Supporting Information

General Procedures. All chemicals were reagent grade and were used as supplied. Technical grade or reagent grade solvents for extraction and chromatography were used without further purification. Silica gel 60 F254 plates (E. Merck) were used for analytical and preparative thin-layer chromatography. Silica gel 60N (spherical, neutral, Kanto Chemical Co., Inc, Tokyo) was used for flash column chromatography (40-100 mm) and open column (100-200 mm) chromatography. 1H and 13C NMR spectra were recorded at ambient temperature (23~24 °C) in CDCl3 using JEOL EX 400 MHz spectrometer. 13C-NMR spectra were taken in CDCl3 unless otherwise mentioned, and CHCl3 (δ 77.0 ppm) was used as an internal standard. Chemical shifts are reported in ppm relative to internal tetramethylsilane (δ = 0.00 ppm or CHCl3 as 7.26 ppm) for 1H and internal CDCl3 (δ = 77.00 ppm) for 13C NMR spectra. Optical rotations were measured with a JASCO DIP-310 polarimeter. MALDI-TOF MS spectra were measured by Shimadzu AXIMA-CFR using DHBA and CHCA as matrix.

General procedure for preparation of glycosyl bromide from thioglycoside
To a solution of thioglycoside (1 equiv.) in CH2Cl2, Br2 solution (1 M in CH2Cl2, 1.2 equiv.) was dropped at 4 °C. The mixture was stirred at 4 °C-room temperature under N2 atmosphere (normally 30 min ~ 2 h). After consuming the thioglycoside, the reaction was quenched with 10% Na2S2O3 aq. and the aqueous layer was extracted with EtOAc. The combined layers were washed with sat. NaHCO3 and brine. After drying the mixture over Na2SO4. The mixture was filtered and concentrated. The residue was purified by silica gel column chromatography.
Yields 1a (94%), 1b (93%), 1c (44%), 6a (46%), 6b (95%), 6c (94%), 9 (94%).

General Procedure for Keck reaction:
A mixture of bromide (1 equiv.), allyl-n-tributylstannane (12 equiv.) and AIBN (15.5 mg/substrate mmol) in PhH (0.2 M solution) was refluxed under N2 atmosphere for 12 h. The mixture was purified by silica gel column chromatography. The α/β ratio is based on integration of 1H-NMR.

General Procedure for chain reaction:
To a solution of bromide (1 equiv.), Bu3SnH (2 equiv) and olefin (15 equiv) in PhH
(substrate concentration 0.2 M), AIBN (16.8 mg/substrate mmol) was added. The mixture was refluxed under N₂ atmosphere for 12 h. After cooling the mixture to room temperature, the mixture was purified by silica gel column chromatography. The α/β ratio is based on integration of ¹H-NMR.

Phenyl

*N*-benzyl-2-amino-4,6-*O*-benzylidene-2,3-*N*,*O*-carbonyl-2-deoxy-1-thio-*α*-D-glucopyranoside¹ (3.00g, 6.31 mmol) in AcOH (16 mL) and H₂O (4 mL) was stirred at 100 °C for 2 h. After concentration, the residue was filtered and washed with ether. The precipitate was dissolved in DMF (10 mL) and imidazole (858 mg, 12.62 mmol) was added. To a solution, TBDPSCl (1.93mL, 7.57 mmol) was dropped. The mixture was stirred at room temperature under N₂ atmosphere overnight. The solution was diluted with EtOAc and washed with sat. NH₄Cl, sat. NaHCO₃ and brine. After concentration, the residue was purified by silica gel column chromatography (hexane:EtOAc 7:3-1:1) to give product (3.08 g, 78%).

¹H-NMR δ 7.67-7.65 (m, 4H), 7.42-7.18 (m, 16H), 4.78-4.68 (m, 3H), 4.11-4.06 (m, 2H), 3.93 (s, 1H), 3.91 (s, 1H), 3.51 (m, 1H), 3.41-3.36 (m, 1H), 1.04 (s, 9H); ¹³C-NMR δ 150.9, 136.3, 135.6, 135.5, 132.4, 132.0, 129.9, 129.0, 128.6, 128.2, 128.1, 127.8, 127.8, 127.5, 86.8, 82.4, 80.5, 69.0, 64.0, 60.2, 47.7, 26.8, 19.3; [α] -54.5 (c 0.73, CHCl₃); calcd for [C₃₆H₃₉NO₅SSi+Na]⁺ 648.2210, found 648.2217.

