Supporting Information

Functional Polycarbonate of a D-Glucal-Derived Bicyclic Carbonate *via* Organocatalytic Ring-Opening Polymerization

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Experimental Section

Materials. Reagents were available from Sigma Aldrich and used as received unless otherwise noted. TU was prepared as previously reported.[1] TU, 4-methylbenzyl alcohol (99%), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; 98%) were dried by stirring in dry THF with CaH_2, filtering, and removing solvent under reduced pressure. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%) was stirred over CaH_2, vacuum distilled, then stored over molecular sieves (3 Å). Dichloromethane (DCM) was purified by passage through a solvent purification system (J.C. Meyer Solvent Systems) and used as a dried solvent. Monomer, **3**, was dried under reduced pressure, over P_2O_5 and stored under Ar environment. Column chromatography was performed on a combiflash Rf4x (Teledyne ISCO) with RediSep Rf Columns (Teledyne ISCO). The prepared polymer sample, **4**, was dried over P_2O_5 under reduced pressure overnight prior to characterizations.

Characterization. ^{1}H, ^{13}C, and homonuclear correlation spectroscopy (COSY) and heteronuclear single-quantum correlation spectroscopy (HSQC) NMR spectra were recorded on a Varian Inova 500 spectrometer. Chemical shifts were referenced to the solvent resonance signals. The data obtained were processed and analyzed using MestReNova software.

IR spectra were recorded on a Shimadzu IR Prestige attenuated total reflectance Fourier transform infrared spectrophotometer (ATR-FTIR) and analyzed using IRsolution v. 1.40 software.

Size exclusion chromatography (SEC) measurements were performed on a Waters Chromatography, Inc. (Milford, MA) system equipped with an isocratic pump model 1515, a differential refractometer model 2414 and a four-column set of 5 μm Guard (50 × 7.5 mm), Styragel HR 4 5 μm DMF (300 × 7.5 mm), Styragel HR 4E 5 μm DMF (300 × 7.5 mm) and

Styragel HR 2 5 μm DMF (300 × 7.5 mm) using DMF (0.05 M LiBr) as the eluent (1.00 mL/min) at 70 °C. Polymer solutions were prepared at a concentration of *ca*. 3–5 mg/mL and an injection volume of 200 μL was used. Data collection and analysis were performed with Empower 2 v. 6.10.01.00 software (Waters, Inc.). The system was calibrated with polystyrene standards (Polymer Laboratories, Amherst, MA) ranging from 615 to 442,800 Da.

Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC822 (Mettler-Toledo, Inc., Columbus, OH) under N_2, with a heating rate of 10 °C/min. Measurements were analyzed using Mettler-Toledo Star^e v.10.00 software. The T_g was taken as the midpoint of the inflection tangent, upon the third heating scan. Thermogravimetric analysis (TGA) was performed under Ar atmosphere using a Mettler Toledo model TGA/SDTA851^e apparatus with a heating rate of 10 °C/min that was coupled to a Pfeiffer ThermoStar/GSD320T3 mass spectrometer.

Synthesis of *iso*-propyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (1). Tri-*O*-acetyl D- glucal (12.0997 g, 44.443 mmol) was added to a flamed dried round bottom flask (150 mL) under nitrogen and dissolved in 100 mL of anhydrous DCM and 4.20 mL of propan-2-ol (3.2995 g, 54.9 mmol). After cooling to 0 °C, boron trifluoride diethyl etherate (2.5547 g, 2.2 mL, 18 mmol) was added dropwise. The ice bath was removed, and the reaction mixture was allowed to stir for additional 30 min until the solution turned a deep purple color. The reaction was quenched by adding 150 mL of saturated solution of $NaHCO_3$ at which point the color of the solution was discharged. After extracting the aqueous layer with DCM (100 mL), the combined organic layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure, resulting in a light amber syrup. The crude was purified by column

chromatography (9:1 hexanes/ethyl acetate), resulting in 10.8427 g (95.2%) of **1** (9:1, α/β) as a colorless liquid.

*Iso-Propyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**1a**).* FTIR (ATR) (cm^{-1}): 2972, 2931, 1739, 1369, 1222, 1099, 1028, 981. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.88–5.86 (ddd, $J_{3\text{-}2}$ = 10.2, $J_{3\text{-}4}$ = 1.7, $J_{3\text{-}1}$ = 1.5, 1H, H-3), 5.82–5.79 (ddd, $J_{2\text{-}3}$ = 10.2, $J_{2\text{-}1}$ = 2.8, $J_{2\text{-}4}$ = 1.9, 1H, H-2), 5.31–5.28 (ddd, $J_{4\text{-}5}$ = 9.6, $J_{4\text{-}2}$ = 1.9, $J_{4\text{-}3}$ = 1.7, 1H, H-4), 5.14–5.12 (dd, $J_{1\text{-}2}$ = 2.8, $J_{1\text{-}3}$ = 1.5, 1H, H-1), 4.25–4.22 (dd, $J_{6\text{-}6'}$ = 11.6, $J_{6\text{-}5}$ = 5.6, 1H, H-6), 4.19–4.16 (dd, $J_{6'\text{-}6}$ = 11.6, $J_{6'\text{-}5}$ = 2.5, 1H, H-6'), 4.17–4.13 (ddd, $J_{5\text{-}4}$ = 2.5, $J_{5\text{-}6}$ = 5.6, $J_{5\text{-}6'}$ = 2.5, 1H, H-5), 4.02–3.95 (septet, J = 6.2, 1H, C*H*(CH_3)(CH_3)), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.26–1.25 (d, J = 6.6, 3H, -CH(C*H*$_3$)(CH_3)), 1.19–1.18 (d, J = 6.6, 3H, -CH(CH_3)(C*H*$_3$)) ppm; ^{13}C NMR(125 MHz, $CDCl_3$, ppm): δ 170.9 (O*C*OCH_3), 170.5 (O*C*OCH_3), 128.9 (C=C), 128.6 (C=C), 92.9 (C1), 70.9 (*C*H(CH_3)(CH_3)), 66.9 (C5), 65.5 (C4), 63.2 (C6), 23.6 (OCO*C*H$_3$), 22.1 (OCO*C*H$_3$), 21.1 (CH(*C*H$_3$)(CH_3)), 20.9 (CH(CH_3)(*C*H$_3$)). ESI MS: calculated [M + Li] for $C_{13}H_{20}O_6$, 279.2345; found, 279.1138.

*Iso-Propyl 4,6-di-O-acetyl-2,3-dideoxy-β-D-erythro-hex-2-enopyranoside (**1b**).* FTIR (ATR): (cm^{-1}) 2972, 2931, 1739, 1369, 1222, 1099, 1028, 981. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.97–5.93 (ddd, $J_{3\text{-}2}$ = 10.3, $J_{3\text{-}4}$ = 3.7, $J_{3\text{-}1}$ = 1.8, 1H, H-3), 5.91–5.88 (ddd, $J_{2\text{-}3}$ = 10.3, $J_{2\text{-}4}$ = 1.5, $J_{2\text{-}1}$ = 1.0, 1H, H-2), 5.22–5.20 (ddd, $J_{4\text{-}5}$ = 7.8, $J_{4\text{-}3}$ = 2.5, $J_{4\text{-}2}$ = 1.5, 1H, H-4), 5.21–5.20 (dd, $J_{1\text{-}3}$ = 1.8, $J_{1\text{-}2}$ = 1.0, 1H, H-1), 4.29–4.25 (dd, $J_{6\text{-}6'}$ = 11.6, $J_{6\text{-}5}$ = 6.0, 1H, H-6), 4.19–4.16 (dd, $J_{6'\text{-}6}$ = 11.6, $J_{6'\text{-}5}$ = 2.5, 1H, H-6'), 4.17–4.13 (ddd, $J_{5\text{-}4}$ = 7.8, $J_{5\text{-}6}$ = 6.0, $J_{5\text{-}6'}$ = 2.5, 1H, H-5), 4.10–4.02 (septet, J = 6.3, 1H, C*H*(CH_3)(CH_3)), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.24–1.23 (d, J = 6.1, 3H, -CH(C*H*$_3$)(CH_3)), 1.18–1.17 (d, J = 6.0, 3H, -CH(CH_3)(C*H*$_3$)) ppm; ^{13}C NMR(125 MHz, $CDCl_3$, ppm): δ 170.9 (O*C*OCH_3), 170.5 (O*C*OCH_3), 131.0 (C=C), 125.8 (C=C), 93.2 (C1), 72.7

(C5), 70.2 (*C*H(CH_3)(CH_3)), 64.5 (C4), 63.5 (C6), 23.6 (OCO*C*H_3), 22.1 (OCO*C*H_3), 21.1 (CH(*C*H_3)(CH_3)), 20.9 (CH(CH_3)(*C*H_3)). ESI MS: calculated [M + Li] for $C_{13}H_{20}O_6$, 279.2345; found, 279.1138.

Synthesis of *Iso*-propyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2). A solution of **1** (10.5 g, 58.6 mmol) in 180 mL of dry methanol under nitrogen at room temperature was treated with a solution of sodium methoxide in methanol (0.80 mL, 4.37 M, 3.5 mmol), and the reaction mixture was stirred at room temperature for 45 min. Solid NH_4Cl (0.5 g) was added, and the mixture was stirred 15 min and then diluted with 200 mL of acetone. The solids were removed by filtration, and the filtrate was concentrated *in vacuo* to afford **2** (7.26 g, 9:1 α/β) in quantitative yield, which was used directly in the next reaction.

*Iso-propyl-2,3-Dideoxy-a-D-erythro-hex-2-enopyranoside (**2a**).* FTIR (ATR): (cm^{-1}) 3500–3150 (br), 2968, 2933, 2877, 1384, 1037, 945. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.96–5.94 (ddd, $J_{3\text{-}2}$ = 10.2, $J_{3\text{-}1}$ = $J_{3\text{-}4}$ = 1.2, 1H, H-3), 5.75–5.72 (ddd, $J_{2\text{-}3}$ = 10.2, $J_{2\text{-}4}$ = 3.0, $J_{2\text{-}1}$ = 2.1, 1H, H2), 5.10–5.08 (dd, $J_{1\text{-}2}$ = 2.1, $J_{1\text{-}3}$ = 1.2, 1H, H-1), 4.24–4.19 (dddd, $J_{4\text{-}5}$ = 9.2, $J_{4\text{-OH}}$ = 8.5, $J_{4\text{-}2}$ = 3.0, $J_{4\text{-}3}$ = 1.7, 1H, H-4), 4.01–3.93 (septet, J = 6.3, 1H, C*H*(CH_3)(CH_3))), 3.91–3.80 (m, 2H, H-6, H-6'), 3.77–3.74 (ddd, $J_{5\text{-}4}$ = 9.2, $J_{5\text{-}6}$ = $J_{5\text{-}6'}$ = 4.6, 1H, H-5), 1.97–1.93 (d, $J_{\text{OH-}6}$ = 7.5, 1H, OH), 1.84–1.81 (d, $J_{\text{OH-}4}$ = 8.5, 1H, OH), 1.25–1.24 (d, J = 6.2, 3H, -CH(C*H*$_3$)(CH_3)), 1.19–1.17 (d, J = 6.2, 3H, -CH(CH_3)(C*H*$_3$)) ppm; ^{13}C NMR(125 MHz, $CDCl_3$, ppm): δ 133.3 (C=C), 126.9 (C=C), 92.7 (C1), 71.39 (C5), 70.60 (*C*H(CH_3)(CH_3)), 64.4 (C4), 62.8 (C6), 23.8 (CH(*C*H_3)(CH_3)), 22.1 (CH(CH_3)(*C*H_3)); ESI MS: calculated [M + Li] for $C_9H_{16}O_4$, 195.1209; found, 195.1201.

*Iso-propyl-2,3-Dideoxy-β-D-erythro-hex-2-enopyranoside (**2b**).* FTIR (ATR): (cm^{-1}) 3500–3150 (br), 2968, 2933, 2877, 1384, 1037, 945. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.04–6.01 (ddd, $J_{3\text{-}2}$ = 10.3, $J_{3\text{-}1}$ = 3.4, $J_{3\text{-}4}$ = 1.7, 1H, H-3), 5.78–5.75 (ddd, $J_{2\text{-}3}$ = 10.3, $J_{2\text{-}1}$ = $J_{2\text{-}4}$ = 1.7, 1H, H2), 5.22–5.21 (dd, $J_{1\text{-}3}$ = 3.4, $J_{1\text{-}2}$ = 1.7, 1H, H-1), 4.20–4.16 m 1H, H-4), 4.11–4.04 (septet, J = 6.3, 1H, C*H*(CH_3)(CH_3)), 3.91–3.82 (m, 2H, H-6, H-6'), 3.77–3.74 (ddd, $J_{5\text{-}4}$ = 9.2, $J_{5\text{-}6}$ = $J_{5\text{-}6'}$ = 4.6, 1H, H-5), 1.97–1.93 (d, $J_{OH\text{-}6}$ = 7.5, 1H, OH), 1.84–1.81 (d, $J_{OH\text{-}4}$ = 8.5, 1H, OH), 1.25–1.24 (d, J = 6.2, 3H, -CH(C*H*$_3$)(CH_3)), 1.19–1.17 (d, J = 6.2, 3H, -CH(CH_3)(C*H*$_3$)) ppm; ^{13}C NMR(125 MHz, $CDCl_3$, ppm): δ 131.2 (C=C), 128.7 (C=C), 94.23 (C1), 71.4 (C5), 70.6 (*C*H(CH_3)(CH_3)), 64.4 (C4), 63.3 (C6), 23.8 (CH(*C*H$_3$)(CH_3)), 22.1 (CH(CH_3)(*C*H$_3$)). ESI MS: calculated [M + Li] for $C_9H_{16}O_4$, 195.1209; found, 195.1201.

Synthesis of Iso-propyl 4,6-carbonate-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3). The diol, **2**, (2.4089 g, 14.923 mmol) was dissolved in dry dichloromethane (600 mL) and anhydrous pyridine (3.5595 g, 3.6 mL, 45 mmol). Triphosgene (2.2166 g, 7.4696 mmol) dissolved in 25 mL of dry dichloromethane was added dropwise over 10 min and the reaction mixture was allowed to stir at room temperature for 3.5 hours. The reaction was quenched with 25 mL of saturated $NaHCO_3$, and the organic layer was washed with saturated NH_4Cl solution (25 mL) and brine (25 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The crude was purified by column chromatography (SiO_2; 1/1 hexane/ethyl acetate) and recrystallized (ether/hexanes) to afford **2** (1.2788 g, 40.0%, 1:0 α/β) as white needle-like crystals. The monomer was dried in a dessicator over P_2O_5, for three days and stored in a glovebox.

*Iso-propyl 4,6-carbonate-2,3-dideoxy-a-D-erythro-hex-2-enopyranoside (**3**).* FTIR (ATR): (cm^{-1}) 2976, 2907, 1755 (carbonate), 1396, 1267, 1238, 1183, 1130, 1120, 1010, 952, 933. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.12–6.10 (ddd, $J_{3\text{-}2}$ = 10.0, $J_{3\text{-}4}$ = 2.7, $J_{3\text{-}1}$ = 1.4, 1H, H3), 5.86–5.83

(ddd, $J_{2\text{-}2}$ = 10.0, $J_{2\text{-}1}$ = $J_{2\text{-}4}$ =2.5, 1H, H2), 5.20–5.18 (dd, $J_{1\text{-}2}$ = 2.5, $J_{1\text{-}3}$ = 1.4, 1H, H-1), 4.66–4.63 (ddd, $J_{4\text{-}5}$ = 9.1, $J_{4\text{-}3}$ = 2.7, $J_{4\text{-}2}$ = 2.5, 1H, H-4), 4.53–4.50 (dd, $J_{6eq\text{-}6ax}$ = 9.7, $J_{6eq\text{-}5}$ = 6.0, 1H, H-6_{eq}), 4.32–4.28 (dd, $J_{6ax\text{-}5}$ = 10.4, $J_{6ax\text{-}6eq}$ = 9.7, 1H, 6_{ax}), 4.23–4.17 (ddd, $J_{5\text{-}6ax}$ = 10.4, $J_{5\text{-}4}$ = 9.1, $J_{5\text{-}6eq}$ = 6.0), 4.02–3.94 (septet, J = 6, 1H, C*H*(CH_3)(CH_3)), 1.26–1.25 (d, J = 6.2, 3H, -CH(C*H*$_3$)(CH_3)), 1.22–1.21 (d, J = 6.2, 3H, -CH(C*H*$_3$)(CH_3)); ^{13}C NMR(125 MHz, $CDCl_3$, ppm): δ 148.0 (carbonate), 129.4 (C=C), 126.83 (C=C), 93.6 (C1), 72.6 (C4), 71.5 (*C*H(CH_3)(CH_3)), 70.3 (C6), 60.9 (C5), 23.8 (CH(*C*H$_3$)(CH_3)), 22.0 (CH(CH_3)(*C*H$_3$)). ESI MS: calculated [M + H] for $C_{10}H_{14}O_5$, 215.0919; found, 215.0917.

