Supporting Information

General Procedure for the Preparation of Thioacids 4, 7, 10 and 12.

To a stirred solution of the appropriate peptide (0.6 mmol) and *N*-hydroxysuccinimide (0.6 mmol) in dry CH_2Cl_2 (7 mL) was added DCC (0.6 mmol) at 0 °C under N_2. Then the mixture was stirred at 0 °C for 30 min, warmed to room temperature and stirred overnight. The resulting precipitate was removed by filtration and washed several times with CH_2Cl_2. The combined filtrate was concentrated to about one-fifth of its original volume and left to stand in the refrigerator for about 2 h. The mixture was filtered again and concentrated to give the corresponding activated ester as a colourless foam, which was immediately dissolved in dry THF (12 mL) followed by addition of DIPEA (0.6 mmol). This mixture was cooled to 0 °C and bubbled with H_2S gas for 1 h, then stirred at room temperature overnight. The solvent was removed in vacuo, and EtOAC-H_2O was added. The pH was adjusted to a value of ~3 by careful addition of 1 N HCl, upon which the organic layer was collected, washed several times with water, dried over $MgSO_4$ and concentrated in vacuo. The resulting thioacid was dried under vacuum and directly used in the next step without purification.

A Typical Procedure for the Synthesis of Thioglycosides 3, 5, 8, 11 and 13.

To a stirred solution of azide **1** (126 mg, 0.3 mmol) in $CHCl_3$ (0.5 mL) was added 2,6-lutidine (48 mg, 0.45 mmol) followed by addition of thioacid **2** (82 mg, 0.4 mmol). The mixture was refluxed overnight under N_2, then concentrated in vacuo to give a residue which was purified by flash column chromatography (petroleum ether/EtOAc, 1:1) to afford the recovered azide **1** (43 mg) and the desired thioglycoside **3** (88 mg, 79% based on recovered starting material): TLC R_f = 0.11 (petroleum ether/EtOAc, 1:1); $[\alpha]_D$ = -17.5° (c 1.2 $CHCl_3$); ^1H NMR ($CDCl_3$) δ 6.82 (t, J = 6.0 Hz, 1H), 5.20 (t, J = 9.2 Hz, 1H), 5.13 (d, J = 8.7 Hz, 1H), 5.07 (t, J = 9.4 Hz, 1H), 5.02 (t, J = 9.3 Hz, 1H), 4.70 (dd, J = 14.3, 6.8 Hz, 1H), 4.64 (d, J = 9.9 Hz, 1H), 4.27 (overlapped dd, J = 14.3, 5.6 Hz, 1H), 4.25 (d, J = 4.1 Hz, 2H), 4.15 (m, 1H), 3.72 (dt, J = 9.8, 3.3 Hz, 1H), 2.08, 2.01, 2.00, 1.98 (4s, 12H), 1.42 (s, 9H), 1.33 (d, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.7, 170.8, 170.0, 169.5, 169.3, 155.4, 82.6, 80.1, 73.7, 69.9, 68.1, 61.6, 39.1, 28.3, 20.8, 20.6, 20.5, 18.3; MALDI-MS m/z 586.8 [M + Na^+], 602.9 [M + K^+]. HRMS (MALDI) calcd for $C_{23}H_{36}N_2O_{12}SNa$ (M + Na^+) 587.1888, found 587.1903.

5: The reaction procedure was identical with that for **3** except thioacid **4** was used instead of **2**. Product **5** (43 mg) was obtained from **1** (48 mg, 0.11 mmol) and **4** (40 mg, 0.15 mmol) after purification by flash column chromatography (petroleum ether/EtOAc, 1:2 → EtOAc) in 83% yield based on recovered azide **1** (13 mg): TLC R_f = 0.26 (EtOAc); $[\alpha]_D$ = -16.1° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.46 (br s, 1H), 7.20 (t, *J* = 5.8 Hz, 1H), 5.25 (d, *J* = 5.9 Hz, 1H), 5.19 (t, *J* = 9.2 Hz, 1H), 5.06 (t, *J* = 9.7 Hz, 1H), 5.00 (t, *J* = 9.2 Hz, 1H), 4.69 (d, *J* = 10.0 Hz, 1H), 4.46 (m, 2H), 4.21 (m, 2H), 4.13 (m, 1H), 4.07 (t, *J* = 6.8 Hz, 1H), 3.80 (dd, *J* = 17.1, 4.9 Hz, 1H), 3.70 (dt, *J* = 9.9, 3.2 Hz, 1H), 2.07, 2.00, 1.99, 1.95 (4s, 12H), 1.40 (s, 9H), 1.34 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 173.5, 171.1, 170.0, 169.6, 169.4, 169.2, 155.9, 82.9, 80.5, 76.2, 73.8, 69.8, 68.2, 61.7, 50.8, 43.0, 39.4, 28.3, 20.8, 20.6, 20.5, 17.7; MALDI-MS m/z 644.1 [M + Na^+], 660.0 [M + K^+]. HRMS (MALDI) calcd for $C_{25}H_{39}N_3O_{13}SNa$ (M + Na^+) 644.2102, found 644.2096.

