Supporting Information

Enzymatic Synthesis and Polymerization of Isosorbide-Based Monomethacrylates for High-T_g Plastics

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Experimental

Alternative Synthesis of D-Isosorbide 5-Methacrylate **M1** (Acyl Donor: Vinyl Methacrylate / Reaction Medium: 2-MeTHF).

Into a 100 mL flask were introduced: D-isosorbide (1.461 g, 10 mmol), 2-MeTHF (20 mL), vinyl methacrylate (2.243 g, 2.4 mL, 20 mmol), and Lipozyme RM IM (267 mg). The mixture was slowly stirred at 20 °C for 60 h. After that the ratio of the unreacted D-isosorbide and the target monoester was estimated to be approximately 3/1 by TLC. The synthesis was terminated by filtering off the enzyme. The filtrate was evaporated to remove the solvent, and the residual crude product was dissolved in EtOAc (60 mL) and washed with saturated $NaHCO_3$ solution (2x10 mL) and brine (2x10 mL). HQ (1 mg) was added to the solution, which was further dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The oily crude product was dissolved in 20 mL of EtOH (95.6%), activated charcoal (0.14 g) was added and the mixture was stirred at 20 °C for 12 h. The charcoal was filtered off using a glass filter covered with filter aid Hyflo® Super Cel® layer (CAS: 68855-54-9). An additional 1 mg of HQ was added to the EtOH solution before evaporation, which afforded 0.512 g (yield: 23.9%) of colourless oily target D-isosorbide 5-methacrylate **M1**. The purity of the product was >96% as determined by ^{1}H NMR spectroscopy; neither 2-methacrylate nor bis-methacrylate of isosorbide was detected in the product. Characterization of the product is given in the Experimental section of the current article.

D-Isosorbide 2-Methacrylate **M2** (Reaction Medium: 2-MeTHF).

The starting D-isosorbide 2-methacrylate-5-acetate **M4** (0.743 g, 2.9 mmol) containing HQMME was dissolved in 2-MeTHF (9.6 mL), and MeOH (0.4 mL) was added. To catalyze methanolysis, immobilized *Candida antarctica* lipase B (Novozym 435; 0.26 g) was introduced into the reaction flask. The process was monitored by TLC until complete conversion was reached after shaking the mixture at RT for 72 h (conversion was ~95% after 48 h incubation). The enzyme was filtered off, the filtrate was evaporated to remove the solvent, and the residual substance was chromatographed over silica gel. HQ (1 mg) was added to the collected fractions; evaporation afforded 594 mg of isosorbide 2-methacrylate **M2** (yield: 95.7%).

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.13 (dq, *J* = 1.5 and 3x1.0 Hz, 1H, H-3mZ), 5.62 (p, *J* = 4x1.5 Hz, 1H, H-3mE), 5.28 (dtd, *J* = 3.6, 2x1.0 and 0.6 Hz, 0.6, 1H, H-2n), 4.65 (ddt, *J* = 5.4, 4.4 and 2x0.5 Hz, 1H, H-4x), 4.53 (dt, *J* = 4.4 and 2x1.0 Hz, 1H, H-3x), 4.32 (dtd, *J* = 7.5, 2x6.0 and 5.4 Hz, 1H, H-5x), 4.09 (dtt, *J* = 10.7, 2x0.9 and 2x0.5 Hz, 1H, H-1x), 4.05 (dddd, *J* =

10.7, 3.6, 0.5 and 0.4 Hz, 1H, H-1n), 3.91 (dd, *J* = 9.5 and 6.0, Hz, 1H, H-6x), 3.58 (ddd, *J* = 9.7, 6.1 and 0.5 Hz, 1H, H-6n), 2.67 (d, *J* = 7.5 Hz, 1H, C5-OH), 1.94 (dd, *J* = 1.6 and 1.0 Hz, 3H, H-4m) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) δ 166.25 (C-1m), 135.60 (C-2m), 126.61 (C-3m), 85.56 (C-3), 81.94 (C-4), 78.55 (C-2), 73.58 (C-1), 73.45 (C-6), 72.28 (C-5), 18.19 (C-4m) ppm.

$[\alpha]^{20}_D$ +68.2 (c 1.1, $CHCl_3$).

IR (ATR) ν_{max} (cm^{-1}): 3433, 1717, 1636, 1161, 1084, 1049.

HRMS (ESI): calcd for $C_{10}H_{14}O_5Na$ $[M + Na]^+$ 237.0733, found 237.0733.

TLC: R_f = 0.37 (PE/EtOAc 1/1); flash chromatography eluent: PE/EtOAc 3/2.

Alternative Synthesis of D-isosorbide 2-Methacrylate-5-Acetate **M2** (Reaction Medium: ACN).

The starting D-isosorbide 2-methacrylate-5-acetate **M4** (2.23 g, 8.7 mmol) containing HQMME was dissolved in ACN (28.8 mL), and MeOH (1.2 mL) was added. To catalyze methanolysis, Novozym 435 (0.8 g) was introduced into the reaction vessel. The process was monitored by TLC until complete conversion was reached after shaking the mixture at RT for 48 h. The enzyme was filtered off, the filtrate was evaporated to remove the solvent, and the residual substance was chromatographed over silica gel. HQ (1 mg) was added to the collected fractions; evaporation afforded 1.81 g of isosorbide 2-methacrylate **M2** (yield: 97.4%). Characterization of the product is given in the former example.

D-Isosorbide 2-Methacrylate-5-Acetate **M4**.

D-Isosorbide 5-acetate **Ac4** (2.82 g, 15 mmol) was dissolved in ACN (75 mL). Methacrylic anhydride (3.08 g, 2.98 mL, 20 mmol) was added followed by Et_3N (4.05 g, 5.58 mL, 40 mmol). The mixture was stirred at RT for 48 h, MeOH (1.0 mL, 25 mmol) was added, and stirring was continued for 12 h. The mixture was evaporated to remove the solvent, the residual substance was dissolved in EtOAc (80 mL), washed with a saturated solution of $NaHCO_3$ (2x30 mL), and brine (2x20 mL). The solution was dried over anhydrous Na_2SO_4, filtered, HQMME (1 mg) was added and the solution was evaporated to dryness. The crude product was further purified by column chromatography over silica gel. Prior to evaporation of collected fractions HQMME (1 mg) was added; 3.687 g of the target diester **M4** was gained (yield: 95.9%).

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.12 (dq, *J* = 1.5 and 3x1.0 Hz, 1H, H-3mZ), 5.62 (p, *J* = 4x1.5 Hz, 1H, H-3mE), 5.26 (dddd, *J* = 3.4, 1.3, 0.9 and 0.7 Hz, 1H, H-2n), 5.16 (ddd, *J* = 6.1, 5.6 and 5.4 Hz, 1H, H-5x), 4.86 (ddt, *J* = 5.4, 4.6 and 2x0.5 Hz, 1H, H-4x), 4.54 (dt, *J* = 4.6 and

2x0.9 Hz, 1H, H-3x), 4.05 (dd, *J* = 10.7 and 3.4 Hz, 1H, H-1n), 4.03 (ddd, *J* = 10.7, 1.3 and 0.9 Hz, 1H, H-1x), 3.97 (dd, *J* = 9.7 and 6.1 Hz, 1H, H-6x), 3.82 (ddd, *J* = 9.7, 5.6 and 0.6 Hz, 1H, H-6n), 2.17 (s, 3H, H-2a), 1.94 (dd, *J* = 1.6 and 1.0 Hz, 3H, H-4m) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) δ 170.43 (C-1a), 166.32 (C-1m), 135.61 (C-2m), 126.62 (C-3m), 85.82 (C-3), 80.69 (C-4), 78.17 (C-2), 73.97 (C-5), 73.46 (C-1), 70.10 (C-6), 20.68 (C-2a), 18.18 (C-4m) ppm.

$[\alpha]^{20}_D$ +123.0 (c 1.3, $CHCl_3$).

IR (ATR) ν_{max} (cm^{-1}): 1721, 1636, 1373, 1238, 1161, 1096.

HRMS (ESI): calcd for $C_{12}H_{16}O_6Na$ $[M + Na]^+$ 279.0839, found 279.0840.

TLC: R_f = 0.40 (PE/EtOAc 2/1); flash chromatography eluent: PE/EtOAc 5/1.

D-Isosorbide 2-Acetate-5-Methacrylate **M3**.

D-Isosorbide 5-methacrylate **M1** (2.57 g, 12 mmol) containing ca 200 ppm of HQ was dissolved in ACN (60 mL). Acetic anhydride (2.45 g, 2.27 mL, 24 mmol) was added on stirring followed by Et_3N (4.86 g, 6.7 mL, 48 mmol). The mixture was stirred at RT for 24 h, then the conversion was almost complete by TLC. MeOH (2 mL, 50 mmol) was added, and the mixture was allowed to stir overnight (14 h). The mixture was evaporated to remove the solvent, the residual substance was dissolved in EtOAc (80 mL), and washed with saturated $NaHCO_3$ solution (3x30 mL), and brine (2x20 mL). The solution was dried over anhydrous Na_2SO_4, filtered, and HQ (2 mg) was added. After evaporation to dryness, the target diester was purified by short-column chromatography over silica gel (2 mg of HQMME was added to the collected fractions prior to evaporation) to afford a pure product **M3** (2.87 g, yield: 93.2%).

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.17 (dq, *J* = 1.5 and 3x 1.0 Hz, 1H, H-3mZ), 5.63 (p, *J* = 4x1.5 Hz, 1H, H-3mE), 5.22 (td, *J* = 2x5.7 and 4.7 Hz, 1H, H-5x), 5.19 (dtd, *J* = 3.4, 2x0.9 and 0.7 Hz, 1H, H-2n), 4.90 (dddd, *J* = 5.6, 4.9, 0.7 and 0.5 Hz, 1H, H-4x), 4.50 (dt, *J* = 4.9 and 2x0.9 Hz, 1H, H-3x), 3.97 (m, 1H, H-1x), 3.96 (m, 1H, H-1n), 3.94 (dd, *J* = 10.1 and 5.7 Hz, 1H, H-6x), 3.90 (ddt, *J* = 10.1, 4.8 and 2x0.5 Hz, 1H, H-6n), 2.08 (s, 3H, H-2a), 1.97 (dd, *J* = 1.6 and 1.0 Hz, H-4m) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) δ 170.20 (C-1a), 166.57 (C-1m), 135.56 (C-2m), 126.96 (C-3m), 85.91 (C-3), 80.85 (C-4), 77.97 (C-2), 74.01 (C-5),73.30 (C-1), 70.66 (C-6), 20.90 (C-2a), 18.36 (C-4m) ppm.

$[\alpha]^{20}_D$ +97.1 (*c* 1.6, $CHCl_3$).

IR (ATR) ν_{max} (cm^{-1}): 1736, 1636, 1373, 1234, 1165, 1096.

HRMS (ESI): calcd for $C_{12}H_{16}O_6Na$ $[M + Na]^+$ 279.0839, found 279.0839.

TLC: R_f = 0.40 (PE/EtOAc 1/1); flash chromatography eluent: PE/EtOAc 5/1.

D-Isosorbide 2-Laurate-5-Methacrylate **M5**.

D-Isosorbide 5-methacrylate **M1** (2.10 g, 9.8 mmol) was dissolved in ACN (30 mL), vinyl laurate (2.88, 3.30 mL, 12.74 mmol) was added followed by catalyst Novozym 435 (2.0 g). After incubation of the mixture at 55 °C for 48 h on stirring, the enzyme was filtered off. The filtrate was evaporated to dryness, and the target diester was purified by short column chromatography over silica gel to afford 2.241 g (yield: 57.7%) of the target compound **M5**.

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.17 (dq, *J* = 1.5 and 3x 1.0 Hz, 1H, H-3mZ), 5.63 (p, *J* = 4x1.5 Hz, 1H, H-3mE), 5.21 (td, *J* = 2x5.7 and 4.8 Hz, 1H, H-5x), 5.20 (m, 1H, H-2n), 4.89 (ddt, *J* = 5.4, 4.9 and 2x 0.5 Hz, 1H, H-4x), 4.49 (dt, *J* = 4.8 and 2x0.9 Hz, 1H, H-3x), 3.97 (dd, *J* = 10.7 and 3.2 Hz, 1H, H-1n), 3.96 (dd, *J* = 10.0 and 5.7 Hz, 1H, H-6x), 3.95 (ddd, *J* = 10.7, 1.2 and 0.9 Hz, 1H, H-1x), 3.89 (dddd, *J* = 10.0, 4.8, 0.5 and 0.3 Hz, 1H, H-6n), 2.31 (dd, *J* = 7.9 and 7.3 Hz, 2H, H-2l), 1.97 (dd, *J* = 1.5 and 1.0 Hz, 3H, H-4m), 1.60 (m, 2H, H-3l), 1.30-1.23 (m, 16H, H-4l – H-11l), 0.88 (t, *J* = 7.2 Hz, 3H, H-12l) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) δ 172.94 (C-1l), 166.65 (C-1m), 135.56 (C-2m), 126.41 (C-3m), 85.98 (C-3), 80.86 (C-4), 77.71 (C-2), 74.06 (C-5), 73.43 (C-1), 70.63 (C-6), 34.12 (C-2l), 31.87 (C-10l), 29.560 (C-6l), 29.55 (C-7l), 29.40 (C-5l), 29.30 (C-8l), 29.19 (C-4l), 29.03 (C-9l), 24.80 (C-3l), 22.66 (C-11l), 18.31 (C-4m), 14.12 (C-12l) ppm.

$[\alpha]^{20}_D$ +44.82 (*c* 1.1, EtOAc).

IR (ATR) ν_{max} (cm^{-1}): 1724, 1638, 1458, 1159, 1096, 758.

HRMS (ESI): calcd for $C_{22}H_{37}O_6$ $[M + H]^+$ 397.2585, found 397.2574.

TLC: R_f = 0.19 (PE/EtOAc 10/1); flash chromatography eluent: PE/EtOAc 10/0.6.

D-Isosorbide 2-Methacrylate-5-Laurate **M6**.

D-Isosorbide 5-laurate **La6** (1.774 g, 5.4 mmol) was dissolved in ACN (40 mL), methacrylic anhydride (1.249 g, 8.1 mmol) was added followed by Et_3N (1.23 g, 1.7 mL, 12.15 mmol). The mixture was stirred at RT for 48 h. TLC analysis indicated complete conversion of the starting material. MeOH (0.4 mL, 10 mmol) was added, and the mixture was stirred for further 16 h. The mixture was evaporated to remove the solvent, the residual substance was dissolved in EtOAc (70 mL), and washed with $NaHCO_3$ saturated solution (2x25 mL), and brine (2x15 mL), the solution was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. Purification of the product over silica gel afforded 1.869 g of homogeneous target compound **M6** (yield: 87.2%).