General Procedure for Polymerization of 3 Using TBD. A solution of initiator, 4-methylbenzyl alcohol, and catalyst, TBD, in dry DCM with a concentration of 10 mg/mL was prepared prior to polymerization. In a 5 mL vial containing a magnetic stir bar in the glovebox, **3** (0.100 g, 0.467 mmol, 1 equiv) and 4-methylbenzyl alcohol (2.282 mg, 0.0187 mmol, 0.04 equiv) were dissolved in DCM (974 μL). TBD (3.236 mg, 0.0233 mmol, 0.05 equiv) was then added to initiate polymerization. The reaction was allowed to stir at 30 °C, and aliquots of samples were taken to monitor the monomer conversion by ^{1}H NMR spectroscopy and GPC. After 10 min of stirring, the reaction mixture was quenched by adding Amberlyst 15 H resin (20–50 mg). The product was precipitated from DCM to methanol and dried in a falcon tube under reduced pressure, yielding a white powder.

General Procedure for Polymerization of 3 Using DBU. A solutions of the initiator, 4-methylbenzyl alcohol, and catalyst, DBU, in dry DCM with a concentration of 10 mg/mL was prepared prior to polymerization. In a 5 mL vial containing a magnetic stir bar in the glovebox, **3** (0.100 g, 0.467 mmol, 1 equiv) and 4-methylbenzyl alcohol (2.282 mg, 0.0187 mmol, 0.04 equiv) were dissolved in DCM (974 μL). DBU (3.539 mg, 3.476 μL, 0.0233 mmol, 0.05 equiv)

was then added to initiate polymerization. The reaction was allowed to stir at 30 °C, and aliquots of samples were taken to monitor the monomer conversion by ^{1}H NMR spectroscopy and GPC. After 10 min of stirring, the reaction mixture was quenched by adding Amberlyst 15 H resin (20–50 mg). The product was precipitated from DCM to methanol and dried in a falcon tube under reduced pressure, yielding a white powder.

General Procedure for Polymerization of 3 using a combination of DBU+TU. A solution of the initiator, 4-methylbenzyl alcohol, and catalysts, DBU and TU, in dry DCM with a concentration of 10 mg/mL were prepared prior to polymerization. In a 5 mL vial containing a magnetic stir bar in the glovebox, **3** (0.117 g, 0.546 mmol, 1 equiv), 4-methylbenzyl alcohol (2.658 mg, 0.0218 mmol, 0.04 equiv), and TU (11.244 mg, 0.0272 mmol, 0.05 eq) were dissolved in DCM (126 μL). DBU (4.141 mg, 4.067 μL, 0.0272 mmol, 0.05 equiv) was then added to initiate polymerization. The reaction was allowed to stir at 30 °C, and aliquots of samples were taken to monitor the monomer conversion by ^{1}H NMR spectroscopy and GPC. After 10 min of stirring, the reaction mixture was quenched by adding Amberlyst 15 H resin (20-50 mg). The product was precipitated from DCM to methanol and dried in a falcon tube under reduced pressure, yielding a white powder.

*Poly(hex-2-enopyranoside)carbonate(**4**).* FTIR (ATR): (cm^{-1}) 2968, 2933, 2877, 1751, 1384, 1037, 945. M_n (NMR) 11800 g/mol; M_n (GPC) 9800 g/mol; PDI = 1.31; T_g = 69 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 7.27–7.26 (d, Ar), 7.19–7.17 (d, Ar), 5.96–5.91 (m, H3), 5.85–5.79 (m, H2), 5.16–5.08 (m, H4+H1), 4.43–4.23 (m, H6), 4.18–4.10 (m, H5), 3.99–3.90 (sept, C*H*(CH_3)(CH_3)), 2.34 (s, C*H*$_3$Ar), 1.21-1.20 (d, CH(C*H*$_3$)(CH_3)), 1.16–1.14, (d, CH(CH_3)(C*H*$_3$)) ppm; ^{13}C NMR(125 MHz, CD_2Cl_2, ppm): δ 155.5–154.6 (carbonate), 129.7 (C=C), 128.2 (C=C),

93.2 (C1), 71.3 (C4), 68.4 (*C*H(CH_3)(CH_3)), 67.1 (C6), 66.9 (C5), 23.9 (CH(*C*H_3)(CH_3)), 22.2 (CH(CH_3)(*C*H_3)). TGA in Ar: $T_{d,\,5\%}$ = 190 °C, $T_{d,50\%}$ = 296 °C.

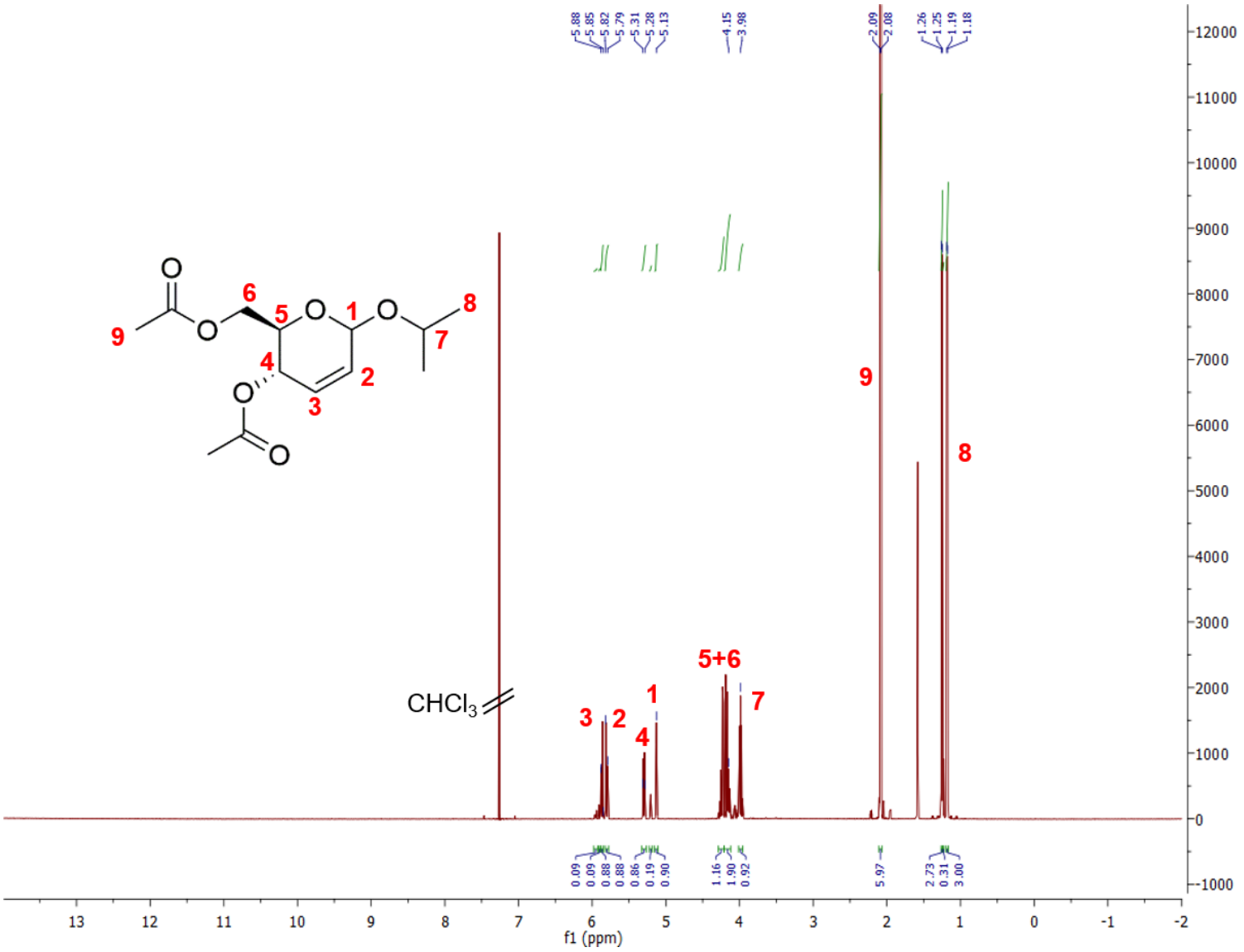


Figure S1. ^{1}H NMR spectrum of compound **1**.

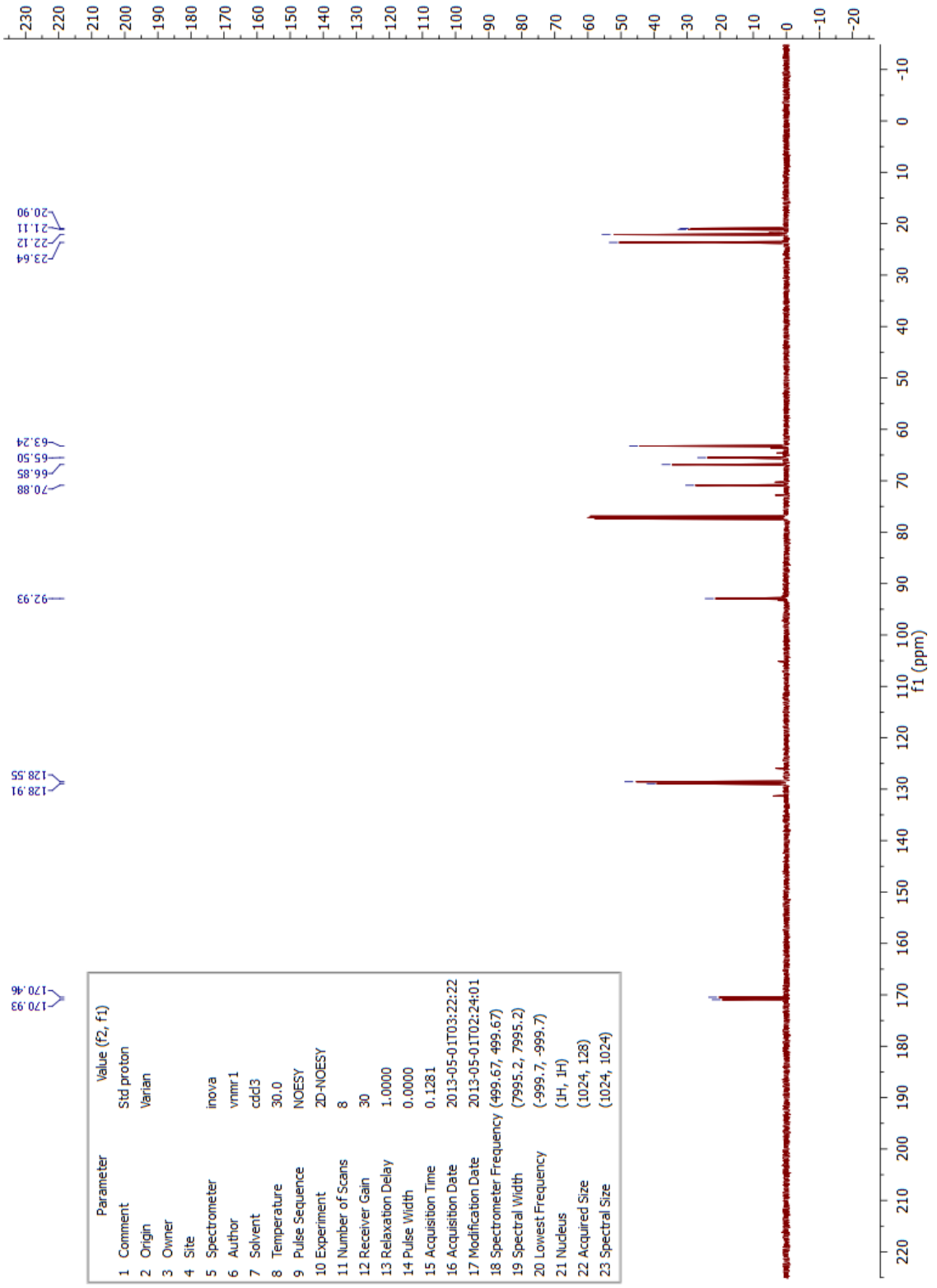


Figure S2. ^{13}C NMR spectrum of compound **1**.

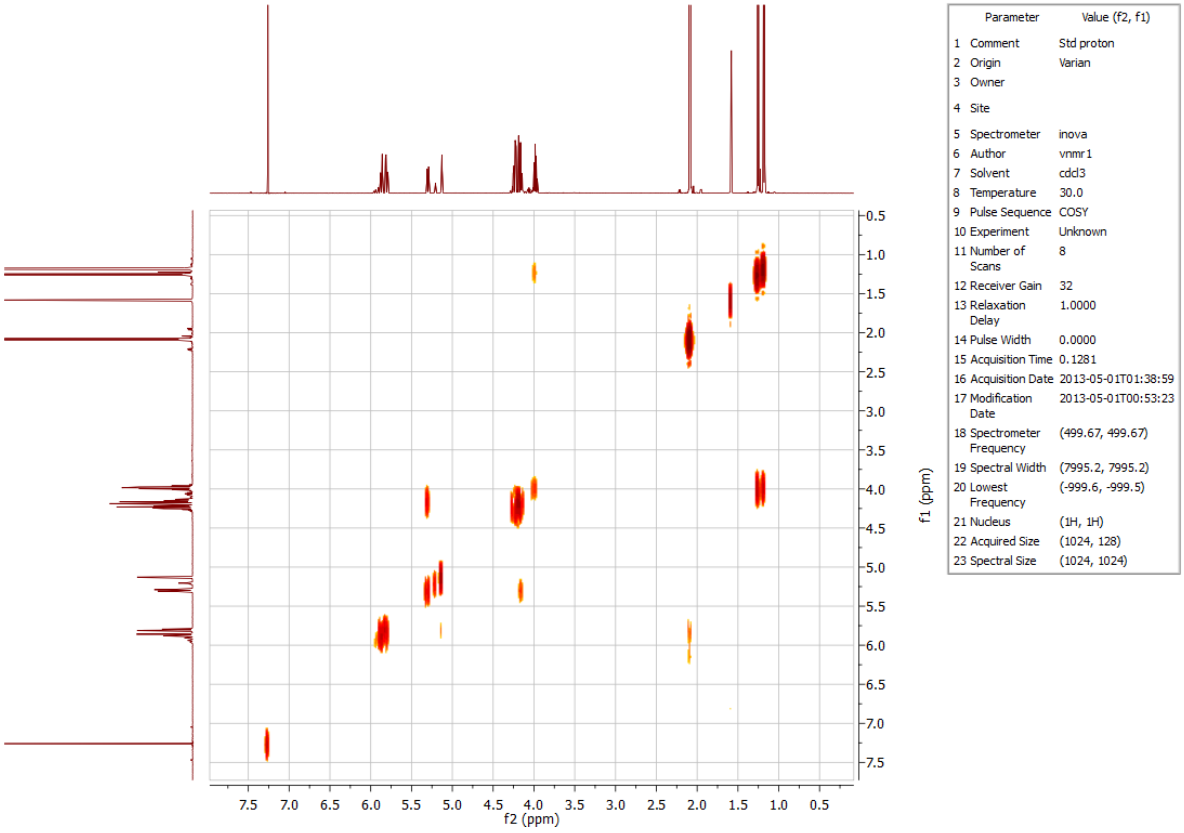


Figure S3. COSY NMR spectrum of compound **1**.

