Supporting Information

Continuous production of amines directly from alkenes via cyclodextrin-mediated hydroaminomethylation using only water as the solvent

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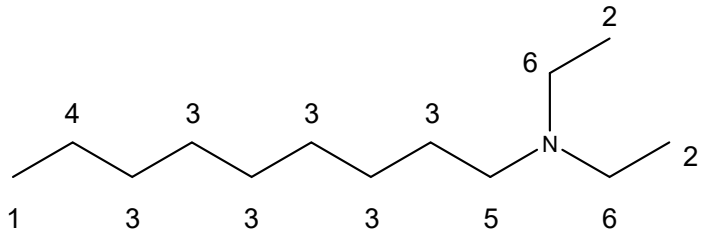
Product Identification

The measurement of NMR spectra was recorded with a 400 MHz spectrometer type BRUKER DVANCE III HD NANOBAY. Deuterated chloroform was used as the solvent for the samples.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, 3H, CH_3), 1.01 (t, 6H, CH_3), 1.26 (m, 12H, CH_2), 1.43 (m, 2H, CH_2), 2.40 (m, 2H, CH_2), 2.52 (q, 4H, CH_2)

^{13}C NMR (400MHz, $CDCl_3$) for the main product N,N,diethylnonylamine: δ =11.78, 14.25, 22.82, 27.09, 27.90, 29.45, 29.75, 29.8, 32.04, 47.03, 53.16



