 (18H, m, aromatic). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 23.3, 28.2, 52.1, 52.6, 66.7, 68.5, 72.8, 73.5, 75.0, 75.7, 77.3, 78.2, 79.0, 80.1, 83.1, 84.5, 127.7, 127.7, 127.9, 128.0, 128.0, 128.1, 128.1, 128.4, 128.5, 138.0, 138.4, 155.3, 171.3. MS (FAB) m/z 750 (M + H). *Anal.* Calcd. for $C_{45}H_{51}NO_9$: C,

72.07; H, 6.86; N, 1.87%. Found: C, 72.09; H, 6.77; N, 2.00%.

*1-Acetyl-N-(tert-butoxycarbonyl)-3-(2′,3′,4′,6′-tetra-O-benzyl-α-D-glucopyranosyl)-L-iso-tryptophan methyl ester (**13b**).* A 5-ml two-necked round-bottomed flask was charged with glucosy-α-1-ethynylalanine **12** (29.3 mg, 0.039 mmol), *o*-iodoacetanilide **4b** (5.1 mg, 0.0195 mmol), $Pd(OAc)_2$ (1.3 mg, 5.85×10^{-3} mmol), PPh_3 (1.5 mg, 5.85×10^{-3} mmol), *n*-Bu_4NCl (5.4 mg, 0.0195 mmol) and Na_2CO_3 (10.3 mg, 0.0975 mmol) and connected to a vacuum/argon line. The flask was evacuated and then filled with argon, this evacuation/filling cycle being conducted three times. These reagents were dissolved in DMF (0.88 ml). The mixture was stirred at 90°C for 16 hr. After cooling to rt, the reaction was quenched with a saturated NH_4Cl solution, and the mixture was extracted with AcOEt (×3). The combined organic extract was successively washed with a saturated NH_4Cl solution (×2), H_2O (×2) and brine (×2), passed through a short column packed with Na_2SO_4, and concentrated. The residue was purified by preparative thin-layer chromatography (Et_2O: hexane = 3:1) to afford **13b** (5.4 mg, 31%) as a yellow oil. $[\alpha]_D^{26}$ +8.2 (*c* 0.38, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 3338, 3029, 2865, 1730, 1677, 1457, 1093. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.67 (3H, s, $COCH_3$), 1.73 (9H, s, $OC(CH_3)_3$), 3.64 (1H, dd, J = 14, 4.5 Hz, H-β), 3.65 (1H, t, J = 2 Hz, H-2′), 3.70 (3H, s, $COOCH_3$), 3.75 (1H, dd, J = 14, 12 Hz, H-β), 3.82 (1H, dd, J = 11, 3 Hz, H-6′), 3.87 (1H, dd, J = 11, 3.5 Hz, H-6′), 3.89 (1H, dd, J = 5.5, 2 Hz, H-3′), 4.01 (1H, dd, J = 8.5, 5.5 Hz, H-4′), 4.10 (1H, d, J = 12 Hz, CH_AH_BPh), 4.31 (1H, d, J = 12 Hz, CH_AH_BPh), 4.32 (1H, ddd, J = 8.5, 3.5, 3 Hz, H-5′), 4.46 (1H, d, J = 12 Hz, CH_CH_DPh), 4.50 (1H, d, J = 12 Hz, CH_EH_FPh), 4.54 (1H, d, J = 12 Hz, CH_EH_FPh), 4.58 (1H, d, J = 12 Hz, CH_CH_DPh), 4.60 (1H, d, J = 12 Hz, CH_GH_HPh), 4.71 (1H, d, J = 12 Hz, CH_GH_HPh), 4.85 (1H, ddd, J = 12, 8, 4.5 Hz, H-α), 5.40 (1H, d, J = 2 Hz, H-1′), 6.90 (1H, d, J = 8 Hz, aromatic), 6.90 (1H, d, J = 8 Hz, aromatic), 7.05–7.17 (5H, m, H-6, H-7 & aromatic), 7.23–7.38 (16H, m, H-5 & aromatic), 7.61 (1H, d, J = 8.5 Hz, N*H*), 8.09 (1H, d, J = 8.5 Hz, H-4). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 22.6, 28.3, 29.2, 51.4, 52.1, 68.5, 68.7, 72.2, 72.9, 73.1, 73.3, 73.4, 76.2, 78.4, 80.9, 84.8, 116.2, 116.9, 117.4, 122.6, 124.1, 127.8, 127.8, 127.9, 128.0, 128.4, 128.6, 134.9, 136.0, 137.3, 137.9, 138.3, 150.3, 170.4, 173.1. MS(FAB) *m/z* 883 (M + H). HRMS(FAB): calcd. for $C_{53}H_{59}N_2O_{10}$ (M + H), 883.4170; found, 883.4101.

