Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Translating Solution to Solid Phase Glycosylation Conditions

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Contents

Materials:

N,N-dimethylformamide (DMF), methanol (MeOH), dichloromethane (DCM), and dry toluene were purchased from BIO-LAB chemicals, Israel. Column chromatography: silica gel 60-120 mesh; thin layer chromatography (TLC): silica gel 60 F254 percolated plates; were purchased from Merck. Merrifield resin and Fmoc-Cl were purchased from CHEM-IMPEX. Pyridine, piperidine, tetrabutylammonium iodide (TBAI), sodium borohydride ($NaBH_4$), Cs_2CO_3, K_2CO_3, 1,4-Dioxane, triflic acid (TfOH) and 6-aminohexan-1-ol were purchased from Sigma-Aldrich, Israel. CsOAc and n-iodosuccinimide (NIS) purchased from ALFA-AESAR. Benzyl chlorofromate (Cbz-Cl) purchased from ACROS Organic. BB **6, 7** from GlycoUniverse GmbH & CO KGaA, Potsdam, Germany. *N*-acetyl glucosamine donors **4, 5** were synthesized following published procedures. For compound **4**, see: Kröck, L.; Esposito, D.; Castagner, B.; Wang, C.-C.; Bindschädler, P.; Seeberger, P. H. *Chem. Sci.* **2012**, *3*, 1617. For compound **5**, see: Bandara, M. D.; Stine, K. J.; Demchenko, A. V. *Carbohydrate Research* **2019**, *483*, 107743.

Methods:

NMR spectra were recorded in Brucker advance-II 500 MHz instrument. Chemical shifts are expressed in δ units. 1D and 2D-NMR were recorded in $CDCl_3$ using BBO-5mm probe unless stated otherwise. Low resolution Mass Spectrometry ESI-MS was performed on LCQ Fleet Ion Trap mass spectrometer (Thermo Scientific). High resolution Mass Spectrometry was recorded on either Agilent 6550 iFunnel Q-TOF LC/MS system or on Q Exactive Plus (Thermo Fisher Scientific). The experimental molecular mass of the compounds was determined from the collected m/z ratio for all the observed multiply charged species. UV measurements were performed on Shimadzu 300pc spectrophotometer by scanning wavelengths from 400 nm to 220 nm in a quartz cuvette (114 - QS Hellma GmbH & Co. KG). The compounds were purified by InterChim puriflash XS 420 with silica flash column F0012-14g-SI-HP 5- µm, and were recorded at a wavelength of 254 nm at room temperature.

RP-HPLC analysis

The crude material was analyzed by HPLC with C18 (5 µm) column at the flow rate of 1.0 mL/min using a general gradient method ramping from 5% to 95% ACN in TDW in 55 min.

Experimental section:

General Photocleavage Procedure:

Linker **2** or **3** immobilized on solid support was suspended in DCM (2 ml) and placed in a 1 cm quartz cuvette with a magnetic bar. The LED lamp was set to pass the beam directly into the solution of the cuvette. The irradiation was performed at 365 nm in a dark room for 3h. Light source was turned off and the suspension of solid support in DCM was collected with a plastic pipette and filtered through a fritted Sep-Pak cartridge (12 ml Capacity, 20 µm porosity Frits). An additional 2 ml of DCM were used to wash the cuvette remove the remaining solid support which also filtered through the same Sep-Pak. The combined DCM filtrate containing the cleaved compound was placed in a small 5 ml glass vial and the DCM was evaporated under reduced pressure.

Glyconeer^{TM} Synthesizer modules

The exact timing and quantity of solvents transferred to the reaction vessel (RV) in each step are controlled by the software and the exact composition of the solution is described for each module in the next section. The system is constantly pressurized using Argon gas so that the specific solvent/reagent is transferred by timing the opening and closing of the appropriate valves

General modules

Module 1: Swelling the resin

The resin was washed with DMF, THF, DCM (six times each with 2 ml). The resin was swollen in 2 ml DCM

Module2: Fmoc Deprotection:

The resin was washed with DMF (six times with 2 ml for 25 s), swollen in 2 ml DMF and the temperature of the RV is adjusted to 25 °C. DMF drained and a 2 ml solution of 20% piperidine in DMF was delivered to the RV. After 5 min the reaction solution was drained through the UV detector and the transmittance recorded. An additional 2 ml of 20% piperidine solution in DMF is delivered to the resin and incubated for another 5 min. After the second deprotection cycle, the resin was washed with DMF (six times with 2 ml for 15 sec).

Module 3: End wash

Rinses/purges all the manifolds at 20 ºC for 20 min.

Automated solution phase optimization glycosylation module: AGO module

A mixture of donors **4**-**8** (0.04 mmol) and linker acceptor **1** (0.007 mmol) was co-evaporated with toluene and dried in high vacuum overnight. The mixtures were dissolved in 8 ml of dry DCM and divided equally to four septum-sealed vials. The RV temperature was set to -40 ℃ and the RV was washed with DCM while temperature was adjusted. When the set temperature was reached, the donor/acceptor mixture was transferred to the RV and 1 ml of activator solution containing 0.01 mmol NIS and TfOH 3.6 µl in a DCM/dioxane 2:1 solution was added. The mixture was allowed to react at a constant temperature while occasionally mixing by argon bubbling. After 25 min the reaction mixture was transferred to a designated tube in the fraction collector where it was immediately quenched with water. This glycosylation cycle was repeated three more times each run, increasing the temperature to-25 ℃, -10 ℃, and finally to 10 ℃.

The quenched reaction mixture collected in the fraction collector tube was diluted with DCM (20 ml) and washed with a 1:1 solution of $NaHCO_3$/$Na_2S_2O_3$. The aqueous layer was extracted twice with DCM (2 × 10 mL) and the combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* to provide crude mixture of linker, product and hydrolyzed donor which was analyzed by HPLC without further purification.

AGA1 glycosylation module

Thioglycoside donors **4**-**8** (6 equiv, 0.18 mmol) were co-evaporated with toluene, dissolved in dry DCM (2 ml), and placed in septum-sealed vials. 41 mg of solid support **2** (loading 0.6 mmol/g) were placed in the RV and swollen according to the above module. After swelling the system was set to reach the

specific temperature that was determined by the optimization studies. During the adjustment of the temperature, RV was repeatedly washed by DCM. When the set temperature was reached, the donor mixture was transferred to the RV and 1 ml of activator solution, containing 0.18 mmol NIS and TfOH 64 µl in a DCM/dioxane (v/v, 2:1) solution, was added. The mixture was allowed to react at a constant temperature while occasionally mixing by argon bubbling. After 25 min the reaction mixture was transferred to a designated tube in the fraction collector and the resin in the reaction vessel was further washed with DCM (six times with 2 ml for 15 sec). The resin was taken out of the RV and photocleaved in DCM as described above. The crude product was analyzed by HPLC/MS and ^{1}H-NMR without any purification.

AGA2 glycosylation module

Thioglycoside donors **4**-**8** (1.5 equiv, 0.04 mmol) were co-evaporated with toluene, dissolved in dry DCM (2 ml), and placed in septum-sealed vials. 41 mg of solid support **2** (loading 0.6 mmol/g) were placed in the RV and swollen according to the above module. After swelling, the system was set to reach the specific temperature that was determined by the optimization studies. During the adjustment of the temperature, RV was repeatedly washed by DCM. When the set temperature was reached, the donor mixture was transferred to the RV and 1 ml of activator solution, containing NIS (0.04 mmol) and TfOH 14.5 µl in DCM/dioxane (v/v, 2:1), was added. The mixture was allowed to react at a constant temperature while occasionally mixing by argon bubbling. After 25 min the reaction mixture was transferred to a designated tube in the fraction collector and the resin in the reaction vessel was further washed with DCM (six times with 2 ml for 15 sec). The resin was taken out of the RV and photocleaved in DCM as described above. The crude product was analyzed by HPLC/MS and ^{1}H- NMR without any purification.

AGA3 glycosylation module

Thioglycoside donors **4**-**8** (1.5 equiv, 0.022 mmol based on loading) were co-evaporated with toluene, dissolved in dry DCM (2 ml), and placed in septum-sealed vials. 41 mg of solid support **3** (loading 0.3 mmol/g) were placed in the RV and swollen according to the above module. After swelling, the system was set to reach the specific temperature that was determined by the optimization studies. During the adjustment of the temperature, RV was repeatedly washed by DCM. When the set temperature was reached, the donor mixture was transferred to the RV and 1 ml of activator solution, containing 0.022 mmol NIS and 8 µl TfOH in DCM/dioxane (v/v, 2:1), was added. The mixture was allowed to react at a constant temperature while occasionally mixing by argon bubbling. After 25 min the reaction mixture was transferred to a designated tube in the fraction collector and the resin in the reaction vessel was further washed with DCM (six times with 2 ml for 15 sec). The resin was taken out of the RV and photocleaved in DCM as described above. The crude product was analyzed by HPLC/MS and ^{1}H-NMR without any purification.

Summary of glycosylation modules and conditions

Glycosylation method	Loading (mmol/g)	Acceptor (mM)	Donor/NIS (mM)	Temperature
AGO (solution)	------	0.6	3.3	-45 °C -10 °C
AGA1	0.6	10.0	60.0	As optimized
AGA2	0.6	10.0	13.3	As optimized
AGA3	0.3	5.0	7.3	As optimized

[a] A summary of the concentration used for acceptor, donor, and activator for each glycosylation strategy. TfOH was used in catalytic amounts. The molarity of the solid support refers to the reactive positions available for glycosylation, which were determined based on loading.

Tables:

Table 1: Automated solution phase manipulations using BB

	Moles (mmol)	**Concentration (mM)**	**Concentration in RV (mM)**
Linker **1**	$1.7*10^{-3}$	8.7	0.6
BB	$1.0*10^{-2}$	5.0	3.0

Table 2: AGA manipulations using 6 eq of the BB (Loading 0.6 mmol/g)

	Moles (mmol)	**Concentration (mM)**	**Concentration in RV (mM)**
Linker **2**	$30*10^{-3}$	15	10
BB	$18*10^{-2}$	90	60

Table 3: AGA manipulations using 1.5 eq of the BB (Loading 0.6 mmol/g)

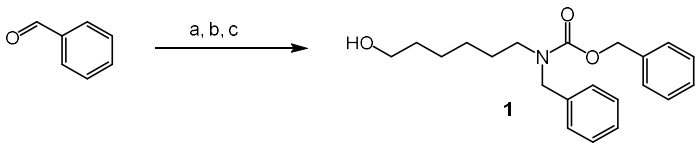
	Moles (mmol)	**Concentration (mM)**	**Concentration in RV (mM)**
Linker **2**	$30*10^{-3}$	15	10
BB	$45*10^{-3}$	22	15

Table 4: AGA manipulations using 1.5 eq of the BB (Loading 0.3 mmol/g)

	Moles (mmol)	**Concentration (mM)**	**Concentration in RV (mM)**
Linker **3**	0.015	7.5	5
BB	0.022	11	7

Synthetic Schemes

Synthesis of benzyl benzyl(6-hydroxyhexyl) carbamate **1**

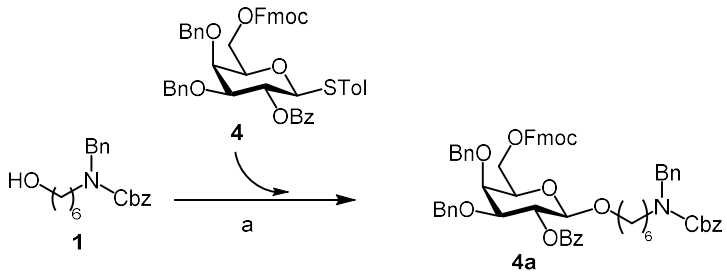


Scheme 1. Synthesis of linker **(1).** Reagents and conditions: a) 6-aminohexan-1-ol (1 equiv), Na_2SO_4, DCM. b) $NaBH_4$ (1.5 equiv), MeOH, 24 h, 25°C. c) Cbz-Cl (2 equiv), 2. Et_3N (2 equiv), K_2CO_3 (3 equiv), MeOH, 2 h, 25°C.

A solution of benzaldehyde (2.98 g, 0.028 mol) and 6-aminohexan-1-ol (3 g, 0.025 mol) was dissolved in DCM (60 ml) and sodium sulfate (Na_2SO_4, 3.63 g, 0.0256 mol) was slowly added, then the reaction was left overnight. The solvent was evaporated to furnish a yellowish foam. The crude imine was dissolved in MeOH (60 ml) and sodium borohydride ($NaBH_4$, 1.45 g, 0.0384 mol) was slowly added under bubbler control. The reaction was left overnight, after that the solvent was evaporated to furnish a yellowish foam. The crude product was dissolved in EtOAc and washed successively with water. The organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated. The crude was dissolved in DCM, then 7.14 ml of Et_3N (0.0512 mol) and 4.25 ml Cbz-Cl (0.02816 mol) were added to a solution of the amine and the mixture was stirred at ambient conditions. After 1 h, potassium carbonate (K_2CO_3, 6.20 g, 44.91 mmol) was added to the mixture and stirred for an additional 1 h. The solution was filtered through celite and solvents were evaporated. The crude was dissolved in DCM and washed successively with HCl (1 M) and water. The organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated. The residue was purified by flash chromatography (EtOAC/Hex) to give **1** (82% over three steps). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.31 - 7.41 (m, 10H), 5.18-5.14 (d, 2H,), 4.46 4.48 (d, 2H), 3.62-3.50 (d, 2H,), 3.30-3.26 (d, 2H), 1.75-1.41 (m, 4H), 1.20-1.34 (m, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$) 156.8, 136.9, 136.8, 132.9, 130.8, 128.5, 128.3, 127.9, 127.8, 127.4, 127.3, 127.2, 127.0, 62.7, 65.5, 50.5, 50.1, 27.6, 26.5, 26.4, 26.3, HRMS for: $[M+Na]^+$, calculated 364.1889; found: 364.1884.

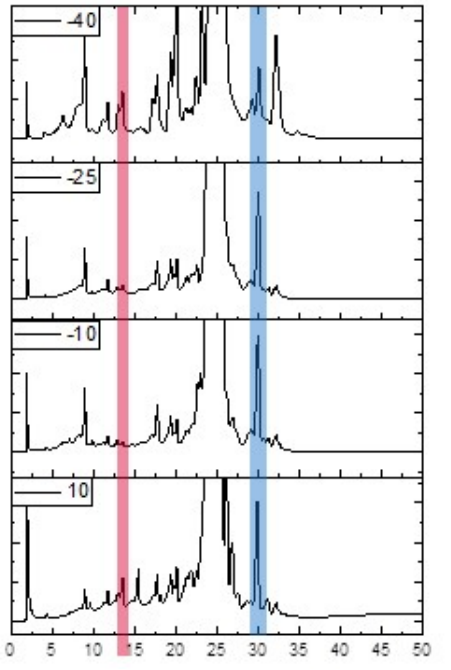
Synthesis, characterization and cleavage efficiency analysis of mono- and disaccharide

Synthesis of **4a** via AGO



Scheme 2: Synthesis of monosaccharide **4a** by AGA. Reagents and conditions: a) DMF, THF, DCM/ dioxane ,**4**, NIS, TfOH.

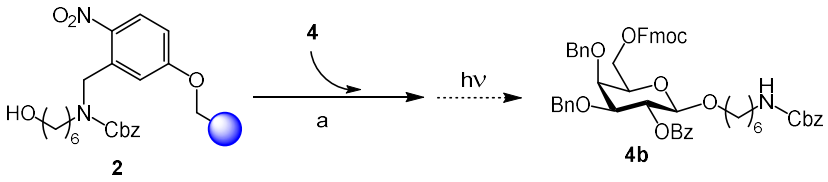
A mixture of linker **1** (0.5 mg) and **4** (7.99 mg) was co-evaporated with toluene and dried under high vacuum overnight, after which time it was dissolved in 2 ml of dry DCM. Linker **1** was glycosylated using AGO module. The crude monosaccharide was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 1032.4293, found 1032.42392.



*RP-HPLC trace of Monosaccharide **4a** recorded at 254 nm.*

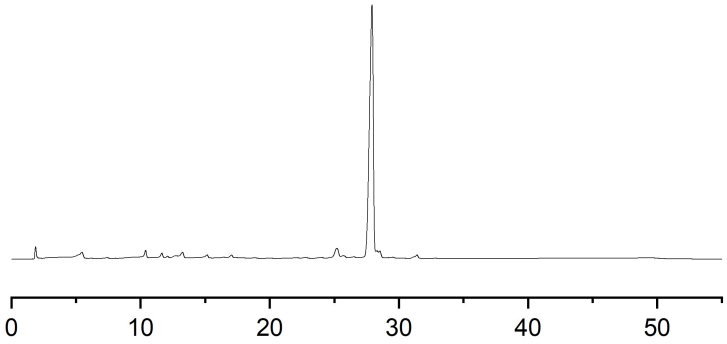
Glycosylation temperature (°C)	Acceptor Area %	4a Area %
-40	43	57
-25	11	89
-10	7	93
10	27	73

Synthesis **4b** via AGA1



Scheme 3: Synthesis of monosaccharide **4b** by AGA. Reagents and conditions: **a)** DMF, THF, DCM, DCM/ dioxane, **4**, NIS, TfOH, 40 min.

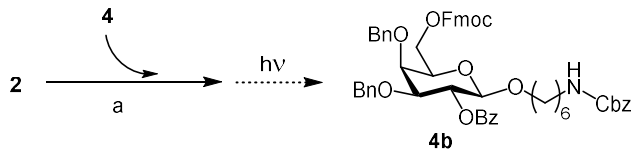
Linker **2** (41 mg, loading 0. 6 mmol/g) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **4** (143 mg) at -10 °C using glycosylation module AGA1. The monosaccharide was photo-cleaved using the breaking beads approach the crude monosaccharide **4b** was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 942.3824, found 942.3828 (Yield 57%), ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.53 – 7.52 (m, 2H), 7.45 – 7.42 (m, 2H), 7.34 – 7.25 (m, 3H), 7.19 – 7.17 (m, 9H), 7.13 – 6.99 (m, 10H), 5.65 – 5.54 (m, 1H), 5.11 (s, 1H), 5.03 – 5.01 (d, 2H), 4.25 – 4.19 (m, 3H), 4.13 – 4.10 (m, 1H), 4.09 – 4.01 (m, 4H), 3.85 – 3.80 (m, 2H), 3.59 – 3.55 (m, 2H), 3.19 – 3.14 (m, 2H), 2.99 – 2.95 (m, 2H),1.52 – 1.42 (m, 6H), 1.07 – 1.05 (m, 3H).



*RP-HPLC trace of **4b** recorded at 254 nm*

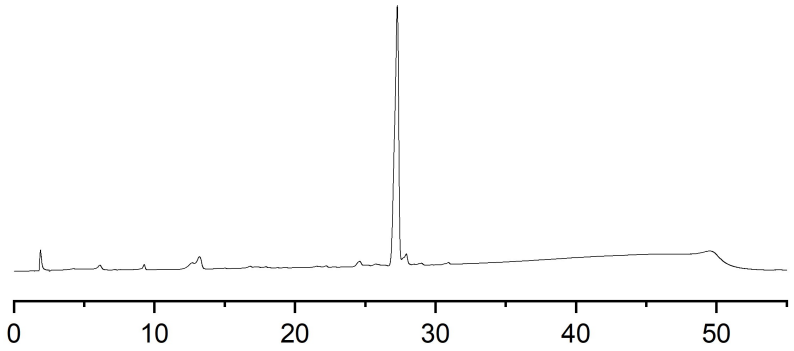
Acceptor	Acceptor area %	4b Area %
2	2	98

Synthesis of **4b** via AGA2



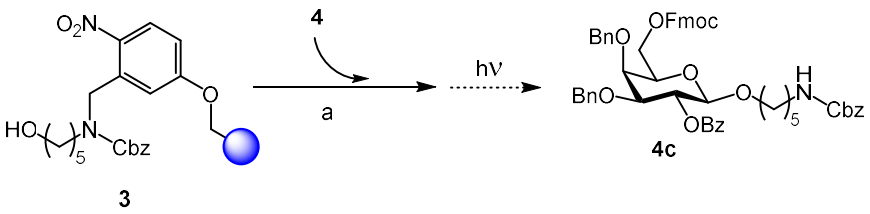
Scheme 4: Synthesis of monosaccharide **4b** by AGA2. Reagents and conditions: a**)** DMF, THF, DCM, DCM/ dioxane, **4**, NIS, TfOH.

