Electronic Supplementary Material (ESI) for ChemComm.

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

From 3D to 4D printing: a reactor for photochemical experiments using hybrid polyurethane acrylates for vat-based polymerization and surface functionalization

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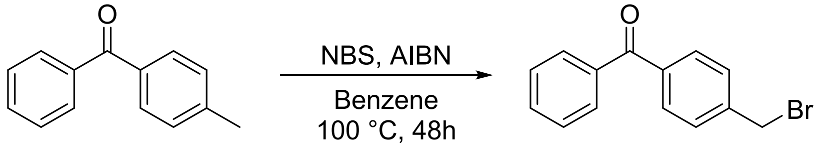
1. Synthesis of catalysts

General

All chemicals and solvents (HPLC grade) were purchased from commercial suppliers and used without further purification.

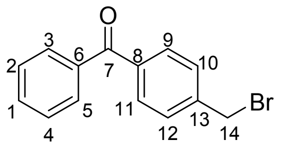
The present ^{1}H and ^{13}C NMR spectra were measured on a Bruker spectrometer of type Bruker Avance III 499 (499 MHz and 125 MHz) and Avance II 300 (300 MHz and 75 MHz). 2D spectra were recorded on a Bruker Avance III 499 (500 MHz or 125 MHz).The internal standard was the proton signal of the deuterated solvent $CDCl_3$ (7.26 ppm (1H), 77.16 ppm (13C)) and CD_3OD (3.31 ppm (1H), 49.00 ppm (13C)) from Deutero. The chemical shift was given in ppm and the coupling constants *J* in Hz. The fine structure of the signals was described by the abbreviations s (singlet), d (doublet), dd (doubled), t (triplet) and m (multiplet). The multiplicity of the carbon signals was determined by APT experiments (attached proton test) and designated by the abbreviations q (CH3), t (CH2), d (CH) and s (quaternary carbon atoms). The assignment of the signals was performed with the help of the 2D-NMR experiments H,H-COSY, H,H-NOESY, HSQC and HMBC..

(4-(Bromomethyl)-benzophenone (13)



12 **13**

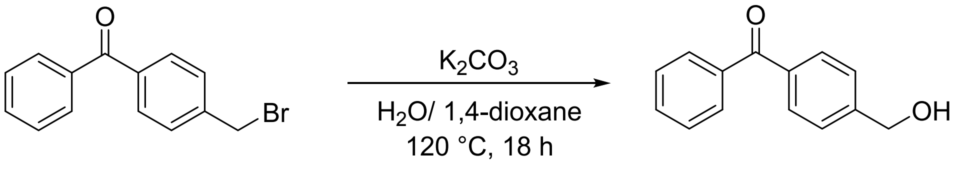
1.96 g (10.0 mmol, 1.0 eq.) 4-methylbenzophenone (**12**), 1.95 g (10.1 mmol, 1.01 eq.) N-bromosuccinimide (NBS) and 23.0 mg (0.14 mmol, 0.01 eq.) azobis(isobutyronitrile) (AIBN) were refluxed in benzene for 48 hours. After cooling, the solvent was removed under reduced pressure, the mixture was absorbed into EtOAc and washed with water (5x30 ml). The combiend organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was obtained as a colorless solid (2.31 g, 8.50 mmol, 85%)..



^{1}H-NMR[1] (499 MHz, $CDCl_3$): *δ* (ppm): 7.82 – 7.76 (m, 4H, H-3, H-5, H-9, H-11), 7.60 (td, *J* = 7.3, 1.3 Hz, 1H, H-1), 7.54 – 7.46 (m, 4H, H-2, H-4, H-10, H-12)), 4.54 (s, 2H, H-14).

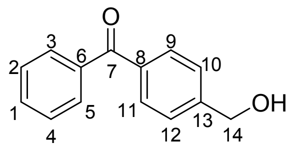
^{13}C-NMR[1] (125 MHz, $CDCl_3$): *δ* (ppm): 196.1 (s, C-7), 142.2 (s, C-13), 137.5 (s, C-6), 137.4 (s, C-8), 132.7 (d, C-1), 130.6 (d, C-3, C-5), 130.1 (d, C-9, C-11), 129.0 (d, C-2, C-4), 128.6 (d, C-10, C-12), 32.4 (t, C-14).

(4-(Hydroxymethyl)-benzophenone (4)



13 **4**

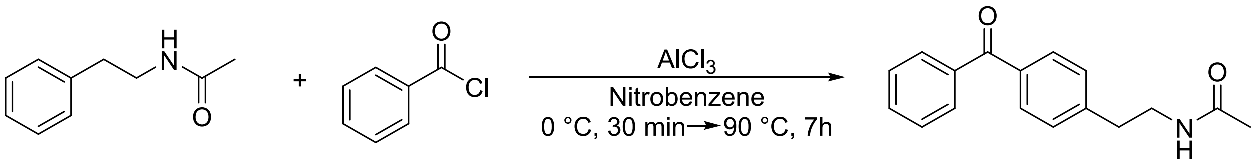
500 mg (1.80 mmol, 1.0 eq.) (4-(bromomethyl)benzophenone (**13**) were dissolved in 5 ml 1,4-dioxane and 995 mg (6.50 mmol, 3-6 eq.) K_2CO_3 were dissolved in 5 ml water. The combined solutions were refluxed for 18 hours. After cooling, the solution was extracted with $CHCL_3$ (3x20ml), the combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was purified by column chromatography ($CHCl_3$, R_f: 0.30) and was obtained as a slightly yellow solid (192 mg, 0.91 mmol, 51%)..



^{1}H-NMR[2] (499 MHz, $CDCl_3$): *δ* (ppm): 7.75 (dq, *J* = 8.2, 2.0 Hz, 4H, H-3, H-5, H-9, H-11), 7.60 – 7.55 (m, 1H, H-1), 7.51 – 7.40 (m, 4H, H-2, H-4, H-10, H-12), 4.76 (s, 2H, H-14), 2.89 (bs, *J* = 15.4 Hz, 1H, OH).

^{13}C-NMR[2] (125 MHz, $CDCl_3$): *δ* (ppm): 196.7 (s, C-7), 145.9 (s, C-13), 137.5 (s, C-6), 136.8 (s, C-8), 132.5 (d, C-1), 132.2 (d, C-9, C-11), 130.0 (d, C-3, C-5), 128.3 (d, C-2, C-4), 126.4 (d, C-10, C-12), 64.4 (t, C-14).