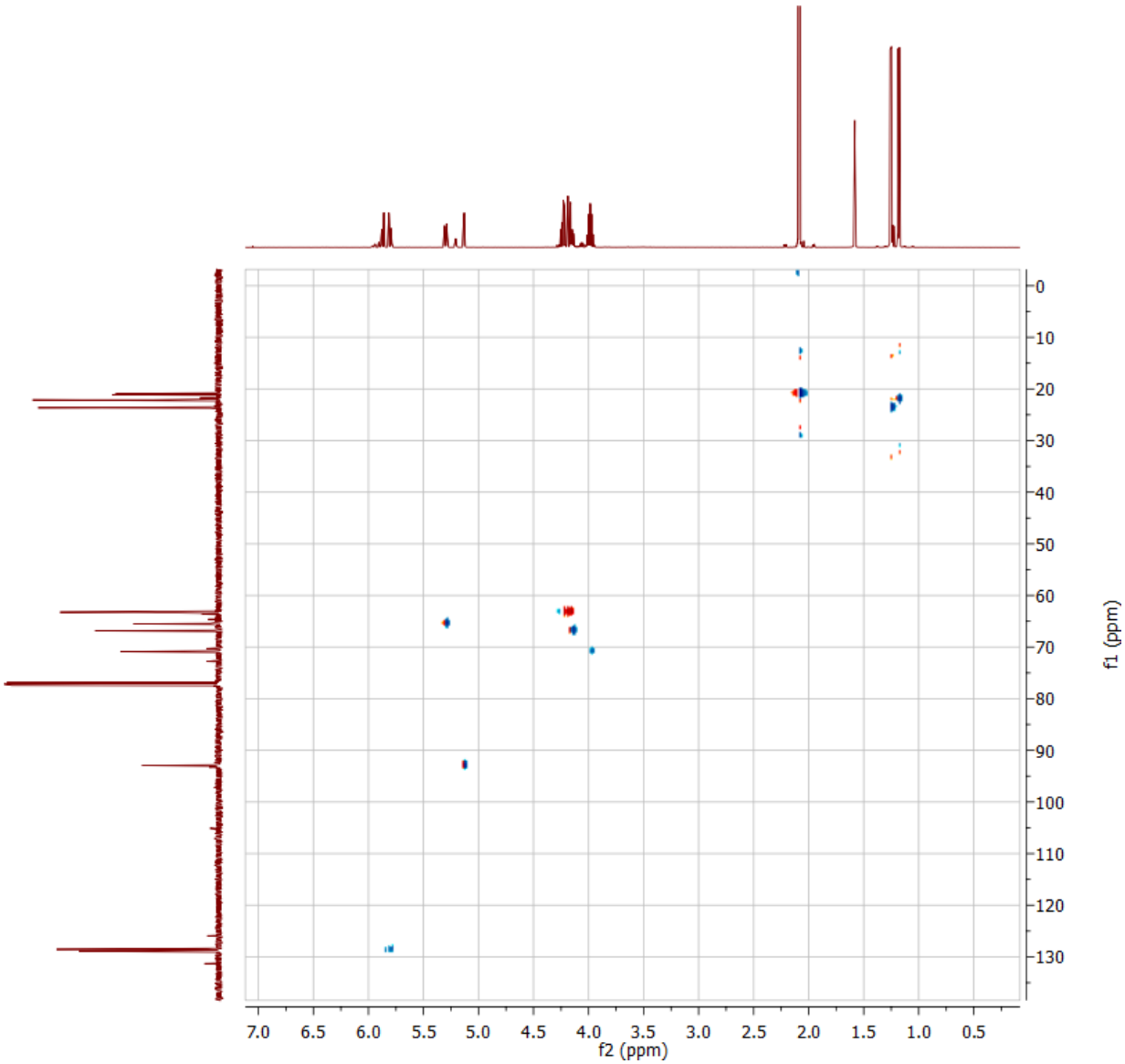


Figure S4. HSQC NMR spectrum of **1**.

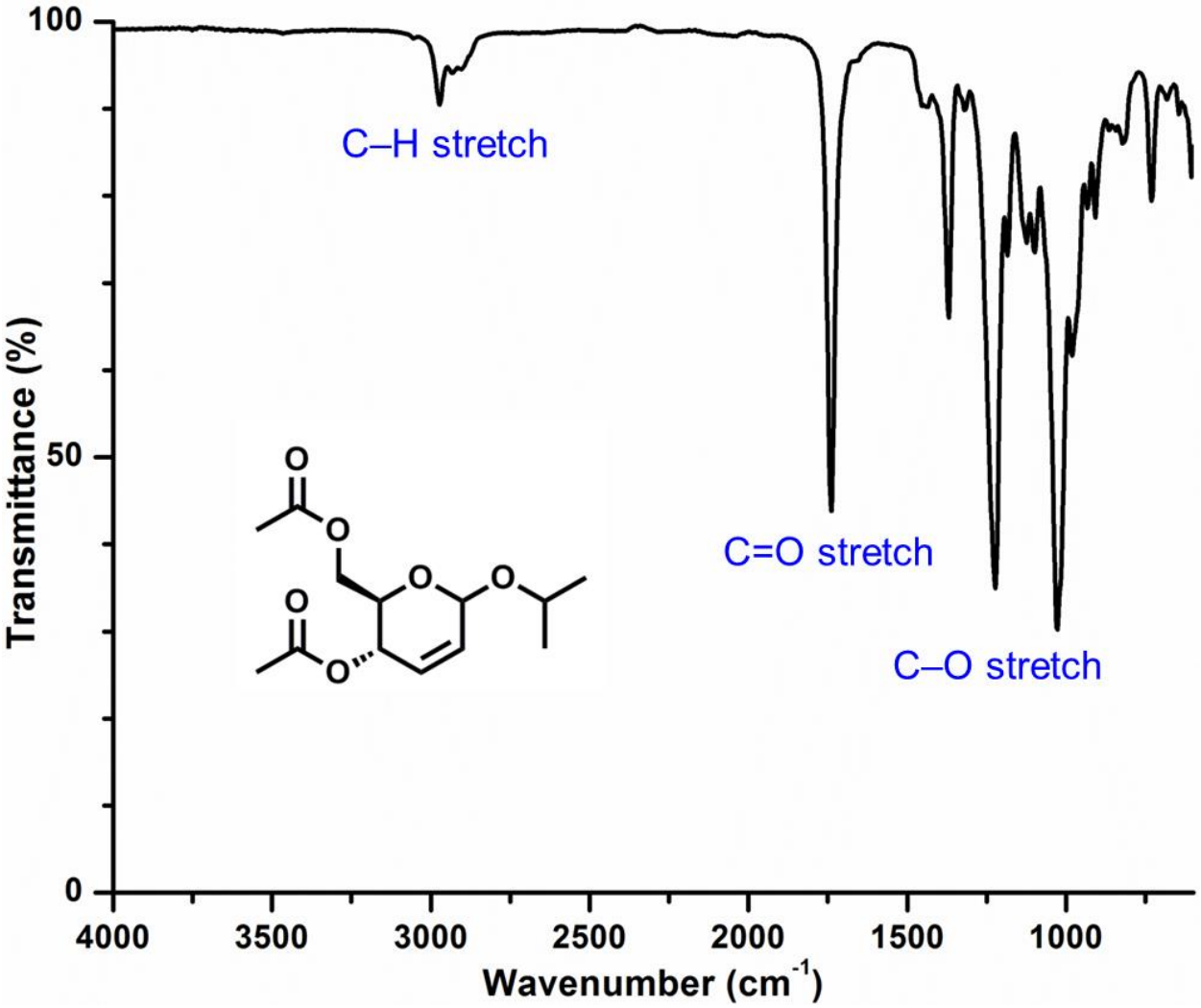


Figure S5. IR spectrum of compound **1** (neat).

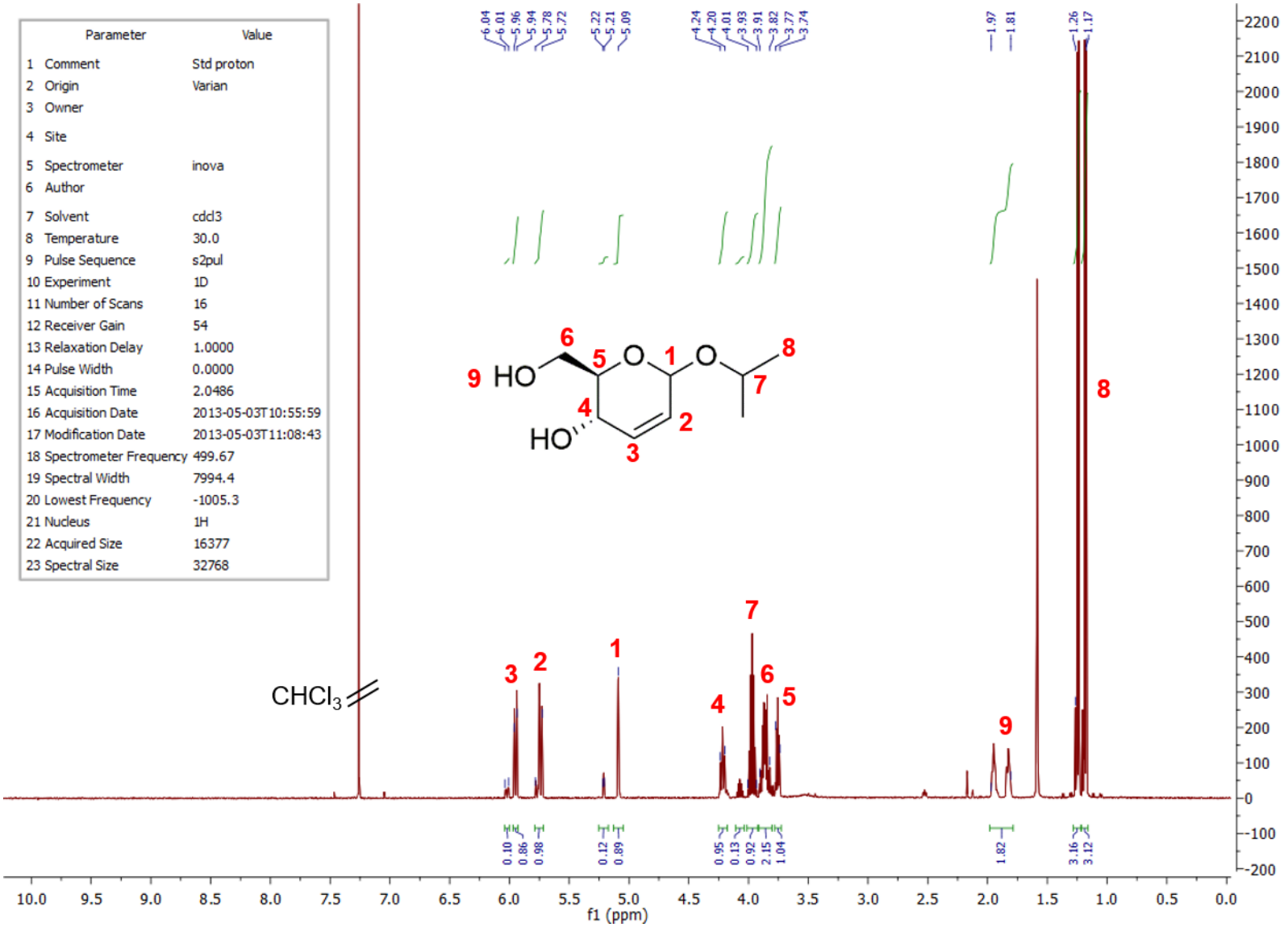


Figure S6. ^{1}H NMR spectrum of compound **2**.

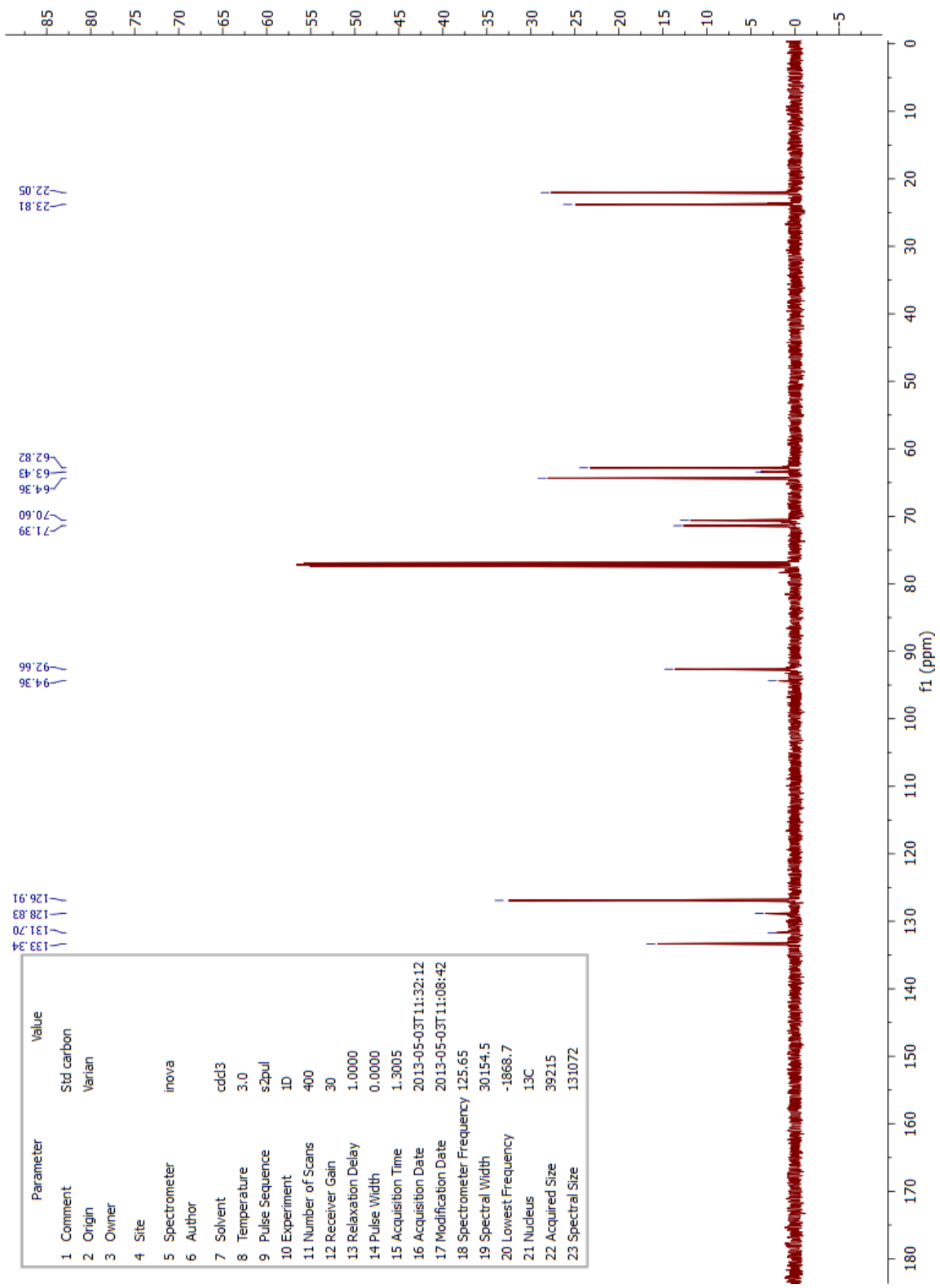


Figure S7. ^{13}C NMR spectrum of **2**.

