Diversified Synthesis and α-Selective Glycosylation of 3-Amino-2,3,6-trideoxy Sugars

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1. General information

All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates (Yantai Chemical Industry Research Institute). The spots on TLC were visualized by warming 10% H$_2$SO$_4$ (10% H$_2$SO$_4$ in ethanol) sprayed plates on a hot plate. Column chromatography was performed using silica gel (Qingdao Marine Chemical Inc., China). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz), and the $^1$H and $^{13}$C NMR chemical shifts were referenced to the solvent or solvent impurity peaks for CDCl$_3$ at $\delta_H$ 7.24 and $\delta_C$ 77.23, for acetone-$d_6$ at $\delta_H$ 2.05 and $\delta_C$ 29.84. Optical rotations were measured at 20 °C with a Rudolph Autopol IV automatic polarimeter using a quartz cell with 2 mL capacity and a 1 dm path length. Concentrations (c) are given in g/100 mL. High resolution mass spectra were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI).

Materials

Prior to running the glycosylation reactions, all reagents except Tf$_2$O and those with low boiling point (<180°C) were dried by repeated azeotropic removal of water using toluene and a rotary evaporator at 27 °C. Solvents for reactions were dried on an Innovative Technologies Pure Solv400 solvent purifier. Molecular sieves (4Å, powder < 50 µm) for reactions were flame dried immediately before use. Trifluoromethanesulfonic anhydride (Tf$_2$O) was purchased from Acros. Bis(trifluoroacetoxy)iodobenzene (PIFA), copper(I) tetrakis(acetonitrile) hexafluorophosphate (Cu(MeCN)$_4$PF$_6$), and all other commercial available chemicals were purchased from Adamas and used without further purification.
2. Improved synthesis of key intermediate 1 and 3a

A dried round bottom flask was deoxygenated for 5 min, t-BuOH (1.6 equiv, 37.4 mmol, 3.58 mL) was added, and then dry THF (15 mL) was added to the bottom at 0°C with rapid stirring. Chlorosulfonyl isocyanate (1.5 equiv, 35.1 mmol, 3.05 mL) was then added, and the solution was stirred for 4 h at 0°C. After this, compound 2 (3 g, 23.4 mmol, 1.0 equiv) dissolved in THF (30 mL) was slowly added to the round bottom flask. Finally, trimethylamine (1.7 equiv, 39.8 mmol, 5.53 mL) was added. The reaction mixture was stirred at rt for 3 h, then quenched by 0.5 mol/L NaHSO₄ solution, the mixture was extracted with EtOAc. The combined organic layer was washed with water, brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product S₁ was dissolved in toluene/CH₃CN (10:1, 234 mL, C = 0.1 mol/L) and p-toluenesulfonic acid monohydrate (0.1 equiv, 445 mg) was added. The reaction mixture was stirred at 80°C for 16 h and then diluted with water. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine and dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by silica gel chromatography (petroleum-EtOAc 2:1) to afford 1 (2.9 g, 65% yield over two steps) as yellow solid. Analytical data for 1 are consistent with our previous reported [1]. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 5.6 Hz, 1H, H₁), 5.89 (d, J = 5.6 Hz, 1H, H₂), 4.94 (d, J = 12.8 Hz, 1H, H₄), 4.36 (dq, J = 6.0, 12.8 Hz, 1H, H₅), 1.61 (d, J = 6.0 Hz, 3H, H₆).

(3aR, 4S)-4-methyl-3a,4-dihydropyrano [4, 3-d] [1, 2, 3] oxathiazole 2,2-dioxide (1)

NaOMe (171 mg, 3.17 mmol, 0.2 equiv) was added to the solution of 1 (3 g, 15.8 mmol, 1.0 equiv) in dry methanol (79 mL, C = 0.2 mol/L) at 0°C. The reaction mixture was stirred for 1 h at 0°C, then 3 h at room temperature. After completion, the mixture was evaporated and extracted with EtOAc. The combined organic layer was washed with water, brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by...
silica gel chromatography (petroleum-EtOAc 5: 1) to afford 3α (2.0 g, 58% yield) and 3β (0.84 g, 24% yield). Analytical data for 3a are consistent with our previous reported [1].

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.12 (d, $J = 4.8$ Hz, 1H, H-1), 4.71 (d, $J = 9.2$ Hz, 1H, H-4), 3.91 (dq, $J = 6.0, 9.2$ Hz, 1H, H-5), 3.34 (s, 3H, -OMe), 3.05 (d, $J = 14.0$ Hz, 1H, H-2a), 2.91 (dd, $J = 4.8, 14.0$ Hz, 1H, H-2b), 1.44 (d, $J = 6.0$ Hz, 3H, H-6).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.72 (d, $J = 9.2$ Hz, 1H, H-4), 4.58 (dd, $J = 2.4, 8.8$ Hz, 1H, H-1), 3.55 (s, 3H, -OMe), 3.49 (dq, $J = 6.0, 9.2$ Hz, 1H, H-5), 3.20 (dd, $J = 2.4, 14.0$ Hz, 1H, H-2a), 2.78 (dd, $J = 8.8, 14.0$ Hz, 1H, H-2b), 1.50 (d, $J = 6.0$ Hz, 3H, H-6).
3. Addition reactions at C3 position

![Chemical structure](image)

Addition reactions at C3 position

a Reaction was carried out with Grignard reagents (2.0-5.0 equiv) unless otherwise specified. b Reaction was carried out with NaBH₄ in 2.3 mmol scale; c Reaction was carried out with NaBD₄; d Reaction was carried out with MeMgBr in 3.2 mmol scale.

**General Procedure A:** To a solution of NaBH₄ (1.1 equiv) in methanol (c = 0.22 M), compound 3αa (1.0 equiv) in methanol (c = 0.2 M) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 5 min and then quenched with water. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with saturated aqueous NaHCO₃, brine and dried over NaSO₄. After evaporation of the solvent, the residue was purified by silica gel column chromatography to afford the cyclic sulfamidate product.

**General Procedure B:** In a typical experimental, a solution of compound 3αa (1.0 equiv) in dry DCM (c = 0.2 M) was cooled at 0°C, Grignard reagents (2.0-5.0 equiv)
were then added dropwise. The reaction was stirred at 0°C for 3 h and then quenched with saturated ammonium chloride aqueous solution. After extraction with EtOAc, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the desired product.

(3aR, 4S, 6R, 7aR)-6-methoxy-4-methylhexahydropyrano [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4a)

Prepared from 3aa (500.0 mg, 2.64 mmol) according to General Procedure A to give 4a (445.0 mg, 88% yield) as white solid. Rf = 0.25 (petroleum-EtOAc 3: 1). m.p. 70-72 °C. [α]D²⁰ -141.9 (c, 1.65 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 5.50 (d, J = 11.6 Hz, 1H, -NH), 4.78 (d, J = 3.6 Hz, 1H, H-1), 4.28 (dd, J = 5.2, 9.6 Hz, 1H, H-4) 4.08-4.14 (m, 1H, H-3), 4.02 (dq, J = 6.0, 9.6 Hz, 1H, H-5), 3.37 (s, 3H, -OCH₃), 2.23 (d, J = 15.6 Hz, 1H, H-2a), 2.05 (ddd, J = 3.6, 15.2 Hz, 1H, H-2b), 1.33 (d, J = 6.0 Hz, H-6). ¹³C NMR (100 MHz, CDCl₃) δ 97.3, 84.4, 61.3, 56.0, 52.7, 29.1, 18.0. HRMS calc. for C₇H₁₃NNaO₅S [M+Na]+: 246.0407, found: 246.0402.

(3aR,4S,6R,7aR)-6-methoxy-4-methylhexahydropyrano[4,3-d][1,2,3]oxathiazole 2,2-dioxide-7a-d (4a')

Prepared from 3aa (500.0 mg, 2.64 mmol) according to General Procedure A to give 4a' (445.0 mg, 88% yield) as white solid. Rf = 0.25 (petroleum-EtOAc 3: 1). m.p. 70-72 °C. [α]D²⁰ -141.9 (c, 1.65 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 5.50 (d, J = 11.6 Hz, 1H, -NH), 4.78 (d, J = 3.6 Hz, 1H, H-1), 4.28 (dd, J = 5.2, 9.6 Hz, 1H, H-4) 4.08-4.14 (m, 1H, H-3), 4.02 (dq, J = 6.0, 9.6 Hz, 1H, H-5), 3.37 (s, 3H, -OCH₃), 2.23 (d, J = 15.6 Hz, 1H, H-2a), 2.05 (ddd, J = 3.6, 15.2 Hz, 1H, H-2b), 1.33 (d, J = 6.0 Hz, H-6). ¹³C NMR (100 MHz, CDCl₃) δ 97.3, 84.4, 61.3, 56.0, 52.7, 29.1, 18.0. HRMS calc. for C₇H₁₃NNaO₅S [M+Na]+: 246.0407, found: 246.0402.

(3aR, 4S, 6R, 7aR)-6-methoxy-4-methylhexahydropyrano [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4b)

Prepared from 3aa (600mg, 3.17 mmol) with CH₃MgBr (3.0 equiv) according to General Procedure B to give 4b (572.5mg, 88% yield) as white solid. Analytical data for 4b has been reported in our previous work. ¹H NMR (400 MHz, CDCl₃) δ 5.83 (brs, 1H, -NH), 4.77 (dd, J = 0.8 Hz, 4.0 Hz 1H, H-1), 4.03-4.12 (m, 2H, H-5, H-4), 3.38 (s, 3H, -OCH₃), 2.20 (dd, J = 0.8, 15.2 Hz, 1H, H-2a), 1.82 (dd, J = 4.0, 15.2 Hz, 1H, H-2b), 1.50 (s, 3H, -CH₃ at C-3), 1.34 (d, J = 6.0 Hz, H-6).
(3aR, 4S, 6R, 7aR)-7a-ethyl-6-methoxy-4-methylhexahydropyran-3,3-dioxide (4c)

Prepared from 3α (20.0 mg, 0.10mmol) with CH$_3$CH$_2$MgBr (5.0 equiv) according to General Procedure B to give 4c (18.0 mg, 82% yield) as white solid. $R_f$ = 0.44 (petroleum-EtOAc 3: 1). m.p. 81-83°C. [$\alpha$]$_{D}$$^{20}$ = 112.7 (c, 2.57 in CHCl$_3$). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.68 (brs, 1H, -NH), 4.79 (d, $J$ = 4.0 Hz, 1H, -H-1), 4.12 (dq, $J$ = 6.0, 9.2 Hz, 1H, -H-5), 4.03 (d, $J$ = 9.2 Hz, 1H, -H-4), 3.38 (s, -OMe), 2.12-2.21 (m, 2H, -CH$_2$), 1.73 (dd, $J$ = 4.0, 15.2 Hz, 1H, H-2a), 1.44-1.53 (m, 1H, H-2b), 1.34 (d, $J$ = 6.0 Hz, 1H, H-6), 0.95 (t, 3H, -CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 97.5, 89.1, 63.1, 55.9, 33.7, 31.3, 18.2, 7.2. HRMS calc. for C$_9$H$_7$NNaO$_2$S [M+Na$^+$]: 274.0720, found: 274.0730.

(3aR, 4S, 6R, 7aR)-7a-allyl-6-methoxy-4-methylhexahydropyran-3,3-dioxide (4d)

Prepared from 3α (14.0 mg, 0.07 mmol) with allylMgBr (2.0 equiv) according to General Procedure B to give 4d (14.7 mg, 84% yield) as white solid. $R_f$ = 0.56 (petroleum-EtOAc 3: 1). m.p. 89-91°C. [$\alpha$]$_{D}$$^{20}$ = 131.0 (c, 0.73 in CHCl$_3$). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.68 (brs, 1H, -NH), 4.79 (d, $J$ = 4.0 Hz, 1H, -H-1), 4.06-4.16 (m, 2H, H-4, H-5), 3.37 (s, 3H, -OMe), 2.81 (dd, $J$ = 2.0, 14.0 Hz, 1H, -CH$_2$-), 2.30 (dd, $J$ = 8.4, 14.0 Hz, 1H, -CH$_2$-), 1.81 (dd, $J$ = 4.0, 15.2 Hz, 1H, H-2a), 1.35 (d, $J$ = 6.0 Hz, 1H, H-6). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.0, 121.0, 97.5, 88.1, 62.4, 61.9, 55.9, 42.5, 34.2, 18.2. HRMS calc. for C$_{10}$H$_{17}$NNaO$_2$S [M+Na$^+$]: 286.0720, found: 286.0730.

(3aR, 4S, 6R, 7aR)-7a-butyl-6-methoxy-4-methylhexahydropyran-3,3-dioxide (4e)

Prepared from 3α (21.0 mg, 0.095 mmol) with $n$-ButylMgBr (5.0 equiv) according to General Procedure B to give 4e (22.3 mg, 84% yield) as white solid. $R_f$ = 0.74 (petroleum-EtOAc 3: 1). m.p. 54-56 °C. [$\alpha$]$_{D}$$^{20}$ = 84.2 (c, 1.75 in CHCl$_3$). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.83 (brs, 1H, -NH), 4.78 (d, $J$ = 3.2 Hz, 1H, H-1), 4.11 (dq, $J$ = 6.0, 9.6 Hz, 1H, H-5), 4.02 (d, $J$ = 9.6 Hz, 1H, H-4), 3.37 (s, 3H, -OMe), 2.19 (d, $J$ = 15.2 Hz, H-2a), 2.09 (dd, $J$ = 9.6, 11.6 Hz, 1H), 1.76 (dd, $J$ = 4.0, 15.2 Hz, H-2b), 1.46-1.44 (m, 2H), 1.34 (d, $J$ = 6.0 Hz, 3H, H-6), 1.31-1.17 (m, 2H), 0.99 (t, $J$ = 7.2, 14.4 Hz, 3H, -CH$_2$CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 97.5, 89.2, 62.8, 62.0, 55.8, 38.2, 34.3, 24.9, 22.8, 18.2, 14.1. HRMS calc. for C$_{11}$H$_{21}$NNaO$_2$S [M+Na$^+$]: 302.1033, found: 302.1043.
(3aR, 4S, 6R, 7aR)-6-methoxy-4-methyl-7a-(3-phenylpropyl) hexahydropyran[4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4f)

Prepared from 3aa (15.5 mg, 0.07 mmol) with 3-phenylpropylMgBr (5.0 equiv) according to General Procedure B to give 4f (16.1 mg, 64% yield) as white solid. Rf = 0.50 (petroleum-EtOAc 3: 1). m.p. 106-108 °C. [α]D20 47.0 (c, 1.12 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.36-7.22 (m, 5H, -Ph), 5.77 (brs, 1H, -NH), 4.18 (dq, J = 6.4, 9.6 Hz, 1H, H-5), 3.43 (s, 3H, -OCH3), 2.79 (ddd, J = 5.6, 8.4, 14.0 Hz, 1H), 2.62 (ddd, J = 7.2, 8.0, 14.0 Hz, 1H), 2.27 (dd, J = 7.2, 13.6Hz, 1H, H-2a), 2.23 (dd, J = 5.6, 8.0 Hz, 1H), 2.87-2.70 (m, 1H), 1.87-1.60 (m, 1H), 1.77 (dd, J = 4.0, 15.2 Hz, 1H, H-2b), 1.40 (d, J = 6.4 Hz, 3H, H-6). 13C NMR (100 MHz, CDCl3) δ 141.81, 128.59, 128.59, 128.53, 128.53, 126.17, 97.39, 89.22, 62.19, 61.97, 55.85, 38.08, 35.75, 34.32, 24.65, 18.19. HRMS calc. for C16H13NNaO3S [M+Na]+: 364.1189, found: 364.1194.