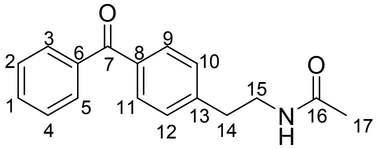
N-(4-Benzoylphenethyl)acetamide (16)



14 **15** **16**

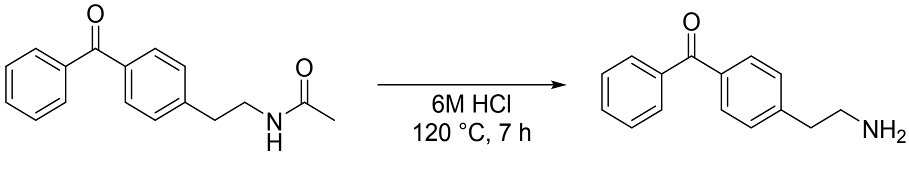
The product was prepared according to literature.[3] Under inert atmosphere, 1.00 g (6.13 mmol, 1.0 eq.) N-phenethylacetamide (**14**) and 0.71 ml (0.86 g, 6.13 mmol, 1.00 eq.) benzoyl chloride (**15**) were added to 3 ml dry nitrobenzene and cooled to 0°C. Within 30 min, 1.63 g (12.2 mmol, 2.0 eq.) $AlCl_3$ was added in portions to the reaction solution. After complete addition, the solution was stirred for seven hours at 90 °C. After cooling, the solution was added to approx. 50 ml conc. HCl and was extracted once with 30 ml Et_2O, so that most of the nitrobenzene was removed from the aqueous phase. The aqueous phase was neutralized with 10% NaOH solution and was extracted with Et_2O (3x30 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. After column chromatographic purification (20 : 1, $CHCl_3$: MeOH, R_f: 0.26) the product could be obtained as a slightly yellow oil (734 mg, 2.75 mmol, 45%).

^{1}H-NMR [3] (499 MHz, $CDCl_3$): δ (ppm): 7.76 (ddd, J = 12.9, 5.5, 4.1 Hz, 4H, H-3, H-5, H-9, H-11), 7.59 (t, J = 7.6 Hz, 1H, H-1), 7.48 (t, J = 7.8 Hz, 2H, H-2, H-4), 7.34 – 7.26 (m, 2H, H-10, H-12), 6.06 (bs, 1H, NH), 3.57 – 3.50 (m, 2H, H-15), 2.91 (t, J = 7.1 Hz, 2H, H-14), 1.95 (s, 3H, H-13).



^{13}C-NMR [3] (125 MHz, $CDCl_3$): δ (ppm): 196.4 (s, C-7), 170.3 (s, C-16), 144.2 (s, C-13), 137.6 (s, C-6), 135.9 (s, C-8), 132.4 (d, C-1), 130.4 (d, C-3, C-5), 129.9 (d, C-9, C-11), 128.6 (d, C-10, C-12), 128.3 (d, C-2, C-4), 40.4 (t, C-15), 35.7 (t, C-14), 23.3 (q, C-17).

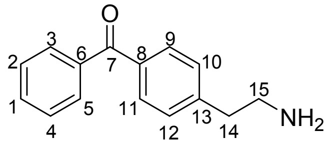
4-(2-Aminoethyl)benzophenone (5)



16 **5**

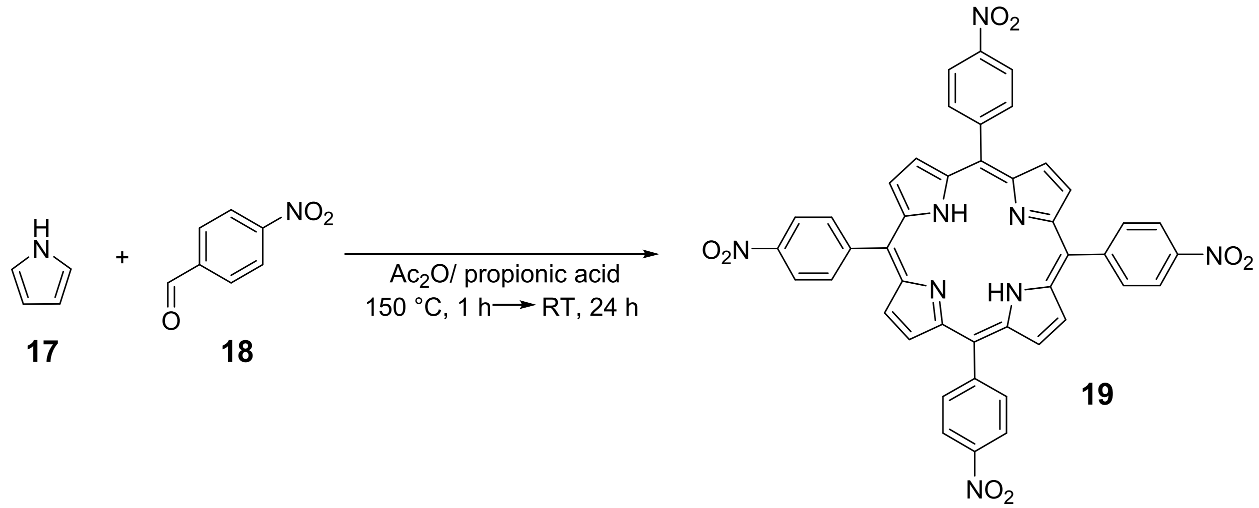
The product was prepared according to literature.[3] 706 mg (2.64 mmol) N-(4-benzoylphenethyl)acetamide (**16**) was dissolved in 5 ml 6 M HCl and was refluxed for 7 hours. After cooling to room temperature, the solution was neutralized with 10% NaOH and the aqueous phase was extracted with EtOAc (3x20 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (20 : 1, $CHCl_3$: MeOH, R_f: 0.74) and was obtained as a colorless solid (46.0 mg, 0.21 mmol, 8%).

^{1}H-NMR[3] (499 MHz, MeOD): *δ* (ppm): 7.77 (td, *J* = 5.7, 2.9 Hz, 4H, H-3, H-5, H-9, H-11), 7.69 – 7.62 (m, 1H, H-1), 7.53 (t, *J* = 7.8 Hz, 2H, H-2, H-4), 7.47 (d, *J* = 8.0 Hz, 2H, H-10, H-12), 3.25 (dd, *J* = 8.9, 6.6 Hz, 2H, H-15), 3.09 (dd, *J* = 9.0, 6.6 Hz, 2H, H-14).



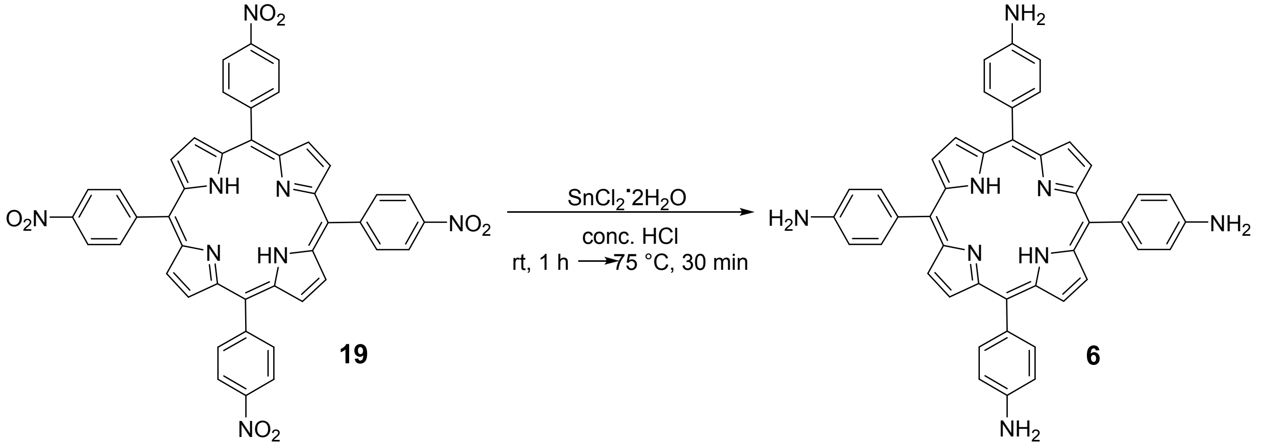
^{13}C-NMR[3] (125 MHz, MeOD): *δ* (ppm): 198.2 (s, C-7), 143.4 (s, C-13), 138.9 (s, C-6), 137.6 (s, C-8), 133.9 (d, C-1), 131.7 (d, C-9, C-11), 130.9 (d, C-3, C-5), 130.0 (d, C-10, C-12), 129.6 (d, C-2, C-4), 41.5 (t, C-15), 34.4 (t, C-14).

