Supporting Information

Chemoenzymatic Synthesis of Glycopeptides Bearing Rare N-Glycan Sequences with or without Bisecting GlcNAc

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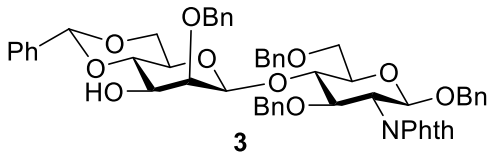
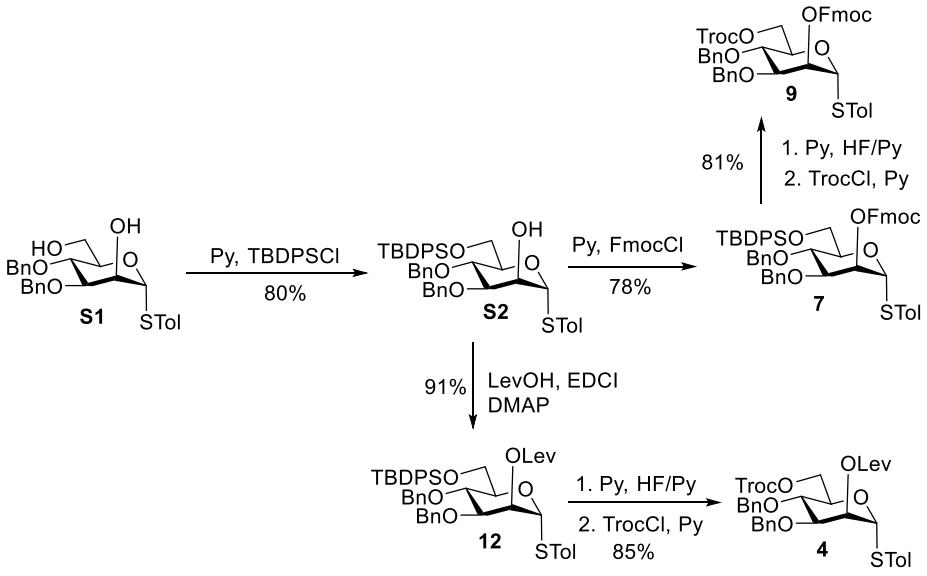
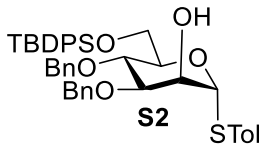


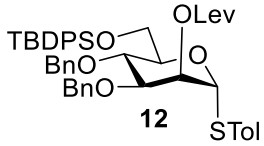
3

Benzyl (2-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (3). Compound **2**[1] (1.0 g) was dissolved in CH_2Cl_2/H_2O (10/1, 10 mL) and DDQ (240 mg, 1.1 equiv) was added at 0°C. The mixture was stirred at room temperature for 4 hours, then it was quenched with sat. $NaHCO_3$. The mixture was extracted with ethyl acetate and washed with sat. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under a reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate/DCM = 3/1/1) and afforded **3** (725 mg, 82%) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.67 (bs, 2 H), 7.47-7.29 (m, 16 H), 7.12-7.05 (m, 6 H), 6.93-6.92 (m, 2 H), 6.84-6.82 (m, 3 H), 5.45 (s, 1 H), 5.13-5.12 (m, 1 H, H-1 of ring B), 5.02 (d, J = 11.5 Hz, 1 H), 4.87-4.77 (m, 3 H), 4.68-4.65 (m, 2 H, H-1 of ring C), 4.52-4.50 (m, 2 H), 4.42 (d, J = 12.0 Hz, 1 H), 4.24-4.19 (m, 3 H), 4.10-4.07 (m, 1 H), 3.77-3.68 (m, 4 H), 3.55-3.50 (m, 3 H), 3.17-3.12 (m, 1 H), 2.33 (bs, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 168.0, 167.7, 138.1, 137.6, 137.2, 137.1, 129.1, 128.6, 128.5, 128.3, 128.2, 128.1 (2 C), 127.9 (2 C), 127.8, 127.7, 127.6 (2 C), 127.0, 126.3, 102.0 (2 C, C-1 of ring C and benzylidene), 97.3 (C-1 of ring B), 79.6, 79.1, 77.2, 76.9, 75.7, 74.7, 74.6, 73.8, 70.9, 70.7, 68.5, 68.3, 66.9, 55.7. HRMS: $C_{55}H_{53}NO_{12}$ $[M + H]^+$ calcd: 920.3646, obsd: 920.3619.



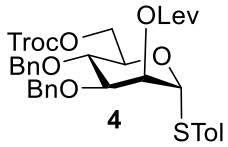


***p*-Methylphenyl 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-*a*-D-mannopyranoside (S2).** To a solution of known compound **S1**[2] (1.08 g, 2.3 mmol) in pyridine (6 ml) was added TBDPSCl (1 ml, 1.2 equiv) at 0 ^{o}C. The reaction was stirred at room temperature for 3 h, after which it was extracted with ethyl acetate and washed with 10% HCl, sat. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate = 5/1) to afford **S2** (1.3 g, 80%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ. 7.74-7.69 (m, 4 H), 7.45-7.30 (m, 15 H), 7.24-7.22 (m, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 5.58 (s, 1 H), 4.93 (d, J = 11.0 Hz, 1 H), 4.78-4.74 (m, 2 H), 4.68 (d, J = 11.0 Hz, 1 H), 4.31-4.30 (m, 1 H), 4.25 (dd, J = 2.5, 10.0 Hz, 1 H), 4.06-4.00 (m, 2 H), 3.93-3.88 (m, 2 H), 2.61 (d, J = 3.0 Hz, 1 H), 2.32 (s, 3 H), 1.07 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ.138.3, 137.7, 137.2, 135.9, 135.6, 133.8, 133.1, 131.5, 130.6, 129.7, 129.5 (2 C), 128.6, 128.4, 128.1, 128.0 (2 C), 127.7 (2 C), 127.5. HRMS: $C_{43}H_{48}O_5SSi$ $[M + NH_4]^+$ calcd: 722.3336, obsd: 722.3329.



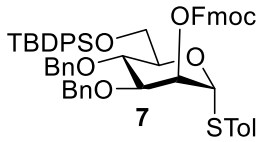
***p*-Methylphenyl 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-levulinyl-1-thio-*a*-D-mannopyranoside (12).** A mixture of compound **S2** (1.19 g, 1.69 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (973 mg, 5.07 mmol) and levulinic acid (LevOH) (0.26 ml) was dissolved in CH_2Cl_2 (10/1, 6 mL) followed by the addition of *N*,*N*-dimethylaminopyridine (DMAP) (206 mg, 0.1 equiv). The mixture was stirred at room temperature for 10 hours, then it was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate = 6/1) and afforded **12** (1.23 g, 91%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ. 7.76-7.72 (m, 4 H), 7.47-7.25 (m, 18 H), 7.08 (d, J = 8.0 Hz, 2 H), 5.66 (s, 1 H), 5.50 (s, 1 H), 4.98 (d, J = 10.5 Hz, 1 H), 4.78 (d, J = 11.5 Hz, 1 H), 4.70 (d, J = 10.5 Hz, 1 H), 4.62 (d, J = 11.0 Hz, 1 H), 4.26 (dd, J = 1.5, 9.0 Hz, 1 H), 4.14-4.09 (m, 2 H), 4.00 (dd, J = 3.0, 9.5 Hz, 1 H), 3.94 (d, J = 11.5 Hz, 1 H),2.81-2.69 (m, 4 H), 2.35 (s, 3 H), 2.16 (s, 3 H), 1.10 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ. 206.2, 172.1, 138.4, 137.8, 137.6, 136.0, 135.5, 133.8, 133.0, 131.9, 130.4, 129.8, 129.6 (2 C), 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 86.4, 78.5, 75.5, 74.3, 73.6, 71.8, 70.7, 62.7, 38.0, 29.9, 28.1, 26.8, 21.2, 19.4. HRMS: $C_{48}H_{54}O_7SSi$ $[M + NH_4]^+$ calcd: 820.3698, obsd: 820.3686.

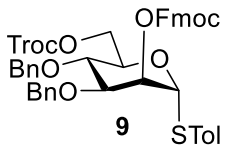


***p*-Methylphenyl 3,4-di-*O*-benzyl-6-*O*-(2,2,2-trichloroethoxylcarbonyl)-2-*O*-levulinyl-1-thio-*a*-D-mannopyranoside (4).** To a solution of compound **12** (1.23 g, 1.53 mmol) in pyridine (8 ml) was added 70% HF/Py (3 ml) at 0^{o}C. The reaction was stirred at room temperature for 3 h, after which it was neutralized by sat. $NaHCO_3$. The mixture was extracted with ethyl acetate and washed with 10% HCl, sat. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The resulted residue was dissolved in pyridine (5 ml) and Troc-Cl (1.5 equiv) was added at 0^{o}C. The reaction was stirred at room temperature for 1 h, after which it was extracted with ethyl acetate and washed sat. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate = 4/1) and afforded **4** (962 mg, 85%) as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ. 7.38-7.28 (m, 12 H), 7.16 (d, *J* = 7.0 Hz, 2 H), 5.63 (s, 1 H), 5.39 (s, 1 H), 4.99 (d, J = 11.0 Hz, 1 H), 4.77-4.74 (m, 3 H), 4.63 (d, J = 11.0 Hz, 1 H), 4.58 (d, J = 11.5 Hz, 1 H), 4.52-4.46 (m, 3 H), 4.00-3.98 (m, 1 H), 3.85-3.81 (m, 1 H), 2.76-2.71 (m, 4 H), 2.34 (s, 3 H), 2.20 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ. 206.3, 171.8, 153.9, 138.3, 137.9, 137.4, 132.8,

130.0, 129.1, 128.5 (2 C), 128.3, 128.1, 128.0 (2 C), 86.4, 77.3, 77.1, 76.9, 76.8, 75.3, 74.1, 71.7, 70.3, 70.0, 67.7, 38.0, 29.9, 28.2, 21.2. HRMS: $C_{35}H_{37}Cl_3O_9S$ $[M + NH_4]^+$ calcd: 756.1568, obsd: 756.1567.

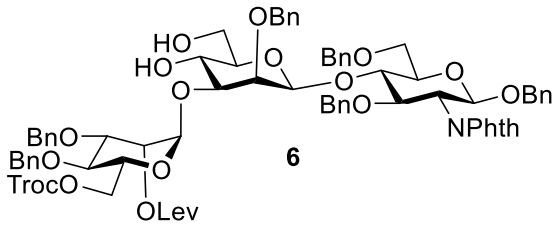


***p*-Methylphenyl 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-1-thio-*α*-D-mannopyranoside (7).** Compound **S2** (1 g, 1.42 mmol) was dissolved in pyridine (2.5 ml) and Fmoc-Cl (1.1 g, 3 equiv) was added at 0ºC. The reaction was stirred at room temperature for 8 h. The mixture was extracted with ethyl acetate and washed with 10% HCl, sat. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate = 9/1) and afforded **7** (1.03 mg, 78%) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ.* 7.81-7.62 (m, 9 H), 7.45-7.22 (m, 21 H), 7.08 (d, J = 8.0 Hz, 2 H), 5.58 (s, 1 H), 5.50 (s, 1 H), 5.00 (d, J = 11.0 Hz, 1 H), 4.82 (d, J = 11.5 Hz, 1 H), 4.71 (d, J = 10.5 Hz, 1 H), 4.67 (d, J = 11.5 Hz, 1 H), 4.47 (d, J = 8.0 Hz, 1 H), 4.36-4.17 (m, 4 H), 4.12 (dd, J = 4.0, 11.5 Hz, 1 H), 4.01 (dd, J = 3.0, 9.5 Hz, 1 H), 3.95 (d, J = 11.0 Hz, 1 H), 2.33 (s, 3 H), 1.10 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ.* 154.9, 143.9, 143.2, 141.3, 141.2, 138.3, 137.7, 136.0, 135.6, 133.9, 133.0, 132.1, 130.3, 129.8, 129.6, 129.5, 128.4 (2 C), 128.0 (2 C), 127.9 (2 C), 127.8, 127.7, 127.5, 127.2 (2 C), 125.4, 125.2 (2 C), 120.1, 120.0 (2 C), 86.3, 78.6, 75.6, 74.4, 74.3, 73.8, 72.0, 70,2, 69.9, 62.8, 46.8, 46.6, 26.8, 21.1, 19.3. HRMS: $C_{58}H_{58}O_7Si$ $[M+NH_4]^+$ calcd: 944.4011, obsd: 944.3995.



***p*-Methylphenyl 3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-**

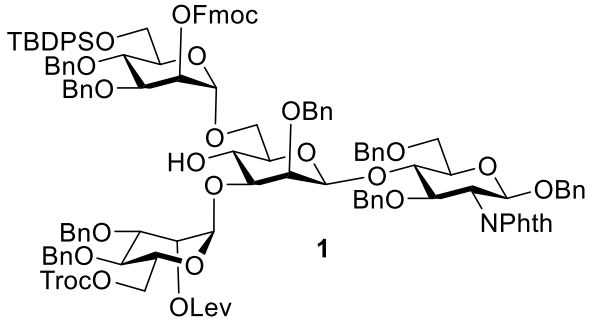
6-*O*-(2,2,2-trichloroethoxylcarbonyl)-1-thio-*a*-D-mannopyranoside (9). Following the procedure of synthesizing compound **4**, compound **9** was obtained in 81% yield from compound **7**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ. 7.80 (dd, J = 3.0, 8.0 Hz, 2 H), 7.66 (t, J = 7.0 Hz, 2 H), 7.44-7.26 (m, 16 H), 7.18 (d, J = 8.0 Hz, 2 H), 5.53 (d, J = 1.0 Hz, 1 H), 5.49-5.48 (m, 1 H), 5.04 (d, J = 11.0 Hz, 1 H), 4.82-4.78 (m, 3 H), 4.70-4.64 (m, 2 H), 5.57-4.50 (m, 3 H), 4.48-4.45 (m, 1 H), 4.38-4.35 (m, 1 H), 4.30-4.27 (m,1 H), 4.05 (dd, J = 3.5, 9.5 Hz, 1 H), 3.97-3.39 (m, 1 H), 2.35 (s,1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ. 154.7, 153.9, 143.4, 143.2, 141.3, 141.2, 138.5, 137.8, 137.4, 133.1, 130.0, 128.6, 128.5, 128.1 (2 C), 128.0 (2 C), 127.9, 127.2 (2 C), 125.4, 125.2, 120.1 (2 C), 86.3, 78.5, 76.9, 76.3, 75.5, 74.3, 74.0, 72.0, 70.5, 70.4, 67.8, 46.6, 21.2. HRMS: $C_{45}H_{41}Cl_3O_9S$ $[M + NH_4]^+$ calcd: 880.1875, obsd: 880.1848.



6

Benzyl [3,4-di-*O*-benzyl-2-*O*-levulinyl-6-*O*-(2,2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (6). A mixture of compound **2** (201 mg, 0.22 mmol), donor **4** (194 mg, 0.26 mmol), and 4 A molecular sieves in DCM (3 ml) was stirred at room temperature for 30 min. Then it was cooled to -60ºC followed by addition of *N*-iodosuccinimide (71 mg, 0.3 mmol) and TfOH (0.004 ml, 0.15 equiv to donor). The reaction was stirred at -30ºC for 1 hour, after which it was quenched by triethylamine and filtered by celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate = 3/1). The resulting trisaccharide was dissolved in 80% acetic acid in water and the mixture was stirred at 90ºC for 3 hours. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (toluene/acetone = 3/1) and afforded **6** (228 mg, 64% for two steps)

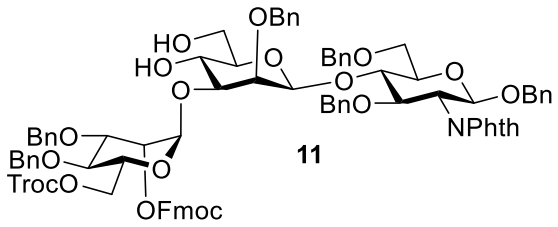
as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ. 7.81-7.53 (m, 5 H), 7.43-7.24 (m, 18 H), 7.18-7.05 (m, 6 H), 6.87-6.82 (m, 5 H), 5.43-5.42 (m, 1 H, H-1 of ring E), 5.16 (d, J = 8.0 Hz, 1 H, H-1 of ring B), 4.96-4.93 (m, 2 H), 4.89-4.82 (m, 2 H), 4.81-4.78 (m, 3 H), 4.74-4.68 (m, 2 H), 4.60 (d, J = 11.0 Hz, 1 H), 4.56-4.49 (m, 4 H, H-1 of ring C), 4.41-4.35 (m, 3 H), 4.29-4.23 (m, 2 H), 4.11-4.07 (m, 1 H), 4.00 (dd, J = 3.0, 9.0 Hz, 1 H), 3.94 (t, J = 9.5 Hz, 1 H), 3.89-3.85 (m, 1 H), 3.82-3.73 (m, 5 H), 3.60-3.53 (m, 2 H), 3.39 (dd, J = 2.5, 9.5 Hz, 1 H), 3.11-3.07 (m, 1 H), 2.76-2.68 (m, 4 H), 2.19 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ. 206.5, 172.0, 167.9, 167.7, 153.9, 138.5, 138.4, 138.1, 137.8, 137.7, 137.2, 128.7, 128.4 (2 C), 128.3, 128.2 (2 C), 128.1 (2 C), 127.9 (2 C), 127.8, 127.7, 127.6, 127.5 (2 C), 127.4, 127.0, 100.8 (C-1 of ring C), 99.0 (C-1 of ring E), 97.3 (C-1 of ring B), 94.5, 81.1, 78.5, 77.9, 77.5, 77.4, 76.9, 76.8, 75.6, 75.0, 74.9, 74.5, 74.3, 73.7 (2 C), 71.6, 70.7, 70.1, 68.8, 68.3, 67.9, 67.8, 62.4, 55.7, 38.0, 29.9, 28.2. HRMS: $C_{76}H_{78}Cl_3NO_{21}$ $[M + 2\ NH_4]^{2+}$ calcd: 740.7402, obsd: 740.7392.



1

Benzyl [3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-(9-fluorenylmethyloxy carbonyl)-*a*-D-mannopyranosyl]-(1→6)-[3,4-di-*O*-benzyl-2-*O*-levulinyl-6-*O*-(2,2,2 -trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-manno pyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (1). A mixture of compound **6** (100 mg, 0.07 mmol), donor **7** (77 mg, 0.08 mmol), and 4 A molecular sieves in DCM (1.5 ml) was stirred at room temperature for 30 min. Then it was cooled to -60ºC followed by addition of *N*-iodosuccinimide (27 mg, 0.12 mmol) and TfOH (0.001 ml, 0.15 equiv to donor). The reaction was stirred at -30 ºC for 1 hours, after which it was quenched by triethylamine and filtered by celite, and

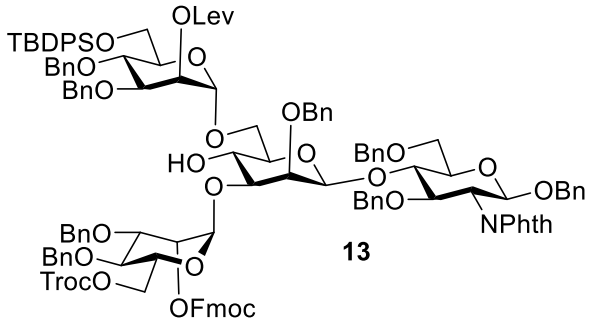
the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate/DCM = 5/2/2) and afforded **1** (86 mg, 55%). ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.81-7.59 (m, 12 H), 7.57-7.05 (m, 45 H), 6.87-6.86 (m, 2 H), 6.67-6.65 (m, 3 H), 5.49-5.48 (m, 1 H, H-1 of ring E), 5.22-5.21 (m, 1 H, H-1 of ring D), 5.16 (bs, 1 H), 5.13 (d, J = 8.0 Hz, 1 H, H-1 of ring B), 5.01-4.94 (m, 4 H), 4.88-4.66 (m, 8 H), 4.62-4.59 (m, 3 H), 4.53-4.49 (m, 4 H, H-1 of ring C), 4.42-4.34 (m, 4 H), 4.28-3.89 (m, 9 H), 3.98-3.89 (m, 5 H), 3.59-3.56 (m, 2 H), 3.35 (dd, J = 3.0, 9.5 Hz, 1 H), 3.15-3.12 (m, 1 H), 2.76-2.71 (m, 4 H), 2.18 (s, 3 H), 1.13 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 206.3, 171.9, 154.7, 154.0, 143.7, 143.3, 141.3, 141.2, 138.7, 138.6, 138.3, 138.2, 138.0, 137.9, 137.7, 137.2, 136.0, 135.7, 133.9, 133.2, 129.7, 129.6, 128.6, 128.4 (2 C), 128.3, 128.2, 128.1 (3 C), 128.0, 127.9 (2 C), 127.8 (3 C), 127.7, 127.6 (2 C), 127.5 (2 C), 127.4 (2 C), 127.1, 126.8, 125.5, 125.3, 119.9, 101.6 (C-1 of ring C), 99.4 (C-1 of ring E), 97.6 (C-1 of ring D), 97.3 (C-1 of ring B), 94.5, 81.4, 79.2, 78.2, 77.7 (2 C), 76.6, 75.6, 75.0, 74.9, 74.2 (2 C), 74.0, 73.7, 73.5, 72.8, 72.4, 71.7, 70.7, 70.1, 70.0, 68.6, 68.5, 68.0, 67.6, 66.7, 62.8, 55.7, 46.6, 38.0, 29.9, 28.2, 26.8, 19.4. HRMS: $C_{127}H_{128}Cl_3NO_{28}Si$ [M + 2 NH_4]$^{2+}$ calcd: 1141.9067, obsd: 1141.9000.



11

Benzyl [3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6-*O*-(2,2,2-trichloroethoxylcarbonyl)- α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-manno pyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (11). A mixture of compound **3** (193 mg, 0.17 mmol), donor **9** (210 mg, 0.25 mmol), and 4 A molecular sieves in DCM (2 ml) was stirred at room temperature for 30 min. Then it was cooled to -60ºC followed by addition of *N*-iodosuccinimide (84 mg, 0.37 mmol) and TfOH (0.004 ml, 0.15 equiv to donor). The reaction was stirred at -30ºC

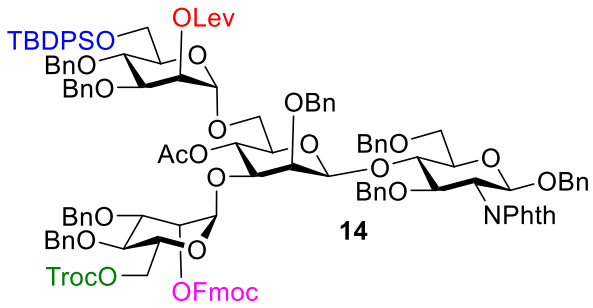
for 1 hours, after which it was quenched by DIPEA and filtered by celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate/DCM = 5/1/1). The resulting trisaccharide was dissolved in 80% acetic acid in water and the mixture was stirred at 90ºC for 3 hours. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (toluene/acetone = 2/1) and afforded **11** (254 mg, 77% for two steps) as a white solid.^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.80 (dd, J = 8.0 Hz, 2 H), 7.67-7.62 (m, 5 H), 7.44-7.30 (m, 19 H), 7.24-7.22 (m, 5 H), 7.15-7.05 (m, 6 H), 6.85-6.84 (m, 5 H), 5.35 (s, 1 H, H-1 of ring D), 5.23 (s, 1 H), 5.14 (d, J = 8.0 Hz, 1 H, H-1 of ring B), 5.00 (d, J = 11.0 Hz, 1 H), 4.94 (d, J = 11.0 Hz, 1 H), 4.88 (d, J = 12.5 Hz, 1 H), 4.84-4.72 (m, 6 H), 4.65 (d, J = 11.0 Hz, 1 H), 4.57-4.50 (m, 4 H, H-1 of ring C), 4.46-4.43 (m, 2 H), 4.39-4.21 (m, 6 H), 4.09-4.06 (m, 1 H), 4.00 (dd, J = 3.0, 9.0 Hz, 1 H), 3.95-3.90 (m, 2 H), 3.84-3.75 (m, 4 H), 3.73 (dd, J = 3.5, 12.0 Hz, 1 H), 3.59-3.57 (m, 1 H), 3.53 (dd, J = 5.0, 11.5 Hz, 1 H), 3.39 (dd, J = 3.0, 9.5 Hz, 1 H), 3.08-3.04 (m, 1 H), . ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 154.7, 153.9, 143.4, 143.2, 141.3, 141.2, 138.5, 138.3, 138.0, 137.8, 137.6, 137.2, 128.6, 128.4 (2 C), 128.3, 128.2, 128.1, 127.9 (2 C), 127.8, 127.7, 127.6, 127.5, 127.4, 127.2 (2 C), 127.0, 125.4, 125.2, 120.1, 120.0, 100.8 (C-1 of ring C), 98.7 (C-1 of ring E), 97.3 (C-1 of ring B), 81.2, 78.4, 78.0, 77.6, 76.8, 75.5, 75.2, 74.8, 74.6, 74.3, 73.8, 73.7, 72.6, 71.9, 70.7, 70.4, 70.3, 68.3, 68.1, 67.5, 62.3, 55.6, 46.6. HRMS: $C_{86}H_{82}Cl_3NO_{21}$ $[M + 2\ NH_4]^{2+}$ calcd: 802.7566, obsd: 802.7570.



13

Benzyl [3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-levulinyl-*a*-D-mannopyranosyl]-(1→6)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6

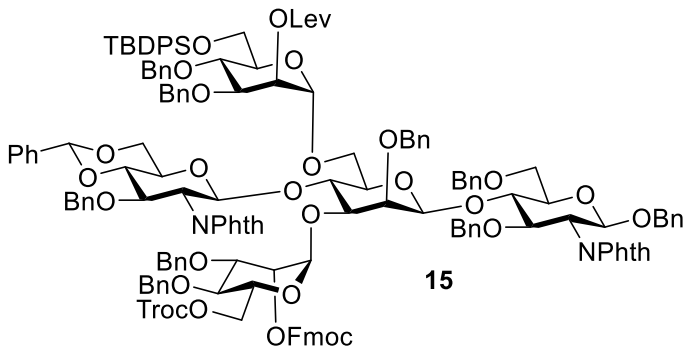
-*O*-(2,2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (13). A mixture of compound **11** (139 mg, 0.09 mmol), donor **12** (85 mg, 0.1 mmol), and 4 A molecular sieves in DCM (2 ml) was stirred at room temperature for 30 min. Then it was cooled to -60ºC followed by addition of *N*-iodosuccinimide (27 mg, 0.12 mmol) and TfOH (0.002 ml, 0.15 equiv to donor). The reaction was stirred at -30ºC for 1 hours, after which it was quenched by DIPEA and filtered by celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate = 2/1) and afforded **13** (86 mg, 55%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ. 7.78-7.60 (m, 11 H), 7.42-7.07 (m, 42 H), 7.04-7.03 (m, 4 H), 7.86-7.85 (m, 2 H), 6.72-6.68 (m, 3 H), 5.33 (s, 1 H), 5.29 (s, 1 H, H-1 of ring E), 5.09 (d, J = 7.5 Hz, 1 H, H-1 of ring B), 5.00 (d, J = 11.0 Hz, 1 H), 4.96 (d, J = 12.0 Hz, 1 H), 4.87 (d, J = 10.5 Hz, 1 H), 4.83 (d, J = 11.5 Hz, 1 H), 4.80-4.72 (m, 7 H, H-1 of ring D), 4.64 (d, J = 11.0 Hz, 1 H), 4.58-4.56 (m, 2 H, H-1 of ring C), 4.53-4.37 (m, 8 H), 4.31-4.17 (m, 5 H), 4.07-3.95 (m, 5 H), 3.92-3.76 (m, 7 H), 3.73 (dd, J = 3.0, 11.0 Hz, 1 H), 3.65 (d, J = 9.5 Hz, 1 H), 3.53 (d, J = 9.5 Hz , 1 H), 3.49 (dd, J = 3.5, 10.5 Hz, 1 H), 3.35 (dd, J = 2.0, 9.5 Hz, 1 H), 3.09-3.05 (m, 1 H), 2.61-2.52 (m, 4 H), 2.06 (s, 3 H), 1.06 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ. 206.2, 171.7, 154.8, 154.0, 143.4, 143.2, 141.3, 141.2, 138.7, 138.6, 138.2, 138.1, 137.9 (2 C), 137.7, 137.2, 135.9, 135.6, 133.8, 133.0, 129.7, 129.6, 128.6, 128.4, 128.3 (2 C), 128.2, 128.1, 128.0 (2 C), 127.9 (2 C), 127.8 (2 C), 127.7 (3 C), 127.6 (3 C), 127.5 (2 C), 127.4, 127.2, 126.8, 125.4, 125.2, 120.0 (2 C), 101.6 (C-1 of ring C), 99.2 (C-1 of ring E), 97.5 (C-1 of ring D), 97.3 (C-1 of ring B), 81.1, 79.3, 77.9 (2 C), 77.7, 76.8, 76.6, 75.5 (2 C), 74.8, 74.2, 74.0, 73.9 (2 C), 73.5, 72.5, 72.3, 71.8, 71.5, 70.7, 70.3, 70.2, 68.7, 68.5, 68.2, 68.0, 66.7, 62.7, 55.7, 46.5, 38.0, 29.8, 28.0, 26,8, 19.4. HRMS: $C_{127}H_{128}Cl_3NO_{28}Si$ $[M + 2\ NH_4]^{2+}$ calcd: 1141.9067, obsd: 1141.8999.



14

Benzyl [3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-levulinyl-*a*-D-mannopyranosyl]-(1→6)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6-*O*-(2,2,2-trichloroethoxylcarbonyl)- α-D-mannopyranosyl]-(1→3)-(4-*O*-acetyl-2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (14). To a solution of compound **13** (150 mg) in pyridine (3 ml) was added acetic anhydride (1.5 ml). The reaction was stirred at room temperature for 3 h, after which it was extracted with ethyl acetate and washed with 10% HCl, sat. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate/DCM = 3/1/1) to afford **14** (139 mg, 91%). ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.81 (dd, J = 2.0, 7.5 Hz, 2 H), 7.73-7.64 (m, 8 H), 7.45-7.28 (m, 26 H), 7.24-7.20 (m, 10 H), 7.12-7.09 (m, 2 H), 7.07-7.04 (m, 4 H), 6.84 (d, J = 7.0 Hz, 2 H), 6.67-6.60 (m, 3 H), 5.37-5.34 (m, 2 H, H-1 of ring E), 5.11 (d, J = 7.5 Hz, 1 H, H-1 of ring B), 5.03 (s, 1 H), 5.00-4.97 (m, 4 H), 4.94 (d, J = 11.0 Hz, 1 H), 4.82-4.77 (m, 6 H, H-1 of ring D), 4.71 (d, J = 11.5 Hz, 1 H), 4.67-4.61 (m, 3 H), 4.59-4.47 (m, 6 H, H-1 of ring C), 4.41-4.33 (m, 4 H), 4.31-4.28 (m, 1 H), 4.24-4.19 (m, 2 H), 4.16-4.12 (m, 1 H), 4.06-3.96 (m, 4 H), 3.85-3.81 (m, 4 H), 3.77 (dd, J = 3.0, 11.0 Hz, 1 H), 3.68-3.65 (m, 2 H), 3.55-3.50 (m, 2 H), 3.44 (dd, J = 2.0, 9.5 Hz, 1 H), 3.27-3.24 (m, 1 H), 2.63-2.54 (m, 4 H), 2.07 (2, 3 H), 2.02 (s, 3 H), 1.07 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 206.3, 171.8, 169.6, 154.6, 154.0, 143.4, 143.1, 141.3 (2 C), 138.9, 138.5, 138.3 (2 C), 138.1, 138.0, 137.5, 137.2, 135.9, 135.6, 133.9, 133.2, 131.7, 129.6, 129.5, 128.6, 128.4 (2 C), 128.3, 128.2 (3 C), 128.1, 128.0 (2 C), 127.9 (2 C), 127.8 (2 C), 127.7, 127.6 (2 C), 127.5 (3 C), 127.4, 127.3, 127.2 (2 C), 126.9, 125.4, 125.1, 120.1 (2 C), 101.4 (C-1 of ring C), 99.5 (C-1 of ring E), 97.8

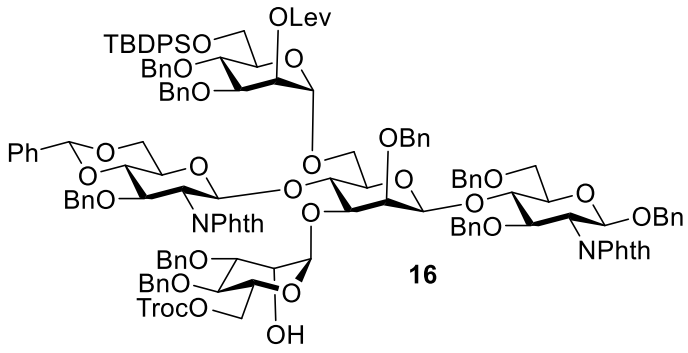
(C-1 of ring D), 97.4 (C-1 of ring B), 94.5, 80.5, 79.3, 78.4, 77.5, 77.3, 76.1, 75.1, 74.8, 74.1 (2 C), 73.9, 73.7, 73.5, 72.8, 72.7, 72.4, 71.8, 71.7, 70.7, 70.3, 68.9, 68.5, 68.2, 66.9, 62.7, 55.6, 46.6, 38.0, 32.0, 29.8, 28.1, 26.8, 20.9, 19.4. HRMS: $C_{129}H_{130}Cl_3NO_{29}Si$ $[M + 2\ NH_4]^{2+}$ calcd: 1162.9120, obsd: 1162.9050.



15

Benzyl [3,4-di-*O*-benzyl-6-*O*-*tert*-Butyldiphenylsilyl-2-*O*-levulinyl-*a*-D-manno pyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6-*O*-(2,2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopy ranoside (15). A mixture of compound **13** (150 mg, 0.07 mmol), donor **8** (119 mg, 0.2 mmol), and 4 A molecular sieves in DCM (2 ml) was stirred at room temperature for 30 min. Then it was cooled to -78ºC followed by addition of a solution of AgOTf (154 mg, 0.6 mmol in DCM/diethyl ether = 1:1) and *p*-TolSCl (0.029 ml). The reaction was allowed to warm up to -30ºC over 40 min, after which it was quenched by DIPEA and filtered by celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate/DCM = 5/1/1) to afford **15** (146 mg, 81%). ^{1}H-NMR (500 MHz, $CDCl_3$): *δ.* 7.83-7.49 (m, 16 H), 7.44-7.27 (m, 27 H), 7.25-7.16 (m, 14 H), 7.12-7.04 (m, 4 H), 7.01-6.96 (m, 5 H), 6.84-6.72 (m, 7 H), 6.63-6.60 (m, 1 H), 6.50-6.48 (m, 2 H), 5.64 (s, 1 H), 5.61 (s, 1 H), 5.36 (s, 1 H), 5.23-5.21 (m, 2 H, H-1 of ring E and H-1 of bisecting GA), 5.03-4.99 (m, 2 H, H-1 of ring B), 4.94-4.92 (m, 2 H, H-1 of ring D), 4.85-4.24 (m, 28 H, H-1 of ring C), 4.20-4.06 (m, 5 H), 4.02-3.97 (m, 5 H), 3.87-3.82 (m, 2 H), 3.76-3.72 (m, 3

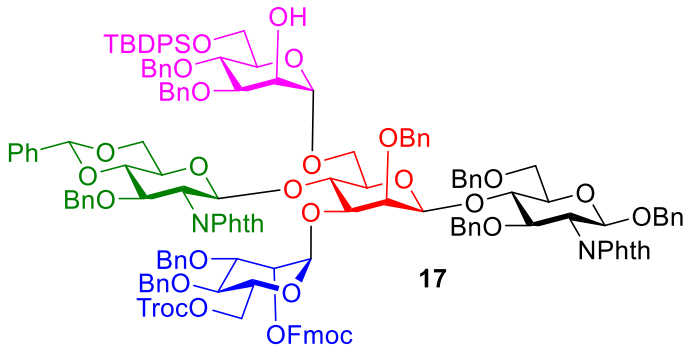
H), 3.65-3.55 (m, 4 H), 3.38-3.60 (m, 1 H), 3.33 (dd, J = 2.5, 12.0 Hz, 1 H), 3.22 (d, J = 10.0 Hz, 1 H), 2.35-2.10 (m, 4 H), 1.93 (s, 3 H), 1.02 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 206.2, 171.3, 155.0, 154.1, 144.2, 143.5, 141.3, 141.1, 139.0, 138.5, 138.4, 138.3, 138.2, 138.0, 137.8, 1376., 137.5, 137.2, 136.0, 135.6, 134.0, 133.1, 131.7, 129.7, 129.5, 128.8, 128.7, 128.5, 128.4 (2 C), 128.3, 128.2, 128.1 (2 C), 128.0 (3 C), 127.9 (2 C), 127.8, 127.7, 127.6 (2 C), 127.5 (2 C), 127.3, 127.2 (2 C), 127.1, 126.8, 126.2, 125.8, 125.4, 119.9, 119.8, 101.1, 100.7 (C-1 of ring C), 99.5 (C-1 of ring E), 98.0 (C-1 of ring D), 97.7 (C-1 of bisecting GA), 97.2 (C-1 of ring B), 82.2, 79.1, 78.8, 78.1, 77.8, 77.1, 76.8, 75.3, 75.1, 75.0, 74.6, 74.5, 74.0, 73.8, 73.5, 73.4, 72.5, 71.9 (2 C), 71.8 (2 C), 70.7, 70.6, 70.2, 68.7, 68.6, 68.3, 66.7, 64.4, 62.6, 55.8, 55.6, 46.8, 37.8, 29.7, 27.9, 26.8, 19.4. HRMS: $C_{155}H_{151}Cl_3N_2O_{34}Si$ $[M + 2\ NH_4]^{2+}$ calcd: 13760.4730, obsd: 1376.4708.



16

Benzyl [3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-levulinyl-*a*-D-mannopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-[3,4-di-*O*-benzyl-6-*O*-(2,2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (16). Following the general procedure for Fmoc removal, compound **16** was obtained in 95% yield from compound **15**. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.74-7.69 (m, 5 H), 7.63-7.15 (m, 37 H), 7.12-7.10 (m, 1 H), 7.06-7.03 (m, 1 H), 7.00-6.97 (m, 1 H), 6.94 (d, J = 7.5 Hz, 2 H), 6.86-6.79 (m, 3 H), 6.74 (d, J = 7.5 Hz, 2 H), 6.61 (t, J = 7.0 Hz, 1 H), 6.48 (t, J = 7.0 Hz, 2 H), 5.55 (s, 1 H), 5.29 (s, 1 H), 5.22 (s, 1 H), 5.20 (d, J = 8.5 Hz, 1 H), 4.98

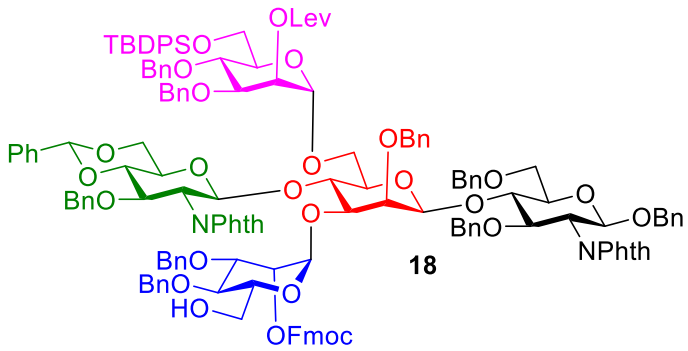
(d, J = 8.0 Hz, 1 H), 4.94-4.91 (m, 2 H), 4.87-4.84 (m, 3 H), 4.81-4.69 (m, 7 H), 4.50-4.32 (m, 10 H), 4.17-4.04 (m, 5 H), 3.98-3.88 (m, 5 H), 3.83-3.69 (m, 6 H), 3.60-3.56 (m, 3 H), 3.52-3.47 (m, 2 H), 3.36-3.32 (m, 2 H), 3.18 (dd, J = 4.0, 12.5 Hz, 1 H), 2.36-2.06 (m, 4 H), 1.91 (s, 3 H), 1.00 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 206.1, 171.3, 154.0, 139.1, 138.5, 138.4 (2 C), 138.1, 137.8, 137.7, 137.3, 137.2, 135.9, 135.6, 134.1, 131.7, 129.8, 129.5, 128.7, 128.6 (2 C), 128.4, 128.3, 128.2 (3 C), 128.1 (2 C), 128.0 (2 C), 127.9, 127.8, 127.7 (2 C), 127.6 (2 C), 127.4 (2 C), 127.2, 126.1, 101.2 (C -1 of ring C), 100.8, 100.6 (C -1 of ring E), 98.7 (C -1 of ring D), 97.8 (C -1 of ring bisecting GA), 97.2 (C -1 of ring B), 82.9, 79.0, 78.6, 77.2, 75.1, 74.8, 74.7, 74.3, 74.2, 74.1, 74.0, 73.5, 73.4, 72.4, 72.2, 71.8, 70.6, 70.0, 68.7, 68.5, 68.3 (2 C), 67.9, 66.0, 56.2, 55.6, 37.7, 26.7, 19.3. HRMS: $C_{140}H_{141}Cl_3N_2O_{32}$ $[M + 2\ NH_4]^{2+}$ calcd: 1265.4489, obsd: 1265.4434.



17

Benzyl [3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-*a*-D-mannopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6-*O*-(2,2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (17). Following the general procedure for Lev removal, compound **17** was obtained in 85% yield from compound **15**. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.82 (d, J = 7.5 Hz, 1 H), 7.78 (d, J = 7.5 Hz, 1 H), 7.77 (d, J = 7.5 Hz, 1 H), 7.74-7.61 (m, 9 H), 7.46-7.28 (m, 23 H), 2.26-7.19 (m, 6 H), 7.17-6.98 (m, 13 H), 6.83-6.80 (m, 3 H), 6.77-6.76 (m, 2 H), 6.73-6.70 (m, 2 H), 6.65 (t, J = 7.5 Hz, 1 H), 6.54 (t, J = 7.5 Hz, 2 H), 5.63 (s, 1

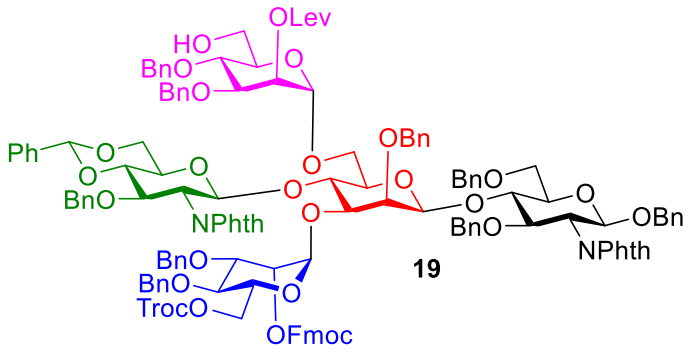
H), 5.61-5.60 (m, 1 H), 5.27 (d, J = 1.5 Hz, 1 H), 5.18 (d, J = 8.0 Hz, 1 H), 5.04 (d, J = 8.5 Hz, 1 H), 5.01 (d, J = 11.0 Hz, 1 H), 4.92 (d, J = 11.5 Hz, 1 H), 4.89 (s, 1 H), 4.85-4.71 (m, 7 H), 4.68-4.31 (m, 17 H), 4.24 (t, J = 9.5 Hz, 1 H), 4.18-4.08 (m, 5 H), 4.03-3.94 (m, 4 H), 3.88-3.80 (m, 5 H), 3.77-3.70 (m, 2 H), 3.67-3.55 (m, 3 H), 3.46-3.42 (m, 2 H), 3.43 (dd, J = 4.5, 12.5 Hz, 1 H), 3.30 (dd, J = 3.0, 10.0 Hz, 1 H), 2.59-2.56 (m, 1 H), 1.00 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 167.3, 155.0, 154.1, 144.2, 143.4, 141.3, 141.1, 139.0, 138.6 (2 C), 138.3, 138.1, 137.9, 137.8, 137.6, 137.5, 137.2, 136.0, 135.7, 134.0, 133.9, 133.3, 131.7, 129.5, 129.4, 128.8, 128.5, 128.4 (2 C), 128.3 (3 C), 128.2, 128.1 (3 C), 128.0 (2 C), 127.9 (2 C), 127.8, 127.7 (3 C), 127.6 (2 C), 127.5 (3 C), 127.2 (2 C), 127.1 (2 C), 126.7, 126.2, 125.8, 125.4, 119.9, 119.8, 101.1 (C -1 of ring C), 100.3, 100.0 (C -1 of ring E), 99.4 (C -1 of ring D), 97.8 (C -1 of bisecting GA), 97.3 (C -1 of ring B), 94.5, 82.2, 80.8, 78.3, 78.2, 77.9, 77.7, 77.2, 76.9, 75.6, 75.3, 74.8, 74.7, 74.4, 74.2, 74.1, 74.0, 73.8 (2 C), 73.4, 72.4, 72.1 (2 C), 71.8, 70.7, 70.6, 70.3, 68.5, 68.2, 66.5, 65.0, 62.9, 55.8, 55.6, 46.8, 26.8, 19.3. HRMS: $C_{150}H_{145}Cl_3N_2O_{32}Si$ $[M + 2\ NH_4]^{2+}$ calcd: 1327.4646, obsd: 1327.4612.



18

Benzyl [3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-levulinyl-*a*-D-mannopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (18). Following the general procedure for Troc removal, compound **18** was obtained in 74% yield from compound

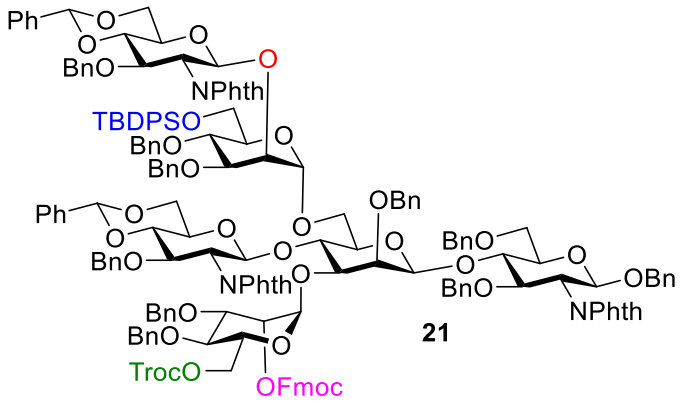
15. ^{1}H-NMR (500 MHz, $CDCl_3$): δ. 7.79-7.60 (m, 15 H), 7.50-7.27 (m, 28 H), 7.24-7.09 (m, 18 H), 7.04-6.97 (m, 5 H), 6.86-6.80 (m, 3 H), 6.75-6.72 (m, 4 H), 6.62 (t, J = 7.5 Hz, 1 H), 6.49-6.46 (m, 2 H), 5.64 (s, 1 H), 5.41 (s, 1 H), 5.33 (s, 1 H), 5.25 (s, 1 H), 5.21 (d, J = 8.5 Hz, 1 H), 4.99-4.97 (m, 2 H), 4.93 (d, J = 11.5 Hz, 1 H), 4.88 (s, 1 H), 4.83 (s, 2 H), 4.80 (d, J = 11.5 Hz, 1 H), 4.73-4.54 (m, 11 H), 4.49-4.05 (m, 18 H), 3.99-3.94 (m, 5 H), 3.89-3.82 (m, 2 H), 3.77-3.61 (m, 7 H), 3.55-3.50 (m, 2 H), 3.34-3.33 (m, 3 H), 2.75 (d, J = 5.5 Hz, 1 H), 2.35-2.21 (m, 4 H), 1.03 (s, 3 H), 1.00 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ. 206.1, 171.3, 167.4, 167.2, 154.9, 144.1, 143.5, 141.3, 141.1, 139.1, 138.5, 138.4, 138.3, 137.9, 137.8, 137.5, 137.2, 136.0, 135.9, 135.6 (2 C), 134.0, 133.1, 131.7 (2 C), 129.7, 129.5, 128.7, 128.5 (2 C), 128.4, 128.3 (4 C), 128.2 (2 C), 128.1 (3 C), 128.0 (4 C), 127.9 (3 C), 127.8, 127.7 (3 C), 127.6 (2 C), 127.5 (2 C), 127.4, 127.3, 127.2 (2 C), 127.1 (2 C), 126.8, 126.2 (2 C), 125.6, 125.4, 123.0, 119.9, 119.8, 101.0 (C -1 of ring C), 100.8, 99.3 (C -1 of ring E), 98.0 (C -1 of ring D), 97.9 (C -1 of bisecting GA), 97.2 (C -1 of ring B), 82.2, 79.1, 78.9, 78.1, 77.5, 75.2, 75.0, 74.6, 74.4, 74.2, 73.8, 73.6, 73.4, 72.5, 72.3, 72.1, 71.9, 71.8, 70.6, 68.7, 68.2, 66.5, 64.5, 62.6, 62.4, 55.9, 55.6, 46.8, 37.8, 31.9, 27.8, 26.7, 22.7, 19.3. HRMS: $C_{152}H_{150}N_2O_{32}Si$ $[M + 2\ NH_4]^{2+}$ calcd: 1289.5308, obsd: 1289.5237.