Linker **2** (41 mg) was glycosylated with **4** using automated synthesizer Glyconeer 2.1 using glycosylation AGA2 at -10 °C. The crude **4b** was photocleaved and characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 942.3824, found 942.3821, HPLC, ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.53 – 7.52 (m, 2H), 7.45 – 7.42 (m, 2H), 7.34 – 7.25 (m, 3H), 7.19 – 7.17 (m, 9H), 7.13 – 6.99 (m, 10H), 5.65 – 5.54 (m, 1H), 5.11 (s, 1H), 5.03 – 5.01 (d, 2H), 4.25 – 4.19 (m, 3H), 4.13 – 4.10 (m, 1H), 4.09 – 4.01 (m, 4H), 3.85 – 3.80 (m, 2H), 3.59 – 3.55 (m, 2H), 3.19 – 3.14 (m, 2H), 2.99 – 2.95 (m, 2H),1.52 – 1.42 (m, 6H), 1.07 – 1.05 (m, 3H).



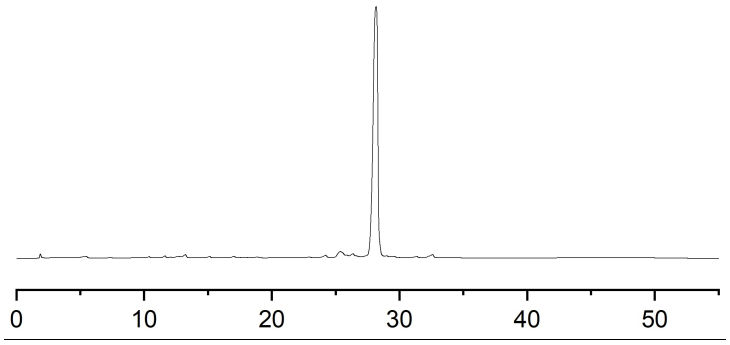
*RP-HPLC trace of **4b** recorded at 254 nm (crude)*

Synthesis of **4c** via AGA3



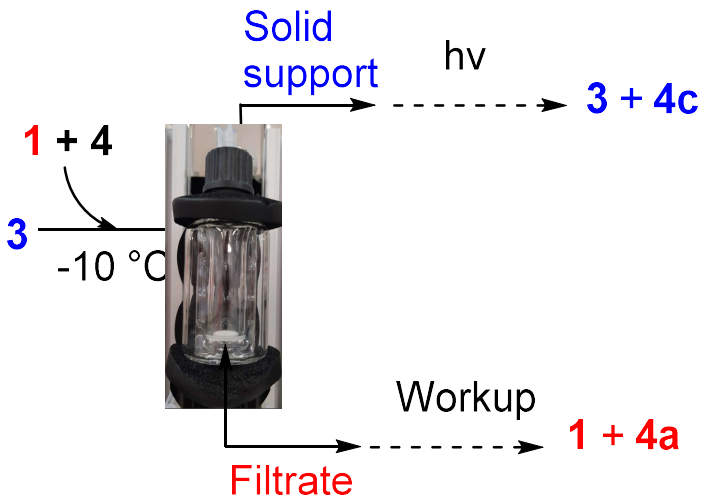
Scheme 5: Synthesis of monosaccharide **4c** by AGA. Reagents and conditions: a) DMF, THF, DCM/dioxane, **4**, NIS, TfOH.

Linker **3** (loading 0.3 mmol/g, 41 mg) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **4** (14.7 mg) at -10 °C using glycosylation AGA3. The monosaccharide was photo-cleaved and the crude **4c** was characterized by HPLC, HRMS for: [M+Na] +, calculated 928.3667, found 928.3666, ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.53 – 7.52 (m, 5H), 7.45 – 7.42 (m, 1H), 7.34 – 7.25 (m, 2H), 7.19 – 7.17 (m, 2H), 7.13 – 6.99 (m, 18H), 5.95 – 5.94 (m, 1H), 5.18 (m, 1H), 5.11 (s, 1H), 5.03 – 5.01 (d, 2H), 4.29 – 4.27 (m, 1H), 4.25 – 4.19 (m, 4H), 4.13 – 4.10 (m, 1H), 4.09 – 4.01 (m, 4H), 3.85 – 3.80 (m, 2H), 3.59 – 3.55 (m, 1H), 3.19 – 3.14 (m, 1H), 2.99 – 2.95 (m, 1H),1.19 – 1.13 (m, 3H), 1.07 – 1.05 (m, 3H) ^{13}C-NMR (125 MHz, $CDCl_3$) 165.2, 156.5, 154.8, 143.3, 143.2, 141.3, 137.9, 137.5, 136.7, 136.6, 133.1, 130.1, 129.8, 128.6, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.2, 127.0, 125.1, 120.1, 101.5, 74.4, 72.3, 72.1, 71.8, 70.0, 69.4, 66.7, 66.6, 66.5, 65.4, 62.7, 46.7, 40.9, 32.2, 29.8, 29.4, 28.9.



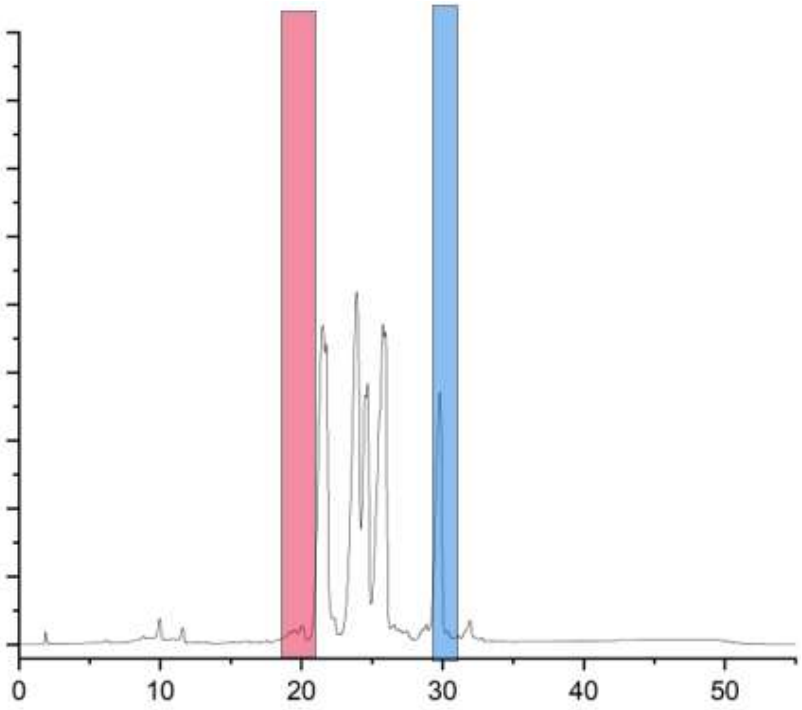
*RP-HPLC trace of **4c** recorded at 254 nm (crude)*

Automated co-assembly of **4a** and **4c** using simultaneous glycosylation of **1** and **3** via AGA3

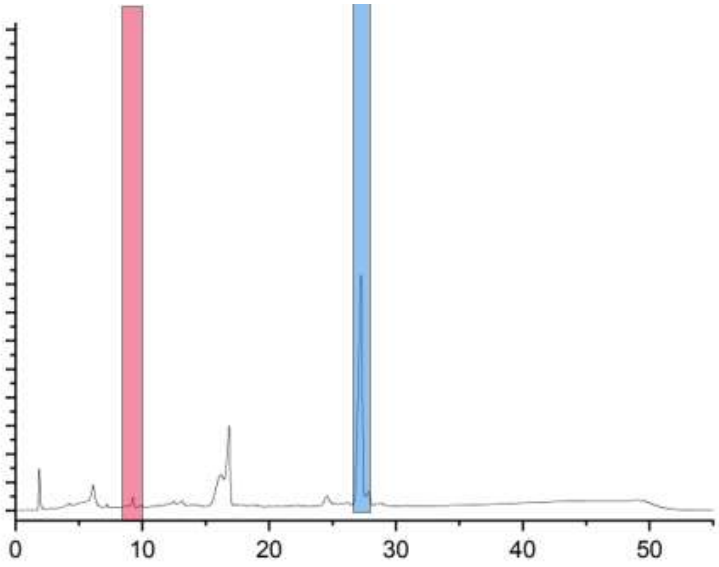


Scheme 6: Co-synthesis of **4a** and **4c** by AGA using one pot glycosylation. Reagents and conditions: a) DMF, THF, DCM, DCM/dioxane, **4**, NIS, TfOH.

A mixture of **1** (4 mg) and **4** (15 mg) was co-evaporated in toluene and dried under high vacuum overnight. The mixture was dissolved in 2 ml of dry DCM. Linker **3** (loading 0.3 mmol/g, 41 mg) was placed in the RV. Both linkers were co-glycosylated at -10 °C with donor **4** by delivery of the mixture of **1** and **4** to the RV containing **3** and activation using NIS/TfOH solution as described for protocol AGA3. The glycosylation mixture was collected and quenched, and the ratio between **1** and **4a** was determined by HPLC after a quick workup. The solid support was washed after glycosylation and later irradiated at 365 nm to yield a mixture containing **3** and **4c** in DCM. The solvent was evaporated and the resulting crude product was analyzed by HPLC to determine the ratio between **3** and **4c**. The glycosylation efficiency of **1** to **4a** and of **3** to **4c** were of comparable ratios.



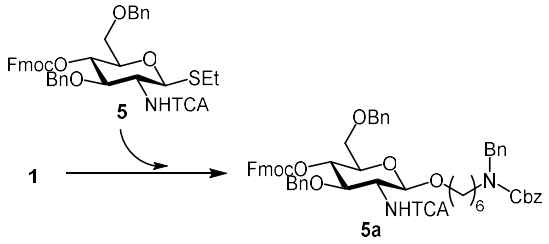
*RP-HPLC trace of **4a** recorded at 254 nm (Crude), red (**1**), blue (**4a**)*



*RP-HPLC trace of **4c** recorded at 254 nm (Crude): red (**1**), blue (**4c**)*

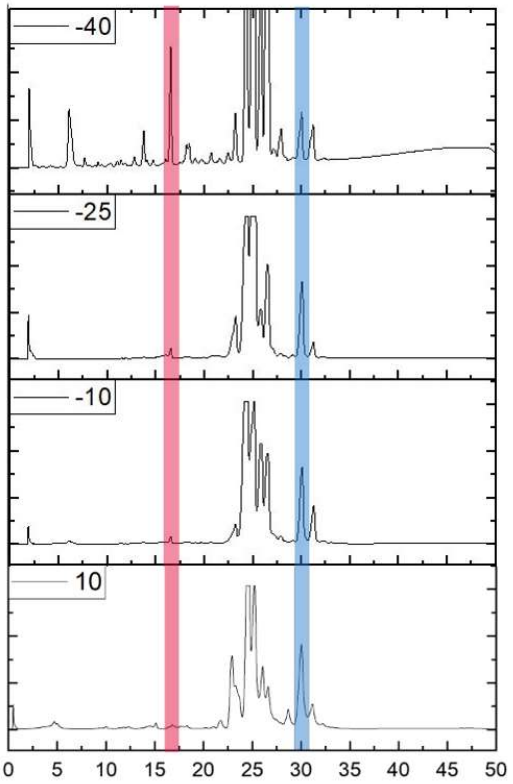
Acceptor	Acceptor area %	Product Area %
3	2	98
1	8	92

AGO of **5a**



Scheme 7: Synthesis of monosaccharide **5a** by AGO. Reagents and conditions: a) DCM, **5**, NIS, TfOH, 25 min.

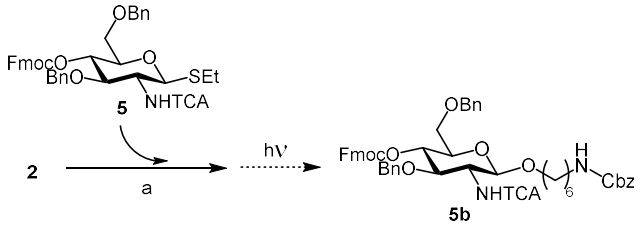
A mixture of (0.5 mg) of **1** and (7.99 mg) of **5** was co-evaporated in toluene and dried in high vacuum overnight, mixture was dissolved in 2 ml of dry DCM. **1** was glycosylated using the Automated Solution Phase Optimization Glycosylation module**.** The crude **5a** was characterized by HPLC, HRMS for: $[M]^+$, calculated 1048.3235, found 1048.3239.



*RP-HPLC trace of **5a** recorded at 254 nm.*

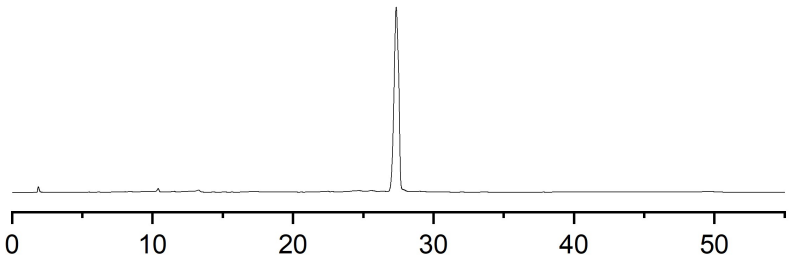
Glycosylation temperature (°C)	Acceptor Area %	5a Area %
-40	25	75
-25	24	76
-10	6	94
10	5	95

Synthesis of **5b** via AGA1



Scheme 8: Synthesis of monosaccharide **5b** by AGA1. Reagents and conditions: a) DMF, THF, DCM, **5**, NIS, TfOH, 25 min, 10 °C.

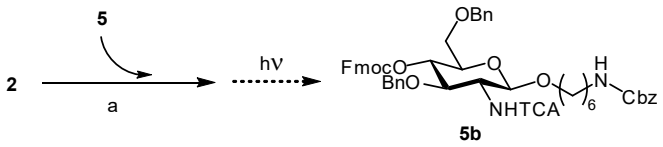
linker **2** (41 mg, loading 0.6) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **5** (136 mg) at 10 °C using glycosylation module AGA1. **5b** was photo-cleaved and the crude **5b** was characterized by HPLC, HRMS: $[M+Na]^+$, calculated 981.2658, found 981.2657 (Yield 45%), ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.92 – 6.99 (m, 23H), 5.95 – 5.94 (m, 1H), 5.18 (d, 1H), 5.11 (s, 1H), 4.60 – 4.72 (m, 4H), 4.13 – 4.10 (m, 1H), 3.50– 4.01 (m, 4H), 3.59 – 3.55 (m, 5H),1.19 – 1.13 (m, 4H).



*RP-HPLC trace of Monosaccharide **5b** recorded at 254 nm (Crude).*

Acceptor	Acceptor Area %	5b Area %
2	1	99

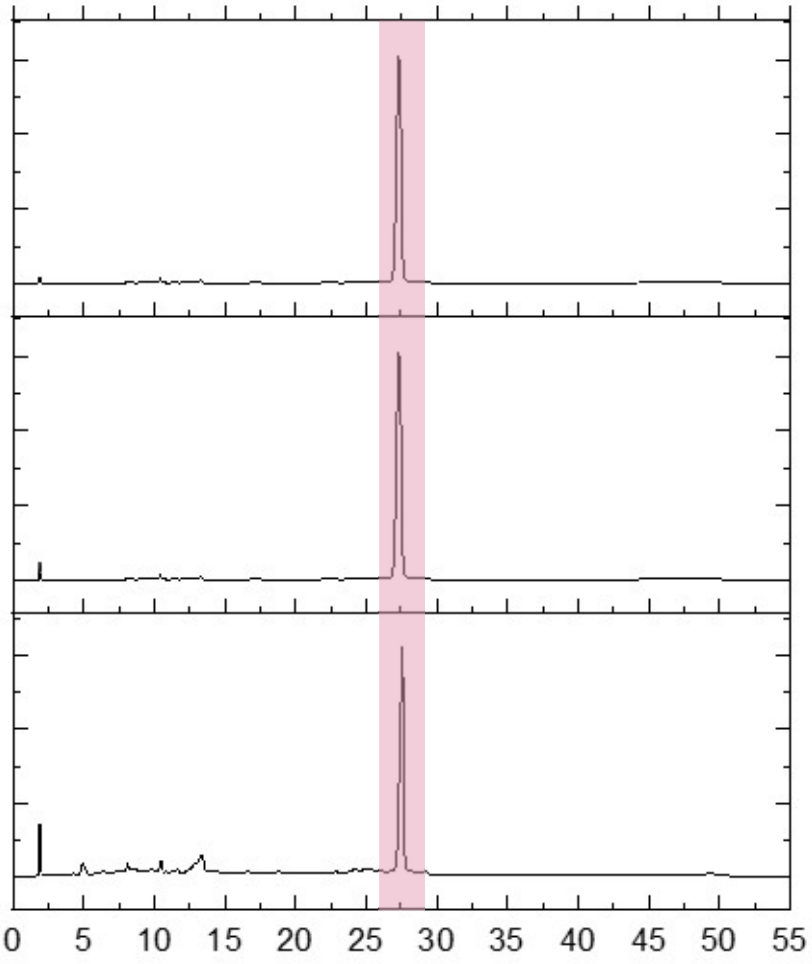
Synthesis of **5b** via AGA2



Scheme 9: Synthesis of monosaccharide **5b** by AGA2. Reagents and conditions: a) DMF, THF, DCM, **5**, NIS, TfOH, 25 min, 10 °C.

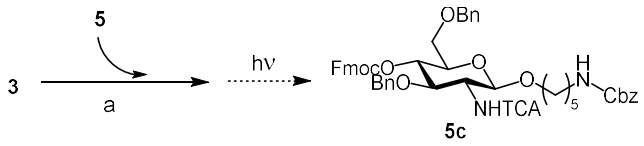
Linker **2** (41 mg, loading 0.6) was glycosylated using automated synthesizer Glyconeer 2.1 with thioglycoside donor **5** (33 mg) at 10 °C using glycosylation module AGA2. **5b** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 981.2658, found 981.2660 (Yield 40 %), ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.82 – 6.79 (m, 23H), 5.75 – 5.64 (m, 1H), 5.21 (d, 1H), 5.11 (s, 1H), 4.68 – 4.72 (m, 4H), 4.15 – 4.10 (m, 1H), 3.50– 4.01 (m, 4H), 3.59 – 3.55 (m, 5H),1.19 – 1.13 (m, 4H).

This experiment was repeated 3 times to prove the reproducibility.



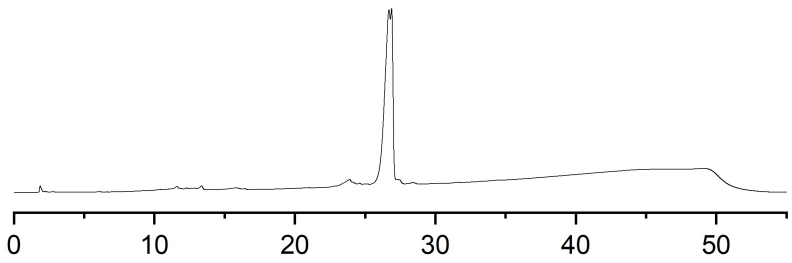
*RP-HPLC trace of Monosaccharide **5b** recorded at 254 nm. (crude)*

Synthesis of **5c** via AGA3



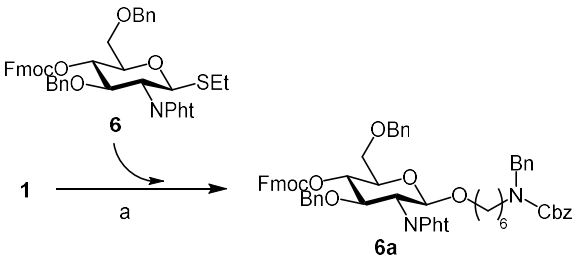
Scheme 10: Synthesis of monosaccharide **5c** by AGA3. Reagents and conditions: a) DMF, THF, DCM/ dioxane, **5**, NIS, TfOH, 25 min, 10 °C

Linker **3** (loading 0.3 mmol/g, 41 mg) was glycosylated using automated synthesizer Glyconeer 2.1 with thioglycoside donor **5** (17.02 mg) at 10 °C module using glycosylation module AGA3. **5c** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 967.2502, found 967.2500 (Yield 43 %), ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.82 – 6.79 (m, 23H), 5.11 (m, 3H), 4.68 – 4.72 (m, 4H), 4.15 – 4.10 (m, 2H), 3.50– 4.01 (m, 3H), 3.49 – 3.35 (m, 4H), 3.19 – 3.20 (m, 2H),1.19 – 1.13 (m, 4H) ,1.09 – 1.10 (m, 2H), ^{13}C-NMR (125 MHz, $CDCl_3$): 162.0, 154.3, 143.3, 141.3, 137.8, 137.5, 128.6, 128.5, 128.4, 128.3, 128.1, 127.3, 127.7, 127.2, 127.0, 125.1, 125.0, 120.1, 98.9, 73.6, 73.0, 70.1, 69.4, 69.4. 65.4, 62.7, 58.8, 46.7, 29.8, 29.5, 22.9.



