Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Iridium Catalysis: Reductive Conversion of Glucan to Xylan

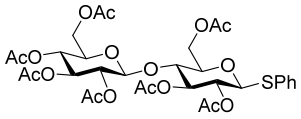
Martin Jæger Pedersen, Robert Madsen and Mads Hartvig Clausen*

1) Table of Contents

2) Materials and Techniques

All materials, reagents and solvents were purchased from Alfa Aesar, Carbosynth, Sigma-Aldrich or TCI chemicals and used without further purification. All solvents were HPLC-grade. The dry solvents were obtained from Innovative Technology PS-MD-7 Pure-solv solvent purification system. Reactions requiring anhydrous conditions were carried out in flame-dried glassware under inert atmosphere, either using argon or nitrogen. Solvents were removed in vacuo at 40 °C. All reactions were monitored by thin-layer chromatography (TLC), performed on Merck aluminum plates precoated with 0.25 mm silica gel 60 F254. Compounds were visualized under UV irradiation and/or heating after applying a solution of $Ce(SO_4)_2$ (2.5 g) and $(NH_4)_6Mo_7O_{24}$ (6.25 g) in 10% aqueous H_2SO_4 (250 mL). Column chromatography was performed using Geduran silica gel 60 with specified solvents given as volume-ratio. NMR spectra were recorded on a Varian Unity Inova 500, Bruker Ascend 400 or Varian Mercury 300 spectrometer. Melting points (m.p.) were measured on a Stuart melting point apparatus SMP30 and reported uncorrected. Optical rotations were measured with a Perkin-Elmer Model 241 Polarimeter with a path length of 1 dm. Chemical shifts (δ) are reported in ppm downfield from TMS ($\delta = 0$) using the solvent resonance as the internal standard, e.g. $CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.16 ppm. NMR samples dissolved in D_2O were using CH_3CN (^{1}H 2.06 ppm, ^{13}C 1.47 ppm) as internal standard. ^{13}C NMR spectra were ^{1}H decoupled. Coupling constants (J) are reported in hertz (Hz), and the field is indicated in each case. Multiplicities are reported as singlet (s), doublet (d), triplet (t) and multiplet (m). IR spectra were recorded neat on a Bruker Alpha-P FT-IR spectrometer and absorption maxima reported in wavenumbers (cm^{-1}). High-resolution mass spectroscopy (HRMS) were recorded on a Agilent 1100 LC system equipped with a photodiode array detector and coupled to a LCT orthogonal time-of-flight (TOF) mass spectrometer (Waters-Micromass, Manchester, UK) with Z-spray electrospray ionization (ESI) source and equipped with a LockSpray probe, all controlled using MassLynx v4.0.

3) Experimental Procedures

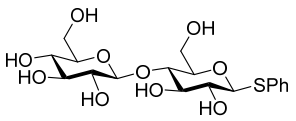


Phenyl hepta-*O*-acetyl-1-thio-β-D-cellobioside (2)

Octa-*O*-acetyl-α-D-cellobiose (8.66 g, 12.8 mmol) was suspended in 33 % HBr in AcOH (50 mL) cooled in an ice bath under an atmosphere of argon. Acetic anhydride (9 mL) was added, the reaction mixture was allowed to reach 23 °C and stirred overnight. The reaction mixture was diluted with 150 mL CH_2Cl_2 and poured into a beaker with 400 mL ice water. This mixture was stirred vigorously before the phases were separated. The aqueous phase was extracted three times with 50 mL CH_2Cl_2. The combined organic phases were neutralized with saturated $NaHCO_3$ (aq), washed with brine, dried with Na_2SO_4, filtered, concentrated and coevaporated with heptane. The resulting crude was recrystallized from CH_2Cl_2/heptane yielding the bromide as colorless needles (8.80 g, 99 %). The compound analyses were in accordance with data from the literature.[1] **m.p.** (CH_2Cl_2/heptane, uncorrected) 185.2-185.7 °C.

Hepta-*O*-acetyl-1-bromo-α-D-cellobioside (8.80 g, 12.6 mmol) was dissolved in 60 mL CH_2Cl_2 before tetrabutylammonium hydrogensulfate (4.27 g, 12.6 mmol) and thiophenol (3.9 mL, 38 mmol) were added. The reaction mixture was stirred at 23 °C for 10 min before 70 mL 1M Na_2CO_3 (aq) were added and the two phases were stirred vigorously for 1 hour and 20 min. The reaction mixture consisting of two phases was separated and the aqueous phase was extracted three times with 40 mL CH_2Cl_2. The combined organic phases were washed with 1M NaOH (aq), H_2O, brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The resulting brownish crude solid was recrystallized from ethanol/H_2O yielding the title product (**2**) as colorless crystals (6.59 g, 72 %). The compound analyses were in accordance with data from the literature.[2]

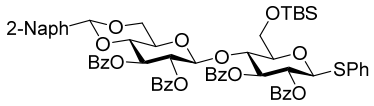
m.p. (EtOH/H_2O, uncorrected) 220.8-221.4 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 2H, *meta*^{Ph}), 7.36 – 7.27 (m, 3H, *ortho*^{Ph}, *para*^{Ph}), 5.19 (t, $^3J_{2,3\sim3,4}$ = 9.1 Hz, 1H, H3), 5.13 (t, $^3J_{2,3\sim3,4}$ = 9.4 Hz, 1H, H3'), 5.05 (t, $^3J_{3,4\sim4,5}$ = 9.5 Hz, 1H, H4'), 4.97 – 4.82 (m, 2H, H2', H2), 4.65 (d, $^3J_{1,2}$ = 10.1 Hz, 1H, H1), 4.55 (dd, $^2J_{6a,6b}$ = 11.9 Hz, $^3J_{5,6a}$ = 1.8 Hz, 1H, H6a), 4.48 (d, $^3J_{1,2}$ = 7.9 Hz, 1H, H1'), 4.36 (dd, $^2J_{6a,6b}$ = 12.5 Hz, $^3J_{5,6a}$ = 4.3 Hz, 1H, H6a'), 4.09 (dd, $^3J_{5,6b}$ = 5.4 Hz, 1H, H6b), 4.02 (dd, $^3J_{5,6b}$ = 2.1 Hz, 1H, H6b'), 3.72 (t, $^3J_{3,4\sim4,5}$ = 9.6 Hz, 1H, H4), 3.68 – 3.55 (m, 2H, H5', H5), 2.11 (s, 3H, CH_3^{Ac}), 2.08 (s, 3H, CH_3^{Ac}), 2.06 (s, 3H, CH_3^{Ac}), 2.02 (s, 3H, CH_3^{Ac}), 2.00 (s, 6H, CH_3^{Ac}), 1.97 (s, 3H, CH_3^{Ac}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.6/170.4/170.4/169.9/169.7/169.4/169.2 (C=O^{Ac}), 133.2 (2C, *ortho*^{Ph}), 131.8 (*ipso*^{Ph}), 129.0 (2C, *meta*^{Ph}), 128.5 (*para*^{Ph}), 100.9 (C1'), 85.6 (C1), 76.9/76.5 (C4, C5), 73.7 (C3), 73.0 (C3'), 72.1 (C5'), 71.7 (C2'), 70.2 (C2), 67.8 (C4'), 62.1 (C6), 61.6 (C6'), 21.0/20.9/20.8/20.7/20.7 (CH_3^{Ac}).



Phenyl 1-thio-β-D-cellobioside (3)

Sodium (720 mg, 31.3 mmol) was reacted with 1 L of CH_3OH under argon at 23 °C before adding this solution to a flask containing phenyl hepta-*O*-acetyl-1-thio-β-D-cellobioside (**2**) (55.89 g, 76.7 mmol) and stirred for one hour. The resulting solution was concentrated to half the volume under reduced pressure and allowed to react for 1.5 hours. The reaction mixture was quenched with 40 mL freshly washed Amberlite IR-120 (H) until the mixture was slightly acidic and stirred for three hours. The mixture was then filtered and concentrated under reduced pressure. This gave the title compound as off-white crystals (33.66 g, 100%). The compound analyses were in accordance with data from the literature.[3]

^{1}H NMR (300 MHz, CD_3OD) δ 7.56 – 7.50 (m, 2H, *meta*^{Ph}), 7.34 – 7.16 (m, 3H, *ortho*^{Ph}, *para*^{Ph}), 4.60 (d, $^3J_{1,2}$ = 9.8 Hz, 1H, H1), 4.39 (d, $^3J_{1,2}$ = 7.8 Hz, 1H, H1'), 3.93 – 3.76 (m, 3H), 3.63 (dd, $^2J_{6a,6b}$ = 11.9 Hz, $^3J_{5,6a}$ = 5.4 Hz, 1H, H6a), 3.58 – 3.48 (m, 2H), 3.46 – 3.15 (m, 6H). **^{13}C NMR** (75 MHz, CD_3OD) δ 134.8 (*ipso*^{Ph}), 132.9 (*meta*^{Ph}), 129.9/128.4 (*ortho*^{Ph}, *para*^{Ph}), 104.4 (C1'), 89.0 (C1), 80.4/ 80.1/ 78.0/ 77.8/ 77.7/ 74.8/ 73.4/ 71.3 (C2, C2', C3, C3', C4, C4', C5, C5'), 62.4/61.8 (C6, C6').



Phenyl 2,2',3,3'-tetra-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-4',6'-*O*-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (4a)

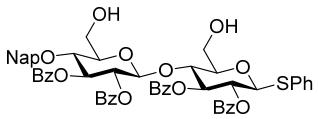
Naphthaldehyde (1.27g, 8.11 mmol) was suspended in 8 mL CH_3OH before trimethyl orthoformate (1.5 mL, 13.5 mmol) and *p*-toluenesulfonic acid mono hydrate (102 mg, 0.54 mmol) were added at 23°C. The reaction mixture turned clear with a yellowish color and after 30 minutes TLC indicated full conversion. The resulting mixture was then concentrated, dissolved in 10 mL dry CH_3CN and added to a suspension of phenyl 1-thio-β-D-cellobioside (**3**) (2.37 g, 5.41 mmol) in 90 mL of dry CH_3CN. The resulting reaction mixture was heated to 60 °C and followed by TLC. After 8 hours TLC indicated full conversion and the reaction mixture was removed from the heat, the acid neutralized with 1.0 mL Et_3N. Observation, neither the starting material nor the product were fully dissolved at any point of time during the course of the reaction. The mixture was concentrated on silica gel and purified by flash chromatography (1:24→1:9, EtOH/CH_2Cl_2), this yielded the phenyl 4',6'-O-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside as a colorless amorphous solid (2.71 g, 88 %).

R_f 0.28 (1:19 CH_3OH/CH_2Cl_2). **$[\alpha]_D^{22}$** = – 58.0 (*c* = 0.993, EtOH). **HRMS** (ESI-TOF) m/z for $C_{29}H_{33}O_{10}S^+$ (MH^+) calculated: 573.1789; found: 573.1786. **^{1}H NMR** (400 MHz, DMSO) δ 8.07 – 7.84 (m, 4H, H^{Naph}), 7.66 – 7.40 (m, 5H, H^{Naph}, *meta*^{Ph}), 7.38 – 7.19 (m, 3H, *ortho*^{Ph}, *para*^{Ph}), 5.76 (s, 1H, CHO_2^{Naph}), 5.54 (d, $^3J_{2,OH}$ = 5.1 Hz, 1H, OH2'), 5.46 (d, $^3J_{2,OH}$ = 6.1 Hz, 1H, OH2), 5.41 (d, $^3J_{3,OH}$ = 4.2 Hz, 1H, OH3'), 4.69 (d, $^3J_{1,2}$ = 9.7 Hz, 1H, H1), 4.68 (t, $^3J_{6a,OH\sim6b,OH}$ = 5.8 Hz, 1H, OH6), 4.59 (d, $^3J_{3,OH}$ = 2.6 Hz, 1H, OH3), 4.56 (d, $^3J_{1,2}$ = 7.8 Hz, 1H, H1'), 4.25 (dd, $^2J_{6a,6b}$ = 9.8 Hz, $^3J_{5,6a}$ = 4.0 Hz, 1H, H6a'), 3.87 – 3.72 (m, 2H, H6a, H6b'), 3.72 – 3.58 (m, 1H, H6b), 3.58 – 3.36

(m, 6H, H3, H3', H4, H4', H5, H5'), 3.25 – 3.02 (m, 2H, H2, H2'). **^{13}C NMR** (101 MHz, DMSO) δ 135.2 (*ipso*^{Ph}), 134.5/ 133.0/ 132.3/ 130.0/ 128.9/ 128.2 /127.7/ 127.6/ 126.5/ 126.3/ 125.4/ 124.2 (C^{Naph}, C^{Ph}), 103.0 (C1'), 100.7 (CHO_2^{Naph}), 86.6 (C1), 80.4 (C4'), 79.0 (C5), 78.4 (C4), 75.9 (C3), 74.4 (C2'), 72.8 (C3'), 72.3 (C2), 67.7 (C6'), 66.0 (C5'), 60.0 (C6). **IR** (neat, cm^{-1}) 3392 (s (br), O-H, stretch), 3059 (m, CH-sp^2), 2969, 2875 (m, CH-sp^3), 1582, 1477 (w, C-C *aromatic*), 1072 (s, C-O).

Phenyl 4',6'-O-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (1.43 g, 2.50 mmol) was dissolved in 12.5 mL dry pyridine and cooled in an ice bath. *tert*-Butyldimethylsilyl chloride (TBSCl) (453 mg, 3.00 mmol) and DMAP (70 mg) were added to the reaction mixture and allowed to reach 23 °C stirring overnight. TLC did not show completion and additional TBSCl (200 mg) was added. TLC revealed full conversion after 6 hours. NMR confirmed conversion to phenyl 6-*O*-*tert*-butyldimethylsilyl-4',6'-*O*-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside. The reaction mixture was cooled to 0 °C and benzoyl chloride (1.4 mL, 12 mmol) was added slowly. The resulting mixture was diluted with 10 mL dry CH_2Cl_2, allowed to reach 23 °C and stirred overnight. Next morning additional benzoyl chloride (0.35 mL, 3.0 mmol) was added to give full conversion. The resulting mixture was diluted with 50 mL CH_2Cl_2 and the remaining benzoyl chloride was quenched by addition of 1 mL CH_3OH. After stirring for ten minutes the resulting mixture was washed with H_2O, 1 M HCl, 0.15 M $CuSO_4$ (aq), H_2O, saturated $NaHCO_3$ (aq) and brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was co-evaporated with heptane, concentrated on silica and purified using Combiflash (15 % → 65 %, EtOAc/heptane) yielding the title compound (**4a**) as a colorless amorphous solid (2.197 g, 80 %).

R_f 0.57 (4:6 EtOAc/heptane). **$[\alpha]_D^{22}$** = – 2.9 (*c* = 1.0, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{63}H_{62}NaO_{14}SSi^+$ (MNa^+) calculated: 1125.3522; found: 1125.3529. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 7.68 (m, 12H, *ortho*^{Bz}, H^{Naph}), 7.66 – 7.18 (m, 20H, *meta*^{Bz}, *para*^{Bz}, H^{Naph}, H^{Ph}), 5.67 (t, $^3J_{2,3\sim3,4}$ = 9.5 Hz, 1H, H3), 5.64 (t, $^3J_{2,3\sim3,4}$ = 9.5 Hz, 1H, H3'), 5.41 (dd, $^3J_{1,2}$ = 7.9 Hz, 1H, H2'), 5.36 (s, 1H, CHO_2^{Naph}), 5.32 (t, $^3J_{1,2\sim2,3}$ = 9.9 Hz, 1H, H2), 4.99 (d, 1H, H1'), 4.82 (d, 1H, H1), 4.16 (t, $^3J_{3,4\sim4,5}$ = 9.5 Hz, 1H, H4), 3.83 (dd, $^2J_{6a,6b}$ = 10.7 Hz, $^3J_{5,6a}$ = 4.9 Hz, 1H, H6a'), 3.75 (dd, $^2J_{6a,6b}$ = 12.0 Hz, $^3J_{5,6a}$ = 2.4 Hz, 1H, H6a), 3.70 (d, 1H, H6b), 3.66 (t, $^3J_{3,4\sim4,5}$ = 9.5 Hz, 1H, H4'), 3.44 (td, $^3J_{5,6b}$ = 9.6 Hz, 1H, H5'), 3.39 (br d, 1H, H5), 2.80 (t, 1H, H6b'), 1.00 (s, 9H, CH_3^{tBu}), 0.14 (s, 3H, CH_3^{TBS}), 0.13 (s, 3H, CH_3^{TBS}). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7/ 165.5/ 165.3/ 164.9 (C=O^{Bz}), 134.1 (*ipso*^{Ph}) 133.7/ 133.5/ 133.3/ 133.2/ 133.2/ 132.9/ 132.2/ 130.4/ 130.0/ 129.9/ 129.5/ 129.5/ 129.2/ 129.0/ 128.6/ 128.5/ 128.5/ 128.4/ 128.2/ 128.1/ 127.7/ 126.5/ 126.2/ 125.7/ 123.7 (C^{Bz}, C^{Naph}, C^{Ph}), 101.5 (CHO_2^{Naph}), 101.3 (C1'), 86.1 (C1), 79.6 (C5), 78.6 (C4'), 75.4 (C4), 74.7 (C3), 72.7 (C2'), 72.4 (C3'), 70.7 (C2), 68.1 (C6'), 66.4 (C5'), 61.0 (C6), 26.1 (CH_3^{tBu}), 18.5 ($C(CH_3)_3^{tBu}$), -4.8, -5.1 (CH_3^{TBS}). **IR** (neat, cm^{-1}) 3062 (w, CH-sp^2), 2951, 2928, 2856 (w, CH-sp^3), 1730 (s, C=O), 1602, 1451 (w, C-C *aromatic*), 1315, 1086 (s, C-O strecth).



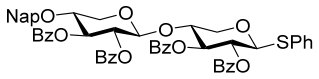
Phenyl 2,2',3,3'-tetra-*O*-benzoyl-4'-*O*-(naphthalen-2-ylmethyl)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (5a)

Phenyl 2,2',3,3'-tetra-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-4',6'-*O*-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (**4a**) (14.22 g, 12.89 mmol) was dissolved in 150 mL dry CH_2Cl_2 and cooled in an ice bath. Then 1M BH_3·THF (64.5 mL) was slowly added to the cooled solution and allowed to stir for 15 minutes before adding $Cu(OTf)_2$ (527 mg). After the addition effervescence was observed and the solution turned from brown to black suspension. When TLC showed completion (overnight), the reaction mixture was neutralized with Et_3N and the remaining BH_3 was quenched by slow addition of CH_3OH (*strong effervescence!*). The reaction mixture was filtered through celite, washed with H_2O and phases separated. The aqueous phase was extracted twice with CH_2Cl_2 and the combined organic phases were washed with saturated $NaHCO_3$ (aq), brine, dried with $MgSO_4$, filtered and concentrated. The resulting crude oil was purified by dry column chromatography (EtOAc/heptane) yielding phenyl 2,2',3,3'-tetra-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-4'-*O*-(naphthalen-2-ylmethyl)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside, as a colorless amorphous solid (11.60 g, 81 %).

R_f 0.33 (3:7 EtOAc/heptane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, $^3J_{o,m}$ = 8.2 Hz, $^4J_{o,p}$ = 0.9 Hz, 2H, *ortho*^{Bz}), 7.94 (dd, $^3J_{o,m}$ = 8.3 Hz, $^4J_{o,p}$ = 1.0 Hz, 2H, *ortho*^{Bz}), 7.91 (dd, $^3J_{o,m}$ = 8.3 Hz, $^4J_{o,p}$ = 1.0 Hz, 2H, *ortho*^{Bz}), 7.76 (dd, $^3J_{o,m}$ = 8.3 Hz, $^4J_{o,p}$ = 1.1 Hz, 2H, *ortho*^{Bz}), 7.68 – 7.31 (m, 20H, *meta*^{Bz} ,*para*^{Bz}, meta^{Ph}, 1,4,5,6,7,8-H^{Nap}), 7.31 – 7.17 (m, 3H, *ortho*^{Ph}, *para*^{Ph}), 7.13 (dd, $^3J_{3,4}$ = 8.4 Hz, $^4J_{1,3}$ = 1.6 Hz, 1H, 3-H^{Nap}), 5.64 (t, $^3J_{2,3\sim3,4}$ = 9.4 Hz, 1H, H3), 5.58 (t, $^3J_{2,3\sim3,4}$ = 9.6 Hz, 1H, H3'), 5.32 (t, $^3J_{1,2\sim2,3}$ = 9.9 Hz, 1H, H2), 5.26 (dd, $^3J_{1,2}$ = 8.0 Hz, 1H, H2'), 4.92 (d, 1H, H1'), 4.79 (d, 1H, H1), 4.64 (d, ^2J = 11.2 Hz, 1H, CH_2^{Nap}), 4.54 (d, 1H, CH_2^{Nap}), 4.12 (t, $^3J_{3,4\sim4,5}$ = 9.5 Hz, 1H, H4), 3.86 – 3.64 (m, 3H, H4', H6a, H6b), 3.48 (dd, $^2J_{6a,6b}$ = 12.3 Hz, $^3J_{5,6a}$ = 1.5 Hz, 1H, H6a'), 3.42 – 3.25 (m, 3H, H5, H5', H6b'), 0.98 (s, 9H, CH_3^{tBu}), 0.13 (s, 6H, CH_3^{TBS}). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7/ 165.3/ 165.2/ 164.9 (C=O^{Bz}), 134.7 (*ipso*^{Ph}), 133.6/ 133.4/ 133.2/ 133.1/ 133.0/ 132.1/ 130.0/ 130.0/ 129.8/ 129.7/ 129.7/ 129.5/ 129.4/ 129.3/ 129.0/ 128.9/ 128.5/ 128.5/ 128.4/ 128.3/ 128.3/ 128.0/ 127.7/ 127.2/ 126.1/ 126.1/ 126.0 (C^{Bz}, C^{Nap}, C^{Ph}), 100.7 (C1'), 86.0 (C1), 79.8 (C5), 75.8/75.1/75.1/75.0/75.0 (C3', C4, C4', C5', CH_2^{Nap}), 74.8 (C3), 72.3 (C2'), 70.7 (C2), 61.2/61.0 (C6, C6'), 26.1 (CH_3^{tBu}), 18.5 ($C(CH_3)_3^{tBu}$), -4.83 (CH_3^{TBS}), -5.06 (CH_3^{TBS}).

Phenyl 2,2',3,3'-tetra-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-4'-*O*-(naphthalen-2-ylmethyl)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (9.24 g, 8.36 mmol) was dissolved in 400 mL CH_3CN and stirred at 22 °C before 14.6 mL 20 % HF (aq) were added. TLC (1:4 EtOAc/toluene) showed completion after two hours. The remaining HF was quenched by adding TMSOMe (46 mL, 330 mmol) and the resulting mixture was left stirring for 30 minutes. Afterwards, 200 mL of saturated $NaHCO_3$ (aq) were added and the resulting phases were separated. The aqueous phase was extracted twice with 300 mL CH_2Cl_2 and the combined organic phases were washed with brine, dried with $MgSO_4$ and filtered. After concentration the resulting crude was purified by dry chromatography (0:1→6:4 EtOAc/heptane) resulting in the title compound (**5a**) as a colorless amorphous solid (7.60 g, 91 %).

R_f 0.59 (1:1 EtOAc/heptane). **m.p.** 184.6-185.7 °C (EtOH/H_2O, uncorrected). **$[\alpha]_D^{22}$** = + 1.6 (*c* = 0.52, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{57}H_{50}NaO_{14}S^+$ (MNa^+) calculated: 1013.2813; found: 1013.2818. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.11 – 7.87 (m, 6H, *ortho*^{Bz}), 7.76 (dd, $^3J_{o,m}$ = 8.2 Hz, $^4J_{o,p}$ = 1.1 Hz, 2H, *ortho*^{Bz}), 7.69 – 7.27 (m, 20H, *meta*^{Bz} ,*para*^{Bz}, meta^{Ph}, 1,4,5,6,7,8-H^{Nap}), 7.26 – 7.06 (m, 4H, *ortho*^{Ph}, *para*^{Ph}, 3-H^{Nap}), 5.68 (t, $^3J_{2,3\sim3,4}$ = 9.3 Hz, 1H, H3), 5.63 (t, $^3J_{2,3\sim3,4}$ = 9.6 Hz, 1H, H3'), 5.38 (t, $^3J_{1,2\sim2,3}$ = 9.7 Hz, 1H, H2), 5.28 (dd, $^3J_{2,3}$ = 9.9 Hz, $^3J_{1,2}$ = 8.0 Hz, 1H, H2'), 4.88 (d, $^3J_{1,2}$ = 10.1 Hz, 1H, H1), 4.85 (d, 1H, H1'), 4.64 (d, ^2J = 11.3 Hz, 1H, CH_2^{Nap}), 4.55 (d, 1H, CH_2^{Nap}), 4.16 (t, $^3J_{3,4\sim4,5}$ = 9.5 Hz, 1H, H4), 3.80 (t, $^3J_{3,4\sim4,5}$ = 9.4 Hz, 1H, H4'), 3.79 – 3.59 (m, 2H, H6a, H6b), 3.45 (br d, 1H, H5), 3.41 – 3.20 (m, 3H, H5', H6a', H6b'). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.7/ 165.3/ 165.1/ 165.09 (C=O^{Bz}), 134.8/ 133.7/ 133.5/ 133.4/ 133.2/ 133.1/ 133.0/ 132.9/ 132.0/ 130.0/ 129.9/ 129.7/ 129.7/ 129.6/ 129.3/ 129.2/ 129.1/ 129.1/ 128.9/ 128.6/ 128.5/ 128.4/ 128.3/ 128.2/ 128.0/ 127.7/ 127.1/ 126.1/ 126.0 (C^{Bz}, C^{Nap}, C^{Ph}), 101.1 (C1'), 86.0 (C1), 79.2 (C5), 75.6 (C5'), 75.4 (C4), 75.0 (C4'), 74.9, 74.9 (C3', CH_2^{Nap}), 74.6 (C3), 72.3 (C2'), 70.7 (C2), 61.1 (C6'), 60.5 (C6). **IR** (neat, cm^{-1}) 3594, 3505 (br w, OH), 3061 (w, CH-sp^2), 2949, 2877 (w, CH-sp^3), 1728 (s, C=O), 1601, 1584, 1451 (w, C-C *aromatic*), 1271, 1091 (m, C-O).