5,10,15,20-Tetrakis(4-nitrophenyl)porphyrin (19)



The product was prepared according to literature.[4] 5.50 g (36.5 mmol, 1.1 eq.) *para*-nitrobenzaldehyde (**18**) and 6 ml Ac_2O were dissolved in 150 ml propionic acid and heated to reflux. 2.30 ml (2.23 g, 33.2 mmol, 1.0 eq.) pyrrole (**17**) was dissolved in 5 ml propionic acid and added to the previous solution. The combined solutions were refluxed for 30 minutes and then allowed to rest for 24 hours at room temperature. The precipitated dark solid was filtered off, washed with approximately 500 ml water and dried under vacuum. In the second step, the solid was refluxed in pyridine for one hour, cooled to room temperature and stored overnight in the refrigerator. A purple solid was filtered off, which was not soluble in any common solvent (95.0 mg, 0.12 mmol, 1%) and was directly used in the next step. The low yield is explained by the complex washing process after the first step.

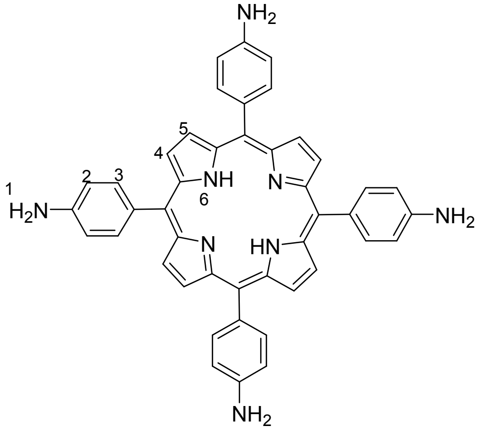
5,10,15,20-Tetrakis(4-aminophenyl)porphyrin 6



19 **6**

The product was prepared according to literature.[5] 95.0 mg (0.12 mmol, 1.0 eq.) $(NO_2)_4$-TPP (**19**)were dissolved in 5 ml conc. HCl solution and stirred under argon for one hour. 0.43 g (1.92 mmol, 16 eq.) $SnCl_2{\cdot}2H_2O$ dissolved in 1 ml conc. HCl solution were added to the $(NO_2)_4$-TPP solution and the reaction solution was heated under argon in a water bath at 75 °C for 30 minutes. Then 6 ml conc. ammonia solution was added for neutralization. The green solid was filtered off, mixed with 10 ml 5% NaOH and stirred vigorously at room temperature for about 30 minutes. The solid was filtered off again and purified by Soxhlet extraction in chloroform. A dark purple, hardly soluble solid was obtained (61.0 mg, 0.10 mmol, 83%).

^{1}H-NMR (499 MHz, $CDCl_3$): δ (ppm): 8.90 (s, 8H, H-4, H-5), 7.9
7.06 (d, J = 8.2 Hz, 8H, H-2), 4.04 (s, 8H, H-1), -2.71 (s, 2H, H-



2. 3D-printing

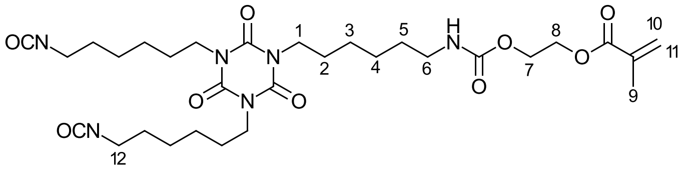
2.1 DLP-Printing

General

Hexamethylene diisocyanate trimer (HDI Trimer) was provided by Covestro Deutschland AG (Desmodur® N3600). Omnirad® BL 750, an initiator blend based on phosphineoxides was kindly provided by IGM-Resins. *Tough* and *Durable* Resins were received from Formlabs. All other chemicals were purchased from Sigma Aldrich and were used as received. FT-IR spectroscopy was conducted on a Bruker Tensor II equipped with an ATR crystal. The evaluation was performed using OPUS Version 7.5 as software. For all spectra a baseline correction was performed and they were normed according to the min-max normalization method on the CH2 peak between 2800 and 3100 cm^{-1}. For all samples, the absorption was measured. UV-vis spectroscopy was measured on a PerkinElmer UV/Vis/NIR Spectrophotometer Lambda 950. 20 x 20 x 0.5 mm printed blocks were used for the measurements with 0.5 wt% and 1 wt% initiator, respectively. Dynamic mechanical analysis was performed on a Seiko SII Exstar 6100 DMS with a frequency of 1 Hz. The experiments were carried out from -150 °C to 250 °C with a heating rate of 2 $Kmin^{-1}$. The glass transition temperature was determined by evaluation of the peak maximum in the loss factor curve.

Synthesis of bifunctional (acrylate and NCO-functionalized) prepolymer

In a typical experiment, the HDI Trimer was heated to 60 °C in a three-neck flask equipped with a stirrer, a condenser and a thermometer. Subsequently, 500 ppm butylhydroxytoluene (BHT) were added as stabilizer. Lastly, hydroxyethylmethacrylate was added dropwise in a 1:1 ratio and the reaction was allowed to take place until the desired isocyanate content was obtained (12.6 %). Products were analyzed by titration and ^{1}H-NMR (600 MHz, C6D6): δ (ppm): 6.17 (s, 1H, H-10), 5.24 (s, H1, H-11), 4.15 (m, 4H, H-7, H-8), 3.80 (dd, 6H, H-1), 2.91 (m, 2H, H-2), 2.55 (dd, 4H, H-12), 1.85 (s, H3, H-9), 1.57 (m, 6H, H-2), 1.17 (m, 6H, H-5), 1.08 (m, 6H, H-3), 1.02 (m, 6H, H-4).



Preparation of printing mixtures

The as synthesized prepolymer was diluted with 30 wt% dipropyleneglycoldiacrylate (DPGDA) and 0.5 wt% or 1 wt% Omnirad® BL 750 were added. The mixture was then transferred into the resin bath of the printer.

Digital Light Processing

Prints were performed on an ASIGA Pro2 75 equipped with a 385 nm radiation source with an energy input of 10 mW/cm². The layer thickness was 100 µm for all prints. Number of Burn-in layers was two. Sliced files were created using the corresponding Composer software.

Table 1. Printing parameters for the different resins printed on the ASIGA Pro2 75.

