SI Content

Transformation from the mass fraction to the water activity regime

The water activity of an aqueous solution is often found to be temperature dependent. To a first approximation this temperature dependence can be assumed to be linear whereas the slope of this linear relationship is concentration dependent. Hence, data of water activity for different concentrations and at least at two different temperatures are needed in order to determine the slope of the linear relationship and its concentration dependence. As described in the paper, we measured the water activity for tetraol solution at mass fractions between 0 and 1 at T^θ = 25°C and fitted the data with equation S1 (Zobrist et al., 2008).

$$a_w\left(w_2, T^\theta\right) = \frac{(1 + a \cdot w_2)}{(1 + b \cdot w_2 + c \cdot w_2^2)}$$ S1

The water activities at a second temperature were derived from the solutions' ice melting temperatures. It was shown previously that the water activity of an aqueous solution at its ice melting temperature is independent of the chemical nature of the solute and can be described with equation S2 (Koop and Zobrist, 2009).

$$
\begin{aligned}
a_{w,ice}(T_m) &= p_{ice}(T_m) \cdot \{p_{liq}(T_m)\}^{-1} \\
&= \left\{exp\left[9.550426 - \frac{5723.265}{T} + 3.53068 \cdot \ln(T) - 0.00728332 \cdot T\right]\right\} \\
&\quad \cdot \left\{exp\left[54.842763 - \frac{6763.22}{T} - 4.21 \cdot \ln(T) - 0.000367 \cdot T\right.\right. \\
&\quad + \tanh(0.0415 \cdot (T - 218.8)) \cdot (53.878 - \frac{1331.22}{T} - 9.44523 \cdot \ln(T) \\
&\quad \left.\left. + 0.014025 \cdot T\right]\right\}^{-1}
\end{aligned}
$$ S2

The ice melting points in this study were determined as the point of maximum slope at the left side of the ice melting peak measured in the heating mode of a differential scanning calorimeter at a heating rate of 10 K/min. This method gives ice melting temperatures that are slightly too high because of the rather high heating rate. Therefore, we did calibration measurements with aqueous sorbitol solutions at different concentrations and heating rates. (Sorbitol is a hexane-hexol and thus structurally similar to tetraol.) From these measurements we concluded a correction value of 0.93 K that is subtracted from the measured tetraol solution ice melting points. The water activity at the heating rate-corrected ice melting points was then calculated using equation S2.

The water activities at 25°C and those at the melting points for the different concentrations was then fitted using equation S3 (Zobrist et al., 2008), whereby the fit parameters *a, b* and *c* obtained from fitting equation S1 were kept fixed

$$a_w(w_2, T) = \frac{(1 + a \cdot w_2)}{(1 + b \cdot w_2 + c \cdot w_2^2)} + (T - T^\theta) \cdot (d \cdot w_2 + e \cdot w_2^2 + f \cdot w_2^3 + g \cdot w_2^4) \qquad \text{S3}$$

The last bracket in the equation is a fourth order polynomial function that is meant to describe the concentration dependence of the slope of the linear fit.

With these equations our measured glass transition temperatures at different mass fractions as well as the corresponding Gordon-Taylor fit can be converted from a mass fraction dependence to a water activity dependence. We note here that this transformation is not exact for several reasons. First we derived the temperature dependence of the water activity by fitting only two points for each concentration. Second we had to correct our ice melting points for a high heating rate which is a potential source for uncertainty. Third our data could not be fitted very well for the entire concentration range with the original fourth-order polynomial equation from Zobrist et al.: we while the fourth order polynomial in equations S3 fitted the low tetraol concentration range very well, we obtained a better fit at medium tetraol concentrations with a second order polynomial (i.e. by setting parameters f and g to zero). To take these uncertainties into account we took the following measures for the data transformation from the mass fraction dependence to the water activity dependence.

We did not transfer the actual Gordon-Taylor fit itself into the water activity regime but the 3σ range of the fit. Furthermore, we did the transformation with both the second order as well as the fourth order polynomial function and then overlapped the resulting ranges. With this procedure we derived a relatively broad glass transition range rather than an actual glass transition line. While this procedure reduces the precision of the glass transition temperature as a function of water activity, it enhances the certainty that the glass transition will take place within the range of glass transition temperatures depicted in figure 4.

Syntheses

General information

Materials used

The following chemicals were obtained from commercial suppliers and were used as received. The quality specified by the supplier is given in parentheses: (*S*)-1,1'-bi-2-naphthol (99%), *tert*-butanol (100%), calcium chloride (85%), citric acid monohydrate (> 99.5%), 2,2-dimethoxypropane (98%), Dowex® 50 WX4 (100 - 200 mesh, Sigma-Aldrich Chemie GmbH), lipase A *Candida antarctica* immobilised on Immobead 150, recombinant from *Aspergillus oryzae* (CAL-A, ≥ 500 U/g, product nr.:41658, Sigma-Aldrich Chemie GmbH), lithium aluminium hydride (for synthesis), maleic acid (99.99%), magnesium sulfate (> 99%), methanol (100%), (*E*)-2-methylbut-2-enedioic acid (99%), (*Z*)-2-methylbut-2-enedioic acid (99+%), *N*-methylmorpholine-*N*-oxide (97%), potassium carbonate (> 99.0%), potassium osmate dihydrate (for synthesis), potassium permanganate (99%), sodium hydroxide (99%), sodium sulphite (98%), concentrated sulfuric acid (95%), toluene (99.9%), vinyl butanoate (> 98.0%.).

Tetrahydrofuran (99.7%) was distilled from sodium/benzophenone prior its use. Solvents used for work-up and chromatography were of technical grade and were distilled prior their use. Deionized water was used for the syntheses.

Comments on the procedures

The temperatures given are the bath temperatures. If no temperature is mentioned, the reaction was performed at room temperature. For reactions performed under argon, the Schlenk technique was applied and argon 4.0 was passed through anhydrous calcium chloride before being used.

Column chromatography was carried out on silica gel (grain size: 0.035 - 0.070 mm, Acros) applying slight pressure. The size of the column and the type of eluent are given as (diameter ✕ length, eluent). Thin layer chromatography (TLC) was performed on silica gel coated aluminium foil (Merck, 60 F254). The compositions of solvent mixtures are given in volume ratios. If not detectable with UV light of λ = 254 nm, the spots were stained by dipping the TLC cards into an aqueous solution of sodium hydroxide (1 M) containing 0.5 wt% potassium permanganate and subsequently drying the TLC card with a heat gun.

Solvent removal was performed by using a rotary evaporator (40 °C, reduced pressure). Solvent residues were removed at room temperature/0.05 mbar, unless otherwise stated.

NMR spectroscopy

NMR spectra were calibrated using the solvent signal as an internal standard [$CDCl_3$: $\delta(^1H) = 7.25$, $\delta(^{13}C) = 77.16$; CD_3OD: $\delta(^1H) = 3.31$, $\delta(^{13}C) = 49.0$]. ^{13}C NMR signal assignment was supported by DEPT 135 experiments.

For quantitative ^1H NMR (qNMR) spectroscopic analysis, maleic acid was used as an internal reference compound, dissolved in the solution of the sample. The ^1H NMR spectra were recorded with a relaxation time of 30 s and the mass fraction of the substance, w_x, was calculated according to equation (S4)

$$w_x = \frac{I_x \cdot N_{ref} \cdot M_x \cdot m_{standard} \cdot w_{ref}}{I_{ref} \cdot N_x \cdot M_{ref} \cdot m_{sample}} \qquad \text{S4}$$

with integrals *I*, numbers of protons *N* causing a specific signal, molar masses *M*, and the mass fractions *w* of compound *x* and *reference compound* (*ref*) and the masses *m* of *sample* and *standard*.

Determination of the ee-values with ^1H NMR spectroscopy

To determine the *ee*-values of diols **3** with ^1H NMR spectroscopy, a mixture of diol **3** and (*S*)-1,1'-bi-2-naphthol in $CDCl_3$ was used. The relative intensities of the signals assigned to the methyl groups in the 2-positions of the enantiomers were determined after signal deconvolution.

Determination of the ee-values with gas chromatography: Gas chromatography was performed on GC-2010 (Shimadzu) equipped with an MN Lipodex E column (length 25.0 m, inner diameter 0.25 mm, film thickness 0.25 μm; Macherey-Nagel) and a flame ionisation detector. N_2 was used as the mobile phase (column flow rate 2.15 mL/min) and two different temperature profiles (Table S1) were applied. 1 μL of a solution of the sample in methanol (~ 1 mg mL^{-1}) was injected. The enantiomeric excess was calculated with the integrals of the GC signals.

Table S1. Temperature profiles 1 and 2 used for GC analysis of diols **3** and butanoates **4** on an MN Lipodex E column. The heating rate was applied to bring the column to the given temperature at which the column was kept for the specified time. Both profiles started at 40 °C and ended at 180 °C.

heating rate / °C min^{-1}	temperature / °C	holding time / min
profile 1		
10	100	0
4	140	0
10	180	0
profile 2		
10	105	2
2	107	2
2	109	3
2	110	3
2	111	3
2	112	3
2	114	3
2	138	0
10	180	0

Table S2. Retention times of the enantiomers during GC analysis on an MN Lipodex E column using temperature profile 1 for diol (2*R*,3*R*)$_x$-**3** and butanoate (2*S*,3*S*)$_x$-**4** and temperature profile 2 for butanoate (2*R*,3*S*)$_x$-**4**. For temperature profiles see Tables S1.

	butanoates **4**		diols **3**		butanoates **4**	
	(2*R*,3*S*)-**4**	(2*S*,3*R*)-**4**	(2*S*,3*S*)-**3**	(2*R*,3*R*)-**3**	(2*S*,3*S*)-**4**	(2*R*,3*R*)-**4**
retention time /min	42.6	42.0	14.6	15.0	18.7	19.1

Specific rotation

Specific rotations were determined with the polarimeter Model 341 by Perkin Elmer Instruments using a cuvette of 100 mm thickness and light of 589 nm at room temperature.

Esterification

Dimethyl 2-methylmaleate (diester (*Z*)-2; dimethyl (*Z*)-2-methylbut-2-enedioate, dimethyl citraconate)

Concentrated sulfuric acid (8.9 mL) was added to a solution of 2-methylmaleic acid (diacid (*Z*)-**1**; 104.7 g, 805 mmol) in methanol (750 mL). The slightly yellow solution was

heated to 115 °C in a Soxhlet extractor with a thimble filled with magnesium sulfate monohydrate (83 g, 690 mmol). After 1 d magnesium sulfate monohydrate (2.2 g, 18 mmol) was added to the reaction mixture. The reaction was monitored by TLC [Et$_2$O/EtOH 9:2, R_f(diacid (Z)-**1**) = 0.00, R_f(diester (Z)-**2**] = 1.00]. After a reaction time of overall 7 d, potassium acetate (17.8 g, 182 mmol) was added to the solution. This way the pH was raised to 6-7. Upon addition of potassium acetate a precipitate formed. The suspension was concentrated (40 °C/ 200 mbar) to about half of its volume and diethyl ether (350 mL) and then water (150 mL) were added. The two phases were separated and the turbid aqueous phase was extracted with diethyl ether (3 x 100 mL). The combined organic phases were washed with an aqueous solution of NaOH (1M, 3 x 20 mL), dried with sodium sulfate, and filtered. The solvent of the filtrate was removed and the yellow liquid residue was distilled giving diester (Z)-**2** (98-99 °C/ 100 mbar; 103.8 g, 82%) as a colourless liquid. The ^{1}H NMR spectrum reveals that the compound was very slightly contaminated with unidentified compounds. ^{1}H NMR (500 MHz, CD$_3$OD): δ = 5.96 (q, J = 1.6 Hz, 1H, CH), 3.78 and 3.70 (2s, 3H each, OCH$_3$), 2.04 (d, J = 1.6 Hz, 3H, CCH$_3$). Data of another batch: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.85 (q, J = 1.6 Hz, 1H, CH), 3.82 and 3.71 (2s, 3H each, OCH$_3$), 2.05 (d, J = 1.6 Hz, 3H, CCH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 169.4 and 165.4 (CO$_2$Me), 145.8 (C=CH), 120.6 (C=CH), 52.4 und 51.9 (OCH$_3$), 20.5 (CCH$_3$).

Dimethyl 2-methylfumarate (diester (E)-2; dimethyl (E)-2-methylbut-2-enedioate, dimethyl mesaconate)

Concentrated sulfuric acid (4.4 mL) was added to a solution of 2-methylfumarate (diacid (E)-**1**; 51.2 g, 393 mmol) in methanol (370 mL). The colourless solution was heated to 115 °C for 7 d in a Soxhlet extractor with a thimble filled with magnesium sulfate monohydrate (80 g, 660 mmol). The reaction was monitored by TLC [Et$_2$O/EtOH 9:2, R_f(diacid (E)-**1**) = 0.00, R_f(diester (E)-**2**) = 1.00]. After 1 d magnesium sulfate monohydrate (1.3 g, 11 mmol) was added to the reaction mixture. The heating was continued until no change between two samples taken with a time difference of 23 h was detected by TLC and ^{1}H NMR spectroscopy. After a reaction time of allover 7 d, potassium acetate (11.7 g, 119 mmol) was added to the solution. This brought the pH value to 7 and caused the formation of a precipitate. The suspension was concentrated (40 °C/ 200 mbar; about 75 mL of the solvent were removed). To the remaining suspension, diethyl ether (100 mL) and then water (100 mL) were added. The two phases were separated and the aqueous phase was extracted with diethyl ether (3 x 80 mL). The combined organic phases were washed with an aqueous solution of sodium hydroxide (1 M, 3 x 15 mL), dried with sodium sulfate, and filtered. The solvent of the filtrate was removed giving a yellow liquid residue (58.9 g). Part of this residue (48.4 g)

was distilled giving diester (*E*)-**2** (85-94 °C/15 mbar; 38.2 g, 62%, which corresponds to an overall yield of 75%) as a colourless liquid. ^{1}H NMR (500 MHz, CD$_3$OD): δ = 6.74 (q, *J* = 1.6 Hz, 1H, CH), 3.80 and 3.76 (2s, 3H each, OCH$_3$), 2.26 (d, *J* = 1.6 Hz, 3H, CCH$_3$). Data of another batch: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.77 (q, *J* = 1.6 Hz, 1H, CH), 3.79 and 3.75 (2s, 3H each, OCH$_3$), 2.28 (d, *J* = 1.6 Hz, 3H, CCH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 167.6 and 166.3 (CO$_2$Me), 143.8 (C=CH), 126.5 (C=CH), 52.6 and 51.7 (OCH$_3$), 14.3 (CCH$_3$).