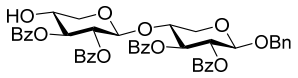


Phenyl 2,2',3,3'-tetra-*O*-benzoyl-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside (6a)

General method for dehydrogenative decarbonylation: Phenyl 2,2',3,3'-tetra-*O*-benzoyl-4'-*O*-(naphthalen-2-ylmethyl)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (**5a**) (0.2 mmol), $[Ir(cod)Cl]_2$ (30 µmol, 15 mol%), *racemic* BINAP (60 µmol) was added to an oven-dried schlenk flask, evacuated and filled with argon three times. Norbornene (0.44 mmol) and 2.0 mL mesitylene (saturated with H_2O, 150 ppm) were added. The flask was fitted with a cold-finger and a slow flow of argon through a syringe was allowed over the reflux ring. The flask was then lowered into a preheated oil bath (170 °C) and refluxed for 16 – 20h before the reaction was stopped by cooling the mixture to room temperature (23 °C). The reaction was purified by loading the reaction mixture directly on to a silica gel and using flash chromatography (1:4→1:2 EtOAc/heptane) yielded the title compound, **6a** as a yellowish amorphous solid (38-50 %).

R_f 0.38 (2:3 EtOAc/heptane). **$[\alpha]_D^{22}$** = + 31.8 (*c* = 0.925, acetone). **HRMS** (ESI-TOF) m/z for $C_{55}H_{46}NaO_{12}S^+$ (MNa^+) calculated: 953.2602; found: 953.2599. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.14 (m, 32H, H^{Bz}, H^{Nap}, H^{Ph}), 5.63 (t, $^3J_{2,3\sim3,4}$ = 7.9 Hz, 1H, H3), 5.52 (t, $^3J_{2,3\sim3,4}$ = 8.0 Hz, 1H, H3'), 5.31 (t, $^3J_{1,2\sim2,3}$ = 8.0 Hz, 1H, H2), 5.16 (dd, $^3J_{2,3}$ = 8.3 Hz, $^3J_{1,2}$ = 6.3 Hz, 1H, H2'), 4.98 (d, $^3J_{1,2}$ = 8.1 Hz, 1H, H1), 4.76 (d, 1H, H1'), 4.61 (d, ^2J = 12.2 Hz, 1H, CH_2^{Nap}), 4.57 (d, 1H, CH_2^{Nap}), 4.16 (dd, $^2J_{5a,5b}$ = 12.1 Hz, $^3J_{4,5a}$ = 4.8 Hz, 1H, H5a), 4.01 (td, $^3J_{3,4\sim4,5b}$ = 8.2 Hz, 1H, H4), 3.63 (dd, $^2J_{5a,5b}$ = 11.8 Hz, $^3J_{4,5a}$ 4.6 Hz, 1H, H5a'), 3.56 (td, $^3J_{3,4\sim4,5b}$ = 7.9, 1H, H4'), 3.48 (dd, $^3J_{4,5b}$ = 8.5 Hz, 1H, H5b), 3.23 (dd, $^3J_{4,5b}$ = 8.1 Hz, 1H, H5b'). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7/ 165.5/ 165.4/ 165.2 (C=O^{Bz}), 135.0 (*ipso*^{Ph}), 133.4/ 133.3/ 133.2/ 133.2/ 133.1/ 132.9/ 132.6/ 130.1/ 129.9/ 129.9/ 129.8/ 129.7/ 129.5/ 129.5/ 129.3/ 129.1/ 128.6/ 128.5/ 128.5/ 128.4/ 128.4/ 128.2/ 128.0/ 127.8/ 126.8/ 126.3/ 126.1/ 125.7 (C^{Bz}, C^{Nap}, C^{Ph}), 101.3 (C1'), 86.8 (C1), 75.9 (C4), 74.2 (C4'), 73.1 (C3), 72.8 (CH_2^{Nap}), 72.4 (C3'), 71.4 (C2'), 70.5 (C2),

65.8 (C5), 62.8 (C5'). **IR** (neat, cm^{-1}) 3061 (w, CH-sp^2), 2945, 2865 (w, CH-sp^3), 1728 (s, C=O), 1601, 1584, 1451 (w, C-C *aromatic*), 1266, 1069 (m, C-O).

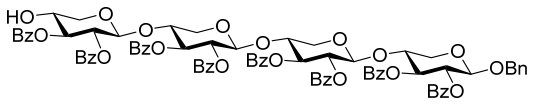


Benzyl 2,2',3,3'-tetra-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-β-D-xylopyranoside (11a)

The starting material phenyl 2,2',3,3'-tetra-*O*-benzoyl-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside, **6a** (196 mg, 0.211 mmol) was evacuated under vacuum in flame-dried glassware for a couple of hours. Then refilled with argon and dissolved in 6 mL dry CH_2Cl_2, before BnOH (27 µL, 0.26 mmol) and NIS (54 mg, 0.24 mmol) were added. The resulting mixture was stirred for 10 minutes at 22 °C and then cooled to -30 °C before TMSOTf (4.0 µL) was added slowly. After stirring for 30 minutes, TLC (1:9 EtOAc/toluene) showed very little conversion and the temperature was raised to -20 °C. After 2 hours of maintaining the temperature, TLC showed completion and the reaction mixture was neutralized with Et_3N. The resulting mixture was then diluted with CH_2Cl_2 and washed with 10 % $Na_2S_2O_3$ (aq), the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered and concentrated. The resulting crude product was purified by column chromatography (0:1→1:19 EtOAc/toluene) to give the desired β-product as a white amorphous solid (108 mg, 55 %) and the α-product as a minor (32.8 mg, 17 %).

The β-product (101 mg, 0.109 mmol) was dissolved in 2.5 mL (1:9) H_2O/CH_2Cl_2 and stirred vigorously at 22 °C. DDQ (50 mg, 0.22 mmol) was added to the mixture and shielded from the light with aluminium foil. After 4 hours TLC showed full conversion and the reaction mixture was diluted with 5 mL CH_2Cl_2 and washed with 5 mL of a mixture containing 0.7 % ascorbic acid, 1.5 % citric acid and 1.0 % NaOH in H_2O. The aqueous phase was extracted twice with 5 mL CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered, concentrated and purified by flash chromatography (1:9 EtOAc/toluene). This yielded the title compound as a colorless amorphous solid, **11a** (84 mg, 54 %, over two steps). The compound analyses were in accordance with data from literature.[4]

HRMS (ESI-TOF) m/z for $C_{45}H_{40}NaO_{13}^+$ (MNa^+) calculated: 811.2361; found: 811.2366. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 7.84 (m, 8H, *ortho*^{Bz}), 7.67 – 7.30 (m, 12H, *meta*^{Bz}, *para*^{Bz}, H^{Nap}), 7.25 – 7.07 (m, 5H, H^{Bn}), 5.58 (dd, $^3J_{2,3}$ = 8.5 Hz, $^3J_{3,4}$ = 7.8 Hz, 1H, H3), 5.34 (dd, $^3J_{1,2}$ = 6.7 Hz, 1H, H2), 5.26 (dd, $^3J_{2,3}$ = 8.1 Hz, $^3J_{1,2}$ = 6.1 Hz, 1H, H2'), 5.18 (dd, $^3J_{3,4}$ = 7.1 Hz, 1H, H3'), 4.82 (d, ^2J = 12.5 Hz, 1H, CH_2^{Bn}), 4.80 (d, 1H, H1'), 4.67 (d, 1H, H1), 4.57 (d, 1H, CH_2^{Bn}), 4.11 – 3.95 (m, 2H, H4, H5a), 3.81 – 3.59 (m, 2H, H4', H5a'), 3.58 – 3.34 (m, 1H, H5b), 3.29 – 3.08 (m, 1H, H5b'), 2.95 (d, $^3J_{4,OH}$ = 5.6 Hz, 1H, OH4'). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2/ 165.6/ 165.4/ 165.1 ($C{=}O^{Bz}$), 136.9/ 133.8/ 133.6/ 133.3/ 133.2/ 130.1/ 130.1/ 129.8/ 129.8/ 129.8/ 129.6/ 129.2/ 128.9/ 128.7/ 128.6/ 128.5/ 128.5/ 128.4/ 128.0/ 127.9 (C^{Bn}, C^{Bz}), 101.1 (C1'), 99.5 (C1), 76.3 (C4), 75.5 (C3'), 72.3 (C3), 71.2 (C2), 70.8 (C2'), 70.5 (CH_2^{Bn}), 68.5 (C4'), 64.5 (C5'), 62.8 (C5). **IR** (neat, cm^{-1}) 3465 (w, OH), 3062 (w, CH-sp^2), 2926, 2859 (w, CH-sp^3), 1729 (s, C=O), 1602, 1584, 1452 (w, C-C *aromatic*), 1273, 1070 (m, C-O).



Benzyl *O*-(2,3-di-*O*-benzoyl-β-D-xylopyranosyl)-(1→4)-*O*-bis[(2,3-di-*O*-benzoyl-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-benzoyl-β-D-xylopyranoside (12a)

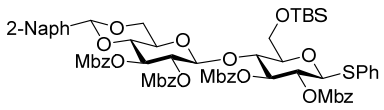
The donor, phenyl 2,2',3,3'tetra-*O*-benzoyl-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside **6a** (110 mg, 0.118 mmol), and the acceptor, benzyl 2,2',3,3'-tetra-*O*-benzoyl-β-D-xylopyranosyl-(1⟶4)-β-D-xylopyranoside **11a** (84.3 mg, 0.107 mmol), were weighed in the same flame-dried flask and co-evaporated three times with toluene, left under vacuum to dry completely and refilled with argon. This mixture was dissolved in 4.5 mL of dry CH_2Cl_2. NIS (28.8 mg, 0.128 mmol) was added and the resulting mixture was left stirring at 22 °C for 15 minutes. Hereafter the mixture was cooled to 0 °C, before adding 0.25 mL of diluted trifluoromethanesulfonic acid in CH_2Cl_2 (5.0 µL to 5.0 mL dry CH_2Cl_2). TLC (1:4 EtOAc/toluene) showed full conversion of the donor after 30 minutes. The mixture was allowed to stir for additional 20 minutes before the reaction was neutralized with Et_3N (15 µL). The neutralized mixture was diluted with 5 mL CH_2Cl_2, washed with 10 % $Na_2S_2O_3$ (aq) and the aqueous phase extracted twice with 5 mL CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered, concentrated and purified by flash chromatography (1:19⟶1:4 EtOAc/toluene) to yield as a colorless powder (114 mg, 66 %).

$[\alpha]_D^{22}$ = + 13.9 (*c* = 0.778, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{94}H_{80}NaO_{25}^+$ (MNa^+) calculated: 1631.4881; found: 1631.4875. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.11 (m, 52H, H^{Bn}, H^{Bz}, H^{Nap}), 5.51 (dd, $^3J_{2,3}$ = 8.3 Hz, $^3J_{3,4}$ = 7.7 Hz, 1H, $H3^I$), 5.48 – 5.42 (m, 2H, $H3^{III}$, $H3^{IV}$), 5.41 (t, $^3J_{2,3\sim3,4}$ = 8.1 Hz, 1H, $H3^{II}$), 5.28 (dd, $^3J_{1,2}$ = 6.7 Hz, 1H, $H2^I$), 5.11 (dd, $^3J_{2,3}$ = 8.3 Hz, $^3J_{1,2}$ = 6.4 Hz, 1H, $H2^{II}$), 5.06 (dd, $^3J_{2,3}$ = 9.0 Hz, $^3J_{1,2}$ = 5.7 Hz, 1H, $H2^{IV}$), 5.05 (dd, $^3J_{2,3}$ = 9.0 Hz, $^3J_{1,2}$ = 5.8 Hz, 1H, $H2^{III}$), 4.79 (d, ^2J = 12.3 Hz, 1H, CH_2^{Bn}), 4.67 (d, 1H, $H1^{II}$), 4.62 (d, 1H, $H1^I$), 4.59 (d, ^2J = 12.1 Hz, 1H, CH_2^{Nap}), 4.54 (br d, 2H, CH_2^{Bn}, CH_2^{Nap}), 4.51 (d, 1H, $H1^{IV}$), 4.44 (d, 1H, $H1^{III}$), 4.03 – 3.87 (m, 2H, H4, $H5a^I$), 3.80 – 3.63 (m, 2H, $H4^{III}$, $H4^{IV}$), 3.60 – 3.47 (m, 2H, $H4^{II}$, $H5a^{II}$), 3.45 – 3.29 (m, 3H, H5b, $H5a^{III}$, $H5a^{IV}$), 3.14 (m, 1H, $H5b^{II}$), 3.05 (dd, $^2J_{5a,5b}$ = 12.2 Hz, $^3J_{4,5b}$ = 8.7 Hz, 1H, $H5b^{IV}$), 3.01 (dd, $^2J_{5a,5b}$ = 12.2 Hz, $^3J_{4,5b}$ = 8.6 Hz, 1H, $H5b^{III}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7/ 165.5/ 165.4/ 165.4/ 165.3/ 165.1/ 165.1/ 165.0 ($C{=}O^{Bz}$), 136.9/ 134.9/ 133.4/ 133.3/ 133.2/ 133.2/ 133.1/ 130.0/ 129.9/ 129.9/ 129.9/ 129.8/ 129.8/ 129.7/ 129.7/ 129.7/ 129.6/ 129.6/ 129.4/ 129.4/ 129.3/ 128.6/ 128.5/ 128.5/ 128.4/ 128.4/ 128.4/ 128.3/ 128.3/ 128.3/ 128.0/ 127.9/ 127.9/127.8/126.8/126.2/126.1/125.7 (C^{Bn}, C^{Bz}, C^{Nap}), 101.1 ($C1^{II}$), 100.9 ($C1^{IV}$), 100.7 ($C1^{III}$), 99.4 ($C1^I$), 76.1 ($C4^I$), 75.6/ 75.4 ($C4^{III}$, $C4^{IV}$), 74.2 ($C4^{II}$), 72.7 (CH_2^{Nap}), 72.4/72.3/72.2/72.2 ($C3^I$, $C3^{II}$, $C3^{III}$, $C3^{IV}$), 71.5 ($C2^{II}$), 71.3/71.3 ($C2^{III}$, $C2^{IV}$), 71.1 ($C2^I$), 70.4 (CH_2^{Bn}), 62.8/62.7 ($C5^I$, $C5^{II}$), 62.4/62.4 ($C5^{III}$, $C5^{IV}$). **IR** (neat, cm^{-1}) 3062 (w, CH-sp^2), 2946, 2866 (w, CH-sp^3), 1729 (s, C=O), 1601, 1584, 1452 (w, C-C *aromatic*), 1268, 1070 (m, C-O).

The starting material benzyl *O*-(2,3-di-O-benzoyl-4-*O*-(naphthalene-2-metyl)-β-D-xylopyranosyl)-(1→4)-*O*-bis[(2,3-di-*O*-benzoyl-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-benzoyl-β-D-xylopyranoside (113 mg, 70.2 µmol) was dissolved in 1.5 mL 1:9 H_2O/CH_2Cl_2 and stirred vigorously at 23 °C. DDQ (32 mg, 0.14 mmol) was added to the mixture and shielded from the light covering the flask with aluminium foil. After 4 hours, TLC showed full conversion and the reaction mixture was diluted with 5 mL CH_2Cl_2 and washed with 10 mL of a mixture containing 0.7 % ascorbic acid, 1.5 % citric acid and 1.0 % NaOH in H_2O. The aqueous phase was extracted twice with 5 mL CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered, concentrated and purified by flash

chromatography (1:19→1:3 EtOAc/toluene). This yielded the title compound **12a** as a colorless amorphous solid (92.1 mg, 89 %) with an appearance of colorless flakes.

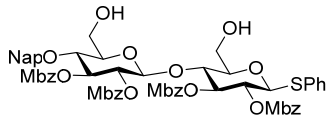
HRMS (ESI-TOF) m/z for $C_{83}H_{72}NaO_{25}^+$ (MNa^+) calculated: 1491.4255; found: 1491.4266. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.28 (m, 37H, H^{Bz}), 7.25 – 7.09 (m, 8H, H^{Bn}, *meta*^{Bz}), 5.51 (dd, $^3J_{2,3}$ = 8.4 Hz, $^3J_{3,4}$ = 7.7 Hz, 1H, $H3^{I}$), 5.45 (t, $^3J_{2,3\sim3,4}$ = 8.1 Hz, 1H, $H3^{II}$), 5.43 (t, $^3J_{2,3\sim3,4}$ = 8.3 Hz, 1H, $H3^{III}$), 5.28 (dd, $^3J_{1,2}$ = 6.7 Hz, 1H, $H2^{I}$), 5.15 (dd, $^3J_{2,3}$ = 8.1 Hz, $^3J_{1,2}$ = 6.0 Hz, 1H, $H2^{IV}$), 5.11 (dd, $^3J_{2,3}$ = 8.3 Hz, $^3J_{1,2}$ = 6.4 Hz, 1H, $H2^{II}$), 5.09 (dd, $^3J_{3,4}$ = 7.1 Hz, 1H, $H3^{IV}$), 5.07 (dd, $^3J_{2,3}$ = 8.5 Hz, $^3J_{1,2}$ = 6.5 Hz, 1H, $H2^{III}$), 4.79 (d, ^2J = 12.3 Hz, 1H, CH_2^{Bn}), 4.68 (d, 1H, $H1^{II}$), 4.62 (d, 1H, $H1^{I}$), 4.54 (d, 1H, $H1^{IV}$), 4.54 (d, 1H, CH_2^{Bn}), 4.46 (d, 1H, $H1^{III}$), 4.04 – 3.89 (m, 2H, H4, $H5a^{I}$), 3.75 (td, $^3J_{3,4\sim4,5b}$ = 8.2 Hz, $^3J_{4,5a}$ = 4.8 Hz, 1H, $H4^{III}$), 3.74 – 3.66 (m, 2H, $H4^{II}$, $H4^{IV}$), 3.63 (dd, $^2J_{5a,5b}$ = 12.0 Hz, $^3J_{4,5a}$ = 4.5 Hz, 1H, $H5a^{IV}$), 3.47 – 3.29 (m, 3H, $H5a^{II}$, $H5a^{III}$, $H5b^{I}$), 3.10 (dd, $^3J_{4,5b}$ = 7.6 Hz, 1H, $H5b^{IV}$), 3.06 (dd, $^2J_{5a,5b}$ = 12.3 Hz, $^3J_{4,5b}$ = 8.7 Hz, 1H, $H5b^{II}$), 3.02 (dd, $^2J_{5a,5b}$ = 12.2 Hz, $^3J_{4,5b}$ = 8.8 Hz, 1H, $H5b^{III}$), 2.91 (d, $^3J_{4,OH}$ = 5.5 Hz, 1H, $4^{IV}OH$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2/ 165.5/ 165.4/ 165.3/ 165.1/ 165.0/ 164.9 ($C{=}O^{Bz}$), 136.9/ 133.8/ 133.6/ 133.4/ 133.4/ 133.3/ 133.2/ 133.1/ 130.1/ 130.0/ 129.9/ 129.9/ 129.8/ 129.7/ 129.7/ 129.6/ 129.6/ 129.4/ 129.3/ 129.2/ 128.8/ 128.7/ 128.6/ 128.6/ 128.6/ 128.5/ 128.4/ 128.4/ 128.3/ 128.3/ 127.9/ 127.9 (C^{Bn}, C^{Bz}), 101.1 ($C1^{II}$), 100.9 ($C1^{III}$), 100.7 ($C1^{IV}$), 99.4 ($C1^{I}$), 76.1 ($C4^{I}$), 75.7/ 75.6/ 75.5 ($C4^{II}$, $C4^{III}$, $C3^{IV}$), 72.3/ 72.2/ 72.2 ($C3^{I}$, $C3^{II}$, $C3^{III}$), 71.5/ 71.4 ($C2^{II}$, $C2^{III}$), 71.1 ($C2^{I}$), 70.6 ($C5^{IV}$), 70.4 (CH_2^{Bn}), 68.5 ($C4^{IV}$), 64.4 ($C5^{IV}$), 62.7 ($C5^{I}$), 62.5/62.4 ($C5^{II}$, $C5^{III}$). **IR** (neat, cm^{-1}) 3427 (br w, OH), 3066 (w, CH-sp^2), 2923, 2853 (w-m, CH-sp^3), 1730 (s, C=O), 1601, 1584, 1452 (w, C-C *aromatic*), 1272, 1070 (m, C-O).



Phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-6-*O*-*tert*-butyldimethylsilyl-4',6'-*O*-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (4b)

Phenyl 2,2',3,3'-tetra-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-4',6'-*O*-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside **4a** (18.42 g, 16.7 mmol) was dissolved in a solution of $NaOCH_3$ in CH_3OH (250 mL, 700 mg Na). CH_3CN (50 mL) was added and reaction mixture was heated to 60 °C for 1.5 h when TLC indicated full conversion of the starting material. The reaction mixture was neutralized with Amberlite™ IR120 (H), filtered, concentrated and purified by flash chromatography (1:19 CH_3OH/CH_2Cl_2) yielding a colorless amorphous compound (10.0 g, 87 %). This was co-evaporated with toluene and dissolved in dry CH_2Cl_2 (80 mL) and cooled in an ice bath. Pyridine (20 mL) and 4-methoxybenzoyl chloride (12.5 g) were added and allowed to stir for 10 minutes before DMAP (800 mg) was added. The resulting mixture was stirred overnight and cooled before additional DMAP (800 mg) and 4-methoxybenzoyl chloride were added at 0 °C, after one hour no change was observed on TLC and the remaining 4-methoxybenzoyl chloride was quenched by slow addition of CH_3OH (5 mL). The mixture was washed with H_2O (100 mL) and the aqueous phase extracted two times with CH_2Cl_2 (2x100 mL). The organic phases were combined and washed two times with 1M HCl, H_2O, 1M HCl, H_2O and brine, dried with $MgSO_4$, filtered and concentrated to give crude colorless oil. After flash chromatography (1:19, EtOAc/toluene) the title compound **4b** was isolated as a colorless amorphous solid (13.87 g, 78 %).

R_f 0.41 (1:9 EtOAc/toluene). **$[\alpha]_D^{22}$** = + 36.6 (*c* = 0.815, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{67}H_{70}NaO_{18}SSi^+$ (MNa^+) calculated: 1245.3944; found: 1245.3943. **^{1}H NMR** (400 MHz, C_6D_6) δ 8.30 – 8.07 (m, 8H, 2,6-H^{Mbz}), 7.80 (br s, 1H, 1-H^{Naph}), 7.57 – 7.35 (m, 6H, H^{Naph}, *meta*^{Ph}), 7.14 – 6.89 (m, 5H, H^{Naph}, *ortho*^{Ph}, *para*^{Ph}), 6.69 – 6.43 (m, 8H, 3,5-H^{Mbz}), 6.15 (t, $^3J_{2,3\sim3,4}$ = 9.4 Hz, 1H, H3'), 6.08 (t, $^3J_{2,3\sim3,4}$ = 9.4 Hz, 1H, H3), 5.95 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{1,2}$ = 7.8 Hz, 1H, H2'), 5.80 (t, $^3J_{1,2\sim2,3}$ = 9.8 Hz, 1H, H2), 5.22 (d, 1H, H1'), 5.16 (s, 1H, CH^{Naph}), 4.64 (d, $^3J_{1,2}$ = 10.1 Hz, 1H, H1), 4.35 (t, $^3J_{3,4\sim4,5}$ = 9.5 Hz, 1H, H4), 3.98 (dd, $^2J_{6a,6b}$ = 10.6 Hz, $^3J_{5,6a}$ = 4.9 Hz, 1H, H6a'), 3.94 (dd, $^2J_{6a,6b}$ = 11.7 Hz, $^3J_{5,6a}$ = 3.1 Hz, 1H, H6a), 3.73 – 3.60 (m, 2H, H5', H6b), 3.55 (t, $^3J_{3,4\sim4,5}$ = 9.4 Hz, 1H, H4'), 3.25 – 3.13 (m, 1H, H6'b), 3.13 (s, 3H, CH_3^{Mbz}), 3.08 (s, 3H, CH_3^{Mbz}), 3.08 (s, 3H, CH_3^{Mbz}), 3.01 (s, 3H, CH_3^{Mbz}), 2.98 (br d, 1H, H5), 1.00 (s, 9H, (CH_3^{tBu}), 0.15 (s, 3H, CH_3^{TBS}), 0.14 (s, 3H, CH_3^{TBS}).**^{13}C NMR** (101 MHz, C_6D_6) δ 165.6/ 165.4/ 165.1/ 165.0 (C=O^{Mbz}), 164.1/ 163.9/ 163.8/ 163.8 (1-C^{Mbz}), 135.0 (*ipso*^{Ph}), 134.0/ 133.4/ 133.3 (2,4a,8a-C^{Naph}), 133.1 (*meta*^{Ph}), 132.5/ 132.3/ 132.2 (2,6-C^{Mbz}), 129.0 (*ortho*^{Ph}), 128.7/ 128.4/ 128.2/ 127.9/ 127.9/ 126.3/ 126.3/ 126.1/ 124.4 (*para*^{Ph}, C^{Naph}), 123.3/ 122.6/ 122.4/ 122.3 (4-C^{Mbz}), 114.3/ 114.1/ 113.9 (3,5-C^{Mbz}), 102.2 (C1'), 101.8 (CH^{Naph}), 86.2 (C1), 79.8 (C5), 78.8 (C4'), 76.4 (C4), 74.9 (C3), 73.2 (C2'), 72.7 (C3'), 71.2 (C2), 68.6 (C6'), 67.2 (C5'), 61.6 (C6), 54.8/54.8/54.8/54.7 (CH_3^{Mbz}), 26.2 (CH_3^{tBu}), 18.6 ($C(CH_3)_3^{tBu}$), -4.7 (CH_3^{TBS}), -5.0 (CH_3^{TBS}).

