Supporting Information

For

PHOTO-IRRADIATION-PROMOTED AMINOETHERIFICATION OF GLYCALS WITH N-ACYLIMINOIODINANE AND ALCOHOLS

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1. General information

Solvents and materials were obtained from commercial suppliers and used without further purification. Analytical thin-layer chromatography was performed using Silica gel 60 plates (Merck, Darmstadt, Germany). Silica gel column chromatography was performed using Kanto silica gel 60 (particle size 63–210 μm, Kanto, Tokyo, Japan) and Chromatorex BW-300 (Fuji silysia, Aichi, Japan). Proton nuclear magnetic resonance (\(^1\)H NMR) spectra were recorded on JNM-AL 400 (JEOL) at 400 MHz or Avance I 600 (Bruker Biospin AG, Switzerland) at 600 MHz. Chemical shifts were reported relative to Me4Si (δ 0.00) in CDCl3. Multiplicity was indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad); brs (broad singlet). Carbon nuclear magnetic resonance (\(^{13}\)C NMR) spectra were recorded on a JNM-AL 400 at 100 MHz or on an Avance I 600 at 150 MHz. Chemical shifts were reported relative to CDCl3 (δ 77.0). Fluorine nuclear magnetic resonance (\(^{19}\)F NMR) spectra were recorded on a JNM-AL 400 at 376 MHz. Infrared spectra were recorded on a FT/IR-4100 Fourier-transform infrared spectrometer (JASCO, Tokyo, Japan) ATR (attenuated total reflectance). High resolution mass spectra were recorded on a LCMS-IT-TOF (Shimadzu, Kyoto, Japan) for ESI-MS. All melting points were measured on BÜCHI M-565 melting point apparatus and are uncorrected.

2. Preparation of N-acyliminoiodinane and substrate

N-acyliminoiodinane 1\(^{1)}\) and glycols 2\(^{1)}\) and 11\(^{2)}\) were prepared by following the literature.

3. Optimized general procedure for the photo-induced aminomethylation

A mixture of glycal 2 or 11 (0.1 mmol, 44.3 mg), iminoiodinane 1 (0.2 mmol, 71.8 mg), and activated molecular sieves 5Å (MS 5Å, 50 mg) in dry dichloromethane (2.0 mL) was stirred at room temperature for 30 min. The reaction mixture was then cooled to 0°C and stirred at the same temperature for 6 h under black light irradiation (λ = 365 nm), when the consumption of glycal was monitored by TLC. To the resulting mixture, was added alcohol (0.1 mmol or 0.3 mmol), and the whole mixture was stirred at room temperature for 30 min before the addition of TMSOTf (0.02 mmol, 3.6 μL). The reaction mixture was further stirred at room temperature overnight. After concentration of the solvent under reduced pressure, direct purification by flash column chromatography on silica gel gave the desired aminoconjugate 6 or 13. The spectral data of 6a-c were reported in the preliminary communication.\(^{1)}\)

**Benzyl 2-deoxyl-2-trifluoroacetamido-3-O-triisopropylsilyl-4,6-O-(1,1-di-tert-butyldisiloxy-1-yl)-β-D-glucopyranoside (13a)**

![Chemical Structure](image)

White solid; m. p. 137.9 °C (decomp.); \(^1\)H-NMR (600 MHz, CDCl3) δ: 7.37–7.26 (5H, m), 6.32 (1H, d, J = 8.2 Hz), 4.90 (1H, d, J = 8.8 Hz, H-1), 4.83 (1H, d, J = 11.5 Hz), 4.55 (1H, d, J = 11.5 Hz), 4.19 (1H, dd, J = 9.9, 4.9 Hz), 4.12 (1H, t, J = 9.1 Hz), 3.95 (1H, t, J = 10.2 Hz), 3.77 (1H, t, J = 8.8 Hz), 3.52 (1H, q, J = 8.8 Hz), 3.41 (1H, td, J = 9.9, 4.8 Hz), 1.12–1.08 (30H, m), 0.99 (9H, s); \(^{13}\)C-NMR (150 MHz, CDCl3) δ: 157.2 (q, J = 37.0 Hz), 136.7, 128.5, 128.1, 128.0, 115.6 (q, J = 288.7 Hz, CF3), 98.2, 79.0, 74.6, 71.0, 70.3, 66.1, 59.7, 27.4, 26.9, 22.8, 19.9, 18.4, 18.2, 13.3; \(^{19}\)F-NMR (376 MHz, CDCl3) δ: −75.84; ESI-HRMS Calcd. for C\(_{32}\)H\(_{33}\)F\(_3\)N\(_2\)O\(_3\)Si\(_2\) [M+H]^+ 660.3369; Found: 660.3370; IR (ATR) 3276, 1701 cm\(^{-1}\); [\(\alpha\)]\(_D\)\(^{25}\) −43.1 (c 1.21, CHCl3).
**Isopropyl 2-deoxy-2-trifluoroacetamido-3-O-triisopropylsilyl-4,6-O-(1,1-di-tert-butylsiloxane-1-yl)-β-D-glucopyranoside (13b)**

![Chemical Structure]