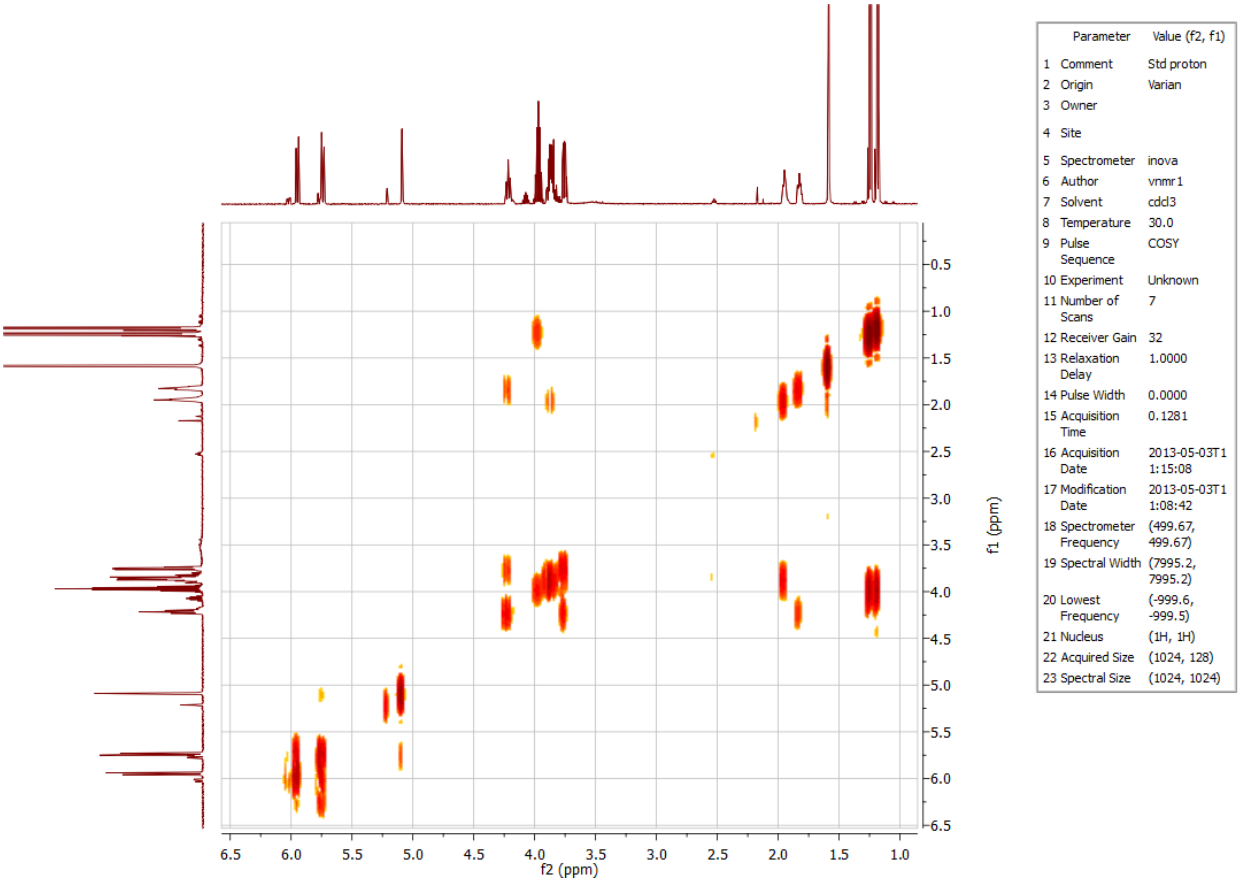
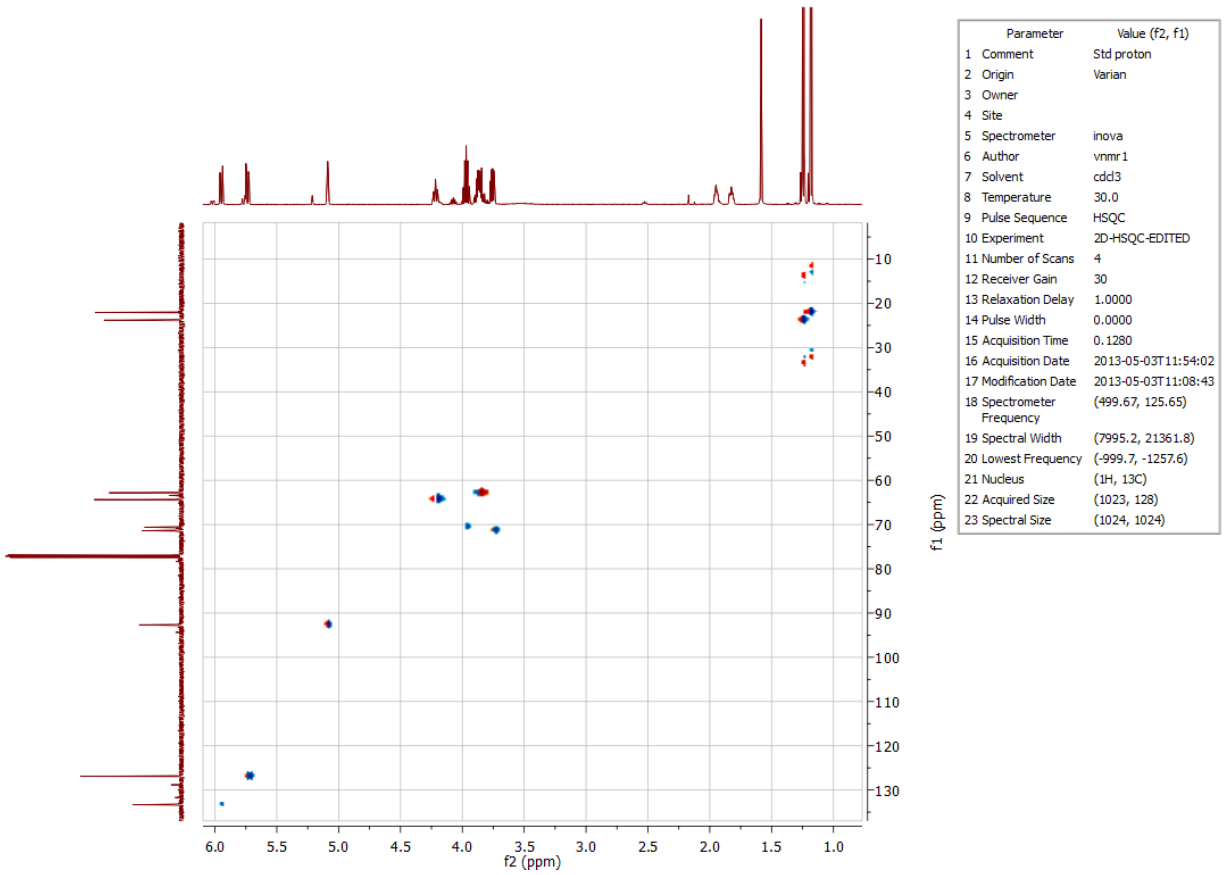


Figure S8. COSY NMR spectrum of compound **2**.



Parameter	Value (f2, f1)
1 Comment	Std proton
2 Origin	Varian
3 Owner	
4 Site	
5 Spectrometer	inova
6 Author	vnmr1
7 Solvent	cdcl3
8 Temperature	30.0
9 Pulse Sequence	HSQC
10 Experiment	2D-HSQC-EDITED
11 Number of Scans	4
12 Receiver Gain	30
13 Relaxation Delay	1.0000
14 Pulse Width	0.0000
15 Acquisition Time	0.1280
16 Acquisition Date	2013-05-03T11:54:02
17 Modification Date	2013-05-03T11:08:43
18 Spectrometer Frequency	(499.67, 125.65)
19 Spectral Width	(7995.2, 21361.8)
20 Lowest Frequency	(-999.7, -1257.6)
21 Nucleus	(1H, 13C)
22 Acquired Size	(1023, 128)
23 Spectral Size	(1024, 1024)

Figure S9. HSQC NMR spectrum of compound **2**.

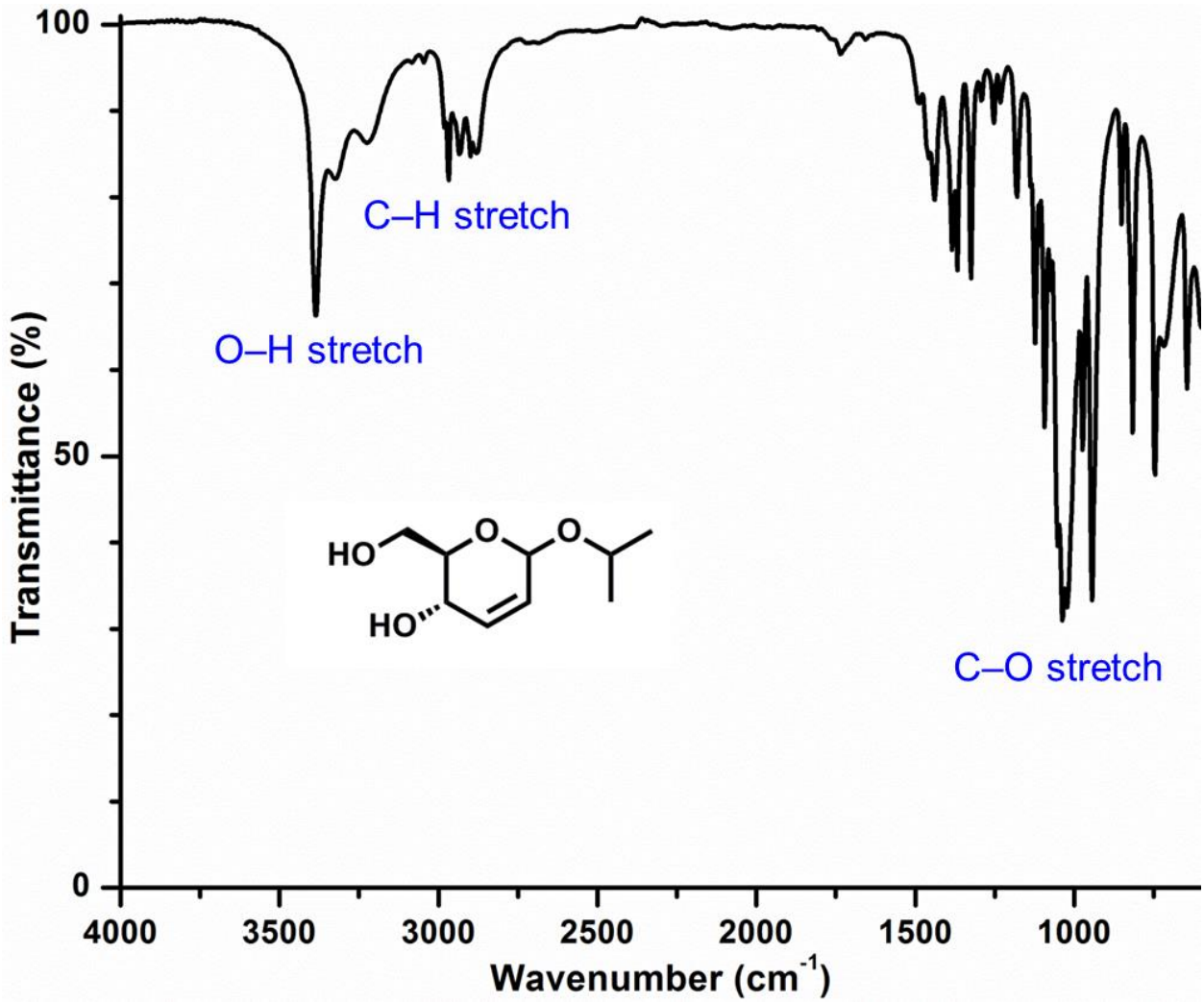


Figure S10. IR spectrum of compound **2** (neat).

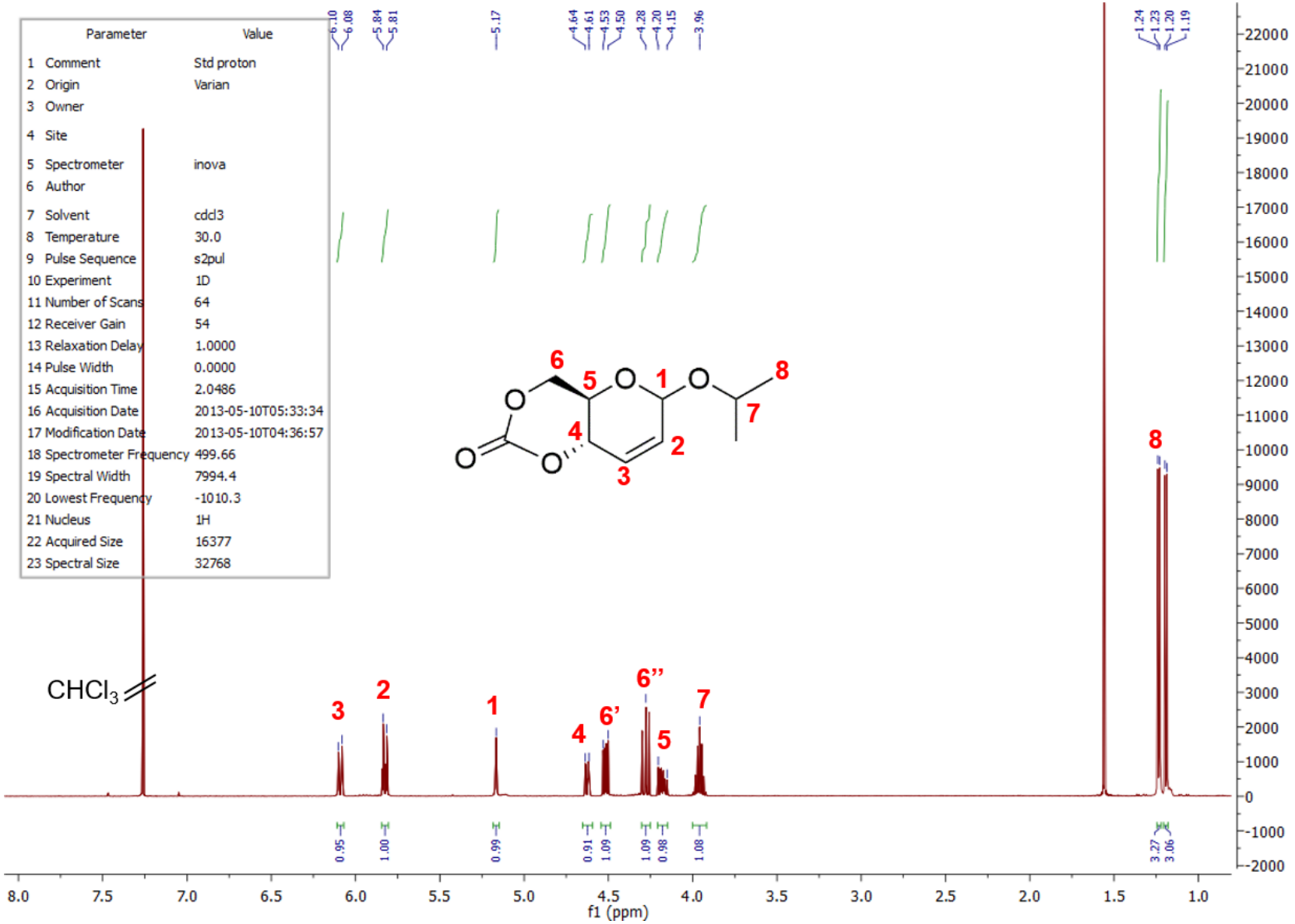


Figure S11. ^{1}H NMR spectrum of compound **3**.