(3aR, 4S, 6R, 7aS)-7a-isopropyl-6-methoxy-4-methylhexahydropyran [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4g)

Prepared from 3aa (14.0 mg, 0.06 mmol) with isoproylMgCl (4.0 equiv) according to General Procedure B to give 4g (8.3 mg, 50% yield) as white solid. Rf = 0.55 (petroleum-EtOAc 3: 1). m.p. 122-124 °C. [α]D20 72.5 (c, 1.39 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.36-7.22 (m, 5H, -Ph), 4.82 (d, J = 4.0 Hz, 1H, H-1), 4.26 (d, J = 9.2 Hz, 1H, H-4), 4.16 (dq, J = 6.0, 9.2 Hz, 1H, H-5), 3.38 (s, 3H, -OMe), 2.41 (dt, J = 6.8 Hz, 1H, -CH-), 1.94 (d, J = 15.2 Hz, 1H, H-2a), 1.80 (dd, J = 4.4, 15.2 Hz, 1H, H-2b), 1.36 (d, J = 6.0 Hz, 1H, H-6), 0.99 (d, J = 6.8 Hz, 3H, -CH3), 0.93 (d, J = 6.8 Hz, 3H, -CH3), 0.93 (d, J = 6.8 Hz, 3H, -CH3). 13C NMR (100 MHz, CDCl3) δ 97.6, 86.2, 66.5, 61.9, 55.9, 31.5, 28.0, 18.3, 17.3, 16.2. HRMS calc. for C10H19NNaO3S [M+Na]+: 288.0876, found: 288.0887.

(3aR, 4S, 6R, 7aS)-7a-cyclopropyl-6-methoxy-4-methylhexahydropyran [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4h)

Prepared from 3aa (13.6 mg, 0.06 mmol) with cyclopoylMgBr (3.0 equiv) according to General Procedure B to give 4h (7.7 mg, 60% yield) as colorless syrup. Rf = 0.47 (petroleum-EtOAc 3: 1). m.p. 70-72 °C. [α]D20 102.9 (c, 0.48 in CHCl3). 1H NMR (400MHz, CDCl3) δ 7.35-7.20 (m, 5H, -Ph), 4.78 (dd, J = 1.6, 4.0Hz, 1H, H-1), 4.17 (dq, J = 6.0, 9.6 Hz, 1H, H-5), 4.00 (d, J = 9.6 Hz, 1H, H-4), 3.38 (s, 1H, -OMe), 2.04 (dd, J = 1.6, 15.2 Hz, H-2a), 1.78 (dd, J = 4.0, 15.2 Hz, H-2b), 1.35 (d, J = 6.0 Hz, 1H, H-6), 1.16-1.23 (m, 1H), 1.09-1.16 (m, 2H), 0.49-0.54 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 97.4, 87.8, 62.8, 62.2, 55.8, 34.5, 19.7, 18.4, 1.8, 1.7. HRMS calc. for C10H17NNaO3S [M+Na]+: 286.0720, found: 286.0732.
(3aR, 4S, 6R, 7aS)-6-methoxy-4-methyl-7a-phenylhexahydropyranol [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4i)

Prepared from 3aa (19.0 mg, 0.07 mmol) with PhMgBr (4.0 equiv) according to General Procedure C to give 4i (16.7 mg, 65% yield) as white solid. Rf = 0.67 (petroleum-EtOAc 3: 1). m.p. 112-114 °C. [α]D20 -108.4 (c, 1.64 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.55-7.58 (m, 2H, -Ph), 7.38-7.42 (m, 2H, -Ph), 7.30-7.34 (m, 1H, -Ph), 6.22 (bs, 1H, -NH), 4.81 (d, J = 4.0 Hz, 1H, H-1), 4.69 (d, J = 9.2 Hz, 1H, H-4), 4.38 (dq, J = 6.0, 9.2 Hz, 1H, H-5), 3.45 (s, 3H, -OMe), 2.31 (dd, J = 15.6 Hz, 1H, H-2a), 2.07 (dd, J = 4.0, 15.6 Hz, 1H, H-2b), 1.46 (d, J = 6.0 Hz, 1H, H-6). 13C NMR (100 MHz, CDCl3) δ 140.4, 129.0, 128.6, 126.0, 97.3, 88.5, 66.3, 62.2, 56.0, 40.4, 18.3. HRMS calc. for C13H17NNaO5S [M+Na]+: 322.0720, found: 322.0729.

(3aR, 4S, 6R, 7aR)-7a-allyl-6-(2-Iodobenzyloxy)-4-methylhexahydropyranol [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4j)

Prepared from 3ga (30.0 mg, 0.07 mmol) with allylMgBr (2.0 equiv) according to General Procedure B to give 4j (23.0 mg, 70% yield) as colorless syrup. Rf = 0.50 (petroleum-EtOAc 3: 1). [α]D20 -130.5 (c, 0.95 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.84 (dd, J = 8.0, 0.8 Hz, 1H, -Ph), 7.34 (ddd, J = m, 2H, -Ph), 7.04 – 6.99 (m, 1H, -Ph), 5.83 – 5.74 (m, 1H, -CH- at allyl group), 5.73 (s, 1H, -NH), 5.23 (d, J = 10.4 Hz, 1H, =CH2), 5.18 (dd, J = 16.8, 1.2 Hz, 1H, =CH2), 5.03 (dd, J = 4.0, 1.2 Hz, 1H, H-1), 4.71 (d, J = 12.4 Hz, 1H, -PhCH), 4.53 (d, J = 12.4 Hz, 1H, -PhCH), 4.23 (dq, J = 9.2, 6.0 Hz, 1H, H-5), 4.09 (dd, J = 9.2, 3.2 Hz, 1H, H-4), 2.83 (dd, J = 14.4, 6.0 Hz, 1H, -CH2-), 2.31 (dd, J = 14.4, 8.4 Hz, 1H, -CH2-), 2.19 (dd, J = 15.6, 1.2 Hz, 1H, H-2a), 1.87 (dd, J = 15.6, 4.0 Hz, 1H, H-2b), 1.35 (d, J = 6.0 Hz, 3H, H-6). 13C NMR (100 MHz, CDCl3) δ 139.88, 138.88, 131.03, 130.28, 129.76, 128.75, 121.13, 99.02, 96.29, 88.06, 74.48, 62.68, 62.29, 42.62, 34.39, 18.24. HRMS calc. for C16H20INaO5S [M+Na]+: 488.0017, found: 487.9999.

(3aR, 4S, 6R, 7aR)-7a-ethyl-6-(1-Octadecanoloxy)-4-methylhexahydropyranol [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (4k)

Prepared from 3da (40.0 mg, 0.087 mmol) with CH3CH2MgBr (5.0 equiv) according to General Procedure B to give 4k (35.0 mg, 83% yield) as white solid. Rf = 0.45 (petroleum-EtOAc 3: 1). m.p. 85-87°C. [α]D20 -100.5 (c, 2.0 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 5.82 (s, 1H, -NH), 4.90 (d, J = 3.2 Hz, 1H, H-1), 4.14 (dq, J = 9.6, 6.4 Hz, 1H, H-5), 4.02 (d, J = 9.6 Hz, 1H, H-4), 3.65 (dt, J = 9.6, 6.4 Hz, 1H), 3.37 (dt, J = 9.6, 6.4 Hz, 1H), 2.23 – 2.12 (m, 2H, -CH2-), 1.71 (dd, J = 15.2, 4.0 Hz, 1H, H-2a), 1.48 (dd, J = 15.6, 7.2, 1.2 Hz, 1H, H-2b), 1.33 (d, J = 6.4 Hz, 3H, H-6), 1.25 (s, 32H), 0.95 (t, J = 7.2 Hz, 3H, -
CH$_3$), 0.85 (t, $J = 6.8$ Hz, 3H, -CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 96.28, 89.21, 68.76, 63.17, 62.22, 33.91, 32.15, 31.37, 29.92, 29.88, 29.86, 29.83, 29.70, 29.58, 29.51, 26.28, 22.91, 18.29, 14.34, 7.27. HRMS calc. for C$_{26}$H$_{51}$NNaO$_5$S [M+Na]$^+$: 512.3387, found: 512.3380.
4. **S$_n$2 reactions at C4 position**

$$\text{R = H } 4a \hspace{1cm} \text{R = Cbz } 5$$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Solvent</th>
<th>Base</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me,} \text{O,} \text{OMe} \text{NR} \text{O,} \text{O,} \text{OMe} \text{Me,} \text{O,} \text{OMe} $</td>
<td>DMF: H$_2$O (10:1)</td>
<td>H$_2$O</td>
<td>CbzCl, Et$_3$N (R = Cbz)</td>
</tr>
<tr>
<td>$\text{Me,} \text{O,} \text{OMe} \text{Me,} \text{O,} \text{OMe} \text{Me,} \text{O,} \text{OMe} $</td>
<td>CH$_3$CN</td>
<td>DIPEA</td>
<td>fac-Ir(mppy)$_3$, p-toluenethiol</td>
</tr>
<tr>
<td>$\text{Me,} \text{O,} \text{OMe} \text{Me,} \text{O,} \text{OMe} \text{Me,} \text{O,} \text{OMe} $</td>
<td></td>
<td></td>
<td>CH$_3$CN, 1 W blue LED</td>
</tr>
</tbody>
</table>

---

$^a$ DMF: H$_2$O (10:1) was used as solvent, $^b$ fac-Ir(mppy)$_3$(1.5% mol), DIPEA (2.0 equiv), p-toluenethiol (2.0 equiv), CH$_3$CN, 1 W blue LED, 4 h. \[2\]

### 4.1 Preparation of compound 5

Benzyl (3aR, 4S, 6R, 7aR)-6-methoxy-4-methyltetrahydropyrano [4, 3-d] [1, 2, 3] oxathiazole-1(4H)-carboxylate 2, 2-dioxide (5)

To a solution of compound 4a (200.0 mg, 0.86 mmol, 1.0 equiv) in dry DCM (1.72 mL, c = 0.5 M) was added CbzCl (0.15 mL, 1.03 mmol, 1.2 equiv) dropwise at 0°C, followed by Et$_3$N (0.60 mL, 4.3 mmol, 5.0 equiv). The resulting mixture was stirred at room temperature for 1 h, then quenched with saturated aqueous NaHCO$_3$. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine, dried over NaSO$_4$. After concentration at reduced pressure, the residue was purified by silica gel column chromatography (petroleum-EtOAc 5:1) to afford 5 (290 mg, 90% yield) as white solid. $R_f = 0.54$ (petroleum-EtOAc 3:1). m.p. 83-85 °C. [$\alpha$]$_{D}^{20}$-91.2 (c, 1.14 in CHCl$_3$). $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 7.31-7.39 (m, 5H, -Ph), 5.30 (dd, $J = 12.4$ Hz, 2H, -CH$_2$-Ph), 4.72 (dd, $J = 6.4$, 8.0 Hz, 1H, H-1), 4.53 (t, $J = 7.2$ Hz, 1H, H-4), 4.27 (ddd, $J = 4.8$, 6.8, 11.6 Hz, 1H, H-3), 4.08(dq, $J = 6.4$, 7.2 Hz, 1H, H-2).
H-5), 3.36 (s, 3H, -OMe), 2.51 (dt, J = 5.2, 14.0 Hz, 1H, H-2a), 1.93 (ddd, J = 8.0, 12.5, 14.0 Hz, 1H, H-2b), 1.37(d, J = 6.4 Hz, 3H, H-6). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.9, 134.5, 128.9, 128.9, 128.9, 128.1, 97.6, 80.0, 69.7, 64.4, 55.5, 53.5, 29.4, 19.0. HRMS calc. for C$_{15}$H$_{16}$NNaO$_2$S [M+Na]$^+$: 380.0774, found: 380.0789.

4.2 Sn2 reactions at C4 position

**General Procedure C**: Nucleophile reagent (5.0 equiv) was added in a single portion to a solution of Cbz protected cyclic sulfamidates (1.0 equiv) in DMF (c = 0.1 M). The resulting mixture was warmed to 60 °C and stirred for 5 h. Upon completion, the reaction mixture was cooled to room temperature and diluted with DCM (c = 0.1 M), treated with 1N aqueous HCl (c = 0.1 M), and allowed to stir for an additional 1 h at room temperature. Once completed, the reaction mixture was poured into saturated NaHCO$_3$ and extracted with EtOAc. The combined organic layers were then washed with water, dried over Na$_2$SO$_4$. After evaporation of the solvent, the residue was purified by flash column chromatography to afford the desired product.

(2S, 3S, 4R, 6R)-4-((benzyloxy)carbonyl) amino)-6-methoxy-2-methyltetrahydro-2H-pyran-3-yl acetate (6a)

Prepared from 5 (30 mg, 0.08 mmol) according to **General Procedure C** with TBAOAc (5.0 equiv) as nucleophile reagent to give 6a (26.1 mg, 92% yield) as colorless syrup. R$_f$ = 0.42 (petroleum-EtOAc 3:1). [a]$_D^{20}$ -102.3 (c, 1.23 in CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28-7.40 (m, 5H, -Ph), 6.10 (d, J = 8.0 Hz, 1H, -NH), 5.13 (d, J = 12.0 Hz, 1H, -CH$_2$Ph), 5.04 (d, J = 12.0 Hz, 1H, -CH$_2$Ph), 4.80 (s, 1H, H-4), 4.76 (d, J = 2.8 Hz, 1H, H-1), 4.08-4.13 (m, 1H, H-5), 3.87-3.93 (m, 1H, H-3), 3.34 (s, 3H, -OMe), 2.12-2.17 (m, 4H, H-2a, -OAc), 1.65 (d, J = 14.4 Hz, H-2b), 1.10 (d, J = 6.4 Hz, 1H, H-6). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.0, 155.5, 136.5, 128.7, 128.7, 128.7, 128.4, 98.6, 69.8, 67.1, 61.1, 55.4, 46.4, 28.6, 21.1, 16.9. HRMS calc. for C$_{17}$H$_{23}$NNaO$_6$ [M+Na]$^+$: 360.1418, found: 360.1404.