White solid; m. p. 200.5 °C (decomp.); ¹H-NMR (600 MHz, CDCl₃) δ: 6.45 (1H, d, J = 7.1 Hz), 5.04 (1H, d, J = 8.8 Hz, H-1), 4.28 (1H, t, J = 9.1 Hz), 4.14 (1H, dd, J = 10.4, 4.9 Hz), 3.93–3.90 (2H, m), 3.74 (1H, t, J = 8.8 Hz), 3.43 (1H, td, J = 9.9, 4.9 Hz), 3.25 (1H, q, J = 8.6 Hz), 1.19 (3H, d, J = 6.0 Hz), 1.16–1.04 (33H, m), 0.99 (9H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 157.2 (q, J = 36.6 Hz), 115.6 (q, J = 288.7 Hz, CF₃), 97.4, 79.2, 74.2, 72.3, 70.2, 66.2, 60.7, 27.4, 27.0, 23.4, 22.8, 21.7, 19.9, 18.4, 18.2, 13.3; ¹⁹F-NMR (376 MHz, CDCl₃) δ: −76.09; ESI-HRMS Calcd. for C₂₉H₃₃F₃NO₆Si₂ [M–H]⁻ 612.3369; Found: 612.3365; IR (ATR) 3275, 1702 cm⁻¹; [α]D²⁵ −19.3 (c 0.69, CHCl₃).

**Cyclopropyl 2-deoxy-2-trifluoroacetamido-3-O-triisopropylsilyl-4,6-O-(1,1-di-tert-butylsiloxane-1-yl)-β-D-glucopyranoside (13c)**

![Chemical Structure]

White solid; m. p. 193.9 °C (decomp.); ¹H-NMR (600 MHz, CDCl₃) δ: 6.44 (1H, d, J = 7.7 Hz), 5.06 (1H, d, J = 8.8 Hz, H-1), 4.27 (1H, t, J = 9.1 Hz), 4.14 (1H, dd, J = 10.4, 4.9 Hz), 3.92 (1H, t, J = 10.2 Hz), 3.74 (1H, t, J = 8.8 Hz), 3.60–3.57 (1H, m), 3.43 (1H, td, J = 9.9, 4.9 Hz), 3.29 (1H, q, J = 8.8 Hz), 1.85–1.84 (1H, m), 1.77–1.75 (1H, m), 1.70–1.67 (2H, m), 1.50–1.49 (1H, m), 1.37–1.33 (1H, m), 1.25–1.21 (2H, m), 1.14–1.12 (2H, m), 1.08–1.05 (30H, m), 0.99 (9H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 157.2 (q, J = 36.6 Hz), 115.6 (q, J = 288.7 Hz, CF₃), 97.2, 79.1, 74.2, 70.2, 66.2, 60.7, 33.4, 31.6, 27.4, 27.0, 25.4, 22.8, 19.9, 18.4, 18.2, 13.3; ¹⁹F-NMR (376 MHz, CDCl₃) δ: −76.03; ESI-HRMS Calcd. for C₃₁H₅₅F₃NO₆Si₂ [M–H]⁻ 652.3682; Found: 652.3669; IR (ATR) 3322, 1703 cm⁻¹; [α]D²⁵ −76.2 (c 0.09, CHCl₃).

**tert-Butyl 2-deoxy-2-trifluoroacetamido-3-O-triisopropylsilyl-4,6-O-(1,1-di-tert-butylsiloxane-1-yl)-β-D-glucopyranoside (13d)**

![Chemical Structure]

White solid; m. p. 168.5 °C (decomp.); ¹H-NMR (600 MHz, CDCl₃) δ: 6.47 (1H, d, J = 6.6 Hz), 5.13 (1H, d, J = 8.2 Hz, H-1), 4.35 (1H, t, J = 8.8 Hz), 4.08 (1H, dd, J = 10.4, 4.9 Hz), 3.92 (1H, t, J = 10.4 Hz), 3.73 (1H, t, J = 8.8 Hz), 3.42 (1H, td, J = 9.9, 5.1 Hz), 3.23 (1H, q, J = 8.6 Hz), 1.20 (9H, s), 1.08–1.05 (30H, m), 1.00 (9H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 157.1 (q, J = 36.2 Hz), 115.6 (q, J = 288.7 Hz, CF₃), 93.5, 79.1, 76.5, 74.0, 69.9, 66.2, 61.1, 28.5, 27.4, 27.0, 22.8, 19.9, 18.4, 18.2, 13.3; ¹⁹F-NMR (376 MHz, CDCl₃) δ: −76.06; ESI-HRMS Calcd. for C₂₉H₃₉F₃NO₆Si₂ [M–H]⁻ 626.3526; Found: 626.3529; IR (ATR) 3307, 1704 cm⁻¹; [α]D²⁰ −12.5 (c 1.61, CHCl₃).

