Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Supporting information

Site-selective introduction of thiols in unprotected glycosides

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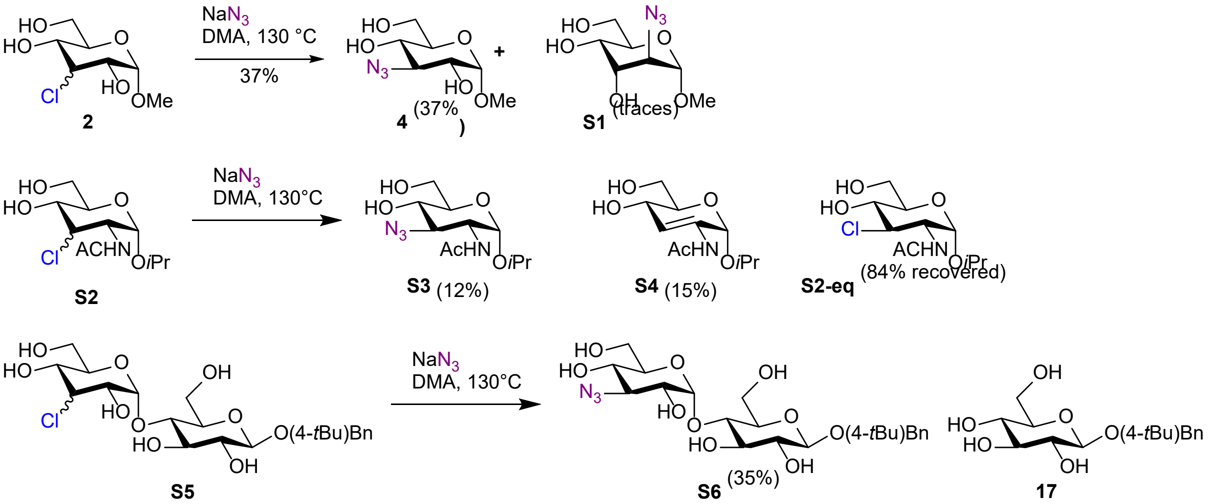
Substitution reactions on 3-chloro sugars

After some experimentation, we found that heating **2**, as a mixture of epimers, with sodium azide in DMA at 130 °C, gave full conversion and provided from a black reaction mixture after column purification 3-azido-glucoside **4** in 37% yield and traces of 2-azido-altroside **S1** (Scheme S1). Similar results were obtained with the substitution of chloro-GlcNAc and chloromaltose.



Scheme S1. Substitution of 3-Cl Glc (**2**), 3-Cl GlcNAc (**S1**) and 3-Cl maltose (**S4**) with azide. For Glc **2**, a mixture of eq/ax of 1/2.7 was used; for GlcNAc **S1**, a mixture of eq/ax of 1.4/1 was used; for maltose **S4**, a mixture of eq/ax of 1/4.4 was used

To gain insight in the reactivity difference between the axial chloride **2a** and the equatorial chloride **2b**, we separated the isomers and studied their behavior in the substitution reaction (Table S1). Heating **2a** for 2 h at 130 °C in the presence of sodium azide gave a dark colored reaction mixture and, according to NMR analysis, full conversion and formation of **4** in 45% yield (entry 2). This confirms the results of Jones *et al.* that in the presence of sodium azide, the axial chloride substituent is prone to elimination and therefore part of the starting material degrades (Figure S1B).[1] Treatment of **2b** in DMA or D_2O with sodium azide did not lead to the axial azide substituent, but surprisingly gave a mixture of 3-azido-glucoside **4** and 2-azido-altroside **S1** in a ratio of 2:1 (entry 4). The direct substitution reaction is unfavorable due to shielding of the $\sigma_{C\text{-}Cl}*$ in the $^4C_1$ chair and, apparently, inversion of the chair to the $^4C_1$ conformer leads to rapid intramolecular S_N2 reaction with the C2-hydroxy group (Figure S1B) forming epoxide **5**. Epoxide **5** is subsequently ring-opened by azide providing **4** and **S1**.[2–4] Epoxide **5** could be isolated by treatment of **2b** with KO*t*Bu in D_2O followed by lyophilization. KO*t*Bu was selected as a base for practical reasons, as the small amounts could be weighted out more accurately. Ring-opening of **5** with sodium azide gave a mixture of **4** and **S1** (entry 6). Finally, when we subjected a mixture of **2a** and **2b** to these conditions, **4** and **S1** were formed in a total NMR yield of 86% (entry 8), and could be separated via column chromatography.

Intrigued by the epoxide formation of **2b**, we also subjected chloro-maltoside to KO*t*Bu in D_2O. This gave epoxide **6** in quantitative yield, which shows the potential of the deoxy-chlorination reaction to obtain epoxides in an unprotected manner.

While these results clearly demonstrate that S_N2 substitution of chlorides with sodium azide is feasible, the reactions with thiols show that for some nucleophiles an S_N1 substitution reaction on the more reactive chloro azo compounds may be more suitable.

Table S1. Screening of substitution reactions on 3-chloro glucose 2

Entry	Ratio chloride eq/ax	Solvent	Nucleophile (eq.)	Temperature (°C)	Time (h)	Conversion SM (%)	NMR yield (%)		
							Epoxide 5	**3-N_3 4**	**2-N_3 S1**
1	0/1	DMA	-	120 130	1 1	0 2	- -	0 0	- -
2	0/1	DMA	NaN_3 (5)	130	2	100	-	45	-
3	0/1	D_2O	NaN_3 (5)	140	4	50	-	<20[a]	-
4	1/0	DMA	NaN_3 (5)	130	2	100	-	65	23
5	1/0	D_2O	NaN_3 (5)	140	2	100	-	65	39
6	1/0	D_2O	KO*t*Bu (1.1)	50	1.5	91	87	-	-
		DMA	NaN_3 (5) NH_4Cl (1)	80 100	1 2	22 84	-	13 52	0 30
7	1/0	D_2O	KOtBu (1.1)	50	1.5	100	89[b]	-	-
8	1/1	D_2O	KO*t*Bu (1.1)	50	1.5	100 of ax-Cl 12 of eq-Cl	80	-	-
		DMA	NaN_3 (5) NH_4Cl (1)	120	3	100	-	67[c]	19[c]

[a] Due to difficult analysis, the small amounts of **4** are estimated to be max. 20%.

[b] This is the isolated yield after column purification.

[c] The yields after column purification are: 31% for **4** and 10% for **S1**.

[d] After heating for one h, 0.1 eq. DIPEA was added and heated again for an additional h.

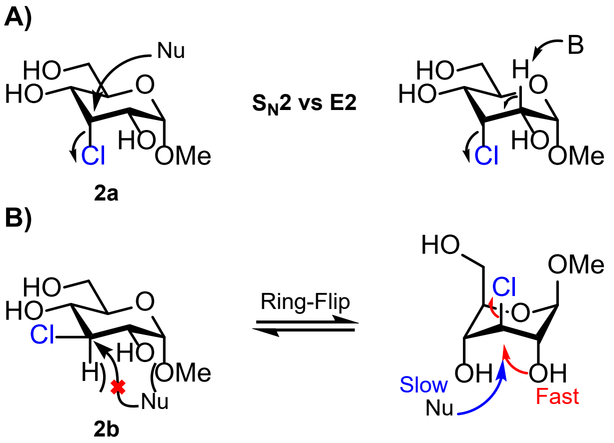
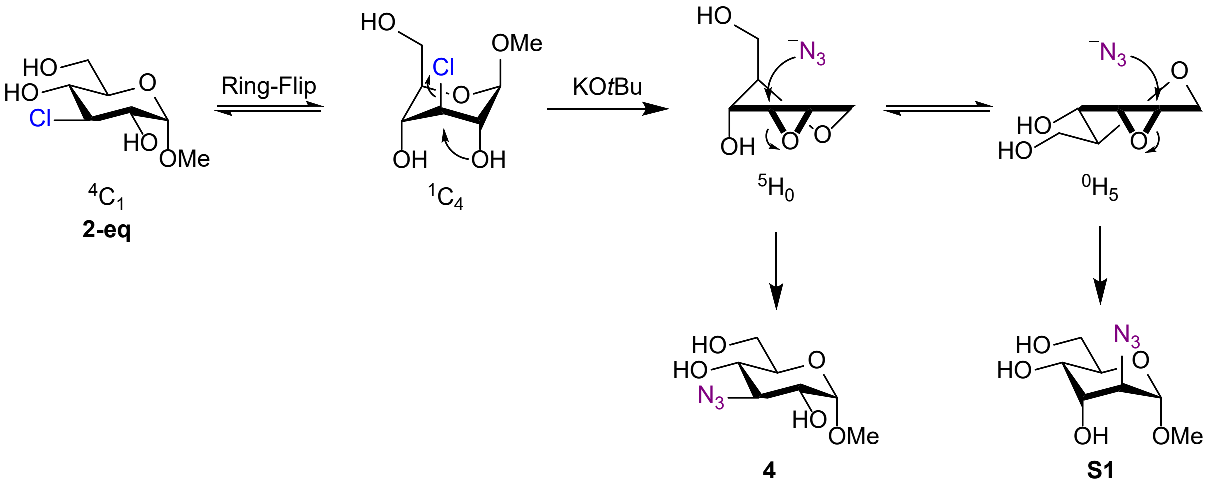


Figure S1. A) Substitution of **2** (1/2.7 eq/ax ratio) with sodium azide; B) Substitution versus elimination of the axial chloride; C) The required ring flip of the equatorial chloride to form the epoxide; D) Isolated products after treatment of solely **2a** or **2b** with either KO*t*Bu or NaN_3; E) Epoxide of maltose.



Scheme S2. Formation of **4** and **S1** from **2-eq**.

Deoxy-thiolation

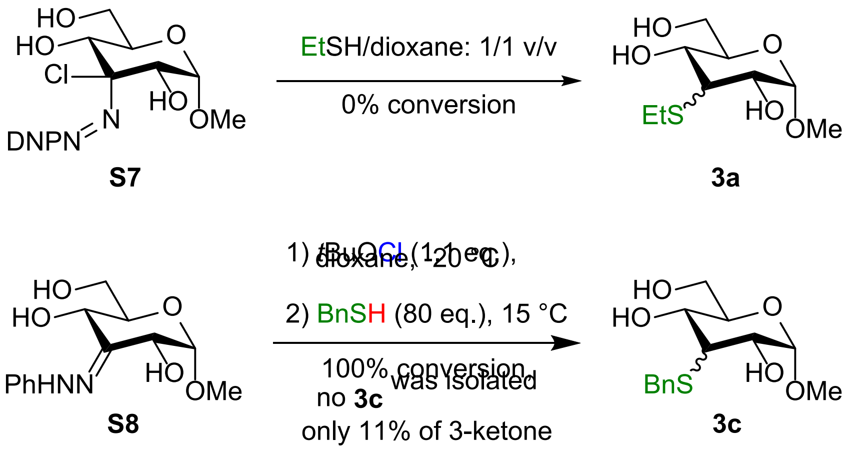
Table S2. Dehydroxy-chlorination and deoxy-thiolation reactions

Entry	Substrate	H-donor (eq.)	Time (min)[a]	Temp. (°C)	Yield thiol (Eq/Ax)	Yield Cl-product (Eq/Ax)	Yield side-product
1[b]	**1**, α-Glc	*t*BuSH (80)	120	-20->60	-	66 (**2**) (1/3.5)	**-**
2[b]	**1**, α-Glc	EtSH (80)	120	-20->40	74 (**3a**) (1/2.6)	19 (**2**) (1/1.4)	-
3	**1**, α-Glc	EtSH (80)	310	-20->10	97 (**3a**) (1/3.7)	-	**-**
4	**1**, α-Glc	PhSH (80)	O.N.	-20->15	80 (**3b**) (1/1.5)	-	-
5	**1**, α-Glc	BnSH (80)	O.N.	-20->15	84 (**3c**) (1/5.1)	-	-
6	**1**, α-Glc	BnSH (80)	O.N.	-20->-5	77 (**3c**) (1/4.6)	-	-
7	**1**, α-Glc	AcSH (80)	300	-20->5	64 (**3d**) (1.3/1)	-	-
8[c]	**1**, α-Glc	AcSH (80)	300	-20->5	58 (**3d**) (1.1/1)	-	-
9	**1**, α-Glc	AcSH (80)	O.N.	-20->-5	56 (**3d**) (1.2/1)	-	-
10	**1**, α-Glc	AcSH (80)	O.N.	-20->-10	52 (**3d**) (1/1.1)	-	-

[a] After addition of the thiol.

[b] Earlier published results.[5]

[c] Scale-up to 6 mmol.



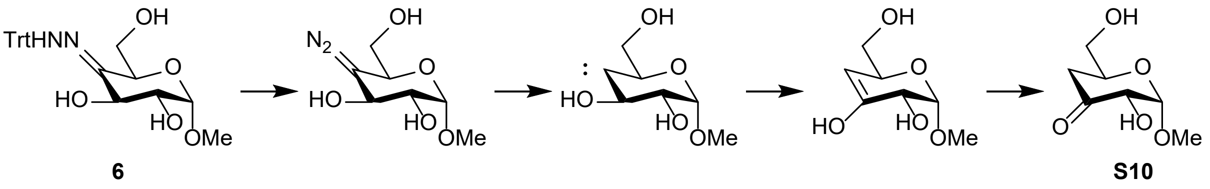
Scheme S3. Failed deoxy-thiolation reactions on **S7** and **S8**.

Table S3. Deoxy-thiolation reactions

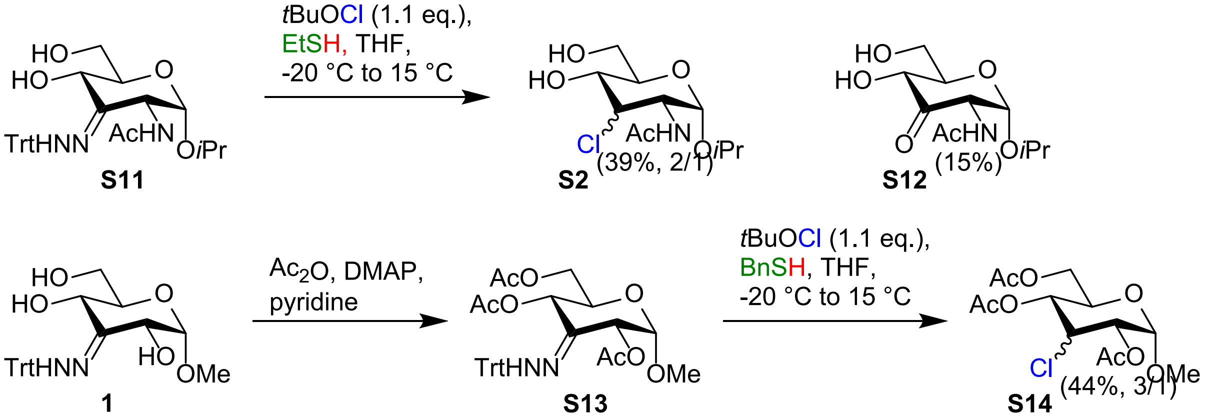
Entry	Substrate	H-donor (eq.)	Time (min)[a]	Temp. (°C)	Yield thiol (Eq/Ax)	Yield Cl-product (Eq/Ax)	Yield side-product
1	**7**, Xylose	EtSH (80)	O.N.	-20->-5	41 (**8a**) (1/5)	-	-
2	**7**, Xylose	BnSH (80)	O.N.	-20->-5	41 (**8b**) (1/5)	-	-
3	**7**, Xylose	AcSH (80)	O.N.	-20->-5	36 (**8c**) (1.5/1)	-	-
4	**9**, 4-TrtHNN-Gal	EtSH (80)	O.N.	-20->15	-	20 (**S9**) (1.8/1)	10 (**S10**)
5	**9**, 4-TrtHNN-Gal	AcSH (80)	O.N.	-20->-5	22 (**10**) (1/3.7)	15 (**S9**) (1/1.4)	40 (**S10**)
6	**11**, Maltose	BnSH (80)	O.N.	-20->-5	57 (**12**) (1/5)	-	-
7	**S11**, GlcNAc	EtSH (80)	O.N.	-20->15	-	39 (**S2**) (2/1)	15 (**S12**)
8	**S13**, Ac-α-Glc	BnSH (80)	O.N.	-20->15	-	44 (**S14**) (3/1)	-
9	**13**, β-Glc	BnSH (80)	O.N.	-20->15	21 (**14**) (1/1.1)	54 (**15**) (1.8/1)	5 (**S15**)
10	**16**, Cellobiose	AcSH (80)	O.N.	-20->15	-	-	47 (**17**)
11	**16**, Cellobiose	BnSH (80)	O.N.	-20->-5	-	-	50 (**17**)

[a] After addition of the thiol.

[b] Scale-up to 6 mmol.



Scheme S4. Proposed mechanism formation of **S10**.



Scheme S5. Attempted deoxy-thiolation reactions on N-acetyl glucosamine **S11** and acetylated trityl hydrazone **S13**. The ratios behind the yield are the equatorial/axial ratios.

Experimental procedures

General procedures

General Information

All solvents used for reaction, extraction, filtration, and chromatography were of commercial grade and used without further purification. Automated flash chromatography was performed on a Reveleris® X2 Flash Chromatography, using Grace® Reveleris Silica flash cartridges (12 grams). ^{1}H-, ^{13}C-, APT-, HSQC-, and COSY-NMR were recorded on a Varian AMX400 spectrometer (400, 101 MHz, respectively) using DMSO-d_6, chloroform-*d*, or methanol-d_4 as solvent. Chemical shifts are given in ppm (δ) relative to the solvent residual peak. Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, t = triplet, q =quartet, m = multiplet), coupling constants J (Hz), and integration. High Resolution Mass measurements were performed using a ThermoScientific LTQ OribitrapXL spectrometer. Microwave reactions were performed with Biotage® Initiator+.

Preparation of *tert*-butyl hypochlorite

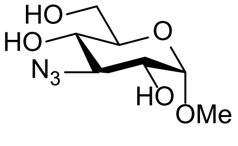
10-15% aqueous NaOCl (100 mL) was diluted with water (150 mL). The solution was cooled to 0 °C and placed in the dark. AcOH (10 mL) and *t*BuOH (15.5 mL) were added in one single portion. The solution was stirred for 15 min. The formed *tert*-butyl hypochlorite formed an immiscible layer on top of the water. The reaction mixture was poured into a separatory funnel and the aqueous layer was discarded. The neat *tert*-butyl hypochlorite layer was washed with sat. aq. $NaHCO_3$ (1× 100 mL), water (1× 50 mL) and filtered over a pipet filled with $CaCl_2$. Neat yellow *tert*-butyl hypochlorite was obtained, which was stored over $CaCl_2$ under N_2 atmosphere in a fridge for a maximum period of one month. When used in a reaction, it was dissolved in the solvent mentioned.

General procedure of following experiments with qNMR.

The starting material was dissolved in a microwave vial with either D_2O or DMA to obtain a solution with a concentration of 0.1 M, followed by the addition of the internal standard. For experiments in D_2O DMSO was used as I.S., while for experiments in DMA 1,2-dichlorobenzene was used. In the case of D_2O, the reaction mixture was shaken and transferred to an NMR tube. ^{1}H-NMR was taken (t0 measurement) with 8 scans (nt=8) and a d1 value of 60 (d1=60). After the NMR measurement, the D_2O mixture was transferred to the microwave vial. When DMA was used, a small amount was taken and concentrated in vacuo before being dissolved in methanol-d_4 followed by t0 measurement. Next, the additive was added and the reaction mixture was heated to the given temperature. The reaction was followed by using the NMR-sample preparation method mentioned earlier.

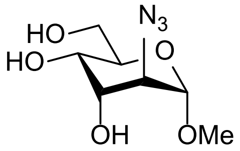
Substitution reactions on chloroglycosides

Methyl 3-azido-3-deoxy-α-D-glucopyranoside (4)



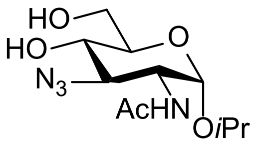
NaN_3 (71 mg, 1.1 mmol, 5.0 eq.) was added in a microwave vial, followed by the addition of a solution of compound **2** (46 mg, 0.22 mmol, 1.0 eq., ax/eq ratio: 1/1) in DMA (2.2 mL). The vial was closed with a cap and heated for two hours at 100 °C in a microwave. NMR analysis showed only 5% conversion, therefore the vial was heated once more for two hours at 130 °C. NMR analysis showed full conversion and the reaction mixture was concentrated *in vacuo*. Purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) gave the title compound (19 mg, 80 µmol, 73% starting from the axial chloride) as an oil. HRMS (ESI neg) m/z calcd for $C_7H_{12}N_3O_5$ $[M\text{-}H]^-$: 218.0782, found: 218.0782. ^{1}H NMR (400 MHz, Methanol-d_4) δ = 4.68 (d, *J*=3.6, 1H), 3.81 (dd, *J*=11.8, 1.9, 1H), 3.69 (dd, *J*=11.8, 5.3, 1H), 3.61 – 3.51 (m, 2H), 3.48 – 3.38 (m, 4H), 3.37 – 3.27 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 100.6, 73.5, 72.3, 70.2, 68.7, 62.3, 55.6.

Methyl 2-azido-2-deoxy-α-D-altropyranoside (S1)



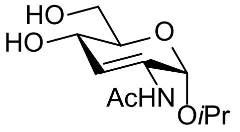
Compound **2** (38.6 mg, 0.18 mmol, ax/eq ratio: 1/1) was dissolved in D_2O (1.8 mL). DMSO (13 µL, 0.18 mmol, 1.0 eq.) was added as internal standard. qNMR (t0) was measured as described in the general procedure. The azide was introduced as described in the general procedure. KO*t*Bu (20 mg, 0.18 mmol, 1.0 eq.) was added and the reaction mixture was heated for 1.5 hours at 50 °C in a microwave. qNMR analysis showed full conversion of the equatorial chloride **2-eq** to epoxide **5**. After lyophilization, the crude was dissolved in DMA (1.8 mL) in a microwave vial, followed by the addition of 1,2-dichlorobenzene (20 µL, 0.18 mmol, 1.0 eq.). qNMR (t0) was measured with 50 µL of the reaction mixture. NaN_3 (59 mg, 0.91 mmol, 5.0 eq.) and NH_4Cl (9.7 mg, 0.18 mmol, 1.0 eq.) were added and the reaction mixture was heated to 120 °C for three hours, after which qNMR (t1) showed full conversion of **2-ax** and **5**. The reaction mixture was concentrated *in vacuo* and purified by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) to give **4** (12.5 mg, 57 µmol, 31%) and **S1** (4.0 mg, 18 µmol, 10%). The analysis of **4** is described *vide supra*. HRMS (ESI neg) m/z calcd for $C_7H_{12}N_3O_5$ $[M-H]^-$: 218.0782, found: 218.0784. ^1H NMR (400 MHz, Methanol-d_4) δ 4.58 (d, *J* = 3.7 Hz, 1H), 3.84 (td, *J* = 6.6, 3.2 Hz, 1H), 3.80 – 3.75 (m, 3H), 3.75 – 3.72 (m, 1H), 3.71 – 3.64 (m, 2H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 101.4, 73.8, 70.6, 67.1, 64.3, 63.0, 55.9.

Isopropyl 2-acetmido-3-azido-2,3-dideoxy-α-D-glucopyranoside (S3)



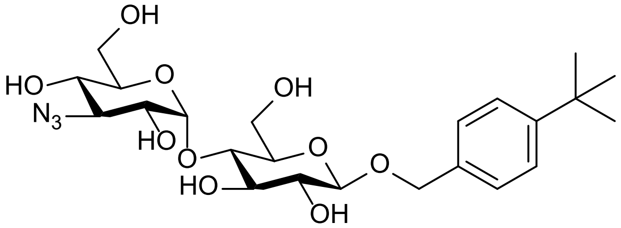
NaN_3 (41 mg, 0.63 mmol, 5.0 eq.) was added in a microwave vial, followed by the addition of a solution of compound **S2**[5] (36 mg, 0.13 mmol, 1.0 eq., ax/eq ratio: 1/1.4) in DMA (2.5 mL). The vial was closed with a cap and heated for two hours at 130 °C in a microwave. The reaction mixture was concentrated *in vacuo*. Purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) gave two fractions. One was a mixture of the title compound (4.3 mg, 15 µmol 29% starting from the axial chloride) and unreacted equatorial chloride **S2-eq** (17.4 mg, 62 µmol, 83% recovered). The other fraction contained compound **S4** (4.7 mg, 19 µmol). The analysis of **S4** is described *vide infra.* HRMS (ESI) m/z calcd for $C_{11}H_{20}N_4O_5Na$ $[M+Na]^+$: 311.1326, found: 311.1322. Because of the overlap with the spectrum of **S2-eq**, only two signals from **S3** can be observed in ^1H NMR. ^1H NMR (400 MHz, Methanol-d_4) δ = 3.61 (dd, *J* = 11.2, 9.3 Hz, 1H), 3.41 (t, *J* = 9.3 Hz, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 173.3, 96.1, 73.8, 71.2, 71.1, 65.6, 62.4, 53.5, 23.6, 22.4, 21.6.

Side product of the azide introduction in GlcNAc (S4)



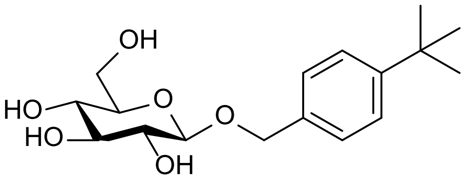
Compound **S4** (4.7 mg, 19 µmol) was isolated during the synthesis of **S3**. HRMS (ESI) m/z calcd for $C_{11}H_{19}NO_5Na$ $[M+Na]^+$: 268.1155, found: 268.1151. ^1H NMR (400 MHz, Methanol-d_4) δ = 6.12 (d, *J*=2.1, 1H), 5.28 (s, 1H), 4.13 (d, *J*=8.9, 1H), 4.02 (p, *J*=6.2, 1H), 3.82 (d, *J*=10.0, 1H), 3.75 – 3.64 (m, 2H), 2.01 (s, 3H), 1.25 (d, *J*=6.2, 3H), 1.18 (d, *J*=6.1, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 172.1, 134.8, 118.1, 94.0, 73.6, 72.0, 64.3, 62.7, 24.1, 23.5, 22.3.

4-tert-butylbenzyl-3-azido-3-deoxy-α-D-maltoside (S6)



NaN_3 (26 mg, 0.40 mmol, 5.3 eq.) was added in a microwave vial, followed by the addition of a solution of compound **S5**[5] (38 mg, 75 µmol, 1.0 eq., ax/eq ratio: 4.4/1) in DMA (1.5 mL). The vial was closed with a cap and heated for two hours at 130 °C in a microwave. NMR analysis showed full conversion and the reaction mixture was concentrated *in vacuo*. Purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 25% MeOH in DCM) gave a mixture of the title compound (13 mg, 26 µmol, 43% starting from the axial chloride) and side product **17** (7.6 mg, 23 µmol, 38% starting from the axial chloride) which could not be separated. HRMS (ESI) m/z calcd for $C_{23}H_{35}N_3O_{10}Na$ $[M+Na]^+$: 536.2215, found: 536.2203. ^1H NMR (400 MHz, Methanol-d_4) δ = 7.38 (q, *J*=8.4, 4H), 5.21 (d, *J*=3.7, 1H), 4.90 (d, *J*=11.7, 1H), 4.66 (d, *J*=11.6, 1H), 4.38 (dd, *J*=12.8, 7.7, 1H), 3.97 – 3.89 (m, 1H), 3.88 – 3.81 (m, 2H), 3.77 – 3.59 (m, 4H), 3.59 – 3.52 (m, 1H), 3.46 (dd, *J*=10.2, 3.6, 1H), 3.44 – 3.39 (m, 1H), 3.36 – 3.22 (m, 8H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 151.9, 136.0, 129.2, 126.2, 103.1, 102.0, 81.0, 77.8, 76.6, 74.8, 74.6, 72.8, 71.7, 70.0, 68.8, 62.4, 62.2, 35.4, 31.8.

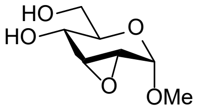
4-tert-butylbenzyl-β-D-glucopyranoside (17)



Compound **17** was formed during the attempted deoxy-thiolation of **16** (Table S3, entry 10 & 11) and the synthesis of **S6**. HRMS (ESI) m/z calcd for $C_{17}H_{26}NO_6Na$ [M+Na]$^+$: 349.1622, found: 349.1622. ^{1}H NMR (400 MHz, Methanol-d_4) δ = 7.43 – 7.33 (m, 4H), 4.91 (d, *J*=11.6, 1H), 4.66 (d, *J*=11.6, 1H), 4.37 (d, *J*=7.7, 1H), 3.92 (dd, *J*=11.9, 2.1, 1H), 3.72 (dd, *J*=11.9, 5.6, 1H), 3.39 – 3.24 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 151.8, 135.9, 129.2, 126.1, 103.1, 78.0, 77.9, 75.1, 71.5, 62.8, 35.3, 31.8.

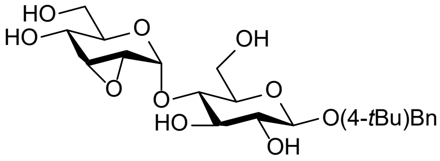
Synthesis of epoxides 5 and 6

Methyl 2,3-anhydro-α-D-glucopyranoside (5)



Compound **2-eq**[5] (0.13 g, 0.62 mmol, 1.0 eq.) was dissolved in D_2O (6.2 mL). DMSO (44 µL, 0.62 mmol, 1.0 eq.) was added as internal standard. KO*t*Bu (76 mg, 0.68 mmol, 1.1 eq.) was added and the reaction mixture was heated for 1.5 hours at 50 °C in a microwave. qNMR analysis showed full conversion. After lyophilization, the crude was purified by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) and lyophilization gave the title compound (83 mg, 0.44 mmol, 70%). HRMS (ESI neg) m/z calcd for $C_7H_{11}O_5$ [M-H]$^-$: 175.0612, found: 175.0614. ^{1}H NMR (400 MHz, Methanol-d_4) δ 4.92 (d, *J* = 3.2 Hz, 1H), 3.87 – 3.78 (m, 2H), 3.68 – 3.59 (m, 2H), 3.54 (dd, *J* = 4.2, 3.2 Hz, 1H), 3.46 (s, 3H), 3.42 – 3.39 (m, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 96.0, 70.9, 66.4, 62.5, 55.9, 55.7, 55.1. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 5.07 (d, *J* = 3.1 Hz, 1H), 3.96 (dd, *J* = 9.6, 1.7 Hz, 1H), 3.87 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.75 – 3.66 (m, 2H), 3.65 – 3.57 (m, 2H), 3.48 (s, 3H).

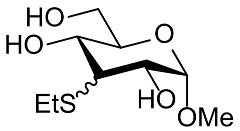
4-tert-butylbenzyl-2,3-anhydro-α-D-maltoside (6)



4-tert-butylbenzyl-3-chloro-3-deoxy-β-D-maltoside[5] (5.0 mg, 9.9 µmol, 1.0 eq.) was dissolved in D_2O (0.47 mL) in an NMR tube. DMSO (1 µL, 9.9 µmol, 1.0 eq.) was added as internal standard. A solution of KO*t*Bu in D_2O (0.5 M, 30 µg, 15 µmol, 1.5 eq.) was added and the reaction mixture was heated for 1.5 hours at 50 °C. NMR analysis showed full conversion. After lyophilization, the title compound was obtained in quantitative yield (5.5 mg). HRMS (ESI pos) m/z calcd for $C_{23}H_{34}O_{10}Na$ [M+Na]$^+$: 493.2044, found: 493.2041. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.56 (d, *J* = 3.0 Hz, 1H), 4.85 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.33 (d, *J* = 7.8 Hz, 1H), 3.85 – 3.76 (m, 3H), 3.75 – 3.67 (m, 3H), 3.58 – 3.51 (m, 3H), 3.36 (dd, *J* = 4.3, 1.1 Hz, 1H), 3.33 – 3.29 (m, 1H), 3.23 (dd, *J* = 9.3, 7.8 Hz, 1H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 134.5, 127.7, 124.7, 101.7, 93.9, 77.4, 75.0, 73.9, 73.9, 70.6, 70.1, 65.2, 61.6, 60.4, 54.6, 53.8, 30.3.

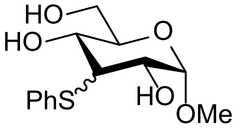
Synthesis of α-Glc derivatives

Methyl 3-S-ethyl-3-deoxy-α-D-allo/glucopyranoside (3a)



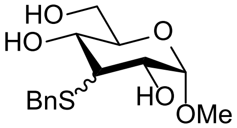
A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **1**[5] (186 mg, 0.40 mmol, 1.0 eq.) and THF (4 mL). The resulting solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature). *tert*-Butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 20 minutes. During this time EtSH was purged for 5 minutes with N_2. Excess EtSH (2.3 mL, 32 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to 10 °C over 5 h, after which the reaction mixture was concentrated *in vacuo*. Purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) gave the title compound (93 mg, 0.39 mmol, 97%). The NMR shows the ratio of equatorial and axial is 1/3.7. Analysis was in agreement with literature.[5]

Methyl 3-*S*-phenyl-3-deoxy-α-D-allo/glucopyranoside (3b)



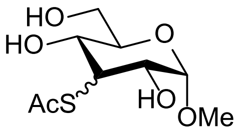
A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **1**[5] (189 mg, 0.40 mmol, 1.0 eq.) and THF (4 mL). The resulting solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature). *tert*-Butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 20 minutes. During this time PhSH was purged for 5 minutes with N_2. Excess PhSH (3.3 mL, 32 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to 15 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and the remaining crude was diluted with pentane/Et_2O (1/1 v/v) and extracted with H_2O (2x). The combined aqueous layers were concentrated *in vacuo* and purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) gave the title compound (92 mg, 0.32 mmol, 80%). The NMR shows the ratio of equatorial and axial is 1/1.5. HRMS (ESI) m/z calcd for $C_{13}H_{18}O_5SNa$ $[M+Na]^+$: 309.0767, found: 309.0767. Reported NMR data is for the major isomer. ^1H NMR (400 MHz, Methanol-d_4) δ = 7.70 – 7.65 (m, 1H), 7.64 – 7.59 (m, 2H), 7.39 – 7.24 (m, 2H), 4.65 (d, *J*=3.5, 1H), 4.01 – 3.96 (m, 1H), 3.93 – 3.64 (m, 5H), 3.44 (s, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 140.6, 135.8, 132.4, 129.7, 129.7, 100.5, 70.6, 69.0, 67.9, 62.4, 61.7, 55.4.

Methyl 3-*S*-benzyl-3-deoxy-α-D-allo/glucopyranoside (3c)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **1**[5] (189 mg, 0.40 mmol, 1.0 eq.) and THF (4 mL). The resulting solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature). *tert*-Butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 20 minutes. During this time BnSH was purged for 5 minutes with N_2. Excess BnSH (3.8 mL, 32 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to 15 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and the remaining crude was diluted with pentane/Et_2O (1/1 v/v) and extracted with H_2O (2x). The combined aqueous layers were concentrated *in vacuo* and purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) gave the title compound (101 mg, 0.34 mmol, 84%). The NMR shows the ratio of equatorial and axial is 1/5.1. HRMS (ESI) m/z calcd for $C_{14}H_{20}O_5SNa$ $[M+Na]^+$: 323.0924, found: 323.0921. Reported NMR data is for the major isomer. ^1H NMR (400 MHz, Methanol-d_4) δ = 7.45 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.18 (m, 1H), 4.54 (d, *J*=3.5, 1H), 3.92 – 3.84 (m, 2H), 3.84 – 3.79 (m, 2H), 3.79 – 3.71 (m, 3H), 3.41 – 3.38 (m, 1H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 139.9, 130.3, 129.4, 127.9, 100.4, 70.4, 68.9, 68.7, 62.5, 55.9, 55.3, 40.7.

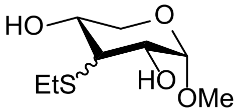
Methyl 3-*S*-acetyl-3-deoxy-α-D-allo/glucopyranoside (3d)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **1**[5] (186 mg, 0.40 mmol, 1.0 eq.) and THF (4 mL). The resulting solution was evacuated and backfilled with N$_2$ (3 times) and then cooled to -20 °C (external temperature). *tert*-Butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N$_2$ bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N$_2$, the reaction was maintained at an external temperature ≤ -15 °C for 20 minutes. During this time AcSH was purged for 5 minutes with N$_2$. Excess AcSH (2.3 mL, 32 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to 5 °C over 7.5 h in the dark, after which TLC analysis showed full conversion. The reaction mixture was concentrated *in vacuo* and purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) gave the title compound (65 mg, 0.26 mmol, 64%). The NMR shows the ratio of equatorial and axial is 1.3/1.0. Analysis was in agreement with literature.[5]

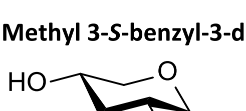
Synthesis of Xylose derivatives

Methyl 3-deoxy-3-*S*-ethyl-α-D-riboso/xylopyranoside (8a)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **7**[5] (167 mg, 0.38 mmol, 1.0 eq.) and THF (4 mL). The resulting yellow solution was evacuated and backfilled with N$_2$ (3 times) and then cooled to -20 °C (external temperature), *tert*-butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise over 1 minute to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N$_2$ bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N$_2$, the reaction was maintained at an external temperature ≤ -15 °C for 35 minutes. During this time EtSH was degassed in a separated flask by purging with N$_2$ for 5 minutes, after which 2.3 mL (30.4 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to -5 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and purified by Grace flash chromatography on a 15 g silica cartridge using heptane/EtOAc (0 to 100% EtOAc in heptane). The products were obtained as an oil (40 mg, 0.19 mmol, 50%). Two fraction were collected of which one fraction contains the axial product and the other contains a mixture of axial- and equatorial-product. The ratio between equatorial- and axial-product is 1/5.3. **3-equatorial/3-axial mix:** HRMS (ESI) m/z calcd for $C_8H_{16}O_4SNa$ [M+Na]$^+$: 231.0662, found: 231.0660. **3-equatorial:** ^{1}H NMR (400 MHz, Methanol-d_4) δ 4.61 (d, *J* = 3.5 Hz, 1H), 3.65 – 3.59 (m, 1H), 3.50 – 3.46 (m, 2H), 3.45 – 3.42 (m, 4H), 2.81 – 2.69 (m, 3H), 1.28 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 100.6, 72.3, 69.9, 63.9, 55.5, 53.8, 49.6, 49.4, 49.2, 49.0, 48.8, 48.6, 48.4, 26.5, 15.3. **3-Axial:** HRMS (ESI) m/z calcd for $C_6H_{11}ClO_4Na$ [M+Na]$^+$: 231.06620, found: 231.0660. ^{1}H NMR (400 MHz, Methanol-d_4) δ 4.39 (d, *J* = 1.8 Hz, 1H), 3.92 (dd, *J* = 11.8, 4.7 Hz, 1H), 3.85 – 3.78 (m, 2H), 3.56 (dd, *J* = 11.8, 2.3 Hz, 1H), 3.48 (s, 3H), 3.12 (t, *J* = 3.3 Hz, 1H), 2.69 – 2.55 (m, 2H), 1.28 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 102.8, 70.8, 68.7, 67.3, 56.4, 52.0, 27.2, 15.3.

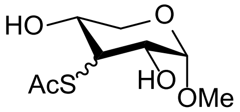
Methyl 3-*S*-benzyl-3-deoxy-α-D-riboso/xylopyranoside (8b)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **7**[5] (167 mg, 0.38 mmol, 1.0 eq.) and THF (4 mL). The resulting yellow solution was evacuated and backfilled with N$_2$ (3 times) and then cooled to -20 °C (external temperature), *tert*-butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise over 1 minute to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light yellow solution was then frozen in a liquid N$_2$ bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N$_2$, the reaction was maintained at an external temperature ≤ -15 °C for 35 minutes. During this time BnSH was degassed in a separated flask by purging with N$_2$ for 5 minutes, after which

3.6 mL (30.4 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to -5 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and the remaining crude was diluted with pentane/Et_2O (1/1 v/v) and extracted with H_2O (2x). The combined aqueous layers were concentrated *in vacuo* and the mixture was purified by Grace flash chromatography on a 15 g silica cartridge using heptane/EtOAc (0 to 70% EtOAc in heptane). The products were obtained as an oil (32 mg, 0.14 mmol, 38%). The equatorial- and axial-products were isolated separately with a ratio of 1/5. **3-equatorial**: HRMS (ESI) m/z calcd for $C_{13}H_{18}O_4SNa$ $[M+Na]^+$: 293.0818, found: 293.0814. ^{1}H NMR (400 MHz, Methanol-d_4) δ = 7.42 – 7.12 (m, 5H), 4.59 (d, *J*=3.5, 1H), 3.97 (d, *J*=1.5, 2H), 3.61 – 3.55 (m, 1H), 3.52 – 3.42 (m, 4H), 3.41 (s, 3H), 2.86 – 2.79 (m, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 140.0, 130.2, 129.4, 127.9, 100.7, 72.5, 70.0, 64.0, 55.5, 53.9, 49.4, 49.2, 49.0, 48.8, 48.6, 37.0. **3-axial**: HRMS (ESI) m/z calcd for $C_{13}H_{18}O_4SNa$ $[M+Na]^+$: 293.0818, found: 293.0815. ^{1}H NMR (400 MHz, Methanol-d_4) δ = 7.39 – 7.19 (m, 5H), 4.26 (d, *J*=1.6, 1H), 3.90 (dd, *J*=11.9, 4.4, 1H), 3.85 – 3.75 (m, 2H), 3.75 – 3.68 (m, 2H), 3.47 (dd, *J*=11.9, 2.1, 1H), 3.43 (s, 3H), 2.99 (t, *J*=3.1, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ = 139.9, 130.1, 129.5, 128.0, 102.8, 70.8, 68.8, 56.5, 49.2, 49.0, 48.8, 48.6, 37.2.

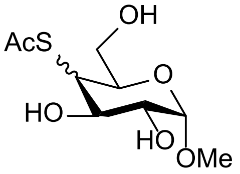
Methyl 3-*S*-acetyl-3-deoxy-α-D-riboso/xylopyranoside (8c)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **7**[5] (167 mg, 0.38 mmol, 1.0 eq.) and THF (4 mL). The resulting yellow solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature), *tert*-butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise over 1 minute to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 35 minutes. During this time AcSH was degassed in a separated flask by purging with N_2 for 5 minutes, after which 2.3 mL (30.4 mmol. 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to -5 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and purified by Grace flash chromatography on a 15 g silica cartridge using heptane/EtOAc (0 to 100% EtOAc in heptane). The products were obtained as an oil (32 mg, 0.14 mmol, 38%). The product was isolated as a mixture of equatorial- and axial-product, with a ratio of 1.5/1. Reported NMR data is for the major isomer. HRMS (ESI) m/z calcd for $C_8H_{13}O_6S$ $[M-H]^-$: 221.0489, found: 221.0486. ^{1}H NMR (400 MHz, Methanol-d_4) δ 4.62 (d, *J* = 3.5 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.64 – 3.56 (m, *2*H), 3.56 – 3.49 (m, 2H), 3.44 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 197.5, 197.2, 100.5, 100.5, 70.9, 68.9, 63.9, 55.5, 52.3, 49.4, 49.2, 49.0, 48.8, 48.6, 30.7.

Synthesis of Gal derivative

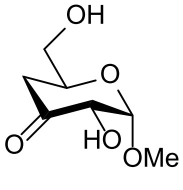
Methyl 4-*S*-acetyl-4-deoxy-α-D-galacto/glucopyranoside (10)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **9**[5] (179 mg, 0.40 mmol, 1.0 eq.) and THF (4 mL). The resulting yellow solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature), *tert*-butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise over 1 minute to the cooled solution of hydrazone and stirred for 25 minutes. The resulting light yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 30 minutes. During this time AcSH was degassed in a separated flask by purging with N_2 for 5 minutes, after which 2.3 mL (32 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to -5 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* purified by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM). Three fractions were obtained: I) 12 mg methyl 4-chloro-4-deoxy-α-D-galacto/glucopyranoside **S9**[5] (58 µmol, 15%, eq/ax ratio: 1/1.4); II) 22 mg **10** (88 µmol, 22%, eq/ax 1/3.7); III) 28 mg **S10** (0.16 mmol, 40%). The equatorial and axial product could not be separated. HRMS (ESI) m/z calcd for $C_9H_{16}O_6SNa$ $[M+Na]^+$: 275.0560, found:

275.0554. Reported NMR data is for the major isomer (axial). ^{1}H NMR (400 MHz, Methanol-d_4) δ 4.77 (d, *J* = 3.7 Hz, 1H), 3.75 – 3.63 (m, 3H), 3.59 (dd, *J* = 12.1, 6.5 Hz, 1H), 3.48 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.42 (s, 3H), 3.41 – 3.36 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 196.2, 101.2, 74.8, 73.0, 71.3, 63.4, 55.6, 48.0, 30.6.

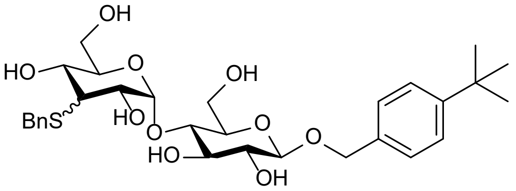
Methyl 3-keto-3,4-deoxy-α-D-glucopyranoside (S10)



Compound **S10** was isolated during the synthesis of **10**. ^{1}H NMR (400 MHz, Methanol-d_4) δ 5.07 (d, *J* = 4.1 Hz, 1H), 4.33 (dd, *J* = 4.1, 1.3 Hz, 1H), 4.08 – 4.00 (m, 1H), 3.69 (dd, *J* = 11.8, 3.5 Hz, 1H), 3.62 (dd, *J* = 11.9, 5.2 Hz, 1H), 3.42 (s, 3H), 2.71 – 2.61 (m, 1H), 2.38 (dd, *J* = 13.9, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 206.4, 103.9, 76.9, 71.8, 65.0, 55.7, 43.3. NMR analysis in DMSO-d6 was in agreement with literature.[6]

Synthesis of maltose derivatives

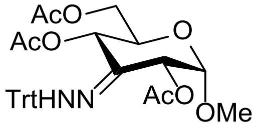
4-tert-butylbenzyl-3-*S*-benzyl-3-deoxy-α-D-maltoside (12)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **11**[5] (196 mg, 0.26 mmol, 1.0 eq.) and THF (2.6 mL). The resulting solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature). *tert*-Butyl hypochlorite (1.24 M in DCM, 0.23 mL, 1.1 eq.) was added dropwise to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 20 minutes. During this time BnSH was degassed by purging with N_2 for 5 minutes. Excess BnSH (2.4 mL, 32 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to -5 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and the remaining crude was diluted with pentane/Et_2O (1/1 v/v) and extracted with H_2O (2x). The combined aqueous layers were concentrated *in vacuo* and the mixture was purified by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM). The title compound was obtained as an oil (86 mg, 0.15 mmol, 57%, eq/ax 1/5). The equatorial- and axial-products were partially isolated. **3-equatorial**: HRMS (ESI) m/z calcd for $C_{30}H_{42}O_{10}SNa$ $[M+Na]^+$: 617.2390, found: 617.2377. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.44 – 7.19 (m, 9H), 5.16 (d, *J* = 3.3 Hz, 1H), 4.90 (d, *J* = 11.7 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H), 4.05 – 3.90 (m, 3H), 3.88 – 3.78 (m, 2H), 3.73 – 3.64 (m, 2H), 3.64 – 3.53 (m, 3H), 3.42 – 3.28 (m, 3H), 2.86 (t, *J* = 10.7 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 139.8, 130.3, 129.4, 129.2, 128.0, 126.2, 103.1, 102.3, 81.4, 77.8, 76.7, 75.6, 74.7, 73.2, 71.6, 69.5, 62.9, 62.2, 53.5, 36.9, 35.4, 31.8. **3-axial**: HRMS (ESI) m/z calcd for $C_{30}H_{43}O_{10}S$ $[M+H]^+$: 595.2571, found: 595.2561. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.42 – 7.19 (m, 9H), 5.13 (d, *J* = 3.4 Hz, 1H), 4.90 (overlap with H_2O peak, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.36 (d, *J* = 7.8 Hz, 1H), 3.95 – 3.85 (m, 6H), 3.83 – 3.70 (m, 3H), 3.68 – 3.55 (m, 2H), 3.41 – 3.36 (m, 1H), 3.36 – 3.32 (m, 1H), 3.31 – 3.26 (m, 1H), 1.33 (d, *J* = 2.1 Hz, 9H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 151.8, 139.9, 135.9, 130.4, 129.4, 129.1, 127.9, 126.1, 103.1, 101.1, 79.2, 77.8, 76.7, 75.0, 71.7, 71.6, 69.4, 68.9, 62.6, 62.2, 55.2, 40.7, 35.3, 31.8.

Synthesis of S13 and S14

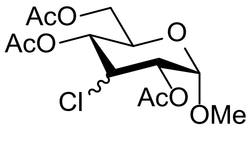
Methyl-2,4,6-O-acetyl-3-(trityl)hydrazone)-α-D-glucopyranoside (S13)



To a solution of **1**[5] (0.30 g, 0.67 mmol, 1.0 eq.) in pyridine (3.3 mL) was added DMAP (11 mg, 90 µmol, 0.14 eq.) and Ac_2O (0.19 mL, 2.0 mmol, 3.0 eq.) at 0 °C, after which the reaction was allowed to warm-up to room temperature and stirred for three hours. The reaction mixture was quenched by the addition of MeOH at 0 °C and diluted with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ (1x), brine (1x), dried over Na_2SO_4, filtered, and concentrated in *vacuo*. Purification by Grace flash chromatography on a 15 g silica cartridge with heptane/EtOAc (0 to 100% EtOAc in heptane) gave the title compound (0.21 g, 0.32 mmol, 47%). HRMS (ESI pos) m/z calcd for

$C_{32}H_{35}N_2O_8$ [M+H]$^+$: 575.2388, found: 575.2374. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.34 – 7.18 (m, 15H), 5.57 (d, *J* = 3.3 Hz, 1H), 5.04 (d, *J* = 9.3 Hz, 1H), 4.83 (d, *J* = 3.3 Hz, 1H), 4.18 (d, *J* = 3.8 Hz, 2H), 3.82 (dt, *J* = 9.0, 3.7 Hz, 1H), 3.32 (s, 3H), 2.08 (s, 6H), 1.54 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 169.4, 169.0, 145.8, 130.0, 129.3, 129.2, 127.7, 127.6, 126.7, 97.7, 73.2, 72.8, 70.3, 69.2, 62.6, 55.2, 20.8, 20.8, 20.3.

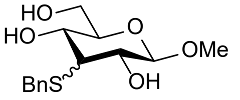
Methyl 2,4,6-tri-*O*-acetyl-3-chloro-3-deoxy-α-D-allo/glucopyranoside (S14)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **S13** (113 mg, 0.20 mmol, 1.0 eq.) and THF (2.0 mL). The resulting solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature). *tert*-Butyl hypochlorite (1.24 M in DCM, 0.18 mL, 1.1 eq.) was added dropwise to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 20 minutes. During this time BnSH was degassed by purging with N_2 for 5 minutes. Excess BnSH (1.8 mL, 16 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to 15 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and the remaining crude was dissolved in MeCN (+/- 5 mL) and washed several times with heptane (total of 150 mL) till TLC analysis showed that all benzyl thiol was removed. The MeCN layer was concentrated *in vacuo* and purification by Grace flash chromatography on a 15 g silica cartridge using heptane/EtOAc (0 to 40% EtOAc in heptane) gave the title compound (29 mg, 86 µmol, 44%, eq/ax 3/1). The equatorial- and axial-products were isolated separately. **3-equatorial**: HRMS (ESI pos) m/z calcd for $C_{13}H_{19}O_8ClNa$ [M+Na]$^+$: 361.0661 and 363.0631, found: 361.0662 and 363.0632. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.16 (t, *J* = 10.1 Hz, 1H), 4.97 (dd, *J* = 10.9, 3.6 Hz, 1H), 4.90 (d, *J* = 3.5 Hz, 1H), 4.29 – 4.18 (m, 2H), 4.10 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.89 (ddd, *J* = 10.0, 4.7, 2.4 Hz, 1H), 3.40 (s, 3H), 2.15 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.1, 169.4, 96.9, 72.7, 70.4, 68.2, 62.1, 58.1, 55.6, 20.9, 20.8, 20.7. **3-axial**: HRMS (ESI pos) m/z calcd for $C_{13}H_{19}O_8ClNa$ [M+Na]$^+$: 361.0661 and 363.0631, found: 361.0660 and 363.0630. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.09 (t, *J* = 4.1 Hz, 1H), 4.97 (dd, *J* = 9.3, 3.6 Hz, 1H), 4.88 (d, *J* = 4.2 Hz, 1H), 4.81 (t, *J* = 3.8 Hz, 1H), 4.40 – 4.31 (m, 2H), 4.27 – 4.18 (m, 1H), 3.45 (s, 3H), 2.18 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.0, 169.6, 97.4, 67.8, 67.0, 63.4, 62.2, 56.8, 56.2, 20.9, 20.9, 20.8.

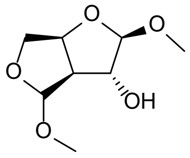
Synthesis of β-Glc derivative

Methyl 3-*S*-benzyl-3-deoxy-β-D-allo/glucopyranoside (14)



A 100 mL flask equipped with a magnetic stir bar was charged with trityl hydrazone **13**[5] (193 mg, 0.40 mmol, 1.0 eq.) and THF (4 mL). The resulting solution was evacuated and backfilled with N_2 (3 times) and then cooled to -20 °C (external temperature). *tert*-Butyl hypochlorite (1.24 M in DCM, 0.35 mL, 1.1 eq.) was added dropwise to the cooled solution of hydrazone and stirred for 15 minutes. The resulting light-yellow solution was then frozen in a liquid N_2 bath and degassed by two freeze-pump-thaw cycles, each time thawing in a -20 °C bath. After backfilling with N_2, the reaction was maintained at an external temperature ≤ -15 °C for 20 minutes. During this time BnSH was purged for 5 minutes with N_2. Excess BnSH (3.8 mL, 32 mmol, 80 eq.) was added to the cooled reaction. The reaction flask was subsequently allowed to warm-up to 15 °C overnight in the dark. The reaction mixture was concentrated *in vacuo* and the remaining crude was diluted with pentane/Et_2O (1/1 v/v) and extracted with H_2O (2x). The combined aqueous layers were concentrated *in vacuo* and purification by Grace flash chromatography on a 15 g silica cartridge using DCM/MeOH (0 to 10% MeOH in DCM) gave a mixture of the title compound (25 mg, 83 µmol, 21%, eq/ax 1/1.1) and rearrangement side product **S15** (4 mg, 20 µmol, 5%). Methyl 3-chloro-3-deoxy-β-D-allo/glucopyranoside **15**[5] (46 mg, 0.22 mmol, 54%, eq/ax 1.8/1) was also isolated. The reported NMR data is for the equatorial isomer, not all signals are given due to overlap. HRMS (ESI) m/z calcd for $C_{14}H_{20}O_5SNa$ [M+Na]$^+$: 323.0924, found: 323.0932. ^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 7.44 – 7.20 (m, 5H), 4.20 (d, *J* = 7.5 Hz, 1H), 4.00 (s, 2H), 3.83 – 3.76 (m, 1H), 3.74 – 3.67 (m, 2H), 3.55 (s, 3H), 3.40 – 3.31 (m, 1H), 3.27 (dd, *J* = 10.7, 7.6 Hz, 1H), 2.61 – 2.54 (m, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 139.8, 130.3, 129.4, 127.9, 106.6, 73.9, 62.9, 57.2, 56.8, 36.8.

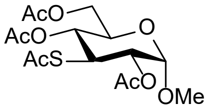
Rearrangement side product (S15)



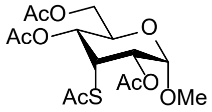
Compound **S15** was isolated as a minor product during the synthesis of **14**. Peaks of OMe are not given due to overlap with **14**. ^{1}H NMR (400 MHz, Methanol-d_4) δ 5.01 (d, *J* = 1.5 Hz, 1H), 4.96 (dd, *J* = 6.5, 3.5 Hz, 1H), 4.82 (s, 1H), 4.22 – 4.16 (m, 1H), 3.95 – 3.92 (m, 1H), 3.92 – 3.86 (m, 1H), 2.63 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 111.8, 109.4, 85.3, 79.5, 74.0, 59.6.

S-glycosides synthesis

Methyl 2,3,4,6-tri-*O*-acetyl-3-S-acetyl-3-deoxy-α-D-allo/glucopyranoside (S16 + S17)



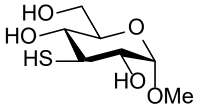
S16



S17

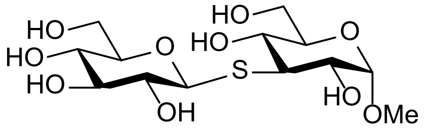
To a solution of compound **3d** (0.14 g, 0.54 mmol, 1.0 eq. eq/ax: 1.1/1) in pyridine (1.8 mL) was added Ac_2O (1.8 mL, 20 mmol, 36 eq.) at 0 °C. After 15 minutes, the reaction mixture was allowed to warm-up to room temperature and stirred for an additional hour. The reaction mixture was quenched by the addition of methanol at 0 °C, diluted with EtOAc and the organic layer was washed with 1 M HCl (2x), sat. aq. $NaHCO_3$ (2x), brine (1x), dried over Na_2SO_4, filtered, and concentrated in *vacuo*. A mixture of the title compounds was obtained in 98% yield (0.20 g, 0.53 mmol). With flash chromatography pentane/EtOAc (0 to 60% EtOAc in pentane) the two compounds could partly be separated to give pure **S16** (32 mg, 85 µmol) and pure **S17** (31 mg, 82 µmol), together with a mix fraction (0.14 g) that contained both **S16** and **S17**. **S16**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.05 (dd, *J* = 11.0, 9.9 Hz, 1H), 4.93 (dd, *J* = 11.8, 3.6 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 4.21 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.99 (ddd, *J* = 9.9, 4.7, 2.4 Hz, 1H), 3.42 (s, 3H), 2.31 (s, 3H), 2.06 (d, *J* = 8.5 Hz, 6H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.3, 170.8, 170.1, 169.5, 96.6, 69.8, 68.6, 67.6, 62.4, 55.4, 44.8, 30.8, 20.9, 20.8, 20.7. HRMS (ESI pos) m/z calcd for $C_{15}H_{22}O_9SNa$ $[M+Na]^+$: 401.0877, found: 401.0873. **S17**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.23 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.13 (dd, *J* = 10.3, 4.2 Hz, 1H), 4.79 (d, *J* = 3.4 Hz, 1H), 4.56 (t, *J* = 4.7 Hz, 1H), 4.26 (dd, *J* = 12.2, 4.7 Hz, 1H), 4.13 (dd, *J* = 12.2, 2.2 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.42 (s, 3H), 2.34 (s, 3H), 2.07 (d, *J* = 4.0 Hz, 6H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.6, 170.8, 169.7, 169.1, 96.6, 77.5, 77.2, 76.8, 67.5, 65.6, 65.3, 62.1, 55.4, 44.0, 30.4, 20.9, 20.8, 20.7. HRMS (ESI pos) m/z calcd for $C_{15}H_{22}O_9SNa$ $[M+Na]^+$: 401.0877, found: 401.0875.

Methyl 3-deoxy-3-thio-α-D-glucopyranoside (18)



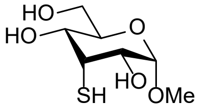
To a solution of **S16** (31 mg, 83 µmol, 1.0 eq.) in MeOH (0.4 mL) was added a solution of sodium methoxide in methanol (4.4 M, 38 µL, 0.24 mmol, 2.0 eq.). After stirring for one hour, TLC showed full conversion of the starting material. The reaction mixture was neutralized with dowex H$^+$ resin, filtered and concentrated *in vacuo* to give the title compound (15 mg, 69 µmol, 83%). NMR analysis was in agreement with literature.[7]

Methyl 3-*S*-β-D-glucopyranosyl-3-deoxy-3-thio-α-D-glucopyranoside (20)



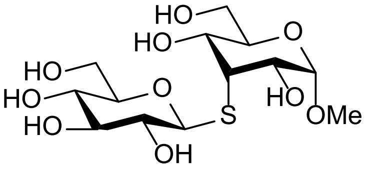
Thiol **18** (15 mg, 69 µmol, 1.0 eq.) was dissolved in MilliQ-H_2O (0.2 mL) and transferred to an Eppendorf containing α-D-glucopyranosyl fluoride[7] (38 mg, 0.21 mmol, 3.0 eq.) and $Ca(OH)_2$ (15 mg, 0.21 mmol, 3.0 eq.). The reaction was stirred vigorously for five hours, after which the reaction mixture was neutralized with 2 M HCl and concentrated *in vacuo*. Purification by Grace flash chromatography on a 15 g spherical silica cartridge using DCM/MeOH (0 to 30% MeOH in DCM) gave the title compound (12 mg, 32 µmol, 47%). HRMS (ESI pos) m/z calcd for $C_{13}H_{24}O_{10}SNa$ $[M+Na]^+$: 395.0982, found: 395.0984. ^{1}H NMR (400 MHz, Methanol-d_4) δ 4.72 (d, *J* = 3.5 Hz, 1H), 4.59 (d, *J* = 9.8 Hz, 1H), 3.89 – 3.80 (m, 2H), 3.75 – 3.64 (m, 2H), 3.63 – 3.53 (m, 2H), 3.46 (s, 3H), 3.41 – 3.32 (m, 4H), 3.26 (dd, *J* = 9.6, 8.5 Hz, 1H), 3.06 (t, *J* = 10.7 Hz, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 100.5, 86.3, 81.9, 79.4, 74.3, 72.2, 71.2, 69.2, 62.8, 62.6, 55.4, 53.6.

Methyl 3-deoxy-3-thio-α-D-allopyranoside (21)



To a solution of **S17** (46 mg, 0.12 mmol, 1.0 eq.) in MeOH (0.6 mL) was added a solution of sodium methoxide in methanol (4.4 M, 55 µL, 0.24 mmol, 2.0 eq.). After stirring for one hour, TLC showed full conversion of the starting material. The reaction mixture was neutralized with dowex H$^+$ resin, filtered and concentrated *in vacuo* to give the title compound (18 mg, 84 µmol, 70%). NMR analysis was in agreement with literature.[7]

Methyl 3-*S*-β-D-glucopyranosyl-3-deoxy-3-thio-α-D-allopyranoside (22)



Thiol **21** (18 mg, 84 µmol, 1.0 eq.) was dissolved in MilliQ-H_2O (0.1 mL) and transferred to an vial α-D-glucopyranosyl fluoride[7] (46 mg, 0.25 mmol, 3.0 eq.) and $Ca(OH)_2$ (19 mg, 0.25 mmol, 3.0 eq.). The reaction was stirred vigorously for five hours, after which the reaction mixture was neutralized with 2 M HCl and concentrated *in vacuo*. Purification by Grace flash chromatography on a 15 g spherical silica cartridge using DCM/MeOH (0 to 30% MeOH in DCM) gave the title compound (12 mg, 33 µmol, 39%). HRMS (ESI pos) m/z calcd for $C_{13}H_{24}O_{10}SNa$ $[M+Na]^+$: 395.0982, found: 395.0982. ^{1}H NMR (400 MHz, Methanol-d_4) δ 4.61 (d, *J* = 3.4 Hz, 1H), 4.34 (d, *J* = 9.8 Hz, 1H), 3.99 – 3.93 (m, 1H), 3.91 – 3.76 (m, 3H), 3.75 (t, 1H), 3.72 – 3.61 (m, 3H), 3.40 – 3.34 (m, 4H), 3.37 – 3.29 (m, 3H), 3.30 – 3.23 (m, 1H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 100.4, 87.7, 82.2, 79.4, 74.7, 71.3, 70.6, 68.9, 67.9, 62.7, 62.4, 55.3, 53.4.

Supplemental references

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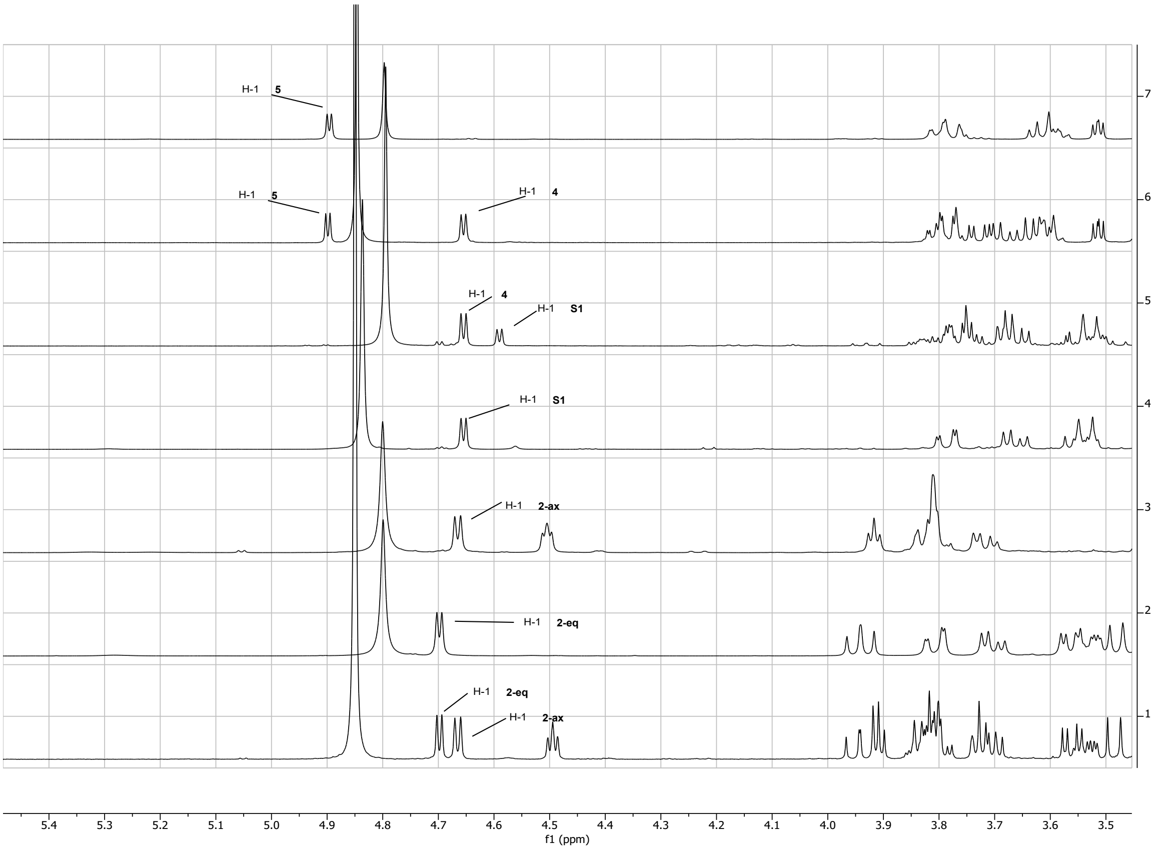
[7] P. Wen, P. Jia, Q. Fan, B. J. McCarty, W. Tang, *ChemSusChem* **2022**, *15*, No. e202102483.

NMR spectra

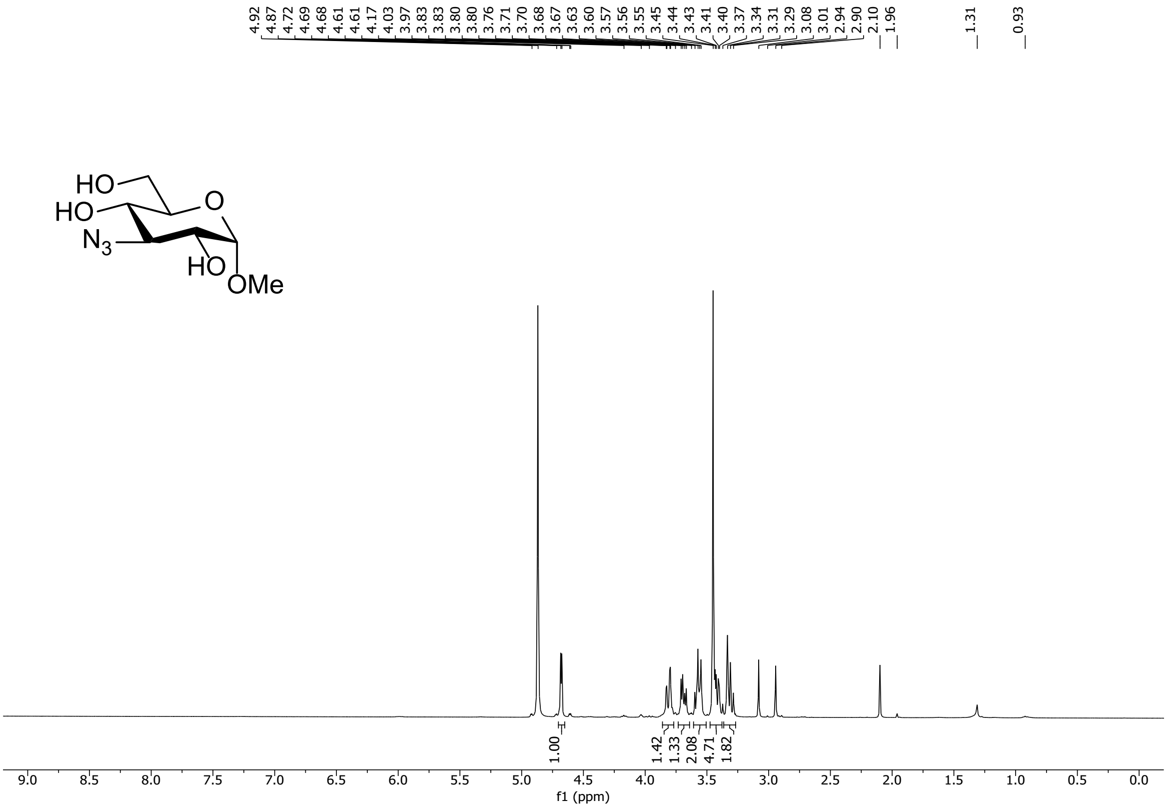
NMR spectra of substitution reactions on chloroglycosides

Comparison of ^{1}H-NMR between compounds **2-ax**, **2-eq**, **4**, **5**, **S1** in CD_3OD.

