

# Diastereoselective Synthesis of the Borylated D-Galactose Monosaccharide 3-Boronic-3-Deoxy-D-Galactose and Biological Evaluation in Glycosidase Inhibition and in Cancer for Boron Neutron Capture Therapy (BNCT)

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## 1. Further Synthetic Details

### 1.1. About the chemical stability of alkene **3**.

It was noticed alkene **3** reacted overtime, when stored at room temperature. Storage in freezing temperature was required and at -25°C the alkene survived unchanged for at least 12 months. Alkene **3** was also found to quickly react in the presence of chloroform. This was noticed during overnight NMR data acquisition. Hence, all data collections measured in solution were carried out in acetone or deuterated acetone, in which the alkene intermediate **3** displays stability over the data collection time.

### 1.2. Hydroboration/borane-trapping optimisation

The trapping of the borane with an organic nucleophile was a challenging transformation. However, it was possible to optimise this reaction and to develop a one-pot procedure with the hydroboration step (see video in Supplementary Information). The trapping was investigated with several organic nucleophiles.

**Trapping with methanol.** Methanol was initially used hoping that an acidic wash would have transformed *in situ* the boronic methyl ether into the corresponding boronic acid. It would have been advantageous to characterise the resulting doubly acetonide-protected boronic acid product and confirm structural integrity before global deprotection. It was however difficult to isolate pure product *via* this route. Methanol trapping was followed by coevaporation with methanol three times. Partitioning in EtOAc/HCl (1 M) afforded the boronic acid product in both layers. Trapping with methanol and purification on silica gel by flash column chromatography afforded – as expected – several products, inclusive of a diastereoisomerically pure C-3 saturated 3-deoxy-1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-xylo-hexose [ $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 5.80 (1H, d,  $J_{\text{H-1,H-2}}$  3.8 Hz, H-1), 4.73 (1H, ddd,  $J_{\text{H-2,H-3}}$  6.1 Hz,  $J_{\text{H-2,H-1}}$  3.8 Hz,  $J_{\text{H-2,H-3'}}$  1.3 Hz, H-2),

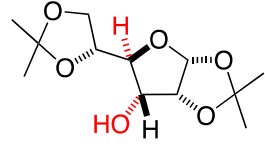
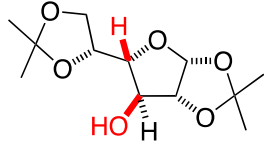
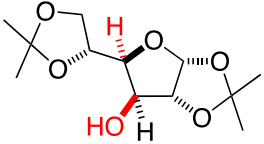
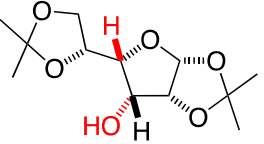
4.44 (1H, dt,  $J_{\text{H-5,H-4}}$  8.2 Hz,  $J_{\text{H-5,H-6}}$  6.8 Hz,  $J_{\text{H-5,H-6'}}$  6.8 Hz, H-5), 4.05 (1H, dd,  $J_{\text{H-6',H-6}}$  8.2 Hz,  $J_{\text{H-6',H-5}}$  6.6 Hz, H-6'), 3.61 (1H, dd,  $J_{\text{H-6,H-6'}}$  8.2 Hz,  $J_{\text{H-6,H-5}}$  6.9 Hz, H-6), 4.11 (1H, td,  $J_{\text{H-4,H-3'}}$  4.0 Hz,  $J_{\text{H-4,H-5}}$  8.4 Hz,  $J_{\text{H-4,H-3}}$  4.0 Hz, H-4), 2.21 (1H, ddd,  $J_{\text{H-3,H-3'}}$  14.4 Hz,  $J_{\text{H-3,H-4}}$  8.5 Hz,  $J_{\text{H-3,H-2}}$  6.2 Hz, H-3), 1.82 (1H, ddd,  $J_{\text{H-3',H-3}}$  14.2 Hz,  $J_{\text{H-3',H-4}}$  4.1 Hz,  $J_{\text{H-3',H-2}}$  1.1 Hz, H-3'), 1.57, 1.45, 1.37, 1.33 (12H, 4 x s, 4 x CH<sub>3</sub>).  $\delta_{\text{c}}$  (CDCl<sub>3</sub>, 100 MHz): 112.9, 110.0 (2 x C<sub>quat</sub> acetonides), 106.5 (C-1), 81.5 (C-4), 80.5 (C-2), 77.7 (C-5), 66.1 (C-6), 33.6 (C-3), 27.4, 26.8, 26.3, 25.3 (4 x CH<sub>3</sub>) (Supplementary Information, Figure S7) and whose characterisation data matched the literature[24-26] ( $R_{\text{f}}$  0.80 in EtOAc as a white crystalline solid) and partially 5,6- and 1,2:5,6-deprotected boron-bearing monosaccharide derivatives. No signal was observed in the <sup>11</sup>B-NMR spectrum.

Other side-products obtained during the optimisation process included oxidised compounds from the borane intermediate, such as:

1,2:5,6-Di-O-isopropylidene- $\alpha$ -D-gulofuranose:  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 5.78 (1H, d,  $J_{\text{H-1,H-2}}$  4.0 Hz, H-1), 4.66 (1H, dd,  $J_{\text{H-2,H-3}}$  6.3 Hz,  $J_{\text{H-2,H-1}}$  4.1 Hz, H-2), 4.47 (1H, dt,  $J_{\text{H-5,H-4}}$  8.4 Hz,  $J_{\text{H-5,H-6}}$  7.1 Hz,  $J_{\text{H-5,H-6'}}$  7.0 Hz, H-5), 4.25-4.19 (2H, m, H-3 and H-6'), 3.90 (1H, dd,  $J_{\text{H-4,H-5}}$  8.5 Hz,  $J_{\text{H-4,H-3}}$  5.7 Hz, H-4), 3.72 (1H, dd,  $J_{\text{H-6,H-6'}}$  8.5 Hz,  $J_{\text{H-6,H-5}}$  7.3 Hz, H-6), 2.65 (1H, d,  $J_{\text{OH-3,H-3}}$  6.5 Hz, OH-3), 1.63, 1.45, 1.43, 1.38 (12H, 4 x s, 4 x CH<sub>3</sub>).  $\delta_{\text{c}}$  (CDCl<sub>3</sub>, 100 MHz): 115.2, 109.4 (2 x C<sub>quat</sub> acetonides), 105.5 (C-1), 84.5 (C-4), 80.0 (C-2), 75.7 (C-5), 69.8 (C-3), 66.5 (C-6), 27.3 (2 x CH<sub>3</sub>), 26.8, 25.4 (2 x CH<sub>3</sub>) (Supplementary Information, Figure S2) and whose characterisation data matched the literature (Table 1, **entry 4**).

1,2:5,6-Di-O-isopropylidene- $\alpha$ -D-galactofuranose:  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 5.85 (1H, d,  $J_{\text{H-1,H-2}}$  3.8 Hz, H-1), 4.52 (1H, d,  $J_{\text{H-2,H-1}}$  3.8 Hz, H-2), 4.33 (1H, app-q,  $J$  6.9 Hz, H-5), 4.08-4.05 (1H, app-s, H-3), 4.05 (1H, dd, partially obscured,  $J$  6.7 Hz, H-6), 3.84 (1H, dd,  $J_{\text{H-4,H-5}}$  7.1 Hz,  $J$  4.3 Hz, H-4), 3.81 (1H, dd,  $J$  6.9 Hz, H-6'), 3.20-3.00 (1H, br s, OH), 1.52, 1.42, 1.35, 1.32 (12H, 4 x s, 4 x CH<sub>3</sub>) and whose characterisation data matched the literature (Table 1, **entry 3**).

**Table S1.** (top) Structures, (middle)  $^1\text{H}$ - and (bottom)  $^{13}\text{C}$ -NMR data in  $\text{CDCl}_3$  for all stereoisomeric 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-aldohexofuranosides at C-3 and C-4: 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-allofuranose (**entry 1**), 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-galactofuranose (**entry 2**), 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranose (**entry 3**), 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-gulofuranose (**entry 4**). Chemical shifts are in ppm and *J* coupling values in Hz.

Entry	1 [27-29]	2 [30-32]	3 [27-29, 33]	4
Structure	 D-Allo	 D-Galacto	 D-Glucos	 D-Gulo

Entry	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	OH	4 x CH <sub>3</sub>	References
1	5.80, d <i>J</i> <sub>H-1,H-2</sub> 3.8	4.59, dd <i>J</i> <sub>H-2,H-3</sub> 5.1 <i>J</i> <sub>H-2,H-1</sub> 4.0	4.08-3.97, m		4.29, ddd <i>J</i> <sub>H-5,H-6/H-4</sub> 6.6 <i>J</i> <sub>H-5,H-6'</sub> 4.9	4.08-3.97, m	3.80, dd <i>J</i> <sub>H-6',H-6</sub> 8.5 <i>J</i> <sub>H-6',H-5</sub> 4.8	2.55, d <i>J</i> <sub>OH,H-3</sub> 8.4	1.56, 1.45, 1.36, 1.35	[28]
	5.82, d <i>J</i> <sub>H-1,H-2</sub> 3.8	4.62, dd <i>J</i> <sub>H-2,H-1</sub> 3.9	4.11-4.00, m		4.31, m	4.11-4.00, m	3.82, dd <i>J</i> <sub>H-6',H-6</sub> 8.4 <i>J</i> <sub>H-6',H-5</sub> 4.8		1.58, 1.47, 1.38	Our data <sup>s</sup>
2	5.80, d <i>J</i> <sub>H-1,H-2</sub> 4.2	4.49, d <i>J</i> <sub>H-2,H-1</sub> 4.2	4.05-3.98, m	3.81-3.75, m	4.30, m	4.05-3.98, m	3.81-3.75, m		1.48, 1.39, 1.31, 1.28	[34]
	5.85, d <i>J</i> <sub>H-1,H-2</sub> 3.8	4.52, d <i>J</i> <sub>H-2,H-1</sub> 3.8	4.08-4.05, app-s	3.84, dd <sup>o</sup> <i>J</i> <sub>H-4,H-5</sub> 7.1, <i>J</i> 4.3	4.33, app-q <i>J</i> 6.9	4.05, dd <sup>o</sup> <i>J</i> 6.7 <sup>o</sup>	3.81, dd <i>J</i> 6.9 <sup>o</sup>	3.20-3.00, br s	1.52, 1.42, 1.35, 1.32	Our data
3	5.94, d <i>J</i> <sub>H-1,H-2</sub> 3.6	4.53, d <i>J</i> <sub>H-2,H-1</sub> 3.6	4.37-4.31, m	4.07, dd <i>J</i> 7.7 <i>J</i> 2.9	4.37-4.31, m	4.17, dd <i>J</i> <sub>H-6,H-6'</sub> 8.6 <i>J</i> <sub>H-6,H-5</sub> 6.3	3.98, dd <i>J</i> <sub>H-6',H-6</sub> 8.6 <i>J</i> <sub>H-6',H-5</sub> 5.4	2.60-2.54, br s	1.49, 1.44, 1.36, 1.32	Our data
4	5.73, d <i>J</i> <sub>H-1,H-2</sub> 4.1	4.61, dd <i>J</i> <sub>H-2,H-1</sub> 4.1 <i>J</i> <sub>H-2,H-3</sub> 6.3	4.22-4.14, m	3.85, dd <i>J</i> <sub>H-4,H-5</sub> 8.7 <i>J</i> <sub>H-2,H-3</sub> 5.9	4.44, dt <i>J</i> <sub>H-5,H-4</sub> 8.6 <i>J</i> <sub>H-5,H-6/6'</sub> 7.0	4.22-4.14, m	3.66, dd <i>J</i> <sub>H-6,H-5</sub> 8.6 <i>J</i> <sub>H-6,H-6'</sub> 7.4	2.68, d <i>J</i> <sub>OH,H-3</sub> 6.4	1.58, 1.40, 1.37, 1.33	[35]
	5.78, d <i>J</i> <sub>H-1,H-2</sub> 4.0	4.66, dd <i>J</i> <sub>H-2,H-3</sub> 6.3 <i>J</i> <sub>H-2,H-1</sub> 4.1	4.25-4.19, m	3.90, dd <i>J</i> <sub>H-4,H-5</sub> 8.5 <i>J</i> <sub>H-4,H-3</sub> 5.7	4.47, dt <i>J</i> <sub>H-5,H-4</sub> 8.4 <i>J</i> <sub>H-5,H-6</sub> 7.1 <i>J</i> <sub>H-5,H-6'</sub> 7.0	4.25-4.19, m	3.72, dd <i>J</i> <sub>H-6,H-6'</sub> 8.5 <i>J</i> <sub>H-6,H-5</sub> 7.3	2.65, d <i>J</i> <sub>OH,H-3</sub> 6.5	1.63, 1.45, 1.43, 1.38	Our data

Entry	C-1	C-2	C-3	C-4	C-5	C-6	2 x C <sub>quat</sub>	4 x CH <sub>3</sub>	References
1	103.9	79.7	75.6	79.1	72.4	65.8	NA	NA	[36, 37]
	104.0	79.6	72.4 <sup>#</sup>	79.1	75.4 <sup>#</sup>	65.7	112.6, 109.6	26.4, 25.3	[38]
	103.7	79.6	78.8	75.5	72.4	65.7	112.6, 109.6	26.5, 26.4, 26.2, 25.2	[28]

	104.0	79.8	79.0	75.6	72.5	65.9	112.9, 109.8	26.6, 26.5, 26.3, 25.3	Our data <sup>§</sup>
2	104.9	87.6	76.1	85.9	75.3	65.6	113.6, 109.9	27.4, 26.8, 26.5, 25.2	[34]
	105.1	87.7	76.1	86.5	75.7	65.8	113.5, 110.0	27.4, 26.7, 26.6, 25.4	Our data
3	105.4	85.2	75.0	81.3	73.3	67.7	NA	NA	[36]
	104.5	85.0	73.1	80.9	72.2	66.0	110.5, 107.8	26.5, 26.0, 26.0, 25.2	[39]
	104.9	84.6	74.5	81.0	72.8	67.3	111.4, 109.2	26.5, 25.9, 25.0	[38]
	104.5	84.4	74.5	80.4	72.8	67.0	111.8, 109.0	25.9, 26.8, 26.2, 25.2	Our data.
4	105.5	80.0	69.8	84.5	75.7	66.5	115.2, 109.4	27.3, 26.8, 25.4	Our data

Legend: <sup>#</sup>Data for these swapped. <sup>§</sup>Data collected by our laboratory in other projects. <sup>ϕ</sup>Other *J* coupling is not discernible due to overlap. <sup>Ⓜ</sup>Partially obscured signal. NA = not available.



**Trapping with a 1,2-diol.** It was reasoned this type of trapping agent should afford a more stable boronate ester intermediate, but it should have still been possible to produce the corresponding boronic acid *in situ* via an acidic treatment that wouldn't also remove the acetonide protecting group. Trapping with esculetin and molecular sieves in DCM at r.t. did not afford the desired product, but an inseparable mixture. Trapping with ethylene glycol provided the desired C-3 boron glycol ester, however could not be purified via re/crystallisation. Isolation by flash column chromatography of the desired product ( $R_f$  0.00-0.10) provided yields in the single digits, likely due to interactions between silica gel and B atoms, and, additionally, due to potential decomposition of the product during purification. To give the deprotected boronic acid 3-boronic-3-deoxy-1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-galactofuranose  $\delta_H$  (CDCl<sub>3</sub>, 400 MHz): 5.77 (1H, d,  $J_{H-1,H-2}$  3.9 Hz, H-1), 4.81 (1H, dd,  $J_{H-2,H-3}$  2.2 Hz,  $J_{H-2,H-1}$  3.7 Hz, H-2), 4.42 (1H, app-q,  $J_{H-5,H-4}$  7.1 Hz, H-5), 4.12 (1H, dd,  $J_{H-4,H-5}$  7.1 Hz,  $J_{H-4,H-3}$  5.7 Hz, H-4), 4.03 (1H, dd,  $J_{H-6,H-6'}$  8.2 Hz,  $J_{H-6,H-5}$  6.6 Hz, H-6), 3.71 (1H, dd,  $J_{H-6',H-6}$  8.1 Hz,  $J_{H-6',H-5}$  7.1 Hz, H-6'), 2.20-1.70 (2H, broad singlet, 2 x OH), 1.69 (1H, dd,  $J_{H-3,H-4}$  5.4 Hz,  $J_{H-3,H-2}$  1.9 Hz, H-3), 1.57, 1.44, 1.36, 1.32 (12Hs, 4 x s, 4 x CH<sub>3</sub>);  $\delta_C$  (CDCl<sub>3</sub>, 100 MHz): 113.2, 110.1 (2 x C<sub>quat</sub> acetonides), 106.6 (C-1), 83.2, 83.1 (C-4, C-2), 77.9 (C-5), 66.2 (C-6) 32.0-30.0 (broad, C-3), 27.7, 26.7 [2 x C], 25.5 (4 x CH<sub>3</sub>);  $\delta_B$  (CDCl<sub>3</sub>, 128 MHz): 33.3. (Supplementary Information, Figure S1)

Removal of the excess borane through addition of excess glycol produced boronate-glycol educts that were difficult to remove completely through attempted recrystallisation, crystallisations or partitioning. For example, using solvent mixtures such as diethyl ether/hexane did not yield any crystalline product or precipitate. We noticed that these boronated educts and boronated monosaccharide derivative tend to be oils with a very large solubility window, ranging from very unipolar (hexane) to very polar (water, methanol).

Trapping of the borane with a more hindered 1,2-diol to form a more stable boronate educt was attempted with pinacol to give product **5** (Scheme 1). This reaction was successful, however purification produced a mixture of D-*galacto* and D-*allo* boronated products and side-products. The boronated products could not be synthesised or isolated reliably. Various purification methods were attempted including by flash column chromatography and prep t.l.c. (with the products were visualised through sprinkling of iodine-soaked silica gel on the plate). The side-products included the saturated 1,2:5,6-di-*O*-isopropylidene-3-deoxy derivative mentioned earlier and oxidised products, such as 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-galactofuranose and 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-allofuranose.

It was attempted to crystallise the excess pinacol out *via* a variety of solvent mixtures covering the polarity range, but unsuccessfully. Boiling off of the pinacol also proved challenging due to its high boiling point (172°C). A further purification protocol utilising a complexation resin[40] also did not afford pure product. Therefore it was deemed appropriate to change the trapping agent.

### 1.3. Purification protocol optimisation (Table 2)

In Purification 1, the reaction mixture (200 mg scale) was filtered to remove excess DEA, however the filtrate appeared to contain product **6** along with some remaining excess DEA. The filtrate was dried and triturated with diethyl ether. This showed a slightly more pure product **6** (the solid fraction), while <sup>1</sup>H-NMR indicated unidentified compound mixture in the filtrate. An additional trituration with PET ether/diethyl ether (5:1) removed impurities which ended in the filtrate, although the excess DEA remained still largely trapped in the solid fraction. Finally product **6** was dissolved in DCM and partitioned with HCl (0.1 M). The excess DEA was successfully removed and product **6** was the sole species migrating to the DCM layer (23% yield).

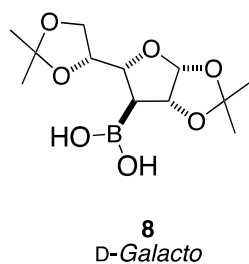
**Table S2.** Summary of the purification methods employed in the optimisation of the purification protocol to product **6**.

Purification	Purification Method	Outcome	Yield
<b>1</b>	Filtration of crude (crude contained <b>6</b> :DEA in 1.0:1.6 ratio)	Filtrate: <b>6</b> and DEA (1.0:0.8 ratio) Solid: mainly DEA and unidentified compounds.	23%
	Diethyl ether trituration	Filtrate: unidentified compounds. Solid: <b>6</b> and DEA (1.0: 0.6 ratio).	
	PET ether/diethyl ether (5:1) partition	Filtrate: unidentified compounds. Solid: <b>6</b> and DEA (1.0: 0.6 ratio).	
	DCM/HCl (0.1 M) wash	DCM layer: pure <b>6</b> . Aqueous layer: small amount of <b>6</b> and DEA (1.0:2.8 ratio).	
<b>2</b>	DCM/HCl (0.1 M) partition 1	DCM layer: <b>6</b> and DEA (1.0:1.9 ratio).	23%
	DCM/HCl (0.1 M) partition 2	DCM layer: <b>6</b> and DEA (1.0:0.7 ratio) and unidentified impurities.	
	DCM/HCl (0.1 M) partition 3	DCM layer: <b>6</b> and DEA (1.0:0.6 ratio) and unidentified compounds.	
	Diethyl ether trituration	Solid: pure <b>6</b> .  Filtrate: unidentified compounds.	
<b>3</b>	Filtration of crude	Filtrate: <b>6</b> and some DEA.  Solid: mainly DEA and unidentified compounds.	58%
	Diethyl ether trituration	Filtrate: unidentified compounds.  Solid: <b>6</b> and DEA.	
	DCM/HCl (0.1 M) partition	DCM layer: pure <b>6</b> .	

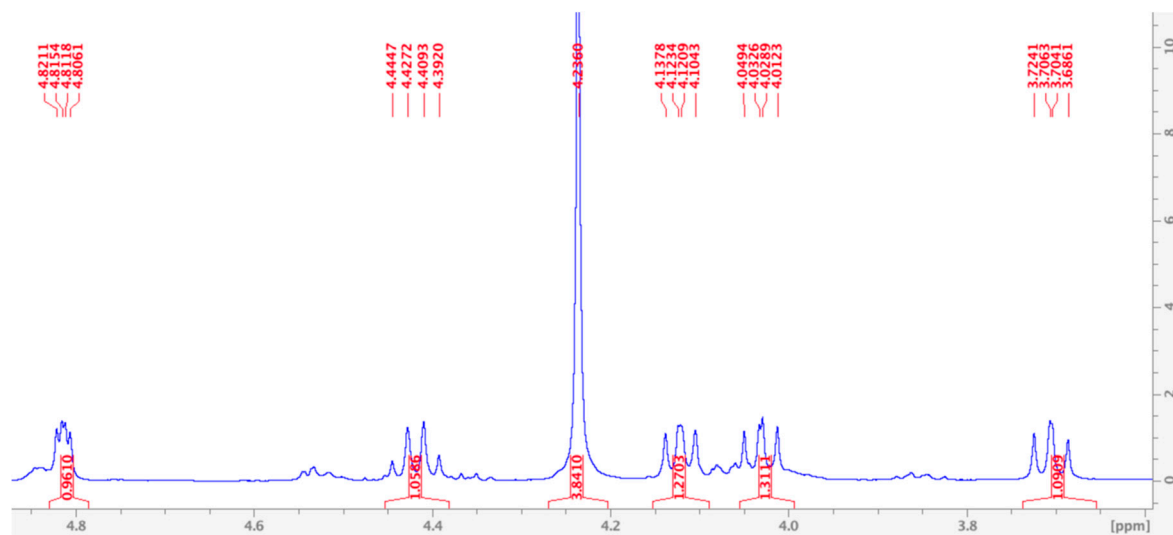
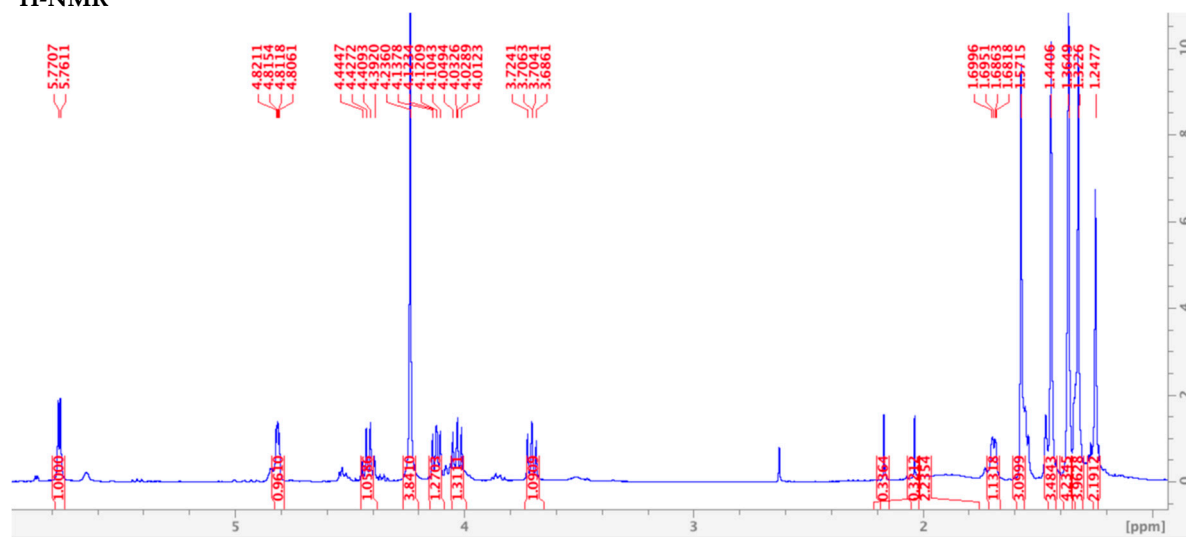
As the yield for purification method 1 was quite low, the second purification method focused on the successful DCM/HCl (0.1 M) partitioning. The reaction mixture (500 mg scale) was dried and then partitioned in DCM/HCl (0.1 M). Although the majority of the DEA was removed in this first partitioning, there was some remaining in the DCM layer along with unidentified compounds. After two additional HCl (0.1 M) washes, the DCM layer still contained unidentified compounds, although a majority of the DEA had been successfully removed. The DCM layer was dried, triturated with diethyl ether and filtered to give pure product **6** (23%) as a white solid, with the unidentified compounds ending up in the filtrate.