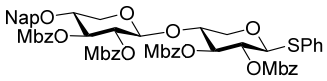


Phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-4'-*O*-(naphthalen-2-ylmethyl)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside (5b)

Phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-6-O-tert-butyldimethylsilyl-4',6'-O-(naphthalen-2-ylmethylidene)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside **4b** (14.55 g, 11.89 mmol) was dissolved in 150 mL dry CH_2Cl_2 and cooled in an ice bath. Then 1 M BH_3·THF (54 mL) was slowly added to the cooled solution and allowed to stir for 15 minutes before adding $Cu(OTf)_2$ (860 mg). After addition, effervescence was observed and the solution turned to a brown-black suspension. When TLC showed completion (overnight), the reaction mixture was neutralized with Et_3N and the remaining BH_3 was quenched by slow addition of CH_3OH (*strong effervescence!*). The reaction mixture was filtered through a pad of celite, washed with H_2O and phases separated. The aqueous phase was extracted twice with CH_2Cl_2 and the combined organic phases were washed with saturated $NaHCO_3$ (aq), brine, dried with $MgSO_4$, filtered and concentrated. The resulting crude oil was dissolved in 450 mL CH_3CN and stirred at 22 °C before 20 % HF (aq, 8.2 mL) was added. When TLC (1:4 EtOAc/toluene) showed full conversion (five hours) the remaining HF was quenched by addition of TMSOMe (65 mL, 476 mmol) and the resulting mixture was stirred for 30 minutes. Afterwards it was diluted with CH_2Cl_2 (250 mL) before 100 mL of saturated $NaHCO_3$ (aq) was added and the resulting phases were separated. The aqueous phase was extracted twice with 150 mL CH_2Cl_2 and the combined organic phases were washed with brine, dried with $MgSO_4$, filtered and concentrated. The resulting crude material was purified by flash chromatography (4:6 EtOAc/toluene) from this a by-product without the naphthalene-2-ylmethyl group was isolated, phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-

β-D-glucopyranosyl-(1⟶4)-1-thio-β-D-glucopyranoside (3.40 g, 29 %) and the title compound **5b** as a colorless amorphous solid (6.30 g, 48 % over two steps).

R_f 0.37 (1:1 EtOAc/toluene). **$[\alpha]_D^{22}$** = + 59.9 (*c* = 0.950, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{61}H_{58}NaO_{18}S^+$ (MNa^+) calculated: 1133.3236; found: 1133.3230. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, $^3J_{2,3=5,6}$ = 8.9 Hz, 2H, 2,6-H^{Mbz}), 7.88 (dd, $^3J_{2,3=5,6}$ = 8.9 Hz, $^4J_{2,4=4,6}$ = 1.7 Hz, 4H, 2,6-H^{Mbz}), 7.68 (d, $^3J_{2,3=5,6}$ = 8.9 Hz, 2H, 2,6-H^{Mbz}), 7.65 – 7.57 (m, 2H, 5,8-H^{Nap}), 7.51 (d, $^3J_{3,4}$ = 8.4 Hz, 1H, 4-H^{Nap}), 7.48 (br s, 1H, 1-H^{Nap}), 7.44 – 7.32 (m, 4H, *meta*^{Ph}, 6,7-H^{Nap}), 7.30 – 7.19 (m, 3H, *ortho*^{Ph}, *para*^{Ph}), 7.15 (dd, $^4J_{1,3}$ = 1.5 Hz, 1H, 3-H^{Nap}), 6.93 – 6.77 (m, 6H, 3,5-H^{Mbz}), 6.66 (d, 2H, 3,5-H^{Mbz}), 5.64 (t, $^3J_{2,3\sim3,4}$ = 9.3 Hz, 1H, H3), 5.57 (t, $^3J_{2,3\sim3,4}$ = 9.6 Hz, 1H, H3'), 5.31 (t, $^3J_{1,2\sim2,3}$ = 9.7 Hz, 1H, H2), 5.23 (dd, $^3J_{2,3}$ = 9.8 Hz, $^3J_{1,2}$ = 8.0 Hz, 1H, H2'), 4.87 (d, $^3J_{1,2}$ = 10.0 Hz, 1H, H1), 4.83 (d, 1H, H1'), 4.65 (d, ^2J = 11.3 Hz, 1H, CH_2^{Nap}), 4.56 (d, 1H, CH_2^{Nap}), 4.11 (t, $^3J_{3,4\sim4,5}$ = 9.4 Hz, 1H, H4'), 3.83 (s, 3H, CH_3^{Mbz}), 3.81 (s, 3H, CH_3^{Mbz}), 3.80 (s, 3H, CH_3^{Mbz}), 3.79 – 3.71 (m, 4H, CH_3^{Mbz}, H6a), 3.68 (dd, $^2J_{6a,6b}$ = 12.4 Hz, $^3J_{5,6b}$ = 2.7 Hz, 1H, H6b), 3.45 (dt, $^3J_{4,5\sim5,6a}$ = 9.5 Hz, 1H, H5), 3.40 (d, $^3J_{5,6}$ = 2.3 Hz, 2H, H6'), 3.34 (dt, 1H, H5'). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2/ 164.9/ 164.8/ 164.6 (C=O^{Mbz}), 163.7/ 163.6/ 163.5/ 163.3 (1-C^{Mbz}), 134.8 (*ipso*^{Ph}), 133.0/ 132.9 (3,4a/8a-C^{Nap}), 132.6 (*meta*^{Ph}), 132.2 (4a/8a-C^{Nap}), 132.0/ 131.8/ 131.6/ 131.6 (2,6-C^{Mbz}), 129.0 (*ortho*^{Ph}), 128.2 (*para*^{Ph}), 128.1 (4-C^{Nap}), 127.9/ 127.6 (5,8-C^{Nap}), 126.9 (1-C^{Nap}), 126.0 (3-C^{Nap}), 125.9/ 125.7 (6,7-C^{Nap}), 121.8/ 121.6/ 121.5/ 121.4 (4-C^{Mbz}), 114.0/ 113.7/ 113.7/ 113.4 (3,5-C^{Mbz}), 101.2 (C1'), 86.0 (C1'), 79.1 (C5), 75.6 (C4'), 75.5 (C5'), 75.1 (C4), 74.7 (CH_2^{Nap}), 74.4 (C3'), 74.3 (C3), 72.0 (C2'), 70.4 (C2), 61.0 (C6'), 60.6 (C6), 55.5/ 55.4/ 55.4/ 55.3 (CH_3^{Mbz}).

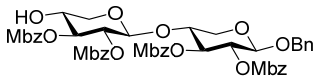


Phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside (6b)

Phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-4'-*O*-(naphthalen-2-ylmethyl)-β-D-glucopyranosyl-(1→4)-1-thio-β-D-glucopyranoside **5b** (5.03 g, 4.53 mmol), $[Ir(cod)Cl]_2$ (456 mg, 0.679 mmol) and *racemic* BINAP (847 mg, 1.36 mmol) were added to a oven-dried schlenk flask and suspended in a solution of norbornene (0.94 g, 10 mmol) in 45 mL mesitylene (saturated with H_2O, 150 ppm). The resulting mixture was subjected to 9 freeze-pump-thaw cycles, the flask was fitted with a cold-finger and lowered into a preheated oil bath (170 °C) and refluxed. A gentle flow of argon through a syringe was allowed over the reflux ring. After TLC showed full conversion of the starting material, the reaction was stopped by cooling the mixture to room temperature (23 °C). The reaction was purified by loading the reaction mixture directly on to silica gel and using flash chromatography (1:99→1:49 Et_2O/CH_2Cl_2) yielded the title compound **6b** as a yellow amorphous solid (1.66 g, 35%).

R_f 0.54 (3:7 EtOAc/toluene). **$[\alpha]_D^{22}$** = + 73.2 (*c* = 1.05, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{59}H_{54}NaO_{16}S^+$ (MNa^+) calculated: 1073.3025; found: 1073.2999. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, $^3J_{2,3=5,6}$ = 8.7 Hz, 2H, 2,6-H^{Mbz}), 7.93 (d, $^3J_{2,3=5,6}$ = 8.5 Hz, 2H, 2,6-H^{Mbz}), 7.84 (d, $^3J_{2,3=5,6}$ = 8.8 Hz, 2H, 2,6-H^{Mbz}), 7.84 (d, $^3J_{2,3=5,6}$ = 8.9 Hz, 2H, 2,6-H^{Mbz}), 7.78 – 7.71 (m, 1H, 5-H^{Nap}), 7.68 – 7.56 (m, 3H, 1,4,8-H^{Nap}), 7.47 – 7.37 (m, 4H, 6,7-H^{Nap}, *meta*^{Ph}), 7.32 – 7.20 (m, 4H, 3-H^{Nap}, *ortho*^{Ph}, *para*^{Ph}), 6.90 – 6.77 (m, 6H, 3,5-H^{Mbz}), 6.72 (d, $^3J_{2,3=5,6}$ = 8.8 Hz, 2H, 3,5-H^{Mbz}), 5.59 (t, $^3J_{2,3\sim3,4}$ = 7.8 Hz, 1H, H3), 5.48 (t, $^3J_{2,3\sim3,4}$ = 7.5 Hz, 1H, H3'), 5.27 (t, $^3J_{1,2\sim2,3}$ = 7.9 Hz, 1H, H2), 5.11 (dd, $^3J_{1,2}$

= 5.8 Hz, 1H, H2'), 4.98 (d, 1H, H1), 4.78 (d, 1H, H1'), 4.65 (d, ^{2}J = 12.0 Hz, 1H, CH_2^{Nap}), 4.58 (d, 1H, CH_2^{Nap}), 4.18 (dd, $^{2}J_{5a,5b}$ = 12.1 Hz, $^{3}J_{4,5a}$ = 4.6 Hz, 1H, H5a), 4.01 (t, $^{3}J_{3,4\sim4,5b}$ = 8.0 Hz, 1H, H4), 3.84 (s, 3H, CH_3^{Mbz}), 3.83 (s, 3H, CH_3^{Mbz}), 3.82 (s, 3H, CH_3^{Mbz}), 3.79 – 3.71 (m, 4H, H5a', CH_3^{Mbz}), 3.57 (td, $^{3}J_{4,5a}$ = 7.4 Hz, $^{3}J_{4,5b}$ = 4.4 Hz, 1H, H4'), 3.50 (dd, 1H, H5b), 3.30 (dd, $^{2}J_{5a,5b}$ = 12.0 Hz, 1H, H5b'). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3/ 165.2/ 165.0/ 164.9 ($C{=}O^{Mbz}$), 163.7/ 163.7/ 163.6 ($1\text{-}C^{Mbz}$), 135.1 (*ipso*^{Ph}), 133.2/ 133.1 (2,4a,8a-C^{Nap}), 132.5 (*meta*^{Ph}), 132.2/ 132.1/ 132.0/ 132.0 ($2,6\text{-}C^{Mbz}$), 129.1 (*ortho*^{Ph}), 128.3 ($4\text{-}C^{Nap}$), 128.1 ($8\text{-}C^{Nap}$), 128.0 (*para*^{Ph}), 127.7 ($5\text{-}C^{Nap}$), 126.8 ($1\text{-}C^{Nap}$), 126.1/ 126.0 ($6,7\text{-}C^{Nap}$), 125.8 ($3\text{-}C^{Nap}$), 122.1/ 121.9/ 121.9/ 121.7 ($4\text{-}C^{Mbz}$), 113.7 ($3,5\text{-}C^{Mbz}$), 100.7 (C1'), 86.9 (C1), 75.4 (C4), 74.1 (C4'), 72.8 (C3), 72.6 (CH_2^{Nap}), 71.4 (C3'), 70.8 (C2'), 70.3 (C2), 65.7 (C5), 62.5 (C5'), 55.6 (3C), 55.5 (CH_3^{Mbz}).



Benzyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-β-D-xylopyranoside (11b)

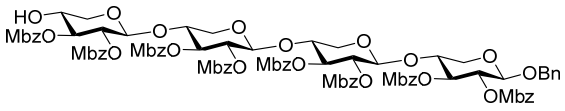
The starting material, phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside **6b** (353 mg, 0.336 mmol) was dissolved in 6 mL dry CH_2Cl_2, then BnOH (69 µL, 0.67 mmol) and 250 mg 4Å MS were added. The resulting mixture was stirred for one hour at 22 °C and then cooled to -75 °C for 30 minutes, before NIS (227 mg, 1.01 mmol) and TfOH (6.0 µL, 67 µmol) were added. The temperature of the acetone bath was slowly raised and, at -40 °C, a color change was observed and the reaction mixture was kept at this temperature for two hours. The resulting mixture was then diluted with CH_2Cl_2 and washed with a solution of 10 % $Na_2S_2O_3$ (aq)/saturated $NaHCO_3$ (1:1), the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered and concentrated.

The resulting amorphous solid was dissolved in 7.5 mL (1:9) H_2O/CH_2Cl_2 and stirred vigorously at 22 °C. DDQ (190 mg, 0.84 mmol) was added to the mixture and shielded from the light covering the flask with aluminium foil. After 4 hours, TLC showed full conversion and the reaction mixture was diluted with 15 mL CH_2Cl_2 and washed with 15 mL of a mixture containing 0.7 % ascorbic acid, 1.5 % citric acid and 1.0 % NaOH in H_2O. The aqueous phase was extracted twice with 15 mL CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered, concentrated and purified by flash chromatography (1:19⟶1:4 EtOAc/toluene). This yielded a colorless amorphous solid as mixture of anomers (240 mg, 1:2 α/β, 79 %, over two steps). The mixture was separated using column chromatography (1:19⟶3:17 Et_2O/CH_2Cl_2), the factions containing the β compound gave a colorless amorphous solid **11b** (65 mg, 1:6 α/β, 21 %)

R_f 0.27 (3:17 Et_2O/CH_2Cl_2). **$[\alpha]_D^{22}$** = – 89 (*c* = 0.26, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{49}H_{48}NaO_{17}^{+}$ (MNa^{+}) calculated: 931.2784; found: 931.2776.

α-anomer *inter alia:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.96 (dd, $^{3}J_{2,3}$ = 10.1 Hz, $^{3}J_{3,4}$ = 9.2 Hz, 1H, H3), 5.15 (d, $^{3}J_{1,2}$ = 3.6 Hz, 1H, H1), 5.03 (dd, 1H, H2), 4.71 (d, ^{2}J = 12.6 Hz, 1H, CH_2^{Bn}), 4.45 (d, 1H, CH_2^{Bn}), 4.09 – 4.01 (m, 1H, H4), 3.80 – 3.72 (m, 1H, H5a), 3.69 – 3.62 (m, 1H, H5b). **^{13}C NMR** (101 MHz, gHSQC, $CDCl_3$) δ 95.2 (C1), 77.4 (C4), 72.3 (C2), 71.3 (C3), 69.7 (CH_2^{Bn}), 60.2 (C5).

β-anomer *inter alia:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.80 (m, 8H, 2,6-H^{Mbz}), 7.23 – 7.10 (m, 5H, H^{Bn}), 6.94 – 6.75 (m, 8H, 3,5-H^{Mbz}), 5.53 (dd, $^3J_{2,3}$ = 8.6 Hz, $^3J_{3,4}$ = 7.9 Hz, 1H, H3), 5.30 (dd, $^3J_{1,2}$ = 6.7 Hz, 1H, H2), 5.22 (dd, $^3J_{2,3}$ = 8.1 Hz, $^3J_{1,2}$ = 5.9 Hz, 1H, H2'), 5.10 (dd, $^3J_{3,4}$ = 6.7 Hz, 1H, H3'), 4.81 (d, ^2J = 12.4 Hz, 1H, CH_2^{Bn}), 4.77 (d, 1H, H1'), 4.64 (d, 1H, H1), 4.57 (d, 1H, CH_2^{Bn}), 4.15 – 3.89 (m, 2H, H4, H5a), 3.84 (s, 6H, CH_3^{Mbz}), 3.83 (s, 3H, CH_3^{Mbz}), 3.82 (s, 3H, CH_3^{Mbz}), 3.79 – 3.70 (m, 2H, H4', H5'a), 3.51 – 3.29 (m, 1H, H5b), 3.29 – 3.04 (m, 1H, H5'b). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1/165.3/165.1/164.8 ($C{=}O^{Mbz}$), 164.0/163.8/163.6/163.5 (1-C^{Mbz}), 137.0 (*ipso*-C^{Bn}), 132.3/132.2/131.9 (2,6-C^{Mbz}), 128.5 (*meta*-C^{Bn}), 127.9/127.9 (*ortho*-C^{Bn}, *para*-C^{Bn}), 122.2/122.0/121.6/121.2 (4-C^{Mbz}), 113.9/113.9/113.7/113.7 (3,5-C^{Mbz}), 101.1 (C1'), 99.6 (C1), 76.3 (C4), 75.5 (C3'), 72.1 (C3), 71.0 (C2), 70.4/70.4 (C3', CH_2^{Bn}), 68.6 (C4'), 64.5 (C5'), 62.9 (C5), 55.6/55.6/55.5 (CH_3^{Mbz}).



Benzyl *O*-(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)-*O*-bis[(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranoside (12b)

Acceptor, benzyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-β-D-xylopyranoside **11b** (298 mg, 0.328 mmol), and donor, phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside **6b** (437 mg, 0.416 mmol), were dissolved in 8.5 mL dry CH_2Cl_2 together with 450 mg 4Å MS and NIS (94 mg, 0.416 mmol). The mixture was stirred for 20 minutes at 22 °C and cooled in an acetone bath to -40 °C, AgOTf (0.66 mL, 0.1 M in dry toluene) was added and the temperature was allowed to increase slowly. When the reaction mixture reached -20 °C, a color change was observed and the reaction mixture was kept around this temperature for 1.5 hours. The resulting mixture was diluted with CH_2Cl_2 and filtered into ice-water, washed with 1:1 $Na_2S_2O_3$ (10 %)/$NaHCO_3$ (saturated), the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered and concentrated.

The resulting amorphous solid was dissolved in 9 mL (1:9) H_2O/CH_2Cl_2 and stirred vigorously at 22 °C. DDQ (190 mg, 0.84 mmol) was added to the mixture and shielded from the light covering the flask with aluminium foil. After 4 hours TLC showed full conversion and the reaction mixture was diluted with 20 mL CH_2Cl_2 and washed with 30 mL of a mixture containing 0.7 % ascorbic acid, 1.5 % citric acid and 1.0 % NaOH in H_2O. The aqueous phase was extracted twice with 10 mL CH_2Cl_2. The combined organic phases were dried with Na_2SO_4, filtered, concentrated and purified by flash chromatography (3:37⟶3:17 Et_2O/CH_2Cl_2). This yielded a colorless amorphous solid **12b** (500 mg, 89 %, over two steps, 1:6 α/β).

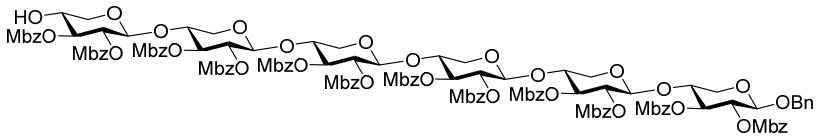
R_f 0.35 (3:17 Et_2O/CH_2Cl_2). **$[\alpha]_D^{22}$** = + 65.8 (*c* = 0.791, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{91}H_{88}NaO_{33}^+$ (MNa^+) calculated: 1731.5100; found: 1731.5121.

α-anomer *inter alia:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (t, $^3J_{2,3\sim3,4}$ = 9.7 Hz, 1H, $H3^{I\alpha}$), 5.15 – 5.11 (m, 1H, $H1^{I\alpha}$), 4.98 (dd, $^3J_{2,3}$ = 10.2 Hz, $^3J_{1,2}$ = 3.5 Hz, 1H, $H2^{I\alpha}$), 4.72 – 4.66 (m, 1H, CH_2^{Bn}), 4.43 (d, ^2J = 12.6 Hz, 1H, CH_2^{Bn}), 4.02 – 3.95 (m, 1H, $H4^{I\alpha}$), 3.74 – 3.68 (m, 1H, $H5a^{I\alpha}$), 3.67 – 3.61 (m, 1H, $H5b^{I\alpha}$).

^{13}C NMR (101 MHz, gHSQC, $CDCl_3$) δ 95.2 ($C1^{I\alpha}$), 76.6 ($C4^{I\alpha}$), 72.1 ($C2^{I\alpha}$), 70.6 ($C3^{I\alpha}$), 69.5 (CH_2^{Bn}), 60.0 ($C5^{I\alpha}$).

β-anomer *inter alia:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.77 (m, 16H, 2,6-H^{Mbz}), 7.24 – 7.14 (m, 5H, H^{Bn}), 6.90 – 6.71 (m, 16H, 3,5-H^{Mbz}), 5.46 (t, $^3J_{2,3\sim3,4}$ = 7.8 Hz, 1H, $H3^{I\beta}$), 5.41 (t, $^3J_{2,3\sim3,4}$ = 7.5 Hz, 1H, $H3^{II}$), 5.41 (t, $^3J_{2,3\sim3,4}$ =

7.9 Hz, 1H, H3^{III}), 5.24 (dd, $^{3}J_{1,2}$ = 6.5 Hz, $^{3}J_{2,3}$ = 8.1 Hz, 1H, H2$^{I\beta}$), 5.13 (dd, $^{3}J_{1,2}$ = 5.8 Hz, $^{3}J_{2,3}$ = 7.8 Hz, 1H, H2^{IV}), 5.07 (dd, $^{3}J_{2,3}$ = 7.6 Hz, $^{3}J_{1,2}$ = 5.9 Hz, 1H, H2^{II}), 5.06 – 5.01 (m, 2H, H2^{III}, H3^{IV}), 4.79 (d, ^{2}J = 12.2 Hz, 1H, CH_2^{Bn}), 4.70 (d, 1H, H1^{II}), 4.62 (d, 1H, H1$^{I\beta}$), 4.59 (d, 1H, H1^{IV}), 4.55 (d, 1H, CH_2^{Bn}), 4.53 (d, $^{3}J_{1,2}$ = 6.0 Hz, 1H, H1^{III}), 4.04 – 3.90 (m, 2H, H4$^{I\beta}$, H5a$^{I\beta}$), 3.89 – 3.66 (m, 28H, CH_3^{Mbz}, H4^{II}, H4^{III}, H4^{IV}, H5a^{IV}), 3.61 (dd, $^{2}J_{5a,5b}$ = 12.2 Hz, $^{3}J_{4,5a}$ = 7.3 Hz, 1H, H5a^{III}), 3.58 (dd, $^{2}J_{5a,5b}$ = 12.0 Hz, $^{3}J_{4,5a}$ = 6.8 Hz, 1H, H5a^{II}), 3.36 (dd, $^{2}J_{5a,5b}$ = 11.1 Hz, $^{3}J_{4,5b}$ = 7.5 Hz, 1H, H5b$^{I\beta}$), 3.21 – 3.08 (m, 3H, H5b^{II}, H5b^{III}, H5b^{IV}). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.11 (C=O^{Mbz}, O3^{IV}), 165.20/ 165.18/ 165.11/ 165.06/ 164.87/ 164.80/ 164.69 (C=O^{Mbz}), 164.04/ 163.85/ 163.66/ 163.64/ 163.59/ 163.54/ 163.53/ 163.50 (1-C^{Mbz}), 137.06 (*ipso*^{Bn}), 132.32/ 132.17/ 132.04/ 131.92/ 131.88/ 131.82 (2,6-C^{Mbz}), 128.45 (*meta*^{Bn}), 127.90 (*ortho*^{Bn}), 127.86 (*para*^{Bn}), 122.09/ 122.06/ 122.05/ 122.02/ 121.87/ 121.80/ 121.57/ 121.20 (4-C^{Mbz}), 113.93/ 113.91/ 113.78/ 113.75/ 113.71/ 113.68/ 113.65 (3,5-C^{Mbz}), 100.48 (C1^{II}, C1^{IV}), 100.27 (C1^{III}), 99.37 (C1$^{I\beta}$), 75.39 (C3^{IV}), 75.34 (C4$^{I\beta}$), 75.27 (C4^{III}), 74.56 (C4^{II}), 71.69 (C3$^{I\beta}$, C3^{II}), 71.42 (C3^{III}), 71.15 (C2^{II}), 71.09 (C2^{III}), 70.81 (C2$^{I\beta}$), 70.29 (CH_2^{Bn}), 70.20 (C2^{IV}), 68.52 (C4^{IV}), 64.32 (C5^{IV}), 62.53 (C5$^{I\beta}$), 62.31 (C5^{III}), 62.08 (C5^{II}), 55.59/ 55.55/ 55.52 (CH_3^{Mbz}).



