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Visible Light Photoredox-Catalyzed *O*-Sialylation Using Thiosialoside Donors

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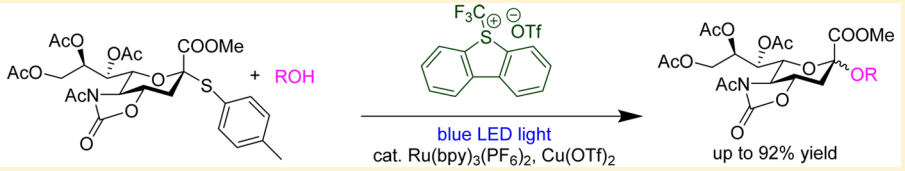
Supporting Information



ABSTRACT: An efficient protocol for the O-sialylation using thiosialoside donors under visible light photocatalysis was developed. Thiosialosides were activated under the irradiation with blue light in the presence of $Ru(bpy)_3(PF_6)_2$ as photocatalyst, Umemoto's reagent as CF_3 radical source and $Cu(OTf)_2$ as an additive in acetonitrile/dichloromethane at −30 °C, and the subsequent reaction with glycosyl acceptors generally produced the desired sialosides in good to excellent yields with the satisfactory α-selectivity.

INTRODUCTION

Sialic acids are involved in a wide variety of physiological and pathological processes.[1−4] The sialic acid moiety usually occurs in poly(oligo)saccharides, glycoproteins, or glycolipids. Chemical syntheses have provided reliable routes to the synthesis of many complex sialosides. However, chemical sialylation by using glycosyl donors of Neu5Ac (the most abundant sialic acid) is challenging, owing to the lack of neighboring C-3 functionality to direct the stereochemical outcome of glycosylations, the tendency of 2,3-elimination to generate glycals arising from the electron-withdrawing carboxylic acid at the anomeric center, and a sterically hindered tertiary oxocarbenium ion intermediate. Over the years, many efforts have been made toward the development of high-yielding and α-selective sialylation methodologies.[5−9] Thioglycosides are versatile donors used in carbohydrate chemistry.[10−13] Nevertheless, thiosialoside donors are 10^5 times less reactive than other corresponding sugar donors.[14] The activation and glycosidation of thiosialoside donors are more difficult. Several activation systems, such as NIS/TfOH,[15,16] DMTST,[17,18] PhSeOTf,[19] TMSOTf,[20] and Ph_2SO/Tf_2O,[21] have been developed to tackle this problem. Our group has also been dedicated to the continuous development of highly efficient glycosylation protocols using thioglycosides as glycosyl donors.[22−25] Recently, photocatalysis has attracted great attention due to its virtue of environmental-friendliness and versatility in organic synthesis,[26−28] but it is addressed less in carbohydrate chemistry. Very recently, we and others have developed several photoinduced glycosylation methods.[29−31] especially, a light-mediated glycosylation reaction using thioglycosides.[30] Based on our previous work, herein we report a new visible light photoredox-catalyzed *O*-sialylation protocol.

RESULTS AND DISCUSSION

In our previous studies, we used Umemoto's reagent **2a** as the CF_3 radical source, $Ru(bpy)_3(PF_6)_2$ as the photocatalyst, $Cu(OTf)_2$ as the additive, and CH_2Cl_2 as the solvent. Encouraged by this work, the coupling reaction of thiosialoside donor **1** with galactoside 3[32] as the acceptor in the presence of Umemoto's reagent and $Cu(OTf)_2$ catalyzed by $Ru(bpy)_3(PF_6)_2$ was reinvestigated (Table 1). Upon the irradiation of blue LEDs (λ_{max} = 465 nm, 4*7 W), when the reaction was performed in CH_2Cl_2 at room temperature in the presence of Umemoto's reagent **2a**, only the glycal side-product was obtained (entry 1). Interestingly, when the reaction was carried out in CH_3CN, the coupled product **4** was isolated only in 23% yield (entry 2), presumably resulting from the effect of acetonitrile participation to stabilize the oxocarbenium ion.[15,33,34] When THF or Et_2O was used as the solvent, no desired product **4** was obtained, either (entries 5 and 6). The yield of the product **4** was improved when a mixed solvent (CH_3CN/CH_2Cl_2) was employed, and the optimal ratio of the solvent was 2/1 (v/v) (entries 3−4). Notably, decreasing the reaction temperature to −30 °C boosted the yield of **4** up to 74% (entries 7−9), but no reaction was detected at lower temperature (entry 10). The α/β selectivity was similar to that reported in the literature.[16] The optimal ratio of donor/acceptor was 1/1.3 (entry 11). Increasing the amount of Umemoto's reagent **2a** did not enhance the yield obviously (entry 12) and the Umemoto's reagent **2b** did not work at all for the sialylation reaction (entry 13). The reaction of

