Supporting Information

Overcoming antibiotic resistance in *Pseudomonas aeruginosa* biofilms using glycopeptide dendrimers

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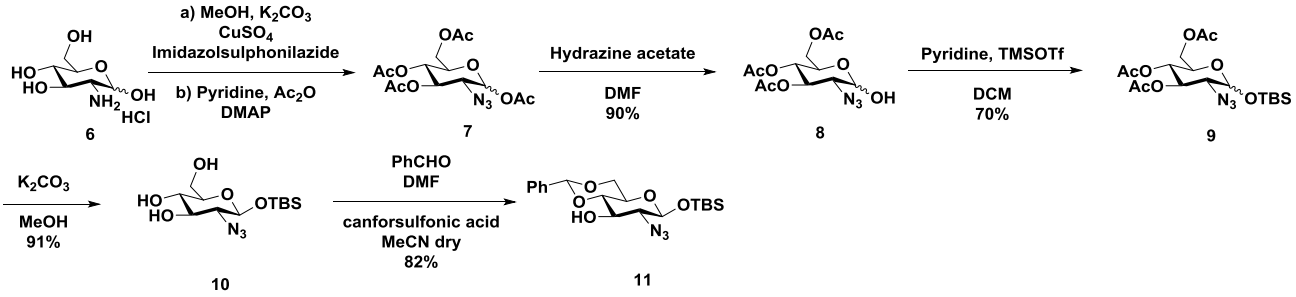
1. Carbohydrate building block synthesis

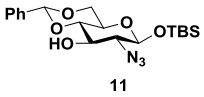
Building block GalA (4-carboxyphenyl-β-D-galactoside), GalB (3-carboxythiopropyl-β-D-thiogalactoside) and cFuc (α-L-fucosylacetic acid) were prepared as described previously.[1, 2]

Synthesis of Le^aC_6 carbohydrate building blocks

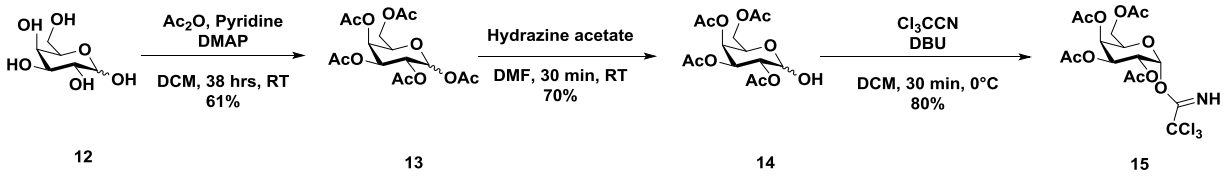


Scheme S1: Synthesis of glucosylated carbohydrate building block for the synthesis of the trisaccharide $\mathbf{Le^aC_6}$ (ref. 1 and 2)

Compound 11

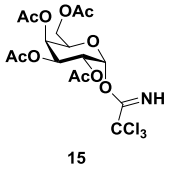


Following a previously reported procedure,[3] **10**[4] (2.95 g, 9.25 mmoL) was dissolved in dry MeCN (37 mL). $PhCH(OMe)_2$ (2.5 mL, 16.65 mmoL) and camphorsulfonic acid (0.38 g, 1.57 mmoL) were added to the reaction mixture and stirred for 90 min. Then, the reaction mixture was treated with TEA until pH = 7, diluted with AcOEt (400 mL) and washed with H_2O (3 x 40 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (eluent EP/AcOEt (7:1) to EP/AcOEt (5:1) to deliver the product **11** as a pale yellow oil (3.15 g, 7.73 mmoL, 84% yield). $\mathbf{[\alpha]^{25}_D}$ **=** - 16.6 (c 0.55 in $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.50-7.35 (m, 5H), 5.52 (s, 1H), 4.28 (part A of a system ABX, *J* = 10.4 Hz, *J* = 4.8 Hz, 1H), 3.77 (at, *J* =9.8 Hz, 1H), 3.59-3.51 (m, 2H), 3.44-3.27 (m, 2H). 0.94 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H). **^{13}C NMR**: (50 MHz, $CDCl_3$) δ: 136.4, 129.0, 128.0, 125.9, 101.6, 97.2, 80.4, 77.3, 76.7, 76.1, 71.4, 68.6, 68.2, 66.0, 25.3, 17.7, -4.5, -5.4.

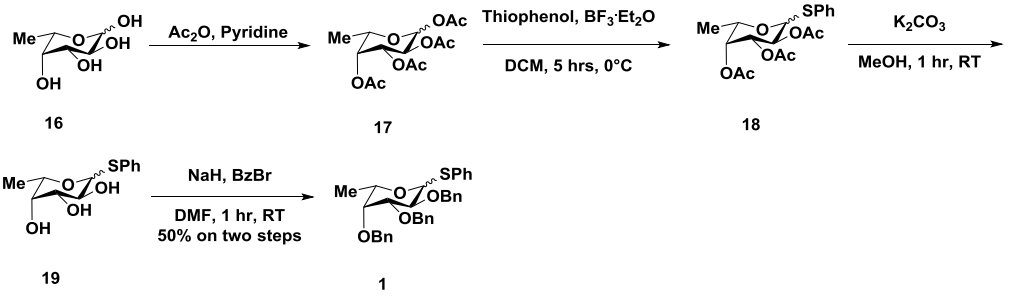


Scheme S2: Synthesis of galactosylated carbohydrate building block for the synthesis of the trisaccharide **Le^{a}C$_6$**

Compound 15

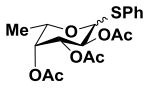


14 (3.71 g, 11.1 mmoL) was dissolved in dry DCM (30 mL) and cooled down to 0°C. DBU (0.32 mL, 2.22 mmoL) and Cl_3CCN (7.8 mL, 77.7 mmoL) were added to the reaction mixture and stirred for 30 min. The reaction mixture was then diluted with DCM (500 mL) and washed with a saturated solution of NH_4Cl (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude was purified by flash chromatography on silica gel (eluent EP/AcOEt (2: 1) + 0.1% TEA) to obtain the product **15** as a white solid (4.04g, 8.22 mmol, 80% yield). **$[\alpha]^{25}_D$ =** - 4.5 (c 1 in $CHCl_3$); **ESI-MS**: m/z 514.03$[M+Na]^+$; **^{1}H NMR** (200 MHz $CDCl_3$) δ: 8.66 (bs, 1H), 6.60 (ad, *J* = 2.8 Hz, 1H), 5.59-5.53 (m, 1H), 5.39 (dd, *J* = 2.8 Hz, *J* = 4.6 Hz, 2H), 4.44 (at, *J* = 6.4 Hz, 1H), 4.23-4.01 (m, 2H), 2.17 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H). **^{13}C NMR**: (50 MHz, $CDCl_3$) δ: 170.2, 170.0, 169.9, 160.9, 93.5, 69.0, 67.5, 67.4, 66.9, 61.2, 20.6.



Scheme S3: Synthesis of fucosylated carbohydrate building block for the synthesis of the trisaccharide **Le^{a}C$_6$ (ref.[5])**

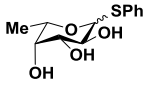
Compound 18[3]



18

17 (3.55 g, 10.7 mmoL) was dissolved in dry DCM (36.7 mL) was cooled down to 0°C. Thiophenol (2.2 mL, 15.06 mmoL) and $BF_3{\cdot}Et_2O$ (1.17 mL, 13.16 mmoL) were added. After completation of the addition, the reaction mixture was slowly heated up to RT and stirred for 5 hrs. Then, the reaction mixture was treated with TEA, diluted with DCM (400 mL), and washed with brine (3 × 40 mL) and with $NaHCO_3$ (3 × 40 mL). The organic phase is then dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (eluent EP/EtOAc (4: 1)) to obtain the product **18** as a pale yellow oil (4.00 g, 10.7 mmoL, 99% yield). **$[\alpha]^{25}_D$ =** -3.0 (c 0.9 in $CHCl_3$). **Elemental analysis:** ($C_{18}H_{22}O_7S$) calculated: C 56.23; H 6.29, found: C 55,18; H 6.19. **^{1}H NMR** (200 MHz $CDCl_3$) δ: 7.28-7.53 (m, 5H, Ph), 5.27 (d, 1H), 5.23 (t, 1H), 5.04 (dd, *J* = 9.9 Hz, *J* = 3.3 Hz), 4.71 (d, *J* = 9.9 Hz, 1H), 3.84 (q, *J* = 6.4 Hz, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 1.97 (s, 3H), 1.24 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (50 MHz $CDCl_3$) δ: 170.5, 170.0, 169.4, 132.3, 128.8, 127.9, 86.5, 73.1, 72.4, 69.0, 67.3, 20.7, 20.5, 16.3.

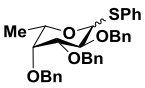
Compound 19[3]



19

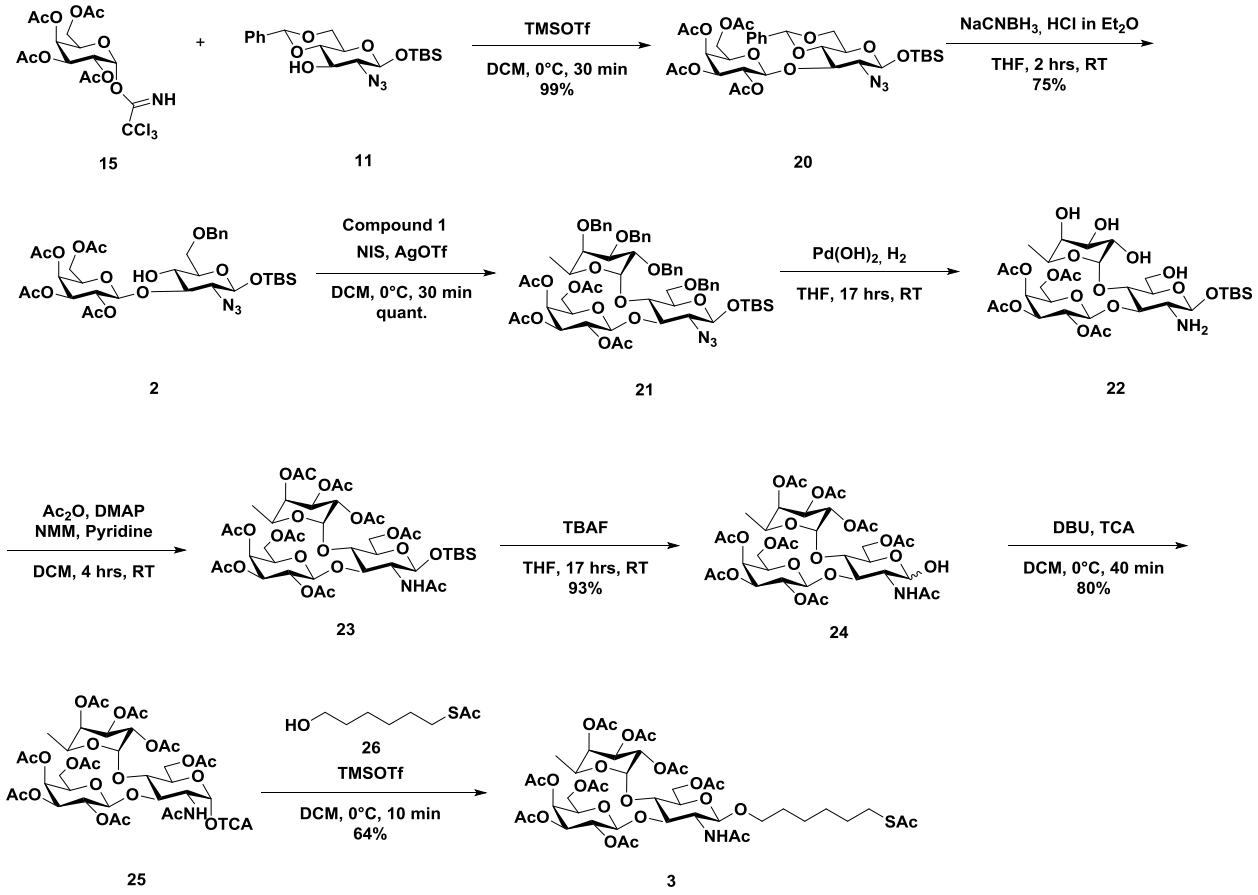
To a solution of **18** (3.84 g, 10.0 mmoL) in MeOH (25 mL) K_2CO_3 (0.42 g, 3.02 mmoL) was added. The reaction mixture was stirred at RT for 90 min. Then, the reaction mixture was concentrated. 2.58 g of crude product **19** were obtained and were used for the next reaction without further purification.

Compound 1[3]



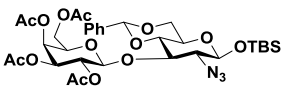
1

To a solution of **19** (2.58 g, 10.0 mmoL) in DMF (17 mL) NaH (60% in oil) (1.45 g, 36.0 mmoL) and BzBr (4.30 mL, 36.25 mmoL) were added at RT. After 1 hr of stirring, the reaction mixture was diluted with MeOH (50 mL) and Et_2O (400 mL) and washed with a saturated solution of NH_4Cl (3 × 40 mL). The organic phase is then dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was crystallized with 15 mL of a mixture Et_2O/hexane (1:3) to obtain **1** as a white solid (2.6 g, 4.94 mmoL, 50% yield over two steps). **$[\alpha]^{25}_D$ =** - 14.0 (c 0.7 in $CHCl_3$). **p.f.** 107-109°C. **Elemental analysis:** calculated $C_{33}H_{30}O_4S$: C 75.83; H 5.79; found: C 75.56; H 5.53. **^{1}H NMR** (200 MHz $CDCl_3$) δ: 7.18-7.60 (m, 20H, Ph), 4.83 (s, 2H, C*H*$_2$Ar), 4.76 (s, 2H, C*H*$_2$Ar), 4.73 (s, 2H, C*H*$_2$Ar), 4.60 (d, 1H, H-1), 3.93 (dd, $J_{2\text{-}1}$ = 9.5 Hz, 1H, H-2), 3.59 (dd, $J_{2\text{-}3}$ = 11.7 Hz, $J_{3\text{-}4}$ = 2.8 Hz, 1H, H-3), 3.52 (q, $J_{5\text{-}6}$ = 6.4 Hz, 1H, H-5), 1.26 (d, $J_{6\text{-}5}$ = 6.4 Hz, 1H, H-6).**^{13}C NMR** (125 MHz $CDCl_3$) δ: 138.7, 138.4, 138.3, 134.3, 131.5, 128.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.9, 87.5, 84.5, 77.1, 76.6, 75.5, 74.6, 74.5, 72.8, 17.28.



Scheme S4: Synthesis of fucosylated carbohydrate building block for the synthesis of the trisaccharide **Le^{a}C$_6$** (ref. 1).

Compound 20[1]

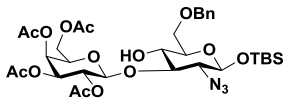


20

To a solution of **11** (1.5 g, 3.97 mmoL) and **15** (2.78 g, 5.96 mmoL) in dry DCM (30 mL), TMSOTf (0.087 g, 0.394 mmoL) was added. After 30 min., the reaction mixture was neutralized with TEA, diluted with DCM (200 mL) and washed with brine (3 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (Biotage SNAP-100 g, flow 15 mL/ min, eluent EP/AcOEt (3: 1) to EP/AcOEt (2: 1)) to obtain the product **20** as a white glassy solid (3.58g, 3.97 mmol, 99% yield). **$[\alpha]^{25}_D$** = - 4.5 (c 1 in $CHCl_3$). **Elemental analysis:** ($C_{33}H_{47}N_3O_{14}Si$) calculated C 53.72; H 6.42; N 5.70, found : C 53.82; H 6.38; N 5.37. **^{1}H NMR** (400 MHz $CDCl_3$) δ: 7.47-7.34 (m, 5H, Ph), 5.53 (s, 1H, C*H*Ph), 5.32 (d, $J_{4b\text{-}3b}$ = 3.6 Hz, 1H, H-4b), 5.26 (dd, $J_{2b\text{-}1b}$ = 8.0 Hz, $J_{2b\text{-}3b}$ = 10.8 Hz, 1H, H-2b), 4.99 (dd, $J_{3b\text{-}4b}$ = 3.2 Hz, $J_{3b\text{-}2b}$ = 10.4 Hz, 1H, H-3b), 4.72 (d, $J_{1b\text{-}2b}$ = 8.0 Hz, 1H, H-1b), 4.60 (d, $J_{1a\text{-}2a}$ = 7.6 Hz, 1H, H-1a), 4.27 (dd, $J_{6a\text{-}5a}$ = 4.8 Hz, $J_{6a\text{-}6'a}$ = 10.4

Hz, 1H, H-6a), 4.06 (A part of an ABX system, $J_{A\text{-}X}$ = 7.6 Hz, $J_{A\text{-}B}$ = 10.4 Hz, 1H, H-6b), 3.87 (B part of an ABX system, $J_{B\text{-}X}$ = 6.0 Hz, $J_{A\text{-}B}$ = 11.2 Hz, 1H, H-6'b), 3.79-71 (m, 2H, H-5b, H-6'a), 3.67 (at, $J_{4a\text{-}3a}$ = 9.2 Hz, 1H, H-4a), 3.46 (at, $J_{3a\text{-}4a}$ = 9.6 Hz, 1H, H-3a), 3.39-3.30 (m, 2H, H-5a,H-2a), 2.11 (s, 3H, COCH_3), 2.07 (s, 3H, COCH_3), 1.97 (s, 3H, COCH_3), 1.93 (s, 3H, COCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.16 (s, 3H, SiCH_3), 0.14 (s, 3H, SiCH_3). **^{13}C NMR**: (100 MHz, $CDCl_3$) δ: 170.3 (Cq), 170.3 (Cq), 170.1 (Cq), 169.5 (Cq), 136.9 (C-Ph), 129.1 (C-Ph), 125.9 (C-Ph), 101.5 (C-1b), 101.2 (CH-Ph), 97.6 (C1a), 79.6 (C-3a).79.3 (C-4a), 70.9 (C-3b), 70.6 (C-5b), 69.2 (C-2b), 68.5 (C-2a, C-6a, C-6'a), 66.8 (C-4b), 66.4 (C-5a), 60.9 (C-6b, C-6'b), 25.4 (SiC(*C*H_3)$_3$), 20.5 (CO*C*H_3), 17.8 (Si*C*(CH_3)$_3$), -4.3 (Si*C*H_3), -5.2 (Si*C*H_3).

Compound 2[1]

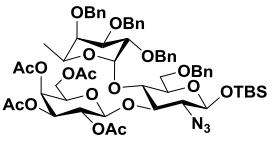


2

To a solution of **20** (1.72 g 1.62 mmoL) in dry THF (34 mL), a solution of $NaBH_3CN$ (1 M in THF, 18 mL, 18.00 mmoL) and a solution of HCl (2 M in ether, 11 mL, 22.00 mmoL) were added dropwise to pH = 1. After 20 min. of stirring, the reaction mixture was neutralized with solid $NaHCO_3$ (1.85 g, 22.0 mmoL), diluted with Et_2O (100 mL) and washed with a saturated solution $NaHCO_3$ (2 × 10mL), and with brine (2 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (eluent EP/AcOEt (3:1) to EP/AcOEt (2: 1) to obtained **2** as a colorless oil (0.87 g, 1.21 mmoL, 75% yield). **$[\alpha]^{25}_D$ =** + 12.5 (c 1 in $CHCl_3$). **Elemental analysis:** ($C_{33}H_{49}N_3O_{14}Si$) calculated: C 53.57; H 6.68; N 5.68, found: C 53.49; H 6.63; N 5.58. **^{1}H NMR** (400 MHz $CDCl_3$) δ: 7.47-7.34 (m, 5H, Ph), 5.38 (d, $J_{4b\text{-}3b}$ = 2.8 Hz, 1H, H-4b), 5.25 (dd, $J_{2b\text{-}3b}$ = 10.4 Hz, $J_{2b\text{-}1b}$ = 8.0 Hz, 1H, H-2b), 5.04 (dd, $J_{3b\text{-}2b}$ = 10.8 Hz, $J_{3b\text{-}4b}$ = 3.6 Hz, 1H, H-3b), 4.57 (s, 2H, CH_2Ar), 4.56 (d, $J_{1b\text{-}2b}$ = 8.4 Hz, 1H, H-1b), 4.53 (d, $J_{1a\text{-}2a}$ = 7.6 Hz, 1H, H-1a), 4.11 (dd, $J_{6b\text{-}6'b}$ = 2.8 Hz, $J_{6b\text{-}5b}$ = 5.6 Hz, 2H, H-6b, H-6'b), 3.98 (at, $J_{5b\text{-}6b}$ = 6.8 Hz, 1H, H-5b), 3.79 (dd, $J_{6a\text{-}5a}$ = 1.2 Hz, $J_{6'a\text{-}6a}$ = 7.6 Hz 1H, H 6a), 3.64 (dd, $J_{6'a\text{-}6a}$ = 10.8 Hz, $J_{6'a\text{-}5a}$ = 6.0 Hz 1H, H-6'a), 3.64 (dd, $J_{6a\text{-}6'a}$ = 10.8 Hz, $J_{6a\text{-}5a}$ = 6.0 Hz 1H, H-6a), 3.53 (at, $J_{4a\text{-}3a}$ = $J_{4a\text{-}5a}$ = 8.8 Hz, 1H, H-4a), 3.40 3.36 (m, 1H, H-5a), 3.27 (dd, $J_{2a\text{-}1a}$ = 7.2 Hz, $J_{2a\text{-}3a}$ = 10.0 Hz, 1H, H-2a), 3.17 (dd, $J_{3a\text{-}2a}$ = 10.0 Hz, $J_{3a\text{-}4a}$ = 8.3 Hz, 1H, H-3a), 2.15 (s, 3H, COCH_3), 2.11 (s, 3H, COCH_3), 2.02 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 0.93 (s, 9H, SiC(CH_3)$_3$), 0.17 (s, 3H, SiCH_3), 0.15 (s, 3H, SiCH_3). **^{13}C NMR**: (100 MHz, $CDCl_3$) δ: 170.4 (Cq), 170.1 (Cq), 170.0 (Cq), 169.4 (Cq), 138 (C-Ar), 128.2 (C-Ar), 127.4 (C-Ar), 102.4 (C-1b), 97.2 (C-1a), 86.3 (C-3a), 75.3 (C-5a), 73.4 (*C*H_2Ar), 71.1 (C-5b), 70.6 (C-3b), 69.4 (C-6a

o C-6'a), 68.9 (C-4a), 68.5 (C-2b), 67.1 (C-2a), 66.8 (C-4b), 61.6 (C-6b o C-6'b), 25.5 (SiC(CH_3)$_3$), 20.4 (COCH_3), 17.9 (SiC(CH$_3$)$_3$), -4.2 (SiCH_3), -5.2 (SiCH_3).

Compound 21



21

A solution of **2** (0.85 g, 1:15 mmoL) and **1** (1.21 g, 2:31 mmoL) in dry DCM (15 mL) was cooled down to -10 °C. NIS (0.51 g, 2.30 mmoL) and AgOTf (0.07 g, 0.25 mmoL) were added and the reaction mixture was stirred for 40 min. at -10°C. The reaction mixture was neutralized with TEA (pH = 7), diluted with DCM (50 mL) and washed with a saturated solution of Na_2SO_4 • 5 H_2O (2 × 5 mL) and brine (2 × 5 mL). The organic phase is then dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (eluent EP/AcOEt (3: 1) to EP/AcOEt (2: 1)) to obtain **21** as a white glassy solid (1.30 g, 1.15 mmol, 99% yield). **[α]$^{25}_{D}$ =** - 12.0 (c 1 in CHCl3). **ESI-MS**: m/z 1178.37 [M + Na]$^+$. **Elemental analysis:** calculated $C_{60}H_{77}N_3O_{18}Si$: C 62.32; H 6.71; N 53.63, found: C 62.12; H 6.70; N 3.37. **^{1}H NMR** (400 MHz $CDCl_3$) δ: 7.23-7.34 (m, 20H, Ph), 5.35 (d, $J_{4b\text{-}3b}$ = 2.8 Hz, 1H, H-4b), 5.07 (m, 3H, H-1b, H-2b, H_1c), 5.02 (d, $J_{3b\text{-}4b}$ = 3.2 Hz,1H, H-3b), 5.00-4.97 (A part of AB system, $J_{A\text{-}B}$ = 12.0, Hz, 1H, CH_2Ar), 4.87-4.84 (A part of AB system, $J_{A\text{-}B}$ = 12.0, Hz, 1H, CH_2Ar), 4.80 (d, $J_{5c\text{-}6c}$ = 6.8 Hz, 1H, H-5c), 4.76-4.73 (B part of AB system, J = 11.6 Hz, 1H, CH_2Ar), 4.69-4.66 (B part of AB system , J = 11.6 Hz, 1H, CH_2Ar), 4.47(d, $J_{1a\text{-}2a}$ = 7.6 Hz, 1H, H-1a), 4.47-4.44 (A part of AB system, J = 12.4, Hz, 1H, CH_2Ar), 4.39-4.36 (B part of AB system, J = 12.8 Hz, 1H, CH_2Ar), 4.15 (dd, $J_{2c\text{-}1c}$ = 4.0 Hz, $J_{2c\text{-}3c}$ = 10.3 Hz,1H, H-2c), 4.09 (dd, $J_{6'b\text{-}5b}$ =8.0 Hz, $J_{6'b\text{-}6b}$ = 10.4 Hz, 1H, H-6b), 3.99-3.81 (m,5H, H-4a, H-6a, H-5b, H-6'b, H-3c), 3.72 (d, $J_{4c\text{-}3c}$ =1.6 Hz 1H, H-4c), 3.57-3.53 (m, 2H, H-3a, H-6'a), 3.34 (ad, J = 9.8 Hz, H-5a), 3.23 (dd, $J_{2a\text{-}1a}$ = 7.6 Hz, $J_{2a\text{-}3a}$ = 10.0 Hz, 1H, H-2a), 2.10 (s, 3H, COCH_3), 2.02 (s, 3H, COCH_3), 1.96 (s, 3H, COCH_3), 1.82 (s, 3H, COCH_3), 1.27 (d, $J_{6c\text{-}5c}$ = 6.4 Hz, 3H, H-6c), 0.91 (s, 9H, SiC(CH_3)$_3$), 0.13 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3). **^{13}C NMR**: (100 MHz, $CDCl_3$) δ:170.4 (Cq), 169.8 (Cq), 169.2 (Cq), 138.7 (C-Ar), 138.6 (C-Ar), 138.2 (C-Ar), 138.1 (C-Ar), 128.6 (C-Ar), 100.6 (C-1b), 97.5 (C-1c), 97.1 (C-1a), 80.7 (C-5b), 77.7 (C-3a), 76.3 (C-4c), 75.7 (C-2c), 74.9 (CH_2Ar), 74.0 (CH_2Ar), 73.3 (C-5a), 73.0 (CH_2Ar), 72.2 (CH_2Ar), 71.3 (C-3c), 70.9 (C-3b), 70.2 (C-4a), 69.7 (C-2a), 68.4 (C-2b), 67.2 (C-4b), 66.8 (C-6a, C-6'a), 66.2 (C-5c), 60.3 (C-6b, C6'b), 25.5 (SiC(CH_3)$_3$), 20.7 (COCH_3), 20.6 (COCH_3), 20.5 (COCH_3), 17.8 (SiC(CH$_3$)$_3$), 16.7 (C-6c), -4.2 (SiCH_3), -5.2 (SiCH_3).

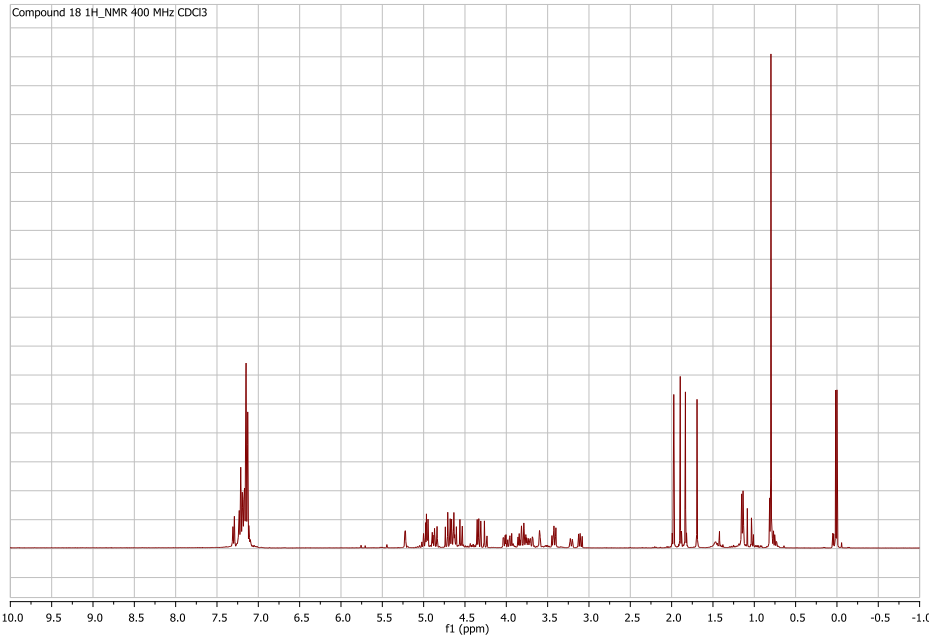


Figure S1: ^{1}H NMR of **21** carbohydrate building block.

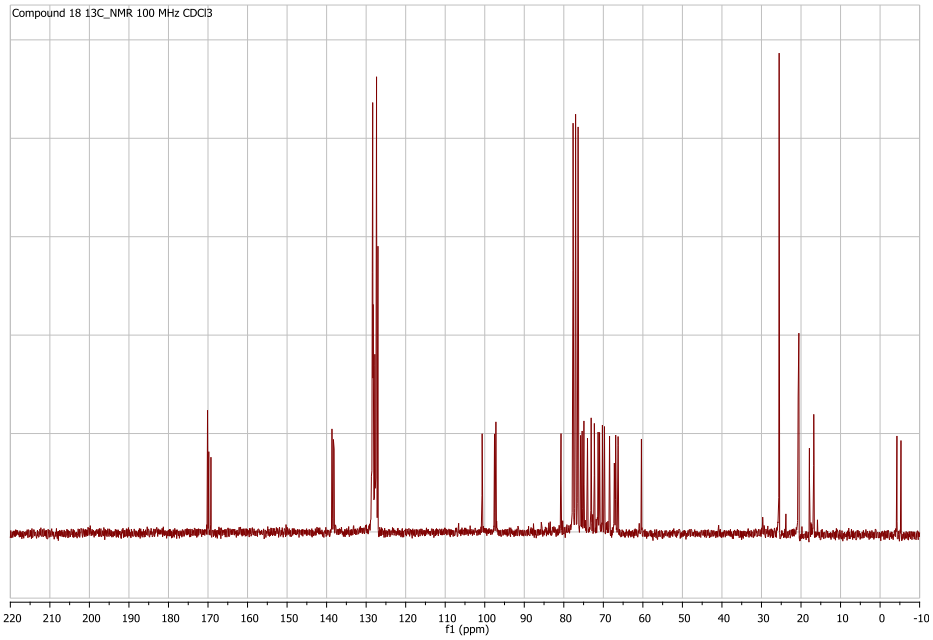
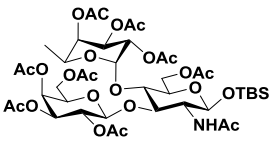


Figure S2: ^{13}C NMR of **21** carbohydrate building block.

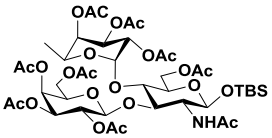
Compound 22



22

To a solution of **21** (0.30 g, 0.26 mmoL), in dry THF (30 mL), glacial acetic acid (0.06 mL, 1.03 mmoL), H_2O (0.5 mL), and $Pd(OH)_2$ (0. 27g, 0.38 mmoL) were added at RT. After the addition, three cycles vacuum/H_2 were performed. Then the reaction mixture was allowed to stir under a hydrogen atmosphere for 17 hrs. Then, the reaction mixture was filtered through Celite and washed with AcOEt. The filtrate was concentrated to obtain **22** as a crude yellow solid. **19** was used crude for the next reaction without further purification.

Compound 23



23

To a solution of **22** (0.26 g, 0.30 mmoL) in dry DCM (5 mL), NMM (0.03 mL, 0:04 mmoL), pyridine (0.42 mL, 6.07mmoL), DMAP (3.0 mg, 0:03 mmoL) and Ac_2O (0.48 mL, 6.07 mmoL) were added at RT. After 4 hrs of stirring at RT, the reaction mixture was diluted with DCM (30 mL) and washed with a saturated solution of NH_4Cl (3 x 5 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (eluent EP/AcOEt (2: 3)) to obtain **23** as a yellow glassy solid (0.12g, 0.12 mmol, 55% yield over two steps). **ESI-MS**: m/z 1002.51 $[M + Na]^+$. **^{1}H NMR** (400 MHz $CDCl_3$) δ: 5.49 (d, $J_{NH\text{-}2a}$ = 8.8 Hz, 1H, NH), 5.39 (d, $J_{4b\text{-}3b}$ = 3.2 Hz, 1H, H-4b), 5.35 (bs, 1H, H-3c), 5.31-5.15 (m, 2H, H-2c, H-4c), 5.09 (dd, $J_{2b\text{-}3b}$ = 10.8 Hz, $J_{2b\text{-}1b}$ = 8.4 Hz, 1H, H-2b), 4.99 (d, $J_{1c\text{-}2c}$ = 3.2 Hz, 1H, H-1c), 4.93 (dd, $J_{3b\text{-}2b}$ = 10.4 Hz, $J_{3b\text{-}4b}$ = 3.6 Hz, 1H, H-3b), 4.75-4.73 (m, 2H, H-1a, H-1b), 4.55-4.44 (m, 2H, H-6a, H-6b), 4.26-4.11 (m, 2H, H-6'b, H-3a), 4.04 (at, *J* = 9.2 Hz, 1H, H-5b), 3.88-3.81 (m, 1H, H-6'a), 3.78-3.71 (m, 2H, H-2a, H-4a), 3.55 - 3.51 (m, 1H, H-5a), 2.17 (s, 3H, COCH_3), 2.15 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), *2*.07 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), 2.00 (s, 3H, COCH_3), 1.97 (s, 3H, COCH_3), 1.94 (s, 3H, COCH_3), 1.24 (d, $J_{6c\text{-}5c}$ = 6.4 Hz, 3H, H-6c),0.85 (s, 9H, SiC(CH_3)$_3$), 0.07 (s, 3H, SiCH_3), 0.06 (s, 3H, SiCH_3). **^{13}C NMR** (100 MHz $CDCl_3$) δ: 170.7 (Cq), 170.4 (Cq), 170.4 (Cq), 170.3 (Cq), 170.2 (Cq), 170.2 (Cq), 169.9 (Cq), 169.8 (Cq), 169.4 (Cq), 100.0 (C-1b), 95.8 (C-1c), 95.5 (C-1a), 73.3 (C-3a), 72.9 (C-4a), 71.4 (C-5a), 71.1 (C-3c), 70.5 (C-3b), 68.4 (C-5b), 68.0 (C-2b), 67.7 (C-2c, C-4c), 66.71 (C-4b), 64.6 (C-5c), 61.9 (C-6a), 60.6 (C-6b), 58.4 (C-2a), 30.9 (CO*C*H$_3$), 25.5 (SiC(*C*H$_3$)$_3$), 23.5 (CO*C*H$_3$), 20.8 (CO*C*H$_3$), 20.8 (CO*C*H$_3$), 20.7 (CO*C*H$_3$), 20.7 (CO*C*H$_3$), 20.6 (CO*C*H$_3$), 20.6 (CO*C*H$_3$), 20.5 (CO*C*H$_3$), 17.7 (C-6c), 15.7 (Si*C*(CH$_3$)$_3$), -4.2 (Si*C*H$_3$), -5.4 (Si*C*H$_3$).

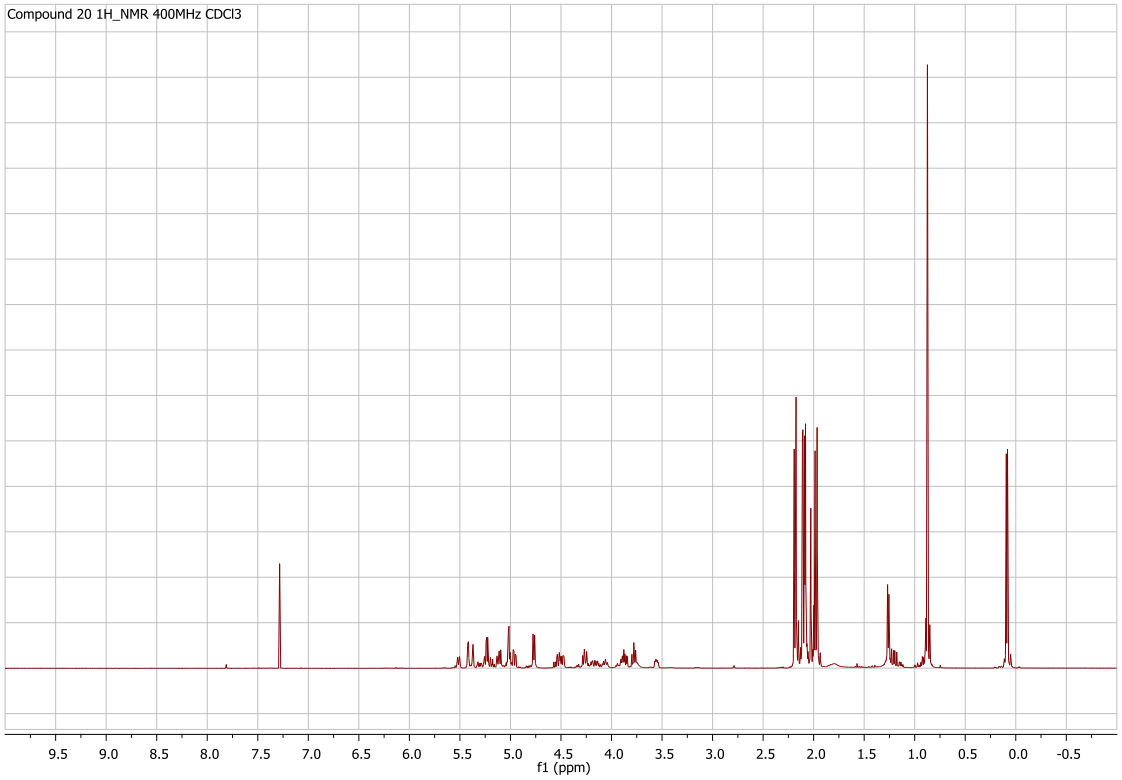


Figure S3: ^{1}H NMR of **23** carbohydrate building block.

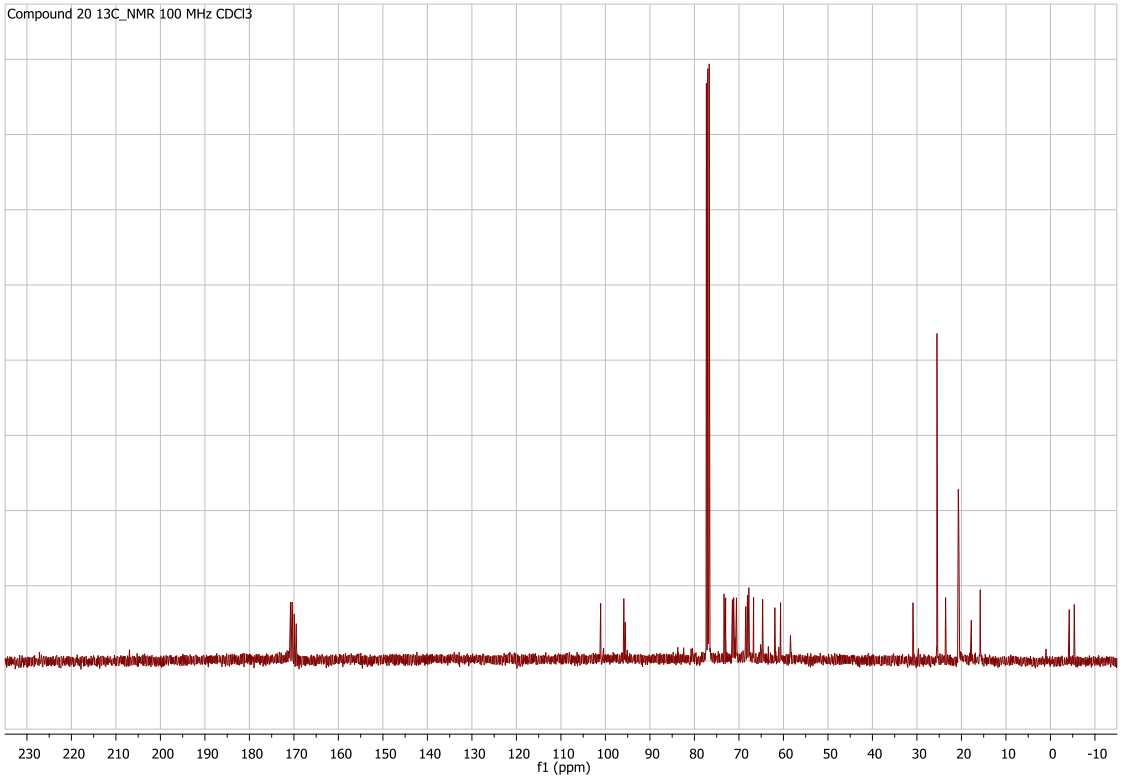
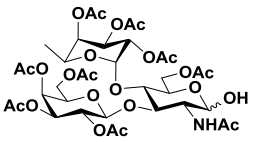


Figure S4: ^{13}C NMR of **23** carbohydrate building block.