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.12 (dq, *J* = 1.5 and 3x 1.0 Hz, 1H, H-3mZ), 5.61 (p, *J* = 4x1.5 Hz, 1H, H-3mE), 5.26 (dddd, *J* = 3.1, 1.5, 0.9 and 0.6 Hz, 1H, H-2n), 5.16 (dt, *J* = 6.1 and 2x5.4 Hz, 1H, H-5x), 4.86 (ddt, *J* = 5.4, 4.7 and 2x0.5 Hz, 1H, H-4x), 4.53 (ddd, *J* = 4.7, 0.9 and 0.7 Hz, 1H, H-3x), 4.02 (dd, *J* = 10.7 and 3.1 Hz, 1H, H-1n), 4.01 (ddd, *J* = 10.7, 1.4 and 0.6 Hz, 1H, H-1x), 3.96 (dd, *J* = 9.8 and 6.0 Hz, 1H, H-6x), 3.82 (ddd, *J* = 9.8, 5.4 and 0.6 Hz, 1H, H-6n), 2.37 (m, 2H, H-2l), 1.93 (dd, *J* = 1.6 and 1.0 Hz, 3H, H-4m), 1.64 (m, 2H, H-3l), 1.34-1.23 (m, 16H, H-4l – H-11l), 0.88 (t, *J* = 7.2 Hz, 3H, H-12l) ppm.

^{13}C NMR (200 MHz, $CDCl_3$) δ 173.26 (C-1l), 166.32 (C-1m), 135.60 (C-2m), 126.59 (C-3m), 85.84 (C-3), 80.71 (C-4), 78.17 (C-2), 73.71 (C-5), 73.35 (C-1), 70.29 (C-6), 33.92 (C-2l), 31.87 (C-10l), 29.56, 29.56, 29.41, 29.30, 29.22 (C-(4l-8l)), 29.03 (C-9l), 24.83 (C-3l), 22.66 (C-11l), 18.18 (C-4m), 14.11 (C-12l) ppm.

$[\alpha]^{20}_D$ +81.2 (*c* 1.2, EtOAc).

IR (ATR) ν_{max} (cm^{-1}): 1724, 1636, 1458, 1157, 1096, 756.

HRMS (ESI): calcd for $C_{22}H_{37}O_6$ $[M + H]^+$ 397.2585, found 397.2569.

TLC: R_f = 0.16 (PE/EtOAc 10/1); flash chromatography eluent: PE/EtOAc 10/0.7.

D-Isosorbide 2-Cyclohexanecarboxylate-5-Methacrylate **M7**.

D-Isosorbide 5-methacrylate **M1** (2.057 g, 9.6 mmol) was dissolved in ACN (50 mL), Et_3N (5 mL) was added to the solution. Cyclohexanecarbonyl chloride (1.7 g, 1.55 mL, 11.6 mmol) was added dropwise on stirring at RT. Stirring was continued at RT ovenight (16 h); TLC analysis indicated incomplete conversion. An additional quantity of cyclohexanecarbonyl chloride (0.66 g, 0.6 mL, 4.5 mmol) was added and stirring was continued for additional 24 h. MeOH (0.8 mL, 20 mmol) was added, and the mixture was allowed to stir for another 3 h. The reaction mixture was evaporated to remove the solvent, EtOAc (80 mL) was added to the residual substance, and the solution obtained was washed with saturated $NaHCO_3$ solution (2x30 mL), and brine (2x15 mL). The solution was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The product was recrystallized from EtOH (20 mL) at -6 °C to afford 1.911 g of the target diester **M7** (yield: 61.4%).

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.17 (dq, *J* = 1.6 and 3x1.0 Hz, 1H, H-3mZ), 5.630 (p, *J* = 4x1.5 Hz, 1H, H-3mE), 5.21 (td, *J* = 2x5.6 and 4.9 Hz, 1H, H-5x), 5.19 (dddd, *J* = 3.4, 1.2, 0.9 and 0.7 Hz, 1H, H-2n), 4.891 (ddt, *J* = 5.3, 4.8 and 2x0.5 Hz, 1H, H-4x), 4.47 (dt, *J* = 4.8 and 2x0.9 Hz, 1H, H-3x), 3.97 (dd, *J* = 10.6 and 3.4 Hz, 1H, H-1n), 3.96 (dd, *J* = 10.0 and 5.8 Hz, 1H, H-6x), 3.93 (dt, *J* = 10.6 and 2x0.9 Hz, 1H, H-1x), 3.89 (ddt, *J* = 10.0, 5.1 and 2x0.5 Hz, 1H, H-6n), 2.30 (tt, *J* = 2x11.3 and 2x 3.6 Hz, 1H, H-1c), 1.97 (dd, *J* = 1.6 and 1.0 Hz, 3H, H-4m),

1.87 and 1.42 (m, 2+2H, H-2,6c, eq and ax), 1.74 and 1.27 (m, 2+2H, H-3,5c, eq and ax), 1.64 and 1.22 (m, 2H, H-4c, eq and ax) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) δ 175.14 (COc), 166.66 (C-1m), 135.56 (C-2m), 126.40 (C-3m), 85.98 (C-3), 80.84 (C-4), 77.50 (C-2), 74.10 (C-5), 73.47 (C-1), 70.57 (C-6), 42.85 (C-1c), 28.80/28.78 (C-2,6c), 25.59 (C-4c), 25.24/25.23 (C-3,5c), 18.31 (C-4m) ppm.

$[\alpha]^{20}_D$ +79.3 (*c* 0.6, EtOAc).

IR (ATR) ν_{max} (cm^{-1}): 1724, 1636, 1161, 1096, 756.

HRMS (ESI): calcd for $C_{17}H_{25}O_6$ $[M + H]^+$ 325.1646, found 325.1632.

TLC: R_f = 0.13 (PE/EtOAc 10/1).

D-Isosorbide 5-Acetate **Ac4** (Reaction Medium: MTBE).

D-Isosorbide (4.38 g; 30 mmol) was introduced into a 250 mL flask on magnetic stirrer, MTBE (60 mL) was added followed by vinyl acetate (12.9 g; 13.8 mL; 150 mmol) on stirring. The acetylation was started by adding a catalyst – Lipozyme RM IM (2.0 g). The reaction mixture was stirred at RT for 79 hrs. Conversion of the starting material was estimated by TLC to be ~95%. The synthesis was terminated by filtering off the enzyme. The filtrate was evaporated to dryness to afford 5.8 g of crude product, that was purified by column chromatography over silica gel. The target compound **Ac4** was gained with 88% yield (4.97 g).

^{1}H NMR (800 MHz, $CDCl_3$) δ 5.10 (dt, *J* = 6.0 and 2x5.3 Hz, 1H, H-5x), 4.81 (dddd, *J* = 5.3, 4.6, 0.6 and 0.5 Hz, 1H, H-4x), 4.36 (dt, *J* = 4.6 and 2x1.0 Hz, 1H, H-3x), 4.28 (bm, 1H, H-2n), 3.88 (dt, *J* = 10.0 and 2x0.9 Hz, 1H, H-1x), 3.88 (dd, *J* = 9.8 and 6.0 Hz, 1H, H-6x), 3.84 (dd, *J* = 10.0 and 3.3 Hz, 1H, H-1n), 3.73 (ddd, *J* = 9.8, 5.3 and 0.6 Hz, 1H, H-6n), 3.12 (bs, 1H, OH), 2.09 (s, 3H, H-2a) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) δ 170.61 (C-1a), 88.04 (C-3), 80.20 (C-4), 75.88 (C-2), 75.42 (C-1), 74.05 (C-5), 70.00 (C-6), 20.61 (C-2a) ppm.

$[\alpha]^{20}_D$ +112.92 (c 2.3, EtOAc).

TLC: R_f = 0.14 (PE/EtOAc 4/5); R_f = 0.30 (PE/EtOAc 1/4); flash chromatography eluent: PE/EtOAc 4/5.

Alternative Synthesis of D-Isosorbide 5-Acetate **Ac4** (Reaction Medium: 2-MeTHF).

D-Isosorbide (2.922 g; 20 mmol) was introduced into a 100 mL flask on magnetic stirrer, 2-MeTHF (40 mL) was added followed by vinyl acetate (8.61 g; 9.24 mL; 0.1 mol) on stirring. The acetylation was started by adding the catalyst – Lipozyme RM IM (1.34 g). The reaction mixture was stirred at RT for 72 hrs. Conversion of the starting material was estimated by TLC

to be ~99%. The synthesis was terminated by filtering off the enzyme. One half of the filtrate was evaporated to remove the solvent, and residual crude product was purified by column chromatography over silica gel. The homogeneous target compound was gained in 90.6% yield (1.71 g).

The other half of the filtrate was evaporated to dryness and the residue was dissolved in EtOAC (70 mL). The solution was washed with sat. $NaHCO_3$ (2x10 ml) and brine (2x10 ml) and dried over anhydrous Na_2SO_4. The solution was evaporated to dryness and the residue was dissolved in 20 mL of EtOH (95.6%), activated charcoal (0.14 g) was added and the mixture was stirred at 20 °C for 12 h. The charcoal was filtered off using a glass filter covered with filter aid Hyflo® Super Cel® layer and the solution was evaporated to dryness to afford 0.924 g of the target compound (yield: 49.1%) containing ca 3% of isosorbide bis-acetate and up to 1% of several minor impurities detectable by ^{1}H NMR. Thus, the purity estimated for the target compound gained after washing and decolorization with charcoal was ~96%. Characterization of the product is given in the former example.

D-Isosorbide 5-Laurate **La6**.

D-Isosorbide (2.19 g, 15 mmol) and MTBE (50 mL) were introduced into a 250 mL flask on a magnetic stirrer. Vinyl laurate (5.09 g, 5.83 mL, 22.5 mmol) was added followed by a catalyst – Lipozyme RM IM (1.0 g). The mixture was stirred for 48 h at RT. After the monitoring by TLC had confirmed the conversion rate to be higher than 90%, the process was terminated by filtering off the enzyme. The filtrate was evaporated to dryness, and the target compound was purified by flash chromatography over silica gel. Homogeneous isosorbide 5-laurate (4.523 g) was gained with 91.8% yield.

^{1}H NMR (800 MHz, $CDCl_3$) δ 5.14 (ddd, *J* = 5.9, 5.4 and 5.1 Hz, 1H, H-5x), 4.84 (ddt, *J* = 5.4, 4.6 and 2x0.6 Hz, 1H, H-4x), 4.39 (dt, *J* = 4.9 and 2x0.9 Hz, 1H, H-3x), 4.31 (dtd, *J* = 3.2, 2x0.9 and 0.6 0.9 Hz, 1H, H-2n), 3.90 (dt, *J* = 10.0 and 2x0.9 Hz, 1H, H-1x), 3.90 (dd, *J* = 9.8 and 7.9 Hz, 1H, H-6x), 3.86 (dd, *J* = 10.1 and 3.2 Hz, 1H, H-1n), 3.76 (ddd, *J* = 9.8, 5.1 and 0.6 Hz, 1H, H-6n), 2.48 (bs, 1H, OH), 2.36 and 2.35 (m, 2H, H-2l), 1.62 (m, 2H, H-3l), 1.33-1.23 (m, 16H, H-4l – H-11l), 0.87 (t, *J* = 7.2 Hz, 3H, H-12l) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) δ 173.36 (C-1l), 88.13 (C-3), 80.28 (C-4), 76.08 (C-2), 75.39 (C-1), 73.80 (C-5), 70.27 (C-6); 33.91 (C-2l), 31.84 (C-10l), 29.55, 29.54, 29.40, 29.28, 29.20, 29.02 (C-(4l-9l)), 24.79 (C-3l), 22.63 (C-11l), 14.08 (C-12l) ppm.

$[\alpha]^{20}_D$ +68.87 (*c* 1.5, EtOAc).

TLC: R_f = 0.29 (PE/EtOAc 1/1); flash chromatography eluent: PE/EtOAc 2/1.

NMR Spectra

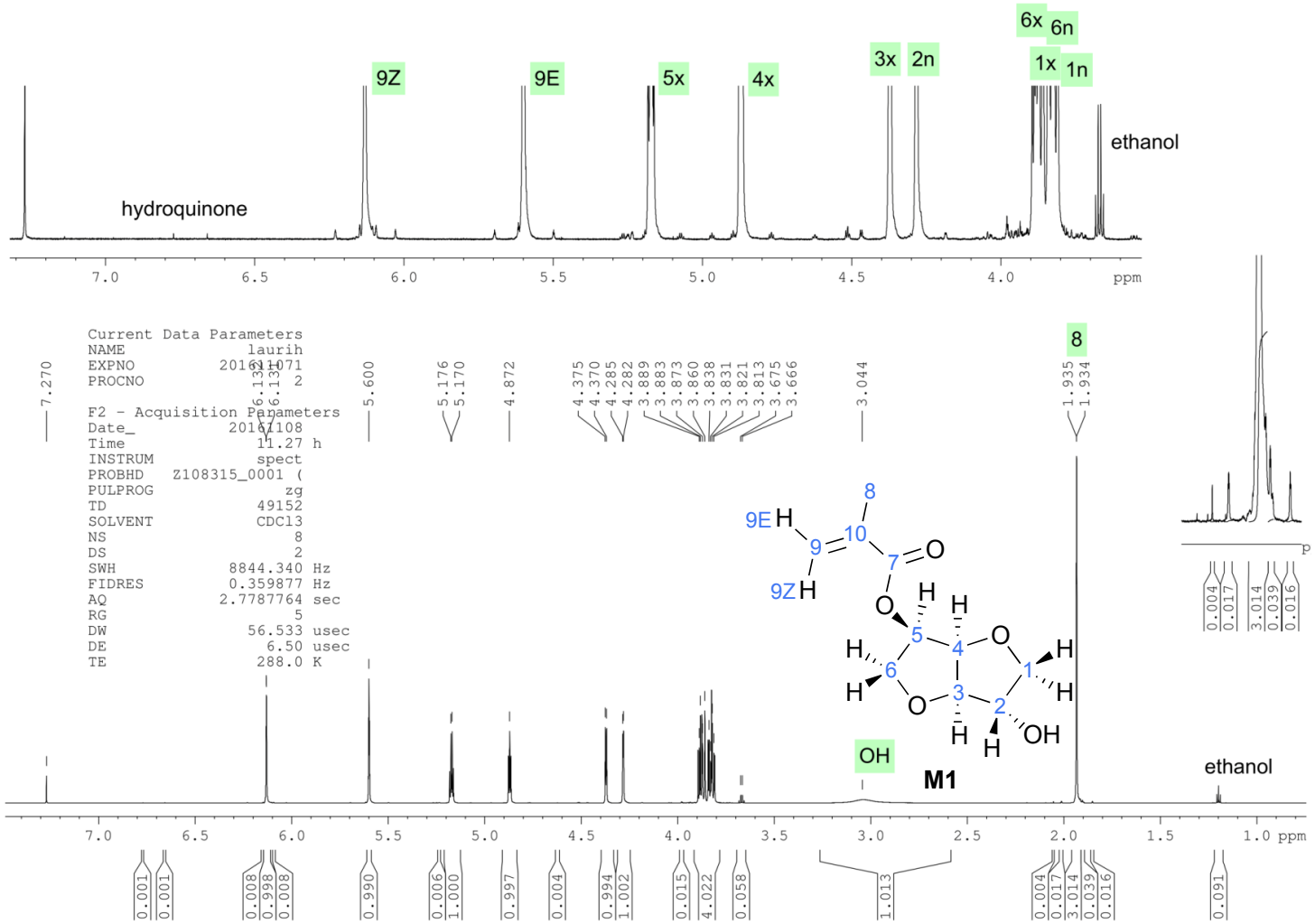

Figure S1. [1]H NMR spectrum of D-isosorbide 5-methacrylate **M1**.