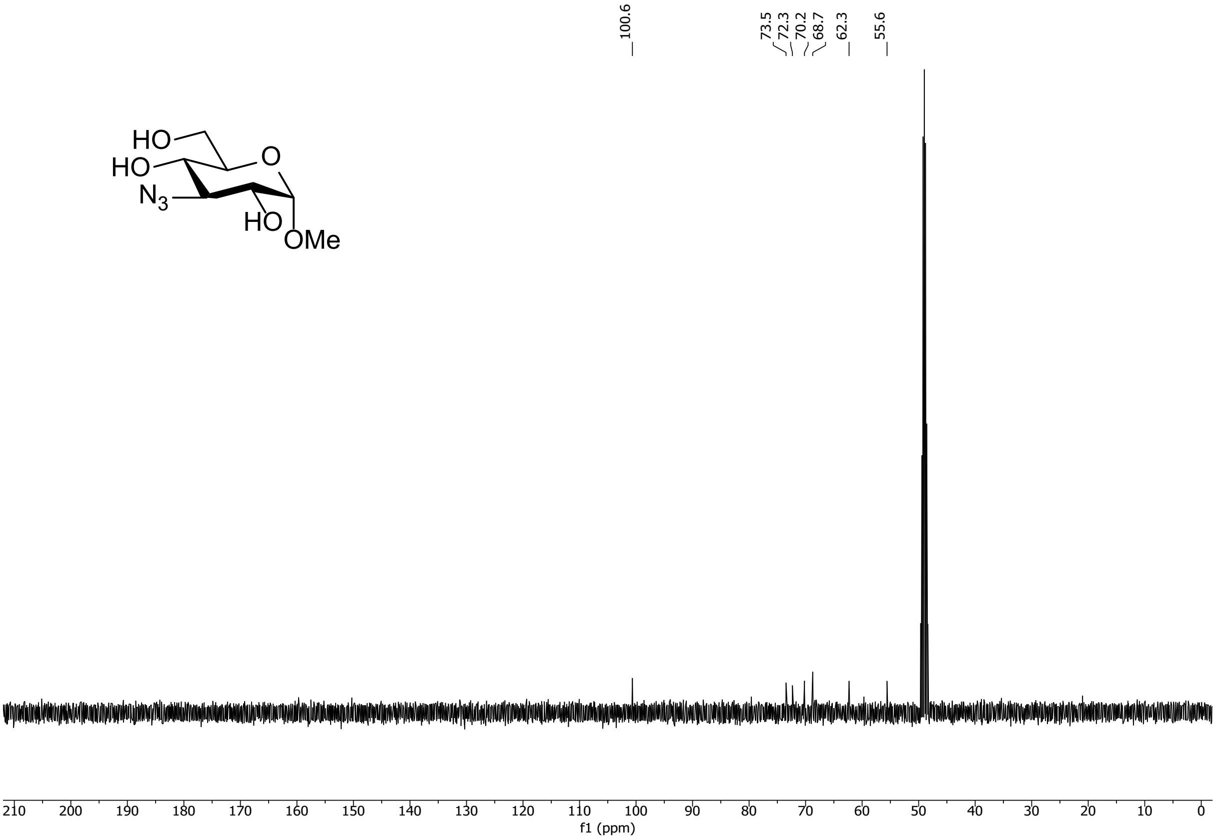


Methyl 3-azido-3-deoxy-α-D-glucopyranoside (4)

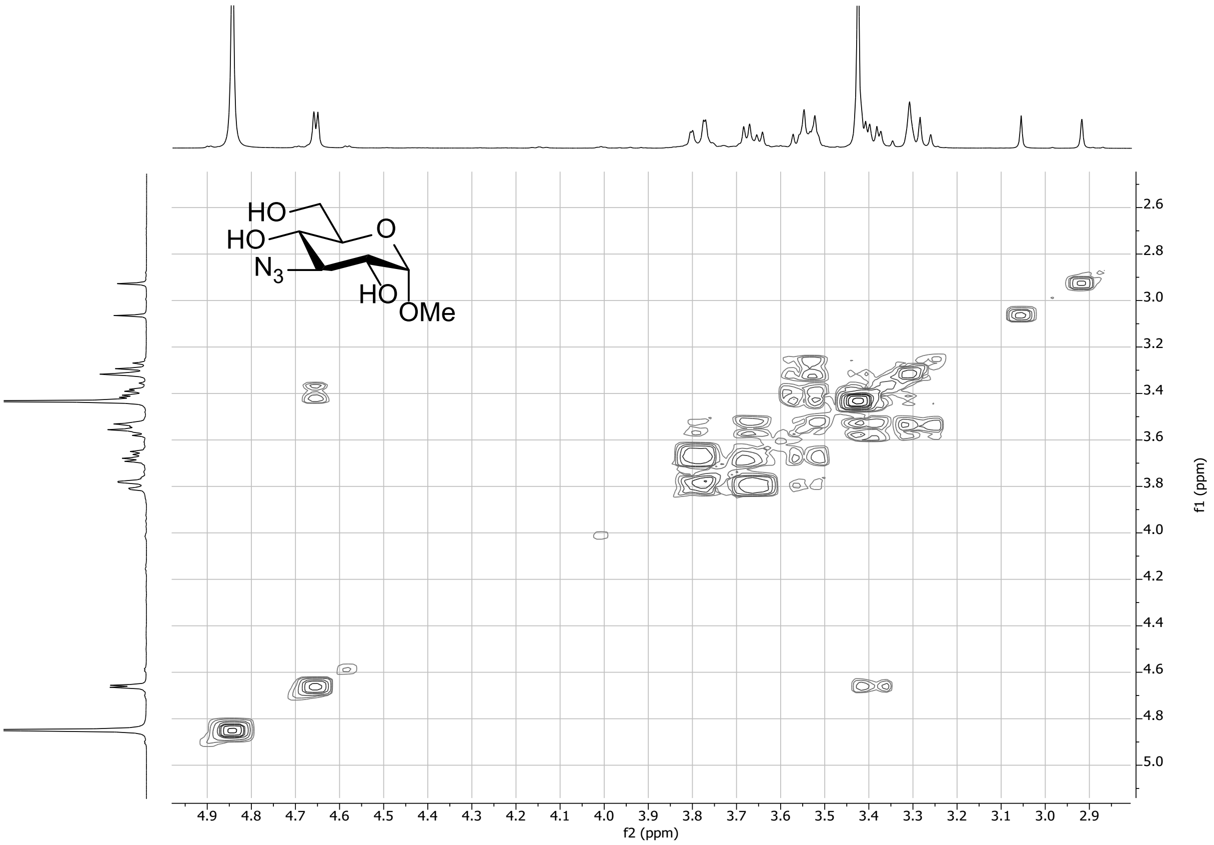
^{1}H NMR, 400 MHz, CD$_3$OD of compound **4**



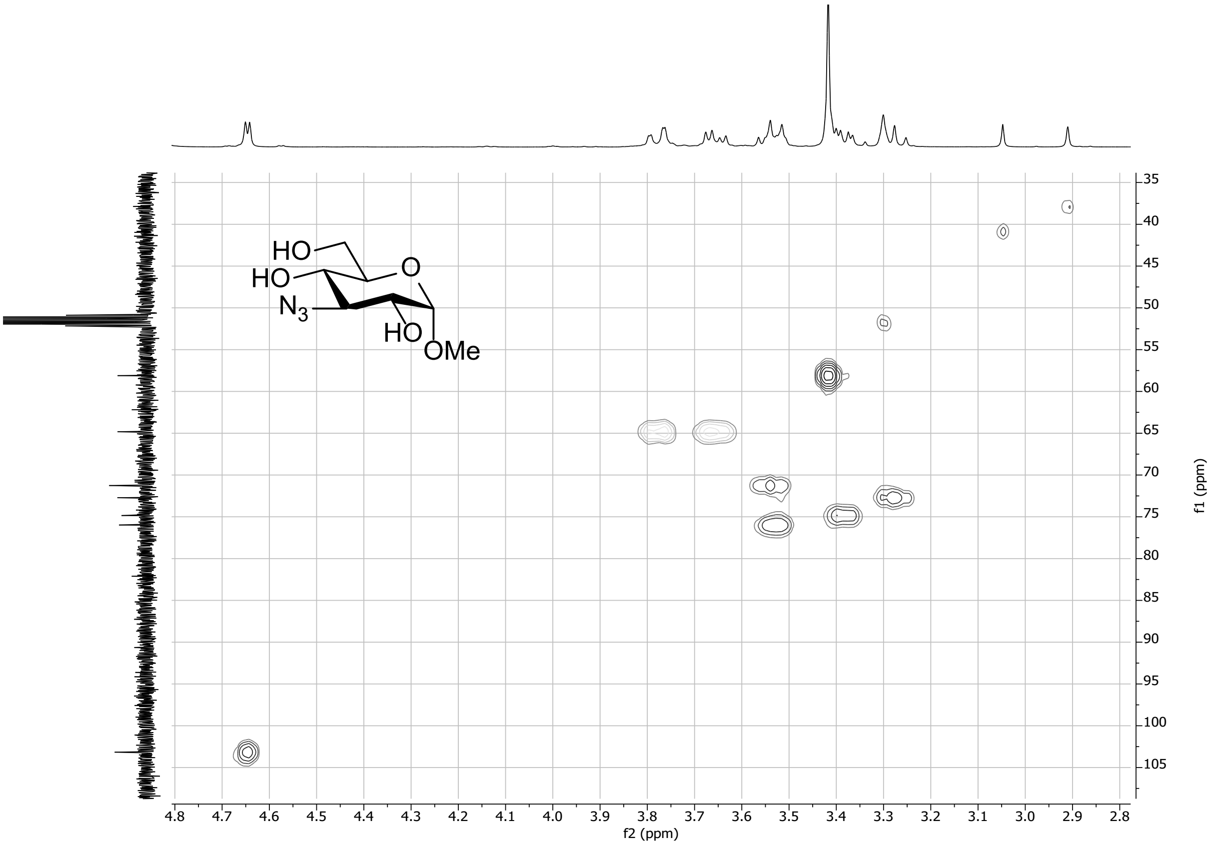
^{13}C NMR, 101 MHz, CD$_3$OD of compound **4**



^{1}H-^{1}H COSY of compound **4**

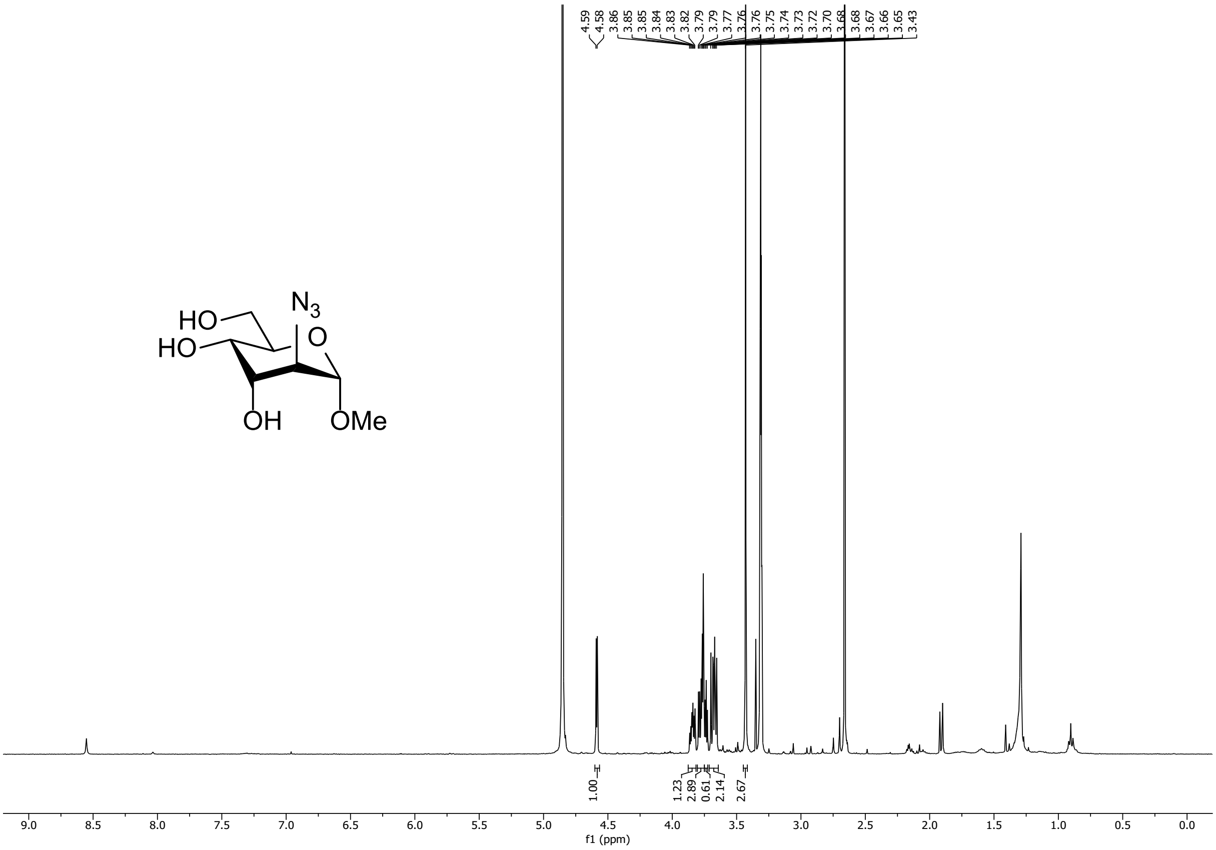


^{1}H-^{13}C HSQC of compound **4**

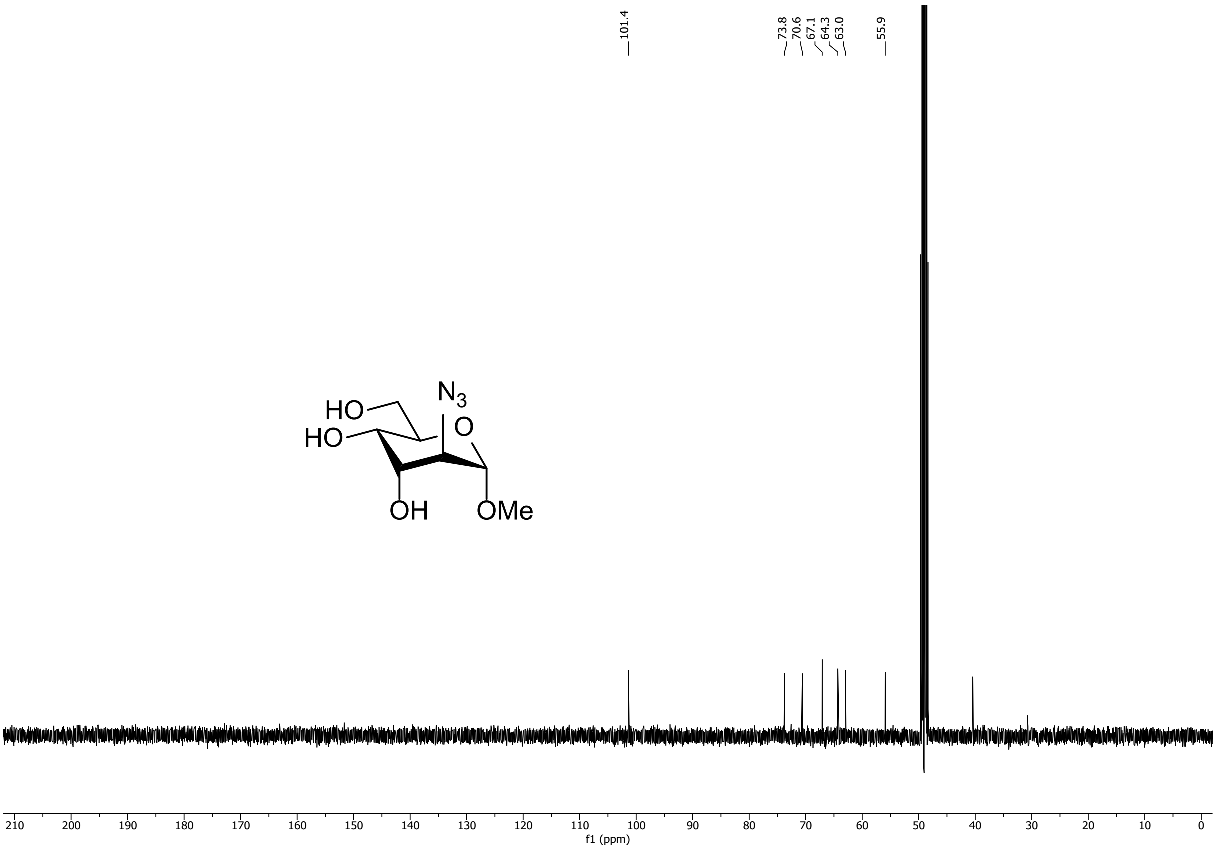


Methyl 2-azido-2-deoxy-α-D-altropyranoside (S1)

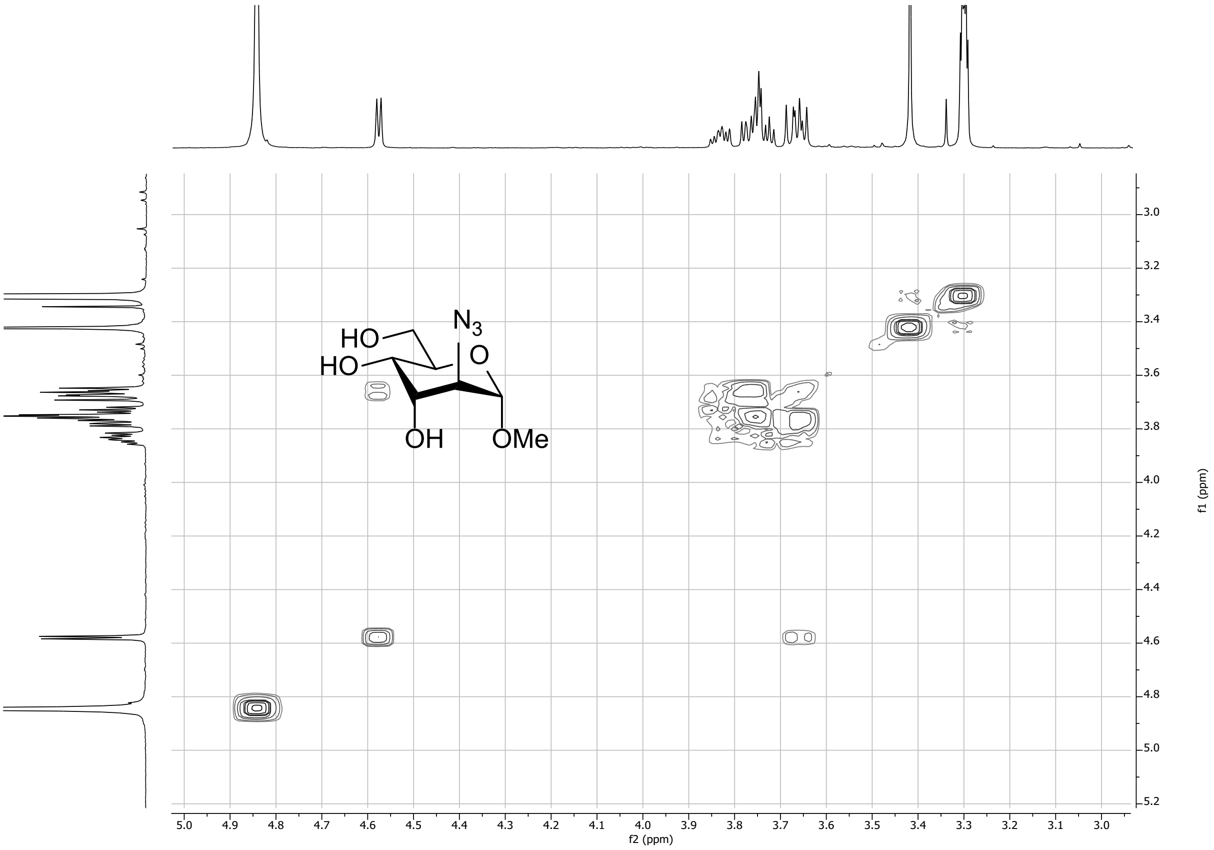
^{1}H NMR, 400 MHz, CD$_3$OD of compound **S1**



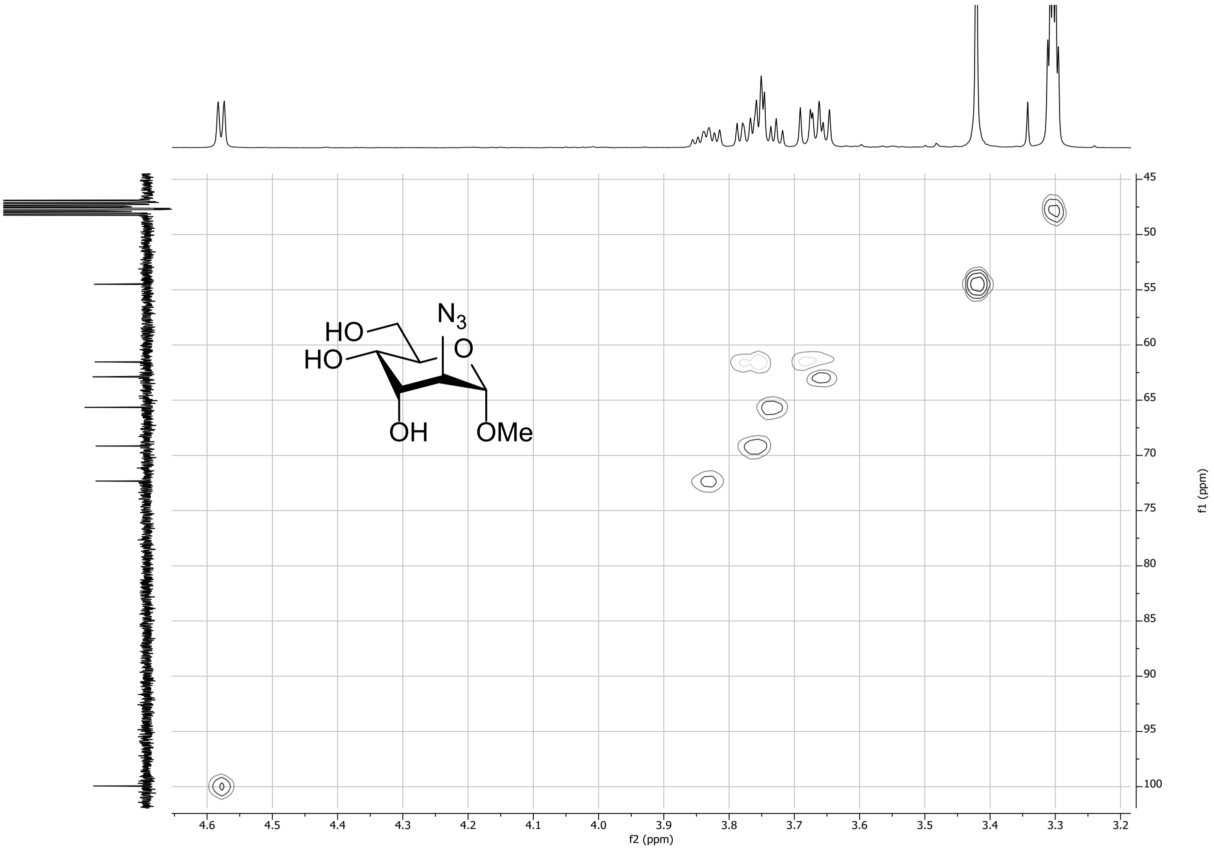
^{13}C NMR, 101 MHz, CD$_3$OD of compound **S1**



^1H-^1H COSY of compound **S1**

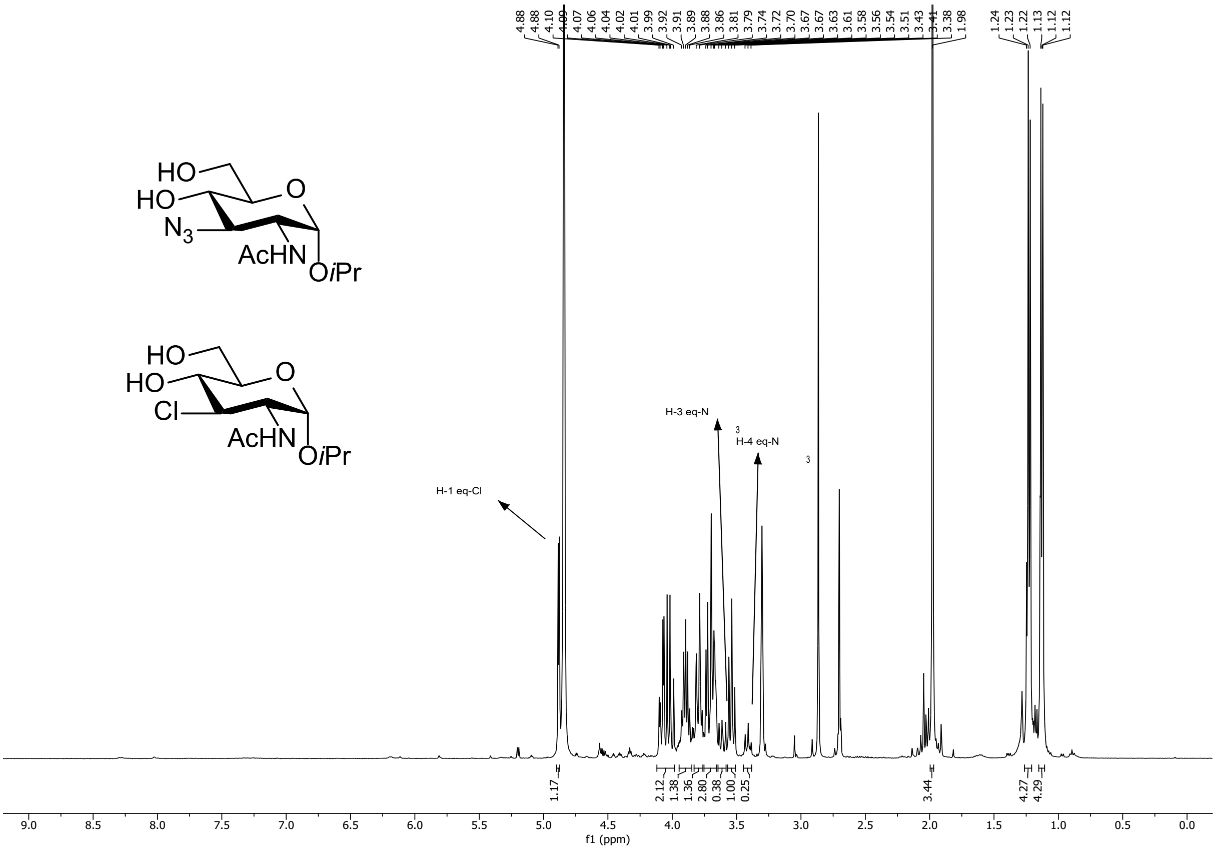


^1H-^{13}C HSQC of compound **S1**

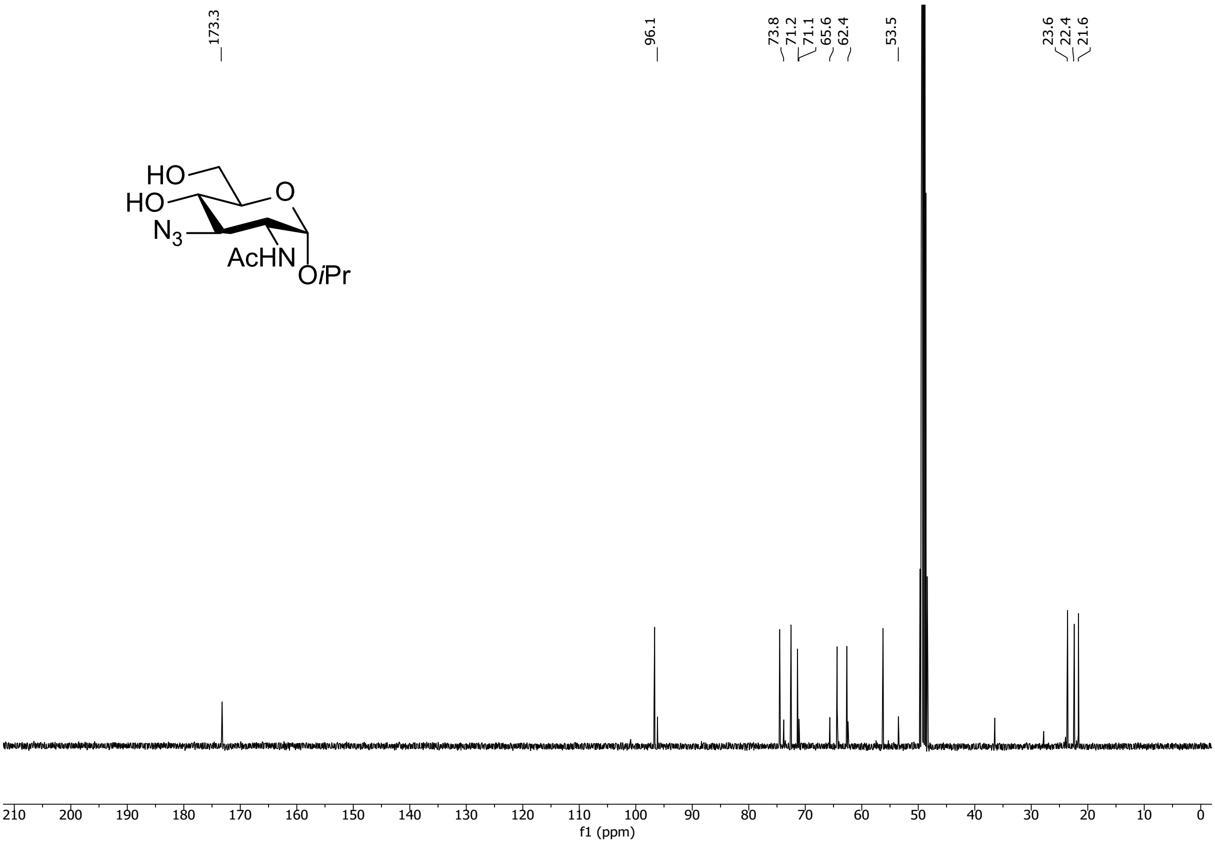


Isopropyl 2-acetmido-3-azido-2,3-dideoxy-α-D-glucopyranoside (S3)

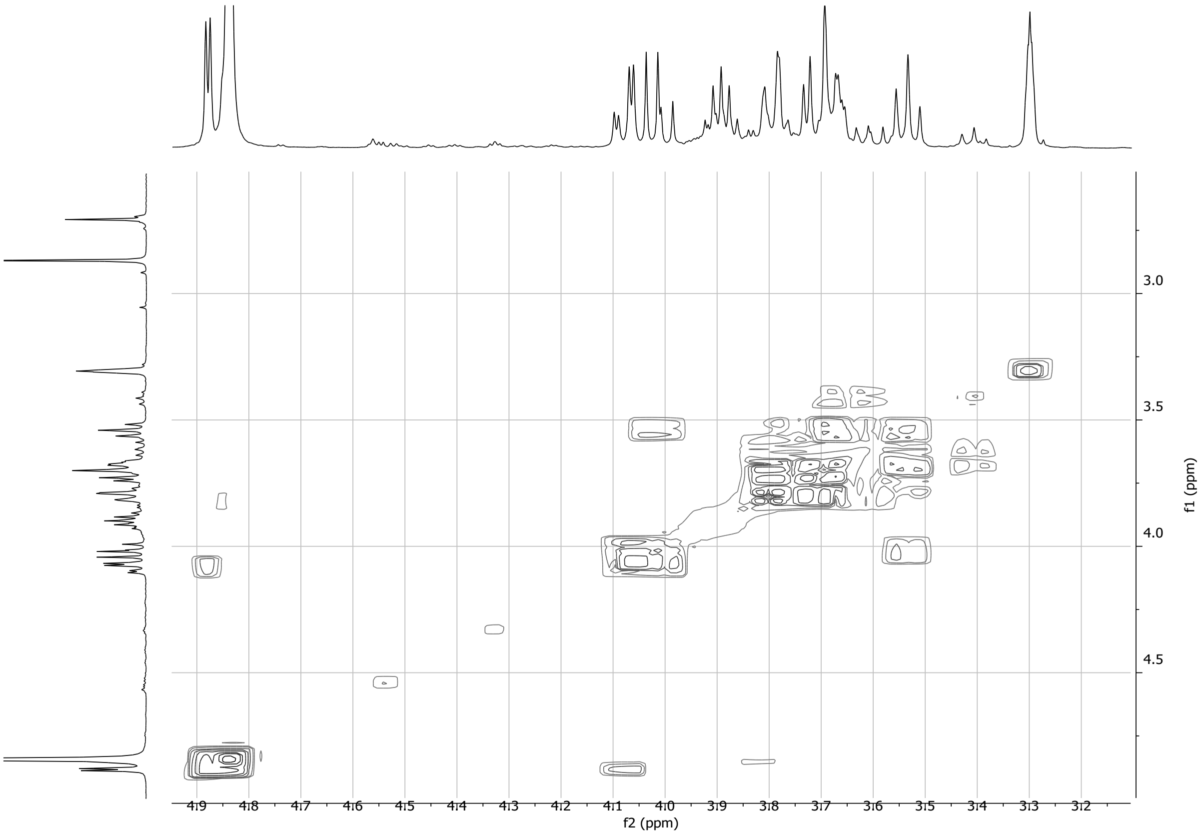
^{1}H NMR, 400 MHz, CD$_3$OD of compound **S3**



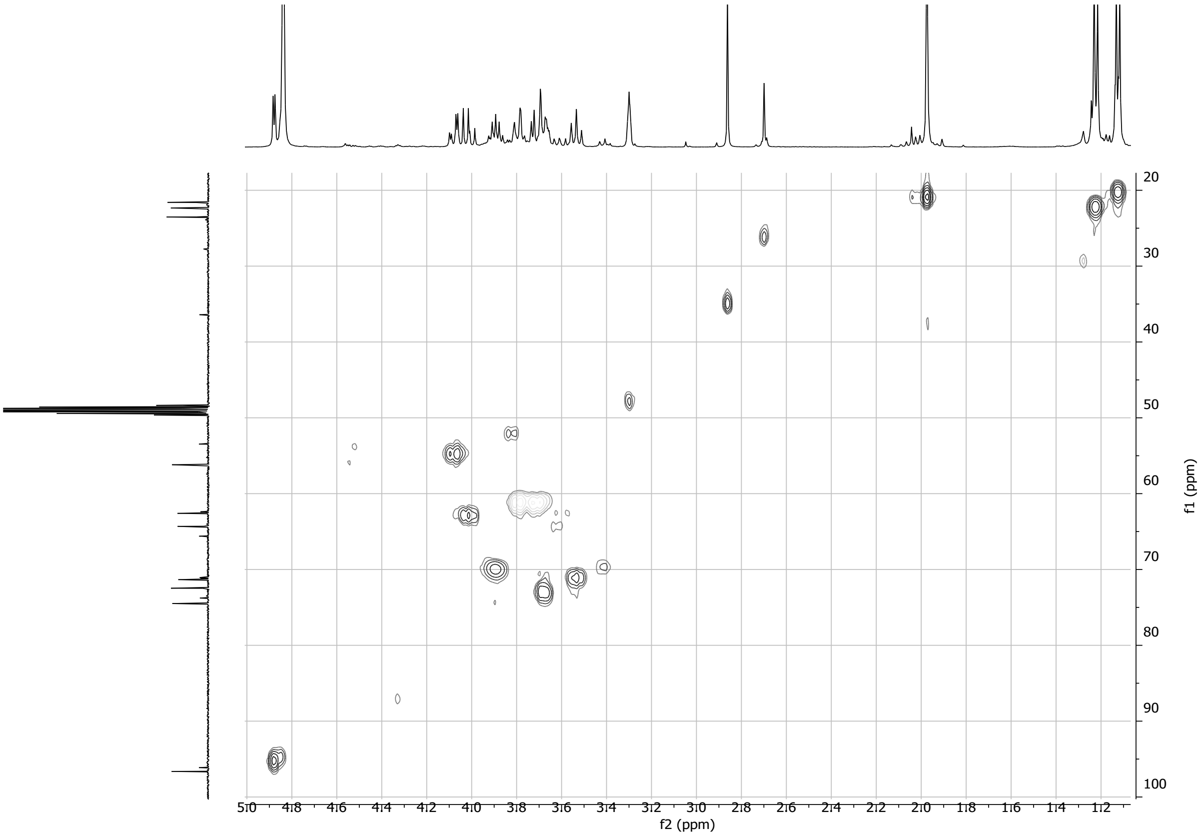
^{13}C NMR, 101 MHz, CD$_3$OD of compound **S3 (the minor peaks)**



^{1}H-^{1}H COSY of compound **S3**

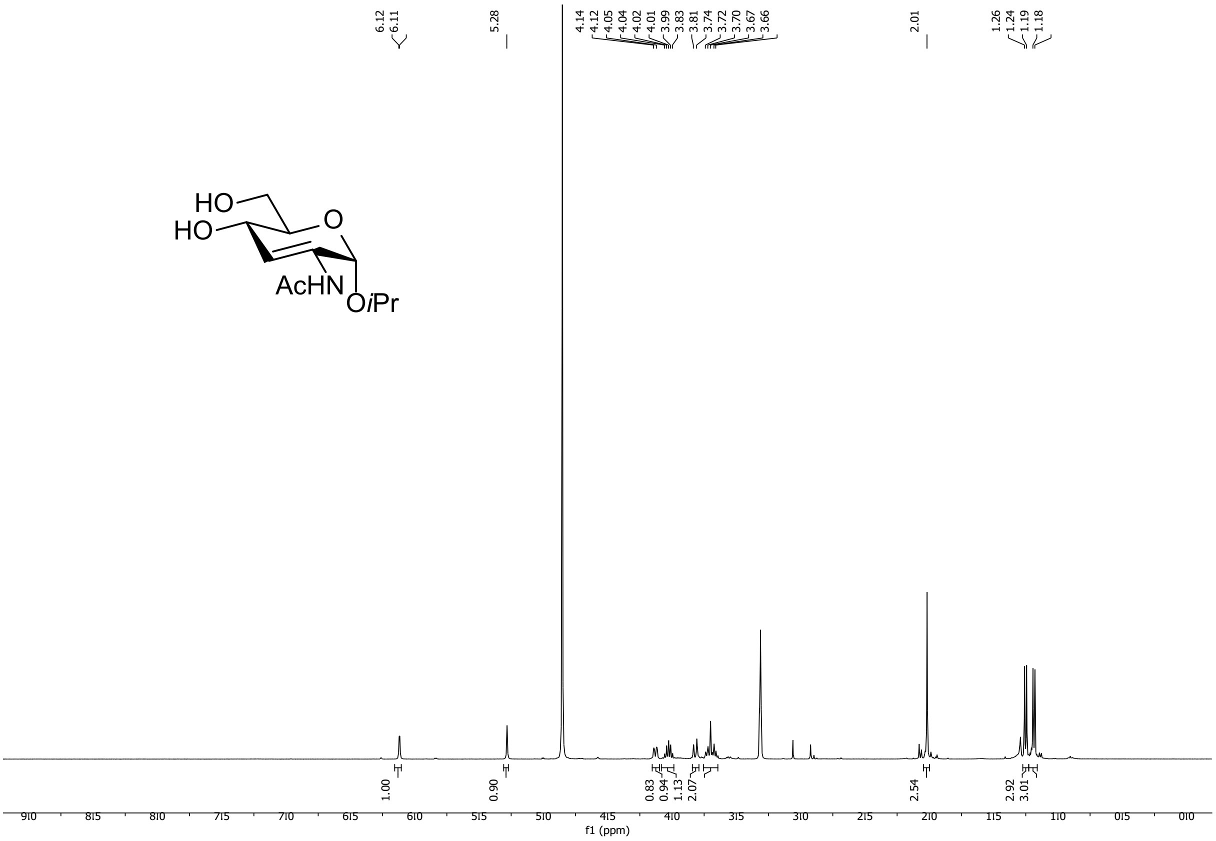


^{1}H-^{13}C HSQC of compound **S3**

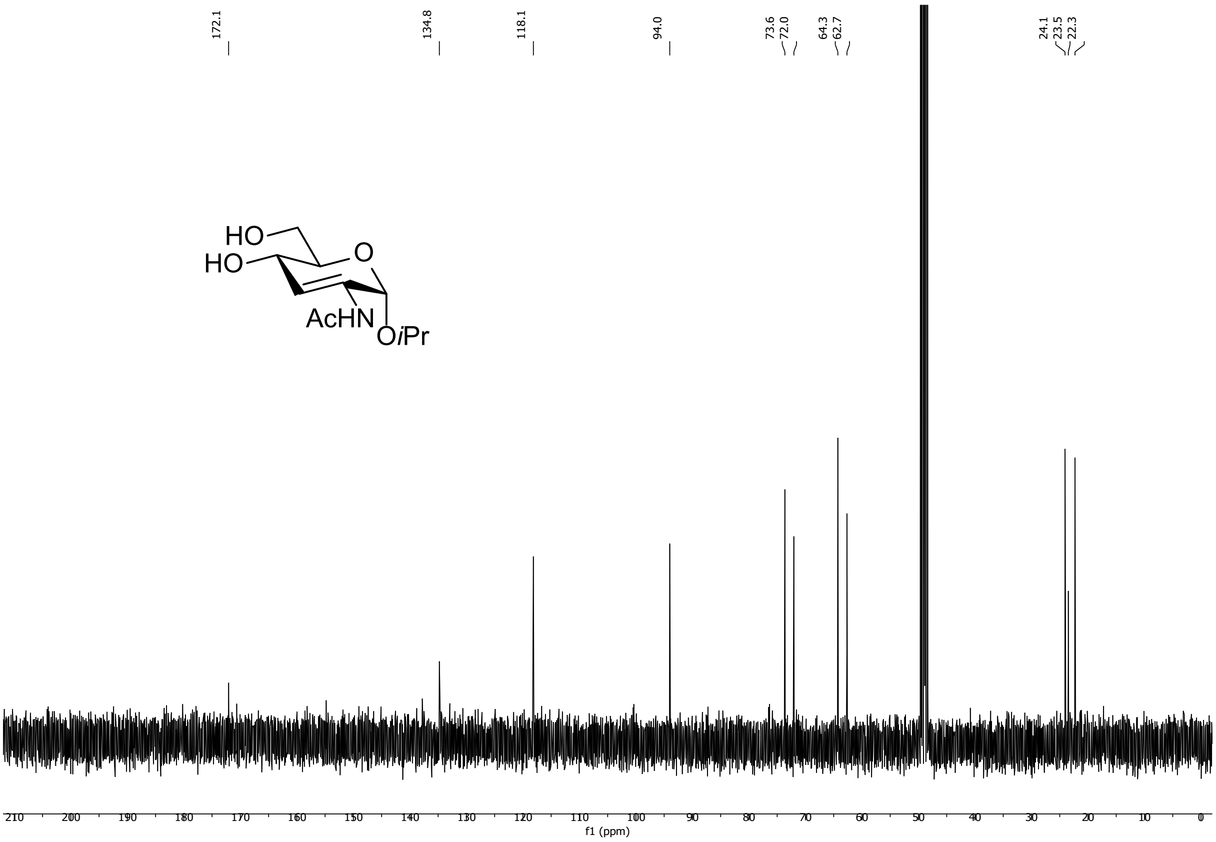


Sideproduct of the azide introduction in GlcNAc (S4)

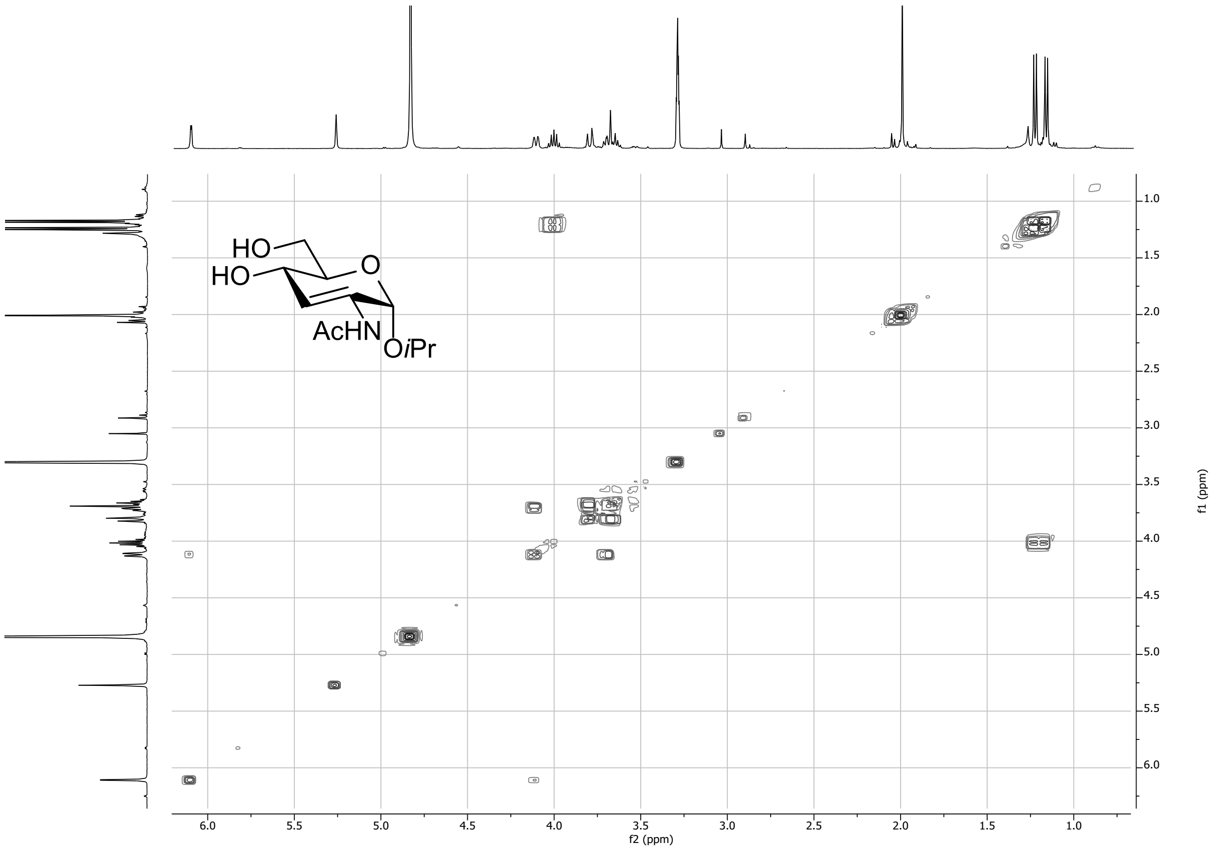
^1H NMR, 400 MHz, CD_3OD of compound **S4**



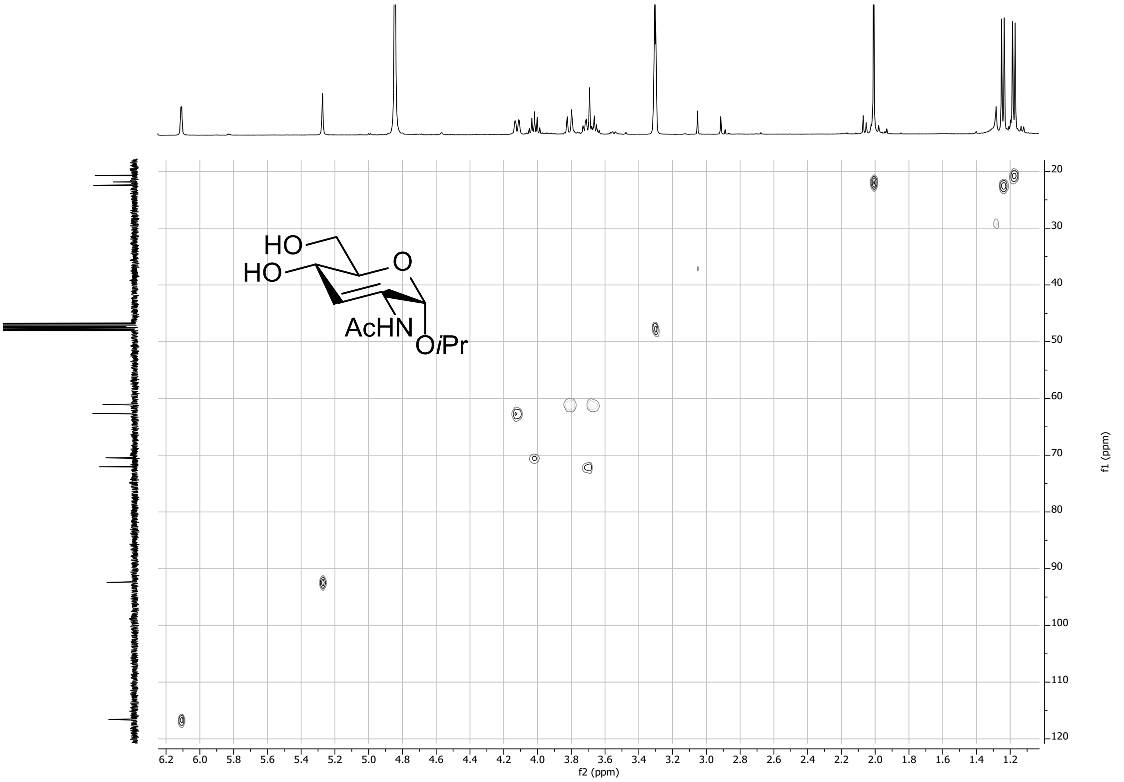
^{13}C NMR, 101 MHz, CD_3OD of compound **S4**



^{1}H-^{1}H COSY of compound **S4**

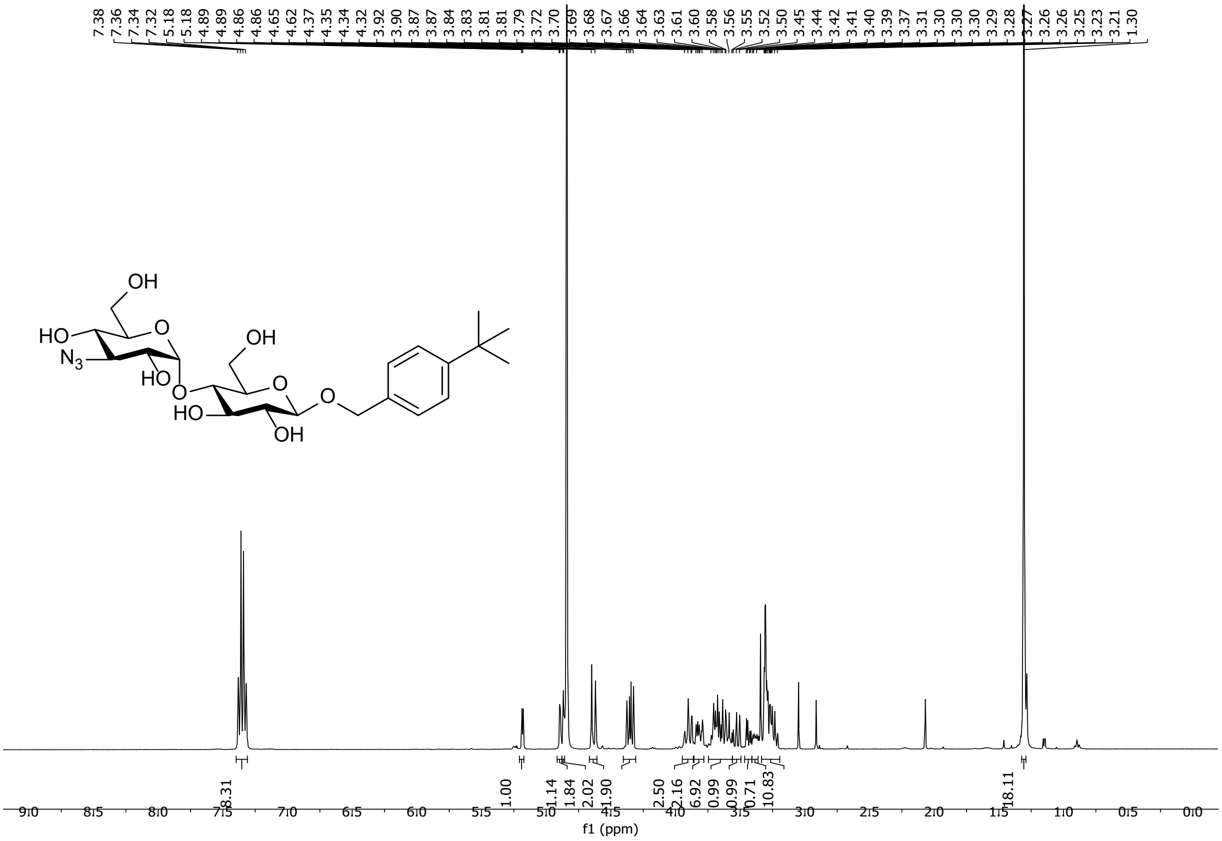


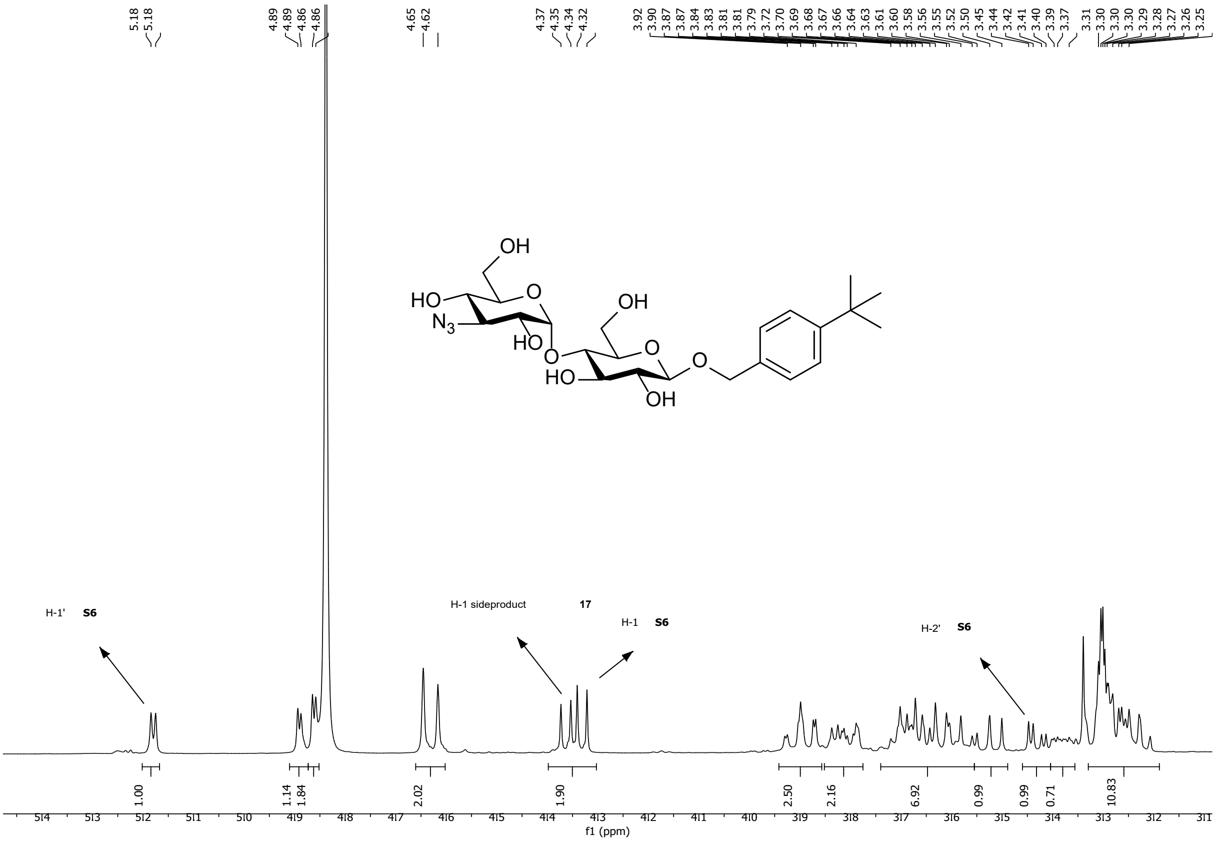
^{1}H-^{13}C HSQC of compound **S4**



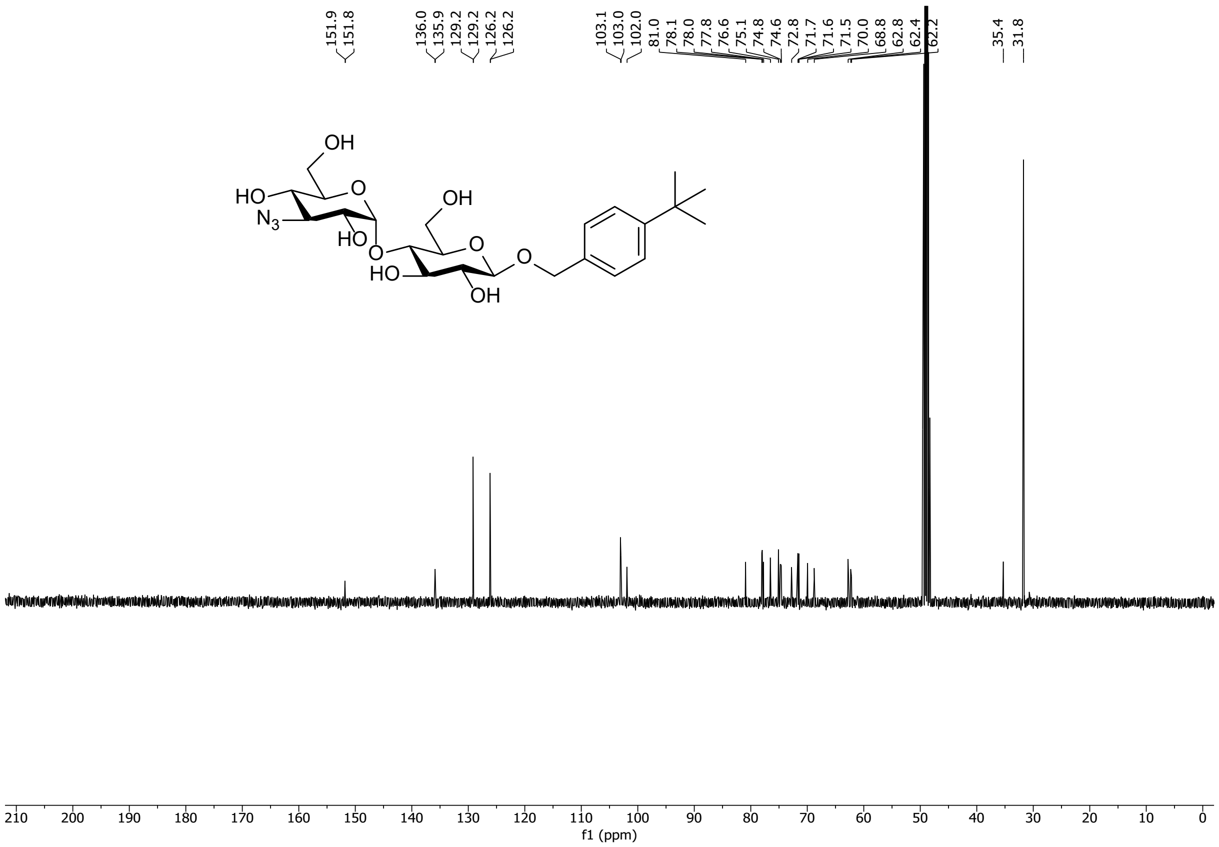
4-tert-butylbenzyl-3-azido-3-deoxy-α-D-maltoside (S6)

^{1}H NMR, 400 MHz, CD$_3$OD of compound **S6**

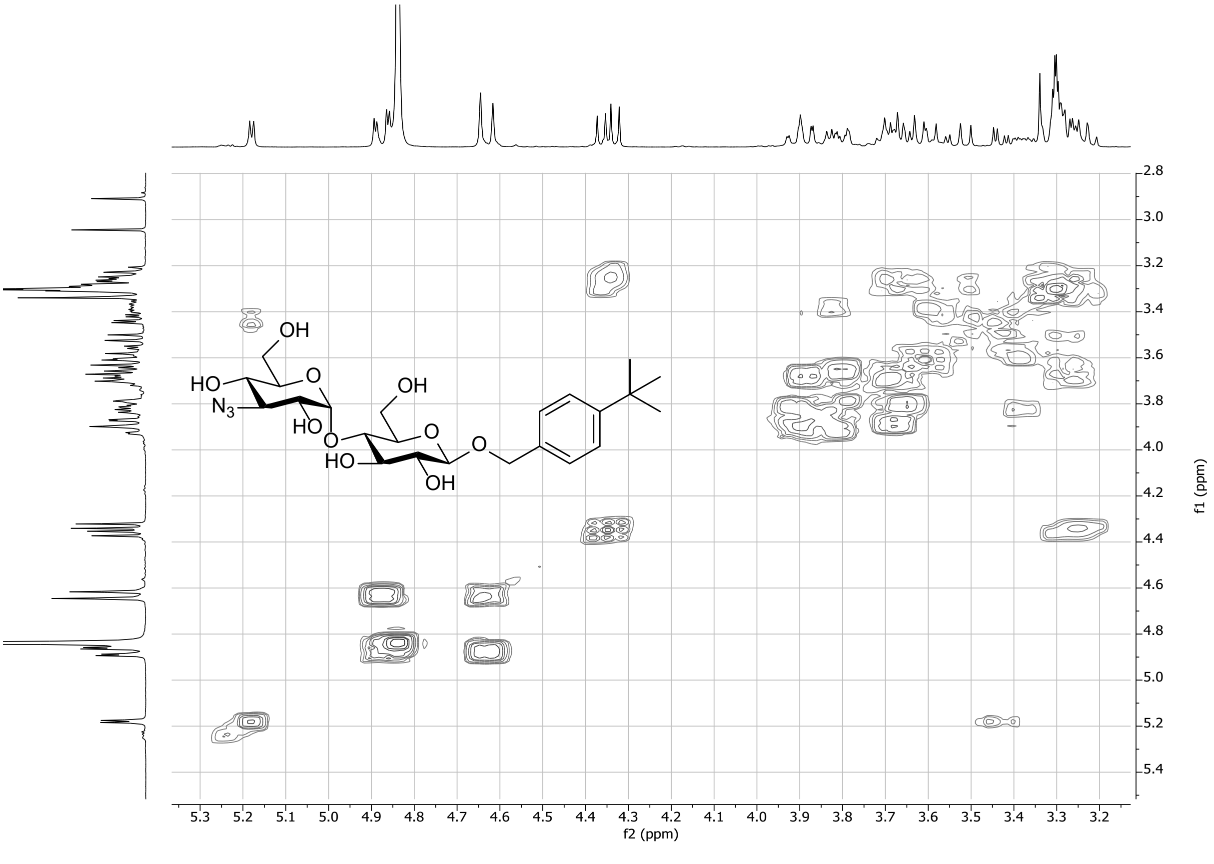




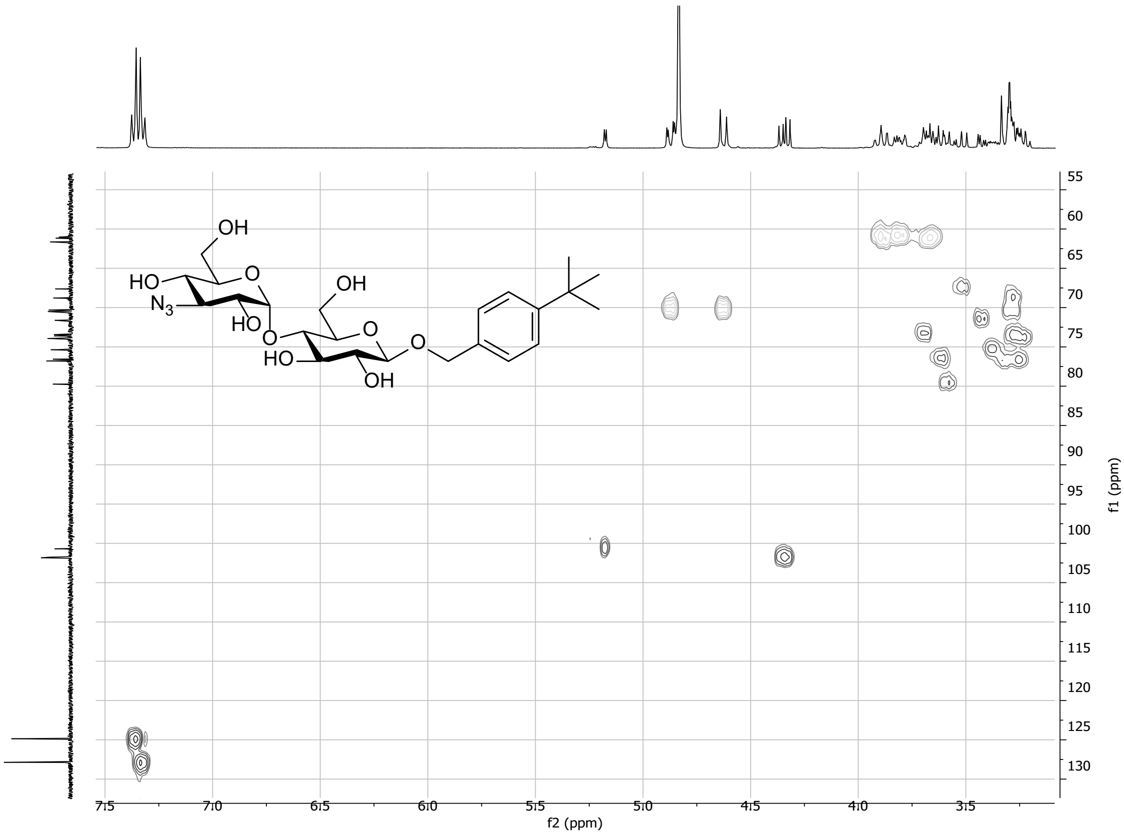
^{13}C NMR, 101 MHz, CD$_3$OD of compound **S6**



^{1}H-^{1}H COSY of compound **S6**

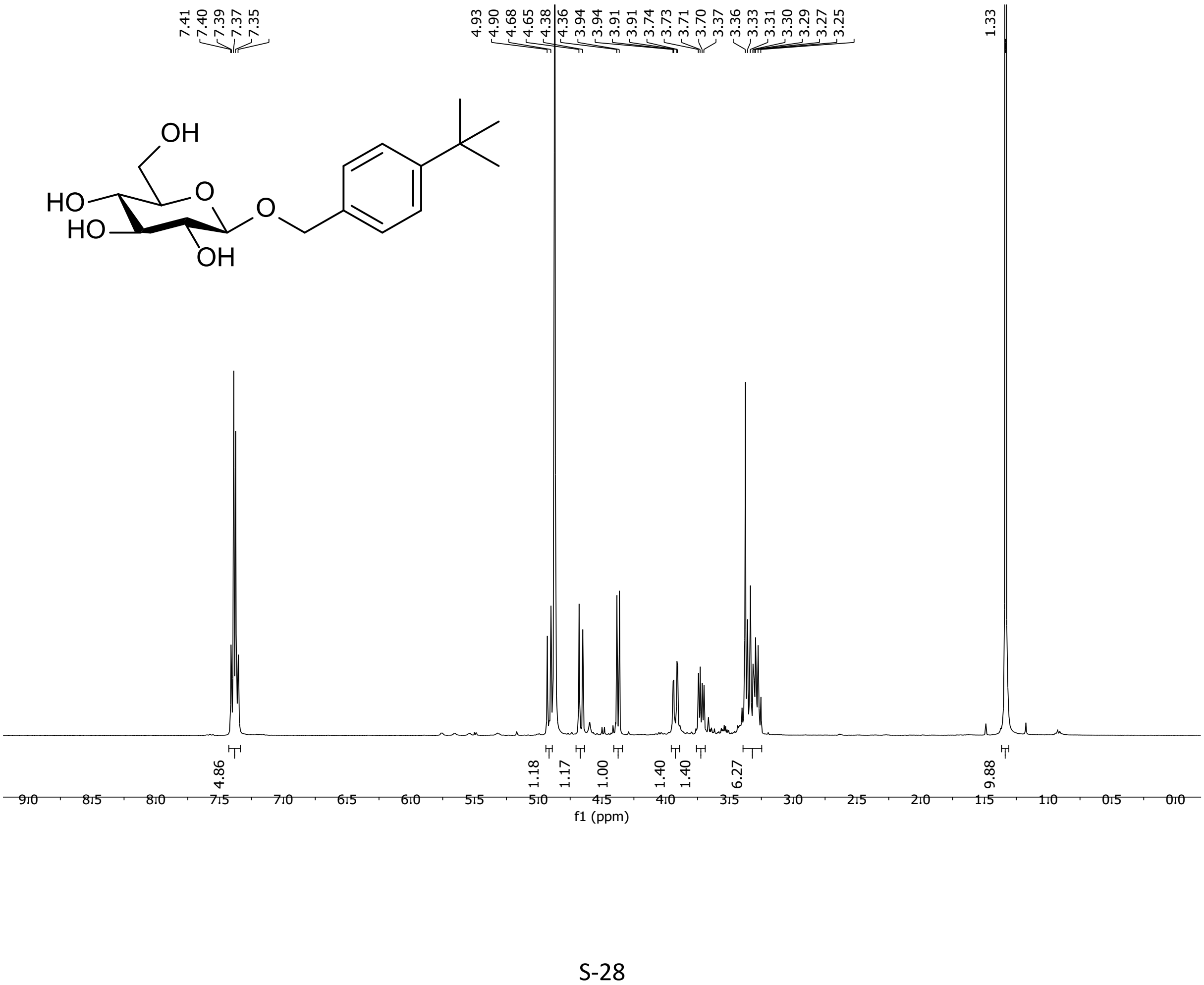


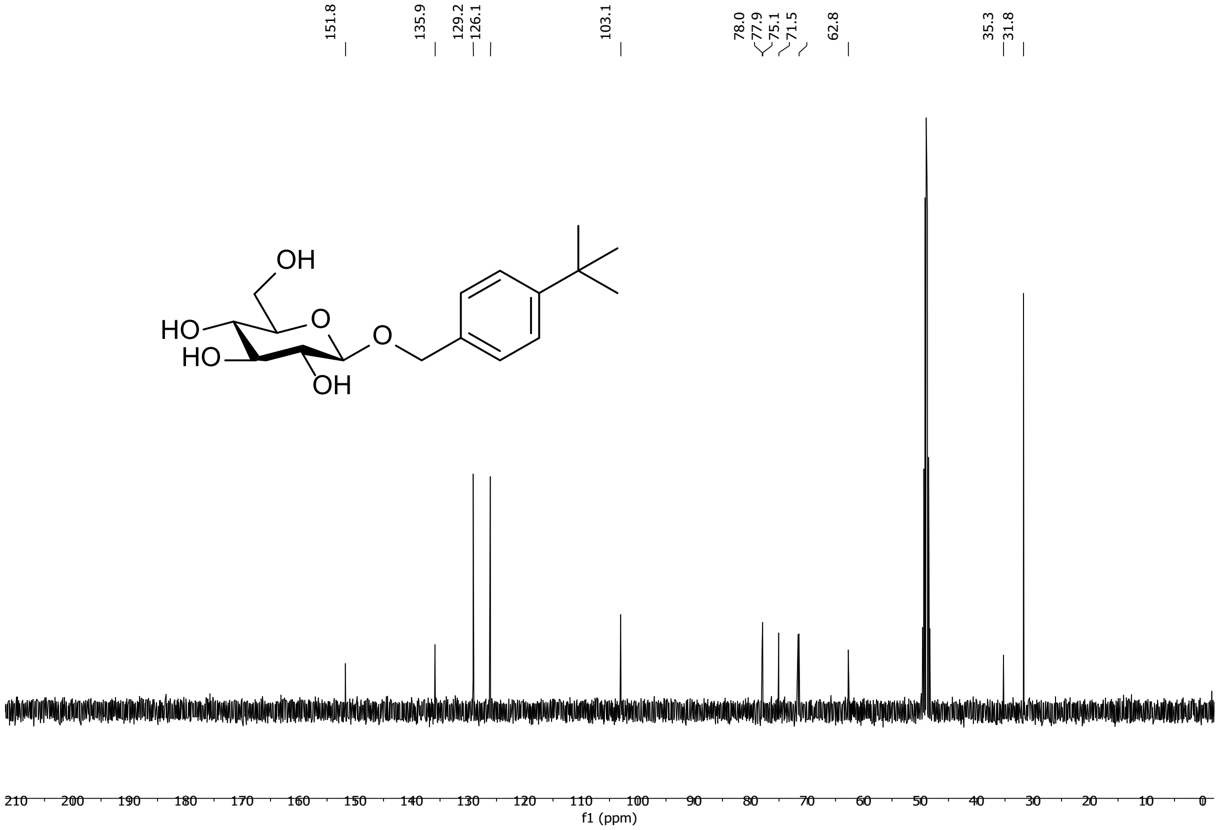
^{1}H-^{13}C HSQC of compound **S6**



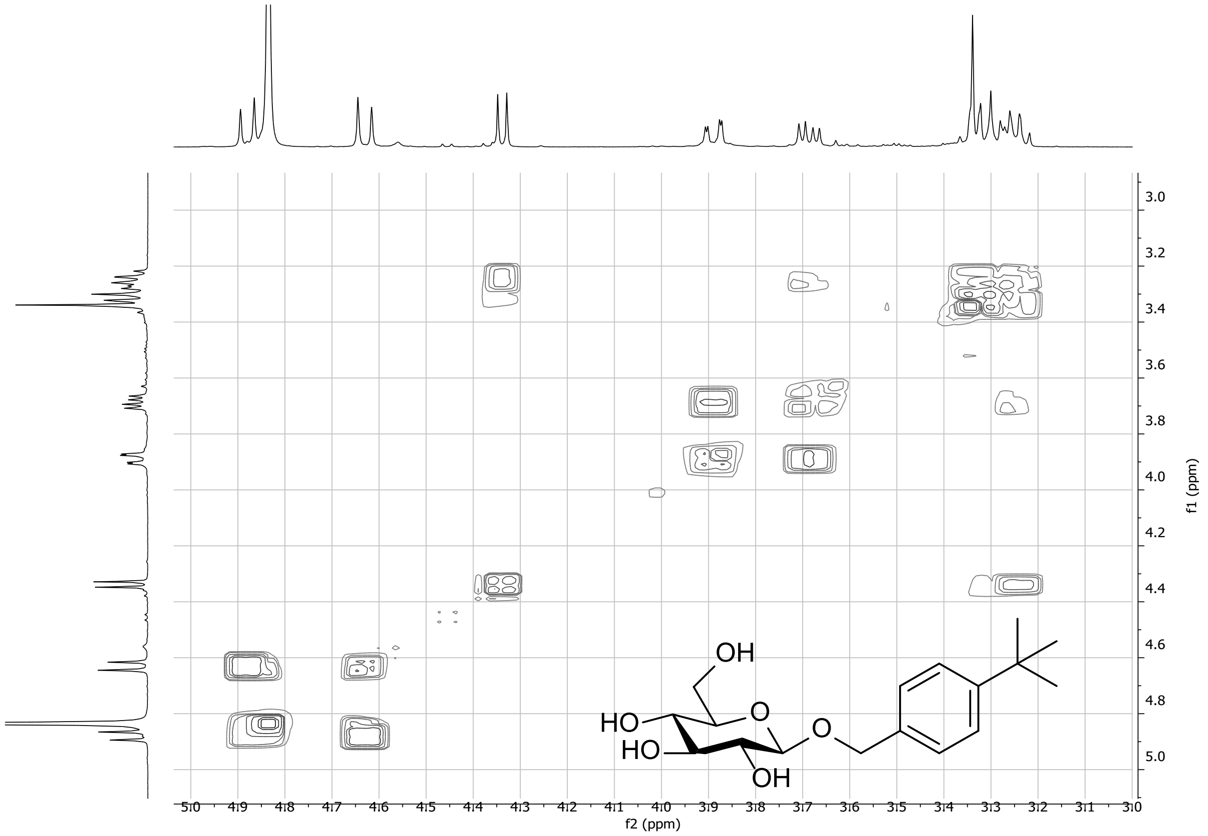
4-tert-butylbenzyl-β-D-glucopyranoside (17)