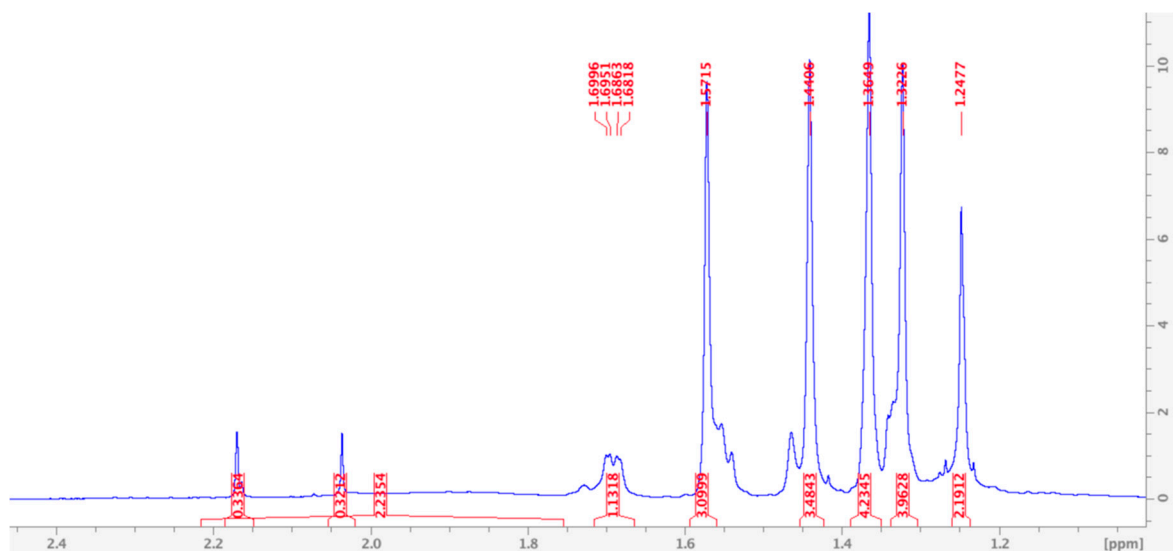
## 2. NMR Spectra

**Figure S1.**  $^1\text{H}$ - (400 MHz),  $^{13}\text{C}$ -NMR (100 MHz), DEPT (100 MHz),  $^{11}\text{B}$ -NMR (128 MHz), COSY and HMBC spectra of 3-boronic-3-deoxy-1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-galactofuranose **8** in  $\text{CDCl}_3$ .



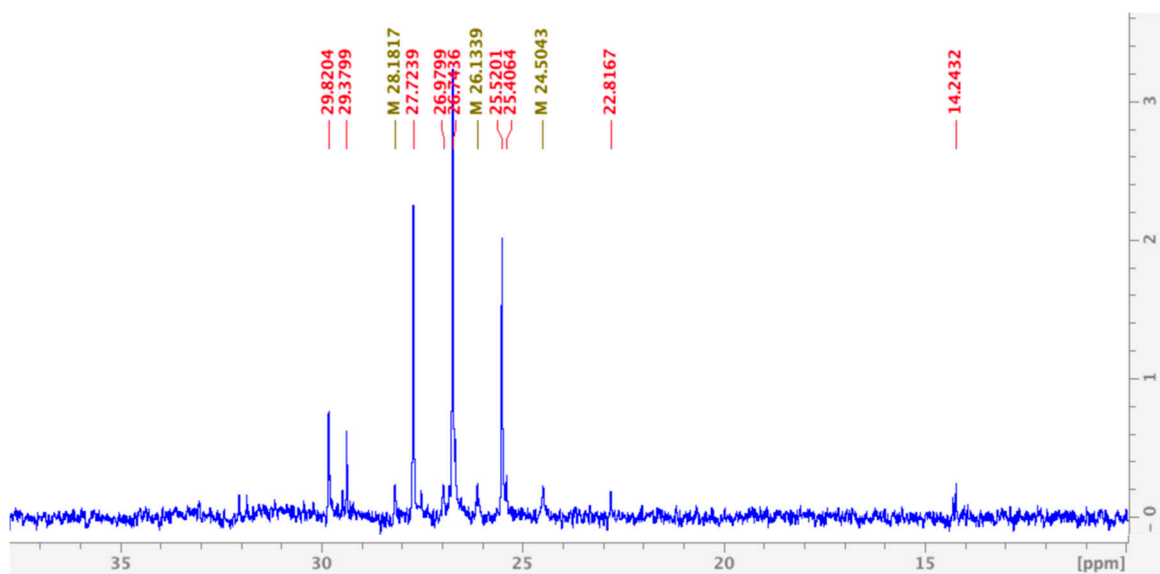
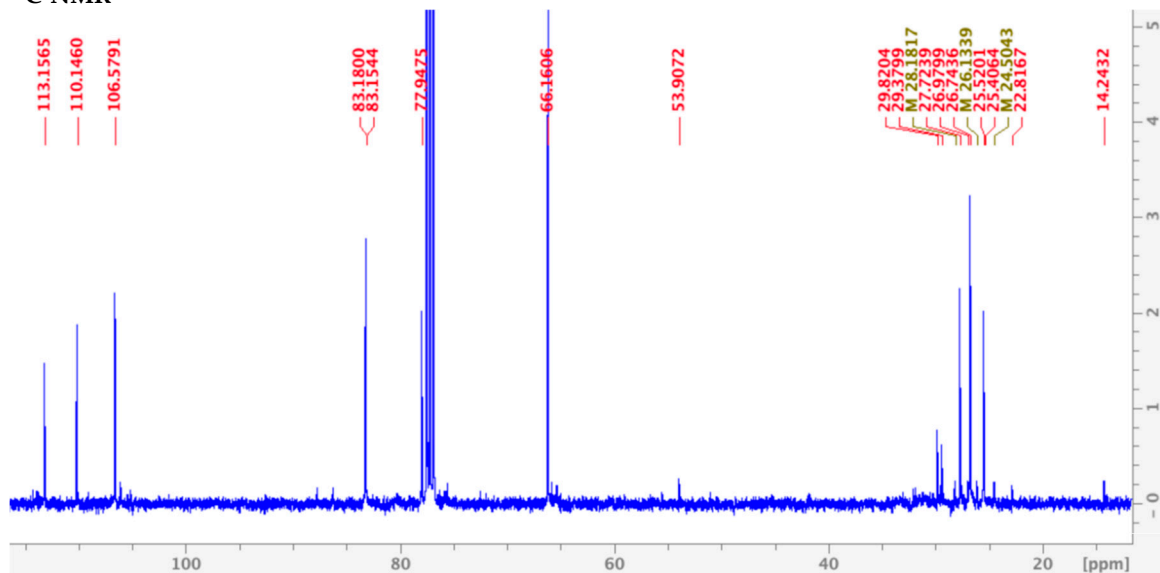
### $^1\text{H}$ -NMR



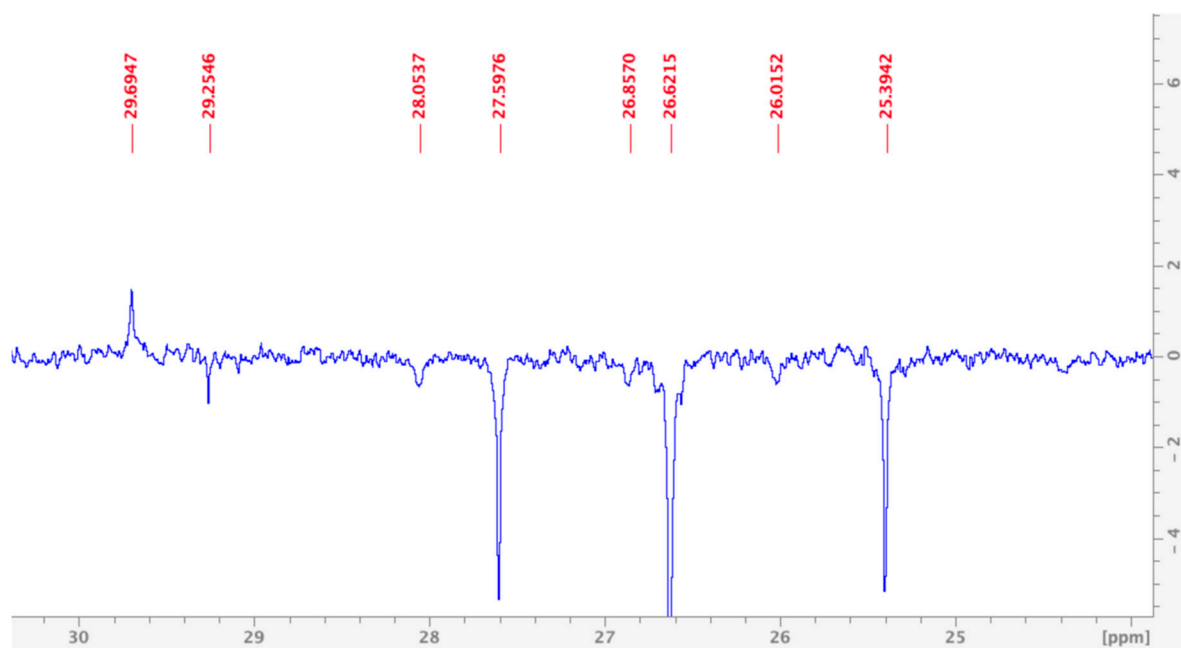
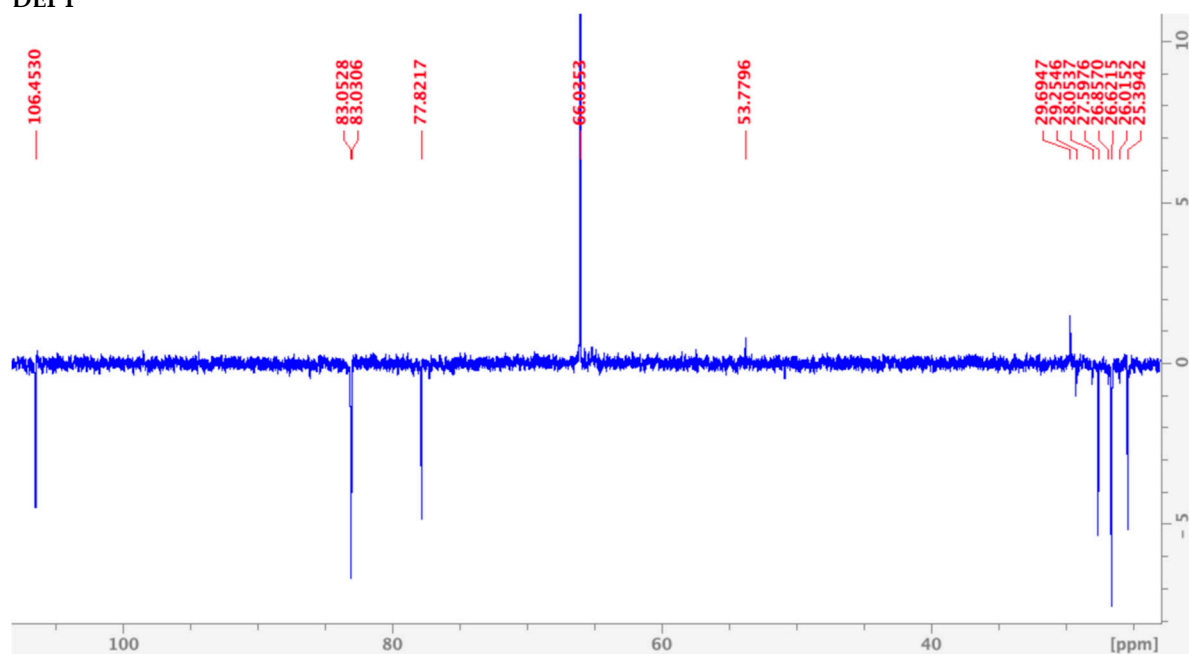


Note, impurity at 4.24 ppm and 1.25 ppm in the  $^1\text{H}$ -NMR spectrum, HMQC-coupled to signals at 62.3 ppm and 29.4 ppm in the  $^{13}\text{C}$ -NMR spectrum.