Compound 24



24

A solution of **23** (0.53 g, 0.58 mmoL) in dry THF (7 mL) was cooled down to -45°C. A solution of glacial acetic acid 2 M in THF (0.03 mL, 0.59 mmoL) and a solution of TBAF 0.2 M in THF (3.38 mL, 0.68 mmoL) were added dropwise at RT. The reaction mixture was stirred at RT for 17 hrs. Then, the reaction mixture was diluted with AcOEt (100 mL) and washed with brine (3 x 10 mL). The crude reaction was purified by flash chromatography on silica gel (eluent AcOEt) to obtain **24** as a yellow glassy solid (0.20 g, 0.23 mmol, 60% yield). $\mathbf{[\alpha]^{25}_D}$ = - 62.6 (C 0.3 in $CHCl_3$). **ESI-MS**: m/z 888.50 $[M + Na]^+$. **^{1}H NMR** (400 MHz $CDCl_3$) δ: 6.08 (bs, 1H, N*H*), 5.4 (d, $J_{4b\text{-}3b}$ = 3.6 Hz, 1H, H-4b), 5.36 (ad, $J_{3c\text{-}2c}$ = 1.6 Hz, 1H, H-3c), 5.27-5.18 (m, 2H, H-2c, H-4c), 5.13-4.99 (m, 3H, H-2b, H-1c, H-1a), 4.91 (dd, $J_{3b\text{-}4b}$ =3.6 Hz, $J_{3b\text{-}2b}$ = 10.4 Hz, 1H, H-3b), 4.75 (d, $J_{1b\text{-}2b}$ = 8.4 Hz, 1H, H-1b), 4.54(A part of a system ABX, $J_{A\text{-}B}$ = 11.2 Hz, $J_{A\text{-}X}$ = 6.0 Hz, 1H, H-6a), 4.50-4.47 (m,1H, H-6b), 4.37-4.31 (m, 1H, H-2a), 4.21 (dd, $J_{6a\text{-}5a}$ = 8.4 Hz, $J_{6a\text{-}6'a}$ = 11.2 Hz, 1H, H-6'a), 4.05- 3.78 (m, 5H, H-3a, H-4a , H5b, H-5a, H-6'b), 2.17 (s, 3H, COCH_3), 2.16 (s, 3H, COCH_3), 2.15 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 2.07 (s, 3H, COCH_3), 2.04 (s, 3H, COCH_3), 1.96 (s, 3H, COCH_3), 1.94 (s, 3H, COCH_3), 1.26 (d, $J_{6c\text{-}5c}$ = 6.8 Hz, 3H, H-6). **^{13}C NMR** (100 MHz $CDCl_3$) δ: 171.0 (Cq), 170.8 (Cq), 170.7 (Cq), 170.5 (Cq), 170.3 (Cq), 170.2 (Cq), 170.0 (Cq), 169.9 (Cq), 169.8 (Cq), 101.5 (*C*-1b), 96.0 (C-1c), 91.9 (C-1a), 75.2 (C-3a), 72.6 (C-4a), 71.5 (C-3c), 71.2 (C-3b), 70.2 (C-5a), 69.6 (C-5b), 68.1 (C-2b), 68.0 (C-2c), 67.7 (C-4c), 66.6 (C-4b), 64.7 (C-5c), 61.4 (C-6b), 60.5 (C-6a), 53.0 (C-2a), 23.5 (CO*C*H_3), 20.9 (CO*C*H_3), 20.8 (CO*C*H_3), 20.6 (CO*C*H_3), 20.5 (CO*C*H_3), 15.7 (C-6c).

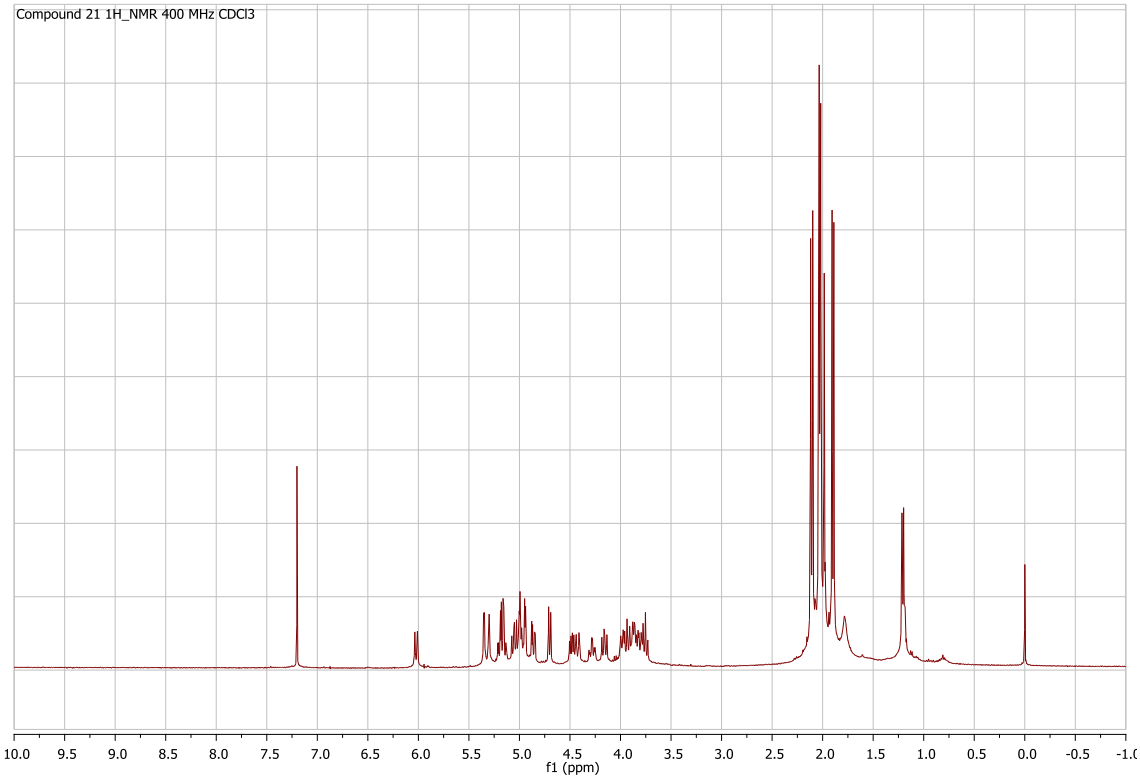


Figure S5: ^{1}H NMR of **24** carbohydrate building block.

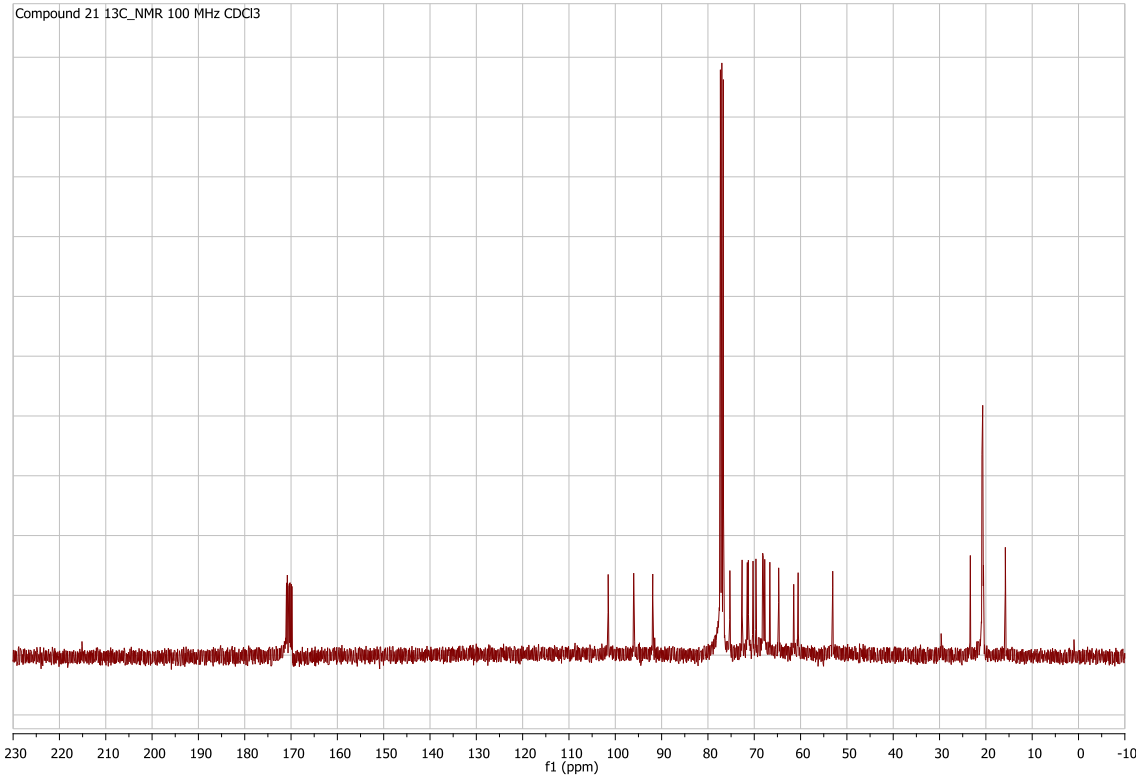
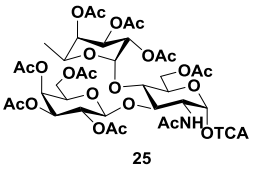


Figure S6: ^{13}C NMR of **24** carbohydrate building block.

Compound 25



25

A solution of **24** (0.17 g, 0.20 mmoL) in dry DCM (4 mL) was cooled down to 0 ° C. DBU (0.01 mL, 0.06 mmoL), and Cl_3CCN (0.20 mL, 2.01 mmoL) were added. After 40 min at this temperature the reaction mixture was diluted with DCM (30 mL) and washed with a saturated solution of NH_4Cl (3 x 5 mL). The organic phase is dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified was purified by flash chromatography on silica gel (eluent EP/AcOEt (1: 3) + 0.1% TEA) to obtain **25** as a yellow oil (0.16g, 0.15 mmol, 80% yield). $\mathbf{[\alpha]^{28}_D}$ **=** - 27.33 (c 0.5 in DCM). **^{1}H NMR** (400 MHz $CDCl_3$) δ: 8.75 (s, 1H, N*H* - OTCA), 6.05 (d, $J_{1a\text{-}2a}$ = 4.0 Hz, 1H, H-1a), 5.55 (ad, $J_{3a\text{-}2a}$ = 10.4 Hz, 1H, H-3a), 5.35 (d, $J_{4b\text{-}3b}$ = 3.6 Hz, 1H, H-4b), 5.32-5.31 (m, 1H, H-3c), 5.23-5.18 (m, 2H, H,1c, H-2c), 5.06 (dd, $J_{2b\text{-}1b}$ = 8.0 Hz, $J_{2b\text{-}3b}$ = 10.4 Hz, 1H, H-2b), 4.98 (q, $J_{5c\text{-}6c}$ = 6.4 Hz, 1H, H-5c), 4.92-4.87 (m, 2H, H-3b, H-4c), 4.68 (d, $J_{1b\text{-}2b}$ = 8.0 Hz, 1H, H-1b), 4.64-4.58 (m, 1H, H-2a), 4.48 (A part of a system AB, $J_{A\text{-}B}$ = 11.2 Hz, $J_{A\text{-}M}$ = 6.0 Hz, 1H, H-6a), 4.37 (ad, $J_{6b\text{-}6'b}$ = 12.4 Hz, 1H, H-6b), 4.18 (dd, $J_{6'a\text{-}6a}$ = 11.6 Hz, $J_{6'a\text{-}5a}$ = 8.0 Hz, 1H, H-6'a), 4.00-3.86 (m, 4H, H-5a, H-4a, H-6'b, H-5b), 2.11 (s, 6H, COCH_3), 2.10 (s, 6H, COCH_3), 2.03 (s, 6H, COCH_3), 2.01 (s, 6H, COCH_3), 2.00 (s, 6H, COCH_3), 1.95 (s, 6H, COCH_3), 1.90 (s, 6H, COCH_3), 1.88 (s, 6H, COCH_3), 1.25 (d, $J_{6c\text{-}5c}$ = 6.8 Hz, 3H, H-6c). **^{13}C NMR** (100 MHz $CDCl_3$) δ: 170.8 (Cq), 170.7 (Cq), 170.4 (Cq), 170.2 (Cq), 170.20 (Cq), 170.1 (Cq), 169.9 (Cq), 169.7 (Cq), 169.5 (Cq), 160.2 (Cq) 101.6 (C-1b), 95.2 (C-1c), 95.6 (C-1a), 90.8 (Cq), 76.0 (C-4a), 72.1 (C-5b), 72.0 (C-4b), 71.4 (C-3b), 71.0 (C-5a), 70.4 (C-2b), 68.2 (C-4c), 68.0 (C-2c), 67.5 (C-3c), 66.5 (C-3a), 64.8(C-5c), 61.1 (C-6b), 60.8 (C-6a), 52.3 (C-2a), 23.3 (CO*C*H_3), 20.7 (CO*C*H_3), 20.70 (CO*C*H_3), 20.64 (CO*C*H_3), 20.61 (CO*C*H_3), 20.56 (CO*C*H_3), 20.5(CO*C*H_3), 20.4 (CO*C*H_3), 17.7 (CO*C*H_3), 15.7 (C-6c).

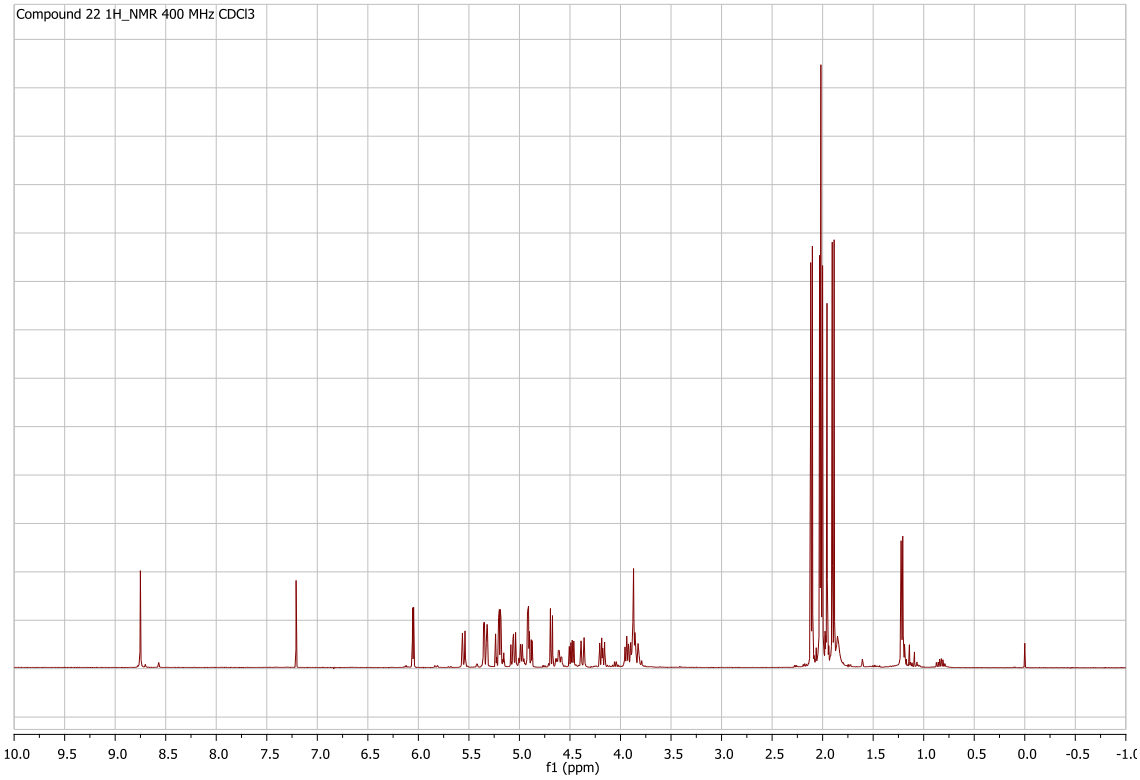


Figure S7: ^{1}H NMR of **25** carbohydrate building block.

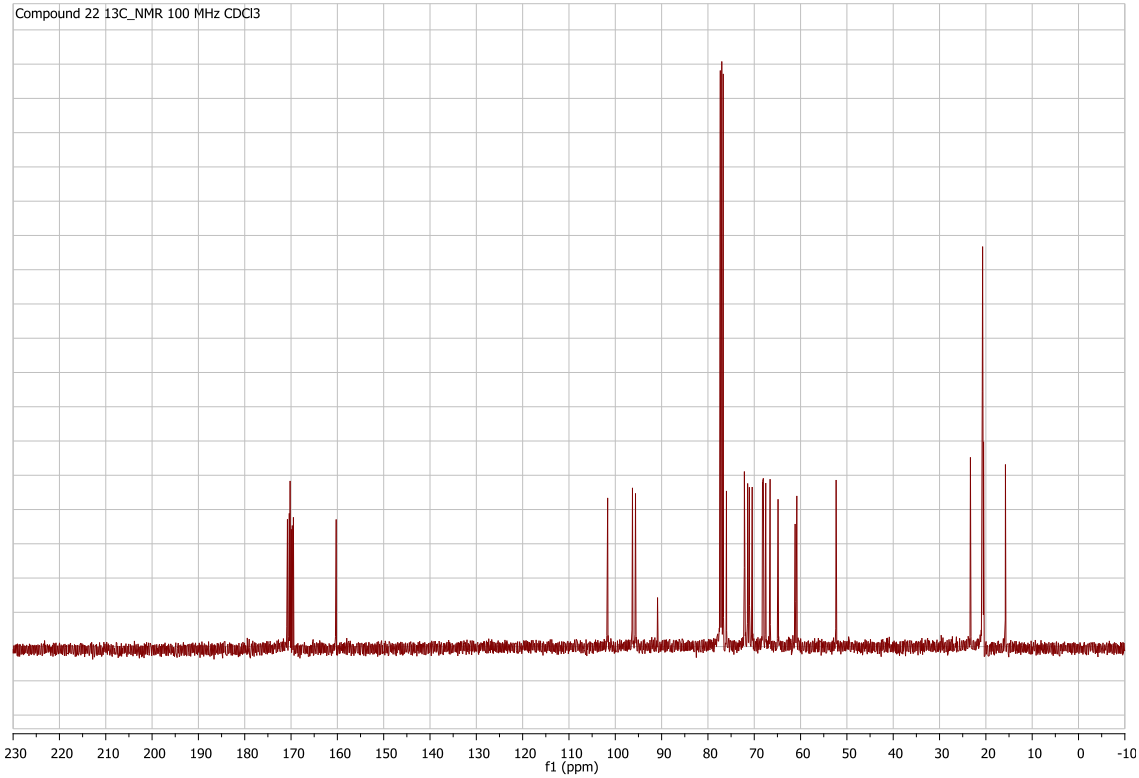
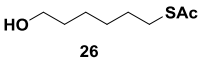


Figure S8: ^{13}C NMR of **25** carbohydrate building block.

Compound 26



26

A solution of 6-chloroesanol (1 g, 7.32 mmoL) in dry DMF (2.5 mL) was warmed up to 60°C. Then, potassium thioacetate (1.25 g, 10.97 mmoL) was added. After 6 hours of stirring at 60°C, the reaction mixture was cooled down to RT, diluted with DCM (500 mL) and washed with brine (3 x 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was filtered on silica gel (eluent EP/AcOEt (2: 1)), to obtain **26** as a brown oil (1.28g, 7.32 mmol, 99% yield). **ESI-MS**: m/z 176.80 $[M + H]^+$.**^{1}H NMR** (500 MHz $CDCl_3$) δ: 3.66 (t, *J* = 5.0 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 1.64-1.56 (m, 4H), 1.49 (bs,1H), 1.42-1.39 (m, 4H), **^{13}C NMR** (125 MHz $CDCl_3$) δ: 190.0, 62.8, 32.5, 30.6, 29.4, 28.9, 28.4, 25.2.

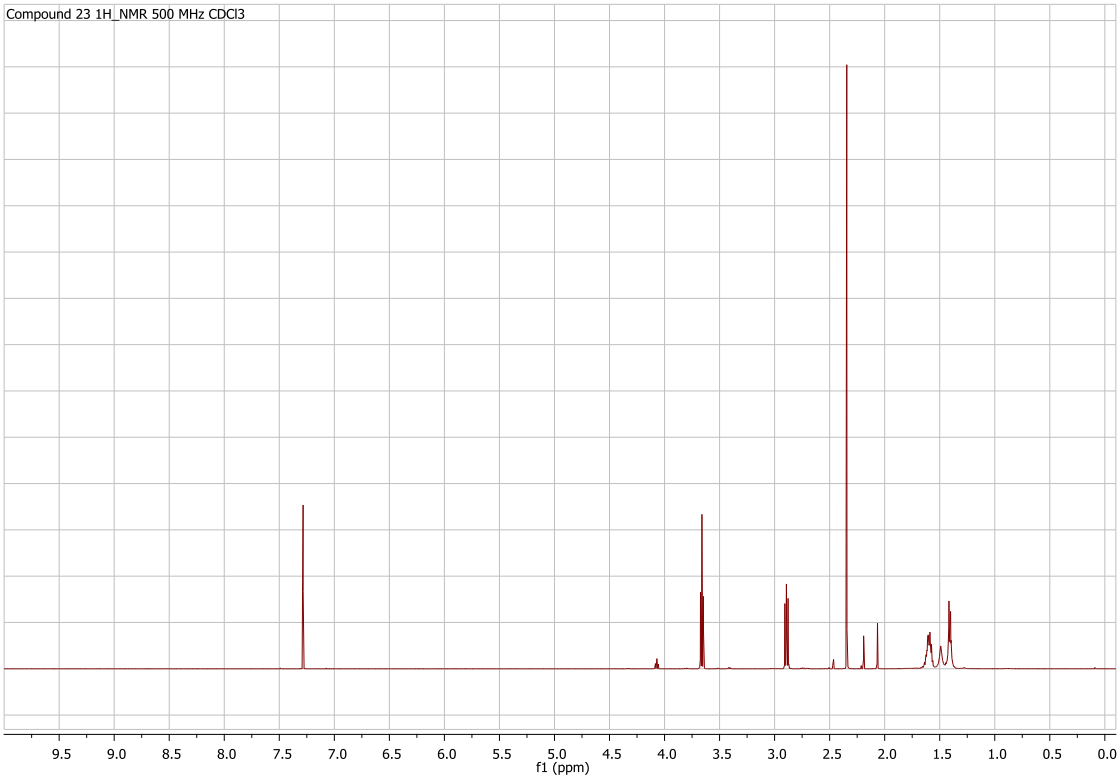


Figure S9: ^{1}H NMR of **26.**

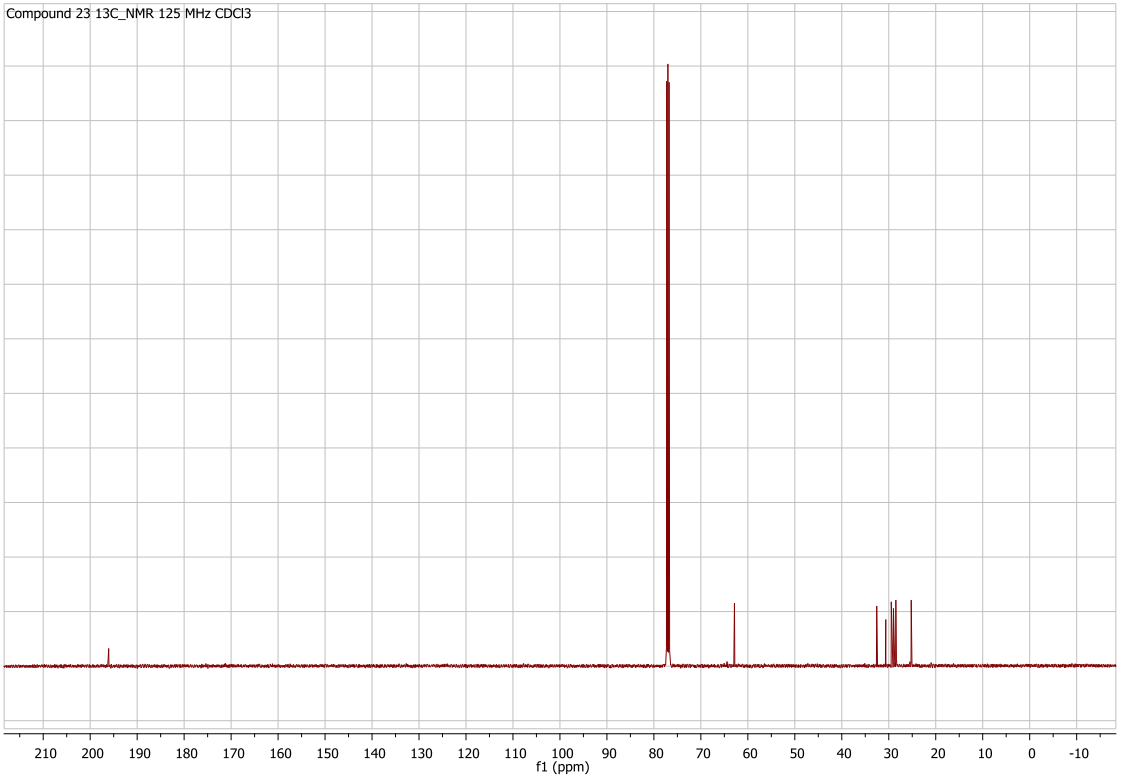
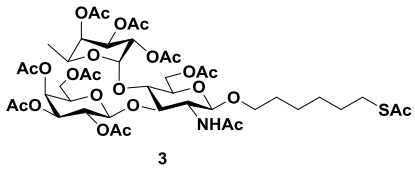


Figure S10: ^{13}C NMR of **26.**

Compound 3



3

A solution of **25** (0.13 g, 0.13 mmoL) and **26** (0.04 g, 0.25 mmoL) in dry DCM (4 mL) was cooled down to 0°C. TMSOTf (0.01 mL, 0.05 mmoL) was added and the reaction mixture was stirred for 20 min. at 0°C. Then, the reaction mixture was neutralized with TEA, diluted with DCM (30 mL) and washed with brine (3 x 5 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (eluent EP/AcOEt (1: 3)) to obtain **3** as a yellow glassy solid (0.09g, 0.08 mmoL, 64% yield). $\mathbf{[\alpha]^{25}_D}$ **=** -146.4 (c 0.5 in $CHCl_3$). **HR-MS:** *m/*z calculated for $C_{44}H_{66}O_{24}NS$ $[M+H^+]^+$: 1024.36900. Found 1024.36831. **^{1}H NMR** (400 MHz $CDCl_3$) δ: 5.90 (bs, 1H, NH), 5.39 (d, $J_{4b\text{-}3b}$ = 3.2 Hz, 1H, H-4b), 5.33 (bs, 1H, H-3c), 5.21 (bs, 2H, H-4c, H-2c), 5.10 (dd, $J_{2b\text{-}1b}$ = 8.0 Hz, $J_{2b\text{-}3b}$ = 10.0 Hz, 1H, H-2b), 4.99 (s, 1H, H-1c), 4.96 (dd, $J_{3b\text{-}4b}$ = 3.6 Hz, $J_{3b\text{-}2b}$ = 10.4Hz, 1H, H-3b), 4.92-4.89 (m, 1H, H-5c), 4.81 (d, $J_{1b\text{-}2b}$ = 8.0 Hz, 1H, H-1b), 4.62 (d, $J_{1a\text{-}2a}$ = 6.8 Hz, 1H, H-1a), 4.46-4.38 (m, 2H, H-6_a, H-6_b), 4.21(dd, $J_{6'b\text{-}6a}$ = 11.6 Hz, $J_{6'b\text{-}5b}$ = 8.0 Hz, 1H, H-6'b), 4.15 (at, *J* = 8.4 Hz 1H, H-3a), 3.93 (dd, $J_{6'a\text{-}6a}$ = 12.4 Hz, $J_{6'a\text{-}5a}$ = 4.4 Hz, 1H, H-6'a), 3.89- 3.75 (m, 3H, H-5b, H-4a, H-1'a), 3.65 (aq, *J* = 7.2 Hz, 1H, H-2a), 3.60-3.56 (m, 1H, H-5a), 3.42-3.39(m. 1H, H-1'b), 2.84 (t, $J_{6'\text{-}5'}$ = 7.6 Hz, 2H, H-6'), 2.31 (s, 3H, SCOCH_3), 2.15 (s, 3H, COCH_3), 2.151(s, 3H, COCH_3), 2.07(s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), *2*.059 (s, 3H, COCH_3), 2.05 (s, 3H, COCH_3), 2.01 (s, 3H, COCH_3), 1.96 (s, 3H, COCH_3), 1.94 (s, 3H, COCH_3), 1.58-148 (m, 4H, H-2', H-3' o H-4', H-5'), 1.39-1. 32 (m, 4H, H-2', H-3' o H-4', H-5'), 1.23 (d, $J_{6c\text{-}5c}$ = 6.4 Hz, 3H, H-6c). **^{13}C NMR** (100 MHz $CDCl_3$) δ: 196.4 (Cq), 170.6 (Cq), 170.5 (Cq), 170.3 (Cq), 170.2 (Cq), 170.1 (Cq), 170.1 (Cq), 169.8 (Cq), 169.3 (Cq), 100.4 (C-1a), 99.5 (C-1b), 95.7 (C-1c), 72.9 (C-3a), 72.6 (C-5a), 71.4 (C-4a), 71.1 (C-3c), 70.7 (C-3b), 68.9 (C-5b), 68.5(C-1'), 68.0 (C-2b) 67.9(C-2c), 67.8(C-4c), 66.8 (C-4b), 64.7 (C-5c), 62.0 (C-6a), 60.3 (C-6b), 56.0 (C-2a), 30.6 (SCO*C*H_3), 29.2 (C-4' o C-5'), 29.0 (C-4' o C-5'), 28.7 (C-6'), 28.1 (C-2' o C-3'), 25.2 (C-2' o C-3'), 23.4 (CO*C*H_3), 20.8 (CO*C*H_3), 20.7 (CO*C*H_3), 20.7 (CO*C*H_3), 15.7 (C-6c).

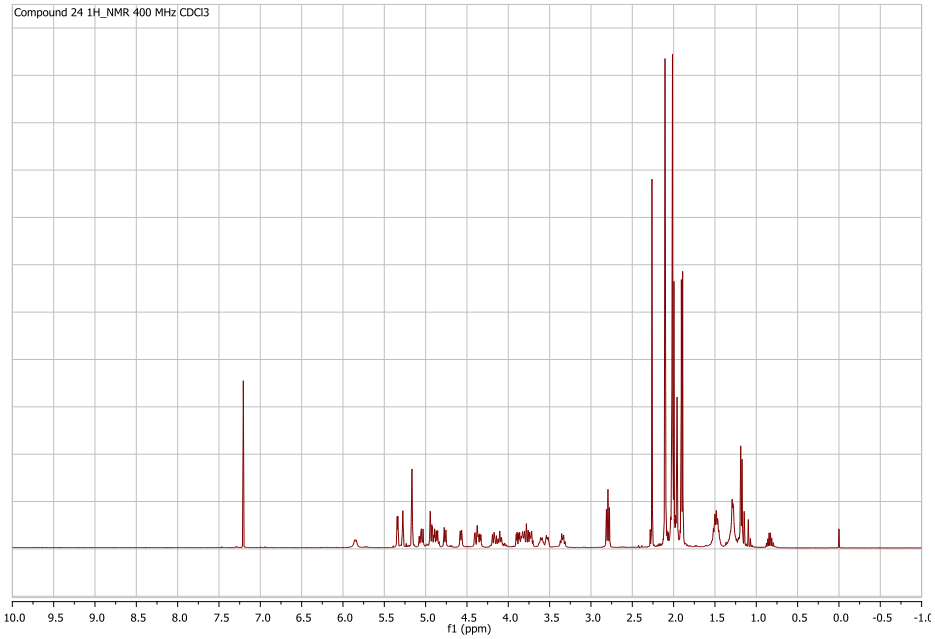


Figure S11: ^{1}H NMR of Le^{a}C$_{6}$ **3** carbohydrate building block.

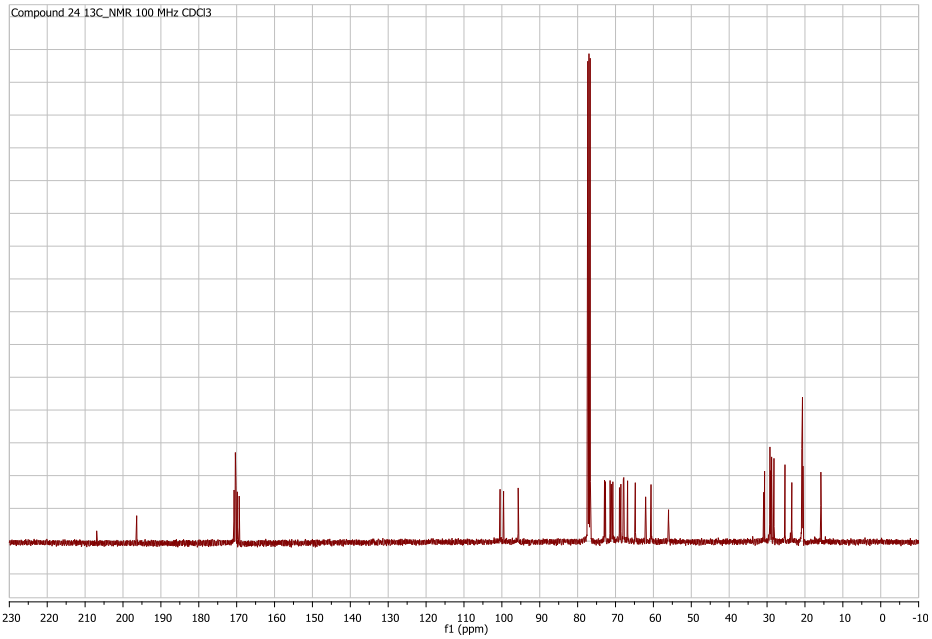
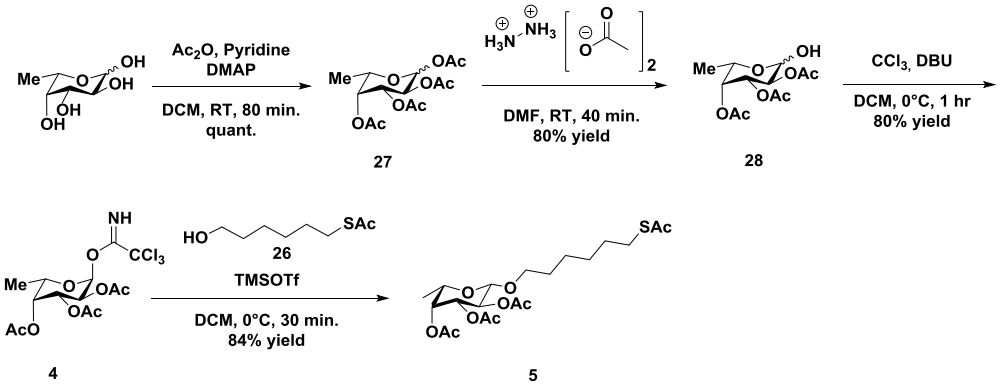


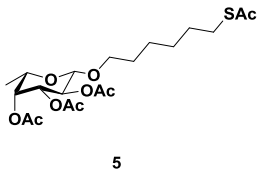
Figure S12: ^{13}C NMR of Le^{a}C$_{6}$ **3** carbohydrate building block.

Synthesis of $FucC_6$ carbohydrate bulding block



Scheme S5: **Synthesis of $FucC_6$ (ref 1)**

Compound 5



5

A solution of **4**[1] (0.78 g, 1.78 mmoL) and **26** (0.63 g, 0.26 mmoL) were dissolved in dry DCM (20 mL) and cooled down to 0°C. TMSOTf (0.05 mL, 0.26 mmoL) was added dropwise. The reaction mixture was stirred for 30 min. and then neutralized with TEA and diluted with DCM (100 mL). The organic phase was washed with brine (2 x 20 mL) and then dried over anhydrous Na_2SO_4, filtered and concentrated. The crude reaction was purified by flash chromatography on silica gel (Biotage SNAP-50 g, flow 15 mL/min, eluent DCM/aceton (98/2) to DCM/acetone (95/5) to obtain the product **5** as a yellow oil (0.67 g, 1.49 mmoL, 84% yield). $\mathbf{[\alpha]^{25}_D}$ = + 4.34 (c 0.57 in DCM). **ESI-MS**: m/z 471.30 $[M + Na]^+$. **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 5.22 (add, *J* = 3.2 Hz, *J* =1.0 Hz, 1H), 5.18-5.12 (m, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.94-3.85 (m, 1H), 3.84-.73 (m, 1H), 3.51-3.36 (m, 1H), 2, 85 (t, *J* = 7.4, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.63-1.47 (m, 4H), 1.44-128 (m, 4H), 1.22 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR**: (50 MHz, $CDCl_3$) δ: 195.5, 170.3, 169.8, 169.0, 100.78, 71.01, 70.0, 69.5, 68.7, 30.3, 29.2, 28.9, 28.7, 28.2, 25.0, 20.5, 20.4, 20.3, 15.8.

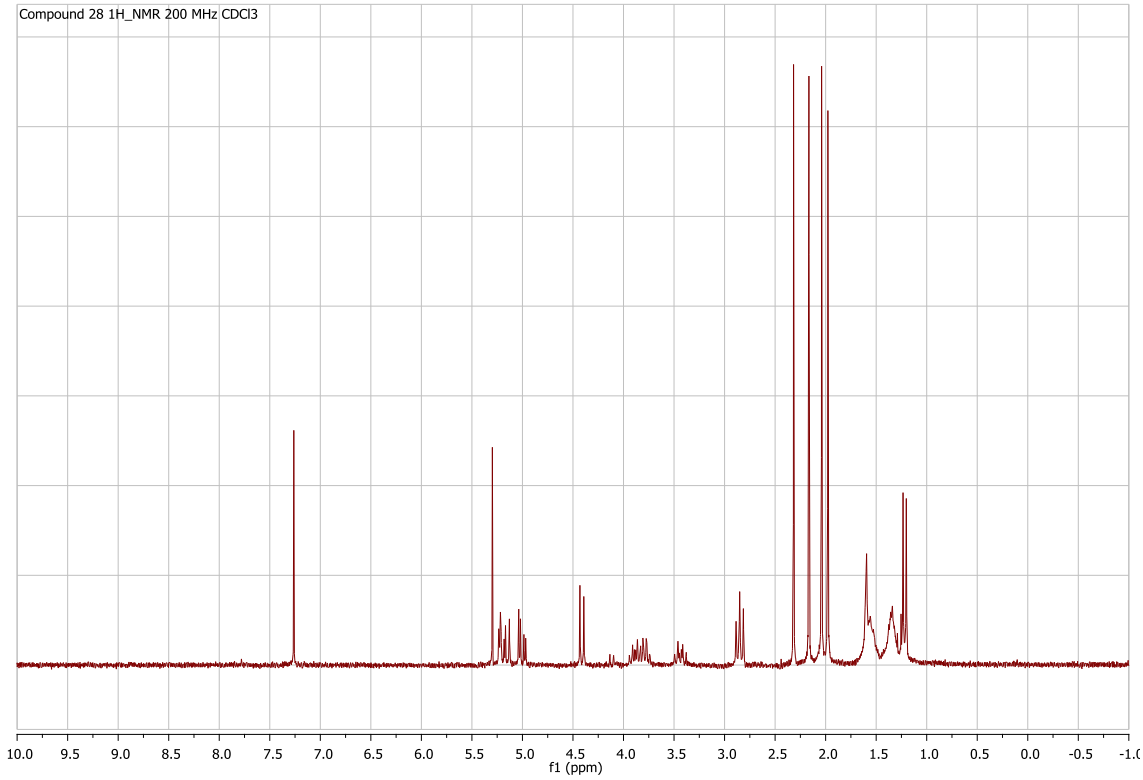


Figure S13: ^{1}H NMR of **FucC$_6$ 5** carbohydrate building block.