Syn-dihydroxylation

rac-(2*R*,3*S*)-Dimethyl 2,3-dihydroxy-2-methylbutandioate (diol *rac*-(2*R*,3*S*)-3)

To a colourless solution of diester (*Z*)-**2** (107.1 g, 677 mmol) and citric acid monohydrate (108.2 g, 515 mmol) in *tert*-butanol (362 mL) and water (362 mL) was added K$_2$OsO$_4$•2 H$_2$O (649 mg, 1.76 mmol). This resulted in a green solution containing a brown solid. To this suspension *N*-methylmorpholine-*N*-oxide (87.4 g, 723 mmol) was added causing a slight temperature rise of the reaction mixture. The resulting brown solution was stirred for 24 h, meanwhile the solution turned green. TLC (Et$_2$O/CH$_2$Cl$_2$ 1:1) revealed an incomplete conversion of diester (*Z*)-**2** (*R$_f$*(diester (*Z*)-**2**) = 1.00, *R$_f$*(diol *rac*-(2*R*,3*S*)-**3**) = 0.52). More *N*-methylmorpholine-*N*-oxide (8.40 g, 70 mmol) was added, whereupon the solution turned brown. After 22 h of stirring no diester (*Z*)-**2** was detected by TLC. Na$_2$SO$_3$ (77.93 g, 618 mmol) was added and the mixture of two liquid phases was stirred for 2.5 h. The aqueous brown phase and the organic colourless phase were separated. The aqueous phase was extracted with a 10:1 mixture of diethyl ether and tetrahydrofuran (6 x 110 mL). The combined organic phases were filtered to remove a brown solid, and the solvents of the filtrate were removed. The colourless solid residue was recrystallised in methanol (46 mL) and the crystals were rinsed with *n*-hexane (8 x 10 mL). This provided diol *rac*-(2*R*,3*S*)-**3** (84.1 g, 65%) as colourless crystals in the form of short needles with a very slight tinge of yellow. The ^{1}H NMR spectrum reveals that the compound was very slightly contaminated with unidentified compounds. ^{1}H NMR (500 MHz, CD$_3$OD): δ = 4.40 (s, 1H, CH), 3.75 and 3.71 (2s, 3H each, OCH$_3$), 1.46 (s, 3H, CCH$_3$). ^{13}C NMR (125 MHz, CD$_3$OD): δ = 176.1 and 173.2 (CO$_2$Me), 78.0 (MeCOH), 76.5 (HCOH), 52.9 und 52.5 (OCH$_3$), 23.1 (CCH$_3$). Data of another batch: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.36 (s, 1H, CH), 3.82 and 3.76 (2s, 3H each, OCH$_3$), 3.34 (broad s, 1 H, MeCOH), 3.07 (broad s, 1H, HCOH), 1.54 (s, 3H, CCH$_3$).

rac-(2*R*,3*R*)-Dimethyl 2,3-dihydroxy-2-methylbutandioate (diol *rac*-(2*R*,3*R*)-3)

To a colourless solution of diester (*E*)-**2** (38.16 g, 241 mmol) and citric acid monohydrate (38.5 g, 183 mmol) in *tert*-butanol (186 mL) and water (186 mL) was added K$_2$OsO$_4$•2H$_2$O (231 mg, 0.63 mmol). This resulted in a green solution containing a brown solid. To this

suspension *N*-methylmorpholine-*N*-oxide (35.05 g, 299 mmol) was added causing a slight temperature rise of the reaction mixture. The brown solution was stirred for 21 h. Analysis of the brown solution with TLC [CH_2Cl_2, R_f(diester (*E*)-**2**) = 0.50, R_f(diol *rac*-(2*R*,3*R*)-**3**) = 0.18] proofed the absence of diester (*E*)-**2**. Na_2SO_3 (31.8 g, 252 mmol) was added which turned the brown solution into a mixture of two liquid phases with a small amount of fine brown solid. This suspension was stirred for 1.5 h. The brown aqueous phase and the colourless organic phase were separated and the aqueous phase was extracted with a 10:1 mixture of diethyl ether and tetrahydrofuran (6 x 55 mL). The solvents of the combined organic phases were removed yielding a turbid colourless viscous liquid, which was filtered through a plug of silica gel (7 cm x 5 cm) using a 1:1 mixture (ca. 830 mL) and then a 3:1 mixture (ca. 400 mL) of diethyl ether and dichloromethane. The solvents of the eluate were removed leaving diol *rac*-(2*R*,3*R*)-**3** (42.3 g, 91%) as a viscous colourless liquid. The ^{1}H NMR spectrum reveals that the compound was very slightly contaminated with unidentified compounds. ^{1}H NMR (500 MHz, CD_3OD): *δ* = 4.36 (s, 1H, CH), 3.77 and 3.76 (2s, 3H each, OCH_3), 1.43 (s, 3H, CCH_3). Data of another batch: ^{1}H NMR (500 MHz, $CDCl_3$): *δ* = 4.34 (d, *J* = 8.1 Hz, 1H, CH), 3.85 and 3.83 (2s, 3H each, OCH_3), 3.60 (s, 1H, MeCOH), 3.30 (d, *J* = 8.5 Hz, 1H, HCOH), 1.50 (s, 3H, CCH_3).

Kinetic resolutions of the diols *rac*-(2*R*,3*S*)-3 and *rac*-(2*R*,3*R*)-3
General considerations

For monitoring the chiral resolutions, a sample (0.1 mL) of the suspension was removed and diluted with $CDCl_3$ (ca. 0.7 mL) and the ^{1}H NMR spectrum of this sample was recorded. The conversion was calculated from the relative intensities of the singlets arising from the methoxy groups of diols and butanoates.

The ratios of butanoates **4** to butanoic acid were calculated from the intensities of the ^{1}H NMR spectroscopic signals of the O_2CCH_2 moieties.

Table S3: *ee*-Values of diols **3** and butanoates **4** determined by gas chromatography (GC) and/or ^{1}H NMR spectroscopy (NMR). The diols and butanoates were obtained through kinetic resolutions of the racemates *rac*-(*2R,3S*)-**3** and *rac*-(*2R,3R*)-**3** and of the enantiomerically enriched diol (*2S,3R*)$_7$-**3**.

	materials obtained by resolutions of	
	racemates x_{method}/ %	(*2S,3R*)$_7$-**3** x_{method}/ %
diol (*2S,3R*)$_X$-**3**	7_{NMR}	65_{NMR}
butanoate (*2R,3S*)$_X$-**4**	86_{GC}	75_{GC}
diol (*2R,3R*)$_X$-**3**	63_{NMR}, 64_{GC}	-
butanoate (*2S,3S*)$_X$-**4**	97_{GC}	-

Resolution of rac-(2R,3S)-3 providing diol (2S,3R)$_7$-3 and butanoate (2R,3S)$_{86}$-4

A mixture of diol *rac*-(*2R,3S*)-**3** (29.13 g, 152 mmol) and vinyl butanoate (184 mL, 1.45 mol) in toluene (700 mL) was tempered at 14 °C. CAL-A (4.12 g) and toluene (36 mL) were added and the yellow suspension was stirred at 14 °C. A reaction control after 17.5 h revealed a 69:31 ratio of diol (*2S,3R*)$_X$-**3** and butanoate (*2R,3S*)$_X$-**4**. After stirring for allover 19.5 h, the suspension was filtered through a Büchner funnel and the filter cake was subsequently rinsed with methanol (150 mL), dichloromethane (50 mL) and diethyl ether (50 mL). The solvents of the filtrate were removed yielding a mixture of colourless crystals and a yellow oil. This mixture consisted essentially of diol (*2S,3R*)$_X$-**3** and butanoate (*2R,3S*)$_X$-**4** in a ratio of 80:20 The mixture was suspended in CH_2Cl_2/Et_2O (1:1, 700 mL), silica gel (50 mL) was added, and the suspension was heated to 40 °C to dissolve as much of the crystals as possible. Then the solvents were removed and the residual fine powder was brought onto the top of a silica gel column (7.0 cm x 28.5 cm). Column chromatography (CH_2Cl_2/Et_2O 1:1) gave a yellow liquid 7:3 mixture (8.7 g; R_f = 0.69) of butanoate (*2R,3S*)$_{86}$-**4** (19% yield) and butanoic acid and a fraction (20.9 g; R_f = 0.25) consisting mainly of diol (*2S,3R*)$_7$-**3**. Recrystallisation of the latter fraction in methanol (11.6 mL) and washing the isolated crystals with *n*-hexane (4 x 10 mL) yielded diol (*2S,3R*)$_7$-**3** (17.1 g, 59%) as colourless needle-shaped crystals.

Analytical data of the fraction which contained butanoate (*2R,3S*)$_{86}$-**4** and butanoic acid: ^{1}H NMR (500 MHz, CDCl$_3$), signals assigned to butanoate (*2R,3S*)$_{86}$-**4**: δ = 5.48 (s, 1H, CH), 3.83 and 3.70 (s, 3H each, OCH$_3$), 2.44 (characteristic pattern with 10 lines (Figure S3), 2H, O$_2$CCH$_2$), 1.70 (sext, *J* = 7.5 Hz, 2H, CH$_2$CH$_3$), 1.44 (s, 3H, CCH$_3$), 0.96 (t, *J* = 7.5 Hz, 3H, CH$_2$CH$_3$), signals assigned to butanoic acid: δ = 2.30 (t, *J* = 7.5 Hz, 2H), 1.63 (sext, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). ee$_{GC}$ = (86 ± 1).

Analytical data of diol (*2S,3R*)$_7$-**3**: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.36 (d, *J* = 8.5 Hz,

1H, CH), 3.82 and 3.76 (2s, 3H each, OCH$_3$), 3.33 (s, 1H, MeCOH), 3.06 (d, J = 8.5 Hz, 1H, HCOH), 1.54 (s, 3H, CCH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 175.0 and 171.9 (CO$_2$Me), 76.6 (MeCOH), 75.6 (HCOH), 53.3 and 52.9 (OCH$_3$), 22.7 (CCH$_3$). ee$_{NMR}$ = (7 ± 1)%

Analytical data of the mixture of diol (2S,3R)$_7$-**3** (6 mg, 0.03 mmol) and (S)-1,1'-bi-2-naphthol (16 mg, 0.06 mmol) in CDCl$_3$ (0.8 mL): ^{1}H NMR (500 MHz, CDCl$_3$), signals assigned to diol (2S,3R)-**3**: δ = 4.34 (d, J = 8.5 Hz, CH), 3.81 and 3.75 (2s, OCH$_3$), 3.33 (s, MeCOH), 3.09 (d, J = 8.5 Hz, HCOH) 1.52 (s, CCH$_3$), signals assigned to diol (2R,3S)-**3**: δ = 4.33 (d, J = 8.5 Hz, CH), 3.81 and 3.75 (2s, OCH$_3$), 3.34 (s, MeCOH), 3.08 (d, J = 8.5 Hz, HCOH) 1.53 (s, CCH$_3$), signals assigned to (S)-1,1'-bi-2-naphthol: δ = 7.96 (apparent d, J = 9.1 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H), 7.36 (m and apparent d with J = 8.9 Hz, 4H), 7.30 (m, 2H), 7.14 (d, J = 8.6 Hz, 2H), 5.10 (s, 2H). The integral ratio of the singlet of diol (2R,3S)-**3** at 1.53 ppm and of the singlet of diol (2S,3R)-**3** at 1.52 ppm was determined by deconvolution of the overlapping signals to be 7160:8200.

Resolution of diol (2*S*,3*R*)$_7$-3 providing diol (2*S*,3*R*)$_{65}$-diol 3 and butanoate (2*R*,3*S*)$_{75}$-4

A mixture of diol (2S,3R)$_7$-**3** (16.78 g, 87 mmol) and vinyl butanoate (106.4 mL, 838 mmol) in toluene (350 mL) was tempered at 14 °C. CAL-A (2.44 g) that had been recovered from the chiral resolution of diol *rac*-(2R,3S)-**3** that is described above was added and the yellow suspension was stirred at 14 °C for 3 d. Because no product formed (^{1}H NMR spectroscopical analysis), commercially obtained CAL-A (1.12 g) was added. Additional CAL-A (0.28 g and 1.70 g) was added at the seventh and twelfth day. After a reaction time of allover 13 d the ratio of diol (2S,3R)$_x$-**3** to butanoate (2R,3S)$_x$-**4** was 69:31. The yellow suspension was filtered through a Büchner funnel and the filter cake was rinsed with toluene (40 mL). The solvent of the filtrate was removed yielding a mixture of colourless crystals and a yellow oil containing, among other components, diol (2S,3R)$_x$-**3** and butanoate (2R,3S)$_x$-**4** in a ratio of 52:48. The mixture was suspended in CH$_2$Cl$_2$ (50 mL), silica gel (8.2 g) was added, and the solvent was removed. The residual fine powder was brought onto the top of a silica gel column (5.0 cm x 33 cm). Column chromatography (CH$_2$Cl$_2$/Et$_2$O 1:1) gave a yellow liquid (5.1 g; R_f = 0.78), consisting of butanoate (2R,3S)$_{75}$-**4** (21% yield) and butanoic acid in a ratio of 83:17, and diol (2S,3R)$_{65}$-**3** (3.4 g, 20%; R_f = 0.24) as a colourless crystalline solid. The filter cake was furthermore rinsed with methanol (6 x 25mL) and diethyl ether (2 x 40 mL). Removal of the solvent of this filtrate gave a colourless solid (8.5 g) consisting mainly of diol (2S,3R)$_x$-**3**, 2 mol% of butanoate (2R,3S)$_x$-**4** and 2 mol% of butanoic acid.

Analytical data of the fraction which contained butanoate (2R,3S)$_{75}$-**4** and butanoic acid:

^{1}H NMR (500 MHz, CDCl$_3$), signals assigned to butanoate (2R,3S)$_{75}$-**4**: δ = 5.50 (s, 1H, CH), 3.85 and 3.72 (s, 3H each, OCH$_3$), 3.54 (broadened s, 1H, OH), 2.46 (characteristic pattern with 10 lines (Figure S3), 2H, O$_2$CCH$_2$), 1.72 (sext, J = 7.5 Hz, 2H, CH$_2$CH$_3$), 1.46 (s, 3H, CCH$_3$), 0.98 (t, J = 7.5 Hz, 3H, CH$_2$CH$_3$); signals assigned to butanoic acid: δ = 2.33 (t, J = 7.5 Hz, 2H), 1.66 (sext, J = 7.5 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$), signals assigned to butanoate (2R,3S)$_{75}$-**4**: δ = 174.5 and 172.9 (CO$_2$Me), 167.7 (PrCO$_2$), 75.7 (HCO$_2$C), 75.1 (MeCOH), 53.6 and 52.7 (OCH$_3$), 35.9 (O$_2$CCH$_2$), 22.8 (HOCCH$_3$), 18.5 (CH$_2$CH$_3$), 13.68 (CH$_2$CH$_3$); signals assigned to butanoic acid: δ = 178.3, 35.8, 18.3, 13.72. ee$_{GC}$ = (75 ± 1).

Analytical data of diol (2S,3R)$_{65}$-**3**: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.36 (d, J = 8.5 Hz, 1H, CH), 3.82 and 3.76 (2s, 3H each, OCH$_3$), 3.33 (s, 1H, MeCOH), 3.06 (d, J = 8.5 Hz, 1H, HCOH) 1.54 (s, 7H, CCH$_3$, H$_2$O). ee$_{NMR}$ = (65 ± 1)%.

Analytical data of the mixture of diol (2S,3R)$_{65}$-**3** (7 mg, 0.04 mmol) and (S)-1,1'-bi-2-naphthol (26 mg, 0.09 mmol) in CDCl$_3$ (0.8 mL): ^{1}H NMR (500 MHz, CDCl$_3$), signals assigned to diol (2S,3R)-**3**: δ = 4.33 (broad s, CH), 3.81 and 3.75 (2s, OCH$_3$), 3.32 (broad s, MeCOH), 3.10 (broad s, HCOH) 1.51 (s, CCH$_3$), signals assigned to diol (2R,3S)-**3**: δ = 4.33 (broad s, CH), 3.81 and 3.75 (2s, OCH$_3$), 3.32 (broad s, MeCOH), 3.10 (broad s, HCOH), 1.52 (s, CCH$_3$); signals assigned to (S)-1,1'-bi-2-naphthol: δ = 7.95 (apparent d, J = 9.1 Hz, 2H), 7.88 (d, J = 8.6 Hz, 2H), 7.36 (m and apparent d with J = 8.9 Hz, 4H), 7.30 (m, 2H), 7.15 (d, J = 8.6 Hz, 2H), 5.13 (s, 2H). The integral ratio of the singlet of diol (2R,3S)-**3** at δ = 1.52 and of the singlet of diol (2S,3R)-**3** at δ = 1.51 was determined by deconvolution to be 1840:8530.

