

# ChemistrySelect

Supporting Information

## **Direct Conversion of Agarose into Alkyl Mono- and Disaccharide Surfactants Based on 3,6-Anhydro L- and D-Galactose Units**

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## Experimental

### General

Agarose was purchased from SIGMA-ALDRICH (A9539-1004, Lot number: SLBD2499V). All commercially available reagents and solvents were used without further purification. TLC analysis was applied on Merck 60 F254 silica gel nonactivated plates; the eluent for TLC plate is CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1; a solution of H<sub>2</sub>SO<sub>4</sub> in EtOH (5%, v/v) and a spatula tip of orcinol was used for plates developing. The crude product was chromatographed by automatic puriFlash 430 equipment (Interchim) with pre-packed silica gel column (SILICA HC 12 g, 25 μm). Positive ion electrospray (ESI+) mass spectra were acquired on MS/MS TOF and the Shimadzu ensemble LC-MS 2020 mass spectrometers. NMR spectra were recorded on a Bruker Avance III 400 spectrometer operating at 400.13 MHz for <sup>1</sup>H, equipped with a BBFO probe with a Z-gradient coil and a GREAT 1/10 gradient unit. The standard temperature was adjusted to 298 K. <sup>13</sup>C NMR spectra were recorded at 100.61 MHz. <sup>1</sup>H chemical shifts (δ) are given in ppm relative to the solvent residual peak and <sup>13</sup>C chemical shifts are relative to the central peak of the solvent signal. Coupling constants were expressed in Hertz (Hz) and the following abbreviations were used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintuplet), sex (sextuplet), m (multiplet), dd (doublet of doublets) and dt (doublet of triplets).

### Calculation of the molar equivalents of polymeric materials

The molar mass of the disaccharidic repeating unit of agarose is 306.74 g mol<sup>-1</sup>. Because the aim of the study was to depolymerize agarose and graft alkyl chain on monosaccharide units, the value of 153.37 g mol<sup>-1</sup> corresponding to half of the molar mass of the disaccharidic repeating unit, was used to calculate the number of moles of monosaccharide unit. Thus, for 500 mg agarose, 1 eq. is 3.26 mmol.

For Amberlyst-15Dry, the concentration of acid sites is 4,7 eq. (mmol) per gram (data sheet from ROHM&HASS). For 1 eq. (3.26 mmol) Amberlyst-15Dry, the mass added is (3.26/4.7) = 0.694 g.

### Synthesis of butyl mono- and disaccharide 3,6-anhydro L- and D-galactose acetals (1)-(4)

To a suspension of agarose (500 mg, 3.26 mmol, 1.0 equiv.) in water (22 mL, 1224.41 mmol, 375 equiv.) and *n*-butanol (36 mL, 396.72 mmol, 121.5 equiv.) was added Amberlyst-15Dry (694 mg, 4.7 mmol g<sup>-1</sup>, 3.26 mmol, 1.0 equiv.). Then, in the presence of a Dean-Stark apparatus filled with *n*-butanol, the temperature was increased to reach 90°C and the reaction mixture was stirred for 22 h under reduced pressure (500 mbar). The reaction mixture was followed by TLC (CH<sub>2</sub>Cl<sub>2</sub>/MeOH (90/10, v/v), the plate was developed by 5 % H<sub>2</sub>SO<sub>4</sub> in EtOH and a spatula tip of orcinol. The reaction mixture was cooled down to room temperature and filtered through a Büchner funnel precoated with celite and rinsed several times with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was neutralized with a 1N aqueous solution of NaOH and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (98/2 to 85/15, v/v) as the eluent to give *n*-butyl monosaccharides and disaccharides (overall yield = 61 %).

#### *n*-Butyl α,β-D-galactopyranoside (1α,β)

After column chromatography, butyl D-galactoside **1** as an anomeric mixture (156 mg, yield 40%) was isolated as a solid. R<sub>f</sub> 0.27 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1 v/v). <sup>1</sup>H NMR (400.13 MHz, MeOD): δ 4.82 (d, 1H, J = 3.3 Hz, H1<sub>α</sub>), 4.22 (d, 1H, J = 7.3 Hz, H1<sub>β</sub>), 3.91-3.90 (m, 1H, H3), 3.82 (δ, 1H, J = 1.4, 6.6 Hz, H4), 3.77-3.42 (m, 6H, H2, H5, H6, OCH<sub>2</sub>), 1.63 (quin, 2H, J = 6.7 Hz, CH<sub>2</sub>), 1.49-1.40 (m, 2H, CH<sub>2</sub>), 0.97 (t, 3H, J = 7.3 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (100.61 MHz, MeOD): δ 103.63 (C1<sub>β</sub>), 98.87 (C1<sub>α</sub>), 75.30, 73.65, 71.19, 70.97, 70.10, 69.70, 69.15, 69.10, 67.46, 67.43, 61, 15, 61.13, 31.49, 19.15, 13.00.

#### 1-(Dibutylacetal)-3,6-anhydro-L-galactopyranoside (2)

After column chromatography, L-galactoside **2** (40 mg, yield 8%) was isolated as an oil R<sub>f</sub> 0.16 (CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400.13 MHz, MeOD): δ 4.50 (d, 1H, J = 7.6 Hz, H1), 4.15 (t, 1H, J = 2.6 Hz, H4), 4.03 (quin, 1H, J = 2.1 Hz, H5), 3.96-3.93 (m, 2H, H3, H6a), 3.81 (dd, 1H, J = 2.1, 9.4 Hz, H6b), 3.76-3.54 (m, 5H, H2, 2 OCH<sub>2</sub>), 1.66-1.56 (m, 4H, 2 CH<sub>2</sub>), 1.49-1.39 (m, 4H, 2 CH<sub>2</sub>), 0.97 (t, 3H, J = 7.3 Hz, CH<sub>3</sub>), 0.96 (t, 3H, J = 7.3 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (100.61 MHz, MeOD): δ 104.40 (C1), 86.22 (C3),

79.98 (C4), 78.36 (C5), 74.85 (C6), 72.50 (C2), 69.14, 68.03 (2 OCH<sub>2</sub>), 33.16, 33.05 (2 CH<sub>2</sub>), 20.38, 20.36 (2 CH<sub>2</sub>), 14.27, 14.20 (2 CH<sub>3</sub>).

### ***n*-Butyl -3,6-anhydro-L-galactopyranoside (3)**

After column chromatography, compound **3** (13 mg, yield 4%) was isolated as an oil. *R*<sub>f</sub> 0.09 (CH<sub>2</sub>Cl<sub>2</sub>). **<sup>1</sup>H NMR (400.13 MHz, MeOD):** δ 4.52 (s, 1H, H1), 4.34 (d, 1H, *J* = 1.7 Hz, H4), 4.19-4.17 (m, 2H, H5, H6a), 4.11 (d, 1H, *J* = 4.7 Hz, H2), 3.92 (dd, 1H, *J* = 3.2, 8.9 Hz, H6b), 3.91 (d, 1H, *J* = 4.6 Hz, H3), 3.78 (dt, 1H, *J* = 6.5, 9.5 Hz, OCH<sub>a</sub>H<sub>b</sub>), 3.36 (dt, 1H, *J* = 6.4, 9.5 Hz, OCH<sub>a</sub>H<sub>b</sub>), 1.62-1.55 (m, 2H, CH<sub>2</sub>), 1.47-1.38 (m, 2H, CH<sub>2</sub>), 0.96 (t, 3H, *J* = 7.4 Hz, CH<sub>3</sub>). **<sup>13</sup>C NMR (100.61 MHz, MeOD):** δ 103.57 (C1), 82.51 (C2), 79.18 (C5), 74.22 (C3), 71.26 (C4), 71.20 (C6), 69.09 (OCH<sub>2</sub>), 32.69 (CH<sub>2</sub>), 20.49 (CH<sub>2</sub>), 14.22 (CH<sub>3</sub>).

### **D-Galactopyranosyl-(1->4')-1'-(dibutylacetal)-3',6'-anhydro-L-galactoside (4)**

After column chromatography, disaccharide **4** (64 mg, yield 9%) was isolated as a solid. *R*<sub>f</sub> 0.11 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1 v/v). **<sup>1</sup>H NMR (400.13 MHz, D<sub>2</sub>O):** δ 4.47 (d, 1H, *J* = 7.8 Hz, H1'), 4.45 (d, 1H, *J* = 7.9 Hz, H1), 4.33-4.29 (m, 1H, H5'), 4.27 (dd, 1H, *J* = 5.0, 3.0 Hz, H4'), 3.96 (m, 1H, H3'), 3.90 (dd, 1H, *J* = 10.0, 5.0 Hz, H6'a), 3.83 (d, 1H, *J* = 3.6 Hz, H4), 3.77 (dd, 1H, *J* = 7.8, 2.2 Hz, H2'), 3.77-3.71 (m, 1H, H6'b), 3.70-3.62 (m, 1H, H6), 3.60 (m, 1H, H5), 3.55 (m, 1H, H3), 3.70-3.49 (m, 4H, 2 OCH<sub>2</sub>), 3.43 (dd, 1H, *J* = 10.0, 7.9 Hz, H2), 1.54-1.42 (m, 4H, 2 CH<sub>2</sub>), 1.34-1.20 (m, 4H, 2 CH<sub>2</sub>), 0.81 (t, 3H, *J* = 7.3 Hz, CH<sub>3</sub>), 0.80 (t, 3H, *J* = 7.3 Hz, CH<sub>3</sub>). **<sup>13</sup>C NMR (100.61 MHz, D<sub>2</sub>O):** δ 102.62 (C1), 102.53 (C1'), 85.76 (C4'), 82.62 (C3'), 75.22 (C5), 75.10 (C5'), 72.90 (C6'), 72.58 (C3), 70.66 (C2), 69.83 (C2'), 68.92 (OCH<sub>2</sub>), 68.47 (C4), 67.65 (OCH<sub>2</sub>), 60.99 (C6), 31.00, 30.95 (2 CH<sub>2</sub>), 18.65, 18.64 (2 CH<sub>2</sub>), 13.05, 13.01 (2 CH<sub>3</sub>).

### **One-pot process to synthesize dodecyl mono- and disaccharide acetal surfactants from agarose (5)-(10)**

To a suspension of agarose (500 mg, 3.26 mmol, 1.0 equiv.) in water (22 mL, 1224.41 mmol, 375 equiv.) and *n*-butanol (36 mL, 396.72 mmol, 121.5 equiv.) was added Amberlyst-15Dry (694 mg, 4.7 mmol/g, 3.26 mmol, 1.0 equiv.). Then, in the presence of a Dean-Stark apparatus filled with *n*-butanol, the temperature was increased to reach 90°C and the reaction mixture was stirred for 22 h under reduced pressure (500 mbar). The reaction mixture was followed by TLC (CH<sub>2</sub>Cl<sub>2</sub>/MeOH (90/10, v/v), the plate was developed by 5 % H<sub>2</sub>SO<sub>4</sub> in EtOH and a spatula tip of orcinol. At room temperature, *n*-dodecanol (2.93 mL, 13.06 mmol, 4.0 equiv.) was added. The mixture was then heated to 70°C and the pressure was progressively reduced to 5 mbar to azeotropically remove water and *n*-butanol. Under these conditions, the reaction mixture was stirred for 4 h. The residue was cooled down to room temperature, diluted in CH<sub>2</sub>Cl<sub>2</sub> and filtered through a Büchner funnel precoated with celite and rinsed several times with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (90/10, v/v). The filtrate was neutralized with a 1N aqueous solution of NaOH and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (98/2 to 90/10, v/v) as the eluent to give the dodecyl monosaccharides and disaccharides **5-8** (overall yield = 45 %) in addition to a mixture of dodecyl/butyl glycosides based on single-tailed disaccharides **9,10** (yield ~ 6%).