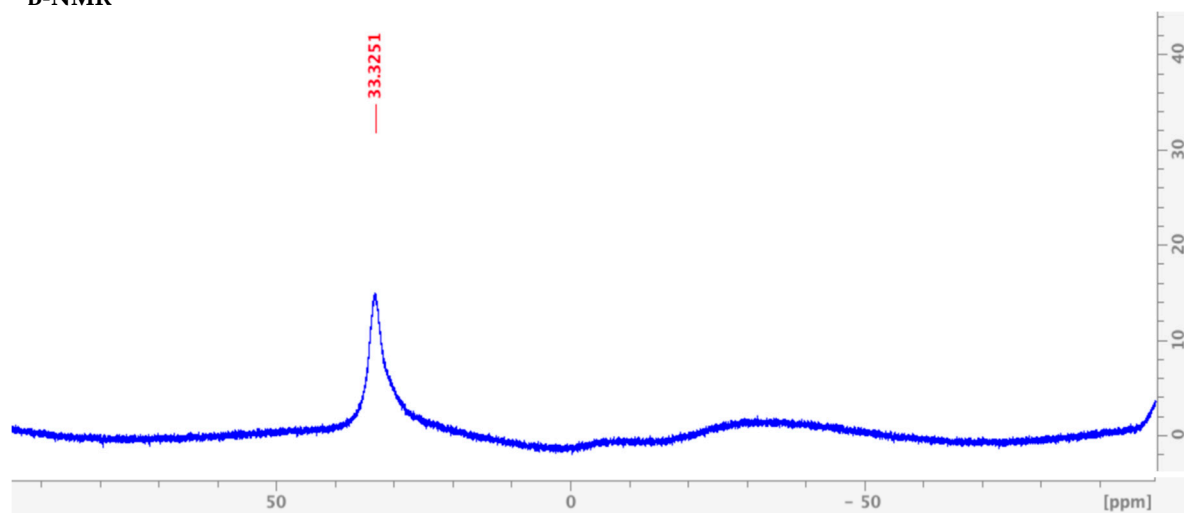
### $^{13}\text{C}$ -NMR



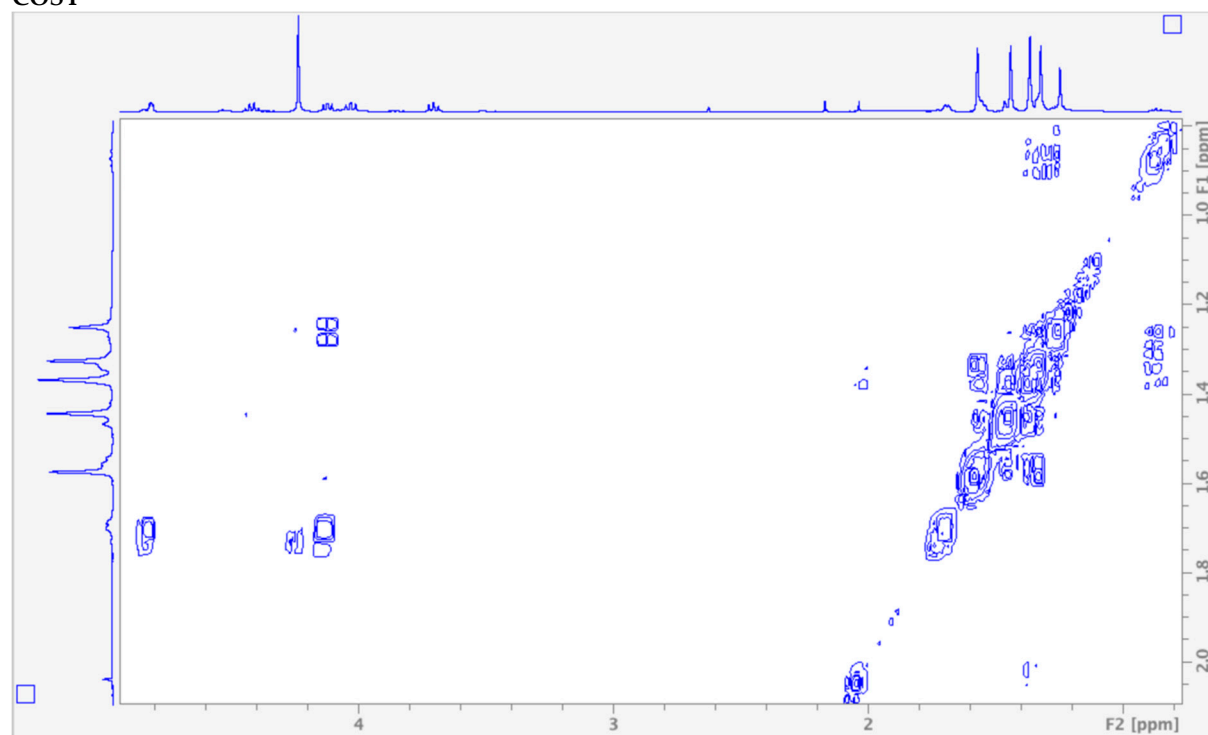
DEPT

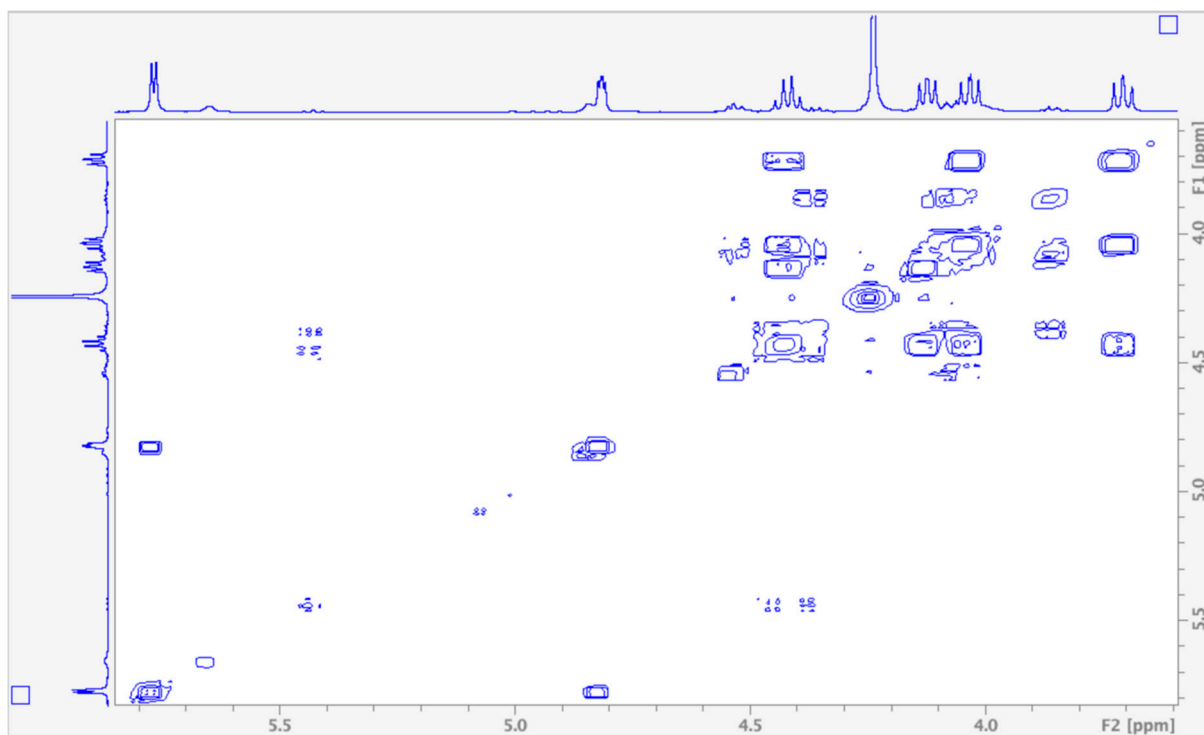


$^{11}\text{B}$ -NMR

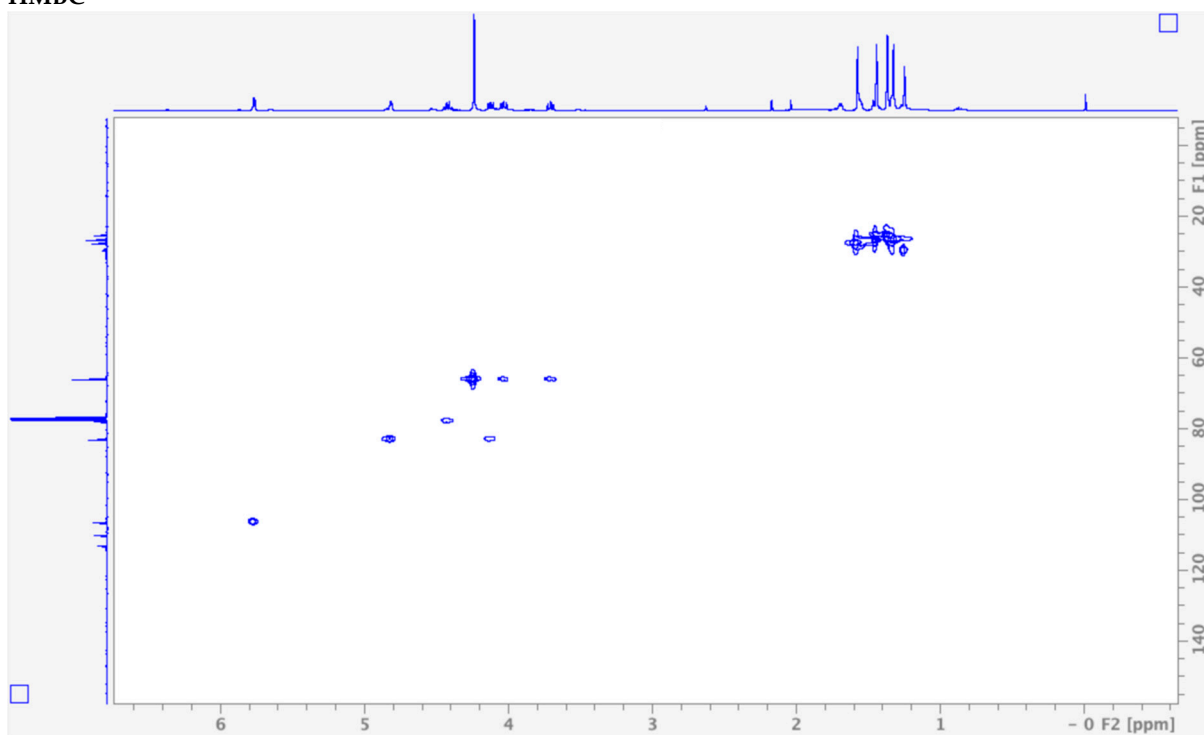


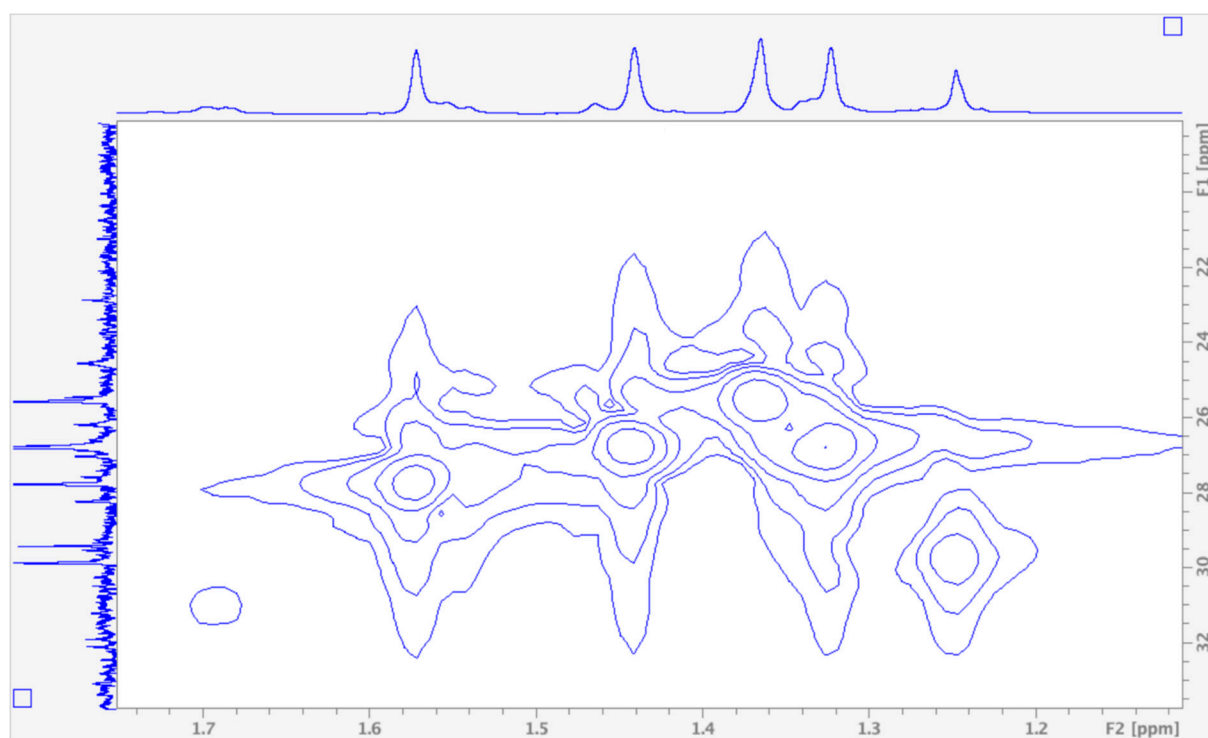
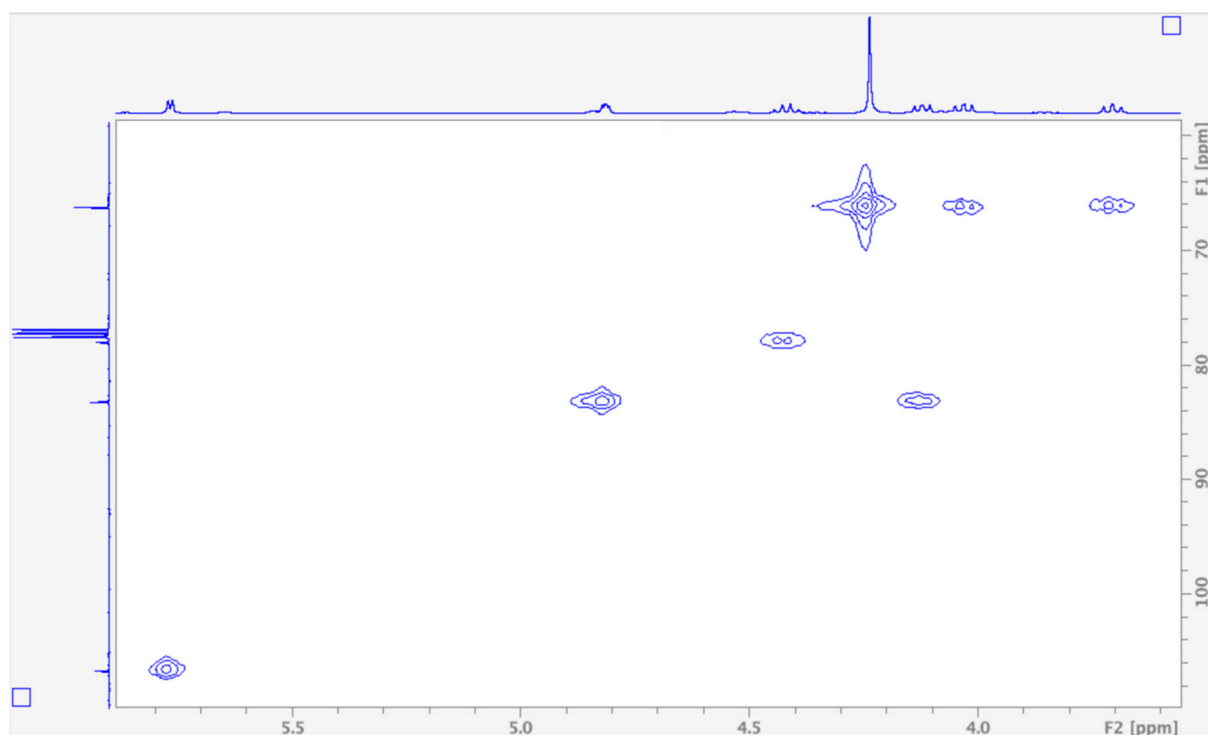
COSY





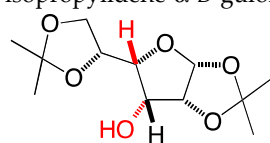
HMBC



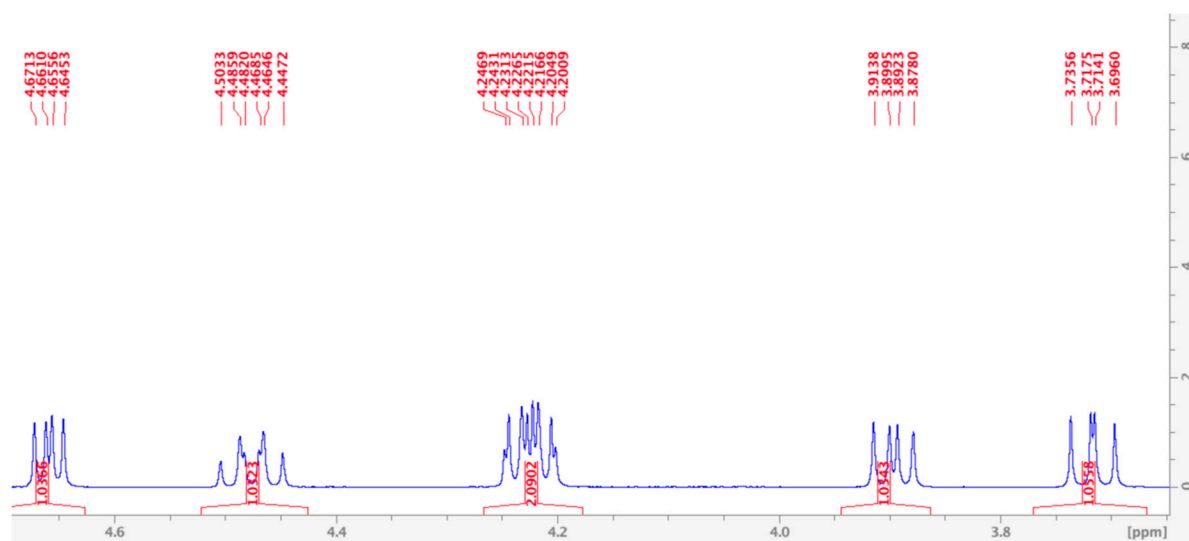
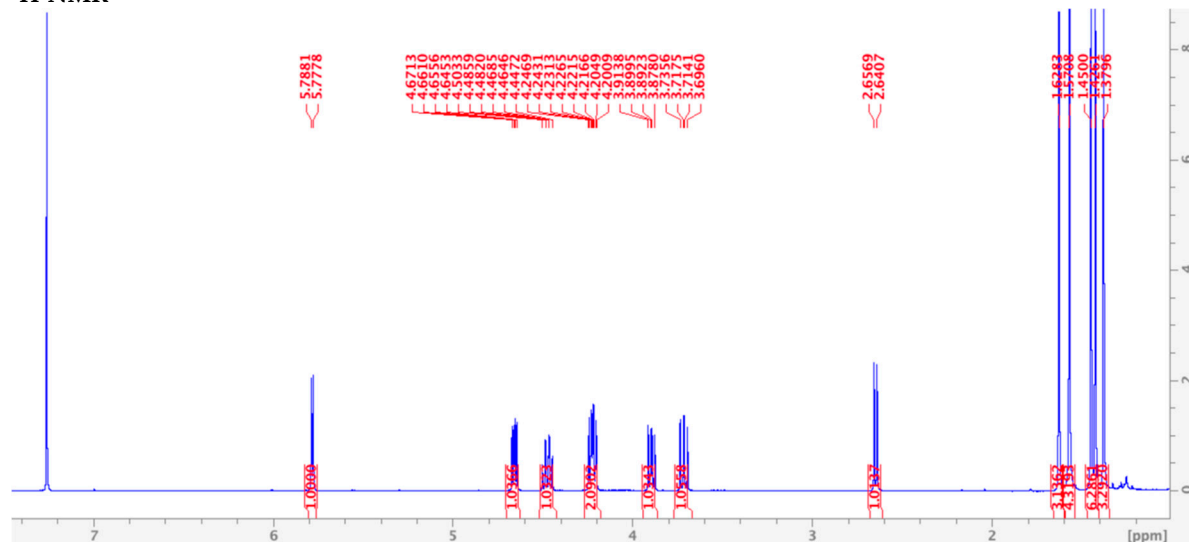




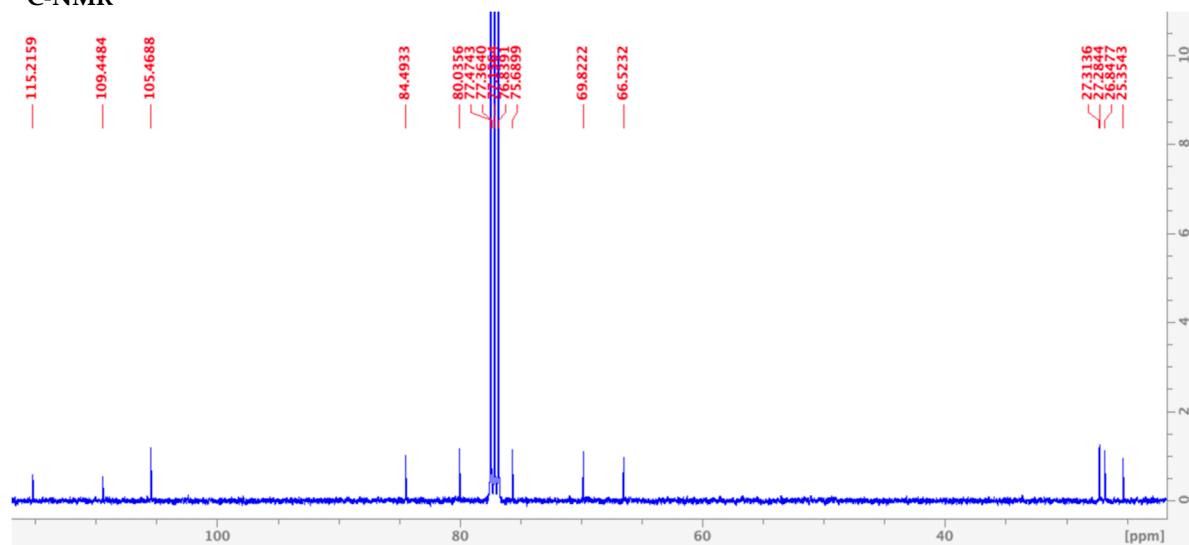
**Figure S2.**  $^1\text{H}$ - (400 MHz),  $^{13}\text{C}$ -NMR (100 MHz), DEPT (100 MHz), COSY and HSQC spectra of 1,2:5,6-Di-O-isopropylidene- $\alpha$ -D-gulofuranose in  $\text{CDCl}_3$ .



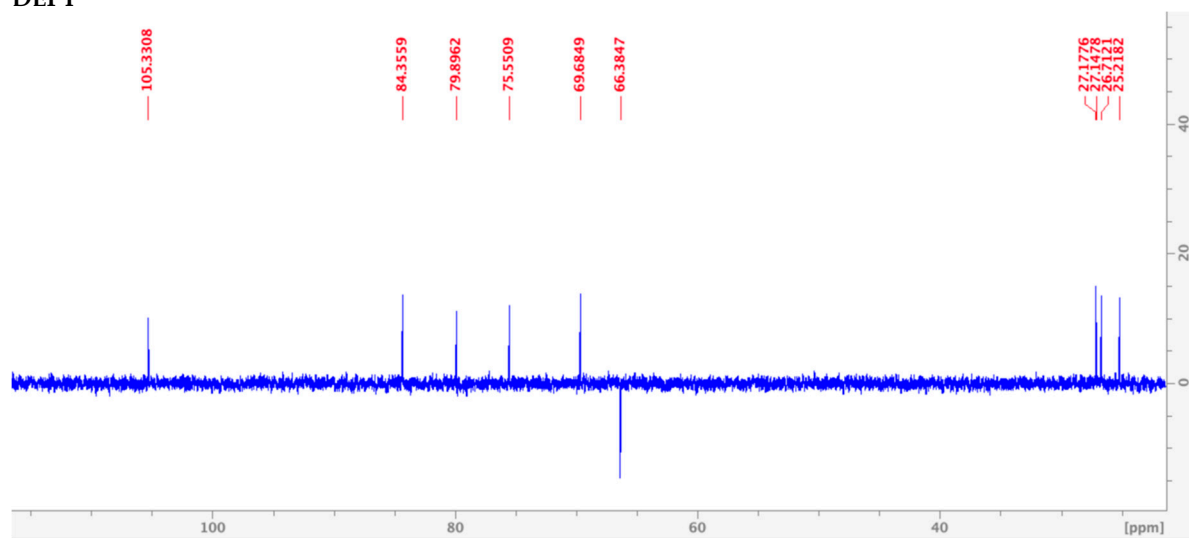
$^1\text{H}$ -NMR



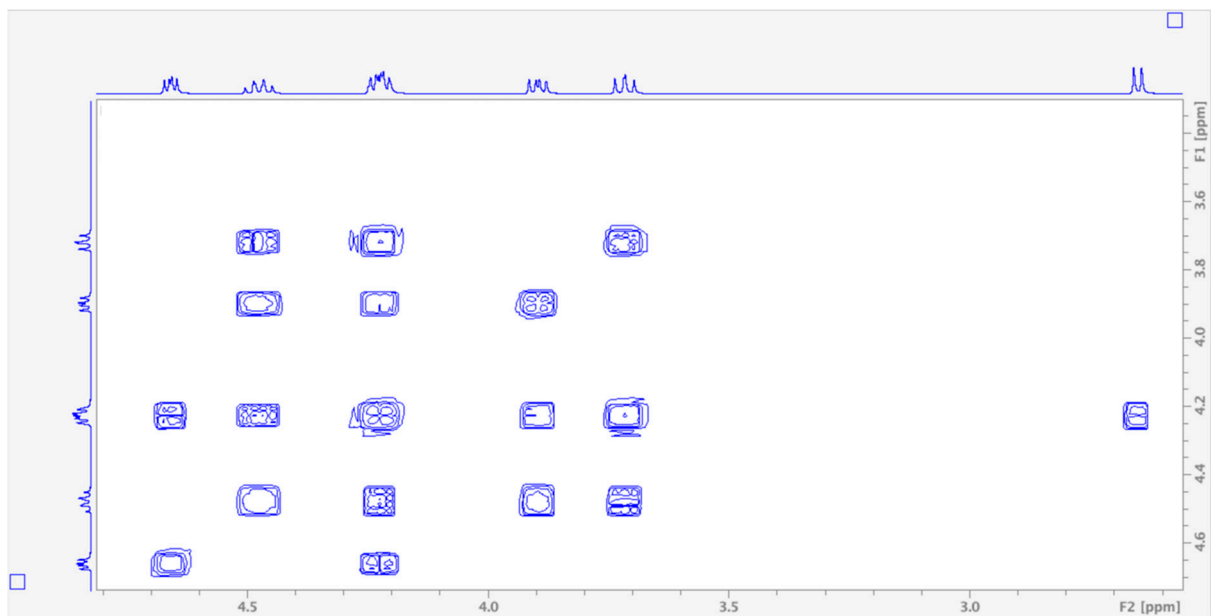
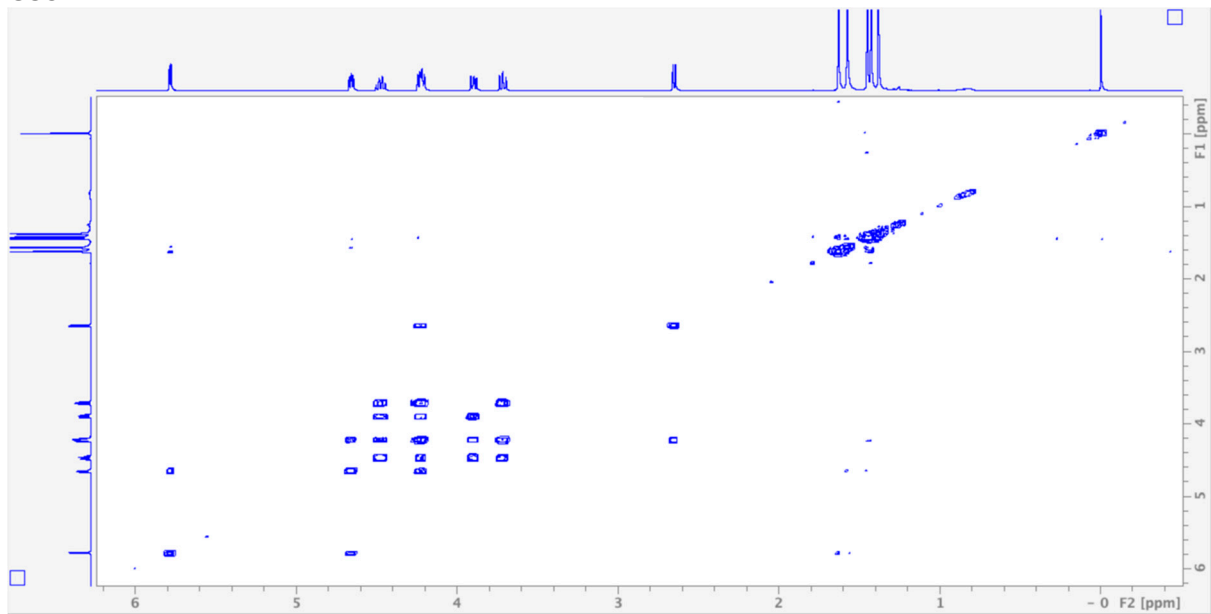
# <sup>13</sup>C-NMR



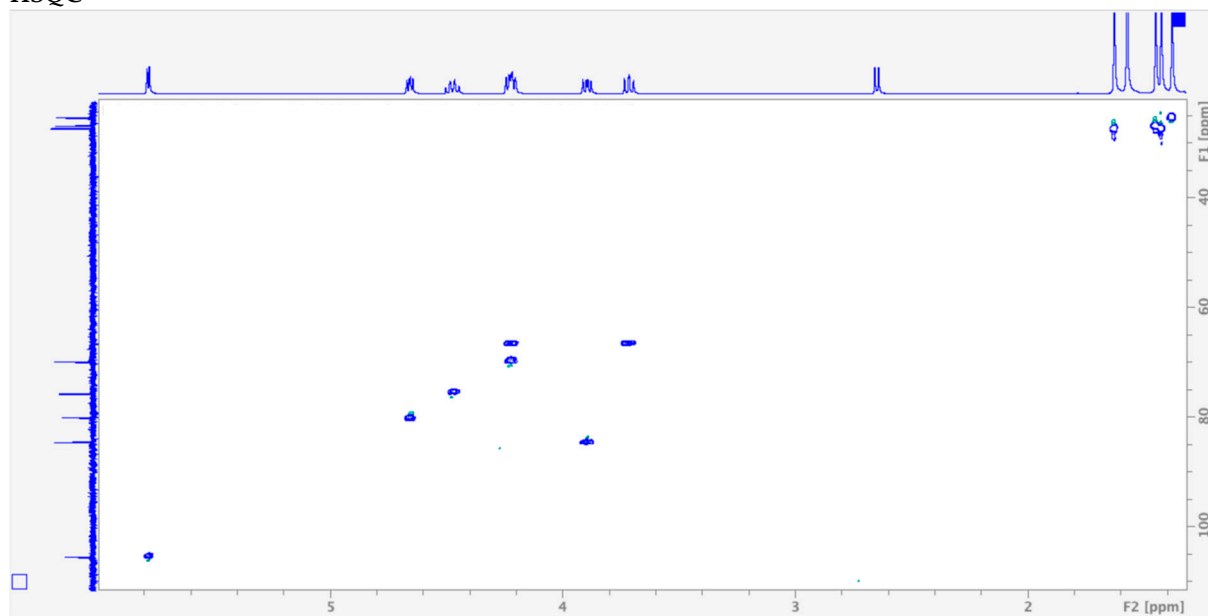
# DEPT



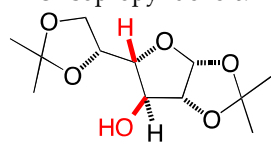
COSY



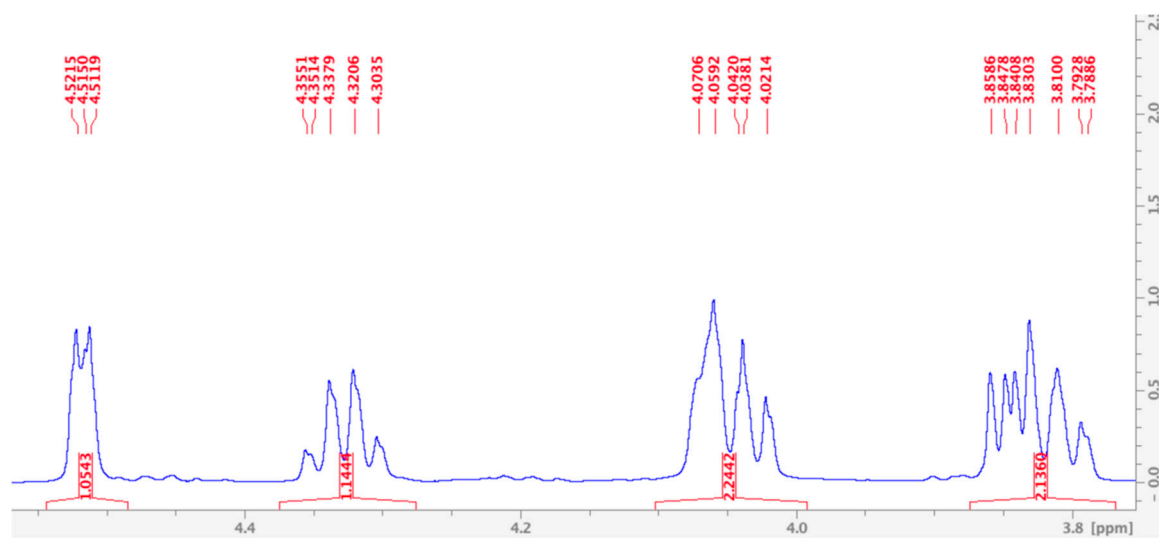
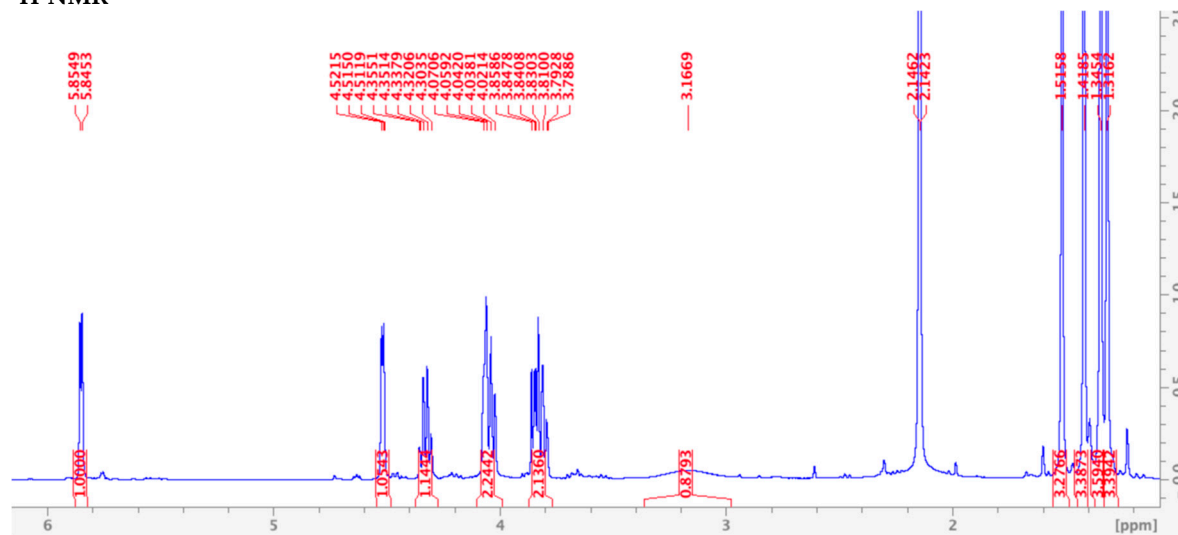
HSQC