Resolution of diol rac-(2R,3R)-3 providing diol (2R,3R)$_{64}$-3 and butanoate (2S,3S)$_{97}$-4

A mixture of diol rac-(2R,3R)-**3** (31.68 g, 165 mmol) and vinyl butanoate (200 mL, 1.58 mol) in toluene (700 mL) was tempered at 14 °C. CAL-A (4.49 g) and toluene (100 mL) were added and the yellow suspension was stirred at 13-14 °C. A reaction control after 40 h gave a ratio of diol (2R,3R)$_x$-**3** to butanoate (2R,3R)$_x$-**4** of 56:44. After stirring for allover 44 h, the suspension was filtered through a Büchner funnel and the filter cake was subsequently rinsed with methanol (230 mL) and diethyl ether (80 mL). The solvents of the filtrate were removed yielding a yellow oil containing, besides minor amounts of other components, diol (2R,3R)$_x$-**3** and butanoate (2R,3R)$_x$-**4** in the ratio of 60:40. The yellow oil was diluted with CH$_2$Cl$_2$/Et$_2$O (1:1, 400 mL), silica gel (60 mL) was added, and the solvents were removed giving a fine powder which was loaded on top of a silica gel column (7.0 cm x 27.5 cm). Column chromatography (CH$_2$Cl$_2$/Et$_2$O 1:1) gave, as the first fraction, a slightly yellow liquid (13.5 g; R_f = 0.7) which consisted of butanoate (2S,3S)$_{97}$-**4** (29% yield) and butanoic acid in a ratio of 83:17, as the second fraction a 18:82 mixture

of butanoate $(2S,3S)_{94}$-**4** and diol $(2R,3R)_{70}$-**3** (6.4 g; R_f = 0.7 and 0.5; the *ee* values were determined with GC), and, as the last fraction, diol $(2R,3R)_{64}$-**3** (11.2 g, 35%; R_f = 0.50) together with a trace of butanoic acid as a yellow oil.

Analytical data of the chromatography fraction which contained butanoate $(2S,3S)_{97}$-**4** and butanoic acid: ^{1}H NMR (500 MHz, CDCl$_3$), signals assigned to butanoate $(2S,3S)_{97}$-**4**: δ = 5.17 (s, 1H, CH), 3.79 and 3.78 (2s, 3H each, OCH$_3$), 3.51 (slightly broadened s, 1H, OH), 2.35 (characteristic pattern with 10 lines (Figure S5), 2H, O$_2$CCH$_2$), 1.64 (sext, J = 7.4 Hz, 2H, CH$_2$CH$_3$), 1.56 (s, 3H, CCH$_3$), 0.94 (t, J = 7.4 Hz, 3H, CH$_2$CH$_3$), signals assigned to butanoic acid: δ = 2.33 (t, J = 7.4 Hz, 2H), 1.60 (sext, J = 7.5 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$), signals assigned to butanoate $(2S,3S)_{97}$-**4**: δ = 173.8 and 172.4 (CO$_2$Me), 167.1 (PrCO$_2$), 76.1 (HCO$_2$C), 75.2 (MeCOH), 53.3 and 52.6 (OCH$_3$), 35.7 (O$_2$CCH$_2$), 22.1 (HOCCH$_3$), 18.3 (CH$_2$CH$_3$), 13.5 (CH$_2$CH$_3$), signals assigned to butanoic acid: δ = 178.1, 35.8, 18.2, 13.7. ee_{GC} = (97 ± 1).

Analytical data of diol $(2R,3R)_{64}$-**3**: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.34 (d, ^3J = 8.5 Hz, 1H, CH), 3.85 and 3.84 (2s, 3H each, OCH$_3$), 3.59 (slightly broadened d, ^4J = 2.3 Hz, 1H, CMeOH) and 3.28 (slightly broadened dd, ^3J = 8.5 Hz, ^4J = 3.4 Hz, 1H, CHOH) 1.50 (s, 3H, CCH$_3$); signals assigned to butanoic acid: δ = 2.33 (t, ^3J = 7.4 Hz, 2H), 1.67 (sext, ^3J = 7.4 Hz, 2H), 0.97 (t, ^3J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, CD$_3$OD): δ = 175.7 and 172.8 (C=O), 78.5 (H$_3$CCOH), 76.9 (HCOH), 53.0 and 52.5 (OCH$_3$), 22.2 (CCH$_3$). ee_{GC} = (64 ± 1)%, ee_{NMR} = (63 ± 1)%.

Analytical data of the mixture of diol $(2R,3R)_{64}$-**3** (5 mg, 0.03 mmol) and (*S*)-1,1'-bi-2-naphthol (28 mg, 0.10 mmol) in CDCl$_3$ (0.8 mL): ^{1}H NMR (500 MHz, CDCl$_3$), signals assigned to diol $(2R,3R)$-**3**: δ = 4.31 (s, CH), 3.823 and 3.815 (2s, OCH$_3$), 1.49 (s, CCH$_3$), signals assigned to diol $(2S,3S)$-**3**: δ = 4.30 (s, CH), 3.828 and 3.815 (2s, OCH$_3$), 1.47 (s, CCH$_3$); signals assigned to (*S*)-1,1'-bi-2-naphthol: δ = 7.95 (apparent d, J = 9.1 Hz, 2H), 7.88 (d, J = 8.6 Hz, 2H), 7.36 (m, 2H), 7.35 (apparent d, J = 9.0 Hz, 2H), 7.30 (m, 2H), 7.15 (d, J = 8.6 Hz, 2H), 5.08 (s, 2H). The integral ratio of the singlet of diol $(2R,3R)$-**3** at 1.49 ppm and of the singlet of diol $(2S,3S)$-**3** at 1.48 ppm was determined by deconvolution to be 115800:26600.

Reduction of the diols 3 to the tetraols
rac-(2*R*,3*S*)-2-Methylbutane-1,2,3,4-tetraol (2-*C*-methyl-D,L-erythritol, rac-(2*R*,3*S*)-tetraol)

The reaction was performed under argon. Diol *rac*-(2*R*,3*S*)-**3** (18.21 g, 95 mmol) was added portionwise within 30 min to the grey suspension of lithium aluminium hydride (14.2 g, 374 mmol) in tetrahydrofuran (550 mL) which was cooled with an ice bath. The ice bath was removed and the suspension was stirred for 19 h. The suspension was

cautiously poured into water (400 mL) which was cooled with an ice bath. The suspension was filtered through a Büchner funnel. The colourless creamy solid, which was retained in the funnel, was rinsed with water (2 x 50 mL) and then with methanol (2 x 50 mL). The combined slightly yellow filtrates were concentrated (40 °C/ 150 mbar). To the residual yellow solution, solid carbon dioxide (ca. 200 g) was added in seven portions until the pH was reduced from 12-14 to 7-8 whereupon a colourless precipitate formed. This precipitate was removed by centrifugation (6000 g, 10 min, 4 °C) and subsequent separation of the solid and the clear liquid phase. The solvents of the orange supernatant liquid were removed giving a mixture of colourless and orange-brown solids. This mixture was suspended in methanol (100 mL) and the suspension was filtered through a Büchner funnel. The powdery colourless filter cake was rinsed with methanol (4 x 20 mL). The solvent of the combined filtrates was removed giving a brown oil (7.84 g) which contained *rac*-(2*R*,3*S*)-tetraol (80±3 wt%, 49% yield).

rac-(2*R*,3*R*)-2-Methylbutane-1,2,3,4-tetraol (2-*C*-methyl-D,L-threitol, *rac*-(2*R*,3*R*)-tetraol)

The reaction was performed under argon. Diol *rac*-(2*R*,3*R*)-**3** (18.23 g, 95 mmol) was added dropwise within 30 minutes to a grey suspension of lithium aluminium hydride (15.2 g, 400 mmol) in dry tetrahydrofuran (550 mL) which was cooled with an ice bath. The ice bath was removed and the mixture was stirred for 22 h. The suspension was cautiously poured into water (400 mL) which was cooled with an ice bath. The resulting colourless suspension was filtered through a Büchner funnel. The colourless creamy filter cake was rinsed with water (2 x 50 mL) and then with methanol (2 x 50 mL). The combined slightly yellow filtrates were concentrated (40 °C/ 150 mbar). To the residual solution, solid carbon dioxide (ca. 150 g) was added in six portions until the pH was reduced from 12-14 to 8-9 whereupon a colourless precipitate formed. This precipitate was removed by centrifugation (6000 g, 10 min, 5 °C) and subsequent separation of the solid from the supernatant clear liquid. The solvents of the orange liquid were removed giving an orange solid which was suspended in methanol (100 mL). The suspension was filtered through a Büchner funnel and the powdery filter cake was rinsed with methanol (5 x 10 mL). The solvent of the combined filtrates was removed giving a brown oil (6.13 g) which contained *rac*-(2*R*,3*R*)-tetraol (80±3 wt%, 38% yield).

(2*S*,3*R*)$_{86}$-2-Methylbutane-1,2,3,4-tetraol (2-*C*-methyl-D-erythritol with ee = 86%, (2*S*,3*R*)$_{86}$-tetraol)

The reaction was performed under argon. The 7:3 mixture of butanoate (2*R*,3*S*)$_{86}$-**4** and butanoic acid (6.60 g containing about 22 mmol of butanoate) was added dropwise within 40 minutes to a grey suspension of lithium aluminium hydride (3.72 g, 98 mmol) in dry tetrahydrofuran (200 mL) which was cooled with a water bath. The dropping funnel was

rinsed with dry tetrahydrofuran (12 mL). Then the water bath was removed, and the suspension was stirred for 20 h. The suspension was cautiously poured into water (200 mL) which was cooled with a water bath. The resulting colourless suspension was filtered through a Büchner funnel. The colourless creamy filter cake was rinsed with water (2 x 20 mL). To the combined filtrates, solid carbon dioxide (ca. 70 g) was added in four portions until the pH was reduced to 8 whereupon a colourless precipitate formed. This precipitate was removed by centrifugation (6000 g, 10 min, 4 °C) and subsequent separation of the liquid from the solid phase. The solvents of the slightly yellow supernatant liquid were removed giving a mixture of a colourless and an orange solid which was suspended in methanol (60 mL). The suspension was filtered through a Büchner funnel and the filter cake was rinsed with methanol (5 x 10 mL). The solvent of the combined yellow filtrates was removed and the residue was suspended in ethanol (26 mL). The precipitate was removed by centrifugation (6000 g, 20 min, 4 °C) and subsequent separation of the liquid from the solid phase. The solvent of the yellow supernatant liquid was removed giving a yellow highly viscous oil (2.2 g) which contained $(2S,3R)_{86}$-tetraol (84±3 wt%, 62% yield).

$(2R,3S)_{65}$-2-Methylbutane-1,2,3,4-tetraol (2-*C*-methyl-L-erythritol with ee = 65%, $(2R,3S)_{65}$-tetraol)

The reaction was performed under argon. Diol $(2S,3R)_{65}$-**3** (1.36 g, 7 mmol) was added within 30 minutes in small portions to a grey suspension of lithium aluminium hydride (0.84 g, 22 mmol) in dry tetrahydrofuran (50 mL) which was cooled with a water bath. The water bath was removed. The suspension was stirred for 5 d and then cautiously poured into water (50 mL) which was cooled with an ice bath. The colourless suspension was filtered through a Büchner funnel. The colourless creamy filter cake was rinsed with water (15 mL) and then with methanol (15 mL). The solvents of the combined filtrates were removed yielding an orange solid. It was dissolved in methanol (50 mL), silica gel was added, and the solvent was removed. The residual fine powder was loaded on top of a silica gel column (4.5 cm x 27.5 cm). Column chromatography (Et_2O/EtOH first 9:2, then 1:1, and finally rinsing with methanol) gave a highly viscous brown oil (0.67 g) containing $(2R,3S)_{65}$-tetraol.

$(2R,3R)_{97}$-2-Methylbutane-1,2,3,4-tetraol (2-*C*-methyl-D-threitol with ee = 97%, $(2R,3R)_{97}$-tetraol)

The reaction was performed under argon. The 83:17 mixture of butanoate$(2S,3S)_{97}$-**4** and butanoic acid (12.99 g containing about 46 mmol of butanoate) was added dropwise within 45 minutes to a grey suspension of lithium aluminium hydride (7.96 g, 210 mmol) in dry tetrahydrofuran (410 mL) which was cooled with a water bath. After the addition was complete, dry tetrahydrofuran (20 mL) was used to rinse the dropping funnel. The

water bath was removed and the suspension was stirred for 20 h. The suspension was cautiously poured into water (395 mL) which was cooled with a water bath. The resulting colourless suspension was filtered through a Büchner funnel. The colourless creamy filter cake was rinsed with water (2 x 50 mL). To the combined filtrates, solid carbon dioxide (ca. 80 g) was added in six portions until the pH was reduced to 8 whereupon a colourless precipitate formed. This precipitate was removed by centrifugation (6000 g, 10 min, 4 °C) and subsequent separation of the liquid from the solid phase. The yellow supernatant liquid was concentrated giving a mixture (~ 50 mL) of a yellow oil and a colourless solid. It was suspended in methanol (20 mL), the suspension was filtered through a Büchner funnel, and the filter cake was rinsed with methanol (4 x 10 mL). The solvents of the combined turbid orange filtrates were removed and the residual orange greasy solid was suspended in ethanol (35 mL). The solid was removed by centrifugation (6000 g, 15 min, 4 °C) and subsequent separation of the liquid from the solid phase. The solvent of the yellow supernatant liquid was removed giving a yellow highly viscous oil (3.4 g) which contained ($2R,3R$)$_{97}$-tetraol (75±3 wt%, 41% yield).

($2S,3S$)$_{64}$-2-Methylbutane-1,2,3,4-tetraol (2-C-methyl-L-erythritol with ee = 64%, ($2S,3S$)$_{64}$-tetraol)

The reaction was performed under argon. Diol ($2R,3R$)$_{64}$-**3** (9.95 g, 52 mmol) that contained a trace of butanoic acid (see above) was added dropwise within 30 minutes to a grey suspension of lithium aluminium hydride (7.05 g, 186 mmol) in dry tetrahydrofuran (380 mL) which was cooled with a water bath. The water bath was removed and the mixture was stirred for 19.5 h. The suspension was cautiously poured into water (250 mL) which was cooled with a water bath. The colourless suspension was filtered through a Büchner funnel and the colourless creamy filter cake was rinsed with water (4 x 10 mL). To the combined filtrates, solid carbon dioxide (ca. 50 g) was added in two portions until the pH was reduced to 8 whereupon a colourless precipitate formed. This precipitate was removed by centrifugation (6000 g, 10 min, 4 °C) and subsequent separation of the liquid from the solid phase. The solvents of the yellow supernatant liquid were removed giving an orange solid. The solid was suspended in methanol (100 mL) and the suspension was filtered through a Büchner funnel. The powdery filter cake was rinsed with methanol (5 x 10 mL). The solvent of the combined filtrates was removed and the residual mixture of a red-brown oil with a colourless solid was suspended in ethanol (65 mL). The precipitate was removed by centrifugation (6000 g, 15 min, 4 °C) and subsequent separation of the liquid from the solid phase. The solvent of the supernatant liquid was removed (finally at 60 °C/ 0.05 mbar) giving a brown highly viscous oil (3.6 g) which contained ($2S,3S$)$_{64}$-tetraol (70±3 wt%; 36 % yield). The oil was dissolved in methanol (50 mL), silica gel was added, and the solvent was removed. The residual fine

powder was loaded on top of a silica gel column (6.5 cm x 23 cm). Column chromatography (Et$_2$O/EtOH 9:2) gave a yellow highly viscous oil (2.3 g; for the removal of residual solvent the oil was kept at 70 °C/ 0.05 mbar) which contained (2S,3S)$_{64}$-tetraol (91±3 wt%, 30% yield).

