

## Supporting Information

### **Aqueous Biphasic Hydroaminomethylation enabled by Methylated Cyclodextrins: Sensitivity analysis for transfer into a Continuous Process**

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Total number of pages: 8 (S1-S8)

Total table of pages: 5 (Table S1- Table S5)

Total number of figures: 9 (Figure S1-Figure S9).

# Additional results of sensitivity analysis

## Analysis of solid content

The solid obtained was analysed by NMR (after dilution with  $\text{CDCl}_3$ ), FT-IR and MALDI experiments. NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz. Mass spectra were recorded on a MALDI-TOF/TOF Bruker Daltonics Ultraflex II in positive reflectron mode with 2,5-DHB as matrix. IR spectra were recorded on Fourier transform infrared spectrophotometer SHIMADZU IRAffinity-1.

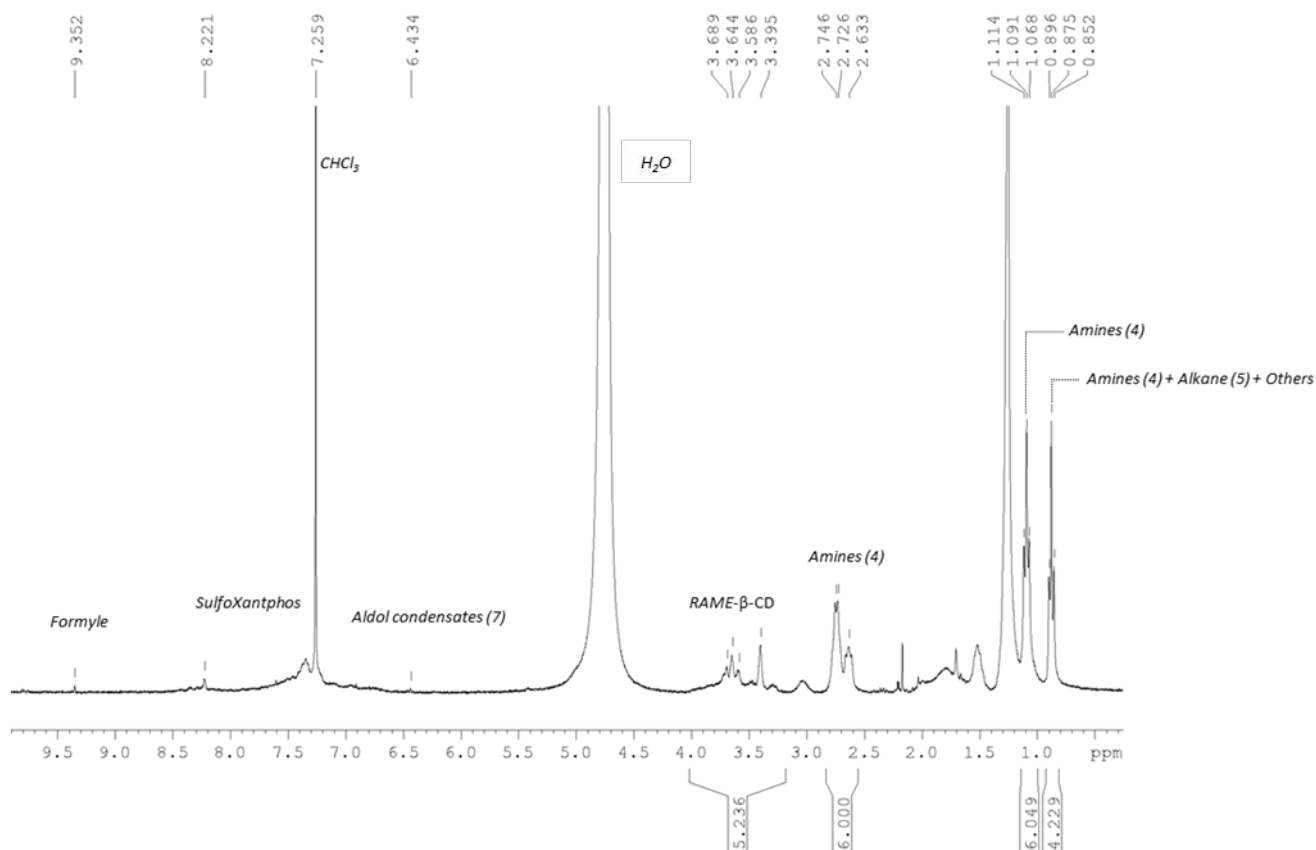


Figure S1:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectrum of isolated solid