(2S, 3S, 4R, 6R)-4-((benzyloxy)carbonyl) amino)-6-methoxy-2-methyltetrahydro-2H-pyran-3-yl acetate (6b)

Prepared from 5 (15 mg, 0.042 mmol) according to **General Procedure C** with KNO$_2$ (5.0 equiv) as nucleophile reagent to give 6b (8.1 mg, 65% yield) as colorless syrup. R$_f$ = 0.20 (petroleum-EtOAc 2:1). [a]$_D^{20}$ -64.0 (c, 1.3 in CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.28 (m, 5H, -Ph), 6.11 (d, J = 7.6 Hz, 1H, -NH), 5.10 (d, J = 12.0 Hz, 1H, -CHPh), 5.03 (d, J = 12.0 Hz, 1H, -CHPh), 4.72 (d, J = 3.6 Hz, 1H, H-1), 4.02 (q, J = 6.6 Hz, 1H, H-5), 3.91 (m, 1H, H-3), 3.48 (s, 1H, H-4), 3.33 (s, 3H, -OMe), 2.57 (s, 1H, -OH), 2.24 (dt, J = 14.8, 4.4 Hz, 1H, H-2a), 1.58 (d, J = 14.8 Hz, 1H, H-2b), 1.21 (d, J = 6.4 Hz, 3H, H-6). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.95, 136.54, 128.74, 128.54, 128.43, 98.73, 77.55, 77.23, 76.91, 68.85, 67.02, 61.95, 55.31, 48.89, 27.82, 16.82. HRMS calc. for
C_{15}H_{21}NNaO_{5} [M+Na]^{+}: 318.1317, found: 318.1325.

S-((2S, 3S, 4R, 6R)-4-(((benzyloxy) carbonyl) amino)-6-methoxy-2-methyltetrahydro-2H-pyran-3-yl) ethanethioate (6c)

Prepared from 5 (30 mg, 0.08 mmol) according to General Procedure C with KSAc (5.0 equiv) as nucleophile reagent to give 6c (26.4 mg, 89% yield) as white solid. R_f = 0.59 (petroleum-EtOAc 3:1). m.p. 83-85 °C. [α]_{D}^{20} -105.1 (c, 1.06 in CHCl_{3}). ¹H NMR (400 MHz, CDCl_{3}) δ 7.11-7.26 (m, 5H, -Ph), 6.12 (d, J = 8.0 Hz, -NHCbz), 5.03 (d, J = 12.0 Hz, 1H, -CH₂), 4.91 (d, J = 12.0 Hz, 1H, -CH₂), 4.57 (d, J = 3.6 Hz, 1H, H-1), 4.18-4.23 (m, 1H, H-3), 3.83-3.88 (m, 1H, H-5), 3.63 (s, 1H, H-4), 3.19 (s, 3H, -OMe), 2.24 (s, 3H, -SAC), 1.86 (dt, J = 3.6, 8.0, 14.8 Hz, 1H, H-2a), 1.53 (d, J = 14.8 Hz, 1H, H-2b), 1.01 (d, J = 6.0 Hz, 1H, H-6). ¹³C NMR (100 MHz, CDCl₃) δ 193.6, 155.4, 136.6, 128.7, 128.7, 128.7, 128.4, 98.8, 67.0, 55.4, 49.3, 47.8, 30.9, 30.2, 18.5. HRMS calc. for C₁₁H₂₂NNaO₅S [M+Na]^{+}: 376.1189, found: 376.1198.

Benzyl ((2S,3S,4R,6R)-3-azido-6-methoxy-2-methyltetrahydro-2H-pyran-4-yl) carbamate (6d)

Prepared from 5 (30 mg, 0.08 mmol) according to General Procedure C with NaN₃ (5.0 equiv) as nucleophile reagent to give 6d (24.5 mg, 92% yield) as colorless syrup. R_f = 0.53 (petroleum-EtOAc 3:1). [α]_{D}^{20} -133.4 (c, 0.87 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 731-7.37 (m, 5H, -Ph), 6.18 (d, J = 7.2 Hz, -NHCbz), 5.13 (d, J = 12.0 Hz, 1H, -CH₂), 5.04 (d, J = 12.0 Hz, 1H, -CH₂), 4.72 (d, J = 3.6 Hz, 1H, H-1), 4.07-4.13 (m, 1H, H-3), 4.02-4.07 (m, 1H, H-5), 3.40 (s, 1H, H-4), 3.32 (s, 3H, -OMe), 2.15 (dt, J = 3.6, 8.8, 14.8 Hz, 1H, H-2a), 1.62 (d, J = 14.8 Hz, 1H, H-2b), 1.25 (d, J = 6.8 Hz, 1H, H-6). ¹³C NMR (100 MHz, CDCl₃) δ 133.6, 136.4, 128.8, 128.6, 128.6, 128.5, 98.5, 67.1, 61.9, 61.2, 55.4, 47.2, 28.2, 17.7. HRMS calc. for C₁₂H₂₀N₂NaO₄ [M+Na]^{+}: 343.1377, found: 343.1367.

Benzyl ((2S,3S,4R,6R)-3-fluoro-6-methoxy-2-methyltetrahydro-2H-pyran-4-yl) carbamate (6e)

Prepared from 5 (30 mg, 0.08 mmol) according to General Procedure C with TBAF·3H₂O (3.0 equiv) as nucleophile reagent and DMF: H₂O 10:1 as solvent to give 6e (12.5 mg, 50% yield) as white solid. R_f = 0.69 (petroleum-EtOAc 3:1). m.p. 75-77 °C. [α]_{D}^{20} -78.7 (c, 0.30 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.36 (m, 5H, -Ph), 6.06 (d, J = 3.2 Hz, 1H, -NH), 5.11 (d, J = 14.2 Hz, 1H), 5.04 (d, J = 14.2 Hz, 1H), 4.76 (d, J = 3.2 Hz, 1H, H-1), 4.26 (dd, J = 3.2, 2J_HF = 45.6 Hz, 1H, H-4), 4.07-4.15 (m, 1H, H-3), 3.98 (dq, J = 6.8 Hz, 2J_HF = 30.8 Hz, 1H, H-5), 3.34 (s, 3H, -OMe), 2.14-2.22 (m, 1H, H-2a), 1.65 (d, J = 14.4 Hz, 1H, H-2b), 1.25 (d, J = 6.8 Hz, H-6). ¹³C NMR (100 MHz, CDCl₃) δ 155.7, 136.4, 128.8, 128.8, 128.6, 128.5, 98.5, 87.7 (J_F-C = 182.7 Hz), 67.1, 61.1 (J_F-C = 18.6 Hz), 55.4, 46.0 (J_F-C = 30.7 Hz), 28.1, 16.3 (J_F-C = 5.9 Hz). HRMS calc. for C₁₃H₂₀FNNaO₄ [M+Na]^{+}: 320.1261, found: 320.1269.
Benzyl ((2S,3S,4R,6R)-3-iodo-6-methoxy-2-methyltetrahydro-2H-pyran-4-yl) carbamate (6f)

KI (220 mg, 1.3 mmol, 5.0 equiv) was added in a single portion to a solution of 5 (95 mg, 0.26 mol, 1.0 equiv) in DMF-H$_2$O cosolvent (10:1, 1.4 ml). The resulting mixture was warmed to 60 °C and stirred for 4 h. After completion, the mixture was diluted with water and extracted with EtOAc. The combined organic layers were washed brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by flash column chromatography to give 6f (71.5 mg, 68% yield) as colorless syrup. R$_f$ = 0.33 (petroleum-EtOAc 4: 1). $[\alpha]_D^{20}$ -142.0 (c, 0.54 in CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.39 (m, 5H, Ph), 6.46 (d, $J$ = 3.2 Hz, -NH), 5.12 (d, $J$ = 12.4 Hz, 1H), 5.03 (d, $J$ = 12.4 Hz, 1H), 4.72 (d, $J$ = 3.6 Hz, 1H, H-1), 4.27 (s, 1H, H-4), 4.17-4.23 (m, 1H, H-5), 3.34 (s, 3H, -OMe), 3.16-3.23 (m, 1H, H-3), 2.63 (dt, $J$ = 4.4, 14.8 Hz, 1H, H-2a), 1.65 (d, $J$ = 14.8 Hz, 1H, H-2b), 1.16 (d, $J$ = 6.0 Hz, 1H, H-6). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.4, 136.4, 128.8, 128.8, 128.6, 98.7, 67.2, 60.5, 55.4, 51.6, 39.5, 28.3, 24.0. HRMS calc. for C$_{15}$H$_{20}$INaO$_4$ [M+Na]$: 428.0329, found: 428.0329.

Benzyl ((2R, 4S, 6S)-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl) carbamate (6g)

A round bottom flask under argon was charged with 6e (24.3 mg, 0.06 mmol), fac-Ir(mppy)$_3$ (0.59 mg, 0.0009 mmol, 0.015 equiv), t-butylmercaptan (15.0 mg, 0.12 mmol, 2.0 equiv). The reaction mixture was deoxygenated with argon for 30 min and then degasified CH$_3$CN (0.6 ml), DIPEA (20.74μl, 0.12 mmol, 2.0 equiv) was injected. The reaction mixture placed in the irradiation apparatus equipped with 1w blue light-emitting diode and was stirred at room temperature for 4 h. After that, the solvent was removed and the residue was purified by column chromatography to give 6g (15.4 mg, 92% yield) as yellow oil. R$_f$ = 0.49 (petroleum-EtOAc 4: 1). $[\alpha]_D^{20}$ -55.9 (c, 1.24 in CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30-7.36 (m, 5H, Ph), 6.19 (d, $J$ = 7.6 Hz, 1H, N-H), 5.07 (dd, $J$ = 12.0 Hz, 2H, -Ph-CH$_2$), 4.75 (d, $J$ = 3.2 Hz, 1H, H-1), 4.01 (dd, $J$ = 4.4, $J$ = 7.6 Hz, 1H, H-3), 3.95 (dq, $J$ = 6.0, $J$ = 6.4 Hz, 1H, H-5), 3.33 (s, 3H, -OMe), 1.82-1.88 (m, 1H, H-4a), 1.78 (dd, $J$ = 2.0, $J$ = 13.6 Hz, 1H, H-2a), 1.71 (d, $J$ = 14.4 Hz, 1H, H-4b), 1.41-1.49 (m, 1H, H-2b), 1.15 (d, $J$ = 6.4 Hz, 3H, H-6). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 155.7, 136.8, 128.7, 128.7, 128.4, 128.4, 98.9, 66.7, 60.0, 55.1, 43.6, 37.3, 33.0, 21.4. HRMS calc. for C$_{15}$H$_{21}$NNaO$_4$ [M+Na]$: 302.1363, found: 302.1372.
5. Functionlization at C1 position

5.1 Optimization of reaction conditions

Table S1: Screening of catalysts

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<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>α:β</th>
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<tr>
<td>1</td>
<td>Cu(MeCN)&lt;sub&gt;4&lt;/sub&gt;PF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>DCE</td>
<td>69(23)</td>
<td>7:1</td>
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<td>2</td>
<td>Cu(OTf)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DCE</td>
<td>20 (68)</td>
<td>1.9:1</td>
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<tr>
<td>3</td>
<td>AgOTf</td>
<td>DCE</td>
<td>36 (35)</td>
<td>5.3:1</td>
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<td>4</td>
<td>PPh&lt;sub&gt;3&lt;/sub&gt;AuNTf&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DCE</td>
<td>62 (20)</td>
<td>5:1</td>
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<td>5</td>
<td>Pd(MeCN)&lt;sub&gt;4&lt;/sub&gt;PF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>DCE</td>
<td>55 (10)</td>
<td>7.1:1</td>
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<td>6</td>
<td>Pd(MeCN)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DCE</td>
<td>53 (14)</td>
<td>5.3:1</td>
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<td>7</td>
<td>PPh&lt;sub&gt;3&lt;/sub&gt;HBr</td>
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<td>71 (13)</td>
<td>7.3:1</td>
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<td>8</td>
<td>p-TsOH•H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>DCE</td>
<td>67 (16)</td>
<td>6.3:1</td>
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<td>9</td>
<td>ReOCl&lt;sub&gt;3&lt;/sub&gt;(SMe&lt;sub&gt;2&lt;/sub&gt;)(OPPh&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>DCE</td>
<td>72 (12)</td>
<td>6.5:1</td>
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<td>Cu(MeCN)&lt;sub&gt;4&lt;/sub&gt;BF&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>71 (11)</td>
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<td>11</td>
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<td>MeCN</td>
<td>72 (13)</td>
<td>7.7:1</td>
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<td>Cu(MeCN)&lt;sub&gt;4&lt;/sub&gt;PF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>PhMe</td>
<td>66 (12)</td>
<td>5:1</td>
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<td>13</td>
<td>Cu(MeCN)&lt;sub&gt;4&lt;/sub&gt;PF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>DCM</td>
<td>75 (15)</td>
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<td>14&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>87</td>
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<td>15&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>Cu(MeCN)&lt;sub&gt;4&lt;/sub&gt;PF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>DCM</td>
<td>95</td>
<td>5.5:1</td>
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<sup>a</sup> Recovery yields of 1 in parentheses. <sup>b</sup> Reaction carried in a sealed tube; <sup>c</sup>Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (0.3 equiv), 60 °C, C = 0.2 M; <sup>d</sup>Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (0.3 equiv), 60 °C, C = 0.2 M, 12 h.
5.2 Functionlization at C1 position

![Diagram of functionalization at C1 position]

General Procedure D: To a solution of compound 1 (1.0 equiv) in dry CH$_2$Cl$_2$ (C = 2.0 mol/L) was added ROH (2.0 - 5.0 equiv) and CuPF$_6$ (MeCN)$_4$ (0.3 equiv) in a sealed tube, the reaction mixture was stirred at 60 °C for 12 h. The mixture was extracted with EtOAc and washed with water and brine. The organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica gel chromatography to afford desired product 3a-g.