19

Benzyl [3,4-di-*O*-benzyl-2-*O*-levulinyl-*a*-D-mannopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6-*O*-(2,2,2-trichloroethoxylcarbonyl) - α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (19). Following the general

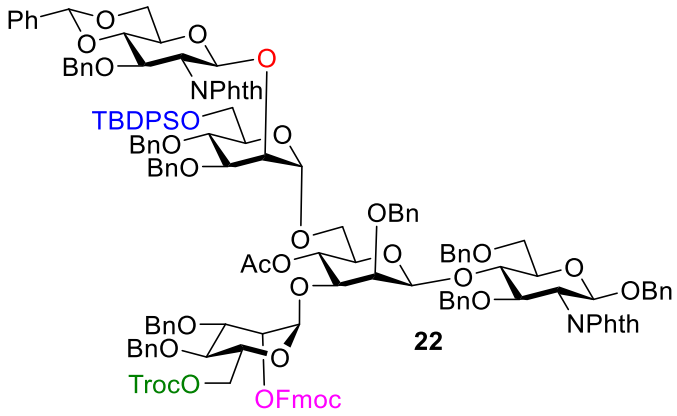
procedure for TBDPS removal, compound **19** was obtained in 81% yield from compound **15**. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.84-7.69 (m, 8 H), 7.44-7.28 (m, 22 H), 7.25-7.17 (m, 16 H), 7.11-7.05 (m, 5 H), 7.02-6.96 (m, 5 H), 6.90-6.86 (m, 3 H), 6.82-6.78 (m, 4 H), 6.66-6.64 (m, 1 H), 6.01-6.58 (m, 2 H), 5.65 (s, 1 H), 5.63 (bs, 1 H), 5.27-5.24 (m, 3 H), 5.02-4.99 (m, 2 H), 4.93 (s, 1 H), 4.84-4.80 (m, 4 H), 4.78-4.77 (m, 2 H), 4.75-4.64 (m, 6 H), 4.61-4.51 (m, 6 H), 4.48-4.38 (m, 8 H), 4.31-4.19 (m, 6 H), 4.1-4.08 (m, 3 H), 4.00-3.93 (m, 2 H), 3.90-3.82 (m, 3 H), 3.76-3.55 (m 9 H), 3.40-3.34 (m, 2 H), 3.23 (dd, J = 2.0, 9.5 Hz, 1 H), 2.59 (dd, J = 3.5, 9.5 Hz, 1 H), 2.37-2.21 (m, 4 H), 1.95 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 206.1, 171.3, 167.5, 155.1, 154.1, 144.3, 143.4, 141.3, 141.1, 138.5, 138.4, 138.2, 138.0, 137.8, 137.6, 137.4, 137.1, 134.2, 128.7, 128.5, 128.4 (3 C), 128.3, 128.2, 128.1, 128.0 (3 C), 127.9 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6 (2 C), 127.5, 127.3 (2 C), 127.2, 127.1, 127.0, 126.2, 125.8, 125.4, 119.9, 119.8, 101.1 (C -1 of ring C), 100.3, 99.5 (C -1 of ring E), 97.5 (C -1 of ring D), 97.2 (C -1 of bisecting GA), 97.1 (C -1 of ring B), 82.2, 78.5, 78.3, 78.1, 77.7, 77.5, 77.2, 76.8, 76.0, 75.2, 75.0, 74.8, 74.6, 74.5, 74.3, 74.1, 74.0, 73.8, 73.4, 72.4, 71.7, 71.6, 71.5, 70.8, 70.6, 70.3, 68.5, 68.3, 66.8, 64.4, 62.3, 55.7, 55.6, 46.9, 37.9, 29.7, 29.6, 27.9. HRMS: $C_{139}H_{133}Cl_3N_2O_{34}$ $[M + 2\ NH_4]^{2+}$ calcd: 1257.4241, obsd: 1257.4250.



21

Benzyl [3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside-(1→2)-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-*a*-D-mannopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6-*O*-(2,

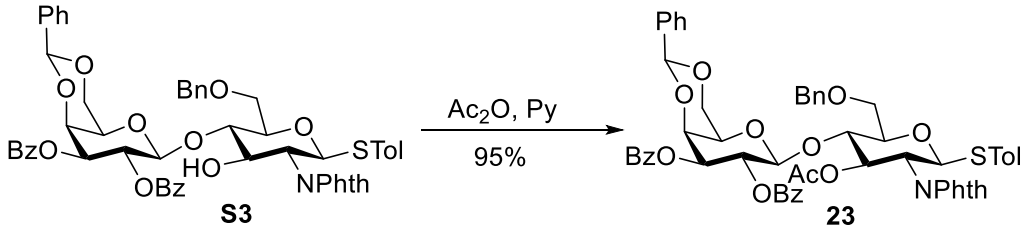
2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (21). Following the general procedure for glycosylation catalyzed by NIS/AgOTf, compound **21** was obtained from **17** in 53% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.72-7.29 (m, 46 H), 7.22-6.75 (m, 38 H), 6.69 (d, J = 8.0 Hz, 1 H), 6.59-6.55 (m, 2 H), 6.48-6.42 (m, 3 H), 5.52 (s, 1 H), 5.47 (s, 1 H, H-1 of ring E), 5.22 (d, J = 8.5 Hz, 1 H, H-1 of GA on 1,6 arm), 5.15 (bs, 2 H, H-1 of bisecting GA and H-1 of ring E), 5.10 (d, J = 8.5 Hz, 1 H, 1-H of ring B), 5.00-4.98 (m, 1 H, 1-H of ring D), 4.89-4.81 (m, 4 H), 4.78-4.50 (m, 20 H), 4.45-4.29 (m, 11 H, H-1 of ring C), 4.23-4.06 (m, 10 H), 3.99-3.85 (m, 5 H), 3.81-3.56 (m, 16 H), 3.46-3.41 (m, 8 H), 3.25 (s, 1 H), 3.20-3.18 (m, 1 H), 3.02 (bs, 1 H), 2.75-2.69 (m, 2 H), 0.79 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 167.5, 167.3, 154.0, 139.1, 138.9, 138.8, 138.7, 138.5, 138.4, 138.2, 138.0 (2 C), 137.9 (2 C), 137.8 (2 C), 137.7, 137.6 (2 C), 137.3, 137.2, 136.0, 135.7, 135.5, 135.4, 134.1, 134.0, 133.9, 133.5, 133.4 (2 C), 133.2, 132.9, 131.7, 131.5, 129.7, 129.3, 129.1, 128.9 (2 C), 128.6 (2 C), 128.5, 128.4 (3 C), 128.2 (2 C), 128.1 (2 C), 128.0 (2 C), 127.9 (2 C), 127.8 (2 C), 127.7 (3 C), 127.6 (2 C), 127.5, 127.4 (3 C), 127.3 (2 C), 127.2 (2 C), 127.1, 126.8, 126.4, 126.2, 126.1, 123.6, 123.5, 123.3, 123.0, 122.9, 101.3 (C-1 of ring E), 101.1 (C-1 of ring D), 101.0 (2 C, C-1 of ring C), 100.9, 97.8 (C-1 of GA on 1,6 arm), 97.4 (C-1 of ring B), 97.2 (C-1 of bisecting GA),, 94.5, 83.2, 82.8, 80.2, 79.9, 79.6 (2 C), 79.4, 79.3, 77.9, 77.2, 76.1, 75.2, 74.9, 74.8, 74.7, 74.6, 74.5, 74.2, 74.1, 74.0, 73.9 (2 C), 73.8, 73.4 (2 C), 73.2, 73.0, 72.6, 72.2, 72.1 (2 C), 70.5, 70.1, 68.6, 68.4, 68.3, 68.2, 68.1, 66.1, 66.0, 65.7, 63.5, 56.2, 55.7, 55.5, 53.4, 26.7. MALDI: $C_{178}H_{168}Cl_3N_3O_{38}Si$ $[M + Na]^+$ calcd: 3114.7, obsd: 1257.4250.



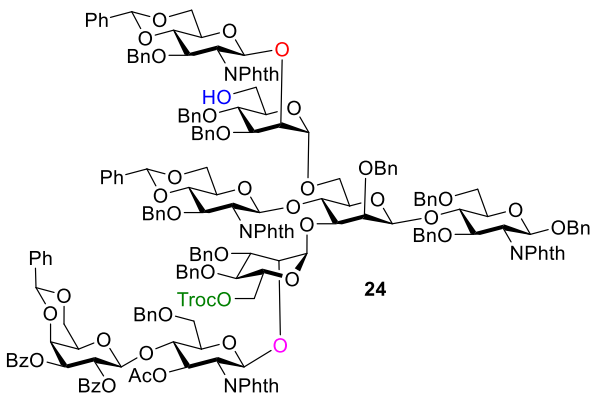
22

Benzyl [3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside-(1→2)-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-*a*-D-mannopyranosyl]-(1→6)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-6-*O*-(2,2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-(4-*O*-acetyl-2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (22). Following the general procedures for Lev removal and glycosylation catalyzed by NIS/AgOTf, compound **22** was obtained from **20** in 71% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 8.05-8.03 (m, 3 H), 7.79-7.73 (m, 3 H), 7.65-7.61 (m, 3 H), 7.57-7.46 (m, 8 H), 7.42-7.28 (m, 25 H), 7.25-7.14 (m, 11 H), 7.09-6.99 (m, 7 H), 6.94-6.91 (m, 3 H), 6.88-6.83 (m, 4 H), 6.63-6.60 (m, 3 H), 5.51 (s, 1 H), 5.39 (t, J = 10.0 Hz, 1 H), 5.05-4.94 (m, 5 H, H-1 of ring B, E and GA on 1,6 arm), 4.82-4.15 (m, 32 H, H-1 of ring C, D), 4.05-4.01 (m, 1 H), 3.96 (dd, J = 3.0, 9.0 Hz, 1 H), 3.91-3.89 (m, 4 H), 3.82-3.70 (m, 6 H), 3.65 (d, J = 10.0 Hz, 1 H), 3.58-3.51 (m, 3 H), 3.26-3.18 (m, 3 H), 3.06-3.01 (m, 1 H), 1.85 (s, 3 H), 0.86 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 169.3, 166.5, 154.6, 154.0, 146.5, 143.4, 143.1, 141.3, 141.2, 139.3, 138.9, 138.6, 138.4, 138.1, 138.0, 137.9, 137.6, 137.5, 137.1, 135.4, 135.3, 134.1, 133.8, 133.5, 133.0, 130.0, 129.7, 129.4, 129.3, 129.1, 128.8, 128.5, 128.6, 128.5, 128.3 (3 C), 128.2 (2 C), 128.1, 128.0 (4 C), 127.9 (4 C), 127.8 (2 C), 127.7, 127.6 (2 C), 127.5 (2 C), 127.4, 127.3 (3 C), 127.2 (3 C), 127.0, 126.1 (2 C), 125.3, 125.1, 124.1, 123.5, 123.1, 123.0, 120.1 (2 C), 114.1, 101.7 (C-1 of ring C), 101.1, 99.5 (C-1 of ring E), 97.9 (C-1 of GA on 1,6 arm), 97.6 (C-1 of ring D), 97.2 (C-1 of ring B), 94.5, 82.7, 80.4, 80.1, 79.7, 78.9, 77.8, 77.2, 76.2, 75.1, 74.9, 74.7, 74.6, 74.5, 74.3, 74.1, 73.9, 73.7, 73.6 (2 C), 73.5, 73.0, 72.3, 72.0, 71.9, 71.8, 70.6,

70.4, 70.3, 69.2, 68.4, 68.1, 66.4, 65.6, 64.0, 55.8, 55.6, 46.6, 26.7, 20.8. HRMS: $C_{152}H_{147}Cl_3N_2O_{33}Si$ $[M + 2\ NH_4]^{2+}$ calcd: 1348.4698, obsd: 1348.4600.

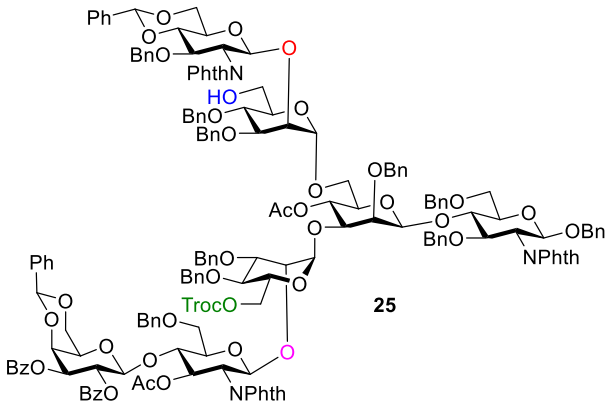


***p*-Methylphenyl (2,3-di-*O*-benzyol-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (23).** To a solution of compound **S3**[3] (100 mg) in pyridine (2 ml) was added acetic anhydride (1 ml). The reaction was stirred at room temperature for 5 h, after which it was extracted with ethyl acetate and washed with 10% HCl, sat. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexanes/ethyl acetate/DCM = 3/1/1) to afford **23** (99 mg, 95%). ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.96-7.92 (m, 4 H), 7.87-7.85 (m, 2 H), 7.75-7.71 (m, 2 H), 7.54-7.46 (m, 5 H), 7.43-7.37 (m, 7 H), 7.35-7.30 (m, 7 H), 7.02 (d, J = 8.0 Hz, 2 H), 5.79 (t, J = 9.5 Hz, 1 H), 5.73 (dd, J = 8.0, 10.0 Hz, 1 H), 5.63 (d, J = 10.5 Hz, 1 H), 5.48 (s, 1 H), 5.22 (dd, J = 3.5, 10.5 Hz, 1 H), 4.82 (d, J = 8.0 Hz, 1 H), 4.73 (d, J = 12.0 Hz, 1 H), 4.51 (d, J = 3.0 Hz, 1 H), 4.47 (d, J = 12.0 Hz, 1 H), 4.35-4.29 (m, 2 H), 4.14 (t, J = 9.5 Hz, 1 H), 4.08 (d, J = 12.5 Hz, 1 H), 3.77 (dd, J = 3.0, 11.5 Hz, 1 H), 3.64 (d, J = 11.0 Hz, 1 H), 3.58 (d, J = 10.0 Hz, 1 H), 3.46 (s, 1 H), 2.29 (s, 3 H), 1.92 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 170.6, 167.7, 167.4, 166.2, 164.6, 138.4, 138.2, 137.5, 134.3, 134.1, 133.7, 133.3, 133.2, 131.8, 131.3, 129.9, 129.7, 129.6, 129.4, 129.0 (2 C), 128.6, 128.4 (2 C), 128.1, 128.0, 127.9, 127.5, 126.4, 123.7, 123.5, 101.1, 100.3, 83.2, 78.8, 74.8, 73.5, 73.4, 73.3, 73.2, 69.4, 68.6, 67.7, 66.3, 54.0, 21.2, 20.5. HRMS: $C_{57}H_{51}NO_{14}S$ $[M + NH_4]^+$ calcd: 1023.3369, obsd: 1023.3364.



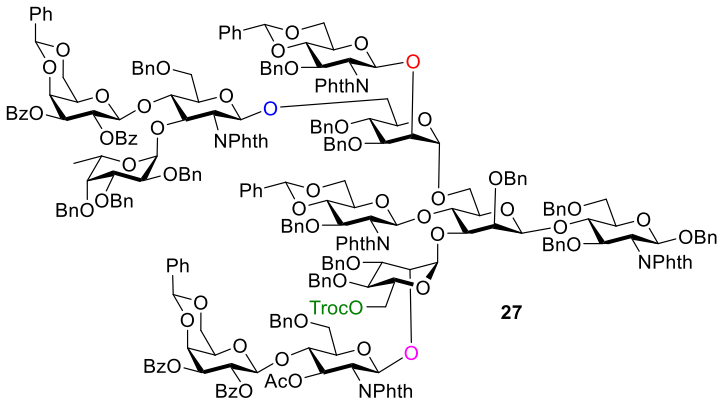
Benzyl [(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(2,2,2-trichloroethoxylcarbonyl)- α-D-mannopyranosyl]-(1→3)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside-(1→4)-[2-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (24). Following the general procedures for Fmoc removal, glycosylation catalyzed by NIS/AgOTf and TBDPS removal, compound **24** was obtained from **21** in 43% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.90 (d, J = 8.0 Hz, 2 H), 7.75-7.68 (m, 7 H), 7.48-7.39 (m, 7 H), 7.36-7.28 (m, 12 H), 7.24-7.13 (m, 10 H), 7.11-7.02 (m, 10 H), 6.99-6.94 (m, 5 H), 6.92-6.88 (m, 2 H), 6.85 (t, J = 7.5 Hz, 1 H), 6.76-6.71 (m, 3 H), 6.65 (d, J = 7.0 Hz, 1 H), 6.57 (t, J = 7.0 Hz, 1 H), 6.50 (t, J = 7.0 Hz, 2 H), 6.08 (t, J = 10.5 Hz, 1 H), 5.82 (d, J = 8.0 Hz, 1 H, H-1 of glucosamine on 1,3 arm), 5.76 (dd, J = 8.0, 9.5 Hz, 1 H), 5.46 (s, 1 H), 5.45 (s, 1 H), 5.15 (s, 1 H), 5.13 (m, 2 H), 5.01 (d, J = 8.0 Hz, 1 H, H-1 of ring B), 4.96 (s, 1 H, H-1 of ring E), 4.94 (s, 1 H, H-1 of ring D) 4.87-4.70 (m, 7 H, H-1 of galactose and bisecting GA), 4.66 (d, J = 11.5 Hz, 1 H), 4.63 (d, J = 11.5 Hz, 1 H), 4.59 (d, J = 12.0 Hz, 1 H), 4.56-4.45 (m, 5 H), 4.43-4.37 (m, 4 H), 4.34-4.26 (m, 4 H, H-1 of GA on 1,6 arm), 4.24-4.11 (m, 5 H, H-1 of ring C), 4.07-3.94 (m, 8 H), 3.90-3.78 (m, 6 H), 3.73 (t, J = 8.0 Hz, 1 H), 3.67-3.55 (m, 6 H), 3.52 (t, J = 9.5 Hz, 1 H), 3.44-3.35 (m, 5 H), 3.22-3.12 (m, 3 H), 2.98-2.92 (m, 2 H), 2.65 (bs, 1 H), 1.96 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 170.6, 166.1, 164.6, 153.5, 138.9, 138.7, 138.4, 138.2 (2 C), 138.1, 138.0 (3 C), 137.6, 137.5 (2 C), 137.3, 137.1, 134.0, 133.8, 133.2,

133.0, 132.8, 131.7, 131.5, 129.9, 129.7, 129.6, 129.3, 129.0, 128.9 (2 C), 128.8 (2 C), 128.6, 128.5, 128.4, 128.3, 128.2 (2 C), 128.1 (3 C), 128.0 (4 C), 127.9 (2 C), 127.8 (3 C), 127.6 (3 C), 127.5, 127.4, 127.3 (2 C), 127.1, 127.0, 126.7, 126.4, 126.1 (2 C), 101.1, 101.0, 100.8 (C-1 of ring C), 100.2 (C-1 of ring E), 98.3 (C-1 of galactose), 97.4 (C-1 of GA on 1,6 arm), 97.2 (C-1 of bisecting GA), 97.0 (C-1 of ring D), 96.6 (C-1 of ring B), 95.7 (C-1 of glucosamine on 1,3 arm), 83.4, 82.6, 78.8, 78.2, 77.2, 76.7, 75.6, 75.1, 74.7, 74.6, 74.5, 74.4, 73.9 (2 C), 73.7, 73.4, 73.2, 73.0, 72.8, 70.9, 70.7, 70.6, 70.3, 69.9, 69.5, 69.2, 68.6, 68.5, 68.4, 68.3, 66.3, 65.5, 65.3, 64.0, 62.7, 55.6, 20.7. MALDI: $C_{197}H_{183}Cl_3N_4O_{50}$ $[M + Na]^+$ calcd: 3535.9, obsd: 3536.2.



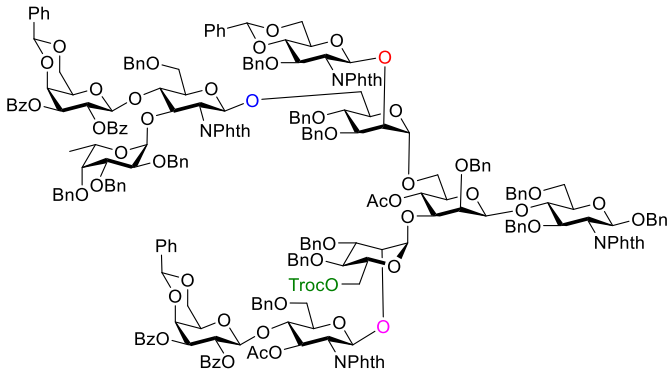
Benzyl [2,3-di-*O*-benzyol-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(2,2,2-trichloroethoxylcarbonyl)-α-D-mannopyranosyl]-(1→3)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside-(1→2)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→6)-[4-*O*-acetyl-2-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (25). Following the general procedures for Fmoc removal, glycosylation catalyzed by NIS/AgOTf and TBDPS removal, compound **25** was obtained from **22** in 70% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.95 (d, J = 7.5 Hz, 2 H), 7.89 (d, J = 7.5 Hz, 2 H), 7.83-7.60 (m, 9 H), 7.53-7.28 (m, 25 H), 7.24-6.91 (m, 19 H), 6.79 (d, J = 7.0 Hz, 2 H), 6.66-6.59 (m, 3 H), 5.78 (dd, J = 9.0, 10.5 Hz, 1 H), 5.73 (dd, J = 8.0, 10.0 Hz, 1 H), 5.57 (s, 1 H), 5.48 (s, 1 H), 5.32 (d, J = 8.5 Hz, 1 H, H-1 of glucosamine on 1,3 arm), 5.19 (dd, J = 3.5, 10.5 Hz, 1 H), 5.04-5.00 (m, 3 H, H-1 of ring B), 4.90-4.85 (m, 2 H), 4.82-4.79

(m, 2 H, H-1 of galactose and ring E), 4.76 (d, J = 12.5 Hz, 1 H), 4.70-4.66 (m, 3 H, H-1 of ring D), 4.62-4.54 (m, 5 H), 4.51-4.23 (m, 13 H, H-1 of ring C), 4.19-4.05 (m, 5 H, H-1 of glucosamine on 1,6 arm), 4.00-3.97 (m, 2 H), 3.91-3.86 (m, 2 H), 3.84-3.80 (m, 2 H), 3.76-3.67 (m, 4 H), 3.63-3.54 (m, 4 H), 3.45-3.38 (m, 5 H), 3.34 (dd, J = 2.0, 10.0 Hz, 1 H), 3.28-3.25 (m, 2 H), 3.05 (dd, J = 3.5, 11.0 Hz, 1 H), 2.92-2.88 (m, 1 H), 1.94 (s, 3 H), 1.86 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ. 170.6, 169.5, 166.2, 164.7, 153.5, 138.8, 138.5, 138.4, 138.2 (2 C), 138.1, 138.0, 137.9, 137.7, 137.5 (2 C), 137.1, 134.0, 133.4, 133.3, 131.7, 131.3, 129.9, 129.6, 129.3, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3 (2 C), 128.2 (5 C), 128.1 (5 C), 128.0, 127.9 (3 C), 127.7, 127.6, 127.5 (3 C), 127.4, 127.1, 126.3, 126.1, 123.5, 123.2, 101.2, 101.0, 100.8 (C-1 of ring C), 100.3 (C-1 of galactose and ring E), 98.3 (C-1 of ring D), 98.1 (C-1 of ring B), 97.1, 96.7 (C-1 of glucosamine on 1,6 arm), 96.6 (C-1 of glucosamine on 1,3 arm), 94.4, 82.5, 82.5, 79.5, 78.1, 78.0, 77.5, 76.6, 76.5, 75.1, 75.0, 74.8, 74.7, 74.6, 74.4 (2 C), 74.2, 74.0, 73.6, 73.4 (2 C), 72.8, 72.3, 72.1, 71.4, 70.9, 70.6, 70.5, 70.3, 70.2, 69.6, 69.5, 69.0, 68.6, 68.5, 68.2, 66.5, 66.4, 65.9, 62.4, 56.0, 55.7, 54.7, 21.0, 20.6. HRMS: $C_{171}H_{162}Cl_3N_3O_{45}$ $[M + 2\ NH_4]^{2+}$ calcd: 1559.0111, obsd: 1559.0071.



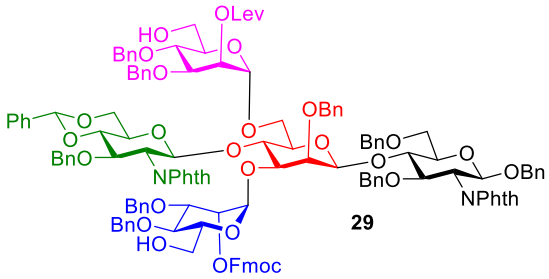
Benzyl [(2,3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside-(1→2)-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl]-(1→6)-[2,3-di-*O*-benzyol-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deo

xy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(2,2,2-trichlor oethoxylcarbonyl)- α-D-mannopyranosyl]-(1→3)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-(2-*O*-benzyl-β-D-mannopyra nosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (27). Following the general procedure for glycosylation catalyzed by NIS/AgOTf, compound **27** was obtained from **24** in 33% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 8.07 (d, J = 8.0 Hz, 2 H), 8.01 (d, J = 7.5 Hz, 2 H), 7.91 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 7.5 Hz, 2 H), 7.64 (t, J = 8.0 Hz, 1 H), 7.56-7.37 (m, 16 H), 7.31-7.28 (m, 9 H), 7.24-7.15 (m, 11 H), 7.14-6.77 (m, 25 H), 6.72-6.70 (m, 2 H), 6.67 (t, J = 8.0 Hz, 1 H), 6.58 (t, J = 7.5 Hz, 1 H), 6.05 (t, J = 10.0 Hz, 1 H), 5.95 (t, J = 9.5 Hz, 1 H), 7.79 (d, J = 8.5 Hz, 1 H), 5.74 (t, J = 9.0 Hz, 1 H, anomeric H), 5.61 (s, 1 H), 5.46 (s, 1 H), 5.35 (s, 1 H), 5.25 (s, 1 H), 5.14-5.08 (m, 3 H), 4.99-4.91 (m, 5 H, 5 anomeric H), 4.88 (d, J = 11.0 Hz, 1 H, anomeric H), 4.79-4.74 (m, 3 H, anomeric H), 4.71 (d, J = 11.0 Hz, 1 H), 4.66-4.59 (m, 3 H), 4.55-4.42 (m, 8 H, anomeric H), 4.40-4.23 (m, 8 H), 4.19-4.02 (m, 9 H, anomeric H), 3.99-3.82 (m, 10 H, anomeric), 3.69-3.54 (m, 7 H), 3.50-3.43 (m, 4 H), 3.38-3.23 (m, 8 H), 3.12-3.05 (m, 2 H), 2.86-2.84 (m, 1 H), 1.94 (s, 3 H), 1.46 (d, J = 6.5 Hz, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 168.3, 167.6, 167.4, 167.3, 166.8, 166.6, 166.0, 165.9, 164.8, 139.6, 139.5 (3 C), 139.4, 138.8, 138.4, 138.3, 138.2, 138.1, 138.0, 137.9 (2 C), 137.6, 137.2, 133.7, 133.4, 131.7, 129.8, 129.7, 129.6, 129.1, 128.8 (2 C), 128.7 (2 C), 128.6 (2 C), 128.5, 128.3, 128.2 (2 C), 128.1 (2 C), 128.0 (3 C), 127.9 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6 (2 C), 127.5 (2 C), 127.4, 127.3 (2 C), 127.2 (2 C), 126.8 (2 C), 125.8 (2 C), 125.7, 123.0, (anomeric C and 3 benzylidenes: 101.1, 101.0, 100.9, 100.4, 100.1, 99.7, 99.6, 98.1, 97.5, 97.2, 97.1), 78.9 (2 C),75.0, 74.9, 74.8 (2 C), 74.4, 73.8 (2 C), 73.6, 73.5 (2 C), 73.4, 72.6, 72.5, 72.4, 71.4, 71.3, 71.1, 70.3, 69.5, 69.1, 68.9, 66.3, 56.6, 55.8, 20.7, 16.4. MALDI: $C_{273}H_{256}Cl_3N_5O_{67}$ $[M + Na]^+$ calcd: 4792.3, obsd: 4791.7.



Benzyl [(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside-(1→2)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→6)-[2,3-di-*O*-benzyol-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-(2,2,2-trichloroethoxylcarbonyl)- α-D-mannopyranosyl]-(1→3)-(4-*O*-acetyl-2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (28). Following the general procedure for glycosylation catalyzed by NIS/AgOTf, compound **28** was obtained from **25** in 74% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 8.07 (d, J = 7.5 Hz, 2 H), 8.01 (d, J = 7.5 Hz, 2 H), 7.97 (d, J = 7.5 Hz, 2 H), 7.90 (d, J = 7.5 Hz, 2 H), 7.79-7.72 (m, 4 H), 7.64-7.60 (m, 4 H), 7.57-7.53 (m, 3 H), 7.50-7.28 (m, 30 H), 7.25-6.97 (m, 33 H), 6.93-6.86 (m, 6 H), 6.82 (d, J = 7.0 Hz, 2 H), 6.68 (t, J = 7.5 Hz, 2 H), 6.63-6.60 (m, 1 H), 5.93 (dd, J = 8.5, 10.0 Hz, 1 H), 5.78-5.70 (m, 2 H), 5.59 (s, 1 H), 5.48 (s, 1 H), 5.38 (s, 1 H), 5.37 (d, J = 8.5 Hz, 1 H, anomeric H), 5.17-5.13 (m, 4 H), 5.03 (d, J = 9.0 Hz, 1 H, anomeric H), 4.94 (d, J = 8.0 Hz, 1 H, anomeric H), 4.90 (d, J = 12.0 Hz, 1 H), 4.83 (d, J = 11.5 Hz, 1 H), 4.79-4.71 (m, 4 H, anomeric H), 4.67-4.53 (m, 11 H, 3 anomeric H), 4.50-4.45 (m, 3 H), 4.41-4.25 (m, 11 H, anomeric H), 4.09-3.82 (m, 13 H, 2 anomeric H), 3.79-3.57 (m, 11 H), 3.53-3.41 (m, 7 H), 3.38-3.62 (m, 2 H), 3.32 (bs, 1 H), 3.22 (bs, 1 H), 3.16 (dd, J = 2.0, 10.0 Hz, 1 H), 3.07-3.03 (m, 1 H), 3.00-2.96 (m, 2 H), 2.60 (d, J = 11.0 Hz, 1 H), 1.94 (s, 3 H), 1.74 (s, 3 H), 1.41 (d, J = 6.5 Hz, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 170.6, 168.9, 167.5, 166.7, 166.2, 165.0, 164.7, 153.5, 139.4 (2 C), 138.9, 138.7, 138.5, 138.3,

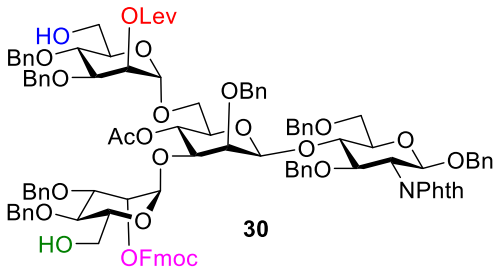
138.2 (3 C), 138.0 (2 C), 137.9 (2 C), 137.7, 137.6 (2 C), 137.1, 133.3, 131.8, 130.0, 129.9, 129.7, 129.6, 129.1 (2 C), 128.9, 128.8 (3 C), 128.7, 128.6, 128.5 (2 C), 128.4 (2 C), 128.3 (2 C), 128.2 (3 C), 128.1 (4 C), 128.0 (3 C), 127.9 (3 C), 127.8 (3 C), 127.7 (2 C), 127.6 (2 C), 127.5, 127.4 (2 C), 127.1, 127.0, 126.9, 126.8, 126.7, 126.4, 126.1, 125.7, 123.5, 122.3, (anomeric C and 3 benzylidenes : 101.6, 101.1, 101.0, 99.6, 98.8, 97.2, 96.7, 96.6, 96.4, 94.5), 82.7, 80.1, 79.1, 78.9, 74.9, 74.8, 74.7, 74.6, 74.2, 74.1, 73.8, 73.7, 73.6 (2 C), 73.5, 73.4, 71.8, 71.6, 71.4 (2 C), 70.8, 70.5, 70.4, 69.4, 69.0, 68.2, 66.4, 66.3, 53.8, 20.7, 20.6, 16.4. MALDI: $C_{178}H_{168}Cl_3N_3O_{38}Si$ [M + Na] $^+$ calcd: 4364.8, obsd: 4367.2.



29

Benzyl [3,4-di-*O*-benzyl-2-*O*-levulinyl-*α*-D-mannopyranosyl]-(1→6)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-(1→3)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (29). Following the general procedure for TBDPS removal, compound **29** was obtained from **18** in 96% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 8.05 (d, J = 7.5 Hz, 2 H), 7.83-7.54 (m, 10.0 Hz, 10 H), 7.45-7.28 (m, 15 H), 7.25-7.04 (m, 13 H), 7.01-6.98 (m, 3 H), 6.88 (d, J = 6.0 Hz, 2 H), 6.81-6.79 (m, 3 H), 6.66-6.57 (m, 3 H), 5.66 (s, 1 H), 5.57 (s, 1 H), 5.27 (s, 1 H), 5.24 (bs, 1 H), 5.02-4.89 (m, 4 H), 4.83-4.78 (m, 3 H), 4.73-4.39 (m, 15 H), 4.33-4.18 (m, 5 H), 4.12-4.05 (m, 3 H), 3.99-3.81 (m, 6 H), 3.76-3.52 (m, 9 H), 3.38-3.30 (m, 3 H), 2.78-2.76 (m, 1 H), 2.29-2.25 (m, 2 H), 2.07-2.00 (m, 2 H), 1.96 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 206.1, 171.3, 167.4, 166.5, 155.0, 144.1, 143.4, 141.3, 141.2, 139.3, 138.5 (2 C), 138.4 (2 C), 138.2, 137.9, 137.8 (2 C), 137.5, 137.1, 134.2, 133.0, 130.0, 129.7, 128.8, 128.5, 128.4, 128.3 (3 C), 128.2, 128.1 (2 C), 128.0 (2 C), 127.9 (2 C), 127.7 (2 C),

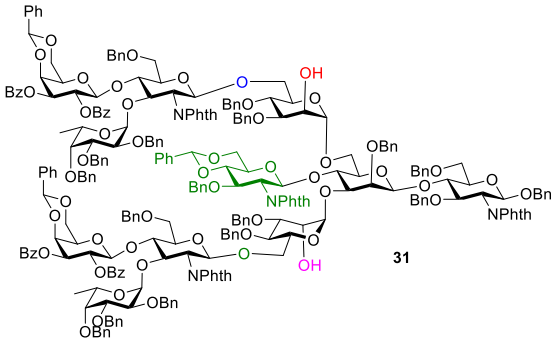
127.6 (2 C), 127.5 (2 C), 127.4, 127.3, 127.2, 127.1, 127.0, 126.2, 125.7, 125.4, 119.9 (2 C), 114.1, 101.1 (C-1 of ring C), 100.5, 99.4 (C-1 of ring E), 97.7 (C-1 of ring D), 97.2 (C-1 of ring B and bisecting GA), 82.2, 78.6, 78.4, 78.1, 77.7, 76.0, 75.2, 75.0, 74.9, 74.6, 74.5, 74.4 (2 C), 74.1 (2 C), 73.8, 73.5, 72.5, 72.4, 72.1, 72.0, 71.8, 71.4, 70.7, 70.6, 69.2, 68.3, 68.2, 64.0, 62.4, 62.3, 55.9, 55.6, 46.8, 37.9, 33.8, 31.9, 29.5, 29.4, 29.2, 28.9, 27.9. HRMS: $C_{136}H_{132}N_2O_{32}$ $[M + 2\ NH_4]^{2+}$ calcd: 1170.4670, obsd: 1170.4664.



30

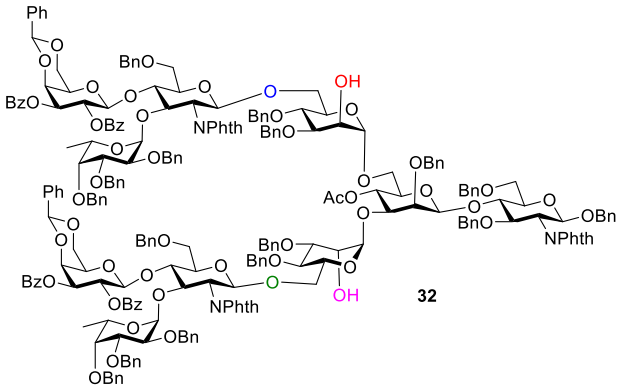
Benzyl [3,4-di-*O*-benzyl-2-*O*-levulinyl-*a*-D-mannopyranosyl]-(1→6)-[3,4-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-(1→3)-(4-*O*-acetyl-2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (30). Following the general procedures for Troc and TBDPS removal, compound **30** was obtained from **14** in 75% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 7.77 (d, J = 7.0 Hz, 2 H), 7.59 (d, J = 7.0 Hz, 2 H), 7.39-7.29 (m, 20 H), 7.24-7.19 (m, 4 H), 7.14-7.08 (m, 5 H), 7.03-7.02 (m, 3 H), 5.39 (t, J = 10.0 Hz, 1 H), 5.19-5.18 (m, 2 H), 5.11 (d, J = 8.0 Hz, 1 H), 4.95-4.90 (m, 4 H), 4.84-4.76 (m, 3 H), 4.71 (d, J = 11.0 Hz, 1 H), 4.64-4.58 (m, 3 H), 4.52-4.47 (m, 3 H), 4.43 (d, J = 11.0 Hz, 1 H), 4.35 (dd, J = 8.0, 9.5 Hz, 1 H), 4.27-4.21 (m, 2 H), 4.19-4.08 (m, 3 H), 3.99 (dd, J = 2.0, 9.0 Hz, 1 H), 3.93 (dd, J = 2.0, 9.0 Hz, 1 H), 3.87-3.83 (m, 2 H), 3.76-3.58 (m, 10 H), 3.51 (d, J = 9.5 Hz, 2 H), 3.37-3.33 (m, 2 H), 2.80-2.63 (m, 5 H), 2.18 (s, 3 H), 2.14 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 206.5, 171.9, 170.0, 154.5, 143.6, 143.3, 141.2 (2 C), 138.5 (2 C), 138.4, 138.2, 138.1, 138.0, 137.7, 137.2, 128.6, 128.4, 128.3 (3 C), 128.2, 128.1 (2 C), 128.0 (2 C), 127.8 (3 C), 127.7 (2 C), 127.6 (2 C), 127.5 (2 C), 127.3, 127.1 (2 C), 126.9, 125.5, 125.2, 119.9 (2 C), 101.1 (C-1 of ring C), 99.4 (C-1

of ring E), 97.8 (C-1 of ring D), 97.4 (C-1 of ring B), 79.0 (2 C), 78.2, 77.7, 76.4, 75.1, 74.9, 74.8, 74.4, 74.3, 74.1, 73.7, 73.2, 72.6, 72.4, 72.3, 71.7, 71.6, 70.7, 70.1, 69.0 (2 C), 68.3, 67.3, 62.2, 55.6, 46.5, 38.1, 28.1, 20.9. HRMS: $C_{110}H_{111}NO_{27}$ $[M + 2\ NH_4]^{2+}$ calcd: 956.9010, obsd: 956.9028.



Benzyl [(2,3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→6)-[(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→3)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (31). Following the general procedures for glycosylation catalyzed by NIS/AgOTf, Lev removal and Fmoc removal, compound **31** was obtained from **29** in 40% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 8.06 (d, J = 6.5 Hz, 4 H), 7.97-7.93 (m, 4 H), 7.76 (bs, 3 H), 7.55-7.35 (m, 48 H), 7.25-6.86 (m, 76 H), 6.65 (d, J = 7.0 Hz, 2 H), 5.51-6.48 (m, 1 H), 6.44-6.41 (m, 2 H), 5.89-5.82 (m, 2 H), 5.60 (s, 1 H), 5.57 (s, 1 H), 5.50 (s, 1 H), 5.30 (s, 1 H), 5.16-5.08 (m, 4 H), 5.03-4.85 (m, 11 H), 4.81-4.59 (m, 16 H), 4.53-4.18 (m, 35 H), 4.15-3.72 (m, 27 H), 3.70-3.42 (m, 20 H), 3.38-3.32 (m, 3 H), 3.26-3.19 (m, 6 H), 3.08 (d, J = 11.0 Hz, 1 H), 2.92-2.90 (m, 1 H), 1.32-1.30 (m, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 166.0 (2 C), 164.8 (2 C), 139.5 (3 C), 138.9, 138.8, 138.7, 138.5, 138.4, 138.3 (2 C), 138.2 (2 C), 138.1, 138.0, 137.7 (2 C), 137.6, 137.4,

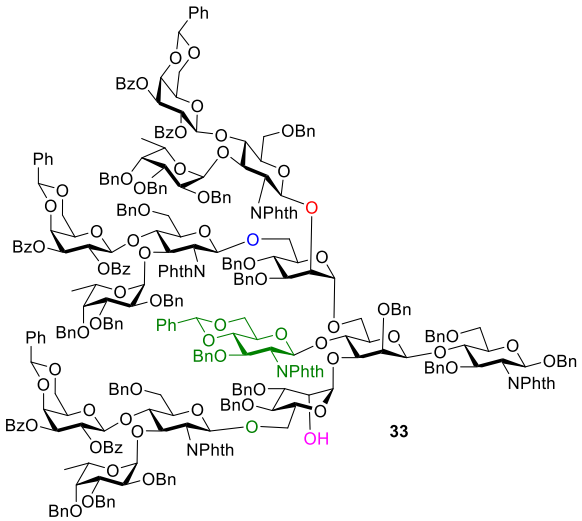
137.3, 134.3, 134.1, 133.5, 133.3, 131.6, 130.9, 129.9, 129.8, 129.3 (2 C), 129.1 (2 C), 129.0, 128.8 (3 C), 128.7, 128.5 (2 C), 128.4 (2 C), 128.3, 128.2 (2 C), 128.1 (3 C), 128.0, 127.9 (3 C), 127.8 (2 C), 127.7 (2 C), 127.6 (3 C), 127.5 (2 C), 127.4 (3 C), 127.3, 127.2, 127.0, 126.9 (3 C), 126.8, 126.6, 126.2, 126.1, 125.8 (2 C), 123.5, [anemoric C and 3 benzylidenes : 101.1, 100.3, 100.1, 99.6 (2 C), 99.4, 99.2, 98.6 (2 C), 97.4 (2 C), 97.3], 82.6, 79.7, 79.6, 79.1, 79.0, 78.9, 78.5, 78.2, 76.2, 75.5, 75.2, 75.0, 74.8, 74.6, 74.5, 74.4 (2 C), 73.8, 73.7 (2 C), 73.5, 73.4 (2 C), 73.0, 72.9, 72.6, 72.5, 72.0, 71.5, 71.4, 71.3, 71.0, 70.7, 70.5, 69.9, 69.1, 69.0, 68.7, 68.4, 68.2, 67.8, 67.7, 67.5, 67.2, 66.4 (2 C), 66.3, 65.8, 65.4, 62.7, 56.7, 56.3, 56.1, 55.6, 53.5, 34.9, 16.4, 16.3. HRMS: $C_{266}H_{254}N4O_{62}$ $[M + Na]^+$ calcd: 4521.9, obsd: 4521.0.



32

Benzyl [(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl]-(1→6)-[(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl]-(1→3)-(4-*O*-acetyl-2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (32). Following the general procedures for glycosylation catalyzed by NIS/AgOTf, Lev removal and Fmoc removal, compound **32** was obtained from **30** in 51% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ*. 8.04 (d, J = 8.0 Hz, 4 H), 7.95-7.91 (m, 4 H), 7.63-7.37 (m, 30 H), 7.32-7.29 (m, 2 H), 7.24-7.10 (m, 25 H), 7.09-6.95 (m, 13 H), 6.92-6.88 (m, 3 H), 6.82 (d, J = 8.0 Hz, 2 H), 6.70 (d, J = 7.5 Hz, 2 H), 6.65-6.58

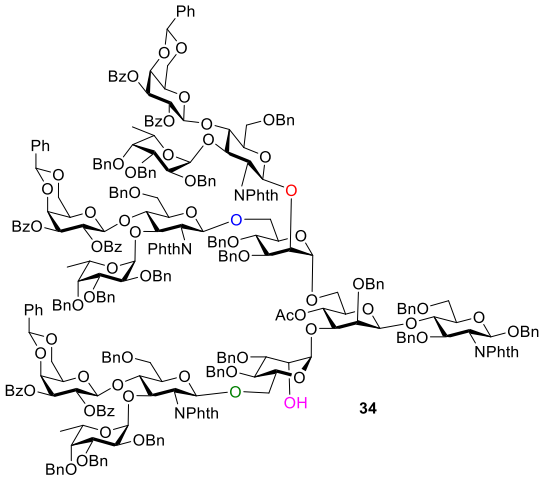
(m, 3 H), 5.85-5.81 (m, 2 H), 5.57 (s, 1 H), 5.55 (s, 1 H), 5.12-5.08 (m, 3 H, anomeric H), 4.97-4.93 (m, 3 H, 3 anomeric H), 4.90-4.87 (m, 3 H), 4.84-4.81 (m, 2 H, anomeric H), 4.79-4.71 (m, 5 H, anomeric H), 4.68-4.65 (m, 3 H, 2 anomeric H), 4.57 (bs, 3 H), 4.54-4.43 (m, 10 H, anomeric H), 4.40-4.32 (m, 5 H), 4.26-4.20 (m, 5 H), 4.18 (d, J = 10.0 Hz, 1 H), 4.15 (bs, 1 H, anomeric H), 4.13-4.09 (m, 2 H), 4.07 (bs, 1 H), 4.04 (d, J = 8.5 Hz, 1 H), 4.01-3.89 (m, 7 H), 3.80 (bs, 1 H), 3.73 (bs, 1 H), 3.65 (bs, 1 H), 3.61-3.52 (m, 9 H), 3.49 (s, 1 H), 3.43-3.10 (m, 17 H), 2.93 (d, J = 10.5 Hz, 1 H), 1.98 (s, 3 H), 1.43-1.40 (m, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 169.5, 166.0 (2 C), 164.7, 139.5 (2 C), 138.9, 138.7, 138.5, 138.4 (2 C), 138.3, 138.1 (2 C), 138.0 (2 C), 137.7, 137.6 (2 C), 137.3, 133.4, 133.3 (2 C), 139.9, 139.8, 129.3, 129.1 (2 C), 128.8 (2 C), 128.7, 128.6, 128.5 (2 C), 128.2 (2 C), 128.2, 128.1 (3 C), 128.0 (5 C), 127.9 (3 C), 127.8, 127.7 (4 C), 127.6, 127.5 (2 C), 127.4, 127.3 (3 C), 127.2, 127.1, 127.0, 126.9 (2 C), 126.7 (2 C), 126.6, 125.7, 123.6, [anomeric C and 2 benzylidenes : 101.0, 100.3, 99.6, 98.9, 98.8 (2 C), 97.4, 97.3 (2 C)], 79.7, 79.4, 79.0 (3 C), 78.9 (2 C), 75.2, 75.1, 75.0 (2 C), 74.8 (2 C), 74.6, 74.4, 74.2, 74.1, 74.0, 73.9, 73.8, 73.6 (2 C), 73.4, 72.9 (2 C), 72.6, 72.4, 72.2, 71.5, 71.4 (3 C), 71.3, 70.6, 70.4, 69.8, 69.0, 68.5, 68.3, 68.1, 67.8, 67.6 (3 C), 66.4, 66.3, 56.5, 56.3, 55.8, 21.0, 16.3 (2 C). MALDI: $C_{240}H_{233}N_3O_{57}$ $[M + Na]^+$ calcd: 4094.5, obsd: 4095.2.



Benzyl [(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido

-β-D-glucopyranosyl-(1→6)-(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→6)-[(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→3)-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-(1→4)-(2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (33). Following the general procedures for Lev removal, glycosylation catalyzed by NIS/AgOTf and Fmoc removal, compound **33** was obtained from **29** in 18% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ.* 8.03 (d, J = 7.0 Hz, 4 H), 7.99 (d, J = 8.0 Hz, 2 H), 7.94-7.89 (m, 6 H), 7.81-7.72 (m, 6 H), 7.60-7.32 (m, 62 H), 7.24-7.82 (m, 107 H), 6.69-6.67 (m, 4 H), 6.31 (t, J = 7.0 Hz, 1 H), 6.06 (t, J = 7.0 Hz, 2 H), 5.91 (t, J = 9.5 Hz, 1 H), 5.85 (t, J = 9.5 Hz, 1 H), 5.76 (t, J = 9.0 Hz, 1 H), 5.59 (s, 1 H), 5.55 (s, 1 H), 5.50 (s, 1 H), 5.30-5.28 (m, 2 H), 5.13-5.02 (m, 6 H), 4.97-4.81 (m, 11 H), 4.78-3.70 (m, 104 H), 3.60-3.44 (m, 20 H), 2.29 (d, J = 8.0 Hz, 2 H), 3.20 (s, 1 H), 3.15 (s, 1 H), 3.05-3.02 (m, 3 H), 3.00-2.93 (m, 3 H), 2.71 (d, J = 11.0 Hz, 1 H), 2.36-2.33 (m, 1 H), 1.28-1.26 (m, 6 H), 1.21-1.20 (m, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ.* 167.5, 167.4, 167.2, 166.6, 166.0, 165.8, 165.0, 164.9, 164.8, 139.6, 139.5 (2 C), 139.4, 138.9, 138.6, 138.5, 138.4, 138.3 (2 C), 138.2 (2 C), 138.1 (2 C), 137.7, 137.6 (2 C), 137.3, 137.2, 133.6, 133.4, 131.6 (2 C), 131.3, 129.9, 129.8, 129.7, 129.6, 129.4, 129.2 (3 C), 129.1, 129.0, 128.9, 128.7, 128.6, 128.5 (3 C), 128.3 (3 C), 128.2 (2 C), 128.2 (2 C), 128.1 (2 C), 128.0 (3 C), 127.9 (3 C), 127.8 (2 C), 127.7, 127.6 (4 C), 127.5, 127.4 (2 C), 127.3 (2 C), 127.2 (2 C), 127.0, 126.9 (3 C), 126.8 (3 C), 126.7 (2 C), 126.5, 126.2, 125.8, 125.7, (anomeric C and 4 benzylidenes : 101.1, 100.8, 100.5, 100.0, 99.6, 99.5, 99.4, 99.3, 97.6, 97.4, 97.3, 95.5), 78.9, 75.3, 75.2, 75.1, 74.9 (2 C), 74.8 (2 C), 74.7, 74.6, 74.3 (2 C), 74.2, 74.0, 73.9 (2 C), 73.7 (2 C), 73.5, 73.4, 73.3 (2 C), 73.0, 72.9, 72.7 (2 C), 72.5, 72.4, 72.3, 71.9, 71.7, 71.6 (2 C), 71.5, 71.4, 71.3, 71.2, 71.0, 70.8, 70.1 (2 C), 70.0, 69.1, 69.0, 67.8, 67.6, 66.4 (2 C),

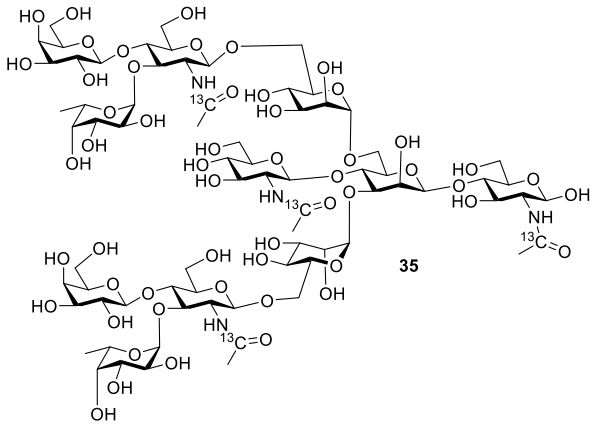
66.3, 66.1 (2 C), 65.9, 56.3, 56.1, 56.0, 55.7, 55.6, 16.5, 16.4, 16.3. HRMS: $C_{341}H_{323}N5O_{79}$ $[M + Na]^+$ calcd: 5778.3, obsd: 5780.9.