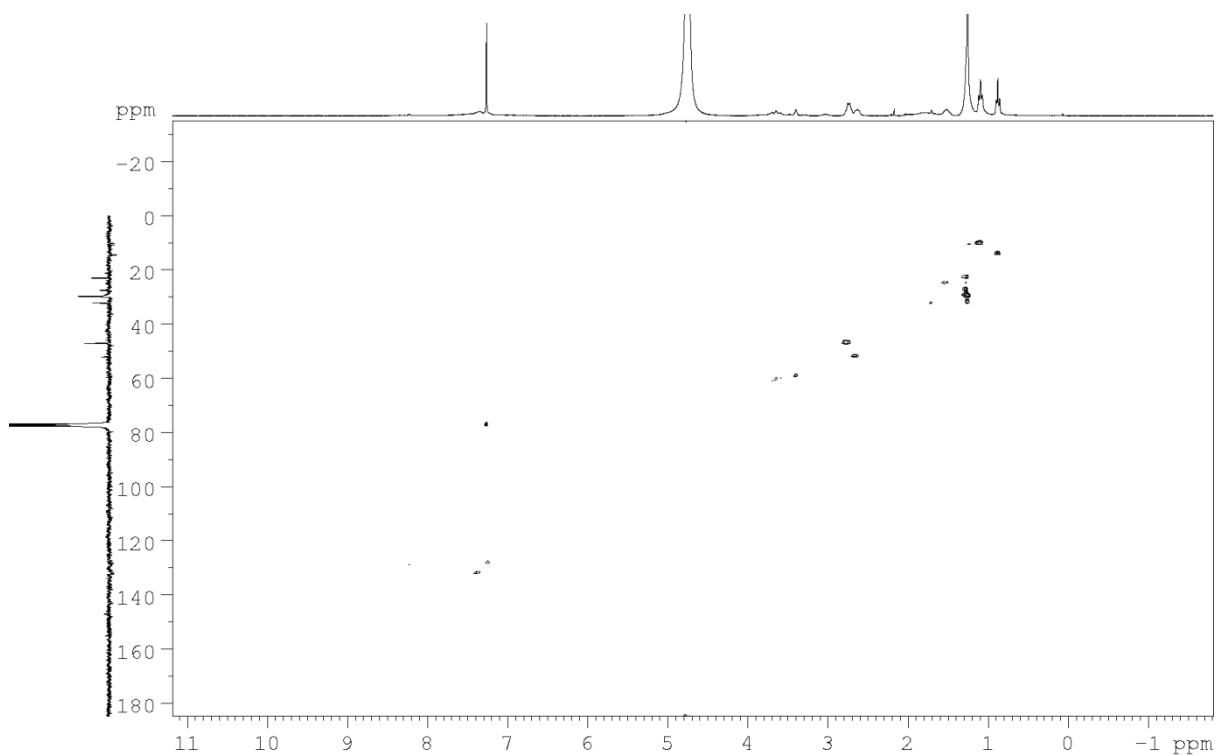


Figure S2: HSQC NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) spectrum of isolated solid