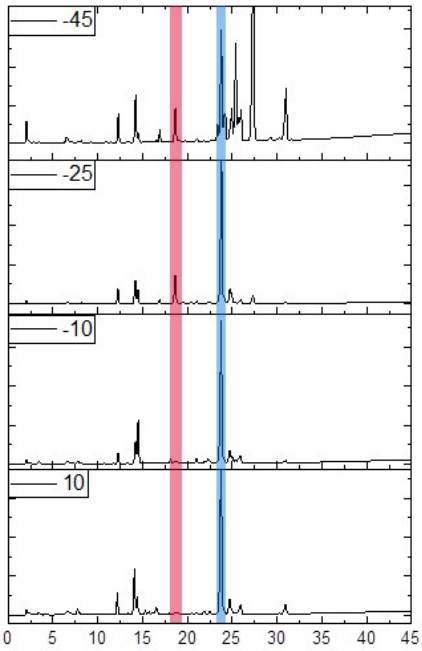
*RP-HPLC trace of Monosaccharide **5c** recorded at 254 nm (Crude)*

Synthesis of **6a** via AGO



Scheme 11: Synthesis of monosaccharide **6a** by AGO. Reagents and conditions: a) DMF, THF, DCM, DCM/ Dioxane, **6**, NIS, TfOH.

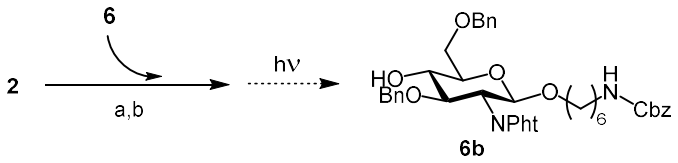
A mixture of (0.5 mg) of linker **1** and (7.6 mg) of **6** was co-evaporated with toluene and dried under high vacuum overnight, after which it was dissolved in 2 ml of dry DCM. The linker was glycosylated using automated solution phase optimization glycosylation module AGO. Crude **6a** was characterized by HPLC, HRMS for: $[M+H]^+$, calculated 1067.5058, found 1067.5060.



*HPLC of crude **6a***

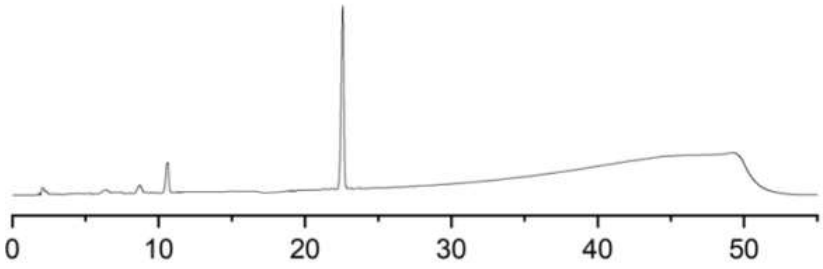
Glycosylation temperature (°C)	Acceptor Area %	6a %
-40	34	66
-25	24	76
-10	8	92
10	4	96

Synthesis of **6b** via AGA1



Scheme 12: Synthesis of monosaccharide **6b** by AGA1. Reagents and conditions: a) DCM/ dioxane, **6**, NIS, TfOH b) 20% piperidine /DMF

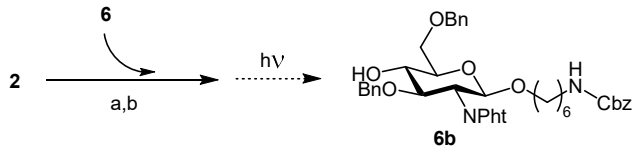
Linker **2** (loading 0. 6 mmol/g) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **6** (136 mg) at 10 ℃ using glycosylation module AGA1. Fmoc was removed and **6b** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 745.3101, found 745.3103 (Yield 52%).



*HPLC of crude monosaccharide **6b** recorded at 254 nm*

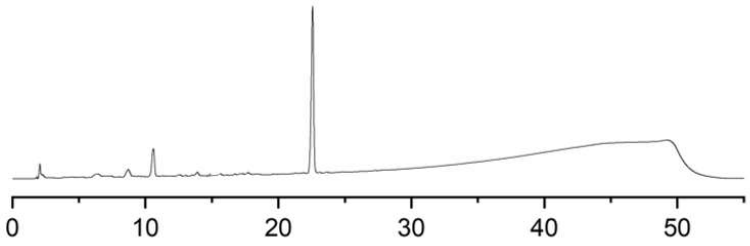
Acceptor	Acceptor Area %	6b Area %
2	7	93

Synthesis of **6b** via AGA2



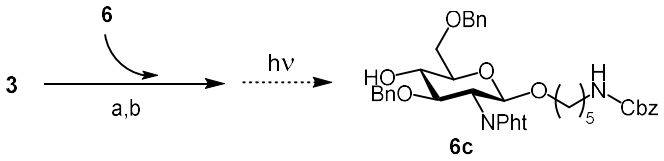
Scheme 13: Synthesis of monosaccharide **6b** by AGA2. Reagents and conditions: a) DMF, THF, DCM, DCM/ dioxane, **6**, NIS, TfOH b) 20% piperidine /DMF

Linker **2** (loading 0.6 mmol/g, 41 mg) was glycosylated with 34 mg of **6** at 10 °C using glycosylation module AGA2. Fmoc was removed and **6b** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$ calculated 745.3101, found 745.3101 (Yield 49%), ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.13 – 6.99 (m, 19H), 6.09 – 6.08 (m, 1H), 5.95 – 5.94 (m, 1H), 5.18 (d, 1H), 5.11 (s, 1H), 4.60 – 4.72 (m, 4H), 4.13 – 4.10 (m, 1H), 3.50– 4.01 (m, 4H), 3.85 – 3.80 (m, 2H), 3.59 – 3.55 (m, 2H),1.19 – 1.13 (m, 5H), 1.07 – 1.05 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) verified by HSQC: 167.7, 167.6, 155.9, 128.0, 127.9, 127.8, 127.8, 127.8, 127.8, 127.8, 127.2, 127.2, 127.1, 125.5, 125.4, 125.3, 125.2, 119.9, 98.9, 82.6 ,71.7, 71.6, 71.3, 71.2, 71.1, 70.6, 70.5, 40.3, 26.5, 26.4, 25.8, 23.2.



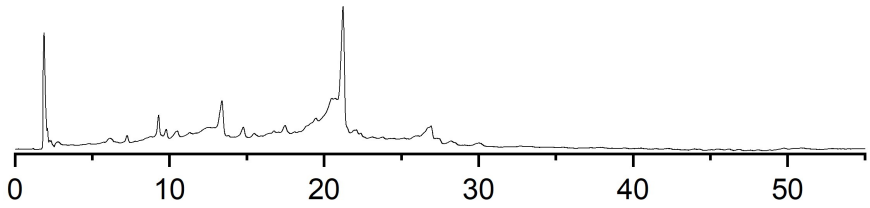
*RP-HPLC trace of **6b** recorded at 254 nm (crude)*

Synthesis of **6c** via AGA3



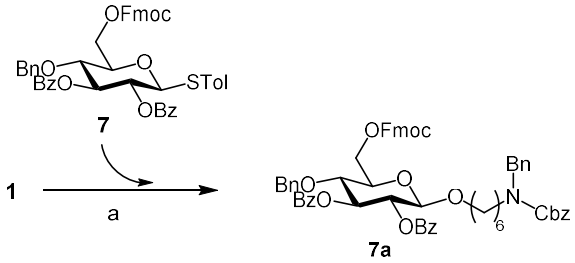
Scheme 14: Synthesis of monosaccharide **6c** by AGA3. Reagents and conditions: a) DMF, THF, DCM/ dioxane, **6**, NIS, TfOH b) 20% Piperidine/DMF.

Linker **3** (loading 0.3 mmol/g, 41 mg) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **6** (16.61 mg) at 10 °C using glycosylation module AGA3. Fmoc was removed and **6c** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$ calculated 731.2945, found 731.2942 (Yield 38%), ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.13 – 6.99 (m, 19H), 5.95-5.11 (m, 3H), 4.60 – 4.72 (m, 4H), 4.13 – 4.10 (m, 1H), 3.50– 4.01 (m, 2H), 3.85 – 3.80 (m, 2H), 3.59 – 3.55 (m, 2H),1.42 – 1.13 (m, 3H), 1.07 – 1.05 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$)140.9, 136.6, 129.7, 129.0, 128.6, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 127.4, 127.0, 125.2, 98.3, 76.8, 74.3, 73.8, 73.5, 70.8, 66.7, 65.4, 62.7, 55.4, 40.8, 29.8, 29.3, 28.8.



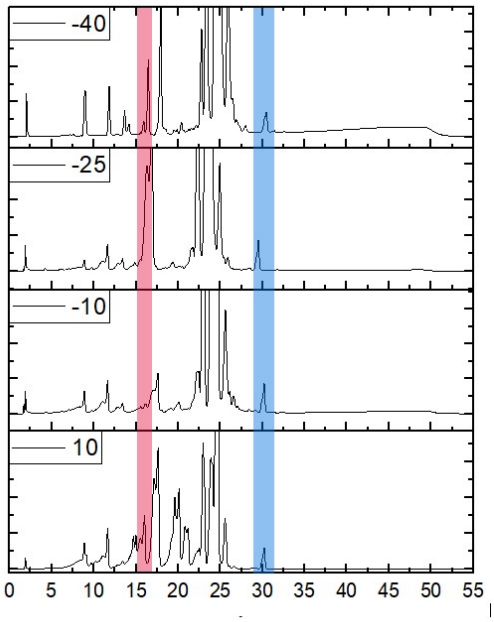
*RP-HPLC trace of Monosaccharide **6c** recorded at 254 nm (crude)*

AGO of **7a**



Scheme 15: Synthesis of monosaccharide **7a** by AGO. Reagents and conditions: a) DMF, THF, DCM/ dioxane, **7**, NIS, TfOH.

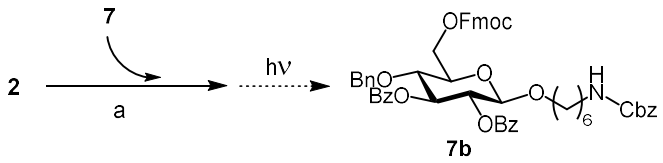
A mixture of (0.5 mg) of **1** and (7.99 mg) of **7** was co-evaporated with toluene and dried under high vacuum overnight, after which it was dissolved in 2 ml of dry DCM. **1** was glycosylated with **6** using AGO module and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 1046.4086, found 1047.4083.



*RP-HPLC trace of Monosaccharide **7a** recorded at 254 nm.*

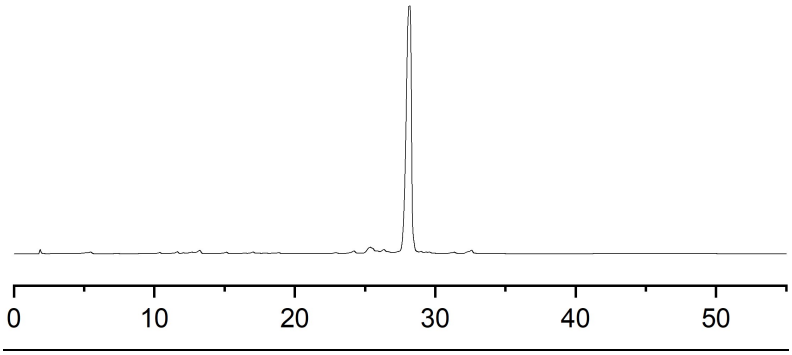
Glycosylation temperature (°C)	Acceptor Area %	Product Area %
-40	58	42
-25	75	25
-10	7	93
10	61	39

Synthesis of **7b** via AGA1



Scheme 16: Synthesis of monosaccharide **7b** by AGA1. Reagents and conditions: a) DMF, THF, DCM, DCM/ dioxane, **7**, NIS, TfOH.

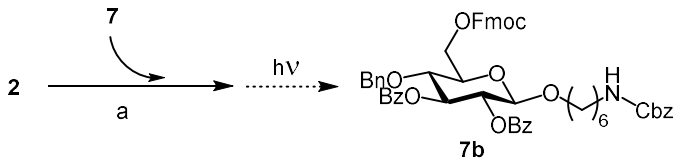
Linker **2** (loading 0. 6 mmol/g) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **7** (143 mg) at (-10 °C) using glycosylation module AGA1**. 7b** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 956.3616, found 956.3619 (Yield 50 %). ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.95 – 7.80 (m, 10H), 7.13 – 7.00 (m, 18H), 5.95 – 5.94 (m, 1H), 5.35-5.25 (m, 1H), 5.22-5.09(m, 1H), 5.07 – 5.01 (d, 2H), 4.30 – 4.27 (m, 1H), 4.26 – 4.20 (m, 4H), 4.15 – 4.10 (m, 1H), 4.10 – 4.01 (m, 4H), 3.89 – 3.82 (m, 2H), 3.59 – 3.55 (m, 1H), 3.19 – 3.14 (m, 1H), 2.99 – 2.95 (m, 2H),1.39 – 1.13 (m, 3H), 1.10 – 1.05 (m, 5H).



*RP-HPLC trace of **7b** recorded at 254 nm (crude)*

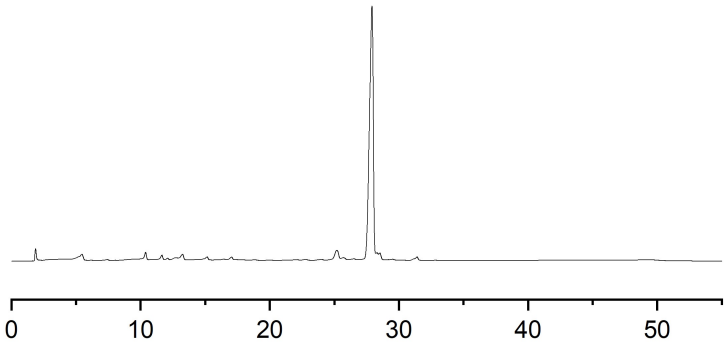
Acceptor	Acceptor Area %	Product Area %
2	8	92

Synthesis of **7b** via AGA2



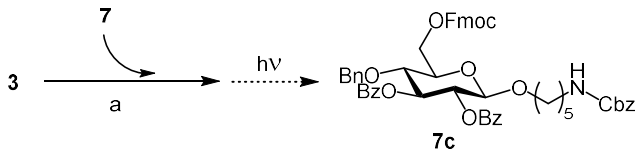
Scheme 17: Synthesis of monosaccharide **7b** by AGA2. Reagents and conditions: a**)** DMF, THF, DCM, DCM/ dioxane, **7**, NIS, TfOH.

Linker **2** (loading 0. 6 mmol/g, 41 mg) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **7** (33 mg) at (-10 °C) using glycosylation module AGA2. **7b** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 956.3616, found 956.3620 (Yield 48%). ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.95 – 7.82 (m, 10H), 7.13 – 6.99 (m, 18H), 5.95 – 5.94 (m, 1H), 5.30-5.25 (m, 1H), 5.22-5.11(m, 1H), 5.03 – 5.01 (d, 2H), 4.29 – 4.27 (m, 1H), 4.25 – 4.19 (m, 4H), 4.13 – 4.10 (m, 1H), 4.09 – 4.01 (m, 4H), 3.85 – 3.80 (m, 2H), 3.59 – 3.55 (m, 1H), 3.19 – 3.14 (m, 1H), 2.99 – 2.95 (m, 2H),1.39 – 1.13 (m, 3H), 1.10 – 1.05 (m, 5H).



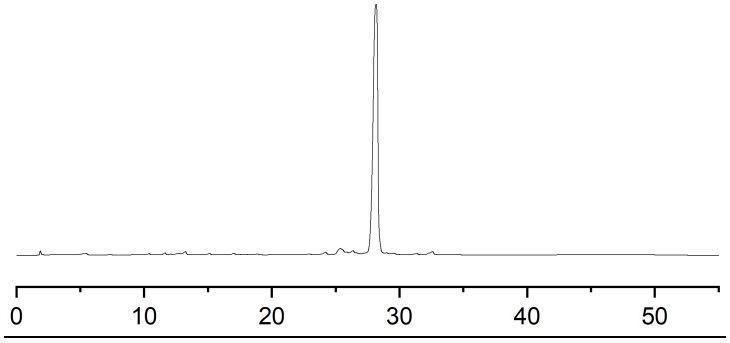
*RP-HPLC trace of **7b** recorded at 254 nm (crude)*

Synthesis of **7c** via AGA3



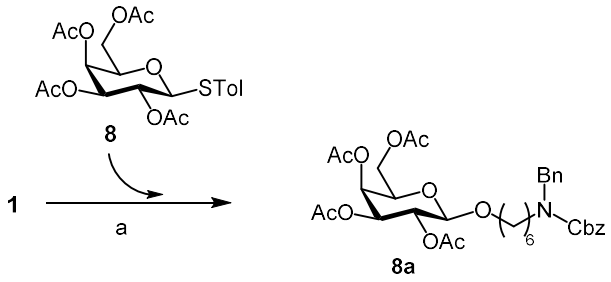
Scheme 18: Synthesis of monosaccharide **7c** by AGA3. Reagents and conditions: a) DMF, THF, DCM/ dioxane, **7**, NIS, TfOH.

Linker **3** (loading 0.3 mmol/g, 41 mg) was glycosylated with thioglycoside donor **7** (15.08 mg) at (-10 °C) using glycosylation module AGA3. **7c** was photo-cleaved and the crude was characterized by HPLC, HRMS for: $[M+Na]^+$, calculated 942.3460, found 942.3462 (Yield 42%). ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.53 – 7.52 (m, 8H), 7.45 – 7.42 (m, 10H), 7.90 – 7.75 (m, 8H), 7.19 – 7.17 (m, 2H), 7.13 – 6.99 (m, 18H), 5.30-5.25 (m, 1H), 5.22-5.11(m, 1H), 5.03 – 5.01 (m, 2H), 4.25 – 4.19 (m, 2H), 4.13 – 4.10 (m, 1H), 4.09 – 4.01 (m, 4H), 3.85 – 3.80 (m, 3H), 3.59 – 3.55 (m, 1H), 3.19 – 3.14 (m, 2H), 3.12 – 3.05 (m, 2H), 1.20 – 1.05 (m, 6H), ^{13}C-NMR (125 MHz, $CDCl_3$)165.7, 155.0, 143.4, 143.2, 141.3, 136.8, 133.3, 130.2, 129.8, 129.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 128.1, 127.9, 127.7, 127.2, 127.1, 125.2, 123.2, 120.1, 101.1, 73.2, 72.0, 70.1, 69.9, 69.9, 66.2, 64.0, 46.7, 32.2, 30.9, 29.8, 28.9, 23.0, 22.9.