To a solution of alcohol (2.00 g, 3.20 mmol) in pyridine (5 mL), Ac₂O (3 mL) was added. After 2 h, the reaction was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc 7:3) to give product (2.00 g, 94%).

¹H-NMR δ 7.66-7.63 (m, 4H), 7.40-7.18 (m, 16H), 5.30 (t, J = 8.8 Hz, 1H), 4.79-4.72 (m,
To a solution of phenyl 2-amino-6-O-benzyl-2,3-N,O-carbonyl-2-deoxy-1-thio-α-D-glucopyranoside (1.00 g, 2.60 mmol) in pyridine (3 mL), Ac₂O (2 mL) and DMAP (50 mg, 0.41 mmol) was added. After stirring at room temperature overnight, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (hexane: EtOAc 7:3) to give the product (1.20 g, 95%).

1H-NMR δ 7.52-7.50 (m, 2H), 7.32-7.19 (m, 8H), 5.33 (t, J = 8.4 Hz, 1H), 4.95 (d, J = 7.6 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.24 (d, J = 10.8 Hz, 1H), 4.22 (d, J = 10.8 Hz, 1H), 3.72 (m, 1H), 3.65 (s, 1H), 3.63 (s, 1H), 3.63 (s, 1H), 2.55 (s, 3H), 2.02 (s, 3H); 13C-NMR δ 172.5, 169.1, 153.2, 137.5, 134.1, 132.0, 128.8, 128.3, 127.8, 127.7, 87.4, 79.3, 79.1, 76.7, 73.6, 68.9, 68.4, 59.8, 24.8, 20.7; [α] = -55.2 (c 1.4, CHCl₃); calcd for [C₂₄H₂₅NO₇SNa]+ 494.1244, found 494.1243.

1H-NMR δ 7.56-7.54 (m, 4H), 7.40-7.15 (m, 11H), 6.24 (d, J = 3.2 Hz, 1H) 5.44 (t, J = 10.0 Hz, 1H), 4.78 (d, J = 14.8 Hz, 1H), 4.63 (t, J = 11.6 Hz, 1H), 4.09 (d, J = 14.8 Hz, 1H), 3.80 (m, 1H), 3.70 (m, 2H), 3.27 (dd, J = 11.2, 2.8 Hz, 1H), 1.98 (s, 3H), 1.01 (s, 9H); 13C-NMR δ 168.7, 159.6, 135.5, 133.7, 132.7, 132.6, 129.8, 129.7, 129.1, 129.0, 128.9, 128.7, 128.1, 127.7, 127.6, 83.9, 75.8, 66.8, 61.2, 61.0, 47.8, 26.8, 20.6, 19.3; calcd for [C₃₃H₃₇NO₇SSi+Na]+ 642.1952, found 642.1950.
1H-NMR δ 7.38-7.36 (m, 3H), 7.28-7.26 (m, 2H), 6.21 (d, J = 3.2 Hz, 1H), 5.30 (t, J = 10.0 Hz, 1H), 4.80 (d, J = 14.4 Hz, 1H), 4.65 (t, J = 10.0 Hz, 1H), 4.27 (dd, J = 12.8, 4.4 Hz, 1H), 4.09-4.04 (m, 2H), 4.01 (m, 1H), 3.31 (dd, J = 11.2, 2.8 Hz, 1H), 2.10 (s, 3H), 2.03 (s, 3H); 13C-NMR δ 170.1, 168.8, 157.3, 133.5, 129.1, 128.8, 128.7, 83.0, 75.3, 74.1, 66.8, 60.8, 47.8, 20.8; [α] 194.0 (c 1.1, CHCl3); calcd for [C18H20BrNO7+Na]+ 464.0315, found 464.0314.

