

# Supplementary Material

## Developing Multicompartment Biopolymer Hydrogel Beads for Tandem Chemoenzymatic One-Pot Process

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## 1. General

<sup>1</sup>H NMR spectrum was recorded with a Bruker Avance III 500 HD (measuring frequency: 500.2 MHz) spectrometer in CDCl<sub>3</sub> solution. Chemical shifts are referenced to the residual peak of CDCl<sub>3</sub>: 7.26 ppm (Gottlieb, H.E.; Kotlyar, V.; Nudelman, A. NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J. Org. Chem.* **1997**, *62*, 7512–7515, doi:10.1021/jo971176v). HPLC experiments were carried out on a Machery-Nagel NUCLEODUR® C18 Gravity-SB (5 μm) column.

## 2. Preparation of Octyl-Grafted Alginate Amide

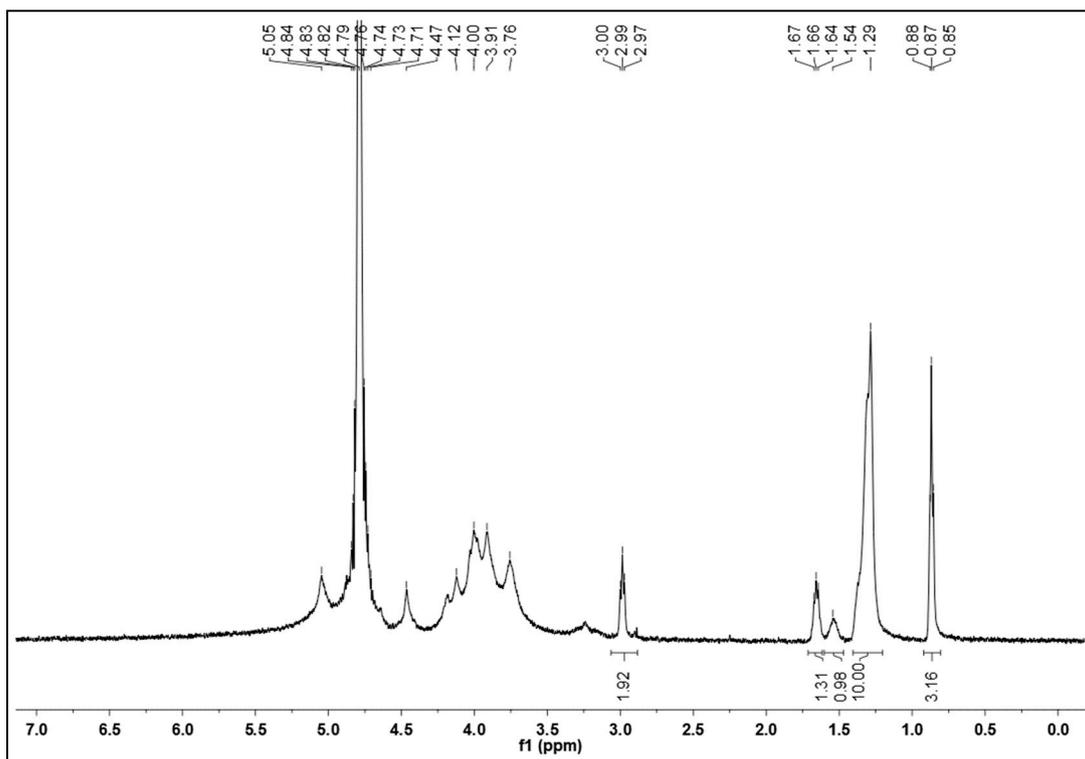
Since we already reported the preparation previously (adapted from: Hu, W.; Li, J.; Hou, H.; Yan, H.; Feng, Y.; Mi, X.; Lin, Q. Preparation and Characterization of Hydrophobic Alginate Derivative Nanocapsules Entrapping I-Cyhalothrin. *Asian J. Chem.* **2013**, *25*, 9904–9908, doi:10.14233/ajchem.2013.15593), we quote it from our previous study:

“Sodium alginate (3.0 g) was dissolved in water (90 ml), resulting in a 3.33% w/v solution. EDC · HCl (0.73 g) was added to this solution and pH was adjusted to 3.4 with HCl<sub>(aq)</sub> (0.5 M). After diluting the solution with 30 ml water (resulting in 2.5% w/v), octyl amine (5.1 ml) was added. Then, the reaction mixture was stirred for 24 h at 35 °C. By adding ethanol (300 ml) after the reaction time, the product was precipitated. The mixture was centrifuged, washed with ethanol (5 x 20 ml) and dried for three days at room temperature. After milling the chunky solid in a ball mill, a fine white powder (2.72 g) was obtained.

