Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Sustainable Synthesis of CO_2–derived Polycarbonates from D-Xylose

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Materials

Reactions were performed under a N_2 or argon atmosphere, using Schlenk and glovebox techniques. Glassware and stainless steel autoclave reactors were oven-dried at 150 °C for 24 hours prior to use. D-Xylose was purchased from Chem-Impex. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from TCI America (Portland, OR), and was degassed and stored in a glovebox under Ar atmosphere. (R,R)-*N,N′*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride was purchased from Strem Chemicals. Bone-dry CO_2 (99.8%) was supplied from a high-pressure cylinder and equipped with a liquid dip tube purchased from Scott Specialty Gases. Tetrahydrofuran (THF), dichloromethane (DCM), and toluene were purified by passage through a solvent purification system (J. C. Meyer Solvent Systems, Inc., Laguna Beach, CA). Tetrabutylammonium iodide (*n*-Bu_4NI) was purchased from Sigma-Aldrich, Co. (St. Louis, MO) and purified by dissolving in acetone and precipitating into diethyl ether. Bis(triphenylphosphine)iminium chloride (PPNCl) was purchased from Sigma-Aldrich, Co. (St. Louis, MO) and was recrystallized from DCM/diethyl ether. Bis(triphenylphosphine)iminium azide ($PPNN_3$) was prepared from a previous procedure[1]. Other chemicals and reagents were purchased from Sigma-Aldrich and were used as received, unless otherwise noted.

Instrumentation, Methods and Analysis

^1H NMR and ^{13}C NMR spectra were recorded on Varian Inova 500 spectrometer (Varian, Inc., Palo Alto, CA), Bruker Avance Neo console with an Ascend magnet, an automated tuning 5 mm broadband iProbe, and a 60 position SampleXpress sample changer, or Bruker Avance Neo console with an Oxford magnet, an automated tuning 5 mm $^1H/^{13}C/^{15}N$ cold probe, and a 24 position SampleCase sample changer interfaced to a UNIX computer using the VnmrJ software. Chemical shifts for ^1H NMR and ^{13}C NMR signals were referenced to the solvent resonance frequencies.

Fourier transform-infrared (FT-IR) spectra were recorded on an IR Prestige 21 system, equipped with a diamond attenuated total reflection (ATR) lens (Shimadzu Corp., Japan), and analyzed using IRsolution *v*. 1.40 software.

Size exclusion chromatography (SEC) eluting with THF was conducted on a Waters chromatography, Inc. (Milford, MA) system equipped with an isocratic pump model 1515, a differential refractometer model 2414, and a three-column set including a guard column (PLgel 5 µm, 50 × 7.5 mm) and two Styragel columns (PLgel 5 µm Mixed C, 500 Å, and 104 Å, 300 × 7.5 mm columns). The system was operated at 40 °C with a flow rate of 1 mL/min. Data were

analyzed using Breeze *v*. 6.20 software from Waters Chromatography, Inc. (Milford, MA). Molar masses were determined relative to polystyrene standards (300–467,000 Da) purchased from Polymer Laboratories, Inc. (Amherst, MA). Polymer solutions were prepared at a concentration of *ca*. 3 mg/mL with 0.05 vol% toluene as flow rate marker and an injection volume of 200 µL was used.

Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC3/700/1190 (Mettler-Toledo, Inc., Columbus, OH) under a nitrogen gas atmosphere. Measurements were performed with heating and cooling rates of 10 °C/min, and three heating and cooling cycles were conducted. Measurements were analyzed using Mettler-Toledo STAR^e *v*. 15.00a software. The T_g was taken as the midpoint of the inflection tangent of the third heating scan.

Thermogravimetric analysis (TGA) was performed under N_2 atmosphere using a Mettler-Toledo TGA2/1100/464, with a heating rate of 10 °C/min. Data were analyzed using Mettler-Toledo STAR^e *v*. 15.00a software.

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed using a Thermo Scientific Q Exactive Focus. Samples were injected (10 µL) using methanol as a mobile phase at a flow rate of 300 µL/min. The Q Exactive Focus HESI source was operated in full MS in positive mode. The mass resolution was tuned to 70000 FWHM at m/z 200. The spray voltage was set to 3.75 kV, and the sheath gas and auxiliary gas flow rates were set to 7 and 0 arbitrary units, respectively. The transfer capillary temperature was held at 250 °C and the S-Lens RF level was set at 50 v. Exactive Series 2.11 /Xcalibur 4.2.47 software was used for data acquisition and processing.

MALDI-TOF mass spectrometry analysis was performed using a Bruker Microflex MALDI-TOF mass spectrometer (Bruker Daltonics) operated using FlexControl software version 3.4. Stock solutions of the matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), polymer analyte, and alkali cation sodium trifluoroacetate (NaTFA) were prepared by dissolving DCTB (25.6 mg) in chloroform ($CHCl_3$) (1 mL), polymer analyte (1.0 mg) in $CHCl_3$ (1 mL), and NaTFA (1.0 mg) in acetone (1 mL) in glass vials. In an Eppendorf tube, DCTB (2 µL), polymer analyte (1 µL), and NaTFA (1 µL) were pipette mixed, and 1 µL of the mixture was spotted onto the target section of a 384 well ground steel MALDI-ToF plate. The spot was left to evaporate to dryness before being inserting the plate into the instrument. Once loaded, spectra were acquired in linear positive ion mode.

X-ray crystal structure analysis was performed after obtaining and mounting a suitable crystal sample. A Leica MZ 75 microscope was used to identify a suitable colorless needle with well-defined faces and dimensions of 0.417 x 0.076 x 0.061 mm^3 (max, intermediate, and min, respectively), from a representative sample of crystals of the same habit. The crystal, mounted on a nylon loop, was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A Bruker Venture X-ray (kappa geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.[3] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Cu-IμS X-ray tube (K_α = 1.5418 Å with a potential of 50 kV and a current of 1.0 mA). Forty-five data frames were taken at widths of 1°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (33 sets) was initiated using omega and phi scans.

Analysis of the X-ray crystal structure data was then performed. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[3] The integration method employed a three-dimensional profiling algorithm, and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data were merged and scaled to produce a suitable data set. The absorption correction program SADABS[4] was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests of the data suggested the space group $P2_12_12_1$. A solution was obtained readily using XT/XS in APEX3.[3,5] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. An absence of additional symmetry or void was confirmed using PLATON (ADDSYM).[7] The structure was refined (weighted least squares refinement on F^2) to convergence.[5,6] Olex2 was employed for the final data presentation and structure plots.[6]

Cambridge Crystallographic Data Centre (CCDC) Deposition Number: 2089312.

Synthetic Procedures

Synthesis of 1,2-*O*-isopropylidene-α-D-xylofuranose (*2*):

Following an adapted procedure:[2] A 0.4 M solution of H_2SO_4 in acetone was prepared by adding H_2SO_4 (10 mL) into acetone (260 mL). D-Xylose (10.2 g, 67.9 mmol) was added, and the mixture was allowed to stir for 30 min at room temperature. The mixture was cooled to 0 °C and Na_2CO_3 (13.3 g, 125 mmol) in water (120 mL) was added slowly *via* an addition funnel. After complete addition, the mixture was further stirred for 3 h at room temperature. The pH of the reaction was elevated to >7 by the addition of solid Na_2CO_3 (14.9 g). The solids were removed by filtration, and the filtrate was evaporated *in vacuo*. The yellow crude oil was purified by SiO_2 flash chromatography (ethyl acetate/hexanes, 3/2, v/v) to give 1,2-*O*-isopropylidene-α-D-xylofuranose (***2***) as a white solid (11.1 g, 58.4 mmol, 86% yield). T_m: 68 – 71 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.97 (d, *J* = 3.7 Hz, 1H), 4.51 (m, 1H), 4.31 (m, 1H), 4.16 (m, 1H), 4.12 – 4.00 (m, 3H), 2.97 (br, 1H), 1.47 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 111.96, 105.00, 85.79, 78.89, 77.04, 61.25, 26.90, 26.30. FT-IR(ATR): 3610 – 3520, 3440 – 3024, 3024 – 2850, 1450, 1381, 1211, 1165, 1056, 1010, 856, 825, 794, 679 cm^{-1}. HRMS (ESI$^+$) Calcd. for (M+Na$^+$) $C_8H_{14}O_5Na^+$ 213.0730; Found: 213.0733.

Synthesis of 1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (*3*):

Following an adapted procedure:[2] To a stirred solution of 1,2-*O*-isopropylidene-α-D-xylofuranose (29.3 g, 158 mmol) and triethylamine (44 mL, 320 mmol) in THF (180 mL) at 0 °C, a solution of tosyl chloride (33.2 g, 174 mmol) in THF (40 mL) was added dropwise. After addition, the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of MeOH, and the solvents were evaporated *in vacuo*. The residue was dissolved in EtOAc and washed with H_2O, saturated $NaHCO_3$, and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. The crude product was recrystallized from ethyl acetate/hexanes to give 1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (***3***) as white crystals (37.1 g, 108 mmol, 68% yield). T_m: 132 – 135 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 5.88 (d, *J* = 3.6 Hz, 1H), 4.52 (m, 1H), 4.37 – 4.34 (m, 2H), 4.32 (m, 1H), 4.16 – 4.11 (m, 1H), 2.46 (s, 3H), 1.46 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 145.42, 132.52, 130.14, 128.15, 112.26, 105.11, 85.20, 77.78, 74.43, 66.47, 26.91, 26.33, 21.78. FT-IR(ATR): 3579 – 3170, 3047 – 2816, 1597, 1450, 1427 – 1311, 1296, 1280 – 1203, 1203 – 1141, 1080, 1072, 964, 902, 833, 810, 756 cm^{-1}. HRMS (ESI$^+$) Calcd. for (M+Na$^+$) $C_{15}H_{20}O_7Na^+$ 367.0822; Found: 367.0812.

Synthesis of 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (*4*):

1,2-*O*-Isopropylidene-5-*O*-tosyl-α-D-xylofuranose (49.7 g, 145 mmol) was dissolved in anhydrous methanol (300 mL). K_2CO_3 (30.3 g, 218 mmol) was added and the mixture was heated at reflux for 3 h. Methanol was evaporated *in vacuo*, and the solid residue was dissolved in CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. The resulting crude liquid product was purified by vacuum distillation over CaH_2 (150 mtorr, b.p. = 54 °C) to yield 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (***4***) as a colorless liquid (19.1 g, 111 mmol, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.28 (d, *J* = 3.7 Hz, 1H), 5.21 (m, 1H), 5.12 (ddd, *J* = 4.5, 4.2, 2.2 Hz, 1H), 4.77 – 4.71 (m, 2H), 4.26 (dd, *J* = 7.7, 2.2 Hz, 1H), 1.42 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 114.06, 108.36, 87.69, 84.76, 78.66, 78.44, 28.03, 27.33. FT-IR(ATR): 3047 – 2900, 2900 – 2854, 1450, 1373, 1280 – 1188, 1157, 1080, 1041, 972, 887, 840 cm^{-1}. HRMS (ESI$^+$) Calcd. for (M+Na$^+$) $C_8H_{12}O_4Na^+$ 195.0628; Found: 195.0627.