34

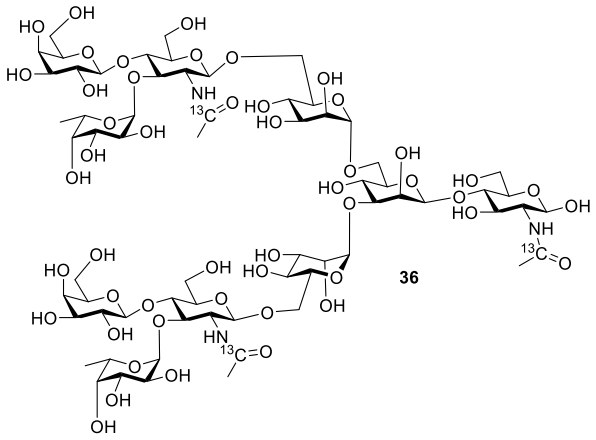
Benzyl [(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyL-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→6)-[(2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*a*-D-mannopyranosyl]-(1→3)-(4-*O*-acetyl-2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (34). Following the general procedures for Lev removal, glycosylation catalyzed by NIS/AgOTf and Fmoc removal, compound **34** was obtained from **30** in 39% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ.* 8.04-8.01 (m, 6 H), 7.93-7.89 (m, 6 H), 7.77-7.72 (m, 2 H), 7.69-7.60 (m, 6 H), 7.55-7.46 (m, 15 H), 7.43-7.36 (m, 13 H), 7.33-7.28 (m, 4 H), 7.25-7.07 (m, 36 H), 7.05-6.96 (m, 15 H), 6.91-6.81 (m, 5 H), 6.77-6.70 (m, 3 H), 6.67 (d, J = 7.0 Hz, 2 H), 6.30-6.21 (m, 3 H), 5.87-5.78 (m, 3 H), 5.57 (s, 1 H), 5.55 (s, 1 H), 5.54 (s, 1 H), 5.34 (t, J = 9.0 Hz, 1 H), 5.14-5.09 (m, 3 H), 5.04 (dd, J = 2.5, 10.5 Hz, 1 H), 4.95-4.88 (m, 5 H), 4.84-4.78 (m, 3 H), 4.76-4.73 (m, 1 H), 4.70-3.38 (m, 77 H), 3.31-3.24 (m, 4 H), 3.18 (s, 1 H), 3.17

(s, 1 H), 3.10 (s, 1 H), 2.99-2.97 (m, 1 H), 2.90-2.78 (m, 4 H), 1.87 (s, 3 H), 1.32 (d, J = 6.5 Hz, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): *δ*. 167.6, 166.0, 165.9, 165.0, 164.7 (2 C), 139.6, 139.5 (3 C), 139.4, 139.2, 139.0 (2 C), 138.7, 138.4, 138.3 (3 C), 138.1, 138.0, 137.9, 137.8, 137.7 (2 C), 137.6 (2 C), 137.3, 134.6, 133.9, 133.5 (2 C), 133.4 (2 C), 133.3 (2 C), 131.6, 131.5, 131.3, 131.2, 129.9, 129.7 (3 C), 129.6, 129.3, 129.1, 129.0, 128.8, 128.7, 128.6 (2 C), 128.5 (3 C), 128.4, 128.3 (2 C), 128.2, 128.1 (2 C), 128.0 (3 C), 127.9 (2 C), 127.8 (2 C), 127.7 (4 C), 127.6 (3 C), 127.5 (3 C), 127.4, 127.3 (3 C), 127.2 (2 C), 127.0 (2 C), 126.9, 126.8, 126.7 (4 C), 126.6, 125.8, 125.7, [anomeric C and 3 benzylidenes : 100.5, 100.0, 99.7, 99.6, 99.5 (3 C), 97.7, 97.5, 97.3, 97.2], 79.2, 79.0 (2 C), 78.9 (2 C), 78.6, 75.2, 75.1, 75.0, 74.8 (2 C), 74.7, 74.4, 74.1, 73.9 (2 C), 73.8, 73.7 (2 C), 73.6 (2 C), 73.5 (2 C), 73.4 (2 C), 73.3, 73.2, 73.1, 72.9, 72.7, 72.6, 72.5 (2 C), 72.3, 71.9, 71.7, 71.4, 71.3 (2 C), 70.6, 70.4, 69.8, 69.1, 69.0, 67.6, 67.5, 66.3 (2 C), 56.2, 56.1, 55.8, 20.8, 16.3 (3 C). MALDI: $C_{315}H_{302}N4O_{74}$ [M + Na] $^+$ calcd: 5350.8, obsd: 5353.9.

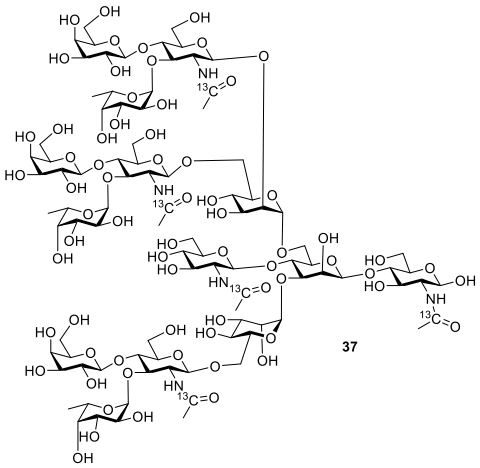


[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido -β-D-glucopyranosyl-(1→6)-*a*-D-mannopyranosyl]-(1→6)-[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1 →6)-*a*-D-mannopyranosyl]--(1→3)-[2-deoxy-2-acetamido-β-D-glucopyranosyl]-(1 →4)-(β-D-mannopyranosyl)-(1→4)-2-deoxy-2-acetamido-β-D-glucopyranose (35). Following the general procedure for global deprotection, compound **35** was obtained from **31** in 73% yield. ^{1}H-NMR (500 MHz, D_2O): *δ*. [anomeric H : 5.06 (s, 1 H), 5.04

(d, J = 1.5 Hz, 1 H), 4.97 (d, J = 3.5 Hz, 1 H), 4.76 (d, J = 3.5 Hz, 1 H), 4.75 (s, 1 H), 4.41-4.35 (m, 3 H), 4.31-4.27 (m, 2 H)], 4.08-4.02 (m, 2 H), 3.96 (bs, 2 H), 3.86-3.41 (m, 57 H), 3.35-3.31 (m, 2 H), 3.27-3.20 (m, 2 H), 1.89-1.85 (m, 12 H), 1.02 (d, J = 6.5 Hz, 6 H). HRMS: $C_{70}{}^{13}C_4H_{124}N_4O_{54}$ [M + 2 H] $^{2+}$ calcd: 969.3680, obsd: 969.3683.

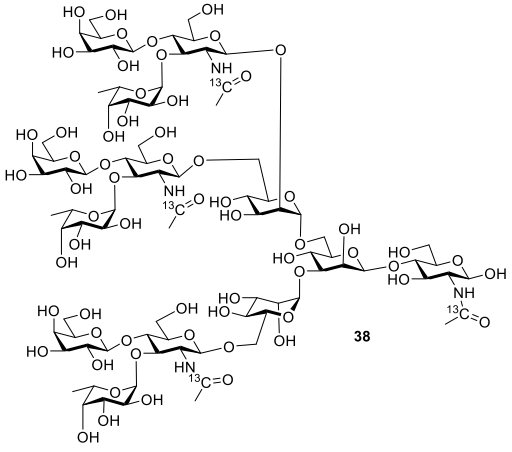


[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→6)-*a*-D-mannopyranosyl]-(1→6)-[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→6)-*a*-D-mannopyranosyl]-(1→3)-(β-D-mannopyranosyl)-(1→4)-2-deoxy-2-acetamido-β-D-glucopyranose (36). Following the general procedure for global deprotection, compound **36** was obtained from **32** in 73% yield. ^{1}H-NMR (500 MHz, D_2O): *δ*. [anomeric H : 5.04 (d, J = 1.8 Hz, 1 H), 4.94 (d, J = 3.5 Hz, 2 H), 4.88 (bs, 1 H), 4.70 (bs, 1 H), 4.68 (bs, 1 H), 4.41 (d, J = 8.5 Hz, 2 H), 4.29-4.26 (m, 2 H)], 4.04-3.98 (m, 3 H), 3.88 (bs, 1 H), 3.85 (bs, 1 H), 3.83 (bs, 1 H), 3.79-3.67 (m, 20 H), 3.62-3.61 (m, 3 H), 3.59-3.54 (m, 10 H), 3.52-3.51 (m, 2 H), 3.50-3.49 (m, 2 H), 3.47 (d, J = 3.5 Hz, 2 H), 3.45-3.41 (m, 6 H), 1.89-1.86 (m, 9 H), 1.01 (d, J = 6.5 Hz, 6 H). HRMS: $C_{63}{}^{13}C_3H_{111}N_3O_{49}$ [M + 2 H] $^{2+}$ calcd: 867.3266, obsd: 867.3253.



37

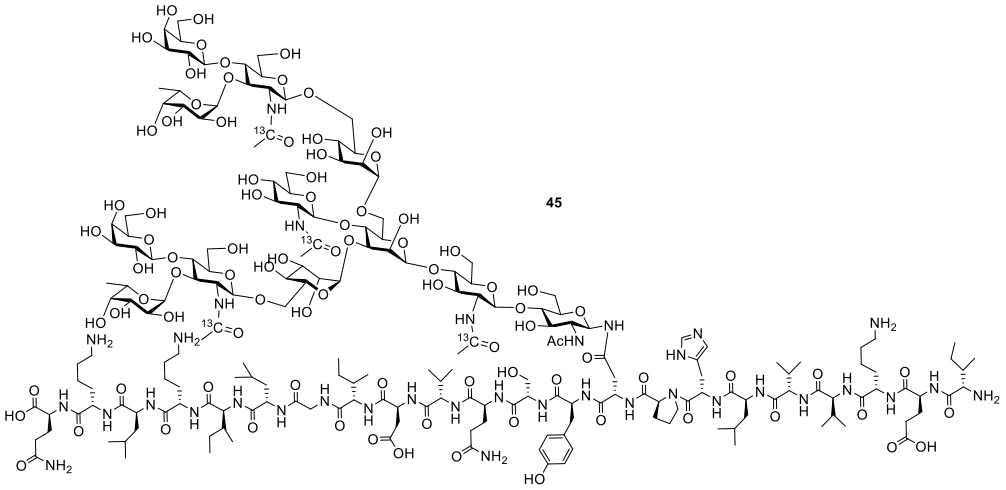
[[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-(1→6)-[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-(1→2)-*a*-D-mannopyranosyl]-(1→6)-[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→6)-*a*-D-mannopyranosyl]--(1→3)-[2-deoxy-2-acetamido-β-D-glucopyranosyl]-(1→4)-(β-D-mannopyranosyl)-(1→4)-2-deoxy-2-acetamido-β-D-glucopyranose (37). Following the general procedure for global deprotection, compound **37** was obtained from **33** in 67% yield. ^{1}H-NMR (500 MHz, D_2O): *δ*. [anomeric H : 5.06 (s, 1 H), 5.04 (d, J = 1.5 Hz, 1 H), 4.99 (d, J = 3.5 Hz, 1 H), 4.97-4.95 (m, 2 H), 4.79 (d, J = 9.0 Hz, 1 H), 4.43-4.39 (m, 3 H), 4.31-4.28 (m, 3 H)], 4.08 (d, J = 10.0 Hz, 2 H), 3.99-3.94 (m, 4 H), 3.87-3.31 (m, 75 H), 3.28-3.24 (m, 3 H), 1.91-1.85 (m, 15 H), 1.03-1.01 (m, 9 H). HRMS: $C_{89}{}^{13}C_5H_{157}N_5O_{68}$ $[M + 2\ H]^{2+}$ calcd: 1225.4647, obsd: 1225.4618.



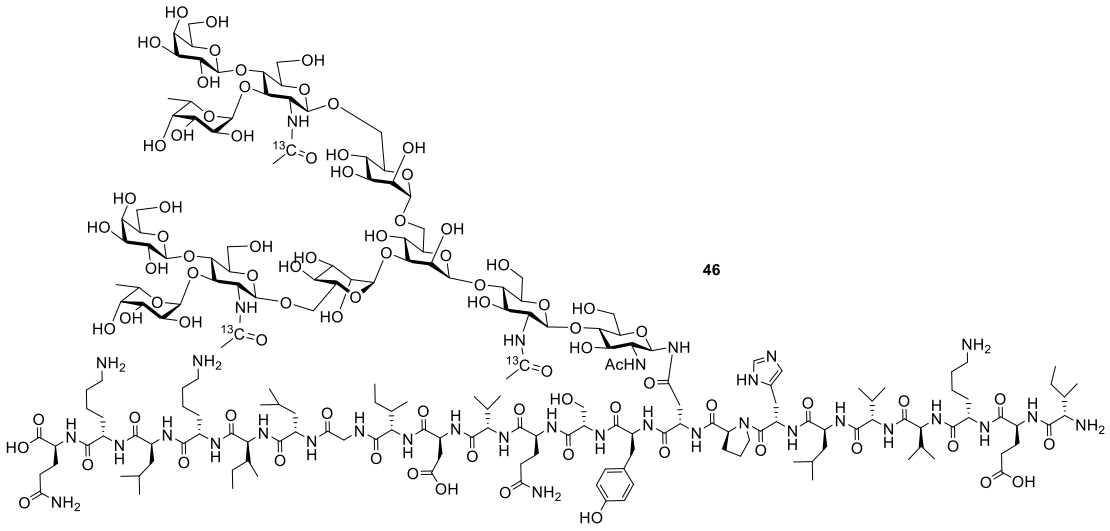
38

[[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-(1→6)-[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-(1→2)-*a*-D-mannopyranosyl]-(1→6)-[(β-D-galactopyranosyl)-(1→4)-(α-L-fucopyranosyl)-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranosyl-(1→6)-*a*-D-mannopyranosyl]--(1→3)-(β-D-mannopyranosyl)-(1→4)-2-deoxy-2-acetamido-β-D-glucopyranose (38). Following the general procedure for global deprotection, compound **38** was obtained from **34** in 67% yield. ^{1}H-NMR (500 MHz, D_2O): δ. [anomeric H : 5.05 (d, J = 3.0 Hz, 1 H), 4.96-4.94 (m, 3 H), 4.90 (bs, 1 H), 4.43-4.40 (m, 3 H), 4.30-4.28 (m, 3 H)], 4.05-3.99 (m, 4 H), 3.93-3.92 (m, 1 H), 3.90-3.41 (m, 68 H), 3.35-3.32 (m, 3 H), 3.26-3.24 (m, 1 H), 1.90-1.85 (m, 12 H), 1.02 (d, J = 6.5 Hz, 9 H). HRMS: $C_{82}{}^{13}C_4H_{144}N_4O_{63}$ $[M + 2\ H]^{2+}$ calcd: 1123.4233, obsd: 1123.4182.

General Procedure for HPLC. Analytical reverse-phase HPLC was carried out on a Waters Alliance e2695 HPLC system equipped with a dual absorbance UV detector and coupled to a single quadrupole mass detector which was used for mass spectrometry analysis. HPLC separation was performed on a C18 column (Thermoscientific Hypersil Gold™, 4.6 X 250 mm, 3µm) at a flow rate of 0.5 mL/min. The column was eluted using a linear gradient of 5-25% MeCN containing 0.1% TFA over 30 min followed by a 20 min isocratic flow of 90% MeCN.



Glycopeptide **44** (20µ*g*, 7.3 nmol) was incubated at 30 °C together with 11-mer glycan oxazoline **39** (140 µg, 73 nmol) and wild type Endo-A enzyme (4 µg) in phosphate buffer (50 mM, pH 6.5, 10 µl). The reaction was monitored by RP-HPLC and ESI mass spectroscopy and was quenched after 4 h using 0.1% aq. TFA. The product was purified by RP-HPLC to give glycopeptide **45** (25 µg, 73%). ESI-MS: Calcd., M = 4657.96; found(*m/z*): 932.26 $[M + 5\ H]^{5+}$, 1165.07 $[M + 4\ H]^{4+}$, 1560.07 $[M + Na + 2\ H]^{3+}$. RP-HPLC retention time, t_R = 38.4 min.



Glycopeptide **44** (50 µg, 18.3 nmol) was incubated at 30 °C together with 10-mer glycan oxazoline **40** (313 µg, 183 nmol) and wild type Endo-A enzyme (4 µg) in phosphate buffer (50 mM, pH 6.5, 10 µl). The reaction was monitored by RP-HPLC and ESI mass spectroscopy and was quenched after 1 h using 0.1% aq. TFA. The product was purified by RP-HPLC to give glycopeptide **46** (53 µg, 65%). ESI-MS: Calcd., M =4453.78; found(m/z): 891.71 $[M + 5\ H]^{5+}$, 1114.43 $[M + 4\ H]^{4+}$, 1485.04 $[M + 3\ H]^{3+}$. RP-HPLC retention time, t_R = 30.6 min.

Table S1. The relative energies of all conformers of compounds **17** and **20** within 6 kcal/mol from the lowest energy conformation based on AM1 semi-empirical calculation. The number of atoms within 5 Å of the free OH group are tabulated below.

	Compound **17**		Compound **20**	
conf #	rel E (Kcal/mol)	# of atoms within 5Å	rel E (Kcal/mol)	# of atoms within 5Å
1	0.0	40	0.00	43
2	1.5	55	0.91	29
3	2.5	34	1.53	46
4	4.1	34	1.70	44
5	4.6	41	1.73	37
6	4.8	41	2.27	33
7	4.9	46	2.92	45
8	5.8	54	3.11	34
9	5.9	48	3.16	34
10	6.0	36	3.38	31
11	average	42.9	3.40	40
12			3.46	50
13			3.53	36
14			3.58	34
15			3.58	41
16			3.60	39
17			3.74	44
18			3.85	39
19			4.06	40
20			4.17	39
21			4.18	29
22			4.24	28
23			4.33	28
24			4.36	28
25			4.40	37
26			4.46	43
27			4.53	16
28			4.73	34
29			4.85	29
30			5.04	49
31			5.09	39
32			5.20	35
33			5.51	38
34			5.58	28
35			5.66	53
36			5.67	35
37			5.67	27

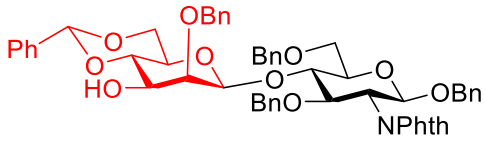
38	5.69	30
39	5.73	32
40	5.75	46
41	5.75	33
42	5.81	26
43	5.86	34
44	5.86	31
45	5.95	33
46	5.97	34
	average	35.9

References:

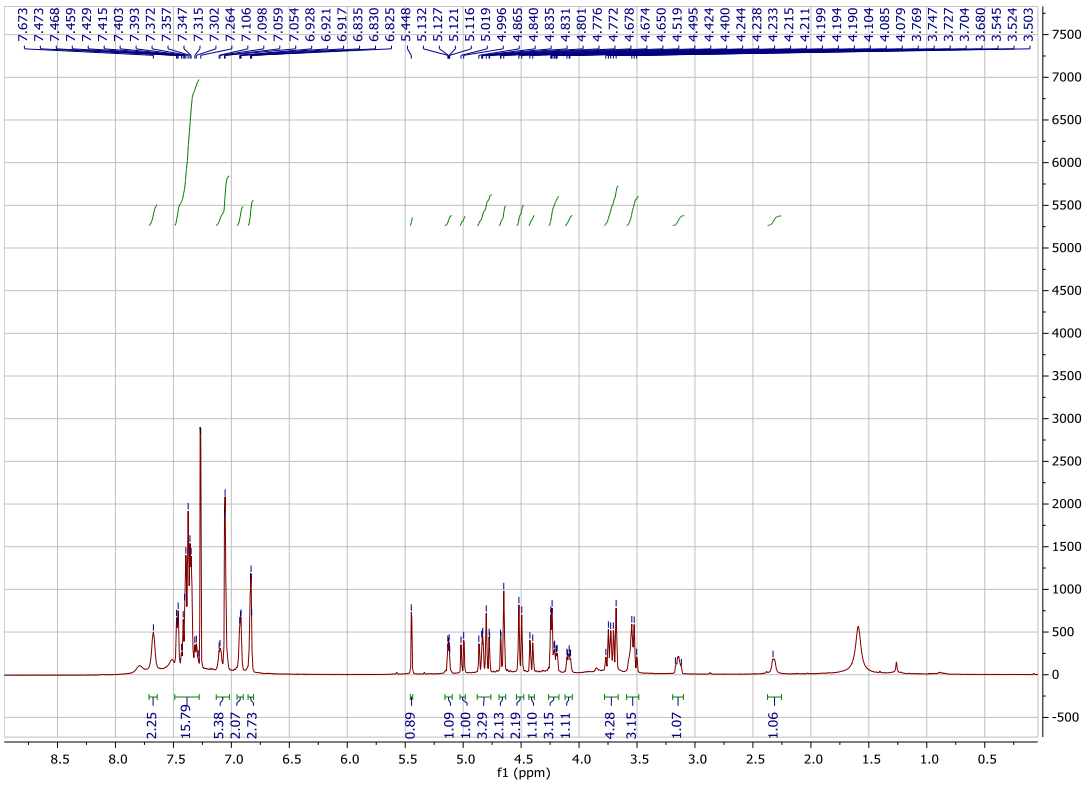
[1] G. Zou, H. Ochiai, W. Huang, Q. Yang, C. Li, L. X. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 18975-18991.

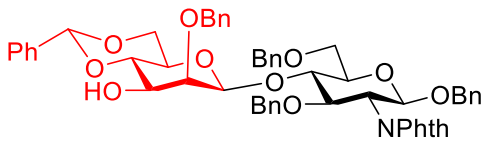
[2] P. S. Patil, T.-J. R. Cheng, M. M. L. Zulueta, S.-T. Yang, L. S. Lico, S.-C. Hung, *Nat. Commun.* **2015**, *6*, 7239.

[3] A. Miermont, Y. Zeng, Y. Jing, X. S. Ye, X. Huang, *J. Org. Chem.* **2007**, *72*, 8958-8961.

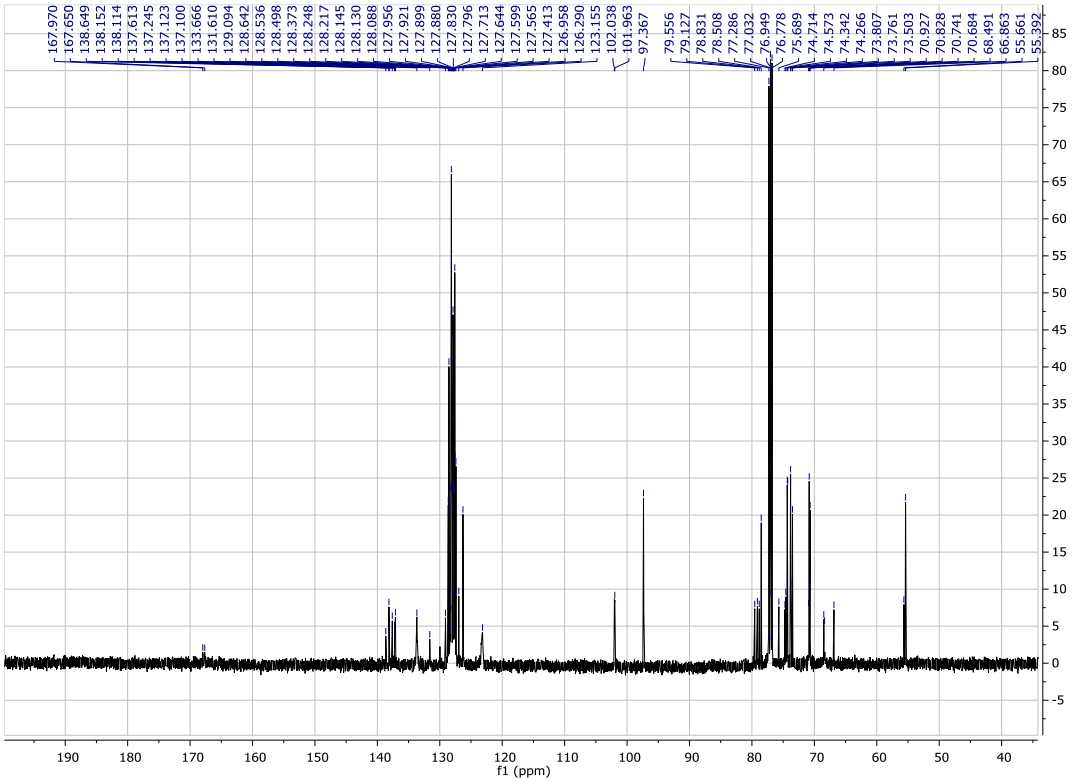


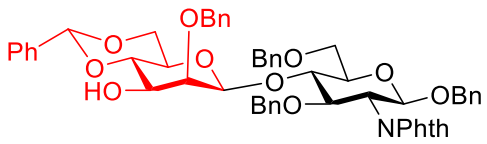
^{1}H-NMR ($CDCl_3$, 500 MHz) of **3**



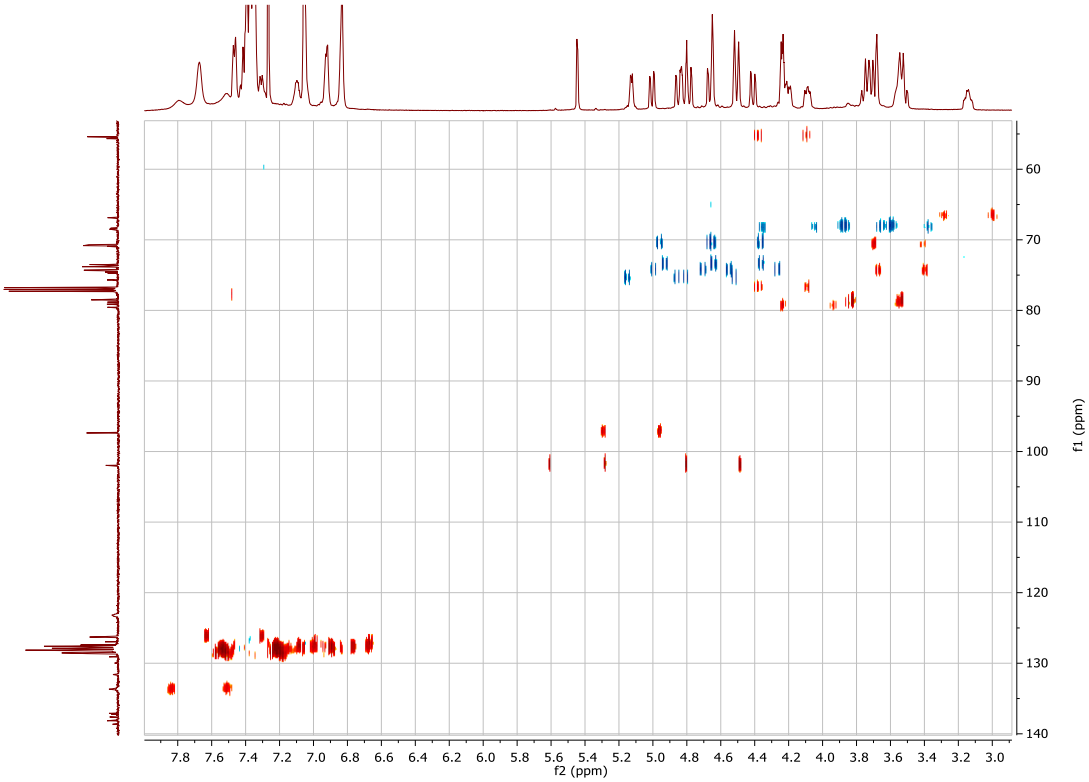


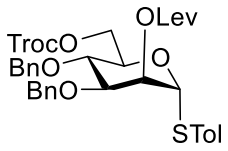
^{13}C-NMR ($CDCl_3$, 125 MHz) of **3**



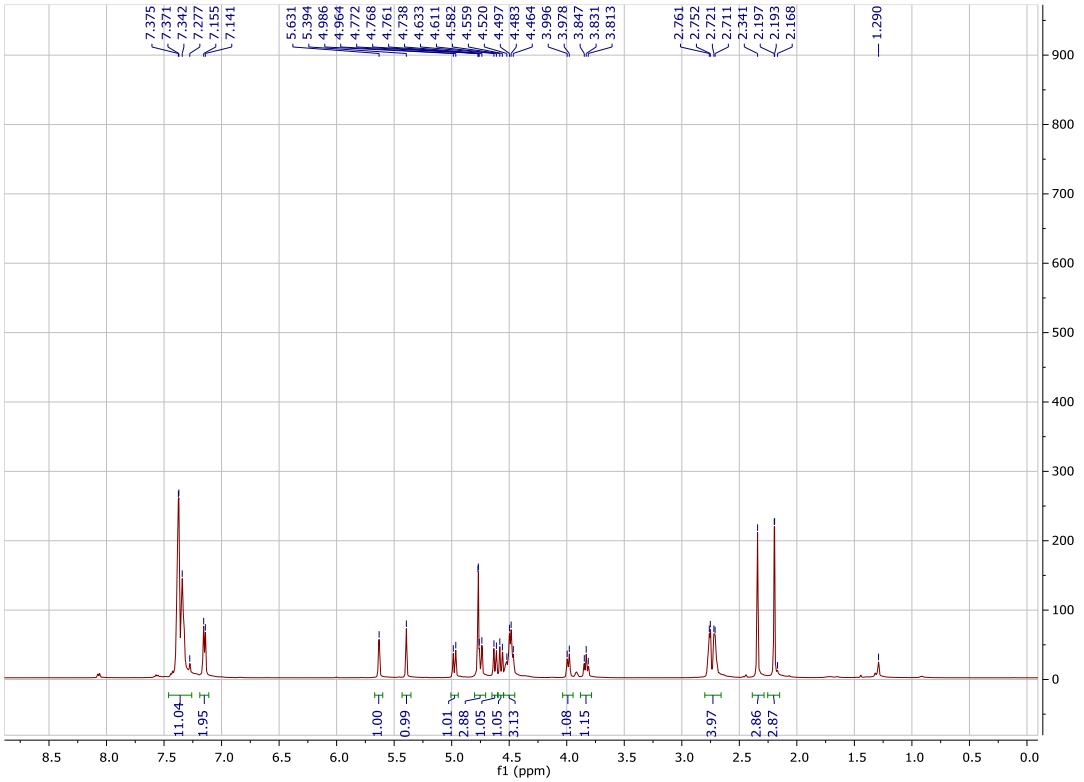


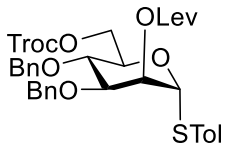
coupled gHSQC ($CDCl_3$, 500 MHz) of **3**





^{1}H-NMR ($CDCl_3$, 500 MHz) of **4**





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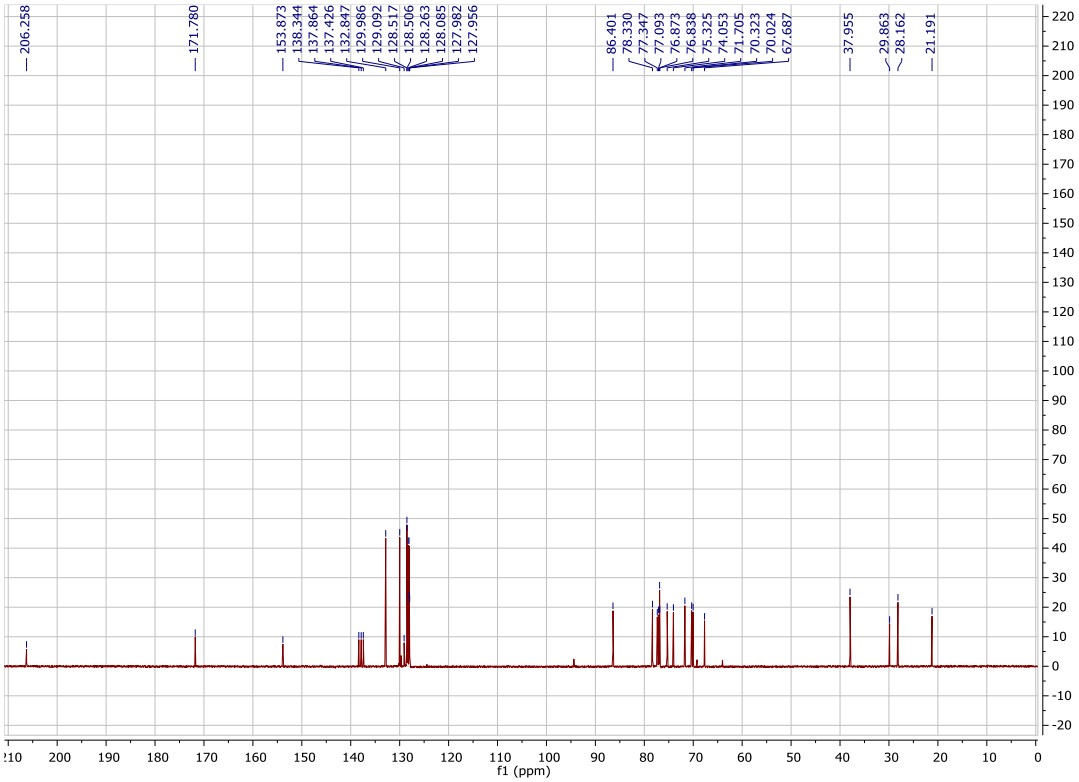
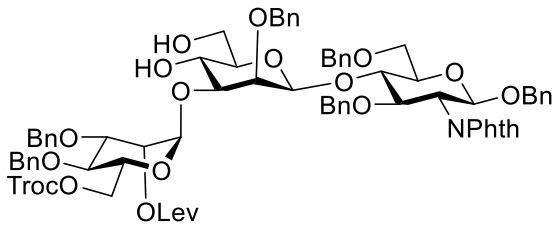
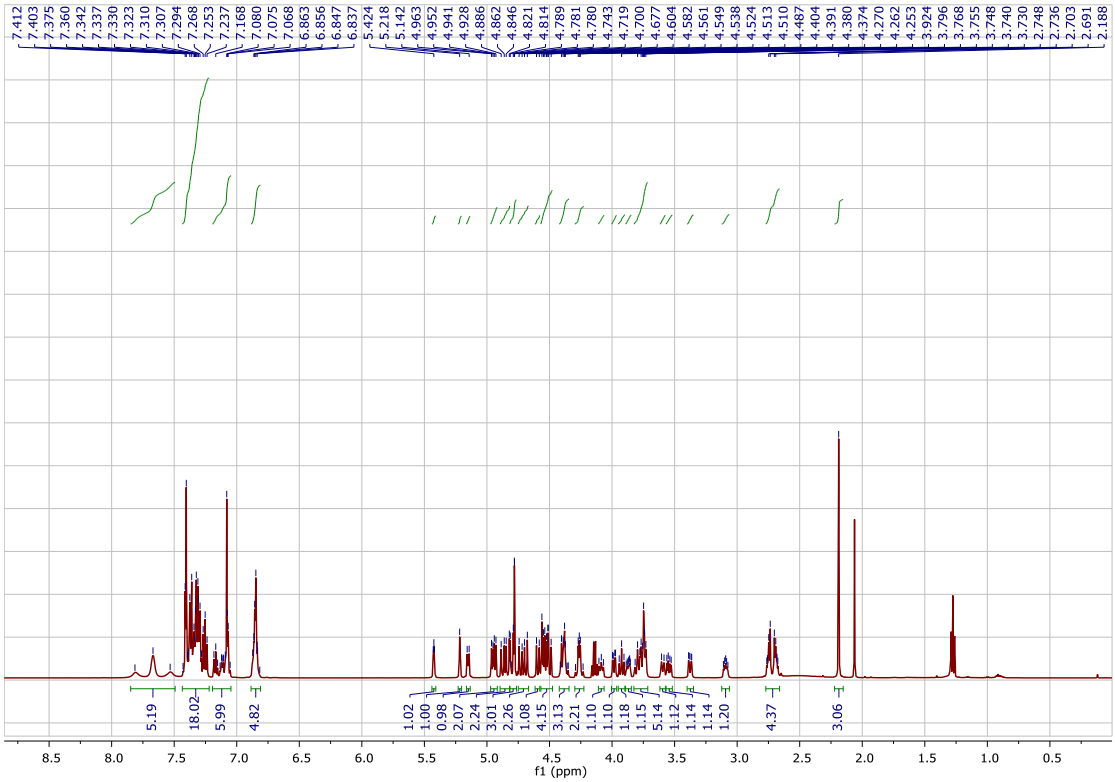
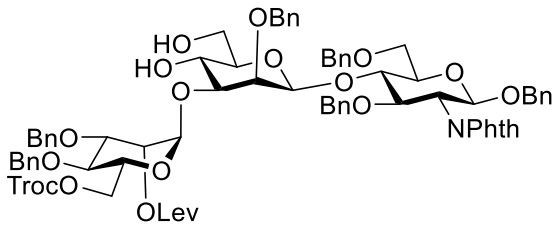




^{1}H-NMR ($CDCl_3$, 500 MHz) of **6**





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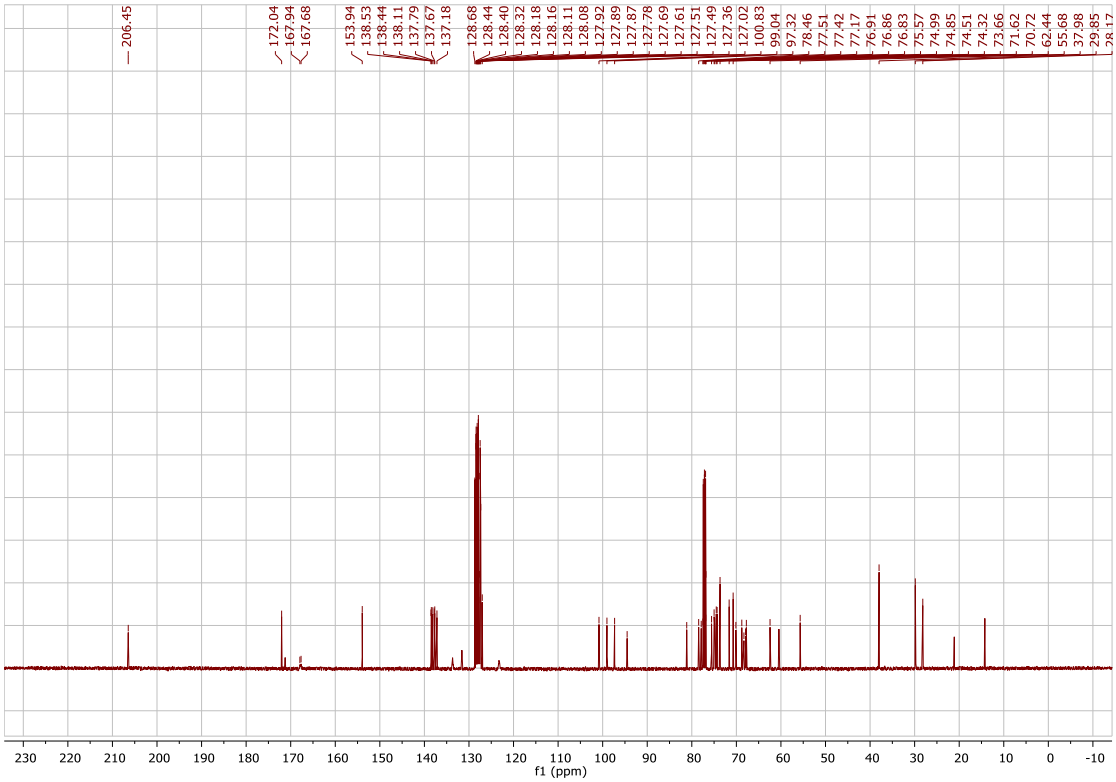
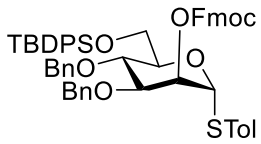
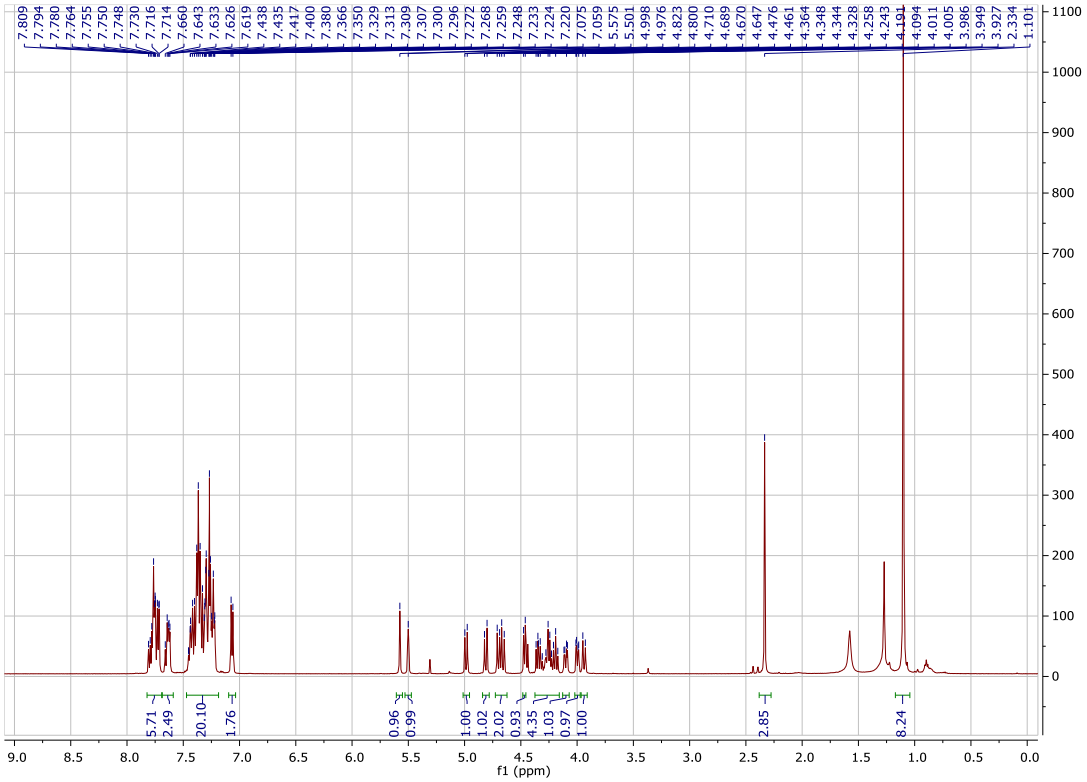
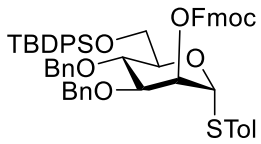




^{1}H-NMR ($CDCl_3$, 500 MHz) of **7**





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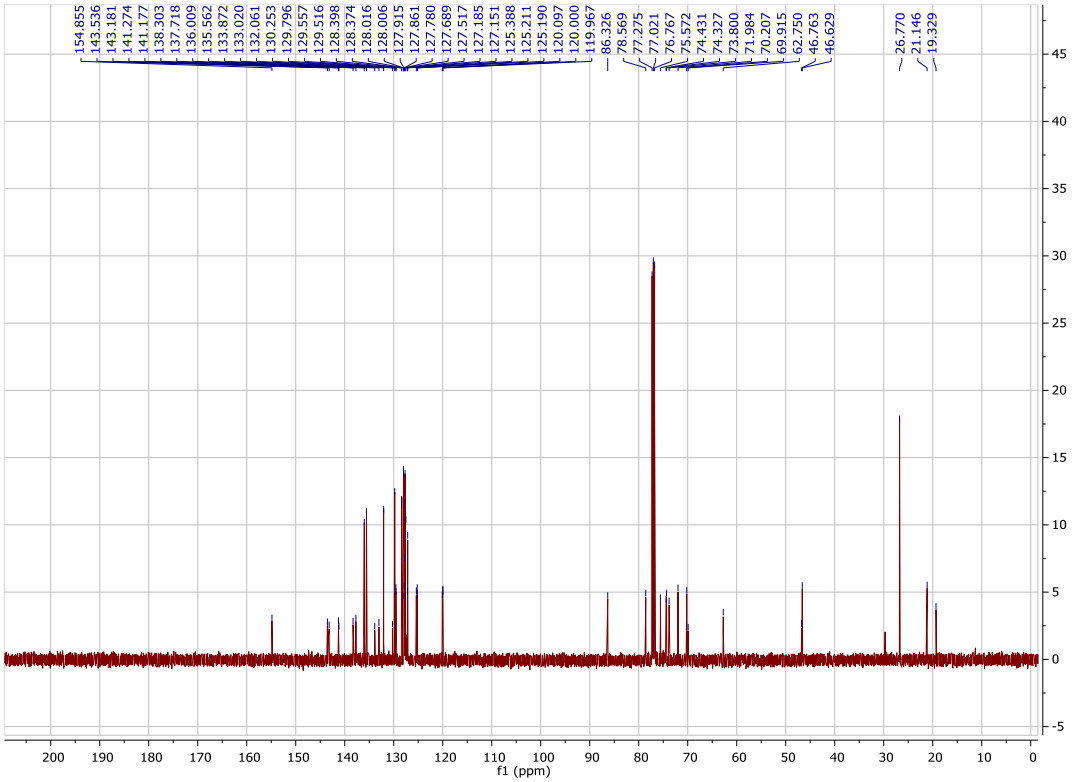
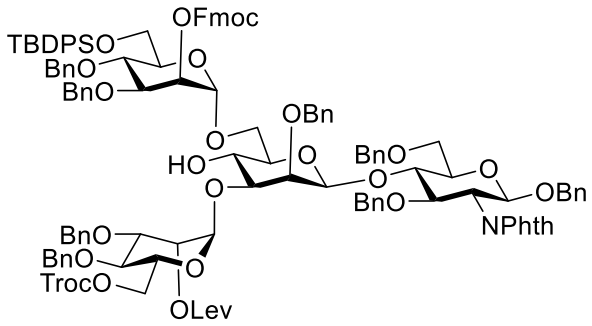
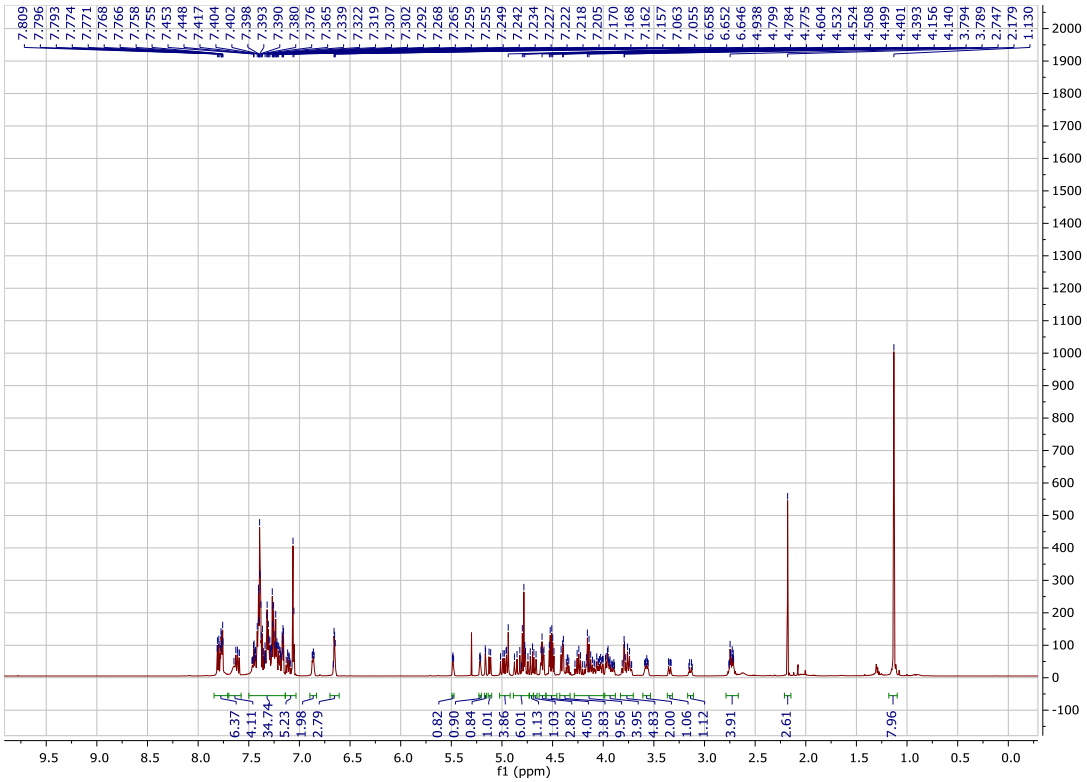
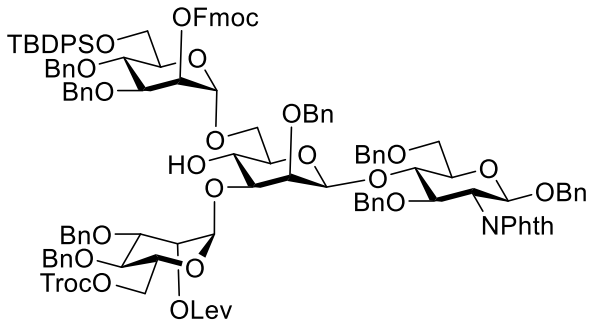