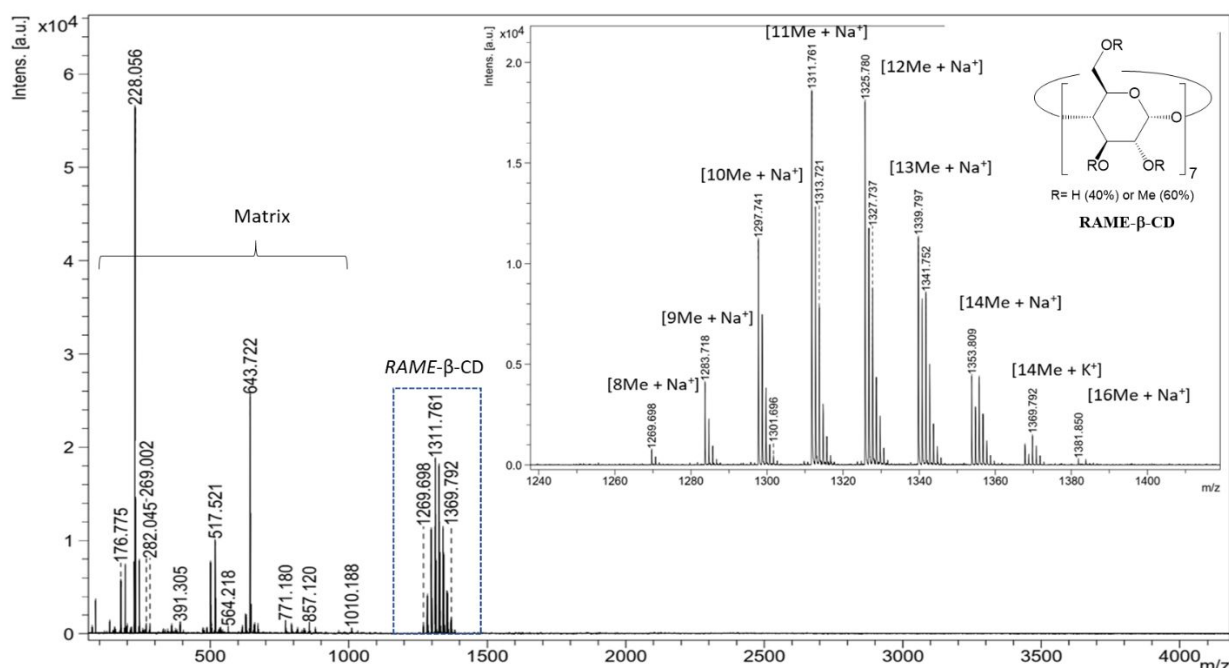


Figure S3: MALDI spectrum of isolated solid

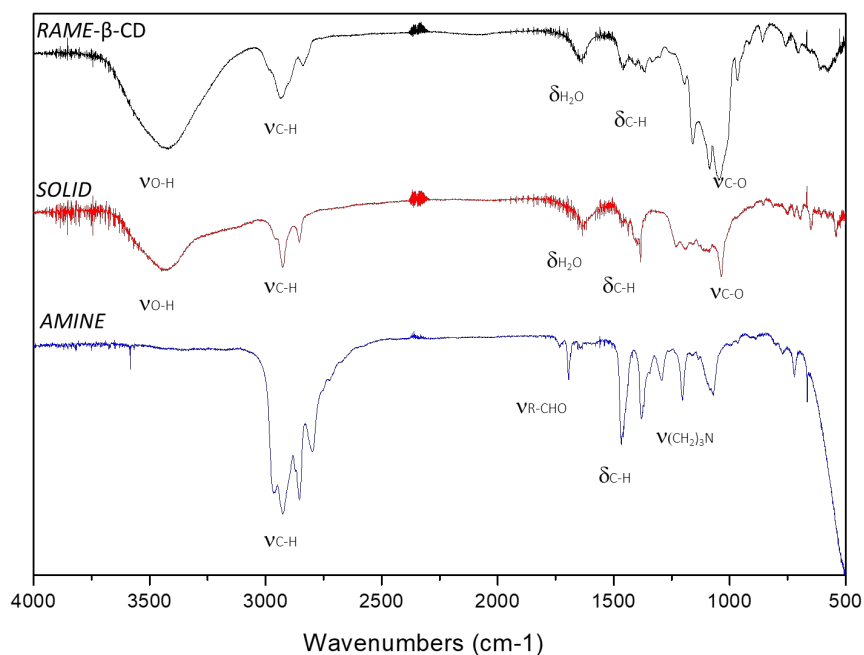


Figure S4: IR spectrum of RAME-β-CD, Solid and Amine

## Additional results to batch experiments

Table S1: Additional results to all 23 conducted batch experiments for the sensitivity analysis in 300 ml autoclave

#	<i>l/b</i>	TOF [h <sup>-1</sup> ]	X [%]	#	<i>l/b</i>	TOF [h <sup>-1</sup> ]	X [%]
1	32.6	11.5	97.5	13	30.6	8.1	99.8
2	32.5	17.5	93.5	14	34.1	11.6	91.2
3	13.9	17.6	94.7	15	20.0	12.4	99.0
4	30.6	8.1	99.8	16	33.8	10.9	89.5
5	32.6	11.5	97.5	17	32.6	11.5	97.5
6	27.9	11.8	97.1	18	29.7	21.1	98.3
7	29.2	12.3	94.3	19	31.1	12.7	96.9
8	30.5	12.3	95.5	20	30.8	11.1	96.3
9	1.1	7.6	96.4	21	33.8	11.8	91.0
10	1.3	7.3	95.1	22	31.1	12.7	96.9
11	32.6	11.5	97.5	23	32.4	11.9	98.3
12	29.7	12.1	98.3				



