Supplementary Information to: **Selective Oxidative Debenzylation of Mono- and Oligosaccharides in the Presence of Azides**

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General Remarks for the Synthesis:

All solvents were distilled before use. Absolute solvents were dried according to standard methods. Optical rotations were measured at ambient temperature on a Perkin-Elmer 241 polarimeter at 589 nm. NMR spectra were recorded on Jeol JNM-EX-270-FT and Bruker Avance 360 instruments. The NMR spectra were assigned by a series of 1D- and 2D-NMR spectra including HH-COSY, HMQC-COSY and HMBC-experiments. HSQC spectra were recorded with and without decoupling. All *J* values are given in Hertz. ESI-TOF-MS spectra were recorded on a Micromass LCT instrument coupled to an Agilent 1100 HPLC.

Flash chromatography was performed on silica gel 60 (230-400 mesh, Merck Darmstadt). Reactions were monitored by thin layer chromatography on coated aluminium plates (silica gel 60 GF_{254}, Merck Darmstadt). Spots were detected by UV-light and charring with a 1:1 mixture of 2 N H_2SO_4 and 0.2 % resorcine monomethylether in ethanol.

O-(3,4,6-Tri-O-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→2)-[O-(3,4,6-tri-O-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→4)]-O-3,6-di-O-acetyl-D-mannopyranose (2)

Using $FeCl_3$:

Trisaccharide **1** (100 mg, 89.2 μmol) and anhydrous $FeCl_3$ (306 mg, 1.88 mmol) were suspended in absolute dichloromethane (5.9 mL) and stirred for 5 h at 0 °C. Further $FeCl_3$ (280 mg, 1.73 mmol) was added and the mixture was stirred for 2 h at 0 °C. To the suspension was added water (6 mL), the mixture was diluted with ethyl acetate (30 mL) and extracted with water. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuum. The remainder was purified by flash chromatography (cyclohexane/acetone 2.5:1) to afford **2** (77.8 mg, 85%).

Using $NaBrO_3$/ $Na_2S_2O_4$:

To a solution of trisaccharide **1** (2.0 g, 1.8 mmol) in ethyl acetate (23 mL) was added a solution of $NaBrO_3$ (1.24 g, 8.1 mmol) in water (18 mL). A solution of $Na_2S_2O_4$ (85 %, 1.47 g, 7.2 mmol) in water (36 mL) was added over 25 min and the mixture was vigorously stirred for 6 h at ambient temperature. The mixture was diluted with ethyl acetate, quenched with

10% sodium thiosulphate (2 mL) and extracted with water. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuum. The remainder was purified by flash chromatography (cyclohexane/ethyl acetate 2.5:1 to 2:1) to afford **2** as a mixture (90 % α) of anomers (1.7 g, 91%): $[\alpha]^{23}_D$ = -36.7 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (360 MHz, DMSO) *δ* 9.61 (d, $J_{NH,2}$ = 9.1 Hz, 1H, NH), 9.48 (d, $J_{NH,2}$ = 9.3 Hz, 1H, NH), 6.99 (d, $J_{OH,1}$ = 4.1 Hz, 1H, OH-1^1), 5.14 (dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H-3^4), 5.08 (dd, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.7 Hz, 1H, H-3^2), 5.01 (dd, $J_{1,2}$ < 1 Hz, $J_{OH,1}$ = 4.1 Hz Hz, 1H, H-1^1), 4.95-4.81 (m, 4H, H-3^1, H-1^4, H-4^2, H-4^4), 4.65 (d, $J_{1,2}$ = 8.3 Hz, 1H, H-1^2), 4.29-4.16 (m, 2H, H-$6a^1$, H-$6a^4$), 4.13 (dd, $J_{5,6}$ = 4.9 Hz, J_{gem} = 12.0 Hz, 1H, H-$6a^2$), 3.97-3.65 (m, 10H, H-$6b^4$, H-2^1, H-4^1, H-2^2, H-$6b^2$, H-5^2, H-5^4, H-5^1, H-2^4, H-$6b^1$), 2.10-1.83 (m, 24 H, OAc); ^{13}C NMR (90 MHz, DMSO) *δ* 170.1, 169.8, 169.6, 169.5, 169.2 (C=O OAc), 156.5 (q, $J_{C,F}$ = 36.5 Hz, C=O TFAc), 156.4 (q, $J_{C,F}$ = 36.5 Hz, C=O TFAc), 115.7 (q, $J_{C,F}$ = 287.5 Hz, C=O CF_3), 115.6 (q, $J_{C,F}$ = 288.7 Hz, C=O CF_3), 99.6 (C-1^2), 98.8 (C-1^4), 90.9 (C-1^1α, $J_{H\text{-}1,C\text{-}1}$ = 174.7 Hz,), 75.8 (C-2^1), 72.7 (C-4^1), 71.8 (C-3^2), 71.8 (C-3^4), 70.8 (C-3^1), 70.7 (C-5^2), 70.6 (C-5^4), 68.2 (C-4^2), 68.2 (C-4^4), 67.3 (C-5^1), 62.2 (C-6^1), 62.0 (C-6^4), 61.9 (C-6^2), 54.2 (C-2^4), 53.2 (C-2^2), 20.5, 20.4, 20.1, 20.0 (OAc); MS (ESI) *m/z* calcd $C_{38}H_{48}F_6N_2O_{24}Na$ $[M+Na]^+$ 1053.24, found 1053.54.

