

Supporting Information

Intensified Continuous Extraction of Switchable Hydrophilicity Solvents Triggered by Carbon Dioxide

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S1. Chemical Properties

Properties of the chemicals used in this work are listed in **Table S1**.

Table S1. Molecular weight, density, and boiling point of the chemicals used in this work.

Chemical	Molecular Weight [g/mol]	Density [g/ml] at 25°C	Boiling Point [°C]
Toluene	92.1	0.867	110.6
Water	18.02	0.998	100.0
Dimethylcyclohexylamine (DMCA), 1	127.23	0.849	160
Dimethylhexylamine (DMHA), 2	129.24	0.744	146-150
Triethylamine (TEA), 3	101.19	0.729	89.28
Di-sec-butylamine (DBA), 4	129.24	0.753	135

S2. Density Measurements

In order to calculate density of an SHS in toluene and DI water, SHS samples with different concentrations were prepared. Volume and mass of each SHS sample mixed with toluene was measured. Next, a known volume of DI water and SHS was injected into the tube-in-tube flow reactor and introduced to carbon dioxide (CO₂) until complete mixing of the SHS and DI water was achieved (*i.e.*, the two-phase solution became single phase). The length of the mixed SHS and DI water segment was then used to calculate the final volume of the SHS and DI water mixture. Measured densities of DMCA in toluene and DI water are shown in **Fig. S1**.

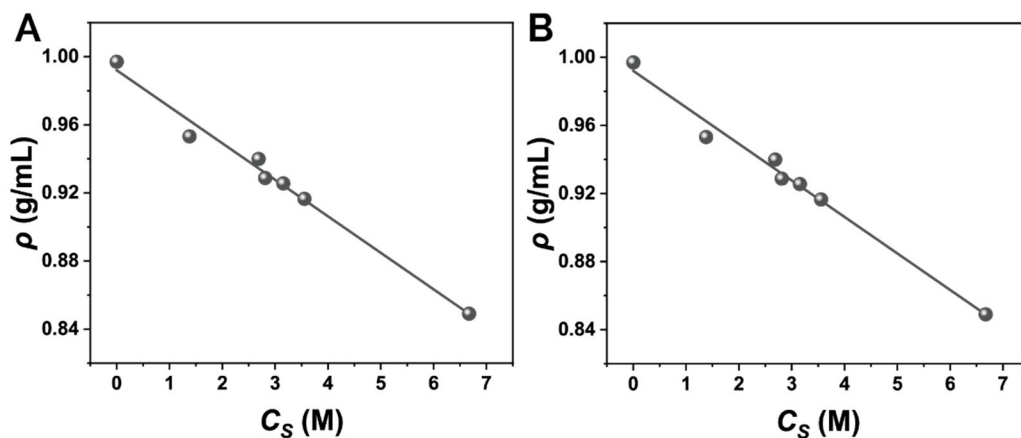


Figure S1. Density calibration curves for various DMCA concentrations in (A) toluene and (B) DI water.

S3. Evaluation of SHS Extraction in Flow

Using the measured density values of SHSs in toluene and DI water, the amount of SHS present in the organic and aqueous phase during the in-flow extraction was calculated with the following steps:

The measured density of the organic phase (**Fig. S1A**) is expressed as,

$$\rho_{org} = a * C_s(t) + \rho_{toluene} = a * \frac{m_{s,org}(t)}{MW_s * V_{org}(t)} + \rho_{toluene} \quad (\text{eqn. S1})$$

where ρ , a , C , t , m , MW , and V represent the density, fitting constant, concentration, time, mass, molecular weight, and volume; subscripts *org*, *aq*, and *s* represent organic phase, aqueous phase, and SHS, respectively. Also, the density of the organic phase, by definition, can be defined as following:

$$\rho_{org} = \frac{m_{org}}{V_{org}} = \frac{m_{toluene}(t) + m_s(t)}{L_{org} * A} \quad (\text{eqn. S2})$$

where L and A are the length and cross-sectional area of the organic phase segment in the continuous flow reactor. Combining equations S1 and S2, and rearranging the equation, the mass of the SHS in the organic phase segment in flow can be expressed as:

$$m_{s,org}(t) = \frac{m_{toluene}(t) - \rho_{toluene} * V_{org}(t)}{\frac{a}{MW_s} - 1} \quad (\text{eqn. S3})$$

Following the calculation shown above, the mass of the SHS in the aqueous phase can be calculated as:

$$m_{s,aq}(t) = \frac{m_{water} - \rho_{aq} * V_{aq}(t)}{\frac{b}{MW_s} - 1} \quad (\text{eqn. S4})$$

where b is a fitting constant from the density calibration graph (**Fig. S1B**) for the aqueous phase.

The SHS extraction efficiency, η , can then be calculated as:

$$\eta = \frac{(\rho_{aq})_f * (V_{aq})_f}{(\rho_{org})_i * (V_{org})_i} = \frac{(m_{s,aq})_f}{(m_{s,org})_i} \quad (\text{eqn. S5})$$

S4. Concentration and Pressure Dependence of DMCA Extraction

At a constant CO₂ pressure, we observed a linear relationship between the characteristic DMCA extraction time, t_e , and DMCA concentration (Fig. S2A), while varying CO₂ pressure at a constant DMCA concentration resulted in a non-linear relationship between the DMCA extraction time and CO₂ pressure (Fig. S2B). The rapid decay of the DMCA extraction time when increasing the CO₂ pressure can be attributed to the reduced mass transfer resistance and higher CO₂ flux into the aqueous phase.