Figure S5: Three phasic reaction solution after reaction in separation funnel from experiment 8



Figure S6: Black solid content precipitation in reactor after reaction (experiment 10)

Table S2: Henry's law constants

T [°C]	H(T,H <sub>2</sub> ) [mol/L]	H(T,CO) [mol/L]
0	0.0184	0.0289
10	0.0171	0.0244
20	0.0161	0.0209
30	0.0151	0.0181
40	0.0143	0.0157
50	0.0136	0.0138
60	0.0129	0.0123
70	0.0124	0.011
80	0.0118	0.0098
90	0.0113	0.0089
100	0.0109	0.0081
110	0.0105	0.0074
120	0.0102	0.0068
130	0.0098	0.0062
140	0.0095	0.0058
150	0.0092	0.0054
160	0.009	0.005
170	0.0087	0.0047
180	0.0085	0.0044
190	0.0083	0.0041
200	0.0081	0.0039
210	0.0079	0.0037
220	0.0077	0.0035
230	0.0076	0.0033
240	0.0074	0.0031
250	0.0073	0.003
260	0.0071	0.0028

## Additional results: reproducibility of data in a 300 ml autoclave

Table S3: Reproducibility results for the HAM of 1-decene and diethylamine under optimized conditions in 300 ml autoclave (reaction profile).

Nr.	X [%]	S4 [%]	Y4 [%]	Y3 [%]	Y2 [%]
24.1	90.9	77.5	70.5	0.3	2.6
24.2	97.1	78.2	76.0	0.1	0.3
24.3	95.9	80.6	80.3	0.1	0.2
<b>Standard Deviation</b>	<b>3.2</b>	<b>1.6</b>	<b>4.9</b>	<b>0.06</b>	<b>1.4</b>

**Reaction conditions:**  $c_{\text{Cat.}}$ : 2.6 mmol/l,  $n_{1\text{-decene}}/n_{\text{Cat.}}$ : 500,  $n_{\text{SXP}}/n_{\text{Cat.}}$ : 2.5,  $n_{\text{CD}}/n_{\text{Cat.}}$ : 15,  $n_{\text{DEA}}/n_{1\text{-decene}}$ : 1.5,  $\phi$ : 0.2, T: 125 °C, p: 30 bar, t: 30h, n: 800 rpm with pitched blade stirrer.

## Additional results: recycling experiments

Table S4: Recycle experiments for the HAM of 1-decene and diethylamine under optimized conditions.

Nr.	Rh-Leaching [ppm]	P-Leaching [ppm/]	l/b	TOF [h <sup>-1</sup> ]	X [%]	S4 [%]	Y4 [%]	Y3 [%]	Y2 [%]
25	10 (0.6%)	4 (0.3%)	26	10	92.9	72	67	0	1
26	10 (0.7%)	16 (1.5%)	6	11	93.8	72	68	0	0
27	52 (3.5%)	42 (3.8%)	2	7	96.2	41	39	0	1

**Reaction conditions:**  $c_{\text{Cat.}}$ : 2.6 mmol/l,  $n_{1\text{-decene}}/n_{\text{Cat.}}$ : 500,  $n_{\text{SXP}}/n_{\text{Cat.}}$ : 2.5,  $n_{\text{CD}}/n_{\text{Cat.}}$ : 12,  $n_{\text{DEA}}/n_{1\text{-decene}}$ : 1.5,  $\phi$ : 0.25, T: 125°C,  $p_{\text{Start}}$ : 30 bar, t: 30 h, n: 800 rpm with pitched blade stirrer.



Figure S7: Reaction solution of recycle run 0 (left) and recycle run 2 (right) after the experiment in separation funnel



