

Supporting Information

for

Synthesis of modified cyclic and acyclic dextrans and comparison of their complexation ability

Kata Tuza^{1*}, László Jicsinszky^{1,2}, Tamás Sohajda¹, István Puskás¹ and Éva Fenyvesi¹

Address: ¹CycloLab Cyclodextrin R&D Laboratory Ltd, Illatos út 7, Budapest, 1097, Hungary and

²Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, via P. Giuria 9, Turin, 10125, Italy

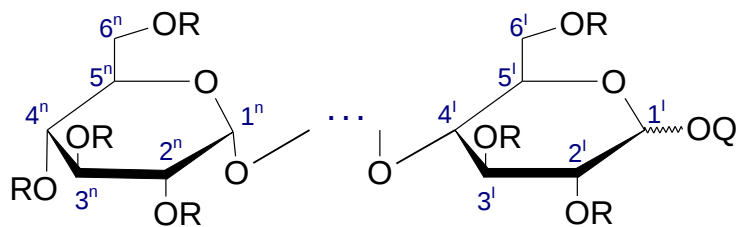
Email: Kata Tuza -tuza@cyclolab.hu

*Corresponding author

Additional NMR and HPLC data

Characterization of the ionic derivatives by NMR

All the NMR spectra including ^1H , HSQC-DEPT (Heteronuclear Single Quantum Coherence - Distortionless Enhancement by Polarization Transfer) were recorded in D_2O on a Varian VXR-300 instrument at 300 MHz.



Q = Bn or H

R = H or $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

n = 2-8

Scheme S1: General scheme of substituted maltooligomers for NMR assignment.

Table S1: Proton assignments of 1-O-benzylated and (2-hydroxy)propylated maltooligosaccharides (chemical shifts are in ppm).

	1-OBn			1-OH		
	G6	G7	G8	G6	G7	G8
Benzyl, Aromatic	7.38-7.45, br m	7.42-7.47, br, m	7.40-7.60, br m	-	-	-
Benzyl, CH ₂ α	4.93, d (J 11 Hz)	4.93, d (J 12 Hz)	4.93, d (J 12 Hz)	-	-	-
Benzyl, CH ₂ β	4.75, d (J 11 Hz)	4.76, d (J 12 Hz)	4.75, d (J 12 Hz)	-	-	-
(2-Hydroxy)prop-yl CH ₂	-	-	-	3.45-3.55, 3.63-68, 3.79-3.84, br	3.43-3.53, 3.61-3.66, 3.76-3.82, br	3.45-3.54, 3.62-3.66, 3.78-3.82, br
(2-Hydroxy)prop-yl CH	-	-	-	3.92-4.04, br	3.91-4.02, br	3.89-4.02, br
(2-Hydroxy)prop-yl CH ₃	-	-	-	1.14, 1.16, br	1.13, 1.15, br	1.13, 1.15, br
H1 ^l α	5.38, br	5.38, br	5.39, br	5.21, 5.52, br	5.20, 5.51, br	5.19, 5.50, br
H1 ^l β	4.52, d (J _{1,2} 7.7 Hz)	4.54, d (J _{1,2} 8 Hz)	4.53, d (J _{1,2} 7.6 Hz)	4.63, d (J _{1,2} 7.6 Hz)	4.62, d (J _{1,2} 7.8 Hz)	4.62, d (J _{1,2} 7.4 Hz)
H2 ^l	3.55, br m	3.55, br m	3.55, br m	3.55-3.72, br, unsubst 3.69, br, subst	3.54-3.68, br, unsubst 3.67, br, subst	3.54-3.68, br, unsubst 3.67, br, subst
H3 ^l	3.82, br m	3.84, br m	3.84, br m	3.76-3.87, br, unsubst 3.71-3.78, br, subst	3.75-3.85, br, unsubst 3.68-3.77, br, subst	3.74-3.86, br, unsubst 3.69-3.76, br, subst
H4 ^l	3.64-3.76, br m	3.58-3.74, br m	3.57-3.75, br m	3.44, br	3.42, br	3.43, br
H5 ^l	3.69-3.71, br m	3.68-3.74, br m	3.89-4.00, br m	4.03, br	4.01, br	4.01, br
H6 ^l	3.73-3.94, br m	3.75-3.96, br m	3.70-3.95, br m	3.74-3.93, br, unsubst 3.78-3.82, br, subst	3.74-3.93, br, unsubst 3.78-3.82, br, subst	3.74-3.93, br, unsubst 3.78-3.82, br, subst
H1 ²⁻⁽ⁿ⁻¹⁾	5.38, br d	5.38, br	5.39, br	5.39, 5.67, br	5.37, 5.65, br	5.37, 5.65, br
H2 ²⁻⁽ⁿ⁻¹⁾	3.60-3.63, br m	3.57-3.67, br m	3.50-3.67, br m	3.55-3.72, br, unsubst 3.69, br, subst	3.54-3.68, br, unsubst 3.67, br, subst	3.54-3.68, br, unsubst 3.67, br, subst

	1-OBn			1-OH		
	G6	G7	G8	G6	G7	G8
H3 ²⁻⁽ⁿ⁻¹⁾	3.82, br m	3.84, br m	3.84, br m	3.76-3.87, br, unsubst 3.71-3.78, br, subst	3.75-3.85, br, unsubst 3.68-3.77, br, subst	3.74-3.86, br, unsubst 3.69-3.76, br, subst
H4 ²⁻⁽ⁿ⁻¹⁾	3.64-3.76, br m	3.58-3.74, br m	3.57-3.75, br m	3.44, br	3.42, br	3.43, br
H5 ²⁻⁽ⁿ⁻¹⁾	3.92-3.97, br m	3.91-4.02, br m	3.62-3.73, br m	3.76-3.87, br, unsubst 3.71-3.78, br, subst	3.75-3.85, br, unsubst 3.68-3.77, br, subst	3.74-3.86, br, unsubst 3.69-3.76, br, subst
H6 ²⁻⁽ⁿ⁻¹⁾	3.73-3.94, br m	3.75-3.96, br m	3.70-3.95, br m	3.74-3.93, br, unsubst 3.78-3.82, br, subst	3.74-3.93, br, unsubst 3.78-3.82, br, subst	3.74-3.93, br, unsubst 3.78-3.82, br, subst
H1 ⁿ	5.38, br d	5.38, br	5.39, br	5.39, 5.67, br	5.37, 5.65, br	5.37, 5.65, br
H2 ⁿ	3.60-3.63, br m	3.57-3.67, br m	3.50-3.67, br m	3.55-3.72, br, unsubst 3.69, br, subst	3.54-3.68, br, unsubst 3.67, br, subst	3.54-3.68, br, unsubst 3.67, br, subst
H3 ⁿ	3.82, br m	3.84, br m	3.84, br m	3.76-3.87, br, unsubst 3.71-3.78, br, subst	3.75-3.85, br, unsubst 3.68-3.77, br, subst	3.74-3.86, br, unsubst 3.69-3.76, br, subst
H4 ⁿ	3.41, t (J _{1,2} 9.1 Hz)	3.39, t (overlapped)	3.40, t (overlapped)	3.44, br	3.42, br	3.42, br
H5 ⁿ	3.33, t (J _{1,2} 8.7 Hz)	3.35, t (overlapped)	3.33, t (overlapped)	3.27, br	3.25, br	3.25, br
H6 ⁿ	3.73-3.94, br m	3.75-3.96, br m	3.70-3.95, br m	3.74-3.93, br, unsubst 3.78-3.82, br, subst	3.74-3.93, br, unsubst 3.78-3.82, br, subst	3.74-3.93, br, unsubst 3.78-3.82, br, subst
1,2-Propylene-glycol CH ₂	-	-	-	-	3.80, br	3.81, br
1,2-Propylene-glycol CH	-	-	-	-	3.83, br	3.84, br
1,2-Propylene-glycol CH ₃	-	-	-	-	1.13, 1.15, br	1.13, 1.15, br

Table S2: Carbon assignments of 1-O-benzylated and (2-hydroxy)propylated maltooligosaccharides (chemical shifts are in ppm, based on DEPT-ed-HSQC experiments).