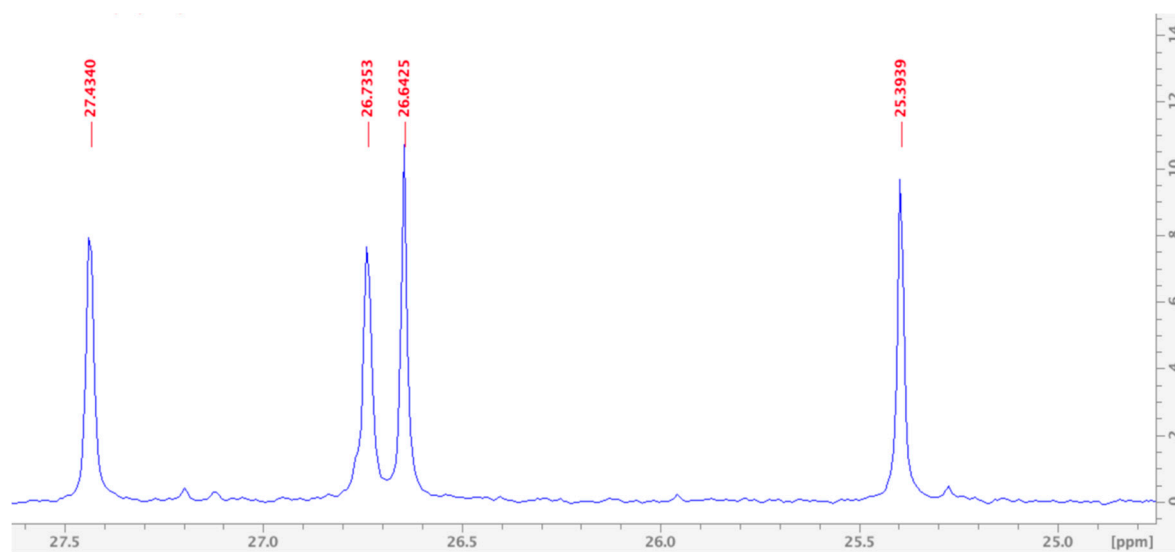
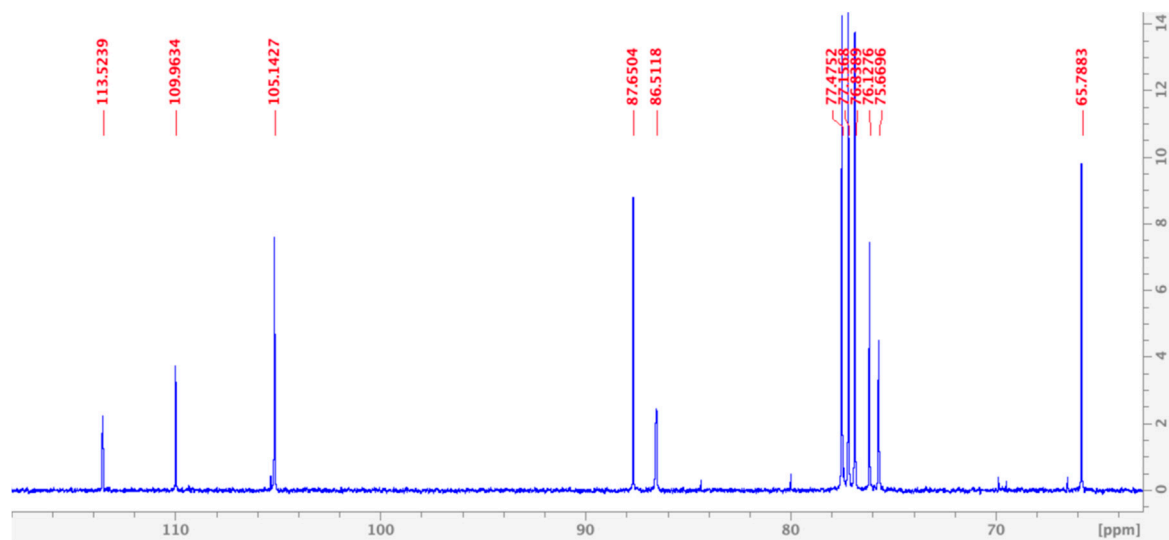
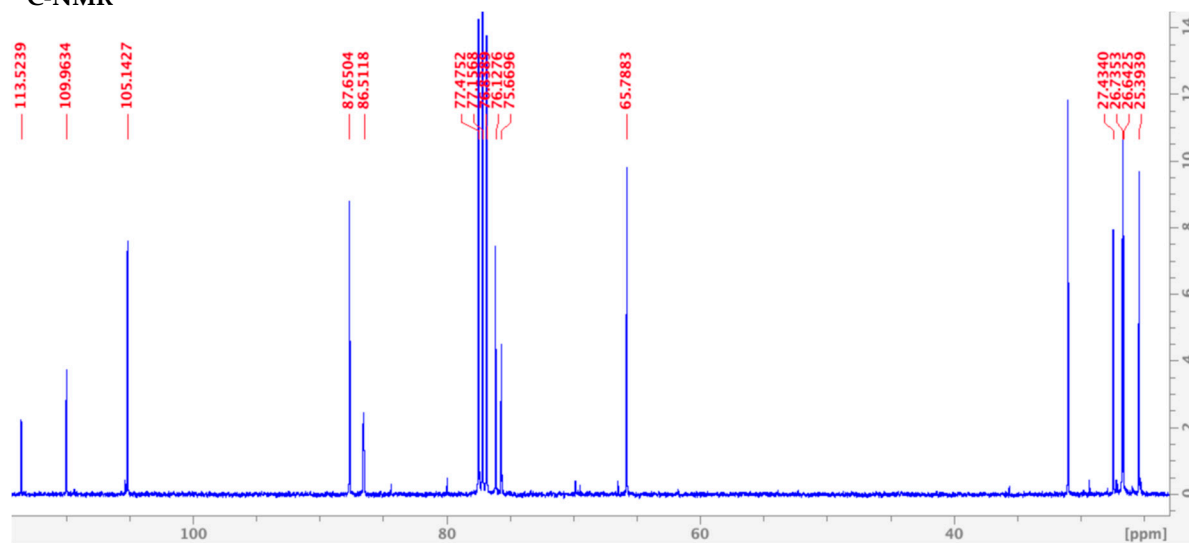
**Figure S3.**  $^1\text{H}$ - (400 MHz),  $^{13}\text{C}$ -NMR (100 MHz), DEPT (100 MHz), COSY, HMQC and HMBC spectra of 1,2:5,6-Di-O-isopropylidene- $\alpha$ -D-galactofuranose in  $\text{CDCl}_3$ .



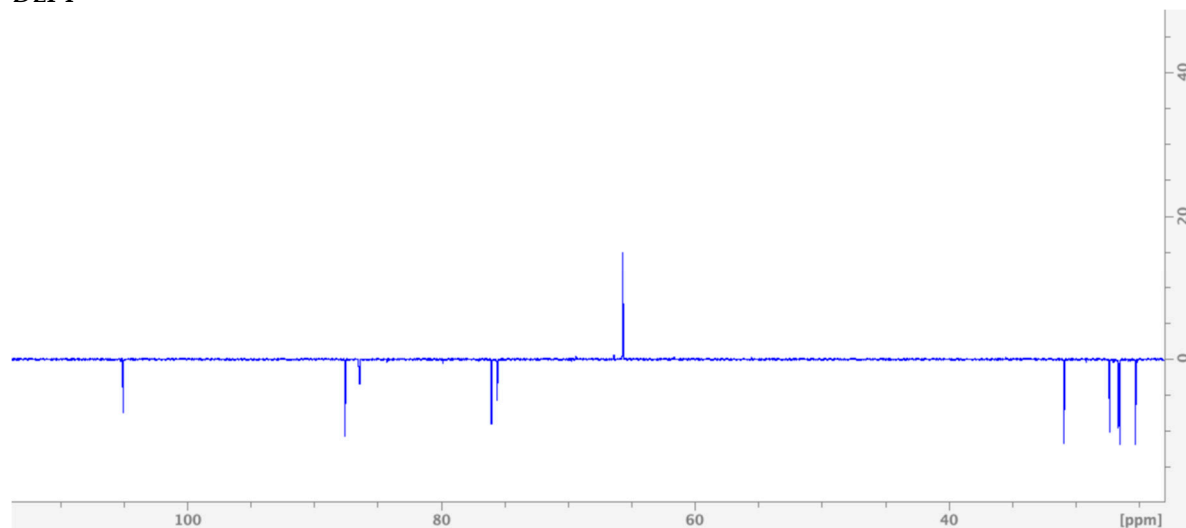
**$^1\text{H}$ -NMR**



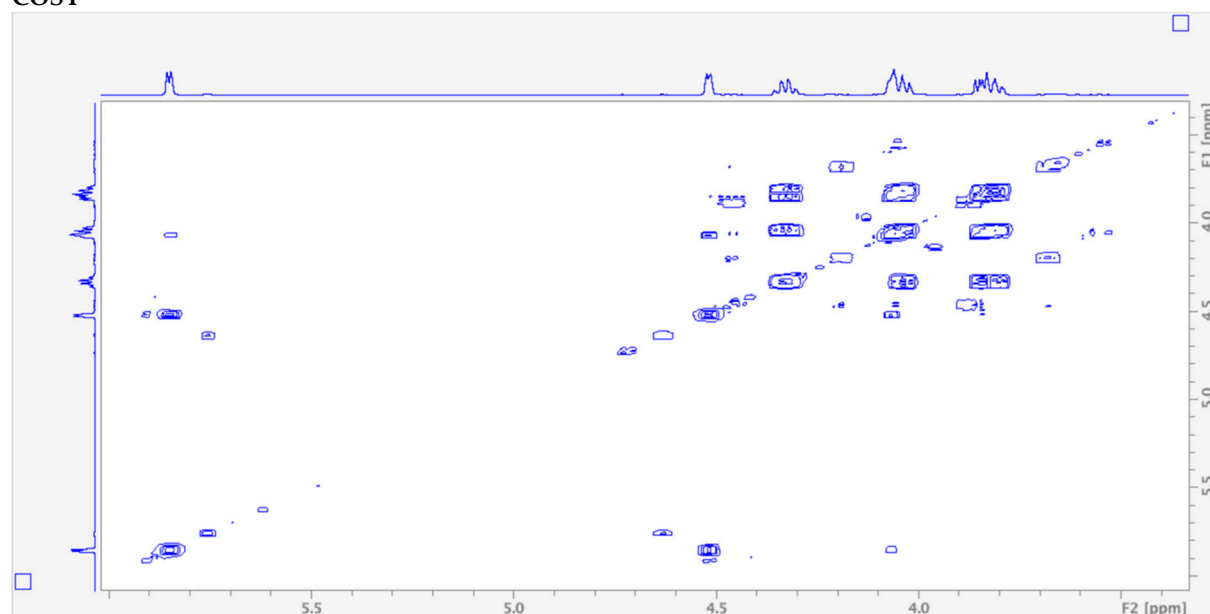
<sup>13</sup>C-NMR



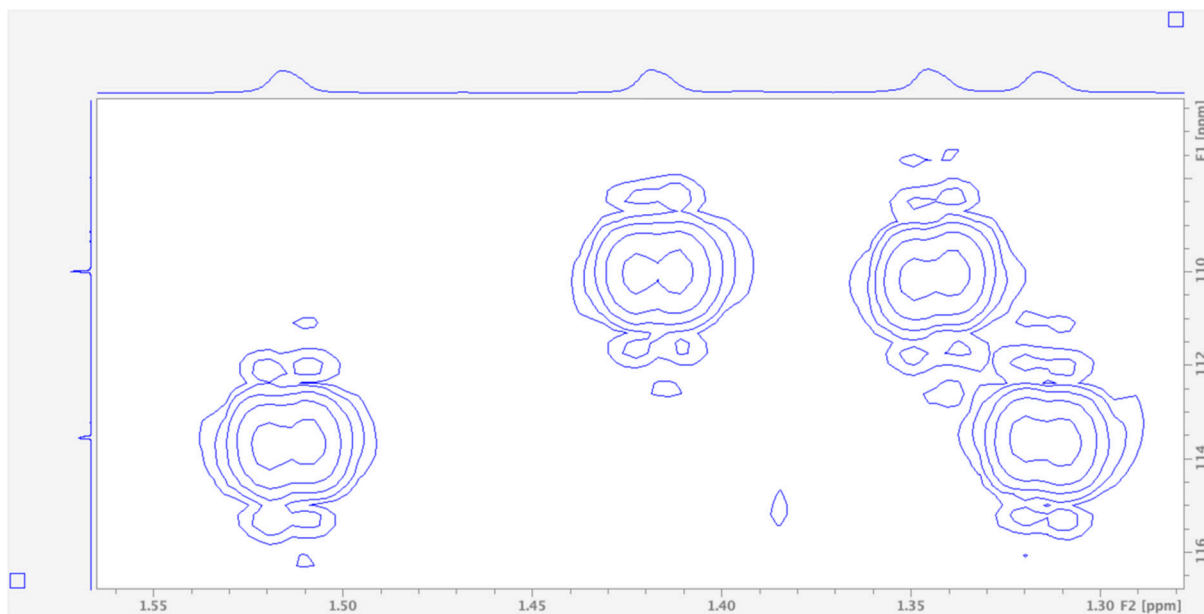
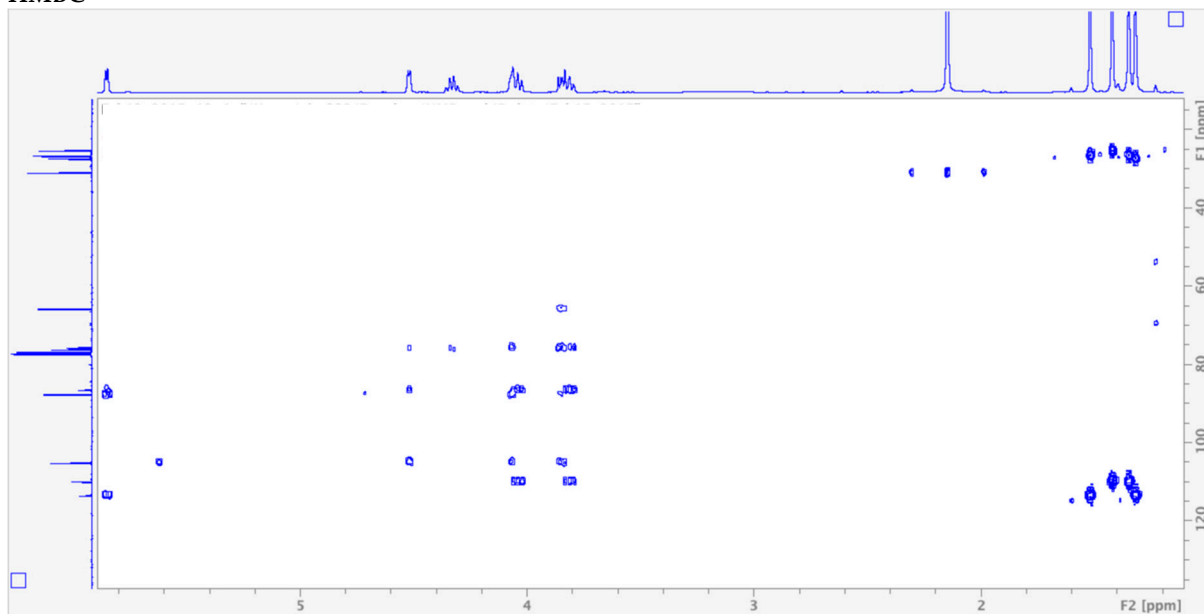
DEPT



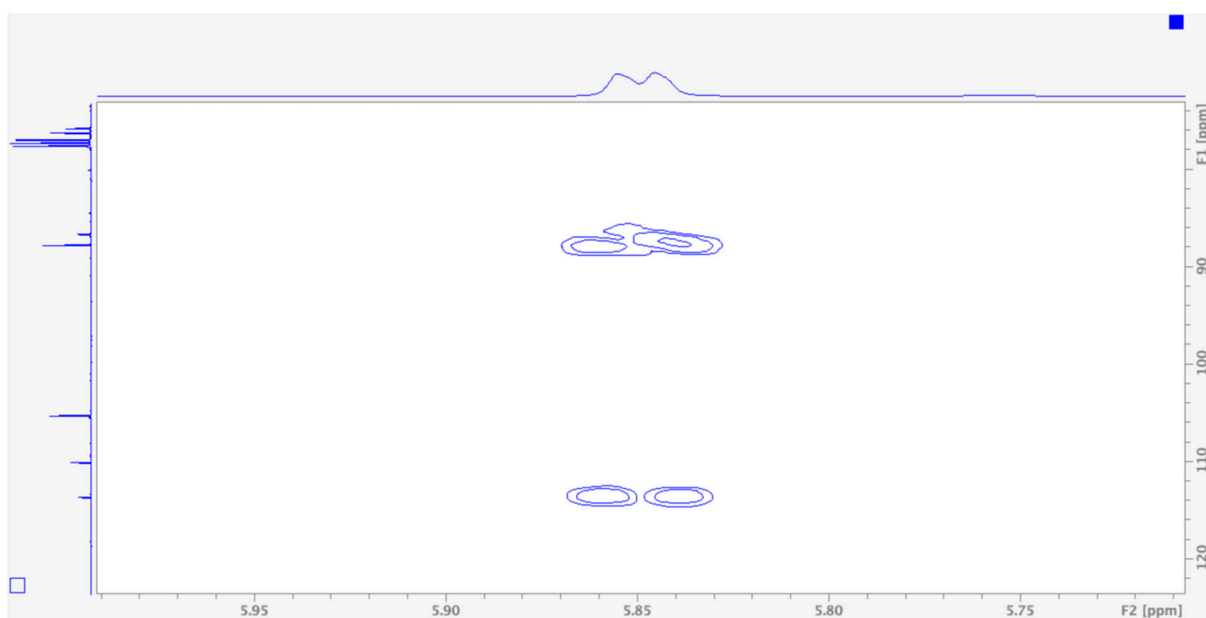
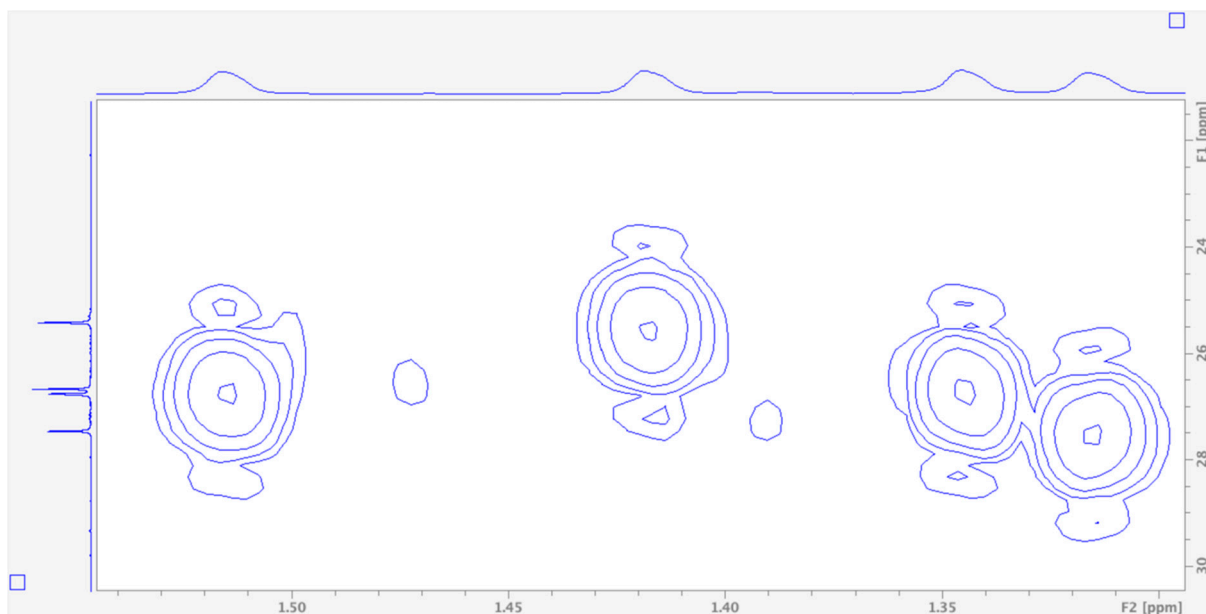
COSY

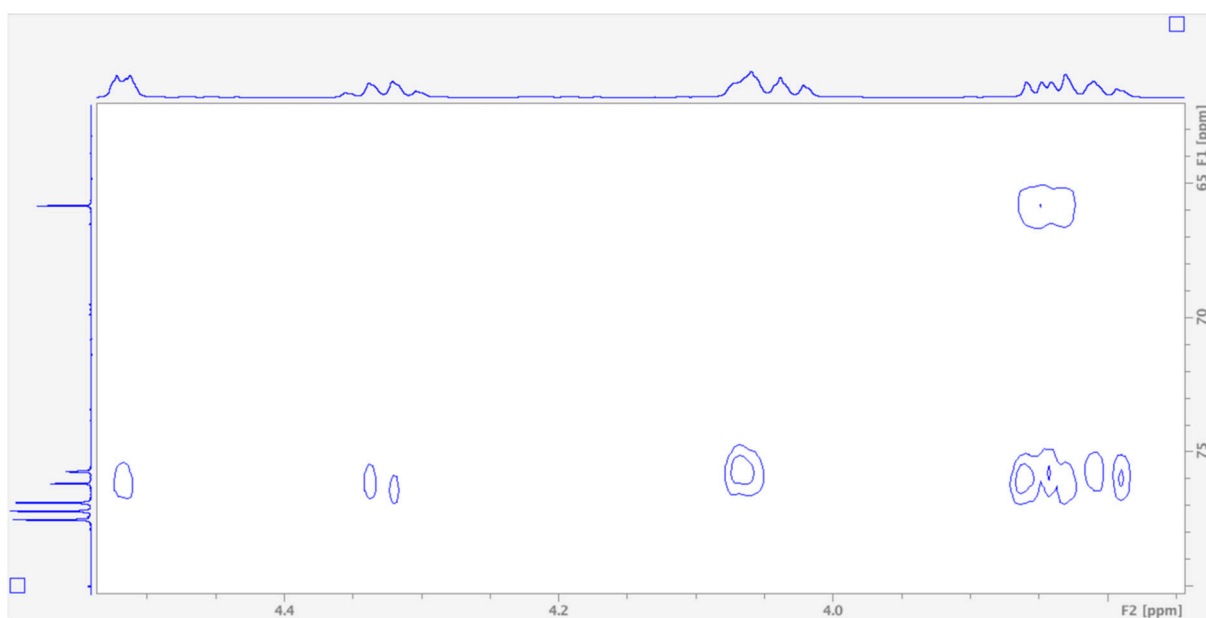
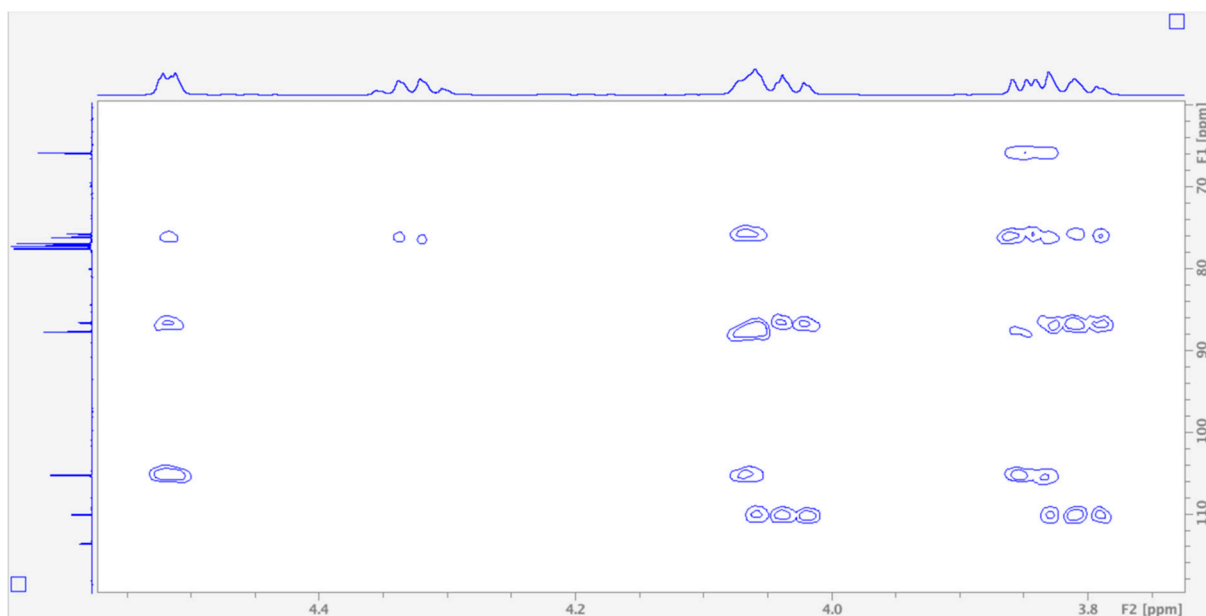