In the following, protons are assigned to the octyl group:

<sup>1</sup>H-NMR (500.2 MHz, D<sub>2</sub>O, 296 K): δ = 0.87 (t, <sup>3</sup>J<sub>H,H</sub> = 5.4 Hz, 3H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 1.29-1.67 (m, 12H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 2.99 (t, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>) ppm.-

The analytical data are in accordance to those reported (W. Hu, J. Li, H. Hou, H. Yan, Y. Feng, X. Mi, Q. Lin, *Asian J. Chem.* **2013**, *25*, 9904).”



**Figure S1.** <sup>1</sup>H NMR spectrum of octyl-grafted alginate amide.

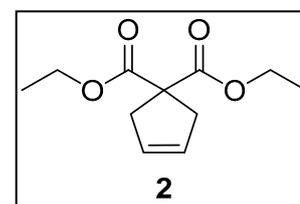
From: Pauly, J.; Gröger, H.; Patel, A.V. Metathesis in water conducted by tailor-made encapsulated Grubbs' catalyst. *Green Chem.* **2018**, *20*, 5179–5187, doi:10.1039/C8GC02164C.

### 3. Synthesis and Analytical Data of Diethyl Cyclopent-3-ene-1,1-dicarboxylate (**2**)

Since we already reported the preparation previously, we quote it from our previous study:

“This substance was synthesised as substrate for the enzymatic ester hydrolysis benchmark experiments. After diethyl 2,2-diallylmalonate (5.45 mmol; 1.31 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 ml), Grubbs’ second-generation catalyst ((1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro-(phenylmethylene)(tricyclohexylphosphine)ruthenium; 0.5 mol%; 0.027 mmol; 23 mg) was added and the resulting reddish solution was stirred for 20 h at room temperature. After the solvent was removed with a rotary evaporator, the product **2** was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 9:1, R<sub>f</sub> = 0.53) and provided as colourless liquid (1.130 g; 98%).

<sup>1</sup>H-NMR (500.2 MHz, CDCl<sub>3</sub>, 296 K): δ = 1.24 (t, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 6H, 2 x CH<sub>2</sub>CH<sub>3</sub>), 3.00 (s, 4H, CH<sub>2</sub>-CH=CH-CH<sub>2</sub>), 4.19 (q, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 4H, 2 x CH<sub>2</sub>CH<sub>3</sub>), 5.60 (s, 2H, CH<sub>2</sub>-CH=CH-CH<sub>2</sub>) ppm.-



The analytical data are in accordance to those reported (F. Michalek, W. Bannwarth, *Helv. Chim. Acta* **2006**, *89*, 1030).”

