Supporting Information

Compartmentalized Droplets for Continuous Flow Liquid-Liquid Interface Catalysis

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Experimental section

Mass spectrometry spectra

1. Materials

Methyltrimethoxysilane (98%), *n*-hexanol (AR), *n*-octanol (AR), cyclohexanol (AR), aniline (AR), 4-methoxyaniline (AR), 4-methylaniline (AR), 4-*iso*propylaniline (AR), tetraethylenepentamine(AR), diethylenetriamine (AR), ethylenediamine (AR), ethanolamine (AR), diethylamine (AR), 3,4-dihydro-2*H*-pyran (98%), cyclohexene oxide (98%), phosphotungstic acid (AR, $H_3PW_{12}O_{40}$), trisodium salt of tri-(*m*-sulfonphenyl)phosphine (TPPTS) and span 80 were purchased from Aladdin (China). Coomassie Brilliant Blue G-250 (CBB) and bovine serum albumin (BSA) were purchased from Sinopharm Chemical Reagent Co., Ltd, (China). Native Lipase B from *Candida Antarctica* (CALB) was purchased from Novozymes. (*R, S*)-1-phenylethyl acetate (98%), and (*R, S*)-1-octen-3-yl acetate (97%) were purchased from Adamas Reagent Co., Ltd, (China). (*R, S*)-2-octanol acetate (98%) and (*R, S*)-4-methyl-2-pentanol acetate (99%) was purchased from Alfa Aesar. Cyclohexane (AR) and Triton X-10 (TX-10, 98%) were obtained from Guangzhou Reagent Company (China). FITC-dextran (CAS No. 60842-46-8) and fluorescein isothiocyanate isomer I (FITC-I, CAS No.3326-32-7) were obtained from Santa Cruz Biotechnology. Nile red (CAS No. 7385-67-3) was obtained from Sigma-Aldrich. Water used in this study was de-ionized water.

2. Characterization and methods

Nitrogen-sorption experiments of hydrophobised silica particles were performed at -196 °C on a Micromeritics ASAP 2020 analyzer. Before measuring, all samples were out gassed at 120 °C under vacuum for 6 h. The surface area was calculated from the adsorption branch in the relative pressure range of 0.05–0.15 using the Brunauer-Emmett-Teller (BET) method. Samples for transmission electron microscopy (TEM) observations were prepared by dispersing the sample powder in ethanol using ultrasound and then allowing a drop of the suspension to evaporate on a copper gird covered with a holey carbon film. The TEM images were obtained on a JEOL-JEM-2000EX instrument. Emulsion droplets were observed using an optical microscope (XSP-8CA, Shanghai, China) equipped with 4 or 10 × magnification lens. X-ray photoelectron spectrum (XPS) was recorded on a Kratos Axis Ultra DLD. The contact angles of water in air on silica particle disks were measured using a Krüss DSA100 instrument. Before measurement, the powder sample was compressed into a disk of thickness approximately 1 mm (*ca.* 2 MPa). A drop of water (1 μL) was injected on the sample disk. The appearance of the water drop was recorded at *ca.* 0.1 second with digital camera. The value of contact angle was determined by a photogoniometric method. UV-Vis determination was conducted on a TU-1900 spectrometer (China). The flow rate of the oil phase is controlled with a flow pump (LC-01P, Jiangshen Technology Co., China). The gas chromatography (GC) analysis was carried out on an Agilent 7890Aanalyzer (SE-30, CatNO.1034-4 or Agilent-113-2532, Cyclodex-B), with a flame ionization detector. The identification of products by MS spectra was performed on a GC-MS instrument (7890A-5975C, HP-5, Agilent).Confocal laser scanning microscopy images were obtained on a Carl Zeiss LSM880 instrument (Germany). The concentration of FITC-dextran in water was 5×10^{-6} M and the excitation wavelength is 488 nm (green). The concentration of Nile red in toluene was 2×10^{-6} M and the excitation wavelength is 559 nm (red). The average droplet size was estimated based on 200 droplets. The surface coverage C is estimated by

$$C = m_p D/4\rho_p V_d d_p$$

where m_p is the mass of solid particle emulsifier, D is the average diameter of an emulsion droplet, ρ_p is the density of the solid particle emulsifier (2.65 gcm^{-3}),V_d is the volume of water and d_p is the solid particle diameter.[1]

3. Material synthesis

Emulsifier preparation. Silica nanospheres were synthesized according to our previous procedure.[2] 1.5 g as-synthesized silica nanospheres (dried at 120 °C for 4 h) was dispersed into toluene (8 mL). Into this suspension, a mixture of 4.5 mmol $(MeO)_3SiCH_3$ and 4.5 mmol $(C_2H_5)_3N$ were added. After heating under reflux for 4 h under a N_2atmosphere, the solid material was isolated by centrifugation, washed four times with toluene and dried, giving methyl-modified silica particles as emulsifier.

FITC-I-labelled emulsifier preparation.1.5 g silica nanospheres (dried at 120 °C for 4 h) was dispersed into toluene (8 mL). A mixture of 0.3 mmol $(MeO)_3SiCH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$, 4.5 mmol $(MeO)_3SiCH_3$and 4.8 mmol $(C_2H_5)_3N$ were added to this suspension. After refluxing for 4 h under a N_2 atmosphere, the silica nanospheres were isolated by centrifugation, washed four times with toluene and dried, resulting in bifunctionalized silica nanospheres. 1 g of the bifunctionalized silica and 0.02 g fluorescein isothiocyanate isomer I (FITC-I) were dispersed into 50 mL ethanol. The mixture was stirred over night at room temperature in the dark. After centrifugation, being washed four times with ethanol and being dried, FITC-I-labelled emulsifier was eventually obtained.