Synthesis of (3aR,4S,6R)-6-methoxy-4-methyl-3a,4,6,7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3aα) and (3aR,4S,6S)-6-methoxy-4-methyl-3a,4,6,7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3aβ)

Prepared from 1 (40.0 mg, 0.21 mmol) with methanol according to General Procedure D to give 3aα (30.3 mg, 65% yield) and 3aβ (10.4 mg, 22% yield). Both are colorless syrup. Analytical data for 3a has been reported in our previous work.$^1$

Synthesis of (3aR,4S,6R)-4-methyl-6-allyloxy-3a,4,6,7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3bα) and (3aR,4S,6S)-4-methyl-6-(pent-4-en-1-yloxy)-3a,4,6,7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3bβ)

Prepared from 1 (40.0 mg, 0.21 mmol) with Allyl alcohol (72 ul, 5.0 equiv) according to General Procedure D to give 3bα (38 mg, 73% yield) and 3bβ (4 mg, 8% yield). Both are colorless syrup.

Analytical data for 3bα: $R_f = 0.25$ (petroleum-EtOAc 3: 1). [$\alpha$]$_D^{20}$ -38.1 (c, 1.9 in CHCl$_3$).$^1$H NMR (400MHz CDCl$_3$): $\delta$ 5.82 (ddd, $J = 22.4, 10.4, 5.2$ Hz, 1H), 5.28 (d, $J = 5.2$ Hz, 1H, H-1), 5.28 – 5.16 (m, 2H), 4.72 (d, $J = 9.2$ Hz, 1H, H-4), 4.11 (dd, $J = 12.8, 5.2$ Hz, 1H), 3.96 (m,2H), 3.06 (d, $J = 14.4$ Hz, 1H, H-2a), 2.93 (dd, $J = 14.3, 4.8$ Hz, 1H, H-2b), 1.43 (d, $J = 6.4$ Hz, 3H, H-6).$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 180.70, 132.81, 118.63, 96.57, 86.57, 69.19, 68.72, 37.41, 18.82.

S16
Synthesis of (3aR,4S,6R)-4-methyl-6-propargyloxy-3a,4,6,7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3ca) and (3aR,4S,6S)-4-methyl-1-6-(pent-4-en-1-yloxy)-3a,4,6,7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3cb)

Prepared from 1 (40.0 mg, 0.21 mmol) with Propargyl alcohol (62.5 ul, 5.0 equiv) according to General Procedure D to give 3ca (36.8 mg, 73% yield) and 3cb (4.7 mg, 9% yield). Both are colorless syrup.

Synthesis of (3aR,4S,6R)-4-methyl-6-(1-Octadecanoloxy)-3a,4,6,7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3da) and (3aR,4S,6S)-4-methyl-1-6-(pent-4-en-1-yloxy)-3a,4,6,7-tetrahydropyrano [4, 3-d] [1, 2, 3] oxathiazole 2,2-dioxide (3db)

Prepared from 1 (40.0 mg, 0.21 mmol) with 1-Octadecanol (114.5mg, 0.42mmol).
according to General Procedure D to give 3da (71 mg, 73% yield) and 3db (4.7 mg, 11% yield). Both are yellow solid.

Analytical data for 3da: R<sub>f</sub> = 0.25 (petroleum-EtOAc 5: 1). m.p. 58-60 ºC. [α]<sub>D</sub><sup>20</sup> = -19.3 (c, 3.0 in CHCl<sub>3</sub>).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.21 (d, J = 4.8 Hz, 1H, H-1), 4.70 (d, J = 9.2 Hz, 1H, H-4), 3.92 (dq, J = 9.2, 6.0 Hz, 1H, H-5), 3.61 - 3.54 (m, 1H), 3.43 - 3.35 (m, 1H), 3.03 (d, J = 14.0 Hz, 1H, H-2a), 2.90 (dd, J = 14.0, 4.8 Hz, 1H, H-2b), 1.42 (d, J = 6.4 Hz, 3H, H-6), 1.23 (s, 32H), 0.86 (t, J = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 180.79, 97.53, 86.61, 68.96, 68.68, 37.57, 32.13, 29.91, 29.87, 29.80, 29.71, 29.57, 29.52, 29.31, 26.19, 22.90, 18.86, 14.32. HRMS calc. for C<sub>24</sub>H<sub>45</sub>NNaO<sub>5</sub>S [M+Na]<sup>+</sup>: 482.2910, found: 482.2890

Analytical data for 3db: R<sub>f</sub> = 0.80 (petroleum-EtOAc 3: 1). m.p. 56-58 ºC. [α]<sub>D</sub><sup>20</sup> = +36.9 (c, 1.3 in CHCl<sub>3</sub>).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.71 (d, J = 9.6 Hz, 1H, H-4), 4.64 (dd, J = 8.8, 2.4 Hz, 1H, H-1), 3.93 – 3.87 (m, 1H), 3.54 – 3.43 (m, 2H), 3.19 (dd, J = 14.0, 2.0 Hz, 1H, H-2a), 2.80 (dd, J = 14.0, 8.8 Hz, 1H, H-2b), 1.49 (d, J = 6.4 Hz, 3H, H-6), 1.23 (s, 32H), 0.86 (t, J = 7.2 Hz, 3H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 181.02, 100.99, 86.56, 72.36, 70.83, 38.78, 32.14, 29.91, 29.87, 29.80, 29.75, 29.67, 29.57, 29.56, 26.12, 22.91, 18.93, 14.33. HRMS calc. for C<sub>24</sub>H<sub>45</sub>NNaO<sub>5</sub>S [M+Na]<sup>+</sup>: 482.2910, found: 482.2909

Synthesis of (3aR, 4S, 6R)-4-methyl-6-(pent-4-en-1-yloxy)-3a, 4, 6, 7-tetrahydropyrano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3eα) and (3aR,4S,6S)-4-methyl-6-(pent-4-en-1-yloxy)-3a, 4, 6, 7-tetrahydropyrano [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (3eβ)

Prepared from 1 (40.0 mg, 0.21 mmol) with 4-penten-1-ol (n-Pen-OH) (43.7ul, 0.42 mmol) according to General Procedure D to give 3eα (47 mg, 80% yield) and 3eβ (8.5 mg, 15% yield). Both are colorless syrup. Analytical data for 3e has been reported in our previous work<sup>[1]</sup>.

<sup>1</sup>H NMR (400MHz CDCl<sub>3</sub>): δ 5.79-5.69 (m, 1H), 5.21 (d, J = 4.8 Hz, 1H, H-1), 5.02-4.95 (m, 2H), 4.70 (d, J = 9.6 Hz, 1H, H-4), 3.92 (dq, J = 6.0, 9.6 Hz, 1H, H-5), 3.60 (dt, J = 6.4, 12.8 Hz, 1H), 3.40 (dt, J = 6.4, 12.8 Hz, 1H), 3.05 (d, J = 14.4 Hz, 1H, H-2a), 2.90 (dd, J = 4.8, 14.4 Hz, 1H, H-2b), 2.10-2.02 (m, 2H), 1.69-1.62 (m, 2H), 1.42 (d, J = 6.0 Hz, 3H, -Me).
Synthesis of (3aR, 4S, 6R)-6-((2-(isopropylthio) benzyl) oxy)-4-methyl-3a, 4, 6, 7-tetrahydropyrano [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (3fα) and (3aR, 4S, 6S)-6-((2-(isopropylthio) benzyl) oxy)-4-methyl-3a, 4, 6, 7-tetrahydropyrano [4, 3-d] - [1, 2, 3] oxathiazole 2, 2-dioxide (3fβ)
Prepared from 1 (500 mg, 2.64 mmol) with (2-(isopropylthio) benzyl alcohol (PTBOH) (960mg, 5.28 mmol) according to General Procedure D to give 3fα (660 mg, 80% yield) and 3fβ (45 mg, 4% yield). Both are colorless syrup. Analytical data for 3f has been reported in our previous work[1].

Synthesis of (3aR, 4S, 6R)-4-methyl-6-(2-Iodobenzyloxy)-3a, 4, 6, 7-tetrahydropryano[4,3-d] [1,2,3] oxathiazole 2,2-dioxide (3gα) and (3aR,4S,6S)-4-methyl-6-(pent-4-en-1-ylxylo)-3a, 4, 6, 7-tetrahydropryano [4, 3-d] [1, 2, 3] oxathiazole 2, 2-dioxide (3gβ)
Prepared from 1 (80.0 mg, 0.42 mmol) 2-Iodobenzyl Alcohol (198mg, 0.84mmol) according to General Procedure D to give 3gα (116 mg, 65% yield) and 3gβ (16 mg, 9% yield). Both are yellow solid.
Analytical data for $3g\alpha$: $R_f = 0.30$ (petroleum-EtOAc 3:1), m.p. 55-57 °C. $[\alpha]^{20}_{D} = -15.6$ (c, 6.0 in CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.0$ Hz, 1H, -Ph), 7.36 - 7.30 (m, 2H, -Ph), 7.03 - 6.97 (m, 1H, -Ph), 5.38 (d, $J = 4.8$ Hz, 1H, H-1), 4.76 (d, $J = 9.4$ Hz, 1H), 4.64 (d, $J = 12.6$ Hz, 1H), 4.50 (d, $J = 12.6$ Hz, 1H), 4.00 (dq, $J = 12.2, 6.2$ Hz, 1H), 3.13 (d, $J = 14.4$ Hz, 1H), 2.98 (dd, $J = 14.4, 4.9$ Hz, 1H), 1.42 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 180.63, 139.60, 138.71, 130.04, 129.33, 128.70, 98.18, 97.36, 86.50, 73.90, 69.59, 37.32, 18.84. HRMS calc. for $C_{13}H_{14}INaO_2S$ [M+Na]$^+$: 445.9529, found: 445.9541.

Analytical data for $3g\beta$: $R_f = 0.60$ (petroleum-EtOAc 3:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 8.0$ Hz, 1H, -Ph), 7.40–7.32 (m, 2H, -Ph), 7.06–6.99 (m, 1H, -Ph), 7.03 (t, $J = 8.4$ Hz, 1H), 4.92 (d, $J = 12.2$ Hz, 1H), 4.79 (dd, $J = 8.8, 2.4$ Hz, 1H, H-1), 4.74 (d, $J = 9.5$ Hz, 1H), 4.68 (d, $J = 12.2$ Hz, 1H), 3.56 – 3.49 (m, 1H), 3.58 – 3.49 (m, 1H), 3.26 (dd, $J = 14.2, 2.4$ Hz, 1H), 1.53 (d, $J = 6.3$ Hz, 3H). Because of the instability of $3g\beta$, the $^{13}$C NMR are not recorded.

*Condition A (Procedure E): 7 (1.5 equiv), Tf₂O (1.5 equiv), DCM, 4Å MS, -40 °C, (reverse addition).

*Condition B (Procedure F): 7 (1.5 equiv), Tf₂O (1.5 equiv), DTBMP (5.0 equiv), DCM, 4Å MS, -40 °C.

*Condition C (Procedure G): 1) 7 (1.5 equiv), Tf₂O (1.5 equiv), DTBMP (5.0 equiv), DCM, 4Å MS, -40 °C; 2) TfOH (0.5 equiv), DCM, 4Å MS, -40 °C. DTBMP = 2, 6-di-tert-butyl-4-methylpyridine. PIFA = [Bis(trifluoroacetoxy) iodo] benzene

6.1 Preparation of donor 7

To a solution of NaBH₄ (44.85 mg, 1.18 mmol) in methanol (c = 0.22 M), compound 3fu (400 mg, 1.08 mmol) in methanol (c = 0.2 M) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 5 min and then quenched with water. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with saturated aqueous NaHCO₃, brine and dried over NaSO₄. After evaporation of the solvent, the crude product treated with a mixed solvent of CH₃CN: H₂O = 10:1 (5.0 ml: 0.5 ml, C = 0.2 mol/L), and then bis(trifluoroacetoxy)iodobenzene (PIFA) (556 mg, 1.3 mmol, 1.2 equiv), the mixture was stirred at room temperature for
10 min and quenched with saturated aqueous NaHCO₃. The reaction was extracted with EtOAc and the organic layer was washed with saturated aqueous NaHCO₃, water and brine sequentially, then dried over Na₂SO₄, and concentrated *in vacuo*. The residue was purified by silica gel chromatography (petroleum-EtOAc 1:1) to give 7 (370 mg, 88%) as colorless syrup. Analytical data for 7: R_f = 0.10 (petroleum-EtOAc 1:1). [α]_D²⁰ = -81.9 (c, 1.5 in CHCl₃).

**General Procedure E (Condition A):** Acceptor (1.0 equiv) were azeotroped with toluene and dissolved in anhydrous CH₂Cl₂ (C = 0.05 mol/L) in the presence of 4 Å MS (100 wt. %) was stirred for 3 min at –40 °C. After addition of Tf₂O (1.5 equiv), the solution was stirred at –40°C for 5 min, and then the glycosyl donor (1.5 equiv) were azeotroped with toluene and dissolved in anhydrous CH₂Cl₂ was added. The reaction mixture was stirred at –40°C for 3 h. The reaction mixture was quenched with saturated aqueous NaHCO₃, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried (Na₂SO₄), concentrated, and purified by silica gel column chromatography.

**General Procedure F (Condition B):** Glycosyl donor (1.5 equiv) and acceptor (1.0 equiv) were azeotroped with toluene and dissolved in anhydrous CH₂Cl₂ (C = 0.05 mol/L). Freshly activated 4 Å molecular sieves were added and then DTBMP (5.0 equiv) was also added to the mixture, and stirred at –40°C for 5 min. After addition of Tf₂O (1.5 equiv), the solution was stirred at –40°C for 3 h. The reaction mixture was quenched with saturated aqueous NaHCO₃, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried (Na₂SO₄), concentrated, and purified by silica gel column chromatography.

**General Procedure G (Condition C):** Glycosyl donor (1.5 equiv) and acceptor (1.0 equiv) were azeotroped with toluene and dissolved in anhydrous CH₂Cl₂ (C = 0.05 mol/L). Freshly activated 4 Å molecular sieves were added and then DTBMP (5.0 equiv) was also added to the mixture, and stirred at –40°C for 5 min. After addition of Tf₂O (1.5 equiv), the solution was stirred at –40°C for 3 h. The reaction mixture was quenched with saturated aqueous NaHCO₃, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried (Na₂SO₄), concentrated, and the crude product were azeotroped with toluene and dissolved in anhydrous CH₂Cl₂ (C = 0.05
mol/L) in the presence of 4 Å MS. After addition of TfOH (0.5 equiv), the solution was stirred at -40°C for 3 h. The reaction mixture was quenched with saturated aqueous NaHCO₃, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried (Na₂SO₄), concentrated, and purified by silica gel column chromatography.