### ***n*-Dodecyl α,β-D-galactopyranoside (5α,β)**

After column chromatography, dodecyl D-galactoside **5** as an anomeric mixture (113 mg, yield 20%) was isolated as a solid. *R*<sub>f</sub> 0.32 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1 v/v). **<sup>1</sup>H NMR (400.13 MHz, MeOD):** δ 4.82 (d, 1H, *J* = 3.1 Hz, H1α), 4.23 (d, 1H, *J* = 7.3 Hz, H1β), 3.91-3.90 (m, 1H, H3), 3.84-3.79 (m, 1H, H4), 3.77-3.45 (m, 6H, H2, H5, H6, OCH<sub>2</sub>), 1.69-1.59 (m, 2H, CH<sub>2</sub>), 1.49-1.31 (m, 18H, 9 CH<sub>2</sub>), 0.92 (t, 3H, *J* = 6.5 Hz, CH<sub>3</sub>). **<sup>13</sup>C NMR (100.61 MHz, MeOD):** δ 103.60 (C1β), 100.30 (C1α), 75.40, 73.74, 72.31, 71.55, 71.06, 70.28, 69.21, 69.11, 62.70, 30.65, 33.07, 30.76, 30.61, 30.48, 27.35, 23.73, 14.45. **MS (ESI+):** *m/z* calcd for C<sub>18</sub>H<sub>36</sub>O<sub>6</sub>Na [M+Na]<sup>+</sup>: 371.24; found: 370.85; *m/z* calcd for C<sub>36</sub>H<sub>72</sub>O<sub>12</sub>Na [2M+Na]<sup>+</sup>: 719.49; found: 719.45.

### **1-(Didodecylacetal)-3,6-anhydro-L-galactopyranoside (6)**

After column chromatography, L-galactoside **6** (94 mg, yield 11%) was isolated as an oil. *R*<sub>f</sub> 0.26 (CH<sub>2</sub>Cl<sub>2</sub>). **<sup>1</sup>H NMR (400.13 MHz, MeOD):** δ 4.49 (d, 1H, *J* = 7.6 Hz, H1), 4.14 (t, 1H, *J* = 2.8 Hz, H4), 4.02 (quin, 1H, *J* = 2.1 Hz, H5), 3.95-3.92 (m, 2H, H3, H6a), 3.80 (dd, 1H, *J* = 21.9, 9.3 Hz, H6b), 3.74-3.53 (m, 5H, H2, 2 OCH<sub>2</sub>), 1.66-1.56 (m, 4H, 2 CH<sub>2</sub>), 1.41-1.31 (m, 36H, 18 CH<sub>2</sub>), 0.92 (t, 6H, *J* = 6.7 Hz, 2 CH<sub>3</sub>). **<sup>13</sup>C NMR (100.61 MHz, MeOD):** δ 102.96 (C1), 84.84 (C3), 78.58 (C4), 76.96 (C5), 73.46 (C6), 71.06 (C2), 67.94, 66.74 (2 OCH<sub>2</sub>), 31.69, 29.43, 29.38, 29.10, 25.87, 22.35 (20 CH<sub>2</sub>), 13.05 (2 CH<sub>3</sub>). **HRMS (ESI+):** *m/z* calcd for C<sub>30</sub>H<sub>60</sub>O<sub>6</sub>Na [M+Na]<sup>+</sup>: 539.4282; found: 539.4286.

### ***n*-Dodecyl -3,6-anhydro-L-galactopyranoside (7)**

After column chromatography, compound **7** (34 mg, yield 6%) was isolated as an oil. *R*<sub>f</sub> 0.14 (CH<sub>2</sub>Cl<sub>2</sub>). **<sup>1</sup>H NMR (400.13 MHz, MeOD):** δ 4.51 (s, 1H, H1), 4.34 (d, 1H, *J* = 1.7 Hz, H4), 4.19-4.17 (m, 2H, H5, H6a), 4.11 (d, 1H, *J* = 4.6 Hz, H2), 3.93-3.90 (m, 2H, H5, H6b), 3.76 (dt, 1H, *J* = 6.7, 9.6 Hz, OCH<sub>a</sub>H<sub>b</sub>), 3.34 (dt, 1H, *J* = 6.5, 9.7 Hz, OCH<sub>a</sub>H<sub>b</sub>), 1.65-1.54 (m, 2H, CH<sub>2</sub>), 1.41-1.31 (m, 18H, 9 CH<sub>2</sub>), 0.92 (t, 3H, *J* = 6.7 Hz, CH<sub>3</sub>). **<sup>13</sup>C NMR (100.61 MHz, MeOD):** δ 103.58 (C1), 82.52 (C2), 79.19 (C5), 74.22 (C3), 71.27 (C4), 71.21 (C6), 69.41 (OCH<sub>2</sub>), 33.08, 30.79, 30.75, 30.74, 30.57, 30.48, 27.41, 23.74 (10 CH<sub>2</sub>), 14.45 (CH<sub>3</sub>). **MS (ESI+):** *m/z* calcd for C<sub>18</sub>H<sub>34</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 353.23; found: 352.90; *m/z* calcd for C<sub>36</sub>H<sub>68</sub>O<sub>10</sub>Na [2M+Na]<sup>+</sup>: 683.47; found: 683.60.

### **D-Galactopyranosyl-(1->4')-1'-(didodecylacetal)-3',6'-anhydro-L-galactoside (8)**

After column chromatography, disaccharide **8** (85 mg, yield 8%) was isolated as a solid. *R*<sub>f</sub> 0.16 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1 v/v). **<sup>1</sup>H NMR (400.13 MHz, MeOD):** δ 4.50 (d, 1H, *J* = 7.8 Hz, H1'), 4.40 (d, 1H, *J* = 7.8 Hz, H1), 4.31-4.28 (m, 1H, H4'), 4.28-4.24 (m, 1H, H5'), 4.11-4.05 (m, 1H, H3'), 3.95-3.89 (m, 1H, H6'a), 3.84-3.75 (m, 3H, H6a, H2', H6'b), 3.73-3.68 (m, 1H, H6b), 3.66-3.56 (m, 2H, OCH<sub>2</sub>), 3.56-3.50 (m, 4H, OCH<sub>2</sub>, H2, H5), 3.48 (dt, 1H, *J* = 9.7, 3.2 Hz, H3), 1.43-1.36 (m, 4H, 2 CH<sub>2</sub>), 1.43-1.36 (m, 36H, 18 CH<sub>2</sub>), 0.90 (t, 6H, *J* = 6.0 Hz, 2 CH<sub>3</sub>). **<sup>13</sup>C NMR (100.61 MHz, MeOD):** δ 104.8 (C1), 104.1 (C1'), 87.3 (C4'), 84.5 (C3'), 77.0 (C5), 76.6 (C5'), 74.9 (C3), 74.6 (C6'), 72.4 (C2), 71.6 (C2'), 70.3 (C4), 69.4, 67.6 (2 OCH<sub>2</sub>), 62.7 (C6), 33.1, 30.9, 30.8, 30.6, 30.54, 30.5, 27.2, 23.85 (20 CH<sub>2</sub>), 14.5 (2 CH<sub>3</sub>). **HRMS (ESI+):** *m/z* calcd for C<sub>36</sub>H<sub>70</sub>O<sub>11</sub>Na [M+Na]<sup>+</sup>: 701.4810; found: 701.4811.

## **Interfacial tension and surface tension characterization**

### **General**

The solutions of products were prepared either in sunflower seed oil (brand "Carrefour", density at 25 °C: 0.92 g/L) or in Milli-Q water according to their solubility. Oil solutions were submitted to interfacial tension measurements and water solutions were prepared for surface tension measurements. Krüss apparatus (K100C) was used for interfacial tension and surface tension measurements, by Du Noüy ring method. The ring was cleaned by propane flame before each measurement.

**Oil solution preparation:** The calculated amount of products was dissolved in 38 mL sunflower seed oil, in order to achieve the desired concentration. The solution was homogenized by ultrasonication at 30 °C for 15 min, then cooled down to room temperature (25 °C) and stabilized at this temperature for at least 4 h before the measurement.

### **Interfacial tension (water/oil) measurement**

The oil solution was firstly placed in a calibrated, clean and dry glass vessel, and the surface tension was measured; secondly, the oil solution was put aside, and the glass vessel was cleaned and dried. Then the platinum ring was cleaned by propane flame, and Milli-Q water was placed in the cleaned vessel to measure the surface tension of water. These two surface tension values of oil solution and pure water were used for the calibration of interfacial tension measurements.