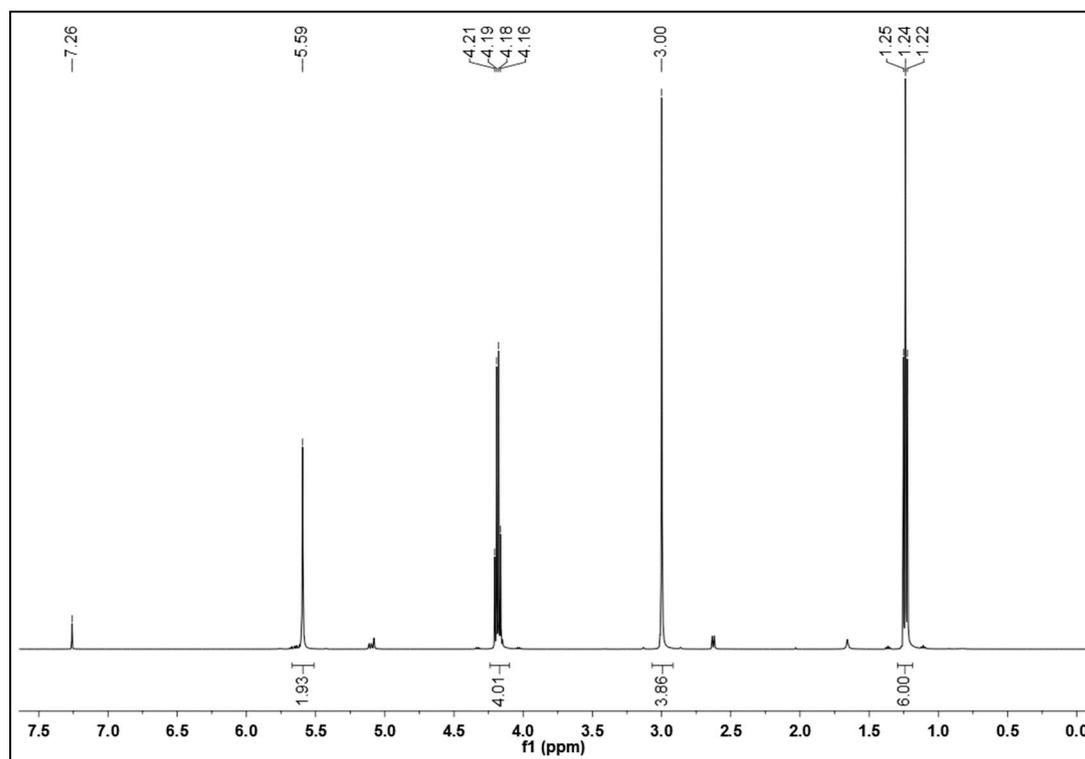


Figure S2. <sup>1</sup>H NMR spectrum of diethyl cyclopent-3-ene-1,1-dicarboxylate (**2**).

From: Pauly, J.; Gröger, H.; Patel, A.V. Catalysts Encapsulated in Biopolymer Hydrogels for Chemoenzymatic One-Pot Processes in Aqueous Media. *ChemCatChem* **2019**, *11*, 1504–1510, doi:10.1002/cctc.201802070.

## 4. HPLC Analysis

### 4.1 General

For the tandem one-pot process, we determined the selectivities of the desired product **3** via HPLC measurements: substances **3** and **4** were analysed alone and subsequently together to develop a suitable method. Then, we determined the **3** / **4** ratios after we recorded series of calibration with defined ratios.

### 4.2 Calibration

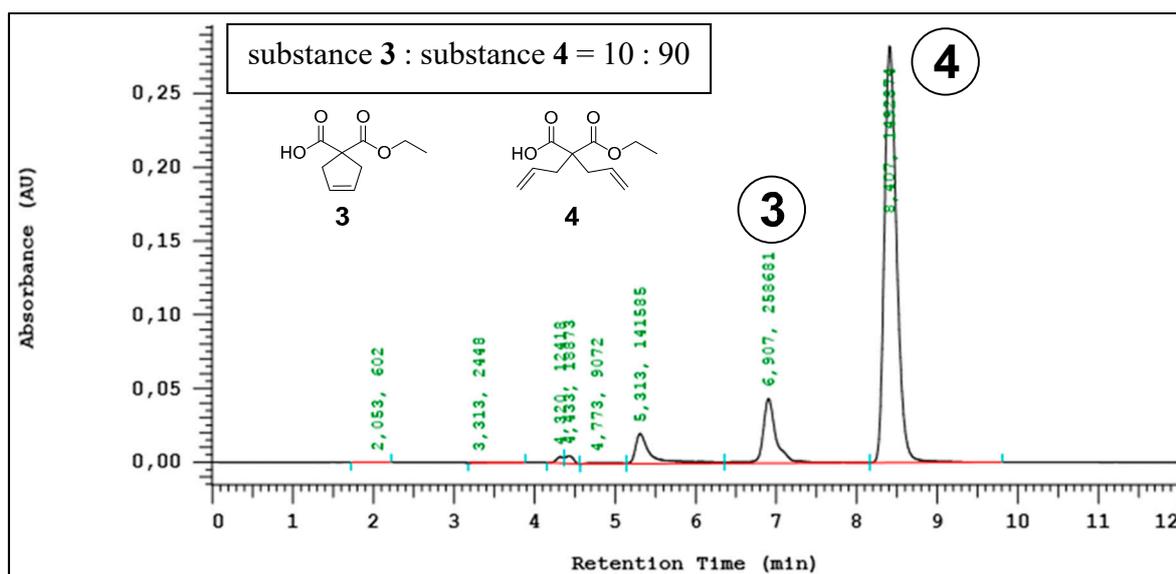


Figure S3. Calibration with 10% substance **3**.