1H-NMR δ 7.36-7.17 (m, 10H), 6.24 (d, J = 3.2 Hz, 1H), 5.43 (t, J = 9.6 Hz, 1H), 4.80 (d, J = 14.8 Hz, 1H), 4.62 (t, J = 10.4 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.39 (d, J = 12.0 Hz, 1H), 3.90 (d, J = 14.8 Hz, 1H), 3.89 (m, 1H), 3.54-3.47 (m, 2H), 3.33 (d, J = 11.6, 3.2 Hz, 1H), 1.97 (t, 3H); 13C-NMR δ 168.7, 157.5, 136.9, 133.7, 129.2, 129.0, 128.8, 128.7, 128.4, 128.1, 128.0, 127.9, 83.7, 75.7, 75.2, 73.6, 67.0, 66.4, 60.7, 47.7, 20.6; [α] 121.2 (c 1.85, CHCl3); calcd for [C29H29NO5S+Na]+ 526.1659, found 526.1653.

1H-NMR δ 7.06 (d, J = 3.2 Hz, 1H), 5.41 (t, J = 10.0 Hz, 1H), 4.76 (t, J = 11.6 Hz, 1H), 4.31 (dd, J = 12.8 Hz, 4.0 Hz, 1H), 4.17 (dd, J = 12.8 Hz, 2.0 Hz, 1H), 4.16 (m, 1H), 3.95 (dd, J = 11.6 Hz, 3.2 Hz, 1H); 13C-NMR δ 170.8, 170.2, 168.7, 152.5, 83.7, 75.4, 73.8, 66.6, 61.0, 60.7, 23.7, 20.8, 20.7; [α] 159.0 (c 2.56, CHCl3); calcd for [C13H16BrNO8+Na]+ 415.9952, found 415.9953.
$^1$H-NMR $\delta$ 6.52 (d, $J = 3.2$ Hz, 1H), 5.50 (bs, 1H), 5.43 (t, $J = 10.0$ Hz, 1H), 4.75 (t, $J = 11.2$ Hz, 1H), 4.30 (dd, $J = 12.4$ Hz, 4.4 Hz, 1H), 4.16 (dd, $J = 12.8$, 2.0 Hz, 1H), 4.16 (dd, $J = 12.8$ Hz, 2.0 Hz, 1H), 4.06 (m, 1H), 3.76 (m, 1H), 2.12 (s, 3H), 2.08 (s, 3H); $^{13}$C-NMR $\delta$ 170.2, 168.8, 157.6, 83.6, 77.6, 73.9, 66.9, 60.9, 59.6, 20.8; $[\alpha]_{149.1}$ (c 1.50, CHCl$_3$).

$^1$H-NMR $\delta$ 7.33-7.15 (m, 5H), 7.08 (d, $J = 2.8$ Hz, 1H), 5.54 (t, $J = 10.0$ Hz, 1H), 4.74 (t, $J = 10.8$ Hz, 1H), 4.58 (d, $J = 12.0$ Hz, 1H), 4.46 (d, $J = 12.0$ Hz, 1H), 3.97-3.91 (m, 2H), 3.60-3.57 (m, 2H), 2.49 (s, 3H), 2.01 (s, 3H); $^{13}$C-NMR $\delta$ 170.8, 168.6, 151.9, 137.0, 128.8, 128.4, 128.1, 127.9, 125.2, 84.4, 75.8, 75.1, 73.6, 66.9, 66.5, 60.9, 23.7, 20.9; $[\alpha]_{242.8}$ (c 2.25, CHCl$_3$); calcd for [C$_{18}$H$_{20}$BrNO$_7$+Na]$^+$ 464.0315, found 464.0307.

$^1$H-NMR $\delta$ 7.34-7.27 (m, 4H), 7.10 (d, $J = 2.8$ Hz, 1H), 5.72 (s, 1H), 4.80 (dd, $J = 2.4$ Hz, 1H), 4.53 (d, $J = 11.6$ Hz, 1H), 4.42 (d, $J = 11.6$ Hz, 1H), 4.25 (d, $J = 12.0$, 2.8 Hz, 1H), 4.21 (t, $J = 6.4$ Hz, 1H), 3.54 (m, 2H), 2.50 (s, 3H), 2.05 (s, 3H); $^{13}$C-NMR $\delta$ 171.4, 168.8, 152.0, 137.0, 128.5, 128.0, 127.9, 85.8, 76.1, 74.0, 73.7, 73.3 66.7, 65.1, 56.9, 23.8, 20.6; $[\alpha]_{162.0}$ (c 0.80, CHCl$_3$); calcd for [C$_{18}$H$_{20}$BrNO$_7$+Na]$^+$ 426.1523, found 426.1527.
$^1$H-NMR δ 5.74 (m, 1H), 5.19 (t, J = 9.6 Hz, 1H), 5.13-5.09 (m, 2H), 4.92 (m, 1H), 4.37 (t, J = 12.4 Hz, 1H), 4.20-4.11 (m, 2H), 4.05 (dd, J = 12.0, 5.2 Hz, 1H), 3.75 (m, 1H), 2.46 (s, 3H), 2.46 (m, 1H), 2.17 (m, 1H), 2.10 (s, 3H), 2.05 (s, 3H); $^{13}$C-NMR δ 171.4, 170.5, 169.0, 152.7, 132.3, 118.0, 75.3, 73.4, 70.7, 68.6, 62.1, 59.5, 29.5, 23.9, 20.7; [α] 89.9 (c 1.2, CHCl₃), calcd for [C₁₆H₂₁NO₈+Na]+ 378.1159, found 378.1157.