^{1}H-NMR ($CDCl_3$, 500 MHz) of **1**





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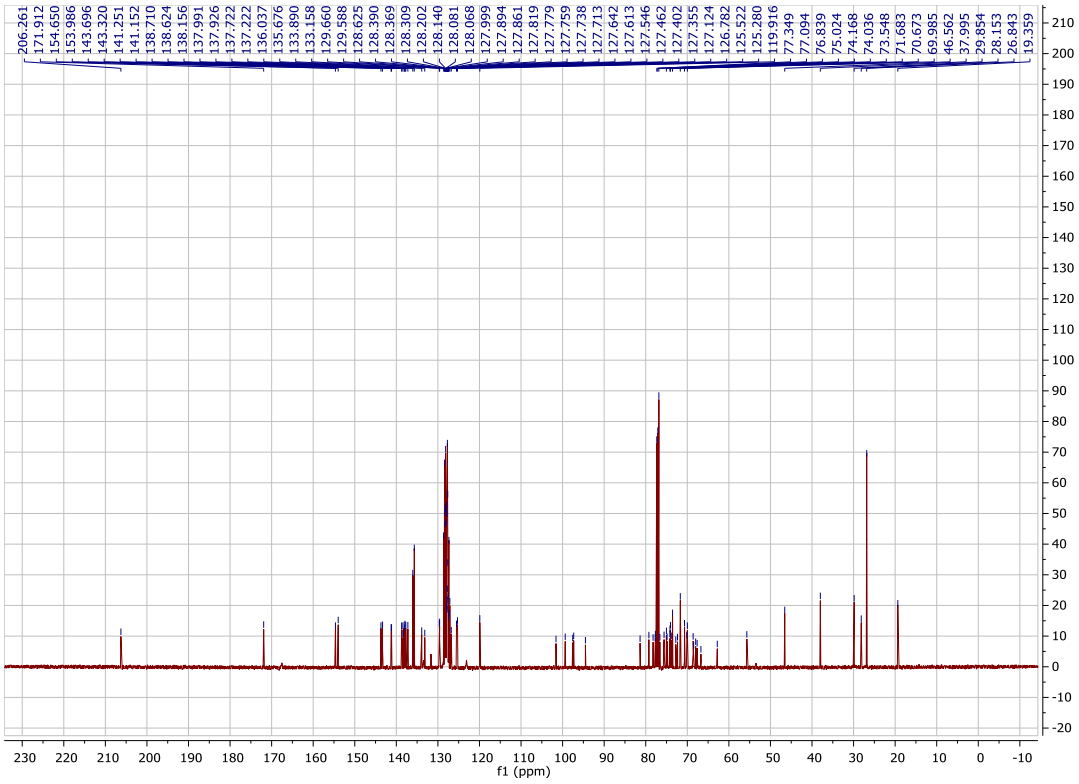
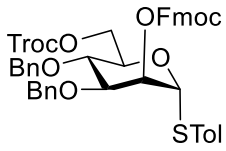
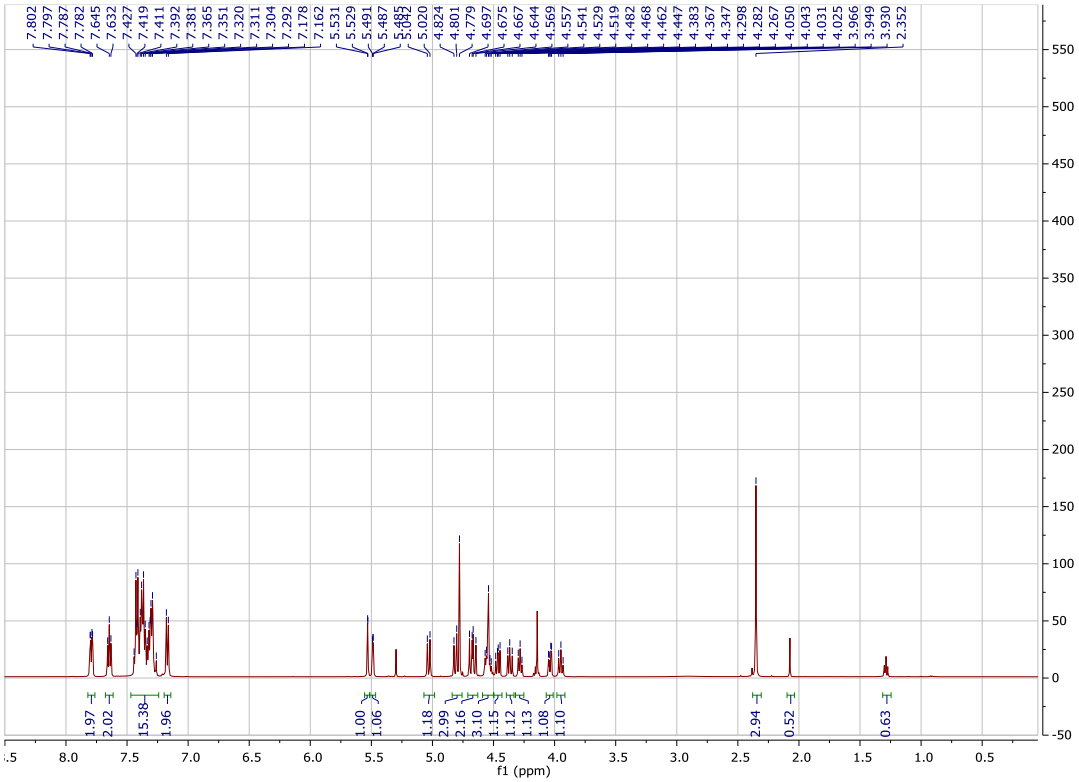
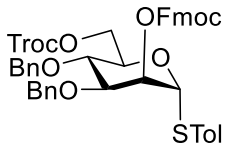




^{1}H-NMR ($CDCl_3$, 500 MHz) of **9**





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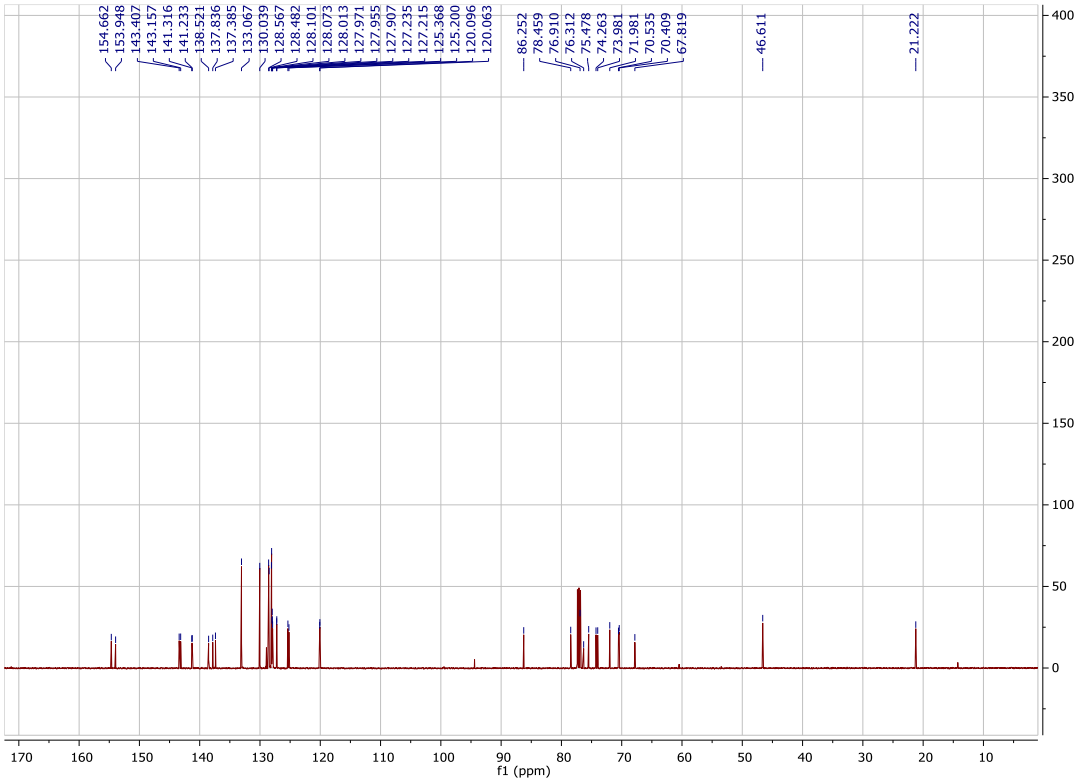
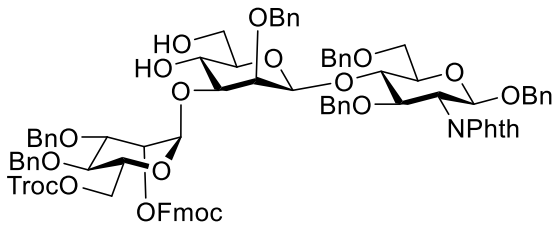
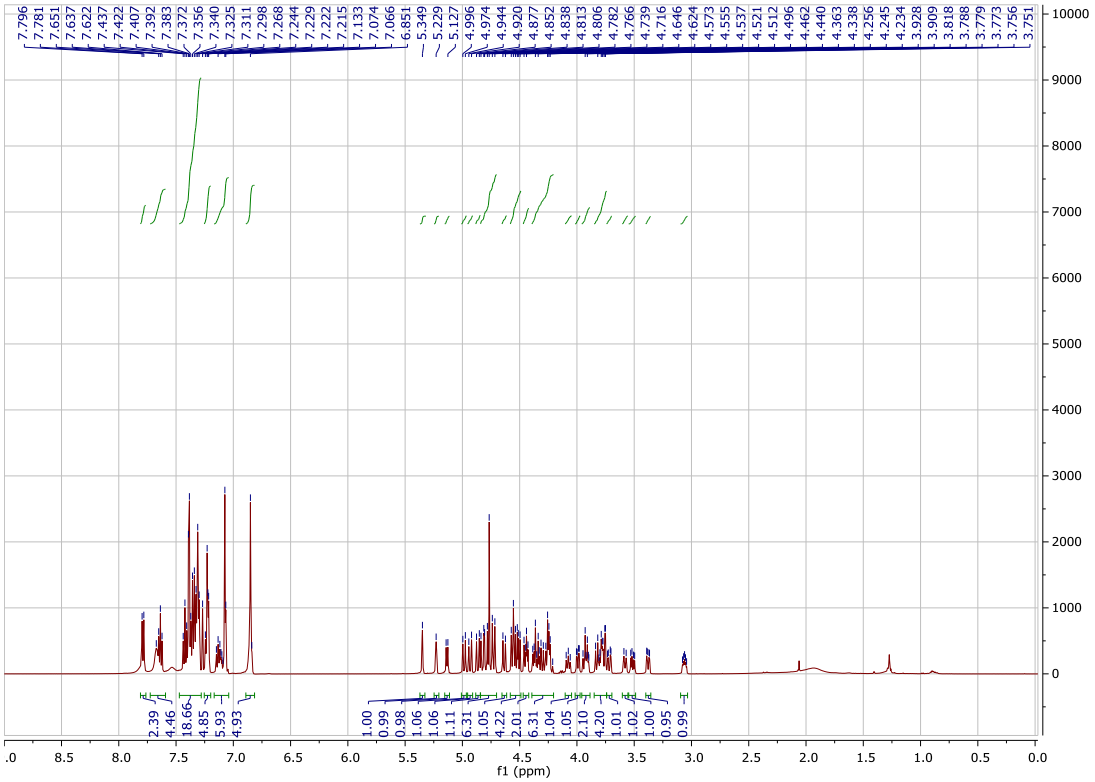
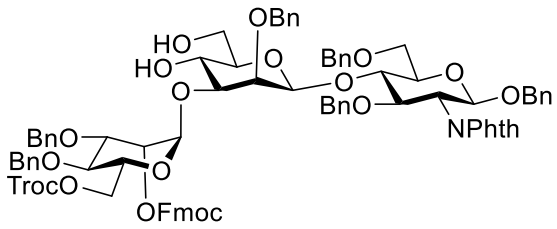




^{1}H-NMR ($CDCl_3$, 500 MHz) of **11**





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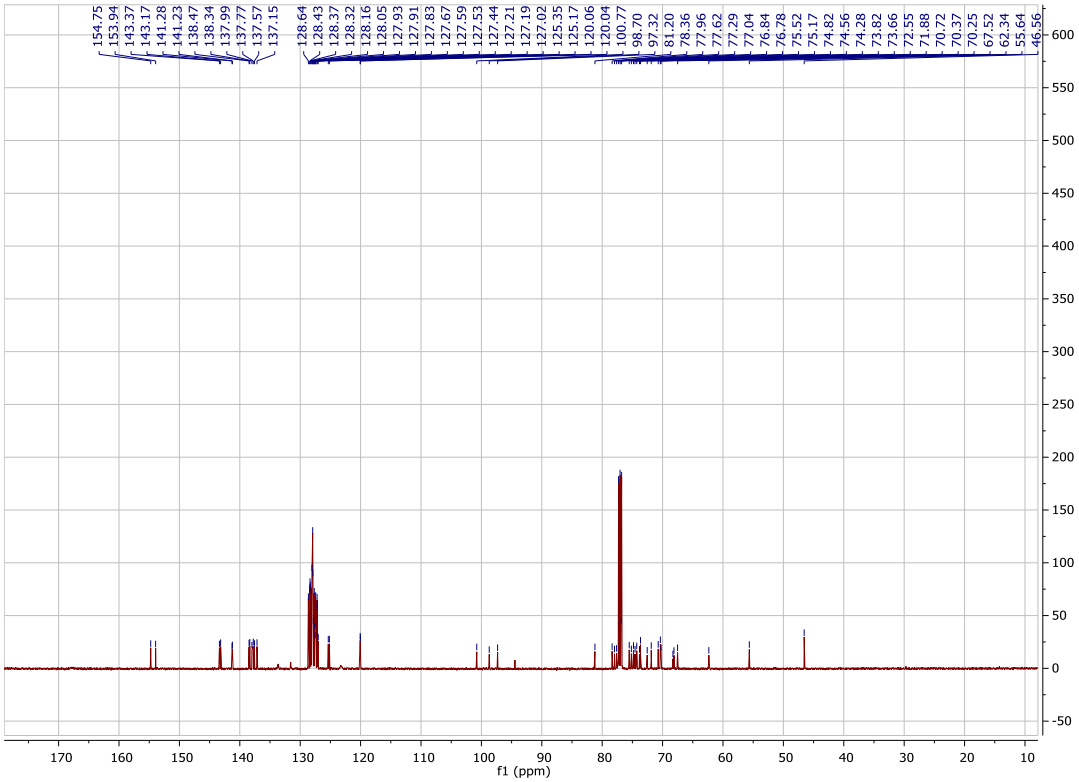
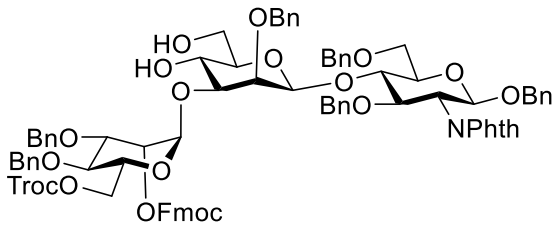
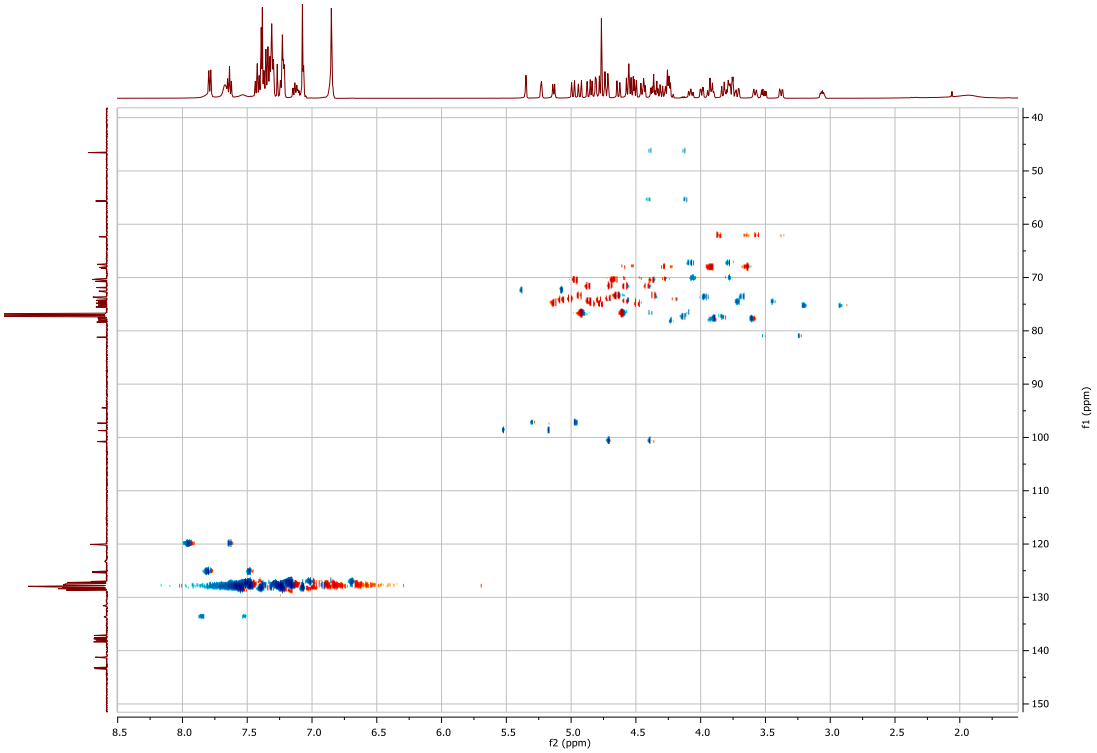
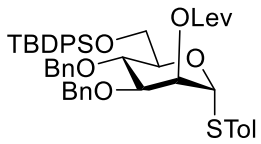


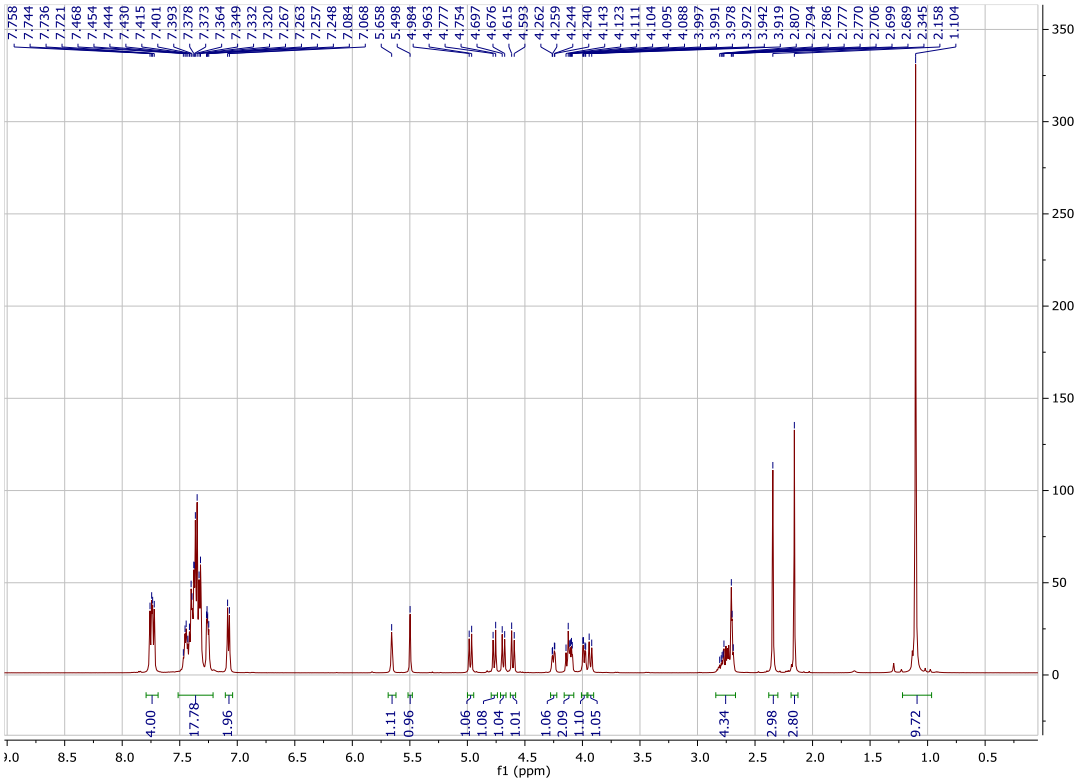


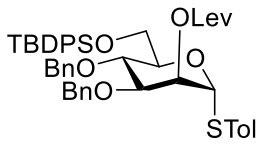
coupled gHSQC ($CDCl_3$, 500 MHz) of **11**



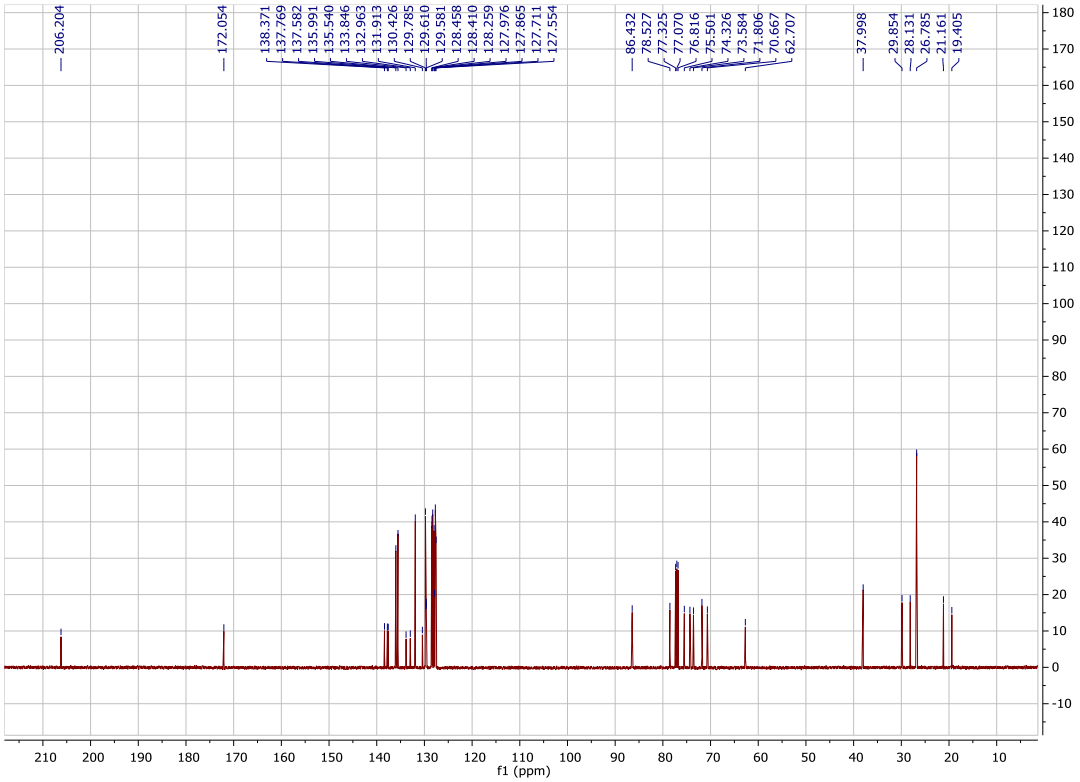


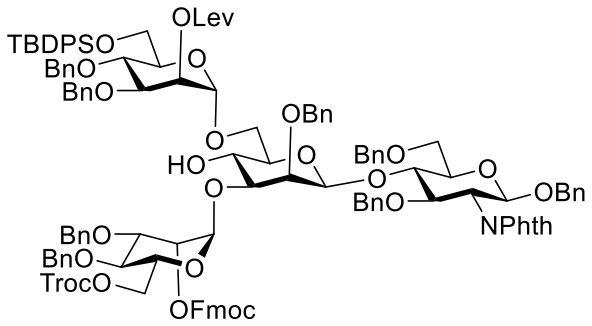
^{1}H-NMR ($CDCl_3$, 500 MHz) of **12**



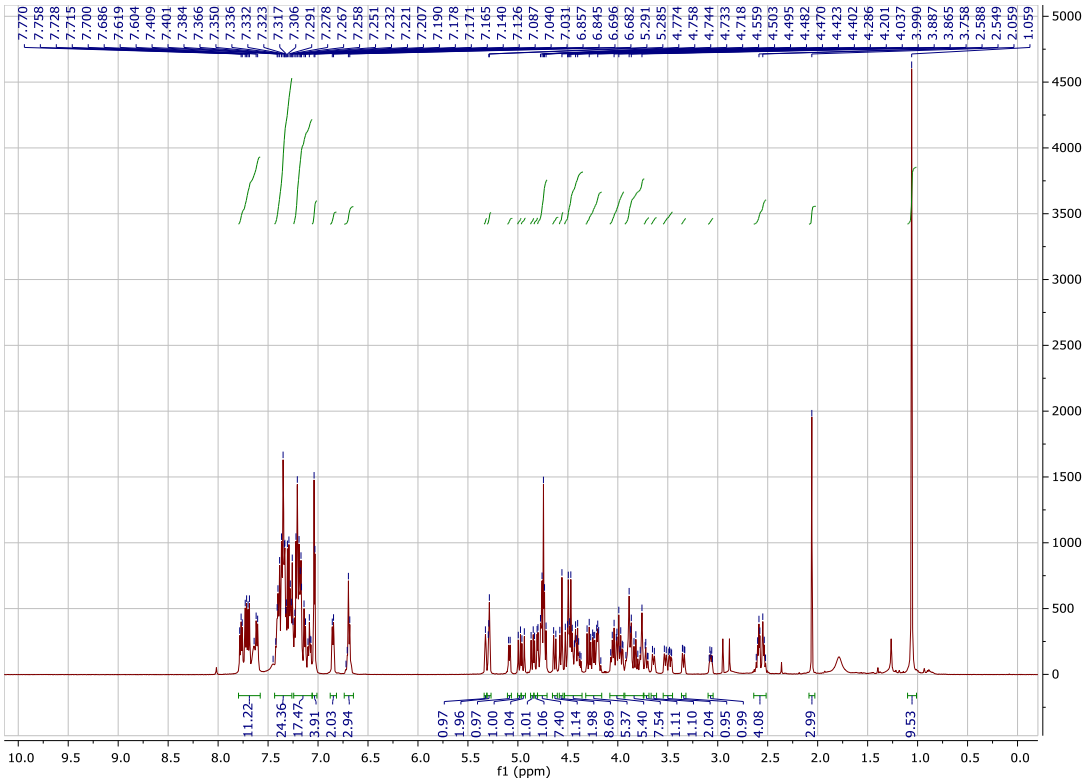


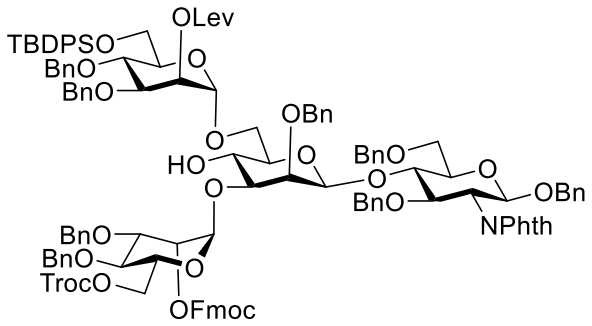
^{13}C-NMR ($CDCl_3$, 125 MHz) of **12**



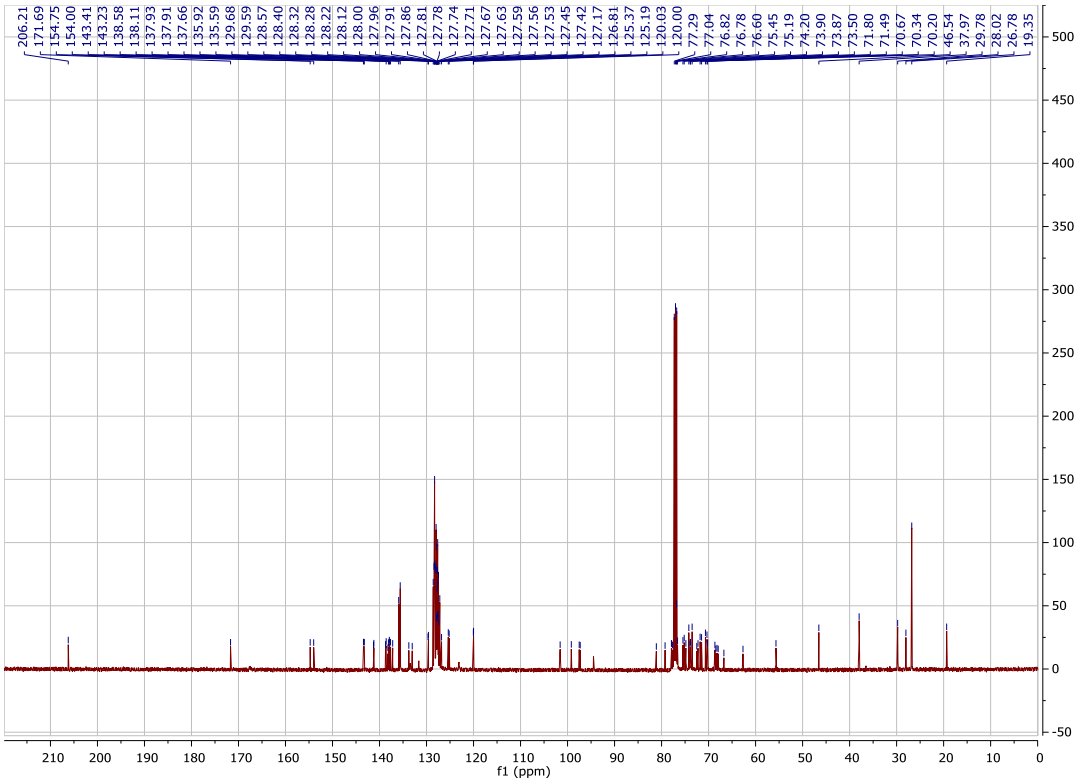


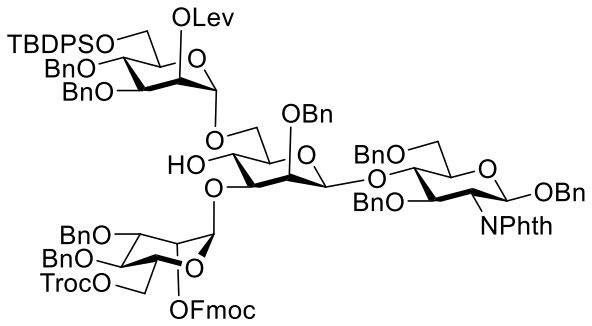
^{1}H-NMR ($CDCl_3$, 500 MHz) of **13**



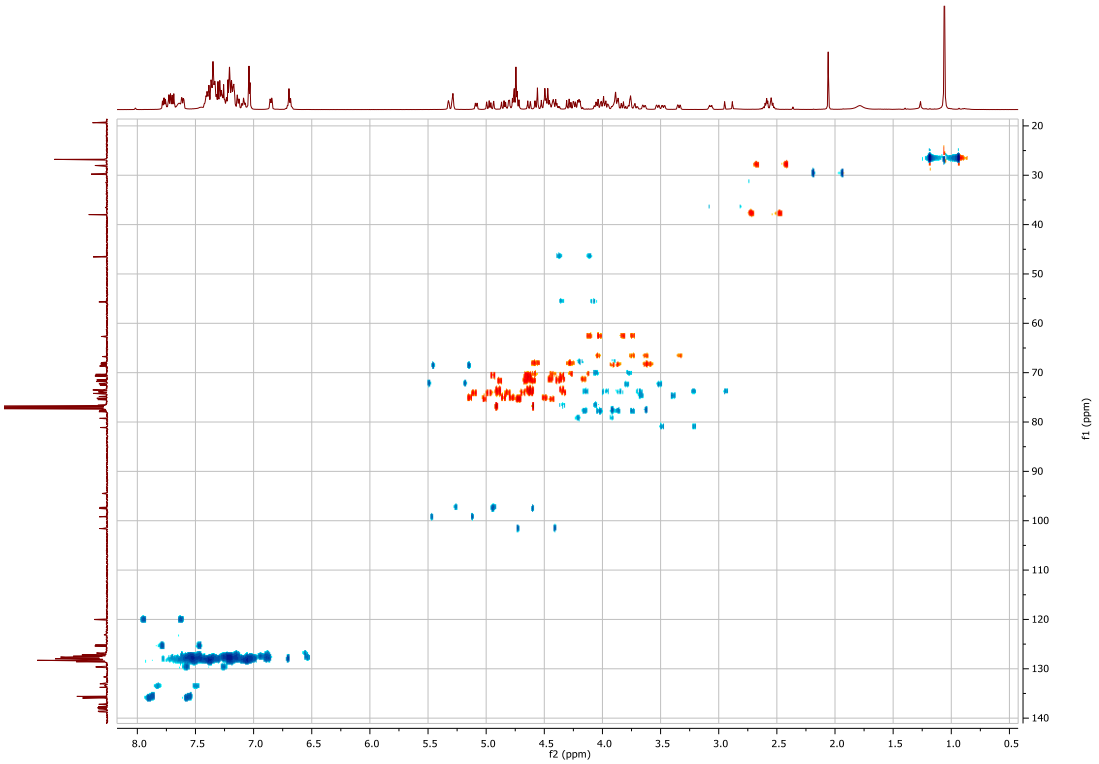


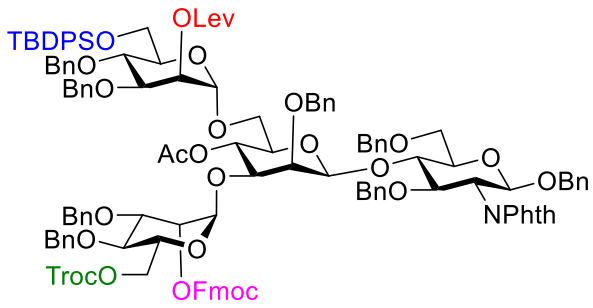
^{13}C-NMR ($CDCl_3$, 125 MHz) of **13**



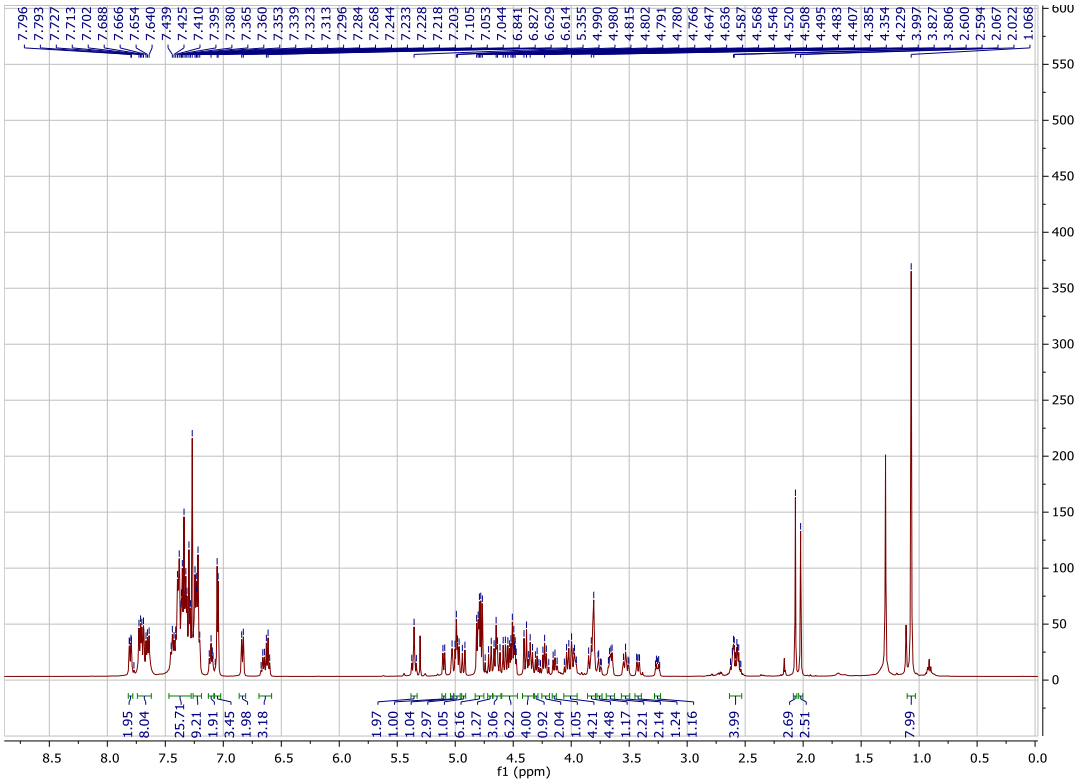


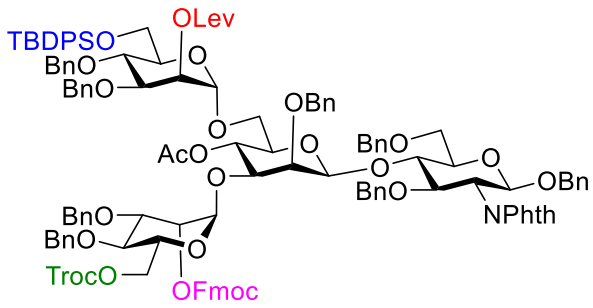
coupled gHSQC ($CDCl_3$, 500 MHz) of **13**



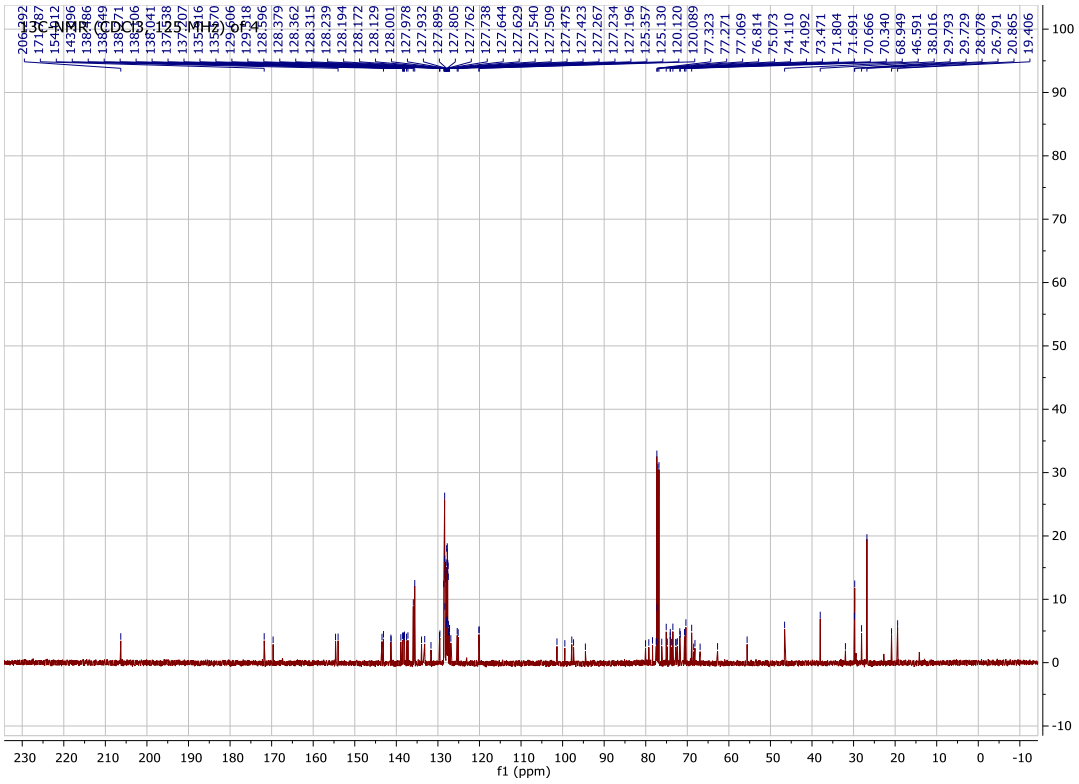


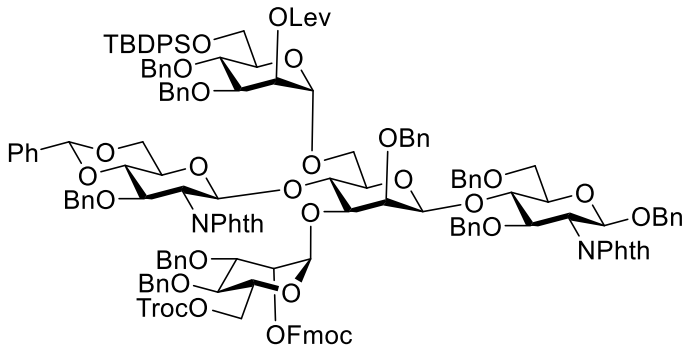
^{1}H-NMR ($CDCl_3$, 500 MHz) of **14**



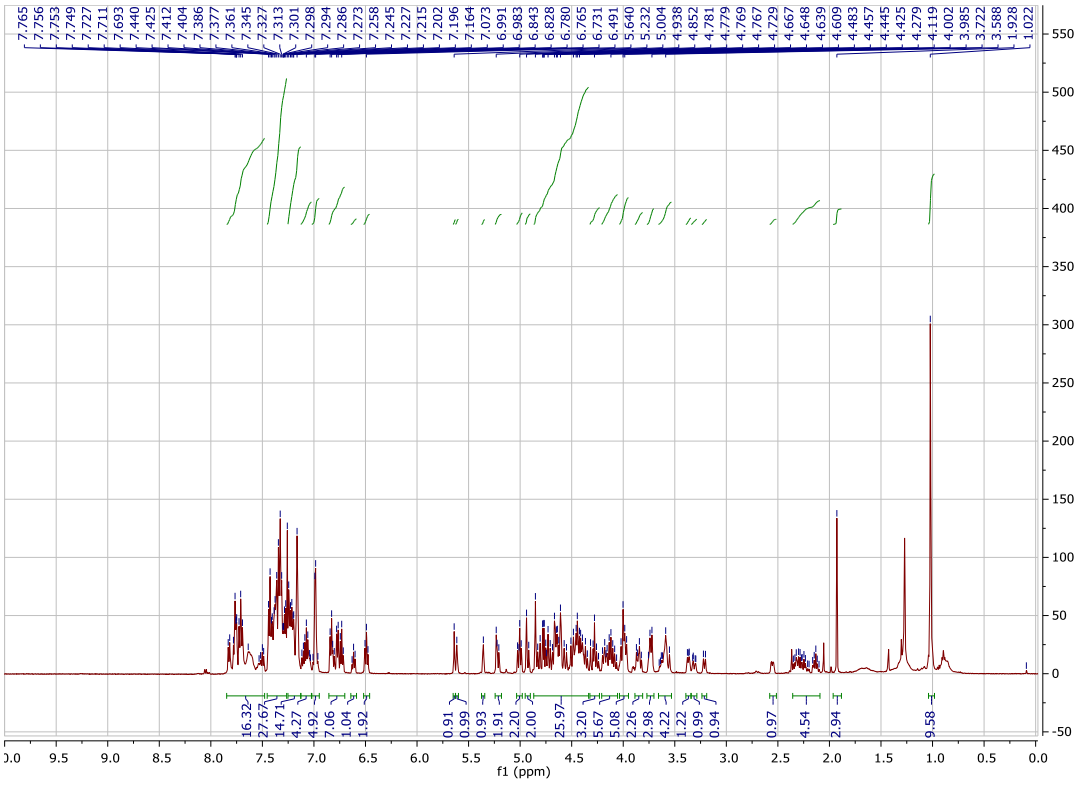


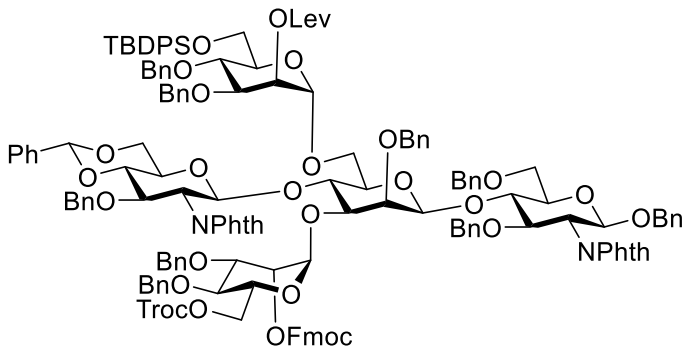
^{13}C-NMR ($CDCl_3$, 125 MHz) of **14**



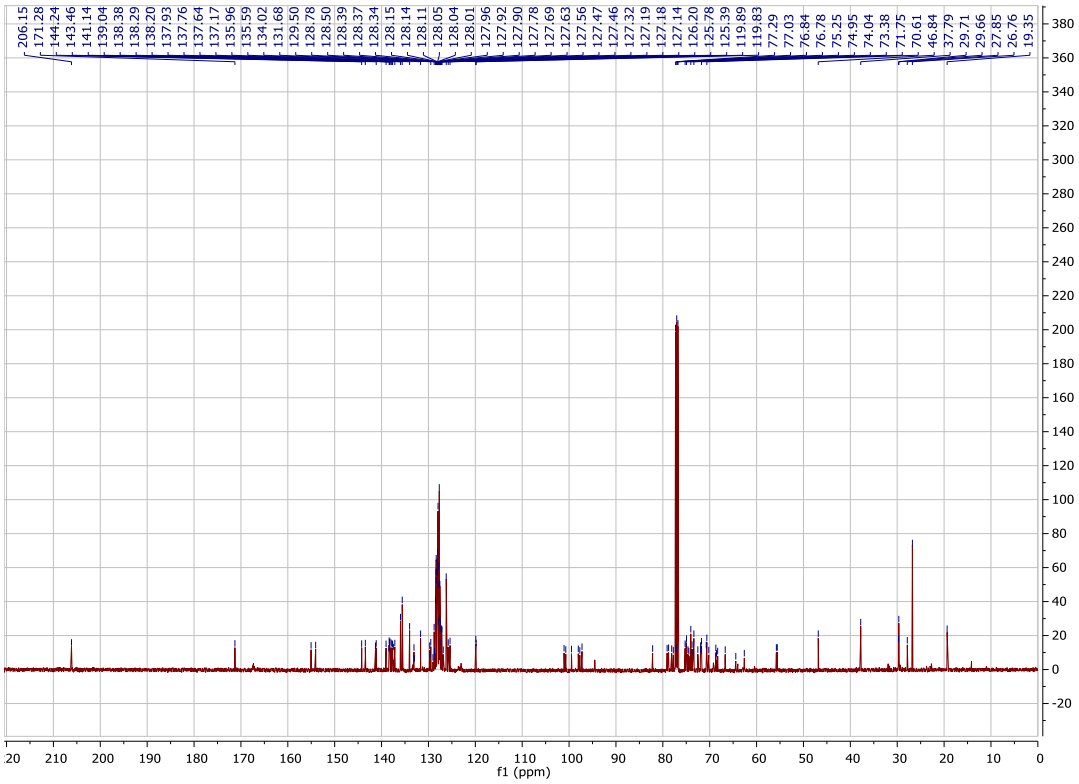


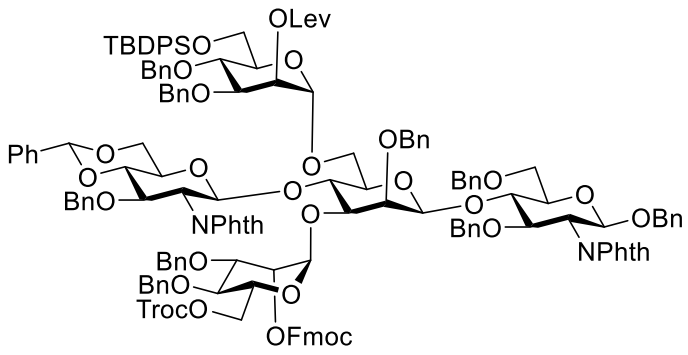
^{1}H-NMR ($CDCl_3$, 500 MHz) of **15**



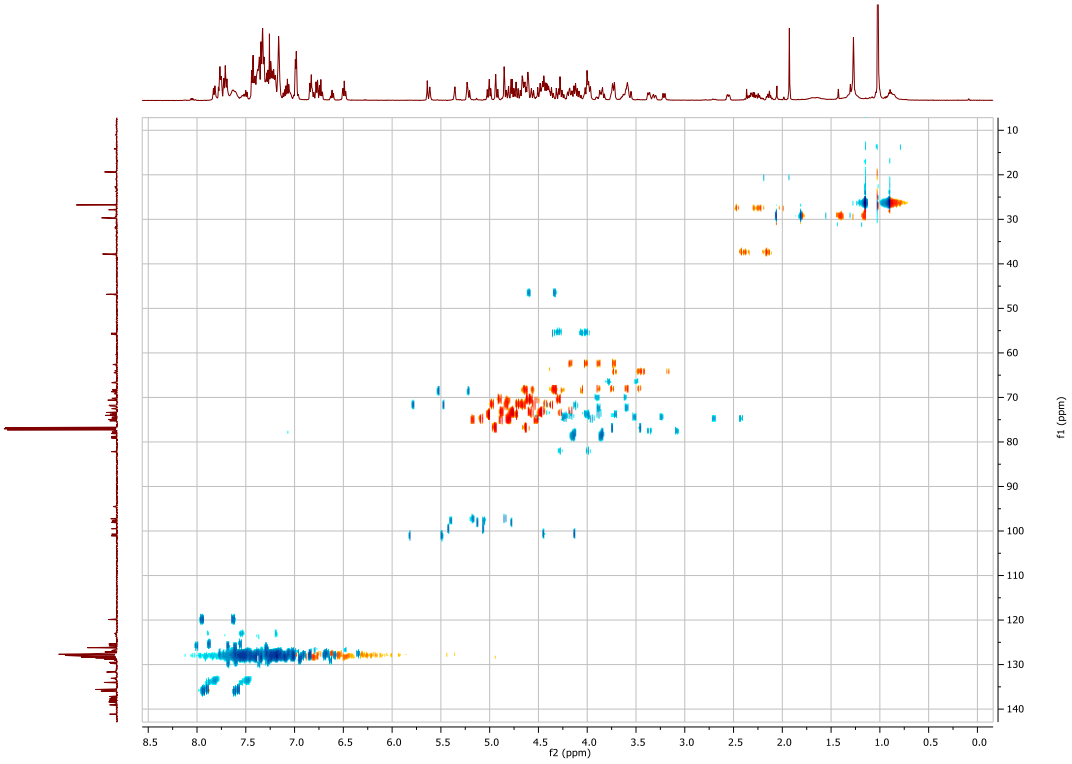


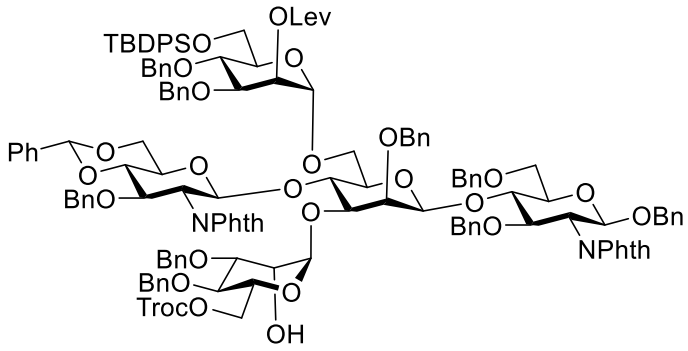
^{13}C-NMR ($CDCl_3$, 125 MHz) of **15**