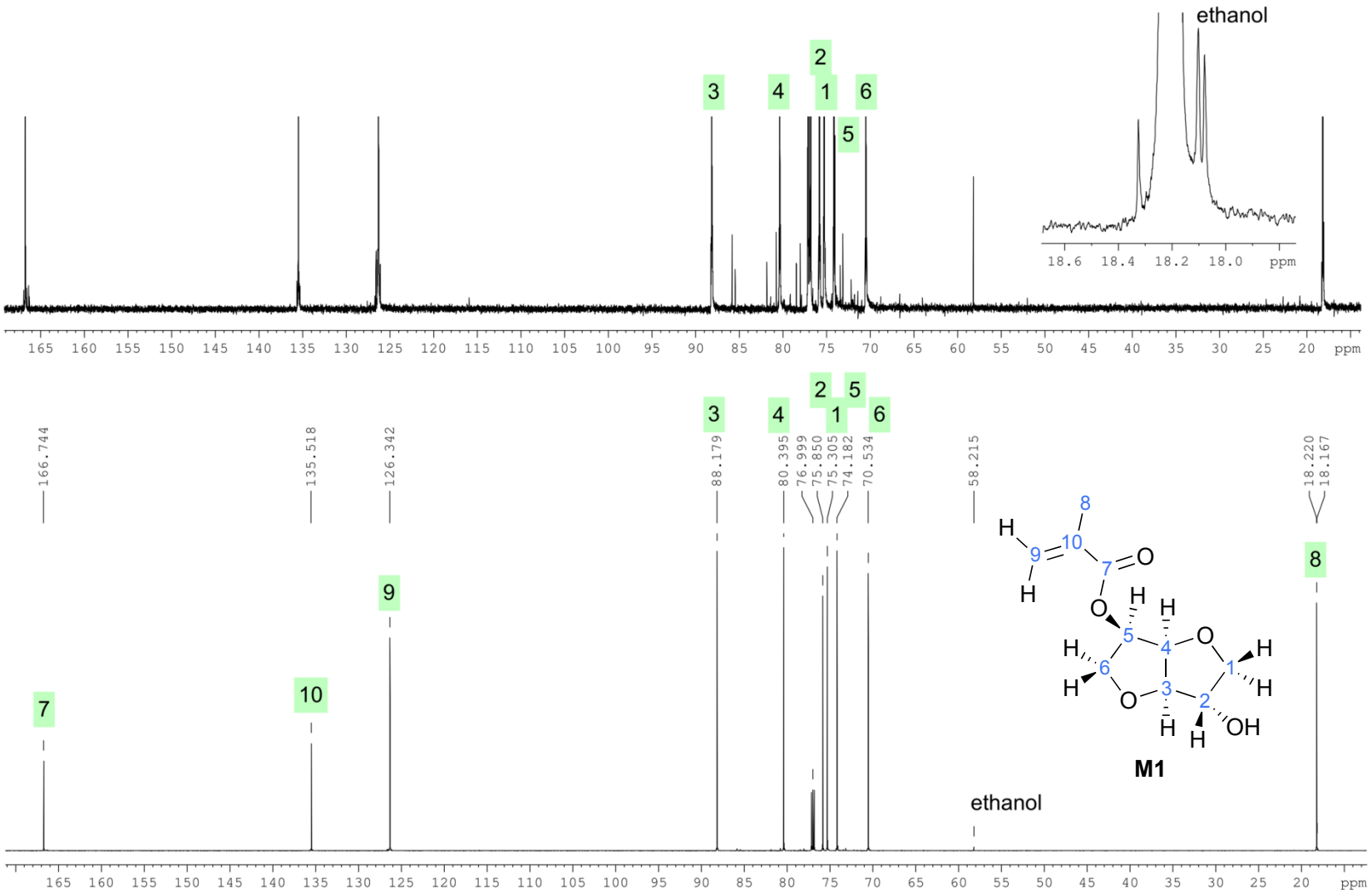

Figure S2. ^{13}C NMR spectrum of D-isosorbide 5-methacrylate **M1**.

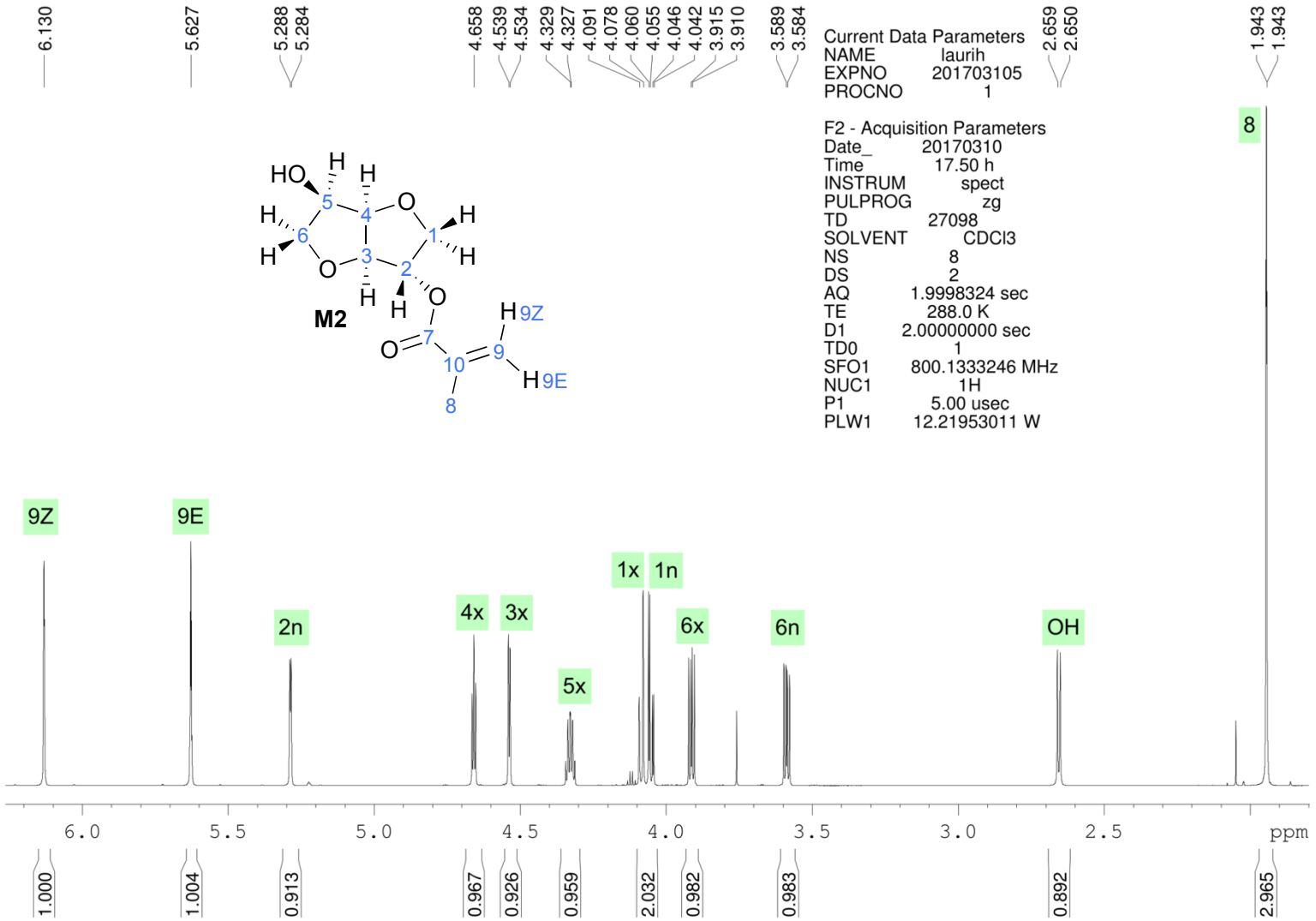

Figure S3. ^{1}H NMR spectrum of D-isosorbide 2-methacrylate **M2**.

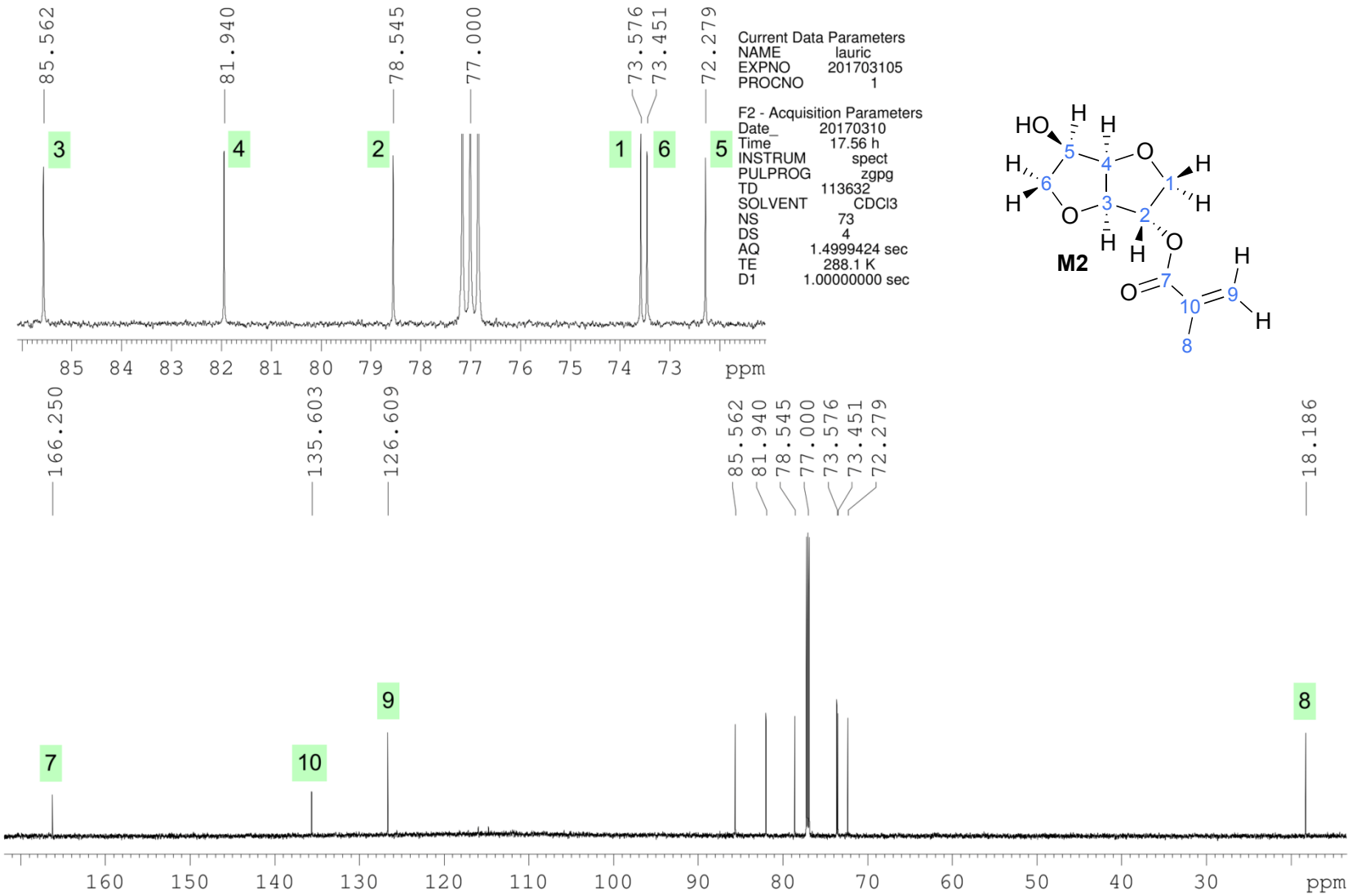

Figure S4. ^{13}C NMR spectrum of D-isosorbide 2-methacrylate **M2**.

