Supporting Information

Accelerated Material-Efficient Investigation of Switchable Hydrophilicity Solvents for Energy-Efficient Solvent Recovery

Suyong Han,† *Keshav Raghuvanshi,*† *and Milad Abolhasani**,†

†Department of Chemical and Biomolecular Engineering
North Carolina State University
911 Partners Way, Raleigh, NC, 27695, USA

*Corresponding Author
E-mail: abolhasani@ncsu.edu
Webpage: www.AbolhasaniLab.com

The supporting information includes 3 Tables, 22 Figures, and 2 Movies in 18 pages.

S1. Chemical Properties

Chemical properties of the species utilized in this study are listed in **Table S1**.

Table S1. *Properties of the Chemical Species Utilized in this Work.*

Chemical	Molecular Weight [g/mol]	Density [g/ml] at 25℃	Boiling Point [℃]
Toluene	92.1	0.867	110.6
Water	18.02	0.998	100.0
Triethylamine (TEA), **1**	127.2	0.849	158.0
Dimethylcyclohexylamine (DMCA), **2**	101.2	0.726	88.8
Di-sec-butylamine (DBA), **3**	129.2	0.742	126.6
Diisopropylethylamine (DIPEA), **4**	129.2	0.753	135.0

S2. NMR Characterization of SHS

S2A. Batch Validation of CO_2-Mediated SHS Extraction

To validate the accuracy of the developed *green* flow chemistry platform for accelerated material-efficient studies of wtichable hydrophilicity solvents (SHSs), a batch SHS extraction experiment under identical process conditions to flow experiments was conducted. For the validation studies, N,N-dimethylcyclohexylamine (DMCA) was used as the exemplary SHS. 1.5 mL of a freshly distilled DMCA from a nitrogen-glove box was added to a 6.0 mL septum vial (Thermo Scientific). Then, 1.4 gm toluene-d_8 was added to the vial, followed by 3.0 mL addition of deuterium oxide (D_2O). In the next step, carbon dioxide (CO_2) bubbled into the vial with a constant flowrate of 5.0 mL/min using a computer-controlled mass flow controller for 8 h. After the SHS extraction was completed, 0.3 mL aliquots of the aqueous and organic phase were collected under nitrogen atmosphere for off-line analysis using ^{1}H and ^{13}C Nuclear magnetic resonance (NMR) spectroscopy (shown below). Analysis of the aqueous and organic phases, following the CO_2-mediated LLE of DMCA resulted in 86 % of the protonated DMCA in the aqueous phase and 14 % of DMCA in the organic phase, which is in agreement with the equilibrium extraction efficiency of DMCA obtained in the single-droplet *green* flow chemistry platform.

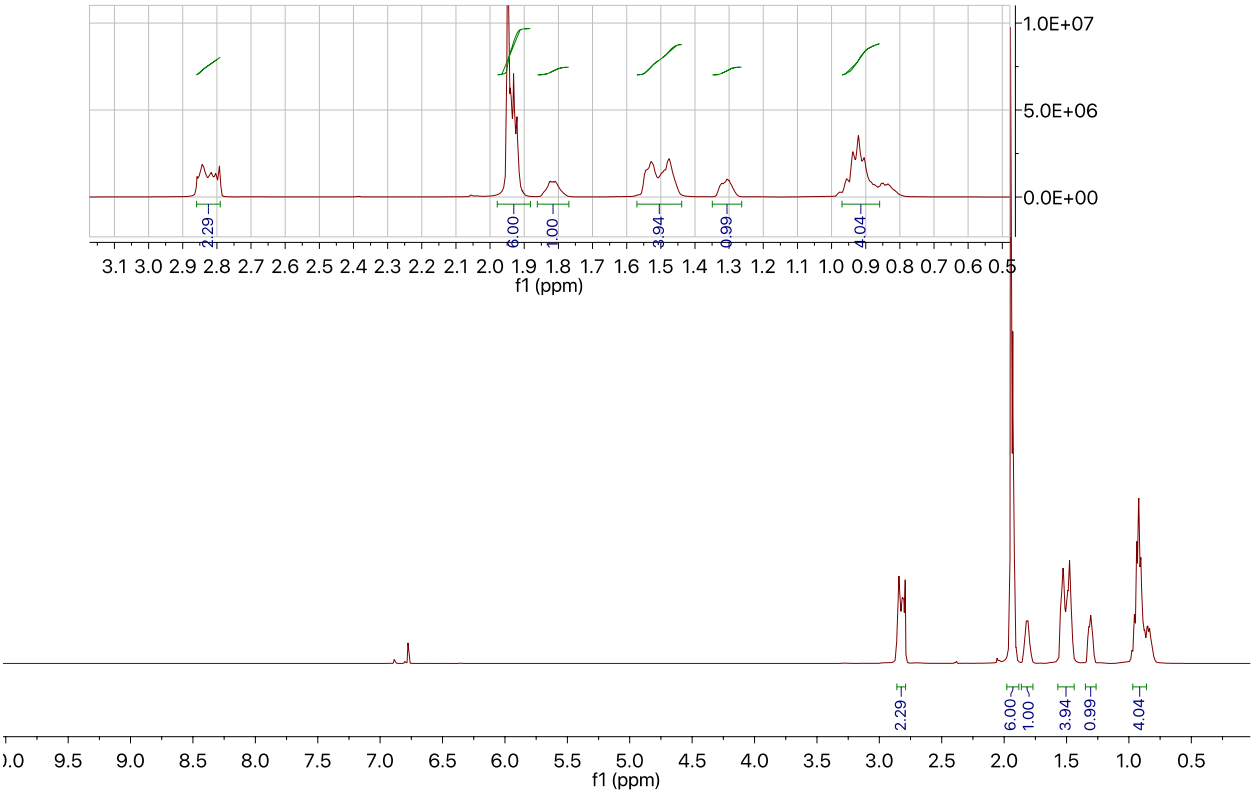

Figure S1. *Before Bubbling CO_2: DMCA in Toluene-d_8 and D_2O mixtute, ^{1}H-NMR*

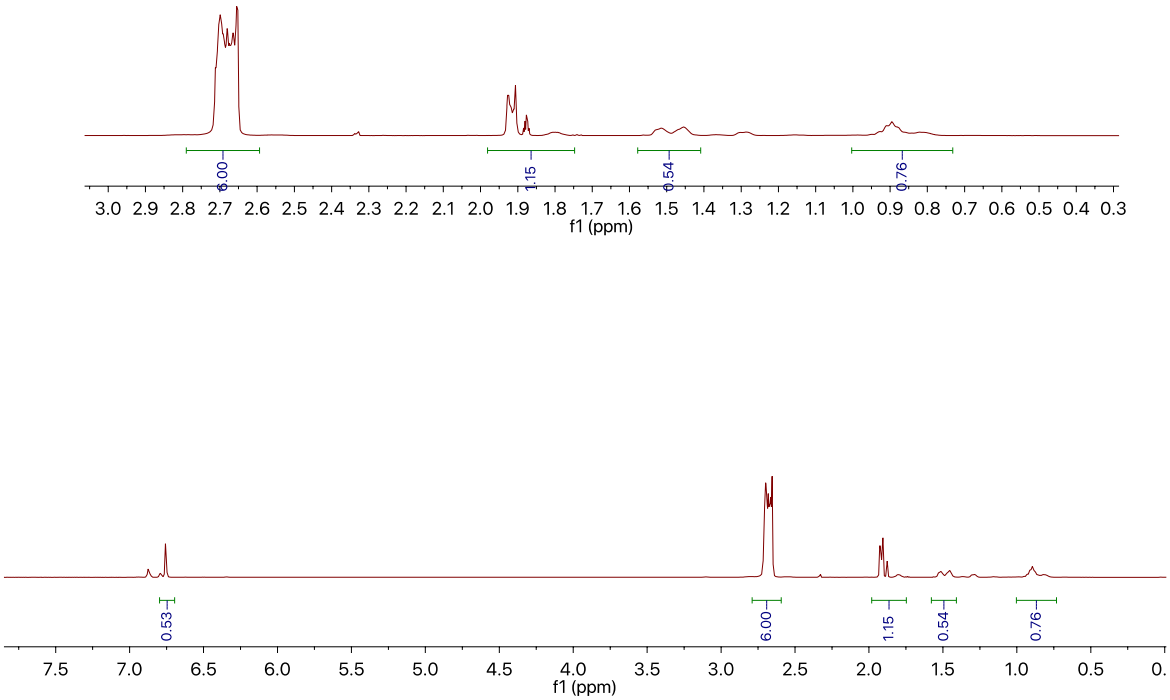

Figure S2. *After Bubbling CO_2 for 8.0 h: DMCA in Toluene-d_8 (Recovered Organic), ^{1}H-NMR*