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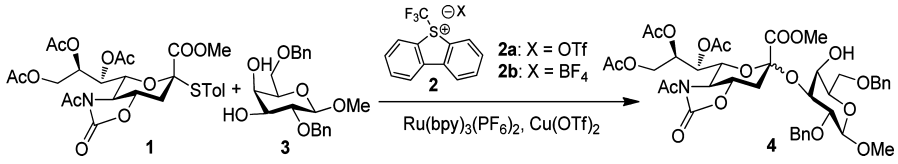
Table 1. Optimization of the Reaction Conditions under Visible Light[a]



entry	ROH (equiv)	activator (equiv)	solvent	T (°C)	α:β[c]	yield[b] (%)
1	**3** (0.8)	**2a** (1.5)	DCM	25	--	0
2	**3** (0.8)	**2a** (1.5)	CH_3CN	25	1.3:1	23
3	**3** (0.8)	**2a** (1.5)	CH_3CN/DCM (2/1)	25	1:1.4	42
4	**3** (0.8)	**2a** (1.5)	CH_3CN/DCM (1/2)	25	1:1.8	33
5	**3** (0.8)	**2a** (1.5)	THF	25	--	0
6	**3** (0.8)	**2a** (1.5)	Et_2O	25	--	0
7	**3** (0.8)	**2a** (1.5)	CH_3CN/DCM (2/1)	0	1:1.2	50
8	**3** (0.8)	**2a** (1.5)	CH_3CN/DCM (2/1)	−20	1:1.5	65
9	**3** (0.8)	**2a** (1.5)	CH_3CN/DCM (2/1)	−30	1:1.3	74
10	**3** (0.8)	**2a** (1.5)	CH_3CN/DCM (2/1)	−40	-	0
11	**3** (1.3)	**2a** (1.5)	CH_3CN/DCM (2/1)	−30	1:1.4	82
12	**3** (1.3)	**2a** (2.0)	CH_3CN/DCM (2/1)	−30	1:1.4	83
13	**3** (1.3)	**2b** (1.5)	CH_3CN/DCM (2/1)	−30	--	0
14	**3** (1.3)	--	CH_3CN/DCM (2/1)	−30	--	0
15[d]	**3** (1.3)	**2a** (1.5)	CH_3CN/DCM (2/1)	−30	--	0
16[e]	**3** (1.3)	**2a** (1.5)	CH_3CN/DCM (2/1)	−30	--	0
17[f]	**3** (1.3)	**2a** (1.5)	CH_3CN/DCM (2/1)	−30	1:1.4	56

[a]General conditions: the reaction was conducted with **1**, **3**, **2**, $Ru(bpy)_3(PF_6)_2$ (0.01 equiv), $Cu(OTf)_2$ (1.3 equiv), and activated 3 Å MS (0.3 g) in anhydrous solvent under the irradiation of LED light. [b]Isolated yield. [c]Ratio was determined by ^1H NMR analysis. [d]No $Cu(OTf)_2$. [e]No light. [f]No 3 Å MS.

thiosialoside donor **1** with acceptor **3** was also explored under the irradiation of UV light, but no improved results were achieved (see the Supporting Information). On the other hand, no desired product was detected in the absence of Umemoto's reagent **2a**, $Cu(OTf)_2$, or the irradiation of blue LEDs (entries 14−16). Thus, the optimized conditions included donor **1** (1.0 equiv), acceptor **3** (1.3 equiv), Umemoto's reagent **2a** (1.5 equiv), $Ru(bpy)_3(PF_6)_2$ (0.01 equiv), $Cu(OTf)_2$ (1.3 equiv), and 3 Å molecular sieves, in CH_3CN/CH_2Cl_2 (2:1) under the irradiation of a blue LED at −30 °C for 1 h.