Purification of the tetraols via diacetonides 5

rac-(2R,3S)-2-Methylbutane-1,2,3,4-tetraol (*rac*-(2R,3S)-tetraol) via diacetonide *rac*-(2R,3S)-5

The reaction mixture was protected from moisture by using a drying tube filled with calcium chloride. *p*-Toluenesulfonic acid monohydrate (1.76 g, 9.2 mmol) was added to *rac*-(2R,3S)-tetraol (7.81 g, 80±3 wt%, 46 mmol) in 2,2-dimethoxypropane (450 mL, 3.67 mol). The reaction mixture was stirred at 40 °C for 46 h. The reaction was monitored by TLC [Et$_2$O/CH$_2$Cl$_2$ 1:1, R_f(*rac*-(2R,3S)-tetraol) = 0.00, R_f(diacetonide *rac*-(2R,3S)-5) = 0.88]. Addition of potassium carbonate (1.58 g, 11 mmol) and, subsequently, addition of an aqueous solution of potassium carbonate (0.5 M, 70 mL) raised the pH from 2 to 8. To the mixture of two liquid phases *n*-hexane (50 mL) was added. The brown aqueous phase and the yellow-orange organic phase were separated. The aqueous phase was extracted with *n*-hexane (3 x 20 mL). The solvents of the combined organic phases were removed. The residual yellow liquid was filtered through a plug of silica gel (2.5 cm x 8 cm, CH$_2$Cl$_2$/Et$_2$O 6:4, 150 mL). The solvents of the eluate were removed giving a mixture (10.0 g) of a crystalline colourless solid with a little bit of yellow oil consisting mainly of diacetonide *rac*-(2R,3S)-5.

Part of this mixture (9.95 g) was suspended in methanol (30 mL) and water (100 mL) and Dowex® 50 WX4 (1.14 g) was added. The suspension was stirred first at room temperature for 1 h, then at 70 °C for 3.5 h and finally at room temperature for 22 h. The reaction was monitored by TLC [Et$_2$O/CH$_2$Cl$_2$ 1:1, R_f(*rac*-(2R,3S)-**tetraol**) = 0.00, R_f(diacetonide *rac*-(2R,3S)-5) = 0.88]. The suspension was filtered and the solvents of the filtrate were removed. The residual oil was dissolved in methanol (30 mL), the solvent was removed (at room temperature as well as at 50 °C/ 0.05 mbar for 1 h) giving *rac*-(2R,3S)-tetraol as a yellow, highly viscous oil (6.13 g, 99±3 wt%, 99% yield).

Analytical data of the material containing the diacetonide *rac*-(2R,3S)-**5**: ^{1}H-NMR (500 MHz, CD$_3$OD), signals assigned to this diacetonide: δ = 4.10 (dd, J = 6.9 Hz, J = 5.9 Hz, 1H, C^{3}H), 4.03 (dd, J = 8.6 Hz, J = 7.0 Hz, 1H, C^{4}H$_2$), 3.99 (d, J = 8.7 Hz, 1H, C^{1}H$_2$), 3.86 (dd, J = 8.6 Hz, J = 5.9 Hz, 1H, C^{4}H$_2$), 3.74 (d, J = 8.7 Hz, 1H, C^{1}H$_2$), 1.39 (s, 3H, CH$_3$), 1.35 (s, 6H, CH$_3$), 1.32 (s, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$).

Analytical data of *rac*-(2R,3S)-tetraol: ^{1}H-NMR (500 MHz, CD$_3$OD): δ = 3.80 (X part of ABX spinsystem, apparent dd with J = 2.7 Hz and 10.4 Hz, 1H, C^{3}H), 3.62-3.56 (AB part

of ABX spinsystem, 2H, C^4H_2), 3.52 and 3.44 (2d with roof effect, J = 11.1 Hz, 1H each, C^1H_2), 1.11 (s, 3H, CH_3). ^{13}C NMR (125 MHz, CD_3OD): δ = 76.1 (C^3), 74.9 (C^2), 68.4 and 63.8 (C^1, C^4), 19.7 (CH_3).

rac-(2R,3R)-2-Methylbutane-1,2,3,4-tetraol (rac-(2R,3R)-tetraol) via diacetonide rac-(2R,3R)-5

The reaction mixture was protected from moisture by using a drying tube filled with calcium chloride. *p*-Toluenesulfonic acid monohydrate (1.37 g, 7.2 mmol) was added to an emulsion of *rac*-(2*R*,3*R*)-tetraol (6.04 g, 80±3 wt%, 35 mmol) in 2,2-dimethoxypropane (350 mL, 2.86 mol). The emulsion was stirred at 35 °C for 4 d. The reaction was monitored by TLC [Et_2O/CH_2Cl_2 1:1, R_f(*rac*-(2*R*,3*R*)-tetraol) = 0.00, R_f(diacetonide *rac*-(2*R*,3*R*)-**5**) = 0.81] and the reaction was continued until no difference was detected between two samples taken with an interval of 18 h. Addition of potassium carbonate (1.32 g, 10 mol) and, subsequently, of an aqueous solution of potassium carbonate (0.5 M, 15 mL) raised the pH from 2 to 8 and gave a mixture of two liquid phases. The solvents were removed and the residue was suspended in diethyl ether (20 mL). The suspension was filtered through a Büchner funnel and the brown granular, soft filter cake was rinsed with diethyl ether (3 x 20 mL). The solvent of the yellow filtrate was removed giving a yellow oil (8.55 g). Column chromatography (4 cm x 40 cm, Et_2O/CH_2Cl_2 1:1) gave diacetonide *rac*-(2*R*,3*R*)-**5** as a colourless oil (6.31 g, 83%; R_f = 0.81).

To this diacetonide *rac*-(2*R*,3*R*)-**5** (6.21 g, 29 mmol) were added methanol (30 mL), water (90 mL), and finally Dowex® 50 WX4 (0.61 g) and the suspension was stirred at room temperature for 1 h and then at 65 °C for 3.5 h. The reaction was monitored by TLC [Et_2O/CH_2Cl_2 1:1, R_f(tetraol *rac*-(2*R*,3*R*)-tetraol) = 0.00, R_f(diacetonide *rac*-(2*R*,3*R*)-**5**) = 0.81]. When TLC analysis indicated a complete conversion, the suspension was filtered, the filter cake was washed with methanol, and the solvents of the filtrate were removed. The residual oil was dissolved in water (30 mL) and the aqueous phase was extracted with diethyl ether (7 x 10 mL). The solvent of the aqueous phase was removed and the highly viscous yellow residue was dissolved in methanol (20 mL). Removal of the solvent (at room temperature as well as at 50 °C/ 0.05 mbar for 1 h) gave *rac*-(2*R*,3*R*)-tetraol as a slightly yellow, highly viscous oil (3.68 g, 98±3 wt%, 93% yield referred to diacetonide *rac*-(2*R*,3*R*)-**5**, 77% referred to *rac*-(2*R*,3*R*)-tetraol).

Analytical data of diacetonide *rac*-(2*R*,3*R*)-**5**: ^1H NMR (500 MHz, CD_3OD): δ = 4.06 (A part of ABX spinsystem, apparent t with J = 6.9 Hz, 1H, C^3H), 4.04 (d, J = 8.7 Hz, 1H, C^1H_2), 4.01 (B part of ABX spinsystem, apparent dd with J = 7.9 Hz and 6.9 Hz, 1H, C^4H_2), 3.86 (X part of ABX spinsystem, apparent dd with J = 7.9 Hz and 6.9 Hz, 1H, C^4H_2), 3.72 (d, J = 8.7 Hz, 1H, C^1H_2), 1.39, 1.38, 1.36, 1.33 and 1.27 (5 s, 3H each, CH_3).

^{13}C NMR (125 MHz, CD$_3$OD): δ = 111.0 and 110.7 ($\underline{C}$Me$_2$), 82.1 (C^2), 80.5 (C^3), 71.9 and 66.5 (C^1, C^4), 27.2, 26.9, 26.6, 25.3, and 23.8 (CH$_3$).

Analytical data of *rac*-(2*R*,3*R*)-tetraol: ^{1}H NMR (500 MHz, CD$_3$OD): δ = 3.74 (X part of ABX spinsystem, apparent dd with J = 2.8 Hz and 10.4 Hz, 1 H, C^{3}H), 3.62-3.57 (AB part of ABX spinsystem, 2 H, C^{4}H$_2$), 3.53 and 3.46 (2d with roof effect, J = 11.1 Hz, 1H each, C^{1}H$_2$), 1.15 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CD$_3$OD): δ = 76.7 (C^3), 74.9 (C^2), 68.0 and 63.6 (C^1, C^4), 21.3 (CH$_3$). Elemental analysis calculated for C$_5$H$_{12}$O$_4$: C, 44.11 and H, 8.88. Found: C, 43.98 and H, 9.03.

(2*S*,3*R*)$_{86}$-2-Methylbutane-1,2,3,4-tetraol ((2*S*,3*R*)$_{86}$-tetraol) via diacetonide (2*S*,3*R*)$_{86}$-5)

Dowex$^®$ 50 WX4 (0.107 g) was added to an emulsion of (2*S*,3*R*)$_{86}$-tetraol (1.03 g, (84 ± 3) w%, 6 mmol) in 2,2-dimethoxypropane (15 mL, 122 mmol) and the emulsion was stirred at 40 °C for 22 h. During this time the suspension turned into a yellow solution with a brown precipitate. ^{1}H NMR spectroscopy indicated an incomplete conversion. 2,2-Dimethoxypropane (10 mL, 82 mmol) was added and the suspension was stirred at 40 °C for 23 h. The suspension was filtered. Potassium carbonate (0.51 g, 3.7 mmol), then *n*-hexane (20 mL), and finally an aqueous solution of potassium carbonate (0.6 M, 25 mL) were added. A mixture of two liquid phases was obtained. The colourless organic phase was separated from the yellow aqueous phase and the aqueous phase was extracted with *n*-hexane (4 x 10 mL). The solvents of the combined organic phases were removed giving a mixture (1.20 g; R_f(CH$_2$Cl$_2$/Et$_2$O 2:1) = 0.7 and 0.4) of a yellow greasy solid and a colourless crystalline solid. This mixture was dissolved in dichloromethane and diethyl ether (2:1, 15 mL) and 8.2 g (48%) of the resulting solution were filtered through silica gel (2.0 cm x 2.5 cm, CH$_2$Cl$_2$/Et$_2$O 2:1). Solvent removal from the eluate gave a colourless crystalline solid (0.53 g; R_f = 0.7 and 0.4) which consisted mainly of diacetonide (2*S*,3*R*)$_{86}$-**5**.

This solid (0.52 g) was suspended in water (30 mL) and methanol (5 mL) together with Dowex$^®$ 50 WX4 (57 mg). The suspension was stirred first at room temperature for 17 h, then at 65 °C 3 h. The reaction was monitored by TLC [CH$_2$Cl$_2$/Et$_2$O 2:1, R_f((2*S*,3*R*)$_{86}$-tetraol) = 0.0] and the reaction was continued until TLC indicated a complete conversion. The suspension was filtered and the solvents of the filtrate were removed (at room temperature as well as at 80 °C/ 0.05 mbar for 2 h) giving (2*S*,3*R*)$_{86}$-tetraol as a yellow, highly viscous oil (0.37 g, 98± 3wt%, 89% yield referred to tetraol). ^{1}H NMR (500 MHz, CD$_3$OD): δ = 3.80 (X part of ABX spinsystem, apparent dd with J = 2.7 Hz and 10.3 Hz, 1H, C^{3}H), 3.62-3.56 (AB part of ABX spinsystem, 2H, C^{4}H$_2$), 3.52 and 3.44 (2d with roof effect, J = 11.1 Hz, 1H each, C^{1}H$_2$), 1.11 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CD$_3$OD): δ = 76.1 (C^3), 75.0 (C^2), 68.5 and 63.8 (C^1, C^4), 19.7 (CH$_3$). Elemental analysis calculated

for $C_5H_{12}O_4$: C, 44.11 and H, 8.88. Found: C, 44.01 and H, 8.96.

(2*R*,3*S*)₆₅-2-Methylbutane-1,2,3,4-tetraol ((2*R*,3*S*)₆₅-tetraol) via diacetonide (2*R*,3*S*)₆₅-5)

The reaction mixture was protected from moisture by using a drying tube filled with calcium chloride. To the emulsion of the brown oil (0.67 g) which contained (2*R*,3*S*)$_{65}$-tetraol (obtained as described in the section of the reduction of diol (2*S*,3*R*)$_{65}$-**3**) in 2,2-dimethoxypropane (49 mL, 0.40 mol) was added *p*-toluenesulfonic acid monohydrate (75 mg, 0.4 mmol). The emulsion was stirred at 40 °C for 1 d. *p*-Toluenesulfonic acid monohydrate (0.210 g, 1.1 mmol) was added to reduce the p*H* value from 7 to 1. The emulsion was stirred at 40 °C for another 4 d. During the reaction time, the emulsion turned into a suspension. The reaction was monitored by TLC [Et$_2$O/CH$_2$Cl$_2$ 1:1, R_f((2*R*,3*S*)$_{65}$-tetraol) = 0.00, R_f(diacetonide (2*R*,3*S*)$_{65}$-**5**) = 0.89] and the reaction was continued until TLC showed no difference between two samples taken with a time gap of 23 h. Potassium carbonate (0.20 g, 1 mmol) and subsequently an aqueous solution of potassium carbonate (1 M, 20 mL) were added and a mixture of two liquid phases formed. The yellow aqueous phase was separated from the slightly yellow organic phase and the aqueous phase was extracted with *n*-hexane (3 x 10 mL). The solvents of the combined organic phases were removed and the residual mixture of a colourless solid and a yellow oil was filtered through silica gel (3 cm x 4 cm, CH$_2$Cl$_2$/Et$_2$O 1:1, 100 mL). The solvents of the eluate were removed providing a colourless crystalline solid with yellow spots (0.50 g; R_f = 0.84, eluent: Et$_2$O/CH$_2$Cl$_2$ 1:1) which consisted mainly of diacetonide (2*R*,3*S*)$_{65}$-**5**.

To an emulsion of this material (0.50 g) in water (20 mL), Dowex® 50 WX4 (44 mg) was added and the suspension was stirred first at room temperature for 19 h, then at 70 °C for 6 h, and afterwards at room temperature for 21 h. The reaction was monitored by TLC [Et$_2$O/CH$_2$Cl$_2$ 1:1, R_f((2*R*,3*S*)$_{65}$-tetraol) = 0.00, R_f(diacetonide (2*R*,3*S*)$_{65}$-**5**) = 0.89] and the reaction was continued until TLC indicated a complete conversion. The suspension was filtered and the solvent was removed giving a highly viscous yellow oil (0.31 g) which was combined with the product of another experiment which had been performed in the same way. The oil (0.60 g) was dissolved in methanol, silica gel (1.3 g) was added, and the solvent was removed. The residual powder was brought on top of a silica gel column (2.5 cm x 20 cm). Column chromatography (Et$_2$O/EtOH 6:4) and removal of the solvent (at room temperature as well as at 50 °C/ 0.05 mbar for 1 h) gave (2*R*,3*S*)$_{65}$-tetraol as a highly viscous colourless oil (0.39 g, 99±3 wt%, 23% yield referred to diol (2*S*,3*R*)$_{65}$-**3**). The ^{1}H NMR spectrum reveals that the compound was very slightly contaminated with unidentified compounds. ^{1}H NMR (500 MHz, CD$_3$OD): δ = 3.80 (X part of ABX spinsystem, apparent dd with J = 2.7 Hz and 10.4 Hz, 1H, C^{3}H), 3.62-3.56 (AB part of

ABX spinsystem, 2H, C^4H_2), 3.52 and 3.44 (2d with roof effect, J = 11.1 Hz, 1H each, C^1H_2), 1.11 (s, 3H, CH_3). ^{13}C NMR (125 MHz, CD_3OD): δ = 76.1 (C^3), 75.0 (C^2), 68.5 and 63.8 (C^1, C^4), 19.7 (CH_3). Elemental analysis calculated for $C_5H_{12}O_4$: C, 44.11 and H, 8.88. Found: C, 44.11 and H, 8.90.

