One pot catalytic conversion of cellulose into biodegradable surfactants

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Electronic Supplementary Information

1. Materials

The α-cellulose (Sigma, particle size estimated by scanning electron microscopy SEM: 20-100 µm; relative crystallinity of about 75% as estimated by XRD analysis according following to the method reported by Hilmioglu *et al.*[1]) and cellulose fibers (Aldrich, particle size: 20-100 µm; relative crystallinity of about 67%) were dried under vacuum at 100 ºC for 24 h before use. Butyl-3-methylimidazolium chloride (Basionic ST 70, ≥ 95% BASF) were purchased from Fluka and used as received. The Amberslyst 15Dry (Aldrich), $H_3PW_{12}O_{40}$ xH_2O (Fluka, reagent for microscopy), Cs_2CO_3 (Aldrich, 99%) *p*-toluenesulfonic acid monohydrate (PTSA, Aldrich, 98%) were used as received. *n*-Butanol, *n*-hexanol and *n*-octanol were purchased to Aldrich and used as received.

2. Catalyst preparation

2.1. $H_{0.5}Cs_{2.5}PW_{12}O_{40}$

The acidic salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as $Cs_{2.5}PW$) was prepared following[2]. Typically, 5.15 g of $H_3PW_{12}O_{40}$ was dissolved in 19.5 mL of water and an aqueous solution composed of 0.63 g of Cs_2CO_3 in 15.6 mL of water was gradually added at a rate of 1 mL.min^{-1} under stirring. After complete addition, the water was evaporated at 40 ºC until a dried solid was obtained. Before reaction the solid was calcined at 300 ºC for 3 h under air. The amount of Cs content in the solid was determined by ICP analysis after that the solid was dissolved in an aqueous NaOH solution.

2.2. Silica-supported heteropolyacid $H_3PW_{12}O_{40}$ (SiO_2-HPW)

Silica-supported catalyst, 50 % PW/SiO_2, was prepared by impregnating Aerosil Degussa (S_{BET} = 209 m^2.g^{-1}) with an aqueous solution of $H_3PW_{12}O_{40}$ following the method of Kozhevnikov *et al.* with slight modification.[3] Typically, 1 g of polyanion was dissolved in 20 mL of distilled water and the solution mixed with 2 g of silica. The mixture was stirred overnight at room temperature and the excess of water was evaporated in a rotary evaporator under vacuum at 50 ºC, followed by drying the solid at 100 ºC for 2 h. The Brønsted-acid sites in this catalyst were determined by the titration method as follows, a sodium hydroxide aqueous solution (0.01 mol.L^{-1}, 20 mL) was added to a catalyst (40 mg), and the mixture was stirred for 2 h at room temperature. After filtration of the solid, the filtrate was titrated by a hydrochloric acid (0.01 mol.L^{-1}) aqueous solution using phenolphthalein. The catalyst was calcined before reaction at 150 ºC for 2 h under vacuum.

2.3. Carbon material bearing SO_3H groups

The carbon material with SO_3H was prepared as reported by Hara *et al.*[4] 20 g of cellulose powder (Avicel, Fluka) was heated for 5 H at 723 K under N_2 flow to produce a black solid, which was reduced to a powder. Then, 7 g of the black powder was boiled in 150 cm^3 of fuming sulphuric acid (20 wt% SO_3H) at 353 K under N_2. After heating for 15 h and cooling to room temperature 1 L of distilled water was added to the mixture to form a black precipitate, which was washed repeatedly in hot distilled water (> 353 K) until impurities such as sulphate ions were no longer detected in the wash water. The Brønsted-acid sites in the solid were determined like for the solid SiO_2-HPW and the quantity of sulfonic groups was determined by elemental analysis.

3. Catalyst characterization

The result from characterisation of different catalysts materials are summarized in Table S1. The solid $Cs_{2.5}PW$ was obtained by a partial exchange of hydrogen atoms in $H_3PW_{12}O_{40}$ by cesium atoms. The structure of the solid obtained was analysed by XRD and FTIR. The IR spectrum showed the characteristic bands at 1081, 984, 888 and 806 cm^{-1} assigned to the asymmetric stretching vibration of the P-O, to the stretching vibration of W=O and the stretching vibration to W-O-W, respectively, which indicate the presence of the $PW_{12}O_{40}^{3-}$ anion after the exchange of protons from $H_3PW_{12}O_{40}$. The amount de Cs, determined by ICP analysis indicate that the Cs, content in the solid $Cs_{2.5}PW$ was of 2.3 cation Cs per Keggin unit so the composition of the final catalyst is $H_{0.7}Cs_{2.3}PW$.

The catalyst SiO_2-HPW was also characterized by XRD and FTIR. The IR spectrum presented two characteristic bands at 985 and 898 cm^{-1} showing the presents of $PW_{12}O_{40}^{3-}$ anion in the structure. The bands located about 1080 and 800 cm^{-1} can not be separated from the characteristic bands of the silica. A titration method revealed that the amount of acid sites was 4.55 $mmol.g^{-1}$.

The carbon material was obtained following the method developed by Hara *et al.*[4] After partial pyrolysis of the cellulose and the black powder obtained was sulfonated in the resence of fuming sulphuric acid. The vibration bonds at 1041 cm^{-1} (SO_3-streching) and 1388 cm^{-1} (O=S=O stretching in SO_3H) in the FTIR spectrum indicate that the resulting material possesses SO_3H groups. Elemental analysis and a titration method revealed that the amount of

SO_3H groups and the amount of acid sites (SO_3H, OH, and COOH) was of 1.10 mmol.g^{-1} and 2.26 mmol.g^{-1} respectively.

Table S1 Characterisation of different catalysts

Catalyst	BET surface area (m^2.g^{-1})	Pore diameter (Å)	Amount of acid (mmol.g^{-1})
$H_3PW_{12}O_{40}$	-	-	1[a]
PTSA	-	-	5.25[a]
$H_{0.5}Cs_{2.5}$	83	17	0.15[a]
SiO_2-HPW	126	17	4.55[b]
A-15	42	20	4.7
C-SO_3H	423	18	2.26[b] (SO_3H: 1.10)[c]

[a] Total amount in the bulk was calculated from the composition. [b] The amount of acid sites were determined by titration method. [c] The amount of SO_3H groups were determined by analysis elemental.

4. Hydrolysis procedure

The cellulose (0.300 g, 1.85 mmol, calculated as anhydroglucose, $C_6H_{10}O_5$) and ionic liquid (6 g) were heated with stirring at 100ºC, ambient pressure until a clear solution was formed (about 30 min), and then water and catalyst were added. The reaction was vigorously stirred and samples were withdrawn, weighed (M_1), and quenched immediately with cold water at different intervals. After neutralisation, if necessary, the sample was filtered and the filtrate solution was diluted to 5 mL and subjected to total reducing sugar (TRS) and analysed by HPLC.