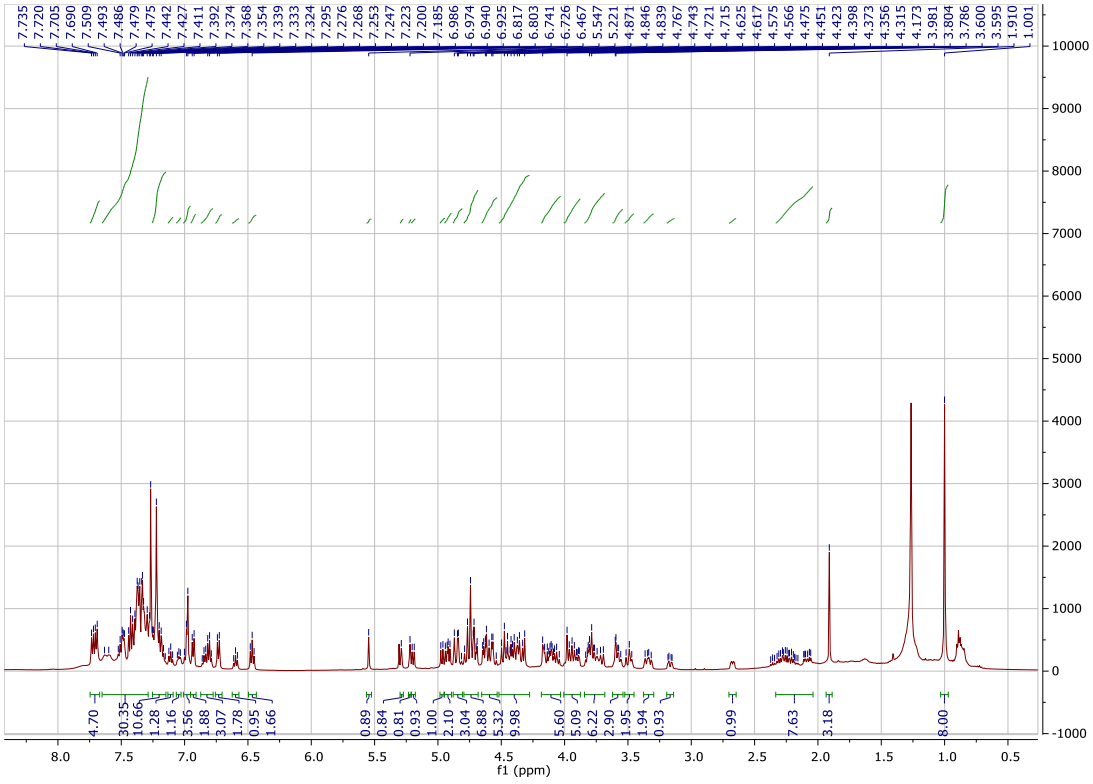


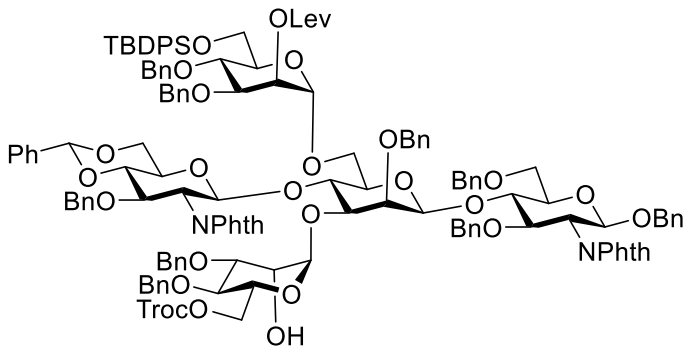
coupled gHSQC ($CDCl_3$, 500 MHz) of **15**



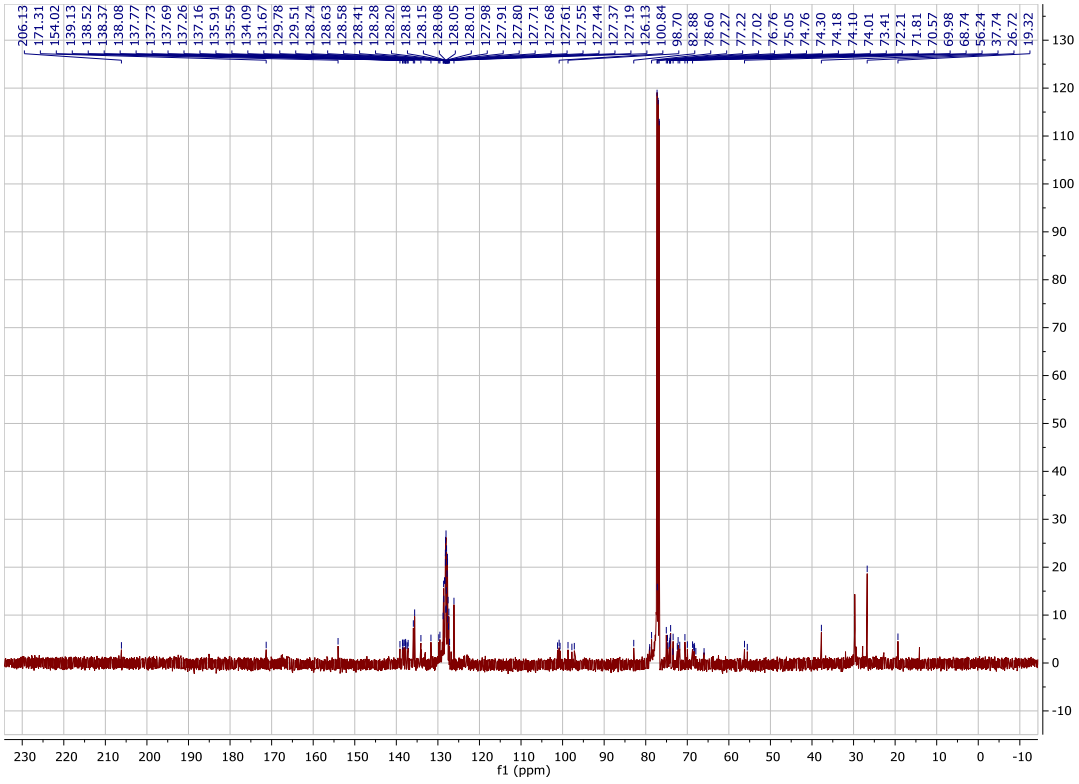


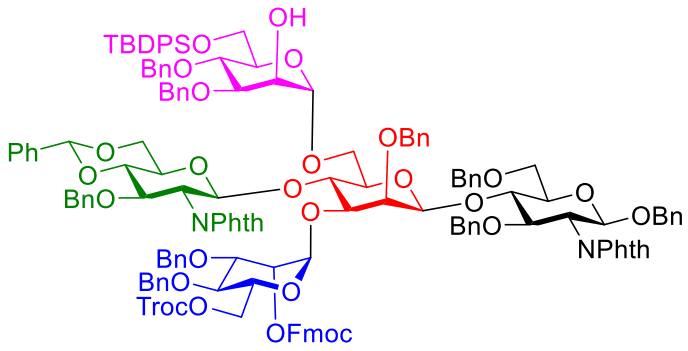
^{1}H-NMR ($CDCl_3$, 500 MHz) of **16**





^{13}C-NMR ($CDCl_3$, 125 MHz) of **16**





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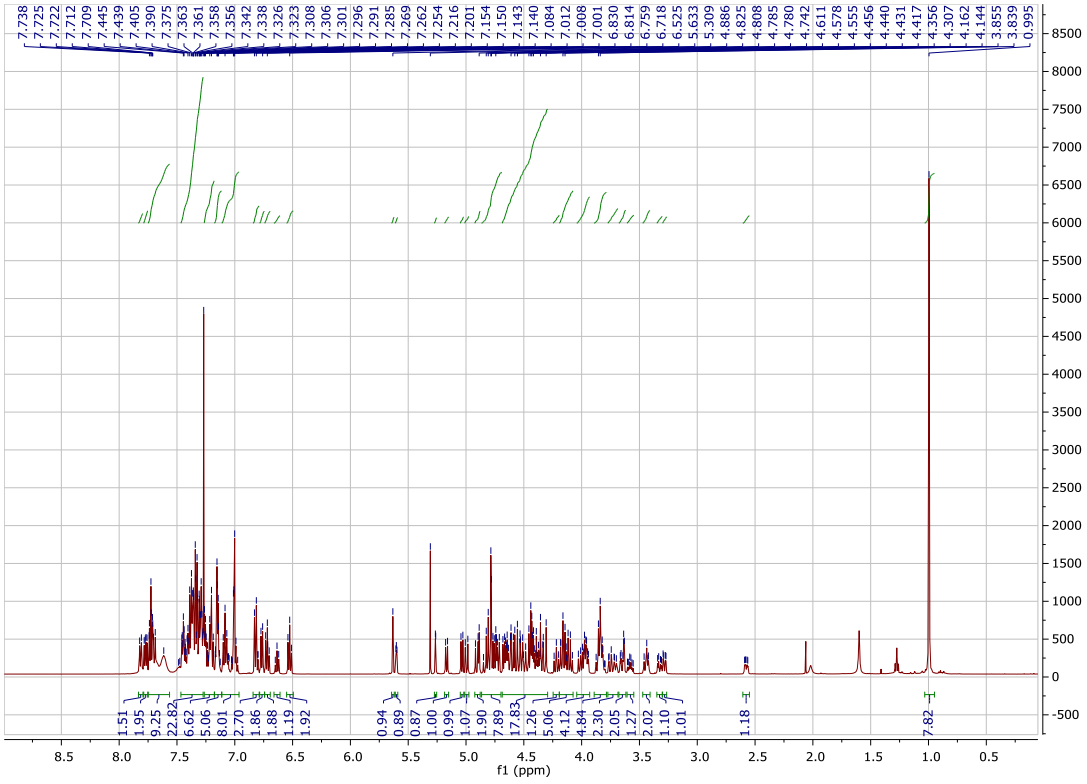
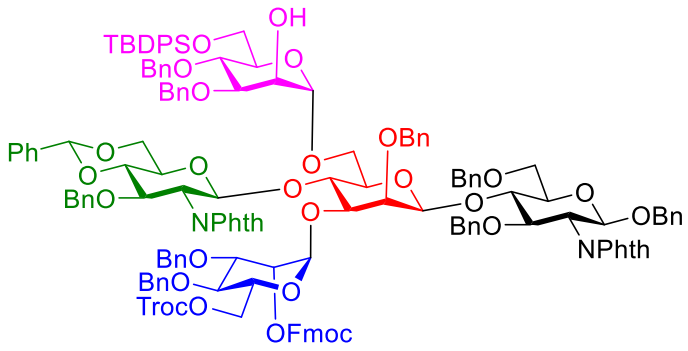
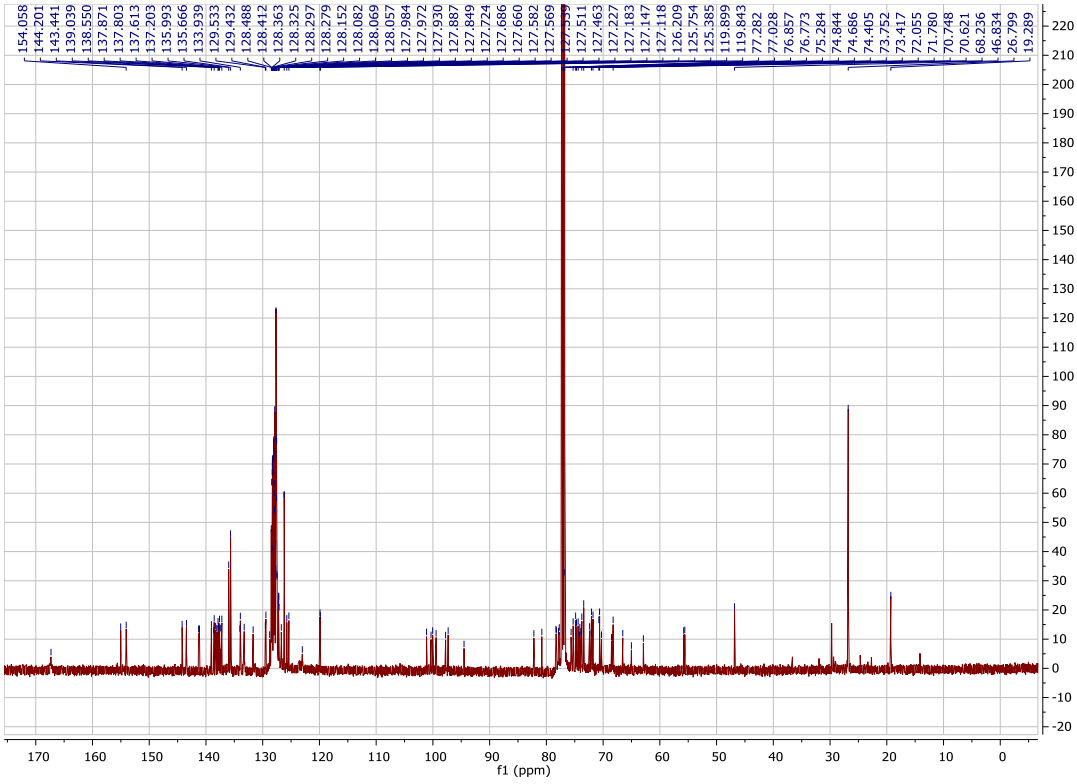
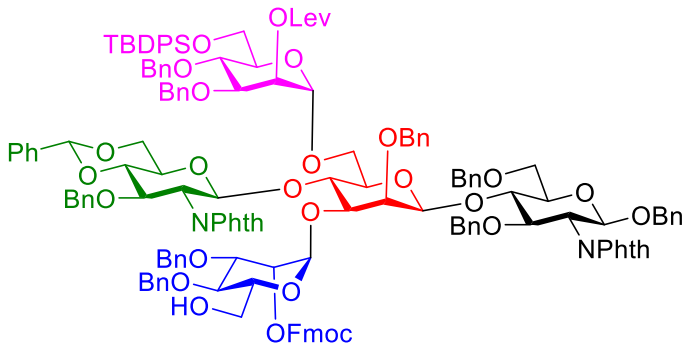


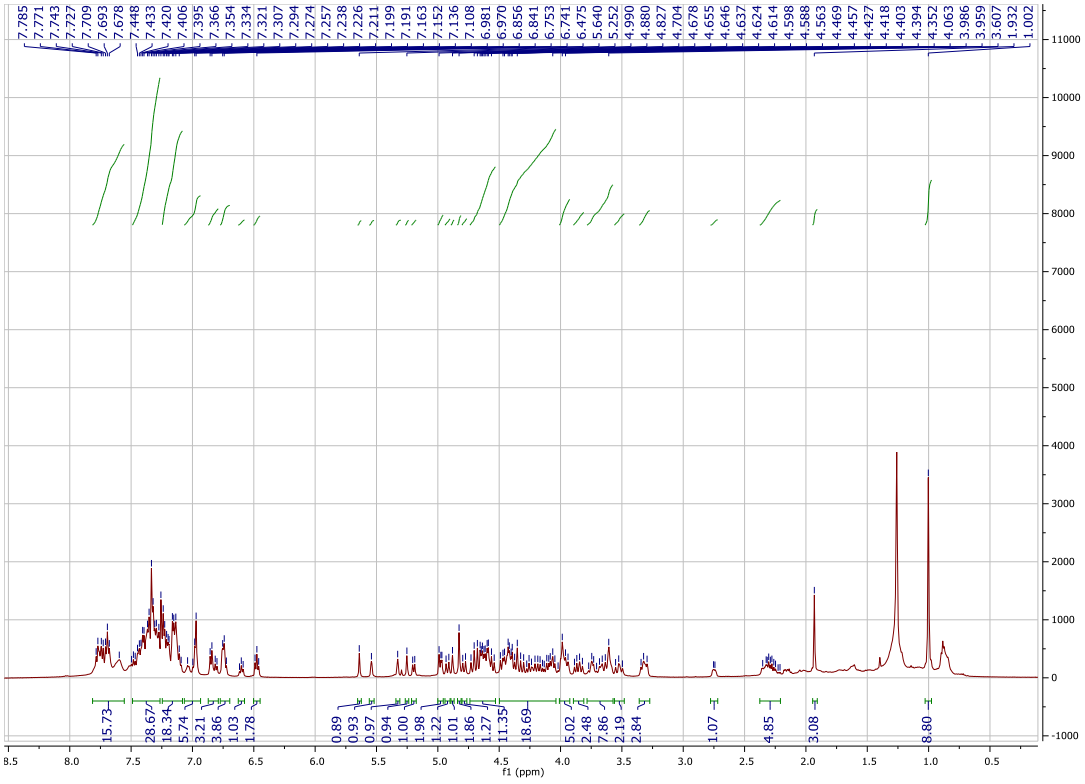


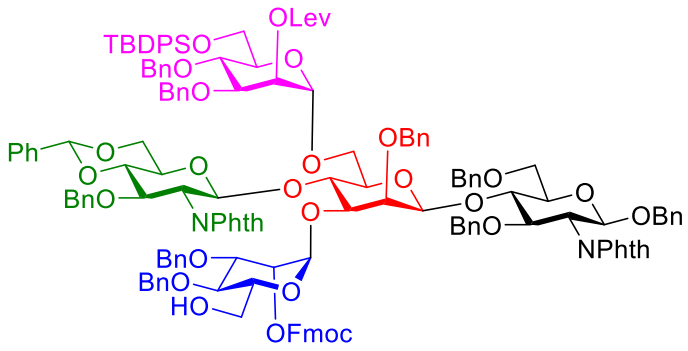
^{13}C-NMR ($CDCl_3$, 125 MHz) of **17**



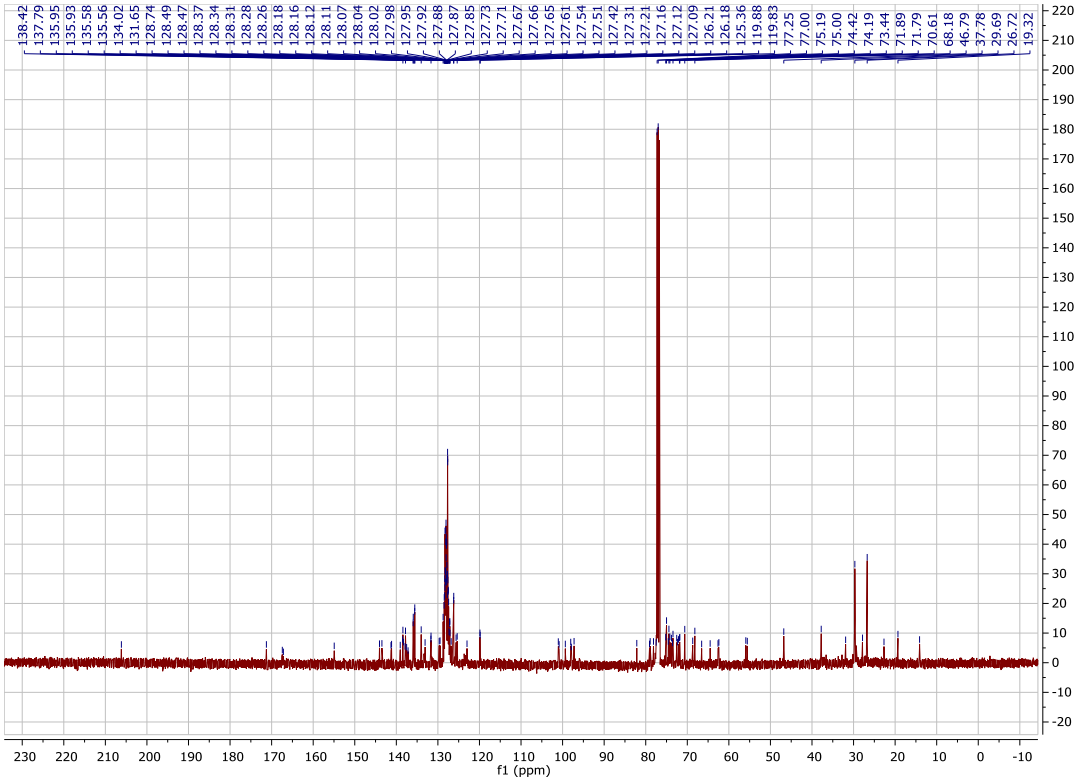


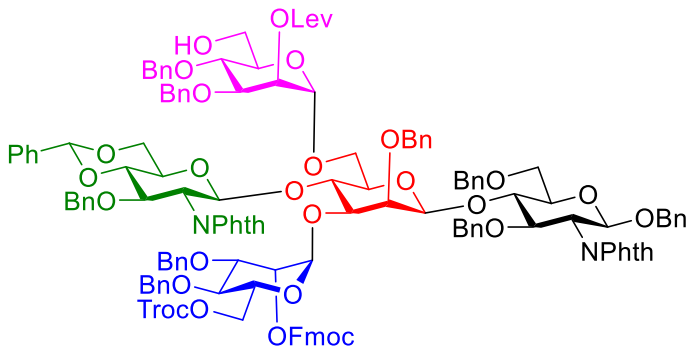
^{1}H-NMR ($CDCl_3$, 500 MHz) of **18**



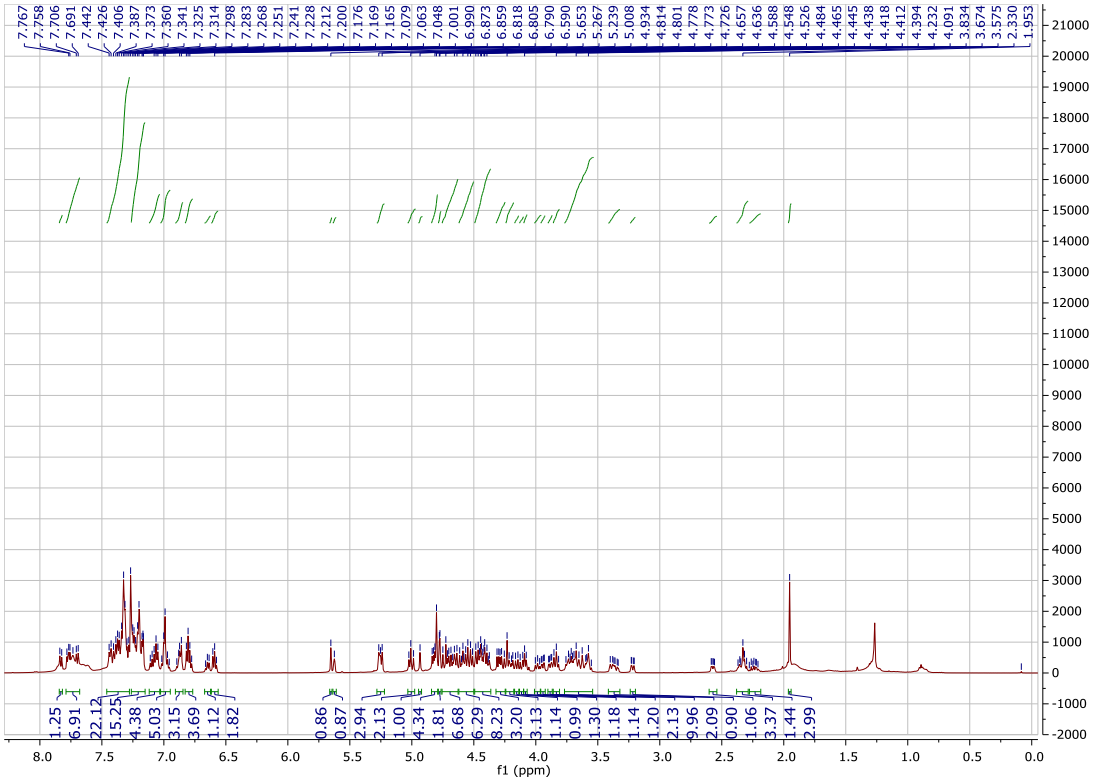


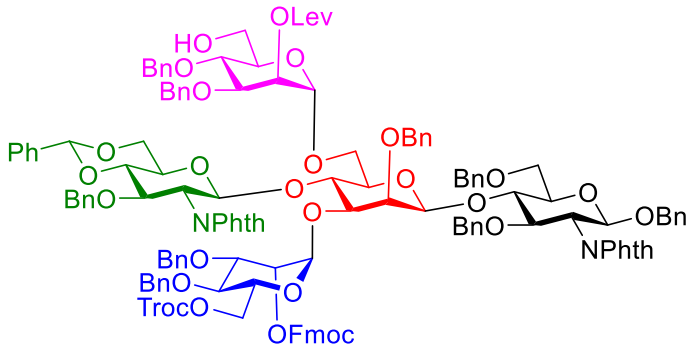
^{13}C-NMR ($CDCl_3$, 125 MHz) of **18**



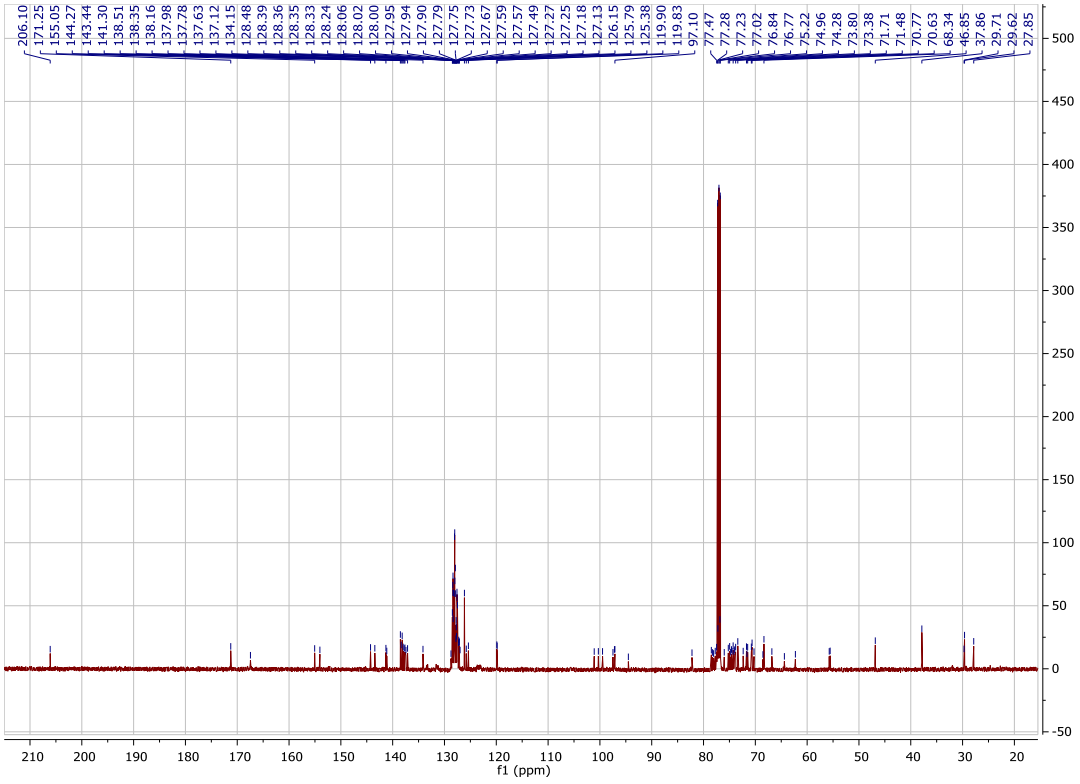


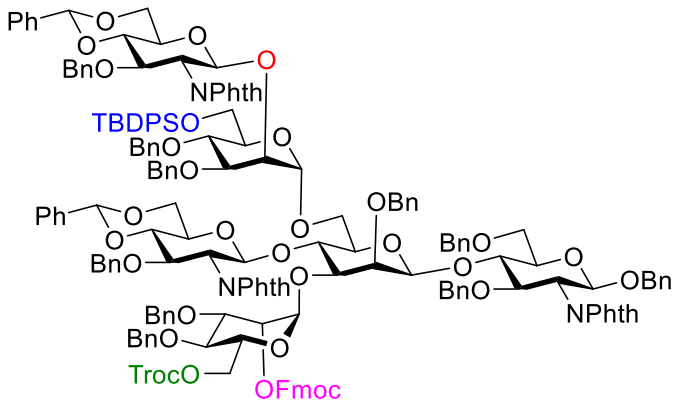
^{1}H-NMR ($CDCl_3$, 500 MHz) of **19**



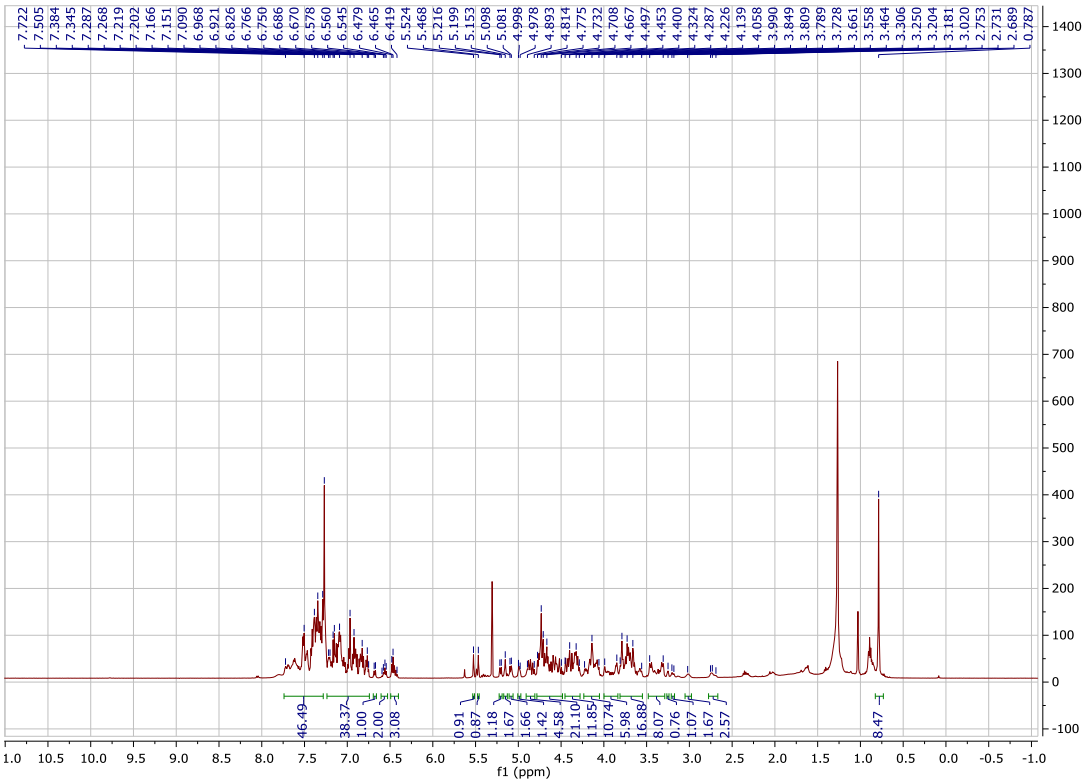


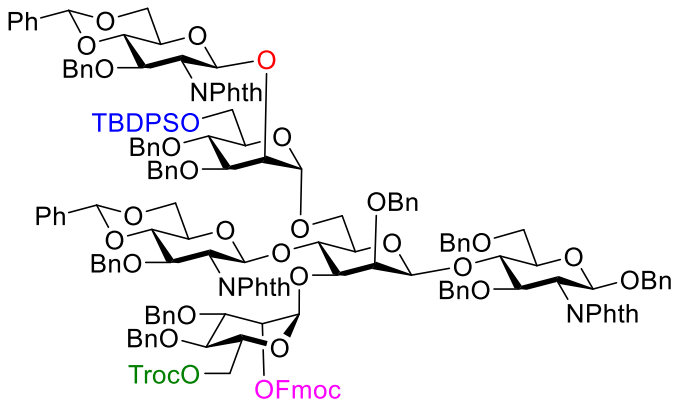
^{13}C-NMR ($CDCl_3$, 125 MHz) of **19**



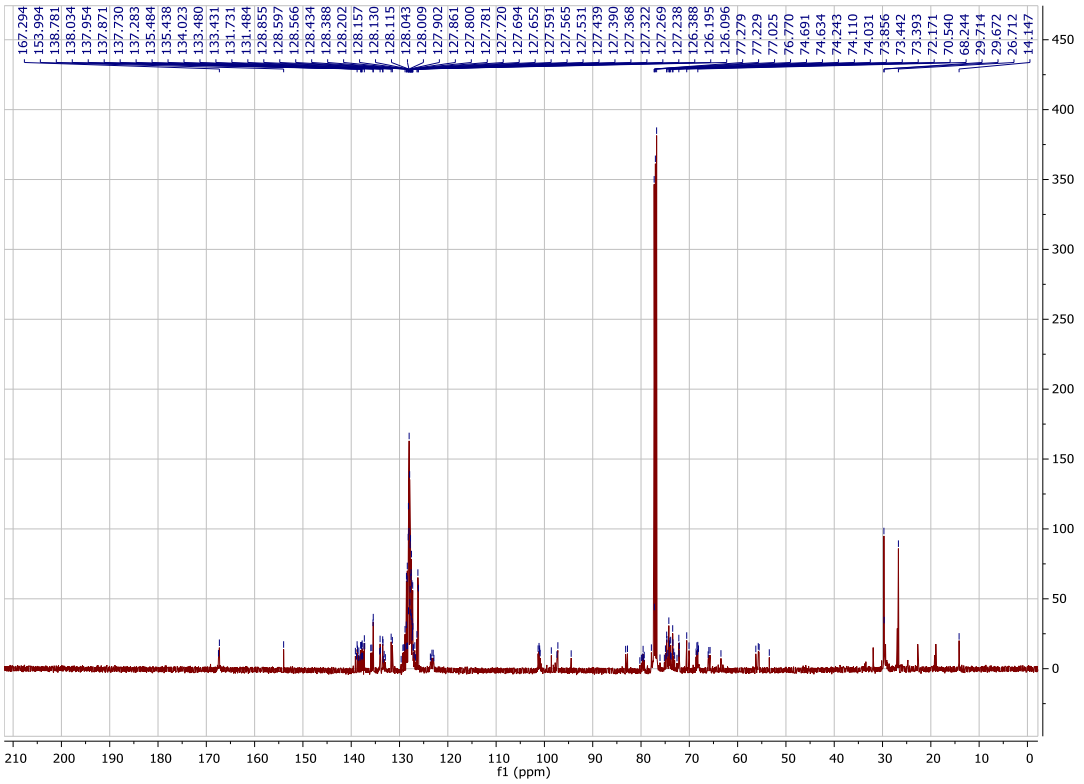


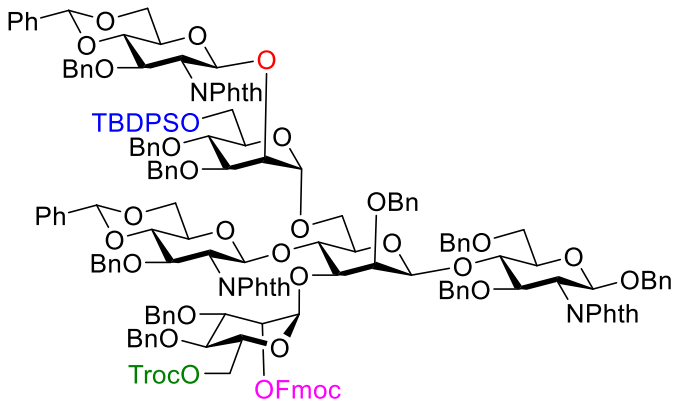
^{1}H-NMR ($CDCl_3$, 500 MHz) of **21**



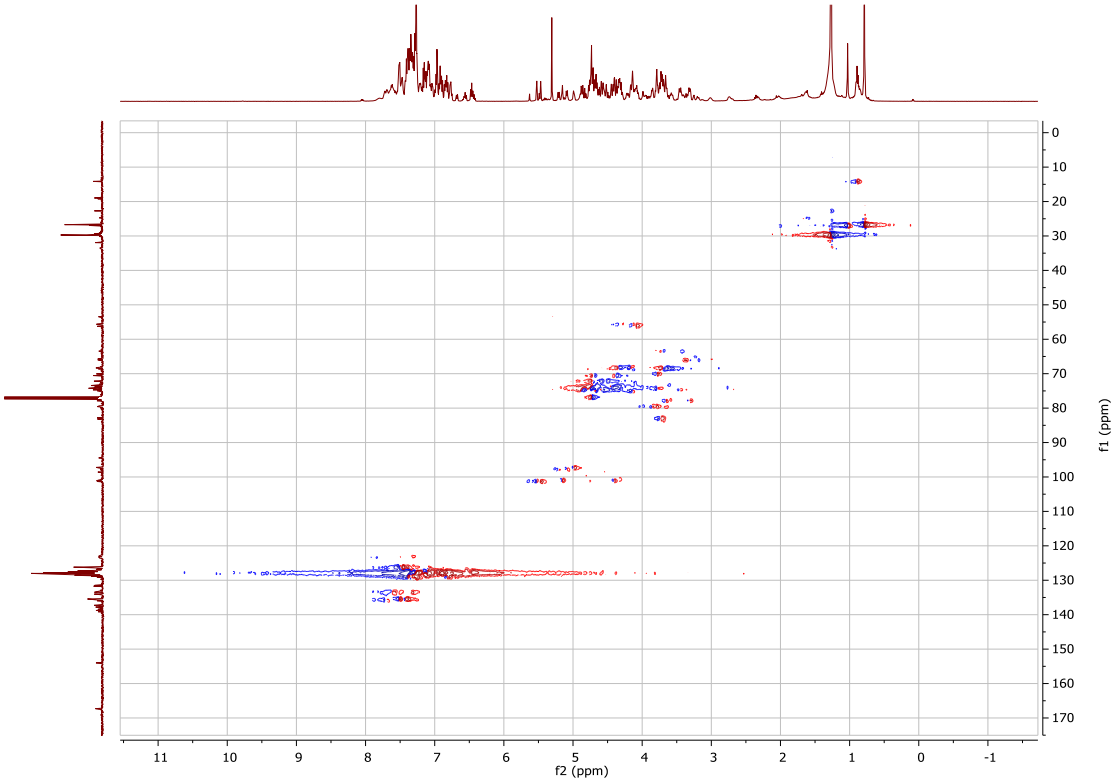


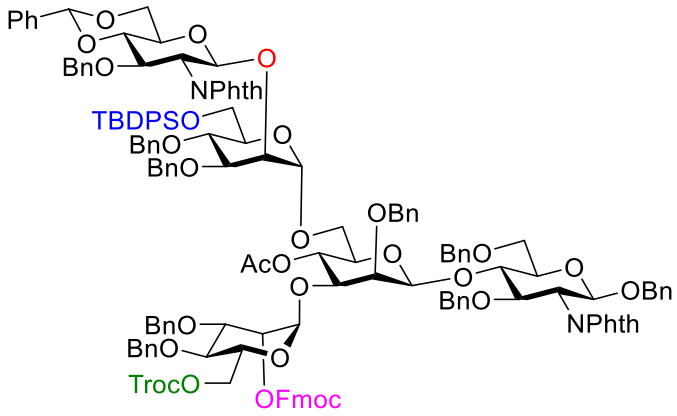
^{13}C-NMR ($CDCl_3$, 125 MHz) of **21**



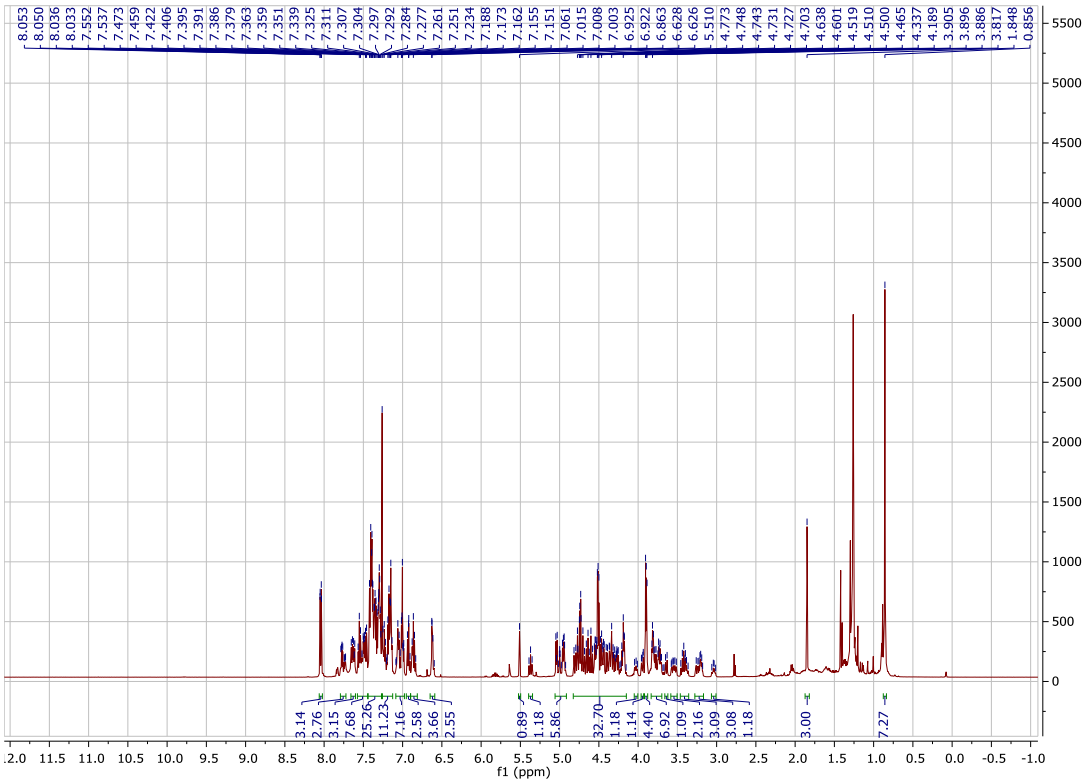


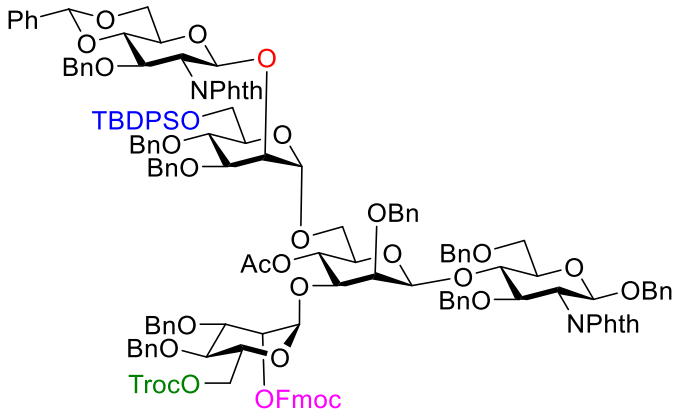
gHSQC ($CDCl_3$, 500 MHz) of **21**



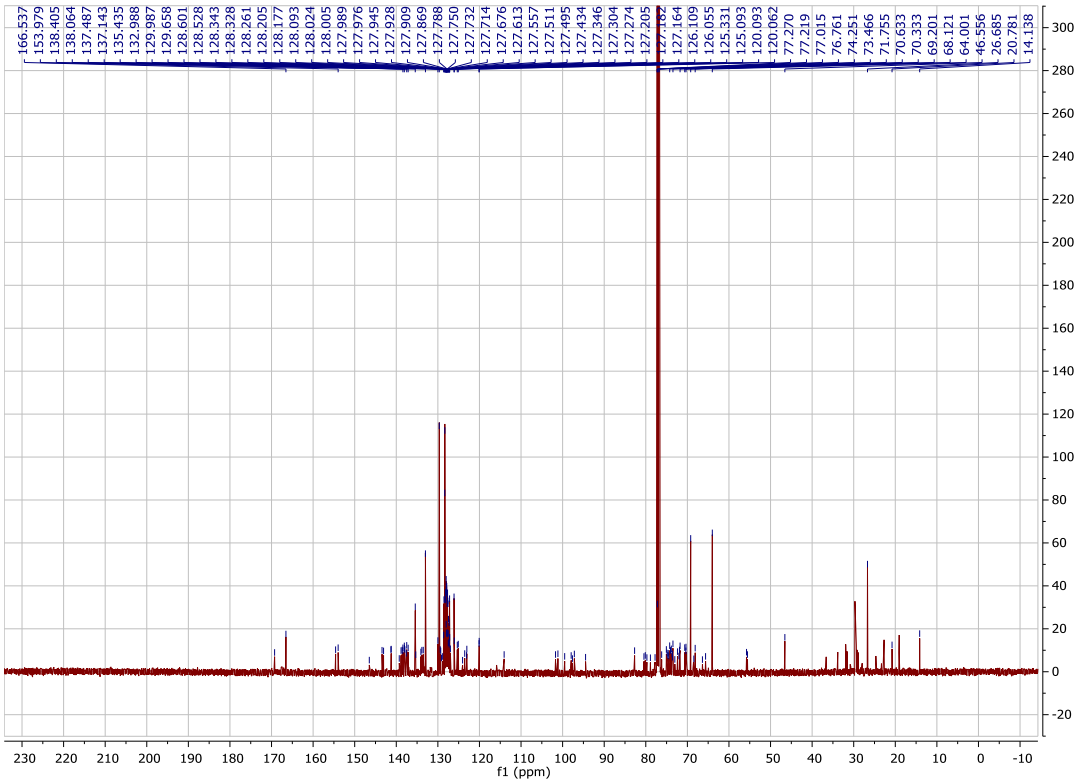


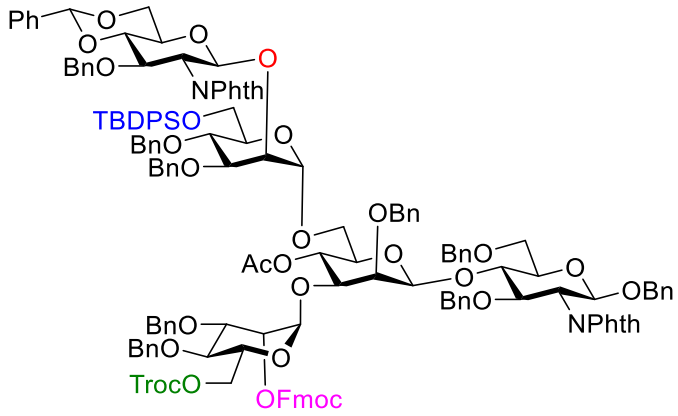
^{1}H-NMR ($CDCl_3$, 500 MHz) of **22**



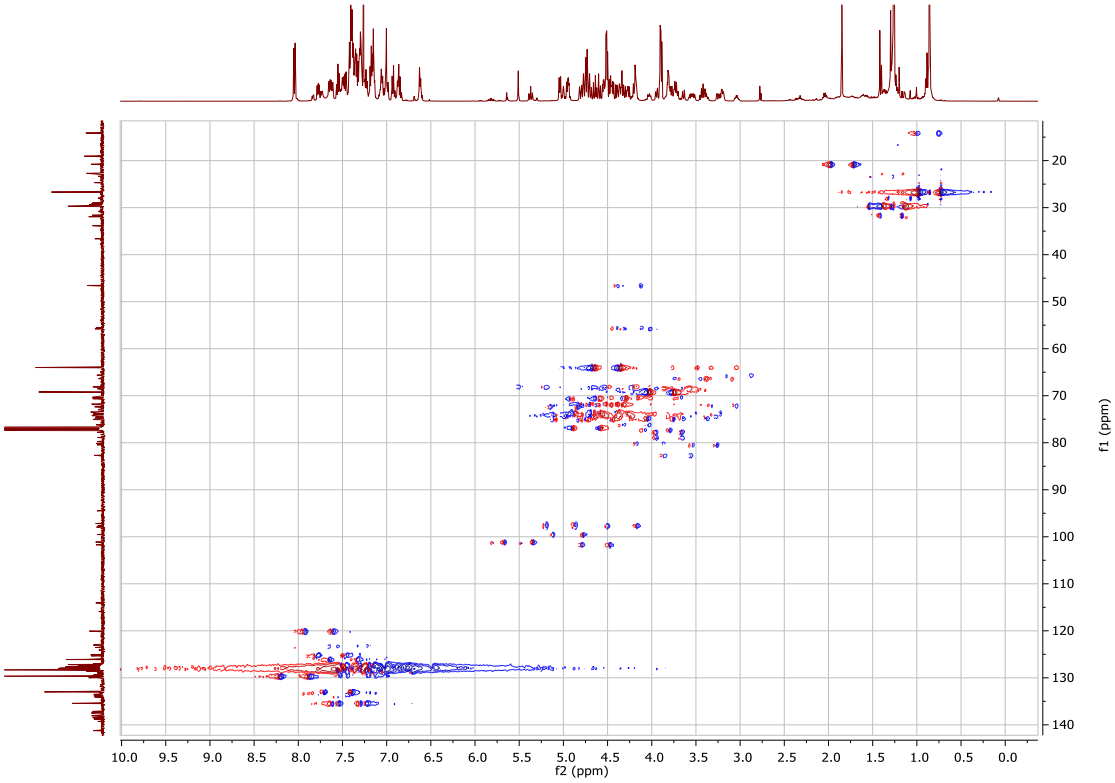


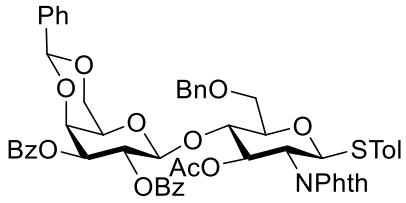
^{13}C-NMR ($CDCl_3$, 125 MHz) of **22**



