Supporting Information

Lipase Catalyzed Epoxy-acid Addition and Transesterification: from Model Molecule Studies to Network Build-up

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1- Characterization of products by 1H NMR spectroscopy and GC-MS analysis

1.1. Characterisation of the different product by ^{1}H NMR

^{1}H NMR analysis of a commercially available 3-phenoxy-1,2-propane diol (95%) and the crude mixture of an addition reaction catalyzed by 2-PI are presented below and allow the attribution of characteristic signals of products **3** (green, 3.9-3.7ppm) and **1-2** (blue and grey, at 4.0 and 5.2ppm) respectively. Integrations gave a relative proportion **1**:**2** of (81:19) for 2-PI catalysed addition reaction.

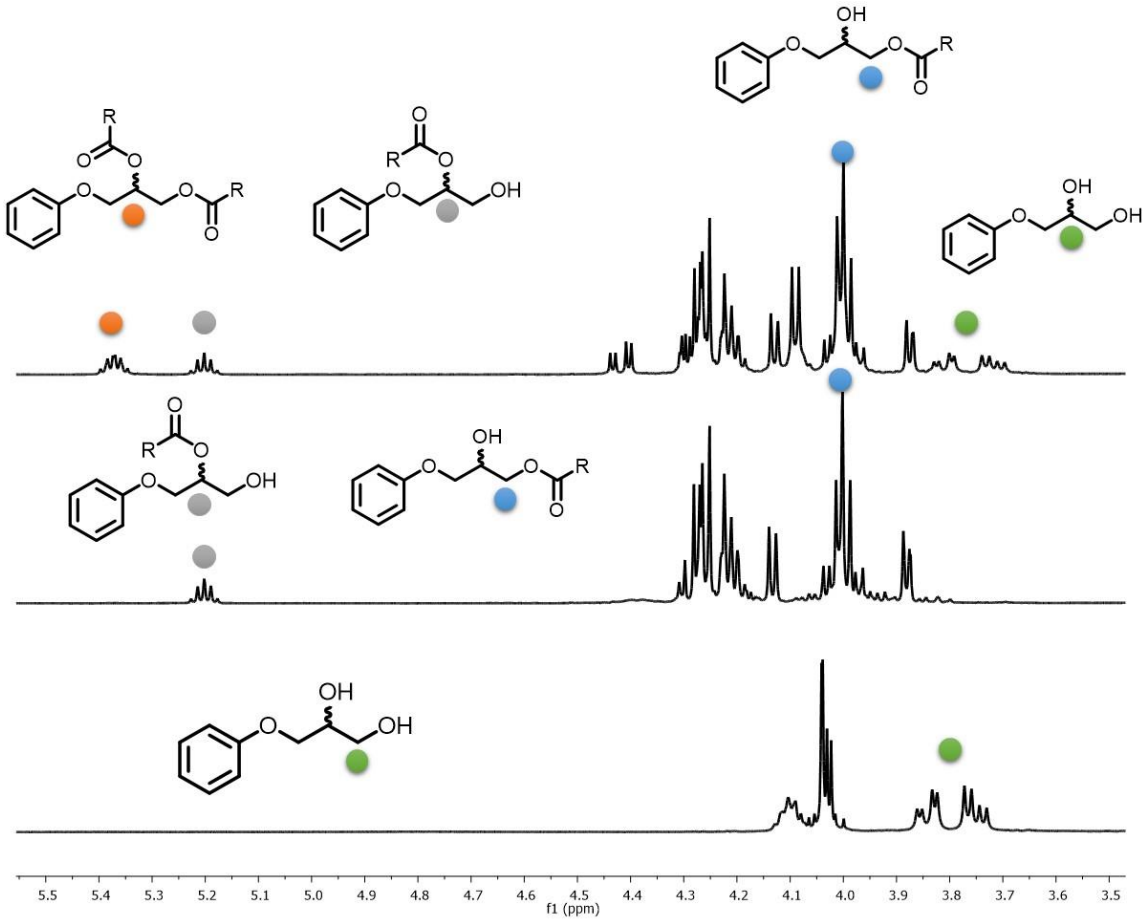
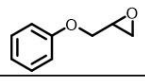
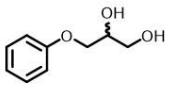
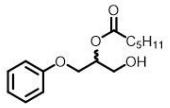
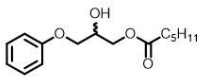
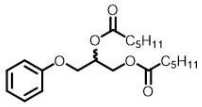


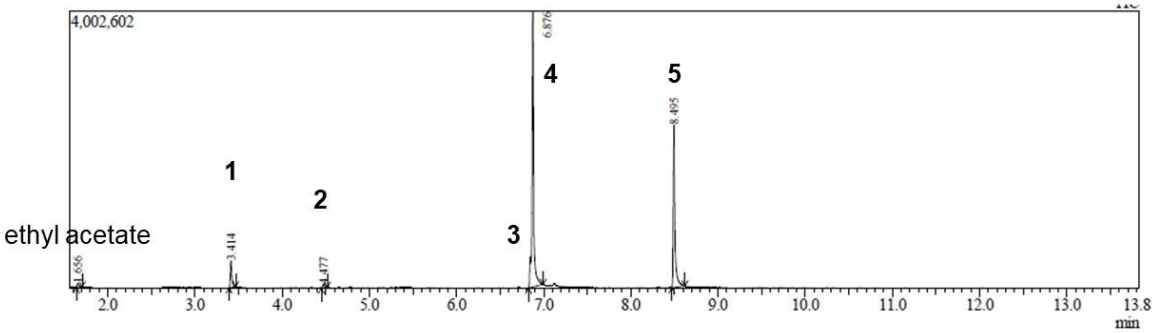
Figure S1. ^{1}H NMR spectroscopy spectra ($CDCl_3$, 400 MHz) of a) the crude mixture (TL100, 72h) b) From the addition the reaction catalyzed by 2-PI (100°C, 3h) and c) commercially available 3-phenoxy-1,2-propane diol (zoom on the epoxy region 2.5-5.5 ppm)

1.2. GC MS spectra

A typical GC-MS spectrum of the crude mixture of reaction (TL100, 48h, conv. 99%) is presented below. Apart from the residual monomer traces of PGE at 3.41 min, the 2 isomers coming from the addition reaction (1 and 2) are discernable at 6.85 and 6.87 min. Diester (4) and diol (3) signals coming from the transesterification reaction are detectable at respectively 8.49 and 4.47. The presence of diol and carboxylic acid (polar compounds not eluted properly) into the reaction mixture prevents any accurate determination of the conversion nor quantitative measurement by this method and ^{1}H NMR spectroscopy was preferred to determine conversions and relative proportions.

Table S1. Analysis of fragments

Peak	Fragment	Elution time (min)	$M_{calculated}$ (in $g.mol^{-1}$)	M_{found} (in $g.mol^{-1}$)
1		3.41	150.15	150.0
2		4.47	168.08	168.0
3		6.85	266.15	266.0
4		6.87	266.15	266.0
5		8.49	364.22	364.0



