Supporting Information

On-demand manufacture of circular 3D printing resins

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Experimental methods

Materials

All reagents were purchased from either Sigma-Aldrich or ThermoScientific and used as received. Lipoic acid (LA) was purchased from the supplement brand Peak Supps. Spectroscopic analysis of the Peak Supps product determined it was similar in composition to a product obtained from a conventional chemical supplier (Acros). The immobilized enzyme Sustine® 110 IM (Novozym®435) was supplied from Novozymes. A packed bed reactor used for the synthesis in flow was obtained from Omnifit glass chromatography columns (length = 150 mm; internal diameter = 6.6 mm, or length = 150 mm; internal diameter = 15 mm).

NMR spectroscopy. All NMR spectroscopy experiments were performed at 298 K on a Bruker DPX-400 NMR instrument equipped with a BBFO smart probe operating at 400 MHz for ^{1}H (100.57 MHz for ^{13}C). ^{1}H NMR spectra are referenced to solvent residual proton (δ = 7.26 for $CDCl_3$) and ^{13}C NMR spectra are referenced to the solvent signal (δ = 77.16 for $CDCl_3$). The resonance multiplicities are described as t (triplet), q (quartet), dq (doublet of quartets), dtd (doublet of triplet of doublets) dddd (doublet of doublet of doublet of doublets), or m (multiplet).

Mass Spectrometry. High Resolution Electrospray Ionization Mass Spectrometry was performed in the School of Chemistry at the University of Birmingham on a Waters Xevo G2-XS QTof Quadrupole Time-of-Flight mass spectrometer.

Fourier-transform Infrared Spectroscopy (FT-IR). All FT-IR spectroscopic analyses were performed on an Agilent Technologies Cary 630 FT-IR spectrometer at a resolution of 4 cm^{-1}. 16 Scans from 600 to 4000 cm^{-1} were performed and the spectra were corrected for background absorbance.

Differential Scanning Calorimetry (DSC). The thermal characteristics of the polymers were determined using differential scanning calorimetry (STARe system DSC3, Mettler Toledo) from −80 to 130 °C at a heating rate of 10 °C·min^{-1} for three heating/cooling cycles unless otherwise specified. The glass transition temperature (T_g) was determined from the inflection point in the second heating cycle of DSC.

Thermogravimetric Analysis (TGA). TGA thermograms were obtained using a Q550 Thermogravimetric Analyzer (TA instrument). Thermograms were recorded under an N_2 atmosphere at a heating rate of 10 °C·min^{-1}, from 10 to 600 °C, with an average sample weight of *ca*. 5 mg. Aluminium pans were used for all samples. Decomposition temperatures were reported as the 5% weight loss temperature ($T_{d,5\%}$).

Digital light processing (DLP) printing. Printing was performed on an unmodified MiiCraft Ultra 125 printer. For each print, 2 base layers were irradiated for 160 s. The buffer layer number was set to 5, and each layer after that was irradiated for 60 s.

Determination of power consumption. The power consumption was recorded using a 4-3680 W energy consumption meter and compared with previously reported processes.[1]

Set up Continuous Flow

Esterification reactions in continuous flow were completed using an EZ Omnifit® glass chromatography column 6.6 mm x 150 mm, 900 psi, with one adjustable end piece to adjust bed height. Plastic tubing was used for maximum flexibility. An AL-300 syringe pump from World Precision Instruments was fitted with a 20 mL (inner diameter 20.1 mm) plastic syringe dispensing at a flow rate of 0.05-0.1 mL min^{-1}. Residence time (τ) was determined using the formula below:

$$Residence\ time\ (\mathrm{min}) = internal\ volume\ (mL)\ /\ flow\ rate\ (mL\ min^{-1})$$

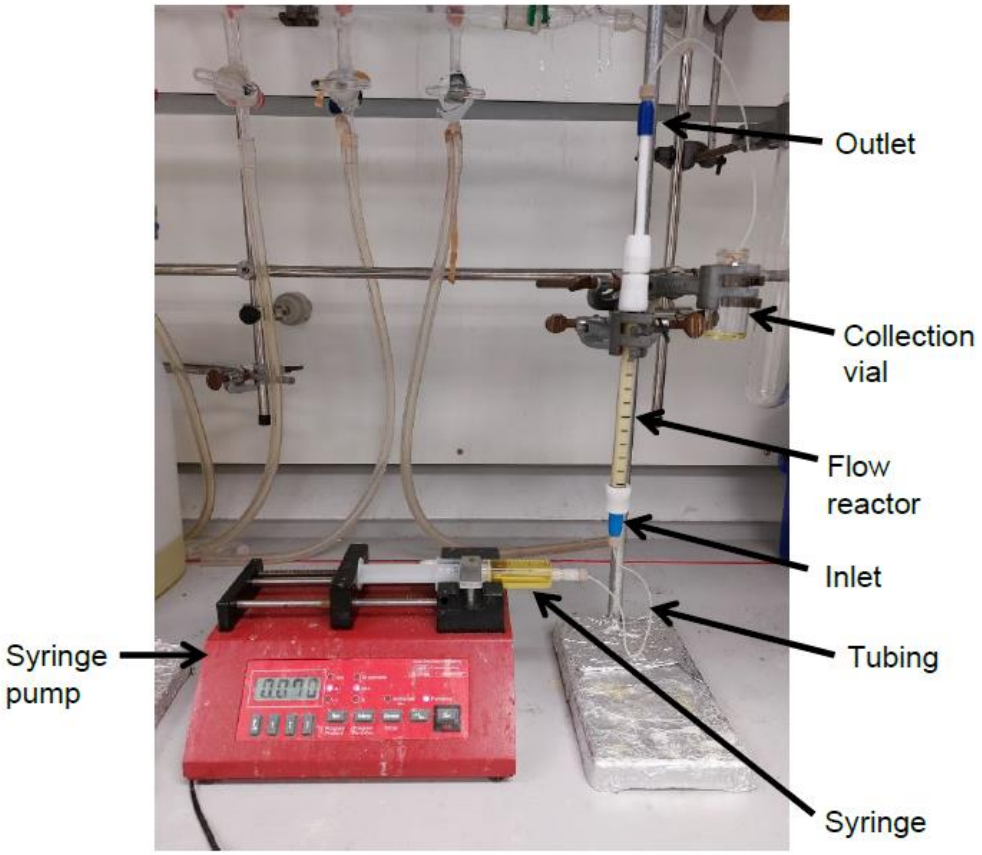
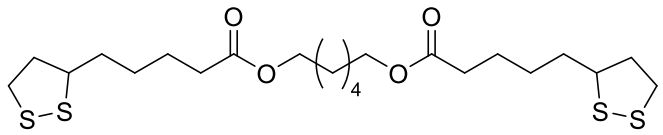


Figure S1. Continuous flow equipment set up with an AL-300 syringe pump fitted with a 20 mL plastic syringe and Onmifit® glass chromatography column.

Experimental procedures

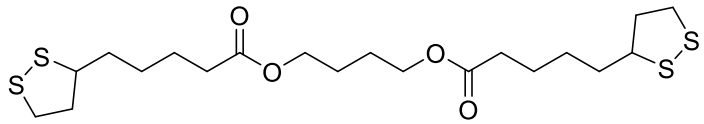
Synthesis of $HexLp_2$ under batch conditions



A 500 mL 1-neck amber coloured round bottom flask (RBF) was charged with lipoic acid (36.7 g, 177.8, 2.1 equiv.), 1,6-hexanediol (10 g, 84.6 mmol, 1 equiv.), DMAP (21.7 g, 177.8 mmol, 2.1 equiv.) and CH_2Cl_2 (200 mL). The solution was cooled in an ice bath for 15 minutes, followed by portion-wise addition of EDC·HCl (34.1 g, 177.8 mmol, 2.1 equiv.) over the course of 10 minutes. The reaction was left shielded from light and allowed to warm up to room temperature under stirring overnight (*ca.* 16 h). The reaction mixture was washed with HCl 1 M (3×100 mL), $NaHCO_3$ (1×100 mL), and brine (1×100 mL). The organic layer was then dried over $MgSO_4$, filtered, and concentrated *in vacuum* to obtain the desired product as a yellow viscous liquid (36 g, 86% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 4.05 (t, J = 6.7 Hz, 4H), 3.56 (dq, J = 8.6, 6.4 Hz, 2H), 3.26 – 2.97 (m, 4H), 2.45 (dtd, J = 13.1, 6.6, 5.3 Hz, 2H), 2.30 (t, J = 7.4 Hz, 4H), 1.90 (dq, J = 12.7, 6.9 Hz, 2H), 1.78 – 1.57 (m, 12H), 1.46 (dddd, J = 15.8, 9.0, 5.4, 1.9 Hz, 4H), 1.41 – 1.27 (m, 4H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ 173.64, 64.35, 56.44, 40.31, 38.58, 34.69, 34.18, 28.85, 28.62, 25.70, 24.80. HMRS (TOF-ASAP) (*m/z*): [M + H] calculated for $C_{22}H_{38}O_4S_4$ H, 495.1731; found 495.1722, FT-IR: 1726 cm^{-1}, C=O ester bond.

