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Electronic Supplementary Information

Integrated Recycling of Polylactide using Biomass into Renewable Fuels: A Combined Experimental and Computational Design Approach.

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1. Analytic methods

1.1. Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on a Bruker Avance III HD 400 and a Bruker Avance II 400 nuclear resonance spectrometer at 25°C. Resonances were referenced to the residual solvent signal, relative to TMS. Data in the ^{1}H and ^{13}C NMR spectra are stated as follows: chemical shift (δ in ppm) (multiplicity, coupling constant (*J* in Hz), integration). To describe the multiplicity of the signals the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof. For a more detailed analysis of the signals various 2D NMR experiments (COSY, HSQC, HMBC) were conducted. Hydrogen and carbon atoms of all molecules are consecutively numbered for a clear and simple classification. For the Bruker Avance III HD 400 the software Topspin (Version 3.5.7) from Bruker and for the Bruker Avance III neo 400 the software TopSpin (Version 4.5.0) from Bruker were used for data acquisition. For visualization and examination of the NMR spectra the software MestReNova (Version 14.2.3-29241) from Mestrelab Research was used.

1.2. Elemental analysis (EA)

Elemental analysis was conducted with an elementar vario EL and an elementar vario EL cube.

1.3. Infrared Spectroscopy (IR)

FT-IR spectra were recorded with a Shimadzu IRTracer 100 using a CsI beam splitter in combination with an ATR unit (Quest model from Specac utilizing a robust monolithic crystalline diamond) in a 2 cm^{-1} resolution. For data acquisition, the software LabSolution IR (Version 2.15) from Shimadzu was used. The obtained IR data are stated as reciprocal wave numbers of the absorption (cm^{-1}). The vibration bands of the spectra are characterized *via* the Chemotion electronic lab notebook (ELN) as follows: vw = very weak, w = weak, m = medium, s = strong and vs = very strong.

1.4. ESI-HRMS

ESI mass spectra were obtained with a *ThermoFisher* Scientific LTQ Orbitrap XL. The source voltage was 4.49 kV, the capillary temperature amounted to 299.54 °C. The tube lens voltage lay between 110 and 130 V.

1.5. General experimental information

The chemicals used were commercially available from Acros Organis, Sigma Aldrich GmbH, TCI GmbH, and Alfa Aesar and used as received. If not stated otherwise, the reactions were performed in contact with air. If needed, solvents and the alcohols used were dried according to literature. The used polymers were provided by bio-mi Ltd. (Croatia). PLA powder (M_n = 56.6 kg mol^{-1}) was cryo-milled to 0.75 mm by the Leibniz Institute for Natural Product Research and Infection Biology - Hans Knöll Institute (HKI, Germany). The bisguanidine organocatalyst TMG$_2$e was synthesized according to literature.[1-3] The zinc bisguanidine catalyst [Zn(DMEG$_2$ch)$_2$)](OTf)$_2$ · THF (**Zn1**) was synthesized according to literature.[4] The experiments conducted are available *via* the Chemotion repository including the obtained data and additional information at 10.14272/collection/LB_2025-09-05.

Table S1: Supplier of the used nucleophiles and solvents.

Chemical	Supplier	Purity
Tetrahydrofuran (THF)	Fisher scientific	Synthesis grade
Methanol	Fisher scientific	Synthesis grade
Ethanol	VWR Chemicals	Analytic reagent grade
Ethylene glycol	Alfa Aesar	99%
Allyl alcohol	Sigma Aldrich	
Propanol	Thermo scientific	99.9%
iso-Propanol	Thermo scientific	99%
Butanol	Sigma Aldrich	99.8%
iso-Butanol	Sigma Aldrich	99.5%
tert-Butanol	Sigma Aldrich	
Pentanol	Thermo scientific	99%
3-Pentanol	Thermo scientific	98%
Hexanol	Thermo scientific	99%
3,3-Dimethyl-1-butanol	Thermo scientific	97%
Benzyl alcohol	Sigma Aldrich	99.8%
Octanol	Thermo scientific	99%

2. General procedure for the alcoholysis

2.1. Depolymerization of PLA in THF (GP1)

For the depolymerization in THF, PLA (1.00 equiv) and catalyst (1.0 mol%) were provided in a Young-type Schlenk tube and dissolved in THF (4 mL) using an external heat source (80 °C). The reaction tube was placed in a preheated oil bath (60 °C, stirring speed = 260 rpm) and the reaction was started by the addition of the used nucleophile (7 equiv). The reaction was monitored using ^{1}H NMR spectroscopy. Catalytic reactions using TMG$_2$e were performed under air and with synthetic grade solvents and reactants.

2.2. Depolymerization of PLA under solvent-free conditions (GP2)

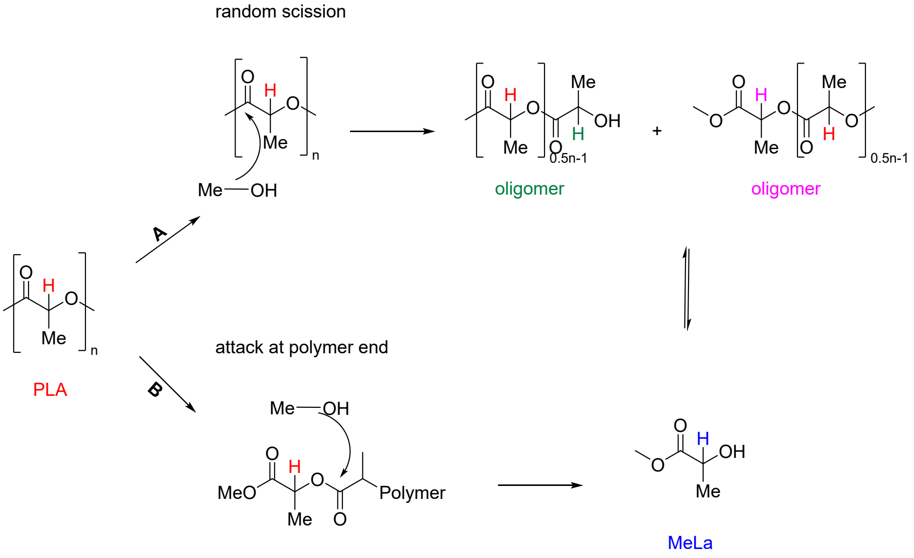
For the depolymerization under solvent-free conditions, PLA (1.00 equiv), catalyst (1.0 mol%) and the used nucleophile (7 equiv) were provided in a Young-type Schlenk tube. The reaction tube was placed in a preheated oil bath (150 °C, stirring speed = 260 rpm) to start the reaction. The reaction was monitored using ^{1}H NMR spectroscopy. Samples were taken by cooling the tube to room temperature under running water to collect a sample. Subsequently, the reaction tube was placed into the oil bath to restart the reaction. Catalytic reactions using TMG$_2$e were performed under air and with synthetic grade solvents and reactants. Under these conditions, we observed the low formation of other not identified oligomeric species.

2.3. Depolymerization of PLA under inert and solvent-free conditions (GP2*)

In a N$_2$ filled glovebox, [Zn(DMEG$_2$ch)$_2$)](OTf)$_2$ · THF (**Zn1**, 1.0 mol%, regarding the ester bonds, synthesized according to literature[5]) was weighed into a Young-type Schlenk tube. PLA (3.47 mmol, 1.00 equiv, bio-mi Ltd.) was added in N$_2$ counterflow. To start the depolymerization, the respective alcohol (24.3 mmol, 7 equiv) was added under N$_2$ counterflow, the Young-type Schlenk tube was placed in an oil bath preheated to 150 °C and stirred with a magnetic stirrer at 260 rpm.

3. Evaluation of the alcoholysis and glycolysis of PLA

3.1. Proposed mechanism



Scheme S1 Proposed mechanism for the depolymerization of PLA using methanol as example under **GP1** conditions (Pathway A). Using smaller alcohols under **GP2** conditions can lead to a change of reaction mechanism to Pathway B. Larger nucleophiles such as BnOH follow Pathway B under **GP1** and **GP2**. For other nucleophiles we found that oligomer formation occurs (Pathway A) under the conditions of **GP2**.

3.2. Determination of X_{int}, S_{RLa}, and Y_{RLa}

The catalytic experiments were analyzed using ^{1}H NMR spectroscopy and the products were not isolated. MeLa, PrLa, BuLa, *i*BuLa, PrLa, PeLa, HeLa, and OcLa were analyzed according to literature.[6-8] EGLa could not be analyzed according to literature due to overlap of the signal of the internal methine group of PLA and the OH signal of EGLa. Instead, the doublet for the methyl group of the lactate moiety was analyzed. Due to the overlap of the signals of the methine proton of EtLa and Me$_2$BuLa and the signals of the protons of the alcohol moiety of one of the oligomer chain-ends, the integral for EtLa and Me$_2$BuLa were calculated according to literature.[6, 9] For BnLa, the signal for the internal methine group of PLA (Int) is overlapped by the CH$_2$ group of the benzylic residue (BnCH_2OR); thus, the amount of PLA ([Int]) was calculated by subtracting the protons of the CH$_2$ units from the overlapped integral of PLA and BnLa using the equation S1. The amount of CH$_2$ units was determined by using the integral of the methine signal of BnLa (BnLa). Due to ^{13}C satellites and the fast depolymerization of PLA this method is not quantitative.

$$Int = \left(Int + BnCH_2OR\right) - \left(2 \cdot (BnLa)\right) \tag{S1}$$

AlLa could only be analyzed after complete conversion of PLA was reached due to the overlap of PLA and signals from the AlOH. For BnLa, the signal for the internal methine group of PLA (Int) is overlapped not only by the oligomer but by the methine signal of the *iso*-propyl residue of the oligomer and the *i*PrLa; thus, the ratio of PLA ([Int]) was calculated by subtracting the integral of the oligomers as described in literature. Further, the integrals of the oligomer and the *i*PrLa were subtracted from the integral at 5.2 ppm to amount for the additional protons of the methine group of the *i*-propyl residue. To obtain [Int] the calculated integral needs to be divided by the sum of the methine signals of the (former) internal methine group of PLA, oligomers, and *i*PrLa.

$$[Int] = \frac{Int - 2 \cdot oligomers - iPrLa}{Int + oligomer + iPrLa - oligomer - iPrLa} \tag{S2}$$

Furthermore, depolymerizations using *t*BuOH and 3PeOH were not successful. We observed several oligomeric species which were not identified further.