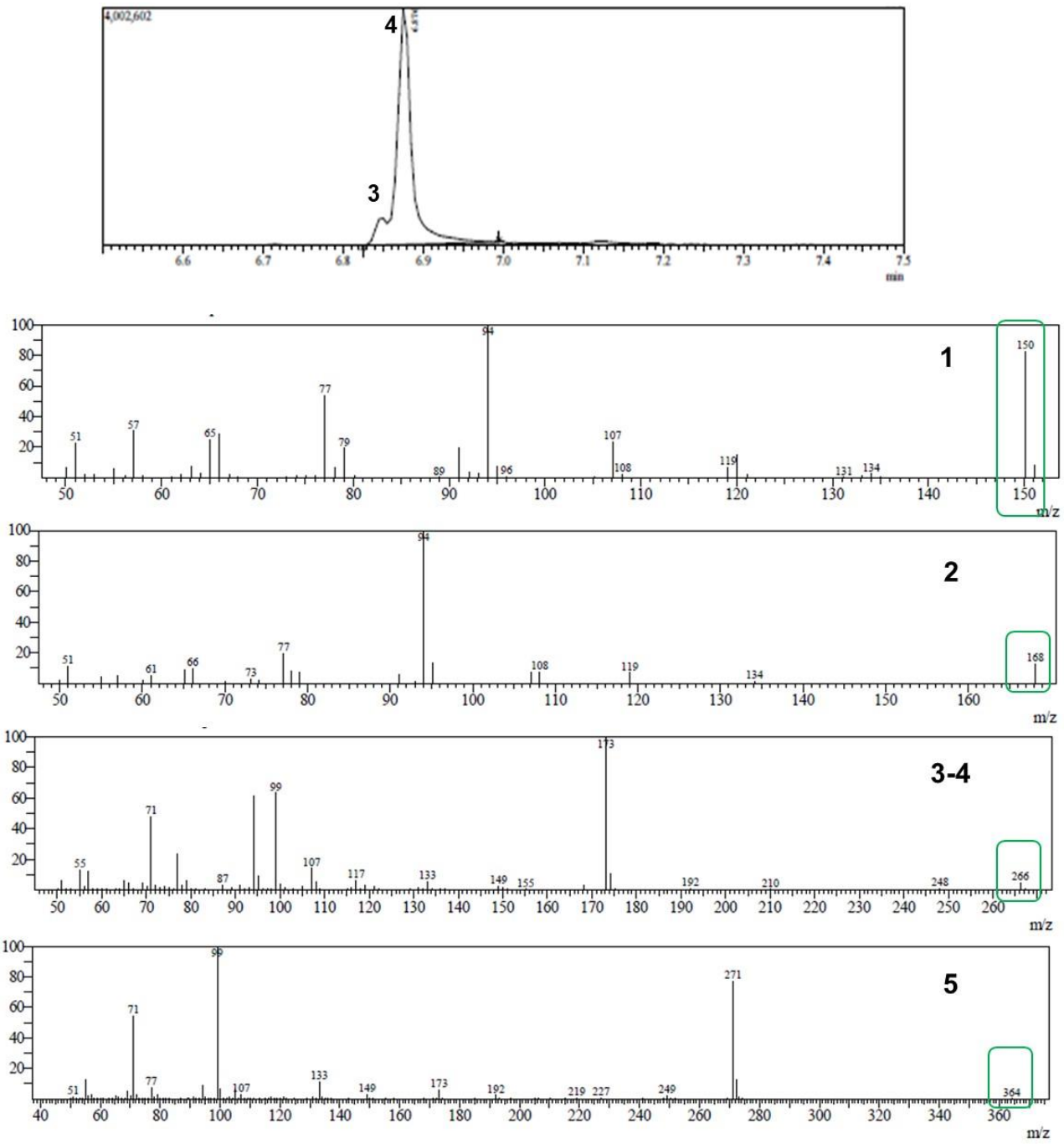


Figure S2. GC-MS analysis of the a) crude mixture (TL100,48h, conv. 99%) b) zoom on the isomers 1-2 region.

1.3. Calculation of the relative proportion

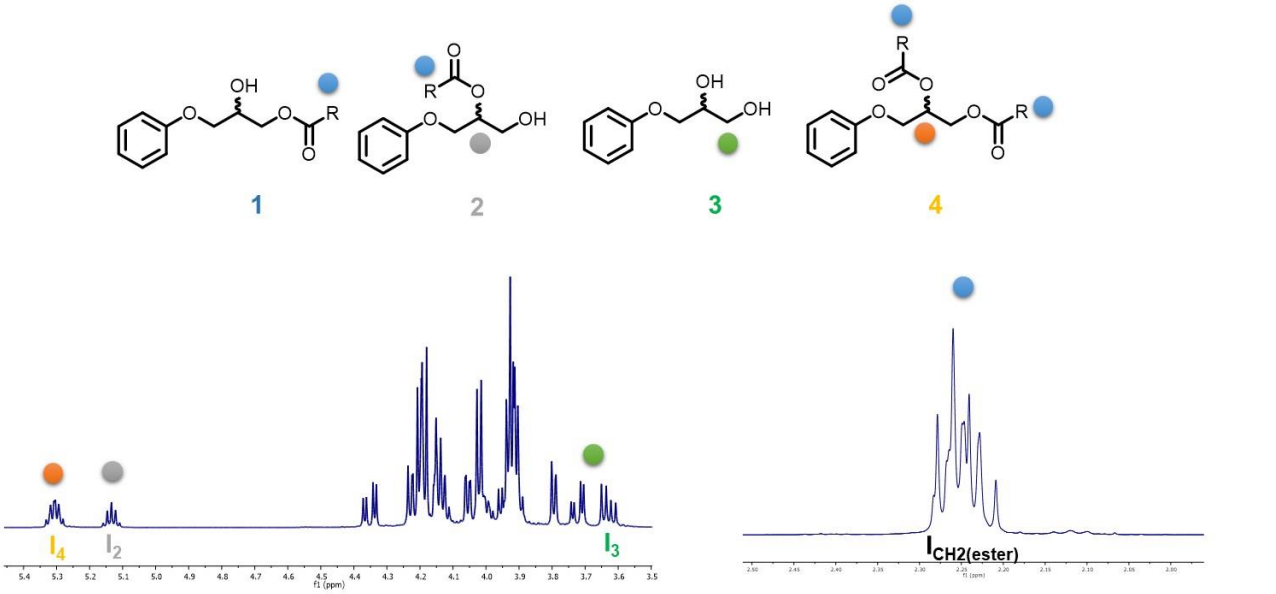
The relative proportion of products 1, 2, 3 and 4 are calculated from ^{1}H NMR spectroscopy measurement at different conversion as follow:

Integrals $I_2(t)$ $I_3(t)$ et $I_4(t)$ are easily discernable but not $I_1(t)$ (overlapping)

$I_{CH2(ester)}$ (t) can be calculated at any time with $I_{CH2(ester)}$ (t) = 2 × conversion(t)

$I_{CH2(ester)}$ (t) = $2I_1$(t) + $2I_2$(t) + $4I_4$(t)
and allow to recalculate I_1(t)

with I_{tot} (t) = I_1(t) + I_2(t) + I_3(t) + I_4(t)
the relative proportion of each product is given by %P = [I_x (t) / I_{tot} (t)] × 100



zoom on the ring-opened epoxy region (3,5-5,5ppm)

signal of the alpha position of the ester group (2,25 ppm)