5. Fisher glycosidation procedure

The cellulose (0.3 g of α-cellulose or 0.6 g of cellulose fibres) and ionic liquid (6 g) were heated with stirring at 100 ºC, ambient pressure until a clear solution was formed (about 30 min). To this cellulose solution the water and the catalyst was added. The reaction was then vigorously stirred for different times. After that time, the alcohol (43 mmol, 23 eq.) was added and the reaction media stirred at 363 K. Then the catalyst was filtrated, 75 mL of water was added, the unreacted alcohol was extracted with heptane and the water was evaporated under vacuum. A sample of a solution obtained was diluted in water to be analysed in HPLC. Finally the crude reaction was filtrated through a silica gel eluted with a MeOH/AcOEt mixture (0/100 and then 5/95) to afford the desired alkyl-α,β-glycoside as an anomeric mixture. The purity of alkylglycosides was confirmed by ^{1}H and ^{13}C NMR analysis.

6. Apparatus for catalysts characterisation and products analysis

The XRD data of C-SO3H and SiO_2-HPW were collected using a Panalytical Cubix PRO diffractometer, using Cu KR radiation (λ) 1.5441 Å.

IR spectra were recorded on a FT-IR Nicolet 710 spectrometer using the KBr pellet technique with a catalyst concentration of 0.5 wt%.

Textural properties were determined from nitrogen isotherms at liquid N_2 temperature using a Micromeritics Tristar apparatus (static volumetric technique). Samples (0.2 g) were first outgassed overnight under vacuum.

Chemical analysis (C, N, H, S) was carried out by using a FISONS Instruments EA 1108 CHNS-0 analyzer ICP (Cs, P, W) with a VARIAN 715-ES.

The amount of total reducing sugars was determined by reaction with 3,5-dinitrosalicylic acid (DNS) (Figure S1). A mixture contained 1 mL of DNS regent, 0.5 mL of reaction sample and 0.5 mL of water was heated for 5 min in a boiling water bath, then cooled to room temperature, and mixed with 10 mL of deionized water. The colour intensity of the mixture was measured in A JASCO V-530 Model spectrophotometer at 540 nm. The concentration of total reducing sugars was calculated based on a standard curve obtained with glucose. The mass of TRS M_T and the yield of TRS were calculated as follows:

$$M_T\ (\text{mg}) = \text{TRS concentration (mg/mL)} \times 12\ (\text{mL}) \times (5/0{,}5) \times (M_0/M_1)$$

$$\text{TRS Yield} = M_T \times 0.9/320 \times 100\%$$

Where, M_T is the mass of TRS, M_0 is the total mass of the reaction solution or solid obtained and M_1 is the mass of sample.

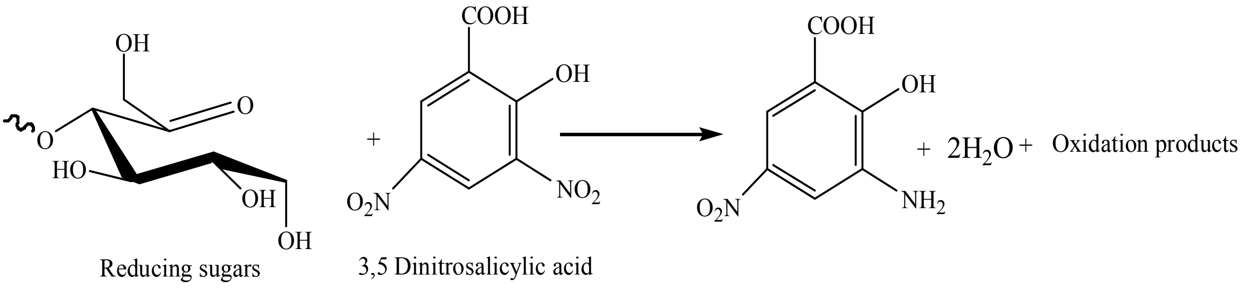

Figure S1 : Dosage of reducing sugars with the 3,5-dinitrosalicylic acid

The analysis of samples was performed at 333 K with a HPLC system composed of a Waters pump (model 1525) and a Waters 2410 differential refractometer. The sugars (glucose, xylose and cellobiose), the dehydration products (HMF and furfural) and alkylglycosides were analysed using an ion –exclusion column (Aminex HPX-87H, Bio-Rad) eluting with an aqueous solution of sulphuric acid (0.004 mol.L^{-1}) as mobile phase. This analysis was operated at a flow rate of 0.6 mL.min^{-1}. Peak identification was established by comparison of the sample peak retention times with the standard solution of the pure compound. The calibration of the peaks was performed using standard solutions of varying concentrations to develop a linear relationship between the peak area and the corresponding concentration.

The molecular product yield [Y (mol%)] was defined as:

$$\mathrm{Y\ (mol\%)} = \frac{n_i}{n_0}$$

Where n_0 and n_i, are the mole number of $C_6H_{10}O_5$ unit in charged cellulose introduced and the mole of component i respectively.

The mass product yield [Y (wt%)] was defined as:

$$\mathrm{Y\ (wt\%)} = \frac{m_i}{m_0}$$

Where m_0 and m_i, are the weight of cellulose put into the reaction and the weight of component i respectively.

The liquid NMR spectra were recorded at room temperature with a BRUKER Avance 300 spectrometer. Spectroscopic data were identified by comparing with those previously reported in the literature.[5]

Hexyl–α,β-glucoside: I.R. (neat, cm^{-1}) ν 3398, 2957, 2933, 2874, 2869, 1460, 1380, 1156, 1080, 1039; ^{1}H NMR (300 MHz, D_2O) δ 0.84-089 (t, *J* = 6.75 Hz, 3H), 1.31 (m, 6H), 1.62 (m, 2H), 3.22-3.95 (m, 8H), 4.43-4.46 (d, *J* = 7.97 Hz, 0.5 H, Hβ), 4.89-4.91 (d, *J* = 3.78 Hz, Hα); ^{13}C NMR (75 MHz, D_2O) δ 13.3 (2 CH_3), 21.9 (2 CH_2), 24.7 (CH_2), 25.1 (CH_2), 28.5 (CH_2), 28.7 (CH_2), 30.8 (2 CH_2), 60.5 (CH_2), 60.7 (CH_2), 68.3 (CH_2α), 69.5 (CH), 69.6 (CH), 70.7 (CH_2β), 71.3 (CH), 71.7 (CH), 73.1 (CH), 75.8 (CH), 75.9 (CH), 98.0 (CHα), 102.1 (CHβ)