The conversion of PLA (X_{int}), the selectivity towards the lactate (S_{RLa}), and the yield of the lactate (Y_{RLa}) were determined according to literature.[6-7]

$$X_{int} = \frac{[Int]}{[Int]_0} \tag{S3}$$

$$S_{RLa} = \frac{[RLa]}{[Int]_0 - [Int]} \tag{S4}$$

$$Y_{RLa} = X_{int} \cdot S_{RLa} \tag{S5}$$

$$[Int]_0 = [Int] + [oligomers] + [RLa] \tag{S6}$$

4. Synthesis and Characterization of Me_2BuLa

3,3-Dimethylbutyl 2-hydroxypropanoate (Me_2BuLa) was synthesized in a 500 mg PLA and a 2.00 g PLA scale to isolate characterize the compound, since no sources of reliable spectroscopic data could be identified. For the 500 mg scale alcoholysis, the reaction was performed as described for a 250 mg scale. For the 2.00 g scale alcoholysis, the reaction conditions were adjusted to larger reaction volume.

4.1. Synthesis of Me_2BuLa (2.00 g scale)

TMG_2e (73.7 mg, 287 µmol, 0.0104 equiv), PLA powder (2.00 g, 27.8 mmol, 1.00 equiv), and 3,3-dimethylbutan-1-ol (8.44 g, 10.0 mL, 82.6 mmol, 2.98 equiv) were provided in a 50 mL Schlenk flask. The flask was equipped with a reflux condenser and placed in a preheated oil bath (150 °C, *t* = 0 min). A ^{1}H NMR sample was collected after 1.5 h, 24 h and 48 h. The reaction was performed under protective atmosphere. After 49 h, the reaction was stopped and the ^{1}H NMR spectroscopic analysis performed yielded a conversion of PLA of 100% and a yield for 3,3-dimethylbutyl 2-hydroxypropanoate (Me_2BuLa) of 75%. All volatile compounds were removed in high vacuum and collected in a cooling trap ($_{\text{oil bath}}$ = 80–100 °C). Me_2BuLa was separated from 3,3-dimethylbutan-1-ol using micro distillation. The obtained fraction contained Me_2BuOH, which was removed in high vacuum ($4 \cdot 10^{-2}$ mbar) at *T* = 80–140 °C. The yield of Me_2BuLa was not determined.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.25–4.15 (m, 3H, C*H*OH, C*H*$_2$O), 3.08 (b, 1H, O*H*), 1.55 (t, *J* = 7.3 Hz, 2H, C*H*$_2$CH$_2$O), 1.37 (dd, *J* = 6.9 Hz, *J* = 0.8 Hz, 3H, CHC*H*$_3$), 0.91 (d, *J* = 0.9 Hz, 9H, CH$_2$(C*H*$_3$)$_3$) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.9 (1C, *C*=O), 66.8 (1C, *C*HOH), 63.5 (1C, CH$_2$*C*H$_2$O), 41.8 (1C, *C*H$_2$CH$_2$O), 29.8 (3C, C(*C*H$_3$)$_3$), 29.6 (1C, *C*(CH$_3$)$_3$), 20.4 (1C, CH*C*H$_3$) ppm.

FTIR (ATR, ṽ) = 3474 (O–H, w), 2959 ($CH_{\text{aliphatic}}$, m), 2906 ($CH_{\text{aliphatic}}$, w), 2870 ($CH_{\text{aliphatic}}$, w), 1731 (C=O, vs), 1478 ($CH_{\text{aliphatic}}$, w), 1466 ($CH_{\text{aliphatic}}$, w), 1396 ($CH_{\text{aliphatic}}$, w), 1367 ($CH_{\text{aliphatic}}$, m), 1311 (w), 1262 (C–O, m), 1215 (C–O, vs), 1204 (C–O, vs), 1127 (C–O, vs), 1086 (C–O, m), 1044 (C–O, s), 964 (m), 928 (w), 864 (w), 761 (w) cm^{-1}.

HRMS (ESI+, MeOH) m/z (%) calc for $C_9H_{18}O_3Na^+$ ($[M+Na]^+$) 197.11481, found 197.11414; calc for $(C_9H_{18}O_3)_2Na^+$ ($[2M+Na]^+$) 371.24040, found 371.23941.

5. Alcoholysis and Glycolysis of PLA using TMG$_2$e and **Zn1**

5.1. Methyl lactate (MeLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[6-7] The ^{1}H NMR spectroscopic data is in good accordance with literature.[6-7]

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.26 (q, *J* = 7.0 Hz, 1H, C*H*), 3.75 (s, 3H, OC*H*$_3$), 1.39 (d, *J* = 6.8 Hz, 3H, CHC*H*$_3$) ppm.

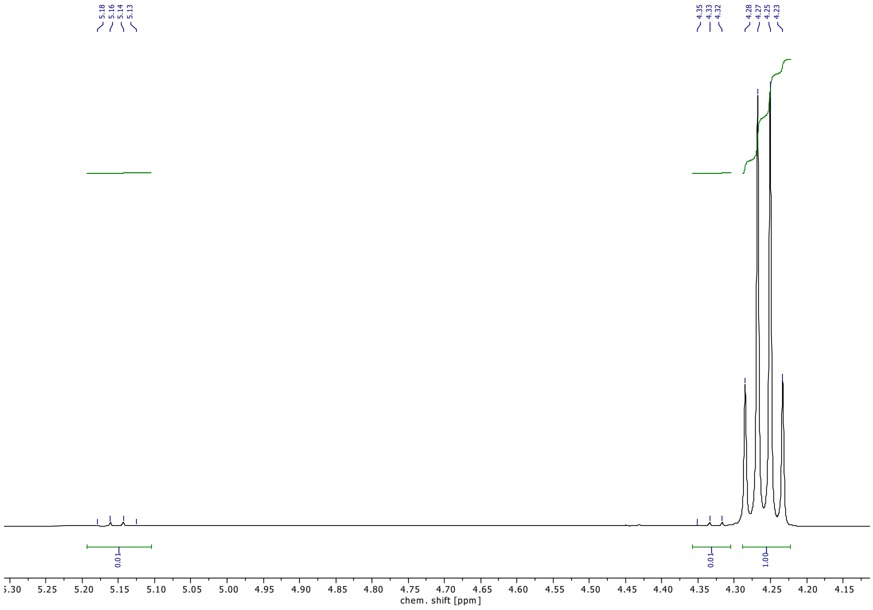


Figure S1. Exemplary ^{1}H NMR spectrum in CDCl$_3$ of the methanolysis of PLA after 5 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.1 equiv MeOH, 150 °C, 260 rpm.

5.2. Ethyl lactate (EtLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[10] The ^{1}H NMR spectroscopic data is in good accordance with literature.[9-10]

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.26 – 4.13 (m, 3H, C*H* + OC*H*$_2$), 1.36 (d, *J* = 6.9 Hz, 3H, CHC*H*$_3$), 1.25 (t, *J* = 7.2 Hz, 3H, CH$_2$C*H*$_3$) ppm.

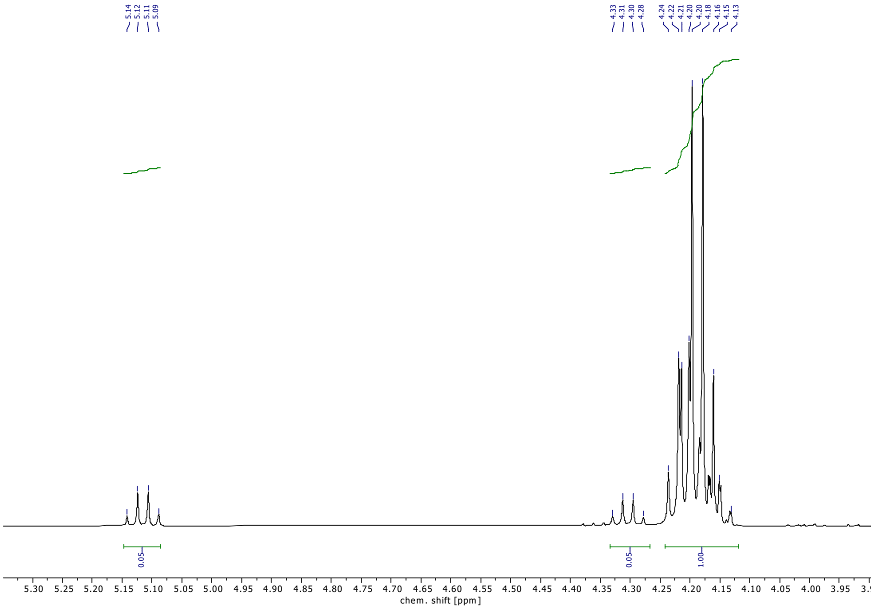


Figure S2. Exemplary ^{1}H NMR spectrum in CDCl$_3$ of the ethanolysis of PLA after10 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 6.9 equiv EtOH, 150 °C, 260 rpm.