3-O-Benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (5) and 2-deoxy-2-phthalimido-β-D-glucopyranosylazide (6)

The dibenzylated azide **4** (41.6 mg, 81 µmol) was dissolved in a solution of DMDO in acetone (2.3 mL, 86 mM, 198 µmol) at -78 °C. The solution was stirred for 80 min at -78 °C, for 6 h at 0 °C and for 15.5 h between 0 °C and 22 °C. The mixture was concentrated in vacuum. The remainder was purified by flash chromatography (cyclohexane/acetone 3:1) to afford **5** (19.1 mg, 56%) and **6** (5.5 mg, 20%).

5: $[\alpha]^{24}_D$ = +22.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (270 MHz, DMSO) *δ* 8.03-7.29 (m, 4H, NPht), 7.05-6.85 (m, 5H, Ar), 5.62 (d, $J_{OH,4}$ = 5.6 Hz, 1H, OH-4), 5.37 (d, $J_{1,2}$ = 9.2 Hz, 1H, H-1), 4.83-4.72 (m, 2H, OH-6, OCH_2), 4.43 (d, J_{gem} = 12.2 Hz, 1H, OCH_2), 4.11 (dd, $J_{2,3}$ = $J_{3,4}$ = 8.6 Hz, 1H, H-3), 3.87-3.73 (m, 2H, H-2, H-6a), 3.67-3.43 (m, 3H, H-6b, H-4, H-5); ^{13}C NMR (68 MHz, DMSO) *δ* 168.0 (C=O NPht), 138.8 (C_q Ar), 135.4 (C-4/5 NPht), 131.2 (C-1/2 NPht), 128.4, 127.9, 127.7 (Ar), 124.0 (C-3/6 NPht), 85.7 (C-1), 79.9 (C-5), 78.9 (C-3), 74.1 (OCH_2), 71.5 (C-4), 60.8 (C-6), 55.3 (C-2); MS (ESI) *m/z* calcd $C_{21}H_{20}N_4O_6Na$ $[M+Na]^+$ 447.13, found 447.21.

6: $[\alpha]^{23}_D$ = -31.5 (*c* 1.0, MeOH); ^{1}H NMR (270 MHz, DMSO) *δ* 8.00-7.45 (m, 4H, NPht), 5.60-5.48 (m, 1H, OH-3), 5.38-5.21 (m, 2H, H-1, OH-4), 4.78-4.68 (m, 1H, OH-6), 4.08 (dd,

$J_{2,3} = J_{3,4}$ = 9.0 Hz, 1H, H-3), 3.82-3.69 (m, 2H, H-2, H-6a), 3.61-3.20 (m, 3H, H-6b, H-5, H-4); ^{13}C NMR (68 MHz, DMSO) δ 168.4 (C=O), 168.1 (C=O), 135.4 (Pht), 135.3 (Pht), 131.8 (Pht-Cq), 131.5 (Pht-Cq), 124.0 (Pht), 123.8 (Pht), 85.8 (C-1), 80.2 (C-5), 70.9 (C-3), 70.6 (C-4), 61.1 (C-6), 57.2 (C-2); MS (ESI) *m/z* calcd $C_{14}H_{14}N_4O_6Na$ $[M+Na]^+$ 357.08, found 357.23.