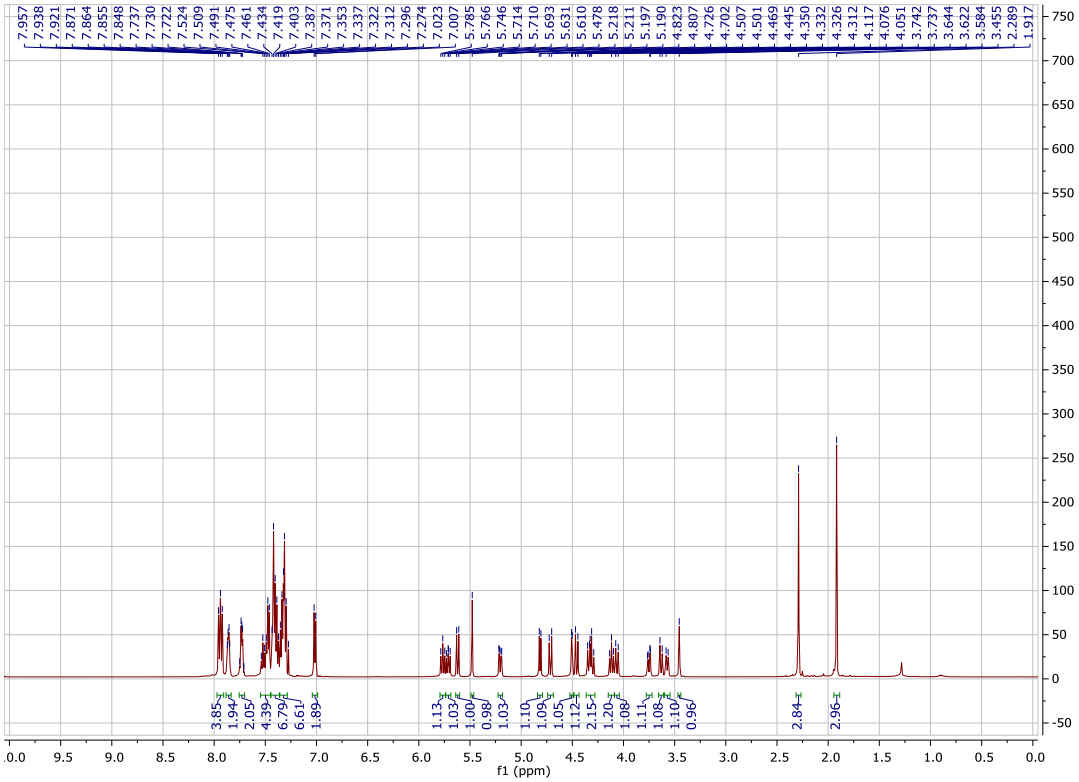


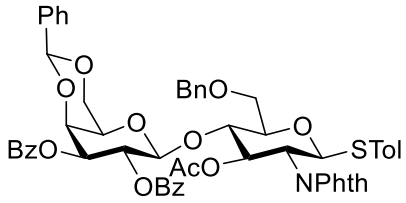
coupled gHSQC ($CDCl_3$, 500 MHz) of **22**



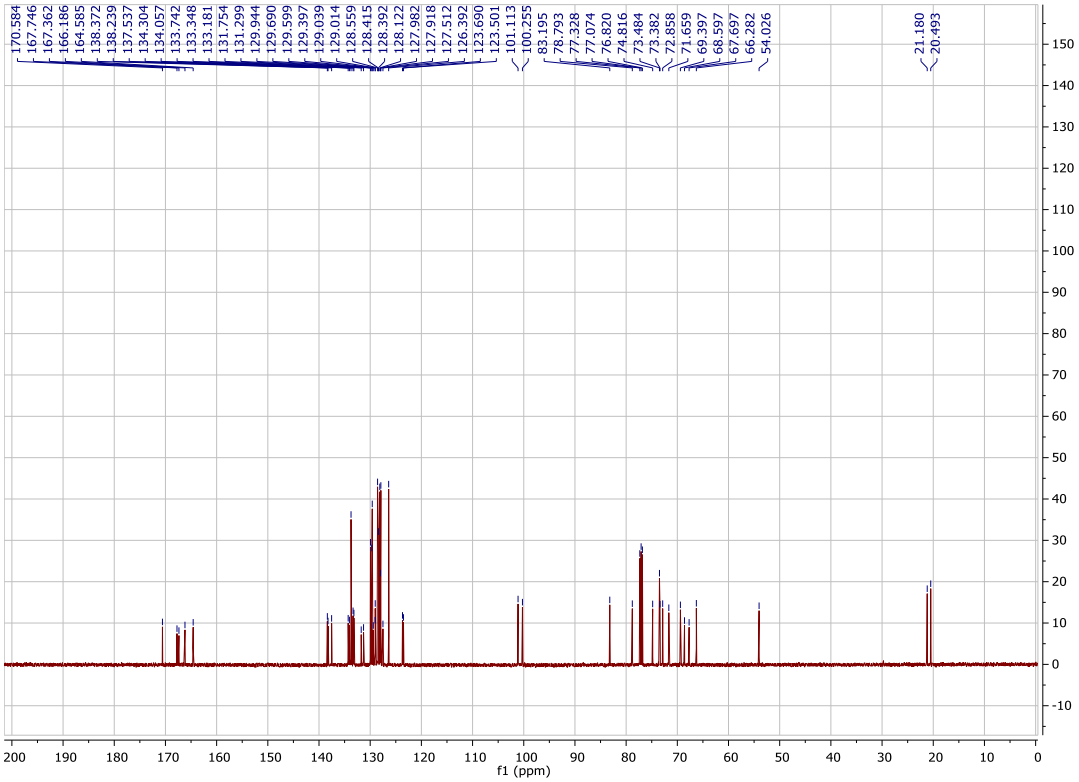


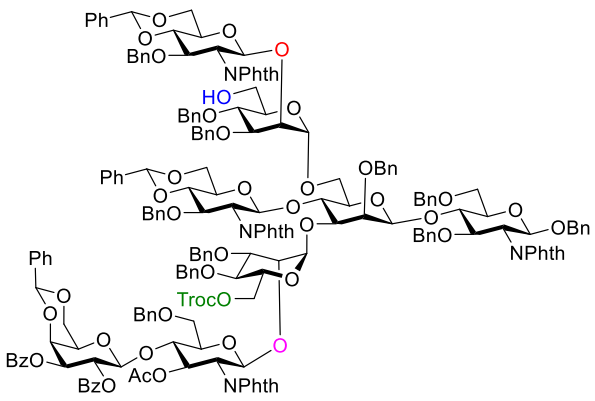
^{1}H-NMR ($CDCl_3$, 500 MHz) of **23**



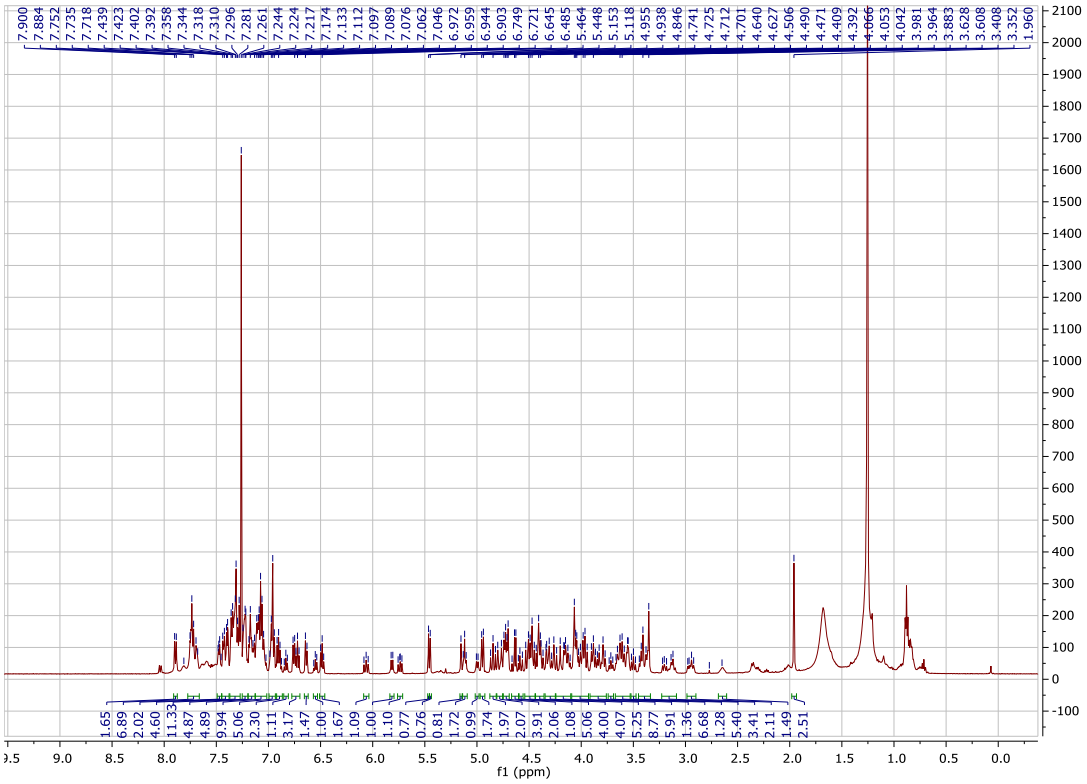


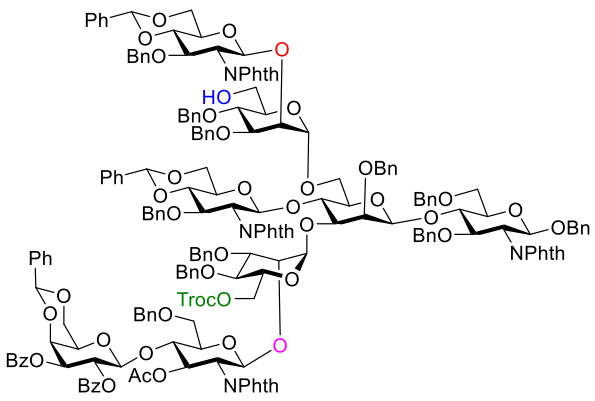
^{13}C-NMR ($CDCl_3$, 125 MHz) of **23**



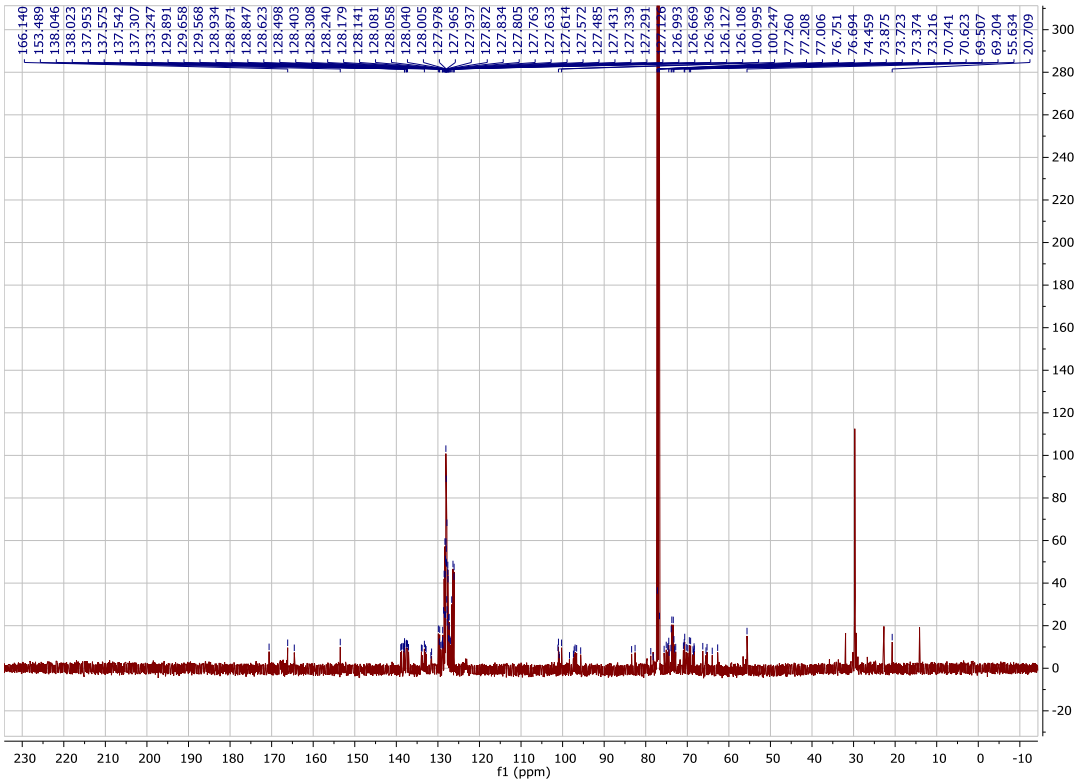


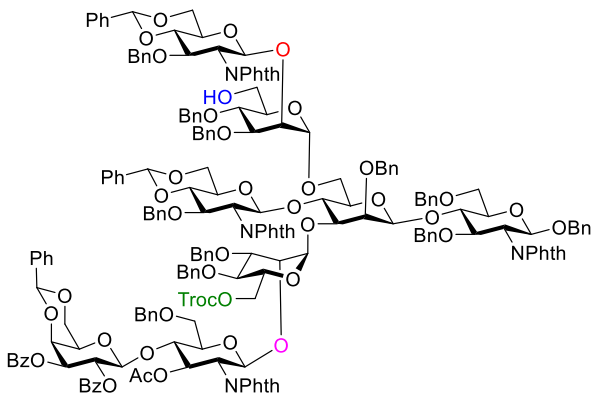
^{1}H-NMR ($CDCl_3$, 500 MHz) of **24**



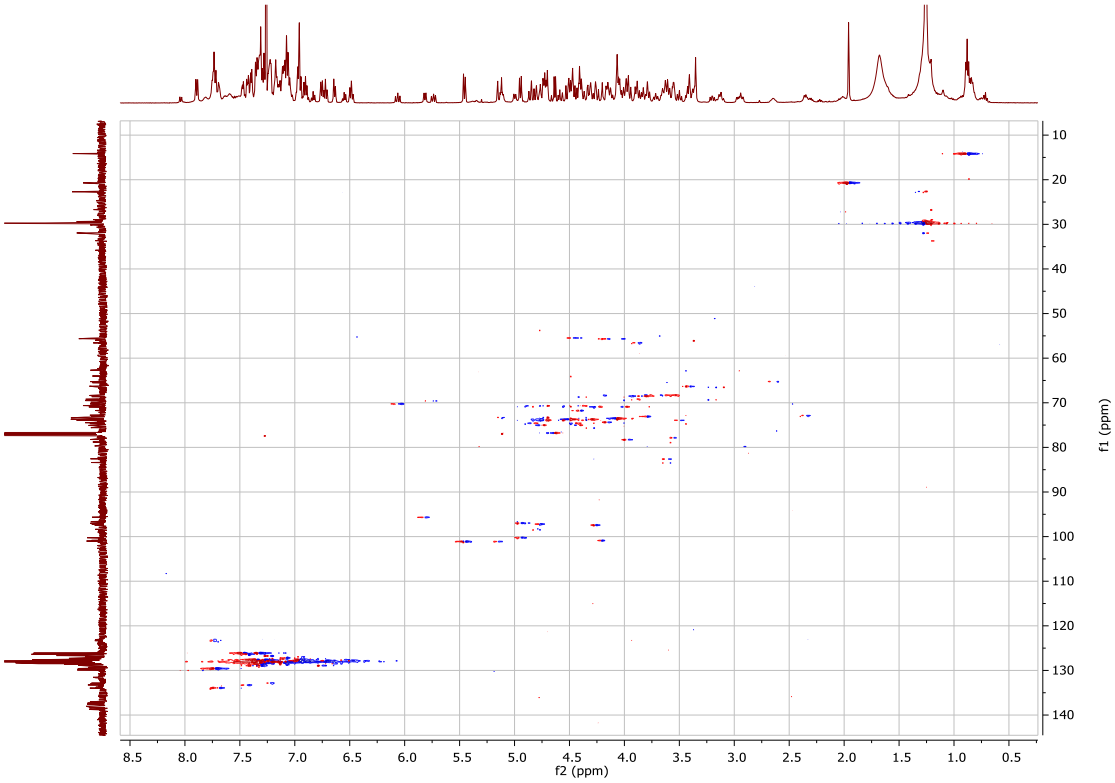


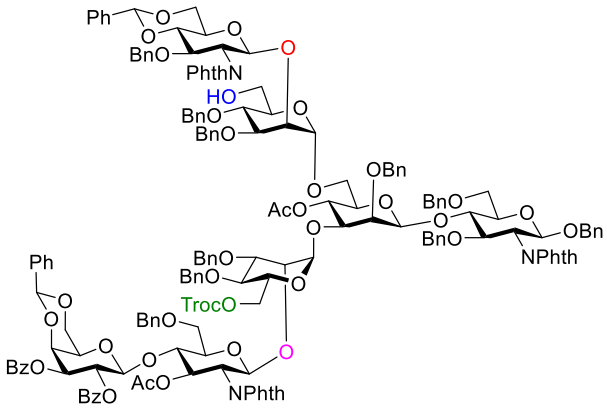
^{13}C-NMR ($CDCl_3$, 125 MHz) of **24**



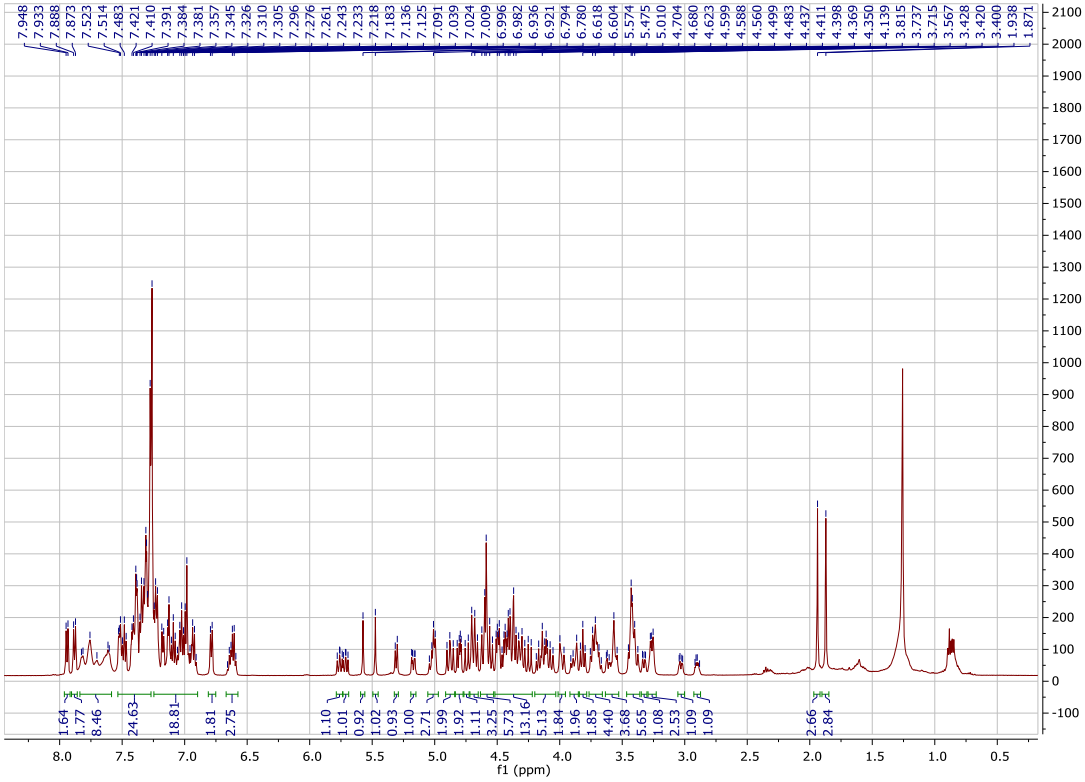


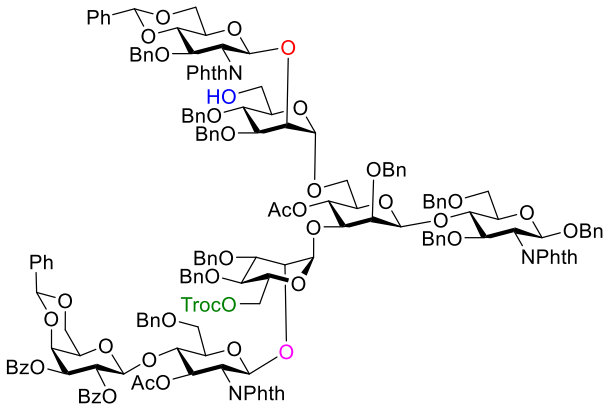
gHSQC ($CDCl_3$, 500 MHz) of **24**



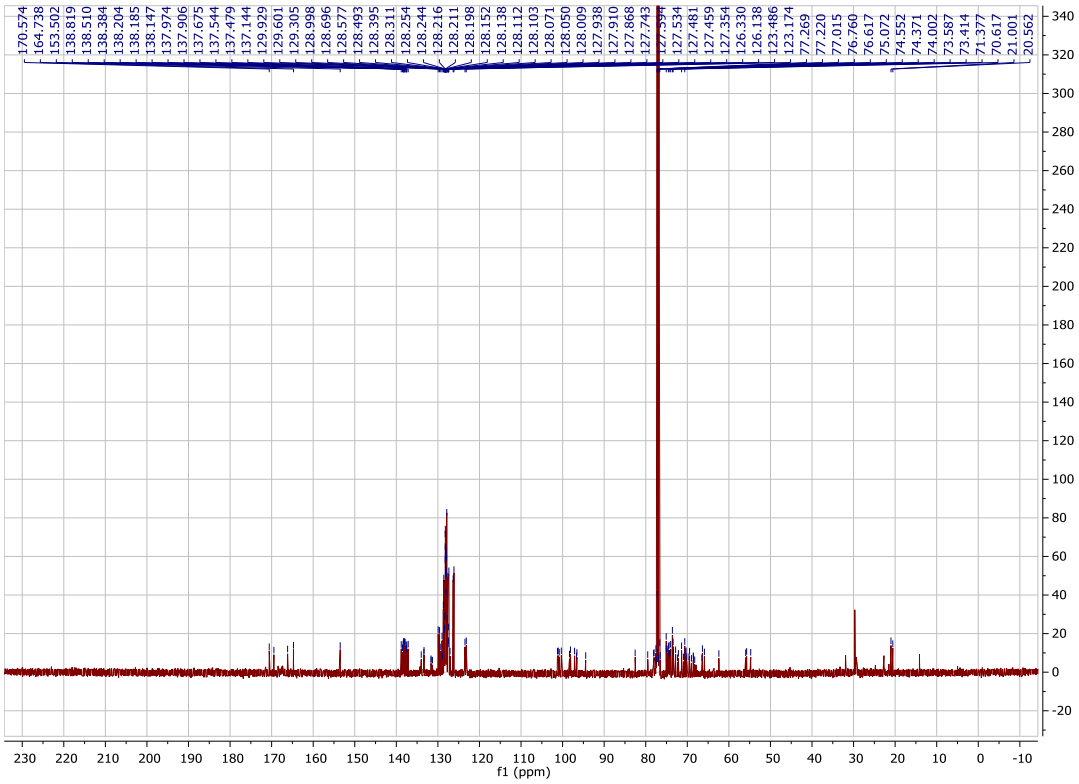


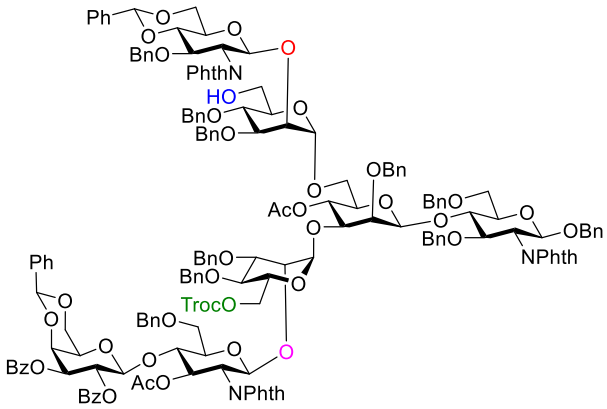
^{1}H-NMR ($CDCl_3$, 500 MHz) of **25**



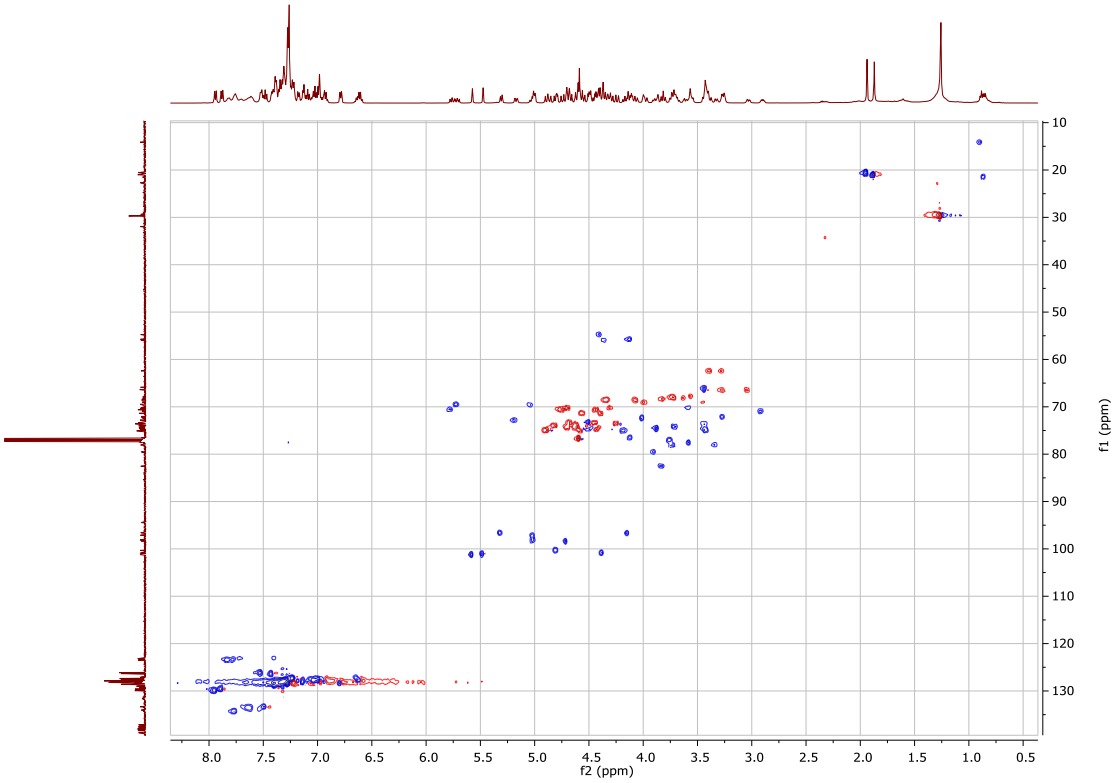


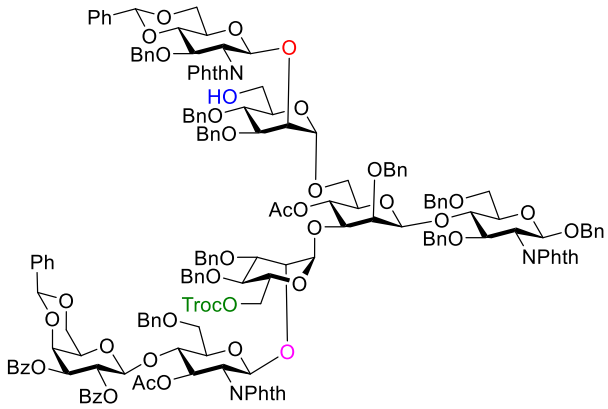
^{13}C-NMR ($CDCl_3$, 125 MHz) of **25**



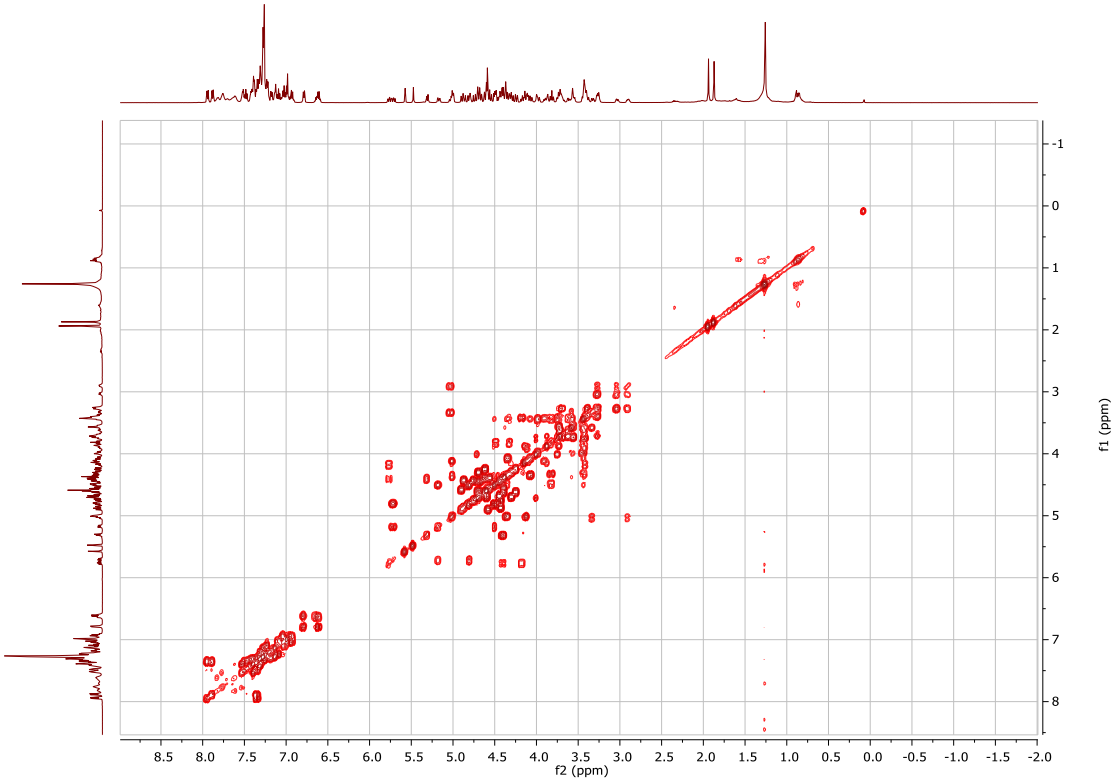


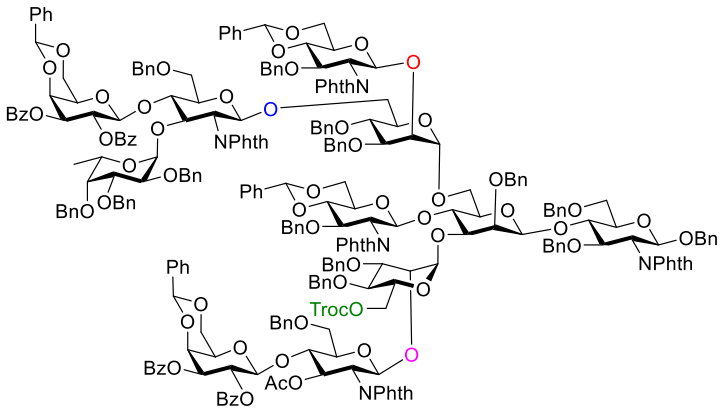
gHSQC ($CDCl_3$, 500 MHz) of **25**



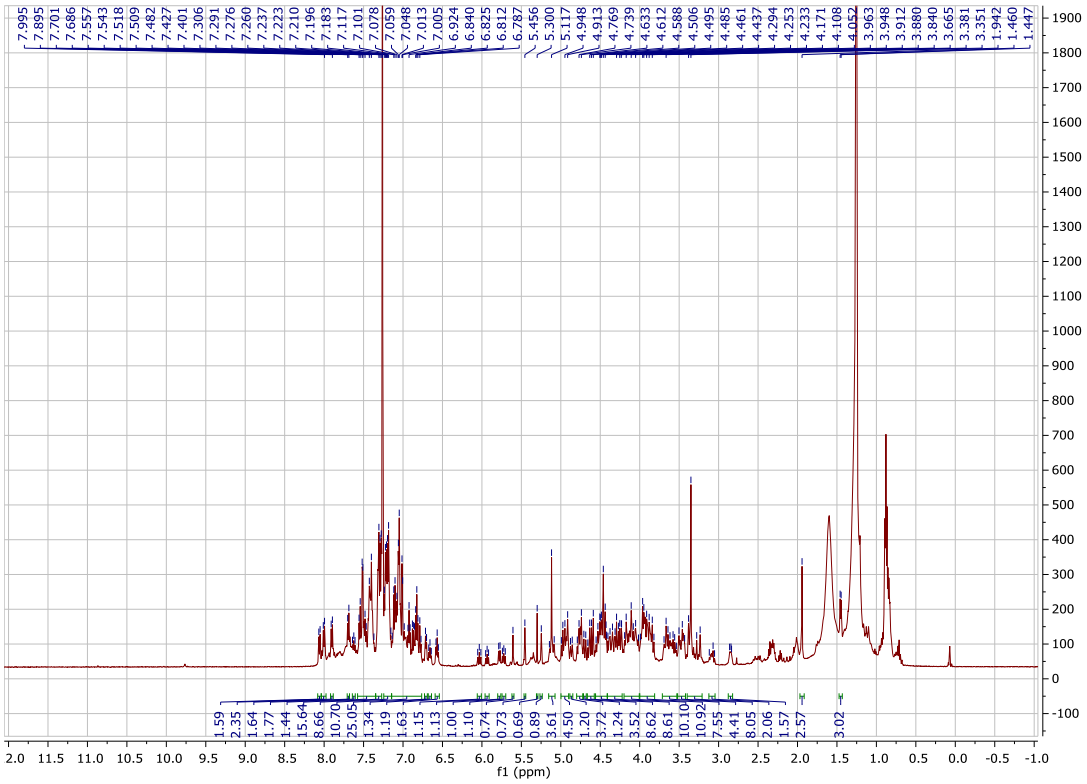


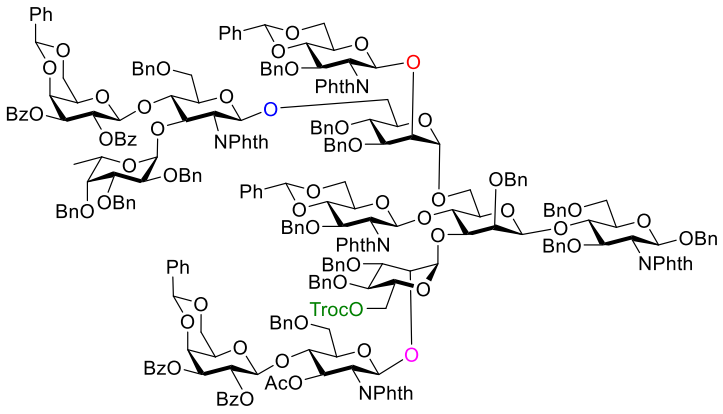
gCOSY ($CDCl_3$, 500 MHz) of **25**



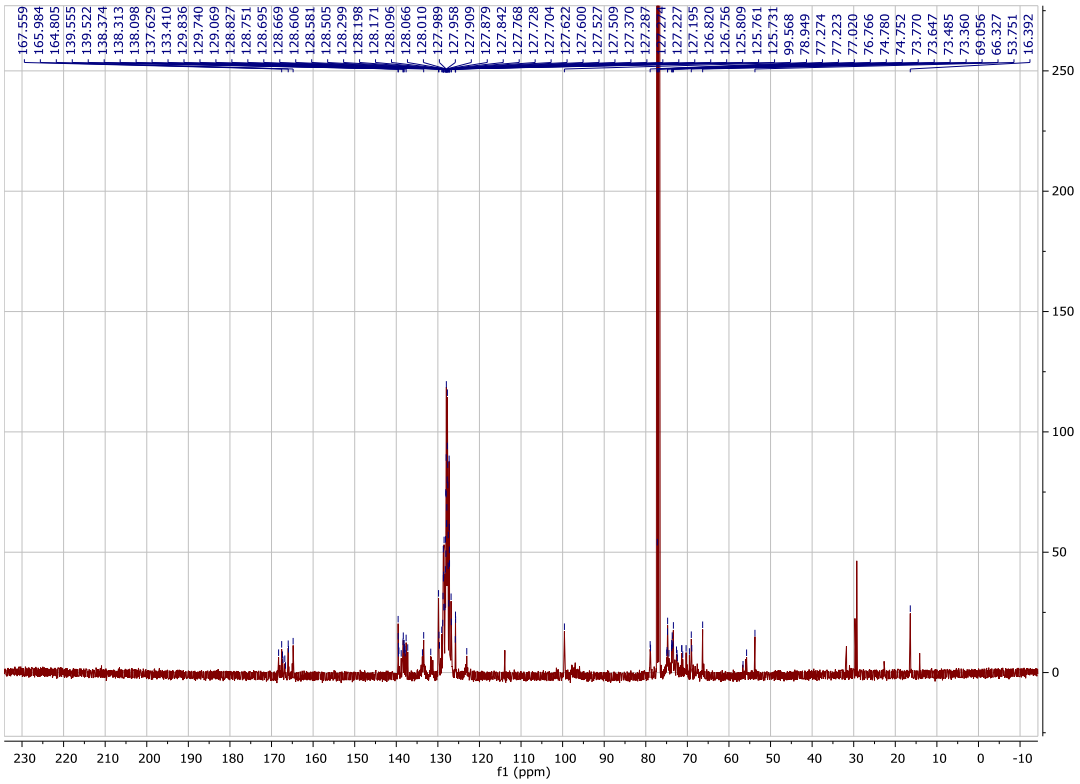


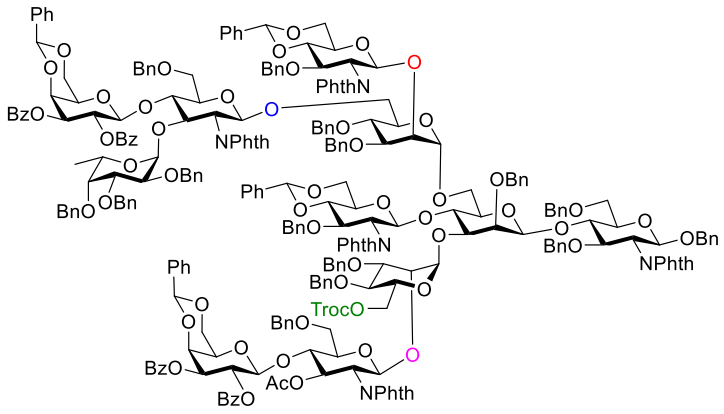
^{1}H-NMR ($CDCl_3$, 500 MHz) of **27**



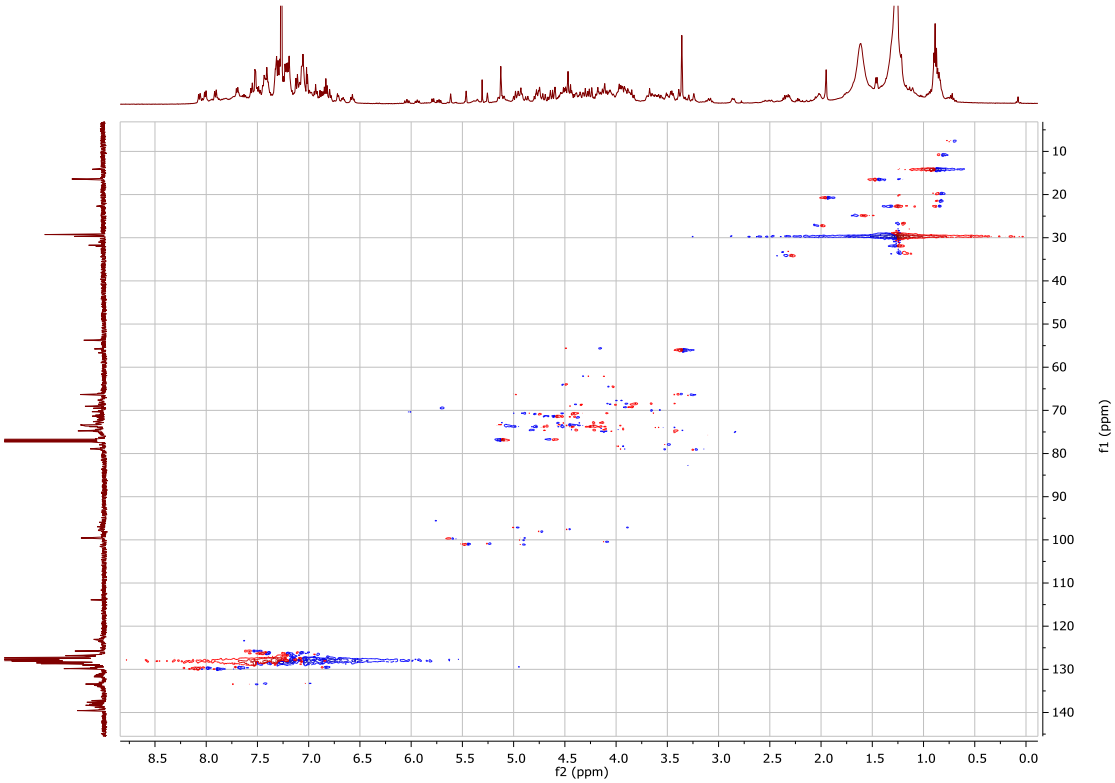


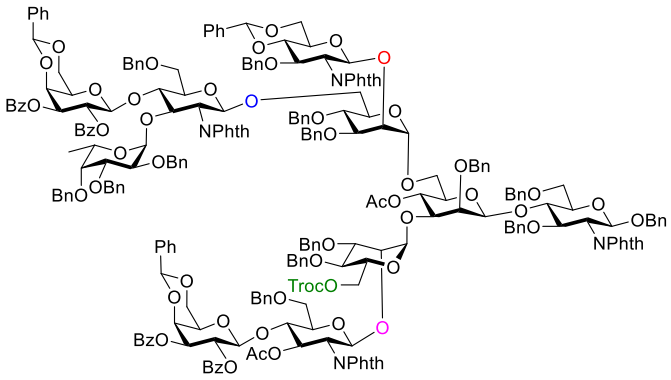
^{13}C-NMR ($CDCl_3$, 125 MHz) of **27**



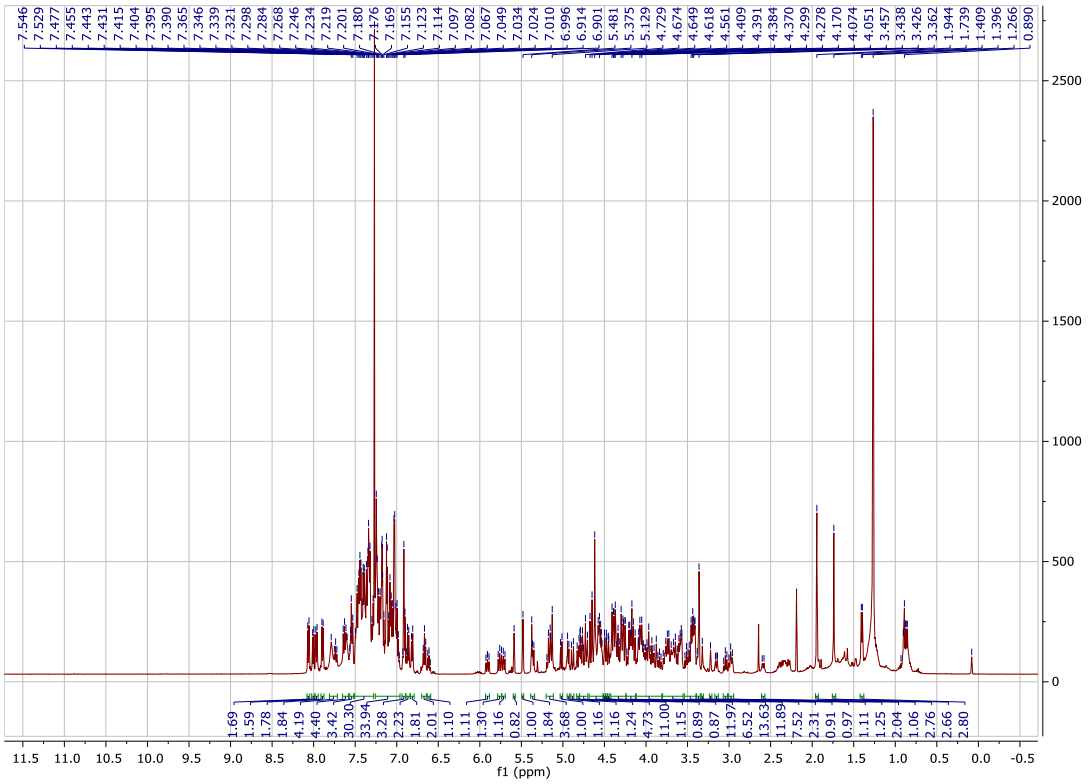


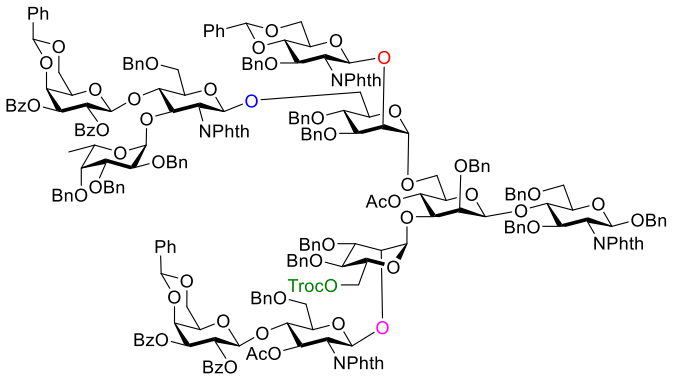
gHSQC ($CDCl_3$, 500 MHz) of **27**



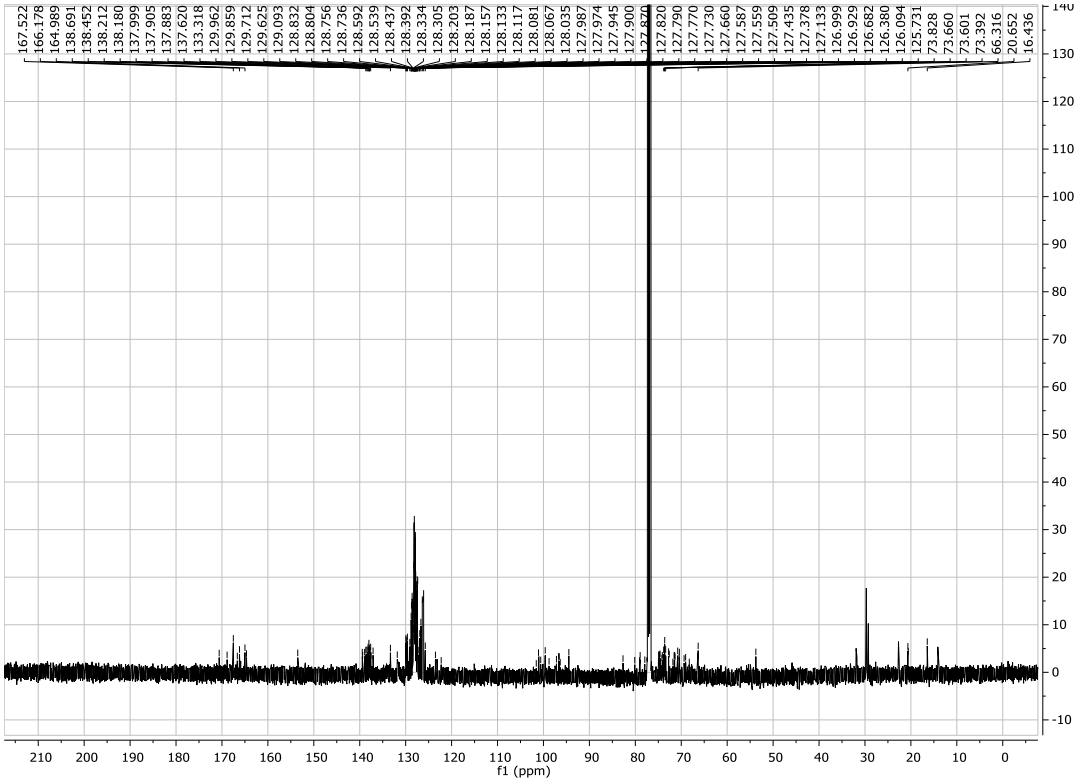


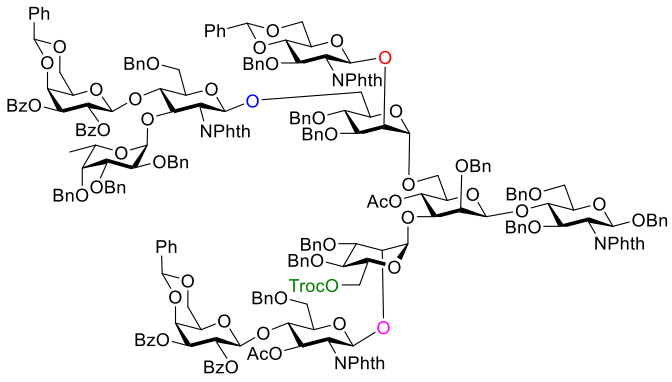
^{1}H-NMR ($CDCl_3$, 500 MHz) of **28**



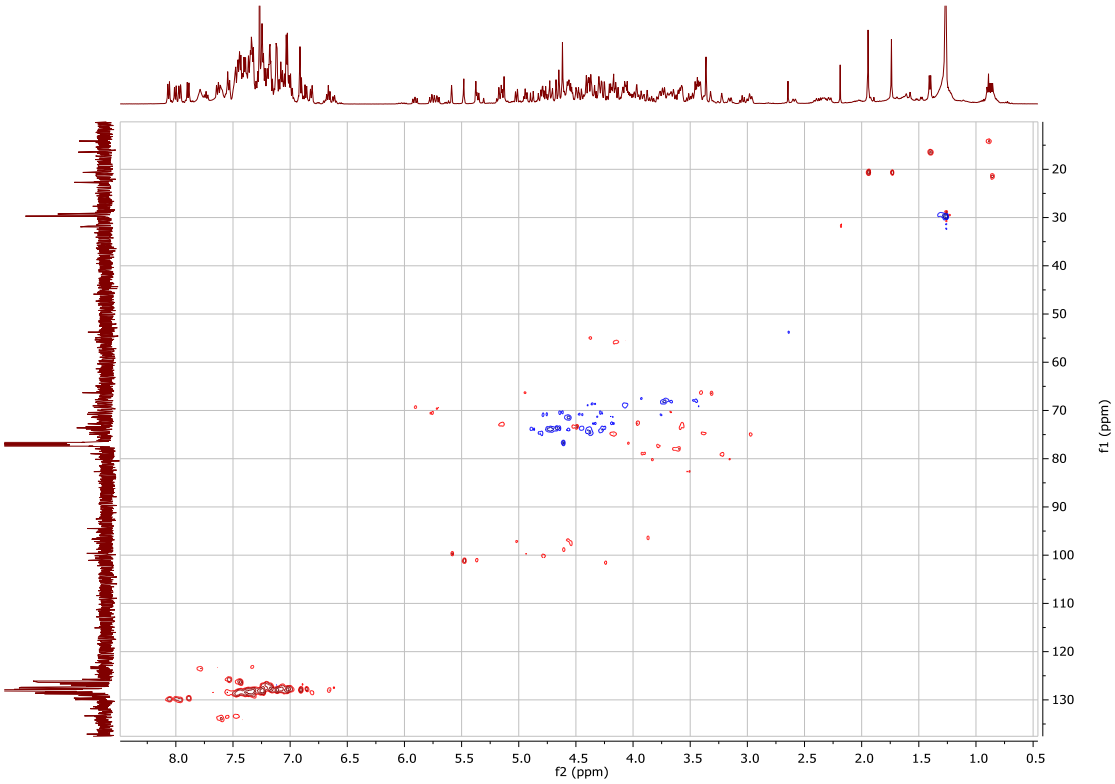


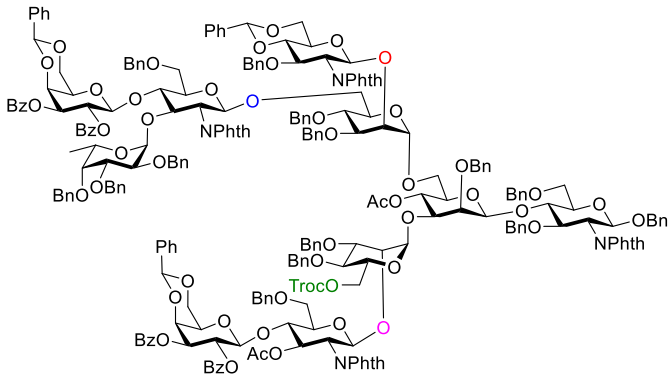
^{13}C-NMR ($CDCl_3$, 125 MHz) of **28**



