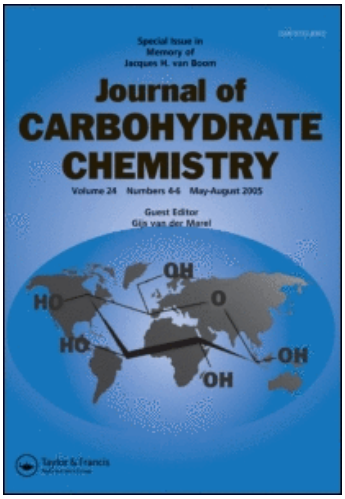

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PREPARATION OF 2-AZIDO-4-*O*-BENZOYL-2, 6-DIDEOXY-3-*O*-METHYL-β-D-ALLOPYRANOSE AND ITS DISACCHARIDE DERIVATIVE

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ABSTRACT

2-Azido-4-*O*-benzoyl-2,6-dideoxy-3-*O*-methyl-D-allopyranose, needed as one of the building blocks for construction of a novel cyclodextrin-like compound, was prepared in the form of crystalline β-anomer **6** from methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside **1**. As a model of α-glycosidation necessary for formation of a cyclic structure, **6** was converted into the corresponding β-glycosyl trichloroacetimidate and coupled with methyl 6-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside **8**, giving α(1→4)-linked disaccharide derivative **9**.

INTRODUCTION

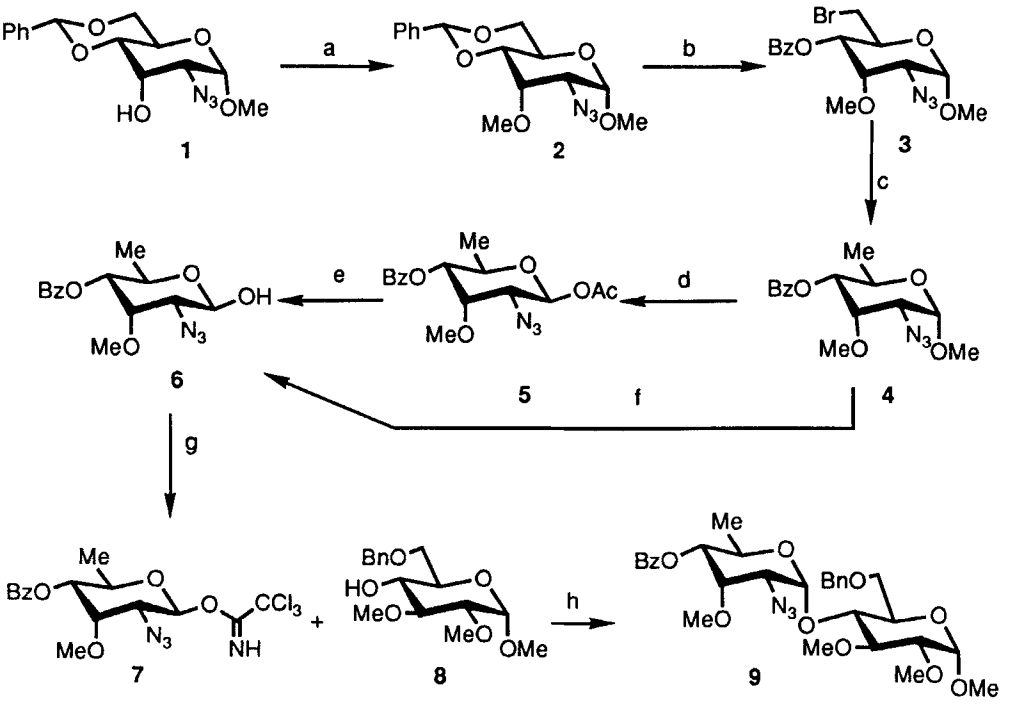
Our recent interests have focused on construction of novel type cyclooligosaccharides with new functions through such successive treatments of the starting ordinary cyclodextrins as ring-opening, selective chemical modifications, and recyclizing. In the course of such studies, we have succeeded in insertion of a D-glucosamine residue into the α-

cyclodextrin skeleton[1], developed a novel recyclization method through addition of iodonium ion to 1,2-unsaturated linear oligosaccharides derived from cyclodextrins, and so on.[2] Now, our attention has been directed towards the preparation of a cyclooligosaccharide which can influence the guest molecules to undergo enantioface-selective reactions. Examination with CPK space-filling molecular models suggested that a 2-amino-2,6-dideoxy-3-*O*-methyl-D-allopyranosyl moiety might be one of the appropriate units to exert the desired ability when inserted into the permethylated α-cyclodextrin skeleton.