O-(3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-O-(3,4,6-tri-O-acetyl-α-D-mannopyranosyl)-(1→3)-[O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-O-(3,4,6-tri-O-acetyl-α-D-mannopyranosyl)-(1→6)]-O-(2,4-di-O-acetyl-β-D-mannopyranosyl)-(1→4)-O-(2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (9)

Heptasaccharide **7** (46 mg, 17.7 µmol) was dissolved in acetic anhydride and pyridine (2 mL, 1:2) at 0 °C and stirred for 24 h at rt. The solution was codistilled with toluene and concentrated in vacuum. The remainder was taken up in dichloromethane (20 mL) and extracted with 1 M HCl and 2 M $KHCO_3$. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuum to afford **8** (47 mg, quant).

To a solution of heptasaccharide **8** (30.2 mg, 11.4 µmol) in ethyl acetate (151 µL) was added a solution of $NaBrO_3$ (15.7 mg, 103 µmol) in water (113 µL). A solution of $Na_2S_2O_4$ (85 %, 18.6 mg, 91 µmol) in water (226 µL) was added over 3 min and the mixture was vigorously stirred for 3.5 h at rt. The mixture was diluted with ethyl acetate (1 mL), quenched with 10% sodium thiosulphate (400 µL) and extracted with water. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuum. The remainder was purified by flash chromatography (dichloromethane/acetone 5:1) to afford **9** (25.2 mg, 97%): $[\alpha]^{22}_D$ = -35.2 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (360 MHz, DMSO) δ 7.96-7.82 (m, 15H, NPht), 7.52-7.46 (m, 1H, NPht), 5.67 (dd, $J_{2,3} = J_{3,4}$ = 10.1 Hz, 1 H, H-3^5), 5.60 (dd, $J_{2,3} = J_{3,4}$ = 10.1 Hz, 1H, H-3$^{5'}$), 5.39 (d, $J_{1,2}$ = 8.4 Hz, 1H, H-1^5), 5.31 (d, $J_{1,2}$ = 9.6 Hz, 1H, H-1^1), 5.26 (d, $J_{1,2}$ = 8.4 Hz, 1H, H-1$^{5'}$), 5.23-5.11 (m, 2H, H-2^3, H-1^2), 5.09-4.83 (m, 9H, OH-3^1, OH-3^2, H-4$^{5'}$, H-4^5, H-4$^{4'}$, H-1^3, H-4^4, H-4^3, H-3^4), 4.75 (dd, $J_{OH,6a} = J_{OH,6b}$ = 5.4 Hz, 1H, OH-6^1), 4.70-4.63 (m, 1H, H-3$^{4'}$), 4.51 (d, $J_{1,2}$ < 1 Hz, 1H, H-1$^{4'}$), 4.46 (dd, $J_{OH,6a} = J_{OH,6b}$ = 5.8 Hz, 1H, OH-6^2), 4.29 (d, $J_{1,2}$ < 1 Hz, 1H, H-1^4), 4.27-3.89 (m, 13H, H-3^1, H-6a$^{5'}$, H-3^2, H-6a^5, H-2^5, H-2$^{5'}$, H-2^4, H-2$^{4'}$, H-5^5, H-6b$^{5'}$, H-6b^5, H-3^3, H-5$^{5'}$), 3.88-3.36 (m, 15H, H-2^2, H-5$^{4'}$, H-2^1, H-6a$^{4'}$, H-6b$^{4'}$, H-6a^1, H-5^3, H-5^4, H-6a^4, H-6b^4, H-4^1, H-4^2, H-6a^3, H-6b^1, H-5^2), 3.35-3.20 (m, 3H, H-5^1, H-6a^2, H-6a^3), 3.08-2.99 (m, 1H, H-6b^2), 2.20 (s, 3H, OAc), 2.08-1.77 (m, 39H, OAc); ^{13}C NMR (90 MHz, DMSO) δ 170.2, 170.1, 170.0, 169.9, 169.8, 169.7, 169.3, 169.2 (C=O OAc), 168.0,