(2*R*,3*R*)₉₇-2-Methylbutane-1,2,3,4-tetraol ((2*R*,3*R*)₉₇-tetraol) via diacetonide (2*R*,3*R*)₉₇-5

A suspension of (2*R*,3*R*)₉₇-tetraol (3.24 g, 75±3 wt%, 18 mmol), 2,2-dimethoxypropane (70 mL, 571 mmol) and Dowex® 50 WX4 (241 mg) was stirred for 24 h at 40 °C. The solvent of the suspension was removed. 2,2-Dimethoxypropane (50 mL, 408 mmol) was added to the residue and the suspension was stirred for 71 h. During this time, more 2,2-dimethoxypropane and Dowex® 50 WX4 were added and the temperature of the oil bath was varied as summarized in table S4.

Table S4: Listing of the additions of 2,2-dimethoxypropane and Dowex® 50 WX4 to the suspension and of the variations of the oil bath temperature. The temperature was set at the given reaction time and was kept for the following period.

Reaction time	2,2-dimethoxypropane	Dowex® 50 WX4	oil bath temp.
0 h	50 mL, 408 mmol	-	40 °C
1 h	-	-	60 °C
2 h	-	97 mg	-
4 h	20mL, 163 mmol	-	-
24 h	-	-	75 °C
29 h	20mL, 163 mmol	-	70 °C
46.5 h	-	60 mg	-

A mixture of a clear solution, a brown solid and a brown highly viscous material was obtained. The solution was separated and the reaction vessel, containing the resin, was rinsed with 2,2-dimethoxypropane (2 x 5 mL, 82 mmol). To the combined clear solutions, Dowex® 50 WX4 (134 mg) was added and the resulting suspension was stirred at 40 °C for 24 h. The suspension was filtered and potassium carbonate (1.47 g, 10.6 mmol) and subsequently a mixture of dichloromethane and diethyl ether (1:1, 15 mL) were added. The suspension was well stirred and filtered. Removal of the solvents of the filtrate gave a yellow oil (3.28 g) showing several spots on the TLC plate (CH_2Cl_2/Et_2O 1:3, R_f = 0.8, 0.6, 0.5, 0.4, 0.3, 0.2, 0). Column chromatography (3.5 cm x 36 cm, CH_2Cl_2/Et_2O 1:2) gave a yellow liquid (1.69 g; R_f = 0.66) which consisted mainly of diacetonide (2*R*,3*R*)₉₇-**5** (43% yield) besides several other chromatography fractions.

The yellow liquid (1.66 g, 8 mmol) was suspended in water (25 mL) and methanol (5 mL)

and Dowex® 50 WX4 (166 mg) was added. The suspension was stirred for 0.5 h and 2 h at 65 °C. The reaction was monitored by TLC [CH_2Cl_2/Et_2O 1:2, R_f((2R,3R)$_{97}$-tetraol) = 0.00, R_f(diacetonide (2R,3R)$_{97}$-**5**) = 0.66] and the reaction was continued until TLC indicated a complete conversion. The suspension was filtered and the solvents were removed from the filtrate (at room temperature as well as at 80 °C/ 0.05 mbar for 3.5 h) providing (2R,3R)$_{97}$-tetraol [0.99 g, 98±3 wt%, 94% yield referred to diacetonide (2R,3R)$_{97}$-**5**, 41% yield referred to tetraol] as a yellow highly viscous oil. The ^{1}H NMR spectrum reveals that the compound was very slightly contaminated with unidentified compounds. ^{1}H NMR (500 MHz, CD_3OD): δ = 3.74 (X part of ABX spinsystem, apparent dd with J = 2.7 Hz and 10.4 Hz, 1 H, C^{3}H), 3.63-3.57 (AB part of ABX spinsystem, 2 H, C^{4}H$_2$), 3.53 and 3.46 (2d with roof effect, J = 11.2 Hz, 1H each, C^{1}H), 1.15 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CD_3OD): δ = 76.7 (C^3), 74.9 (C^2), 68.0 and 63.7 (C^1, C^4), 21.3 (CH$_3$).

(2S,3S)$_{64}$-2-methylbutane-1,2,3,4-tetraol ((2S,3S)$_{64}$-tetraol via diacetonide (2S,3S)$_{64}$-5

The reaction mixture was protected from moisture by using a drying tube filled with calcium chloride. *p*-Toluenesulfonic acid monohydrate (0.326 g, 1.7 mmol) was added to an emulsion of (2S,3S)$_{64}$-tetraol (2.28 g, 91±3 wt%, 15 mmol) in 2,2-dimethoxypropane (166 mL, 1.36 mol) and the emulsion was stirred to 40 °C for 1 d. *p*-Toluenesulfonic acid monohydrate (0.156 g, 0.8 mmol) was added. The emulsion was stirred at 40 °C for another 4 d. During the reaction time the emulsion turned into a mixture of a brown solution with a colourless solid. The reaction was monitored by TLC [Et_2O/CH_2Cl_2 1:1, R_f((2S,3S)$_{64}$-**tetraol**) = 0.00, R_f(diacetonide (2S,3S)$_{64}$-**5**) = 0.89] and the reaction was continued until TLC showed no difference between two samples taken with an interval of 23 h. Potassium carbonate (0.36 g, 3 mmol) and then an aqueous solution of potassium carbonate (1 M, 100 mL) were added giving a mixture of two liquid phases. The yellow aqueous phase was separated from the orange organic phase and the aqueous phase was extracted with *n*-hexane (3 x 30 mL). The solvents of the combined organic phases were removed and the residual brown liquid was filtered through silica gel (1.5 cm x 11 cm, CH_2Cl_2/Et_2O, 1:1, 150 mL). The solvents of the eluate were removed yielding a brown liquid (3.96 g; R_f = 0.84 and 0.50 with Et_2O/CH_2Cl_2 1:1 as the eluent) which consisted mainly of diacetonide (2S,3S)$_{64}$-**5**.

To an emulsion of this brown liquid (3.96 g) in methanol (15 mL) and water (15 mL), Dowex® 50 WX4 (0.246 g) was added and the suspension was stirred at 70 °C for 5 h. The reaction was monitored by TLC [Et_2O/CH_2Cl_2 1:1, R_f((2S,3S)$_{64}$-tetraol) = 0.00, R_f(diacetonide (2S,3S)$_{64}$-**5**) = 0.89] and was continued until TLC indicated a complete conversion. The suspension was concentrated (40 °C/150 mbar) and then filtered. To the yellow filtrate, water (10 mL) was added and the resulting solution was washed with

dichloromethane (5 mL) and then diethyl ether (3 x 10 mL). The solvent of the aqueous phase was removed giving a yellow highly viscous oil (2.0 g) which was dissolved in water (15 mL). The solution was washed with diethyl ether (3 x 10 mL) and the solvent of the aqueous phase was removed (at room temperature as well as at 50 °C/ 0.05 mbar for 1.5 h) giving ($2S,3S$)$_{64}$-tetraol (98±3 wt%; A mistake forbids us to report a yield. The 2.0 g of the material obtained before the last purification step indicates a yield of max. 82% referred to tetraol and a yield of max. 28% referred to diol ($2R,3R$)$_{64}$-**3**)) as a slightly yellow, highly viscous oil. The ^1H NMR spectrum reveals that the compound was very slightly contaminated with unidentified compounds. ^1H NMR (500 MHz, CD$_3$OD): δ = 3.74 (X part of ABX spinsystem, apparent dd with J = 2.7 Hz and 10.4 Hz, 1 H, C^{3}H), 3.63-3.57 (AB part of ABX spinsystem, 2 H, C^{4}H$_2$), 3.53 and 3.46 (2d with roof effect, J = 11.1 Hz, 1H each, C^{1}H$_2$), 1.15 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CD$_3$OD): δ = 76.7 (C^3), 74.9 (C^2), 68.0 and 63.6 (C^1, C^4), 21.3 (CH$_3$).

NMR spectra

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
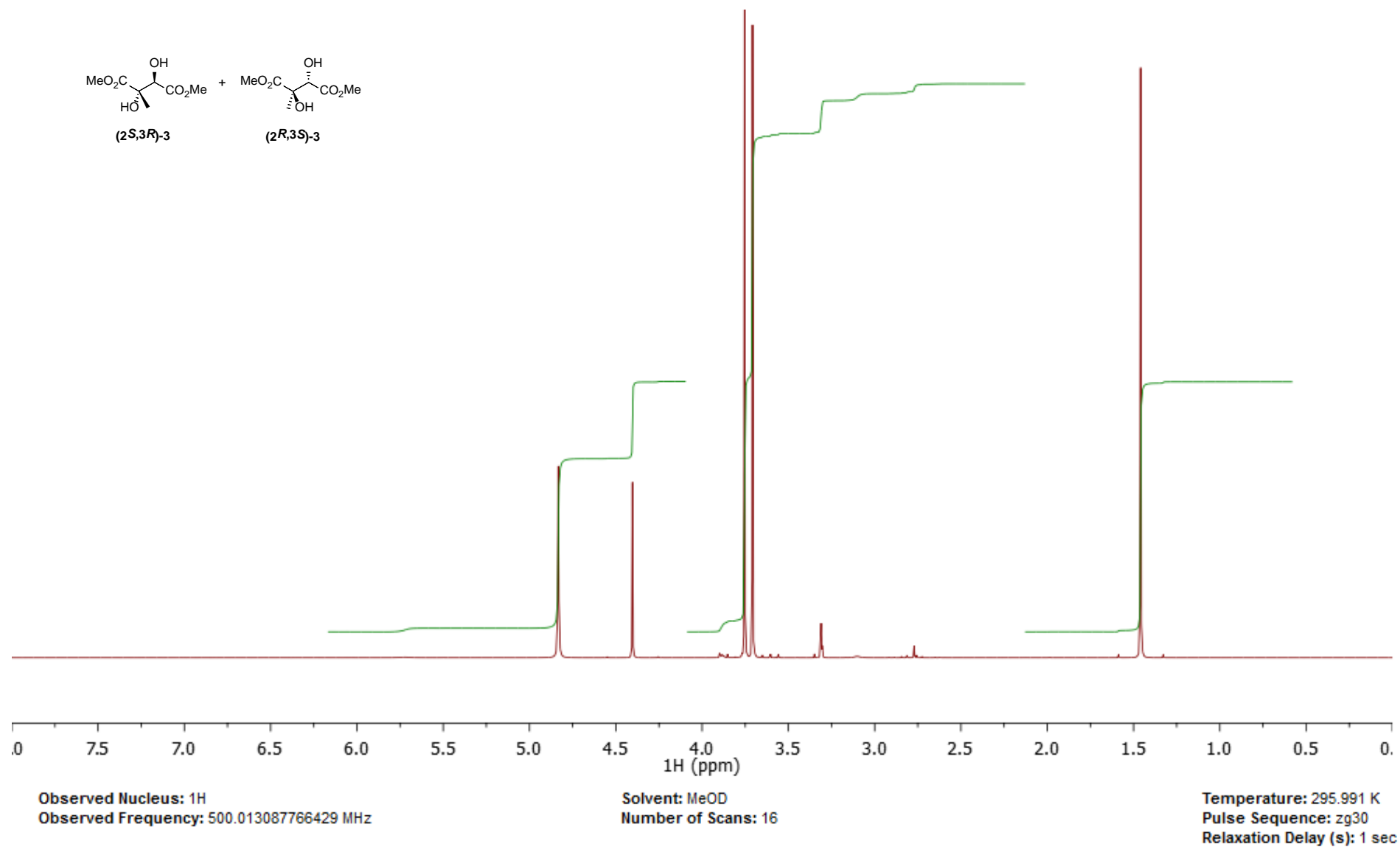
Figure S1. ¹H NMR spectrum of diol *rac*-(*2R,3S*)-**3**.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
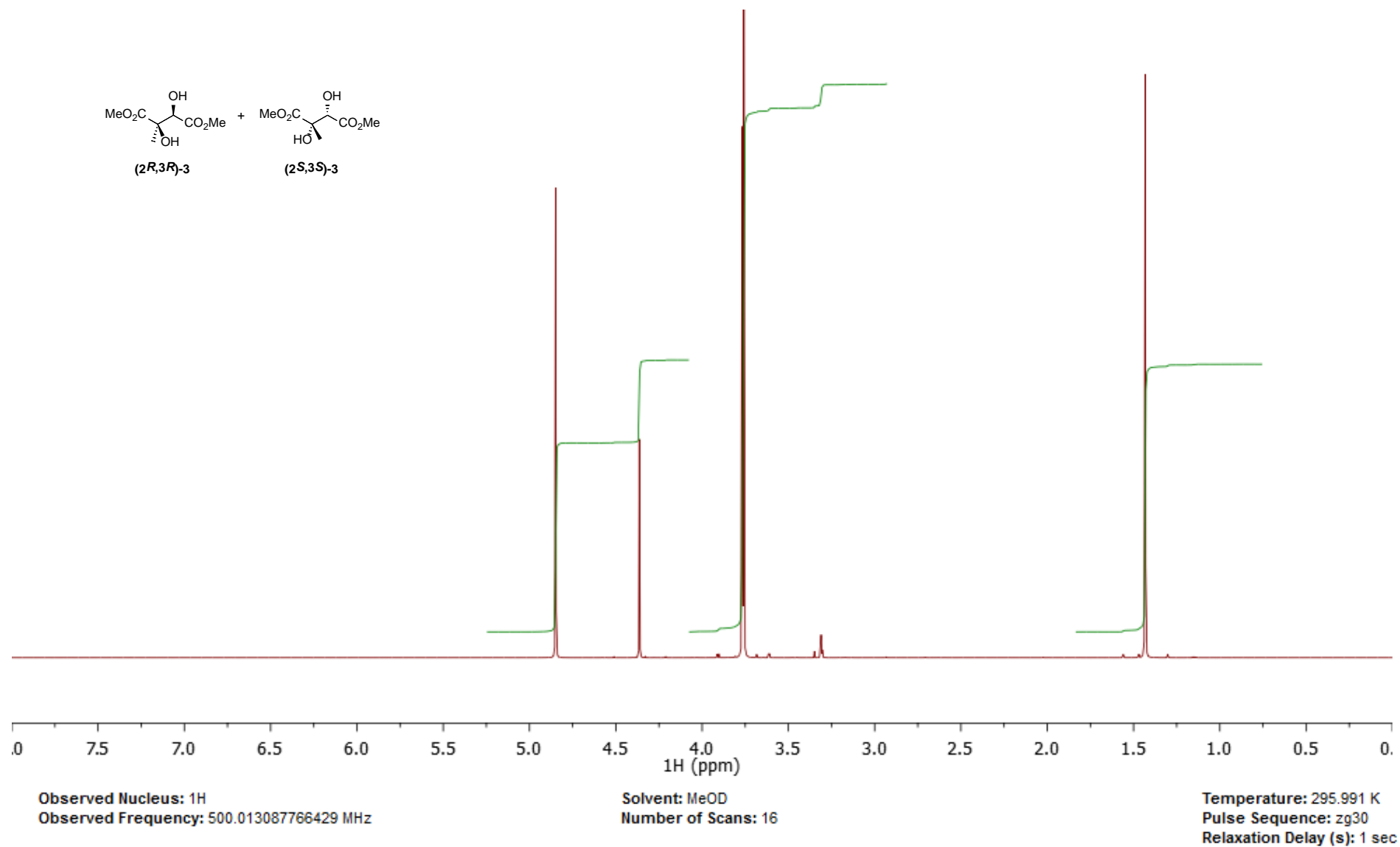
Figure S2. ¹H NMR spectrum of diol *rac*-(2*R*,3*R*)-**3**.
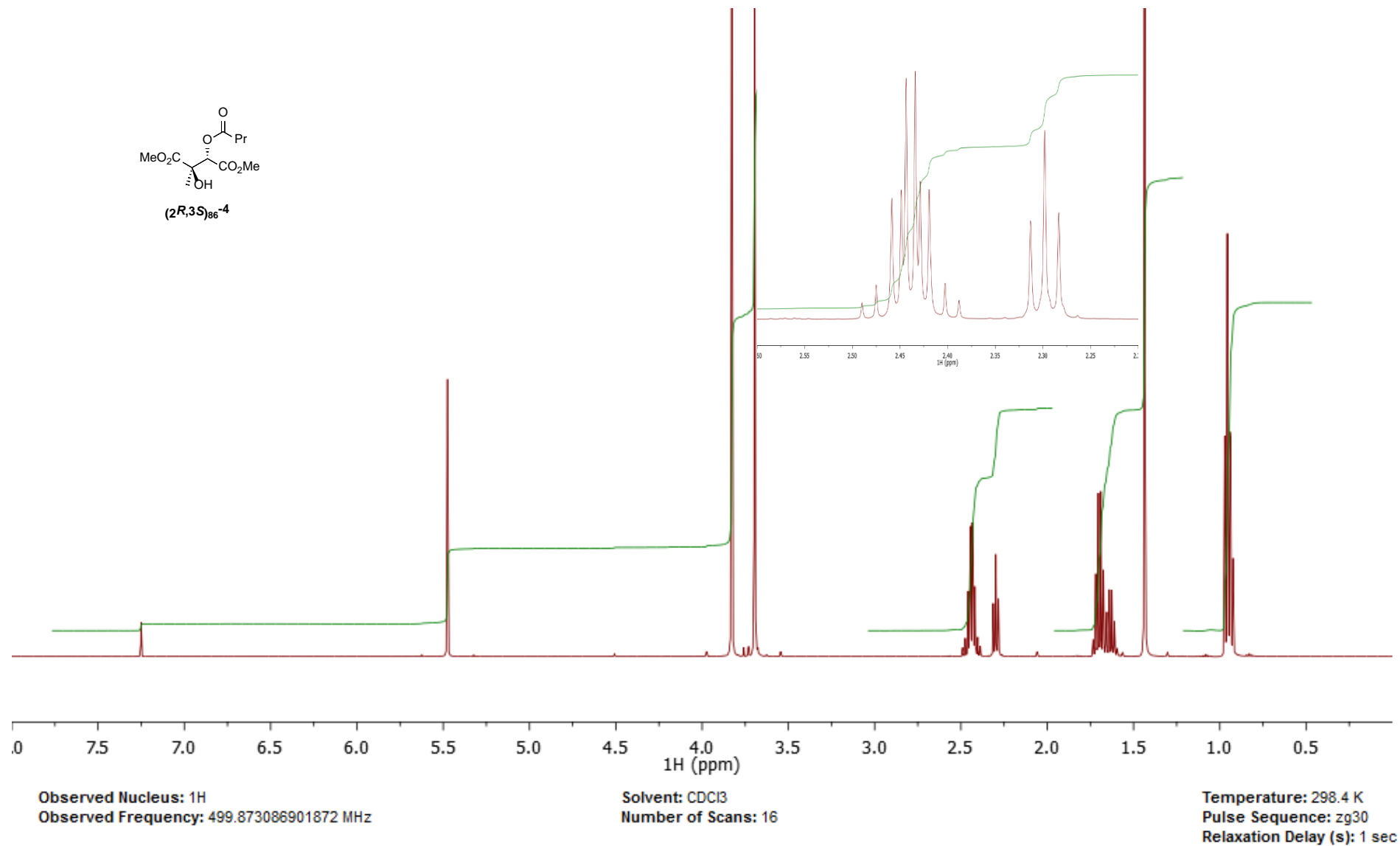
Figure S3. ^{1}H NMR spectrum of a 7:3 mixture of butanoate $(2R,3S)_{86}$-**4** and butanoic acid.