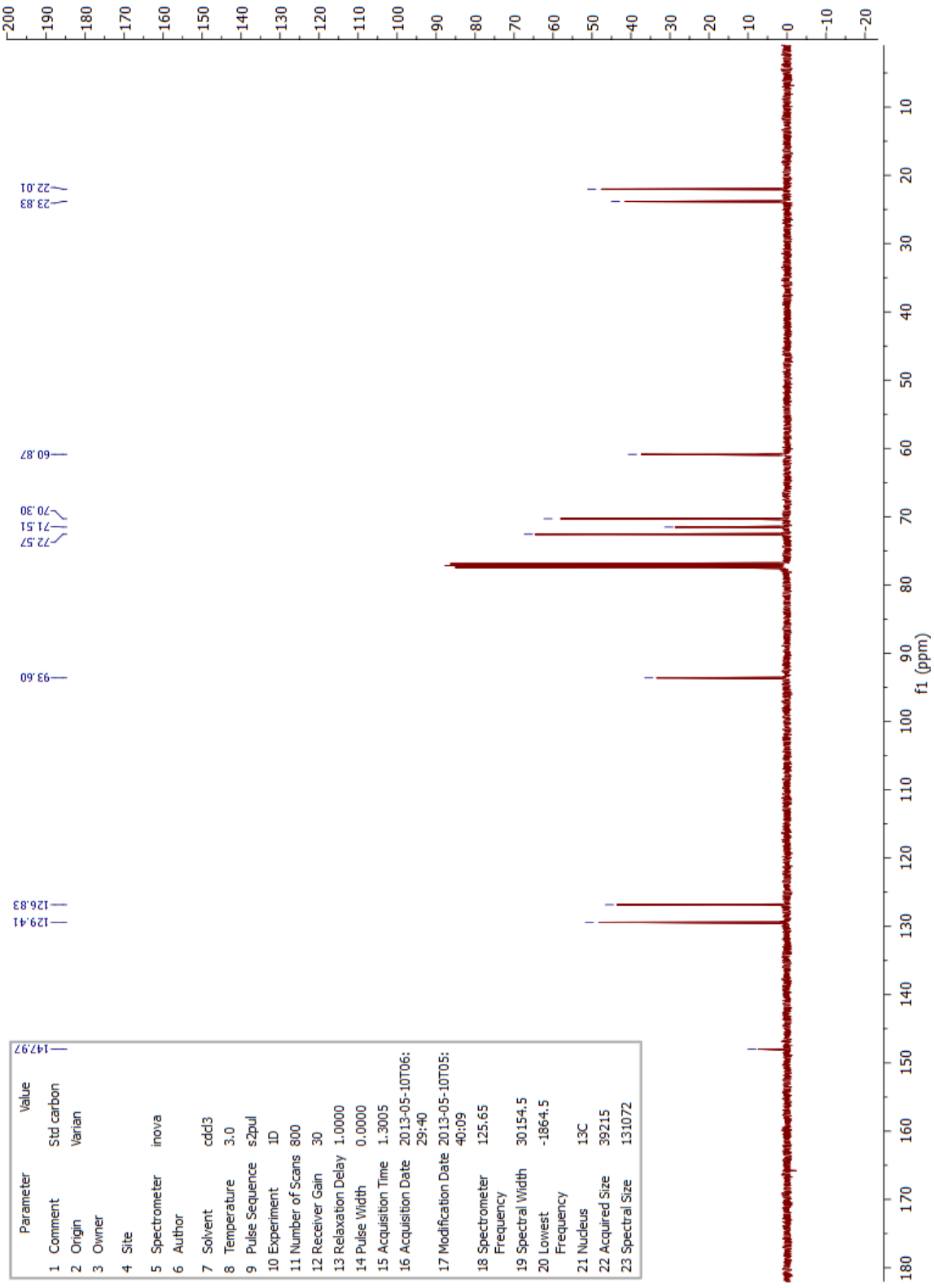


Figure S12. ^{13}C NMR spectrum of compound **3**.

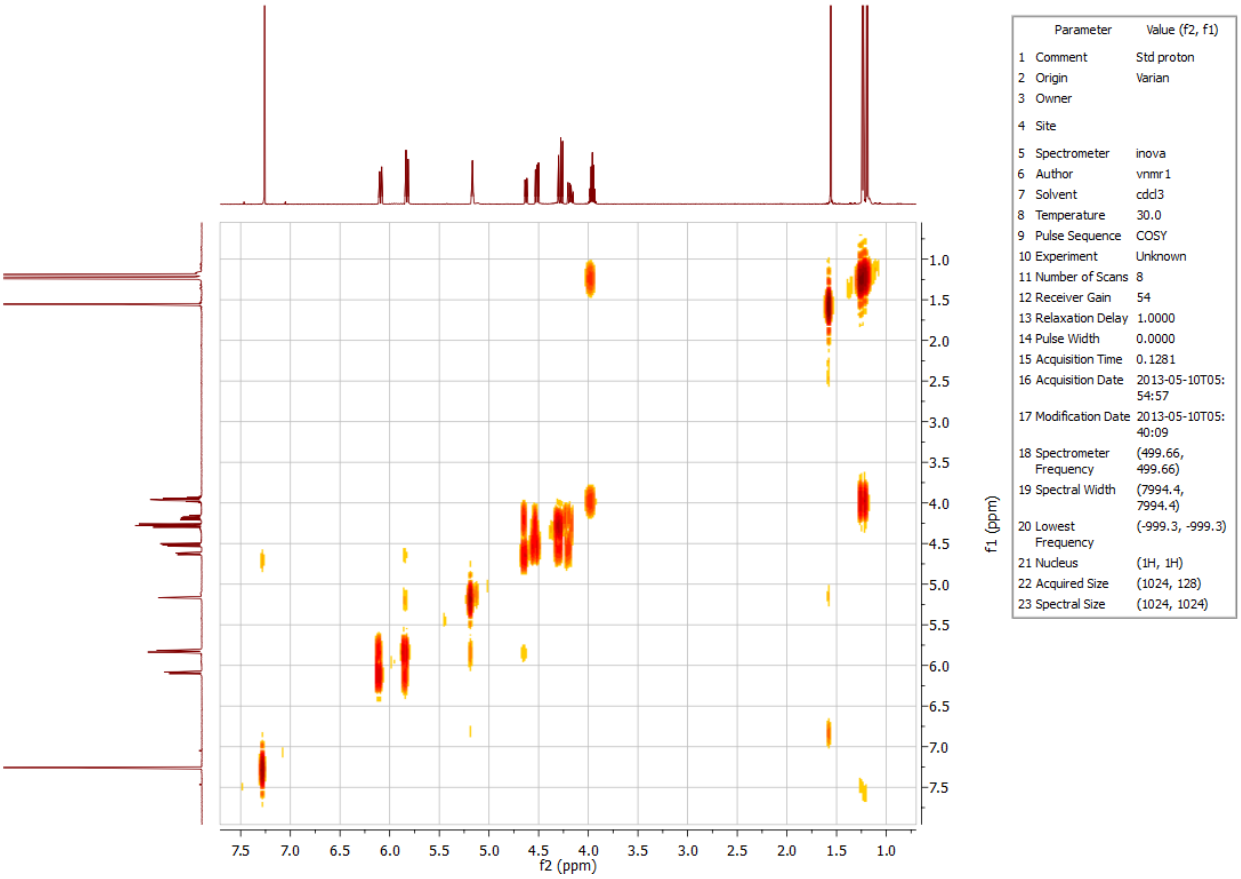
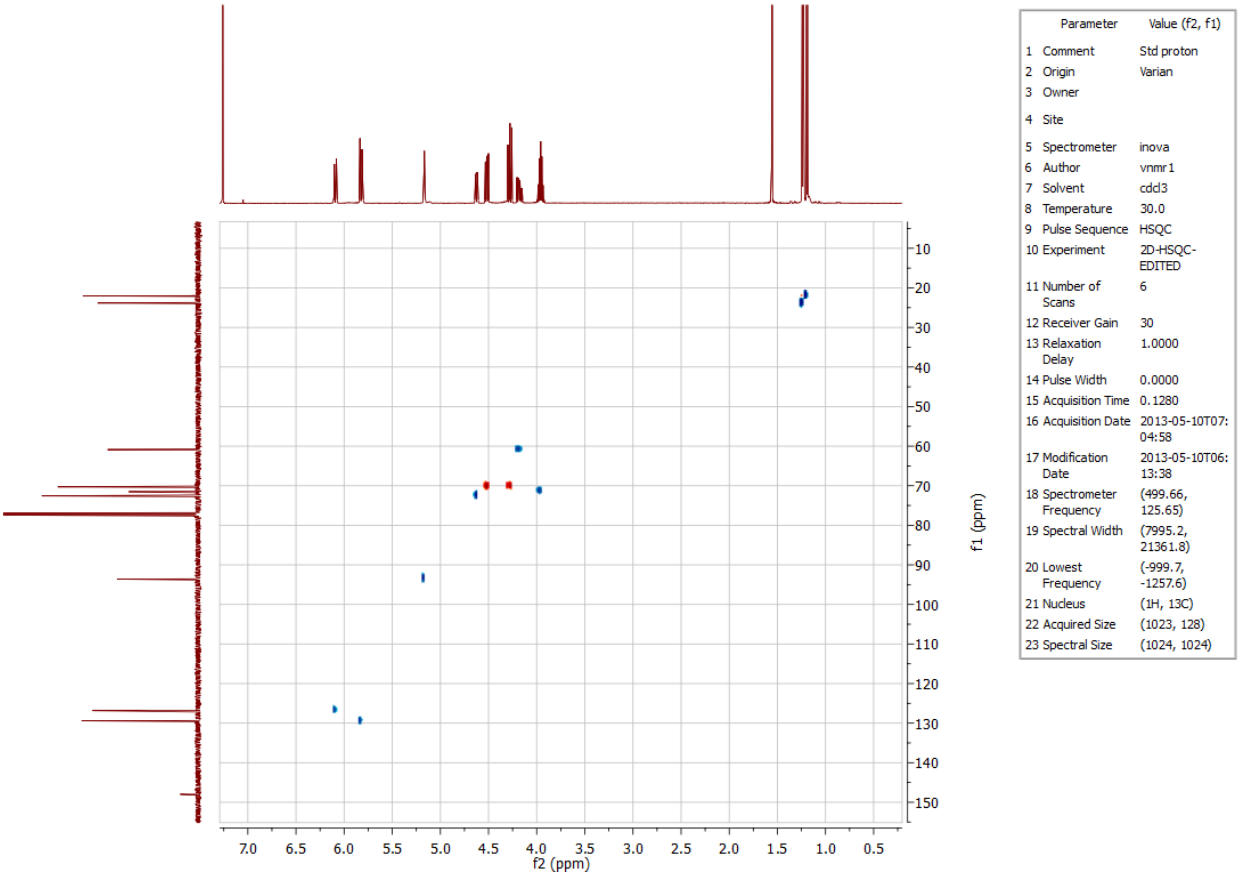


Figure S13. COSY NMR spectrum of compound **3**.



	Parameter	Value (f2, f1)
1	Comment	Std proton
2	Origin	Varian
3	Owner	
4	Site	
5	Spectrometer	inova
6	Author	vnmr1
7	Solvent	cdcl3
8	Temperature	30.0
9	Pulse Sequence	HSQC
10	Experiment	2D-HSQC-EDITED
11	Number of Scans	6
12	Receiver Gain	30
13	Relaxation Delay	1.0000
14	Pulse Width	0.0000
15	Acquisition Time	0.1280
16	Acquisition Date	2013-05-10T07:04:58
17	Modification Date	2013-05-10T06:13:38
18	Spectrometer Frequency	(499.66, 125.65)
19	Spectral Width	(7995.2, 21361.8)
20	Lowest Frequency	(-999.7, -1257.6)
21	Nucleus	(1H, 13C)
22	Acquired Size	(1023, 128)
23	Spectral Size	(1024, 1024)

Figure S14. HSQC NMR spectrum of compound **3**.

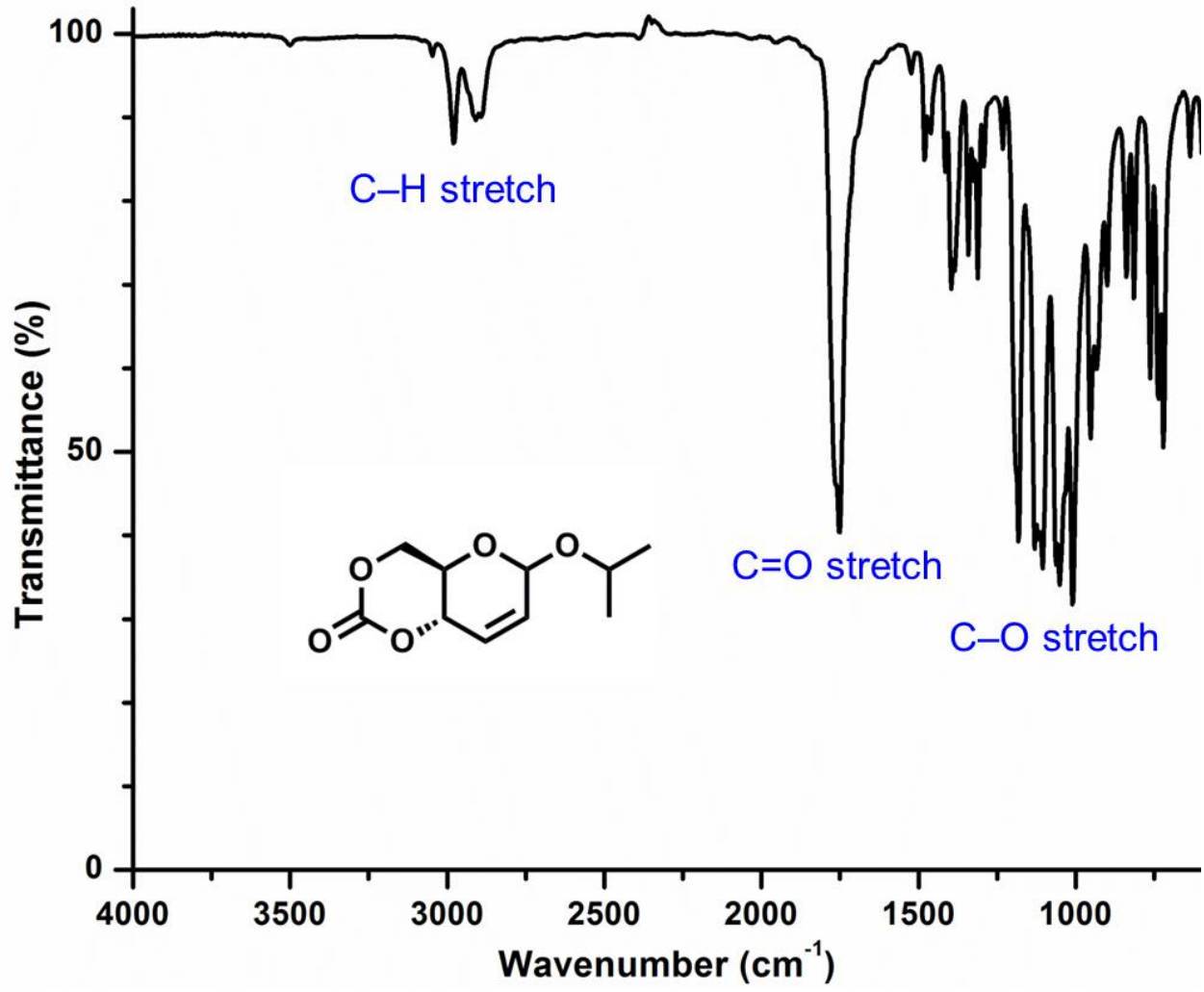


Figure S15. IR spectrum of compound **3** (neat).

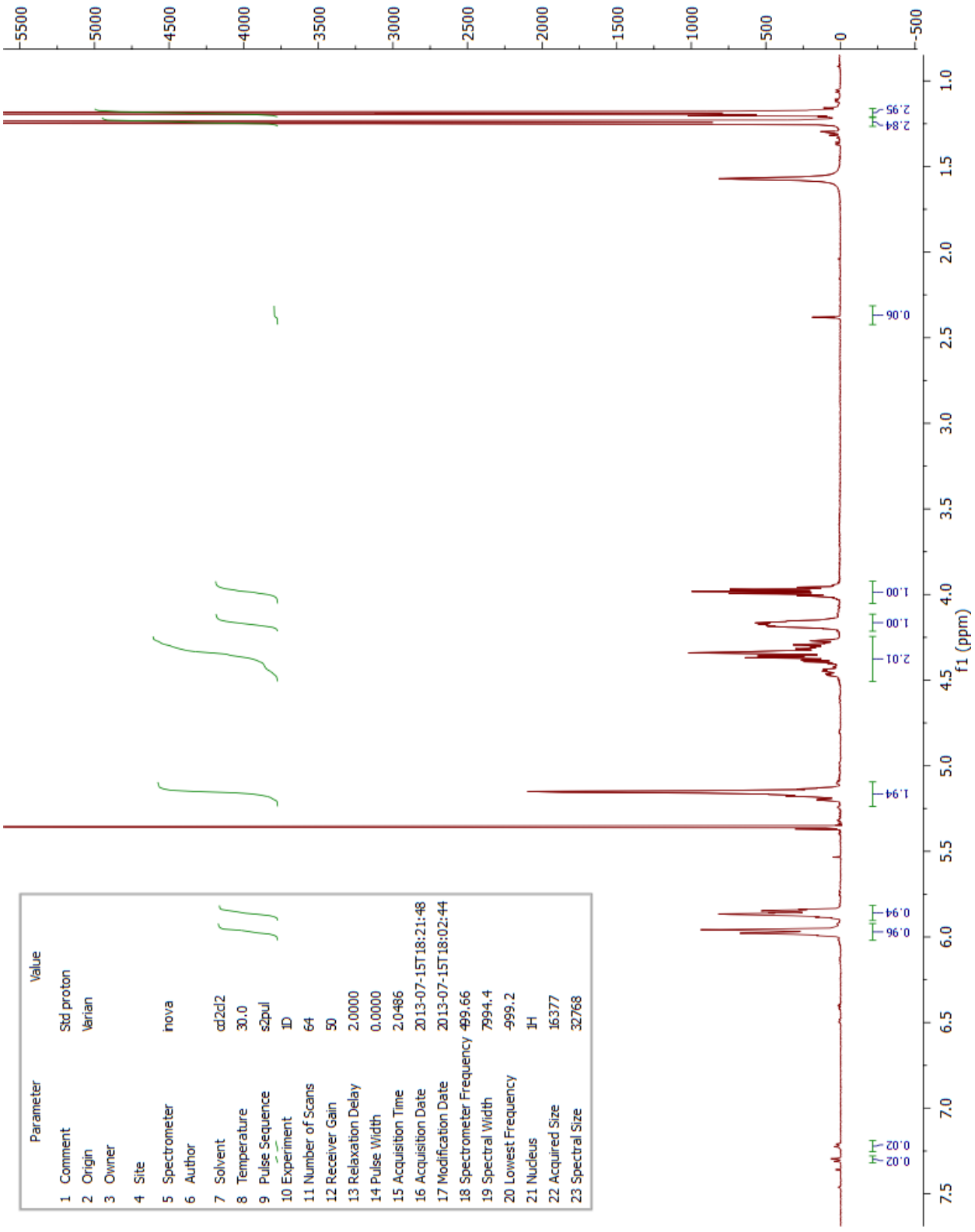


Figure S16. ^{1}H NMR spectrum of compound **4**.