You need to add text on preparation of more monodisperse emulsions

4. General procedure for preparing continuous flow Pickering emulsion

A glass column with a sand filter and a valve at the bottom was used as the column reactor. The inner diameter of the column is 1.34 or 2.0 cm and the pore diameter of the sand filter is 4.5-9 μm. A given volume of Pickering emulsion was poured into this column forming a packed bed. If needed, the column was wrapped with a thermo-jacket for heating. The continuous oil phase was continuously pumped into the column from the top, and the downstream was collected from the outlet of the column. The flow rate of oil was tuned through a flow pump and also determined based on the volume of the collected liquid per unit time.

5. Compartmentalization of water droplet towards water-soluble reagents

Indicator experiment. The flow Pickering emulsion column was packed with two portions of Pickering emulsions in the upper layer and lower layer, respectively. The lower Pickering emulsion consists of 9 mL of aqueous NaOH (0.001 M, 0.003 g of Congo Red), 4.5 mL of toluene and 0.18 g of silica particle emulsifier. The upper Pickering emulsion consisted of 9 mL of aqueous H_2SO_4 (0.001 M, 0.003 g of Congo Red), 4.5 mL of toluene and 0.18 g of silica particle emulsifier. After the column was packed with these two layers of Pickering emulsion, fresh toluene was continuously pumped in the top of column and the layer height of toluene was kept at 5 cm. The flow rate of the continuous phase was controlled at 2 mL h^{-1}.

Retention fraction determination. A FPE column was set up with 18 mL of aqueous solution of a water-soluble reagent (a given concentration), 9 mL of toluene or *n*-octane (only for CALB and TPPTS) and 0.36 g of emulsifier. The examined water-soluble reagents included H_2SO_4 (0.1 M), $H_3PW_{12}O_{40}$ (0.01 M), TPPTS (1×10^{-4} M), CALB (0.1 mg mL^{-1} protein), tetraethylenepentamine (0.1 M), diethylenetriamine (0.1 M), ethylenediamine (0.1 M) and ethanolamine (0.1 M). After flowing for 120 h with a flow rate of 2 mL h^{-1}, the Pickering emulsion collected from the FPE column was demulsified through centrifugation. The obtained aqueous solution was titrated with either 0.025 M NaOH or 0.05 M HCl (repeating three times to get an average value). For TPPTS and CALB, UV-Vis spectrophotometry was used to determine their concentration. To eliminate the possible effect of the presence of silica (water-soluble reagent was adsorbed on silica particles), the fresh Pickering emulsion was subjected to the same treatment for titration. The retention fraction is the ratio of the amount of water-soluble reagent after flow to its amount before flow.

6. Determination of partition coefficient of organic bases

The partition coefficient (K_{ow}) of organic base between toluene and water was determined with the following method. A mixture of 25 mL of aqueous base (1 M) and 25 mL of toluene was stirred for 12 h at room temperature to reach equilibrium. After phase separation, 5 mL of aqueous phase (bottom layer) was withdrawn and titrated with an HCl solution (phenolphthalein as indicator), thus giving the concentration of organic base in water. The concentration of organic base in toluene is calculated based on the difference between the initial concentration of amine in water and the determined concentration after equilibrium. This experiment was repeated three times to obtain an average value. The partition coefficient (K_{ow}) between toluene and water is the ratio of the base concentration in toluene to the base concentration in water at equilibrium.

7. Continuous flow Pickering emulsion reactions

H_2SO_4-containing Pickering emulsions for synthesizing ethers. A mixture of 3.6 mL of aqueous H_2SO_4 (0.1 M), 1.8 mL of toluene and 0.072 g of emulsifier was stirred at 2000 rpm for 5 min yielding a Pickering emulsion. This Pickering emulsion was gently poured into a glass column (1.34 cm in inner diameter) with a sand filter (4.5-9 μm in pore diameter) and valve at the bottom. The substrates including 3, 4-dihydro-2*H*-pyran and alcohol (mole ratio is 1:1) was dissolved in toluene (0.25 M). This toluene solution was pumped with a given velocity to the top of the column reactor and passed through the column whose temperature was kept at 50 °C. The outflow from the column bottom was sampled for GC analysis at intervals. The product was further confirmed with GC-MS. For the reactions of *n*-octanol and 3, 4-dihydro-2*H*-pyran, the H_2SO_4 concentration is 0.5 M. To determine the retention fraction of H_2SO_4, at the end of flow reaction the Pickering emulsion was poured out and subjected to demulsification through centrifugation for phase separation. The obtained water solution was diluted with deionized water to 18 mL. This aqueous solution was titrated with a NaOH solution (0.01 M, repeating three times to get an average value). To eliminate the possible effect of the presence of silica (H_2SO_4 was adsorbed on silica particles), the fresh Pickering emulsion was subjected to the same treatment for titration. The retention fraction is the ratio of the amount of H_2SO_4 after reaction to the amount of H_2SO_4 before reaction.

HPA-containing Pickering emulsions for ring opening of epoxides. A mixture of 30 mL of aqueous phosphotungstic acid (HPA) solution (0.01 M), 15 mL of toluene and 0.9 g of emulsifier was stirred at 2000 rpm for 5 min leading to a Pickering emulsion. This Pickering emulsion was poured in to a glass column reactor (3.6 cm in inner diameter) with a sand filter (4.5-9 μm in pore size) and valve at the bottom. Cyclohexene oxide and amine with mole ratio of 1:1 were dissolved in toluene (0.5 M). This toluene solution of reactants was pumped with a given velocity into the top of the column reactor and passed through the column whose temperature was kept at 50 °C. The outflow from the column reactor was sampled for GC analysis at intervals. The product was further confirmed with GC-MS. The retention rate of HPA was obtained according to the above procedure for H_2SO_4.