![Diagram 1](image1.png)

$^1$H-NMR δ 7.29-7.19 (m, 5H), 5.76 (m, 1H), 5.25 (t, J = 9.0 Hz, 1H), 5.09-5.03 (m, 2H), 4.87 (m, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.31 (t, J = 12.2 Hz, 1H), 4.03 (dd, J = 12.4 Hz, 4.8 Hz, 1H), 3.67 (m, 1H), 3.51-3.47 (m, 2H), 2.41 (s, 3H), 2.13 (m, 1H), 1.92 (s, 3H); $^{13}$C-NMR δ 171.3, 168.9, 152.8, 137.4, 132.6, 128.2, 127.8, 127.6, 117.8, 75.6, 73.6, 73.4, 72.4, 69.2, 68.4, 59.3, 29.9, 24.0, 20.8; [α] 126.8 (c 1.86, CHCl₃), calcd for [C₂₁H₂₅NO₇+Na]+ 426.1523; found 426.1527.

![Diagram 2](image2.png)

$^1$H-NMR δ 5.22 (t, J = 9.6 Hz, 1H), 5.04 (m, 1H), 4.84 (s, 1H), 4.76 (s, 1H), 4.38 (t, J = 10.0 Hz, 1H), 4.18 (dd, J = 12.0, 5.2 Hz, 1H), 4.09 (dd, J = 12.0, 2.4 Hz, 1H), 4.05 (dd, J = 12.4, 5.2 Hz, 1H), 3.78 (m, 1H), 2.44 (s, 3H), 2.44-2.42 (m, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 2.05-2.00 (m, 1H); $^{13}$C-NMR δ 171.3, 170.5, 169.0, 152.8, 140.4, 113.8, 75.4, 72.4, 70.6, 68.6, 62.2, 59.7, 32.9, 23.9, 21.9, 20.7, 20.7; [α] 105.1 (c 0.84, CHCl₃), calcd for [C₁₇H₂₃NO₈+Na]+ 392.1316, found 392.1315.

![Diagram 3](image3.png)

$^1$H-NMR δ 7.34-7.24 (m, 5H), 5.73 (m, 1H), 5.08 (s, 1H), 4.96-4.54 (m, 2H), 4.41 (m,
1H), 4.52 (d, J = 11.6 Hz, 1H), 4.43-4.34 (m, 3H), 3.91 (t, J = 6.0 Hz, 1H), 3.48-3.46 (m, 2H), 2.46 (s, 3H), 2.05 (s, 1H), 205 (s, 3H); 13C-NMR δ 171.6, 169.0, 152.8, 137.3, 132.7, 128.3, 127.8, 127.8, 117.9, 77.2, 74.4, 73.8, 73.6, 69.8, 67.8, 65.9, 55.7, 29.1, 24.2, 20.8; [α] 51.7 (c 1.00, CHCl3); calcd for [C21H25NO7+Na]+ 426.1523, found 426.1520.

\[
\text{AcO} \quad \text{O} \quad \text{Bn} \\
\text{O} \quad \text{N} \quad \text{Ac} \\
\text{CN}
\]

1H-NMR δ 7.29-7.19 (m, 5H), 5.26 (t, J = 8.4 Hz, 1H), 4.77 (m, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.22 (t, J = 12.4 Hz, 1H), 4.07 (m, 1H), 3.64 (m, 1H), 3.58-3.50 (m, 2H), 2.43 (s, 3H), 2.39-2.29 (m, 2H), 1.97 (m, 1H), 1.94 (s, 3H), 1.67 (m, 1H), 13C-NMR δ 171.4, 168.9, 152.5, 137.2, 128.3, 127.8, 118.7, 75.3, 73.7, 73.3, 73.2, 69.1, 68.2, 58.8, 23.4, 21.8, 20.7, 14.2; [α] 87.7 (c 0.90, CHCl3); calcd for [C21H24N2O7+Na]+ 439.1476, found 439.1463.