Figure S3. Analysis method for relative proportion calculation

1.4. ^{1}H NMR spectroscopy comparison with non-catalyzed reactions

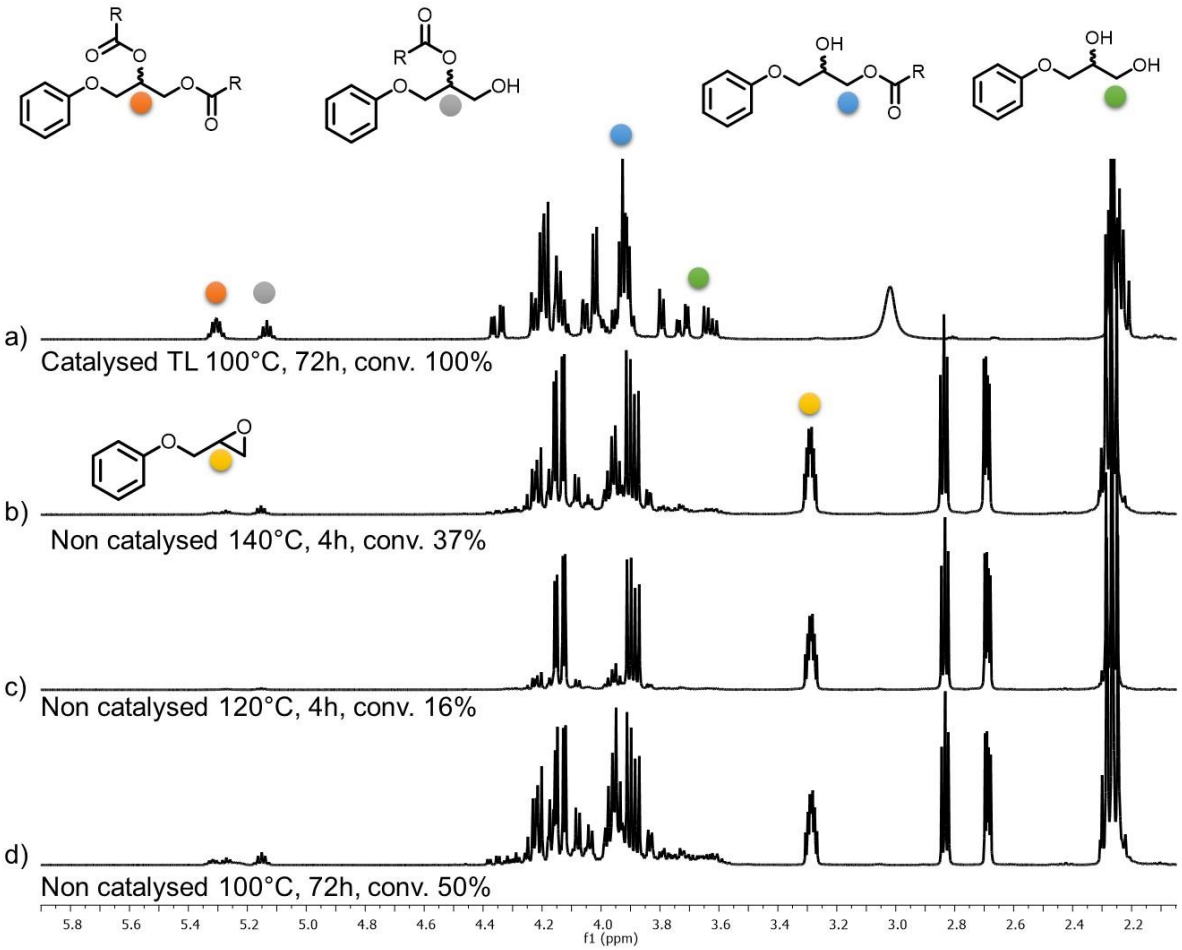


Figure S4. ^{1}H NMR analysis of the crude product of reaction in catalyzed (a) and non-catalyzed control reactions (b, c and d)

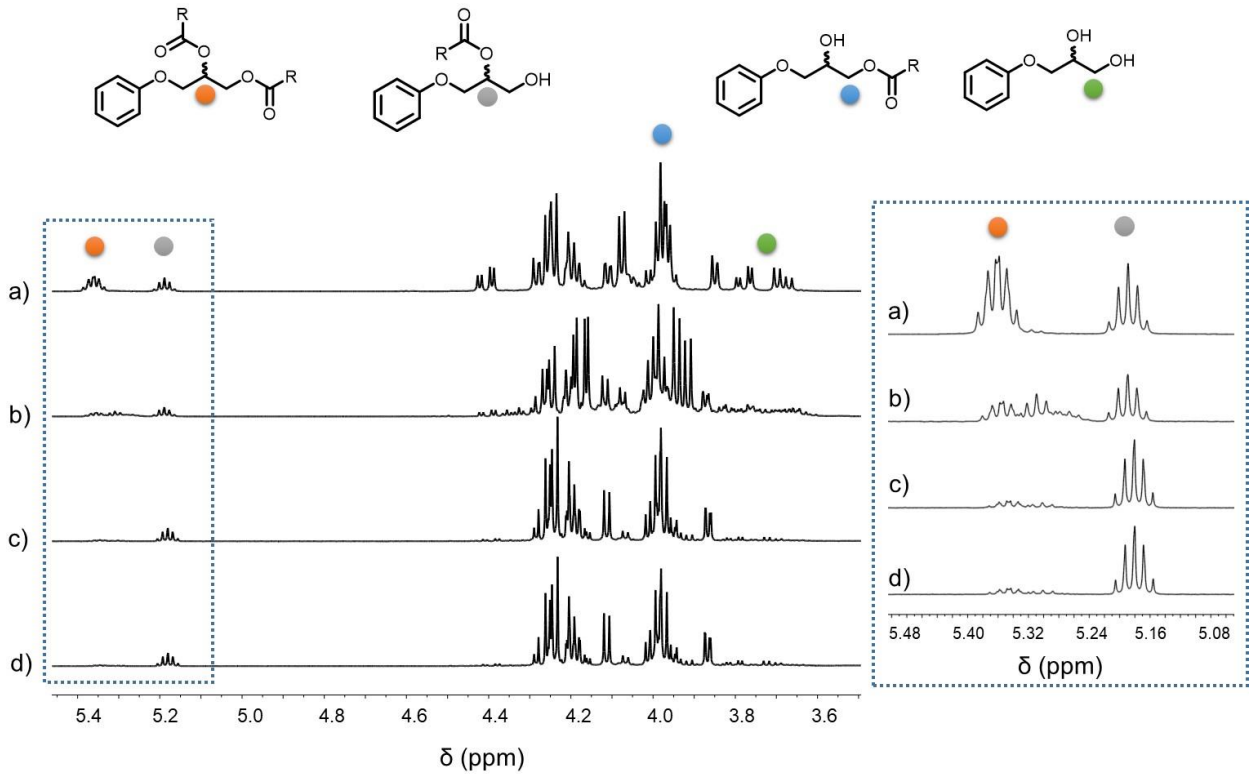


Figure S5. ^{1}H NMR analysis of the crude product of reaction in Lipase TL- (TL100, a) non catalyzed- (NC100, b), TDL- (TDL100, c) and BSA-(BSA100, d) catalyzed acid epoxy-addition (48h, 100°C, Table 1)

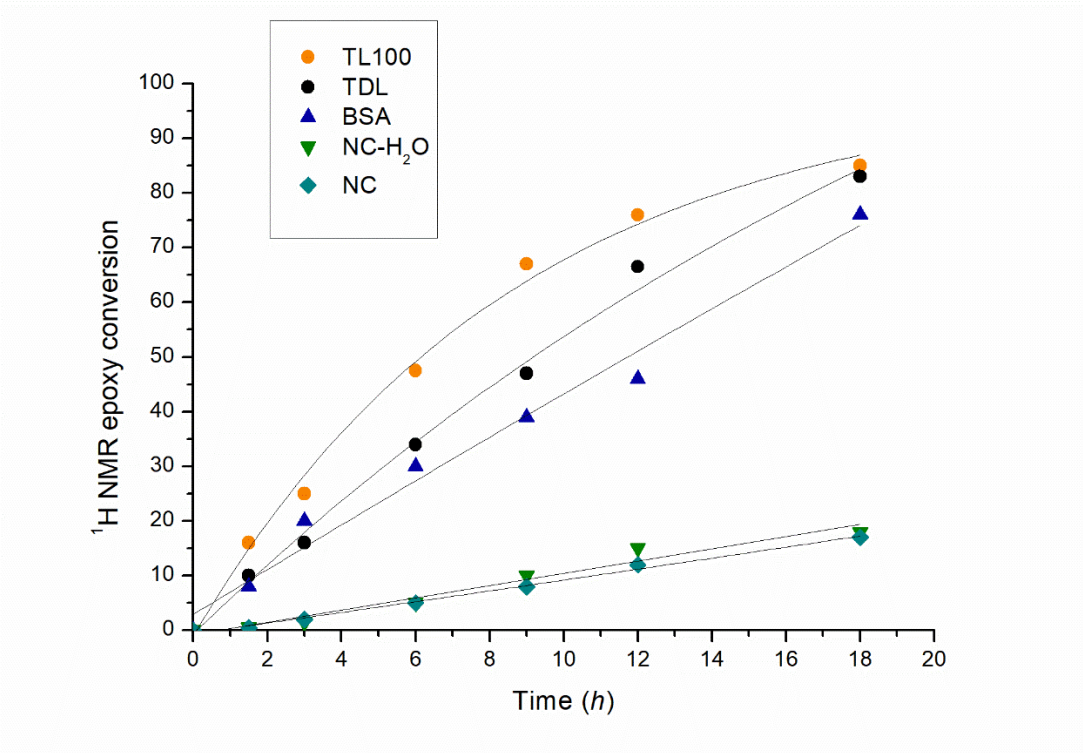
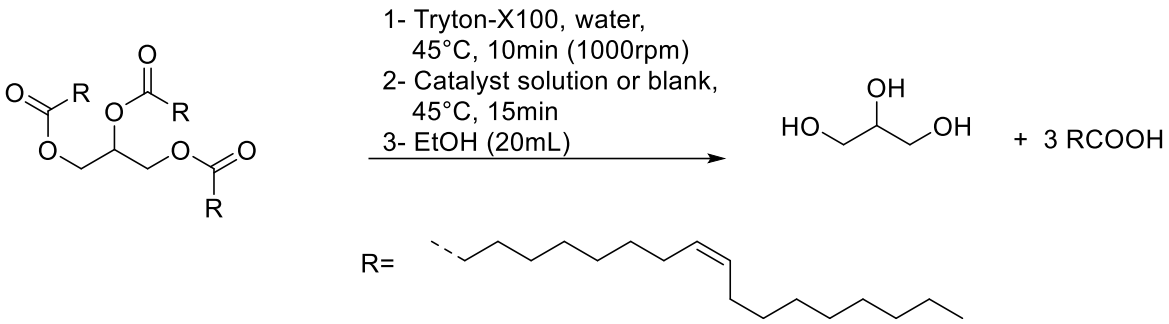