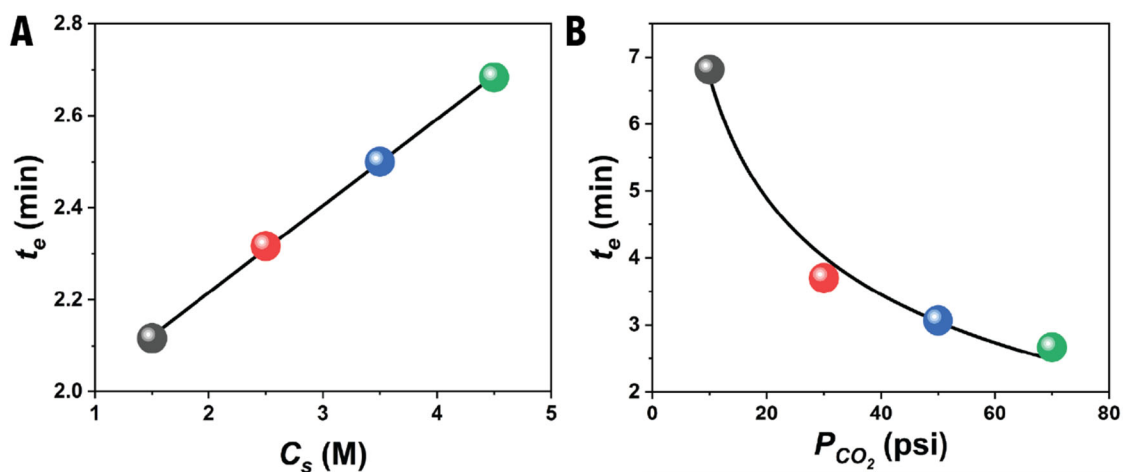


Figure S2. (A) The characteristic DMCA extraction time vs. concentrations of DMCA at $P=70$ psig, $R=1$, $L=2$ m, $Q=250$ μ L/min. (B) The characteristic DMCA extraction time vs. CO₂ pressure at $C_s=4.5$ M, $R=1$, $L=2$ m, $Q=250$ μ L/min.

S5. In-line Phase Separation Module

The segmented flow of the raffinate (hydrophobic SHS and toluene, red) and the extract (hydrophilic SHS and DI water, blue), after leaving the flow reactor where the CO₂-triggered SHS extraction occurred, was fed into the AeosTM ePTFE membrane-based tube-in-tube module for in-line phase separation (**Fig. S3**). Complete liquid-liquid phase separation was accomplished by a real-time PID process controller (LabVIEW) adjusting the hydrodynamic resistance across the raffinate stream. Two optical phase sensors (PS1 and PS2) were attached to each outlet stream of the raffinate and extract while a digital pressure regulator (DPR) was connected to the outlet of the raffinate stream. The voltage readout of the phase sensors could capture complete or incomplete liquid-liquid phase separation in real-time. The liquid-liquid phase separation is governed by balancing the hydrodynamic resistance between the membrane and (i) raffinate and (ii) extract outlets. As soon as the phase sensors detect an incomplete phase separation in one of the outlet streams through a change in the voltage baseline (custom-built LabVIEW script), a PID controller adjusts the raffinate outlet pressure through the DPR (connected to a pressurized nitrogen source) until there is complete separation of the two phases (*i.e.*, constant voltage readout from both PS1 and PS2), shown in **Fig. S3**.

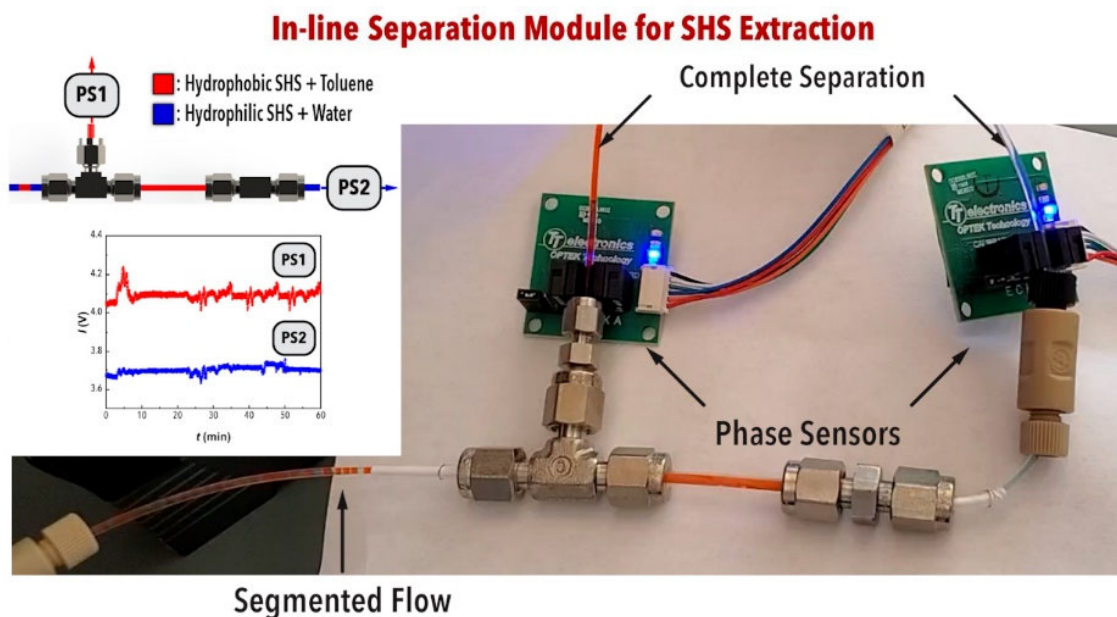


Figure S3. In-line phase separation module for continuous CO₂-triggered SHS extraction. Schematic of separation module is shown in top left with optical phase sensor value for clear separation value.