Observed Nucleus: 1H
Observed Frequency: 499.873086901872 MHz

Solvent: CDCl3
Number of Scans: 16

Temperature: 298.4 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec

Observed Nucleus: 1H
Observed Frequency: 499.863086840118 MHz

Solvent: CDCl3
Number of Scans: 16

Temperature: 298.1 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
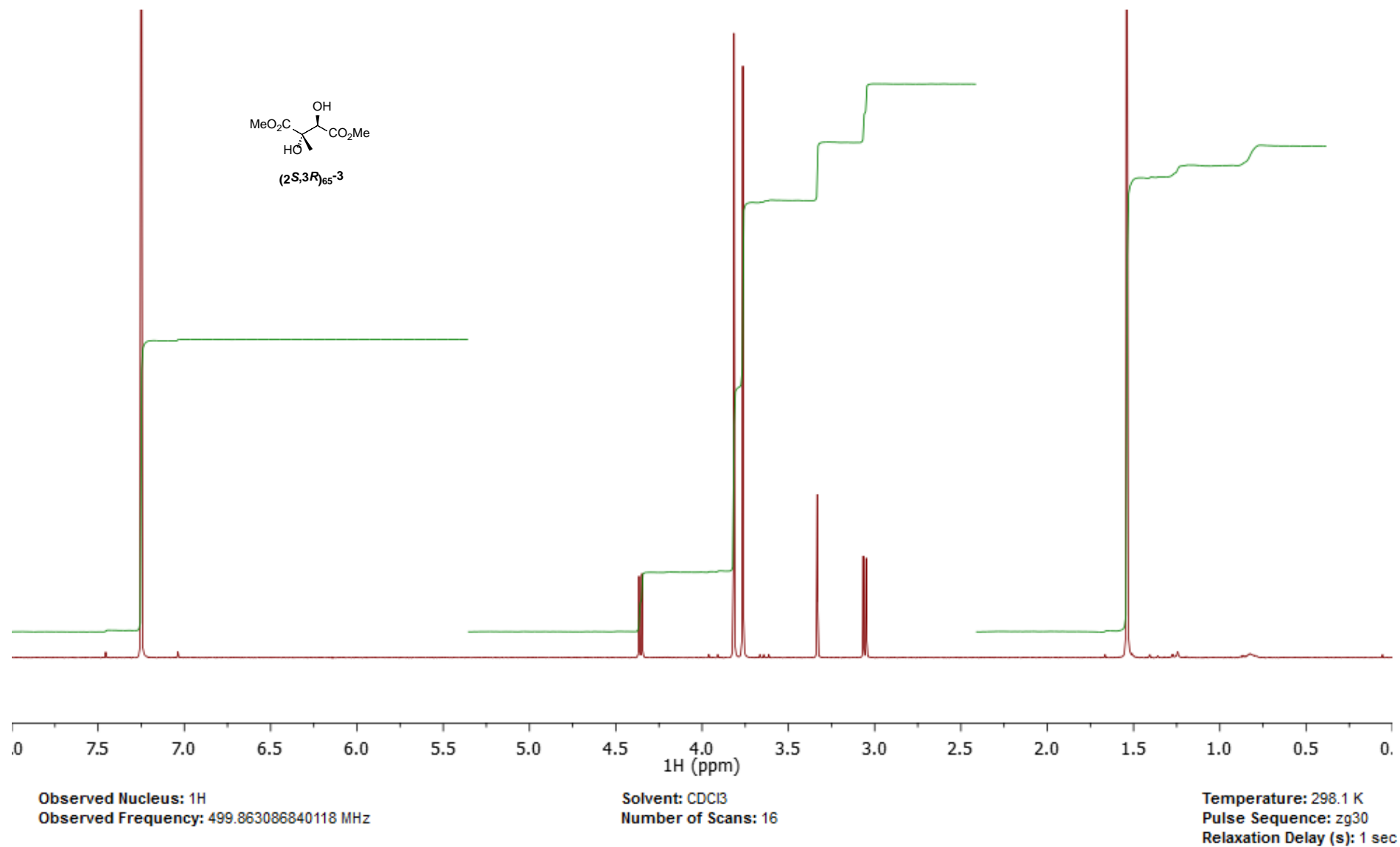
Figure S4. ¹H NMR spectrum of diol (2*S*,3*R*)₆₅-**3**.

Observed Nucleus: 1H
Observed Frequency: 499.873086901872 MHz

Solvent: CDCl3
Number of Scans: 16

Temperature: 298.4 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
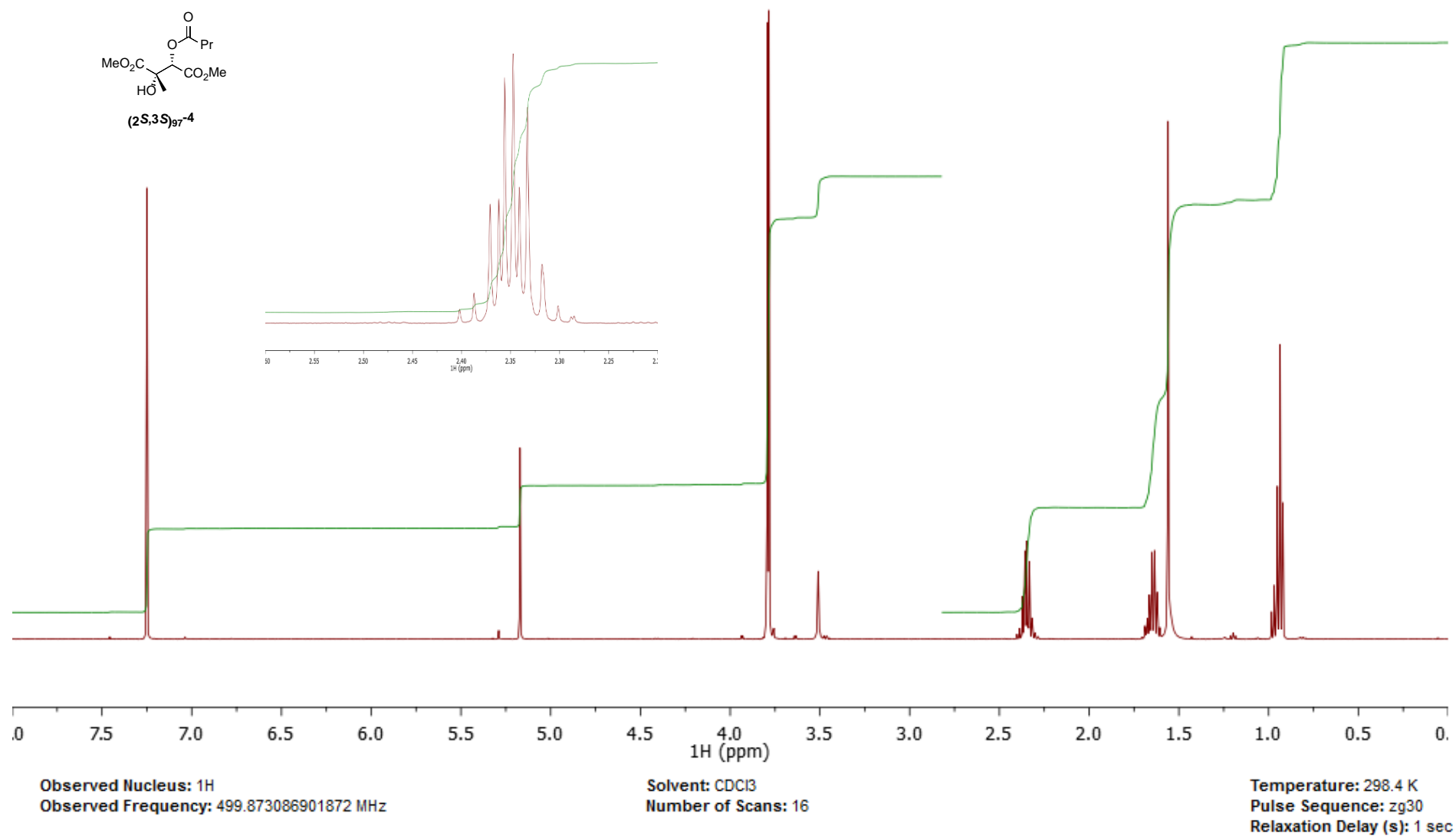
Figure S5. ¹H NMR spectrum of 83:17 mixture of butanoate $(2S,3S)_{97}$-**4** and butanoic acid. The characteristic 10 lines pattern for the protons O_2CCH_2 of the butanoate $(2S,3S)_{97}$-**4** overlaps with the triplet for the protons O_2CCH_2 of butanoic acid.