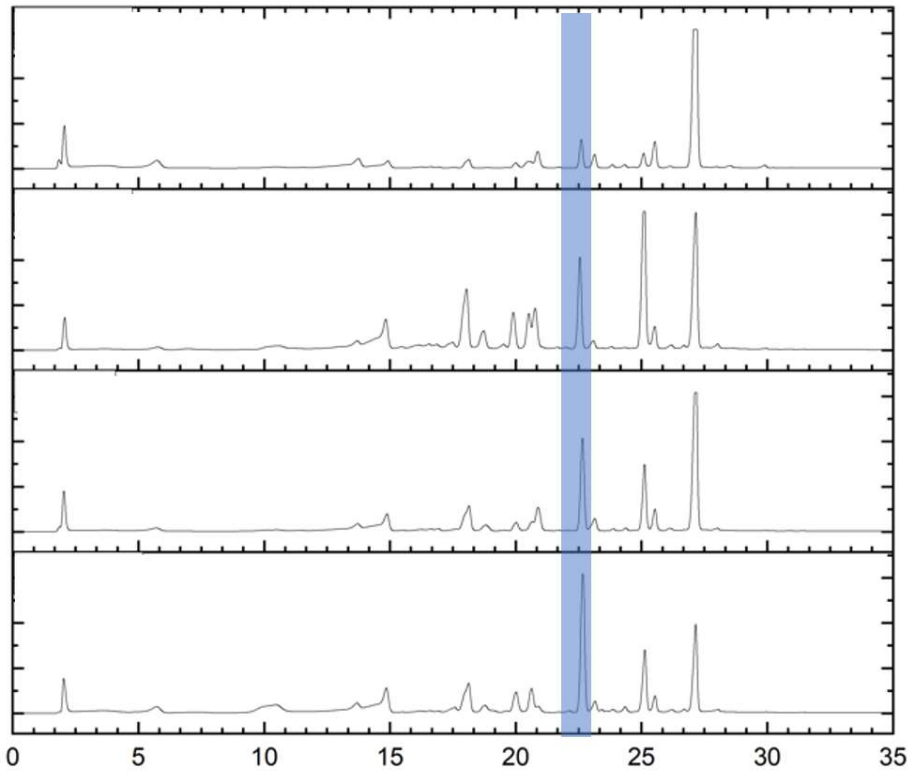
*RP-HPLC trace of **7c** recorded at 254 nm (crude)*

Synthesis of **8a** using AGO module



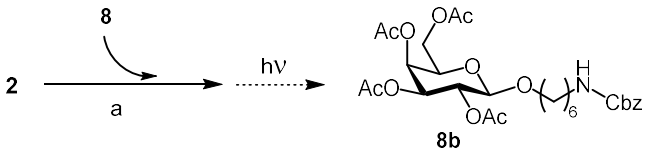
Scheme 19: Synthesis of monosaccharide **8a** by AGO. Reagents and conditions: a) DMF, DCM, THF, DCM/ dioxane ,**8**, NIS, TfOH.

A mixture of (0.5 mg) of **1** and (4.7 mg) of **8** was co-evaporated with toluene and dried in high vacuum overnight, after which time it was dissolved in 2 ml of Dry DCM. **1** was glycosylated with **8** using AGOmodule and the crude was characterized by HPLC, MS to show no product.



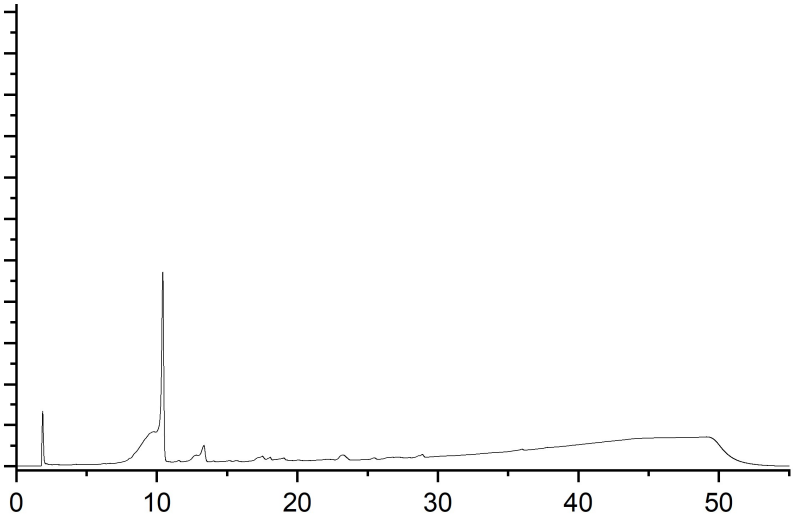
*RP-HPLC trace of Monosaccharide **8a** recorded at 254 nm. The peak at 23.5 min correlates with **1**.and all the other peaks were collected and checked by HRMS, none of the peaks show the mass of monosaccharide **8a***

Synthesis of **8b** via AGA1



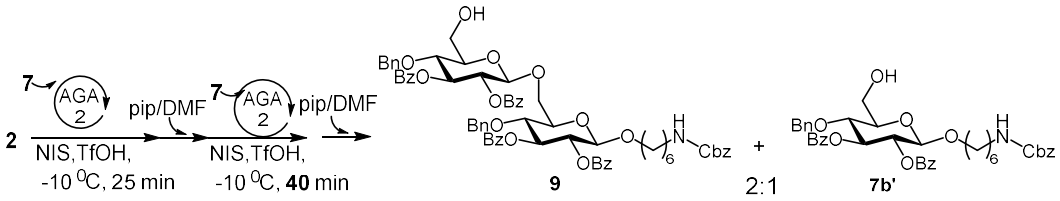
Scheme 20: Synthesis of monosaccharide by **8b** AGA1. Reagents and conditions: a) DMF, THF, DCM DCM/ dioxane, **8**, NIS, TfOH.

Linker **2** (loading 0.6 mmol/g) was glycosylated using automated synthesizer Glyconeer 2.1. with thioglycoside donor **8** (81.7 mg) at -10 ℃ using AGA1 glycosylation module. Reaction outcome was photo-cleaved the crude compound **8b** was characterized by HPLC, MS and showed no trace of the product.



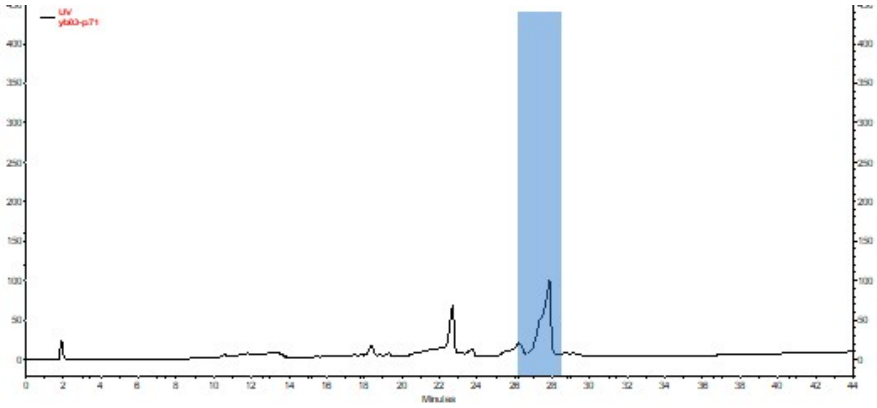
*RP-HPLC trace of Monosaccharide **8b** recorded at 254 nm*

Synthesis of **9** via AGA2



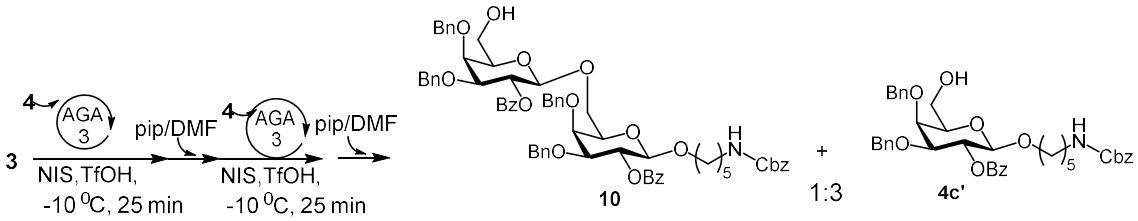
Scheme 21: Synthesis of disaccharide by AGA. Reagents and conditions: DCM/ dioxane, **7**, NIS, TfOH,20% Piperidine in DMF.

2 (41 mg, loading 0.6 mmol/g) was glycosylated with 33.02 mg of **7** using glycosylation module AGA2 at -10 °C for 25 min. After the glycosylation, Fmoc was removed using 20% piperidine in DMF and another glycosylation was performed using glycosylation module AGA2 at -10 °C for 40 min. The sample was photo-cleaved and the crude disaccharide **9** was characterized by HPLC. The ratio between di- (**9**) and monosaccharide (**7b'**) was 65:35. The crude was purified by RP-prepHPLC and the disaccharide was characterized by HRMS for: $[M+Na]^+$, calculated 1194.4453, found 1194.4452 (Yield 53%). ^{1}H-NMR (500 MHz, $CDCl_3$), 7.95-7.92 (m, 9H), 7.45 7.42 (m, 15H), 7.19 7.17 (m, 10H), 6.96-6.93 (m, 1H), 6.09-6.08 (m, 1H), 5.95-5.94 (m, 1H), 5.18 (d, 1H), 5.11 (s, 1H), 5.03-5.01 (d, 1H), 4.95-4.93 (d, 1H), 4.81-4.78 (d, 1H), 4.64-4.62 (m, 1H), 4.58-4.55 (m, 2H), 4.50-4.46 (m, 1H), 4.38-4.36 (d, 1H), 4.34-4.32 (m, 1H), 4.29-4.27 (m, 1H), 4.25-4.19 (m, 4H), 4.18-4.14 (m, 1H), 4.13-4.10 (m, 2H), 4.09-4.01 (m, 4H), 3.85-3.80 (m, 2H), 3.59-3.55 (m, 2H), 3.19-3.14 (m, 2H), 2.99-2.95 (m, 2H),1.19-1.13 (m, 5H), 1.07-1.05 (m, 3H).



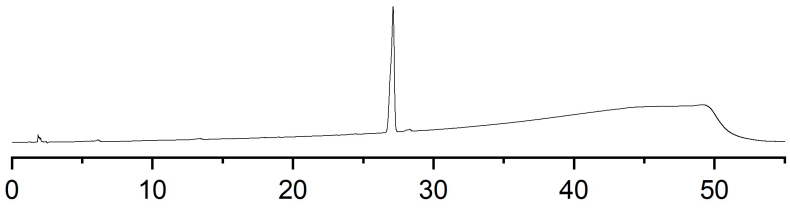
*RP-HPLC trace of disaccharide **9** recorded at 254 nm (crude) The peak at 23.2 min correlates with **7b'** and The peak at 28.01(blue) min correlates with **9**.*

Synthesis of **10** via AGA3



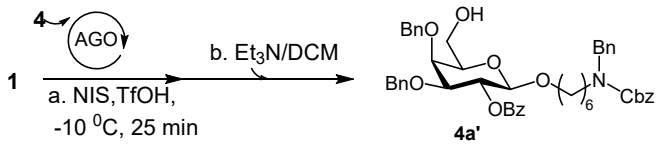
Scheme 22: Synthesis of disaccharide **10** by AGA. Reagents and conditions: DMF, THF, DCM, DCM/ dioxane, **4**, NIS, TfOH, 20% Piperidine in DMF, 30 min, 25 °C

3 (41 mg, loading 0.3 mmol/g) was glycosylated with 15.02 mg of **4** using glycosylation module AGA3 at -10 °C. After the glycosylation, Fmoc was removed using 20% piperidine in DMF and another glycosylation cycle using the exact conditions was performed. Fmoc was removed using 20% piperidine in DMF. The sample was photo-cleaved and the ratio between di- (**10**) and monosaccharide (**4c'**) in the crude determined by HPLC to be 25:75. The crude was purified by RP-prep HPLC and the disaccharide was characterized by HRMS for: $[M+Na]^+$, calculated 1152.4716, found 1152.4713. ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.53 – 7.52 (m, 4H), 7.45 – 7.42 (m, 1H), 7.34 – 7.25 (m, 14H), 7.19 – 7.17 (m, 2H), 7.13 – 6.99 (m, 18H),, 6.96 – 6.93 (m, 1H), 6.09 – 6.08 (m, 1H), 5.95 – 5.94 (m, 1H), 5.18 (d, 1H), 5.11 (s, 1H), 5.03 – 5.01 (d, 1H), 4.95 – 4.93 (d, 1H), 4.81 – 4.78 (d, 1H), 4.64 – 4.62 (m, 1H), 4.58 – 4.55 (m, 2H), 4.50 – 4.46 (m, 1H), 4.38 – 4.36 (d, 1H), 4.34 – 4.32 (m, 1H), 4.29 – 4.27 (m, 1H), 4.25 – 4.19 (m, 4H), 4.18 – 4.14 (m, 1H), 4.13 – 4.10 (m, 1H), 4.09 – 4.01 (m, 4H), 3.85 – 3.80 (m, 2H), 3.59 – 3.55 (m, H), 3.19 – 3.14 (m, 1H), 2.99 – 2.95 (m, 1H),1.19 – 1.13 (m, 3H), 1.07 – 1.05 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 165.3, 156.5, 141.7, 138.3, 130.1, 137.6, 137.6, 136.7, 136.6, 133.1, 130.2, 129.8, 129.7, 129.8, 129.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 125.2, 101.7, 101.3, 76.8, 75.0, 74.3, 74.1, 73.8, 72.1, 71.9, 71.8, 69.4, 66.6, 66.5, 62.7, 62.0, 40.9, 32.2, 29.8, 29.4, 29.3.



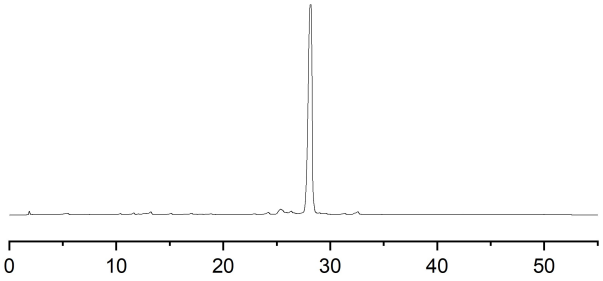
*RP-HPLC trace of Disaccharide **10** recorded in 254 nm (after purification)*

Synthesis of **4a'** via AGO



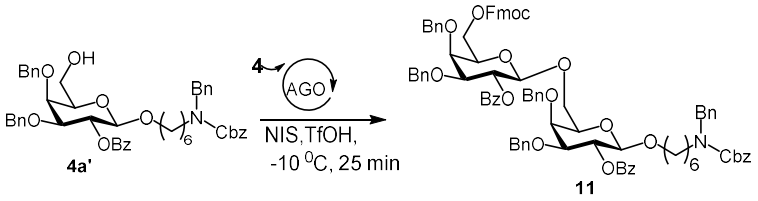
Scheme 23: Synthesis of monosaccharide **4a'**. Reagents and conditions: reactor wash DMF, THF, DCM, DCM/ dioxane, a) **4**, NIS, TfOH, and b) Et_3N, /DCM overnight, 25 °C.

A mixture of **1** (4 mg) and **4** (60 mg) was co-evaporated with toluene and dried under high vacuum overnight. The dry mixture was dissolved in 2 ml of dry DCM and placed in a sealed vial and was glycosylated using AGO module at -10 °C to provide crude **4a.** After workup, the crude **4a** was purified using a prep HPLC. After purification, **4a** (1 mmol) was treated with a solution of Et_3N (3 mmol) in 1ml of DCM overnight at room temperature under argon. The crude was quenched with water and neutralized using diluted HCl solution. The organic phase was separated, dried over $MgSO_4$, evaporated, dissolved in ACN/TDW and purified using prep-HPLC and kept under high vacuum before the next glycosylation. The purified **4a'** was was characterized by analytical HPLC and HRMS for: $[M]^+$, calculated 787.3720, found 787.3724.



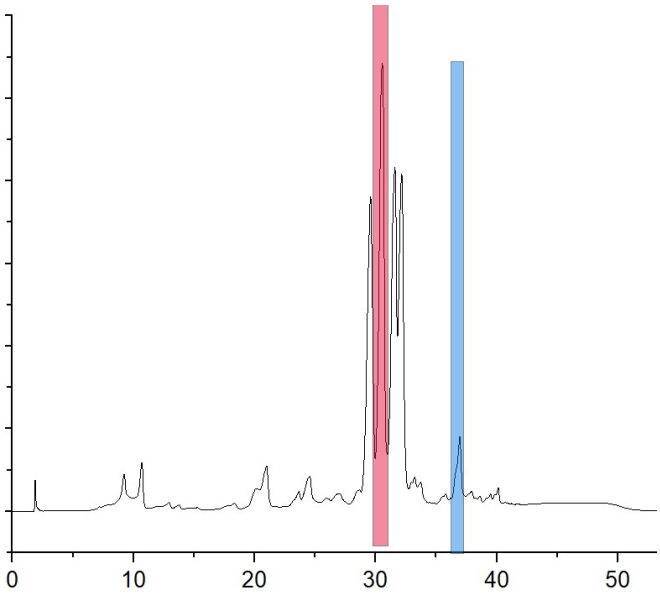
*RP-HPLC trace of **4a'** recorded at 254 nm (after purification)*

Synthesis of **11** via AGO



Scheme 24: Synthesis of disaccharide **11** by AGA. Reagents and conditions: DMF, THF, DCM, DCM/ dioxane, **4a'**, NIS, TfOH,

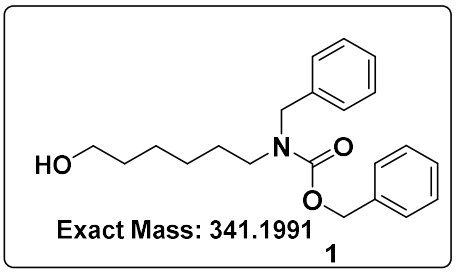
A mixture **4a'** (0.0017 mmol, 1.3 mg) and **4** (0.0026 mmol, 17.2 mg) was co-evaporated with toluene and dried in high vacuum overnight. The dried mixture was dissolved in 2 ml of Dry DCM placed in a septum-sealed vial and was glycosylated using AGO module at -10 °C. After glycosylation, the mixture was collected and quenched as described before. The crude disaccharide was characterized by analytical HPLC to determine the degree of glycosylation efficiency from **4a'** to **11.** MS for: $[M]^+$, calculated 1455.61 found 1455.61.