General procedure for the ring-opening copolymerization of 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose and CO_2 to afford poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate)s (*5*):

Under an argon atmosphere, (salen)CrCl (26 mg, 0.041 mmol), PPNCl (45 mg, 0.077 mmol), 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (501 mg, 2.91 mmol), and toluene (500 µL) were added to a 10 mL stainless steel autoclave reactor that was previously dried overnight at 150 °C. The reactor was pressurized with 3.0 MPa CO_2 and placed in a preheated oil bath (110 °C) and stirred for 72 hours. The reactor was cooled in an ice bath for 10 min and pressure was released slowly. A small aliquot of the resulting foam-like solid was collected and dissolved into $CDCl_3$ for ^{1}H NMR analysis. The remaining majority of the polymer sample was dissolved into a minimal amount of DCM, precipitated into an acidic methanol solution, and purified by precipitation from DCM into methanol twice to afford ***5*** as a white solid (182 mg, 36% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.94 (m, 1H), 5.10 (m, 1H), 4.70 – 4.58 (m, 1H), 4.51 (m, 1H), 4.40 (m, 1H), 4.38 – 4.24 (m, 1H), 1.66 (s, 1H), 1.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.57, 153.92, 153.38, 112.64, 104.94, 83.07, 79.99, 76.29, 64.63, 26.79, 26.32. FT-IR(ATR): 3047 – 2900, 2900 – 2854, 1450, 1373, 1280-1188, 1157, 1080, 1041, 972, 887, 840 cm^{-1}. TGA in N_2, 180 – 260 °C, 100% weight loss. T_g = 121 °C. $M_{n\,SEC}$ = 8.9 kDa, $Đ$ = 1.08.

Synthesis of 1,2-*O*-isopropylidene-α-D-xylofuranose carbonate (*6*):

Under an argon atmosphere, zinc iodide (185 mg, 0.58 mmol), *n*-Bu_4NI (645 mg, 1.74 mmol), 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (1.02 g, 5.92 mmol), and toluene (3 mL)

were added to a 10 mL stainless steel autoclave reactor that had been previously dried at 150 °C overnight. The reactor was pressurized with 3.0 MPa CO_2 and placed in a preheated oil bath (110 °C) and stirred for 24 hours. The reactor was cooled in an ice bath for 10 min and pressure was slowly released. A small aliquot of the resulting foam-like solid was collected and dissolved into $CDCl_3$ for ^1H NMR analysis. Ethyl acetate was added to the reaction mixture, and the solution was filtered through Celite®. The solvents were removed *in vacuo*, and the residue was purified by SiO_2 flash chromatography (hexanes/ethyl acetate ,1/1, v/v) to give a white solid (653 mg, 3.02 mmol, 52% yield). The 1,2-*O*-isopropylidene-α-D-xylofuranose carbonate (***6***) product was further purified by recrystallization in toluene to afford colorless needles (370 mg, 1.71 mmol, 30% yield). T_m: 135 – 138 °C. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 6.00 (d, J = 3.7 Hz, 1H), 4.87 (m, 1H), 4.74 (m, 1H), 4.60 (m, 1H), 4.56 – 4.52 (m, 2H), 1.50 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 146.36, 113.15, 105.33, 83.96, 82.48, 69.29, 66.85, 26.78, 26.31. FT-IR(ATR):3630 – 3290, 3075 2840, 1735, 1471, 1450, 1340, 1324, 1293, 1246, 1190, 1136, 1079, 1023, 835, 760, 704 cm^{-1}. HRMS (ESI^+) Calcd. for ($M+Na^+$) $C_8H_{12}O_4Na^+$ 239.0526; Found: 239.0524. Cambridge Crystallographic Data Centre (CCDC) Deposition Number: 2089312.

General procedure for the organobase-catalyzed ring-opening polymerization of 1,2-*O*-isopropylidene-α-D-xylofuranose carbonate to afford poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate)s (*7*):

1,2-*O*-Isopropylidene-α-D-xylofuranose carbonate was dried under vacuum over P_2O_5 for 3 d before being transferred to a glovebox for storage and manipulation under an inert atmosphere. To a solution of 1,2-*O*-isopropylidene-α-D-xylofuranose carbonate (501 mg, 2.32 mmol) in DCM (4 mL) in a scintillation vial, 4-methylbenzyl alcohol (3.21 mg, 0.023 mmol) in DCM (200 µL) was added via micropipette while stirring. After fitting the vial with a septum, the reaction mixture was transferred to a fume hood equipped with a Schlenk line. Organobase catalyst TBD (2 mol% relative to monomer, 0.046 mmol) as a stock solution in DCM (210 µL) was added *via* syringe to the reaction mixture under N_2 atmosphere. After allowing to stir for 4 h, the reaction vial was opened to air and quenched by addition of benzoic acid as a solution in DCM. The mixture was concentrated *in vacuo*, dissolved in a minimal amount of DCM, and precipitated into methanol thrice to afford ***7*** as a white solid (356 mg, 70% yield). ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 5.94 (m, 1H), 5.17 – 5.05 (m, 1H), 4.64 (m, 1H), 4.51 – 4.27 (m, 2H), 1.50 (m, 3H), 1.32 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.57, 153.91,153.39, 112.64, 104.92, 83.07, 80.02, 76.31, 68.09, 64.63, 26.79, 26.32, 25.74. FT-IR(ATR): 3740 – 3450, 3040 – 2820, 1750, 1458, 1374,

1329 – 1183, 1163, 1138 – 926, 891, 855, 782 cm^{-1}. TGA in N_2, 200 – 280 °C, 100% weight loss. T_g = 125 °C. $M_{n\ SEC}$ = 10.2 kDa, $Đ$ = 1.08.

Figures

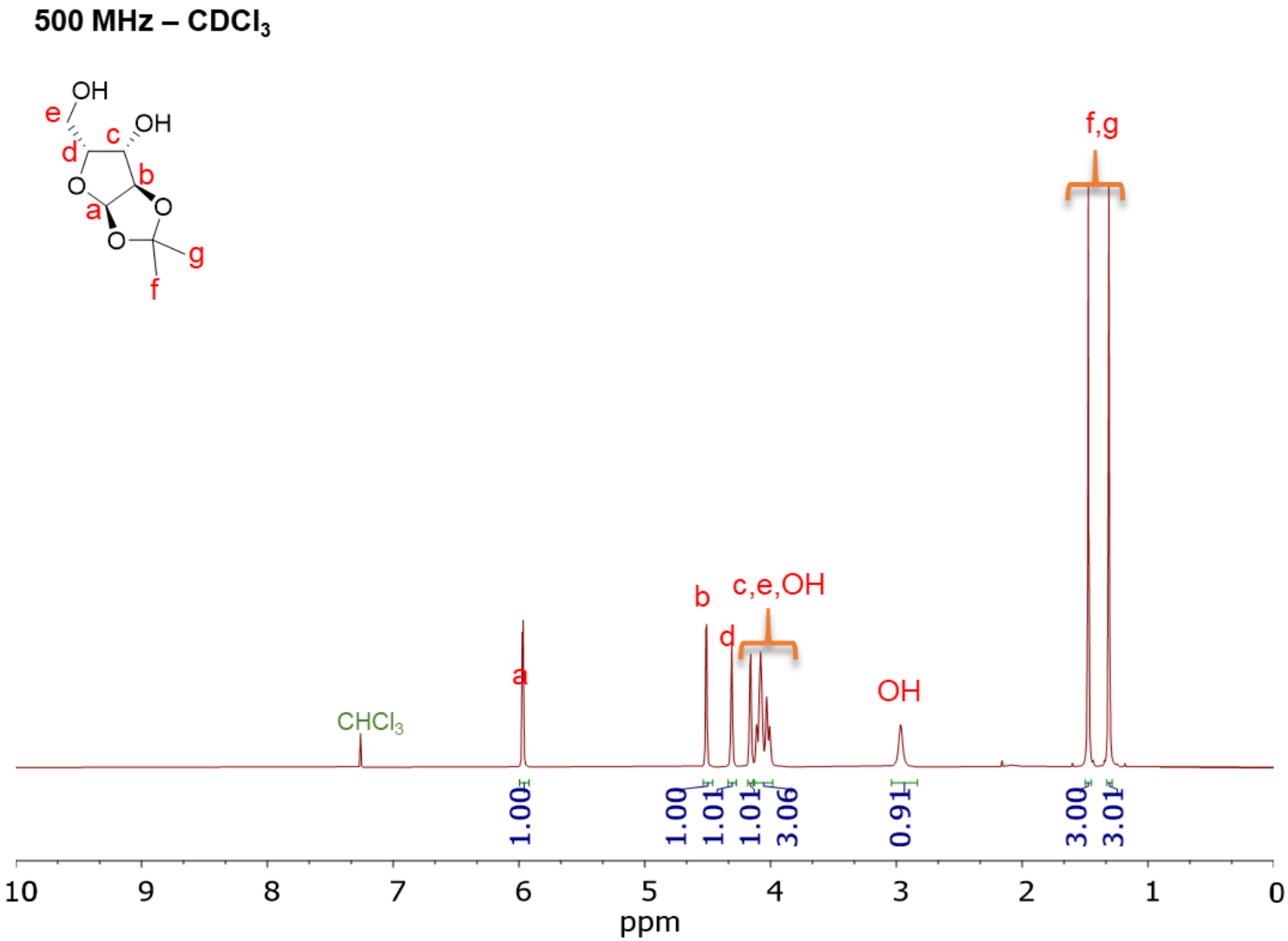

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1,2-*O*-isopropylidene-α-D-xylofuranose (***2***).