With the optimized conditions in hand, the scope of this sialylation reaction was investigated by varying both the donors and the acceptors (Table 2). The coupling reactions of donor **1** with 1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranoside (**5**)[35] or methyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (**6**)[36] gave the corresponding disaccharides **12** and **13** in good yields with excellent α-stereoselectivity (α only, entry 1; α:β > 10:1, entry 2). The coupling reaction of donor **1** and the secondary alcohol methyl 2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**7**)[37] under the standard conditions provided the disaccharide **14** in 72% isolated yield with β-anomer as the major product (α:β = 1:6, entry 3), which is similar to those reported using the NIS/TfOH system.[16] When the tertiary alcohol 1-adamantanol (**8**) was used as the acceptor, the yield was still good but the α-selectivity was moderate (α:β = 2.6:1, entry 4). The glycosylation of acceptor **5** with the *N*-acetyl-protected sialoside donor **10**[38] also proceeded smoothly in high yield with good α-selectivity (α:β = 4.2:1, entry 5). It is noteworthy that the good yield and excellent α-stereoselectivity were obtained by the coupling of donor **1** with the sialyl acceptor **9**[39] (α only, entry 6). Interestingly, it was reported that 1-adamantanyl thiosialoside **11** can be activated by NIS/TfOH,[15] but it was found that the donor **11** is inert in this promoter system, resulting from the severe steric hindrance of 1-adamantanyl thiosialoside **11** (entry 7). Thus, our method might find its applications in the orthogonal synthesis of sialic acid-containing oligosaccharides using thioglycosides as building blocks.

On the basis of our observations in this work and previous work,[30] we proposed the possible mechanism (Figure 1). In the presence of visible light, the Umemoto's reagent **2a** was reduced by the excited state $*[Ru(bpy)_3]^{2+}$ to afford a CF_3 radical, which reacted with the sulfur atom in thiosialoside donor to generate the radical intermediate **A** and *p*-tolyl-(trifluoromethyl)sulfide. The glycosyl radical intermediate **A** was then oxidized by $[Ru(bpy)_3]^{3+}$ to give the glycosyl cation **C**. Finally, a glycosyl coupling reaction of the glycosyl cation **C** with an acceptor occurred, yielding the sialoside product. In the absence of $Cu(OTf)_2$, only the glycal product was detected (Table 1, entry 15). Thus, it seemed that $Cu(OTf)_2$ may not only play an important role in increasing the amount of CF_3 radical in thiosialoside activation, but also act as an extra triflate source to stabilize the oxocarbenium ion intermediate.

In summary, we have developed a visible-light photoredox-catalyzed *O*-sialylation method. This method employed $Ru(bpy)_3(PF_6)_2$ as photocatalyst, Umemoto'a reagent as CF_3 radical source, and $Cu(OTf)_2$ as an additive. Under these conditions, thiosialosides were activated and coupled with glycosyl acceptors in the acetonitrile/dichloromethane mixed solvent at −30 °C by the irradiation of blue LED, generally producing sialosides in good to excellent yields with satisfactory α-stereoselectivities. Further studies on the applications of this method in the synthesis of some biologically important sialic acid-containing oligosaccharides are underway in our laboratory.

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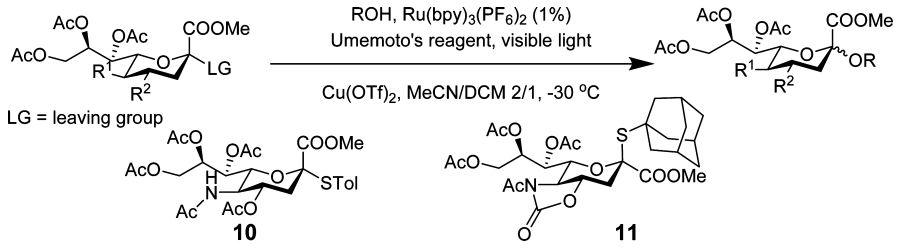
Table 2. Sialylation Reactions under the Irradiation of Visible Light[a]



entry	donor	acceptor	disaccharide	yield[b](%)	(α:β)[c]
1	1	5	12	92	α only
2	1	6	13	85	>10:1
3	1	7	14	72	1:6
4	1	8	15	85	2.6:1
5	10	5	16	90	4.2:1
6	1	9	17	75	α only[d]
7	11	5	12	0	–