	Burn-in exposure time / s	**Model layer exposure time / s**
Hybrid PUA 0.5 wt% initiator	10	4
Hybrid PUA 1 wt% initiator	6	3
Formlabs Tough	18	11
Formlabs Durable	15	8

NCO-titration

The isocyanate content on the surface of 3D printed parts was determined by titration according to DIN EN ISO 14896. In brief, the surface of a 10 x 10 x 4 mm, 3D printed block was measured and 5 mL dibutylamine (DBA) in Xylol (0.1 M) were added to the sample. Subsequently, 50 mL acetone were added and the mixture was stirred for 5 minutes. Upon addition of three drops phenol red, the excess of DBA was titrated against hydrochloric acid (HCl) (0.1 M), and the isocyanate content was determined by

$$g/cm^2 - NCO = \frac{(V_B - V_V) \cdot c\,(HCl) \cdot M(NCO)}{A_{3D}},$$

with V_B as the consumption of HCl from reference measurements without a sample, V_V as the consumption of HCl during sample titration and A_{3D} as the surface of the 3D printed sample.

Post-Processing

After printing, the parts were boiled in water for 5 hours or until all isocyanate groups were converted, as determined by IR-spectroscopy. Figure 1 gives the FT-IR-spectra before and after post-treatment with water. The disappearance of the isocyanate signal at 2275 cm^{-1} indicates a quantitative conversion of all isocyanate groups.

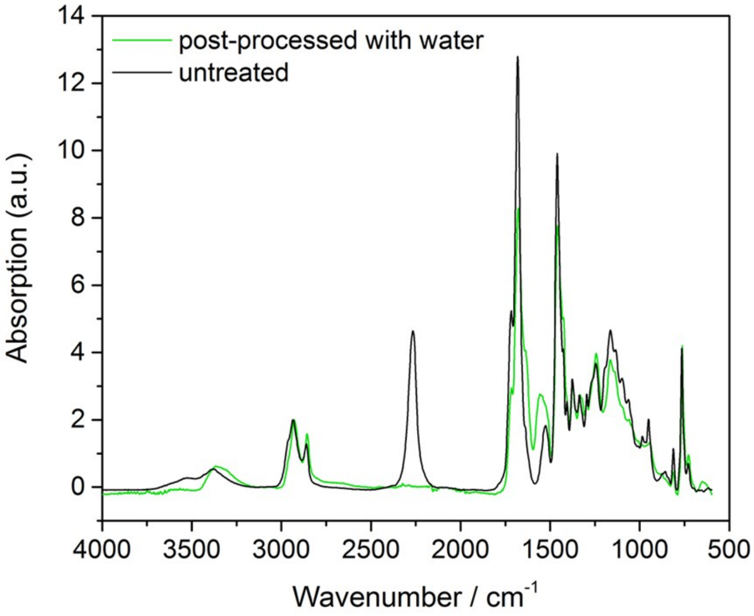


Figure 1. ATR-FTIR spectra of the 3D printed part post-processed with water.

Solvent compatibility

To test the solvent compatibility, 10 x 10 x 4 mm^3 post-processed printed blocks, as well as printed blocks of *Tough* and *Durable* were immersed into water, ethanol, dichloromethane (DCM), dimethylformamide (DMF), tetrahydrofurane (THF), toluene and acetone for 24 h. The solvent uptake was determined gravimetically by

$$Solvent\ uptake = \frac{m_s - m_i}{m_i} \cdot 100\%,$$

where m_s is the weight of the printed part after swelling in the respective solvent and m_i is the weight before immersion.

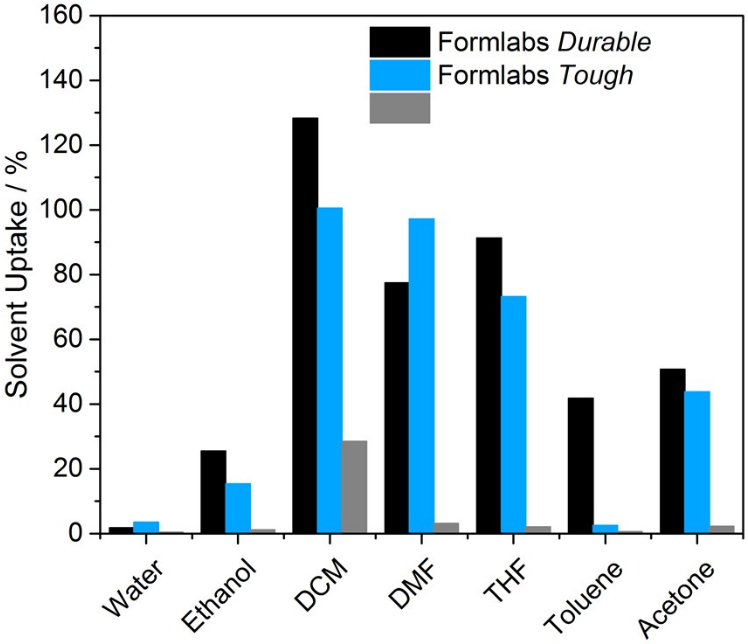


Figure 2. Solvent uptake of 3D printed parts in various solvents.

Dynamic Mechanical Analysis

Mechanical properties of the post-processed hybrid resin were determined by dynamic mechanical analysis, as illustrated in figure 3. Samples were measured before and after reaction with water in order to illustrate the increase in crosslinking density as well as in the glass transition temperature that changed from 44 °C to 130 °C. The results reveal, that the reaction with water leads to a temperature stable material with high mechanical strength.

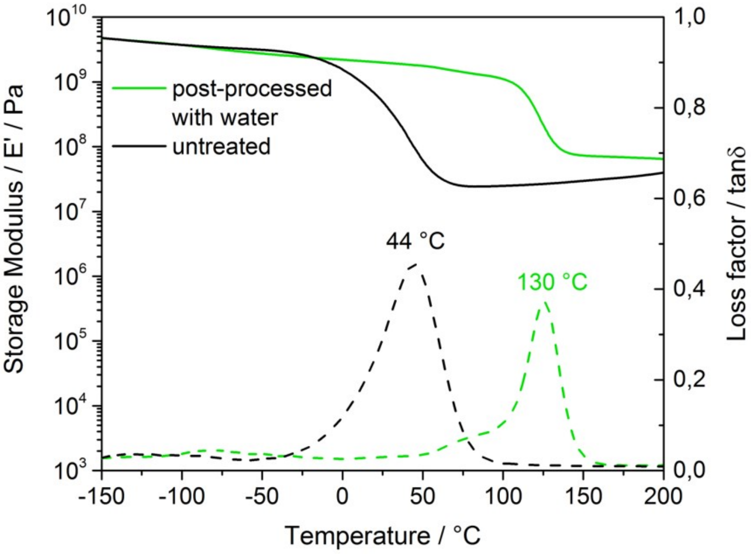


Figure 3. Dynamic Mechanical Analysis of the resin post-processed with water as well as unprocessed, giving the storage modulus as a function of temperature (compact line) as well as the loss factor curve in dependence on the temperature (dotted line).

Post-functionalization

For post-functionalization, the respective sensitizer were diluted in chloroform with a concentration of 0.5 mol/L. Subsequently, the surface of the flowmeter cover was wetted with the solution and the reaction was allowed to take place in the oven at 80 °C over night. In case of the aminobenzophenone derivative containing a hydroxyl groups, catalytic amounts of dibutyltindilaurate were added. After reaction, excess sensitizer was removed by washing for 10 min. in an ultrasonic bath using appropriate solvents. At last, IR-measurements were performed as illustrated in figure 4. The disappearance of the isocyanate signal at 2275 cm^{-1} was used as indication for a successful functionalization reaction.