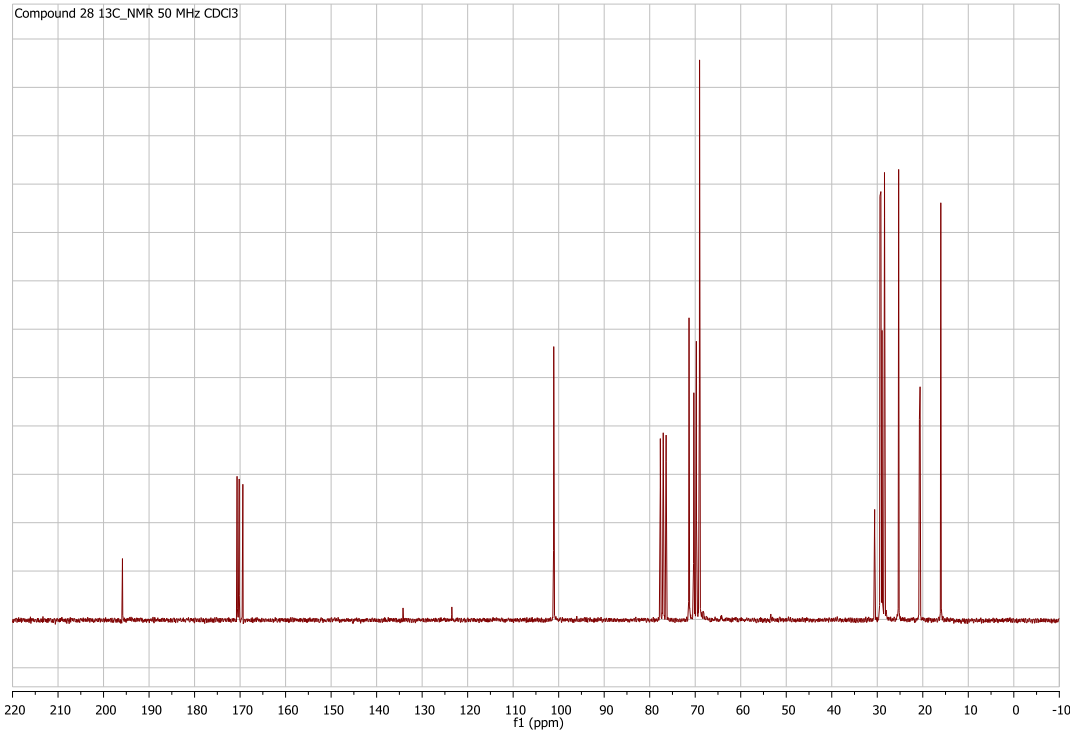


Figure S14: ^{13}C NMR of **FucC$_6$ 5** carbohydrate building block.

2. Glycopeptide and peptide dendrimer synthesis

FD1-Cys: (cFuc-KPL)$_2$*K*FC (33.5 mg, 23 μmol, 18%). MS (ESI+) calc for $C_{68}H_{113}N_{13}O_{19}S$ $[M+H]^+$: 1448.81, found: 1447.80.

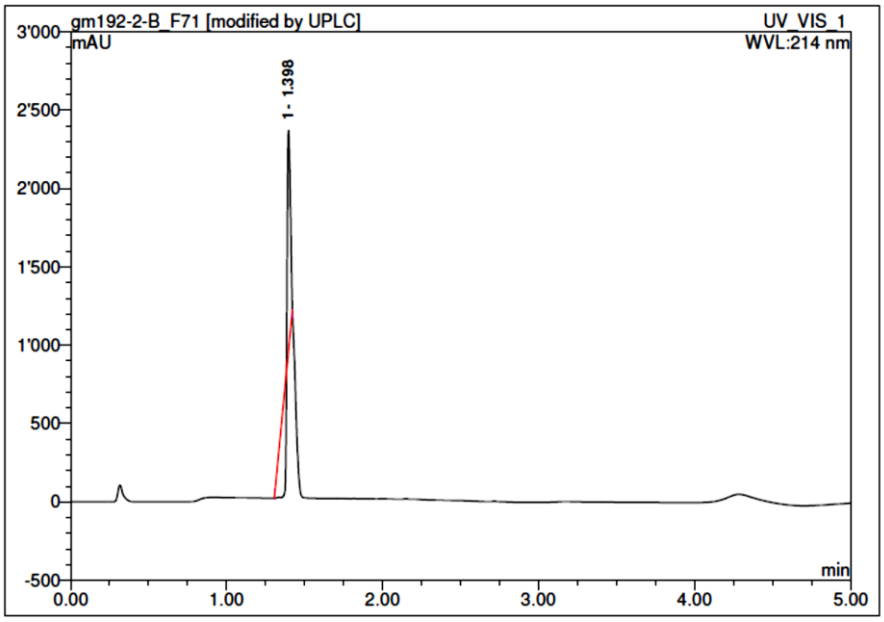


Figure S15: Analytical RP-UHPLC of **FD1-Cys**.

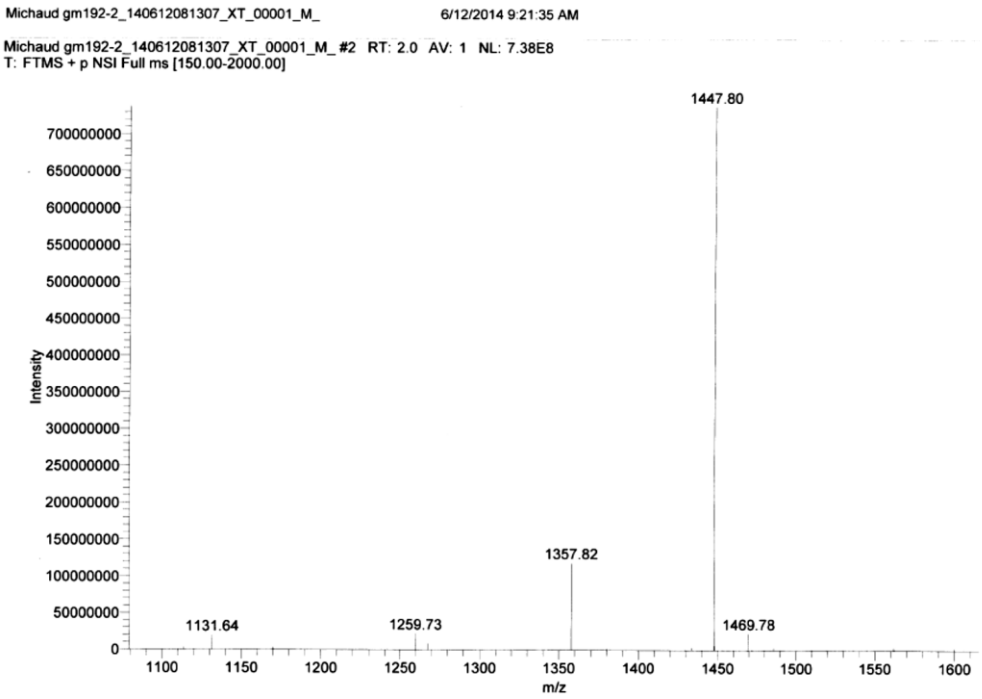
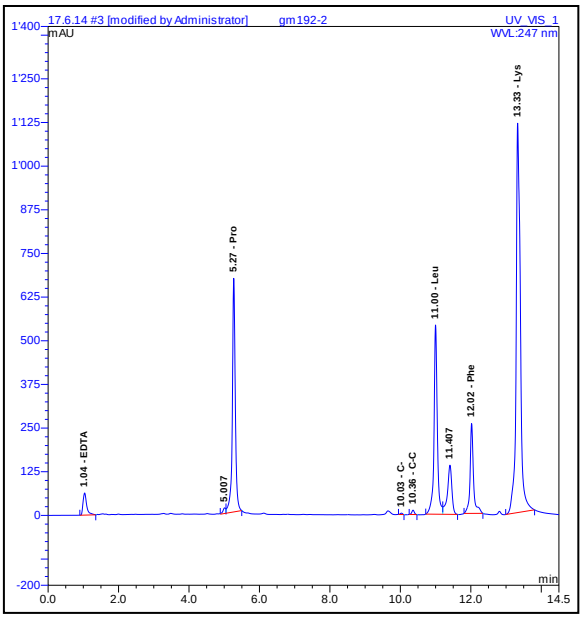


Figure S16: ESI-MS of **FD1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,02	0,104	7,62	63,34		471,65	EDTA
5,27	5,28	0,079	65,16	668,78		3897,98	Pro
10,03	10,05	0,068	0,27	3,88		29,92	C-
10,36	10,35	0,075	1,03	12,47		96,11	C-C
11,00	11,01	0,087	59,05	541,67		3639,09	Leu
12,02	12,03	0,085	28,71	257,16		1835,65	Phe
13,33	13,36	0,121	156,33	1114,80		4766,95	Lys
Total:						14737,35	

Figure S17: Amino acid analysis of **FD1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Pro	3897.98	2	2.21
Leu	3639.09	2	2.06
Phe	1835.65	1	1.04
Lys	4766.95	3	2.70

GalAG1-Cys: (GalA-KPL)$_2$*K*FC (79 mg, 48 µmol, 39%). MS (ESI+) calc for $C_{78}H_{117}N_{13}O_{23}S$ [M+H]+: 1636.82, found: 1637.82 (z=1), 819.41 (z=2).

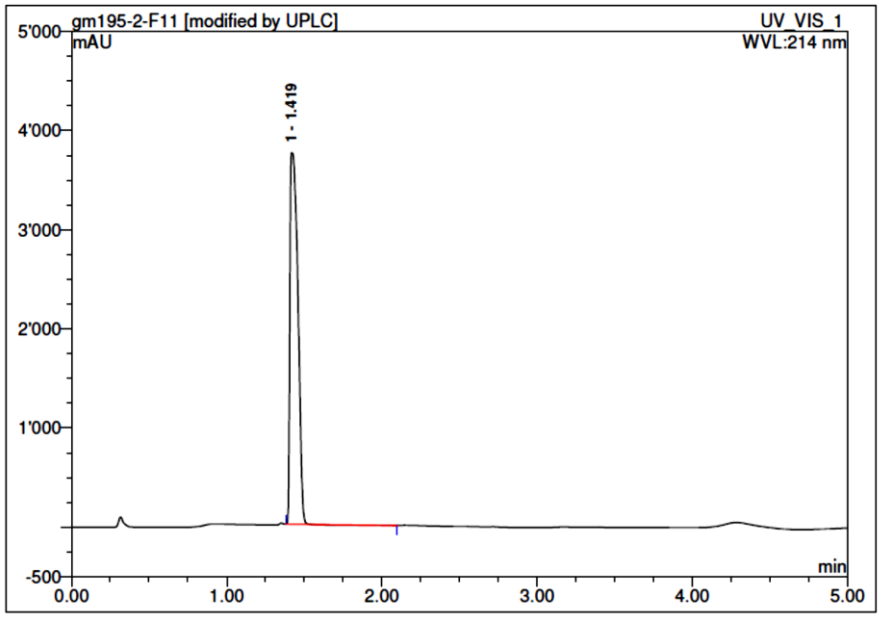


Figure S18: Analytical RP-UHPLC of **GalAG1-Cys**.

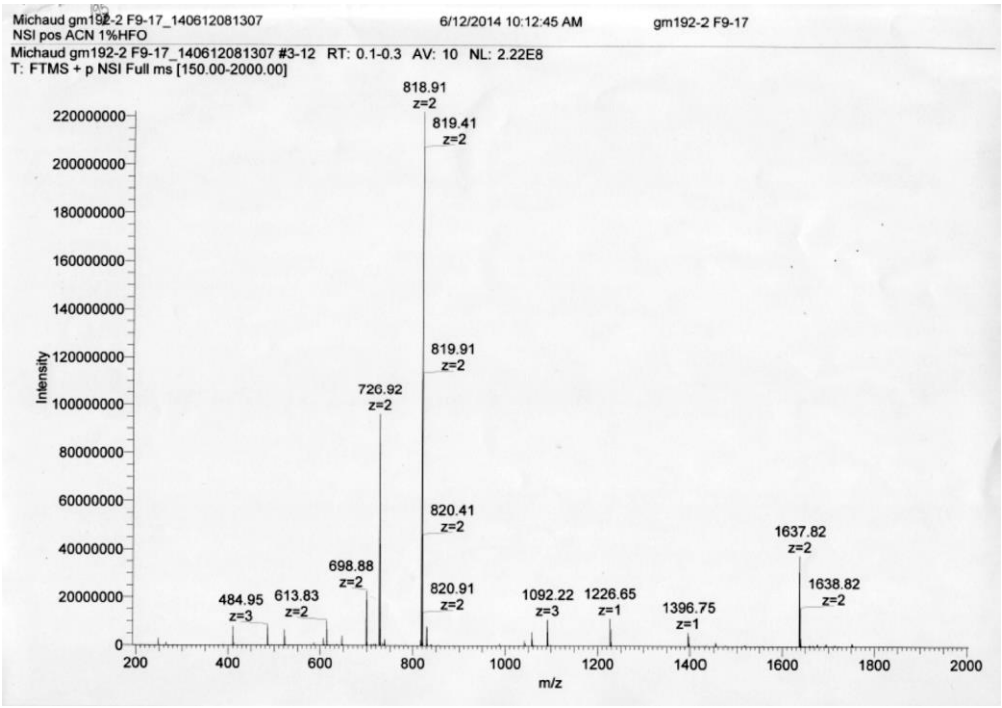
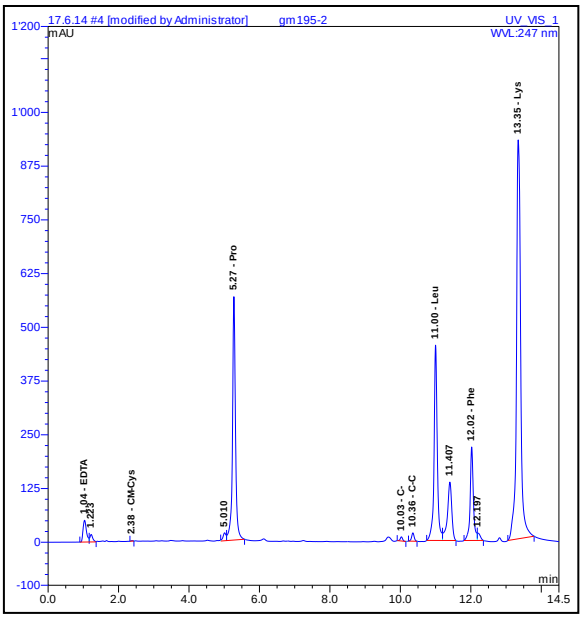


Figure S19: ESI-MS of **GalAG1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,02	0,102	5,66	50,52		376,21	EDTA
2,38	2,37	0,057	0,06	1,12		8,10	CM-Cys
5,27	5,28	0,079	55,82	566,09		3299,45	Pro
10,03	10,05	0,070	0,73	9,56		73,69	C-
10,36	10,35	0,075	1,63	19,31		148,83	C-C
11,00	11,01	0,086	48,24	454,37		3052,59	Leu
12,02	12,03	0,085	22,87	217,35		1551,47	Phe
13,35	13,36	0,115	128,75	927,83		3967,46	Lys
Total:						12477,81	

Figure S20: Amino acid analysis of **GalAG1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Pro	3299.45	2	2.10
Leu	3052.59	2	2.10
Phe	1551.47	1	1.07
Lys	3967.46	3	2.73

GalBG1-Cys: (GalB-KPL)$_2$*K*FC (29.5 mg, 18 µmol, 15%). MS (ESI$^+$) calc. for $C_{70}H_{117}N_{13}O_{21}S_3$ $[M+H]^+$: 1572.77, found: 1573.78 (z=1), 786.89 (z=2).

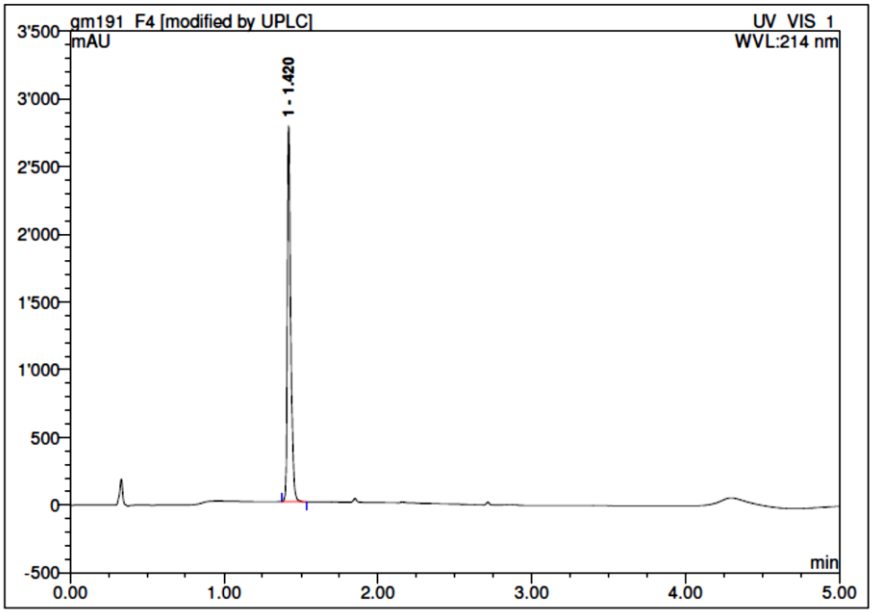


Figure S21: Analytical RP-UHPLC of **GalBG1-Cys**.

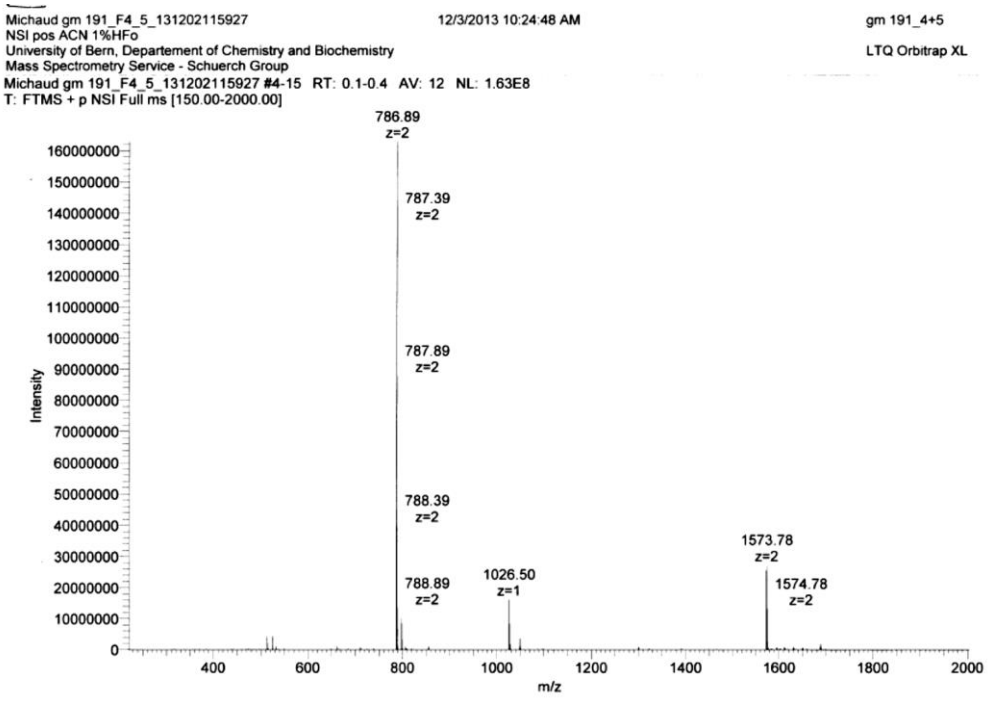
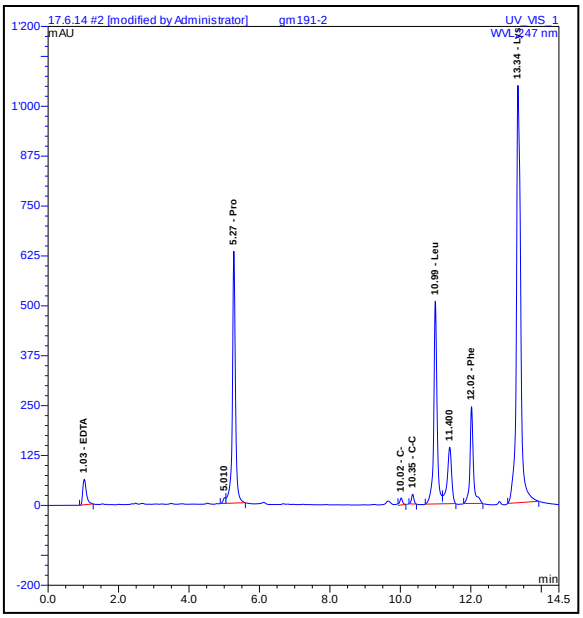


Figure S22: ESI-MS of **GalBG1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,03	1,02	0,106	7,55	63,80		475,10	EDTA
5,27	5,28	0,080	63,19	630,61		3675,51	Pro
10,02	10,05	0,079	1,59	17,48		134,76	C-
10,35	10,35	0,073	1,95	24,27		187,10	C-C
10,99	11,01	0,087	55,26	507,93		3412,38	Leu
12,02	12,03	0,085	27,02	242,27		1729,36	Phe
13,34	13,36	0,120	148,94	1045,27		4469,65	Lys
Total:						14083,84	

Figure S23: Amino acid analysis of **GalBG1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Pro	3675.51	2	2.21
Leu	3412.38	2	2.05
Phe	1729.36	1	1.04
Lys	4469.65	3	2.69

Het1G1-Cys: cFuc-KPL*K*(GalA-KPL)FC (63 mg, 41 µmol, 33%). MS (ESI+) calc for $C_{73}H_{115}N_{13}O_{21}S$ $[M+H]^+$: 1542.82, found: 1543.81 (z=1), 771.91 (z=2).

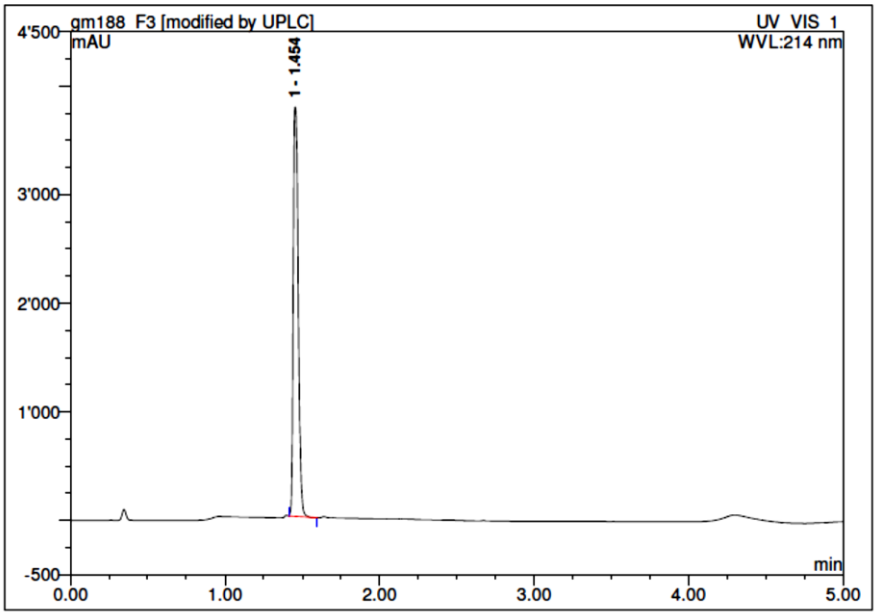


Figure S24: Analytical RP-UHPLC of **Het1G1-Cys**.

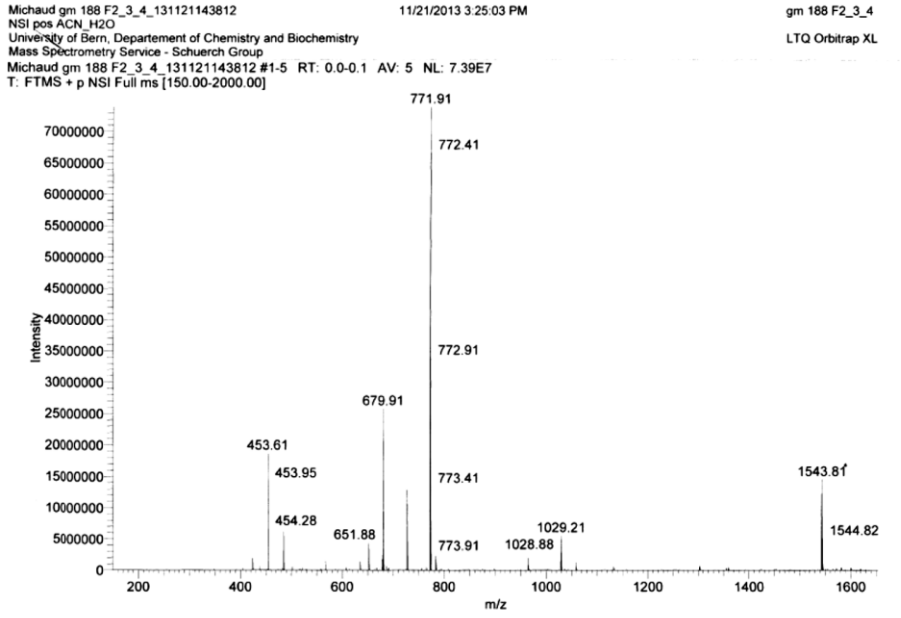
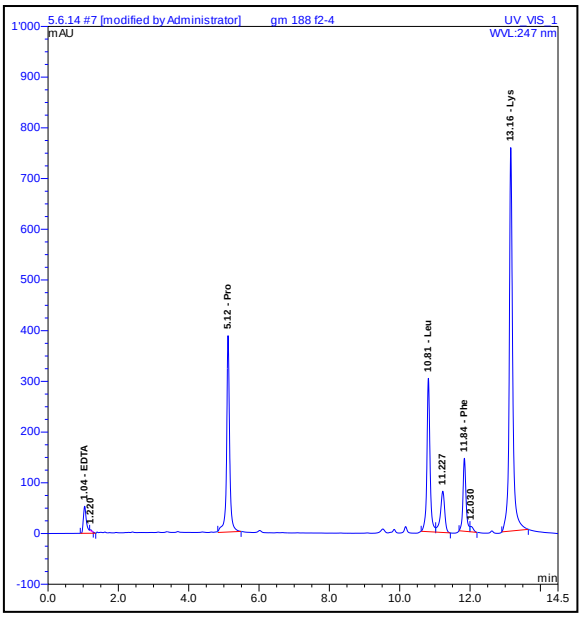


Figure S25: ESI-MS of **Het1G1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,02	0,086	5,74	53,35		318,09	EDTA
5,12	5,14	0,078	38,76	387,17		2253,79	Pro
9,84	9,88	0,067	0,42	5,86		44,00	C-
10,17	10,18	0,077	1,13	12,73		95,62	C-C
10,81	10,84	0,085	31,05	302,38		2057,96	Leu
11,84	11,85	0,084	14,38	143,73		1062,85	Phe
13,16	13,18	0,090	86,29	756,02		3263,41	Lys
Total:						9095,72	

Figure S26: Amino acid analysis of **Het1G1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Pro	2253.79	2	2.09
Leu	2057.96	1	1.91
Phe	1062.85	1	0.98
Lys	3263.41	3	3.02

Het2G1-Cys: GalA-KPL*K*(cFuc-KPL)FC (50 mg, 32 µmol, 26%). MS (ESI+) calc for $C_{73}H_{115}N_{13}O_{21}S$ $[M+H]^+$: 1542.82, found: 1543.81 (z=1), 771.91 (z=2).

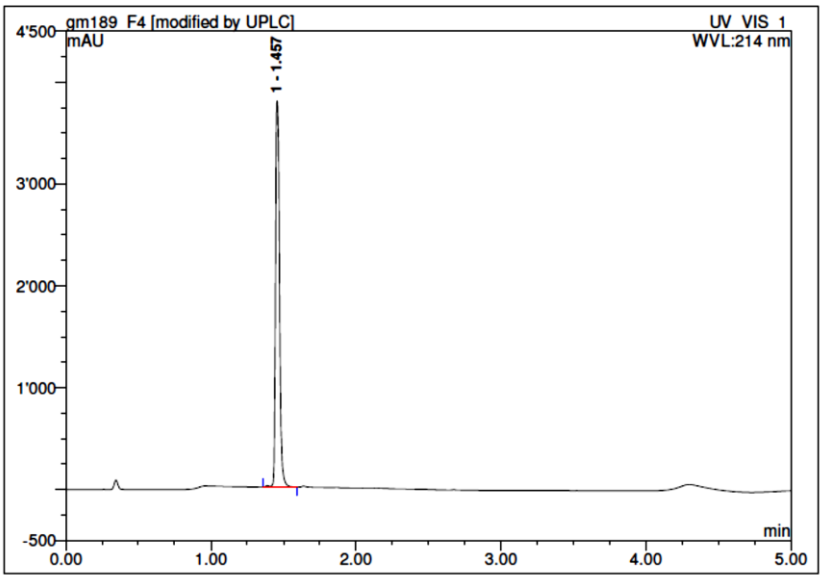


Figure S27: Analytical RP-UHPLC of **Het2G1-Cys**.

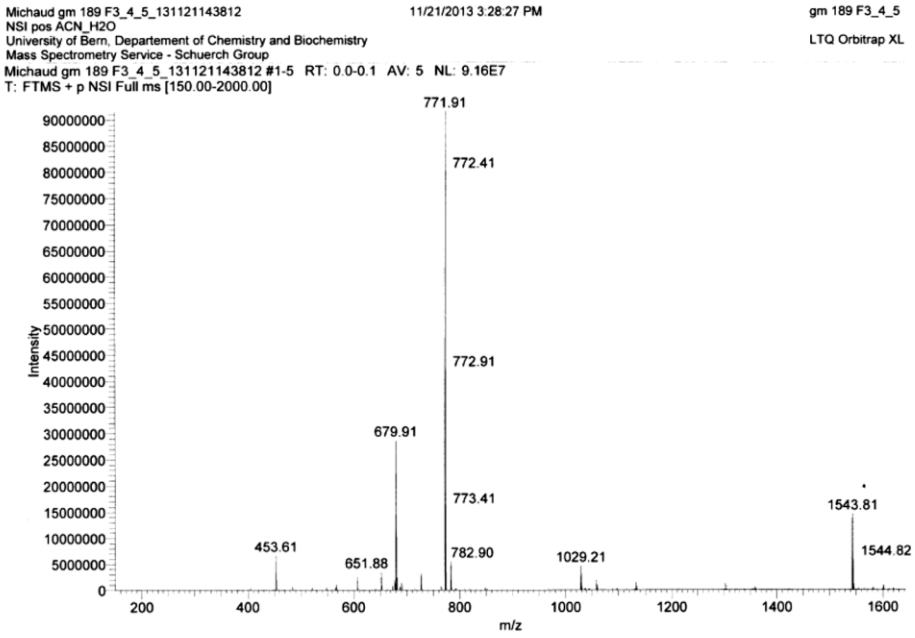
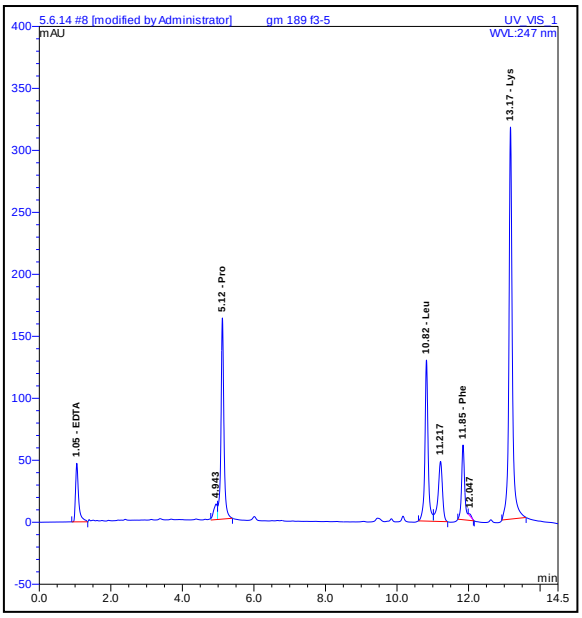


Figure S28: ESI-MS of **Het2G1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,05	1,02	0,082	4,70	47,17		281,27	EDTA
5,12	5,14	0,078	15,54	162,22		944,30	Pro
9,84	9,88	0,069	0,16	2,16		16,20	C-
10,17	10,18	0,071	0,31	4,08		30,66	C-C
10,82	10,84	0,084	13,45	129,92		884,18	Leu
11,85	11,85	0,084	6,37	60,28		445,78	Phe
13,17	13,18	0,087	34,86	316,25		1365,13	Lys
Total:						3967,52	

Figure S29: Amino acid analysis of **Het2G1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Pro	944.30	2	2.08
Leu	884.18	2	1.94
Phe	445.78	1	0.98
Lys	1365.13	3	3.00

Het3G1-Cys: cFuc-KPL*K*(GalB-KPL)FC (52 mg, 34 µmol, 28% yield). MS (ESI^+) calc. for $C_{69}H_{115}N_{13}O_{20}S_2$ $[M+H]^+$: 1510.79, found: 1510.79 (z=1), 755.90 (z=2).

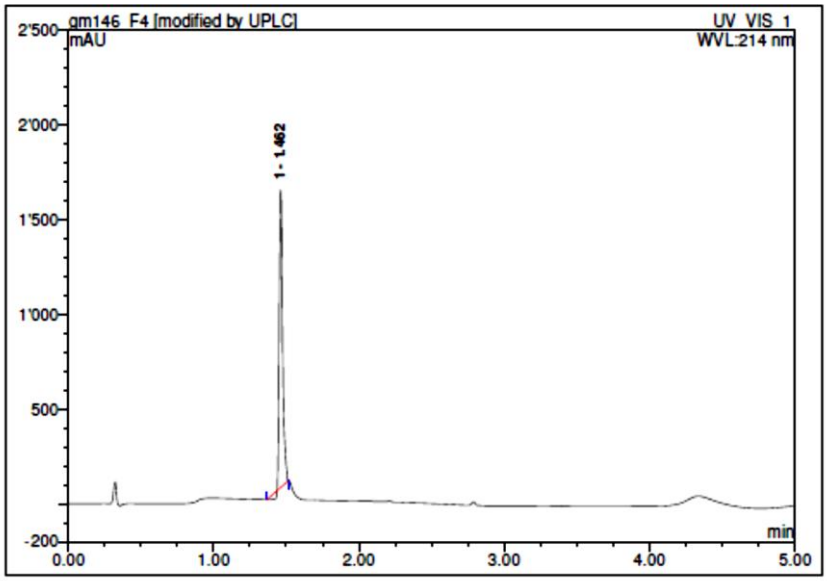


Figure S30: Analytical RP-UHPLC of **Het3G1-Cys**.

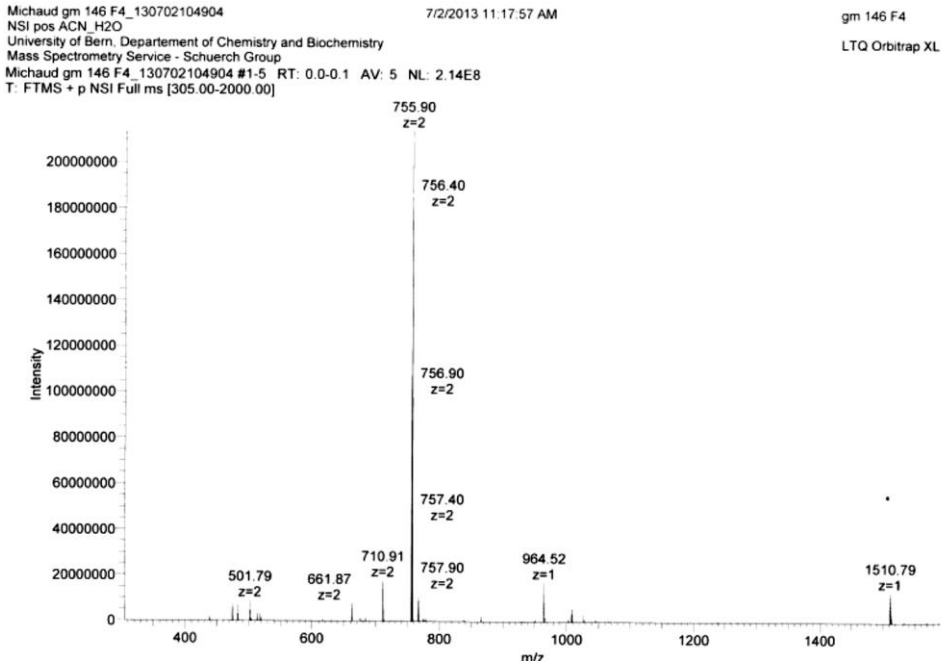


Figure S31: ESI-MS of **Het3G1-Cys**.

Het4G1-Cys: GalB-KPL*K*(cFuc-KPL)FC (50 mg, 33 μmol, 26%). MS (ESI^+) calc. for $C_{69}H_{115}N_{13}O_{20}S_2$ $[M+H]^+$: 1510.79, found: 1510.78 (z=1), 755.90 (z=2).

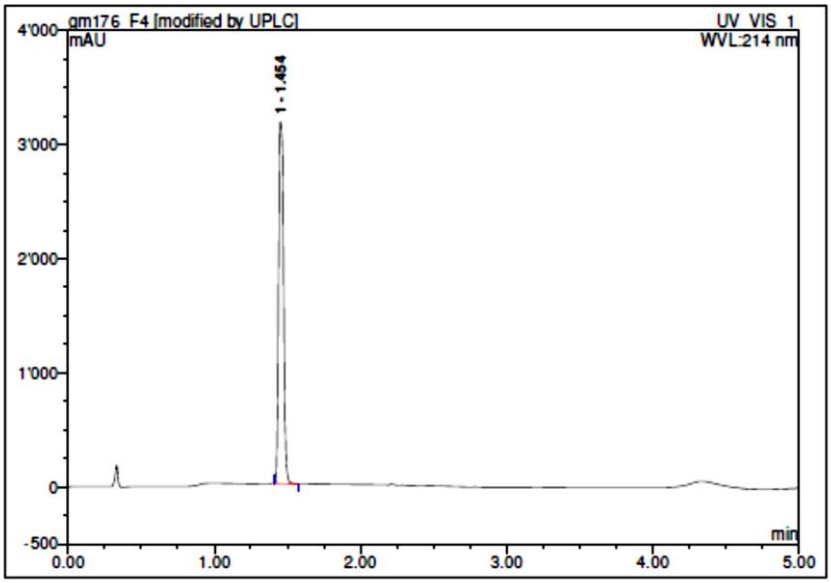


Figure S32: Analytical RP-UHPLC of **Het4G1-Cys**.

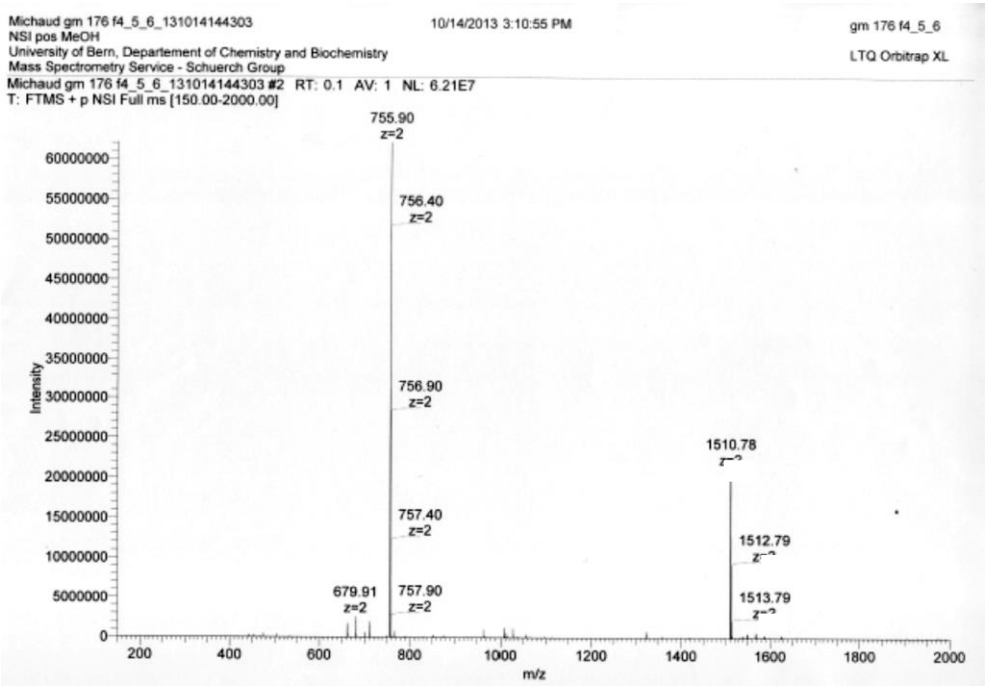


Figure S33: ESI-MS of **Het1G1-Cys**.