8: The reaction procedure was identical with that for **3** except azide **6** was used in place of **1** and thioacid **7** was used instead of **2**. Product **8** (49 mg) was obtained from **6** (58 mg, 0.14 mmol) and **7** (70 mg, 0.18 mmol) after purification by flash column chromatography (petroleum ether/EtOAc, 1:1 → 1:2) in 76% yield based on recovered azide **6** (21 mg): TLC R_f = 0.15 (petroleum ether/EtOAc, 2:3); $[\alpha]_D$ = +1.8° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 5.6 Hz, 1H), 6.19 (d, *J* = 7.2 Hz, 1H), 5.42 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.23 (t, *J* = 9.9 Hz, 1H), 5.04 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.62 (d, *J* = 9.9 Hz, 1H), 4.58 (dd, *J* = 14.2, 6.2 Hz, 1H), 4.47 (dd, *J* = 8.5, 4.8 Hz, 2H), 4.40 (dd, *J* = 14.3, 6.0 Hz, 1H), 4.25 (dd, *J* = 11.4, 7.0 Hz, 1H), 4.05 (dd, *J* = 11.4, 5.5 Hz, 1H), 3.94 (t, *J* = 6.7 Hz, 1H), 3.69 (s, 3H), 2.82 (dd, *J* = 15.7, 4.1 Hz, 1H), 2.58 (dd, *J* = 15.6, 6.3 Hz, 1H), 2.16, 2.05, 2.04, 1.96 (4s, 12H), 1.92 (m, 1H), 1.43 (s, 9H), 1.42 (overlapped m, 1H), 1.21 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 171.9, 171.12, 171.07, 170.5, 170.2, 169.9, 155.7, 82.7, 80.3, 75.2, 71.7, 67.5, 67.1, 61.6, 56.8, 52.0, 50.9, 38.7, 37.5, 28.3, 24.9, 20.75, 20.72, 20.6, 20.5, 15.5, 11.5; MALDI-MS m/z 758.1 [M + Na^+], 774.1 [M + K^+]. HRMS (MALDI) calcd for $C_{31}H_{49}N_3O_{15}SNa$ (M + Na^+) 758.2783, found 758.2811.

11: The reaction procedure was identical with that for **3** except azide **9** was used in place of **1** and thioacid **10** was used instead of **2**. Product **11** (48 mg) was obtained from **9** (77 mg, 0.11 mmol) and **10** (67 mg, 0.15 mmol) after purification by flash column chromatography (toluene/acetone, 3:1 → 1:1) in 65% yield based on recovered azide **9** (29 mg): TLC R_f = 0.07 (petroleum ether/EtOAc, 1:2); $[\alpha]_D$ = -5.4° (c 0.7 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 10H), 7.18 (d, J = 7.1 Hz, 1H), 6.76 (t-like, 1H), 6.20 (d, J = 7.0 Hz, 1H), 5.20-5.01 (m, 8H), 4.95 (t, J = 4.9 Hz, 1H), 4.90 (dd, J = 9.6, 2.7 Hz, 1H), 4.73 (dd, J = 12.4, 1.5 Hz, 1H), 4.63 (dd, J = 14.6, 7.1 Hz, 1H), 4.56 (m, 4H), 4.37 (dd, J = 12.5, 4.0 Hz, 1H), 4.22 (m, 2H), 4.07 (dd, J = 12.2, 4.1 Hz, 1H), 4.01 (dd, J = 12.5, 1.8 Hz, 1H), 3.76 (t, J = 9.6 Hz, 1H), 3.62 (m, 2H), 2.40 (m, 2H), 2.10, 2.06, 2.00, 1.99, 1.96 (5s, 21H), 1.38 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.8, 172.4, 170.9, 170.4, 170.2, 169.8, 169.6, 169.2, 168.9, 156.4, 136.3, 135.4, 128.6, 128.5, 128.4, 128.12, 128.09, 127.96, 100.7, 82.9, 75.9, 73.2, 72.9, 72.0, 71.6, 70.3, 67.7, 67.1, 67.0, 61.5, 61.2, 54.3, 48.2, 39.5, 32.3, 28.7, 21.0, 20.6, 20.5, 17.9; MALDI-MS m/z 1128.9 [M + Na^+], 1144.9 [M + K^+]. HRMS (MALDI) calcd for $C_{50}H_{63}N_3O_{23}SNa$ (M + Na^+) 1128.3472, found 1128.3448. Anal. Calcd for $C_{50}H_{63}N_3O_{23}S$ (1106.11): C, 54.29; H, 5.74; N, 3.80. Found: C, 54.77; H, 5.88; N, 4.15.