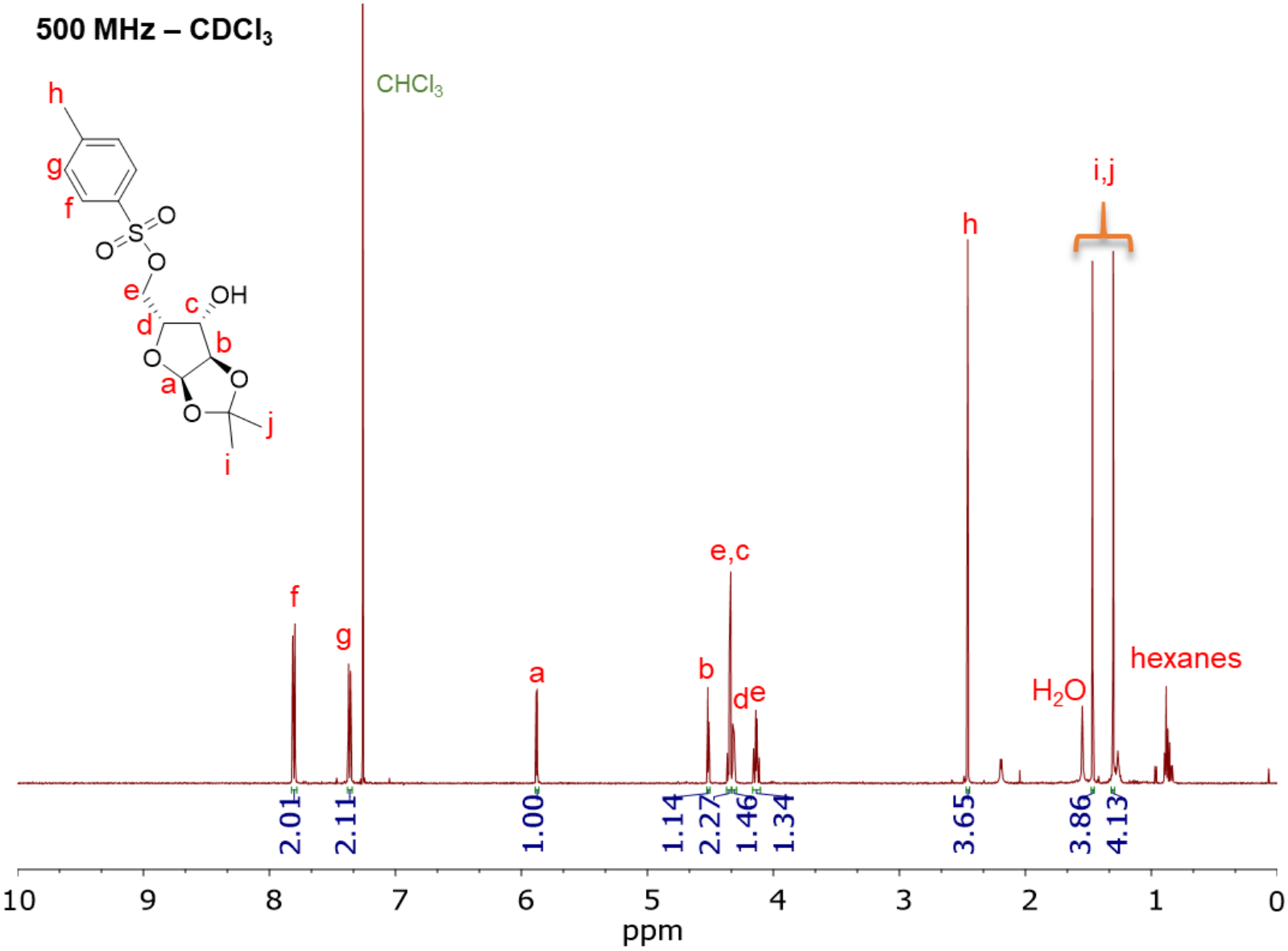

Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (***3***).

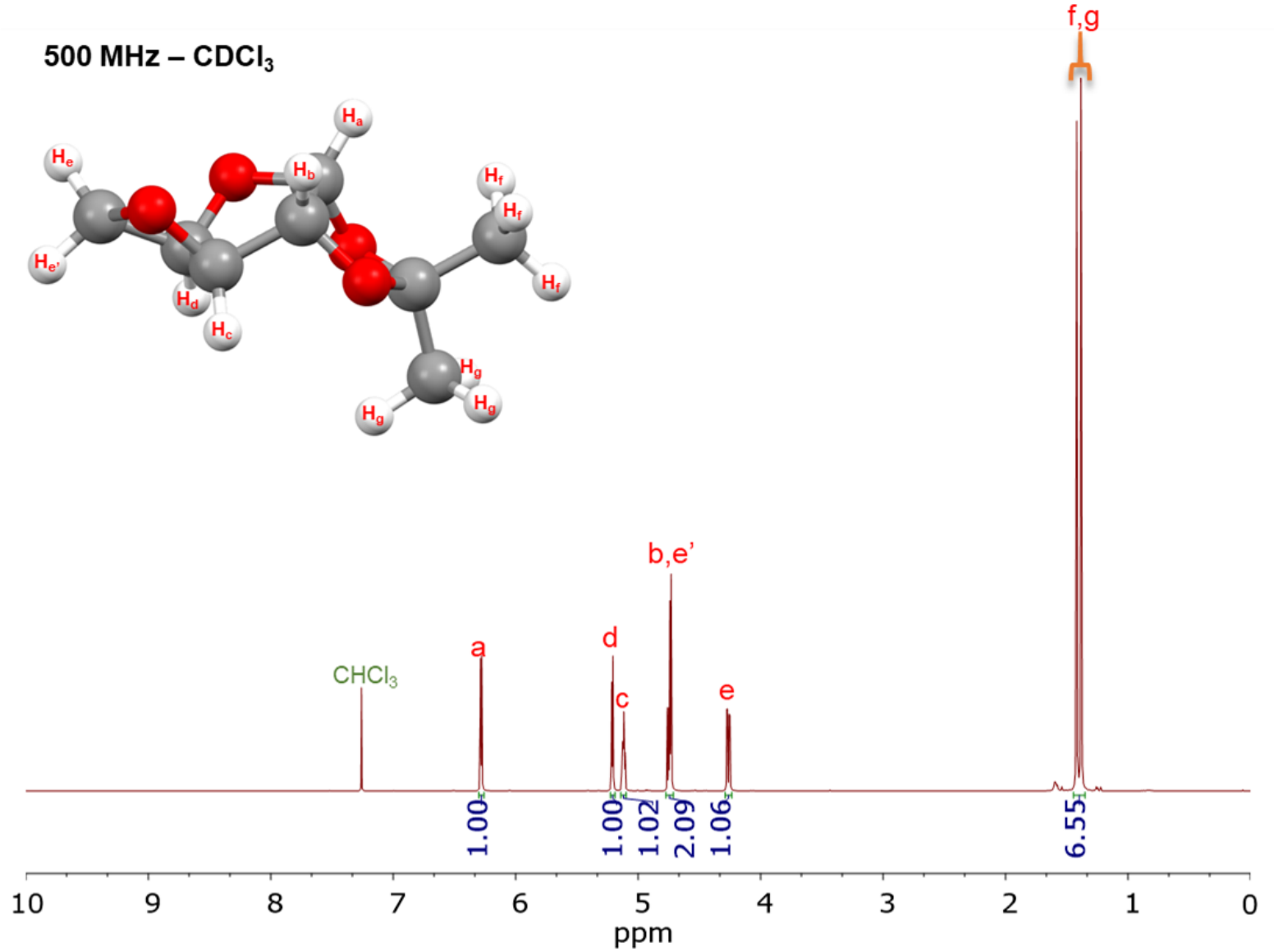

Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (***4***).

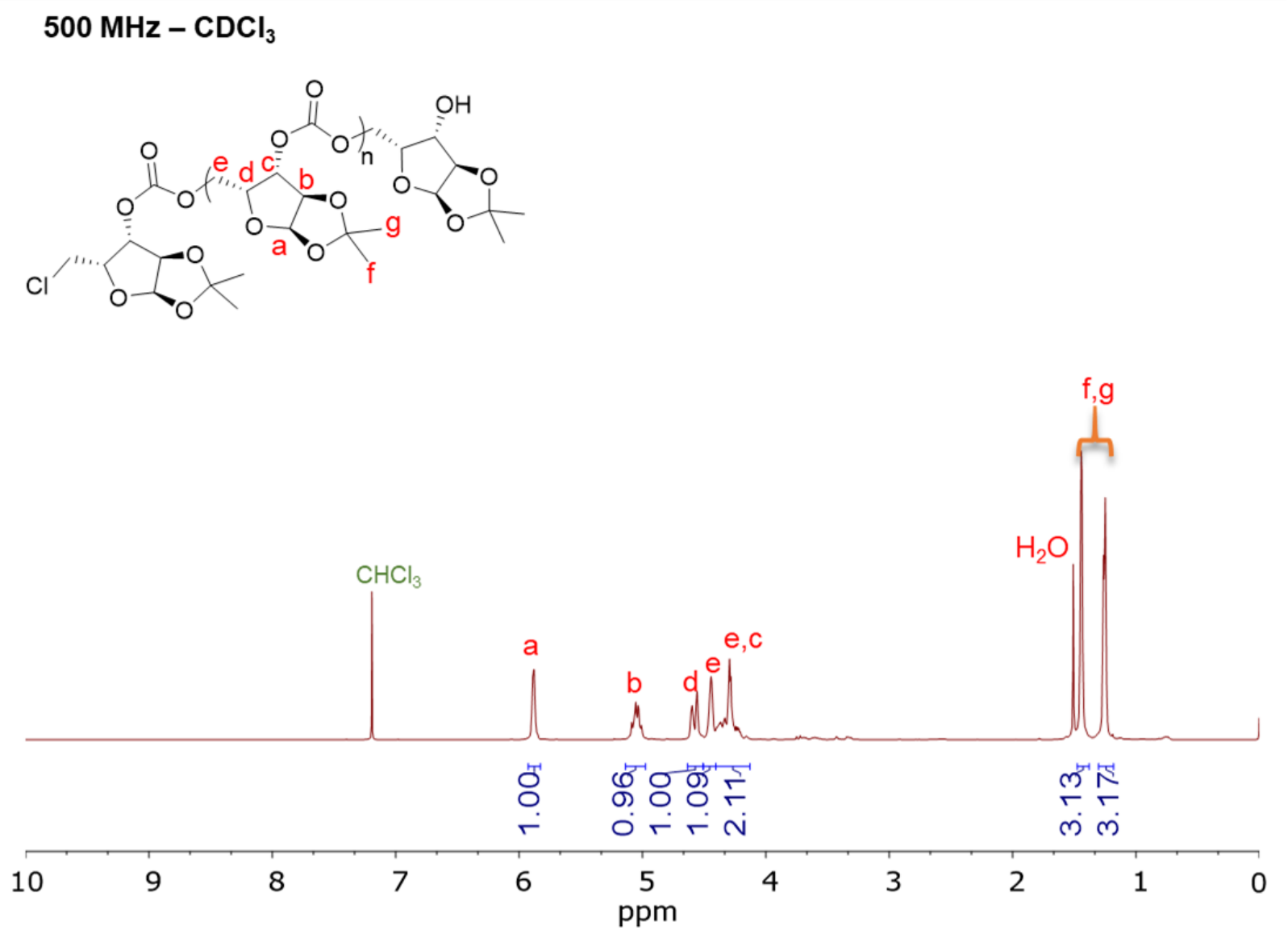

Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate) (***5***).