Hexyl–α,β-xyloside: I.R. (neat, cm^{-1}) ν 3390, 2957, 2932, 2875, 2872, 1469, 1379, 1154, 1091, 1045; ^1H NMR (300 MHz, D_2O) δ 0.84-0.88 (t, *J* = 6.62 Hz, 3H), 1.30 (m, 6H), 1.60 (m, 2H), 3.20-3.96 (m, 7H), 4.37-4.40 (d, *J* = 7,88 Hz, 0.5Hβ), 4.86-4.88 (d, *J* = 3.68, 0.5Hα); ^{13}C NMR (75 MHz, D_2O) δ 13.3 (2 CH_3), 21.9 (2 CH_2), 24.7 (CH_2), 25.0 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 30.8 (2 CH_2), 61,0 (CH_2), 65.1 (CH_2), 68.4 (CH_2α), 69.2 (CH), 69.4 (CH), 70.8 (CH_2β), 71.3 (CH), 73.0 (CH), 73.2 (CH), 75.8 (CH), 98.2 (CHα), 102.9 (CHβ)

Octyl–α,β–glucoside: : I.R. (neat, cm^{-1}) ν 3393, 2956, 2928, 2874, 2857, 1468, 1380, 1155, 1080,1033; ^1H NMR (300 MHz, D_2O) δ 0.81-084 (t, *J* = 6.85 Hz, 3H), 1.24 (m, 10H), 1.60 (m, 2H), 3.20-3.88 (m, 8H), 4.37-4.40 (d, *J* = 7.92 Hz, 0.5 H, Hβ), 4.85-4.86 (d, *J* = 4.24 Hz, Hα); ^{13}C NMR (75 MHz, D_2O) δ 13.5 (CH_3), 22.2 (2 CH_2), 25.3 (CH_2), 25.6 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 28.9 (2 CH_2), 31.4 (2 CH_2), 60.3 (CH_2), 60.7 (CH_2), 68.3 (CH_2α), 69.2 (CH), 69.5 (CH), 70.5 (CH_2β), 71.3 (CH), 71.7 (CH), 73.1 (2 CH), 75.8 (CH), 98.2 (CHα), 102.3 (CHβ)

Octyl–α,β-xyloside: I.R. (neat, cm^{-1}) ν 3396, 2928, 2874, 2858, 1468, 1379, 1152, 1092, 1045; ^1H NMR (300 MHz, CD_4O) δ 0.87-0.92 (t, *J* = 6.42 Hz, 3H), 1.30 (m, 10H), 1.60 (m, 2H), 3.14-3.81 (m, 7H), 4.17-4.19 (d, *J* = 7,53 Hz, 0.5Hβ), 4.69-4.70 (d, *J* = 3.60, 0.5H); ^{13}C NMR (75 MHz, CD_4O) δ 14.4 (CH_3), 23.7 (CH_2), 27.2 (CH_2), 27.4 (CH_2), 30.4 (2 CH_2), 30.5 (CH_2), 30.6 (CH_2), 30.7 (CH_2), 30.8 (CH_2), 33.0 52 CH_2), 63.0 (CH_2), 66.9 (CH_2), 69.3 (CH_2α), 70.9 (CH_2β), 71.2 (CH), 71.6 (CH), 73.6 (CH), 74.9 (CH), 75.2 (CH), 77.9 (CH), 100.4 (CHα), 105.1 (CHβ)