5.3. Propyl lactate (PrLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[11] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 11] The harsher conditions of **GP2** lead to the formation of unidentified depolymerization products which are observable after 48 h *via* ^{1}H NMR spectroscopy. This could be due to racemization of the lactates during the reactions or the formation of different oligomeric species. Under the conditions of **GP1**, the formation of side products was reduced successfully.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.23 (q, J = 6.9 Hz, 1H, C*H*), 4.14 – 4.03 (m, 2H, OC*H*$_2$), 1.69 – 1.60 (m, 2H, $CH_2CH_2CH_3$), 1.38 (d, J = 6.9 Hz, 3H, CHC*H*$_3$), 0.91 (t, J = 7.4 Hz, 3H, CH$_2$C*H*$_3$) ppm.

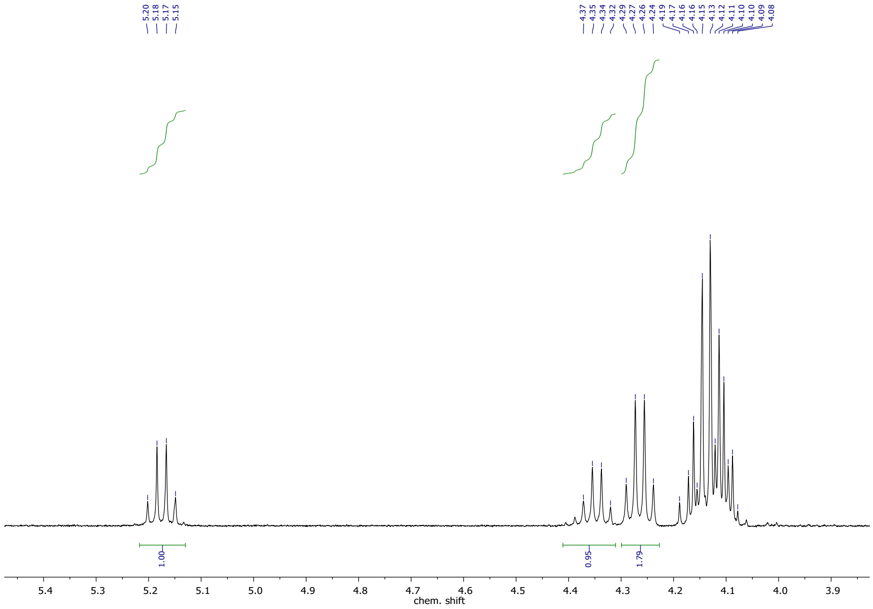


Figure S3. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the propanolysis of PLA after 1 h. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.3 equiv PrOH, 150 °C, 260 rpm.

5.4. Propyl lactate (PrLa; GP2*)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[11] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 11]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.24 (q, J = 6.9 Hz, 1H, C*H*), 4.11 – 4.01 (m, 2H, OC*H*$_2$), 1.68 – 1.57 (m, 2H, $CH_2CH_2CH_3$), 1.34 (d, J = 6.9 Hz, 3H, CHC*H*$_3$), 0.89 (t, J = 7.4 Hz, 3H, CH$_2$C*H*$_3$) ppm.

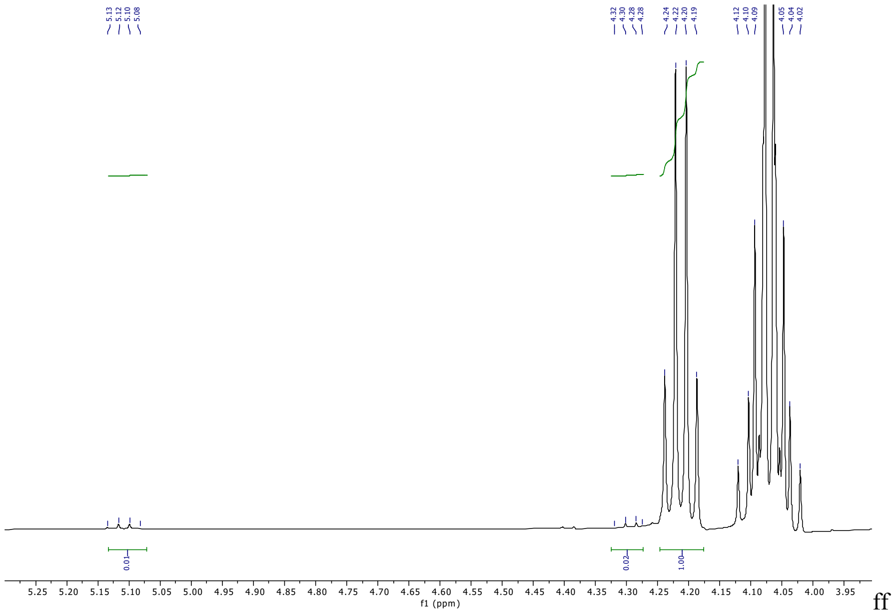


Figure S4. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the propaneolysis of PLA after 1 h. Reaction conditions (**GP2***): 250 mg PLA, 1.0 mol% **Zn1**, 7.3 equiv PrOH, 150 °C, 260 rpm.

5.5. Butyl lactate (BuLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[6-7, 12] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 12]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.22 (q, *J* = 6.9 Hz, 1H, C*H*), 4.18 – 4.07 (m, 2H, CH_2O), 1.63-1.56 (m, 2H, $CH_2CH_2CH_2$), 0.89 (t, *J* = 7.4 Hz, 3H, CH_2CH_3) ppm.

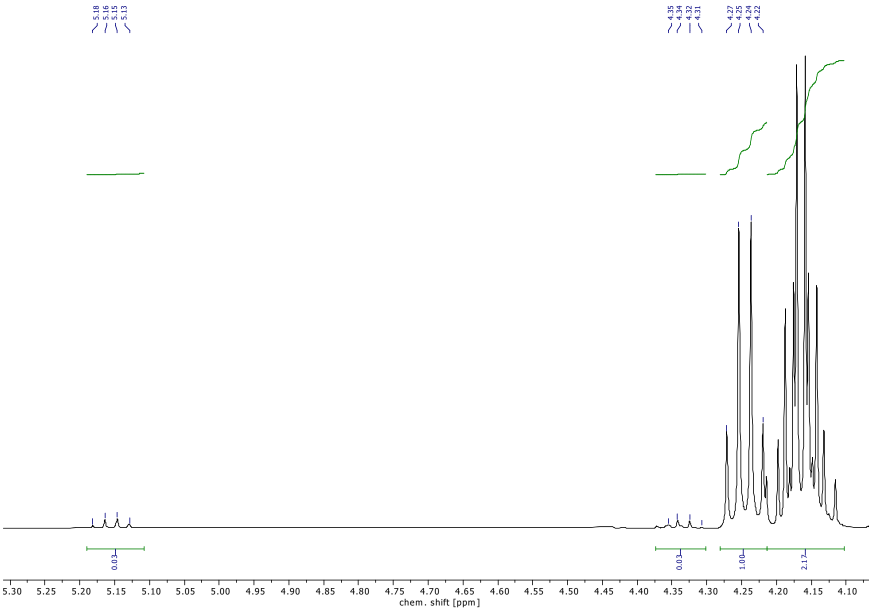


Figure S5. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the butanolysis of PLA after 180 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG_2e, 7.2 equiv BuOH, 150 °C, 260 rpm.

5.6. Pentyl lactate (PeLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[6-7, 13] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 13]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.19 (q, *J* = 6.9 Hz, 1H, C*H*), 4.14 – 4.03 (m, 2H, CH_2O), 1.63 – 1.55 (m, 2H, CH_2CH_2O), 1.34 (d, *J* = 6.9 Hz, 3H, $CHCH_3$) ppm.

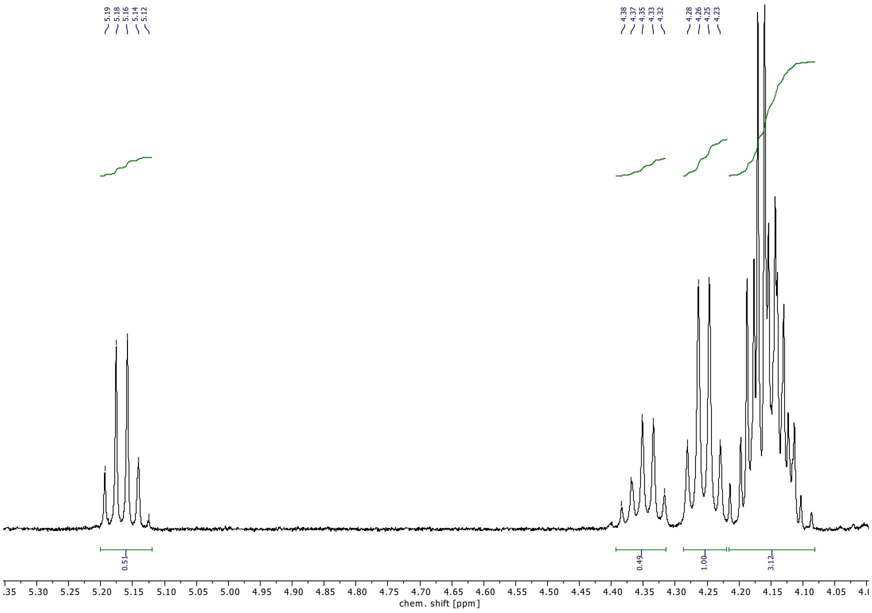


Figure S6. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the pentanolysis of PLA after 25 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG_2e, 7.2 equiv pentanol, 150 °C, 260 rpm.