Benzyl *O*-(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)-*O*-tetrakis[(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranoside (13)

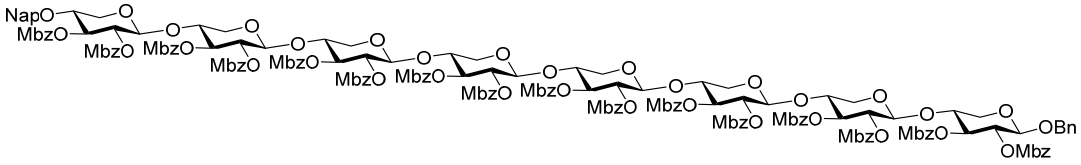
Acceptor, benzyl *O*-(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)-*O*-bis[(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranoside **12b** (475 mg, 0.278 mmol), and donor, phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside **6b** (371 mg, 0.353 mmol), were dissolved in 7.1 mL dry CH_2Cl_2 together with NIS (79 mg, 0.353 mmol) and 550 mg 4Å MS was suspended in the resulting solution. The mixture was stirred for 30 minutes at 22 °C and cooled in an acetone bath to -30 °C, AgOTf (0.56 mL, 0.1 M in dry toluene) was added and the temperature was allowed to slowly increase. When the reaction mixture reached -10 °C, a color change was observed and the reaction mixture was kept around this temperature for 2 hours. The resulting mixture was diluted with CH_2Cl_2 and filtered into ice-water, washed with 1:1 $Na_2S_2O_3$ (10 %)/$NaHCO_3$ (saturated), the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered, concentrated and purified by column chromatography (1:9⟶3:7 EtOAc/toluene). This afforded isolation of the remaining acceptor **15** (38 mg, 8%) and the coupling product (662 mg) as colorless flakes.

From this material, a portion (301 mg, 0.114 mmol) was dissolved in 2.6 mL 1:9 H_2O/CH_2Cl_2 and stirred vigorously at 22 °C. DDQ (64 mg, 0.28 mmol) was added to the mixture and shielded from the light covering the flask with aluminium foil. After 3 hours, TLC showed full conversion and the reaction mixture was diluted with 10 mL CH_2Cl_2 and washed with 10 mL of a mixture containing 0.7 % ascorbic acid, 1.5 % citric acid and 1.0 % NaOH in H_2O. The aqueous phase was extracted twice with 10 mL CH_2Cl_2. The combined organic phases were dried with Na_2SO_4, filtered, concentrated and purified by flash chromatography (1:4⟶1:3 EtOAc/toluene). This yielded a colorless amorphous solid, **13** (267 mg, 84 %, over two steps, 1:6 α/β).

R_f 0.49 (1:1 EtOAc/toluene). **$[\alpha]_D^{22}$** = + 55.8 (*c* = 0.550, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{133}H_{128}NaO_{49}^+$ ($M(100)Na^+$) calculated: 2532.7450; found: 2532.7252.

α-anomer *inter alia:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.90 (t, $^3J_{2,3\sim3,4}$ = 9.7 Hz, 1H, $3H^{I\alpha}$), 5.12 (m, 1H, $H1^{I\alpha}$), 4.98 (m, 1H, $H2^{I\alpha}$), 4.69 (d, ^2J = 12.4 Hz, 1H, CH_2^{Bn}), 4.43 (d, 1H, CH_2^{Bn}), 3.99 (m, 1H, $H4^{I\alpha}$), 3.70 (m, 1H, $H5a^{I\alpha}$), 3.65 (m, 1H, $H5b^{I\alpha}$). **^{13}C NMR** (101 MHz, gHSQC, $CDCl_3$) δ 95.1 ($C1^{I\alpha}$), 76.5 ($C4^{I\alpha}$), 72.0 ($C2^{I\alpha}$), 70.6 ($C3^{I\alpha}$), 69.4 (CH_2^{Bn}), 59.9 ($C5^{I\alpha}$).

β-anomer *inter alia:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.72 (m, 24H, 3,5-H^{Mbz}), 7.25 – 7.07 (m, 5H, Ph^{Bn}), 6.93 – 6.67 (m, 24H, 2,6-H^{Mbz}), 5.46 (t, $^3J_{2,3\sim3,4}$ = 7.8 Hz, 1H, $H3^{I\beta}$), 5.40 (t, $^3J_{2,3\sim3,4}$ = 7.9 Hz, 1H, $H3^{V}$), 5.39 (t, $^3J_{2,3\sim3,4}$ = 7.6 Hz, 1H, $H3^{II}$), 5.36 (t, $^3J_{2,3\sim3,4}$ = 7.5 Hz, 1H, $H3^{III}$/$H3^{IV}$), 5.35 (t, $^3J_{2,3\sim3,4}$ = 7.6 Hz, 1H, $H3^{III}$/$H3^{IV}$), 5.24 (dd, $^3J_{1,2}$ = 6.4 Hz, 1H, $H2^{I\beta}$), 5.13 (dd, $^3J_{2,3}$ = 7.8, $^3J_{1,2}$ = 5.8 Hz, 1H, $H2^{VI}$), 5.06 (dd, $^3J_{1,2}$ = 5.9 Hz, 1H, $H2^{II}$), 5.03 (dd, $^3J_{1,2}$ = 6.2 Hz, 1H, $H2^{V}$), 5.03 (dd, $^3J_{3,4}$ = 6.8 Hz, 1H, $H3^{VI}$), 4.99 (dd, $^3J_{1,2}$ = 5.9 Hz, 1H, $H2^{III}$/$H2^{IV}$), 4.99 (dd, $^3J_{1,2}$ = 6.0 Hz, 1H, $H2^{III}$/$H2^{IV}$), 4.79 (d, ^2J = 12.3 Hz, 1H, CH_2^{Bn}), 4.69 (d, 1H, $H1^{II}$), 4.62 (d, 1H, $H1^{I\beta}$), 4.58 (d, 1H, $H1^{VI}$), 4.55 (d, 1H, CH_2^{Bn}), 4.53 – 4.46 (m, 3H, $H1^{III}$, $H1^{IV}$, $H1^{V}$), 4.06 – 3.88 (m, 2H, $H4^{I\beta}$, $H5a^{I\beta}$), 3.85 – 3.81 (m, 24H, CH_3^{Mbz}), 3.81 – 3.80 (m, 6H, CH_3^{Mbz}), 3.79 (s, 3H, CH_3^{Mbz}), 3.77 (s, 3H, CH_3^{Mbz}), 3.76 – 3.63 (m, 6H, $H4^{II}$, $H4^{III}$, $H4^{IV}$, $H4^{V}$, $H4^{VI}$, $H5a^{VI}$), 3.63 – 3.50 (m, 4H, $H5a^{II}$, $H5a^{III}$, $H5a^{IV}$, $H5a^{V}$), 3.36 (dd, $^2J_{5a,5b}$ = 11.3 Hz, $^3J_{4,5b}$ = 7.4 Hz, 1H, $H5b^{I\beta}$), 3.22 – 3.00 (m, 5H, $H5b^{II}$, $H5b^{III}$, $H5b^{IV}$, $H5b^{V}$, $H5b^{VI}$). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 166.99 ($C{=}O^{Mbz}$, $O3^{VI}$), 165.03 (2C)/ 164.94 (2C)/ 164.92/ 164.71/ 164.65 (2C)/ 164.63 (2C)/ 164.54 ($C{=}O^{Mbz}$), 163.92/ 163.71/ 163.50 (4C)/ 163.45/ 163.40 (4C)/ 163.35 (1-C^{Mbz}), 136.93 (*ipso*^{Bn}), 132.18 (2C)/ 132.02 (2C)/ 131.88 (2C)/ 131.82 (6C)/ 131.78 (10C)/ 131.68 (2C, 2,6-C^{Mbz}), 128.30 (2C, *meta*^{Bn}), 127.75 (2C, *ortho*^{Bn}), 127.71 (*para*^{Bn}), 121.96/ 121.93 (2C)/ 121.89/ 121.84 (2C)/ 121.73 (3C)/ 121.65/ 121.43/ 121.05 (4-C^{Mbz}), 113.79 (2C)/ 113.77 (2C)/ 113.62 (4C)/ 113.56/ 113.54 (3C)/ 113.50 (2C, 3,5-C^{Mbz}), 100.36 ($C1^{II}$), 100.30 ($C1^{VI}$), 100.15/ 99.80 (2C, $C1^{III}$, $C1^{IV}$, $C1^{V}$), 99.23 ($C1^{I\beta}$), 75.26 ($C3^{VI}$), 75.19 ($C4^{I\beta}$), 75.10 ($C4^{II}$), 74.41/ 74.22 (2C, $C4^{III}$, $C4^{IV}$, $C4^{V}$), 71.54 (2C, $C3^{I\beta}$, $C3^{II}$), 71.23/ 71.18/ 71.15 ($C3^{III}$, $C3^{IV}$, $C3^{V}$), 71.03/ 70.96 ($C2^{II}$, $C2^{V}$), 70.78 (2C, $C2^{III}$, $C2^{IV}$), 70.66 ($C2^{I\beta}$), 70.15 (CH_2^{Bn}), 70.04 ($C2^{VI}$), 68.41 ($C4^{VI}$), 64.16 ($C5^{II}$), 62.39 ($C5^{I\beta}$), 62.16/ 61.89/ 61.83/ 61.78 ($C5^{III}$, $C5^{IV}$, $C5^{V}$, $C5^{VI}$), 55.44/ 55.40/ 55.38 (12C, CH_3^{Mbz}).



Benzyl *O*-(2,3-di-*O*-(4-methoxybenzoyl)-4-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl)-(1→4)-*O*-hexakis[(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranoside (14)

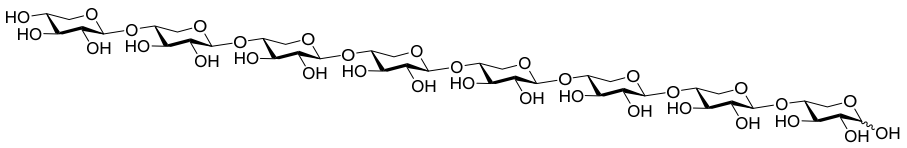
Acceptor, benzyl *O*-(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)-*O*-tetrakis[(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranoside **13** (236 mg, 0.094 mmol), and donor, phenyl 2,2',3,3'-tetra-*O*-(4-methoxybenzoyl)-4'-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside **6b** (127 mg, 0.121 mmol), were dissolved in 2.5 mL dry CH_2Cl_2 together with 200 mg 4Å MS and NIS (27.2 mg, 0.121 mmol). The mixture was stirred for 30 minutes at 22 °C and

cooled in an acetone bath to -40 °C, AgOTf (0.19 mL, 0.1 M in dry toluene) was added and the temperature was allowed to slowly increase. When the reaction mixture reached -14 °C, a color change was observed and the reaction mixture was kept around -10 °C for 6 hours, until TLC indicated full conversion. The resulting mixture was diluted with CH_2Cl_2 and filtered into ice-water, washed with 1:1 $Na_2S_2O_3$ (10%)/$NaHCO_3$ (saturated), the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered, concentrated and purified by column chromatography (2:8⟶3:7 EtOAc/toluene) to afford the remaining acceptor (27.8 mg, 12%) and the title compound **14** (273 mg, 84 %) as a colorless solid.

R_f 0.52 (2:3 EtOAc/toluene). **$[\alpha]_D^{22}$** = + 48.4 (*c* = 0.901, $CHCl_3$). **HRMS** (ESI-TOF) m/z for $C_{186}H_{176}NaO_{65}^+$ ($M(100)Na^+$) calculated: 3473.0392; found: 3473.0056.

α-anomer *inter alia:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.89 (t, $^3J_{2,3\sim3,4}$ = 9.7 Hz, 1H, $H3^{I\alpha}$), 5.12 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, $H1^{I\alpha}$), 4.99 (m, 1H, $H2^{I\alpha}$), 4.69 (d, ^2J = 12.7 Hz, 1H, CH_2^{Bn}), 4.43 (d, 1H, CH_2^{Bn}), 3.99 (m, 1H, $H4^{I\alpha}$), 3.71 (m, 1H, $H5a^{I\alpha}$), 3.64 (m, 1H, $H5b^{I\alpha}$). **^{13}C NMR** (101 MHz, gHSQC, $CDCl_3$) δ 95.3 ($C1^{I\alpha}$), 76.7 ($C4^{I\alpha}$), 73.1 ($C2^{I\alpha}$), 70.7 ($C3^{I\alpha}$), 69.6 (CH_2^{Bn}), 60.0 ($C5^{I\alpha}$).

β-anomer *inter alia:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.76 (m, 32H, 2,6-H^{Mbz}), 7.76 – 7.70 (m, 1H, 5-H^{Nap}), 7.67 – 7.55 (m, 3H, 1-H^{Nap}, 4-H^{Nap}, 8-H^{Nap}), 7.47 – 7.37 (m, 2H, 6-H^{Nap}, 7-H^{Nap}), 7.24 (dd, $^3J_{3,4}$ = 8.4 Hz, $^4J_{1,3}$ = 1.8 Hz, 1H, 3-H^{Nap}), 7.22 – 7.07 (m, 5H, H^{Bn}), 6.91 – 6.65 (m, 32H, 3,5-H^{Mbz}), 5.46 (t, $^3J_{2,3\sim3,4}$ = 7.9 Hz, 1H, $H3^{I\beta}$), 5.43 (t, $^3J_{2,3\sim3,4}$ = 7.2 Hz, 1H, $H3^{VIII}$), 5.41 – 5.27 (m, 6H, $H3^{II}$, $H3^{III}$, $H3^{IV}$, $H3^{V}$, $H3^{VI}$, $H3^{VII}$), 5.24 (dd, $^3J_{2,3}$ = 8.2 Hz, $^3J_{1,2}$ = 6.4 Hz, 1H, $H2^{I\beta}$), 5.06 (dd, $^3J_{2,3}$ = 7.6 Hz, $^3J_{1,2}$ = 5.8 Hz, 1H, $H2^{II}$), 5.04 – 4.92 (m, 6H, $H2^{III}$, $H2^{IV}$, $H2^{V}$, $H2^{VI}$, $H2^{VII}$, $H2^{VIII}$), 4.79 (d, ^2J = 12.4 Hz, 1H, CH_2^{Bn}), 4.69 (d, 1H, H1'), 4.64 (d, ^2J = 12.1 Hz, 1H, CH_2^{Nap}), 4.61 (d, 1H, $H1^{I\beta}$), 4.59 (d, $^3J_{1,2}$ = 5.5 Hz, 1H, $H1^{VIII}$), 4.56 (d, 1H, CH_2^{Nap}), 4.54 (d, 1H, CH_2^{Bn}), 4.53 – 4.45 (m, 5H, $H1^{III}$, $H1^{IV}$, $H1^{V}$, $H1^{VI}$, $H1^{VII}$), 4.04 – 3.88 (m, 2H, H4, $H5a^{I\beta}$), 3.85 – 3.71 (m, 50H, 16xCH_3^{Mbz}, $H4^{VII}$, $H5a^{VIII}$), 3.71 – 3.47 (m, 12H, $H4^{II}$, $H4^{III}$, $H4^{IV}$, $H4^{V}$, $H4^{VI}$, $H4^{VIII}$, $H5a^{II}$, $H5a^{III}$, $H5a^{IV}$, $H5a^{V}$, $H5a^{VI}$, $H5a^{VII}$), 3.36 (dd, $^2J_{5a,5b}$ = 11.2 Hz, $^3J_{4,5b}$ = 7.5 Hz, 1H, $H5b^{I\beta}$), 3.26 (dd, $^2J_{5a,5b}$ = 12.1 Hz, $^3J_{4,5b}$ = 7.4 Hz, 1H, $H5b^{VIII}$), 3.20 – 3.01 (m, 6H, $H5b^{II}$, $H5b^{III}$, $H5b^{IV}$, $H5b^{V}$, $H5b^{VI}$, $H5b^{VII}$). **^{13}C NMR** (101 MHz, CDCl3) δ 165.3/165.2/165.1/165.1/164.8/164.8 (16C, C=O^{Mbz}), 163.6/163.5 (1-C^{Mbz}), 137.1 (*ipso*^{Bn}), 135.1 (2-C^{Nap}), 133.2/133.1 (4a-C^{Nap}, 8a-C^{Nap}), 132.2/132.0/131.9/131.9 (16x2,6-C^{Mbz}), 128.4 (*meta*^{Bn}), 128.3/128.0 (4-C^{Nap}, 8-C^{Nap}), 127.89 (*ortho*^{Bn}), 127.85 (*para*^{Bn}), 127.7 (5-C^{Nap}), 126.7 (1-C^{Nap}), 126.1/126.0 (6-C^{Nap}, 7-C^{Nap}), 125.8 (3-C^{Nap}), 122.1/122.0/121.8/121.7 (16x4-C^{Mbz}), 113.7/113.7/113.6 (3,5-C^{Mbz}), 100.5 ($C1^{II}$), 100.2 ($C1^{VIII}$), 100.1/100.0 ($C1^{III}$, $C1^{IV}$, $C1^{V}$, $C1^{VI}$, $C1^{VII}$), 99.4 ($C1^{I\beta}$), 75.3 ($C4^{I\beta}$), 74.7 ($C4^{VII}$), 74.5/74.4 ($C4^{II}$, $C4^{III}$, $C4^{IV}$, $C4^{V}$, $C4^{VI}$), 74.0 ($C4^{VIII}$), 72.5 (CH_2^{Nap}), 71.7 ($C3^{I\beta}$), 71.6/71.4/71.3/71.3 ($C3^{II}$, $C3^{III}$, $C3^{IV}$, $C3^{V}$, $C3^{VI}$, $C3^{VII}$), 71.2 ($C3^{VIII}$), 71.0/70.9 ($C2^{II}$, $C2^{III}$, $C2^{IV}$, $C2^{V}$, $C2^{VI}$, $C2^{VII}$), 70.8 ($C2^{I\beta}$), 70.6 ($C2^{VIII}$), 70.3 (CH_2^{Bn}), 62.6 ($C5^{I\beta}$), 62.3 ($C5^{VIII}$), 62.1/62.0/61.9 ($C5^{II}$, $C5^{III}$, $C5^{IV}$, $C5^{V}$, $C5^{VI}$, $C5^{VII}$), 55.5/55.5 (16xCH_3^{Mbz}).



β-D-Xylopyranosyl-(1→4)-hexakis[β-D-xylopyranosyl-(1→4)]-D-xylopyranose (15)

Benzyl *O*-(2,3-di-*O*-(4-methoxybenzoyl)-4-*O*-(naphthalen-2-ylmethyl)-β-D-xylopyranosyl)-(1→4)-*O*-hexakis[(2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→4)]-2,3-di-*O*-(4-methoxybenzoyl)-β-D-xylopyranoside **14** (247 mg, 71.6 µmol) was dissolved in 15 mL dry THF together with 3 mL dry CH_3OH and $NaOCH_3$ (124 mg 2.3 mmol) was added. The reaction mixture was stirred at 70 °C overnight and neutralized freshly washed Amberlite IR-120 (H), filtered and concentrated. The resulting crude was triturated with Et_2O resulting in a colorless amorphous solid (81 mg), further purified through a short pad of reverse-phase silica gel (H_2O/ CH_3CN 0.1 % AcOH) to give a colorless amorphous solid (45.2 mg).

This was dissolved in 15 mL (1:2) H_2O/THF and flushed with N_2 before Pd/C (10%, 26 mg) was added. The atmosphere was exchanged with H_2 and stirred at 22 °C overnight. Additional Pd/C (10%, 30 mg) was added and the reaction progress was analyzed by LCMS and H_2-balloon was replenished until full conversion was indicated. The reaction mixture was filtered through celite, the flask and filter were washed with hot water and the filtrate concentrated. This crude material was dissolved and filtered through a short pad of reverse-phase silica gel (H_2O/CH_3OH) to give a colorless amorphous solid (29.8 mg), which was purified further by size exclusion chromatography on Sephadex G-25 (1% 1-butanol in H_2O) yielding an off-white fluffy powder after freeze-drying (17.5 mg, 23 %). The compound analyses were in accordance with ^{13}C NMR data from the literature.[4] Additionally, we report ^{1}H and ^{13}C NMR spectra.

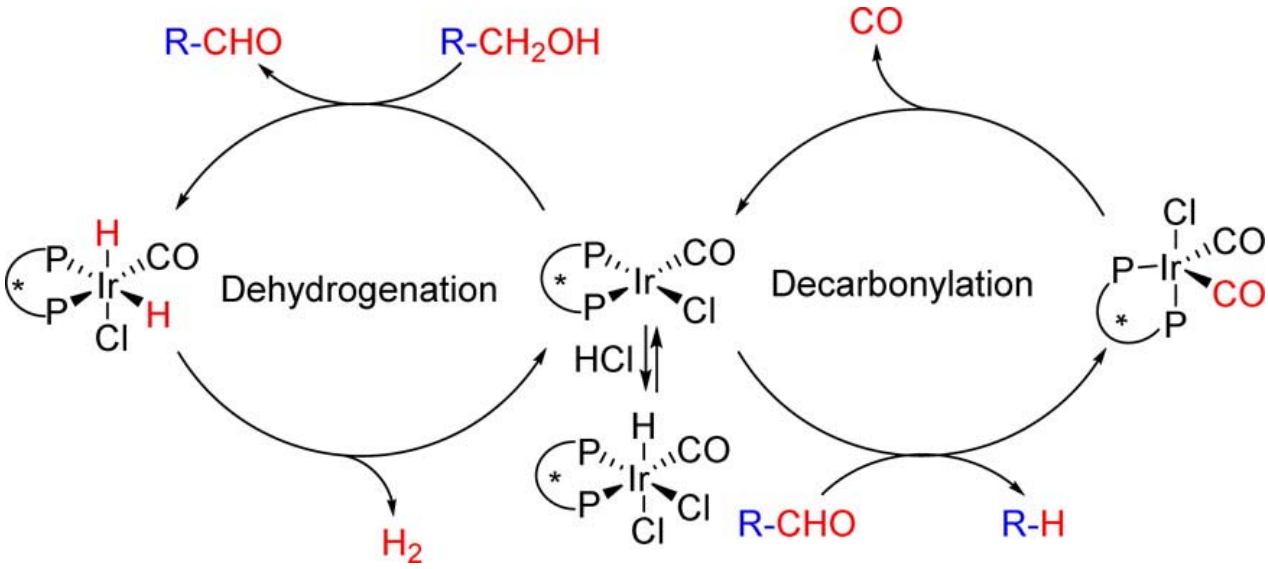
HRMS (ESP-TOF) m/z for $C_{40}H_{66}NaO_{33}^+$ (MNa^+) calculated: 1097.3379; found: 1097.3373.

α-anomer *inter alia:* **^{1}H NMR** (500 MHz, D_2O) δ 5.18 (d, J = 3.7 Hz, 1H, $H1^{I\alpha}$), 3.86 – 3.72 (m, 4H, $H3^{I\alpha}$, $H4^{I\alpha}$, $H5a^{I\alpha}$, $H5b^{I\alpha}$), 3.54 (t, J = 9.4 Hz, 1H, $H2^{I\alpha}$). **^{13}C NMR** (126 MHz, D_2O) δ = 92.6 ($C1^{I\alpha}$), 77.2 ($C4^{I\alpha}$), 72.0 ($C2^{I\alpha}$), 71.5 ($C3^{I\alpha}$), 59.4 ($C5^{I\alpha}$).