**Preparation of disaccharide (9a) under condition A**

Prepared from acceptor (25.0 mg, 0.054 mmol, 1.0 equiv) according to **General Procedure E** with donor 7 (31.4 mg, 0.081 mmol, 1.5 equiv) and Tf₂O (13.6 ul, 0.081 mmol, 1.5 equiv) in anhydrous CH₂Cl₂ (1.08 ml, C = 0.05 mol/L) to give disaccharide 9aa (26.7 mg, 76%) as white solids and 9aβ (2.2mg, 4%) as colorless syrup.

Analytical data for **9aa**: R₇ = 0.20 (petroleum-EtOAc 3:1). m.p. 162 - 164 °C. [α]D²⁰+39.2 (c, 3.5 in CHCl₃). ¹H NMR (400 MHZ, CD₃ODCD₃) δ 7.45 – 7.23 (m, 15H, -Ph), 6.27 (d, J = 10.0 Hz, 1H,-NH), 5.08 (d, J = 10.8 Hz, 1H,-CHPh), 5.03 (t, J = 4.0 Hz, 1H, H-1), 4.84 (d, J = 3.2 Hz, 1H, H-1), 4.77 (d, J = 10.8 Hz, 1H,-CHPh), 4.74 (d, J = 12.0 Hz, 1H,-CHPh), 4.63 (d, J = 12.0 Hz, 1H,-CHPh), 4.52 (d, J = 12.0 Hz, 1H,-CHPh), 4.36 (dd, J = 9.6, 6.0 Hz, 1H,H-4), 4.24 (dq, J = 12.0, 6.0 Hz, 1H,H-5), 4.08 (dq, 1H, J = 11.2, 5.6 Hz,H-3), 3.85 (t, J = 9.0 Hz, 1H, H-6a), 3.79 (t, J = 9.0 Hz, 1H, H-6b), 3.76 – 3.64 (m, 3H, H-3',H-4', H-5'), 3.60 (dd, J = 9.2, 3.6 Hz, 1H, H-2'), 3.35 (s, 3H,-OMe), 2.11 (m, 2H,H-2), 0.69 (d, J = 6.4 Hz, 3H,H-6).¹³C NMR (100 MHZ, CD₃ODCD₃) δ 140.22 (Ph), 139.62 (Ph), 139.20 (Ph), 129.14 (Ph), 129.07 (Ph), 128.78 (Ph), 128.76 (Ph), 128.65 (Ph), 128.59 (Ph), 128.42 (Ph), 128.36 (Ph), 127.94 (Ph), 98.25 (C-1), 97.01 (C-1), 85.17 (C-4), 82.02 (C-2), 79.91 (C-6), 76.25, 75.46 (CH₂Ph), 73.86 (CH₂Ph), 72.86 (CH₂Ph), 71.07, 69.43, 63.42 (C-5), 55.26 (OCH₃), 52.57 (C-3), 30.67 (C-2), 18.06 (C-6). HRMS calc. for C₃₄H₄₁NNaO₁₀S [M+Na]⁺: 678.2343, found: 678.2339.

Analytical data for **9aβ**: R₇ = 0.25 (petroleum-EtOAc 3:1). [α]D²⁰+12.0 (c, 1.7 in CHCl₃). ¹H NMR (400 MHZ, CD₃ODCD₃) δ 7.43 – 7.25 (m, 15H, -Ph), 6.82 (d, J = 6.4 Hz, 1H,-NH), 5.34 (dd, J = 8.4, 2.4 Hz, 1H,H-1), 4.90 (d, J = 11.2 Hz, 1H,-CHPh), 4.83 (d, J = 3.2 Hz, 1H, H-1), 4.73 (d, J = 12.0 Hz, 1H,-CHPh), 4.71 (d, J = 12.0 Hz, 1H,-CHPh), 4.69 (d, J = 12.4 Hz, 1H,-CHPh), 4.60 (d, J = 12.4 Hz, 1H,-CHPh), 4.52 (d, J = 12.4 Hz, 1H,-CHPh), 4.45 – 4.32 (m, 2H,H-3,H-4), 3.89 (m, 3H,H-5,H-6), 3.74 – 3.68 (m, 1H,H-5), 3.66 – 3.57 (m, 2H,H-3',H-4'), 3.50 (dd, J = 9.6, 3.6 Hz, 1H,H-2), 3.38 (s, 3H,-OMe), 2.22 (dt, J = 14.4, 2.8 Hz, 1H,H-2a), 1.96 – 1.89 (m, 1H,H-2b), 1.22 (d, J = 6.0 Hz, 3H,H-6).¹³C NMR (100 MHZ, CD₃ODCD₃) δ 140.03 (Ph), 139.83 (Ph), 139.71 (Ph), 129.13 (Ph), 129.09 (Ph), 129.03 (Ph), 128.97 (Ph), 128.59 (Ph), 128.35, (Ph) 128.30 (Ph), 128.16 (Ph), 128.09 (Ph), 99.34 (C-1), 98.11 (C-1'), 83.21, 81.98, 81.24, 77.13, 75.89 (CH₂Ph), 73.59 (CH₂Ph), 72.75 (CH₂Ph), 70.83, 70.43, 69.15, 55.18
(OCH₃), 53.86, 33.02 (C-2), 18.38 (C-6). HRMS calc. for C₃₄H₄₁NNaO₁₀S [M+Na]+: 678.2343, found: 678.2348.

**Preparation of disaccharide (9b) under condition A**

Prepared from acceptor (20.0 mg, 0.054 mmol, 1.0 equiv) according to **General Procedure E** with donor 7 (31.7 mg, 0.081 mmol, 1.5 equiv) and Tf₂O (13.7 ul, 0.081 mmol, 1.5 equiv) in anhydrous CH₂Cl₂ (1.08 ml, C = 0.05 mol/L) to give disaccharide 9ba (22.0 mg, 70%) as white solid.

Analytical data for 9ba: Rf = 0.35 (petroleum-EtOAc 3: 1). m.p. 157 - 159 °C. [α]b²⁰ =-50.2 (c, 2.0 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.27 (m, 5H, -Ph), 5.41 (t, J = 9.6 Hz, 1H, H-3'), 5.13 (br s, 1H, -NH), 4.87 (d, J = 3.6 Hz, 1H, H-1'), 4.85 (dd, J = 4.0, 2.4 Hz, 1H, H-1), 4.79 (dd, J = 10.0, 4.0 Hz, 1H, H-2'), 4.71 (d, J = 12.0 Hz, 1H, -CHPh), 4.43 (d, J = 12.0 Hz, 1H, -CHPh), 4.19 (dd, J = 9.6, 5.6 Hz, 1H, H-4), 4.02 (dq, J = 9.6, 6.0 Hz, 1H, H-5'), 3.93 (m, 2H, H-3',H-4), 3.76 (dt, J = 9.6, 2.4 Hz, 1H, H-5), 3.61 (d, J = 2.0 Hz, 2H, H-6'), 3.37 (s, 3H, -OMe), 2.03 (s, 3H, -OAc), 2.01 (s, 3H, -OAc), 1.78 – 1.68 (m, 2H, H-2), 1.25 (d, J = 6.0 Hz, 3H, H-6). ¹³C NMR (100 MHz, CDCl₃) δ 170.54 (C=O), 170.15 (C=O), 137.44 (Ph), 128.78 (Ph), 128.50 (Ph), 128.30 (Ph), 97.56 (C-1'), 97.08 (C-1), 83.98 (C-4), 76.42 (C-4'), 73.91 (C₂H₂Ph), 71.51 (C-2'), 71.11 (C-3), 69.42 (C-5'), 68.00 (C-6), 62.65 (C-5), 55.65 (OCH₃), 52.03 (C-3), 29.64 (C-2), 21.16 (COCH₃), 20.94 (COCH₃), 17.80 (C-6). HRMS calc. for C₂₄H₃₃NNaO₁₂S [M+Na]+: 582.1615, found: 582.1611.

**Preparation of disaccharide (9c) under condition B**

Prepared from acceptor (25.0 mg, 0.06 mmol, 1.0 equiv) according to **General Procedure F** with donor 7 (35.2 mg, 0.09 mmol, 1.5 equiv) and Tf₂O (15.2 ul, 0.09 mmol, 1.5 equiv) in anhydrous CH₂Cl₂ (1.2 ml, C = 0.05 mol/L) to give disaccharide 9ca (18.2 mg, 47%) and 9cf (17.9 mg, 47%), both are colorless syrup.

**Preparation of disaccharide (9c) under condition C**

Prepared from acceptor (25.0 mg, 0.06 mmol, 1.0 equiv) according to **General Procedure G** with donor 7 (35.2 mg, 0.09 mmol, 1.5 equiv), Tf₂O (15.2 ul, 0.09 mmol, 1.5 equiv), DTH (61.6 mg, 0.30 mmol, 5.0 equiv) in anhydrous CH₂Cl₂ (1.2 ml, C = 0.05 mol/L) and TIOH (2.65 ul, 0.03 mmol, 0.5 equiv) to give disaccharide 9ca (15 mg, 41%) and 9cf (3.0 mg, 8%), both are colorless syrup.

Analytical data for 9ca: Rf = 0.20 (petroleum-EtOAc 3: 1). [α]b²⁰ =-44.4 (c, 1.9 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.24 (m, 10H, -Ph), 5.37 (d, J = 11.6 Hz, 1H, -NH), 5.20 (d, J = 10.8 Hz, 1H, -CHPh), 4.88 (d, J = 2.8 Hz, 1H, H-1), 4.71 (d, J = 12.0 Hz, 1H, -CHPh), 4.70 (d,
\[ J = 10.8 \text{ Hz}, 1H, -\text{CHPh}, 4.59 \text{ (d, } J = 12.0 \text{ Hz, } 1H, -\text{CHPh}), 4.56 \text{ (d, } J = 3.6 \text{ Hz, } 1H, H-1'), 4.30 \text{ (dd, } J = 12.0, 2.0 \text{ Hz, } 1H, H-4), 4.25 \text{ (dt, } J = 11.6, 6.0 \text{ Hz, } 1H, H-5), 4.17 \text{ (dd, } J = 10.0, 4.8 \text{ Hz, } 1H, H-5'), 4.08 \text{ (m, } 2H, H-3, H-4), 3.84 \text{ (t, } J = 9.2 \text{ Hz, } 1H, H-6a), 3.79 \text{ (ddd, } J = 10.0, 4.0, 2.8 \text{ Hz, } 1H, H-3'), 3.63 \text{ (t, } J = 9.6 \text{ Hz, } 1H, H-6b), 3.58 \text{ (dd, } J = 9.2, 3.6 \text{ Hz, } 1H, H-2'), 3.36 \text{ (s, } 3H, -\text{OME}), 2.22 - 2.16 \text{ (dt, } J = 14.8, 1.6 \text{ Hz, } 1H, H-2a), 2.08 - 1.98 \text{ (m, } 4H, -\text{OAc, } H-2b), 0.70 \text{ (d, } J = 6.0 \text{ Hz, } 3H, H-6). \]

\[ ^{13}C \text{ NMR (101 MHz, } \text{CDCl}_3 \text{)} \delta 170.83 \text{ (C=O), 138.76 (Ph), 137.82 (Ph), 128.78 (Ph), 128.46 (Ph), 128.35 (Ph), 127.98 (Ph), 127.67 (Ph), 97.86 (C-1'), 97.06 (C-1), 84.47 (C-4), 80.95 (C-2), 79.06, 77.06 (C-6'), 75.47 (\text{CH}_2\text{Ph}), 73.40 (\text{CH}_2\text{Ph}), 68.65, 62.68, 62.43, 55.74 (-\text{OCH}_3), 52.20 (C-3), 29.79 (C-2), 21.07 (\text{COCH}_3), 17.45 (C-6). \text{ HRMS calc. for C}_{29}\text{H}_{37}\text{NNaO}_{13}\text{S [M+Na]}^{+}: 630.1979, \text{ found: 630.1989.} \]

Analytical data for 9cβ: \( R_f = 0.10 \) (petroleum-EtOAc 3: 1). \( [\alpha]_D^{20} +16.5 \) (c, 1.9 in CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta 7.43 - 7.27 \) (m, 10H, -Ph), 5.06 (d, \( J = 11.6 \) Hz, 1H, -CHPh), 4.94 (dd, \( J = 6.8, 4.4 \) Hz, 1H, H-1), 4.75 (d, \( J = 12.4 \) Hz, 1H, -CHPh), 4.65 (d, \( J = 12.0 \) Hz, 1H, -CHPh), 4.60 (d, \( J = 3.6 \) Hz, 1H, H-1'), 4.56 (d, \( J = 11.6 \) Hz, 1H, -CHPh), 4.26 (dd, \( J = 12.0, 2.4 \) Hz, 1H, H-4), 4.21 - 4.08 (m, 3H, H-3, H-4, -NH), 3.93 - 3.83 (m, 2H, H-3', H-6a), 3.77 - 3.67 (m, 2H, H-5, H-5'), 3.61 (dd, \( J = 10.0, 8.8 \) Hz, 1H, H-6b), 3.49 (dd, \( J = 9.6, 3.6 \) Hz, 1H, H-2), 3.36 (s, 3H, -OME), 2.03 (s, 3H, -OAc), 1.71 (m, 2H, H-2), 1.23 (d, \( J = 6.4 \) Hz, 3H, H-6). \(^{13}C\) NMR (100 MHz, CDCl₃) \( \delta 170.94 \) (C=O), 139.08 (Ph), 137.95 (Ph), 129.06 (Ph), 128.78 (Ph), 128.34 (Ph), 127.89 (Ph), 98.09 (C-1', C-1), 82.85 (C-4), 82.29 (C-3'), 79.81 (C-2'), 76.05 (CH₂Ph), 75.29 (C-6), 73.44 (CH₂Ph), 68.82 (C-5), 68.21 (C-5'), 63.24 (C-4), 55.52 (-OCH₃), 53.27 (C-3), 31.95 (C-2), 21.15 (COCH₃), 18.14 (C-6). \text{ HRMS calc. for C}_{29}\text{H}_{37}\text{NNaO}_{13}\text{S [M+Na]}^{+}: 630.1979, \text{ found: 630.1962.} \]

Preparation of disaccharide (9d) under condition C

Prepared from acceptor (25.0 mg, 0.054 mmol, 1.0 equiv) according to **General Procedure G** with donor 7 (31.4 mg, 0.081 mmol, 1.5 equiv), Tf₂O (13.6 ul, 0.081 mmol, 1.5 equiv), DTBMP (55.4 mg, 0.27 mmol, 5.0 equiv) in anhydrous CH₂Cl₂ (1.08 ml, C = 0.05 mol/L) and TfOH (2.38 ul, 0.027 mmol, 0.5 equiv) to give disaccharide 9da (29 mg, 83%) as white solid.