13: The reaction procedure was identical with that for **3** except azide **6** was used in place of **1** and thioacid **12** was used instead of **2**. Product **13** (41 mg) was obtained from **6** (53 mg, 0.13 mmol) and **12** (87 mg, 0.17 mmol) after purification by flash column chromatography (petroleum ether/EtOAc, 1:1 → 1:3) in 72% yield based on recovered azide **6** (25 mg): TLC R_f = 0.42 (EtOAc); $[\alpha]_D$ = -40.3° (c 0.7 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.26 (d, J = 9.4 Hz, 1H), 6.62 (t, J = 5.8 Hz, 1H), 6.10 (d, J = 8.8 Hz, 1H), 5.42 (d, J = 3.2 Hz, 1H), 5.22 (t, J = 9.9 Hz, 1H), 5.05 (dd, J = 10.1, 3.4 Hz, 1H), 4.63 (d, J = 9.9 Hz, 1H), 4.54 (q-like, 2H), 4.46-4.32 (m, 3H), 4.24 (dd, J = 11.6, 7.0 Hz, 1H), 4.06 (dd, J = 11.5, 5.5 Hz, 1H), 3.94 (t, J = 6.5 Hz, 1H), 3.72 (m, 1H), 3.64 (m, 1H), 2.84 (dd, J = 15.6, 4.3 Hz, 1H), 2.57 (dd, J = 15.6, 5.4 Hz, 1H), 2.16, 2.05, 2.04, 1.96 (4s, 12H), 2.15-1.90 (overlapped m, 5H), 1.42 (s, 18H), 1.00 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 171.2, 170.9, 170.5, 170.2, 170.0, 169.9, 155.8, 82.8, 81.3, 80.4, 75.2, 71.7, 67.5, 67.2, 61.6, 59.8, 55.8, 51.4, 47.2, 38.8, 37.4, 31.2, 29.1, 28.3, 27.9, 24.9, 20.79, 20.75, 20.67, 20.5, 19.4, 17.6; MALDI-MS m/z 883.8 [M + Na^+], 899.7 [M + K^+]. HRMS (MALDI) calcd for $C_{38}H_{60}N_4O_{16}SNa$ (M + Na^+) 883.3625, found 883.3640. Anal. Calcd for $C_{38}H_{60}N_4O_{16}S$ (860.97): C, 53.01; H, 7.02; N, 6.51. Found: C, 53.44; H, 7.06; N, 6.30.

General Procedure for the Preparation of GTM-Br 14 – 22.

To a stirred solution of the appropriate glycosylthiol (0.8 mmol) in CH_2Br_2 (12 mL) was added K_2CO_3 (1.6 mmol). The resulting mixture was stirred at room temperature until the disappearance of the starting material, as determined by TLC (typically 5 h). At this time, the solid was removed by filtration and the filtrate was concentrated. The residue was purified by flash column chromatography to give the corresponding glycosylthiomethyl bromide.

14: TLC R_f = 0.38 (petroleum ether/EtOAc, 1.3:1); $[\alpha]_D$ = -118.0° (c 1.1 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.25 (t, J = 9.2 Hz, 1H), 5.07 (t, J = 9.9 Hz, 1H), 5.05 (t, J = 9.2 Hz, 1H), 4.77 (d, J = 10.2 Hz, 1H), 4.73, 4.52 (AB peak, J = 11.0 Hz, 2H), 4.23 (dd, J = 12.5, 4.9 Hz, 1H), 4.12 (dd, J = 12.5, 2.4 Hz, 1H), 3.75 (ddd, J = 10.0, 4.9, 2.4 Hz, 1H), 2.04, 2.01, 1.99, 1.97 (4s, 12H); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.0, 169.3, 81.8, 76.2, 73.6, 69.7, 68.1, 61.8, 31.9, 20.6, 20.5; MALDI-MS m/z 479.5 [M + Na^+], 495.5 [M + K^+]. Anal. Calcd for $C_{15}H_{21}BrO_9S$ (457.29): C, 39.40; H, 4.63. Found: C, 39.25; H, 4.61.