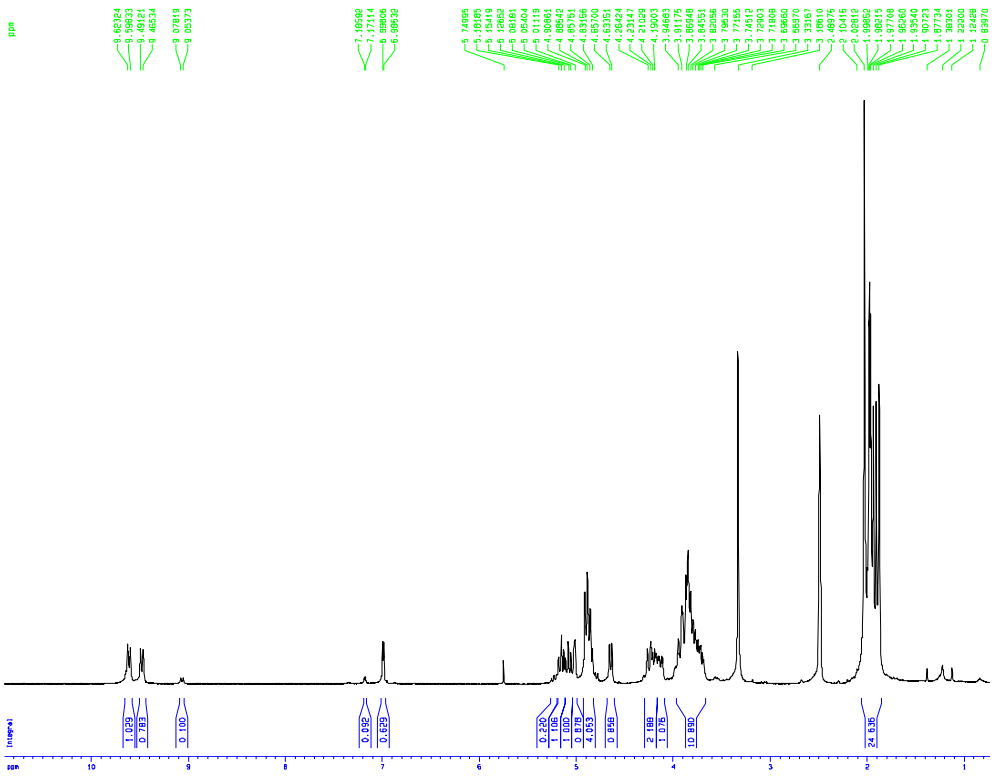
167.6, 167.3, 167.3 (C=O NPht), 135.1, 134.9, 134.6, 134.5 (C-4/5 NPht), 131.5, 131.0, 130.7, 130.6, 130.5 (C-1/2 NPht), 123.6, 123.4 (C-3/6 NPht), 98.0 (C-$1^3\beta$, $J_{C\text{-}1,H\text{-}1}$ = 162.8 Hz), 97.9 (C-$1^2\beta$, $J_{C\text{-}1,H\text{-}1}$ = 167.5 Hz), 97.8 (C-$1^{4'}\alpha$, $J_{C\text{-}1,H\text{-}1}$ = 174.7 Hz), 96.9 (C-$1^4\alpha$, $J_{C\text{-}1,H\text{-}1}$ = 173.8 Hz), 96.0 (C-$1^{5'}\beta$, $J_{C\text{-}1,H\text{-}1}$ = 167.9 Hz), 95.8 (C-$1^5\beta$, $J_{C\text{-}1,H\text{-}1}$= 167.6 Hz), 85.0 (C-$1^1\beta$, $J_{C\text{-}1,H\text{-}1}$ = 167.4 Hz), 79.0 (C-4^1), 78.8 (C-4^2), 76.8 (C-5^2), 75.1 (C-5^1), 73.6 (C-3^3), 73.3 (C-$2^{4'}$), 72.9 (C-2^4), 71.0 (C-5^5), 71.0 (C-$5^{5'}$), 71.0 (C-5^3), 70.1 (C-2^3), 69.7 (C-3^5), 69.7 (C-$3^{5'}$), 69.4 (C-3^4), 68.9 (C-3^1), 68.8 (C-3^2), 68.6 (C-$3^{4'}$), 68.5 (C-4^3), 68.1(C-4^5), 68.1 (C-$4^{5'}$), 67.6 (C-$5^{4'}$), 67.3 (C-5^4), 67.0 (C-6^3), 64.5 (C-4^4), 64.3 (C-$4^{4'}$), 61.9 (C-6^4), 61.7 (C-6^5), 61.7 (C-$6^{5'}$), 61.6 (C-$6^{4'}$), 60.1 (C-6^1), 59.4 (C-6^2), 57.0 (C-2^2), 55.8 (C-2^1), 53.8 (C-2^5), 53.8 (C-$2^{5'}$), 20.9, 20.5, 20.4, 20.2, 20.1, 20.0 (OAc); MS (ESI) *m/z* calcd $C_{102}H_{111}N_7O_{53}Na$ $[M+Na]^+$ 2304.61, found 2304.02.