5.7. Hexyl lactate (HeLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[6-7, 14-15] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 14-15]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.23 (q, J = 6.9 Hz, 1H, CHCH$_3$), 4.19 – 4.08 (m, 2H, CH_2O), 1.66 – 1.58 (m, 1H, CH_2CH$_2$O), 1.38 (d, J = 6.9 Hz, 3H, CHCH_3) ppm.

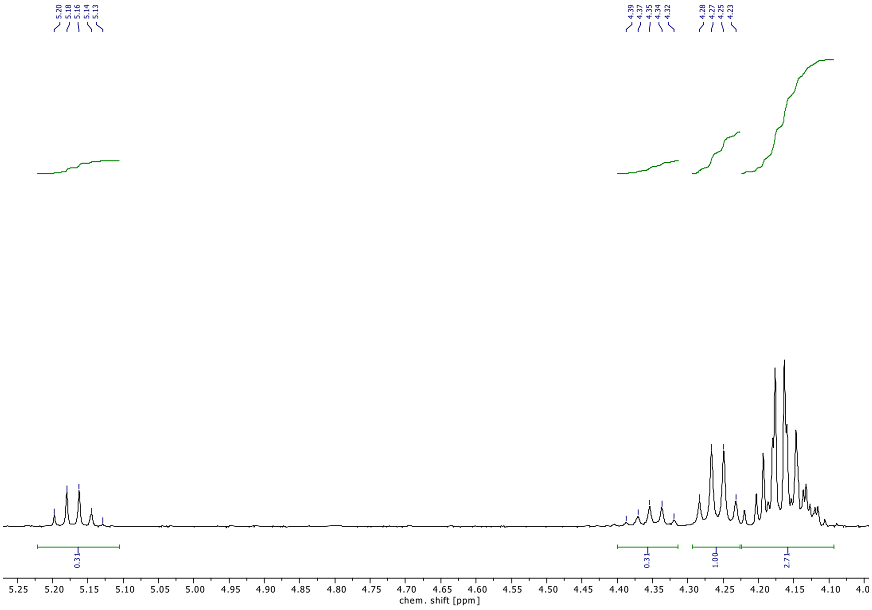


Figure S7. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the hexanolysis of PLA after 25 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.1 equiv hexanol, 150 °C, 260 rpm.

5.8. Octyl lactate (OcLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[6-7, 13, 15] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 13, 15] We could not identify all signals due to overlapping OcOH signals.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.23 (q, J = 6.9 Hz, 1H, CHCH$_3$), 4.19 – 4.08 (m, 2H, CH_2O), 1.67 – 1.58 (m, 1H, CH_2CH$_2$O), 1.38 (d, J = 6.9 Hz, 3H, CHCH_3) ppm.

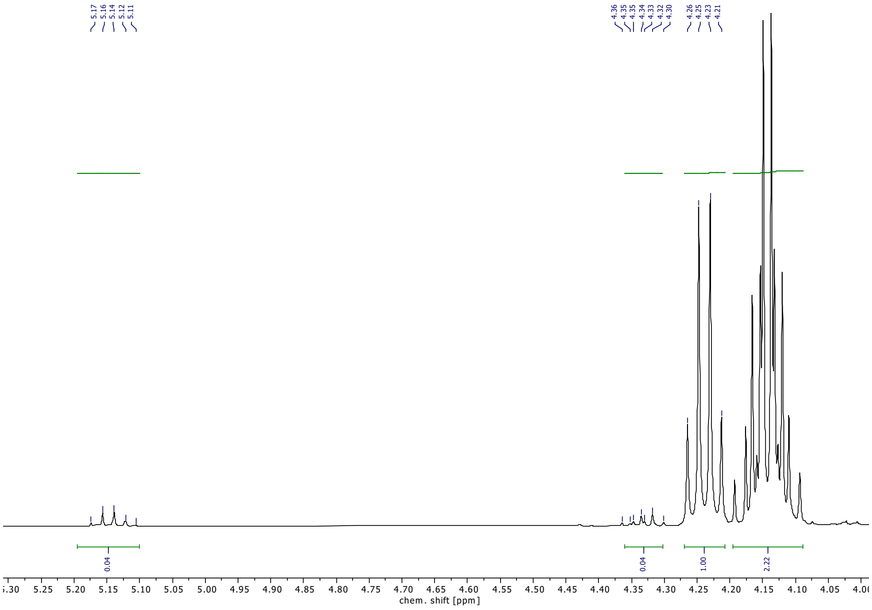


Figure S8. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the octanolysis of PLA after 48 h. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.1 equiv octanol, 150 °C, 260 rpm.

5.9. Octyl lactate (OcLa; GP2*)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[6-7, 13, 15] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 13, 15] We could not identify all signals due to overlapping OcOH signals.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.20 (q, J = 6.9 Hz, 1H, CHCH$_3$), 4.15 – 4.04 (m, 2H, CH_2O), 1.60 (p, J = 6.7 Hz, 1H, CH_2CH$_2$O), 1.35 (d, J = 6.8 Hz, 3H, CHCH_3) ppm.

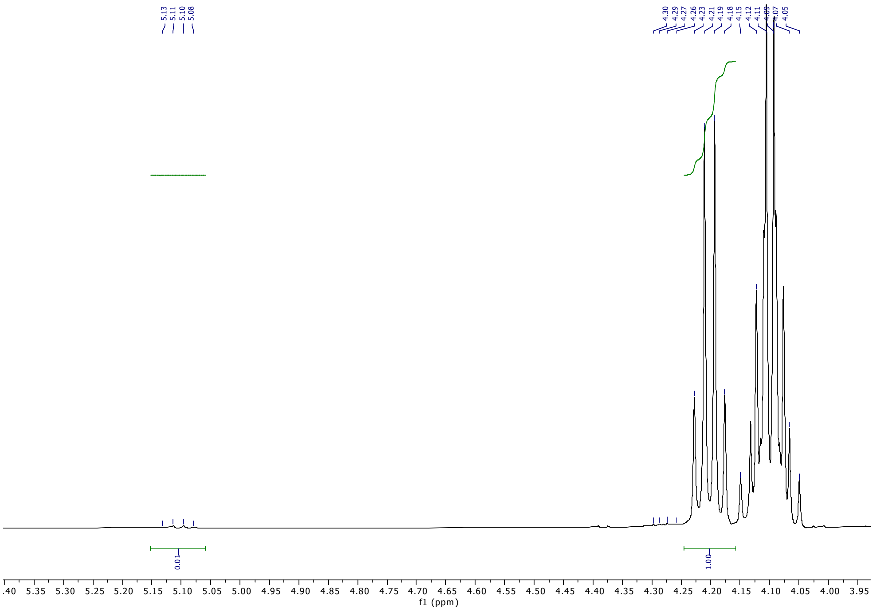


Figure S9. Exemplary ^{1}H NMR spectrum in CDCl$_3$ of the octanolysis of PLA after 1 h. Reaction conditions (**GP2***): 250 mg PLA, 1.0 mol% **Zn1**, 7.1 equiv octanol, 150 °C, 260 rpm.

5.10. *iso*-Propyl lactate (*i*PrLa; GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[11, 16] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8] Due to the overlap of the internal methine of PLA with the methine functionality of the *iso*-propyl residue of the product a quantitative analysis was aggravated. Moreover, unidentified depolymerization products are still observable after 48 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 5.08 – 4.93 (CH(CH$_3$)$_2$ + oligomer), 4.34 – 4.25 (oligomer), 4.15 (q, J = 6.9 Hz, 1H, CHCH$_3$), 1.33 (d, J = 6.9 Hz, 3H, CHCH_3), 1.22 – 1.19 (m, 6H, CH(CH_3)$_2$).

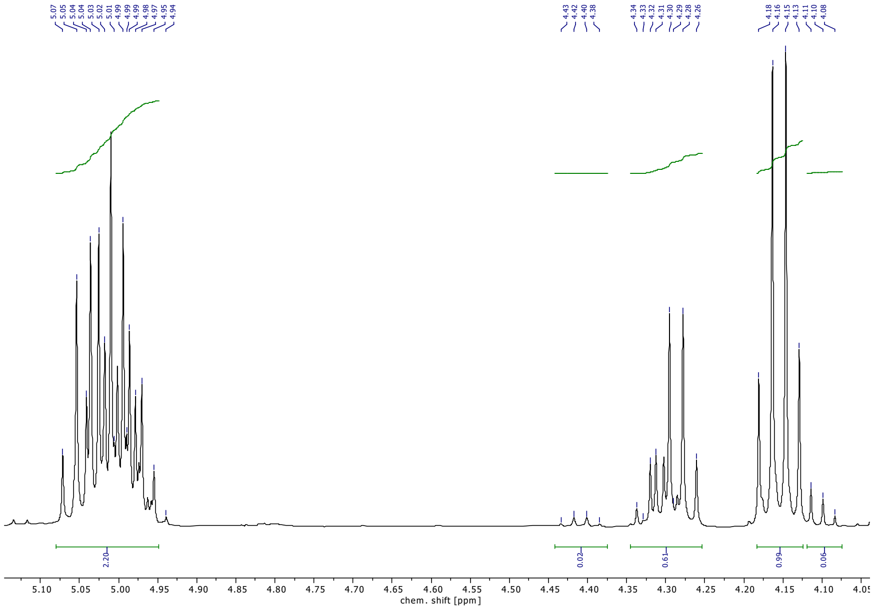


Figure S10. Exemplary 1H NMR spectrum in CDCl$_3$ of the alcoholysis of PLA using *iso*-propanol after 1 h. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.2 equiv *i*PrOH, 150 °C, 260 rpm.

