**Supporting Information**

**Nitrogen-Centered Radical Mediated Anomeric Specific Cascade Amidoglycosylation of Glycals**

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# **1. General methods**

Anhydrous DCE and MeCN were refluxed with CaH2 and freshly distilled prior to use; anhydrous Toluene were distilled over sodium and benzophenone ketyl under nitrogen atmosphere; anhydrous EtOAc, Et3N and Pyridine were dealed with fully dried 4Å molecular sieves; all other solvents and reagents were used from commercial sources without further purifications. All reactions sensitive to air or moisture were carried out in glovebox under argon atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. The silica gel (200-300 meshes) was used for column chromatography. Thin layer chromatographies (TLC) were carried out on GF254 plates (0.25 mm layer thickness).

1H NMR, 13C NMR experiments were performed on Bruker AM-400 or DRX-600 NMR spectrometer at ambient temperature. The residual solvent protons (1H) or the solvent carbons (13C) were used as internal standards. 1H NMR data were presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). Chemical shifts (δ) were given in ppm with reference to solvent signals [1H NMR: CDCl3 (7.26), Acetone-*d6* (2.05); 13C NMR: CDCl3 (77.16), Acetone-*d6* (29.84, 206.26)]. The following abbreviations are used in reporting NMR data: s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplet; m, multiplet. HRMS (ESI) was taken on Agilent 6540 Q-TOF spectrometer. Optical rotations were recorded on Jasco P-2000 polarimeter Na-lamp, λ= 589 nm.

# **2. Additional optimization of reaction conditions**

## Screening of solvents



|  |  |  |  |
| --- | --- | --- | --- |
| entry | solvents | temp (℃) | yield*b*(%) |
| 1 | DCE | RT | 22% |
| 2 | DCE | 50 | 38% |
| 3 | DCM | reflux | <5% |
| 4 | THF | 50 | <5% |
| 5 | MeNO2 | 50 | 16% |
| 6 | Toluene | 50 | <5% |
| **7** | **MeCN** | **50** | **56%** |

*a*Reactions were performed with **1** (0.25 mmol), **2** (0.3 mmol), TEMPO (0.05 mmol) and NFSI (0.75 mmol) in solvent (1.0 mL) for 3 h under argon atmosphere. *b*Isolated yields by silica gel column chromatography.

## Screening of various bases for formation of 2-amino-2-deoxyglycoside **3**



|  |  |  |
| --- | --- | --- |
| entry | bases | yield*b*(%) |
| 1 | Na2CO3 | 53% |
| 2 | K2CO3 | 50% |
| **3** | **NaHCO3** | **57%** |
| 4 | KHCO3 | 46% |
| **5** | **Na2HPO4** | **58%** |
| 6 | K2HPO4 | 49% |
| 7 | Na3PO4 | 42% |
| 8 | K3PO4 | 43% |
| 9 | Pyridine | 35% |
| 10 | Et3N | 12% |

*a*Reactions were performed with **1** (0.25 mmol), **2** (0.3 mmol), TEMPO (0.05 mmol), NFSI (0.75 mmol) and base (0.3 mmol) in MeCN (1.0 mL) at 50℃ for 3 h under argon atmosphere. *b*Isolated yields by silica gel column chromatography.

## Screening of amounts of NFSI and TEMPO



|  |  |  |  |
| --- | --- | --- | --- |
| entry | NFSI | TEMPO | yield*b*(%) |
| 1 | 3.0 eq | 0.2 eq | 58% |
| 2 | 2.0 eq | 0.2 eq | 67% |
| **3** | **1.2 eq** | **0.2 eq** | **76%** |
| **4*c*** | **1.2 eq** | **0.2 eq** | **75%** |
| 5*c* | 1.2 eq | 0.3 eq | 62% |
| 6*c* | 1.2 eq | 0.1 eq | 72% |

*a*Reactions were performed with **1** (0.25 mmol), **2** (0.3 mmol), TEMPO, NFSI and NaH2PO4 (0.3 mmol) in MeCN (1.0 mL) at 50℃ for 3 h under argon atmosphere. *b*Isolated yields by silica gel column chromatography. *c*Reactions were performed without Na2HPO4.

## Screening of temperatures



|  |  |  |
| --- | --- | --- |
| entry | temp. (℃) | yield*b*(%) |
| 1 | 25 | 66% |
| 2 | 40 | 71% |
| **3** | **50** | **75%** |
| 4 | 60 | 70% |

*a*Reactions were performed with **1** (0.25 mmol), **2** (0.3 mmol), TEMPO (0.05 mmol) and NFSI (0.3 mmol) in MeCN (1.0 mL) for 3 h under argon atmosphere. *b*Isolated yields by silica gel column chromatography.