*N,1-bis(tert-Butoxycarbonyl)-3-(2′,3′,4′,6′-tetra-O-benzyl-α-D-glucopyranosyl)-L-iso-tryptophan methyl ester (**13c**).* This was prepared in a 30% yield by coupling **12** (22 mg, 0.030 mmol) and **4c** (10.0 mg, 0.030 mmol) in a similar manner to that described for **13b**. $[\alpha]_D^{25}$ +6.2 (*c* 0.39, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 3336, 3031, 2865, 1733, 1455, 1091. ^{1}H-NMR (DMSO-d_6, at 80°C, 600 MHz) δ: 1.14 (9H, s, $OC(CH_3)_3$), 1.68 (9H, s, $OC(CH_3)_3$), 3.43 (1H, dd, J = 14, 6 Hz, H-β), 3.52–3.57 (1H, m, H-β), 3.55 (3H, s, $COOCH_3$), 3.74 (1H, t, J = 2.5 Hz, H-2′), 3.75 (1H, dd, J = 10.5, 4 Hz, H-6′), 3.78(1H, dd, J = 10.5, 5 Hz, H-6′), 3.92 (1H, dd, J = 8, 5.5 Hz, H-4′), 4.00 (1H, dd, J = 5.5, 2.5 Hz, H-3′), 4.03 (1H, d, J = 12 Hz, CH_AH_BPh), 4.14 (1H, ddd, J = 8, 5, 4 Hz, H-5′), 4.39 (1H, d, J = 12 Hz, CH_AH_BPh), 4.48–4.52 (1H, m, H-α), 4.50 (1H, d, J = 12 Hz, CH_CH_DPh), 4.53 (1H, d, J = 12 Hz, CH_CH_DPh), 4.58 (1H, d, J = 11.5 Hz, CH_EH_FPh), 4.69 (1H, d, J = 12 Hz, CH_GH_HPh), 4.71 (1H, d, J = 11.5 Hz, CH_EH_FPh), 4.71 (1H, d, J = 12 Hz, CH_GH_HPh), 5.38 (1H, d, J = 2.5 Hz, H-1′), 6.84 (1H, d, J = 7 Hz, aromatic), 7.06 (1H, t, J = 7.5 Hz, aromatic), 7.10 (1H, t, J = 8 Hz, H-6), 7.23 (1H, t, J = 8 Hz, H-5), 7.25–7.38 (19H, m, aromatic & N*H*), 7.50 (1H, d, J = 8 Hz, H-7), 8.01 (1H, d, J = 8 Hz, H-4). ^{13}C-NMR (DMSO-d_6, at 80°C, 150 MHz) δ: 27.9, 28.0, 28.1, 51.7, 53.0, 68.2, 69.6, 71.9, 72.2, 72.7, 74.3, 76.0, 78.5, 79.5, 80.0, 80.1, 80.9, 115.1, 122.2, 123.8, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.2, 128.28, 128.34, 133.7, 135.8, 138.6, 150.0, 172.4. HRMS(FAB): calcd. for $C_{56}H_{65}N_2O_{11}$ (M + H), 941.4588; found, 941.4560.