	1-OBn			1-OH		
	G6	G7	G8	G6	G7	G8
Benzyl, Aromatic	128.8, br	128.9	128.8, br	-	-	-
Benzyl, CH ₂ α	71.4, 71.7	71.6, 71.7	71.5, 71.7	-	-	-
Benzyl, CH ₂ β	71.6	71.6	71.5, 71.7	-	-	-
(2-Hydroxy)prop-yl CH ₂	-	-	-	76.1, 76.3, 76.4	76.1, 76.2, 76.4	76.1, 76.3
(2-Hydroxy)prop-yl CH	-	-	-	72.6, 73.1	73.1, 73.2	72.7, 73.1
(2-Hydroxy)prop-yl CH ₃	-	-	-	18.2	18.2	18.2
C1 ^I α	99.8, br	99.7, br	99.6-99.7, br	91.8, 98.4	91.7, 98.3	91.9, 98.3
C1 ^I β	101.2	101.2	101.2	95.6	95.7	95.8
C2 ^I	74.7	74.7	74.6	71.5, 72.8, unsubst 77.4, subst	71.5, 72.6, unsubst 77.2, subst	71.4, 72.6, unsubst 76.9, subst
C3 ^I	71.3	71.3	71.3	70.9 unsubst 74.7, subst	70.8 unsubst 74.8, subst	70.7, 71.1 unsubst 74.7, subst
C4 ^I	76.3-77.1, br	76.3-77.0, br	76.4-77.0, br	79.9	79.9	79.9
C5 ^I	72.9	72.9	73.4	66.3	66.6	66.1
C6 ^I	60.5-60.9, br	60.5-60.9, br	60.5-60.9, br	60.4, 60.6, unsubst 69.3, subst	60.5, unsubst 69.2, subst	60.4, unsubst 69.3, subst
C1 ²⁻⁽ⁿ⁻¹⁾	99.8	99.7	99.6-99.7, br	96.7, 99.6	96.7, 99.5	96.7, 99.6
C2 ²⁻⁽ⁿ⁻¹⁾	71.6-71.7	71.6-71.7	71.6-71.7	71.5, 72.8, unsubst 77.4, subst	71.5, 72.6, unsubst 77.2, subst	71.4, 72.6, unsubst 76.9, subst

	1-OBn			1-OH		
	G6	G7	G8	G6	G7	G8
C3 ²⁻⁽ⁿ⁻¹⁾	71.3	71.3	71.3	70.9 unsubst 74.7, subst	70.8 unsubst 74.8, subst	70.7, 71.1 unsubst 74.7, subst
C4 ²⁻⁽ⁿ⁻¹⁾	76.3-77.1, br	76.3-77.0, br	76.4-77.0, br	79.9	79.9	79.9
C5 ²⁻⁽ⁿ⁻¹⁾	73.4	73.5	73.0, 73.6	66.3	66.6	66.1
C6 ²⁻⁽ⁿ⁻¹⁾	60.5-60.9, br	60.5-60.9, br	60.5-60.9, br	60.4, 60.6, unsubst 69.3, subst	60.5, unsubst 69.2, subst	60.4, unsubst 69.3, subst
C1 ⁿ	99.8	99.7	99.6-99.7, br	96.7, 99.6	96.7, 99.5	96.7, 99.6
C2 ⁿ	71.6-71.7	71.6-71.7	71.6-71.7	71.5, 72.8, unsubst 77.4, subst	71.5, 72.6, unsubst 77.2, subst	71.4, 72.6, unsubst 76.9, subst
C3 ⁿ	71.3	71.3	71.3	70.9 unsubst 74.7, subst	70.8 unsubst 74.8, subst	70.7, 71.1 unsubst 74.7, subst
C4 ⁿ	69.4	69.4	69.4	69.4	69.3	69.2
C5 ⁿ	73.1	73.1	73.1	73.9	74.3	73.9
C6 ⁿ	60.5-60.9, br	60.5-60.9, br	60.5-60.9, br	60.4, 60.6, unsubst 69.3, subst	60.5, unsubst 69.2, subst	60.4, unsubst 69.3, subst
1,2-Propylene-glycol CH ₂	-	-	-	-	64.5	65.6
1,2-Propylene-glycol CH	-	-	-	-	64.7	65.6
1,2-Propylene-glycol CH ₃	-	-	-	-	18.2	18.2

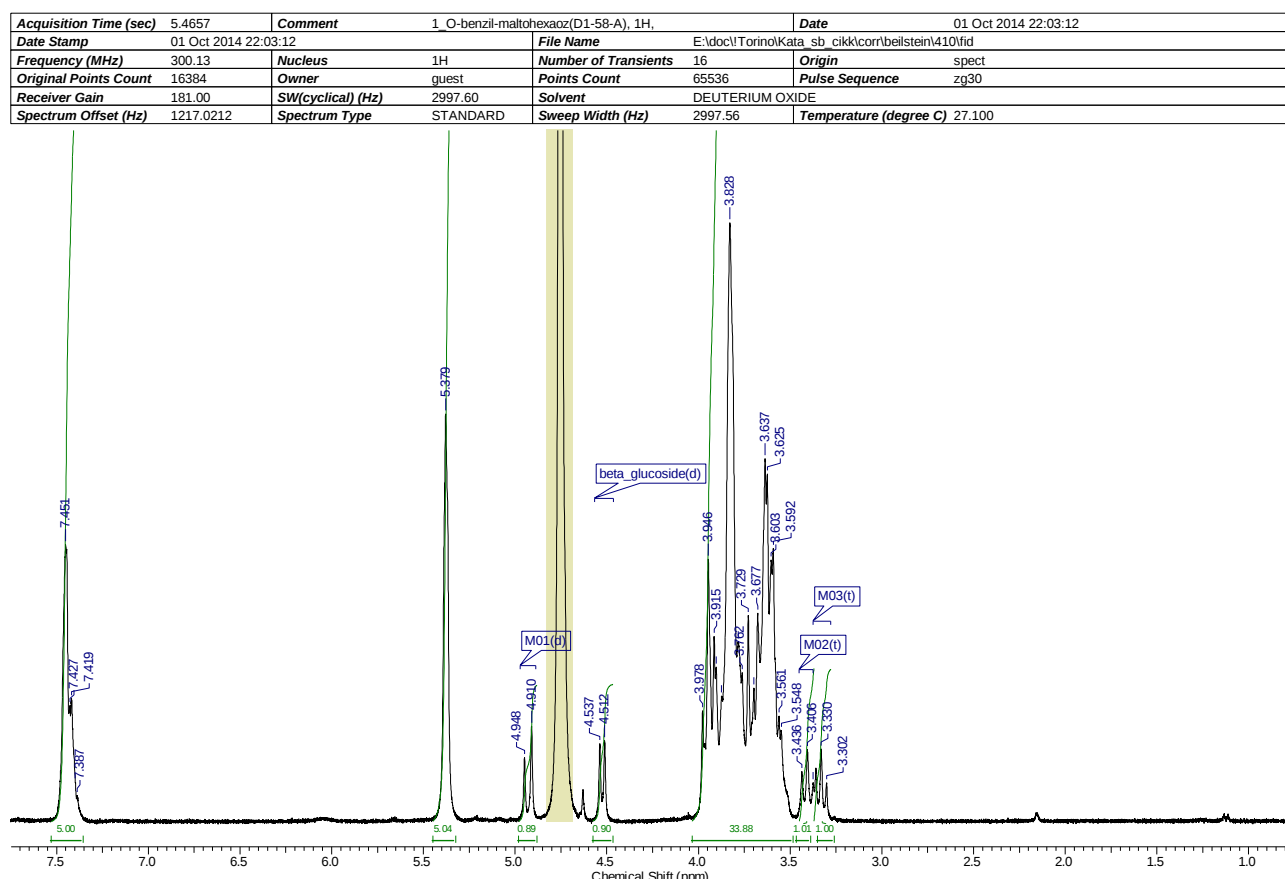


Figure S1: 300 MHz proton spectrum of 1-O-benzil-maltohexaoz.