[a]General conditions: donor (0.050 mmol, 1.0 equiv), acceptor (0.065 mmol, 1.3 equiv), **2a** (0.075 mmol, 1.5 equiv), $Ru(bpy)_3(PF_6)_2$ (0.0005 mmol, 0.01 equiv), $Cu(OTf)_2$ (0.065 mmol, 1.3 equiv), 3 Å MS (0.3 g) in MeCN/DCM (2:1, 2.0 mL) under the irradiation of blue LEDs at −30 °C for 1 h. [b]Isolated yield. [c]Determined by ^1H NMR analysis of the crude reaction mixture. [d]The anomeric configuration of new compound was assigned according to $^3J_{C-1,H-3ax}$ by selective-proton-decoupling ^{13}C NMR.[40]

EXPERIMENTAL SECTION

General Information. All reagents and solvents were purchased from commercial suppliers and were used without further purification unless otherwise specified. The molecular sieves were activated using an oven by heating at 400 °C for 6 h. All reactions were performed in an atmosphere of dry argon. All organic extracts were dried over sodium sulfate and concentrated under vacuum. Chromatographic purification was carried out over silica gel (200——300 mesh). Experiments upon visible-light irradiation were carried out using household blue LED lamps (λ_{max} = 465 nm, 4*7 W). Analytical thin-layer chromatography was performed with silica gel 60 F_{254} precoated on aluminum plates and visualized by UV light and/or by staining with acidic ceric ammonium molybdate. High-resolution mass spectra were recorded with FTMS spectrometer. ^1H, ^{13}C, 2D NMR spectra were recorded at a 400 or 600 MHz spectrometer at 25 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in deuterated chloroform. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.16 ppm). The following standard abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, and br = broad.

General Sialylation Procedure. A mixture of donor (0.050 mmol, 1.0 equiv), acceptor (0.065 mmol, 1.3 equiv), 5-(trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (**2a**) (0.075 mmol, 1.5 equiv), $Ru(bpy)_3(PF_6)_2$ (0.0005 mmol, 0.01 equiv), copper(II) trifluoromethanesulfonate (0.065 mmol, 1.3 equiv) and activated 3 Å powdered molecular sieves (0.3 g) in anhydrous CH_3CN/CH_2Cl_2 (2/1, 2.0 mL) was stirred for 2 h under argon, and then cooled to −30 °C. The reaction mixture was stirred and irradiated

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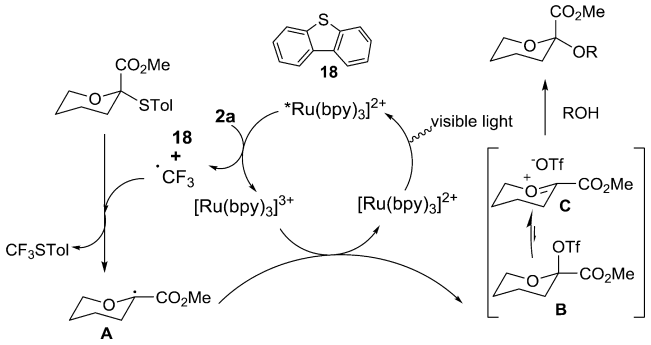

Figure 1. Mechanistic proposal for visible light photoredox-catalyzed *O*-sialylation.

by blue light emitting diodes (LED) at −30 °C for 1 h, and then the light was turned off and the solution was stirred at the same temperature for 2 h and quenched with triethylamine (100 μL). The mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with water and saturated NaCl solution, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with petroleum ether/tetrahydrofuran) to afford the desired coupled product.

