Supplementary information for:

Toward upscaled biocatalytic preparation of lactone buildings blocks for polymer applications

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Figure S2. Picture of the up-scaled reaction set-up (500 mL).

Figure S3. Composition of the isolated products adsorbed on the denatured protein of the 500 mL-scale reaction with ketone substrate **1** at 7.42 min (11.7 %), lactone **1b** at 11.16 min (35.4 %), lactone **1a** at 11.36 min (48.8 %), and the methyl esters **1a'** and **1b'** at 11.74 min (4.1 %).

Figure S4. HSQC spectrum of the isolated products from the upscaled reaction (500 mL), containing the targeted lactone products **1a** and **1b** with the corresponding methyl ester ring opened products **1a'** and **1b'**.

Figure S5. Kinetics of the formation of the methyl ester **1a'** and **1b'** after dilution with methanol (50 % v v^{-1}) of the model reaction containing the chemically synthesized lactones **1a** and **1b** in buffer. The percentage of methyl esters was calculated from GC-FID analysis.
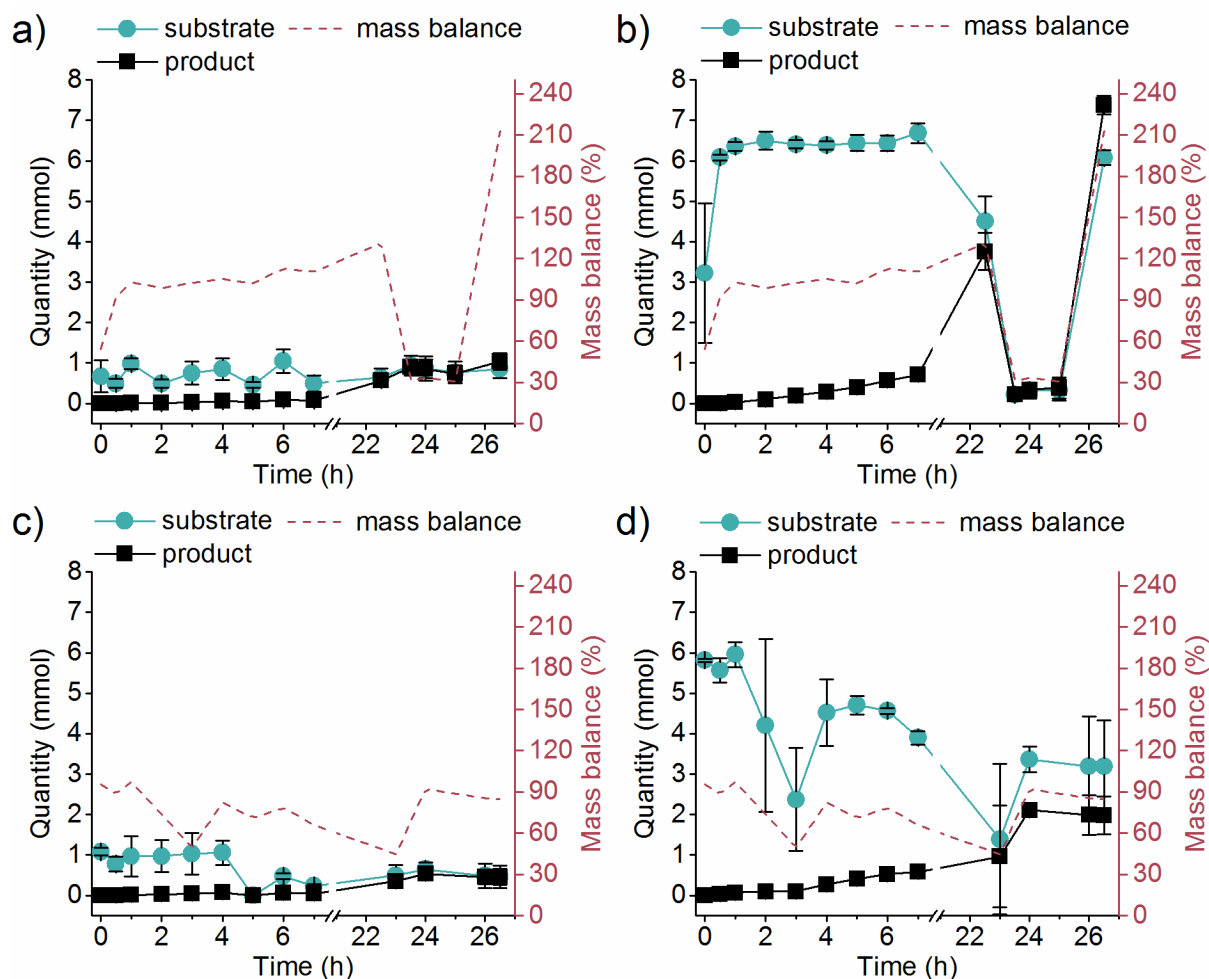
Figure S1. Kinetics of the biphasic reactions with quantity of substrate and product in mmol as a function of time for a) the aqueous phase of the toluene biphasic system, b) the organic phase of the toluene biphasic system, c) the aqueous phase of the n-butyl acetate biphasic system, and d) the organic phase of the n-butyl acetate biphasic system. The mass balance is shown in dotted red line (right axis), calculated as $(n_{sub,\ aq} + n_{sub,\ org} + n_{prod,\ aq} + n_{prod,\ org}) / n_{sub,\ initial} \times 100$, with $n_{sub,\ initial} = 7.2$ mmol. Reaction condition: 7.2 mmol of substrate, 5 % v v^{-1} TmCHMO, [GDH] = 0.1 mg mL^{-1}, [NADP$^+$] = 250 μM, [glucose] = 375 mM, 30 mL aqueous phase + 10 mL organic phase (toluene or n-butyl acetate), 250 rpm, air flow 8 mL min^{-1}.