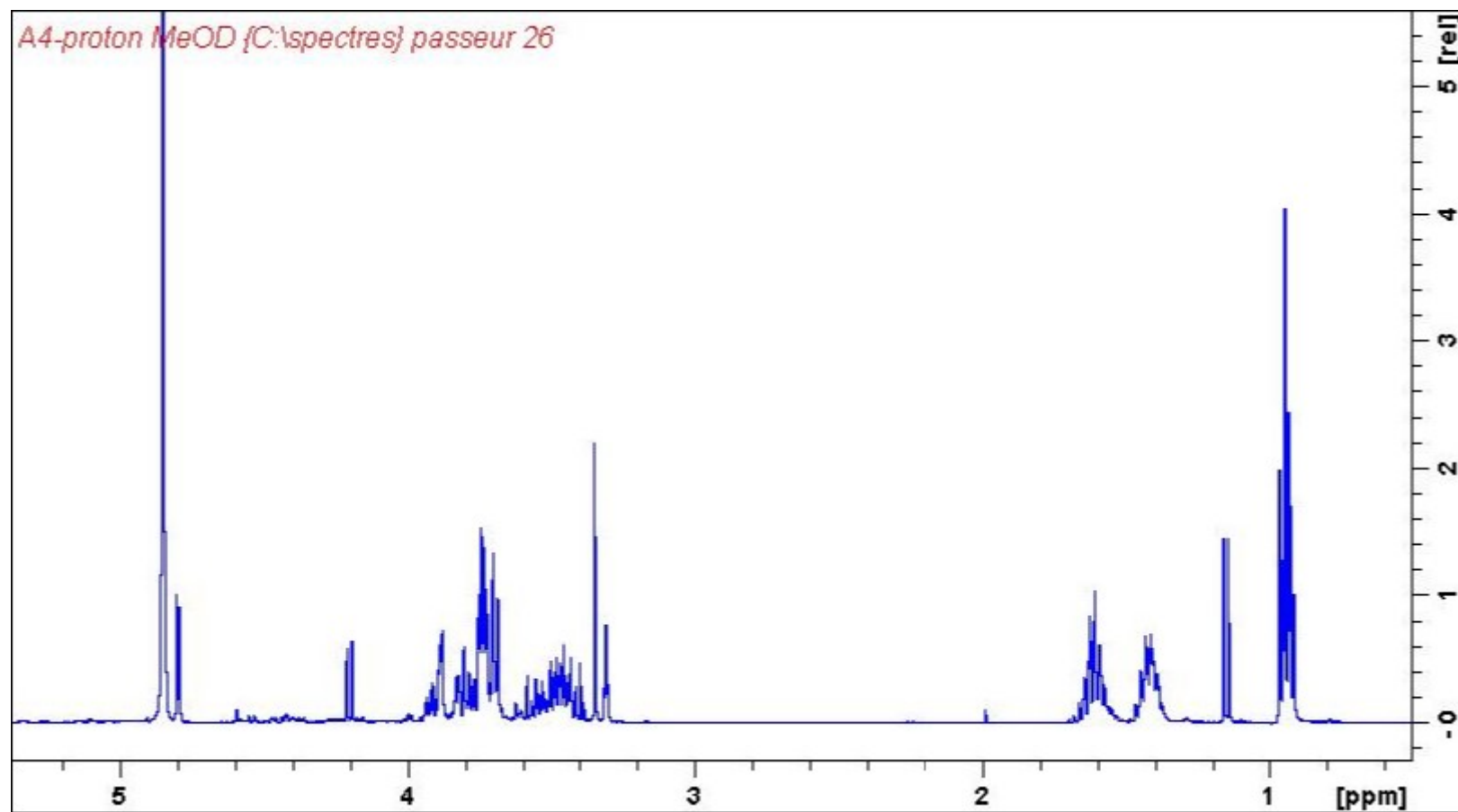
At last, the oil solution was carefully added on the water already in the glass vessel, by a polystyrene pipette without forming any individual droplets, and the two-phase system was stabilized for at least 5 minutes before the measurement of interfacial tension. Once the test was launched, the propane flame cleaned ring was slowly emerged into the solution and the interface would be detected automatically. The interfacial tension was measured successively until standard deviation is within ± 0.1 mN m<sup>-1</sup>, the maximum measurement number is 10. The temperature was maintained at 25 °C ± 0.1 °C by circulating water.

**Water solution preparation:** The calculated amount of sample was dissolved in 5.5 mL Milli-Q water to achieve the desired concentration. The solution was homogenized by ultrasonic at 30 °C for 15 min, then cooled down to room temperature (25 °C) and stabilized at this temperature for at least 4 h before the measurement.

### **Surface tension measurement**

5 mL water solution was carefully introduced (without bubbles or foam) into a PTFE coated conic vessel and the measurement would be conducted automatically with pre-defined number of dilutions (30). After every surface tension measurement at one concentration, the solution was diluted with Milli-Q water by 765 Dosimat (Metrohm) to the next concentration and then homogenized by magnetic stirring for 60 s, followed by stabilization for another 60 s before the surface tension measurement began. Surface tension value at each concentration was determined by 5 successive measurements and the standard deviation was limited within  $\pm 0.1 \text{ mN m}^{-1}$ . The temperature was maintained at  $25 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$  by circulating water.

**Figure S1**  $^1\text{H}$  NMR spectrum in MeOD of *n*-Butyl  $\alpha,\beta$ -D-galactopyranoside ( $1\alpha,\beta$ ).



**Figure S2** 2D-HMBC spectrum (4.85-3.65 ppm / 76-66 ppm) in MeOD of *n*-Butyl  $\alpha,\beta$ -D-galactopyranoside ( $1\alpha,\beta$ ). Correlations between OCH<sub>2</sub> of the butyl chain and the anomeric protons.

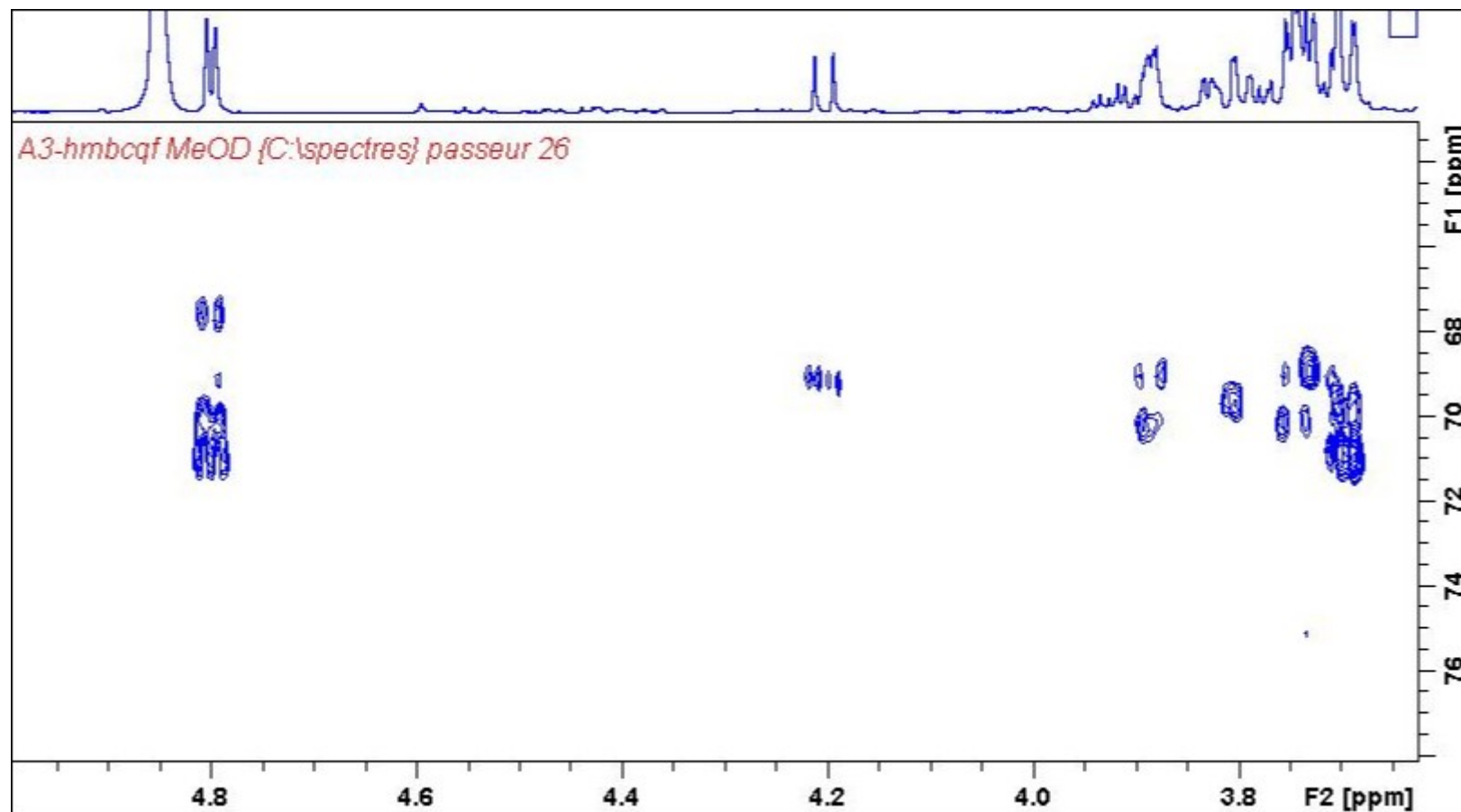


Figure S3  $^1\text{H}$  NMR spectrum in MeOD of dibutyl acetal (**2**).

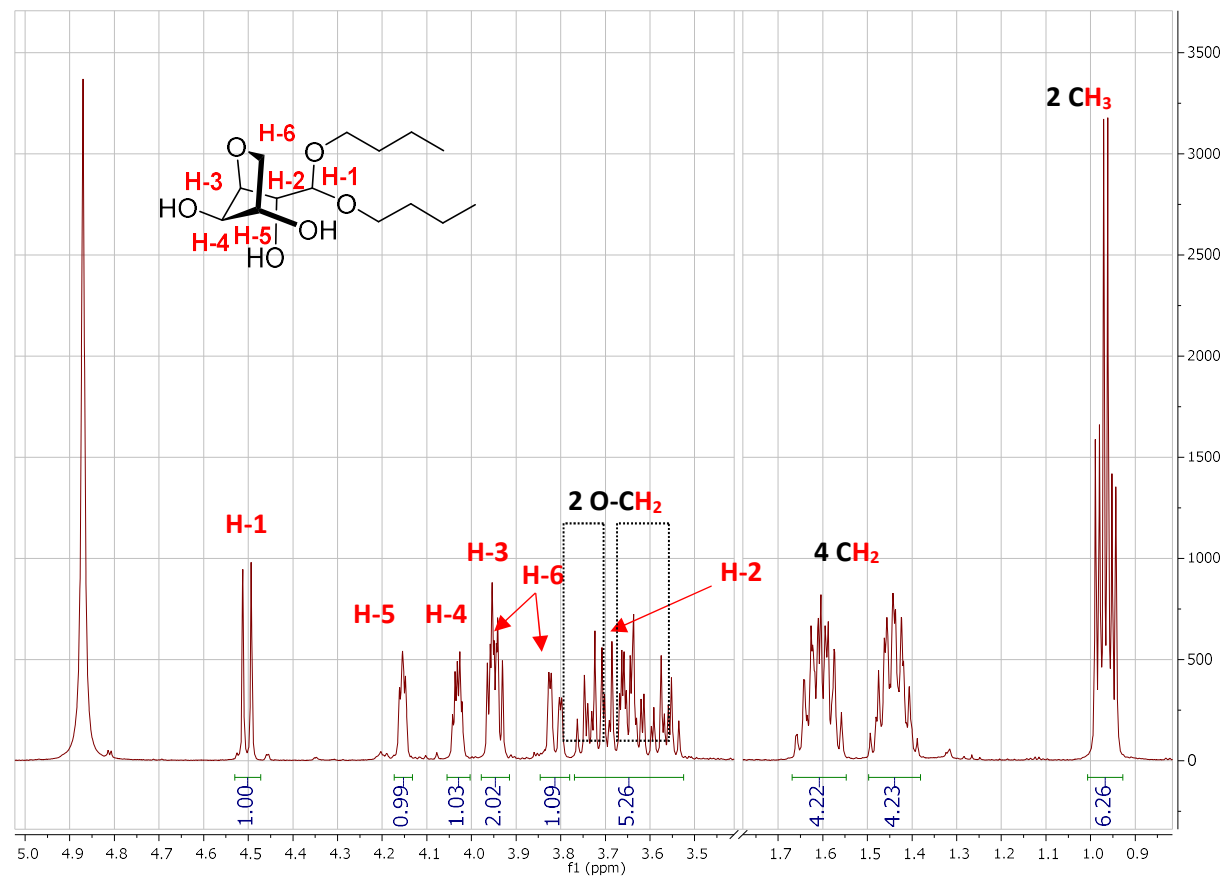




Figure S4 2D-COSY spectrum (3.45-4.55 ppm) in MeOD of dibutyl acetal (2).