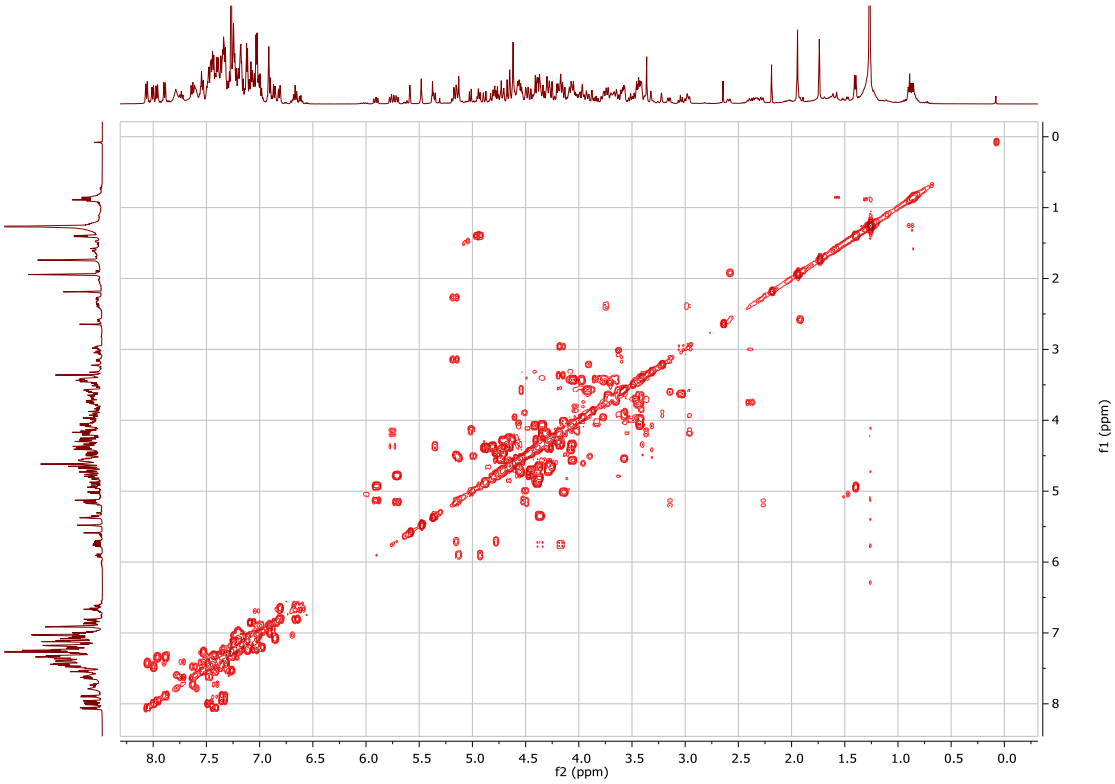


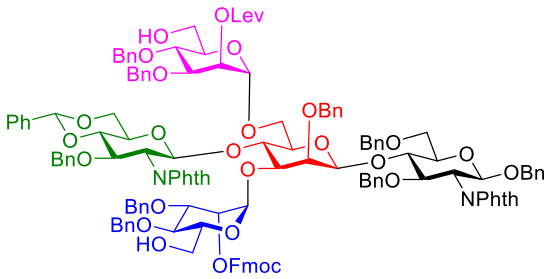
gHSQC ($CDCl_3$, 500 MHz) of **28**





gCOSY ($CDCl_3$, 500 MHz) of **28**





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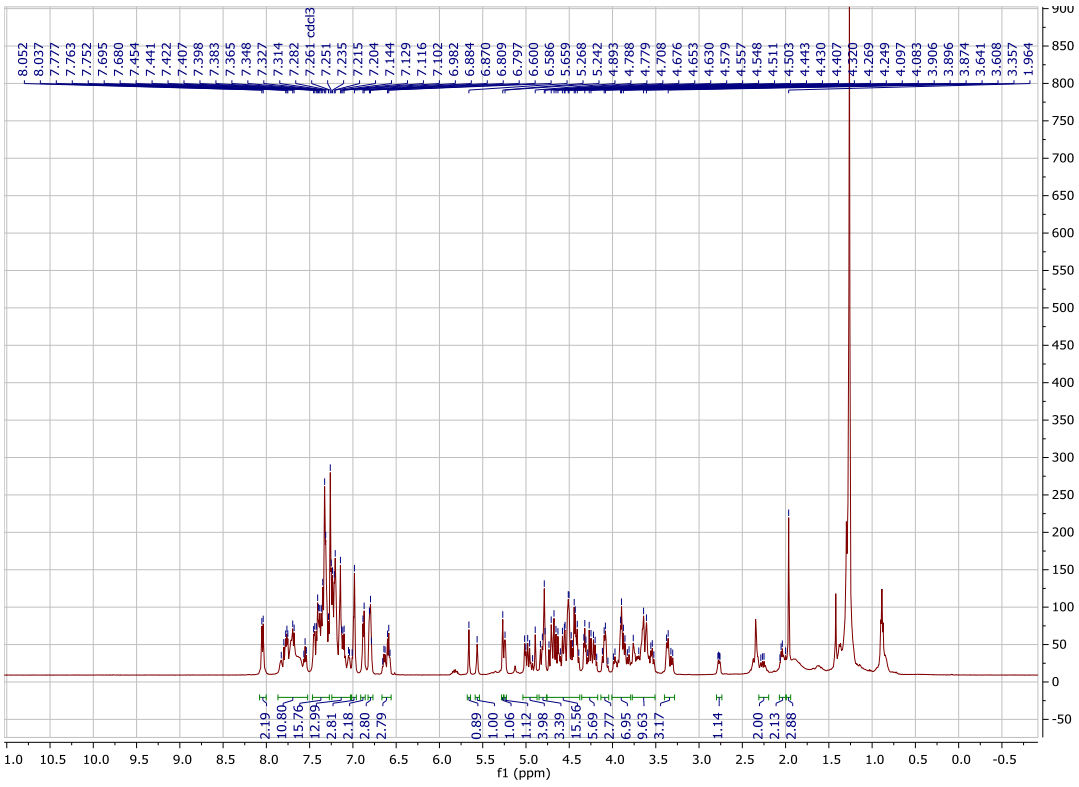
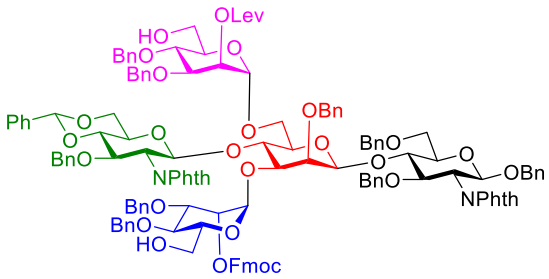
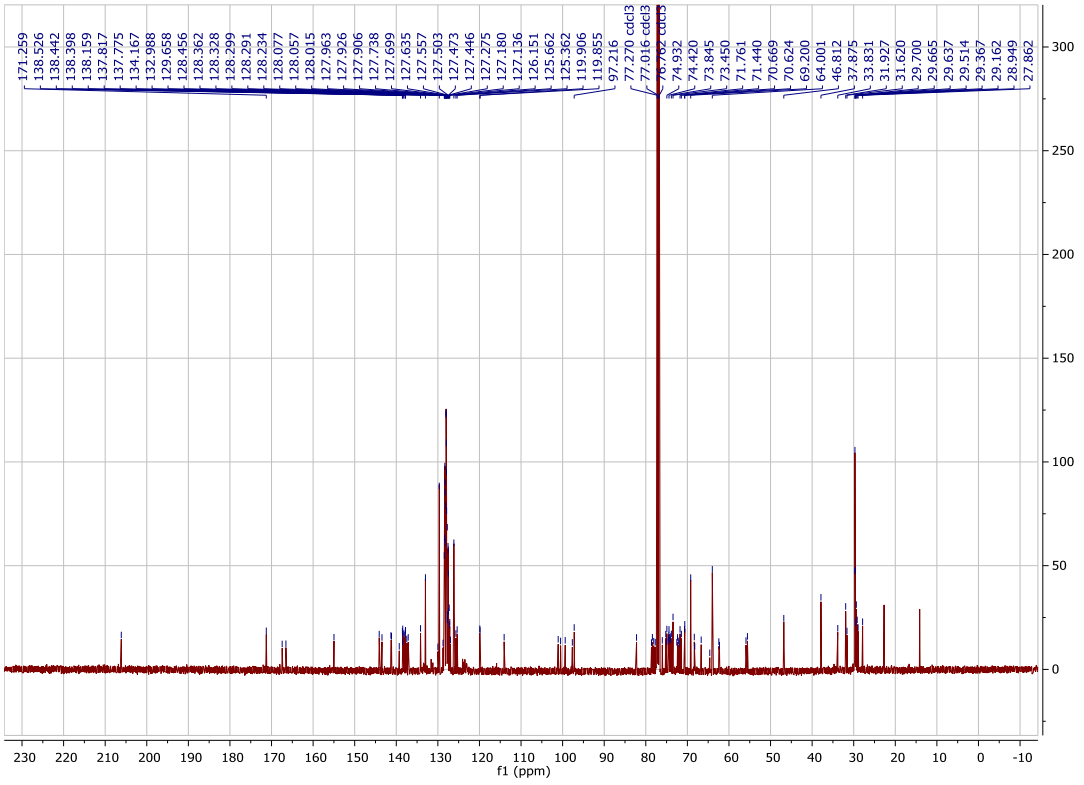
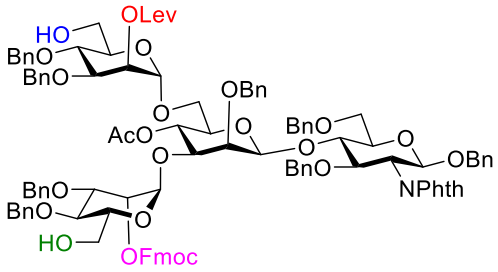


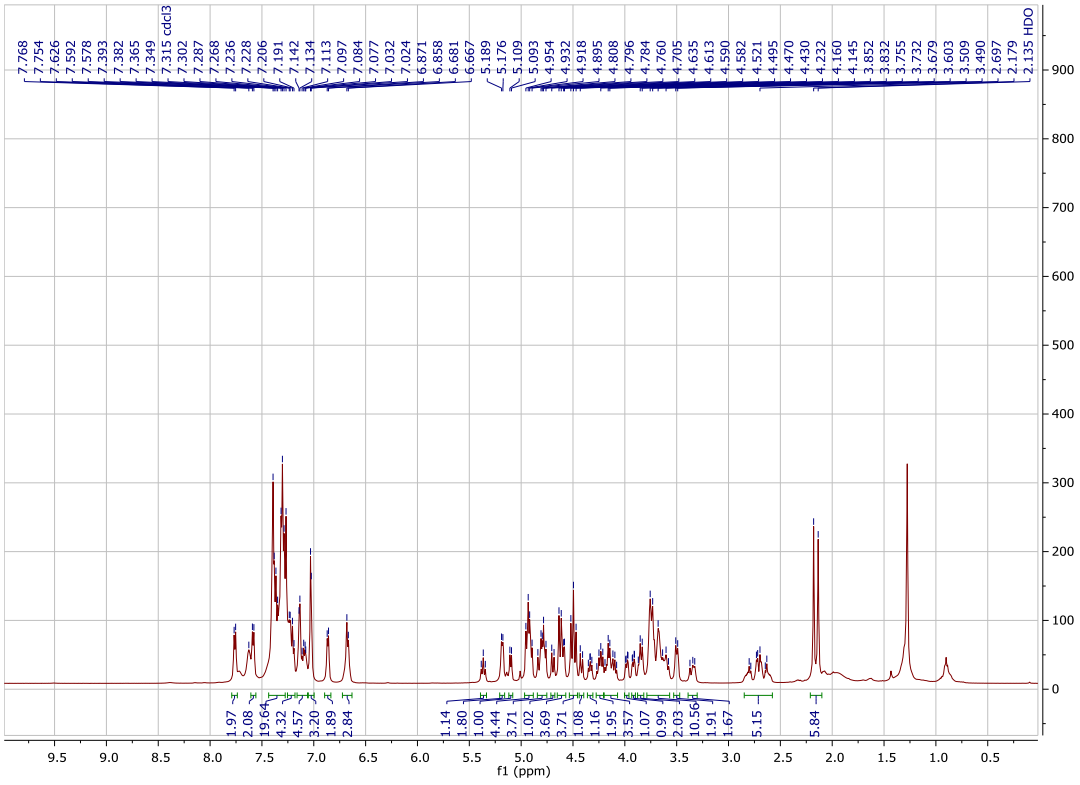


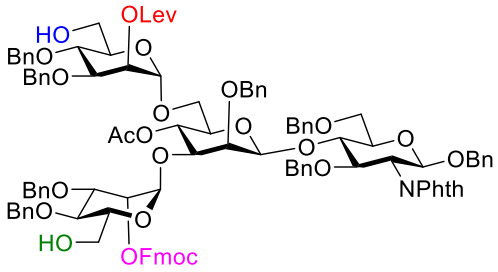
^{13}C-NMR ($CDCl_3$, 125 MHz) of **29**



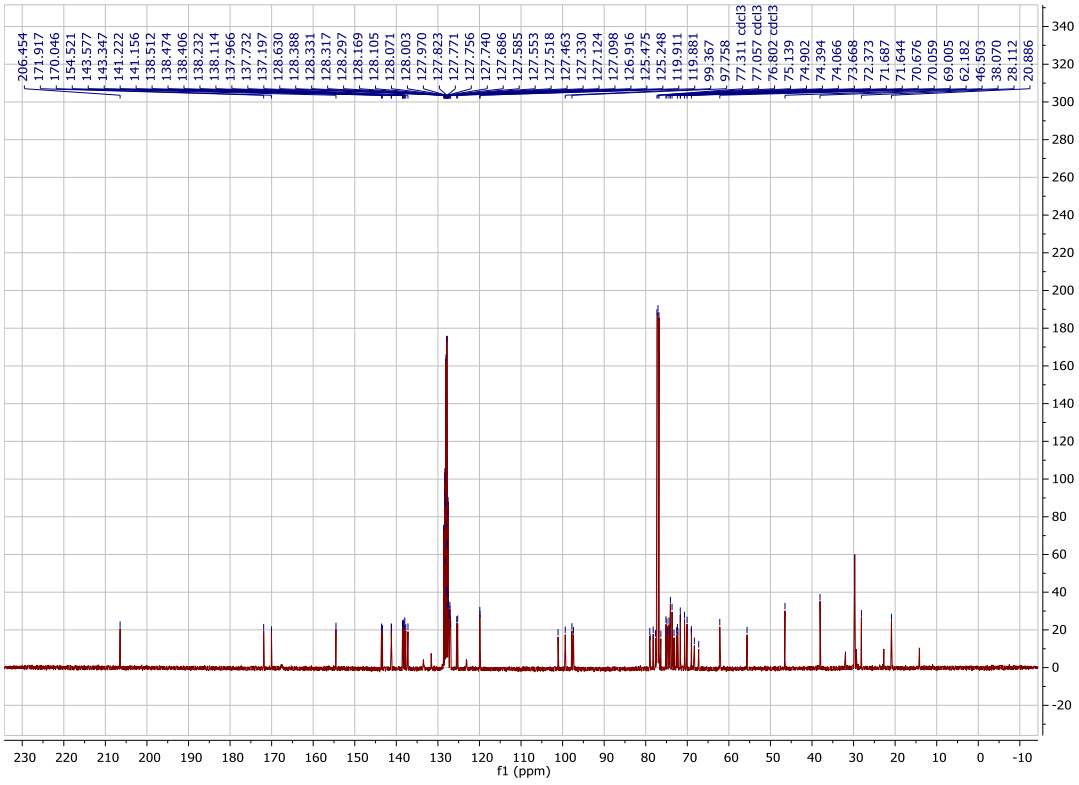


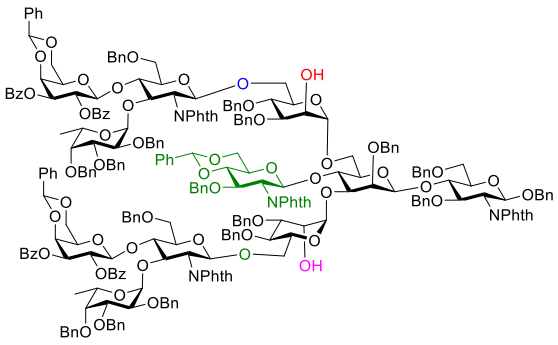
^{1}H-NMR ($CDCl_3$, 500 MHz) of **30**



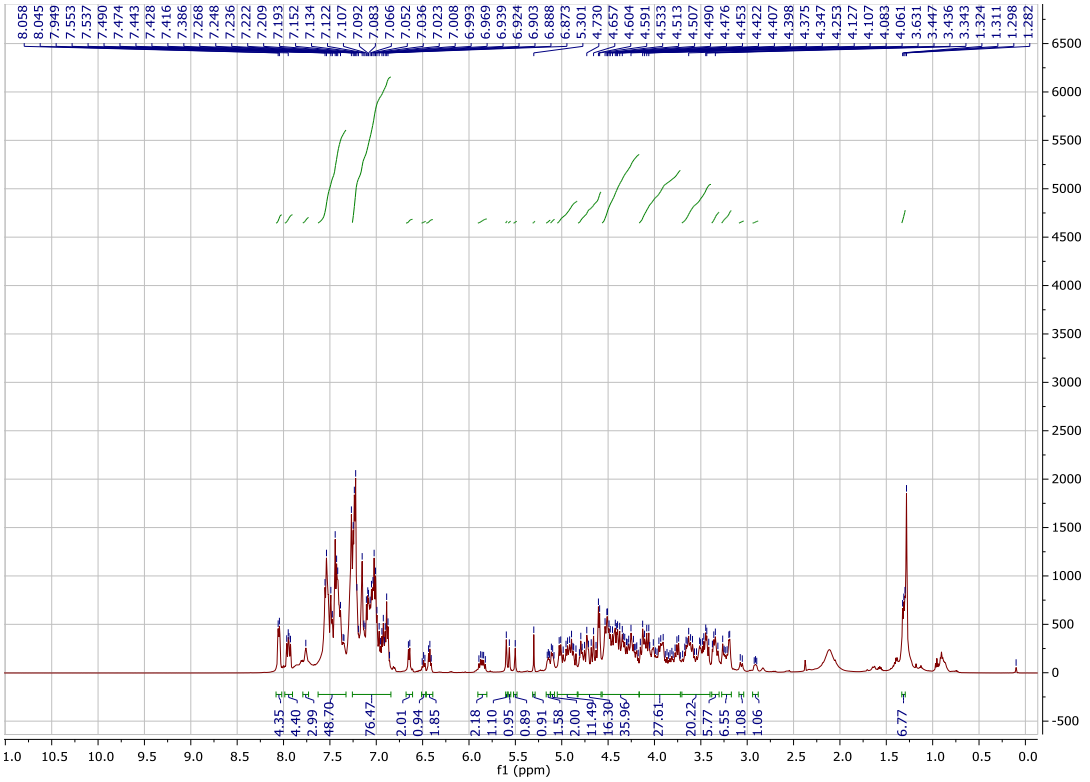


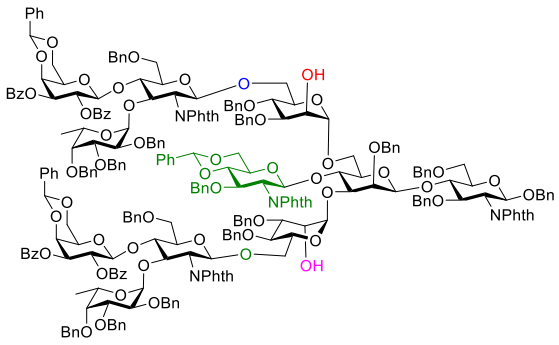
^{13}C-NMR ($CDCl_3$, 125 MHz) of **30**



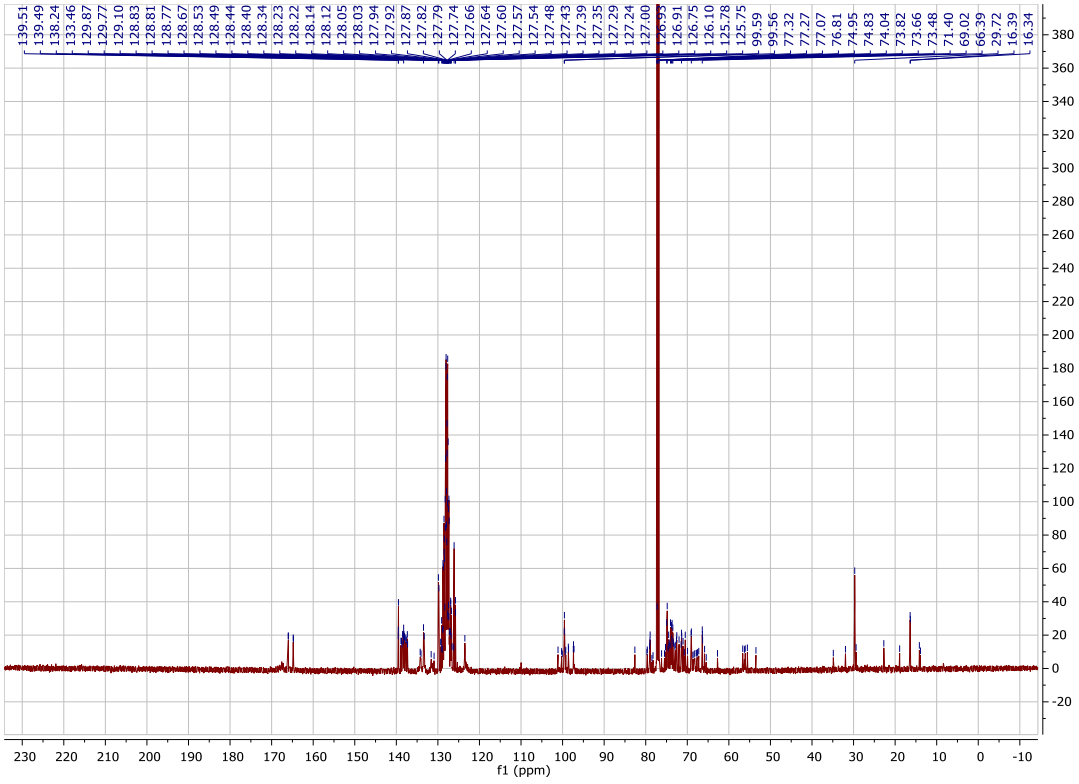


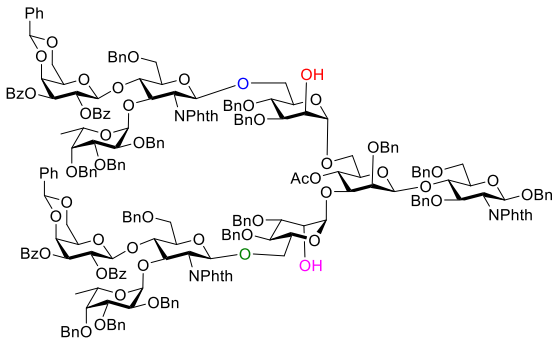
^{1}H-NMR ($CDCl_3$, 500 MHz) of **31**



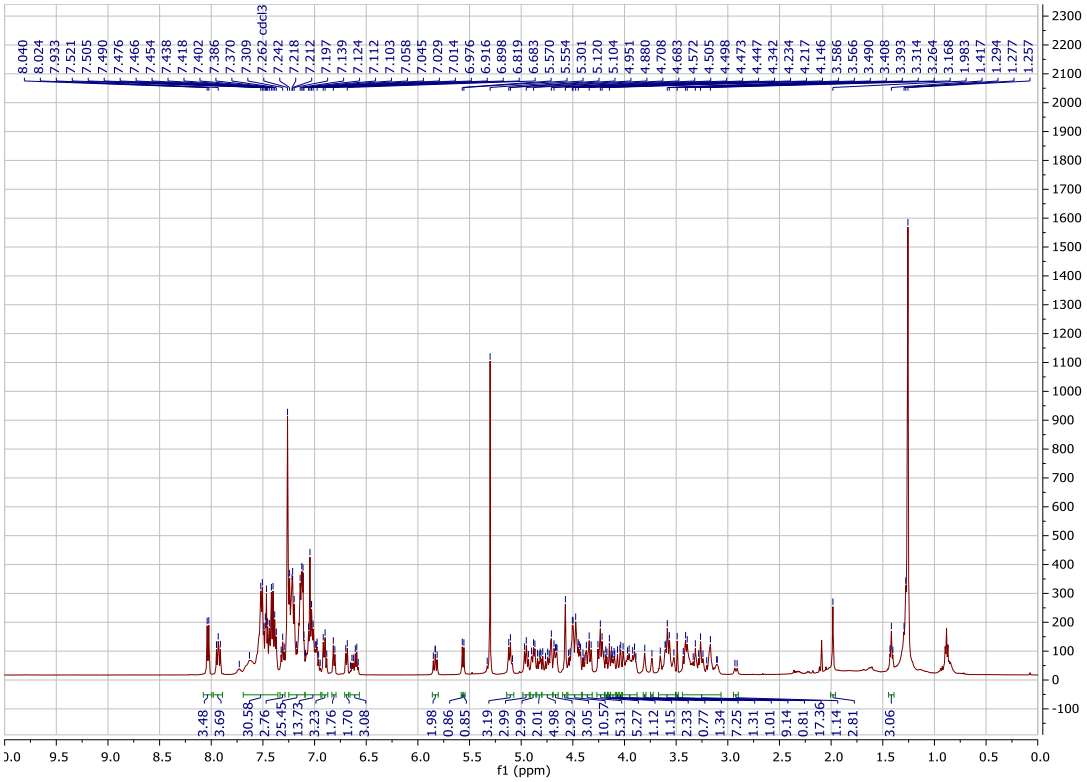


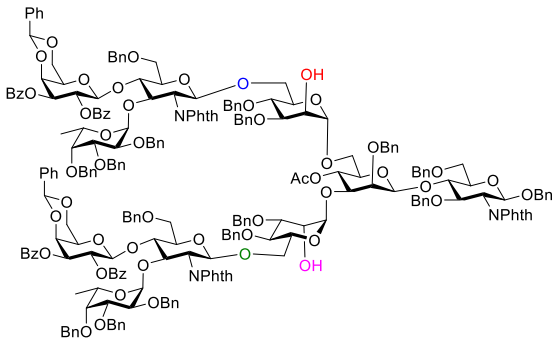
^{13}C-NMR ($CDCl_3$, 125 MHz) of **31**



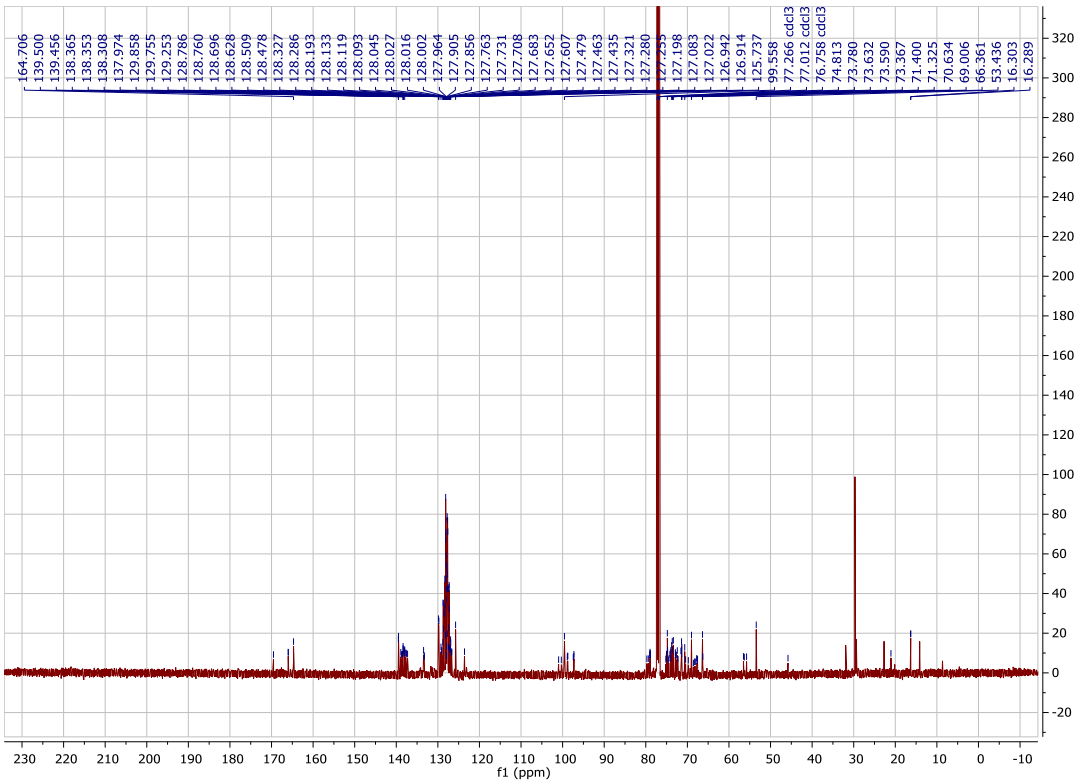


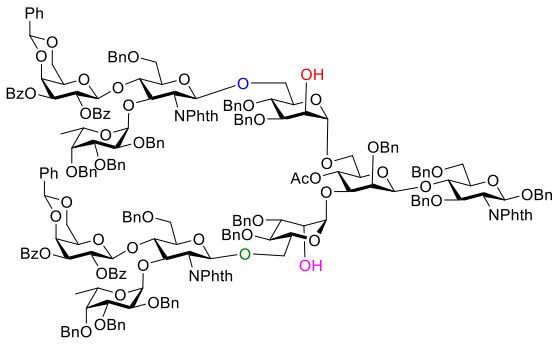
^{1}H-NMR ($CDCl_3$, 500 MHz) of **32**



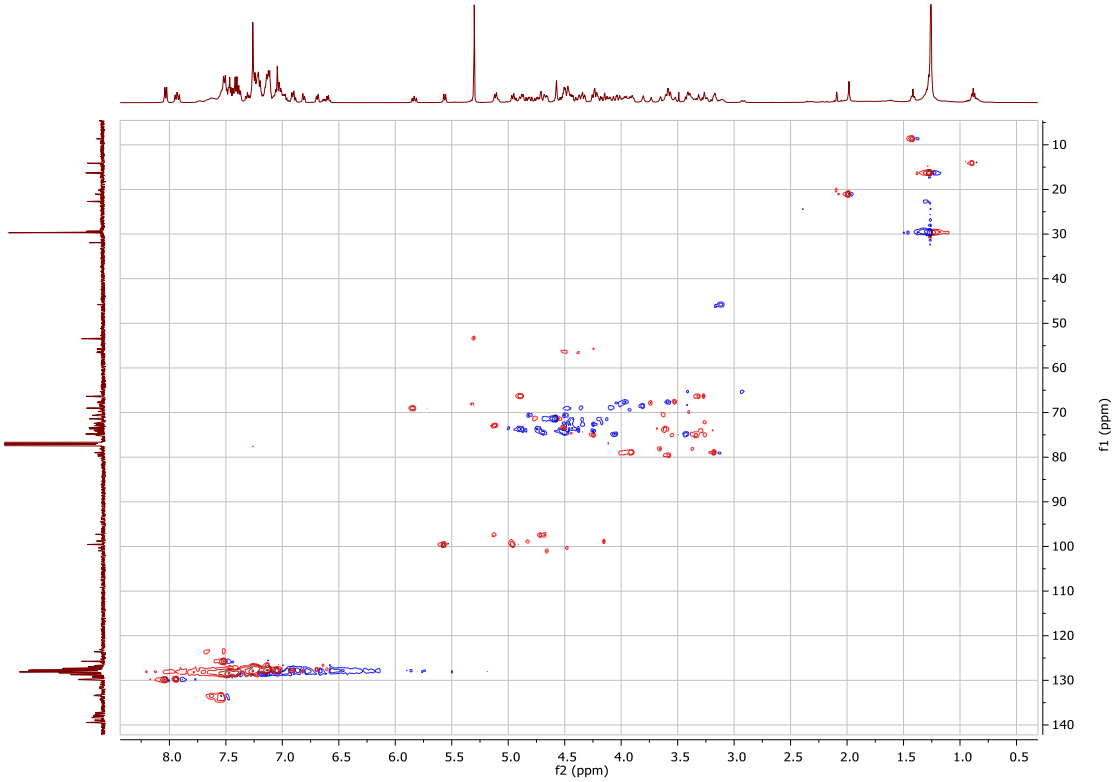


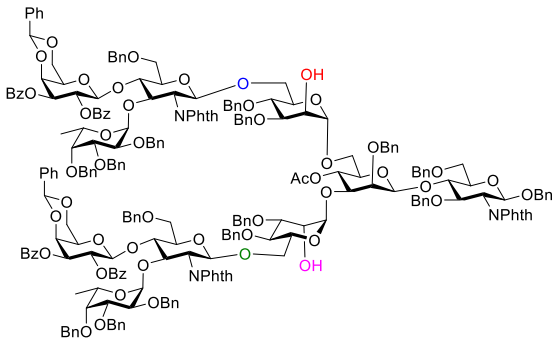
^{13}C-NMR ($CDCl_3$, 125 MHz) of **32**



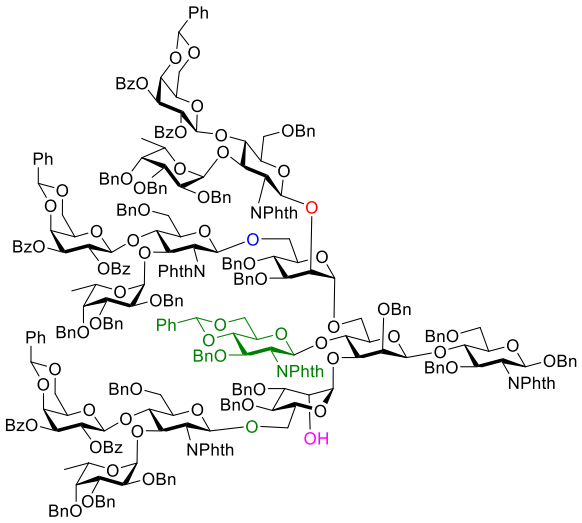


gHSQC ($CDCl_3$, 500 MHz) of **32**

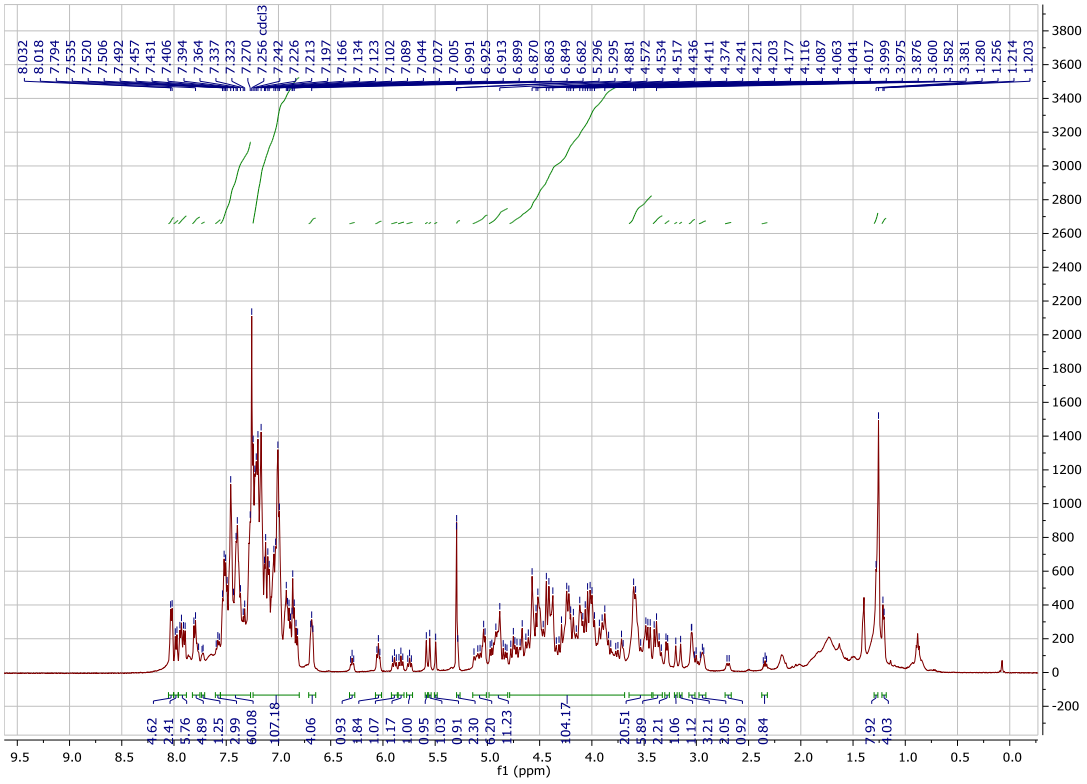


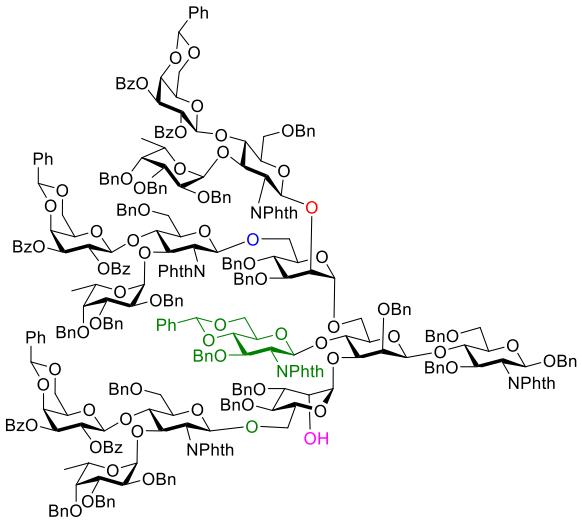


gCOSY ($CDCl_3$, 500 MHz) of **32**

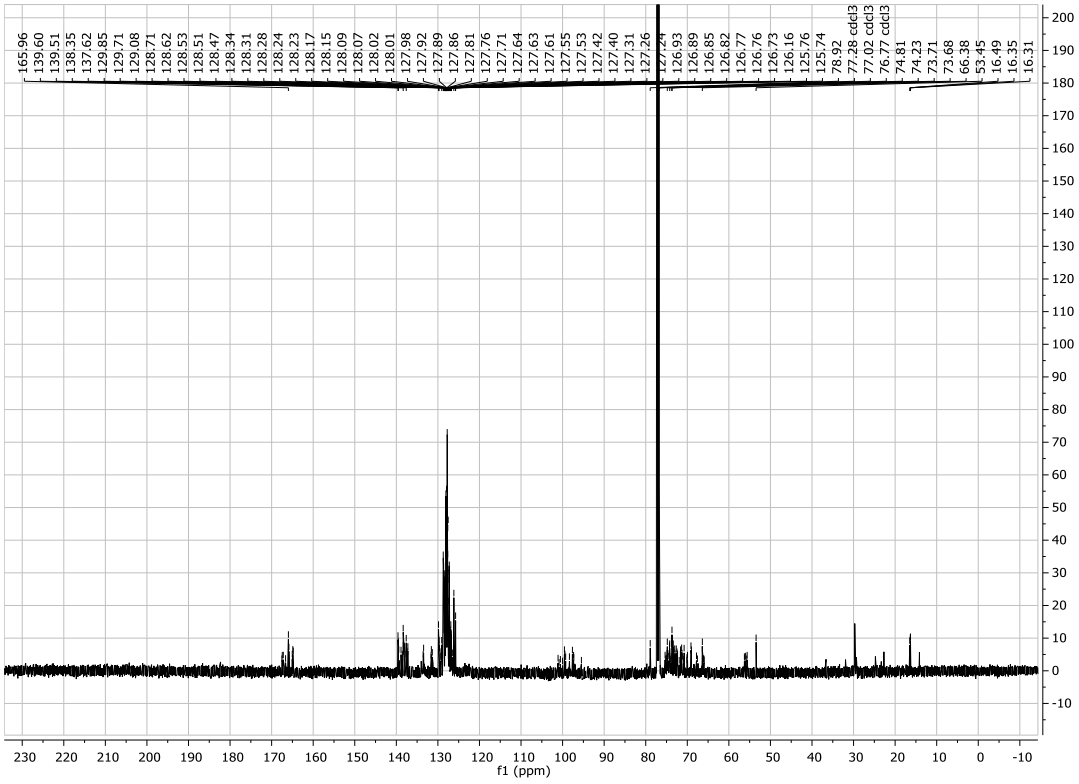


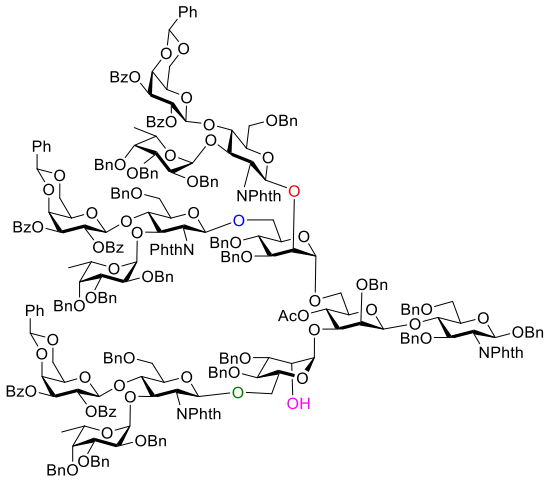
^{1}H-NMR ($CDCl_3$, 500 MHz) of **33**



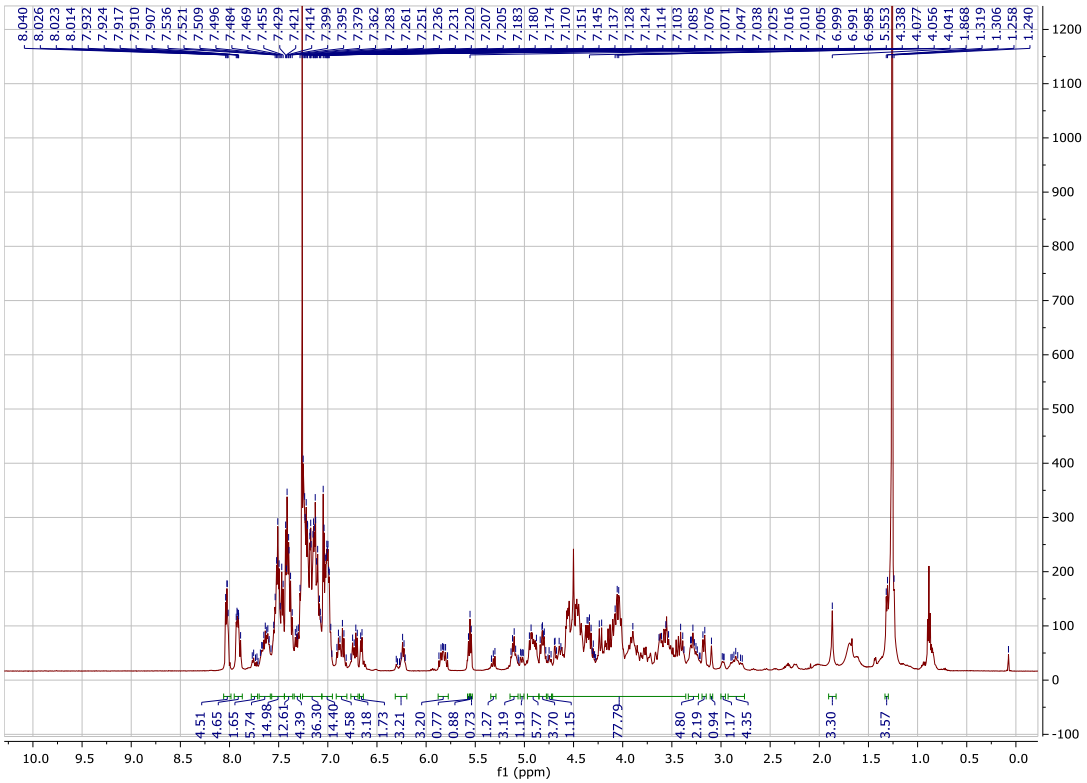


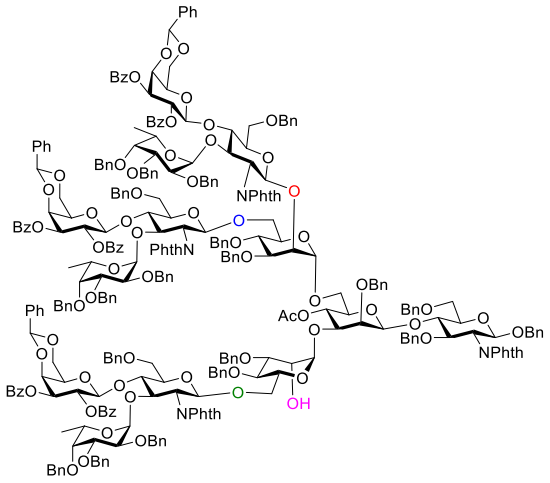
^{13}C-NMR ($CDCl_3$, 125 MHz) of **33**