Figure S6. Kinetic plot at early stage of addition reaction for TL-catalysed addition at 100°C, TDL-catalysed addition at 100°C and non-catalysed reactions

2. Enzymatic Assays



Scheme S1. Hydrolysis in emulsion of triolein under different conditions

Table S2. Enzymatic activity measured by titration (colorimetric analysis) of oleic acid under various conditions (45°C, 15min), titration with KOH (0.0535 M) of duplicate samples using naphtolphthalein as end-point indicator.

Catalyst : Lipase TL (20 mg), Lipase TL+PGE (20mg in 200 mg of PGE), BSA (20mg), Lipase TL100 (20 mg, neat lipase after thermal treatment at 100°C 72h without solvent) and Lipase TL100+PGE (20mg in 200 mg of PGE after thermal treatment at 100°C 72h) Lipase TL120+PGE (20mg in 200 mg of PGE after thermal treatment at 120°C 10h)

Assay	Catalyst	Veq (in mL)[a]	Recalculated Veq (in mL)[b]	Activity ($U.g^{-1}$)[c]
1 (blank)	none	2.45 ± 0.10	0	-
2 (blank 2)	PGE	2.55 ± 0.15	0	-
3	Lipase TL	5.00 ± 0.10	2.55 ± 0.10	460 ± 10
4	Lipase TL+PGE	11.35 ± 1.75	8.80 ± 1.75	1580 ± 315
5	BSA	2.85 ± 0.10	0.40 ± 0.10	70 ± 10
6	Lipase TL100	2.25 ± 0.10	≥ 0	≥ 0

7	Lipase TL100+PGE	3.80 ± 0.10	1.25 ± 0.10	250 ± 10
8	Lipase TL120+PGE	2.30 ± 0.10	≥ 0	≥ 0
9	Lipase TL100+PGE 0.3 w.%H_2O	3.90 ± 0.10	1.35 ± 0.15	265 ± 20
10	Lipase TL100+PGE 6 w.%H_2O	2.25 ± 0.10	≥ 0	≥ 0
11	Extracted Lipase TL after 72h at 100°C	3.90 ± 0.35	1.45 ± 0.35	270 ± 75
12	Extracted Lipase TL after 12h at 120°C	2.05 ± 0.10	≥ 0 (*)	≥ 0
13	Extracted Lipase TL after 6h at 140°C	2.10 ± 0.10	≥ 0 (*)	≥ 0

a) Corresponds to the total volume of KOH solution added b) Recalculated volume is obtained by subtraction of V_{eq} (for non catalyzed reaction or in presence of epoxide) in V_{eq} total c) U = $\mu mol.min^{-1}$ (*) Lipase extracted from RGE140 were found to be insoluble in water, this phenomena was also observed for the thermally degraded Lipase TL (200°C, 3h).

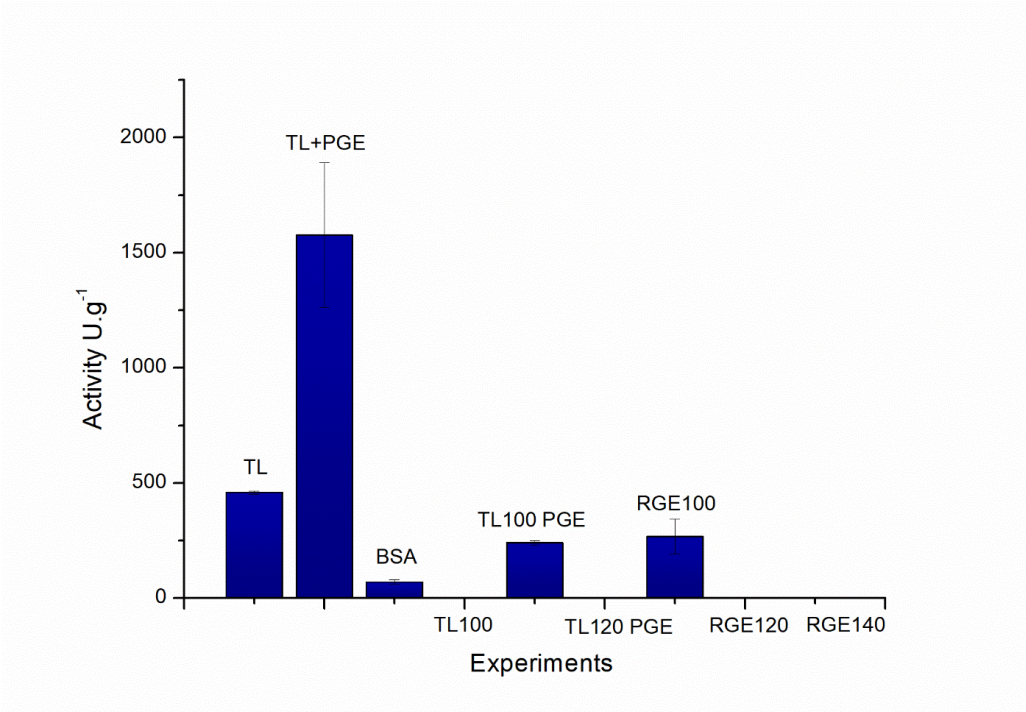


Figure S7. Enzymatic activity measured by titration (colorimetric analysis) of oleic acid under various conditions (45°C, 15min), titration with KOH (0.0535 M) of duplicate samples using naphtolphthalein as end-point indicator

2. Water as co-catalyst

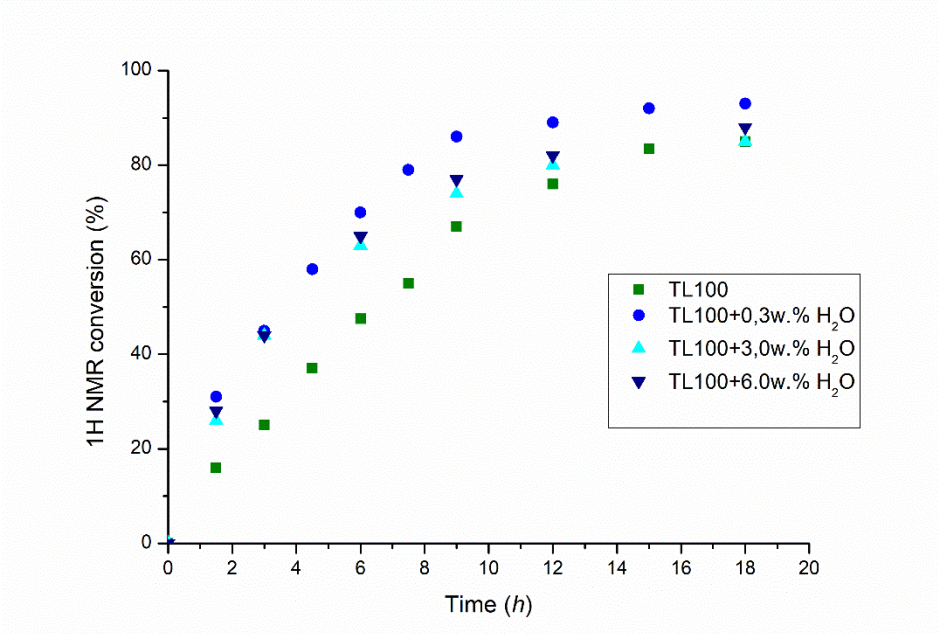


Figure S8. Kinetic experiment of addition reaction catalysed by Lipase TL performed with different water amount (0, 0.3, 3 and 6 w.%) at 100°C.