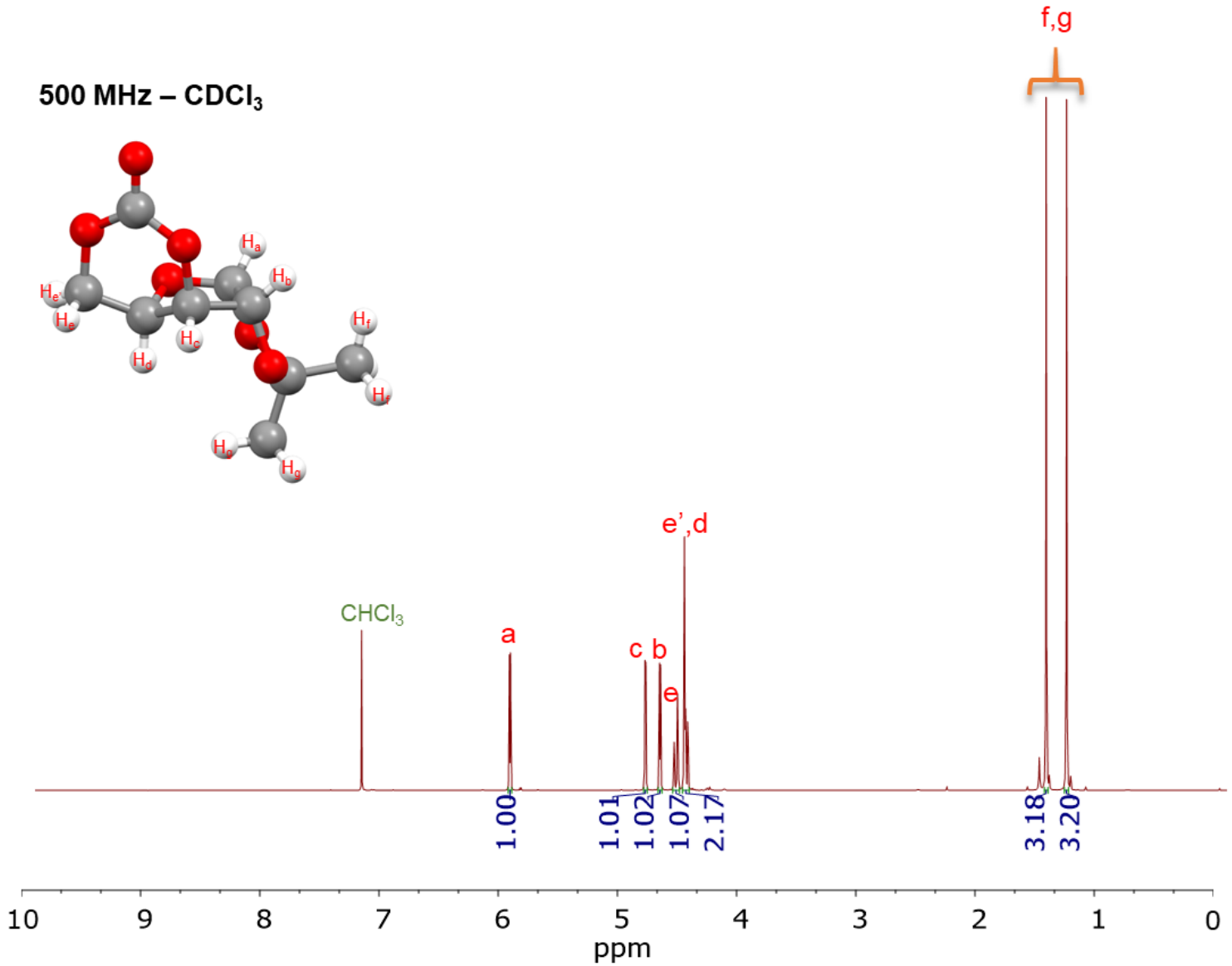

Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1,2-*O*-isopropylidene-α-D-xylofuranose carbonate (***6***).

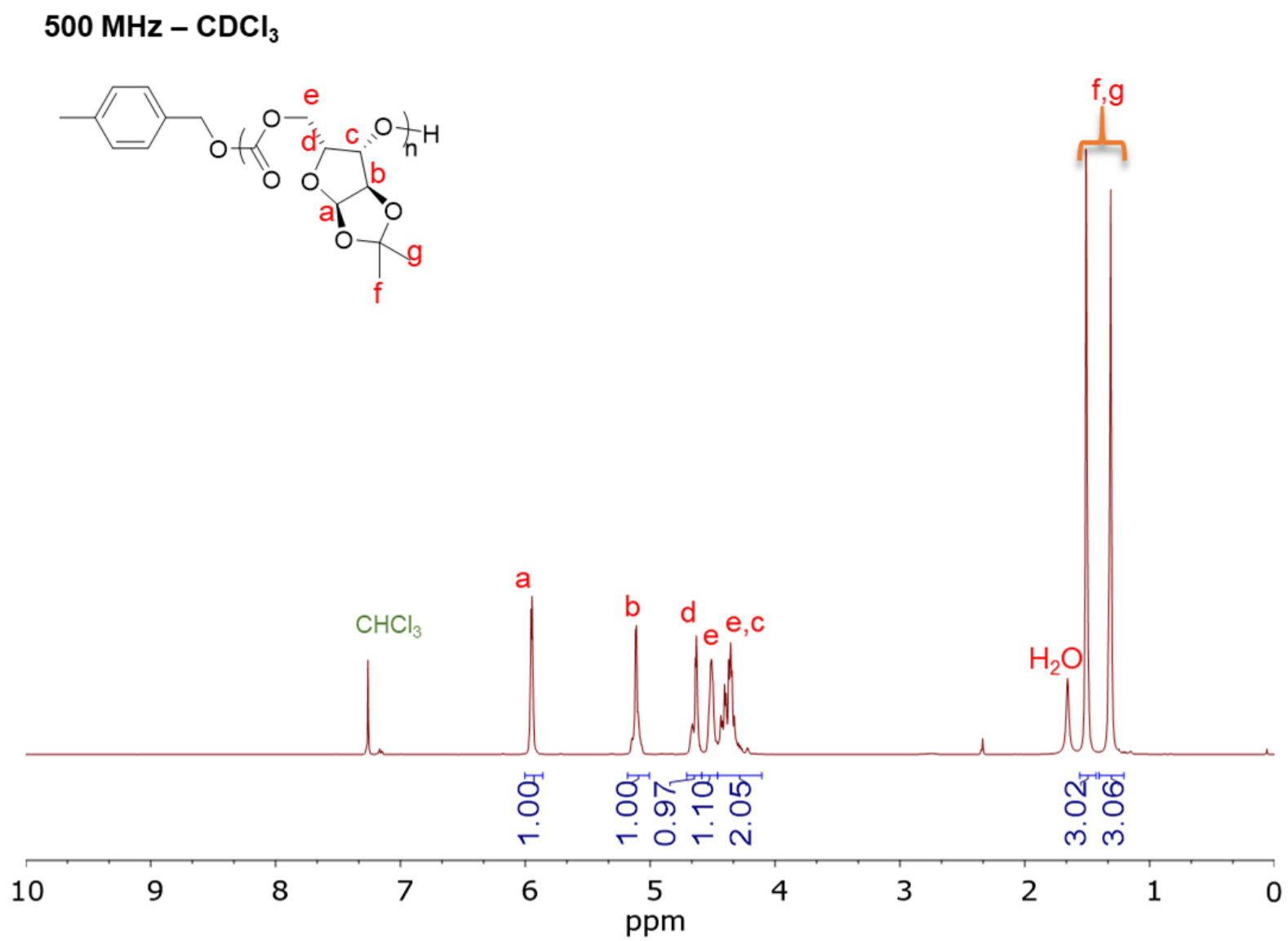

Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate) (***7***).

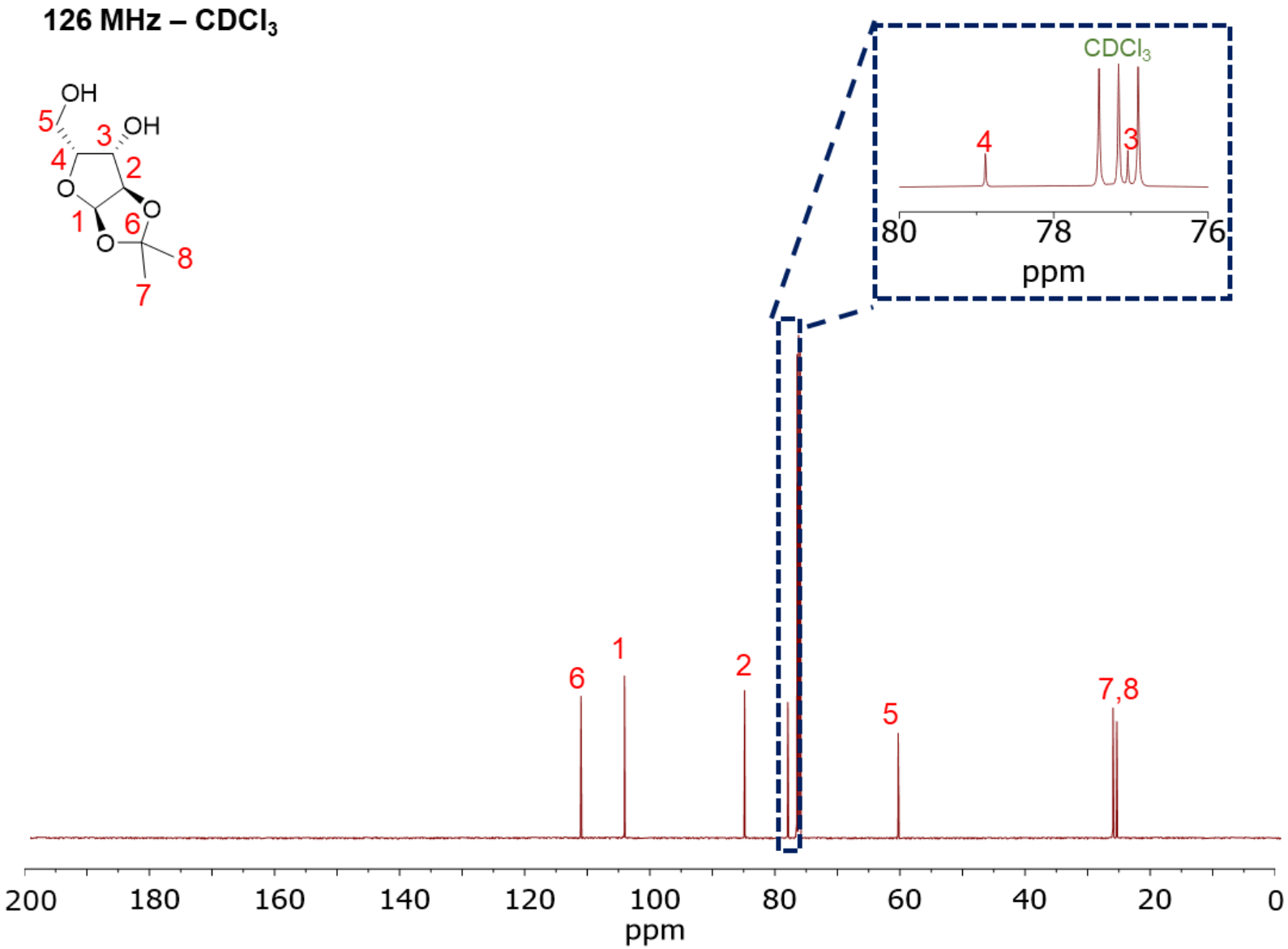

Figure S7. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1,2-*O*-isopropylidene-α-D-xylofuranose (***2***).