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\text{AcO} \quad \text{O} \quad \text{Bn} \\
\text{O} \quad \text{N} \quad \text{Ac} \\
\text{CO2Me}
\]

1H-NMR δ 7.28-7.19 (m, 5H), 5.25 (t, J = 9.2 Hz, 1H), 4.75 (m, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.30 (t, J = 10.0 Hz, 1H), 4.00 (dd, J = 12.4, 5.6 Hz, 1H), 3.63 (m, 1H), 3.59 (s, 3H), 3.45 (m, 2H), 2.45-2.28 (m, 2H), 2.42 (s, 3H), 2.03 (m, 1H), 1.93 (s, 3H), 1.55 (m, 1H); 13C-NMR δ 173.0, 171.3, 168.9, 152.8, 137.3, 128.3, 127.8, 127.7, 75.6, 74.0, 73.6, 72.1, 69.0, 68.2, 59.4, 51.9, 30.5, 25.0, 20.8, 20.3; [α] 88.6 (c 1.25, CHCl3); calcd for [C22H27NO9+Na]+ 472.1578, found 472.1572.

Detectable peak; 1H-NMR δ 7.36 (m, 2H), 7.35 (m, 1H), 7.29 (dd, J = 8.0, 1.0 Hz, 2H),
5.60 (ddddd, J = 17.1, 10.0, 7.0, 6.6 Hz, 1H), 5.14 (dd, J = 10.1 Hz, 9.6 Hz, 1H), 4.48 (d, J = 14.6 Hz, 1H), 4.28 (d, J = 14.6 Hz, 1H), 4.17 (dd, J = 12.6, 5.0 Hz, 1H), 4.29 (dd, J = 12.1 Hz, 10.1 Hz, 1H), 4.06 (dd, J = 12.6, 2.0 Hz, 1H), 4.06 (ddd, J = 11.1, 5.1, 3.1 Hz, 1H), 3.71 (ddd, J = 9.6, 5.0, 2.0 Hz, 1H), 3.50 (dd, J = 12.1, 5.1 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H); 13C-NMR δ 170.6, 169.2, 158.8, 134.8, 132.6, 129.1, 129.0, 128.6, 118.2, 74.8, 73.7, 70.9, 68.9, 62.2, 60.4, 49.2, 29.3, 20.7, 20.7; calcd for [C21H25NO7+Na]+ 426.1523, found 426.1524.

Detectable peak; 1H-NMR δ 7.36-7.29 (m, 5H), 5.71 (ddddd, J = 17.1, 10.1, 6.5, 6.5 Hz, 1H), 5.23 (dd, J = 10.6, 9.1 Hz, 1H), 5.01 (br, J = 10.1 Hz, 1H), 4.88 (ddddd, J = 17.1, 1.5, 1.5, 1.5 Hz, 1H), 4.67 (d, J = 16.1 Hz, 1H), 4.45 (d, J = 17.1 Hz, 1H), 4.21 (dd, J = 12.1, 5.1 Hz, 1H), 4.17 (dd, J = 11.6, 10.6 Hz, 1H), 4.12 (dd, J = 12.1, 2.5 Hz), 3.50 (m, 1H), 3.29 (ss, J = 11.6, 9.1 Hz, 1H), 2.30 (m, 1H), 2.11 (s, 3H), 2.04 (m, 1H), 2.05 (s, 3H), 13C-NMR δ 159.3, 132.7, 126.9, 118.1, 79.9, 76.7, 67.8, 62.2, 62.1, 48.4, 36.5 20.7, 20.7.