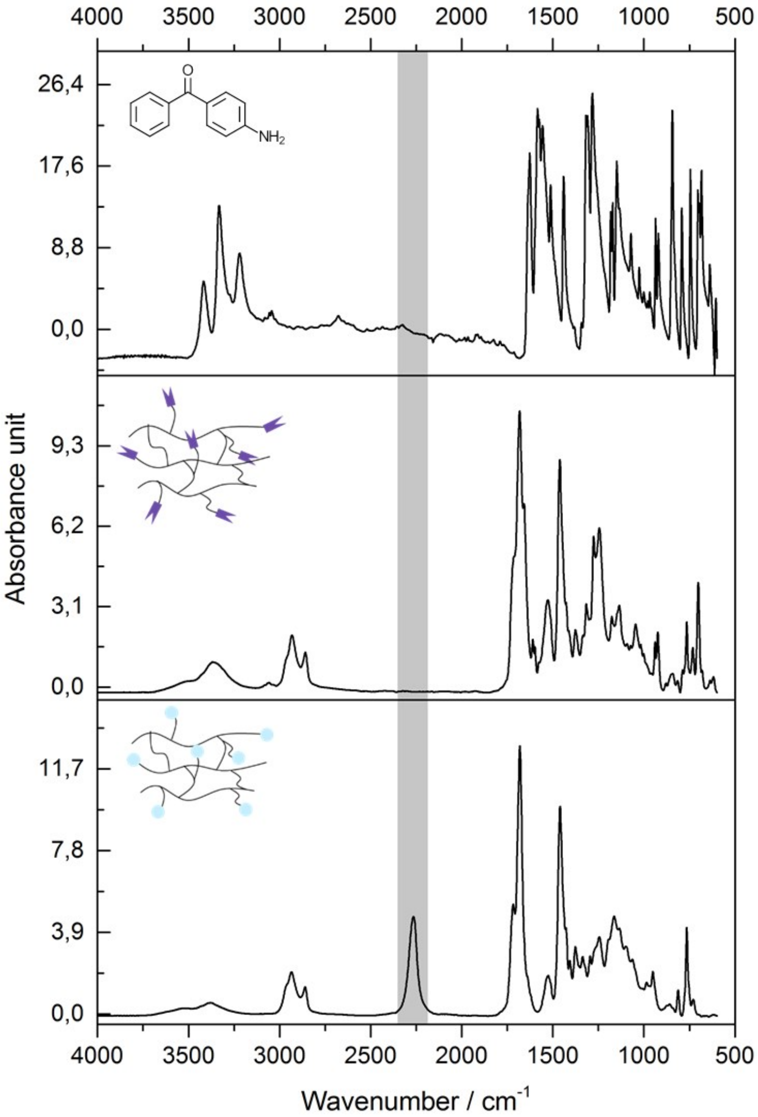


Figure 4. IR measurements from top to bottom: pure aminobenzophenone, functionalized reactor cover with aminobenzophenone, unfunctionalized reactor cover.

2.2. FDM-Printing

Fused Deposition Modelling: Prints were performed on an *Ultimaker 3*. The filament was purchased from *Ultimaker*. The layer thickness was 100 µm for all prints. GCode files were created using the corresponding *Cura* software.

Print Settings

filament	PP
extruder temperature	220 °C
print bed temperature	85 °C
layer height	0.1 mm
wall thickness	1.14 mm
building plate adhesion type	Brim (in addition, a adhesion sheet was used)
print speed	25 mm/s
infill	100 %
Support material	PP

2.3. Parts to be printed

2.3.1. Flowmeter[6]

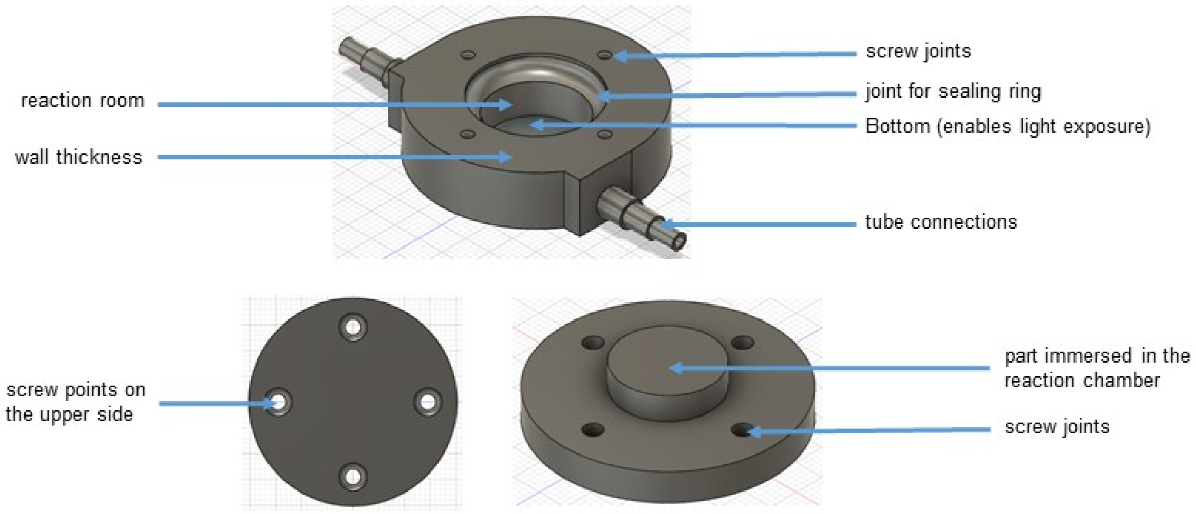


Figure 5: CAD designs of both the cover and the reaction chamber of the flowmeter.[6]

Table 2: Dimensions of the flow reactor.[6]

	Measurements	
Reaction chamber		
total height		10.3 mm
Bottom thickness		0.5mm
reaction room	Height	6.3 mm
	Ø	16.9 mm
	Volume	1.23 cm^3
Joint for sealing ring	Height	3.5 mm (rounded off to 2.5 mm)
	Ø	21.5 mm
Screw joints	Ø	2.042 mm (Thread ANSI 0.99#3)
Wall thickness		11.8 mm
Tube connections	I Ø	2 mm
	O Ø	3 – 5 mm

	Length	15 mm
Cover		
Total height		9.5 mm
part immersed in the reaction chamber	Height	4.3 mm
	Ø	16.6 mm
Screw joints	Top Ø	5.5 mm (rounded of to 1.2 mm)
	Bottom Ø	3.1 mm
assembled reactor	Height	15.5 mm