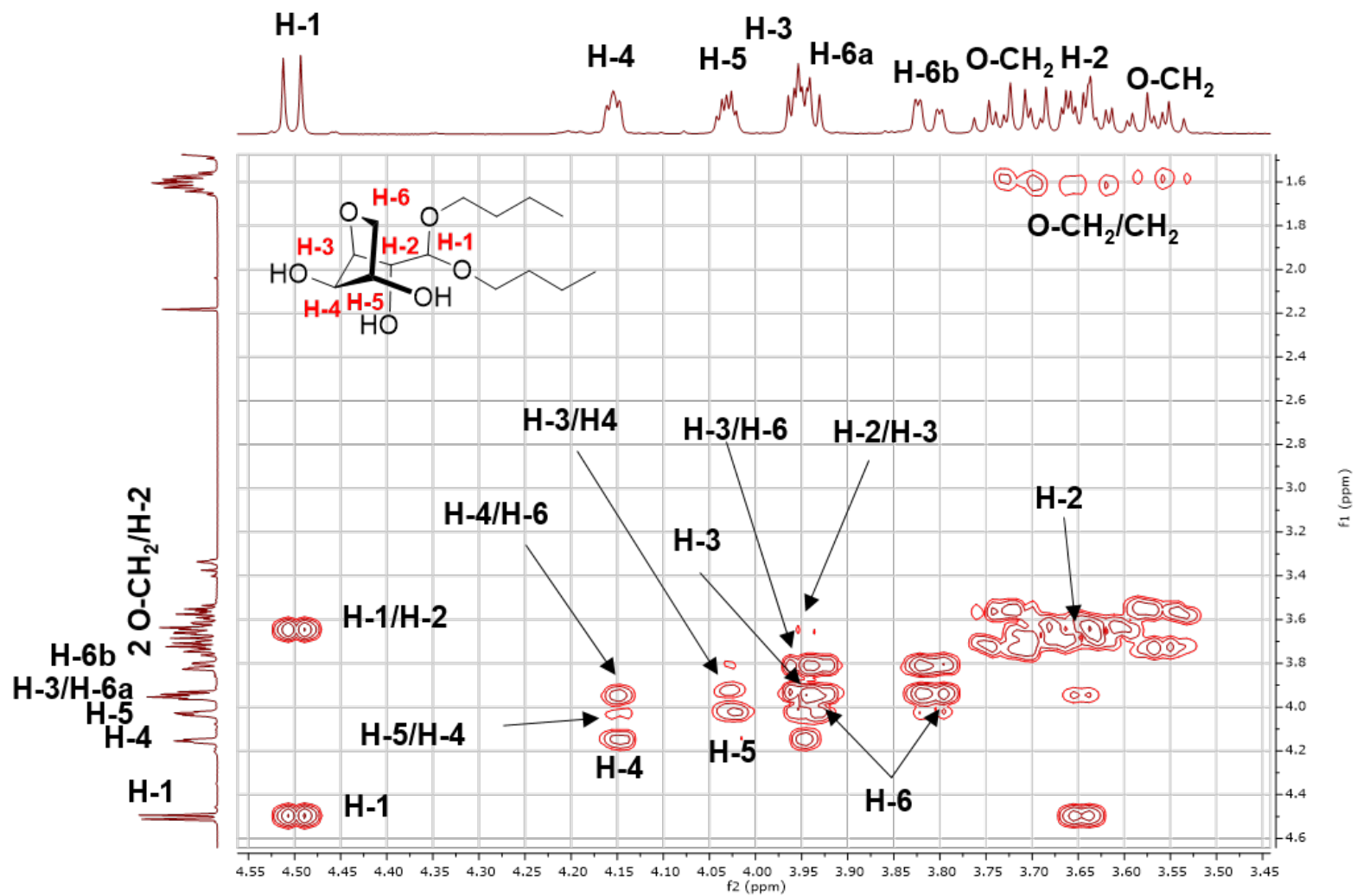


Figure S5  $^1\text{H}$  NMR spectrum in MeOD of *n*-butyl-3,6-anhydro-L-galactopyranoside (**3**).

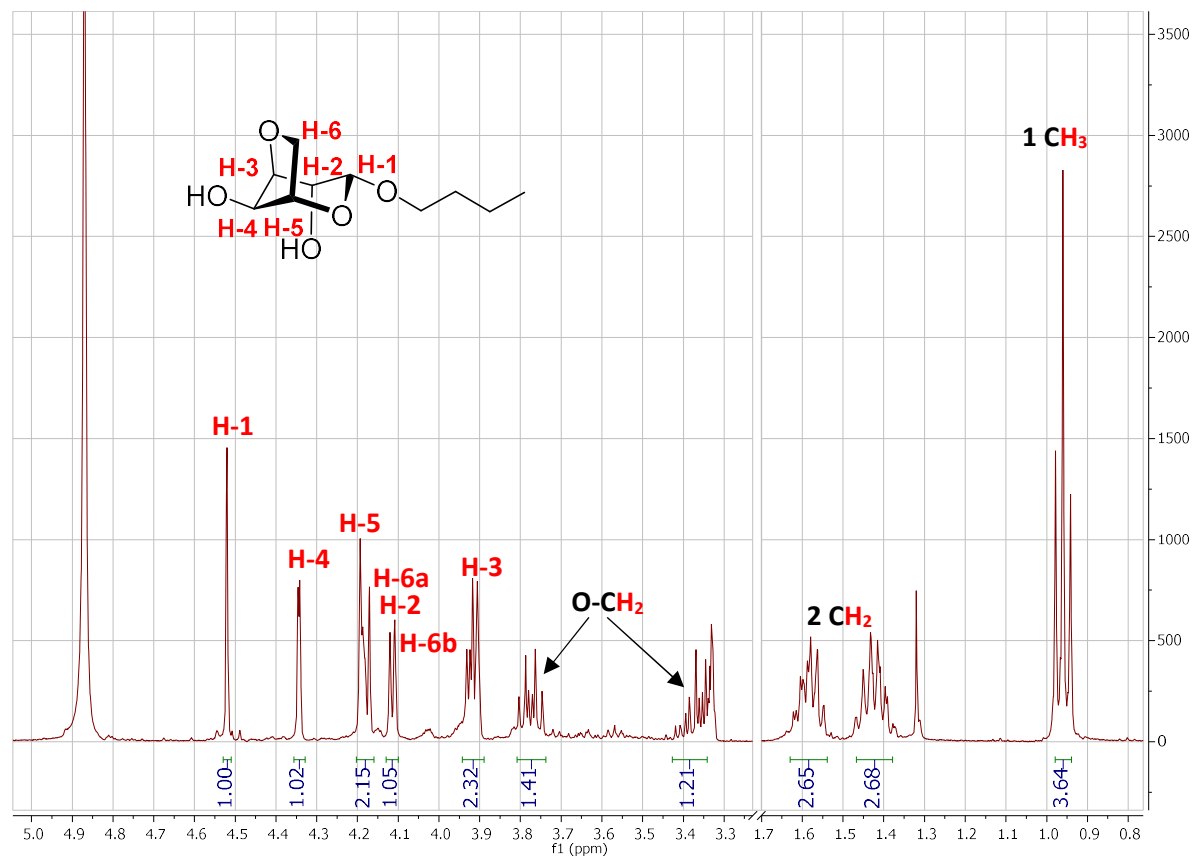


Figure S6 2D-COSY spectrum(4.6-3.1 ppm) in MeOD of *n*-butyl-3,6-anhydro-L-galactopyranoside (**3**).

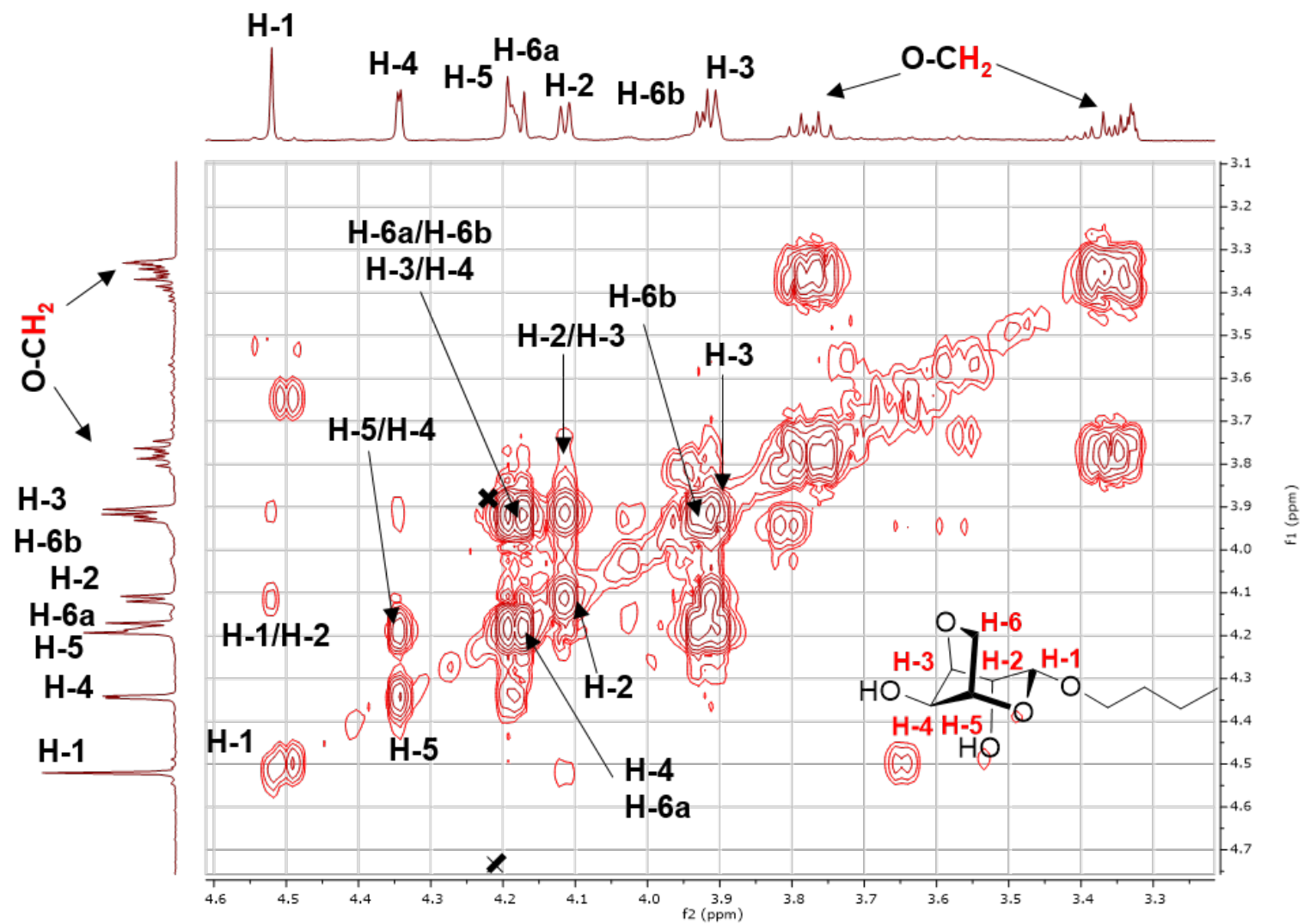


Figure S7 2D-HSQC spectrum (4.55-4.30 ppm / 60-105 ppm) in D<sub>2</sub>O of dimeric acetal (**4**).