CALB -catalyzed kinetic resolution of racemic ester. A mixture of 40 mL of enzyme solution (0.1 $mgmL^{-1}$, 0.5 M Na_2HPO_4), 20 mL of *n*-octane and 1.2 g of emulsifier was stirred at 2000 rpm for 5 min resulting in a Pickering emulsion. This Pickering emulsion was then poured into a glass column reactor (3.6 cm in inner diameter) with a sand filter (4.5-9 μm in pore diameter) and valve at the bottom. Racemic acetates were dissolved in *n*-octane (0.25 M). This solution was continuously pumped into the column and passed through the column reactor with a given velocity whose temperature was maintained at 35 °C. The outflow from the column bottom was sampled for GC at intervals. The product was further confirmed with GC-MS. Every time the collected eluent was up to 400 mL, Pickering emulsion was poured out and demulsified for tuning pH and supplying water (acetic acid is released from reaction to lower the pH, water as one of the reactants is consumed). After the pH was tuned to 8-9 using *ca.*2 ml sodium hydroxide solution, this mixture was re-emulsified and then filled into the column reactor to continue to run. To determine the retention fraction of CALB, after reaction the Pickering emulsion was poured out and subjected to demulsification through centrifugation for phase separation. The amount of CALB in the obtained aqueous phase was determined with the Bradford method.[3]Toeliminate the possible effect that CALB was adsorbed on silica particles, the Pickering emulsion before reaction was subjected to the same treatment to determine the amount of CALB. The retention fraction is the ratio of the amount of CALBafter reaction to the amount of CALB before reaction.

Determination of protein content (Bradford method). Coomassie Brilliant Blue G-250 (100 mg, CBB) and 100 mL of phosphoric acid (85% w/v) were dispersed into 50 mL of ethanol (95%). The resulting solution was then diluted to 1 L with deionized water. The final composition of the solution is 0.01% (w/v) Coomassie Brilliant Blue G-250, 4.7% (w/v) ethanol and 8.5% (w/v) phosphoric acid.

Protein assay. A UV-Vis standard curve for Bovine Serum Albumin (BSA) assay was obtained using different protein concentrations with 0.02, 0.04, 0.06, 0.08 and 0.1 mg mL^{-1}. 1 mL of the sample solution was added into 4 mL of CBB solution. The resultant mixture was incubated for 10 min at room temperature for UV-Vis determination (595 nm). A blank experiment was also conducted in the absence of protein.

8. Batch reactions

H_2SO_4–catalyzed addition reactions. The batch biphasic reactions were conducted in a 20 mL glass vial. 8 mL of aqueous sulfuric acid (0.5 M) and 4 mL of toluene containing *n*-octanol and 3,4-dihydro-2*H*-pyran(1: 1, 0.25 M) were charged into this vial. If needed, the reaction mixture was stirred with a magnetic stir bar (10 mm in length, 900 rpm) at 50 °C. An aliquot of oil phase was taken at intervals for monitoring conversions by GC. The procedures for batch Pickering emulsion reactions are the same as the conventional batch biphasic reactions except for the addition of 0.16 g of emulsifier and stirring at 2000 rpm for 5 min (emulsification) before reaction.

HPA-catalyzed ringopening reactions. The batch biphasic reactions were conducted in a 20 mL glass vial. 10 mL of aqueous phosphotungstic acid solution (0.01 M) and 5 mL of toluene containing aniline and cyclohexene oxide (1: 1, 0.5 M) were charged into this vial. If needed, the reaction mixture was stirred with a magnetic stir bar (10 mm in length, 900 rpm) at 50 °C. An aliquot of oil phase was taken at intervals for monitoring conversions by GC. The procedures for batch Pickering emulsion reactions are the same as the conventional batch biphasic reactions except for the addition of 0.3 g of emulsifier and stirring at 2000 rpm for 5 min (emulsification) before reaction.

CALB-catalyzed kinetic resolution of racemic ester. The batch biphasic reactions were conducted in a 20 mL glass vial. 10 mL of enzyme solution (0.1 mg mL^{-1} protein) and 5 mL of *n*-octane containing (*R, S*)-1-phenylethyl acetate (0.25 M) were charged into the vial. If needed, the reaction mixture was stirred with a magnetic stir bar (10 mm in length, 900 rpm) at 35 °C. An aliquot of oil phase was taken at intervals for monitoring conversions by GC. The procedures for batch Pickering emulsion reactions are the same as the conventional batch biphasic reactions except for the addition of 0.3 g of emulsifier and stirring at 2000 rpm for 5 min (emulsification) before reaction.

References

(1) Gautier, F.; Destribats, M.; Perrier-Cornet, R.; Dechézelles, J. F.; Giermanska, J.; Héroguez, V.; Ravaine, S.; Leal-Calderon, F.; Schmitt, V. *Phys. Chem. Chem. Phys.* **2007**, *9*, 6455.

(2) Kong, D. Y.; Zhang, C. M.; Xu, Z. H.; Li, G. G.; Hou, Z. Y.; Lin, J. *J. Colloid Interface Sci.* **2010**, *352*, 278.

(3) Bradford, M. M. *Anal. Biochem.* **1976**, *72*, 248.

TableS1. Characterisation of water-in-oil Pickering emulsions formulated with different amounts of silica particle emulsifier.

