Supporting Information

Endolysins of *Bacillus anthracis* Bacteriophages Recognize Unique Carbohydrate Epitopes of Vegetative Cell Wall Polysaccharides with High Affinity and Selectivity

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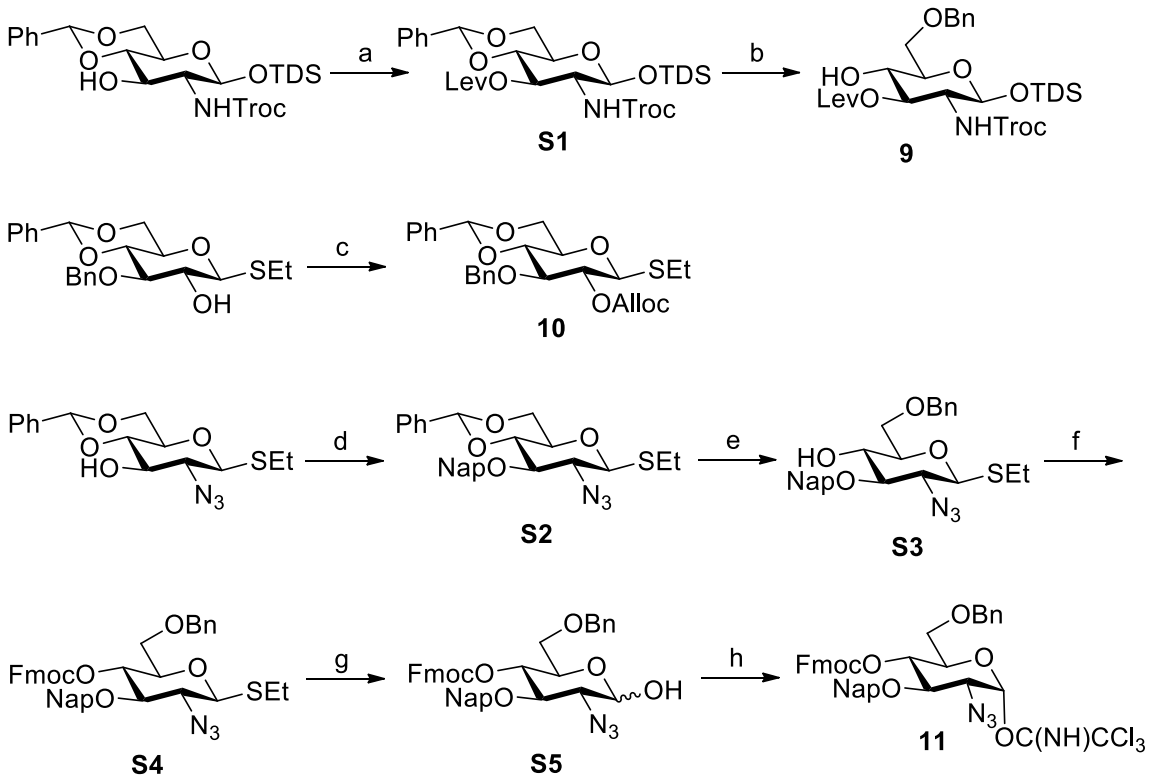
[a]**Scheme S1**. Preparation of building blocks



[a]Reagents and conditions: (a) levulinic acid, DCC, DMAP, DCM (95%); (b) Et_3SiH, TfOH, DCM, -78 ^oC (81%); (c) allyl chloroformate, TMEDA, DMAP, DCM (86%); (d) NapBr, NaH, DMF, 0 ^oC (94%); (e) Et_3SiH, TfOH, DCM, -78^o C (85%); (f) FmocCl, Py/DCM, (82%); (g) NBS, acetone/water (88%); (h) Cl_3CCN, NaH, DCM (91%).

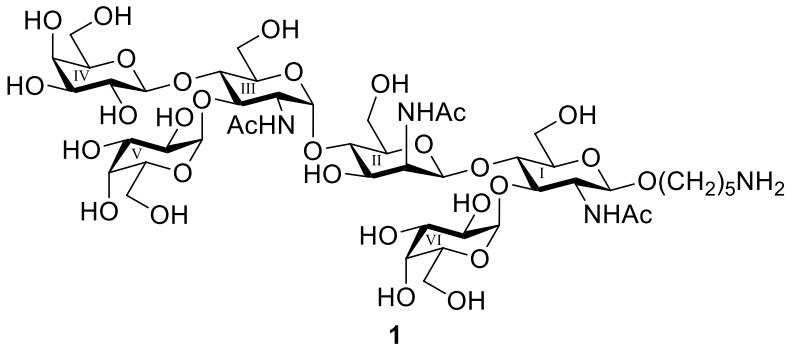


Figure S1. Target **1**: sugar ring marked with Roman numeral I-VI were used as superscript notations in NMR analysis.

Dimethylthexylsilyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S1). To a stirred and cooled (0 ^{o}C) solution of dimethylthexylsilyl 4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy)carbonyl-amino-*β*-D-glucopyranoside[1] (5.02 g, 8.61 mmol), 4-dimethylaminopyridine (53 mg, 0.43 mmol) and *N*,*N'*-dicyclohexylcarbodiimide (5.32 g, 25.8 mmol) in DCM (120 mL) were added levulinic acid (2.64 mL, 25.8 mmol). The reaction mixture turned into cloudy immediately. After stirring for 2 h, the precipitated urea was filtered off and the filtrate (400 mL) was washed with saturated $NaHCO_3$ (2 × 300 mL) brine (300 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4, v/v) to give **S1** (5.57 g, 95%) as an amorphous white solid: R_f = 0.25 (EtOAc/hexanes, 1/4, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.32 (m, 5H), 5.48 (s, 1H, >C*H*Ph), 5.30 (t, 1H, *J* = 10 Hz, H-3), 5.18 (d, *J* = 9.5 Hz, 1H, N*H*Troc), 4.84 (d, 1H, *J* = 8 Hz, H-1), 4.74-4.66 (m, 2H, OC$H_2$$CCl_3$), 4.27 (dd, 1H, *J* = 5 Hz and 10.5 Hz, H-6e), 3.77 (t, 1H, *J* = 10.3 Hz, H-6a), 3.68 (t, 1H, *J* = 9.5 Hz, H-4), 3.64-3.58 (m, 1H, H-2), 3.50-3.45 (m, 1H, H-5), 2.77-2.51 (m, 4H), 2.11 (s, 3H), 1.62-1.56 (m, 1H), 0.85-0.81 (m, 12H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.13, 172.97, 154.45, 137.23, 129.11, 128.31, 126.28, 101.33, 96.76 (C-1), 95.64, 79.02 (C-4), 74.86 , 71.97 (C-3), 68.67 (C-6), 66.25 (C-5), 58.88 (C-2), 38.07, 34.03, 29.85, 28.14, 24.86, 20.07, 18.64, -1.79, -3.25. HR MALDI-TOF MS: m/z: calcd for $C_{29}H_{42}Cl_3NO_9Si$ $[M+Na]^+$: 704.1592; found: 704.1616.

Dimethylthexylsilyl 6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (9). Acccording to general procedure for reductive opening of a 4,6-benzylidene, compound **9** was prepared from a mixture of the compound **S1** (1.00 g, 1.47 mmol) and 4 Å molecular sieves (380 mg) in DCM (49 mL) with

triethylsilane (0.59 mL, 3.7 mmol) and triflic acid (0.29 mL, 3.3 mmol). The reaction was kept at -78 ^{o}C over a period of 1 h. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 2/3, v/v) to give **9** (0.81 g, 81%) as an amorphous white solid: R_f = 0.21 (EtOAc/hexanes, 2/3, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.25 (m, 5H), 5.04-5.00 (m, 2H, H-3 and N*H*Troc), 4.74-4.55 (m, 4H, OCH_2Ph and OCH_2CCl$_3$), 4.71 (d, 1H, J = 8 Hz, H-1), 3.78-3.70 (m, 3H, H-4, H-6a and H-6e), 3.61-3.55 (m, 1H, H-2), 3.53-3.50 (m, 1H, H-5), 3.19 (s, 1H, O*H*), 2.78-2.49 (m, 4H), 2.15 (s, 3H), 1.62-1.56 (m, 1H), 0.84-0.78 (m, 12H), 0.16 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.57, 173.58, 154.43, 138.20, 128.56, 127.83, 127.73, 96.36 (C-1), 95.67, 75.93 (C-3), 74.81, 74.67 (C-5), 73.77, 70.51 (C-4), 70.16 (C-6), 57.95 (C-2), 38.42, 34.13, 29.92, 28.41, 24.96, 20.16, 18.69, -1.71, -3.26. HR MALDI-TOF MS: m/z: calcd for $C_{29}H_{44}Cl_3NO_9Si$ $[M+Na]^+$: 706.1749; found: 706.1777.

Ethyl 2-*O*-allyloxycarbonyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside (10). To a stirred and cooled (0 ^{o}C) solution of ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside[2] (3.15 g, 7.84 mmol), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (1.76 mL, 11.8 mmol) and 4-dimethylaminopyridine (286 mg, 2.34 mmol) in DCM (45 mL) were added allyl chloroformate (2.09 mL, 19.6 mmol). After stirring at room temperature for 16 h, the reaction mixture was diluted with DCM (300 mL) and was washed with saturated $NaHCO_3$ (2 × 250 mL) brine (250 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/8, v/v) to give **10** (3.16 g, 86%) as an amorphous white solid: R_f = 0.35 (EtOAc/hexanes, 1/6, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.25 (m, 10H), 5.96-5.88 (m, 1H, OCH_2CH=CH_2), 5.56 (s, 1H, >C*H*Ph), 5.38-5.25 (m, 2H, OCH_2CH=CH_2), 4.88 (d, 1H, J = 11.5 Hz, OC*H*HPh), 4.83 (dd, 1H, J = 8.5 Hz and 10 Hz, H-2), 4.70 (d, 1H, J = 12 Hz,

OC*H*HPh), 4.65 (d, *J* = 6 Hz, 2H, OCH_2CH=CH_2), 4.51 (d, 1H, *J* = 8 Hz, H-1), 4.36 (dd, 1H, *J* = 5 Hz and 10.5 Hz, H-6e), 3.81-3.72 (m, 3H, H-3, H-4 and H-6a), 3.50-3.45 (m, 1H, H-5), 2.74-2.69 (m, 2H), 1.25 (t, 1H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.30, 138.19, 137.25, 131.49, 129.19, 128.41, 127.90, 127.81, 126.15, 119.13, 101.36, 84.24 (C-1), 81.44 (C-4), 80.05 (C-3), 75.77 (C-2), 74.76, 70.74 (C-5), 69.02 , 68.67 (C-6), 24.37, 14.97. HR MALDI-TOF MS: m/z: calcd for $C_{26}H_{30}O_7S$ $[M+Na]^+$: 509.1610; found: 509.1645.

Ethyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2-methylnaphthyl)-1-thio-*β*-D-glucopyranoside (S2). To a stirred and cooled (0 ^oC) solution of ethyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-*β*-D-glucopyranoside[3] (3.78 g, 11.2 mmol) and 2-(bromomethyl)naphthalene (3.72 g, 16.8 mmol) in DMF (50 mL) under an atmosphere of Ar were added sodium hydride (896 mg, 22.4 mmol, 60% in oil) in small portion. After stirring for 1 h at room temperature, the reaction was quenched by the addition of MeOH (50 mL). The organic solution was diluted with DCM (300 mL) and was washed with water (2 × 250 mL) and brine (250 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/12, v/v) to give **S2** (5.03 g, 94%) as an amorphous white solid: R_f = 0.26 (EtOAc/hexanes, 1/10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82-7.38 (m, 12H), 5.60 (s, 1H, >C*H*Ph), 5.10-4.97 (m, 2H, OCH_2Nap), 4.37-4.32 (m, 2H, H-1 and H-6e), 3.79-3.73 (m, 2H, H-4 and H-6a), 3.68 (t, 1H, *J* = 9 Hz, H-3) 3.49 (dd, 1H, *J* = 9 Hz and 10 Hz, H-2), 3.45-3.41 (m, 1H, H-5) 2.79-2.71 (m, 2H), 1.31 (t, 1H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.28, 135.32, 133.39, 133.25, 129.28, 128.48, 128.34, 128.14, 127.85, 127.27, 126.30, 126.22, 126.20, 126.12, 101.51, 85.10 (C-1), 81.63 (C-4), 80.88 (C-3), 75.16 (C-2), 70.55 (C-5), 68.65 (C-6),

65.99 (C-2), 25.08, 15.18. HR MALDI-TOF MS: m/z: calcd for $C_{26}H_{27}N_3O_4S$ $[M+Na]^+$: 500.1620; found: 500.1649.

Ethyl 2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(2-methylnaphthyl)-1-thio-*β*-D-glucopyranoside (S3). Acccording to general procedure for reductive opening of a 4,6-benzylidene, compound **S3** was prepared from a mixture of compound **S2** (1.00 g, 2.10 mmol), and 4 Å molecular sieves (1.5 g) in DCM (70 mL) with triethylsilane (0.84 mL, 5.2 mmol) and triflic acid (0.41 mL, 4.6 mmol). The reaction was kept at -78 ^oC over a period of 1 h. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4, v/v) to give **S3** (850 mg, 85%) as an amorphous white solid: R_f = 0.31 (EtOAc/hexanes, 1/3, v/v). ^1H NMR (500 MHz, $CDCl_3$): δ 7.85-7.28 (m, 12H), 5.08-5.00 (m, 2H, OCH_2Nap), 4.58-4.52 (m, 2H, OCH_2Ph), 4.30 (d, 1H, J = 10 Hz, H-1), 3.75-3.68 (m, 3H, H-4, H-6a and H-6e), 3.44-3.39 (m, 3H, H-2, H-3 and H-5), 2.77 (s, 1H, OH), 2.76-2.68 (m, 2H), 1.30 (t, 3H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.70, 135.53, 133.42, 133.21, 128.60, 128.51, 128.12, 128.01, 127.87, 127.11, 126.30, 126.16, 126.09, 84.54 (C-3), 84.40 (C-1), 77.96 (C-5), 75.44, 73.83, 72.51 (C-4), 70.52 (C-6), 65.60 (C-2), 24.78, 15.19. HR MALDI-TOF MS: m/z: calcd for $C_{26}H_{29}N_3O_4S$ $[M+Na]^+$: 502.1776; found: 502.1825.

Ethyl 2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-3-*O*-(2-methylnaphthyl)-1-thio-*β*-D-glucopyranoside (S4). To a stirred solution of **S3** (1.52 g, 3.17 mmol) in DCM (30 mL) and pyridine (15 mL) under an atmosphere of Ar were added fluorenylmethyloxycarbonyl chloride (2.46 g in 10 mL DCM, 9.51 mmol) slowly. After stirring for 16 h, the reaction mixture was diluted with DCM (300 mL) and was washed with water (250 mL), 1M HCl (2 × 250 mL) and brine (250 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 10/1→8/1, v/v) to give **S4** (1.82 g,

82%) as an amorphous white solid: R_f = 0.22 (EtOAc/hexanes, 1/6, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.19 (m, 20H), 4.96 (d, 1H, *J* = 11.5 Hz, OC*H*HNap), 4.89 (t, 1H, *J* = 9.3 Hz, H-4), 4.83 (d, 1H, *J* = 11.5 Hz, OC*H*HNap), 4.48 (s, 2H, CH_2CHFmoc), 4.31 (d, 1H, *J* = 10.5 Hz, H-1), 4.25-4.15 (m, 2H, OCH_2Ph), 3.99 (t, 1H, *J* = 7.3 Hz, CH$_2$C*H*Fmoc), 3.63-3.57 (m, 4H, H-3, H-5 and H-6a and H-6e), 3.49 (t, 1H, *J* = 9.8 Hz, H-2), 2.81-2.69 (m, 2H), 1.31 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.37, 143.28, 143.23, 141.40, 141.38, 137.96, 134.99, 133.31, 133.15, 128.44, 128.28, 128.08, 128.03, 127.78, 127.77, 127.70, 127.27, 126.90, 126.21, 126.10, 125.91, 125.18, 125.09, 120.20, 84.46 (C-1), 82.49 (C-3), 77.31(C-5), 75.52 (C-4), 75.50, 73.67, 70.12, 69.64 (C-6), 65.84 (C-2), 46.72, 24.89, 15.23. HR MALDI-TOF MS: m/z: calcd for $C_{41}H_{39}N_3O_6S$ $[M+Na]^+$: 724.2457; found: 724.2479.

***O*-[2-Azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-3-*O*-(2-methylnaphthyl)]-*α*-D-glucopyranosyl Trichloroacetimidate (11).** To a stirred solution of **S4** (1.02 g, 1.46 mmol) in a mixture of acetone and water (4/1, v/v, 15 mL) was added *N*-bromosuccinimide (1.30 g, 7.30 mmol). After stirring for 40 min, the reaction mixture was diluted with DCM (150 mL) and washed with saturated $NaHCO_3$ (2 × 150 mL), brine (150 mL). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/3, v/v) to give **S5** as an inseparable mixture of *α*- and *β*-anomer (803 mg, 88%) as an amorphous white solid: R_f = 0.20 (EtOAc/hexanes, 1/4, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{39}H_{35}N_3O_7$ $[M+Na]^+$: 680.2373; found: 680.2411. To a stirred solution of *α*- and *β*-hemiacetals **S5** (310 mg, 0.472 mmol) in DCM (5.5 mL) was added trichloroacetonitrile (0.472 mL, 4.72 mmol) followed by sodium hydride (10 mg, 0.236 mmol, 60% in oil) under an atmosphere of Ar. After stirring at room temperature for 30 min, the reaction mixture was

filtered, and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4, v/v) to give **11** (344 mg, 91%) as an amorphous white solid: R_f = 0.36 (EtOAc/hexanes, 1/4, v/v). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (s, 1H), 7.76-7.19 (m, 20H), 6.45 (d, 1H, *J* = 3.6 Hz, H-1), 5.17 (t, 1H, *J* = 9.9 Hz, H-4), 5.00-4.85 (m, 2H, OC*H*$_2$Nap), 4.48 (d, 2H, *J* = 2.7 Hz, OC*H*$_2$Ph), 4.31-4.11 (m, 4H, H-3, H-5 and C*H*$_2$CHFmoc), 4.01 (t, 1H, *J* = 6.9 Hz, CH$_2$C*H*Fmoc), 3.78 (dd, 1H, *J* = 3.6 Hz and 10.2 Hz, H-2), 3.64-3.55 (m, 2H, H-6a and H-6e); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.76, 154.31, 143.30, 143.28, 141.46, 141.45, 137.82, 134.87, 133.37, 133.22, 128.49, 128.36, 128.15, 128.11, 127.93, 127.88, 127.85, 127.83, 127.36, 127.05, 126.29, 126.18, 125.99, 125.22, 125.13, 120.26, 120.25, 94.60 (C-1), 90.98, 77.93 (C-3), 75.40, 74.95 (C-4), 73.79, 71.77 (C-5), 70.33, 68.45 (C-6), 62.80 (C-2), 46.79.

Dimethylthexylsilyl *O*-(2-*O*-allyloxycarbonyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (15). A mixture of the glucosyl acceptor **9** (450 mg, 0.657 mmol) and glucosyl donor **10** (415 mg, 0.853 mmol), 4 Å molecular sieves (1.3 g) in DCM (15 mL) was stirred under an atmosphere of Ar for 1 h. The reaction was cooled (-20 ^{o}C) and NIS (230 mg, 1.02 mmol) was added followed by the addition of TMSOTf (30 μL, 0.17 mmol). After stirring for 1 h, the reaction was quenched by the addition of Et_3N (0.5 mL). The mixture was filtered, and the filtrate (180 mL) was washed with 10% $Na_2S_2O_3$ (160 mL) and brine (160 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/3, v/v) to give **15** (614 mg, 86%) as an amorphous white solid: R_f = 0.33 (EtOAc/hexanes, 1/3, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-7.25 (m, 15H), 5.91-5.83

(m, 1H, OCH_2CH=CH_2), 5.53 (s, 1H, >C*H*Ph), 5.34-5.22 (m, 2H, OCH_2CH=CH_2), 5.08 (t, 1H, *J* = 10 Hz, H-3^I), 4.98 (d, 1H, *J* = 9 Hz, H-1, N*H*Troc), 4.87-4.50 (m, 11H, H-1^I, H-1^{II}, H-2^{II}, , OCH_2CH=CH_2, OCH_2CCl_3 and two OCH_2Ph), 4.30 (dd, 1H, *J* = 5 Hz and 10 Hz, H-$6e^{II}$), 3.91 (t, 1H, *J* = 9.3 Hz, H-4^I), 3.78-3.62 (m, 5H, H-$6a^I$, H-$6e^I$, H-3^{II}, H-4^{II} and H-$6a^{II}$), 3.58-3.52 (m, 1H, H-2^I), 3.40 (d, 1H, *J* = 8.5 Hz, H-5^I), 3.27-3.22 (m, 1H, H-5^{II}), 2.72-2.49 (m, 4H), 2.16 (s, 3H), 1.60-1.56 (m, 1H), 0.85-0.81 (m, 12H), 0.15 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.29, 172.45, 154.28, 154.18, 138.32, 137.29, 131.58, 129.22, 128.60, 128.45, 128.40, 127.90, 127.79, 127.75, 126.19, 119.27, 101.35, 101.18 (C-1^I), 96.26 (C-1^{II}), 95.67, 81.31 (C-4^{II}), 78.94 (C-3^{II}), 77.40 (C-2^{II}), 75.96 (C-4^I), 74.84 (C-5^I), 74.42, 73,49, 72.83 (C-3^I), 68.92, 68.68 (C-6^{II}), 67.95 (C-6^I), 66.25 (C-5^{II}), 58.48 (C-2^I), 38.04, 34.16, 30.09, 28.19, 24.99, 20.19, 20.16, 18.69, -1.74, -3.19. HR MALDI-TOF MS: m/z: calcd for $C_{53}H_{68}Cl_3NO_{16}Si$ $[M+Na]^+$: 1130.3271; found: 1130.3321.

Dimethylthexylsilyl *O*-(3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (16). To a stirred solution of **15** (565 mg, 0.509 mmol) in THF (10 mL) and water (1 mL) was added tetrakis(triphenylphosphine)palladium(0) (295 mg, 0.255 mmol) under an atmosphere of Ar. After stirring for 3 h, the reaction mixture was filtered through a short pad of silica gel and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 2/5→1/2, v/v) to give **16** (475 mg, 91%) as an amorphous white solid: R_f= 0.29 (EtOAc/hexanes, 2/5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-7.23 (m, 15H), 5.52 (s, 1H, >C*H*Ph), 5.36 (br s, 1H, N*H*Troc), 5.17 (t, 1H, *J* = 10 Hz, H-3^I), 4.92-4.55 (m, 7H, H-1^I, OCH_2CCl_3 and two OCH_2Ph), 4.36 (d, 1H, *J* = 6.5 Hz, H-1^{II}), 4.28 (dd, 1H, *J* = 5 Hz and 10.5 Hz, H-$6e^{II}$), 3.82 (br s, 3H, H-4^I, H-$6a^I$ and H-$6e^I$), 3.73 (t,

1H, J = 10.3 Hz, H-6a^{II}), 3.62-3.59 (m, 3H, H-2^{I}, H-5^{I} and H-4^{II}), 3.53 (t, 1H, J = 8.8 Hz, H-3^{II}), 3.41-3.38 (m, 1H, H-2^{II}), 3.32-3.27 (m, 1H, H-5^{II}), 2.71-2.51 (m, 4H), 2.15 (s, 3H), 1.62-1.57 (m, 1H), 0.85-0.82 (m, 12H), 0.16 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.88, 173.25, 154.58, 138.85, 137.76, 137.40, 129.12, 128.58, 128.37, 128.33, 127.92, 127.86, 127.59, 126.19, 104.35 (C-1^{I}), 101.28, 96.07 (C-1^{II}), 95.86, 81.43 (C-4^{II}), 80.80 (C-3^{II}), 77.52 (C-4^{I}), 74.82, 74.64 (C-5^{I}), 74.29 (C-2^{II}), 73.80, 73.58 (C-3^{I}), 68.80 (C-6^{II}), 68.41 (C-6^{I}) , 66.46 (C-5^{II}), 58.12, (C-2^{I}), 37.94, 34.17, 30.04, 28.15, 24.90, 20.24, 20.17, 18.74, 18.70 -1.58, -2.89. HR MALDI-TOF MS: m/z: calcd for $C_{49}H_{64}Cl_3NO_{14}Si$ $[M+Na]^+$: 1046.3059; found: 1046.3082.

Dimethylthexylsilyl *O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (17). To a stirred and cooled (0 ^{o}C) solution of **16** (455 mg, 0.444 mmol) and 4-dimethylaminopyridine (6.5 mg, 0.053 mmol) in DCM (6 mL) and pyridine (1.5 mL) under an atmosphere of Ar were added triflic anhydride (0.38 mL, 2.3 mmol) slowly. After stirring for 3 h, the reaction mixture was diluted with DCM (180 mL) and washed with saturated $NaHCO_3$ (2 × 150 mL), brine (150 mL). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure to afford an amorphous yellow solid. To a stirred solution of the crude product in DMF (8 mL) was added sodium azide (175 mg, 2.69 mmol). After stirring at 55 ^{o}C for 18 h, the reaction mixture was diluted with DCM (180 mL) and was washed with water (150 mL) and brine (150 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4, v/v) to give **17** (401 mg, 86% over 2 steps) as an amorphous white solid: R_f = 0.20 (EtOAc/hexanes, 1/4, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.23 (m, 15H), 5.54 (s,

1H, >C*H*Ph), 5.15 (t, 1H, *J* = 10 Hz, H-3^{I}), 5.04 (d, 1H, *J* = 8.5 Hz, N*H*Troc), 4.79-4.46 (m, 7H, H-1^{I}, OCH_2CCl$_3$ and two OCH_2Ph), 4.55 (s, 1H, H-1^{II}), 4.25 (dd, 1H, *J* = 4.8 Hz and 10.3 Hz, H-6e^{II}), 3.97 (t, 1H, *J* = 9.5 Hz, H-4^{I}), 3.87 (t, 1H, *J* = 9.5 Hz, H-4^{II}), 3.79-3.66 (m, 4H, H-6a^{I}, H-6e^{I}, H-2^{II} and H-6a^{II}), 3.63-3.50 (m, 3H, H-2^{I}, H-5^{I} and H-3^{II}), 3.18-3.14 (m, 1H, H-5^{II}), 2.80-2.49 (m, 4H), 2.15 (s, 3H), 1.62-1.57 (m, 1H), 0.85-0.81 (m, 12H), 0.16 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 206.44, 172.53, 154.35, 138.02, 137.92, 137.40, 129.15, 128.71, 128.63, 128.39, 128.16, 128.01, 127.97, 127.72, 126.19, 101.69, 99.82 (C-1^{II}), 96.40 (C-1^{I}), 95.64, 78.48 (C-4^{II}), 76.58 (C-3^{II}), 75.55 (C-4^{I}), 74.82, 74.35 (C-5^{I}), 73.86, 72.95, 72.62 (C-3^{I}), 68.75 (C-6^{I}), 68.51 (C-6^{II}), 67.41 (C-5^{II}), 63.58 (C-2^{II}), 58.36 (C-2^{I}), 38.12, 34.14, 30.03, 28.31, 24.95, 20.16, 20.13, 18.68, -1.75, -3.15. HR MALDI-TOF MS: m/z: calcd for $C_{49}H_{63}Cl_3N_4O_{13}Si$ [M+Na]$^{+}$: 1071.3124; found: 1071.3166.

Dimethylthexylsilyl *O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (18). Acccording to general procedure for reductive opening of a 4,6-benzylidene, compound **18** was prepared from a mixture of the compound **17** (250 mg, 0.24 mmol) and 4 Å molecular sieves (380 mg) in DCM (8 mL) with triethylsilane (96 μL, 0.60 mmol) and triflic acid (47 μL, 0.53 mmol). The reaction was warmed to -40 ^{o}C over a period of 1 h. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **18** (163 mg, 65%) as an amorphous white solid: R_f = 0.31 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36-7.23 (m, 15H), 5.15 (t, 1H, *J* = 10 Hz, H-3^{I}), 4.97 (d, 1H, *J* = 8.5 Hz, N*H*Troc), 4.72-4.48 (m, 10H, H-1^{I}, H-1^{II}, three OCH_2Ph and OCH_2CCl$_3$), 3.98 (t, 1H, *J* = 9.5 Hz, H-4^{I}), 3.77-3.66 (m, 6H, H-6a^{I}, H-6e^{I}, H-2^{II}, H-4^{II}, H-6a^{II} and H-6e^{II}), 3.63-3.54 (m, 2H, H-2^{I} and H-5^{I}), 3.31-3.24 (m, 1H, H-3^{II} and H-5^{II}), 2.65-2.46 (m, 4H), 2.04 (s, 3H), 1.61-

1.56 (m, 1H), 0.85-0.81 (m, 12H), 0.15 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.74, 172.91, 154.33, 138.10, 138.06, 137.69, 128.80, 128.67, 128.66, 128.29, 128.04, 128.02, 127.94, 127.73, 98.84 (C-1^{II}), 96.51 (C-1^{I}), 95.66, 80.64 (C-3^{II}), 74.92, 74.87 (C-4^{I}), 74.84 (C-5^{I} and C-5^{II}), 74.48, 73.83, 73.60, 72.08 (C-3^{I}), 70.30 (C-6^{II}), 68.94 (C-6^{I}), 67.98 (C-4^{II}), 61.23 (C-2^{II}), 58.47 (C-2^{I}), 38.05, 34.15, 29.85, 28.10, 24.96, 20.16, 18.69, -1.73, -3.18. HR MALDI-TOF MS: m/z: calcd for $C_{49}H_{65}Cl_3N_4O_{13}Si$ $[M+Na]^+$: 1073.3281; found: 1073.3255.

Dimethylthexylsilyl *O*-[2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-3-*O*-(2-methylnaphthyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (8). According to general procedure of TMSOTf-mediated glycosylation for synthesis of *α*-anomers, compound **8** was prepare from a mixture of the acceptor **18** (0.100 g, 0.0950 mmol) and trichloroacetimidate **11** (152 mg, 0.190 mmol), 4 Å molecular sieves (380 g) in a mixture Et_2O/DCM (6 mL) with catalytic TMSOTf (6.5 μL, 0.036 mmol). The reaction time was 1.5 h. The resulting yellow oil, a separable mixture of *α*- and *β*-anomer (*α*/*β* = 8/1), was purified by flash chromatography over silica gel twice (1st time: EtOAc/hexanes, 1/3, v/v; 2nd time: acetone/toluene, 0/1→1/40) to give **8** (87 mg, 54% of *α*-anomer after purification) as an amorphous white solid: R_f = 0.28 (acetone/toluene, 1/15, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.13 (m, 35H), 5.67 (d, 1H, *J* = 4 Hz, H-1^{III}), 5.18 (t, 1H, *J* = 10 Hz, H-3^{I}), 5.01 (d, 1H, *J* = 9.0 Hz, N*H*Troc), 4.98 (t, 1H, *J* = 9.8 Hz, H-4^{III}), 4.92-4.77 (m, 2H, OCH_2Nap), 4.69-4.65 (m, 4H, H-1^{I}, H-1^{II} and OCH_2CCl$_3$), 4.55-4.50 (m, 6H, three OCH_2Ph), 4.36-4.14 (m, 4H, OCH_2Ph and CH_2CHFmoc), 4.03-3.91 (m, 4H, H-4^{I}, H-4^{II}, H-3^{III} and CH$_2$C*H*Fmoc), 3.81-3.79 (m, 2H, H-2^{II} and H-5^{III}), 3.72-3.57 (m, 7H, H-2^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-3^{II}, H-6a^{II} and H-6e^{II}), 3.35-3.26 (m, 4H, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III}), 2.60-2.33 (m, 4H),

2.00 (s, 3H), 1.62-1.56 (m, 1H), 0.85-0.81 (m, 12H), 0.16 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.72, 173.08, 154.34, 154.31, 143.40, 143.32, 141.46, 138.26 138.11, 137.94, 137.15, 135.19, 133.40, 133.18, 128.79, 128.76, 128.64, 128.40, 128.35, 128.30, 128.24, 128.12, 128.10, 128.07, 128.02, 127.84, 127.80, 127.72, 127.38, 127.32, 126.76, 126.24, 126.10, 125.88, 125.20, 125.11, 120.23, 98.45 (C-1^{II}), 97.75 (C-1^{III}), 96.56 (C-1^{I}), 95.66, 82.29 (C-3^{II}), 77.78 (C-3^{III}), 75.50 (C-4^{III}), 75.03, 74.93 (C-4^{I} and C-5^{II}), 74.79 (C-5^{I}), 74.54, 73.92, 73.72, 73.23, 71.93 (C-3^{I}), 71.63, 70.91 (C-4^{II}), 70.11, 69.65 (C-5^{III}), 69.01 (C-$6^{I\ and\ II}$), 68.50 (C-6^{III}), 62.95 (C-2^{III}), 60.87 (C-2^{II}), 58.59 (C-2^{I}), 46.80, 37.93, 34.19, 29.82, 27.99, 25.01, 20.20, 18.72, -1.68, -3.18. HR MALDI-TOF MS: m/z: calcd for $C_{88}H_{98}Cl_3N_7O_{19}Si$ $[M+Na]^+$: 1712.5650; found: 1712.5682.