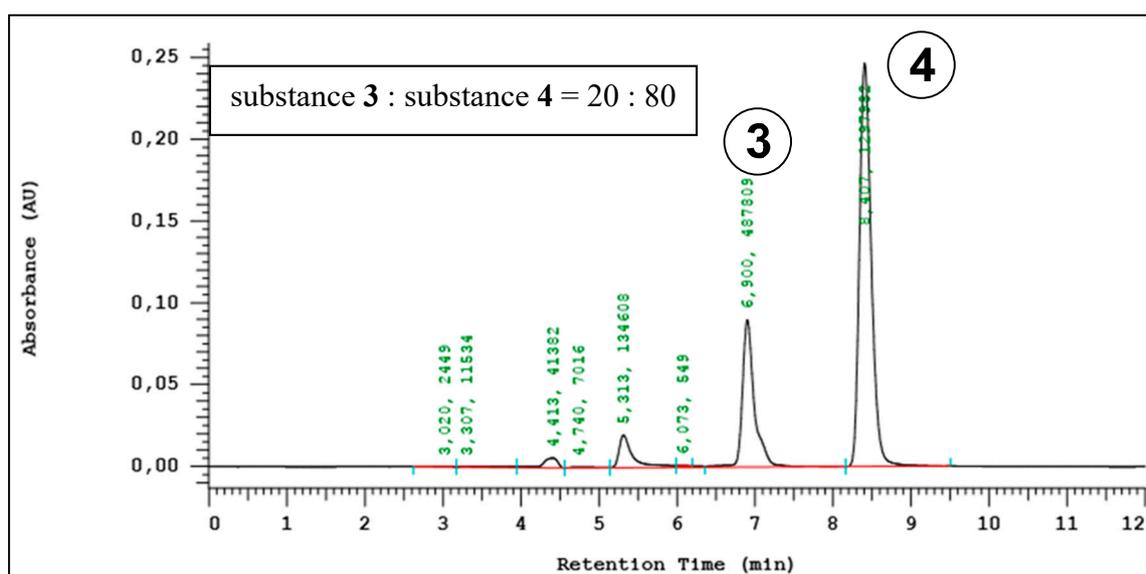


Figure S4. Calibration with 20% substance **3**.

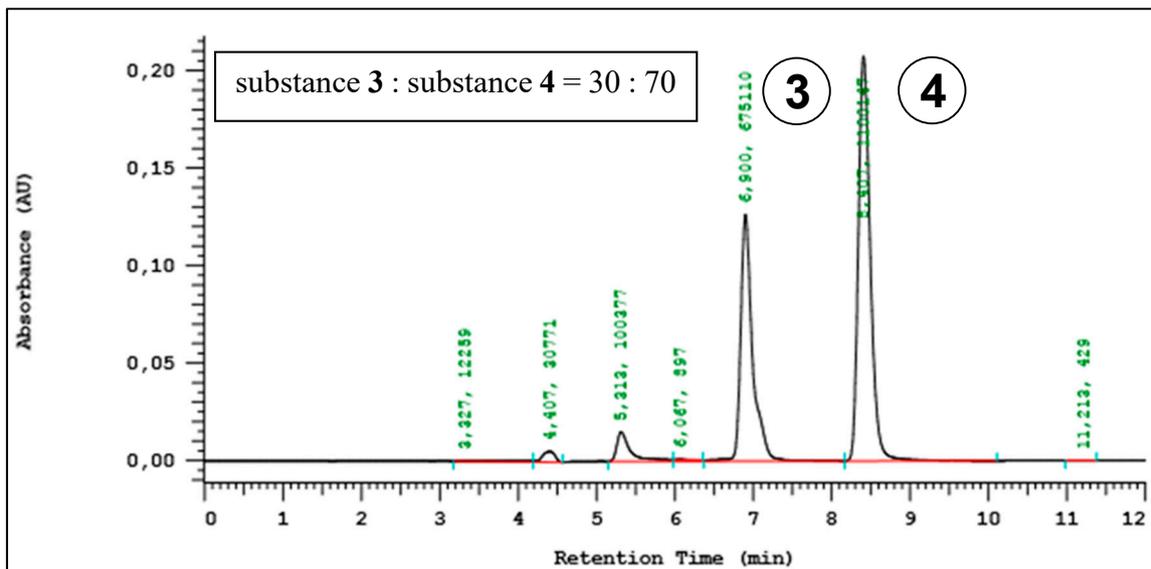


Figure S5. Calibration with 30% substance 3.