This paper describes the preparation of crystalline 2-azido-4-*O*-benzoyl-2,6-dideoxy-3-*O*-methyl-β-D-allopyranose **6**, a precursor of the aforementioned amino sugar, and its α-glycosidation reaction with the 4-hydroxyl group of a methyl α-D-glucopyranoside derivative as a model for longer chain maltooligosaccharide derivatives. The α-glycosidation was needed for cyclic structure formation to be required later.

RESULTS AND DISCUSSION

Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside **1**, which had been first prepared by Ali and Richardson,[3] was chosen as the starting material for the preparation of **6**. Treatment of **1** with dimethyl sulfate in oxolane (THF) in the presence of sodium hydride gave the 3-*O*-methyl derivative **2** in almost quantitative yield. Oxidative ring opening of the benzylidene acetal with *N*-bromosuccinimide (NBS)-barium carbonate in the mixture of carbon tetrachloride-1,1,2,2-tetrachloroethane[4] gave the 6-bromo-6-deoxy derivative **3** in moderately good yield. Compound **3** was then dehalogenated by selective reduction with sodium cyanoborohydride in hexamethylphosphoric triamide (HMPA) at 70 °C in the presence of sodium iodide to give the 2-azido-2,6-dideoxy derivative **4** in quantitative yield.[5] This reaction did not proceed without sodium iodide. In order to hydrolyze the glycosidic bond, **4** was heated with acetic acid-water (3:1 v/v) in the presence of 1% hydrochloric acid,[6] giving crystalline 2-azido-4-*O*-benzoyl-2,6-dideoxy-3-*O*-methyl-β-D-allopyranose (**6**) in 60% yield. The yield of this conversion was greatly improved by employing a two-step procedure of acetolysis[7] followed by basic deacetylation at the anomeric position.[8] Thus, **4** was treated with acetic anhydride-concd H_2SO_4 (100:1 v/v) at 0 °C to give the β-

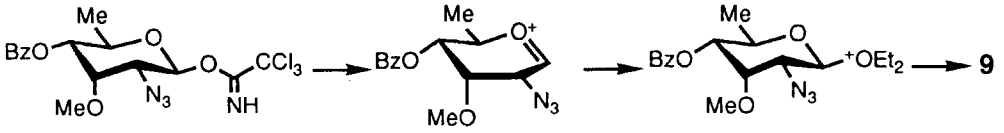


a) $(MeO)_2SO_2$, NaH, THF, 98%; b) NBS, $BaCO_3$, CCl_4-1,1,2,2-tetrachloroethane, 90%; c) $NaBH_3CN$, NaI, HMPA, 100%; d) Ac_2O, H_2SO_4, 97%; e) K_2CO_3, MeOH, 0 °C, 98%; f) AcOH - H_2O, 1% HCl, reflux, 3 h, 60%; g) K_2CO_3, CCl_3CN, CH_2Cl_2, 83%; h) TMSOTf, 4A-MS, Et_2O, -15 °C, 3 h, 83%.

glycosyl acetate **5** in 97% yield, with a ^1H NMR H-1 signal at δ 6.05 and a $J_{1,2}$ = 8.55 Hz. Compound **5** underwent subsequent treatment with potassium carbonate in methanol at 0 °C, to give **6** as crystals in 98% yield. In the ^1H NMR spectrum of **6**, the anomeric proton appeared as a doublet of doublets at 5.17 ppm with $J_{1,2}$ = 8.09 Hz and $J_{1,OH}$ = 5.45 Hz, suggesting that **6** had a β-configuration at C-1. It was quite interesting that both **5** and **6** had the β-configuration at C-1, as similar acetolysis of glucopyranoside derivatives generally gives α-acetates in excess[7,8] and free hemiacetals like **6** usually exist in an equilibrium mixture of α and β anomers.[6,7,8] Possibly the methoxyl group at C-3 in the reactants sterically hinder formation of α-isomers due to the 1,3-diaxial interaction. On treatment of **6** with trichloroacetonitrile and potassium carbonate[9] in dichloromethane, the β-

imidate **7** was formed as the kinetically controlled product. In the ^1H NMR spectrum of **7**, H-1 appears as a doublet ($J_{1,2}$ = 8.57 Hz) at δ 6.56 ppm.