***O*-[2-Azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-3-*O*-(2-methylnaphthyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl Trichloroacetimidate (20).** To a stirred and cooled (0^o C) solution of **8** (185 mg, 0.109 mmol) in THF (5 mL) was added HF·Py (1 mL) under an atmosphere of Ar. After stirring at room temperature for 12 h, the mixture was diluted with DCM (150 mL) and washed with saturated $NaHCO_3$ (2 × 120 mL), brine (120 mL). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2→2/3, v/v) to give **19** (156 mg, 92%) as an inseparable mixture of *α*- and *β*-anomer as an amorphous white solid: R_f = 0.24 (EtOAc/hexanes, 2/3, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{80}H_{80}Cl_3N_7O_{19}$ $[M+Na]^+$: 1570.4472; found: 1570.4521. To a stirred solution of *α*- and *β*-hemiacetals **19** (156 mg, 0.100 mmol) in DCM (3.9 mL) was added trichloroacetonitrile (0.10 mL, 1.0 mmol) followed by potassium carbonate (69 mg, 0.50 mmol) under an atmosphere

of Ar. After stirring for 2 h, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **20** (155 mg, 91%) as an amorphous white solid: R_f = 0.35 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (s, 1H), 7.75-7.15 (m, 35H), 6.42 (d, 1H, J = 3 Hz, H-1^{I}), 5.69 (d, 1H, J = 3.5 Hz, H-1^{III}), 5.39 (t, 1H, J = 10.3 Hz, H-3^{I}), 5.21 (d, 1H, J = 9 Hz, N*H*Troc), 5.01 (t, 1H, J = 9.8 Hz, H-4^{III}), 4.93 (d, 1H, J = 11 Hz, OC*H*HNap), 4.86-4.80 (m, 2H, OCH_2CCl$_3$), 4.71 (d, 1H, J = 12 Hz, OC*H*HPh), 4.65 (d, 1H, J = 12 Hz, OC*H*HNap), 4.53-4.18 (m, 12H, H-2^{I}, H-4^{I}, H-1^{II}, CH_2CHFmoc and seven protons from OCH_2Ph), 4.08-3.94 (m, 4H, H-5^{I}, H-4^{II}, H-3^{III} and CH$_2$C*H*Fmoc), 3.83-3.68 (m, 6H, H-6a^{I}, H-6e^{I}, H-2^{II}, H-6a^{II}, H-6e^{II} and H-5^{III}), 3.60 (dd, 1H, J = 3.3 Hz and 8.8 Hz, H-3^{II}), 3.38-3.29 (m, 4H, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III}), 2.62-2.26 (m, 4H), 2.00 (s, 3H); ^{13}C NMR (HSQC, 125 MHz, $CDCl_3$): δ 128.88, 128.56, 128.28, 128.22, 127.96, 127.85, 127.78, 127.37, 126.87, 126.11, 125.18, 120.23, 98.60 (C-1^{II}), 97.74 (C-1^{III}), 95.32 (C-1^{I}), 82.39 (C-3^{II}), 77.76 (C-3^{III}), 75.59 (C-4^{III}), 75.17 (C-5^{II}), 75.04, 74.49, 74.14, 73.84, 73.48 (C-4^{I}), 73.27, 72.85 (C-5^{I}), 71.64, 70.80 (C-4^{II}), 70.28 (C-3^{I}), 70.18, 69.95 (C-6^{II}), 69.70 (C-5^{III}), 68.60 (C-6^{III}), 68.13 (C-6^{I}), 63.01 (C-2^{III}), 60.66 (C-2^{II}), 54.38 (C-2^{I}), 46.89, 37.77, 29.80, 27.87.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-[2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-3-*O*-(2-methylnaphthyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (21).** According to general procedure of TMSOTf-mediated glycosylation for synthesis of *β*-anomers, compound **21** was prepare from a mixture of *N*-benzyl-*N*-benzyloxycarbonyl-5-aminopentanol[4] (81 mg, 0.25 mmol) and donor **20** (140 mg, 0.083 mmol), 4 Å molecular sieves (330 mg) in DCM (4 mL) with

catalytic TMSOTf (3.5 μL, 0.019 mmol). The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 0/1→1/2, v/v) to give **21** (131 mg, 85%) as an amorphous white solid: R_f = 0.37 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68-7.09 (m, 45H), 5.61 (d, 1H, J = 3.5 Hz, H-1^{III}), 5.34-5.07 (m, 4H, H-3^{I}, N*H*Troc and NC[=O]C*H*$_2$Ph), 4.93 (t, 1H, J = 9.5 Hz, H-4^{III}), 4.87-4.72 (m, 2H, OC*H*$_2$Nap), 4.66-4.59 (m, 2H, OC*H*$_2$CCl$_3$), 4.48-4.09 (m, 14H, H-1^{I}, H-1^{II}, NC*H*$_2$Ph, C*H*$_2$CHFmoc and four OC*H*$_2$Ph), 3.95-3.87 (m, 4H, H-4^{I}, H-4^{II}, H-3^{III} and CH$_2$C*H*Fmoc), 3.76-3.51 (m, 9H, H-2^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-6a^{II} and H-6e^{II} and H-5^{III}), 3.29-3.10 (m, 8H, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III} and two C*H*$_2$-Linker), 2.55-2.28 (m, 4H), 1.94 (s, 3H), 1.477-1.42 (m, 4H, two C*H*$_2$-Linker), 1.24-1.17 (m, 2H, C*H*$_2$-Linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.69, 172.86, 156.86, 156.41, 154.39, 154.26, 143.35, 143.27, 141.40, 138.26, 138.05, 137.99, 137.88, 137.12, 136.98, 135.13, 133.34, 133.13, 128.73, 128.71, 128.58, 128.35, 128.26, 128.17, 128.07, 128.00, 127.79, 127.74, 127.68, 127.46, 127.35, 127.26, 126.71, 126.19, 126.05, 125.83, 125.14, 125.05, 120.18, 101.29 (C-1^{I}), 98.15 (C-1^{II}), 97.70 (C-1^{III}), 95.83, 82.21 (C-3^{II}), 77.66 (C-3^{III}), 75.47 (C-4^{III}), 74.95, 74.77 (C-4^{I} and C-5^{II}), 74.63, 74.42 (C-5^{I}), 73.83, 73.67, 73.15, 71.70 (C-3^{I}), 71.53, 70.88 (C-4^{II}), 70.05, 69.66, 69.60 (C-5^{III}), 68.81 (C-6$^{I\text{ and }II}$), 68.48 (C-6^{III}), 67.33, 62.90 (C-2^{III}), 60.81 (C-2^{II}), 56.59 (C-2^{I}), 50.68, 50.47, 47.30, 46.75, 46.32, 37.89, 29.83, 29.76, 29.22, 29.00, 27.91, 27.36, 23.19. HR MALDI-TOF MS: m/z: calcd for $C_{100}H_{103}Cl_3N_8O_{21}$ $[M+Na]^+$: 1879.6201; found: 1879.6189.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-[2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(2-methylnaphthyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (22).** To a stirred solution of **21** (164

mg, 0.0882 mmol) in DCM (8 mL) was added triethylamine (2 mL). After stirring for 2 h, the reaction mixture was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 2/5→1/2, v/v) to give **22** (142 mg, 98%) as an amorphous white solid: R_f = 0.25 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.20 (m, 37H), 5.68 (d, 1H, J = 3.5 Hz, H-1^{III}), 5.41-5.00 (m, 6H, H-3^{I}, N*H*Troc, NC[=O]CH_2Ph and OCH_2Nap), 4.81-4.28 (m, 14H, H-1^{I}, H-1^{II}, OCH_2CCl$_3$, NCH_2Ph and four OCH_2Ph), 4.10-4.01 (m, 2H, H-4^{I}, H-4^{II}), 3.85-3.61 (m, 11H, H-2^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-6a^{II} and H-6e^{II}, H-3^{III}, H-4^{III} and H-5^{III}), 3.43-3.21 (m, 8H, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III} and two CH_2-Linker), 2.76-2.36 (m, 4H), 2.03 (s, 3H), 1.64-1.42 (m, 4H, two CH_2-Linker), 1.41-1.20 (m, 2H, CH_2-Linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.74, 172.93, 156.89, 156.45, 154.39, 138.40, 138.05, 137.98, 137.71, 137.17, 135.75, 133.49, 133.24, 128.72, 128.59, 128.56, 128.51, 128.27, 128.14, 128.10, 128.01, 127.99, 127.86, 127.83, 127.65, 127.47, 127.19, 126.95, 126.29, 126.14, 126.09, 101.32 (C-1^{I}), 98.18 (C-1^{II}), 97.84 (C-1^{III}), 95.83, 82.34 (C-3^{II}), 79.39 (C-3^{III}), 75.20, 74.79 (C-4^{I}), 74.65 (C-5^{I} and C-5^{II}), 74.45, 73.83, 73.22, 73.01 (C-4^{III}), 71.67, 71.59 (C-3^{I}), 70.57 (C-5^{III}), 70.26, 70.17 (C-4^{II}), 69.65, 69.53 (C-6^{III}), 68.81 (C-6$^{I\text{ and }II}$), 67.34, 62.81 (C-2^{III}), 60.87 (C-2^{II}), 56.57 (C-2^{I}), 50.70, 50.47, 47.31, 46.33, 37.85, 29.85, 29.74, 29.23, 29.02, 27.87, 27.37, 23.20. HR MALDI-TOF MS: m/z: calcd for $C_{85}H_{93}Cl_3N_8O_{19}$ $[M+Na]^+$: 1657.5520; found: 1657.5539.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-*O*-[2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(2-methylnaphthyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (23).** According to general procedure of TMSOTf-mediated glycosylation for

synthesis of *β*-anomers, compound **23** was prepare from a mixture of the acceptor **22** (131 mg, 0.0800 mmol) and trichloroacetimidate **13** (127 mg, 0.200 mmol), 4 Å molecular sieves (400 mg) in DCM (5 mL) with catalytic TMSOTf (7.2 μL, 0.040 mmol). The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **23** (149 mg, 88%) as an amorphous white solid: R_f = 0.28 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.03 (m, 52H), 5.70 (d, 1H, *J* = 4 Hz, H-1^{III}), 5.42-5.12 (m, 6H, H-3^{I}, H-2^{IV}, N*H*Troc, NC[=O]CH_2Ph and OC*H*HNap), 4.96 (d, 1H, *J* = 11 Hz, OC*H*HPh), 4.83 (d, 1H, *J* = 11 Hz, OC*H*HNap), 4.75-4.42 (m, 17H, H-1^{I}, H-1^{II}, NCH_2Ph, OCH_2CCl$_3$ and eleven protons from OCH_2Ph), 4.28 (d, 1H, *J* = 8 Hz, H-1^{IV}), 4.14-4.11 (m, 2H, H-4^{II} and OC*H*HPh), 4.05-3.56 (m, 16H, H-2^{I}, H-4^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-6a^{II}, H-6e^{II}, H-3^{III}, H-4^{III}, H-4^{IV}, H-5^{IV}, H-6a^{IV}, OC*H*HPh and C*H*H-Linker), 3.30-3.21 (m, 9H, H-5^{II}, H-2^{III}, H-5^{III}, H-6a^{III}, H-3^{IV}, H-6e^{IV} and three protons from CH_2-Linker), 3.11 (dd, 1H, *J* = 5 Hz and 8.2 Hz, H-6e^{III}), 2.57-2.30 (m, 4H), 2.03 (s, 3H), 1.88 (s, 3H), 1.64-1.41 (m, 4H, two CH_2-Linker), 1.40-1.19 (m, 2H, CH_2-Linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.74, 172.94, 172.85, 169.37, 156.89, 156.42, 154.47, 154.34, 138.89, 138.35, 138.17, 138.09, 138.03, 137.87, 137.15, 136.40, 133.43, 132.99, 128.74, 128.70, 128.60, 128.57, 128.50, 128.43, 128.38, 128.36, 128.33, 128.25, 128.19, 128.11, 128.08, 128.01, 128.00, 127.95, 127.87, 127.79, 127.77, 127.71, 127.65, 127.62, 127.50, 127.42, 127.38, 126.47, 126.41, 125.77, 125.58, 101.25 (C-1^{I}), 100.79 (C-1^{IV}), 98.09 (C-1^{II}), 97.44 (C-1^{III}), 95.82, 82.44, 80.56, 77.79, 76.75, 75.14, 74.97, 74.72, 74.59, 74.47, 73.83, 73.67, 73.41, 73.23, 72.72, 72.03, 71.85, 71.72, 71.40, 69.67, 69.25, 68.79, 67.93, 67.32, 67.10, 63.02, 61.01, 56.51, 50.68, 50.44, 47.29, 46.30, 37.82, 29.83, 29.76, 29.23, 28.95, 27.94, 27.87, 27.33, 23.18, 21.08. HR MALDI-TOF MS: m/z: calcd for $C_{114}H_{123}Cl_3N_8O_{25}$ $[M+Na]^+$: 2131.7563; found: 2131.7597.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (24).** According to general procedure for deprotection of Nap ethers, compound **24** was prepare from **23** (124 mg, 0.0587 mmol) with DDQ (40 mg, 0.18 mmol) in a mixture of DCM/water (6 mL). The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **24** (90.3 mg, 78%) as an amorphous white solid: R_f = 0.22 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.19 (m, 45H), 5.67 (d, 1H, *J* = 3.5 Hz, H-1^{III}), 5.32 and 4.91 (two br s, 1H, N*H*Troc), 5.37 (dd, 1H, *J* = 8 Hz and 10 Hz, H-2^{IV}), 5.28-5.14 (m, 3H, H-3^{I} and NC[=O]C*H*$_2$Ph), 4.94 (d, 1H, *J* = 11.5 Hz, OC*H*HPh), 4.76-4.42 (m, 18H, H-1^{I}, H-1^{II}, NC*H*$_2$Ph, OC*H*$_2$CCl$_3$ and twelve protons from OC*H*$_2$Ph,), 4.28 (d, 1H, *J* = 8 Hz, H-1^{IV}), 4.22 (d, 1H, *J* = 12 Hz, OC*H*HPh), 4.11 (t, 1H, *J* = 9.3 Hz, H-4^{II}), 4.02 (t, 2H, *J* = 9 Hz, H-4^{I} and H-3^{III}), 3.89 (d, 1H, *J* = 2.5 Hz, H-4^{IV}), 3.86-3.59 (m, 13 H, H-2^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-6a^{II} and H-6e^{II}, H-4^{III}, H-6a^{IV}, H-6e^{IV}, H-5^{IV} and C*H*H-Linker), 3.48-3.22 (m, 8H, H-5^{II}, H-5^{III}, H-6a^{III} and H-6e^{III}, H-3^{IV} and three protons from C*H*$_2$-Linker), 3.13 (dd, 1H, *J* = 3.5 Hz and 10.5 Hz, H-2^{III}), 2.57-2.29 (m, 4H), 2.01 (s, 3H), 1.81 (s, 3H), 1.73-1.45 (m, 4H, two C*H*$_2$-Linker), 1.41-1.20 (m, 2H, C*H*$_2$-Linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.83, 173.07, 172.97, 169.29, 156.93, 156.46, 154.47, 154.35, 138.40, 138.35, 138.12, 138.09, 137.91, 137.81, 137.52, 137.18, 137.12, 136.99, 128.80, 128.74, 128.72, 128.70, 128.60, 128.54, 128.52, 128.44, 128.41, 128.30, 128.27, 128.19, 128.16, 128.10, 128.04, 127.93, 127.81, 127.68, 127.58, 127.52, 127.47, 127.40, 127.20, 101.75 (C-1^{IV}), 101.36 (C-1^{I}), 98.26 (C-1^{II}), 97.45 (C-1^{III}), 95.86, 82.50, 80.93, 80.38, 74.80 , 74.74, 74.66, 74.50, 74.11, 73.96, 73.89, 73.73, 72.75, 72.38, 72.31, 71.70, 71.21, 70.27, 69.70,

69.36, 68.92, 68.80, 68.63, 67.65, 67.36, 62.63, 61.02, 56.53, 50.72, 50.48, 47.33, 46.36, 37.83, 29.89, 29.85, 29.76, 29.55, 29.27, 29.01, 28.00, 27.86, 27.39, 23.22, 20.99. HR MALDI-TOF MS: m/z: calcd for $C_{103}H_{115}Cl_3N_8O_{25}$ $[M+Na]^+$: 1991.6937; found: 1991.6949.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-[*O*-(2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl)-(1→3)]-*O*-(2-azido-6-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (25).** According to general procedure of TMSOTf-mediated glycosylation for synthesis of *α*-anomers, compound **25** was prepare from a mixture of the acceptor **24** (60.0 mg, 0.0304 mmol) and trichloroacetimidate **14** (52.1 mg, 0.0760 mmol), 4 Å molecular sieves (170 mg) in a mixture of Et_2O/DCM (3mL) with catalytic TMSOTf (3.7 μL, 0.0206 mmol). The reaction time was 2 h. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **25** (54.7 mg, 72%) as an amorphous white solid: R_f = 0.25 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43-7.13 (m, 65H), 5.73 (s, 1H, H-1^V), 5.65 (d, 1H, J = 3.6 Hz, H-1^{III}), 5.55-5.15 (m, 5H, H-3^I, H-2^{IV}, N*H*Troc and NC[=O]CH_2Ph), 4.85-4.35 (m, 27H, H-1^I, H-1^{II}, H-1^{IV}, NCH_2Ph, OCH_2CCl$_3$ and twenty protons from OCH_2Ph), 4.23 (t, 1H, J = 8.1 Hz, H-3^{III}), 4.13-3.97 (m, 8H, H-4^I, H-4^{II}, H-4^{III}, H-5^{IV}, H-2^V, H-3^V and OCH_2Ph), 3.90 (s, 1H, H-4^V), 3.83 (s, 1H, H-4^{IV}), 3.61-3.38 (m, 18H, H-2^I, H-5^I, H-6a^I, H-6e^I, H-2^{II}, H-3^{II}, H-6a^{II}, H-6e^{II}, H-2^{III}, H-5^{III}, H-6a^{III}, H-6e^{III}, H-6a^{IV}, H-6e^{IV}, H-6a^V, H-6e^V and CH_2-Linker), 3.30-3.10 (m, 5H, H-5^{II}, H-3^{IV}, H-5^V and CH_2-Linker), 2.56-2.31 (m, 4H), 1.98 (s, 3H), 1.88 (s, 3H), 1.71-1.41 (m, 4H, two CH_2-Linker), 1.42-1.22 (m, 2H, CH_2-Linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.68, 172.90, 172.81, 168.99, 156.88, 156.42, 154.46, 154.33, 139.28, 139.18, 139.01, 138.58, 138.55, 138.47, 138.20, 138.03, 138.00,

137.99, 137.87, 137.83, 137.30, 137.07, 136.93, 128.77, 128.70, 128.56, 128.51, 128.49, 128.33, 128.28, 128.27, 128.23, 128.21, 128.18, 128.14, 128.05, 127.99, 127.98, 127.94, 127.89, 127.85, 127.77, 127.72, 127.62, 127.57, 127.48, 127.31, 127.24, 127.20, 101.24 (C-1^{IV}), 100.48 (C-1^{I}), 98.16 (C-1^{II}), 97.36 (C-1^{III}), 96.43 (C-1^{V}), 95.83, 82.04, 80.72, 78.42, 76.36, 75.85, 75.52, 75.10, 74.80, 74.65, 74.59, 74.49, 73.86, 73.64, 73.50, 73.29, 73.19, 72.45, 72.38, 71.93, 71.80, 71.72, 71.67, 71.45, 71.26, 70.42, 69.98, 69.47, 69.23, 68.78, 68.08, 68.03, 67.32, 62.64, 60.90, 56.48, 50.68, 50.44, 47.29, 46.31, 37.79, 29.84, 29.80, 29.73, 29.24, 28.96, 27.96, 27.85, 27,34, 23.19, 21.05. HR MALDI-TOF MS: m/z: calcd for $C_{137}H_{149}Cl_3N_8O_{30}$ $[M+Na]^+$: 2513.9343; found: 2513.9377.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-[*O*-(2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl)-(1→3)]-*O*-(2-azido-6-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (26).** According to general procedure for deprotection of Lev esters, compound **26** was prepare form **25** (50.2 mg, 0.0201 mmol) with hydrazine acetate (3.7 mg, 0.0402 mmol) in a mixture of MeOH/DCM (2 mL). The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **26** (44.8 mg, 93%) as an amorphous white solid: R_f = 0.25 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47-7.23 (m, 65H), 5.74 (s, 1H, H-1^{V}), 5.61 (d, 1H, J = 3.6 Hz, H-1^{III}), 5.54 (br s, 1H, N*H*Troc), 5.36 (t, 1H, J = 9 Hz, H-2^{IV}), 5.30-5.26 (m, 2H, NC[=O]CH_2Ph), 4.95-4.41 (m, 27H, H-1^{I}, H-1^{II}, H-1^{IV}, NCH_2Ph, OCH_2CCl$_3$ and ten OCH_2Ph), 4.33-3.21 (m, 35H, H-2^{I}, H-3^{I}, H-4^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-4^{II}, H-5^{II}, H-6a^{II}, H-6e^{II}, H-2^{III}, H-3^{III}, H-4^{III}, H-5^{III}, H-6a^{III}, H-6e^{III}, H-3^{IV}, H-4^{IV}, H-5^{IV}, H-6a^{IV}, H-6e^{IV}, H-2^{V}, H-3^{V}, H-4^{V}, H-5^{V} H-6a^{V}, H-6e^{V}, OCH_2Ph and two CH_2-

Linker), 1.98 (s, 3H), 1.74-1.43 (m, 4H, two CH_2-Linker), 1.40-1.22 (m, 2H, CH_2-Linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.14, 168.92, 156.89, 156.36, 154.30, 154.17, 139.22, 139.16, 138.98, 138.57, 138.56, 138.19, 138.06, 138.04, 138.03, 137.84, 137.23, 137.09, 137.05, 136.91, 128.77, 128.74, 128.71, 128.56, 128.54, 128.53, 128.35, 128.32, 128.25, 127.99, 127.94, 127.92, 127.86, 127.85, 127.82, 127.67, 127.57, 127.49, 127.38, 127.33, 127.28, 100.70 (C-1^{II} and C-1^{IV}), 100.01 (C-1^{I}), 97.71 (C-1^{III}), 96.67 (C-1^{V}), 95.78, 82.02, 81.52, 80.64, 78.56, 76.36, 76.16, 75.00, 74.86, 74.71, 74.65, 74.62, 74.59, 73.97, 73.74, 73.71, 73.59, 73.53, 73.44, 73.32, 72.60, 72.39, 71.90, 71.84, 71.75, 71.38, 70.58, 69.76, 69.38, 68.63, 68.18, 67.33, 62.12, 61.27, 58.05, 50.68, 50.45, 47.39, 46.30, 29.86, 29.82, 29.52, 29.29, 29.10, 28.00, 27.37, 23.26, 21.09. HR MALDI-TOF MS: m/z: calcd for $C_{132}H_{143}Cl_3N_8O_{28}$ $[M+Na]^+$: 2415.8975; found: 2415.9011.

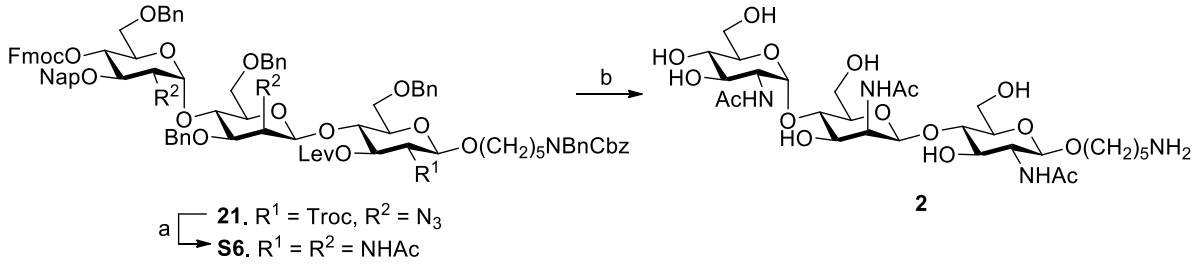
***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-[*O*-(2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl)-(1→3)]-*O*-(2-azido-6-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-[*O*-(2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl)-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (27).** According to general procedure of TMSOTf-mediated glycosylation for synthesis of *α*-anomers, compound **27** was prepare from a mixture of the acceptor **26** (40.0 mg, 0.0167 mmol) and trichloroacetimidate **14** (34.3 mg, 0.0501 mmol), 4 Å molecular sieves (130 mg) in a mixture of Et_2O/DCM (2mL) with catalytic TMSOTf (2.3 μL, 0.0206 mmol). The reaction time was 2 h. The resulting yellow oil, a separable mixture of *α*- and *β*-anomer (*α*/*β* > 20/1), was purified by flash chromatography over silica gel (EtOAc/hexanes, 2/5, v/v) to give **27** (31.7 mg, 65% of *α*-anomer after purification) as an amorphous white solid: R_f = 0.30 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.11 (m, 85H), 6.26 (br s, 1H, N*H*Troc), 5.72 (s, 1H, H-1^{V}),

5.61 (d, 1H, J = 4.2 Hz, H-1^{III}), 5.23 (dd, 1H, J = 8.4 and 9.6 Hz, H-2^{IV}), 5.17-5.14 (m, 3H, H-1^{VI} and NC[=O]CH_2Ph), 4.90-4.43 (m, 33H, H-1^{II}, NCH_2Ph, OCH_2CCl$_3$ and fourteen OCH_2Ph), 4.39-3.05 (m, 42H, H-1^{I}, H-2^{I}, H-3^{I}, H-4^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-4^{II}, H-5^{II}, H-6a^{II}, H-6e^{II}, H-2^{III}, H-3^{III}, H-4^{III}, H-5^{III}, H-6a^{III}, H-6e^{III}, H-1^{IV}, H-3^{IV}, H-4^{IV}, H-5^{IV}, H-6a^{IV}, H-6e^{IV}, H-2^{V}, H-3^{V}, H-4^{V}, H-5^{V} H-6a^{V}, H-6e^{V}, H-2^{VI}, H-3^{VI}, H-4^{VI}, H-5^{VI} H-6a^{VI}, H-6e^{VI}, OCH_2Ph and two CH_2-Linker), 1.85 (s, 3H), 1.69-1.60 (m, 4H, two CH_2-Linker), 1.40-1.22 (m, 2H, CH_2-Linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.97, 156.87, 156.31, 154.19, 139.39, 139.24, 139.11, 138.99, 138.79, 138.68, 138.66, 138.48, 138.32, 138.25, 138.11, 138.09, 137.04, 128.76, 128.73, 128.60, 128.56, 128.55, 128.51, 128.45, 128.40, 128.37, 128.33, 128.31, 128.29, 128.28, 128.25, 128.20, 128.19, 128.14, 128.10, 128.03, 128.01, 127.99, 127.95, 127.89, 127.86, 127.82, 127.79, 127.77, 127.75, 127.70, 127.63, 127.53, 127.35, 127.25, 127.19, 101.01 (C-1^{IV}), 100.58 (C-1^{I}), 98.68 (C-1^{VI}), 97.93 (C-1^{II}), 97.37 (C-1^{III}), 96.54 (C-1^{V}), 96.08, 92.15, 82.63, 80.77, 79.36, 78.92, 78.44, 76.30, 76.07, 75.89, 75.73, 75.63, 75.29, 74.85, 74.79, 74.75, 74.70, 74.37, 74.18, 73.73, 73.70, 73.57, 73.53, 73.47, 73.33, 73.26, 72.87, 72.43, 71.91, 71.85, 71.83, 71.13, 70.43, 70.27, 69.88, 69.56, 69.26, 69.08, 68.02, 67.31, 62.74, 60.87, 54.80, 50.67, 50.38, 47.35, 46.37, 32.13, 29.85, 29.42, 29.30, 29.10, 28.00, 27.37, 23.26, 21.09. HR MALDI-TOF MS: m/z: calcd for $C_{166}H_{177}Cl_3N_8O_{33}$ $[M+Na]^+$: 2938.1381; found: 2938.1432.

5-Aminopentyl *O*-(*β*-D-galactopyranosyl)-(1→4)-[*O*-(*α*-D-galactopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-[*O*-(*α*-D-galactopyranosyl)-(1→3)]-2-acetamido-2-deoxy-*β*-D-glucopyranoside (1). According to general procedure for reduction of azido and Troc groups, compound **28** was prepare from **27** (31.7 mg, 0.0109 mmol) with zinc metal power (35 mg, 0.54 mmol) in AcOH/Ac_2O/THF (4 mL) and saturated $CuSO_{4(aq)}$ (0.2 mL). The resulting yellow oil

was purified by flash chromatography over silica gel (MeOH/DCM, 1/30, v/v) to give **28** (22.0 mg, 72%) as an amorphous white solid: R_f = 0.29 (MeOH/DCM, 1/15, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{169}H_{186}N_4O_{34}$ $[M+Na]^+$: 2838.2846; found: 2838.2864. According to general procedure for ester and carbamate deprotection, deprotected compound was prepared from **28** (22.0 mg, 7.81 μmol) with NaOMe in a methanolic solution (0.10 mL, 1.0 M, 0.10 mmol) in a mixture of MeOH/DCM (3 mL). According to general procedure for hydrogenolysis, compound **1** was prepared from the crude product of previous step with $Pd(OH)_2/C$ (50 mg, 20 wt.%, Degussa type) in a mixture of ^{t}BuOH/AcOH/H_2O (4 mL). Compound **1** (6.5 mg, 69% over 2 steps) was obtained as an amorphous white solid. ^{1}H NMR (500 MHz, D_2O): δ 5.63 (d, 1H, J = 3.5 Hz, H-1^{VI}), 5.52 (d, 1H, J = 3.5 Hz, H-1^{V}), 5.30 (d, 1H, J = 3.5 Hz, H-1^{III}), 4.94 (s, 1H, H-1^{II}), 4.58-4.53 (m, 3H, H-1^{I}, H-2^{II} and H-1^{IV}), 4.16-3.72 (m, 34H), 3.71-3.53 (m, 3H), 3.06-3.00 (m, 2H), 2.11 (s, 3H), 2.06 (s, 6H), 1.78-1.53 (m, 4H), 1.48-1.35 (m, 2H); ^{13}C NMR (HSQC, 150 MHz, D_2O): δ 102.62 (C-1^{IV}), 101.00 (C-1^{I}), 99.29 (C-1^{V}), 98.63 (C-1^{II}), 98.46 (C-1^{III}), 97.74 (C-1^{VI}), 76.93, 75.97, 75.73, 75.46, 75.43, 75.25, 74.75, 73.48, 72.78, 72.77, 72.19, 71.33, 71.17, 71.11, 70.37, 69.98, 69.57, 69.47, 69.17, 69.02, 68.89, 68.82, 65.33, 61.18, 60.86, 60.47, 60.18, 59.60, 58.96, 54.79, 53.89, 53.04, 49.08, 39.54, 28.24, 26.57, 22.46, 22.33, 22.31. HR MALDI-TOF MS: m/z: calcd for $C_{47}H_{82}N_4O_{31}$ $[M+Na]^+$: 1221.4861; found: 1221.4888.

[a]**Scheme S2**. Synthesis of trisaccharide **2**

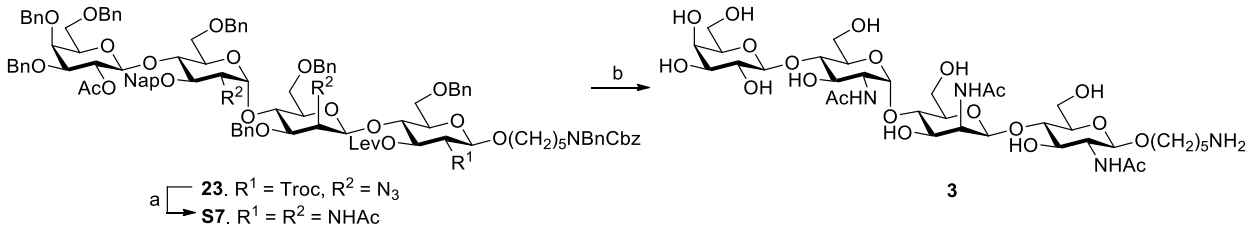


[a]Reagents and conditions: (a) Zn, AcOH/Ac_2O/THF, $CuSO_{4(aq)}$ (64%); (b) NaOMe, MeOH/DCM followed by $Pd(OH)_2$/C, H_2, ^{t}BuOH/AcOH/H_2O (72%, 2 steps).

5-Aminopentyl *O*-(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (2). According to general procedure for reduction of azido and Troc groups, compound **S6** was prepare from **21** (33.4 mg, 0.0180 mmol) with zinc metal power (59 mg, 0.91 mmol) in AcOH/Ac_2O/THF (6 mL) and saturated $CuSO_{4(aq)}$ (0.2 mL). The resulting yellow oil was purified by flash chromatography over silica gel (MeOH/DCM, 1/30, v/v) to give **S6** (20.2 mg, 64%) as an amorphous white solid: R_f = 0.31 (MeOH/DCM, 1/15, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{103}H_{112}N_4O_{22}$ $[M+Na]^+$: 1779.7666; found: 1779.7689. According to general procedure for ester and carbamate deprotection, deprotected compound was prepared from **S6** (20.2 mg, 0.0115 mmol) with NaOMe in a methanolic solution (0.12 mL, 1.0 M, 0.12 mmol) in a mixture of MeOH/DCM (4.5 mL). According to general procedure for hydrogenolysis, compound **2** was prepared from the crude product of previous step with $Pd(OH)_2$/C (50 mg, 20 wt.%, Degussa type) in a mixture of ^{t}BuOH/AcOH/H_2O (4 mL). Compound **2** (5.9 mg, 72% over 2 steps) was obtained as an amorphous white solid. ^{1}H NMR (500 MHz, D_2O): δ 5.34 (d, 1H, J = 3.5 Hz, H-1^{III}), 4.95 (s, 1H, H-1^{II}), 4.58-4.54 (m, 2H, H-1^{I} and H-2^{II}), 4.12 (dd, 1H, J = 4.5 Hz and 9.5 Hz, H-3^{II}), 3.98-3.88 (m, 6H, H-$6a^{I}$, H-$6e^{I}$, H-$6a^{II}$, H-$6e^{II}$, H-2^{III} and C*H*H-Linker), 3.86-

3.73 (m, 8H, H-2^{I}, H-3^{I}, H-4^{I}, H-4^{II}, H-3^{III}, H-4^{III} H-6a^{III} and H-6e^{III}), 3.69-3.62 (m, 2H, H-5^{I} and C*H*H-Linker), 3.57-3.53 (m, 2H, H-5^{II} and H-5^{III}), 3.04 (t, 2H, *J* = 7.5 Hz, CH_2-Linker), 2.12 (s, 3H), 2.08 (s, 6H), 1.75-1.69 (m, 2H, CH_2-Linker), 1.67-1.62 (m, 2H, CH_2-Linker), 1.48-1.43 (m, 2H, CH_2-Linker); ^{13}C NMR (HSQC, 125 MHz, D_2O): δ 101.35 (C-1^{I}), 99.41 (C-1^{II}), 98.32 (C-1^{III}), 79.12 (C-4^{I}), 75.35 (C-5^{I}), 74.66 (C-5^{II}), 73.17 (C-3^{I} and C-4^{III}), 72.96 (C-3^{II}), 72.53 (C-3^{III}), 70.89 (C-4^{II}), 70.36, 69.99 (C-5^{III}), 60.78 (C-6^{II}), 60.66 (C-6^{I}), 60.37 (C-6^{III}), 55.43 (C-2^{I}), 53.93 (C-2^{II}), 53.90 (C-2^{III}), 28.22, 26.58, 22.33, 22.22, 22.15. HR MALDI-TOF MS: m/z: calcd for $C_{29}H_{52}N_4O_{16}$ $[M+Na]^+$: 735.3276; found: 735.3304.