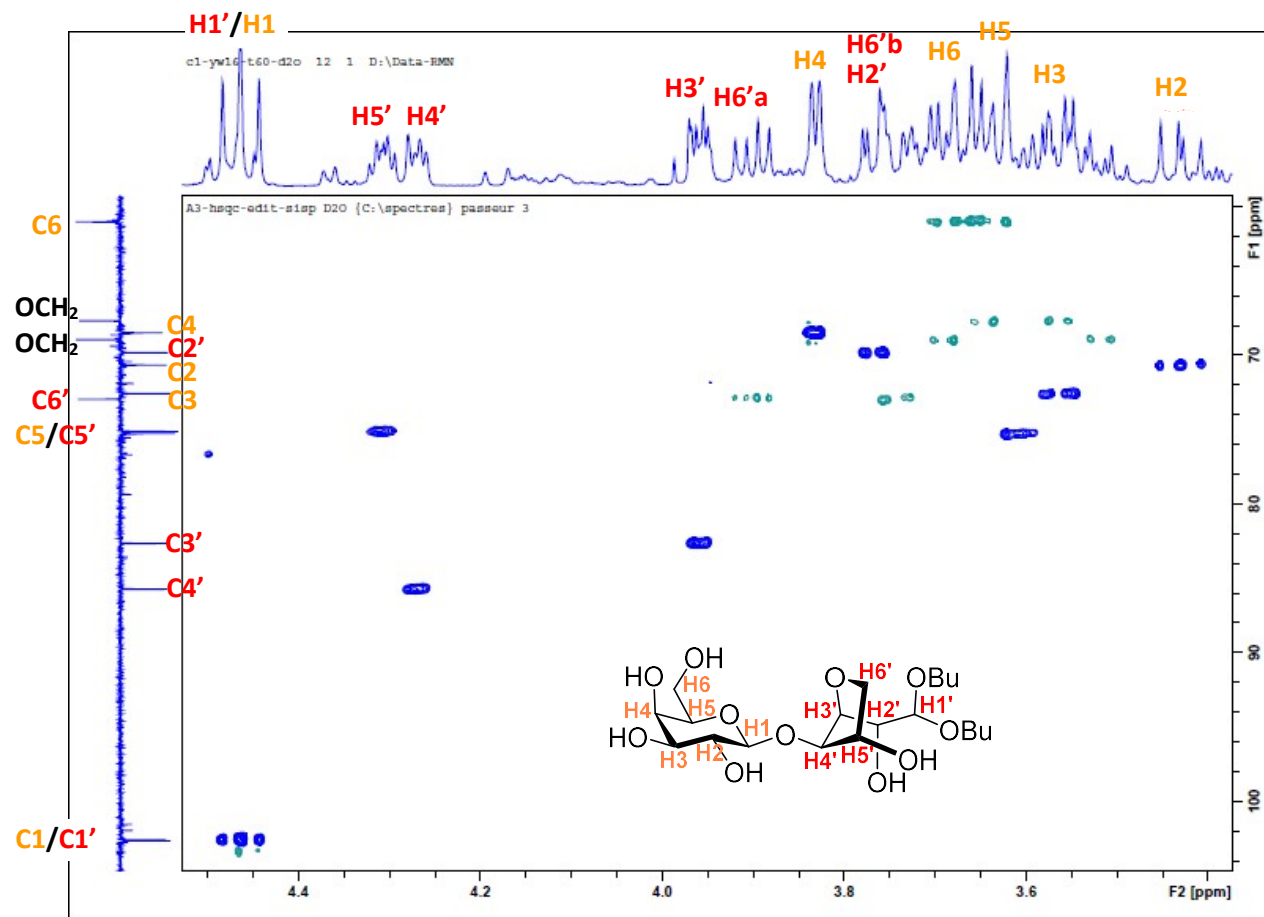


Figure S8 2D-HMBC spectrum (4.55-4.30 ppm / 60-105 ppm) in D<sub>2</sub>O of dimeric acetal (4).

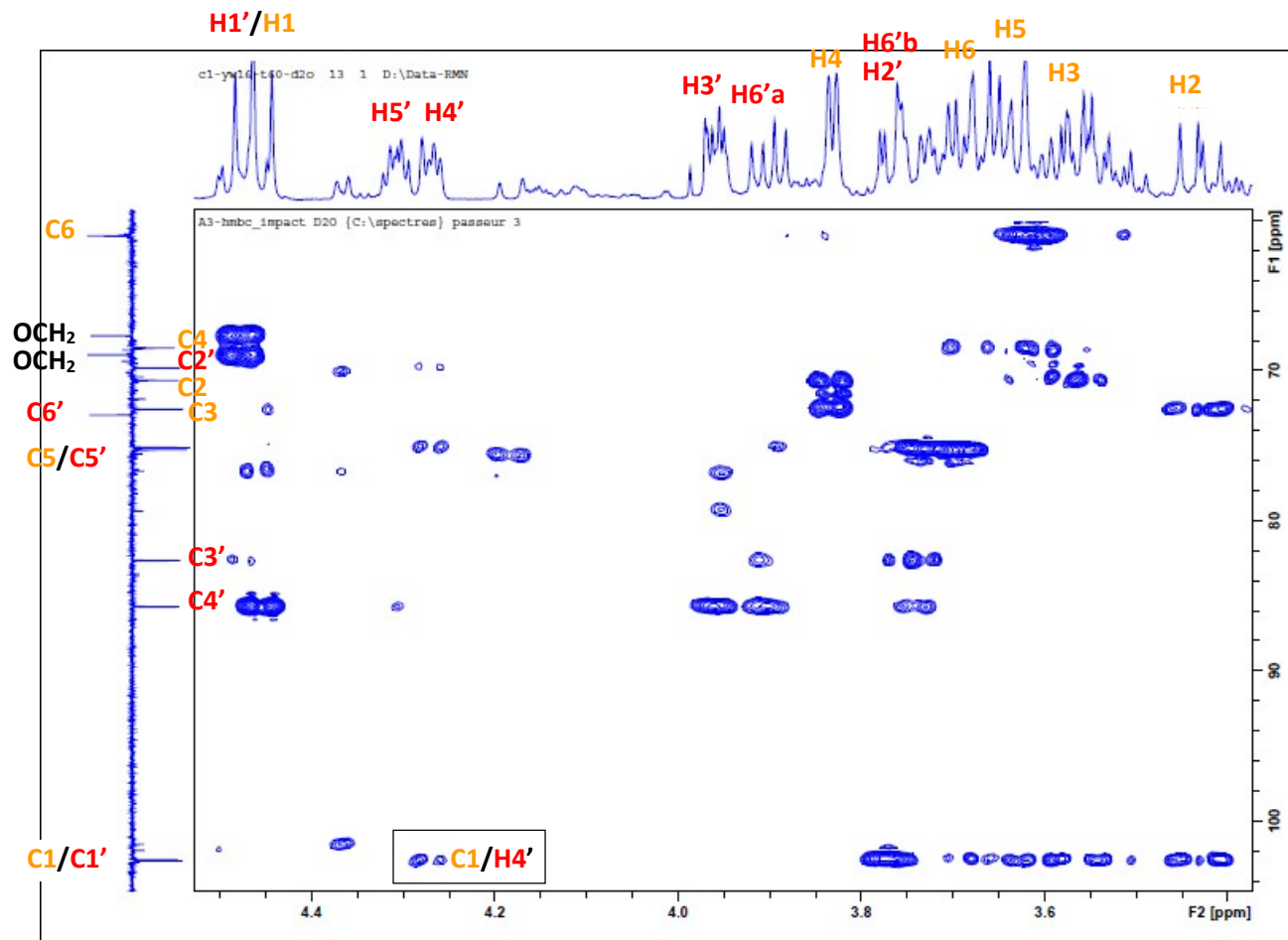


Figure S9  $^1\text{H}$  NMR spectrum in MeOD of L-galactoside (6).

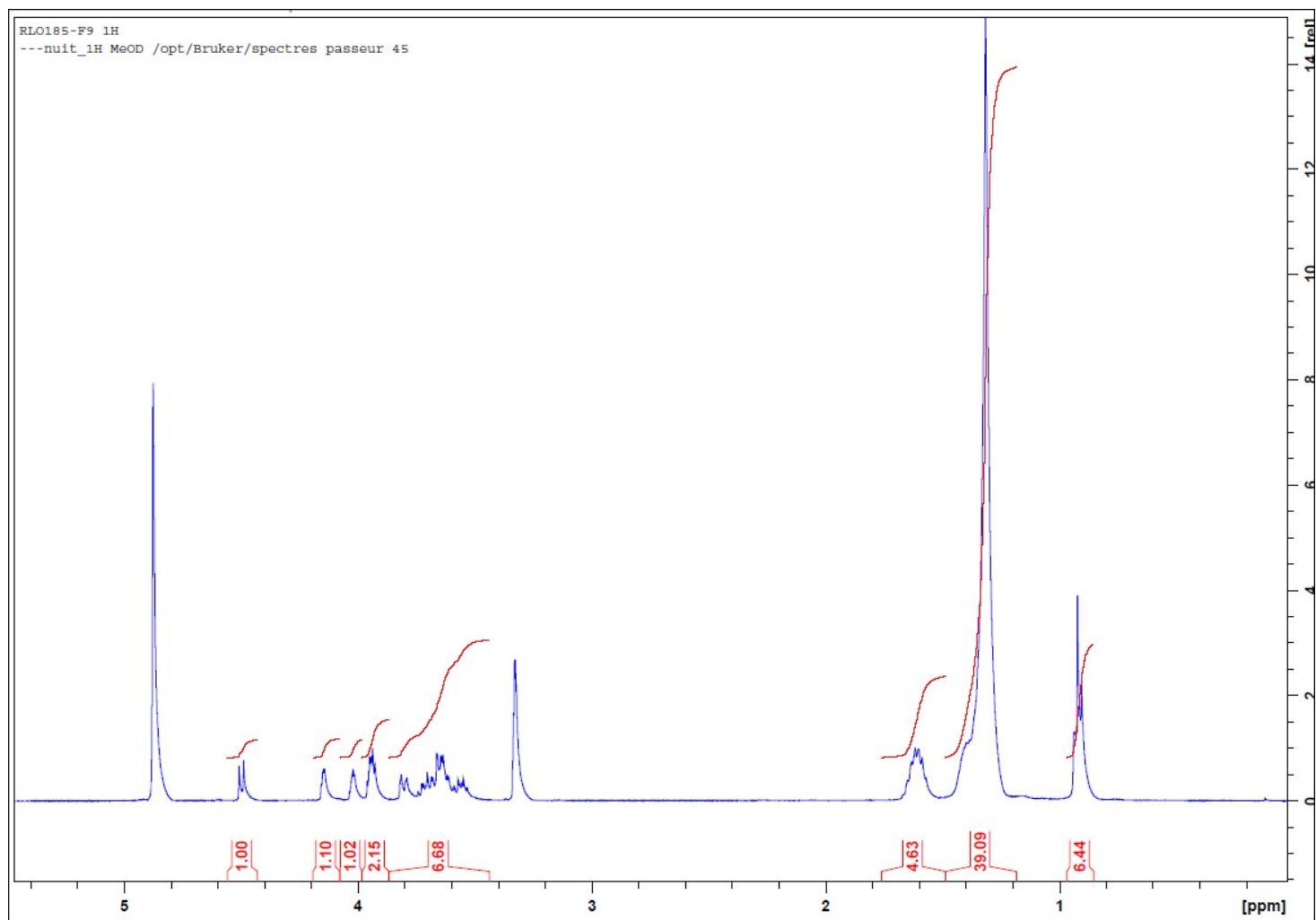


Figure S10  $^{13}\text{C}$  (JMod) NMR spectrum in MeOD of L-galactoside (6).