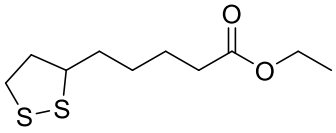
Synthesis of $ButLp_2$ under batch conditions



Lipoic acid (5.1 g, 24.7 mmol, 2.1 equiv.) was dissolved in CH_2Cl_2 (15 mL) in a 20 mL vial covered in foil. To this was added 1,4-butanediol (1.06 g, 11.8 mmol, 1 equiv.) and Novozym®435 (500 mg). The vial was then placed on an orbital shaker at 250 rpm for 24 hours. After this, the catalyst was filtered out and the organic layer was washed with $NaHCO_{3\,(aq.)}$ saturated solution (3×30 mL), brine (3×30 mL), and then dried over $MgSO_4$. After filtration, the product was concentrated *in vacuum* to yield a mixture of $ButLp_2$ and 1,4-butanediol (<8% molar content by ^{1}H NMR spectroscopy). The product was purified *via* column chromatography (1:1 Hexane:Ethyl acetate) to yield a yellow liquid (3.52 g, 64% yield).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 4.09 (ddt, J = 5.3, 3.8, 1.4 Hz, 4H), 3.56 (dq, J = 8.4, 6.4 Hz, 2H), 3.25 – 3.02 (m, 4H), 2.46 (dtd, J = 13.1, 6.6, 5.4 Hz, 2H), 2.32 (t, J = 7.4 Hz, 4H), 1.90 (dq, J = 12.8, 6.9 Hz, 2H), 1.80 – 1.60 (m, 12H), 1.57 – 1.39 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.61, 63.96, 56.48, 40.37, 38.63, 34.74, 34.19, 28.90, 25.47, 24.82. HMRS (TOF-ASAP) (*m/z*): [M + H] calculated for $C_{20}H_{34}O_4S_4$ 466.134: found 466.1351. FT-IR: 1730 cm^{-1}, C=O ester bond.

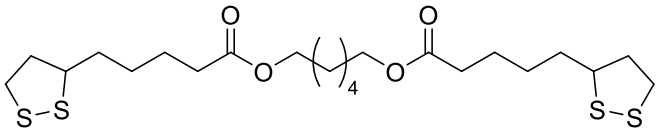
Synthesis of $EtLp_1$ under continuous flow conditions



The continuous flow reactor was loaded with Novozym®435 (500 mg). The catalyst was allowed to swell to its maximum volume by pumping CH_2Cl_2 at 0.7 mL min^{-1} for 10 minutes at room temperature using a syringe pump. The flow rate was adjusted to 0.1 mL min^{-1} allowing CH_2Cl_2 to pump through for a further 10 minutes. A solution of lipoic acid (5 g, 24.2 mmol, 1 equiv.) and CH_2Cl_2 (10 mL) was prepared in a 20 mL vial covered in aluminium foil. To this was added ethanol (1.5 mL, 25.4 mmol, 1.05 equiv.) and shaken to obtain a homogeneous solution. A syringe was filled with the prepared solution and was pumped through the reactor at 0.1 mL min^{-1}. The crude product was collected at 1 hour intervals to calculate conversion *vs*. time and the samples were analysed by ^{1}H NMR spectroscopy. Spectroscopic data are in agreement with previously reported information.[2]

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 4.12 (q, J = 7.2 Hz, 2H), 3.56 (dq, J = 8.4, 6.4 Hz, 1H), 3.23 – 3.05 (m, 2H), 2.45 (dtd, J = 13.1, 6.5, 5.4 Hz, 1H), 2.31 (t, J = 7.4 Hz, 2H), 1.91 (dq, J = 12.9, 6.9 Hz, 1H), 1.77 – 1.57 (m, 3H), 1.57 – 1.37 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ 173.69, 60.41, 56.44, 40.30, 38.57, 34.67, 34.20, 28.83, 24.77, 14.32.

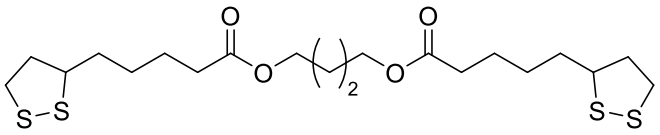
Synthesis of $HexLp_2$ under continuous flow conditions



The continuous flow reactor was loaded with Novozym®435 (2.0 g). The catalyst was allowed to swell to its maximum volume by pumping CH_2Cl_2 at 0.7 mL min^{-1} for 10 minutes at room temperature using a syringe pump. The flow rate was adjusted to 0.1 mL min^{-1} allowing CH_2Cl_2 to pump through for a further 10 minutes. A solution of lipoic acid (7.5 g, 36.4 mmol, 2 equiv.) and CH_2Cl_2 (15 mL) was prepared in a 20 mL vial covered in aluminium foil. To this was added 1,6-hexanediol (2.15 g, 18.2 mmol, 1 equiv.) and shaken at 250 rpm to obtain a homogeneous solution. A syringe was filled with the prepared solution and was pumped through the reactor at 0.1 mL min^{-1}. The crude product was collected at 1 hour intervals to calculate conversion *vs*. time and the samples were analysed by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 4.06 (t, J = 6.7 Hz, 4H), 3.57 (dq, J = 8.4, 6.4 Hz, 2H), 3.23 – 3.06 (m, 4H), 2.46 (dtd, J = 12.9, 6.5, 5.3 Hz, 2H), 2.31 (t, J = 7.4 Hz, 4H), 1.90 (dq, J = 12.7, 7.0 Hz, 2H), 1.77 – 1.54 (m, 12H), 1.54 – 1.41 (m, 4H), 1.40 – 1.32 (m, 4H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ 173.72, 64.43, 56.50, 40.37, 38.63, 34.75, 34.25, 28.92, 28.68, 25.76, 24.86.

Synthesis of ButLp$_2$ under continuous flow conditions



The continuous flow reactor was loaded with Novozym®435 (2.0 g). The catalyst was allowed to swell to its maximum volume by pumping CH_2Cl_2 at 0.7 mL min^{-1} for 10 minutes at room temperature using a syringe pump. The flow rate was adjusted to 0.1 mL min^{-1} allowing CH_2Cl_2 to pump through for a further 10 minutes. A solution of lipoic acid (7.5 g, 36.4 mmol, 2 equiv.) and CH_2Cl_2 (15 mL) was prepared in a 20 mL vial covered in aluminium foil. To this was added 1,4-butanediol (1.64 g, 18.2 mmol, 1 equiv.) and shaken to obtain a homogeneous solution. A syringe was filled with the prepared solution and was pumped through the reactor at 0.1 mL min^{-1}. The crude product was collected at 1 hour intervals and the samples were analysed by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 4.09 (t, 4H), 3.57 (dq, J = 8.3, 6.4 Hz, 2H), 3.24 – 3.05 (m, 4H), 2.46 (dtd, J = 12.9, 6.5, 5.4 Hz, 2H), 2.32 (t, J = 7.4 Hz, 4H), 1.90 (dq, J = 12.6, 7.0 Hz, 2H), 1.79 – 1.56 (m, 12H), 1.56 – 1.34 (m, 4H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ 173.63, 63.98, 56.49, 40.37, 38.64, 34.74, 34.20, 28.91, 25.48, 24.83.

Photocurable resins preparation

Two packed bed reactors [Omnifit glass chromatography column: length = 150 mm; internal diameter = 6.6 mm] were loaded with Novozym®435 (800 mg). The catalyst was allowed to swell to its maximum volume by pumping CH_2Cl_2 at 0.7 mL min^{-1} for 10 min at room temperature using a syringe pump (20 mL syringe; internal diameter = 20.1 mm). The flow rate was adjusted to 0.1 mL min^{-1}, allowing CH_2Cl_2 to pump through for a further 10 minutes.

Two solutions of lipoic acid (7.5 g, 36.4 mmol, 2 equiv.) and CH_2Cl_2 (15 mL) were prepared in two different 20 mL scintillation vials and covered with foil. To one of these, 1,4-hexanediol (2.15 g, 18.2 mmol, 1 equiv.) was added while ethanol (2.55 mL, 43.7 mmol, 1.2 equiv.) was added to the other. Both vials were shaken at 250 rpm to obtain a homogeneous solution. The solutions were pumped into each reactor at a flow rate of 0.1 mL min^{-1}. The outlets of each reactor were connected at a T-junction. The products were collected in a separating funnel and was concentrated by bubbling nitrogen through. The composition of the final resin was analysed *via* ^{1}H NMR spectroscopy.