[a]**Scheme S3**. Synthesis of tetrasaccharide **3**

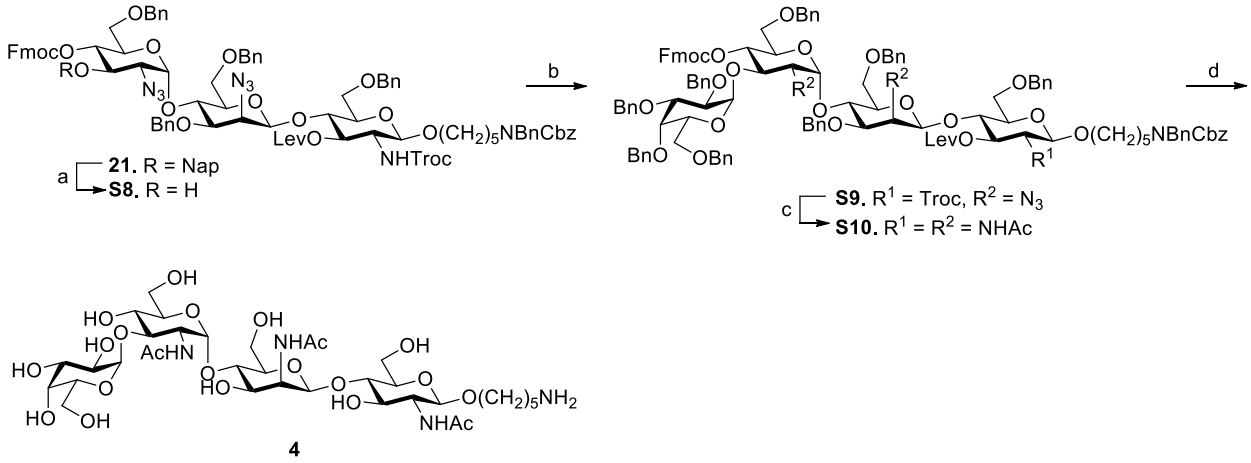


[a]Reagents and conditions: (a) Zn, AcOH/Ac_2O/THF, $CuSO_{4(aq)}$ (66%); (b) NaOMe, MeOH/DCM followed by $Pd(OH)_2$/C, H_2, ^{t}BuOH/AcOH/H_2O (75%, 2 steps).

5-Aminopentyl *O*-(*β*-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (3). According to general procedure for reduction of azido and Troc groups, compound **S7** was prepare from **23** (32.6 mg, 0.0154 mmol) with zinc metal power (50 mg, 0.77 mmol) in AcOH/Ac_2O/THF (5 mL) and saturated $CuSO_{4(aq)}$ (0.2 mL). The resulting yellow oil was purified by flash chromatography over silica gel (MeOH/DCM, 1/30, v/v) to give **S7** (20.4 mg, 66%) as an amorphous white solid: R_f = 0.30 (MeOH/DCM, 1/15, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{117}H_{132}N_4O_{26}$ $[M+Na]^+$: 2031.9028; found:

2031.9056. According to general procedure for ester and carbamate deprotection, deprotected compound was prepared from **S7** (20.4 mg, 0.0102 mmol) with NaOMe in a methanolic solution (0.11 mL, 1.0 M, 0.11 mmol) in a mixture of MeOH/DCM (4 mL). According to general procedure for hydrogenolysis, compound **3** was prepared from the crude product of previous step with $Pd(OH)_2/C$ (50 mg, 20 wt.%, Degussa type) in a mixture of $^tBuOH/AcOH/H_2O$ (3 mL). Compound **3** (6.7 mg, 75% over 2 steps) was obtained as an amorphous white solid. ^1H NMR (500 MHz, D_2O): δ 5.32 (d, 1H, J = 4 Hz, H-1^{III}), 4.92 (s, 1H, H-1^{II}), 4.54-4.50 (m, 3H, H-1^{I}, H-2^{II} and H-1^{IV}), 4.09 (dd, 1H, J = 4.5 Hz and 9.5 Hz), 3.99-3.85 (m, 9H), 3.84-3.68 (m, 10H), 3.64-3.52 (m, 5H), 3.01 (t, 2H, J = 7.5 Hz), 2.09 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.72-1.66 (m, 2H), 1.65-1.58 (m, 2H), 1.44-1.40 (m, 2H); ^{13}C NMR (HSQC, 125 MHz, D_2O): δ 103.03 (C-1^{IV}), 101.32 (C-1^{I}), 99.48 (C-1^{II}), 97.90 (C-1^{III}), 79.07, 78.69, 78.63, 75.54, 75.21, 74.60, 73.24, 72.90, 72.72, 72.52, 71.65, 71.16, 70.30, 69.45, 68.74, 61.17, 60.73, 60.47, 59.96, 55.41, 53.88, 53.51, 39.48, 28.23, 25.72, 22.32, 22.23, 22.42. HR MALDI-TOF MS: m/z: calcd for $C_{35}H_{62}N_4O_{21}$ $[M+Na]^+$: 897.3804; found: 897.3835.

[a]**Scheme S4**. Synthesis of tetrasaccharide **4**



[a]Reagents and conditions: (a) DDQ, DCM/H_2O (92%); (b) **14**, TMSOTf, Et_2O/DCM, -55 °C to 0 °C (82%); (c) Zn, $AcOH/Ac_2O$/THF, $CuSO_{4(aq)}$ (67%); (d) NaOMe, MeOH/DCM followed by $Pd(OH)_2/C$, H_2, $^tBuOH/AcOH/H_2O$ (73%, 2 steps).

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-[2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S8).** According to general procedure for deprotection of Nap ether, compound **S8** was prepare from **21** (74.5 mg, 0.0401 mmol) with DDQ (27 mg, 0.12 mmol) in a mixture of DCM/water (3 mL). The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **S8** (63.4 mg, 92%) as an amorphous white solid: R_f = 0.24 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.16 (m, 38H), 5.67 (d, 1H, J = 3.5 Hz, H-1^{III}), 5.40-4.92 (m, 4H, H-3^{I}, N*H*Troc and NC[=O]CH_2Ph), 4.81 (t, 1H, J = 9.5 Hz, H-4^{III}), 4.78-4.30 (m, 14H, H-1^{I}, H-1^{II}, NCH_2Ph, OCH_2CCl$_3$ and four OCH_2Ph), 4.21-4.19 (m, 3H, CH$_2$C*H*Fmoc and CH_2CHFmoc), 4.05-3.99 (m, 3H, H-4^{I}, H-4^{II} and H-3^{III}), 3.84-3.58 (m, 9H, H-2^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-6a^{II} and H-6e^{II} and H-5^{III}), 3.42-3.17 (m, 8H, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III} and two CH_2-Linker), 2.62-2.39 (m, 4H), 2.02 (s, 3H), 1.71-1.40 (m, 4H, two CH_2-Linker), 1.32-1.18 (m, 2H, CH_2-Linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.75, 172.91, 156.92, 156.50, 155.32, 154.43, 143.34, 143.27, 141.54, 141.51, 138.23 138.07, 138.01, 137.86, 137.13, 128.73, 128.76, 128.74, 128.62, 128.43, 128.33, 128.29, 128.17, 128.13, 128.04, 127.85, 127.78, 127.50, 127.39, 125.23, 125.18, 120.32, 101.34 (C-1^{I}), 98.20 (C-1^{II}), 97.63 (C-1^{III}), 95.85, 82.30 (C-3^{II}), 75.61 (C-4^{III}), 74.84 (C-4^{I} and C-5^{II}), 74.69 (C-5^{I}), 74.49, 73.88, 73.66, 73.20, 71.73 (C-3^{I}), 71.55, 70.64 (C-4^{II} and C-3^{III}), 70.48, 70.39, 69.71 (C-5^{III}), 69.54 (C-6$^{I\text{ and }II}$), 69.27, 68.89 (C-6^{III}), 67.98, 67.38, 63.43 (C-2^{III}), 60.83 (C-2^{II}), 56.61 (C-2^{I}), 50.72, 50.51, 47.33, 46.91, 46.34, 37.92, 29.89, 29.81, 29.55, 29.31,

27.93, 27.40, 23.23. HR MALDI-TOF MS: m/z: calcd for $C_{89}H_{95}Cl_3N_8O_{21}$ $[M+Na]^+$: 1739.5575; found: 1739.5600.

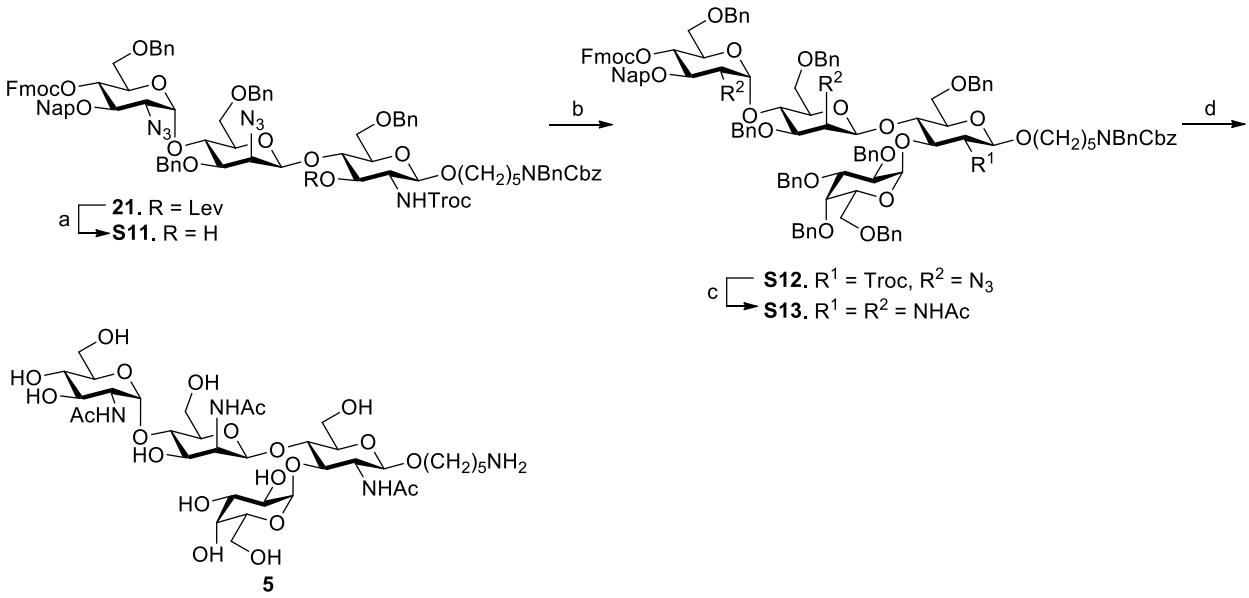
***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-(2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl)-(1→3)-*O*-[2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S9).** According to general procedure of TMSOTf-mediated glycosylation for synthesis of *α*-anomers, compound **S9** was prepare from a mixture of the acceptor **S8** (68.2 mg, 0.0397 mmol) and trichloroacetimidate **14** (67.9 mg, 0.0994 mmol), 4 Å molecular sieves (200 mg) in a mixture of Et_2O/DCM (3 mL) with catalytic TMSOTf (3.6 μL, 0.0199 mmo). The reaction time was 1.5 h. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **S9** (72.9 mg, 82%) as an amorphous white solid: R_f = 0.29 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.11 (m, 58H), 5.76 (d, 1H, J = 4 Hz, H-1^{III}), 5.37-5.14 (m, 5H, H-3^{I}, H-1^{IV}, N*H*Troc and NC[=O]CH_2Ph), 4.99 (t, 1H, J = 9.3 Hz, H-4^{III}), 4.91 (d, 1H, J = 11 Hz, OC*H*HNap), 4.74-4.29 (m, 23H, H-1^{I}, H-1^{II}, OC*H*HNap, NCH_2Ph, OCH_2CCl$_3$ and eight OCH_2Ph), 4.26-4.87 (m, 11H, H-4^{I}, H-4^{II}, H-3^{III}, H-5^{III}, H-2^{IV}, H-3^{IV}, H-4^{IV}, H-5^{IV}, CH$_2$C*H*Fmoc and CH_2CHFmoc), 3.82-3.56 (m, 10H, H-2^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-6a^{II}, H-6e^{II}, H-6a^{IV} and H-6e^{IV}), 3.42-3.16 (m, 8H, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III} and two CH_2-Linker), 2.57-2.33 (m, 4H), 1.99 (s, 3H), 1.68-1.42 (m, 4H, two CH_2-Linker), 1.36-1.18 (m, 2H, CH_2-Linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.76, 172.91, 156.92, 156.45, 154.48, 154.10, 143.59, 143.13, 141.44, 141.35, 139.01, 138.87, 138.61, 138.32, 138.07, 137.95, 137.11, 136.97, 128.79, 128.78, 128.74, 128.61, 128.56, 128.44, 128.35, 128.34, 128.31, 128.29, 128.24, 128.15, 128.04, 127.90,

127.86, 127.74, 127.66, 127.64, 127.51, 127.47, 127.40, 127.38, 127.30, 127.24, 125.42, 125.13, 120.17, 101.30 (C-1^{I}), 99.37 (C-1^{IV}), 98.19 (C-$1^{II\ and\ III}$), 95.85, 82.23, 78.90, 76.24, 76.01, 75.11, 75.08, 74.81, 74.72, 74.66, 74.48, 73.89, 73.62, 73.59, 73.16, 73.11, 73.01, 71.76, 71.69, 71.50, 70.82, 70.29, 70.03, 69.62, 69.18, 69.04, 68.87, 68.79, 67.37, 62.30, 60.81, 56.59, 50.72, 50.47, 47.33, 46.53, 46.34, 37.87, 32.16, 29.89, 29.78, 29.29, 29.00, 27.90, 27.39, 23.23. HR MALDI-TOF MS: m/z: calcd for $C_{123}H_{129}Cl_3N_8O_{26}$ $[M+Na]^+$: 2261.7981; found: 2261.7993.

5-Aminopentyl *O*-(*α*-D-galactopyranosyl)-(1→3)-*O*-(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (4). According to general procedure for reduction of azido and Troc groups, compound **S10** was prepare from **S9** (36.7 mg, 0.0164 mmol) with zinc metal power (53 mg, 0.82 mmol) in AcOH/Ac_2O/THF (5.5 mL) and saturated $CuSO_{4(aq)}$ (0.2 mL). The resulting yellow oil was purified by flash chromatography over silica gel (MeOH/DCM, 1/30, v/v) to give **S10** (23.5 mg, 67%) as an amorphous white solid: R_f = 0.33 (MeOH/DCM, 1/15, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{126}H_{138}N_4O_{27}$ $[M+Na]^+$: 2161.9446; found: 2161.9469. According to general procedure for ester and carbamate deprotection, deprotected compound was prepared from **S10** (23.5 mg, 0.0110 mmol) with NaOMe in a methanolic solution (0.11 mL, 1.0 M, 0.11 mmol) in a mixture of MeOH/DCM (4.5 mL). According to general procedure for hydrogenolysis, compound **4** was prepared from the crude product of previous step with $Pd(OH)_2$/C (50 mg, 20 wt.%, Degussa type) in a mixture of ^{t}BuOH/AcOH/H_2O (5 mL). Compound **4** (7.0 mg, 73% over 2 steps) was obtained as an amorphous white solid. ^{1}H NMR (500 MHz, D_2O): δ 5.43 (d, 1H, J = 4 Hz, H-1^{IV}) 5.28 (d, 1H, J = 4 Hz, H-1^{III}), 4.93 (s, 1H, H-1^{II}), 4.56-4.50 (m, 2H, H-1^{I}, H-2^{II}), 4.11 (dd, 1H, J = 4.5 Hz and 9.5 Hz), 4.08-3.86 (m, 9H), 3.84-3.68 (m, 12H), 3.66-3.58 (m, 2H), 3.54-3.48 (m, 1H), 3.00 (t,

2H, J = 7.5 Hz), 2.08 (s, 3H), 2.05 (s, 6H), 1.71-1.65 (m, 2H), 1.62-1.58 (m, 2H), 1.44-1.36 (m, 2H); ^{13}C NMR (HSQC, 125 MHz, D_2O): δ 101.33 (C-1^{I}), 99.43 (C-1^{IV}), 99.40 (C-1^{II}), 98.76 (C-1^{III}), 79.05, 77.10, 76.42, 76.26, 75.19, 74.59, 73.74, 73.59, 72.89, 72.86, 72.51, 71.18, 70.63, 70.30, 69.46, 69.29, 68.70, 60.92, 60.70, 60.39, 60.32, 55.39, 53.88, 52.40, 39.46, 28.23, 26.58, 22.28, 22.26, 22.10. HR MALDI-TOF MS: m/z: calcd for $C_{35}H_{62}N_4O_{21}$ $[M+Na]^+$: 897.3804; found: 897.3842.

[a]**Scheme 5**. Synthesis of tetrasaccharide **5**



[a]Reagents and conditions: (a) H_2NNH_2, HOAc, DCM/MeOH; (94%); (b) **14**, TMSOTf, Et_2O/DCM, -55 °C to 0 °C (66%, α/β > 20/1); (c) Zn, AcOH/Ac_2O/THF, $CuSO_{4(aq)}$ (62%); (d) NaOMe, MeOH/DCM followed by $Pd(OH)_2/C$, H_2, ^{t}BuOH/AcOH/H_2O (78%, 2 steps).

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-[2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-3-*O*-(2-methylnaphthyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S11).** According to general procedure

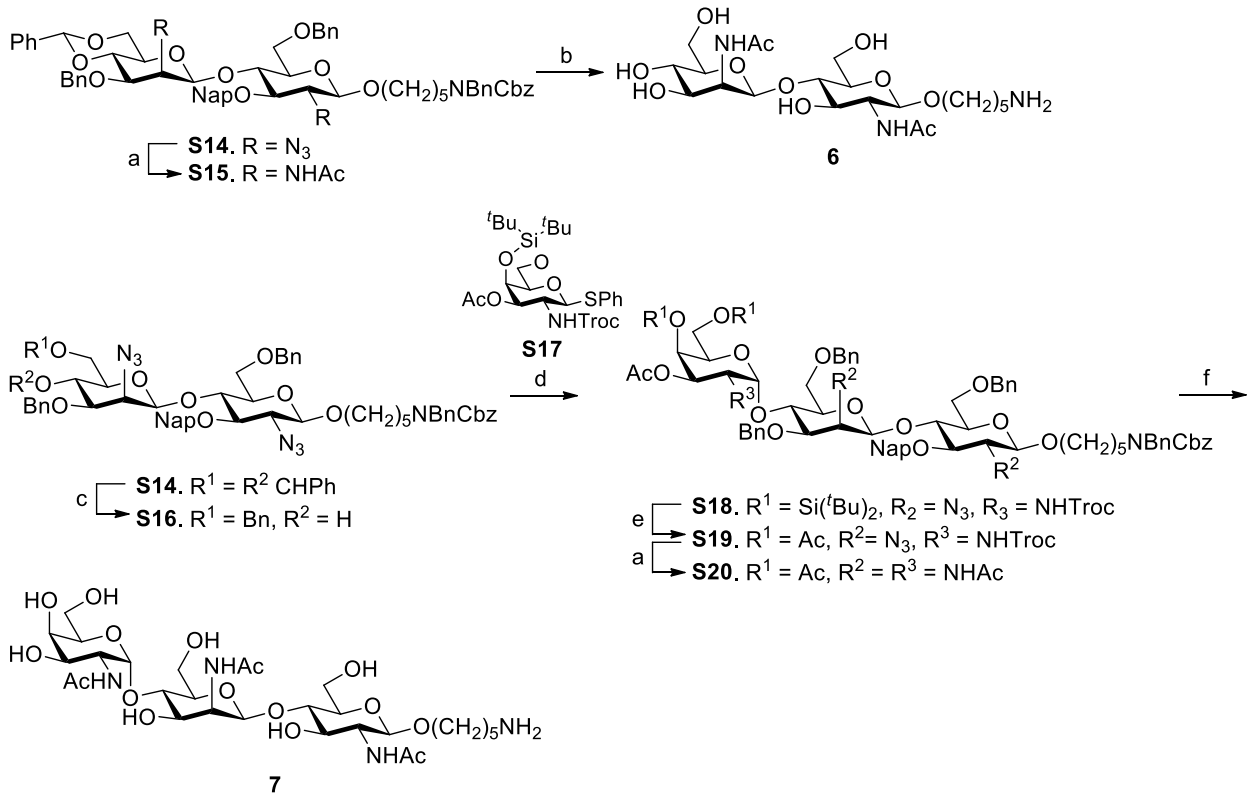
for deprotection of Lev esters, compound **S11** was prepare form **21** (72.3 mg, 0.0389 mmol) with hydrazine acetate (7.2 mg, 0.078 mmol) in a mixture of MeOH/DCM (3 mL). The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 2/5, v/v) to give **S11** (64.4 mg, 94%) as an amorphous white solid: R_f = 0.37 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.16 (m, 45H), 5.60 (d, 1H, J = 4 Hz, H-1^{III}), 5.42-5.16 (m, 3H, N*H*Troc and NC[=O]CH_2Ph), 4.95-4.77 (m, 3H, H-4^{III} and OCH_2Nap), 4.72-4.21 (m, 16H, H-1^{I}, H-1^{II}, CH_2CHFmoc, OCH_2CCl$_3$, NCH_2Ph and four OCH_2Ph), 4.01 (t, 1H, J = 6.8 Hz, CH$_2$C*H*Fmoc), 3.94-3.56 (m, 11H, H-3^{I}, H-4^{I}, H-6a^{I}, H-6e^{I}, H-2^{II}, H-3^{II}, H-4^{II}, H-6a^{II}, H-6e^{II}, H-3^{III} and H-5^{III}), 3.52-3.18 (m, 10H, H-2^{I}, H-5^{I}, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III} and two CH_2-Linker), 1.68-1.44 (m, 4H, two CH_2-Linker), 1.36-1.21 (m, 2H, CH_2-Linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.33, 143.32, 141.49, 138.30, 138.11, 137.85, 137.54, 136.94, 135.10, 133.39, 133.19, 128.85, 128.74, 128.64, 128.48, 128.43, 128.32, 128.22, 128.20, 128.10, 128.03, 127.91, 127.83, 127.50, 127.33, 126.74, 126.27, 126.13, 125.84, 125.13, 125.04, 120.26, 100.87 (C-1^{I}), 100.11 (C-1^{II}), 98.07 (C-1^{III}), 95.84, 82.19 (C-3^{I}), 81.95 (C-3^{II}), 77.43 (C-3^{III}), 75.22 (C-4^{III}), 75.03, 74.63, 74.48 (C-5^{I} and C-5^{II}), 73.81, 73.77, 73.69, 73.63, 72.35 (C-4^{I} and C-4^{II}), 71.89, 71.32, 70.08, 69.93, 69.79 (C-6$^{I\text{ and }II}$), 69.44 (C-5^{III}), 68.72, 68.36 (C-6^{III}), 67.36, 62.74 (C-2^{III}), 61.20 (C-2^{II}), 58.04 (C-2^{I}), 50.49, 47.43, 46.83, 46.34, 29.89, 29.16, 28.04, 27.40, 23.29. HR MALDI-TOF MS: m/z: calcd for $C_{95}H_{97}Cl_3N_8O_{19}$ $[M+Na]^+$: 1781.5833; found: 1781.5855.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-[2-azido-6-*O*-benzyl-2-deoxy-4-*O*-(9-fluorenylmethyloxycarbonyl)-3-*O*-(2-methylnaphthyl)-*α*-D-glucopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-[*O*-(2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl)-(1→3)]-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S12).** According to general procedure of TMSOTf-mediated

glycosylation for synthesis of α-anomers, compound **S12** was prepare from a mixture of the acceptor **S11** (72.5 mg, 0.0412 mmol) and trichloroacetimidate **14** (70.4 mg, 0.103 mmol), 4 Å molecular sieves (220 mg) in a mixture of Et_2O/DCM (4 mL) with catalytic TMSOTf (3.8 µL, 0.0206 mmol). The reaction time was 1.5 h. The resulting yellow oil, a separable mixture of α- and β-anomer (α/β > 20/1), was purified by flash chromatography over silica gel (EtOAc/hexanes, 2/5, v/v) to give **S12** (62.1 mg, 66% of α-anomer after purification) as an amorphous white solid: R_f = 0.31 (EtOAc/hexanes, 2/5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7. 77-7.14 (m, 45H), 6.30 (br s, 1H, N*H*Troc), 5.65 (d, 1H, J = 3.5 Hz, H-1^{III}), 5.25 (br s, 1H, H-1^{IV}), 5.19 (d, 2H, J = 13 Hz, NC[=O]CH_2Ph), 5.01 (t, 1H, J = 9.8 Hz, H-4^{III}), 4.92-4.38 (m, 23H, H-1^{II}, OCH_2Nap, OCH_2CCl$_3$, NCH_2Ph and eight OCH_2Ph), 4.33 (d, 1H, J = 6.5 Hz, H-1^{I}), 4.28-4.17 (m, 3H, H-3^{I} and CH_2CHFmoc), 4.08-3.92 (m, 7H, H-4^{I}, H-2^{II}, H-4^{II}, H-2^{IV}, H-4^{IV}, H-5^{IV} and CH$_2$C*H*Fmoc), 3.91-3.56 (m, 11H, H-2^{I}, H-5^{I}, H-6a^{I}, H-6e^{I}, H-6a^{II}, H-6e^{II}, H-3^{III}, H-5^{III}, H-3^{IV}, H-6a^{IV} and H-6e^{IV}), 3.48 (br s, 1H, H-3^{II}), 3.40-3.17 (m, 8H, H-5^{II}, H-2^{III}, H-6a^{III} and H-6e^{III} and two CH_2-Linkers), 1.56-1.40 (m, 4H, two CH_2-Linkers), 1.36-1.17 (m, 2H, CH_2-Linkers); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.86, 156.31, 154.29, 154.21, 143.38, 143.36, 141.45, 139.03, 138.70, 138.49, 138.17, 137.93, 136.91, 135.20, 133.38, 133.16, 128.75, 128.72, 128.58, 128.57, 128.56, 128.49, 128.47, 128.43, 128.39, 128.33, 128.31, 128.25, 128.18, 128.10, 128.04, 128.01, 127.99, 127.93, 127.91, 127.80, 127.79, 127.72, 127.64, 127.45, 127.35, 127.30, 126.67, 126.21, 126.06, 125.82, 125.15, 125.08, 120.21, 120.20, 101.05 (C-1^{I}), 98.45 (C-1^{IV}), 97.90 (C-1^{III}), 97.76 (C-1^{II}), 96.13, 82.78, 79.24, 77.88, 76.14, 75.95, 75.30, 75.18, 74.92, 74.81, 74.64, 74.42, 73.79, 73.75, 73.68, 73.08, 72.73, 71.80, 71.09, 70.06, 69.96, 69.83, 69.57, 68.26, 67.32, 62.90, 60.48, 55.38, 50.70, 50.40, 47.37, 46.82, 46.38, 29.87, 29.40, 28.11, 27.64, 23.38. HR MALDI-TOF MS: m/z: calcd for $C_{129}H_{131}Cl_3N_8O_{24}$ $[M+Na]^+$: 2303.8239; found: 2303.8261.

5-Aminopentyl *O*-(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-[*O*-(*α*-D-galactopyranosyl)-(1→3)]-2-acetamido-2-deoxy-*β*-D-glucopyranoside (5). According to general procedure for reduction of azido and Troc groups, compound **S13** was prepare from **S12** (35.5 mg, 0.0156 mmol) with zinc metal power (51 mg, 0.78 mmol) in AcOH/Ac_2O/THF (5 mL) and saturated $CuSO_{4(aq)}$ (0.2 mL). The resulting yellow oil was purified by flash chromatography over silica gel (MeOH/DCM, 1/30, v/v) to give **S13** (21.0 mg, 62%) as an amorphous white solid: R_f = 0.33 (MeOH/DCM, 1/15, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{132}H_{140}N_4O_{25}$ $[M+Na]^+$: 2203.9704; found: 2203.9753. According to general procedure for ester and carbamate deprotection, deprotected compound was prepared from **S13** (21.0 mg, 9.63 μmol) with NaOMe in a methanolic solution (0.10 mL, 1.0 M, 0.10 mmol) in a mixture of MeOH/DCM (4 mL). According to general procedure for hydrogenolysis, compound **5** was prepared from the crude product of previous step with $Pd(OH)_2$/C (50 mg, 20 wt.%, Degussa type) in a mixture of ^{t}BuOH/AcOH/H_2O (4 mL). Compound **5** (6.6 mg, 78% over 2 steps) was obtained as an amorphous white solid. ^{1}H NMR (500 MHz, D_2O): δ 5.62 (d, 1H, J = 4 Hz, H-1^{IV}) 5.32 (d, 1H, J = 4 Hz, H-1^{III}), 4.92 (s, 1H, H-1^{II}), 4.58-4.52 (m, 2H, H-1^{I}, H-2^{II}), 4.12-3.99 (m, 3H), 3.97-3.72 (m, 18H), 3.68-3.51 (m, 4H), 3.03 (t, 2H, J = 7.5 Hz), 2.11 (s, 3H), 2.05-2.04 (two s, 6H), 1.73-1.67 (m, 2H), 1.65-1.60 (m, 2H), 1.45-1.38 (m, 2H); ^{13}C NMR (HSQC, 125 MHz, D_2O): δ 101.14 (C-1^{I}), 98.72 (C-1^{IV}), 98.38 (C-1^{II}), 97.92 (C-1^{III}), 78.86, 75.66, 75.13, 73.19, 72.76, 71.30, 70.93, 70.69, 70.37, 70.02, 69.49, 69.24, 68.85, 60.80, 60.72, 60.69, 60.45, 54.90, 53.96, 53.91, 39.52, 28.16, 26.84, 22.41, 22.33, 22.15. HR MALDI-TOF MS: m/z: calcd for $C_{35}H_{62}N_4O_{21}$ $[M+Na]^+$: 897.3804; found: 897.3839.

[a]**Scheme S6**. Synthesis of oligosaccharides **6** and **7**



[a]Reagents and conditions: (a) Zn, AcOH/Ac_2O/THF, $CuSO_{4(aq)}$ (82% for **S15**, 69% for **S20**); (b) $Pd(OH)_2$/C, H_2, ^{t}BuOH/AcOH/H_2O (76%) (c) Et_3SiH, TfOH, DCM, 4Å MS, -78^o C to -40 ^{o}C (74%) (d) NIS, TMSOTf, DCM, 0 ^{o}C (70%); (e) HF·Py, THF followed by Ac_2O, Py (88%, 2 steps); (f) NaOMe, MeOH/DCM followed by $Pd(OH)_2$/C, H_2, ^{t}BuOH/AcOH/H_2O (71%, 2 steps).