S6. NMR Characterization of SHS

S6A. NMR Spectra of SHSs

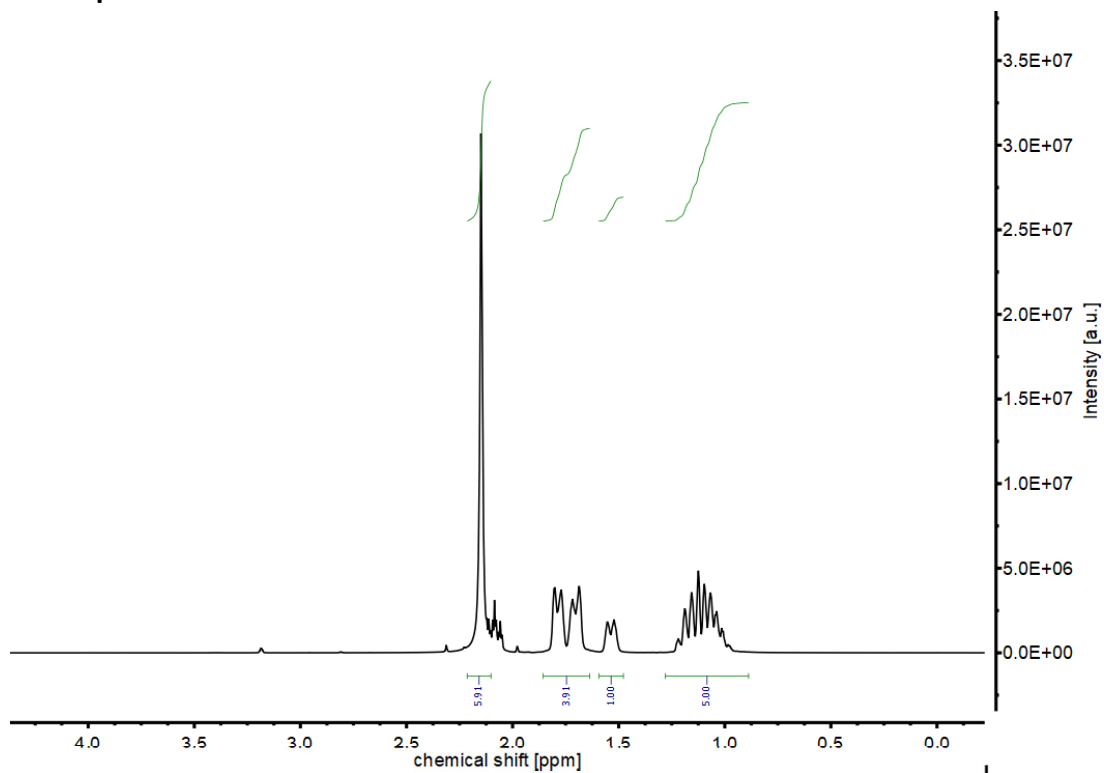


Figure S4. ^1H NMR spectra of *N,N*-dimethylcyclohexylamine (DMCA)

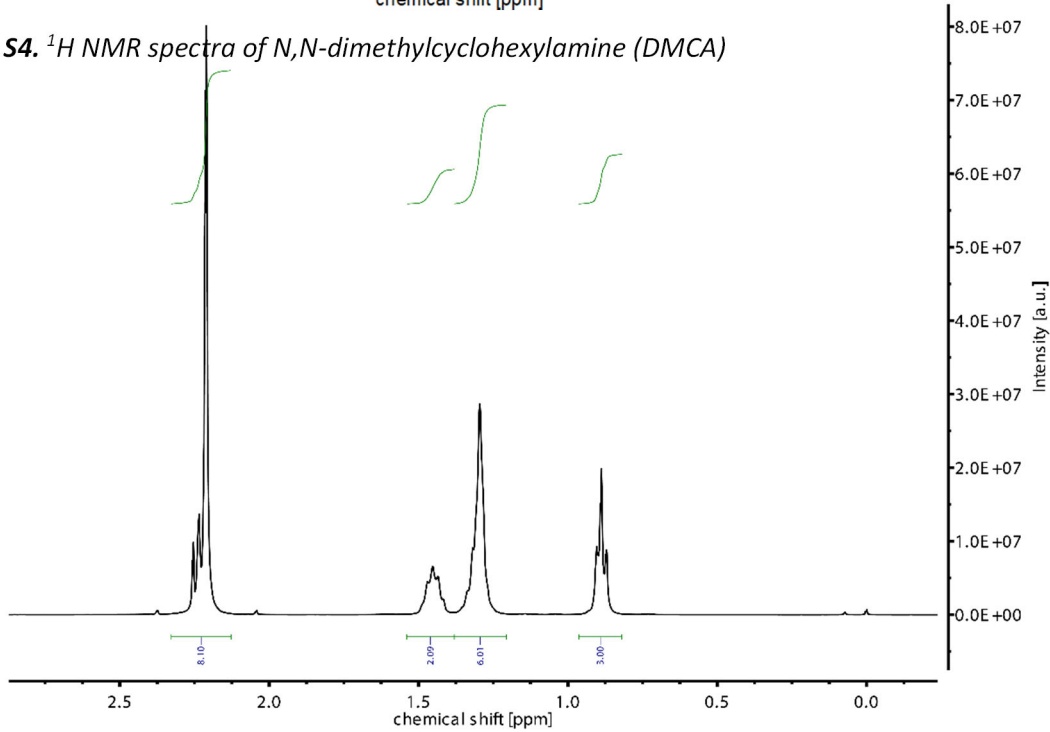


Figure S5. ^1H NMR spectra of *N,N*-dimethylhexylamine (DMHA)