S3
Phenyl 2-deoxyl-2-trifluoroacetamido-3-O-triisopropylsilyl-4,6-O-(1,1-di-tert-butylsiloxane-1-yl)-β-D-glucopyranoside (13e)

White solid; m. p. 213.2 °C (decomp.); 1H-NMR (600 MHz, CDCl3) δ: 7.28 (2H, t, J = 8.0 Hz), 7.06 (1H, t, J = 7.4 Hz), 6.96 (2H, d, J = 8.2 Hz), 6.44 (1H, d, J = 8.2 Hz), 5.41 (1H, d, J = 8.8 Hz, H-1), 4.23-4.20 (2H, m), 3.96 (1H, t, J = 10.2 Hz), 3.86 (1H, t, J = 8.8 Hz), 3.76 (1H, q, J = 8.8 Hz), 3.55 (1H, td, J = 9.7, 4.9 Hz), 1.19–1.06 (30H, m), 1.01 (9H, s); 13C-NMR (150 MHz, CDCl3) δ: 157.4 (J = 38.4 Hz), 157.0, 129.6, 123.4, 117.1, 115.6 (q, J = 288.7 Hz, CF3), 98.2, 78.8, 74.6, 70.6, 66.1, 59.5, 27.4, 27.0, 22.8, 19.9, 18.4, 18.2, 13.3; 19F-NMR (376 MHz, CDCl3) δ: −75.87; ESI-HRMS Calcd. for C31H33F3NO5Si2 [M−H]− 646.3213; Found: 646.3216; IR (ATR) 3256, 1704 cm−1; [α]D0 20 −25.1 (c 0.17, CHCl3).

2-Naphthyl 2-deoxyl-2-trifluoroacetamido-3-O-triisopropylsilyl-4,6-O-(1,1-di-tert-butylsiloxane-1-yl)-β-D-glucopyranoside (13f)

White solid; m. p. 227.7 °C (decomp.); 1H-NMR (600 MHz, CDCl3) δ: 7.78–7.73 (3H, m), 7.45 (1H, t, J = 7.1 Hz), 7.38 (1H, t, J = 7.1 Hz), 7.31 (1H, d, J = 1.6 Hz), 7.14 (1H, dd, J = 9.1, 2.5 Hz), 6.54 (1H, d, J = 7.7 Hz), 5.56 (1H, d, J = 8.2 Hz, H-1), 4.28–4.23 (2H, m), 3.99 (1H, t, J = 10.2 Hz), 3.90 (1H, t, J = 8.8 Hz), 3.83 (1H, q, J = 8.8 Hz), 3.63 (1H, td, J = 9.9, 4.9 Hz), 1.11–1.08 (30H, m), 1.02 (9H, s); 13C-NMR (150 MHz, CDCl3) δ: 157.4 (q, J = 37.0 Hz), 154.7, 134.1, 130.2, 129.8, 127.7, 127.2, 126.6, 124.7, 118.7, 115.6 (q, J = 288.7 Hz, CF3), 111.8, 98.3, 78.8, 74.6, 70.7, 66.1, 59.5, 27.4, 27.0, 22.8, 20.0, 18.4, 18.2, 13.3; 19F-NMR (376 MHz, CDCl3) δ: −76.06; ESI-HRMS Calcd. for C35H35F3NO5Si2 [M−H]− 696.3369.; Found: 696.3363; IR (ATR) 3360, 1706 cm−1; [α]D0 20 −3.6 (c 0.19, CHCl3).

2-Deoxyl-2-trifluoroacetamido-3-O-triisopropylsilyl-4,6-O-(1,1-di-tert-butylsiloxane-1-yl)-β-D-glucopyranosyl-(1→O) -N-benzoxycarbonyl-L-serine methyl ester (13g)

White solid; m. p. 178.9 °C (decomp.); 1H-NMR (600 MHz, CDCl3) δ: 7.36–7.30 (5H, m), 6.43 (1H, dd, J = 16.5, 7.7 Hz), 5.56 (1H, d, J = 7.7 Hz), 5.13 (1H, d, J = 12.6 Hz), 5.09 (1H, d, J = 12.6 Hz), 4.82 (1H, d, J = 8.8 Hz, H-1), 4.48–4.45 (1H, m), 4.14 (2H, td, J = 9.2, 4.0 Hz), 4.07 (1H, t, J = 6.7 Hz), 3.88 (1H, t, J = 10.4 Hz), 3.82 (1H, dd, J = 10.2, 3.0 Hz), 3.74 (3H, s), 3.72 (1H, d, J = 9.3 Hz), 3.46 (1H, q, J = 8.8 Hz), 3.38 (1H, td, J = 9.9, 4.9 Hz), 1.08–1.05 (30H, m), 0.98 (9H, s); 13C-NMR (150 MHz, CDCl3) δ: 170.1, 157.3 (J = 37.0 Hz), 156.0, 136.2, 128.5, 128.1, 128.0, 115.6 (J = 288.7 Hz, CF3), 99.4, 78.8, 74.7, 70.5, 69.0, 67.1, 66.0, 59.1, 54.0, 52.7, 27.4, 26.9, 22.8, 19.9, 18.40, 18.2, 13.31; 19F-NMR (376 MHz,
CDCl₃ δ: −75.71; ESI-HRMS Calcd. for C₃₁H₆₁F₃N₂O₁₀Si₂Na [M+Na]⁺ 829.3709; Found:829.3693; IR (ATR) 3318, 1709 cm⁻¹; [α]D₂⁵ −10.8 (c 0.10, CHCl₃).