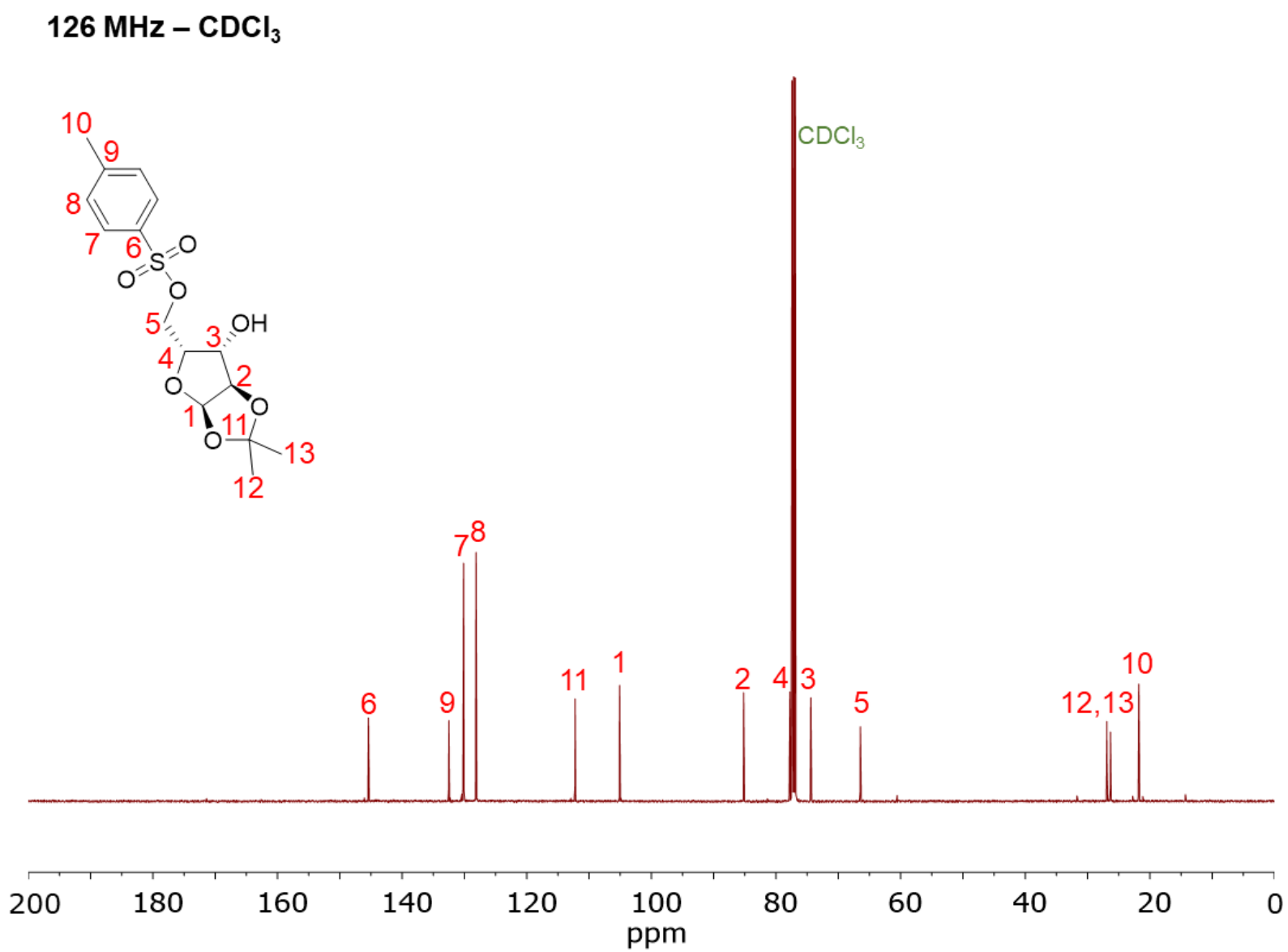

Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (***3***).

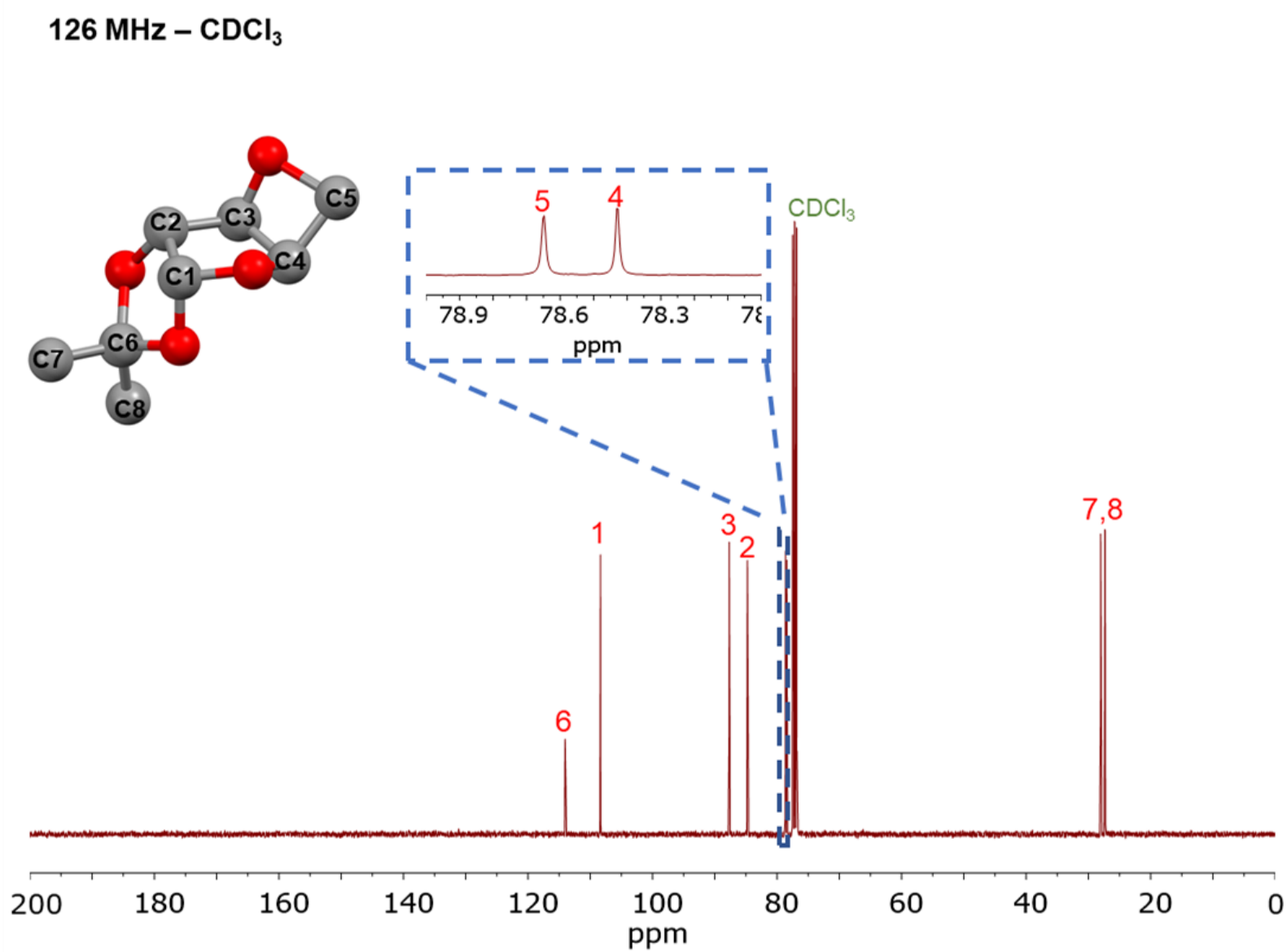

Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (***4***).

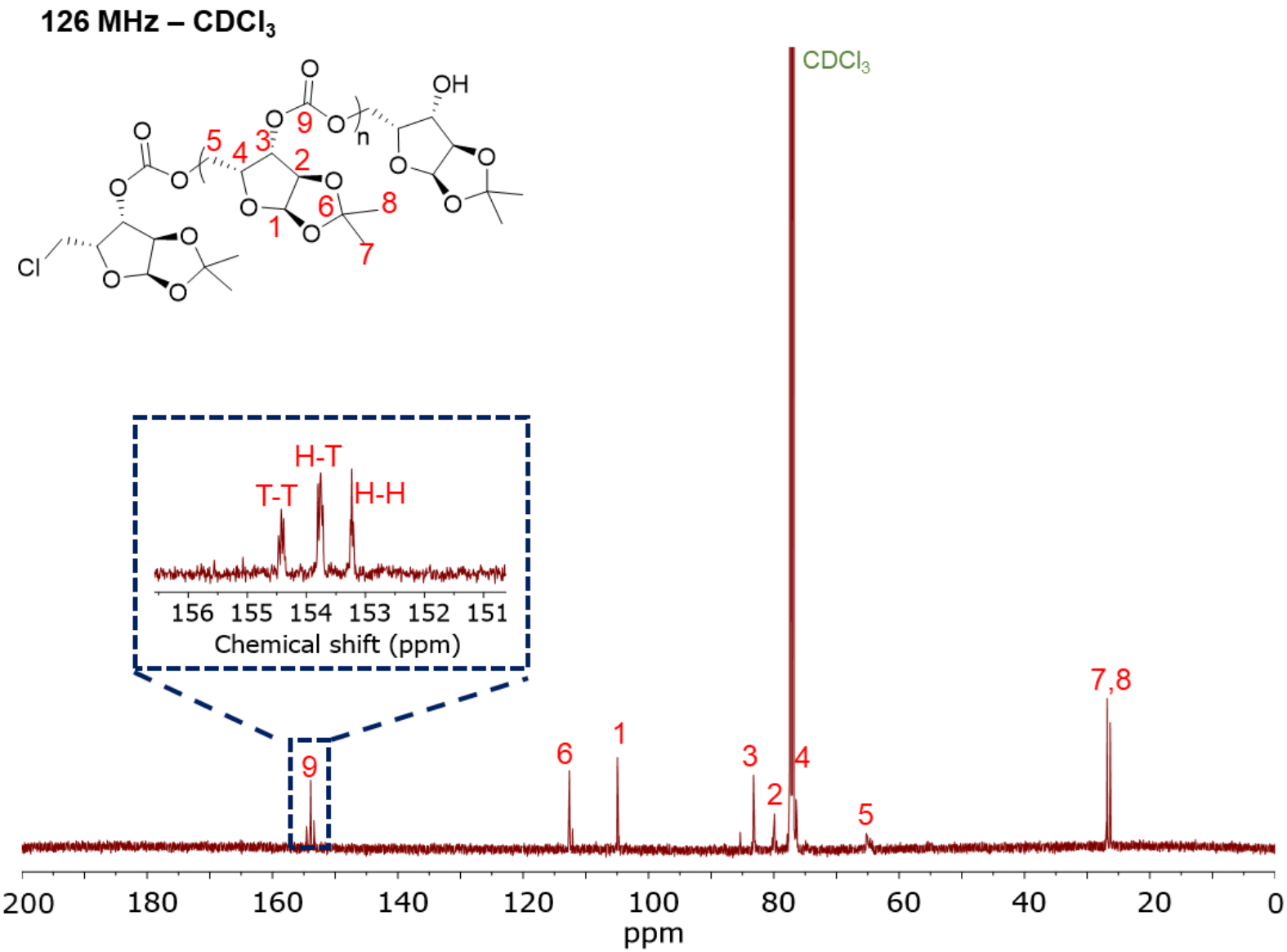

Figure S10. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate) (***5***).