# HMBC

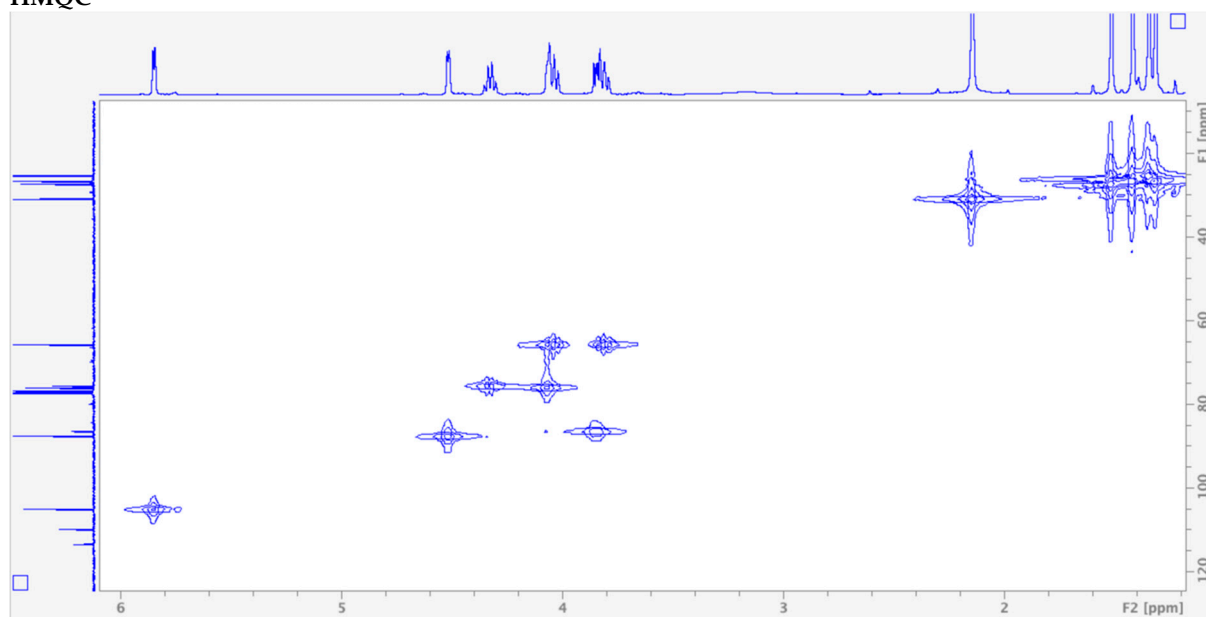




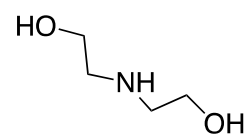




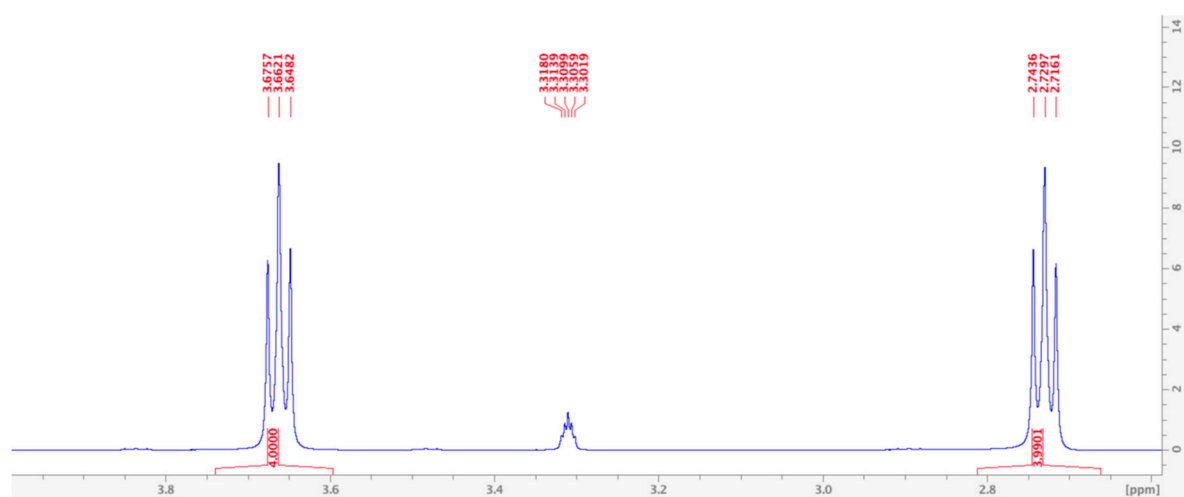
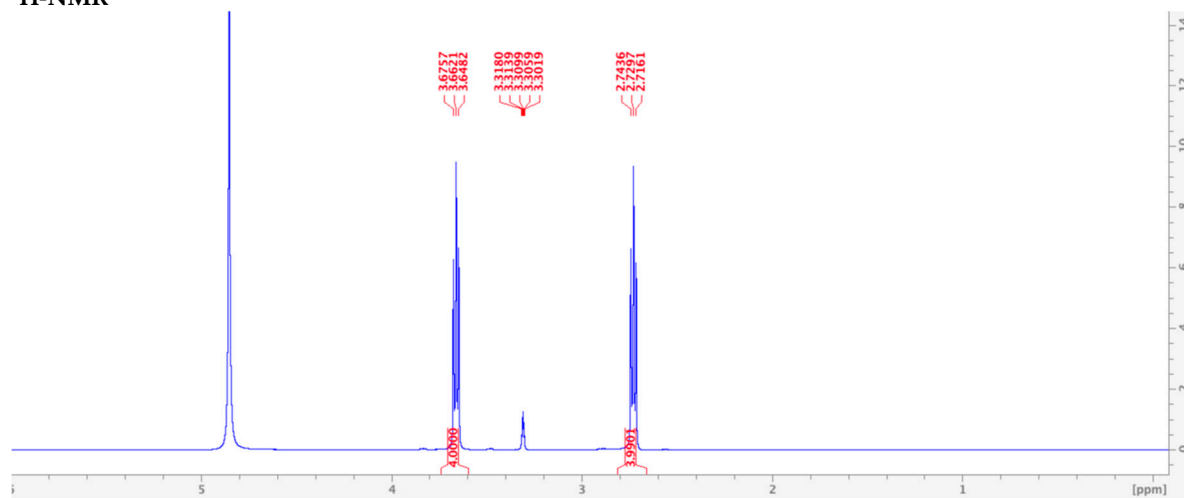
# HMQC



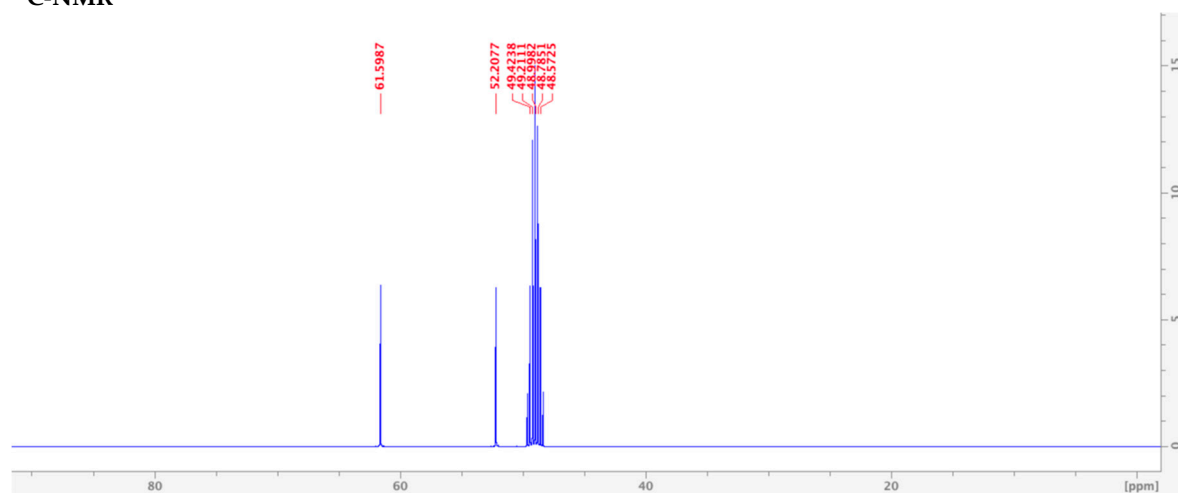
**Figure S4.**  $^1\text{H}$ - (400 MHz) and  $^{13}\text{C}$ -NMR (100 MHz) spectra of diethanolamine (DEA) in  $\text{CD}_3\text{OD}$ .



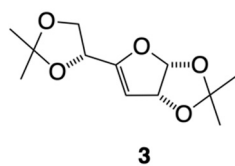
$^1\text{H}$ -NMR



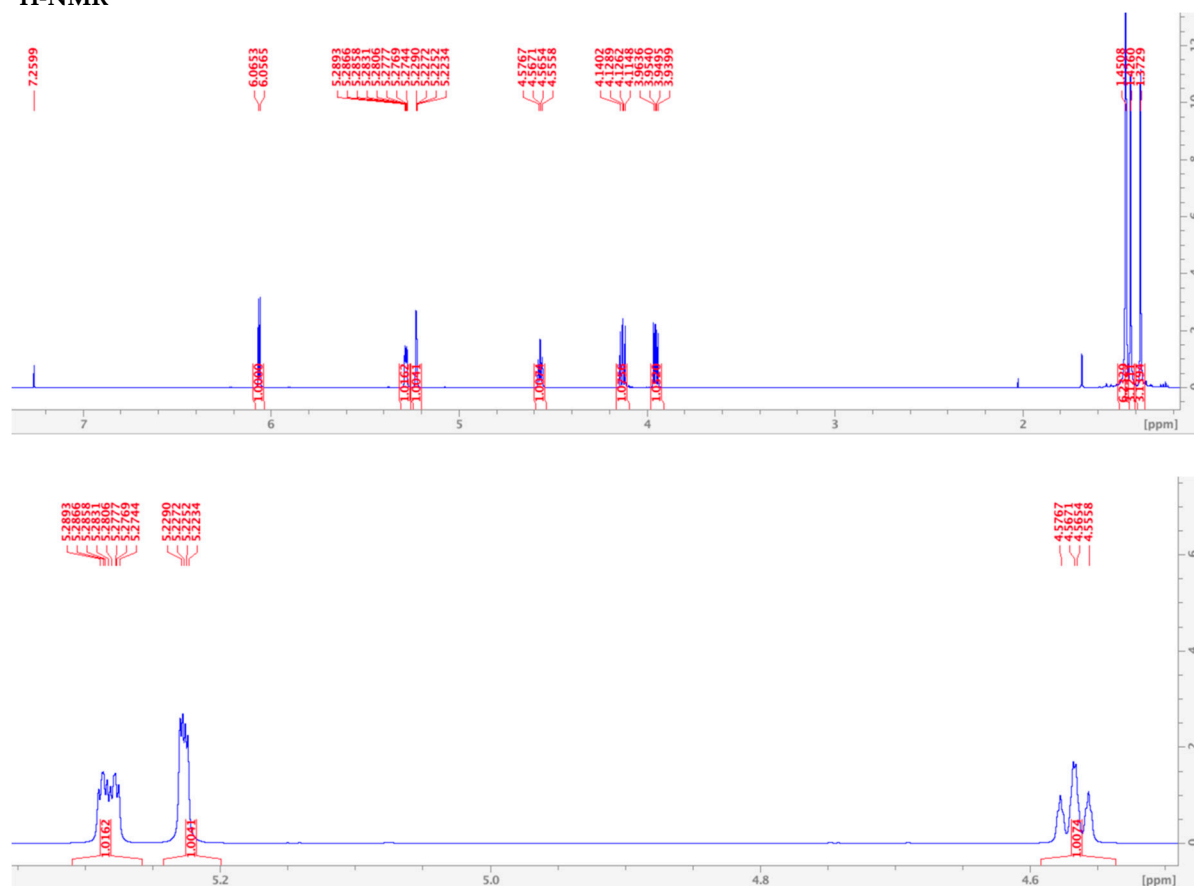
$^{13}\text{C}$ -NMR



**Figure S5.**  $^1\text{H}$ - (400 MHz) and  $^{13}\text{C}$ -NMR (100 MHz) spectra of 3-deoxy-1,2;5,6-di-*O*-isopropylidene- $\alpha$ -D-erythro-hex-3-enofuranose **3** in  $\text{CDCl}_3$ .

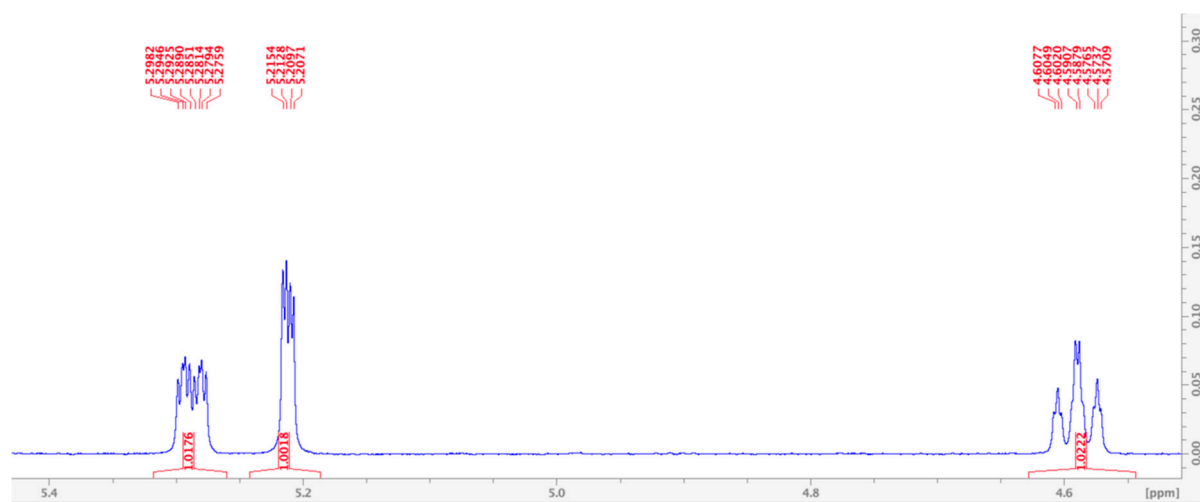
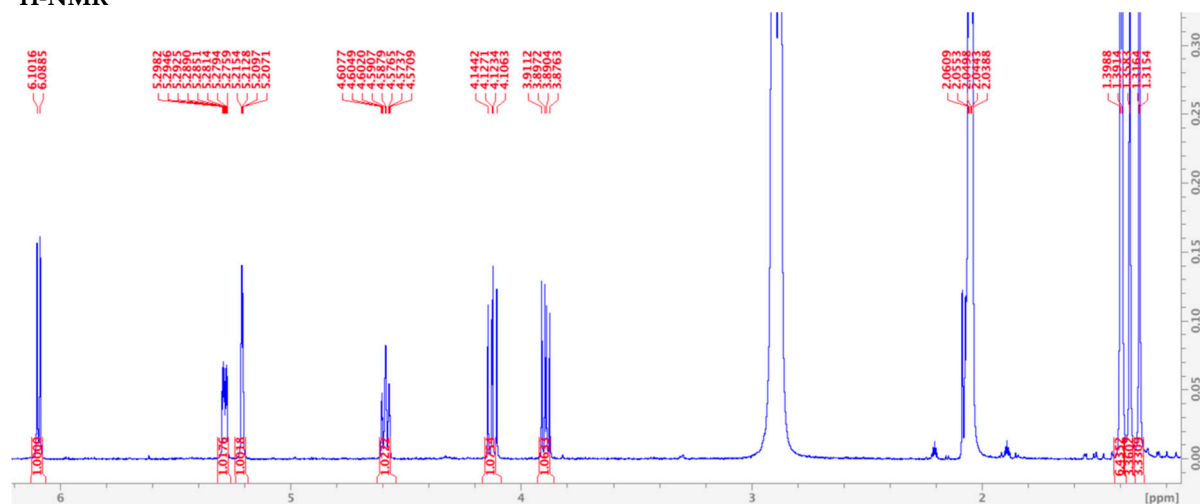


**$^1\text{H}$ -NMR**

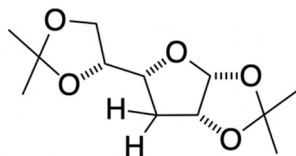


**Figure S6.**  $^1\text{H}$ - (400 MHz) and  $^{13}\text{C}$ -NMR (100 MHz) spectra of 3-deoxy-1,2;5,6-di-*O*-isopropylidene- $\alpha$ -D-erythro-hex-3-enofuranose **3** in acetone- $\text{d}_6$ .

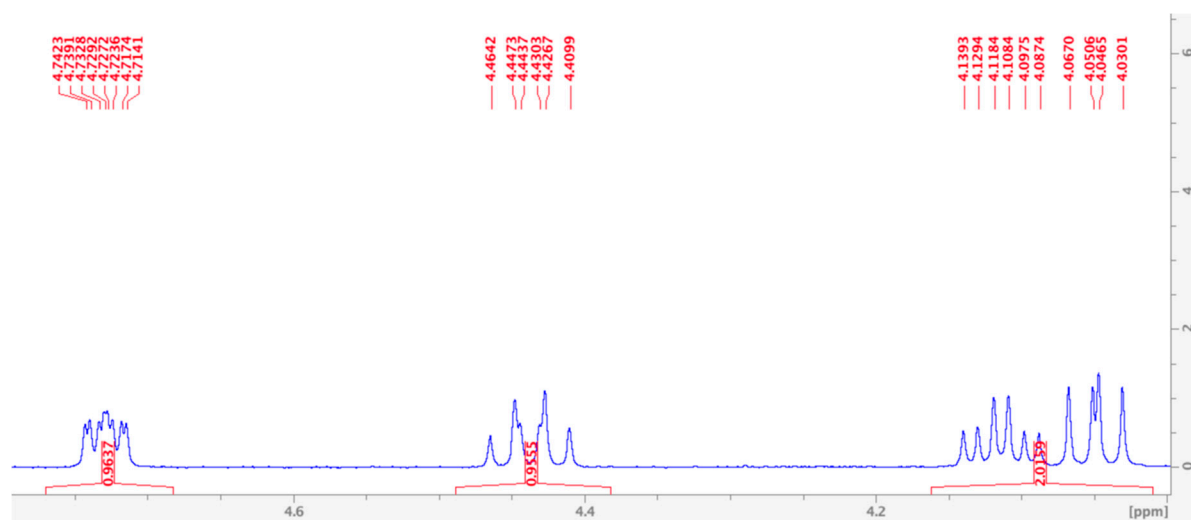
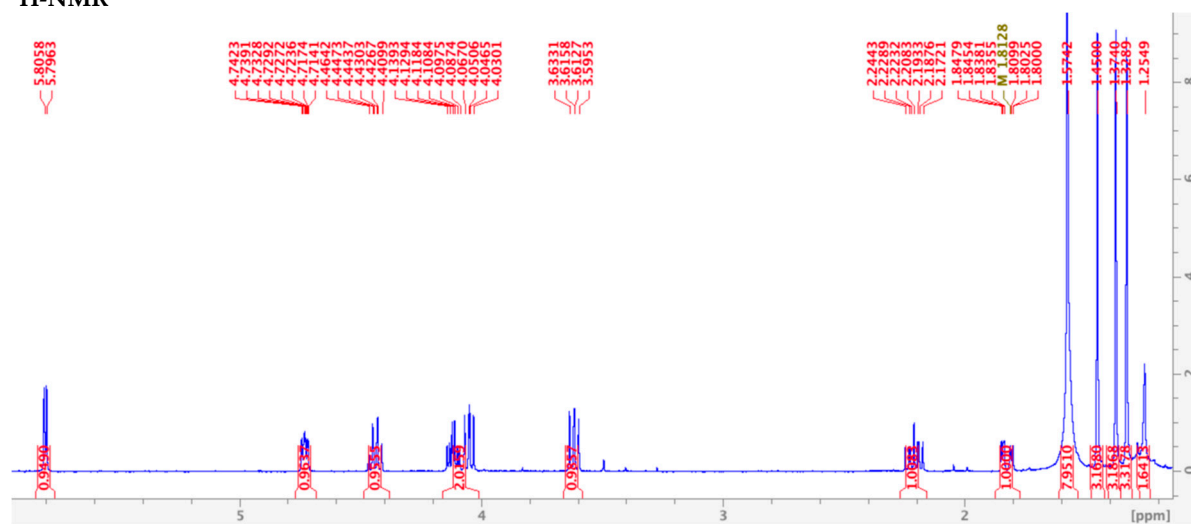
**$^1\text{H}$ -NMR**



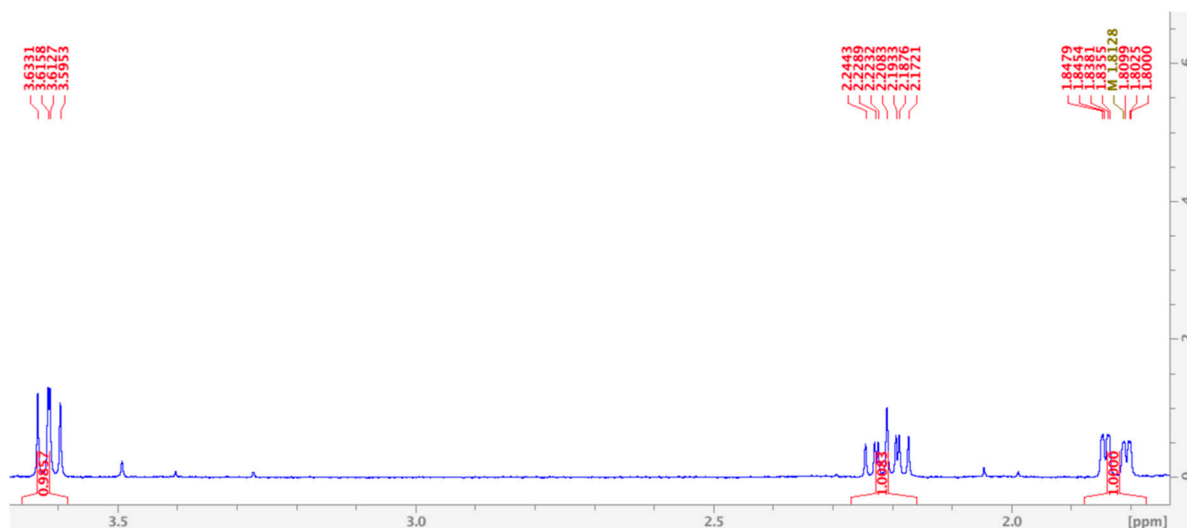
**Figure S7.**  $^1\text{H}$ - (400 MHz),  $^{13}\text{C}$ -NMR (100 MHz), COSY and HSQC spectra of 3-deoxy-1,2:5,6-di-O-isopropylidene- $\alpha$ -D-xylo-hexose in  $\text{CDCl}_3$ .