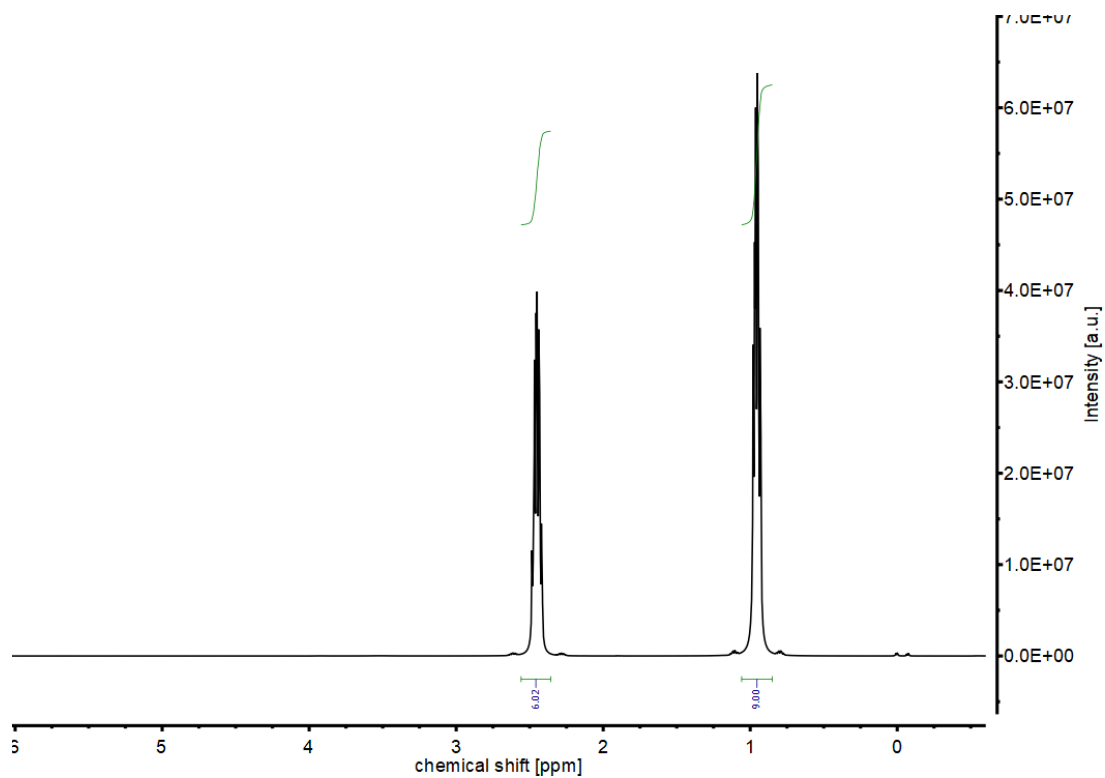


Figure S6. ¹H NMR spectra of triethylamine (TEA)

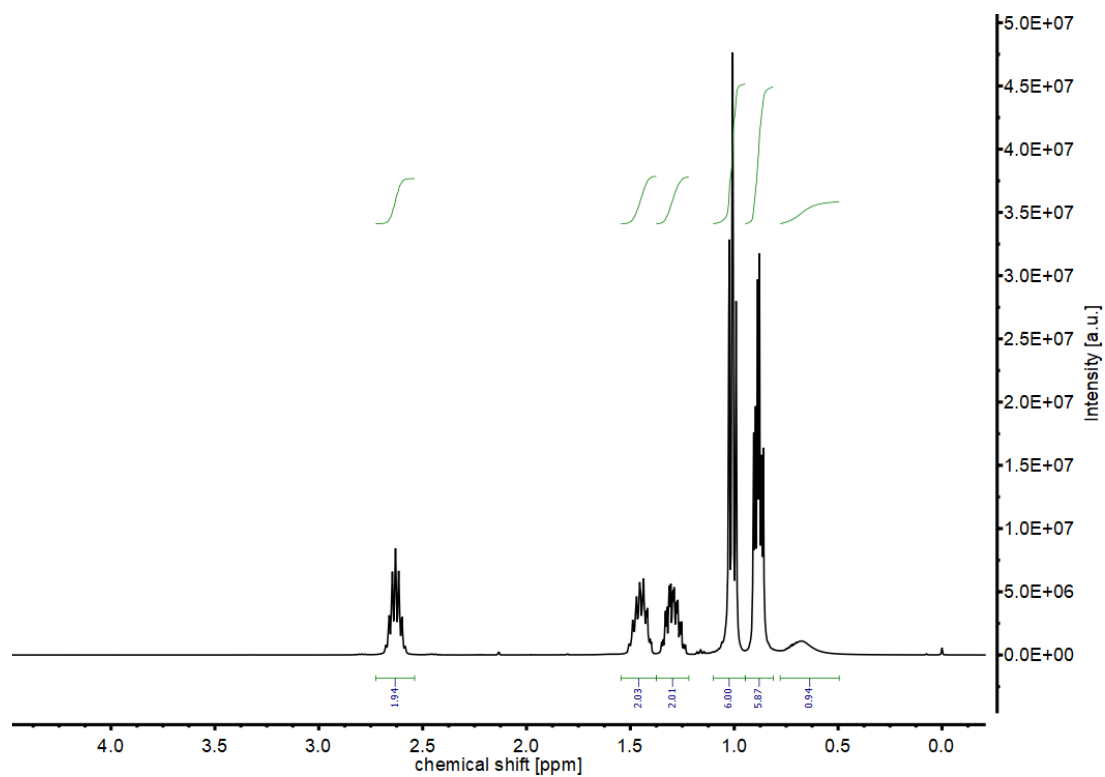


Figure S7. ¹H NMR spectra of di-sec-butylamine (DBA)

S6B. Extraction of DMCA

Extraction of DMCA was performed with deuterated toluene and water for NMR analysis. For internal standard, dibromoethane was used for the organic phase and 1,4-dioxane was used for the aqueous phase. In order to check the precision of NMR characterization, we prepared three identical aqueous samples after complete extraction of DMCA, which resulted in an equilibrium extraction efficiency of $87.3\% \pm 1.9\%$ (**Figure S10-12**). Bruker Avance III 700 MHz NMR spectrometer was used.