Transmission of reactor bottom

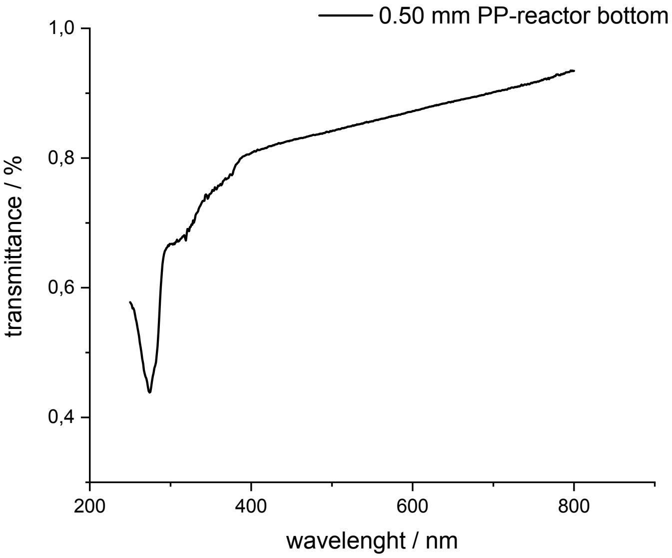


Figure 6: Transmittance of the 0.50 mm PP reactor bottom (Transmittance 0-1 = 0%-100%)

2.3.2. Injection Port

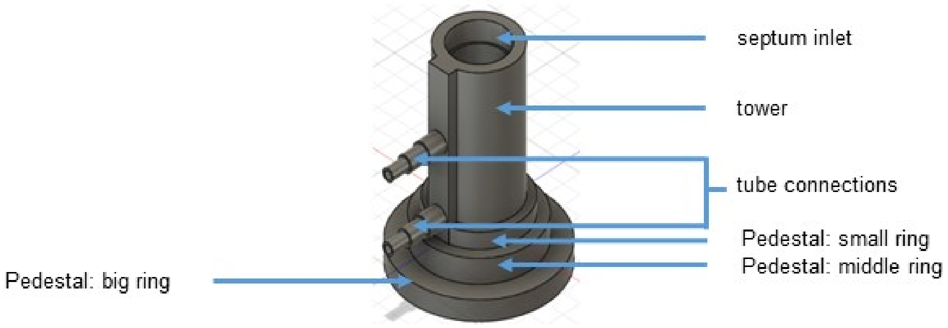


Figure 7: CAD-Design of Injection port for substrate and solvent.[6]

Table 3: Dimensions of the injection port.[6]

	Measurements	
Full height		50.0 mm
Tower	External height	35.0 mm
	Inner height	36.0 mm
	I Ø	13.3 mm
	O Ø	20.0 mm
	Wall thickness	3.35 mm
	Volume without septum	50.0 cm^3
	Volume with septum	43.1 mm^3
Inlet septum	Top Ø	14.5 mm
	Bottom Ø	13.3 mm
Pedestal	Height	15.0 mm
	big ring Ø	40.0 mm
	middle ring Ø	30.0 mm
	small ring Ø	24.3 mm
Tube connections	I Ø	2.00 mm
	O Ø	3.00 – 5.00 mm
	Length	15.0 mm

3. Flow-Experiments

3.1. Experimental Setup

The two parts of the reactor were joined together by means of a sealing ring and four screws. Afterwards the flow reactor was built up as a loop reactor with silicone tubes, a peristaltic pump (or similar) and the injection port with septum and cannula. The light source, a 2.75 W UV LED (λ = 365 nm) for the DLP reactors and a 30 W white LED for the FDM reactor, was directly under the reactor bottom.

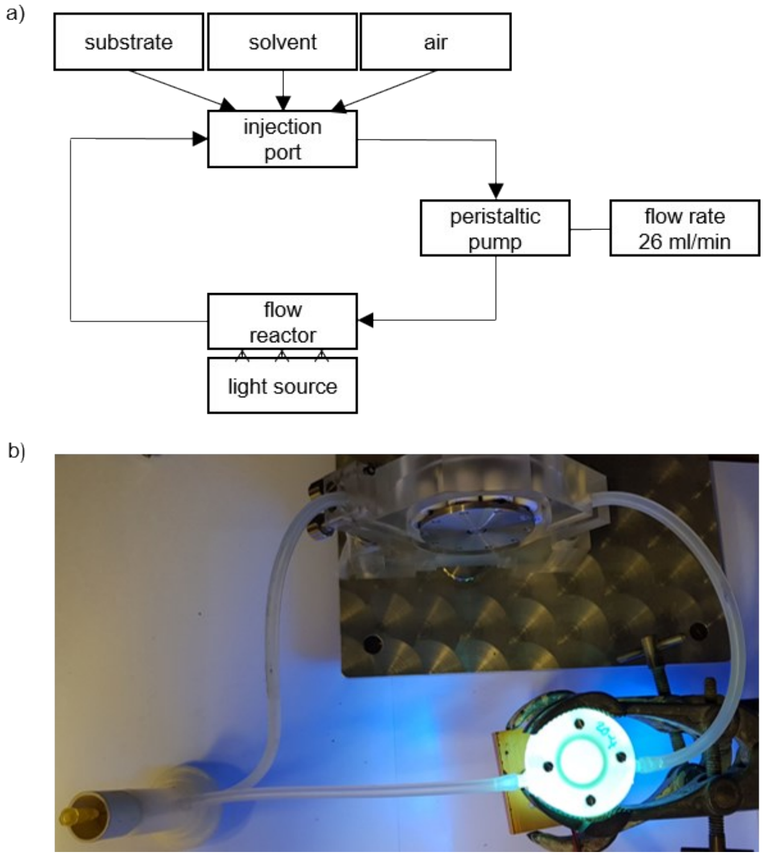
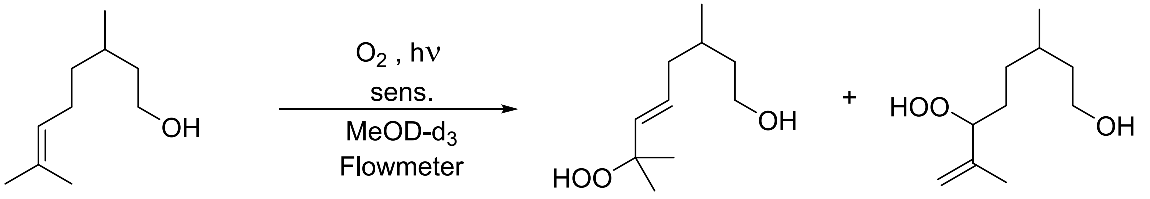


Figure 8: a) Block-Diagramm of flow reaction and b) Experimental Setup of reaction in flowmeter using a 2.75 W UV-LED (λ = 365 nm).

3.2. Photooxygenation of citronellol



7 **8a** **8b**

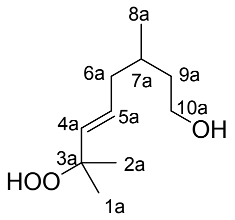
280 mg (1.80 mmol) Citronellol (**7**) was dissolved in 6 ml deuterated methanol (c = 0.30 mol/L). The solution was drawn up with a syringe and injected through the septum into the injection port of the reaction setup of the flowmeter. After addition of the entire solution (not to few air bubbles), the flow reactor was irradiated with the corresponding lightsource. During the reaction solvent could be added by means of the injection port. The products, (*E*)-7-hydroperoxy-3,7-dimethyloct-5-en-1-ole (**8a**) and 6-hydroperoxy-3,7-dimethyloct-7-en-1-ol (**8b**), were analyzed directly from the reaction solution by NMR spectroscopy. The results are presented in table 4.