Het5G1-Cys: cFuc-KKL*K*(GalA-KKL)FC (29.4 mg, 18 µmol, 15%). MS (ESI^+) calc. for $C_{75}H_{125}N_{15}O_{21}S$ $[M+H]^+$: 1604.90, found: 1604.90 (z=1), 802.95 (z=2).

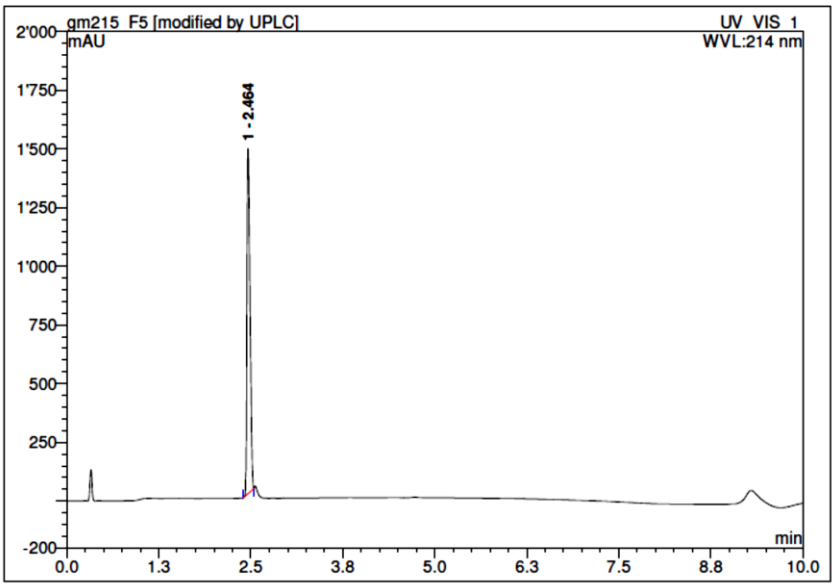


Figure S34: Analytical RP-UHPLC of **Het5G1-Cys**.

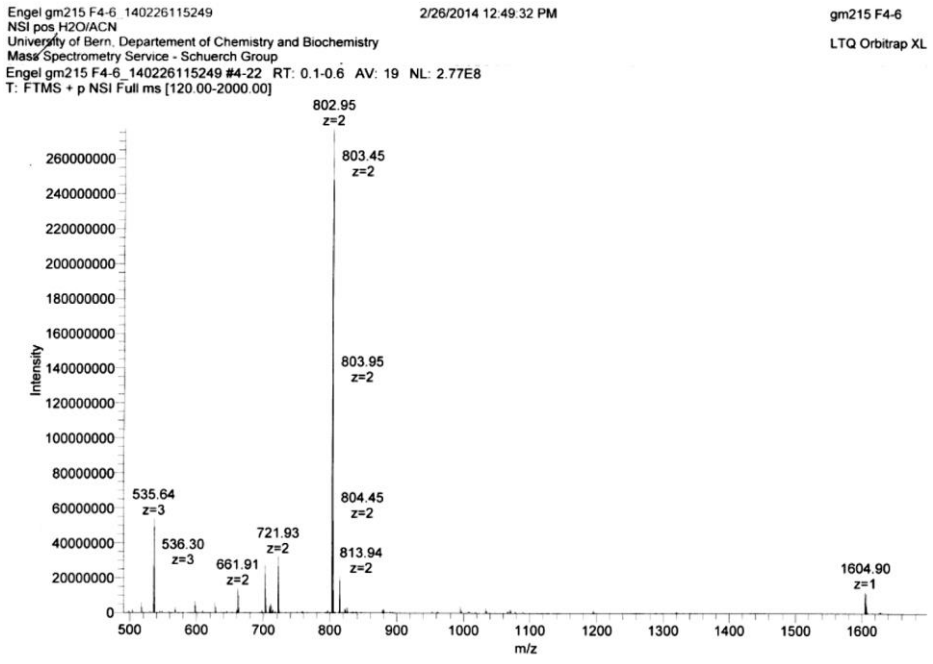
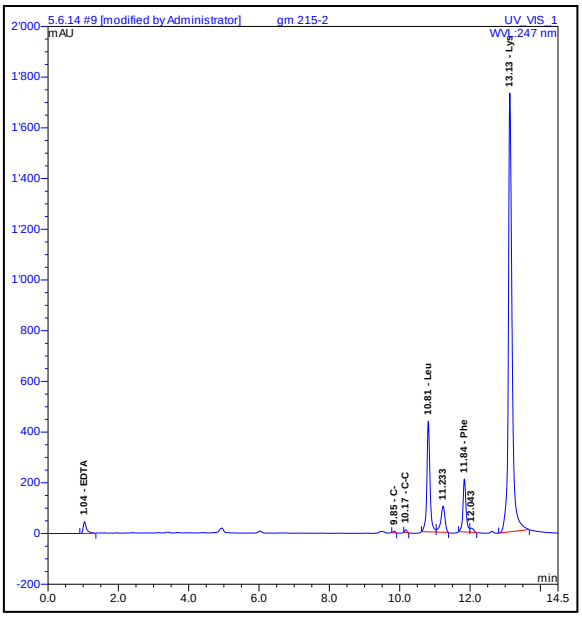


Figure S35: ESI-MS of **Het5G1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,02	0,090	5,19	46,07		274,68	EDTA
9,85	9,88	0,065	0,44	6,52		48,97	C-
10,17	10,18	0,066	0,77	11,17		83,89	C-C
10,81	10,84	0,085	44,67	435,17		2961,65	Leu
11,84	11,85	0,084	20,98	209,04		1545,77	Phe
13,13	13,18	0,100	212,05	1729,77		7466,71	Lys
Total:						12381,67	

Figure S36: Amino acid analysis of **Het5G1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Leu	2961.65	2	1.98
Phe	1545.77	1	1.03
Lys	7466.71	5	4.99

Het6G1-Cys: GalA-KKL*K*(cFuc-KKL)FC (32.5 mg, 20 µmol, 16%). MS (ESI^+) calc. for $C_{75}H_{125}N_{15}O_{21}S$ $[M+H]^+$: 1604.90, found: 1604.90 (z=1), 802.95 (z=2), 535.64 (z=3).

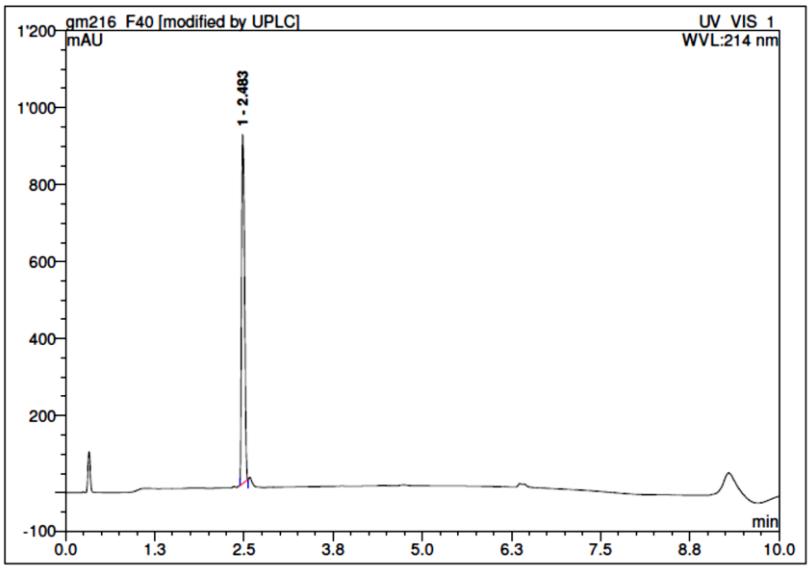


Figure S37: Analytical RP-UHPLC of **Het6G1-Cys**.

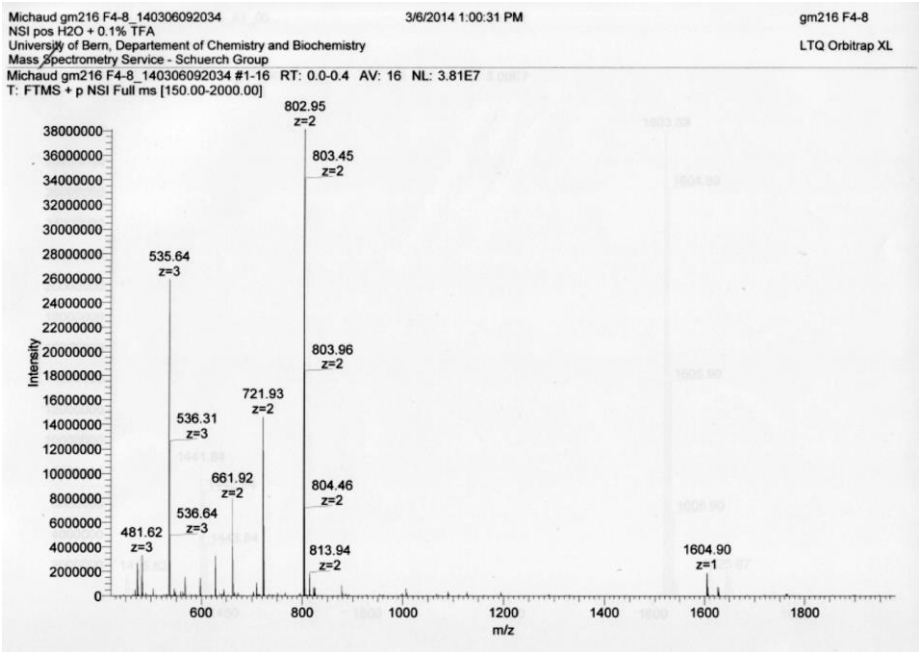
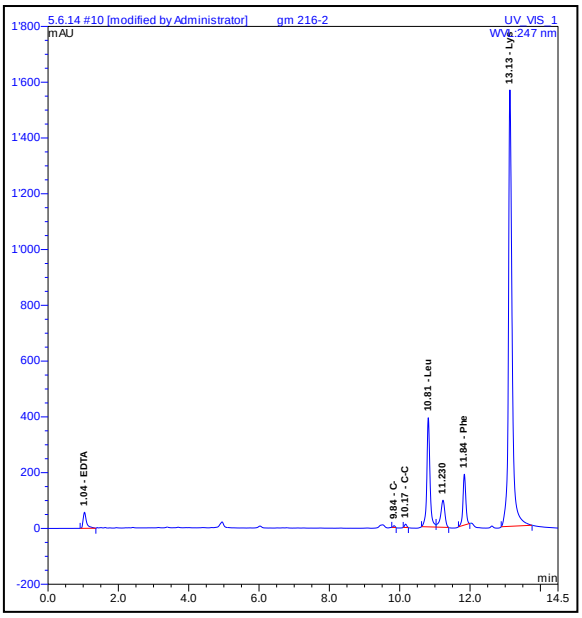


Figure S38: ESI-MS of **Het6G1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,02	0,091	6,38	57,52		342,98	EDTA
9,84	9,88	0,063	0,40	6,20		46,59	C-
10,17	10,18	0,068	0,83	11,76		88,30	C-C
10,81	10,84	0,085	40,12	391,24		2662,66	Leu
11,84	11,85	0,082	16,89	182,26		1347,75	Phe
13,13	13,18	0,098	189,58	1564,64		6753,90	Lys
Total:						11242,18	

Figure S39: Amino acid analysis of **Het6G1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Leu	2662.66	2	1.98
Phe	1347.75	1	1.00
Lys	6753.90	5	5.02

Het7G1-Cys: cFuc-KKL*K*(GalB-KKL)FC (66 mg, 42 µmol, 34%). MS (ESI^+) calc. for $C_{71}H_{125}N_{15}O_{20}S_2$ $[M+H]^+$: 1572.88, found: 1573.88 (z=1), 787.44 (z=2), 525.30 (z=3).

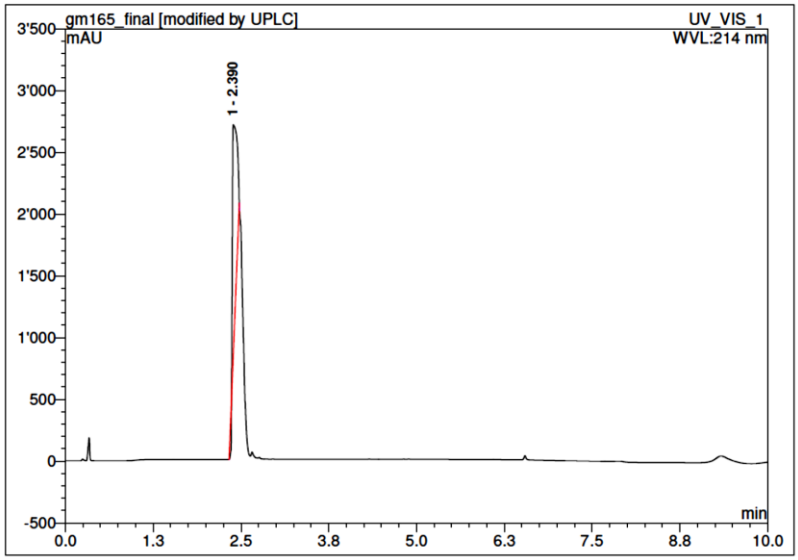


Figure S40: Analytical RP-UHPLC of **Het7G1-Cys**.

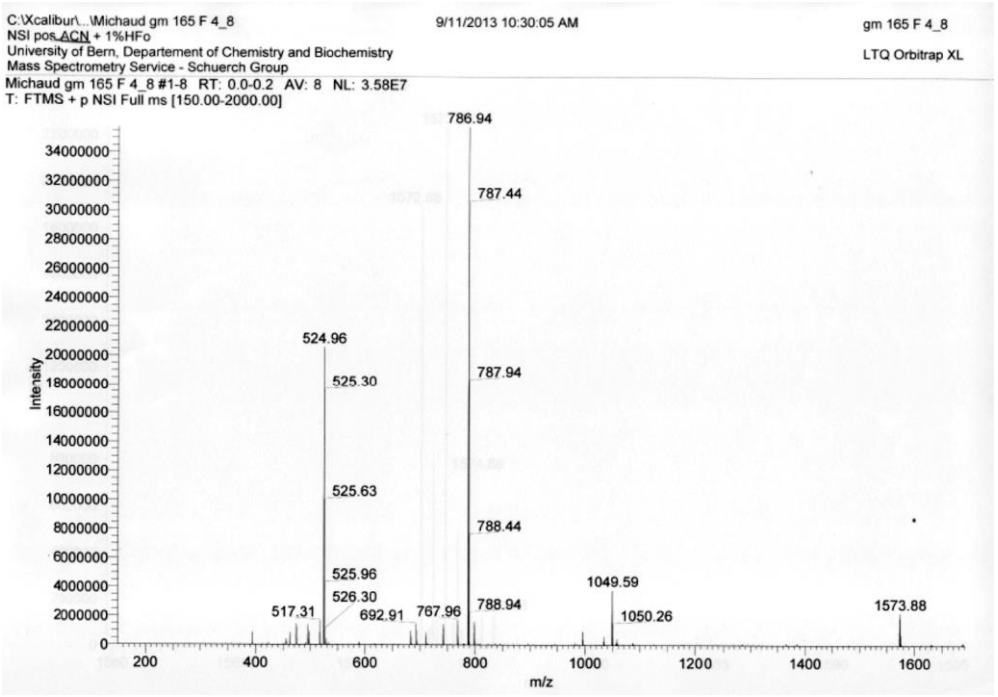
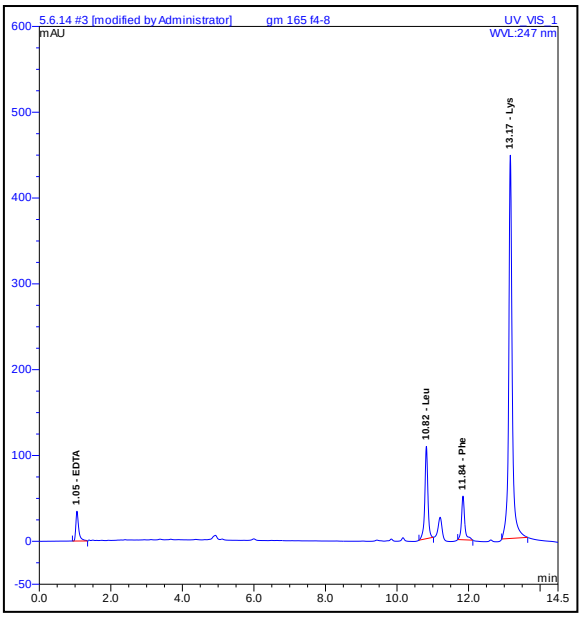


Figure S41: ESI-MS of **Het7G1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,05	1,02	0,077	3,22	34,70		206,89	EDTA
10,82	10,84	0,083	10,56	107,50		731,65	Leu
11,84	11,85	0,083	5,28	50,85		375,99	Phe
13,17	13,18	0,088	50,13	446,63		1927,90	Lys
Total:						3242,42	

Figure S42: Amino acid analysis of **Het7G1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Leu	731.65	2	1.93
Phe	375.99	1	0.99
Lys	1927.90	5	5.08

Het8G1-Cys: GalB-KKL*K*(cFuc-KKL)FC (52 mg, 33 µmol, 26%). MS (ESI^+) calc. for $C_{71}H_{125}N_{15}O_{20}S_2$ $[M+H]^+$: 1572.88, found: 1572.87 (z=1), 766.04 (z=2), 524.90 (z=3).

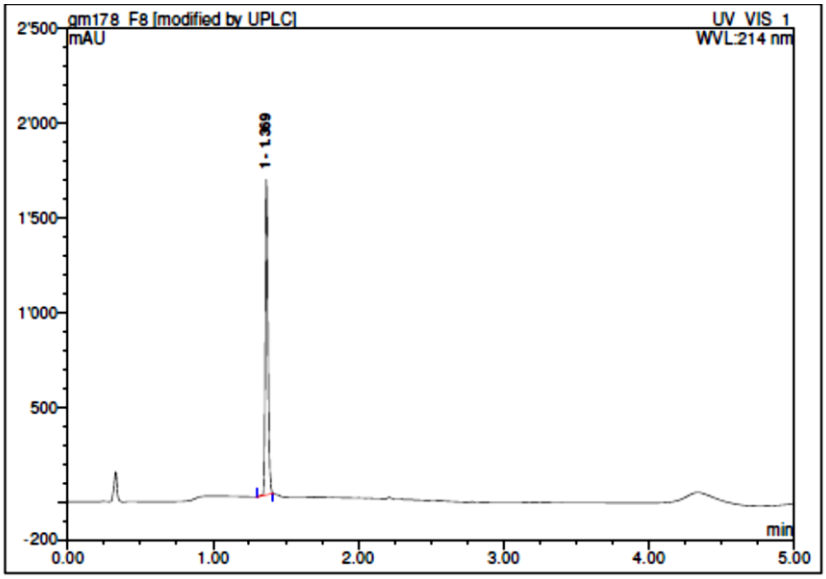


Figure S43: Analytical RP-UHPLC of **Het8G1-Cys**.

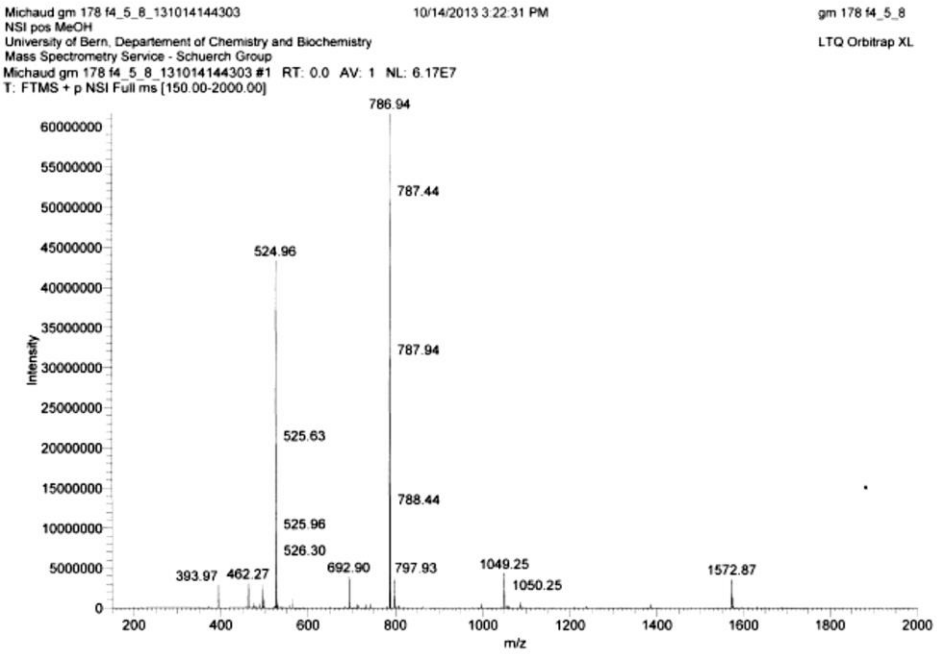
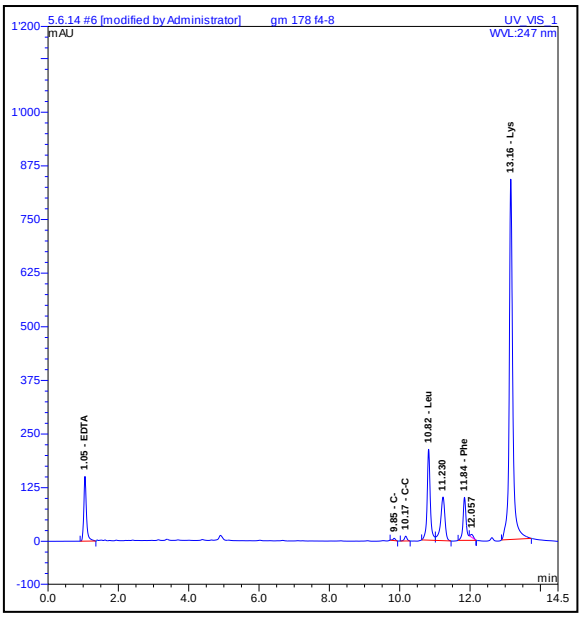


Figure S44: ESI-MS of **Het8G1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,05	1,02	0,072	13,01	150,71		898,63	EDTA
9,85	9,88	0,071	0,43	5,28		39,67	C-
10,17	10,18	0,077	0,97	11,08		83,20	C-C
10,82	10,84	0,084	21,56	211,62		1440,24	Leu
11,84	11,85	0,085	11,26	100,22		741,06	Phe
13,16	13,18	0,092	98,19	839,61		3624,25	Lys
Total:						6827,06	

Figure S45: Amino acid analysis of **Het8G1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Leu	1440.24	2	1.98
Phe	741.06	1	1.02
Lys	3624.25	5	4.99

ClAcG1 : (ClAc-KI)$_2$(*K*HI) (89 mg, 86 µmol, 70%). MS (ESI+) calc for $C_{46}H_{81}Cl_2N_{13}O_9$ $[M+H]^+$: 1030.58, found: 1029.57

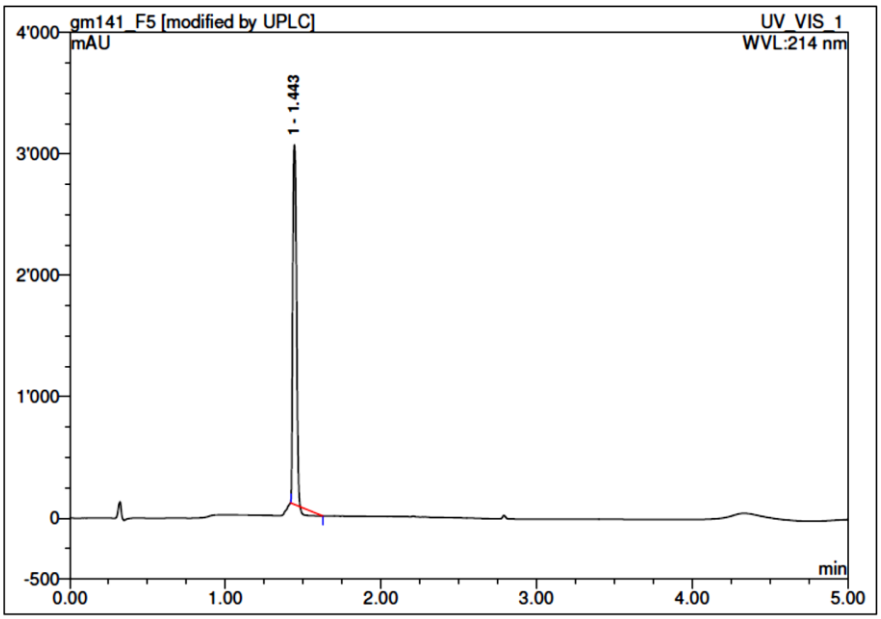


Figure S46: Analytical RP-UHPLC of **ClAcG1**.

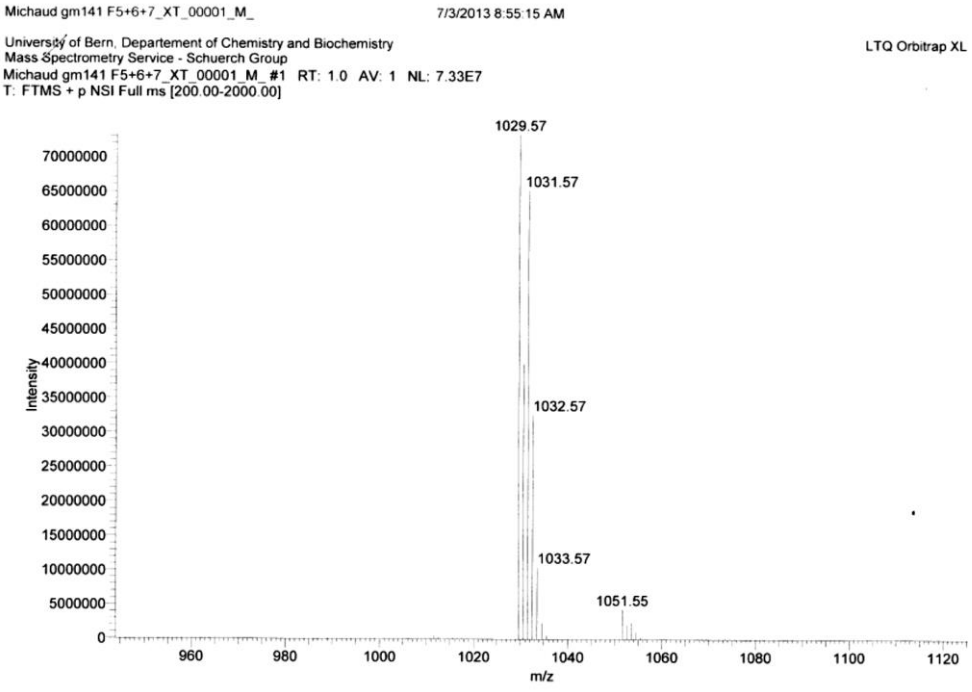


Figure S47: ESI-MS of **ClAcG1**.

AcG1-Cys: (Ac-KPL)$_2$*K*FC (37.8 mg, 33 μmol, 19%). MS (ESI$^+$) calc. for $C_{56}H_{93}N_{13}O_{11}S$ $[M+H]^+$: 1156.69, found: 1156.69 (z=1), 578.85 (z=2).

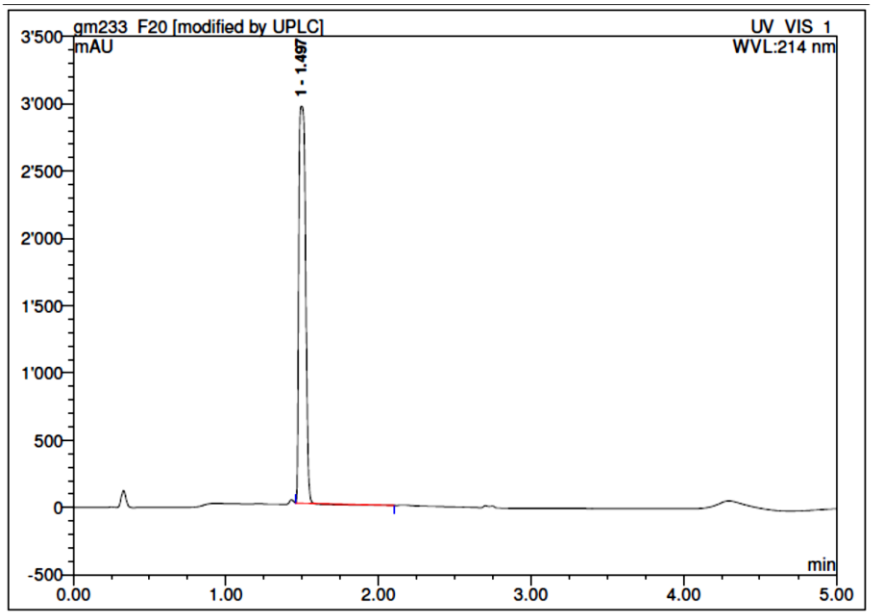


Figure S48: Analytical RP-UHPLC of **AcG1-Cys**.

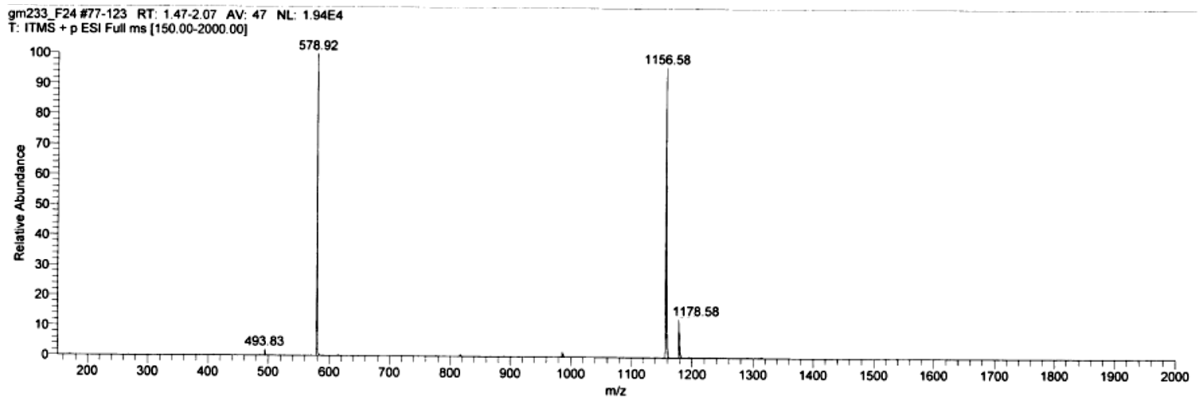
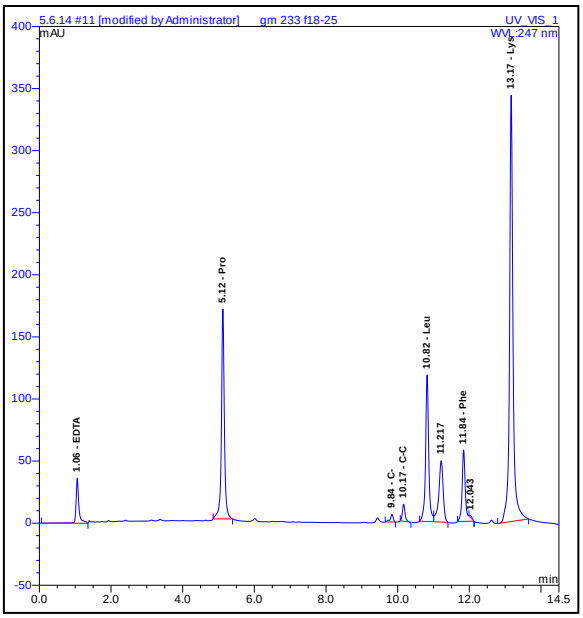


Figure S49: ESI-MS of **AcG1-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,06	1,02	0,069	3,37	36,14		215,49	EDTA
5,12	5,14	0,077	16,16	169,03		983,96	Pro
9,84	9,88	0,075	0,59	6,05		45,45	C-
10,17	10,18	0,074	1,17	13,83		103,85	C-C
10,82	10,84	0,083	12,01	117,85		802,06	Leu
11,84	11,85	0,084	6,07	57,43		424,68	Phe
13,17	13,18	0,087	38,65	343,28		1481,80	Lys
Total:						4057,29	

Figure S50: Amino acid analysis of **AcG1-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Pro	983.96	2	2.13
Leu	802.06	2	1.74
Phe	424.68	1	0.92
Lys	1481.80	3	3.21

AcG1K-Cys: (Ac-KKL)$_2$*K*FC (75.9 mg, 62 µmol, 50%). MS (ESI$^+$) calc. for $C_{59}H_{104}N_{14}O_{11}S$ $[M+H]^+$: 1217.78, found: 1218.78 (z=1), 609.89 (z=2).

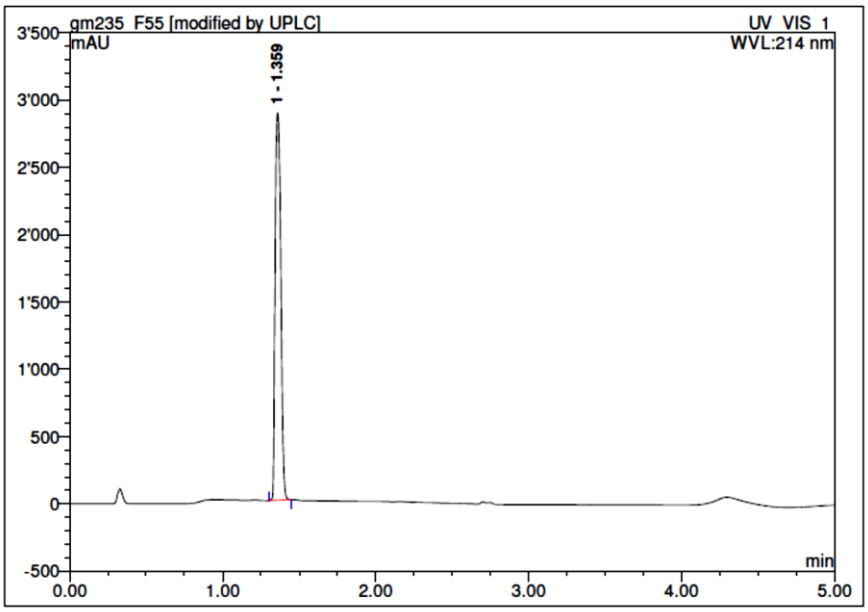


Figure S51: Analytical RP-UHPLC of **AcG1K-Cys**.

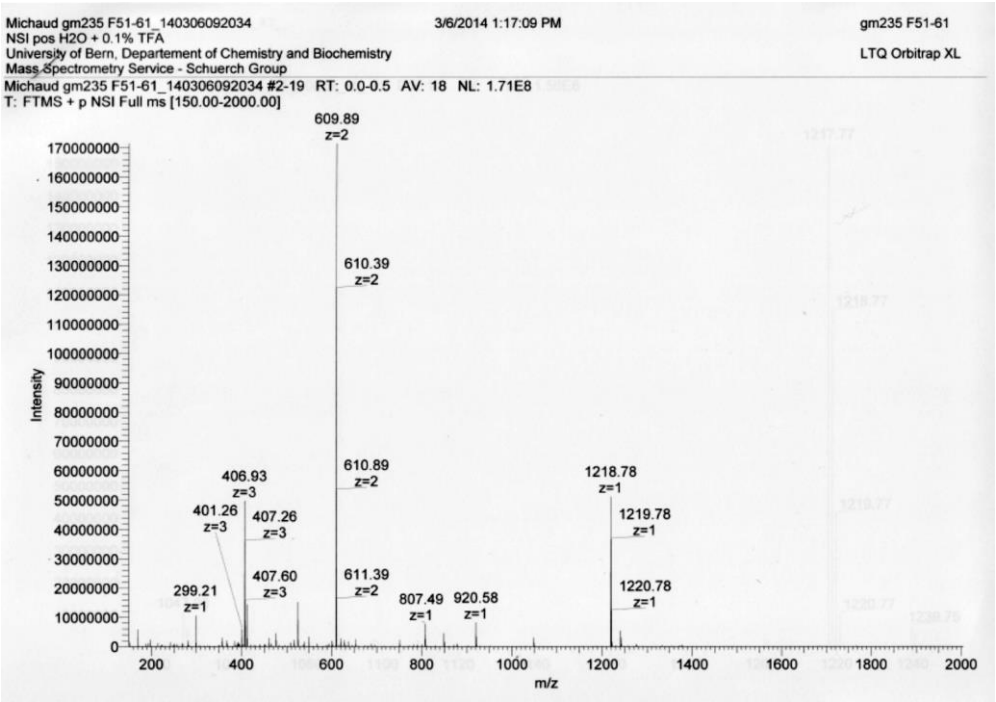
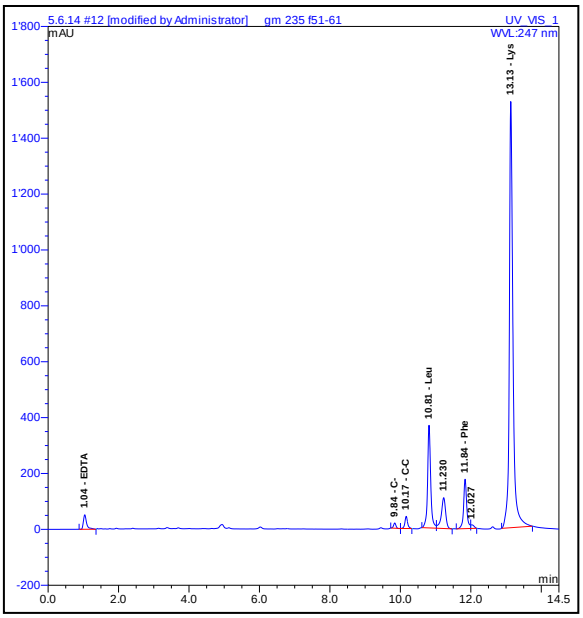


Figure S52: ESI-MS of **AcG1K-Cys**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,02	0,088	5,50	51,84		309,13	EDTA
9,84	9,88	0,071	1,44	18,67		140,23	C-
10,17	10,18	0,076	3,90	43,50		326,73	C-C
10,81	10,84	0,084	37,27	367,21		2499,17	Leu
11,84	11,85	0,085	18,20	176,86		1307,83	Phe
13,13	13,18	0,097	182,50	1525,09		6583,18	Lys
Total:						11166,29	

Figure S53: Amino acid analysis of **AcG1K-Cys**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Leu	2499.17	2	1.92
Phe	1307.83	1	1.01
Lys	6583.18	5	5.07

NG2: $(KPL)_4(KKI)_2KHI$ (8 mg, 2.88 µmol, 44%). MS (ESI^+) calc $C_{140}H_{241}N_{35}O_{23}$ $[M+H]^+$: 2781.88, found: 2781.88 (z=1), 1391.95 (z=2), 928.30 (z=3), 696.48 (z=4), 557.38 (z=5).

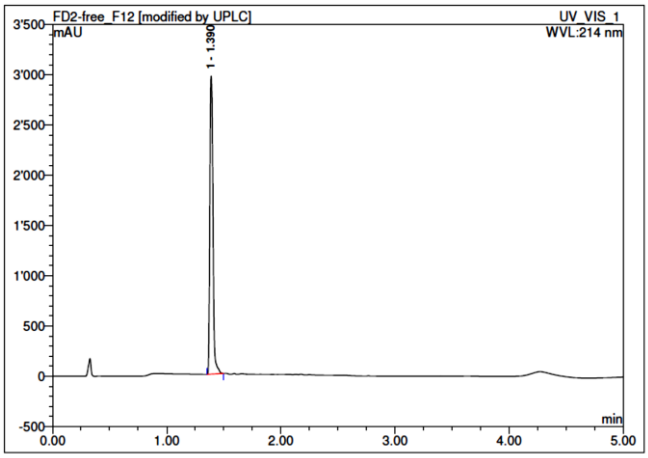


Figure S54: Analytical RP-UHPLC of **NG2**.