Methyl 5-Acetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2 → 3)-methyl 2,6-di-O-benzyl-β-D-galactopyranoside ***(4α)***. Colorless oil, 82% yield (34.0 mg) (mixture of α and β isomers); α isomer was isolated and the spectra are in the accordance with those reported in the literature.[16] Column chromatography conditions: petroleum ether: tetrahydrofuran 4:1 to 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.26 (m, 10H), 5.57 (dd, *J* = 7.3, 1.6 Hz, 1H), 5.43 (dt, *J* = 7.1, 2.7 Hz, 1H), 5.00 (s, 1H), 4.83 (d, *J* = 11.8 Hz, 1H), 4.69 (d, *J* = 11.7 Hz, 1H), 4.57 (s, 2H), 4.48 (dd, *J* = 9.4, 1.4 Hz, 1H), 4.43 (dd, *J* = 12.5, 2.6 Hz, 1H), 4.33 (d, *J* = 7.7 Hz, 1H), 4.05 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.00−3.91 (m, 2H), 3.90−3.87 (m, 1H), 3.85−3.77 (m, 4H), 3.75−3.61 (m, 4H), 3.57 (s, 3H), 3.58−3.54 (m, 1H), 2.88−2.75 (m, 2H), 2.48 (s, 3H), 2.27 (s, 3H), 2.23−2.15 (m, 1H), 2.11 (s, 3H), 2.03 (s, 3H), 1.89 (s, 3H).

Methyl 5-acetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2 → 6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranoside ***(12)***. Colorless oil, 92% yield (33.0 mg). The spectra are in the accordance with those reported in the literature.[16] Column chromatography conditions: petroleum ether: tetrahydrofuran 5:1 to 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (d, *J* = 6.9 Hz, 1H), 5.51 (d, *J* = 5.0 Hz, 1H), 5.45 (dt, *J* = 6.5, 2.7 Hz, 1H), 4.63−4.56 (m, 2H), 4.37−4.29 (m, 2H), 4.23 (d, *J* = 8.0 Hz, 1H), 4.16 (dd, *J* = 12.2, 6.3 Hz, 1H), 4.06−3.96 (m, 1H), 3.93−3.84 (m, 2H), 3.80 (s, 3H), 3.76−3.68 (m, 1H), 3.65−3.57 (m, 1H), 2.90 (dd, *J* = 12.2, 3.4 Hz, 1H), 2.49 (s, 3H), 2.16−2.09 (m, 7H), 2.05 (s, 3H), 1.54 (s, 3H), 1.42 (s, 3H), 1.33 (brs, 6H).

Methyl 5-acetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2 → 6)-methyl 2,3,4-tri-O-benzyl-β-D-galactopyranoside ***(13α)***. Colorless oil, 85% yield (35.0 mg, mixture of α and β isomers); α isomer was isolated and the spectra are in the accordance with those reported in the literature.[16] Column chromatography conditions: petroleum ether: tetrahydrofuran 5:1 to 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.21 (m, 15H), 5.55 (d, *J* = 7.4 Hz, 1H), 5.40 (dt, *J* = 6.9, 2.6 Hz, 1H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.81−4.65 (m, 4H), 4.56 (d, *J* = 10.5 Hz, 1H), 4.35 (dd, *J* = 12.2, 2.5 Hz, 1H), 4.31 (d, *J* = 7.5 Hz, 1H), 4.06 (dd, *J* = 12.2, 6.8 Hz, 1H), 4.03−3.94 (m, 1H), 3.94−3.87 (m, 2H), 3.84−3.76 (m, 1H), 3.70 (t, *J* = 9.7 Hz, 1H), 3.64 (s, 3H), 3.61−3.52 (m, 5H), 2.87 (dd, *J* = 12.3, 3.2 Hz, 1H), 2.48 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.05−1.94 (m, 4H).

Methyl 5-acetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate-(2 → 3)-methyl 2,4,6-tri-O-benzyl-β-D-galactopyranoside ***(14β)***. Colorless oil, 72% yield (33.0 mg, mixture of α and β isomers); β isomer was isolated and the spectra are in the accordance with those reported in the literature.[16] Column chromatography conditions: petroleum ether: tetrahydrofuran 5:1 to 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.26 (m, 15H), 5.36−5.33 (m, 1H), 5.10 (d, *J* = 8.2 Hz, 1H), 4.80−4.72 (m, 2H), 4.71−4.64 (m, 2H), 4.61−4.50 (m, 3H), 4.25 (d, *J* = 7.6 Hz, 1H), 4.12 (dd, *J* = 9.9, 2.4 Hz, 2H), 3.97 (dd, *J* = 12.2, 8.6 Hz, 1H), 3.84 (d, *J* = 2.6 Hz, 1H), 3.74−3.64 (m, 4H), 3.54 (s, 3H), 3.46 (s, 3H), 3.47−3.42 (m, 2H), 2.65 (dd, *J* = 6.2, 2.5 Hz, 1H), 2.46 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03−1.99 (m, 1H), 1.98 (s, 3H).