## Additional results: reaction profile in a 2100 ml autoclave

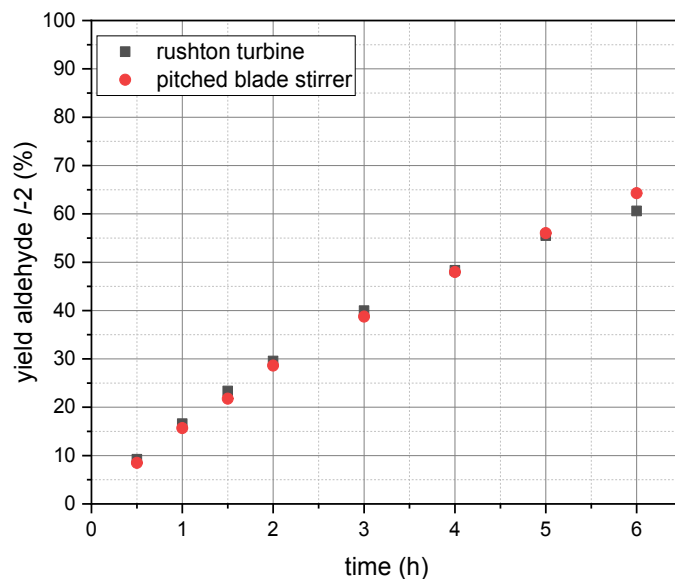


Figure S8: Comparison of blade stirrer and rushton turbine for the hydroformylation of 1-decene in a 2100 ml autoclave.

Reaction conditions:  $c_{\text{Cat.}}$ : 1.8 mmol/l,  $n_{1\text{-decene}}/n_{\text{Cat.}}$ : 1000,  $n_{\text{SXP}}/n_{\text{Cat.}}$ : 2.5,  $n_{\text{CD}}/n_{\text{Cat.}}$ : 12,,  $\phi$ : 0.25, T: 120°C, p: 40 bar, t: 30h.

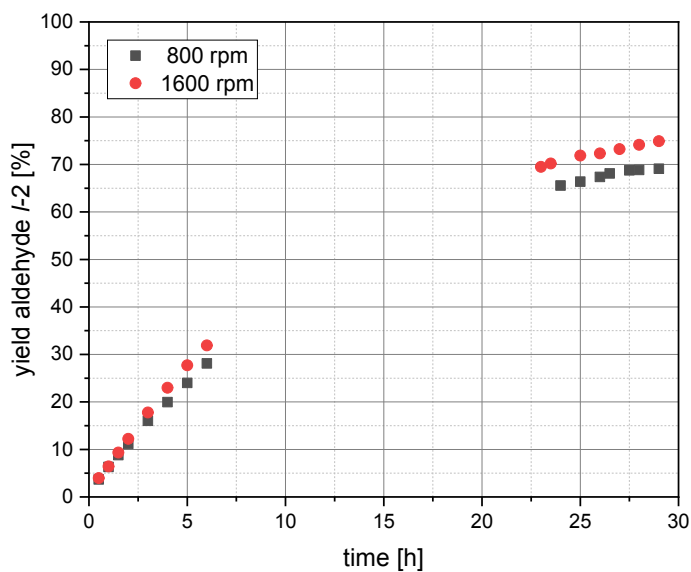


Figure S9: Comparison of the stirrer using a Rushton turbine for the hydroformylation of 1-decene in a 2100 ml autoclave.

Reaction conditions:  $c_{\text{Cat.}}$ : 1.8 mmol/l,  $n_{1\text{-decene}}/n_{\text{Cat.}}$ : 1000,  $n_{\text{SXP}}/n_{\text{Cat.}}$ : 2.5,  $n_{\text{CD}}/n_{\text{Cat.}}$ : 12,,  $\phi$ : 0.25, T: 120°C, p: 40 bar, t: 30h, Rushton turbine.



Table S5: Extended results for the HAM of 1-decene and diethylamine under optimized conditions in 2100 ml autoclave (reaction profile).

#	SCP	$\sum Y_{MP}$ [%]	$\sum Y_{SP}$ [%]	<i>l/b</i>	TOF [h <sup>-1</sup> ]	X [%]	S 4 [%]	Y 4 [%]	Y 3 [%]	Y 2 [%]
28	N	83	14	33.6	13.5	98.4	83	82	0	1

MP = Main products (aldehyde **2** + enamine **3** + amine **4**); SP= By-products (alkanes **5** + alcohol **6** + aldol condensates **7**)

**Reaction conditions:**  $c_{Cat.}$ : 2.6 mmol/l,  $n_{1-decene}/n_{Cat.}$ : 500,  $n_{SXP}/n_{Cat.}$ : 2.5,  $n_{CD}/n_{Cat.}$ : 15,  $n_{DEA}/n_{1-decene}$ : 1.5,  $\phi$ : 0.2, t: 30 h, T: 125°C,  $p_{Start}$ : 40 bar, n: 800 rpm with Rushton turbine.