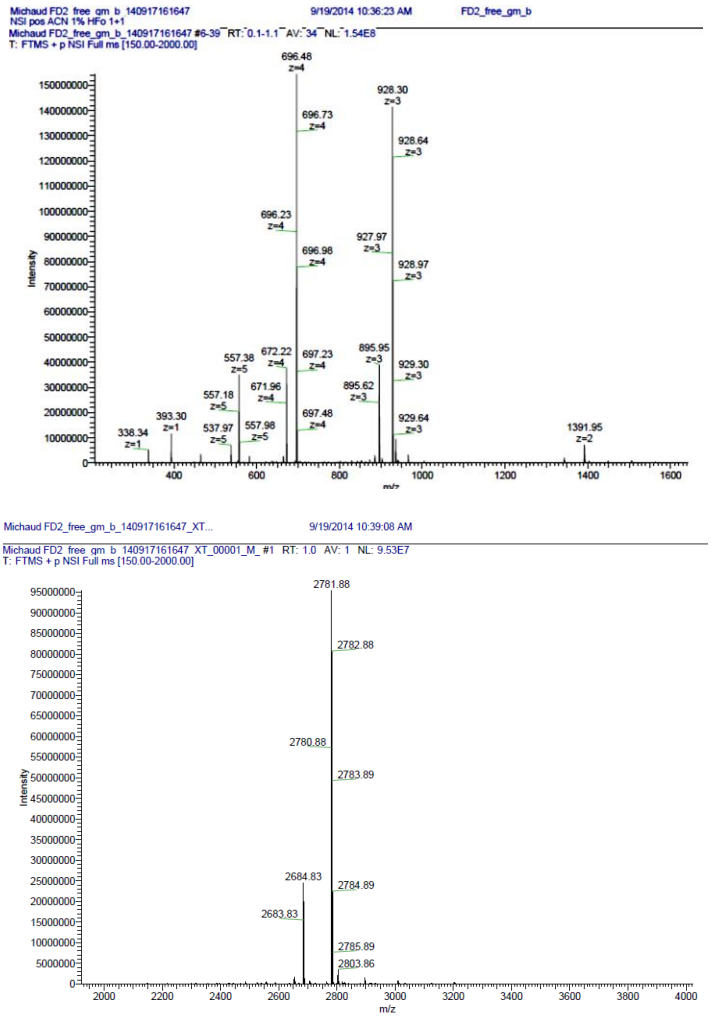
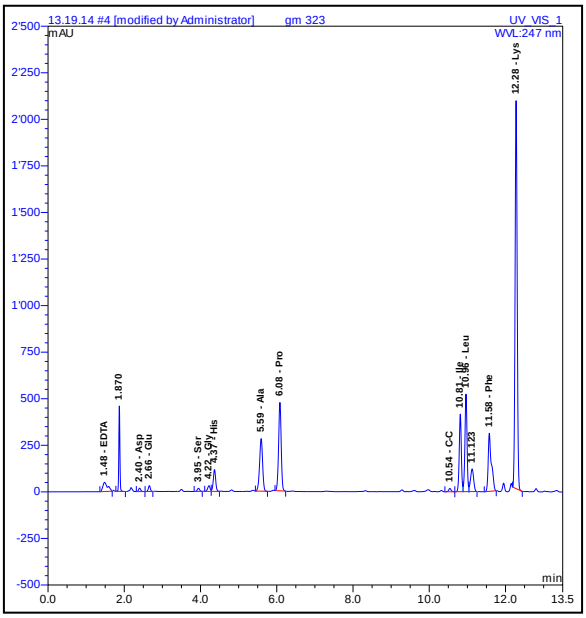


Figure S55: ESI-MS of **NG2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,48	1,45	0,112	7,26	49,30		248,70	EDTA
4,37	4,36	0,067	8,52	116,78		598,65	His
6,08	6,09	0,072	37,19	474,17		2155,78	Pro
10,54	10,57	0,066	1,33	17,86		55,40	C-C
10,81	10,81	0,058	26,40	416,30		1757,03	Ile
10,96	10,96	0,059	33,56	523,17		2217,63	Leu
11,58	11,56	0,075	29,97	311,91		578,82	Phe
12,28	12,29	0,059	132,47	2082,12		4750,14	Lys
Total:						12362,15	

Figure S56: Amino acid analysis of **NG2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
His	598.65	1	1.14
Pro	2155.78	4	4.11
Ile	1757.03	3	3.35
Leu	2217.63	4	4.23
Phe	578.82	2	1.10
Lys	4750.14	9	9.06

ClAcD2 : (ClAc-KPL)$_4$(*K*KI)$_2$*K*HI (42.5 mg, 15 µmol, 17%). MS (ESI+) calc MS (ESI$^+$) calc. for $C_{130}H_{227}Cl_4N_{33}O_{25}$ $[M+H]^+$: 2791.64, found: 2791.64.

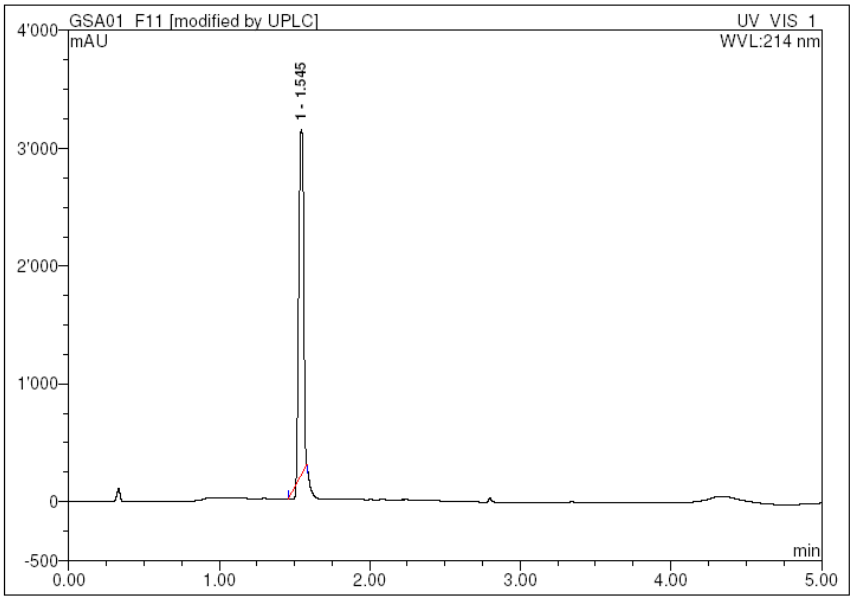


Figure S57: Analytical RP-UHPLC of **ClAcD2**.

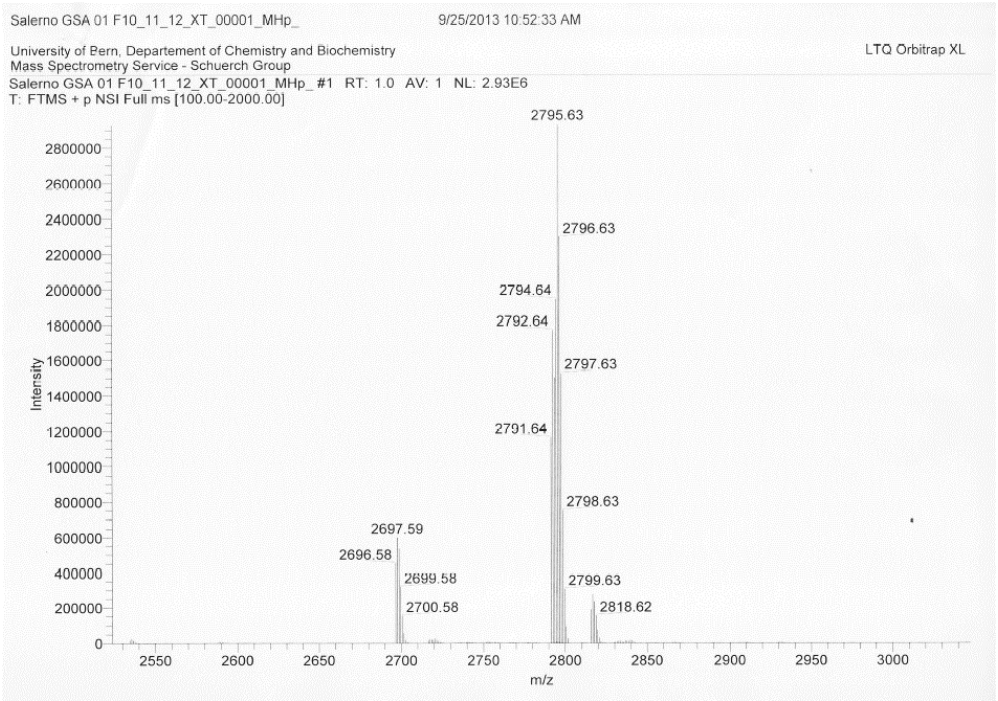


Figure S58: ESI-MS of **ClAcD2**.

FD2x: (cFuc-KPL)$_4$(*K*FCxKI)$_2$*K*HI (7.9 mg, 2.05 μmol, 70%). MS (ESI+) calc for $C_{182}H_{305}N_{39}O_{47}S_2$ $[M+H]^+$: 3854.22, found: 3854.23.

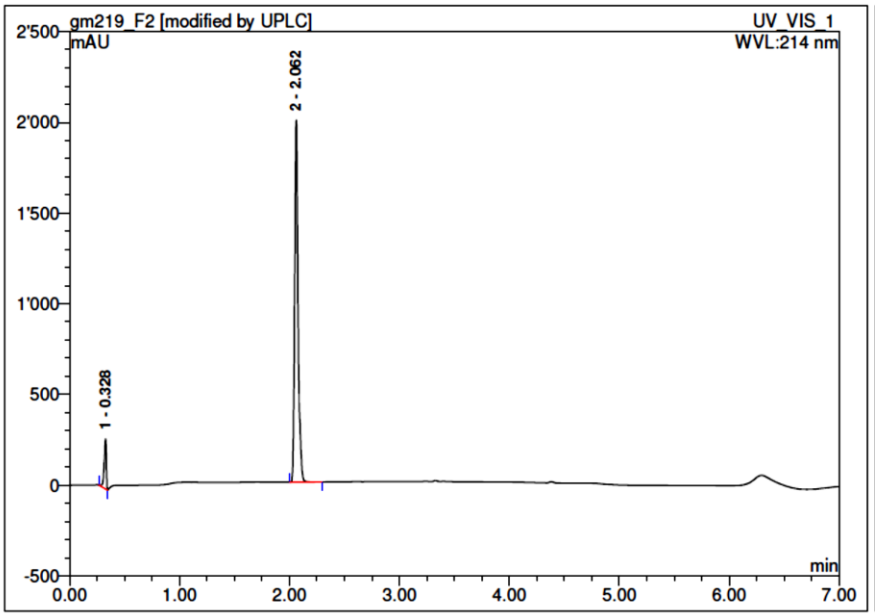


Figure S59: Analytical RP-UHPLC of **FD2x**.

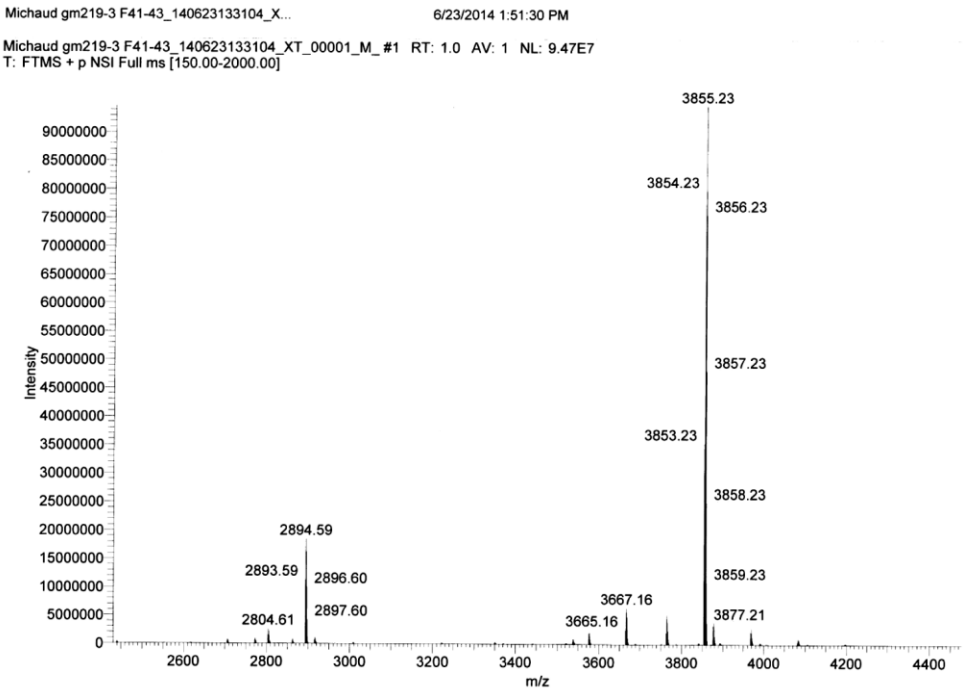
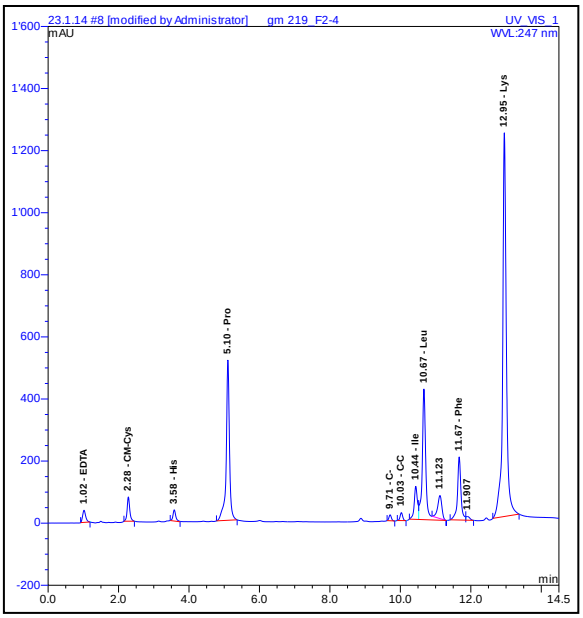


Figure S60: ESI-MS of **FD2x**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,02	1,02	0,092	3,91	38,99		322,11	EDTA
2,28	2,30	0,074	6,73	78,14		433,12	CM-Cys
3,58	3,60	0,078	3,30	35,94		202,81	His
5,10	5,13	0,083	55,43	515,70		2563,75	Pro
9,71	9,77	0,074	1,49	18,85		83,46	C-
10,03	10,07	0,078	2,15	25,53		113,08	C-C
10,44	10,48	0,099	11,37	106,36		601,91	Ile
10,67	10,73	0,090	49,75	420,51		2481,33	Leu
11,67	11,72	0,090	23,09	202,97		1275,17	Phe
12,95	13,01	0,096	152,38	1235,76		4541,23	Lys
Total:						12617,97	

Figure S61: Amino acid analysis of **FD2x**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	433.12	2	2.08
His	202.81	1	0.40
Pro	2563.75	4	5.04
Ile	601.91	3	1.18
Leu	2481.33	4	4.88
Phe	1275.17	2	2.51
Lys	4541.23	9	8.92

GalAG2x: (GalA-KPL)$_4$(*K*FCxKI)$_2$*K*HI (2.9 mg, 0.7 μmol, 24%). MS (ESI+) calc for $C_{202}H_{313}N_{39}O_{55}S_2$ $[M+H]^+$: 4230.24, found: 4231.24.

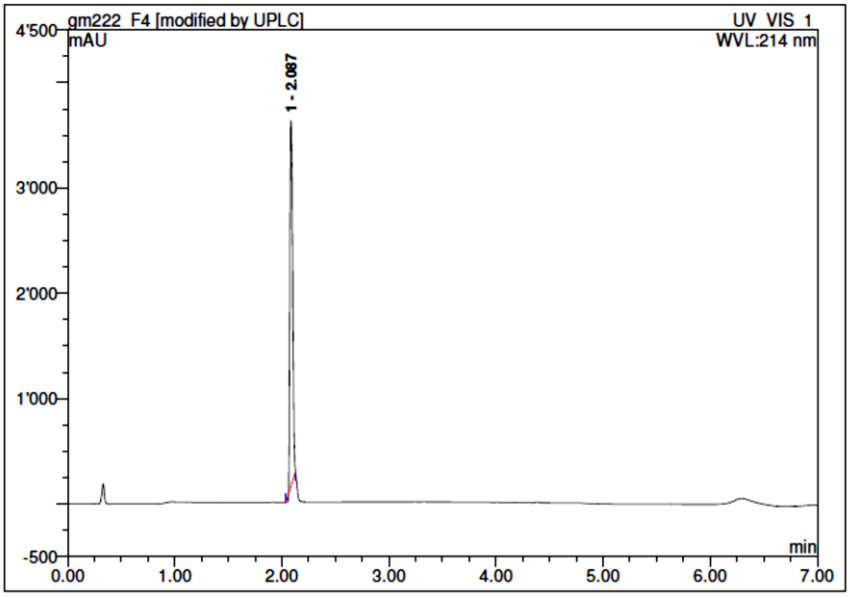


Figure S62: Analytical RP-UHPLC of **GalAG2x**.

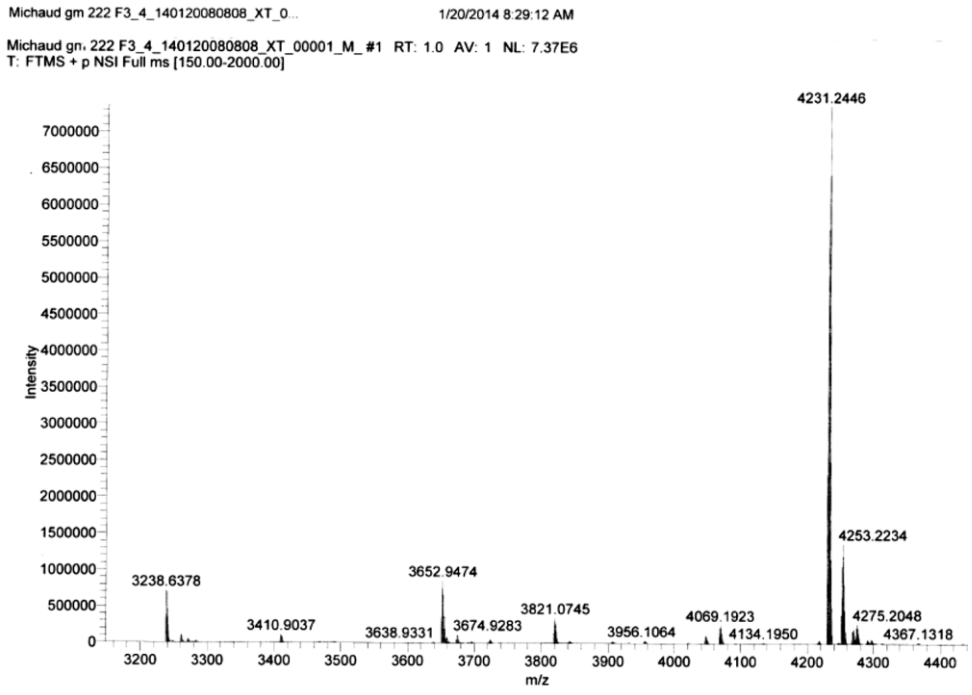
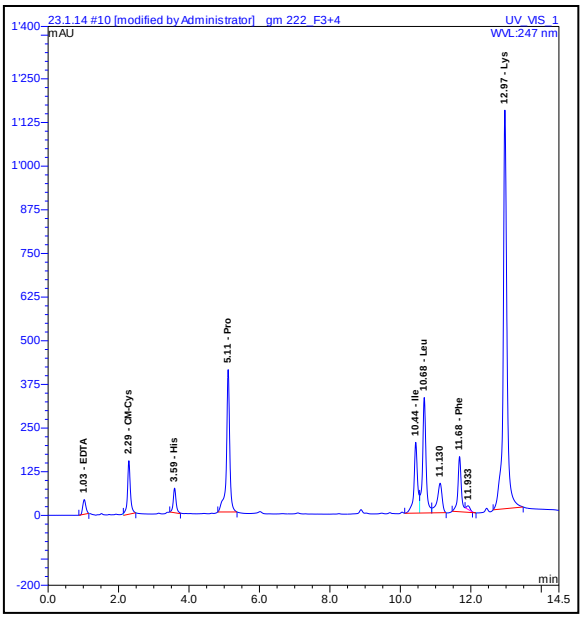


Figure S63: ESI-MS of **GalAG2x**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,03	1,02	0,096	4,23	42,01		347,09	EDTA
2,29	2,30	0,076	14,49	153,16		848,99	CM-Cys
3,59	3,60	0,079	6,59	70,36		397,09	His
5,11	5,13	0,083	44,20	407,52		2025,94	Pro
10,44	10,48	0,092	23,75	202,46		1145,75	Ile
10,68	10,73	0,092	37,80	330,55		1950,48	Leu
11,68	11,72	0,089	18,97	157,81		991,44	Phe
12,97	13,01	0,097	143,77	1141,23		4193,86	Lys
Total:						11900,65	

Figure S64: Amino acid analysis of **GalAG2x**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	848.99	2	2.01
His	397.09	1	0.94
Pro	2025.94	4	4.80
Ile	1145.75	3	2.71
Leu	1950.48	4	4.62
Phe	991.44	2	2.15
Lys	4193.86	9	9.93

GalBG2x: (GalB-KPL)$_4$(*K*FCxKI)$_2$*K*HI (3.8 mg, 0.9 µmol, 32%). MS (ESI$^+$) calc. for $C_{186}H_{313}N_{39}O_{51}S_6$ $[M+H]^+$: 4102.15, found: 4103.15.

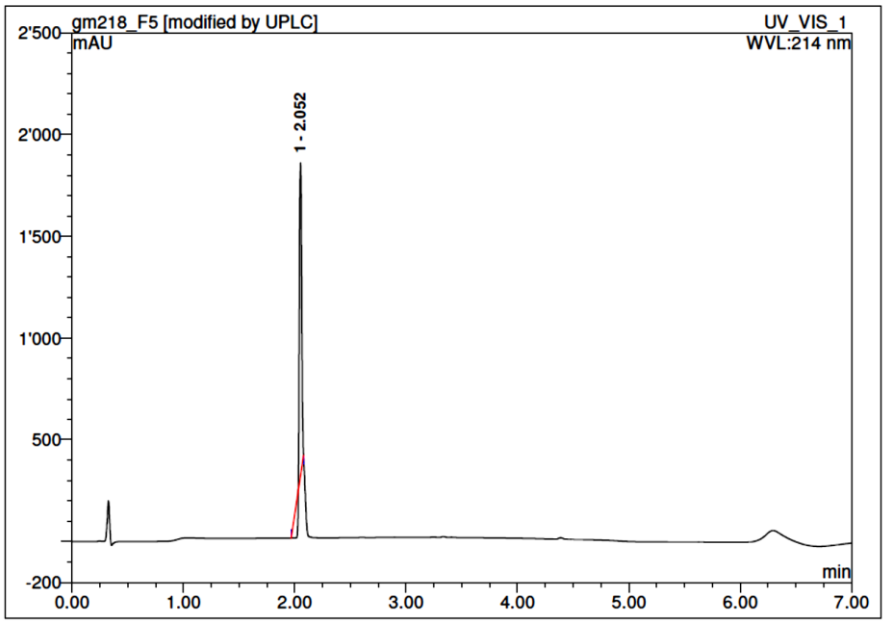


Figure S65: Analytical RP-UHPLC of **GalBG2x**.

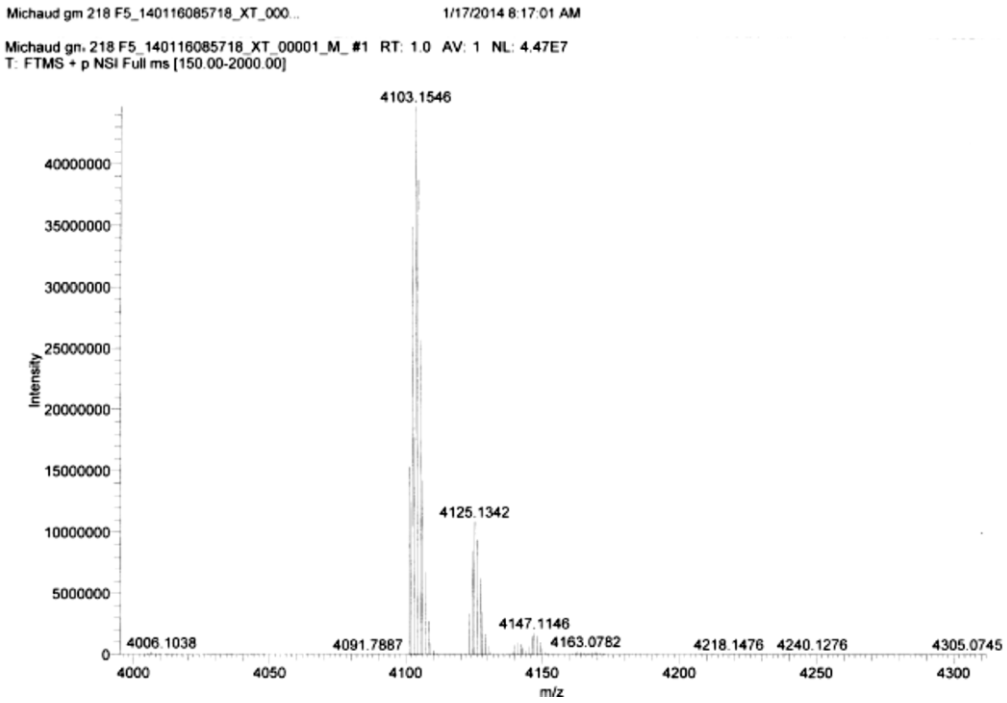
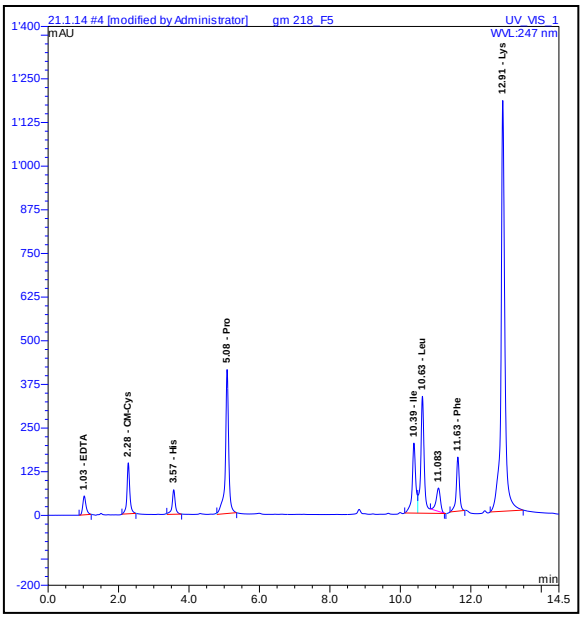


Figure S66: ESI-MS of **GalBG2x**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,03	1,02	0,093	5,71	54,17		393,55	EDTA
2,28	2,27	0,075	13,35	145,94		1056,53	CM-Cys
3,57	3,56	0,081	7,25	70,22		503,61	His
5,08	5,08	0,082	44,61	412,06		2579,91	Pro
10,39	10,38	0,092	23,03	200,40		1426,94	Ile
10,63	10,63	0,090	40,70	334,63		2499,47	Leu
11,63	11,62	0,087	16,02	154,76		1266,74	Phe
12,91	12,92	0,096	149,25	1175,88		5452,68	Lys
Total:						15179,44	

Figure S67: Amino acid analysis of **GalBG2x.**

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	1056.53	2	0.85
His	503.61	1	0.43
Pro	2579.91	4	5.27
Ile	1426.94	3	1.27
Leu	2499.47	4	5.01
Phe	1266.74	2	2.73
Lys	5452.68	9	9.44

Het1G2: (cFuc-KPL*K*(Gal-KPL)FCxKI)$_2$*K*HI (10.3 mg, 2.55 µmol, 88%). MS (ESI$^+$) calc. for $C_{192}H_{309}N_{39}O_{51}S_2$ $[M+H]^+$: 4042.23, found: 1011.81 (z=4), 809.65 (z=5), 674.88 (z=6).

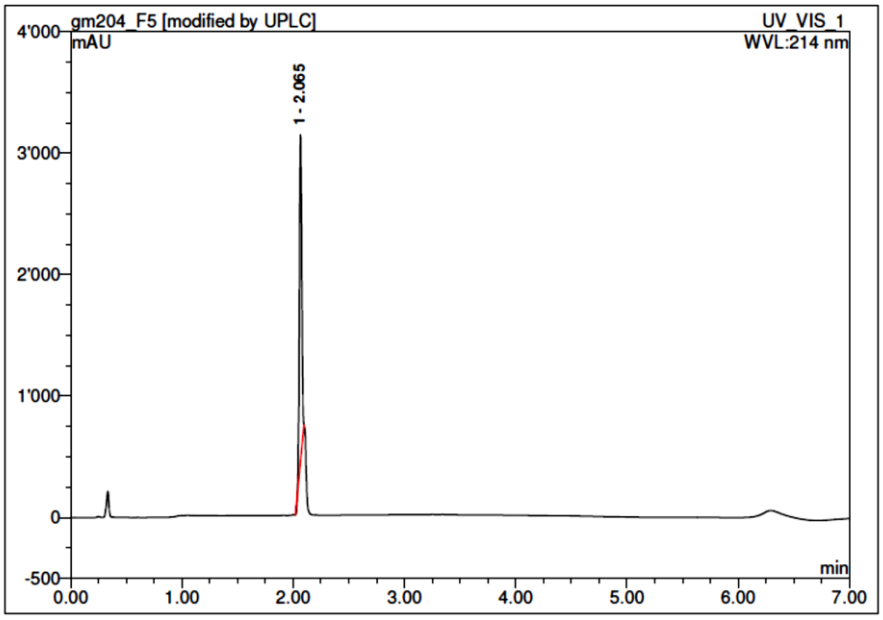


Figure S68: Analytical RP-UHPLC of **Het1G2**.

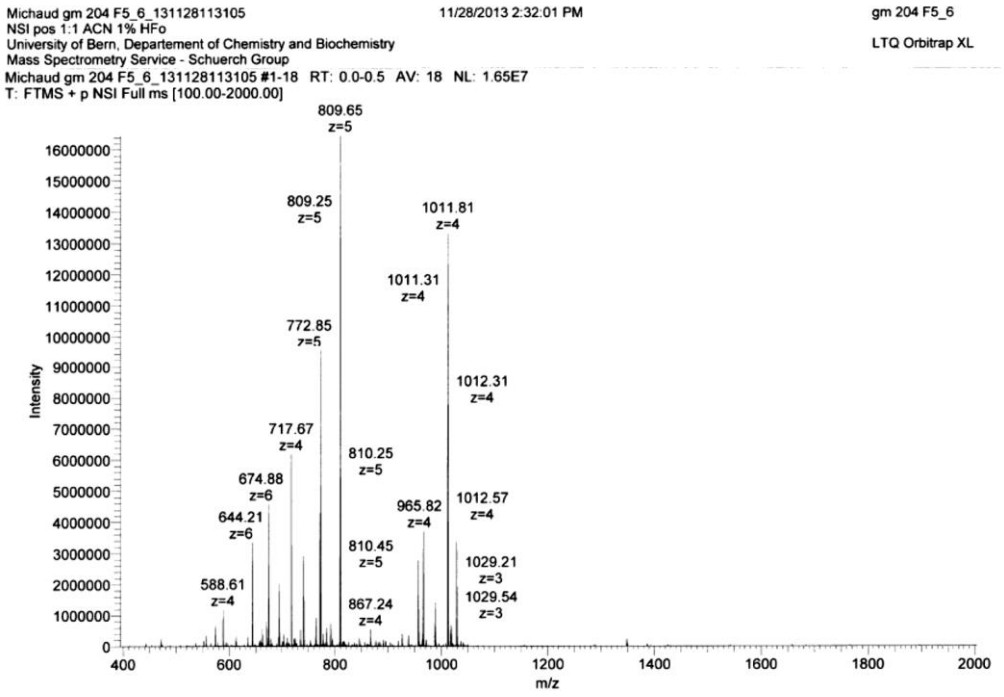
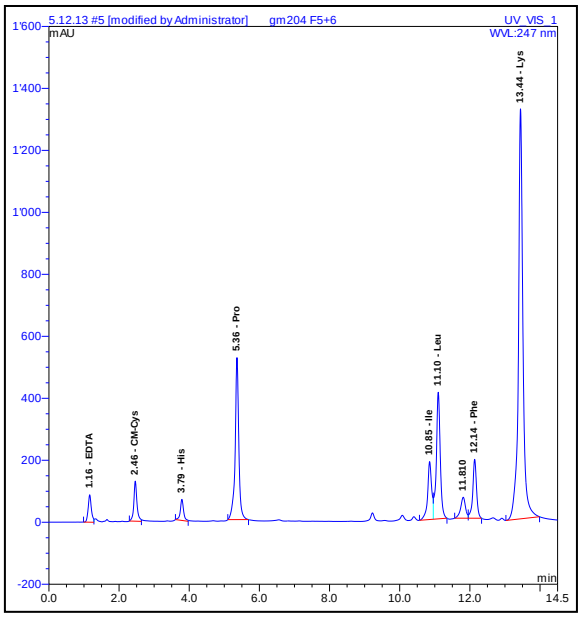


Figure S69: ESI-MS of **Het1G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,16	1,14	0,092	9,29	88,38		713,68	EDTA
2,46	2,46	0,084	13,38	129,20		1004,21	CM-Cys
3,79	3,79	0,089	7,41	68,01		500,74	His
5,36	5,37	0,096	62,94	522,60		3553,83	Pro
10,85	10,85	0,115	24,83	186,89		1517,88	Ile
11,10	11,10	0,109	53,47	408,40		3453,81	Leu
12,14	12,12	0,105	23,65	189,99		1780,94	Phe
13,44	13,45	0,117	198,59	1322,93		6959,01	Lys
Total:						19484,10	

Figure S70: Amino acid analysis of **Het1G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	1004.21	2	1.34
His	500.74	1	0.67
Pro	3553.83	4	4.73
Ile	1517.88	3	2.02
Leu	3453.81	4	4.60
Phe	1780.94	2	2.37
Lys	6959.01	9	9.27

Het2G2: (GalA-KPL*K*(cFuc-KPL)FCxKI)$_2$*K*HI (9.3 mg, 2.3 µmol, 79%). MS (ESI$^+$) calc. for $C_{192}H_{309}N_{39}O_{51}S_2$ $[M+H]^+$: 4042.23, found: 4042.23.

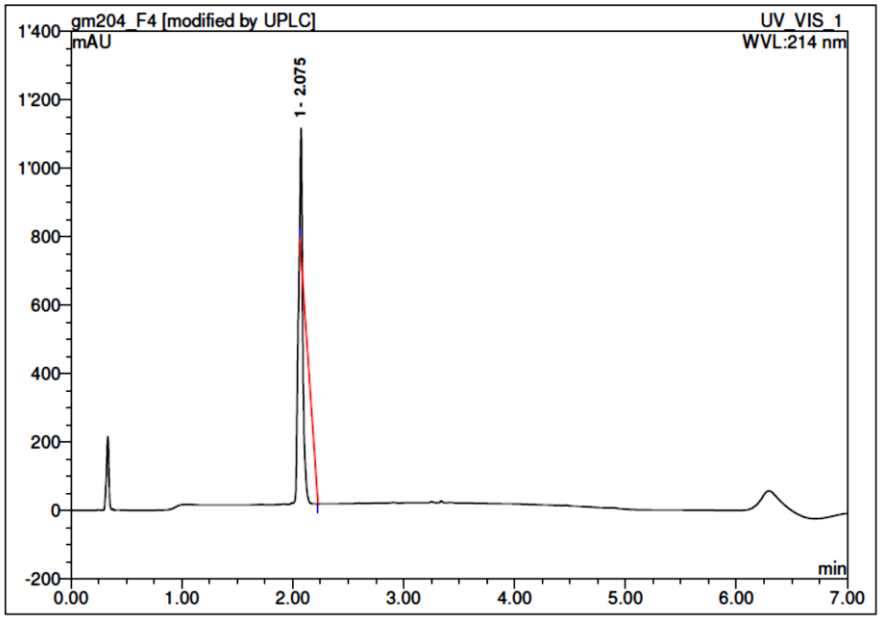


Figure S71: Analytical RP-UHPLC of **Het2G2**.

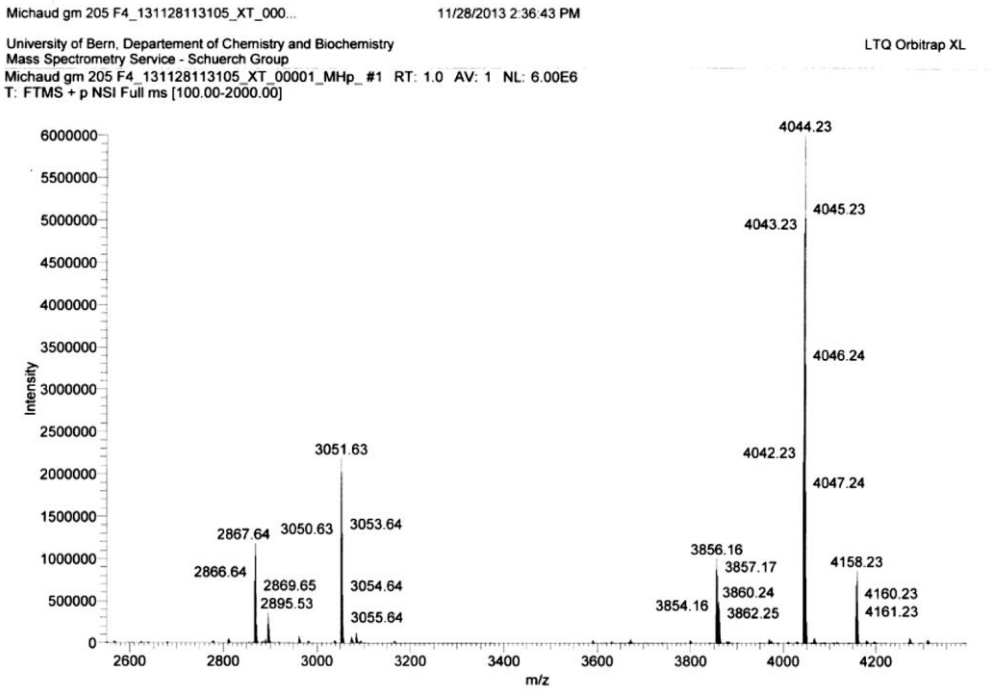
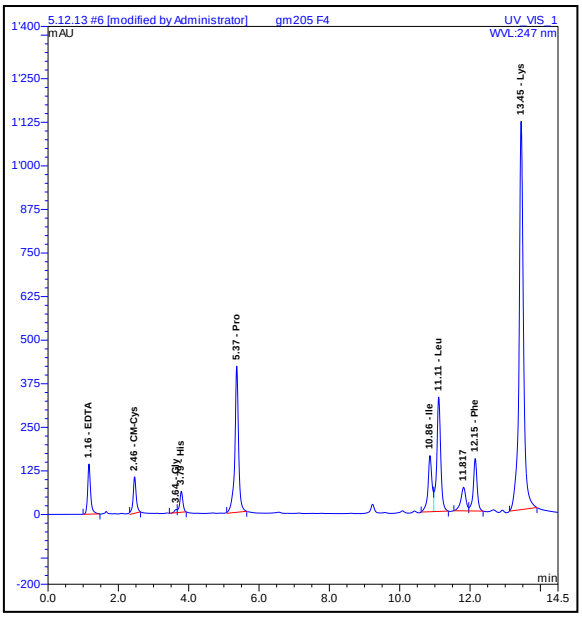


Figure S72: ESI-MS of **Het2G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,16	1,14	0,080	13,88	143,72		1160,62	EDTA
2,46	2,46	0,084	10,61	104,55		812,60	CM-Cys
3,79	3,79	0,088	6,10	59,92		441,16	His
5,37	5,37	0,096	51,27	419,19		2850,60	Pro
10,86	10,85	0,114	21,22	161,02		1307,73	Ile
11,11	11,10	0,109	43,00	327,86		2772,66	Leu
12,15	12,12	0,106	18,94	150,37		1409,58	Phe
13,45	13,45	0,115	162,47	1113,71		5693,07	Lys
Total:						16448,03	

Figure S73: Amino acid analysis of **Het2G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	812.60	2	1.33
His	441.16	1	0.72
Pro	2850.60	4	4.66
Ile	1307.73	3	2.14
Leu	2772.66	4	4.53
Phe	1409.58	2	2.31
Lys	5693.07	9	9.31

Het3G2: (cFuc-KPL*K*(GalB-KPL)FCxKI)$_2$*K*HI (3.6 mg, 0.9 µmol, 31%). MS (ESI$^+$) calc. for $C_{184}H_{309}N_{39}O_{49}S_4$ $[M+H]^+$: 3978.19, found: 3978.18.