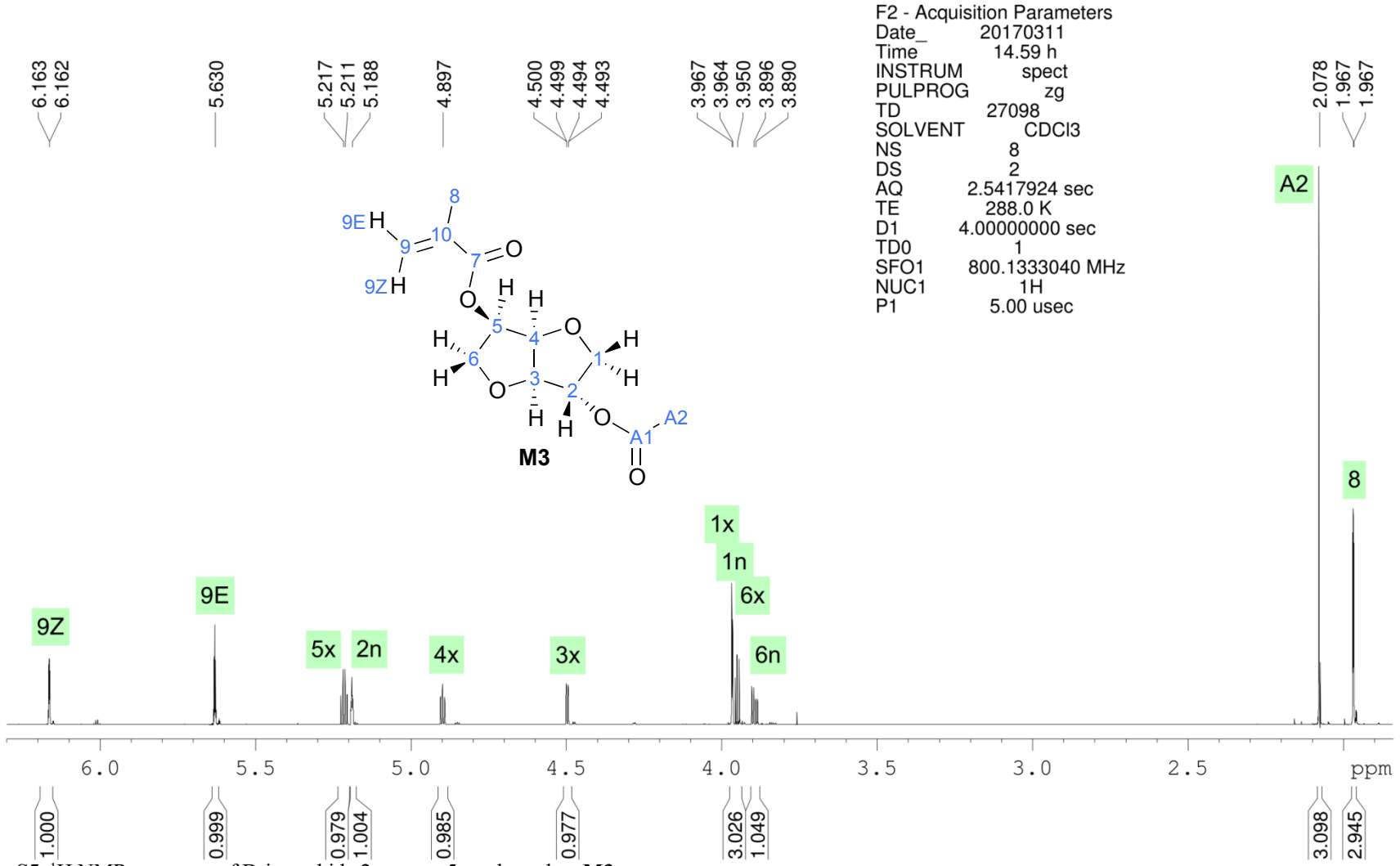

Figure S5. ^{1}H NMR spectrum of D-isosorbide 2-acetate-5-methacrylate **M3**.

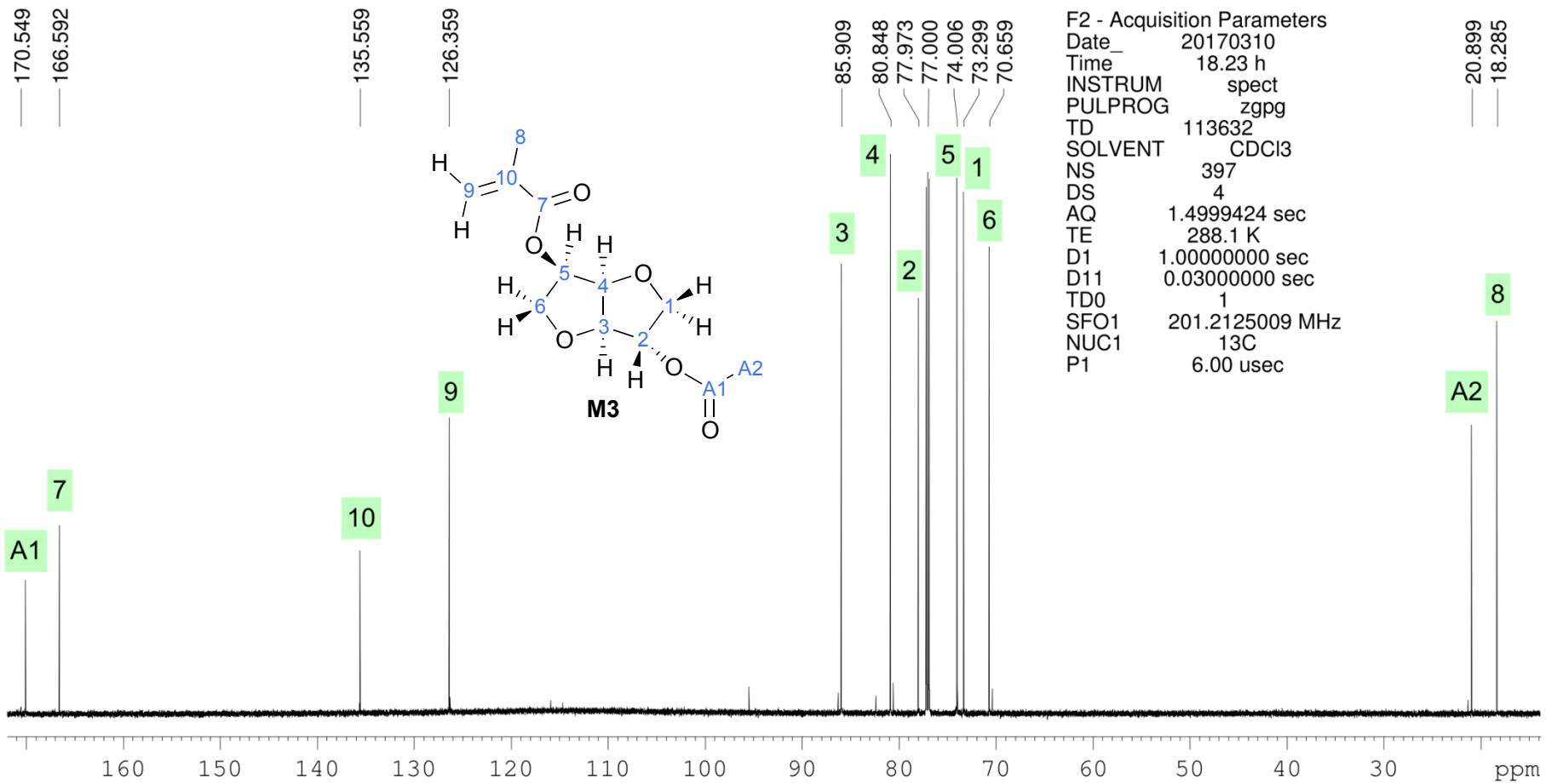

Figure S6. ^{13}C NMR spectrum of D-isosorbide 2-acetate-5-methacrylate **M3**.

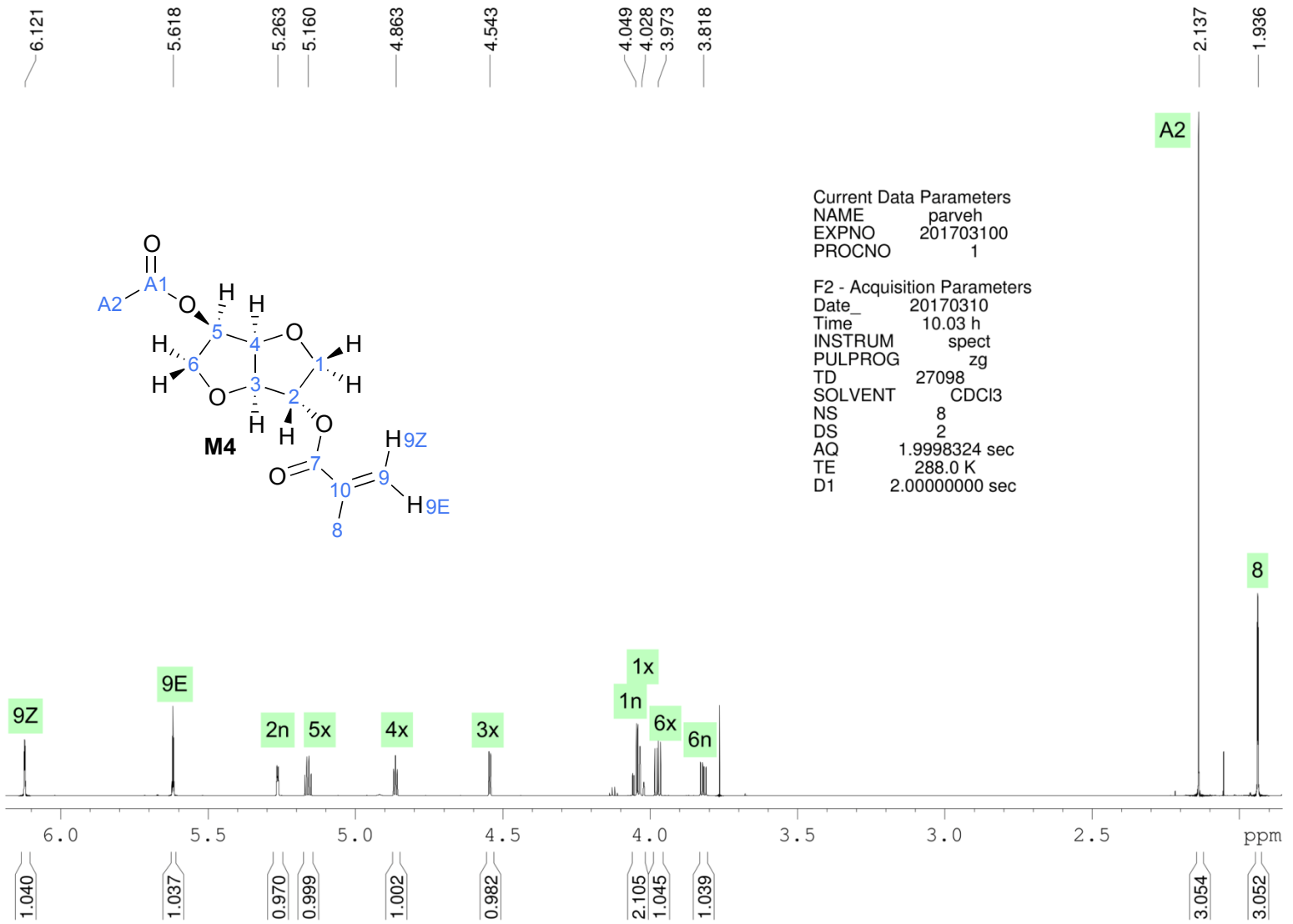

Figure S7. [1]H NMR spectrum of D-isosorbide 2-methacrylate-5-acetate **M4**.

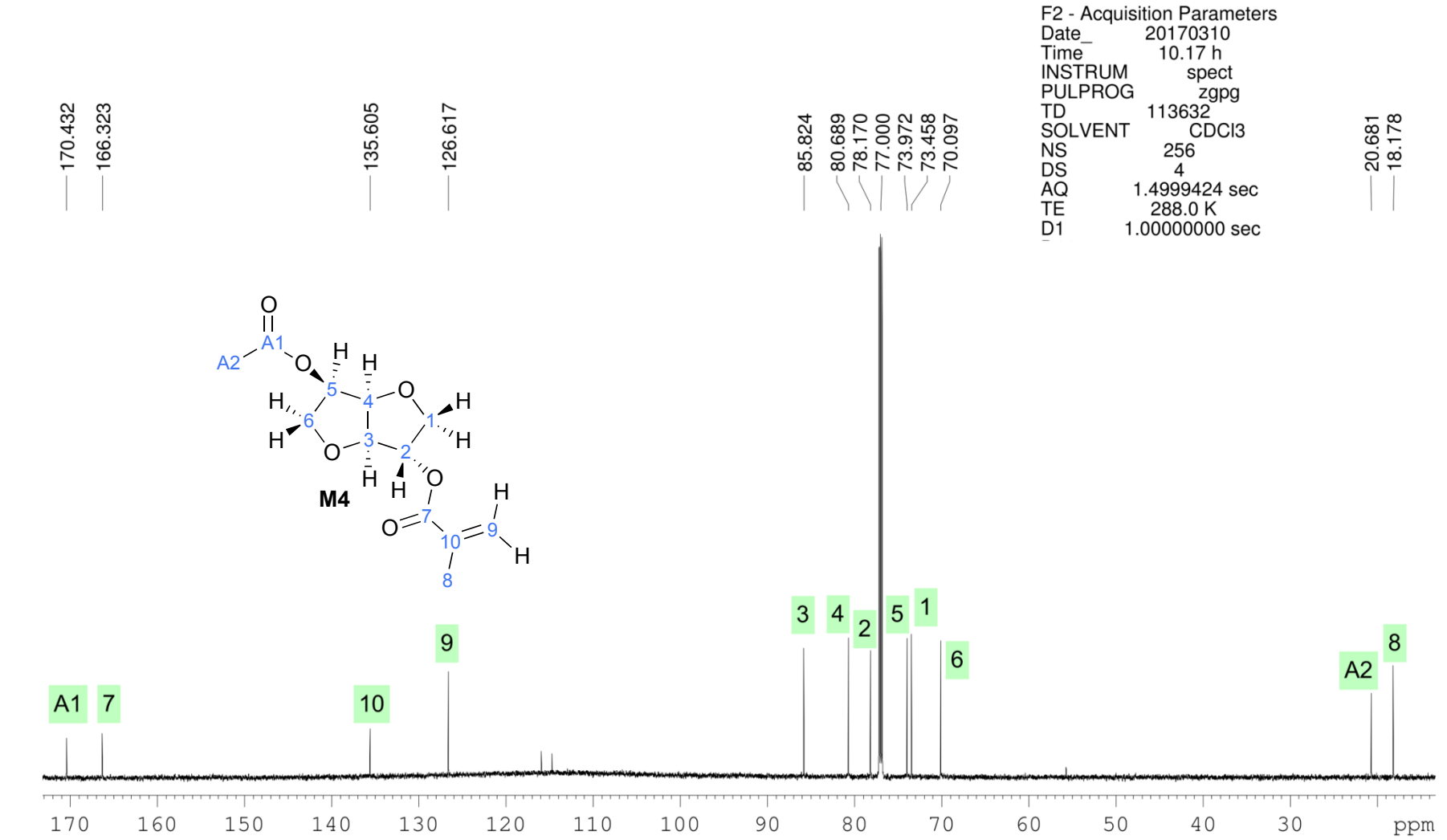

Figure S8. ^{13}C NMR spectrum of D-isosorbide 2-methacrylate-5-acetate **M4**.