15: TLC R_f = 0.49 (petroleum ether/EtOAc, 2:1); $[\alpha]_D$ = -27.2° (c 1.1 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 8.09-7.80 (m, 8H), 7.60-7.26 (m, 12H), 6.03 (t, J = 9.5 Hz, 1H), 5.73 (t, J = 9.8 Hz, 1H), 5.65 (t, J = 9.5 Hz, 1H), 5.22 (d, J = 10.1 Hz, 1H), 4.85, 4.55 (AB peak, J = 10.9 Hz, 2H), 4.66 (dd, J = 12.3, 2.9 Hz, 1H), 4.53 (dd, J = 12.3, 5.7 Hz, 1H), 4.28 (ddd, J = 9.8, 5.6, 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 165.8, 165.5, 165.0, 164.9, 133.3, 133.1, 133.0, 129.7, 129.6, 129.51, 129.45, 129.3, 128.5, 128.4, 128.2, 128.1, 81.9, 76.4, 73.8, 70.4, 69.3, 62.9, 32.0; MALDI-MS m/z 727.0 [M + Na^+], 743.0 [M + K^+]. Anal. Calcd for $C_{35}H_{29}BrO_9S$ (705.58): C, 59.58; H, 4.14. Found: C, 59.55; H, 4.36.

16: TLC R_f = 0.26 (petroleum ether/EtOAc, 1:1); $[\alpha]_D$ = -70.1° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.33 (d, J = 3.1 Hz, 1H), 5.25 (t, J = 9.1 Hz, 1H), 5.10 (dd, J = 10.4, 7.9 Hz, 1H), 5.00 (t, J = 9.7 Hz, 1H), 4.93 (dd, J = 10.4, 3.4 Hz, 1H), 4.76, 4.52 (AB peak, J = 10.0 Hz, 2H), 4.72 (d, J = 10.9 Hz, 1H), 4.49 (m, 2H), 4.08 (m, 3H), 3.86 (t, J = 6.9 Hz, 1H), 3.81 (t, J = 9.2 Hz, 1H), 3.68 (ddd, J = 9.8, 5.0, 1.7 Hz, 1H), 2.13, 2.10, 2.04, 2.03, 1.94 (5s, 21H); ^{13}C NMR ($CDCl_3$) δ 169.9, 169.8, 169.6, 169.3, 168.7, 100.5, 81.1, 76.7, 75.6, 73.2, 70.6, 70.4, 69.8, 68.8, 66.4, 61.6, 60.7, 31.8, 20.5, 20.4, 20.3, 20.1; MALDI-MS m/z 768.5 [M + Na^+]. Anal. Calcd for $C_{27}H_{37}BrO_{17}S\cdot H_2O$ (763.55): C, 42.47; H, 5.15. Found: C, 42.44; H, 5.00.

17: TLC R_f = 0.28 (petroleum ether/EtOAc, 1:1); $[\alpha]_D$ = -97.2° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.22 (t, J = 9.1 Hz, 1H), 5.11 (t, J = 9.3 Hz, 1H), 5.02 (t, J = 9.3 Hz, 1H), 4.99 (t, J = 9.2 Hz, 1H), 4.89 (t, J = 9.0 Hz, 1H), 4.53 (dd, J = 12.1, 1.9 Hz, 1H), 4.74 (d, J = 10.1 Hz, 1H), 4.70, 4.50 (AB peak, J = 10.9 Hz, 2H), 4.49 (d, J = 7.9 Hz, 1H), 4.33 (dd, J = 12.5, 4.5 Hz, 1H), 4.08 (dd, J = 12.1, 5.2 Hz, 1H), 4.01 (dd, J = 12.4, 2.2 Hz, 1H), 3.77 (t, J = 9.5 Hz, 1H), 3.65 (m, 2H), 2.09, 2.05, 2.01, 2.00, 1.99, 1.97, 1.94 (7s, 21H); ^{13}C NMR ($CDCl_3$) δ 170.0, 169.8, 169.7, 169.2, 169.1, 168.9, 168.6, 100.3, 81.2, 76.7, 75.9, 72.9, 72.5, 71.5, 71.2, 69.7, 67.5, 61.5, 61.3, 31.8, 20.4, 20.2, 20.1; MALDI-MS m/z 768.4 [M + Na^+], 784.4 [M + K^+]. Anal. Calcd for $C_{27}H_{37}BrO_{17}S$ (745.54): C, 43.50; H, 5.00. Found: C, 43.38; H, 5.07.