NMR spectra

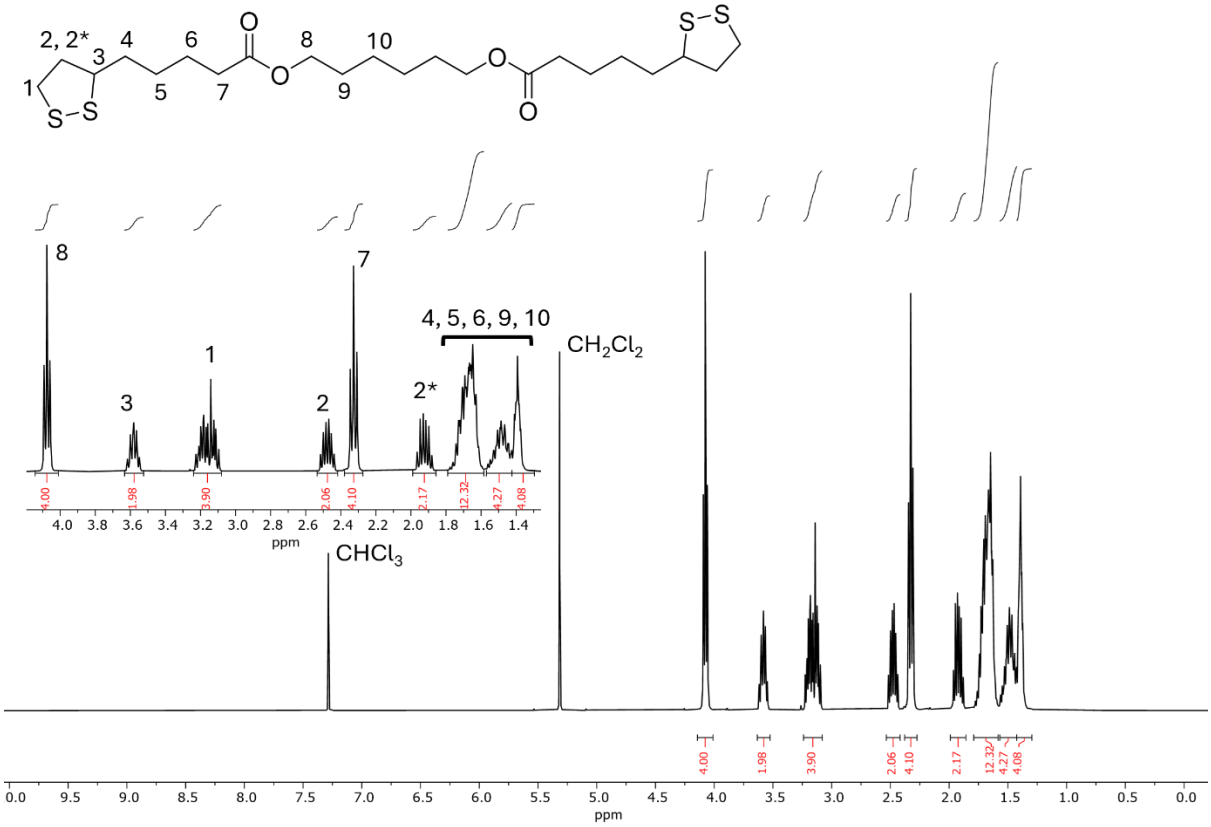


Figure S2. ^{1}H NMR spectrum of $HexLp_2$ prepared in batch – $CDCl_3$, 400 MHz, 298 K.

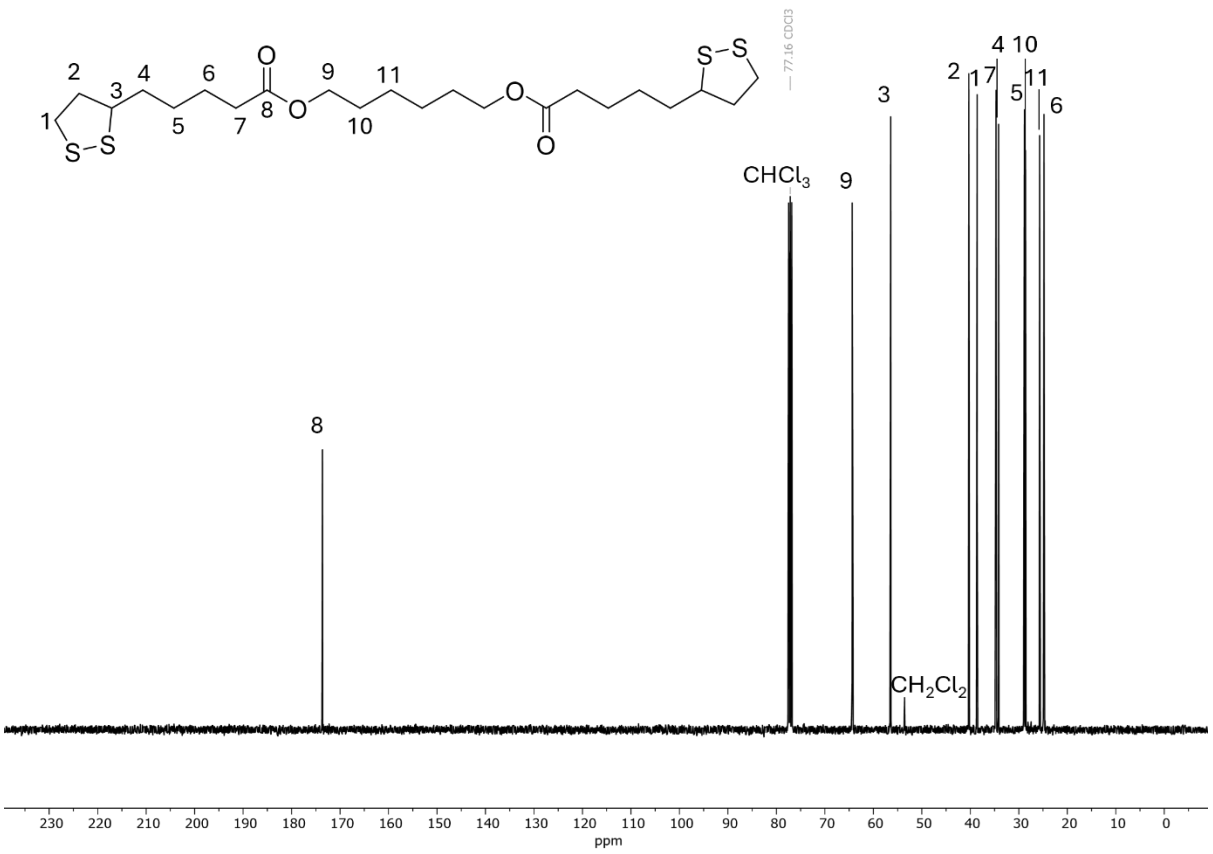


Figure S3. ^{13}C NMR spectrum of $HexLp_2$ prepared in batch – $CDCl_3$, 100.57 MHz, 298 K.

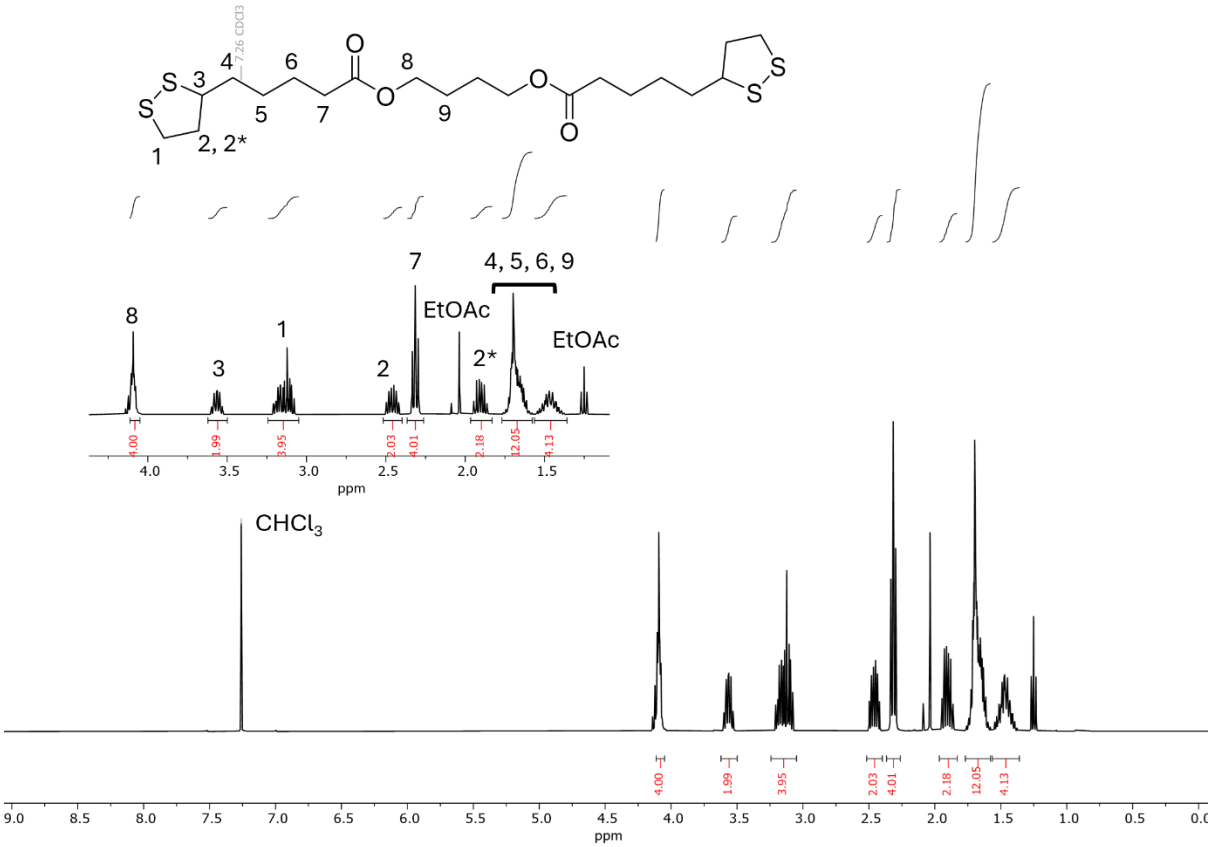


Figure S4. ^{1}H NMR spectrum of ButLp$_2$ prepared in batch – $CDCl_3$, 400 MHz, 298 K.