Disaccharide (13h)

White solid; m. p. 148.5 °C (decomp.); ¹H-NMR (600 MHz, CDCl₃) δ: 6.72 (1H, dd, J = 15.6, 8.5 Hz), 5.49 (1H, d, J = 4.9 Hz), 4.90 (1H, d, J = 8.2 Hz, H-1), 4.58 (1H, dd, J = 8.2, 2.2 Hz), 4.30 (1H, dd, J = 4.9, 2.2 Hz), 4.18–4.16 (3H, m), 3.94–3.88 (3H, m), 3.74 (1H, t, J = 8.8 Hz), 3.67 (1H, dd, J = 10.7, 6.9 Hz), 3.54 (1H, q, J = 8.8 Hz), 3.42 (1H, t, J = 9.9, 4.9 Hz), 1.49 (3H, s), 1.43 (3H, s), 1.32–1.32 (6H, m), 1.09–1.05 (30H, m), 0.99 (9H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 157.4 (q, J = 37.0 Hz), 115.7 (q, J = 288.7 Hz, CF₃), 109.4, 109.4, 108.7, 108.7, 99.8, 96.3, 79.0, 74.5, 71.1, 70.7, 70.4, 70.3, 68.2, 67.2, 66.1, 59.1, 27.4, 27.0, 25.9, 25.8, 24.9, 24.4, 22.8, 19.9, 18.4, 18.2, 13.3; ¹⁹F-NMR (376 MHz, CDCl₃) δ: −75.75; ESI-HRMS Calcd. for C₃₇H₆₅F₆N₃O₆Si₂ [M–H]⁻ 812.4064; Found: 812.4054; IR (ATR) 3312, 1745 cm⁻¹; [α]D₂⁰ −48.1 (c 0.40, CHCl₃).

Disaccharide (13i)

White solid; m. p. 63. 1 °C (decomp.); ¹H-NMR (600 MHz, CDCl₃) δ: 7.34–7.25 (15H, m), 6.34 (1H, d, J = 7.7 Hz), 4.97 (1H, d, J = 11.0 Hz), 4.84–4.76 (4H, m), 4.64 (1H, d, J = 12.1 Hz), 4.56 (1H, d, J = 3.8 Hz), 4.50 (1H, d, J = 11.0 Hz), 4.14–4.10 (2H, m), 4.00–3.95 (2H, m), 3.89 (1H, t, J = 10.2 Hz), 3.74–3.71 (2H, m), 3.58 (1H, dd, J = 10.7, 4.7 Hz), 3.49–3.46 (2H, m), 3.40–3.37 (2H, m), 3.33 (3H, s), 1.12–1.07 (30H, m), 0.99 (9H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 157.1 (q, J = 37.0 Hz), 138.8, 138.2, 138.1, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 115.6 (q, J = 288.7 Hz, CF₃), 99.2, 98.0, 81.9, 79.7, 78.9, 77.7, 75.6, 74.7, 74.5, 73.3, 70.3, 69.3, 67.8, 66.0, 59.6, 55.1, 27.3, 27.0, 22.8, 19.9, 18.4, 18.2, 13.3; ¹⁹F-NMR (376 MHz, CDCl₃) δ: −75.57; ESI-HRMS Calcd. for C₅₃H₇₈F₁₁N₄O₆Si₂ [M+Cl]⁺ 1052.4760; Found: 1052.4719; IR (ATR) 3306, 1745 cm⁻¹; [α]D₁⁵ −8.3 (c 0.07, CHCl₃).

S5
4. Synthesis of bioactive compound

Benzyl \((R)\)-(2,3-dihydroxypropyl)carbamate (S1)

\[
\begin{align*}
\text{HO} & \xrightarrow{\text{Cbz-Cl, K}_2\text{CO}_3} \xrightarrow{\text{THF/H}_2\text{O}} \text{HO} \\
\text{OH} & \xrightarrow{\text{S1, 93\%}} \text{NHCbz}
\end{align*}
\]

To a solution of commercially available \((R)\)-3-amino-1,2-propanediol (1.0 g, 11 mmol) in THF (30 mL) was added potassium carbonate (4.6 g, 33 mmol) in water (15 mL). The reaction mixture was cooled to 0 °C, and benzyl chloroformate (1.6 g, 11 mmol) was added dropwise. The reaction mixture was then warmed up to room temperature and stirred at the same temperature for overnight. The reaction mixture was diluted with water and extracted with EtOAc (3 × 25 mL). Combined organic layer was washed with brine (25 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give analytically pure title compound as white solid (2.3 g, 93% yield); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.35–7.34\ (5\text{H}, \text{m}), 5.12\ (3\text{H}, \text{s}), 3.80–3.77\ (1\text{H}, \text{m}), 3.63–3.58\ (2\text{H}, \text{m}), 3.38–3.33\ (2\text{H}, \text{m}), 2.60\ (1\text{H}, \text{br s}), 2.48\ (1\text{H}, \text{br s}); \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)) \(\delta: 157.6, 136.2, 128.6, 128.2, 128.1, 71.1, 67.1, 63.8, 43.3\). The NMR spectra were consistent with literature data.