β-anomer *inter alia:* **^{1}H NMR** (500 MHz, D_2O) δ 4.58 (d, $^{3}J_{1,2}$ = 7.9 Hz, 1H, $H1^{I\beta}$), 4.48 (d, $^{3}J_{1,2}$ = 7.6 Hz, 6H, $H1^{II}$, $H1^{III}$, $H1^{IV}$, $H1^{V}$, $H1^{VI}$, $H1^{VII}$), 4.45 (d, $^{3}J_{1,2}$ = 7.9 Hz, 1H, $H1^{VIII}$), 4.10 (dd, $^{2}J_{5a,5b}$ = 11.8 Hz, $^{3}J_{4,5a}$ = 5.3 Hz, 6H, $H5a^{II}$, $H5a^{III}$, $H5a^{IV}$, $H5a^{V}$, $H5a^{VI}$, $H5a^{VII}$), 4.05 (dd, $^{2}J_{5a,5b}$ = 11.9 Hz, $^{3}J_{4,5a}$ = 5.5 Hz, 1H, $H5a^{I\beta}$), 3.97 (dd, $^{2}J_{5a,5b}$ = 11.6 Hz, $^{3}J_{4,5a}$ = 5.5 Hz, 1H, $H5a^{VIII}$), 3.85 – 3.68 (m, 7H, $H4^{I\beta}$, $H4^{II}$, $H4^{III}$, $H4^{IV}$, $H4^{V}$, $H4^{VI}$, $H4^{VII}$), 3.68 – 3.58 (m, 2H, $H3^{I\beta}$, $H4^{VIII}$), 3.55 (t, $^{3}J_{2,3\sim3,4}$ = 9.2 Hz, 6H, $H3^{II}$, $H3^{III}$, $H3^{IV}$, $H3^{V}$, $H3^{VI}$, $H3^{VII}$), 3.42 (t, $^{3}J_{2,3\sim3,4}$ = 9.2 Hz, 2H, $H3^{VIII}$,$H5b^{I\beta}$), 3.37 (dd, $^{3}J_{4,5b}$ = 10.4 Hz, 6H, $H5b^{II}$, $H5b^{III}$, $H5b^{IV}$, $H5b^{V}$, $H5b^{VI}$, $H5b^{VII}$), 3.33 – 3.26 (m, 7H, $H2^{II}$, $H2^{III}$, $H2^{IV}$, $H2^{V}$, $H2^{VI}$, $H2^{VII}$, $H5b^{VIII}$), 3.25 (dd, $^{3}J_{2,3}$ = 9.4 Hz, 1H, $H2^{VIII}$), 3.24 (dd, $^{3}J_{2,3}$ = 9.4 Hz, 1H, $H2^{I\beta}$). **^{13}C NMR** (126 MHz, D_2O) δ = 102.4 ($C1^{VIII}$), 102.3 (6C, $C1^{II}$, $C1^{III}$, $C1^{IV}$, $C1^{V}$, $C1^{VI}$, $C1^{VII}$) , 97.1 ($C1^{I\beta}$), 76.98/ 76.96/ 76.92 (7C, $C4^{I\beta}$, $C4^{II}$, $C4^{III}$, $C4^{IV}$, $C4^{V}$, $C4^{VI}$, $C4^{VII}$), 76.2 ($C3^{VIII}$), 74.6 ($C2^{I\beta}$), 74.5 ($C3^{I\beta}$), 74.2 (6C, $C3^{II}$, $C3^{III}$, $C3^{IV}$, $C3^{V}$, $C3^{VI}$, $C3^{VII}$), 73.4 ($C2^{VIII}$), 73.3 (6C, $C2^{II}$, $C2^{III}$, $C2^{IV}$, $C2^{V}$, $C2^{VI}$, $C2^{VII}$), 69.8 ($C4^{VIII}$), 65.8 ($C5^{VIII}$), 63.6 (7C, $C5^{I\beta}$, $C5^{II}$, $C5^{III}$, $C5^{IV}$, $C5^{V}$, $C5^{VI}$, $C5^{VII}$).

4) Mechanism – dehydrogenative decarbonylation

The mechanism of the dehydrogenative decarbonylation can be summarized by the two coupled catalytic cycles seen below (adapted from reference [5])



5) References

[1] P. G. Scheurer, F. Smith, *J. Am. Chem. Soc.* **1954**, *76*, 3224.

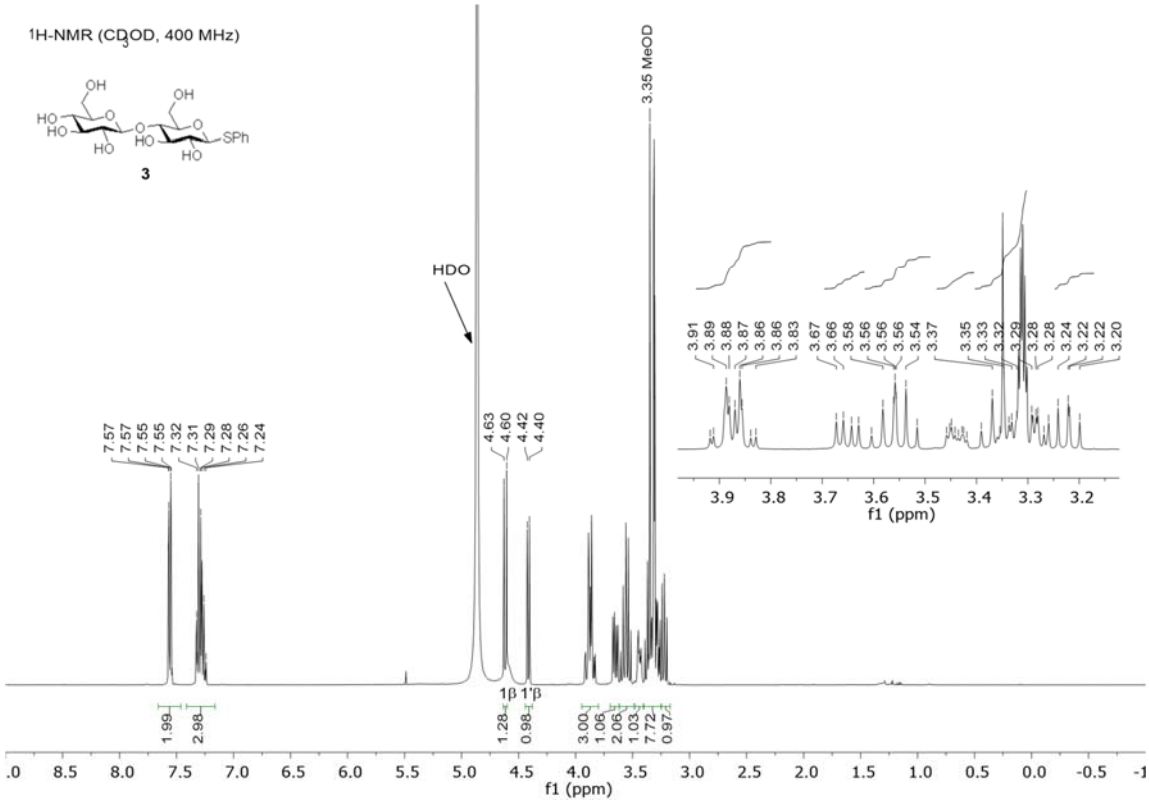
[2] F. D. Tropper, F. O. Andersson, C. Grand-Maître, R. Roy, *Synthesis (Stuttg).* **1991**, *1991*, 734–736.

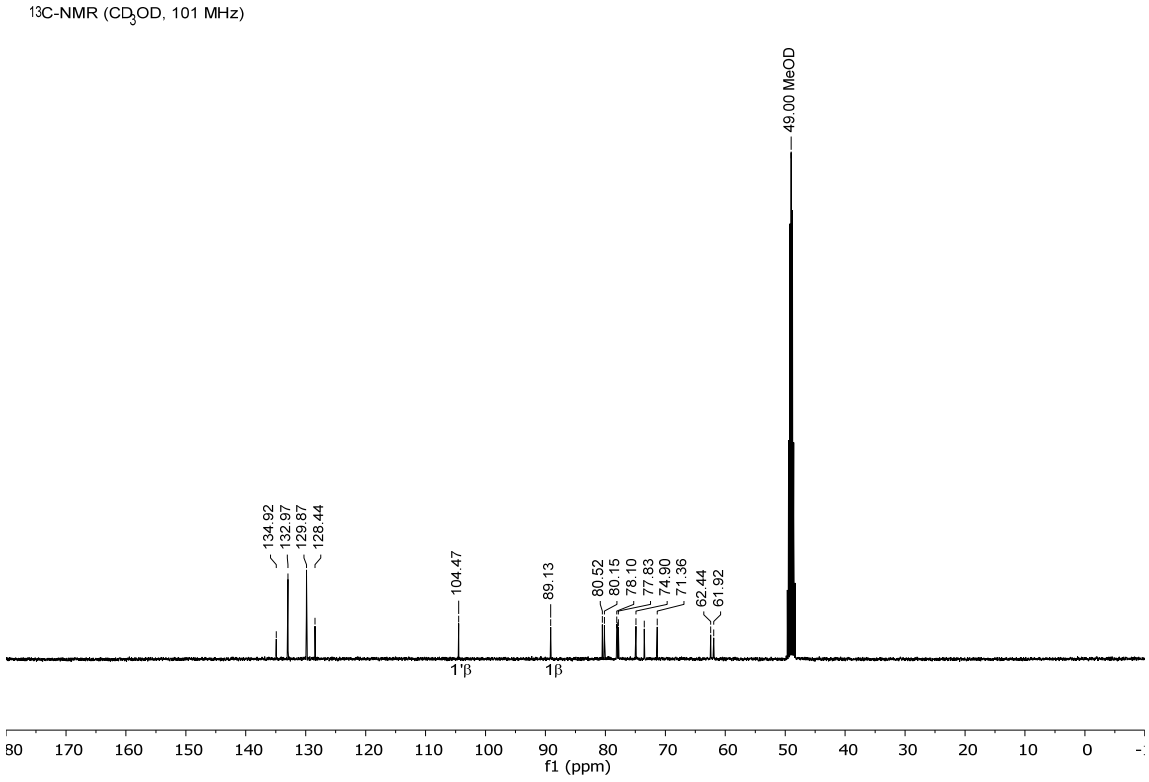
[3] V. Jadhav, C. M. Pedersen, M. Bols, *Org. Biomol. Chem.* **2011**, *9*, 7525–34.

[4] K. Takeo, Y. Ohguchi, R. Hasegawa, S. Kitamura, *Carbohydr. Res.* **1995**, *278*, 301–313.

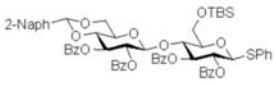
[5] E. K. Olsen, T. Singh, P. Harris, P. G. Anderson and R. Madsen, *J. Am. Chem. Soc.*, 2015, **137**, 834–842.

6) NMR spectra



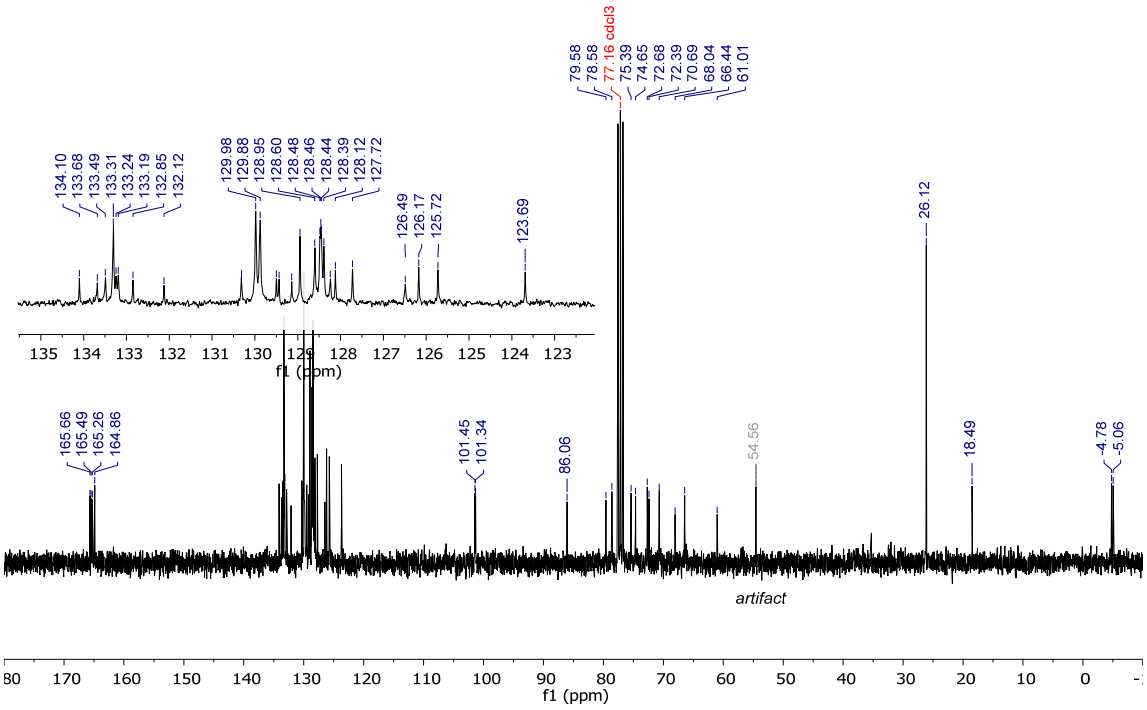


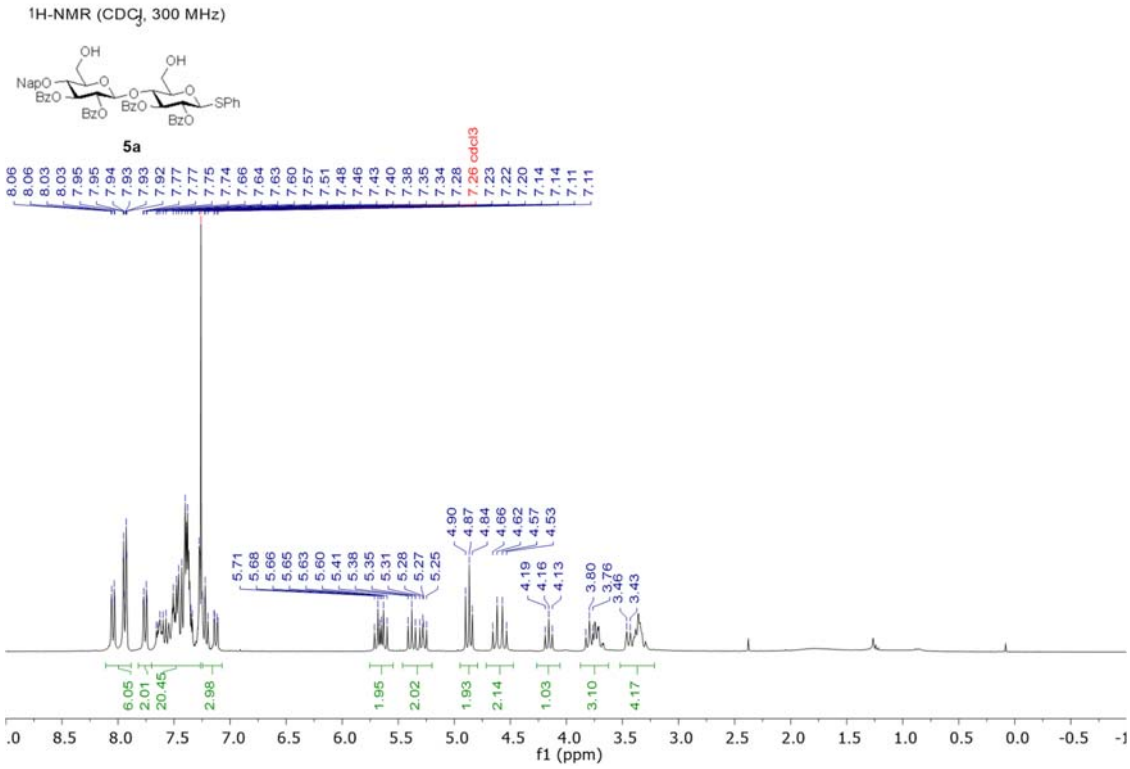
1H-NMR ($CDCl_3$, 300 MHz)

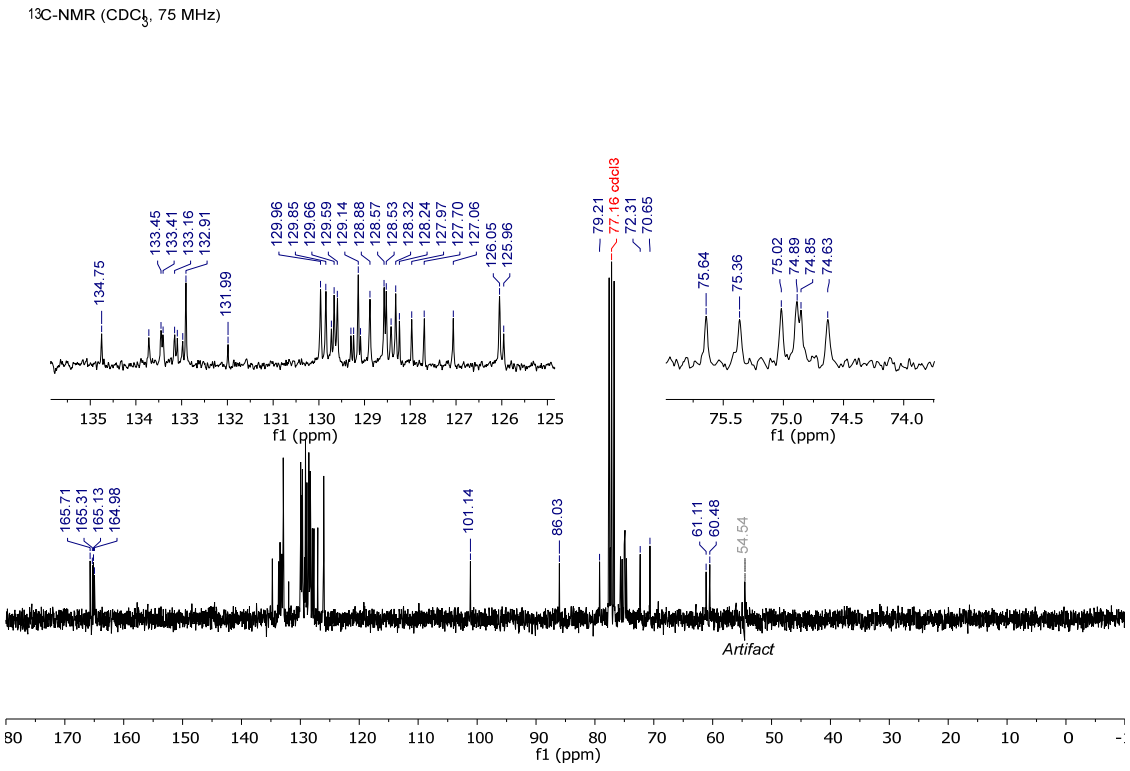


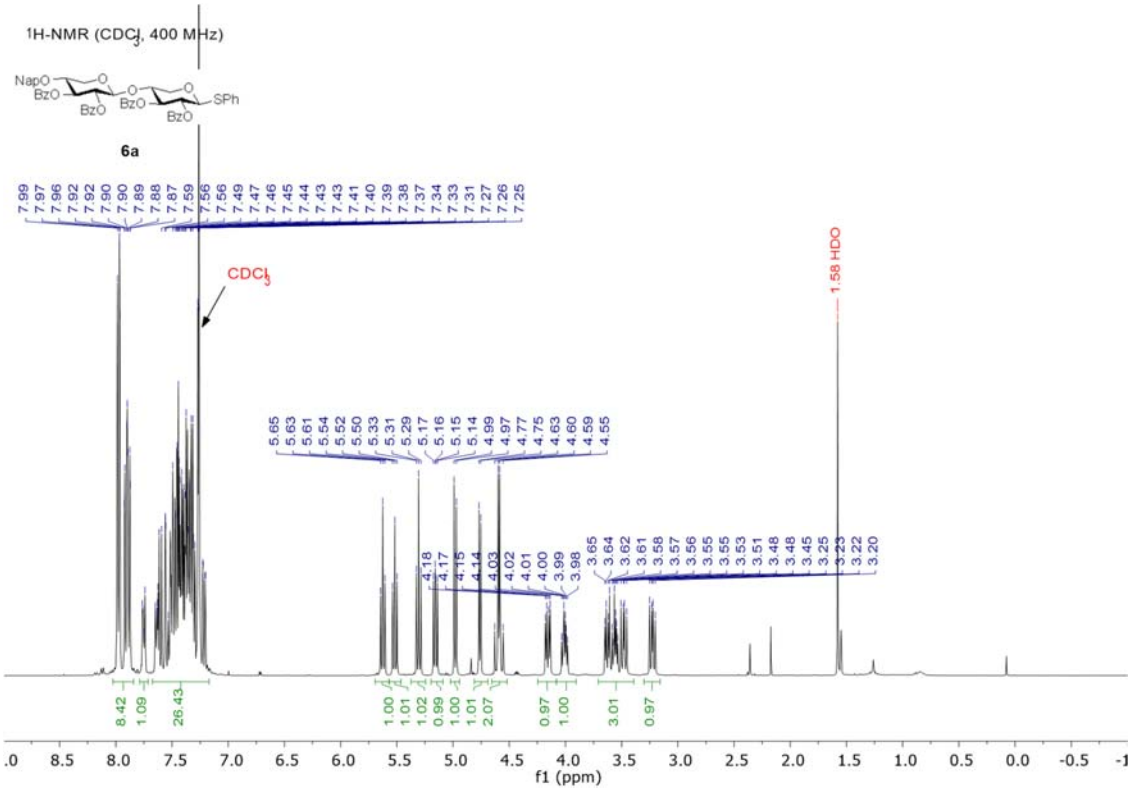
4a

13C-NMR ($CDCl_3$, 75 MHz)




1H-NMR (CDCl3, 300 MHz)
5a
f1 (ppm)