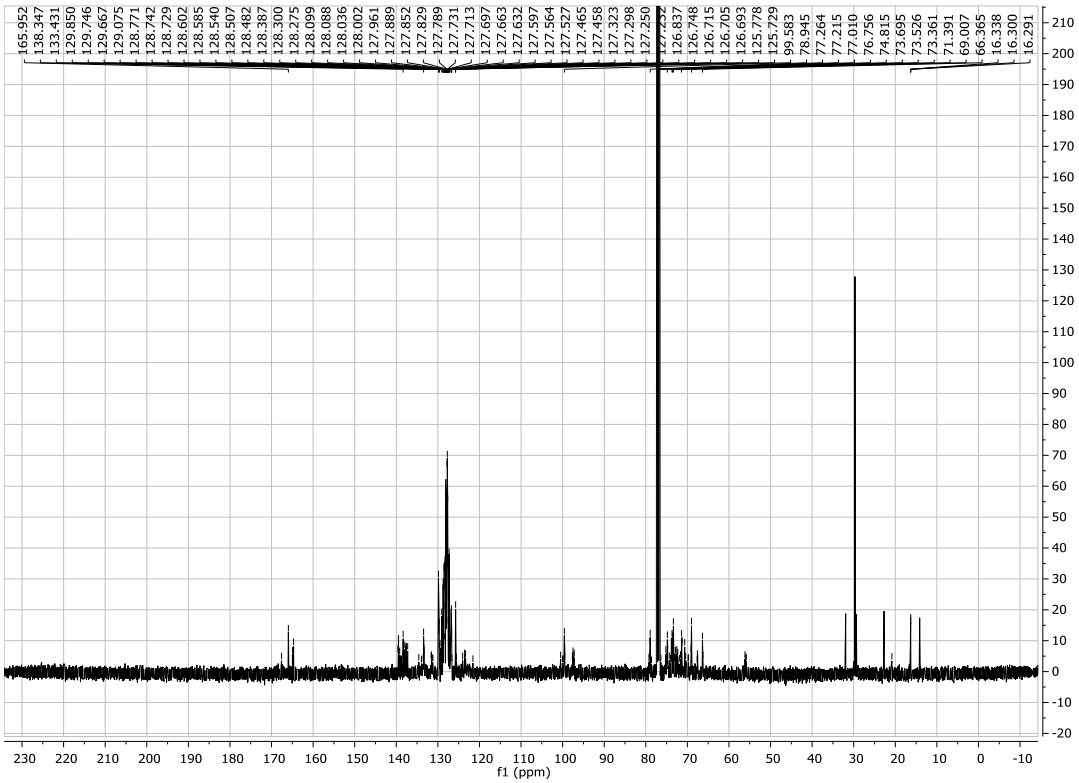


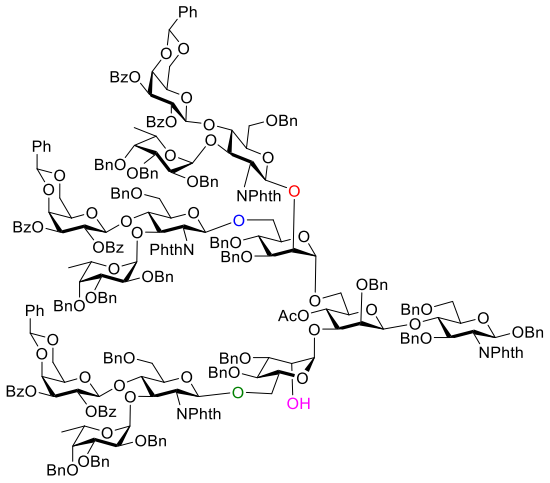
^{1}H-NMR ($CDCl_3$, 500 MHz) of **34**



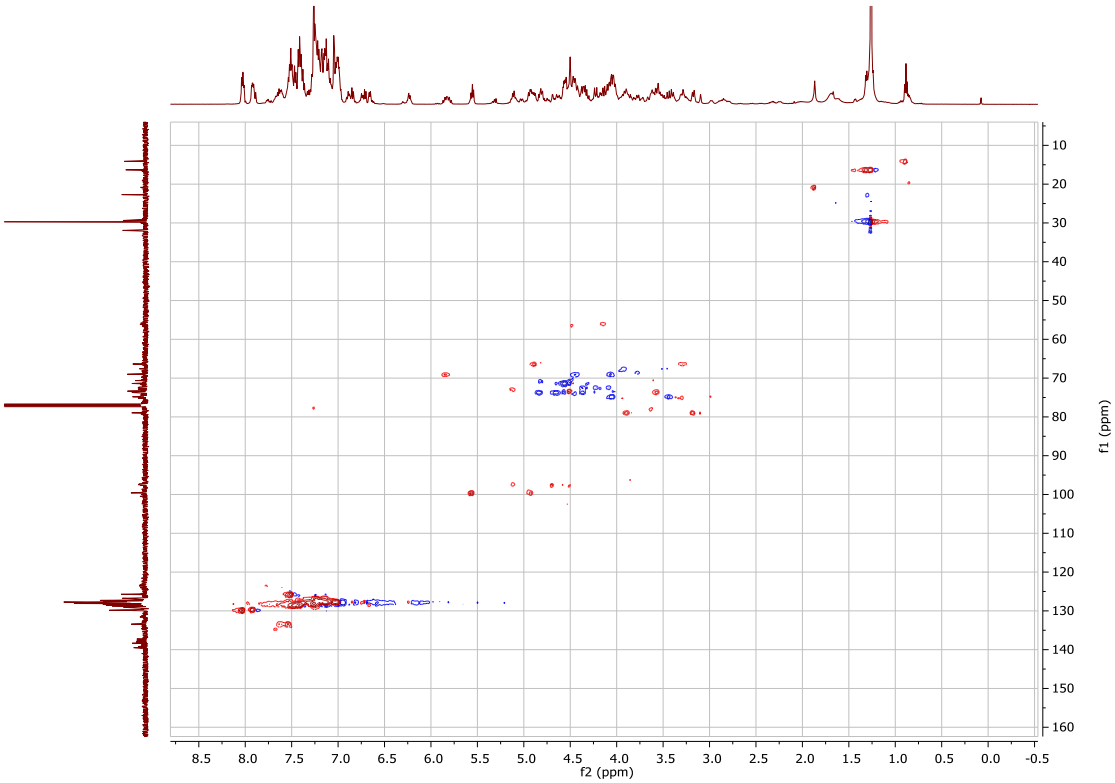


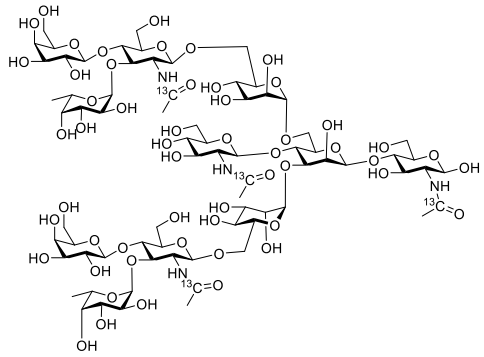
^{13}C-NMR ($CDCl_3$, 125 MHz) of **34**



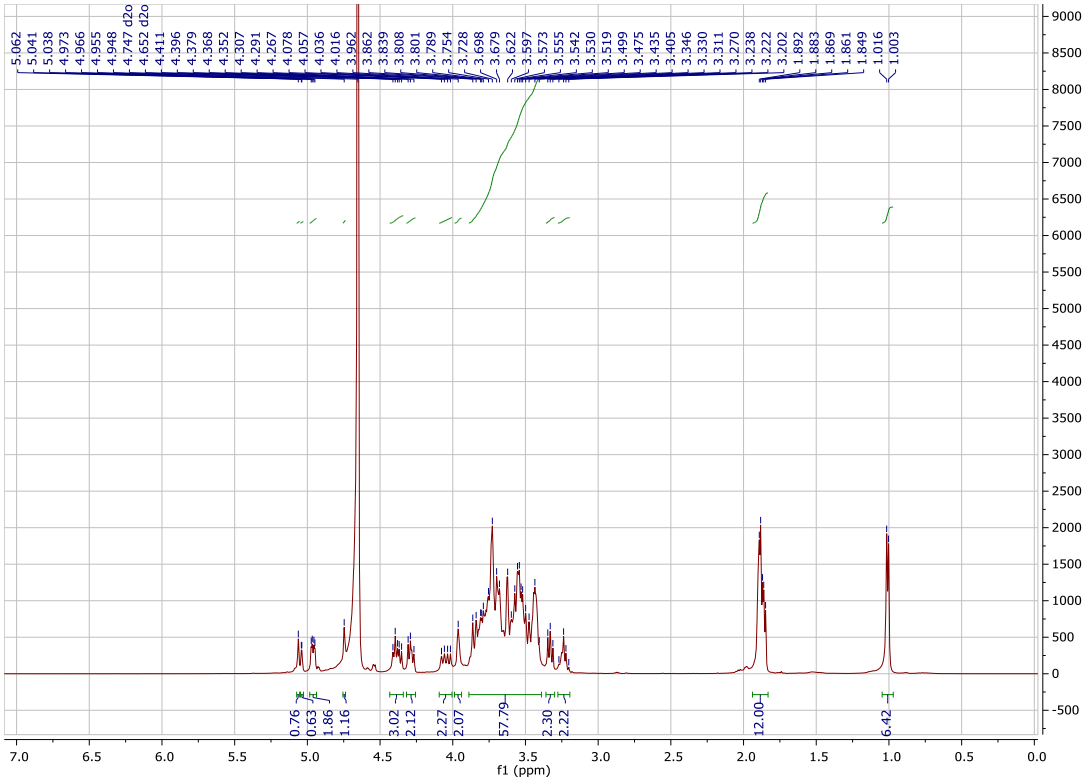


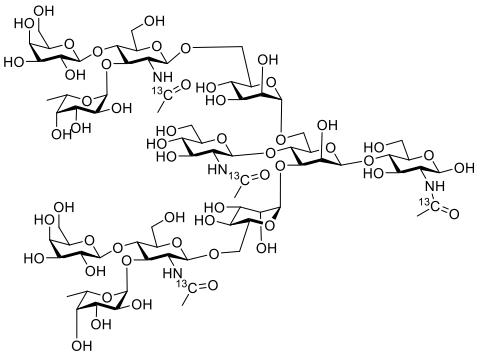
gHSQC ($CDCl_3$, 500 MHz) of **34**



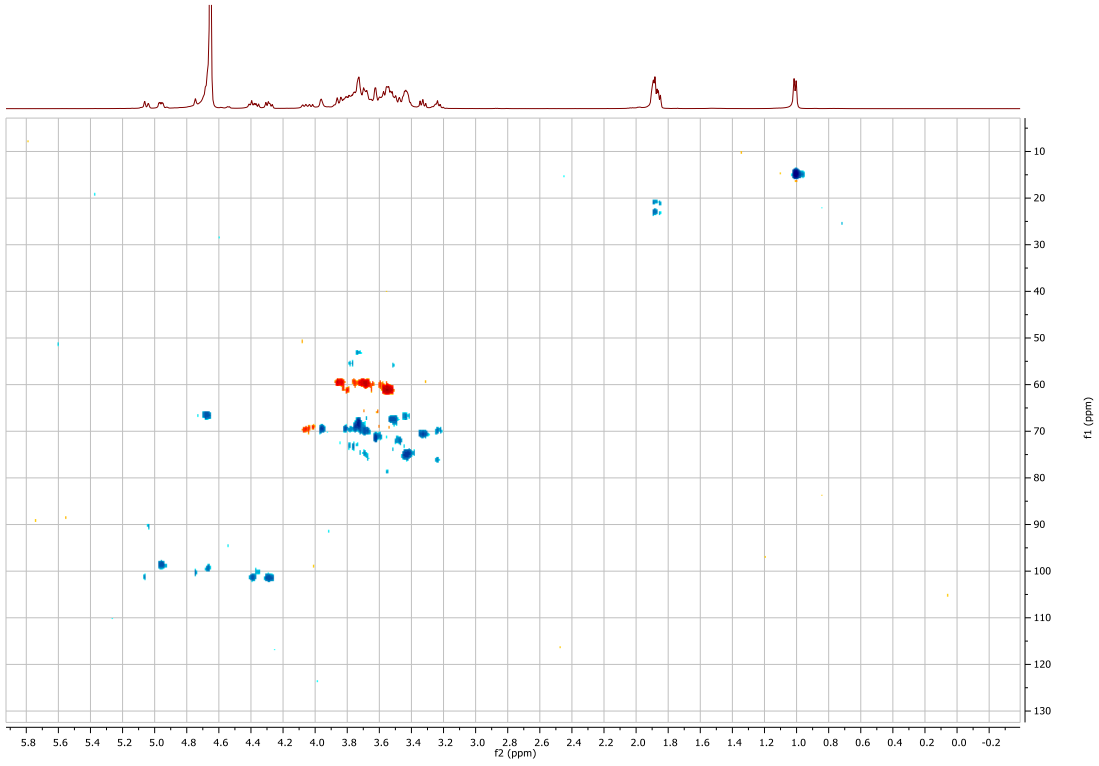


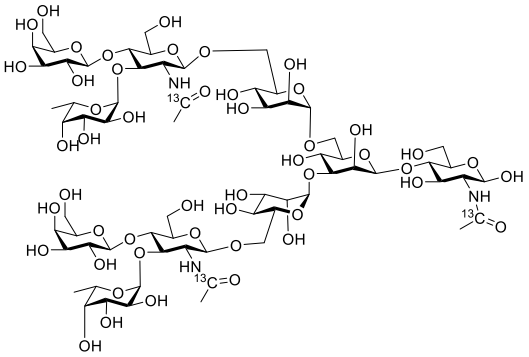
^{1}H-NMR (D_2O, 500 MHz) of **35**



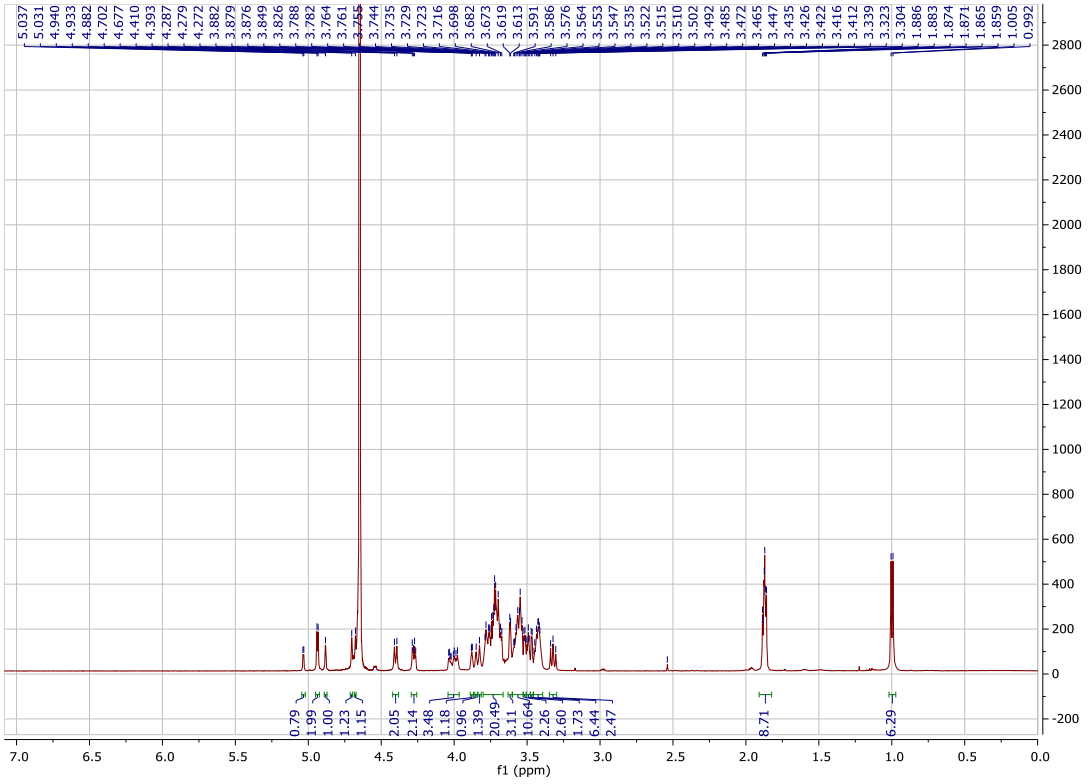


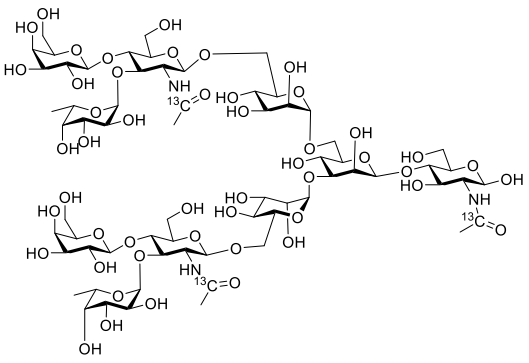
gHSQC (D_2O, 500 MHz) of **35**



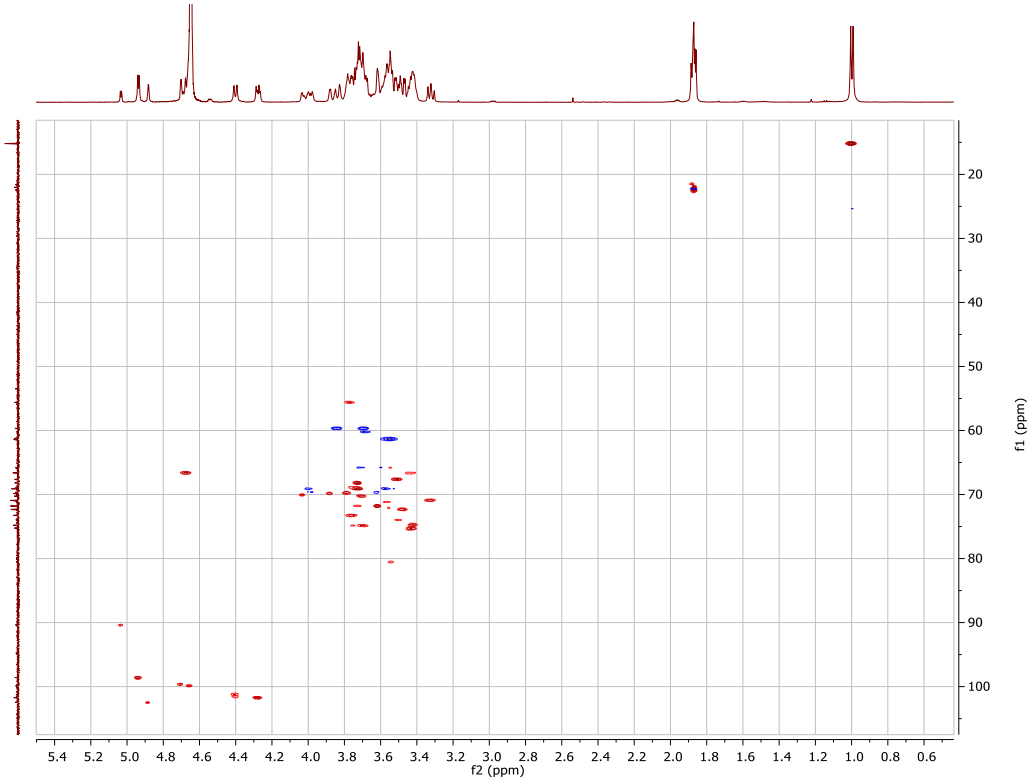


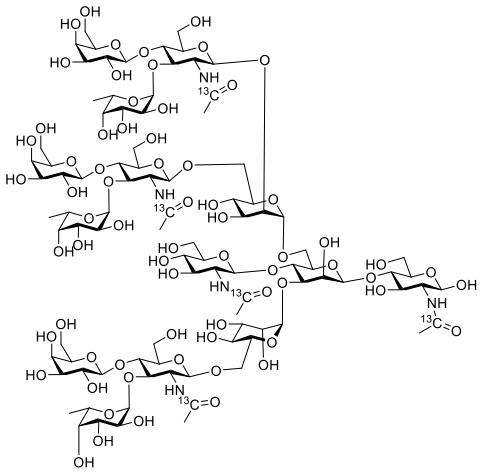
^{1}H-NMR (D_2O, 500 MHz) of **36**



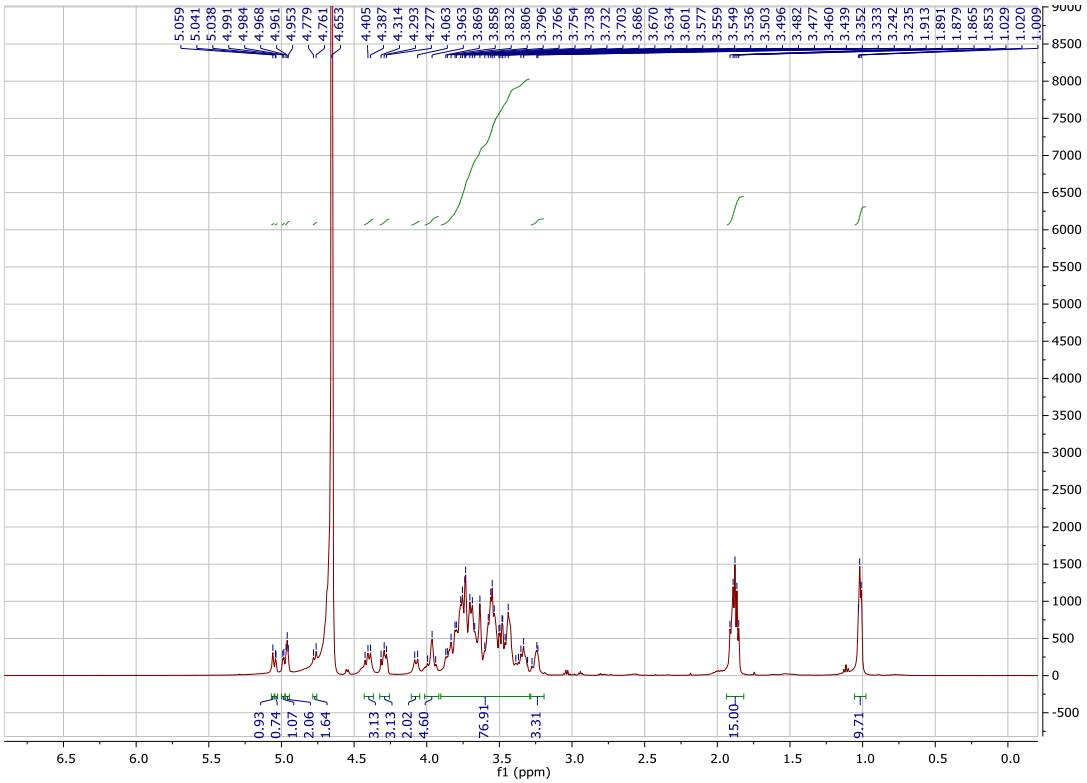


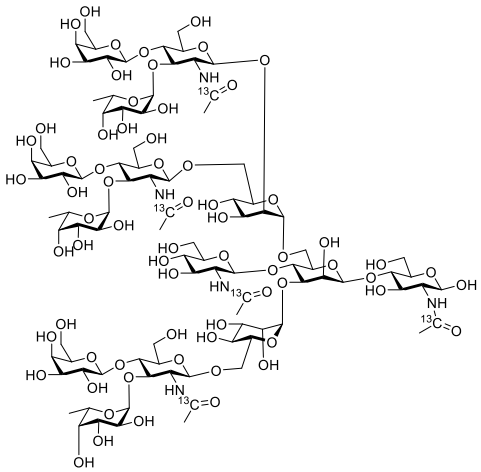
gHSQC (D_2O, 500 MHz) of **36**



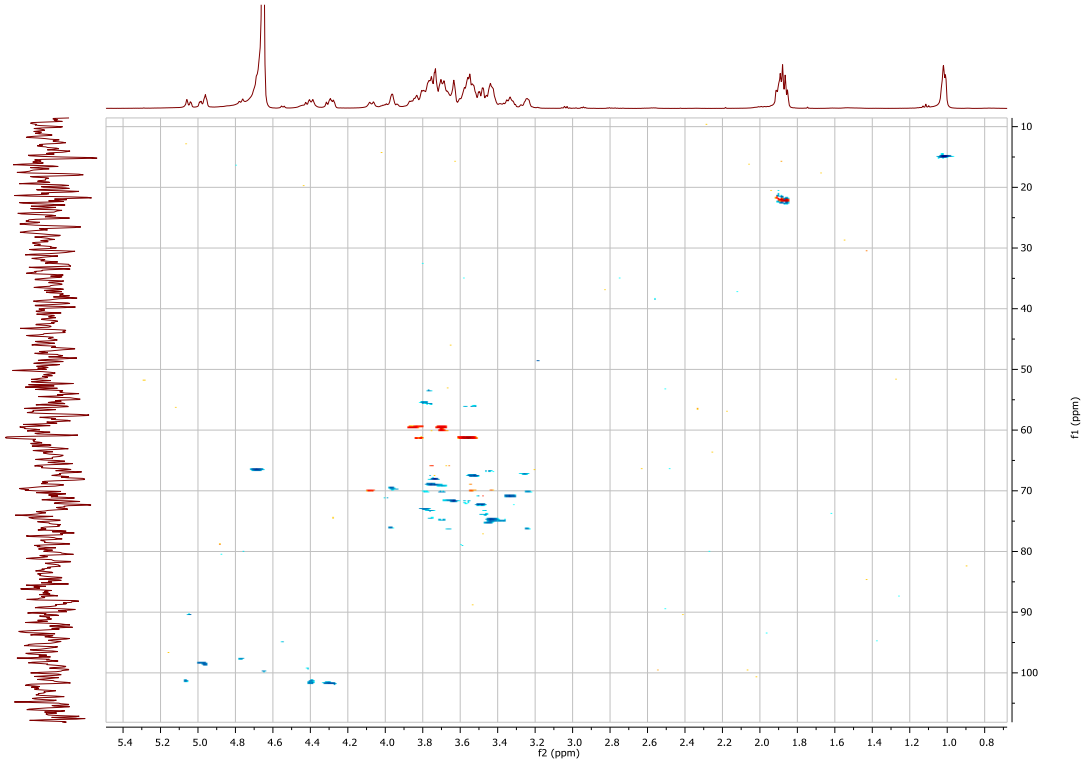


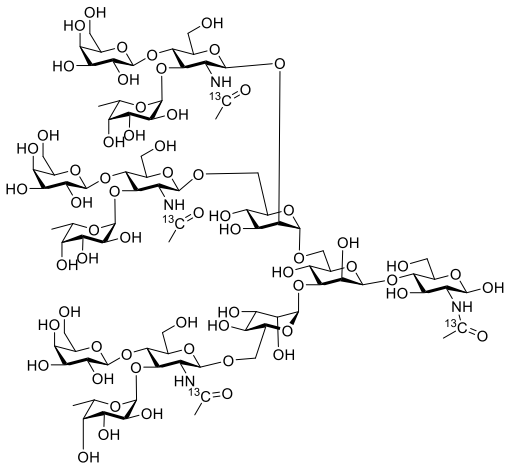
^{1}H-NMR (D_2O, 500 MHz) of **37**



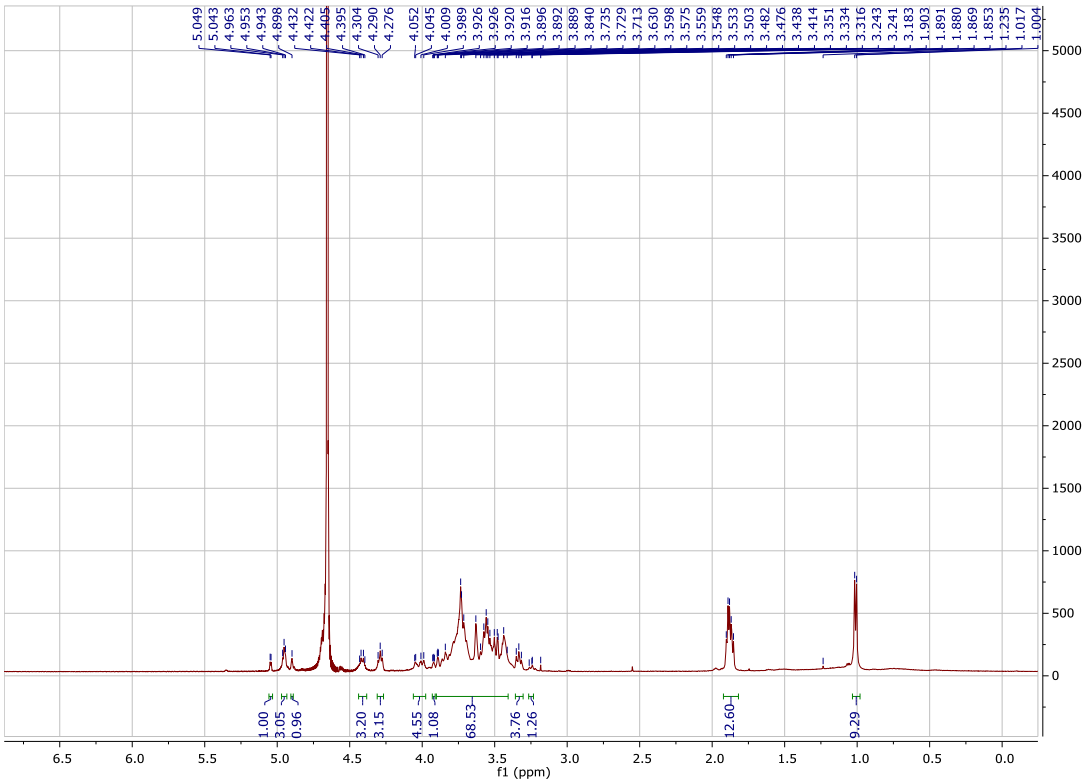


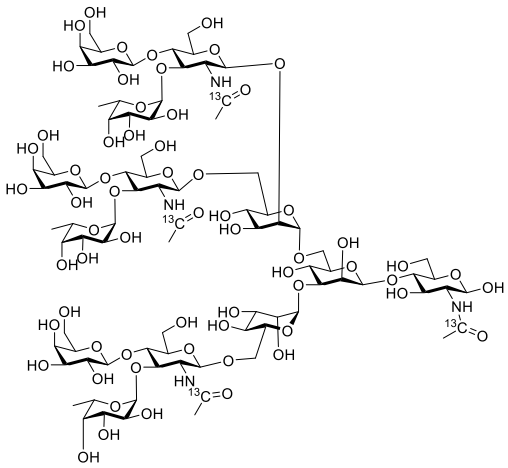
gHSQC (D_2O, 500 MHz) of **37**



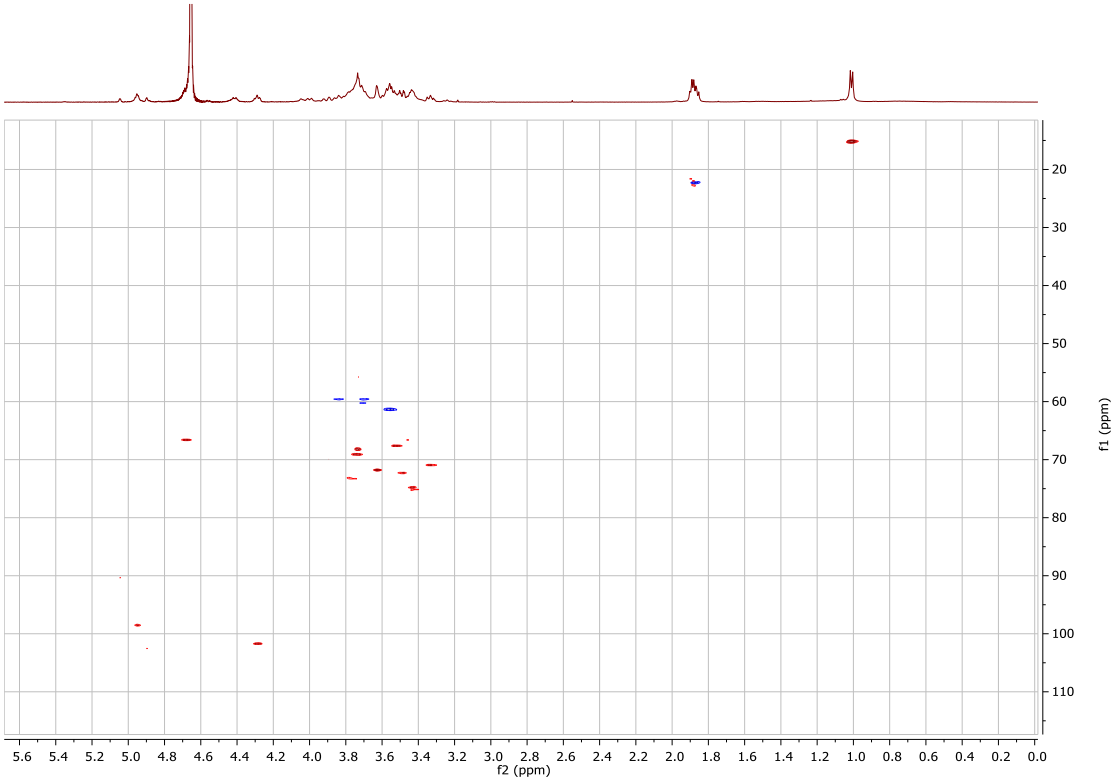


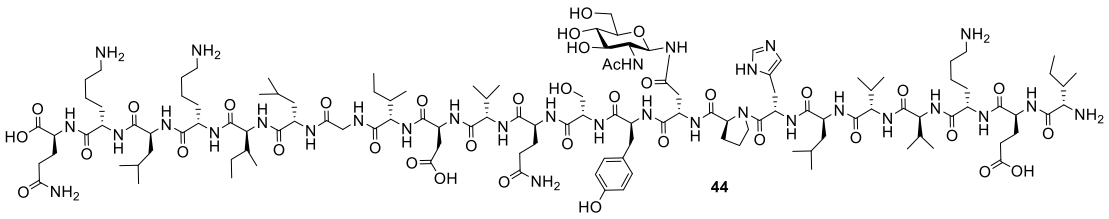
^{1}H-NMR (D_2O, 500 MHz) of **38**



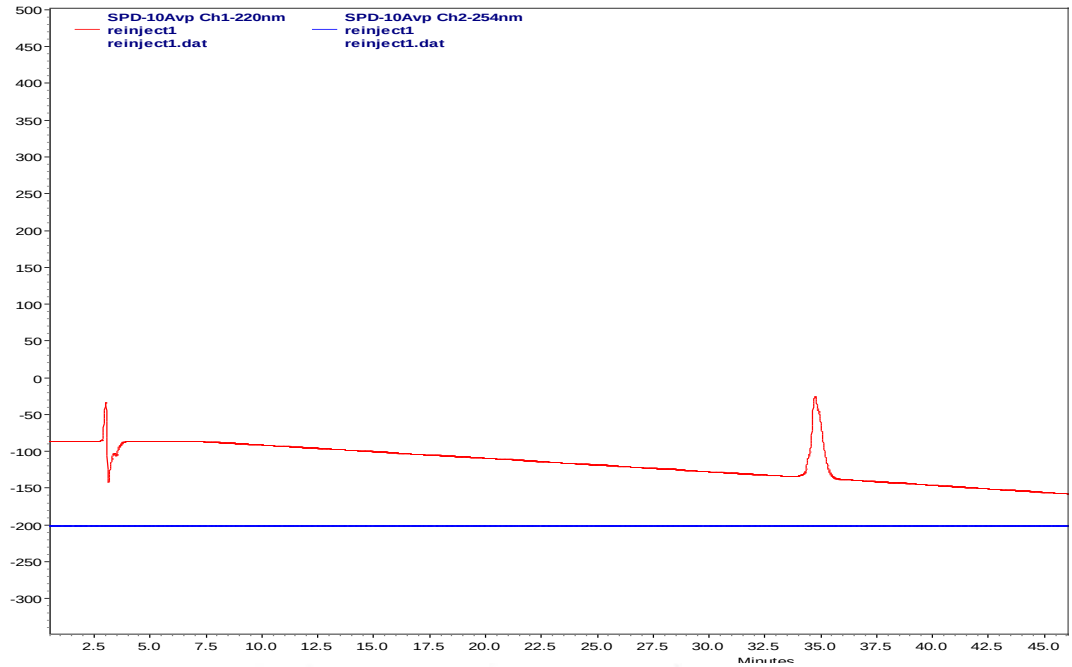


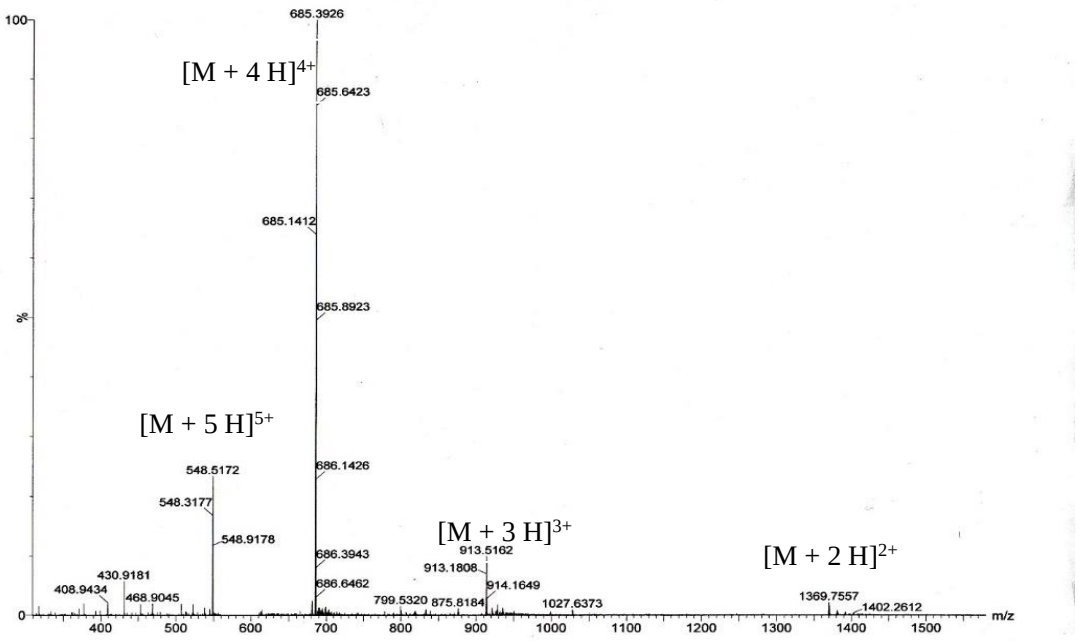
gHSQC (D_2O, 500 MHz) of **38**

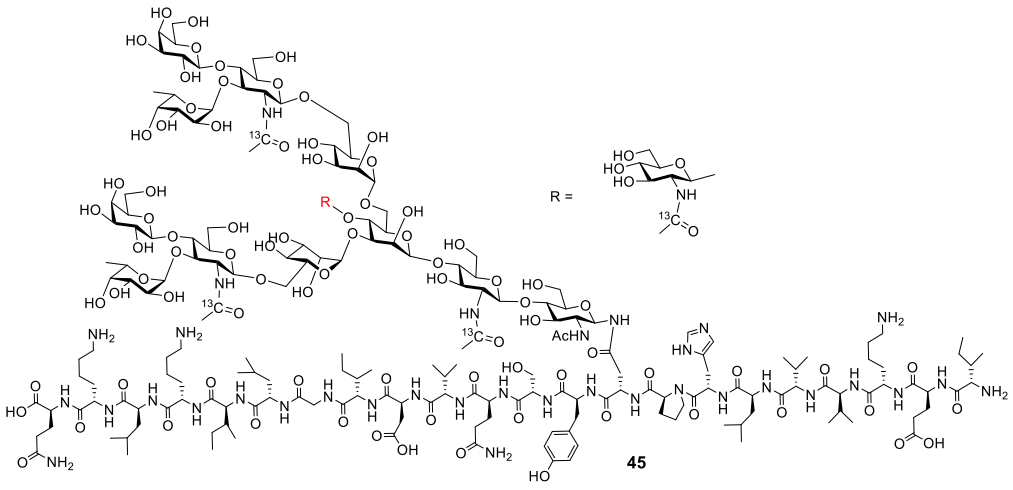




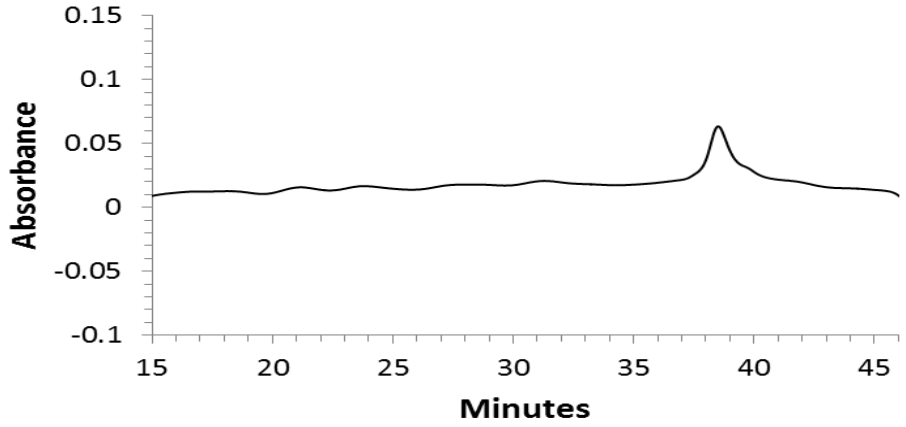
44


SPD-10Avp Ch1-220nm
reinject1
reinject1.dat
SPD-10Avp Ch2-254nm
reinject1
reinject1.dat
Minutes

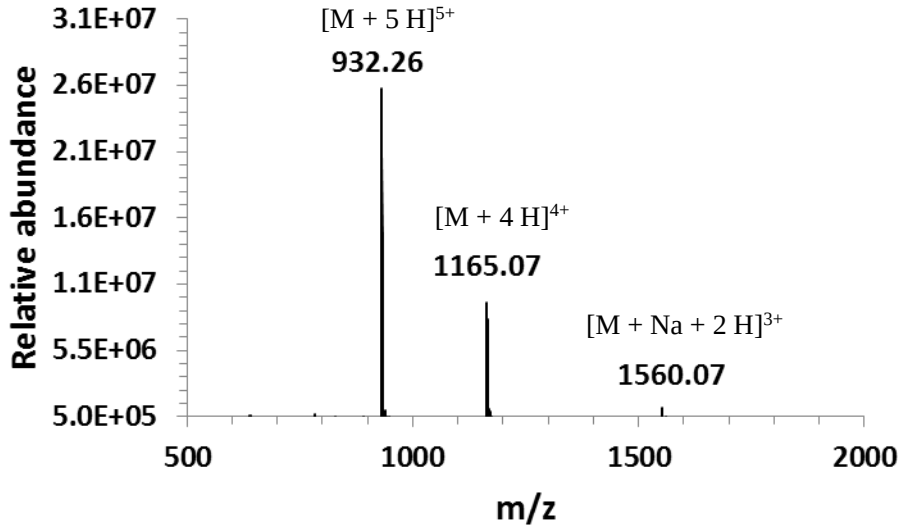

[M + 4 H]4+
[M + 5 H]5+
[M + 3 H]3+
[M + 2 H]2+
685.3926
685.6423
685.1412
685.8923
686.1426
548.5172
548.3177
548.9178
686.3943
686.6462
913.5162
913.1808
914.1649
430.9181
408.9434
468.9045
799.5320
875.8184
1027.6373
1369.7557
1402.2612
m/z

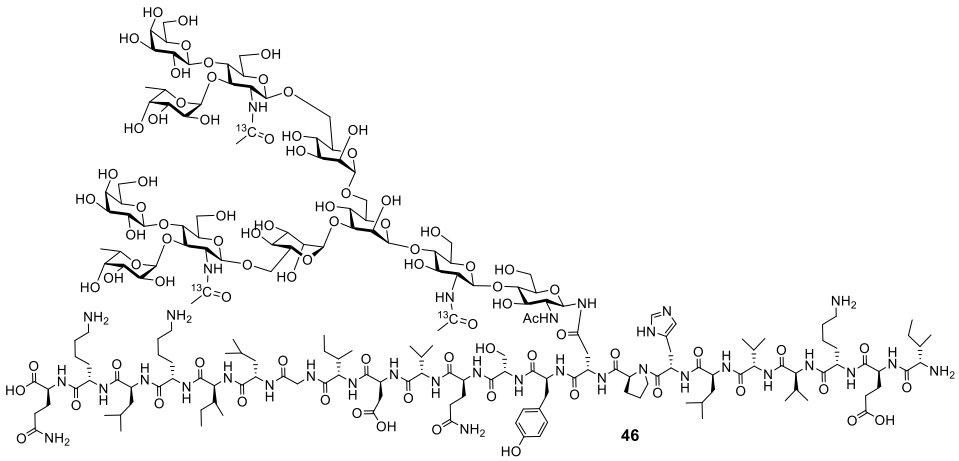


HPLC of glycopeptide **45**



MS of compound **45**





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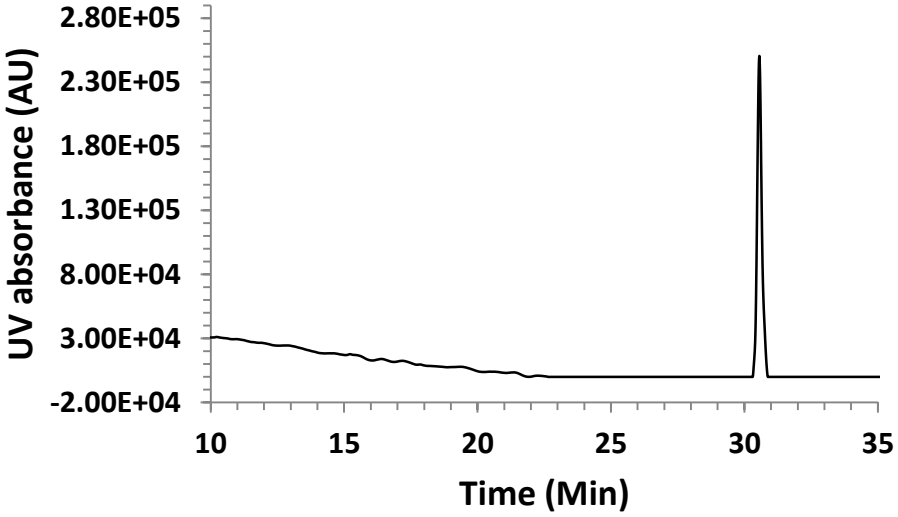
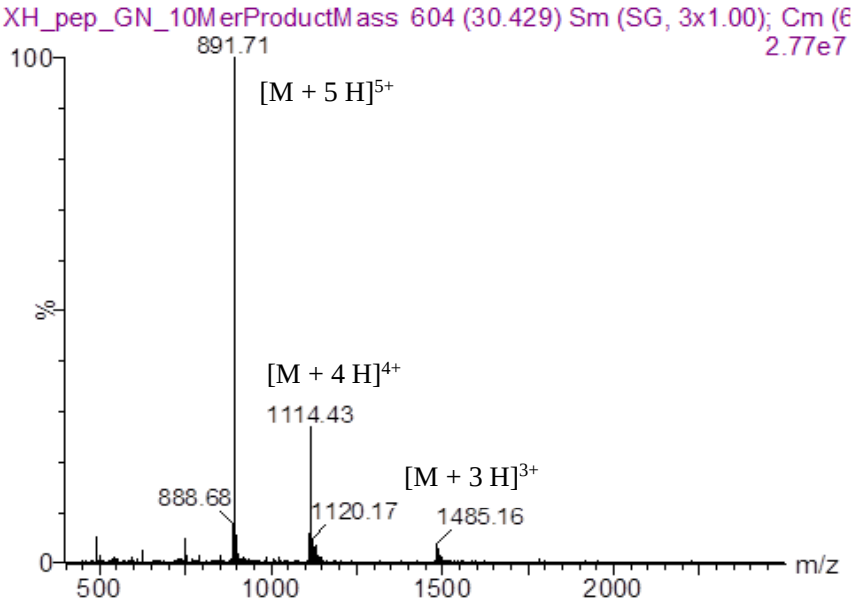
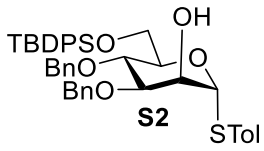
HPLC of glycopeptide **46**

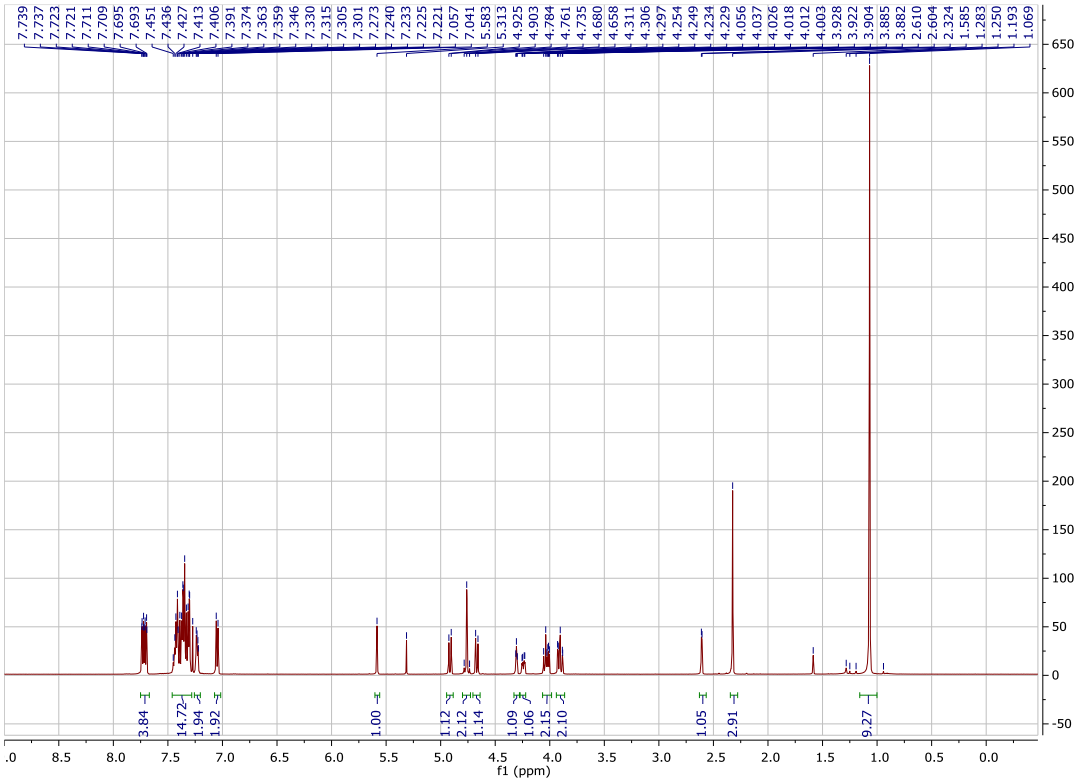


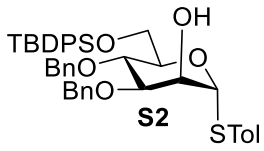
MS of compound **46**





^{1}H-NMR ($CDCl_3$, 500 MHz) of **S2**





^{13}C-NMR ($CDCl_3$, 125 MHz) of **S2**