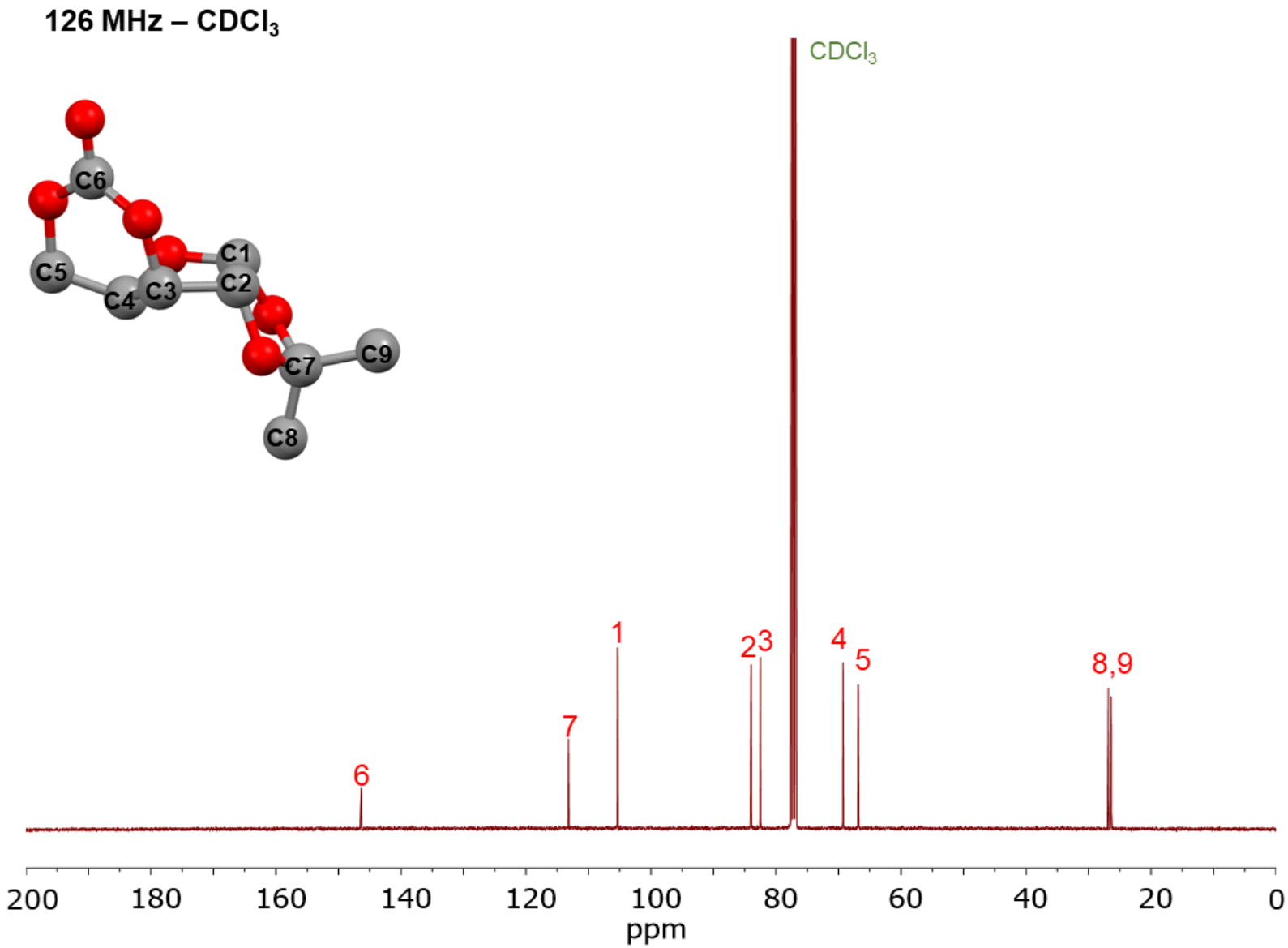

Figure S11. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1,2-*O*-isopropylidene-α-D-xylofuranose carbonate (***6***).

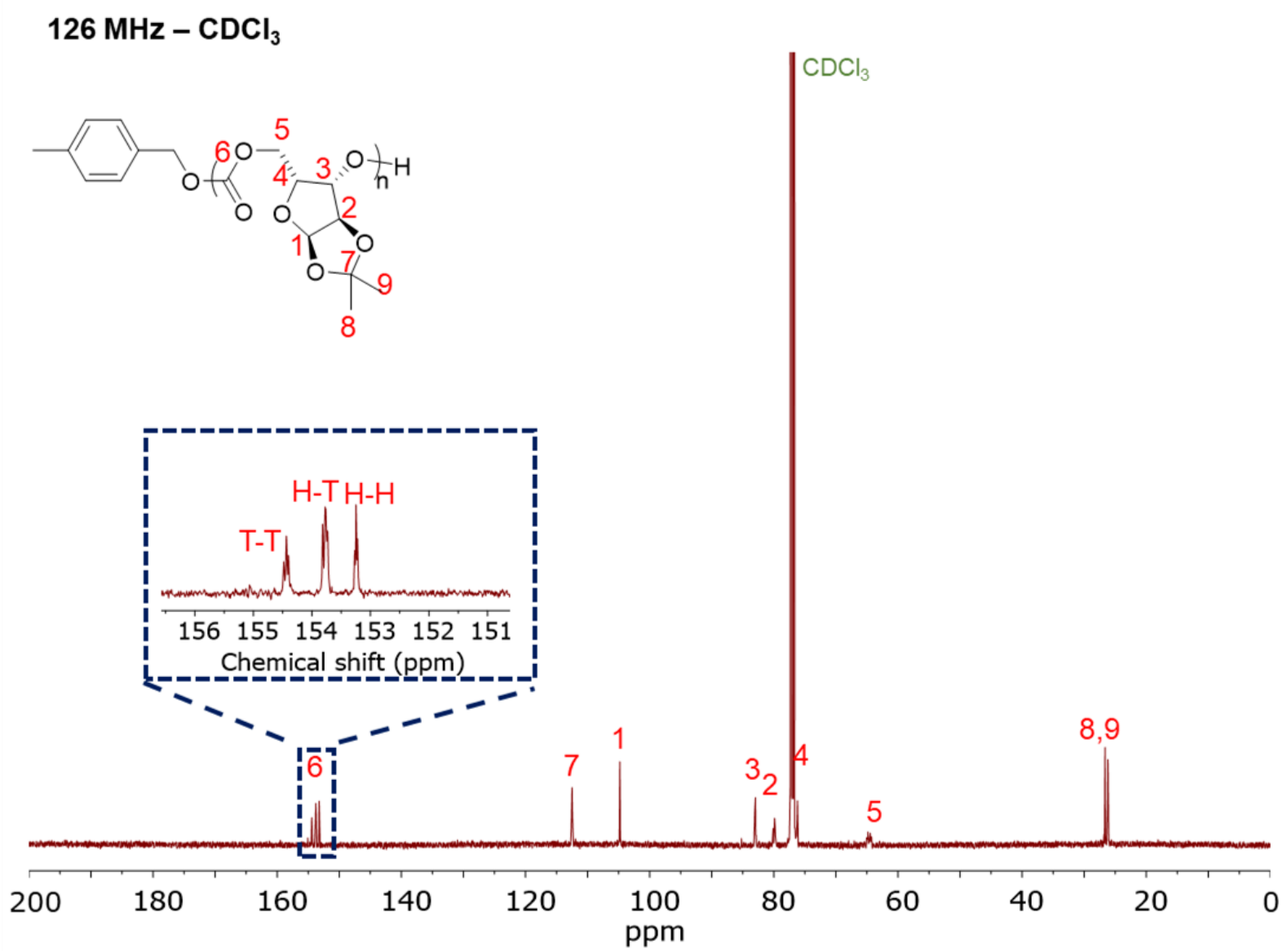

Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate) (***7***).

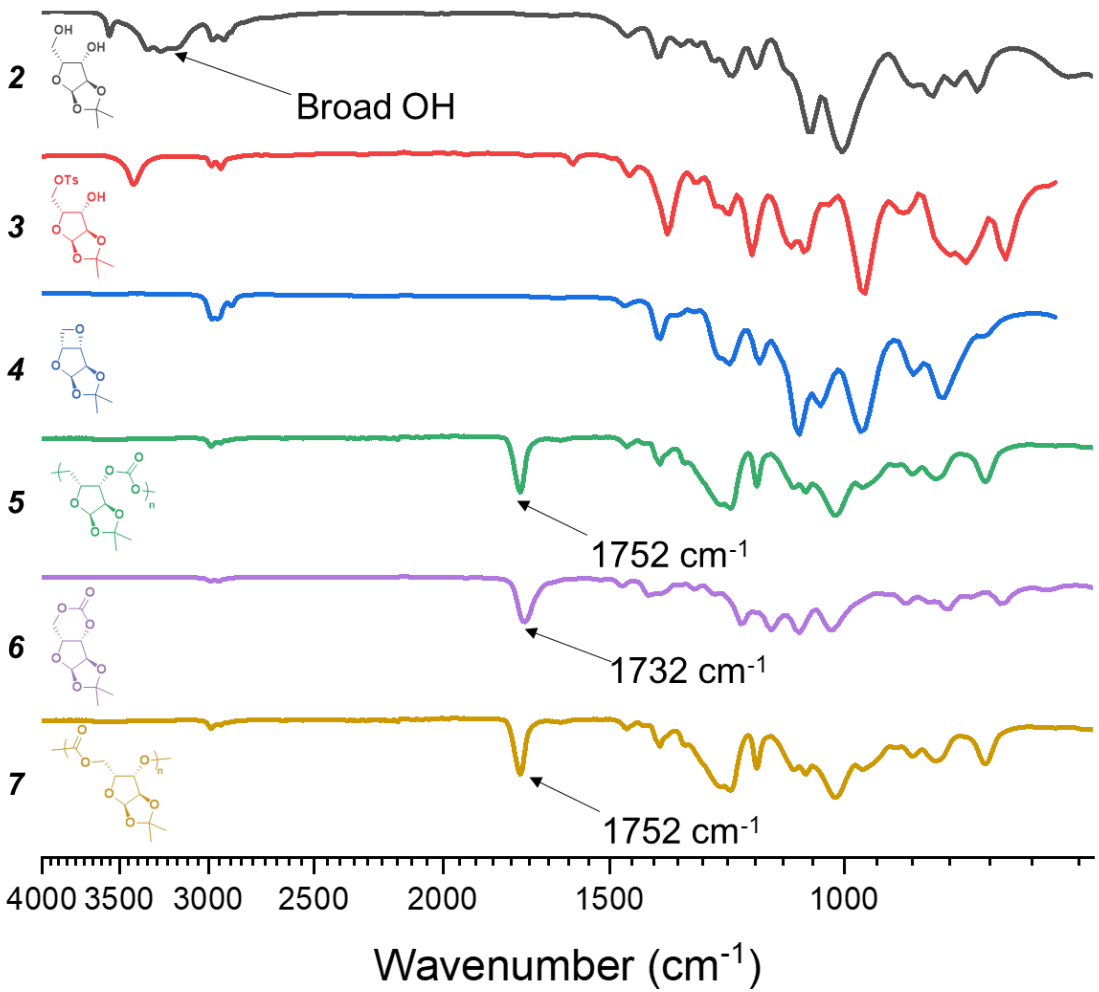

Figure S13. FTIR spectra of compounds ***2***-***7***.