# **3. Experimental details**

## a) List of glycal donors



## b) List of glycosyl acceptors



## c) Preparation of glycal donors and glycosyl acceptors

**2**, **G2**, **G6**, **S1**, **S2**, **S3** and **S8** are commercially available. Other glycosyl donors and acceptors were prepared according to the reported literature procedure. (**1**, **G1, G4, G5, G7, G8)**[1](**S4, S5**)[2] **(S6, S7**)[3] **G3**[4]

## General amidoglycosylation procedure

To an oven-dried 15 mL reaction tube equipped with a stir bar in the glove box, 0.3 mmol NFSI, 0.3 mmol glycosyl acceptor and 0.05 mmol TEMPO were added. Then dry MeCN (500 µL) was added to dissolve the reactants and reagents. The reaction tube was sealed and moved out of the glove box. Glycal donor (0.25 mmol) was dissolved in dry MeCN (500 µL) and added to the above reaction mixture at a constant speed by a syringe over 2 h at 50℃. Then the reaction was stirred for additional 1 hour at 50℃ until glycal donorwas completely consumed (monitored by TLC)**.** Thereaction solution was concentrated *in vacuum* to give the residue, which was subjected to flash chromatographic column to afford the corresponding amidoglycosylation products.

## Gram scale experiment



To an oven dried 50 mL round-bottom flask with a stir-bar in the glovebox, NFSI (6 mmol, 1.89 g), glycosyl acceptor **2** (6 mmol, 1.56 g) and TEMPO (1 mmol, 156 mg) was dissolved in dry MeCN (15 mL). The flask was sealed and moved out of the glove box. Glycal donor **1** (5 mmol, 2.08 g) was dissolved in dry MeCN (5 mL) and was added to the mixture at a constant speed by a syringe over 2 h at 50℃. Then the reaction was stirred for additional 3 hours. Then the reaction solution was concentrated *in* *vacuum* to give fuscous residue, which was purified by flash chromatography on silica gel (Petroleum ether/acetone 80/10 to 60/10 as eluent, to afford the amidoglycosylation product **3** (3.11 g, 64% yield).

## Conversion of disulfonyl group to Ac group



Disaccharide **3** (110 mg, 0.11 mmol) was dried by azeotropic distillation with anhydrous toluene (3 × 5 mL), transferred to a one-piece reflux apparatus with the aid of 5 mL of anhydrous THF, and concentrated in *vacuum*. The vessel was charged with fresh THF (5 mL) and DMPU (1.64 mL), degassed (three freeze-pump-thaw cycles), and placed under argon. SmI2 (2.26 mmol, 23 mL of a 0.1 M solution in THF) was added via syringe and the solution was refluxed for 18 h until all disaccharide **3** was consumed (as judged by the solution color and TLC) [5]. Then the reaction flask was moved to room temperature and Ac2O (34 mg, 0.57 mmol, 32 µL) was added to the reaction. The mixture was stirred for 1 h. The solution was concentrated in *vacuum*, dissolved in 20 mL of EtOAc, washed with saturated NaHCO3 (2 × 50 mL), dried over Na2SO4, and concentrated in *vacuum* to give fuscous residue, which was purified by flash chromatography on silica gel (Petroleum ether/acetone 40/10 as eluent) to afford 2-acetylamino-2-deoxyglycoside **20** as a colorless oil (64 mg, 77% yield). (*c* 0.8, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.37 – 7.22 (m, 13H), 7.19 (d, *J* = 7.1 Hz, 2H), 5.55 (d, *J* = 8.1 Hz, 1H), 5.50 (d, *J* = 4.9 Hz, 1H), 4.85 – 4.75 (m, 2H), 4.73 – 4.65 (m, 2H), 4.64 – 4.50 (m, 4H), 4.33 – 4.26 (m, 1H), 4.16 (d, *J* = 7.9 Hz, 1H), 4.02 – 3.91 (m, 3H), 3.79 – 3.60 (m, 5H), 3.54 (d, *J* = 9.1 Hz, 1H), 1.89 (s, 3H), 1.51 (s, 3H), 1.42 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 170.65, 138.65, 138.37, 138.29, 128.54, 128.48, 128.19, 127.99, 127.91, 127.86, 127.81, 127.69, 109.47, 108.79, 101.31, 96.42, 81.38, 78.59, 75.10, 74.75, 74.63, 73.61, 71.33, 70.80, 70.57, 69.11, 68.95, 67.98, 56.30, 26.24, 26.12, 25.16, 24.50, 23.73. HRMS (ESI) calcd. for C41H51N O11Na [M + Na]+: 756.3354, found 756.3354. The NMR data was according with the reported literature.[6]