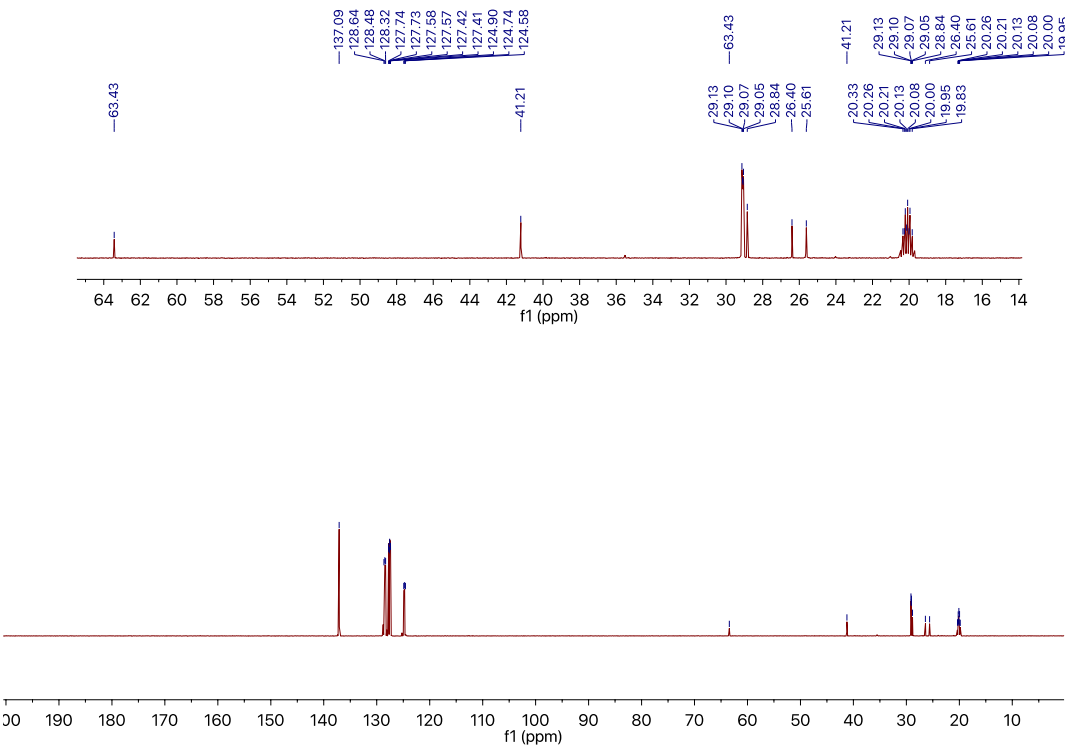

Figure S3. *After Bubbling CO_2 for 8.0 h: DMCA in Toluene-d_8 (Recovered Organic), ^{13}C-NMR*

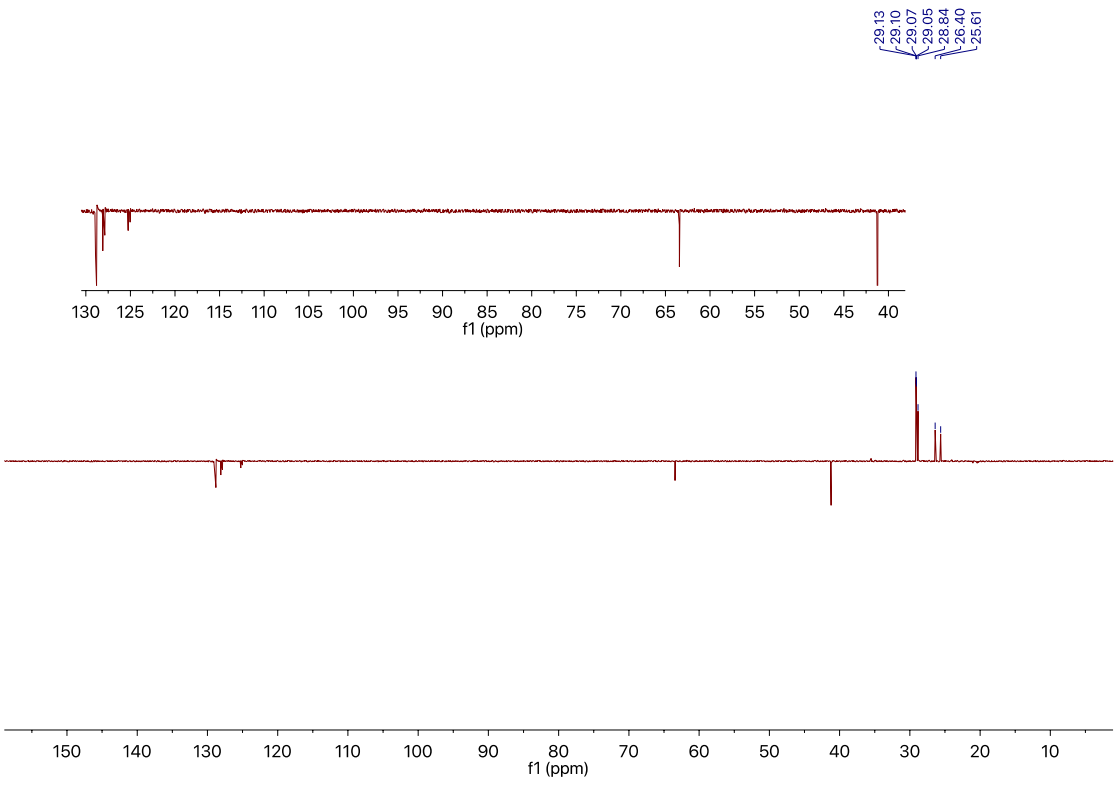

Figure S4. *After Bubbling CO_2 for 8.0 h: DMCA in Toluene-d_8 (Recovered Organic), ^{13}C-APT-NMR*