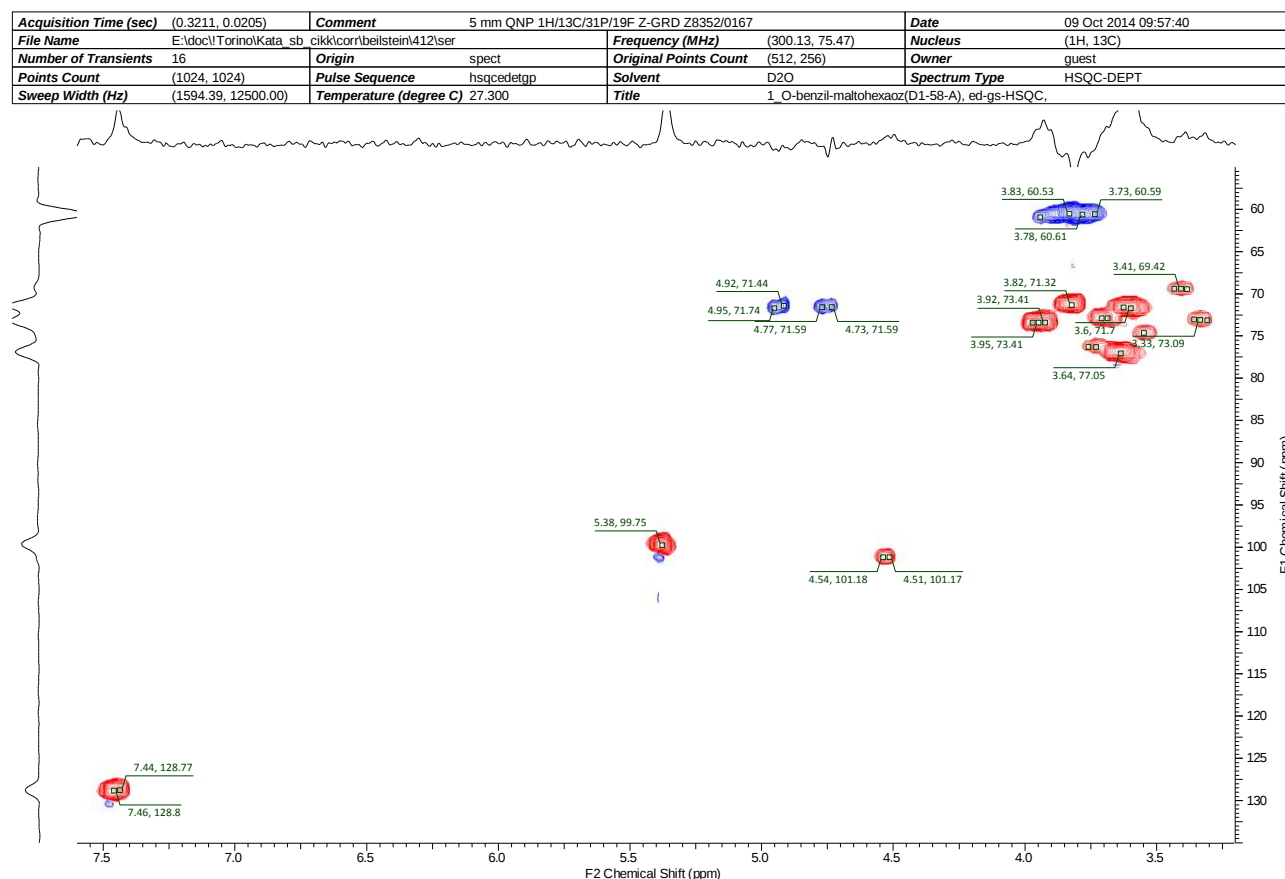


Figure S2: DEPT-ed-HSQC spectrum of 1-O-benzil-maltohexaoz.

Acquisition Time (sec)	5.4657	Comment	1 O-benzil-maltoheptaaz(D1-58-B), 1H,	Date	02 Oct 2014 02:14:56
Date Stamp	02 Oct 2014 02:14:56	File Name	E:\doc\Torino\Kata sb cikk\corn\beilstein\430\fid		
Frequency (MHz)	300.13	Nucleus	1H	Number of Transients	16
Original Points Count	16384	Owner	guest	Points Count	65536
Receiver Gain	181.00	SW(cyclical) (Hz)	2997.60	Solvent	DEUTERIUM OXIDE
Spectrum Offset (Hz)	1216.0607	Spectrum Type	STANDARD	Sweep Width (Hz)	2997.56
				Temperature (degree C)	27.400

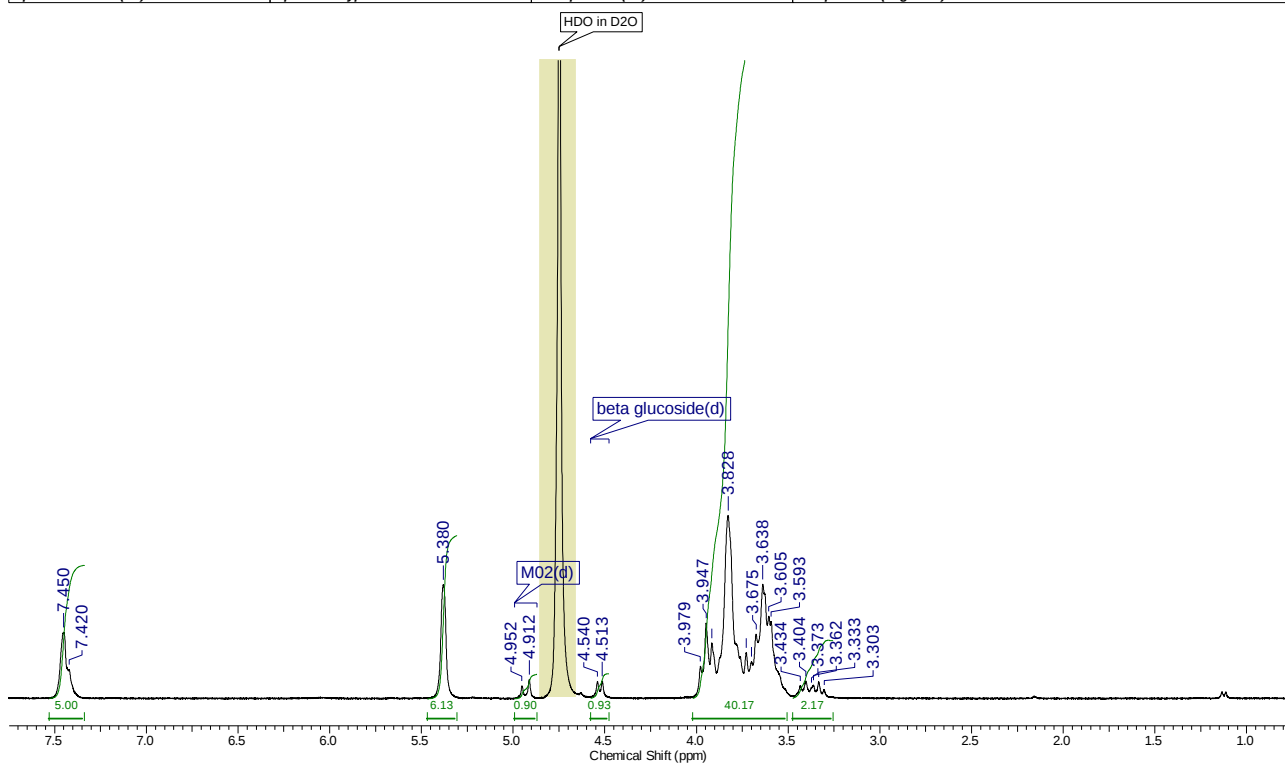


Figure S3: 300 MHz proton spectrum of 1-O-benzylmaltoheptaose.