Benzyl \((R)\)-(3-((tert-butyldimethylsilyl)oxy)-2-hydroxypropyl)carbamate (S2)

\[
\begin{align*}
\text{HO} & \xrightarrow{\text{TBSCI, imidazole}} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{HO} \\
\text{OH} & \xrightarrow{\text{S1, 93\%}} \text{NHCbz}
\end{align*}
\]

To a stirred solution of S1 (2.3 g, 10.2 mmol) and imidazole (1.0 g, 15 mmol) in dichloromethane (25 mL) was added a solution of TBSCI (1.6 g, 11 mmol) in dichloromethane (10 mL) at 0 °C dropwise. The reaction mixture was stirred at room temperature for 1 h, before being quenched with 1 M aqueous HCl (20 mL). The mixture was extracted with CHCl\(_3\) (3 × 25 mL), and the combined organic phase was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give title compound as colorless oil (3.4 g, 95%), which was used for the next reaction without further purification; \(^1\)H-NMR (600 MHz, CDCl\(_3\)) \(\delta: 7.36–7.35\ (4\text{H}, \text{m}), 7.32–7.31\ (1\text{H}, \text{m}), 5.20\ (1\text{H}, \text{brs}), 5.10\ (2\text{H}, \text{s}), 3.76–3.75\ (1\text{H}, \text{m}), 3.65\ (1\text{H}, \text{d}, J = 9.9\ \text{Hz}), 3.53\ (1\text{H}, \text{dd}, J = 9.9, 6.0\ \text{Hz}), 3.43–3.42\ (1\text{H}, \text{m}), 3.21–3.17\ (1\text{H}, \text{m}), 2.72\ (1\text{H}, \text{brs}), 0.89\ (9\text{H}, \text{s}), 0.07\ (6\text{H}, \text{s}); \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)) \(\delta: 157.0, 136.5, 128.5, 128.1, 128.0, 70.9, 66.8, 64.7, 43.7, 25.8, 18.2, –5.5\). The NMR spectra were consistent with literature data.

Benzyl \((R)\)-(2-(benzyloxy)-3-((tert-butyldimethylsilyl)oxy)propyl)carbamate (S3)

\[
\begin{align*}
\text{HO} & \xrightarrow{\text{TFOH, ether, rt, 5 h}} \xrightarrow{\text{S3, 50\%}} \text{HO} \\
\text{OH} & \xrightarrow{\text{S2}} \text{NHCbz}
\end{align*}
\]

To a stirred solution of S2 (600 mg, 1.77 mmol) and benzyl 2,2,2-trichloroacetimidate (500 \(\mu\text{L}, 2.66\ \text{mmol}) in ether (6.0
mL) was added trifluoromethanesulfonic acid (3 × 20 μL), and the reaction mixture was stirred at room temperature for 5 h before being quenched with Et₃N (500 μL). After the volatiles were removed under reduced pressure, the residue was directly purified by flash column chromatography on silica gel to give title compound as colorless oil (380 mg, 50%); ¹H-NMR (600 MHz, CDCl₃) δ: 7.35–7.32 (10H, m), 5.10–5.09 (3H, m), 4.66 (1H, d, J = 11.5 Hz), 4.57 (1H, d, J = 11.5 Hz), 3.72 (1H, dd, J = 10.7, 5.2 Hz), 3.65 (1H, dd, J = 10.7, 5.8 Hz), 3.58–3.57 (1H, m), 3.50 (1H, dt, J = 13.4, 5.4 Hz), 3.30–3.26 (1H, m), 0.89 (9H, s), 0.05 (6H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 156.3, 138.2, 136.6, 128.4, 128.3, 127.9, 127.9, 127.7, 127.6, 77.8, 71.9, 66.5, 63.5, 42.0, 25.7, 18.1, −5.6; ESI-HRMS Calcd. for C₃₂H₄₂NO₄Si [M+H]⁺ 430.2408; Found: 430.2408; IR (ATR) 3347, 1708 cm⁻¹; [α]ᵣ²¹⁺ +23.4 (c 0.48, CHCl₃).

**Benzyl (R)-benzyl(2-(benzoxyl)-3-((tert-butyldimethylsilyl)oxy)propyl)carbamate (S4)**

\[
\begin{align*}
&\text{TBSO} \quad \text{OBn} \\
&\quad \text{S3} \\
&\quad \text{BnBr} \\
&\quad \text{NaH} \\
&\quad \text{DMF} \\
&\quad \text{rt, 3 h} \\
&\quad \text{TBSO} \quad \text{OBn} \\
&\quad \text{S4, 92%} \\
\end{align*}
\]

To a stirred solution of S3 (380 mg, 0.88 mmol) in DMF (5.0 mL) was added NaH (60% oil suspension 53 mg, 1.33 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. BnBr (130 μL, 1.1 mmol) was then added dropwise at room temperature, and the reaction mixture was stirred at the same temperature for 3 h, before being quenched with water (10 mL). The whole mixture was extracted with n-hexane (3 × 10 mL), and the combined organic phase was concentrated under reduced pressure to give crude product, which was purified by flash column chromatography on silica gel to give title compound as colorless oil (420 mg, 92% yield); mixture of rotamers; ¹H-NMR (600 MHz, CDCl₃) δ: 7.30–7.24 (14H, m), 7.13 (1H, d, J = 7.1 Hz), 5.16–5.13 (2H, m), 4.68 (1H, t, J = 14.0 Hz), 4.59 (1H, d, J = 13.2 Hz), 4.54–4.47 (2H, m), 3.74 (2H, m), 3.61–3.55 (1H, m), 3.48–3.42 (1H, m), 3.28–3.22 (1H, m), 0.86 (9H, s), 0.01 (6H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 156.7, 156.3, 138.8, 138.5, 137.9, 137.9, 136.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.3, 127.3, 127.1, 78.4, 78.3, 72.4, 67.3, 67.2, 63.9, 63.6, 51.6, 51.6, 48.4, 47.5, 25.9, 25.8, 18.2, −5.4; ESI-HRMS Calcd. for C₃₁H₄₂NO₄Si [M+H]⁺ 520.2878; Found: 520.2874; IR (ATR) 1701 cm⁻¹; [α]ᵣ¹⁵ +53.0 (c 0.08, CHCl₃).