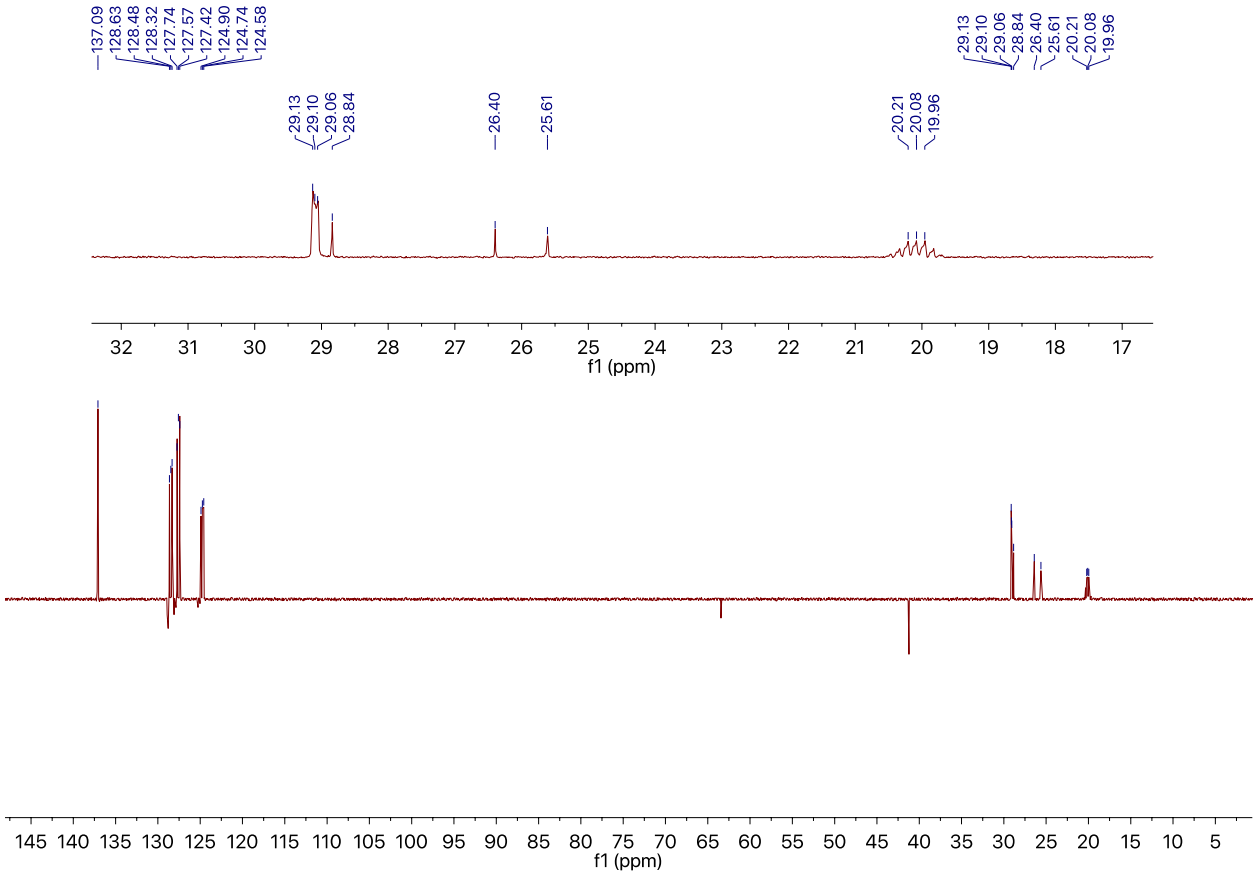

Figure S5. *After Bubbling CO_2 for 8.0 h: DMCA in Toluene-d_8 (Recovered Organic) ^{13}C-2D-NMR*

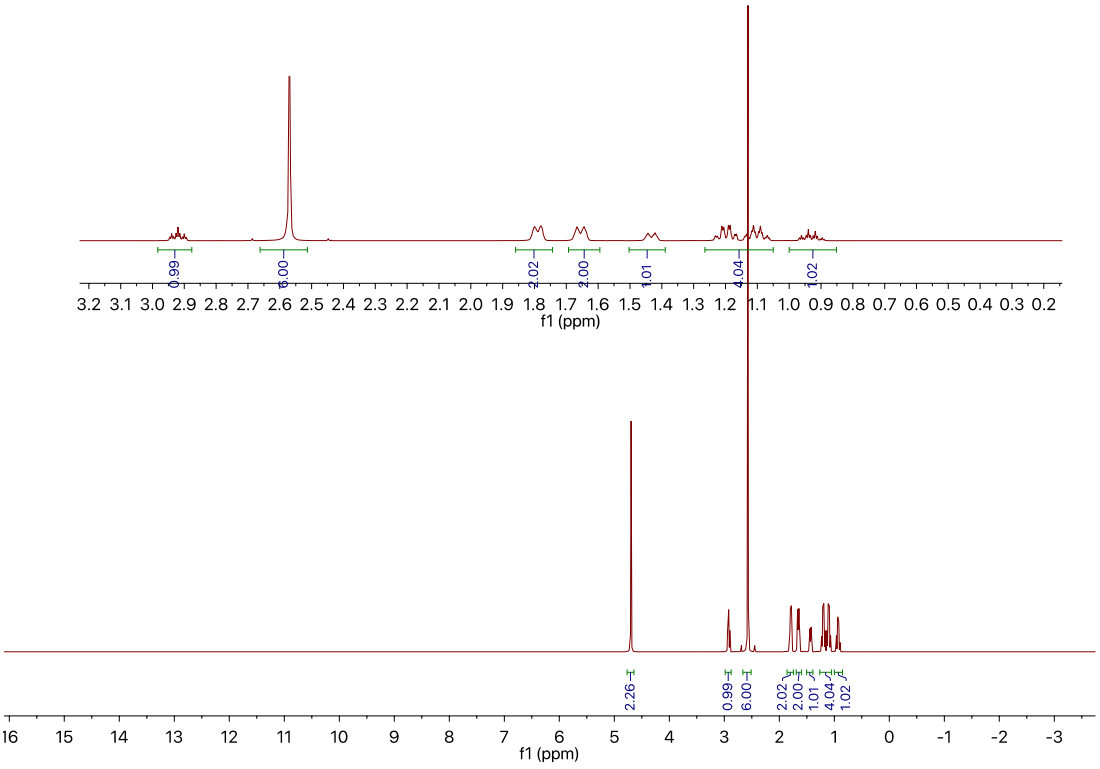

Figure S6. *After Bubbling CO_2 for 8.0 h: DMCA in D_2O (Recovered SHS), ^{1}H-NMR*

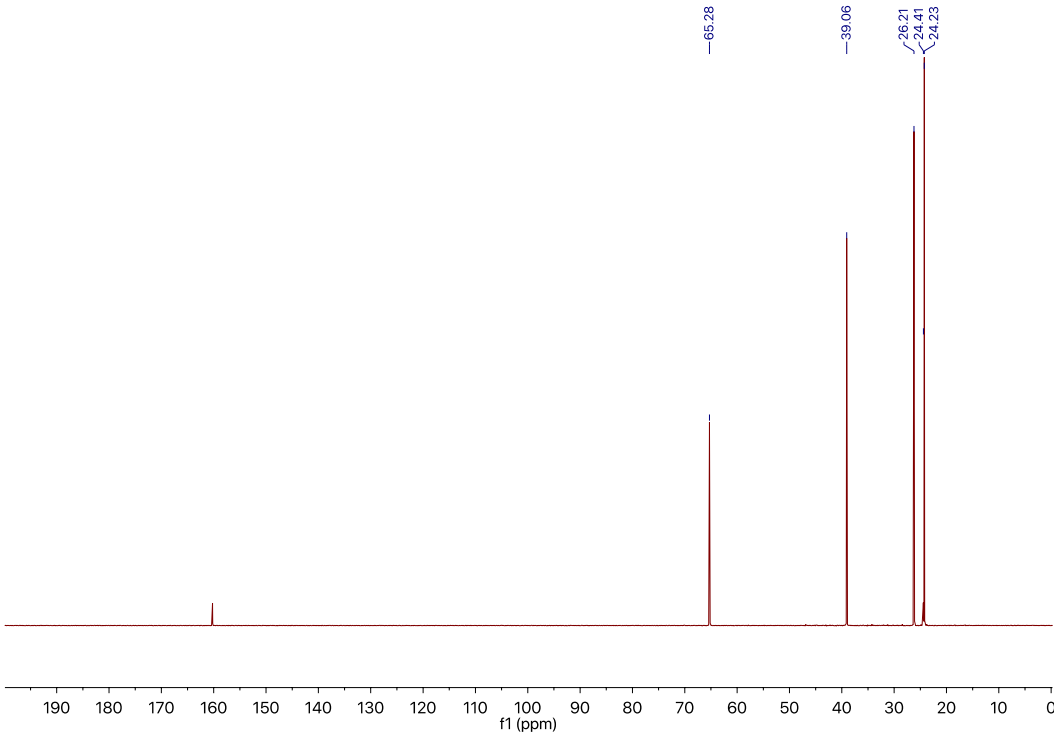

Figure S7. *After Bubbling CO_2 for 8.0 h: DMCA in D_2O (Recovered SHS), ^{13}C-NMR*