3. Relative proportion: effect of water addition as co-catalyst

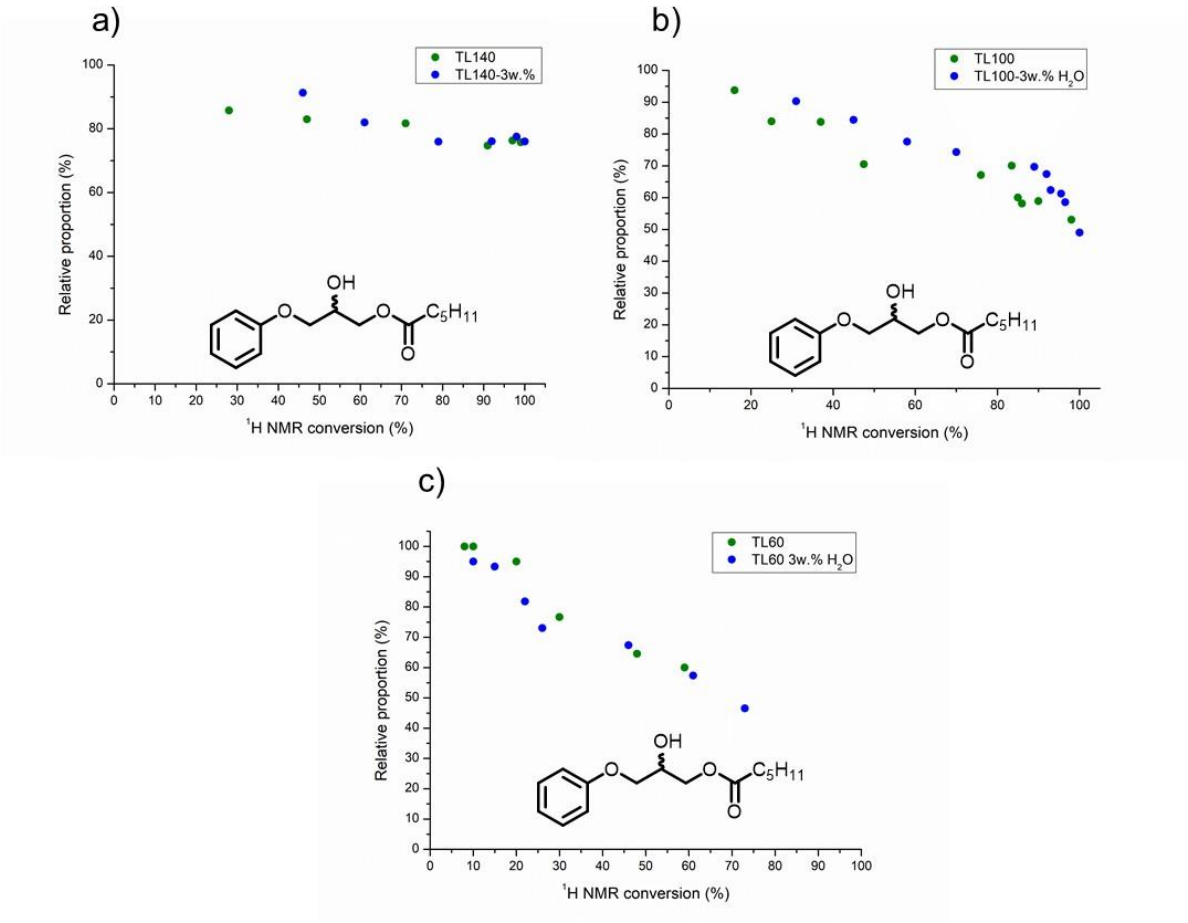


Figure S9. Relative proportion of **1** in Lipase-catalysed (green dots) and Lipase + 3w.% water (blue dots) catalysed addition at a) 140°C , b) 100°C and c) 60°C.

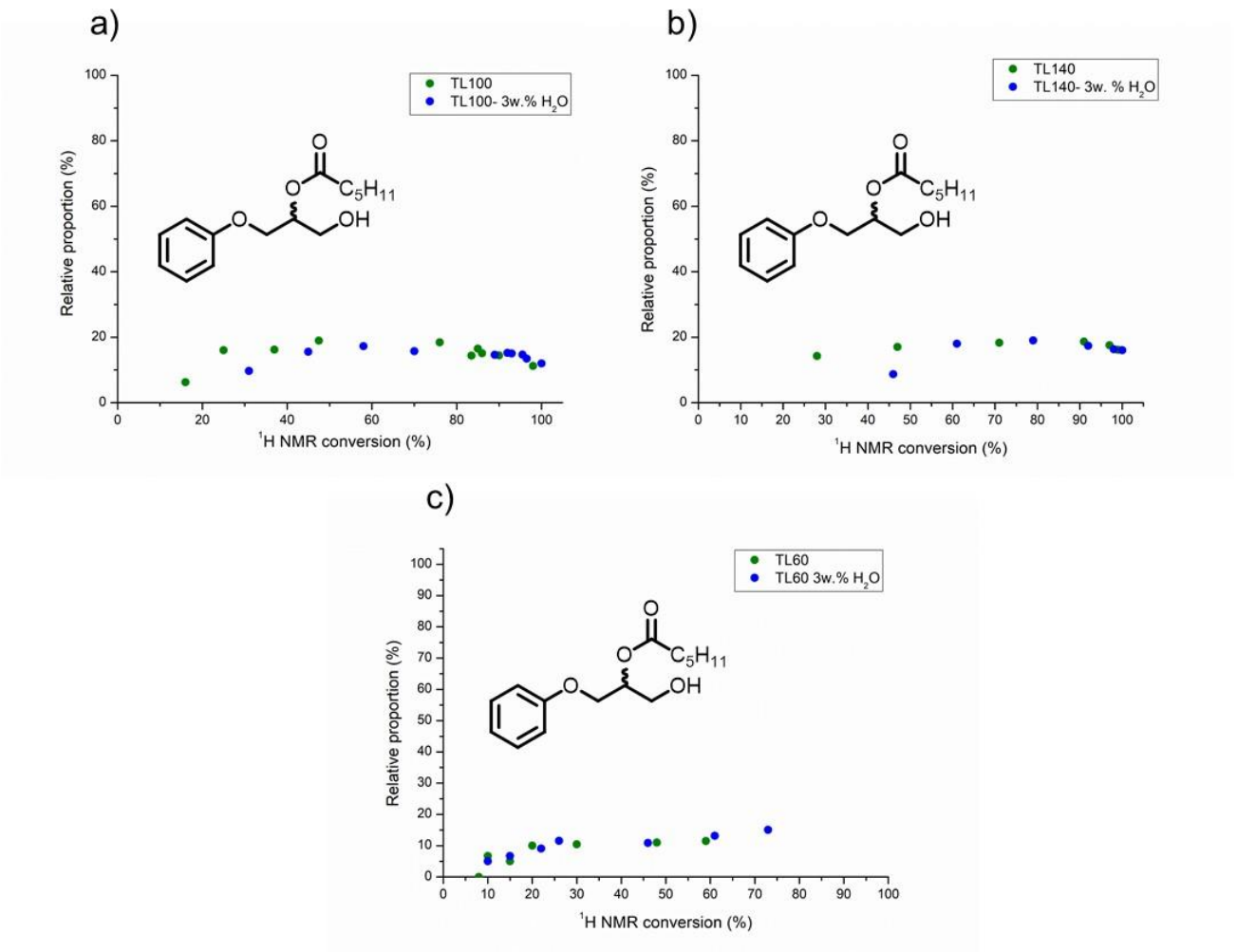


Figure S10. Relative proportion of **2** in Lipase-catalysed (green dots) and Lipase + 3w.% water (blue dots) catalysed addition at a) 140°C , b) 100°C and c) 60°C.