5-Aminopentyl *O*-(2-acetamido-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (6). According to general procedure for reduction of azido and Troc groups, compound **S15** was prepare from **S14**[5] (49.0 mg, 0.0441 mmol) with zinc metal power (143 mg, 2.20 mmol) in AcOH/Ac_2O/THF (12 mL) and saturated $CuSO_{4(aq)}$ (0.2 mL). The resulting yellow oil was purified by flash chromatography over silica gel (MeOH/DCM, 1/30, v/v) to give **S15** (41.3 mg, 82%) as an amorphous white solid: R_f = 0.35 (MeOH/DCM, 1/15, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{68}H_{75}N_3O_{13}$ $[M+Na]^+$: 1164.5198; found: 1164.5220. According to general procedure for hydrogenolysis, compound **6** was prepared from **S15** with

$Pd(OH)_2/C$ (100 mg, 20 wt.%, Degussa type) in a mixture of $^tBuOH/AcOH/H_2O$ (10 mL). Compound **6** (14.0 mg, 76%) was obtained as an amorphous white solid. ^1H NMR (500 MHz, D_2O): δ 4.92 (s, 1H, H-1^{II}), 4.58 (d, 1H, J = 4 Hz, H-2^{II}), 4.52 (d, 1H, J = 6.5 Hz, H-1^{I}), 3.95-3.82 (m, 5H, H-$6e^{I}$, H-3^{II}, H-$6a^{II}$, H-$6e^{II}$ and C*H*H-Linker), 3.77-3.72 (m, 4H, H-2^{I}, H-3^{I}, H-4^{I} and H-$6a^{I}$), 3.64-3.60 (m, 1H, C*H*H-Linker), 3.57-3.46 (m, 3H, H-5^{I}, H-4^{II} and H-5^{II}), 3.01 (t, 2H, J = 8.3 Hz, CH_2-Linker), 2.09 (s, 3H), 2.06 (s, 3H), 1.73-1.66 (m, 2H, CH_2-Linker), 1.65-1.59 (m, 2H, CH_2-Linker), 1.45-1.40 (m, 2H, CH_2-Linker); ^{13}C NMR (HSQC, 125 MHz, D_2O): δ 103.79 (C-1^{I}), 102.11 (C-1^{II}), 81.59 (C-4^{I}), 79.22 (C-5^{II}), 77.23 (C-5^{I}), 75.01 (C-3^{I}), 74.77 (C-3^{II}), 72.88, 69.32 (C-4^{II}), 63.00 (C-$6^{I\ and\ II}$), 58.25 (C-2^{I}), 55.90 (C-2^{II}), 42.13, 30.82, 29.11, 25.03, 24.81, 24.77. HR MALDI-TOF MS: m/z: calcd for $C_{21}H_{39}N_3O_{11}$ $[M+Na]^+$: 532.2482; found: 532.2521.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(2-methylnaphthyl)-*β*-D-glucopyranoside (S16).** Acccording to general procedure for reductive opening of a 4,6-benzylidene, compound **S16** was prepared from a mixture of compound **S14**[5] (265 mg, 0.239 mmol) and 4 Å molecular sieves (400 mg) in DCM (7.9 mL) with triethylsilane (95 μL, 0.59 mmol) and triflic acid (46 μL, 0.52 mmol). The reaction was warmed to -40 ^oC over a period of 1 h. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **S16** (196 mg, 74%) as an amorphous white solid: R_f = 0.31 (EtOAc/hexanes, 1/2, v/v). ^1H NMR (500 MHz, $CDCl_3$): δ 7.84-7.11 (m, 32H), 5.18-5.14 (m, 3H, NC[=O]CH_2Ph and OC*H*HNap), 4.96 (d, 1H, J = 11.5 Hz, OC*H*HNap), 4.66 (d, 1H, J = 12 Hz, OC*H*HNap), 4.59 (s, 1H, H-1^{II}), 4.56-4.43 (m, 5H, NCH_2Ph and three protons from OCH_2Ph), 4.21-4.16 (m, 2H, OCH_2Ph), 3.95 (t, 1H, J = 9.3 Hz, H-4^{I}), 3.87-3.84 (m, 1H, C*H*H-Linker), 3.80-3.68 (m, 4H, H-$6a^{I}$, H-$6e^{I}$, H-2^{II} and H-4^{II}), 3.49-3.37 (m, 6H, H-2^{I}, H-3^{I}, H-5^{I}, H-$6a^{II}$, H-$6e^{II}$ and C*H*H-Linker),

3.28-3.13 (m, 4H, H-3^{II}, H-5^{II} and CH_2-Linker), 2.80 (s, 1H, hydroxyl proton), 1.68-1.46 (m, 4H, two CH_2-Linker); 1.42-1.26 (m, 2H, CH_2-Linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.89, 156.45, 138.02, 137.81, 137.76, 136.91, 136.18, 133.37, 133.05, 128.66, 128.63, 128.54, 128.48, 128.42, 128.10, 128.07, 128.01, 127.95, 127.92, 127.83, 127.78, 127.71, 127.61, 127.38, 126.63, 126.21, 126.07, 125.83, 102.19 (C-1^{I}), 99.56 (C-1^{II}), 81.25 (C-3^{I}), 80.42 (C-3^{II}), 77.02 (C-4^{I}), 75.05, 74.51 (C-5^{I}), 74.34 (C-5^{II}), 73.73, 73.60, 72.20, 70.94 (C-6^{II}), 69.98, 69.09 (C-4^{II}), 68.63 (C-6^{I}), 67.24, 66.24 (C-2^{I}), 61.59 (C-2^{II}), 50.60, 50.34, 47.20, 46.26, 29.27, 27.93, 27.50, 23.27. HR MALDI-TOF MS: m/z: calcd for $C_{64}H_{69}N_7O_{11}$ $[M+Na]^+$: 1134.4953; found: 1134.4979.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-[3-*O*-acetyl-4,6-*O*-di-*tert*-butylsilylene-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*α*-D-galactopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(2-methylnaphthyl)-*β*-D-glucopyranoside (S18).** A mixture of the glycosyl acceptor **S16** (92.5 mg, 0.0833 mmol) and donor **S17**[6] (62.7 mg, 0.10 mmol), 4 Å molecular sieves (250 mg) in DCM (3 mL) was stirred under an atmosphere of Ar for 1 h. The reaction was cooled (-20 ^{o}C) and NIS (34 mg, 0.15 mmol) was added followed by the addition of TMSOTf (4.0 μL, 0.022 mmol). After stirring for 1.5 h, the reaction was quenched by the addition of pyridine (0.1 mL). The mixture was filtered, and the filtrate (100 mL) was washed with 10% $Na_2S_2O_3$ (80 mL) and brine (80 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4, v/v) to give **S18** (95.0 mg, 70%) as an amorphous white solid: R_f = 0.33 (EtOAc/hexanes, 2/5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82-7.06 (m, 32H), 6.21 (d, 1H, J = 9.5 Hz, N*H*Troc), 5.20-5.12 (m, 4H, H-1^{III}, NC[=O]CH_2Ph and OC*H*HNap), 5.00 (d, 1H, J = 11.5 Hz, OC*H*HNap), 4.87 (d, 1H, J = 12.5 Hz, OC*H*HPh), 4.77 (dd, 1H, J = 2,5 Hz and 11 Hz,

H-3^{III}), 4.69-4.33 (m, 11H, H-1^{II} , H-2^{III}, H-4^{III}, OC*H*$_2$CCl$_3$, NC*H*$_2$Ph and four proton from OC*H*$_2$Ph), 4.22-4.17 (m, 2H, H-1^{I} and OC*H*HPh), 3.97-3.83 (m, 5H, H-4^{I}, H-6a^{I}, H-6e^{I}, H-4^{II} an C*H*H-Linker), 3.72 (s, 3H, H-2^{II}, H-6a^{III} and H-6e^{III}), 3.46-3.19 (m, 10H, H-2^{I}, H-3^{I}, H-5^{I}, H-3^{II}, H-6a^{II}, H-6e^{II}, H-5^{III} and three protons from C*H*$_2$-Linker), 2.64 (m, 1H, H-5^{II}), 2.08 (s, 3H), 1.66-1.48 (m, 4H, two C*H*$_2$-Linker); 1.42-1.28 (m, 2H, C*H*$_2$-Linker), 1.03 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.30, 156.87, 156.41, 154.48, 138.20, 138.09, 137.16, 136.42, 136.19, 133.35, 133.03, 129.00, 128.76, 128.70, 128.62, 128.45, 128.39, 128.12, 128.08, 128.04, 127.99, 127.86, 127.63, 127.60, 127.45, 126.41, 126.21, 126.06, 125.93, 102.33 (C-1^{I}), 100.43 (C-1^{III}), 99.34 (C-1^{II}), 95.84, 80.96 (C-3^{I}), 79.80 (C-3^{II}), 77.44 (C-4^{I}), 77.03 (C-5^{II}), 75.63, 74.99, 74.78 (C-5^{I}), 74.66, 74.34, 73.82, 73.68 (C-4^{II}), 73.33, 71.63 (C-3^{III}), 70.97, 70.47 (C-4^{III}), 70.09, 68.83 (C-6$^{II \text{ and } III}$), 68.37 (C-5^{III}), 67.31, 66.88 (C-6^{I}), 66.42 (C-2^{I}), 60.78 (C-2^{II}), 50.68 , 50.41, 49.65 (C-2^{III}), 47.23, 46.32, 29.85, 29.35, 27.69, 27.42, 27.31, 23.43, 23.35, 21.13, 20.88. HR MALDI-TOF MS: m/z: calcd for $C_{83}H_{99}Cl_3N_8O_{18}Si$ $[M+Na]^+$: 1651.5810; found: 1651.5842.

***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl *O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*α*-D-galactopyranosyl]-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(2-methylnaphthyl)-*β*-D-glucopyranoside (S19).** To a stirred and cooled (0^{o} C) solution of **S18** (88 mg, 0.054 mmol) in THF (3 mL) was added HF·Py (0.5 mL) under an atmosphere of Ar. After stirring at room temperature for 5 h, the mixture was diluted with DCM (100 mL) and washed with saturated $NaHCO_3$ (2 × 80 mL), brine (80 mL). The organic layer was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The crude product was dissolved in pyridine (2 mL) and acetic anhydride (0.1 mL, 1 mmol) was added. After stirring for 12 h, the reaction mixture was diluted with DCM (100 mL) and washed with

saturated $NaHCO_3$ (2 × 80 mL) and brine (80 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/2, v/v) to give **S19** (74.8 mg, 88% over 2 steps) an amorphous white solid: R_f = 0.29 (EtOAc/hexanes, 1/2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.14 (m, 32H), 6.59 (d, 1H, *J* = 9.5 Hz, N*H*Troc), 5.29 (d, 1H, *J* = 2.5 Hz, H-4^{III}), 5.18-5.14 (m, 4H, H-1^{III}, NC[=O]C*H*$_2$Ph and OC*H*HNap), 5.03 (dd, 1H, *J* = 3.3 Hz and 11.3 Hz, H-3^{III}), 4.97 (d, 1H, *J* = 12 Hz, OC*H*HNap), 4.85 (d, 1H, *J* = 12 Hz, OC*H*HPh), 4.67 (d, 2H, *J* = 12 Hz, OC*H*HPh and OC*H*HCCl$_3$), 4.52-4.36 (m, 7H, H-1^{II}, OC*H*HCCl$_3$, three protons from OC*H*$_2$Ph and NC*H*$_2$Ph), 4.30-4.21 (m, 3H, H-1^{I}, H-2^{III} and OC*H*HPh), 4.01-3.92 (m, 4H, H-4^{I}, H-4^{II}, H-5^{III} and H-6e^{III}), 3.88-3.84 (m, 2H, H-6a^{III} and C*H*H-Linker), 3.78 (br d, 1H, *J* = 2.5 Hz, H-2^{II}), 3.75-3.70 (m, 2H, H-6a^{I} and H-6e^{I}), 3.54-3.37 (m, 6H, H-2^{I}, H-3^{I}, H-5^{I}, H-6a^{II}, H-6e^{II} and C*H*H-Linker), 3.26-3.22 (m, 3H, H-3^{II}, C*H*$_2$-Linker), 2.77-2.75 (m, 1H, H-5^{II}), 2.14 (s, 3H), 1.98 (s, 3H), 1.88 (s, 3H), 1.67-1.47 (m, 4H, two C*H*$_2$-Linker); 1.42-1.26 (m, 2H, C*H*$_2$-Linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.05, 170.61, 170.42, 170.38, 156.88, 156.35, 154.56, 138.24, 138.09, 138.02, 136.96, 136.12, 133.36, 133.05, 129.12, 128.81, 128.74, 128.70, 128.61, 128.56, 128.43, 128.10, 128.07, 128.04, 127.99, 127.94, 127.84, 127.62, 127.52, 127.45, 126.45, 126.23, 126.03, 125.96, 102.33 (C-1^{I}), 100.70 (C-1^{III}), 99.40 (C-1^{II}), 95.80, 80.75 (C-3^{I}), 78.84 (C-3^{II}), 77.13 (C-4^{I}), 75.66 (C-5^{II}), 75.06, 74.80 (C-4^{II}), 74.65, 74.37, 73.82 (C-5^{I}), 73.27, 70.60, 70.10, 68.99 (C-6^{I}), 68.88 (C-3^{III}), 68.38 (C-6^{II}), 67.99 (C-5^{III}), 67.49 (C-4^{III}), 67.30, 66.44 (C-2^{I}), 62.20 (C-6^{III}), 60.50 (C-2^{II}), 50.68 (C-2^{III}), 50.41, 47.23, 46.30, 31.08, 29.86, 29.35, 28.00, 27.58, 23.35, 20.88, 20.74. HR MALDI-TOF MS: m/z: calcd for $C_{79}H_{87}Cl_3N_8O_{20}$ $[M+Na]^+$: 1595.5000; found: 1595.5023.

5-Aminopentyl *O*-(2-acetamido-2-deoxy-*α*-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-*β*-D-mannopyranosyl)-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (7). According to general procedure for reduction of azido and Troc groups, compound **S20** was prepare from **S19** (35.2 mg, 0.0224 mmol) with zinc metal power (73 mg, 1.1 mmol) in AcOH/Ac_2O/THF (7 mL) and saturated $CuSO_{4(aq)}$ (0.2 mL). The resulting yellow oil was purified by flash chromatography over silica gel (MeOH/DCM, 1/30, v/v) to give **S20** (22.7 mg, 69%) as an amorphous white solid: R_f = 0.32 (MeOH/DCM, 1/15, v/v). HR MALDI-TOF MS: m/z: calcd for $C_{82}H_{96}N_4O_{21}$ $[M+Na]^+$: 1495.6465; found: 1495.6479. According to general procedure for ester and carbamate deprotection, deprotected compound was prepared from **S20** (22.7 mg, 0.0154 mmol) with NaOMe in a methanolic solution (0.16 mL, 1.0 M, 0.16 mmol) in a mixture of MeOH/DCM (4 mL). According to general procedure for hydrogenolysis, compound **7** was prepared from the crude product of previous step with $Pd(OH)_2/C$ (50 mg, 20 wt.%, Degussa type) in a mixture of ^{t}BuOH/AcOH/H_2O (5 mL). Compound **7** (8.3 mg, 76% over 2 steps) was obtained as an amorphous white solid. ^{1}H NMR (500 MHz, D_2O): δ 5.32 (d, 1H, J = 4 Hz, H-1^{III}), 4.92 (s, 1H, H-1^{II}), 4.55-4.51 (m, 2H, H-1^{I} and H-2^{II}), 4.21 (dd, 1H, J = 4.3 Hz and 11.3 Hz, H-2^{III}), 4.09 (dd, 1H, J = 4.8 Hz and 9.3 Hz, H-3^{II}), 4.03-4.01 (m, 2H, H-4^{III} and H-5^{III}), 3.96-3.88 (m, 5H, H-6e^{I}, H-6a^{II}, H-6e^{II}, H-3^{III} and C*H*HLinker), 3.79-3.70 (m, 7H, H-2^{I}, H-3^{I}, H-4^{I}, H-6a^{I}, H-4^{II}, H-6a^{III} and H-6e^{III}), 3.64-3.52 (m, 3H, H-5^{I}, and H-5^{II} and C*H*HLinker), 3.01 (t, 2H, J = 7.8 Hz, CH_2-Linker), 2.09 (s, 3H), 2.06 (s, 6H), 1.75-1.66 (m, 2H, CH_2-Linker), 1.65-1.59 (m, 2H, CH_2Linker), 1.45-1.39 (m, 2H, CH_2Linker); ^{13}C NMR (HSQC, 125 MHz, D_2O): δ 101.34 (C-1^{I}), 99.41 (C-1^{II}), 98.49 (C-1^{III}), 79.14 (C-4^{I}), 75.38 (C-5^{I}), 74.61 (C-5^{II}), 73.24 (C-3^{I}), 72.91 (C-3^{II}), 72.50 (C-4^{II}), 71.88 (C-5^{III}), 70.32, 68.62 (C-4^{III}), 67.64 (C-3^{III}), 61.38 (C-6^{III}), 60.74 (C-6^{II}), 60.29 (C-6^{I}), 55.38 (C-2^{I}), 53.84 (C-2^{II}), 49.95 (C-2^{III}), 39.48, 28.24, 26.55, 22.28,

22.24, 22.15. HR MALDI-TOF MS: m/z: calcd for $C_{29}H_{52}N_4O_{16}$ $[M+Na]^+$: 735.3276; found: 735.3301.

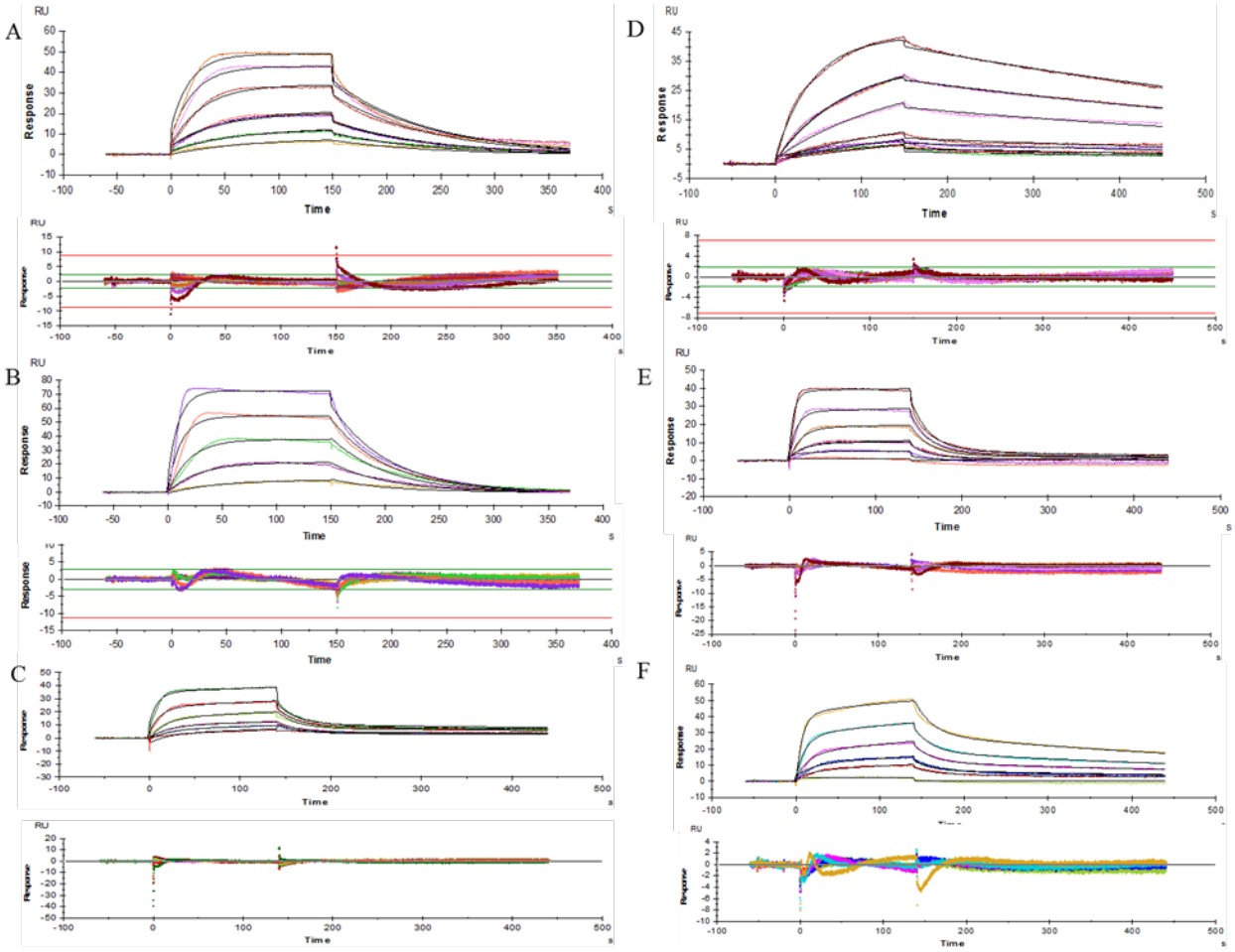


Figure S2. Sensorgrams and corresponding residual plots of the concentration-dependent kinetic analysis for the binding of compounds **1** and **3-7** with immobilized C-terminal PlyL (3000 Ru). A) **1** at concentrations from the bottom to top of 6.25, 12.5, 25, 50, 80 and 100 µM, fitting with 1:1 binding model. B) **3** at concentrations from the bottom to top of 0.2, 1, 2, 4 and 5 µM, fitting with 1:1 binding model. C) **4** at concentrations from the bottom to top of 15.6, 62.5, 125, 250,500 and 1000 µM, fitting with two-state binding model. D) **5** at concentrations from the bottom to top of 3.12, 6.25, 12.5, 25, 50 and 100 µM, fitting with 1:1 binding model. E) **6** and F) **7** at concentrations from the bottom to top of 7.8, 31.2, 62.5, 125, 250 and 500 µM, fitting with two-state binding model.

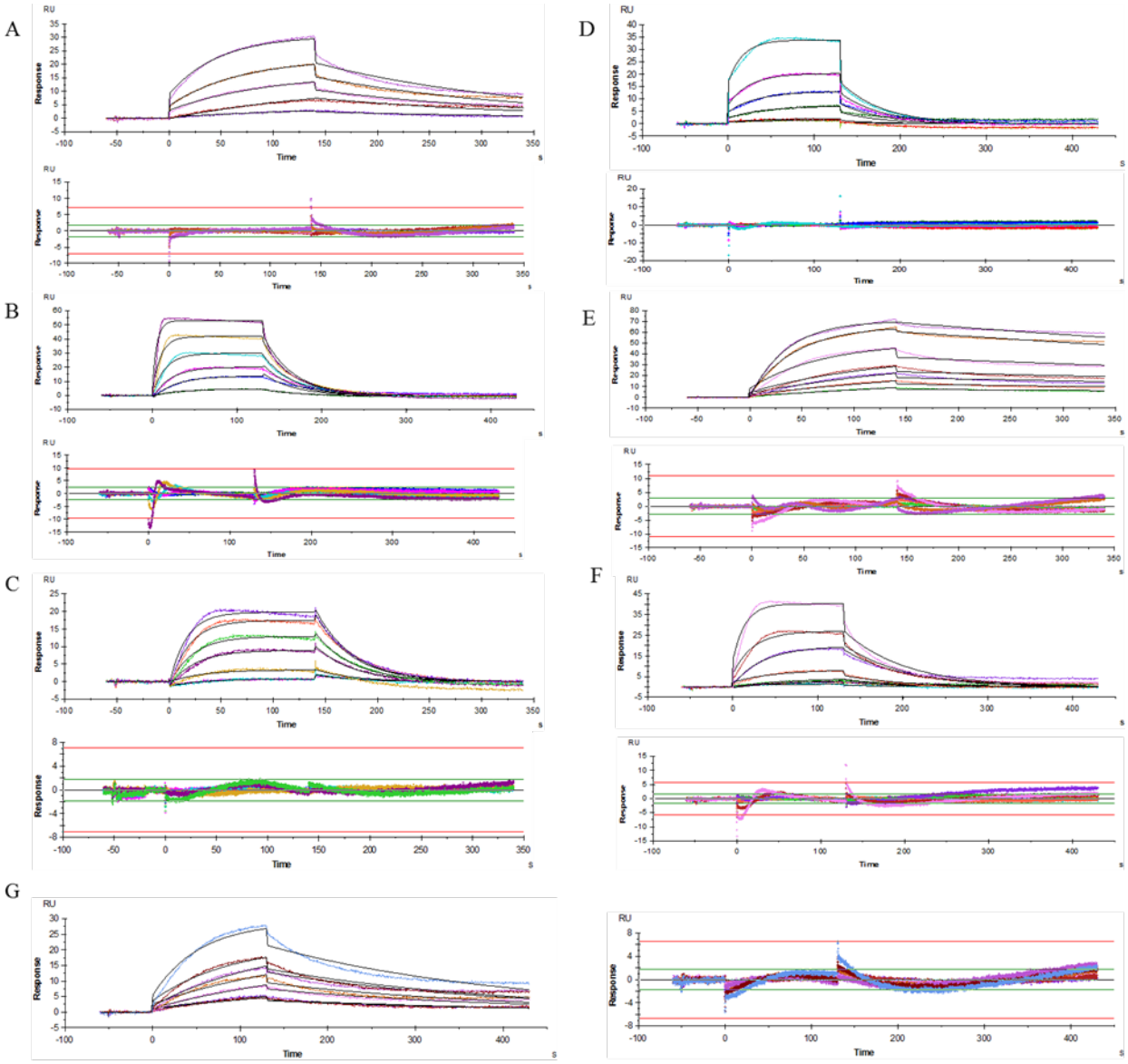


Figure S3. Sensorgrams and corresponding residual plots of the concentration-dependent kinetic analysis for the binding of compounds **1-7** with immobilized C-terminal PlyG (3500 Ru). A) **1** at concentrations from the bottom to top of 3.12, 6.25, 30, 50, 80 µM, fitting with 1:1 binding model. B) **2** at concentrations from the bottom to top of 0.78, 3.12, 6.25, 12.5, 25 and 50 µM, fitting with 1:1 binding model. C) **3** at concentrations from the bottom to top of 0.1, 0.5, 1.5, 2, 3 and 4 µM, fitting with 1:1 binding model. D) **4** at concentrations from the bottom to top of 3.9, 7.8, 31.2, 62.5, 125, and 250 µM, fitting with two-state binding model. E) **5** at concentrations from the bottom to top of 3.12, 6.25, 12.5, 25, 50, 80 and 100 µM, fitting with 1:1 binding model. F) **6** at concentrations from the bottom to top of 1.56, 3.12, 6.25, 25, 50, 100 and 200 µM, fitting with two-state binding model. G) **7** at concentrations from the bottom to top of 1.56, 3.12, 6.25, 12.5 and 50 µM, fitting with two-state binding model.

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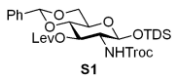
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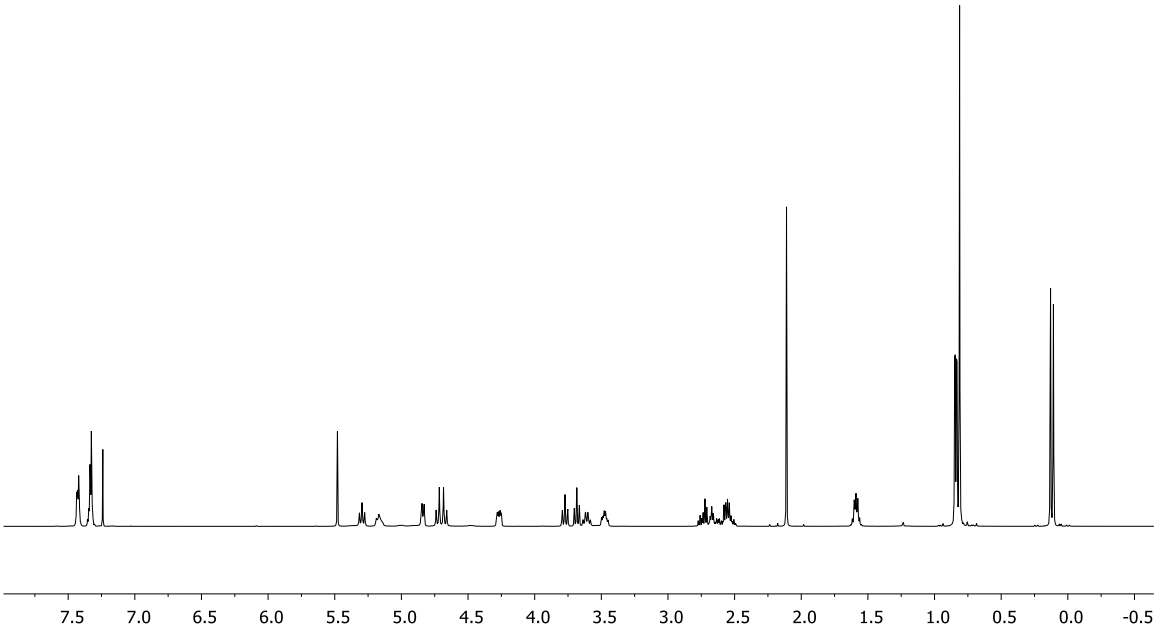
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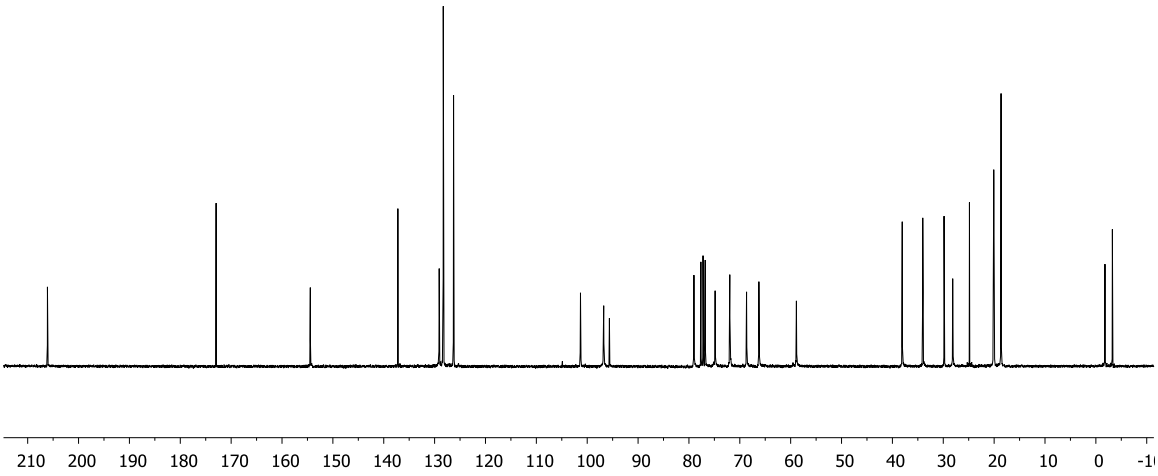
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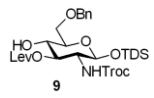
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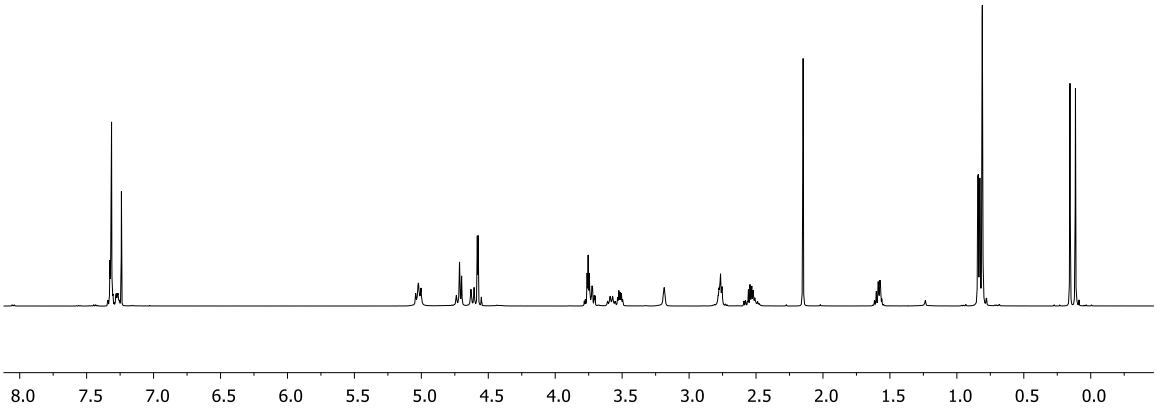
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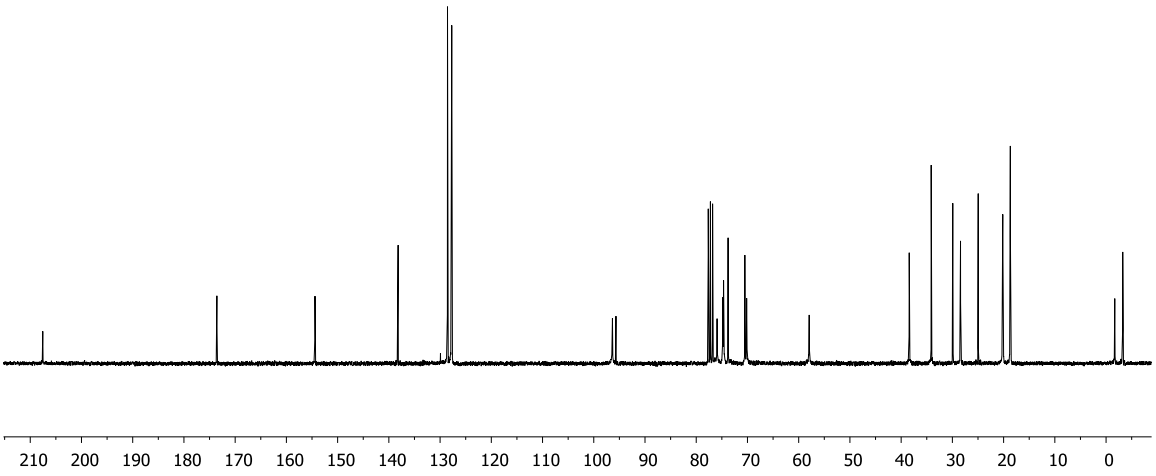
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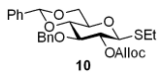
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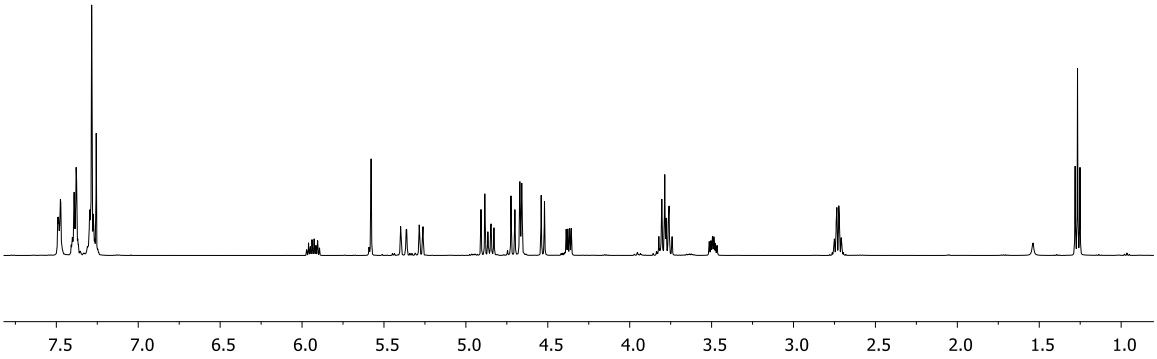
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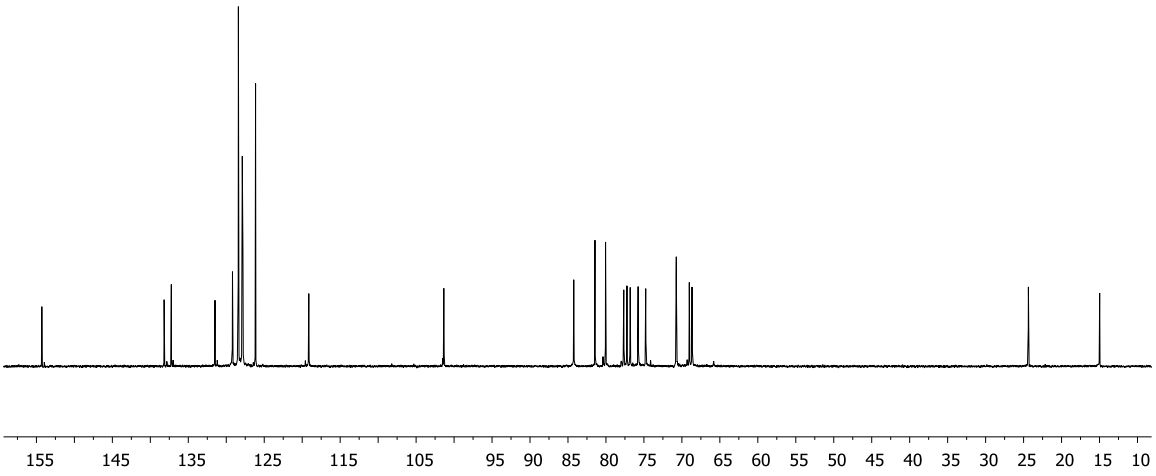
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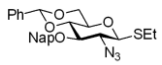
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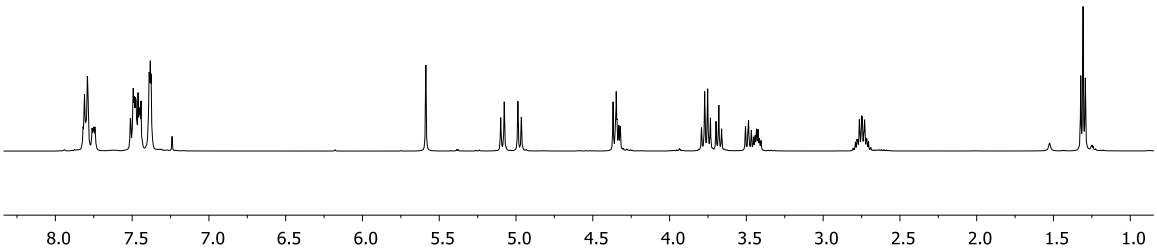
SEt
N3