Finally, reactivity of the imidate **7** as the glycosyl donor was examined by attempting to couple it with the known glucopyranoside[10] **8** bearing a free hydroxyl group at C-4. When trimethylsilyl trifluromethanesulfonate (TMSOTf) and diethyl ether were employed as the promoter and the solvent respectively, the glycosidation reaction smoothly proceeded with high stereoselectivity, giving the α-linked disaccharide **9** in 83% yield. In the ^1H NMR spectrum of **9**, H-1' appears at δ 5.58 ppm as a doublet ($J_{1',2'}$ = 4.27 Hz).



The highly stereoselective formation of α-linked disaccharide through the reaction using such a glucosyl donor of the *allo*-configuration as **7** was in sharp contrast to the predominant formation of β-anomers like **5** and **6** in acetolysis or hydrolysis of the corresponding methyl glycoside **4**. This was probably because the glycosidation reaction involved participation of the solvent leading to a β-oxonium ion intermediate as suggested by Wegmann and Schmidt.[11] Thus, the oxocarbenium ion **10**, first generated from **7** led to the β-oxonium ion intermediate **11**, which underwent an S_N2 type of replacement with the glycosyl acceptor **8**, giving α-linked disaccharide **9**. A potent reverse anomeric effect would stabilize the β-configuration of the diethyloxonium (Et_2O^+) group in **11**, restricting the nucleophile to attack the anomeric position from the α-side.

EXPERIMENTAL

General methods. Melting points were determined with an Ishii micro-melting point apparatus and are uncorrected. Analytical samples were dried at 60-65 °C over phosphorus pentoxide for 5-6 h *in vacuo*. Optical rotations were measured with a JASCO DIP-370 polarimeter. IR spectra were recorded with a Shimadzu-FTIR-8100M spectrophotometer. ^1H NMR

spectra were recorded for solutions in $CDCl_3$ using tetramethylsilane as the internal standard at 500 MHz with a JEOL JNM-GSX-500 for compounds **2**, **3**, **4**, **5** and **7**, and at 270 MHz with JEOL JNM-EX-270 for compounds **6** and **9**. ^{13}C NMR spectra were recorded at 25 °C for solutions in $CDCl_3$ at 67.5 MHz, using a JEOL JNM-EX-270 spectrometer, and chemical shifts are given in ppm down-field for tetramethylsilane.

Methyl 2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-allopyranoside (2). To a solution of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside[3] **1** (4.0 g, 13.0 mmol) in THF (100 mL) was added sodium hydride (0.47 g, 19.5 mmol). After stirring at room temperature for 5 min, dimethyl sulfate (1.9 mL, 20 mmol) was added to the reaction mixture which was further stirred for 1 h. Methanol and diethyl ether were successively added to the mixture. The organic layer was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residual oil was applied to a column of silica gel employing hexane-ethyl acetate (3:1 v/v) as the eluant to give product **2** (4.1 g, 98 %): mp 146-147 °C; $[\alpha]_D^{20}$ +85.0° (*c* 0.69, $CHCl_3$); ν_{max} (KBr) 2112.3, 1043.6 cm^{-1}; ^1H NMR δ 2.99 (t, 1H, $J_{2,3} = J_{2,1}$ = 3.74 Hz, H-2), 3.52 (s, 3H, OMe), 3.58 (dd, 1H, $J_{4,3}$ = 3.74 Hz, $J_{4,5}$ = 9.46 Hz, H-4), 3.66 (s, 3H, OMe), 3.70 (t, 1H, $J_{6a,6b} = J_{6a,5}$ = 10.07 Hz, H-6a), 4.04 (t, 1H, $J_{3,4} = J_{3,2}$ = 3.06 Hz, H-3), 4.31 (m, 1H, H-5), 4.34 (dd, 1H, $J_{6b,5}$ = 5.18 Hz, $J_{6b,6a}$ = 10.07 Hz, H-6b), 4.78 (d, 1H, $J_{1,2}$ = 3.74 Hz, H-1), 5.50 (s, 1H, PhC*H*), 7.38 (m, 3H, phenyl), 7.48 (m, 2H, phenyl); ^{13}C NMR δ 56.48, 57.68 (2 OMe), 57.74 (C-6), 61.51, 69.15, 78.78, 79.68 (ring carbons), 100.04 (C-1), 102.01 (benzylidene), 126.18, 128.32, 129.18, 137.38 (aromatic carbons).