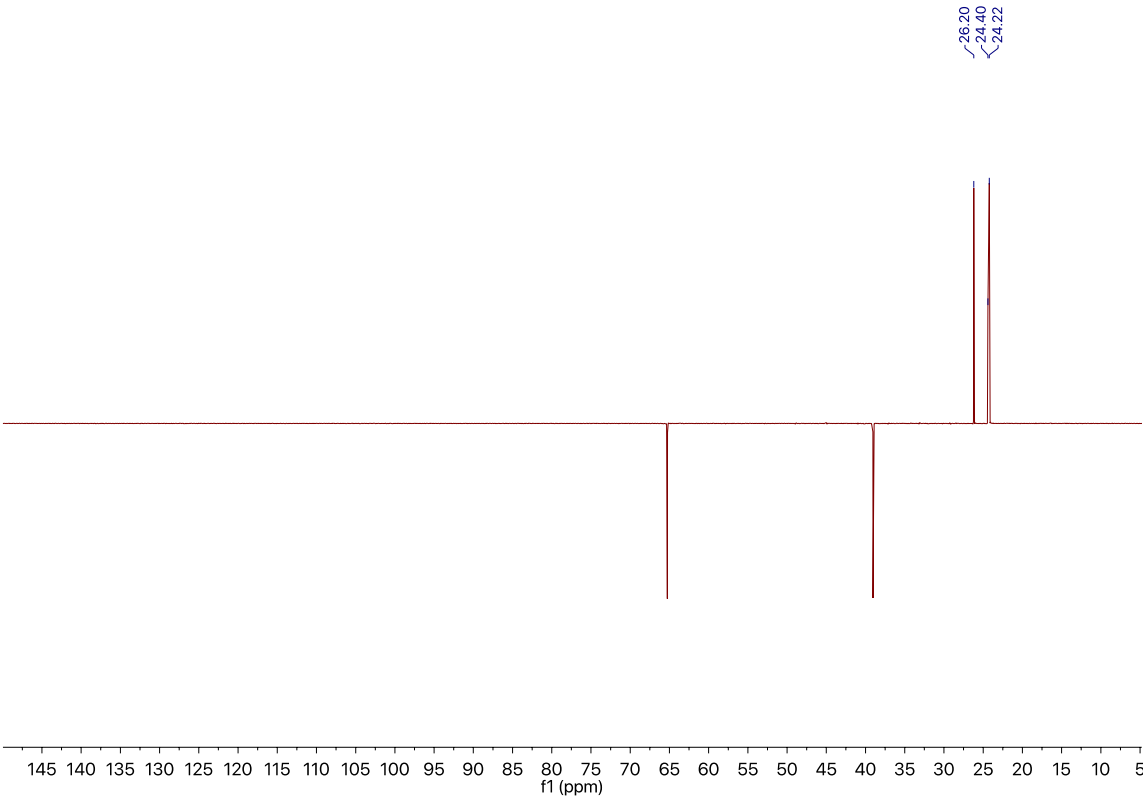

Figure S8. *After Bubbling CO_2 for 8.0 h: DMCA in D_2O (Recovered SHS), ^{13}C-APT-NMR*

S2B. Amine Characterizations

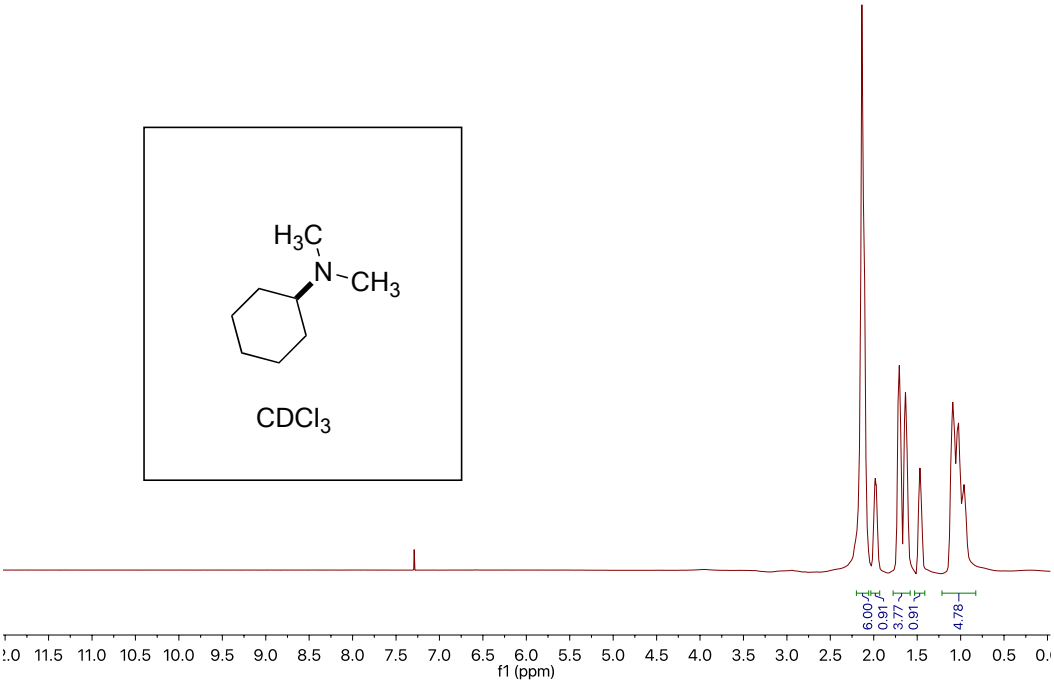

Figure S9. *[1]H-NMR (700 MHz, Chloroform-d) spectra of DMCA; δ = 2.14 (s, 6H), 2.02 – 1.92 (m, 1H), 1.75 – 1.58 (m, 4H), 1.47 (s, 1H), 1.13 – 0.92 (m, 5H).*