18: TLC R_f = 0.26 (petroleum ether/EtOAc, 2.3:1); $[\alpha]_D$ = -152.6° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.18 (t, *J* = 7.5 Hz, 1H), 4.97 (t, *J* = 7.8 Hz, 1H), 4.92 (m, 2H), 4.72, 4.53 (AB peak, *J* = 11.0 Hz, 2H), 4.24 (dd, *J* = 11.9, 4.7 Hz, 1H), 3.48 (dd, *J* = 11.9, 8.1 Hz, 1H), 2.06, 2.05, 2.03 (3s, 9H); ^{13}C NMR ($CDCl_3$) δ 169.3, 169.2, 168.9, 81.8, 70.7, 69.0, 67.9, 64.5, 32.4, 20.4, 20.3. Anal. Calcd for $C_{12}H_{17}BrO_7S$ (385.23): C, 37.41; H, 4.45. Found: C, 37.60; H, 4.16.

19: TLC R_f = 0.27 (petroleum ether/EtOAc, 2.3:1); $[\alpha]_D$ = -127.6° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.30 (m, 1H), 5.21 (dd, *J* = 8.1, 7.3 Hz, 1H), 5.13 (dd, *J* = 8.0, 3.3 Hz, 1H), 4.89 (d, *J* = 7.3 Hz, 1H), 4.74, 4.54 (AB peak, *J* = 11.0 Hz, 2H), 4.10 (dd, *J* = 12.6, 4.5 Hz, 1H), 3.71 (dd, *J* = 12.7, 2.3 Hz, 1H), 2.10, 2.07, 2.03 (3s, 9H); ^{13}C NMR ($CDCl_3$) δ 169.8, 169.5, 169.2, 82.1, 69.7, 68.1, 67.1, 65.0, 32.8, 20.6, 20.5, 20.4; MALDI-MS m/z 406.8 [M + Na^+]. Anal. Calcd for $C_{12}H_{17}BrO_7S$ (385.23): C, 37.41; H, 4.45. Found: C, 37.20; H, 4.80.

20: TLC R_f = 0.52 (EtOAc); $[\alpha]_D$ = -185.5° (c 0.8 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.74 (d, *J* = 9.4 Hz, 1H), 5.19 (t, *J* = 9.4 Hz, 1H), 5.10 (t, *J* = 9.4 Hz, 1H), 4.81 (d, *J* = 10.5 Hz, 1H), 4.79, 4.56 (AB peak, *J* = 10.9 Hz, 2H), 4.20 (m, 3H), 3.75 (ddd, *J* = 9.5, 4.9, 2.5 Hz, 1H), 2.07, 2.02, 1.94 (3s, 12H); ^{13}C NMR ($CDCl_3$) δ 171.1, 170.6, 170.2, 169.2, 82.8, 76.2, 73.6, 68.3, 62.0, 52.7, 33.0, 23.1, 20.7, 20.6, 20.5; MALDI-MS m/z 478.0 [M + Na^+], 494.0 [M + K^+].

21: TLC R_f = 0.28 (petroleum ether/EtOAc, 2:1); $[\alpha]_D$ = -81.9° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.54 (d, *J* = 9.1 Hz, 1H), 5.28 (t, *J* = 10.0 Hz, 1H), 5.08 (t, *J* = 9.7 Hz, 1H), 4.88 (d, *J* = 10.5 Hz, 1H), 4.77, 4.57 (AB peak, *J* = 11.0 Hz, 2H), 4.76, 4.64 (AB peak, *J* = 12.1 Hz, 2H), 4.25 (dd, *J* = 12.5, 5.0 Hz, 1H), 4.15 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.91 (q, *J* = 10.0 Hz, 1H), 3.79 (ddd, *J* = 9.9, 5.0, 2.3 Hz, 1H), 2.06, 2.01, 2.00 (3s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.7, 170.6, 169.3, 154.1, 95.2, 82.5, 76.1, 74.5, 73.1, 68.5, 62.0, 54.7, 32.4, 20.7, 20.5; MALDI-MS m/z 609.6 [M + Na^+], 625.7 [M + K^+]. Anal. Calcd for $C_{16}H_{21}BrCl_3NO_9S$ (589.67): C, 32.59; H, 3.59; N, 2.38. Found: C, 32.63; H, 3.83; N, 2.18.