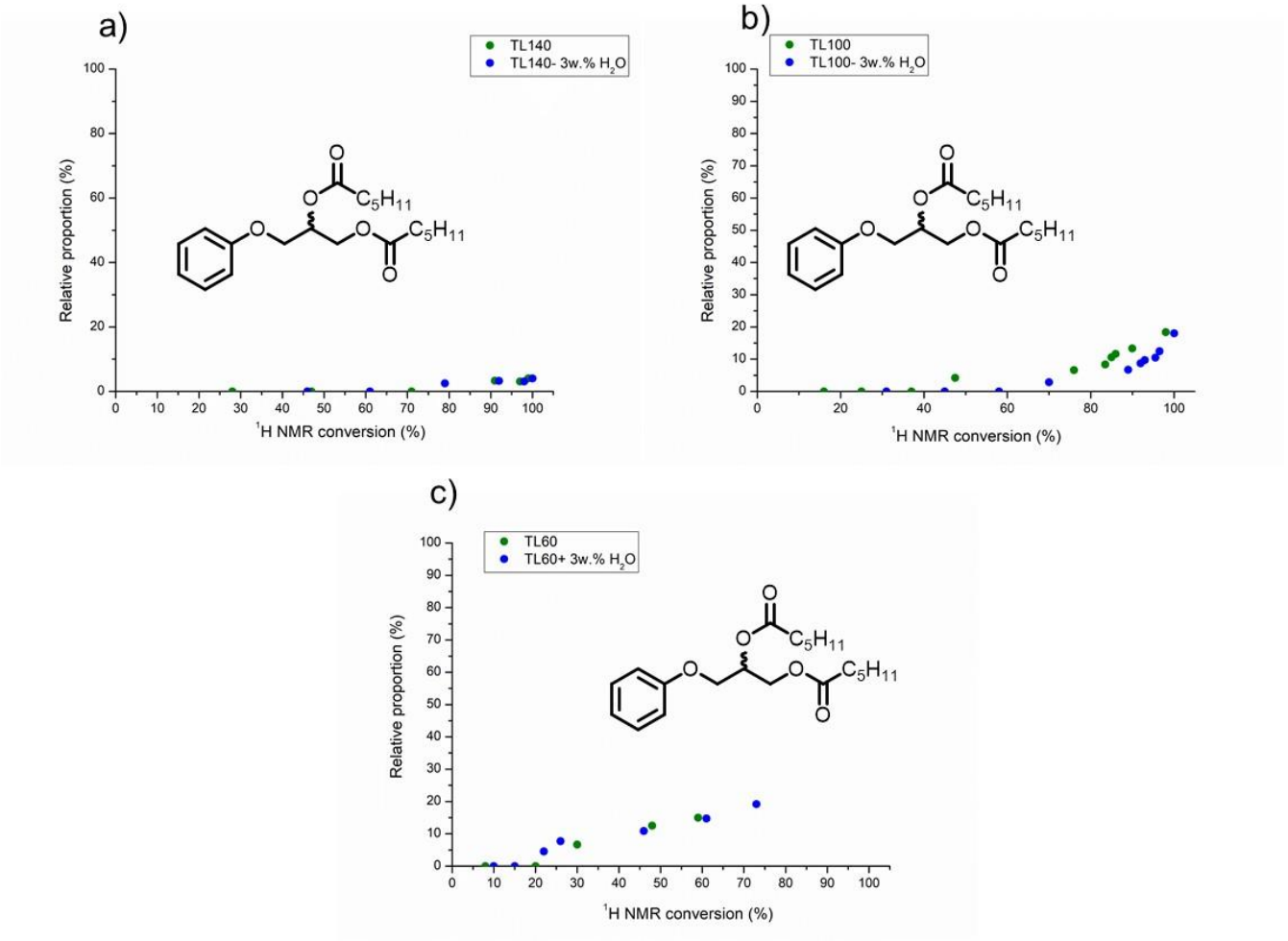


Figure S11. Relative proportion of **4** in Lipase-catalysed (green dots) and Lipase + 3w.% water (blue dots) catalysed addition at a) 140°C , b) 100°C and c) 60°C.

4. Chemical network analysis

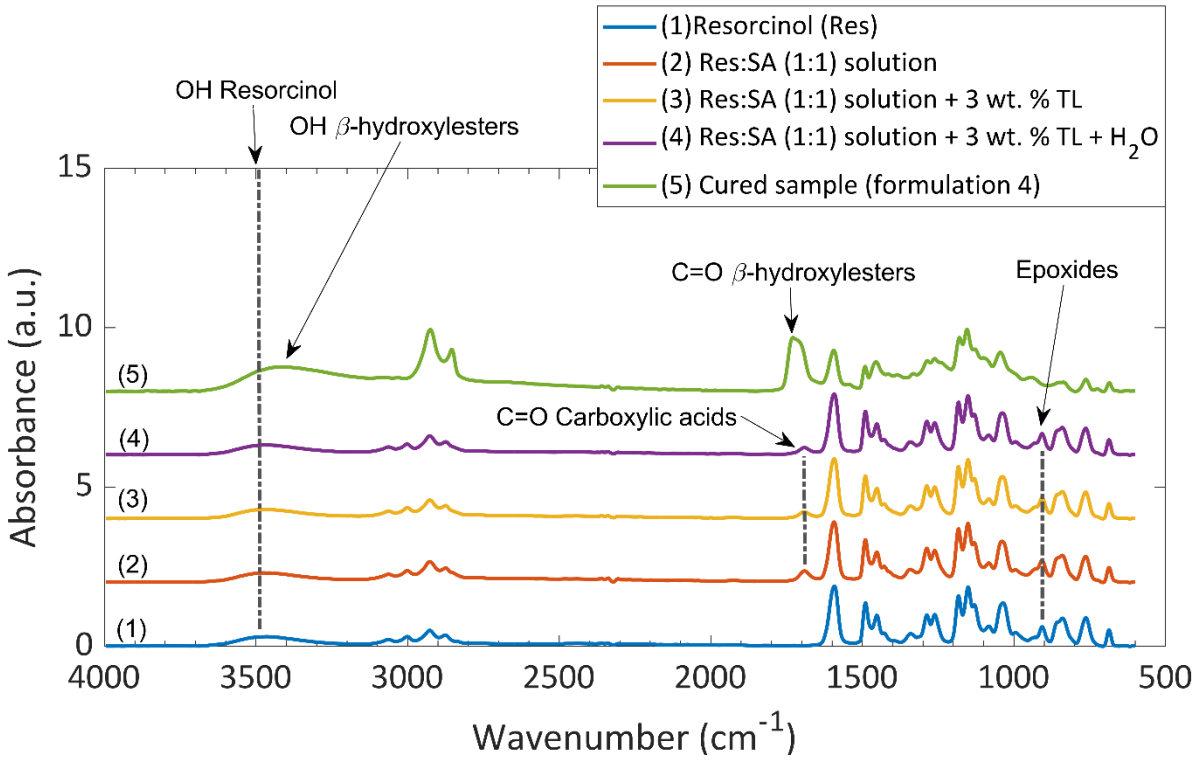


Figure S12. FT-IR spectra of 1) resorcinol diglycidyl ether, 2) resorcinol diglycidyl ether and sebacic acid (1:1), 3) resorcinol diglycidyl ether, sebacic acid (1:1), and Lipase TL (3 w.%), 4) resorcinol diglycidyl ether, sebacic acid (1:1), Lipase TL (3 w.%) and water (0.3w.%) and 5) of the cured sample (72h, 100°C, formulation 4)