S2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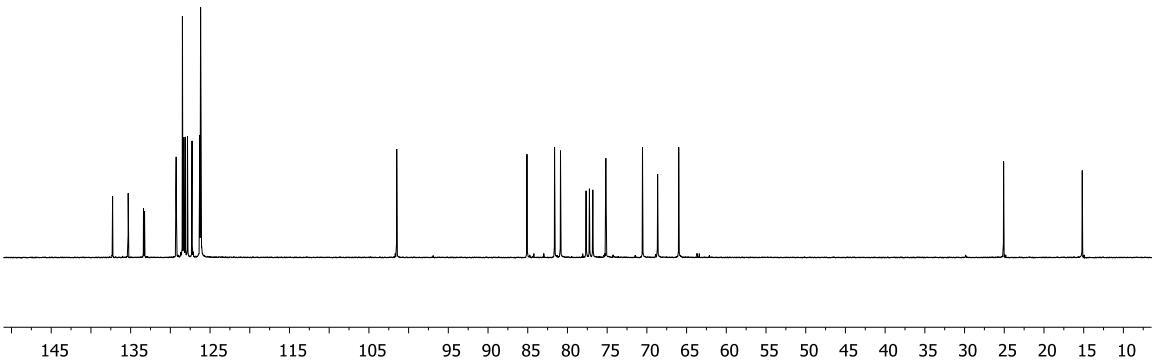
1.0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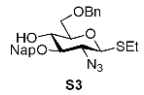
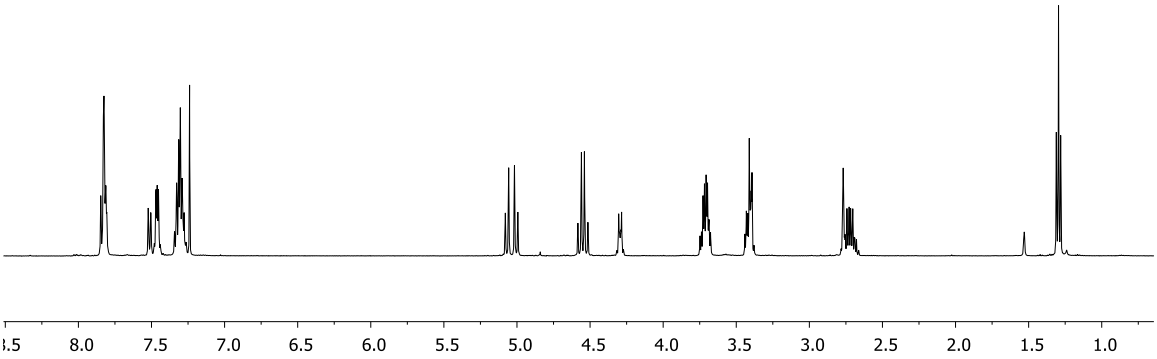

OBn
HO
O
NapO
SEt
N3

S3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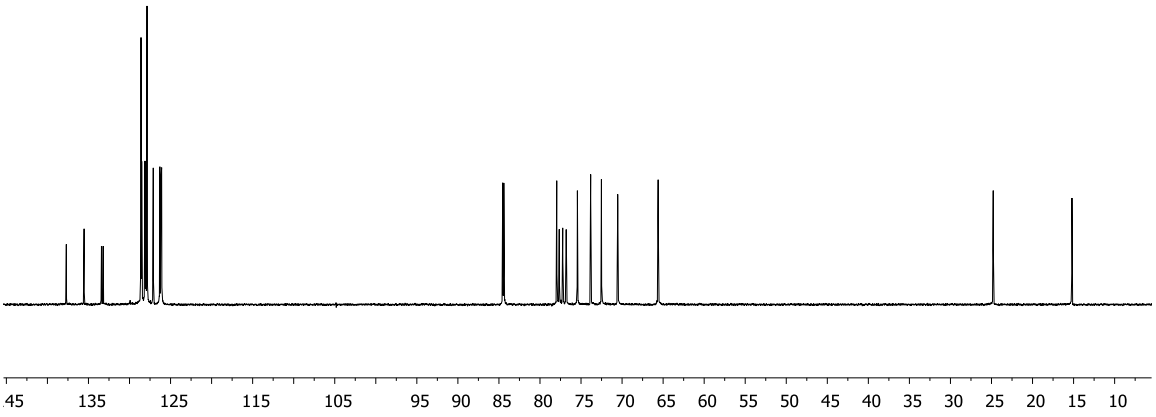
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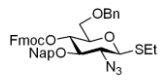
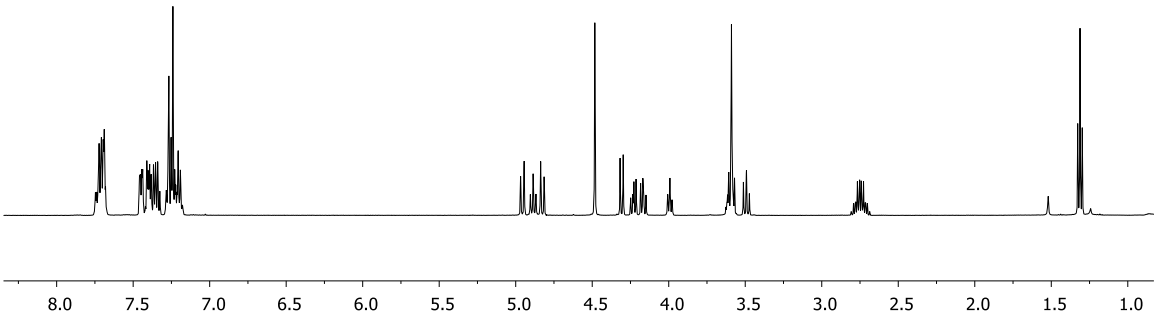

OBn
FmocO
NapO
O
SEt
N3

S4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4.0
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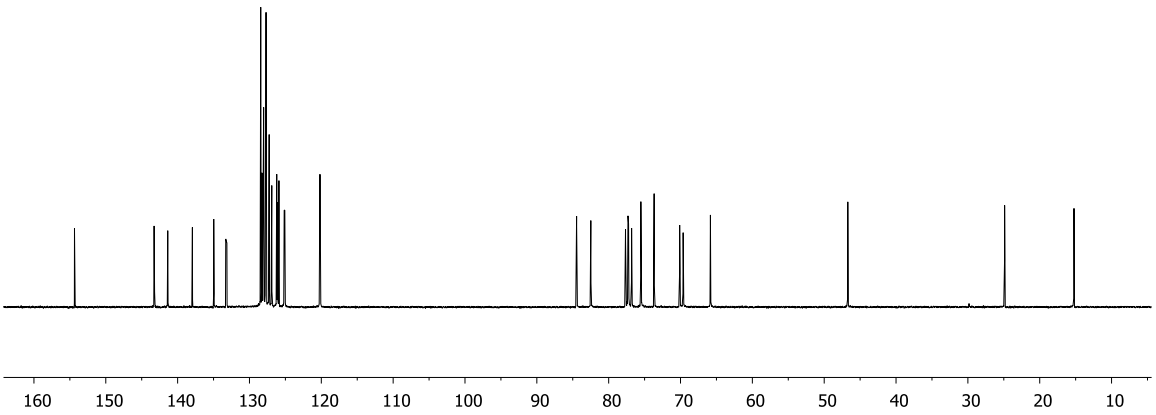
3.0
2.5
2.0
1.5
1.0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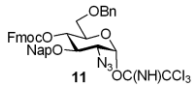
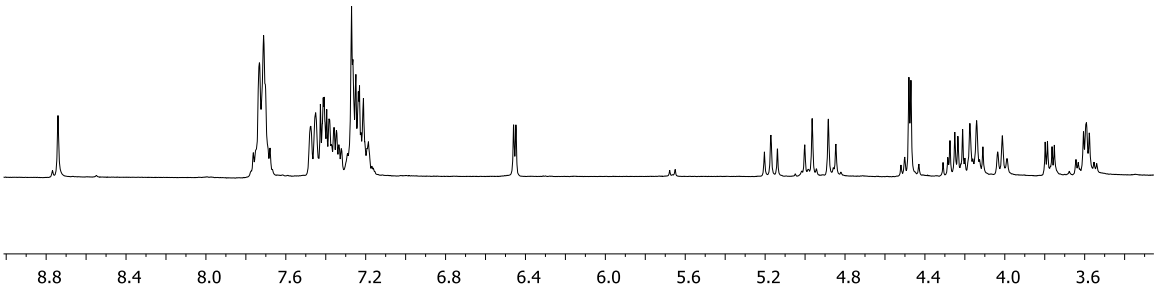

OBn
FmocO
NapO
O
N3
OC(NH)CCl3
11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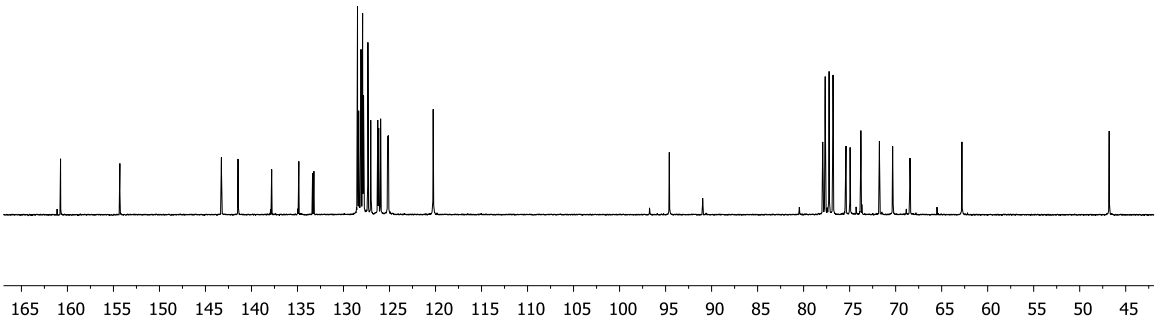
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6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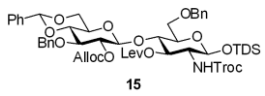
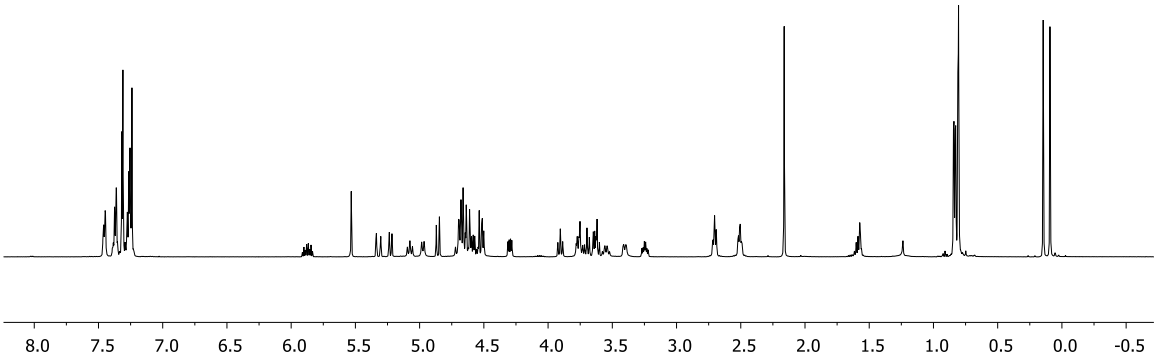

Ph
BnO
AllocO
LevO
OBn
OTDS
NHTroc

15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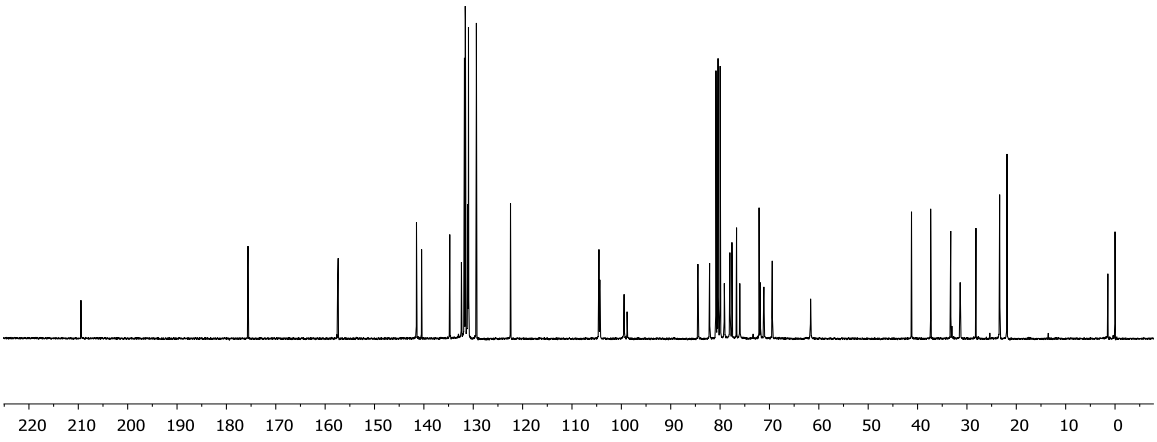
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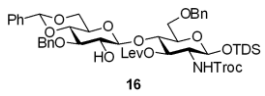
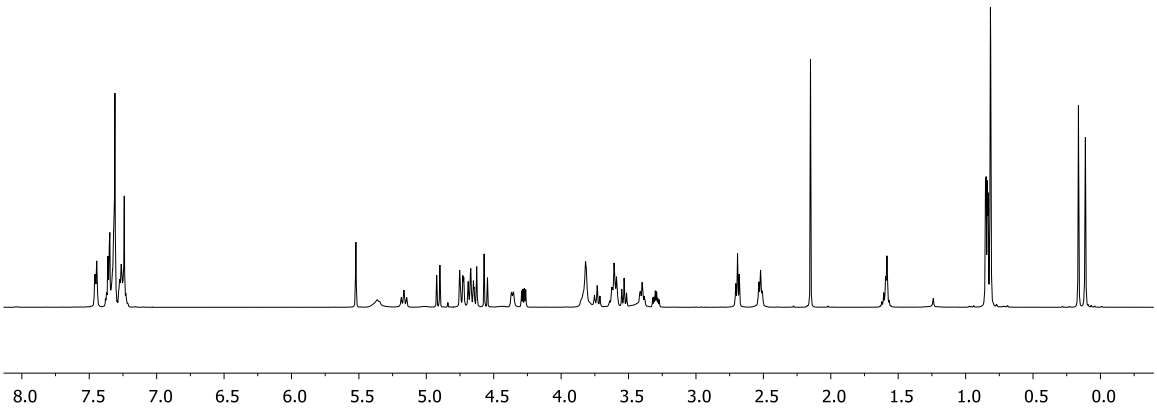

Ph
BnO
HO
LevO
OBn
OTDS
NHTroc

16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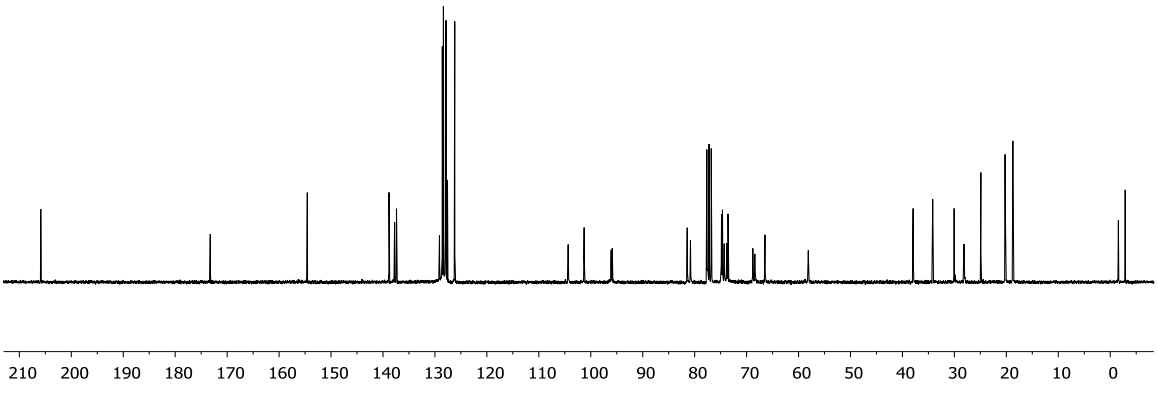
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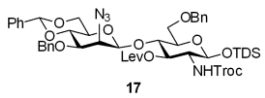
Ph
O
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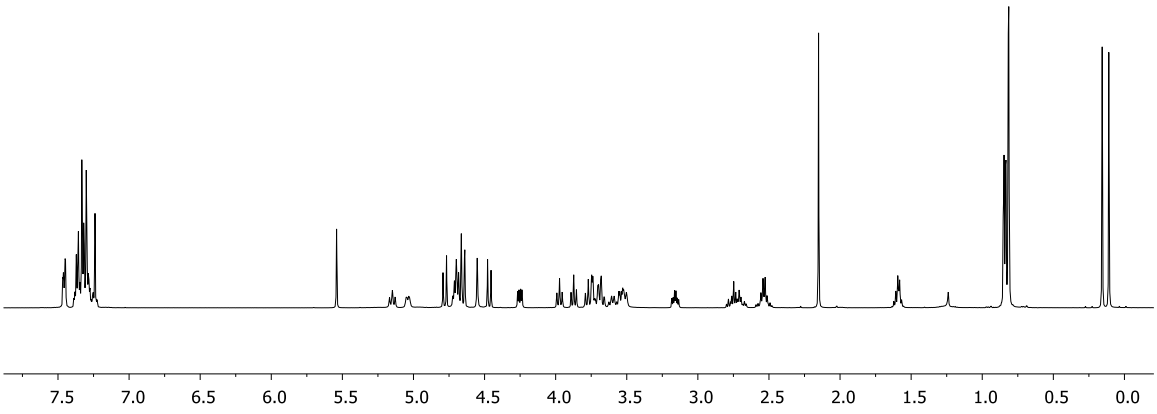
BnO
N3
O
O
LevO
OBn
O
OTDS
NHTroc

17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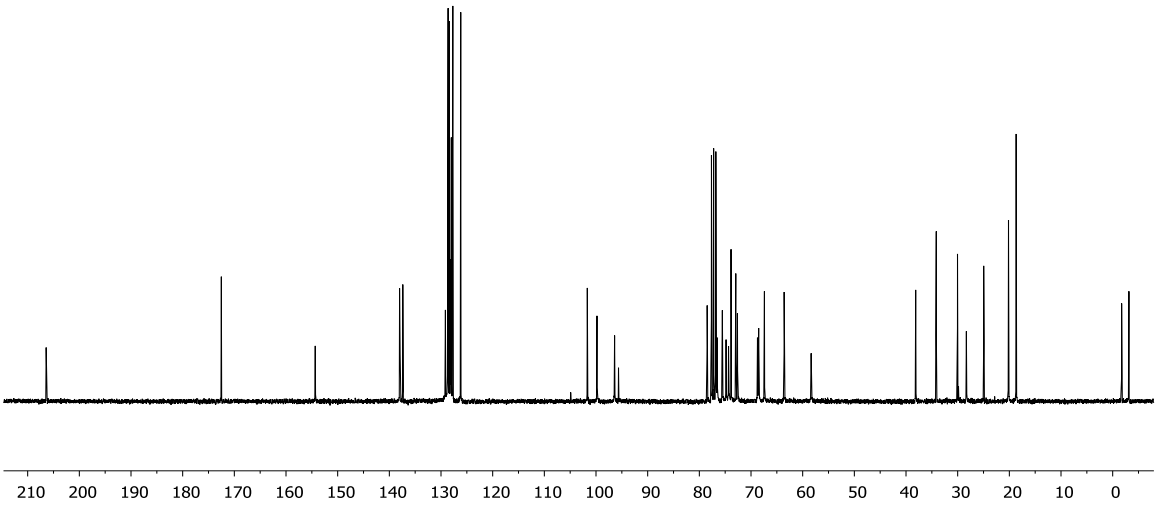
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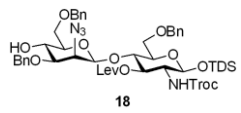
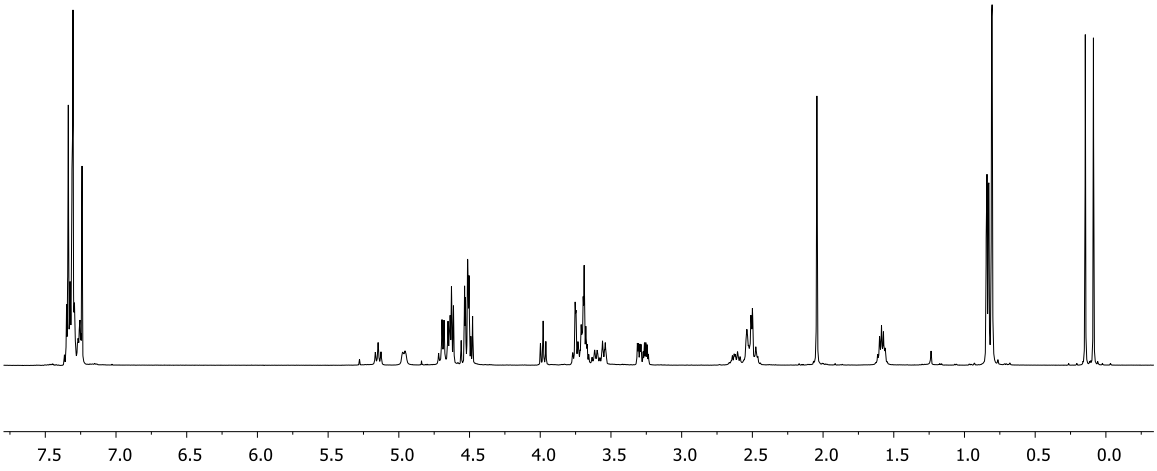

OBn
N3
HO
BnO
O
LevO
OBn
O
OTDS
NHTroc

18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4.5
4.0
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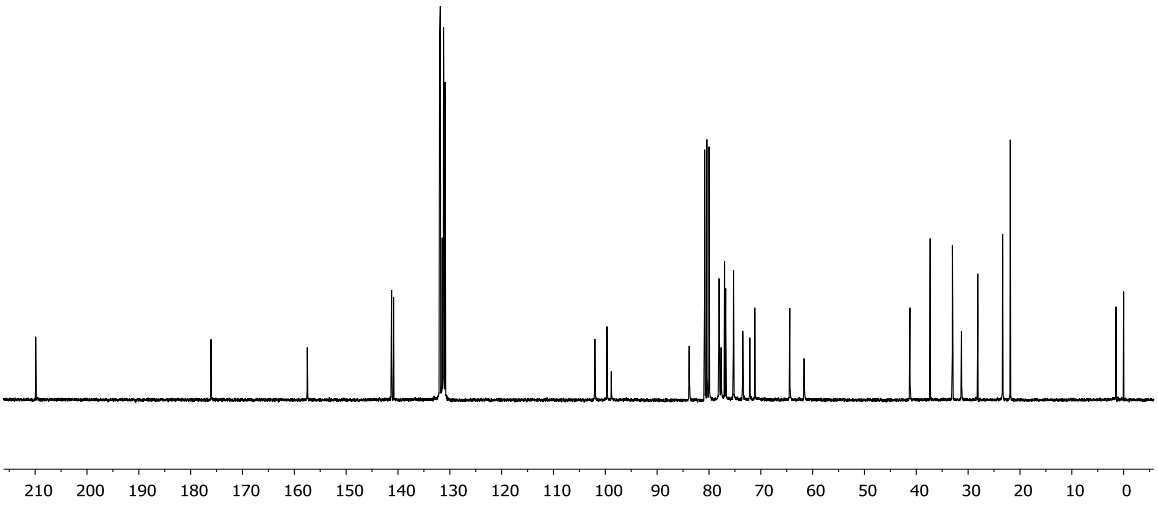
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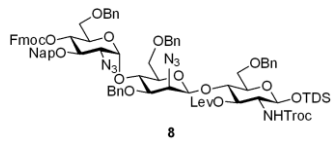
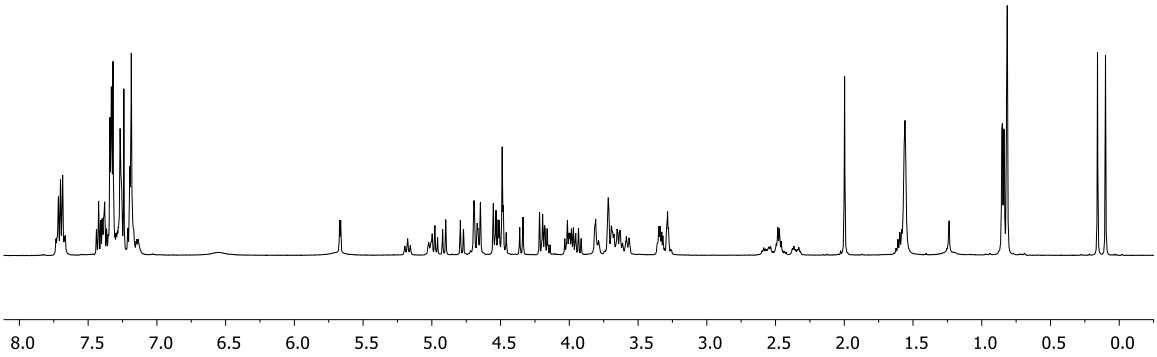

OBn
FmocO
NapO
N3
OBn
N3
OBn
BnO
LevO
OTDS
NHTroc

8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7.0
6.5
6.0
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4.5
4.0
3.5
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2.0
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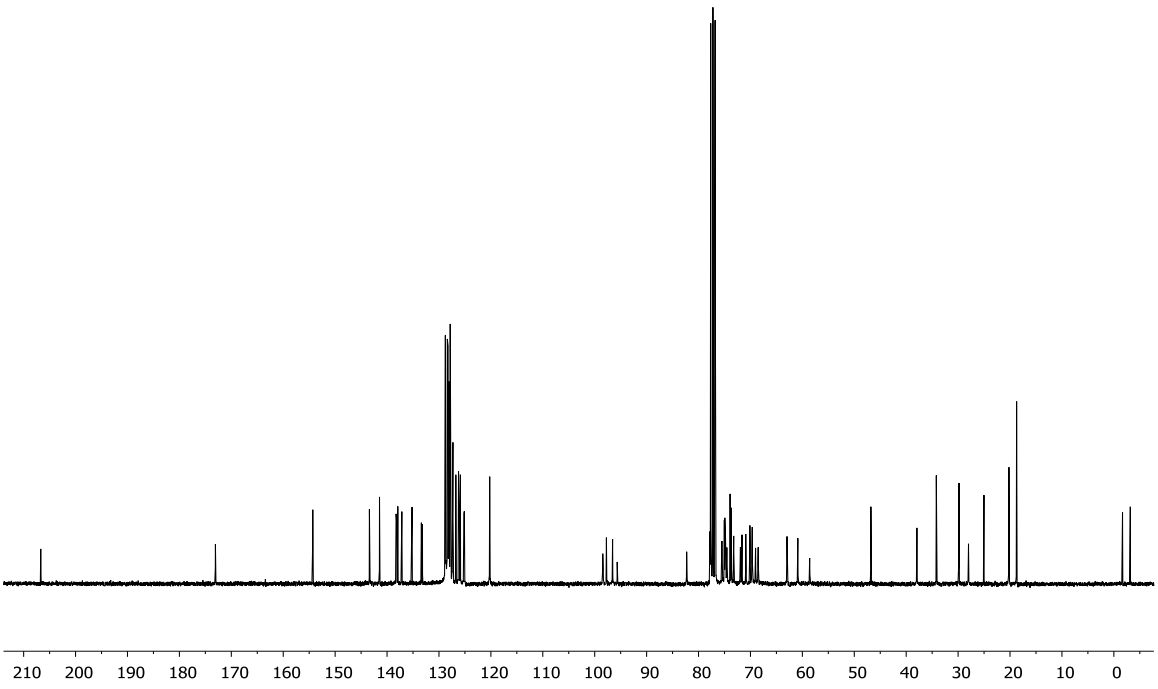
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10
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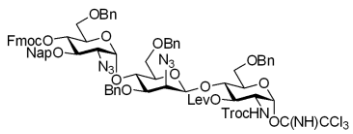
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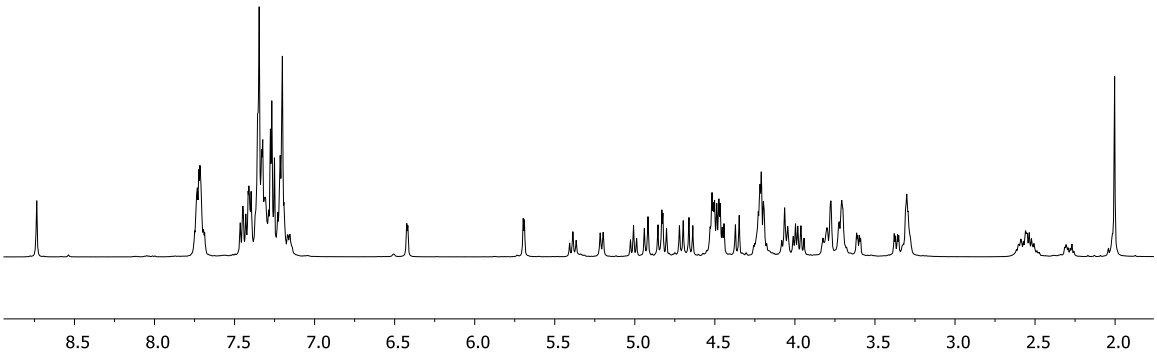
FmocO
NapO
N3
OBn
N3
OBn
BnO
O
LevO
TrocHN
OC(NH)CCl3

20


8.5
8.0
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7.0
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6.0
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5.0
4.5
4.0
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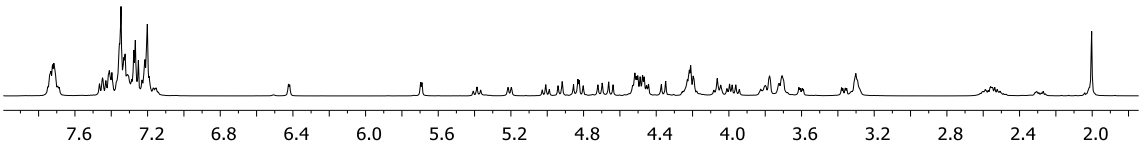
3.0
2.5
2.0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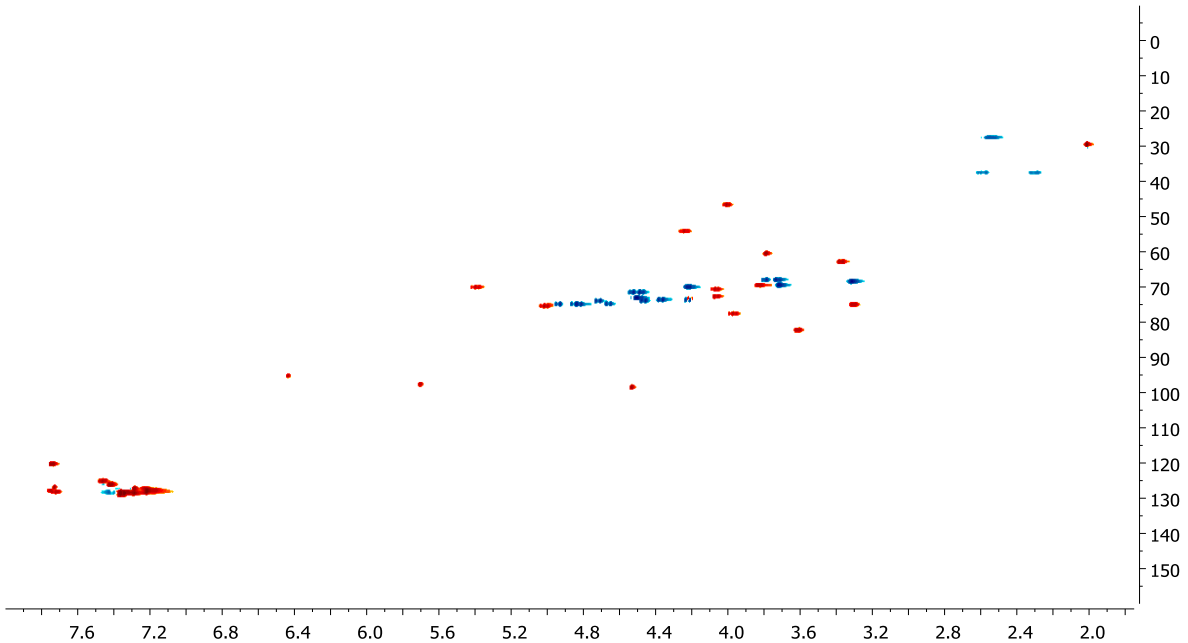
2.0