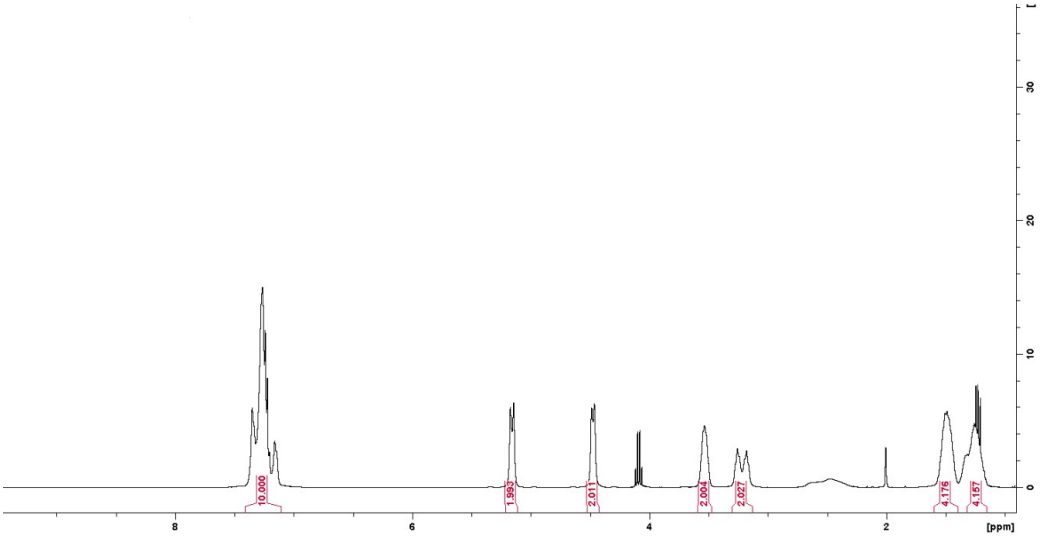


*RP-HPLC trace of **4f** recorded at 254 nm (Crude)*

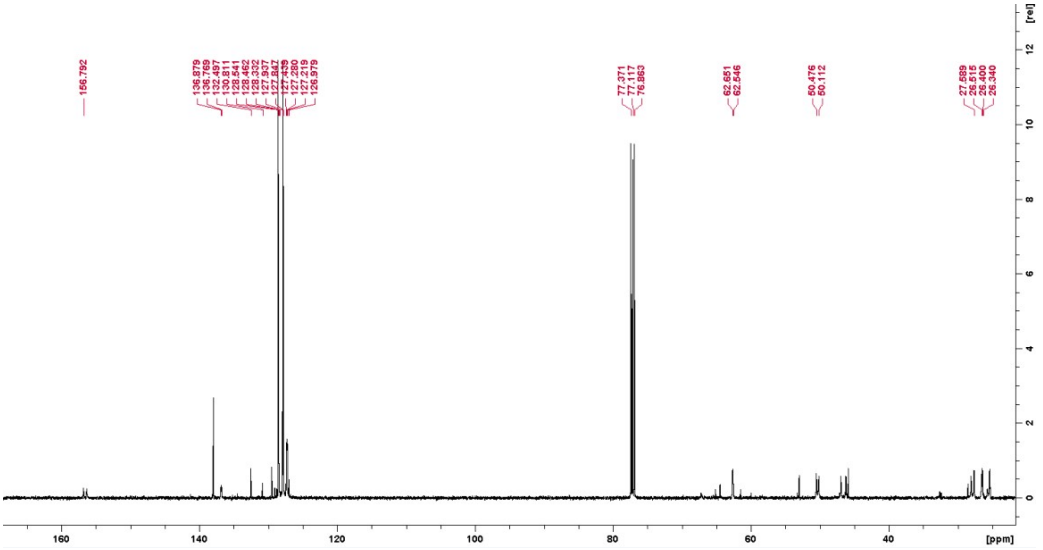
Acceptor	4a' area %	11 area %
4a'	84	16

Compound 1:

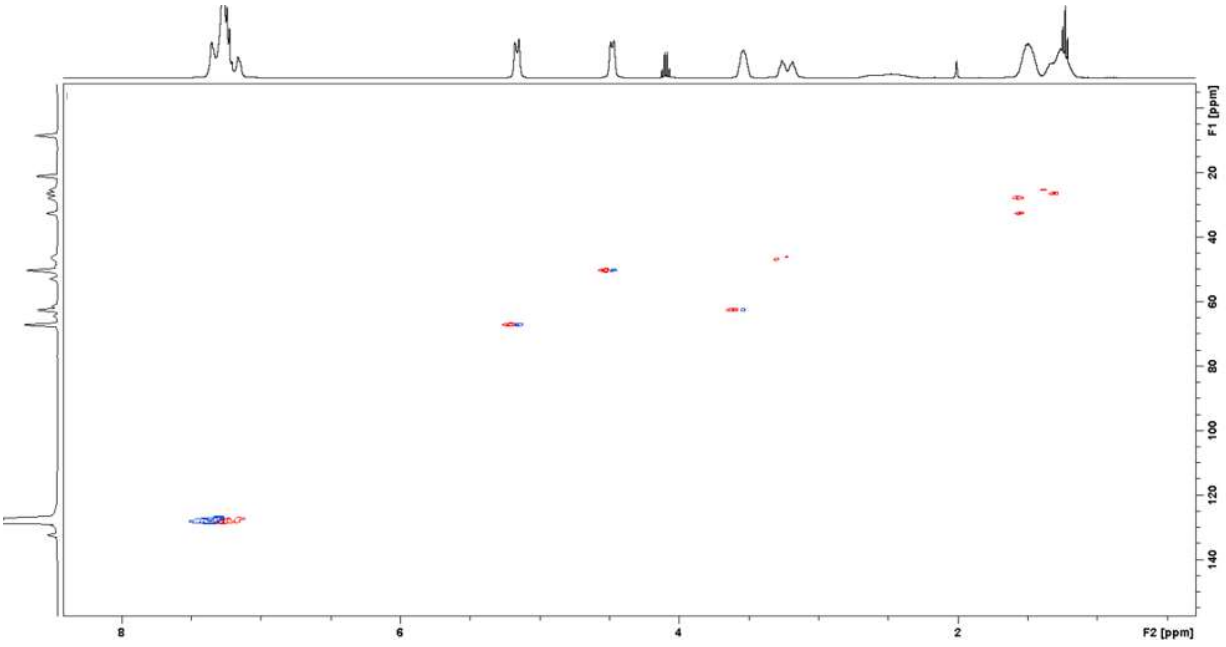




^{1}H-NMR of **1** recorded at 500 MHz

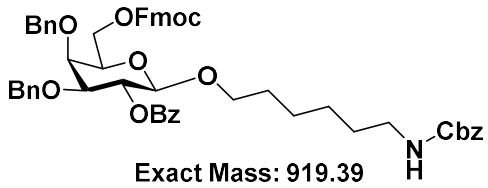


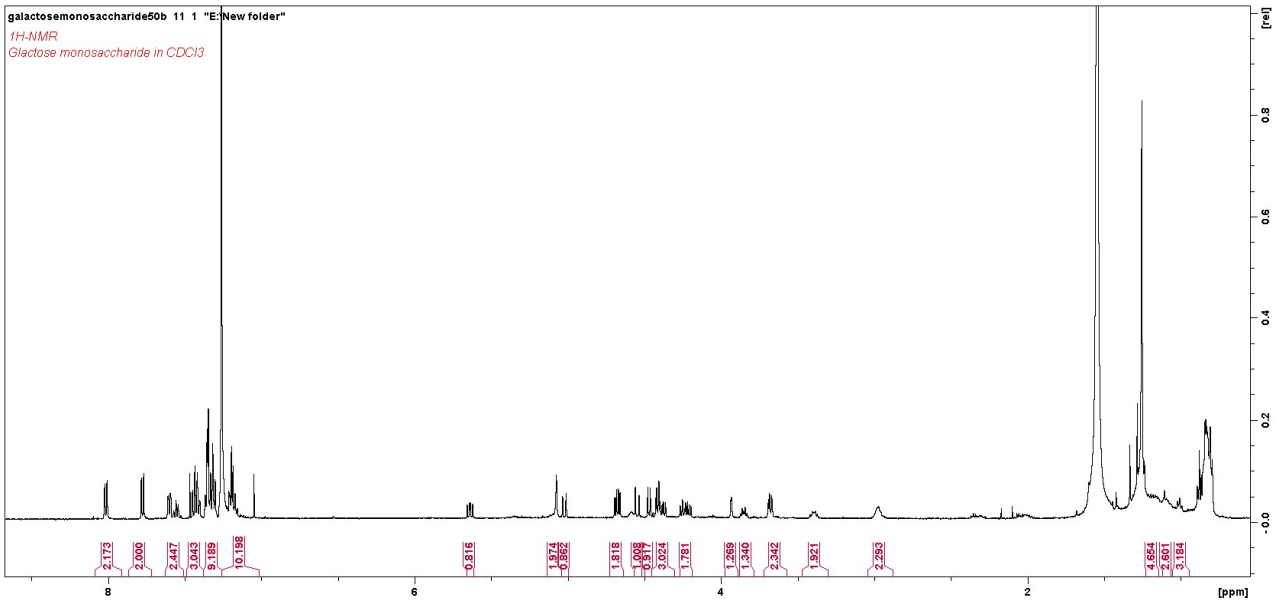
^{13}C-NMR of compound 1 recorded at 125 MHz



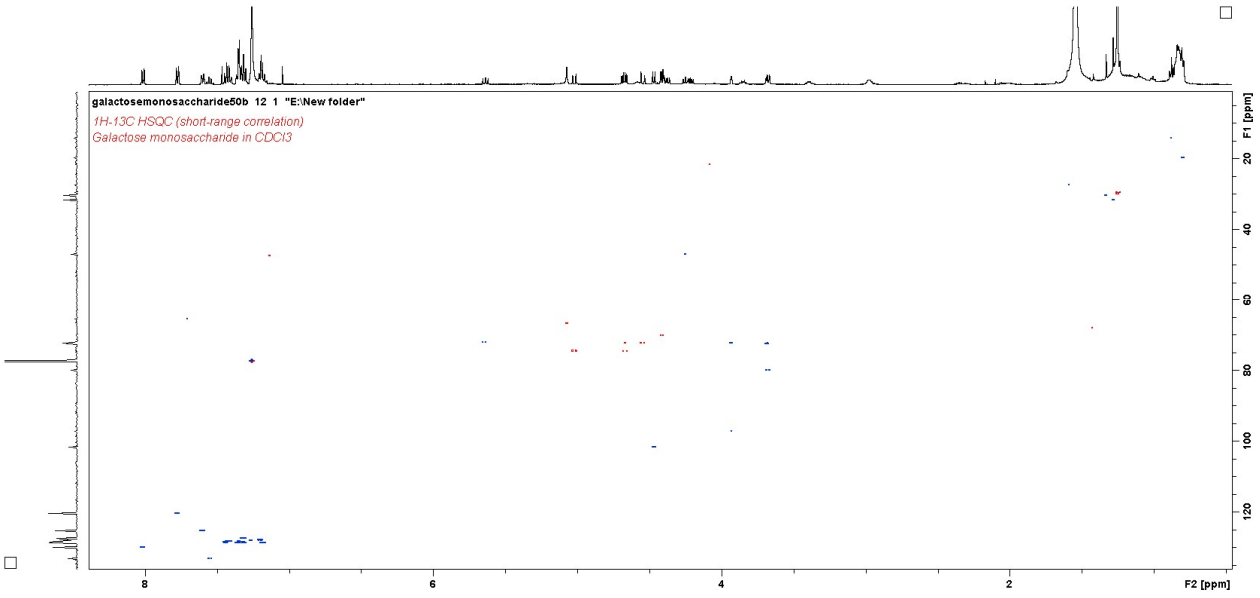
HSQC of compound **1**

Compound 4b:



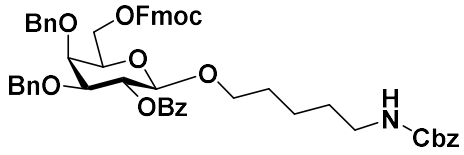


^{1}H-NMR of compound **4b** recorded at 500 MHz

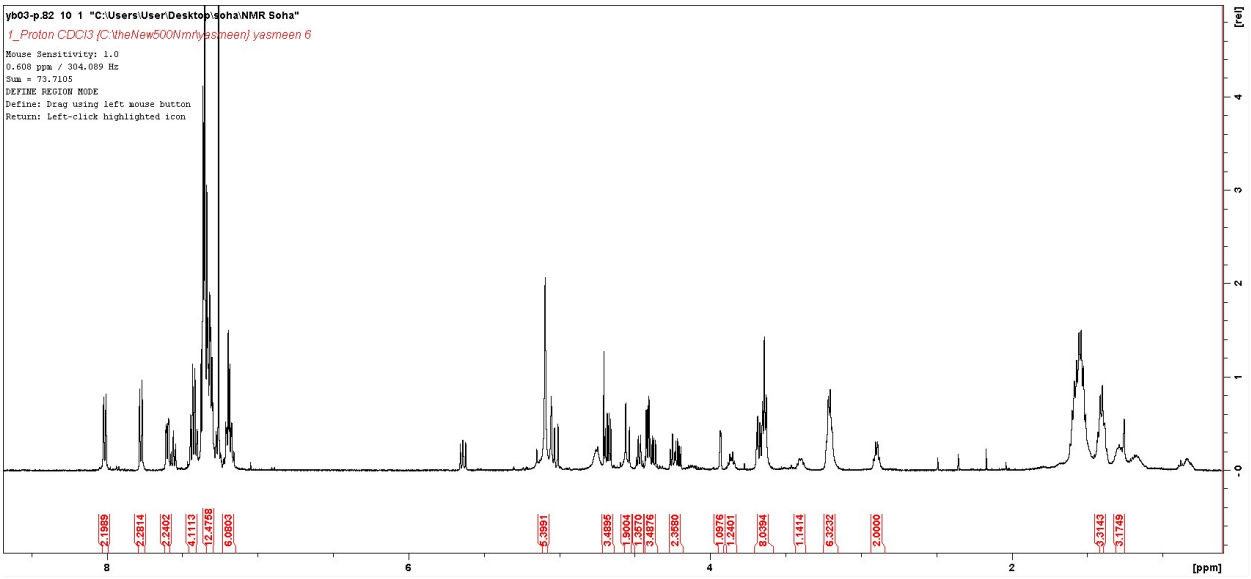


HSQC of compound **4b**

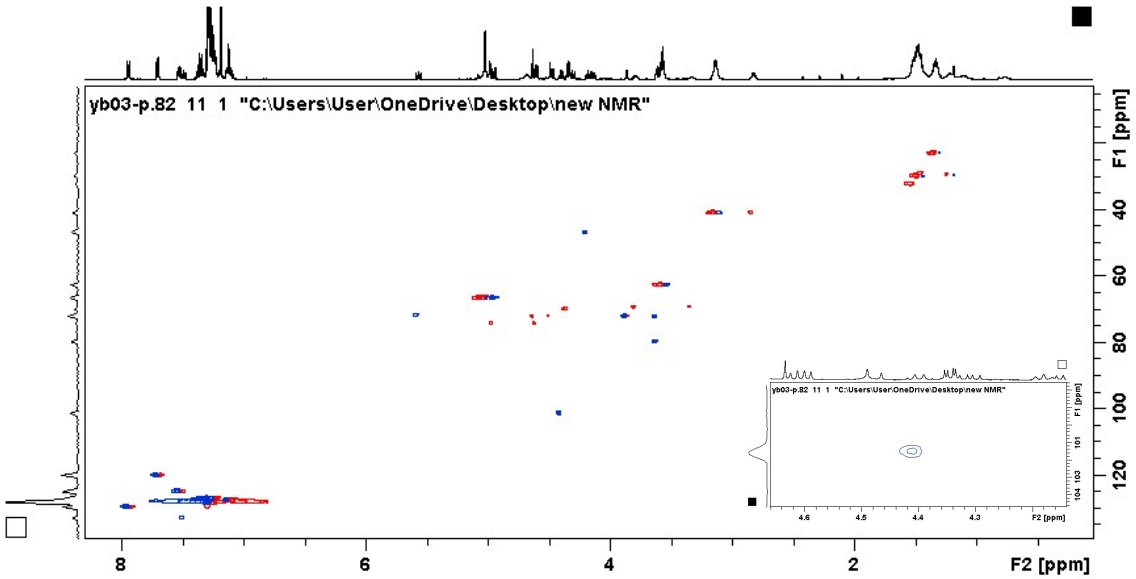
Compound 4c:



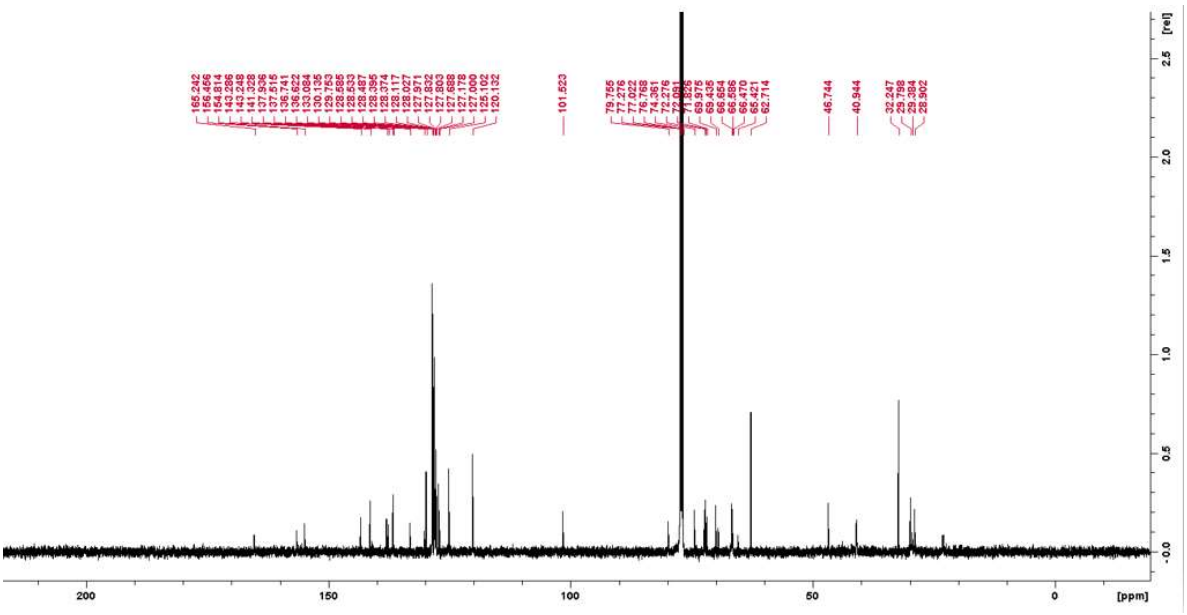
Exact Mass: 905.38



^{1}H-NMR of compound **4c** recorded at 500 MHz

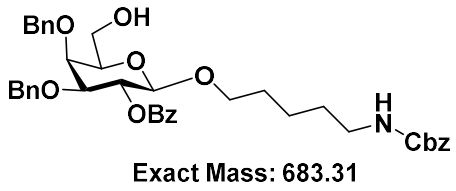


HSQC of compound **4c**

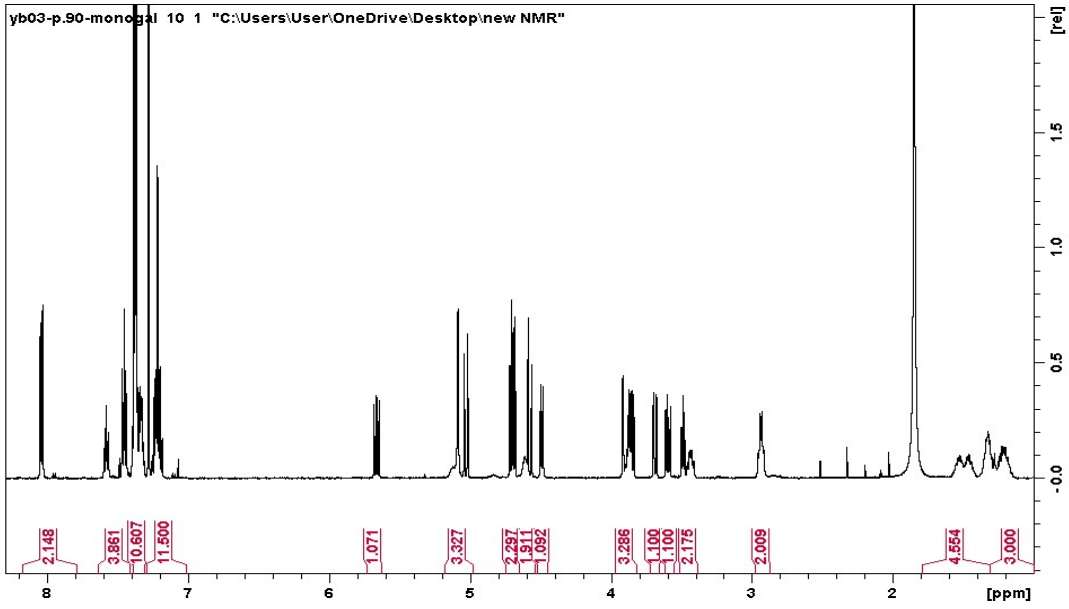


^{13}H-NMR of compound **4c** recorded at 125 MHz

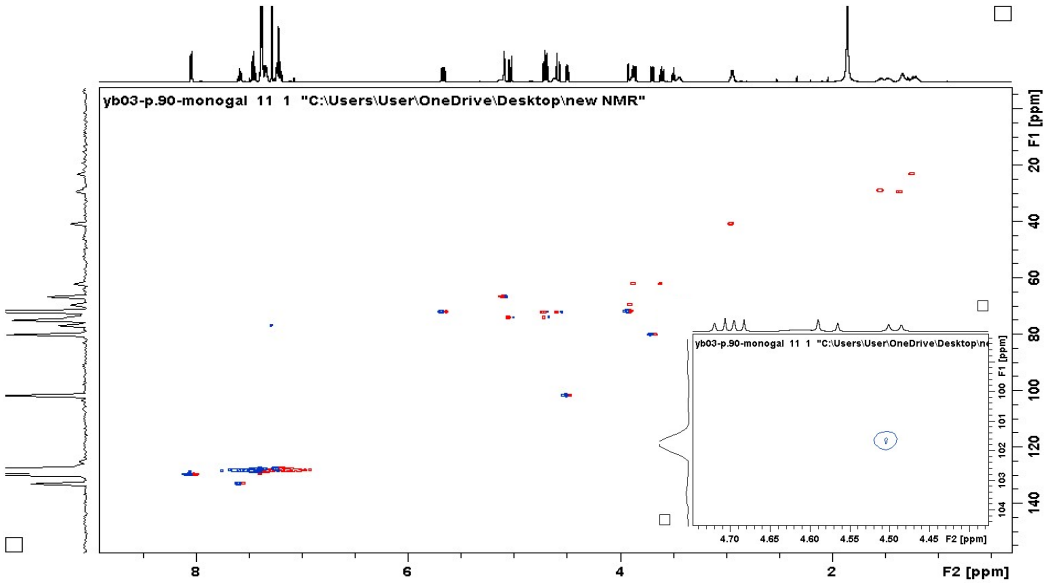
Compound 4c':