13C-NMR (CDCl3, 75 MHz)
Artifact
f1 (ppm)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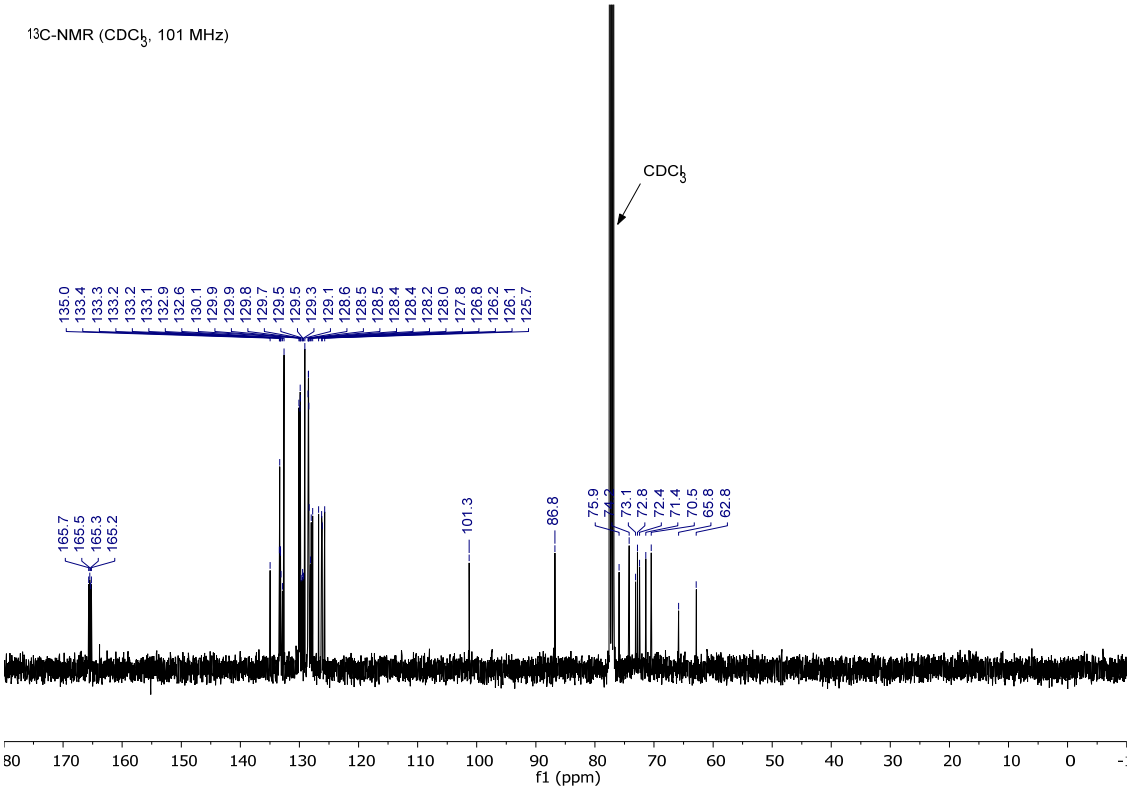
NapO
BzO
BzO
BzO
BzO
SPh
6a
CDCl3
1.58 HDO
f1 (ppm)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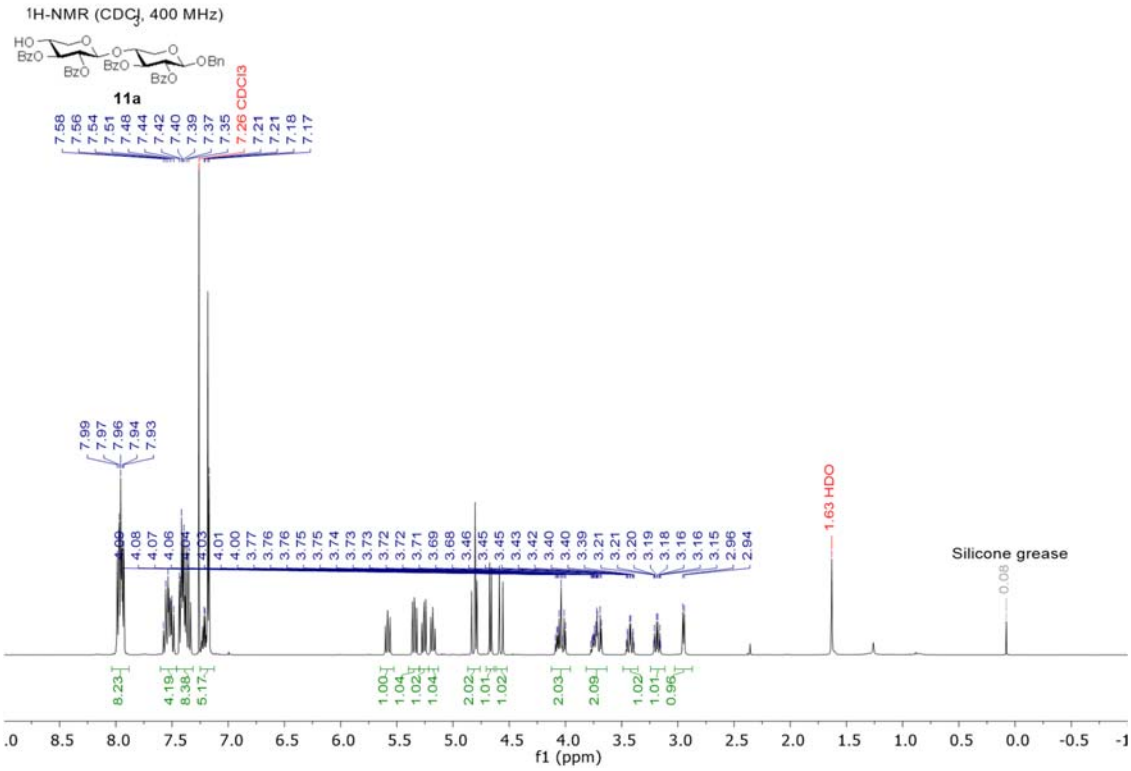
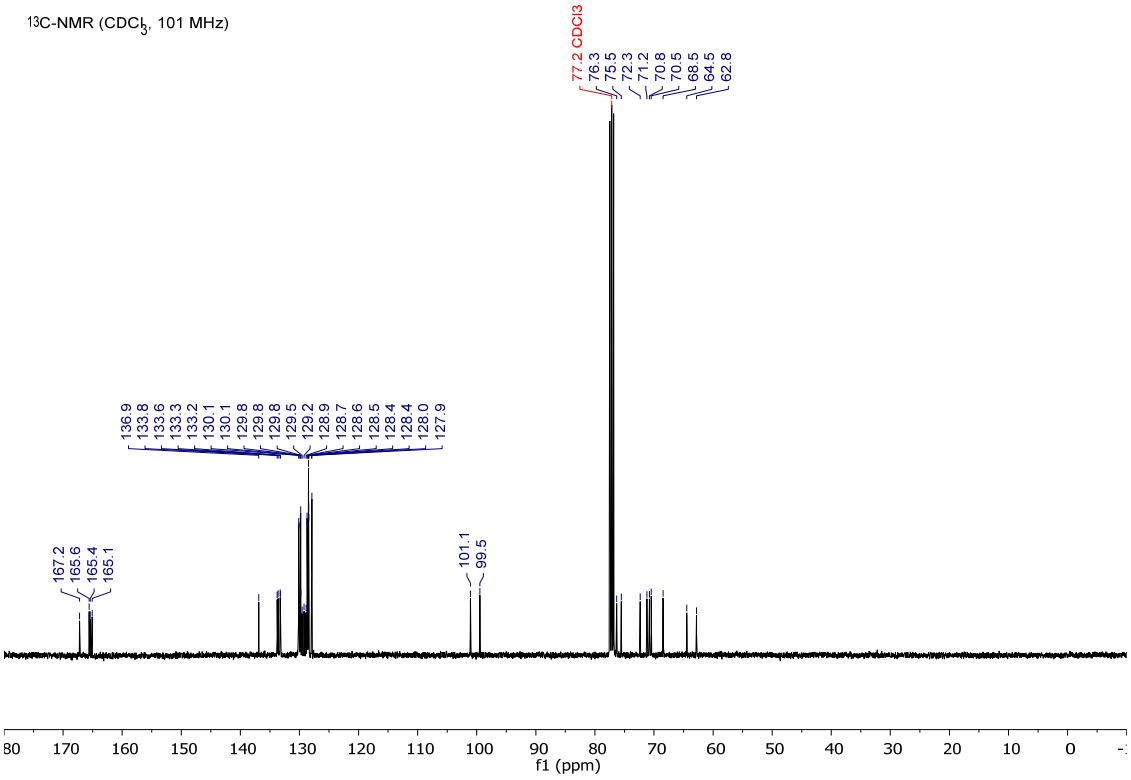
CDCl3
165.7
165.5
165.3
165.2
101.3
86.8
75.9
73.1
72.8
72.4
71.4
70.5
65.8
62.8
f1 (ppm)