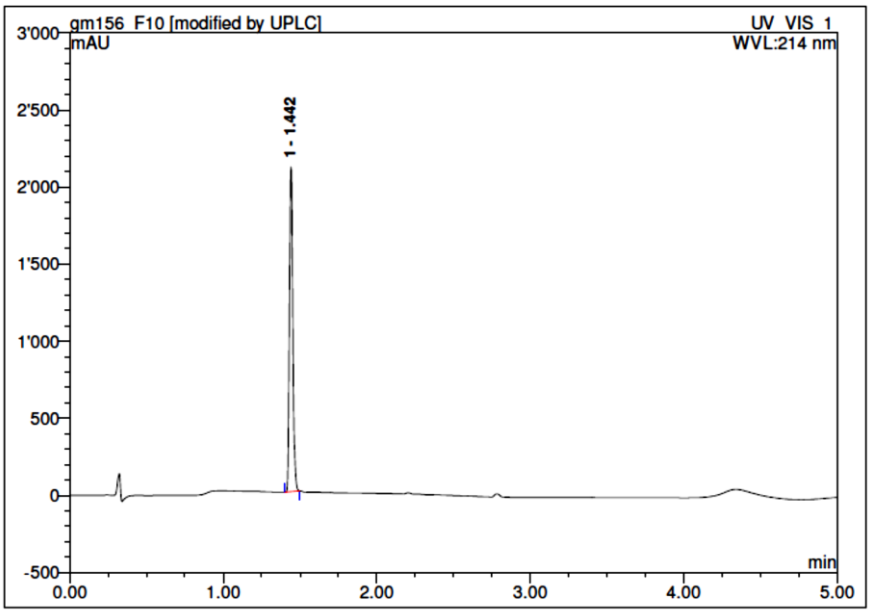


Figure S74: Analytical RP-UHPLC of **Het3G2**.

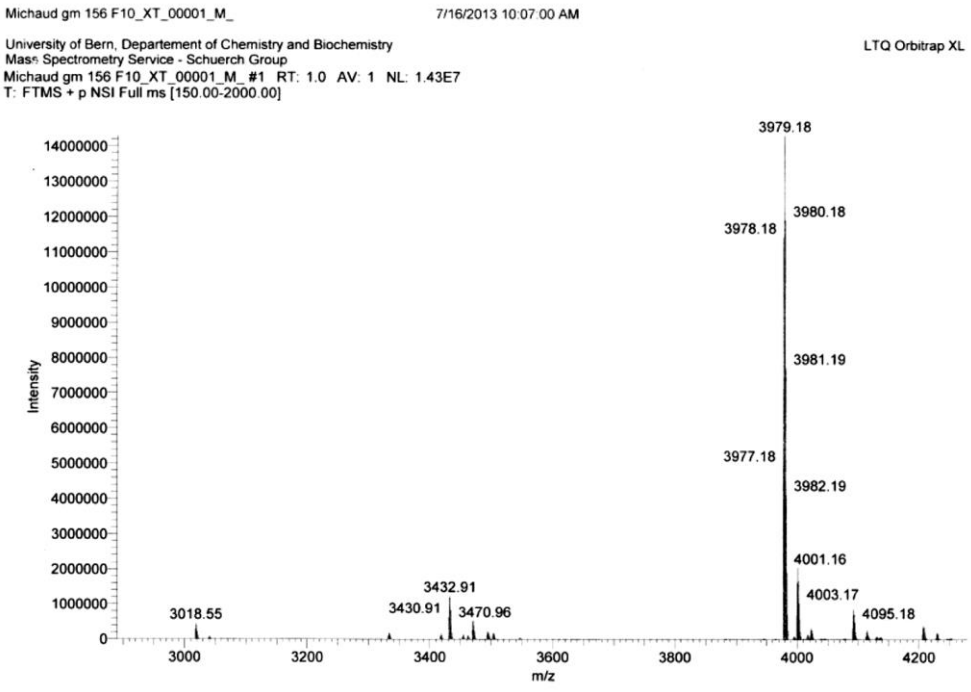
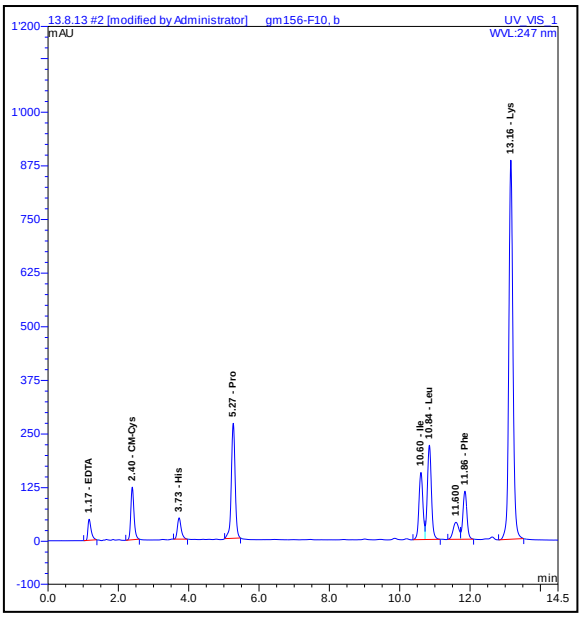


Figure S75: ESI-MS of **Het3G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,17	1,16	0,094	5,21	49,00		354,13	EDTA
2,40	2,39	0,094	12,88	122,54		854,41	CM-Cys
3,73	3,73	0,112	6,18	49,45		409,12	His
5,27	5,27	0,112	33,58	267,89		1743,70	Pro
10,60	10,60	0,122	20,51	156,37		1191,56	Ile
10,84	10,85	0,122	29,36	219,53		1718,04	Leu
11,86	11,86	0,121	14,83	111,81		902,02	Phe
13,16	13,18	0,122	120,15	883,30		3859,80	Lys
Total:						11032,79	

Figure S76: Amino acid analysis of **Het3G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	854.41	2	1.76
His	409.12	1	0.75
Pro	1743.70	4	3.75
Ile	1191.56	3	2.03
Leu	1718.04	4	3.75
Phe	902.02	2	1.97
Lys	3859.80	9	8.00

Het4G2: (GalB-KPL*K*(cFuc-KPL)FCxKI)$_2$*K*HI (7.3 mg, 1.84 µmol, 63%). MS (ESI$^+$) calc. for $C_{184}H_{309}N_{39}O_{49}S_4$ $[M+H]^+$: 3978.19, found: 3978.19 (z=1), 1991.10 (z=2).

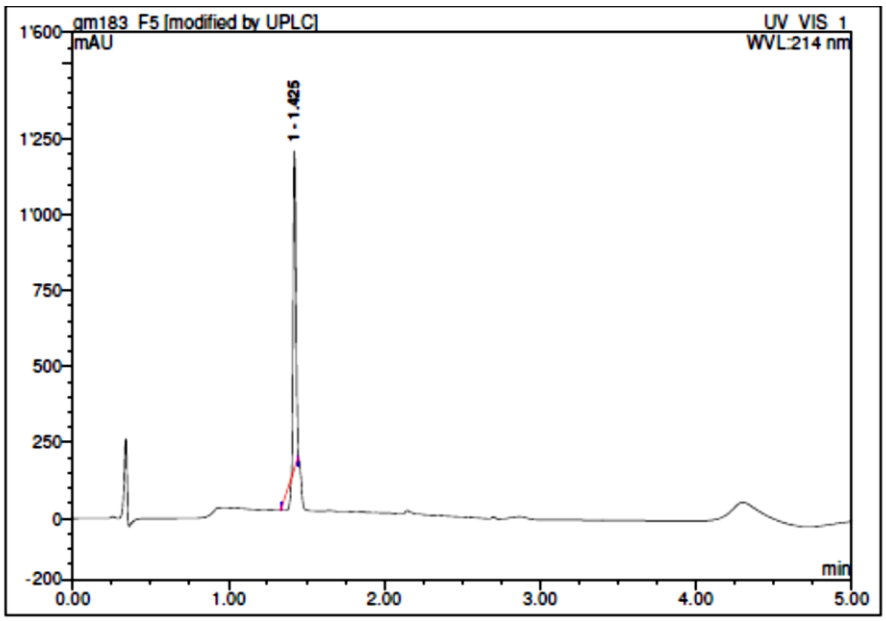


Figure S77: Analytical RP-UHPLC of **Het4G2**.

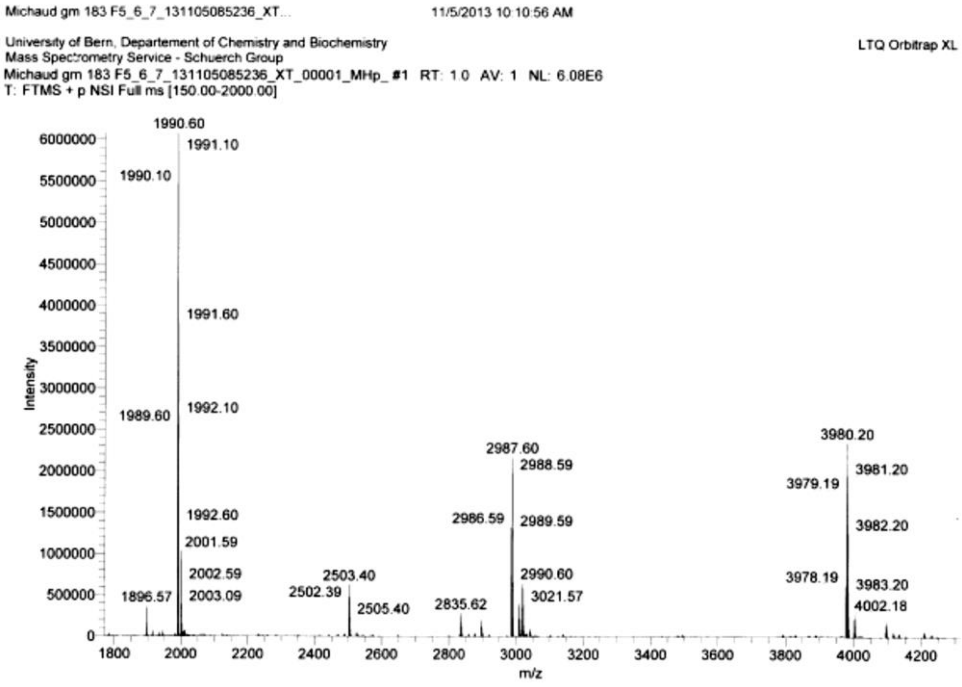
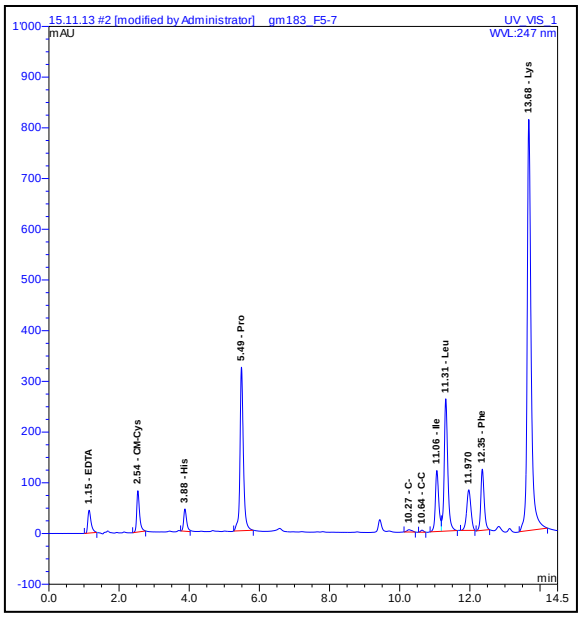


Figure S78: ESI-MS of **Het4G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,15	1,14	0,095	4,83	45,01		264,79	EDTA
2,54	2,53	0,080	7,58	81,42		544,20	CM-Cys
3,88	3,88	0,086	4,31	44,00		281,51	His
5,49	5,50	0,093	35,85	322,42		1951,19	Pro
10,27	10,34	0,166	0,72	4,42		24,70	C-
10,64	10,64	0,092	0,39	4,05		22,63	C-C
11,06	11,08	0,100	13,62	120,23		849,07	Ile
11,31	11,34	0,102	30,87	260,83		1869,69	Leu
12,35	12,37	0,099	13,35	120,53		964,97	Phe
13,68	13,71	0,107	105,42	810,43		3826,43	Lys
Total:						10599,19	

Figure S79: Amino acid analysis of **Het4G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	544.20	2	1.32
His	281.51	1	0.68
Pro	1951.19	4	4.74
Ile	849.07	3	2.06
Leu	1869.69	4	4.54
Phe	964.97	2	2.35
Lys	3826.43	9	9.30

Het5G2: (cFuc-KKL*K*(GalA-KKL)FCxKI)$_2$*K*HI (6.6 mg, 1.58 µmol, 54%). MS (ESI$^+$) calc. for $C_{196}H_{329}N_{43}O_{51}S_2$ $[M+H]^+$: 4166.40, found: 4166.40 (z=1), 1390.14 (z=3), 1042.86 (z=4), 834.49 (z=5), 695.57 (z=6).

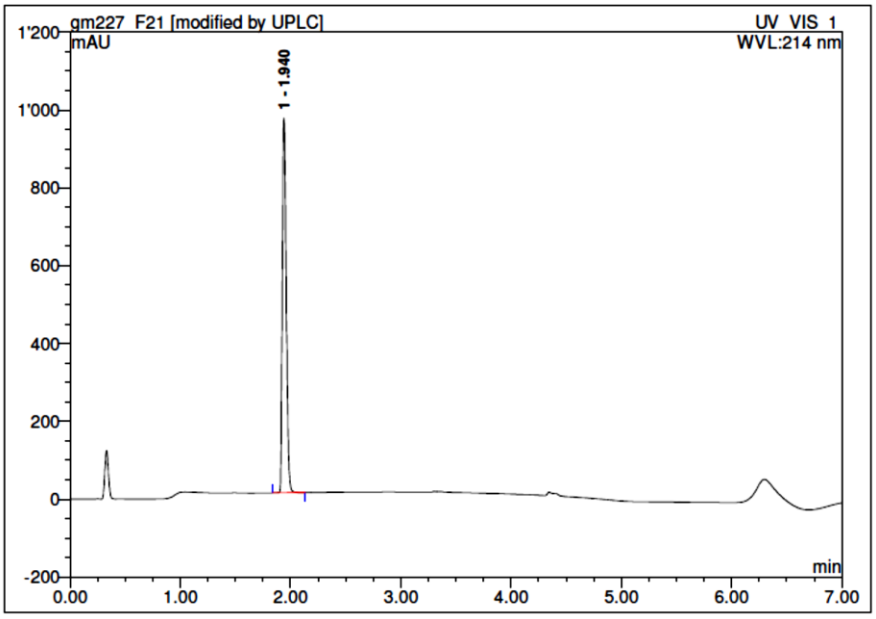
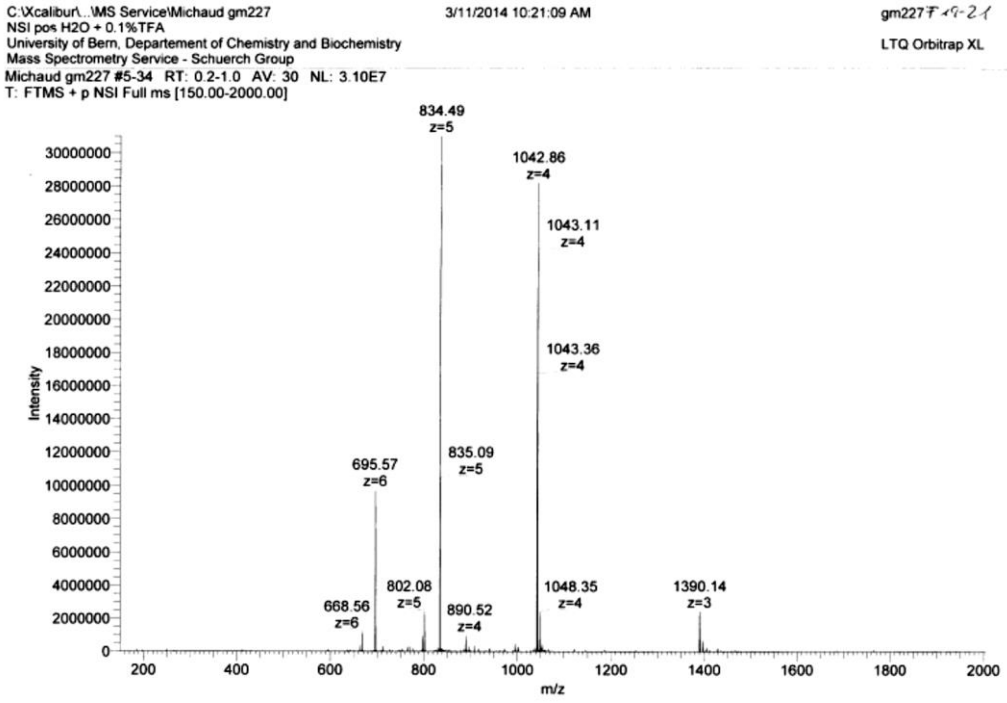


Figure S80: Analytical RP-UHPLC of **Het5G2**.



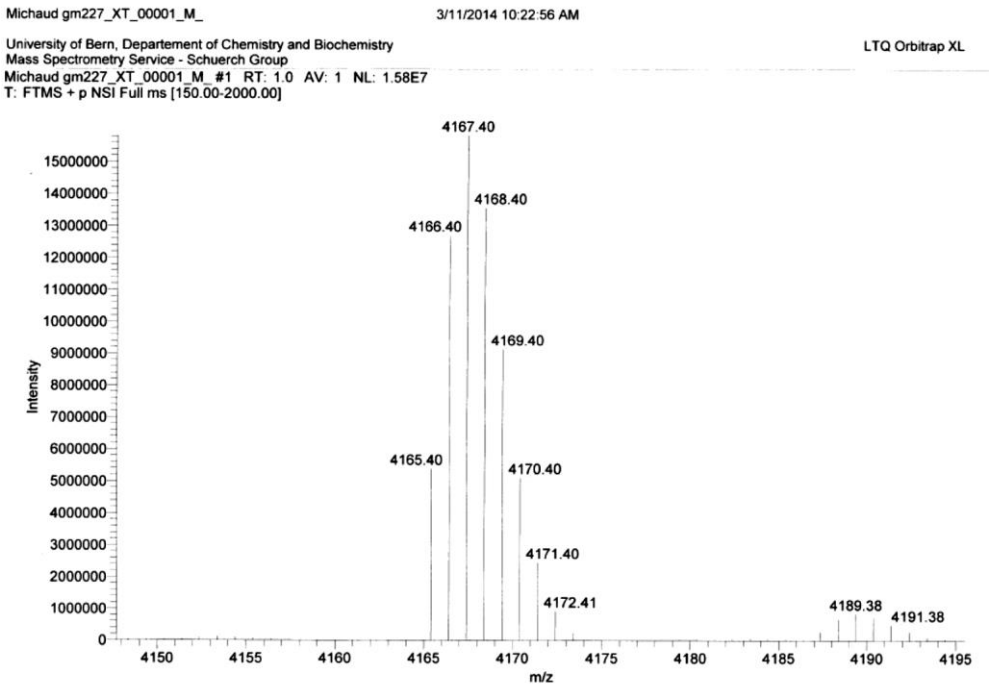
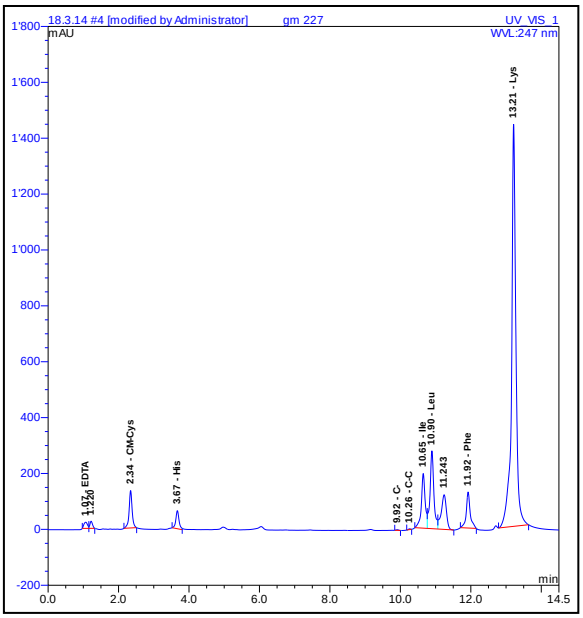


Figure S81: ESI-MS of **Het5G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,07	1,04	0,120	2,59	21,97		289,53	EDTA
2,34	2,35	0,084	13,35	133,76		1193,81	CM-Cys
3,67	3,68	0,090	6,79	64,67		553,76	His
9,92	9,98	0,081	0,18	2,13		16,77	C-
10,26	10,28	0,068	0,20	2,82		22,22	C-C
10,65	10,68	0,102	24,52	195,51		1577,64	Ile
10,90	10,93	0,102	35,29	278,41		2207,22	Leu
11,92	11,93	0,099	16,73	128,71		1147,35	Phe
13,21	13,24	0,108	206,10	1438,71		7469,14	Lys
Total:						14477,42	

Figure S82: Amino acid analysis of **Het5G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	1193.81	2	2.11
His	553.76	1	0.98
Ile	1577.64	3	2.79
Leu	2207.22	4	3.90
Phe	1147.35	2	2.03
Lys	7469.14	13	13.20

Het6G2: (GalA-KKL*K*(cFuc-KKL)FCxKI)$_2$*K*HI (7.1 mg, 1.7 µmol, 59%). MS (ESI$^+$) calc. for $C_{196}H_{329}N_{43}O_{51}S_2$ $[M+H]^+$: 4166.40, found: 4166.40.

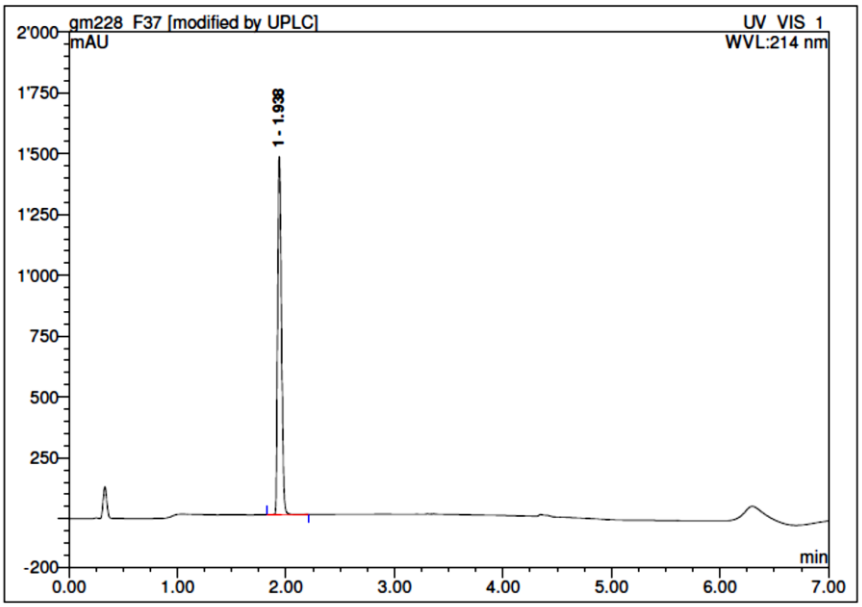


Figure S83: Analytical RP-UHPLC of **Het6G2**.

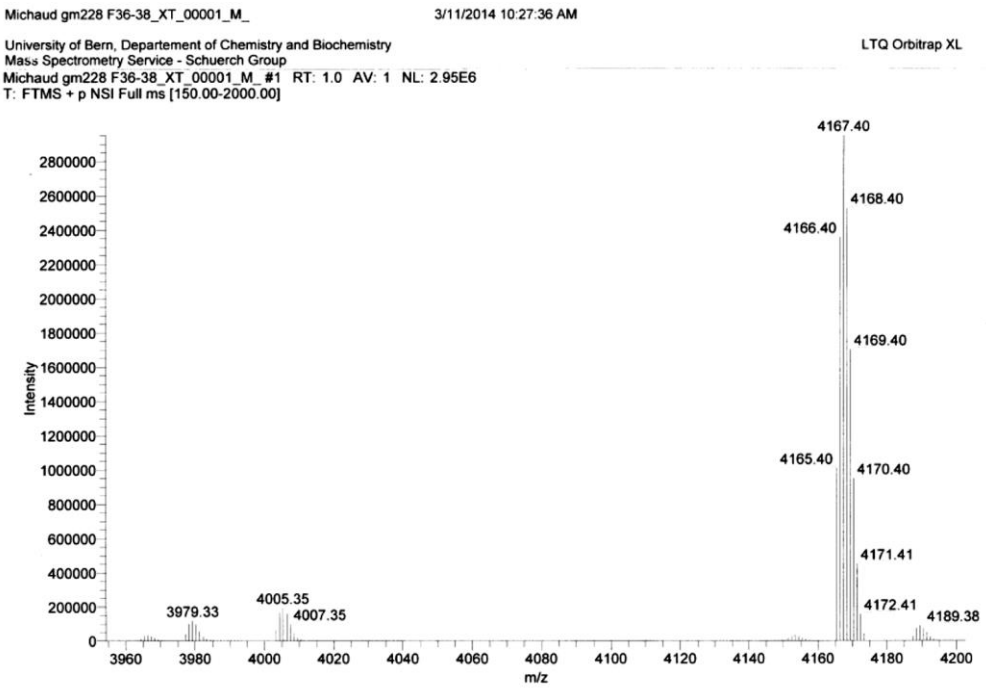
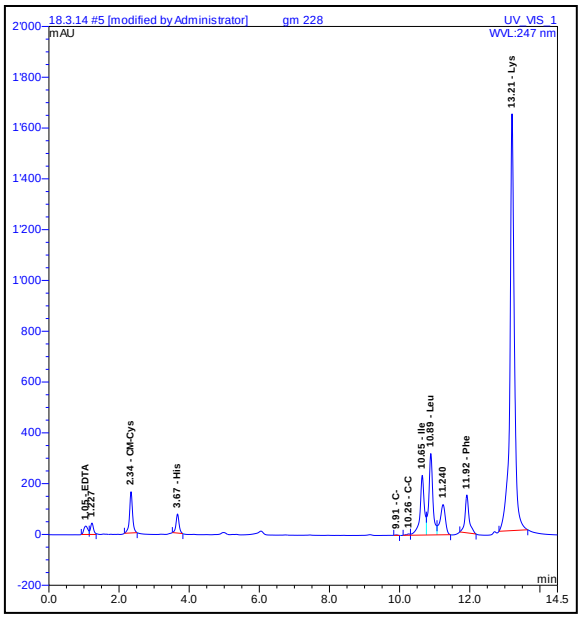


Figure S84: ESI-MS of **Het6G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,05	1,04	0,137	4,38	32,92		433,83	EDTA
2,34	2,35	0,084	16,16	162,16		1447,30	CM-Cys
3,67	3,68	0,088	7,52	75,00		642,27	His
9,91	9,98	0,082	0,15	1,85		14,59	C-
10,26	10,28	n.a.	0,63	5,11		40,22	C-C
10,65	10,68	0,110	33,19	234,81		1894,77	Ile
10,89	10,93	0,108	42,34	320,39		2540,08	Leu
11,92	11,93	0,102	19,79	148,96		1327,83	Phe
13,21	13,24	0,114	242,30	1640,57		8517,06	Lys
Total:						16857,96	

Figure S85: Amino acid analysis of **Het6G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	1447.30	2	2.21
His	642.27	1	0.98
Ile	1894.77	3	2.89
Leu	2540.08	4	3.88
Phe	1327.83	2	2.03
Lys	8517.06	13	13.01

Het7G2: (cFuc-KKL*K*(GalB-KKL)FCxKI)$_2$*K*HI (8.3 mg, 2.02 µmol, 69%). MS (ESI$^+$) calc. for $C_{188}H_{329}N_{43}O_{49}S_4$ $[M+H]^+$: 4102.36, found: 4102.36.

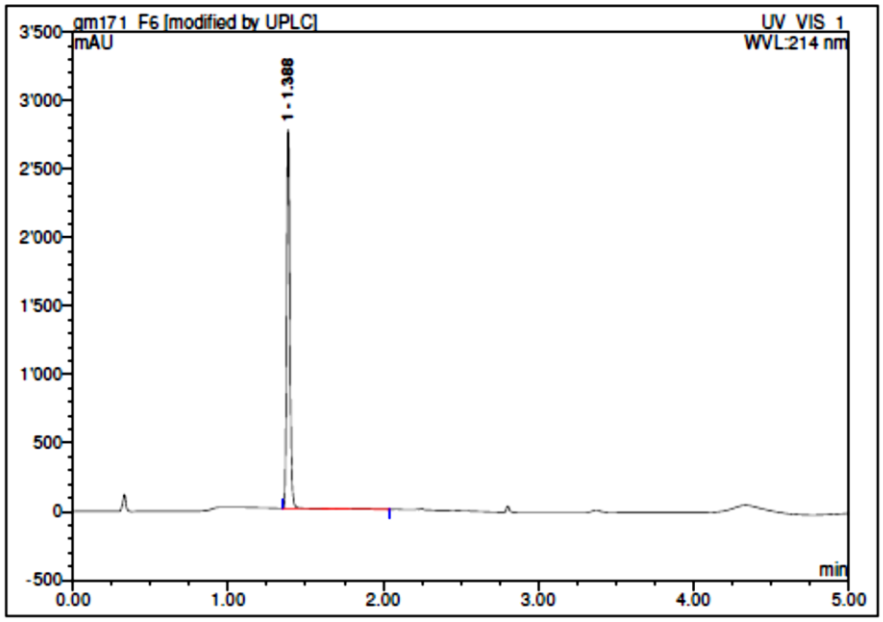


Figure S86: Analytical RP-UHPLC of **Het7G2**.

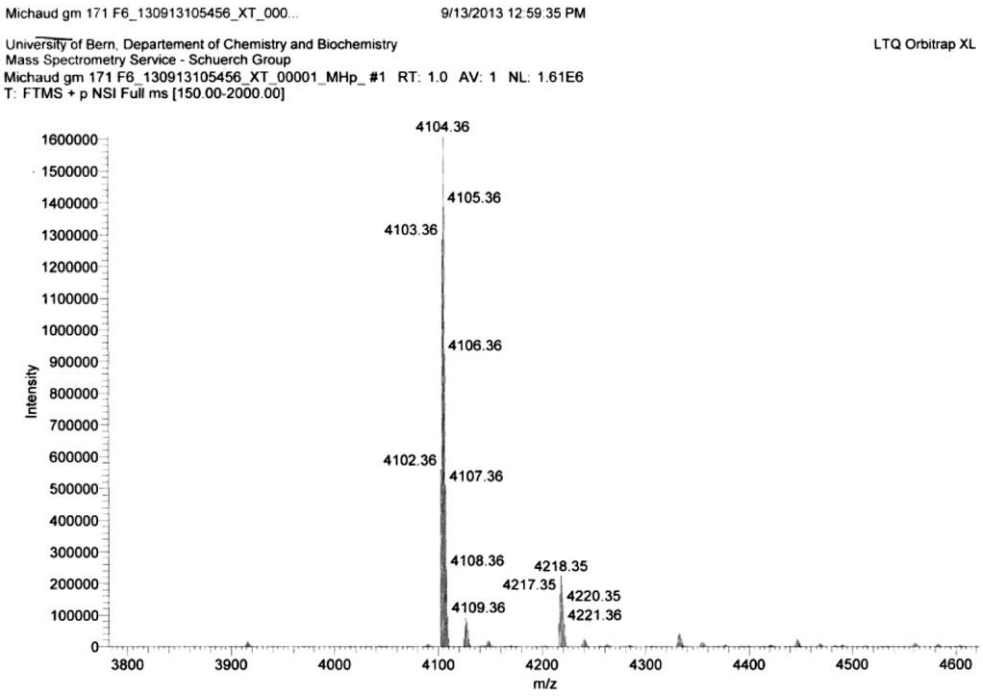
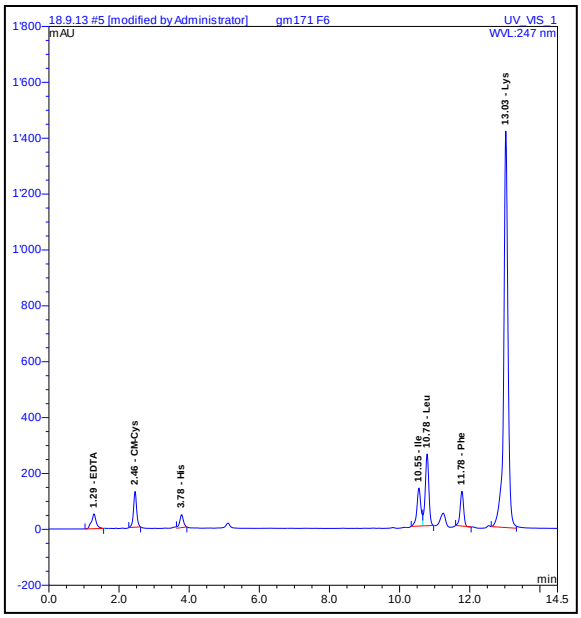


Figure S87: ESI-MS of **Het7G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,29	1,27	0,127	8,14	52,82		628,06	EDTA
2,46	2,46	0,090	13,19	128,01		934,73	CM-Cys
3,78	3,78	0,108	5,68	46,22		414,08	His
10,55	10,55	0,113	17,68	136,13		1029,19	Ile
10,78	10,79	0,107	30,56	256,76		2069,45	Leu
11,78	11,78	0,103	14,08	124,57		1028,50	Phe
13,03	13,06	0,116	199,64	1418,74		7149,46	Lys
Total:						13253,48	

Figure S88: Amino acid analysis of **Het7G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	934.73	2	1.85
His	414.08	1	0.82
Ile	1029.19	3	2.04
Leu	2069.45	4	4.10
Phe	1028.50	2	2.04
Lys	7149.46	13	14.16

Het8G2: (GalB-KKL*K*(cFuc-KKL)FCxKI)$_2$*K*HI (6.8 mg, 1.66 µmol, 57%). MS (ESI$^+$) calc. for $C_{188}H_{329}N_{43}O_{49}S_4$ $[M+H]^+$: 4102.36, found: 4102.36.

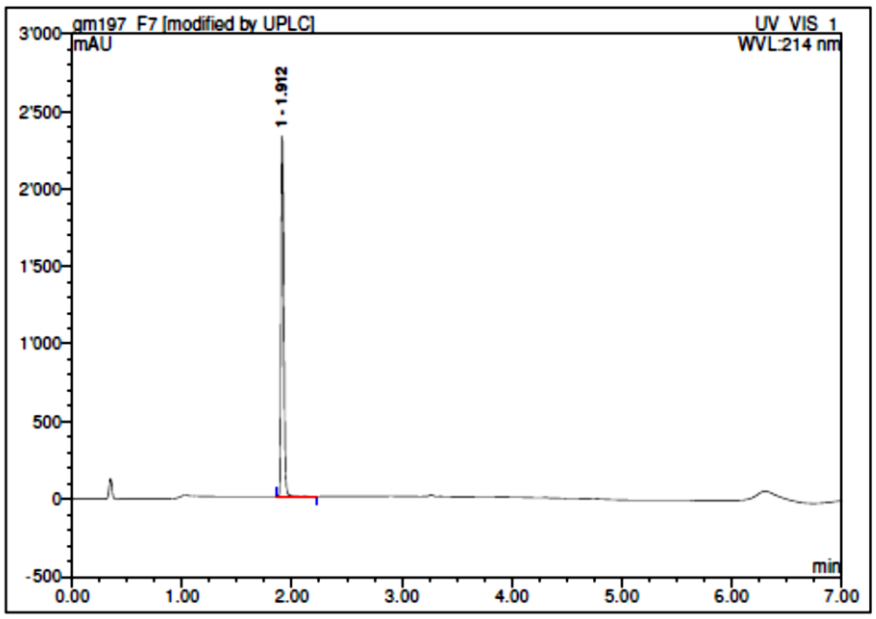


Figure S89: Analytical RP-UHPLC of **Het8G2**.

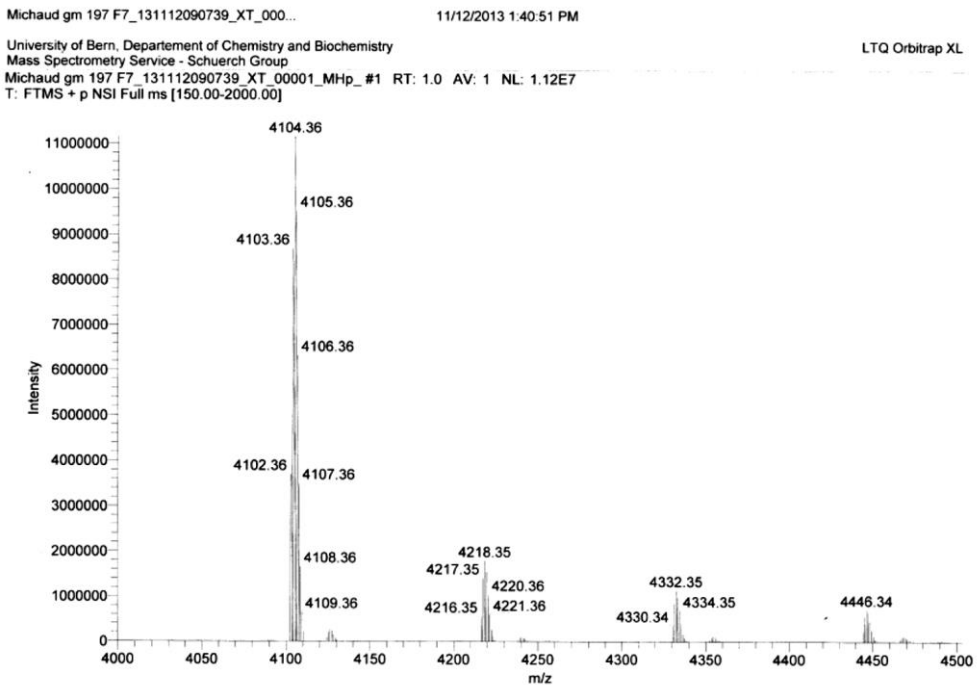
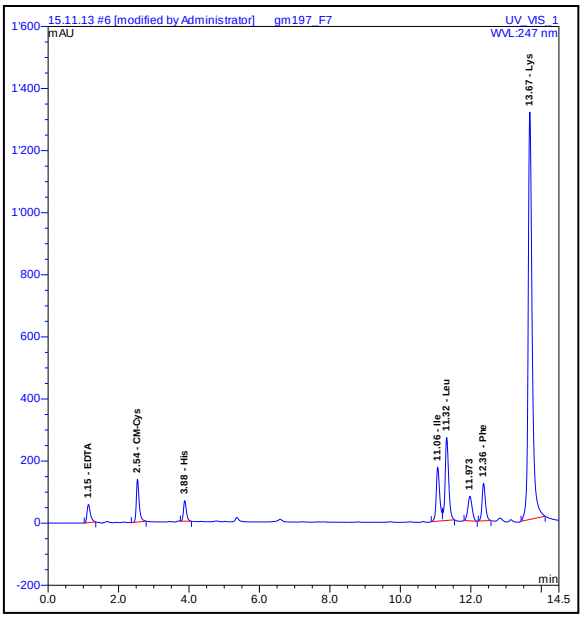


Figure S90: ESI-MS of **Het8G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,15	1,14	0,100	6,49	58,22		342,53	EDTA
2,54	2,53	0,080	12,89	137,81		921,10	CM-Cys
3,88	3,88	0,086	6,31	66,13		423,15	His
11,06	11,08	0,100	19,68	173,95		1228,49	Ile
11,32	11,34	0,101	30,86	266,82		1912,62	Leu
12,36	12,37	0,099	13,38	120,66		966,02	Phe
13,67	13,71	0,111	172,28	1312,03		6253,33	Lys
Total:						12047,24	

Figure S91: Amino acid analysis of **Het8G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	921.10	2	1.97
His	423.15	1	0.90
Ile	1228.49	3	2.62
Leu	1912.62	4	4.09
Phe	966.02	2	2.06
Lys	6253.33	13	13.36

AcG2x: (Ac-KPL)$_4$(*K*FCxKI)$_2$KHI (4.8 mg, 1.47 μmol, 50%). MS (ESI$^+$) calc. for $C_{158}H_{265}N_{39}O_{31}S_2$ $[M+H]^+$: 3269.99, found: 3270.99.