5.11. *iso*-Propyl lactate (*i*PrLa; GP2*)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[11, 16] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.03 (hept, *J* = 6.2 Hz, 1H, $CH(CH_3)_2$), 4.17 (q, *J* = 6.9 Hz, 1H, $CHCH_3$), 1.35 (d, *J* = 6.9 Hz, 3H, $CHCH_3$), 1.22 (dd, *J* = 6.3, 2.6 Hz, 6H, $CH(CH_3)_2$).

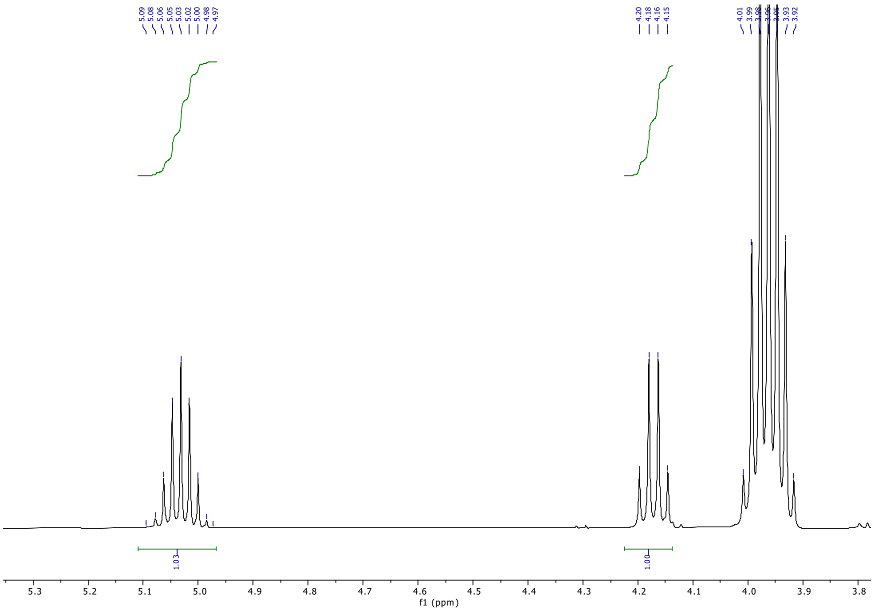


Figure S11. Exemplary 1H NMR spectrum in $CDCl_3$ of the alcoholysis of PLA using *iso*-propanol after 2 h. Reaction conditions (**GP2***): 250 mg PLA, 1.0 mol% **Zn1**, 7.2 equiv *i*PrOH, 150 °C, 260 rpm.

5.12. *iso*-Butyl lactate (*i*BuLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[11-12] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 12]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.26 (q, *J* = 6.9 Hz, 1H, $CHCH_3$), 4.00 – 3.88 (m, 2H, CH_2O), 1.40 (d, *J* = 6.9 Hz, 3H, $CHCH_3$), 0.93, 0.91 (d, *J* = 6.8, 3H, $CH(CH_3)_2$) ppm.

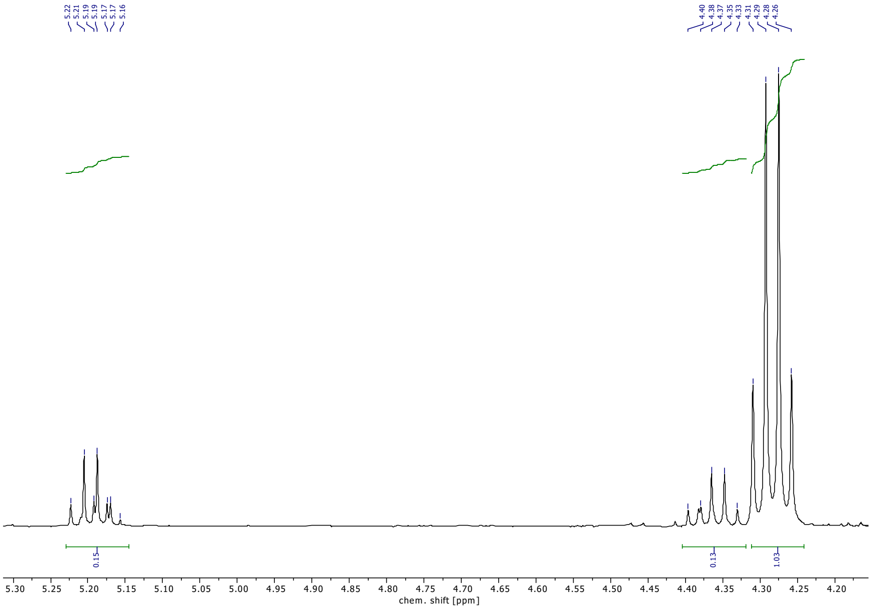


Figure S12. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the *iso*-butanolysis of PLA after 180 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG_2e, 7.3 equiv *i*BuOH, 150 °C, 260 rpm.

5.13. 3,3-Dimethylbutyl lactate (Me$_2$BuLa; GP1+GP2)

The alcoholysis was analyzed according to literature.[6-8, 10]
^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.25 – 4.13 (m, 3H, CHCH$_3$+CH_2O), 1.55 (dd, J = 8.3, 6.6 Hz, 2H, CH_2O), 1.37 (d, J = 6.9 Hz, 3H, CHCH_3), 0.91 (d, J = 2.6 Hz, 9H, CH$_2$(CH_3)$_3$) ppm.

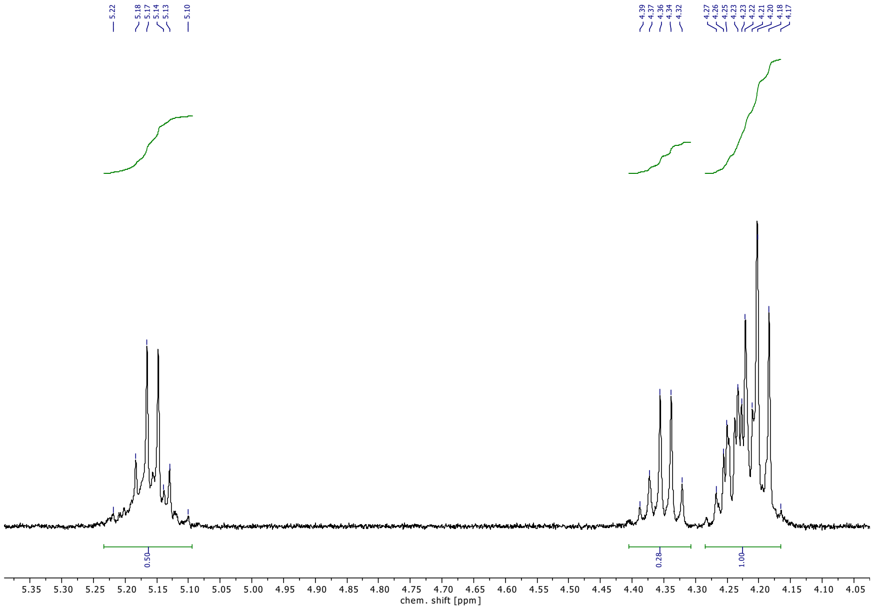


Figure S13. Exemplary ^{1}H NMR spectrum of the alcoholysis in CDCl$_3$ of PLA using 3,3-dimethylbutan-1-ol after 5 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.1 equiv 3,3-dimethylbutan-1-ol, 150 °C, 260 rpm.

5.14. *tert*-Butyl lactate (*t*BuLa; GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature. No depolymerization was observed conducting **GP1**. Following **GP2**, slow conversion of PLA was observed to various depolymerization species. The product mixture was not analyzed further.

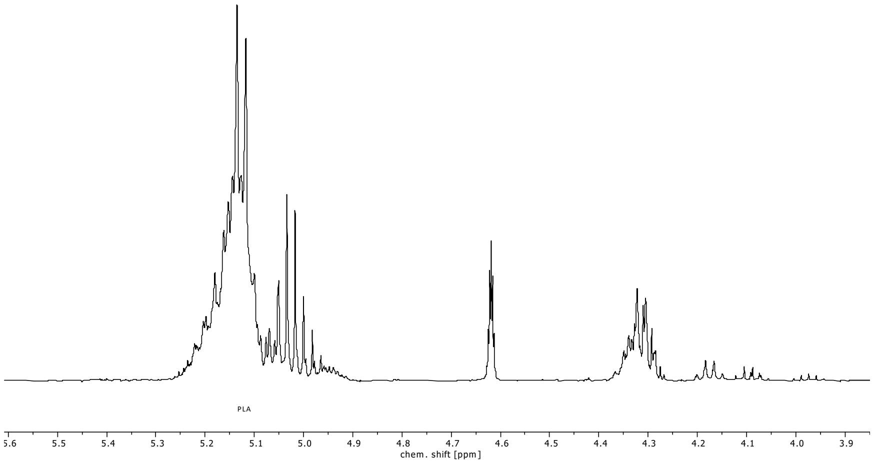


Figure S14. Exemplary ^{1}H NMR spectrum in CDCl$_3$ of the *tert*-butanolysis of PLA after 72 h. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.0 equiv *t*BuOH, 4 mL THF, 60 °C, 260 rpm.