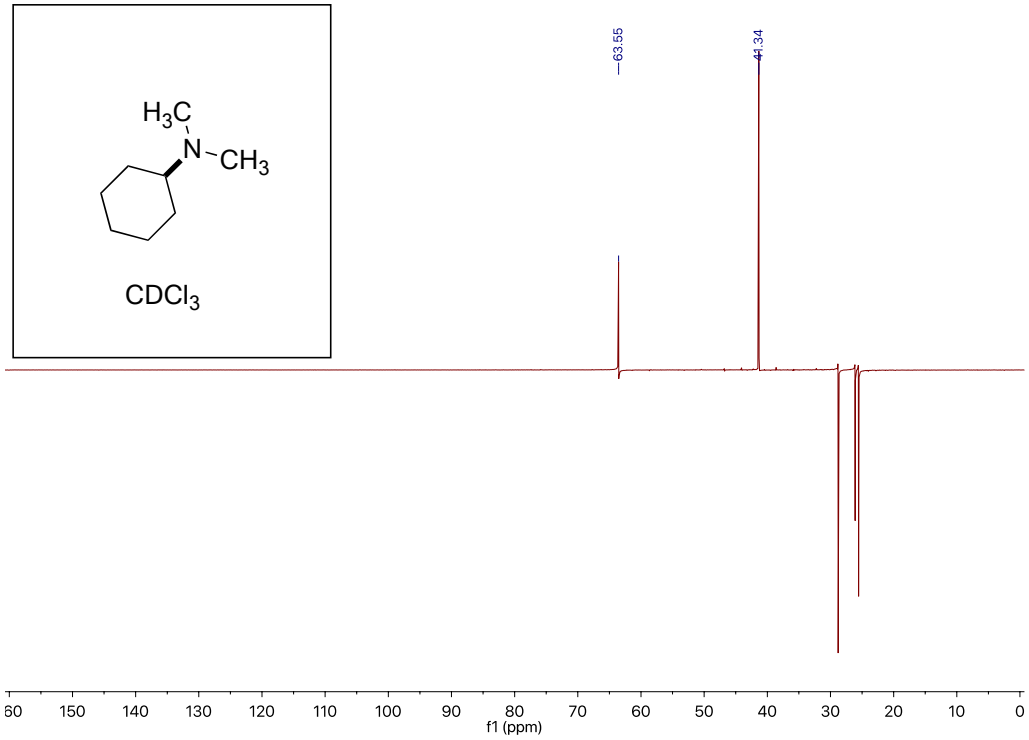

Figure S10. *[13]C-APT-NMR spectra of DMCA*

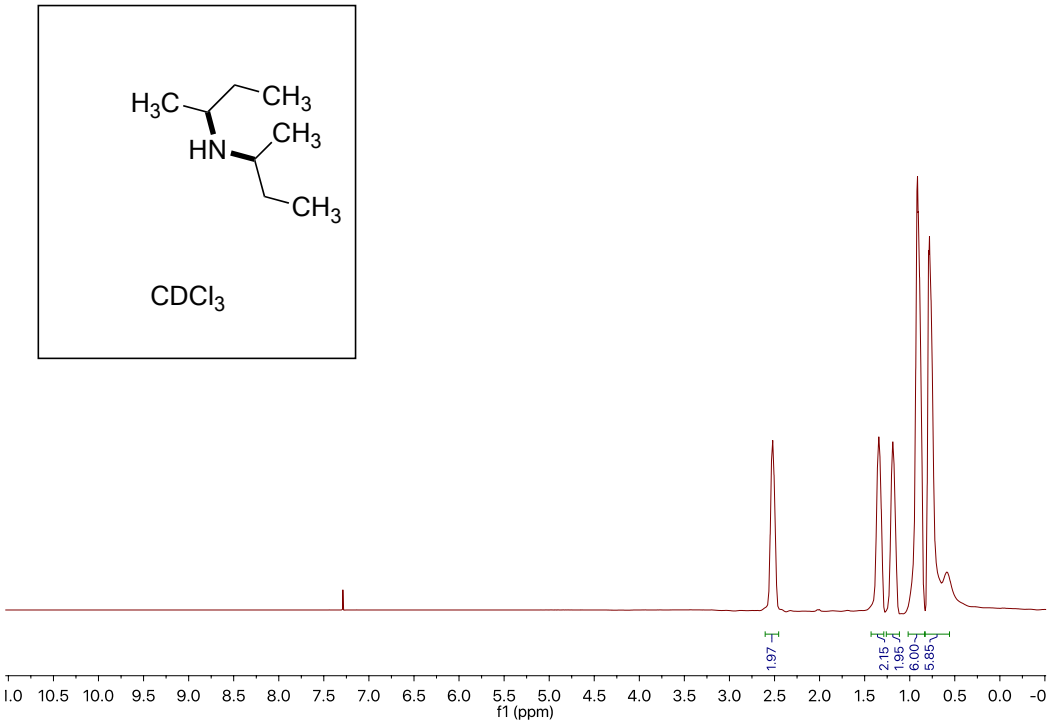

Figure S11. *[1]H-NMR (700 MHz, Chloroform-d) spectra of DBA; δ = 2.52 (tt, J = 12.0, 6.0 Hz, 2H), 1.39 – 1.28 (m, 2H), 1.24 – 1.16 (m, 2H), 0.94 – 0.89 (m, 6H), 0.81 – 0.72 (m, 6H).*

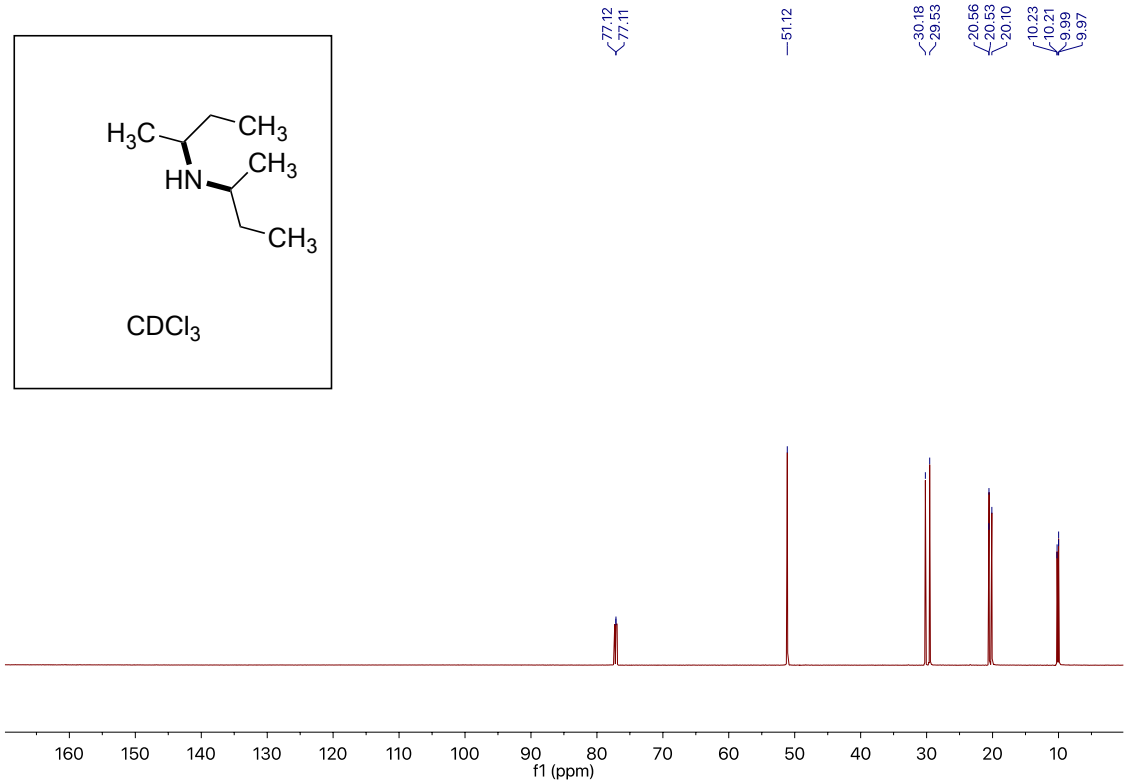

Figure S12. *[13]C-APT-NMR spectra of DBA*

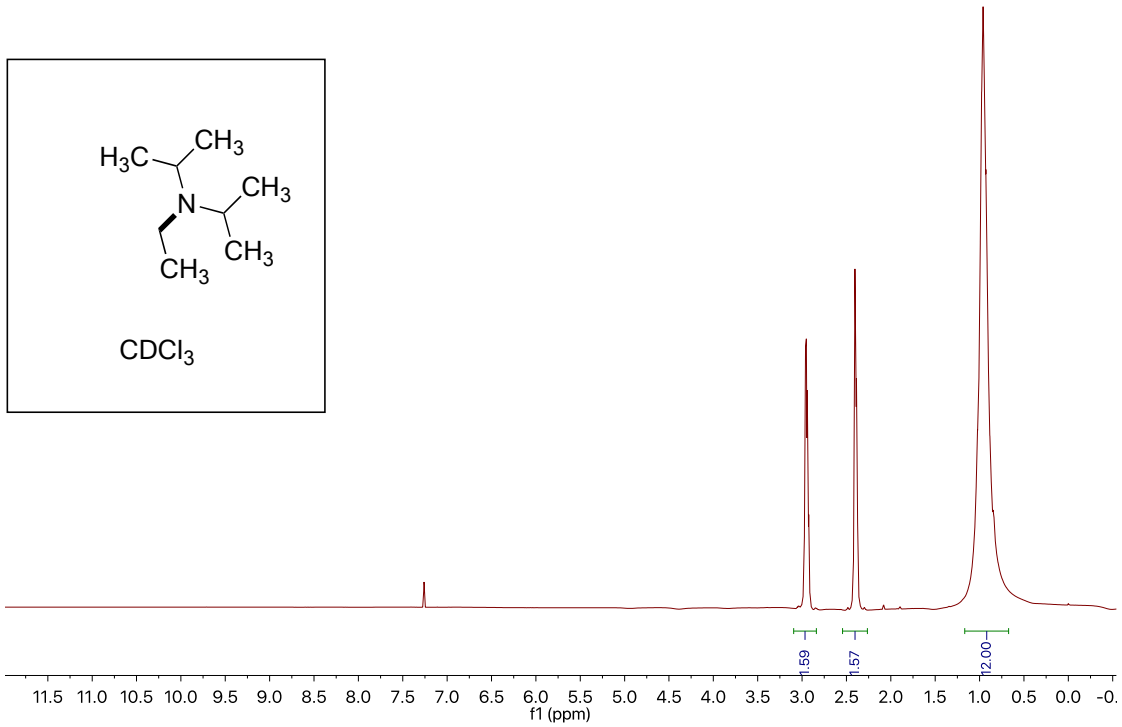

Figure S13. *[1]H-NMR (700 MHz, Chloroform-d) spectra of DIPEA δ = 2.95 (dt, J = 13.3, 6.7 Hz, 2H), 2.40 (q, J = 6.4, 5.6 Hz, 2H), 1.10 – 0.81 (m, 12H).*