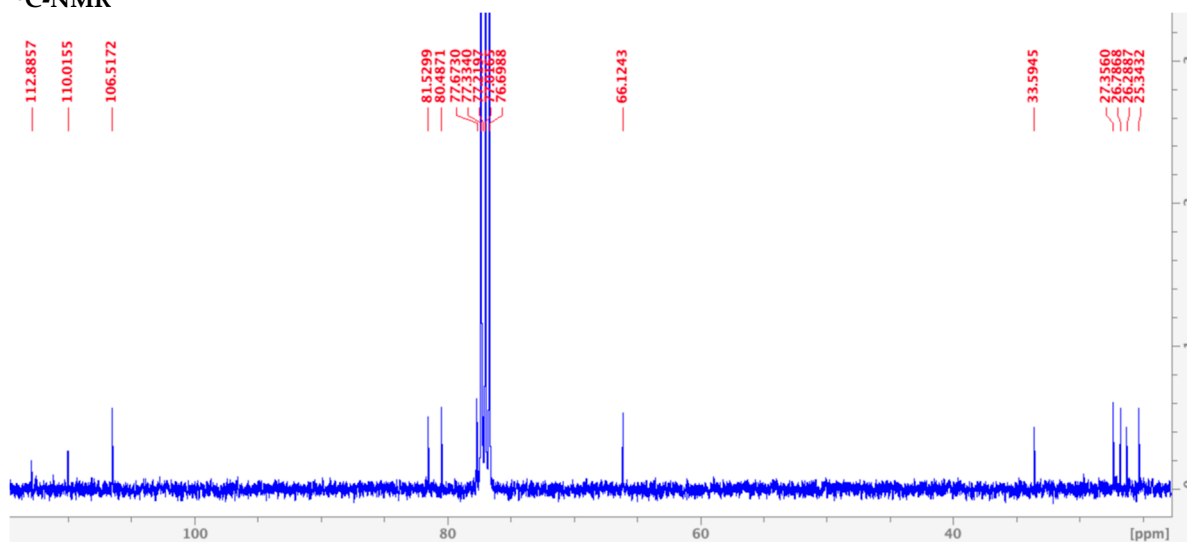
# $^1\text{H}$ -NMR



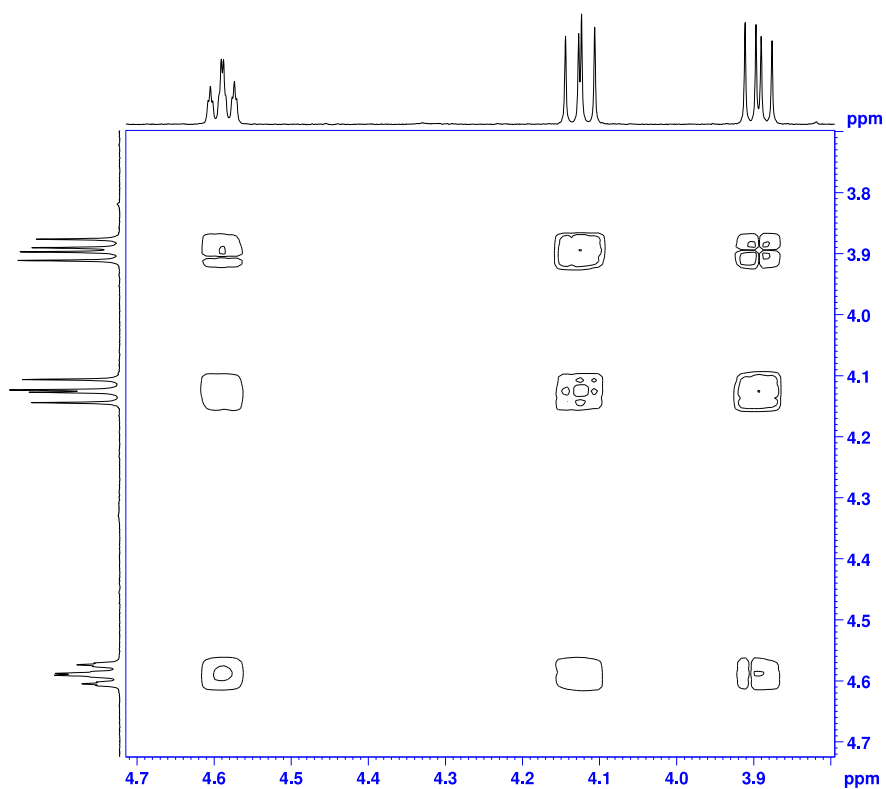
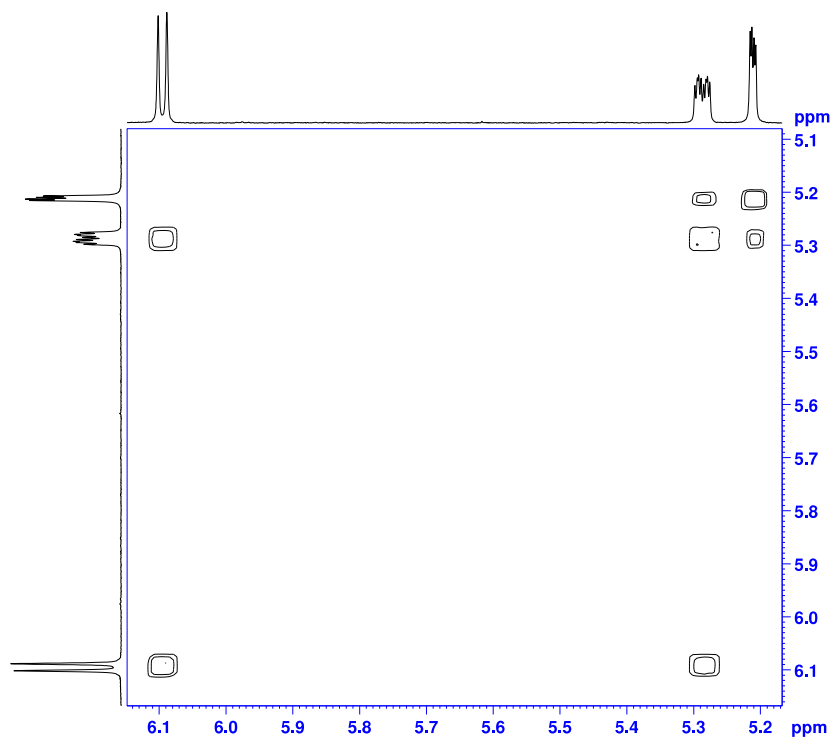


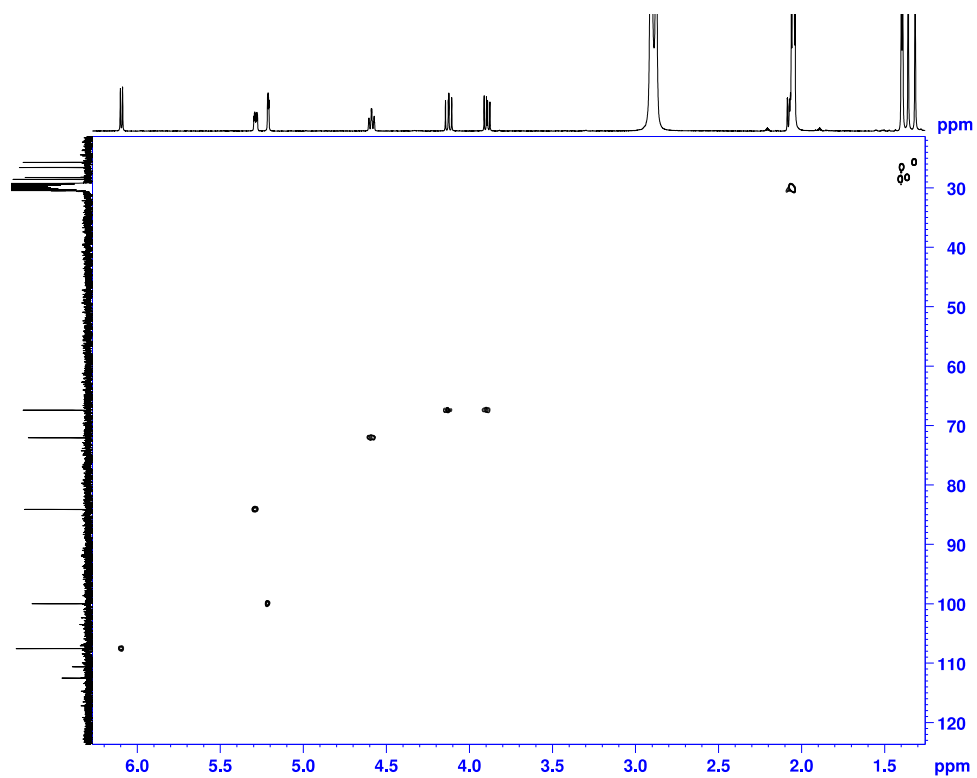


### <sup>13</sup>C-NMR

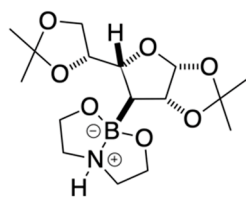


### COSY



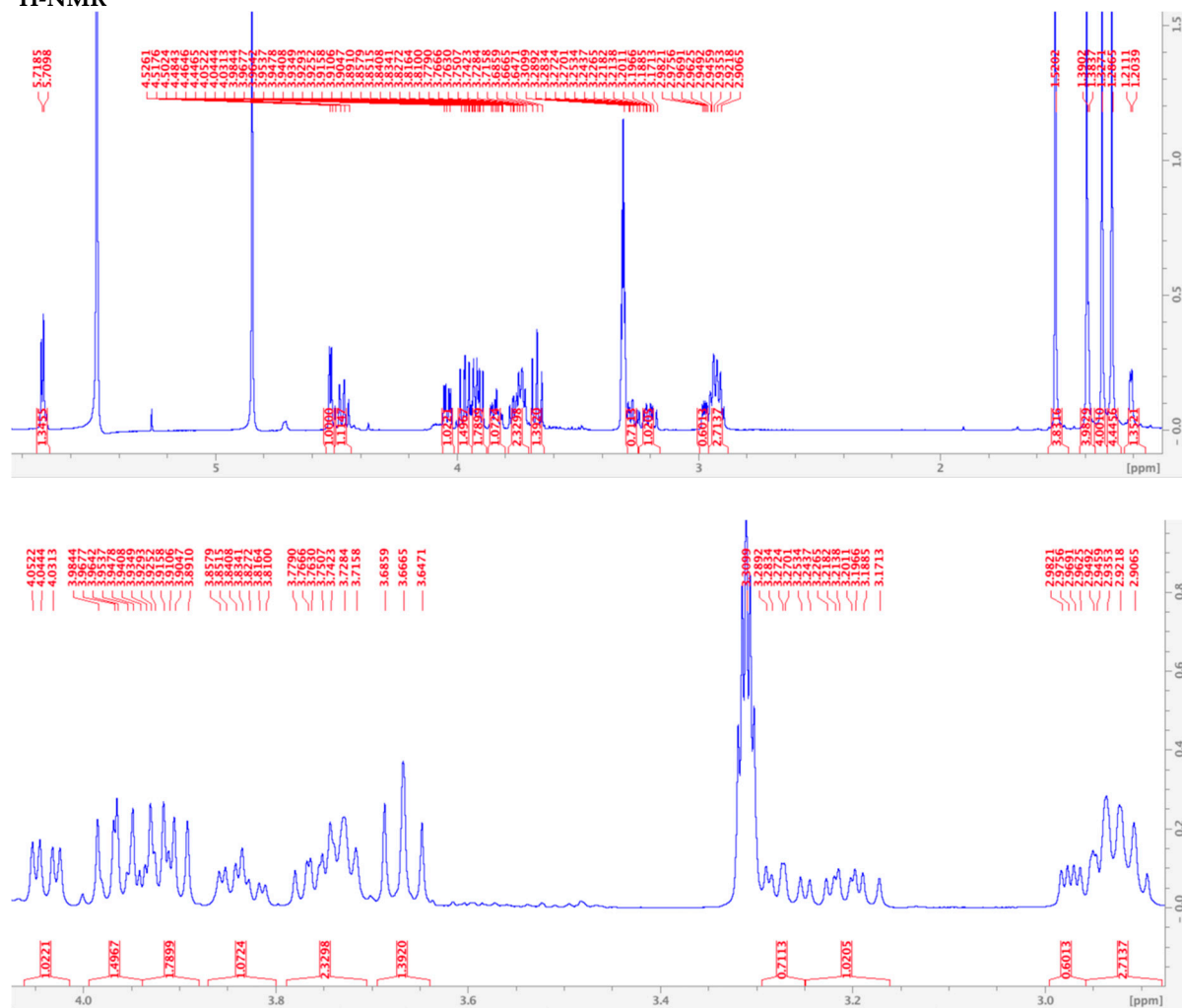


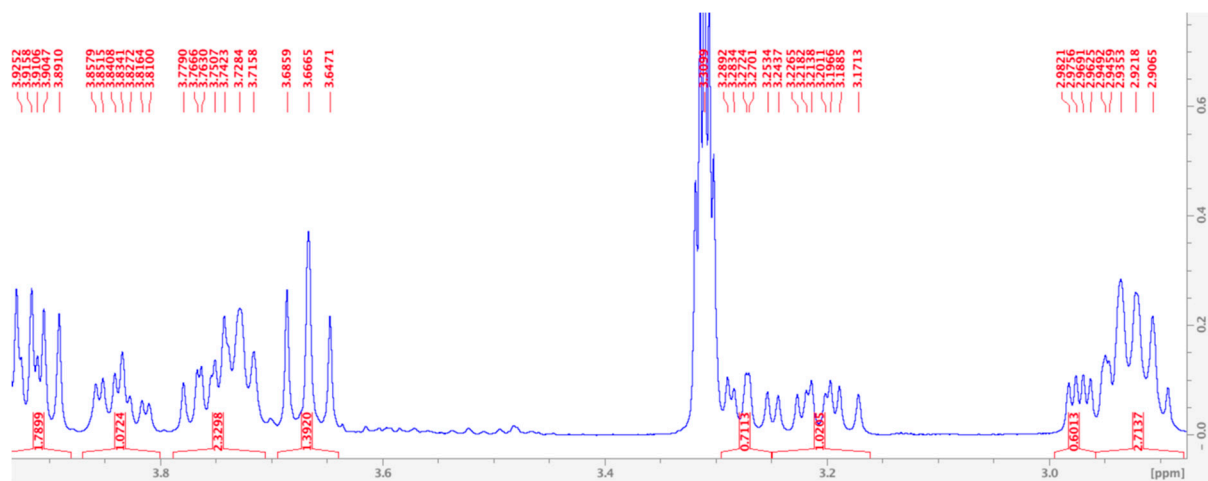
**Figure S8.**  $^1\text{H}$ - (400 MHz) spectrum of 3-deoxy-3-boronodiethanolamine-1,2:5,6-di-O-isopropylidene- $\alpha$ -D-galactofuranose **6** in  $\text{CD}_3\text{OD}$ .



**6**  
D-Galacto

$^1\text{H}$ -NMR





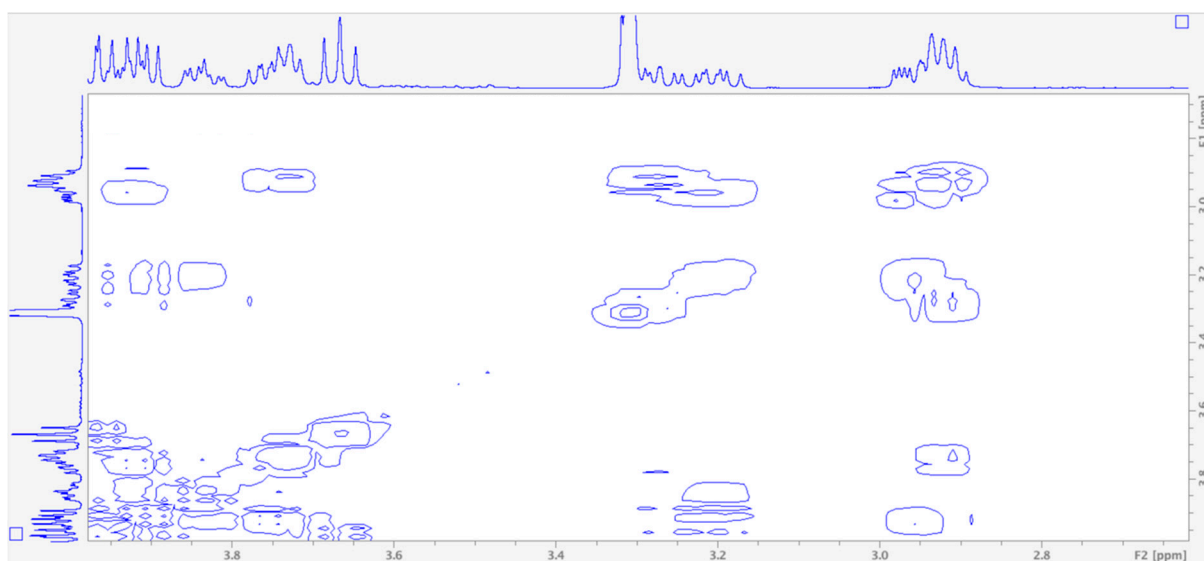
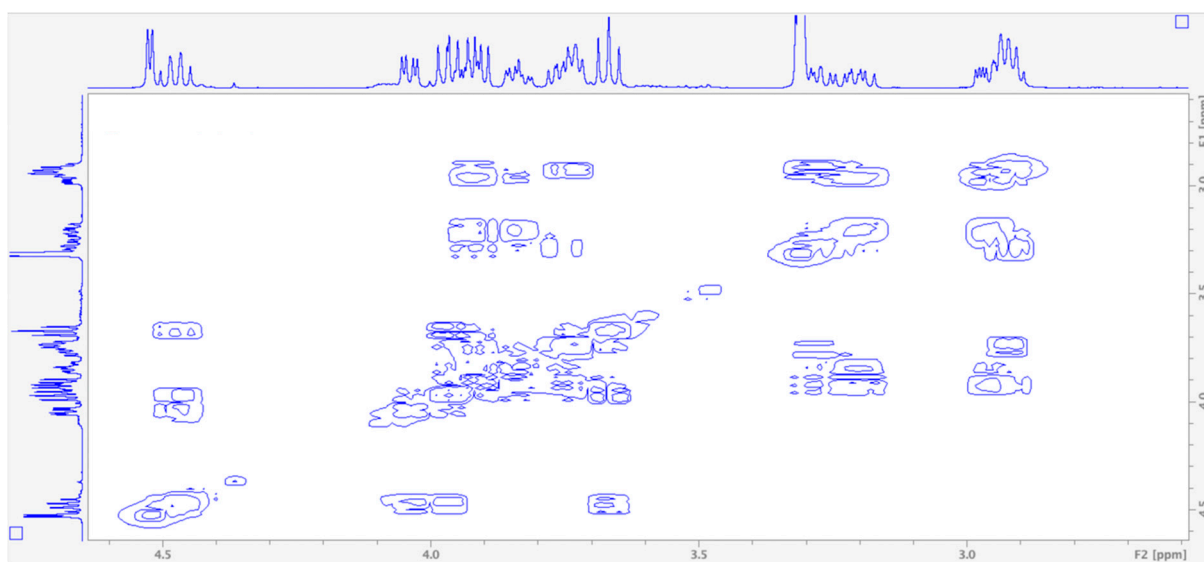
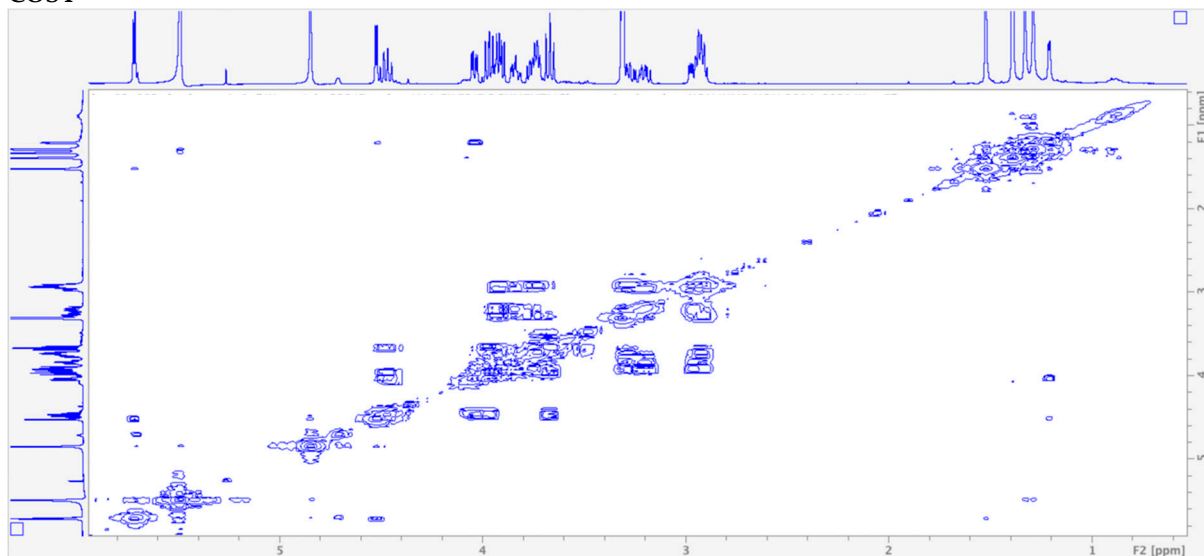
<sup>1</sup>H-NMR

13C NMR spectrum of compound 10a in CDCl<sub>3</sub>. The spectrum shows peaks at 112.9374, 110.7243, 110.4895, 108.1691, 108.0610, 86.4836, 85.7452, 80.3298, 67.3988, 67.2401, 63.8365, 63.7245, 59.9001, 59.8008, 52.7723, 52.7233, 51.3808, 49.2092, 49.1961, 49.2488, 49.2118, 48.7661, 48.5731, 48.3605, 27.8024, 26.4023, 26.3676, and 25.6005 ppm. The x-axis is labeled [ppm] and ranges from 0 to 120. The legend indicates M 37.8862, M 36.6034, and M 35.2351.

1H NMR spectrum of compound 10 in CDCl<sub>3</sub>. The spectrum shows several peaks in the aromatic region (6.5-7.0 ppm), a multiplet in the aliphatic region (4.5-5.5 ppm), and a cluster of peaks in the aliphatic region (2.5-3.0 ppm). A large solvent peak for CDCl<sub>3</sub> is visible at 7.26 ppm. The x-axis is labeled [ppm] and ranges from 0 to 10.

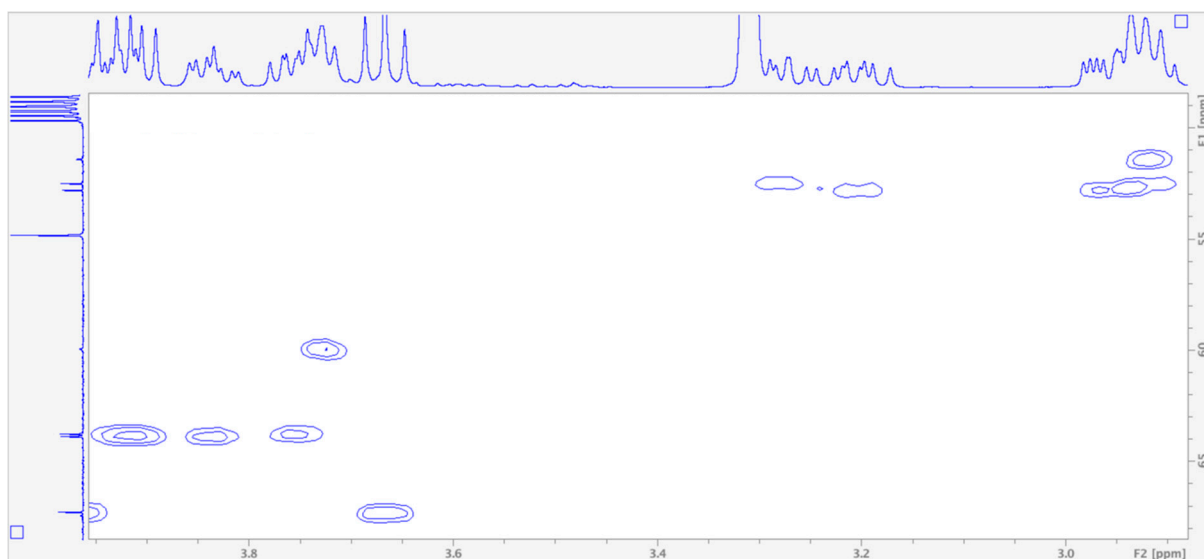
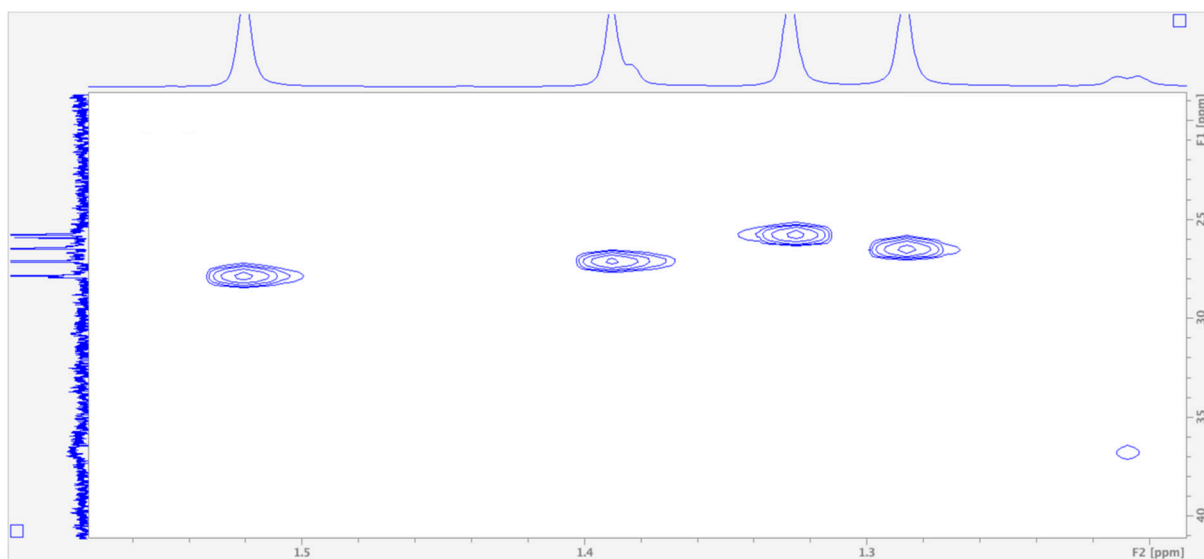
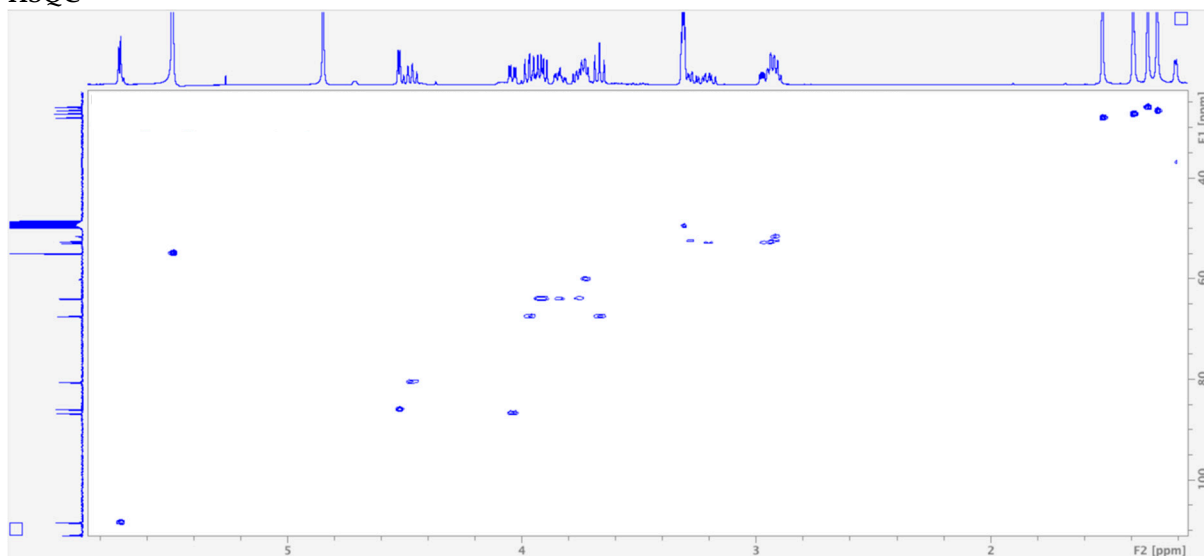
Chemical Shift (ppm)	Assignment
7.1129399	M
7.1107254	M
7.1081720	M
6.854867	M
6.857451	M
6.803323	M
6.674033	M
6.672953	M
6.638390	M
6.637266	M
5.598934	M
5.47975	M
5.27820	M
5.26834	M
5.13747	M
2.78037	M
2.69690	M
2.69690	M
2.57062	M