Acquisition Time (sec)	(0.3244, 0.0205)	Comment	5 mm QNP 1H/13C/31P/19F Z-GRD Z8352/0167	Date	09 Oct 2014 10:12:06
File Name	E:\doc\Torino\Kata sb cikk\corn\beilstein\432\ser	Frequency (MHz)	(300.13, 75.47)	Nucleus	(1H, 13C)
Number of Transients	16	Origin	spect	Original Points Count	(512, 256)
Points Count	(1024, 1024)	Pulse Sequence	hsqcetdtp	Solvent	D2O
Sweep Width (Hz)	(1578.28, 12500.00)	Temperature (degree C)	27.600	Spectrum Type	HSQC-DEPT
		Title	1 O-benzil-maltoheptaaz(D1-58-B), 1H,		

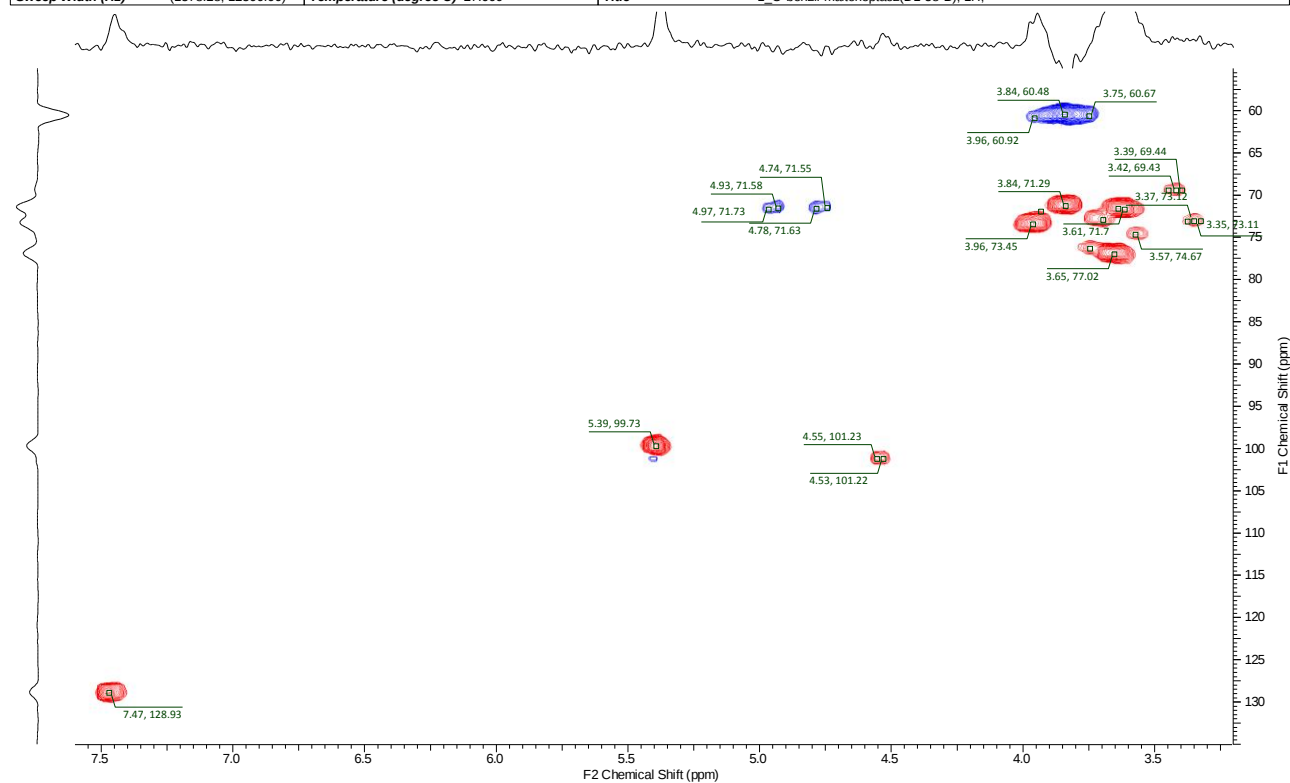


Figure S4: DEPT-ed-HSQC spectrum of 1-O-benzylmaltoheptaose.

Acquisition Time (sec)	5.4657	Comment	1 O-benzil-maltootaoz(D1-58-C), 1H,	Date	02 Oct 2014 04:20:48
Date Stamp	02 Oct 2014 04:20:48	File Name	E:\doc\Torino\Kata_sb_cikk\corr\beilstein\440\fid		
Frequency (MHz)	300.13	Nucleus	1H	Number of Transients	16
Original Points Count	16384	Owner	guest	Points Count	65536
Receiver Gain	181.00	SW(cyclical) (Hz)	2997.60	Solvent	DEUTERIUM OXIDE
Spectrum Offset (Hz)	1216.7925	Spectrum Type	STANDARD	Sweep Width (Hz)	2997.56
				Temperature (degree C)	27.500

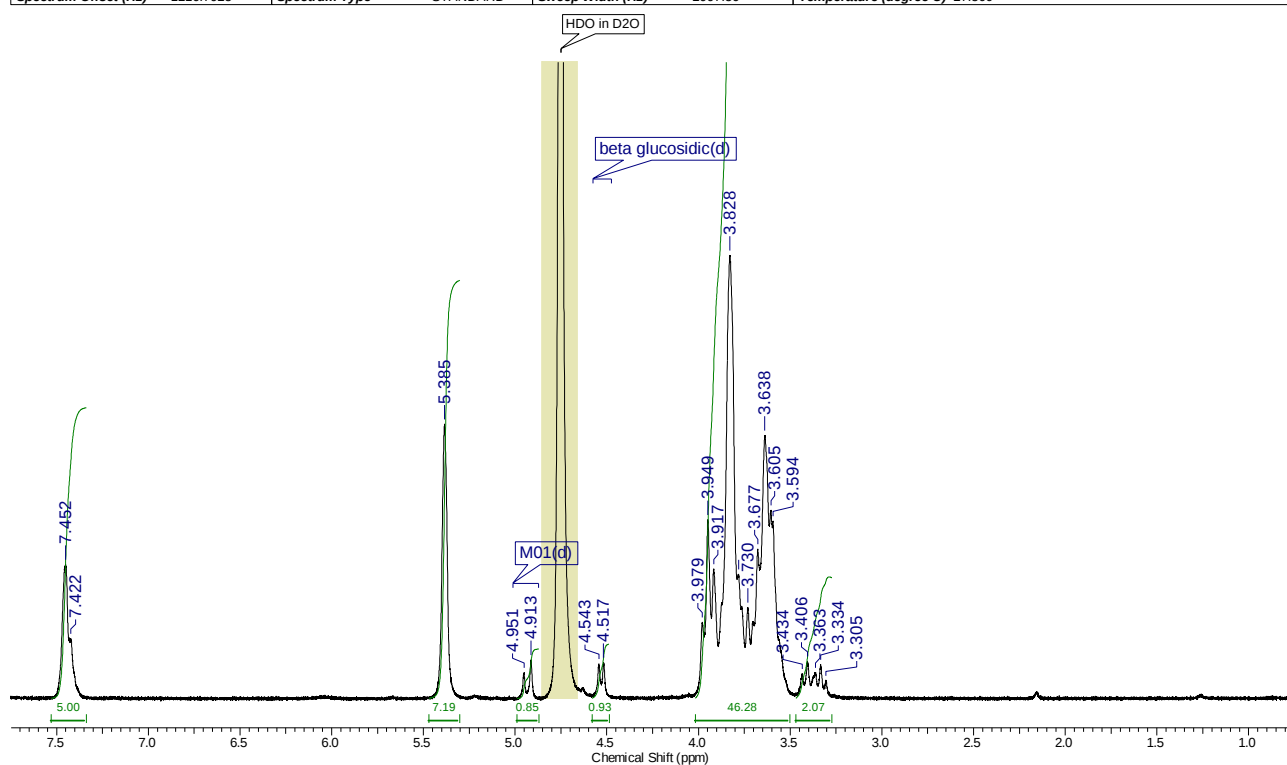


Figure S5: 300 MHz proton spectrum of 1-O-benzylmaltootaoz.

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File Name	E:\doc\Torino\Kata_sb_cikk\corr\beilstein\412\ser	Frequency (MHz)	(300.13, 75.47)	Nucleus	(1H, 13C)
Number of Transients	16	Origin	spect	Original Points Count	(512, 256)
Points Count	(1024, 1024)	Pulse Sequence	hsqcetgpg	Solvent	D2O
Sweep Width (Hz)	(1594.39, 12500.00)	Temperature (degree C)	27.300	Spectrum Type	HSQC-DEPT
		Title	1 O-benzil-maltohexaoz(D1-58-A), ed-gs-HSQC,		