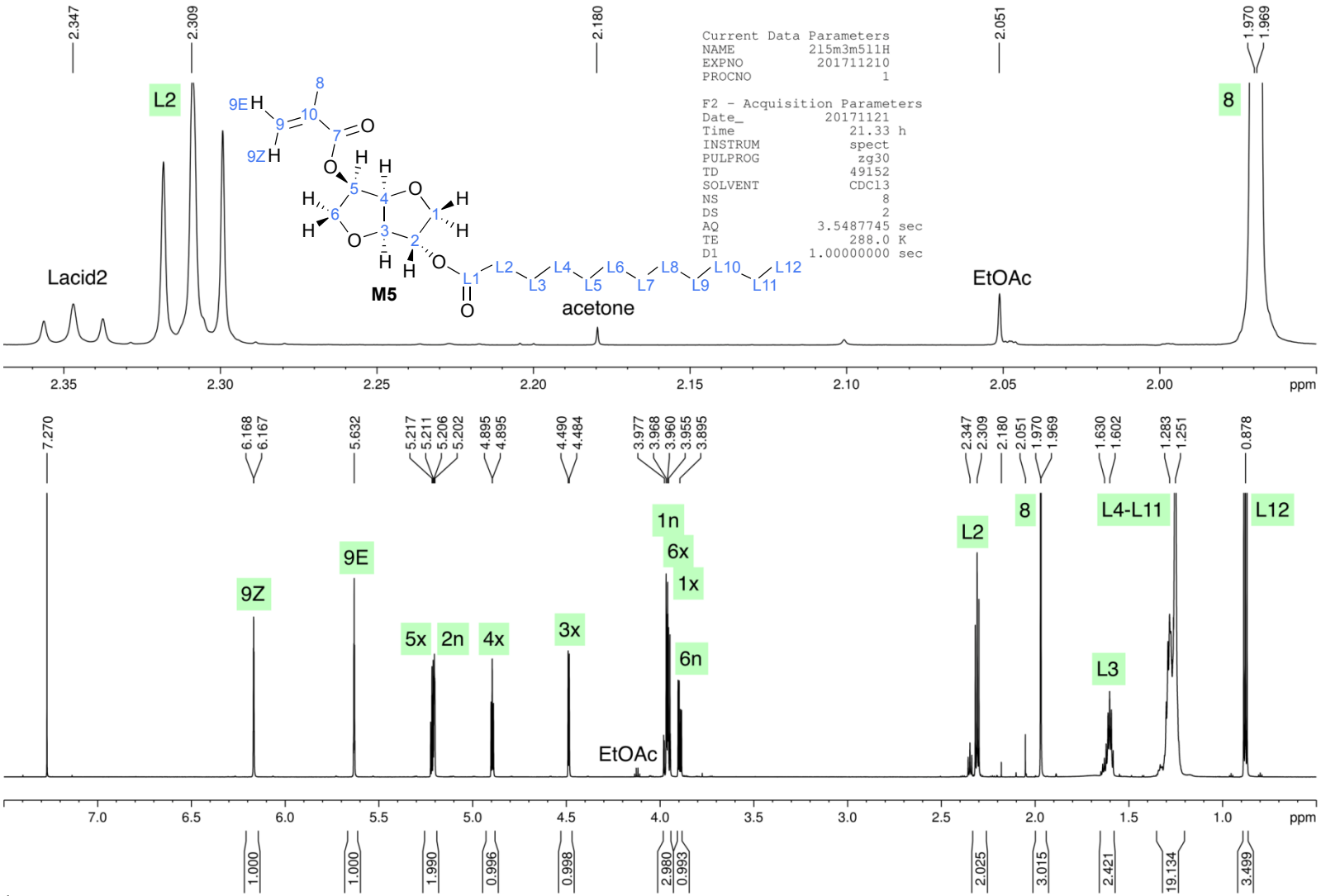

Figure S9. [1]H NMR spectrum of D-isosorbide 2-laurate-5-methacrylate **M5**.

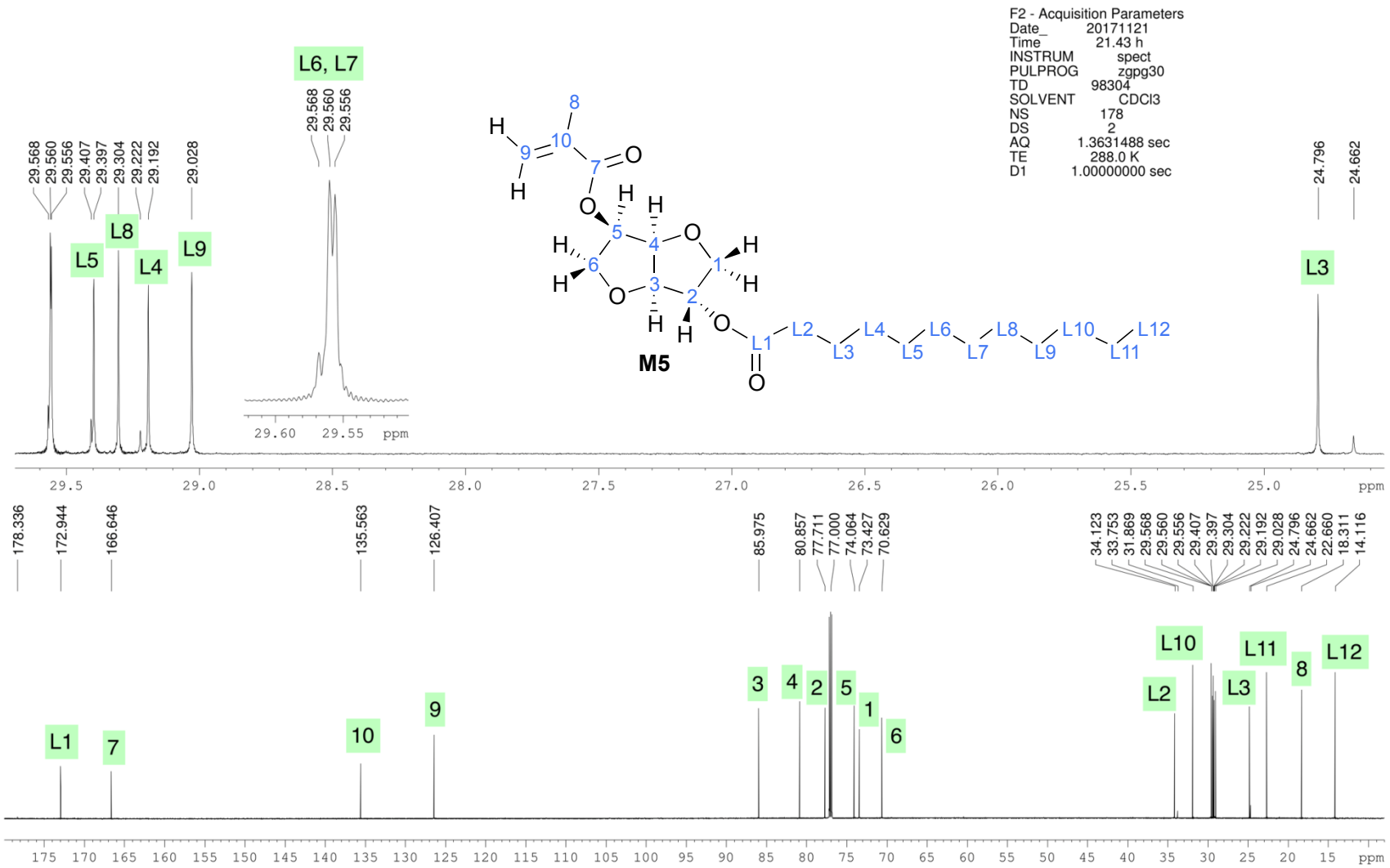

Figure S10. ^{13}C NMR spectrum of D-isosorbide 2-laurate-5-methacrylate **M5**.

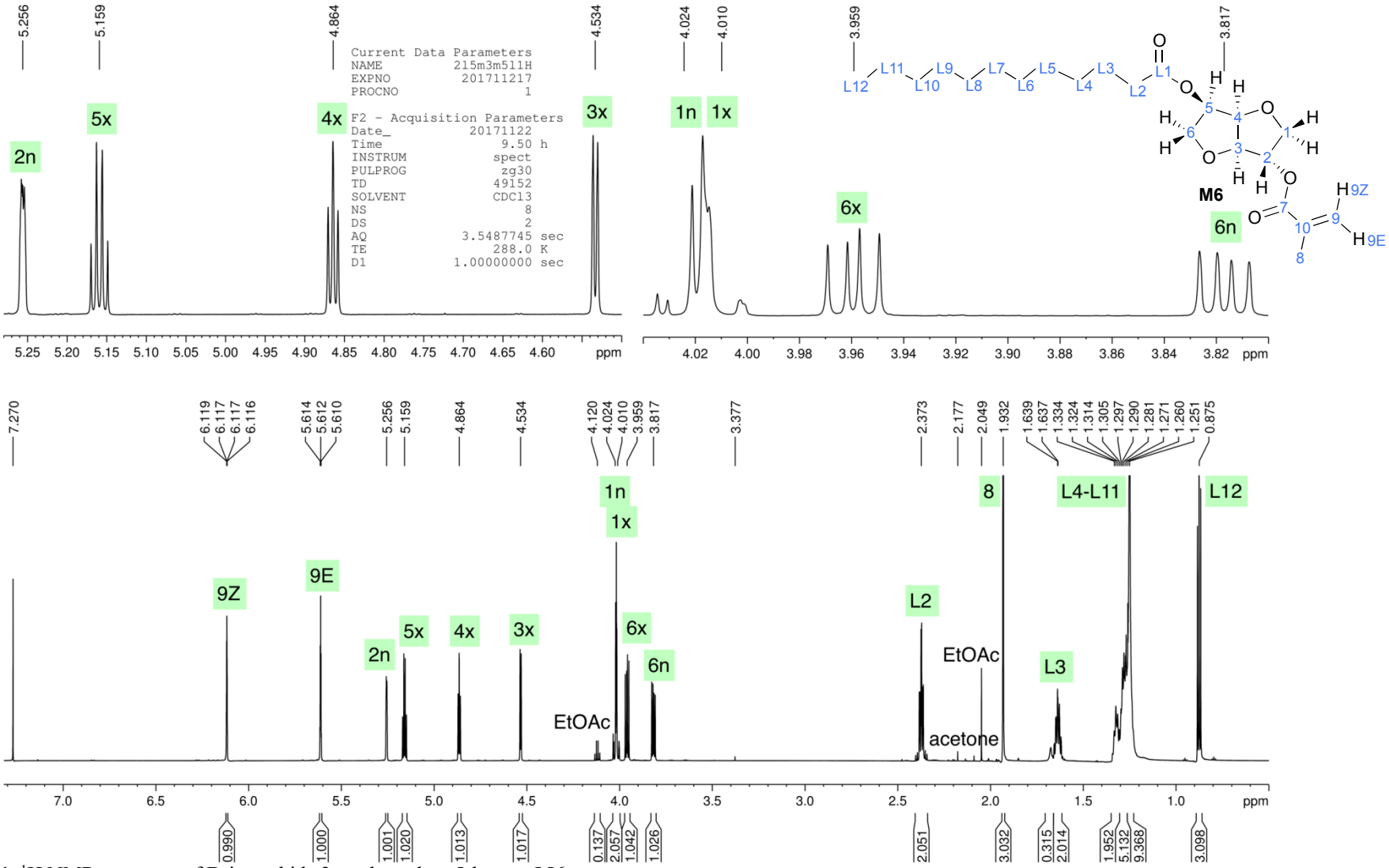

Figure S11. [1]H NMR spectrum of D-isosorbide 2-methacrylate-5-laurate **M6**.

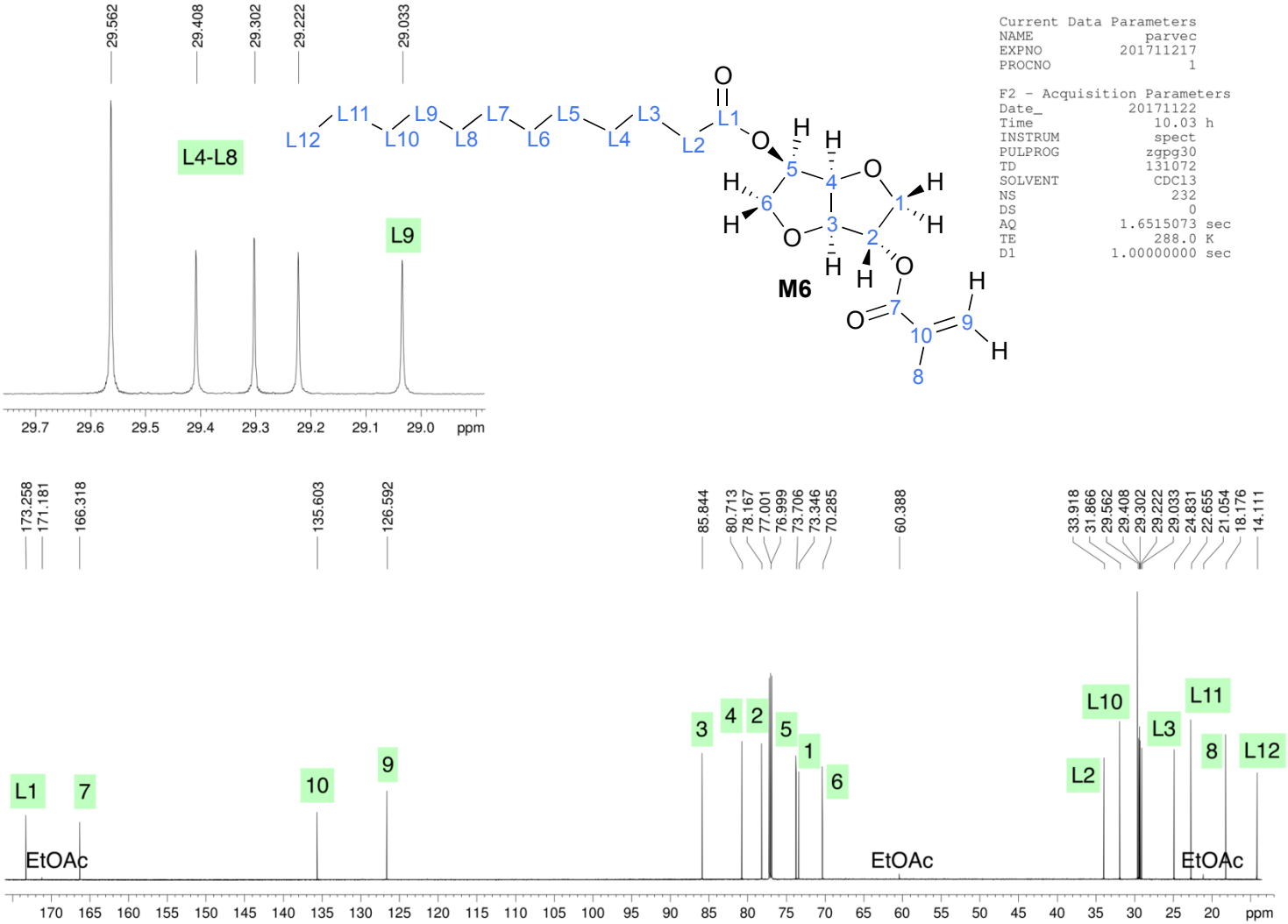

Figure S12. ^{13}C NMR spectrum of D-isosorbide 2-methacrylate-5-laurate **M6**.