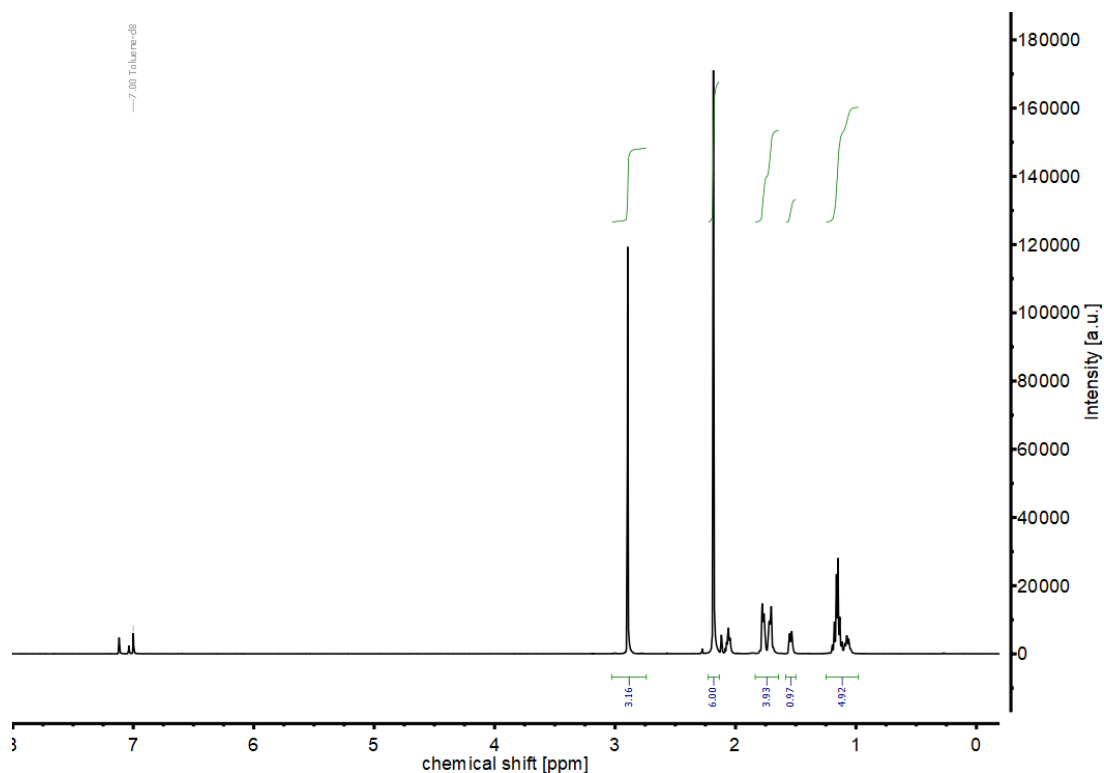


Figure S8. ^1H NMR spectra of initial organic phase: toluene- d_8 , DMCA, and dibromoethane (internal standard)

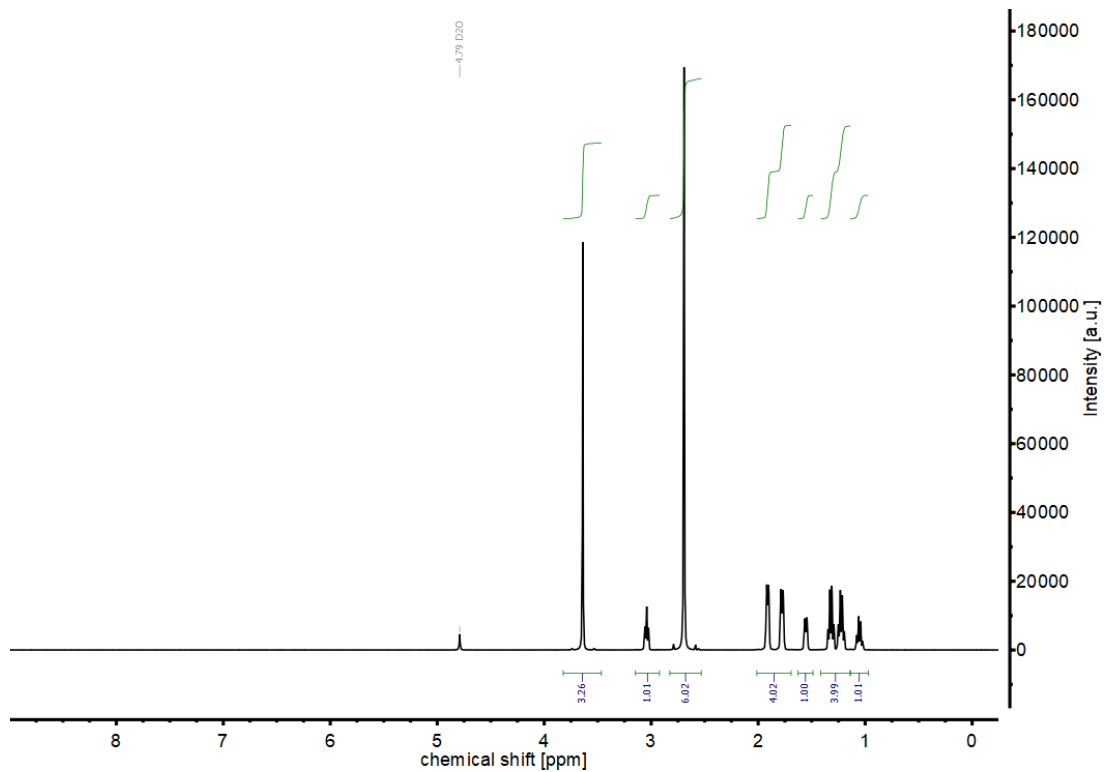


Figure S9. ^1H NMR spectra of aqueous phase after complete extraction: D_2O , protonated DMCA, and 1,4-dioxane (internal standard)

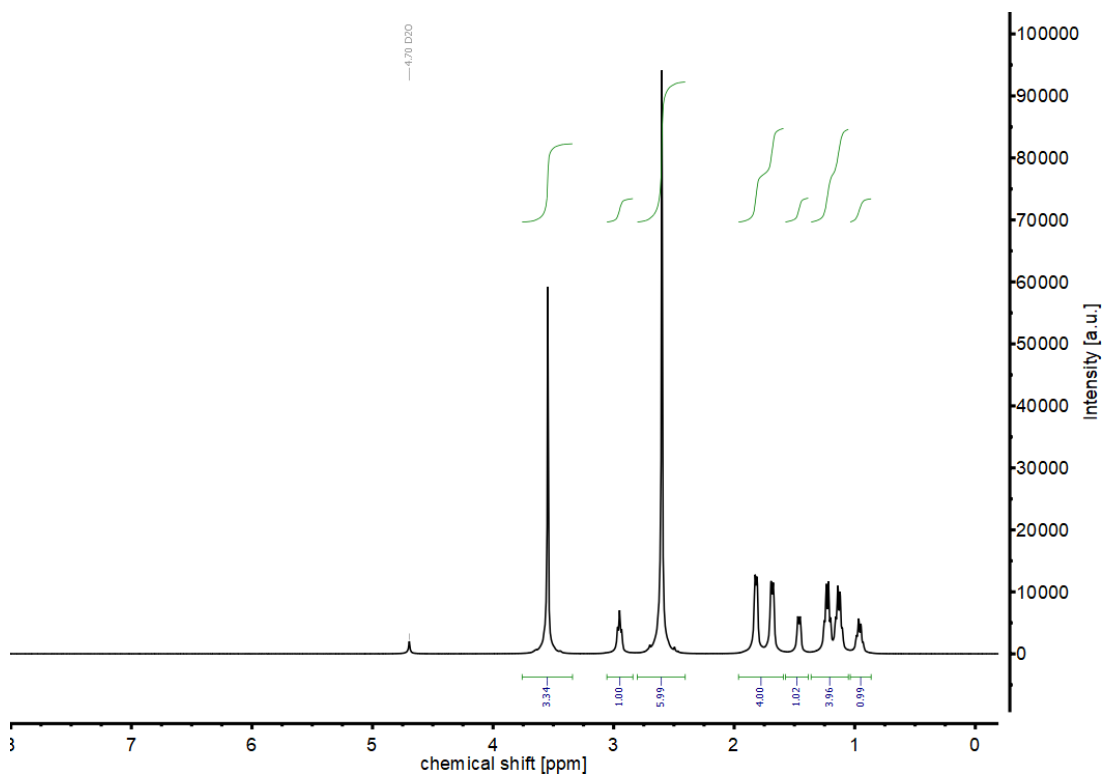


Figure S10. ^1H NMR spectra of aqueous phase after complete extraction: D_2O , protonated DMCA, and 1,4-dioxane (internal standard)