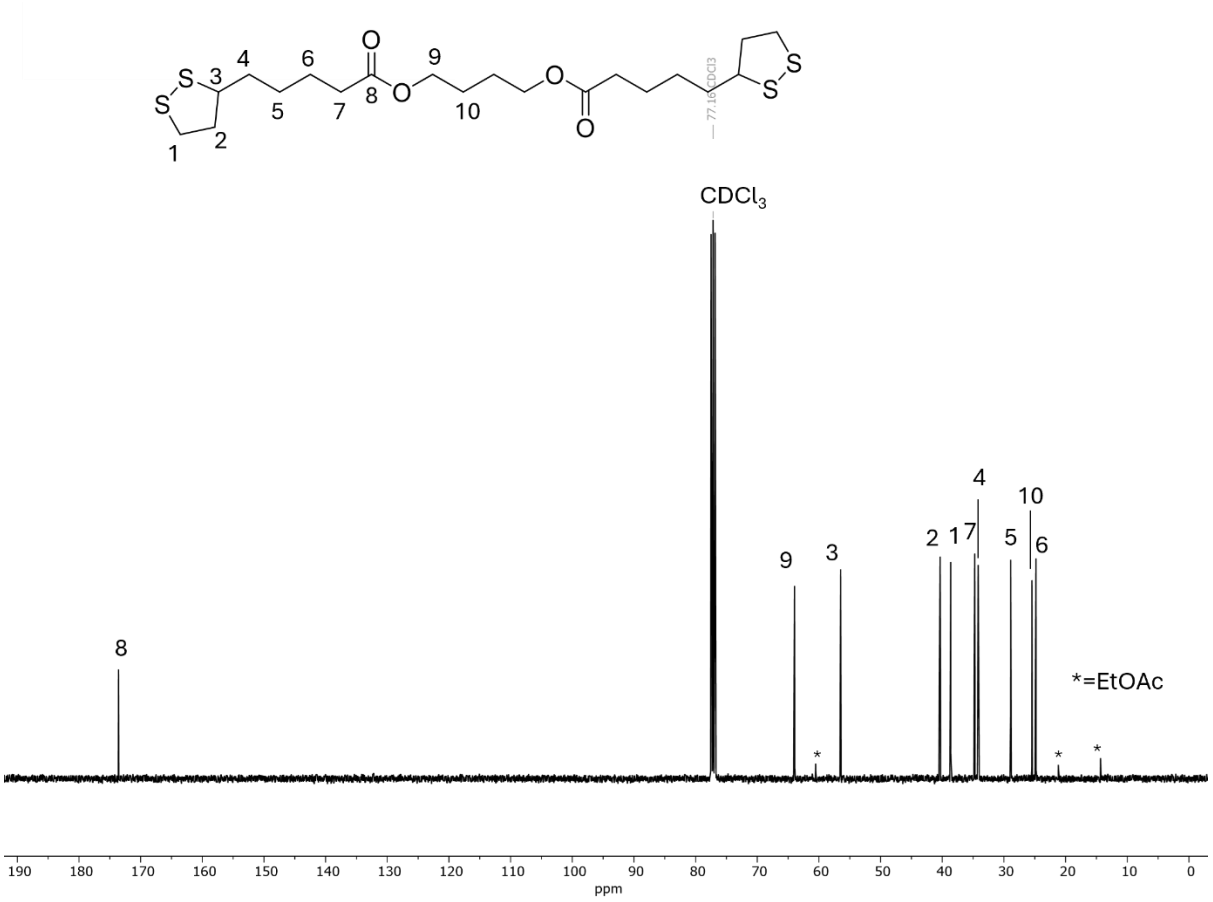


Figure S5. ^{13}C NMR spectrum of $ButLp_2$ prepared in batch $CDCl_3$, 100.57 MHz, 298 K.

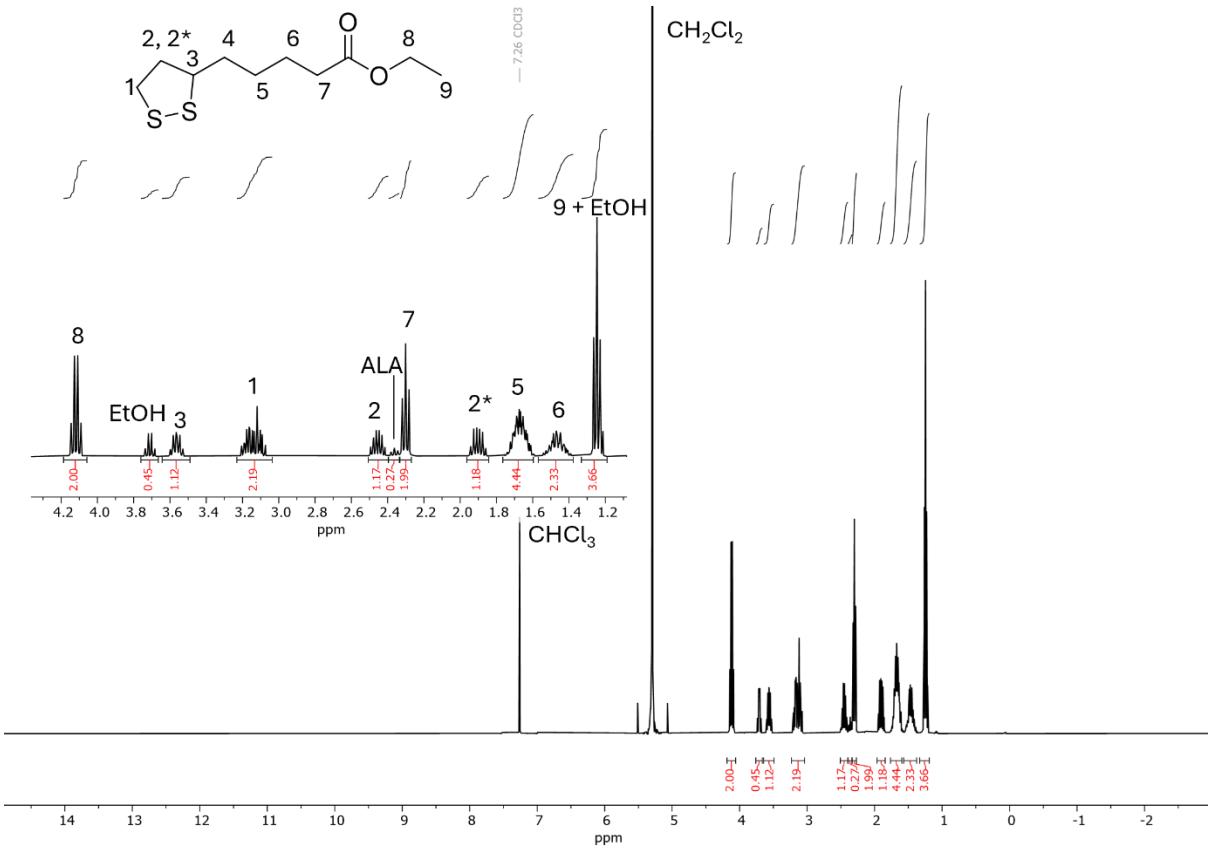


Figure S6. ^{1}H NMR spectrum of EtLp$_1$ prepared under continuous flow conditions – $CDCl_3$, 400 MHz, 298 K.