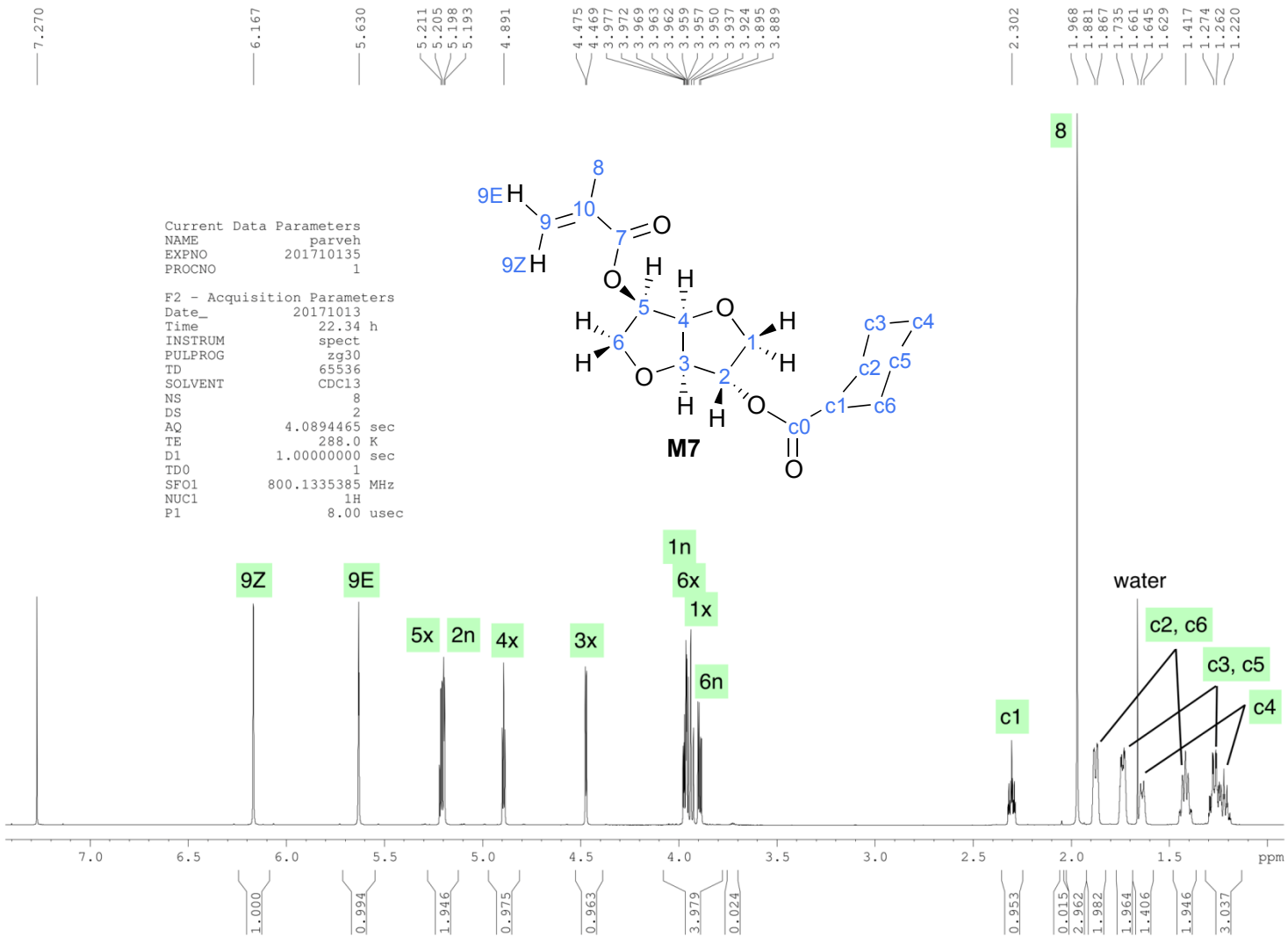

Figure S13. ^{1}H NMR spectrum of D-isosorbide 2-cyclohexanecarboxylate-5-methacrylate **M7**.

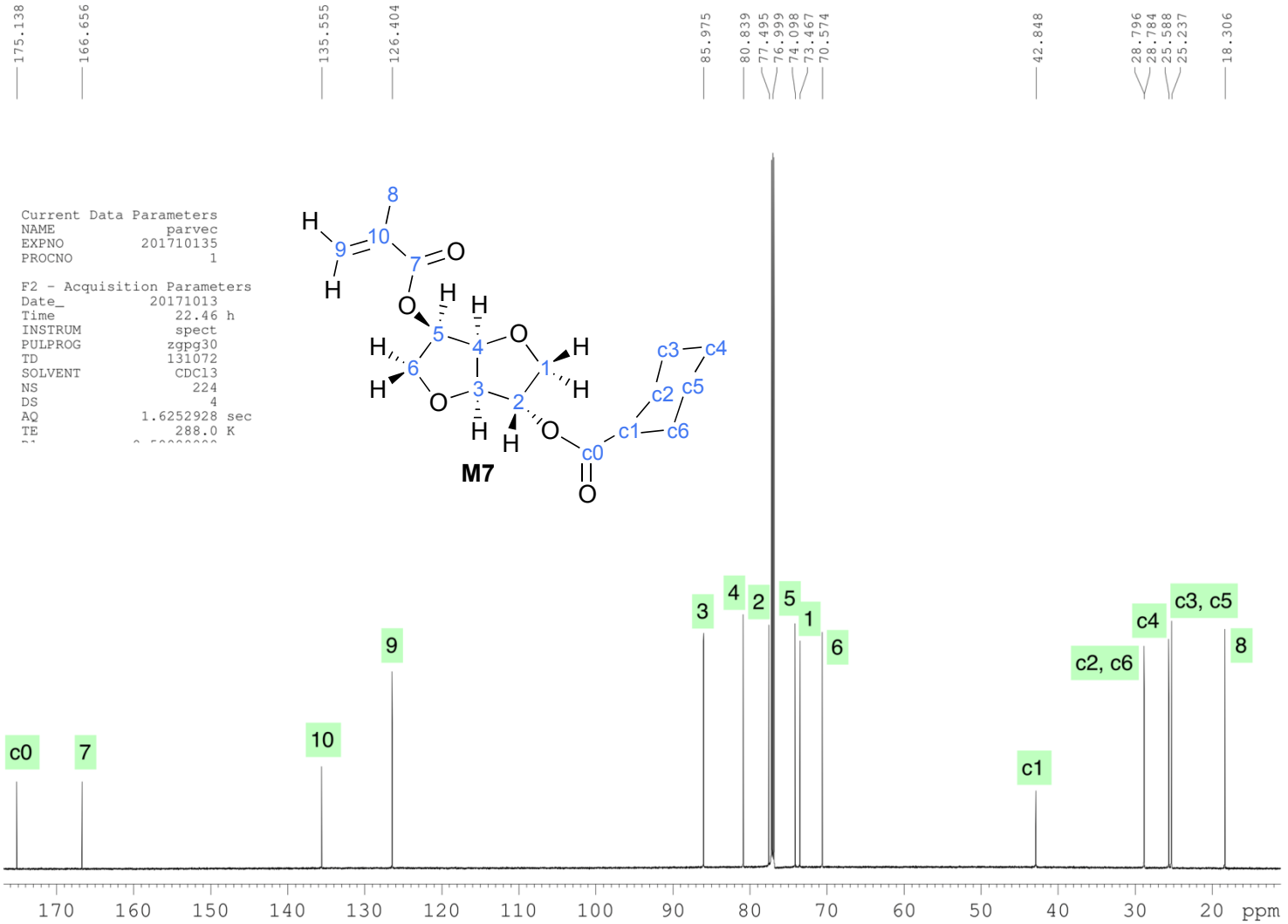

Figure S14. ^{13}C NMR spectrum of D-isosorbide 2-cyclohexanecarboxylate-5-methacrylate **M7**.

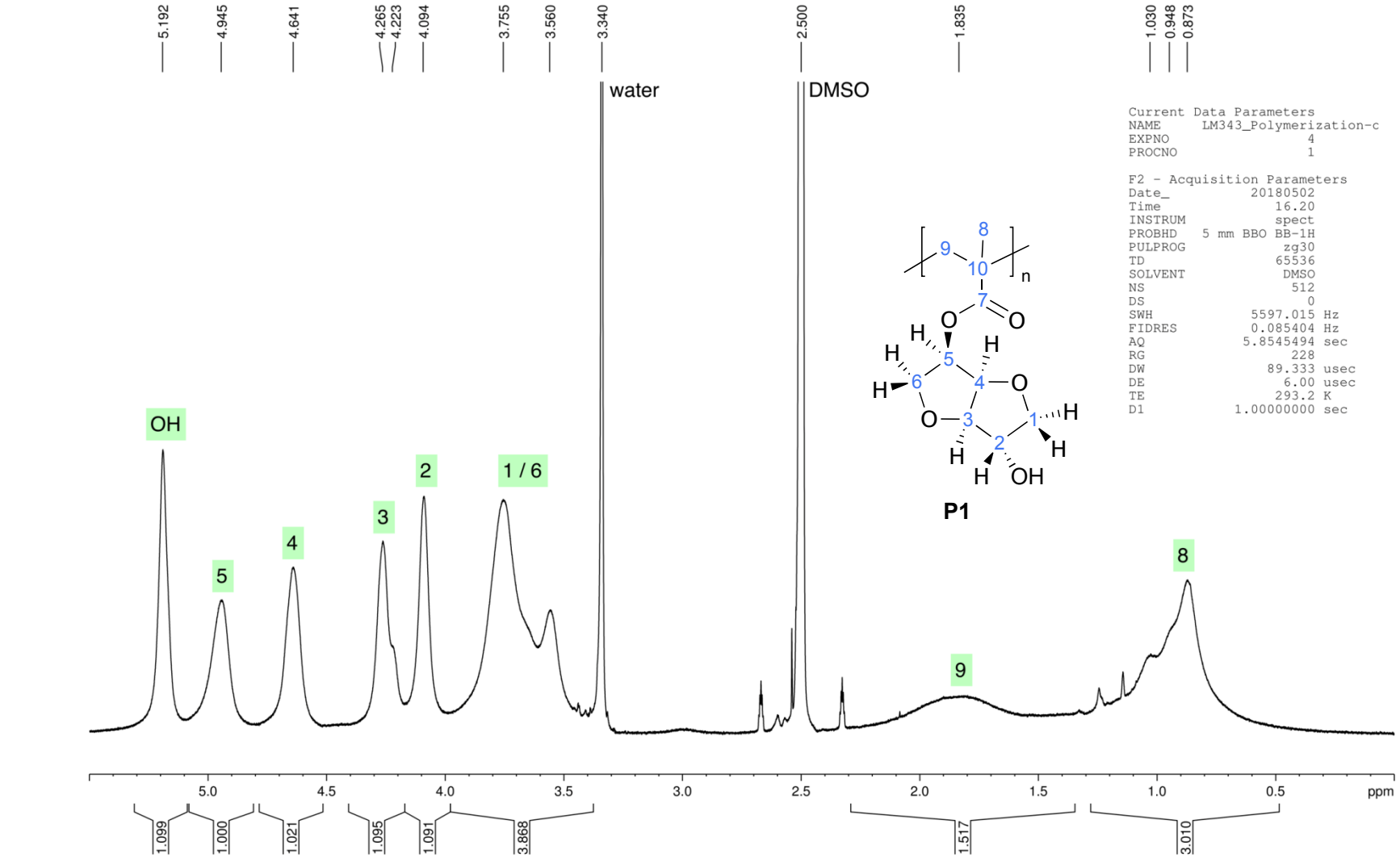

Figure S15. ^{1}H NMR spectrum of polymer **P1**.

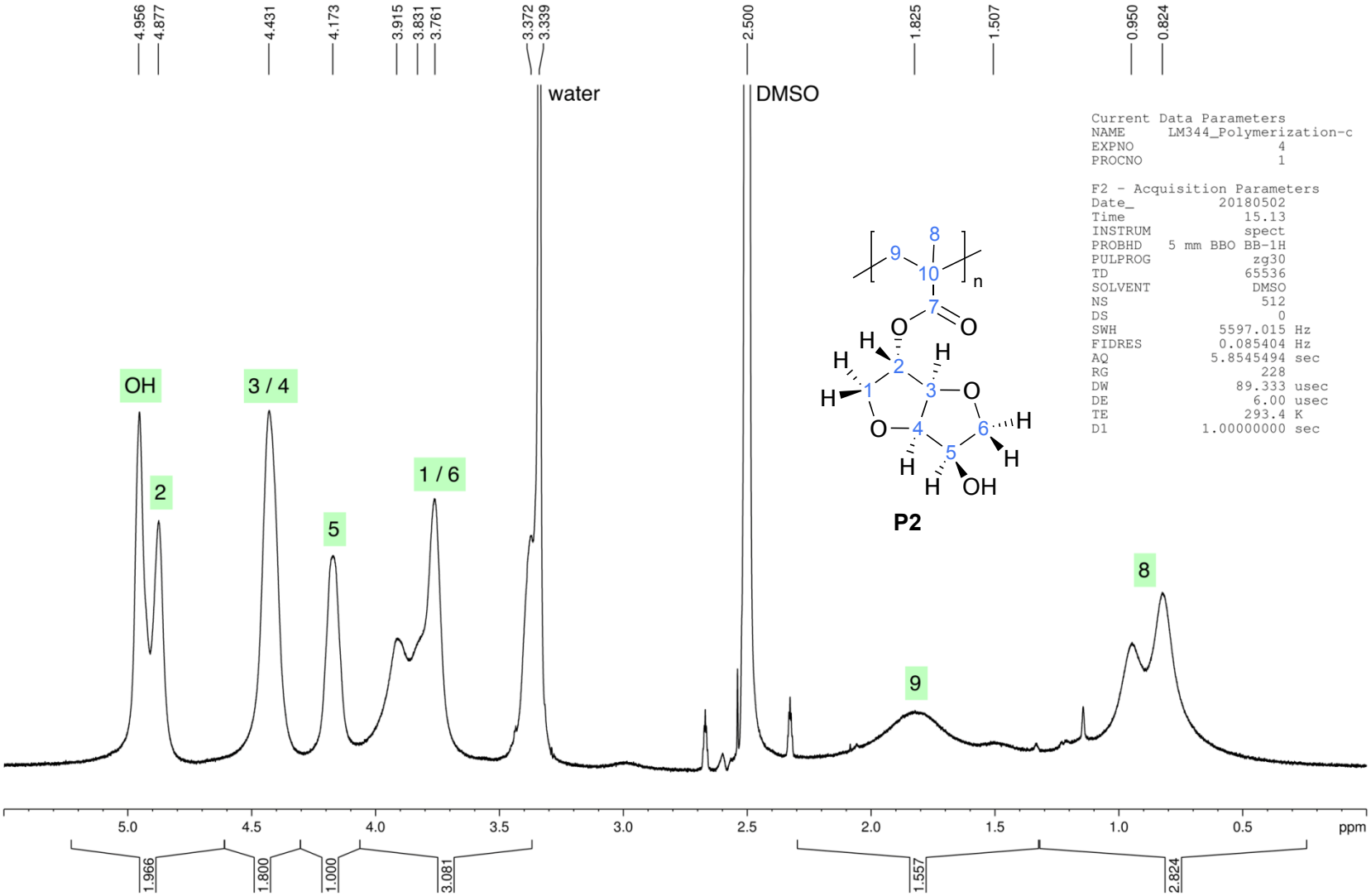

Figure S16. ^{1}H NMR spectrum of polymer **P2**.