*N-(tert-Butoxycarbonyl)-1-(4-toluenesulfonyl)-3-(2′,3′,4′,6′-tetra-O-benzyl-α-D-glucopyranosyl)-L-iso-tryptophan methyl ester (**13d**).* This was prepared in an 89% yield by coupling **12** (73 mg, 0.098 mmol) and **4d** (18.2 mg, 0.0488 mmol) in a similar manner to that described for **13b**. $[\alpha]_D^{26}$ +47 (*c* 0.16, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 3349, 3030, 2867, 1748, 1713, 1454, 1367, 1175, 1090. ^{1}H-NMR (DMSO-d_6, at 80°C, 600 MHz) δ: 1.19 (9H, s, $OC(CH_3)_3$), 2.09 (3H, s, $ArCH_3$), 3.48 (1H, dd, J = 5.5, 14.5 Hz, H-β), 3.57 (3H, s, $COOCH_3$), 3.65 (1H, dd, J = 10, 14.5 Hz, H-β), 3.64 (1H, t, J = 2.5 Hz, H-2′), 3.70 (1H, dd, J = 4.5, 11 Hz, H-6′), 3.72(1H, dd, J = 5, 11 Hz, H-6′), 3.76 (1H, d, J = 12 Hz, CH_AH_BPh), 3.83(1H, dd, J = 5.5, 7.5 Hz, H-4′), 3.89 (1H, dd, J = 2.5, 5.5 Hz, H-3′), 4.03 (1H, d, J = 12 Hz, CH_AH_BPh), 4.06 (1H, ddd, J = 4.5, 5, 7.5 Hz, H-5′), 4.46 (1H, d, J = 12 Hz, CH_CH_DPh), 4.49 (1H, d, J = 12 Hz, CH_CH_DPh), 4.51 (1H, d, J = 11.5 Hz, CH_EH_FPh), 4.58 (2H, s, CH_GH_HPh), 4.63 (1H, d, J = 11.5 Hz, CH_EH_FPh), 4.62 (1H, m, H-α), 5.31 (1H, d, J = 2.5 Hz, H-1′), 6.69 (2H, d, J = 7.5 Hz, aromatic), 7.04 (2H, t, J = 7.5 Hz, aromatic), 7.10 (1H, t, J = 8 Hz, H-6), 7.10 (2H, d, J = 8.5 Hz, H-3″ of Ts), 7.09–7.11 (1H, aromatic), 7.20 (1H, d, J = 8 Hz, N*H*), 7.26 (1H, t, J = 8 Hz, H-5), 7.23–7.31(15H, m, aromatic), 7.46 (1H, d, J = 8 Hz, H-7), 7.51 (2H, d, J = 8.5 Hz, H-2″ of Ts), 8.01 (1H, d, J = 8 Hz, H-4). ^{13}C-NMR (DMSO-d_6, at 80°C,

150 MHz) δ: 20.8, 28.1, 28.9, 51.8, 54.2, 68.0, 69.4, 71.9, 72.1, 72.3, 72.7, 74.2, 75.9, 78.6, 79.4, 79.8, 114.6, 121.6, 124.6, 127.3, 127.3, 127.3, 127.4, 127.5, 127.6, 127.7, 128.2, 128.3, 134.1, 136.3, 138.5, 145.1, 172.3. MS(FAB) m/z 995 (M+H). HRMS(FAB): calcd. for $C_{58}H_{63}N_2O_{11}S$ (M+H), 995.4153; found, 995.4075.

Acknowledgments

We are grateful to Professor J. M. Cook (University of Wisconsin-Milwaukee) for valuable discussion and encouragement to publish our preliminary results. We also thank Mr. K. Koga (analytical laboratory in this school) for measurement of 2D NMR spectra. This work was financially supported by JSPS-RFTF (96L00504) and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan (No. 12760077).

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