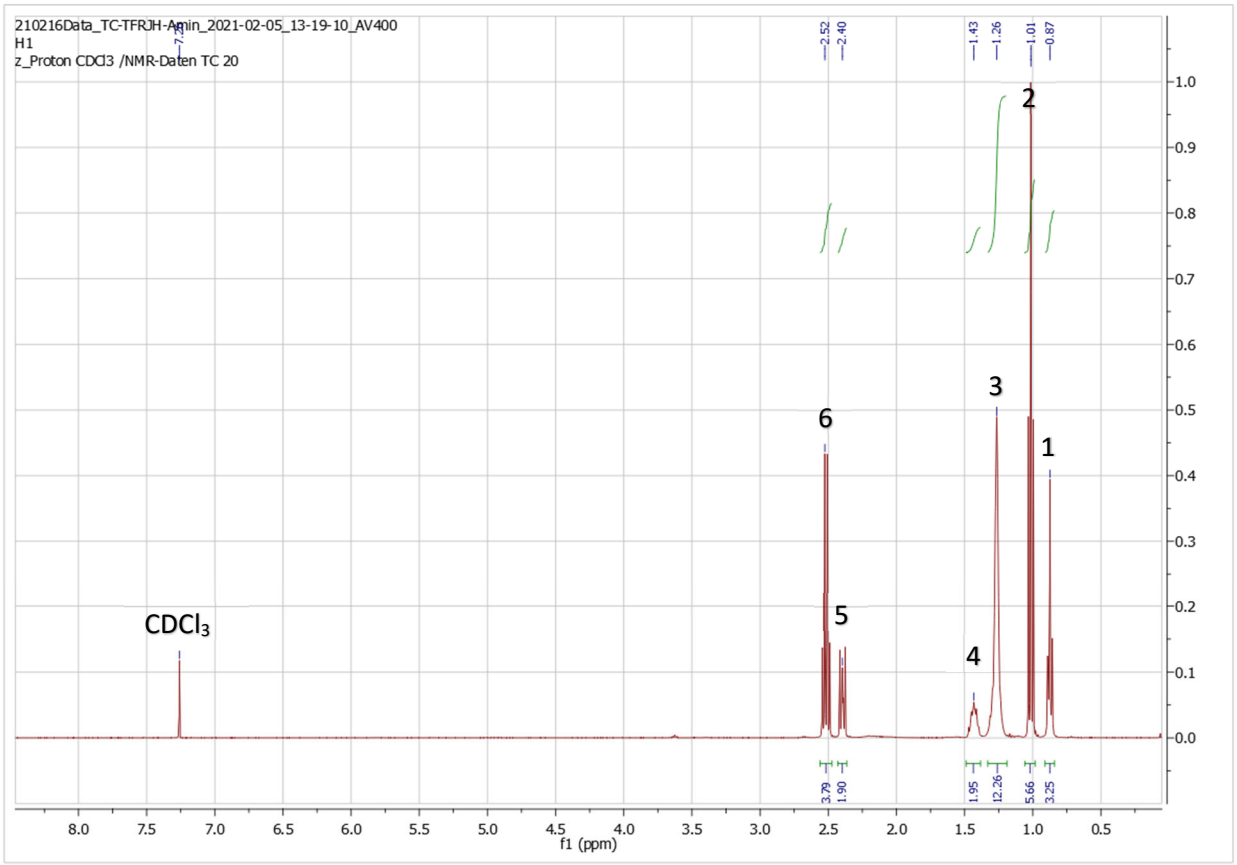


Figure S1: ^{1}H NMR (400MHz, $CDCl_3$) for the main product N,N,diethylnonylamine:

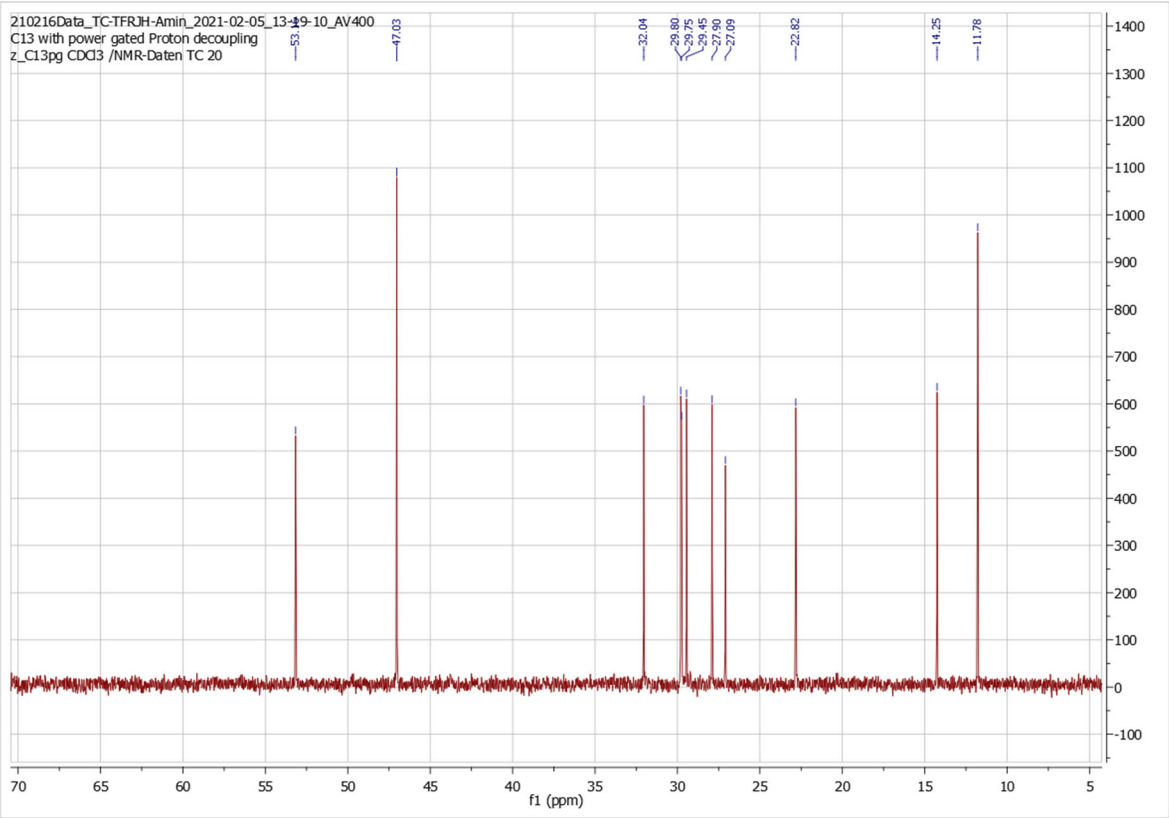


Figure S2: ^{13}C NMR (400MHz, $CDCl_3$) for the main product N,N,diethylnonylamine.

Batch Experiments

Recycling experiment

The reaction temperature was set to 120 °C, with a pressure of 30 bar and a molar ratio of hydrogen to carbon monoxide of 2:1. The organic volume fraction φ was 0.2. The molar ratio of catalyst to ligand to CD was set to 1:7:15, and mixing was assured using a pitched blade stirrer set to 800 rpm combined with a baffle system. The catalyst preforming time was set to 2 h, and the reaction time was decreased from 30 h to 24 h compared to the referenced publication.

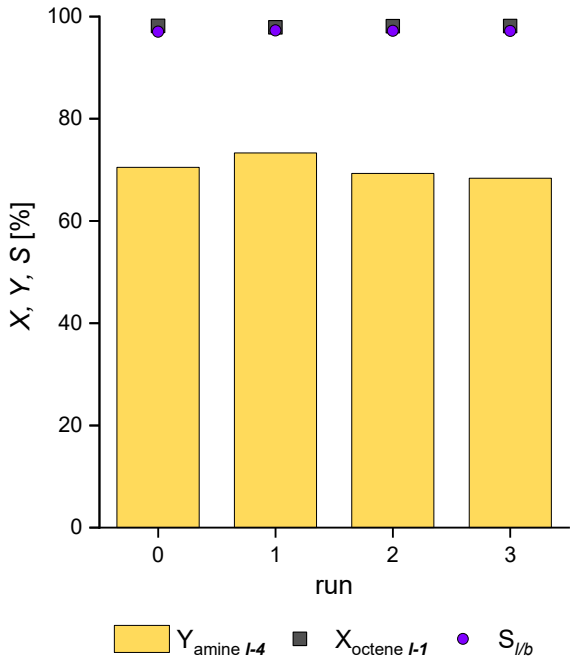


Figure S3: Recycle experiments for the hydroaminomethylation of octene ***l*-1** with diethylamine. Conditions: T = 120 °C; p = 35 bar; n_{CO}/n_{H2} = 1:2; u = 800 rpm; c_{Rh} = 3.2 mmol L^{-1}; $n_P:n_{Rh}$ = 7; $V_{liq.}$= 100ml; φ = 0.2; $n_{DEA}:n_{l\text{-}1}$ = 1.5; $n_{CD}:n_{Rh}$ = 15; t = 24 h; $n_{l\text{-}1,\text{per run}}$ = 0.117 mol; preforming$_{run0}$: T = 120 °C; p = 30 bar; n_{CO}/n_{H2} = 1:1; u = 800 rpm; t = 2 h.

Table S1: ICP-OES measurements of organic phase after the recycle experiments for the hydroaminomethylation of 1-octene with diethylamine. Leaching of catalyst and ligand were calculated based on the remaining masses after the previous run.