^{1}H NMR, 400 MHz, CD$_3$OD of compound **17**



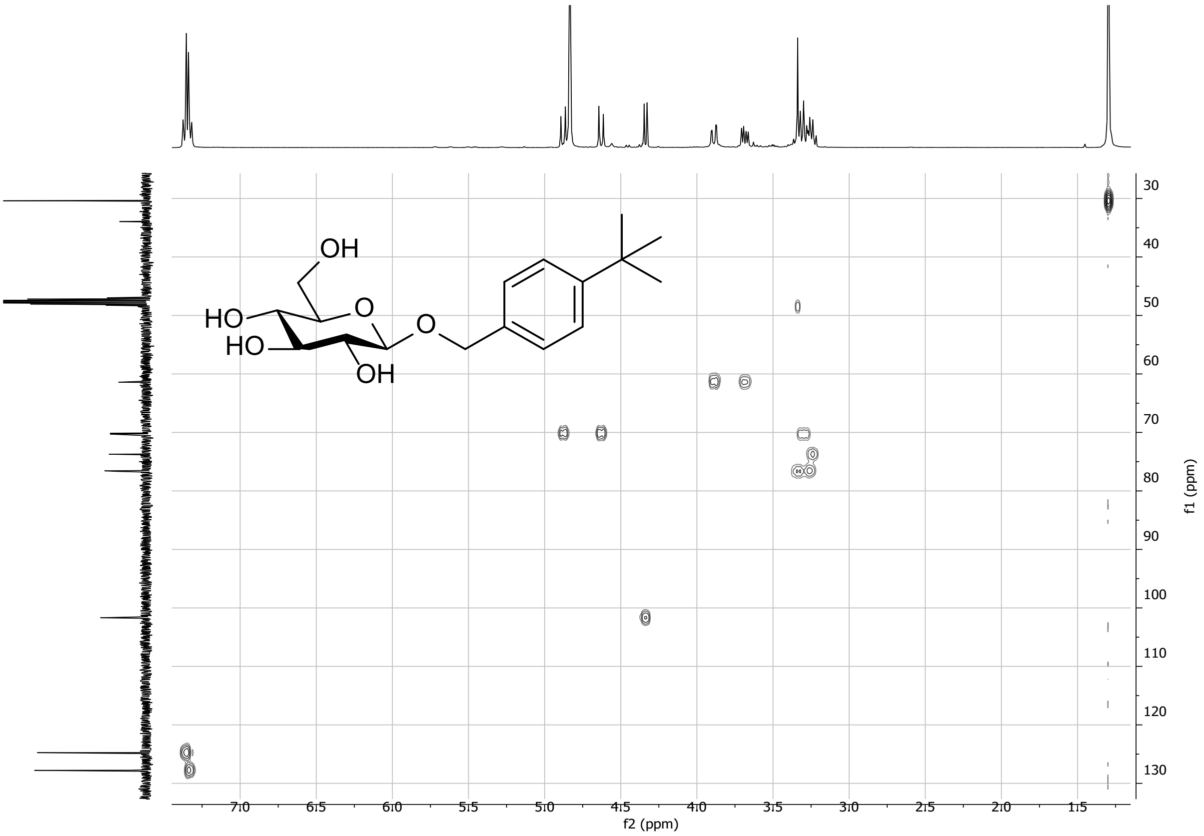


^{13}C NMR, 101 MHz, CD$_3$OD of compound **17**



^{1}H-^{1}H COSY of compound **17**

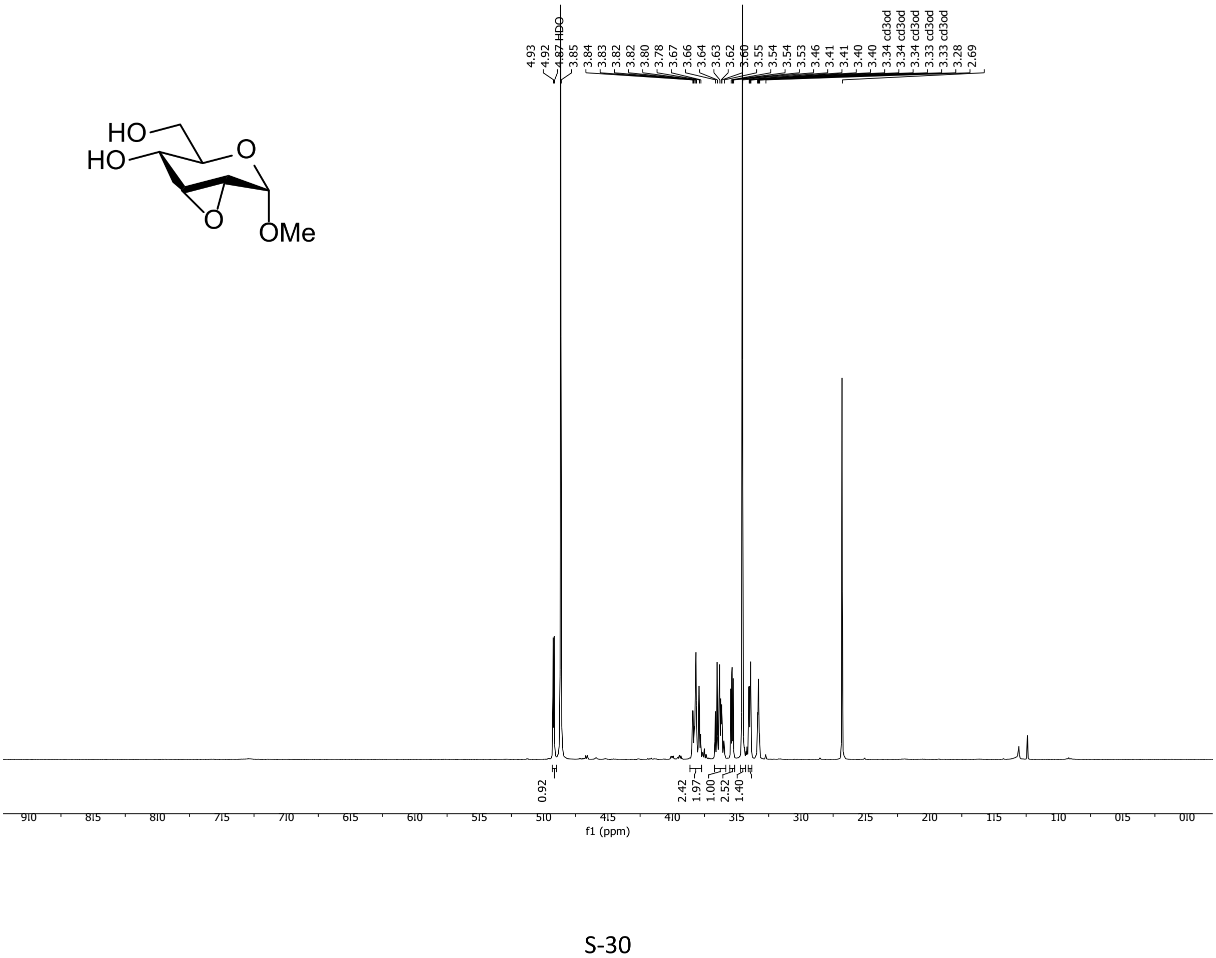
^{1}H-^{13}C HSQC of compound **17**



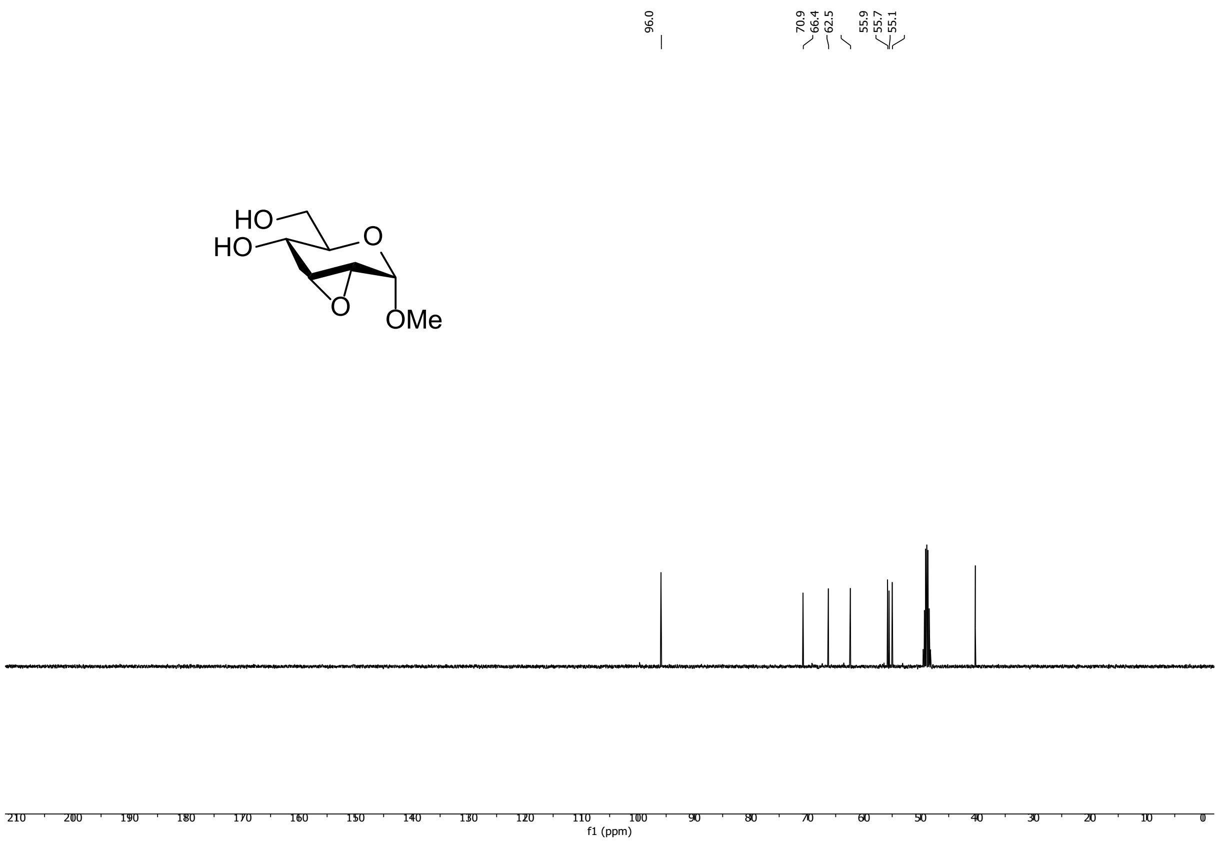
NMR spectra of epoxides 5 and 6

Methyl 2,3-anhydro-α-d-glucopyranoside (5)

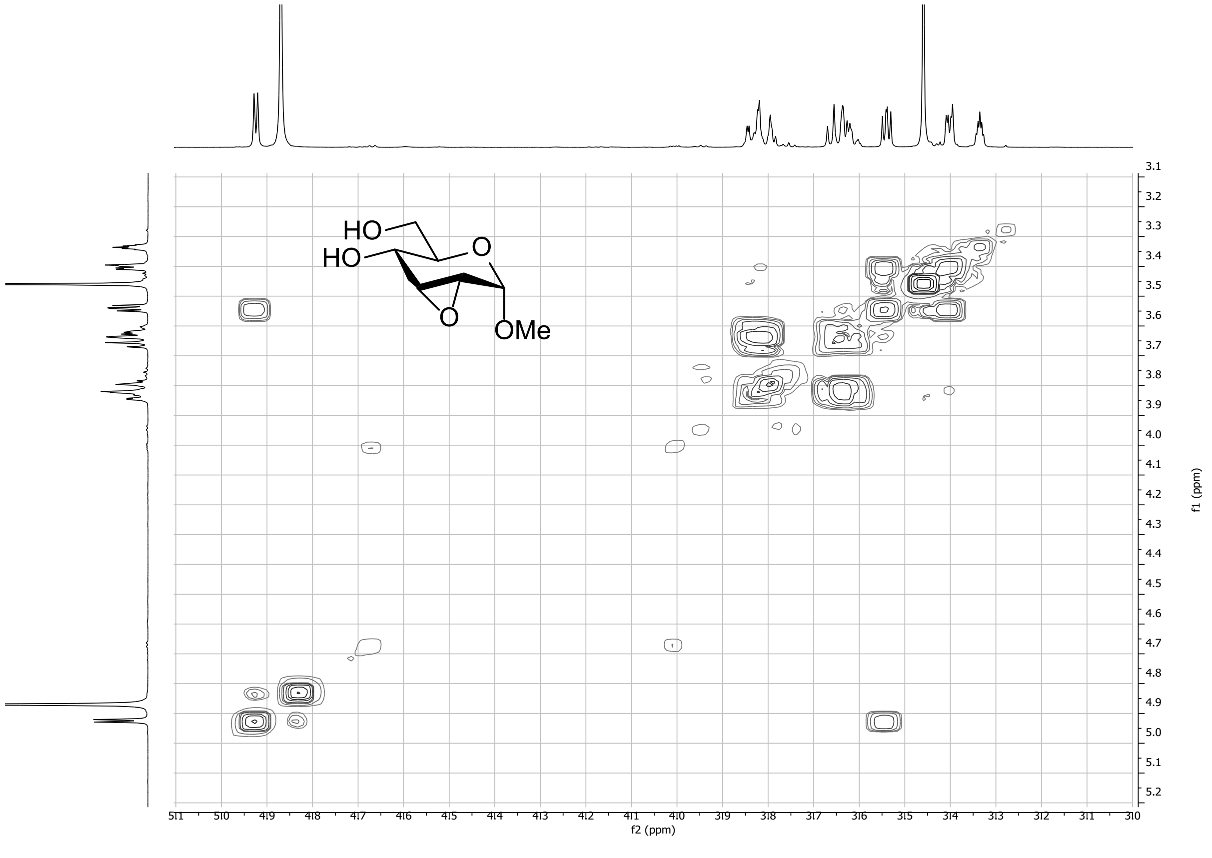
^{1}H NMR, 400 MHz, CD₃OD of compound **5**



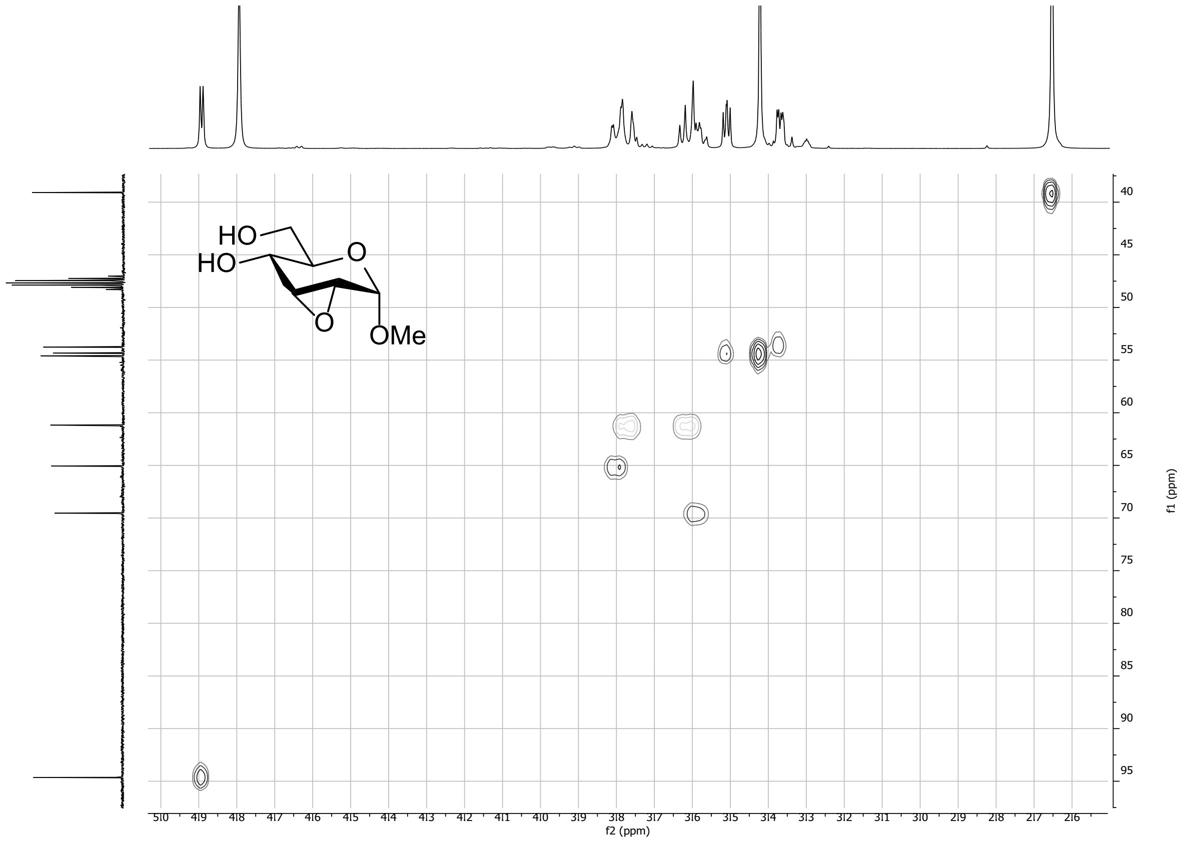
^{13}C NMR, 101 MHz, CD$_3$OD of compound **5**



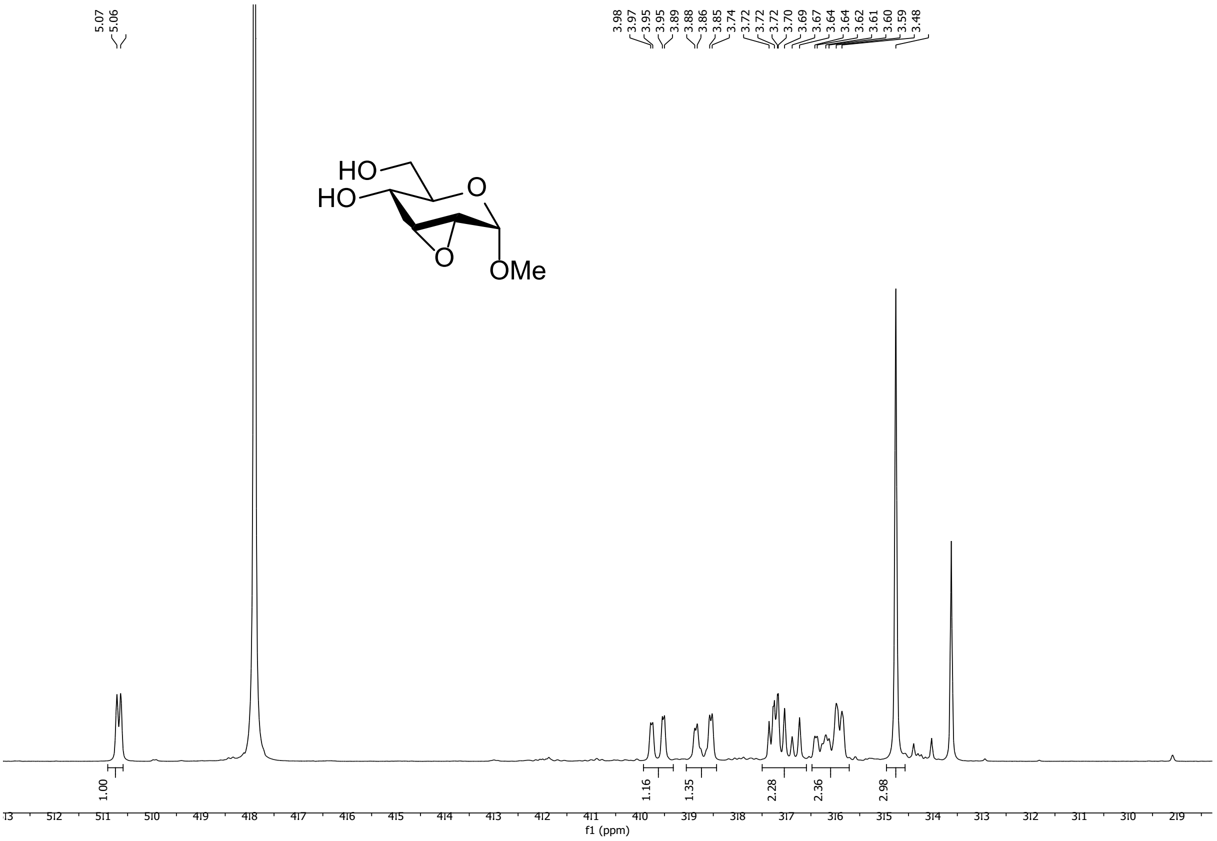
^{1}H-^{1}H COSY of compound **5** in CD$_3$OD



^{1}H-^{13}C HSQC of compound **5** in CD_3OD

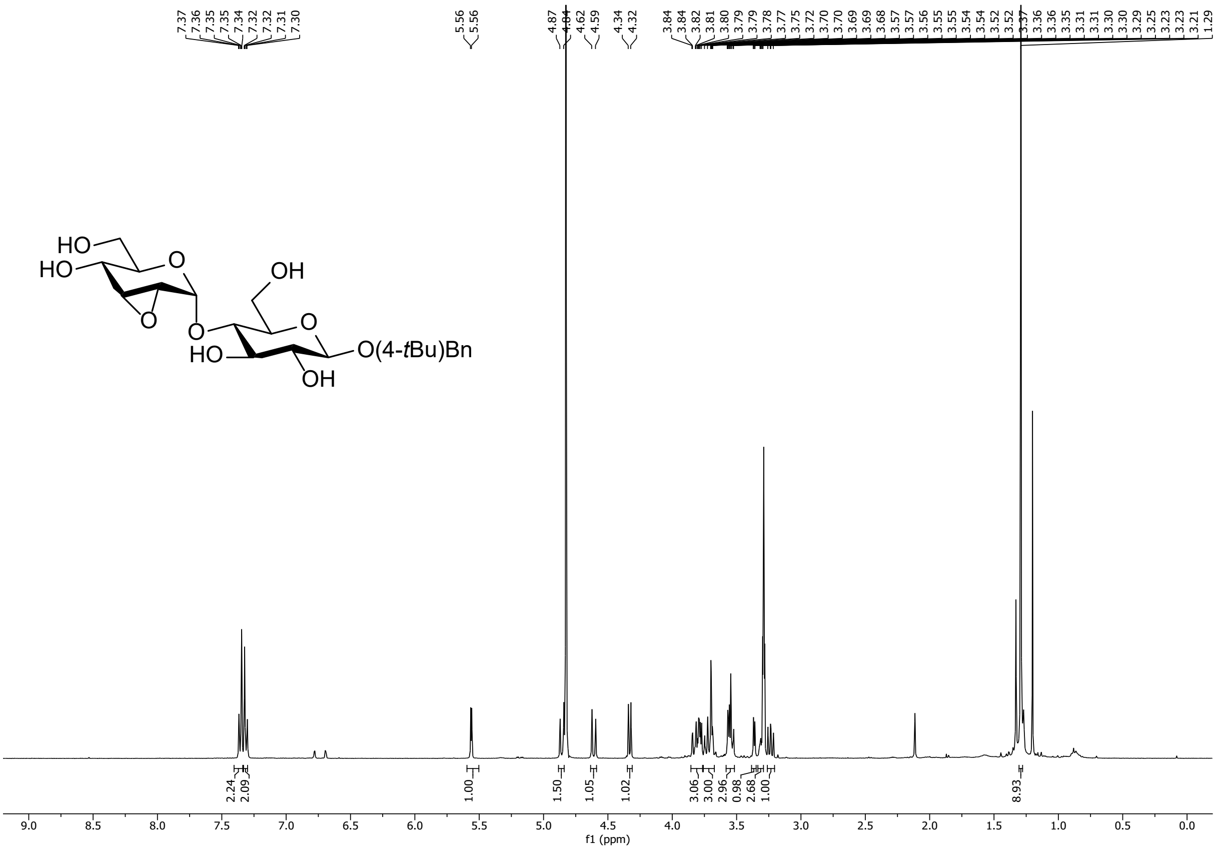


^{1}H NMR, 400 MHz, D_2O of compound **5**

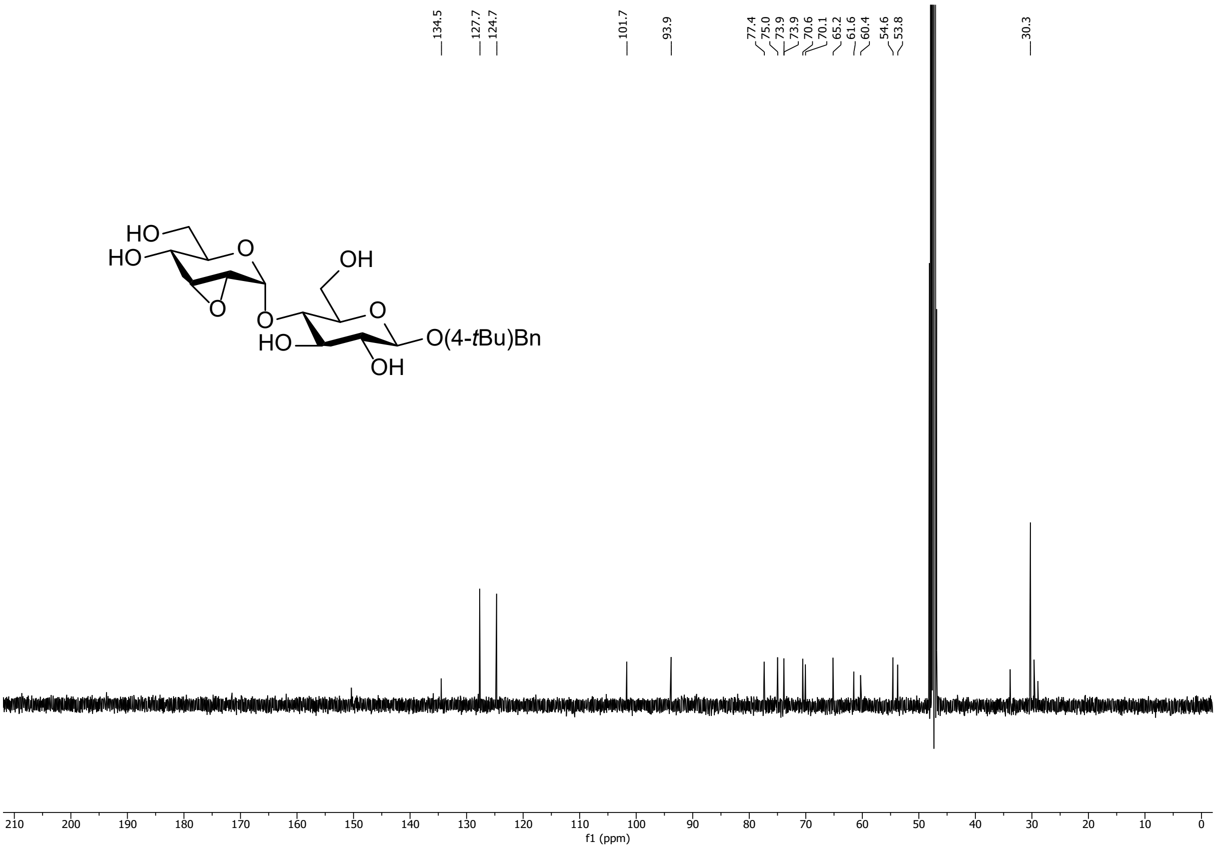


4-tert-butylbenzyl-2,3-anhydro-α-D-maltoside (6)

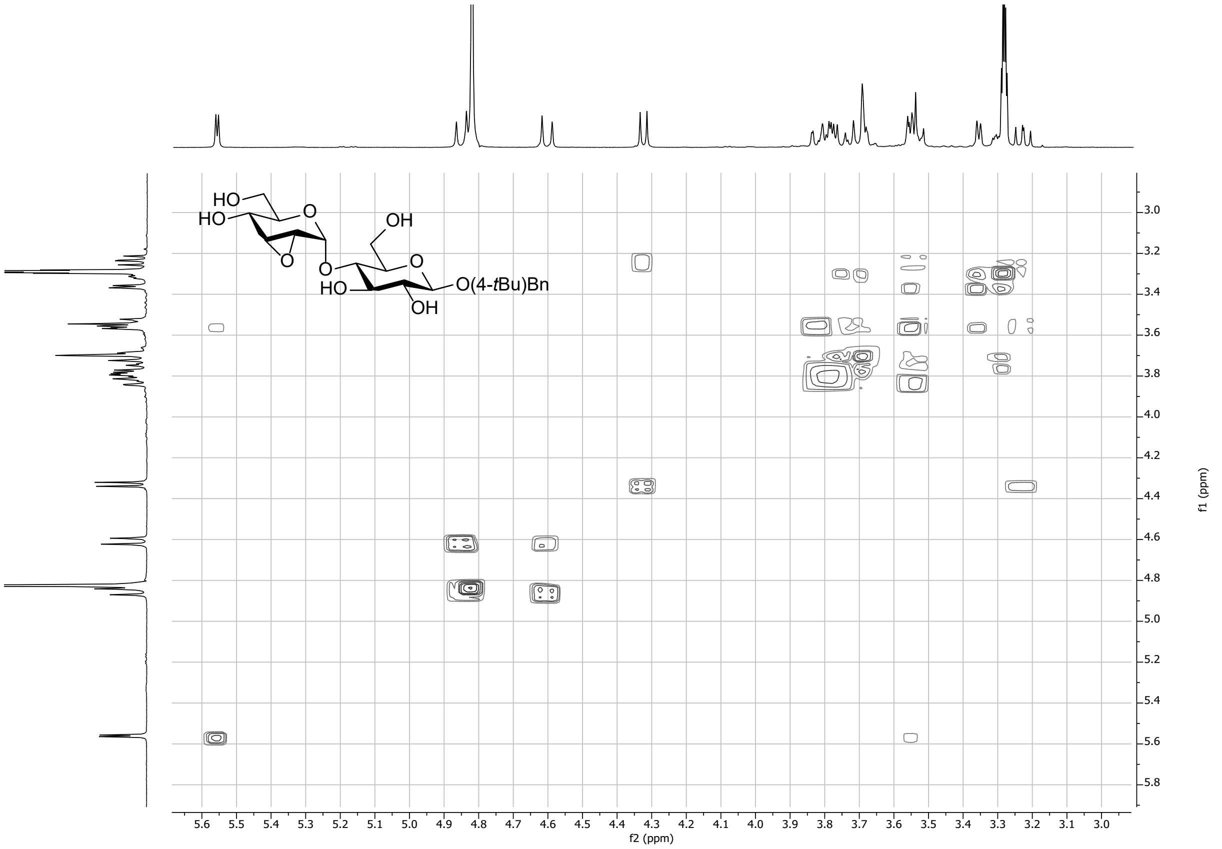
^{1}H NMR, 400 MHz, CD$_3$OD of compound **6**



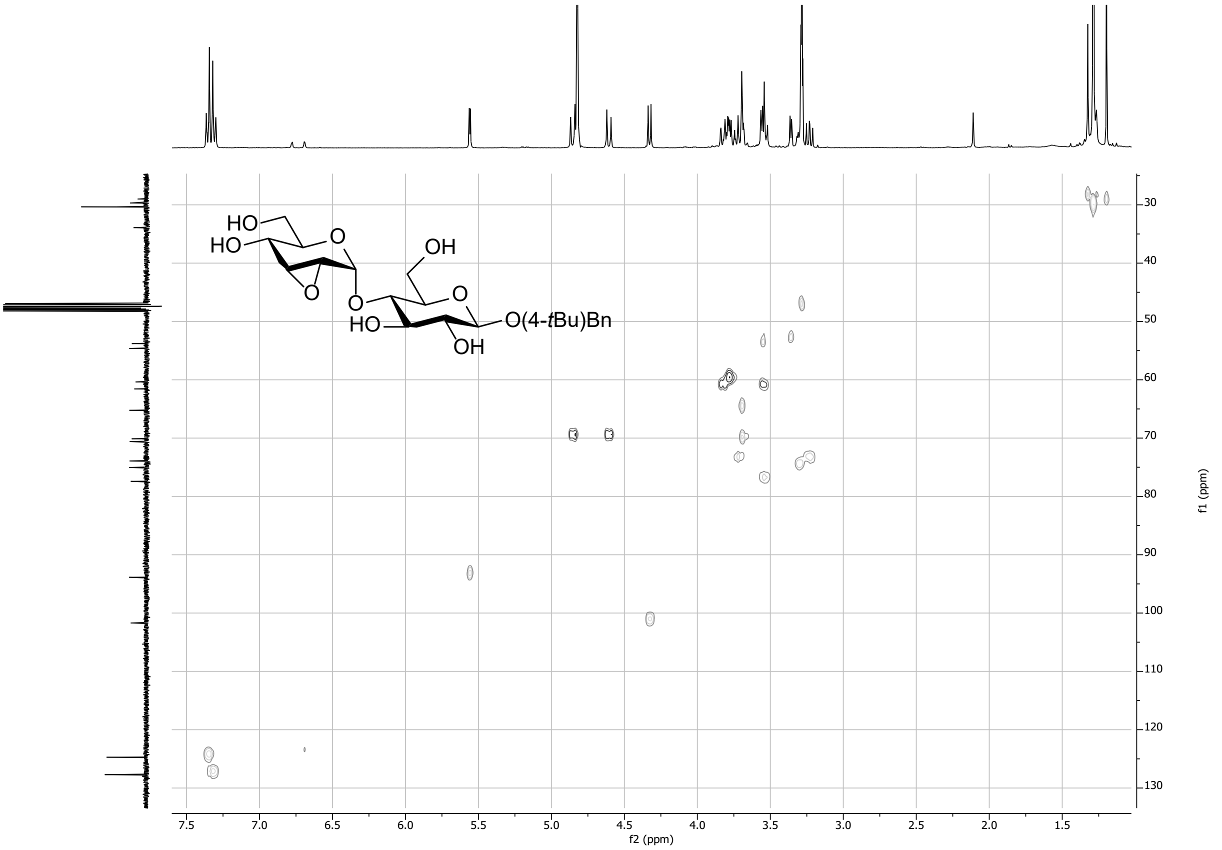
^{13}C NMR, 101 MHz, CD$_3$OD of compound **6**



^{1}H-^{1}H COSY of compound **6** in CD_3OD



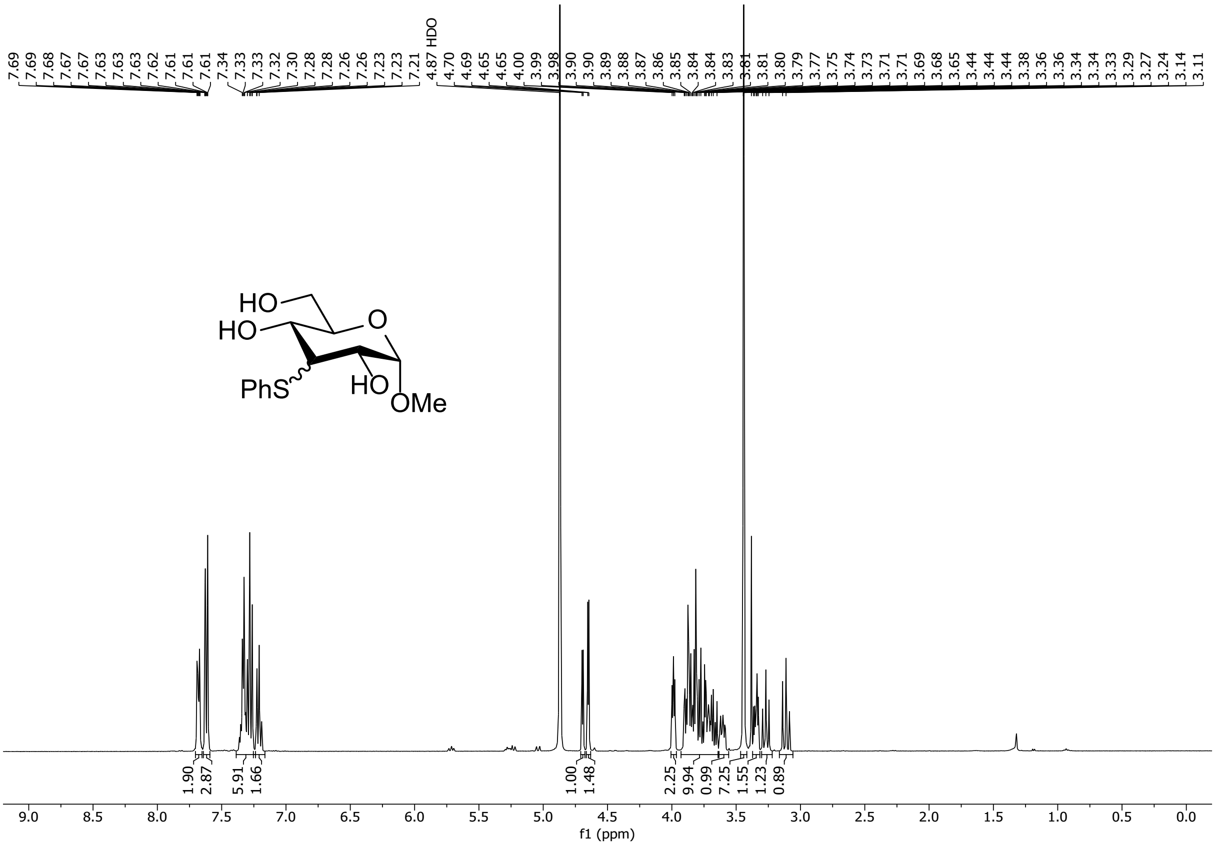
^{1}H-^{13}C HSQC of compound **6** in CD_3OD

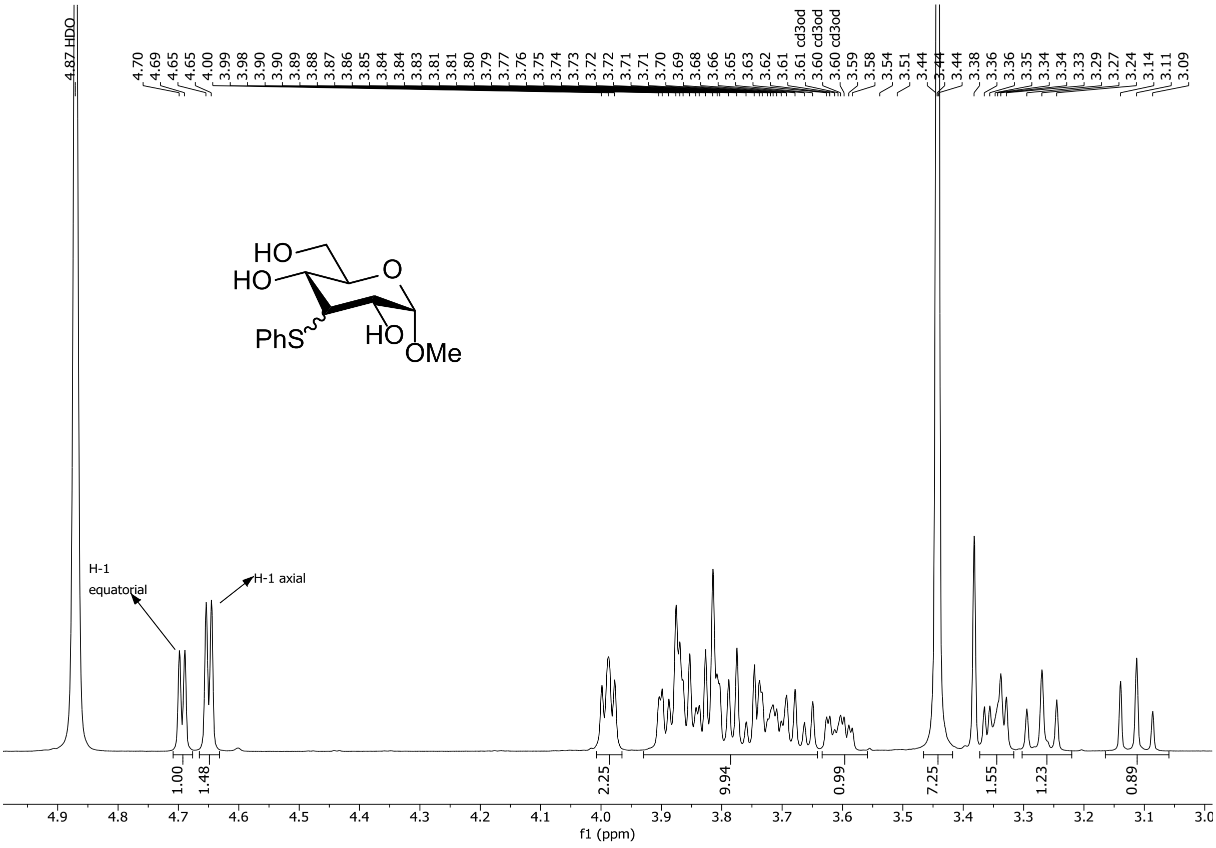


NMR spectra of α-Glc derivatives

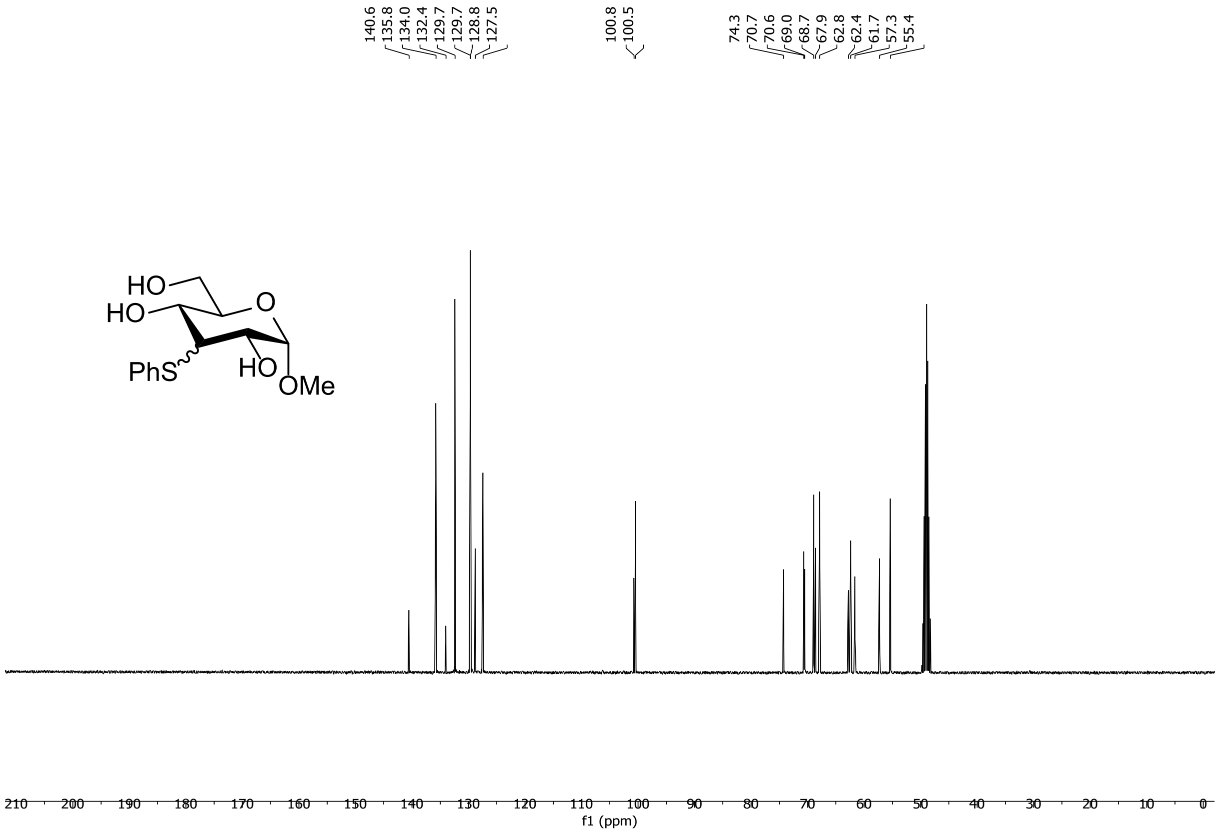
Methyl 3-S-phenyl-3-deoxy-α-D-allo/glucopyranoside (3b)

^{1}H NMR, 400 MHz, CD$_3$OD of compound **3b**

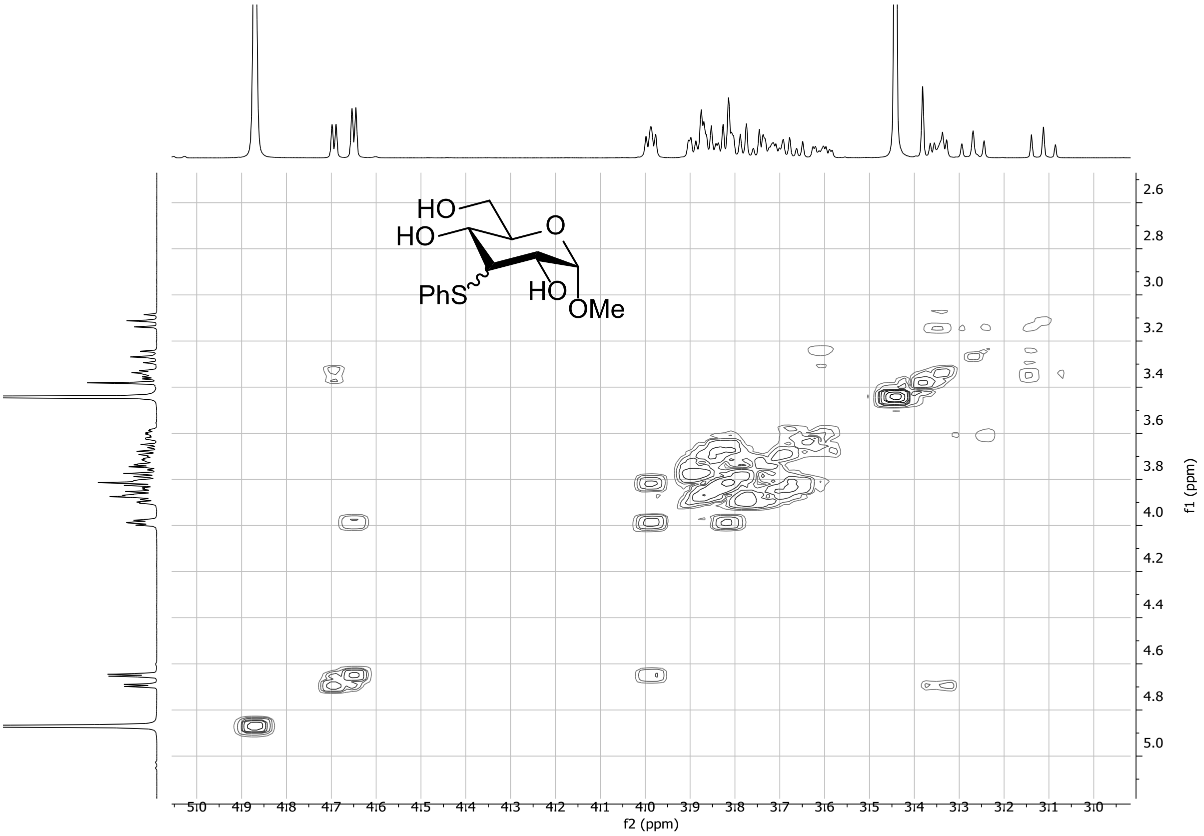




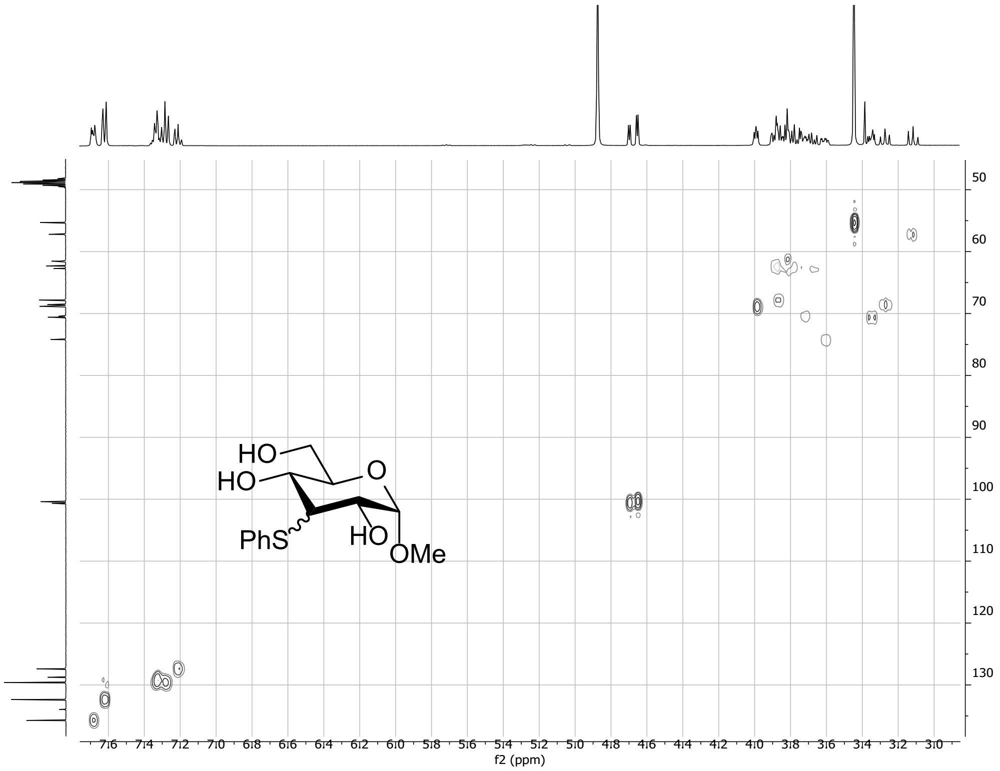
^{13}C NMR, 101 MHz, CD_3OD of compound **3b**



^1H-^1H COSY of compound **3b**

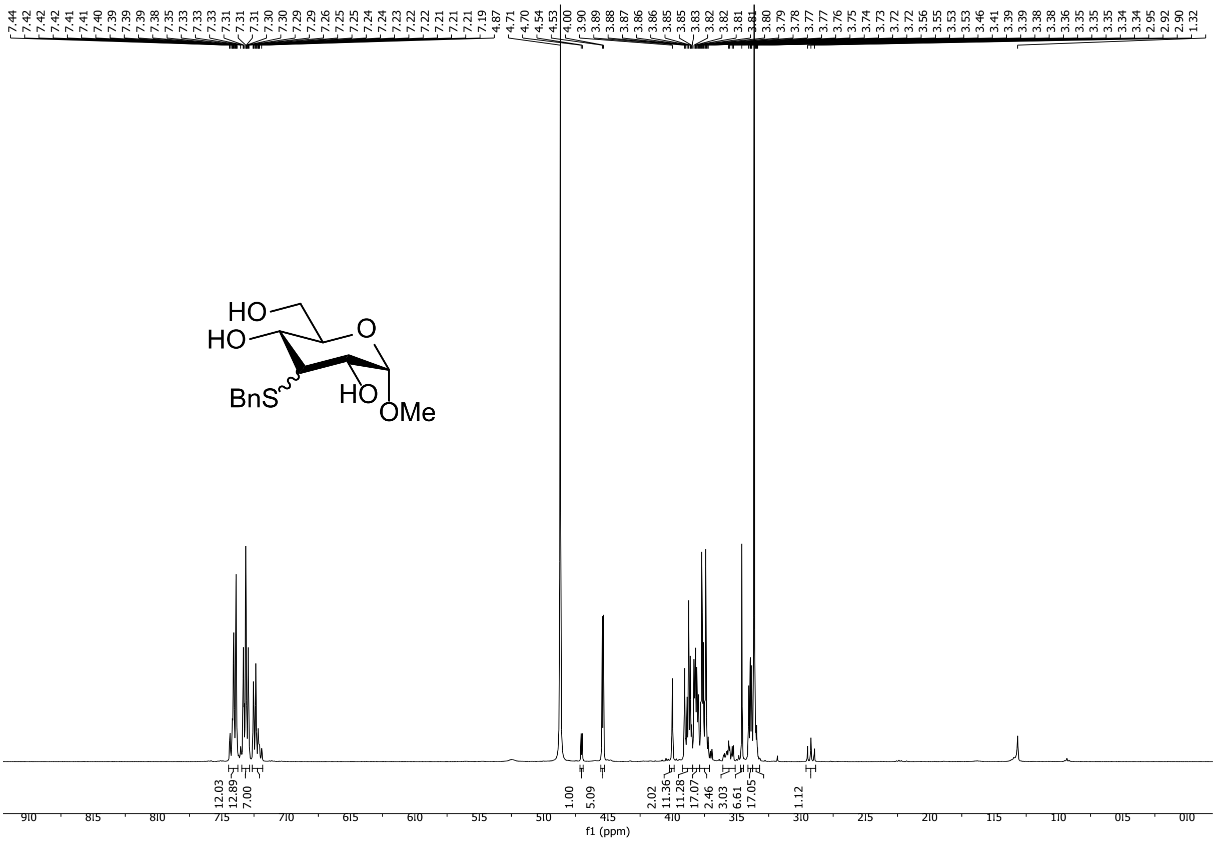


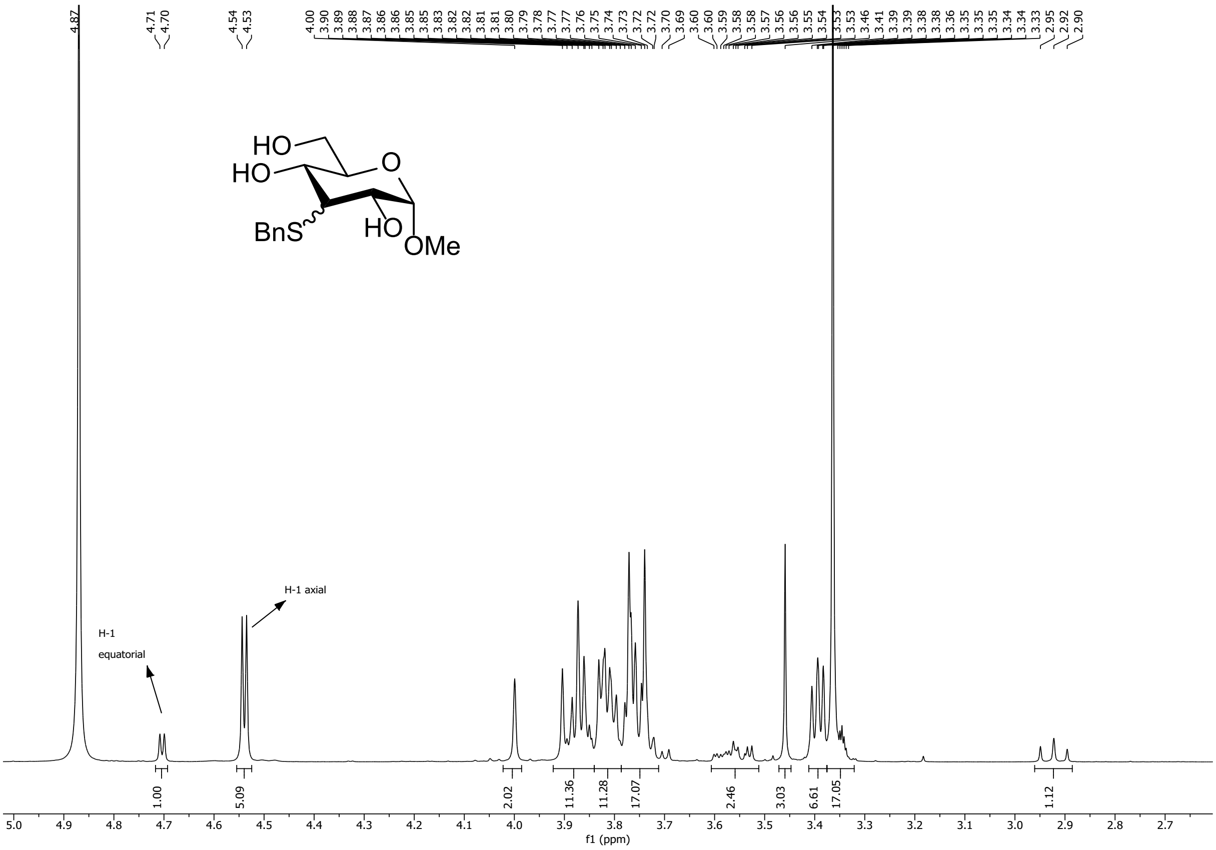
^{1}H-^{13}C HSQC of compound **3b**



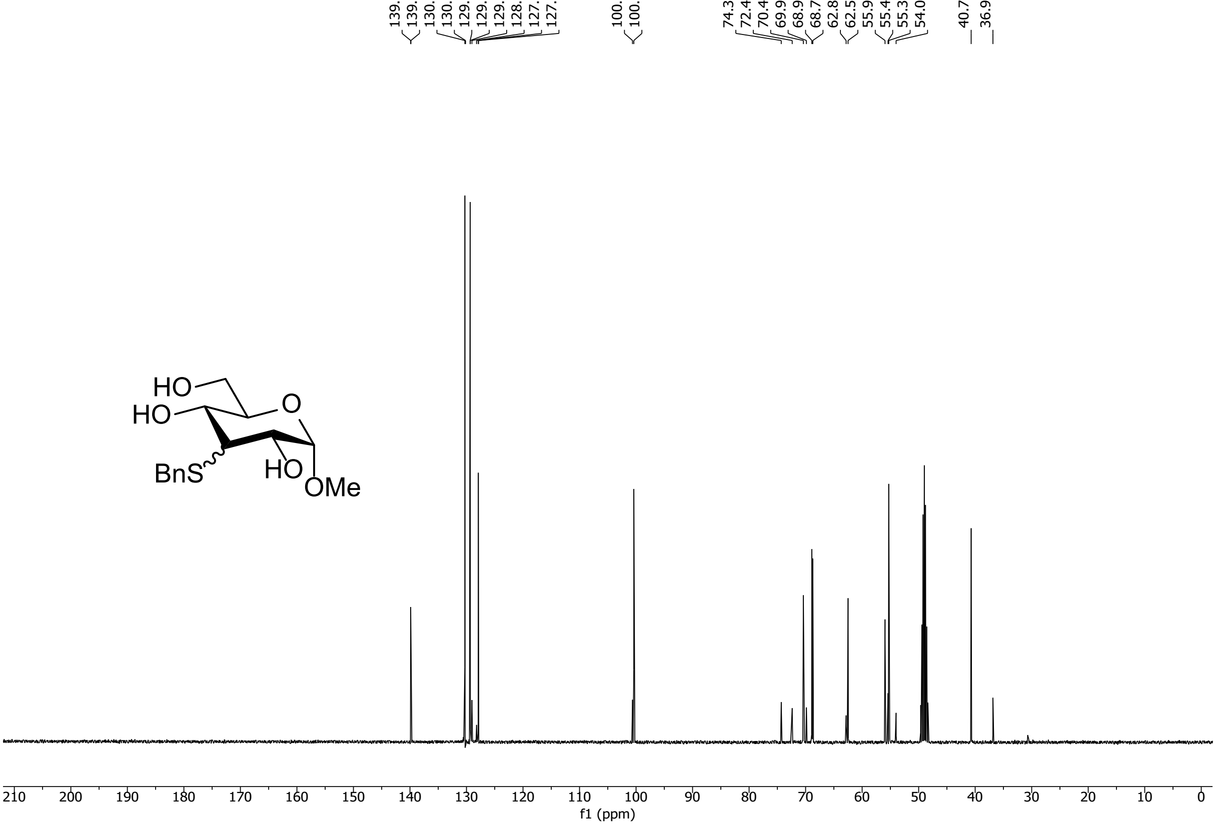
Methyl 3-S-phenyl-3-deoxy-α-D-allo/glucopyranoside (3c)

^{1}H NMR, 400 MHz, CD$_3$OD of compound **3c**

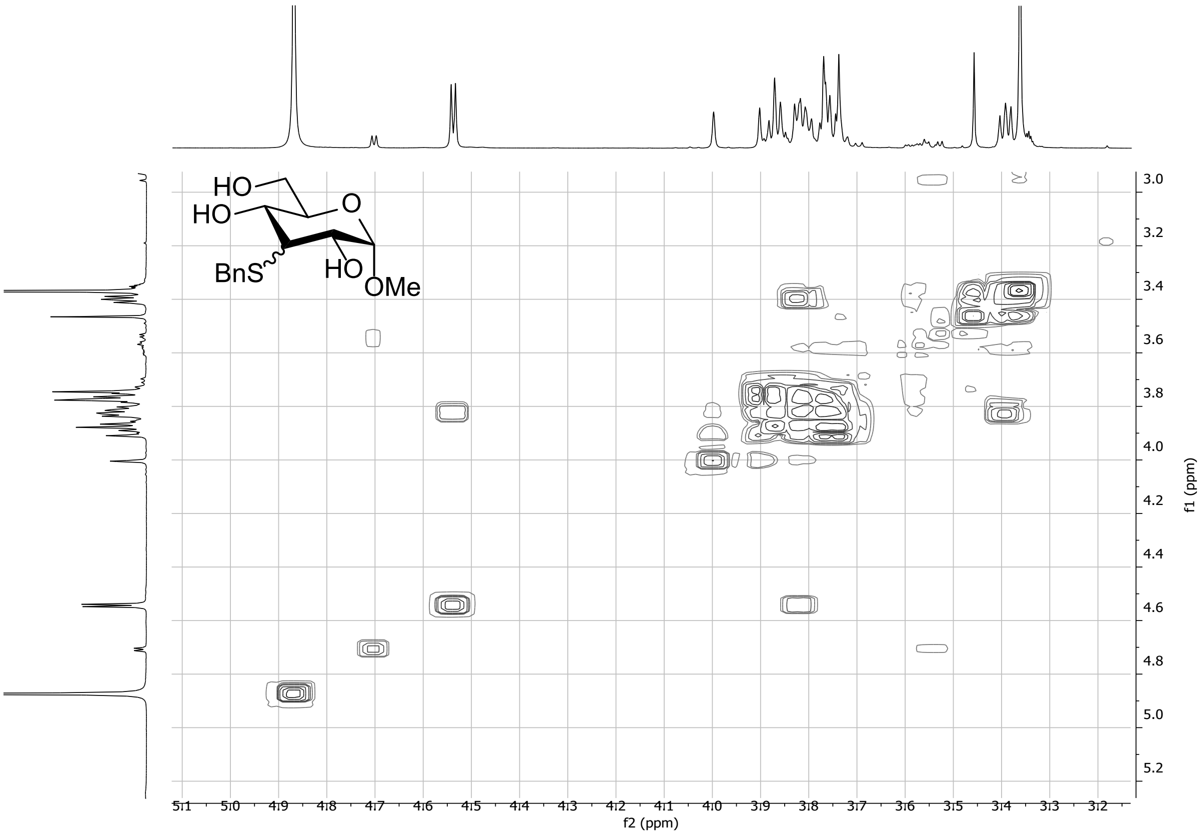




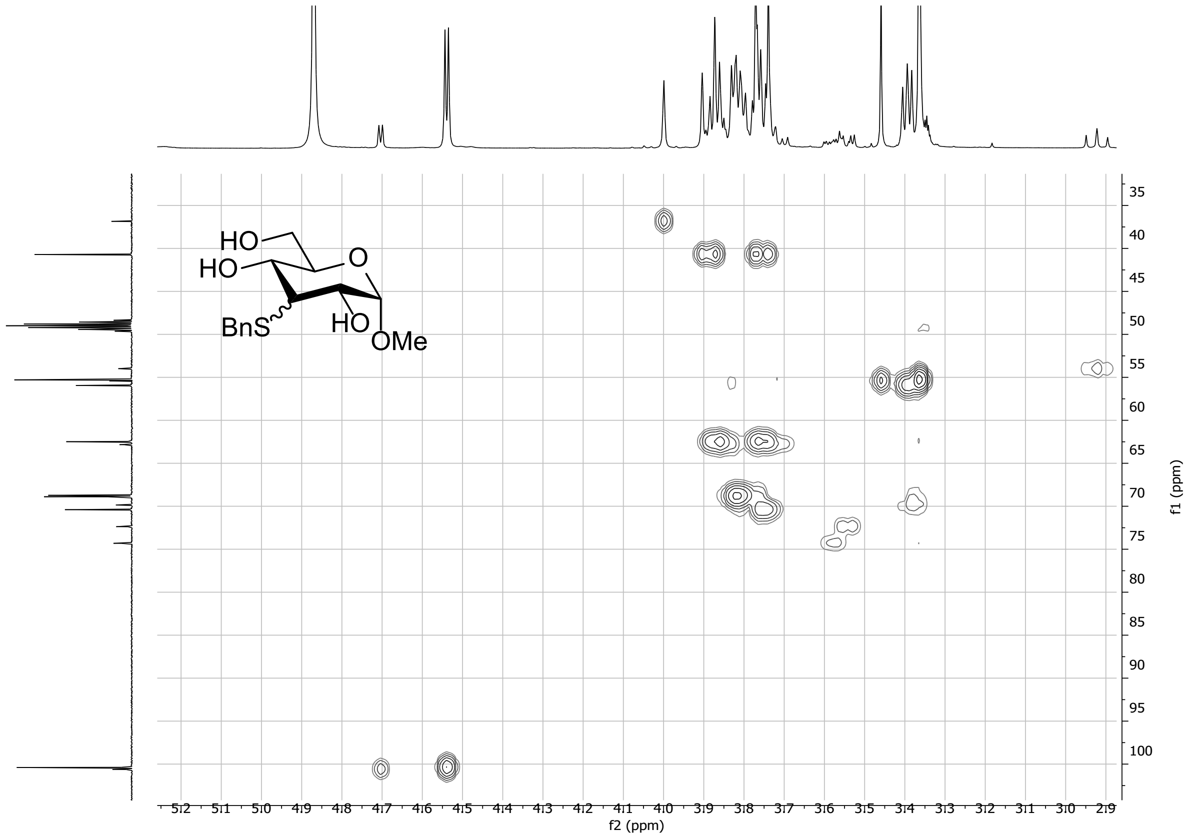
^{13}C NMR, 101 MHz, CD$_3$OD of compound **3c**



^{1}H-^{1}H COSY of compound **3c**



^{1}H-^{13}C HSQC of compound **3c**

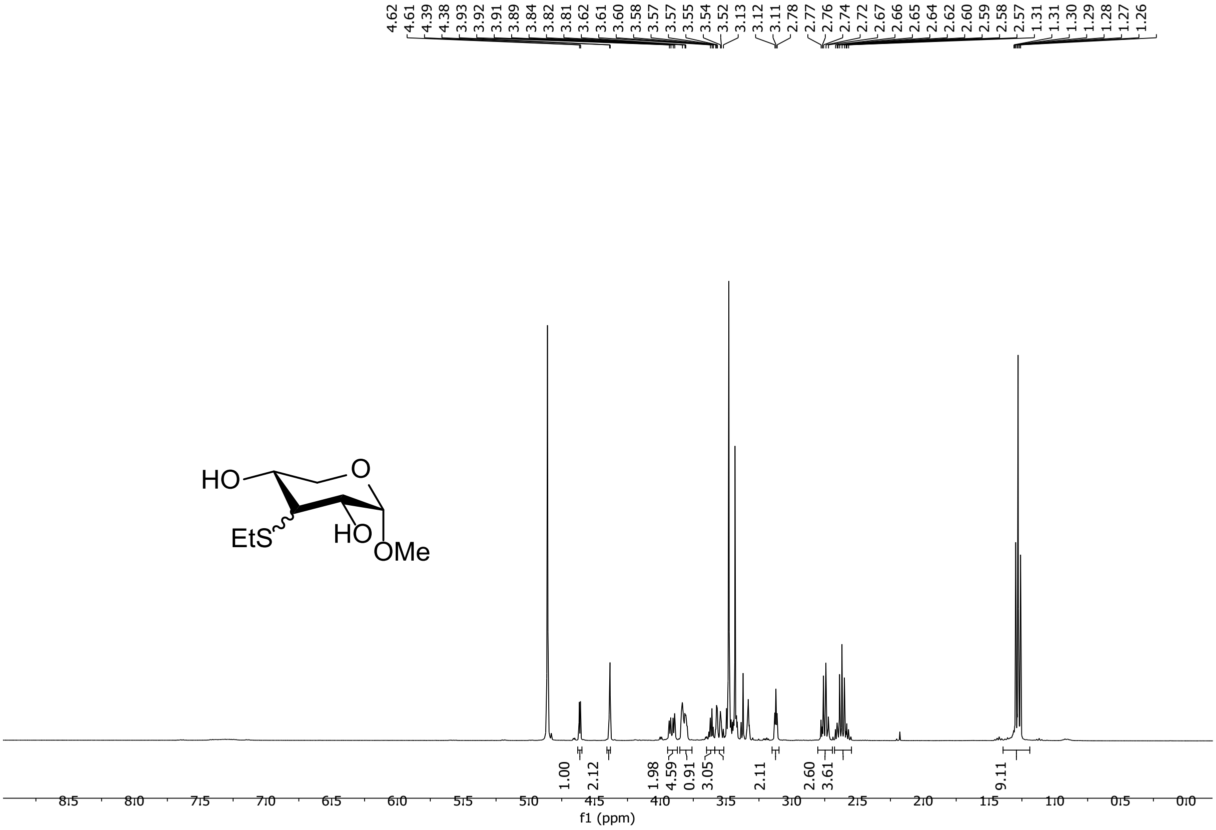


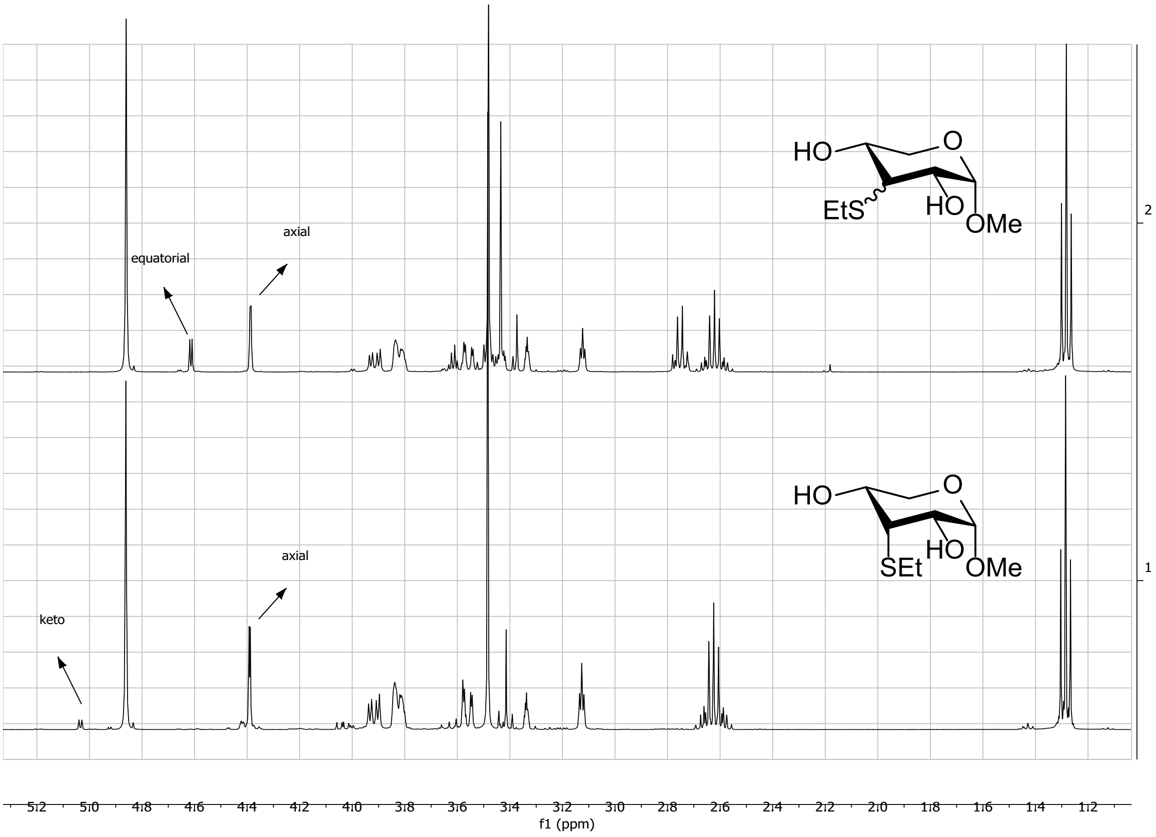
NMR spectra of Xyl derivatives

Methyl 3-deoxy-3-*S*-ethyl-α-ᴅ-riboso/xylopyranoside (8a)