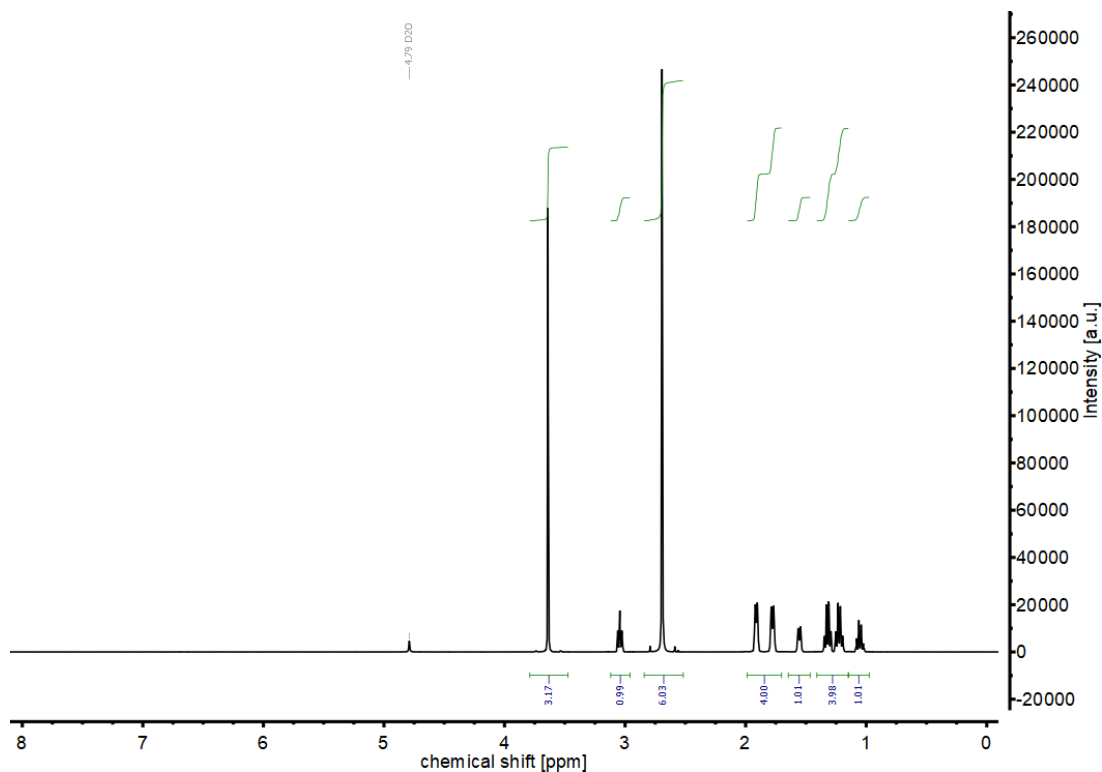


Figure S11. ^1H NMR spectra of aqueous phase after complete extraction: D_2O , protonated DMCA, and 1,4-dioxane (internal standard)

S6C. Transient Extraction of DMCA. To quantify the transient extraction behavior of DMCA, three samples were collected with residence times of 1 min, 1.25 min, and 1.66 min, resulting in 53.6%, 68.8%, and 77.9% extraction efficiencies, respectively (**Figure S13-15**). Extraction of DMCA was performed with deuterated toluene and water for NMR analysis. For internal standard, dibromoethane was used for the organic phase and 1,4-dioxane was used for the aqueous phase. Bruker NEO 400 MHz NMR spectrometer was used.

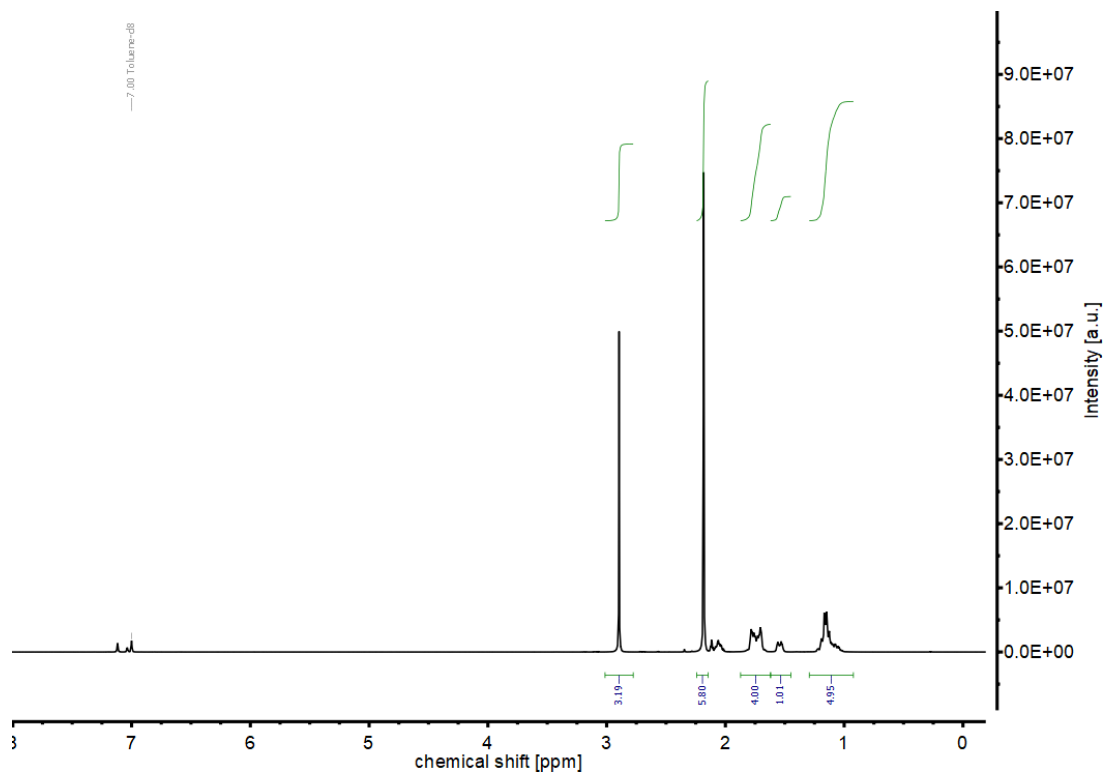


Figure S12. ^1H NMR spectra of initial organic phase: toluene- d_8 , DMCA, and dibromoethane (internal standard)