Observed Nucleus: 1H
Observed Frequency: 499.873086901872 MHz

Solvent: CDCl3
Number of Scans: 16

Temperature: 298.4 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
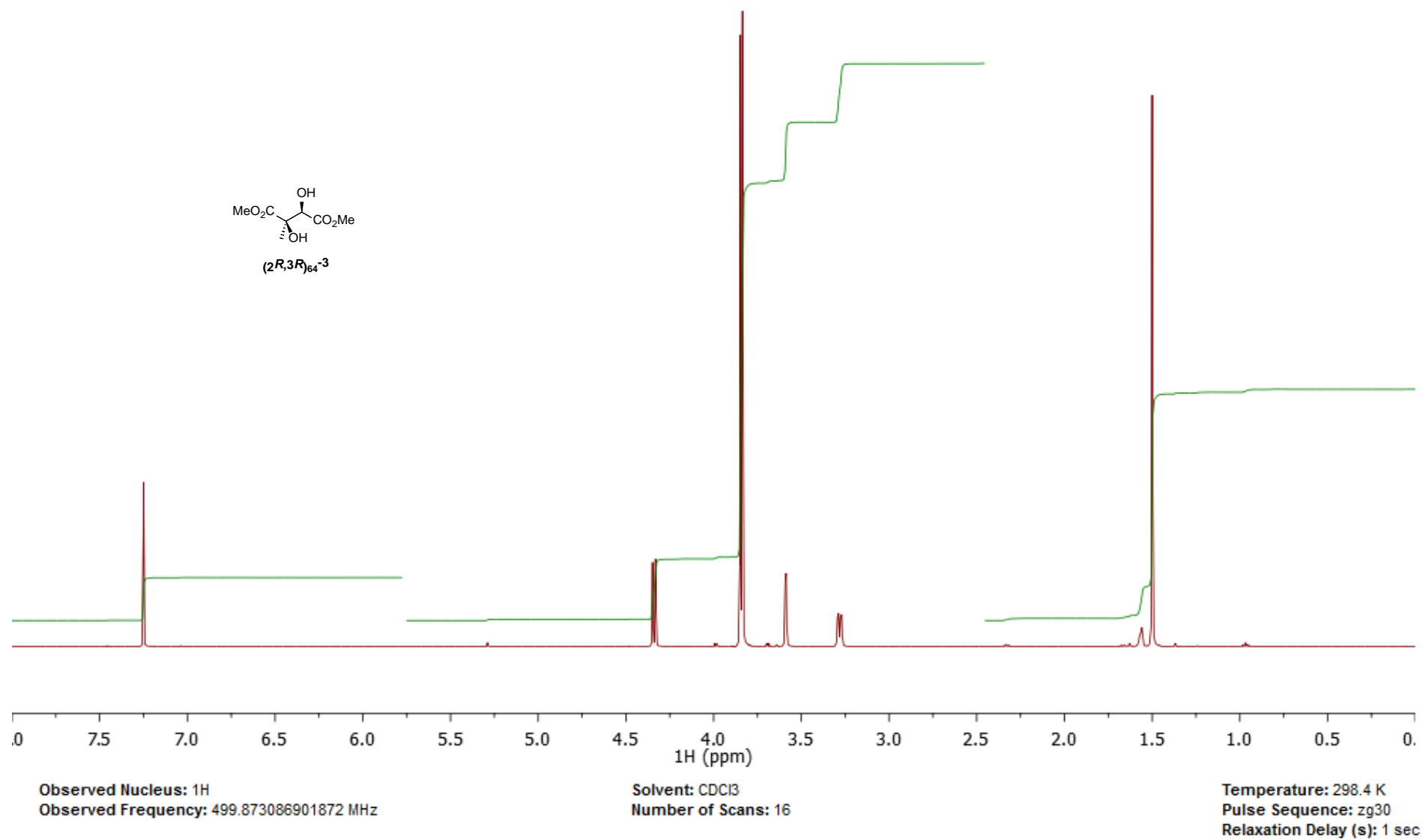
Figure S6. ^{1}H NMR spectrum of diol $(2R,3R)_{64}$-**3**.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
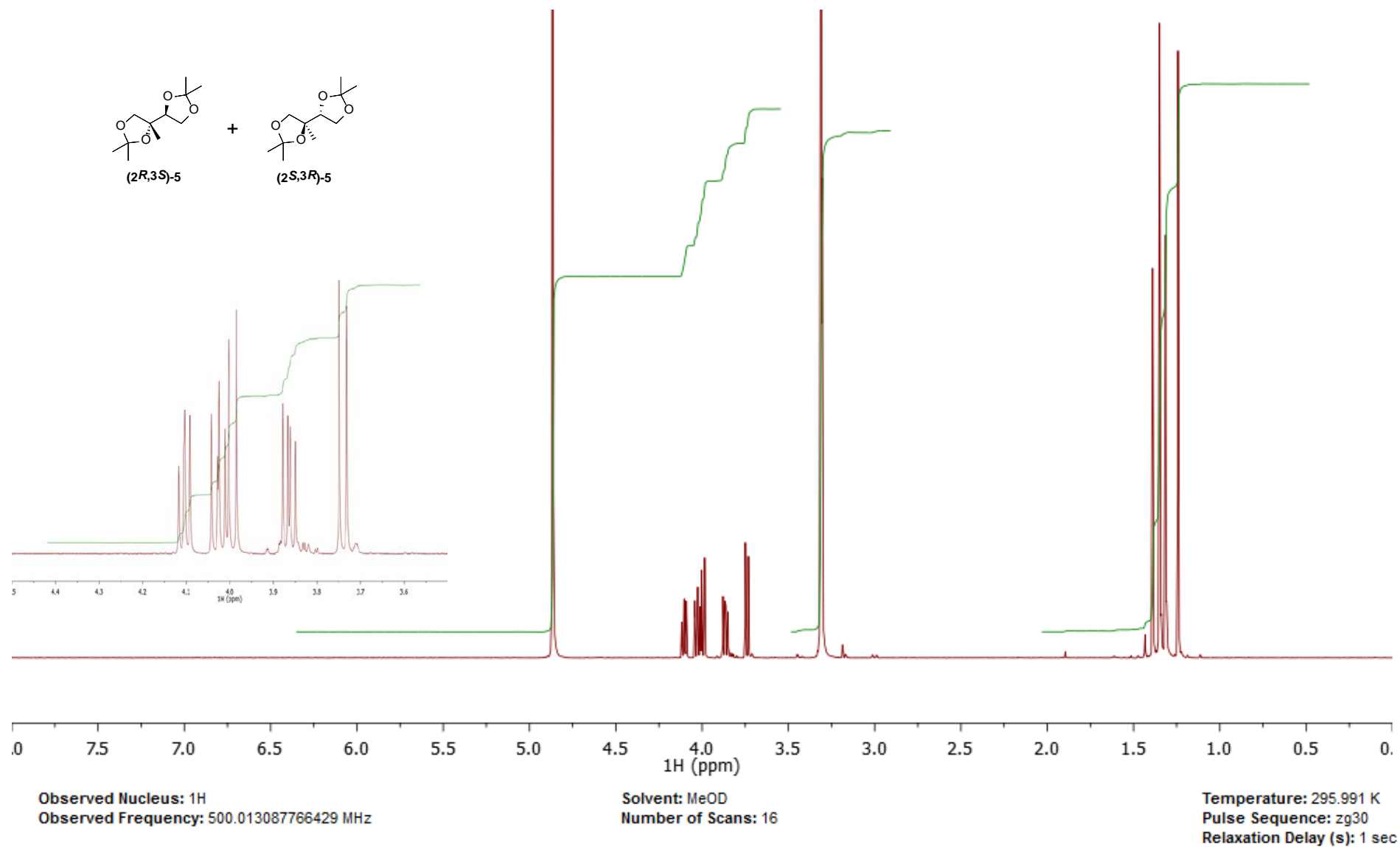
Figure S7. ¹H NMR spectrum of diacetonide *rac*-(2*R*,3*S*)-**5**.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
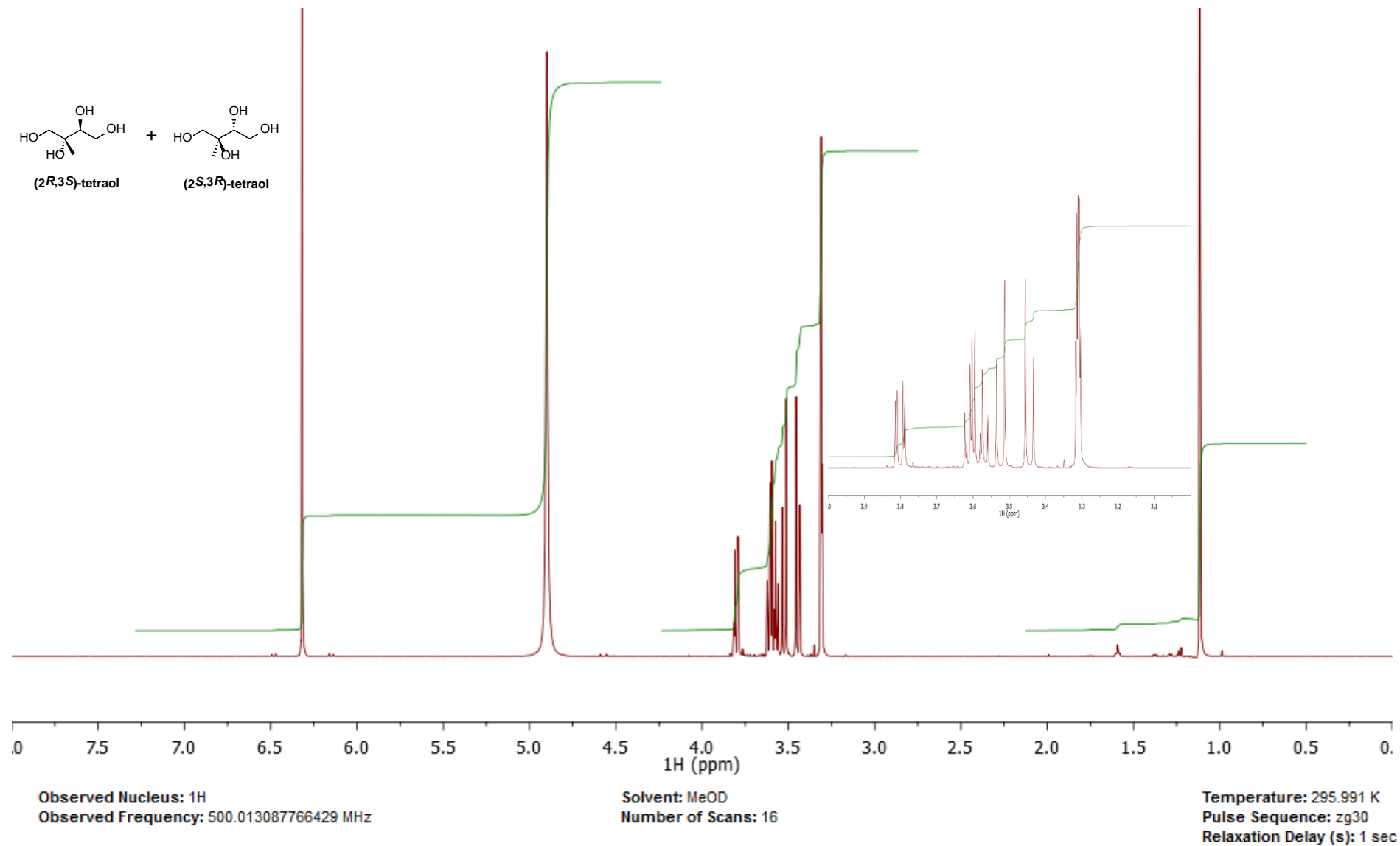
Figure S8. ¹H NMR spectrum of *rac*-(2*R*,3*S*)-tetraol. Maleic acid had been added for the purpose of content determination by qNMR.
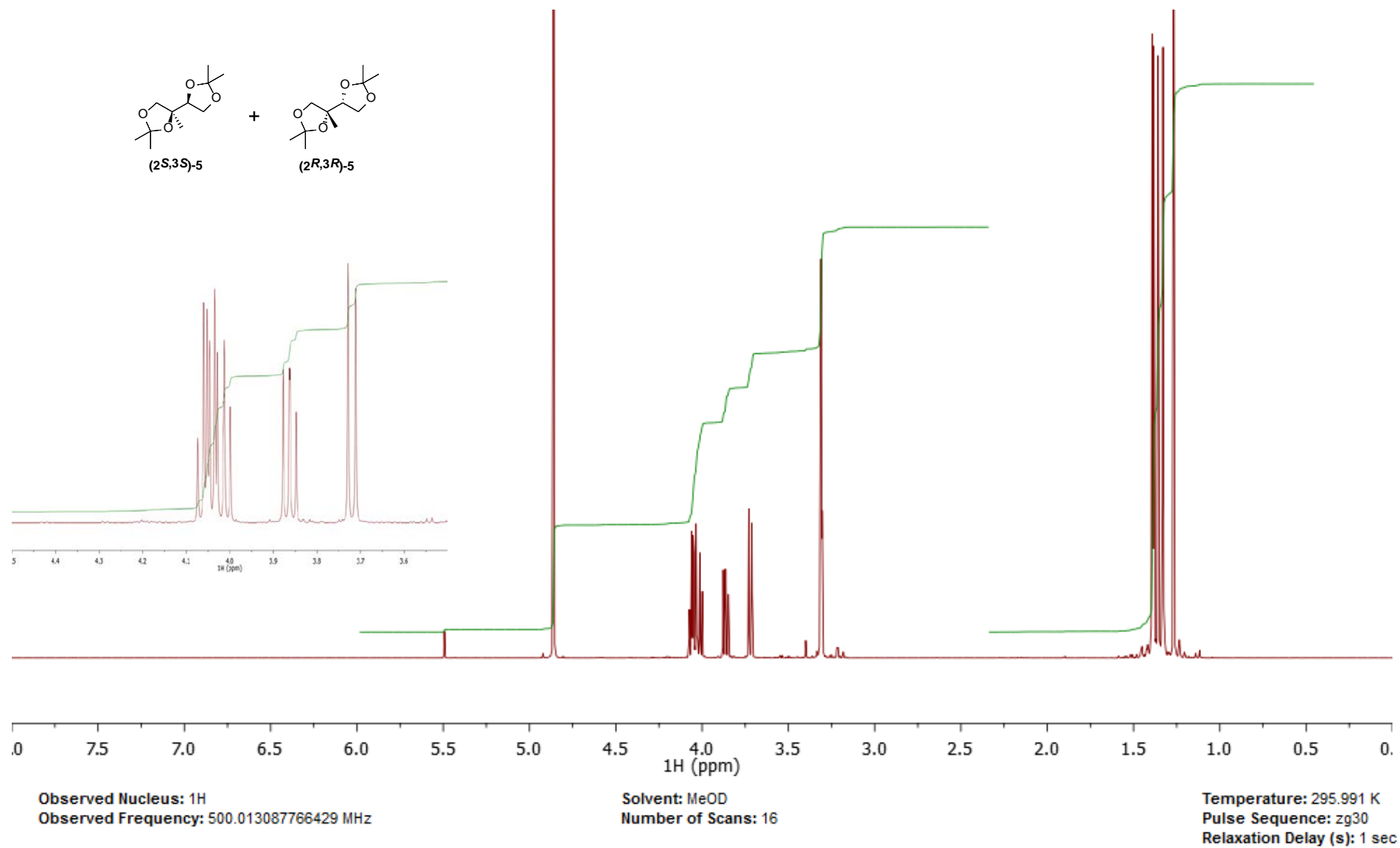
Figure S9. ¹H NMR spectrum of diacetonide *rac*-(2*R*,3*R*)-**5**.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 30 sec
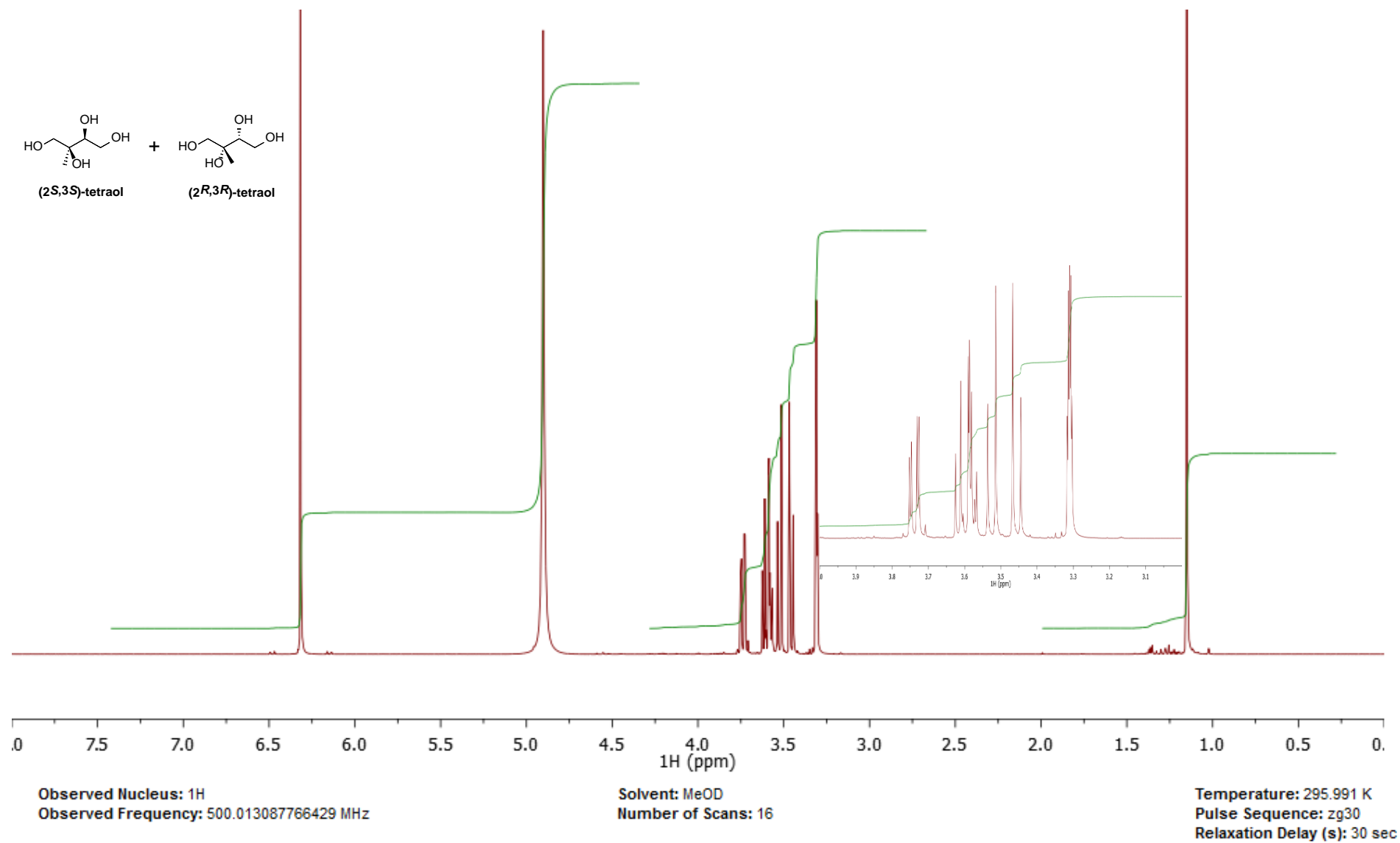
Figure S10. ¹H NMR spectrum of *rac*-(2*R*,3*R*)-tetraol. Maleic acid had been added for the purpose of content determination by qNMR.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 30 sec
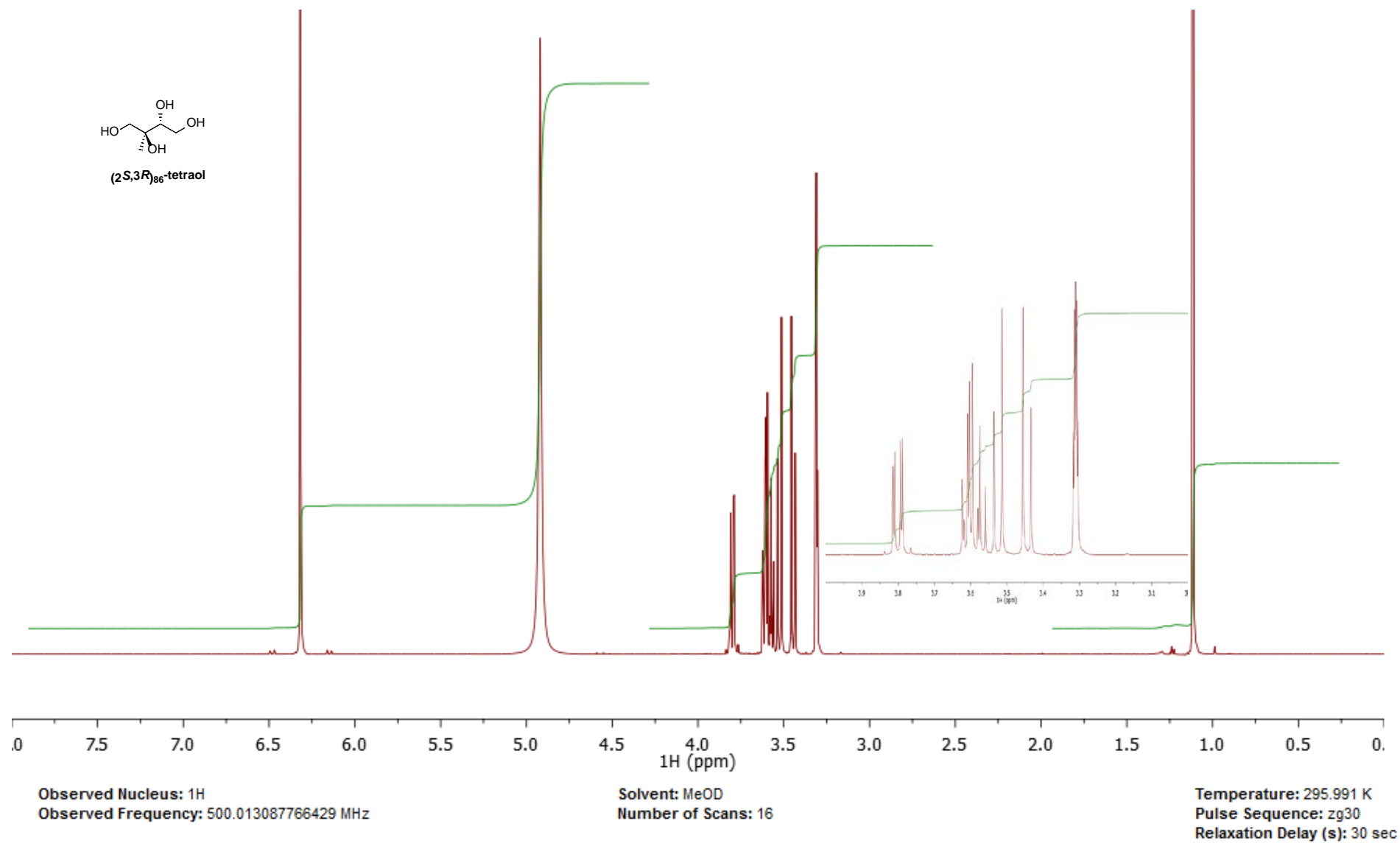
Figure S11. ¹H NMR spectrum of (2S,3R)₈₆-tetraol. Maleic acid had been added for the purpose of content determination by qNMR.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 30 sec
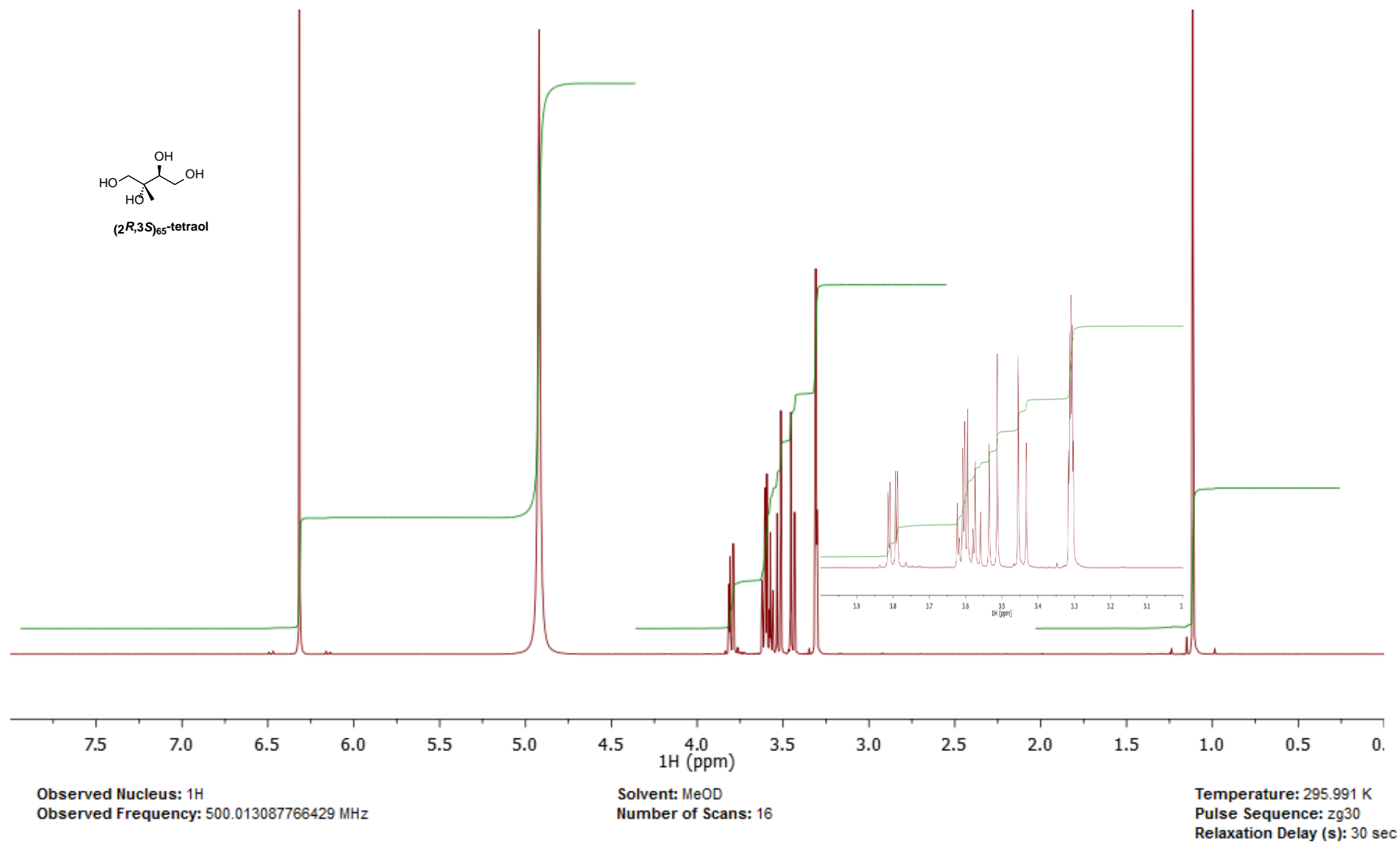
Figure S12. ^{1}H NMR spectrum of (2R,3S)$_{65}$-tetraol. Maleic acid had been added for the purpose of content determination by qNMR.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 30 sec
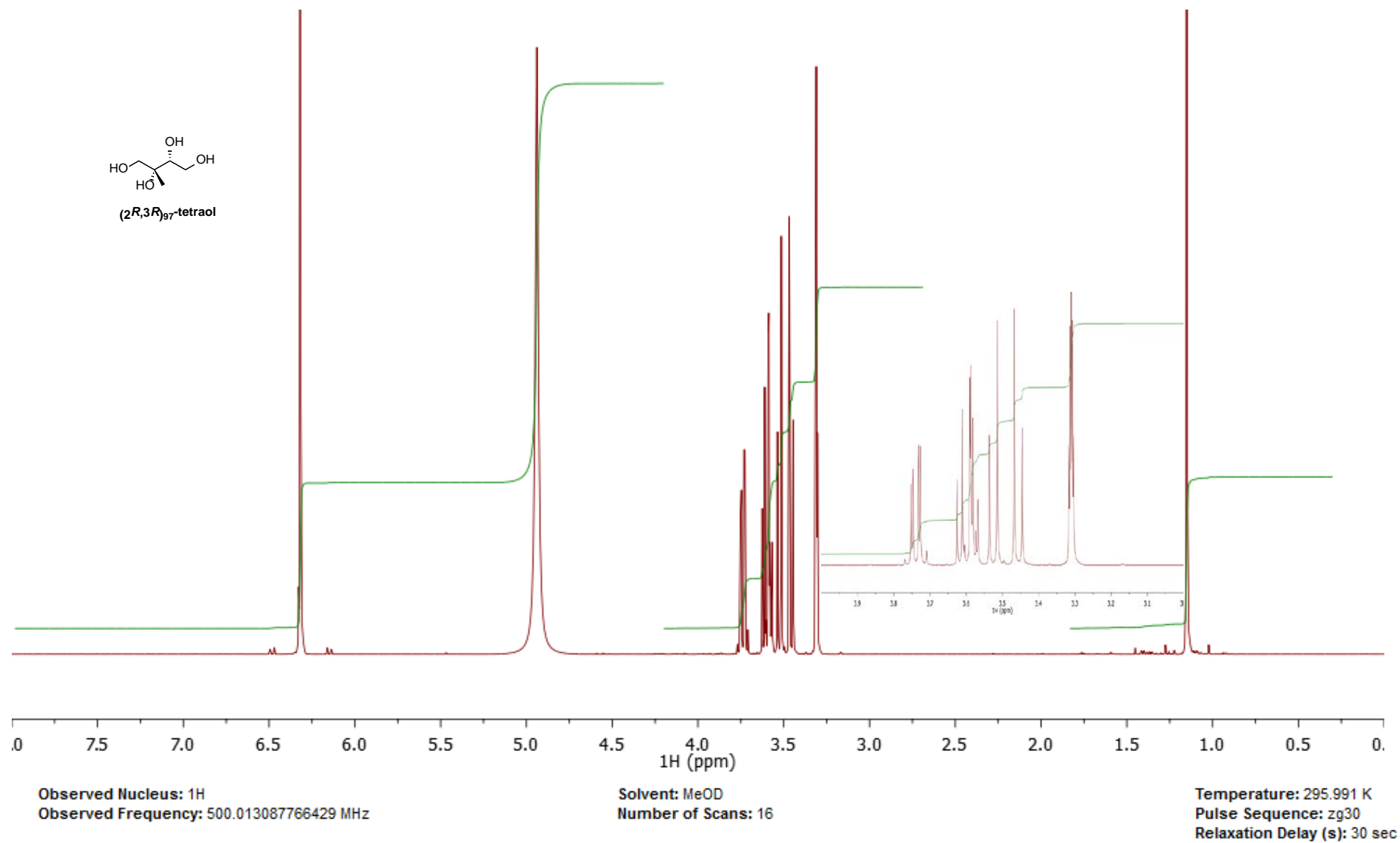
Figure S13. ^{1}H NMR spectrum of $(2R,3R)_{97}$-tetraol. Maleic acid had been added for the purpose of content determination by qNMR.