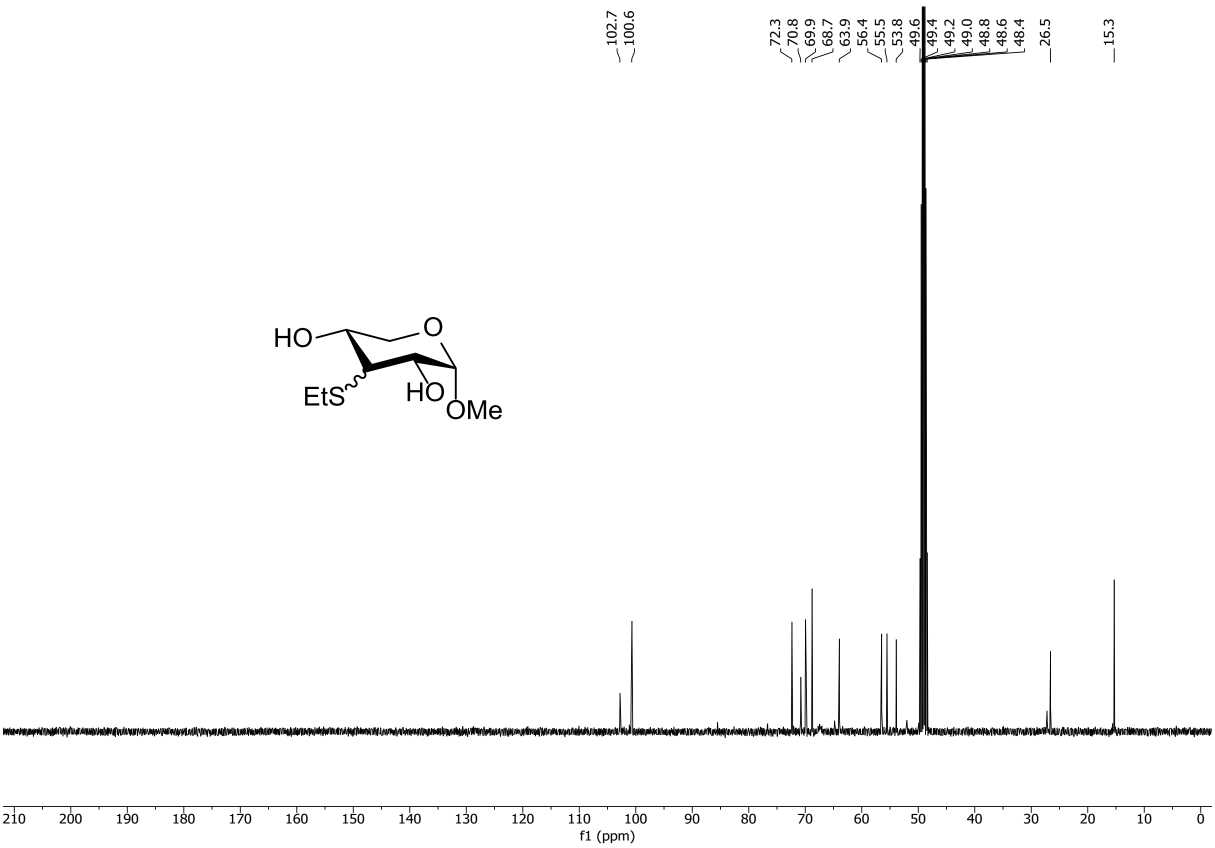
Equatorial/axial mixture:

^{1}H NMR, 400 MHz, CD_3OD of compound **8a**

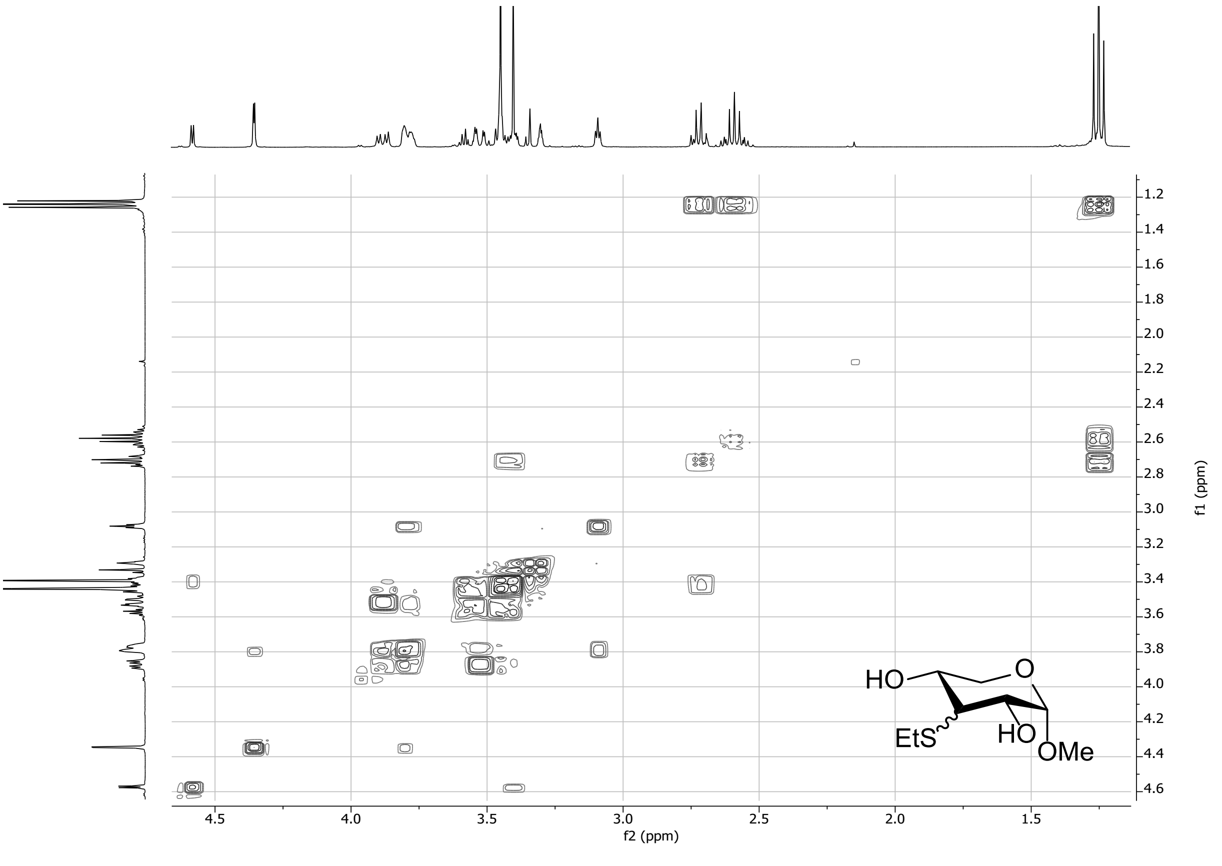




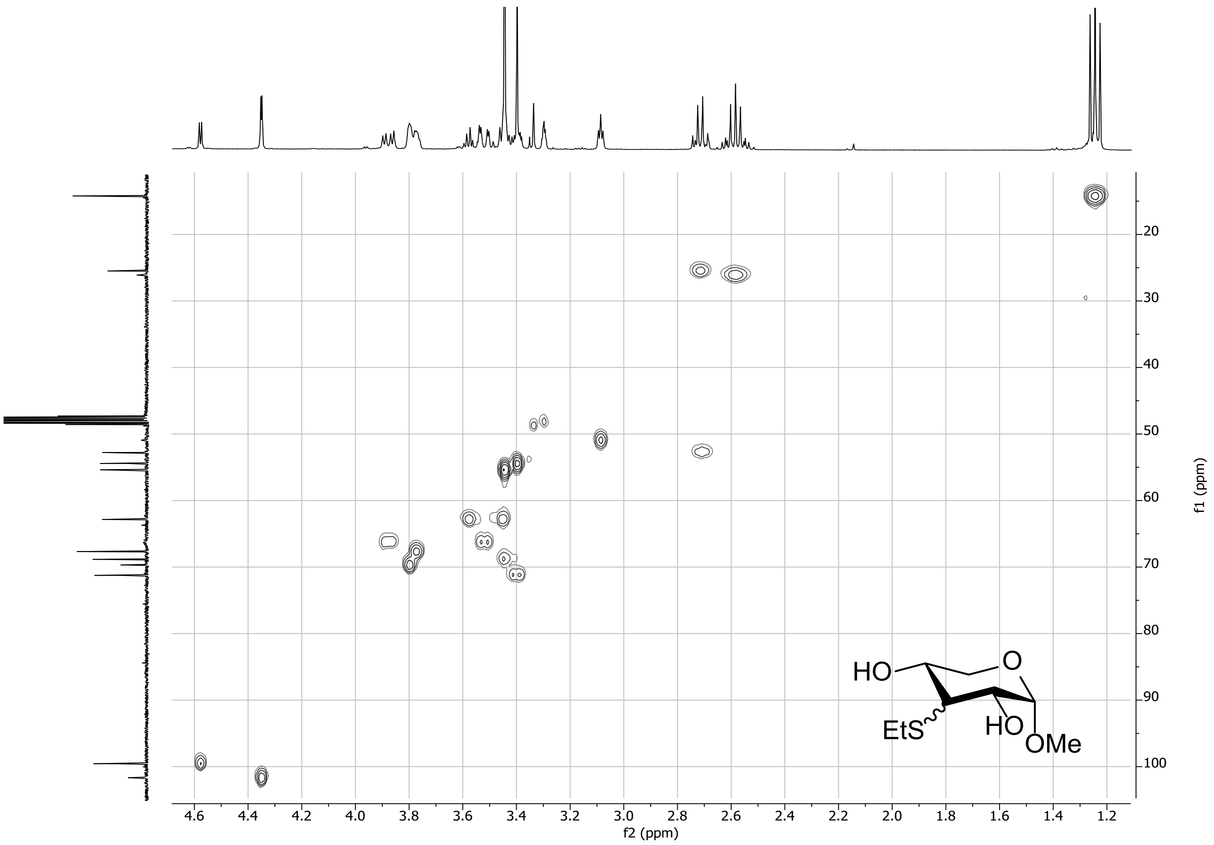
^{13}C NMR, 101 MHz, CD$_3$OD of compound **8a**



^{1}H-^{1}H COSY of compound **8a**

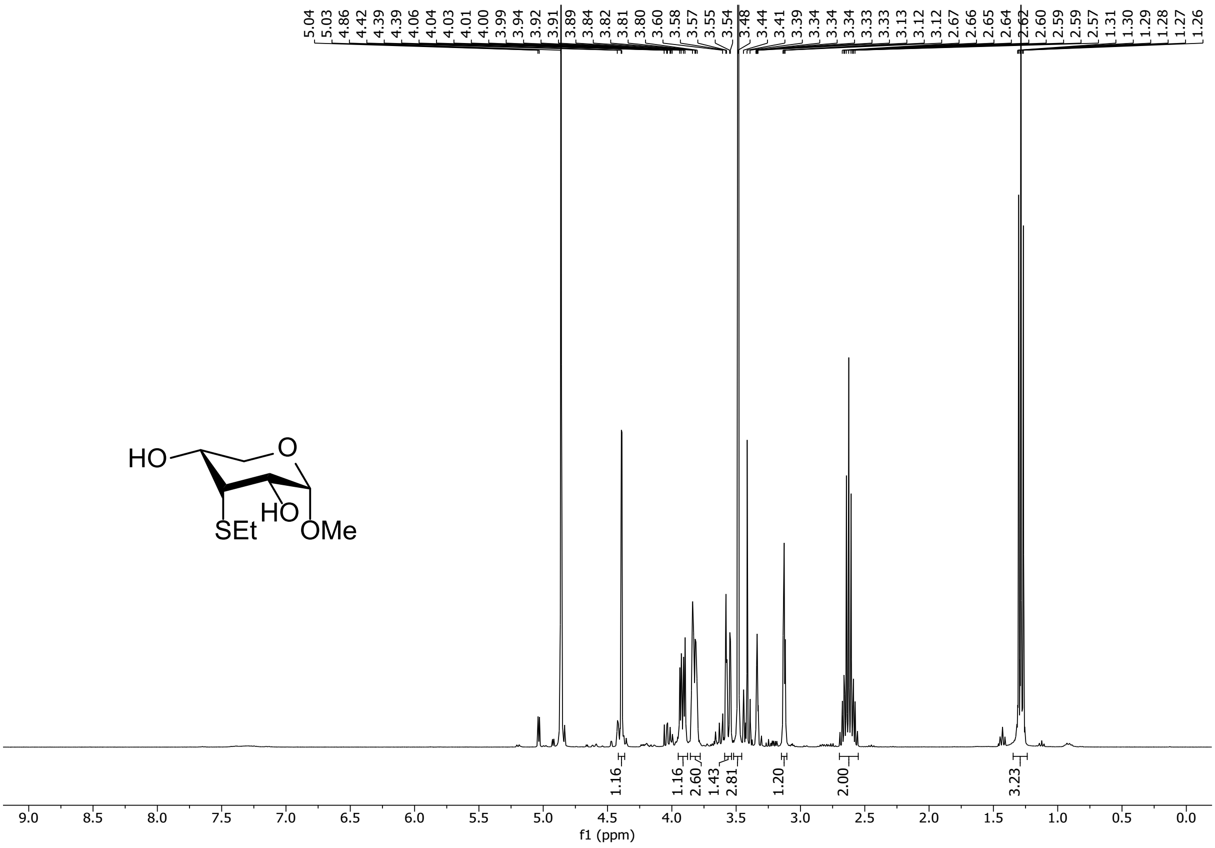


^{1}H-^{13}C HSQC of compound **8a**

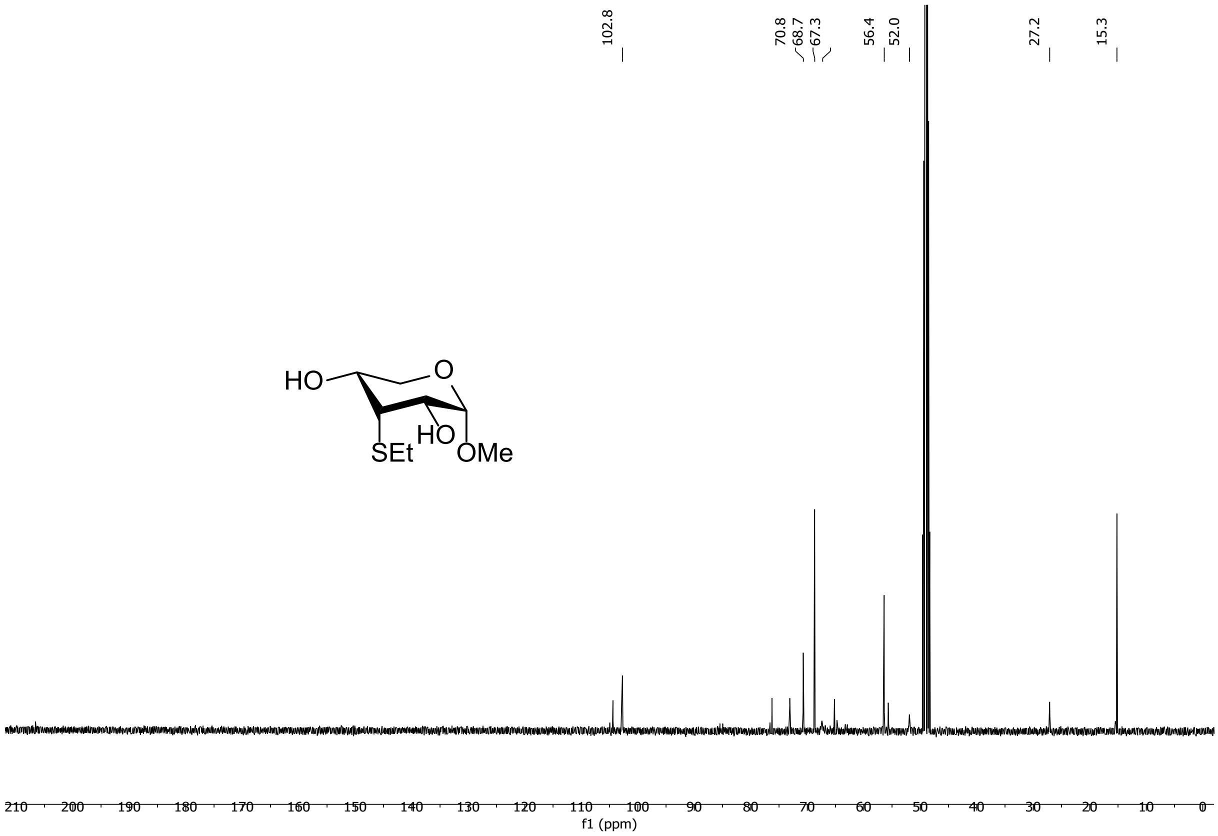


^{1}H NMR, 400 MHz, CD$_3$OD of compound **8a**

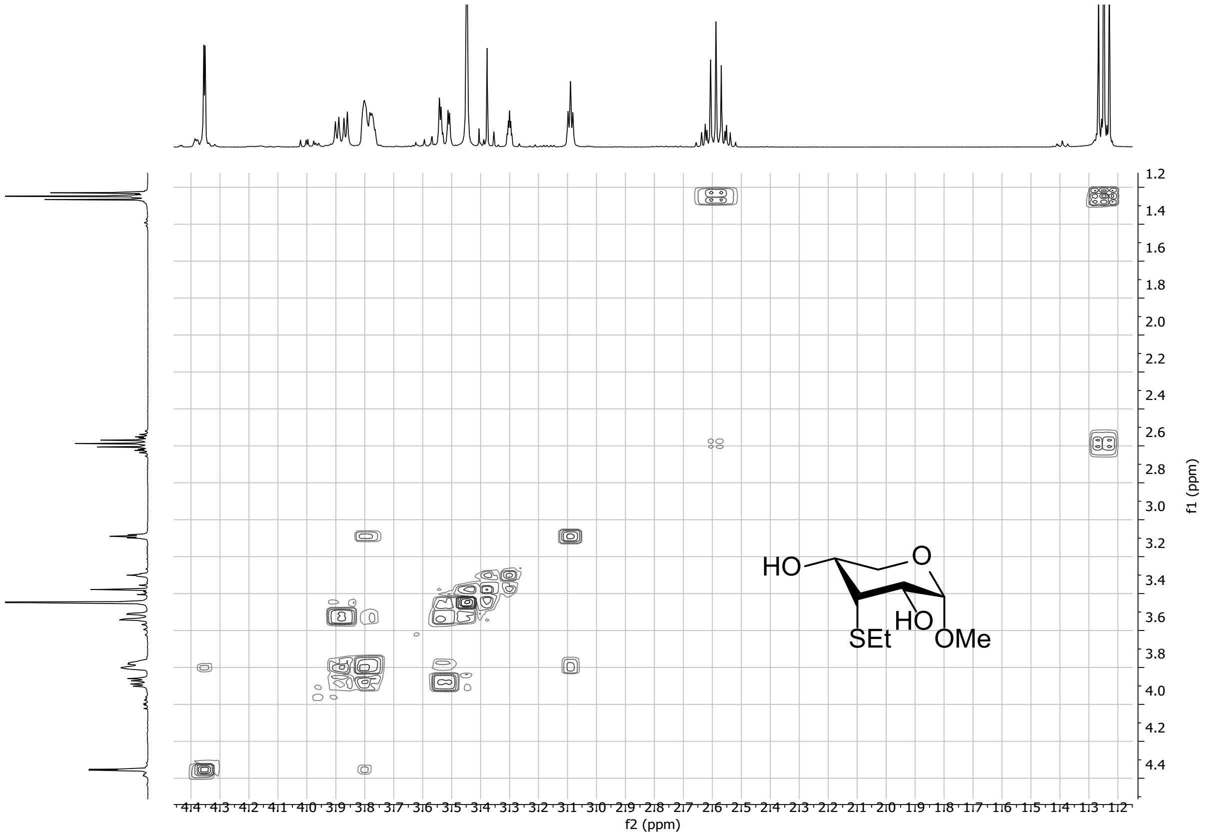
Axial:



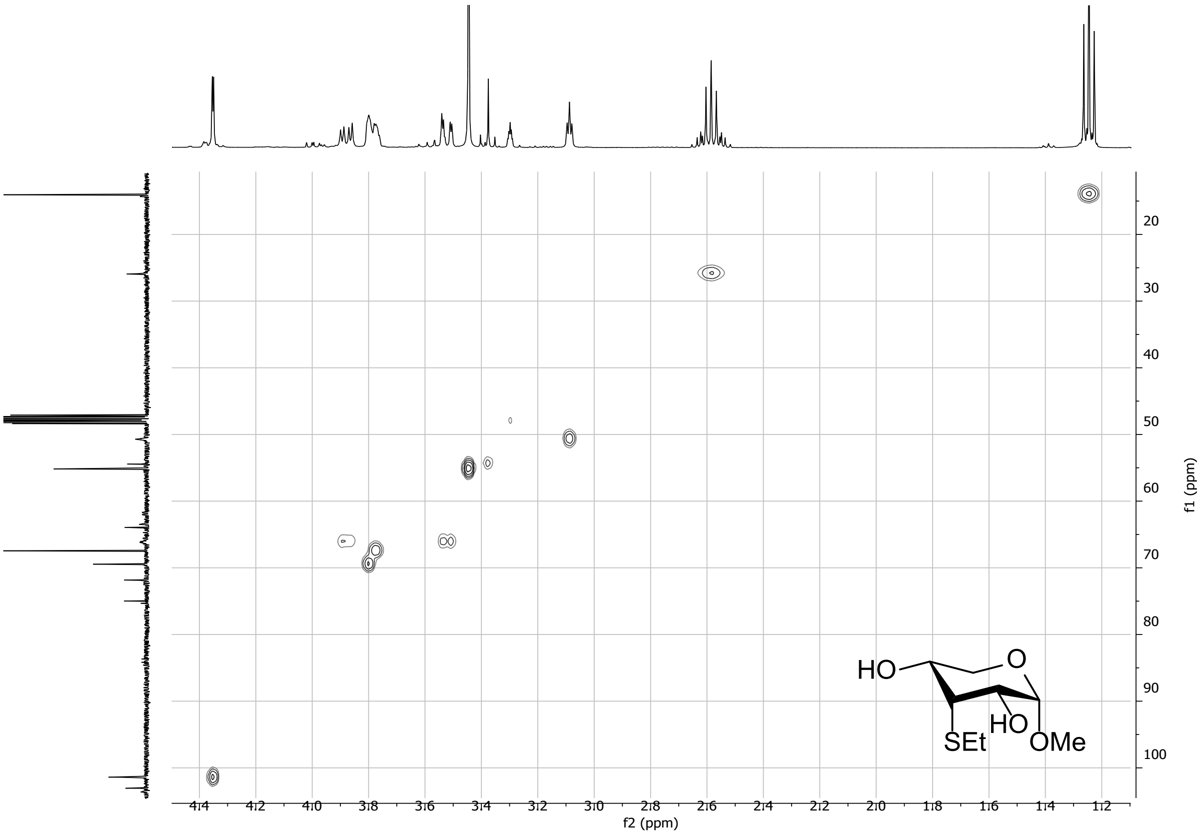
^{13}C NMR, 101 MHz, CD$_3$OD of compound **8a**



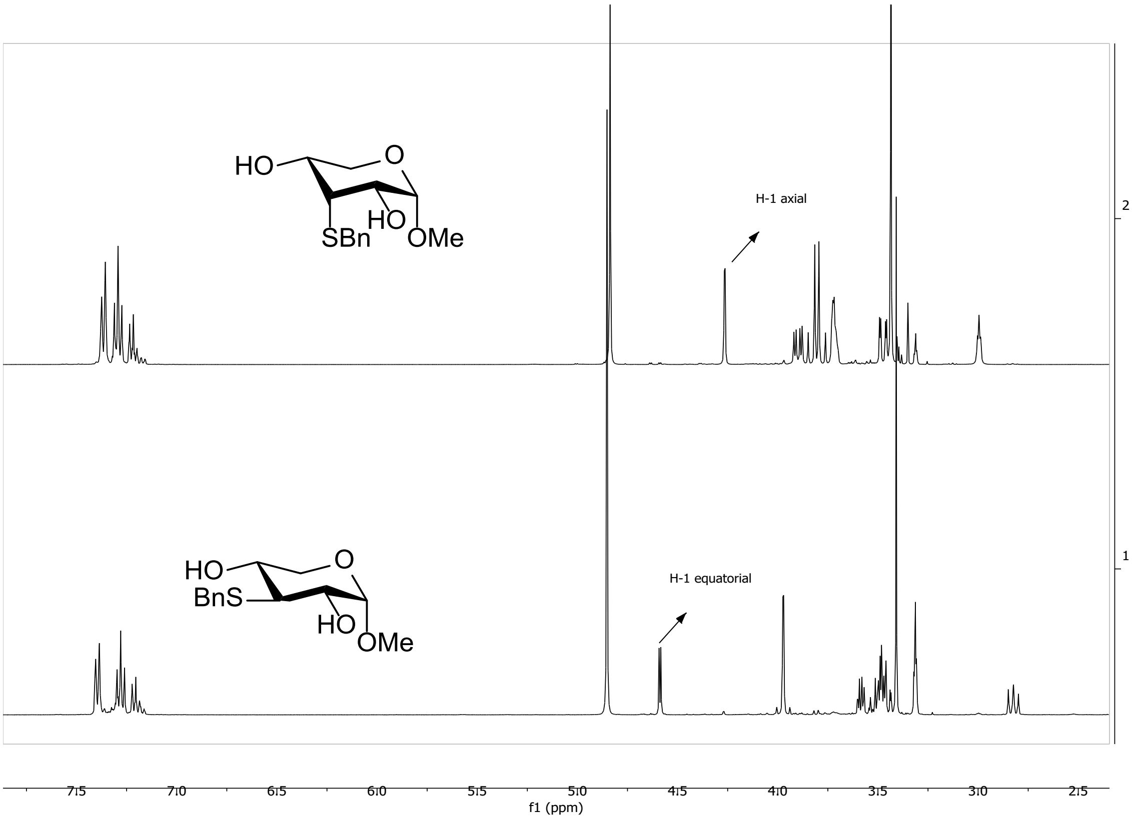
^{1}H-^{1}H COSY of compound **8a**



^{1}H-^{13}H HSQC of compound **8a**

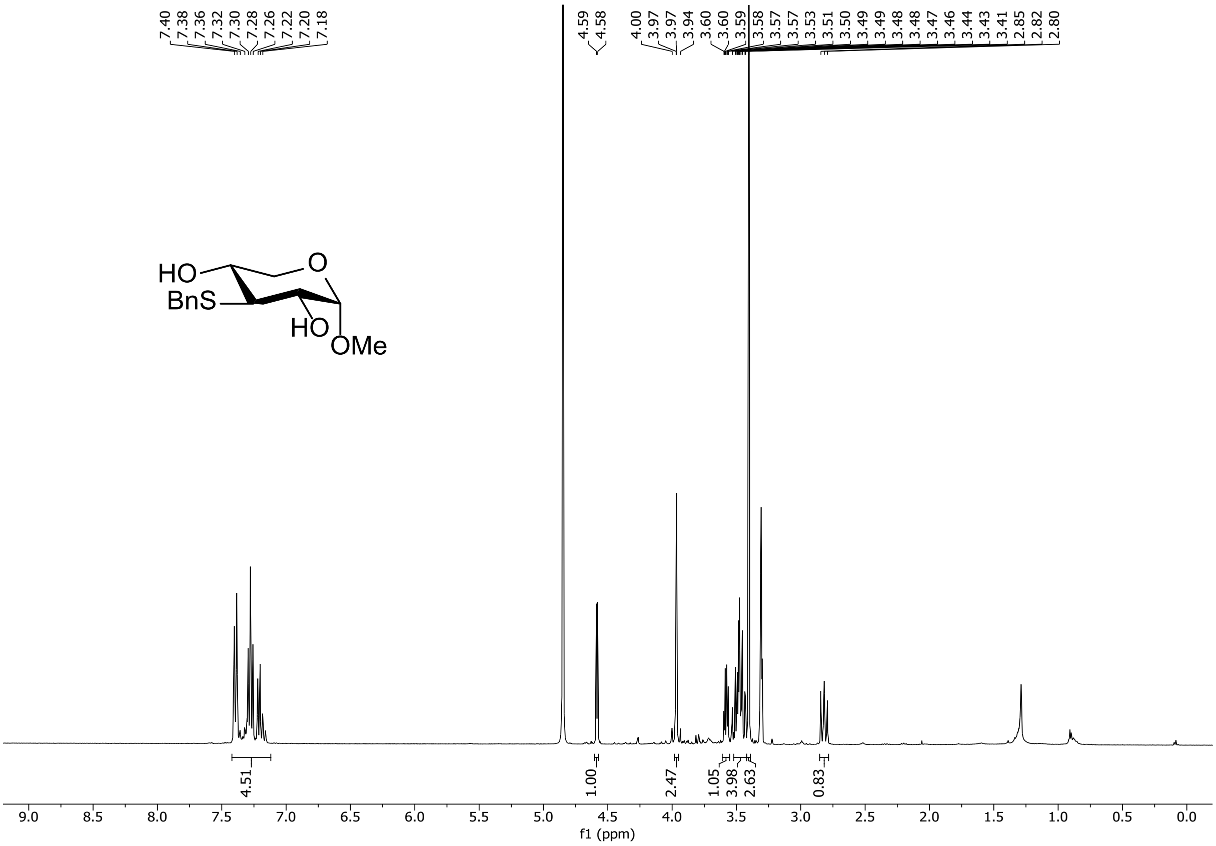


Methyl 3-S-benzyl-3-deoxy-α-D-riboso/xylopyranoside (8b)

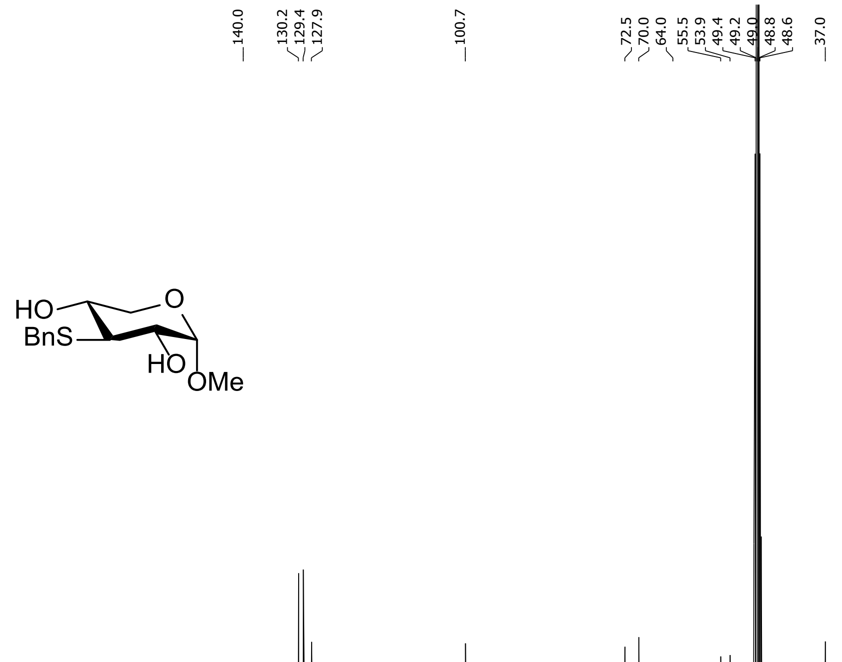


Equatorial:

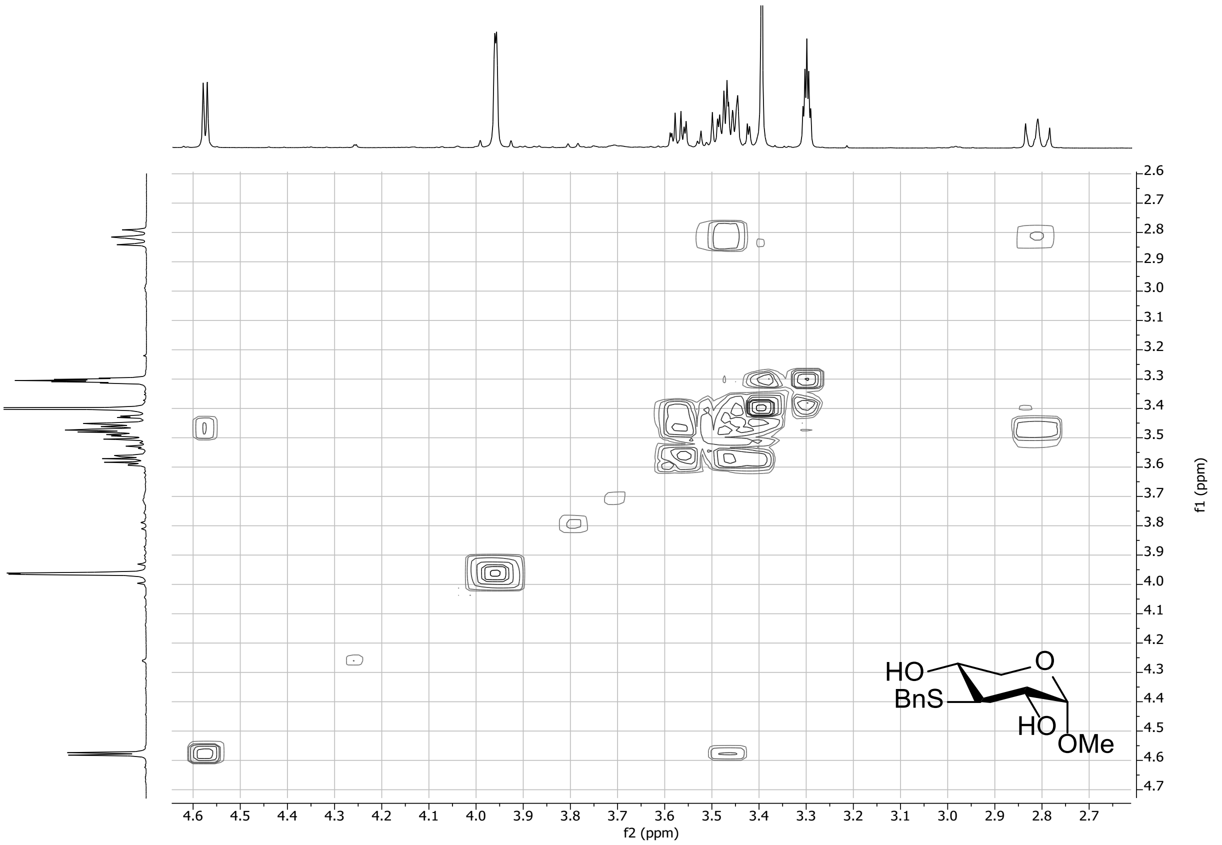
^{1}H NMR, 400 MHz, CD_3OD of compound **8b**



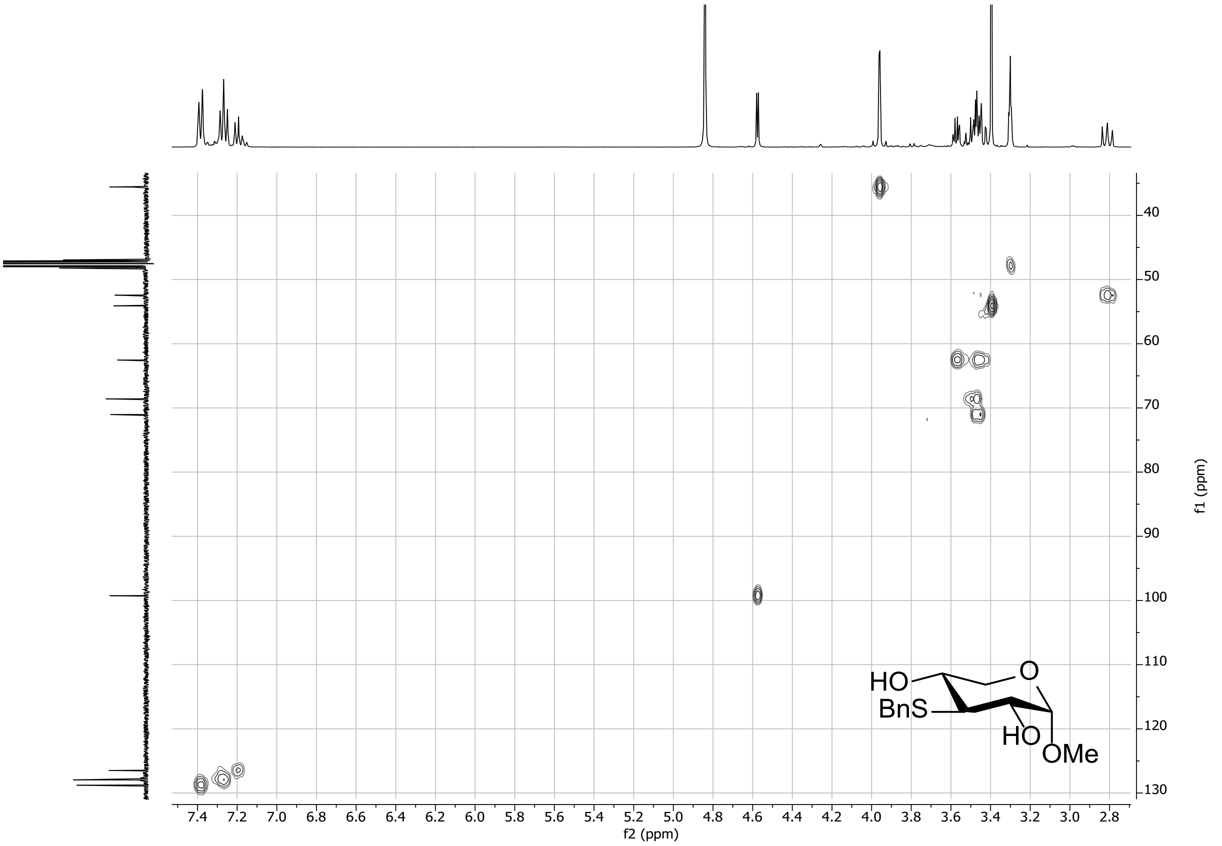
^{13}C NMR, 101 MHz, CD_3OD of compound **8b**



^1H-^1H COSY of compound **8b**

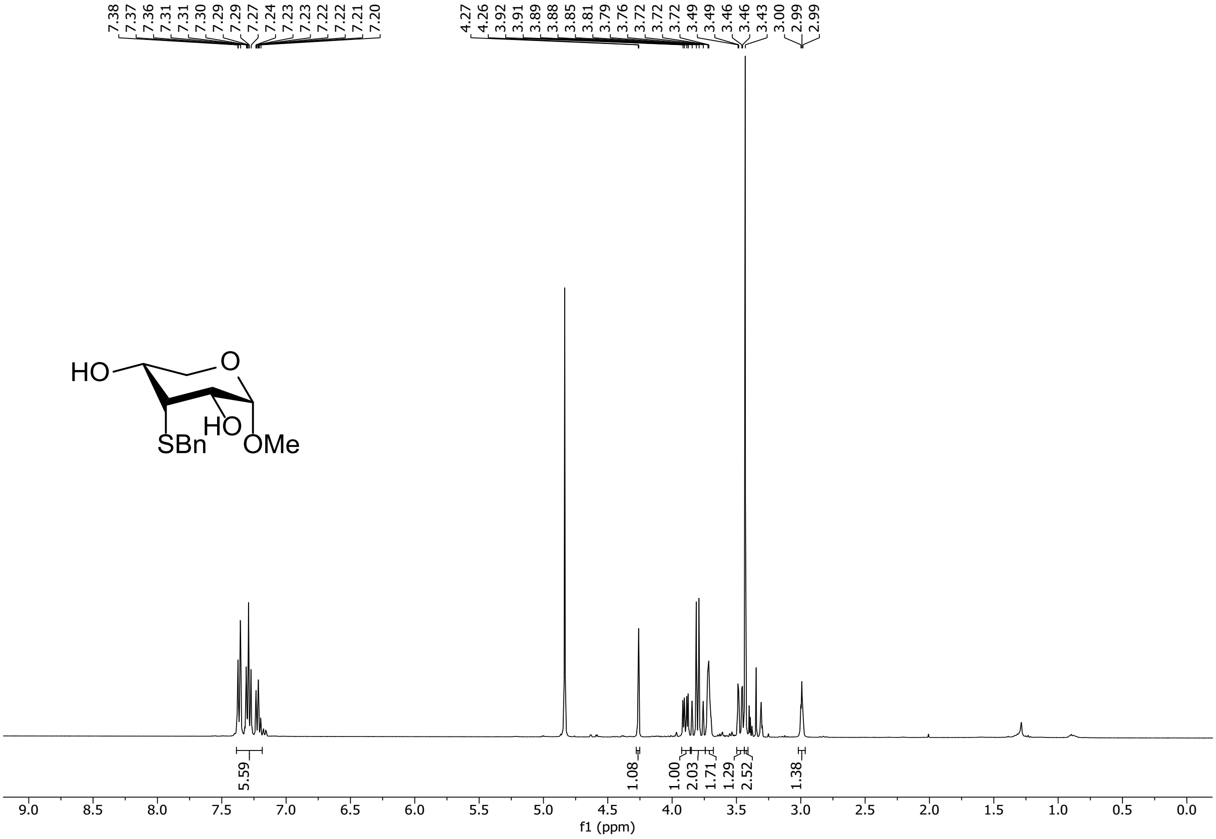


^1H-^{13}C HSQC of compound **8b**

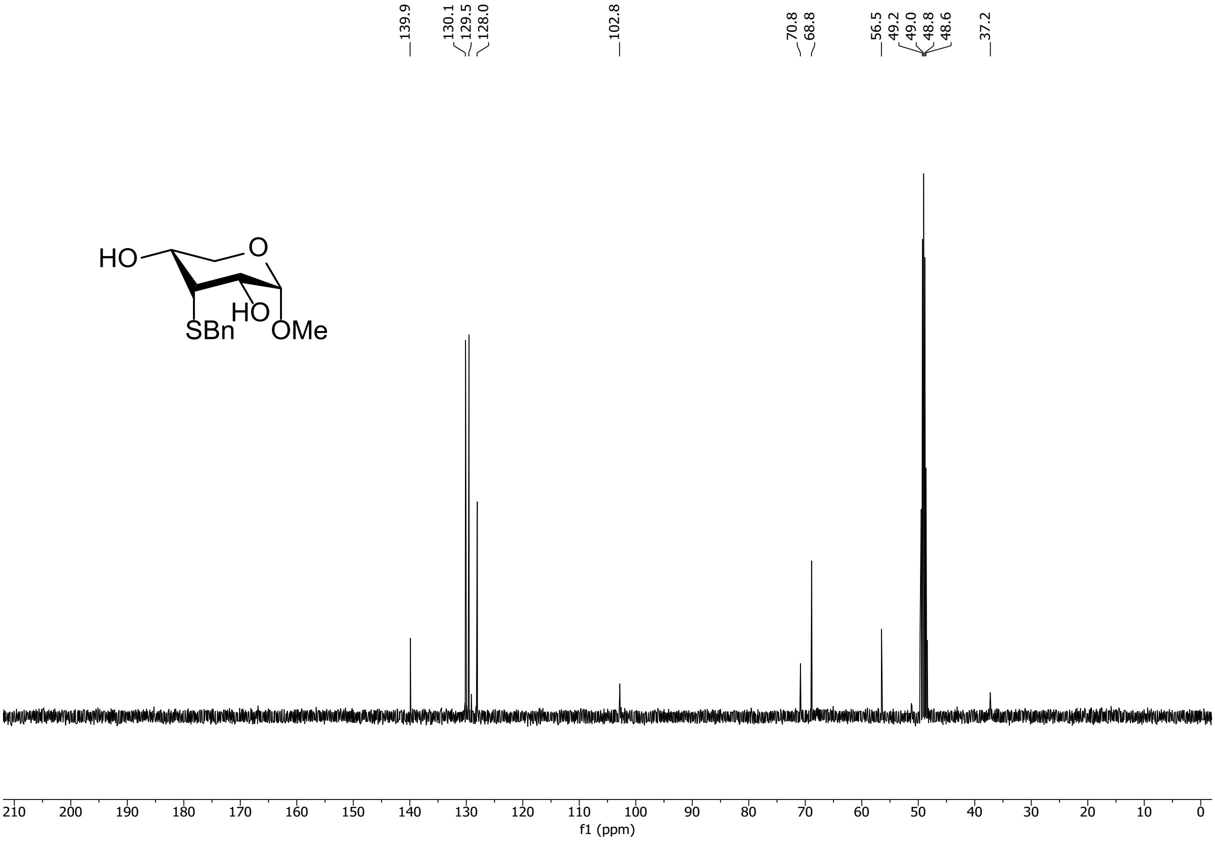


Axial:

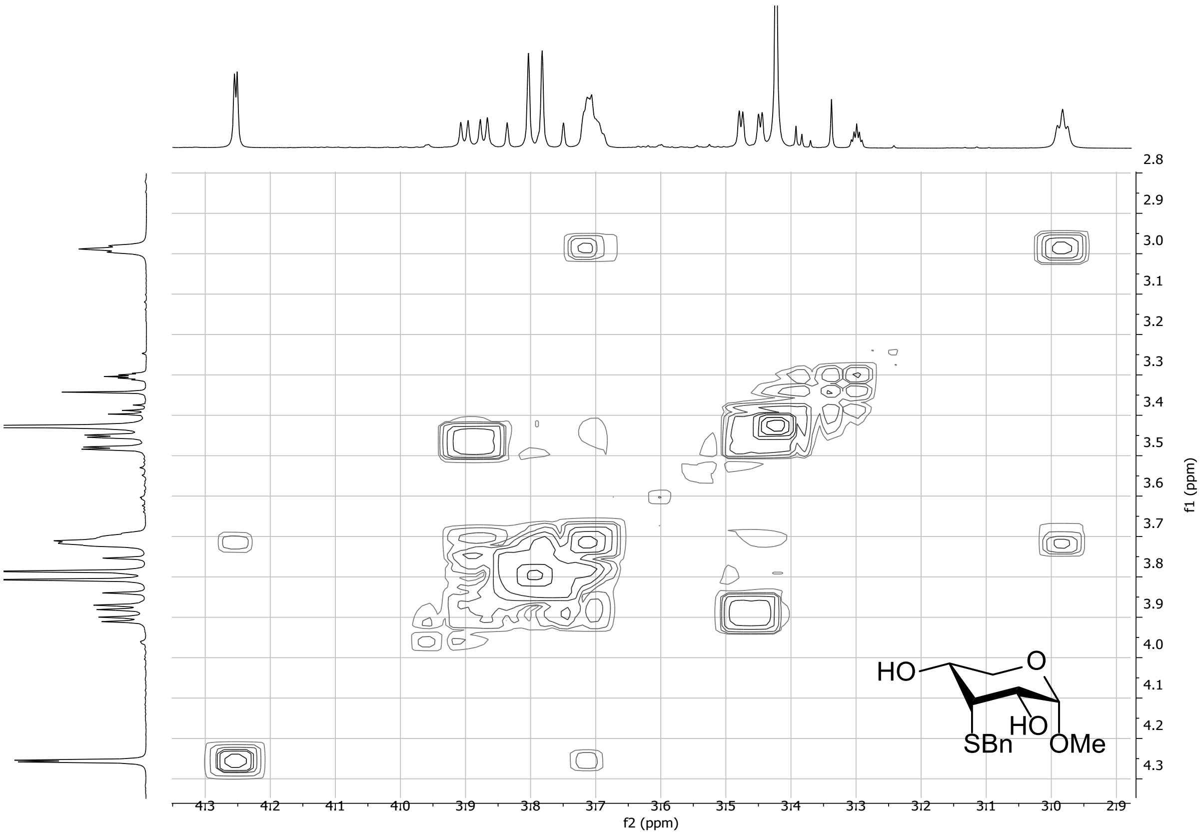
^{1}H NMR, 400 MHz, CD$_3$OD of compound **8b**



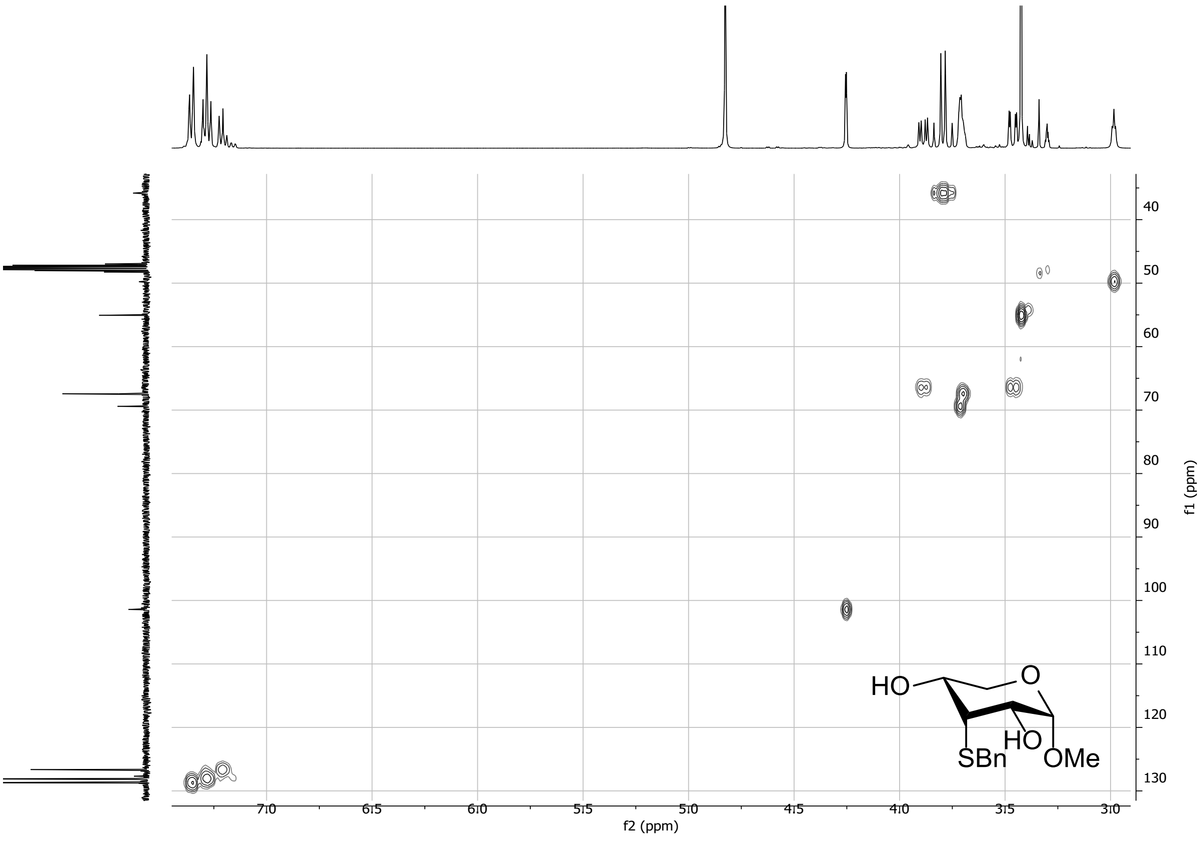
^{13}C NMR, 101 MHz, CD$_3$OD of compound **8b**



^{1}H-^{1}H COSY of compound **8b**

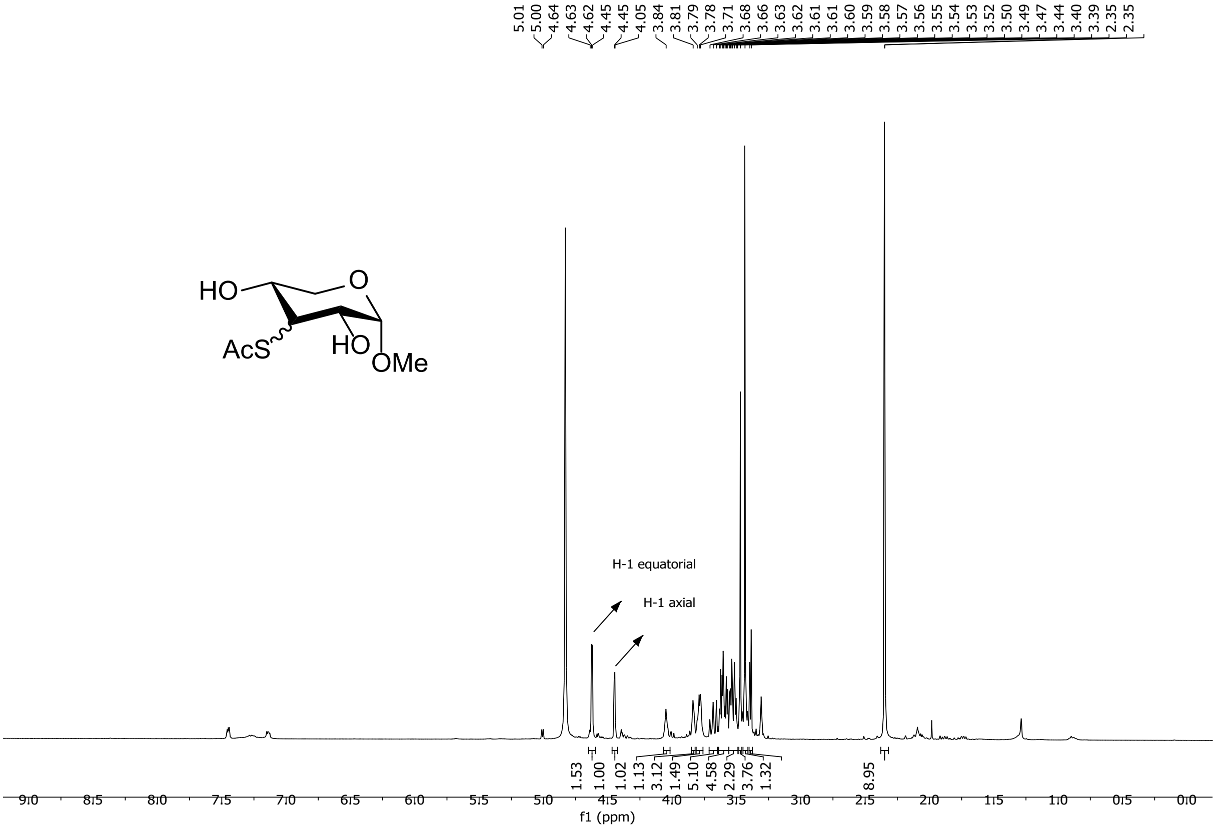


^{1}H-^{13}C HSQC of compound **8b**

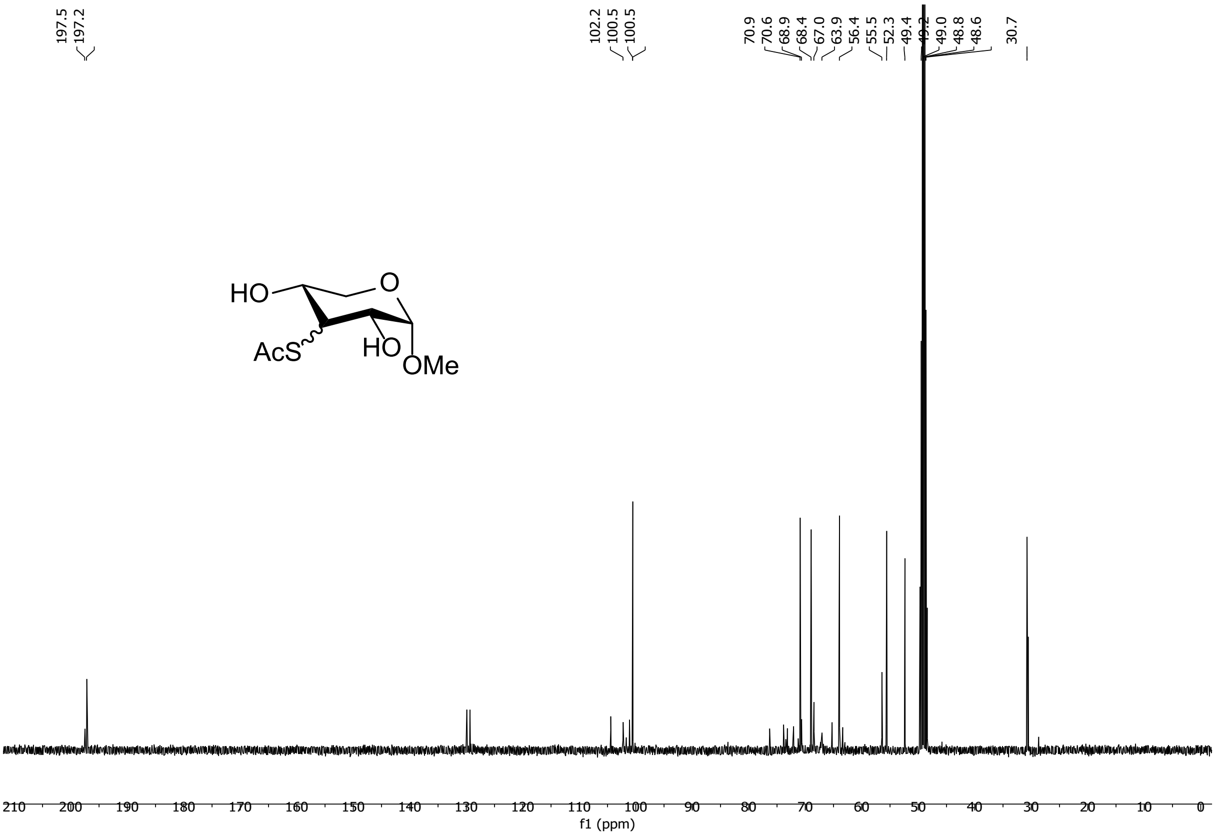


Methyl 3-S-acetyl-3-deoxy-α-D-riboso/xylopyranoside (8c)

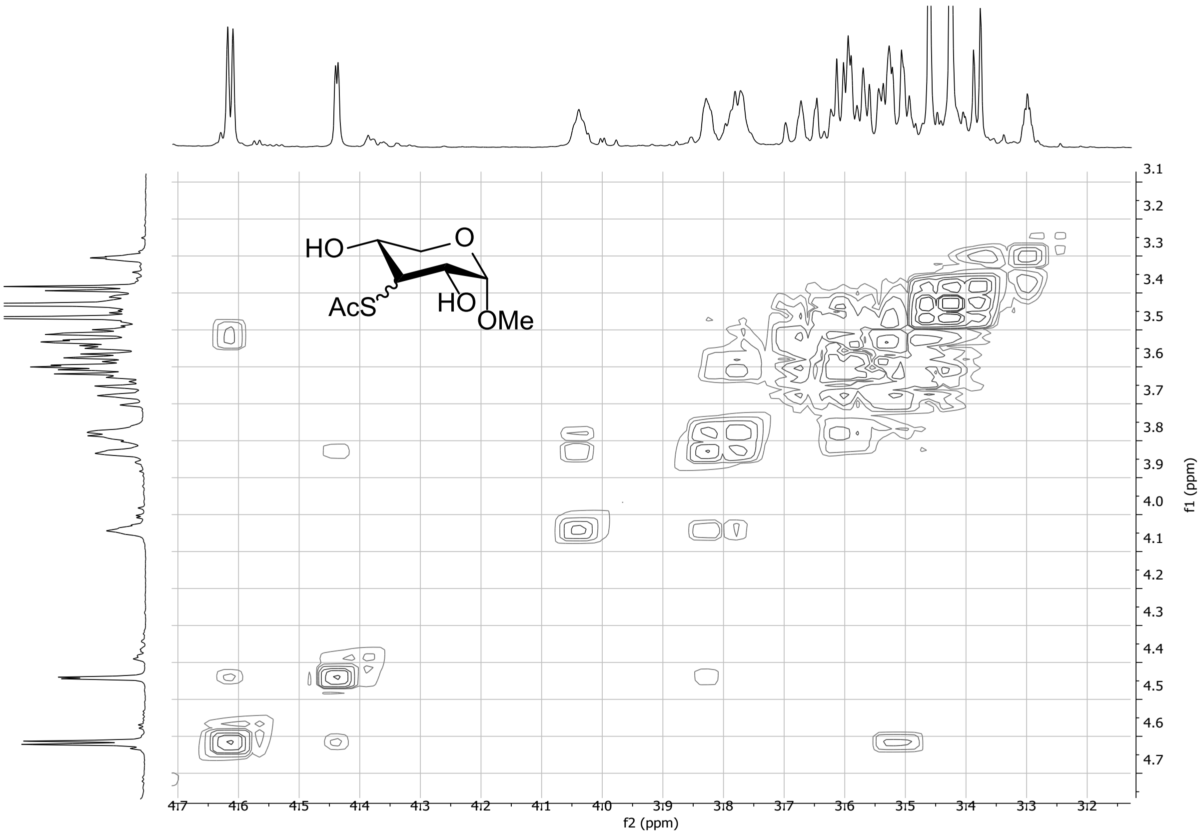
^{1}H NMR, 400 MHz, CD$_3$OD of compound **8c**



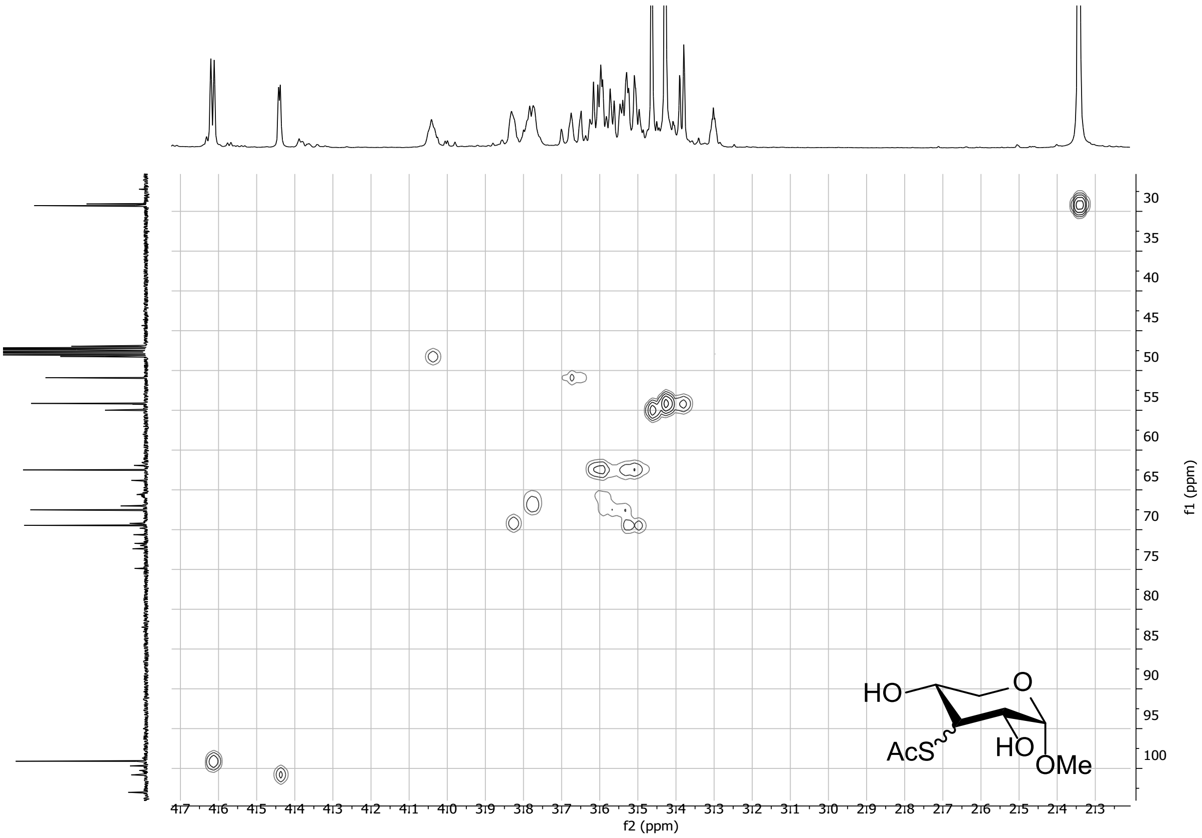
^{13}C NMR, 101 MHz, CD$_3$OD of compound **8c**



^{1}H-^{1}H COSY of compound **8c**



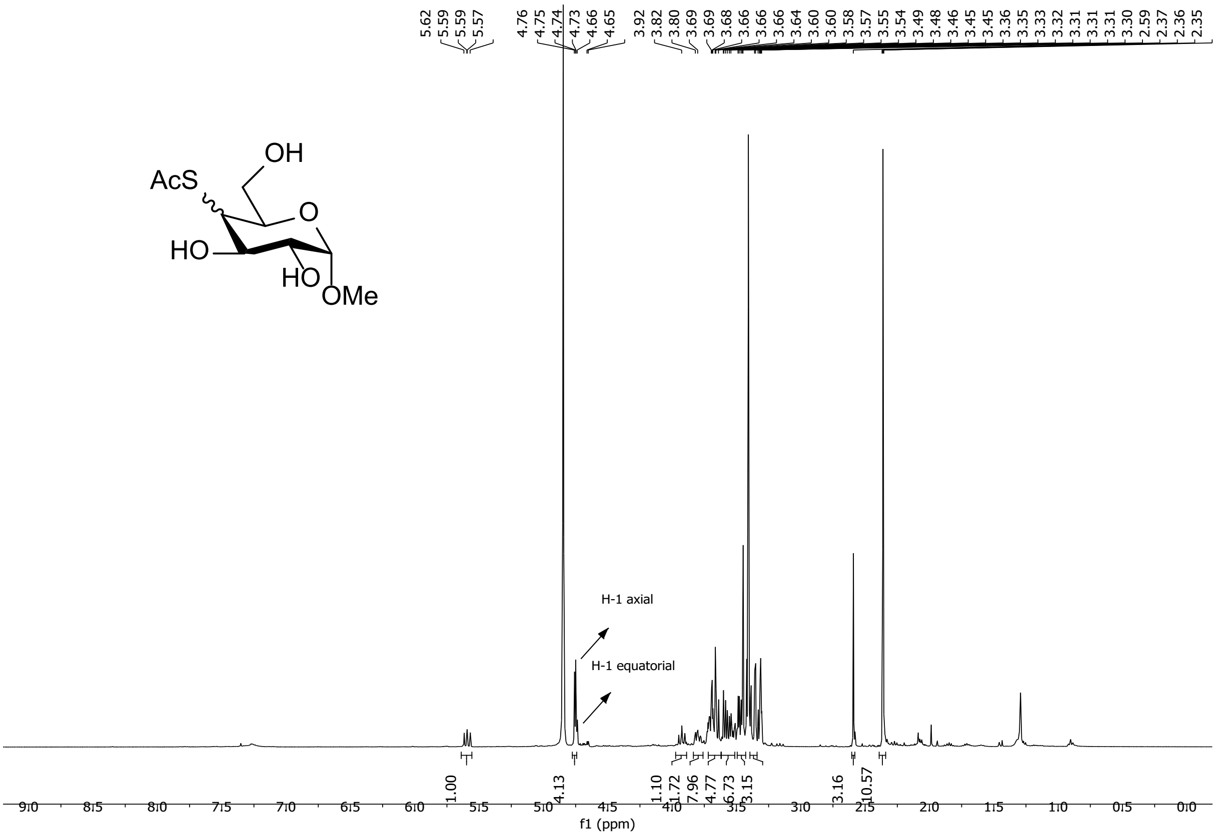
^{1}H-^{13}C HSQC of compound **8c**



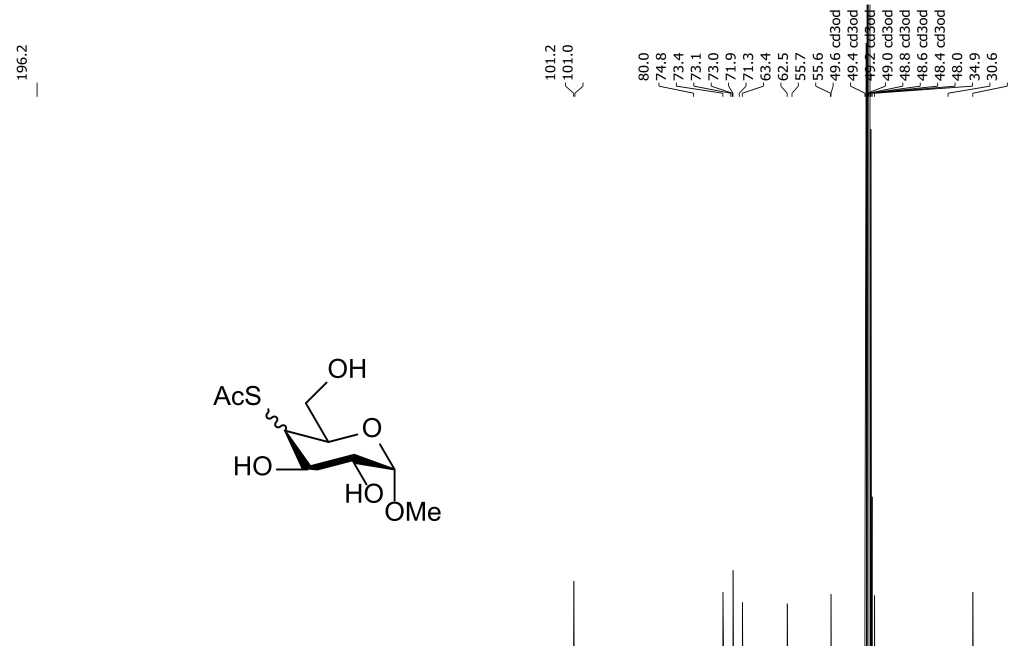
NMR spectra of Gal derivative and side product S10

Methyl 4-S-acetyl-4-deoxy-α-D-galacto/glucopyranoside (10)

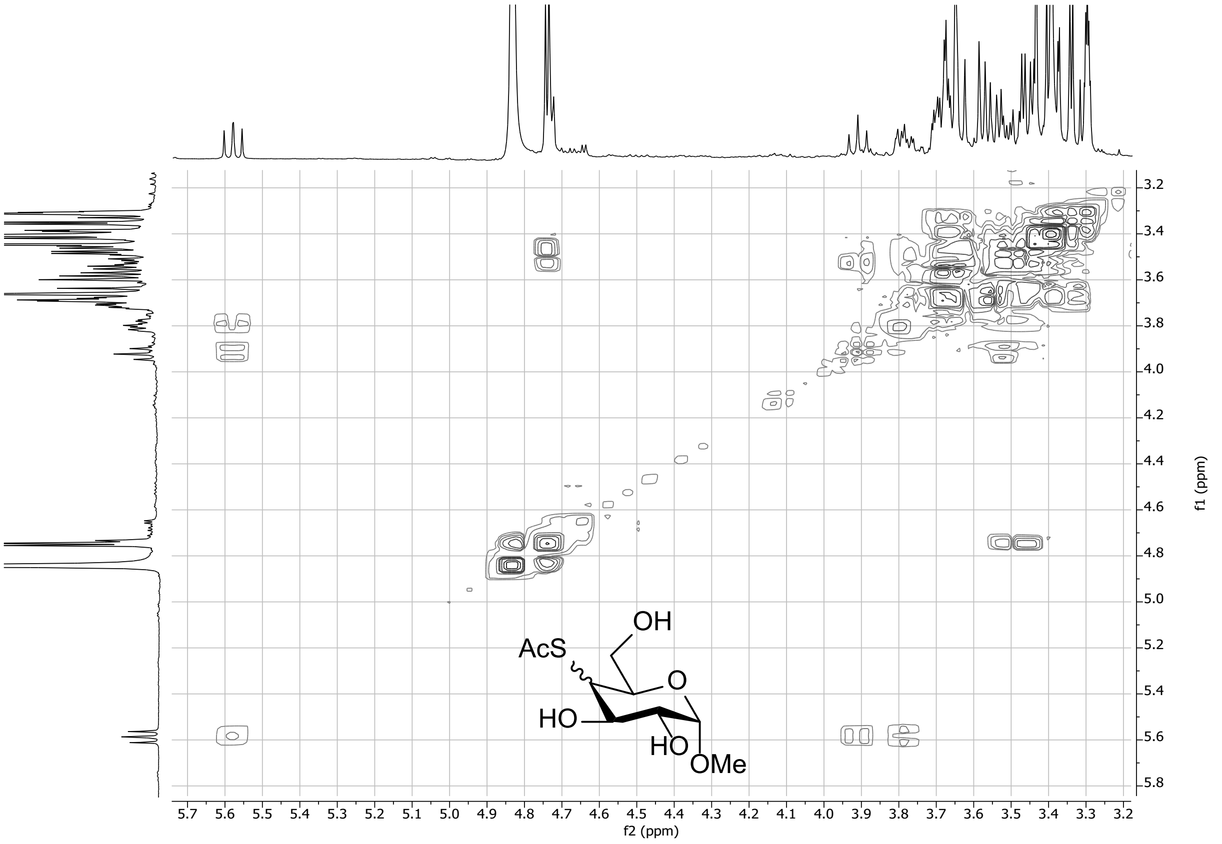
^{1}H NMR, 400 MHz, CD$_3$OD of compound **10**