1H-NMR (CDCl3, 400 MHz)
11a
7.26 CDCl3
1.63 HDO
Silicone grease
f1 (ppm)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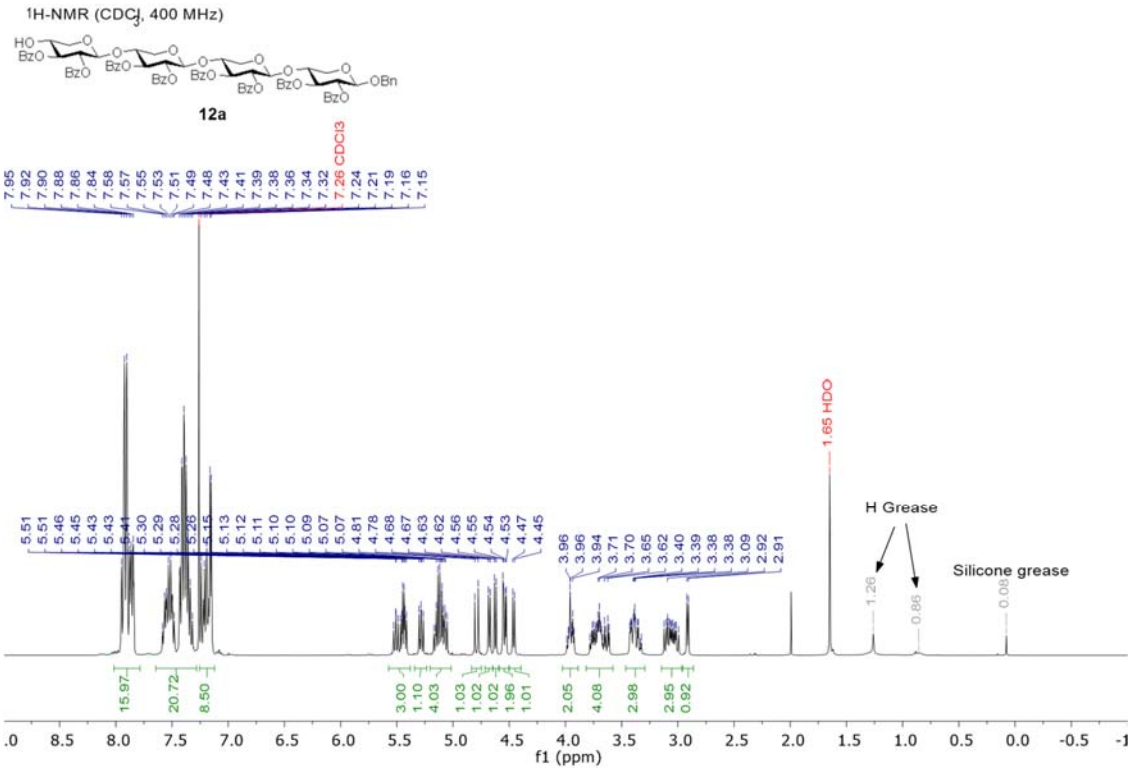
77.2 CDCl3
f1 (ppm)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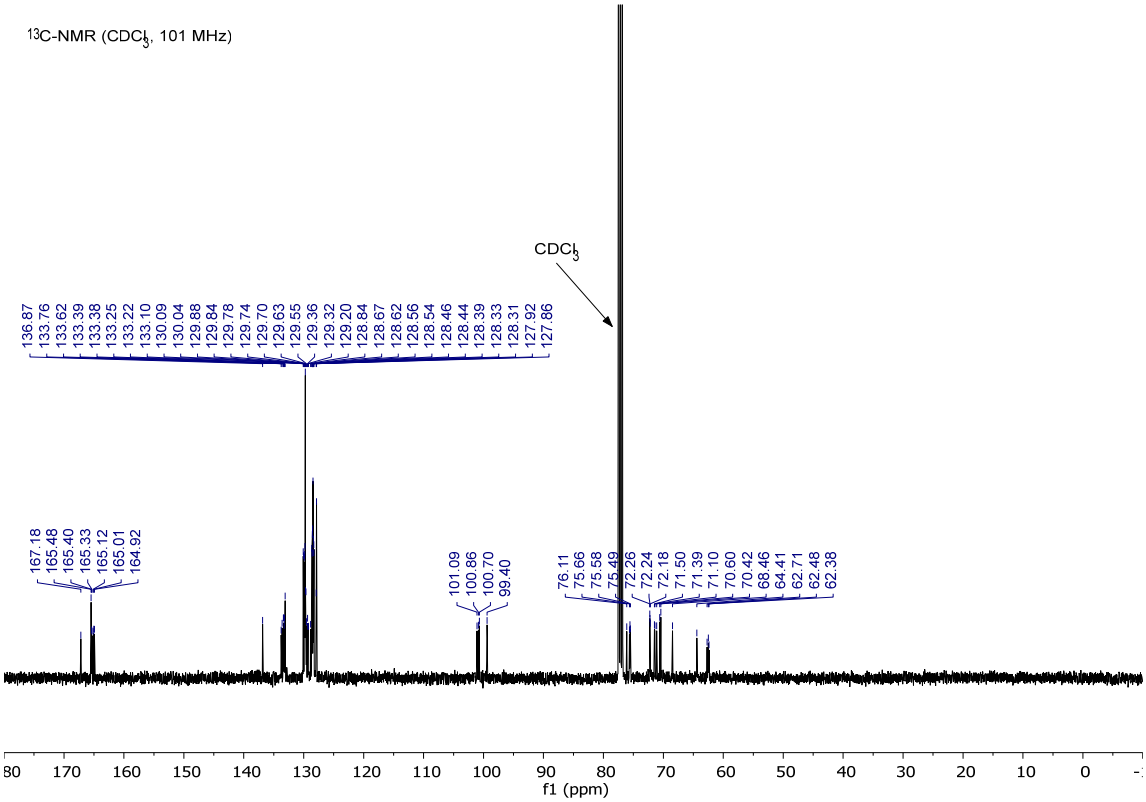
12a
7.26 CDCl3
1.65 HDO
H Grease
Silicone grease
f1 (ppm)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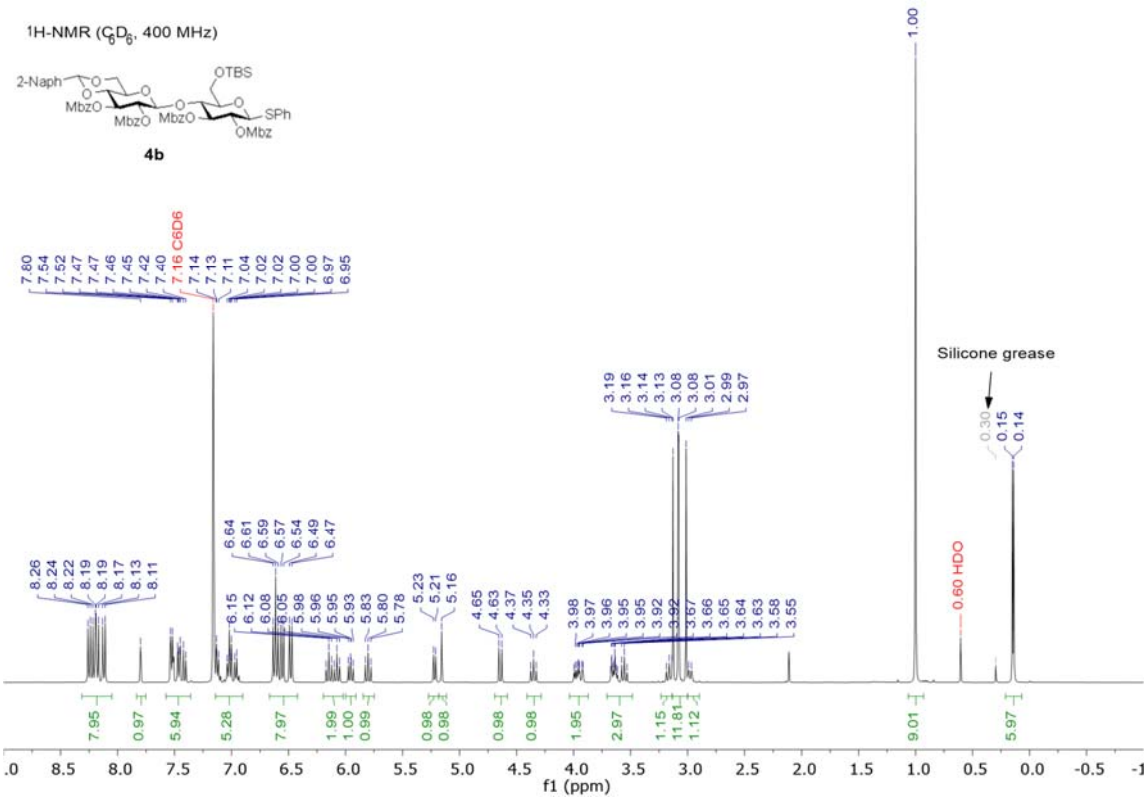
CDCl3
f1 (ppm)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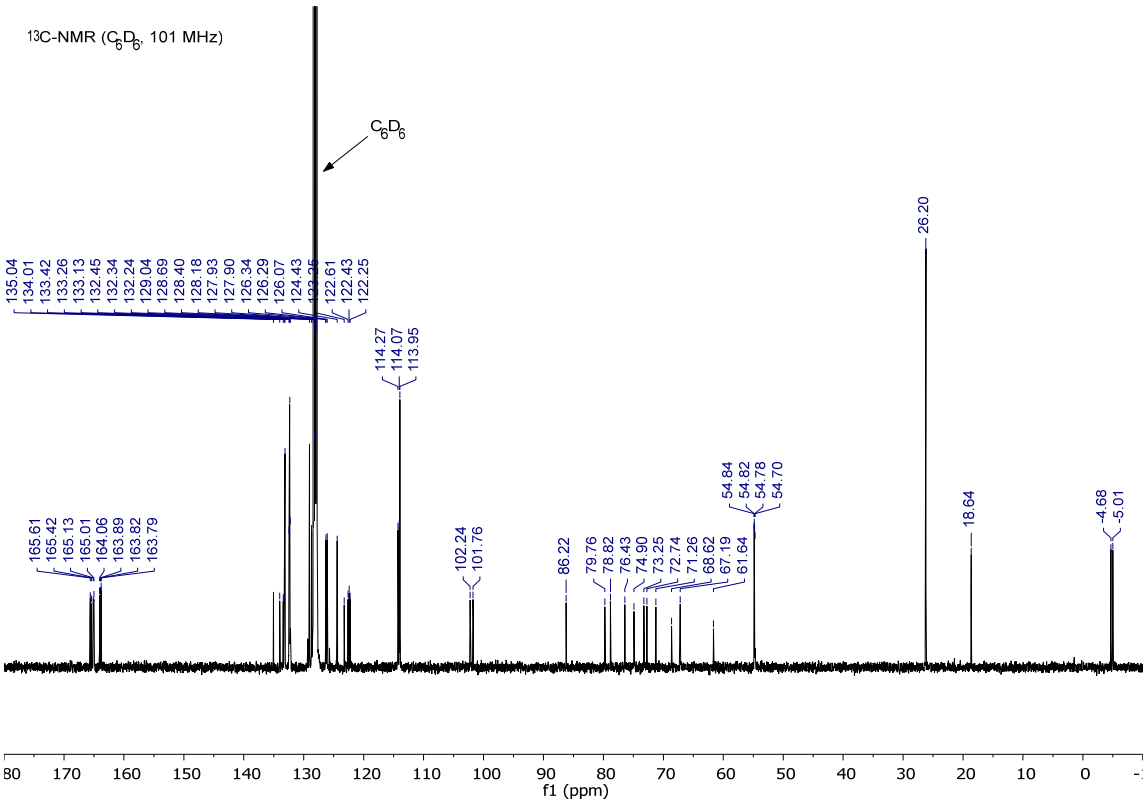
2-Naph
OTBS
MbzO
MbzO
MbzO
SPh
OMbz
4b
Silicone grease
0.60 HDO
C6D6
f1 (ppm)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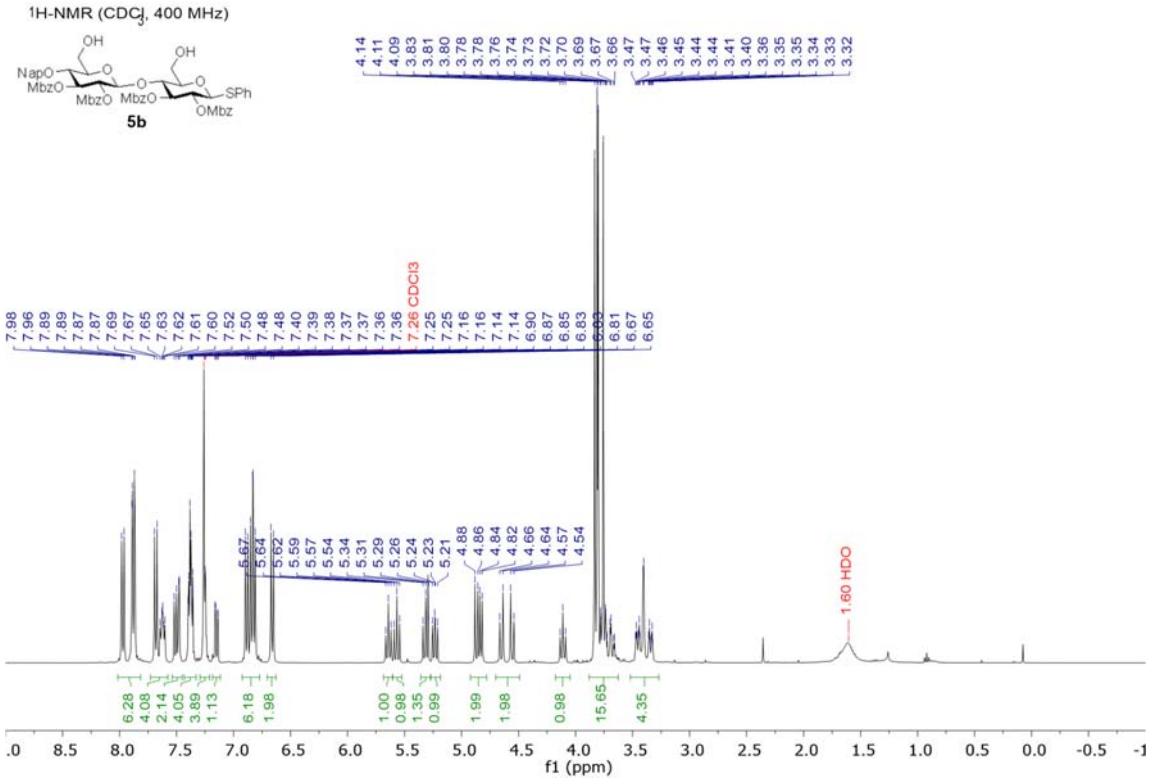
C6D6
f1 (ppm)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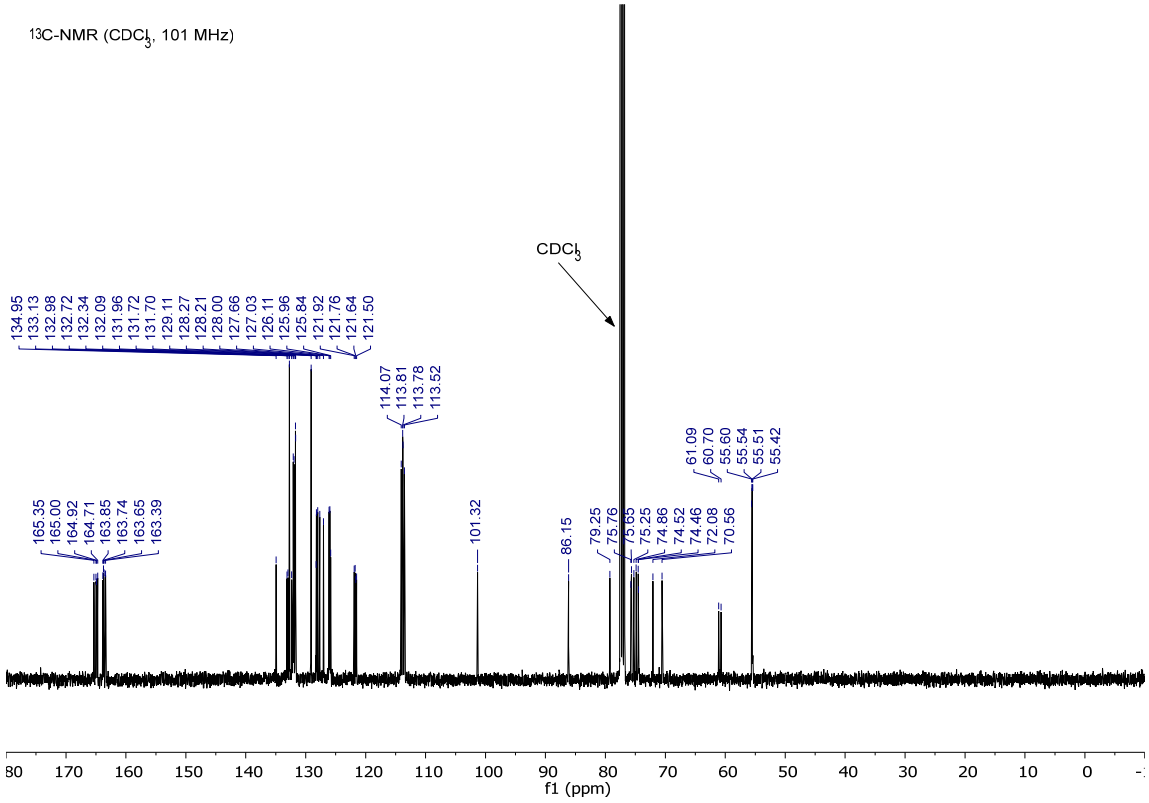
NapO
MbzO
MbzO
MbzO
OH
OH
O
O
O
SPh
OMbz
5b
7.26 CDCl3
1.60 HDO
f1 (ppm)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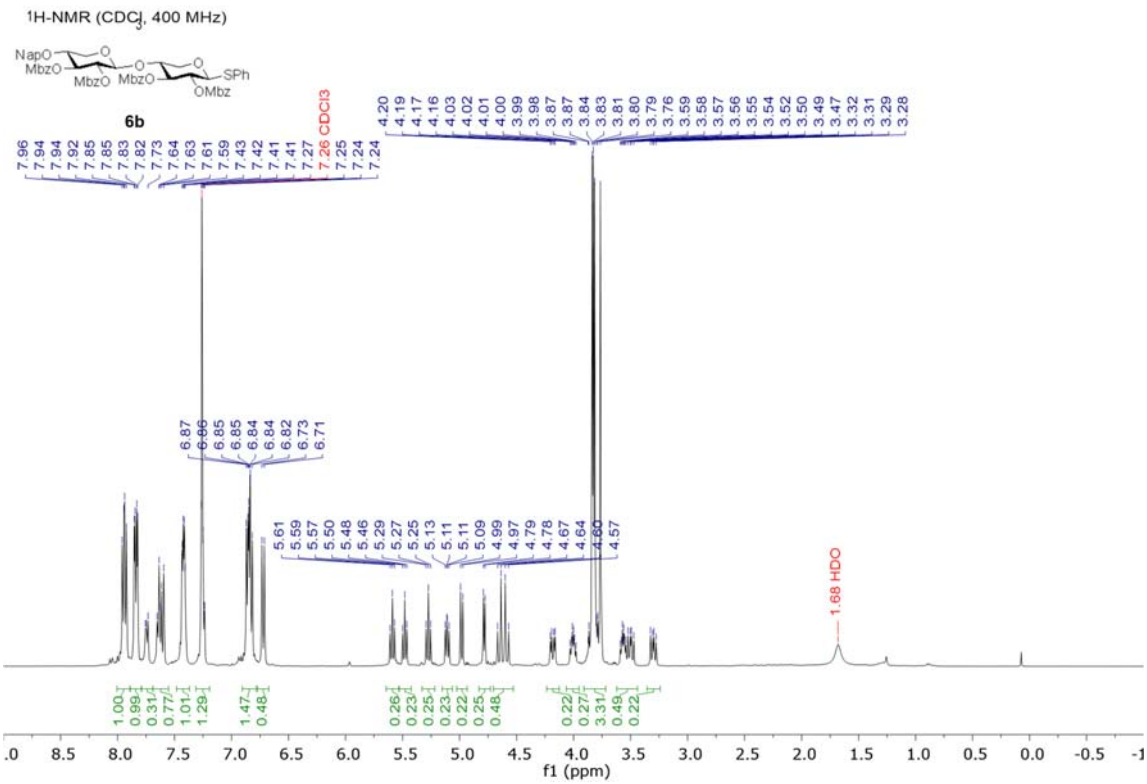
CDCl3
f1 (ppm)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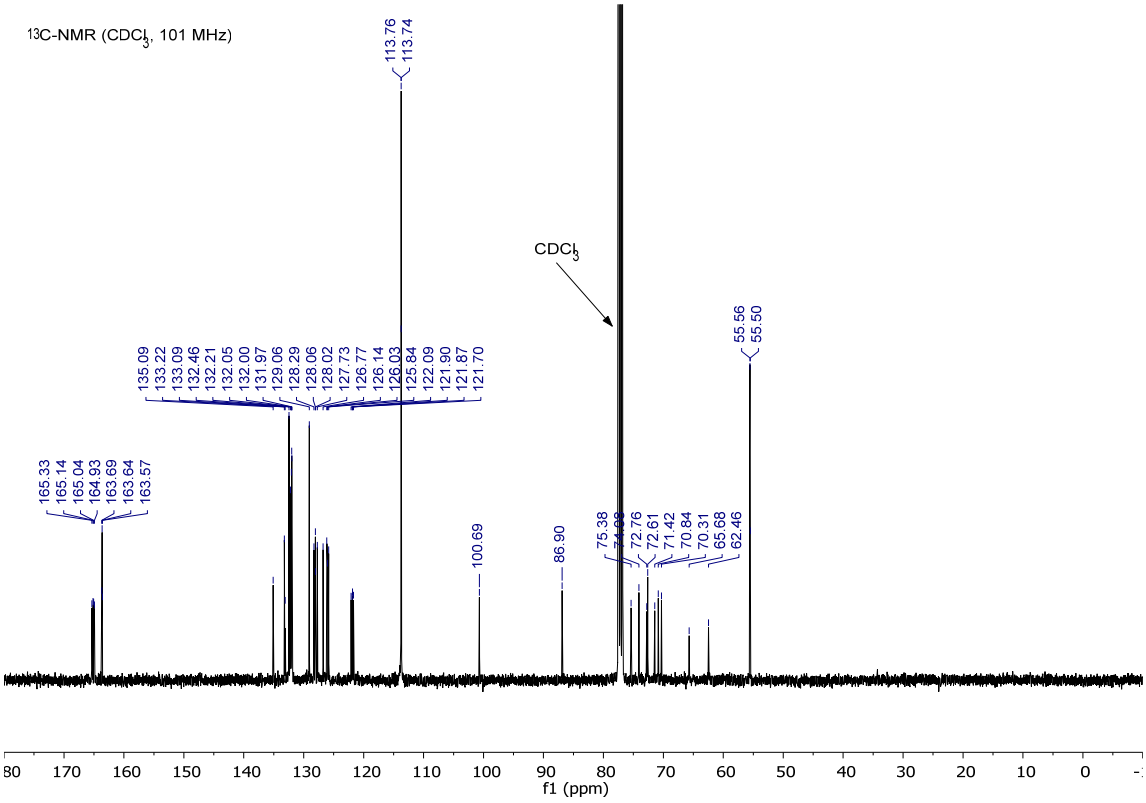
NapO
MbzO
MbzO
MbzO
MbzO
SPh
OMbz
6b
7.26 CDCl3
1.68 HDO
f1 (ppm)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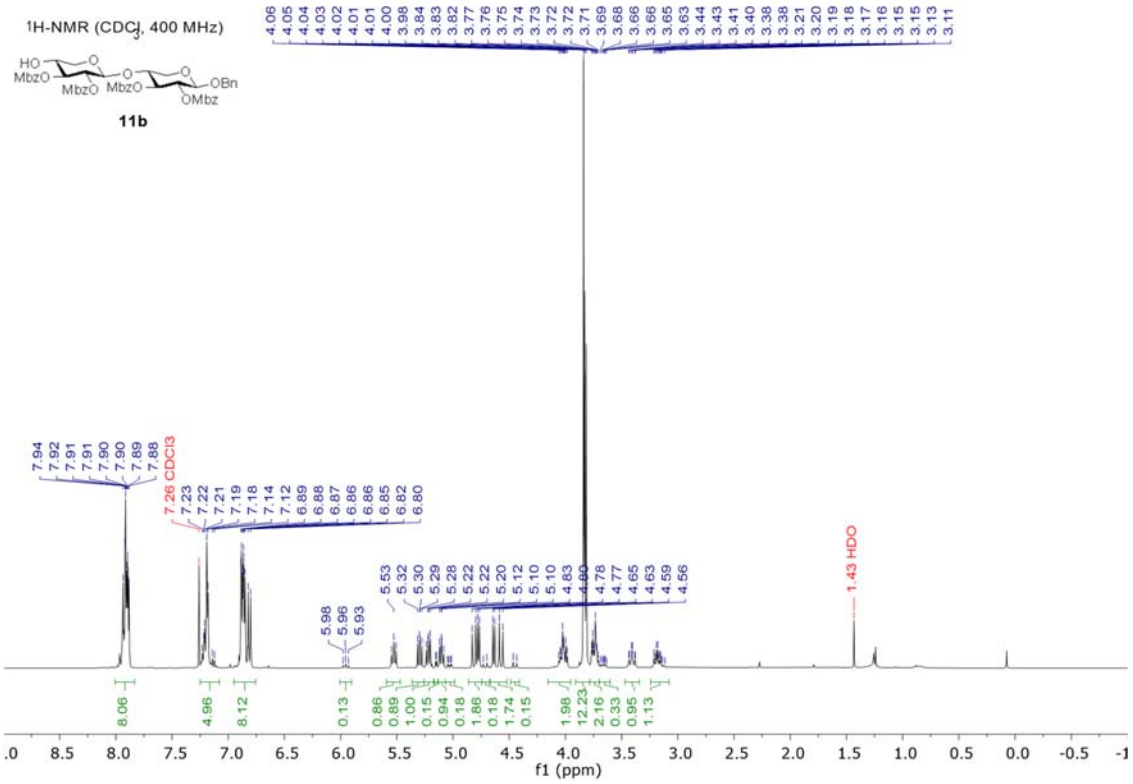
CDCl3
f1 (ppm)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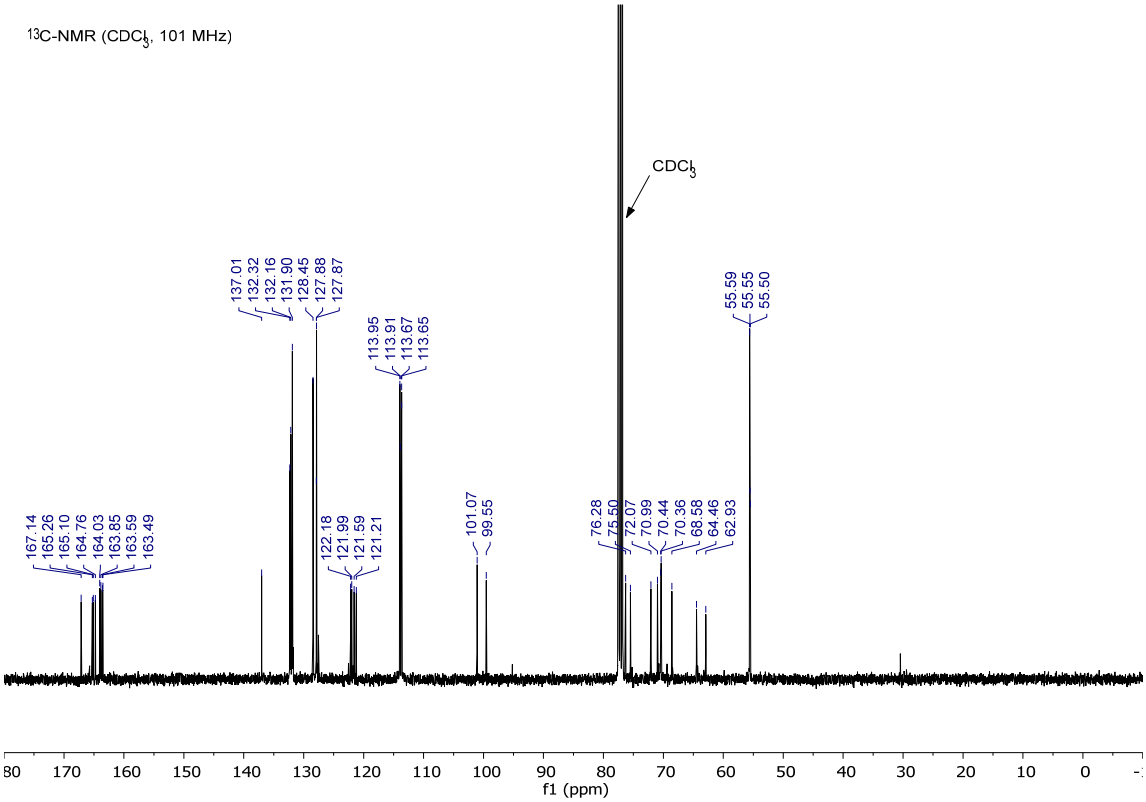
11b
7.26 CDCl3
1.43 HDO
f1 (ppm)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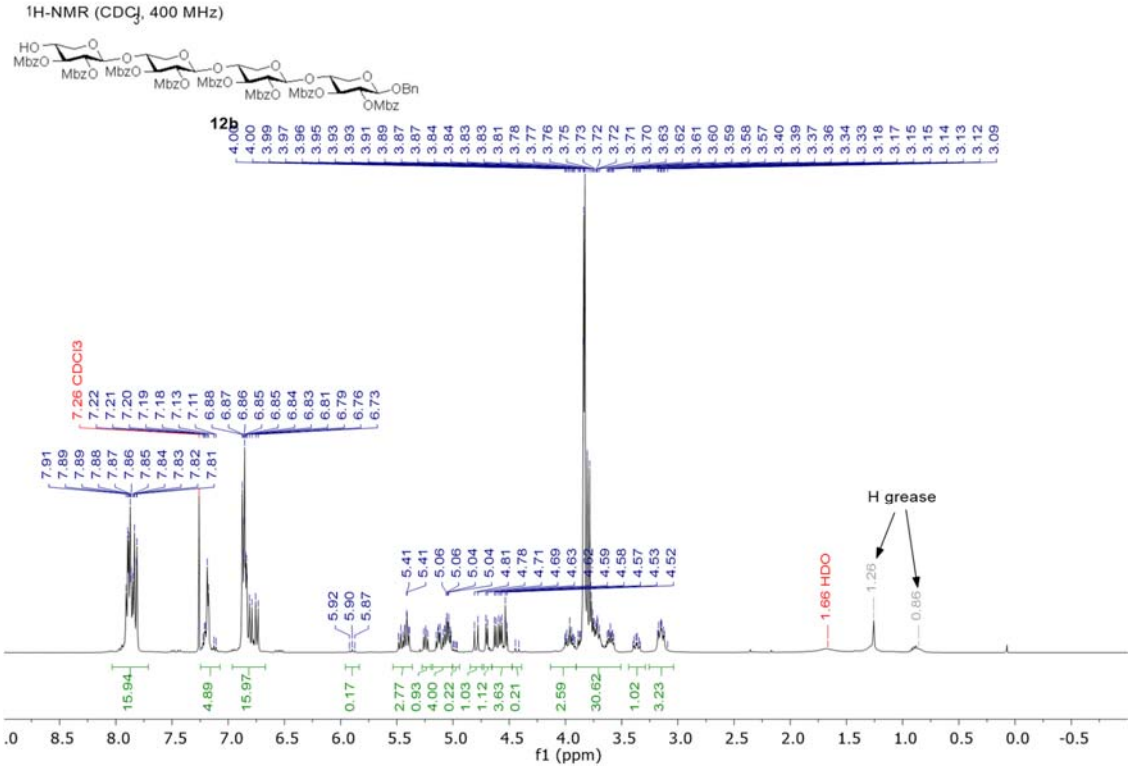
CDCl3
f1 (ppm)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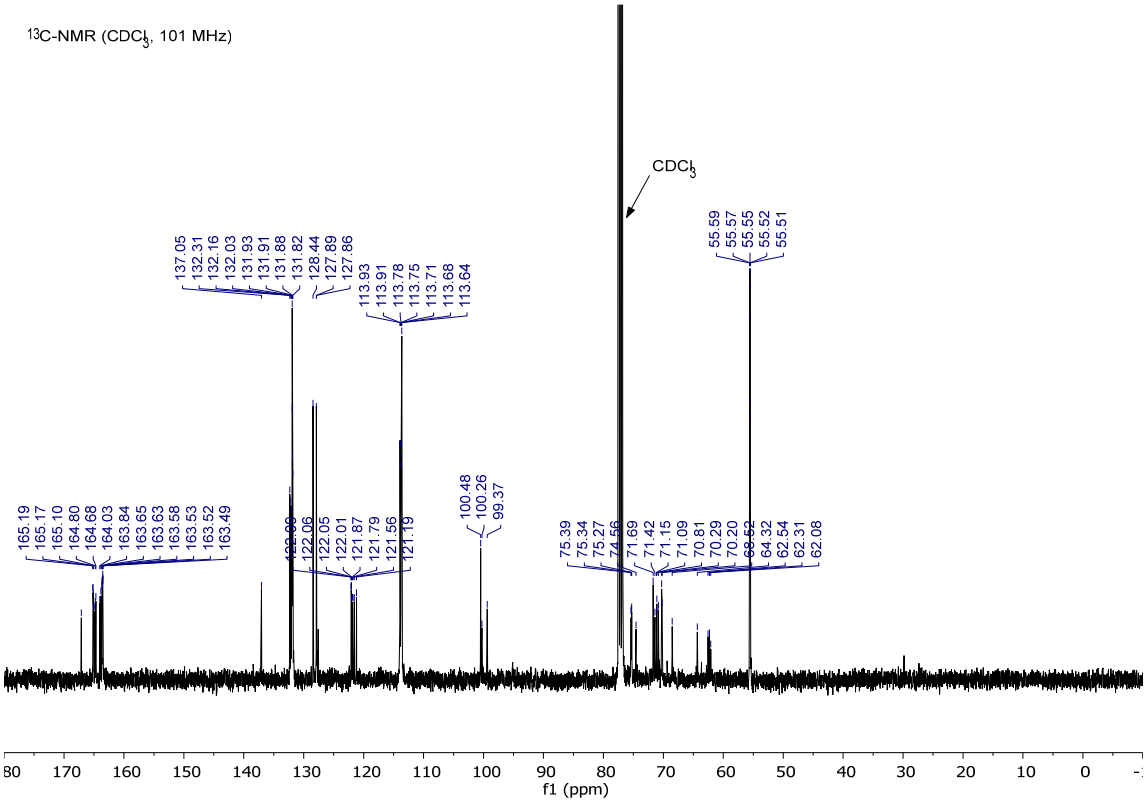
12b
7.26 CDCl3
H grease
1.66 HDO
1.26
0.86
f1 (ppm)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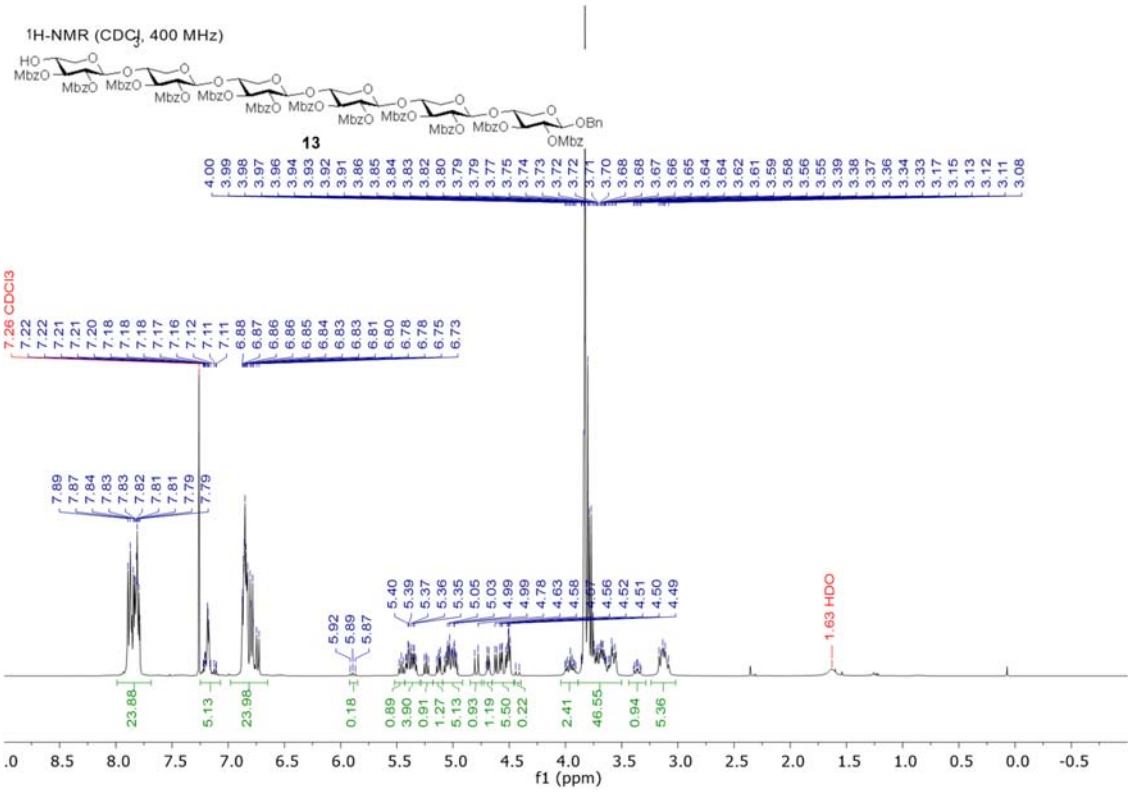
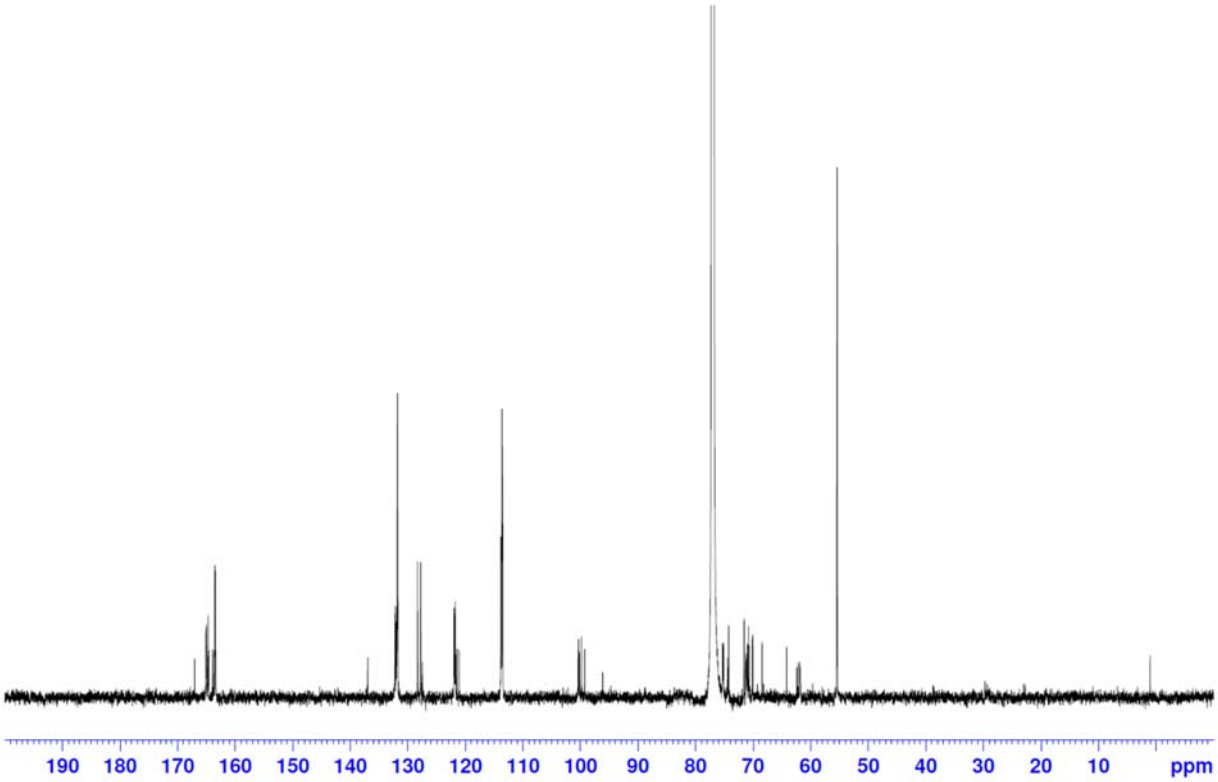
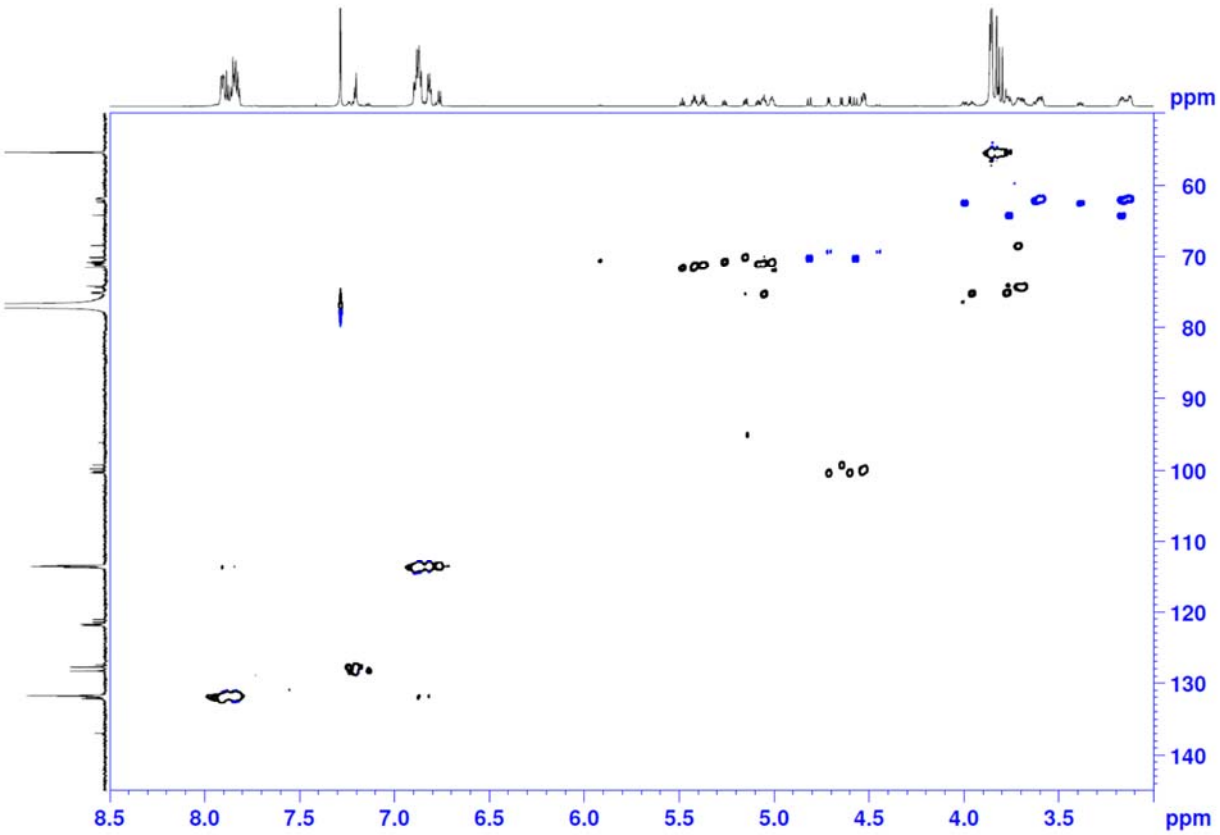
CDCl3
f1 (ppm)