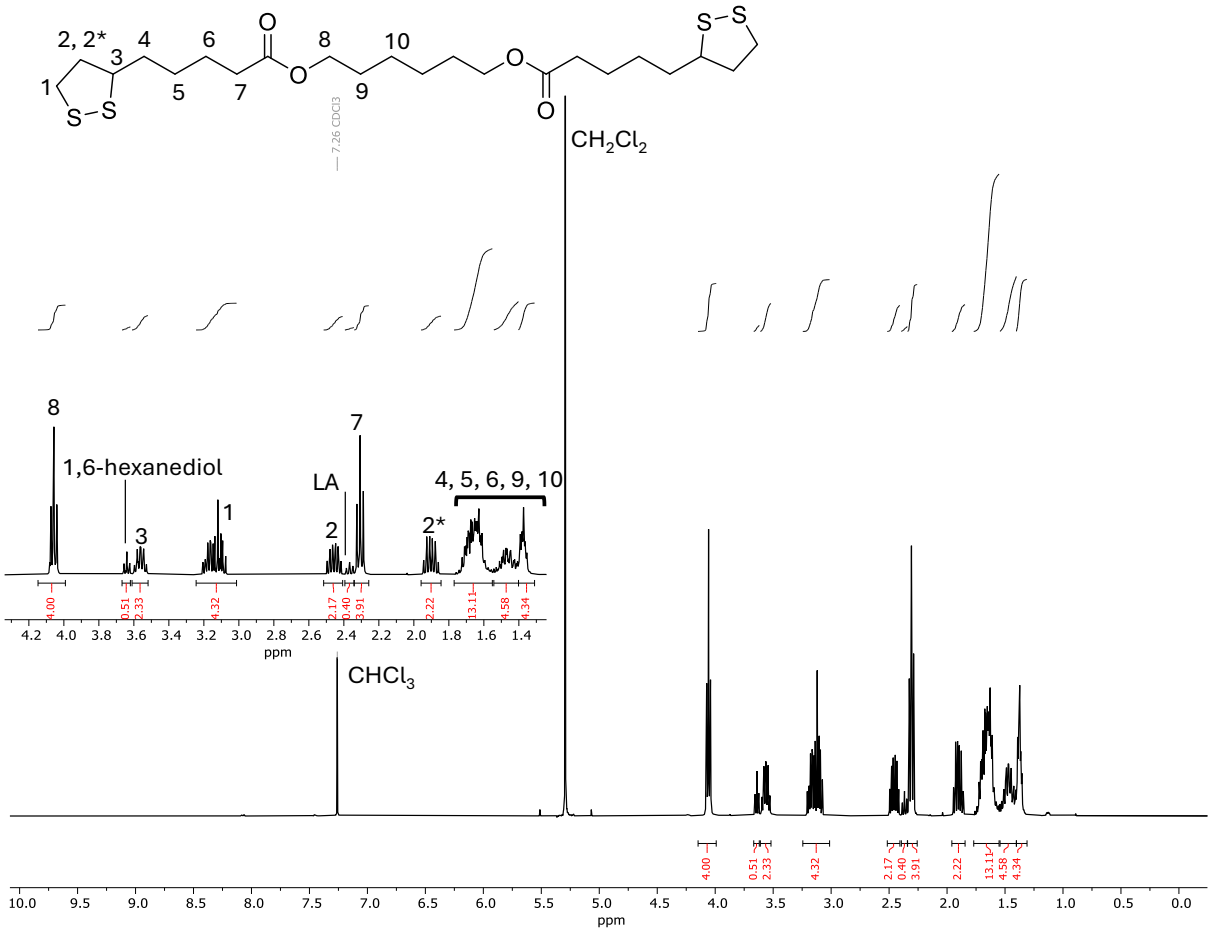


Figure S7. ^{1}H NMR spectrum of HexLp$_2$ prepared under continuous flow conditions – $CDCl_3$, 400 MHz, 298 K.

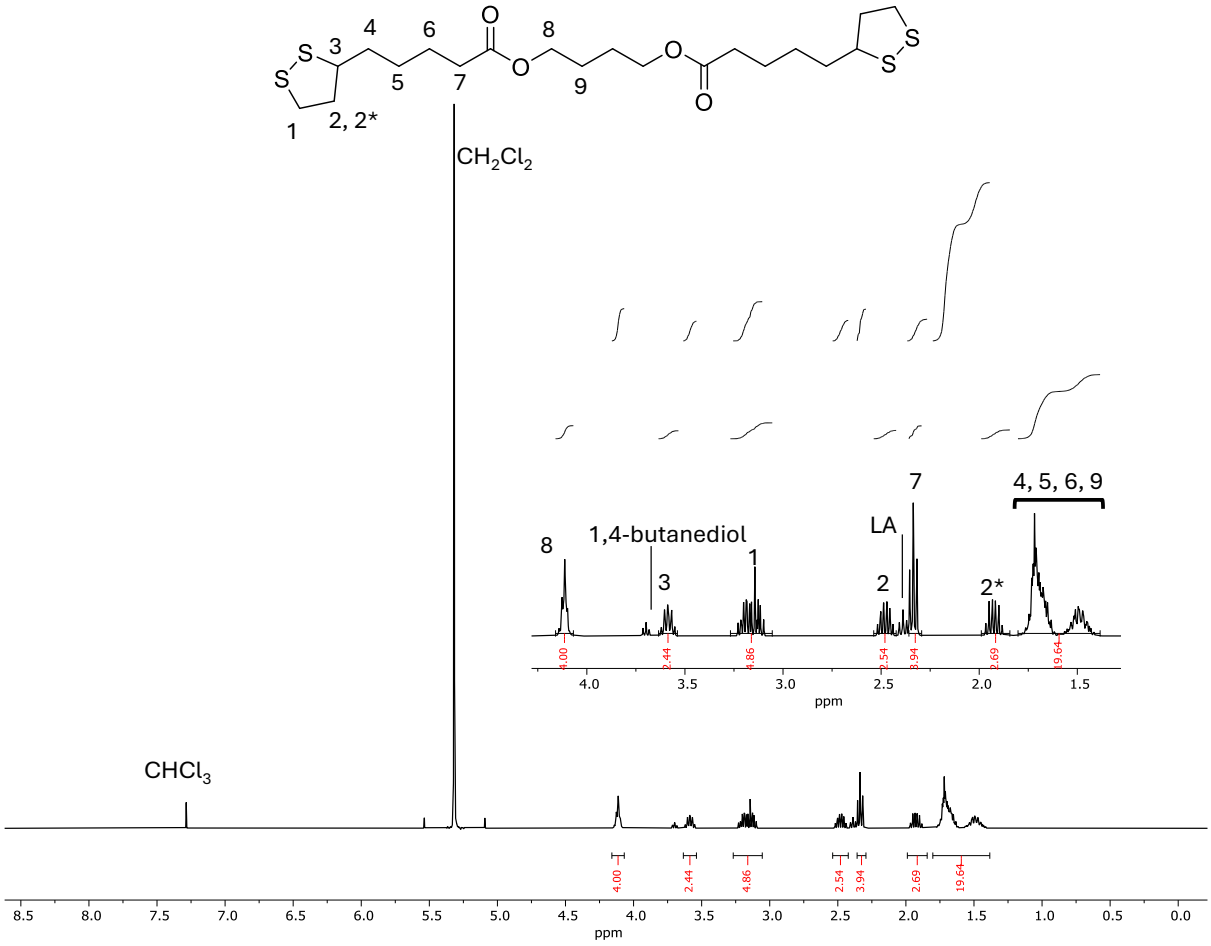


Figure S8. ^{1}H NMR spectrum of ButLp$_2$ prepared under continuous flow conditions – $CDCl_3$, 400 MHz, 298 K.