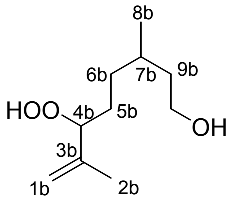
Table 4: Results of photooxygenation of citronellol (**7**) in 3D-printed, post-functionalized reactors.

reactor	immobilized sensitizer	reaction time [h]	conversion[a] [%]
FDM	TPP[b]	7	quant.
DLP	$(NH_2)_4$TPP[b] (**6**)	36	82
DLP	ABP (**3**)	14	28
"	"	28	51
DLP	OH-CH_2-BP (**4**)	14	23
"	"	28	40
DLP	NH_2-$(CH_2)_2$-BP[c] (**5**)	14	9

[a] Conversion was determined by NMR-spectroscopically directly from the crude reaction solution, the products were not further isolated; [b] light source: 30 W white LED; [c] light source: 2.75 W 365 nm LED.

^{1}H- NMR (499 MHz; MeOD):





Characteristic signals for isomer **8a**: δ (ppm): 5.58-5.50 (m, 2H, H-4a, 5b) 1.19 (s, 6H, H-1a, H-2a).

Characteristic signals for isomer **8b**: δ (ppm): 4.82 (m, 2H, H-1b), 4.1 (t, *J* = 6.81 Hz, 1H, H-4b), 2.00-1.94 (dt, *J* = 14.3, 1H, 5.4 Hz, H-5b), 1.87-1.78 (m, 1H, H-5b), 1.61 (s, 3H, H-2b).

Mixture of both isomers, not clearly assignable: δ (ppm): 3.52-3.46 (m, 4H, H-10), 1.56-1.46 (m, 6H, CH_2), 1.22-1.34 (m, 4H, CH_2), 0.82-0.79 (dd, *J* = 6.6, 1.8 Hz, 6H, H-8).

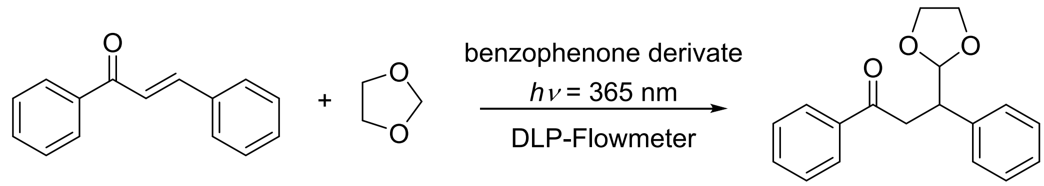
^{13}C-NMR (75 MHz, $CDCl_3$):

Characteristic signals for isomer **8a**: δ (ppm): 137.0 (d, C-4a od. 5a), 129.7 (d, C-4a od. 5a), 82.5 (s, 3a), 41.1 (t, C-6a), 40.2 (t, C-9a), 24.9 (q, 1a, 2a),

Characteristic signals for isomer **8b**: δ (ppm): 145.8/145.7 (s, C-3b), 114.2/114.1 (t, C-1b), 90.7/90.6 (d, C-4b), 40.7/40.5 (t, 9b), 34.1 (t, 6b), 29.3/ 29.1 (t, C-5b), 17.0/16.9 (q, 2b).

Mixture of both isomers, not clearly assignable: δ (ppm): 60.1 (t, C- 10a, 10b), 30.8 (d, C-7), 30.5 (d, C-7), 19.9 (2C, q, 8a, 8b).

3.3. Photoinduced hydrogen atom transfer (PHAT)



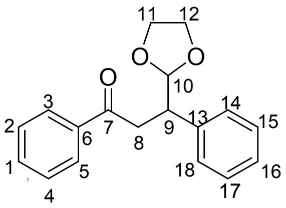
9 **10** **11**

132 mg (0.64 mmol) chalcone (**9**) was dissolved in 6.40 ml 1,3-dioxolane (**10**) (c = 0.1 mol/L) and filled into the inlet by means of a syringe. After addition of the complete solution (no air bubbles!), 365 nm UV-LED lamps (2.75 W) were used for illumination. After 13 hours the reaction was stopped and the 1,3-dioxolane (46) was evaporated under reduced pressure. The product, 3-(1,3-dioxolane-2-yl)-1,3-diphenylpropan-1-one (**11**) was purified by column chromatography (10 : 1 : 0.1, cHex : EtOAc : NEt_3) and was obtained as a colorless oil. The results are shown in table 5.

Table 5: Results of PHAT reaction of chalcone (**9**) and 1,3-dioxolane (**10**) in 3D-printed, functionalized reactors.

reactor	PHAT cat.[a]	reaction time [h]	Yield[%][b]

DLP	ABP	13	13
DLP	OH-CH_2-BP **4**	13	3



^{1}H-NMR (499 MHz, $CDCl_3$): δ (ppm): 8.00 – 7.89 (m, 2H, H-3, H-5), 7.55 – 7.49 (m, 1H, H-1), 7.42 (dd, J = 8.4, 7.1 Hz, 2H, C_{ar}), 7.38 – 7.17 (m, 5H, C_{ar}, C-16,), 5.09 (d, J = 3.8 Hz, 1H, C-10), 3.91 – 3.75 (m, 5H, H-11, H-12, H-9), 3.57 (dd, J = 17.0, 5.5 Hz, 1H, H-8), 3.37 (dd, J = 17.0, 8.2 Hz, 1H, H-8).

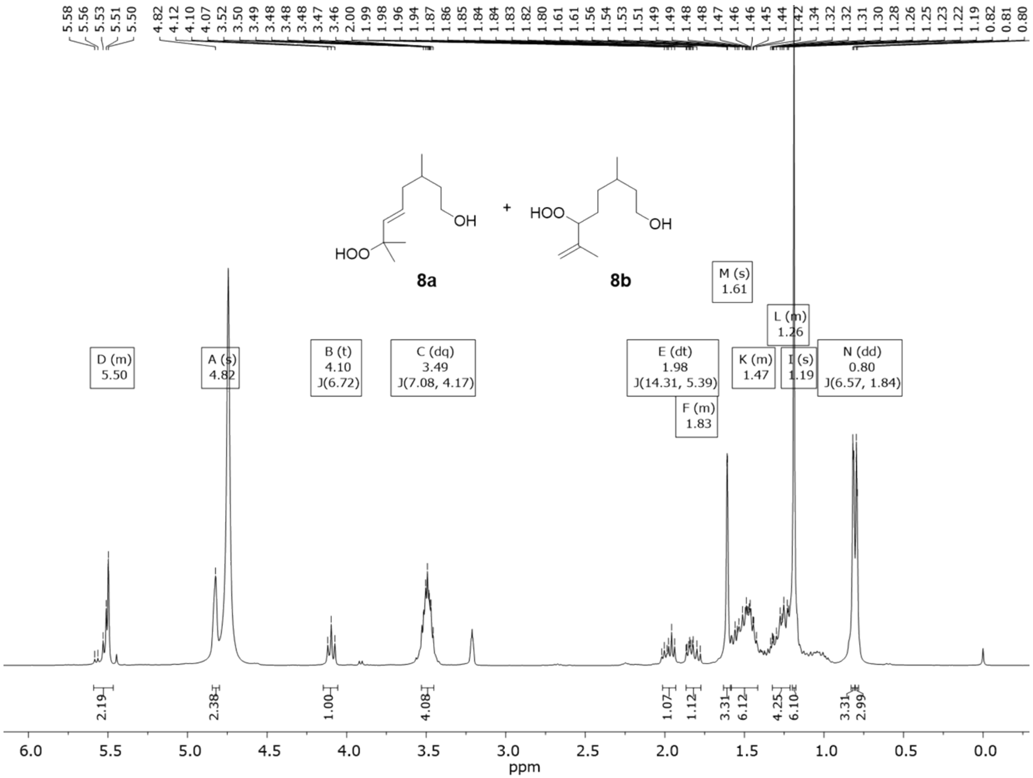
^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm): 198.4 (s, C-7),144.0 (s, C-6), 140.0 (s, C-13), 132.9 (d, C-1), 128.7 (d, C_{ar}), 128.4 (d, C_{ar}), 128.3 (d, C_{ar}), 128.1 (d, C-3, C-5), 127.0 (d, C-16),105.9 (d, C-10), 64.9 (2C, t, C-11, C-12), 44.7 (d, C-9), 38.9 (t, C-8).