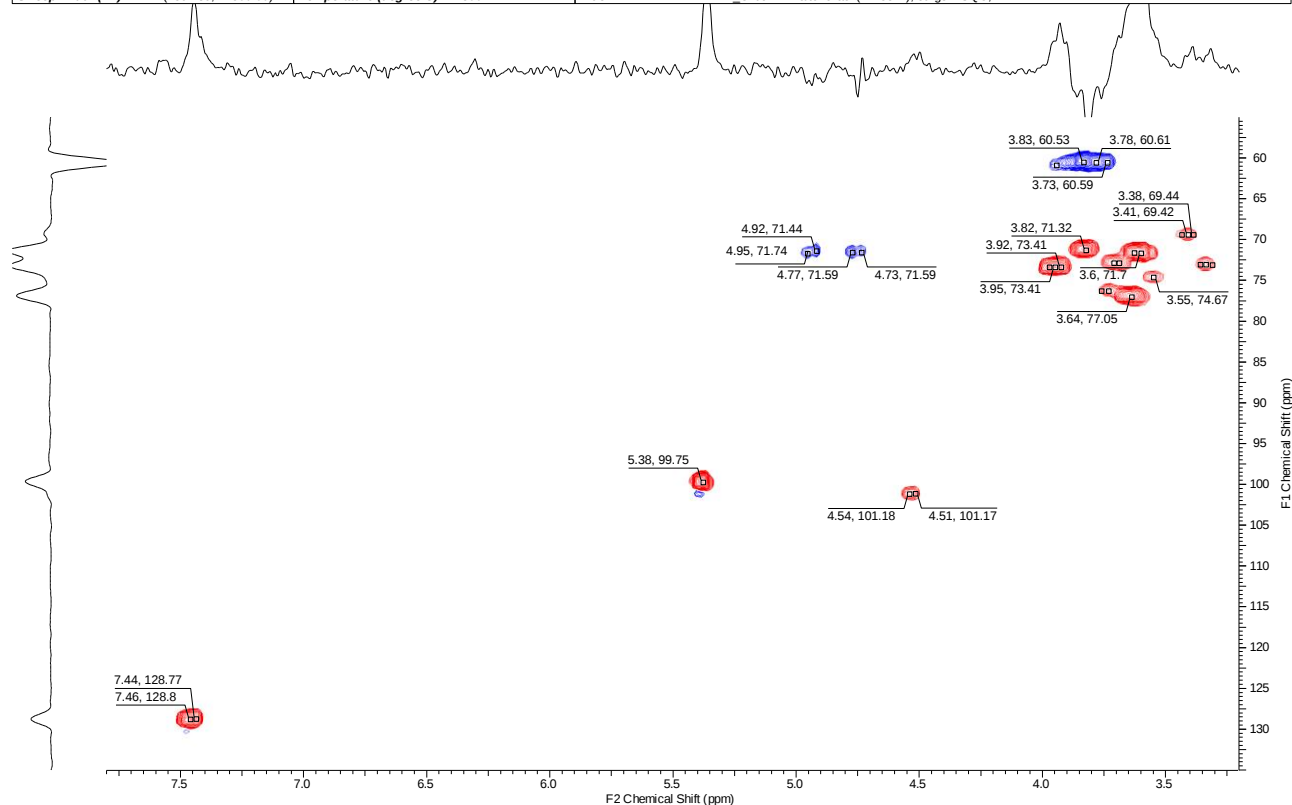


Figure S6: DEPT-ed-HSQC spectrum of 1-O-benzylmaltootaoz.

Acquisition Time (sec)	5.4657	Comment	(2hidrox)propil-maltohexaoz(D1-68-A), 1H,	Date	02 Oct 2014 00:09:04
Date Stamp	02 Oct 2014 00:09:04	File Name	E:\doc\Torino\Kata_sb_cikk\com\beilstein\420\fid	Frequency (MHz)	300.13
Nucleus	1H	Number of Transients	16	Origin	spect
Points Count	65536	Pulse Sequence	zg30	Original Points Count	16384
Spectrum Offset (Hz)	1217.0212	Spectrum Type	STANDARD	Receiver Gain	181.00
				SW(cyclical) (Hz)	2997.60
				Sweep Width (Hz)	2997.56
				Temperature (degree C)	27.600
				Solvent	DEUTERIUM OXIDE

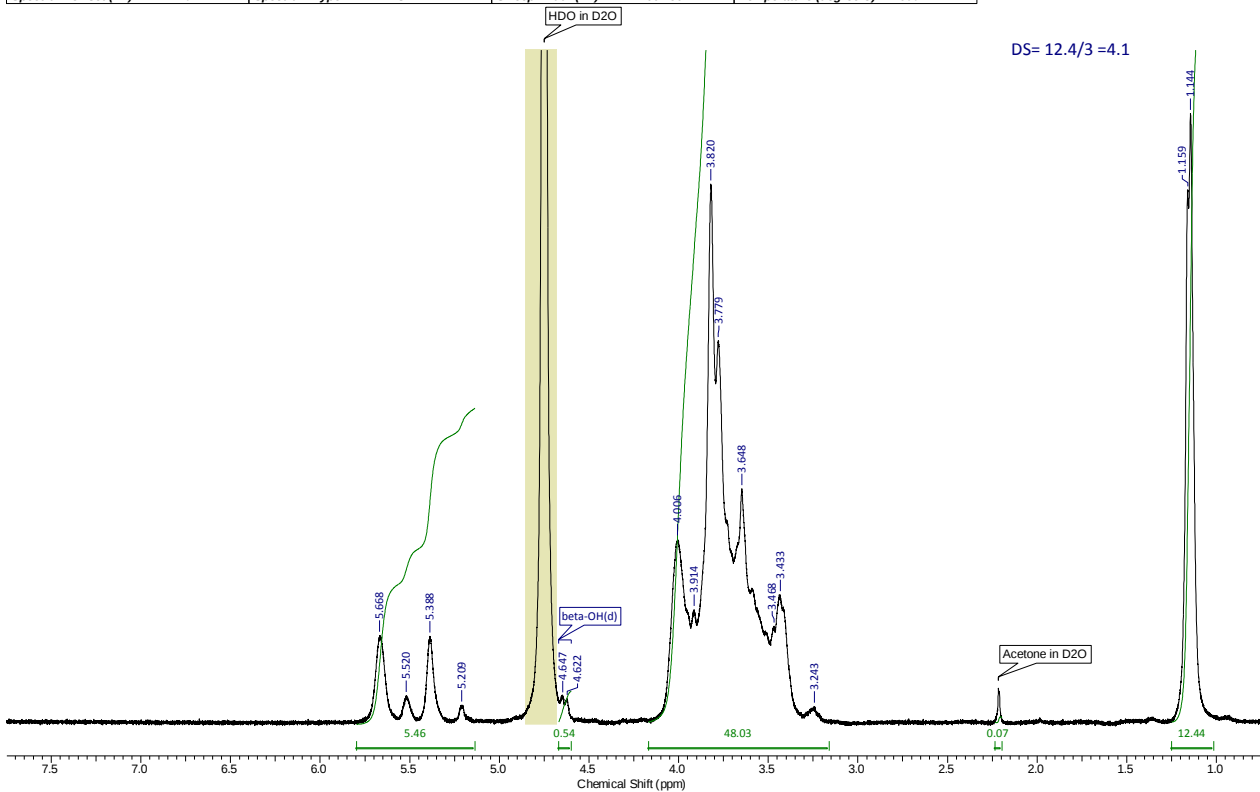


Figure S7: 300 MHz proton spectrum of (2-hydroxy)propylated maltohexaose.

Acquisition Time (sec)	(0.2851, 0.0205)	Comment	5 mm QNP 1H/13C/31P/19F Z-GRD Z8352/0167	Date	09 Oct 2014 10:37:24
File Name	E:\doc\Torino\Kata_sb_cikk\com\beilstein\422\ser	Frequency (MHz)	(300.13, 75.47)	Nucleus	(1H, 13C)
Number of Transients	16	Origin	spect	Original Points Count	(512, 256)
Points Count	(2048, 1024)	Pulse Sequence	hsqcetgpg	Owner	guest
Sweep Width (Hz)	(1795.98, 12500.00)	Temperature (degree C)	27.600	Spectrum Type	HSQC-DEPT
		Title	(2hidrox)propil-maltohexaoz(D1-68-A), gs-HSQC,		