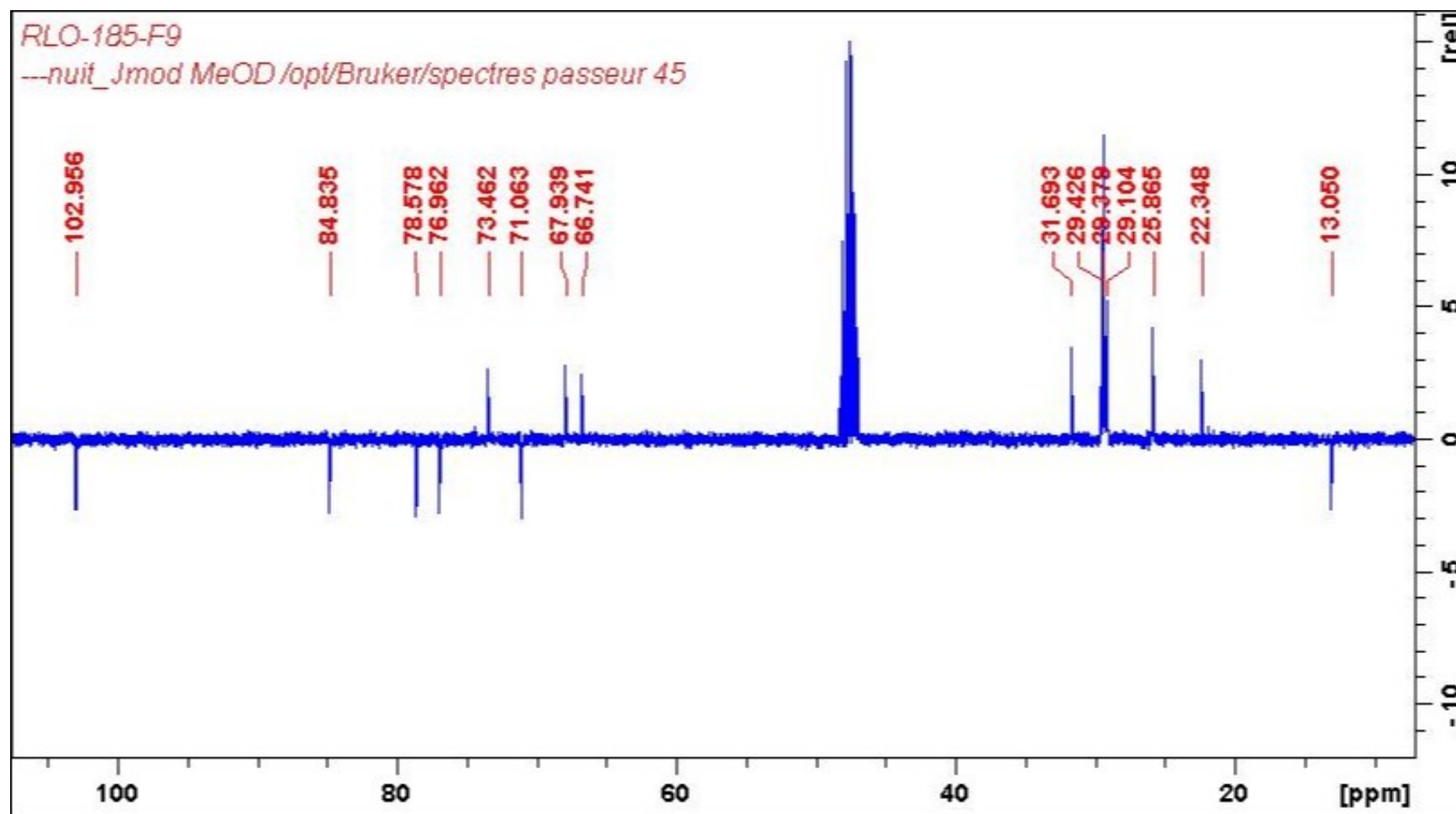


Figure S11  $^1\text{H}$  NMR spectrum in MeOD of L-galactoside (7).

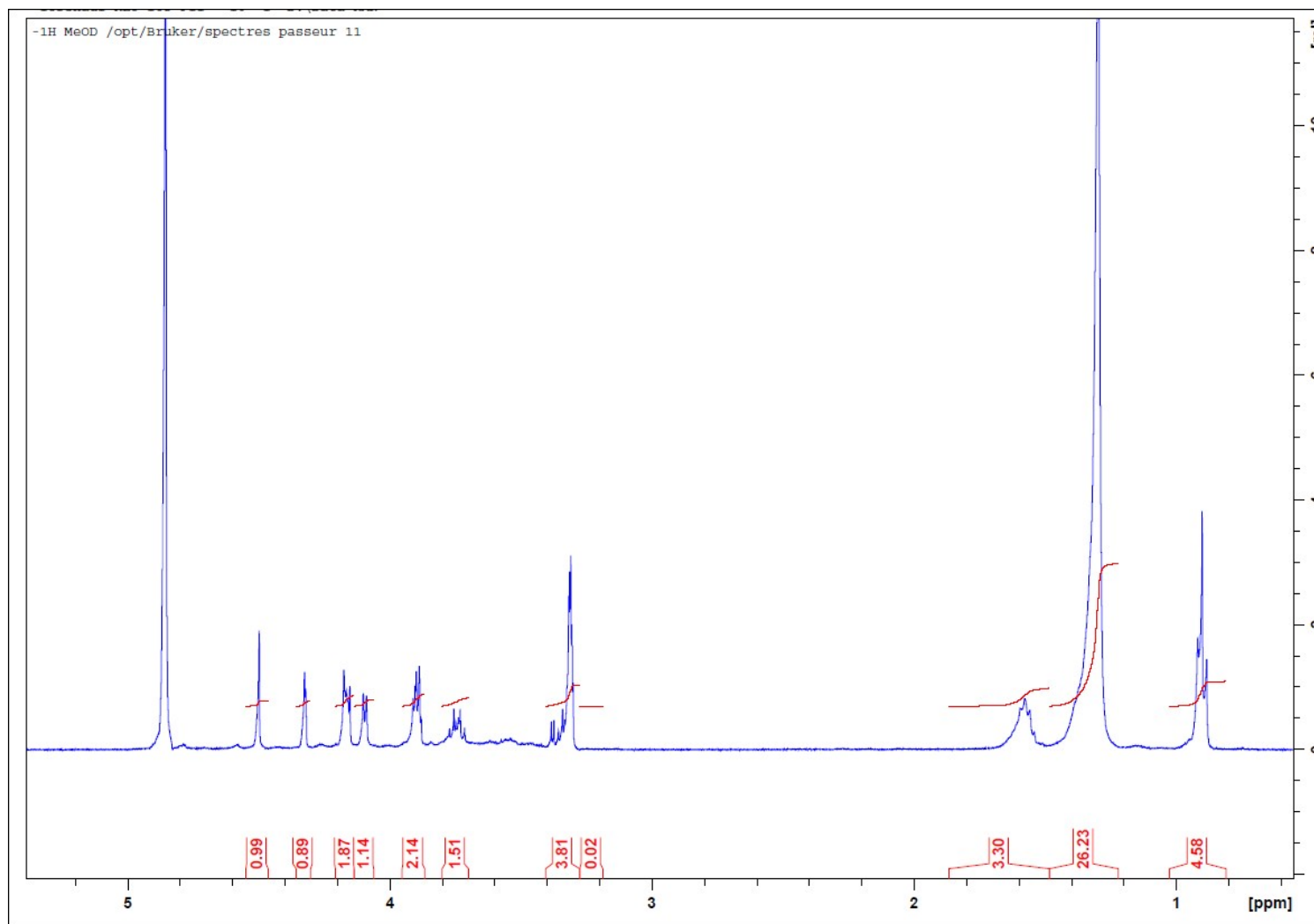
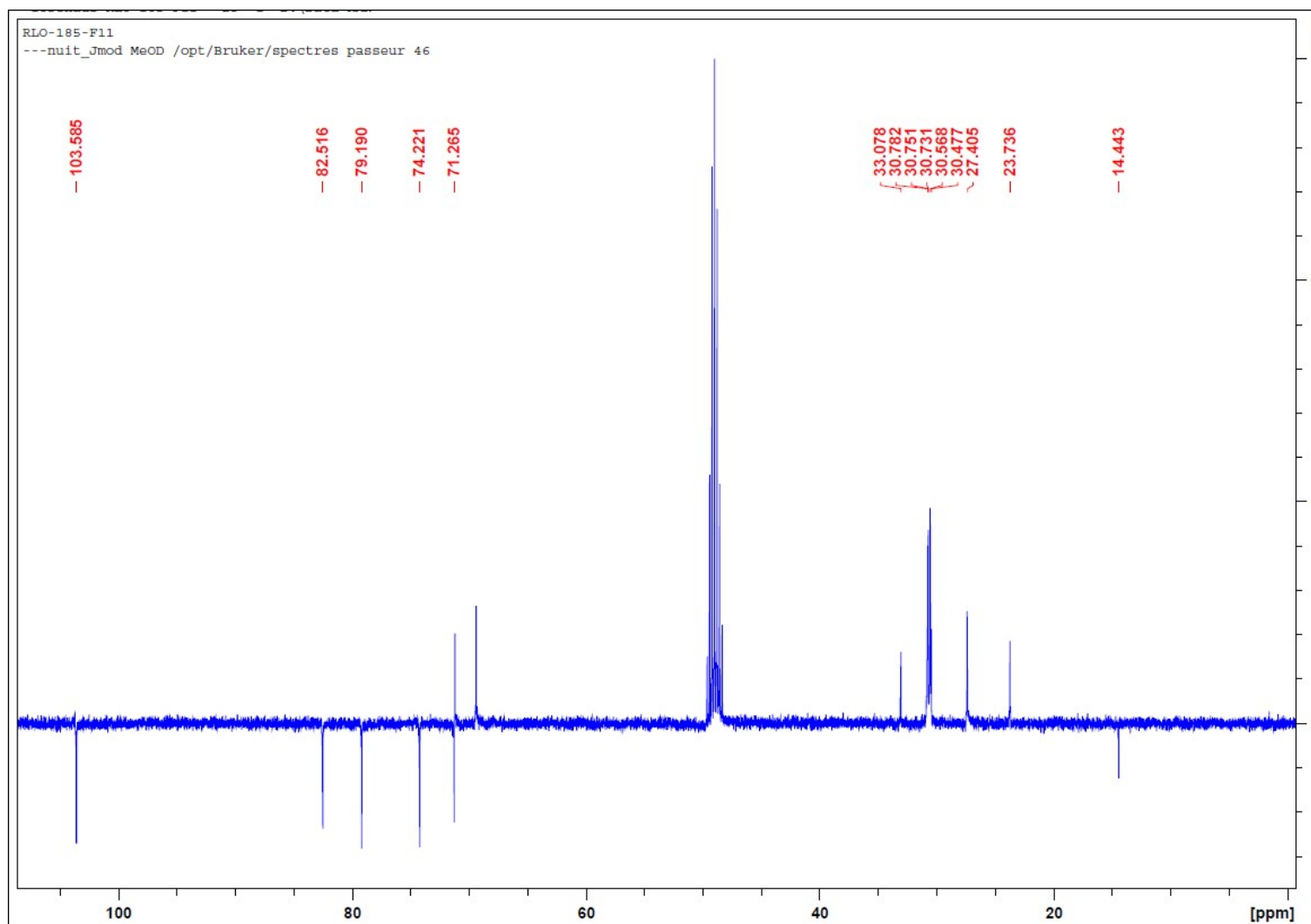