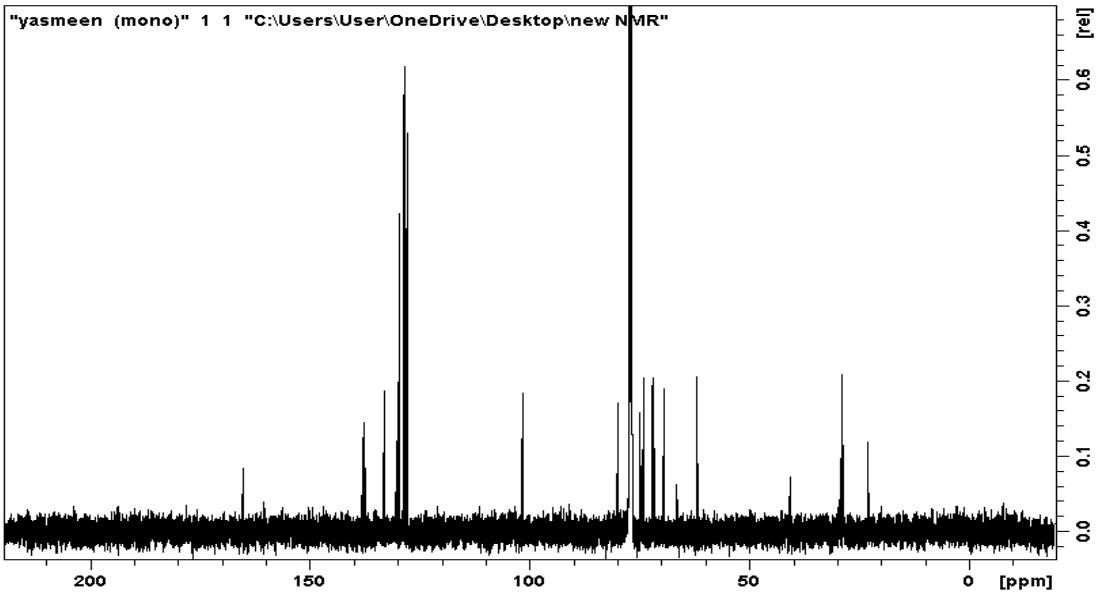
Exact Mass: 683.31



[1]H-NMR of compound **4c'** recorded at 500 MHz

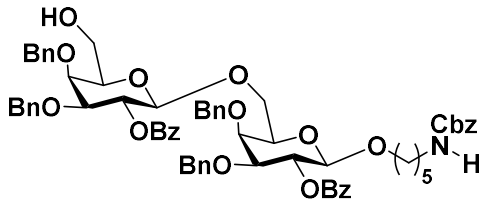


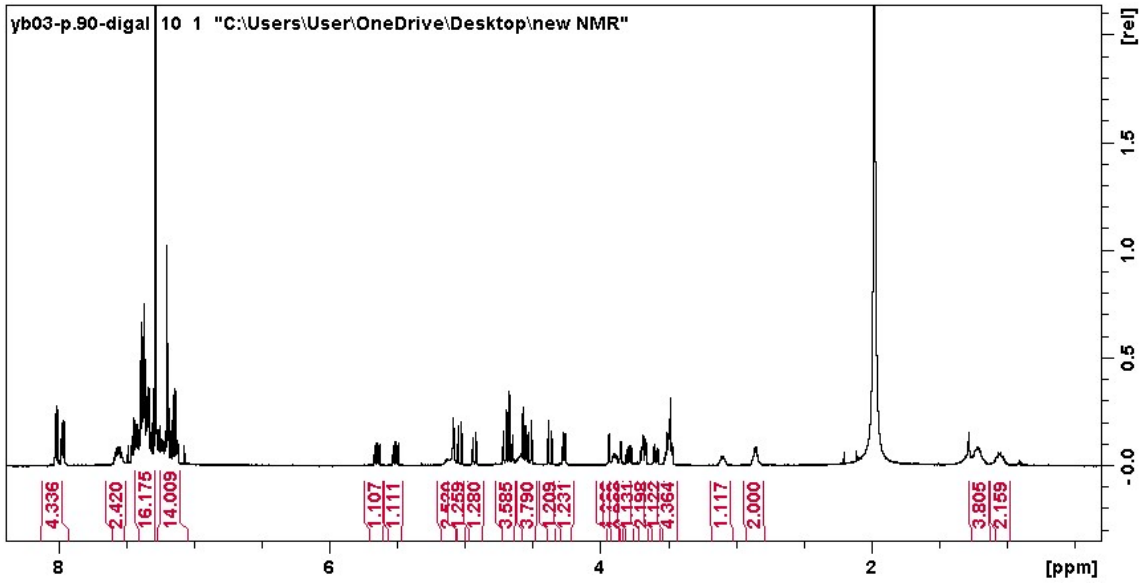
HSQC of compound **4c'**



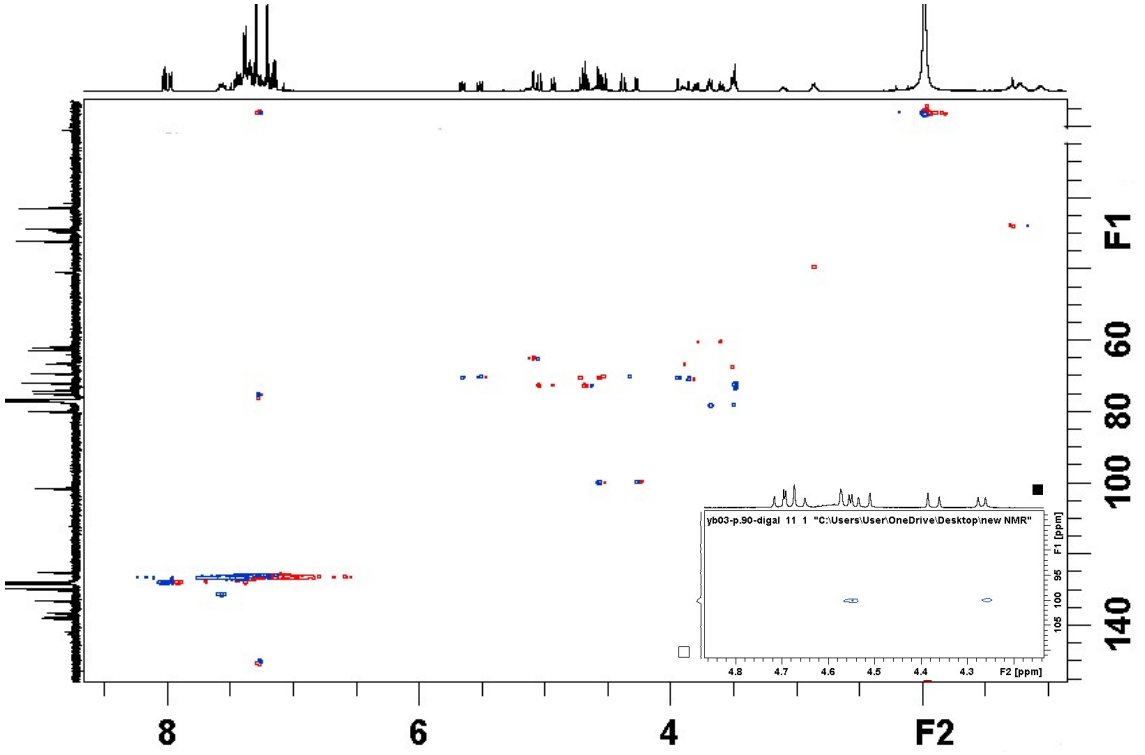
^{13}C-NMR of compound **4c'** recorded at 125 MHz

Compound 10:

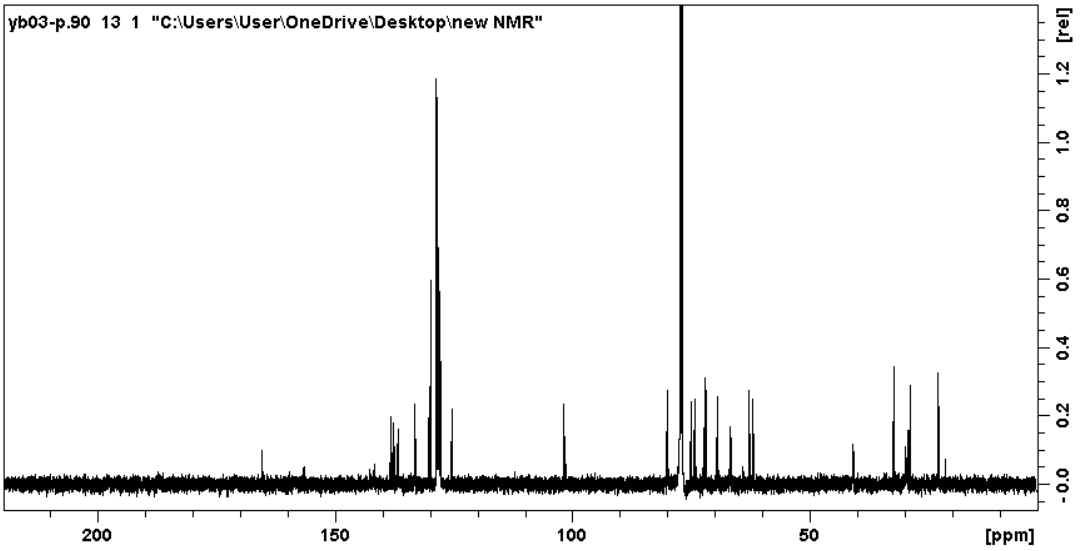




^{1}H-NMR of compound **10** recorded at 500 MHz

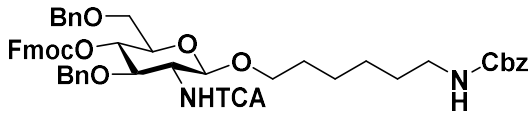


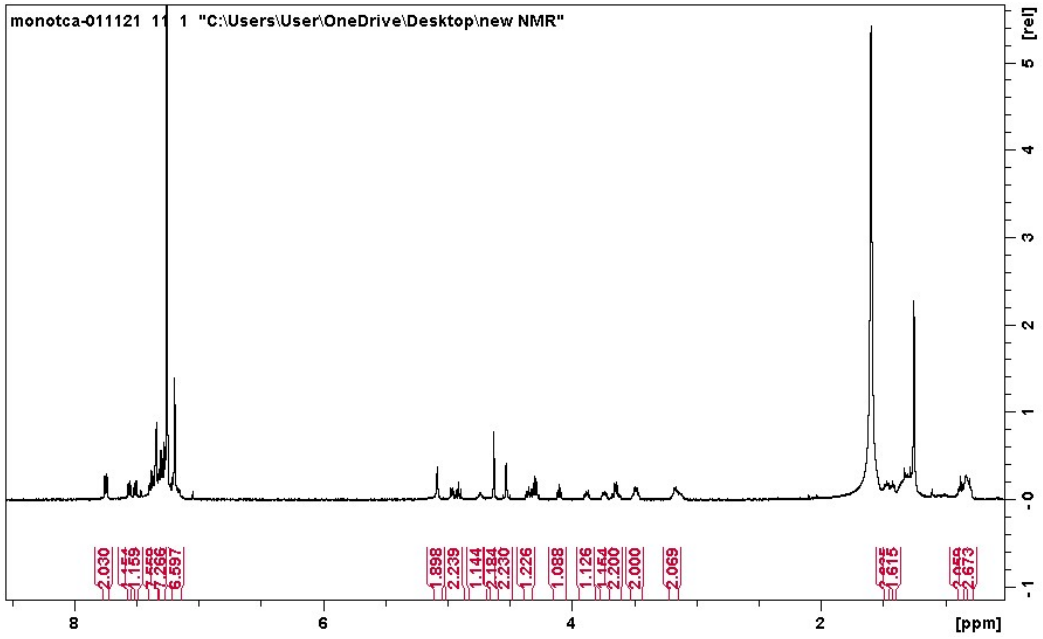
HSQC of compound **10**



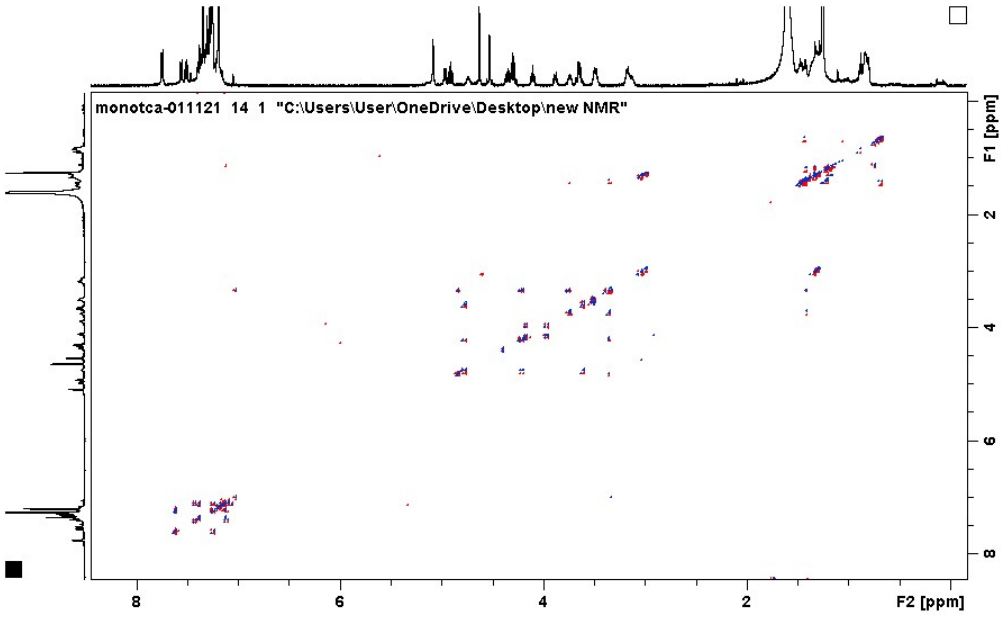
^{13}C-NMR of compound **10** recorded at 125 MHz

Compound 5b:

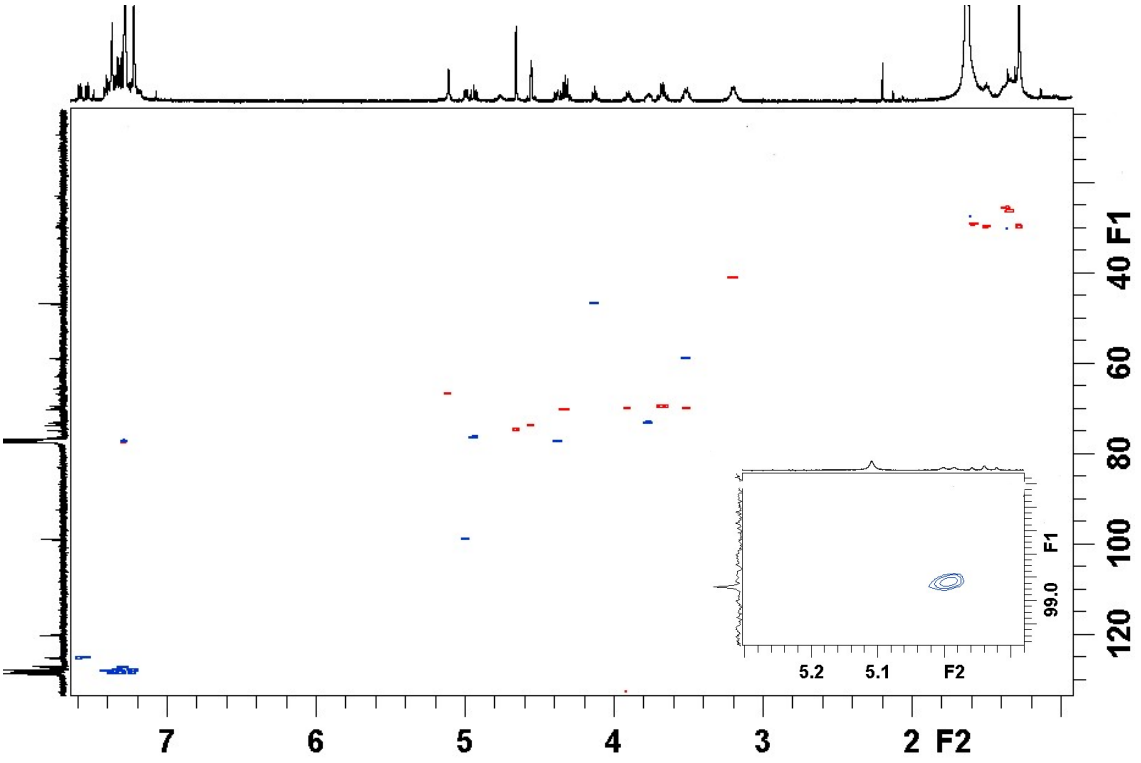




^{1}H-NMR of compound **5b** recorded at 500 MHz

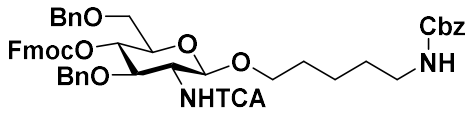


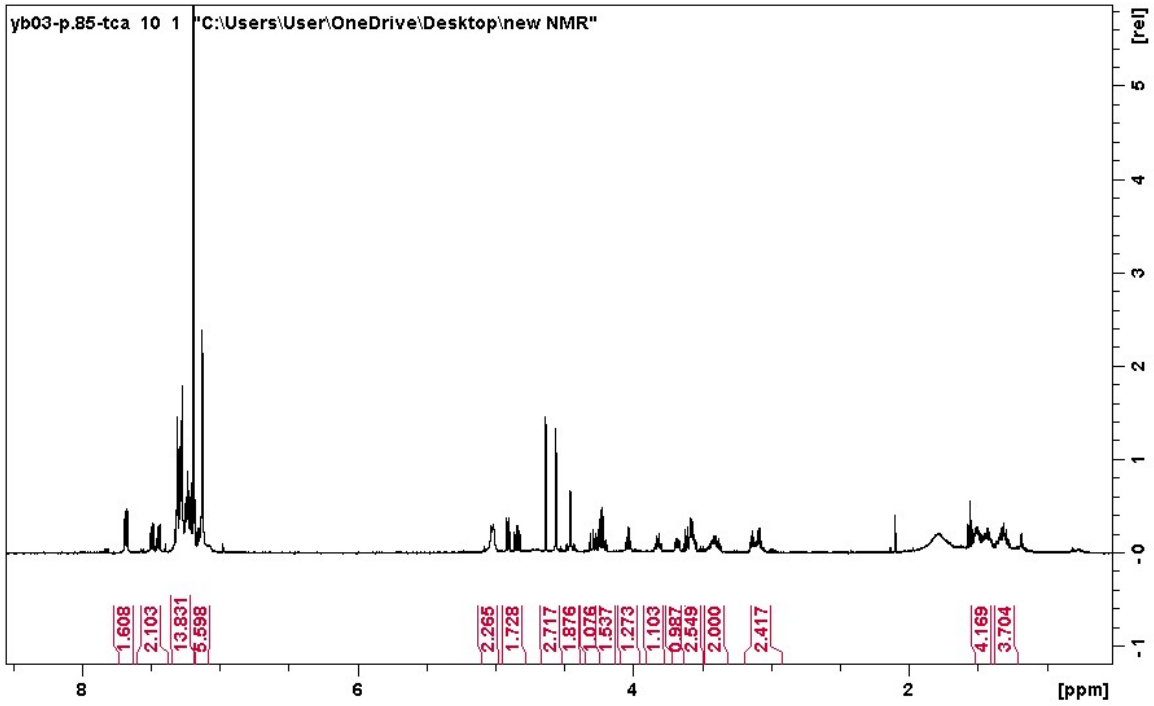
COSY of compound **5b**



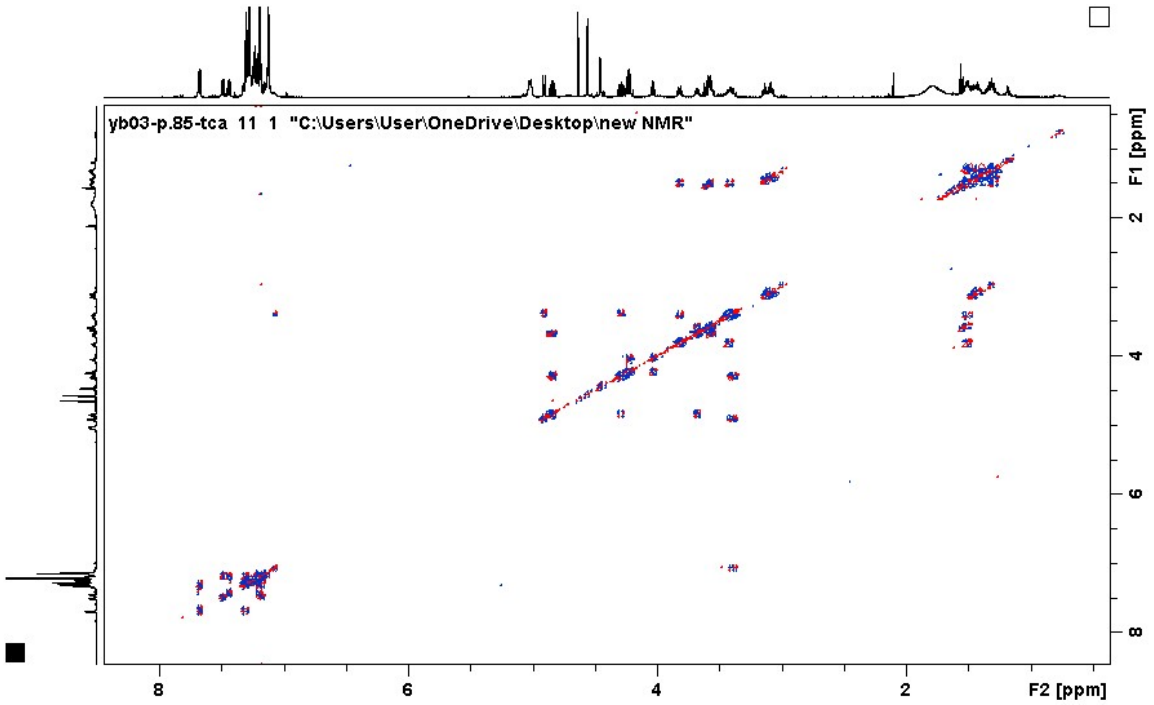
HSQC of compound **5b**

Compound 5c:

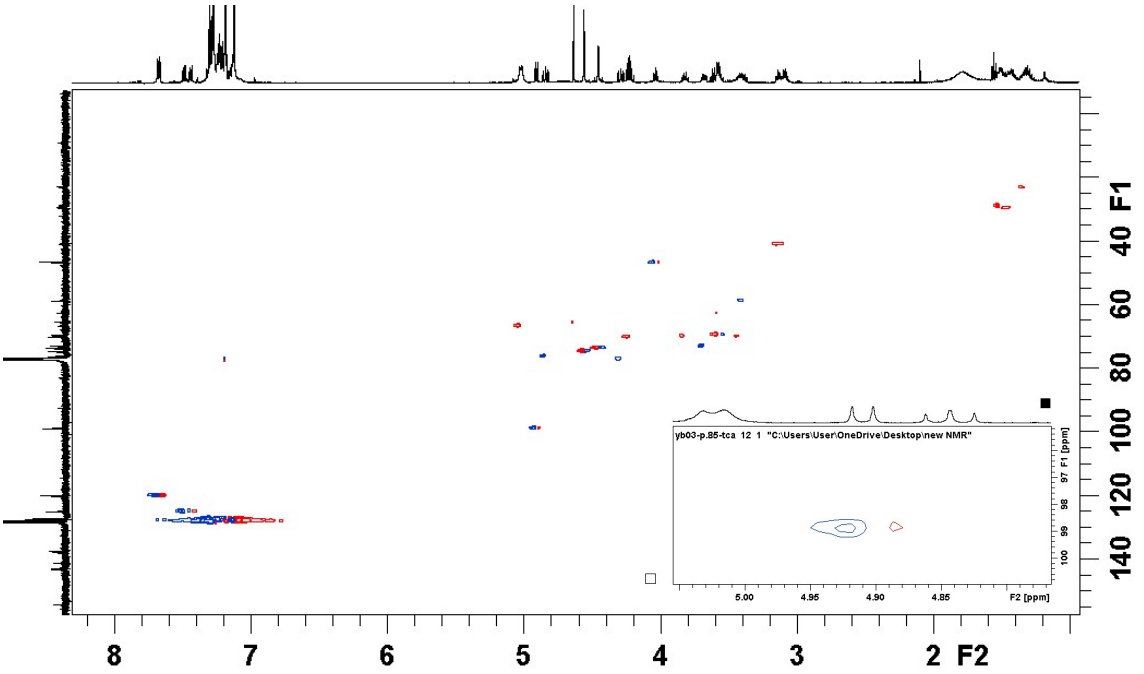




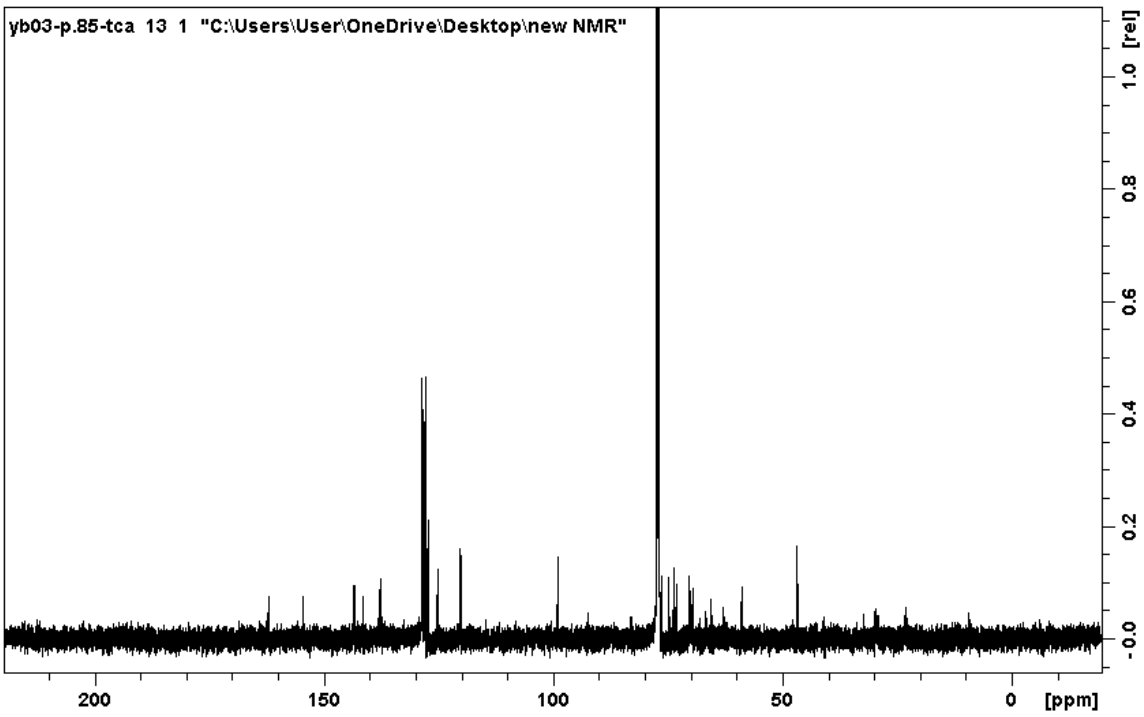
^{1}H-NMR of compound **5c** recorded at 500 MHz



COSY of compound **5c**

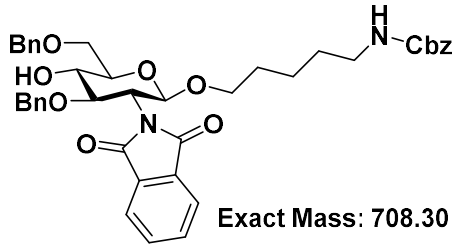


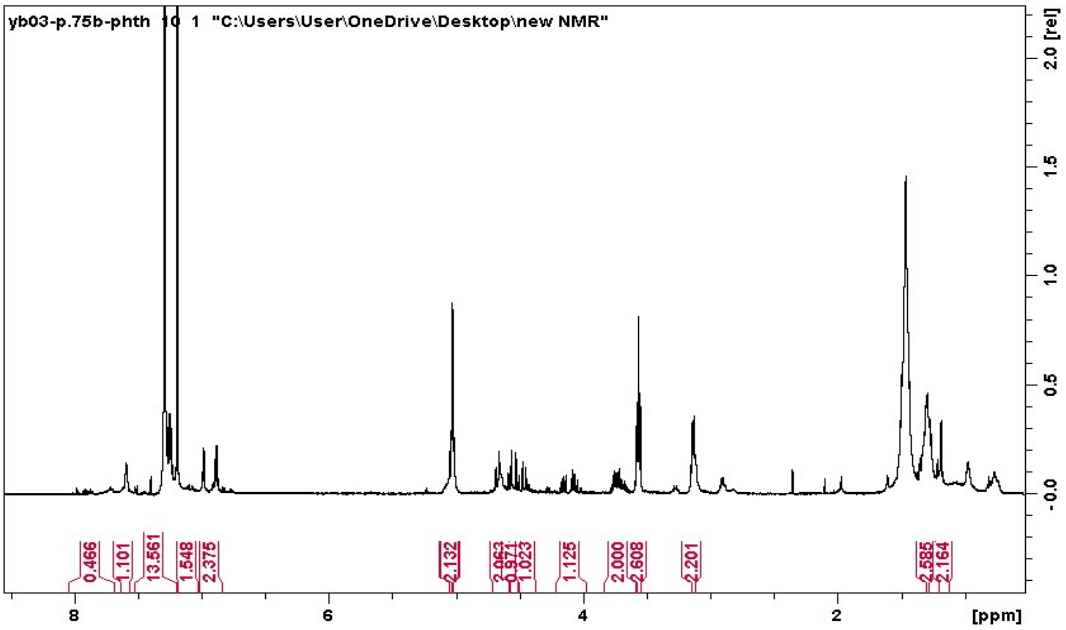
HSQC of compound **5c**



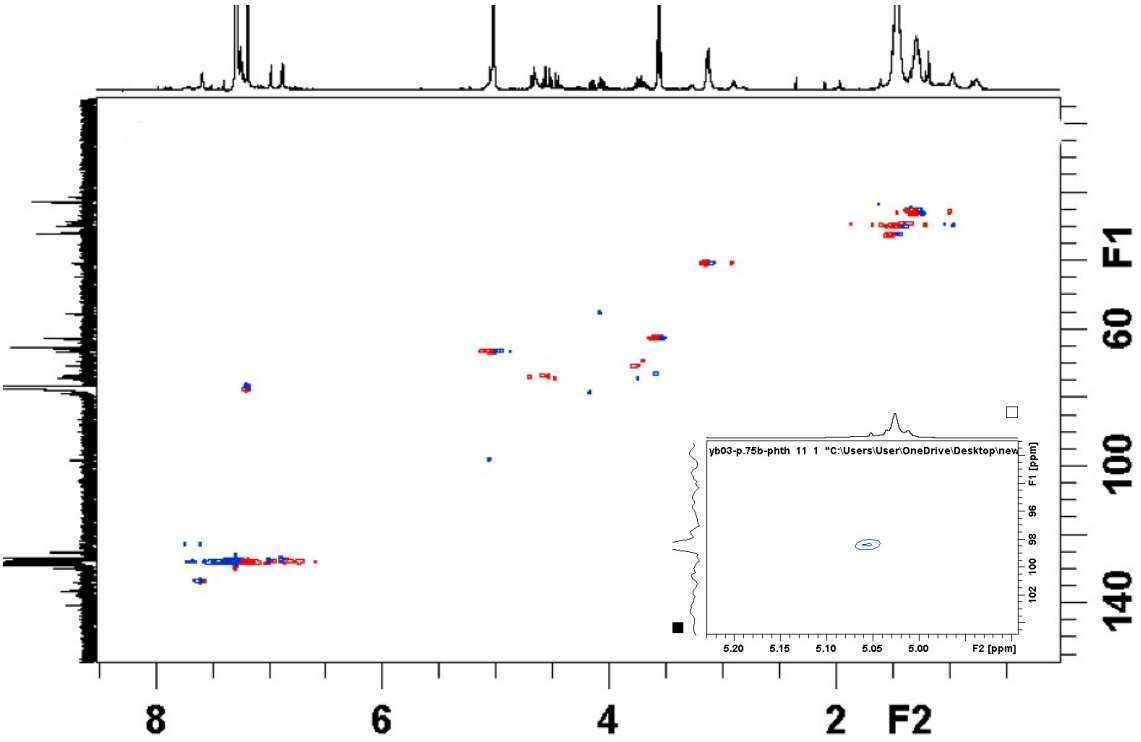
^{13}C-NMR of compound **5c** recorded at 125 MHz

Compound 6b:



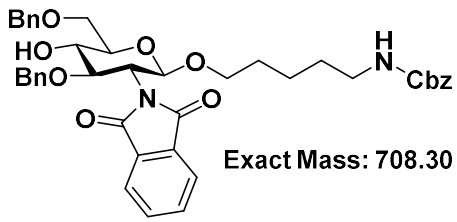


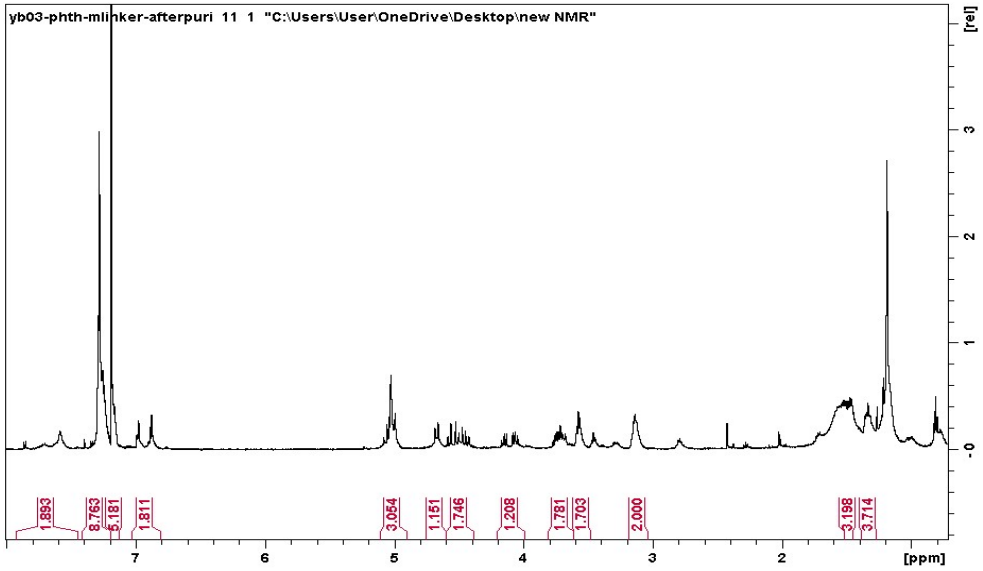
[1]H-NMR of compound **6b** recorded at 500 MHz



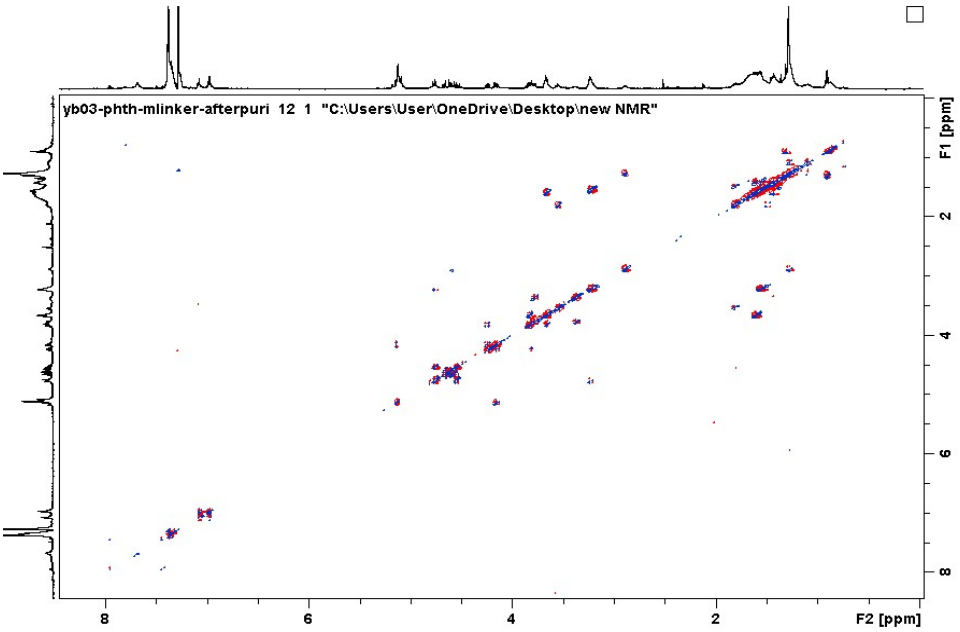
HSQC of compound **6b**

Compound 6c:

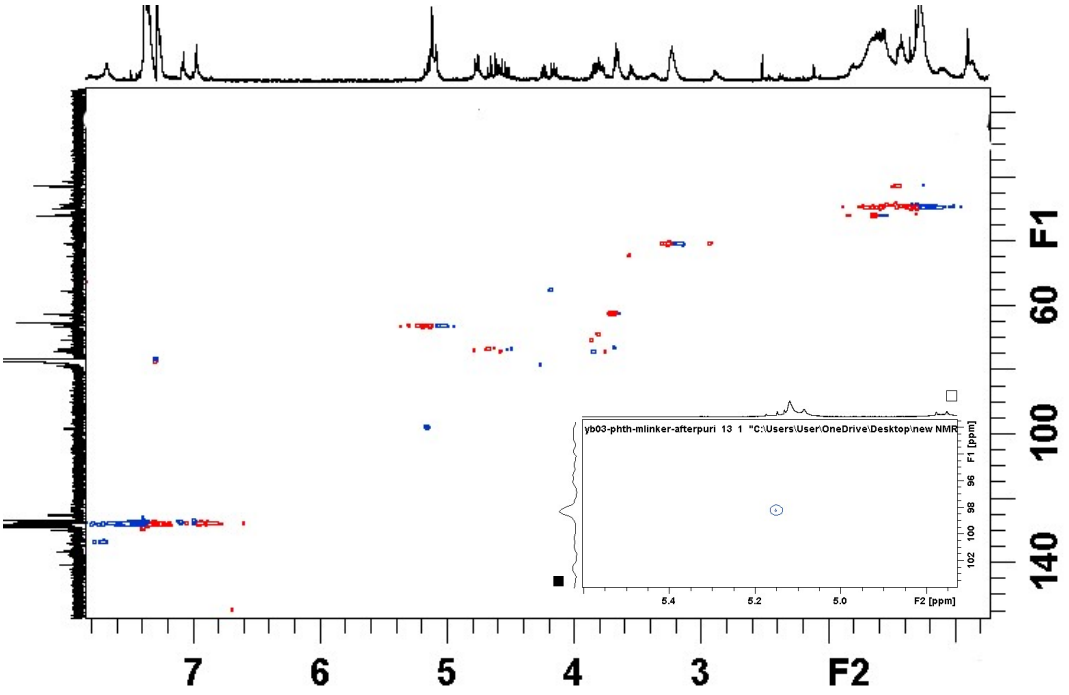




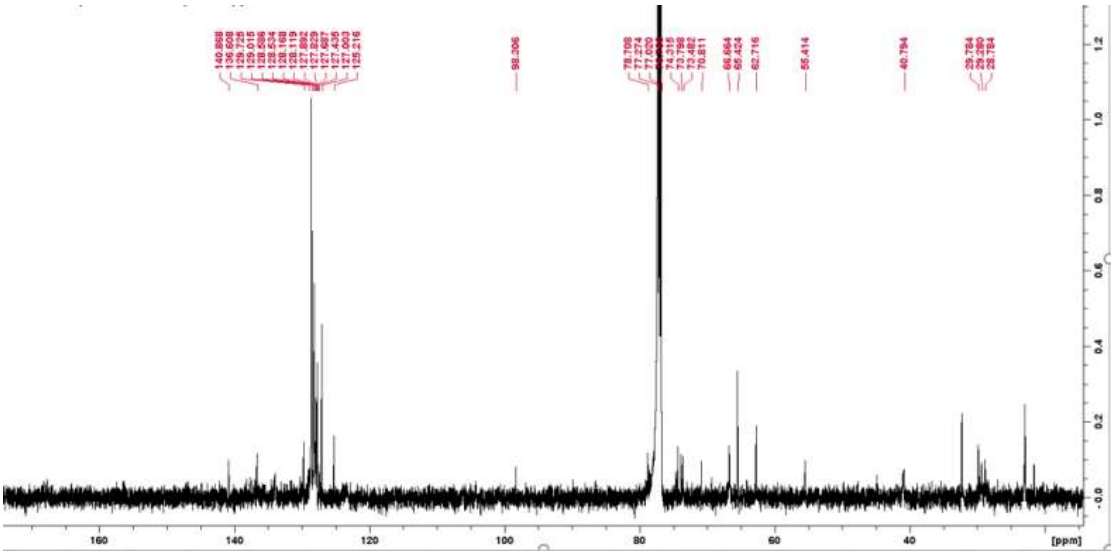
^{1}H-NMR of compound **6c** recorded at 500 MHz