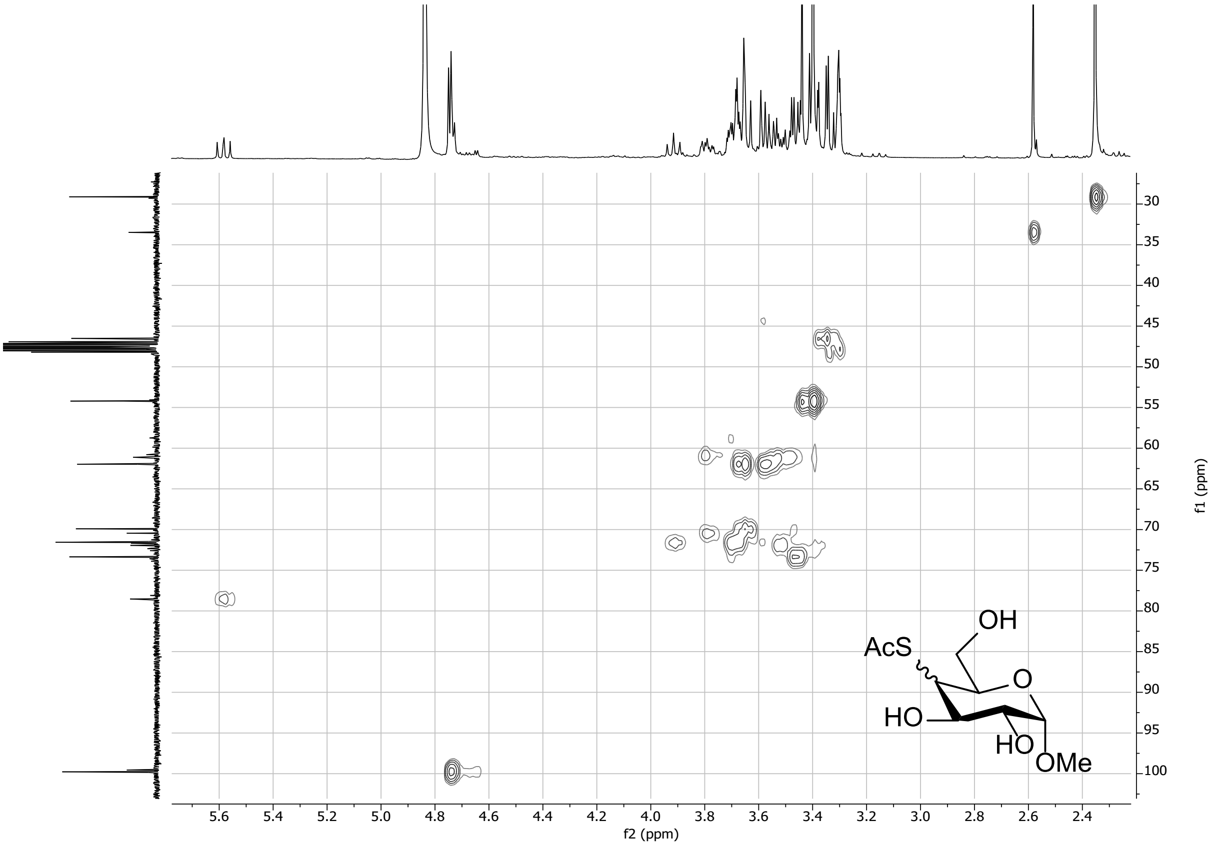
^{13}C NMR, 101 MHz, CD$_3$OD of compound **10**



^{1}H-^{1}H COSY of compound **10**

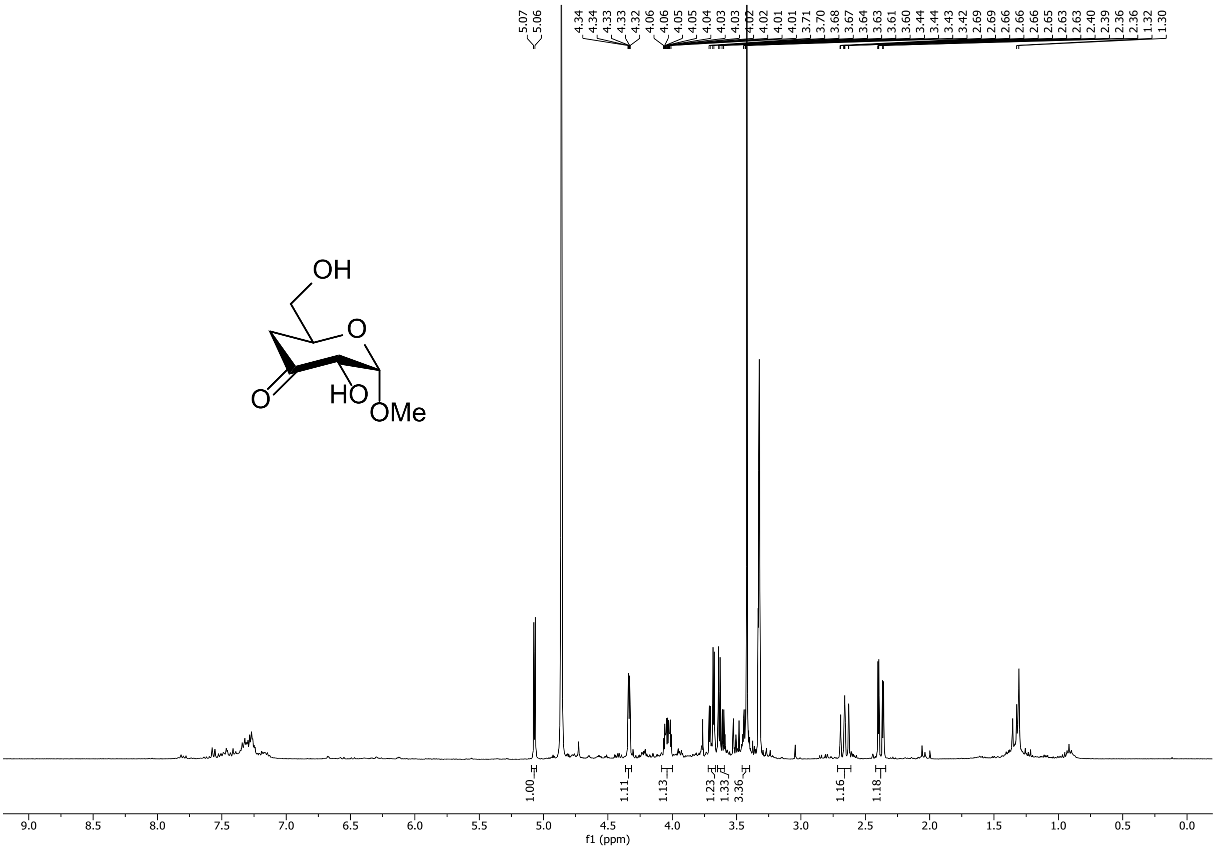


^{1}H-^{13}C HSQC of compound **10**

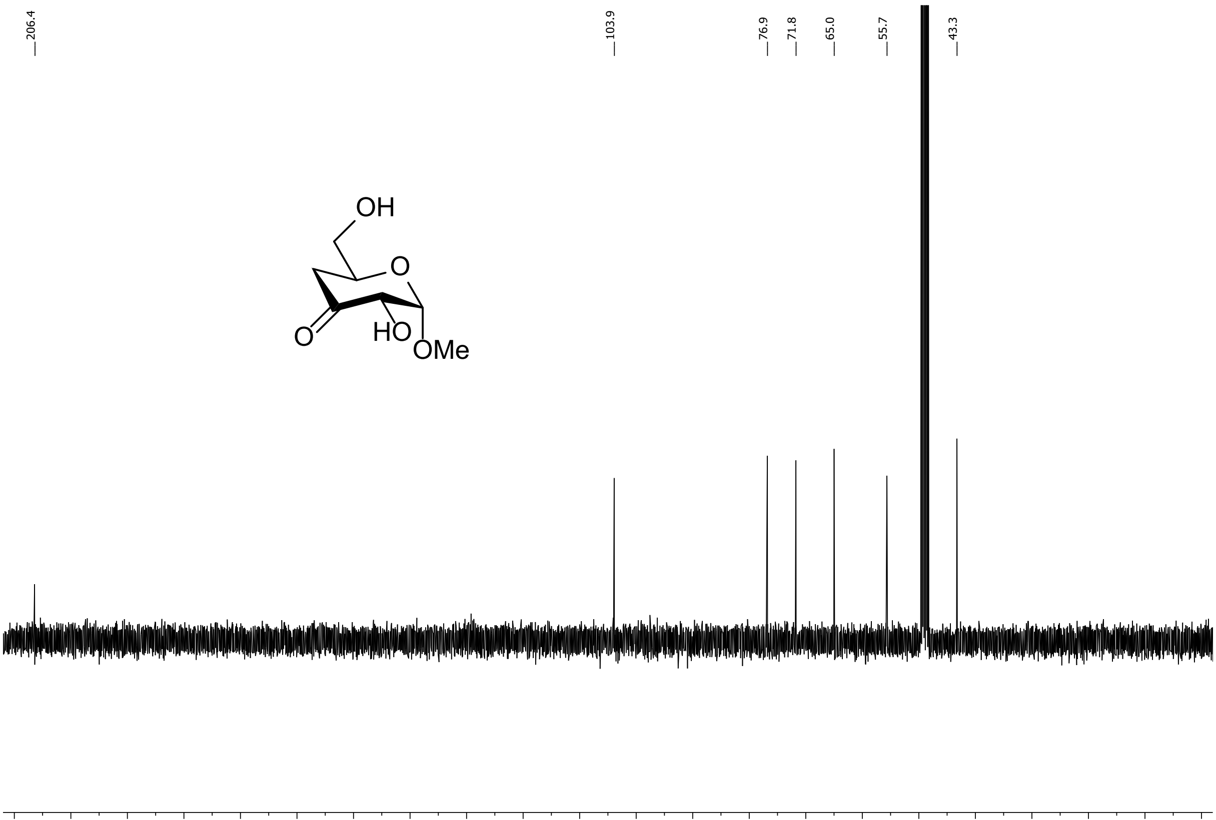


Methyl 3-keto-3,4-deoxy-α-D-glucopyranoside (S10)

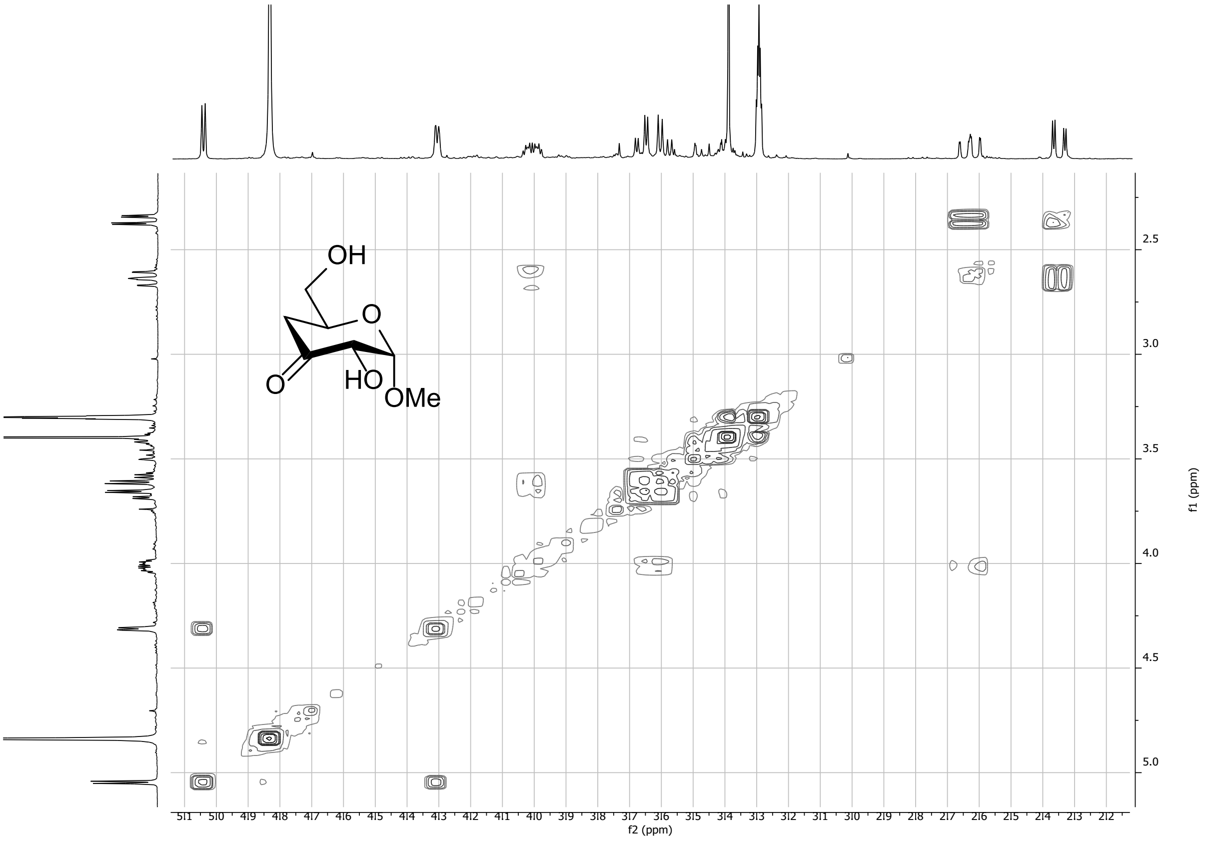
^{1}H NMR, 400 MHz, CD$_3$OD of compound **S10**



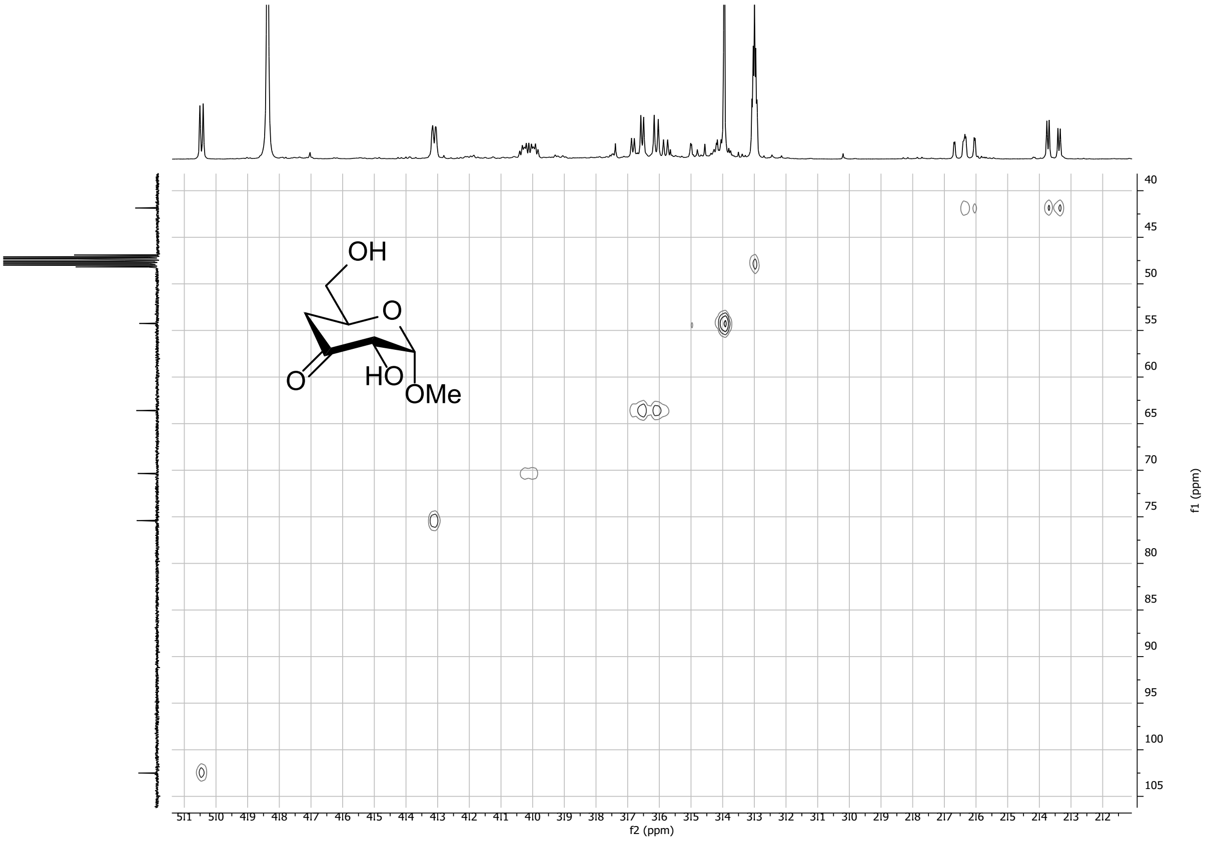
^{13}C NMR, 101 MHz, CD$_3$OD of compound **S10**



^{1}H-^{1}H COSY of compound **S10**



^{1}H-^{13}C HSQC of compound **S10**

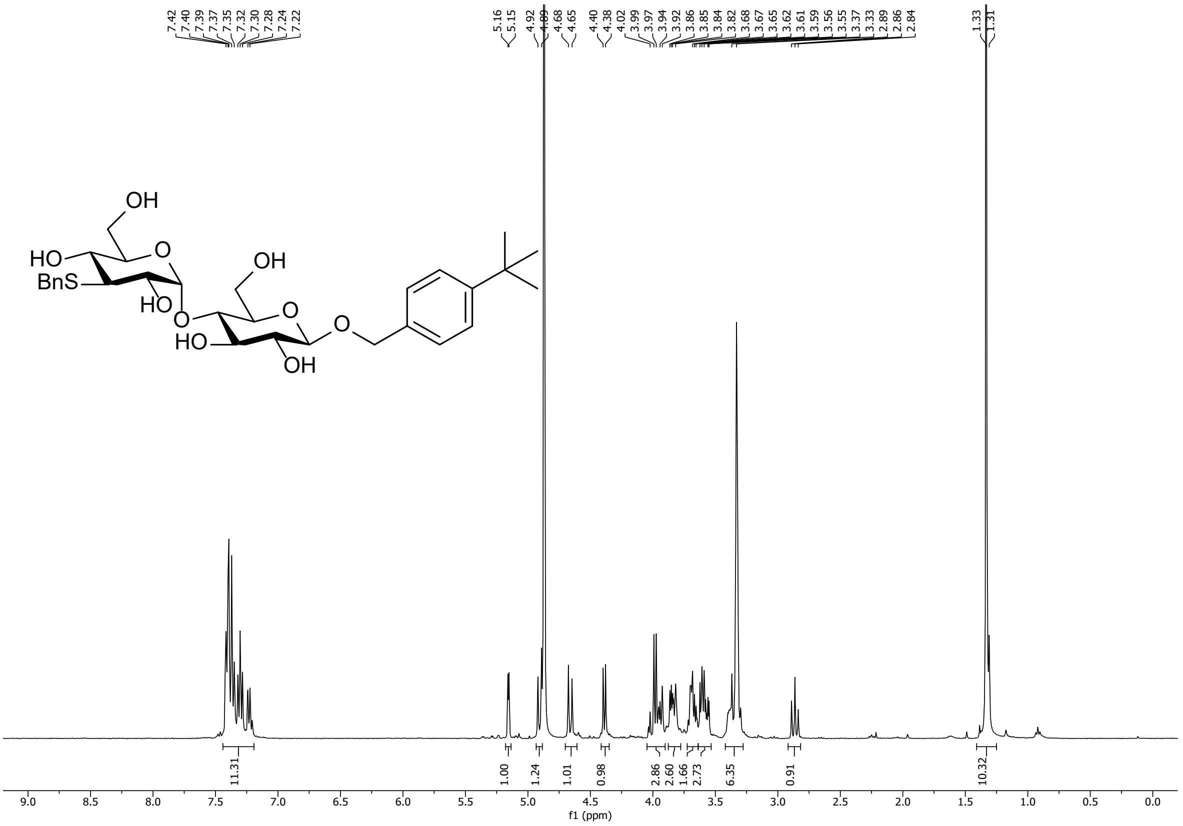


NMR spectra of maltose derivative

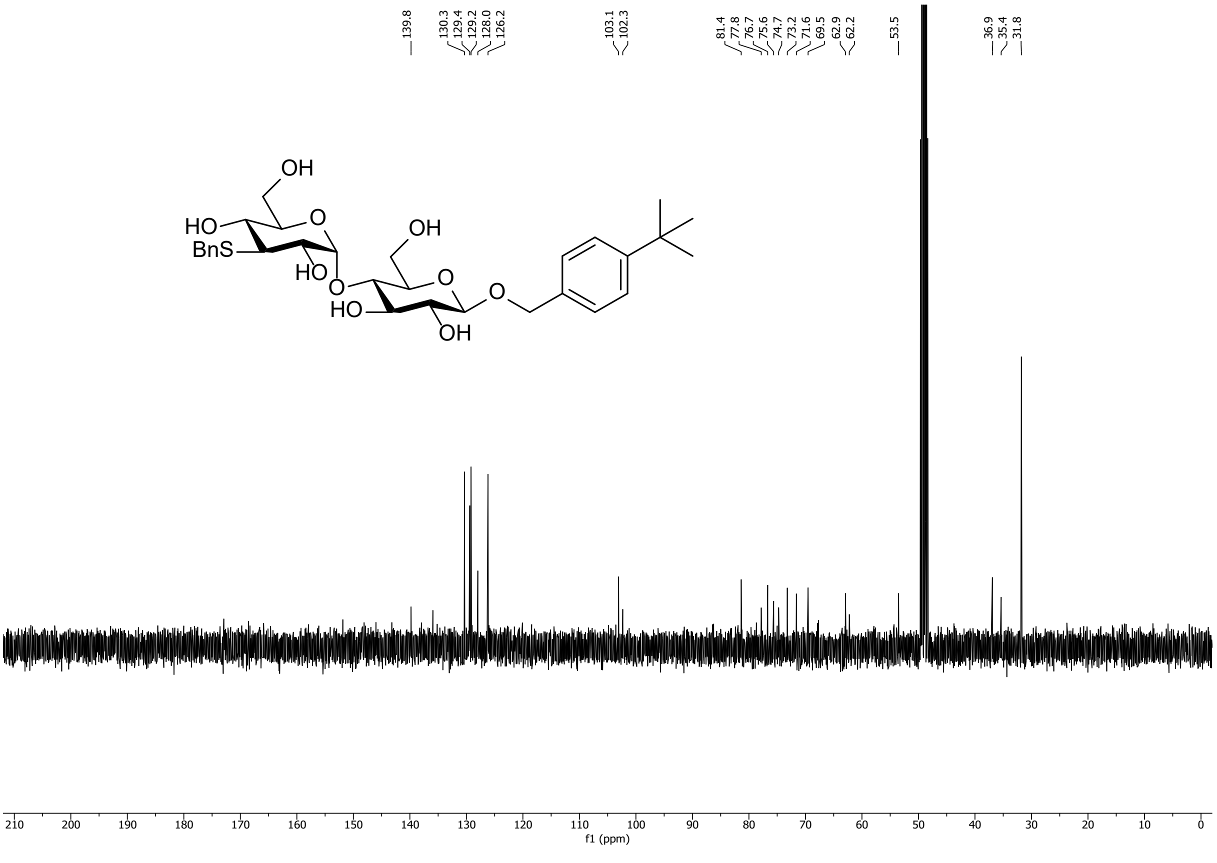
4-tert-butylbenzyl-3-S-benzyl-3-deoxy-α-D-maltoside (12)

Equatorial:

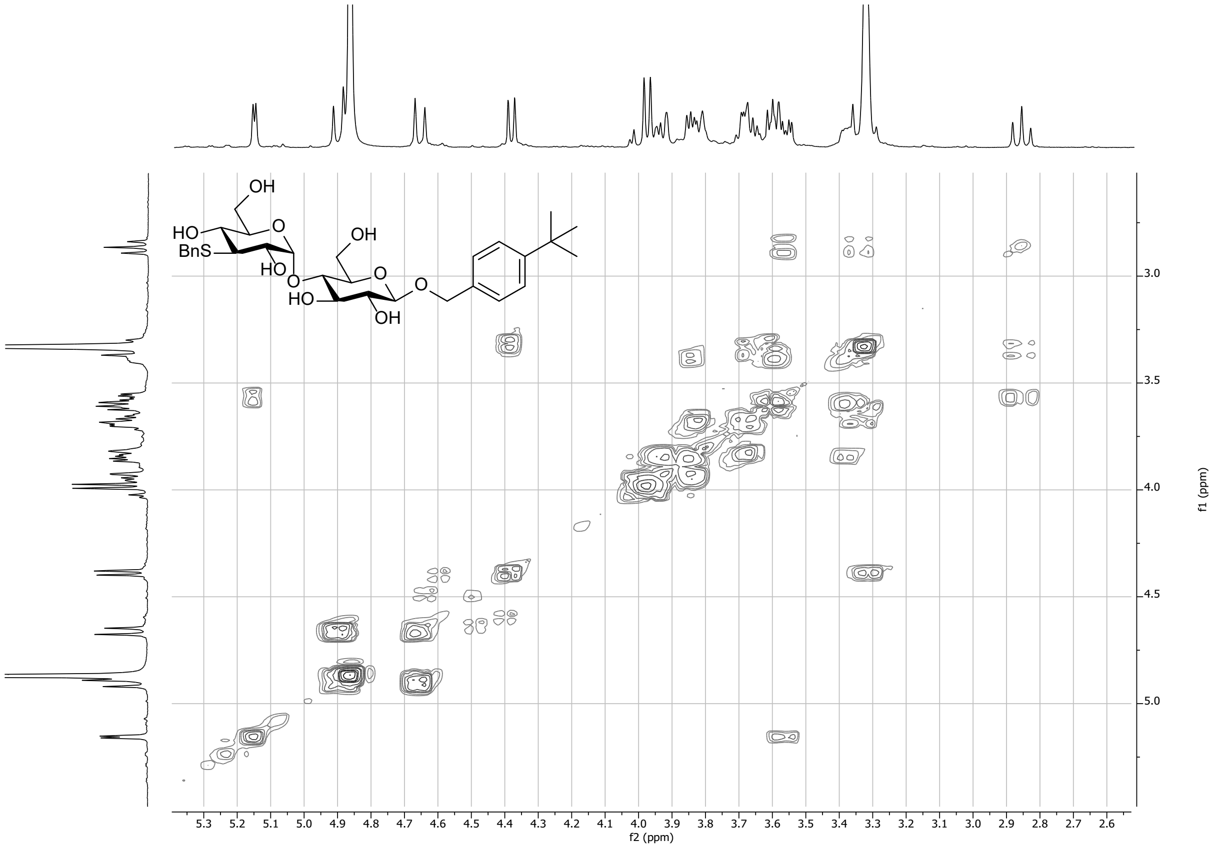
^{1}H NMR, 400 MHz, CD$_3$OD of compound **12**



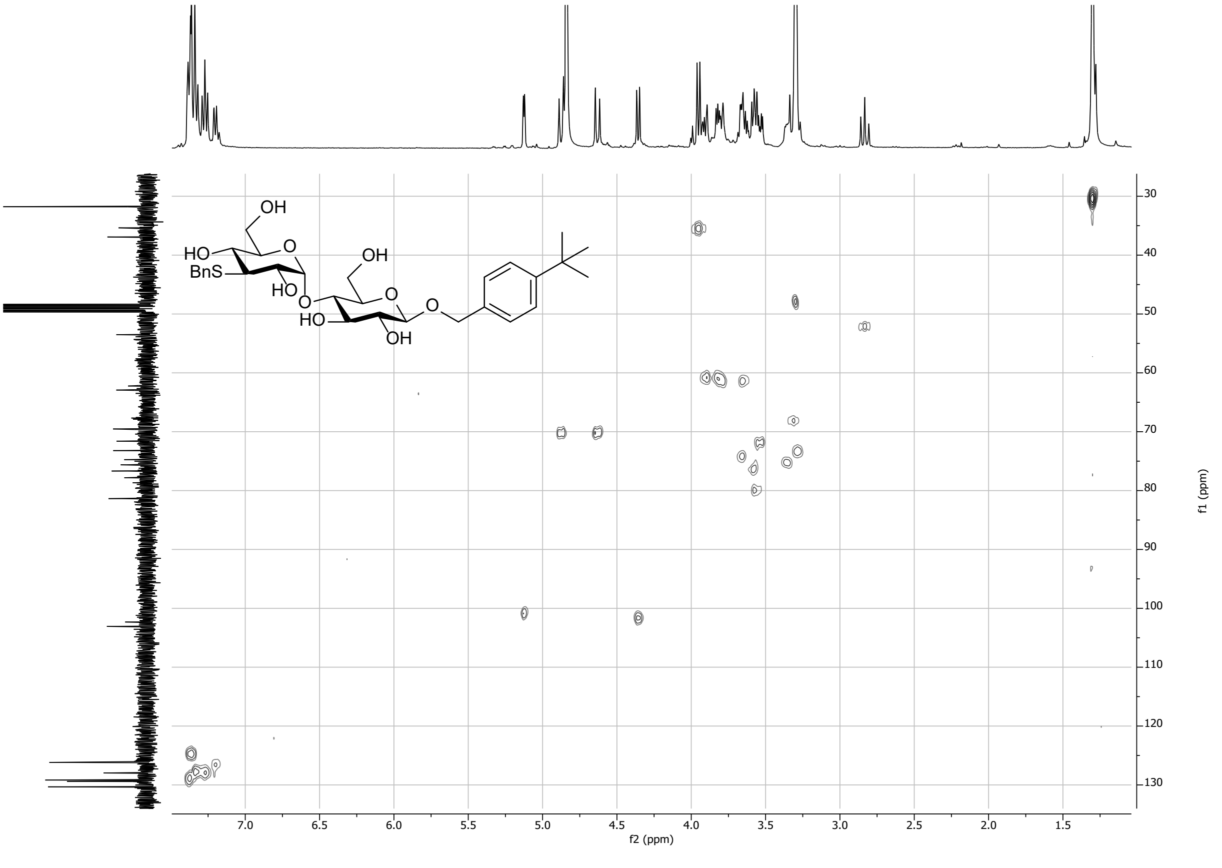
^{13}C NMR, 101 MHz, CD$_3$OD of compound **12**



^{1}H-^{1}H COSY of compound **12**

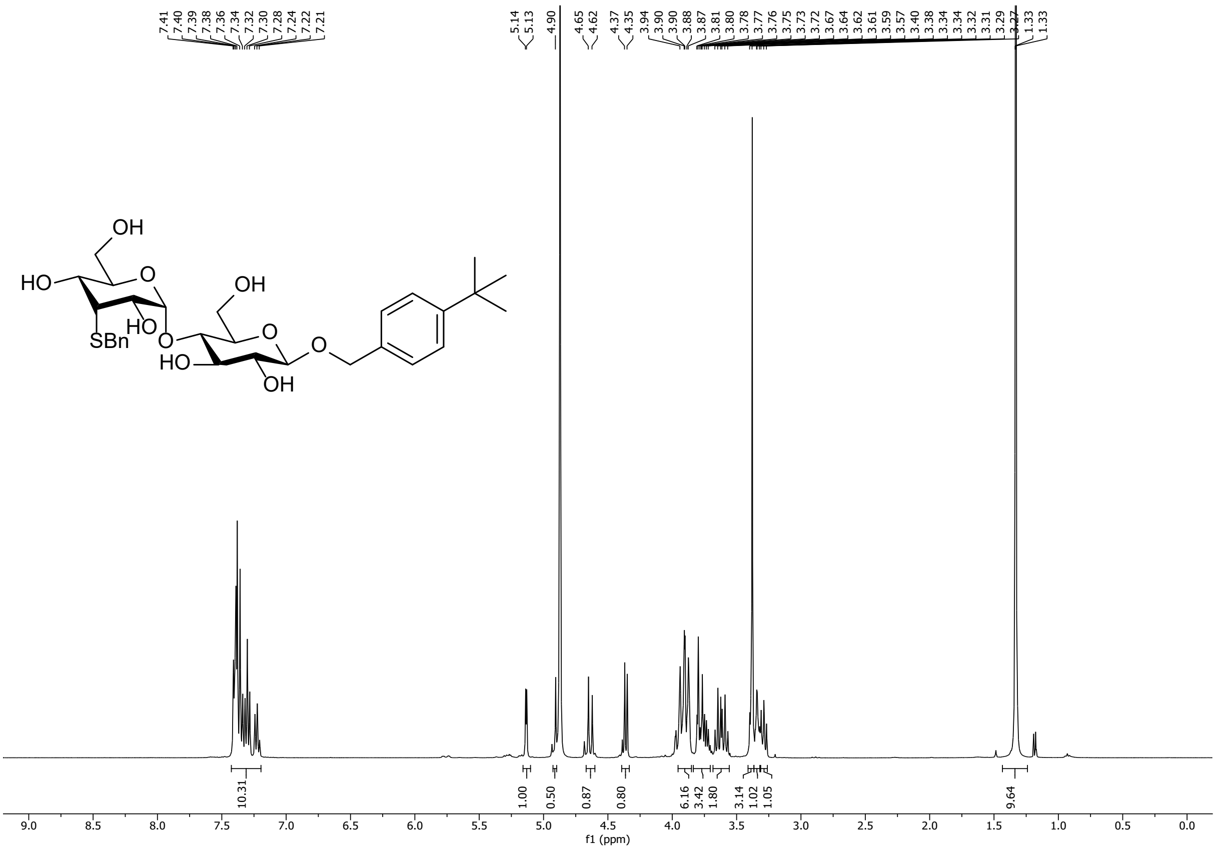


^{1}H-^{13}C HSQC of compound **12**

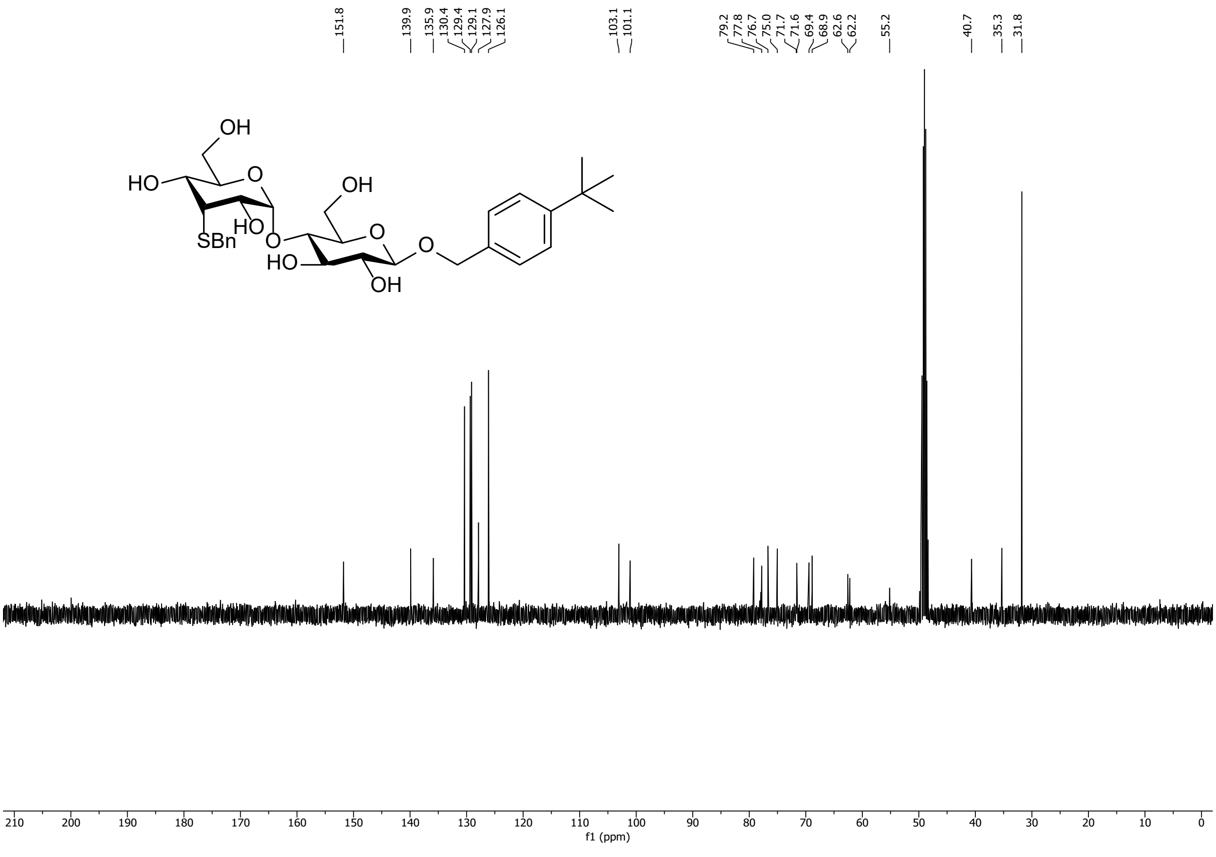


Axial:

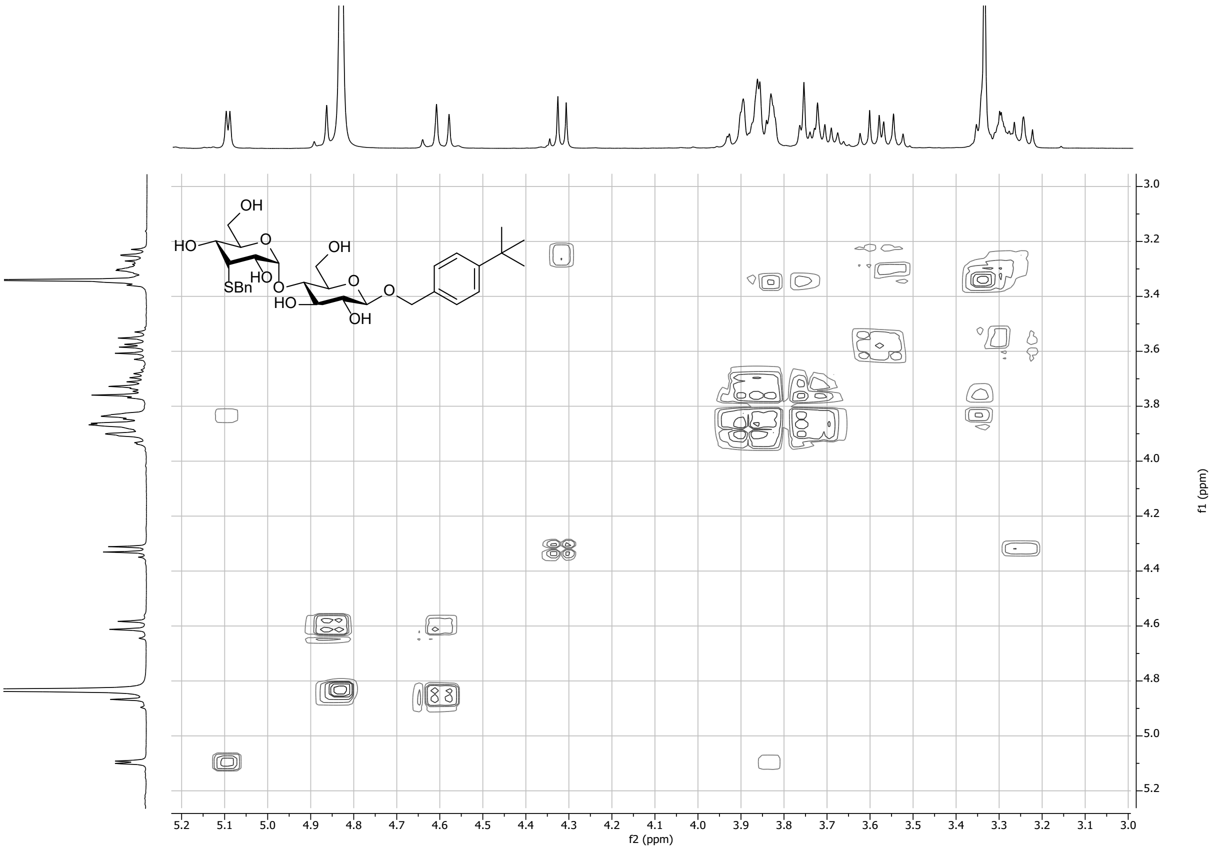
^{1}H NMR, 400 MHz, CD$_3$OD of compound **12**



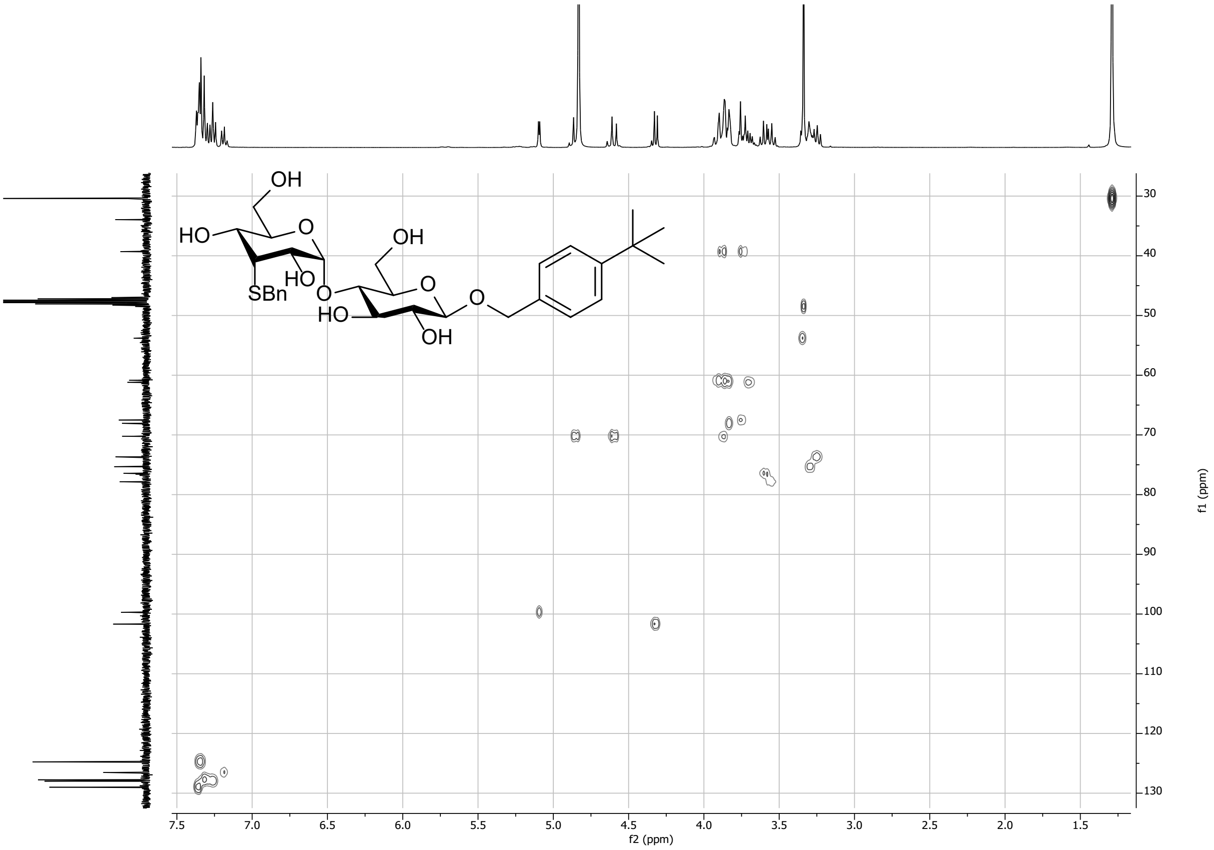
^{13}C NMR, 101 MHz, CD$_3$OD of compound **12**



^{1}H-^{1}H COSY of compound **12**



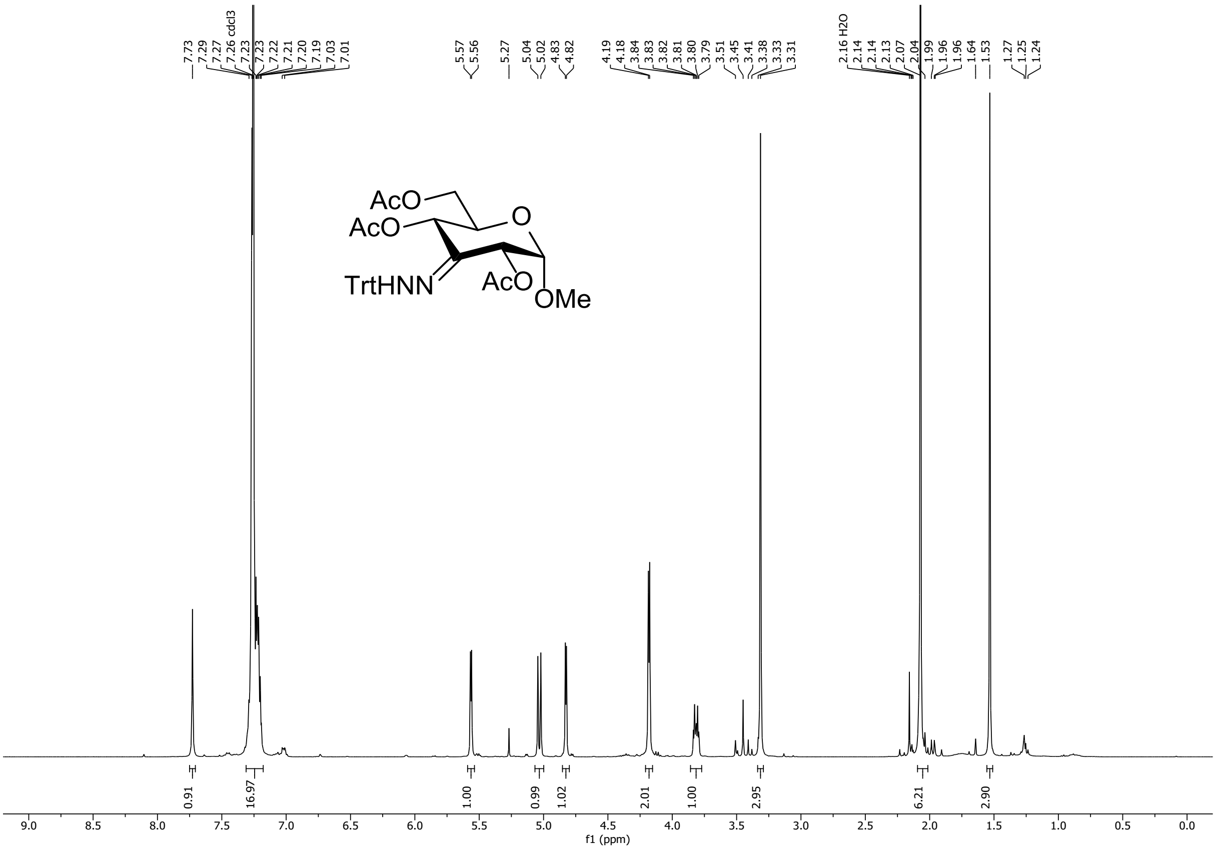
^{1}H-^{13}C HSQC of compound **12**



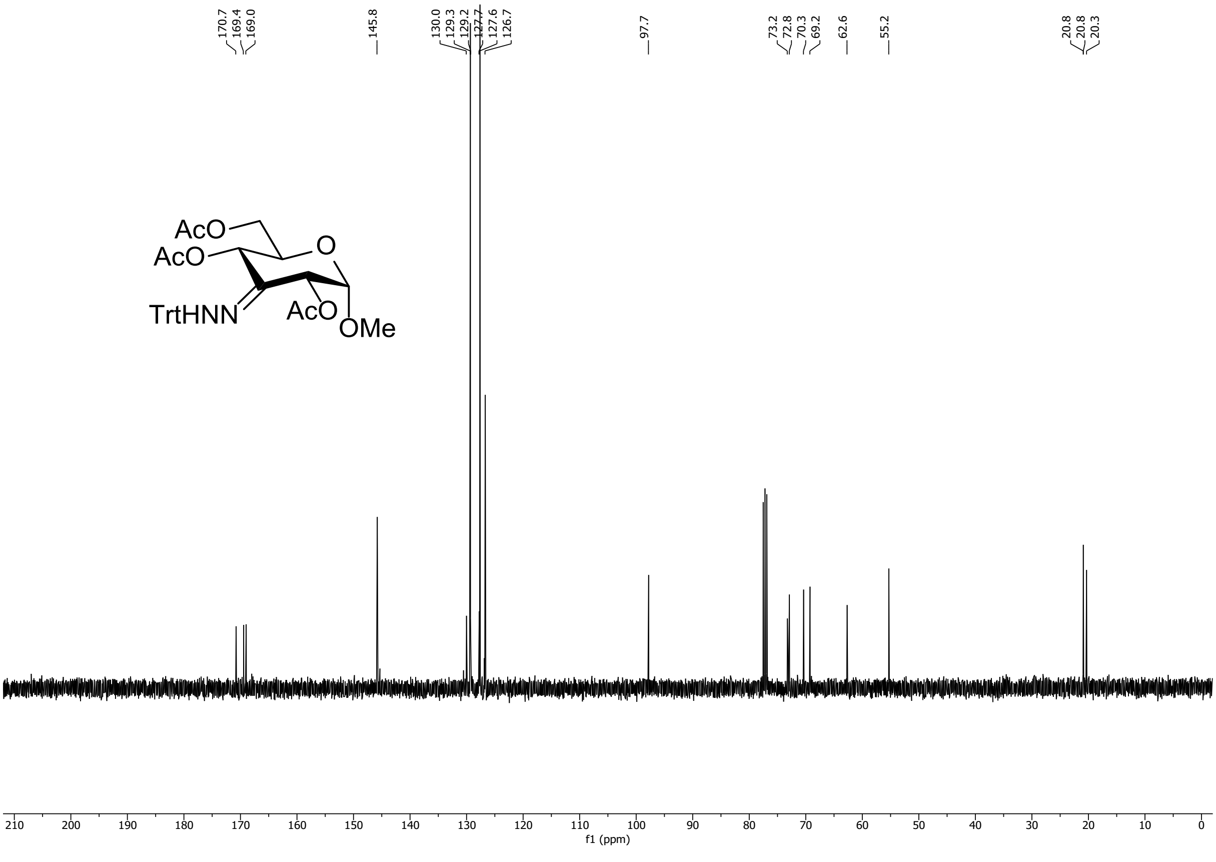
NMR spectra of S13 and S14

Methyl-2,4,6-O-acetyl-3-(trityl)hydrazone)-α-D-glucopyranoside (S13)

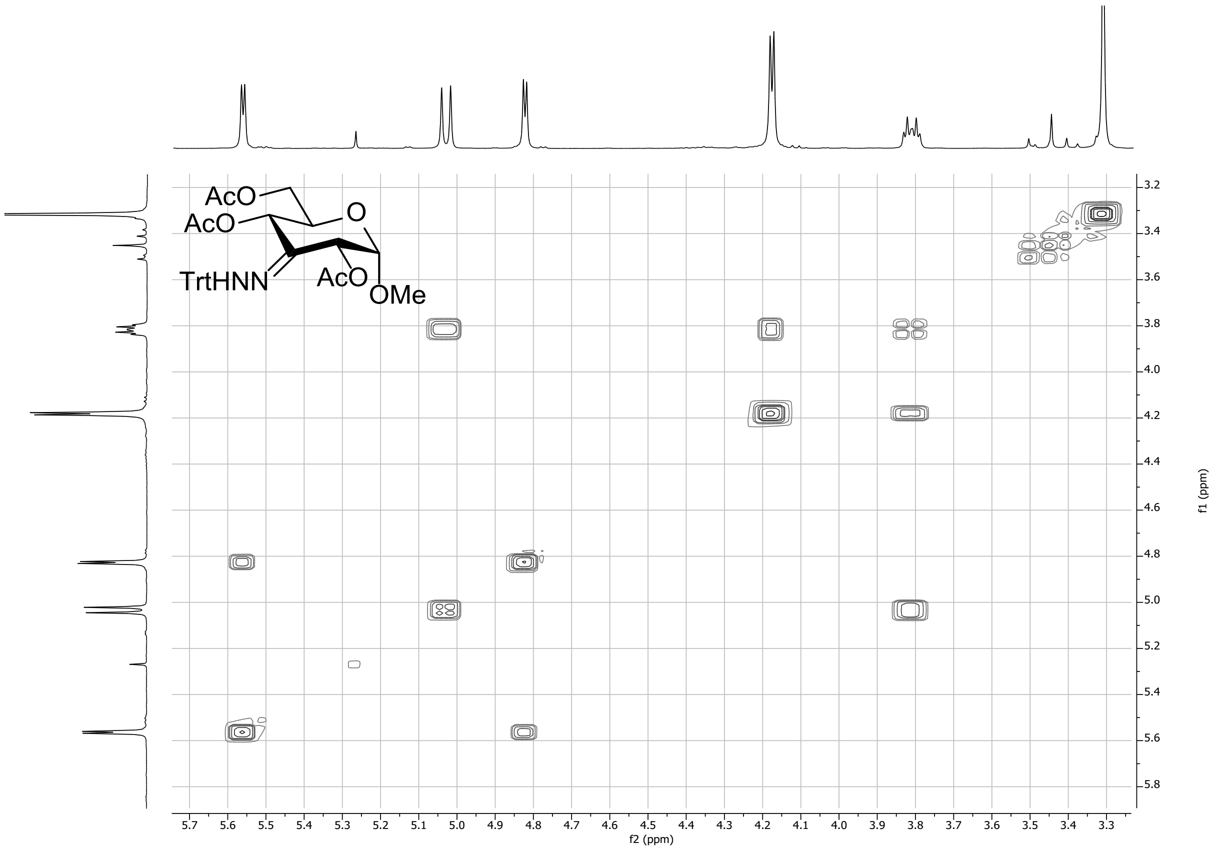
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S13**



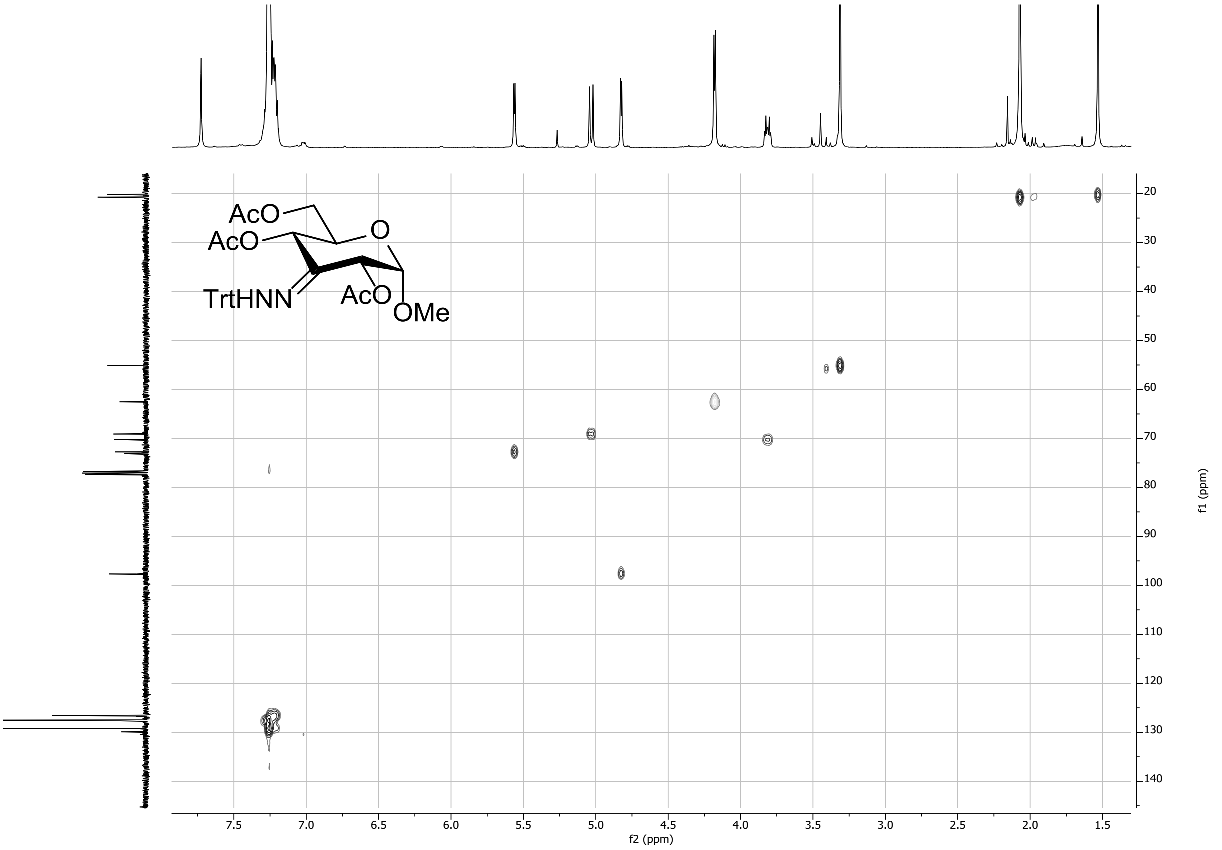
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S13**



^{1}H-^{1}H COSY of compound **S13**



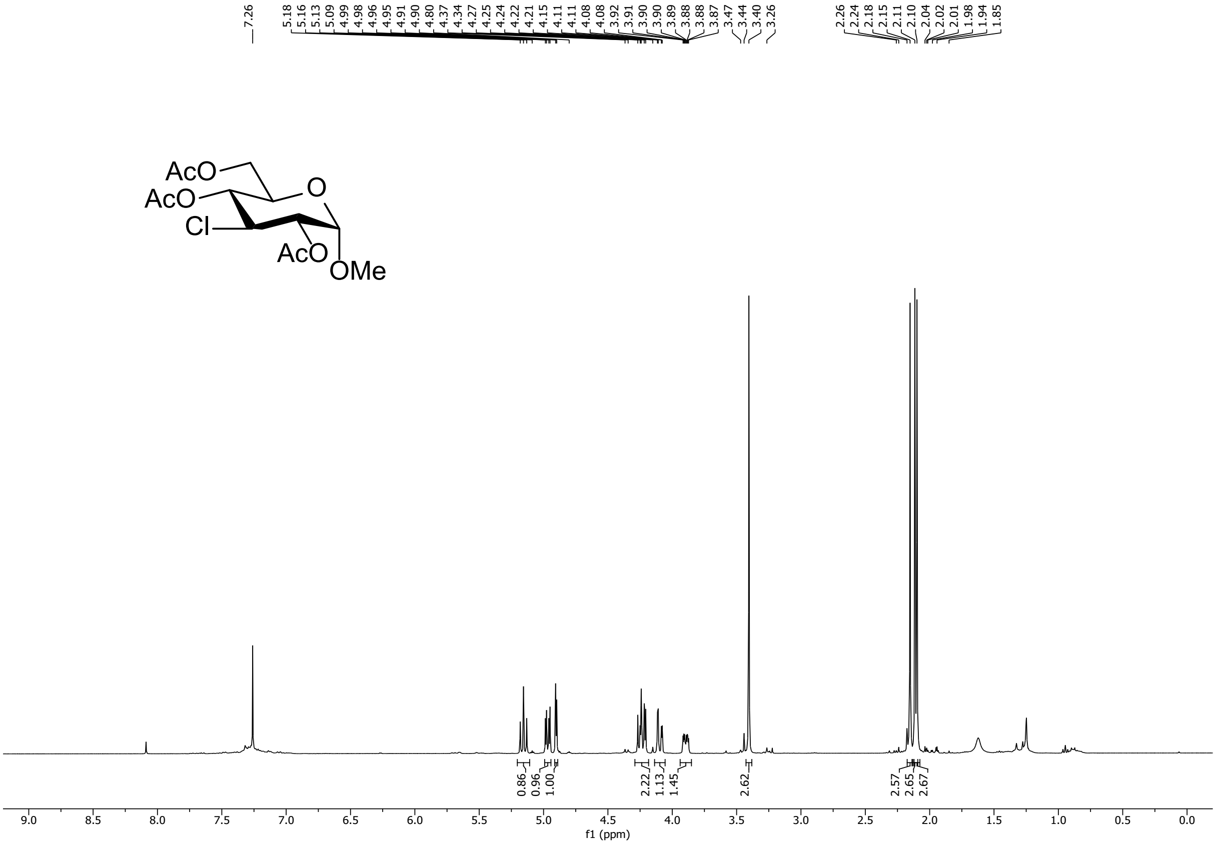
^{1}H-^{13}C HSQC of compound **S13**



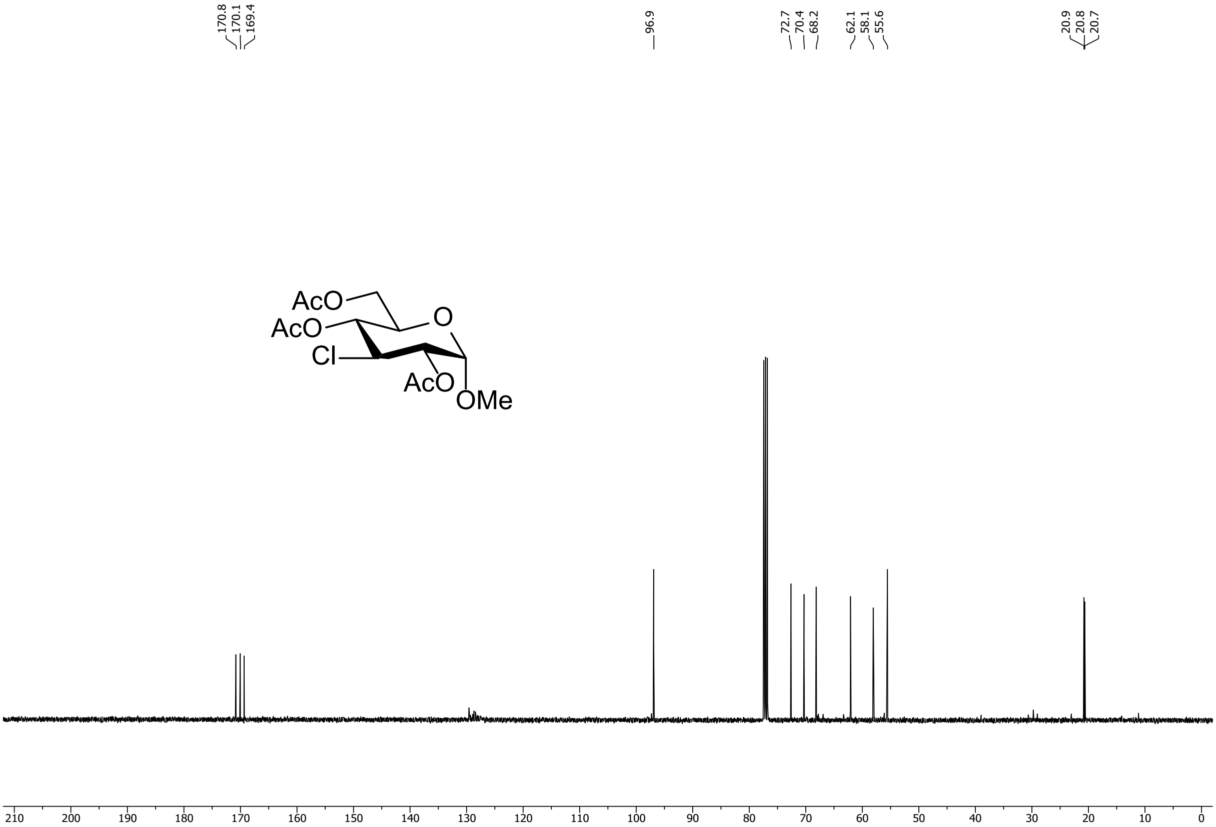
Methyl 2,4,6-tri-O-acetyl-3-chloro-3-deoxy-α-D-allo/glucopyranoside (S14)

Equatorial:

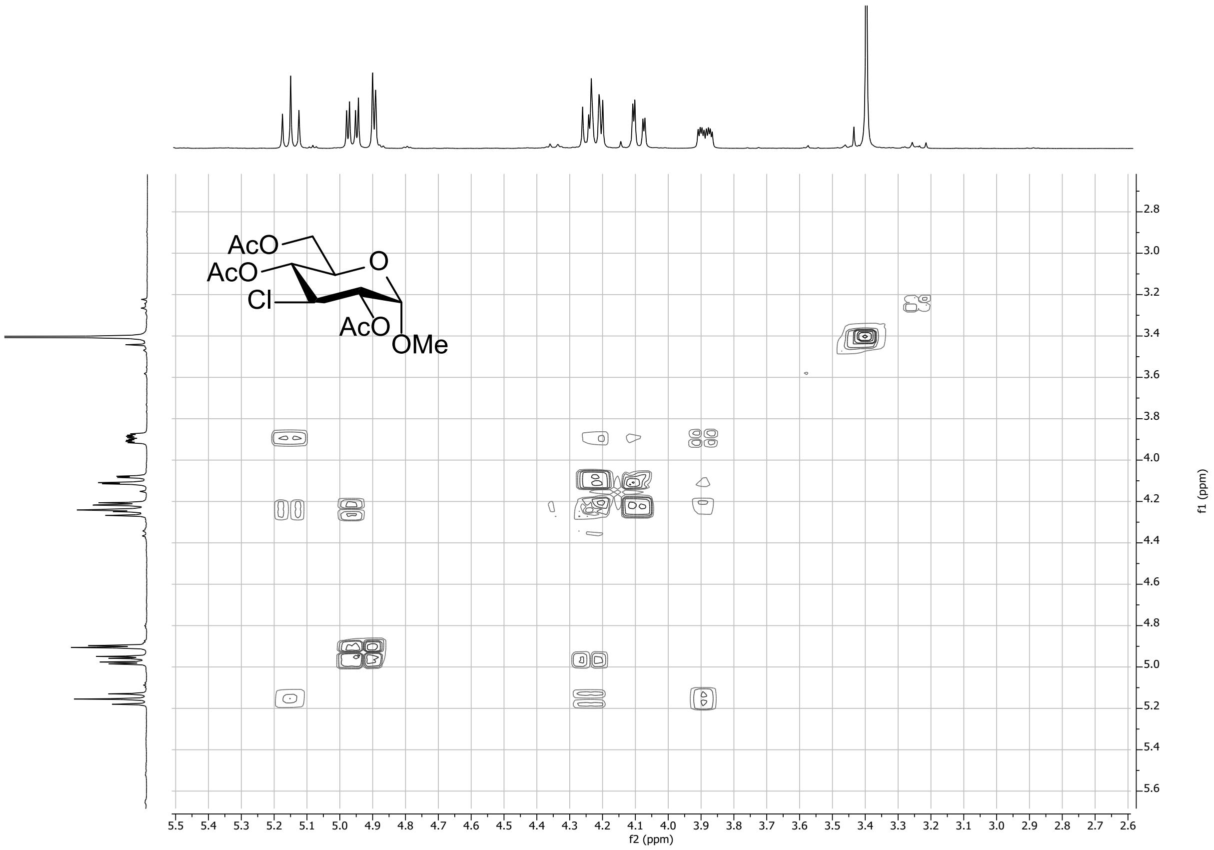
^{1}H NMR, 400 MHz, CDCl$_3$ of compound **S14**



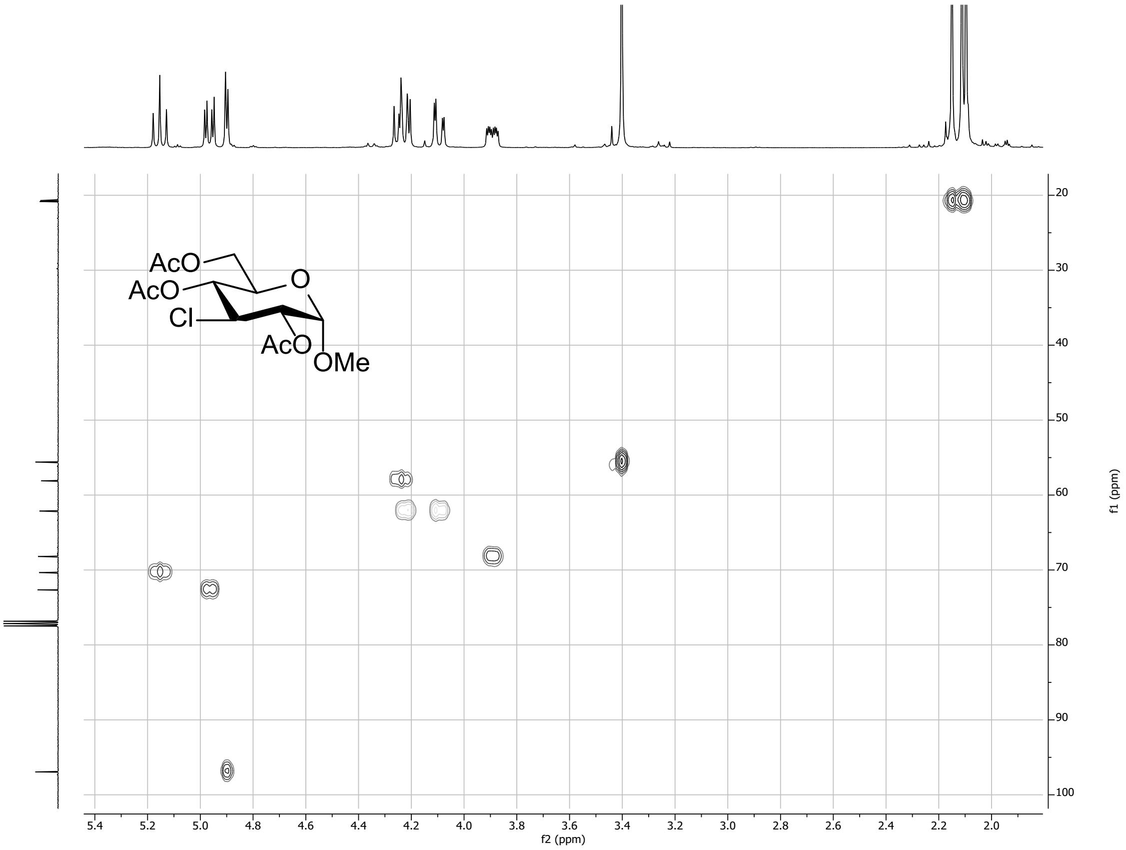
^{13}C NMR, 101 MHz, CDCl$_3$ of compound **S14**