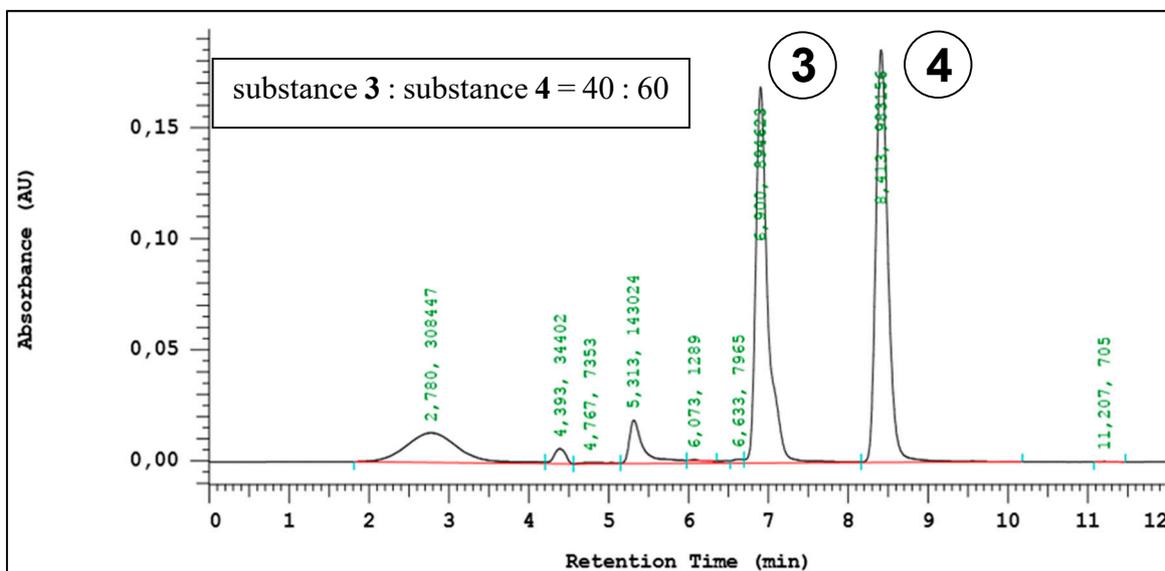


Figure S6. Calibration with 40% substance 3.

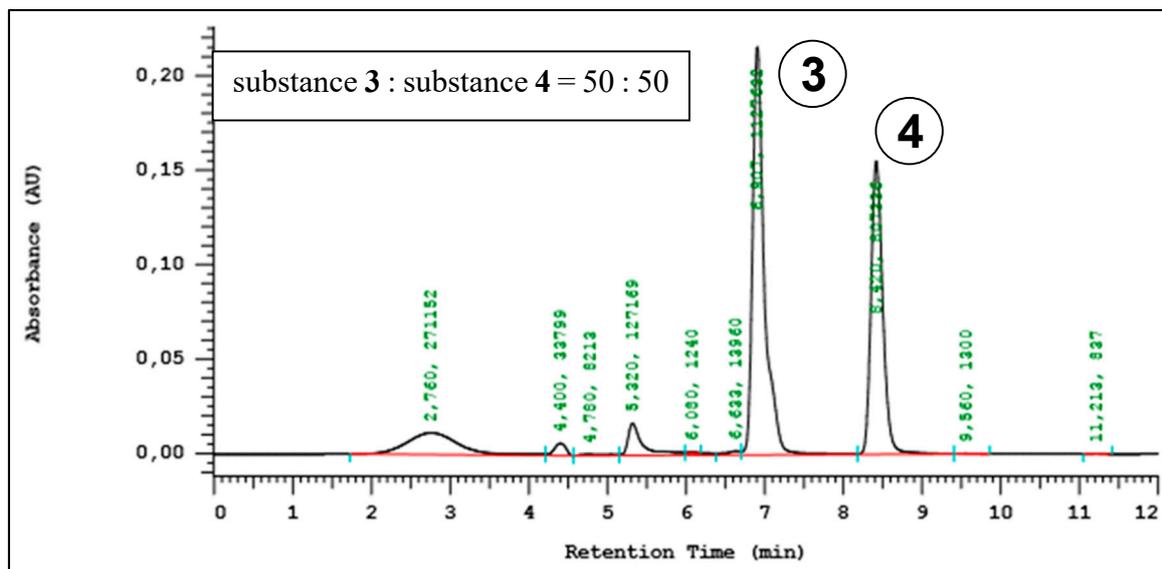


Figure S7. Calibration with 50% substance 3.