overhead
stirrer

pH electrode

condensor
(cold water)

air flow
(sintered frit)

NaOH
dosing
(1M)

double
jacketed
reactor

syringe pump

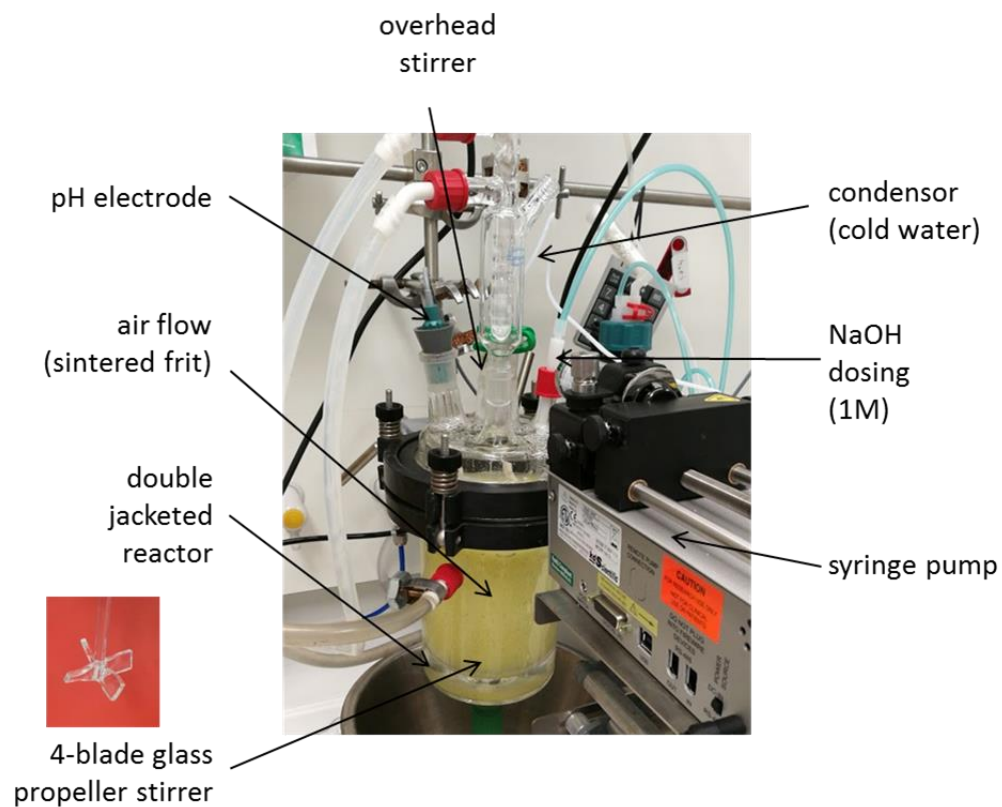4-blade glass
propeller stirrer

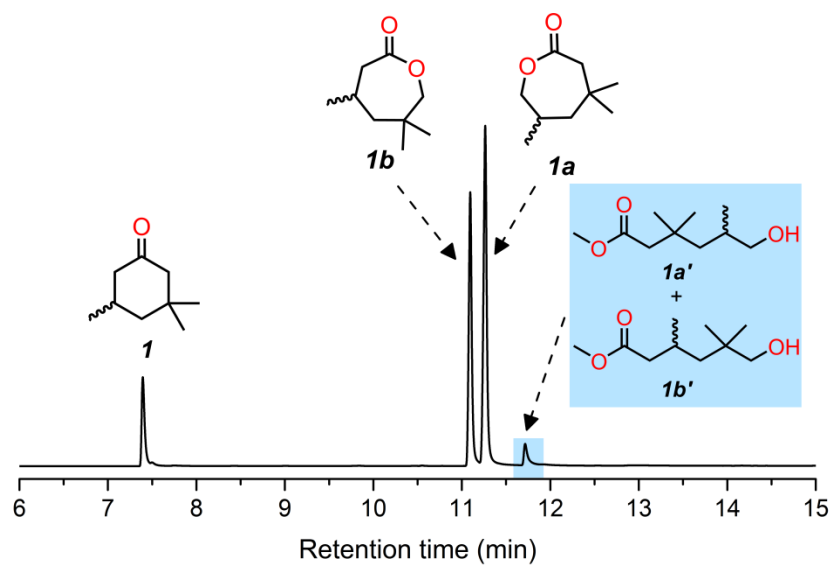**Figure S2**. Picture of the up-scaled reaction set-up (500 mL).