# **4. Characterization of new compounds**

**Compound 3:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 80/10 to 60/10 as the eluent), **3** was obtained as a colorless oil (182 mg, 75% yield, β/α > 20/1). (*c* 0.9, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.50 (dt, *J* = 35.4, 7.6 Hz, 4H), 7.33 (dt, *J* = 15.5, 6.4 Hz, 10H), 7.22 – 7.15 (m, 5H), 7.07 (s, 2H), 5.50 (d, *J* = 4.3 Hz, 1H), 4.93 (d, *J* = 7.8 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.70 (d, *J* = 10.7 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.54 (dd, *J* = 18.2, 11.6 Hz, 5H), 4.47 – 4.38 (m, 1H), 4.28 (d, *J* = 4.3 Hz, 1H), 4.16 (d, *J* = 7.9 Hz, 1H), 3.91 (d, *J* = 6.3 Hz, 2H), 3.79 – 3.70 (m, 3H), 3.51 (d, *J* = 9.5 Hz, 1H), 3.15 – 3.10 (m, H), 1.54 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 141.26, 140.26, 138.81, 138.26, 138.01, 133.89, 133.38, 129.25, 129.20, 128.99, 128.66, 128.53, 128.32, 128.18, 128.04, 127.94, 127.30, 109.22, 108.89, 99.80, 96.53, 80.79, 75.22, 74.91, 74.06, 73.87, 71.14, 70.82, 68.60, 67.46, 66.89, 65.71, 26.33, 25.30, 24.83. HRMS (ESI) calcd. for C51H57NO14S2Na [M + Na]+: 994.3113, found 994.3110.

**Compound 4:** Following the General Glycosylation Procedure: After purification by flash chromatographic column (petroleum ether/acetone 50/10 to 30/10 as the eluent), **4** was obtained as a colorless oil (126 mg, 68% yield, β/α > 20/1). (*c* 0.9, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.10 (d, *J* = 7.5 Hz, 2H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.52 (m, 4H), 7.51 – 7.45 (m, 2H), 5.51 (d, *J* = 5.0 Hz, 1H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.55 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.34 – 4.24 (m, 2H), 4.18 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.99 – 3.89 (m, 3H), 3.66 – 3.57 (m, 2H), 3.49 (s, 3H), 3.42 (s, 3H), 3.35 – 3.24 (m, 3H), 3.12 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H), 1.32 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 141.77, 139.99, 133.55, 133.36, 129.68, 129.08, 128.55, 128.36, 109.18, 108.82, 99.47, 96.38, 82.16, 82.12, 74.76, 71.22, 70.88, 70.78, 70.74, 67.28, 66.94, 65.67, 60.18, 59.67, 59.52, 26.21, 25.19, 24.74. HRMS (ESI) calcd. for C33H45NO14S2Na [M + Na]+: 766.2174, found 766.2173.

 

**Compound 5:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 80/10 as the eluent), **5** was obtained as a colorless oil (154 mg, 70% yield, β/α > 20/1). (*c* 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.13 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.40 – 7.39 (m, 2H), 7.35 – 7.34 (m, 3H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.22 – 7.21 (m, 3H), 7.14 – 7.12 (m, 2H), 5.53 (s, 1H), 5.52 (m, 1H), 5.04 (d, *J* = 8.1 Hz, 1H), 4.85 (d, *J* = 11.7 Hz, 1H), 4.58 (dd, *J* = 17.5, 9.2 Hz, 2H), 4.45 (t, *J* = 9.5 Hz, 1H), 4.35 (dd, *J* = 10.4, 4.9 Hz, 1H), 4.31 – 4.26 (m, 1H), 4.16 (t, *J* = 9.6 Hz, 2H), 3.91 (t, *J* = 5.9 Hz, 1H), 3.84 – 3.75 (m, 3H), 3.50 (td, *J* = 9.7, 5.0 Hz, 1H), 3.13 (dd, *J* = 10.3, 6.0 Hz, 1H), 1.56 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H). 13C NMR(100 MHz, CDCl3) δ 141.19, 140.17, 138.40, 137.07, 133.66, 133.24, 129.31, 129.01, 128.52, 128.29, 128.27, 128.00, 127.24, 127.08, 125.98, 109.14, 108.67, 101.16, 100.97, 96.32, 83.74, 73.34, 70.93, 70.65, 70.56, 68.71, 68.30, 66.53, 65.89, 65.35, 26.10, 25.04, 24.69. HRMS (ESI) calcd. for C44H49NO14S2Na [M + Na]+: 902.2487, found 902.2491.