Anal. Calcd for $C_{15}H_{19}N_3O_5$: C, 56.07; H, 5.96, N,13.08. Found: C, 55.92; H, 5.98; N, 13.04.

Methyl 2-Azido-4-*O*-benzoyl-6-bromo-2,6-dideoxy-3-*O*-methyl-α-D-allopyranoside (3). To a suspension containing compound **2** (4.0 g, 12.5 mmol) in carbon tetrachloride (200 mL) and 1,1,2,2-tetrachloroethane (12 mL) were added NBS (2.4 g, 13.3 mmol) and barium carbonate (1.2 g, 6.2 mmol). The resulting suspension was heated under reflux for 2.5 h and filtered while hot. The residue was washed with two portions (20 mL) of hot carbon tetrachloride. The combined filtrate and washings were concentrated *in vacuo* to give an oil that was dissolved in diethyl ether (200 mL). The solution was washed with three times of water (20 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Chromatography of the residual oil on silica gel with hexane-ethyl acetate (4:1 v/v) as the eluant provided product **3** (3.7 g,

75%): mp 101-102 °C; $[\alpha]_D^{20}$ +178.8° (*c* 0.50, $CHCl_3$); ν_{max} (KBr) 3063.3, 2110.4, 1732.3, 1259.7 cm^{-1}; ^1H NMR δ 3.11 (t, 1H, $J_{2,3} = J_{2,1} = 4.28$ Hz, H-2), 3.54 (s, 3H, OMe), 3.57 (s, 3H, OMe), 3.69 (dd, 1H, $J_{6a,6b} = 11.90$ Hz, $J_{6a,5} = 5.80$ Hz, H-6a), 3.78 (dd, 1H, $J_{6b,5} = 2.44$ Hz, $J_{6b,6a} = 11.90$ Hz, H-6b), 4.19 (t, 1H, $J_{3,4} = J_{3,2} = 4.28$ Hz, H-3), 4.59 (m, 1H, H-5), 4.91 (d, 1H, $J_{1,2} = 4.28$ Hz, H-1), 5.05 (dd, 1H, $J_{4,3} = 4.28$ Hz, $J_{4,5} = 10.08$ Hz, H-4), 7.49 (t, 2H, J = 7.78 Hz phenyl), 7.63 (t, 1H, J = 7.78 Hz, phenyl), 8.07 (m, 2H, phenyl); ^{13}C NMR δ 44.15 (C-6), 56.57, 57.34 (2 OMe), 62.07, 64.76, 70.59, 79.03 (ring carbons), 99.71 (C-1), 128.73, 128.86, 129.78, 133.80 (aromatic carbons), 165.18 (C=O).

Anal. Calcd for $C_{15}H_{18}N_3BrO_5$: C, 45.01; H, 4.50; N, 10.50; Br, 19.99. Found: C, 44.77; H, 4.49; N, 10.14; Br, 20.07.

Methyl 2-Azido-4-*O*-benzoyl-2,6-dideoxy-3-*O*-methyl-α-D-allopyranoside (4). Sodium cyanoborohydride (691 mg, 11 mmol) was added to a mixture of **3** (2.2 g, 5.5 mmol) and sodium iodide (1.2 g, 8.3 mmol) in HMPA (40 mL). The mixture was stirred overnight at 70 °C, diluted with water, and extracted with diethyl ether. The extract was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*, giving a syrup. The syrup was chromatographed on a column of silica gel with hexane-ethyl acetate (3:1 v/v) as the eluant, yielding product **4** (1.8 g, 100%): mp 65-66 °C; $[\alpha]_D^{20}$ +236° (*c* 0.27, $CHCl_3$); ν_{max} (KBr) 2110.4, 1716.9, 1178.6 cm^{-1}; ^1H NMR δ 1.24 (d, 3H, $J_{6,5} = 6.41$ Hz, H-6), 3.07 (t, 1H, $J_{2,3} = J_{2,1} = 3.66$ Hz, H-2), 3.53 (s, 3H, OMe), 3.55 (s, 3H, OMe), 4.09 (t, 1H, $J_{3,4} = J_{3,2} = 3.66$ Hz, H-3), 4.40 (m, 1H, H-5), 4.79 (dd, 1H, $J_{4,3} = 3.66$ Hz, $J_{4,5} = 10.07$ Hz, H-4), 4.81 (d, 1H, $J_{1,2} = 3.66$ Hz, H-1), 7.48 (t, 2H, J = 7.63 Hz, phenyl), 7.61 (t, 1H, J = 7.63 Hz, phenyl), 8.08 (d, 2H, J = 7.63 Hz, phenyl); ^{13}C NMR δ 17.07 (C-6), 56.46, 57.75 (2 OMe), 61.11, 62.03, 74.50, 79.28 (ring carbons), 99.56 (C-1), 128.66, 128.75, 129.77, 133.56 (aromatic carbons), 165.58 (C=O).