0
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150
7.6
7.2
6.8
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3.6
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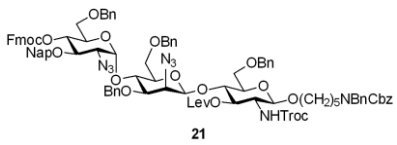
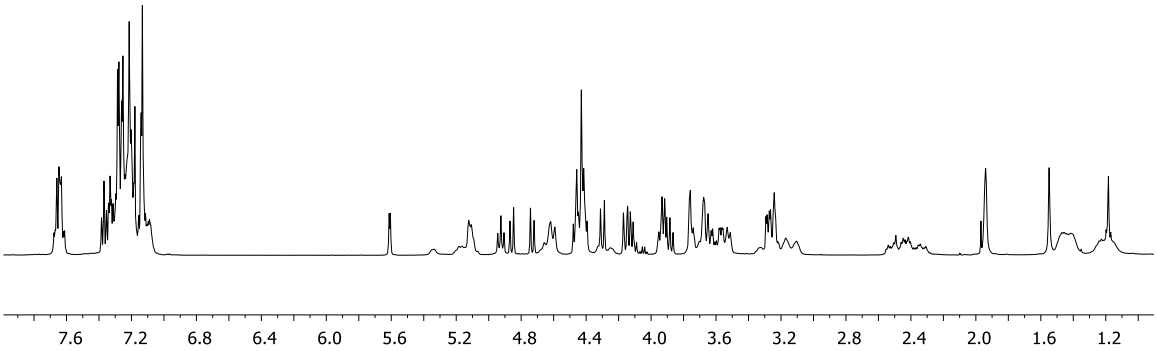
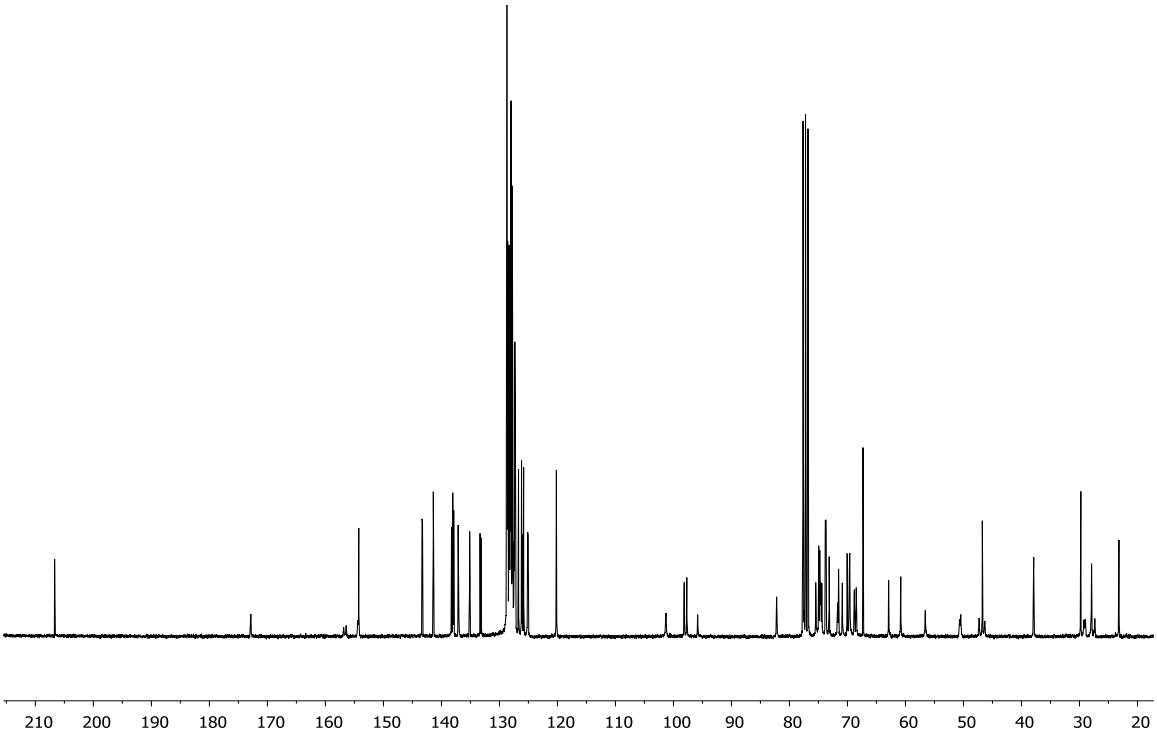
2.4
2.0


OBn
FmocO
NapO
N3
O
BnO
OBn
N3
O
OBn
O
LevO
O
O(CH2)5NBnCbz
NHTroc

21


7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2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80
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50
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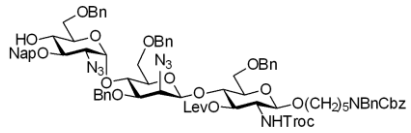
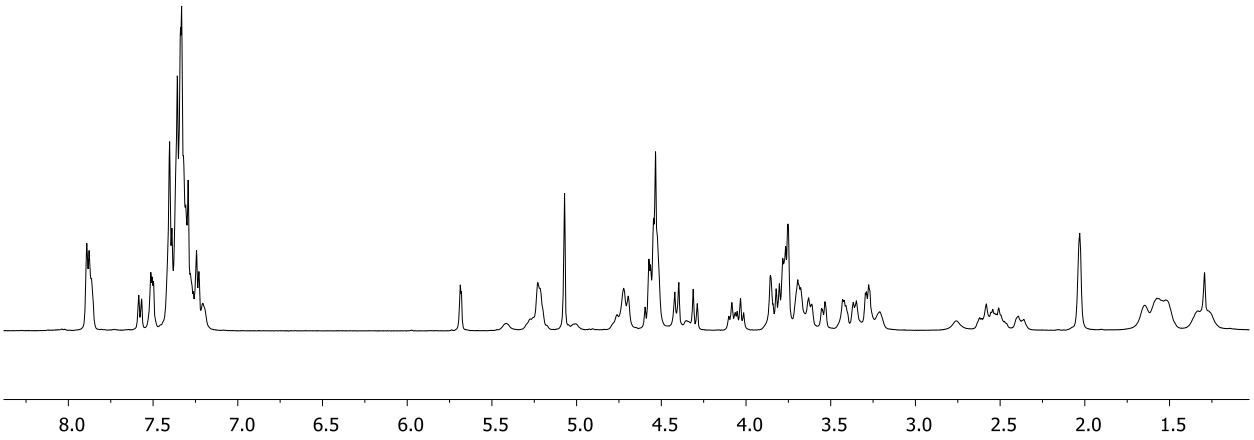
30
20


OBn
HO
NapO
N3
OBn
N3
OBn
O
BnO
O
LevO
O
O(CH2)5NBnCbz
NHTroc

22


8.0
7.5
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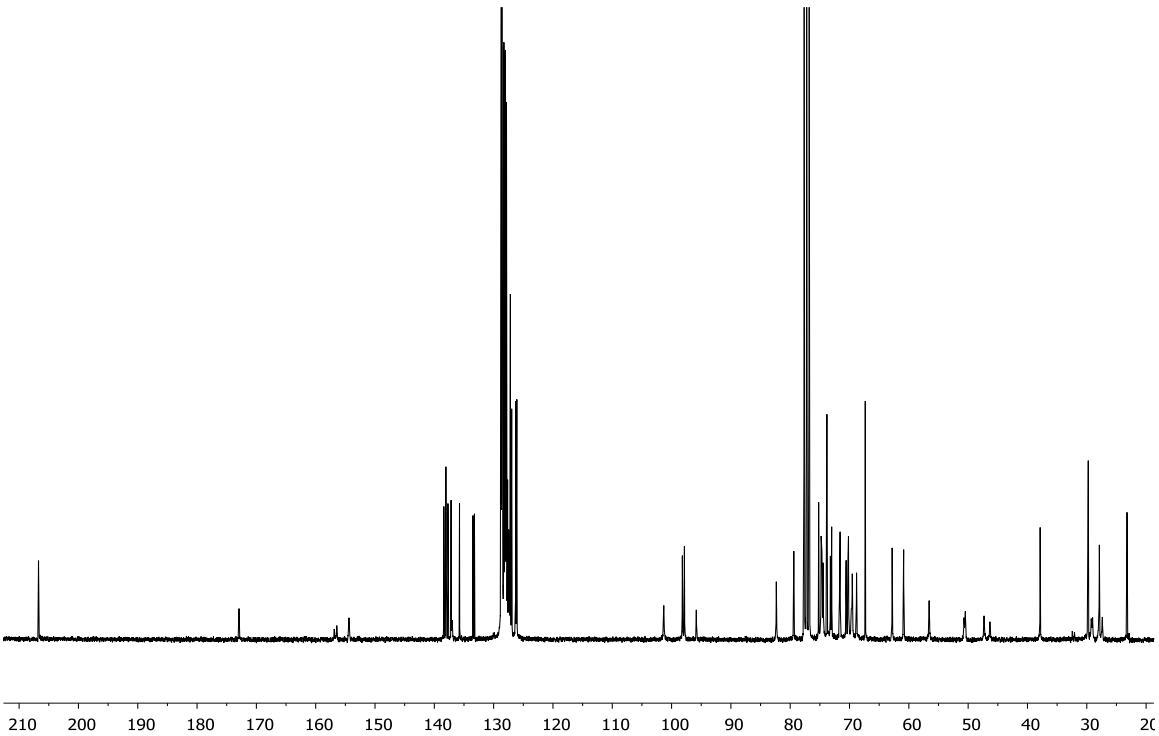
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


210
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180
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100
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80
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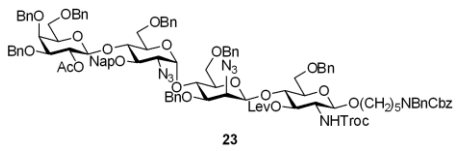
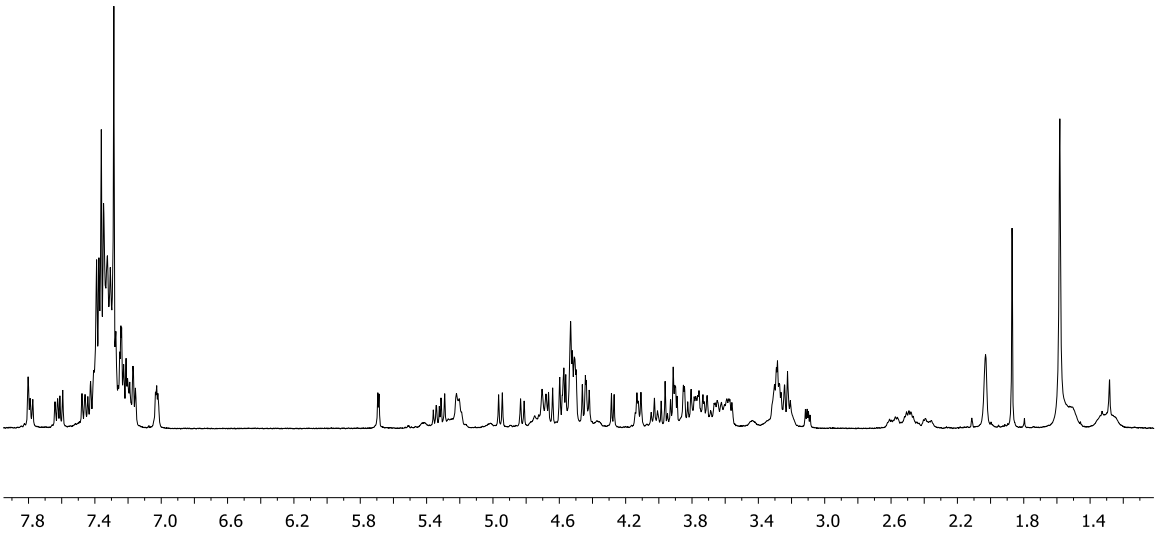
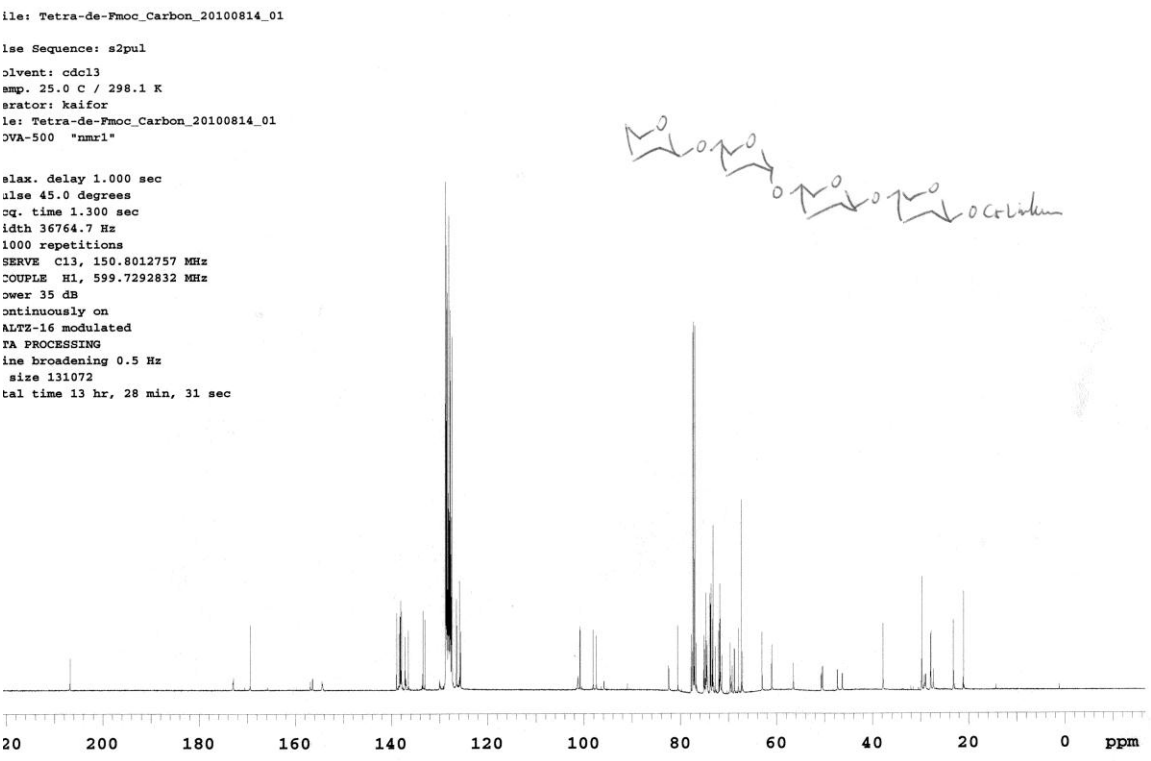
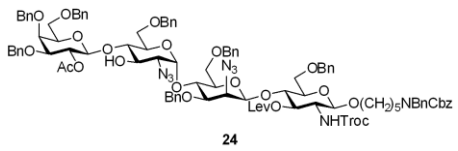
30


BnO
OBn
OBn
BnO
AcO
NapO
OBn
N3
N3
OBn
BnO
LevO
O(CH2)5NBnCbz
NHTroc

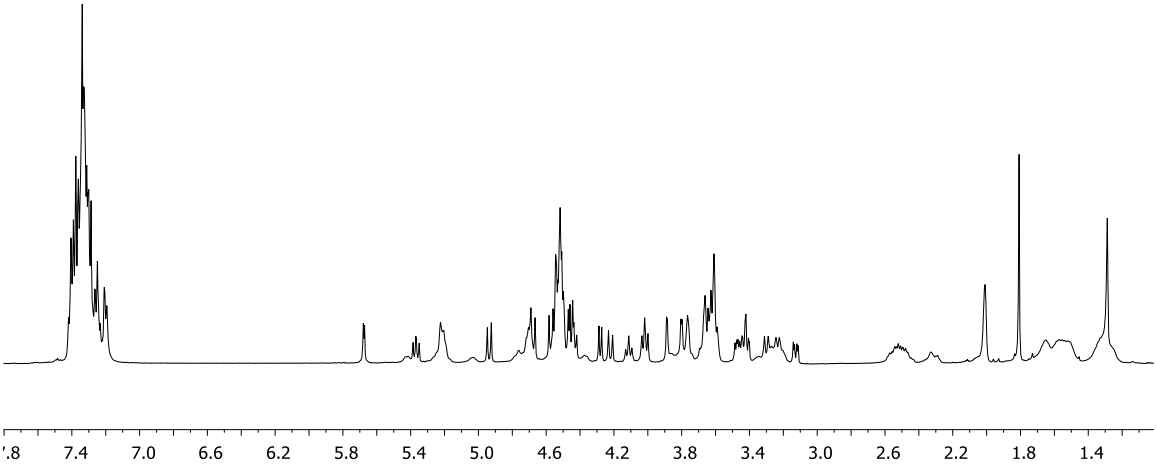
23

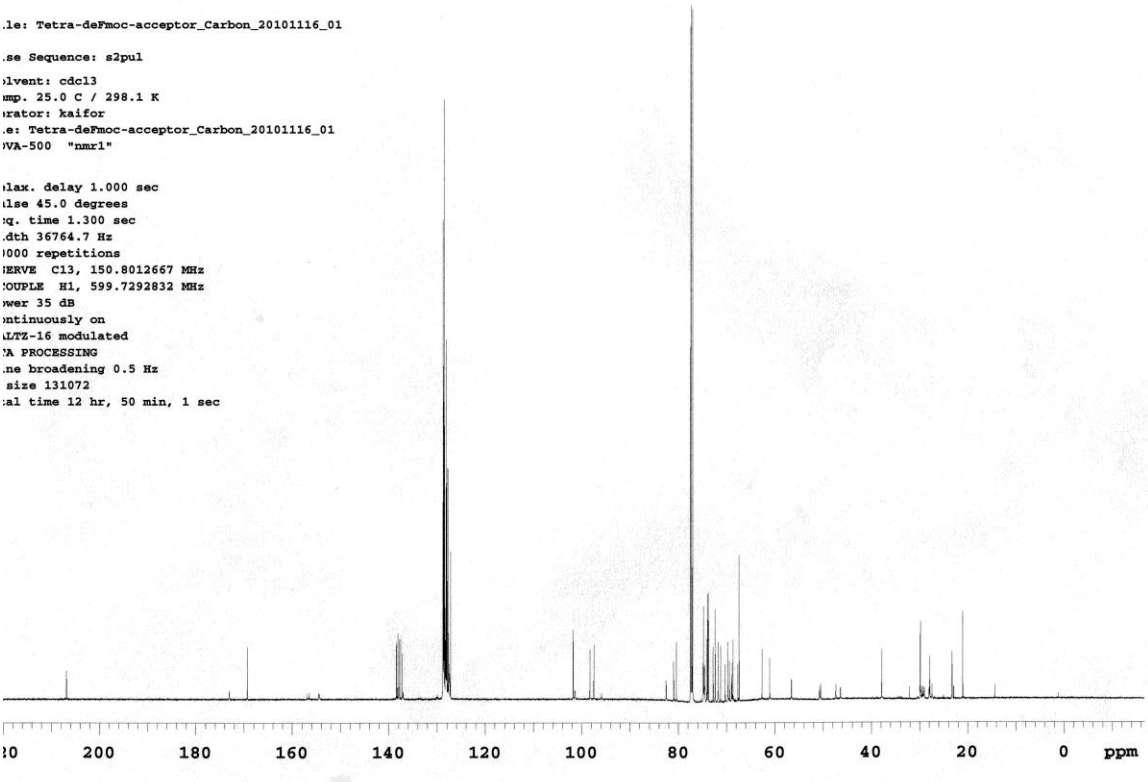

7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4

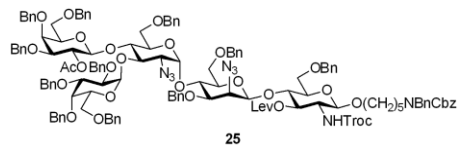

ile: Tetra-de-Fmoc_Carbon_20100814_01
lse Sequence: s2pul
olvent: cdcl3
emp. 25.0 C / 298.1 K
erator: kaifor
le: Tetra-de-Fmoc_Carbon_20100814_01
OVA-500 "nmr1"
elax. delay 1.000 sec
ulse 45.0 degrees
oq. time 1.300 sec
idth 36764.7 Hz
1000 repetitions
SERVE C13, 150.8012757 MHz
COUPLE H1, 599.7292832 MHz
ower 35 dB
ontinuously on
ALTZ-16 modulated
TA PROCESSING
ine broadening 0.5 Hz
size 131072
tal time 13 hr, 28 min, 31 sec
20
200
180
160
140
120
100
80
60
40
20
0
ppm


BnO
OBn
AcO
HO
N3
LevO
NHTroc
O(CH2)5NBnCbz

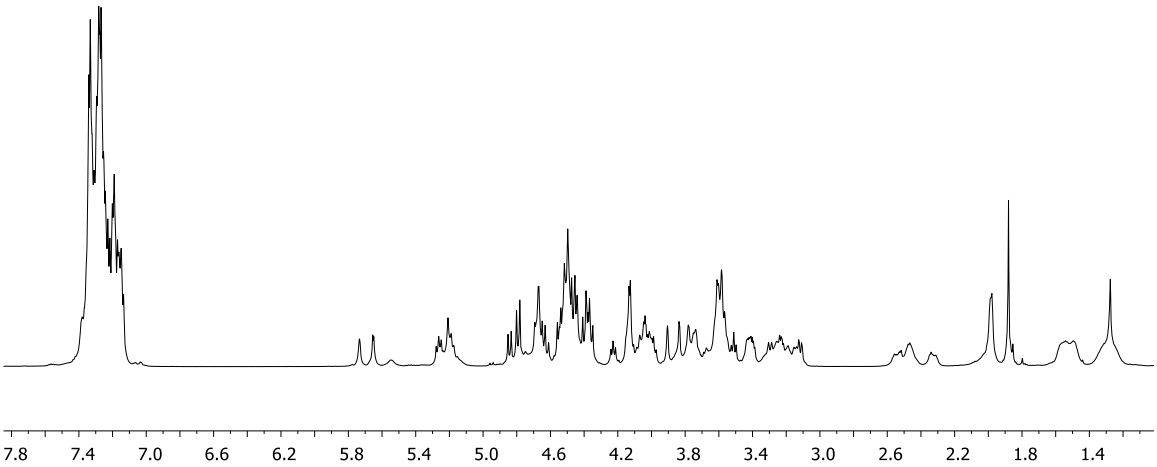
24

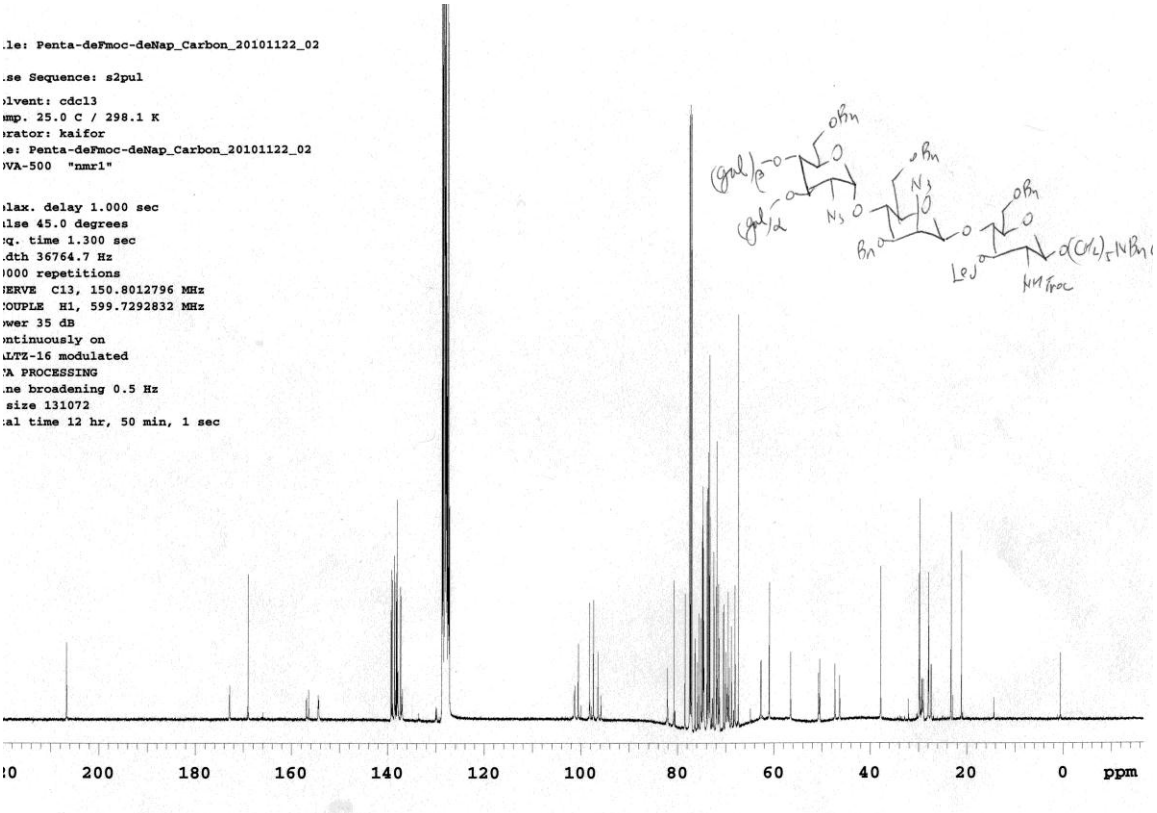

7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4

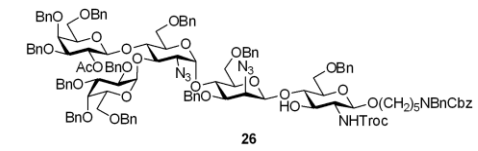

.le: Tetra-deFmoc-acceptor_Carbon_20101116_01
.se Sequence: s2pul
)lvent: cdcl3
mp. 25.0 C / 298.1 K
rator: kaifor
.e: Tetra-deFmoc-acceptor_Carbon_20101116_01
VA-500 "nmr1"
)lax. delay 1.000 sec
)lse 45.0 degrees
:q. time 1.300 sec
.dth 36764.7 Hz
)000 repetitions
:ERVE C13, 150.8012667 MHz
:OUPLE H1, 599.7292832 MHz
)wer 35 dB
)ntinuously on
)LTZ-16 modulated
:A PROCESSING
.ne broadening 0.5 Hz
size 131072
:al time 12 hr, 50 min, 1 sec
:0
200
180
160
140
120
100
80
60
40
20
0
ppm


BnO
OBn
AcO
LevO
NHTroc
N_3
$O(CH_2)_5NBnCbz$

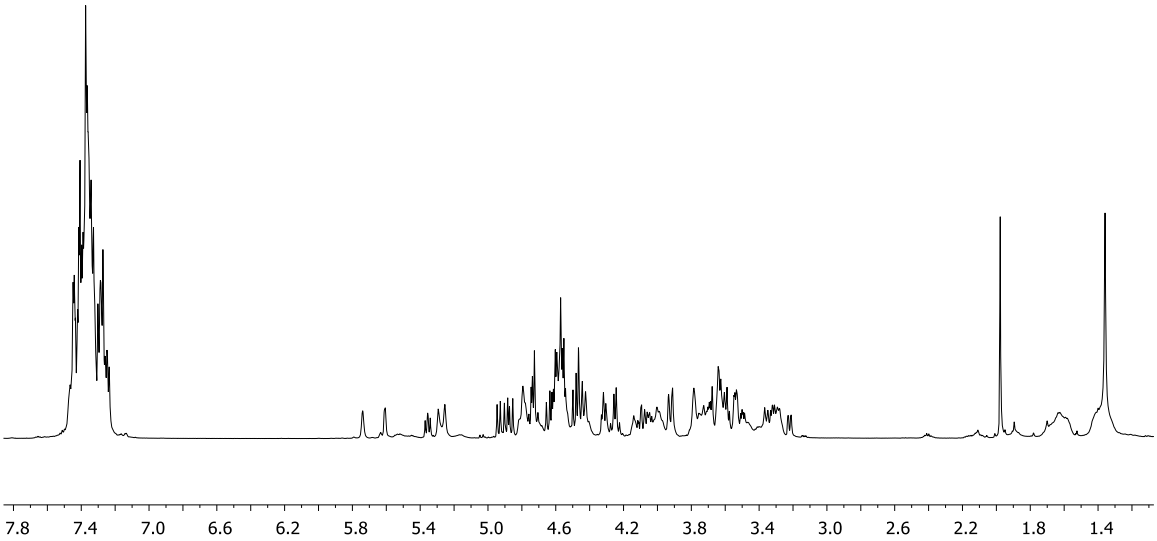
25

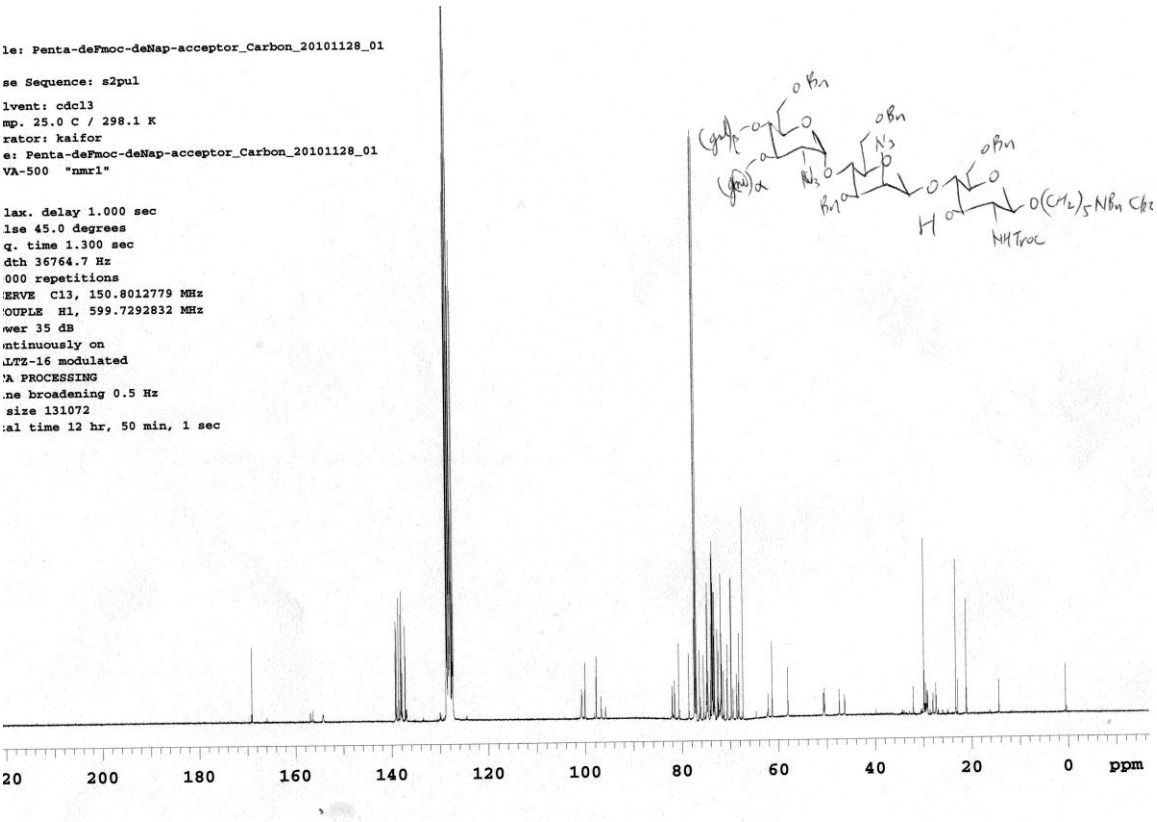

7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4

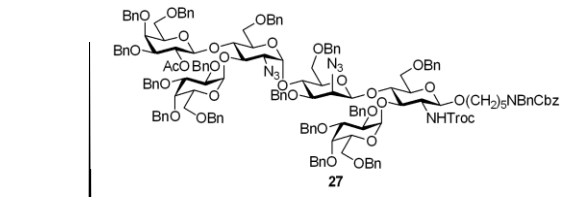

.le: Penta-deFmoc-deNap_Carbon_20101122_02
.se Sequence: s2pul
)lvent: cdcl3
mp. 25.0 C / 298.1 K
rator: kaifor
.e: Penta-deFmoc-deNap_Carbon_20101122_02
VA-500 "nmr1"
)lax. delay 1.000 sec
ilse 45.0 degrees
:q. time 1.300 sec
.dth 36764.7 Hz
)000 repetitions
ERVE C13, 150.8012796 MHz
COUPLE H1, 599.7292832 MHz
)wer 35 dB
)ntinuously on
ALTZ-16 modulated
'A PROCESSING
.ne broadening 0.5 Hz
size 131072
:al time 12 hr, 50 min, 1 sec
:0
200
180
160
140
120
100
80
60
40
20
0
ppm