AutoPhase Ambiguous Phase

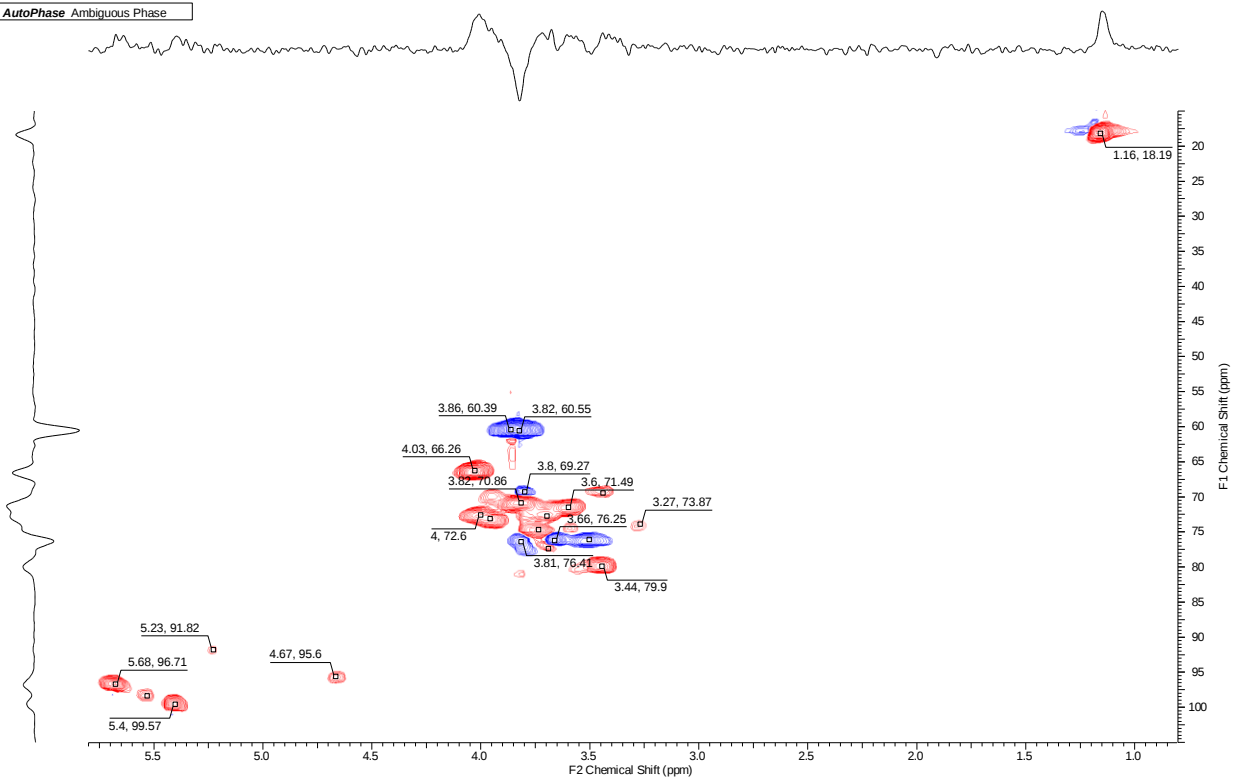


Figure S8: DEPT-ed-HSQC spectrum of (2-hydroxy)propylated maltohexaose.

Acquisition Time (sec)	5.4657	Comment	(2-hidroxy)propil-heptaaz(D1-68-B), 1H,	Date	02 Oct 2014 14:48:00
Date Stamp	02 Oct 2014 14:48:00	File Name	E:\doc\Torino\Kata_sb_cikk\corn\beilstein\450\fid	Frequency (MHz)	300.13
Nucleus	1H	Number of Transients	16	Origin	spect
Points Count	65536	Pulse Sequence	zq30	Original Points Count	16384
Spectrum Offset (Hz)	1218.1189	Receiver Gain	181.00	SW(cyclical) (Hz)	2997.60
		Spectrum Type	STANDARD	Temperature (degree C)	26.100
		Sweep Width (Hz)	2997.56	Solvent	DEUTERIUM OXIDE

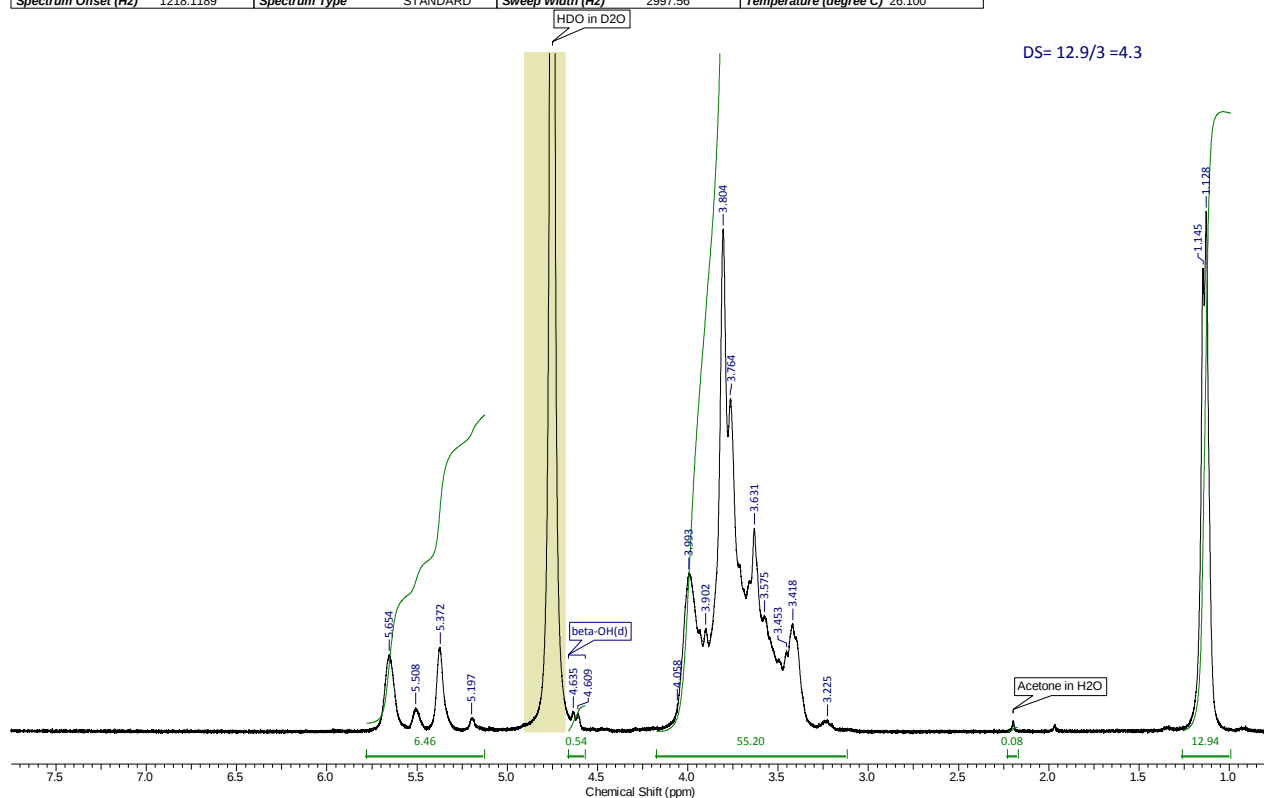


Figure S9: 300 MHz proton spectrum of (2-hydroxy)propylated maltoheptaose.

Acquisition Time (sec)	(0.2834, 0.0205)	Comment	5 mm QNP 1H/13C/31P/19F Z-GRD Z8352/0167	Date	08 Oct 2014 17:21:10
File Name	E:\doc\Torino\Kata_sb_cikk\corn\beilstein\452\ser	Frequency (MHz)	(300.13, 75.47)	Nucleus	(1H, 13C)
Number of Transients	16	Origin	spect	Original Points Count	(512, 256)
Points Count	(1024, 1024)	Pulse Sequence	hsqcetdgp	Solvent	D2O
Spectrum Type		Temperature (degree C)	26.200	Title	(2-hidroxy)propil-heptaaz(D1-68-B), 1H,
Sweep Width (Hz)	(1806.36, 12500.00)				