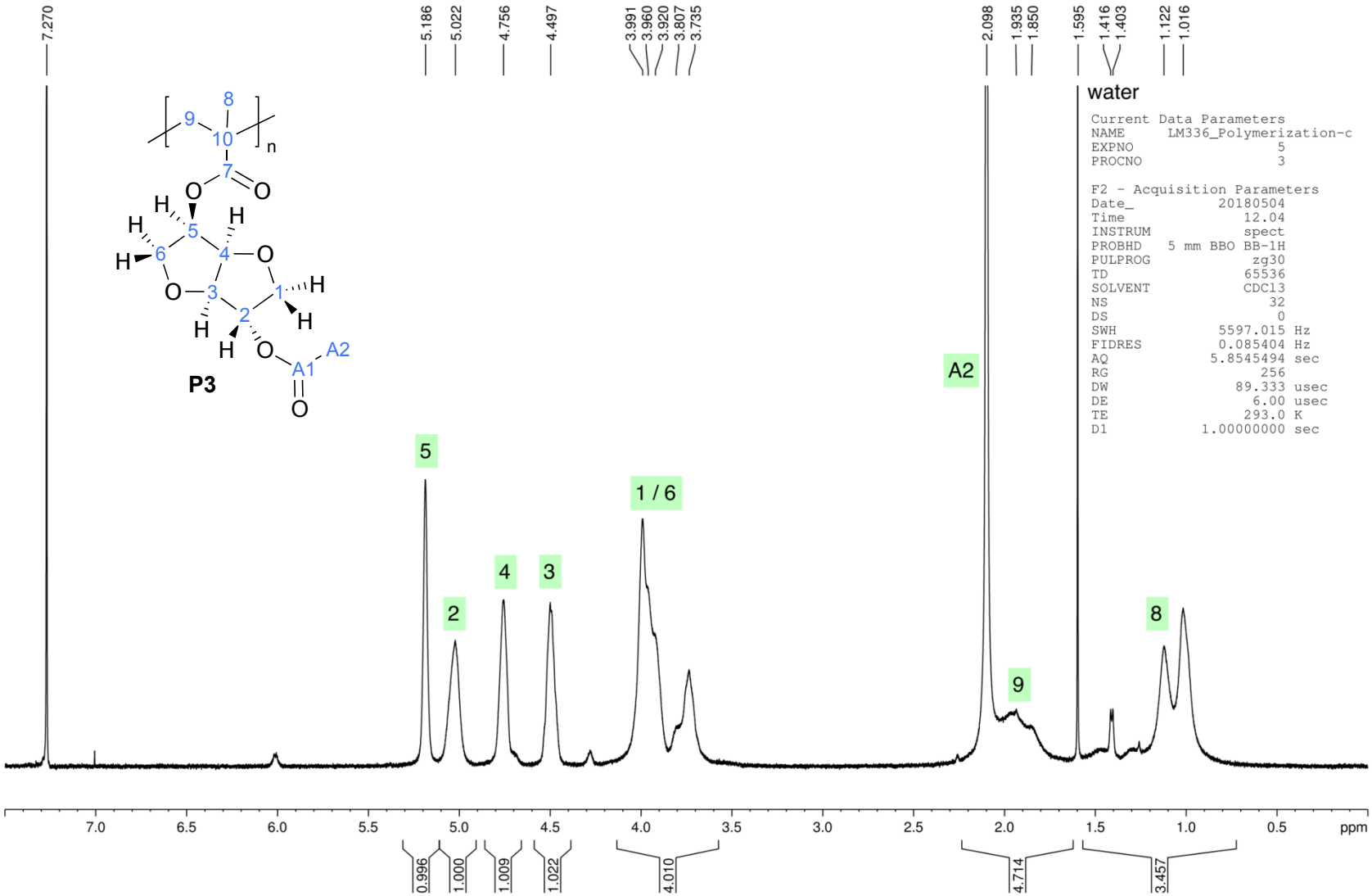

Figure S17. ^{1}H NMR spectrum of polymer **P3**.

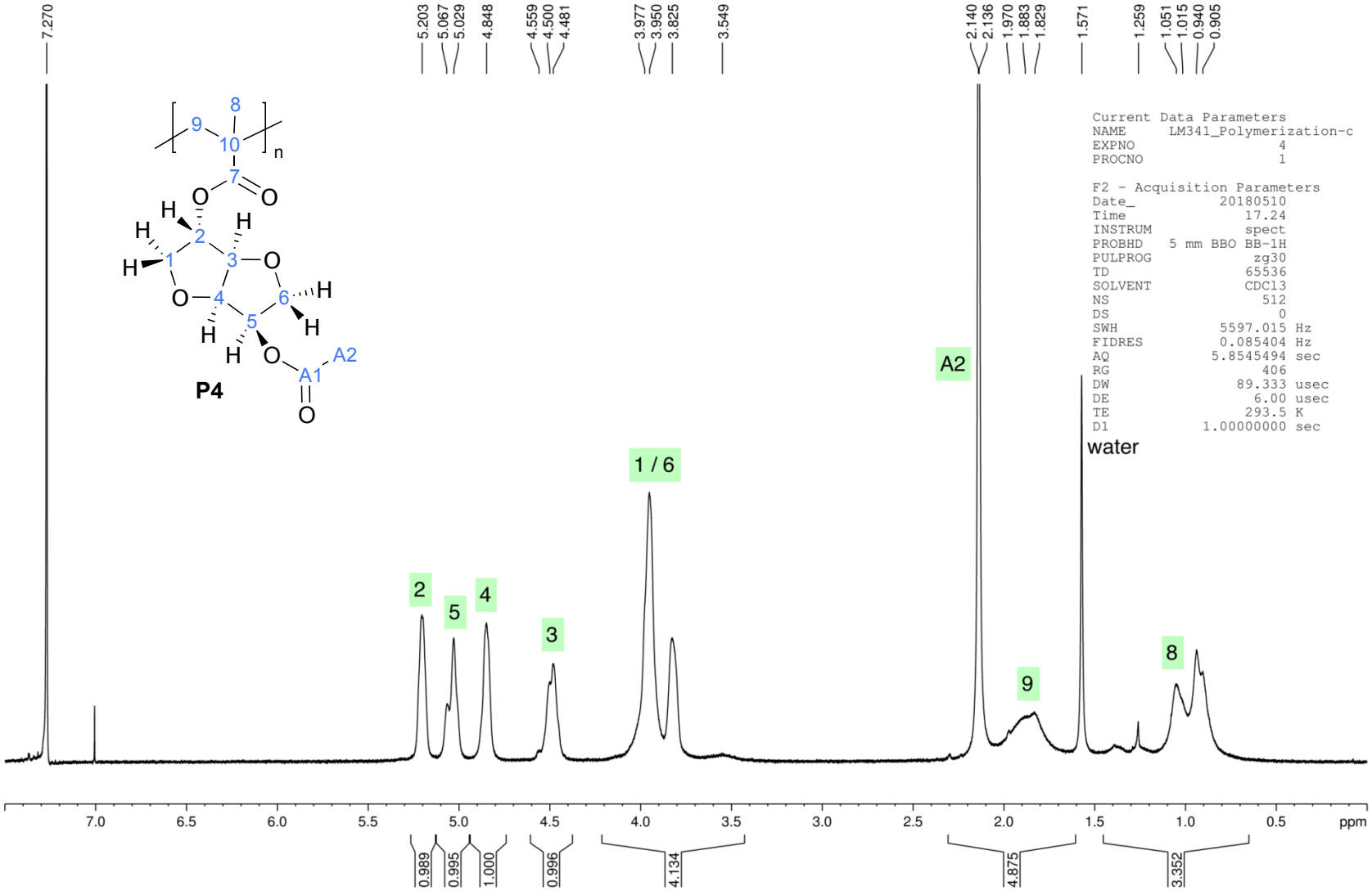

Figure S18. ^{1}H NMR spectrum of polymer **P4**.

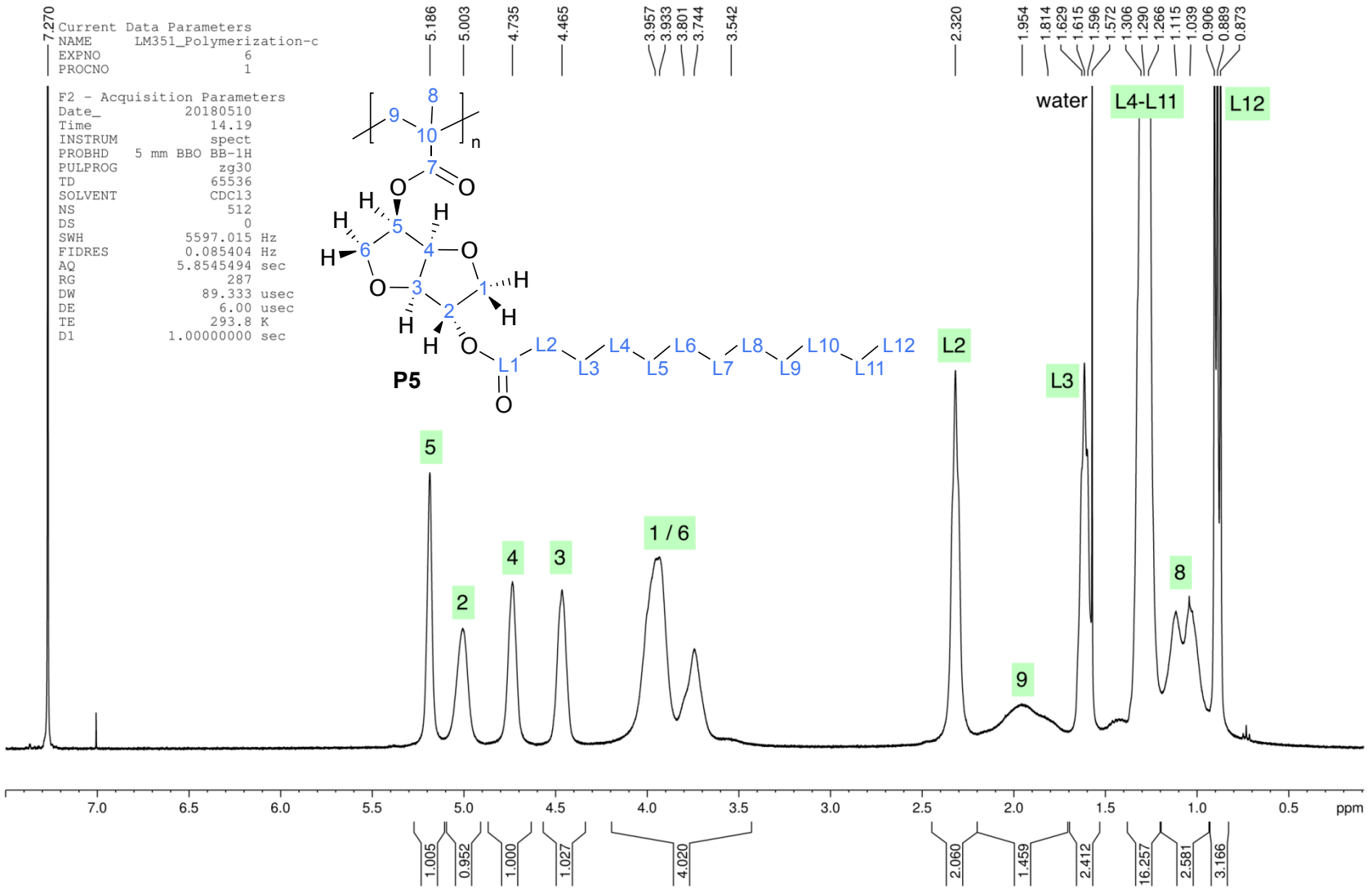

Figure S19. ^{1}H NMR spectrum of polymer **P5**.