BnO
OBn
AcO
N3
HO
O(CH2)5NBnCbz
NHTroc

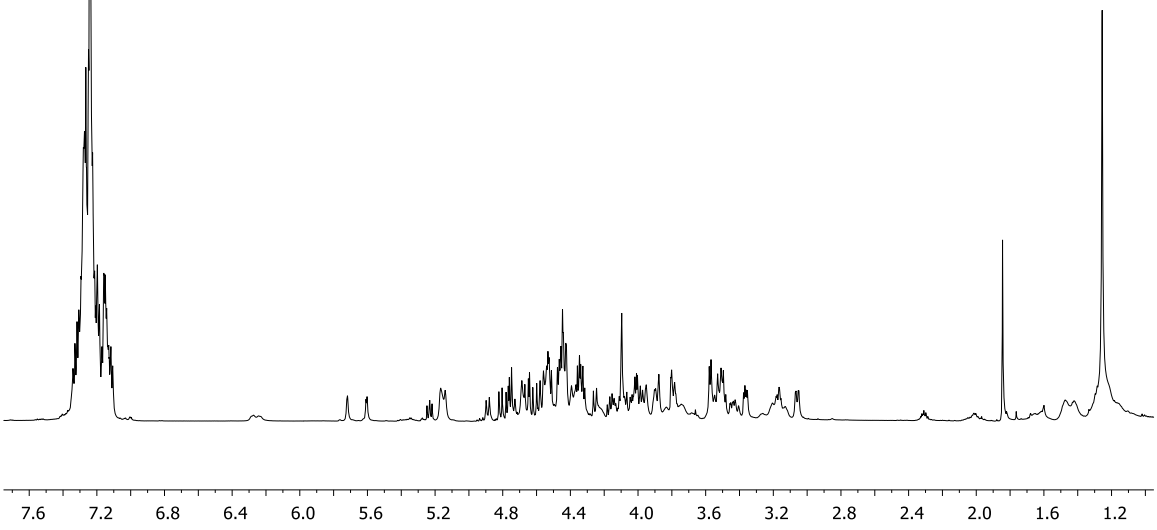
26

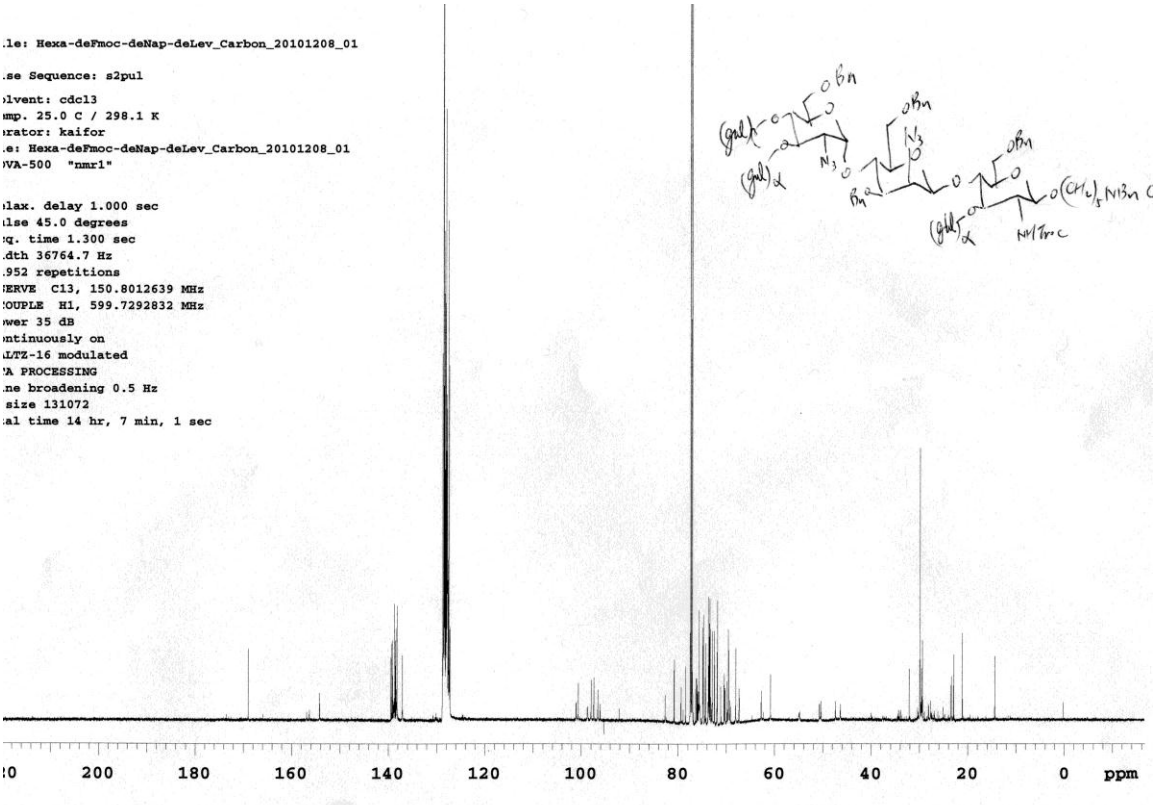

7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4

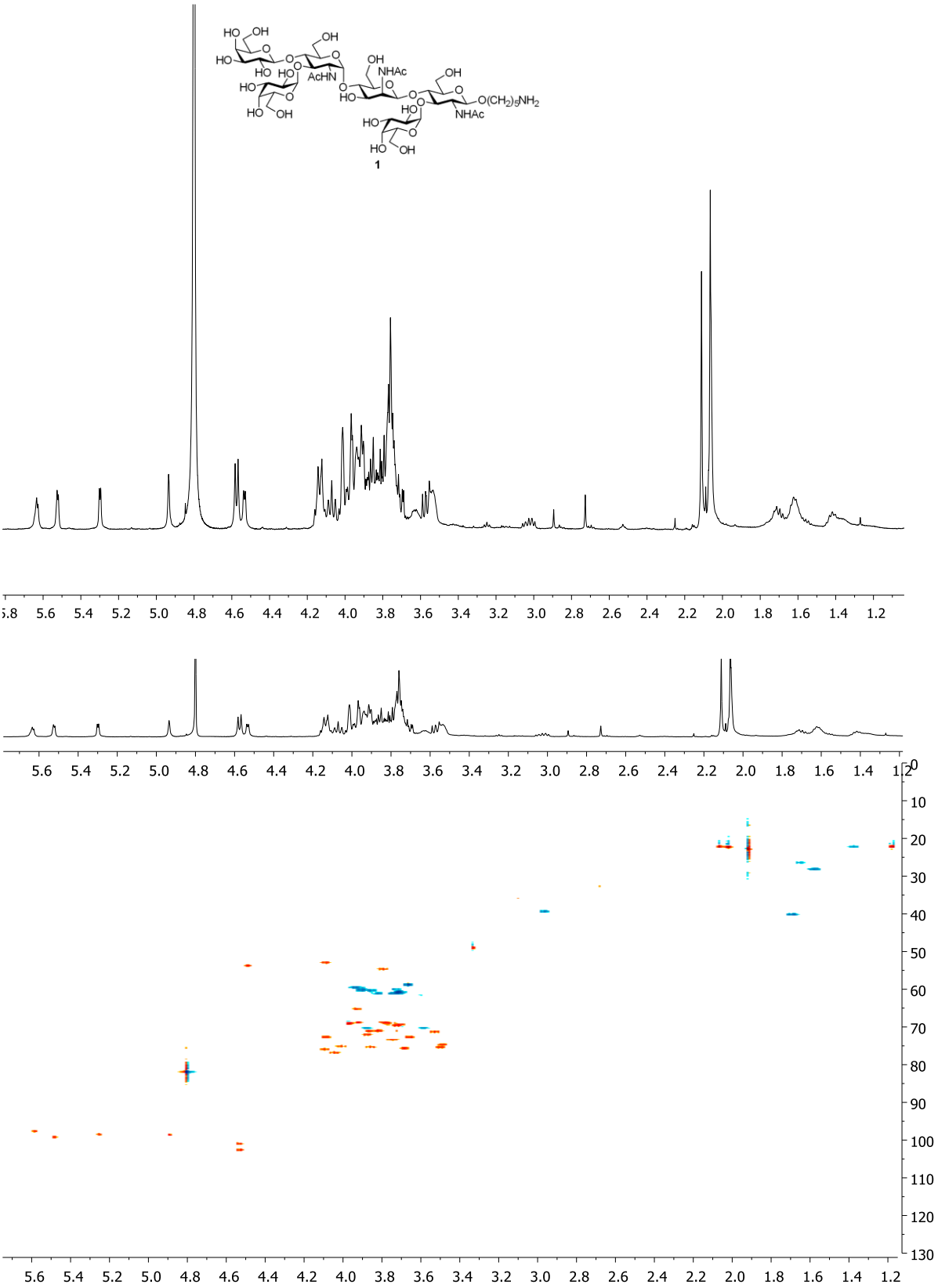

le: Penta-deFmoc-deNap-acceptor_Carbon_20101128_01
se Sequence: s2pul
lvent: cdcl3
mp. 25.0 C / 298.1 K
rator: kaifor
e: Penta-deFmoc-deNap-acceptor_Carbon_20101128_01
VA-500 "nmr1"
lax. delay 1.000 sec
lse 45.0 degrees
q. time 1.300 sec
dth 36764.7 Hz
000 repetitions
ERVE C13, 150.8012779 MHz
OUPLE H1, 599.7292832 MHz
wer 35 dB
ntinuously on
LTZ-16 modulated
A PROCESSING
ne broadening 0.5 Hz
size 131072
al time 12 hr, 50 min, 1 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

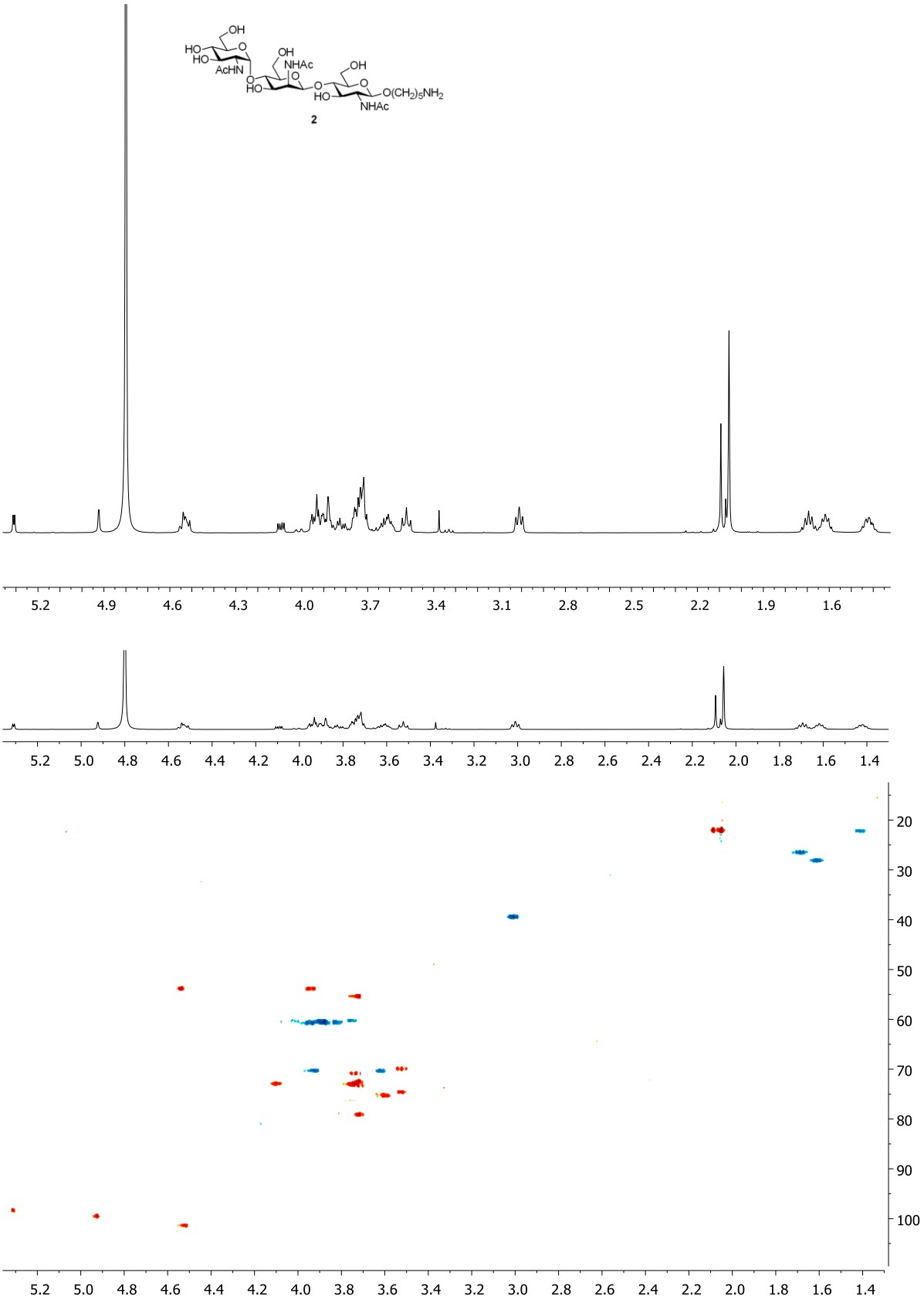

BnO
OBn
AcO
N3
O(CH2)5NBnCbz
NHTroc

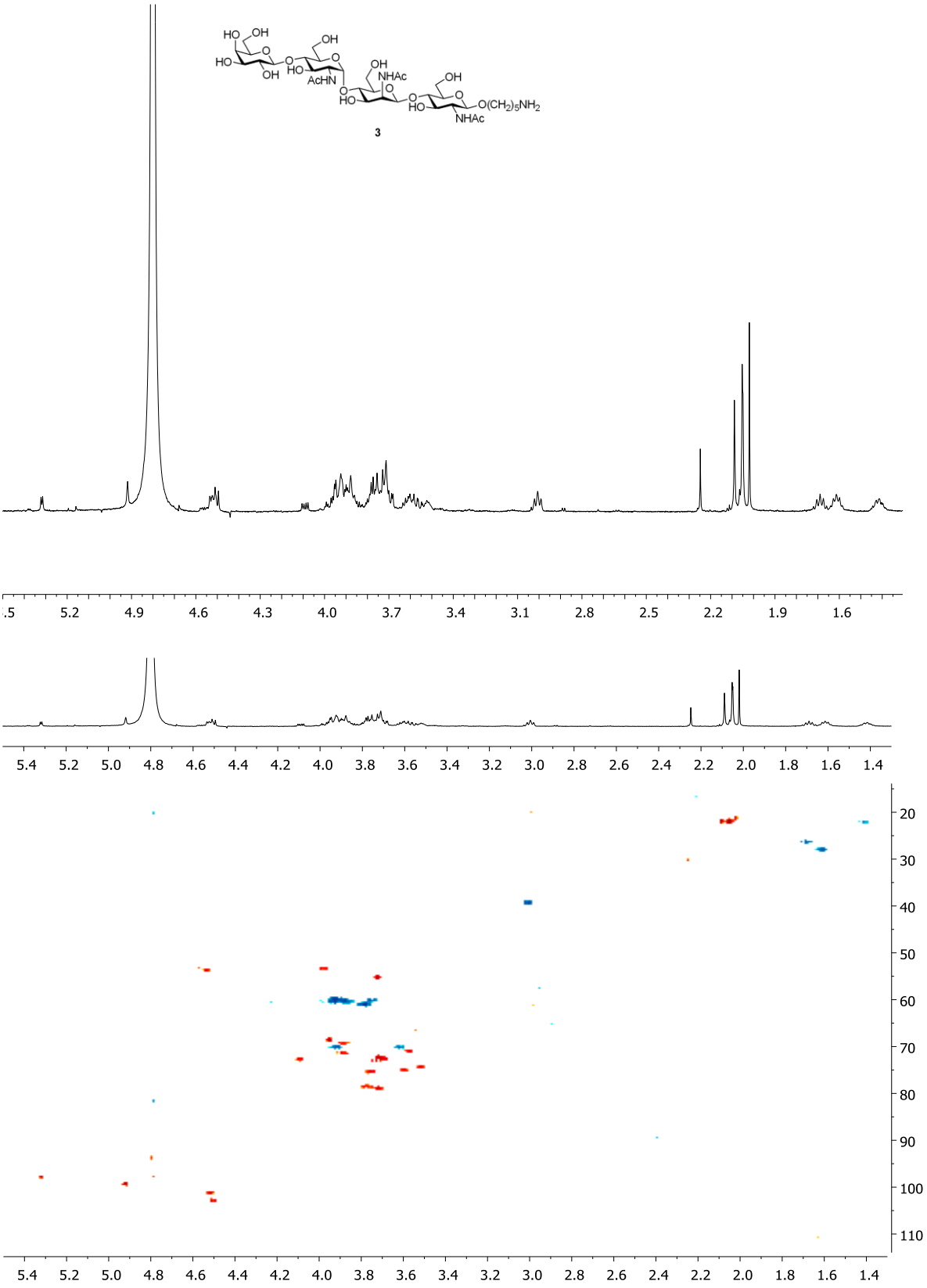
27

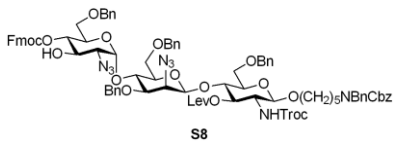

7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2


.le: Hexa-deFmoc-deNap-deLev_Carbon_20101208_01
.se Sequence: s2pul
)lvent: cdcl3
mp. 25.0 C / 298.1 K
rator: kaifor
.e: Hexa-deFmoc-deNap-deLev_Carbon_20101208_01
VA-500 "nmr1"
lax. delay 1.000 sec
lse 45.0 degrees
q. time 1.300 sec
.dth 36764.7 Hz
.952 repetitions
ERVE C13, 150.8012639 MHz
OUPLE H1, 599.7292832 MHz
wer 35 dB
ntinuously on
LTZ-16 modulated
A PROCESSING
.ne broadening 0.5 Hz
size 131072
al time 14 hr, 7 min, 1 sec
200
180
160
140
120
100
80
60
40
20
0
ppm

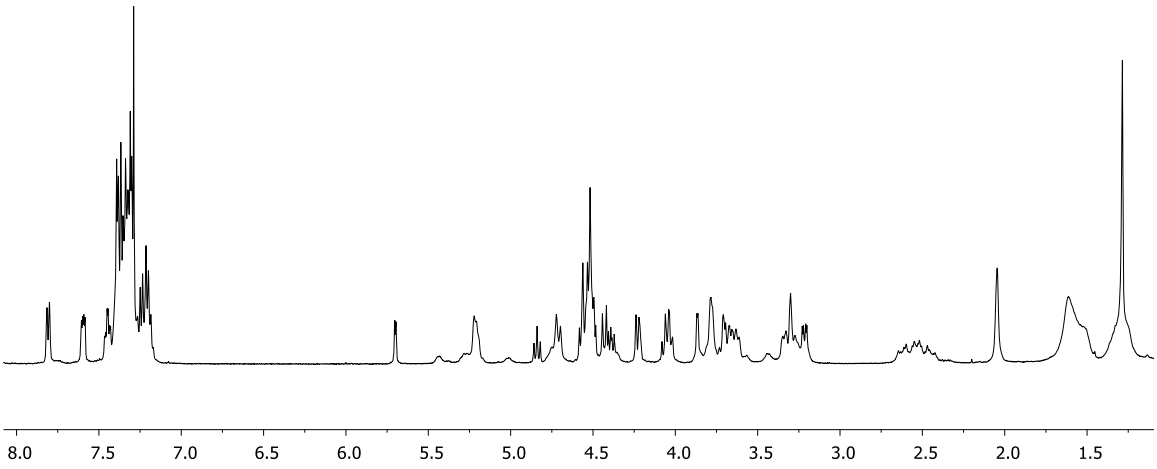

1
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
10 20 30 40 50 60 70 80 90 100 110 120 130

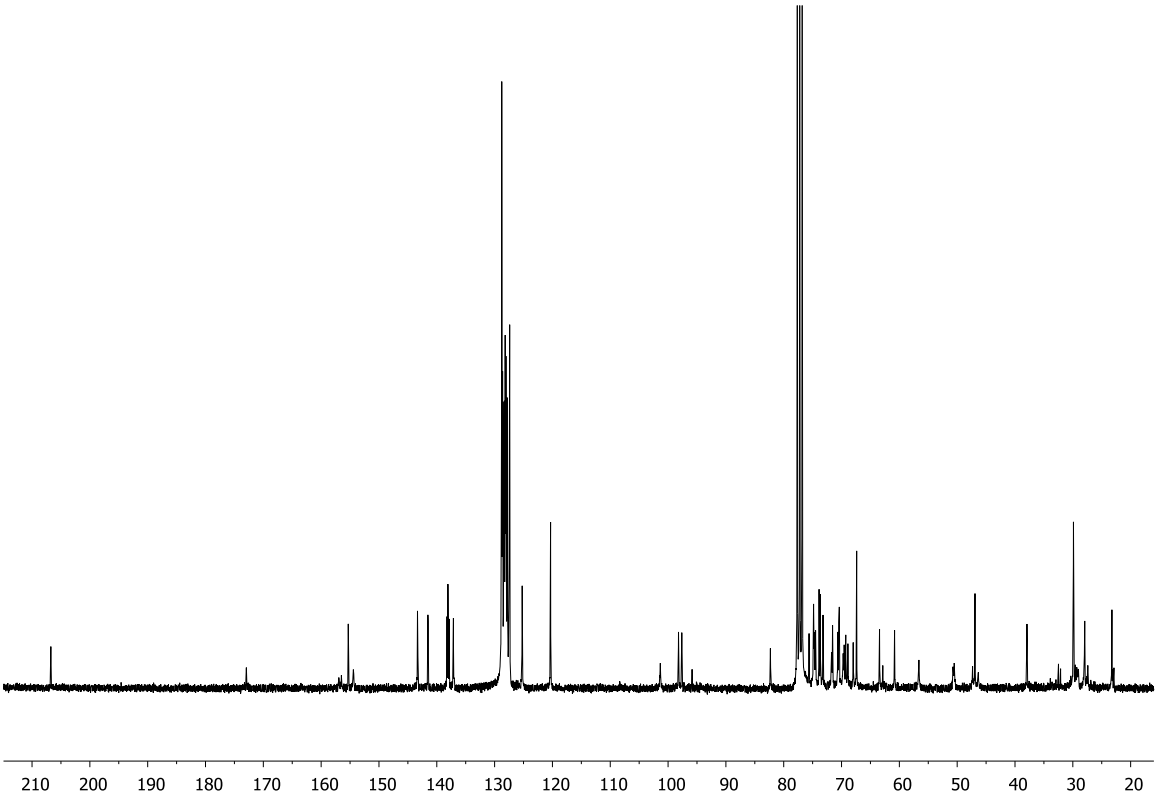

OH
HO
HO
O
AcHN
OH
NHAc
O
HO
O
HO
OH
O
O(CH2)5NH2
NHAc
2
5.2 4.9 4.6 4.3 4.0 3.7 3.4 3.1 2.8 2.5 2.2 1.9 1.6
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
20 30 40 50 60 70 80 90 100
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4

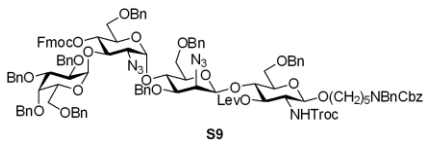

HO
OH
O
HO
OH
O
HO
AcHN
OH
O
HO
OH
NHAc
O
HO
O
HO
OH
O
O(CH2)5NH2
NHAc
3
5.2
4.9
4.6
4.3
4.0
3.7
3.4
3.1
2.8
2.5
2.2
1.9
1.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
20
30
40
50
60
70
80
90
100
110


OBn
FmocO
HO
N3
OBn
N3
OBn
BnO
LevO
O(CH2)5NBnCbz
NHTroc

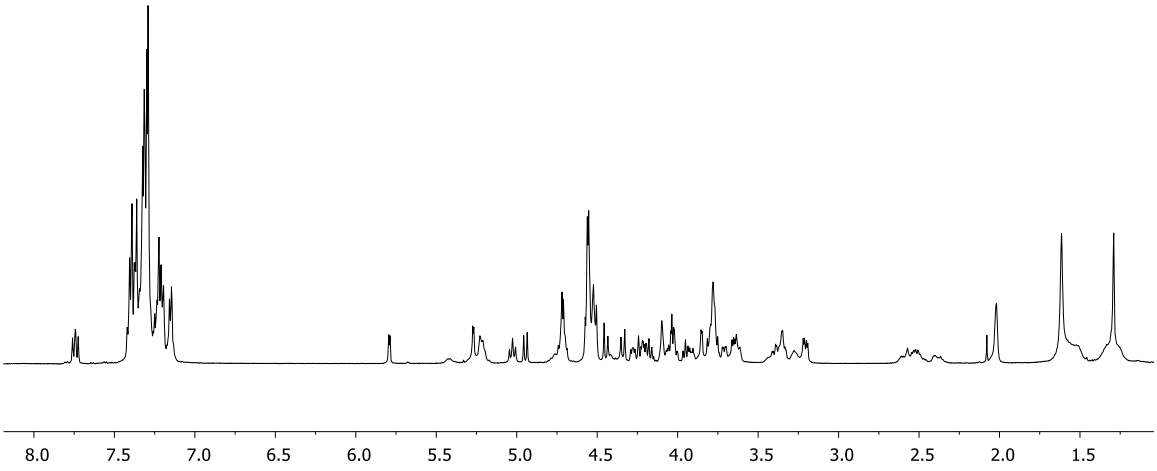
S8

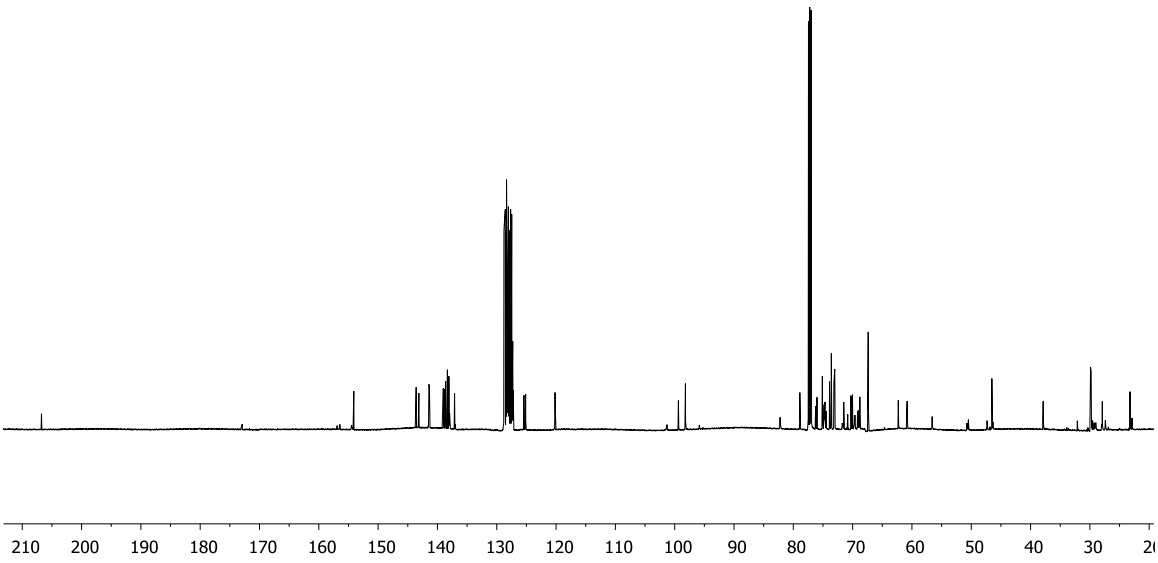

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

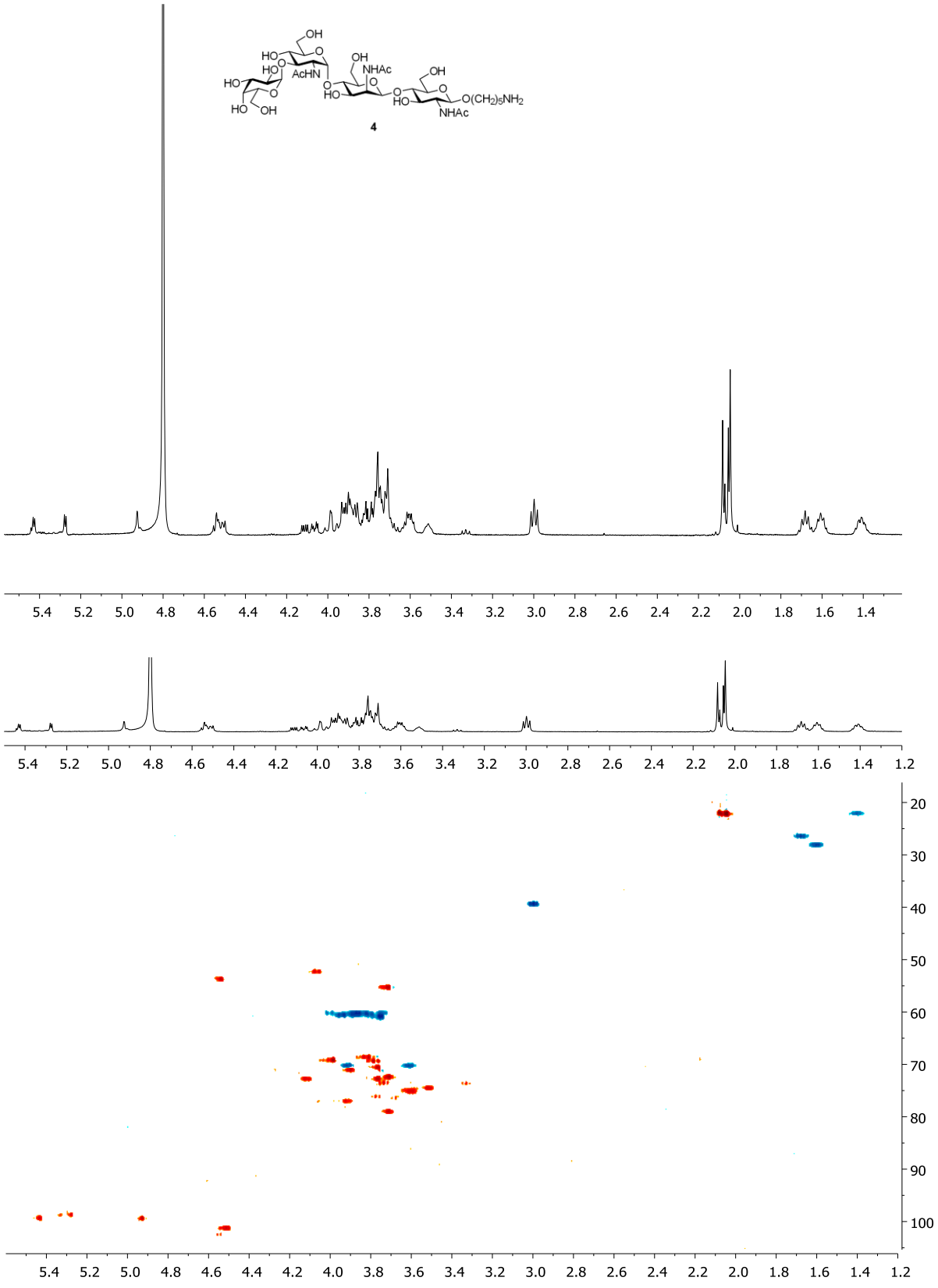

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

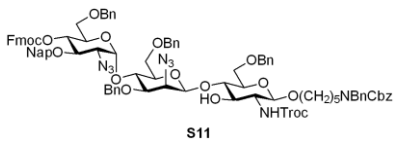

OBn
FmocO
BnO
N3
OBn
N3
OBn
BnO
BnO
OBn
BnO
LevO
O(CH2)5NBnCbz
NHTroc

S9

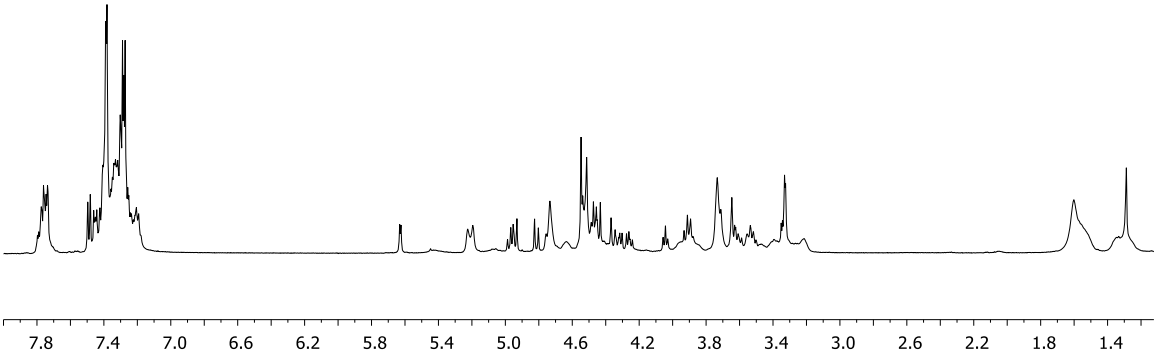

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

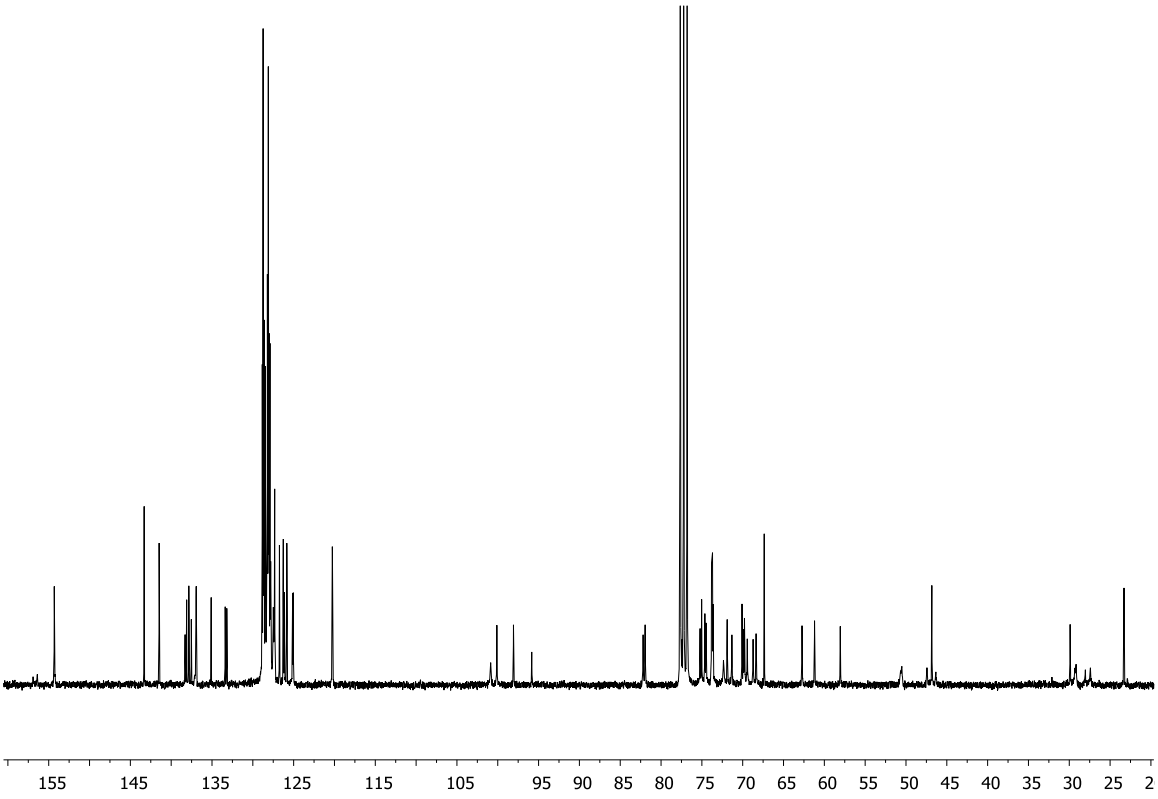

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30

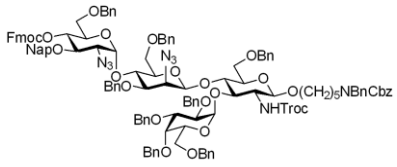

4
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
20 30 40 50 60 70 80 90 100
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2