^{1}H-^{1}H COSY of compound **S14**

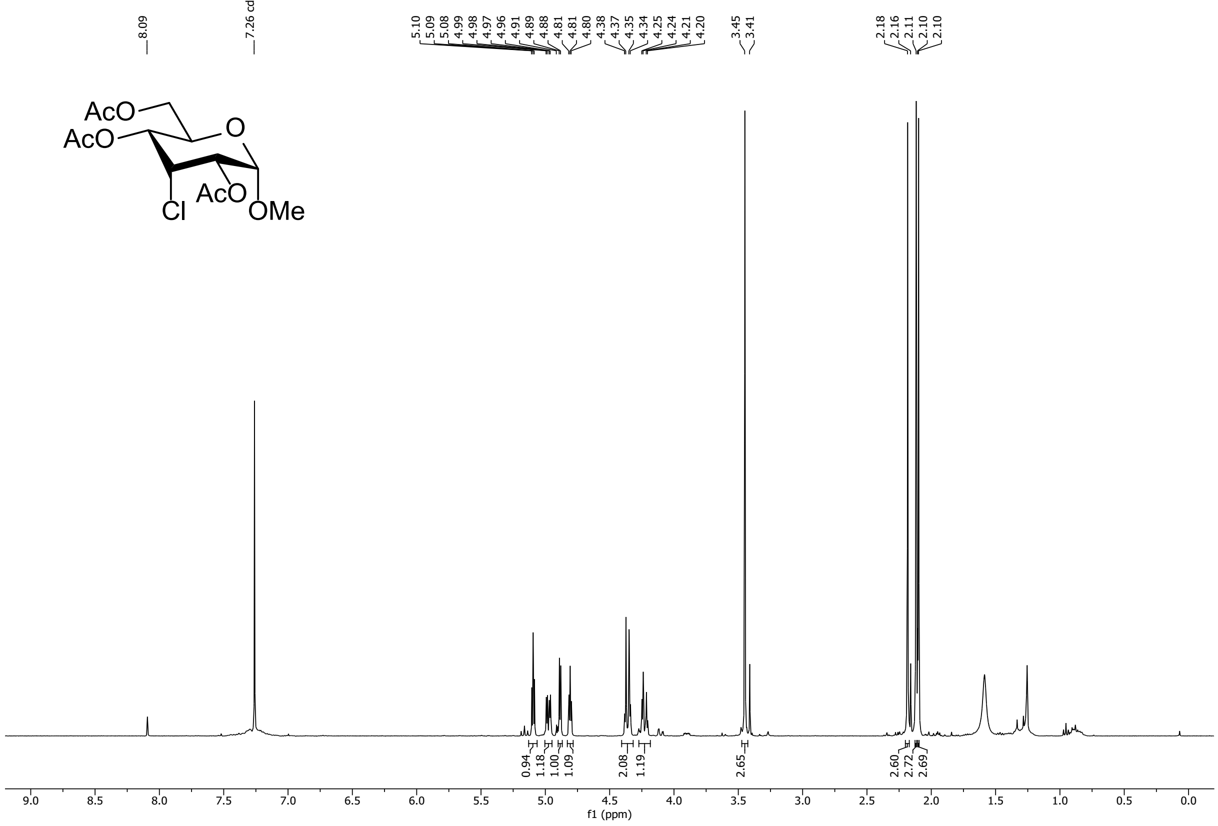


^{1}H-^{13}C HSQC of compound **S14**

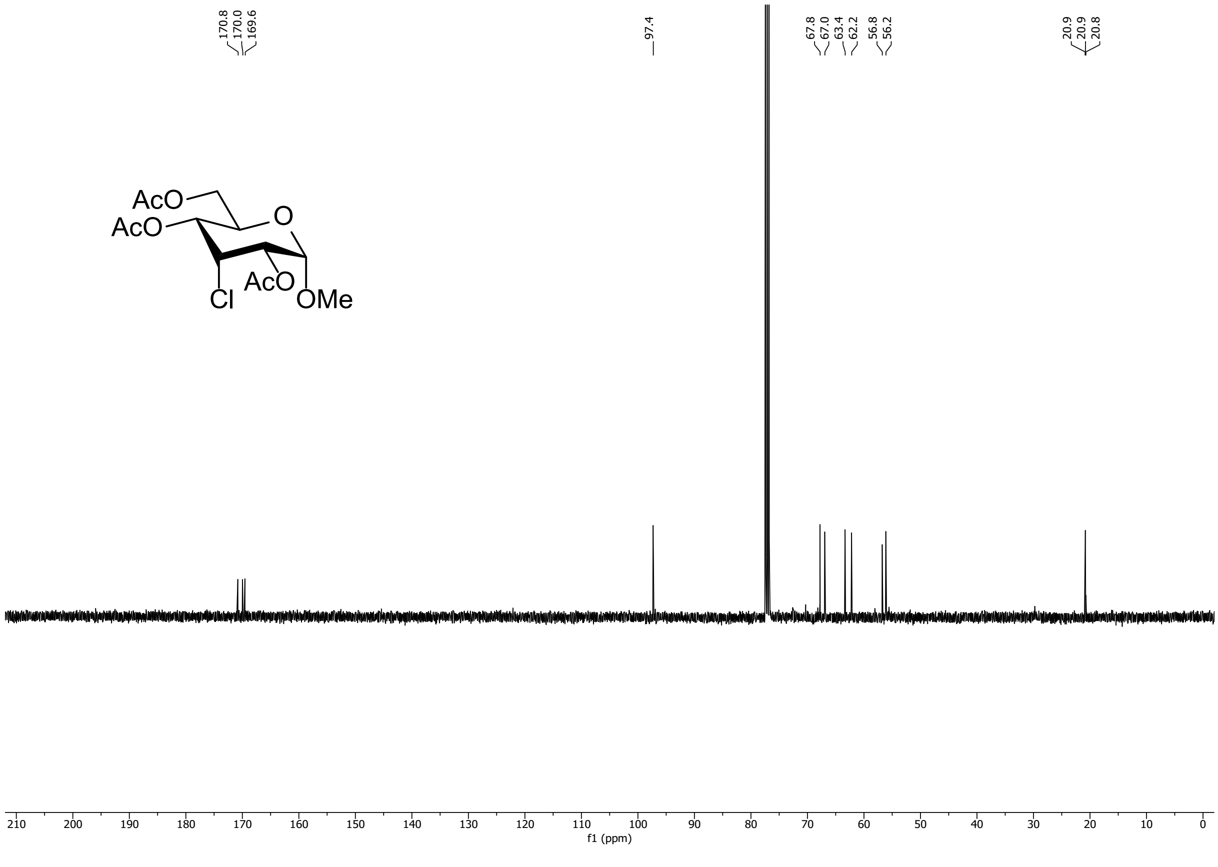


Axial:

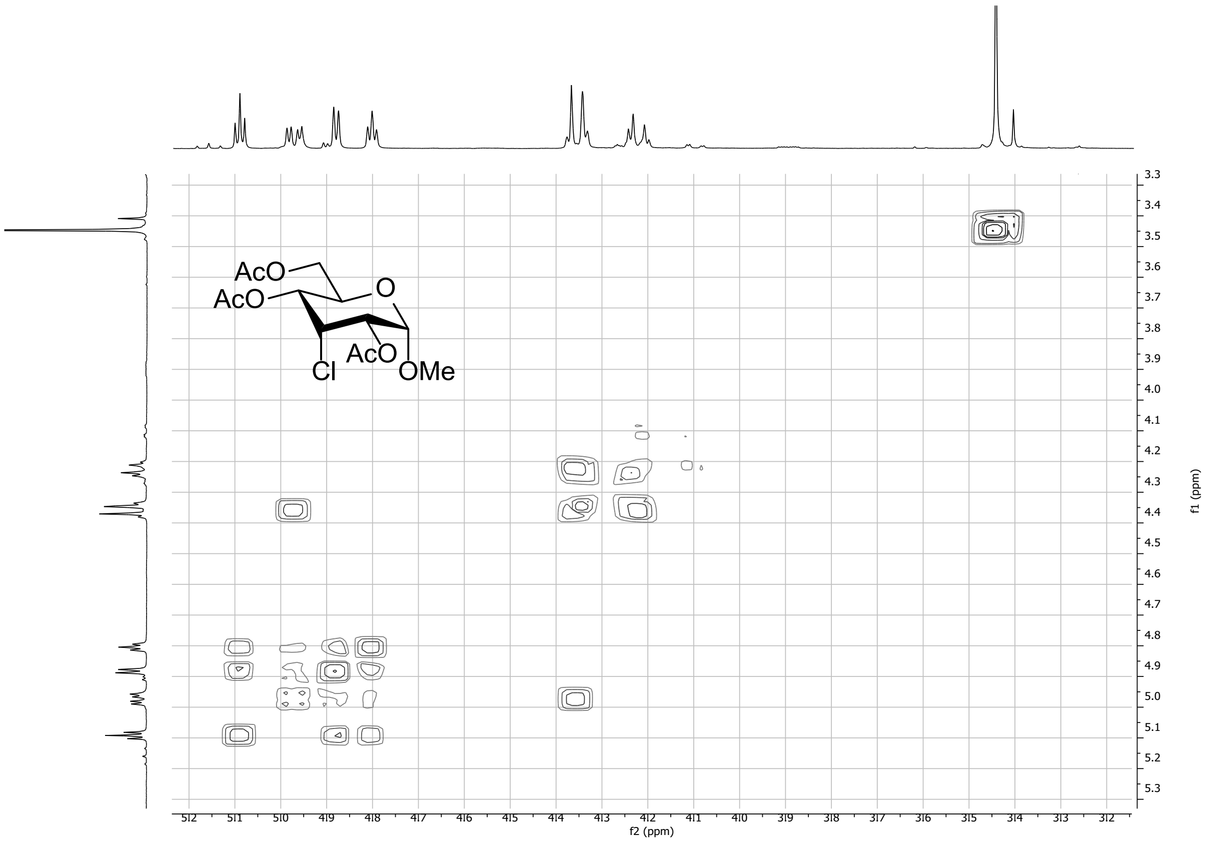
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S14**



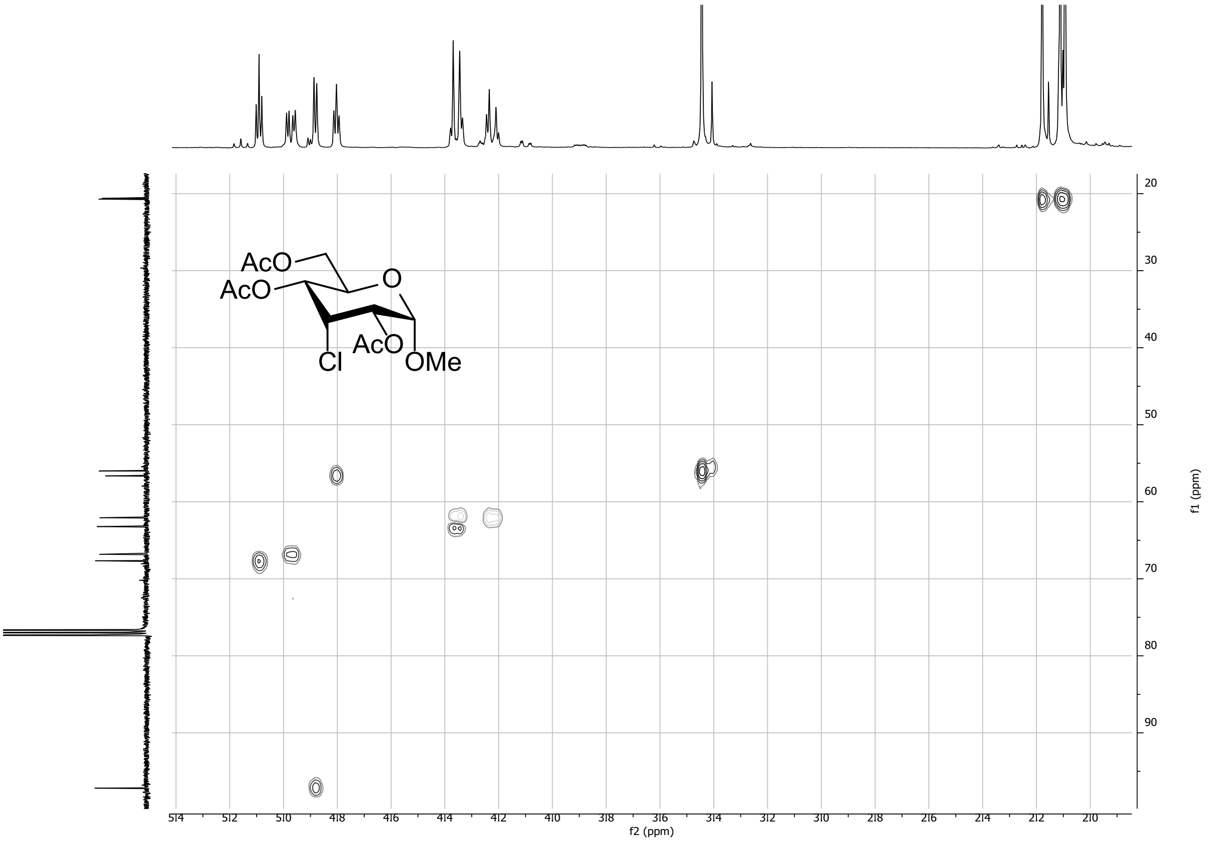
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S14**



^{1}H-^{1}H COSY of compound **S14**



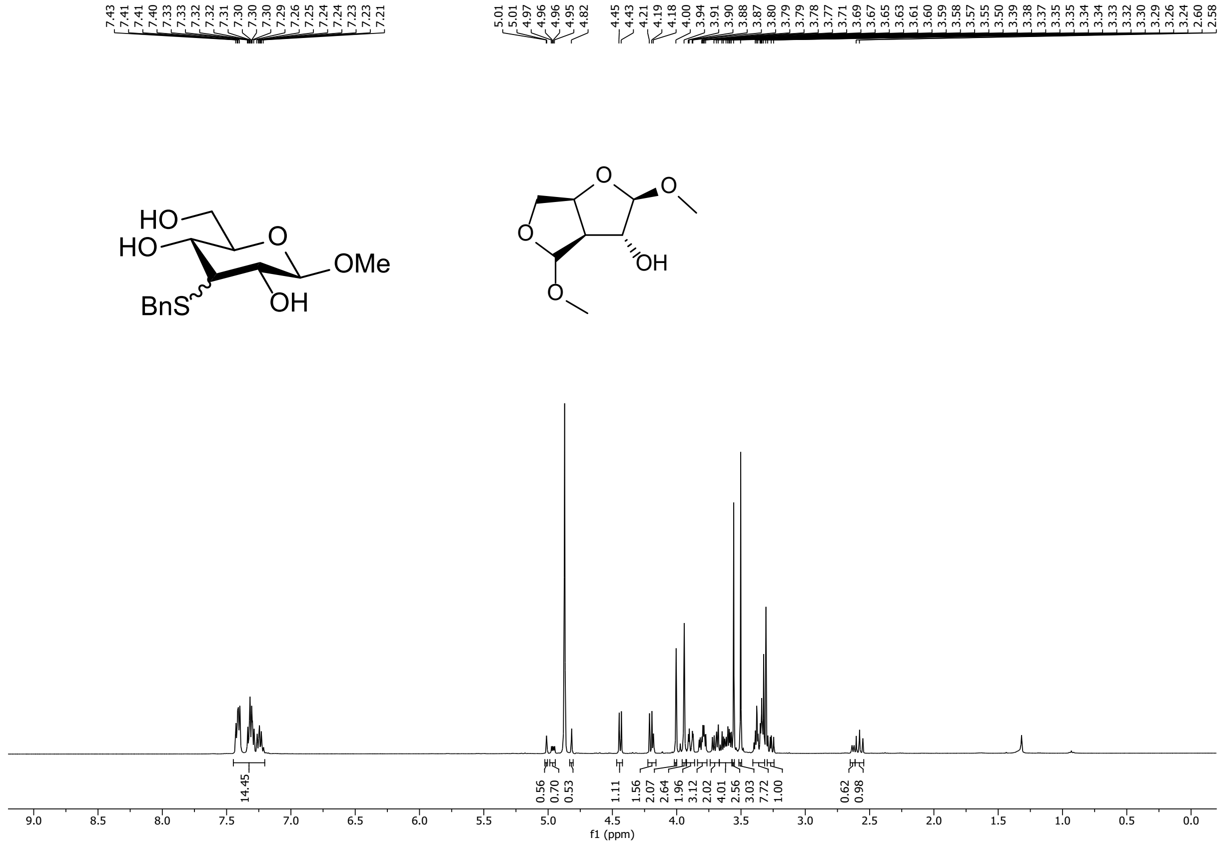
^{1}H-^{13}C HSQC of compound **S14**

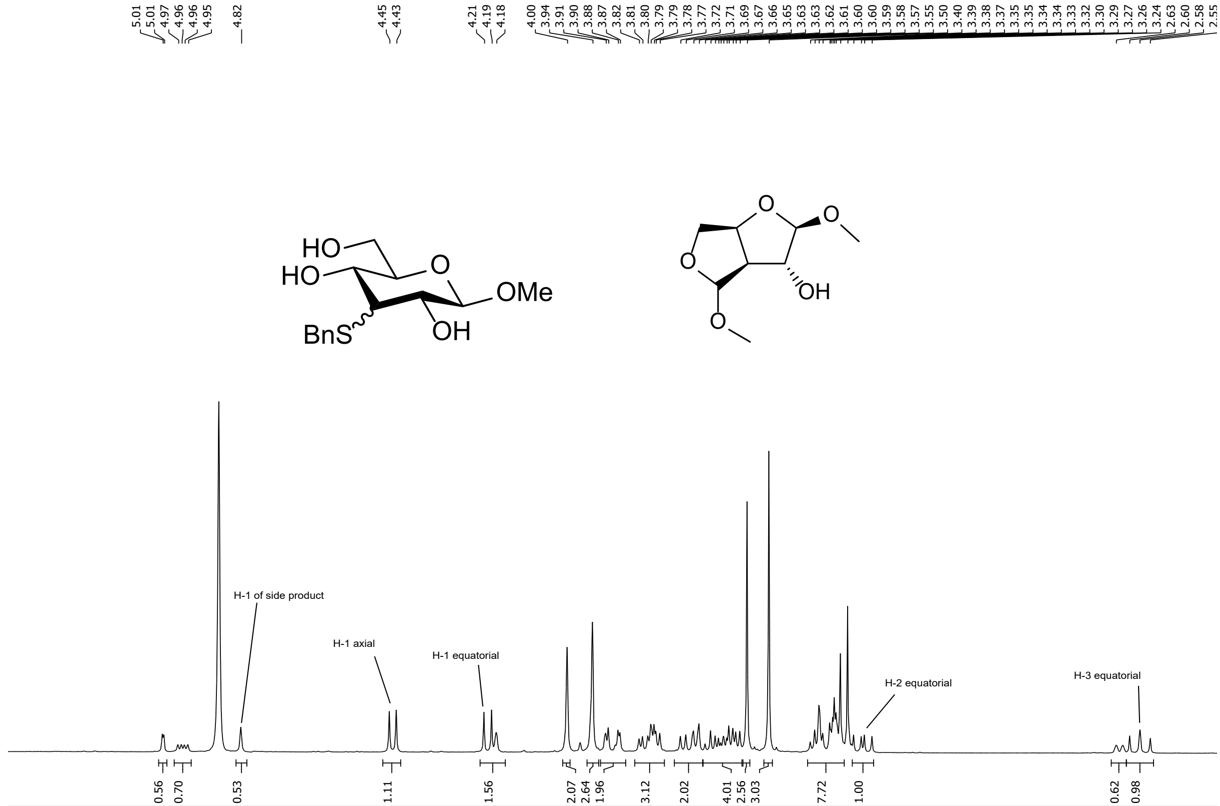


NMR spectra of β-glucose derivative and sideproduct S15

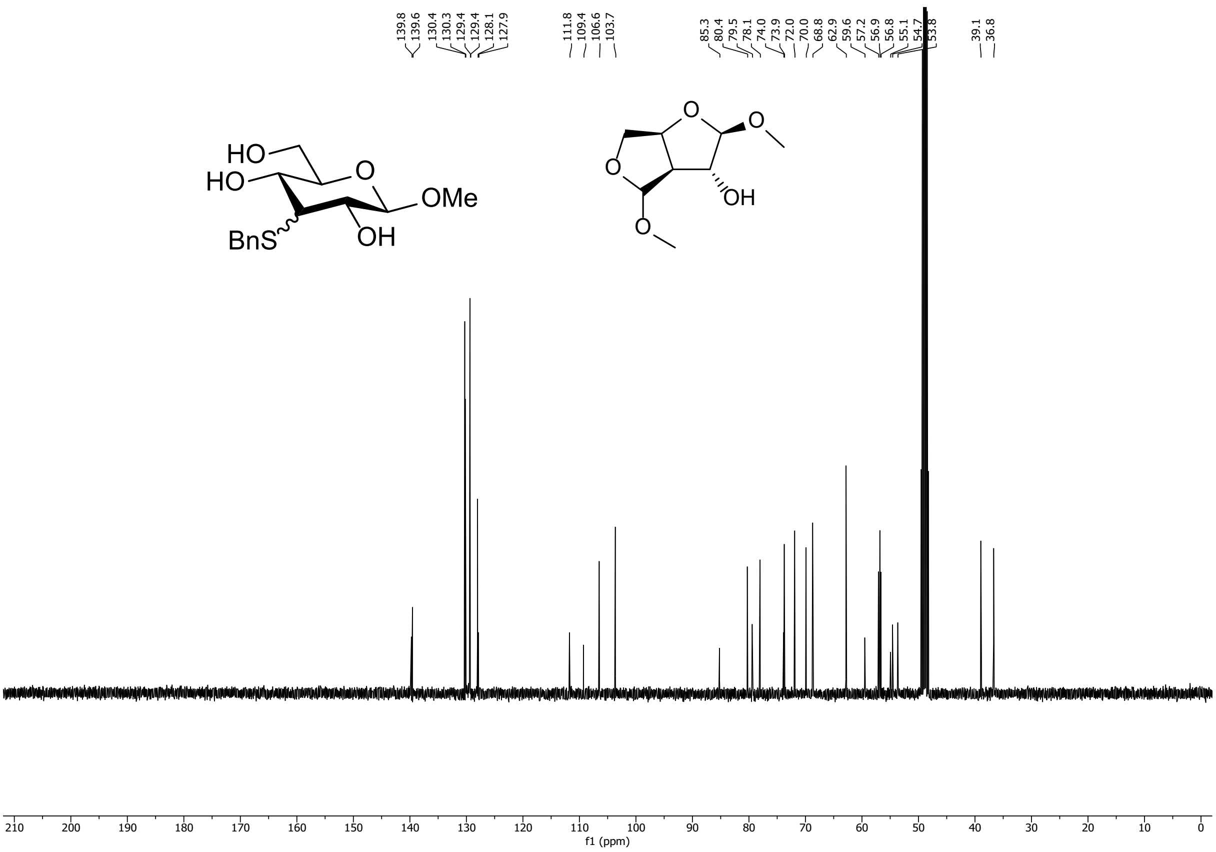
Methyl 3-S-benzyl-3-deoxy-β-ᴅ-allo/glucopyranoside (14) and sideproduct (S15)

^{1}H NMR, 400 MHz, CD$_3$OD of compounds **14** and **S15**

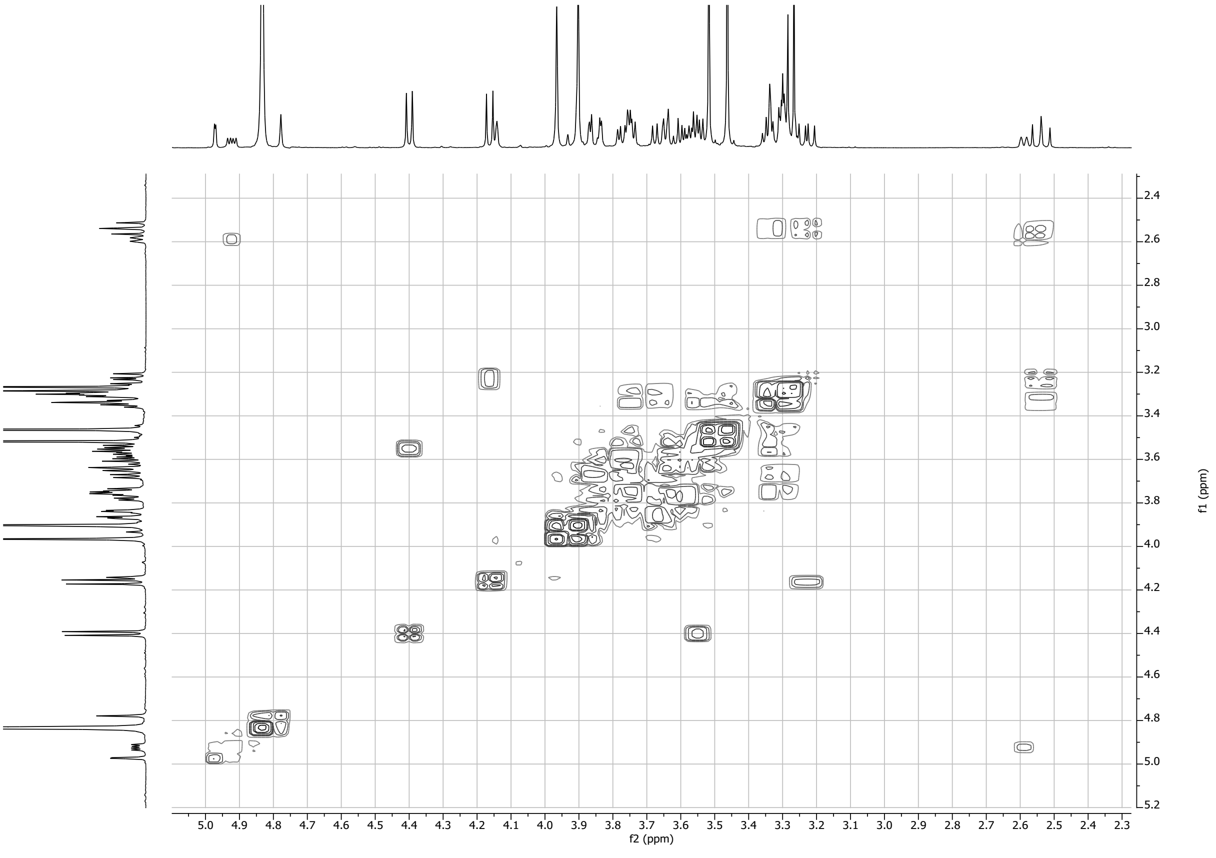




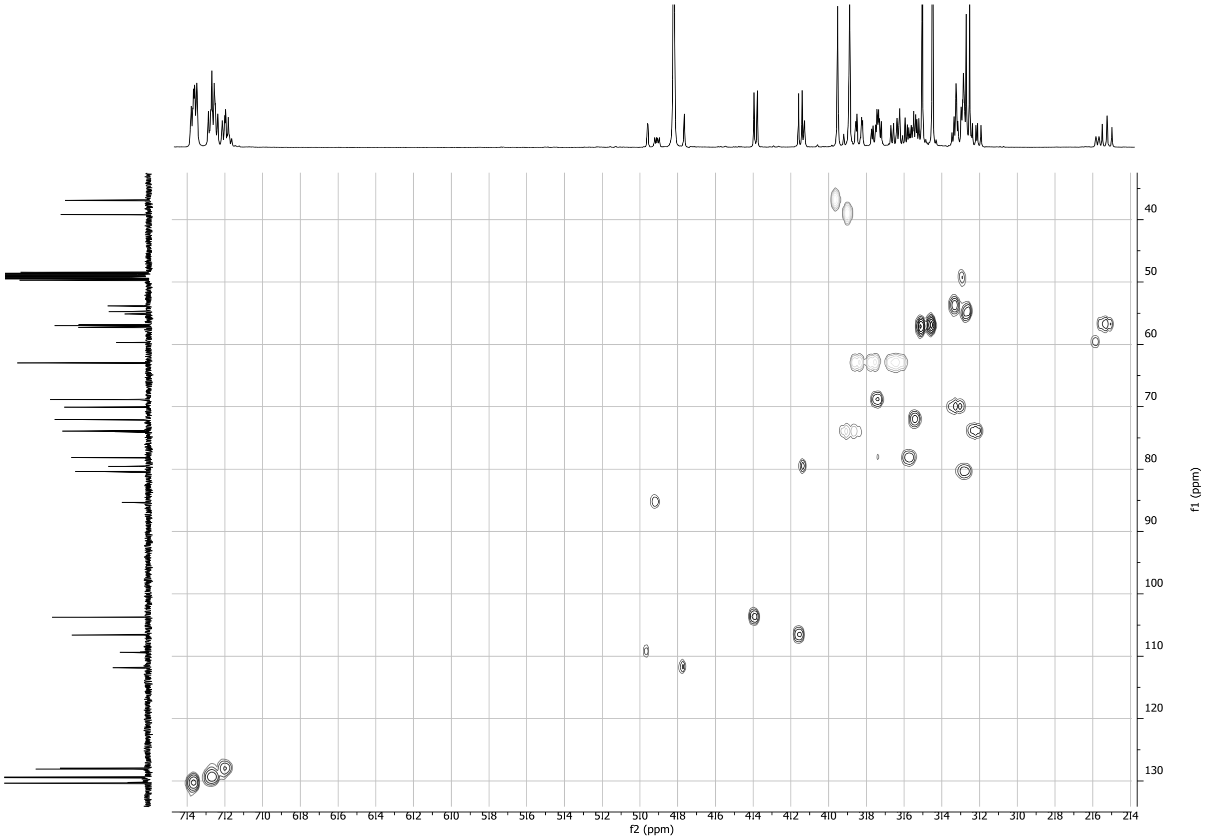
^{13}C NMR, 101 MHz, CD$_3$OD of compounds **14** and **S15**



^{1}H-^{1}H COSY of compounds **14** and **S15**



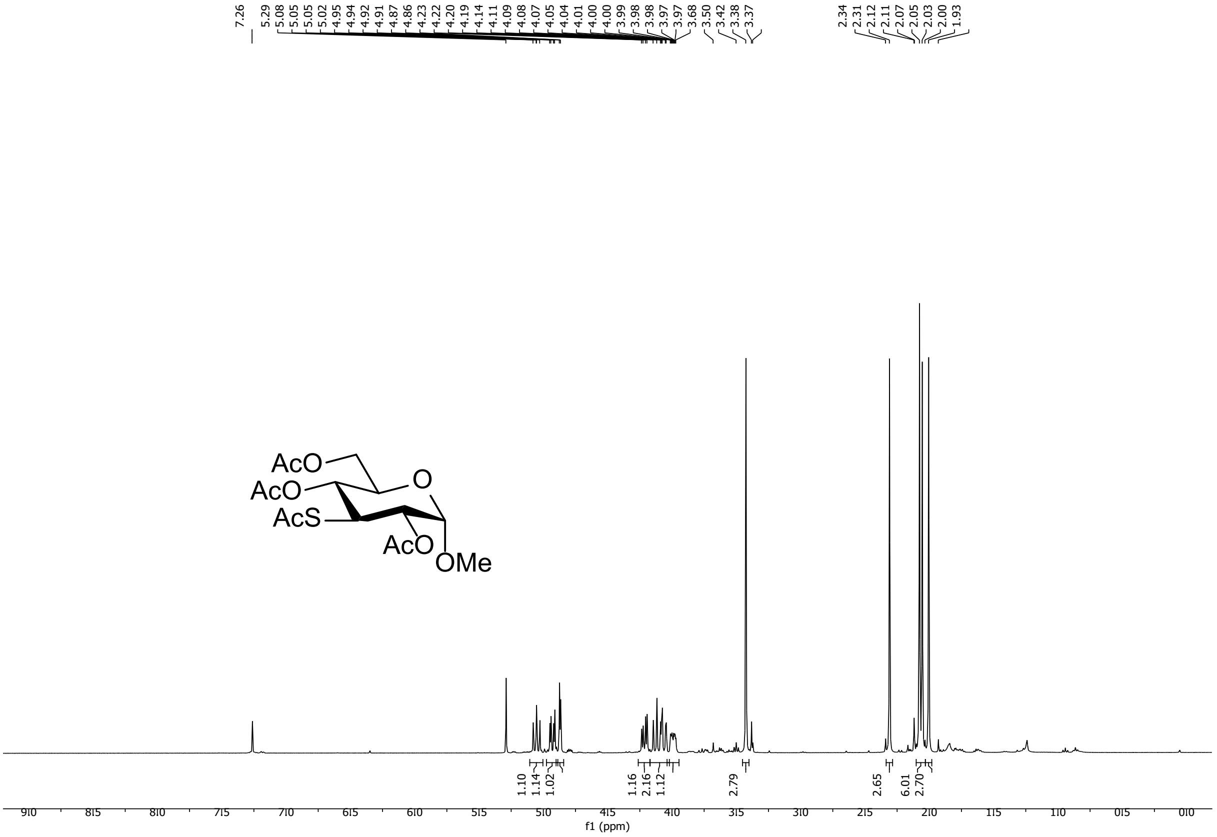
^1H-^{13}C HSQC of compounds **14** and **S15**



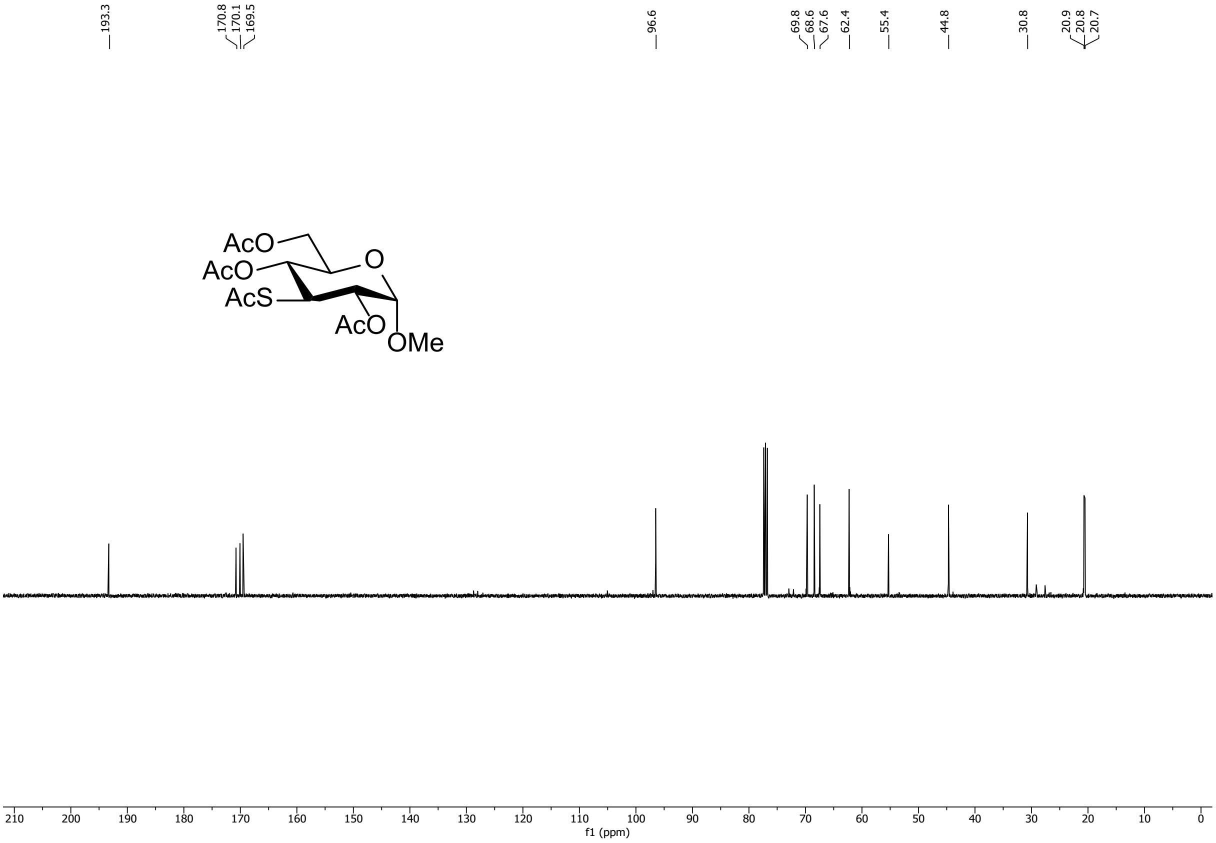
NMR of S16, S17, and S-glycosides 20 and 22

Methyl 2,3,4,6-tri-O-acetyl-3-S-acetyl-3-deoxy-α-D-glucopyranoside (S16)

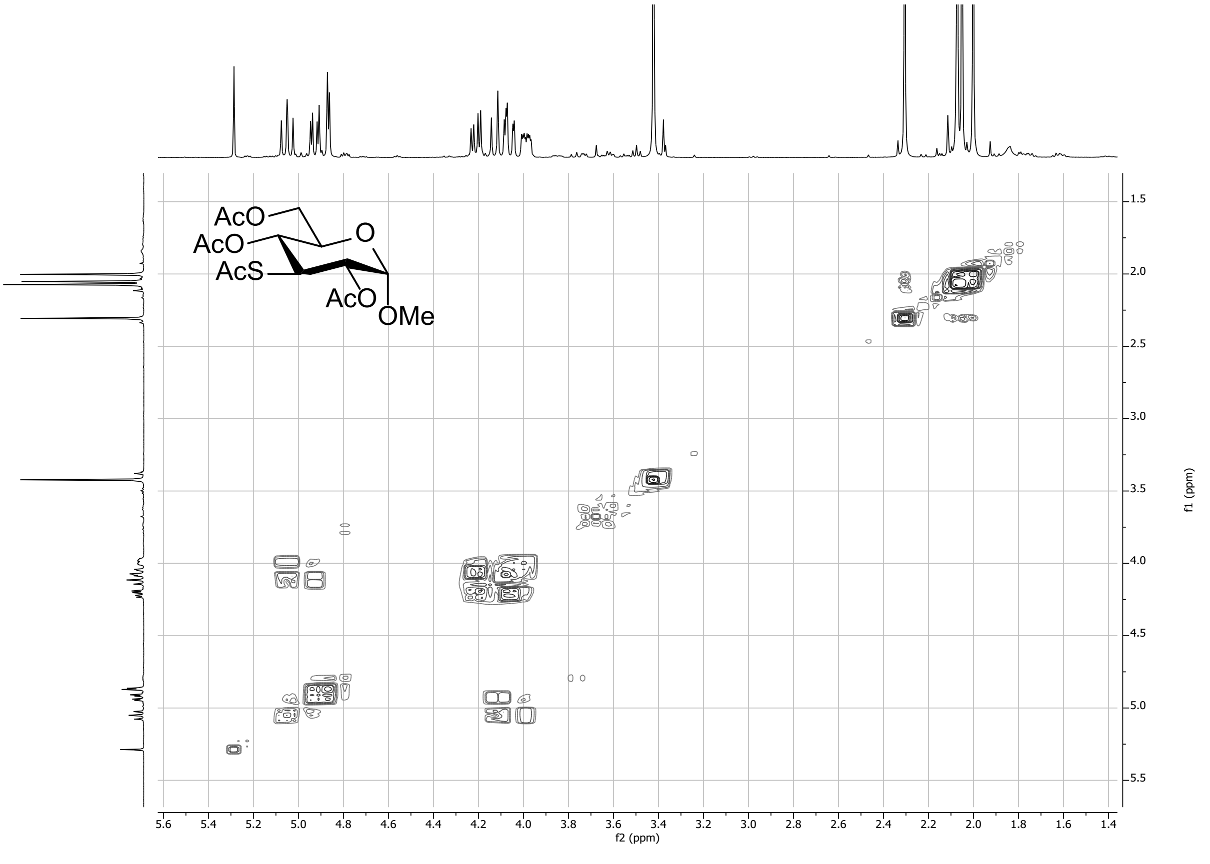
^1H NMR, 400 MHz, $CDCl_3$ of compound **S16**



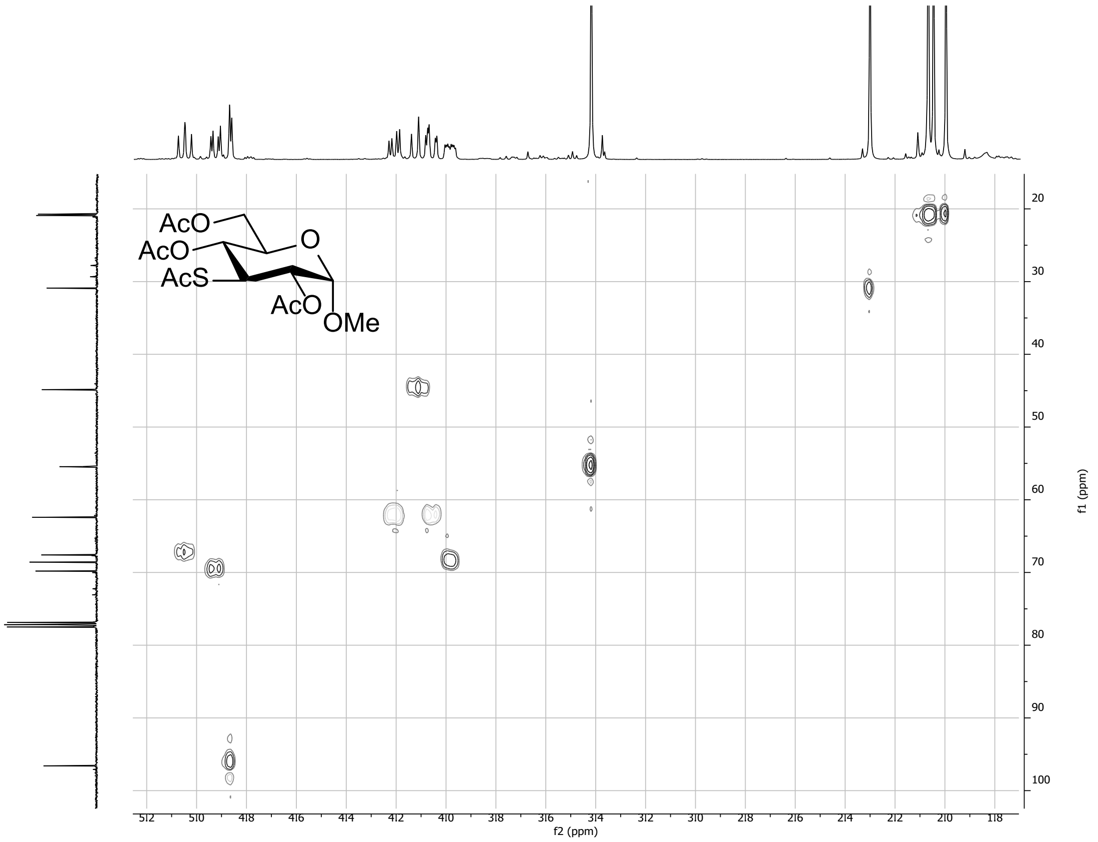
^{13}C NMR, 101 MHz, CDCl$_3$ of compound **S16**



^{1}H-^{1}H COSY of compound **S16**

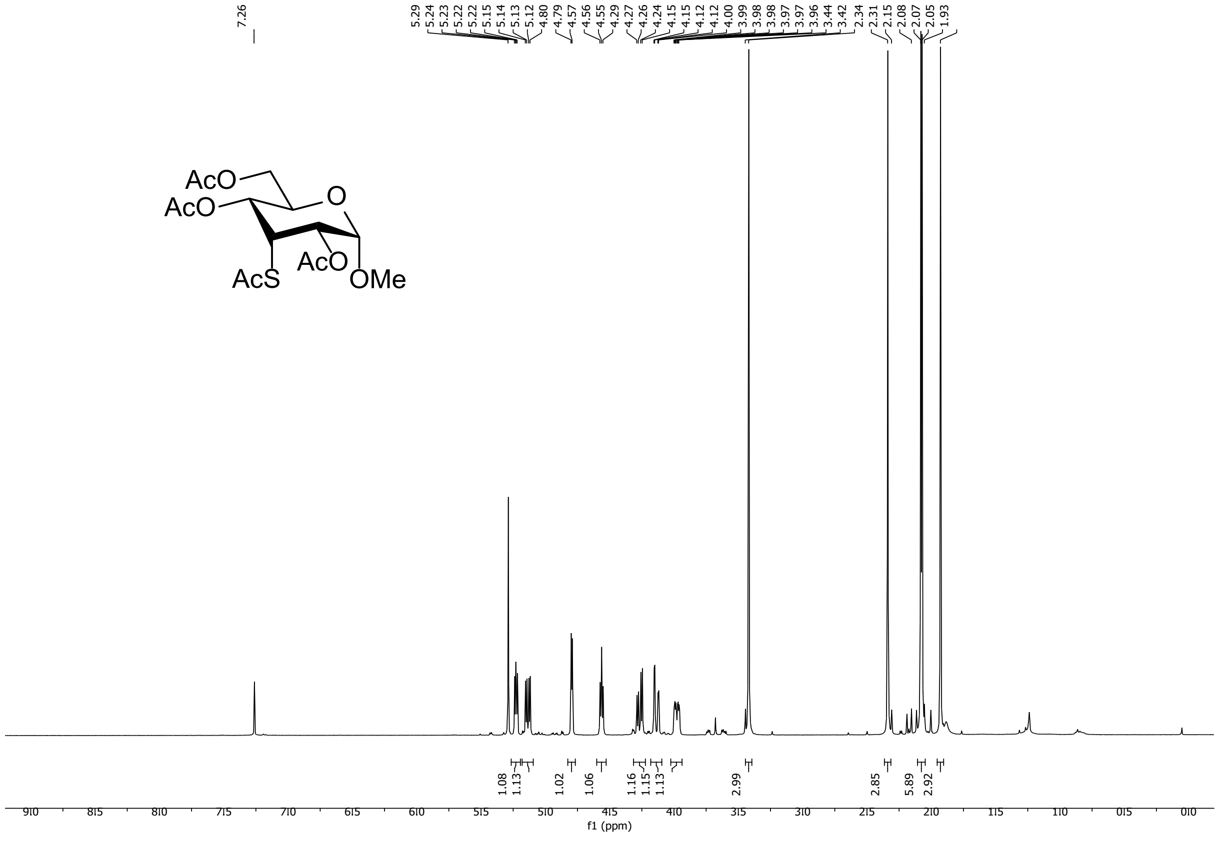


^{1}H-^{13}C HSQC of compound **S16**

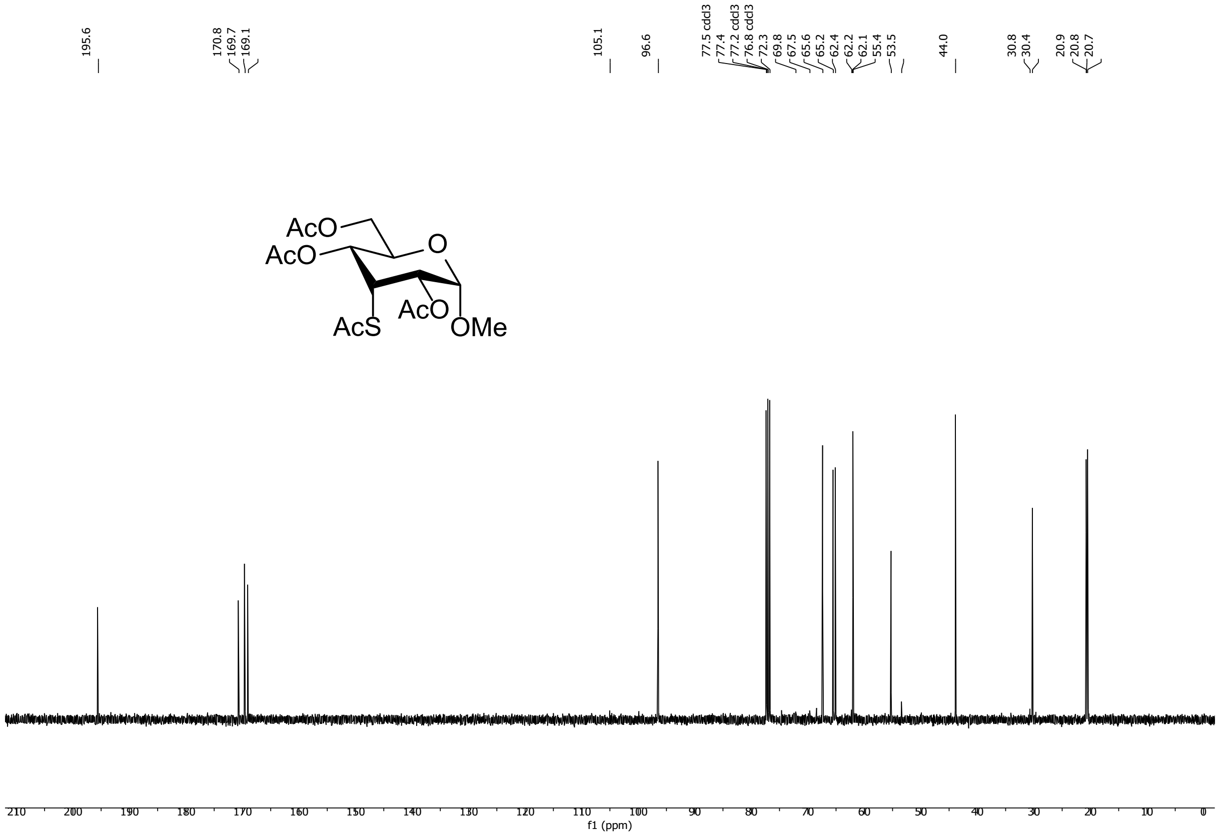


Methyl 2,3,4,6-tri-O-acetyl-3-S-acetyl-3-deoxy-α-D-allopyranoside (S17)

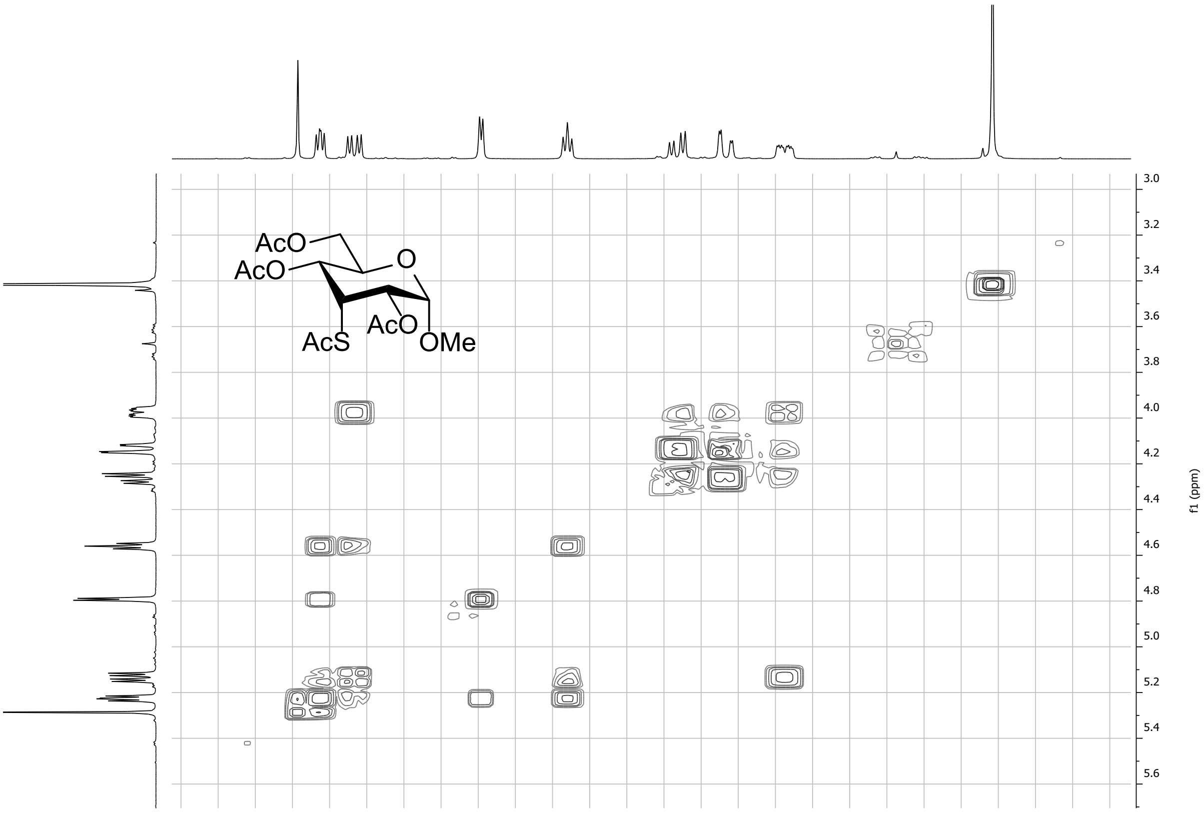
^{1}H NMR, 400 MHz, CDCl$_3$ of compound **S17**



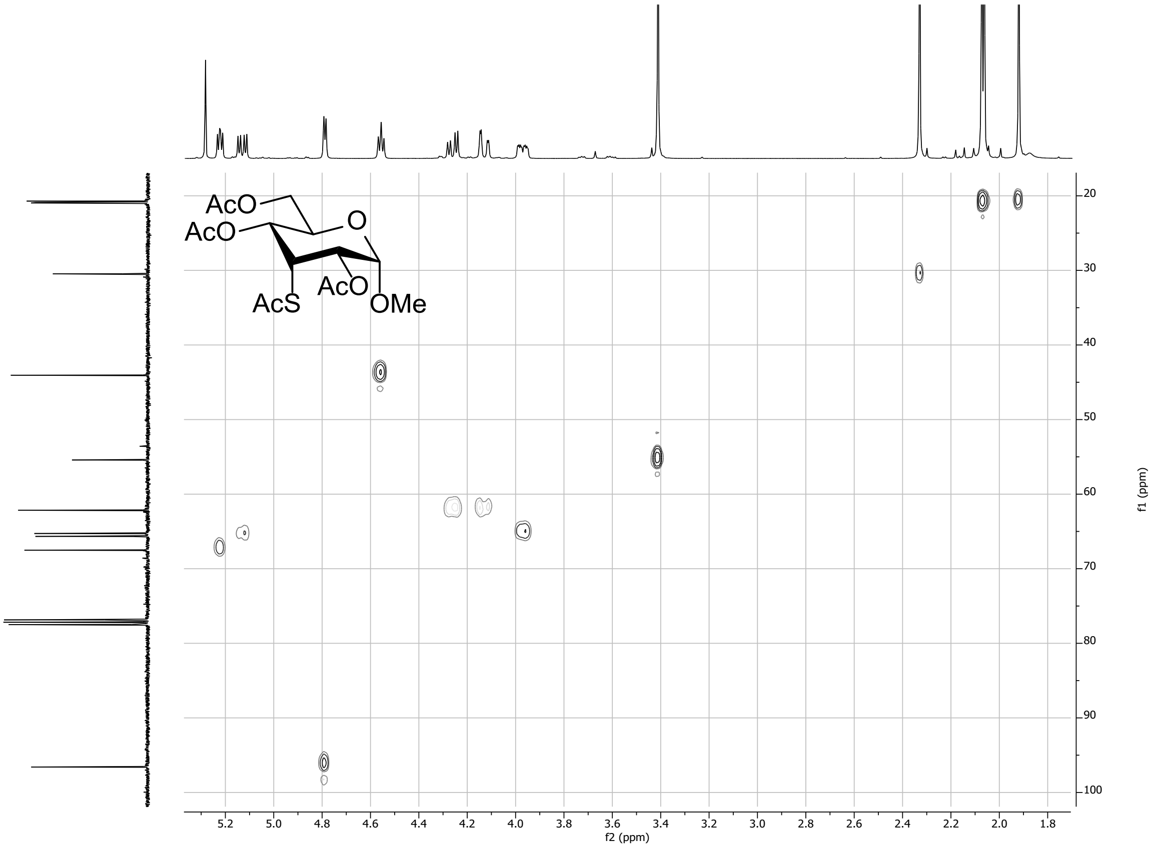
^{13}C NMR, 101 MHz, CDCl$_3$ of compound **S17**



^{1}H-^{1}H COSY of compound **S17**

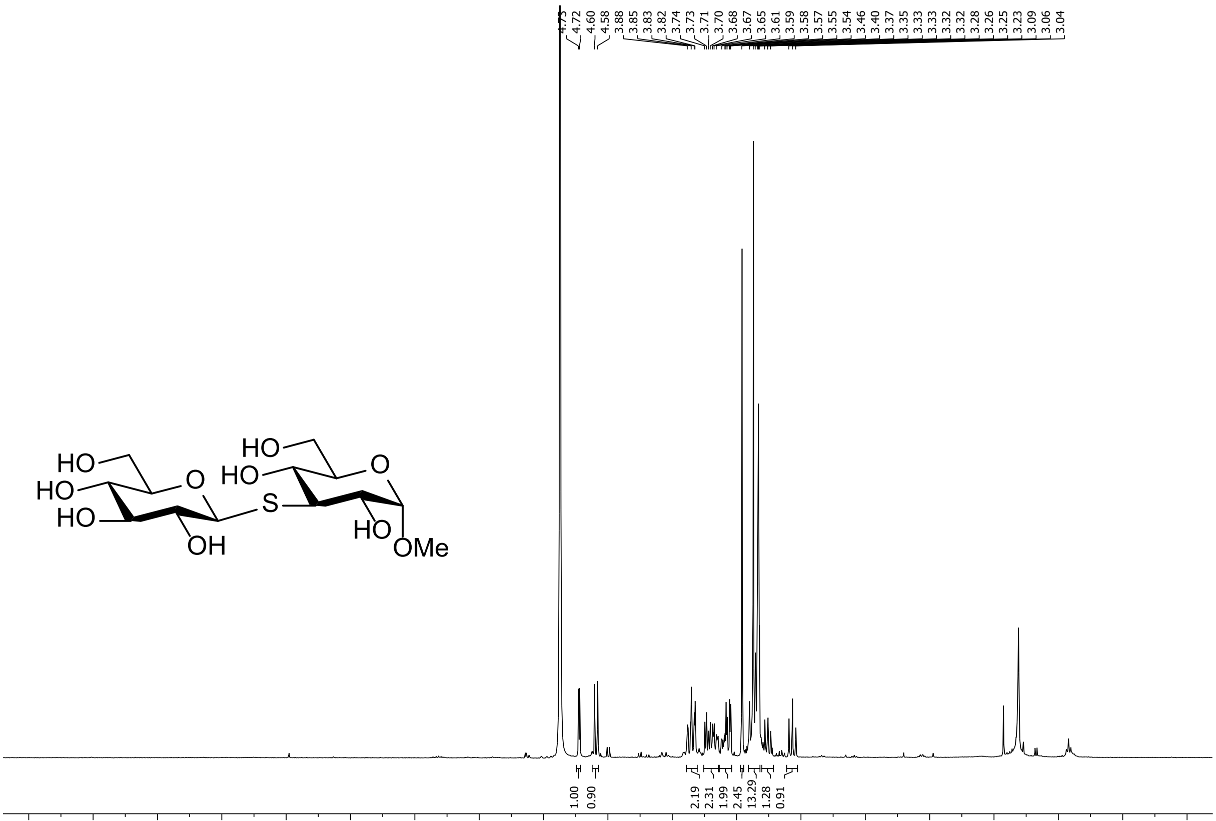


^{1}H-^{13}C HSQC of compound **S17**

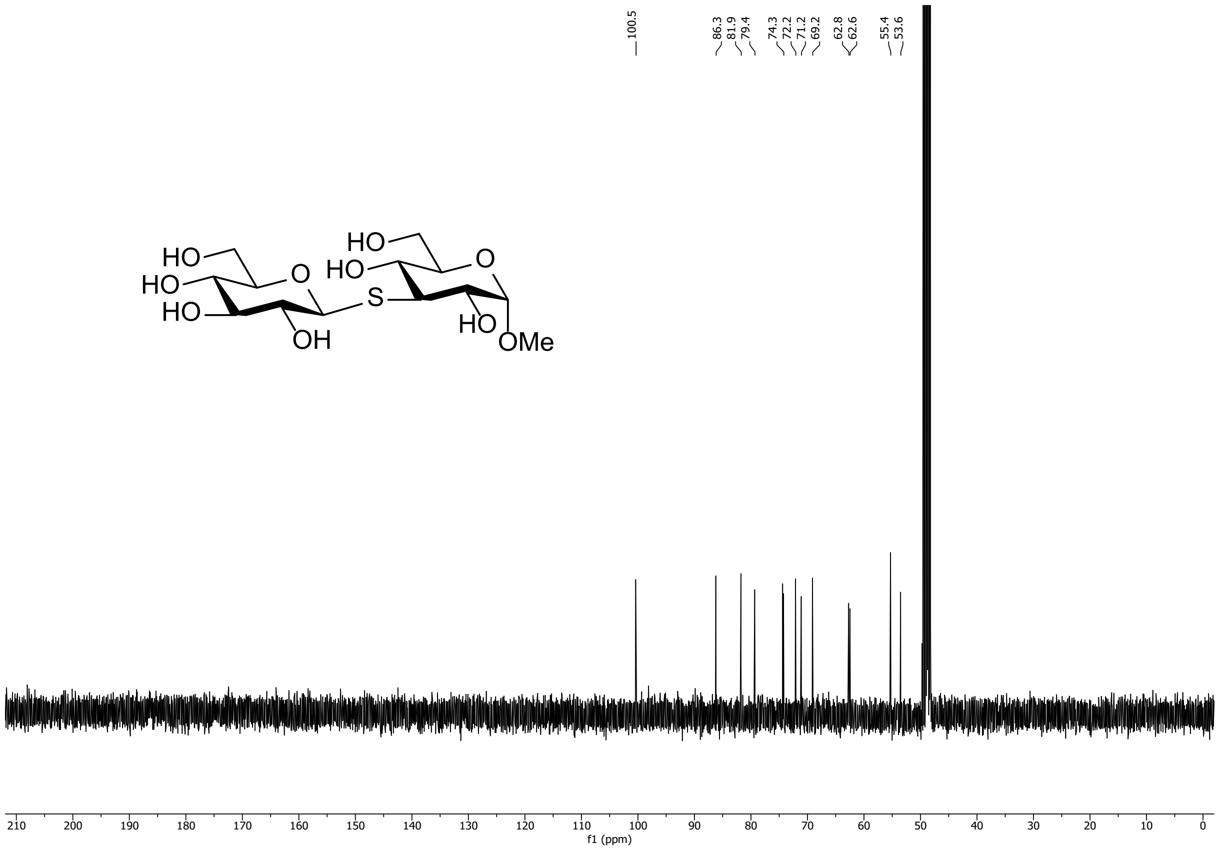


Methyl 3-S-β-D-glucopyranosyl-3-deoxy-3-thio-α-D-glucopyranoside (20)

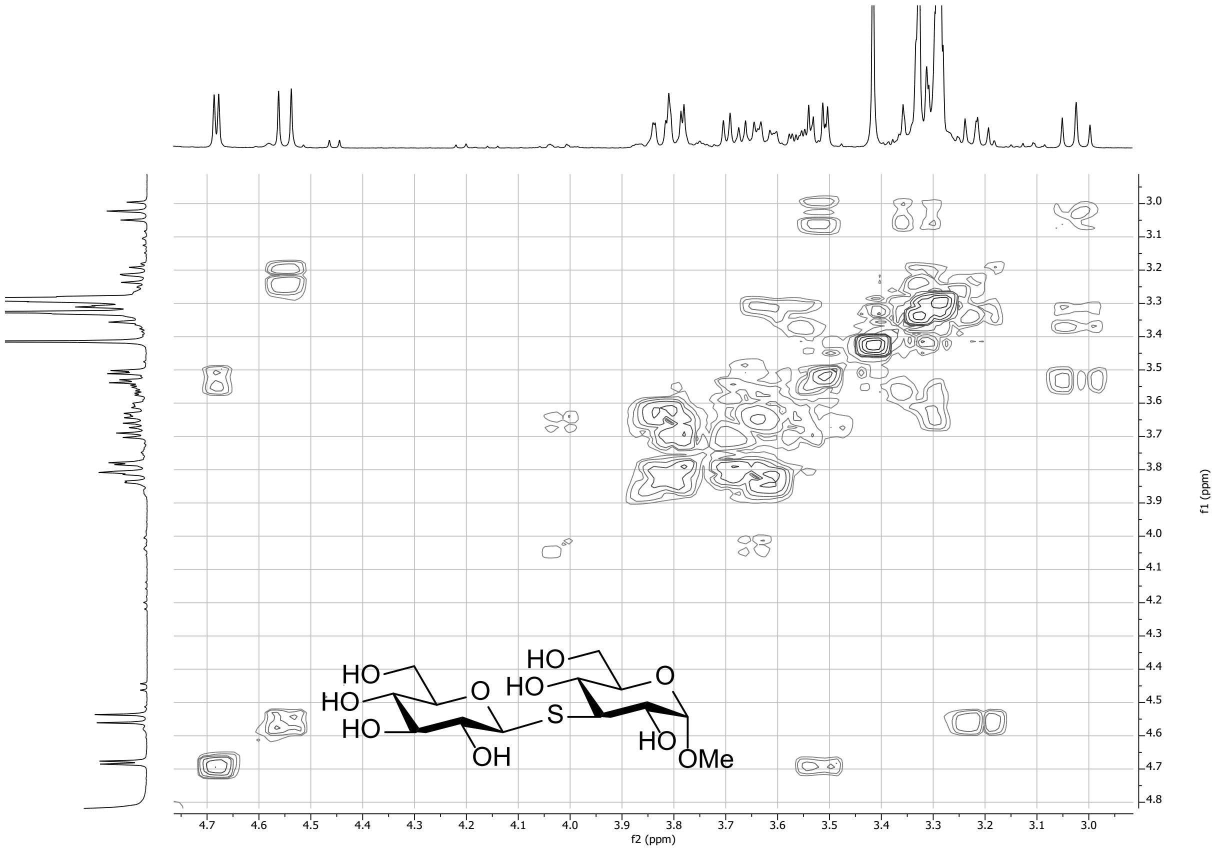
^{1}H NMR, 400 MHz, CDCl$_3$ of compound **20**



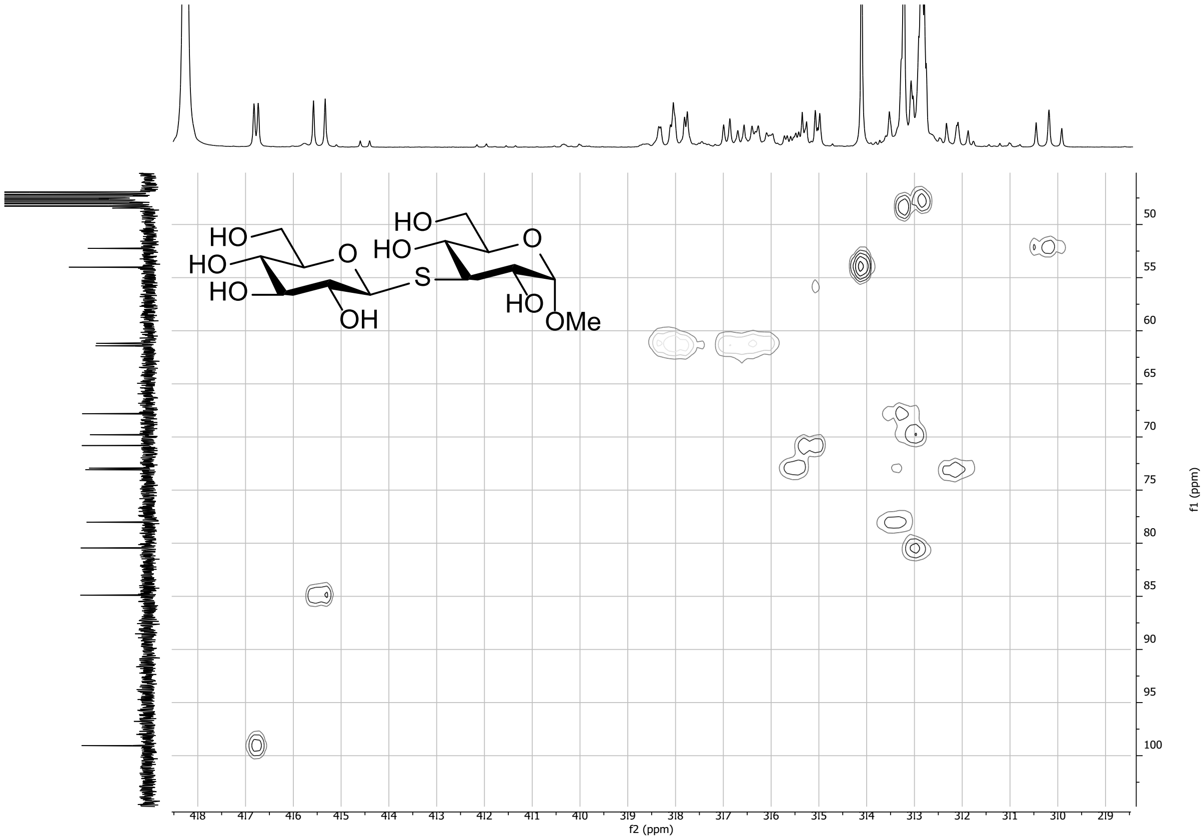
^{13}C NMR, 101 MHz, CDCl$_3$ of compound **20**



^{1}H-^{1}H COSY of compound **20**

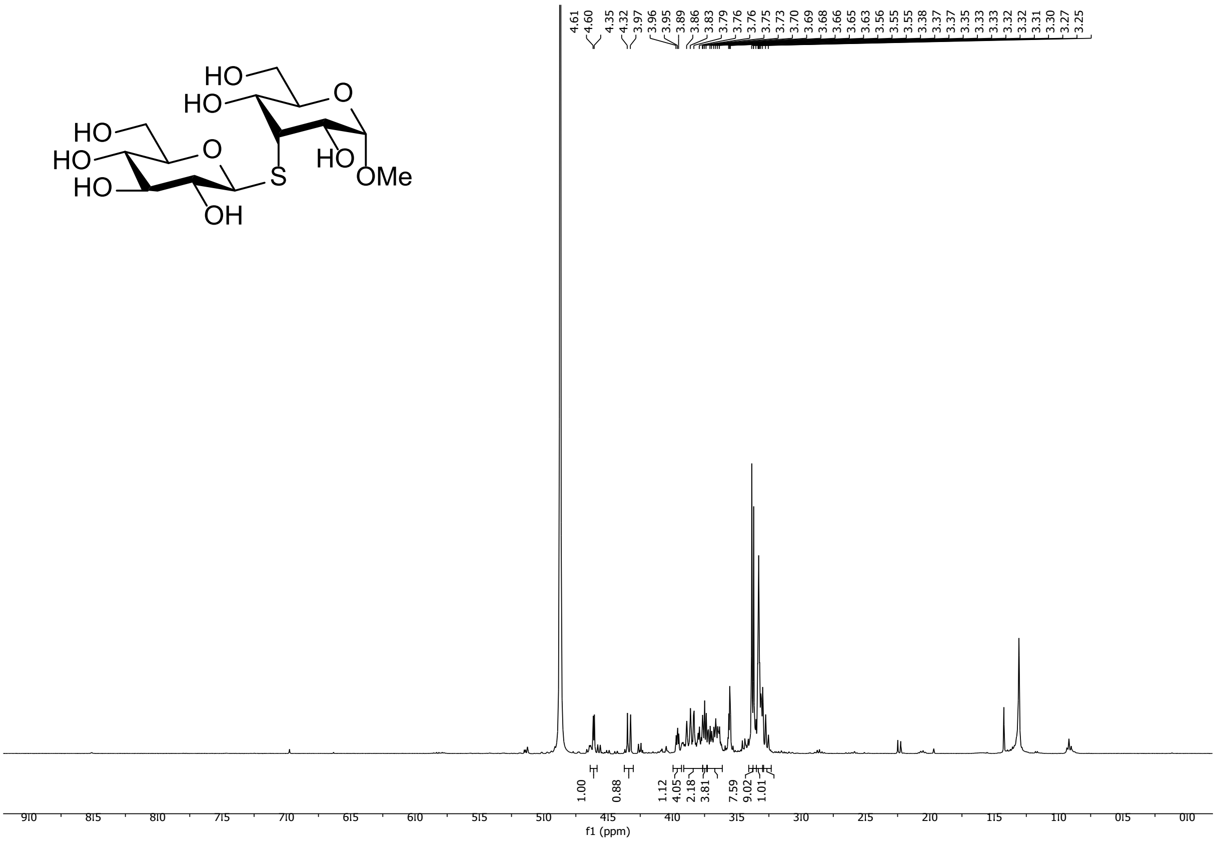


^1H-^{13}C HSQC of compound **20**

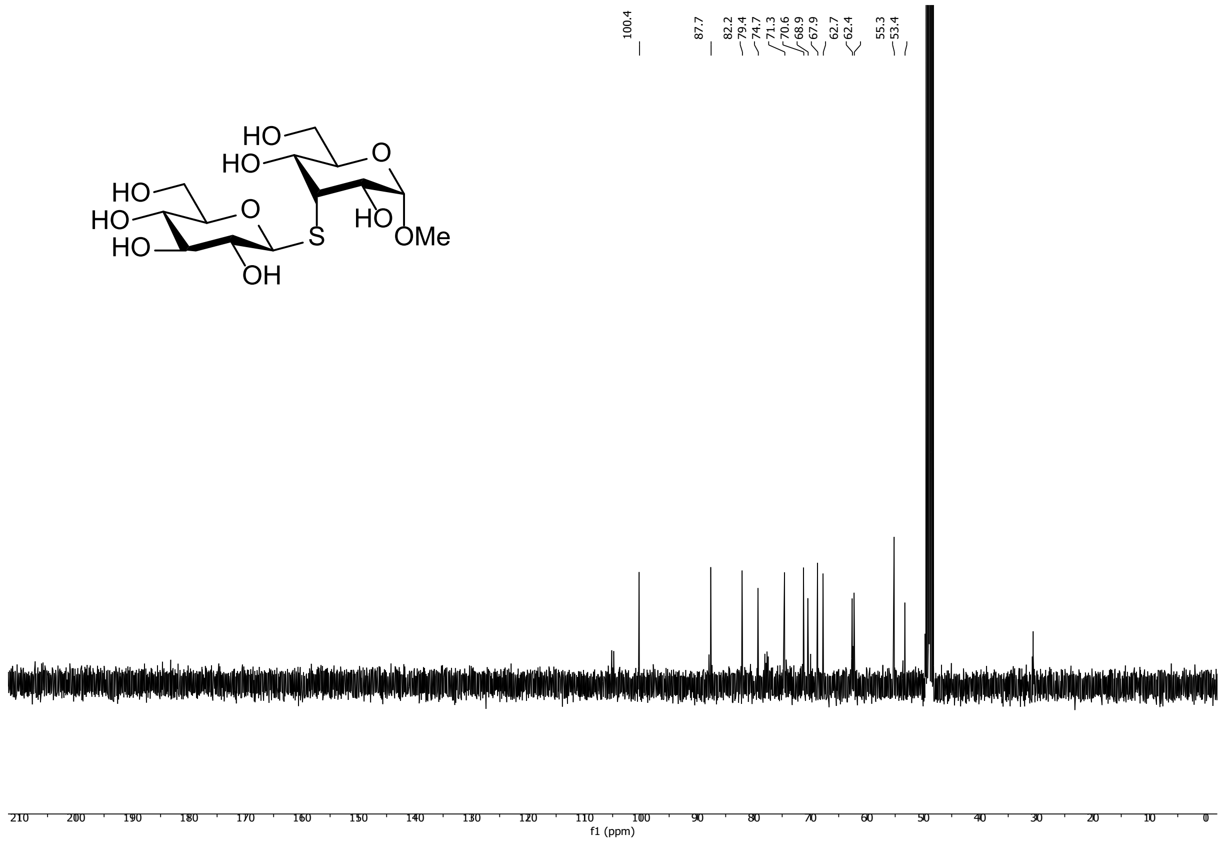


Methyl 3-S-β-D-glucopyranosyl-3-deoxy-3-thio-α-D-allopyranoside (22)