References

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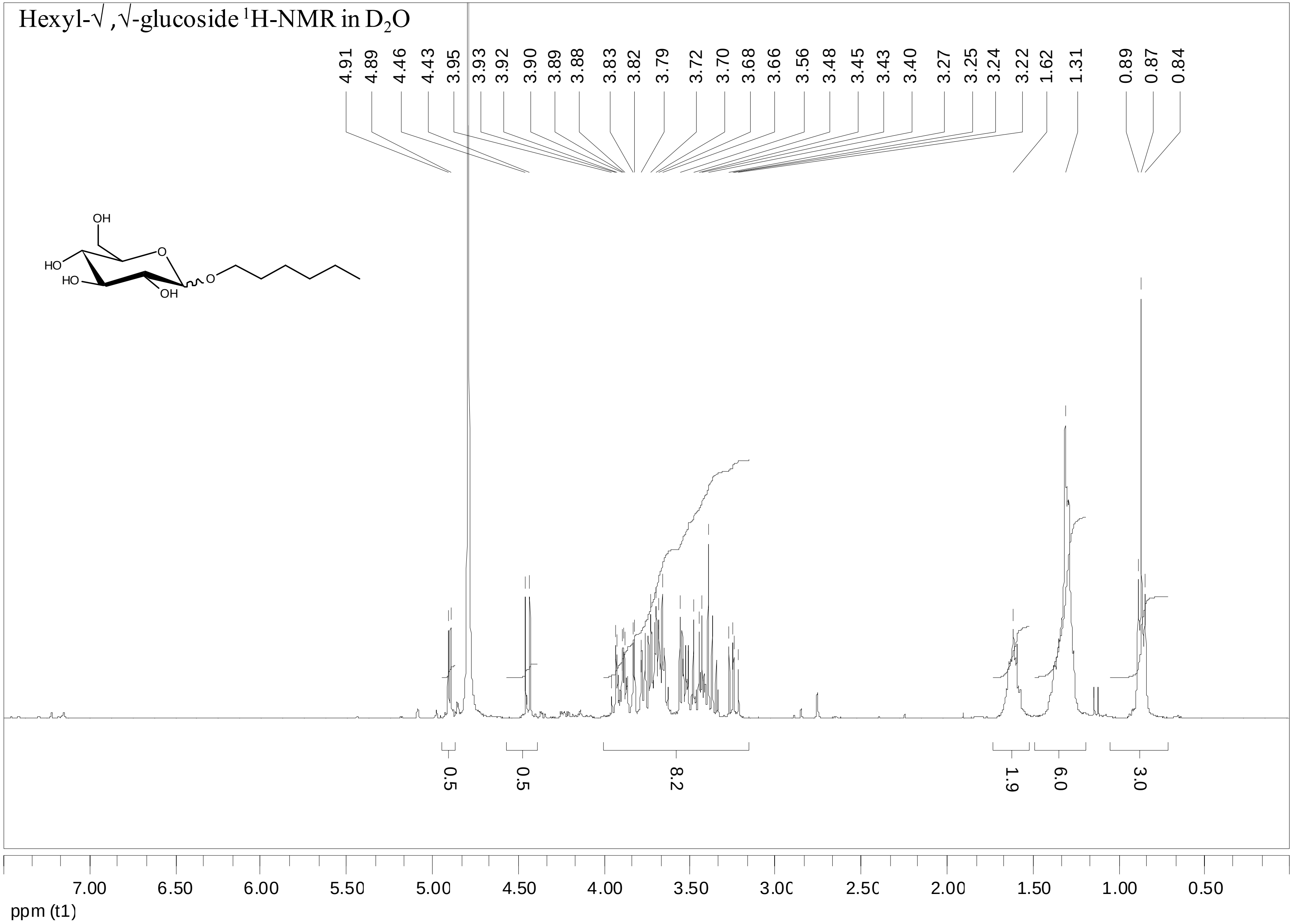
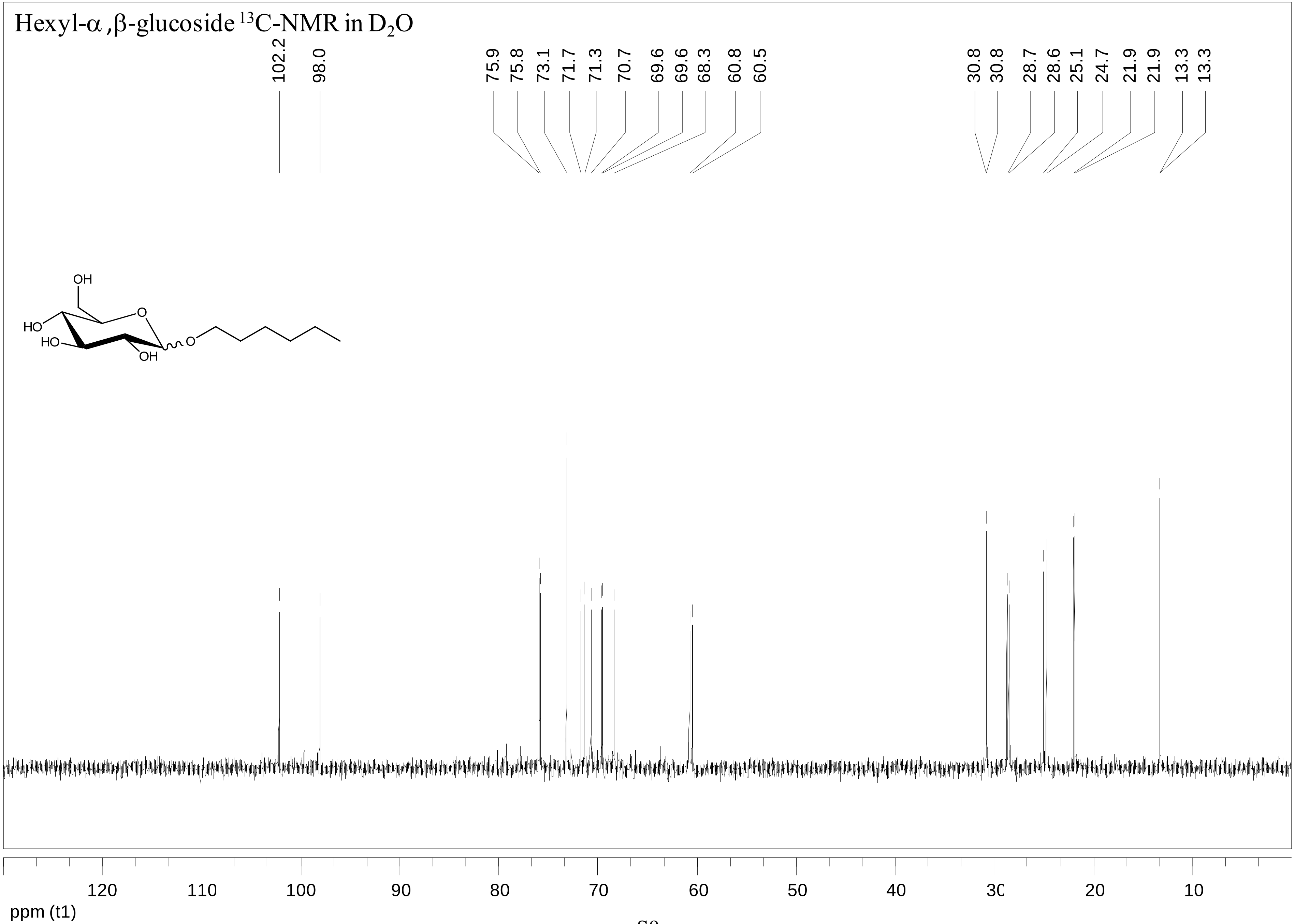
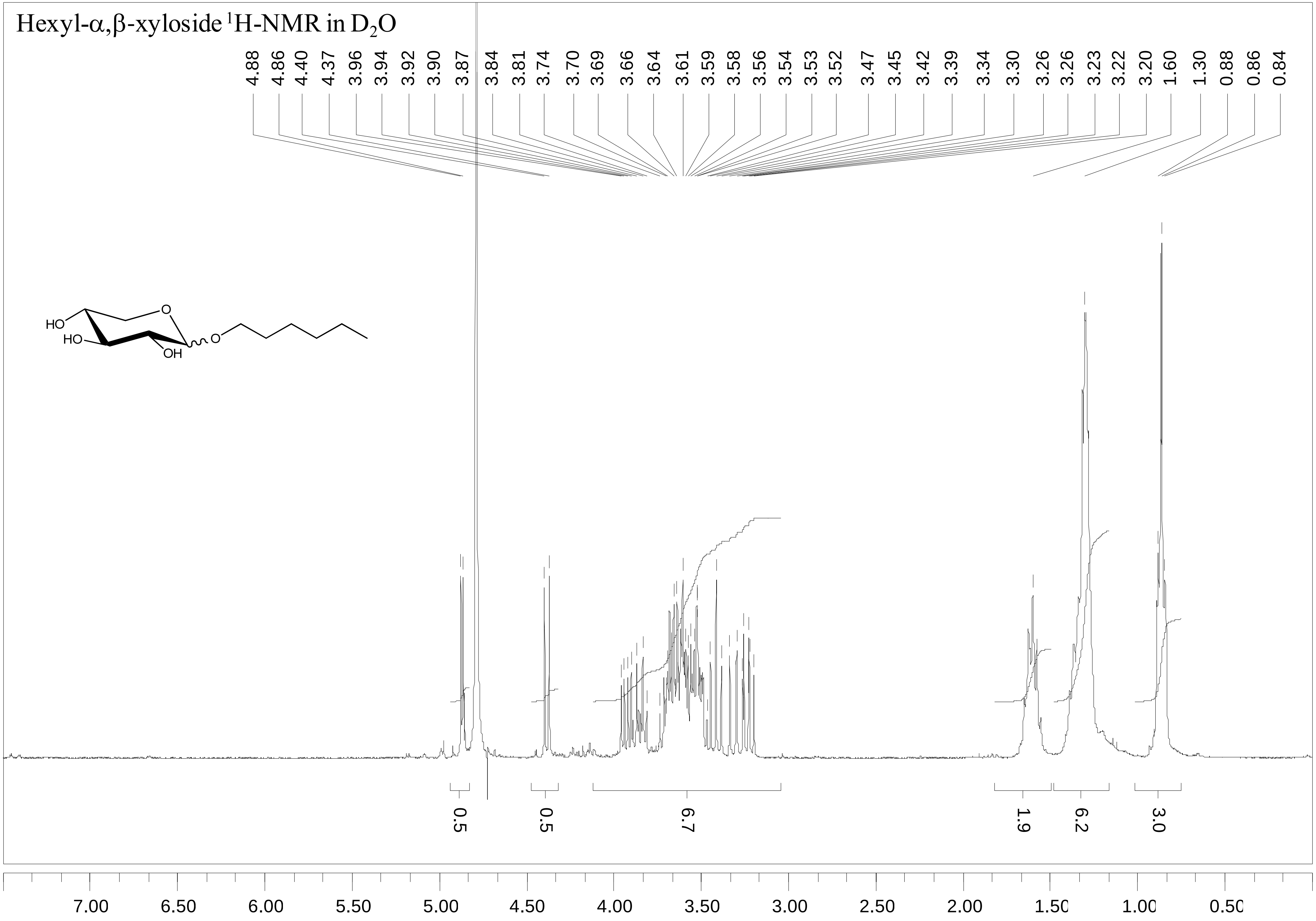
7. ^{1}H and ^{13}C NMR spectra