OBn
FmocO
NapO
N3
OBn
N3
OBn
BnO
O
HO
O(CH2)5NBnCbz
NHTroc

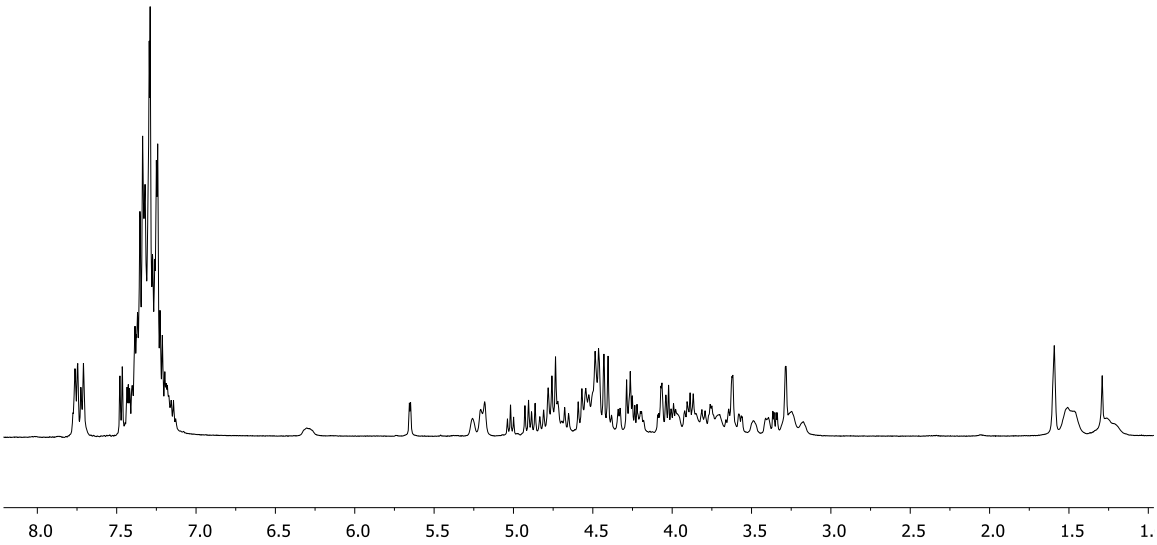
S11

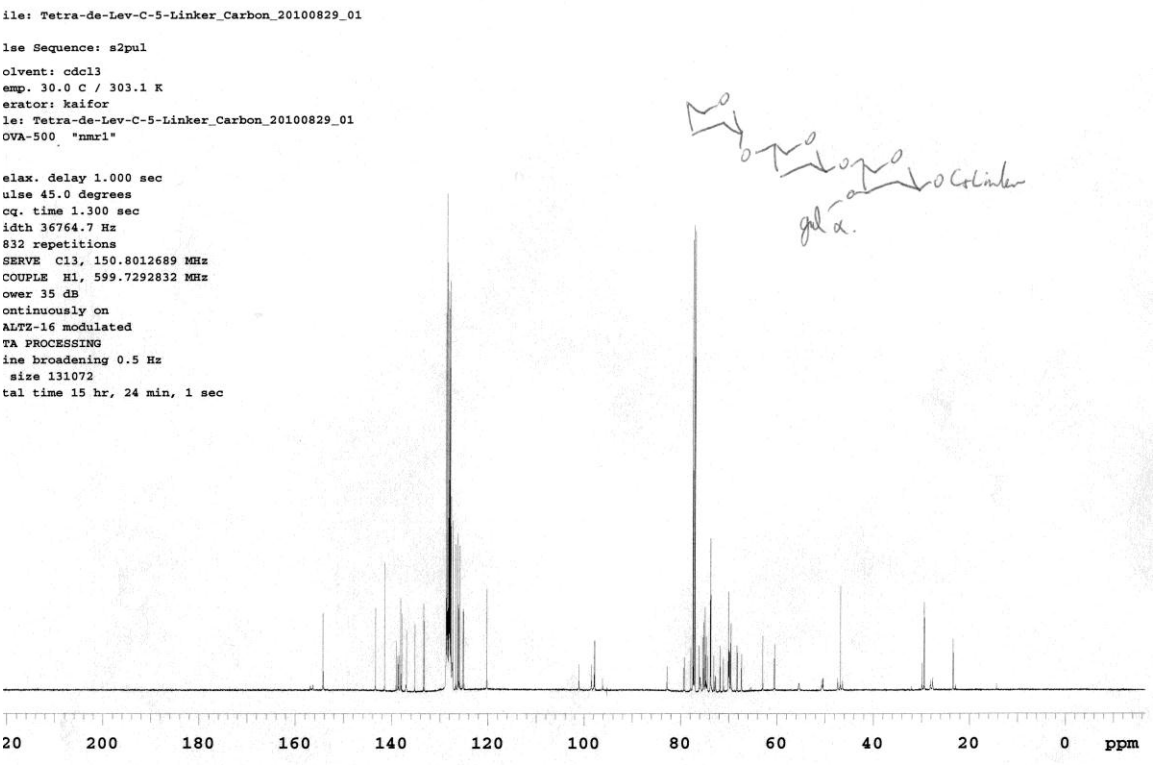

7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4

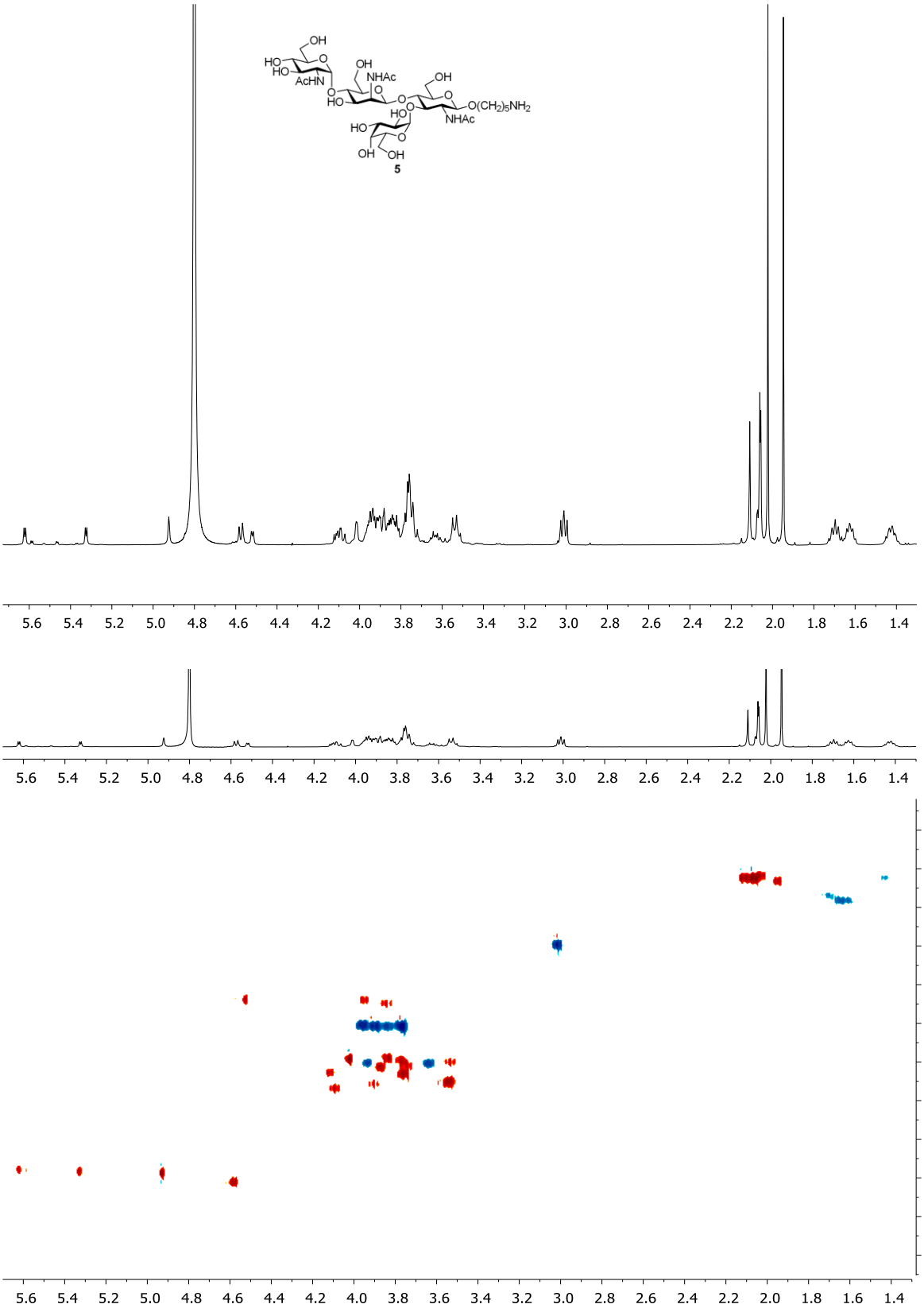

155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
2

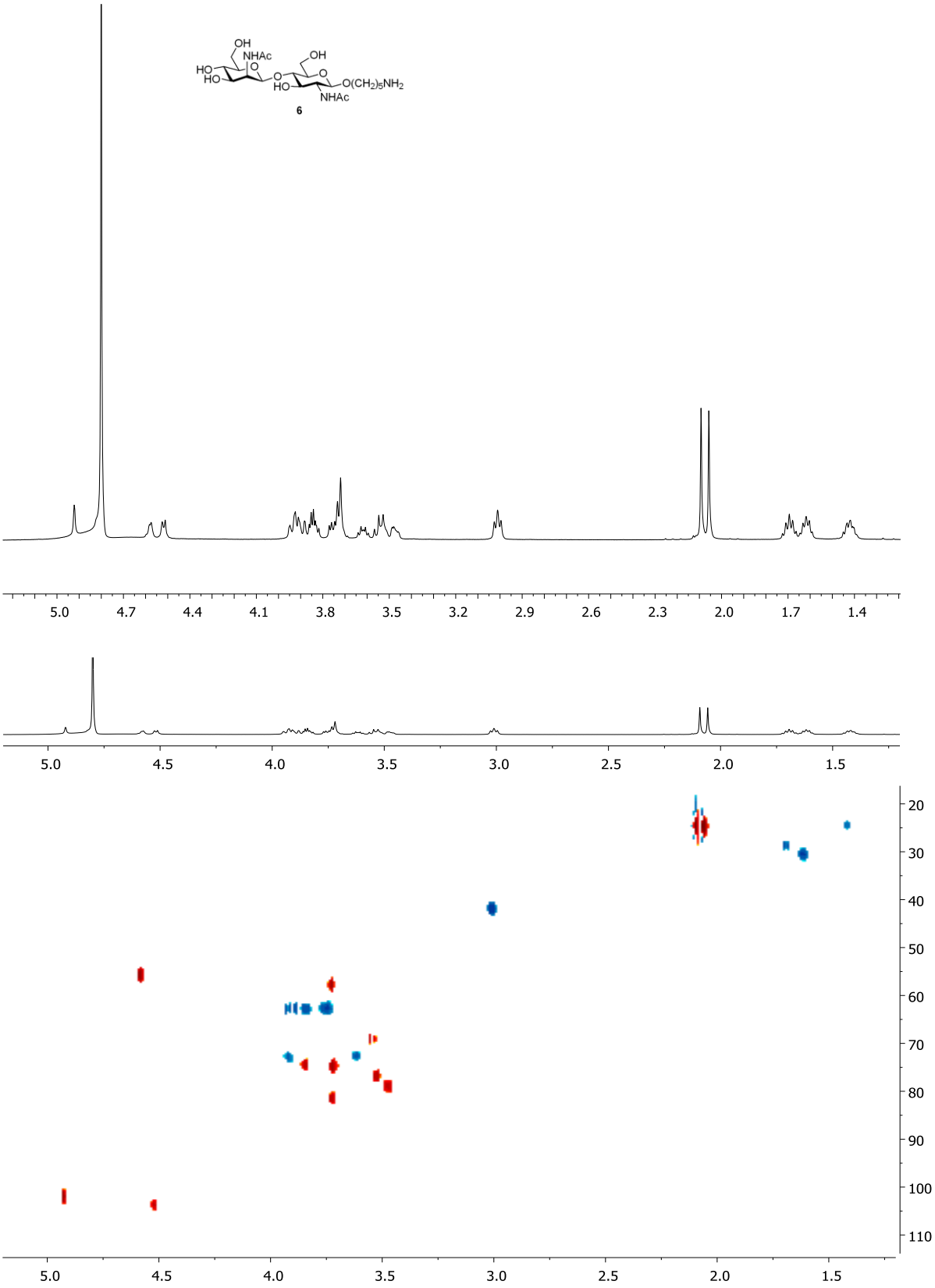

OBn
FmocO
NapO
N3
BnO
OBn
N3
OBn
O(CH2)6NBnCbz
NHTroc
BnO
BnO
BnO
OBn

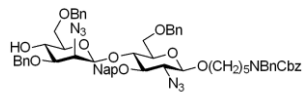
S12


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

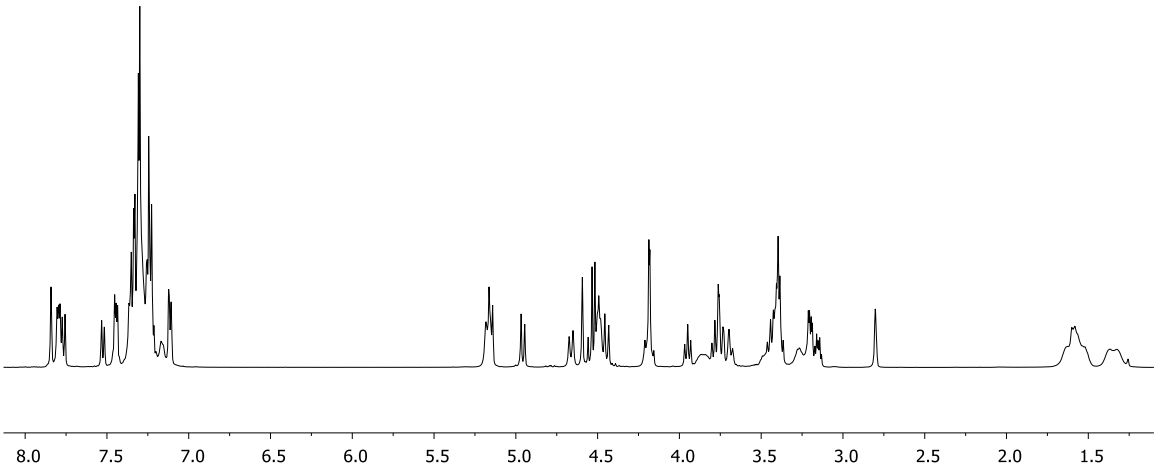

ile: Tetra-de-Lev-C-5-Linker_Carbon_20100829_01
lse Sequence: s2pul
olvent: cdcl3
emp. 30.0 C / 303.1 K
erator: kaifor
le: Tetra-de-Lev-C-5-Linker_Carbon_20100829_01
OVA-500 "nmr1"
elax. delay 1.000 sec
ulse 45.0 degrees
cq. time 1.300 sec
idth 36764.7 Hz
832 repetitions
SERVE C13, 150.8012689 MHz
COUPLE H1, 599.7292832 MHz
ower 35 dB
ontinuously on
ALTZ-16 modulated
TA PROCESSING
ine broadening 0.5 Hz
size 131072
tal time 15 hr, 24 min, 1 sec
20
200
180
160
140
120
100
80
60
40
20
0
ppm

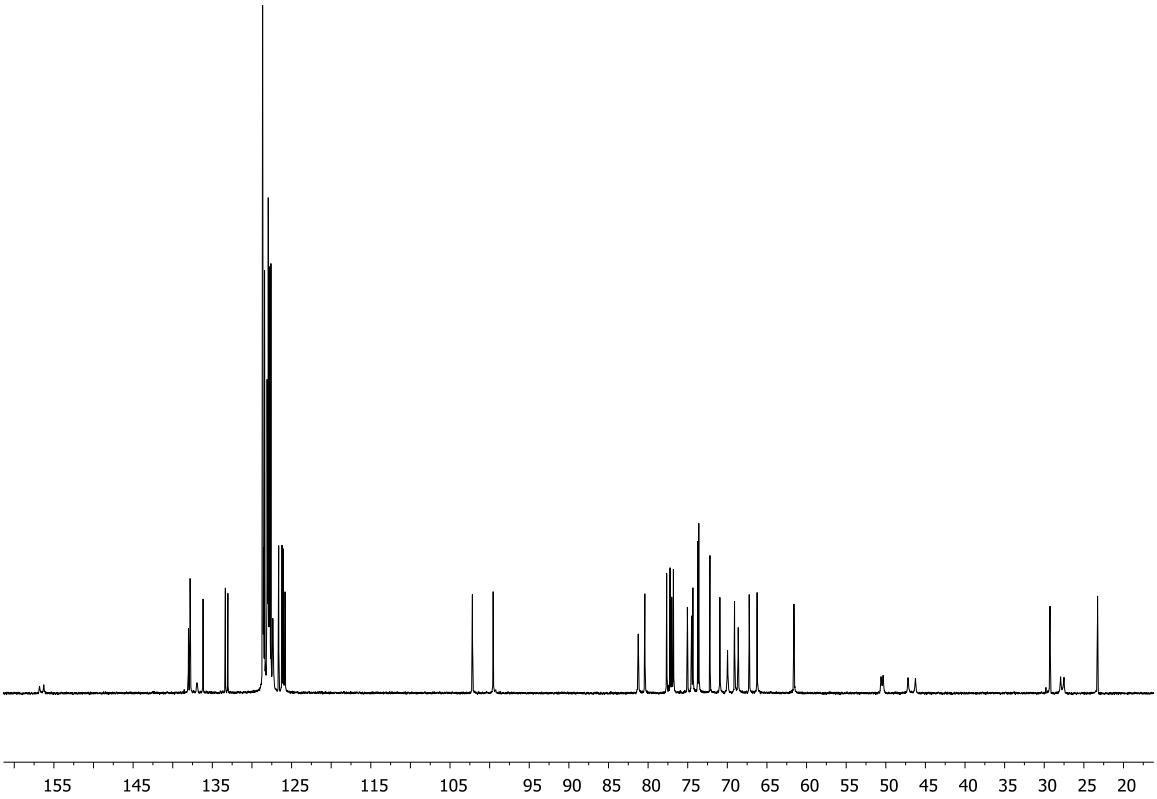

OH
HO
HO
AcHN
O
OH
NHAc
O
HO
O
OH
O
O(CH2)5NH2
HO
O
NHAc
HO
HO
O
OH
OH
5
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
10 20 30 40 50 60 70 80 90 100 110 120


OH
NHAc
HO
HO
O
O
OH
HO
O
O(CH2)5NH2
NHAc
6
5.0
4.7
4.4
4.1
3.8
3.5
3.2
2.9
2.6
2.3
2.0
1.7
1.4
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
20
30
40
50
60
70
80
90
100
110
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


OBn
N3
OBn
HO
BnO
O
NapO
O
O(CH2)5NBnCbz
N3

S16


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


155
145
135
125
115
105
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85
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65
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55
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35
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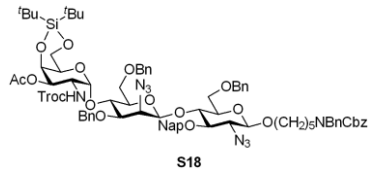
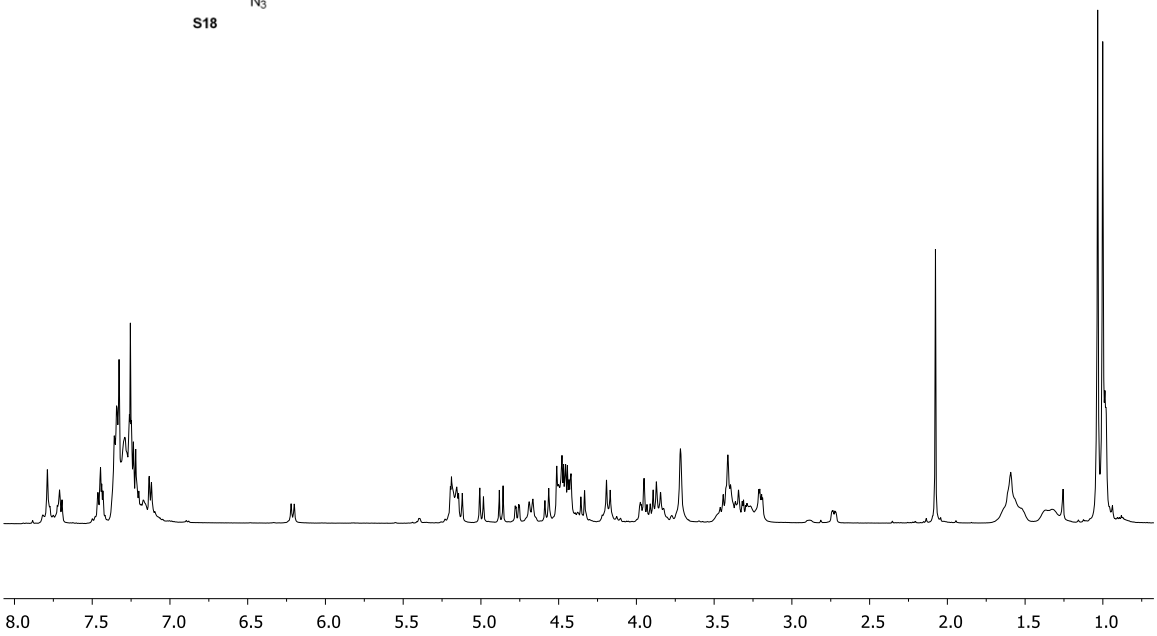
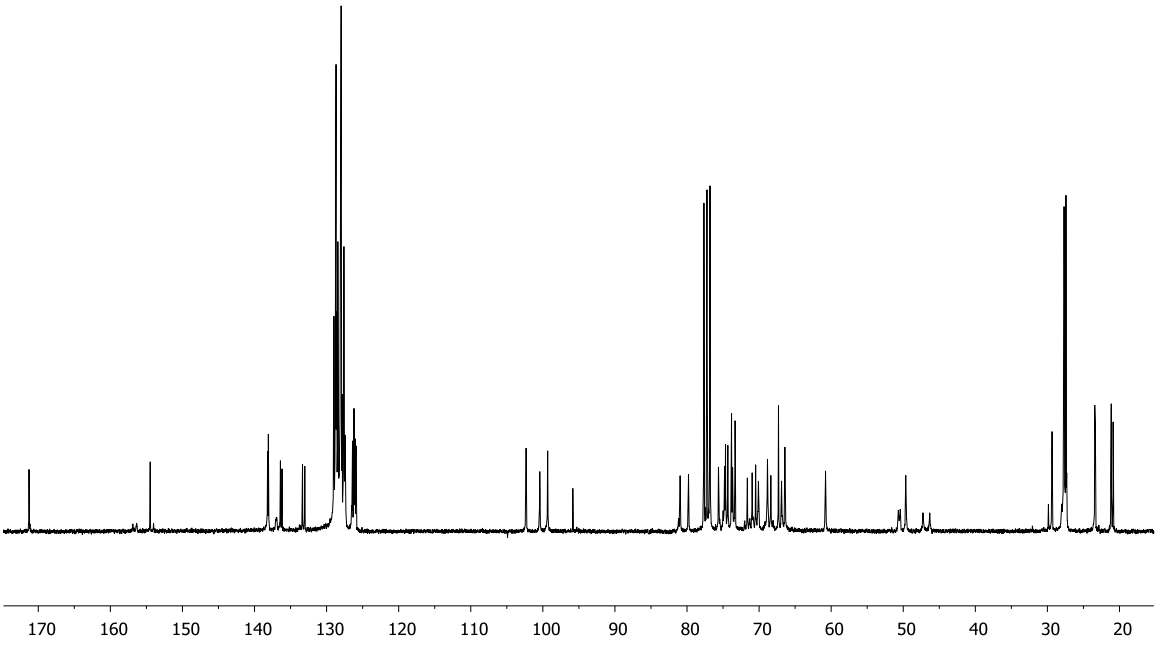
25
20


tBu
tBu
Si
AcO
TrocHN
BnO
OBn
N3
NapO
OBn
O(CH2)5NBnCbz
N3

S18


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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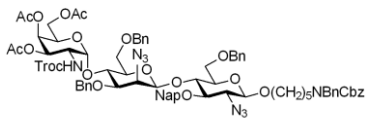
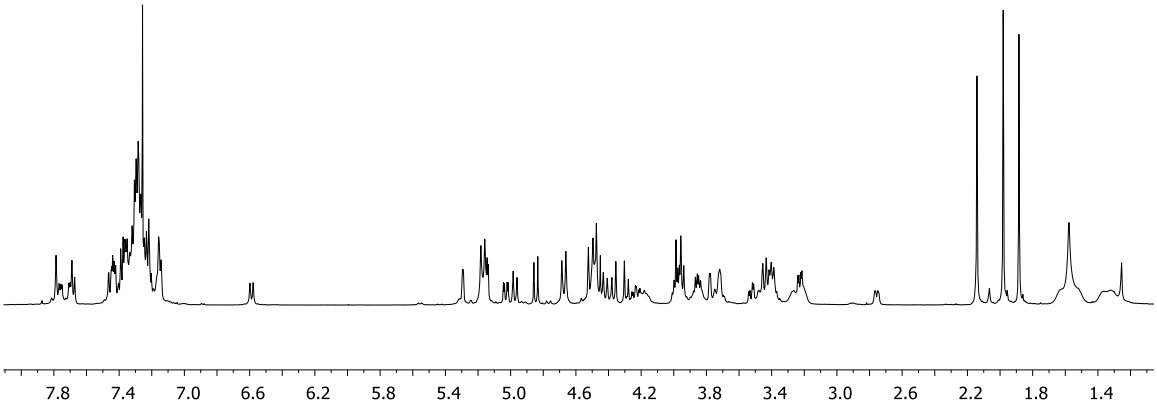
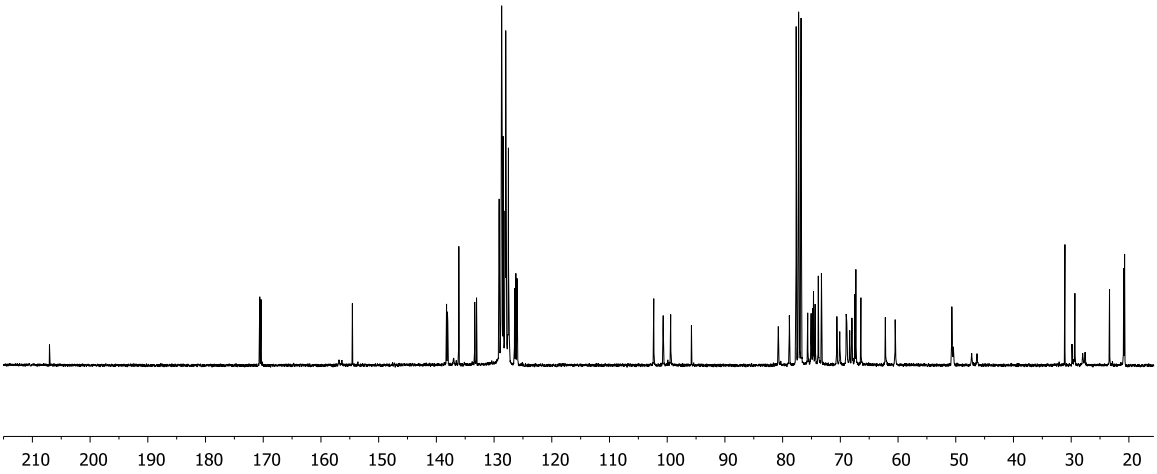
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


AcO
OAc
AcO
TrocHN
BnO
OBn
N3
O
NapO
OBn
O
O(CH2)5NBnCbz
N3

S19


7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4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190
180
170
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100
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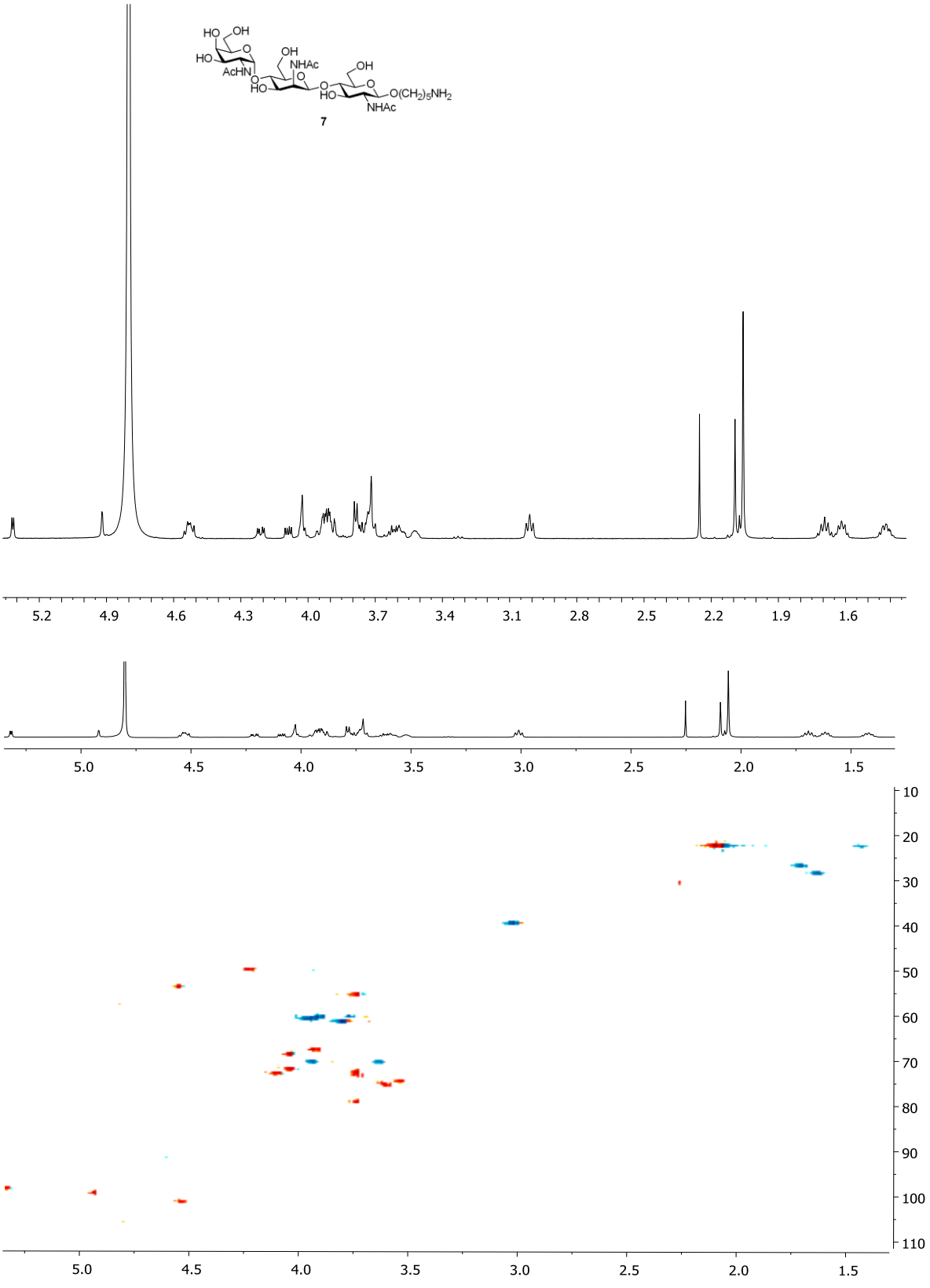
30
20


HO
OH
O
HO
AcHN
OH
NHAc
O
HO
O
HO
OH
O
O(CH2)5NH2
NHAc
7
5.2
4.9
4.6
4.3
4.0
3.7
3.4
3.1
2.8
2.5
2.2
1.9
1.6
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
10
20
30
40
50
60
70
80
90
100
110