**Compound 6:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 80/10 as the eluent), **6** was obtained as a colorless oil (147 mg, 71% yield, β only). (*c* 0.3, CHCl3); 1H NMR (400 MHz, *d*6-acetone) δ 8.19 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.60 (dd, *J* = 17.1, 7.8 Hz, 3H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.32 – 7.20 (m, 5H), 5.50 (d, *J* = 5.1 Hz, 1H), 4.94 (d, *J* = 8.3 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.60 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.52 (dd, *J* = 10.6, 8.3 Hz, 1H), 4.34 (dd, *J* = 5.1, 2.3 Hz, 1H), 4.28 (dd, *J* = 10.6, 8.4 Hz, 1H), 4.19 (dd, *J* = 6.9, 5.2 Hz, 2H), 3.91 (t, *J* = 5.5 Hz, 1H), 3.82 (tdd, *J* = 16.1, 10.1, 6.2 Hz, 4H), 3.33 (td, *J* = 9.9, 5.7 Hz, 1H), 2.97 (dd, *J* = 9.7, 5.6 Hz, 1H), 1.56 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H), 1.32 (s, 6H). 13C NMR (100 MHz, *d*6-acetone) δ 141.21, 141.00, 139.19, 134.03, 133.34, 129.30, 128.94, 128.62, 128.45, 127.86, 127.31, 126.93, 108.53, 108.22, 100.73, 99.08, 96.34, 77.29, 76.32, 72.69, 70.70, 70.59, 70.51, 68.09, 66.76, 66.40, 65.07, 61.70, 25.58, 25.55, 24.33, 23.87, 18.46. HRMS (ESI) calcd. for C40H49NO14S2Na [M + Na]+: 854.2487, found 854.2487.

**Compound 7:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/EtOAc 20/10 as the eluent), **7** was obtained as a white powder (76 mg, 37% yield, β only).(*c* 1.0, CHCl3); 1H NMR(400 MHz, CDCl3) δ 8.04 (d, *J* = 7.7 Hz, 4H), 7.62 (dd, *J* = 15.0, 7.5 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 4H), 5.51 (t, *J* = 4.2 Hz, 2H), 5.31 (dd, *J* = 11.6, 3.1 Hz, 1H), 5.21 (d, *J* = 7.9 Hz, 1H), 4.80 (dd, *J* = 11.5, 7.9 Hz, 1H), 4.54 (dd, *J* = 7.8, 2.3 Hz, 1H), 4.29 (dd, *J* = 4.9, 2.4 Hz, 1H), 4.16 - 4.05 (m, 2H), 4.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.00 – 3.90 (m, 2H), 3.86 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.52 (dd, *J* = 10.8, 5.6 Hz, 1H), 2.16 (s, 3H), 2.05 (s, 3H), 1.57 (s, 3H), 1.53 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 170.52, 170.27, 169.84, 140.49, 139.93, 133.98, 133.68, 129.35, 129.09, 128.90, 128.71, 109.30, 108.87, 101.55, 96.38, 70.94, 70.78, 70.73, 70.65, 69.28, 68.57, 67.66, 66.48, 61.31, 61.04, 26.20, 26.16, 25.12, 24.92, 20.81, 20.75, 20.32. HRMS (ESI) calcd. for C38H45NO17S2Na [M + Na]+: 850.2021, found 850.2024.



**Compound 8:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 50/10 to 30/10 as the eluent), **8** was obtained as a colorless oil (123 mg, 66% yield, β/α > 20/1). (*c* 0.7, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.14 (d, *J* = 7.0 Hz, 2H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.57 (dd, *J* = 15.1, 7.6 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.54 (d, *J* = 4.9 Hz, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.65 – 4.51 (m, 2H), 4.28 (d, *J* = 7.1 Hz, 1H), 4.19 (d, *J* = 8.2 Hz, 1H), 4.00 (q, *J* = 5.5 Hz, 2H), 3.85 (d, *J* = 8.5 Hz, 1H), 3.66 (s, 1H), 3.63 – 3.48 (m, 4H), 3.46 (s, 3H), 3.38 (s, 3H), 2.95 (s, 3H), 1.48 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 142.35, 139.62, 133.16, 133.12, 129.62, 128.98, 128.02, 127.95, 109.04, 108.78, 99.60, 96.27, 80.22, 73.82, 72.92, 71.22, 70.66, 70.39, 67.29, 66.96, 62.80, 60.93, 59.26, 56.25, 26.10, 26.09, 25.12, 24.58. HRMS (ESI) calcd. for C33H45NO14S2Na [M + Na]+: 766.2174, found 766.2173.