Analytical data for 9da: \( R_f = 0.25 \) (petroleum-EtOAc 3: 1). m.p. 142 - 144 °C. \( [\alpha]_D^{20} +22.6 \) (c, 1.9 in CHCl₃). \(^1\)H NMR (400 MHz, CD₃OD₃) \( \delta 7.45 - 7.20 \) (m, 15H, -Ph), 6.08 (s, 1H, -NH), 4.98 (d, \( J = 11.2 \) Hz, 1H, -CHPh), 4.90 (d, \( J = 2.8 \) Hz, 1H, H-1'), 4.89 (d, \( J = 11.6 \) Hz, 1H, -CHPh), 4.85 (d, \( J = 2.8 \) Hz, 1H, H-1), 4.80 (d, \( J = 11.2 \) Hz, 1H, -CHPh), 4.72 (d, \( J = 12.0 \) Hz, 1H, -CHPh), 4.68 (d, \( J = 12.0 \) Hz, 1H, -CHPh), 4.67 (d, \( J = 11.2 \) Hz, 1H, -CHPh), 4.50 (dd, \( J = 9.6, 5.2 \) Hz, 1H, H-4), 4.16 (m, 2H, H-5, H-3), 3.91 (t, \( J = 9.2 \) Hz, 1H, H-6a'), 3.82 (dd, \( J = 10.4, 2.4 \) Hz, 1H, H-3'), 3.72 (dt, \( J = 10.0, 2.4 \) Hz, 1H, H-5'), 3.49 (s, 3H, -OME).
3.63 (dd, J = 10.0, 2.8 Hz, 1H, H-4'), 3.57 – 3.51 (m, 2H, H-2', H-6b'), 3.37 (s, 3H, OMe), 2.24 – 2.14 (m, 2H, H-2), 1.25 (d, J = 6.0 Hz, 3H, H-6). 13C NMR (100 MHz, CD3OD) δ 140.17 (Ph), 139.69 (Ph), 139.67 (Ph), 129.07 (Ph), 129.00 (Ph), 128.92 (Ph), 128.63 (Ph), 128.61 (Ph), 128.38 (Ph), 128.31 (Ph), 128.13 (Ph), 98.48 (C-1'), 96.08 (C-1), 85.35 (C-4), 82.47 (C-6), 81.41 (C-2'), 77.76 (C-5'), 75.81 (CH2Ph), 75.27 (CH2Ph), 72.92 (CH2Ph), 70.15 (C-3'), 65.11 (C-4'), 62.47 (C-5), 55.38 (OCH3), 53.40 (C-3), 29.76 (C-2), 18.07 (C-6). HRMS calc. for C34H31NNaO10S [M+Na]+: 678.2349, found: 678.2353.

**Preparation of disaccharide (9e) under condition C**

Prepared from acceptor (20.0 mg, 0.058 mmol, 1.0 equiv) according to **General Procedure G** with donor 7 (33.7 mg, 0.087 mmol, 1.5 equiv), Tf2O (14.6 ul, 0.087 mmol, 1.5 equiv), DTBMP (59.5 mg, 0.29 mmol, 5.0 equiv) in anhydrous CH2Cl2 (1.16 ml, C = 0.05 mol/L) and TfOH (2.56 ul, 0.029 mmol, 0.5 equiv) to give disaccharide 9eα (14.5 mg, 47%) as white solid and 9eβ (7 mg, 22%) as colorless syrup.

![Chemical Structure Image]

Analytical data for 9eα: Rf = 0.30 (petroleum-EtOAc 3: 1). m.p. 155 - 157 °C. [α]D^20 +41.0 (c, 0.8 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 6.28 (d, J = 4.0 Hz, 1H, H-1'), 5.45 (dd, J = 3.2, 1.2 Hz, 1H, H-3'), 5.29 (dd, J = 10.4, 3.2 Hz, 1H, H-4'), 5.20 (d, J = 11.6 Hz, 1H, -NH), 5.03 (d, J = 2.8 Hz, 1H, H-1), 4.29 – 4.20 (m, 2H, H-4, 4-Ha), 4.13 – 4.00 (m, 4H, H-2, H-5', H-6b, H-6, H-3), 3.94 (dq, J = 9.6, 6.0 Hz, 1H, H-5), 2.19 (s, 3H, -OAc), 2.15 (t, J = 2.0 Hz 1H, H-2a), 2.13 (s, 3H, -OAc), 2.17 (dt, J = 14.2, 4.0 Hz 1H, H-2'b), 2.02 (s, 3H, -OAc), 2.01 (s, 3H, -OAc), 1.32 (d, J = 6.0 Hz, 3H, H-6). 13C NMR (100 MHz, CDCl3) δ 170.57 (C=O), 170.16 (C=O), 170.02 (C=O), 169.86 (C=O), 99.03 (C-1'), 90.72 (C-1'), 83.82 (C-4), 74.22, 69.19 (C-4), 68.40, 67.82 (C-3), 62.44 (C-5), 61.23 (C-6), 52.03 (C-3), 29.47 (C-2), 21.14 (COCH3), 20.89 (COCH3), 20.85 (COCH3), 20.84 (COCH3), 17.81 (C-6). HRMS calc. for C20H29NNaO14S [M+Na]+: 562.1200, found:562.1200.

![Chemical Structure Image]

Analytical data for 9eβ: Rf = 0.35 (petroleum-EtOAc 3: 1). [α]D^20 +18 (c, 0.6 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 6.38 (d, J = 3.6 Hz, 1H, H-1'), 5.45 (dd, J = 3.2, 1.2 Hz, 1H, H-3'), 5.18 (dd, J = 10.4, 3.2 Hz, 1H, H-4'), 4.97 (d, J = 7.2 Hz, 1H, -NH), 4.95 (dd, J = 6.4, 2.8 Hz, 1H, H-1), 4.35 (dd, J = 9.6, 6.4 Hz, 1H, H-4), 4.33 – 4.24 (m, 3H, H-2', H-5', H-3), 4.06 (dd, J = 6.8, 1.2 Hz, 2H, H-6), 3.95 (dq, J = 9.6, 6.0 Hz, 1H, H-5), 2.13 (s, 3H, -OAc), 2.13 (s, 3H, -OAc), 2.03 (s, 3H, -OAc), 2.01 (s, 3H, -OAc), 2.00 – 1.91 (m, 2H, H-2), 1.33 (d, J = 6.0 Hz, 3H, H-6). 13C NMR (100 MHz, CDCl3) δ 170.64 (C=O), 170.29 (C=O), 170.24 (C=O), 169.71 (C=O), 95.33 (C-1'), 90.06 (C-1'), 82.43 (C-4), 70.08 (C-2'), 69.20 (C-5'), 68.38 (C-5'), 68.15 (C-4), 67.86 (C-3'), 61.57 (C-6), 51.87 (C-3), 31.83 (C-2), 21.26 (COCH3), 21.05 (COCH3), 20.89 (COCH3), 20.81 (COCH3), 18.89 (C-6). HRMS calc. for C20H29NNaO14S [M+Na]+: 562.1200, found:562.1195.
Preparation of disaccharide (9f) under condition C

Prepared from acceptor (25.0 mg, 0.054 mmol, 1.0 equiv) according to General Procedure G with donor 7 (31.4 mg, 0.081 mmol, 1.5 equiv), Tf₂O (13.6 ul, 0.081 mmol, 1.5 equiv), DTBMP (55.4 mg, 0.27 mmol, 5.0 equiv) in anhydrous CH₂Cl₂ (1.08 ml, C = 0.05 mol/L) and TfOH (2.38 ul, 0.027 mmol, 0.5 equiv) to give disaccharide 9fa (22.5 mg, 64%) and 9fb (7.5 mg, 21%), both are colorless syrup.

Analytical data for 9fa: Rf = 0.20 (petroleum-EtOAc 3: 1). [α]D²⁰ +24.3 (c, 1.0 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.25 (m, 15H), 5.61 (br s, 1H, -NH), 5.45 (d, J = 2.8 Hz, 1H, H-1),4.81 (d, J = 11.6 Hz, 1H, -CHPh), 4.76 (d, J = 12.0 Hz, 1H,-CHPh), 4.67 (d, J = 3.6 Hz, 1H, H-1'), 4.66 (d, J = 12.0 Hz, 1H,-CHPh), 4.65 (d, J = 12.0 Hz, 1H,-CHPh),4.55 (d, J = 12.4 Hz, 1H, -CHPh), 4.52 (d, J = 12.0 Hz, 1H, -CHPh), 4.23 (dd, J = 9.6, 5.2 Hz, 1H, H-4), 4.20 – 4.12 (m, 2H, H-5, H-4), 4.11 – 4.05 (m, 1H, H-3), 3.95 – 3.85 (m, 2H, H-6a, H-3'),3.80 (dd, J = 10.0, 3.6 Hz, 1H, H-2), 3.62 – 3.50 (m, 2H, H-6b, H-5), 3.35 (s, 3H, -OMe), 2.21 (dt, J = 15.6, 2.0 Hz, 1H, H-2a), 1.92 (dt, J = 15.6, 4.8 Hz, 1H, H-2b), 1.20 (d, J = 6.0 Hz, 3H, H-6). ¹³C NMR (100 MHz, CDCl₃) δ 138.29 (Ph), 138.19 (Ph), 137.99 (Ph), 128.69 (Ph), 128.67 (Ph), 128.64 (Ph), 128.43 (Ph), 128.16 (Ph), 128.01 (Ph), 127.81 (Ph), 98.49 (C-1’), 96.82 (C-1), 84.36 (C-4), 78.51, 76.48 (C-2'), 74.31, 73.97 (CH₂Ph), 73.72 (CH₂Ph), 73.69 (CH₂Ph), 68.88, 68.65, 62.16, 55.69 (OCH₃), 52.55 (C-3), 29.27 (C-2), 18.13 (C-6). HRMS calc. for C₃₄H₄₁NNaO₁₆S [M+Na]⁺: 678.2349, found: 678.2358.

Analytical data for 9fb: Rf = 0.15 (petroleum-EtOAc 3: 1). [α]D²⁰ +23.0 (c, 0.5 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.25 (m, 15H), 4.84 (dd, J = 7.2, 2.4 Hz, 1H, H-1), 4.82 (d, J = 12.0 Hz, 1H, -CHPh), 4.81 (d, J = 12.4 Hz, 1H, -CHPh), 4.66 (d, J = 12.4 Hz, 1H, -CHPh), 4.64 (d, J = 12.0 Hz, 1H, -CHPh), 4.61 (s, 1H, H-1’), 4.54 (d, J = 11.6 Hz, 1H, -CHPh), 4.45 (d, J = 11.6 Hz, 1H, -CHPh), 4.43 – 4.38 (m, 2H, H-6), 4.28 – 4.20 (m, 2H, H-3, H-5),3.95 – 3.75 (m, 4H, H-5, H-4, H-2', -NH), 3.54 – 3.42 (m, 2H, H-3, H-4), 3.33 (s, 3H, -OMe), 2.13 – 2.04 (m, 1H, H-2a), 1.99 (ddd, J = 6.8, 4.0, 2.0 Hz, 1H, H-2b), 1.26 (d, J = 6.0 Hz, 3H, H-6). ¹³C NMR (101 MHz, CDCl₃) δ 138.84 (Ph), 138.70 (Ph), 137.43 (Ph), 128.95 (Ph), 128.84 (Ph), 128.59 (Ph), 128.56 (Ph), 128.54 (Ph), 128.49 (Ph), 128.27 (Ph), 127.98 (Ph), 127.78 (Ph), 127.70 (Ph), 99.02 (C-1), 97.64 (C-1), 82.60 (C-6), 76.70, 75.85, 74.17 (CH₂Ph), 73.78 (CH₂Ph), 73.71 (CH₂Ph), 72.50, 68.61, 68.22,55.74 (OCH₃), 52.69 (C-3), 32.13 (C-2), 18.19 (C-6). HRMS calc. for C₃₄H₄₁NNaO₁₆S [M+Na]⁺: 678.2349, found:678.2342.
Preparation of disaccharide (9g) under condition C

Prepared from diosgenin (40.0 mg, 0.096 mmol, 1.0 equiv) according to General Procedure G with donor 7 (56.3 mg, 0.145 mmol, 1.5 equiv), Tf₂O (24.3 μL, 0.145 mmol, 1.5 equiv), DTBMP (99.0 mg, 0.48 mmol, 5.0 equiv) in anhydrous CH₂Cl₂ (1.92 mL, C = 0.05 mol/L) and TFOH (4.25 μL, 0.048 mmol, 0.5 equiv) to give disaccharide 9gα (41.0 mg, 70%) and 9gβ (8.2 mg, 14%), both are white solids.

Analytical data for 9gα: Rf = 0.40 (petroleum-EtOAc 3: 1). m.p. 175 - 177 ºC. [α]D20 = -122.0 (c, 1.5 in CHCl₃). 1H NMR (400 MHz, CDCl₃) δ 5.74 (d, J = 11.2 Hz, 1H, -NH), 5.33 (d, J = 4.8 Hz, 1H, H-6), 5.09 (d, J = 3.2 Hz, 1H, H-1'), 4.39 (dd, J = 15.2, 7.6 Hz, 1H, H-16), 4.27 (dd, J = 9.6, 4.8 Hz, 1H, H-4'), 4.13 (m, 2H, H-5', H-3'), 3.47 (m, 2H, H-26), 3.35 (t, J = 11.2 Hz, 1H), 2.40 – 1.04 (m, 26H), 1.31 (d, J = 6.0 Hz, 3H, H-19), 1.01 (s, 3H, H-19), 0.95 (d, J = 7.2 Hz, 3H, H-27), 0.77 (s, 3H, -CH₃), 0.76 (s, 3H, -CH₃). 13C NMR (101 MHz, CDCl₃) δ 140.02, 122.50, 109.52, 93.71, 84.64, 81.01, 77.09, 67.08, 62.32, 61.81, 56.68, 53.01, 50.26, 41.83, 40.49, 39.94, 38.22, 37.35, 37.09, 32.91, 32.06, 31.61, 30.51, 29.64, 29.53, 29.02, 21.04, 19.60, 18.09, 17.35, 16.49, 14.74. HRMS calc. for C₃₃H₅₂NO₇S [M+H]⁺: 606.3464, found: 606.3478.