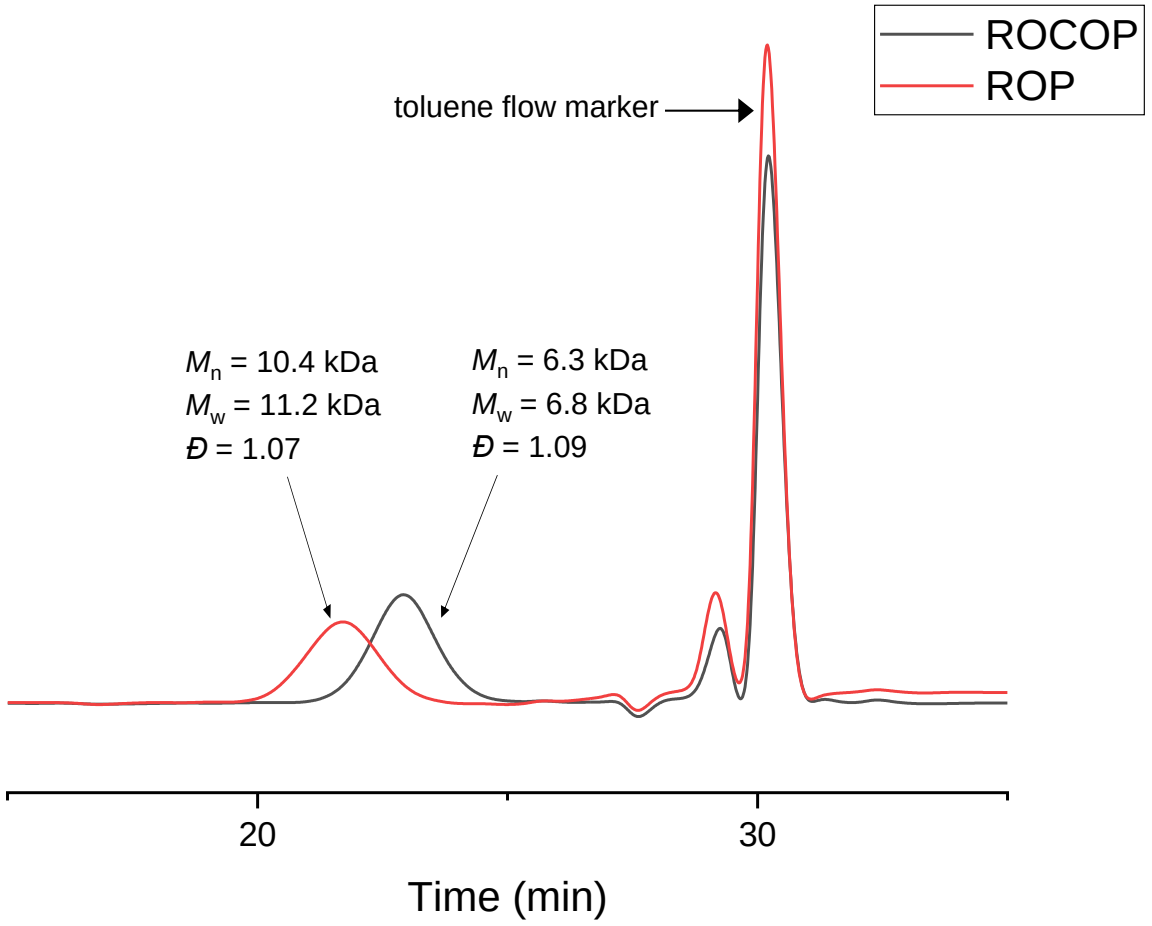

Figure S14. SEC traces of poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate) generated from ROCOP (***5***, black trace) and TBD catalyzed ROP (***7***, red trace).

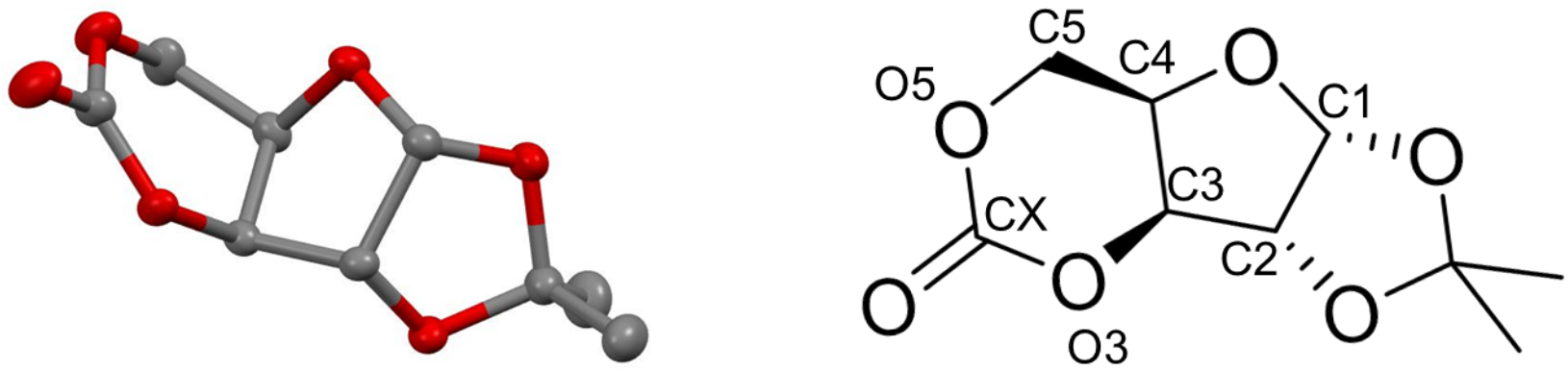

Figure S15. Thermal ellipsoid from the x-ray crystal structure analysis (CCDC Deposition Number: 2089312) and chemical structure of 1,2-*O*-isopropylidene-α-D-xylofuranose carbonate (***6***).

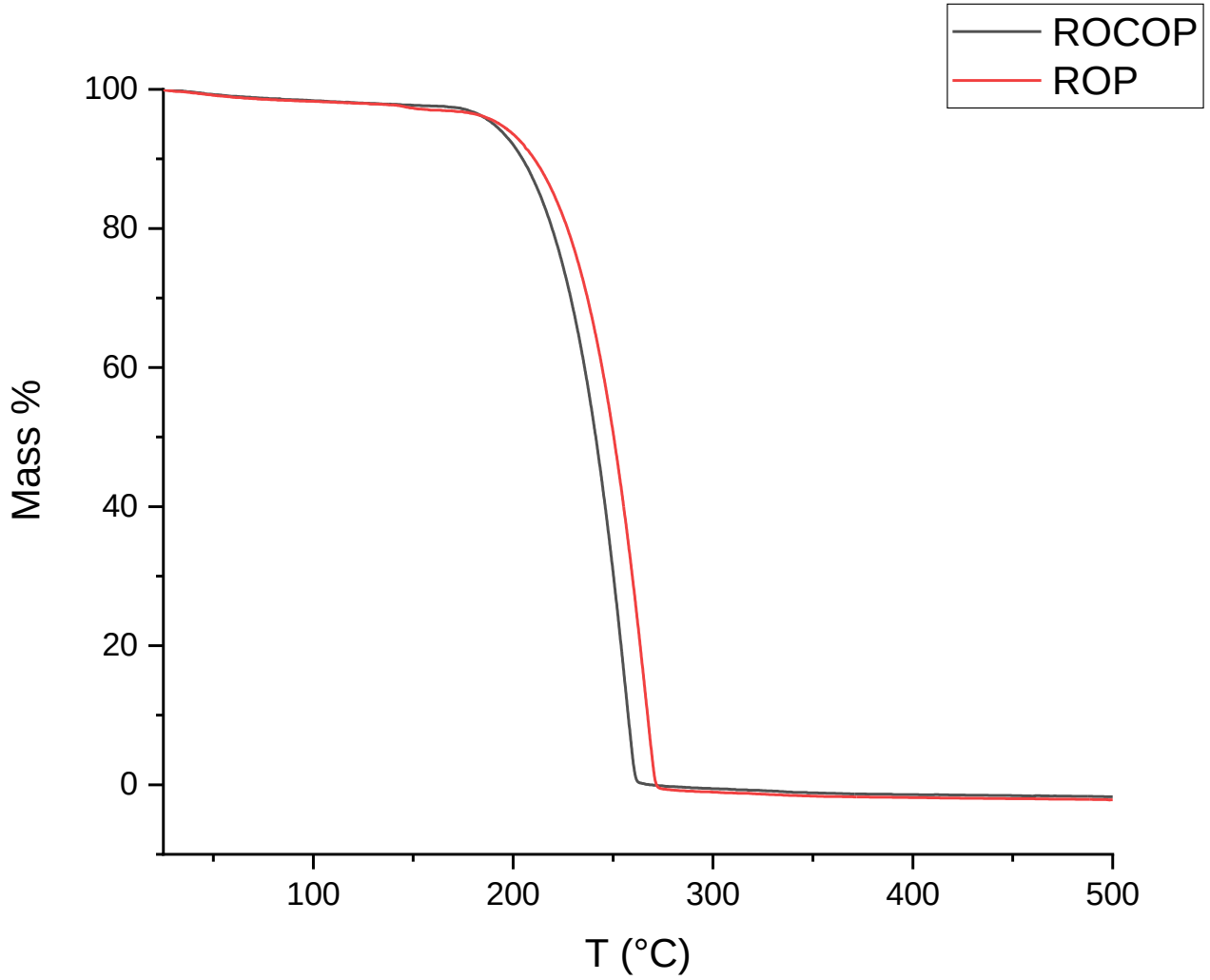

Figure S16. TGA traces of poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate) generated from ROCOP (***5***, black trace) and TBD catalyzed ROP (***7***, red trace).

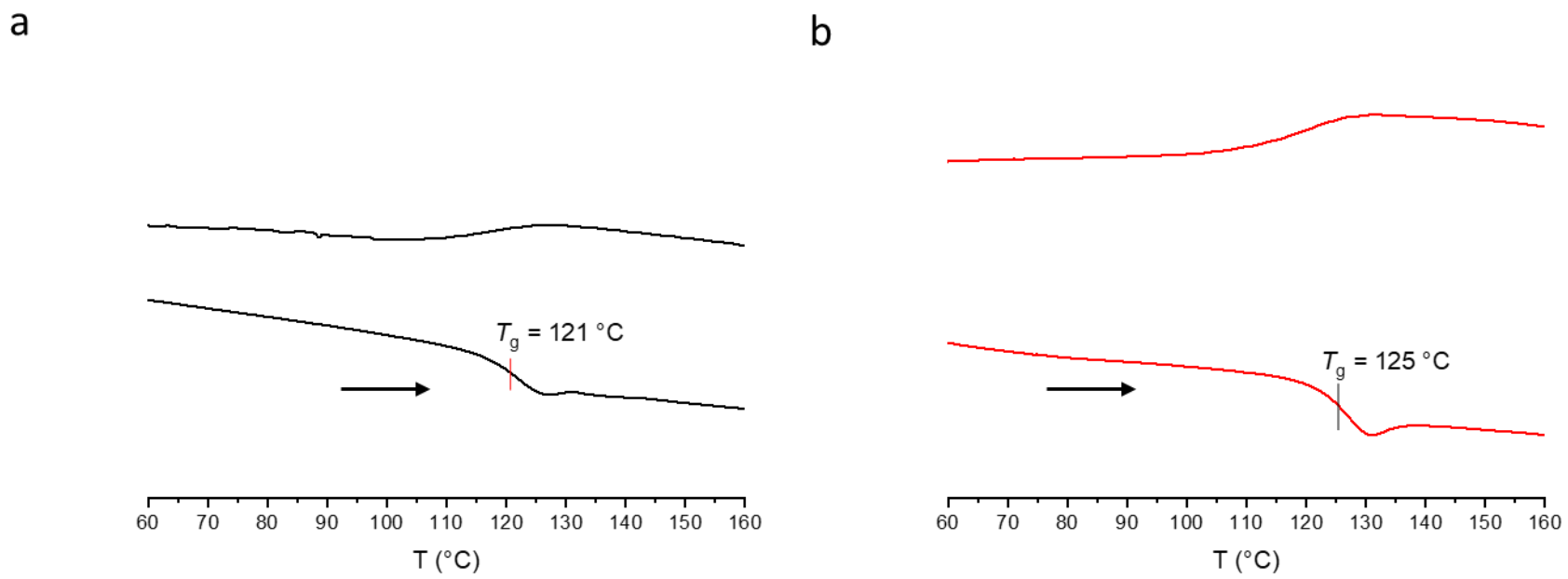

Figure S17. DSC traces of poly(1,2-*O*-isopropylidene-α-D-xylofuranose carbonate) generated from (a) ROCOP (***5***, black trace) and (b) TBD catalyzed ROP (***7***, red trace). The glass transition temperature (T_g) is labeled on the thermograms. Arrows indicate the direction of temperature ramping.