O-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-α-D-mannopyranosyl-(1→3)-{O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-α-D-mannopyranosyl-(1→6)}-O-β-D-mannopyranosyl-(1→4)-O-(2-acetamido--deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosylazide (10)

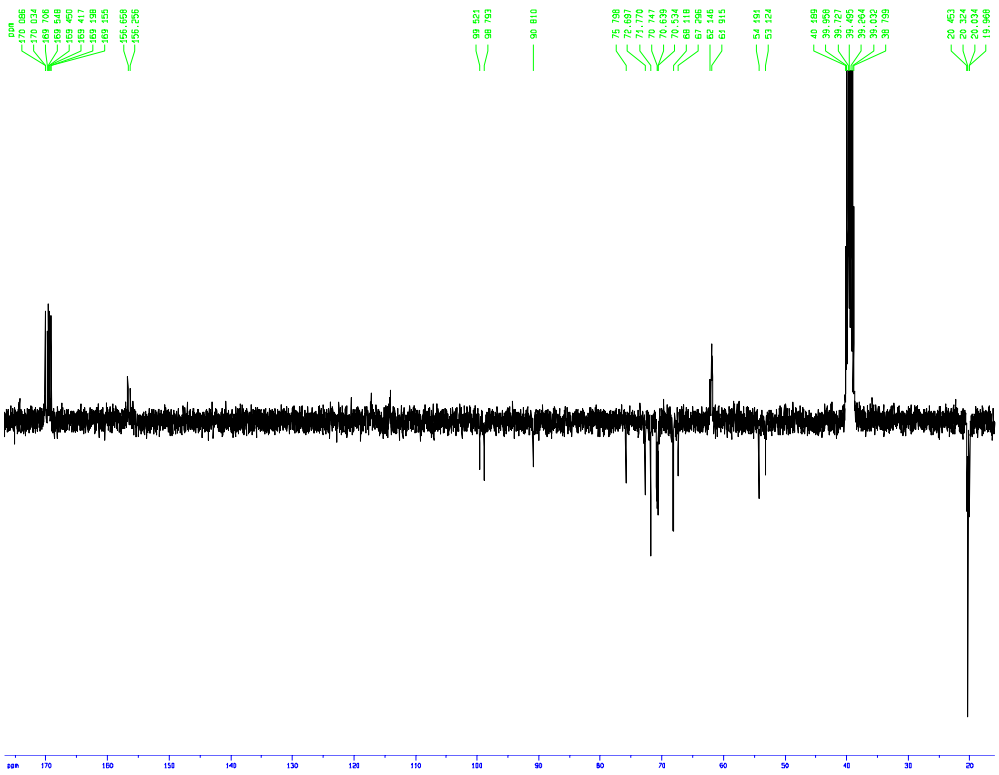
Heptasaccharide **9** (39.3 mg, 17.2 μmol) was dissolved in *n*-butanol (2.2 mL) and ethylene diamine (577 μL, 8.6 mmol) and stirred for 21 h at 90 °C. The mixture was codistilled with toluene and concentrated in vacuum. The remainder was diluted in a mixture of acetic anhydride, methanol and water (2.45 mL, 1:10:1.5) and stirred for 18 h at rt. The solution was codistilled with toluene and concentrated in vacuum. The remainder was dissolved in water (1.8 mL) and purified by reversed phase extraction on two connected SepPak catridges (Waters SepPak C18 Classic; 330 mg each). Elution of each batch was performed with acetonitrile/water (10 mL each, 0, 2.5, 5 and 10 % acetonitrile). The product eluted with 0 % acetonitrile/water and was lyophilized. Further purification was achieved by gel filtration (Hi Load Superdex 30, 16 x 600 mm, 0.1 M NH_4HCO_3, 0.75 mL/min) yielding azide **10** (16.9 mg, 73%): $[\alpha]^{28}_D$ = -9.0 (*c* 0.5, H_2O); ^{1}H NMR (360 MHz, D_2O) δ 4.92 (d, $J_{1,2}$ < 1 Hz, 1H, H-1^4), 4.72 (d, $J_{1,2}$ < 1 Hz, 1H, H-$1^{4'}$), 4.57-4.53 (m, 2H, H-1^3, H-1^1), 4.41 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1^2), 4.38-4.33 (m, 2H, H-1^5, H-$1^{5'}$), 4.07-4.03 (m, 1H, H-2^3), 4.00-3.97 (m, 1H, H-2^4), 3.93-3.89 (m, 1H, H-$2^{4'}$), 3.81-3.64 (m, 9H, H-$6a^3$, H-$6a^4$, H-$6a^5$, H-$6a^{5'}$, H-$6a^{4'}$, H-3^4, H-$3^{4'}$, H-$6a^2$, H-$6a^1$), 3.63-3.47 (m, 15H, H-$6b^3$, H-4^3, H-2^2, H-3^1, H-3^3, H-$6b^5$, H-$6b^{5'}$, H-$6b^2$, H-2^1, H-3^2, H-5^4, H-4^1, H-2^5, H-$2^{5'}$, H-$6b^1$), 3.46-3.28 (m, 11H, H-4^2, H-$6b^4$, H-$6b^{4'}$, H-$5^{4'}$, H-5^3, H-5^2, H-5^1, H-3^5, H-$3^{5'}$, H-4^4, H-$4^{4'}$), 3.27-3.19 (m, 4H, H-4^5, H-$4^{5'}$, H-5^5, H-$5^{5'}$), 1.88 (s, 3H, NAc), 1.87-1.84 (m, 9H, NAc); ^{13}C NMR (90 MHz, D_2O) δ 176.4, 176.3,