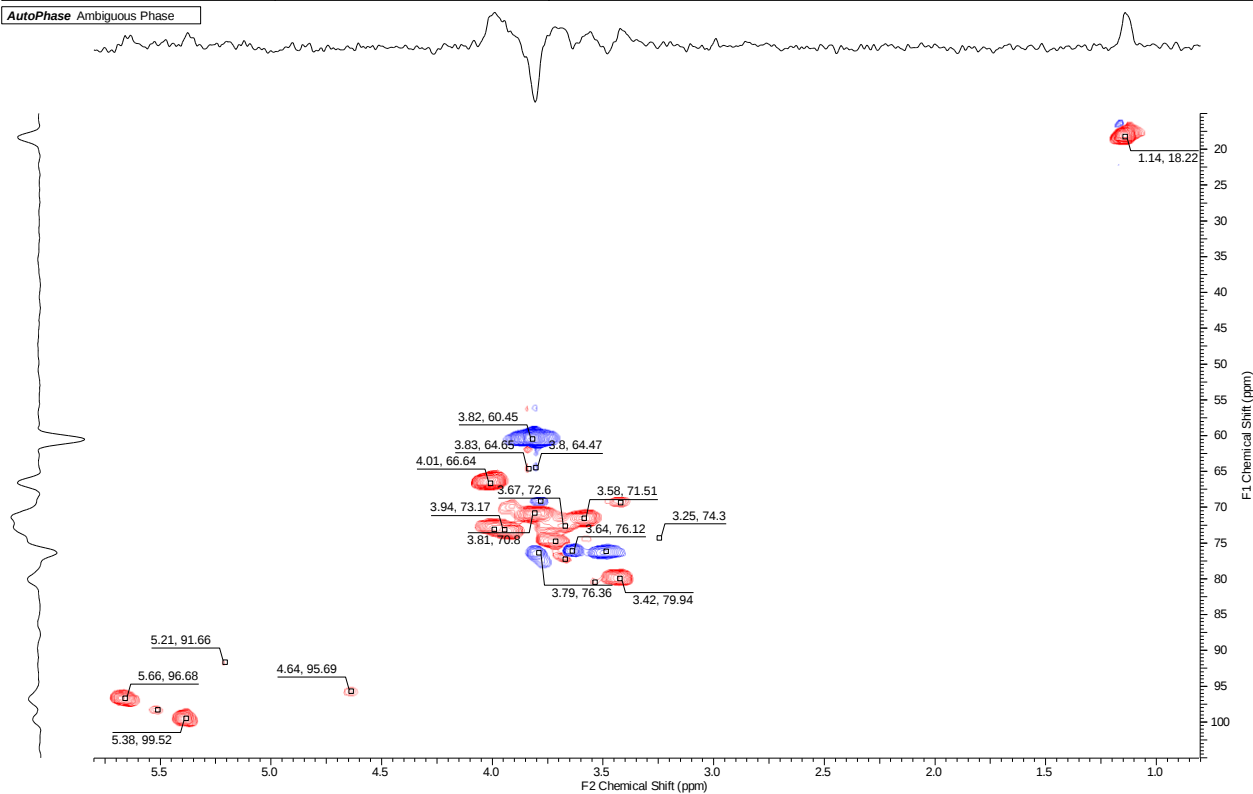


Figure S10: DEPT-ed-HSQC spectrum of (2-hydroxy)propylated maltoheptaose.

Acquisition Time (sec)	5.4657	Comment	(2-hidroxy)propil-oktaoz(D1-68-C), 1H,	Date	02 Oct 2014 16:53:52
Date Stamp	02 Oct 2014 16:53:52	File Name	E:\doc\Torino\Kata_sb_cikk\com\beilstein460\fid	Frequency (MHz)	300.13
Nucleus	1H	Number of Transients	16	Origin	spect
Points Count	65536	Pulse Sequence	zg30	Original Points Count	16384
Spectrum Offset (Hz)	1217.6157	Receiver Gain	181.00	SW(cyclical) (Hz)	2997.60
		Spectrum Type	STANDARD	Solvent	DEUTERIUM OXIDE
		Sweep Width (Hz)	2997.56	Temperature (degree C)	26.100

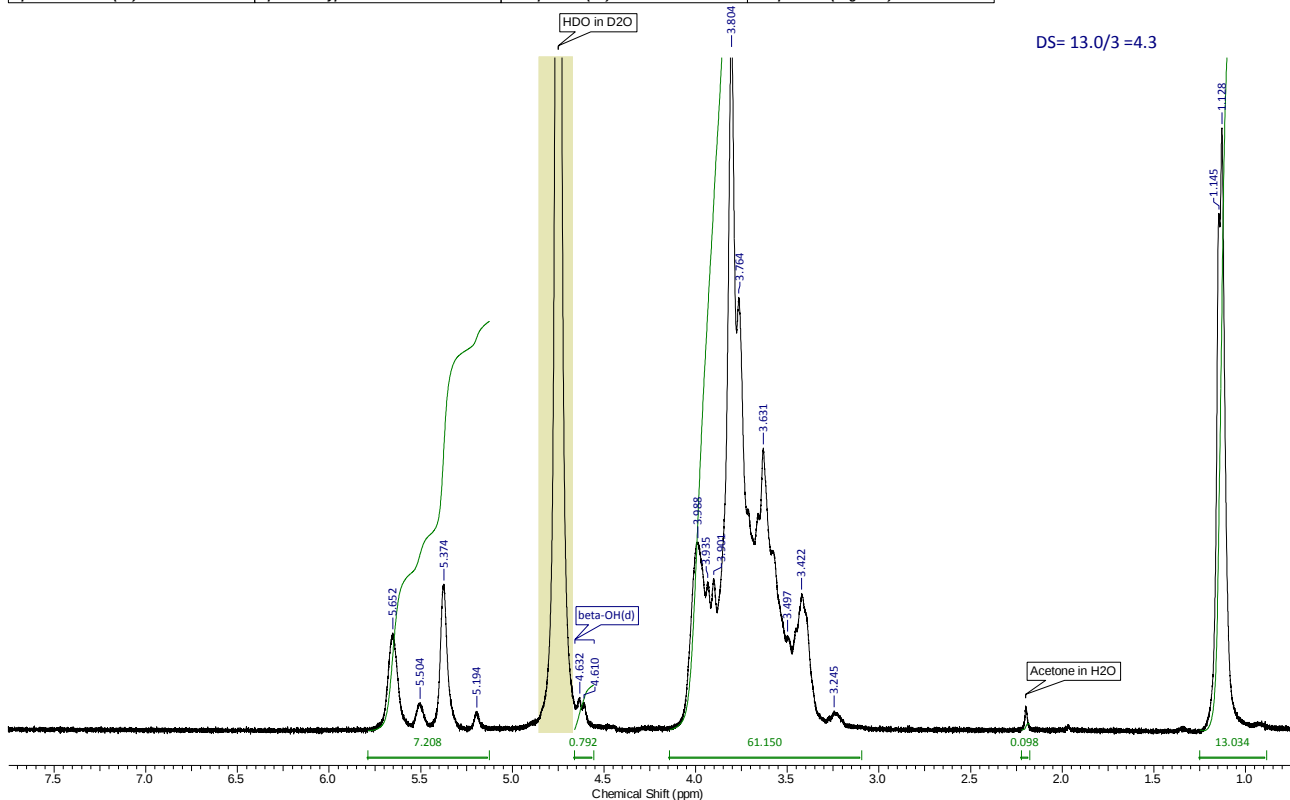


Figure S11: 300 MHz proton spectrum of (2-hydroxy)propylated maltooctaose.

Acquisition Time (sec)	(0.2834, 0.0205)	Comment	5 mm QNP 1H/13C/31P/19F Z-GRD Z8352/0167	Date	08 Oct 2014 15:48:14
File Name	E:\doc\Torino\Kata_sb_cikk\com\beilstein462\ser	Frequency (MHz)	(300.13, 75.47)	Nucleus	(1H, 13C)
Number of Transients	16	Origin	spect	Original Points Count	(512, 256)
Points Count	(1024, 1024)	Pulse Sequence	hsqcetgpg	Solvent	D2O
Sweep Width (Hz)	(1806.36, 12500.00)	Temperature (degree C)	26.200	Spectrum Type	HSQC-DEPT
		Title	(2-hidroxy)propil-oktaoz(D1-68-C), 1H,		