Particleconcentration (wt.%)	$D_{droplet}$[a] (μm)	$V_{emulsion}$[b] (mL)	V_{H_2O}[c] (mL)	V_{octane}[d] (mL)	$H_{emulsion}$[e] (cm)
1.0	92	37.0	30	7.0	11.1
2.0	76	38.6	30	8.6	11.6
3.0	48	40.0	30	10.0	12.0
4.0	39	41.6	30	11.6	12.5
5.0	30	43.0	30	13.0	12.9

[a]$D_{droplet}$ is the average diameter of emulsion droplets; [b]$V_{emulsion}$ is the volume of Pickering emulsion; [c]V_{H_2O} is the water content in the emulsion; [d]V_{octane} is the *n*-octane content in the emulsion; [e]$H_{emulsion}$ is the emulsion height in the column.

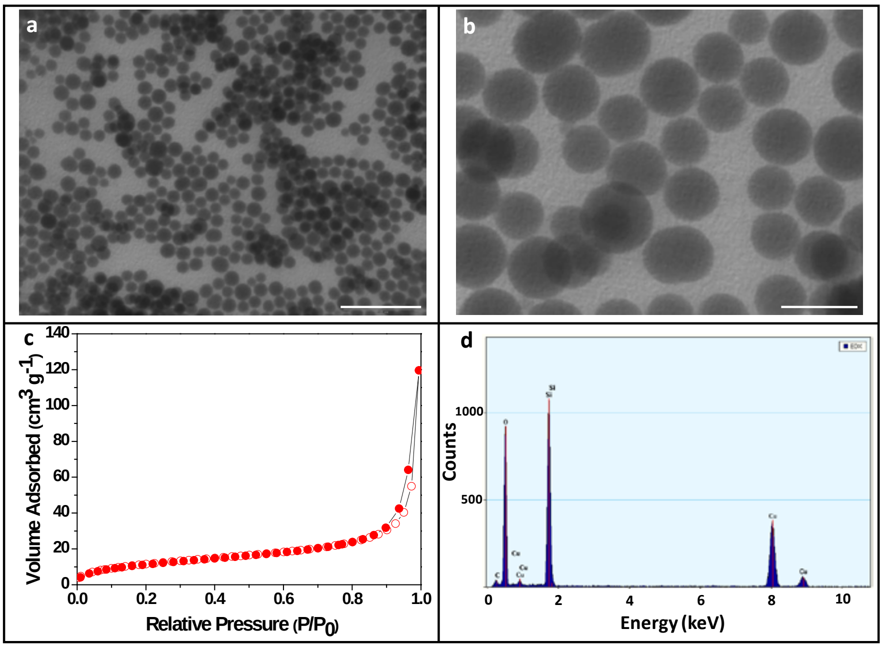

Figure S1. Characterization of silica particle emulsifier. (a) TEM image, scale bar = 500 nm; (b) TEM image, scale bar = 100 nm; (c) N_2 adsorption (open points)–desorption (filled points) isotherms. The specific surface area is 44 m^2 g^{-1}; (d) EDX spectrum (Cu from Cu grid).

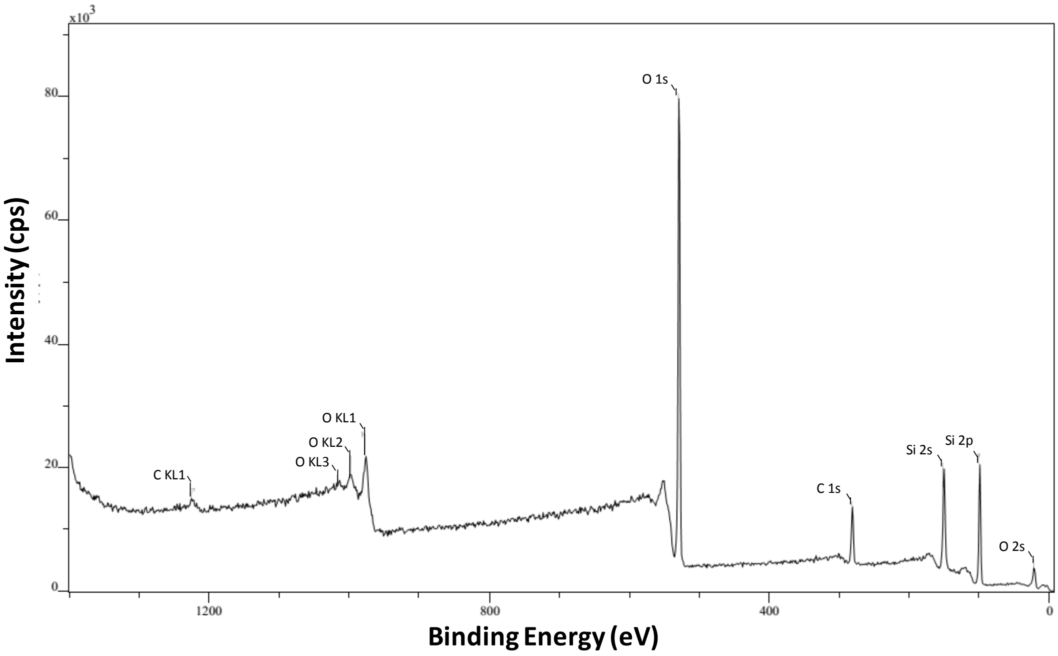

Figure S2. X-Ray photoelectron spectrum of silica particle emulsifier.