5.15. Pentan-3-yl 2-hydroxypropanoate (3PeLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[17] No depolymerization was observed conducting **GP1**. Following **GP2**, slow conversion of PLA was observed. The product mixture was not analyzed further.

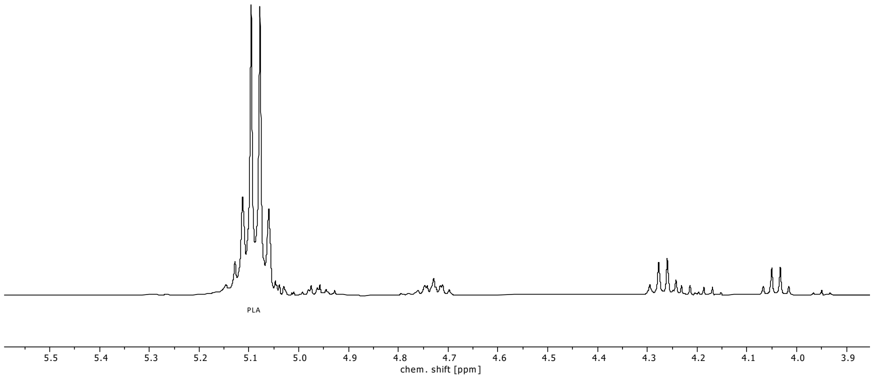


Figure S15. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the alcoholysis of PLA using 3-pentanol after 3 h. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG_2e, 7.2 equiv 3-PeOH, 4 mL THF, 60 °C, 260 rpm.

5.16. Allyl lactate (AlLa; GP1+GP2)

The alcoholysis was analyzed using ^{1}H NMR spectroscopy as described in literature.[10-11, 18] The ^{1}H NMR spectroscopic data is in good accordance with literature.[8, 11] Due to the overlap of the methine signal of PLA with a signal of the allyl alcohol used a quantitative evaluation was aggravated. We propose fast depolymerization of PLA due to the good fit of the integration of the visible signals od AlLa. Furthermore, we could not identify a signal of the methyl group of PLA.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.90 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H, $CH_2=CH$), 5.32 (dq, *J* = 17.3, 1.4 Hz, 1H, $CH=CH$), 4.70 – 4.59 (m, 2H, CH_2O), 4.28 (q, *J* = 6.9 Hz, 1H, CH), 1.41 (d, *J* = 6.9 Hz, 3H, $CHCH_3$) ppm.

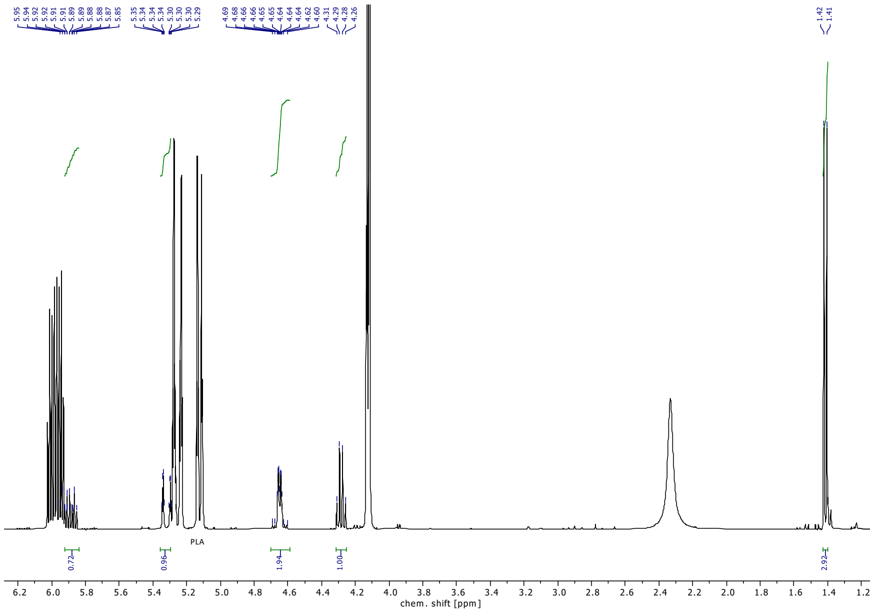


Figure S16. Exemplary ^{1}H NMR spectrum in $CDCl_3$ of the alcoholysis of PLA using allyl alcohol after 24 h. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG_2e, 7.2 equiv AllylOH, 150 °C, 260 rpm.

5.17. Benzyl lactate (BnLa; GP1+GP2)

The alcoholysis was analyzed using ^1H NMR spectroscopy as described in literature.[18-20] The ^1H NMR spectroscopic data is in good accordance with literature.[18-20] No oligomer formation is observed under the given reaction conditions. Furthermore, the signal for the internal methine group of the PLA is overlapped by the signal for the OCH_2 group of the BnLa.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.11 (s, 2H, CH_2O), 4.21 (q, *J* = 6.9 Hz, 1H, $CHCH_3$), 1.33 (d, *J* = 6.9 Hz, 3H, $CHCH_3$) ppm.

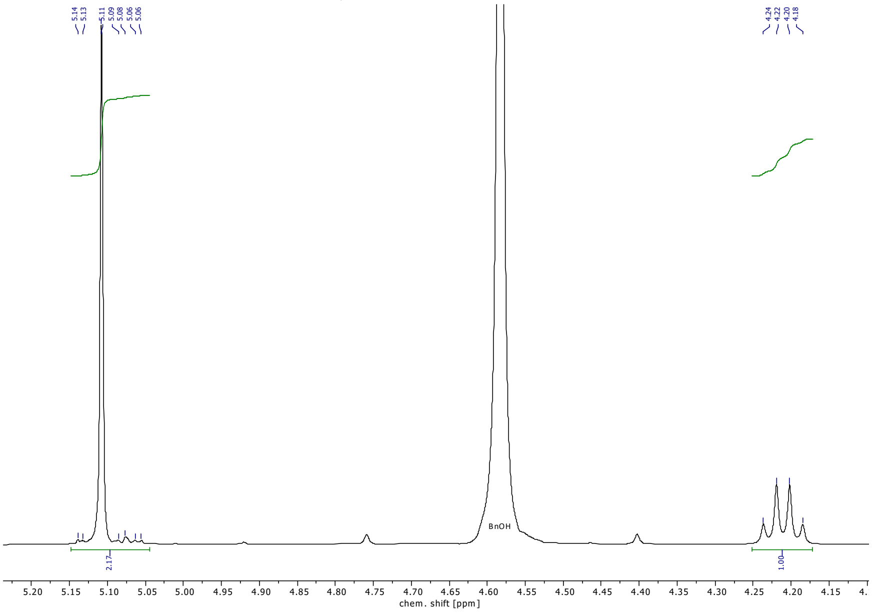


Figure S17. Exemplary ^1H NMR spectrum in $CDCl_3$ of the alcoholysis of PLA using benzyl alcohol after 25 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG_2e, 7.2 equiv BnOH, 150 °C, 260 rpm.

5.18. 2-Hydroxyethyl 2-hydroxypropanoate (EGLa; GP2)

The glycolysis was analyzed using ^1H NMR spectroscopy as described in literature.[10-11, 21] The ^1H NMR spectroscopic data is in good accordance with literature.[10-11, 21] Due to the overlap of the methine signal of PLA with a signal of the ethylene glycol used a quantitative evaluation was aggravated. We propose fast depolymerization of PLA due to the good fit of the integration of the visible signals of EGLa. Furthermore, we could not identify the signal of the methyl group of PLA.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.37 – 4.13 (m, 3H, $CH+OCH_2$), 3.77 (t, *J* = 4.6 Hz, 2H, CH_2OH), 1.38 (d, *J* = 6.9 Hz, 3H, $CHCH_3$) ppm.

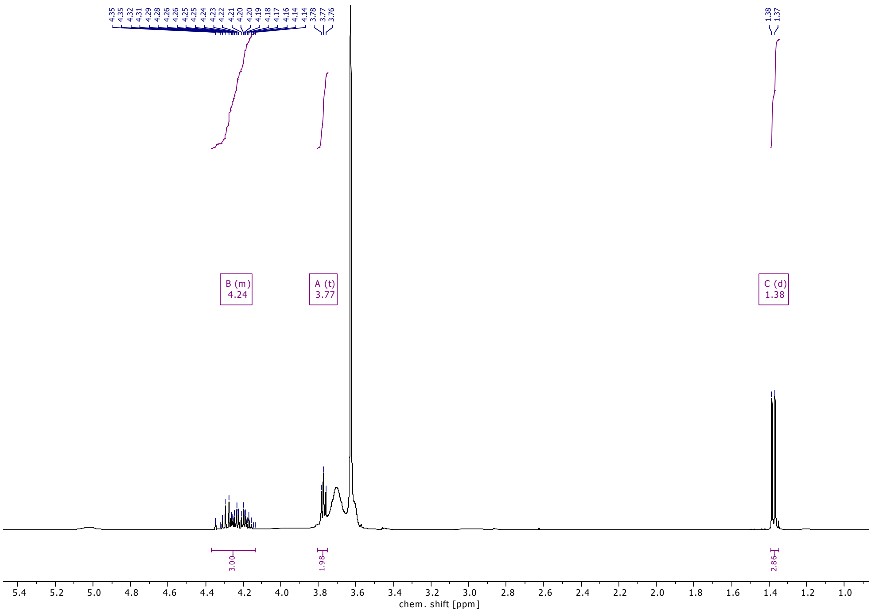


Figure S18. Exemplary ^1H NMR spectrum in $CDCl_3$ of the glycolysis of PLA after 180 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG_2e, 7.2 equiv EG, 150 °C, 260 rpm.