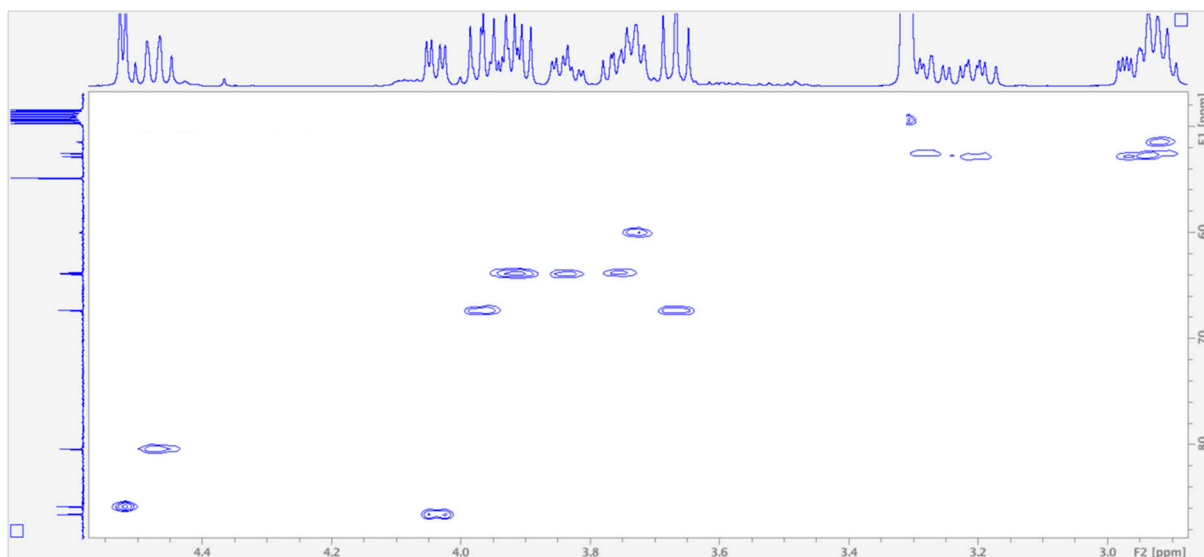
# COSY



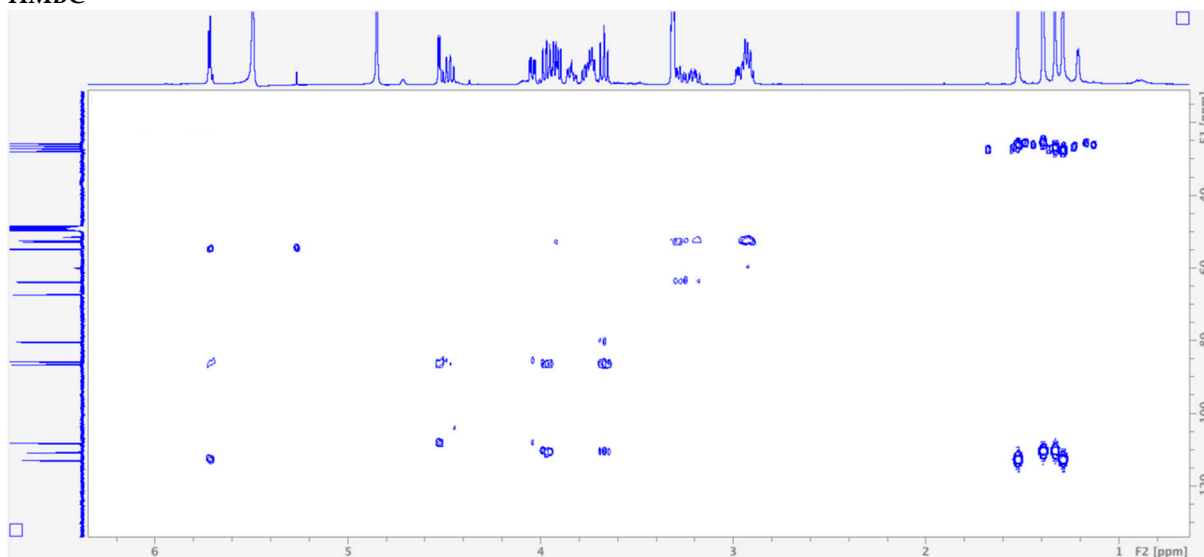


# HSQC

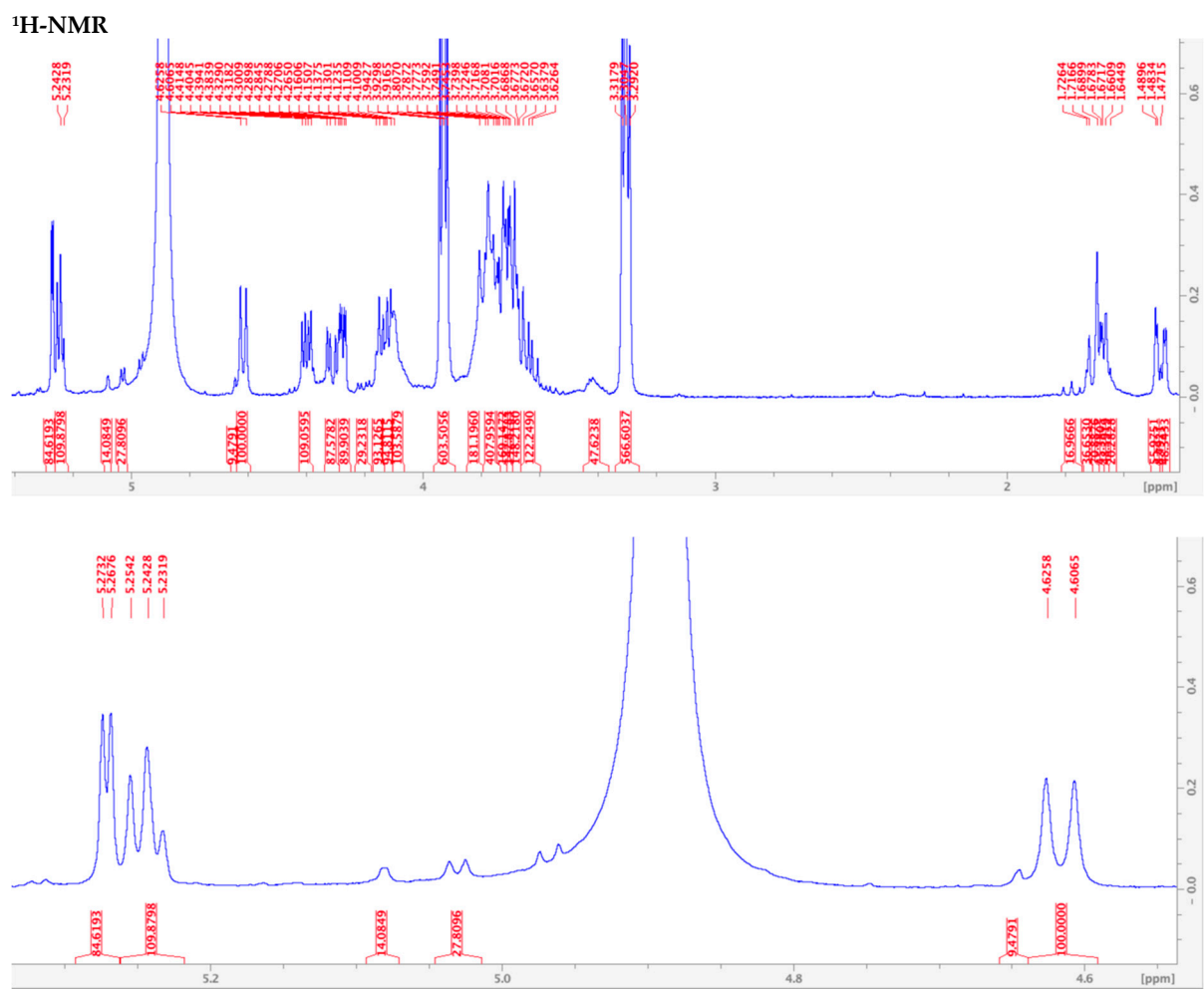


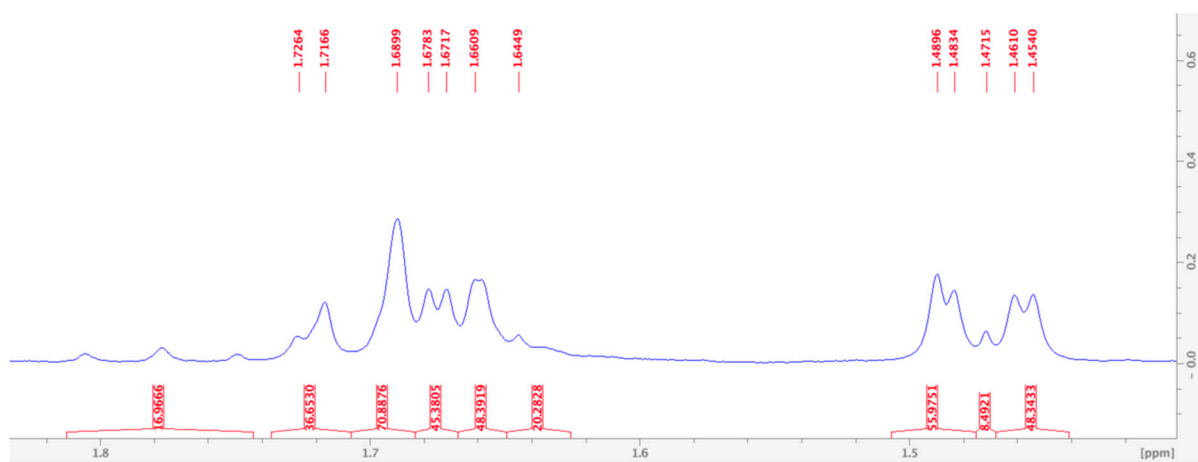
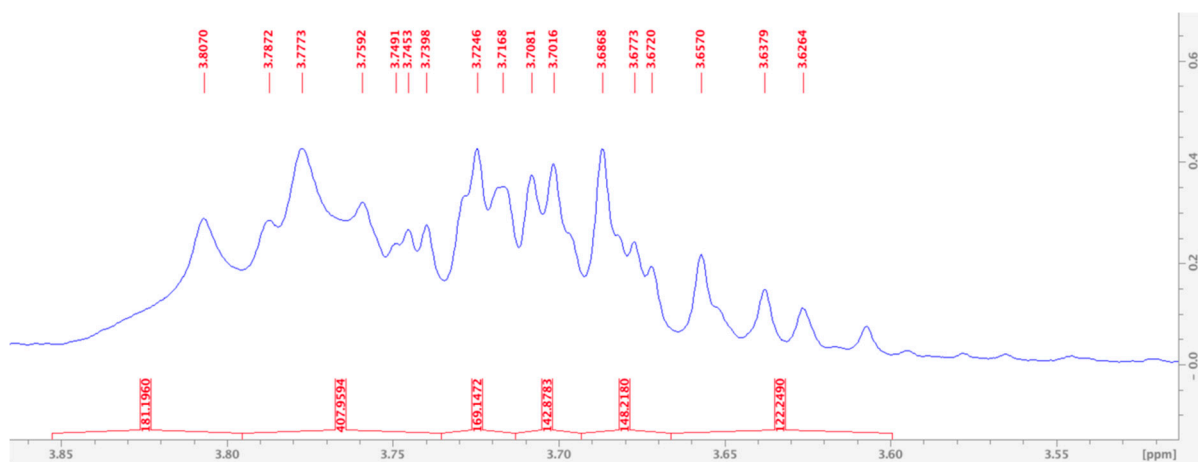
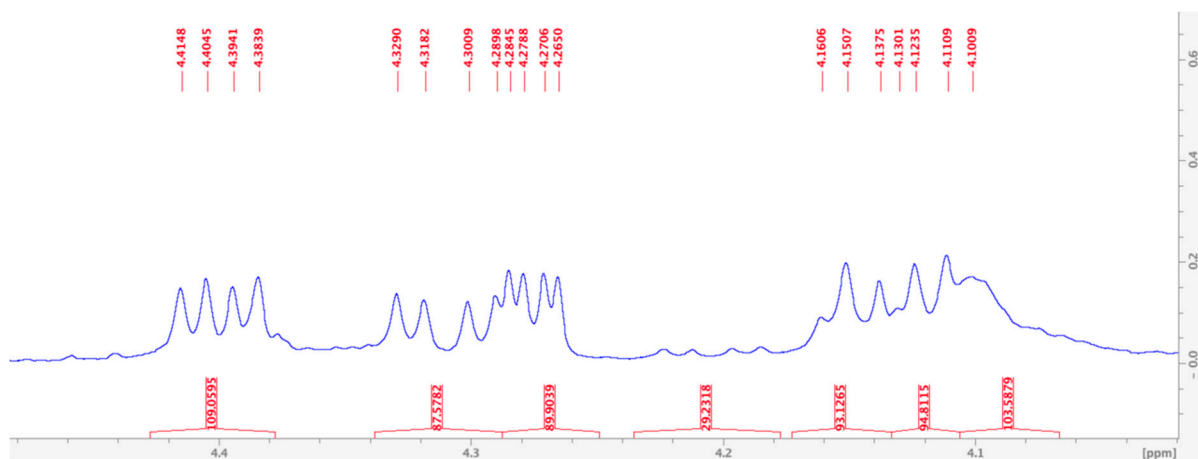


### HMBC

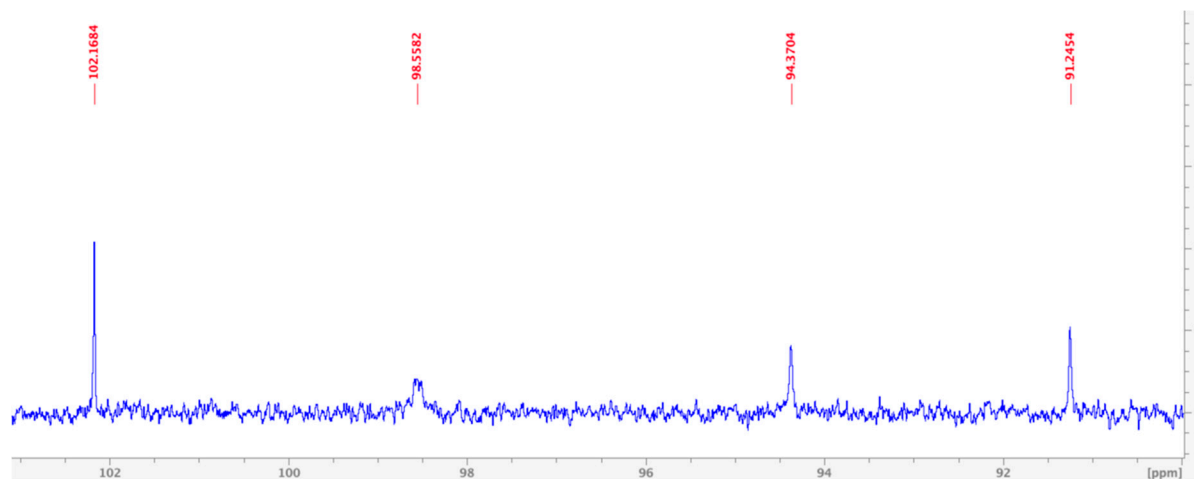
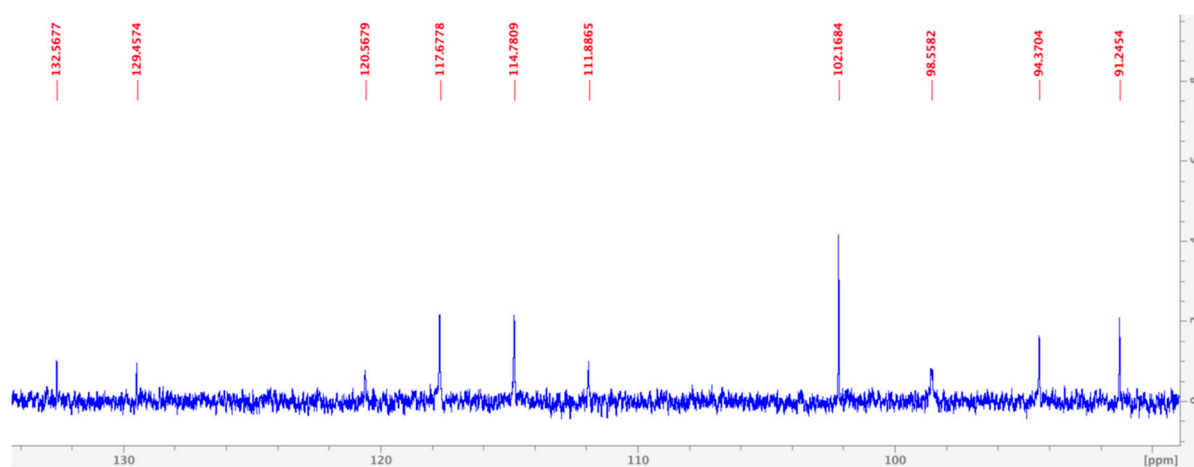
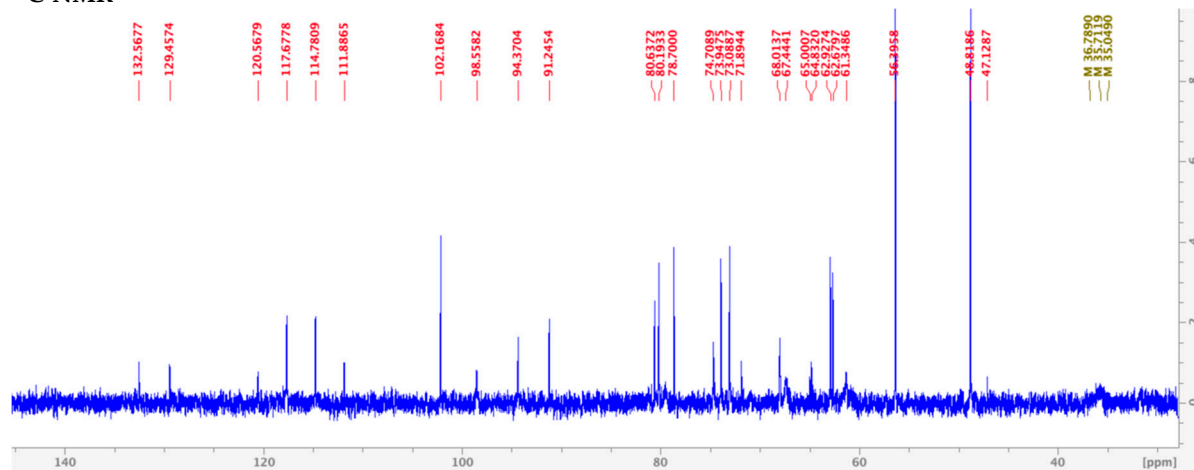


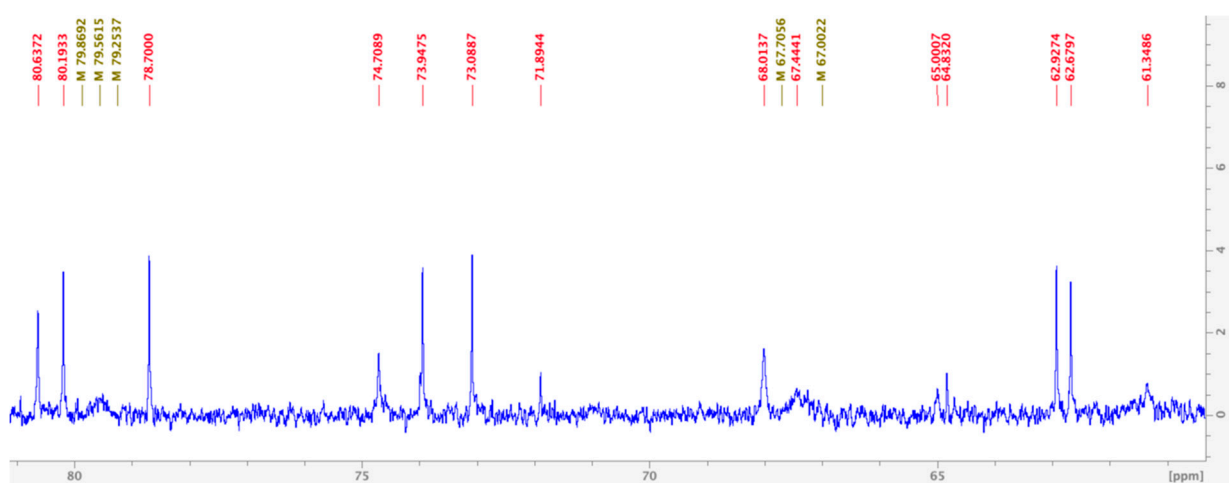
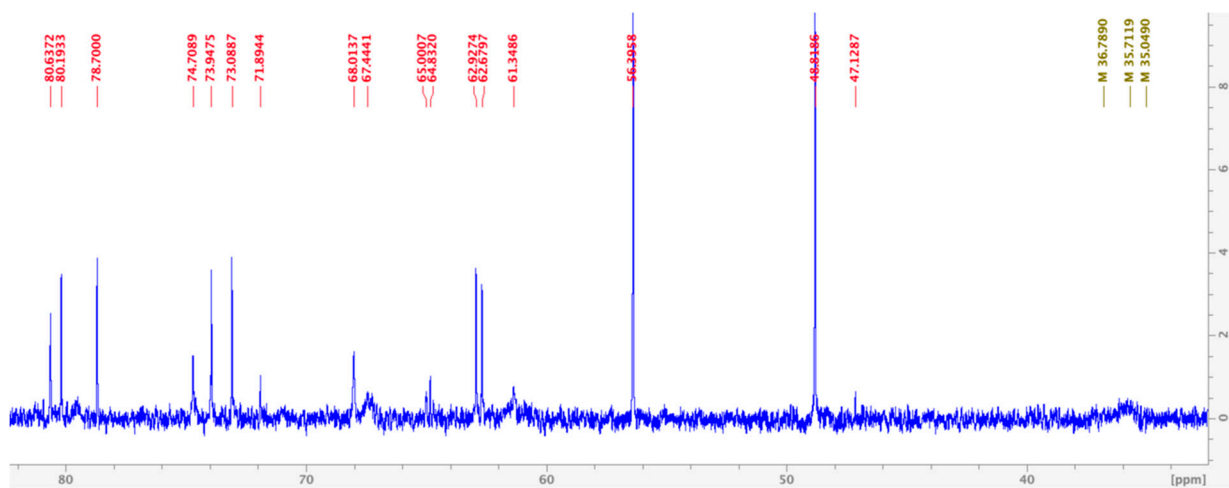
**7**  
*D-Galacto*