Run:		0	1	2	3
$w_{Rh,org}$	[ppm]	1	1	1	1
L_{Rh}	[%]	0,21	0,21	0,21	0,22
$w_{P,org}$	[ppm]	8	6	7	7
L_P	[%]	0,25	0,19	0,22	0,22

Increased CD-concentration:

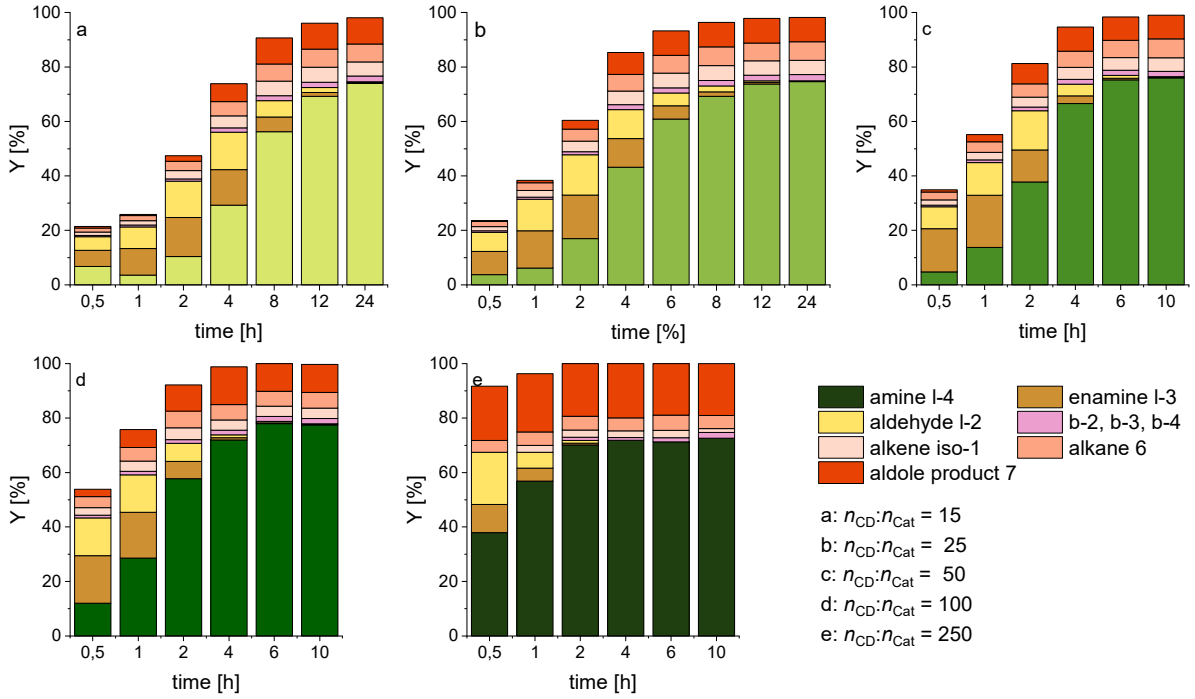


Figure S4: Yield over time for the HAM in dependency of the CD to catalyst ratio as presented in Figure 5 in the main part. Conditions: T = 120 °C; p = 35 bar; n_{CO}/n_{H2} = 1:2; u = 800 rpm; c_{Rh} = 3.2 mmol L^{-1}; n_P:n_{Rh} = 7; φ = 0.2; n_{DEA}:$n_{1\ Alkene}$ = 1.5; n_{CD}:n_{Rh} = 50 to 250; preforming: T = 120 °C; p = 35 bar; n_{CO}/n_{H2} = 1:1; u = 800 rpm; t > 12 h

Additional Results: Reducing catalyst concentration at high cyclodextrine Concentrations:

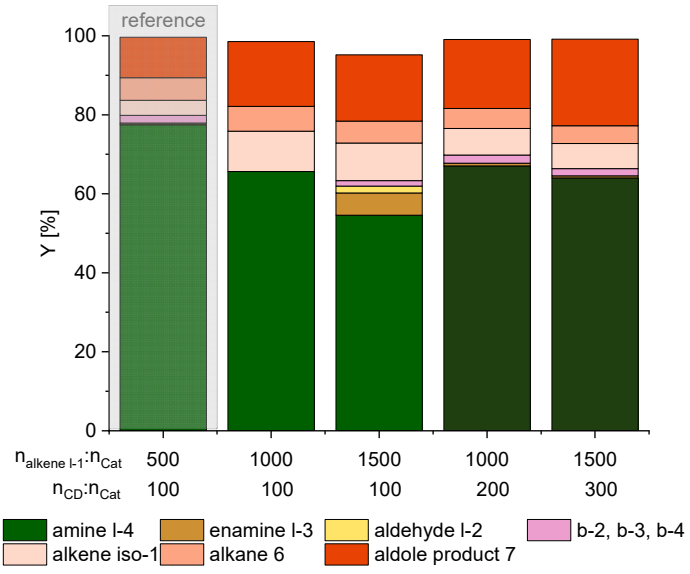


Figure S5: Yield over time for various substrate to catalyst and cyclodextrine to Catalyst ratios of the hydroaminomethylation of 1- octene with diethylamine. Conditions: T = 120 °C; p = 35 bar; n_{CO}/n_{H2} = 1:2; n = 800 rpm; c_{Rh} = 1.1 to 3.2 mmol L-1; n_P:n_{Rh} = 7; φ = 0.2; n_{DEA}:$n_{1\ Alkene}$ = 1.5; t = 10 h; preforming: T = 120 °C; p = 35 bar; n_{CO}/n_{H2} = 1:1; n = 800 rpm; t > 12 h

Continuous Experiments

First continuous experiment

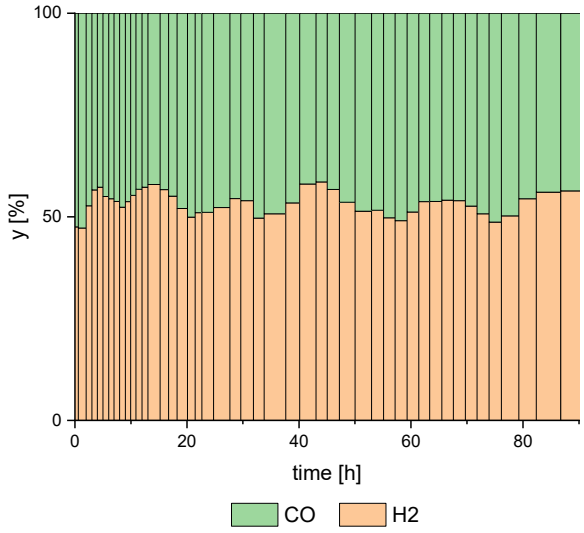


Figure S6: Mole fraction of gasses in reactor during the first continuous experiment.

Second continuous experiment

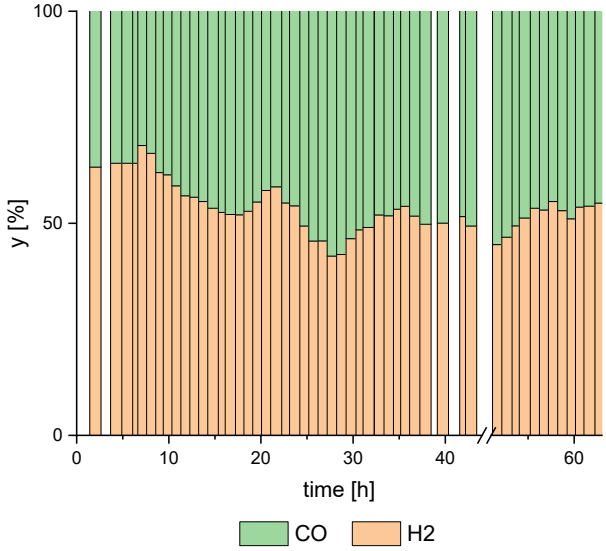


Figure S7: Mole fraction of gasses in reactor during the second continuous experiment.