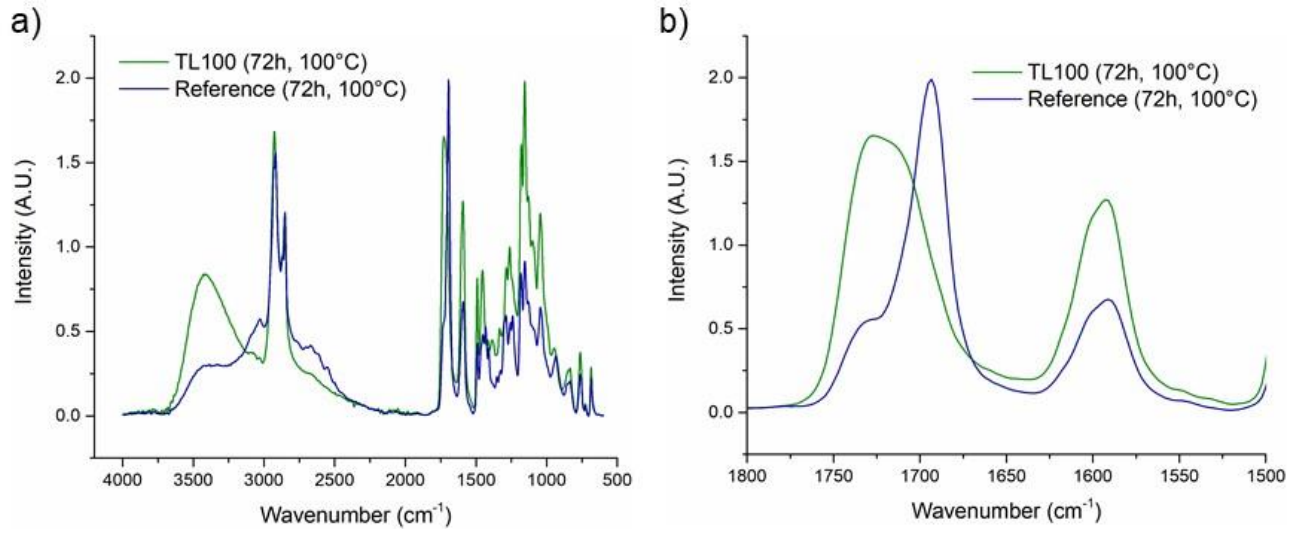


Figure S13. Comparison of FT-IR spectra diglycidyl ether and sebacic acid (1:1) after 72h at 100°C and resorcinol diglycidyl ether sebacic acid (1:1), and Lipase TL (3 w.%), water (0.3 w.%) after 72h at 100°C a) full spectrum and b) zoom on the carbonyl region (1800-1500 cm^{-1})

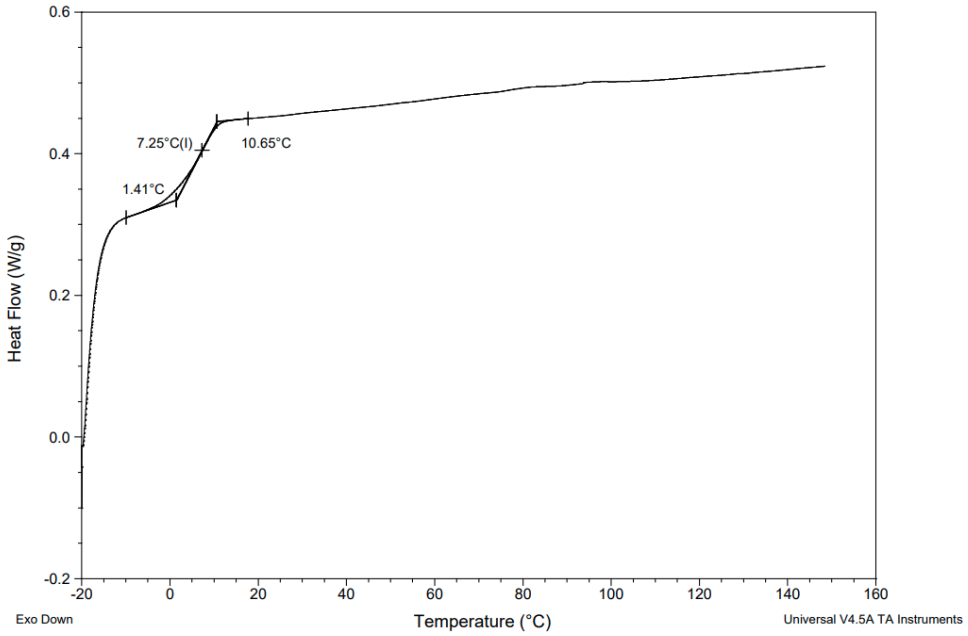


Figure S14. DSC analysis of a chemical network synthesised by reacting resorcinol diglycidyl ether, sebacic acid (1:1) and catalysed by Lipase TL (3 w.%) and water (0.3w.%) (72h, 100°C)

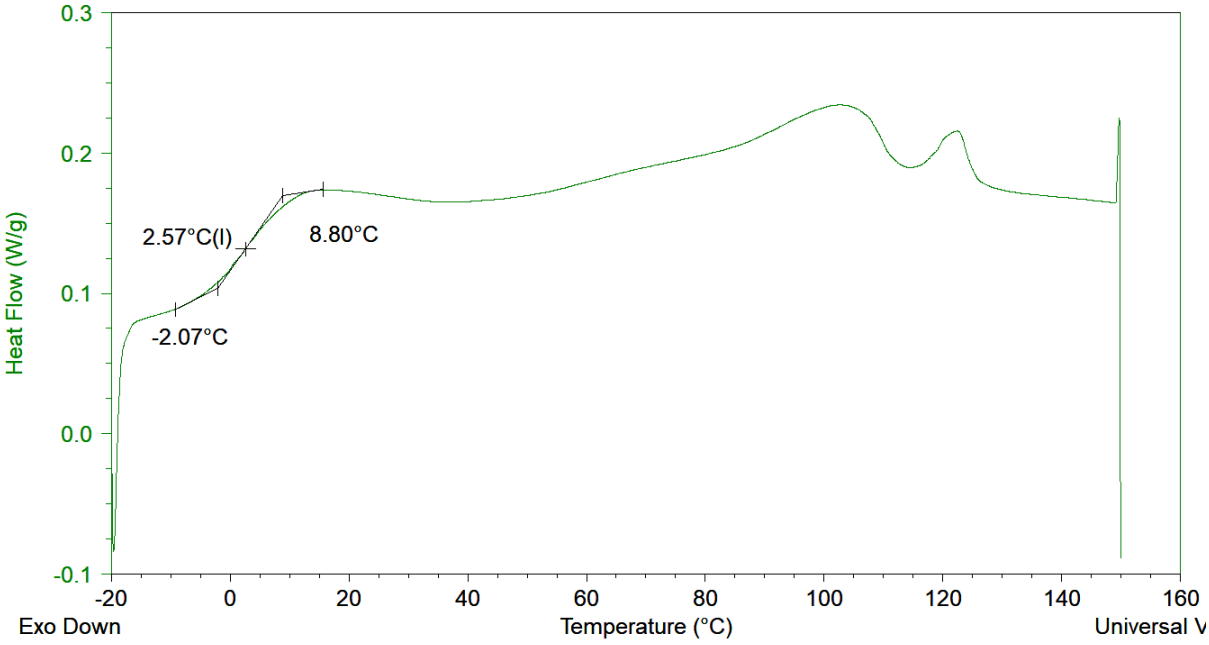


Figure S15. DSC analysis of a chemical network synthesised by reacting resorcinol diglycidyl ether, sebacic acid (1:1) (72h, 100°C)

Figure S16. Picture of chemical networks before (on top) and after (below) swelling in toluene (60°C, 7 days)

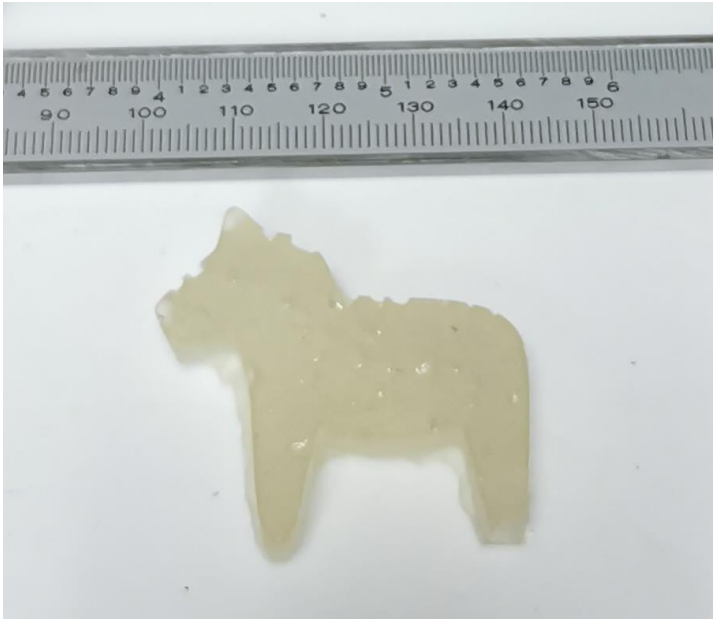


Figure S17. Picture of a referenced chemical networks prepared by reacting resorcinol diglycidyl ether and sebacic acid at 100°C for 72h.