(2S,3S)₆₄-tetraol

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: MeOD
Number of Scans: 16

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 30 sec
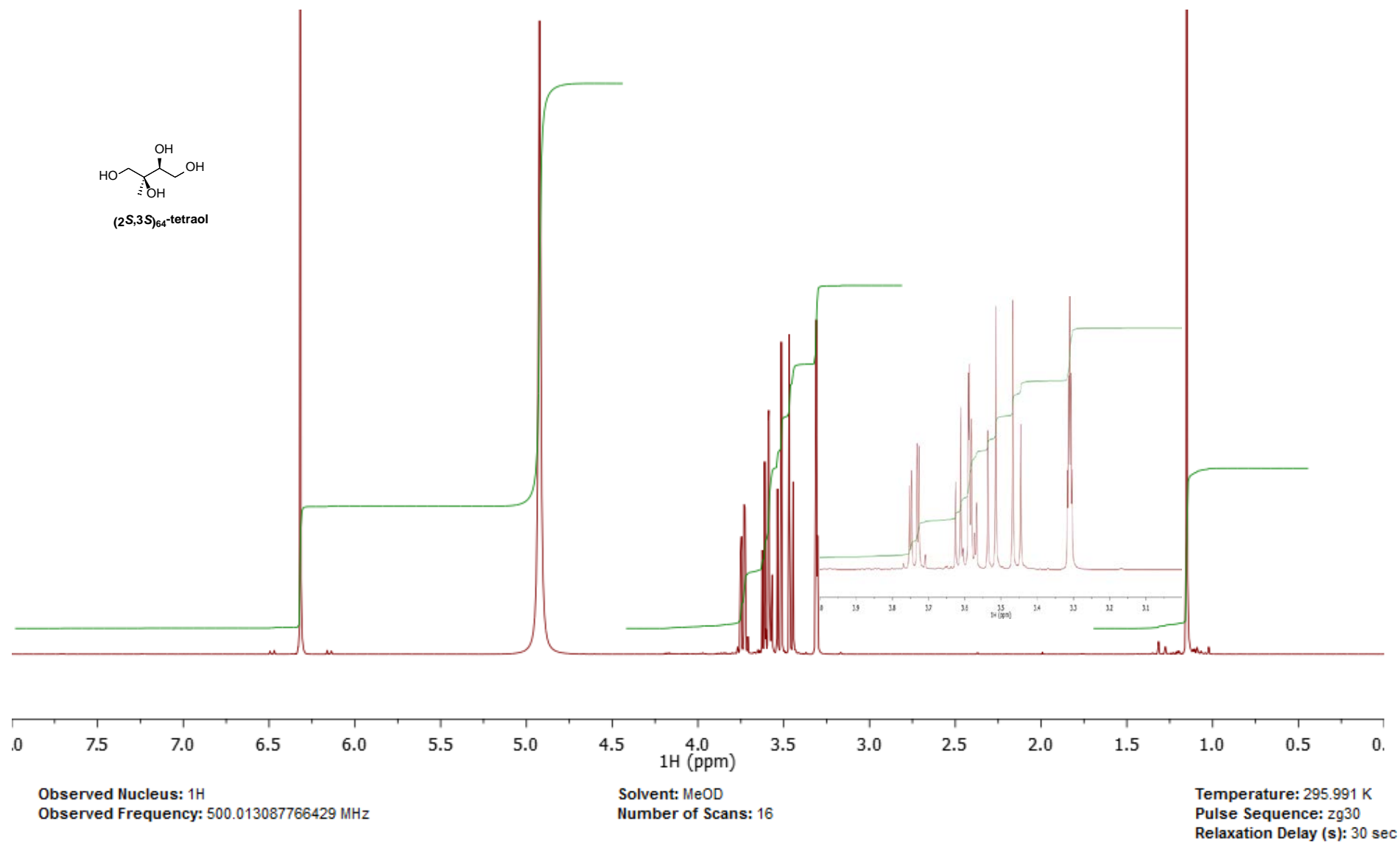
Figure S14. ¹H NMR spectrum of (2S,3S)₆₄-tetraol. Maleic acid had been added for the purpose of content determination by qNMR.

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