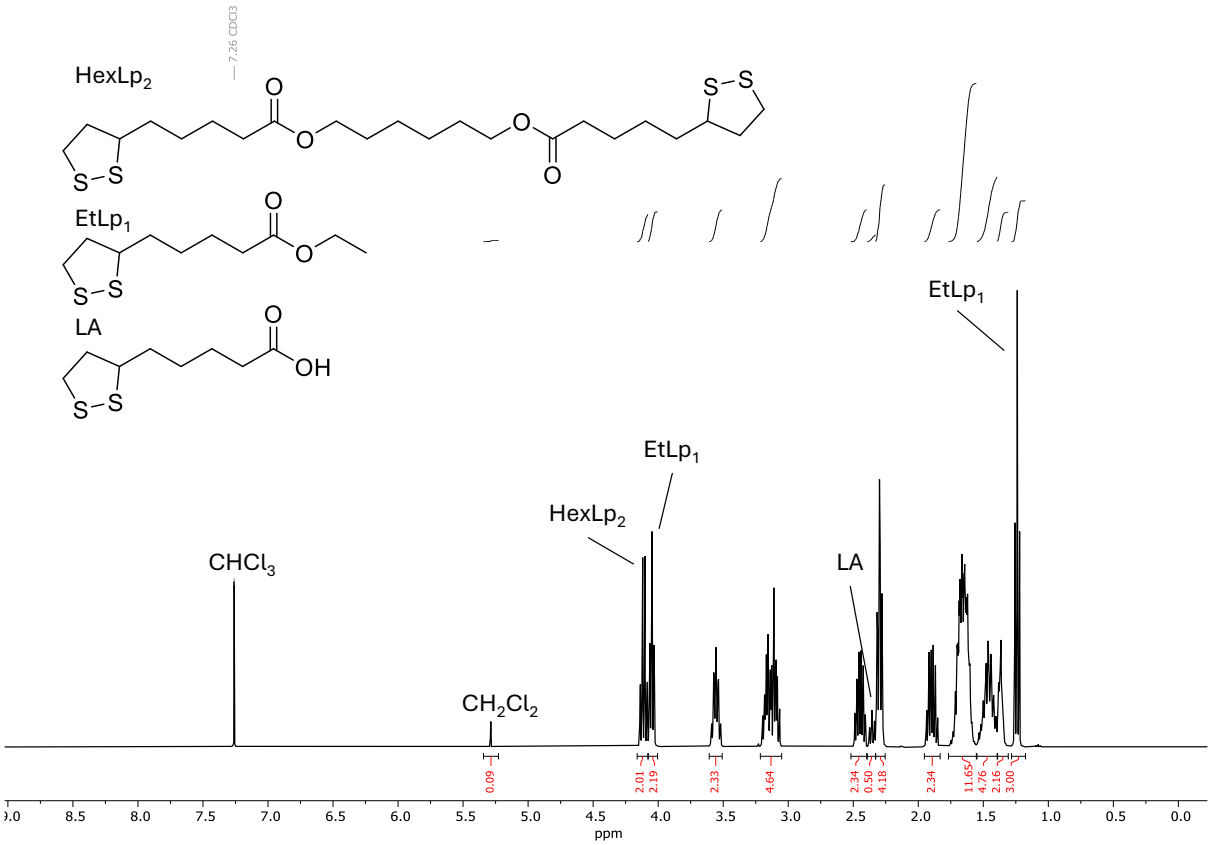


Figure S9. ^{1}H NMR spectrum of $HexLp_2$:$EtLp_1$:LA (57:31:12 mol%) resin prepared under continuous flow conditions – $CDCl_3$, 400 MHz, 298 K.

FT-IR of monomers

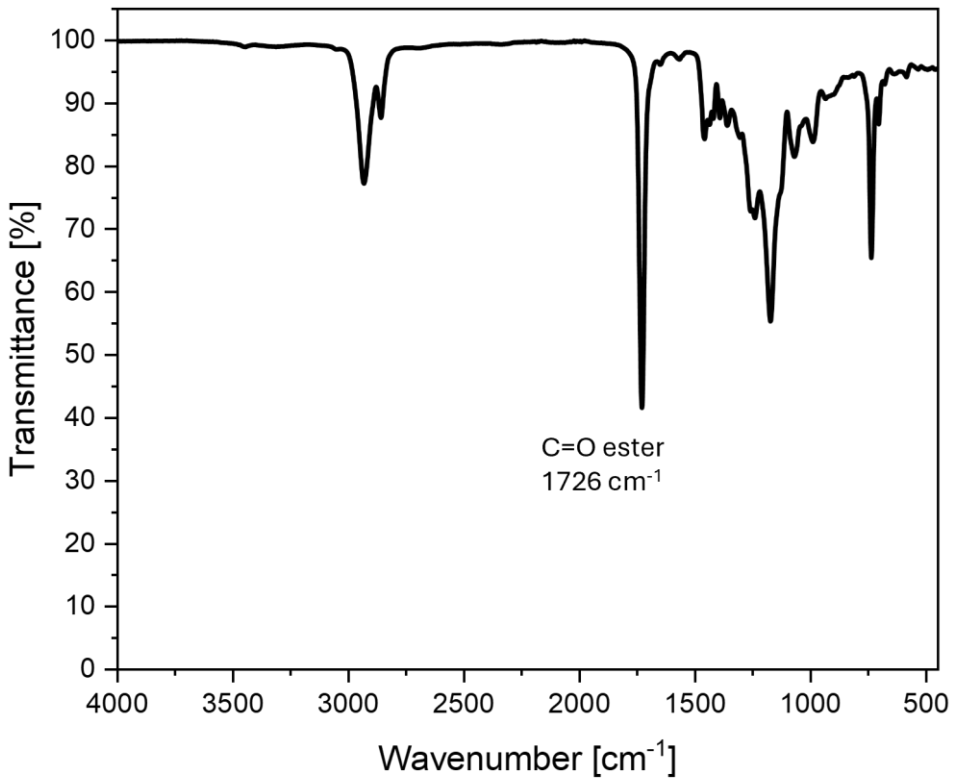


Figure S10. FT-IR spectrum of $HexLp_2$.

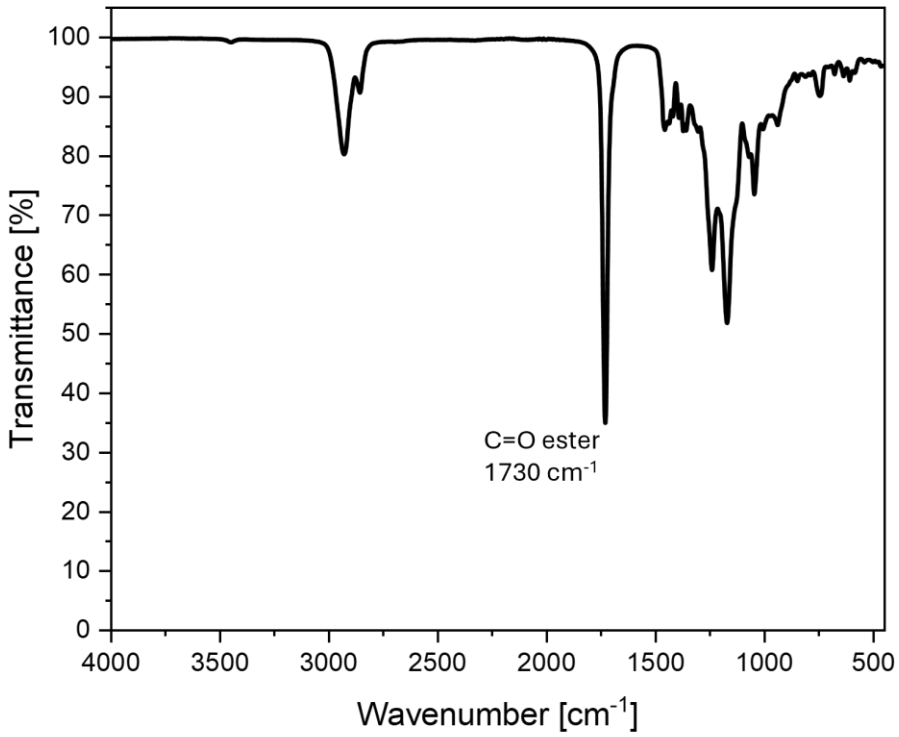


Figure S11. FT-IR spectrum of ButLp2.

Continuous flow experiments

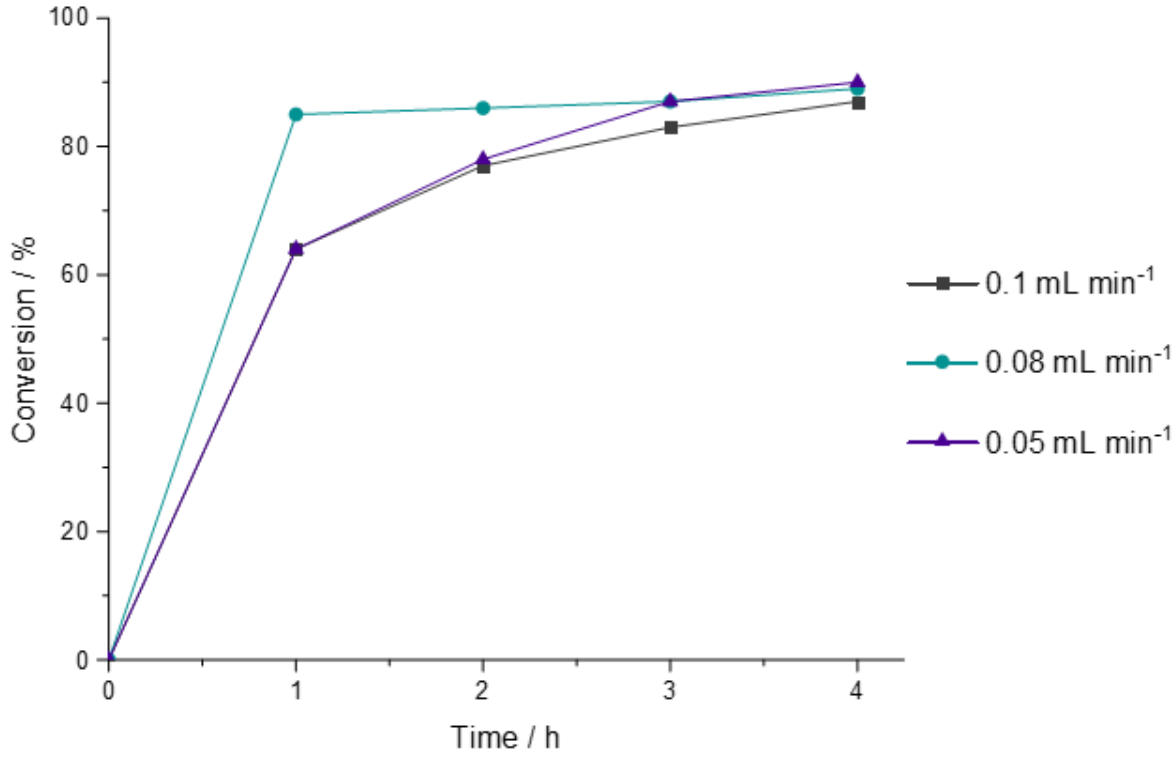


Figure S12. LA to $HexLp_2$ plot of conversion *vs*. time at different flow rates, in CH_2Cl_2 calculated by ^1H NMR spectroscopy.