**Benzyl (R)-benzyl(2-(benzoxyl)-3-hydroxypropyl)carbamate (16)**

\[
\begin{align*}
&\text{TBSO} \quad \text{OBn} \\
&\quad \text{S4} \\
&\quad \text{TBAF} \\
&\quad \text{THF} \\
&\quad \text{rt, 2 h} \\
&\quad \text{HO} \quad \text{OBn} \\
&\quad \text{16, 94%} \\
\end{align*}
\]

To a stirred solution of S4 (420 mg, 0.81 mmol) in THF (10 mL) was added 1 M TBAF solution in THF (1.0 mL) and the reaction mixture was stirred at room temperature for 2 h. Concentration under reduced pressure gave crude product, which was directly purified by flash column chromatography on silica gel to give title compound as colorless oil (240 mg, 94% yield); mixture of rotamers; ¹H-NMR (600 MHz, CDCl₃) δ: 7.28–7.19 (15H, m), 5.18 (2H, s), 4.62–4.53 (4H, m), 3.65–3.29 (6H, m); ¹³C-NMR (150 MHz, CDCl₃) δ: 157.6, 138.1, 137.4, 136.3, 128.6, 128.5, 128.5, 128.1, 127.9, 127.8, 127.7, 127.4, 78.0, 71.8, 67.7, 60.7, 51.8, 46.4; ESI-HRMS Calcd. for C₂₅H₃₀NO₄Li [M+Li]⁺ 412.2095; Found: 412.2100; IR (ATR) 3347, 1708 cm⁻¹; [α]ᵣ¹⁵ +21.0 (c 0.22, CHCl₃).
Aminoglycoside (17)

Following the optimized general procedure for the photo-induced aminoetherification of glycals using 2 (44.3 mg, 0.10 mmol) and 16 (31.5 mg, 0.10 mmol), the title compound was given as white solid (48.5 mg, 51% yield); mixture of rotamers; $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$: 7.28–7.23 (13H, m), 7.09–7.08 (2H, m), 6.33 (1H, d, $J = 7.7$ Hz), 5.17 (1H, d, $J = 12.1$ Hz), 5.09 (1H, d, $J = 12.6$ Hz), 4.86 (1H, d, $J = 3.3$ Hz), 4.69–4.62 (2H, m), 4.53 (1H, d, $J = 12.1$ Hz), 4.46–4.34 (4H, m), 4.11–4.02 (3H, m), 3.75–3.70 (3H, m), 3.51–3.13 (2H, m), 1.07–1.05 (39H, m); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$: 157.5 (q, $J = 37.3$ Hz), 156.2, 137.9, 137.5, 136.5, 128.6, 128.5, 128.0, 127.8, 127.7, 127.4, 127.2, 115.9 (q, $J = 284.9$ Hz, CF$_3$), 97.7, 76.3, 74.0, 71.9, 70.1, 68.1, 67.3, 67.0, 66.3, 51.6, 50.3, 47.6, 27.4, 27.4, 23.4, 20.8, 18.1, 18.0, 12.8; $^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: –75.23; ESI-HRMS Calcd. for C$_{50}$H$_{73}$F$_3$N$_2$O$_9$Si$_2$Na [M+Na]$^+$ 981.4699; Found: 981.4691; IR (ATR) 1726, 1697 cm$^{-1}$; $[\alpha]_D^{15}$ +53.6 (c 0.25, CHCl$_3$).

Triol (18)