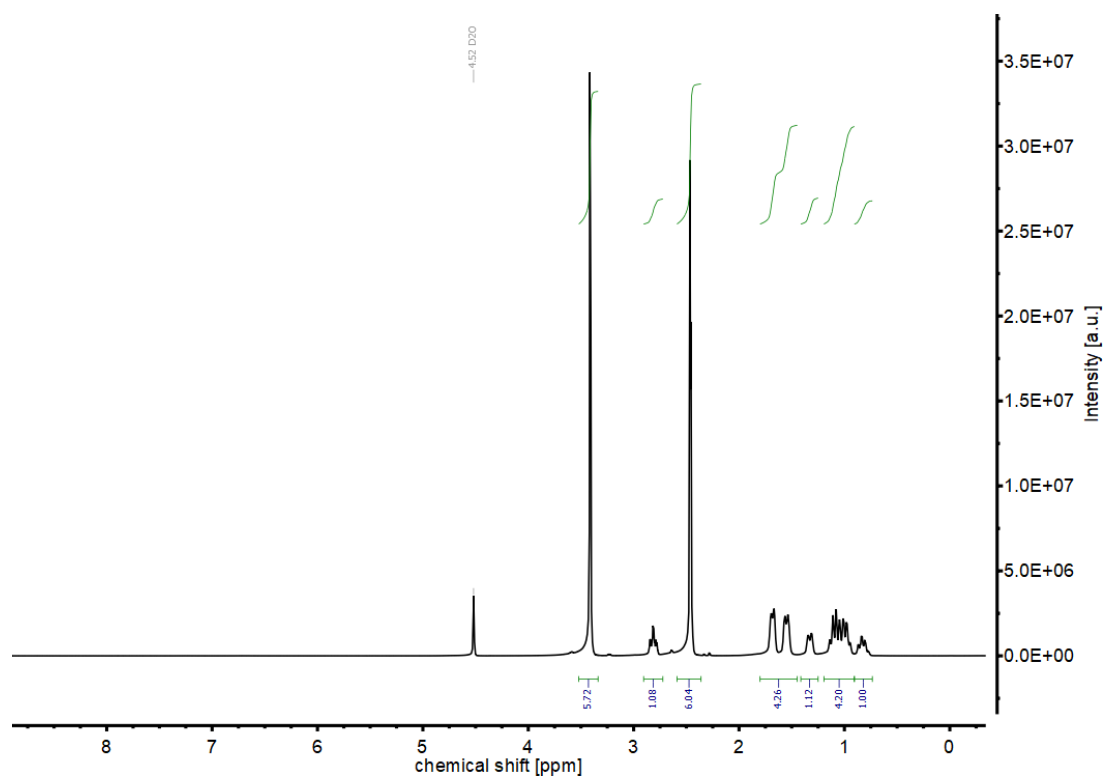


Figure S13. ^1H NMR spectra of aqueous phase after complete extraction: D_2O , protonated DMCA, and 1,4-dioxane (internal standard)

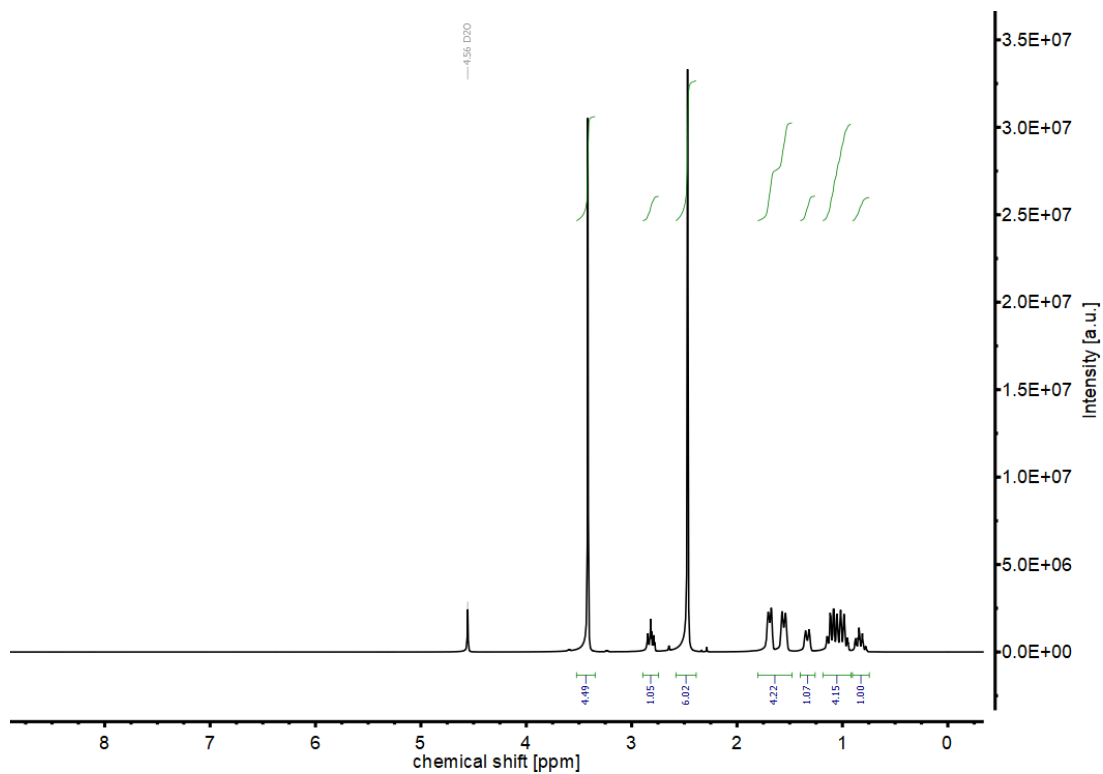


Figure S14. ^1H NMR spectra of aqueous phase after complete extraction: D_2O , protonated DMCA, and 1,4-dioxane (internal standard)