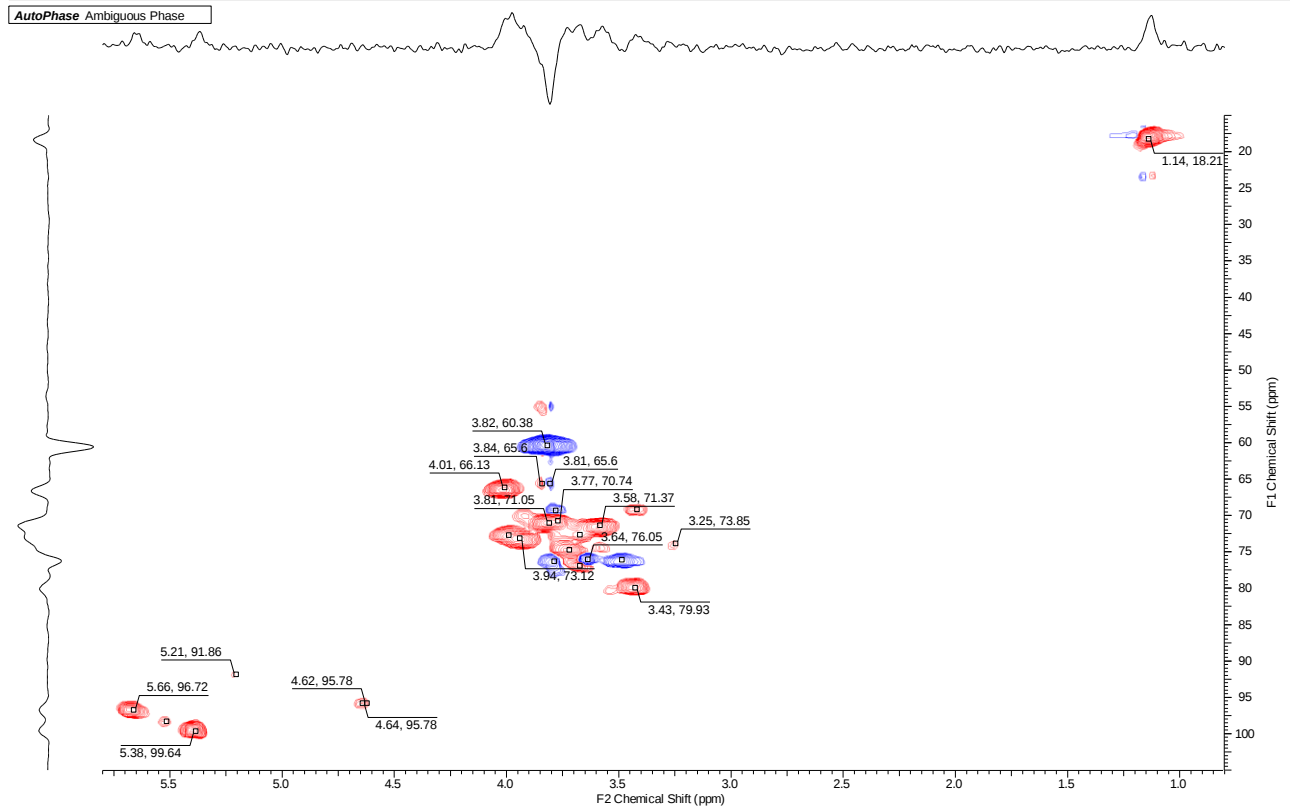


Figure S12: DEPT-ed-HSQC spectrum of (2-hydroxy)propylated maltooctaose.

Characterization of the benzylated maltooligomers with HPLC

Agilent HPLC measuring system with Refractive Index Detector and/or DAD detector was used.

The used HPLC column was Inertsil HILIC, 150 × 4.6 mm, particle size 5 µm (GL Sciences Inc.)

The most appropriate mobile phase contained acetonitrile:water = 69:31.

The flow rate was 1.0 mL/min. The column temperature was set to 30 °C; the injection volume from the sample solution (concentration: 2 mg/mL mobile phase) was 100 µL.

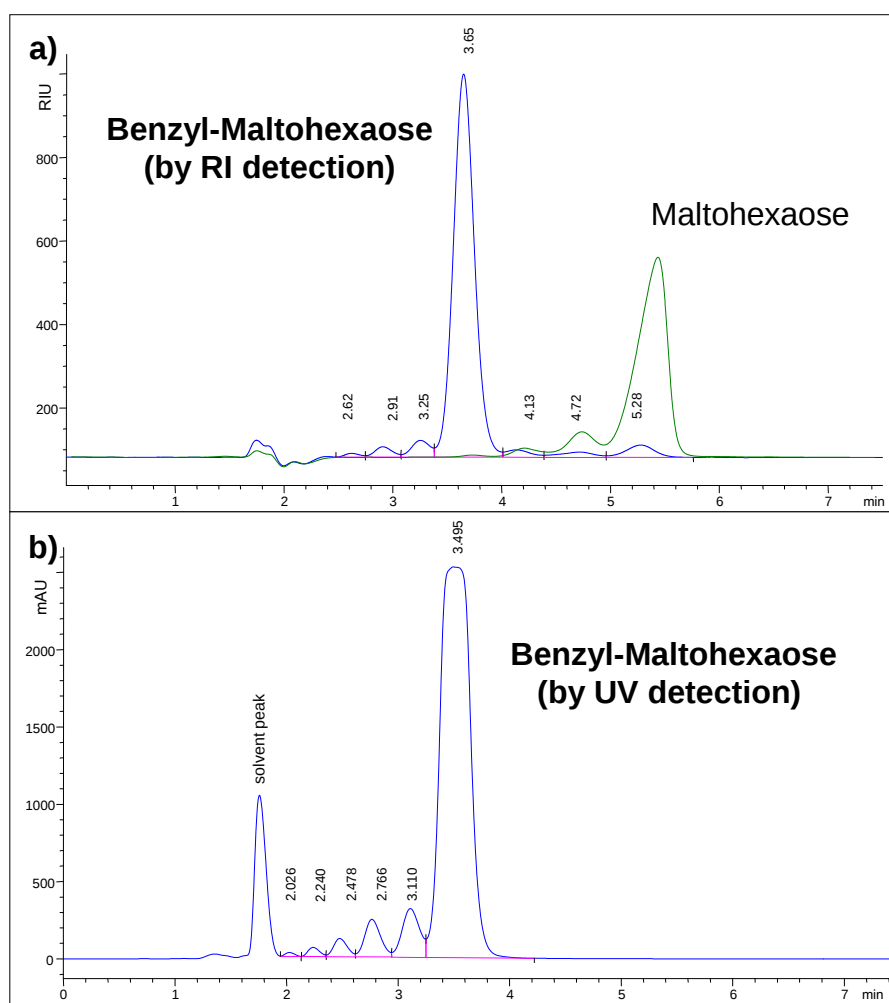


Figure S13: HPLC chromatogram of 1-O-benzylmaltohexaose and maltohexaose using refractive index detector (a) and DAD detector (b).

Table S3: Area percentage of the peaks detected by HPLC.

sample	Composition (in area %)								
	Retention time of peak (min.)								
	2.6	2.9	3.3	3.6	4.1	4.6	5.1/5.3	5.9	6.6
Benzyl-Maltohexaose	0.6	1.9	3.3	86.5	1.9	2.0	3.9		
Benzyl-Maltoheptaose	0.2	1.0	3.2	7.5	79.0	2.5	2.7	3.8	
Benzyl-Maltooctaose	0.4	1.1	2.6	4.8	5.5	75.6	2.9	2.2	5.1

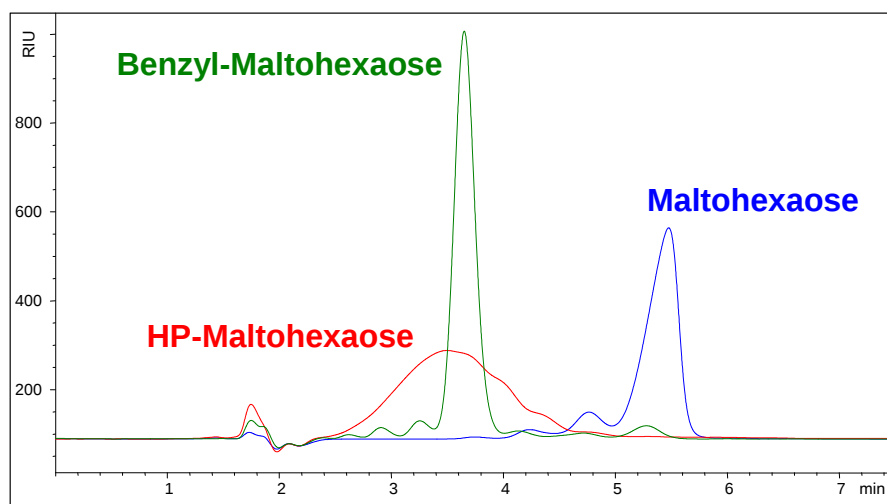


Figure S14: HPLC chromatogram of HP-maltohexaose compared to maltohexaose and O-benzyl-maltohexaose.