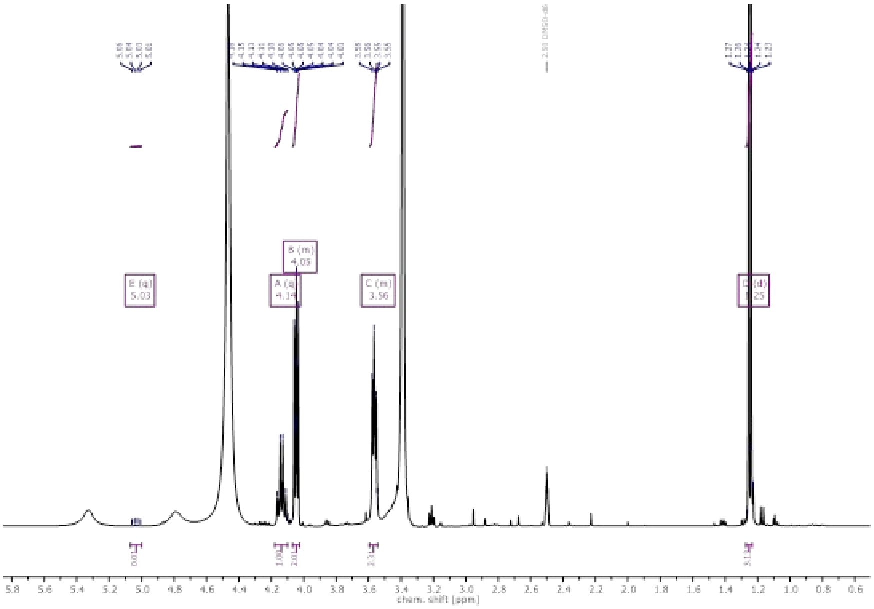


Figure S19. Exemplary ^{1}H NMR spectrum in DMSO-d_6 of the glycolysis of PLA after 2880 min. Reaction conditions (**GP2**): 250 mg PLA, 1.0 mol% TMG$_2$e, 7.2 equiv EG, 150 °C, 260 rpm.

6. Results for the depolymerization of PLA

6.1. Depolymerization using TMG_2e following GP1

Table S2 Overview over depolymerization of PLA using TMG_2e and different nucleophiles following **GP1**.

Entry	Nu	#C	n_{PLA} [mmol]	n_{cat} [µmol]	V_{Nu} [mL]	*t* [h]	X_{int}[a] [%]	S_{RLa}[a] [%]	Y_{RLa}[a] [%]
1[b]	EtOH	2	3.47	34.7	1.44	1	89	21	18
						3	94	57	54
						19.5	100	100	100
2	EtOH	2	3.47	34.7	1.44	0.5	60	13	8
						1	96	28	27
						3	98	67	66
						6	100	84	84
						48	100	100	100
3	PrOH	3	3.47	34.7	1.9	24	100	93	93
4	PrOH	3	3.47	34.7	1.9	24	100	96	96
						48	100	98	98
5	AlOH	3	3.47	34.7	1.7	0.5	100	100	100
6	BuOH	4	3.47	34.7	2.3	1	25	3	1
						3	80	15	12
						24	100	71	70
						48	100	85	85
7	*i*BuOH	4	3.47	34.7	2.3	1	21	0	0
						3	86	20	15
						24	100	72	72
						48	100	88	88
8	*t*BuOH	4	3.47	34.7	1.3	24	small amount of oligomer formation observable		
9	PeOH	5	3.47	34.7	2.7	24	98	78	77
10	PeOH	5	3.47	34.7	2.7	24	100	79	79
						48	100	91	91
						120	100	98	98
11	PeOH	5	3.47	34.7	2.7	24	100	81	81
						48	100	91	91
12	3PeOH	5	3.47	34.7	2.7	24	0	0	0
						48	0	0	0
13	3PeOH	5	3.47	34.7	2.7	24	0	0	0
14	HeOH	6	3.47	34.7	3.1	24	93	76	70
15[b]	HeOH	6	3.47	34.7	3.1	24	88	83	74
						48	91	93	84
16	HeOH	6	3.47	34.7	3.1	24	98	86	85
						48	100	94	94
17	Me_2BuOH	6	3.47	34.7	1.5	48	100	75	75
18	Me_2BuOH	6	3.47	34.7	1.5	24	97	35	34
						48	100	46	46
19[b]	OcOH	8	3.47	34.7	3.8	24	57	75	43
						48	78	81	63
20	OcOH	8	3.47	34.7	3.8	24	71	75	53
						48	91	83	76

a X_{int}, S_{RLa}, Y_{RLa} were calculated from ^1H NMR spectroscopic analysis according to literature[6, 10] or as described in chapter 3.2. **b** Variations of the results of repeated experiments can be explained by the influence of impurities in the used chemicals as well as the less-controlled conditions during the experiments and the uncertainties of the ^1H NMR spectroscopic analysis.

6.2. Depolymerization using TMG_2e following GP2

Table S3 Overview over depolymerization of PLA using TMG_2e and different nucleophiles following **GP2**.

Entry	Nu	#C	n_{PLA} [mmol]	n_{cat} [µmol]	V_{Nu} [mL]	t [h]	X_{int}^{a} [%]	S_{RLa}^{a} [%]	Y_{RLa}^{a} [%]
1	MeOH	1	3.47	34.7	1.0	0.08	100	98	98
2	EtOH	2	3.47	34.7	1.4	0.08	89	75	67
						0.17	100	75	75
						0.25	100	79	79
						1	100	89	89
						3	100	94	94
						24	100	100	100
3	EG	2	3.47	34.7	1.4	1	–	–	–
						48	100	–	100
4	PrOH	3	3.47	34.7	1.8	0.42	89	42	37
						1	99	49	48
						3	100	69	69
						24	100	96	96
						48	100	98	98
5	*i*PrOH	3	3.47	34.7	1.9	1	64	19	12
						24	100	36	36
						48	100	45	45
6	AlOH	3	3.47	34.7	1.7	0.42	100	100	100
7	BuOH	4	3.47	34.7	2.2	0.58	98	83	82
						3	100	94	94
						24	100	98	98
8	*i*BuOH	4	3.47	34.7	2.3	0.17	82	27	22
						1	82	26	21
						3	98	79	78
						48	100	96	96
9	*t*BuOH	4	3.47	34.7	2.3	2	PLA is slowly depolymerized. We did not identify the formed oligomeric species.		
10	*t*BuOH	4	3.47	34.7	2.3	72			
11	*t*BuOH	4	3.47	34.7	2.3	72			
12	PeOH	5	3.47	34.7	2.7	0.42	99	51	50
						1	100	65	65
						3	100	77	77
						24	100	96	96
						48	100	98	98
13	3PeOH	5	3.47	34.7	2.7	48	PLA is slowly depolymerized		
14	HeOH	6	3.47	34.7	3.1	0.42	100	62	62
						1	100	77	77
						3	100	91	91
						24	100	98	98
15	Me_2BuOH	6	3.47	34.7	3.1	1	75	22	17
						3	100	33	33
						24	100	64	64
						48	100	71	71
16	BnOH	7	3.47	34.7	2.6	0.42	85	100	85
						1	89	100	89
						24	99	100	99
17	OcOH	8	3.47	34.7	3.9	0.42	100	44	44
						3	98	85	83
						24	100	91	91
						48	100	93	93

a X_{int}, S_{RLa}, Y_{RLa} were calculated from ^{1}H NMR spectroscopic analysis according to literature[6, 10] or as described in chapter 3.2.

6.3. Depolymerization using Zn1 following GP2*

Table S4 Overview over depolymerization of PLA using **Zn1** and different nucleophiles following **GP2***.

Entry	Nu	#C	n_{PLA} [mmol]	n_{cat} [µmol]	V_{Nu} [mL]	t [h]	X_{int}^{a} [%]	S_{RLa}^{a} [%]	Y_{MRLa}^{a} [%]
1	PrOH	3	3.47	34.7	1.0	1	100	98	98
2	*i*PrOH	3	3.47	34.7	1.4	1	98	98	98
						2	99	98	97
3	OcOH	8	3.47	34.7	3.9	1	100	98	98

a X_{int}, S_{RLa}, Y_{RLa} were calculated from ^{1}H NMR spectroscopic analysis according to literature[6, 10] or as described in chapter 3.2.