Methyl (1-adamantanyl 5-acetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranoside)-onate ***(15α)***. Colorless oil, 85% yield (26.0 mg, mixture of α and β isomers); α isomer was isolated and the spectra are in the accordance with those reported in the literature.[16] Column chromatography conditions: petroleum ether: tetrahydrofuran 5:1 to 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (d, *J* = 9.2 Hz, 1H), 5.49−5.40 (m, 1H), 4.76 (d, *J* = 9.6 Hz, 1H), 4.40 (dd, *J* = 12.4, 3.1 Hz, 1H), 4.12 (dd, *J* = 11.5, 5.1 Hz, 1H), 3.95−3.86 (m, 1H), 3.77 (s, 3H), 3.62−3.69 (m, 1H), 2.83 (dd, *J* = 12.1, 3.4 Hz, 1H), 2.51 (s, 3H), 2.22−2.00 (m, 13H), 1.89−1.82 (m, 6H), 1.63−1.58 (m, 6H).

Methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero-D--D-galacto-non-2-ulopyranosylonate-(2 → 6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranoside ***(16)***. Colorless oil, 90% yield (33.0 mg, an inseparable mixture of α and β isomers); column chromatography conditions: petroleum ether: tetrahydrofuran 5:1 to 4:1. The spectra of α and β mixture are in the accordance with those reported in the literature.[41]

Methyl 5-acetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2 → 9)-[(5-acetamido-2,4,7-tri-O-benzoyl-3,5-dideoxy-2-β-D-glycero-D--D-galacto-2-nonulopyranose)onate] ***(17)***. White foam, 75% yield (41.0 mg); column chromatography conditions: petroleum ether: tetrahydrofuran 2.5:1 to 1.5:1; $[\alpha]^{24}_D$ = +11.0 (c = 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, *J* = 7.1 Hz, 4H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.60−7.43 (m, 5H), 7.38 (t, *J* = 7.6 Hz, 2H), 5.80 (d, *J* = 9.5 Hz, 1H), 5.70 (td, *J* = 10.8, 4.4 Hz, 1H), 5.51 (d, *J* = 6.6 Hz, 1H), 5.39 (d, 9 Hz, 1H), 5.33−5.27 (m, 1H), 4.64−4.53 (m, 2H), 4.40−4.25 (m, 3H), 3.99−3.90 (m, 2H), 3.85 (s, 3H), 3.68 (s, 3H), 3.77−3.59 (m, 2H), 3.56−3.49 (m, 1H), 3.03 (s, 1H), 2.91 (dd, *J* = 13.4, 4.6 Hz, 1H), 2.68 (dd, *J* = 12.1, 3.3 Hz, 1H), 2.46 (s, 3H), 2.20 (t, *J* = 12.3 Hz, 1H), 2.09 (s, 3H), 2.02 (s, 3H), 1.95 (t, *J* = 12.7 Hz, 1H), 1.90 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.1, 170.3, 170.1, 169.9, 168.5 ($^3J_{C-1,H-3ax}$ = 5.9 Hz), 166.9, 166.4, 165.5, 164.4, 153.6, 134.0, 133.4, 133.2, 130.1 129.99, 129.96, 129.8, 129.3, 128.8, 128.7, 128.5, 128.4, 99.2, 97.9, 76.2, 74.7, 72.0, 71.9, 69.8, 69.7, 69.6, 68.1, 67.8, 63.0, 58.9, 53.2, 53.0, 49.2, 37.2, 35.9, 29.7, 29.1, 24.6, 23.9, 23.2, 21.1, 20.9, 20.6. HRMS (ESI) Calcd for $C_{52}H_{56}N_2O_{24}Na$ ($[M + Na]^+$): 1115.3121; found: 1115.3115.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00999.

Optimization of the reaction conditions under UV, and NMR spectra for compounds (PDF)

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Notes

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