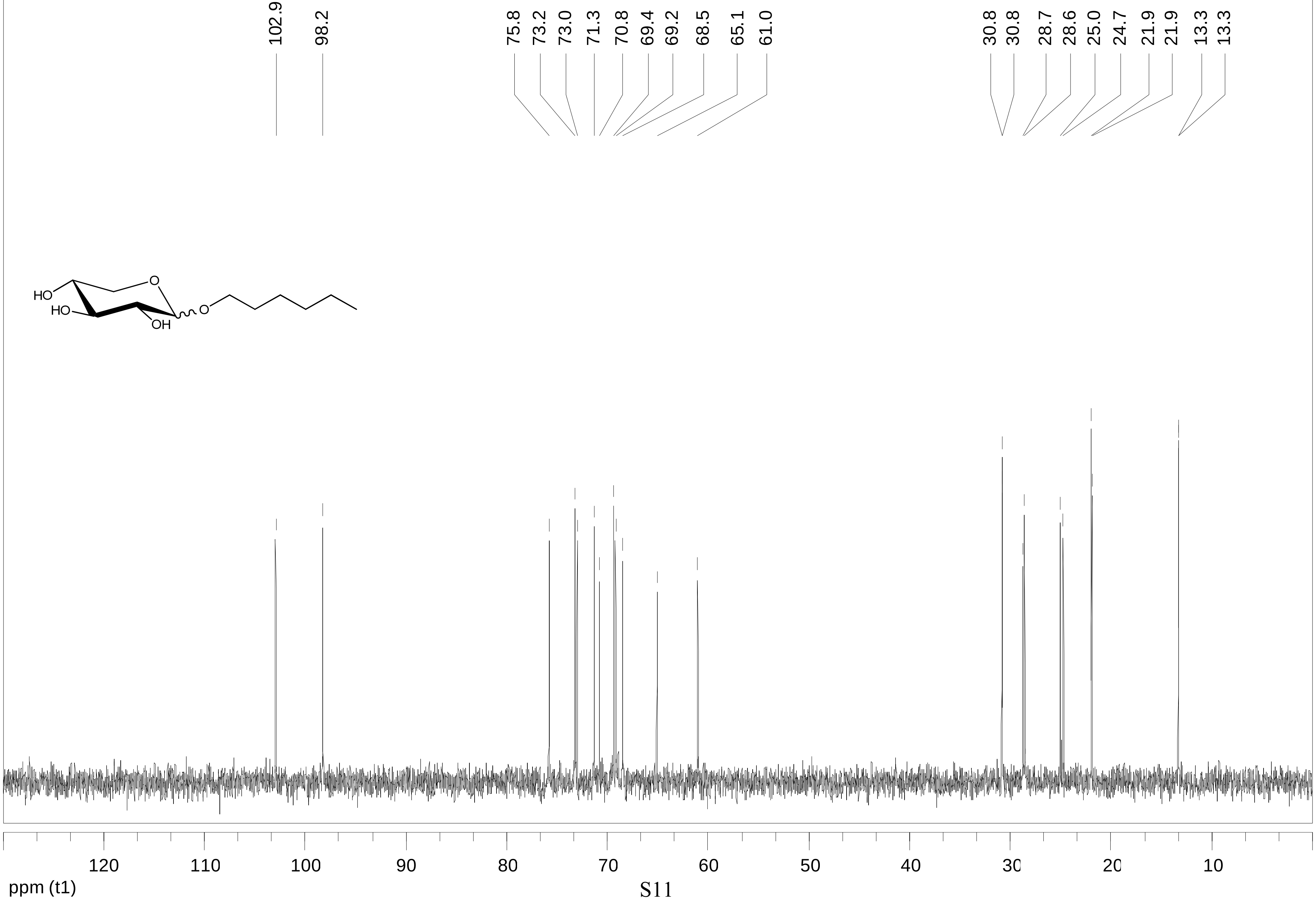


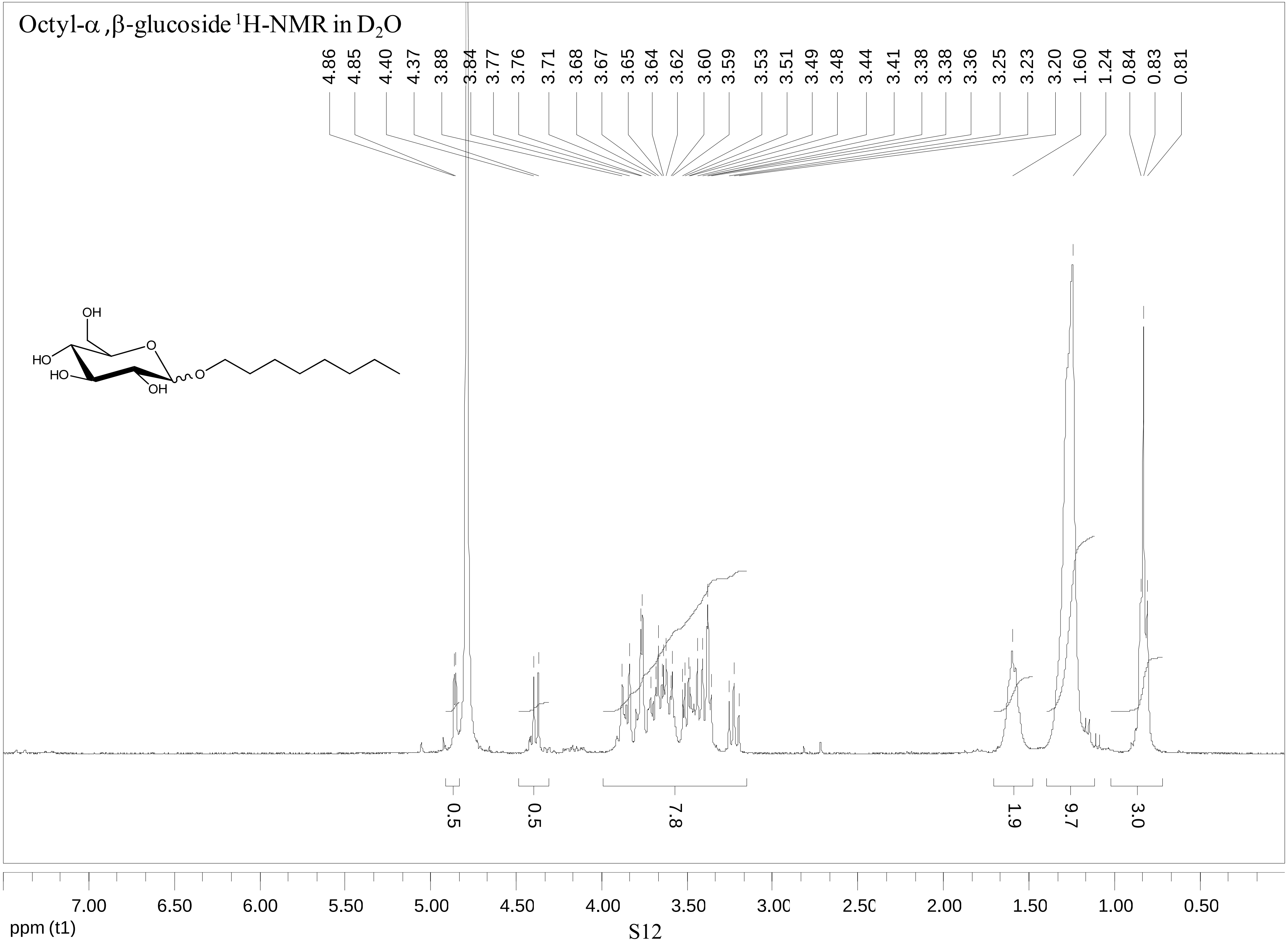

Hexyl-α,β-glucoside ^{13}C-NMR in D_2O
102.2
98.0
75.9
75.8
73.1
71.7
71.3
70.7
69.6
69.6
68.3
60.8
60.5
30.8
30.8
28.7
28.6
25.1
24.7
21.9
21.9
13.3
13.3
OH
O
HO
HO
OH
O
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)