**Compound 9:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 80/10 to 60/10 as the eluent), **9** was obtained as a colorless oil (199 mg, 82% yield, β only). (*c* 0.9, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.47 (dt, *J* = 15.5, 7.5 Hz, 4H), 7.36 – 7.31 (m, 5H), 7.29 – 7.24 (m, 8H), 7.19 – 7.08 (m, 4H), 5.52 (d, *J* = 4.9 Hz, 1H), 5.02 (d, *J* = 7.9 Hz, 1H), 4.85 (dd, *J* = 10.9, 8.0 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.54 (dd, *J* = 7.9, 2.2 Hz, 1H), 4.45 (dt, *J* = 17.2, 11.5 Hz, 4H), 4.29 – 4.21 (m, 2H), 4.15 (dd, *J* = 14.9, 9.6 Hz, 2H), 4.03 – 3.94 (m, 3H), 3.69 – 3.53 (m, 3H), 3.41 (dd, *J* = 11.9, 7.9 Hz, 1H), 1.48 (s, 3H), 1.42 (s, 3H), 1.30 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 142.21, 139.44, 138.58, 137.89, 137.36, 133.16, 133.05, 129.25, 128.97, 128.46, 128.26, 128.23, 128.20, 128.09, 127.99, 127.86, 127.83, 127.57, 127.52, 109.02, 108.77, 99.81, 96.26, 79.40, 74.41, 73.48, 73.44, 73.06, 71.67, 71.18, 70.69, 70.63, 68.22, 67.39, 66.90, 62.79, 26.10, 25.14, 24.57. HRMS (ESI) calcd. for C51H57NO14S2Na [M + Na]+: 994.3113, found 994.3111.

**Compound 10:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 50/10 to 30/10 as the eluent), **10** was obtained as a colorless oil (139 mg, 78% yield, β/α > 20/1). (*c* 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.16 (d, *J* = 7.8 Hz, 2H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.65 – 7.45 (m, 6H), 5.46 (d, *J* = 4.9 Hz, 1H), 4.96 (d, *J* = 8.1 Hz, 1H), 4.46 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.30 (dd, *J* = 10.8, 8.1 Hz, 1H), 4.23 (dd, *J* = 4.9, 2.1 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.82 (dd, *J* = 10.7, 8.3 Hz, 2H), 3.68 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.50 (s, 3H), 3.45 – 3.39 (m, 1H), 3.33 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.03 (s, 3H), 2.88 – 2.80 (m, 1H), 1.52 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H), 1.29 (t, *J* = 3.0 Hz, 6H). 13C NMR (100 MHz, CDCl3) δ 141.58, 140.07, 133.55, 133.40, 129.60, 128.82, 128.81, 128.15, 108.93, 108.47, 99.70, 96.05, 88.12, 81.25, 71.04, 70.33, 70.23, 67.08, 66.04, 65.94, 60.38, 59.21, 26.34, 26.09, 24.97, 24.34, 17.67. HRMS (ESI) calcd. for C32H43NO13S2Na [M + Na]+: 736.2068, found 736.2065.

**Compound 11:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 80/10 to 60/10 as the eluent), **11** was obtained as a colorless oil (168 mg, 78% yield, β/α > 20/1). (*c* 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.12 (d, *J* = 7.9 Hz, 2H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (q, *J* = 7.5 Hz, 3H), 7.37 – 7.27 (m, 6H), 7.25 – 7.13 (m, 6H), 5.46 (d, *J* = 4.9 Hz, 1H), 4.97 (d, *J* = 8.1 Hz, 1H), 4.73 (t, *J* = 10.2 Hz, 2H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.53 (dd, *J* = 10.7, 8.1 Hz, 1H), 4.45 (dd, *J* = 8.0, 1.8 Hz, 1H), 4.31-4.26 (m, 3H), 3.92 (d, *J* = 8.3 Hz, 1H), 3.85 – 3.75 (m, 1H), 3.64 (dd, *J* = 9.8, 5.5 Hz, 1H), 3.48 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.41 – 3.20 (m, 2H), 1.54 (s, 3H), 1.43 (s, 3H), 1.34-1.31 (m, 9H). 13C NMR (100 MHz, CDCl3) δ 141.03, 140.10, 138.49, 137.75, 133.67, 133.37, 129.29, 129.08, 128.77, 128.49, 128.17, 128.06, 127.92, 127.84, 127.06, 127.04, 108.88, 108.45, 100.06, 96.04, 86.22, 79.95, 75.00, 73.39, 71.20, 71.06, 70.31, 70.12, 67.24, 66.01, 65.90, 26.39, 26.11, 24.96, 24.36, 17.94. HRMS (ESI) calcd. for C44H51NO13S2Na [M + Na]+: 888.2694, found 888.2696.