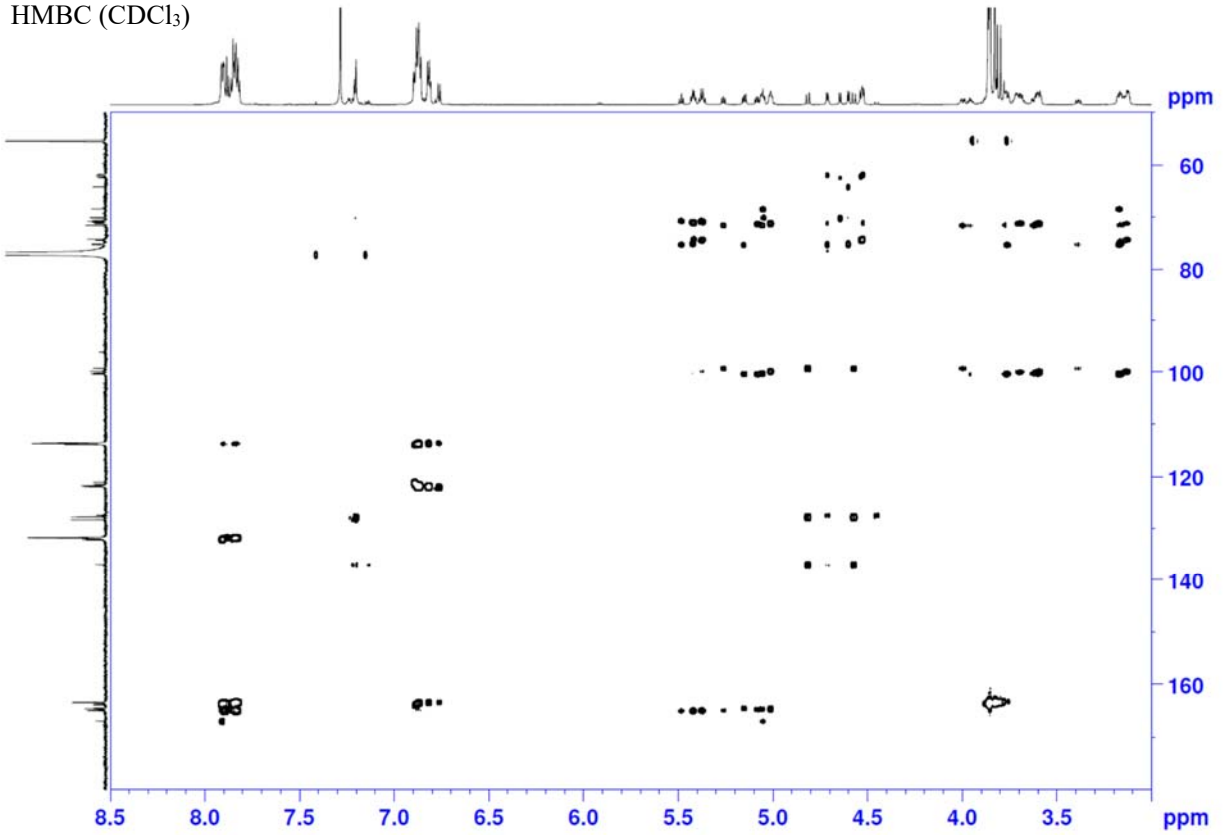
^{13}C NMR ($CDCl_3$, 200 MHz)

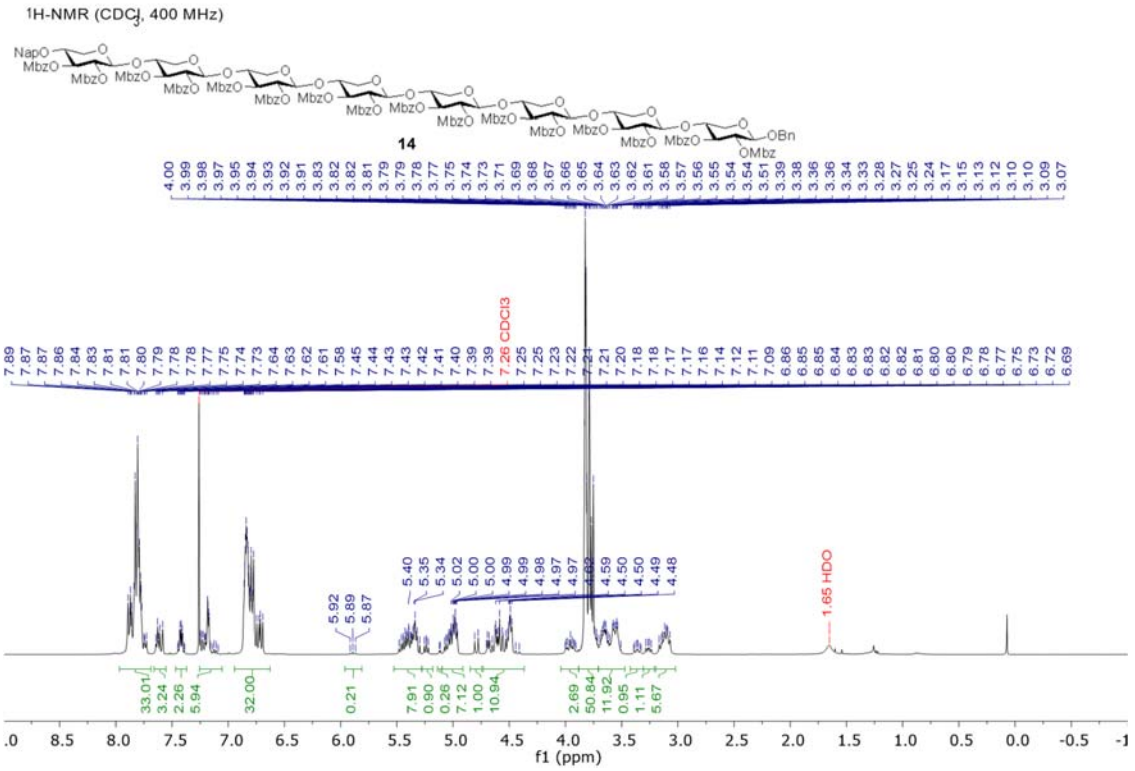


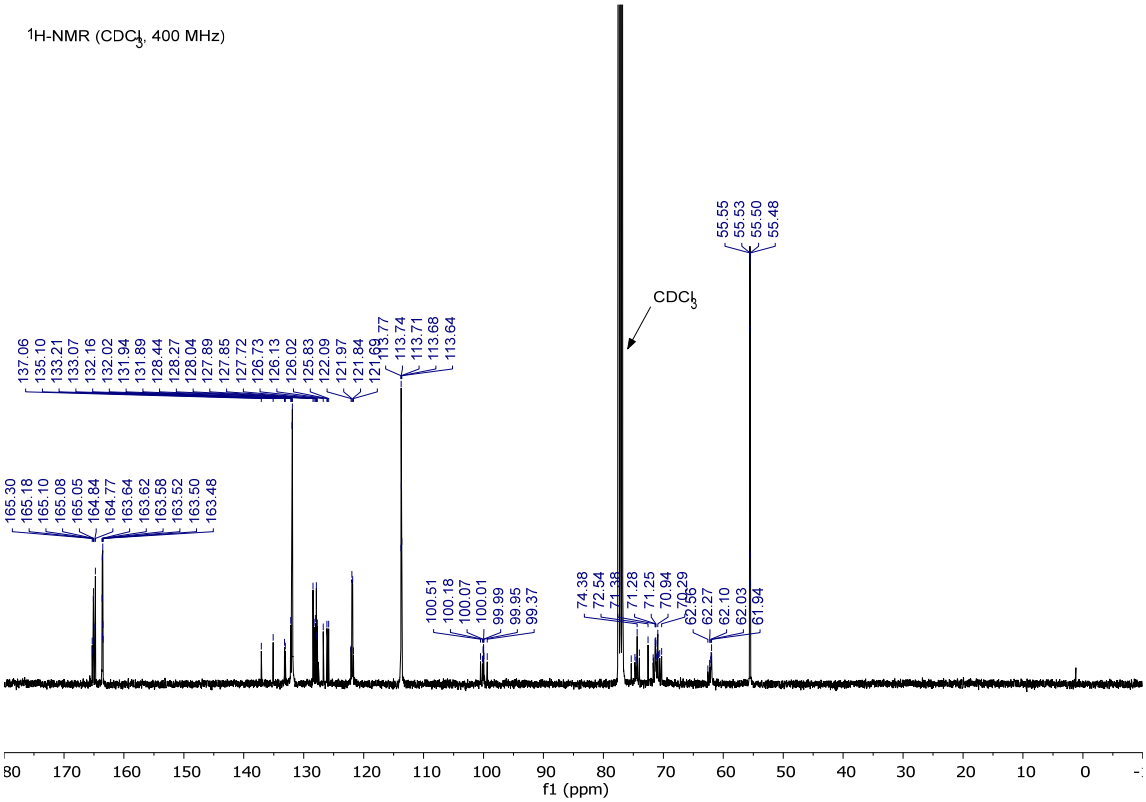
HSQC ($CDCl_3$)

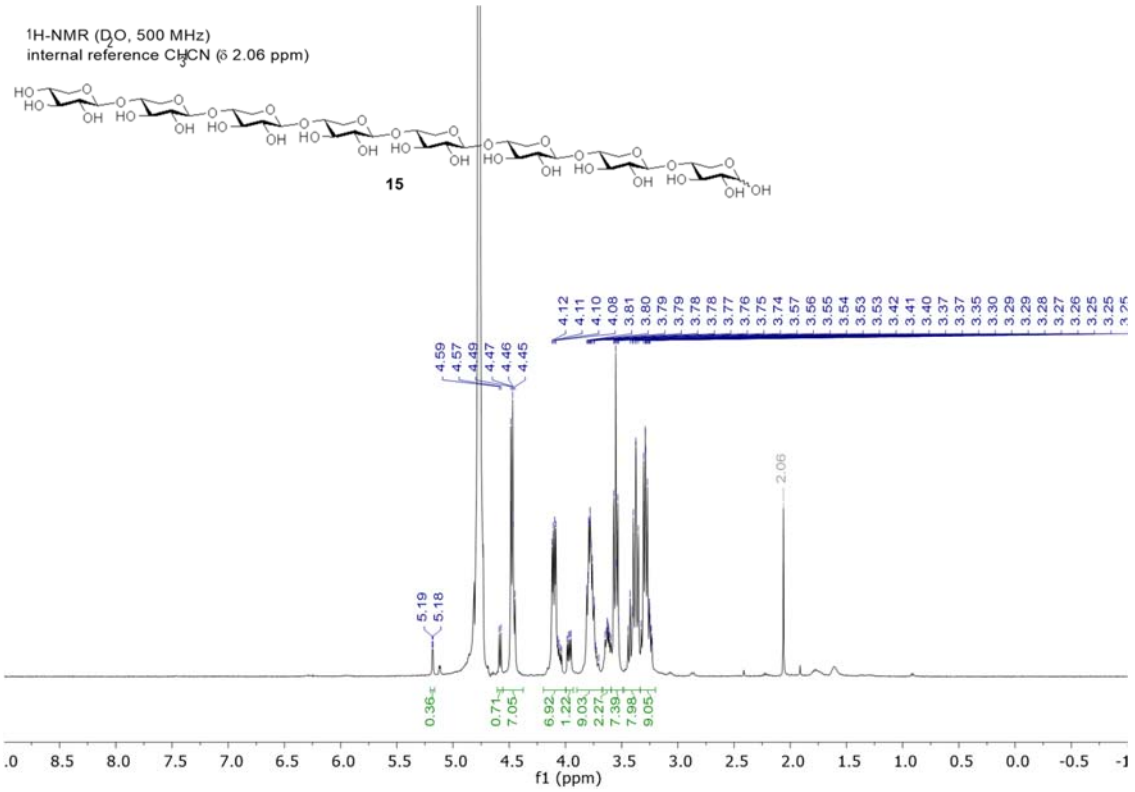


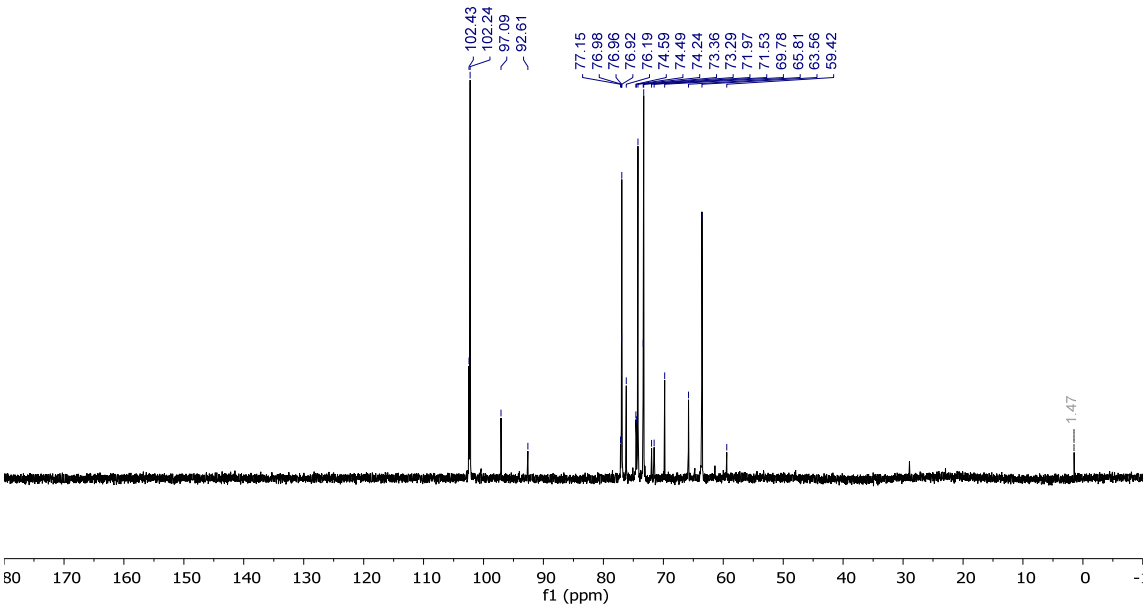
HMBC ($CDCl_3$)

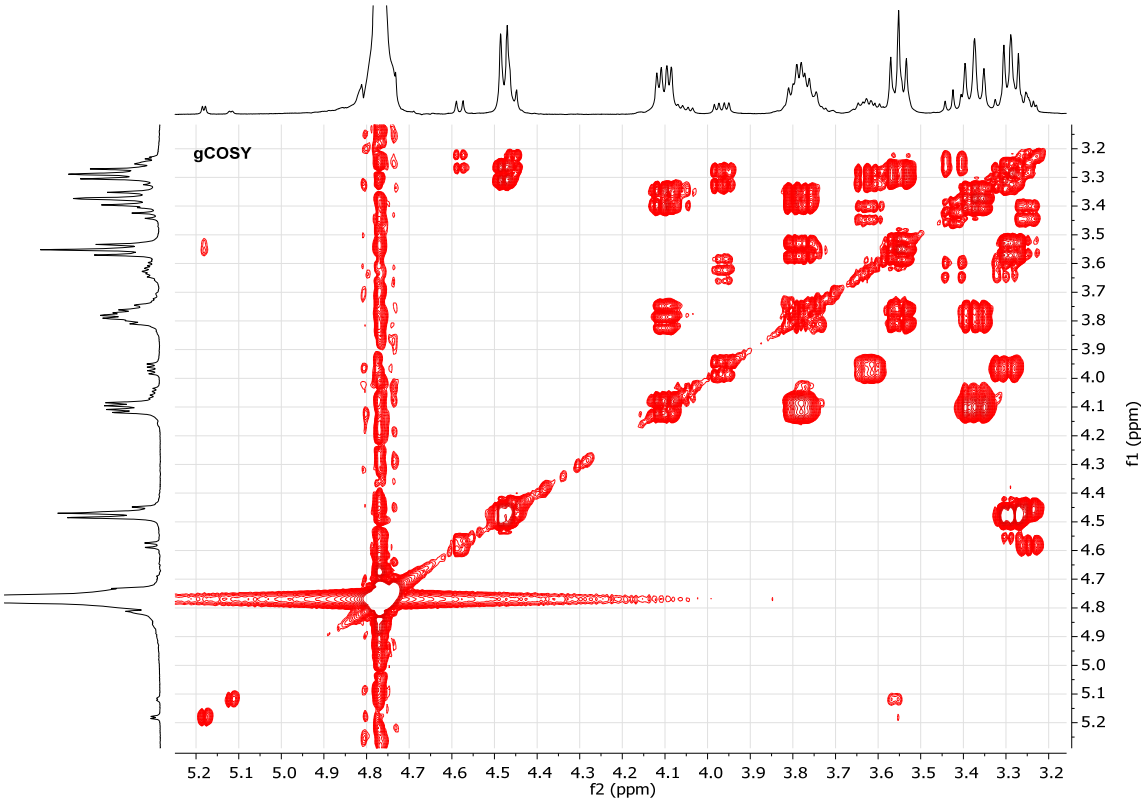


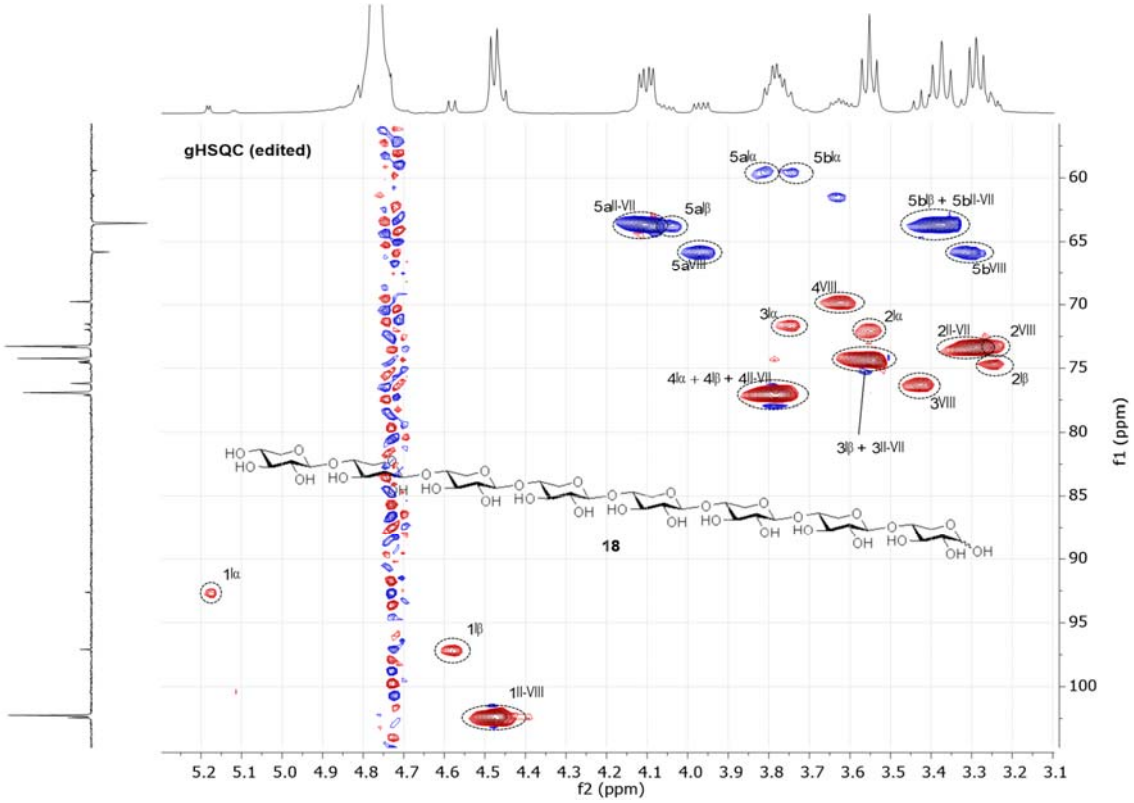

1H-NMR (CDCl3, 400 MHz)
14
CDCl3
1.65 HDO
f1 (ppm)


1H-NMR (CDCl3, 400 MHz)
CDCl3
f1 (ppm)


1H-NMR (D2O, 500 MHz)
internal reference CH3CN (δ 2.06 ppm)
15
f1 (ppm)

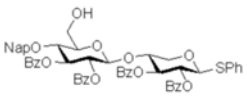

13C-NMR (D2O, 126 MHz)
internal reference CH3CN (δ 1.47 ppm)
f1 (ppm)


gCOSY
f2 (ppm)
f1 (ppm)

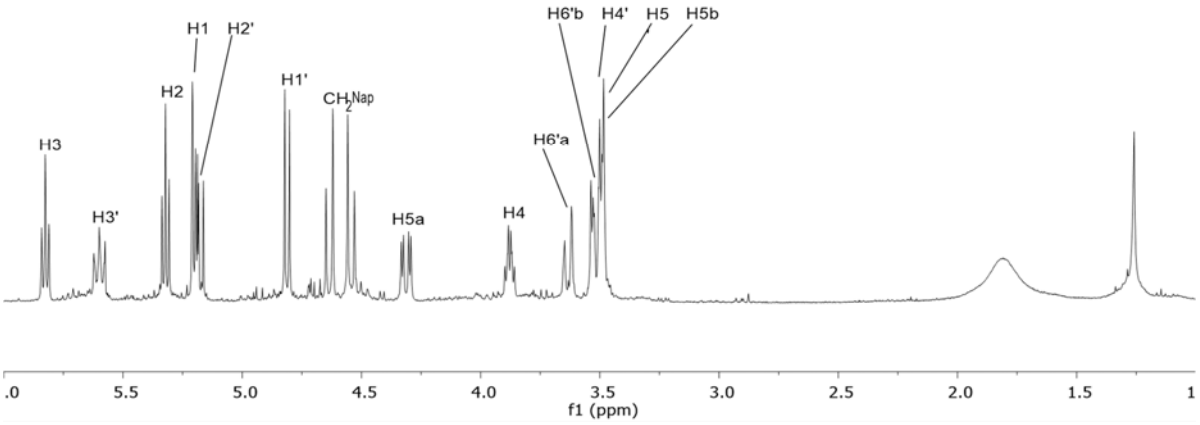

gHSQC (edited)
5aα
5bα
5aII-VII
5aβ
5aVIII
5bβ + 5bII-VII
5bVIII
4VIII
3α
2α
2II-VII
2VIII
4α + 4β + 4II-VII
2β
3VIII
3β + 3II-VII
18
1α
1β
1II-VIII
f2 (ppm)
f1 (ppm)

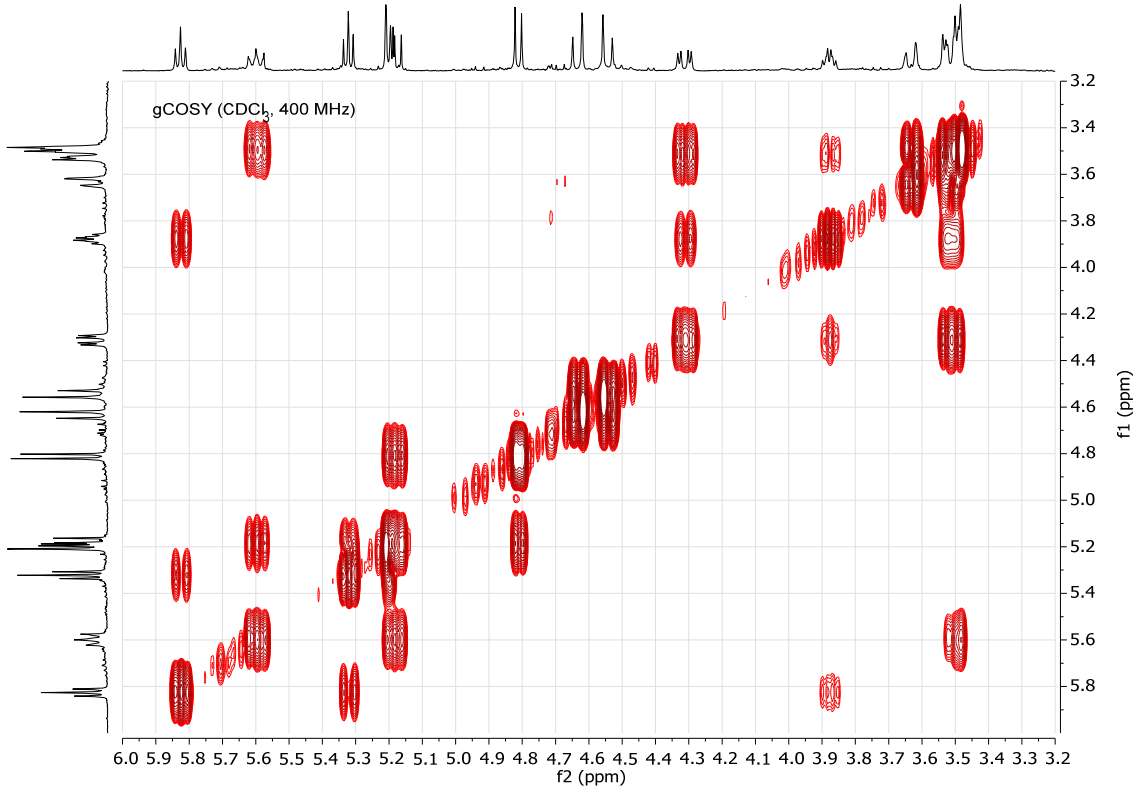
7) Intermediates from dehydrogentive decarbonylation of 5a

^{1}H NMR ($CDCl_3$, 400 MHz)

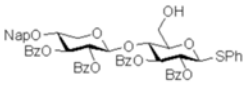


β-D-Glup-(1-4)-β-D-Xylp-SPh





^{1}H NMR ($CDCl_3$, 400 MHz)



β-D-Xyl*p*-(1-4)-β-D-Glu*p*-SPh