Hexyl-α,β-xyloside ^{1}H-NMR in D_2O

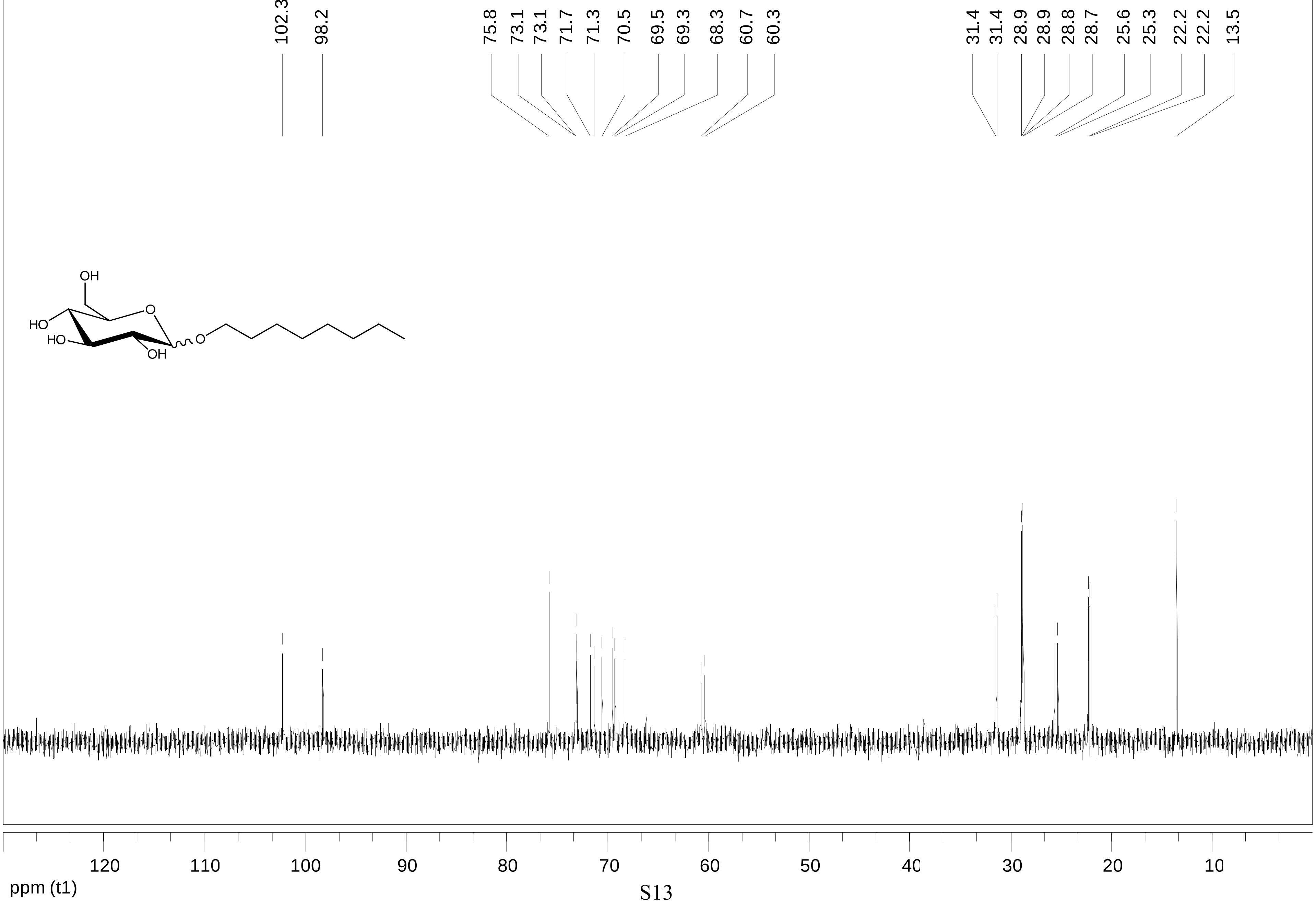
Hexyl-α,β-xyloside ^{13}C-NMR in D_2O

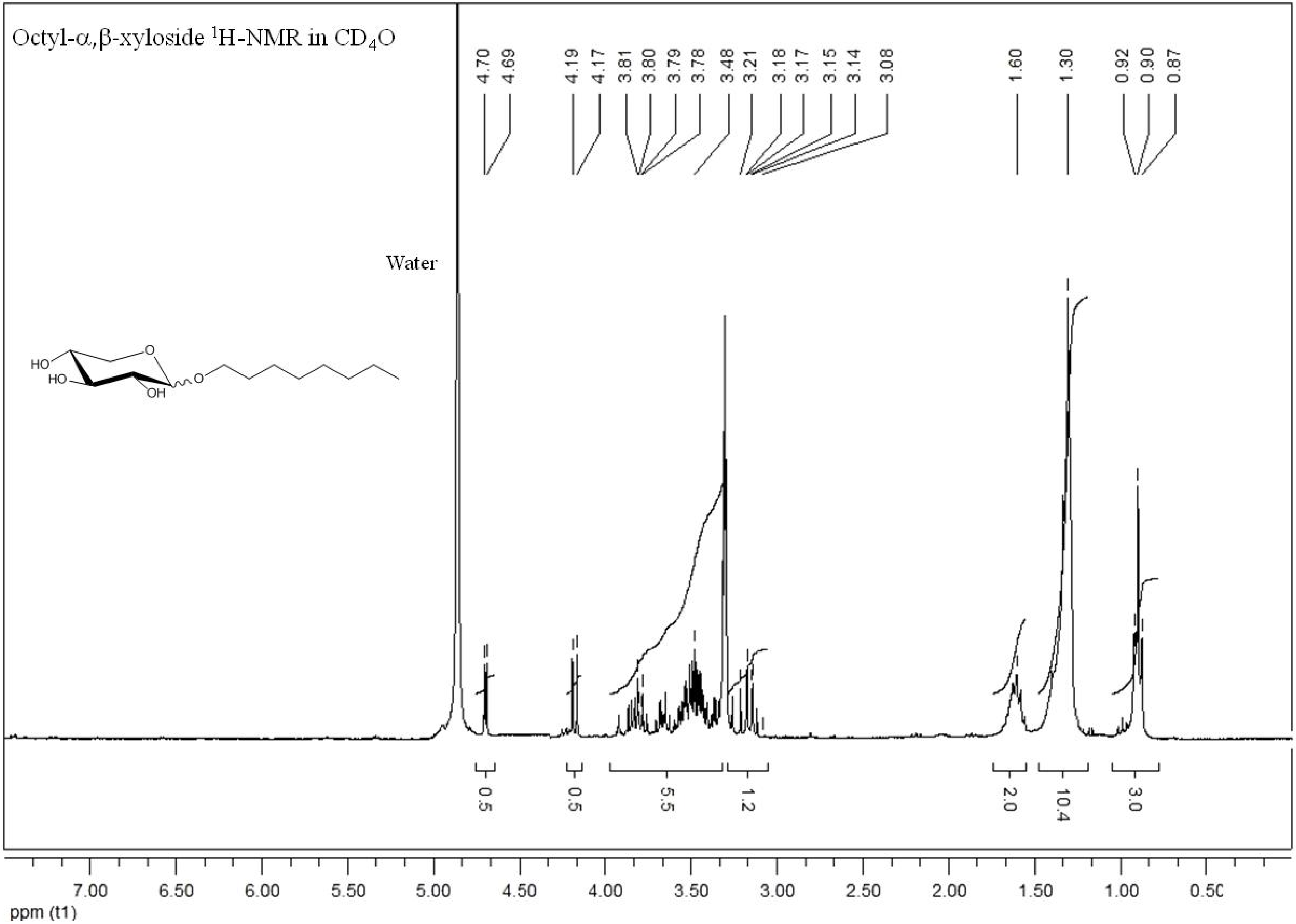


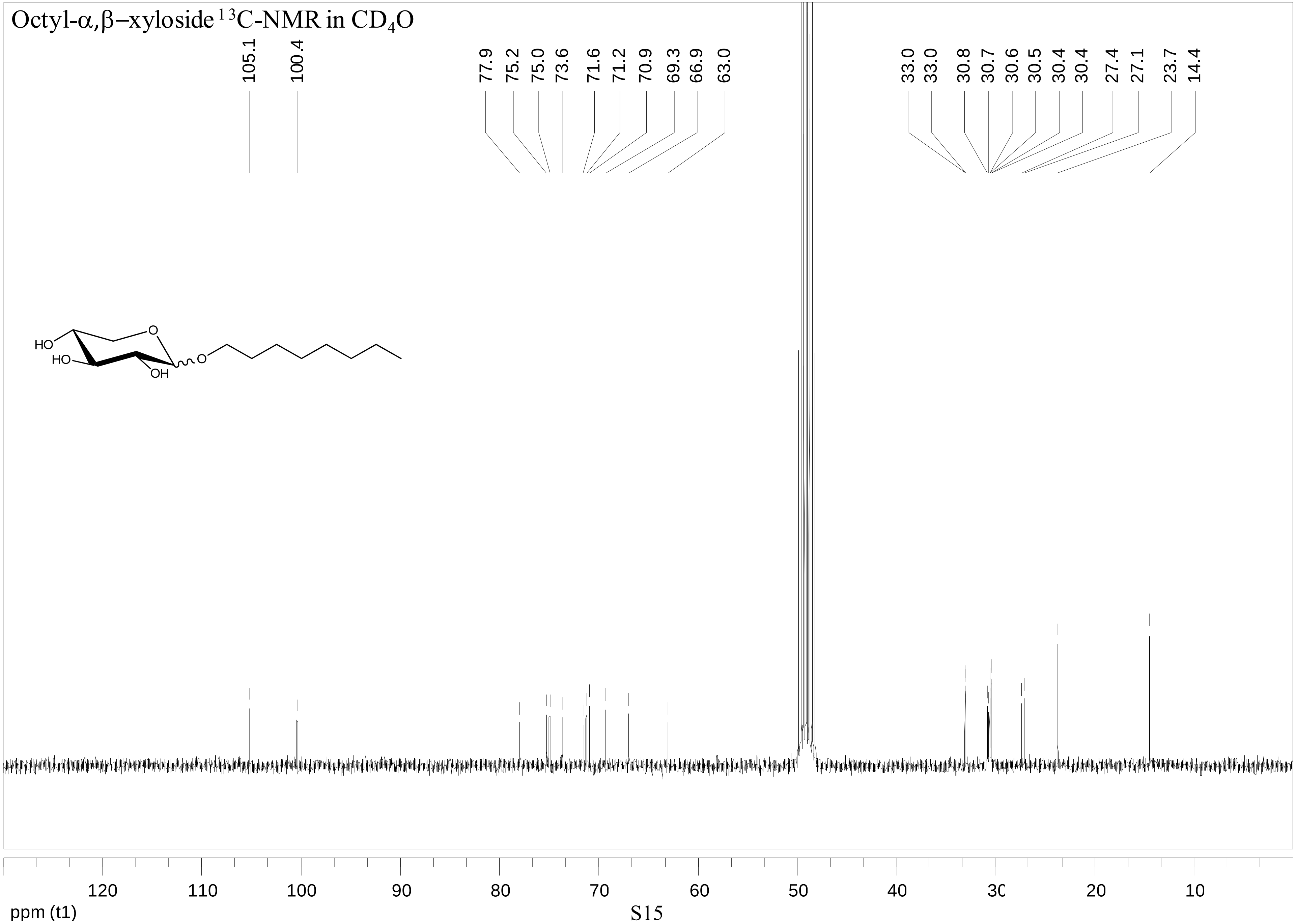


Octyl-α ,β-glucoside ^{1}H-NMR in D_2O