176.2 (C=O NAc), 103.0 (C-1^2), 102.4 (C-1^3), 101.2 (C-1^4), 101.2 (C-1^5), 101.2 (C-$1^{5'}$), 98.6 (C-$1^{4'}$), 90.1 (C-1^1), 82.1 (C-3^3), 81.1 (C-4^1), 80.3 (C-4^2), 78.1 (C-2^4), 78.1 (C-5^2), 77.9 (C-$2^{4'}$), 77.4 (C-5^5), 77.4 (C-$5^{5'}$), 76.0 (C-5^1), 75.9 (C-5^3), 75.2 (C-$5^{4'}$), 75.0 (C-3^5), 74.9 (C-$3^{5'}$), 74.5 (C-5^4), 73.9 (C-3^1), 73.6 (C-3^2), 71.8 (C-2^3), 71.5 (C-4^5), 71.5 (C-$4^{5'}$), 71.1 (C-3^4), 71.0 (C-$3^{4'}$), 69.0 (C-4^4), 68.9 (C-$4^{4'}$), 67.5 (C-4^3), 67.3 (C-6^3), 63.3 (C-$6^{4'}$), 63.2 (C-6^4), 62.2 (C-6^5), 62.2 (C-$6^{5'}$), 61.5 (C-6^1), 61.5 (C-6^2), 56.9 (C-2^5), 56.9 (C-$2^{5'}$), 56.5 (C-2^2), 56.1 (C-2^1), 23.9, 23.8, 23.7 (NAc); MS (ESI) *m/z* calcd $C_{50}H_{83}N_7O_{35}Na$ $[M+Na]^+$ 1364.48, found 1365.86.

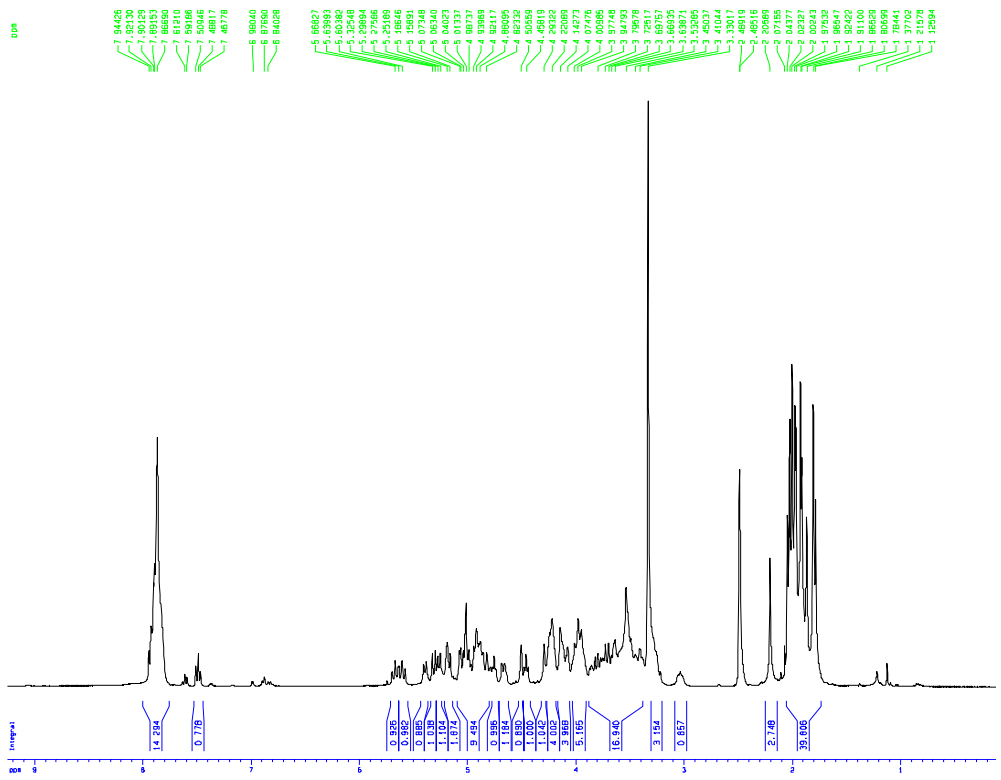
^{1}H NMR and ^{13}C NMR of New Compounds