Third continuous experiment

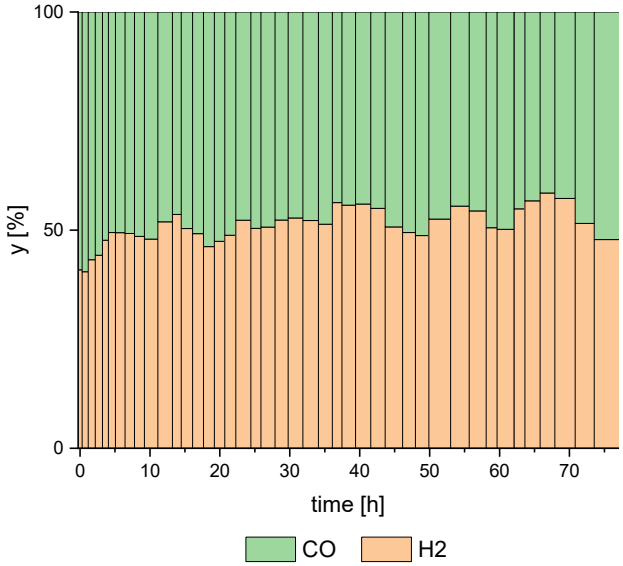


Figure S8: Mole fraction of gasses in reactor during the third continuous experiment.

Detection of CD loss to product phase *via* MS:

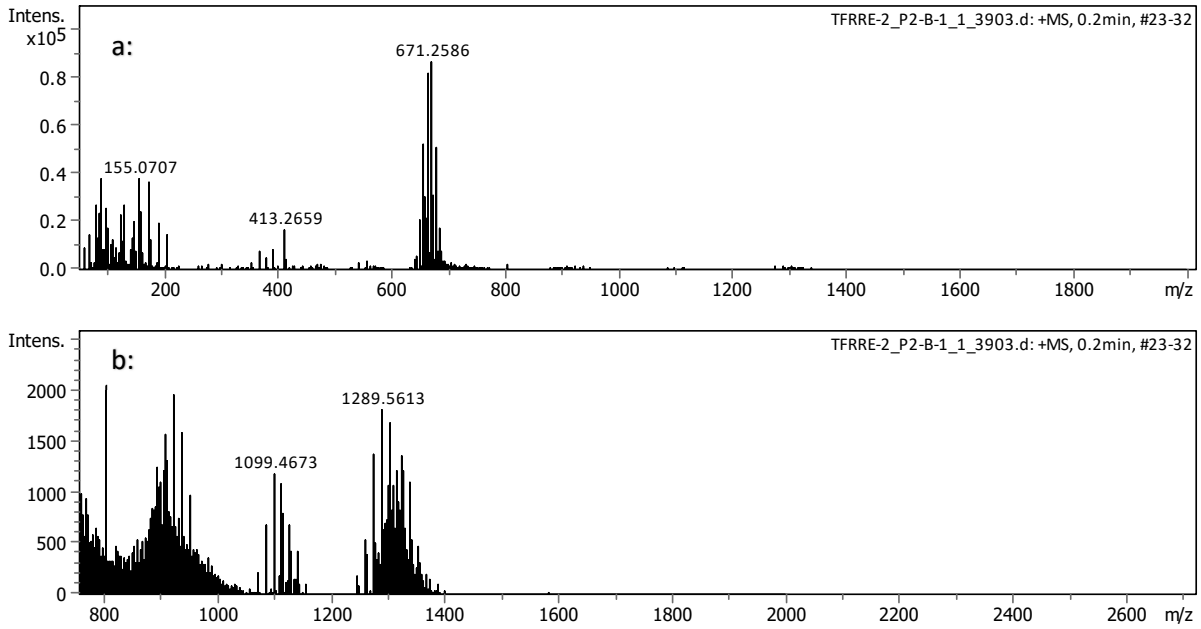
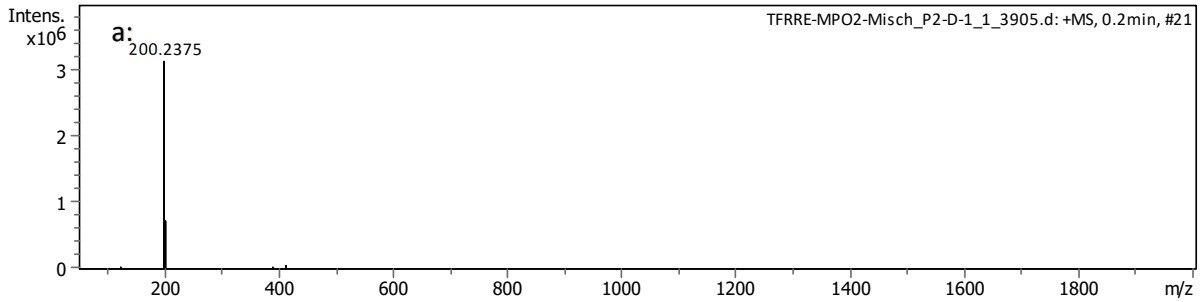