**Compound 12:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 60/10 as the eluent), **12** was obtained as a colorless oil (190 mg, 83% yield, β only). (*c* 0.6, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 3H), 7.30 – 7.25 (m, 4H), 7.18 (dt, *J* = 12.2, 7.5 Hz, 11H), 7.06 – 6.99 (m, 2H), 4.94 (d, *J* = 8.1 Hz, 1H), 4.80 (s, 1H), 4.67 (dd, *J* = 19.5, 11.1 Hz, 2H), 4.59 – 4.52 (m, 2H), 4.49 (d, *J* = 2.9 Hz, 1H), 4.46 (s, 1H), 4.40 (dd, *J* = 18.5, 8.7 Hz, 2H), 4.29 (dd, *J* = 10.5, 8.5 Hz, 1H), 3.80 (dd, *J* = 9.2, 5.0 Hz, 1H), 3.70-3.66 (m, 3H), 3.52 (t, *J* = 9.5 Hz, 1H), 3.45 (d, *J* = 9.8 Hz, 1H), 3.16 (s, 3H), 3.06 (dd, *J* = 9.7, 5.0 Hz, 1H), 1.41 (s, 3H), 1.22 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 140.74, 139.97, 138.48, 137.96, 137.77, 133.83, 133.37, 129.14, 129.12, 128.83, 128.46, 128.38, 128.12, 127.86, 127.83, 127.78, 127.75, 127.15, 112.11, 109.52, 99.43, 85.05, 84.23, 82.15, 80.48, 80.46, 74.95, 74.72, 73.81, 73.59, 69.01, 68.57, 65.55, 54.97, 26.50, 25.01. HRMS (ESI) calcd. for C48H53NO13S2Na [M + Na]+: 938.2851, found 938.2854.

**Compound 13:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 80/10 as the eluent), **13** was obtained as a colorless oil (200 mg, 68% yield, β/α > 20/1). (*c* 0.5, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.27 (m, 20H), 7.26 – 7.17 (m, 10H), 7.10 (dd, *J* = 8.9, 6.6 Hz, 4H), 7.02 (d, *J* = 3.1 Hz, 2H), 4.99 (d, *J* = 8.3 Hz, 1H), 4.97 (d, *J* = 12.6 Hz, 1H), 4.79 (dd, *J* = 11.6, 3.3 Hz, 2H), 4.75 – 4.57 (m, 5H), 4.55 – 4.47 (m, 5H), 4.38 – 4.30 (m, 1H), 4.18 (d, *J* = 11.8 Hz, 1H), 4.00 – 3.92 (m, 2H), 3.73 (ddd, *J* = 21.2, 17.3, 9.0 Hz, 4H), 3.52 – 3.43 (m, 2H), 3.29 (s, 3H), 3.27 – 3.21 (m, 1H), 3.16 (t, *J* = 9.5 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 141.53, 139.94, 138.87, 138.57, 138.51, 138.35, 138.10, 137.77, 133.39, 129.21, 128.87, 128.76, 128.51, 128.45, 128.40, 128.34, 128.22, 128.17, 128.05, 128.00, 127.97, 127.84, 127.80, 127.75, 127.69, 127.62, 127.58, 126.97, 126.84, 99.90, 97.50, 82.14, 80.60, 80.56, 79.68, 78.45, 75.78, 75.00, 74.65, 74.59, 73.70, 73.50, 73.14, 69.73, 68.78, 68.39, 65.97, 55.34. HRMS (ESI) calcd for C67H69NO14S2Na [M + Na]+: 1198.4052, found 1198.4050.

**Compound 14:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 40/10 as the eluent), **14** was obtained as a colorless oil (202 mg, 66% yield, β only). (*c* 0.9, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.15 (d, *J* = 7.9 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.94 (t, *J* = 8.2 Hz, 4H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.52 (dd, *J* = 16.0, 8.4 Hz, 4H), 7.45 – 7.26 (m, 11H), 7.23 – 7.21 (m, *J* = 7.3, 3.4 Hz, 8H), 7.11 – 7.07 (m, 4H), 6.99 – 6.96 (m, 2H), 6.14 (t, *J* = 9.8 Hz, 1H), 5.27 (t, *J* = 9.9 Hz, 1H), 5.21 (dd, *J* = 10.2, 3.5 Hz, 1H), 5.07 (d, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 7.4 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.63 (d, *J* = 10.6 Hz, 1H), 4.54 – 4.43 (m, 4H), 4.36 (t, *J* = 10.9 Hz, 2H), 4.26 (t, *J* = 9.2 Hz, 1H), 3.82 (d, *J* = 10.3 Hz, 1H), 3.69 – 3.62 (m, 2H), 3.58 (d, *J* = 10.2 Hz, 1H), 3.45 (d, *J* = 9.3 Hz, 1H), 3.36 (s, 3H), 3.34 – 3.28 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 166.00, 165.72, 165.62, 141.52, 139.74, 138.55, 137.92, 137.72, 133.64, 133.46, 133.39, 133.27, 133.07, 129.96, 129.88, 129.65, 129.31, 129.20, 129.12, 128.92, 128.87, 128.47, 128.45, 128.41, 128.36, 128.29, 128.11, 128.00, 127.81, 127.79, 127.69, 126.97, 126.90, 99.29, 96.23, 80.85, 80.29, 74.82, 74.67, 73.84, 73.63, 72.26, 70.54, 70.11, 68.78, 68.37, 67.75, 66.07, 55.72. HRMS (ESI) calcd. for C67H63NO17S2Na [M + Na]+: 1240.3430, found 1240.3431.