Anal. Calcd for $C_{15}H_{19}N_3O_5 \cdot 0.25H_2O$: C, 55.29; H, 6.03; N, 12.90. Found: C, 55.36; H, 5.84; N, 12.91.

2-Azido-4-*O*-benzoyl-2,6-dideoxy-3-*O*-methyl-β-D-allopyranose (6). a) To a solution of **4** (400 mg, 1.25 mmol) in a mixture of acetic acid and water (37 mL, 3:1 v/v) was added hydrochloric acid (37%, 1 mL). The mixture was heated under reflux for 3 h, quenched by addition of sodium hydrogen carbonate and extracted with chloroform (3 x 20 mL). The chloroform solution was washed with water, dried ($MeSO_4$) and concentrated *in vacuo*, giving a syrup which was then chromatographed with hexane-ethyl acetate (3:1 v/v) as eluent to give **6** (230 mg, 60%).

b) To a solution of compound **4** (1.6 g, 5.0 mmol) in acetic anhydride (50 mL) was added concd sulfuric acid (0.5 mL) at 0 °C. The mixture was stirred for 30 min, quenched by addition of anhydrous sodium carbonate, and concentrated *in vacuo*. The residue was taken up in diethyl ether, washed with water, and dried ($MgSO_4$) to give a β-anomer of 1-*O*-acetate **5** (1.7 g, 97%): ^{1}NMR δ 1.26 (d, 3H, $J_{6,5}$ = 6.11 Hz, H-6), 2.18 (s, 3H, OAc), 3.45 (dd, 1H, $J_{2,1}$ = 8.55 Hz, $J_{2,3}$ = 2.74 Hz, H-2), 3.53 (s, 3H, OMe), 4.06 (t, 1H, $J_{3,4}$ = $J_{3,2}$ = 2.74 Hz, H-3), 4.31 (m, 1H, H-5), 4.75 (dd, 1H, $J_{4,5}$ = 10.07 Hz, $J_{4,3}$ = 2.74 Hz, H-4), 6.05 (d, 1H, $J_{1,2}$ = 8.55 Hz, H-1), 7.50-8.08 (5H, phenyl). Compound **5** (1.1 g) was dissolved in MeOH (100 mL), and potassium carbonate (1.1 g) was added to the solution at 0 °C. The suspension was stirred for 15 min, and quenched with Dowex 50W-X8 (H^+ form) resin. Filtration of the resin, followed by concentration *in vacuo* yielded the crude product **6**, which was applied to a column of silica gel employing hexane-ethyl acetate (3:1 v/v) as the eluant to give pure **6** (0.95 g, 98 %): mp 108-109 °C; $[\alpha]_D^{20}$ +39.6° (*c* 0.21, $CHCl_3$); ν_{max} (KBr) 2110.4, 1724.6, 1151.6 cm^{-1}; ^{1}H NMR δ 1.28 (d, 3H, $J_{6,5}$ = 6.27 Hz, H-6), 3.28 (dd, 1H, $J_{2,3}$ = 2.26 Hz, $J_{2,1}$ = 8.09 Hz, H-2), 3.33 (d, 1H, $J_{OH,1}$ = 5.45 Hz, OH), 3.53 (s, 3H, OMe), 4.01 (t, 1H, $J_{3,4}$ = $J_{3,2}$ = 2.26 Hz, H-3), 4.23 (dq, 1H, $J_{5,4}$ = 8.09 Hz, $J_{5,6}$ = 6.27 Hz, H-5), 4.76 (dd, 1H, $J_{4,3}$ = 2.64 Hz, $J_{4,5}$ = 8.09 Hz, H-4), 5.17 (dd, 1H, $J_{1,2}$ = 8.09 Hz, $J_{1,OH}$ = 5.45 Hz, H-1), 7.51 (2H, phenyl), 7.62 (1H, phenyl), 8.08 (2H, phenyl); ^{13}C NMR δ 17.54 (C-6), 61.67 (OMe), 63.67, 68.18, 74.88, 78.24 (ring carbons), 93.62 (C-1), 128.66, 129.31, 129.77, 133.62 (aromatic carbons), 165.62 (C=O).