Figure S12  $^{13}\text{C}$  (JMod) NMR spectrum in MeOD of L-galactoside (7).



**Figure S13**  $^1\text{H}$  NMR spectrum in MeOD of dimeric acetal (**8**)

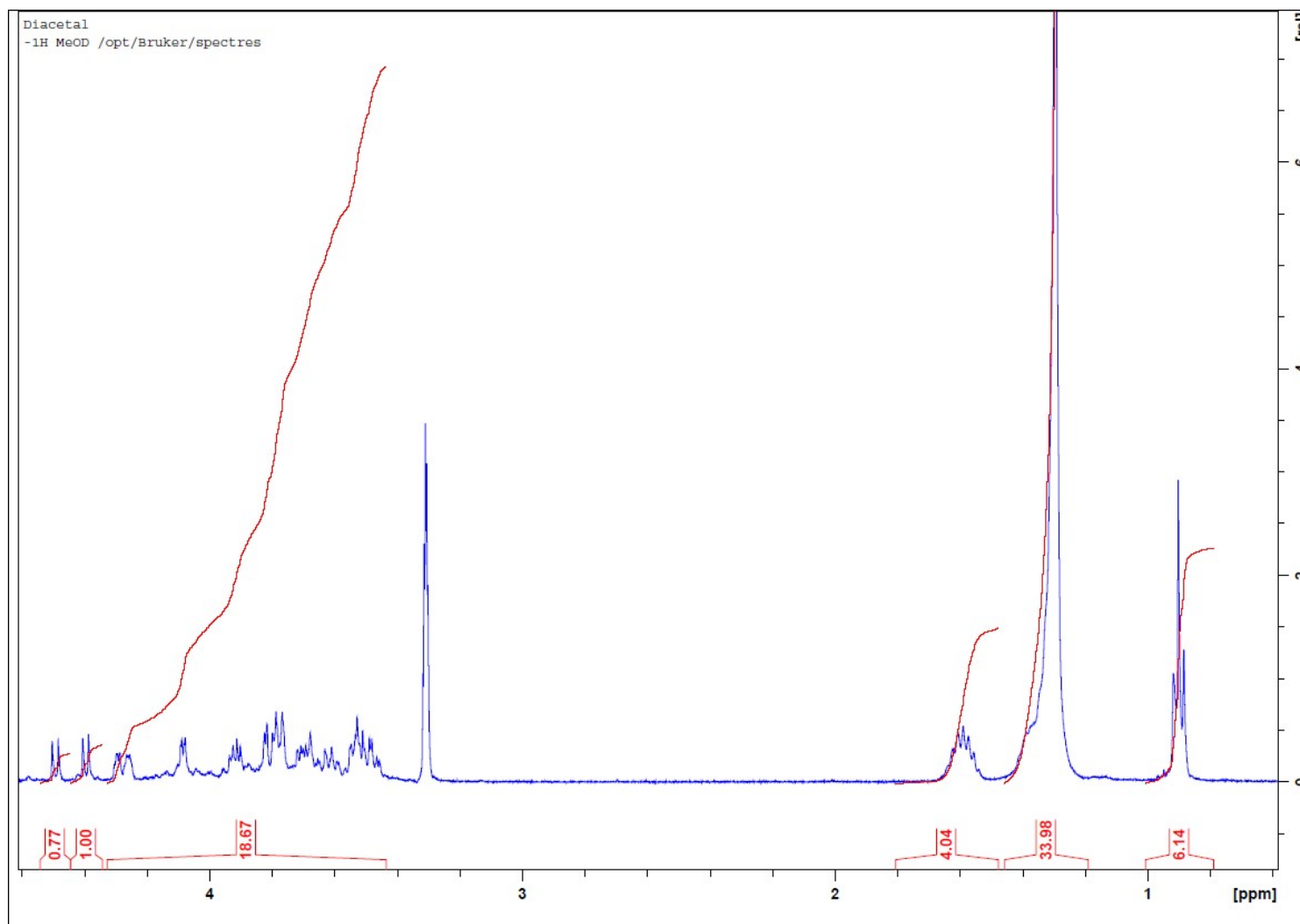
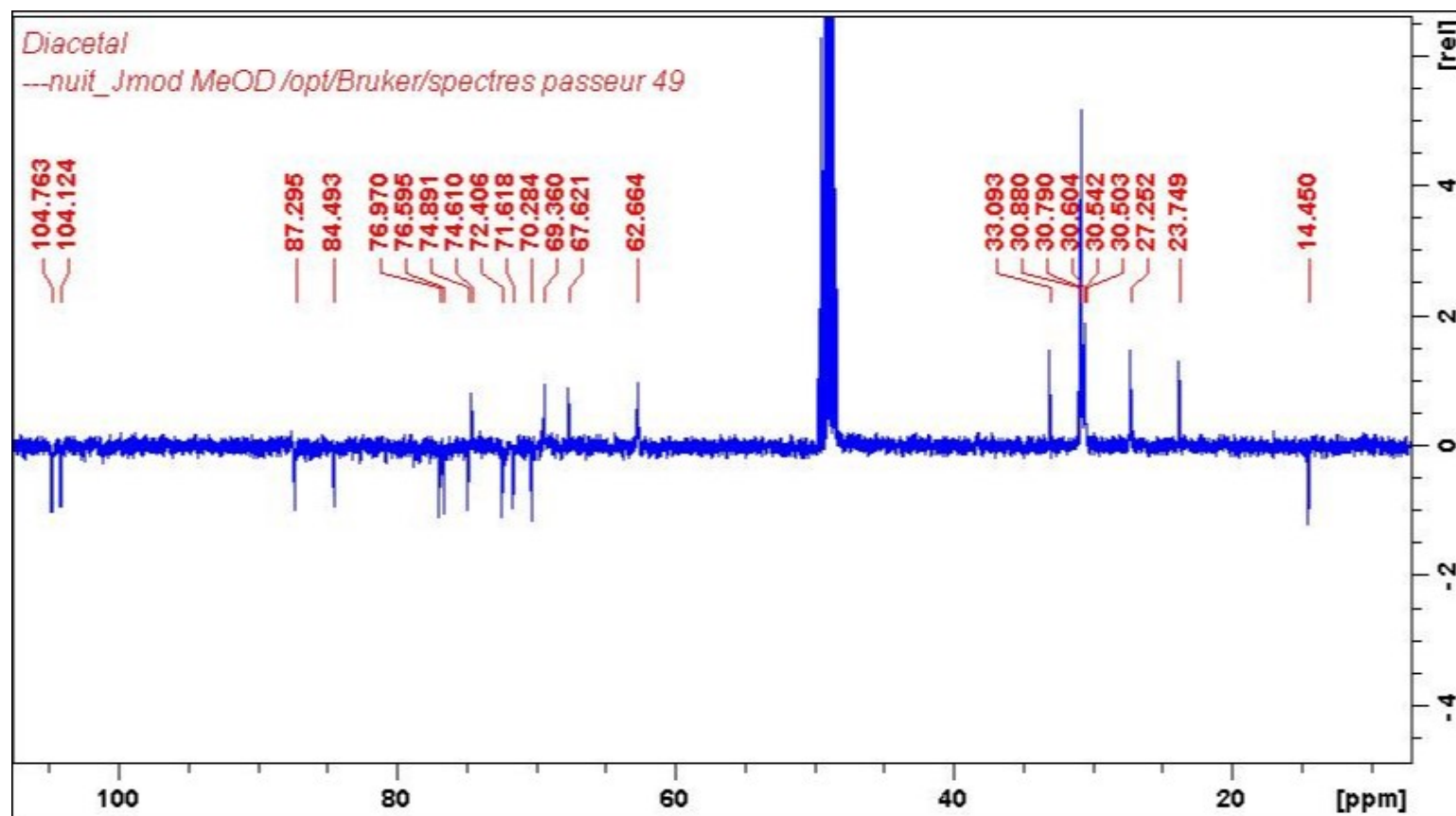
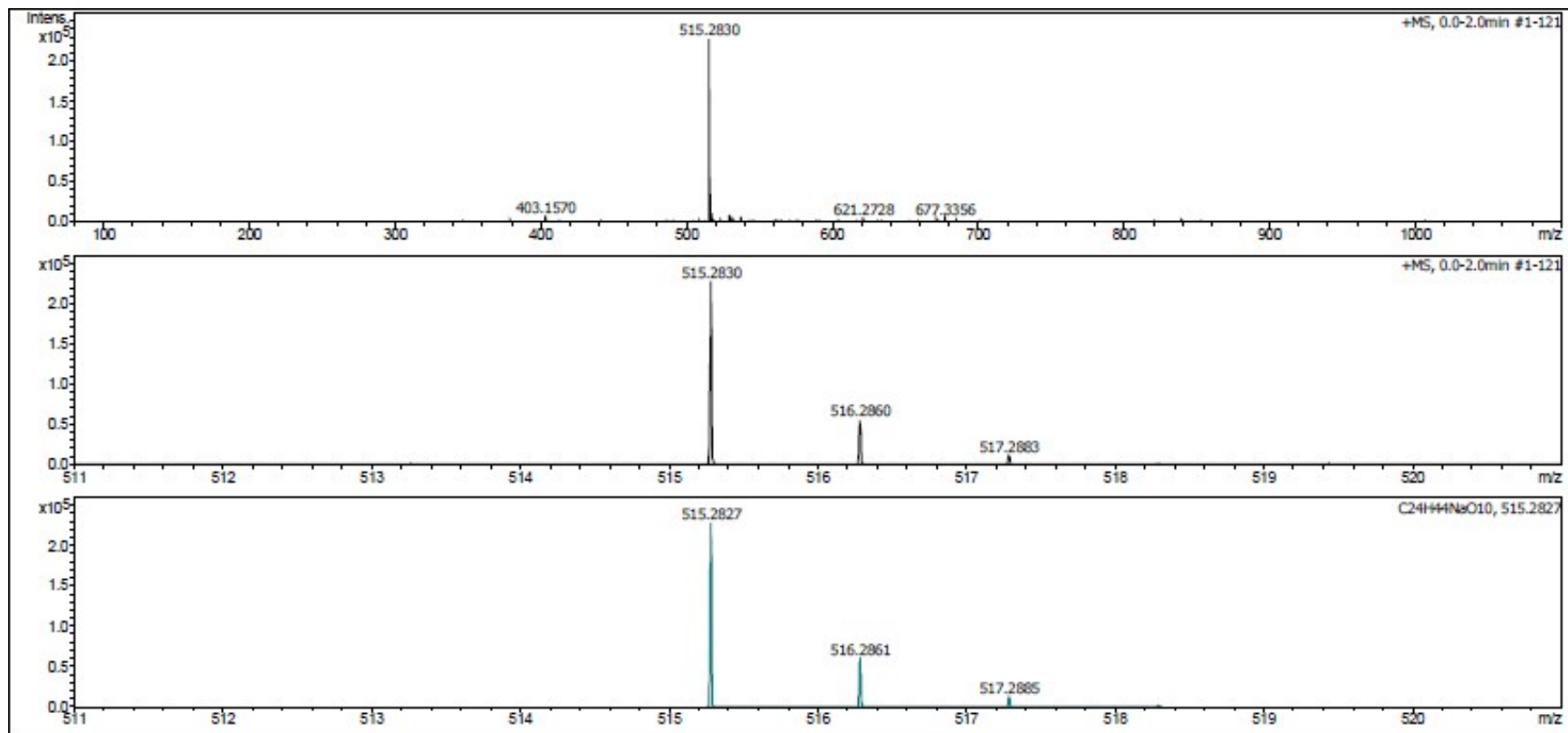