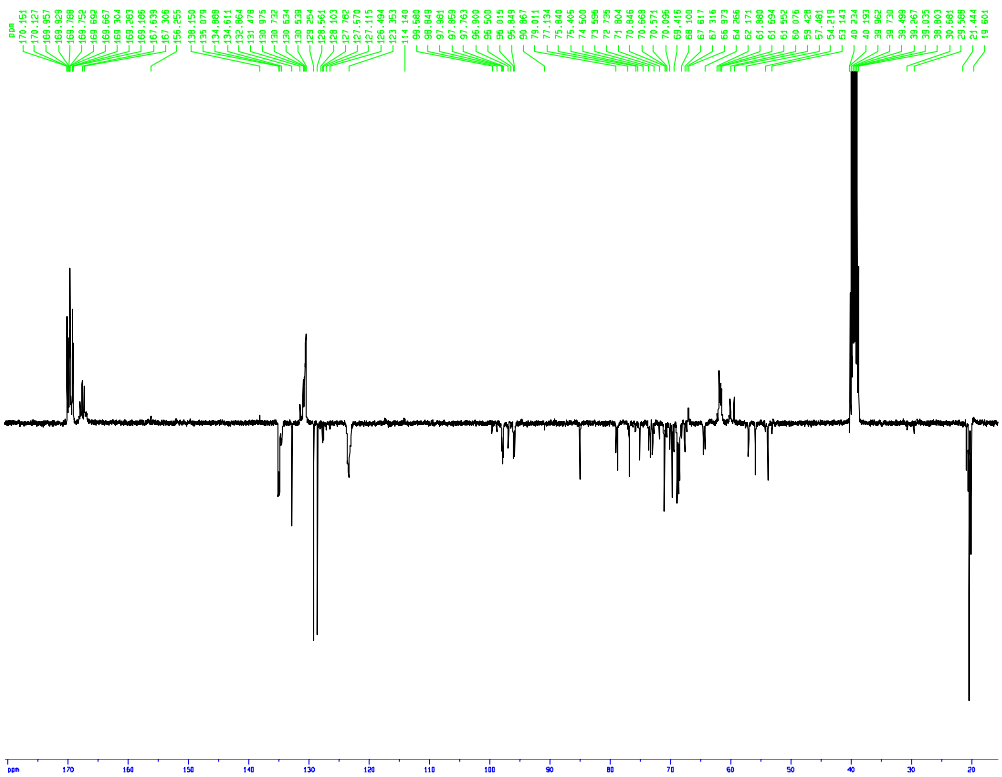
^{1}H NMR of **2** (DMSO)