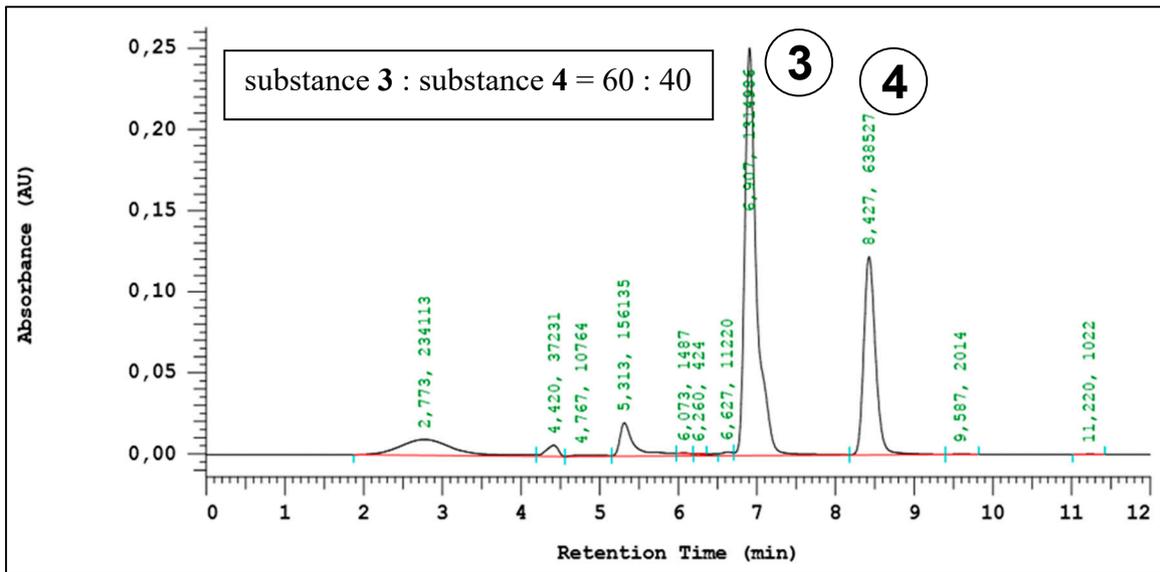


Figure S8. Calibration with 60% substance 3.

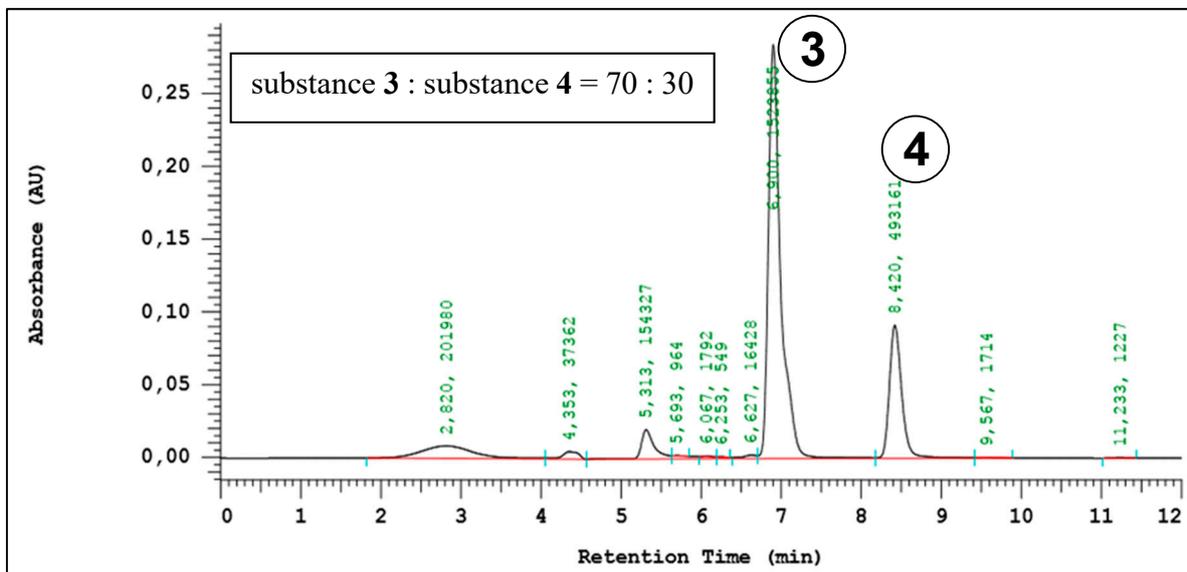


Figure S9. Calibration with 70% substance 3.