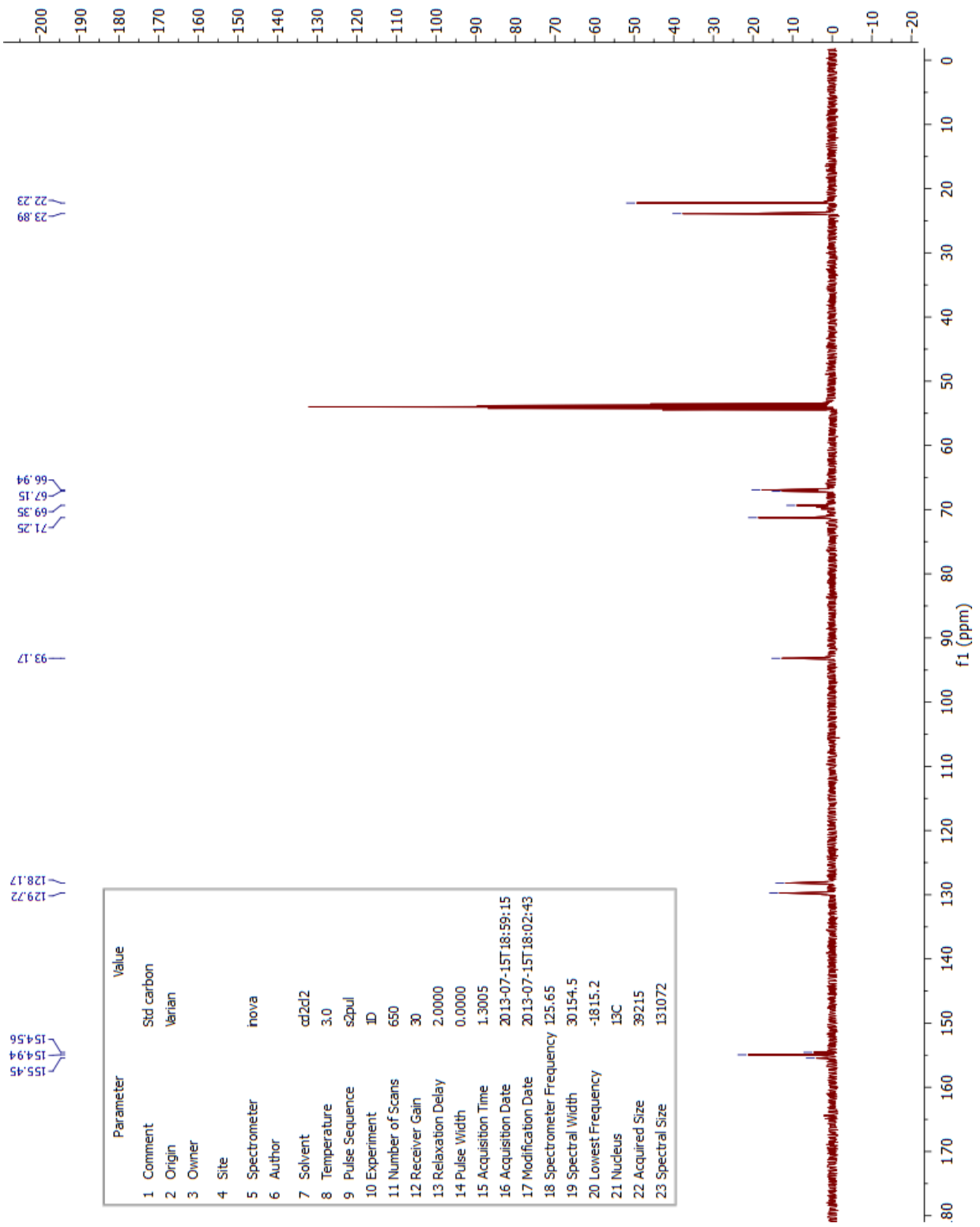


Figure S17. ^{13}C NMR spectrum of compound **4**.

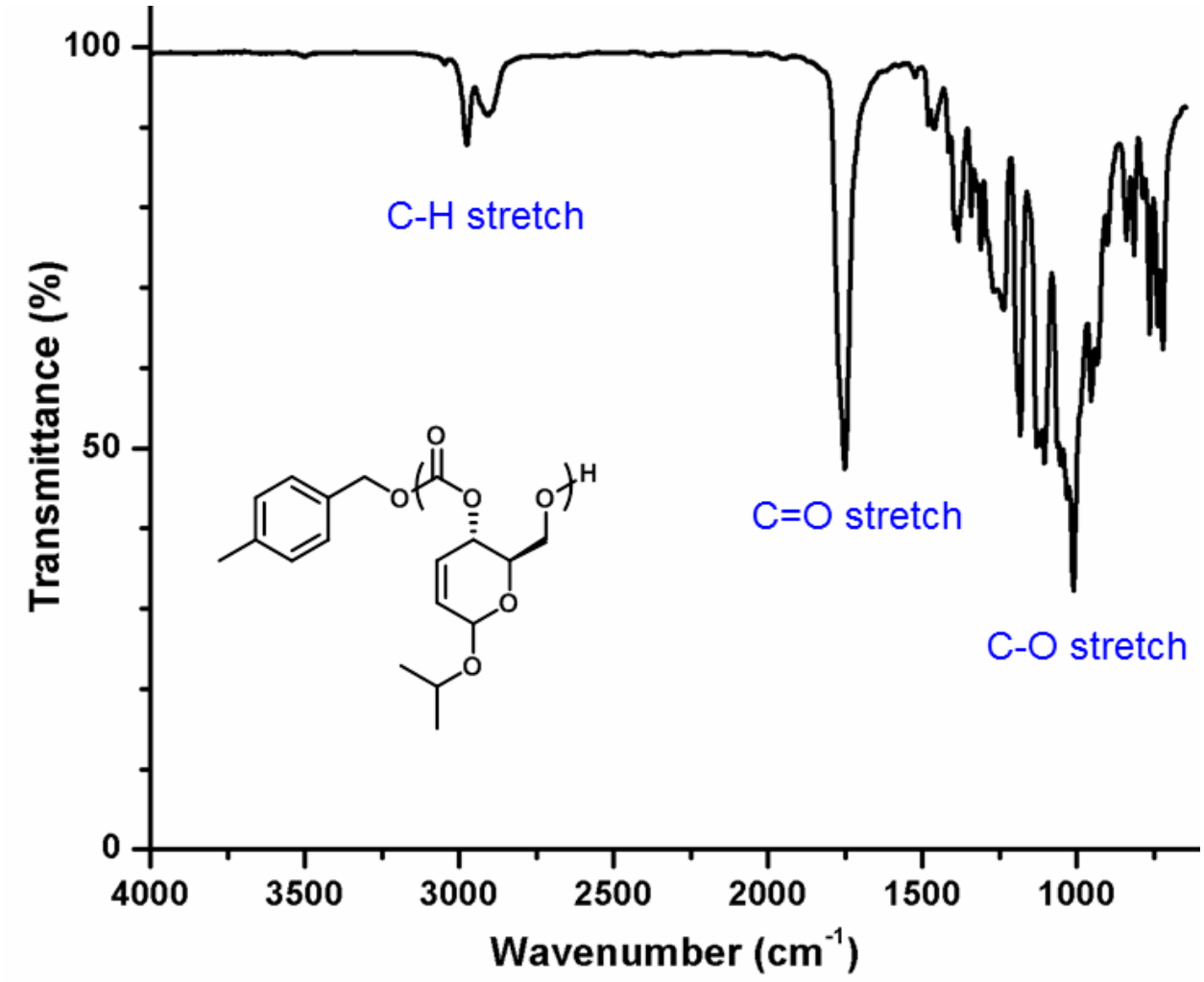
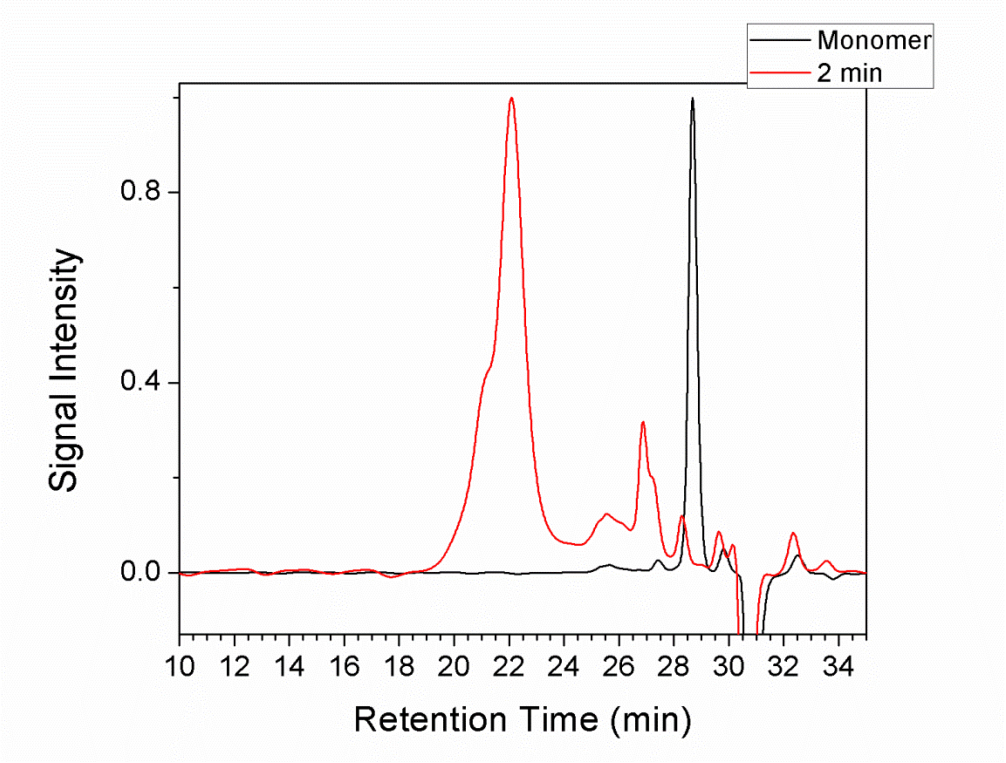
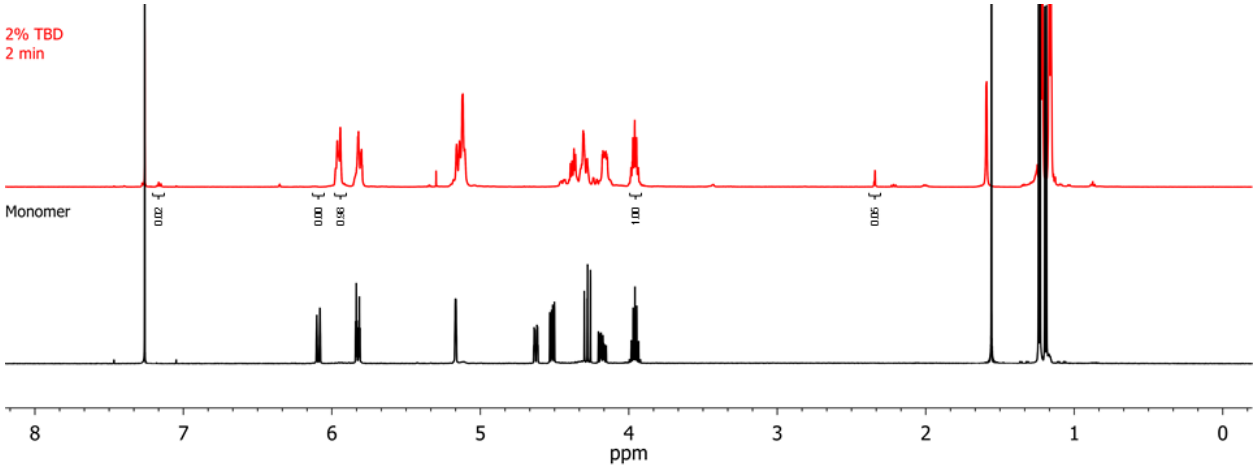


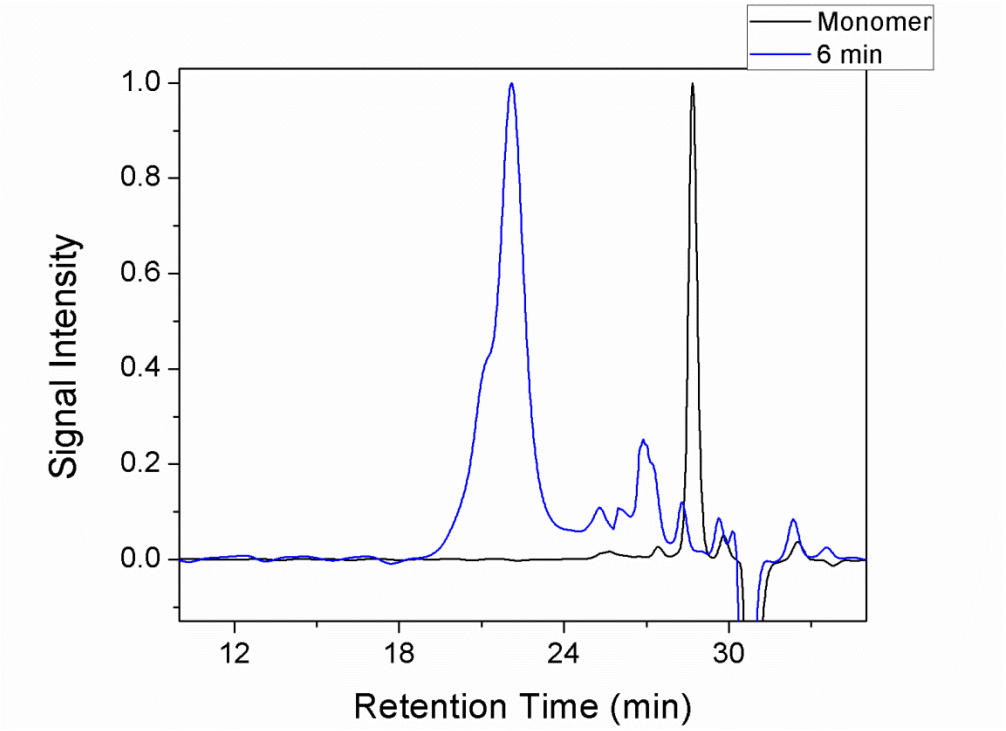
Figure S18. IR spectrum of compound **4** (neat).