22: TLC R_f = 0.14 (petroleum ether/EtOAc, 2:1); $[\alpha]_D$ = -23.0° (c 1.0 $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.84 (br s, 2H), 7.72 (m, 2H), 5.87 (dd, *J* = 10.1, 9.2 Hz, 1H), 5.74 (d, *J* = 10.7 Hz, 1H), 5.19 (dd, *J* = 10.1, 9.3 Hz, 1H), 4.71, 4.48 (AB peak, *J* = 11.0 Hz, 2H), 4.44 (t, *J* = 10.6 Hz, 1H), 4.33 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.19 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.96 (ddd, *J* = 10.2, 4.8, 2.2 Hz, 1H), 2.10, 2.02, 1.84 (3s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.5, 169.9, 169.4, 167.4, 167.0, 134.5, 131.4, 131.0, 123.7, 80.1, 76.1, 71.2, 68.6, 61.9, 53.2, 31.7, 20.7, 20.5, 20.3; MALDI-MS m/z 566.0 [M + Na^+], 581.9 [M + K^+]. Anal. Calcd for $C_{21}H_{22}BrNO_9S{\cdot}0.5H_2O$ (553.38): C, 45.58; H, 4.19; N, 2.53. Found: C, 45.59; H, 3.75; N, 2.54.

General Procedure for the Synthesis of Thioglycosides 24, 26 and 30.

To a solution of the appropriate GTM-Br (0.14 mmol) and Cys or HCy derivative (0.13 mmol) in EtOAc (2 mL) was added 2 mL of 10% Na_2CO_3 followed by addition of TBAHS (170 mg, 0.5 mmol). The mixture was vigorously stirred at room temperature for 8 h, then diluted with EtOAc and washed successively with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, concentrated in vacuo to give a residue which was purified by flash column chromatography to afford the corresponding desired product.

24: TLC R_f = 0.28 (petroleum ether/EtOAc, 3:2); $[\alpha]_D$ = -86.1° (c 1.0 $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.30 (m, 5H), 5.31 (d, *J* = 7.9 Hz, 1H), 5.17 (t, *J* = 9.3 Hz, 1H), 5.13 (q-like, 2H), 5.02 (t, *J* = 9.4 Hz, 1H), 4.98 (t, *J* = 9.2 Hz, 1H), 4.70 (d, *J* = 10.2 Hz, 1H), 4.54 (m, 1H), 4.18 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.05 (dd, *J* = 12.5, 2.2 Hz, 1H), 3.74 (AB peak, *J* = 13.6 Hz, 2H), 3.64 (ddd, *J* = 9.9, 4.7, 2.2 Hz, 1H), 3.13 (dd, *J* = 14.0, 4.4 Hz, 1H), 2.87 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.00, 1.96, 1.945, 1.937 (4s, 12H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.6, 170.5, 170.0, 169.3, 155.0, 135.0, 128.62, 128.56, 128.4, 81.4, 80.3, 75.9, 73.8, 69.7, 68.2, 67.5, 61.9, 53.4, 33.5, 33.1, 28.2, 20.6, 20.5; MALDI-MS m/z 710.7 [M + Na^+], 726.7 [M + K^+]. Anal. Calcd for $C_{30}H_{41}NO_{13}S_2{\cdot}H_2O$ (705.79): C, 51.05; H, 6.14; N, 1.98. Found: C, 50.78; H, 5.55; N, 1.96.

26: TLC R_f = 0.28 (petroleum ether/EtOAc, 1:1); $[\alpha]_D$ = -59.6° (c 1.0 $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 6.3 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 5.92 (m, 1H), 5.68 (d, *J* = 7.9 Hz, 1H), 5.40-5.27 (m, 3H), 5.23 (t, *J* = 9.0 Hz, 1H), 5.11 (dd, *J* = 10.3, 7.8 Hz, 1H), 5.00 (t, *J* = 9.9 Hz, 1H), 4.95 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.74 (d, *J* = 10.2 Hz, 1H), 4.67 (m, 3H), 4.50 (dd, *J* = 12.2, 1.3 Hz, 1H), 4.45 (d, *J* = 7.6 Hz, 1H), 4.42 (d, J = 6.4 Hz, 2H), 4.25 (t, J = 6.8 Hz, 1H), 4.10 (m, 3H), 3.88-3.73 (m, 4H), 3.62 (m, 1H), 3.21 (dd, J = 14.3, 4.3 Hz, 1H), 2.98 (dd, J = 14.1, 6.6 Hz, 1H), 2.15, 2.10, 2.05, 2.04, 2.03, 1.97 (6s, 21H); ^{13}C NMR ($CDCl_3$) δ 170.2, 170.0, 169.9, 169.6, 169.0, 155.7, 143.7, 141.3, 131.2, 127.7, 127.1, 125.0, 120.0, 119.3, 101.0, 81.2, 76.9, 76.1, 73.7, 70.9, 70.7, 70.1, 69.1, 67.2, 66.6, 66.4, 62.0, 60.8, 53.5, 47.1, 33.4, 33.1, 20.75, 20.69, 20.5, 20.4; MALDI-MS m/z 1070.9 [M + Na^+]. Anal. Calcd for $C_{48}H_{57}NO_{21}S_2$ (1048.10): C, 55.01; H, 5.48; N, 1.34. Found: C, 54.65; H, 5.60; N, 1.27.