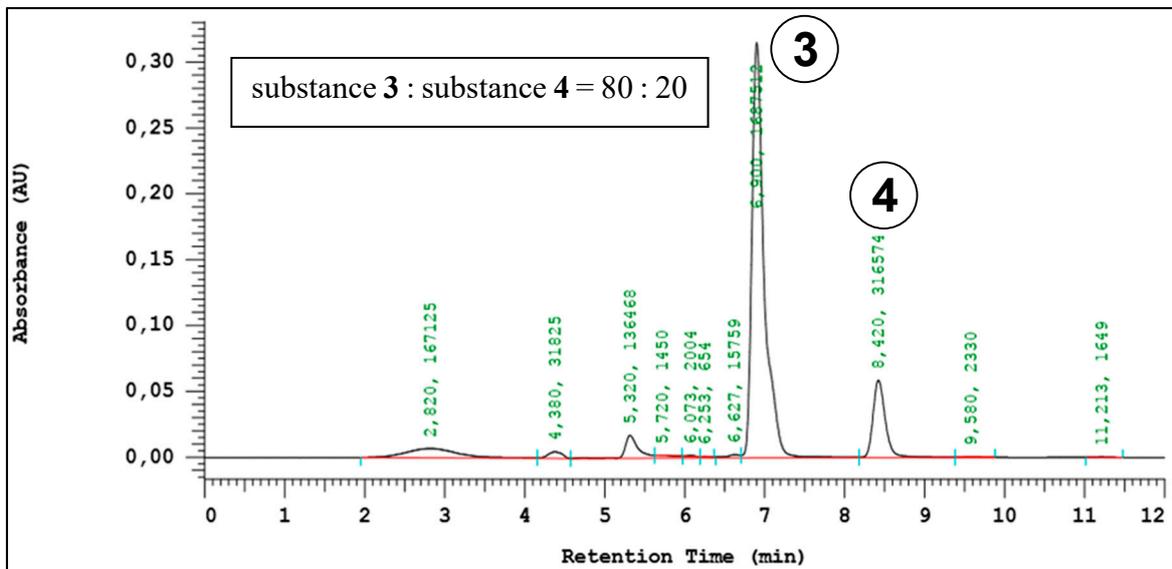


Figure S10. Calibration with 80% substance 3.

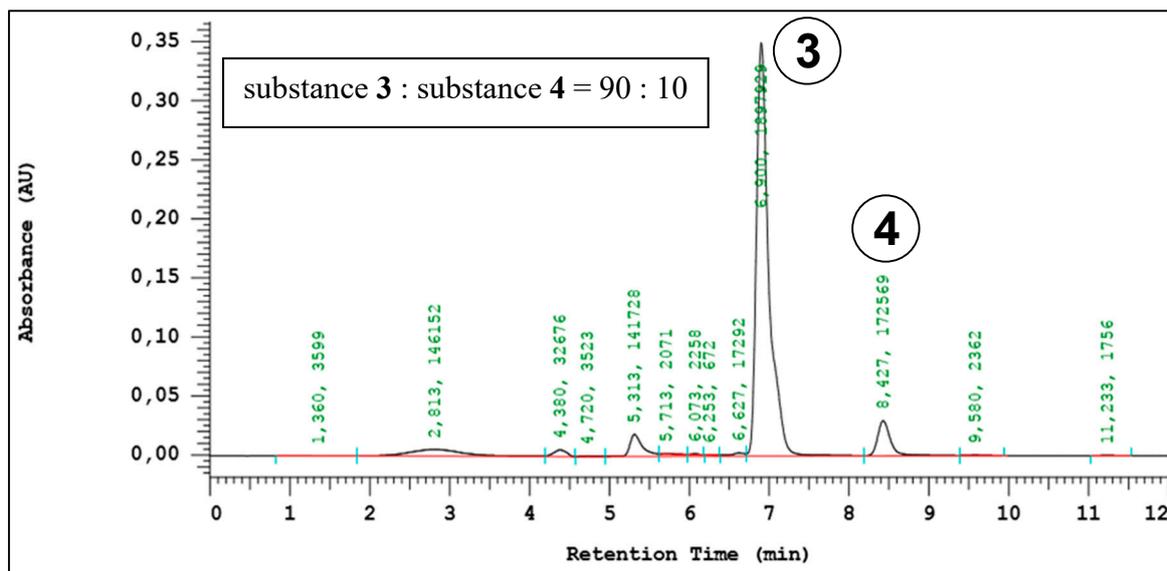


Figure S11. Calibration with 90% substance 3.

Table S1. Values for calibration of substance 3.