**Compound 15:** Following the general amidoglycosylation procedure, but 0.3 mmol Na2HPO4 was added as additive and dry MeCN/DCE (1/1) was selected as solvent. After purification by flash chromatographic column (petroleum ether/acetone 80/10 as the eluent), **15** was obtained as a colorless oil (143 mg, 53% yield, β only).(*c* 0.9, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.16 (d, *J* = 7.7 Hz, 2H), 8.05 (t, *J* = 9.4 Hz, 2H), 7.53 – 7.40 (m, 5H), 7.38 – 7.26 (m, 15H), 7.22 – 7.20 (m, 7H), 7.16 – 7.13 (m, 4H), 5.56 (d, *J* = 7.8 Hz, 1H), 5.40 (s, 1H), 4.94 (d, *J* = 12.5 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.68 (d, *J* = 10.7 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.52 (dd, *J* = 10.4, 2.6 Hz, 1H), 4.48 – 4.41 (m, 3H), 4.41 – 4.32 (m, 2H), 4.25 (d, *J* = 3.7 Hz, 1H), 4.16 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.91 (t, *J* = 9.3 Hz, 1H), 3.80 (t, *J* = 9.5 Hz, 1H), 3.67 – 3.51 (m, 4H), 3.45 – 3.41 (m, 1H), 3.31 – 3.23 (m, 2H), 3.22 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 140.88, 140.39, 139.03, 138.56, 138.26, 137.86, 137.16, 133.52, 133.20, 129.62, 129.15, 128.81, 128.71, 128.49, 128.45, 128.32, 128.28, 128.22, 128.12, 128.05, 127.96, 127.88, 127.73, 127.49, 127.00, 126.86, 126.03, 101.13, 99.03, 98.50, 80.54, 80.13, 80.07, 78.95, 74.52, 74.40, 74.34, 74.05, 73.42, 73.10, 69.03, 68.26, 66.85, 62.12, 55.13. HRMS (ESI) calcd. for C60H61NO14 S2Na [M + Na]+: 1106.3426, found 1106.3426.

**Compound 16:** Following the general amidoglycosylation procedure, but 0.3 mmol Na2HPO4 was added as additive and dry MeCN/DCE (1/1) was selected as solvent. After purification by flash chromatographic column (petroleum ether/acetone 80/10 as the eluent), **16** was obtained as a colorless oil (173 mg, 64% yield, β only). (*c* 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.27 – 8.24 (m, 4H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.42 (m, 5H), 7.35 – 7.34 (m, 7H), 7.31 – 7.17 (m, 11H), 7.14 – 7.10 (m, 5H), 7.03 (d, *J* = 7.3 Hz, 2H), 5.53 (s, 1H), 5.47 (d, *J* = 7.8 Hz, 1H), 4.94 (d, *J* = 3.4 Hz, 1H), 4.76 (dd, *J* = 10.5, 8.1 Hz, 1H), 4.65 – 4.52 (m, 5H), 4.34 (dd, *J* = 10.1, 4.7 Hz, 1H), 4.29 (d, *J* = 11.2 Hz, 1H), 4.21 – 4.13 (m, 1H), 4.00 (d, *J* = 11.1 Hz, 1H), 3.94 – 3.81 (m, 3H), 3.75 (dd, *J* = 14.7, 11.0 Hz, 4H), 3.61 (t, *J* = 9.2 Hz, 1H), 3.56 – 3.49 (m, 2H), 3.54 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 141.16, 140.48, 139.09, 138.41, 137.97, 137.75, 137.37, 133.58, 133.46, 130.54, 129.23, 128.88, 128.69, 128.48, 128.20, 128.19, 127.90, 127.80, 127.76, 127.67, 127.07, 126.86, 126.54, 126.06, 101.36, 101.27, 82.71, 79.90, 78.55, 77.73, 77.64, 74.48, 74.30, 74.18, 73.46, 71.17, 69.26, 68.55, 66.01, 62.25, 55.71.HRMS (ESI) calcd. for C60H61NO14 S2Na [M + Na]+: 1106.3426, found 1106.3427.