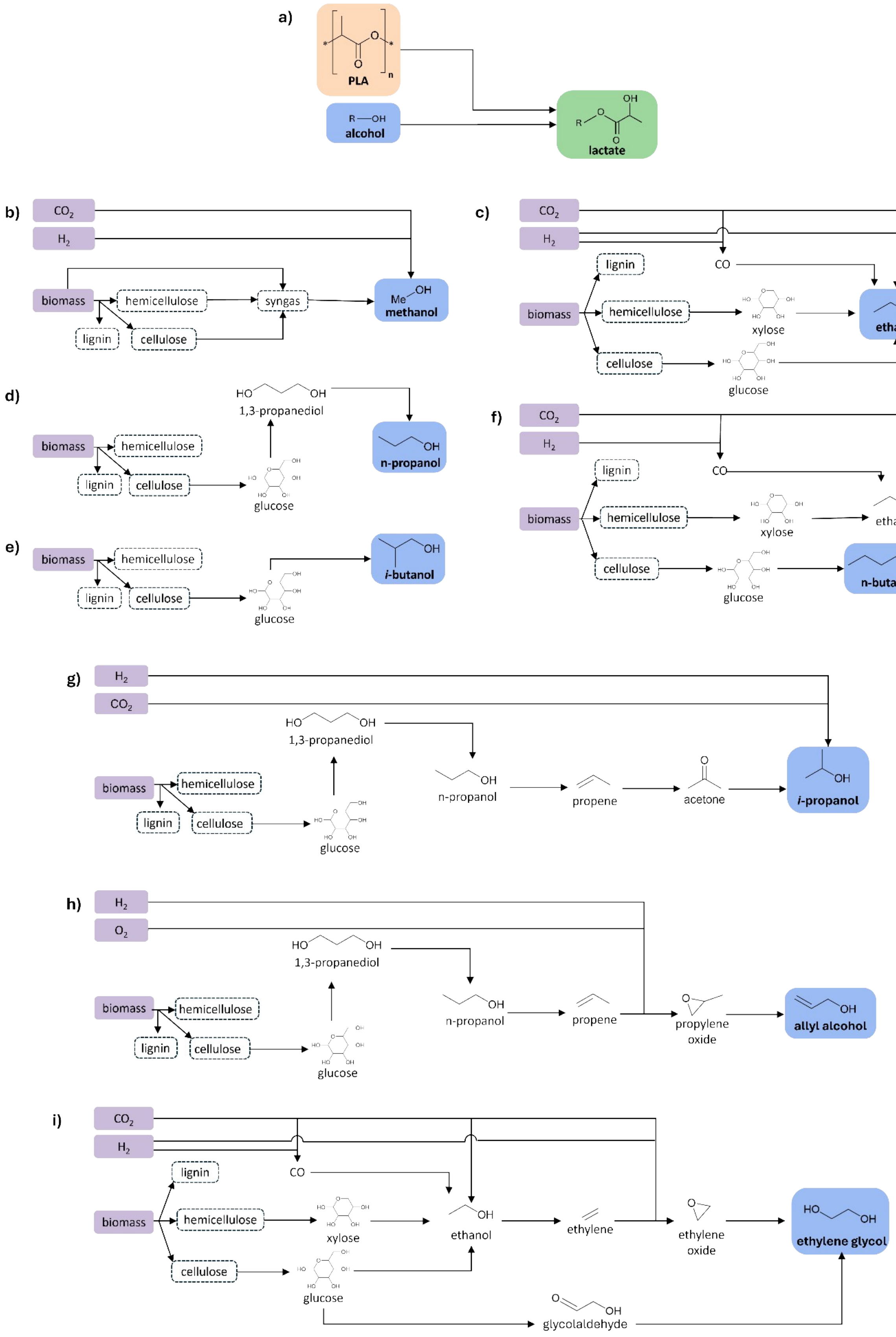
7. New data used in the RNFA analysis

For the pathway screening performed in this work, yield data listed in Table S5 were used in addition to data introduced in previous publications (see manuscript).

Table S5 Reaction selectivity of the reaction steps introduced in this work

Educts	Products	Yield	Reference
Glycerol	Allyl alcohol	98%	26
1,2-propandiol	Allyl alcohol	47%	27
propylene oxide	Allyl alcohol	88.9%	28
propylene, H2	propylene oxide, water	98%	29
Waste_oil, methanol	Glycerol, FAME	95%	30

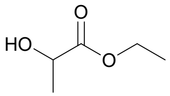
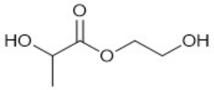
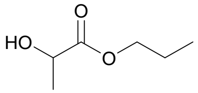
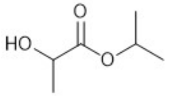
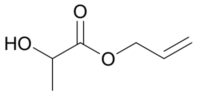
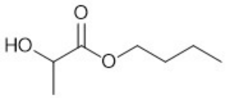
8. Production pathways present in the results shown in Figure 5

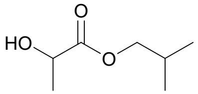
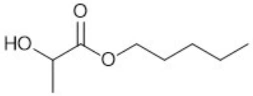
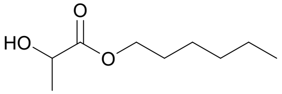
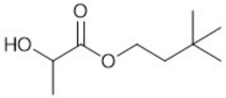
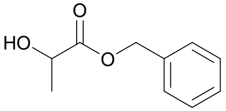
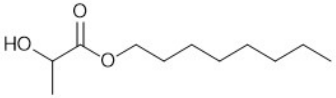


Scheme 2. Collection of all alternative and sequential pathways to produce the respective lactates from lignocellulosic biomass and renewable CO_2 and H_2. Each of the points in the pareto front of Figure 5 corresponds to one or a combination of pathways.

9. Product library

Table S6 Product library

Entry	Abbrevation	Name	Sum formular	SMILES	InChI	Molecular Structure	Reference
1	MeLa	methyl 2-hydroxypropanoate	$C_4H_8O_3$	COC(C(C)O)=O	InChI=1S/C4H8O3/c1-3(5)4(6)7-2/h3,5H,1-2H3		[8]
2	EtLa	ethyl 2-hydroxypropanoate	$C_5H_{10}O_3$	CCOC(C(C)O)=O	InChI=1S/C5H10O3/c1-3-8-5(7)4(2)6/h4,6H,3H2,1-2H3		[8]
3	EGLa	2-hydroxyethyl 2-hydroxypropanoate	$C_5H_{10}O_4$	OC(C)C(OCCO)=O	InChI=1S/C5H10O4/c1-4(7)5(8)9-3-2-6/h4,6-7H,2-3H2,1H3		[11]
4	PrLa	propyl 2-hydroxypropanoate	$C_6H_{12}O_3$	CCCOC(C(C)O)=O	InChI=1S/C6H12O3/c1-3-4-9-6(8)5(2)7/h5,7H,3-4H2,1-2H3		[8]
5	*i*PrLa	isopropyl 2-hydroxypropanoate	$C_6H_{12}O_3$	CC(C)OC(C(C)O)=O	InChI=1S/C6H12O3/c1-4(2)9-6(8)5(3)7/h4-5,7H,1-3H3		[8]
6	AlLa	allyl 2-hydroxypropanoate	$C_6H_{10}O_3$	C=CCOC(C(C)O)=O	InChI=1S/C6H10O3/c1-3-4-9-6(8)5(2)7/h3,5,7H,1,4H2,2H3		[11]
7	BuLa	butyl 2-hydroxypropanoate	$C_7H_{14}O_3$	OC(C)C(OCCCC)=O	InChI=1S/C7H14O3/c1-3-4-5-10-7(9)6(2)8/h6,8H,3-5H2,1-2H3		[8]

8	*i*BuLa	isobutyl 2-hydroxypropanoate	$C_7H_{14}O_3$	CC(C)COC(C(C)O)=O	InChI=1S/C7H14O3/c1-5(2)4-10-7(9)6(3)8/h5-6,8H,4H2,1-3H3		[8]
9	PeLa	pentyl 2-hydroxypropanoate	$C_8H_{16}O_3$	OC(C)C(OCCCCC)=O	InChI=1S/C8H16O3/c1-3-4-5-6-11-8(10)7(2)9/h7,9H,3-6H2,1-2H3		[8]
10	HeLa	hexyl 2-hydroxypropanoate	$C_9H_{18}O_3$	OC(C)C(OCCCCCC)=O	InChI=1S/C9H18O3/c1-3-4-5-6-7-12-9(11)8(2)10/h8,10H,3-7H2,1-2H3		[8]
11	Me_2BuLa	3,3-dimethylbutyl 2-hydroxypropanoate	$C_9H_{18}O_3$	O=C(C(O)C)OCCC(C)(C)C	InChI=1S/C9H18O3/c1-7(10)8(11)12-6-5-9(2,3)4/h7,10H,5-6H2,1-4H3		CAS number: 1856855-09-8 (racemate), 1847539-49-4 (S-isomer), 1841308-93-7 (L-isomer)
12	BnLa	benzyl 2-hydroxypropanoate	$C_{10}H_{12}O_3$	OC(C)C(OCC1=CC=CC=C1)=O	InChI=1S/C10H12O3/c1-8(11)10(12)13-7-9-5-3-2-4-6-9/h2-6,8,11H,7H2,1H3		[18-19]
13	OcLa	octyl 2-hydroxypropanoate	$C_{11}H_{22}O_3$	OC(C)C(OCCCCCCCC)=O	InChI=1S/C11H22O3/c1-3-4-5-6-7-8-9-14-11(13)10(2)12/h10,12H,3-9H2,1-2H3		[8]

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