Octyl-α,β–glucoside ^{13}C-NMR in D_2O

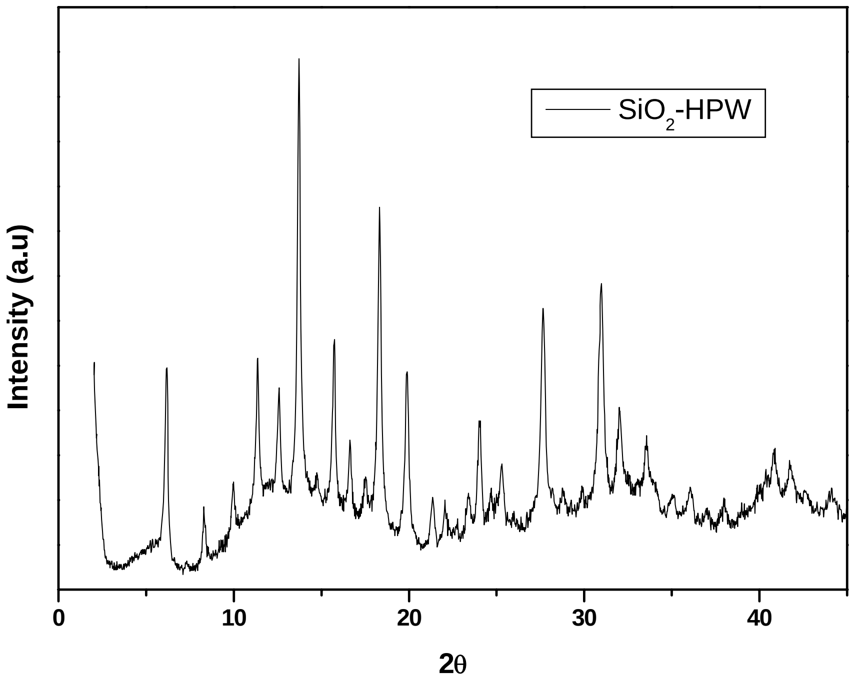


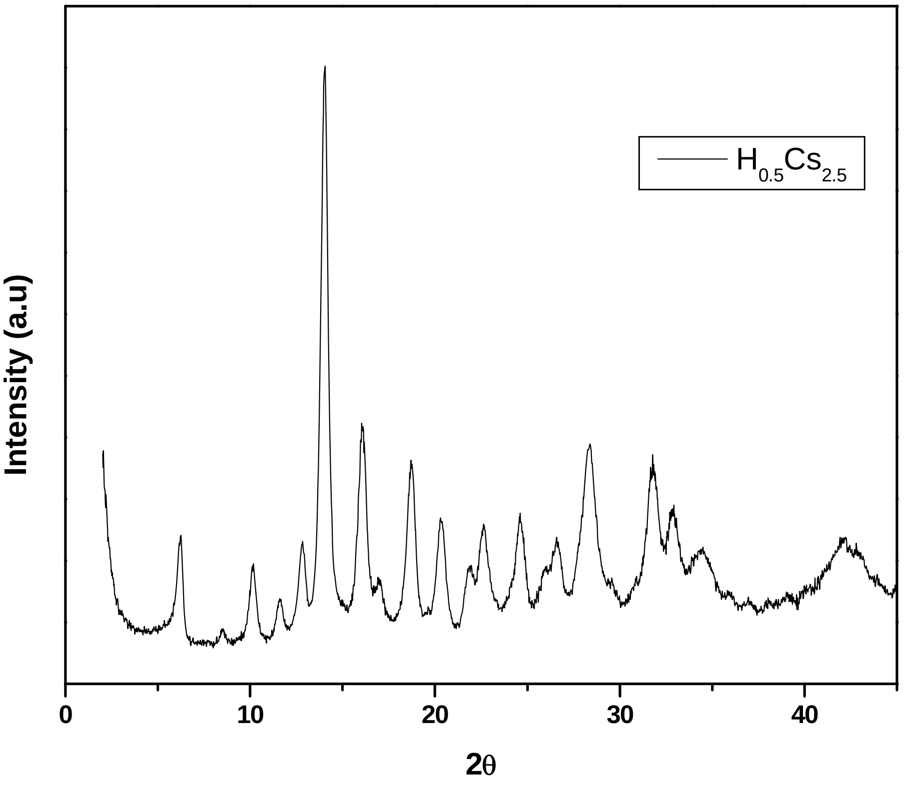

Octyl-α,β-xyloside ¹H-NMR in CD₄O
Water
HO
HO
OH
O
O
4.70
4.69
4.19
4.17
3.81
3.80
3.79
3.78
3.48
3.21
3.18
3.17
3.15
3.14
3.08
1.60
1.30
0.92