Analytical data for 9gβ: Rf = 0.50 (petroleum-EtOAc 3: 1). m.p. 160 - 162 ºC. [α]D20 = -84.8 (c, 1.0 in CHCl₃). 1H NMR (400 MHz, CDCl₃) δ 5.33 (d, J = 5.0 Hz, 1H, H-6), 4.94 (dd, J = 8.0, 2.0 Hz, 1H, H-1'), 4.61 (m, 1H, -NH), 4.47 – 4.31 (m, 3H, H-16, H-3', H-4'), 3.96 (dq, 1H, J =12.0, 6.4 Hz, H-5'), 3.54 (ddd, J = 15.6, 11.2, 3.6 Hz, 1H, H-26a), 3.45 (dd, J = 11.2, 3.2 Hz, 1H, H-26b), 3.35 (t, J = 11.2 Hz, 1H), 2.40 – 1.02 (m, 26H), 1.35 (d, J = 6.0 Hz, 3H, H-6'), 0.99 (s, 3H, H-19), 0.95 (d, J = 7.2 Hz, 3H, H-27), 0.77 (s, 3H, -CH₃), 0.76 (s, 3H, -CH₃). 13C NMR (101 MHz, CDCl₃) δ 140.73, 122.02, 109.51, 95.11, 83.10, 81.02, 78.14, 68.55, 67.06, 62.29, 56.70, 53.37, 50.23, 41.82, 40.47, 40.35, 39.96, 37.18, 37.04, 32.91, 32.27, 32.05, 31.62, 31.59, 30.50, 29.01, 28.20, 21.05, 19.56, 18.60, 17.35, 16.49, 14.74. HRMS calc. for C₃₃H₅₂NO₇S [M+H]⁺: 606.3464, found: 606.3474.
Preparation of disaccharide (9h) under condition C

Prepared from Cholesterol (18.0 mg, 0.047 mmol, 1.0 equiv) according to General Procedure G with donor 7 (27.2 mg, 0.07 mmol, 1.5 equiv), TES (11.7 ul, 0.07 mmol, 1.5 equiv), DTBMP (47.8 mg, 0.23 mmol, 5.0 equiv) in anhydrous CH2Cl2 (0.94 ml, C = 0.05 mol/L) and TEOH (2.07 ul, 0.024 mmol, 0.5 equiv) to give disaccharide 9ha (19 mg, 70%) and 9hb (2 mg, 7%), both are white solids.

Analytical data for 9ha: Rf = 0.20 (petroleum-EtOAc 10: 1). m.p. 168 - 170 °C. [α]D 20 -109.6 (c, 1.2 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 5.75 (d, J = 11.2 Hz, 1H, -NH), 5.33 (dd, J = 5.2Hz, 1H, H-6), 5.09 (d, J = 3.2 Hz, 1H, H-1), 4.27 (dd, J = 9.6, 5.2 Hz, 1H, H-4), 4.18 - 4.06 (m, 2H, H-3, H-5), 3.47 (m, 1H, H-3), 2.35 - 2.27 (m, 1H,H-4a), 2.22 - 2.12 (m, 2H), 2.09 - 1.91 (m, 3H), 1.89 - 1.75 (m, 3H), 1.70 - 0.91 (m, 21H), 1.31 (d, J = 6.4 Hz, 3H, H-6'), 0.99 (s, 3H, H-21), 0.89 (d, J = 6.8 Hz, 3H, H-18), 0.85 (d, J = 1.8 Hz, 3H, H-26), 0.83 (d, J = 1.8 Hz, 3H, H-27), 0.65 (s, 3H, H-19).

13C NMR (100 MHz, CDCl3) δ 139.98 (C-5), 122.78 (C-19), 93.68 (C-1'), 84.65 (C-4'), 77.15, 61.80, 56.93, 56.36, 53.02, 50.34, 42.54, 39.94, 39.73, 38.22, 37.39, 36.95, 36.40, 35.99, 32.15, 32.06, 29.64, 29.55, 28.44, 28.23, 24.50, 24.03, 23.04 (C-27), 22.78 (C-26), 21.25, 19.58 (C-21), 18.93 (C-18), 18.10 (C-6'), 12.07 (C-19). HRMS calc. for C33H55NNaO5S [M+Na]+: 600.3693, found:600.3709.

Analytical data for 9hb: Rf = 0.10 (petroleum-EtOAc 10: 1). m.p. 164 - 166 °C. [α]D 20 -29.2 (c, 0.5 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 5.34 (d, J = 5.2 Hz, 1H, H-6), 4.94 (dd, J = 8.0, 2.4 Hz, 1H, H-1), 4.61 (d, J = 6.0 Hz, 1H, -NH), 4.45 - 4.29 (m, 2H, H-3, H-4'), 3.95 (dq, J = 8.8, 6.0 Hz, 1H, H-5'), 3.61 - 3.45 (m, 1H, H-3), 2.36 - 2.23 (m, 2H), 2.11 (dt, J = 14.9, 2.8 Hz, 1H, H-2a), 2.05 - 1.91 (m, 3H), 1.88 - 1.74 (m, 3H), 1.70 - 1.00 (m, 21H),1.35 (d, J = 6.0 Hz, 3H, H-6'), 0.97 (s, 3H, H-21), 0.89 (d, J = 6.8 Hz, 3H, H-18), 0.85 (d, J = 1.8 Hz, 3H, H-26), 0.83 (d, J = 1.8 Hz, 3H H-27), 0.65 (s, 3H, H-19). 13C NMR (100 MHz, CDCl3) δ 140.70 (C-5), 122.32 (C-6'), 95.10 (C-1'), 83.10 (C-4'), 78.23, 68.55 (C-5'), 56.97, 56.36, 53.38 (C-3'), 50.33, 42.54, 40.39, 39.97, 39.73, 37.23, 36.91, 36.40, 36.00, 32.93 (C-2'), 32.14, 32.09, 28.44, 28.23, 24.50, 24.04, 23.04 (C-27), 22.78 (C-26), 21.27, 19.54 (C-21), 18.94 (C-18), 18.60 (C-6'), 12.08 (C-19). HRMS calc. for C33H55NNaO5S [M+Na]+: 600.3693, found:600.3697.
7. Modification of diosgenin

To a suspension of LiAlH₄ (3.8 mg, 0.1 mmol, 3.0 equiv) in dry THF (0.1 ml), compound 9g-α (20 mg, 0.033 mmol, 1.0 equiv) in dry THF (0.23 ml) was added dropwise at 0 °C. The reaction mixture was stirred at r.t for 3 h and then quenched with Na₂SO₄·10H₂O and filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography (petroleum-EtOAc-Et₃N 100: 5: 10) to afford the 11a (15 mg, 85%) as white solid. Analytical data for 11a: Rᶠ = 0.40 (DCM- MeOH 10: 1), m.p. 195 - 197 ºC. [α]D²⁰ =-85.0 (c, 1.0 in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 5.30 (d, J = 4.0 Hz, 1H, H-6), 5.00 (s, 1H, H-1’), 4.38 (dd, J = 15.2, 7.2 Hz, 1H, H-16), 4.30-3.90 (br s, 3H, -OH, -NH₂), 3.82 (dt, J = 12.0, 6.4 Hz, 1H, H-5’), 3.70 (s, 1H, H-4’), 3.51 – 3.40 (m, 3H, H-3’, H-26), 3.35 (t, J = 10.8 Hz, 1H), 2.35 – 2.12 (m, 3H), 2.02 – 1.35 (m, 19H), 1.26 (d, J = 6.0 Hz, 3H, H-6’), 1.20 – 1.02 (m, 4H), 1.00 (s, 3H, H-19), 0.95 (d, J = 6.8 Hz, 3H, H-27), 0.77 (s, 3H, -CH₃), 0.76 (s, 3H, -CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 140.45, 122.03, 109.48, 102.08, 94.70, 81.00, 77.75, 69.70, 67.06, 63.74, 62.32, 56.76, 50.24, 49.51, 41.83, 40.47, 39.99, 38.44, 37.50, 37.09, 32.29, 32.07, 31.63, 30.51, 29.91, 29.57, 29.02, 21.11, 19.64, 18.26, 17.35, 16.52, 14.75. HRMS calc. for C₃₃H₅₄NO₅ [M+H]⁺: 544.4002, found: 544.4004.
To a solution of 9ga (40mg, 0.066 mmol, 1.0 equiv) in dry DCM (0.66 ml, c = 0.1 mmol/ml) was added CbzCl (11.3ul, 0.08 mmol, 1.2 equiv) dropwise at 0°C, followed by Et3N (45.7ul, 0.33 mmol, 5.0 equiv). The resulting mixture was stirred at room temperature for 1 h, then quenched with saturated aqueous NaHCO3. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine, dried over Na2SO4. After concentration at reduced pressure, t the residue was purified by silica gel column chromatography (petroleum-EtOAc 4: 1) to afford the 10 (48mg, 98%) as white solid.

Analytical data for 10: Rf = 0.50 (petroleum-EtOAc 3: 1). m.p. 150 - 152 °C. [α]D20 -110.7 (c, 1.0 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.40 – 7.30 (m, 5H, -Ph), 5.36 – 5.25 (m, 3H, H-6, -CH2Ph), 5.02 – 4.93 (t, J = 6.8 Hz, 1H, H-1’), 4.51 (t, J = 7.2 Hz, 1H, H-4’), 4.38 (dd, J = 14.8, 7.6 Hz, 1H, H-3’), 4.25 (m, J = 12.0, 6.0 Hz, 1H, H-3’), 4.13 (dq, J = 13.2, 6.4 Hz, 1H, H-5’), 3.52 – 3.42 (m, 2H, H-26’), 3.35 (t, J = 11.2 Hz, 1H), 2.55 – 1.02 (m, 26H), 1.34 (d, J = 6.4 Hz, 3H, H-6’), 0.99 (s, 3H, H-19’), 0.95 (d, J = 6.8 Hz, 3H, H-27’), 0.77 (s, 3H, -CH3), 0.76 (s, 3H, -CH3). 13C NMR (1010 MHz, CDCl3) δ 149.94, 140.67, 134.58, 128.93, 128.90, 128.14, 121.87, 109.51, 94.66, 81.02, 80.19, 69.70, 67.07, 64.28, 62.31, 56.71, 53.63, 50.30, 41.82, 40.48, 39.98, 38.91, 37.45, 37.08, 32.29, 32.06, 31.63, 31.60, 30.52, 30.03, 29.92, 29.02, 21.05, 19.58, 19.13, 17.35, 16.50, 14.74. HRMS calc. for C41H77NNaO8S [M+Na]+: 762.3652, found: 762.3625.

Prepared from 10 (15mg, 0.02 mmol) with TBAOAc (30.5 mg, 0.1 mmol, 5.0 equiv) according to General Procedure C to give 11b (13 mg, 95% yield) as white solid. Analytical data for 11b: Rf = 0.45 (petroleum-EtOAc 3: 1). m.p. 148 - 150 °C. [α]D20 -129.0 (c, 1.4 in CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.43 – 7.27 (m, 5H, -Ph), 6.24 (d, J = 8.0 Hz, 1H, -NH), 5.31 (d, J = 4.0 Hz, 1H, H-6’), 5.17 (d, J = 12.0 Hz, 1H, -CHPh), 5.03 (d, J = 12.4 Hz, 2H, H-1’, -CHPh), 4.80 (s, 1H, H-4’), 4.39 (dd, J = 14.8, 7.2 Hz, 1H, H-16’), 4.20 (dt, J = 12.8, 6.0 Hz, 1H, H-5’), 3.92-3.80 (m, 1H, H-3’), 3.52 – 3.40 (m, 2H, H-26’), 3.35 (t, J = 10.8 Hz, 1H), 2.40 – 1.10 (m, 26H), 2.11 (s, 3H, -OAc), 1.07 (d, J = 6.4 Hz, 3H, H-6’), 1.00 (s, 3H, H-19’), 0.95 (d, J = 7.2 Hz, 3H, H-27’), 0.77 (s, 3H, -CH3), 0.76 (s, 3H, -CH3). 13C NMR (100 MHz, CDCl3) δ 170.02, 155.61, 140.46, 136.88, 128.69, 128.48, 128.29, 122.07, 109.49, 95.16, 81.01, 76.73, 69.97, 67.05, 66.85, 62.30, 61.39, 56.69, 50.27, 46.49, 41.81, 40.47, 39.96, 38.58, 37.44, 37.09, 32.27, 32.05, 31.61, 31.59, 30.50, 29.80, 29.07, 29.01, 21.12, 20.14, 19.63, 17.34, 16.89, 16.48, 14.73. HRMS calc. for C43H67NNaO8 [M+Na]+: 742.4306, found: 742.4289.
Prepared from 10 (20 mg, 0.027mmol) with KSAc (15.4mg, 0.135mmol, 5.0equiv) according to **General Procedure C** to give 11c (18.8 mg, 94% yield) as white solid. Analytical data for 11c: \( R_f = 0.55 \) (petroleum-EtOAc 3: 1). m.p. 95-97 °C. \([\alpha]_D^{20} = -119.7\) (c, 1.5 in CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.40 – 7.26 (m, 5H, -Ph), 6.39 (d, \( J = 7.6 \) Hz, 1H, -NH), 5.30 (d, \( J = 4.0 \) Hz, 1H, -H-6), 5.21 (d, \( J = 12.4 \) Hz, 1H, -CHPh), 5.03 (d, \( J = 12.4 \) Hz, 1H, -CHPh), 4.99 (d, \( J = 2.0 \) Hz, 1H, H-1'), 4.46 – 4.33 (m, 2H, H-16, H-5'), 3.95 (m, 1H, H-3'), 3.77 (s, 1H, H-4'), 3.44 (m, 2H, H-26), 3.35 (s, \( J = 10.9 \) Hz, 1H), 2.36 (s, 3H, -SAc), 2.32 – 1.13 (m, 26H), 1.11 (d, \( J = 6.4 \) Hz, 3H, H-6'), 1.01 (s, 3H, H-19), 0.95 (d, \( J = 7.2 \) Hz, 3H, H-27), 0.77 (s, 3H, -CH₃), 0.76 (s, 3H, -CH₃). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 193.71, 155.47, 140.46, 136.94, 128.70, 128.54, 128.29, 122.04, 109.50, 95.33, 81.01, 76.78, 67.06, 66.83, 62.29, 61.06, 56.69, 50.25, 49.40, 47.96, 41.81, 40.47, 39.96, 38.56, 37.45, 37.09, 32.27, 32.05, 31.61, 31.59, 30.98, 30.65, 30.51, 29.83, 29.01, 21.04, 19.64, 18.55, 17.35, 16.49, 14.73. HRMS calc. for \( \text{C}_{43}\text{H}_{61}\text{NNaO}_{7} \) [M+Na]⁺: 758.4060, found: 758.4058.