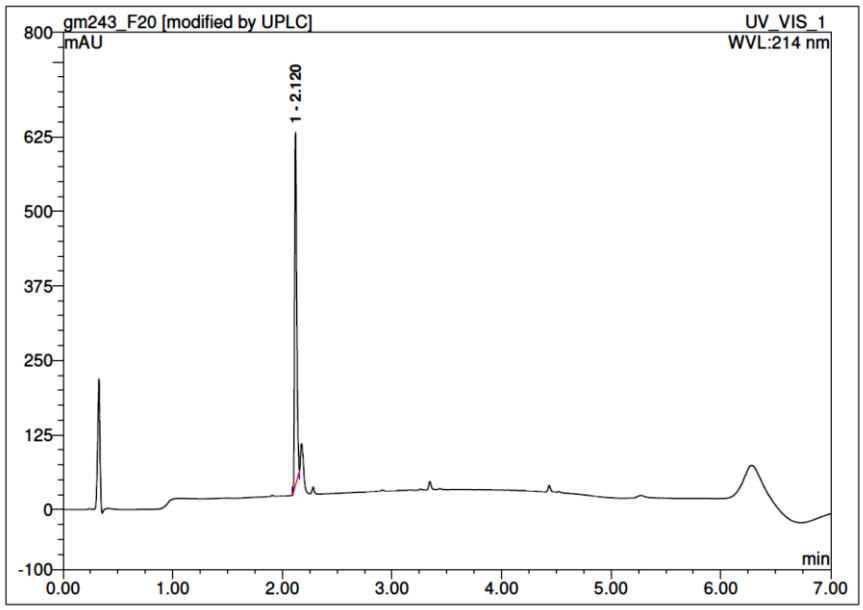


Figure S92: Analytical RP-UHPLC of **AcG2x**.

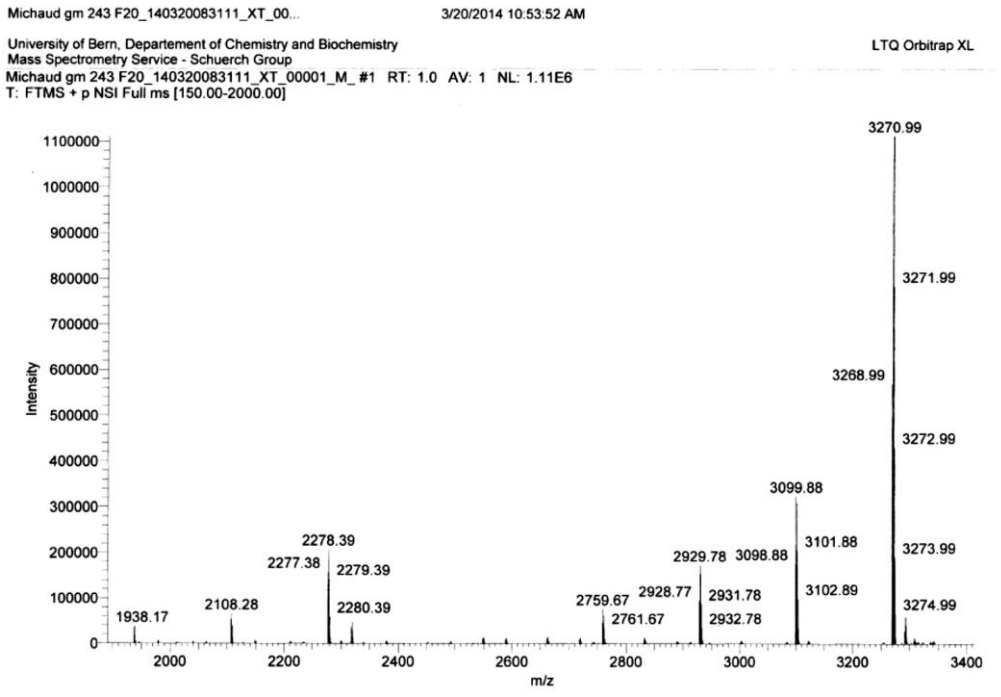
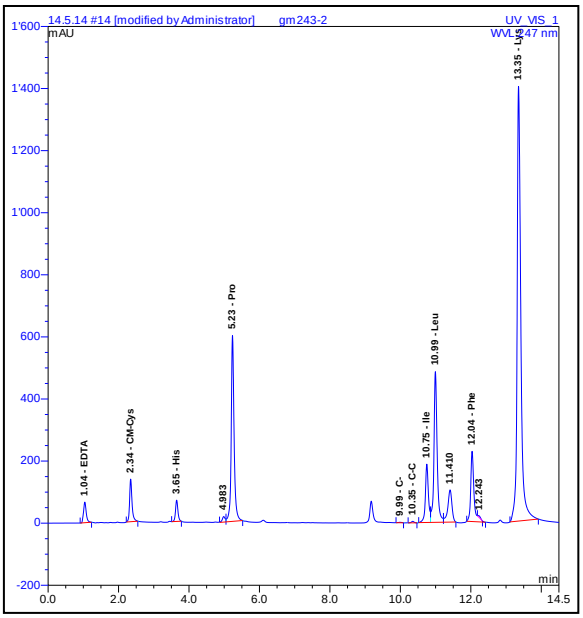


Figure S93: ESI-MS of **AcG2x**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,02	0,079	5,89	66,32		608,10	EDTA
2,34	2,34	0,067	10,97	137,15		993,05	CM-Cys
3,65	3,65	0,070	5,44	68,46		436,81	His
5,23	5,25	0,078	56,59	598,31		3461,43	Pro
9,99	10,08	0,102	0,15	1,39		8,87	C-
10,35	10,38	0,078	0,40	4,79		30,61	C-C
10,75	10,77	0,084	18,65	187,92		1255,32	Ile
10,99	11,03	0,087	51,34	485,35		3299,63	Leu
12,04	12,06	0,085	24,47	226,00		1687,57	Phe
13,35	13,40	0,101	171,22	1399,82		6026,24	Lys
Total:						17807,62	

Figure S94: Amino acid analysis of **AcG2x**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	993.1	2	1.45
His	436.8	1	0.64
Pro	3461.4	4	5.04
Ile	1255.3	3	1.83
Leu	3299.6	4	4.81
Lys	6026.2	9	8.78

AcG2xK: (Ac-KKL)$_4$(*K*FCxKI)$_2$KHI (5.9 mg, 1.74 μmol, 60%). MS (ESI$^+$) calc. for $C_{164}H_{287}N_{41}O_{31}S_2$ $[M+H]^+$: 3392.17, found: 3393.18.

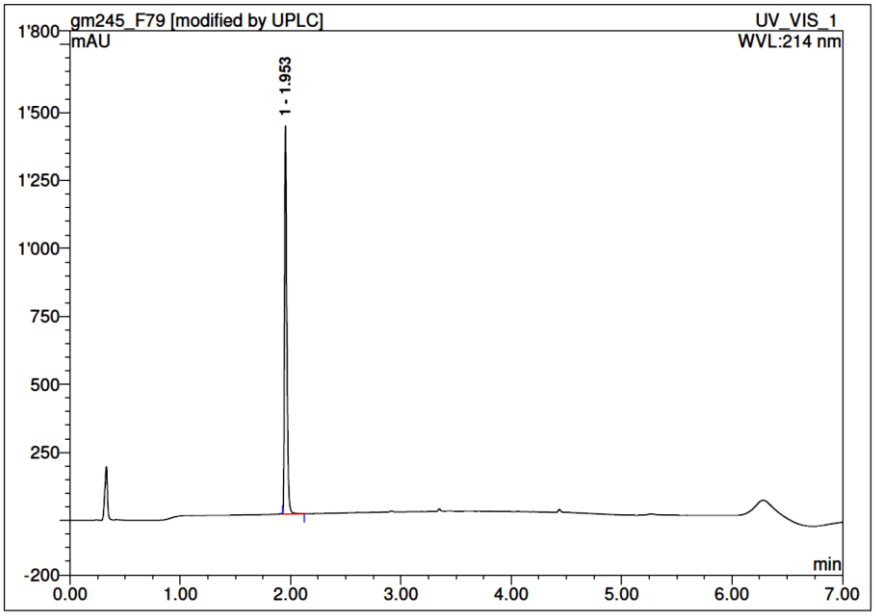


Figure S95: Analytical RP-UHPLC of **AcG2xK**.

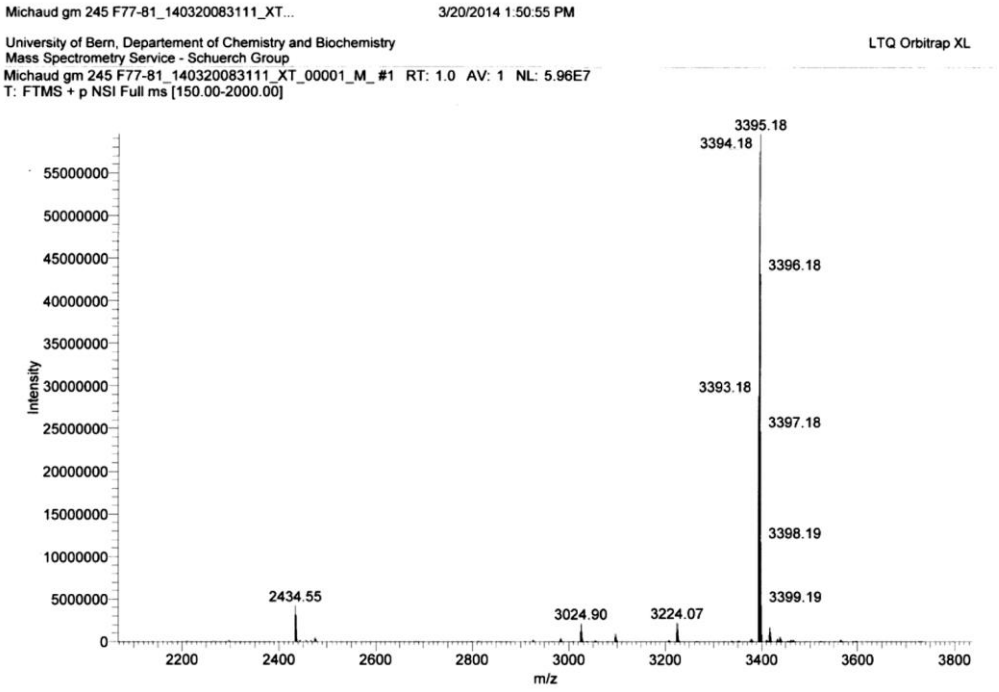
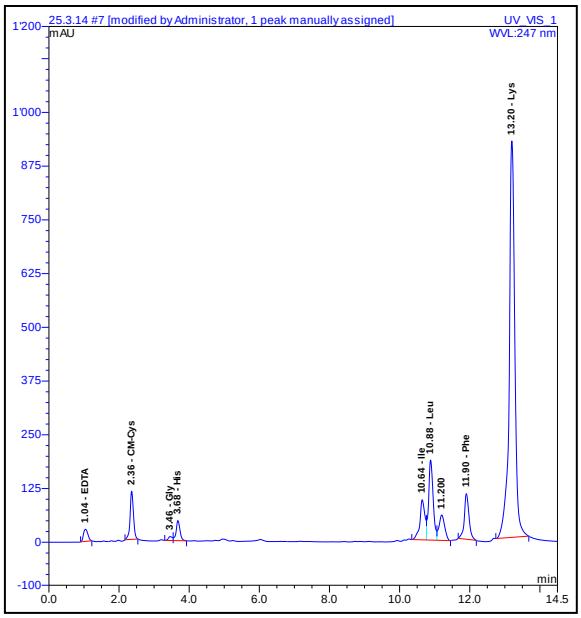


Figure S96: ESI-MS of **AcG2xK**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,04	1,04	0,143	4,10	28,07		388,67	EDTA
2,36	2,36	0,098	12,45	112,14		1175,53	CM-Cys
3,46	3,46	n.a.	1,20	9,06		91,10	Gly
3,68	3,69	0,110	5,95	46,57		479,74	His
10,64	10,70	0,164	15,62	93,23		892,76	Ile
10,88	10,94	0,133	27,90	186,19		1785,42	Leu
11,90	11,97	0,132	16,46	106,19		1152,26	Phe
13,20	13,25	0,150	171,33	922,17		6903,20	Lys
Total:						12868,68	

Figure S97: Amino acid analysis of **AcG2xK**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
CM-Cys	1175.53	2	2.38
His	479.74	1	0.97
Ile	892.8	3	1.81
Leu	1758.4	4	3.56
Phe	1152.3	2	2.33
Lys	6903.2	13	13.96

FucC$_6$G2: (FucC$_6$-KPL)$_4$(*K*KI)$_2$*K*HI (2.5 mg, 0.7 µmol, 31%). MS (ESI+) calc MS (ESI$^+$) calc for $C_{178}H_{319}N_{33}O_{45}S_4$ [M+H]$^+$: 3768.27, found: 3768.27.

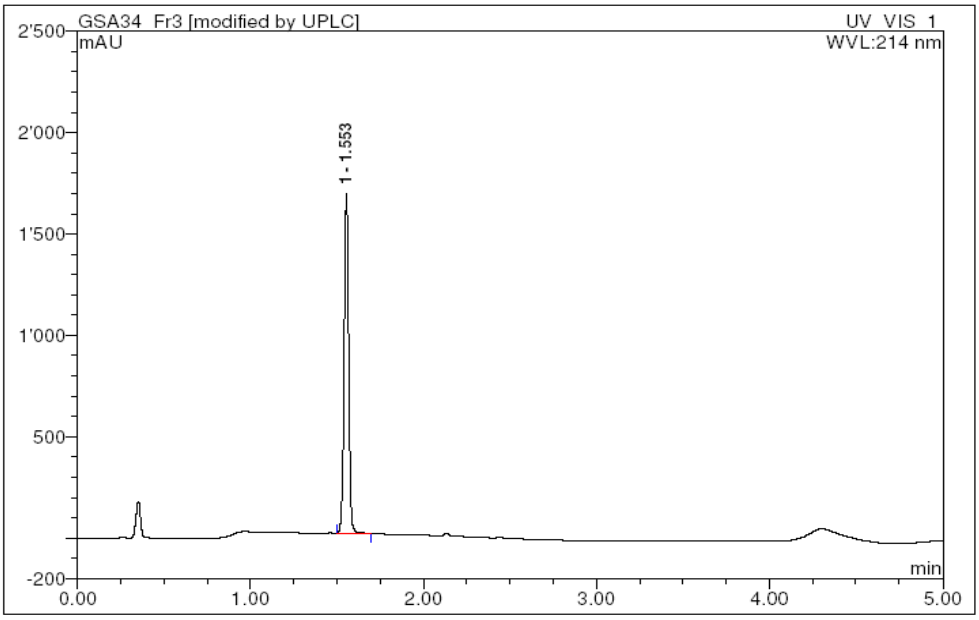


Figure S98: Analytical RP-UHPLC of **FucC$_6$G2**.

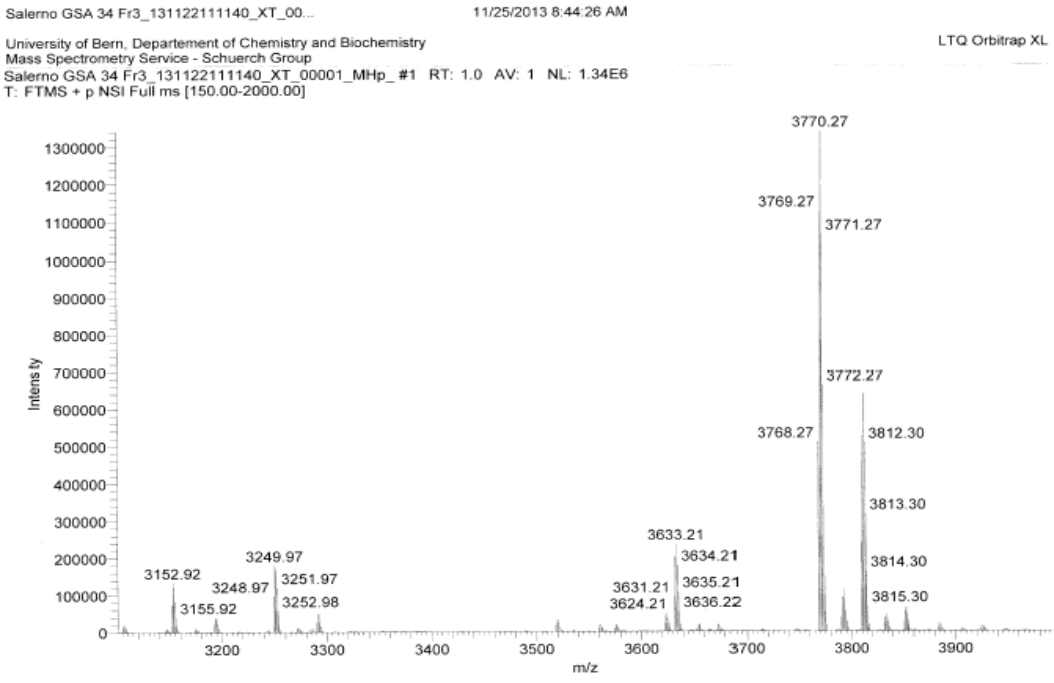
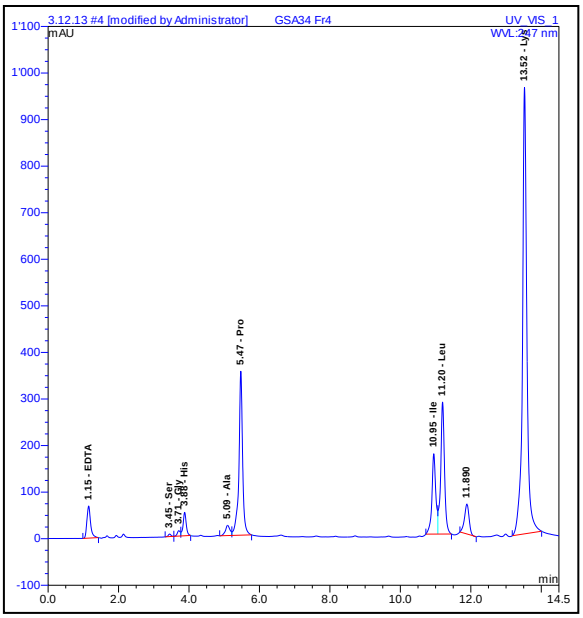


Figure S99: ESI-MS of **FucC$_6$G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1.15	1.14	0.107	8.32	68.91		456.64	EDTA
3.88	3.89	0.088	5.19	50.33		375.99	His
5.47	5.49	0.094	42.95	352.04		2371.16	Pro
10.95	10.96	0.108	22.01	172.43		1373.02	Ile
11.20	11.21	0.106	35.90	283.20		2351.26	Leu
13.52	13.53	0.113	138.82	958.41		5052.99	Lys
Total:						11981.06	

Figure S100: Amino acid analysis of **FucC_6G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
His	375.99	1	0.67
Pro	2371.16	4	4.21
Ile	1373.02	3	2.44
Leu	2351.26	4	4.18
Lys	5052.99	9	8.98

Le^{a}C$_{6}$G2: (LeA-KPL)$_4$(*K*KI)$_2$*K*HI (8 mg, 1.5 µmol, 63%). MS (ESI$^+$) calc $C_{234}H_{411}N_{37}O_{85}S_4$ $[M+H]^+$: 5228.80, found: 5228.80. $[M+H+TFA]^+$: 5342.80, found: 5342.78. $[M+H+2TFA]^+$: 5456.80, found 5457.78.

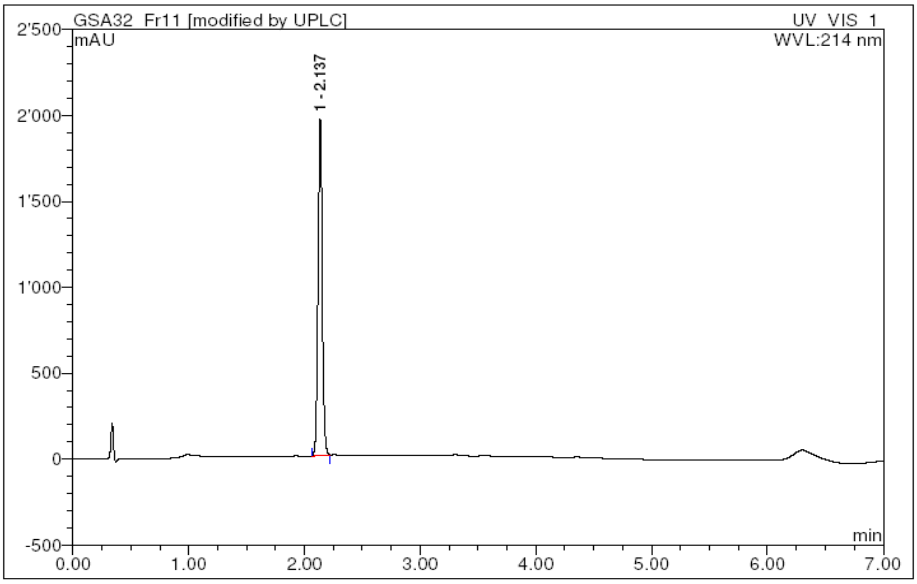


Figure S101: Analytical RP-UHPLC of **Le^{a}C$_{6}$G2**.

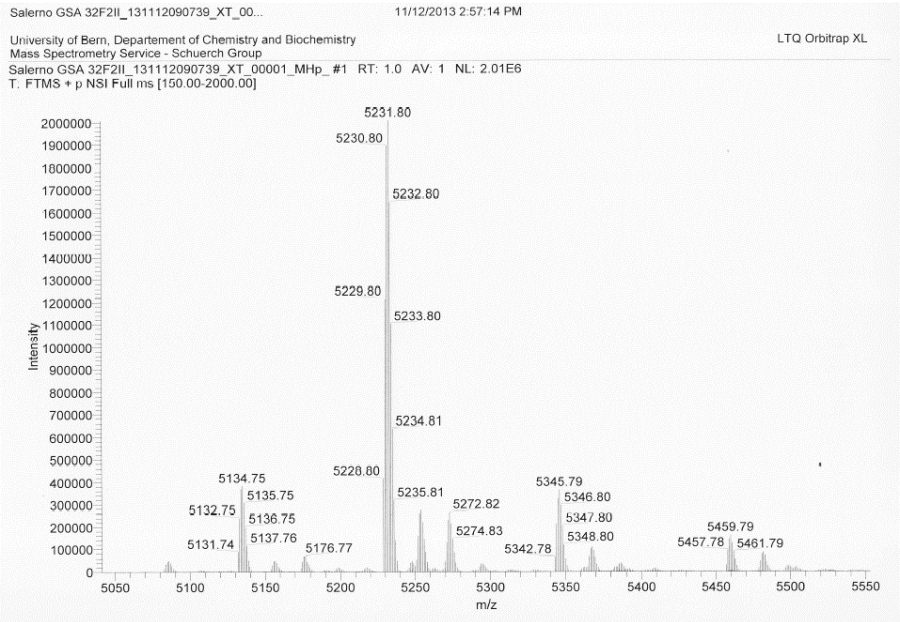
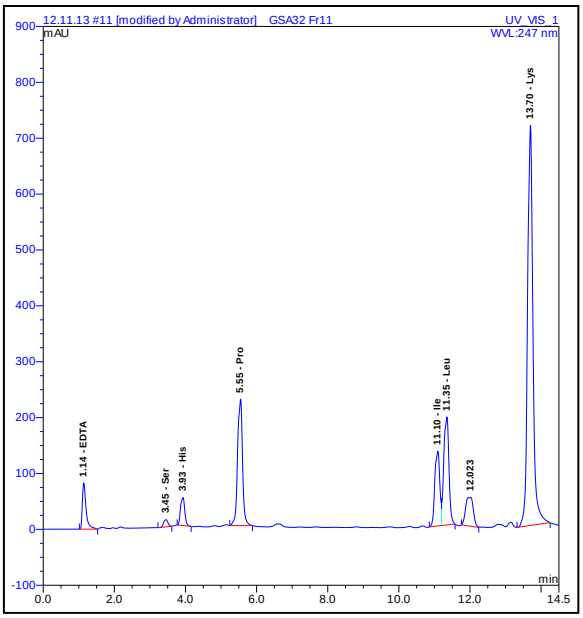


Figure S102: ESI-MS of **Le^{a}C$_{6}$G2**.



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,14	1,14	0,102	10,03	82,60		280,90	EDTA
3,45	3,47	0,137	1,80	12,85		120,80	Ser
3,93	3,92	0,132	6,89	50,16		446,88	His
5,55	5,56	0,148	36,45	226,49		1886,25	Pro
11,10	11,11	0,159	21,72	133,88		1331,08	Ile
11,35	11,37	0,161	32,56	193,29		1965,18	Leu
13,70	13,72	0,159	125,29	715,90		4658,45	Lys
Total:						10689,54	

Figure S103: Amino acid analysis of **Le^{a}C$_{6}$G2**.

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
His	446.88	1	0.90
Pro	1886.25	4	3.80
Ile	1331.08	3	2.68
Leu	1965.18	4	3.96
Lys	4658.45	9	9.38

(Het2G1-Cys)$_2$: (GalA-KPL*K*(cFuc-KPL)FC)$_2$ (1.4 mg, 0.45 µmol, 7.1%). MS (ESI$^+$) calc $C_{146}H_{228}N_{26}O_{42}S_2$ $[M+H]^+$: 3083.69, found: 3084.60 (z=1), 1028.54 (z=3), 771.66 (z=4).

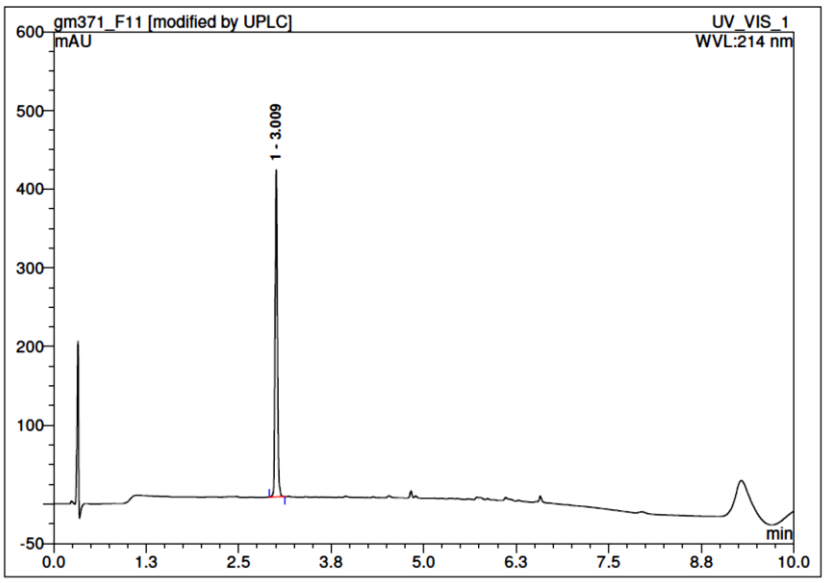


Figure S104: Analytical RP-UHPLC of **(Het2G1-Cys)$_2$.**

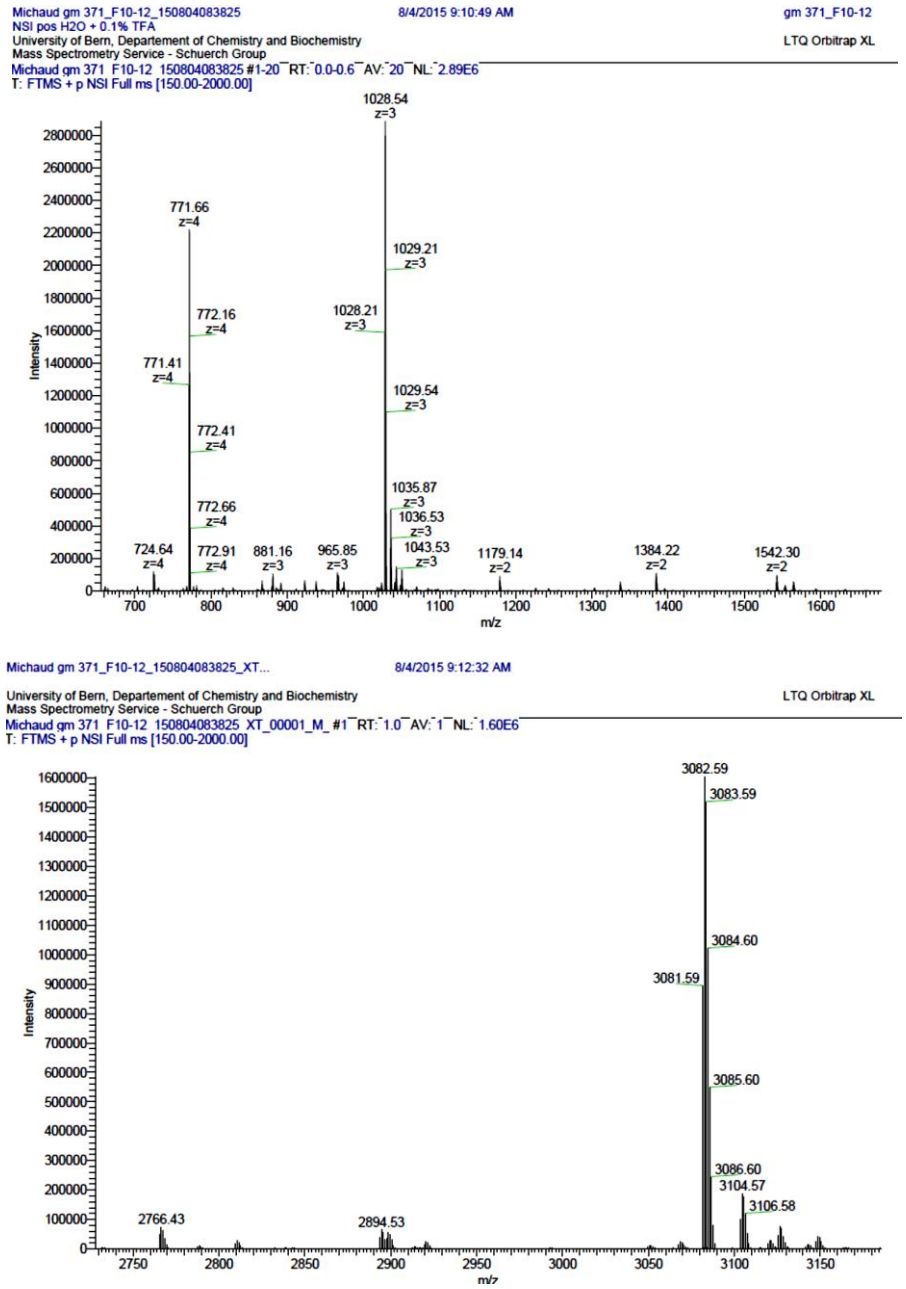
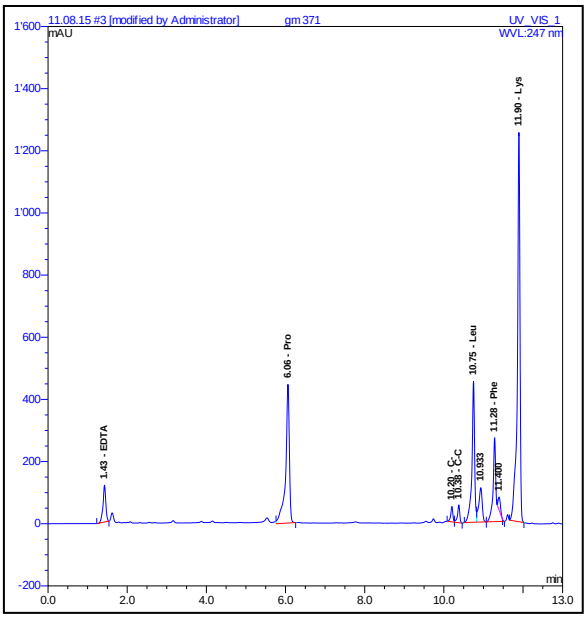


Figure S105: ESI-MS of **(Het2G1-Cys)$_2$.**



RT	RT (STD)	PW(50%)	Area	Height	n.a.	Amount	Peak Name
min	min	min	mAU*min	mAU	n.a.	pmol	
1,43	1,36	0,069	9,65	118,19		879,76	EDTA
6,06	6,08	0,079	48,75	445,90		2698,30	Pro
10,75	10,76	0,060	35,61	453,24		2153,04	Leu
11,28	11,29	0,061	25,39	269,81		1316,65	Phe
11,90	11,90	0,060	97,27	1251,95		3396,13	Lys
Total:						10443,87	

Figure S106: ESI-MS of **(Het2G1-Cys)$_2$.**

Amino Acid	Amount pmol	Quantity Calc	Quantity obs
Pro	2698.30	4	4.51
Ile	2153.04	4	3.60
Phe	1316.65	2	2.20
Lys	3396.13	6	5.68

3. Isothermal Titration Calorimetry (ITC)

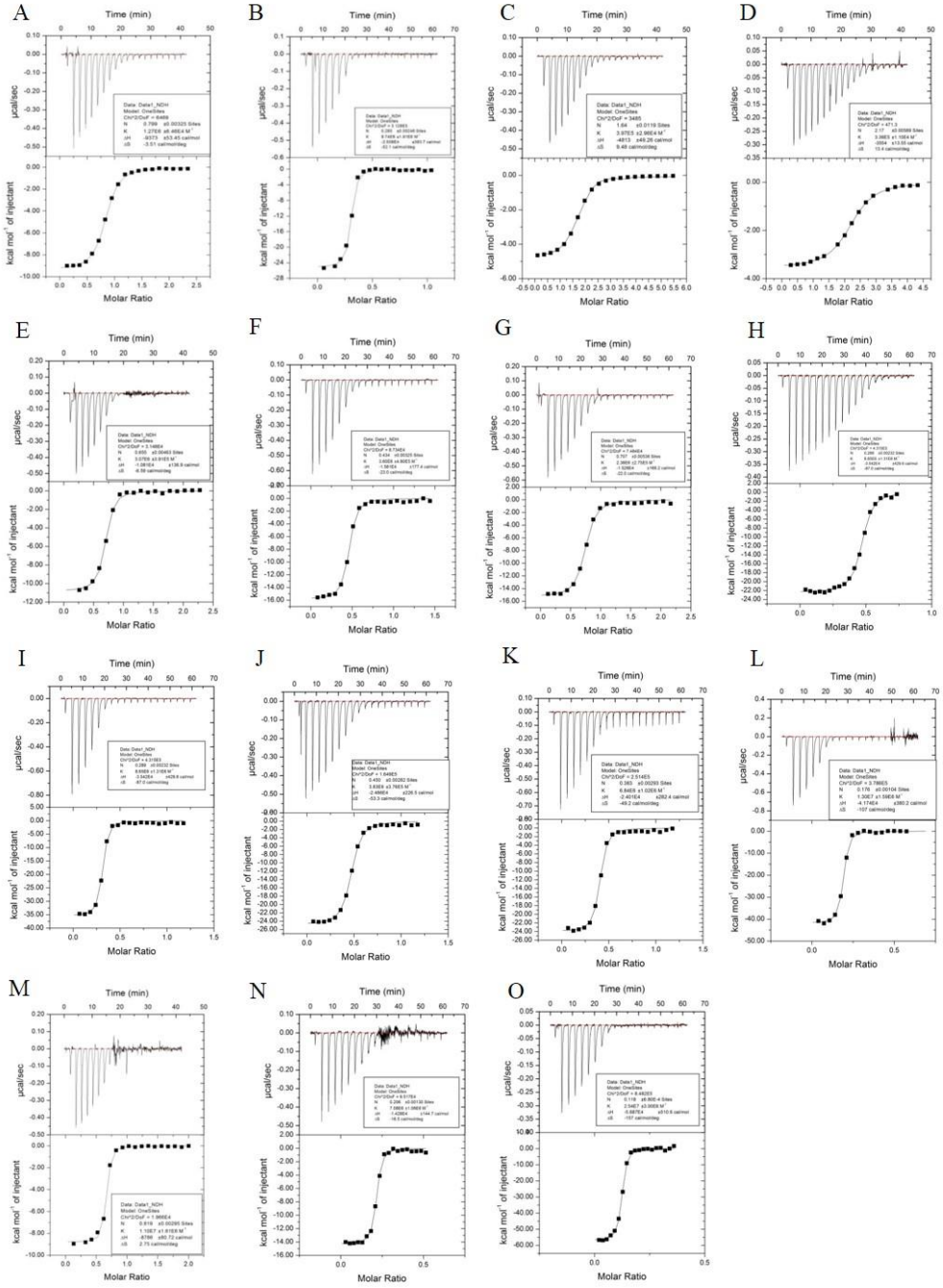


Figure S107: Thermodynamic parameters and dissociation constants K_D are reported as an average of two independent runs from ITC in 20 mM Tris, 100 mM NaCl, 100 µM $CaCl_2$, pH=7.5. Isothermal Titration Calorimetry (ITC) data are for LecB binding. Titration concentrations for Ligand/LecB are indicated in brackets: A) **FD0** (0.5 mM/0.044 mM); B) **FD1** (0.25 mM/0.0496 mM); C), **Het1G1** (0.0457 mM/0.5 mM), D) **Het2G1** (0.0497 mM/0.95 mM); E) **FD1-Cys** (0.0497 mM/0.5 mM); F) **Het1G2** (0.42 mM/0.042 mM); G) **Het2G2** (0.42 mM/0.042 mM); H) **Het3G2** (0.15 mM/0.042 mM); I) **Het4G2** (0.24 mM/0.042 mM); J) **Het7G2** (0.24 mM/0.042 mM); K) **Het8G2** (0.24 mM/0.042 mM); L) **FD2** (0.1 mM/0.028 mM); M) **FD2x** (0.052 mM/0.5 mM); N) **FucC_6G2** (0.3 mM/0.08 mM); O) **Le^aC_6G2** (0.07 mM/0.042 mM).

Determination of thermodynamic parameters and binding constants for the interaction of glycopeptide dendrimers with LecA.