COSY of compound **6c** recorded at 500 MHz

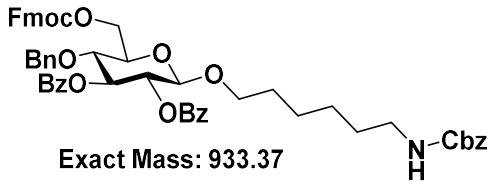


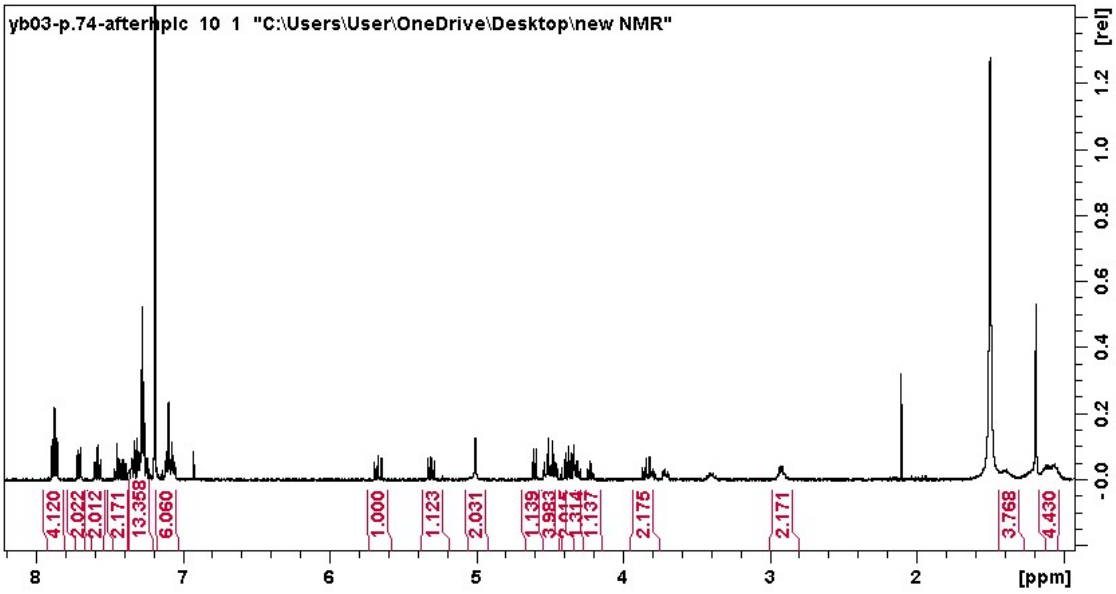
HSQC of compound **6c**



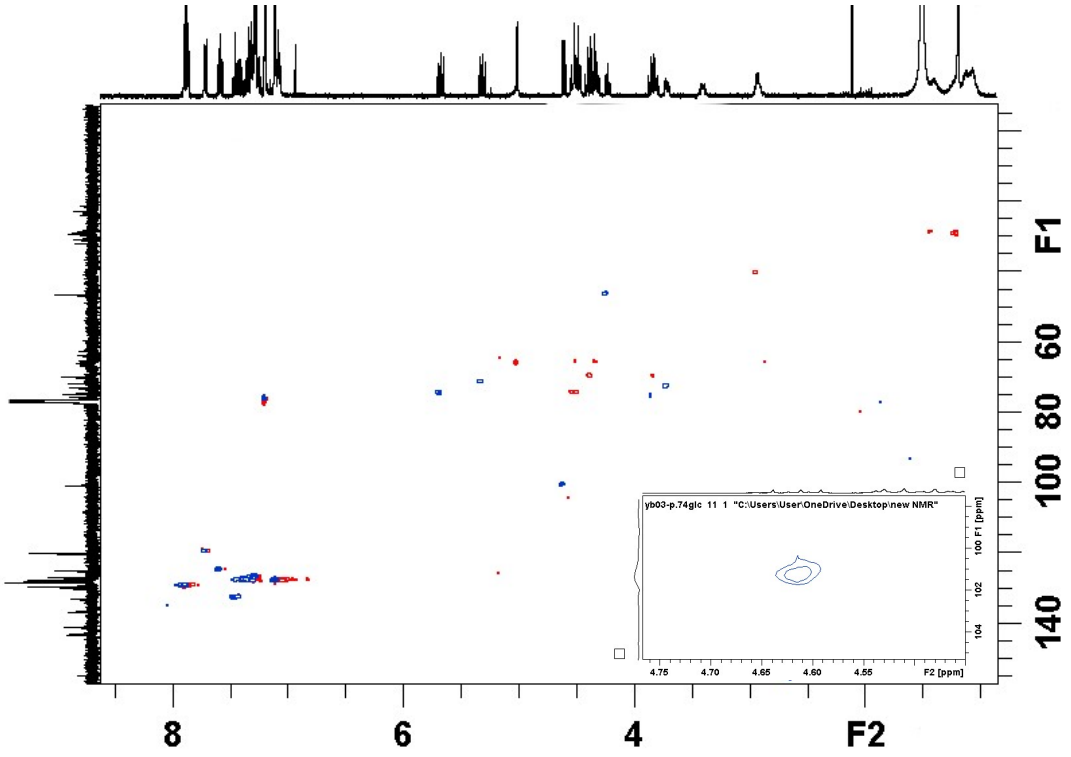
^{13}C-NMR of compound **6c** recorded at 125 MHz

Compound 7b:



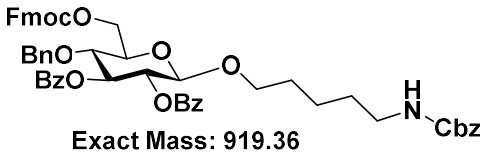


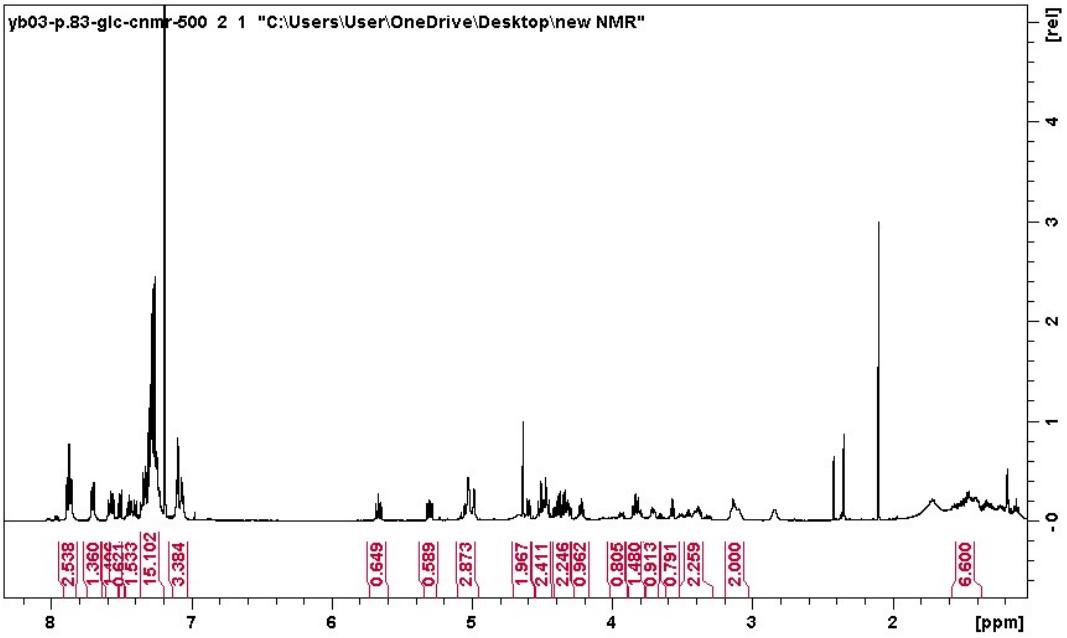
^{1}H-NMR of compound **7b** recorded at 500 MHz



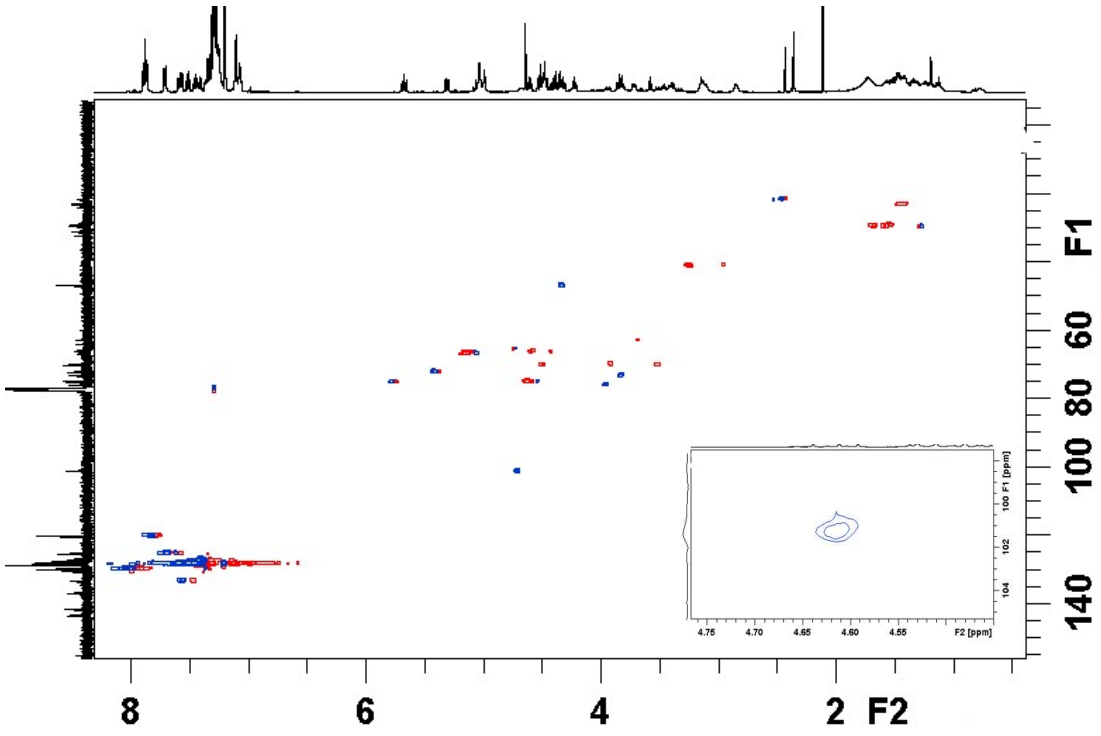
HSQC of compound **7b**

Compound 7c:

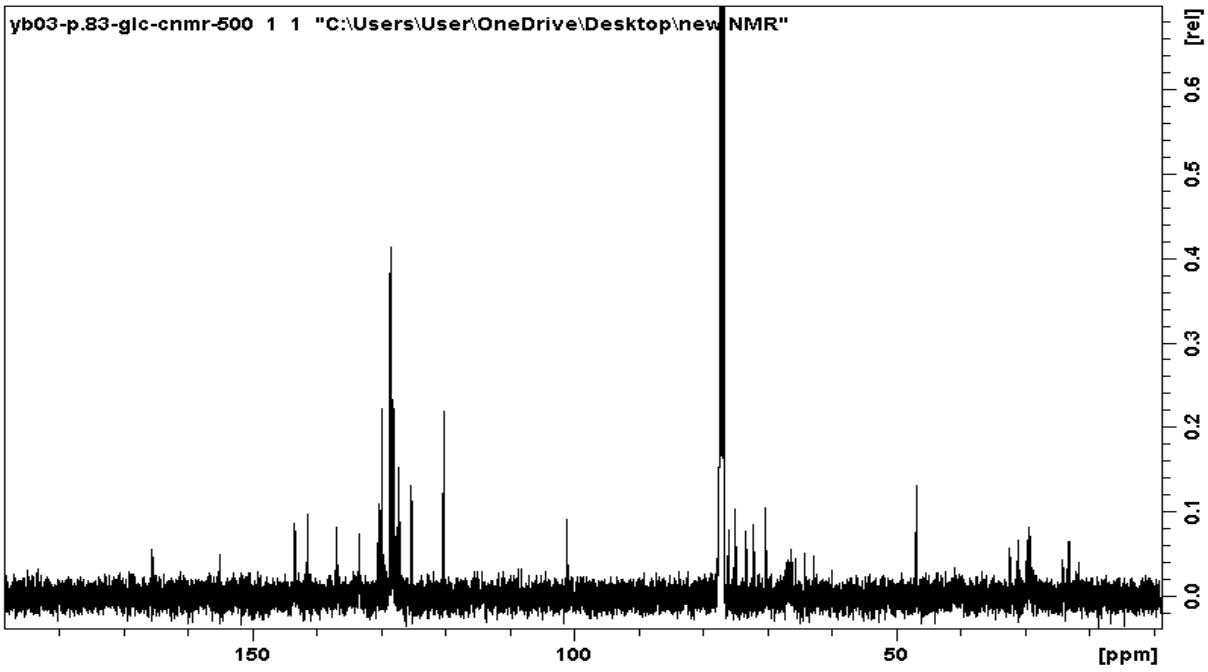




^{1}H-NMR of compound **7c** recorded at 500 MHz

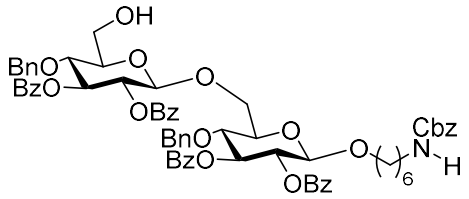


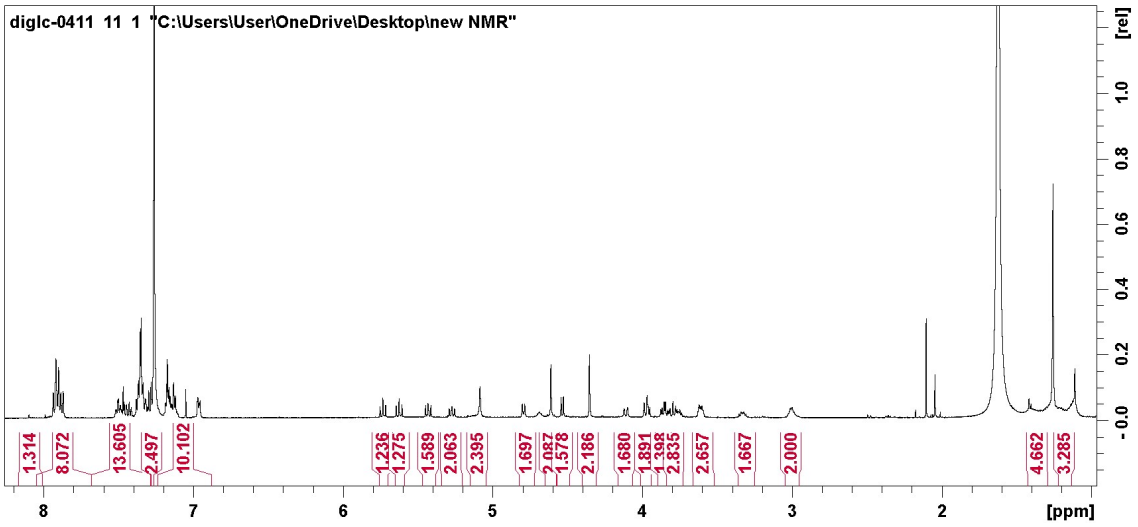
HSQC of compund **7c**



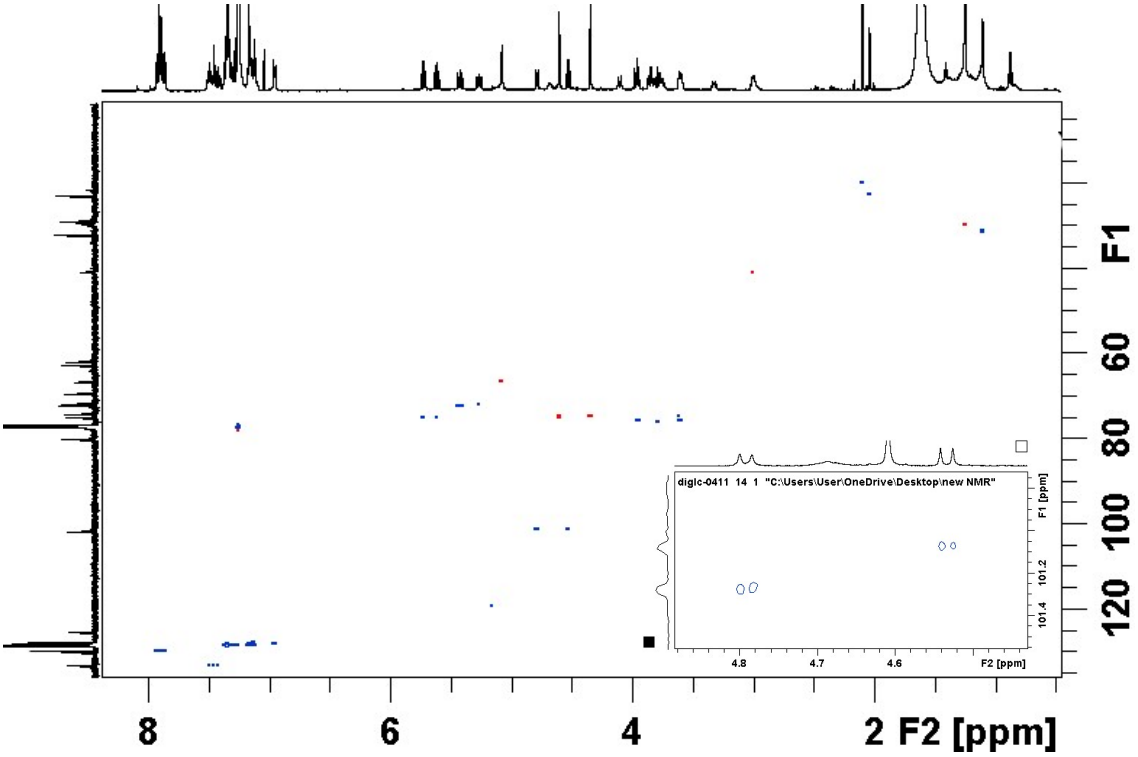
^{13}C-NMR of compound **7c** recorded at 125 MHz

Compound 9:





^{1}H-NMR of compound **9** recorded at 500 MHz



HSQC of compound **9**

References

[1] a) M. D. Bandara, K. J. Stine, A. V. Demchenko, Carbohyd Res 2019, 483; b) L. Krock, D. Esposito, B. Castagner, C. C. Wang, P. Bindschadler, P. H. Seeberger, Chem Sci 2012, 3, 1617-1622.

[2] Y. Bakhatan, I. Alshanski, D. Grunhaus, M. Hurevich, Org Biomol Chem 2020, 18, 4183-4188.