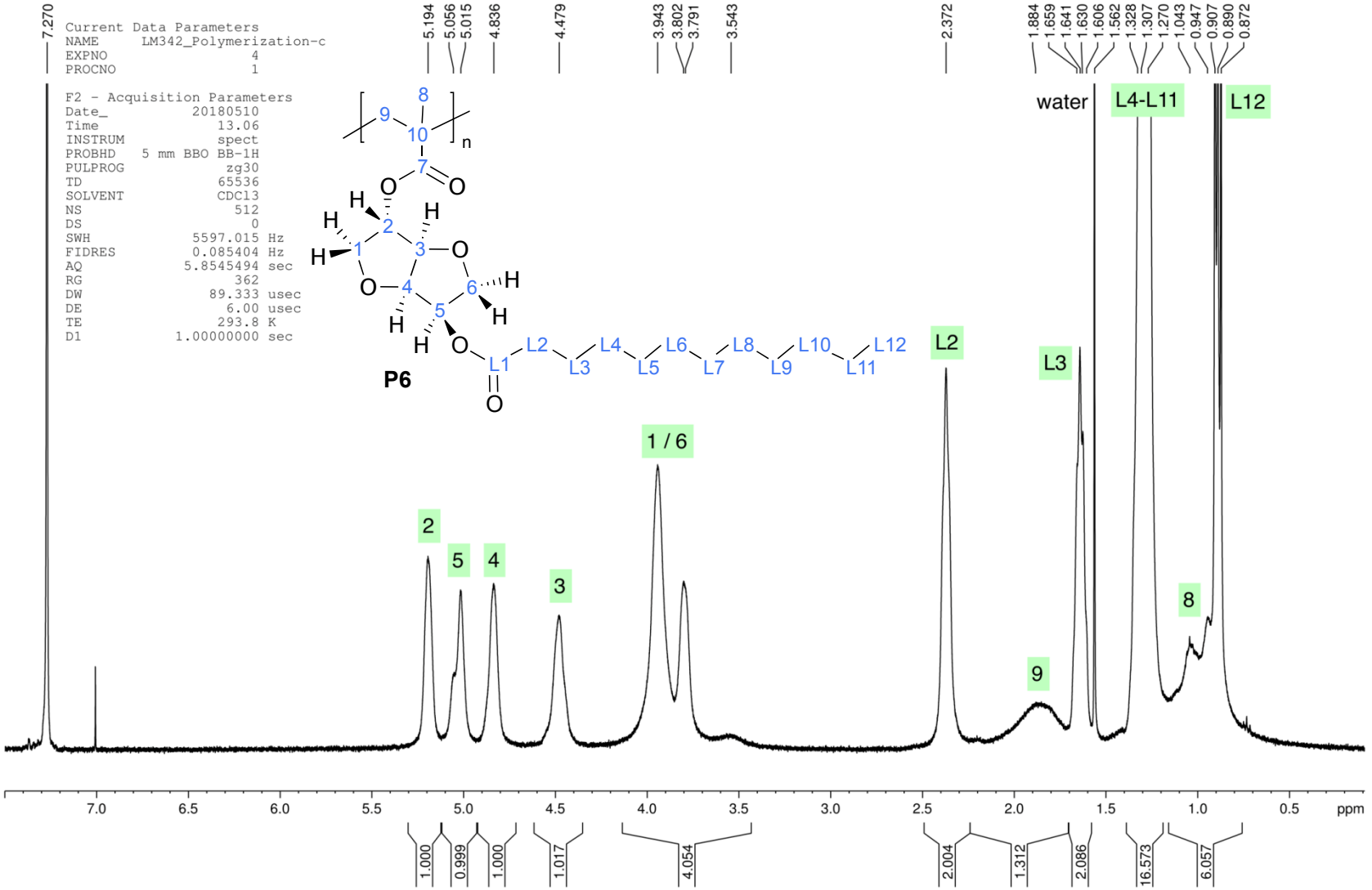

Figure S20. ^{1}H NMR spectrum of polymer **P6**.

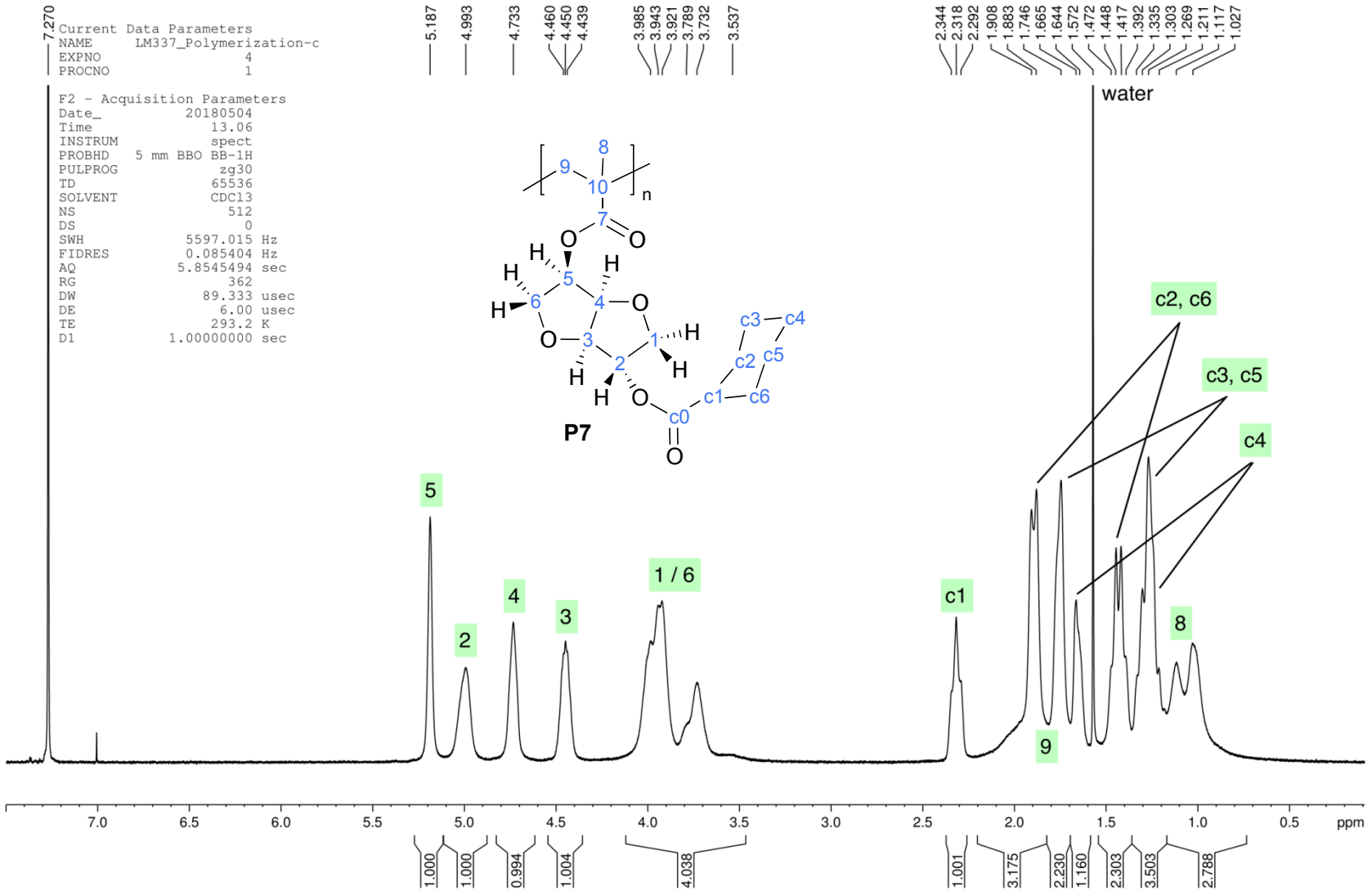

Figure S21. ^{1}H NMR spectrum of polymer **P7**.

DSC Graphs

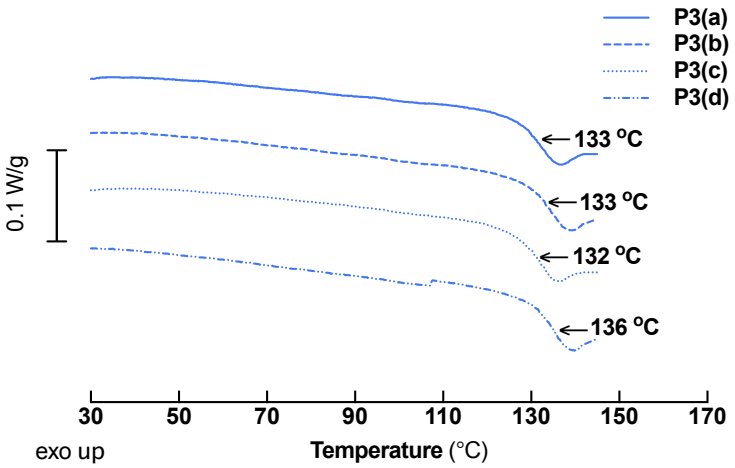

Figure S22. DSC heating curves of polymers **P3(a–d)**. T_g values are indicated at the respective transitions.

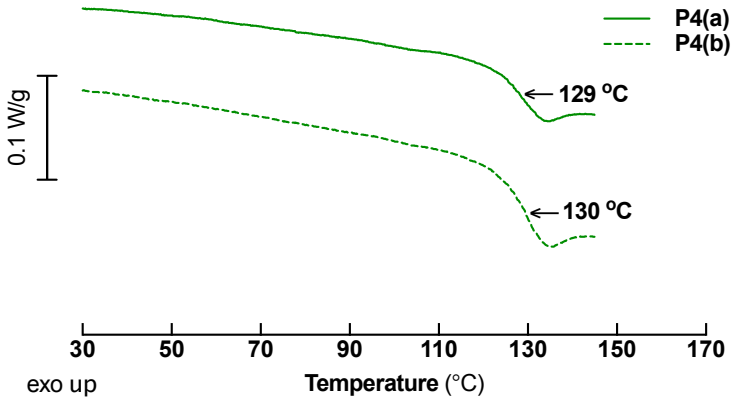

Figure S23. DSC heating curves of polymers **P4(a,b)**. T_g values are indicated at the respective transitions.

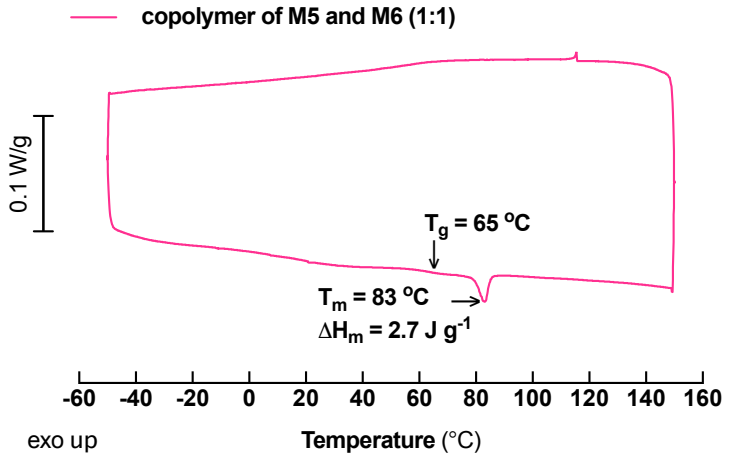

Figure S24. DSC heating and cooling curves of copolymer of **M5** and **M6** (1:1). T_g value is indicated at the respective transition.

SEC Curves

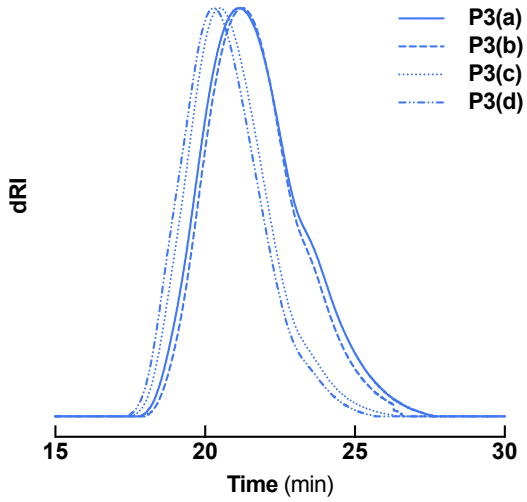

Figure S25. SEC in THF with differential refractive index (dRI) detector of polymers **P3(a–d)**.

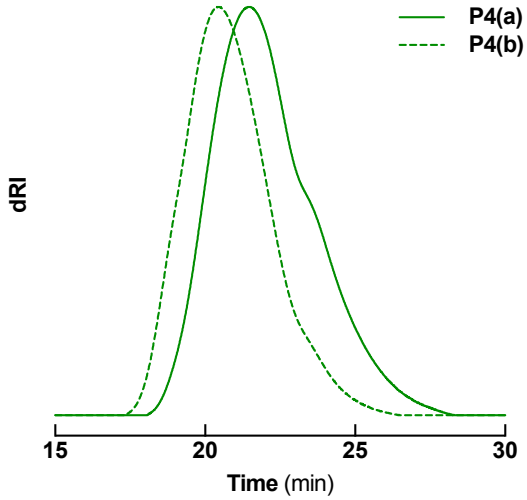

Figure S26. SEC in THF with differential refractive index (dRI) detector of polymers **P4(a,b)**.

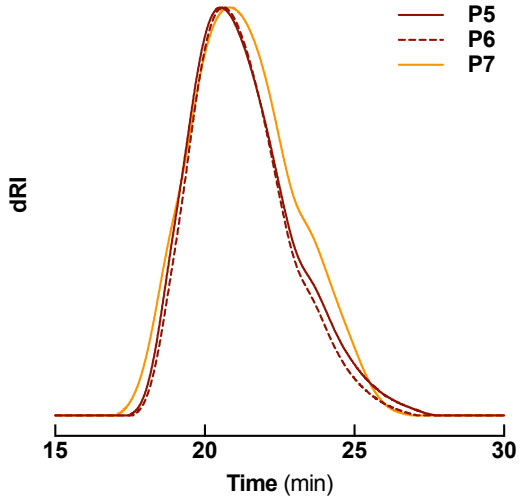

Figure S27. SEC in THF with differential refractive index (dRI) detector of polymers **P5**, **P6** and **P7**.

Evaluation of the Solubility of Isosorbide Polymethacrylates

The solubility of the different isosorbide polymethacrylates was investigated by mixing small samples (about 5 mg) with a range of selected solvents (1 mL). The mixture was stirred for 24 h at room temperature. The results of the dissolution tests were divided into two categories, soluble and insoluble, based on visual inspection. If the samples were found to be completely dissolved, they were considered as soluble; if not, they were considered as nonsoluble.

Table S1. Solubility of the Isosorbide Polymethacrylates at 21 °C.

	solvent[a]								
polymer	**H_2O** **δ = 48 (s)**	**MeOH** **δ = 43 (s)**	**1-BuOH** **δ = 23 (s)**	**DMSO** **δ = 25 (m)**	**THF** **δ = 19 (m)**	**Et_2O** **δ = 15 (m)**	**ACN** **δ = 24 (p)**	**$CHCl_3$** **δ = 19 (p)**	**toluene** **δ = 18 (p)**
P1	–	–	–	+	–	–	–	–	–
P2	–	–	–	+	–	–	–	–	–
P3(a)	–	–	–	+	+	–	+	+	–
P4(a)	–	–	–	+	+	–	+	+	–
P5	–	–	–	–	+	–	–	+	+
P6	–	–	–	–	+	–	–	+	+
P7	–	–	–	–	+	–	–	+	+

[a]The symbols "+" and "–" indicate solubility and nonsolubility, respectively. Solubility parameters (δ, $MPa^{1/2}$) were obtained from the *Polymer Handbook* (J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, D. Bloch. *Polymer Handbook, 4th ed.*, John Wiley and Sons, New York, 1999), and the letters s, m, and p denote strongly, moderately, and poorly hydrogen-bond-forming solvents, respectively.