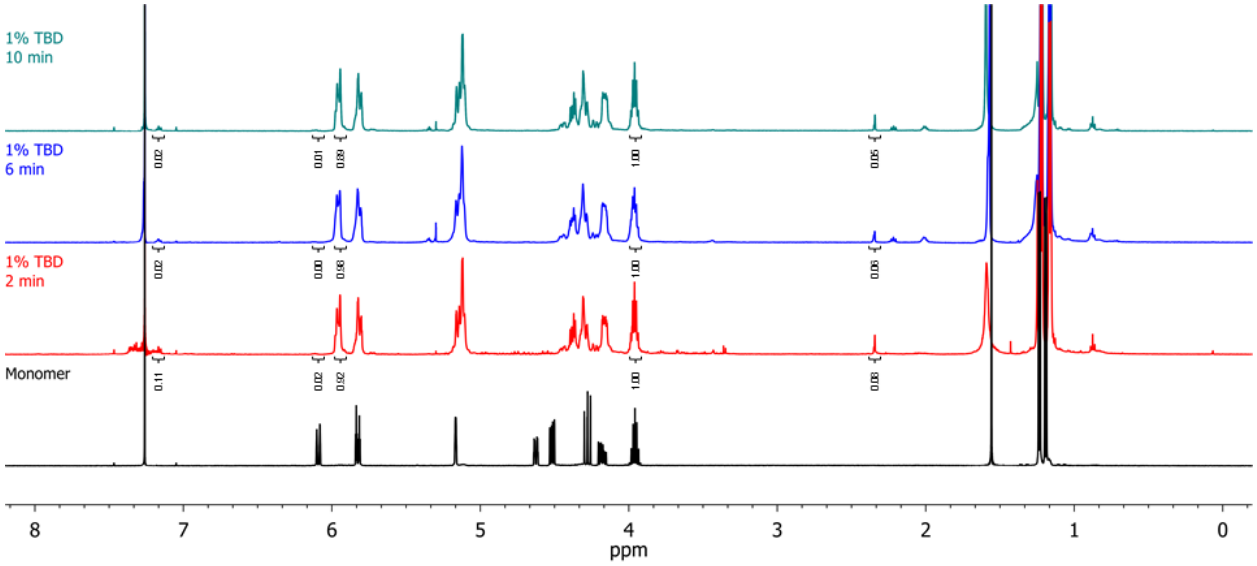




Catalyst	Catalyst mol %	$[M]_0/[I]_0$[a]	$[M]$[b]	Time (min)	Conv (%)[c]	M_n (g/mol)[c]	M_n (g/mol)[d]	M_w (g/mol)[d]	PDI[d]
TBD	2	50	0.3	2	>99	11800	9800	12500	1.31

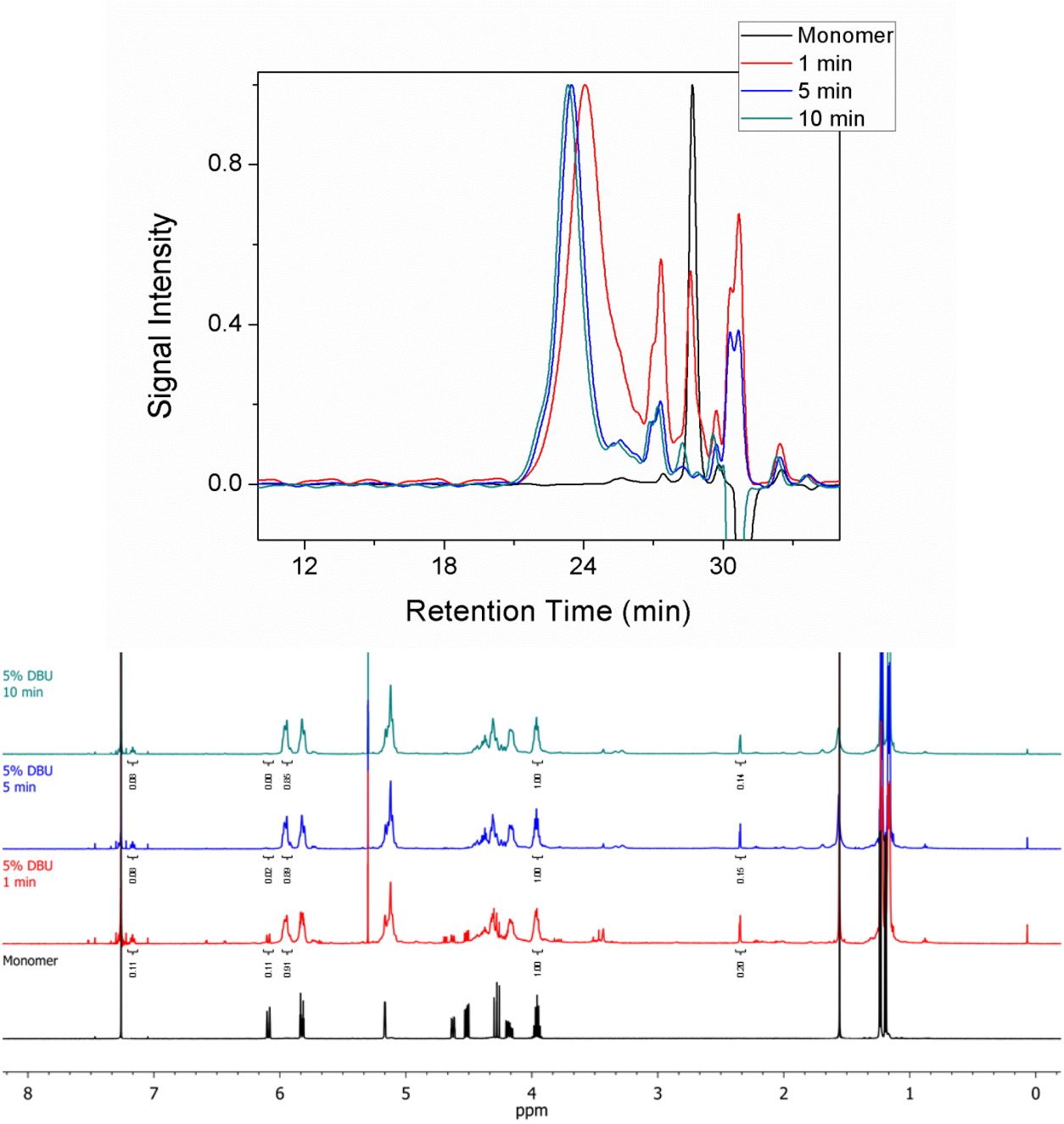
Figure S19. Molecular weight analysis by GPC and end group analysis (^{1}H NMR in $CDCl_3$) of compound **4** (2 mol% TBD) at 2 min.





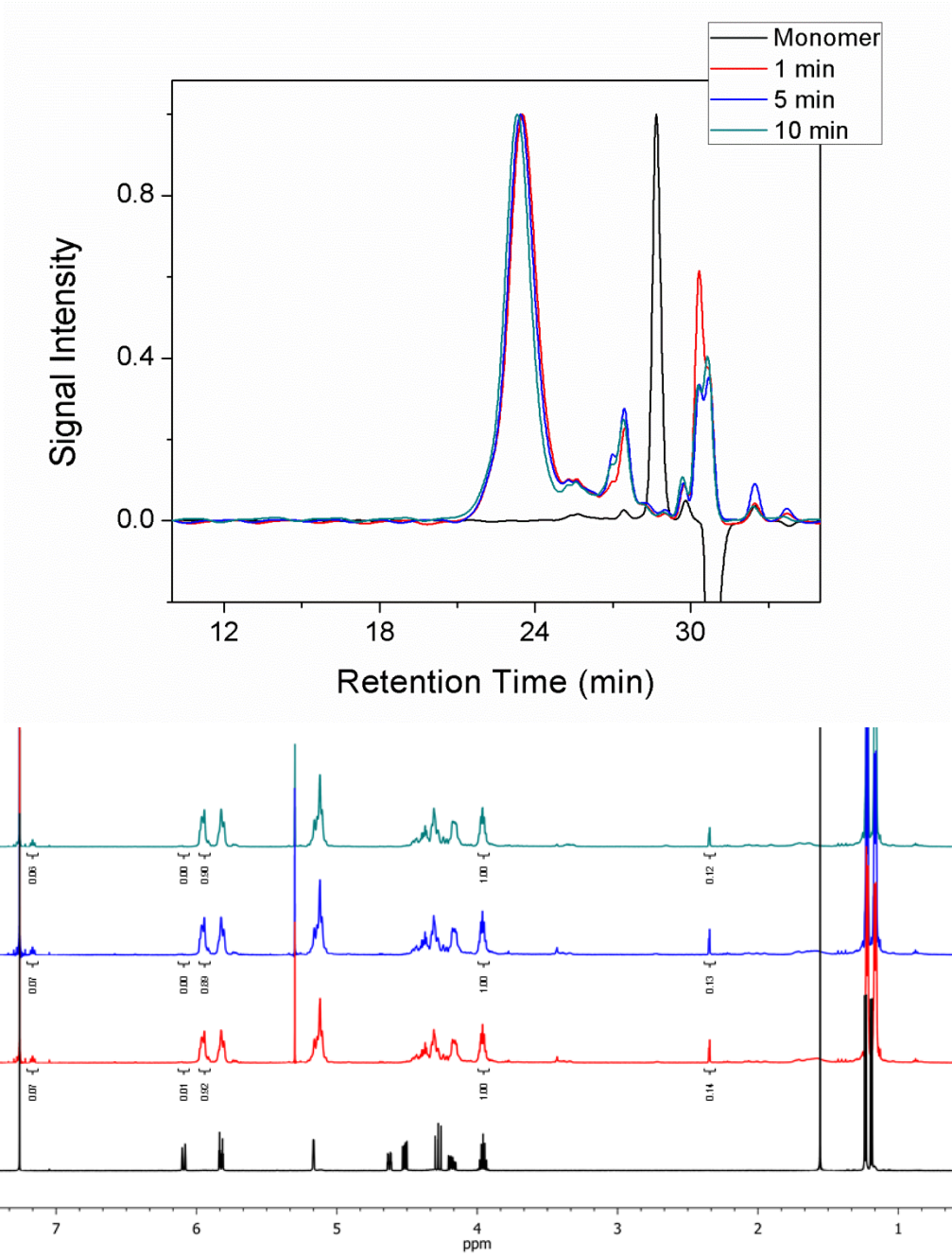
Catalyst	Catalyst mol %	$[M]_0/[I]_0$[a]	$[M]$[b]	Time (min)	Conv (%)[c]	M_n (g/mol)[c]	M_n (g/mol)[d]	M_w (g/mol)[d]	PDI[d]
TBD	1	50	0.3	2	98	7600	8500	10800	1.27
				6	>99	10800	9400	11400	1.21
				10	>99	11500	9900	12900	1.30

Figure S20. Molecular weight analysis by GPC and end group analysis (^{1}H NMR in $CDCl_3$) of compound **5** (1 mol% TBD) at 2, 6, and 10 min.



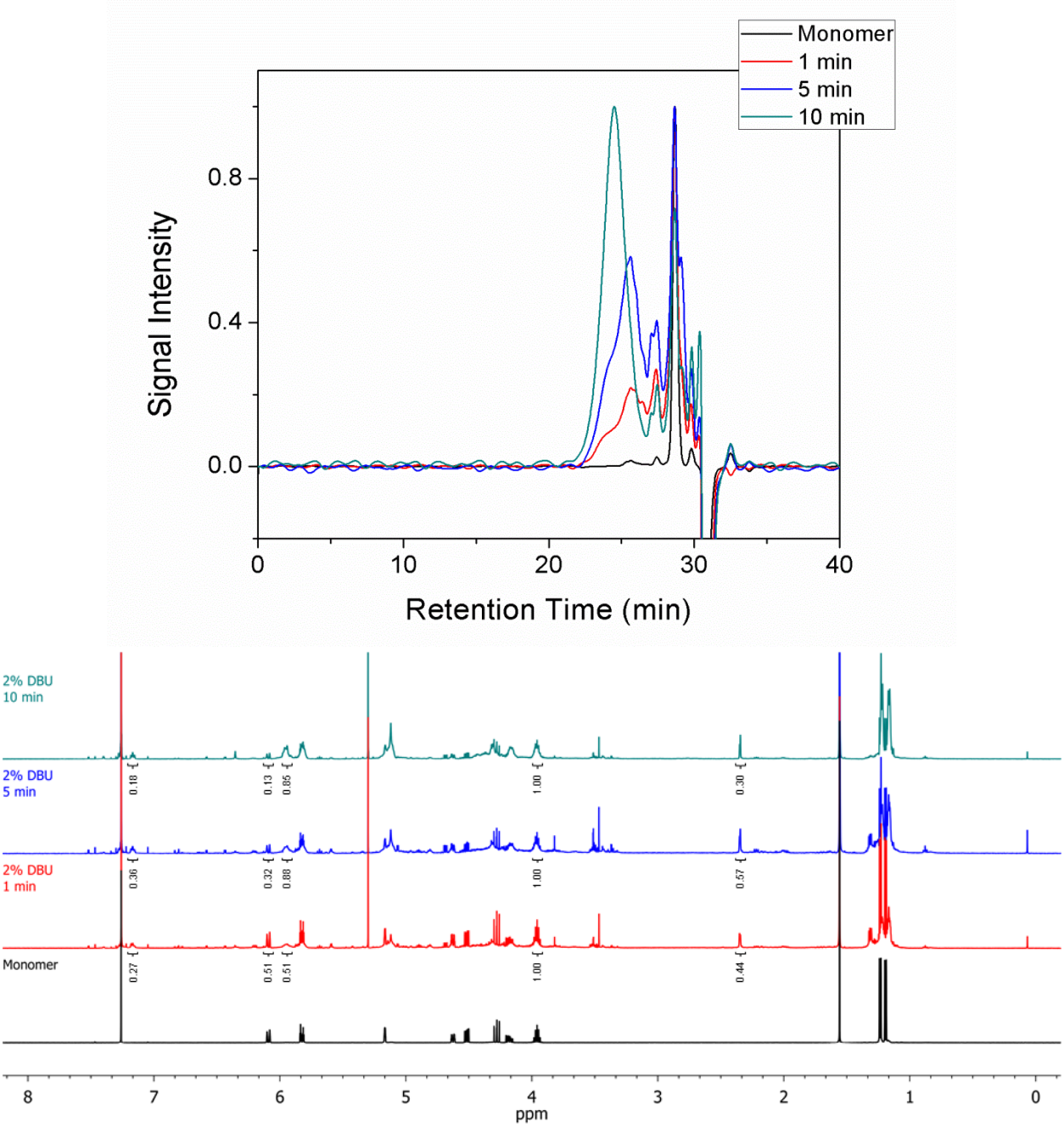
Catalyst	Catalyst mol %	$[M]_0/[I]_0$[a]	$[M]$[b]	Time (min)	Conv (%)[c]	M_n (g/mol)[c]	M_n (g/mol)[d]	M_w (g/mol)[d]	PDI[d]
DBU	5	25	0.3	1	89	2900	2100	2600	1.24
				5	98	4000	3400	3900	1.15
				10	>99	4200	3800	4300	1.13

Figure S21. Molecular weight analysis by GPC and end group analysis (^{1}H NMR in $CDCl_3$) of compound **6** (5 mol% DBU) at 1, 5, and 10 min.