To a stirred solution of 17 (60 mg, 0.063 mmol) in THF (2.0 mL) was added 1 M TBAF solution in THF (320 $\mu$L), and the reaction mixture was stirred at room temperature for 12 h. After THF was removed under reduced pressure, the residue was directly purified by flash column chromatography on silica gel to give triol 18 as white solid (32 mg, 77% yield); mixture of rotamers; $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$: 7.76–7.07 (15H, m), 6.68 (1H, brs), 5.14 (1H, d, $J = 12.6$ Hz), 5.10 (1H, d, $J = 12.1$ Hz), 4.85 (1H, d, $J = 2.7$ Hz), 4.58 (1H, d, $J = 15.9$ Hz), 4.53 (1H, d, $J = 12.1$ Hz), 4.44 (1H, d, $J = 11.5$ Hz), 4.38 (2H, m), 4.03 (1H, s), 3.95–3.69 (7H, m), 3.64–3.58 (1H, m), 3.39 (1H, dd, $J = 10.4, 2.7$ Hz), 3.31–3.12 (1H, m), 2.94 (1H, brs), 1.97 (1H, brs); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$: 158.8 (q, $J = 37.0$ Hz), 156.4, 137.7, 137.2, 136.3, 128.6, 128.5, 128.5, 128.1, 127.9, 127.8, 127.7, 127.5, 127.3, 115.9 (q, $J = 286.5$ Hz, CF$_3$), 97.2, 75.6, 71.8, 70.1, 69.7, 69.2, 67.6, 66.1, 63.0, 51.5, 51.3, 47.4; $^{19}$F-NMR (376 MHz, CDCl$_3$) $\delta$: –74.85; ESI-HRMS Calcd. for C$_{33}$H$_{38}$F$_3$N$_2$O$_9$ [M+H]$^+$ 663.2524; Found: 663.2535; IR (ATR) 3424, 1719, 1696 cm$^{-1}$; $[\alpha]_D^{20}$ +61.9 (c 0.14, CHCl$_3$).
To a mixture of 18 (8.3 mg, 0.013 mmol), TEMPO (0.1 mg, 0.63 μmol), KBr (0.1 mg, 1.3 μmol), and TBAB (0.2 mg, 0.63 μmol) in dichloromethane/saturated aqueous NaHCO₃ solution (1.0 mL/1.0 mL) was added NaClO in saturated aqueous NaHCO₃ solution (7.5 mM, 2.0 mL) dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 30 min before being quenched with saturated aqueous Na₂S₂O₃/NaCl solution (3.0 mL). The mixture was extracted with EtOAc (3 × 2.0 mL), and the combined organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give crude aldehyde, which was used without further purification for the next reaction. The crude aldehyde was dissolved in MeOH (2.0 mL), and K₂CO₃ (3.5 mg, 0.025 mmol) and Ohira-Bestmann reagent 19 (2.25 μL, 0.015 mmol) were successively added. The reaction mixture was stirred at room temperature for 4 h. After MeOH was removed under reduced pressure, the resulting residue was directly purified by column chromatography on silica gel to afford title compound as white solid (6.5 mg, 79% overall yield); mixture of rotamers; ¹H-NMR (600 MHz, CDCl₃) δ: 7.80–7.09 (15H, m), 6.51 (1H, brs), 5.20 (1H, d, J = 12.6 Hz), 5.14 (1H, d, J = 12.6 Hz), 4.84 (1H, d, J = 2.7 Hz), 4.72 (1H, s), 4.62–4.58 (2H, m), 4.51–4.38 (3H, m), 4.01 (1H, s), 3.96–3.79 (3H, m), 3.59 (1H, d, J = 7.7 Hz), 3.43 (1H, dd, J = 10.7, 2.5 Hz), 3.15–3.08 (2H, m), 2.77 (1H, brs), 2.59 (1H, s); ¹³C-NMR (150 MHz, CDCl₃) δ: 159.0 (q, J = 38.4 Hz), 156.3, 137.6, 137.2, 136.3, 128.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.6, 127.3, 115.9 (q, J = 38.4 Hz), 156.3, 137.6, 137.2, 136.3, 128.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.6, 127.3, 115.9 (q, J = 286.5 Hz, CF₃), 97.1, 78.7, 75.2, 75.0, 71.7, 70.7, 69.0, 67.6, 65.9, 62.6, 51.4, 50.9, 46.8; ¹⁹F-NMR (376 MHz, CDCl₃) δ: -74.65; ESI-HRMS Calcd. for C₃₄H₃₆F₃N₂O₈ [M+H]+ 657.2418; Found: 657.2411; IR (ATR) 3425, 3290, 2112, 1695 cm⁻¹; [α]D¹⁸ +72.1 (c 0.09, CHCl₃).

Triazole (22)

To a stirred mixture of 20 (25 mg, 38 μmol), tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (2.0 mg, 3.8 μmol), azide 21 (9.4 mg, 76 μmol), and sodium ascorbate (1.5 mg, 7.6 μmol) in MeOH (2.0 mL) / H₂O (100 μL) was added CuSO₄·5H₂O (9.5 mg, 3.8 μmol), and the reaction mixture was stirred at room temperature for 30 min. After methanol was concentrated under reduced pressure, the residue was directly purified by flash column chromatography on silica gel to give triazole 22 (24 mg, 78% yield) as white solid; mixture of rotamers; ¹H-NMR (600 MHz, CDCl₃) δ: 8.09–6.93 (20H, m), 6.70 (1H, brs), 5.21 (1H, s), 5.15 (1H, d, J = 12.1 Hz), 5.10 (1H, d, J = 12.1 Hz), 4.94 (1H, d, J = 2.7 Hz), 4.63–4.37 (5H,
m), 4.28 (1H, s), 4.09 (1H, s), 3.89–3.81 (5H, m), 3.67 (1H, s), 3.58 (1H, brs), 3.46 (1H, dd, \( J = 10.4, 2.7 \) Hz), 3.36 (1H, brs), 3.20 (1H, dd, \( J = 14.0, 5.2 \) Hz); \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)) \( \delta: \) 160.5, 158.7 (q, \( J = 37.0 \) Hz), 156.4, 145.4, 137.9, 137.8, 137.3, 136.3, 130.4, 128.6, 128.5, 128.1, 127.9, 127.7, 127.5, 127.5, 127.3, 121.8, 115.9 (q, \( J = 286.9 \) Hz, CF\(_3\)), 114.7, 112.5, 106.3, 97.4, 75.4, 69.1, 67.5, 66.5, 66.1, 55.6, 51.5, 51.2, 47.2; \(^{19}\)F-NMR (376 MHz, CDCl\(_3\)) \( \delta: \) ‒74.76; ESI-HRMS Calcd. for C\(_41\)H\(_{43}\)F\(_3\)N\(_5\)O\(_9\) [M+H]\(^{+}\) 806.3007; Found: 806.3007; IR (ATR) 3439, 3276, 1697 cm\(^{-1}\); \([\alpha]_D^{15}\) +55.0 (c 0.14, CHCl\(_3\)).