Prepared from 10 (15 mg, 0.02 mmol) with Na₃ (6.5 mg, 0.1 mmol, 5.0 equiv) according to **General Procedure C** to give 11d (12 mg, 87% yield) as white solid. Analytical data for 11d: \( R_f = 0.52 \) (petroleum-EtOAc 3: 1). m.p. 110 – 112 °C. \([\alpha]_D^{20} = -115.0\) (c, 1.2 in CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.39 – 7.30 (m, 5H, -Ph), 6.34 (d, \( J = 7.6 \) Hz, 1H, -NH), 5.31 (d, \( J = 4.0 \) Hz, 1H, -H-6), 5.16 (d, \( J = 12.4 \) Hz, 1H, -CHPh), 5.03 (d, \( J = 14.2 \), 7.6 Hz, 1H, -H-16), 4.18 (dd, \( J = 13.2 \), 6.4 Hz, 1H, H-3'), 4.03 (s, 1H, H-4'), 3.50 – 3.31 (m, 4H), 2.35 – 1.02 (m, 26H), 1.21 (d, \( J = 6.8 \) Hz, 3H, H-19'), 1.00 (s, 3H, H-19), 0.95 (d, \( J = 7.2 \) Hz, 3H, H-27), 0.77 (s, 3H, -CH₃), 0.76 (s, 3H, -CH₃). \(^{13}\)C NMR (100 MHz, CDCl₃) \( \delta \) 155.68, 140.35, 136.74, 128.76, 128.38, 122.15, 109.50, 95.06, 81.01, 76.76, 67.06, 66.91, 62.31, 61.94, 61.47, 56.68, 50.26, 47.32, 41.82, 40.47, 39.97, 38.58, 37.44, 37.08, 32.27, 32.05, 31.61, 30.51, 29.82, 29.02, 28.62, 21.05, 19.63, 17.74, 17.34, 16.49, 14.73. HRMS calc. for \( \text{C}_{44}\text{H}_{58}\text{NaNO}_6 \) [M+Na]⁺: 725.4254, found: 725.4280.
8. Reference


9. NMR Spectra

Figure S1. $^1$H NMR spectrum of 4a (CDCl$_3$, 400 MHz)

Figure S2. $^{13}$C NMR spectrum of 4a (CDCl$_3$, 100 MHz)
Figure S3. $^1$H NMR spectrum of 4a' (CDCl$_3$, 400 MHz)

Figure S4. $^1$H NMR spectrum of 4a' (CDCl$_3$, 400 MHz)
Figure S5. $^1$H NMR spectrum of 4c (CDCl$_3$, 400 MHz)

Figure S6. $^{13}$C NMR spectrum of 4c (CDCl$_3$, 100 MHz)
Figure S7. $^1$H NMR spectrum of 4d (CDCl$_3$, 400 MHz)

Figure S8. $^{13}$C NMR spectrum of 4d (CDCl$_3$, 100 MHz)
Figure S9. $^1$H NMR spectrum of 4e (CDCl$_3$, 400 MHz)

Figure S10. $^{13}$C NMR spectrum of 4e (CDCl$_3$, 100 MHz)
Figure S11. $^1$H NMR spectrum of 4f (CDCl$_3$, 400 MHz)

Figure S12. $^{13}$C NMR spectrum of 4f (CDCl$_3$, 100 MHz)
Figure S13. $^1$H NMR spectrum of 4g (CDCl$_3$, 400 MHz)

Figure S14. $^{13}$C NMR spectrum of 4g (CDCl$_3$, 100 MHz)
Figure S15. $^1$H NMR spectrum of 4h (CDCl$_3$, 400 MHz)

Figure S16. $^{13}$C NMR spectrum of 4h (CDCl$_3$, 100 MHz)
Figure S17. $^1$H NMR spectrum of 4i (CDCl$_3$, 400 MHz)

Figure S18. $^{13}$C NMR spectrum of 4i (CDCl$_3$, 100 MHz)
Figure S19. $^1$H NMR spectrum of 4j (CDCl$_3$, 400 MHz)

Figure S20. $^{13}$C NMR spectrum of 4j (CDCl$_3$, 100 MHz)
Figure S21. $^1$H NMR spectrum of 4k (CDCl$_3$, 400 MHz)

Figure S22. $^{13}$C NMR spectrum of 4k (CDCl$_3$, 100 MHz)
Figure S23. $^1$H NMR spectrum of 5 (CDCl$_3$, 400 MHz)

Figure S24. $^{13}$C NMR spectrum of 5 (CDCl$_3$, 100 MHz)
Figure S25. $^1$H NMR spectrum of 6a (CDCl$_3$, 400 MHz)

Figure S26. $^{13}$C NMR spectrum of 6a (CDCl$_3$, 100 MHz)
Figure S27. $^1$H NMR spectrum of 6b (CDCl$_3$, 400 MHz)

Figure S28. $^{13}$C NMR spectrum of 6b (CDCl$_3$, 100 MHz)
Figure S29. $^1$H NMR spectrum of 6c (CDCl$_3$, 400 MHz)

Figure S30. $^{13}$C NMR spectrum of 6c (CDCl$_3$, 100 MHz)
Figure S31. $^1$H NMR spectrum of 6d (CDCl$_3$, 400 MHz)

Figure S32. $^{13}$C NMR spectrum of 6d (CDCl$_3$, 100 MHz)
Figure S33. $^1$H NMR spectrum of 6e (CDCl$_3$, 400 MHz)

Figure S34. $^{13}$C NMR spectrum of 6e (CDCl$_3$, 100 MHz)
Figure S35. $^1$H NMR spectrum of 6f (CDCl$_3$, 400 MHz)

Figure S36. $^{13}$C NMR spectrum of 6f (CDCl$_3$, 100 MHz)
Figure S37. $^1$H NMR spectrum of 6g (CDCl$_3$, 400 MHz)

Figure S38. $^{13}$C NMR spectrum of 6g (CDCl$_3$, 100 MHz)
Figure S39. $^1$H NMR spectrum of 3bα (CDCl$_3$, 400 MHz)

Figure S40. $^{13}$C NMR spectrum of 3bα (CDCl$_3$, 100 MHz)
Figure S41. $^1$H NMR spectrum of 3bβ (CDCl$_3$, 400 MHz)

Figure S42. $^{13}$C NMR spectrum of 3bβ (CDCl$_3$, 100 MHz)
Figure S43. $^1$H NMR spectrum of 3ca (CDCl$_3$, 400 MHz)

Figure S44. $^{13}$C NMR spectrum of 3ca (CDCl$_3$, 100 MHz)
Figure S45. $^1$H NMR spectrum of 3cβ (CDCl$_3$, 400 MHz)

Figure S46. $^{13}$C NMR spectrum of 3cβ (CDCl$_3$, 100 MHz)
Figure S47. $^1$H NMR spectrum of 3da (CDCl$_3$, 400 MHz)

Figure S48. $^{13}$C NMR spectrum of 3da (CDCl$_3$, 100 MHz)
Figure S49. $^1$H NMR spectrum of 3dβ (CDCl$_3$, 400 MHz)

Figure S50. $^{13}$C NMR spectrum of 3dβ (CDCl$_3$, 100 MHz)
Figure S51. $^1$H NMR spectrum of 3ga (CDCl$_3$, 400 MHz)

Figure S52. $^{13}$C NMR spectrum of 3ga (CDCl$_3$, 100 MHz)
Figure S53. $^1$H NMR spectrum of 3g$\beta$ (CDCl$_3$, 400 MHz)
Figure S54. $^1$H NMR spectrum of 7 (CDCl$_3$, 400 MHz)

Figure S55. $^{13}$C NMR spectrum of 7 (CDCl$_3$, 100 MHz)
Figure S56. $^1$H NMR spectrum of 9aa (acetone-$d_6$, 400 MHz)

Figure S57. $^{13}$C NMR spectrum of 9aa (acetone-$d_6$, 100 MHz)
Figure S58. $^1$H - $^1$H COSY spectrum of 9aa (acetone-$d_6$, 400 MHz)

Figure S59. HSQC spectrum of 9aa (acetone-$d_6$)
Figure S60. $^1$H NMR spectrum of 9αβ (acetone-$d_6$, 400 MHz)

Figure S61. $^{13}$C NMR spectrum of 9αβ (acetone-$d_6$, 100 MHz)
Figure S62. $^1$H - $^1$H COSY spectrum of 9aβ (acetone-$d_6$, 400 MHz)

Figure S63. HSQC spectrum of 9aβ (acetone-$d_6$)
Figure S64. $^1$H NMR spectrum of 9b (CDCl$_3$, 400 MHz)

Figure S65. $^{13}$C NMR spectrum of 9b (CDCl$_3$, 100 MHz)
Figure S6. $^1$H - $^1$H COSY spectrum of 9b (CDCl$_3$, 400 MHz)

Figure S67. HSQC spectrum of 9b (CDCl$_3$)
Figure S68 $^1$H NMR spectrum of 9ca (CDCl$_3$, 400 MHz)

Figure S69 $^{13}$C NMR spectrum of 9ca (CDCl$_3$, 100 MHz)
Figure S70 $^1$H - $^1$H COSY spectrum of 9ca (CDCl$_3$, 400 MHz)

Figure S71 HSQC spectrum of 9ca (CDCl$_3$)
Figure S72 $^1$H NMR spectrum of 9cβ (CDCl$_3$, 400 MHz)

Figure S73 $^{13}$C NMR spectrum of 9cβ (CDCl$_3$, 100 MHz)
Figure S74 $^1$H - $^1$H COSY spectrum of 9cβ (CDCl$_3$, 400 MHz)

Figure S75 HSQC spectrum of 9cβ (CDCl$_3$)
Figure S76 $^1$H NMR spectrum of 9d (acetone-$d_6$, 400 MHz)

Figure S77 $^{13}$C NMR spectrum of 9d (acetone-$d_6$, 100 MHz)
Figure S78 $^1$H - $^1$H COSY spectrum of 9d (acetone-$d_6$, 400 MHz)

Figure S79 HSQC spectrum of 9d (acetone-$d_6$)
Figure S80 $^1$H NMR spectrum of 9ea (CDCl$_3$, 400 MHz)

Figure S81 $^{13}$C NMR spectrum of 9ea (CDCl$_3$, 100 MHz)
Figure S82 $^1$H - $^1$H COSY spectrum of 9ea (CDCl$_3$, 400 MHz)

Figure S83 HSQC spectrum of 9ea (CDCl$_3$)
Figure S84  $^1$H NMR spectrum of 9eβ (CDCl$_3$, 400 MHz)

Figure S85  $^{13}$C NMR spectrum of 9eβ (CDCl$_3$, 100 MHz)
Figure S86 $^1$H - $^1$H COSY spectrum of 9eβ (CDCl₃, 400 MHz)

Figure S87 HSQC spectrum of 9eβ (CDCl₃)
Figure S8 $^1$H NMR spectrum of 9fa (CDCl$_3$, 400 MHz)

Figure S9 $^{13}$C NMR spectrum of 9fa (CDCl$_3$, 100 MHz)
Figure S90  $^1$H - $^1$H COSY spectrum of 9fa (CDCl$_3$, 400 MHz)

Figure S91. HSQC spectrum of 9fa (CDCl$_3$)
Figure S92. $^1$H NMR spectrum of 9fβ (CDCl$_3$, 400 MHz)

Figure S93. $^{13}$C NMR spectrum of 9fβ (CDCl$_3$, 100 MHz)
Figure S94. $^1\text{H} - ^1\text{H}$ COSY spectrum of $9\text{f}\beta$ (CDCl$_3$, 400 MHz)

Figure S95. HSQC spectrum of $9\text{f}\beta$ (CDCl$_3$)
Figure S96. $^1$H NMR spectrum of 9ga (CDCl$_3$, 400 MHz)

Figure S97. $^{13}$C NMR spectrum of 9ga (CDCl$_3$, 100 MHz)
Figure S98. $^1$H NMR spectrum of 9gβ (CDCl$_3$, 400 MHz)

Figure S99. $^{13}$C NMR spectrum of 9gβ (CDCl$_3$, 100 MHz)
**Figure S100** $^1$H NMR spectrum of 9α (CDCl$_3$, 400 MHz)

**Figure S101** $^{13}$C NMR spectrum of 9α (CDCl$_3$, 100 MHz)
Figure S102 \( ^1H \cdot ^1H \) COSY spectrum of 9ha (CDCl\(_3\), 400 MHz)

Figure S103 HSQC spectrum of 9ha (CDCl\(_3\))
Figure S104 $^1$H NMR spectrum of $9\beta$ (CDCl$_3$, 400 MHz)

Figure S105 $^{13}$C NMR spectrum of $9\beta$ (CDCl$_3$, 100 MHz)
Figure S106  $^1$H - $^1$H COSY spectrum of 9hβ (CDCl$_3$, 400 MHz)

Figure S107 HSQC spectrum of 9hβ (CDCl$_3$)
Figure S108 $^1$H NMR spectrum of 11a (CDCl$_3$, 400 MHz)

Figure S109 $^{13}$C NMR spectrum of 11a (CDCl$_3$, 100 MHz)
Figure S110  $^1$H NMR spectrum of 10 (CDCl$_3$, 400 MHz)

Figure S111  $^{13}$C NMR spectrum of 10 (CDCl$_3$, 100 MHz)
Figure S112. $^1$H NMR spectrum of 11b (CDCl$_3$, 400 MHz)

Figure S113. $^{13}$C NMR spectrum of 11b (CDCl$_3$, 100 MHz)
Figure S114. $^1$H NMR spectrum of 11c (CDCl$_3$, 400 MHz)

Figure S115. $^{13}$C NMR spectrum of 11c (CDCl$_3$, 100 MHz)
Figure S116. $^1$H NMR spectrum of 11d (CDCl$_3$, 400 MHz)

Figure S117. $^{13}$C NMR spectrum of 11d (CDCl$_3$, 100 MHz)