**Compound 17:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 50/10 as the eluent), **17** was obtained as a colorless oil (165 mg, 71% yield, β/α > 20/1). (*c* 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.33 (m, 5H), 7.30 – 7.21 (m, 9H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.11 – 7.04 (m, 2H), 5.46 (d, *J* = 8.6 Hz, 1H), 4.81 (dd, *J* = 14.5, 9.9 Hz, 2H), 4.71 (d, *J* = 10.7 Hz, 1H), 4.66 – 4.48 (m, 5H), 4.46 – 4.38 (m, 1H), 4.28 – 4.18 (m, 1H), 4.05 (dd, *J* = 9.6, 3.8 Hz, 1H), 3.75 – 3.72 (m, 3H), 3.68 (s, 3H), 3.47 (d, *J* = 9.8 Hz, 1H), 3.12 (dd, *J* = 9.6, 3.2 Hz, 1H), 1.49 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 170.57, 155.74, 140.69, 140.27, 138.54, 137.95, 137.66, 133.93, 133.34, 129.08, 129.01, 128.73, 128.49, 128.45, 128.40, 128.18, 127.86, 127.78, 127.15, 126.98, 98.59, 80.44, 80.31, 79.81, 74.96, 74.81, 73.86, 73.64, 68.33, 68.06, 65.01, 53.66, 52.45, 28.46. HRMS (ESI) calcd. for C48H54NO13S2Na [M + Na]+: 953.2960, found 953.2960.

**Compound 18:** Following the general amidoglycosylation procedure: After purification by flash chromatographic column (petroleum ether/acetone 80/10 as the eluent), **18** was obtained as a colorless oil (150 mg, 63% yield, β/α > 20/1).(*c* 0.8, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.35 (m, 8H), 7.32 – 7.24 (m, 10H), 7.22 – 7.17 (dd, 5H), 7.11 – 7.05 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.03 (s, 2H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.71 (d, *J* = 10.8 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.55 – 4.39 (m, 5H), 3.85 – 3.75 (m, 2H), 3.72 (s, 2H), 3.52 (d, *J* = 9.8 Hz, 1H), 3.16 (dd, *J* = 15.9, 9.3 Hz, 1H), 2.50 – 2.34 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 157.35, 141.08, 140.03, 138.51, 138.00, 137.81, 137.19, 133.71, 133.25, 130.51, 129.92, 129.28, 129.07, 128.73, 128.59, 128.43, 128.19, 128.12, 127.93, 127.82, 127.70, 127.46, 127.10, 114.81, 99.86, 80.63, 80.53, 74.86, 74.68, 73.72, 73.55, 70.16, 70.04, 68.65, 65.98, 34.92. HRMS (ESI) calcd. for C54H53NO10S2Na [M + Na]+: 962.3003, found 962.3003.

**Compound 19:** Following the general amidoglycosylation procedure, but 0.3 mmol Na2HPO4 was added as additive and dry MeCN/DCE (1/1) was selected as solvent. After purification by flash chromatographic column (petroleum ether/acetone 80/10 as the eluent), **19** was obtained as a colorless oil (127 mg, 51% yield, β only). (*c* 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.16 (d, *J* = 7.8 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.38 – 7.27 (m, 13H), 7.24 – 7.14 (m, 6H), 5.17 (d, *J* = 8.0 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.67 (dd, *J* = 25.9, 11.5 Hz, 2H), 4.56 (d, *J* = 11.9 Hz, 2H), 4.53 – 4.45 (m, 1H), 4.29 (dd, *J* = 22.8, 10.0 Hz, 2H), 3.80 – 3.67 (m, 3H), 3.60 – 3.51 (m, 1H), 3.41 – 3.29 (m, 1H), 2.43 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.05 (dt, *J* = 12.7, 9.0 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.77 (t, *J* = 12.8 Hz, 3H), 1.62 – 1.60 (m, 3H), 1.55 – 1.43 (m, 2H), 1.25 – 1.10 (m, 6H), 0.89 – 0.82 (m, 5H), 0.76 – 0.68 (m, 4H), 0.66 – 0.55 (m, 1H).13C NMR (100 MHz, CDCl3) δ 221.31, 141.15, 140.29, 138.46, 138.11, 137.80, 133.63, 133.22, 129.69, 129.14, 128.61, 128.46, 128.39, 128.23, 128.06, 127.87, 127.80, 127.72, 127.66, 127.04, 126.88, 99.68, 80.64, 79.88, 79.06, 74.64, 74.44, 73.44, 72.80, 68.89, 66.36, 54.43, 51.43, 47.81, 44.74, 36.98, 35.87, 35.64, 35.05, 33.75, 31.60, 30.90, 29.34, 29.29, 28.30, 21.79, 20.49, 13.83, 12.38. HRMS (ESI) calcd. for C58H67NO10S2Na [M + Na]+: 1024.4099, found 1024.4102.

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# **6. Copies of 1H NMR and 13C NMR spectra**







































