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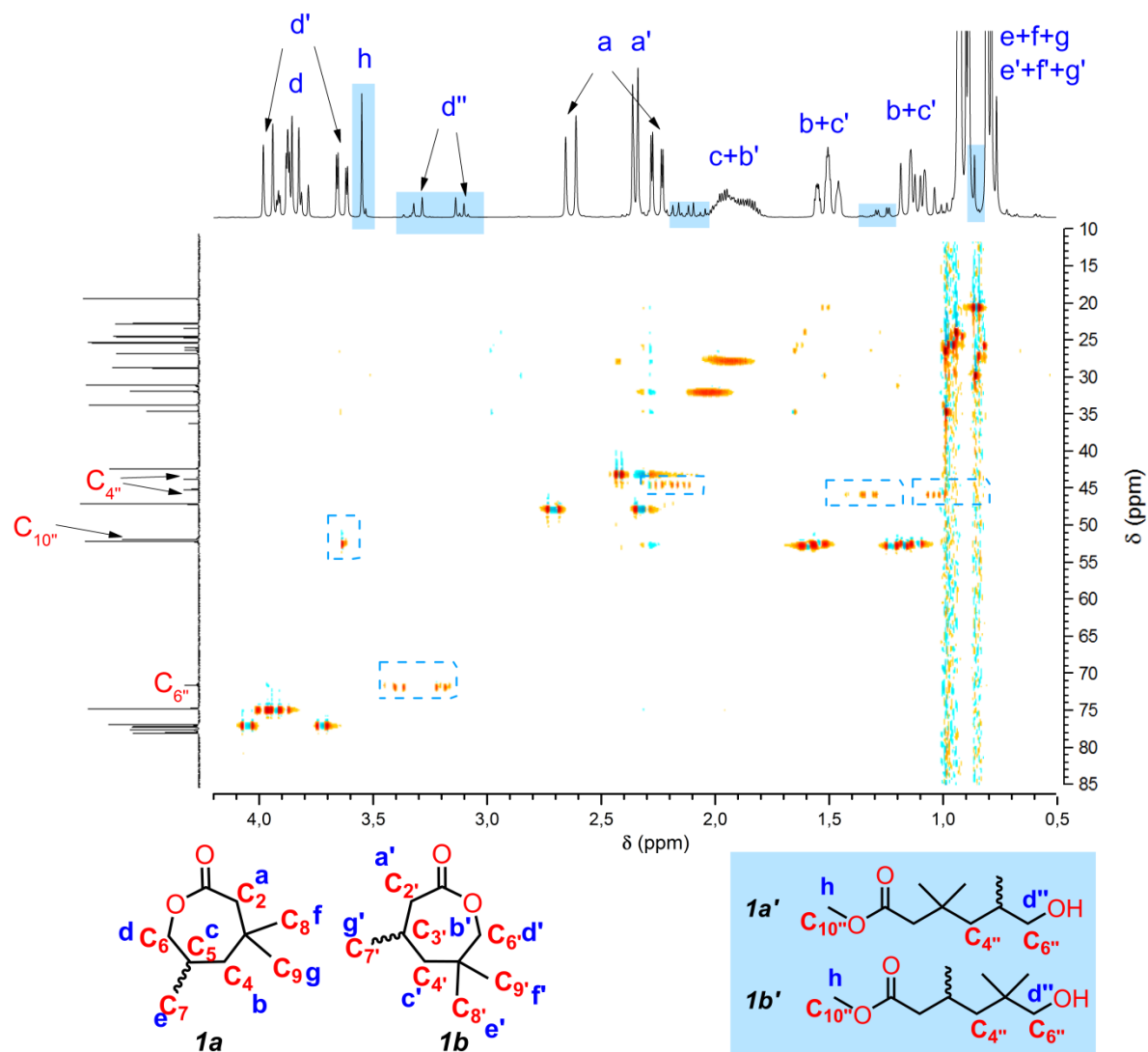
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Figure S4. HSQC spectrum of the isolated products from the upscaled reaction (500 mL), containing the targeted lactone products **1a** and **1b** with the corresponding methyl ester ring opened products **1a'** and **1b'** (proton of the methyl esters ring opened products highlighted in blue).
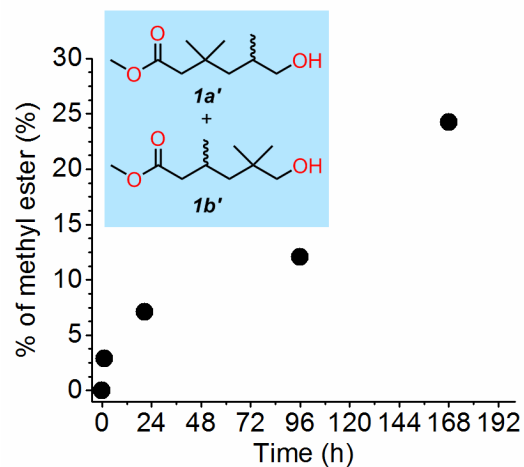
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