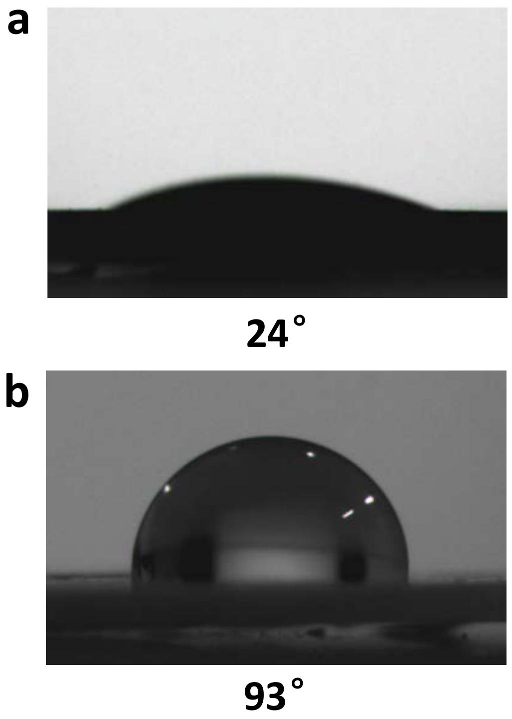

Figure S3. Appearance of a water droplet in air on a disk of compressed silica particles for (a) unmodified silica and (b) hydrophobically modified silica. The contact angles given are through the water drop.

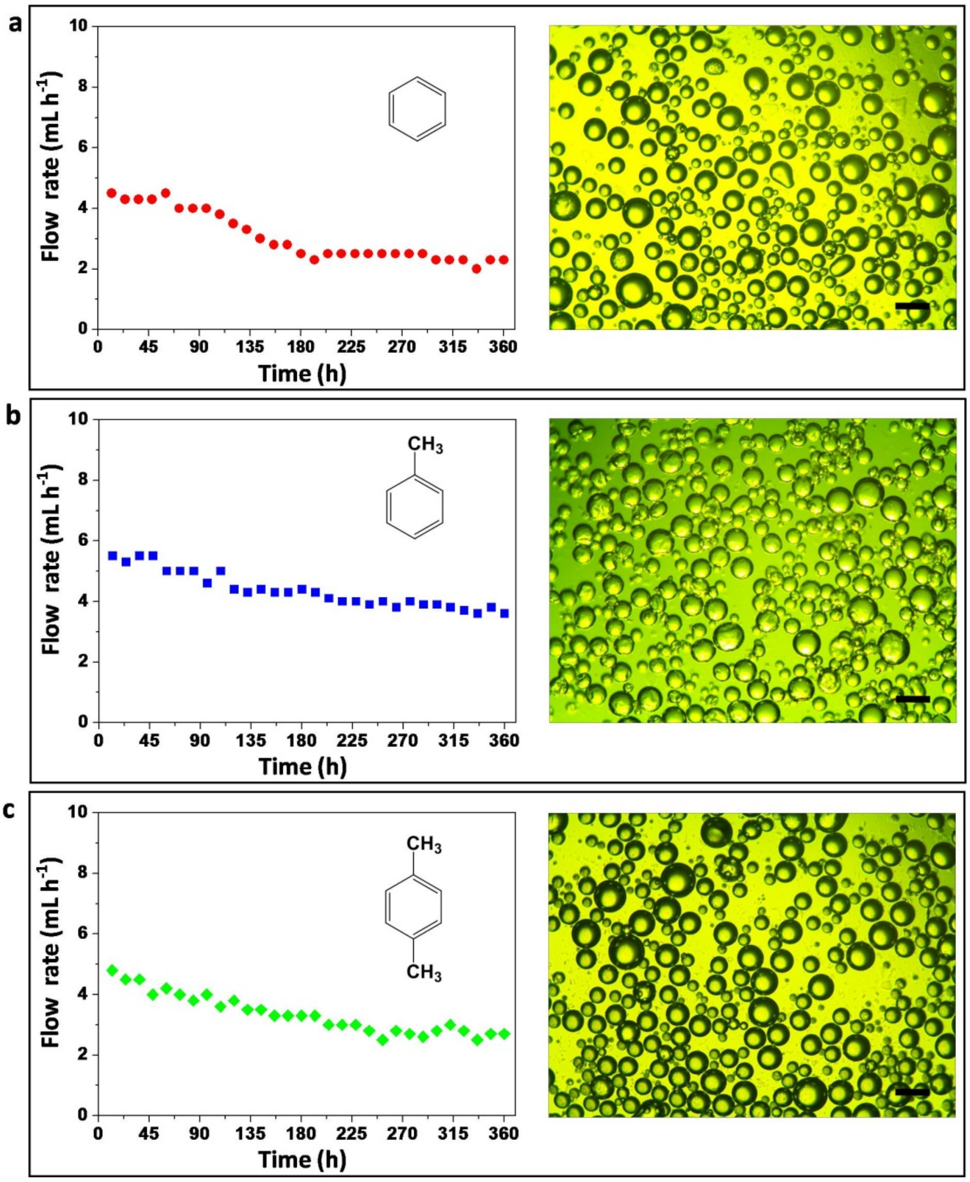

Figure S4. Flow rate of oil with time through the FPE column using different oil phases and optical microscopy images of the Pickering emulsions (scale bar = 100 μm). (a) benzene, (b) toluene, (c) *p*-xylene. The emulsion composition consists of *ca.* 30 mL H_2O, 0.9 g solid emulsifier, 11 mL benzene or 13 mL toluene or 10 mL *p*-xylene.