30: TLC R_f = 0.47 (petroleum ether/EtOAc, 1:1); $[\alpha]_D$ = -78.8° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.61 (d, J = 8.6 Hz, 1H), 6.20 (d, J = 9.1 Hz, 1H), 5.32 (d, J = 8.3 Hz, 1H), 5.26 (t, J = 9.8 Hz, 1H), 5.06 (t, J = 9.8 Hz, 1H), 5.02 (overlapped, 1H), 4.70 (m, 2H), 4.55 (dd, J = 8.6, 4.7 Hz, 1H), 4.27 (m, 1H), 4.24 (dd, J = 12.3, 4.8 Hz, 1H), 4.10 (dd, J = 12.2, 1.9 Hz, 1H), 3.92 (t, J = 10.3 Hz, 1H), 3.90, 3.76 (AB peak, J = 14.1 Hz, 2H), 3.83 (m, 1H), 3.71 (s, 3H), 2.70 (t-like, J = 5.9 Hz, 2H), 2.05, 1.99, 1.98 (3s, 9H), 2.00 (overlapped, 3H), 1.41 (s, 9H), 1.40 (m, 1H), 1.20 (m, 1H), 0.89 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.1, 171.2, 170.6, 170.2, 169.3, 155.5, 154.2, 95.5, 82.4, 80.3, 75.7, 74.3, 73.4, 68.7, 62.1, 56.5, 54.6, 53.3, 52.1, 37.5, 33.6, 28.2, 27.5, 24.9, 20.6, 20.4, 15.4, 11.4; MALDI-MS m/z 892.1 [M + Na^+], 908.1 [M + K^+]. Anal. Calcd for $C_{32}H_{50}Cl_3N_3O_{14}S_2$ (871.24): C, 44.12; H, 5.78; N, 4.82. Found: C, 44.31; H, 5.49; N, 4.80.

Compound **30** was further transformed into **31** according to our previous procedure.[24]

31: TLC R_f = 0.14 (petroleum ether/EtOAc, 1:2); $[\alpha]_D$ = -76.0° (c 0.4 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.84 (d, J = 8.2 Hz, 1H), 6.27 (d, J = 7.6 Hz, 1H), 5.51 (d, J = 7.9 Hz, 1H), 5.21 (t, J = 9.7 Hz, 1H), 5.06 (t, J = 9.4 Hz, 1H), 4.89 (d, J = 10.6 Hz, 1H), 4.53 (dd, J = 8.6, 4.9 Hz, 1H), 4.22 (dd, J = 12.3, 4.8 Hz, 1H), 4.20 (overlapped, 2H), 4.11 (dd, J = 12.3, 2.4 Hz, 1H), 3.83 (AB peak, J = 13.6 Hz, 2H), 3.75 (overlapped, 1H), 3.71 (s, 3H), 2.69 (m, 2H), 2.05, 2.00, 1.99, 1.94 (4s, 12H), 1.95 (overlapped, 3H), 1.42 (s, 9H), 1.41 (m, 1H), 1.20 (m, 1H), 0.89 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.1, 171.4, 170.8, 170.7, 170.5, 169.3, 155.7, 82.6, 80.4, 75.9, 73.7, 68.6, 62.2, 56.6, 53.6, 52.9, 52.1, 37.7, 33.0, 32.0, 28.3, 27.6, 25.0, 23.2, 20.7, 20.62, 20.56, 15.5, 11.5; MALDI-MS m/z 760.7 [M + Na^+], 776.7 [M + K^+]. HRMS (MALDI) calcd for $C_{31}H_{51}N_3O_{13}S_2Na$ (M + Na^+) 760.2763, found 760.2775. Anal. Calcd for $C_{31}H_{51}N_3O_{13}S_2$ (737.88): C, 50.46; H, 6.97; N, 5.69. Found: C, 50.90; H, 7.34; N, 5.44.