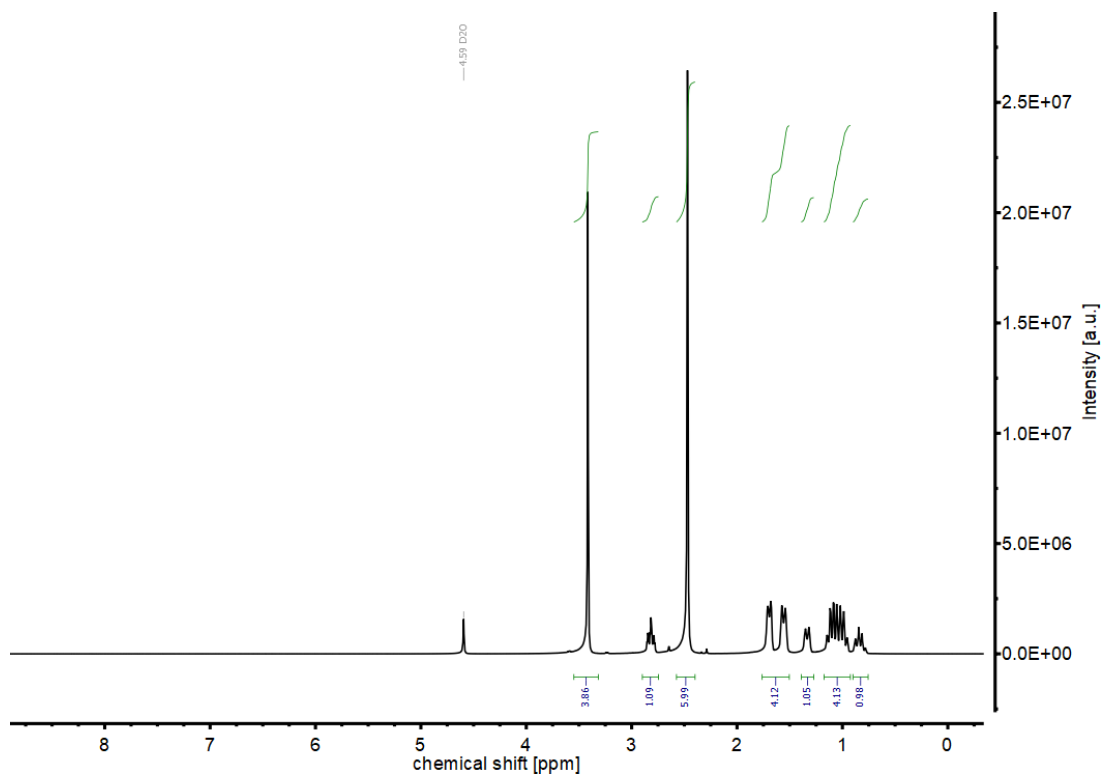


Figure S15. ^1H NMR spectra of aqueous phase after complete extraction: D_2O , protonated DMCA, and 1,4-dioxane (internal standard)

S7. Scale Out Flow Chemistry Platform

Scale Out of SHS Extraction

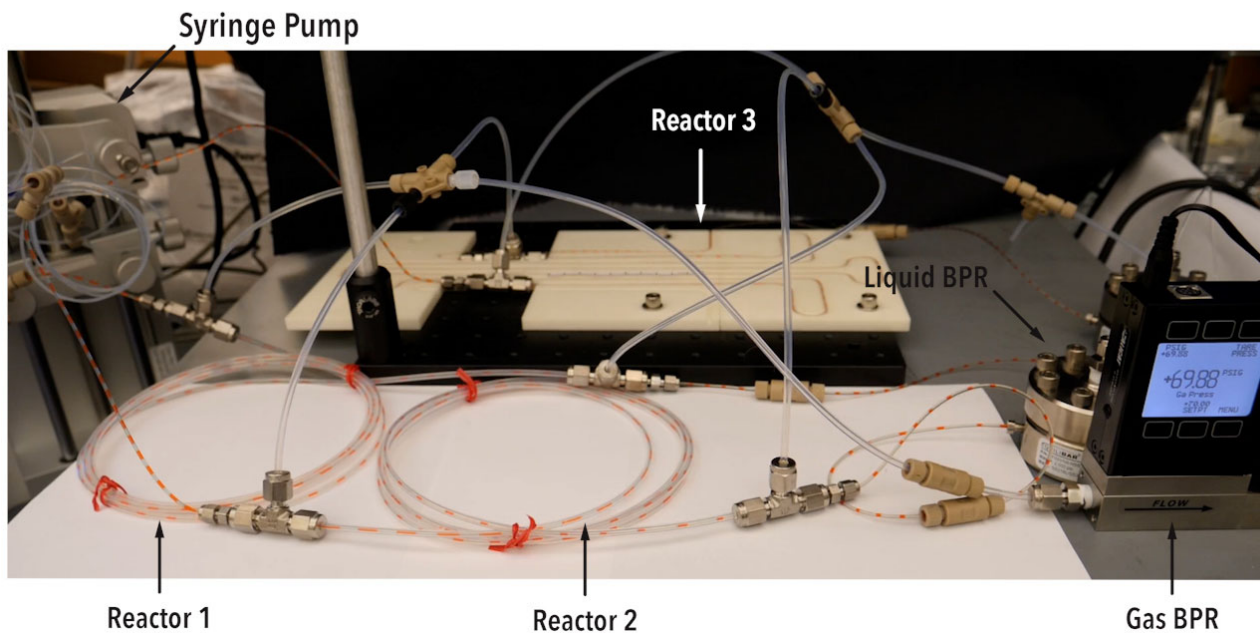


Figure S16. Experimental setup of the scale out flow chemistry platform.

S8. Supplementary Movie

M1. Green flow chemistry-enabled studies of energy-efficient SHS extraction with in-line phase separation and scale out approach. Successful application of the developed flow chemistry approach resulted in high-throughput extraction of SHSs.