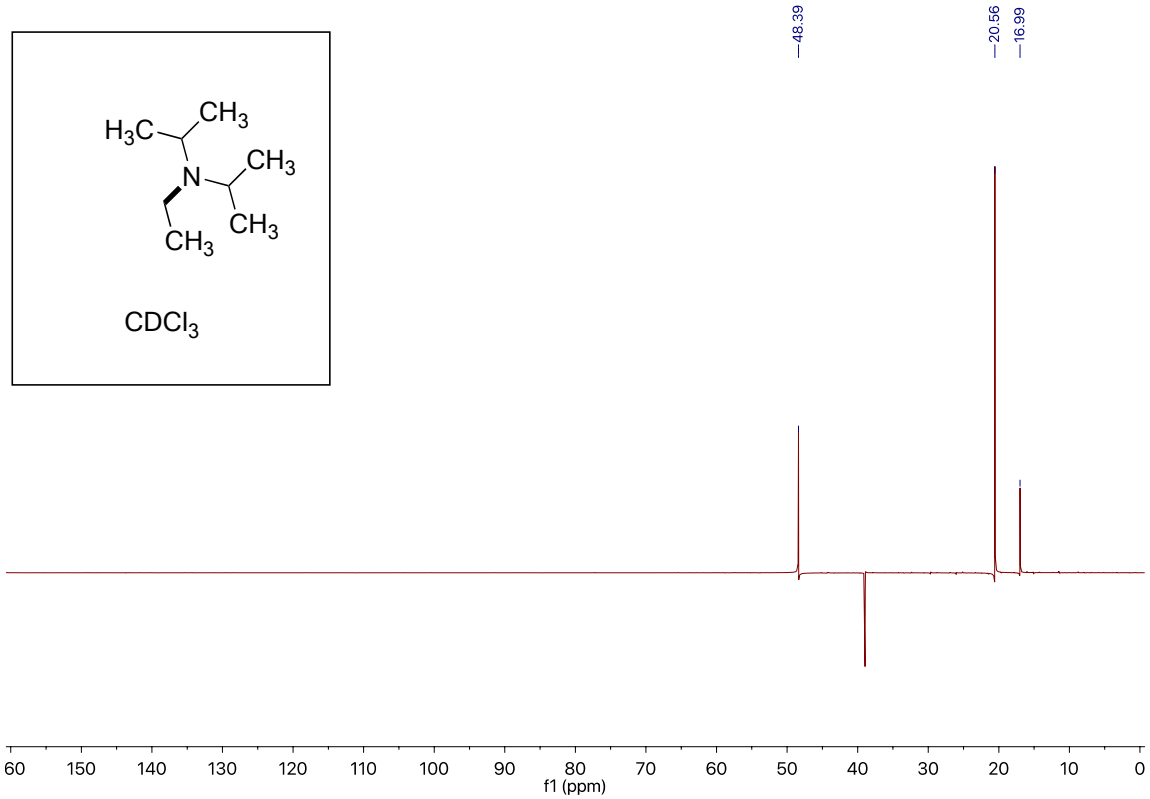

Figure S14. *[13]C-APT-NMR spectra of DIPEA*

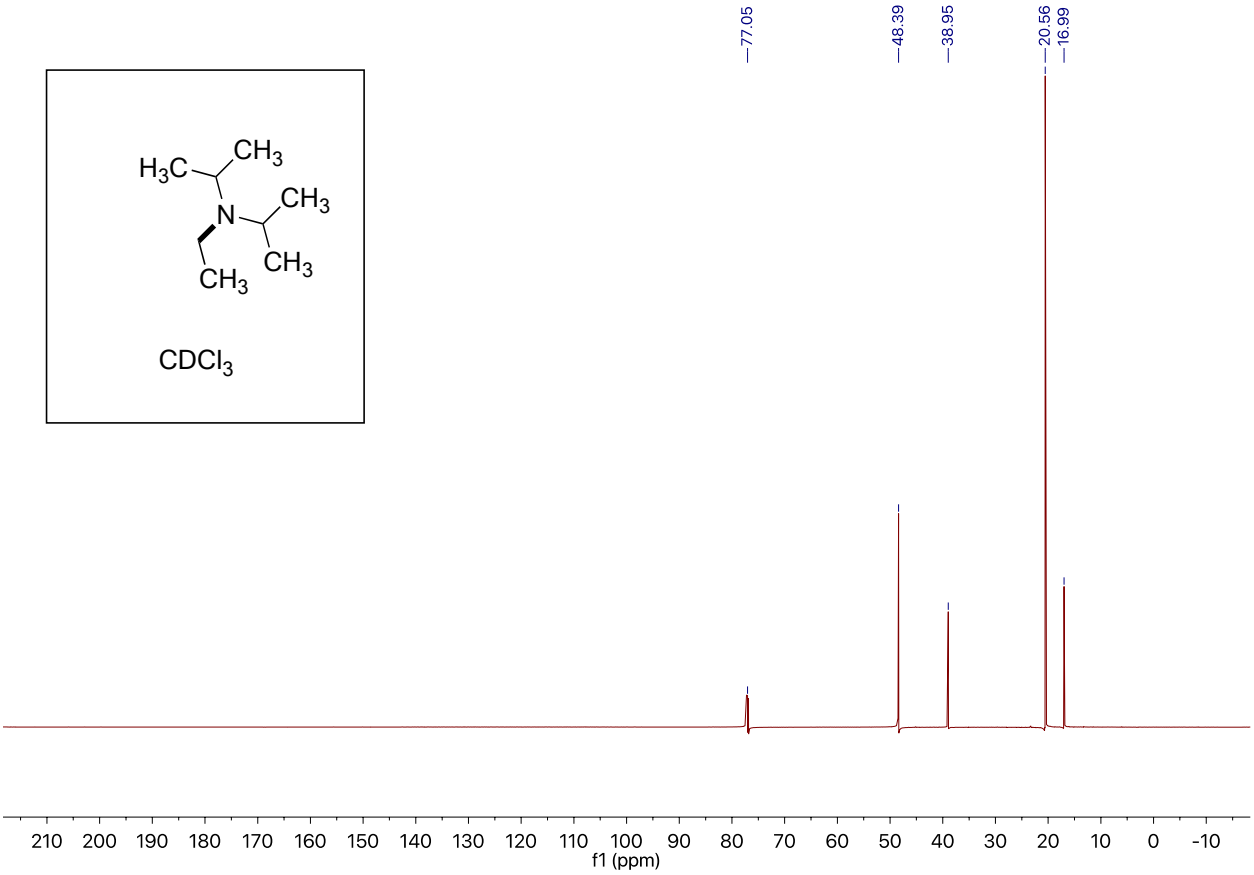

Figure S15. *^{13}C-NMR spectra of DIPEA*

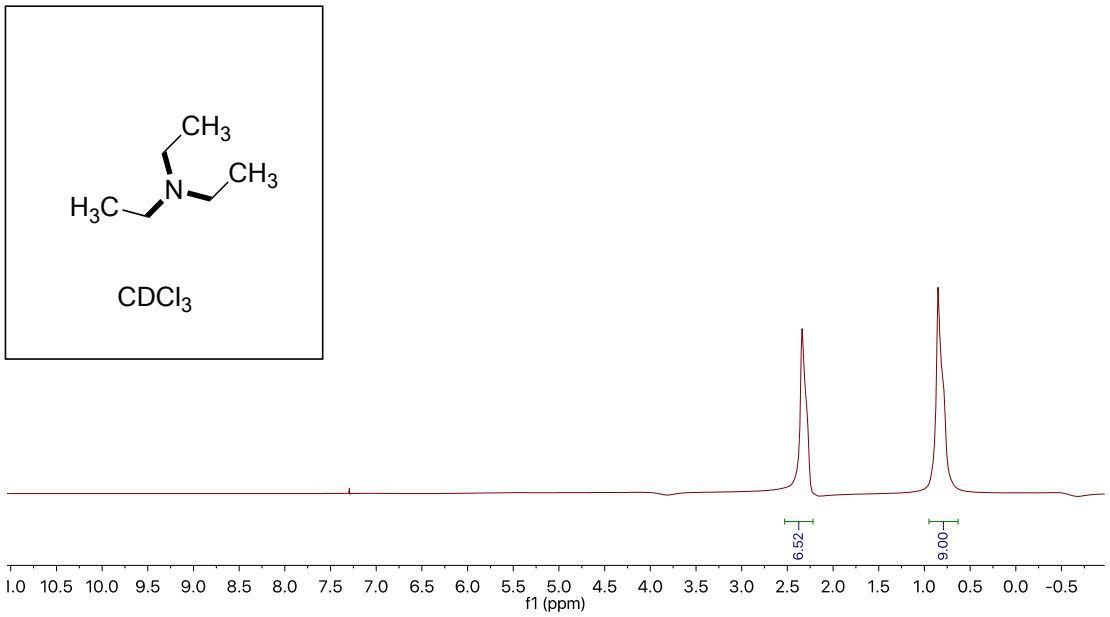

Figure S16. *[1]H-NMR (700 MHz, Chloroform-d) spectra of TEA; δ = 2.33 (d, J = 12.9 Hz, 6H), 0.85 (s, 9H).*