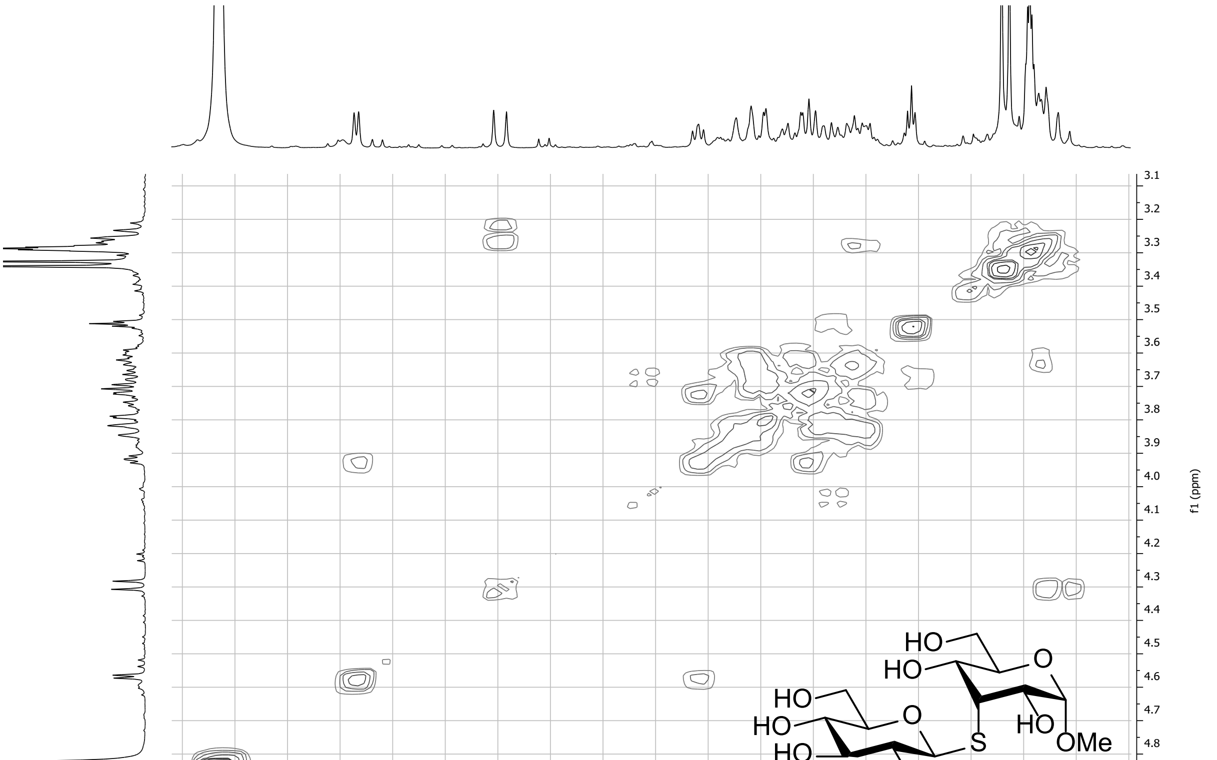
^1H NMR, 400 MHz, $CDCl_3$ of compound **22**



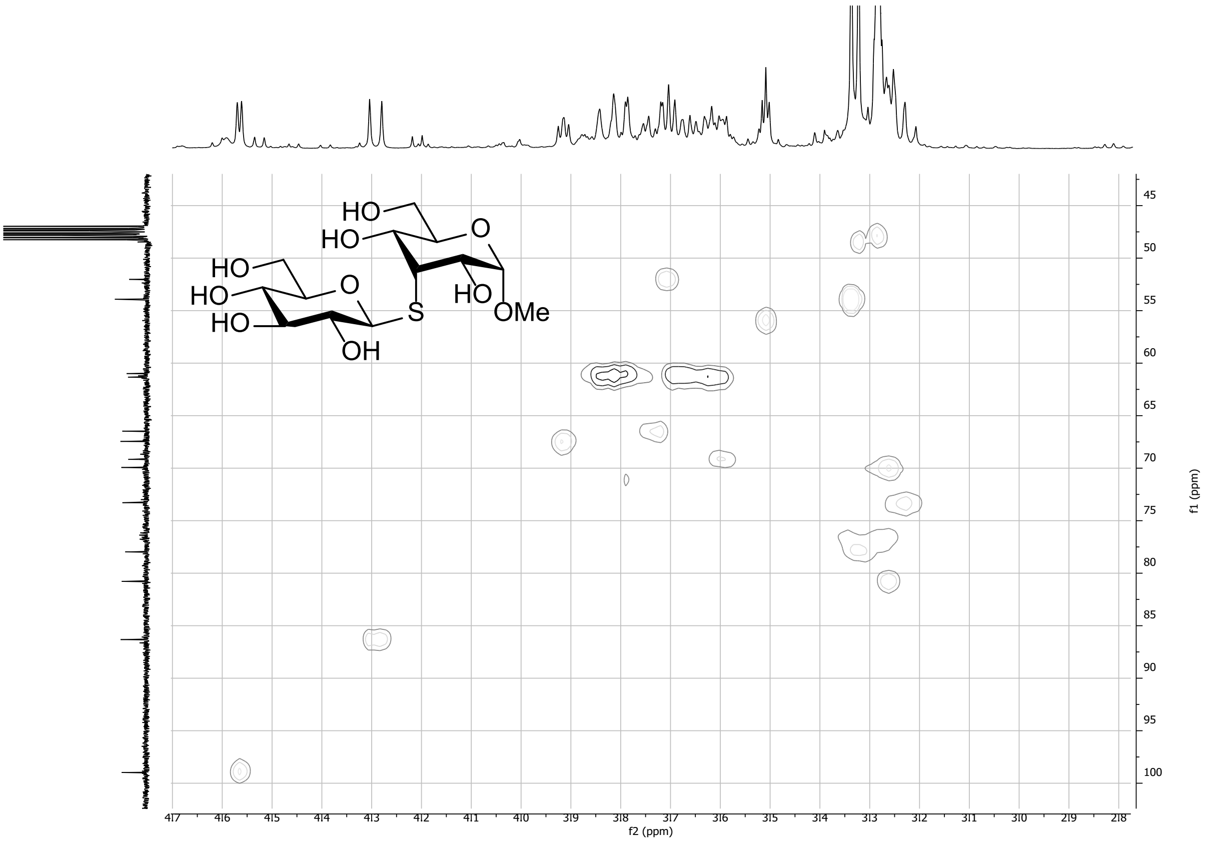
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **22**



^{1}H-^{1}H COSY of compound **22**



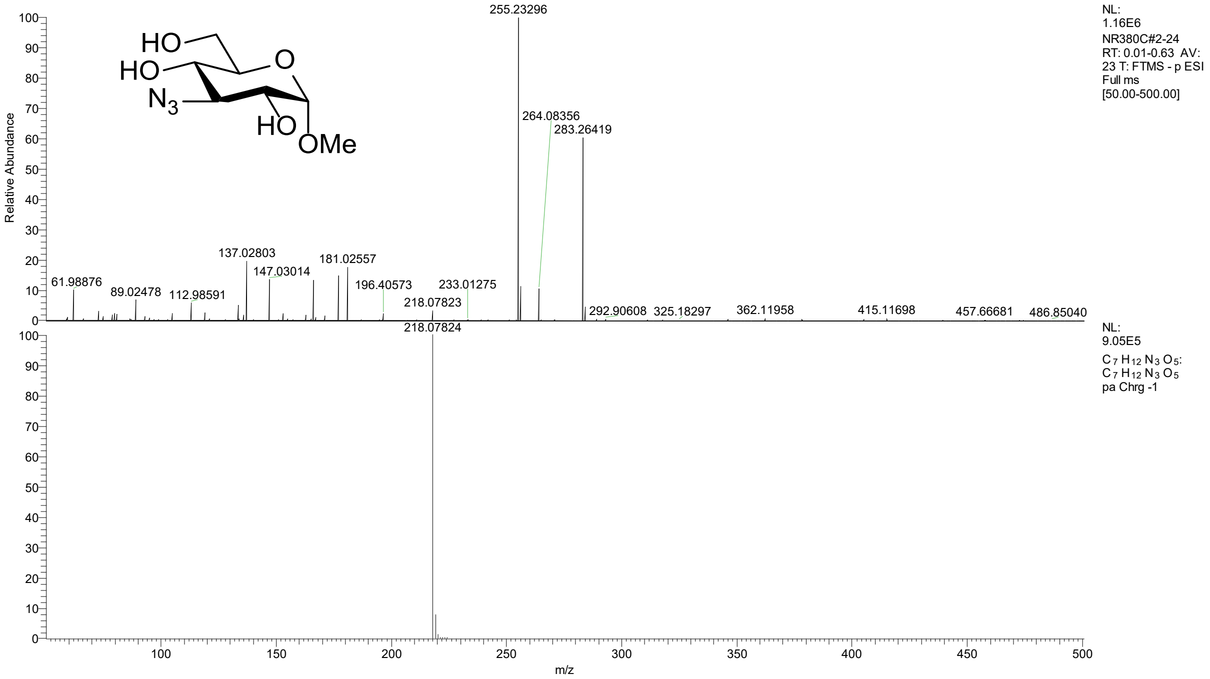
^{1}H-^{13}C HSQC of compound **22**

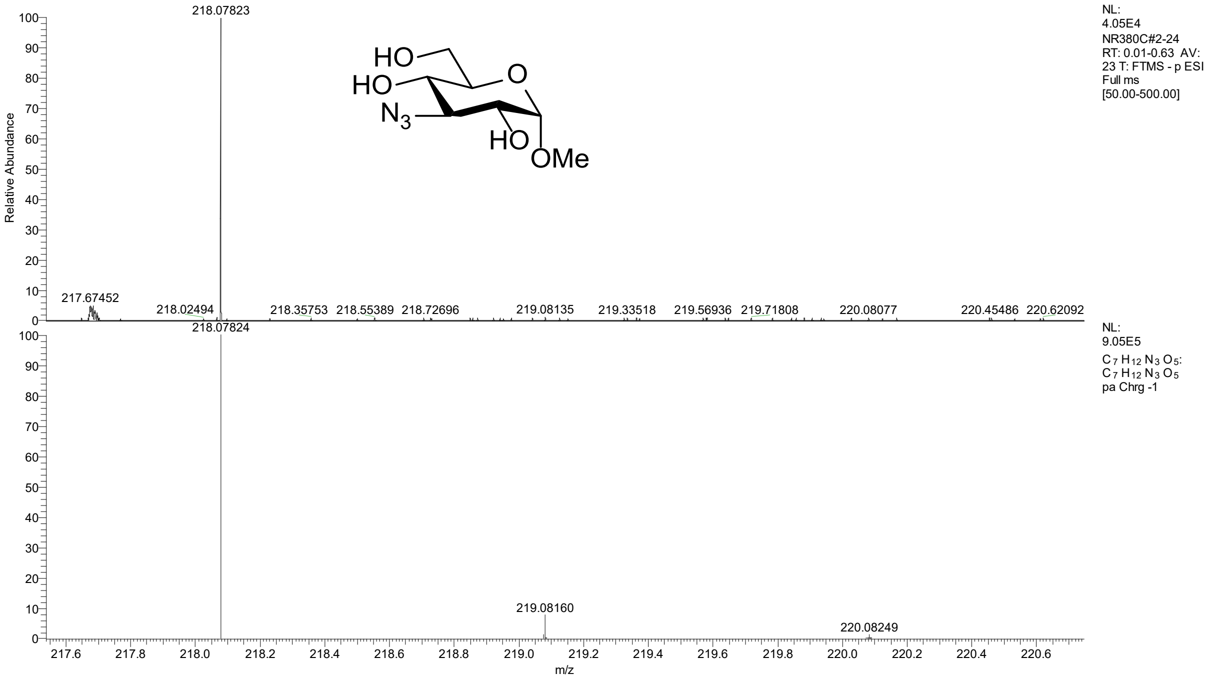


HRMS spectra

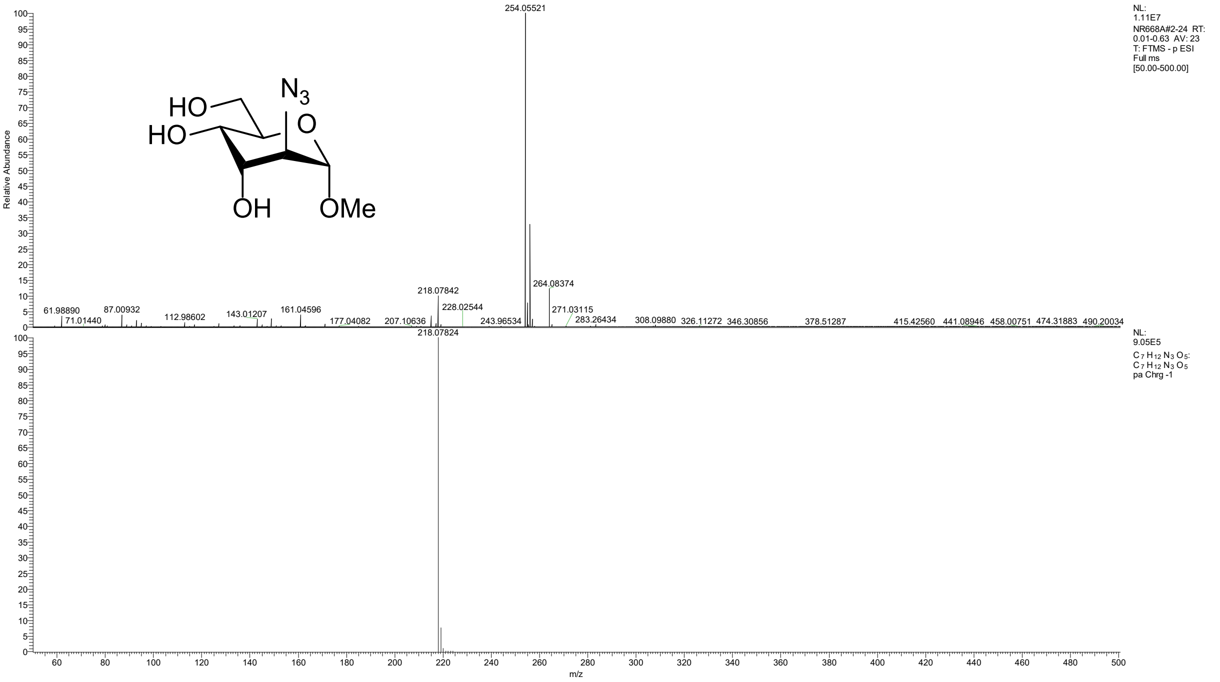
HRMS spectra of substitution reactions on chloroglycosides

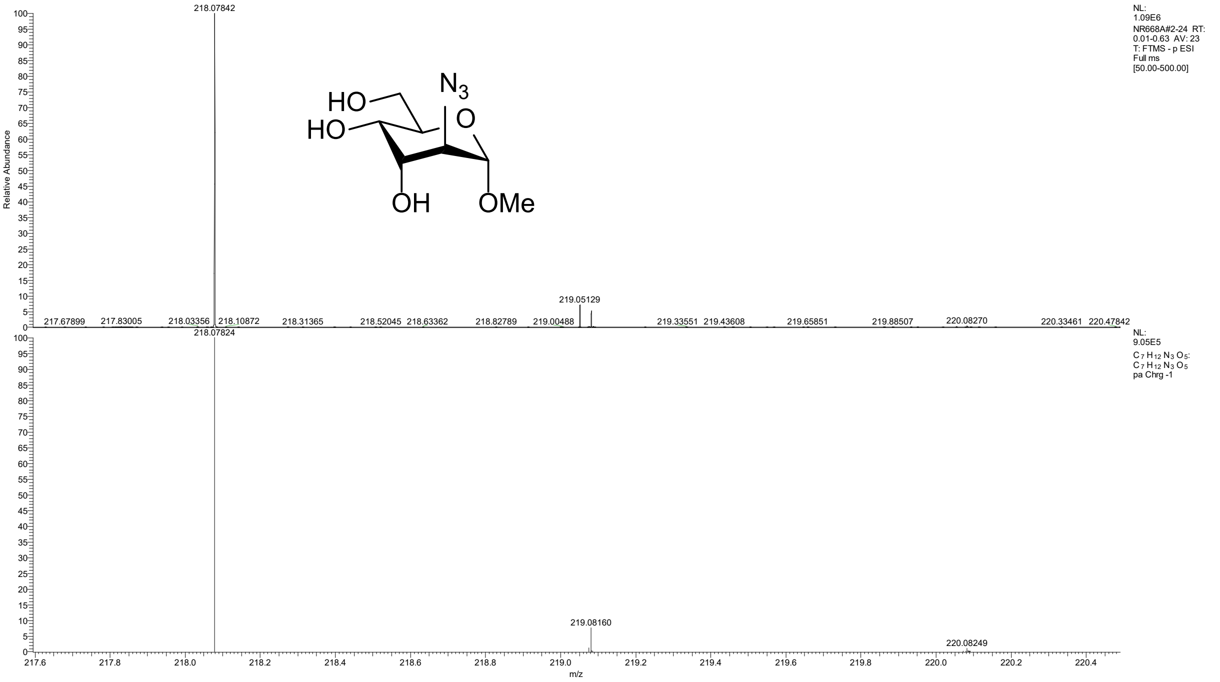
Methyl 3-azido-3-deoxy-α-D-glucopyranoside (4)



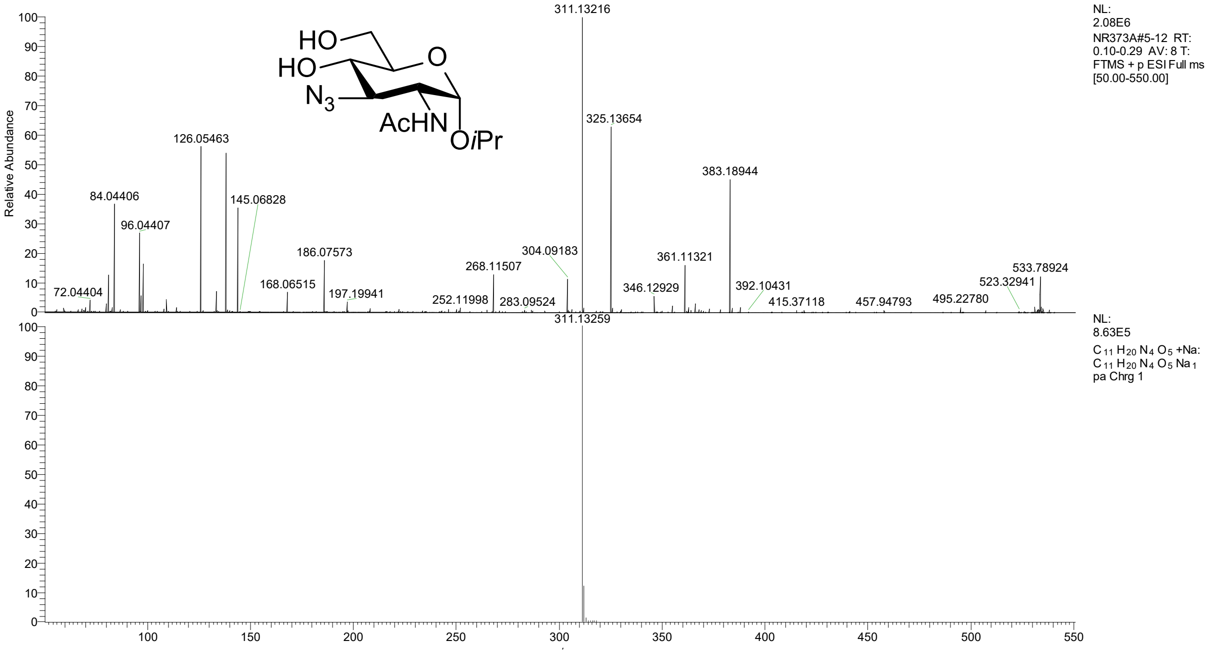


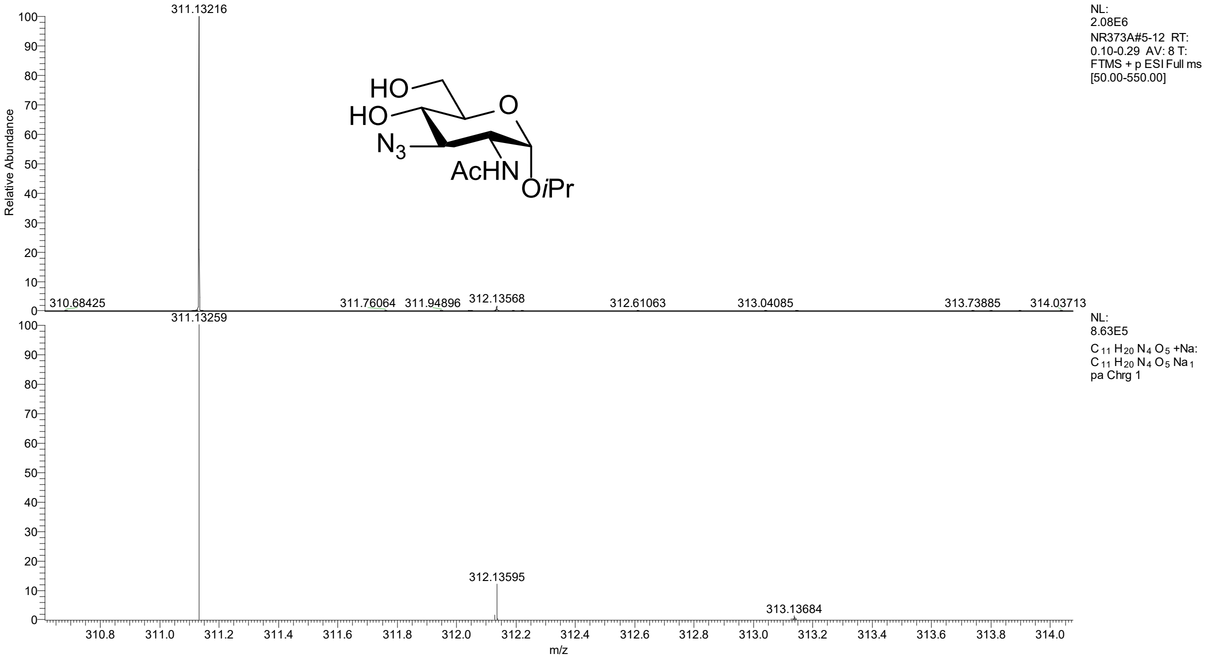
Methyl 2-azido-2-deoxy-α-D-altropyranoside (S1)



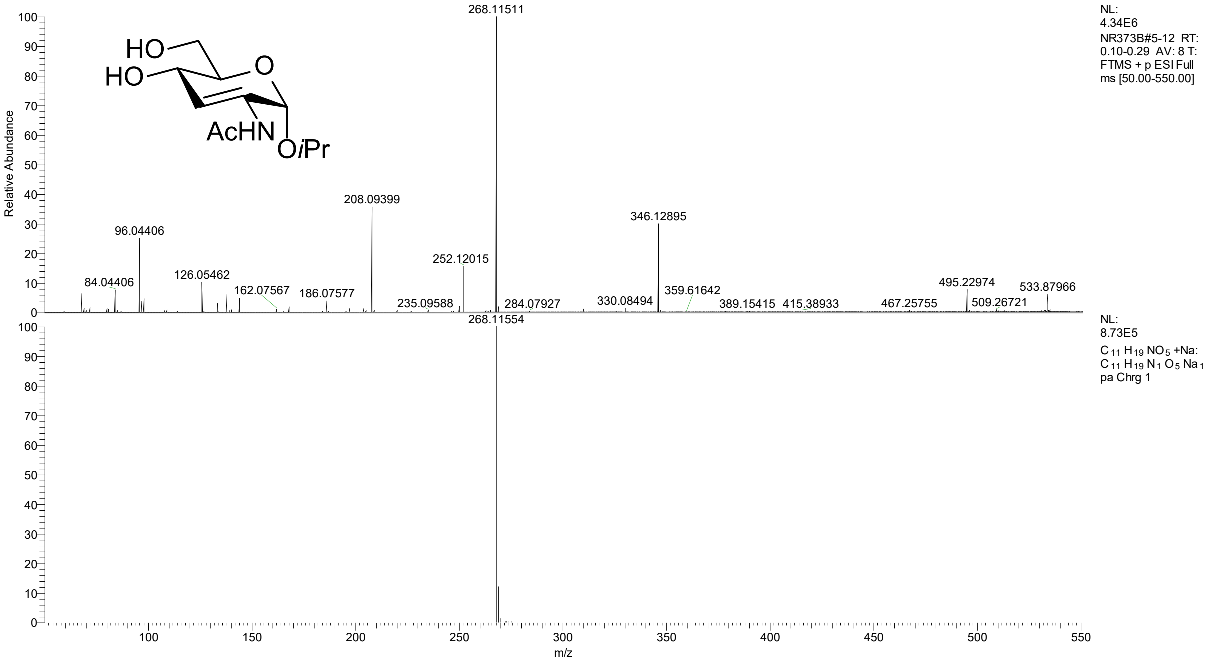


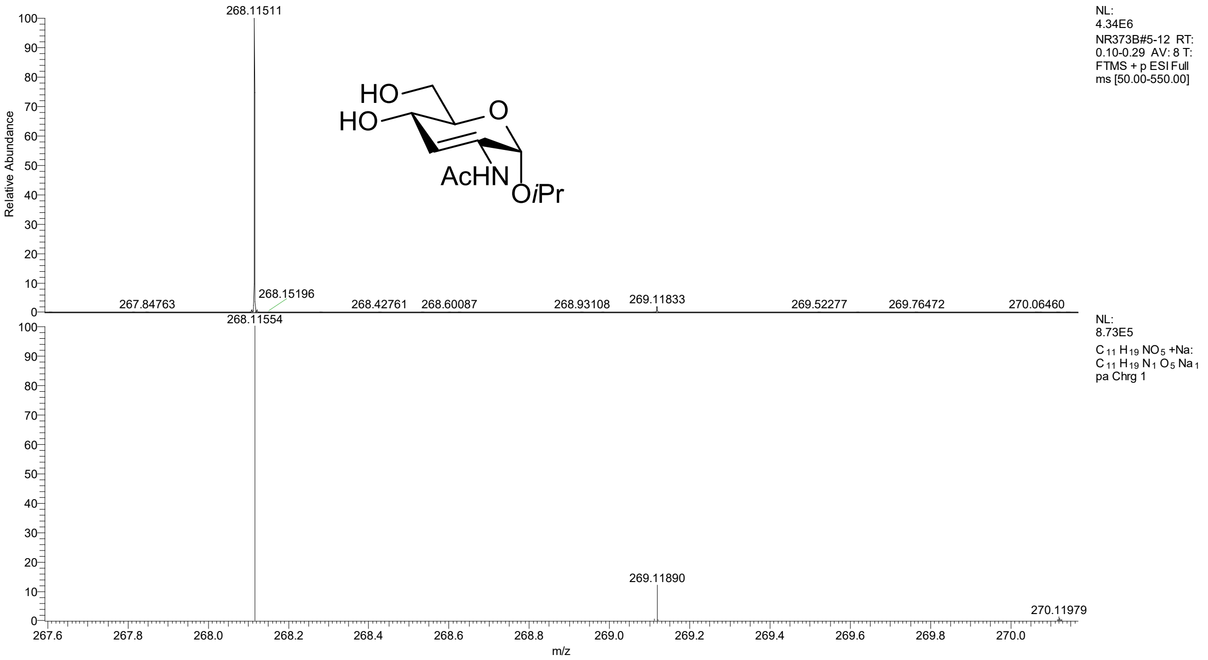
Isopropyl 2-acetmido-3-azido-2,3-dideoxy-α-ᴅ-glucopyranoside (S3)



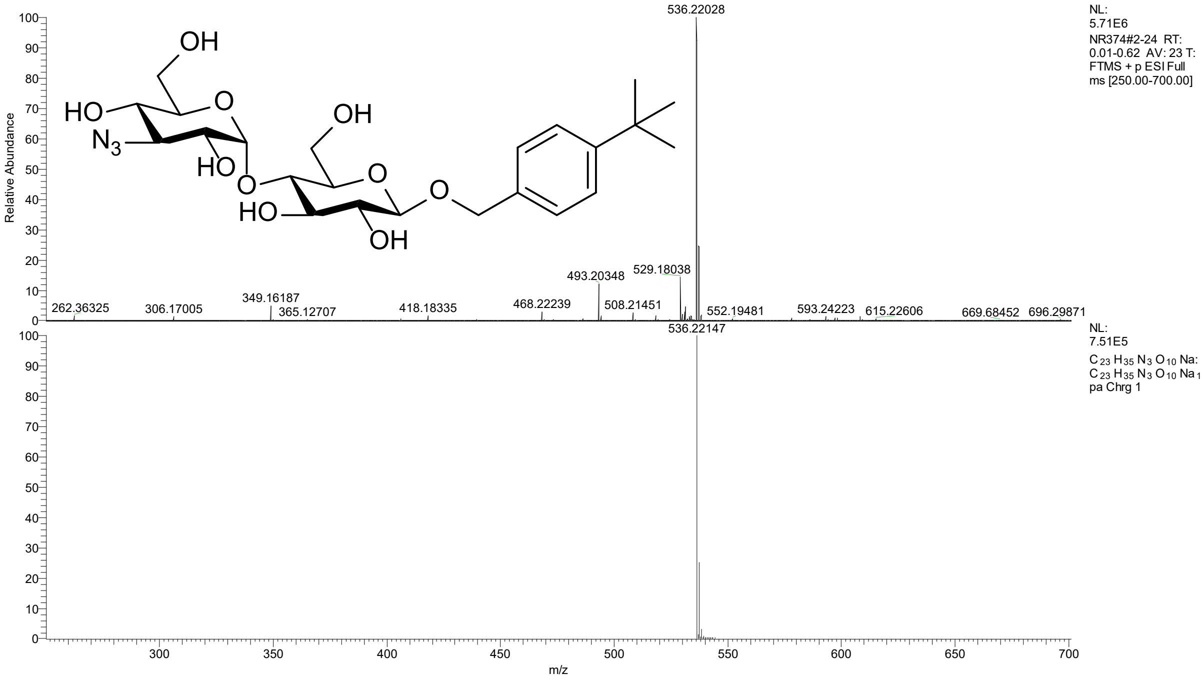


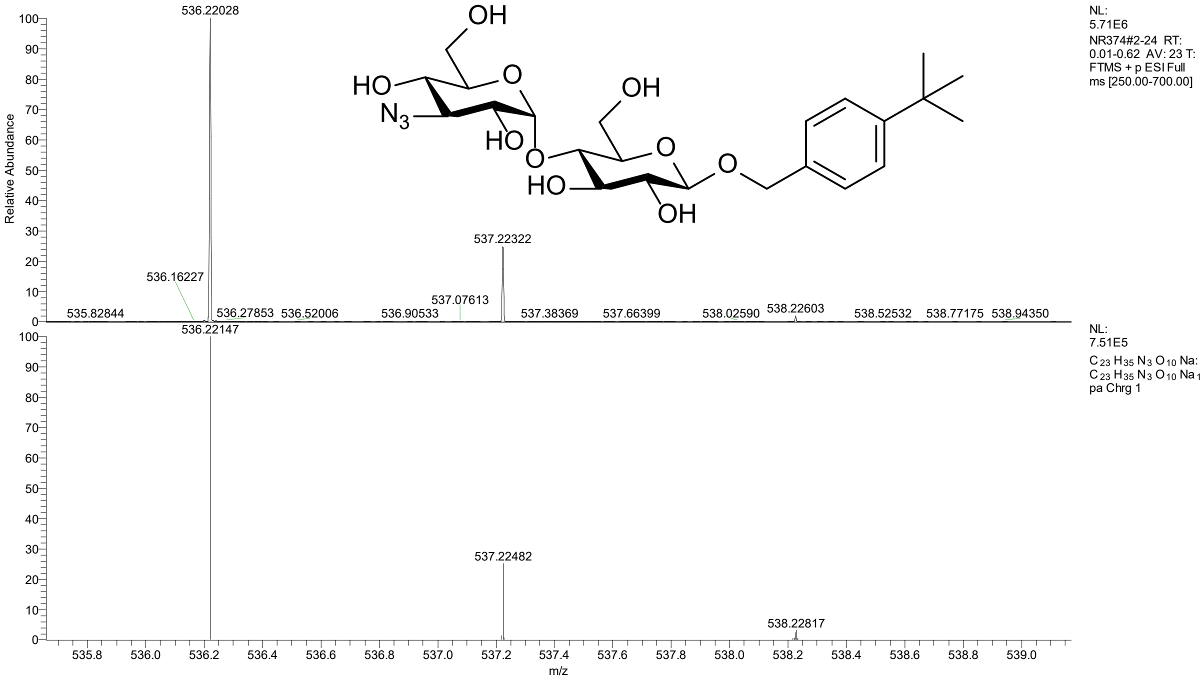
Sideproduct of the azide introruction on GlcNAc (S4)



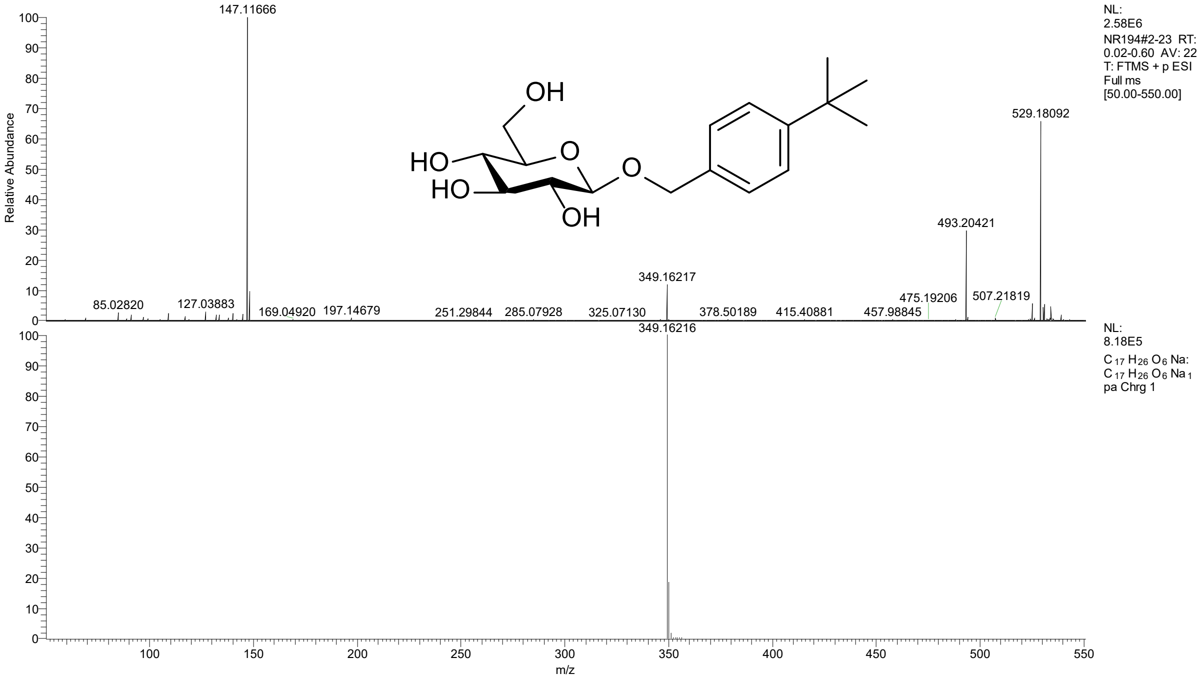


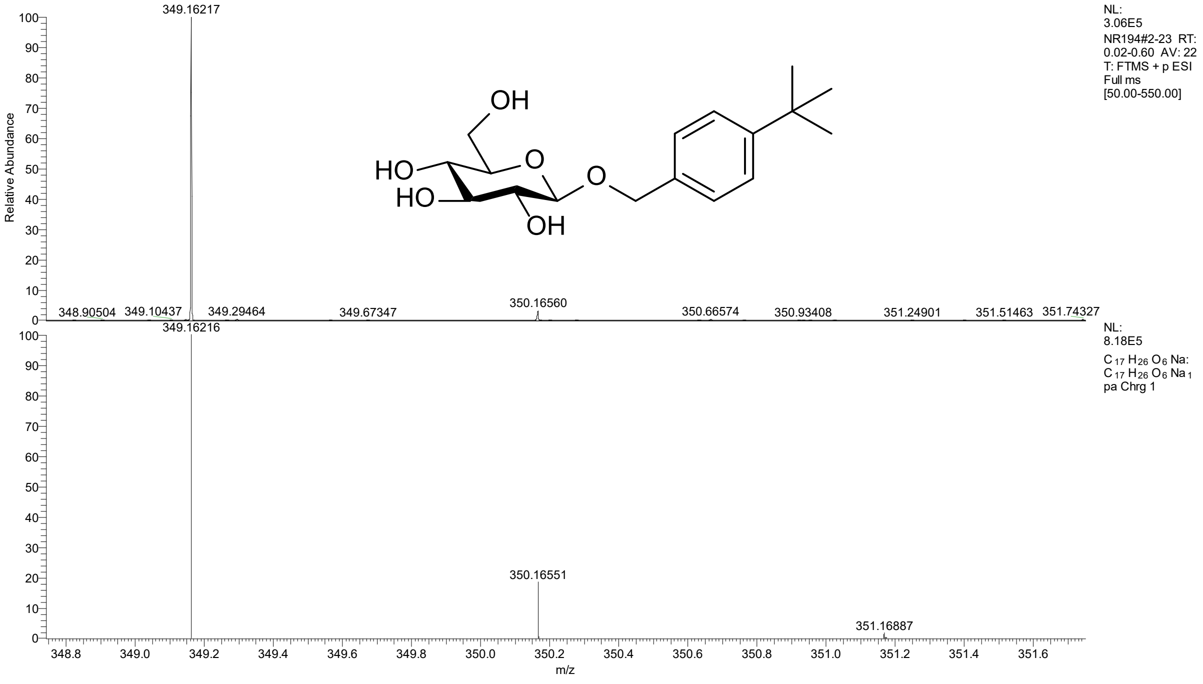
4-tert-butylbenzyl-3-azido-3-deoxy-α-D-maltoside (S6)





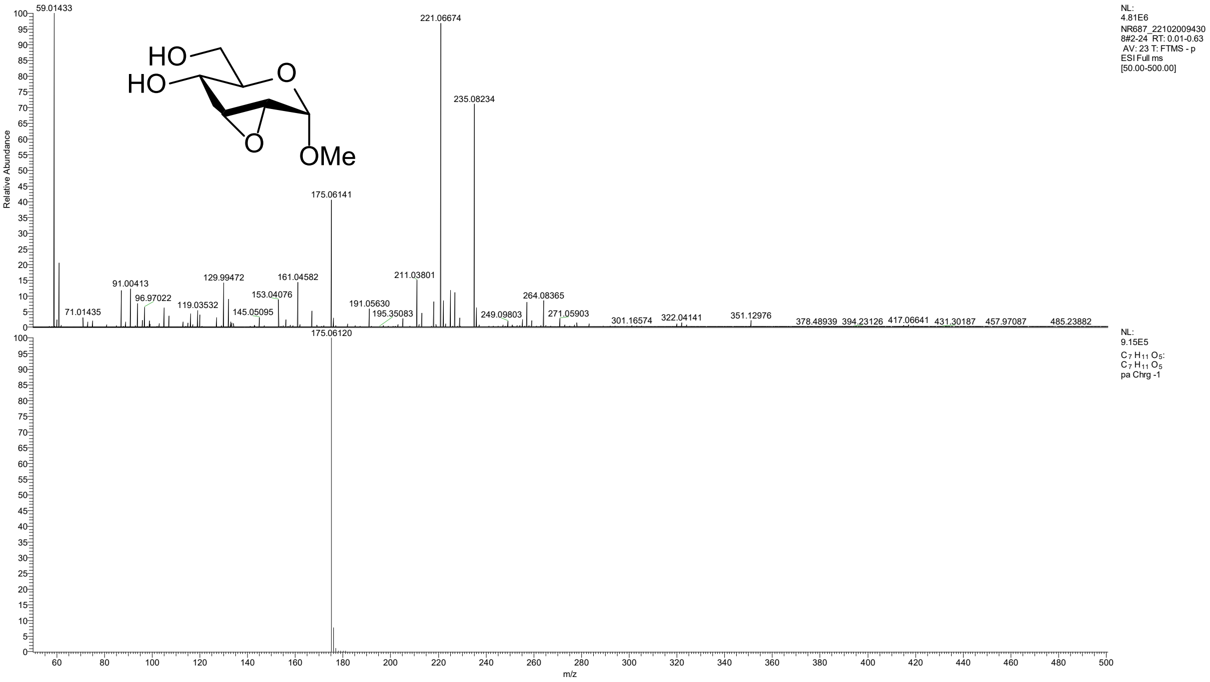
4-tert-butylbenzyl-β-D-glucopyranoside (17)

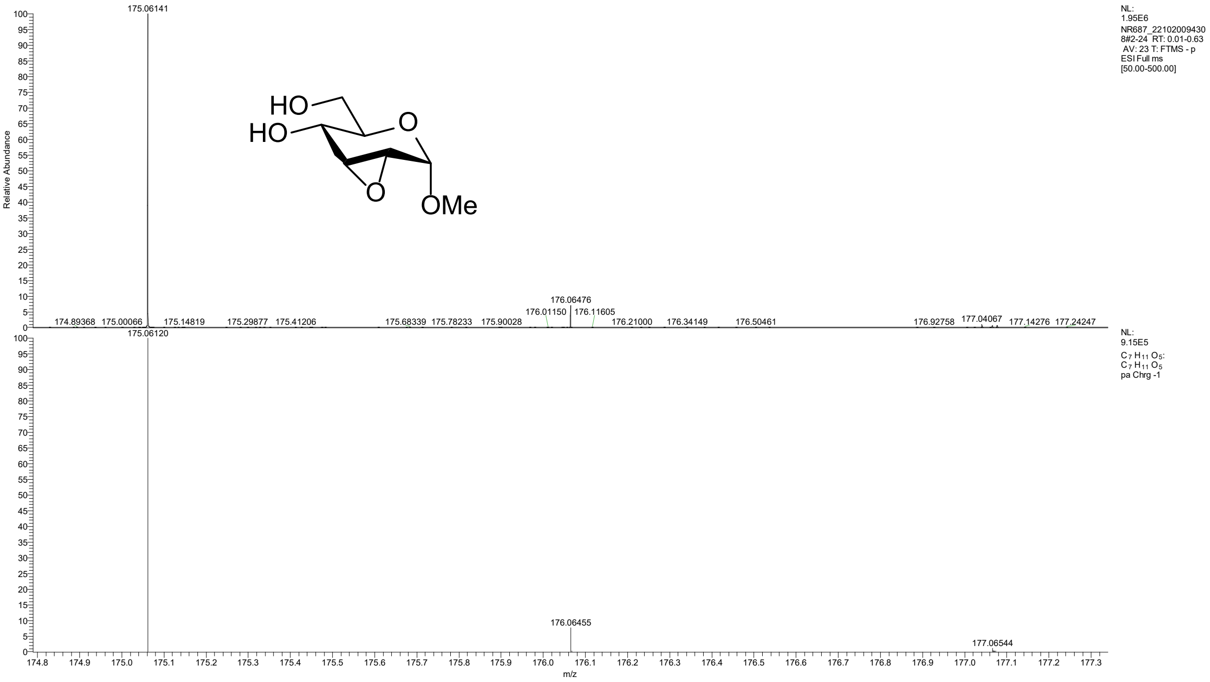




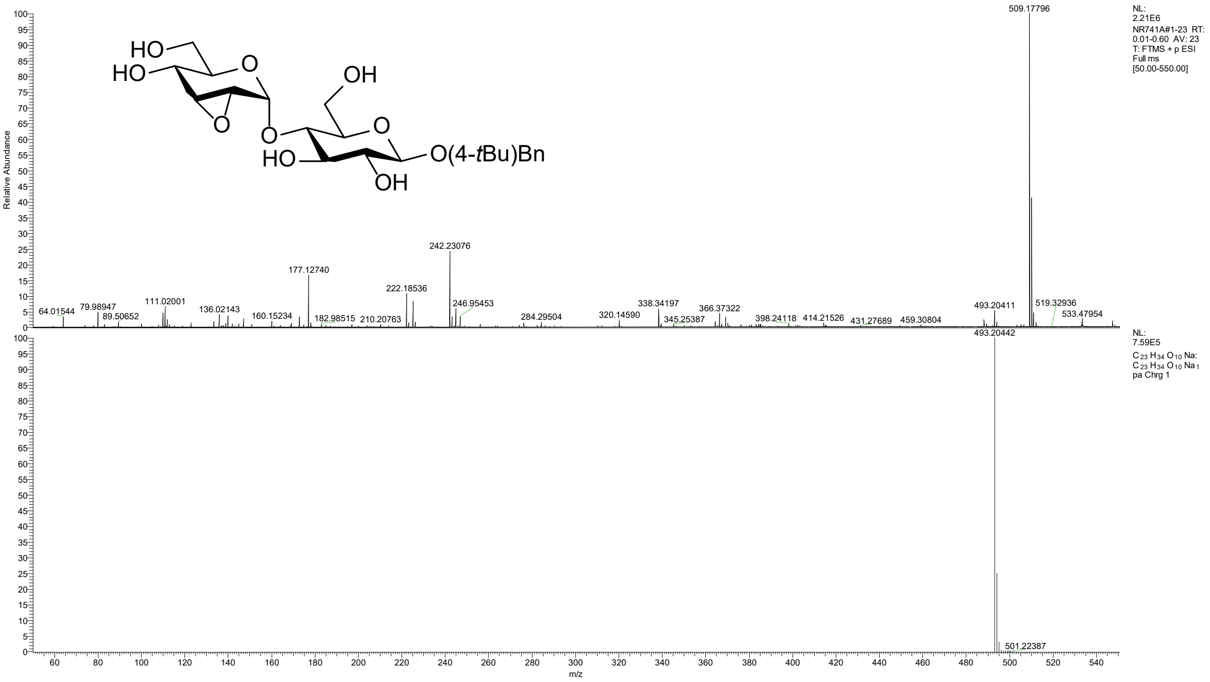
HRMS spectra of epoxides 5 and 6

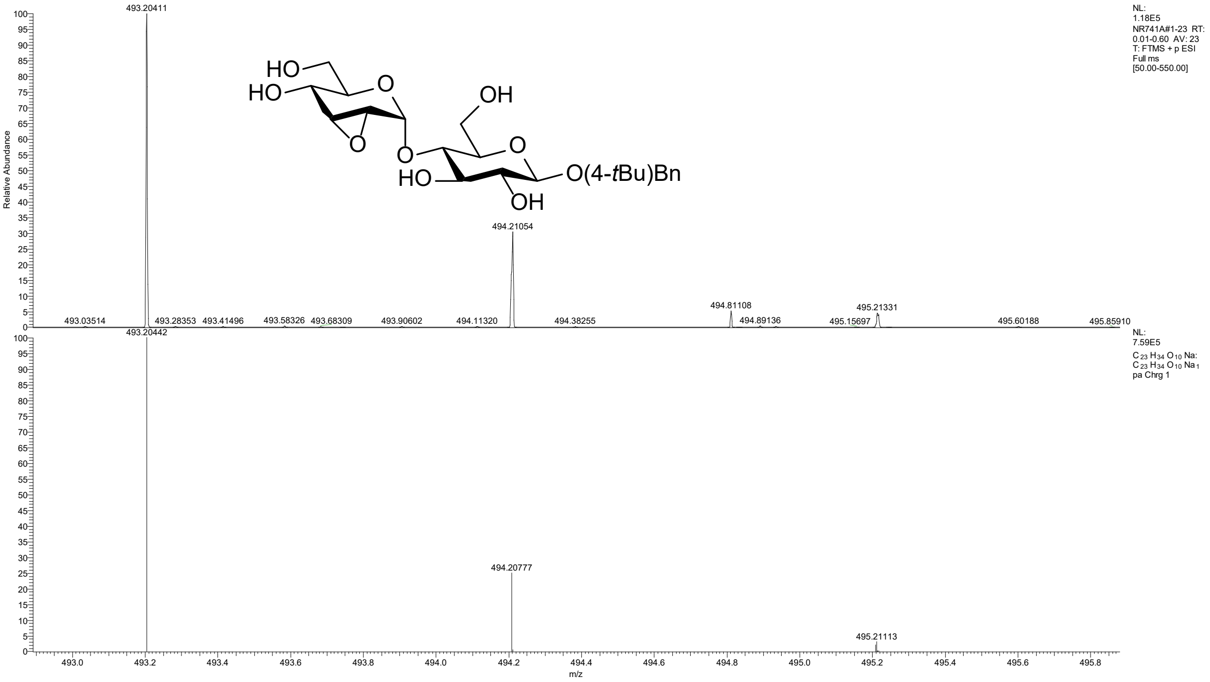
Methyl 2,3-anhydro-α-D-glucopyranoside (5)





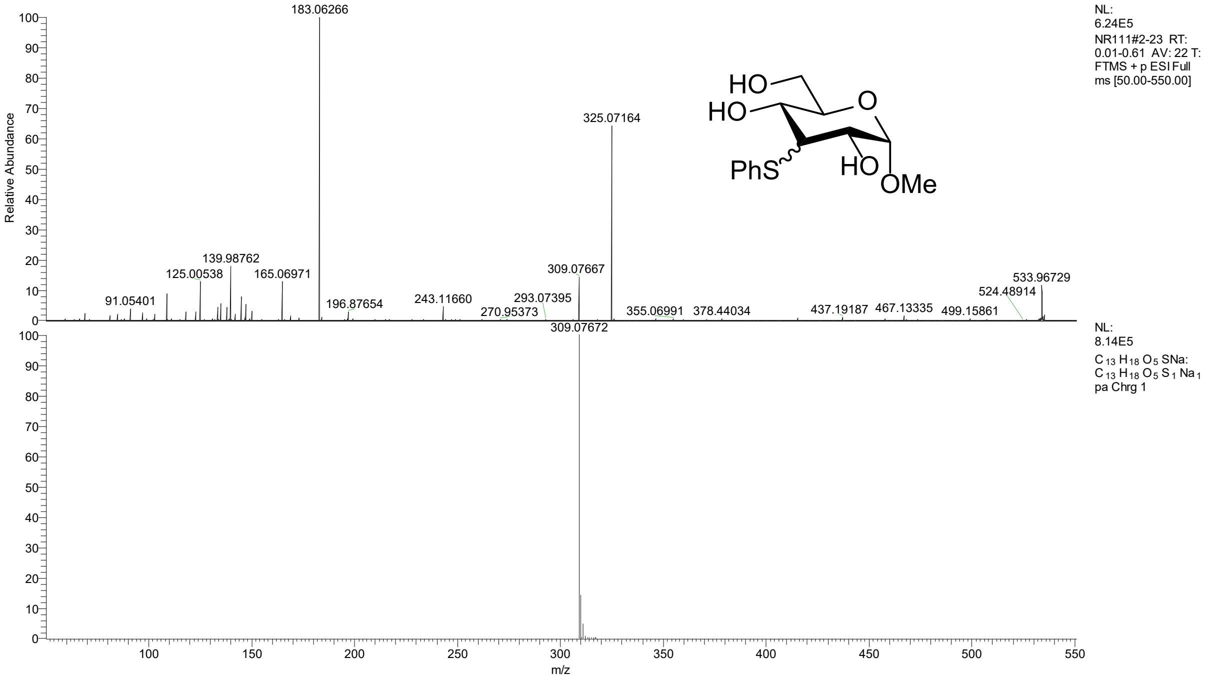
4-tert-butylbenzyl-2,3-anhydro-α-D-maltoside (6)

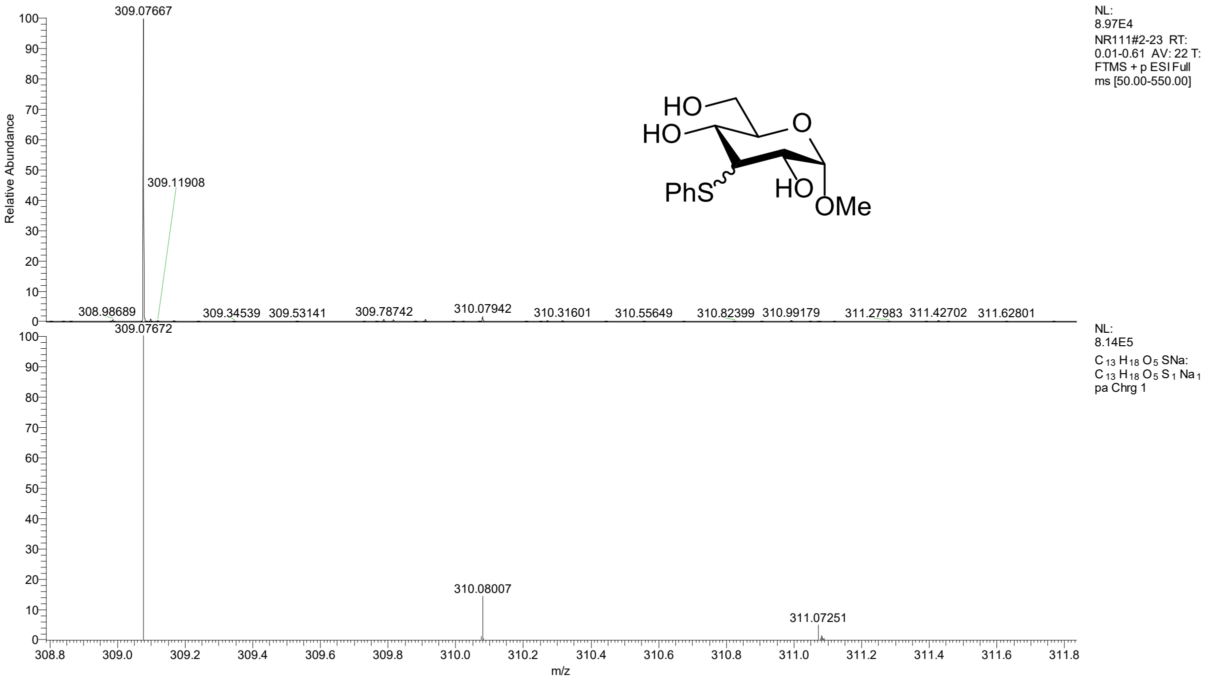




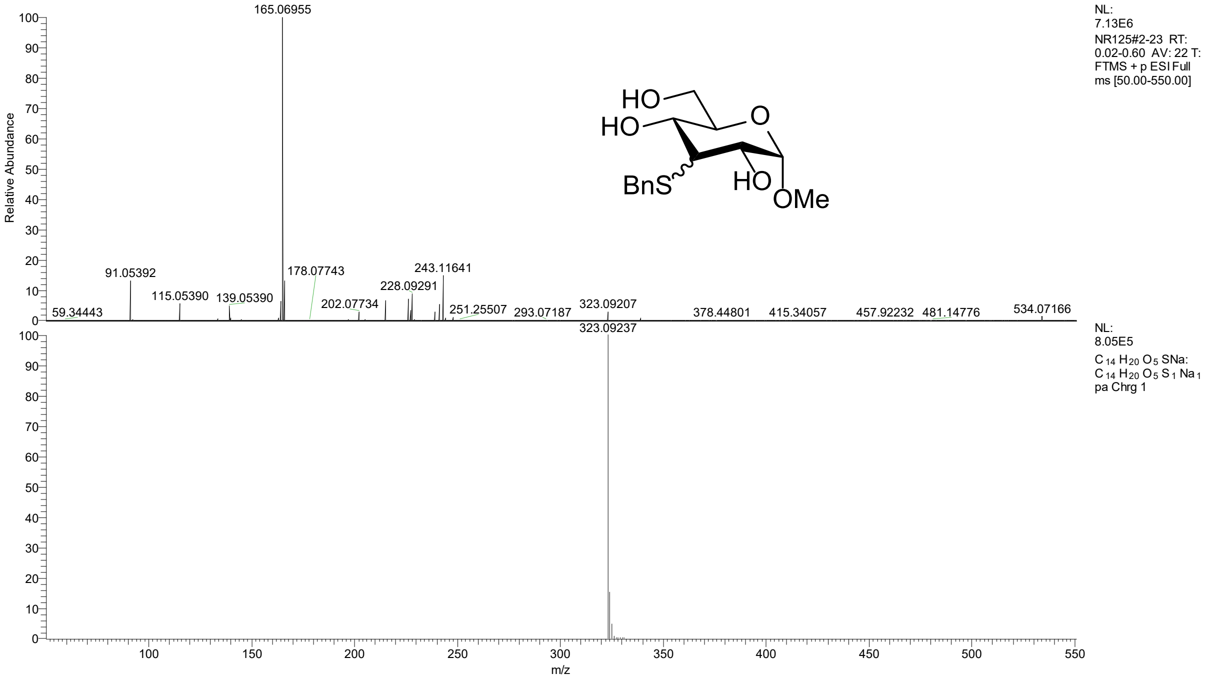
HRMS spectra of α-Glc derivatives

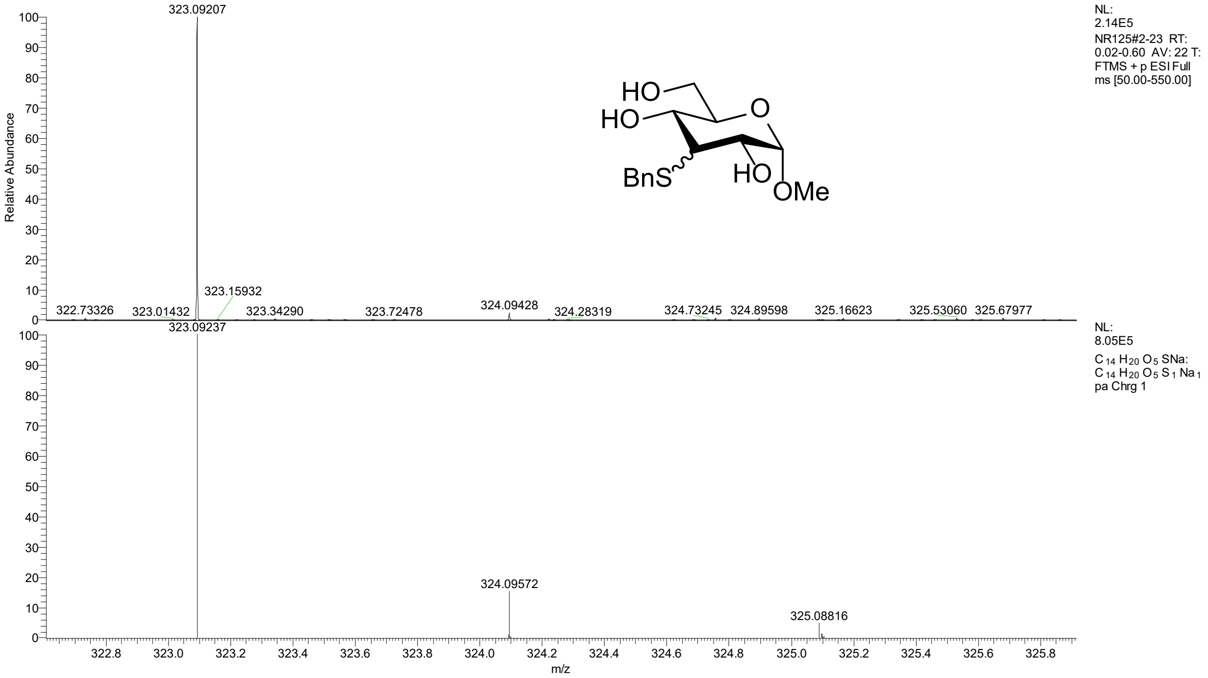
Methyl 3-S-phenyl-3-deoxy-α-D-allo/glucopyranoside (3b)





Methyl 3-S-benzyl-3-deoxy-α-D-allo/glucopyranoside (3c)

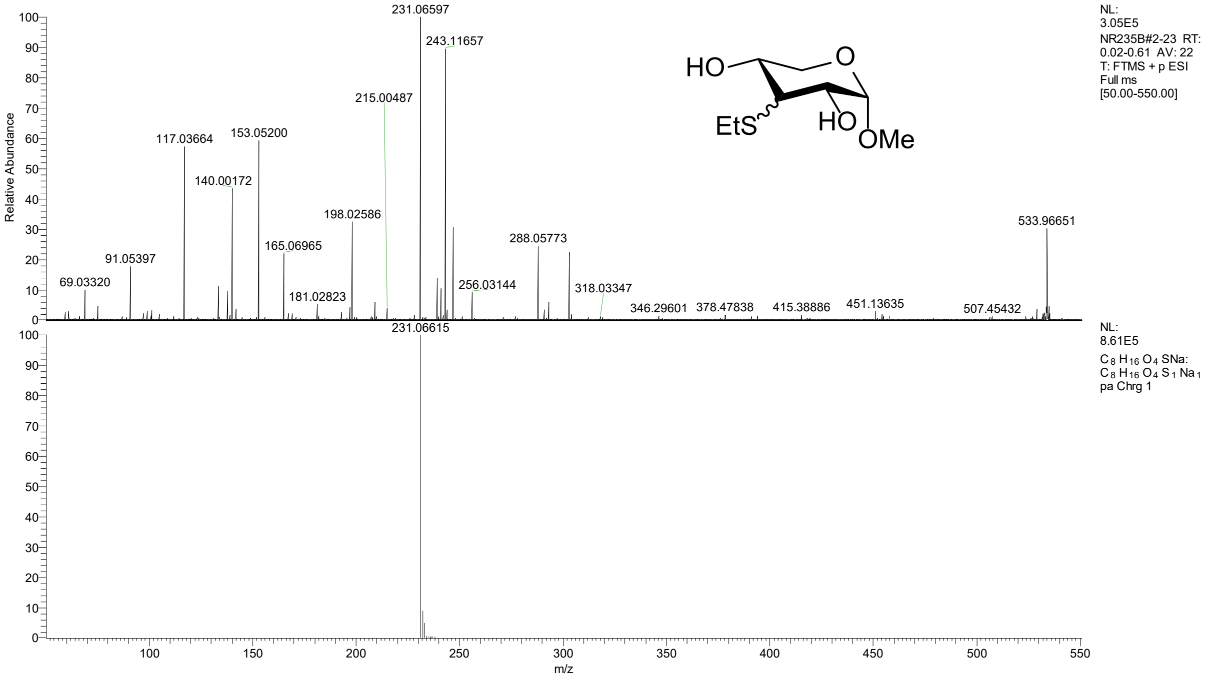


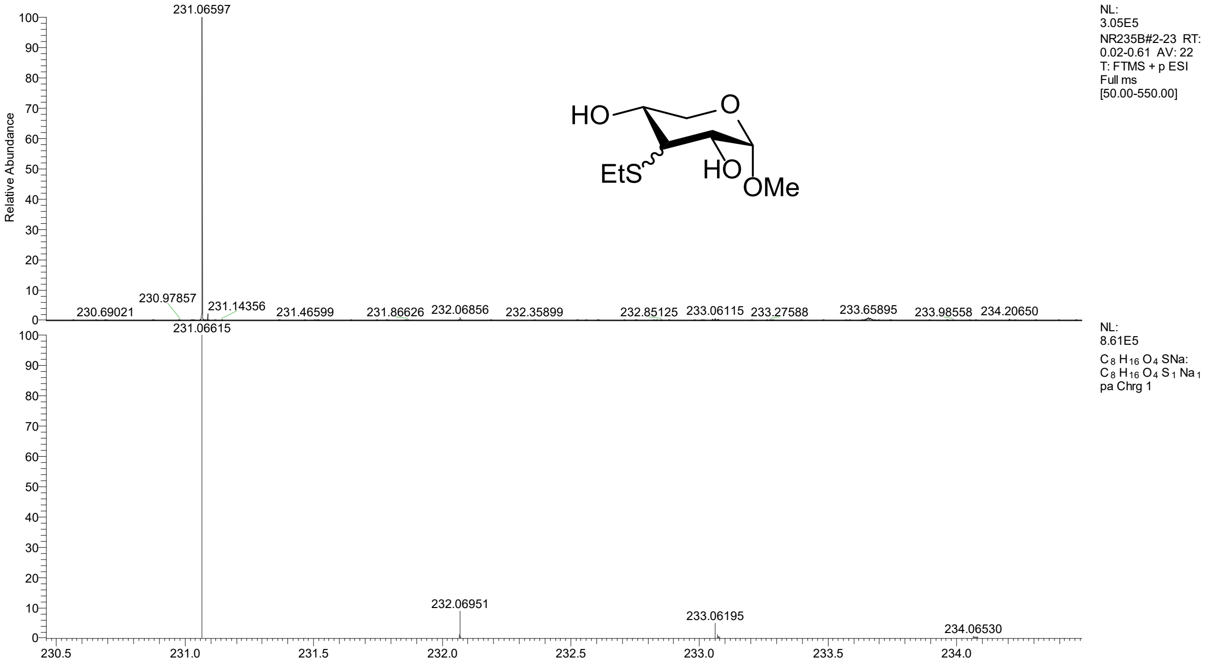


HRMS spectra of Xyl derivatives

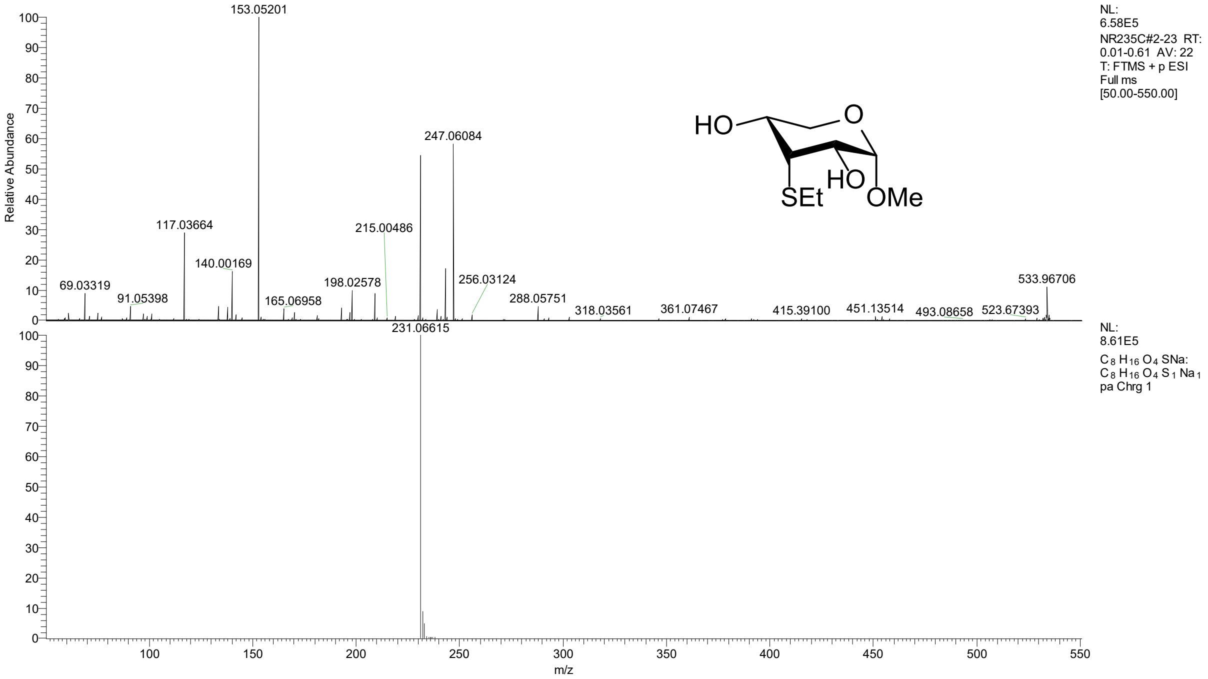
Methyl 3-deoxy-3-S-ethyl-α-D-riboso/xylopyranoside (8a)

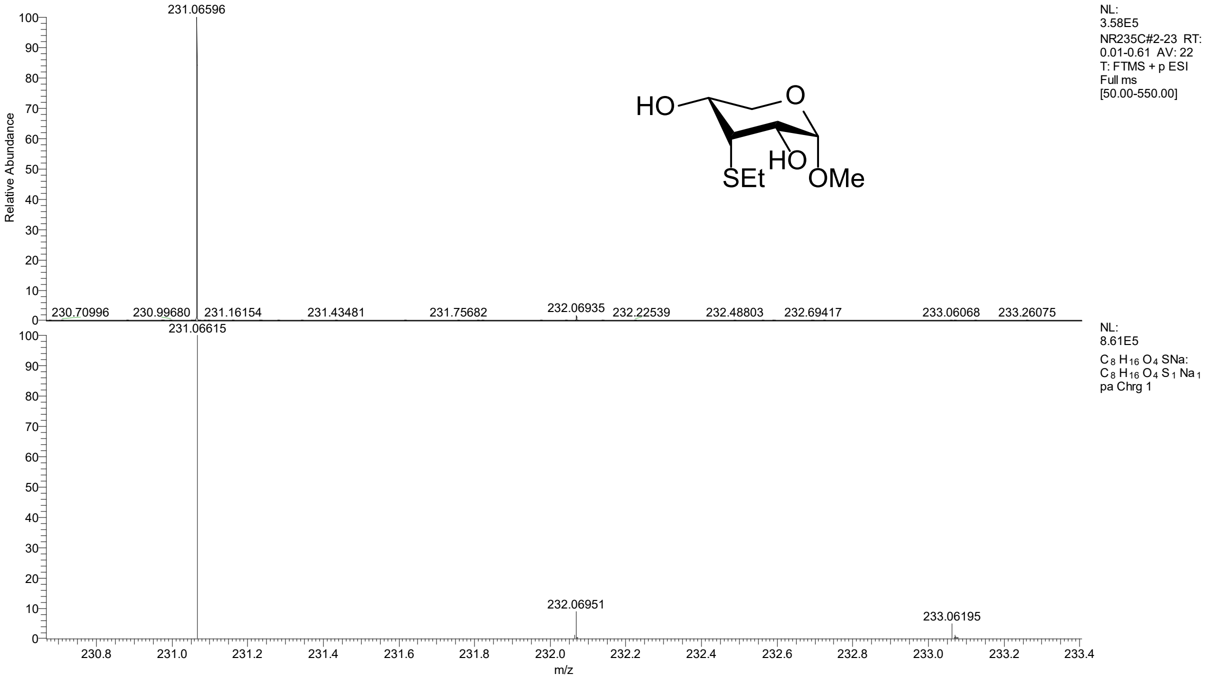
Equatorial/axial mix:





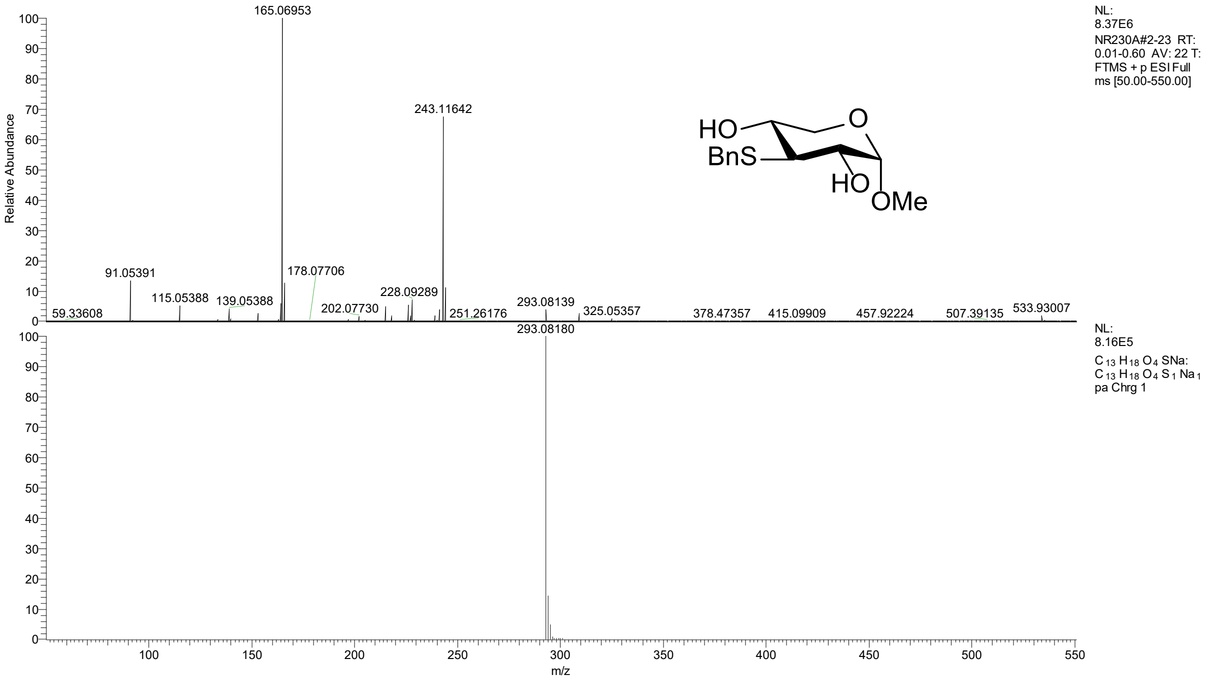
Axial:

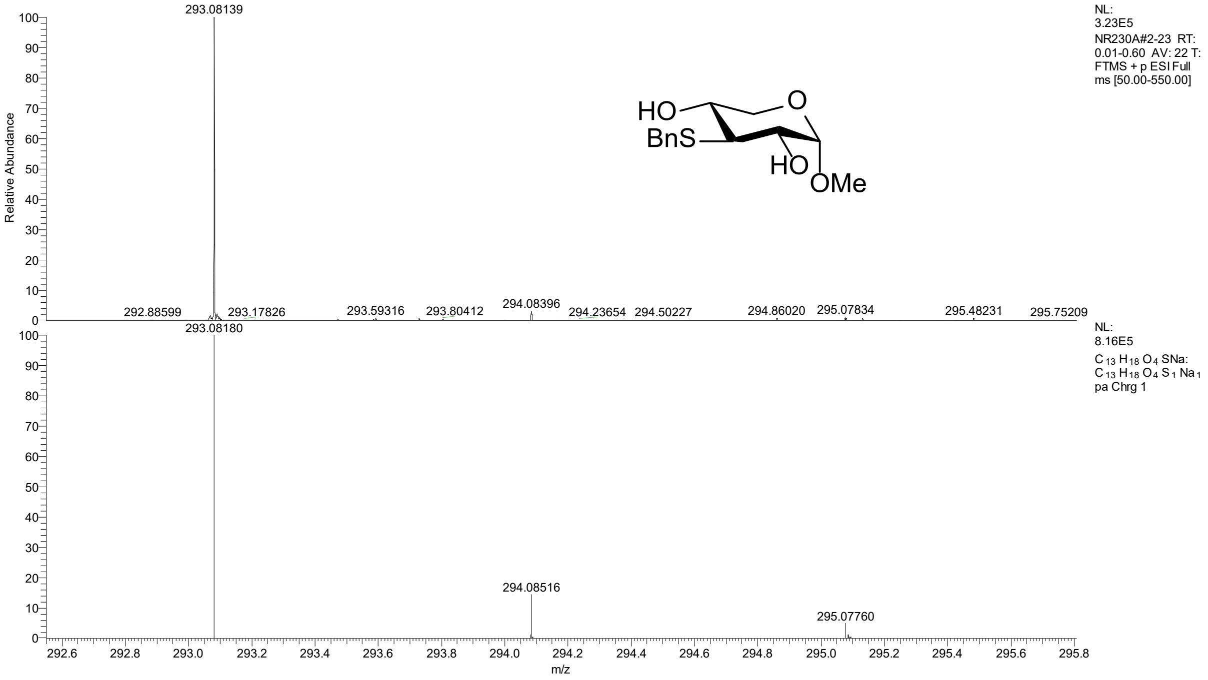

153.05201
247.06084
117.03664
215.00486
140.00169
69.03319
91.05398
165.06958
198.02578
256.03124
288.05751
318.03561
361.07467
415.39100
451.13514
493.08658
523.67393
533.96706
231.06615
Relative Abundance
m/z
NL:
6.58E5
NR235C#2-23 RT:
0.01-0.61 AV: 22
T: FTMS + p ESI
Full ms
[50.00-550.00]
NL:
8.61E5
C 8 H 16 O 4 SNa:
C 8 H 16 O 4 S 1 Na 1
pa Chrg 1
HO
O
HO
SEt
OMe


231.06596
230.70996
230.99680
231.16154
231.43481
231.75682
232.06935
232.22539
232.48803
232.69417
233.06068
233.26075
231.06615
232.06951
233.06195
Relative Abundance
m/z
NL:
3.58E5
NR235C#2-23 RT:
0.01-0.61 AV: 22
T: FTMS + p ESI
Full ms
[50.00-550.00]
NL:
8.61E5
C 8 H 16 O 4 SNa:
C 8 H 16 O 4 S 1 Na 1
pa Chrg 1
HO
O
HO
SEt
OMe

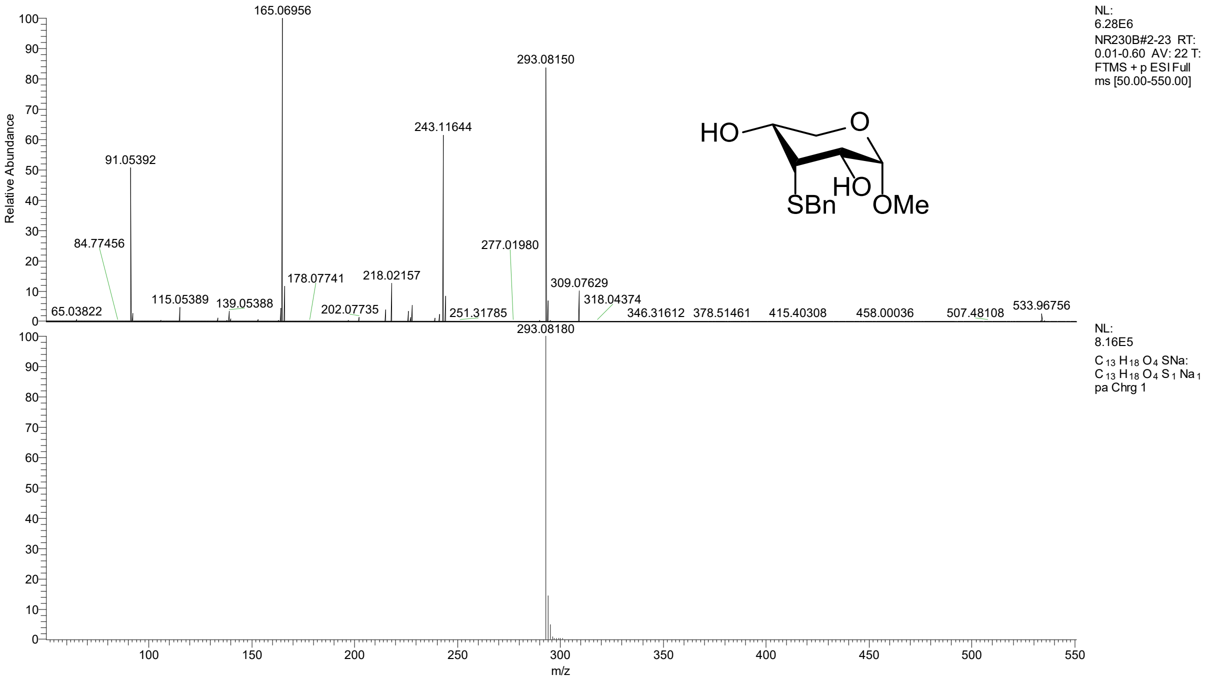
Methyl 3-S-benzyl-3-deoxy-α-D-riboso/xylopyranoside (8b)

Equatorial:

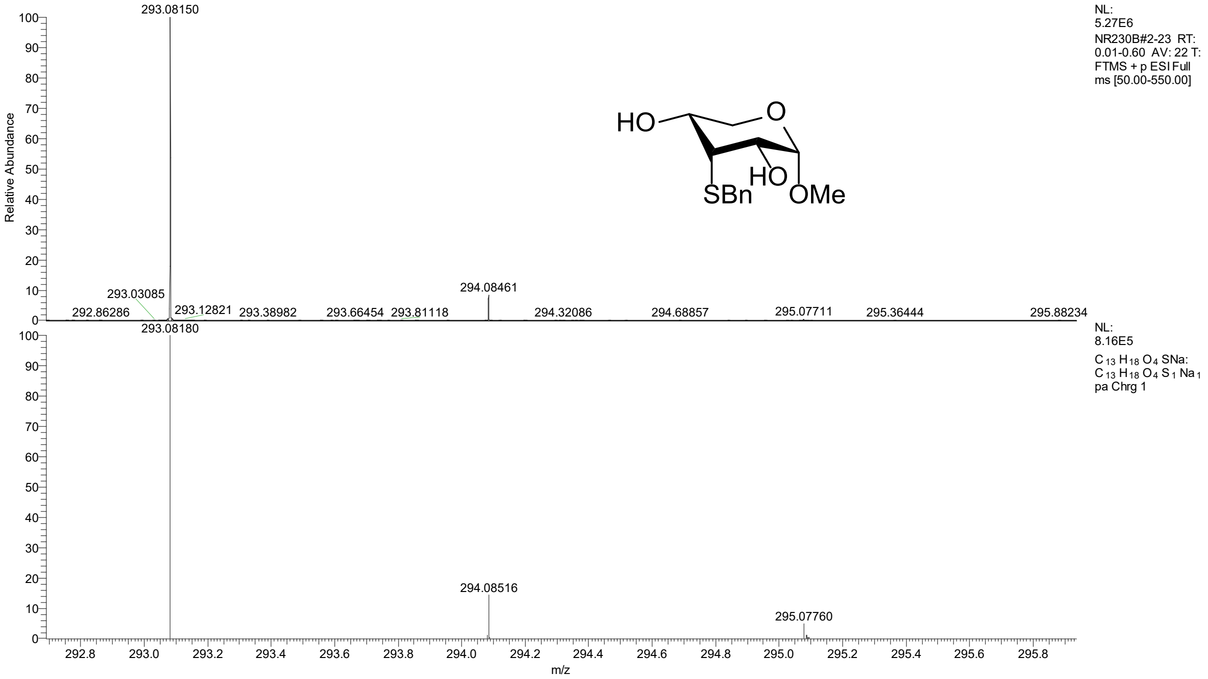




Axial:

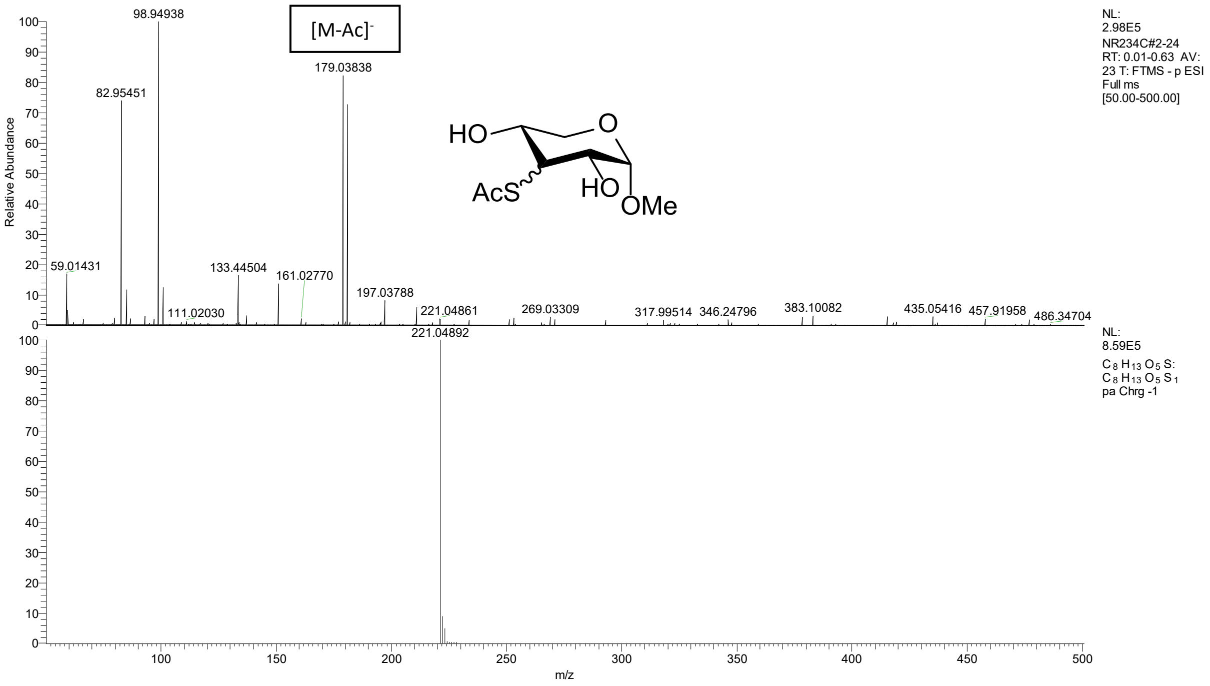


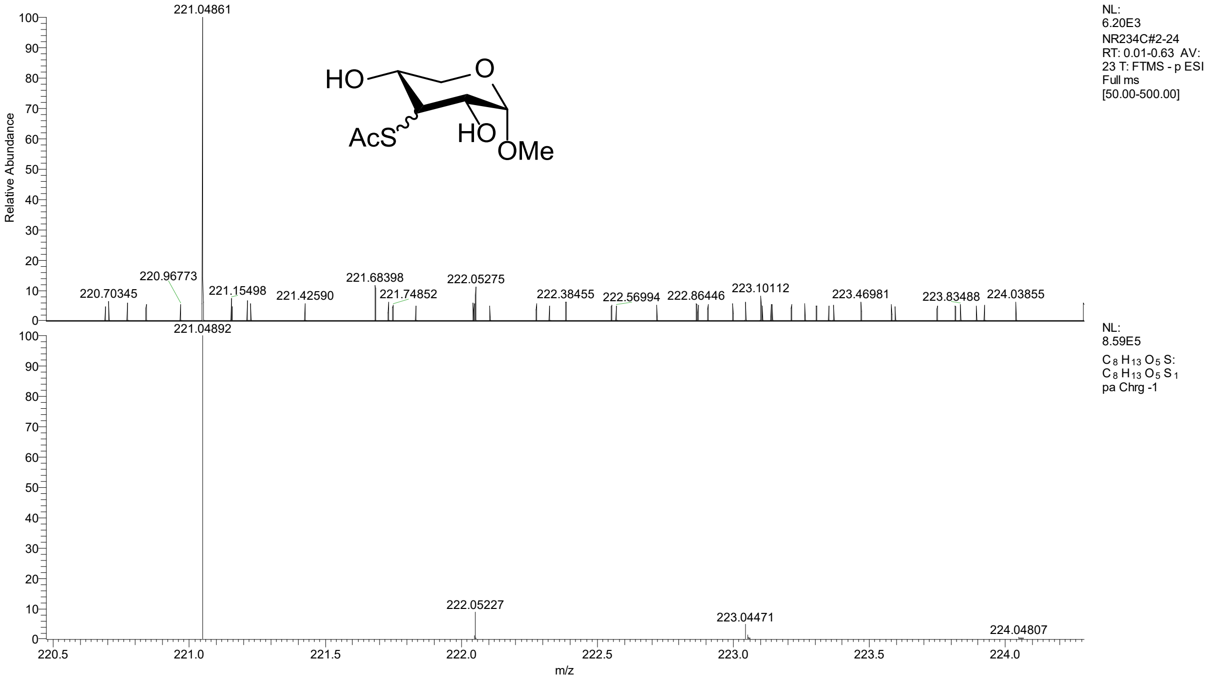
Relative Abundance
m/z
165.06956
293.08150
243.11644
91.05392
84.77456
277.01980
178.07741
218.02157
309.07629
318.04374
65.03822
115.05389
139.05388
202.07735
251.31785
346.31612
378.51461
415.40308
458.00036
507.48108
533.96756
293.08180
NL:
6.28E6
NR230B#2-23 RT:
0.01-0.60 AV: 22 T:
FTMS + p ESI Full
ms [50.00-550.00]
NL:
8.16E5
C 13 H 18 O 4 SNa:
C 13 H 18 O 4 S 1 Na 1
pa Chrg 1
HO
O
HO
SBn
OMe



Relative Abundance
m/z
293.08150
293.03085
292.86286
293.12821
293.38982
293.66454
293.81118
294.08461
294.32086
294.68857
295.07711
295.36444
295.88234
293.08180
294.08516
295.07760
NL:
5.27E6
NR230B#2-23 RT:
0.01-0.60 AV: 22 T:
FTMS + p ESI Full
ms [50.00-550.00]
NL:
8.16E5
C 13 H 18 O 4 SNa:
C 13 H 18 O 4 S 1 Na 1
pa Chrg 1
HO
O
HO
SBn
OMe

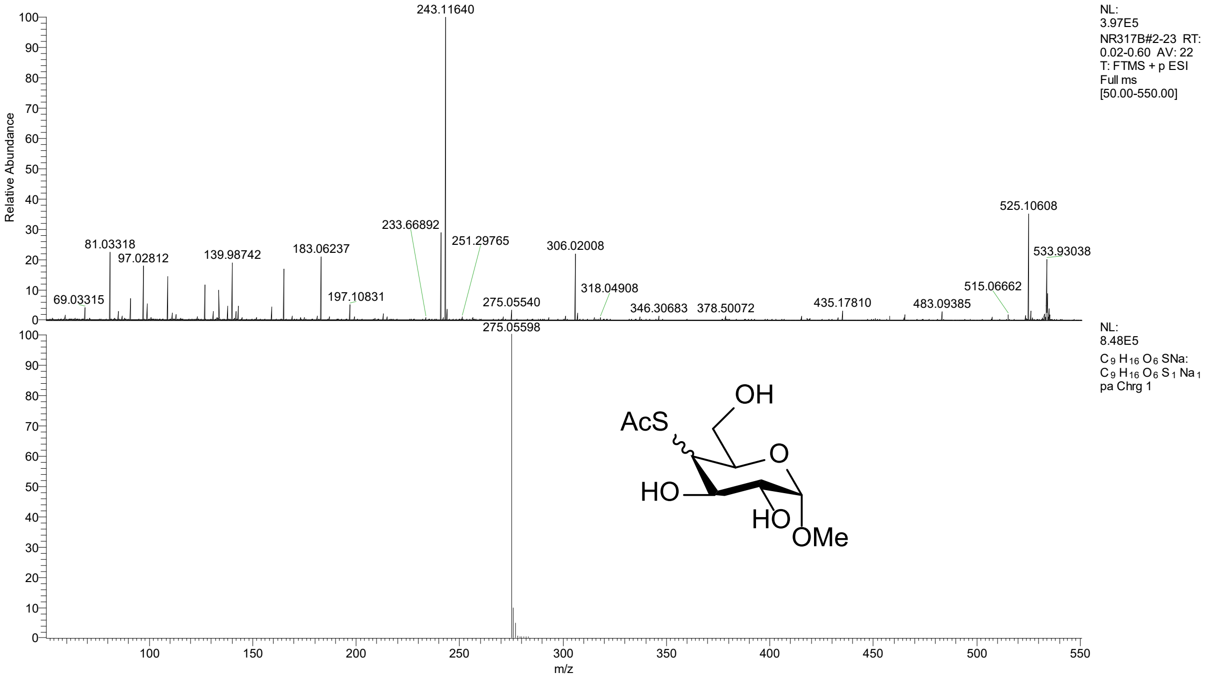
Methyl 3-S-acetyl-3-deoxy-α-D-riboso/xylopyranoside (8c)

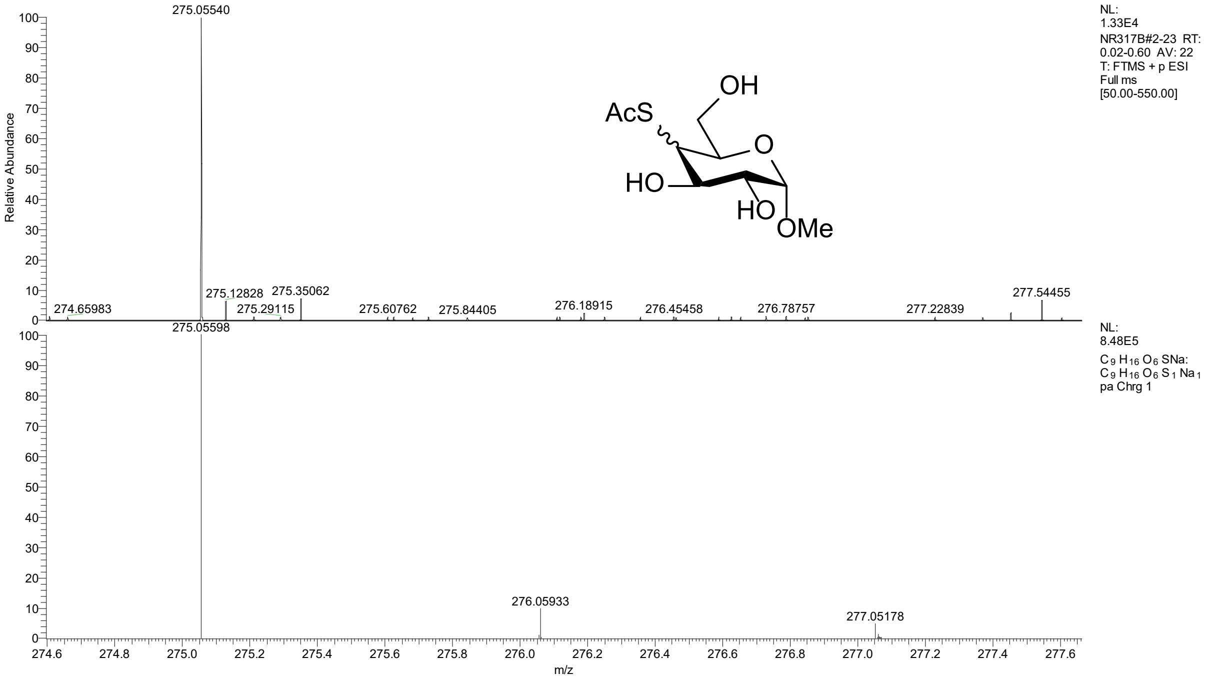




HRMS spectra of Gal derivative

Methyl 4-S-acetyl-4-deoxy-α-D-galacto/glucopyranoside (10)

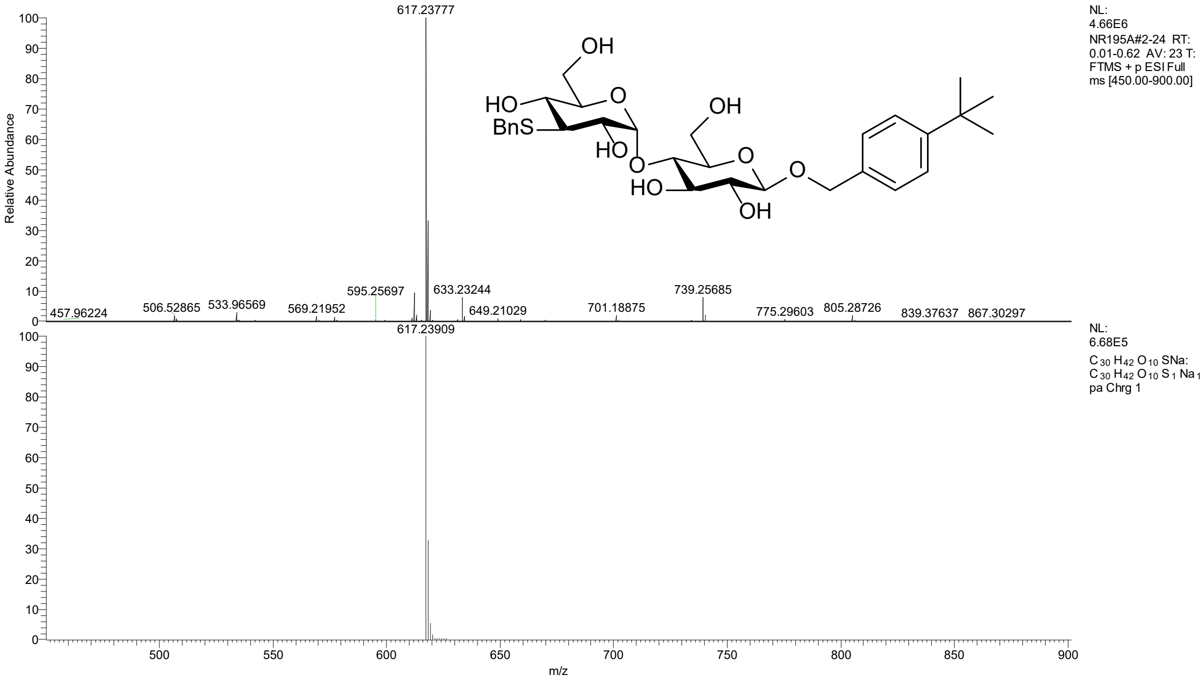


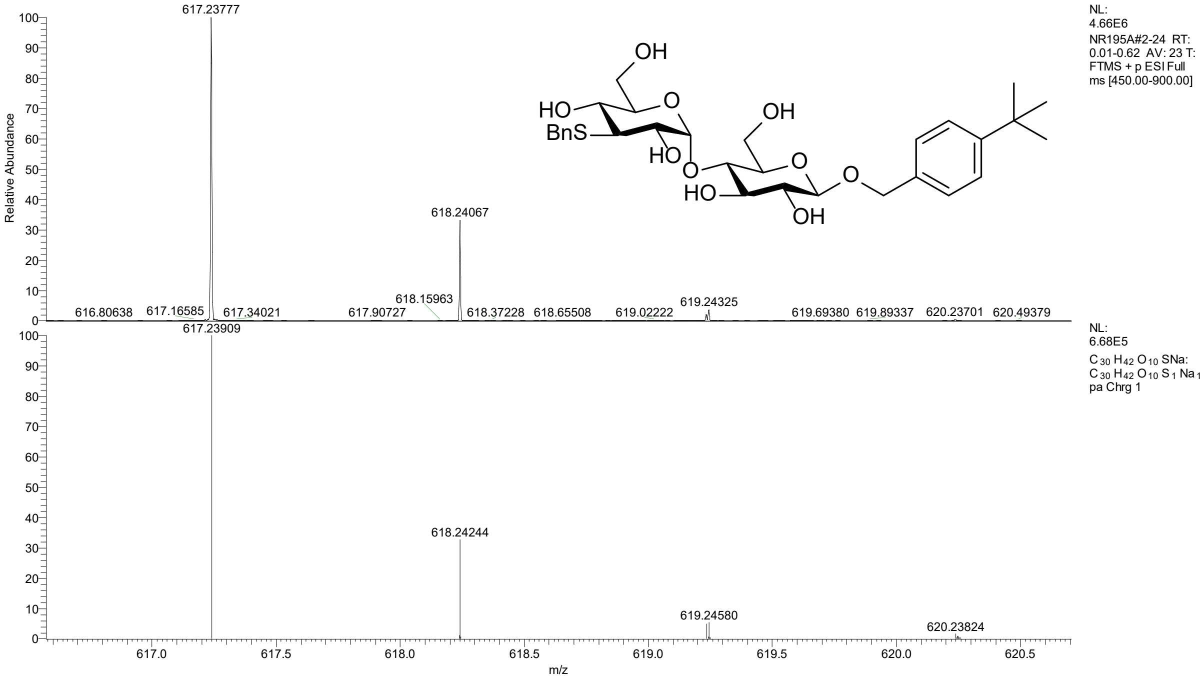


HRMS spectra of maltose derivative

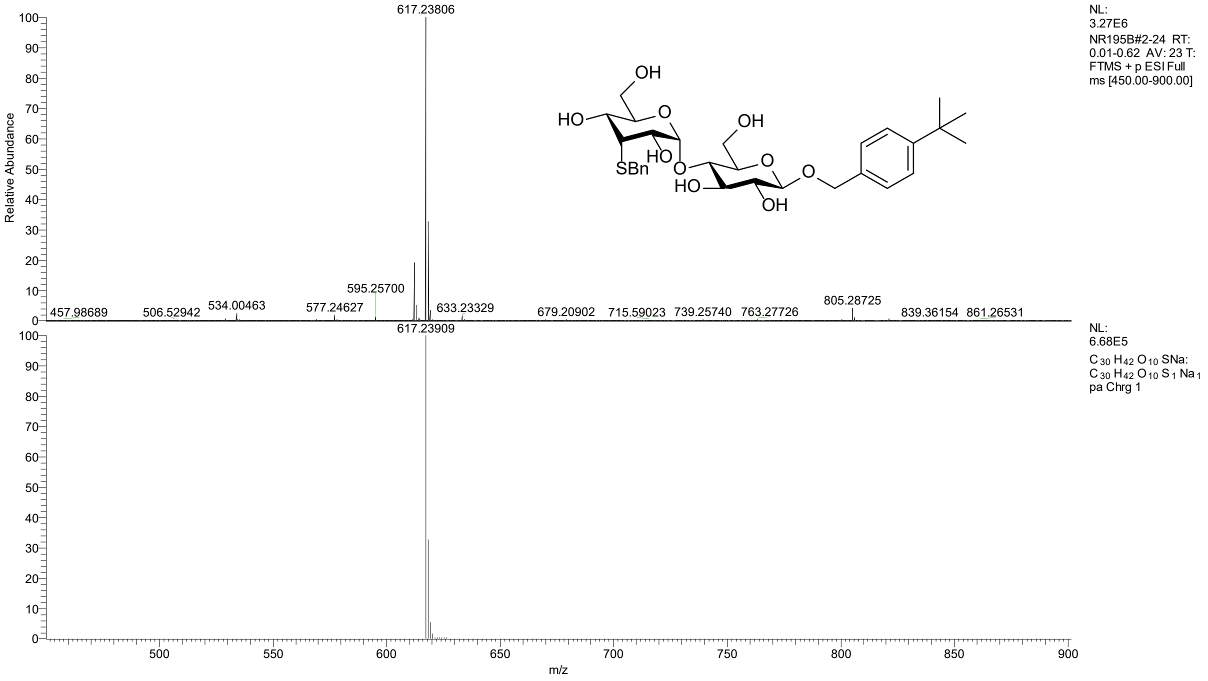
4-tert-butylbenzyl-3-S-benzyl-3-deoxy-α-D-maltoside (12)

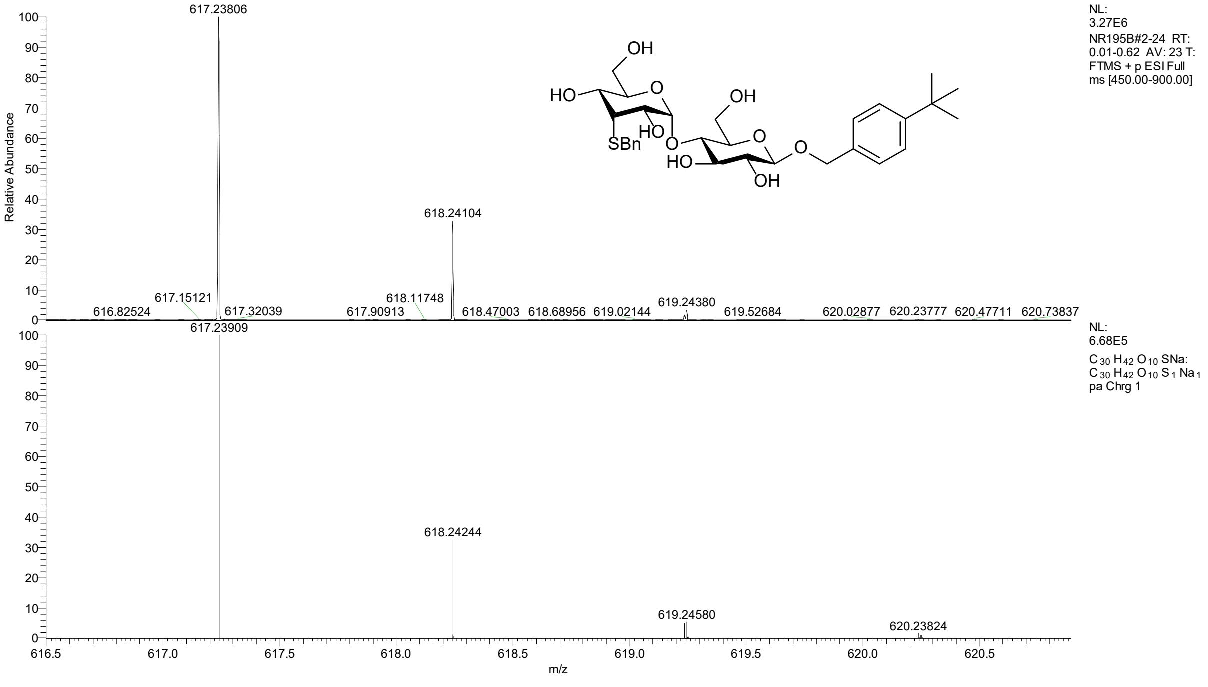
Equatorial:





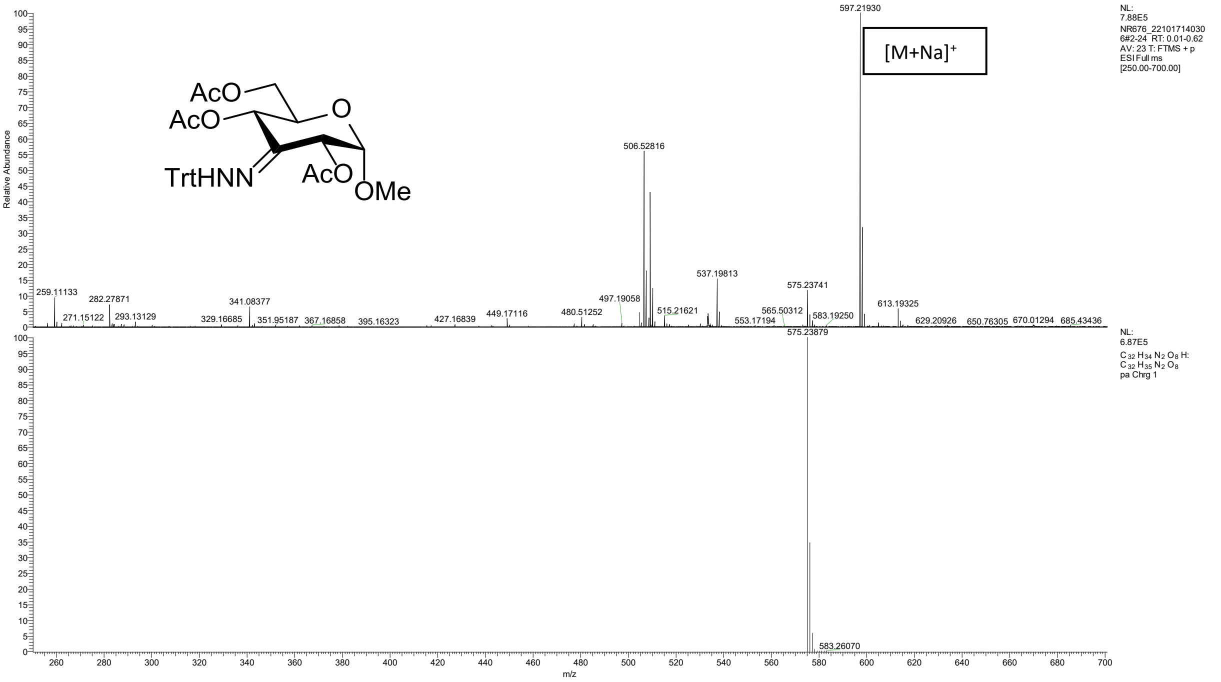
Axial:

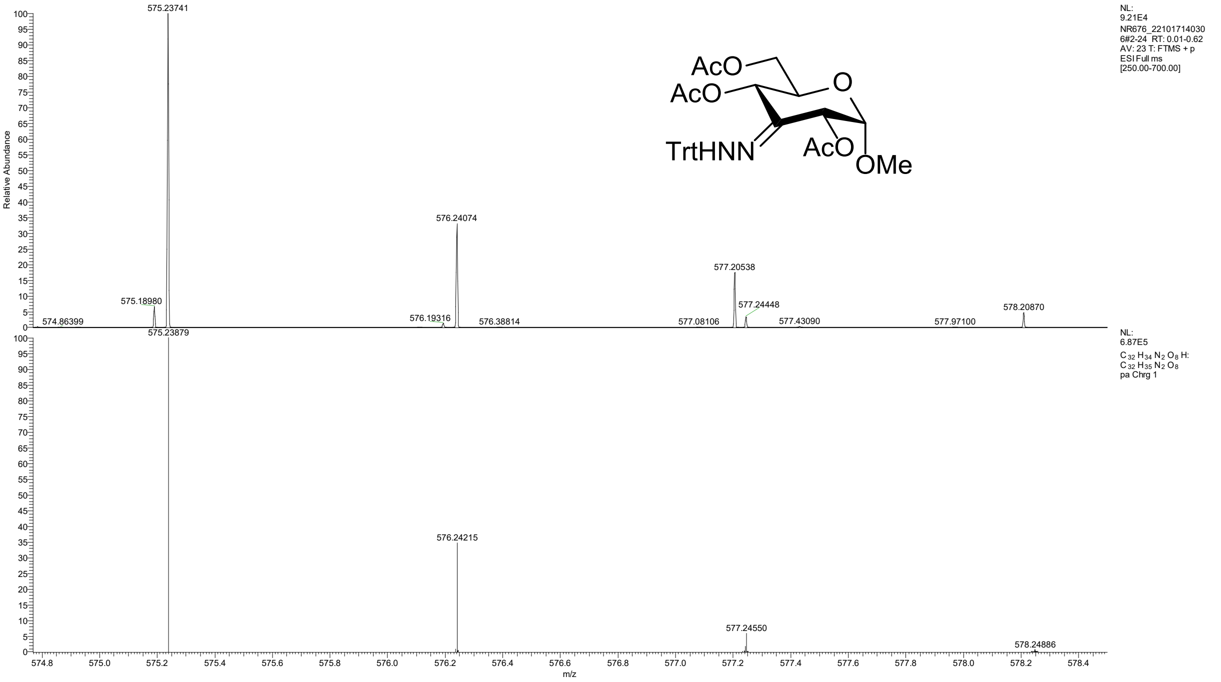

617.23806
595.25700
457.98689
506.52942
534.00463
577.24627
633.23329
679.20902
715.59023
739.25740
763.27726
805.28725
839.36154
861.26531
617.23909
Relative Abundance
m/z
NL:
3.27E6
NR195B#2-24 RT:
0.01-0.62 AV: 23 T:
FTMS + p ESI Full
ms [450.00-900.00]
NL:
6.68E5
$C_{30}H_{42}O_{10}SNa$:
$C_{30}H_{42}O_{10}S_1Na_1$
pa Chrg 1
OH
HO
O
HO
SBn
O
OH
O
HO
OH
O


617.23806
618.24104
616.82524
617.15121
617.32039
617.90913
618.11748
618.47003
618.68956
619.02144
619.24380
619.52684
620.02877
620.23777
620.47711
620.73837
617.23909
618.24244
619.24580
620.23824
Relative Abundance
m/z
NL:
3.27E6
NR195B#2-24 RT:
0.01-0.62 AV: 23 T:
FTMS + p ESI Full
ms [450.00-900.00]
NL:
6.68E5
$C_{30}H_{42}O_{10}SNa$:
$C_{30}H_{42}O_{10}S_1Na_1$
pa Chrg 1
OH
HO
O
HO
SBn
O
OH
O
HO
OH
O

HRMS spectra of S13 and S14

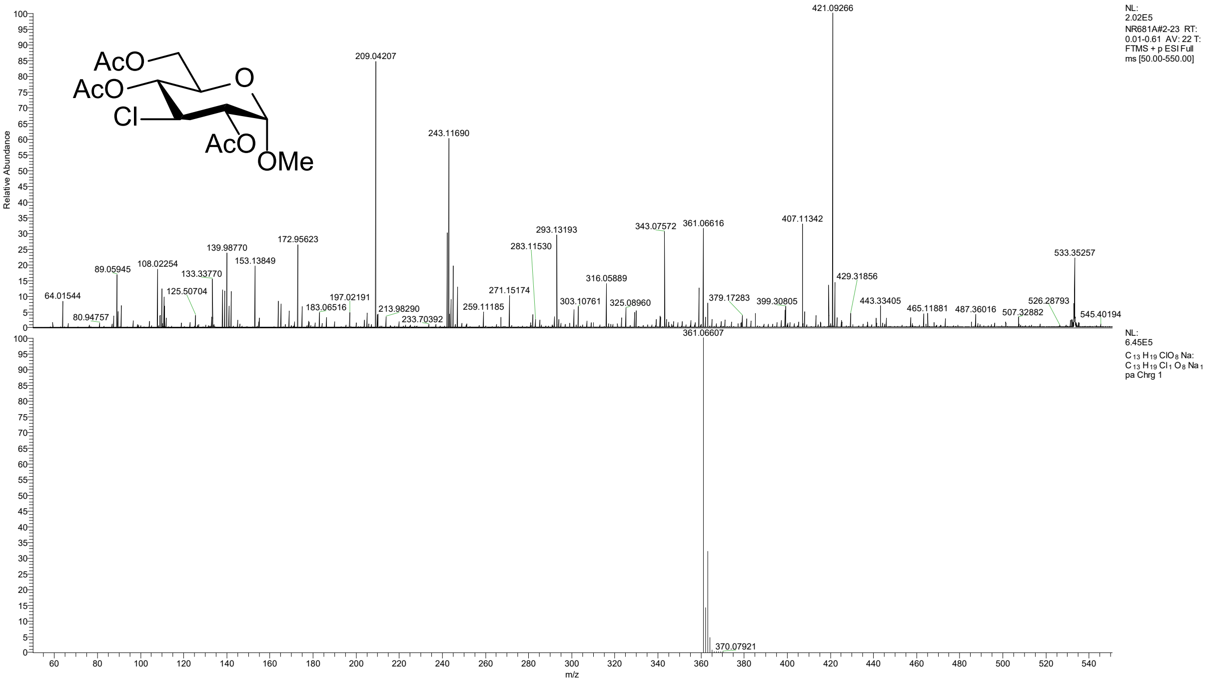
Methyl-2,4,6-O-acetyl-3-(trityl)hydrazone)-α-D-glucopyranoside (S13)

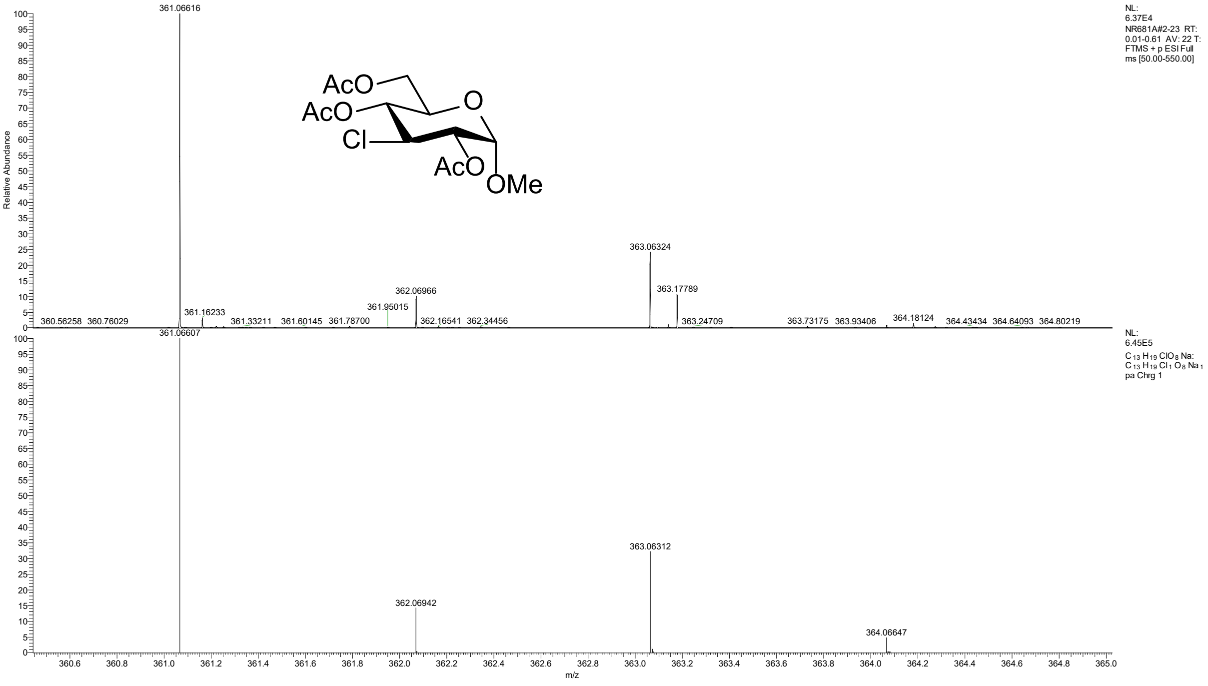




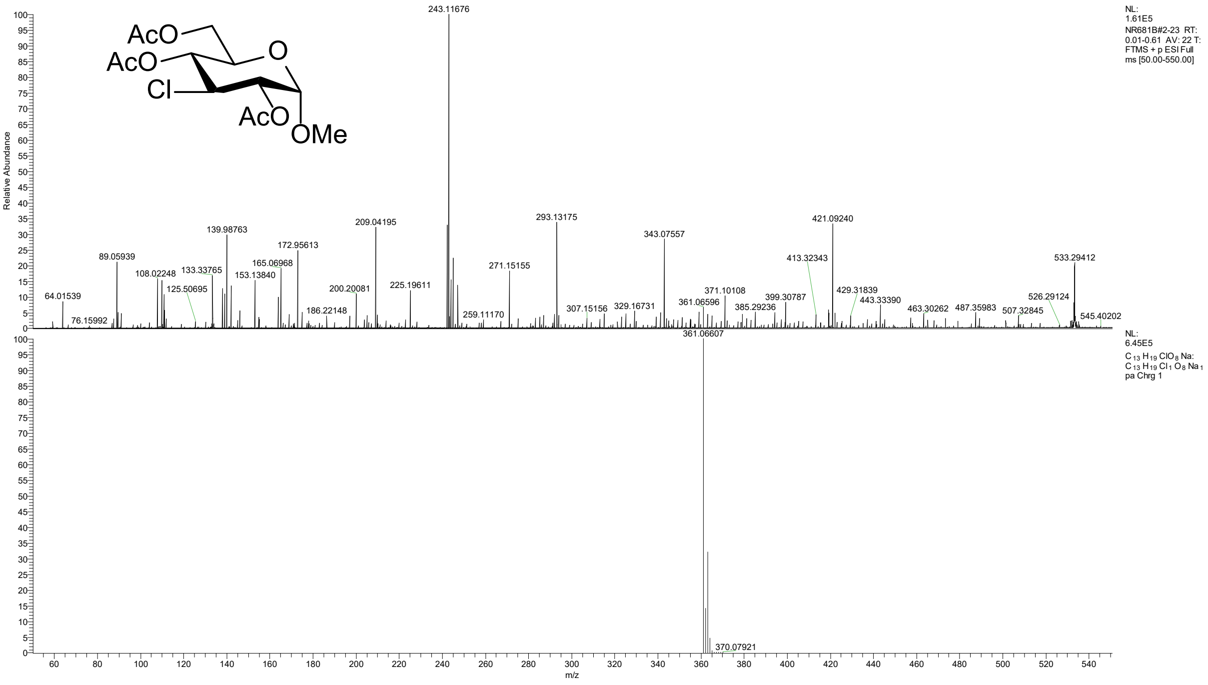
Methyl 2,4,6-tri-O-acetyl-3-chloro-3-deoxy-α-D-allo/glucopyranoside (S14)

Equatorial:

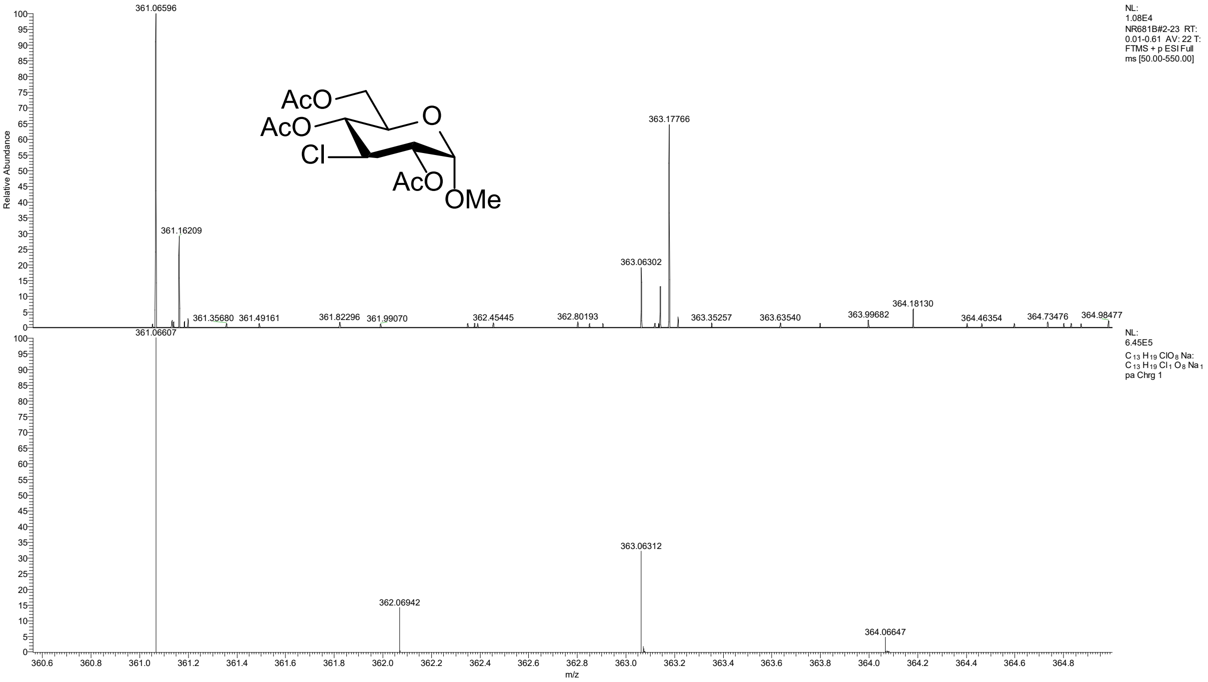




Axial:



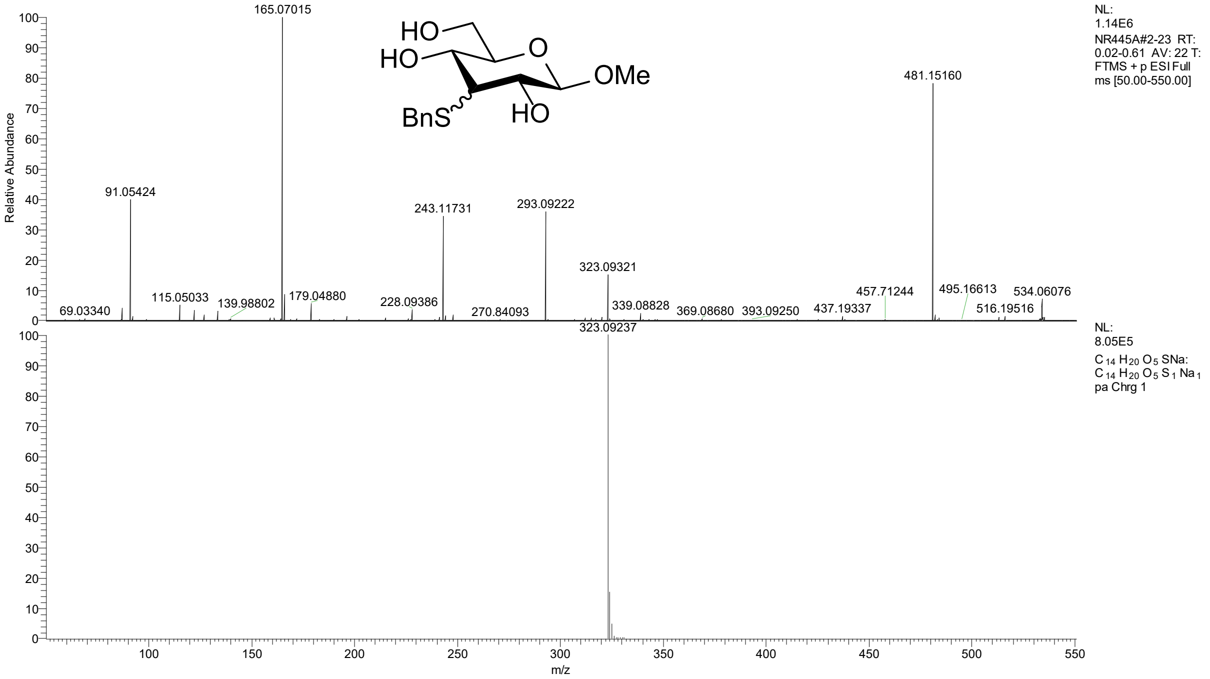
AcO
AcO
O
Cl
AcO
OMe
Relative Abundance
243.11676
139.98763
209.04195
293.13175
343.07557
421.09240
89.05939
172.95613
108.02248
133.33765
165.06968
153.13840
125.50695
200.20081
225.19611
271.15155
413.32343
533.29412
64.01539
76.15992
186.22148
259.11170
307.15156
329.16731
361.06596
371.10108
385.29236
399.30787
429.31839
443.33390
463.30262
487.35983
507.32845
526.29124
545.40202
NL: 1.61E5
NR681B#2-23 RT: 0.01-0.61 AV: 22 T: FTMS + p ESI Full ms [50.00-550.00]
361.06607
370.07921
NL: 6.45E5
C 13 H 19 ClO 8 Na: C 13 H 19 Cl 1 O 8 Na 1 pa Chrg 1
m/z

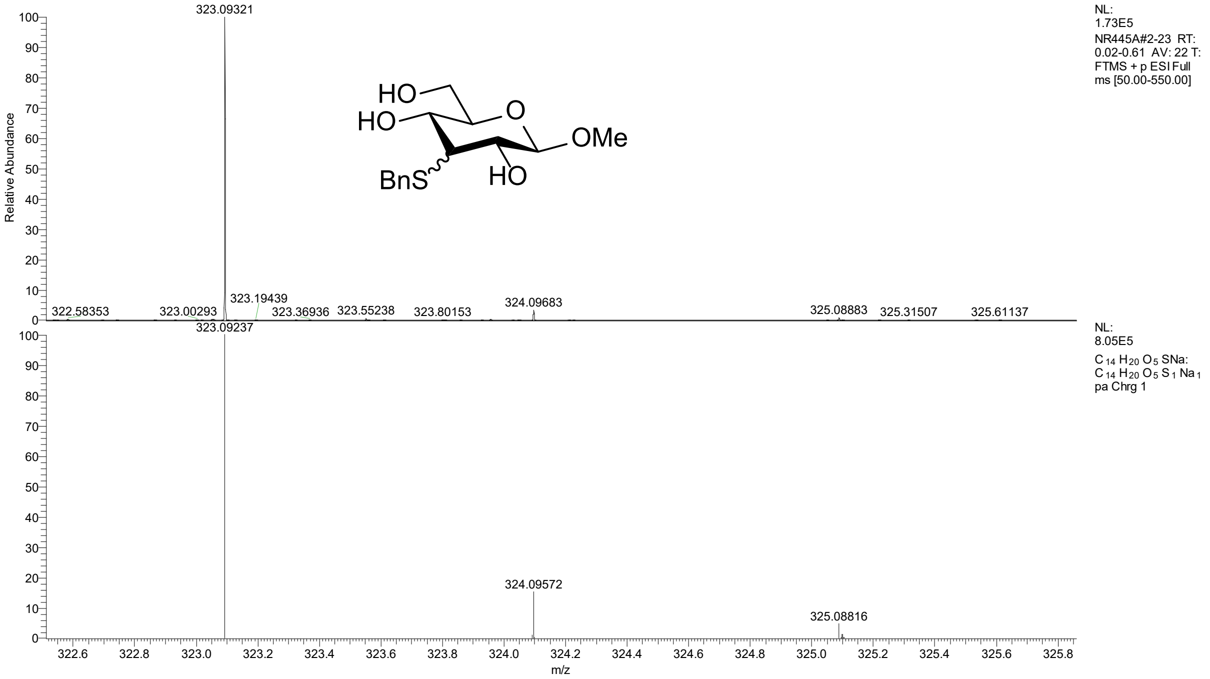


Relative Abundance
361.06596
361.16209
361.35680
361.49161
361.82296
361.99070
362.45445
362.80193
363.06302
363.17766
363.35257
363.63540
363.99682
364.18130
364.46354
364.73476
364.98477
AcO
AcO
O
Cl
AcO
OMe
NL: 1.08E4
NR681B#2-23 RT: 0.01-0.61 AV: 22 T: FTMS + p ESI Full ms [50.00-550.00]
361.06607
362.06942
363.06312
364.06647
NL: 6.45E5
C 13 H 19 ClO 8 Na: C 13 H 19 Cl 1 O 8 Na 1 pa Chrg 1
m/z

HRMS spectra of β-Glc derivative

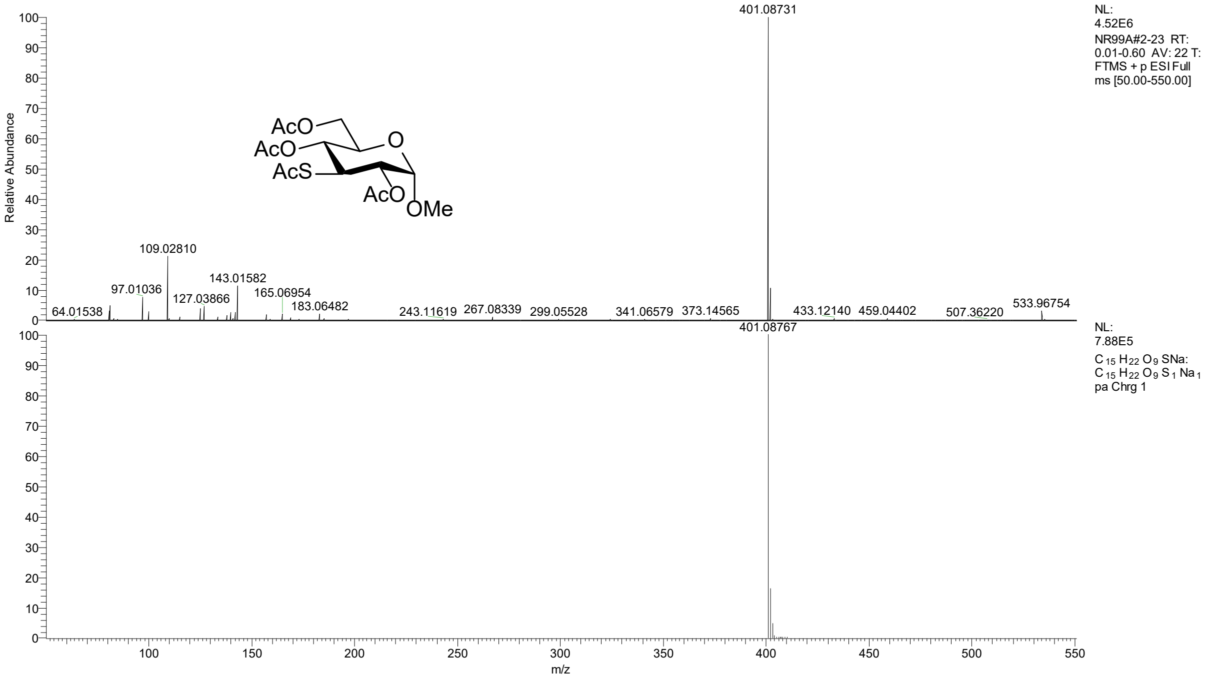
Methyl 3-S-benzyl-3-deoxy-β-D-allo/glucopyranoside (14)

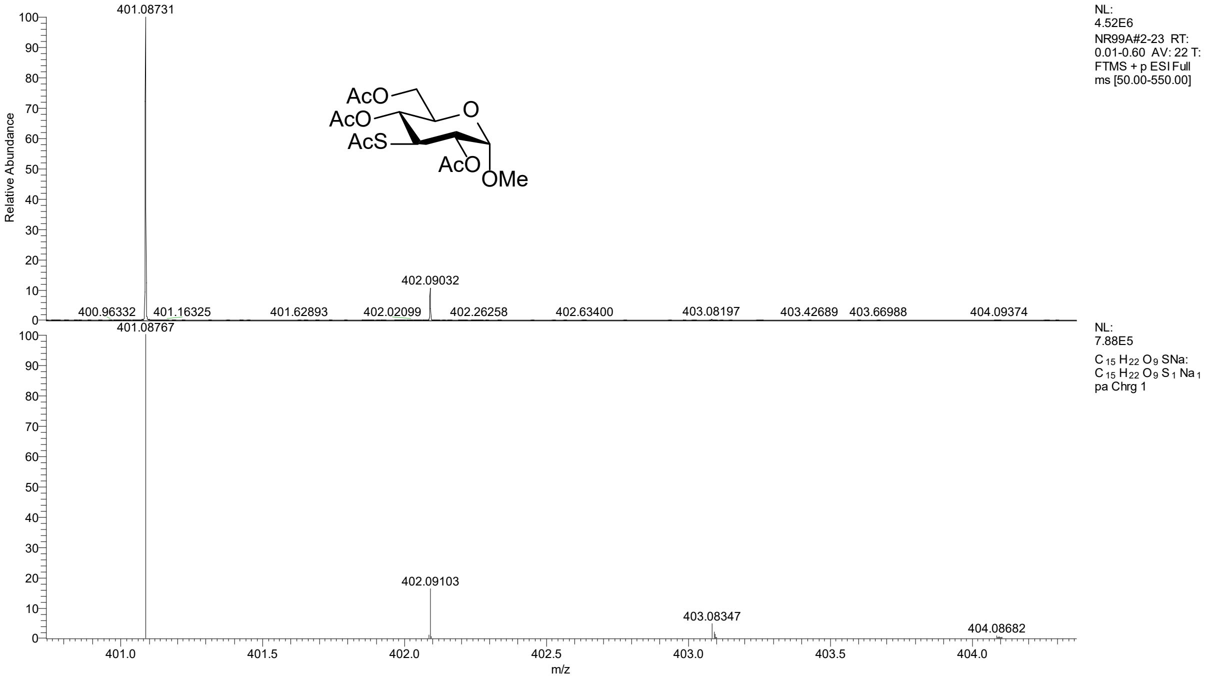




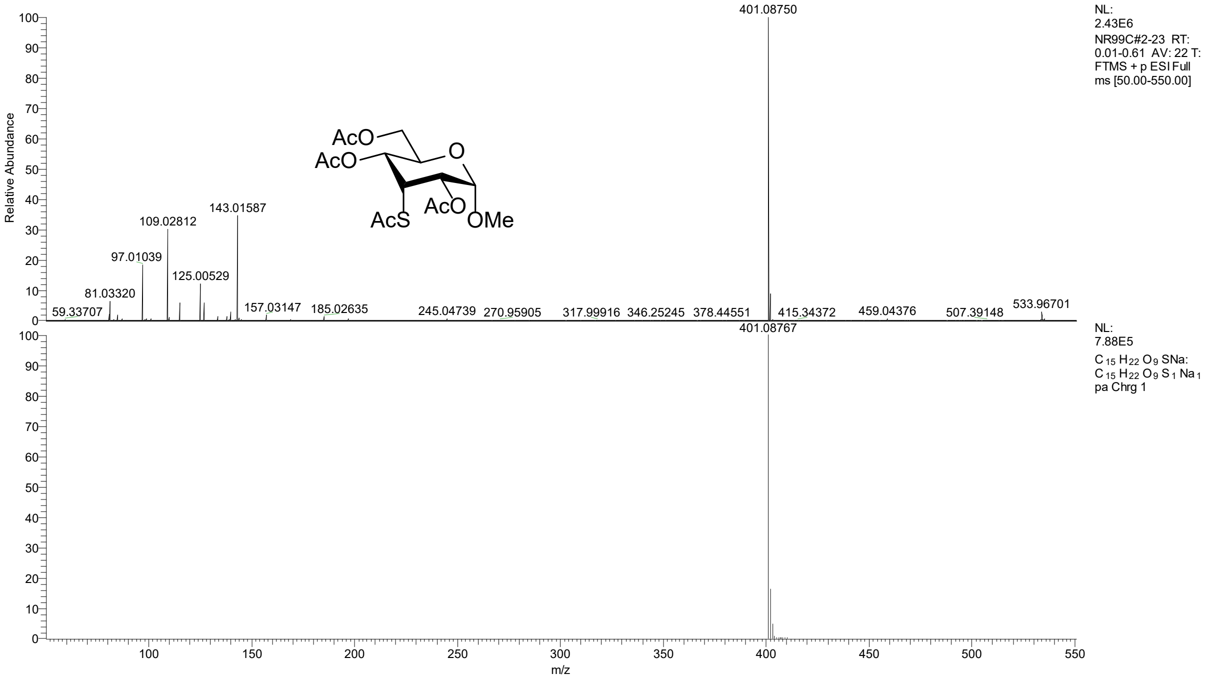
HRMS of S16, S17, and S-glycosides 20 and 22

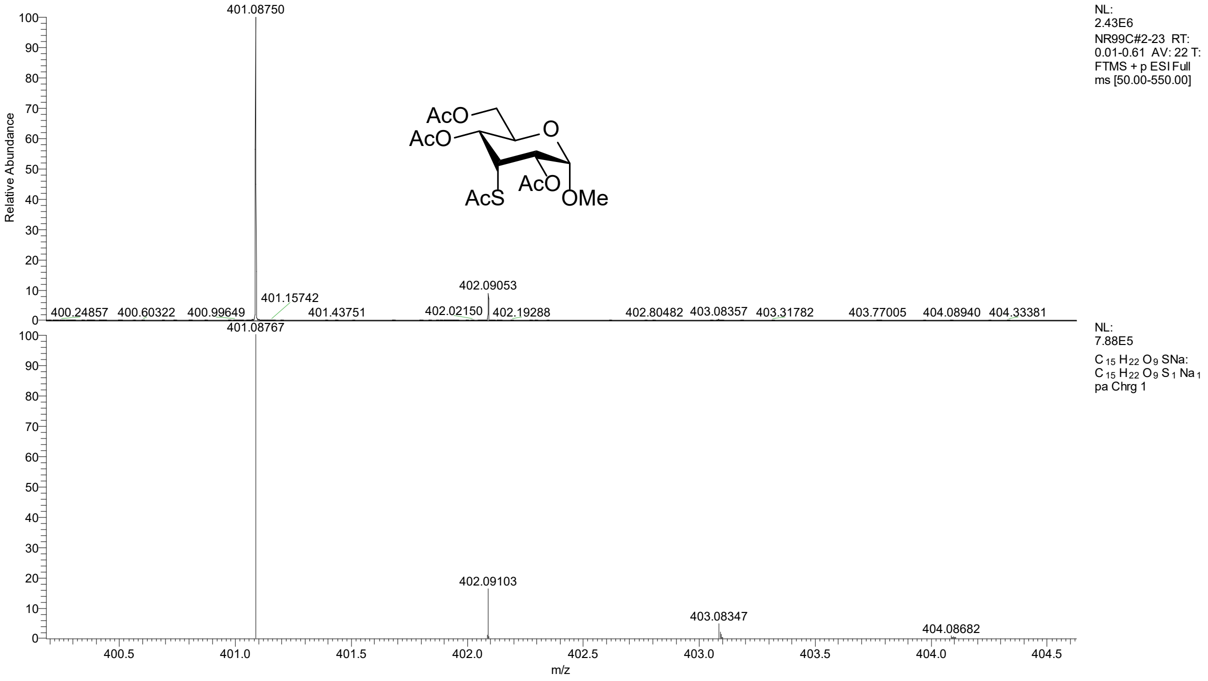
Methyl 2,3,4,6-tri-O-acetyl-3-S-acetyl-3-deoxy-α-D-glucopyranoside (S16)



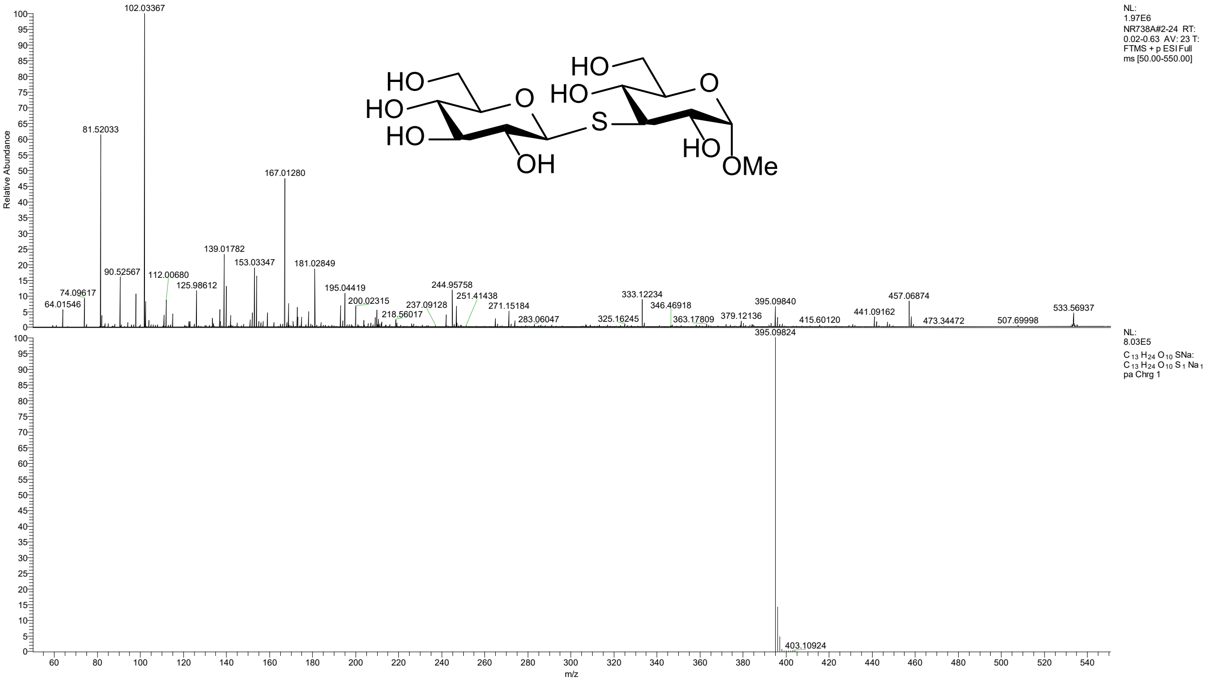


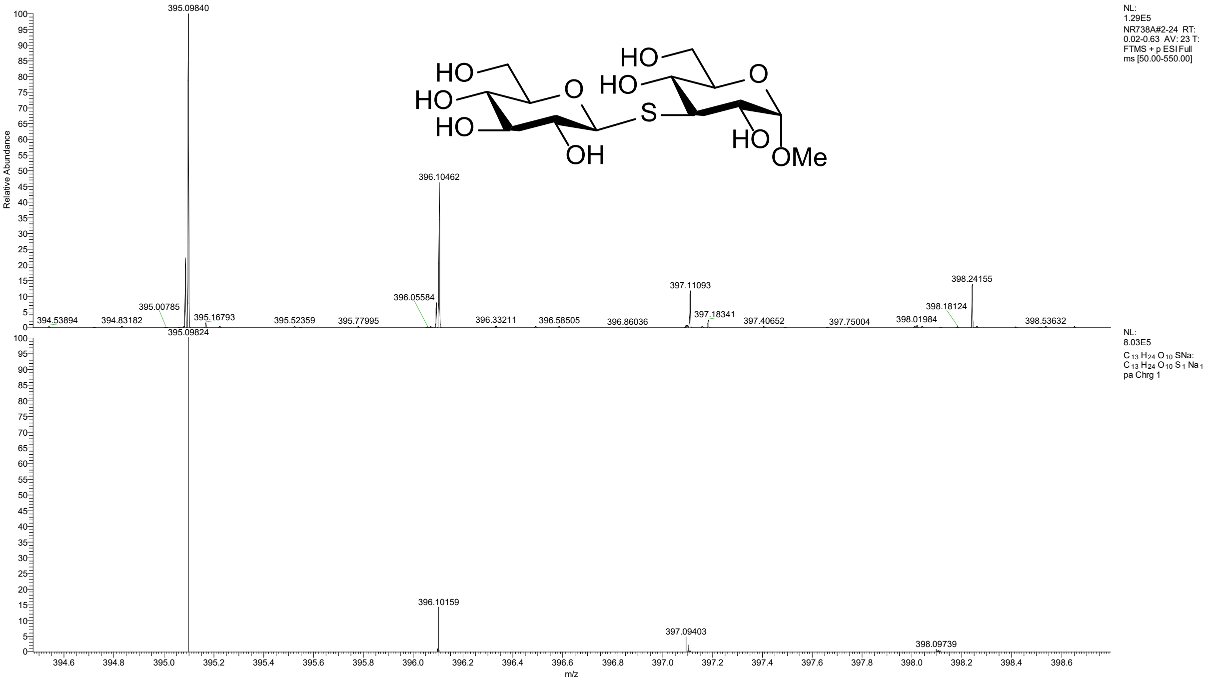
Methyl 2,3,4,6-tri-O-acetyl-3-S-acetyl-3-deoxy-α-D-allopyranoside (S17)





Methyl 3-S-β-D-glucopyranosyl-3-deoxy-3-thio-α-D-glucopyranoside (20)





Methyl 3-S-β-D-glucopyranosyl-3-deoxy-3-thio-α-D-allopyranoside (22)