**ASGPR ligand (15)**

To a solution of 22 (24 mg, 30 \( \mu \)mol) and HCOONH\(_4\) (100 mg, 1.6 mmol) in MeOH (2.0 mL) was added Pd black (50 mg, 0.47 mmol), and the reaction mixture was stirred at room temperature for 6 h. After MeOH was removed under reduced pressure, the reaction mixture was diluted with saturated aqueous NaCl solution (2.0 mL) and extracted with MeCN / EtOAc (3 × 1.0 mL / 1.0 mL). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure to give the crude product, which was purified by preparative TLC on NH silica gel (EtOAc / MeOH 10:1) to obtain 15 as white solid (9.4 mg, 54% yield); \(^1\)H-NMR (600 MHz, CD\(_3\)OD) \( \delta: \) 8.39 (1H, s), 7.40 (1H, t, \( J = 8.2 \) Hz), 7.34–7.32 (2H, m), 7.27–7.20 (4H, m), 7.17 (1H, t, \( J = 7.1 \) Hz), 6.99 (1H, d, \( J = 8.2 \) Hz), 5.12 (1H, s), 4.98 (1H, d, \( J = 3.8 \) Hz), 4.60 (1H, d, \( J = 11.5 \) Hz), 4.50 (1H, d, \( J = 11.5 \) Hz), 4.37 (1H, dd, \( J = 11.3, 3.6 \) Hz), 4.08–4.07 (2H, m), 3.86 (1H, dd, \( J = 11.0, 3.8 \) Hz), 3.82 (3H, s), 3.60–3.57 (1H, m), 3.52 (1H, dd, \( J = 11.3, 4.1 \) Hz), 2.82–2.71 (2H, m) (three O-H protons and two N-H protons were not observed); \(^{13}\)C-NMR (150 MHz, CD\(_3\)OD) \( \delta: \) 162.3, 159.2 (q, \( J = 38.4 \) Hz), 139.4, 131.9, 129.4, 129.4, 129.1, 128.8, 123.4, 117.5 (q, \( J = 287.1 \) Hz, CF\(_3\)), 115.7, 113.5, 107.4, 99.0, 73.1, 72.0, 72.0, 68.5, 68.3, 56.2, 52.2, 43.3 (only major peaks are picked up, because the compound 15 was found to be decomposed in CD\(_3\)OD during \(^{13}\)C-NMR measurement, possibly due to the methanolysis of the anomeric position); \(^{19}\)F-NMR (376 MHz, CD\(_3\)OD) \( \delta: \) ‒76.67; ESI-HRMS Calcd. for C\(_{26}\)H\(_{31}\)F\(_3\)N\(_5\)O\(_7\) [M+H]\(^{+}\) 582.2170; Found: 582.2169.

**5. References**

6. Copies of $^1$H and $^{13}$C NMR charts

Compound **13a**, $^1$H-NMR (600 MHz, CDCl$_3$)

![1H-NMR spectrum of compound 13a](image)

Compound **13a**, $^{13}$C-NMR (150 MHz, CDCl$_3$)

![13C-NMR spectrum of compound 13a](image)
Compound 13b, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 13b, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound 13c, $^1$H-NMR (600 MHz, CDCl$_3$)
Compound 13d, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 13d, $^{13}$C-NMR (150 MHz, CDCl$_3$)

S14
Compound 13e, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 13e, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound 13f, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 13f, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound 13g. $^1$H-NMR (600 MHz, CDCl$_3$)

![H-NMR spectrum of 13g](image)

Compound 13g. $^{13}$C-NMR (150 MHz, CDCl$_3$)

![C-NMR spectrum of 13g](image)
Compound 13h, $^1$H-NMR (600 MHz, CDCl₃)

Compound 13h, $^{13}$C-NMR (150 MHz, CDCl₃)
Compound 13i, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 13i, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound S1, ^1^H-NMR (400 MHz, CDCl₃)

Compound S1, ^13^C-NMR (150 MHz, CDCl₃)
Compound S2, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound S2, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound S3, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound S3, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound S4, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound S4, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound 16, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 16, $^{13}$C-NMR (600 MHz, CDCl$_3$)
Compound 17, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 17, $^{13}$C-NMR (150 MHz, CDCl$_3$)

S25
Compound 18, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 18, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound 20, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 20, $^{13}$C-NMR (150 MHz, CDCl$_3$)
Compound 22, $^1$H-NMR (600 MHz, CDCl$_3$)

Compound 22, $^{13}$C-NMR (600 MHz, CDCl$_3$)
Compound 15, $^1$H-NMR (600 MHz, CD$_3$OD)

Compound 15, $^{13}$C-NMR (150 MHz, CD$_3$OD)