% Substance 3	% Substance 4	Integral substance 3	Integral substance 4	$\frac{\text{Integral substance 3}}{\text{Integral substance 4}}$
10	90	258681	1492874	0.147
20	80	487809	1297982	0.273
30	70	675110	1100147	0.380
40	60	894623	983156	0.476
50	50	1127632	807336	0.582
60	40	1314986	638527	0.673
70	30	1523855	493161	0.755
80	20	1687512	316574	0.842
90	10	1897929	172569	0.916

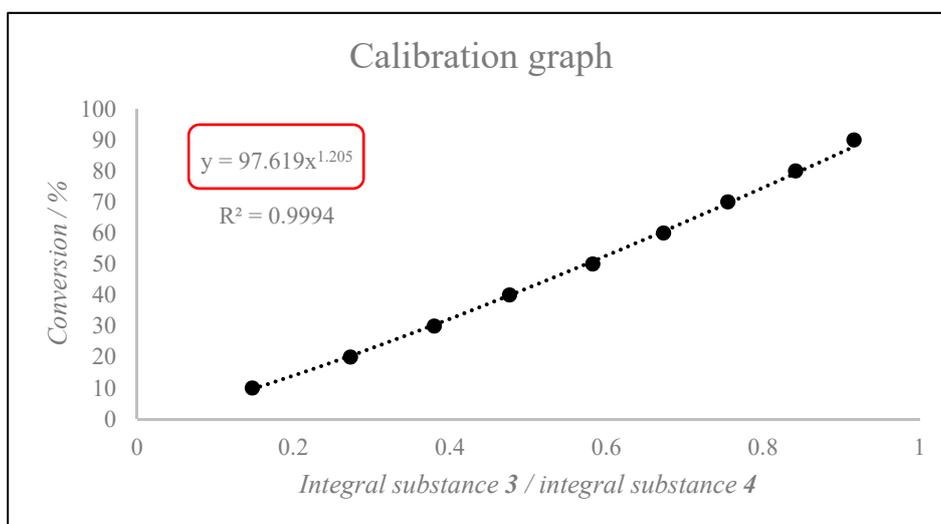


Figure S12. Calibration graph for determining the amount of substance 3.

### 4.3 Example for Determination of Selectivity

Catalysts co-encapsulated in multicompartiment beads with three layers of alginate amide.

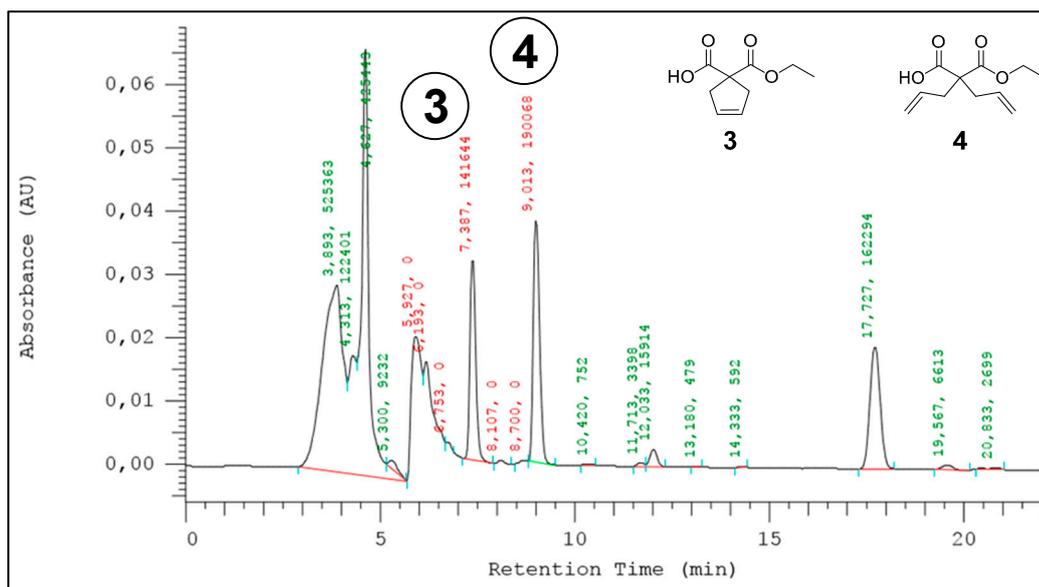


Figure S13. Exemplary chromatogram for determination of selectivity.

Table S2. Exemplary calculation of selectivity.

Integral substance 3	Integral substance 4	$\frac{\text{Integral substance 3}}{\text{Integral substance 4}}$	Product 3 / %
141644	190068	0.427	$97.619 \cdot 0.427^{1.205} = 35$