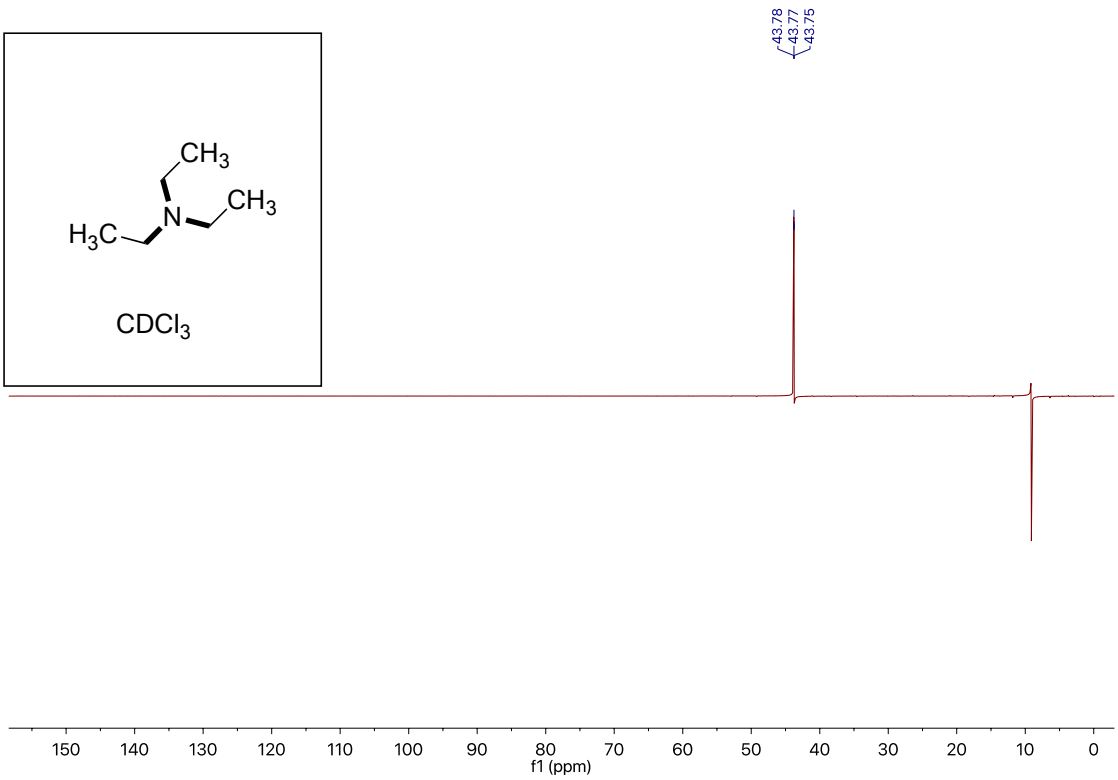

Figure S17. *[13]C-APT-NMR spectra of TEA*

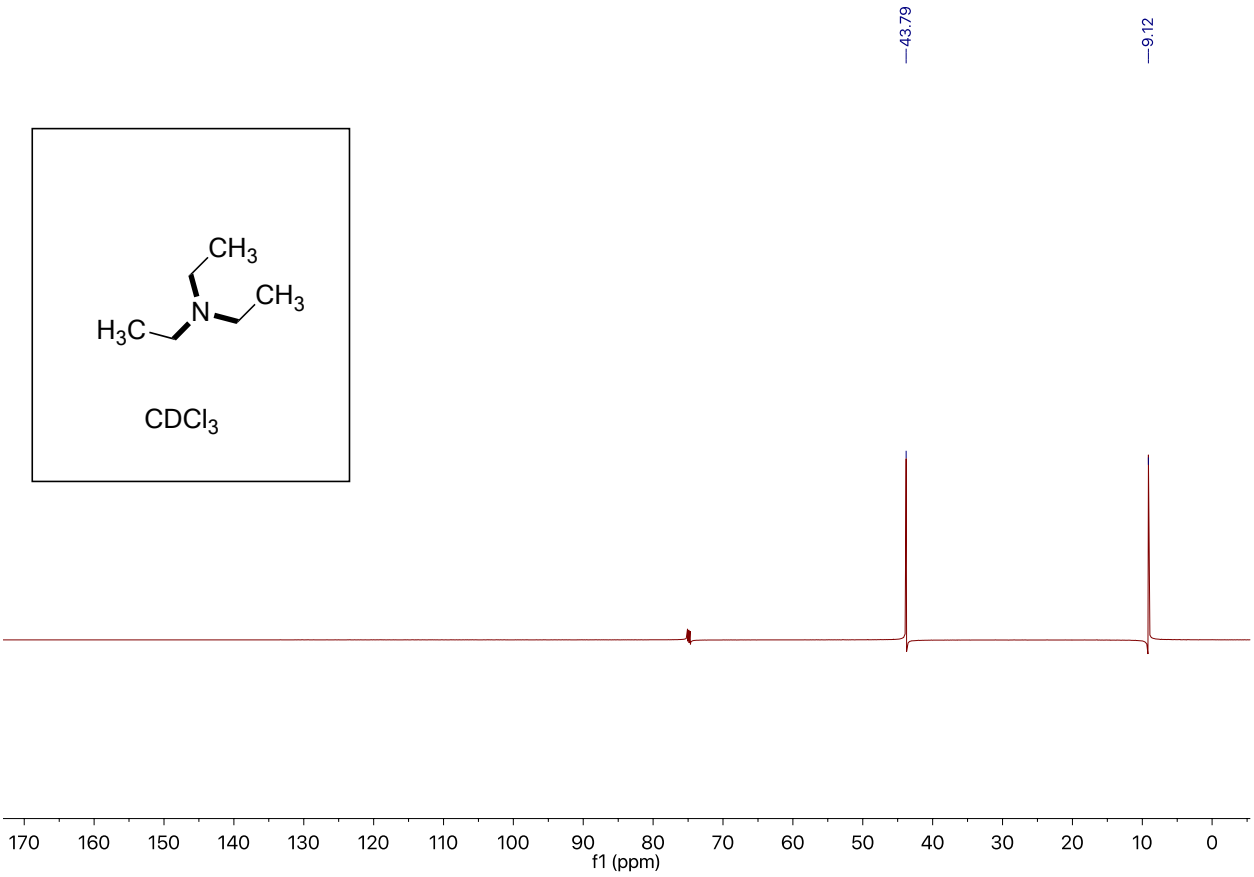

Figure S18. *^{13}C-NMR spectra of TEA*

S3. Density Measurements

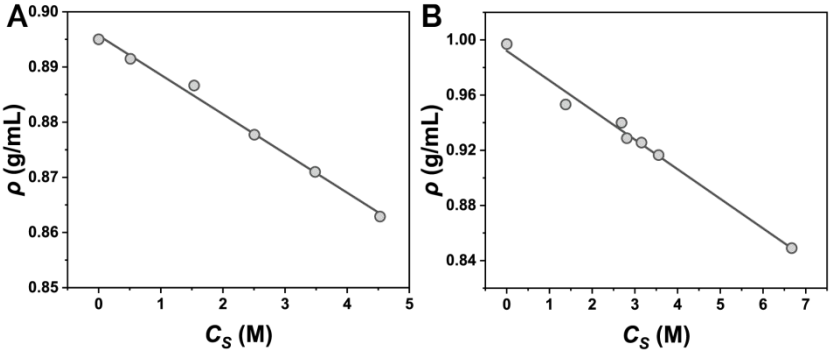

Figure S19. *Density calibration for different DMCA concentrations in (A) toluene and (B) water.*

Density of SHS in water and toluene were determined for different SHS concentrations. Density calibration experiments were carried out with two different methods. For the toluene and SHS mixture, a pre-determined amount of toluene was measured in a vial and weighed. Then various amounts of SHS was added to the vial and weighed. After two liquids were mixed, volume of the resulting mixture was measured. Based on the volume of the resulting mixture and mass of SHS, molar concentration was calculated and fitted as shown in **Figure S19**. The DI water and SHS mixture density calibration was conducted in flow using a procedure similar to the extraction experiment. A pre-determined volume of DI water and SHS mixture (1 µL -3 µL each) was injected into the tube-in-tube flow reactor and final volume of the mixture was measured using a high-resolution digital camera. Mass of SHS was obtained using its reported density. Density calibration graph for aqueous mixture is shown in **Figure S19**.