Figure S9: Mass spectrum of a reference aqueous solution with CD concentration of .1mg/ml. a: whole spectrum, b: zoomed in lower intensities



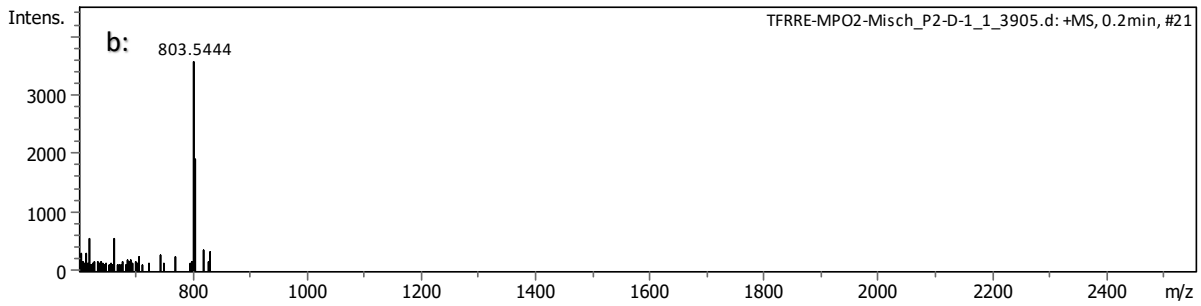


Figure S10: Mass spectrum product solution of third continuous experiment. a: whole spectrum, b: zoomed in lower intensities

Calibration:

Analysis of product mixtures was done with a gas chromatography by Agilent Technologies (7890A) with a flame ionization detector and a capillary column type HP-5 (30m x 0.32mm x 0.25µm). For this purpose, 0.6 g of Tetrahydrofuran as the solvent, 0.05 of di-*n*-butylether as the internal standard, and 0.35 g of sample were used.

Table S2: Heat profile for the GC-FID analysis.

	Rate [°C/min]	Target Value [°C]	Hold Time [min]
T_{Start}		40	3
Ramp 1	7.5	150	0
Ramp 2	40	320	0
T_{End}		320	8

Table S3: Retention times and response factors for the GC- FID analysis.

Spezies	Retention Time [min]	Response Factor
DEA, Diethylamin	1.77	1.0483
***l*-1**, 1-Octen	4.26	1.3434
6, Octan	4.43	1.3642
***iso*-1**, Iso- Octen	4.58- 4.74	1.3434
***b*-2**, b-Nonanal	10.4	0.8928
***l*-2**, l-Nonanal	11.25	0.8928
Nonanol	12.4	0.9516
***b*-4**, b-amine	12.56	0.9603
***b*-3**, b-enamine	14.65	0.9603
***l*-4**, l-amine	15.92	0.9603
***l*-3**, l-enamine	16.79	0.9603
7, aldol condensate	20.0-21.5	0.6377