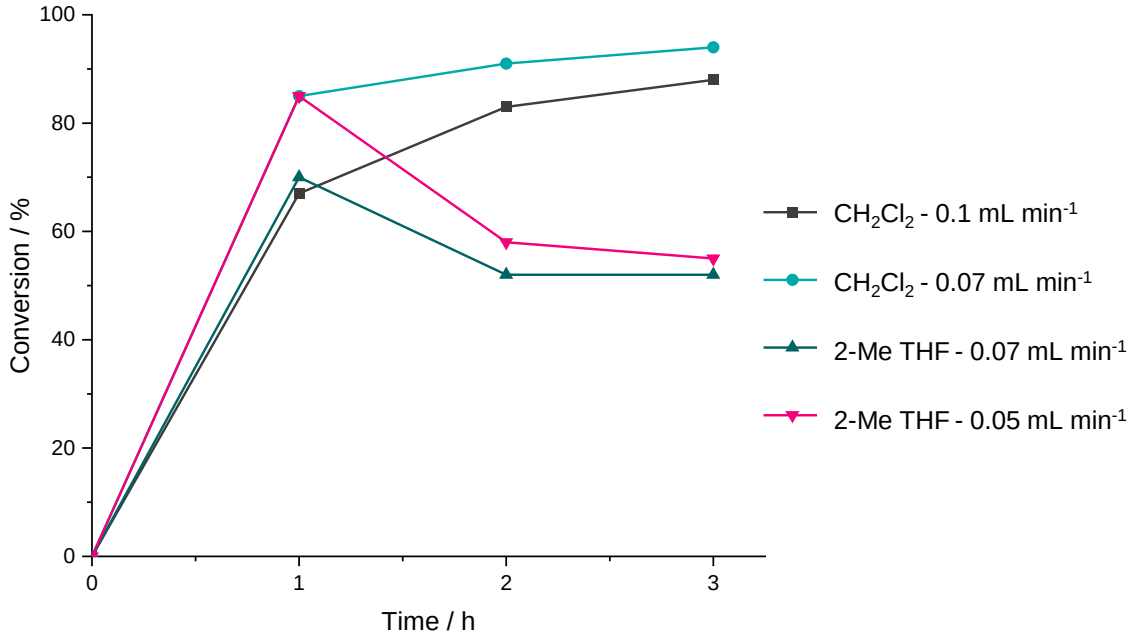


Figure S13. LA to $EtLp_1$ plot of conversion *vs*. time in CH_2Cl_2 and 2-Me THF calculated by ^1H NMR spectroscopy.

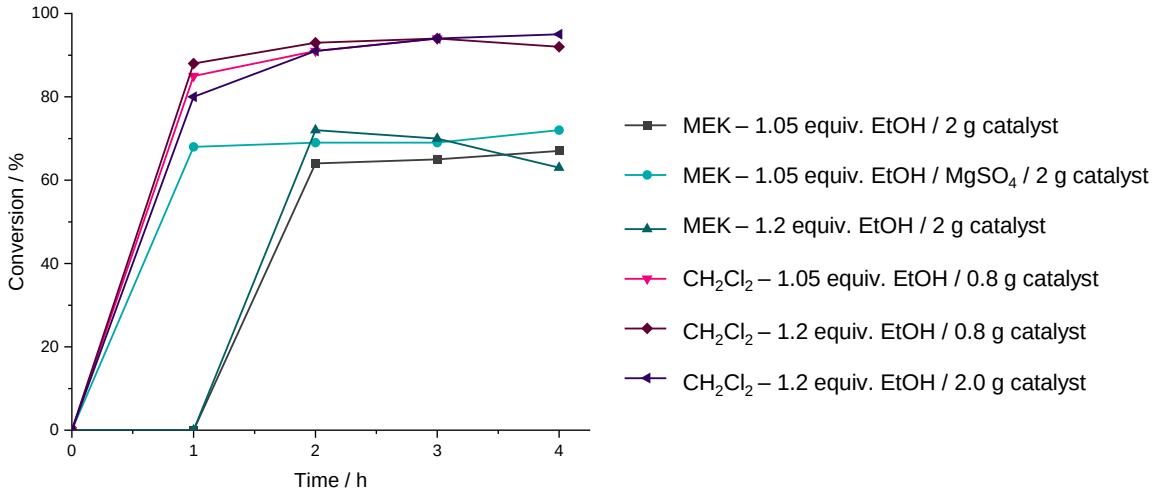


Figure S14. LA to EtLp$_1$ plot of conversion *vs*. time in CH_2Cl_2 and MEK calculated by ^{1}H NMR spectroscopy.

2D photosets and DSC thermograms

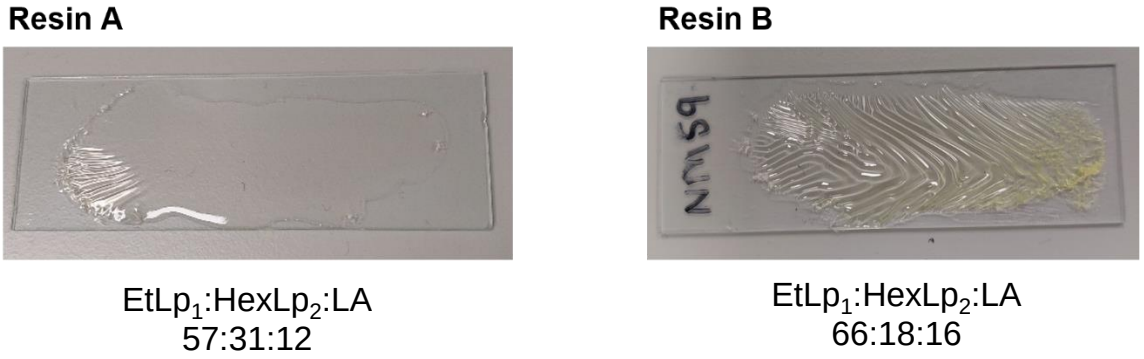


Figure S15. 2D photosets of $EtLp1_1$:$HexLp_2$ resin with varying $EtLp1_1$:$HexLp_2$:LA composition expressed in mol%.

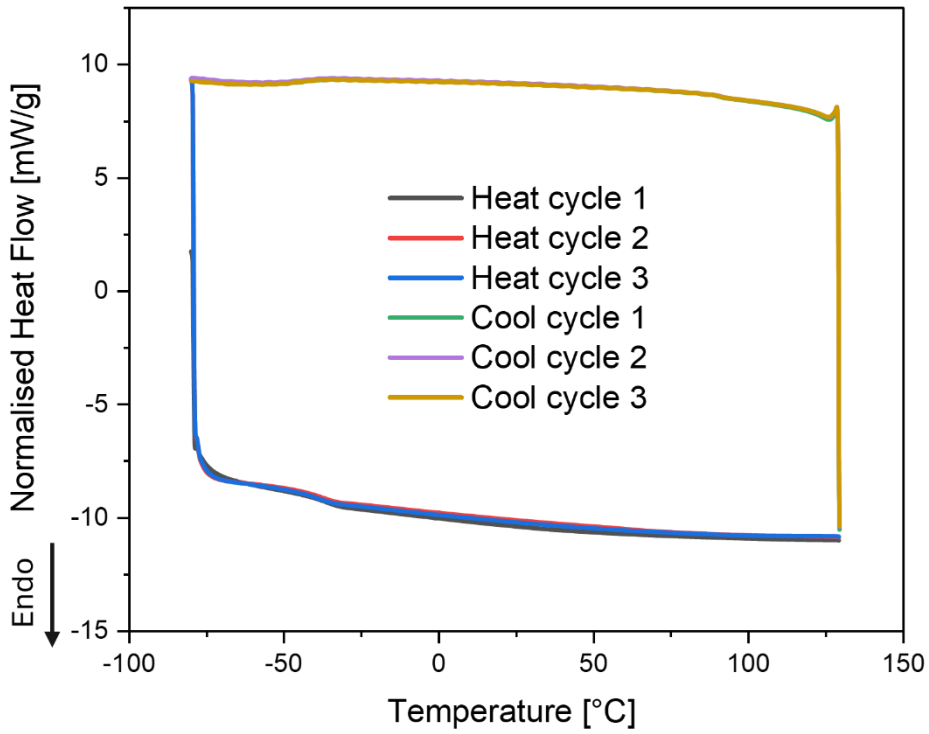


Figure S16. DSC thermogram of Resin A (57:31:12, $EtLp_1$: $HexLp_2$:LA) after post curing at 60 °C for 24 h (−80 – 130 °C, 10 °C×min^{-1}, N_2)