The amount of SHS in both aqueous and organic phase before and after extraction in flow was determined with following equations. Density of the organic phase is defined as

$$\rho_{\text{org}} = \frac{m_{org}}{V_{org}} = \frac{m_{toluene}(t) + m_s(t)}{L_{org} * A} \quad \text{(eqn. S1)}$$

where ρ, V, m, L, t, and A are density, volume, mass, length, time, and cross-sectional area; subscripts *org, aq,* and *s* represent the organic phase, aqueous phase, and SHS, respectively. From **Figure S19A**, the density of SHS in toluene is defined as

$$\rho_{org} = a * C_s(t) + \rho_{toluene} = a * \frac{m_{s,org}(t)}{MW_s * V_{org}(t)} + \rho_{toluene} \quad \text{(eqn. S2)}$$

where C_s, MW, and a are concentration, molecular weight, and slope of the density calibration graph shown in **Figure S19A**. Then, combining equations **S1** and **S2** and rearraigning the resulting euqation in terms of the mass of SHS leads to the following equation:

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

Similarly, mass of SHS in the aqueous phase can be calculated using the following equations:

$$\rho_{\text{aq}} = \frac{m_{aq}}{V_{aq}} = \frac{m_{water} + m_s(t)}{L_{aq} * A} \quad \text{(eqn. S4)}$$

$$\rho_{aq} = b * C_s(t) + \rho_{water} = b * \frac{m_{s,aq}(t)}{MW_s * V_{aq}(t)} \quad \text{(eqn. S5)}$$

$$m_{s,aq}(t) = \frac{m_{water} - \rho_{aq} * V_{aq}(t)}{\frac{b}{MW_s} - 1} \qquad \text{(eqn.S6)}$$

where b is the slope of the density calibration graph shown in **Figure S19B**.

While the aqueous phase (DI water) and all tested SHSs showed neglible volume loss (no measurable change in volume) in the sing-droplet flow reactor over 10 min of the oscillatory movement with different flow velocities, the toluene slug showed 3%-6% volume loss during the oscillation in 10 min (**Figure S20**).

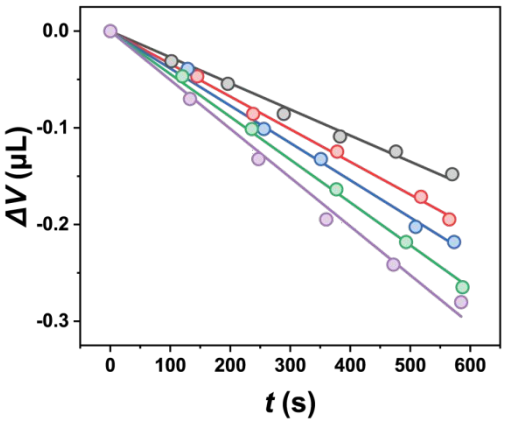

Figure S20. *Mass loss of a toluene slug oscillating in the microreactor for 10 min at flow velocities, U = 5 mm/s (Black), 10 mm/s (Red), 15 mm/s (Blue), 20 mm/s (Green), and 25 mm/s (Purple).*

S4. MATLAB Image Analysis

A custom-developed image processing code (MATLAB) was utilized for accurate volume measurement/tracking of each phase during the CO_2-mediated SHS extraction process in flow. For each bi-phasic slug, such as the one shown in **Figure S21A**, an RGB intensity gradient (I') along the centerline of the microreactor at different positions (X) was calculated (**Figure S21B**). With background subtraction and image filtering, minimum and maximum points of each RGB channel were identified and converted into the slug length and volume using a pixel to mm ratio.

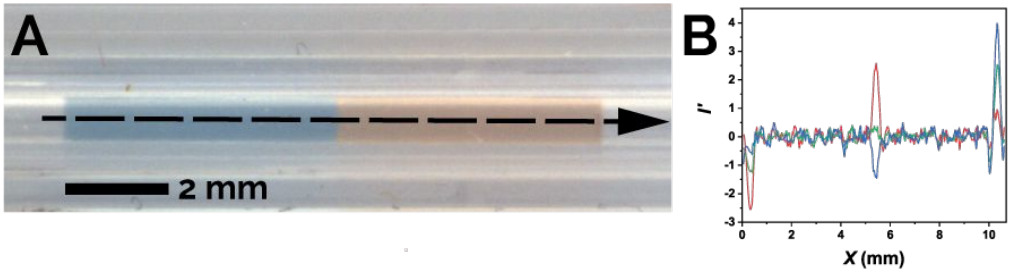

Figure S21. *(A) An exemplary color image of the bi-phasic slug within the microreactor. The dashed line shows the centerline of the microchannel. (B) RGB intensity gradient along the microchannel centerline with a bi-phasic slug present. Organic phase (red): toluene and 4.5M DMCA labeled with Sudan Red dye; Aqueous phase (blue): DI water labeled with Indigo Carmine Dye.*

S5. Table of Abbreviations and Symbols

Table 2. *List of Abbreviations*

Abbreviation	Definition
SHS	Switchable Hydrophilicity Solvents
LLE	Liquid-Liquid Extraction
TEA	Triethylamine
DMCA	N,N-dimethylcyclohexylamine
DBA	Di-*sec*-butylamine
DIPEA	N,N-diisopropylethylamine
FEP	Fluorinated Ethylene Propylene
CO_2	Carbon Dioxide
N_2	Nitrogen

Table 3. *List of Symbols*

Symbol	Definition
ρ	Density
V	Volume
m	Mass
aq	Aqueous Phase
org	Organic Phase
s	SHS
i	Initial
f	Final
t	Time
U	Velocity
C_S	Concentration of SHS
L	Reactor Length
P	Pressure
R_i	Aqueous to Organic Phase Volume Ratio
D	Distribution Ratio
w	Mass fraction

S6. De-wetting and Full engulfment of a Bi-phasic Slug

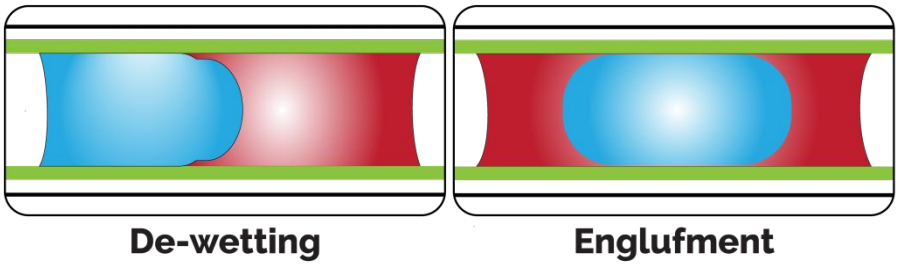

Figure S22. *De-wetting and complete engulfment of the aqueous phase in the organic phase.*

S7. Supplementary Videos

Movie S1. Video of the CO_2-triggered SHS extraction process in the single-droplet *green* flow chemistry platform. Camera frame rate is 30 fps. C_S = 4.5 M, R_i = 1, U = 467 mm/s, L = 6 cm, and P = 30 psig. Organic phase (red): toluene and 4.5M DMCA labeled with Sudan Red dye; Aqueous phase (blue): DI water labeled with Indigo Carmine Dye.

Movie S2. Video of three bi-phasic slugs conducting the CO_2-mediated SHS extraction process, simultaneously. in the microreactor. Camera frame rate is 30 fps. C_S = 4.5 M, R_i = 1, U = 467 mm/s, L = 6 cm, and P = 30 psig. Organic phase (red): toluene and 4.5M DMCA labeled with Sudan Red dye; Aqueous phase (blue): DI water labeled with Indigo Carmine Dye.