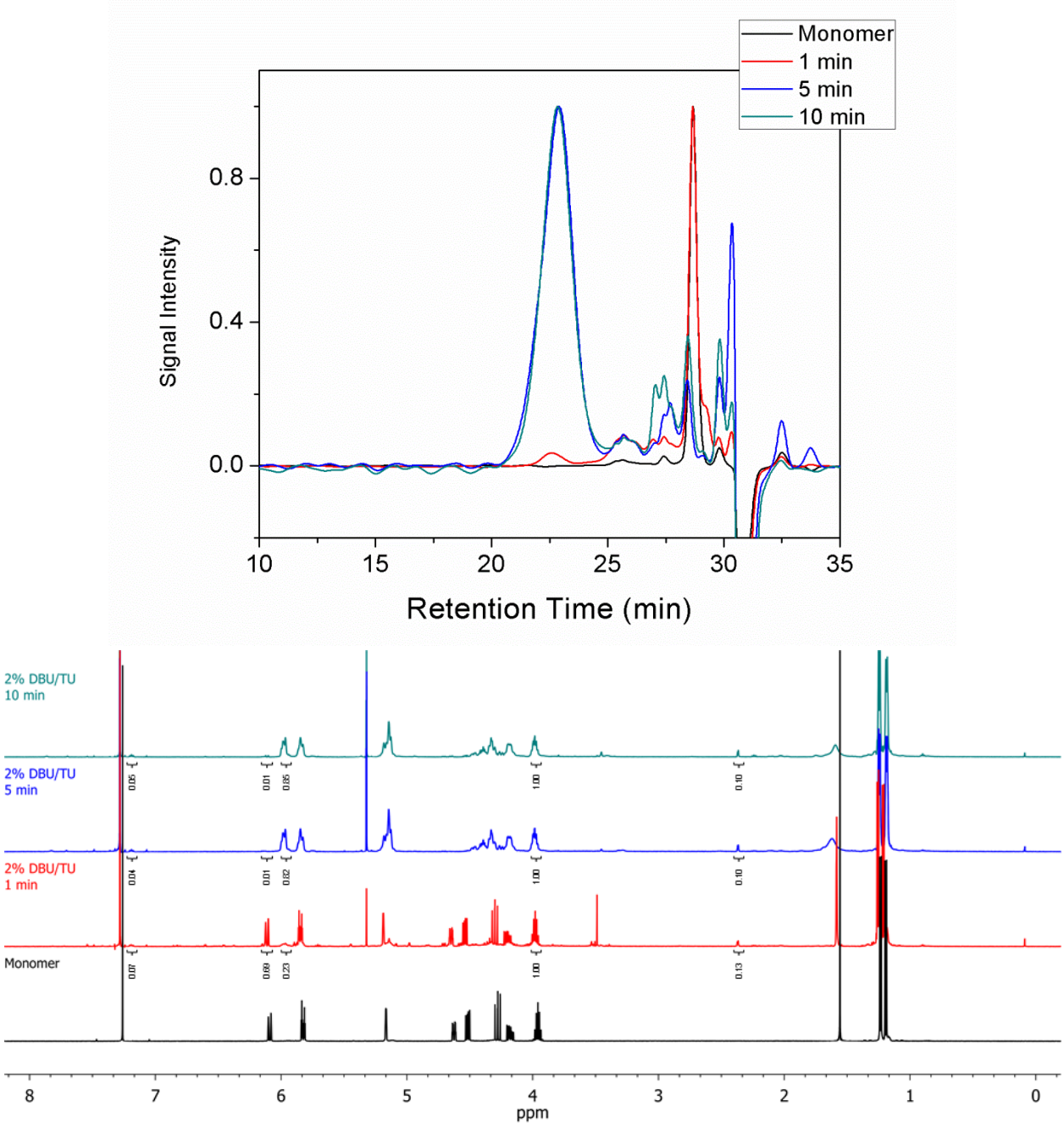
Catalyst	Catalyst mol %	$[M]_0/[I]_0$[a]	[M][b]	Time (min)	Conv (%)[c]	M_n (g/mol)[c]	M_n (g/mol)[d]	M_w (g/mol)[d]	PDI[d]
DBU/TU	5	25	0.3	1	99	4400	3300	3700	1.12
				5	>99	4600	3400	3800	1.12
				10	>99	5000	3700	4200	1.14

Figure S22. Molecular weight analysis by GPC and end group analysis (^{1}H NMR in $CDCl_3$) of compound **7** (5 mol% DBU/TU) at 1, 5, and 10 min.



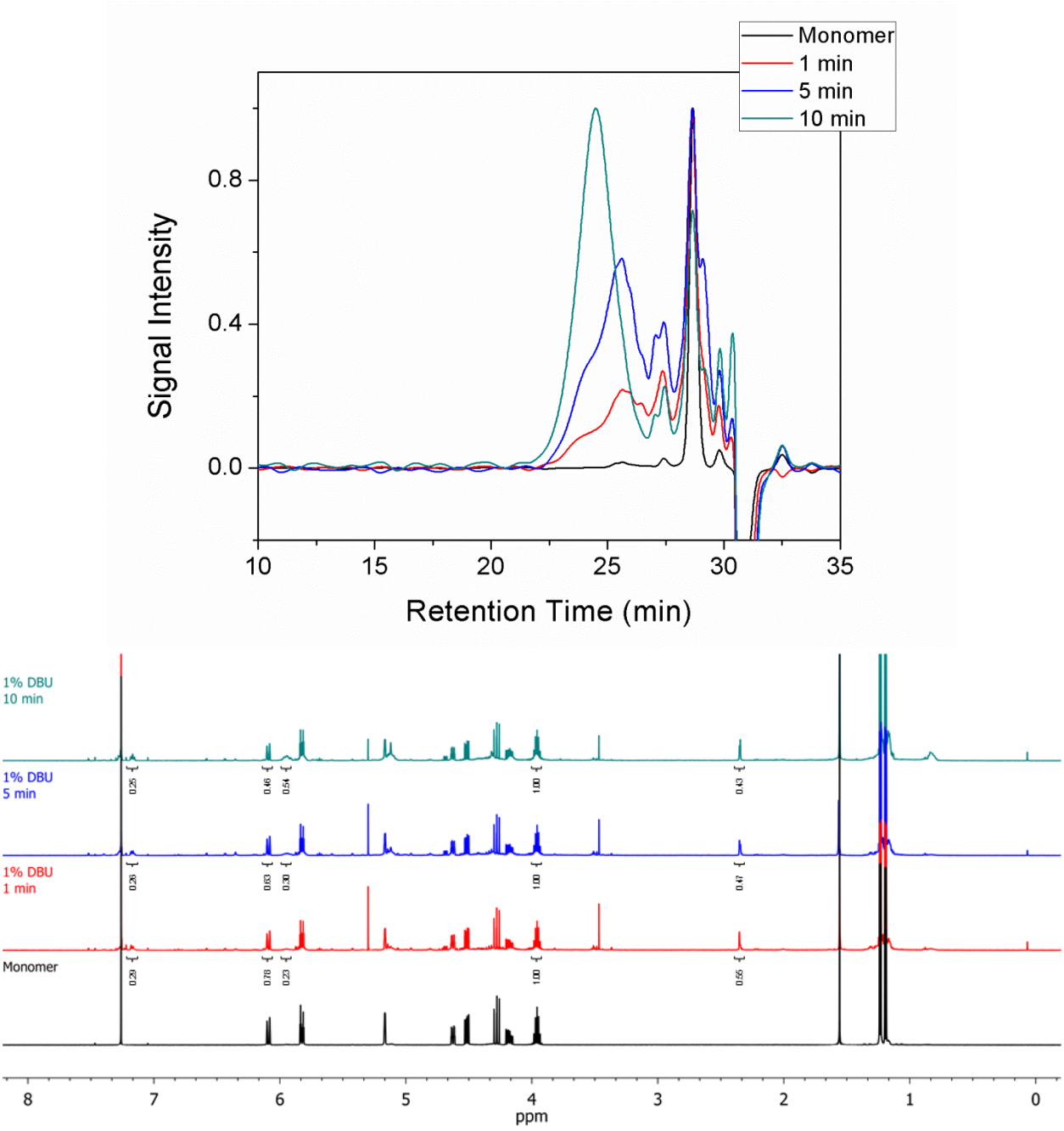
Catalyst	Catalyst mol %	$[M]_0/[I]_0$[a]	$[M]$[b]	Time (min)	Conv (%)[c]	M_n (g/mol)[c]	M_n (g/mol)[d]	M_w (g/mol)[d]	PDI[d]
DBU	2	25	0.3	1	49	800	950	1300	1.37
				5	68	1000	1000	1400	1.40
				10	86	1800	1600	2100	1.31

Figure S23. Molecular weight analysis by GPC and end group analysis (^{1}H NMR in $CDCl_3$) of compound **8** (2 mol% DBU) at 1, 5, and 10 min.



Catalyst	Catalyst mol %	$[M]_0/[I]_0$[a]	[M][b]	Time (min)	Conv (%)[c]	M_n (g/mol)[c]	M_n (g/mol)[d]	M_w (g/mol)[d]	PDI[d]
DBU/TU	2	25	0.3	1	31	1200	780	810	1.03
				5	>99	5500	5000	6000	1.20
				10	>99	5700	5000	5900	1.18

Figure S24. Molecular weight analysis by GPC and end group analysis (^{1}H NMR in $CDCl_3$) of compound **9** (2 mol% DBU) at 1, 5, and 10 min.



Catalyst	Catalyst mol %	$[M]_0/[I]_0$[a]	$[M]$[b]	Time (min)	Conv (%)[c]	M_n (g/mol)[c]	M_n (g/mol)[d]	M_w (g/mol)[d]	PDI[d]
DBU	1	25	0.3	1	22	300	210	220	1.05
				5	37	600	480	590	1.23
				10	54	1000	610	840	1.38

Figure S25. Molecular weight analysis by GPC and end group analysis (^{1}H NMR in $CDCl_3$) of compound **10** (1 mol% DBU) at 1, 5, and 10 min.

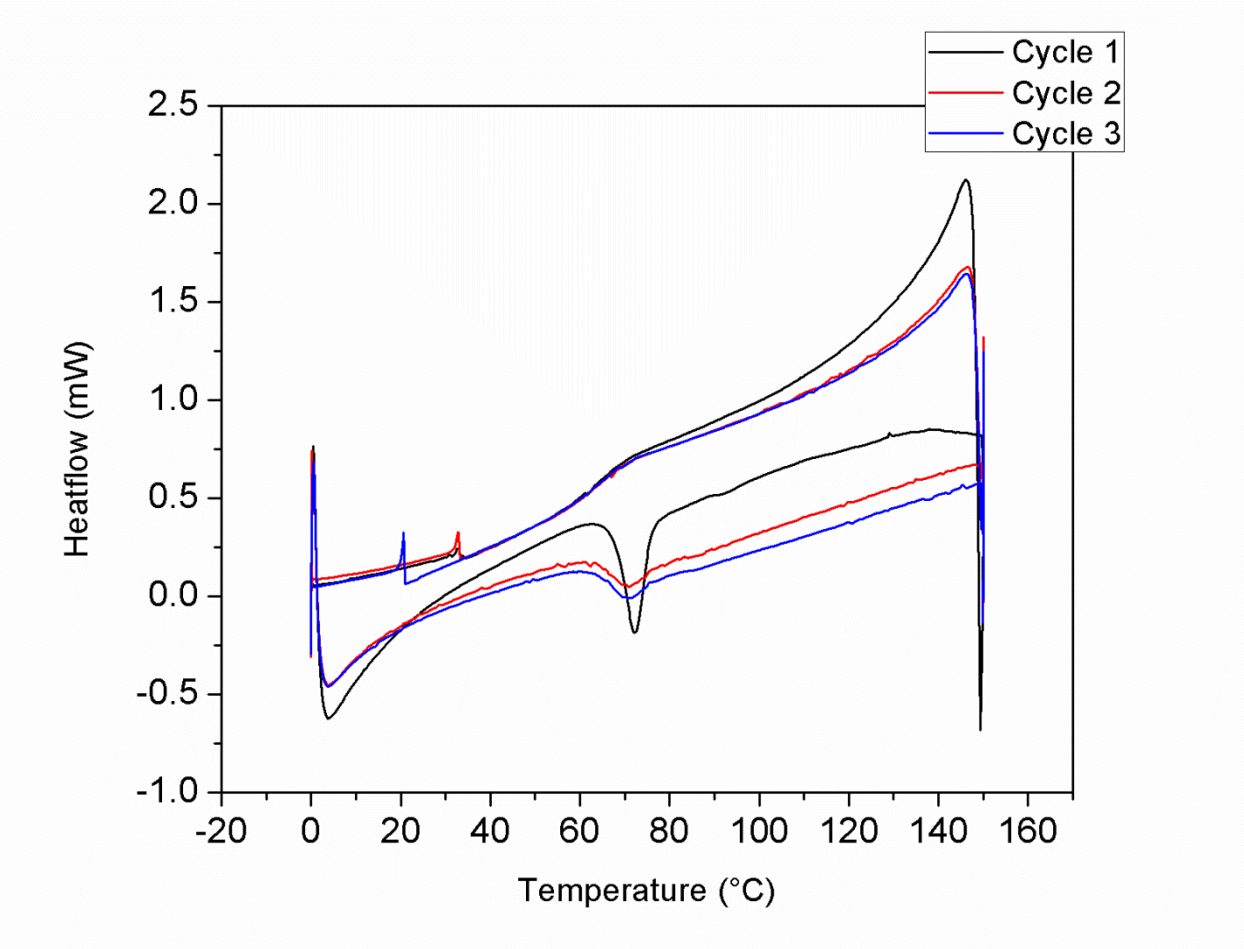


Figure S26. DSC analysis of compound **4**.

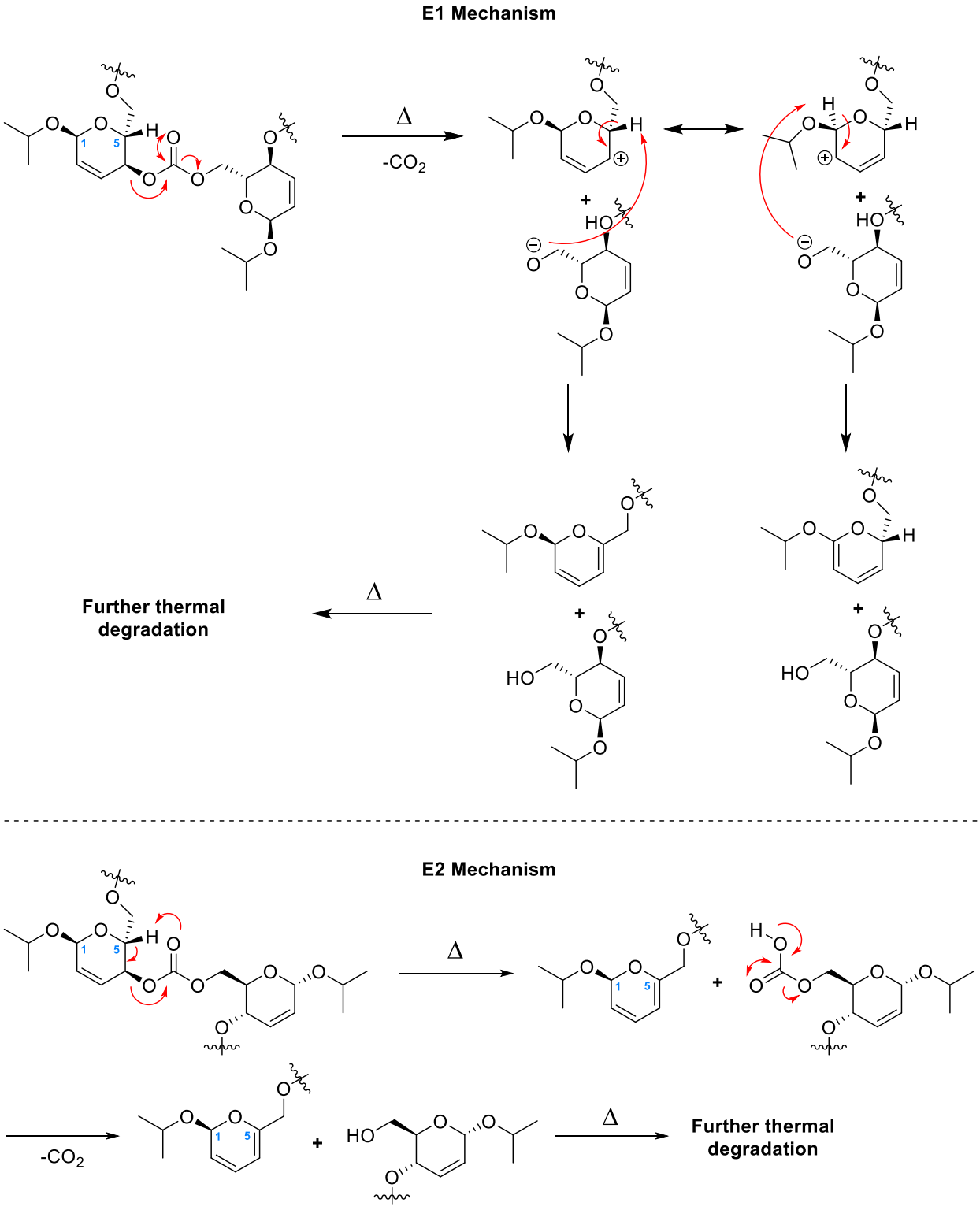


Figure S27. Two proposed mechanisms for thermal degradation of compound **4**.

(1) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L., *Macromolecules* **2006,** *39* (23), 7863-7871.