28: To a solution of GTM-Br **16** (60 mg, 80 μmol) and tripeptide **27** (29 mg, 77 μmol) in 2 mL of DMF was added 0.45 mL of pH 8.5 solution of $NaHCO_3$ followed by addition of 0.85 mL of H_2O. The resulting mixture was stirred at room temperature for 7 h, then diluted with EtOAc and washed successively with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, concentrated in vacuo to give a residue which was purified by flash column chromatography (petroleum ether/EtOAc, 1:1 → 1:3) to afford the desired product **28** (58 mg, 73%) as a white amorphous solid: TLC R_f = 0.57 (EtOAc); $[\alpha]_D$ = -59.4° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.11 (d, J = 7.3 Hz, 1H), 6.77 (d, J = 7.4 Hz, 1H), 5.36 (d, J = 8.2 Hz, 1H), 5.31 (d, J = 3.3 Hz, 1H), 5.24 (t, J = 9.0 Hz, 1H), 5.07 (dd, J = 10.3, 7.8 Hz, 1H), 4.98 (t, J = 9.8 Hz, 1H), 4.92 (dd, J = 10.6, 3.3 Hz, 1H), 4.72 (d, J = 10.1 Hz, 1H), 4.48 (m, 4H), 4.37 (m, 1H), 4.08 (m, 3H), 3.85 (t, J = 6.9 Hz, 1H), 3.78 (m, 3H), 3.70 (s, 3H), 3.66 (overlapped m, 1H), 3.00 (dd, J = 14.0, 6.0 Hz, 1H), 2.79 (dd, J = 14.2, 7.6 Hz, 1H), 2.11, 2.08, 2.04, 2.02, 2.00, 1.92 (6s, 21H), 1.40 (s, 9H), 1.37 (d, J = 7.0 Hz, 3H), 1.36 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 173.0, 171.2, 170.4, 170.2, 170.04, 169.96, 169.6, 168.9, 155.4, 101.0, 81.3, 80.4, 76.8, 76.1, 73.6, 71.0, 70.7, 70.3, 69.1, 66.7, 61.9, 60.8, 53.4, 52.4, 48.9, 48.1, 34.1, 33.0, 28.2, 20.8, 20.7, 20.6, 20.5, 20.4, 18.1, 17.9; MALDI-MS m/z 1064.1 [M + Na^+], 1080.1 [M + K^+]. Anal. Calcd for $C_{42}H_{63}N_3O_{23}S_2$ (1042.09): C, 48.41; H, 6.09; N, 4.03. Found: C, 48.38; H, 6.05; N, 4.34.

33: The reaction procedure was identical with that for **28** except GTM-Br **17** was used in place of **16** and peptide **32** was used instead of **27**. Column chromatography was performed with EtOAc/MeOH 30:1. The *S*-neoglycopeptide **33** was isolated as a white amorphous solid in 69% yield: TLC R_f = 0.49 (EtOAc/MeOH, 20:1); $[\alpha]_D$ = -47.8° (c 0.6 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 1H), 7.26 (d, J = 6.7 Hz, 1H), 6.44 (br s, 1H), 5.85 (br s, 1H), 5.62 (d, J = 7.2 Hz, 1H), 5.26 (t, J = 9.2 Hz, 1H), 5.13 (t, J = 9.3 Hz, 1H), 5.03 (t, J = 9.6 Hz, 1H), 4.96 (t, J = 9.7 Hz, 1H), 4.90 (t, J = 9.0 Hz, 1H), 4.73 (d, J = 10.1 Hz, 1H), 4.52 (m, 2H), 4.49 (d, J = 8.0 Hz, 1H), 4.42-4.34 (m, 2H), 4.29 (m, 1H), 4.11 (m, 2H), 4.02 (dd, J = 12.4, 1.9 Hz, 1H), 3.78 (m, 3H), 3.65 (m, 3H), 2.70 (m, 1H), 2.59 (m, 1H), 2.12, 2.06, 2.03, 2.00, 1.98, 1.96 (6s, 21H), 2.10 (overlapped m, 2H), 1.43 (s, 9H), 1.39 (d, J = 7.4 Hz, 3H), 1.19 (d, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 174.6, 171.6, 170.7, 170.5, 170.1, 170.0, 169.9, 169.4, 169.3, 156.3, 100.7, 81.4, 80.6, 76.3, 73.4, 72.9, 72.0, 71.6, 70.1, 67.9, 67.2, 61.9, 61.6, 59.1, 52.9, 48.9, 33.0, 31.2, 29.7, 28.3, 27.8, 21.0, 20.7, 20.6, 20.5, 18.9, 17.9; MALDI-MS m/z 1093.4 [M + Na^+], 1109.4 [M + K^+]. Anal. Calcd for $C_{43}H_{66}N_4O_{23}S_2$ (1071.13): C, 48.22; H, 6.21; N, 5.23. Found: C, 48.40; H, 6.52; N, 5.07.