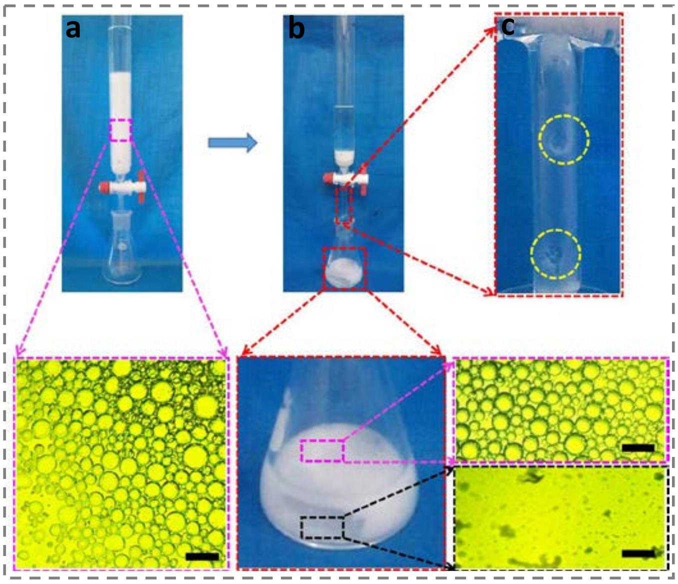

Figure S5. Flow behavior for the surfactant-stabilized water-in-oil emulsion in the column. This emulsion is composed of 0.18 g of Span 80, 30 mL of water and 18 mL of *n*-octane. (a) Appearance of the surfactant-stabilized emulsion in the column before flow and its optical micrograph, (b) appearance of surfactant-stabilized emulsion after flow and the outflow and their optical micrographs, (c) appearance of the outflow (more magnified) where water droplets appear on the column surface and in the outflow. Scale bar = 100 μm.

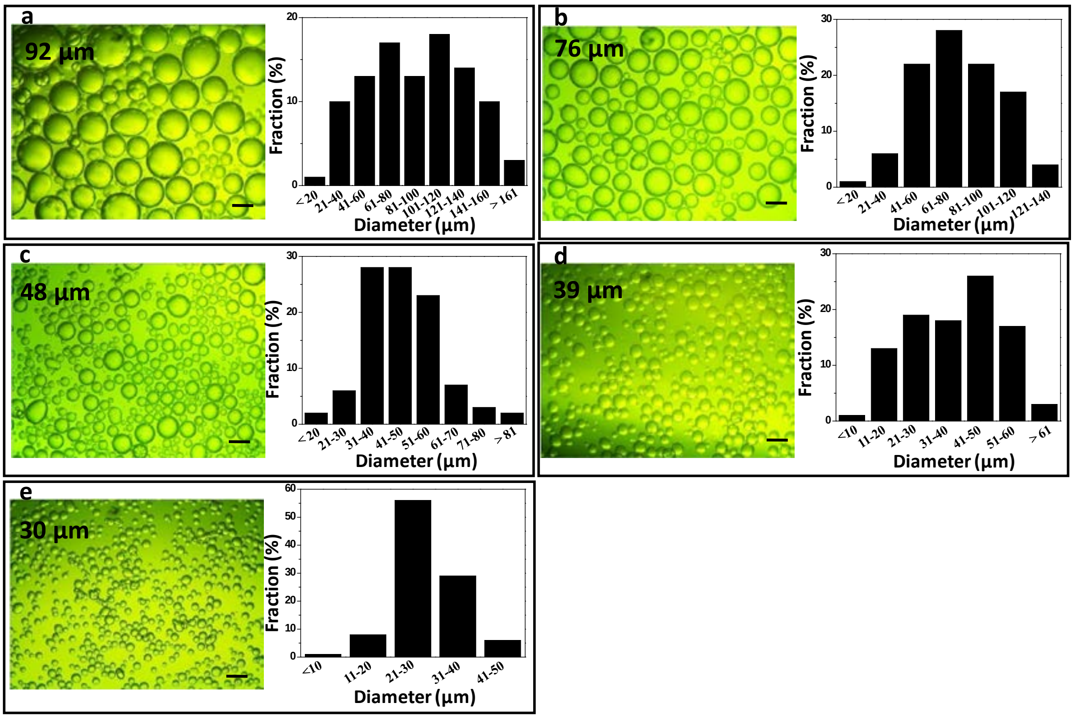

Figure S6. Optical micrographs for Pickering emulsions and their droplet size distributions, scale bar = 100 μm. Pickering emulsions were formulated with *n*-octane as oil phase and different amount of solid emulsifier: (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 4 wt.%,(e) 5 wt.%. The detailed composition is summarized in Table S1.

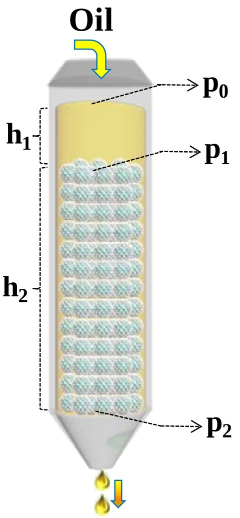

Figure S7. Sketch of the model for the oil flow through the interstices between compartmentalized droplets.

Definition of symbols: v - fluid velocity; V - volumetric flow rate; k - permeability of fluid; μ -dynamic viscosity of oil; ρ - fluid density; p_0 - atmospheric pressure; p_1 - pressure at the boundary between oil phase and Pickering emulsion; p_2 - pressure at the column bottom; g- acceleration due to gravity; h_1 - height of oil; h_2 - height of Pickering emulsion; S – cross-sectional area of column.
Using Darcy's law,[54] the flow (driven by gravity) is:

$$v = \frac{k}{\mu}\frac{\Delta \mathrm{p}}{\Delta \mathrm{x}} \tag{1}$$

where v = V/S, Δx is the distance along the flow direction ($\Delta x = h_2$), Δp is the pressure gradient between the oil surface and the column bottom and can be estimated by

$$\Delta \mathrm{p} = \mathrm{p}_1 = \rho g h_1 \tag{2}$$

Then eq. (1) can be expressed by

$$k = \frac{V \mu h_2}{S \rho g h_1} \tag{3}$$

According to Carman-Kozeny empirical formula, k can be estimated by[55]

$$k = \frac{\varepsilon^3}{180(1-\varepsilon)^2} D^2 \tag{4}$$

where, ε is the voidage of the packed column (ε=0.36 for a packed bed by random packing of microspheres);[59] D is the average droplet diameter. Accordingly,

$$V = \frac{\varepsilon^3}{180(1-\varepsilon)^2}\frac{S \rho g h_1}{\mu h_2} D^2 \tag{5}$$

where $S = 3.14 \times 10^{-4}$ m^2, $\rho = 0.7$ g mL^{-1}, $h_1 = 3.9$ cm, $h_2 = 11.1$ cm, $\mu = 0.52 \times 10^{-3}$ Pa s.