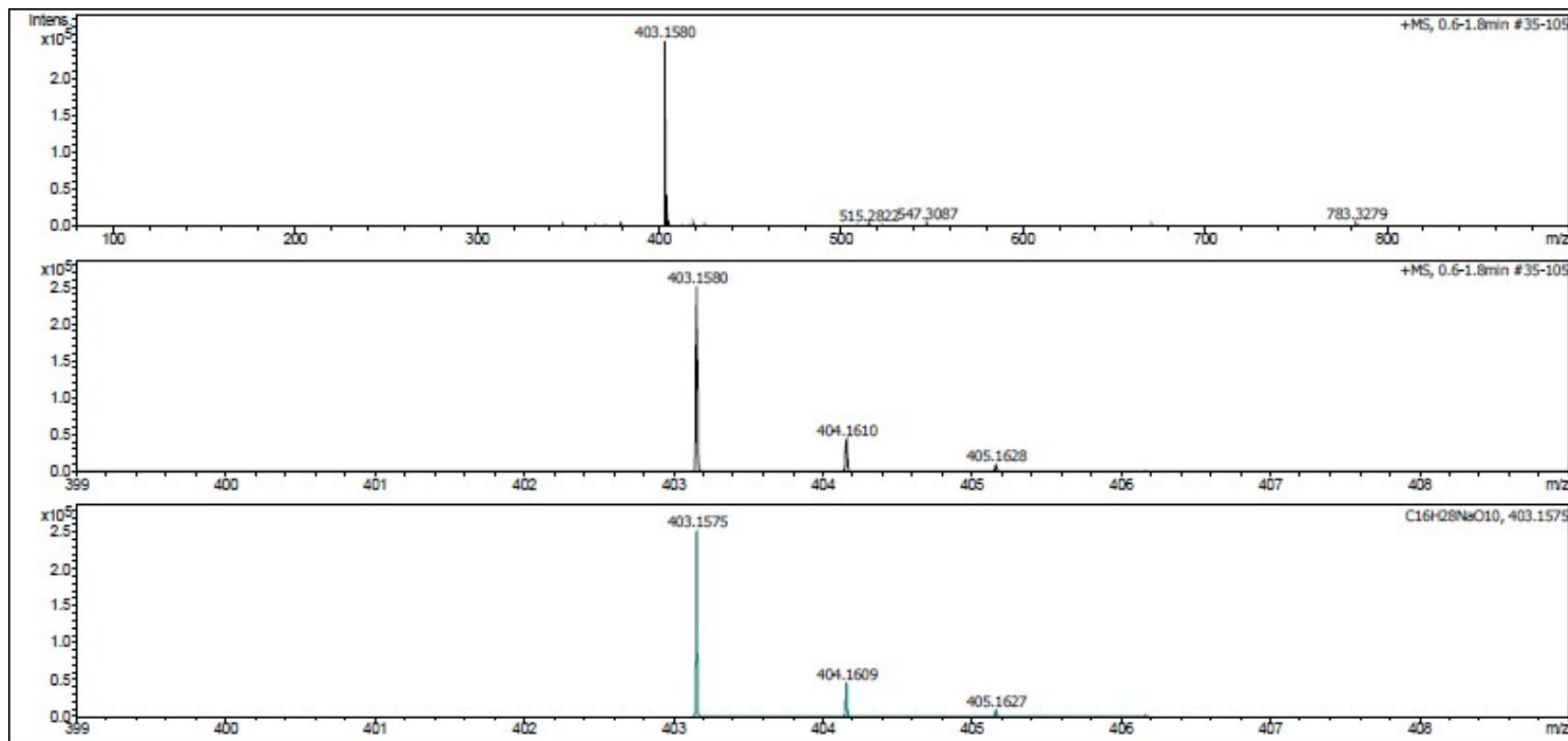
Figure S14  $^{13}\text{C}$  (JMod) NMR spectrum in MeOD of dimeric acetal (**8**)



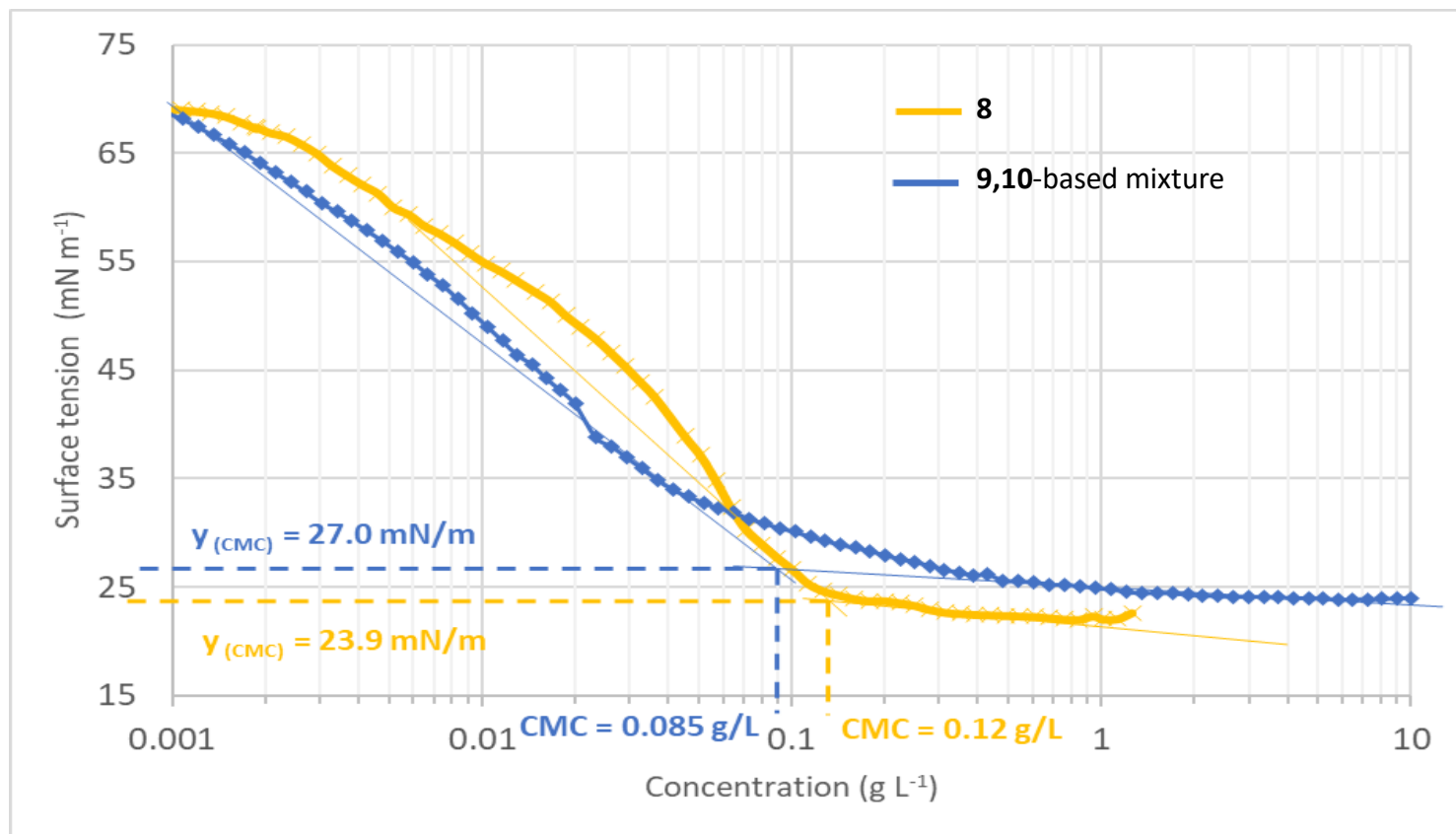
**Figure S15** Electrospray (ESI+) mass spectra of dodecyl 4-*O*-( $\beta$ -D-galactopyranosyl)-3,6-anhydro- $\alpha$ -L-galactopyranosides **9** affording the peak at  $m/z$  515.2830 corresponding to the sodium adduct ions  $[M+Na]^+$ .



**Figure S16** Electrospray (ESI+) mass spectra of dodecyl butyl 4-*O*-( $\beta$ -D-galactopyranosyl)-3,6-anhydro- $\alpha$ -L-galactopyranosides **10** affording the peak *m/z* 403.1580 corresponding to the sodium adduct ions  $[M+Na]^+$ .



**Figure S17** Curves of surface tension ( $\gamma$ ) versus log concentration (C) for disaccharide **8** and **9,10**-based mixture.



**Figure S18** Curve of surface tension ( $\gamma$ ) versus log concentration (C) for **5-10**-based surfactant composition.