Detectable peak; 1H-NMR δ 7.19-7.41 (m, 10H), 5.56-5.70 (m, 1H), 5.24 (t, J = 9.6 Hz, 1H), 5.07 (d, J = 10.0 Hz, 1H), 5.01 (d, J = 17.2 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 14.8 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.26 (t, J = 11.2 Hz, 1H), 4.25 (d, J = 14.8 Hz, 1H), 4.07 (ddddd, J = 11.2, 4.8, 4.0 Hz, 1H), 3.64 (ddddd, J = 8.8, 3.6, 2.8 Hz, 1H), 3.41-3.58 (m, 3H), 2.35-2.48 (m, 1H), 1.95 (s, 3H), 1.83-2.03 (m, 1H); 13C-NMR δ 168.8, 158.7, 137.3, 134.6, 132.7, 128.9, 128.8, 128.4, 128.2, 127.8, 127.6, 118.0, 75.2, 73.7, 73.5, 72.0, 69.2, 68.0, 60.2, 49.1, 29.4, 20.8; MALDI-TOFMS: calcd for C26H29NO6Na:474.19 [M+Na]+; found 474.52.
Detectable peak; $^1$H-NMR $\delta$ 7.33 (m, 6H), 7.29 (m, 4H), 5.61 (ddd, $J = 17.2$, 10.3, 6.9 Hz, 1H), 5.05 (br.d. $J = 10.3$ Hz, 1H), 4.98 (br.d, $J = 17.2$ Hz, 1H), 4.44 (d, $J = 14.9$ Hz, 1H), 4.29 (d, $J = 14.9$ Hz, 1H), 4.20 (ddd, $J = 12.0$, 9.8 Hz, 1H), 4.00 (ddd, $J = 10.3$, 5.2, 3.5 Hz, 1H), 3.95 (ddd, $J = 9.8$, 8.6, 2.9 Hz, 1H), 3.70 (ddd, $J = 10.3$, 4.0 Hz, 1H), 3.62 (dd, $J = 10.3$, 4.6 Hz, 1H), 3.53 (ddd, $J = 8.6$, 4.6, 4.0 Hz, 1H), 3.39 (dd, $J = 12.0$, 5.2 Hz, 1H), 2.97 (d, $J = 2.9$ Hz, 1H), 2.95 (dd, $J = 9.8$, 8.6, 2.9 Hz, 1H), 2.40 (br.ddd, $J = 15.4$, 10.3, 6.9 Hz, 1H), 1.85 (ddd, $J = 15.4$, 6.9, 3.5 Hz, 1H); $^{13}$C-NMR $\delta$ 159.4, 137.3, 135.0, 133.0, 128.9, 128.9, 128.4, 128.3, 127.8, 127.7, 117.8, 77.3, 73.7, 73.6, 72.8, 70.6, 69.6, 60.1, 49.0, 29.3; MALDI-TOFMS: calcd for C$_{24}$H$_{27}$NO$_{5}$ 409.1, found 410.24.

Detectable peak; $^1$H-NMR $\delta$ 7.58-7.63 (m, 4H), 7.25-7.45 (m, 11H), 5.60-5.70 (m, 1H), 5.13 (t, $J = 10.0$ Hz, 1H), 5.05 (ddd, $J = 11.6$, 1.2 Hz, 1H), 4.99 (dd, $J = 17.2$, 1.2 Hz, 1H), 4.45 (d, $J = 14.4$ Hz, 1H), 4.31 (d, $J = 14.4$ Hz, 1H), 4.26 (t, $J = 10.4$ Hz, 1H), 4.00-4.08 (m, 1H), 3.63-3.68 (m, 2H), 3.54-3.59 (m, 1H), 3.46 (ddd, $J = 12.0$, 5.2 Hz, 1H), 2.35-2.47 (m, 1H), 1.93 (s, 3H), 1.80-1.90 (m, 1H), 1.01 (s, 9H); $^{13}$C-NMR $\delta$ 168.8, 158.8, 135.5, 135.4, 134.8, 133.0, 132.9, 132.8, 129.6, 129.5, 128.9, 128.8, 128.3, 127.5, 127.4, 117.9, 75.2, 73.7, 73.5, 69.1, 62.9, 60.6, 49.2, 29.4, 26.8, 20.8, 19.3; MALDI-TOFMS: calcd for C$_{33}$H$_{41}$NO$_{6}$SiNa : 622.26 [M+Na]$^+$; found 622.69.