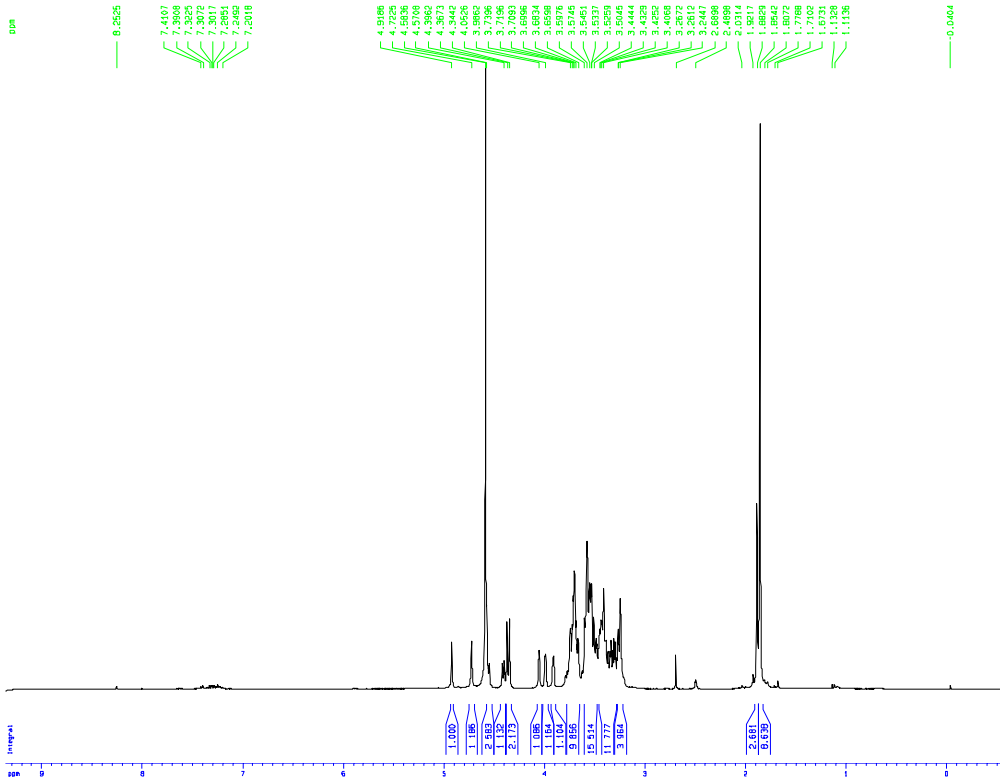
^{13}C NMR of **2** (DMSO)



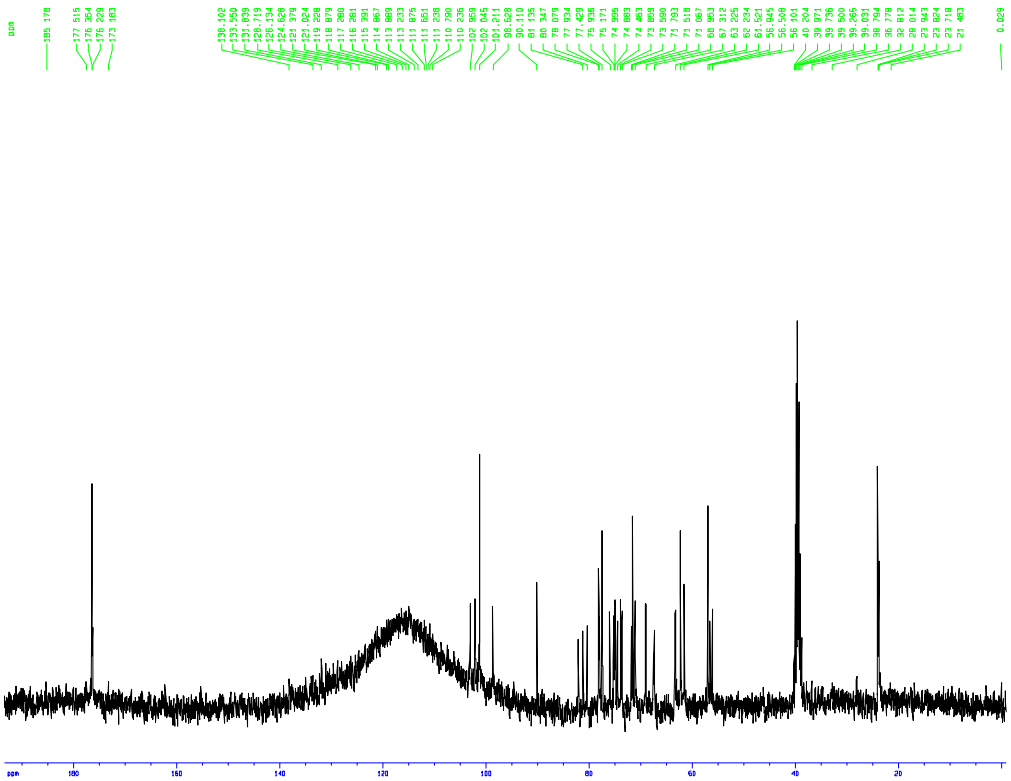
^{1}H NMR of **9** (DMSO)



^{13}C NMR of **9** (DMSO)



^{1}H NMR of **10** (DMSO)



^{13}C NMR of **10** (DMSO)