Table S1. Reaction kinetics of alternating CO_2/xylose oxetane (***4***) copolymerization catalyzed by (salen)CrCl/PPNCl[a]

Entry	Catalyst	Cocatalyst	Time (hours)	% conv.[b]	% Copolymer[c]	% Cyclic Carbonate[c]
1	(salen)CrCl	PPNCl	1	7 ± 0.9	47 ± 1.4	53 ± 1.4
2	(salen)CrCl	PPNCl	2	8 ± 0.3	48 ± 2.5	52 ± 2.5
3	(salen)CrCl	PPNCl	4	11 ± 0.9	33 ± 1.0	67 ± 1.0
4	(salen)CrCl	PPNCl	8	16 ± 0.6	27 ± 2.0	73 ± 2.0
5	(salen)CrCl	PPNCl	16	20 ± 2.7	29 ± 3.4	71 ± 3.4
6	(salen)CrCl	PPNCl	24	29 ± 2.6	42 ± 2.3	58 ± 2.3
7	(salen)CrCl	PPNCl	48	39 ± 1.7	46 ± 1.6	54 ± 1.6
8	(salen)CrCl	PPNCl	72	52 ± 4.2	58 ± 5.0	42 ± 5.0

[a]Reactions were performed in toluene at 110 °C at [(salen)CrCl]:[cocatalyst]:[xylose oxetane] = 1:2:75 molar ratios in a 10 mL autoclave in triplicate. Degrees of alternation were >99% for all samples, based on ^{1}H NMR spectroscopy. [b]Oxetane conversions were determined by ^{1}H NMR spectroscopy of the crude mixtures. [c]Molar ratios of the copolymer *vs* the cyclic product selectivities were determined by ^{1}H NMR spectroscopy of the crude mixtures.

Table S2. Crystal data and structure refinement for IPXFC

Identification code	IPXFC	
Empirical formula	C9 H12 O6	
Formula weight	216.19	
Temperature	110.0 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.9247(2) Å	α = 90°.
	b = 10.1052(4) Å	β = 90°.
	c = 16.3411(6) Å	γ = 90°.
Volume	978.35(6) $Å^3$	
Z	4	
Density (calculated)	1.468 Mg/m^3	
Absorption coefficient	1.080 mm^{-1}	
F(000)	456	
Crystal size	0.417 x 0.076 x 0.061 mm^3	
Theta range for data collection	5.146 to 70.123°.	
Index ranges	-7<=h<=6, -12<=k<=12, -19<=l<=19	
Reflections collected	24949	
Independent reflections	1860 [R(int) = 0.0175]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4684 and 0.3879	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1860 / 0 / 138	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0222, wR2 = 0.0562	
R indices (all data)	R1 = 0.0224, wR2 = 0.0565	
Absolute structure parameter	0.03(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.154 and -0.183 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for IPXFC. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
O(1)	4441(2)	2807(1)	3959(1)	23(1)
O(2)	5589(2)	2010(1)	2330(1)	29(1)
O(3)	8485(2)	3149(1)	2969(1)	22(1)
O(4)	9061(2)	1250(1)	2349(1)	33(1)
O(5)	6834(2)	5512(1)	4501(1)	24(1)
O(6)	4546(2)	4044(1)	5150(1)	31(1)
C(1)	4584(3)	3738(2)	3296(1)	21(1)
C(2)	7020(2)	4169(1)	3307(1)	20(1)
C(3)	7532(2)	4250(1)	4219(1)	20(1)
C(4)	5824(2)	3274(1)	4600(1)	21(1)
C(5)	3997(3)	3058(2)	2511(1)	27(1)
C(6)	7755(3)	2104(2)	2545(1)	23(1)
C(7)	5502(3)	5336(2)	5223(1)	25(1)
C(8)	6969(3)	5402(2)	5982(1)	34(1)
C(9)	3610(3)	6335(2)	5211(1)	38(1)

Table S4. Bond lengths [Å] and angles [°] for IPXFC

O(1)-C(1)	1.4376(18)
O(1)-C(4)	1.4112(17)
O(2)-C(5)	1.4487(19)
O(2)-C(6)	1.3341(19)
O(3)-C(2)	1.4556(17)
O(3)-C(6)	1.3354(18)
O(4)-C(6)	1.2027(19)
O(5)-C(3)	1.4179(17)
O(5)-C(7)	1.4312(18)
O(6)-C(4)	1.4089(18)
O(6)-C(7)	1.4283(18)
C(1)-H(1)	1.0000
C(1)-C(2)	1.508(2)
C(1)-C(5)	1.495(2)
C(2)-H(2)	1.0000
C(2)-C(3)	1.524(2)
C(3)-H(3)	1.0000
C(3)-C(4)	1.5441(19)
C(4)-H(4)	1.0000
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(7)-C(8)	1.515(2)
C(7)-C(9)	1.508(2)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(4)-O(1)-C(1)	107.85(11)
C(6)-O(2)-C(5)	121.34(12)

C(6)-O(3)-C(2)	124.30(11)
C(3)-O(5)-C(7)	108.47(11)
C(4)-O(6)-C(7)	110.25(11)
O(1)-C(1)-H(1)	110.7
O(1)-C(1)-C(2)	103.69(11)
O(1)-C(1)-C(5)	109.41(12)
C(2)-C(1)-H(1)	110.7
C(5)-C(1)-H(1)	110.7
C(5)-C(1)-C(2)	111.42(12)
O(3)-C(2)-C(1)	111.19(11)
O(3)-C(2)-H(2)	111.9
O(3)-C(2)-C(3)	106.85(11)
C(1)-C(2)-H(2)	111.9
C(1)-C(2)-C(3)	102.55(12)
C(3)-C(2)-H(2)	111.9
O(5)-C(3)-C(2)	107.92(11)
O(5)-C(3)-H(3)	113.4
O(5)-C(3)-C(4)	104.63(11)
C(2)-C(3)-H(3)	113.4
C(2)-C(3)-C(4)	103.28(11)
C(4)-C(3)-H(3)	113.4
O(1)-C(4)-C(3)	107.18(11)
O(1)-C(4)-H(4)	111.4
O(6)-C(4)-O(1)	110.23(12)
O(6)-C(4)-C(3)	104.84(11)
O(6)-C(4)-H(4)	111.4
C(3)-C(4)-H(4)	111.4
O(2)-C(5)-C(1)	111.12(12)
O(2)-C(5)-H(5A)	109.4
O(2)-C(5)-H(5B)	109.4
C(1)-C(5)-H(5A)	109.4
C(1)-C(5)-H(5B)	109.4
H(5A)-C(5)-H(5B)	108.0
O(2)-C(6)-O(3)	120.31(13)

O(4)-C(6)-O(2)	119.85(14)
O(4)-C(6)-O(3)	119.84(13)
O(5)-C(7)-C(8)	110.66(13)
O(5)-C(7)-C(9)	108.40(13)
O(6)-C(7)-O(5)	105.21(12)
O(6)-C(7)-C(8)	109.67(13)
O(6)-C(7)-C(9)	108.42(14)
C(9)-C(7)-C(8)	114.09(14)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

Symmetry transformations used to generate equivalent atoms.

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for IPXFC; the anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	23(1)	24(1)	1(1)	1(1)	-6(1)
O(2)	18(1)	34(1)	36(1)	-12(1)	-1(1)	-1(1)
O(3)	16(1)	23(1)	28(1)	-6(1)	2(1)	-1(1)
O(4)	24(1)	29(1)	47(1)	-14(1)	1(1)	4(1)
O(5)	30(1)	18(1)	25(1)	-2(1)	5(1)	-2(1)
O(6)	33(1)	28(1)	31(1)	-7(1)	12(1)	-9(1)
C(1)	17(1)	24(1)	23(1)	2(1)	2(1)	1(1)
C(2)	19(1)	17(1)	22(1)	0(1)	3(1)	1(1)
C(3)	19(1)	17(1)	23(1)	-1(1)	0(1)	-1(1)
C(4)	20(1)	20(1)	22(1)	1(1)	0(1)	-2(1)
C(5)	18(1)	36(1)	27(1)	-4(1)	-1(1)	2(1)
C(6)	19(1)	25(1)	26(1)	-4(1)	2(1)	-2(1)
C(7)	29(1)	23(1)	24(1)	-2(1)	4(1)	-3(1)
C(8)	43(1)	31(1)	26(1)	-1(1)	-2(1)	-3(1)
C(9)	36(1)	38(1)	40(1)	-5(1)	6(1)	9(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for IPXFC

	x	y	z	U(eq)
H(1)	3560	4508	3393	25
H(2)	7239	5040	3027	23
H(3)	9137	4039	4356	24
H(4)	6606	2530	4887	25
H(5A)	2459	2682	2552	32
H(5B)	4002	3711	2060	32
H(8A)	8154	4728	5947	50
H(8B)	6040	5241	6468	50
H(8C)	7662	6281	6021	50
H(9A)	4232	7225	5285	57
H(9B)	2548	6141	5655	57
H(9C)	2821	6287	4685	57

Table S7. Torsion angles [°] for IPXFC

O(1)-C(1)-C(2)-O(3)	75.42(13)
O(1)-C(1)-C(2)-C(3)	-38.47(13)
O(1)-C(1)-C(5)-O(2)	-62.60(16)
O(3)-C(2)-C(3)-O(5)	158.06(10)
O(3)-C(2)-C(3)-C(4)	-91.51(13)
O(5)-C(3)-C(4)-O(1)	108.79(12)
O(5)-C(3)-C(4)-O(6)	-8.36(14)
C(1)-O(1)-C(4)-O(6)	92.87(13)
C(1)-O(1)-C(4)-C(3)	-20.68(14)
C(1)-C(2)-C(3)-O(5)	-84.92(12)
C(1)-C(2)-C(3)-C(4)	25.51(13)
C(2)-O(3)-C(6)-O(2)	7.2(2)
C(2)-O(3)-C(6)-O(4)	-173.61(14)
C(2)-C(1)-C(5)-O(2)	51.47(16)
C(2)-C(3)-C(4)-O(1)	-4.06(14)
C(2)-C(3)-C(4)-O(6)	-121.21(12)
C(3)-O(5)-C(7)-O(6)	-26.72(15)
C(3)-O(5)-C(7)-C(8)	91.66(14)
C(3)-O(5)-C(7)-C(9)	-142.53(13)
C(4)-O(1)-C(1)-C(2)	37.49(14)
C(4)-O(1)-C(1)-C(5)	156.46(11)
C(4)-O(6)-C(7)-O(5)	21.18(16)
C(4)-O(6)-C(7)-C(8)	-97.86(16)
C(4)-O(6)-C(7)-C(9)	136.98(14)
C(5)-O(2)-C(6)-O(3)	3.0(2)
C(5)-O(2)-C(6)-O(4)	-176.18(14)
C(5)-C(1)-C(2)-O(3)	-42.17(16)
C(5)-C(1)-C(2)-C(3)	-156.05(12)
C(6)-O(2)-C(5)-C(1)	-32.76(19)
C(6)-O(3)-C(2)-C(1)	13.63(18)
C(6)-O(3)-C(2)-C(3)	124.79(14)
C(7)-O(5)-C(3)-C(2)	131.11(12)

C(7)-O(5)-C(3)-C(4)	21.60(14)
C(7)-O(6)-C(4)-O(1)	-122.96(13)
C(7)-O(6)-C(4)-C(3)	-7.92(16)

Symmetry transformations used to generate equivalent atoms.

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