Anal. Calcd for $C_{14}H_{17}N_3O_5$: C, 54.72; H, 5.54; N, 13.68. Found: C, 54.43; H, 5.49; N, 13.57.

4-*O*-(2-Azido-4-*O*-benzoyl-2,6-dideoxy-3-*O*-methyl-α-D-allopyranosyl)-6-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (9). To a stirring solution of **6** (307 mg, 1 mmol) in dichloromethane (10 mL) were added trichloroacetonitrile (1 mL, 10 mmol) and potassium carbonate (1.38 g, 10 mmol) at room temperature under an argon atmosphere. The mixture was stirred overnight and chromatographed directly with hexane-ethyl acetate (3:1 v/v) to give the glycosyl trichloroacetimidate **7** (375 mg, 83 %): ^{1}NMR δ 6.58 (d, 1H, $J_{1,2}$ = 8.57 Hz). A suspension of methyl 6-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside[10] **8** (131 mg, 0.42 mmol), **7** (190 mg, 0.42 mmol) and powdered 4A molecular sieves (400 mg) in dry diethyl ether (120 mL) was stirred at -15 °C, and TMSOTf (19 μL) was added to the mixture. After 3 h of stirring, the reaction mixture was neutralized with Et_3N (60 μL), filtered

through celite and washed with Et_2O. The organic layer was washed with water (2 x 5 mL) and brine, dried ($MgSO_4$), concentrated *in vacuo*, and chromatographed with toluene-ethyl acetate (2:1 v/v) as the eluant to give product **9** (210 mg, 83%): mp 107-108 °C; $[\alpha]_D^{20}$ +187° (*c* 0.13, $CHCl_3$); ν_{max} (KBr) 2112.3, 1732.3, 1581.8, 1097 cm^{-1}; ^1H NMR δ 1.07 (d, 3H, $J_{6',5'}$ = 6.27 Hz, H-6'), 3.01 (t, 1H, $J_{2',3'} = J_{2',1'}$ = 4.27 Hz, H-2'), 3.30 (dd, 1H, $J_{2,3}$ = 9.24 Hz, $J_{2,1}$ = 3.30 Hz, H-2), 3.45 (s, 3H, OMe), 3.50 (s, 3H, OMe), 3.52 (s, 3H, OMe), 3.66 (s, 3H, OMe), 3.77-3.85 (m, 5H, H-3, 4, 5, 6), 4.06 (t, 1H, $J_{3',4'} = J_{3',2'}$ = 4.29 Hz, H-3'), 4.34 (m, 1H, H-5'), 4.67 (ABq, 2H, benzyl), 4.74 (dd, 1H, $J_{4',5'}$ = 10.82 Hz, $J_{4',3'}$ = 4.29 Hz, H-4'), 4.88 (d, 1H, $J_{1,2}$ = 3.30 Hz, H-1), 5.58 (d, 1H, $J_{1',2'}$ = 4.27 Hz, H-1'), 7.25-7.40 (m, 5H, phenyl), 7.49 (t, 2H, J = 7.58 Hz, phenyl), 7.62 (t, 1H, J = 7.58 Hz, phenyl), 8.05 (d, 2H, J = 7.25 Hz, phenyl); ^{13}C NMR δ 16.92 (C'-6), 55.27, 57.71, 58.72, 60.30 (4 OMe), 61.34 (C-6), 61.77, 69.20, 69.54, 72.70, 73.36, 74.75, 82.69, 83.86 (ring carbons), 97.16, 97.37 (C-1,1'), 127.31, 127.43, 128.33, 128.64, 129.46, 129.75, 133.54, 138.45 (aromatic carbons), 165.58 (C=O).

Anal. Calcd for $C_{30}H_{39}N_3O_{10}$: C, 59.89; H, 6.53; N, 6.98. Found: C, 59.79; H, 6.52; N, 6.58

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