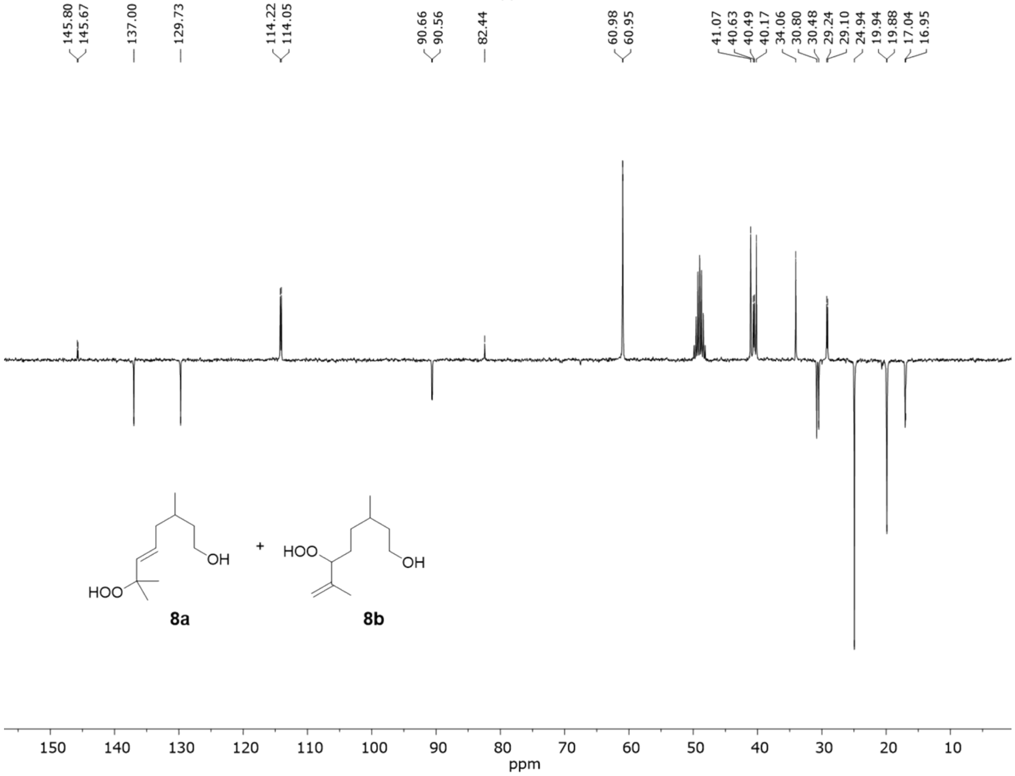
For comparison – the experiment in solution:

91.0 mg (0.50 mmol, 0.4 eq.) benzophenone and 260 mg (1.25 mmol, 1.0 eq.) chalcone (**9**) were dissolved in 30.0 ml (31.8 g, 430 mmol, 344 eq.) 1,3-dioxolane (**10**) and flooded with argon for ten minutes. The reaction solution was exposed for 24 hours at λ = 350 nm. The reaction mixture was analyzed by GC-MS and 52% of product **11** was obtained. After column chromatographic purification (10 : 1 : 0.1, cHex : EtOAc : NEt_3) a colorless oil could be obtained in 18% yield (65.0 mg, 0.23 mmol).

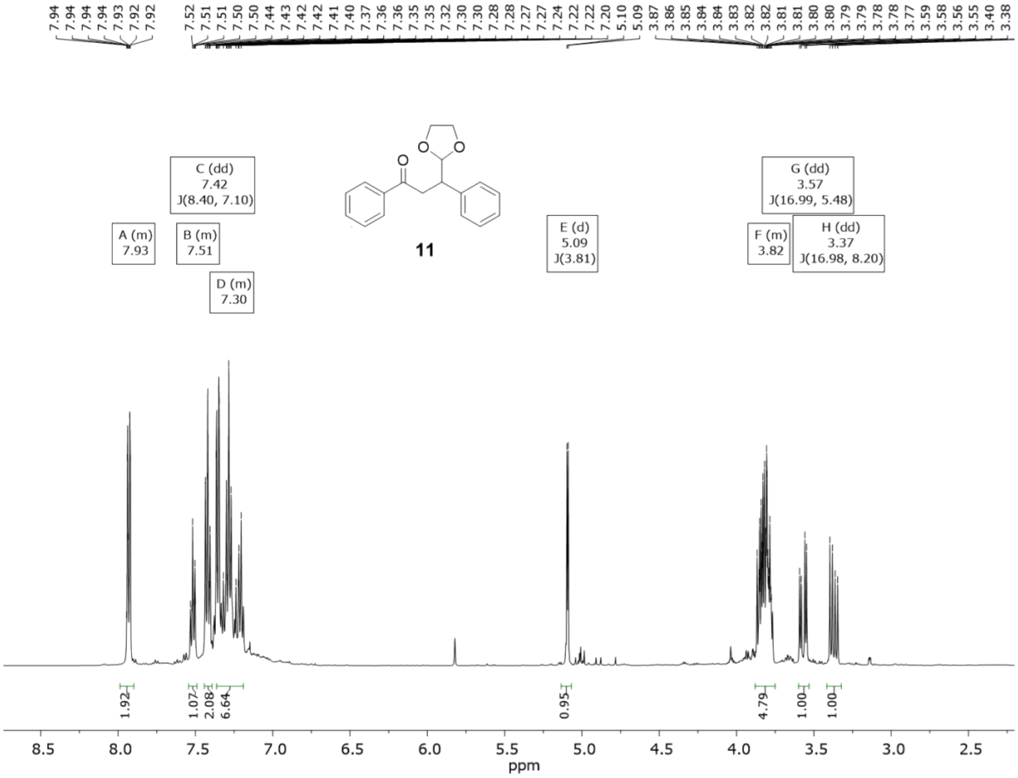
3.4. NMR-Spectra of products obtained in flow reactions

(E)-7-Hydroperoxy-3,7-dimethyloct-5-en-1-ole (8a) und 6-Hydroperoxy-3,7-dimethyloct-7-en-1-ol (8b)





3-(1,3-Dioxolane-2-yl)-1,3-diphenylpropan-1-one (11)



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