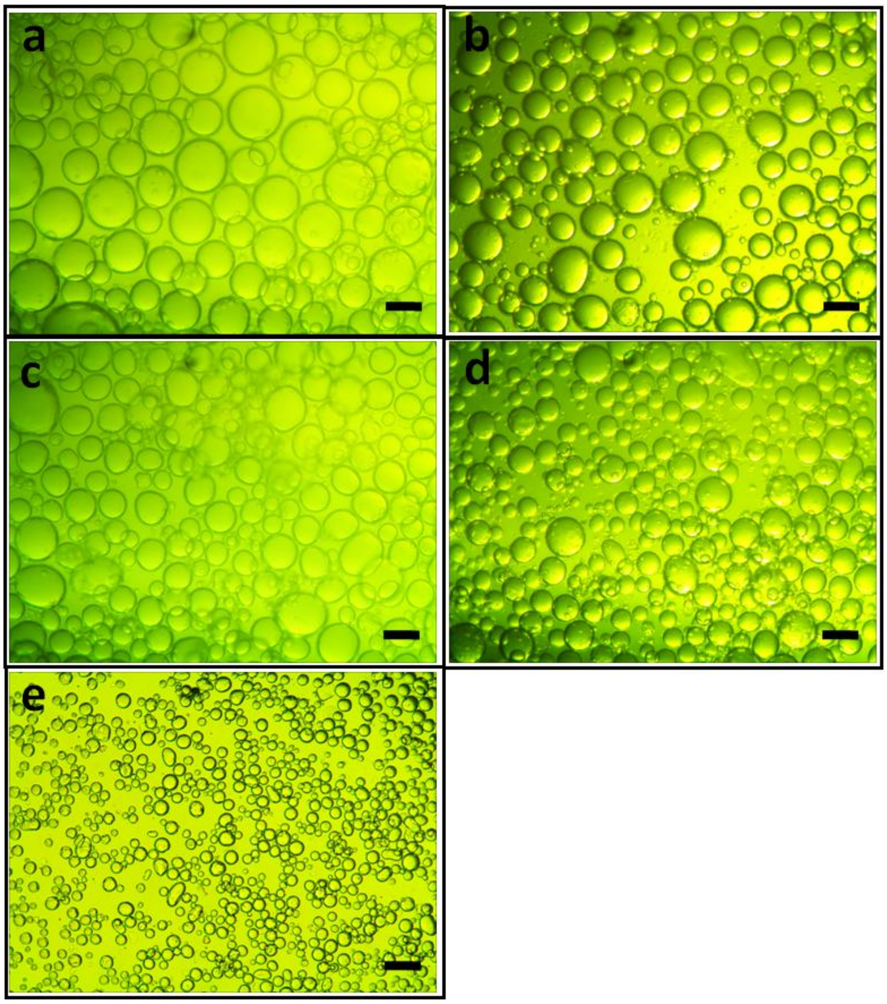

Figure S8. Optical micrographs for Pickering emulsions using different amounts of emulsifier after flow for 360 h (*n*-octane as oil phase). Scale bar = 100 μm. (a) 1wt.%, (b) 2wt.%, (c) 3wt.%, (d) 4wt.%, (e) 5 wt.%.

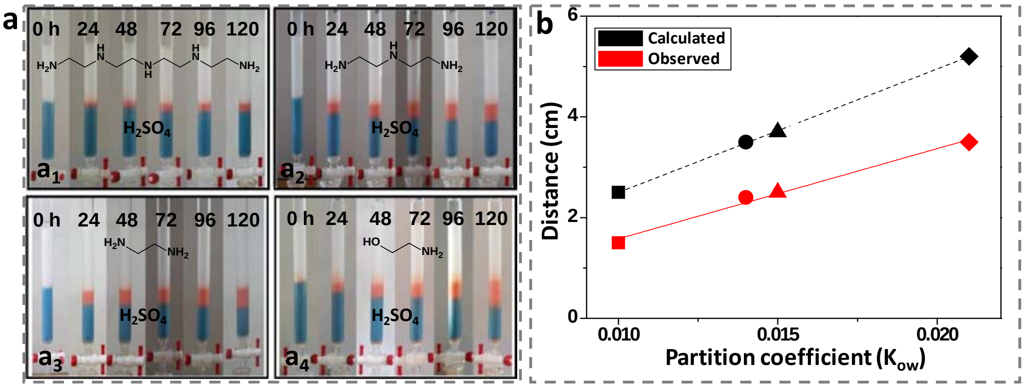

Figure S9. (a) Appearance of Pickering emulsion columns with time for a high concentration of base (0.1 M) in the upper layer and with a low concentration of H_2SO_4 (0.001 M) and Congo Red in the lower layer for different bases given. The upper layer of the Pickering emulsion was formulated with 9 mL aqueous amine, 4.5 mL toluene and 0.18 g emulsifier. The lower layer contained 9 mL aqueous H_2SO_4, 4.5 mL toluene, 0.18 g emulsifier and 0.003 g of Congo Red. The flow rate of oil phase is 2 mL h^{-1}. (b) Theoretical (black) and experimental (red) points for the relationship between the distance moved by the red front after 120 hand the partition coefficient (K_{ow}) of the base between toluene and water. Square, circle, triangle and diamond represent tetraethylenepentamine, diethylenetriamine, ethylenediamine and ethanolamine, respectively.