Detectable peak; $^1$H-NMR $\delta$ 7.15-7.45 (m, 10H), 5.25 (t, $J = 9.6$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.40 (d, $J = 14.4$ Hz, 1H), 4.35 (d, $J = 14.4$ Hz, 1H),
4.15 (t, J = 10.8 Hz, 1H), 3.95-4.05 (m, 1H), 3.45-3.63 (m, 3H), 3.45 (dd, J = 10.8, 4.4 Hz, 1H), 2.20-2.32 (m, 1H), 2.06-2.20 (m, 1H), 2.35-2.48 (m, 1H), 1.96 (s, 3H), 1.83-2.03 (m, 1H), 1.22-1.35 (ddd, J = 13.6, 7.6, 5.2 Hz, 1H); 13C-NMR δ 168.8, 158.5, 137.1, 134.6, 128.9, 128.6, 128.3, 128.1, 127.8, 127.7, 118.4, 74.9, 73.6, 72.8, 72.6, 68.9, 67.8, 60.2, 49.5, 21.1, 20.7, 14.1; MALDI-TOFMS: calcd for C26H28N2O6Na: 487.18 [M+Na]+; found 487.40.

Detectable peak; 1H-NMR δ 7.63 (m, 2H), 7.62 (m, 2H), 7.37 (m, 4H), 7.43 (m, 4H), 7.33 (m, 2H), 7.29 (m, 1H), 7.29 (m, 2H), 5.56 (ddt, J = 17.2, 10.3, 6.9 Hz, 1H), 5.00 (br.d, J = 10.3 Hz, 1H), 4.92 (br.d, J = 17.2 Hz, 1H), 4.41 (d, J = 14.6 Hz, 1H), 4.32 (d, J = 14.6 Hz, 1H), 3.94 (m, 1H), 3.94 (m, 1H), 3.85 (dd, J = 10.6, 4.6 Hz, 1H), 3.81 (dd, J = 10.6, 4.8 Hz, 1H), 3.45 (dd, J = 9.1, 4.8, 4.6 Hz, 1H), 3.33 (dd, J = 12.1, 5.1 Hz, 1H), 3.01 (d, J = 2.9 Hz, 1H), 13C-NMR δ 159.6, 135.2, 132.7, 132.6, 135.6, 135.5, 133.1, 130.0, 129.9, 129.0, 129.0, 128.4, 127.8, 127.8, 117.8, 77.1, 73.7, 73.7, 71.2, 64.7, 60.2, 49.1, 29.4, 26.8, 19.4; calcd for C33H39NO5Si+Na 580.88, found 557.26.

Detectable peak; 1H-NMR δ 7.58-7.63 (m, 4H), 7.25-7.45 (m, 11H), 5.17 (t, J = 9.2 Hz, 1H), 4.45 (d, J = 14.8 Hz, 1H), 4.33 (d, J = 14.8 Hz, 1H), 4.14 (t, J = 10.0 Hz, 1H), 3.92-4.01 (m, 1H), 3.67 (d, J = 3.6 Hz, 2H), 3.50 (dd, J = 12.4, 5.6 Hz, 1H), 3.40-3.47 (m, 1H), 2.24-2.32 (m, 1H), 2.05-2.12 (m, 1H), 1.95 (s, 3H), 1.83-1.92 (m, 1H), 1.22-1.35 (m, 1H), 1.02 (s, 9H); 13C-NMR δ 168.7, 158.5, 135.4, 135.4, 134.8, 132.8, 132.6, 129.7, 129.1, 128.9, 128.6, 127.6, 127.5, 118.2, 75.0, 74.0, 72.3, 68.7, 62.6, 60.5, 49.6, 26.8, 21.2, 20.7, 19.3, 13.8; MALDI-TOFMS: calcd for C33H41N2O6Si : 613.27 [M+H]+; found 613.81.
Electronic Supplementary Material (ESI) for Chemical Communications
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DFILE C:\WIN98\COMMON\DEFAULT.A
CONST
DATE Mon May 30 13:45:04 2011
QNB GC 1H
EXPOD NON
OCIFREQ 399.65 MHz
OSERET 124.00 KHz
OCBINT 10500.0 Hz
OPOINT 32768
OCNQR 7995.1 Hz
OCNCS 16
AQCOMM 4.099 sec
PD 2.901 sec
PFG 5.8 us
INPUC 1H
CTEMPO 22.3 c
SLVRT CCL3
EXSRF 7.24 ppm
RF 0.12 Hz
RGAIN 21

[Diagram with chemical structures and NMR peaks labeled]