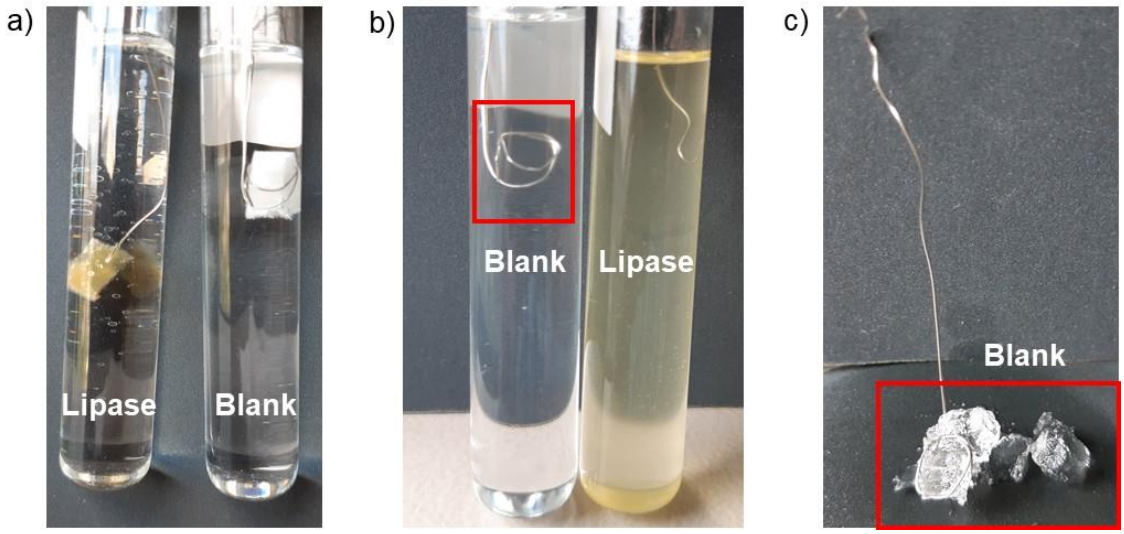


Figure S18. a) Dissolution tests in benzyl alcohol for the referenced resorcinol diglycidyl ether/sebacic acid (1:1) network and resorcinol diglycidyl ether/sebacic acid (1:1) network prepared by Lipase-H_2O-catalyzed (72h at 100°C) b) after 3 days at 100°C c) picture of the swollen gel for the non-catalyzed network.

5. Experiments with lipase recovery after cure:

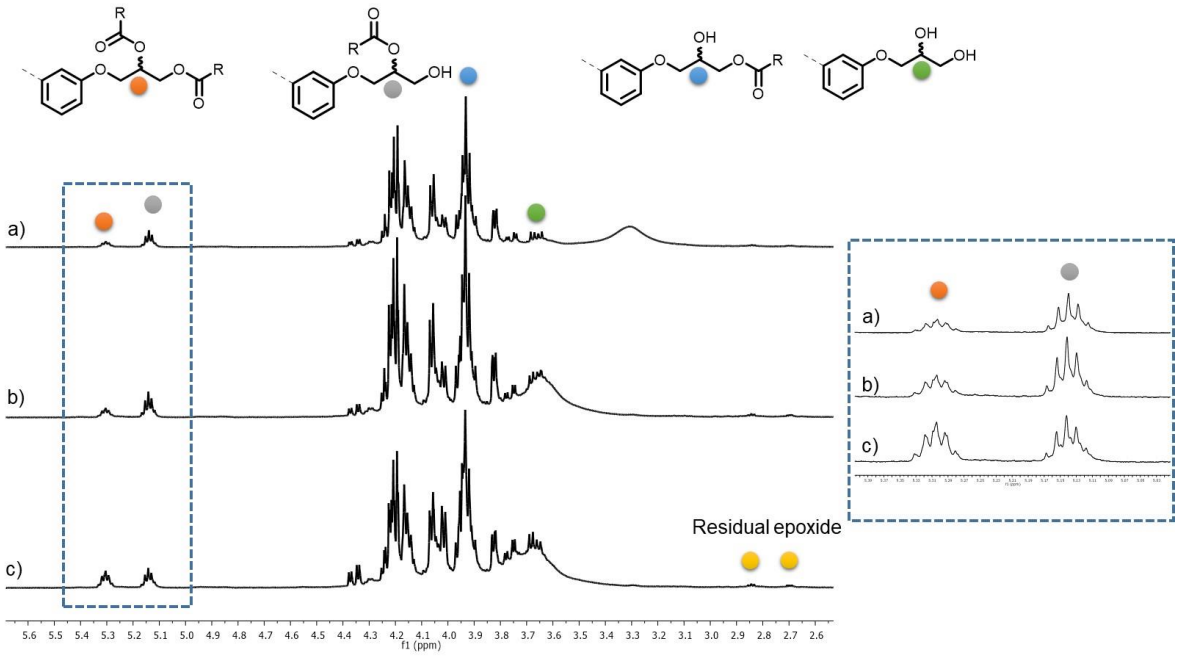


Figure S19. ^1H NMR analysis of the crude product of reaction in Lipase TL catalysed reaction between resorcinol diglycidyl ether and hexanoic acid at a) 140°C for 6h, b) 120°C for 12h and c) 100°C for 72h.

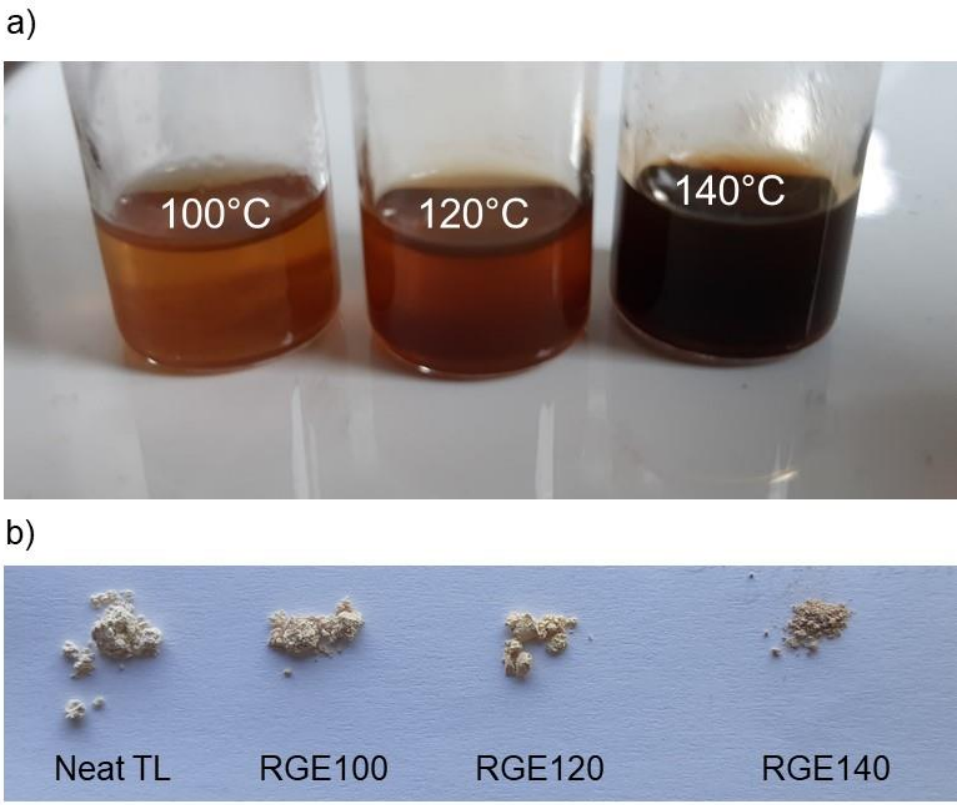


Figure S20. a) Picture of the reaction media in Lipase TL catalysed reaction between resorcinol diglycidyl ether and hexanoic acid and b) Picture of neat Lipase TL extracted Lipase TL after curing in the resin model