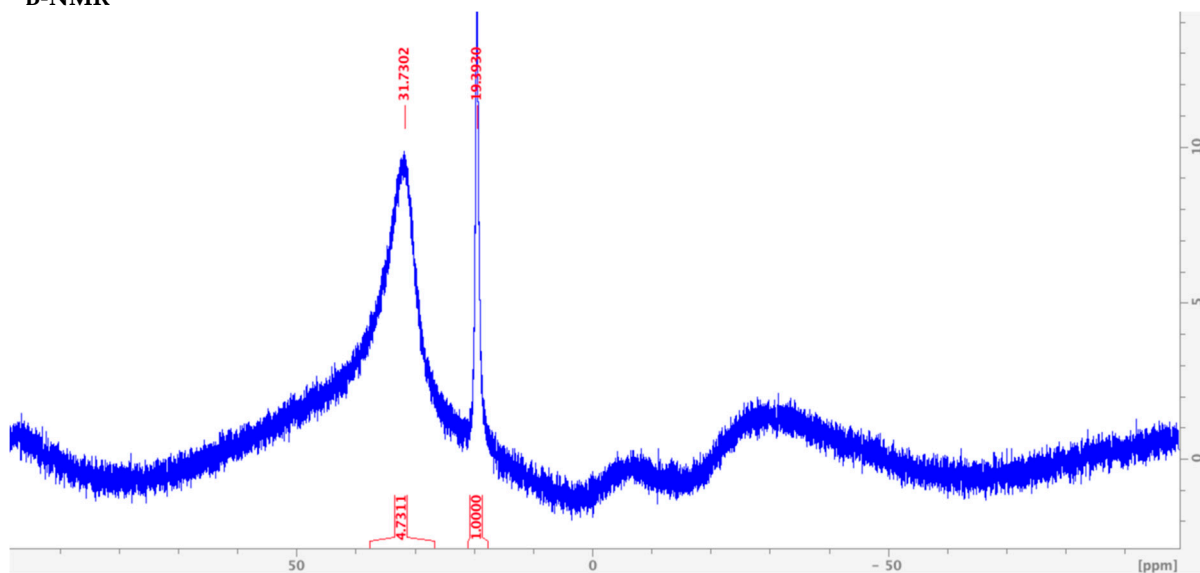


<sup>13</sup>C-NMR

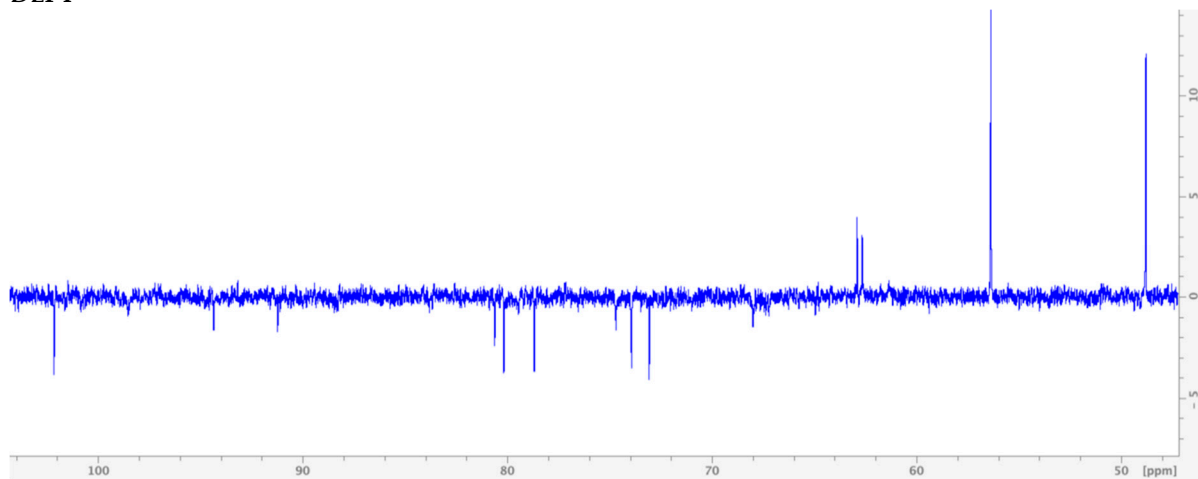




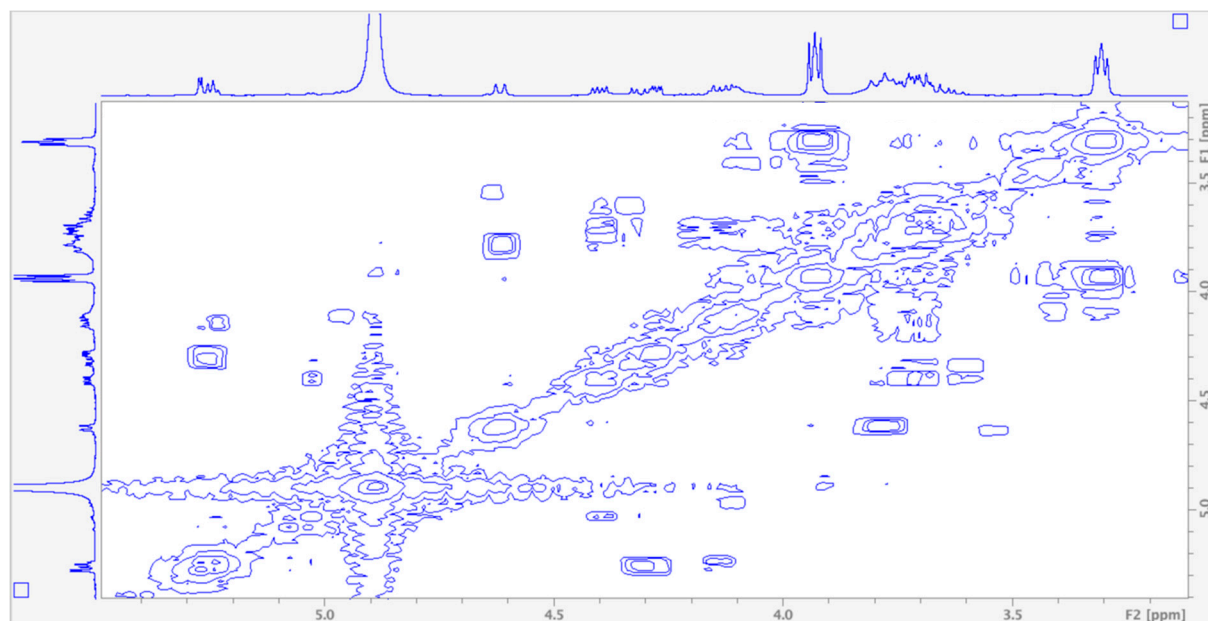
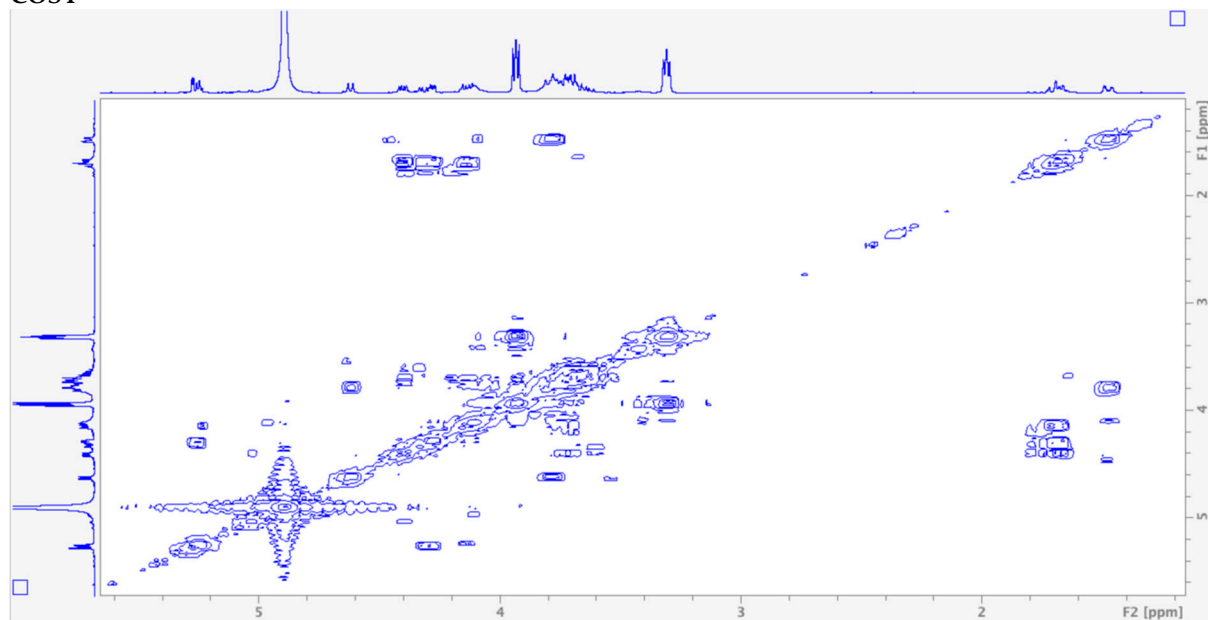
# <sup>11</sup>B-NMR

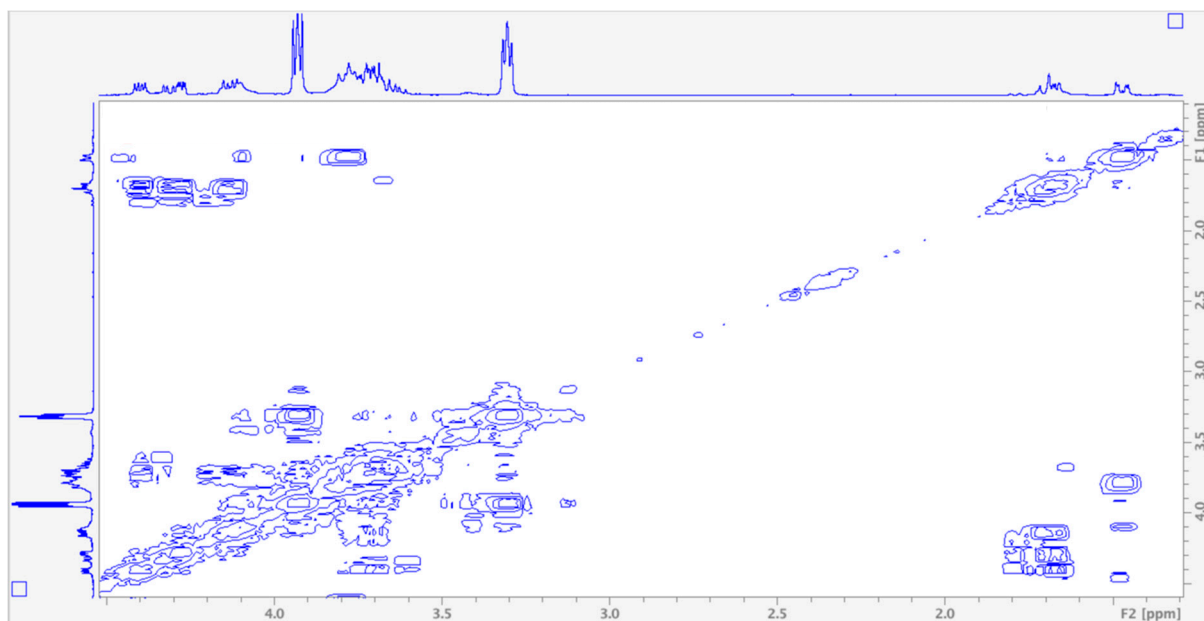


DEPT

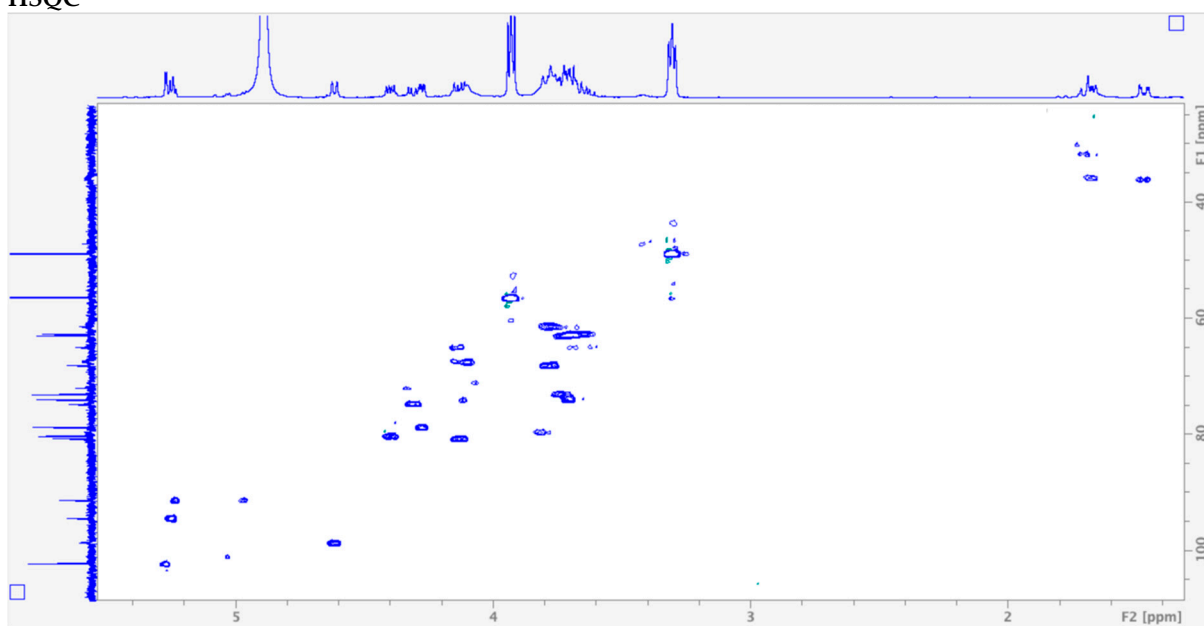


COSY

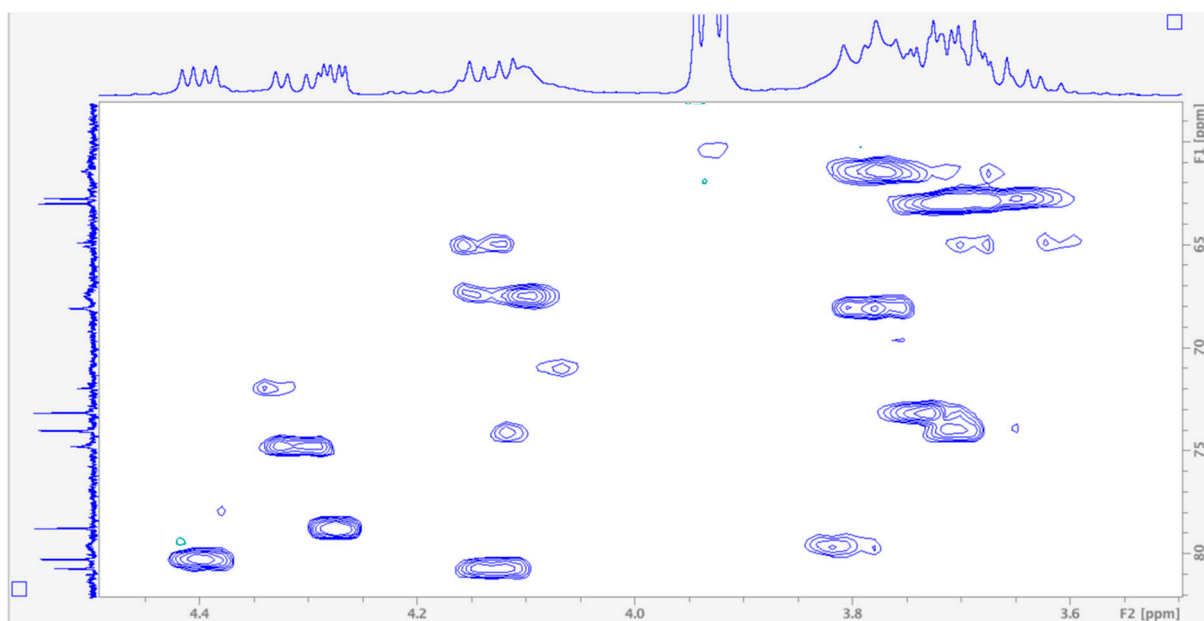
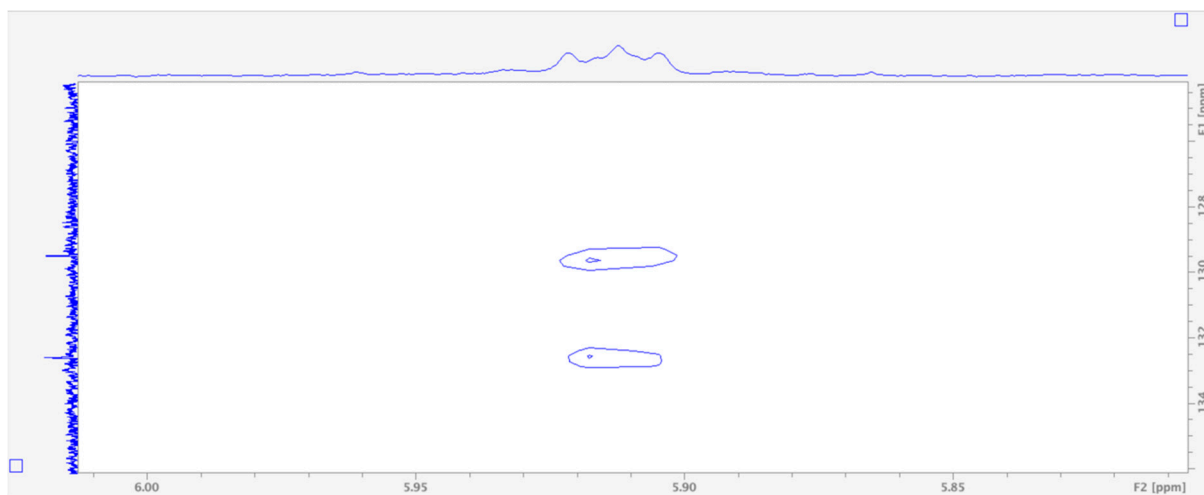
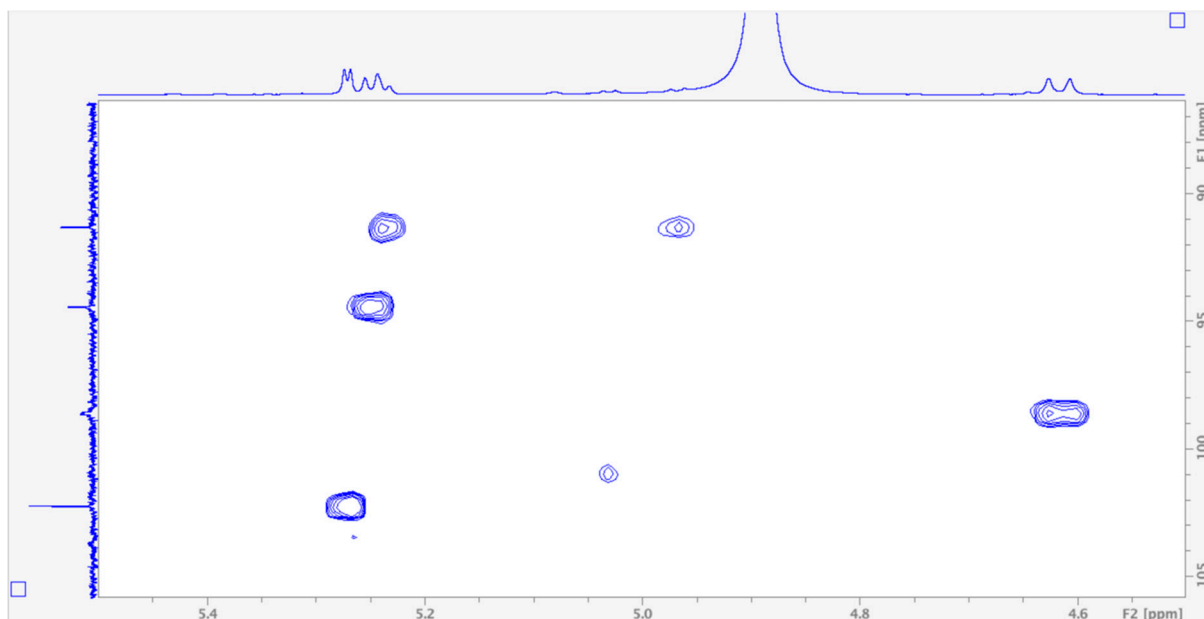


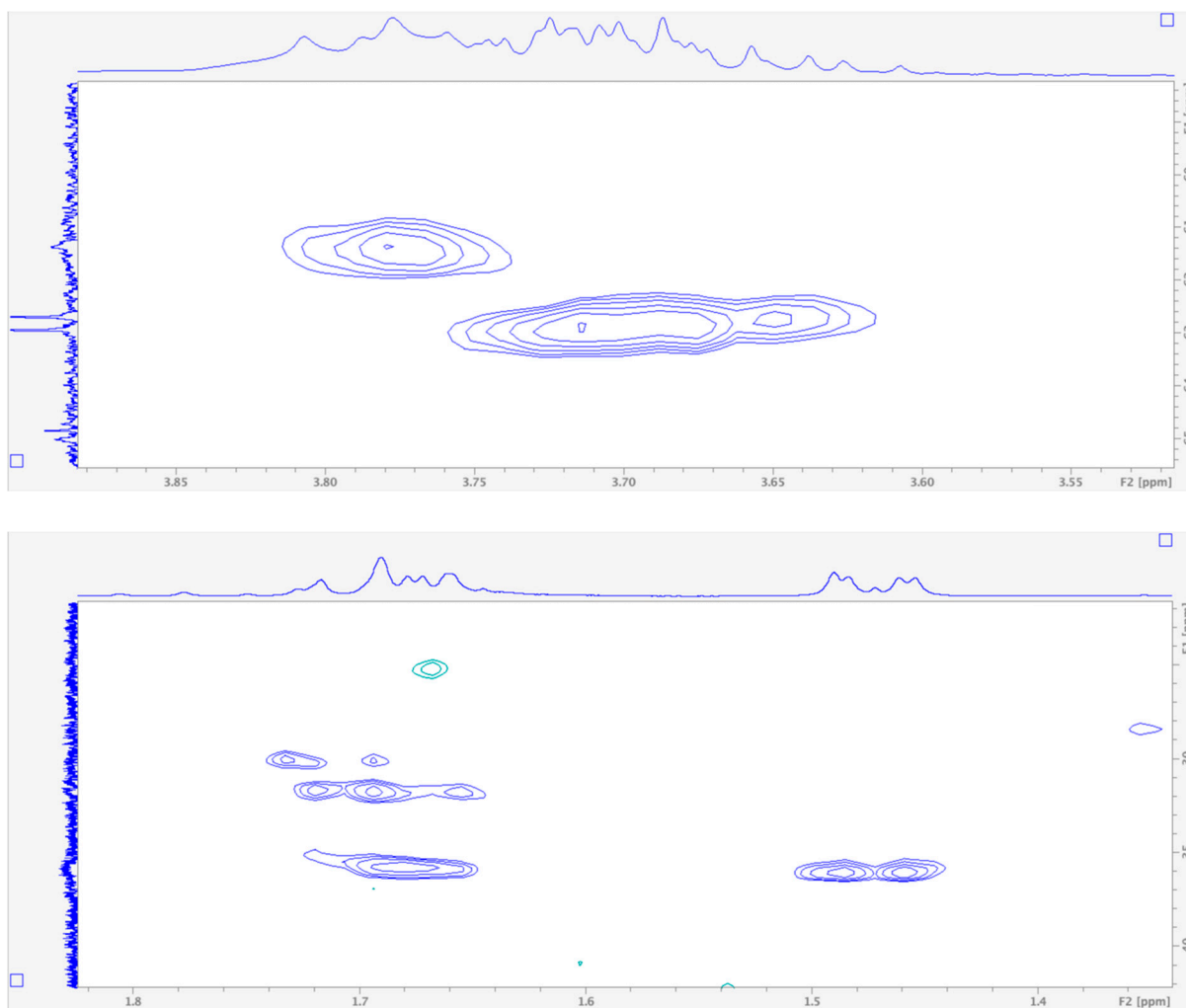


HSQC









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