0.90
0.87
0.5
0.5
5.5
1.2
2.0
10.4
3.0
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)

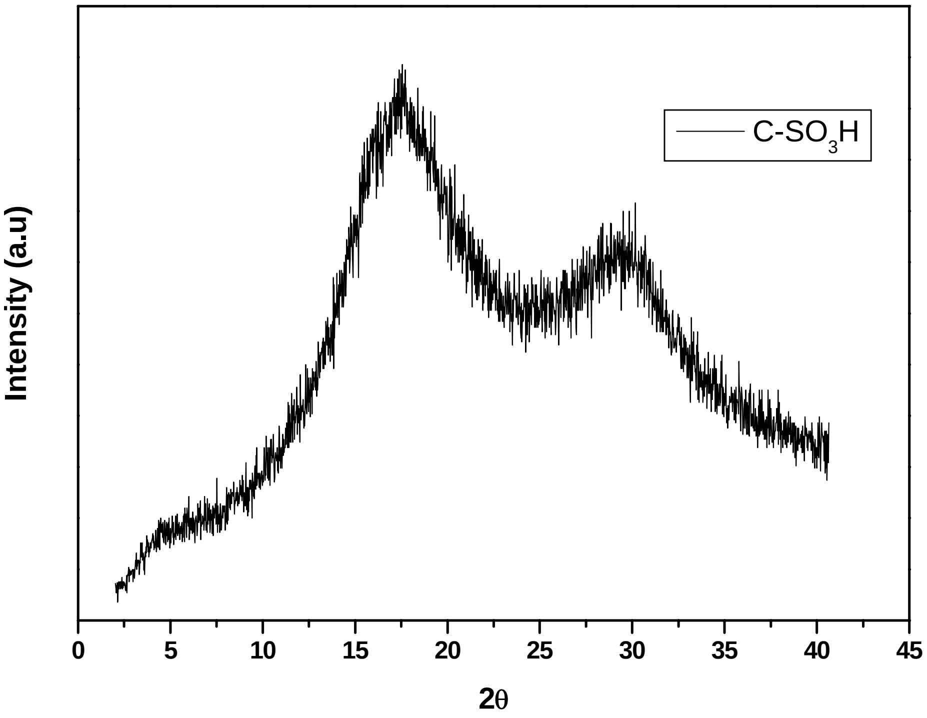


Octyl-α,β–xyloside ^{13}C-NMR in CD_4O

8. XRD spectra






Intensity (a.u)
C-SO$_3$H
0
5
10
15
20
25
30
35
40
45
2θ