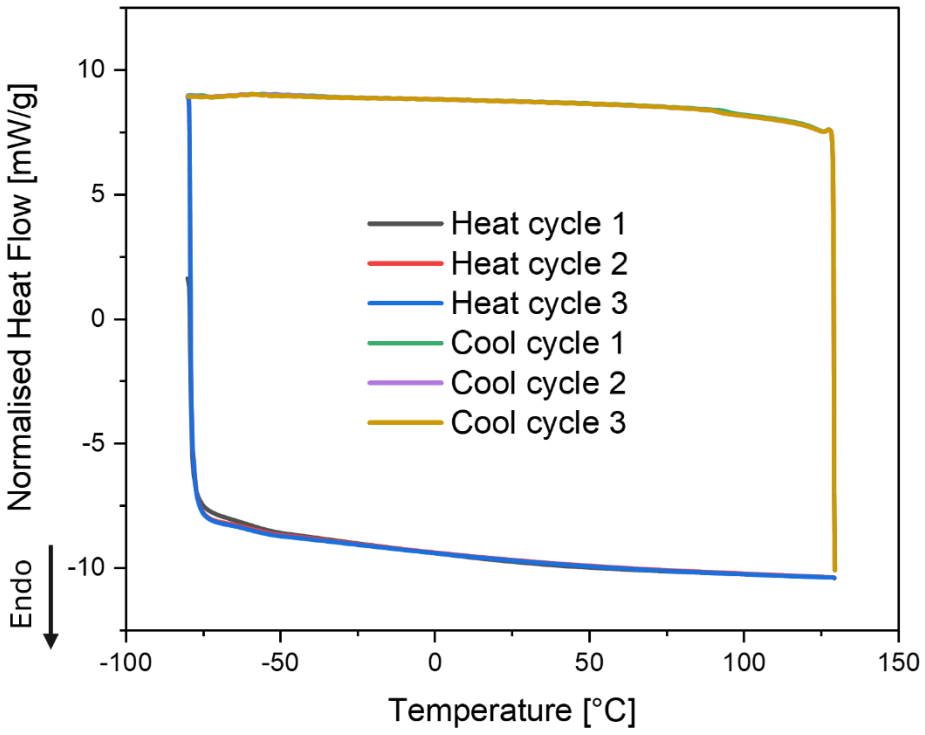


Figure S17. DSC thermogram of Resin B (66:18:16, $EtLp_1$: $HexLp_2$:LA) after post curing at 60 °C for 24 h (−80 – 130 °C, 10 °C×min^{-1}, N_2)

Green chemistry metrics

Atom economy AE. The atom economy was calculated according to the equation introduced by Anastas and Eghbali.[3]

$$AE = \frac{molecular\ weigth\ product}{molecular\ weight\ reagents}\ x\ 100$$

EDC coupling (petrochemical esterification)

$$AE = \frac{MW\ EtLp1}{MW\ EtOH+MW\ LA+MW\ DMAP+MW\ EDC*HCl} * 100 = \frac{234.37}{206.32+46.07+122.17+155.24} * 100 = 44$$

Continuous flow enzymatic esterification (the enzyme has not been considered as it is continuously recycled)

$$AE = \frac{MW\ EtLp1}{MW\ EtOH + MW\ LA} = \frac{234.37}{206.33 + 46.07} * 100 = 93$$

E factor. The E factor was calculated according to the equation of Sheldon.[4]

Both *E* factors show relatively high values due to the laboratory scale, where comparatively large amounts of solvents are required. To better assess the impact of the actual waste generated by the reactions, the *E* factors were also calculated, excluding all solvents.

$$E\ factor = \frac{mass\ waste}{mass\ product}$$

EDC coupling (petrochemical esterification)

$$E\ factor = \frac{m_{unreacted\ LA} + m_{unreacted\ EtOH} + m_{DMAP} + m_{Urea\ from\ EDC} + m_{solvent}}{m_{EtLp1}} =$$

$$E\ factor = \frac{4.4\ g + 1.03\ g + 11.8\ g + 20.1\ g + 266\ g}{17.8\ g} = 17.04$$ (including the solvent)

$$E\ factor = \frac{4.4\ g + 1.03\ g + 11.8\ g + 20.1\ g}{17.8\ g} = 2.097$$ (without solvent)

Continuous flow enzymatic esterification (the enzyme has not been considered as it is continuously recycled)

$$E\ factor = \frac{m_{unreacted\ LA} + m_{unreacted\ EtOH} + m_{solvent}}{m_{EtLp1}} =$$

$$E\ factor = \frac{0.1 + 0.16 + 6.9}{2.8} = 2.57$$ (including the solvent)

$$E\ factor = \frac{0.1 + 0.16}{2.8} = 0.093$$ (without solvent)

Table S1. Reaction parameter and sustainability comparison factors of atom economy and *E* factor of the petrochemical epoxidation (EDC) and the enzymatic epoxidation (Enz).[a]

	Reaction Time	**Yield /%**	**Power/ kWh**	**Atom Economy**	***E* factor**
EDC	16 h	78%	0.513	44	2.097[b] / 17.04[c]
Enz	320 mins[d]	94%	0.067	93	0.093[b] /2.57[c]

[a]See above for calculations. [b]Solvents included. [c]Solvents excluded. [d]τ = 40 mins (5 h 20 min needed to treat 20 g). *EDC* stands for petrochemical esterification, *Enz* stands for enzymatic esterification.

Life Cycle Assessment Analysis

LCA inventory

The starting compound and the product were identical for both reactions. The main differences were the reaction conditions, including the chemicals used and reaction time. The workup of the reaction to obtain the designated product was included in the assessment. The functional unit in this study is 100 g of ester.

The primary data was collected from experiments at the laboratory scale. This applies to both the inputs and outputs of the chemical products and the energy consumption data. For energy consumption data, the electricity consumption of the laboratory equipment was measured using an electricity meter. The background data used for basic chemicals such as solvents, reagents comes from the Ecoinvent-3 database, and the Rest of Europe data was preferred. The datasets used were expanded with the background data of the process during the initial input. For chemicals not available in the database, they were replaced with alternative chemicals or their process was created in the software.

Table S2. Inventory analysis for LCA of production of 100 g of lipoate ester.

Inventory Item	Unit	Input	Output	Comments
Esterification with EDC				
(N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) (EDC HCl)	g	78.7		
Dichloromethane	g	1,132		
Dimethylaminopropylamine (DMAPA)	g	42		Substitute for DMAP
Ethanol	g	20		
Stearic Acid	g	117		Substitute for Lipoic acid
Hydrochloric Acid (1 M solution)	g	1277		
Sodium Bicarbonate	g	425		
Brine	g	425		
Magnesium sulphate	g	4		
Ester Product	g		100	Calculated considering 78% yield
Electricity for reaction (Stirring plate)[a]	kWh	0.320		Measured with electricity meter
Electricity for solvent removal[a]	kWh	0.1935		Measured with electricity meter
Enzymatic Esterification				
Dichloromethane	g	141		
Ethanol	g	21		
Supported Enzyme[b]	g	3.2	3.2	Catalyst is used within a packed bed reactor
Stearic Acid	g	98		
Ester Product			100	Calculated considering 94% yield
Electricity for reaction (Syringe pump)[a]	kWh	0.055		Measured with electricity meter
Electricity for solvent removal[a]	kWh	0.055		Measured with electricity meter

[a]Electricity, high voltage | market for electricity, high voltage | Cut-off, S

[b]Enzyme, Alpha-amylase, Novozyme Liquozyme/kg/RER

Midpoint indicator assessment

Table S3. Environmental impacts due to the preparation of 100 g of ethyl ester computed using ReCiPe 2016 (E) V1.08.

Impact category	Unit	Petrochemical Esterification		Enzymatic Esterification
		Purification	*Synthesis*	
Global warming	kg CO_2 eq	1.106	12.784	0.492
Stratospheric ozone depletion	kg CFC11 eq	0.000	0.000	0.000
Ionizing radiation	kBq Co-60 eq	0.074	0.378	0.007
Ozone formation, Human health	kg NOx eq	0.001	0.058	0.002
Fine particulate matter formation	kg PM2.5 eq	0.000	0.026	0.001
Ozone formation, Terrestrial ecosystems	kg NOx eq	0.001	0.059	0.002
Terrestrial acidification	kg SO_2 eq	0.003	0.074	0.003
Freshwater eutrophication	kg P eq	0.000	0.002	0.000
Marine eutrophication	kg N eq	0.000	0.002	0.000
Terrestrial ecotoxicity	kg 1,4-DCB	4.529	16.824	0.623
Freshwater ecotoxicity	kg 1,4-DCB	0.078	0.182	0.007
Marine ecotoxicity	kg 1,4-DCB	0.022	936.653	36.576
Human carcinogenic toxicity	kg 1,4-DCB	0.000	40.361	1.589
Human non-carcinogenic toxicity	kg 1,4-DCB	0.038	747.646	29.174
Land use	m^2a crop eq	0.016	0.045	0.002
Mineral resource scarcity	kg Cu eq	0.006	0.013	0.000
Fossil resource scarcity	kg oil eq	0.265	4.423	0.155
Water consumption	m^3	0.011	0.088	0.002

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