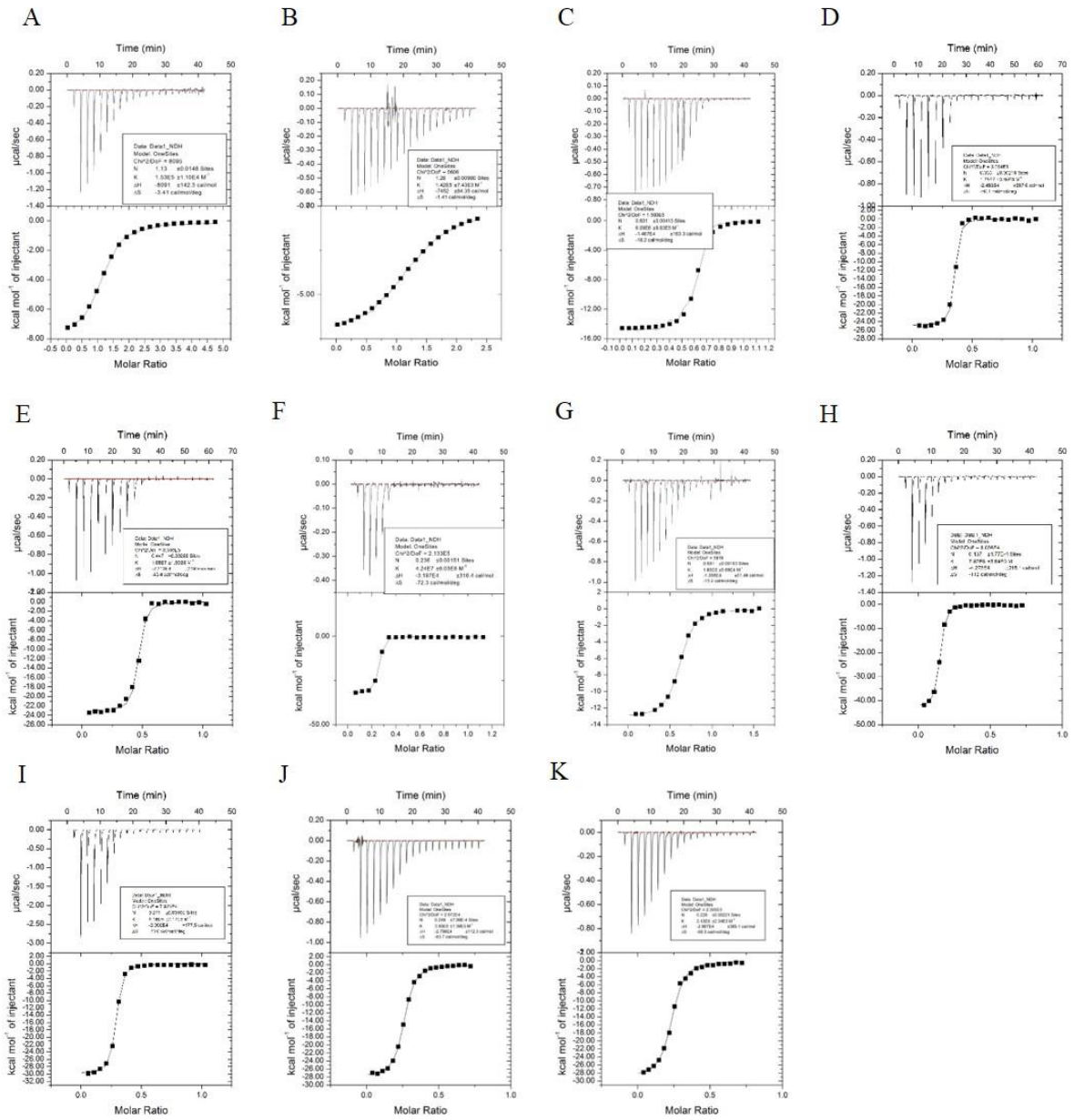


Figure S108: Thermodynamic parameters and dissociation constants K_D are reported as an average of two independent runs from ITC in 20 mM Tris, 100 mM NaCl, 100 µM $CaCl_2$, pH=7.5. Isothermal Titration Calorimetry (ITC) data are for LecA binding. Titration concentrations for Ligand/LecB are indicated in brackets: A) **Het1G1** (1.2 mM/0.051 mM); B) **Het2G1** (0.57 mM/0.05 mM); C) **GalAG1-Cys** (0.255 mM/0.05 mM); D) **Het1G2** (0.25 mM/0.05 mM); E) **Het2G2** (0.25 mM/0.05 mM); F) **GalAG2x** (0.0909 mM/0.0166 mM); G) **GalBG1-Cys** (0.4 mM/0.0526 mM); H) **Het3G2** (0.5 mM/0.1 mM); I) **Het4G2** (0.1 mM/0.05 mM); J) **Het7G2** (0.175 mM/0.05 mM); K) **Het8G2** (0.175 mM/0.05 mM)

4. Biofilm Inhibition and Dispersal assays

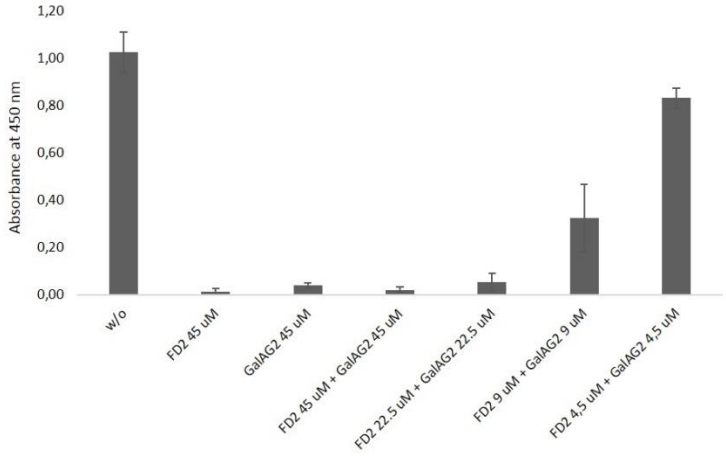


Figure S109: Inhibition of *Pseudomonas aeruginosa* strain PA01 biofilms by using **FD2** and **GalAG2** simultaneously. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the presence of the indicated amount of glycopeptide dendrimers. Viable biofilms were stained with WST-8/PES. Wells incubated without compound (w/o), background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. Data are mean ± SD.

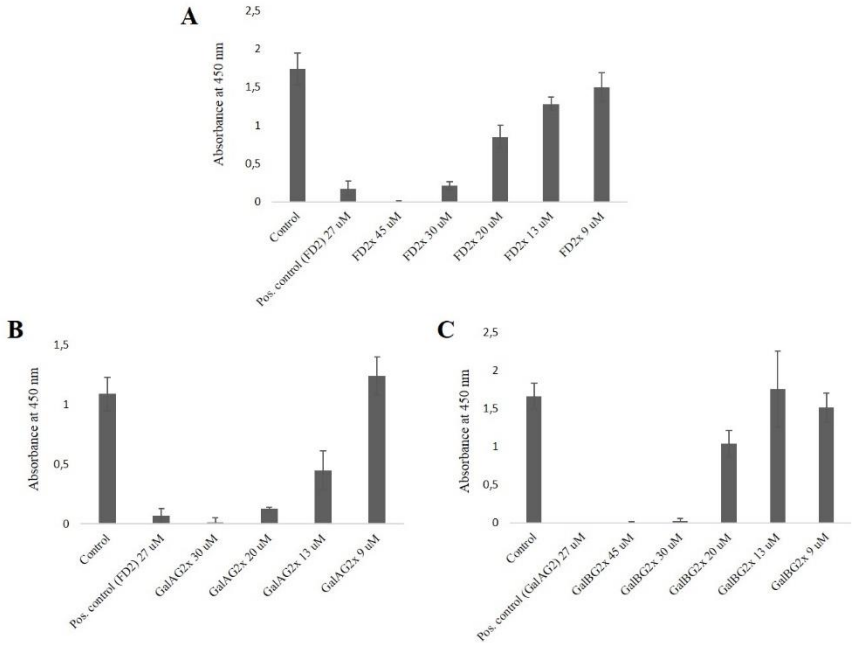


Figure S110: Inhibition of *Pseudomonas aeruginosa* strain PA01 biofilms by glycopeptide dendrimers. A) **FD2x**, B) **GalAG2x**, C) **GalBG2x**. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the presence of the indicated amount of glycopeptide dendrimers. Viable biofilms were stained with WST-8/PES. Wells incubated without compound (w/o), 27 µM **FD2** (positive control) and background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. The minimum inhibition concentration (MBIC) is defined as the lowest concentration causing complete biofilm inhibition. Data are mean ± SD.

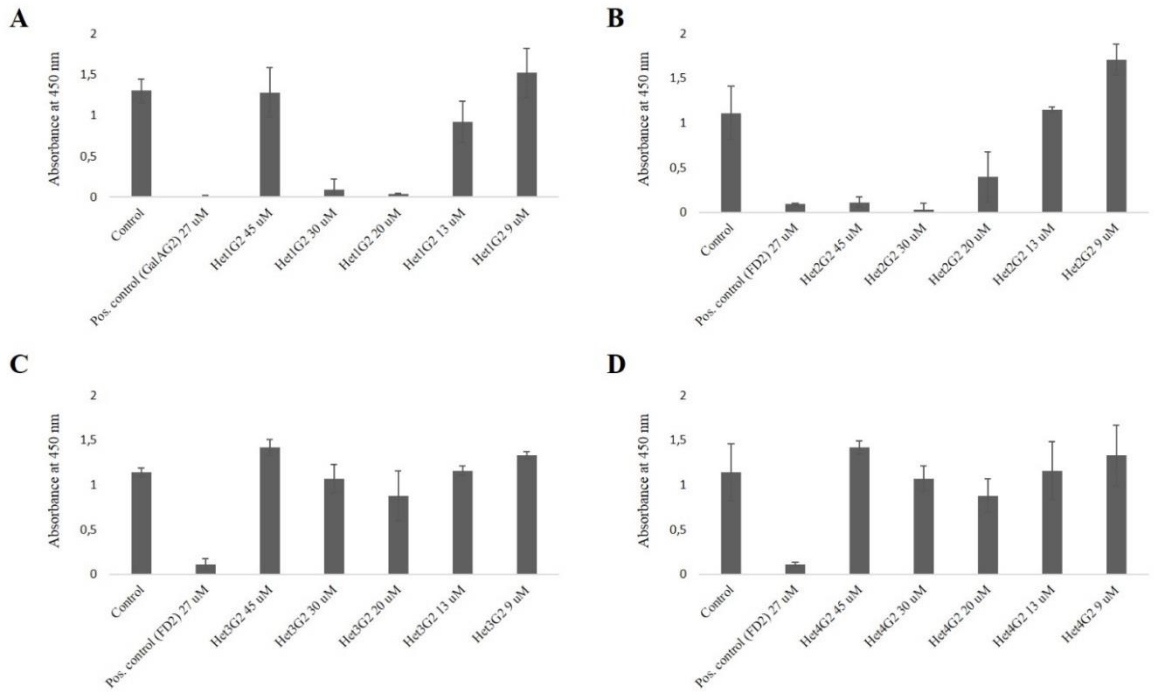


Figure S111: Inhibition of *Pseudomonas aeruginosa* strain PA01 biofilms by glycopeptide dendrimers. A) Het1G2, B) Het2G2, C) Het3G2, D) Het4G2. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the presence of the indicated amount of glycopeptide dendrimers. Viable biofilms were stained with WST-8/PES. Wells incubated without compound (w/o), 27 µM FD2 (positive control) and background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. The minimum inhibition concentration (MBIC) is defined as the lowest concentration causing complete biofilm inhibition. Data are mean ± SD.

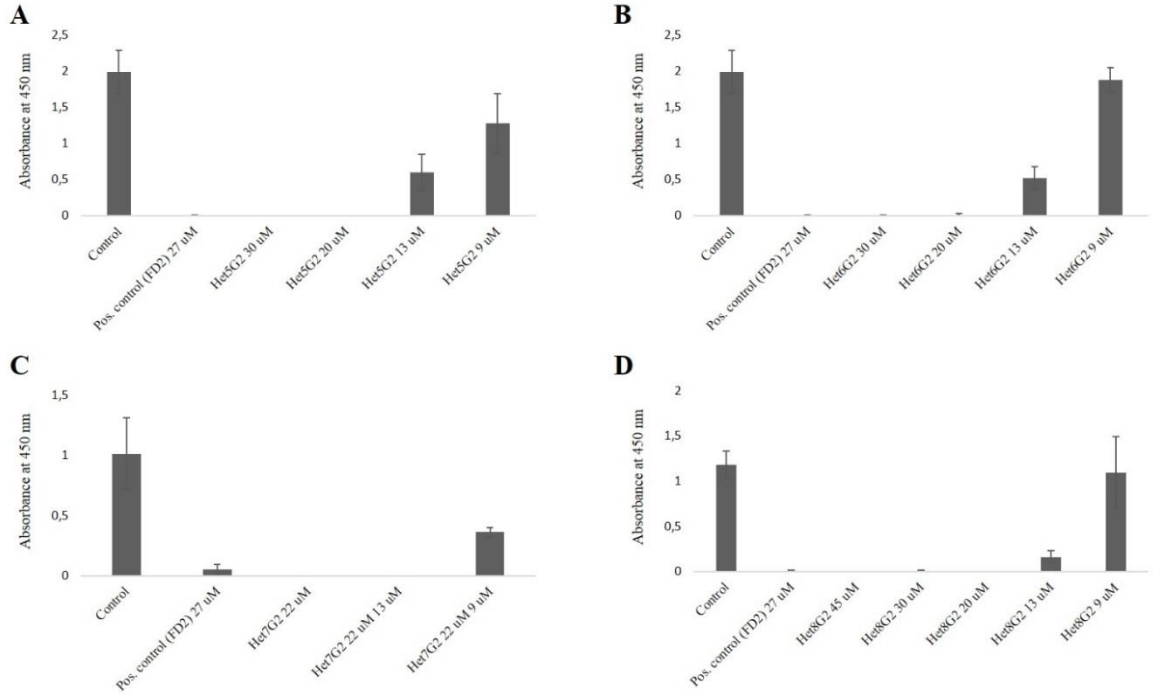


Figure S112: Inhibition of *Pseudomonas aeruginosa* strain PA01 biofilms by glycopeptide dendrimers. A) **Het5G2**, B) **Het6G2**, C) **Het7G2**, D) **Het8G2**. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the presence of the indicated amount of glycopeptide dendrimers. Viable biofilms were stained with WST-8/PES. Wells incubated without compound (w/o), 27 µM **FD2** (positive control) and background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. The minimum inhibition concentration (MBIC) is defined as the lowest concentration causing complete biofilm inhibition. Data are mean ± SD.

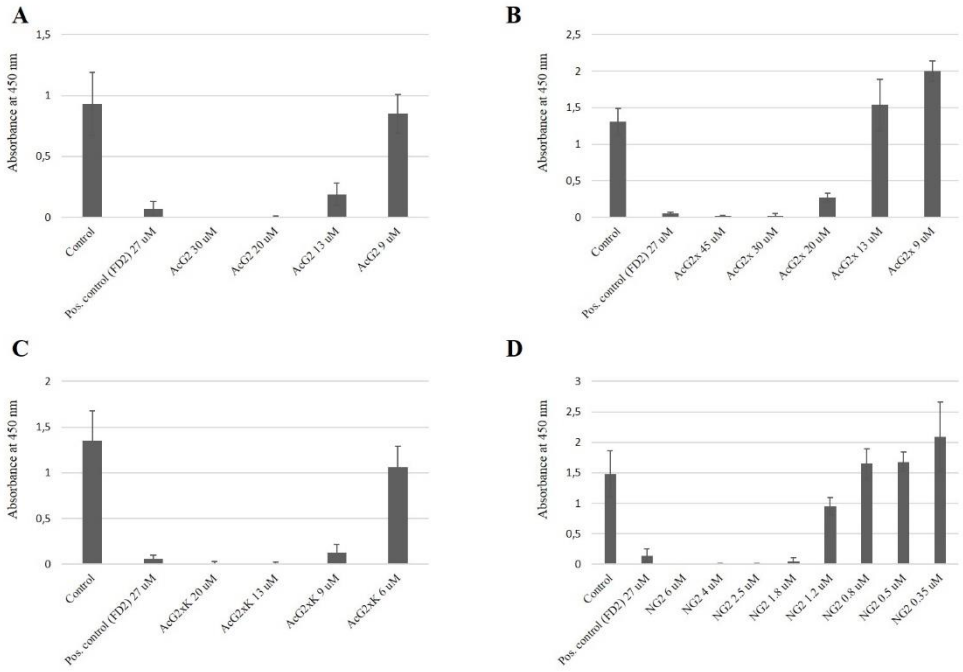


Figure S113: Inhibition of *Pseudomonas aeruginosa* strain PA01 biofilms by glycopeptide dendrimers. A) **AcG2**, B) **AcG2x**, C) **AcG2xK**, D) **NG2**. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the presence of the indicated amount of glycopeptide dendrimers. Viable biofilms were stained with WST-8/PES. Wells incubated without compound (w/o), 27 µM **FD2** (positive control) and background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. The minimum inhibition concentration (MBIC) is defined as the lowest concentration causing complete biofilm inhibition. Data are mean ± SD.

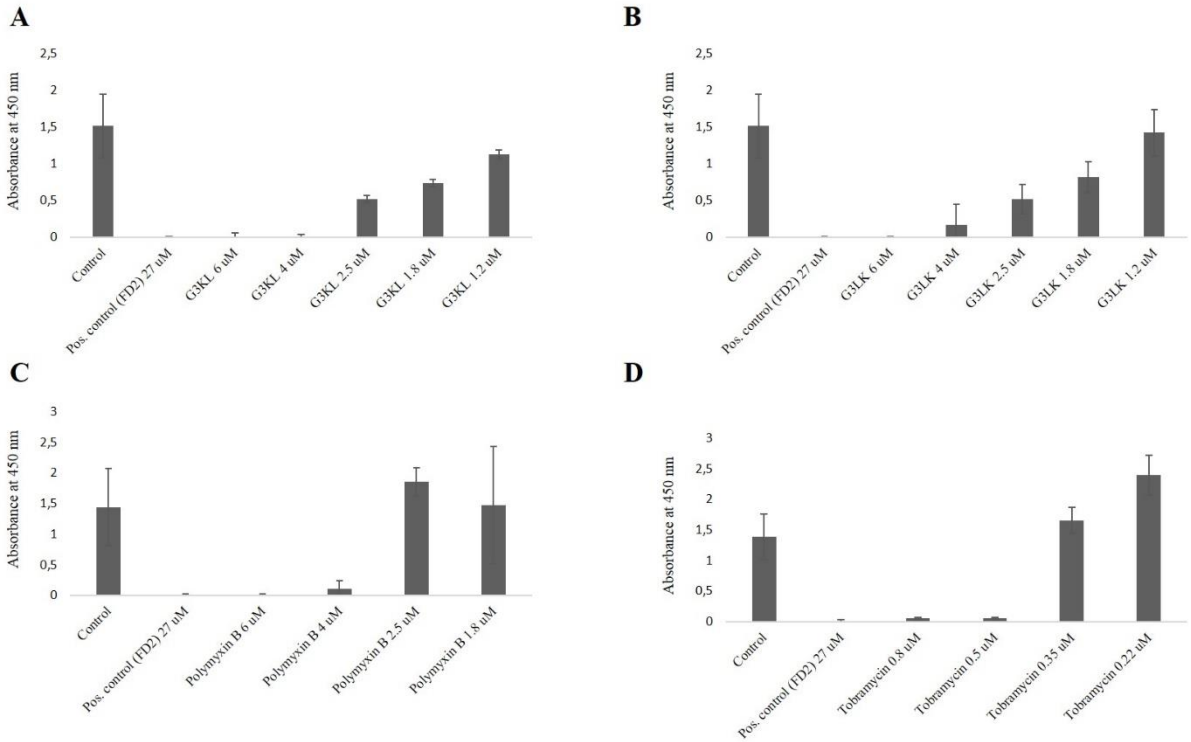


Figure S114: Inhibition of *Pseudomonas aeruginosa* strain PA01 biofilms by glycopeptide dendrimers. A) **G3KL**, B) **G3LK**, C) **Polymyxin B**, D) **Tobramycin**. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the presence of the indicated amount of glycopeptide dendrimers. Viable biofilms were stained with WST-8/PES. Wells incubated without compound (w/o), 27 µM **FD2** (positive control) and background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. The minimum inhibition concentration (MBIC) is defined as the lowest concentration causing complete biofilm inhibition. Data are mean ± SD.

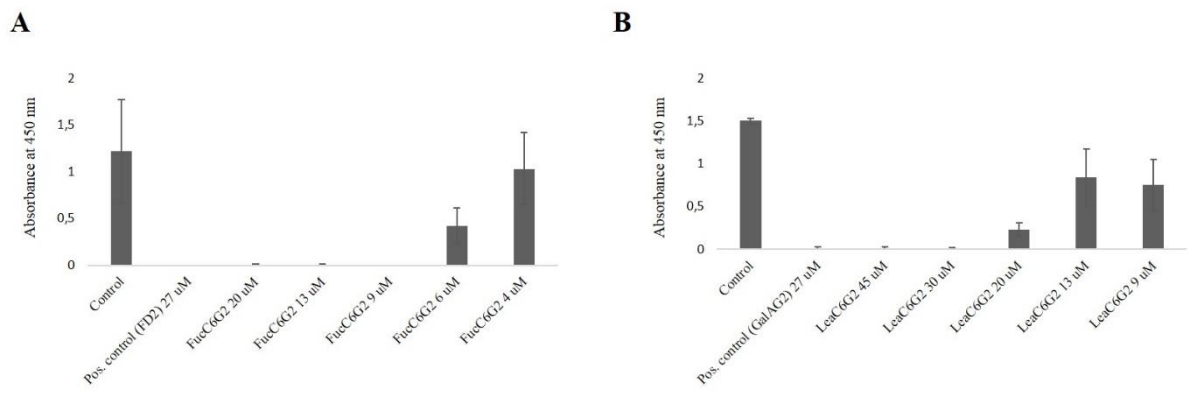


Figure S115: Inhibition of *Pseudomonas aeruginosa* strain PA01 biofilms by glycopeptide dendrimers. A) **FucC_6G2**, B) **Le^aC_6G2**. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the presence of the indicated amount of glycopeptide dendrimers. Viable biofilms were stained with WST-8/PES. Wells incubated without compound (w/o), 27 µM **FD2** (positive control) and background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. The minimum inhibition concentration (MBIC) is defined as the lowest concentration causing complete biofilm inhibition. Data are mean ± SD.

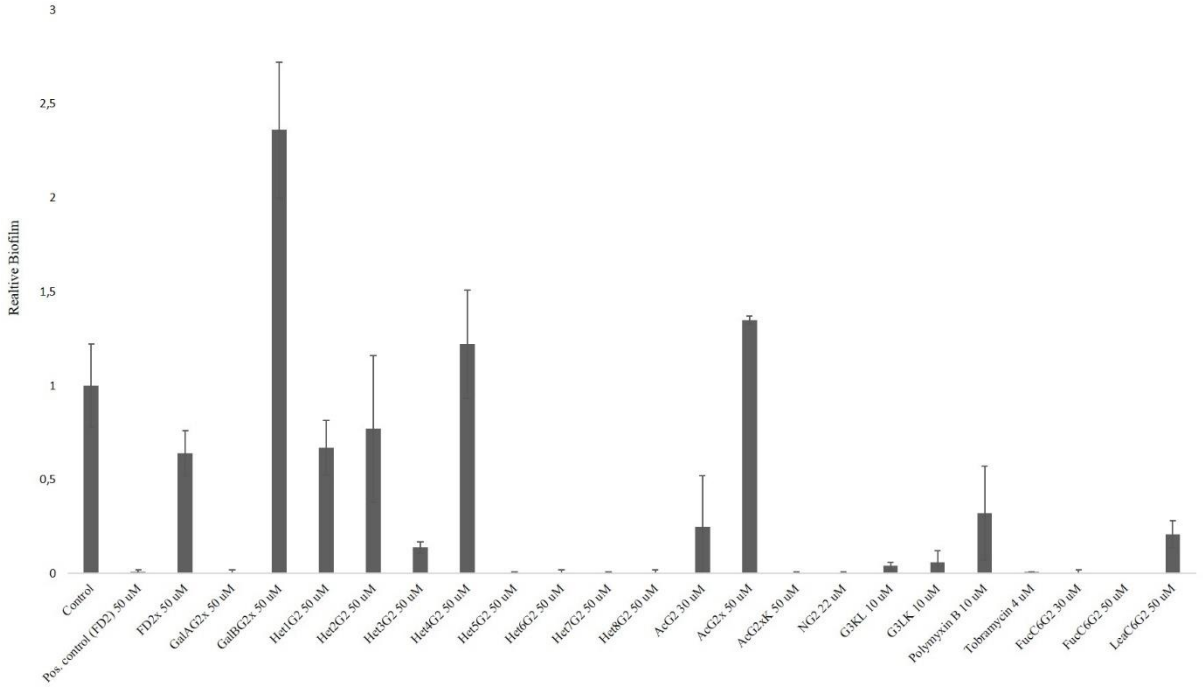


Figure S116: Dispersal of *Pseudomonas aeruginosa* strain PA01 biofilms. Biofilms were grown on microtiter plates inoculated with PA01 for 24 hours at 37°C in the absence of any compounds. Planktonic bacteria were removed and the biofilms were incubated with glycopeptide dendrimers for another 24 hours. Viable biofilms were stained with WST-8/PES and quantified by measuring absorbance at 450 nm. The "relative biofilm" is the relative absorbance value compared to control. Wells incubated without compound (w/o), 50 µM **FD2** (positive control) and background absorbance (growth media without bacteria) were used as the corresponding controls. All measurements were performed in triplicates. The control was set up to a value of 1. Dispersal efficiency of the compounds was calculated in relation to the control. Data are mean ± SD.

5. Broth Microdilution Assays

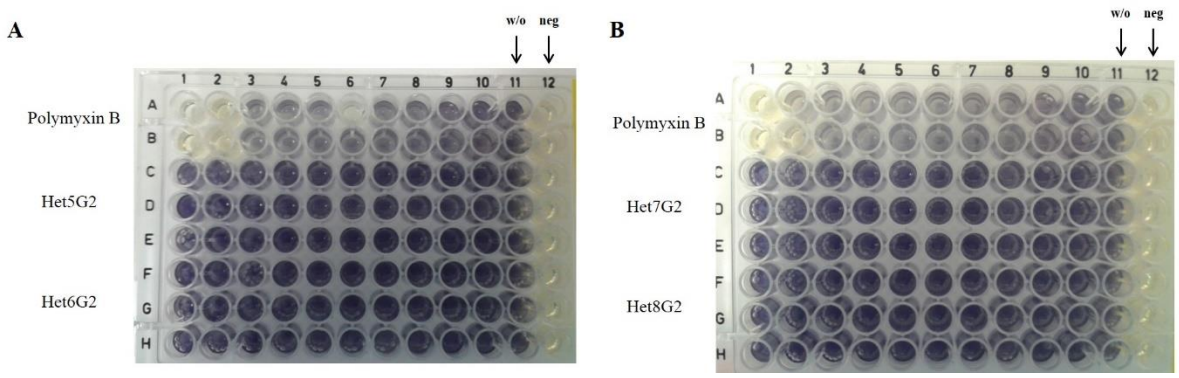


Figure S117: Broth Microdilution Method to determine the MIC values of A) **Het5G2** (raw C-E) and **Het6G2** (raw F-H), B) **Het7G2** (raw C-E) and **Het8G2** (raw F-H); 2-fold dilution series starting from 64 µM (left side). **Polymyxin B** (dilution starting from 64 µg/mL) was used as a reference (raw A-B). Raw 11 is used as growing control without compound (w/o) and raw 12 is used as a negative. All measurements were performed in triplicates.

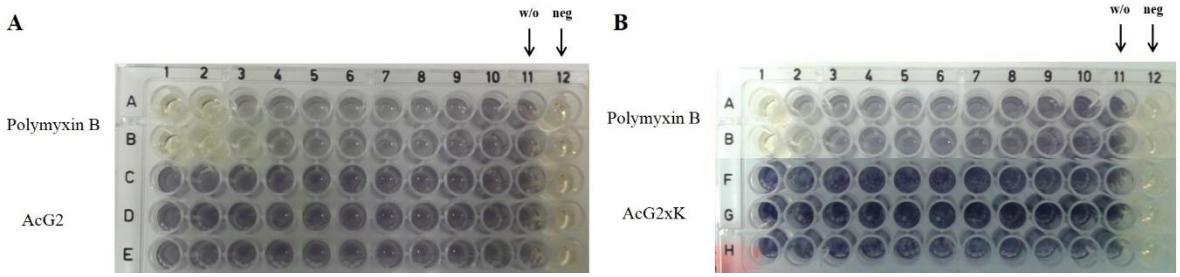


Figure S118: Broth Microdilution Method to determine the MIC values of A) **AcG2** (raw C-E), B) **AcG2xK** (raw F-G); 2-fold dilution series starting from 64 µM (left side). **Polymyxin B** (dilution starting from 64 µg/mL) was used as a reference (raw A-B). Raw 11 is used as growing control without compound (w/o) and raw 12 is used as a negative. All measurements were performed in triplicates.

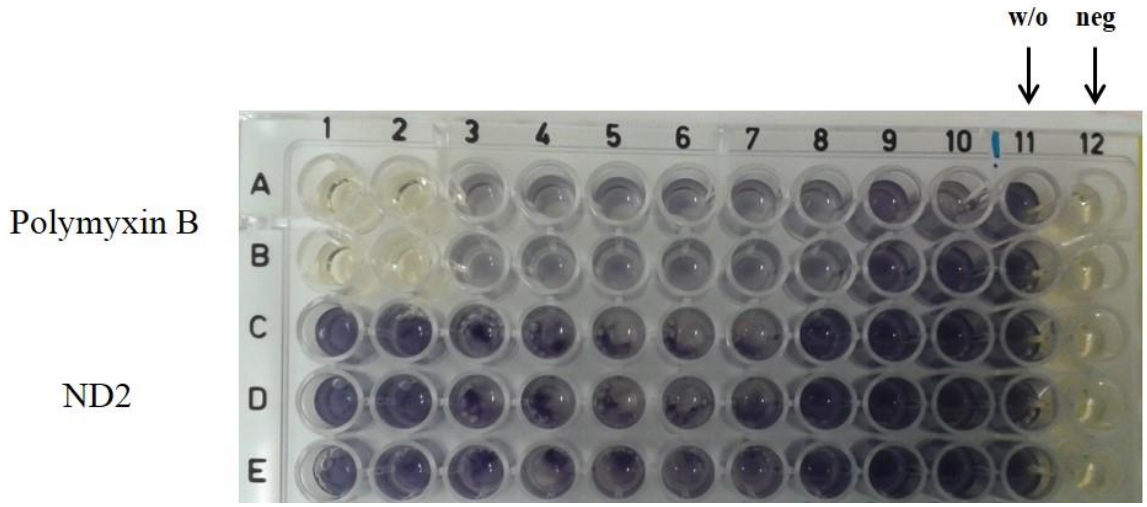


Figure S119: Broth Microdilution Method to determine the MIC values of **ND2** (raw C-E); dilution starting from 64 µM (left side). **Polymyxin B** (dilution starting from 64 µg/mL) was used as a reference (raw A-B). Raw 11 is used as growing control without compound (w/o) and raw 12 is used as a negative control. All measurements were performed in triplicates.

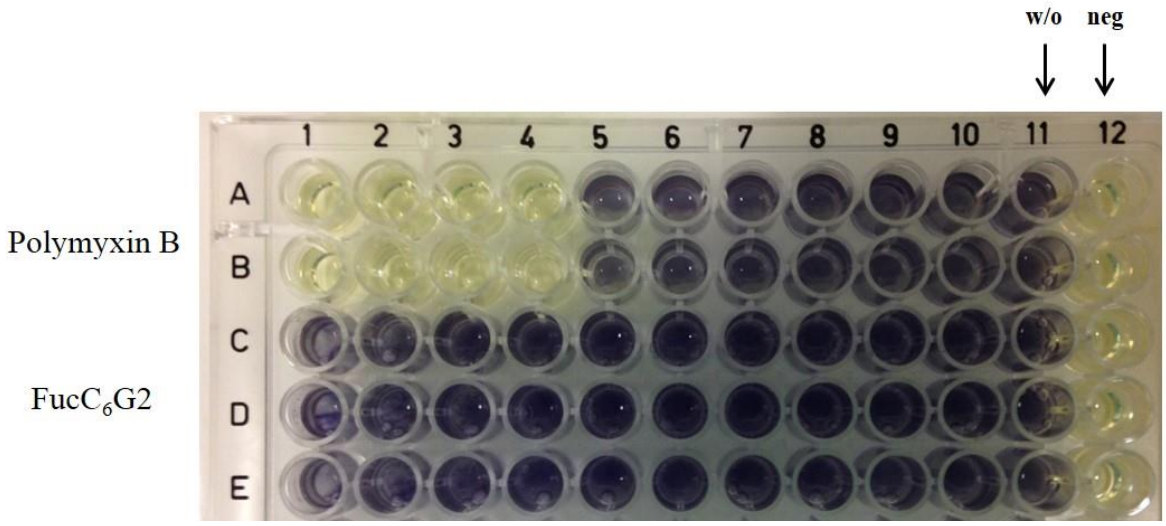


Figure S120: Broth Microdilution Method to determine the MIC values of **FucC$_6$G2** (raw C-E); dilution starting from 64 µM (left side). **Polymyxin B** (dilution starting from 128 µg/mL) was used as a reference (raw A-B). Raw 11 is used as growing control without compound (w/o) and raw 12 is used as a negative control. All measurements were performed in triplicates.

6. *Pseudomonas aeruginosa* Biofilm Inhibition and Dispersal Assay quantifying Bacterial Cell Viability

Table S1: Bacterial cell viability assays

		MBIC assay		Dispersal Assay	
		OD600	**Number of PA01**	**OD600**	**Number of PA01**
FD2					
	50 µM			0.02 ± 0.03	nd
	27 µM	1.24 ± 0.23	23 colonies to		
	30 µM				
GalAG2					
	30 µM	2.79[a)]	6-11 colonies	nd	nd
	20 µM	1.14 [a)]	uncountable	nd	nd
FD2x					
	50 µM			2.02 [a)]	uncountable
	45 µM	0.91 ± 0.27	uncountable		
GalAG2x					
	30 µM	0.05 [a)]	no colonies		
	20 µM	1.03 [a)]	1 colonies		
	13 µM	1.76 [a)]	~ 18 colonies		
	9 µM	7.77 [a)]	5-9 colonies		
GalBG2x					
	50 µM			0.71 [a)]	uncountable
	45 µM	1.48 [a)]	20-30 colonies		
	30 µM	1.59 [a)]	~ 30 colonies		
	20 µM	1.22 [a)]	uncountable		
Het2G2					
	50 µM	1.90 [a)]	uncountable		
	30 µM	0.97 ± 0.19	uncountable		
Het3G2					
	50 µM			1.11 [a)]	uncountable
	45 µM	0.96 [a)]	uncountable		
	30 µM	1.03 [a)]	uncountable		
	20 µM	1.07 [a)]	uncountable		
	13 µM	0.93 [a)]	uncountable		
	9 µM	1.00 [a)]	uncountable		
Het4G2					
	50 µM	1.10 [a)]	uncountable		
	30 µM	0.97 [a)]	uncountable		
Het5G2					
	50 µM	0.08 [a)]	no colonies	0.00 [a)]	nd
Het6G2					
	50 µM			0.00 [a)]	no colonies
	30 µM	0.01 [a)]	no colonies		
	20 µM	0.00 [a)]	no colonies		
	30 µM	0.97 [a)]	uncountable		
	10 µM	0.88 [a)]	uncountable		
Het7G2					
	50 µM			0.00 [a)]	no colonies
	20 µM	0.00 [a)]	no colonies		
	13 µM	0.00 [a)]	no colonies		
	9 µM	0.80 [a)]	uncountable		
Het8G2					
	50 µM			0.00 ± 0.00	nd
	20 µM	0.00± 0.00	no colonies		
	13 µM	1.06 ± 0.12	uncountable		
	9 µM	1.36 [a)]	uncountable		
	50 µM			0.03 ± 0.04	nd
	30 µM	0.00 ± 0.00	no colonies		
	20 µM	0.72 ± 0.31	uncountable		
	13 µM	1.25 ± 0.15	uncountable		
	9 µM	1.21 ± 0.21			
AcG2x					
	50 µM			0.88 ± 0.15	uncountable
	30 µM	0.03 [a)]	no colonies		
	20 µM	1.14 [a)]			

AcG2xK					
	50 µM			0.00 ± 0.00	nd
	20 µM	0.00 [a)]	no colonies		
	6 µM	0.75 [a)]	7 colonies to		
NG2					
	50 µM			0.00 ± 0.00	no colonies
	22 µM			0.00 ± 0.00	no colonies
	11 µM			0.46 ± 0.18	uncountable
	9 µM	0.00 ± 0.00	no colonies		
	6 µM	0.00 ± 0.00	no colonies	0.73 [a)]	uncountable
	4 µM	0.00 ± 0.00	no colonies	0.73 [a)]	uncountable
	2.5 µM	0.00 ± 0.00	no colonies		
	1.8 µM	1.06 ± 0.13	uncountable		
	1.2 µM	0.90 ± 0.33	uncountable		
	0.8 µM	0.94 ± 0.08	uncountable		
	0.2 µM	0.98 [a)]	uncountable		
G3KL					
	10 µM			0.42 ± 0.12	uncountable
	6 µM	0.00 ± 0.00	no colonies		
	4 µM	0.45 ± 0.00	uncountable	0.69 [a)]	uncountable
	2.5 µM	0.95 [a)]	uncountable		
	1.8 µM	1.08 [a)]	uncountable		
G3LK					
	10 µM			0.54 ± 0.03	uncountable
	9 µM	0.00 ± 0.00	no colonies		
	6 µM	0.92 ± 0.15	uncountable	0.70 [a)]	uncountable
	4 µM	0.75 ± 0.13	uncountable		
	2.5 µM	1.00 ± 0.07	uncountable		
Polymyxin B					
	10 µM			0.81 ± 0.12 [c)]	uncountable
	6 µM	0.00 ± 0.00 [c)]	no colonies		
	4 µM	0.00 ± 0.00 [c)]	no colonies	0.22 [a)]	uncountable
	2.5 µM	1.16 ± 0.15 [c)]	uncountable		
	1.8 µM	1.11 ± 0.13 [c)]	uncountable		
Tobramycin					
	4 µM			0.00 ± 0.00	no colonies
	2.5 µM	0.00 ± 0.00	no colonies		
	1.8 µM	0.00 ± 0.00	no colonies		
	1.2 µM	0.00 ± 0.00	no colonies		
	0.8 µM	0.00 ± 0.00	no colonies		
	0.5 µM	0.04 ± 0.02	no colonies		
	0.35 µM	1.27 ± 0.37	uncountable		
$FucC_6G2$					
	30 µM			0.01 ± 0.01	no colonies
	20 µM	0.57 [a)]	~ 18 colonies		
	13 µM	0.96 [a)]	~ 27 colonies		
	9 µM	1.46 [a)]	~ 30 colonies		
	6 µM	0.98 [a)]	uncountable		
	4 µM	1.11 [a)]	uncountable		

For OD_{600} measurements, the 200 µL of the supernatant were added to 5 mL of LB medium and shacken at 37°C for 7-8 hours. The OD_{600} was measured and compared to the w/o supernatant. **For CFU plating**, the 200 µL of the supernatant was added to the first well of a 96-well sterile, F-bottomed polystyrene microtiter plate (TPP, untreated) and diluted serially by ½ (raw 1 to 6) in 180 µL NaCl 0.9%. 4 µL of the raw 6 were plated on LB agar and incubated at 37°C for 24 hours. All measurements were performed in duplicates. [a)] The cell viability assay was performed once and confirmed by CFU plating. [c)] These measurements were performed in triplicates.

7. Growth Curve Control Studies

Table S2: Growth curve control study of **ND2**, **AcG2** and **Het7G2**

Time	OD_{600} (control)	OD_{600} (Tobramycin 100 μM)	OD_{600} (**NG2** 6 μM)	OD_{600} (**AcG2** 50 μM)	OD_{600} (**Het7G2** 30 μM)
t = 0	0,075	0,075	0,075	0,075	0,075
t = 2h45	0,156	0,053	0,14	0,18	0,15
t = 4h30	0,174	0,042	0,17	0,24	0,2
t = 6h15	0,3	0,048	0,41	0,43	0,34
t = 7h30	0,235	0,052	0,238	0,314	0,32
t = 8h30	0,21	0,055	0,31	0,43	0,34
t = 9h	0,197	0,065	0,3	0,91	0,45
t = 10h	0,6	0,049	0,289	0,266	0,32

An overnight culture of P. aeruginosa PAO1 was standardized to an OD600 of 0.75. 20 μL aliquots were inoculated into test wells containing 180 μL LB medium without (control) or the indicated amounts of compounds. The 96-well plate was shaken at 37°C and 180 rpm over a time period of 10 hours. All measurements were performed in duplicate.

8. Crystallographic Data

Structural data	**Het1G1.LecB**
Beam Line	PX-III
Wavelength(Å)	1.0000
Resolution(Å)	47.51 - 2.13
Cell dimension	
Space group	P63 2 2
Unit cell(Å)	105.107, 105.107, 111.092, 90, 90, 120
Measured reflection/unique	392917/38033
Average multiplicity	10.33
Completeness (%)	99.55
Average I/σ(I)	14.95
Correlation CC (1/2) (%)	99.8
Wilson B-factor	30.7
Refinement	
Resolution range (Å)	47.51 - 2.13
R_{work} (%)	0.2050
R_{free} (%)	0.2460
Average Biso ($Å^2$)	53.1
All atoms	1840
Solvent atoms	79
RMSD from ideality angles (°)	1.320
Bonds (Å)	0.010
Protein Data Bank deposition code	5D2A

Structural data	**Het1G1.LecB**
Beam Line	PX-III
Wavelength(Å)	1.0000
Resolution(Å)	47.51 - 2.13
Cell dimension	
Space group	P63 2 2
Unit cell(Å)	105.107, 105.107, 111.092, 90, 90, 120
Measured reflection/unique	392917/38033
Average multiplicity	10.33
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Average I/σ(I)	14.95
Correlation CC (1/2) (%)	99.8
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R_{work} (%)	0.2050
R_{free} (%)	0.2460
Average Biso ($Å^2$)	53.1
All atoms	1840
Solvent atoms	79
RMSD from ideality angles (°)	1.320
Bonds (Å)	0.010
Protein Data Bank deposition code	5D2A

9. References

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