Notes: It can be surmised that at total amount of base needed to enter the region in order to sustain the propagation of the front is $v\ [\phi\ (q_o+q_o) + (1-\phi)\ K_{ow}\ q_o]\ \delta t$. Here v, ϕ, K_{ow}, q_o and p_o are the propagate velocity under steady state, volume fraction of droplets, partition coefficient of base between oil and water phases,[61] initial concentration of base in the droplets and initial concentration of acid in the droplets, respectively. Equating this amount then with that entering the region, the equation can be simply expressed by,

$$V(1-\phi)K_{ow}q_0 = v[\phi(q_0+p_0)1+(1-\phi)K_{ow}q_0] \qquad (1)$$

where V is the flow velocity of the oil phase, λ is the ratio of the initial acid to base in the two types of droplets, *i.e.* (p_o/q_o). Then the distance of color change x is given by

$$x = vt = \frac{V(1-\phi)t}{[\phi(1+\lambda)/K_{ow}\ ]+(1-\phi)} \qquad (2)$$

where the flow rate is 2 mL h^{-1}, the radius of the column is 0.67 cm, the volume fraction of oil $\phi = 1/3$, the ratio of the initial concentration acid to base in the two types of droplets λ=0.01. According to eq. 2, the corresponding results including observed and calculated distances are listed below:

Partition coefficient, observed red front shift distance and calculated red front shift distance

Organic base (0.1 M)	K_{ow}	Observed distance (cm)	Calculated distance (cm)
Tetraethylenepentamine	0.010	1.5	2.5
Diethylenetriamine	0.014	2.4	3.5
Ethylenediamine	0.015	2.5	3.7
Ethanolamine	0.021	3.5	5.2

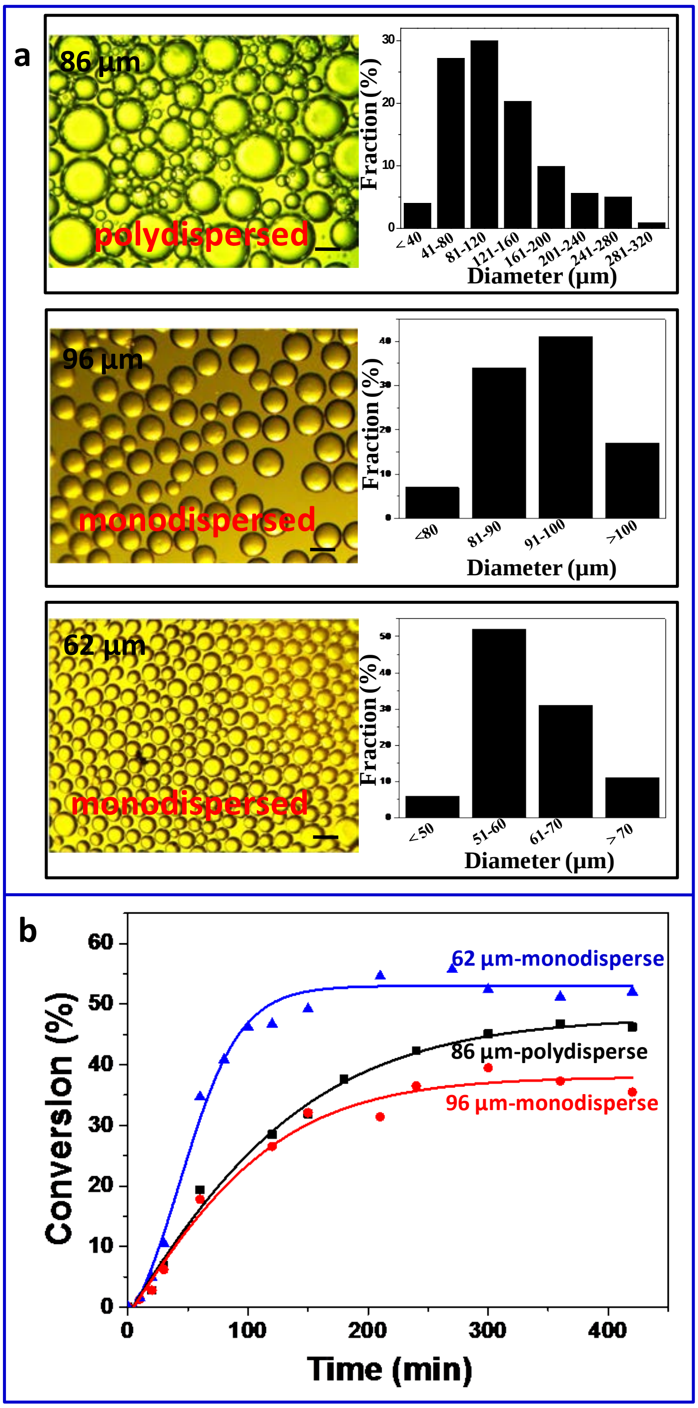

Figure S10. (**a**) Optical micrographs for polydispersed and monodispersed Pickering emulsions and their droplet size distributions, scale bar = 100 *µ*m. (b) Conversions with time for the addition reaction of *n*-octanol with 3, 4-dihydro-2*H*-pyran in these flow Pickering emulsion systems. All emulsion droplets were formulated with 1 wt.% emulsifier, other reaction conditions are the same as in Figure 6.

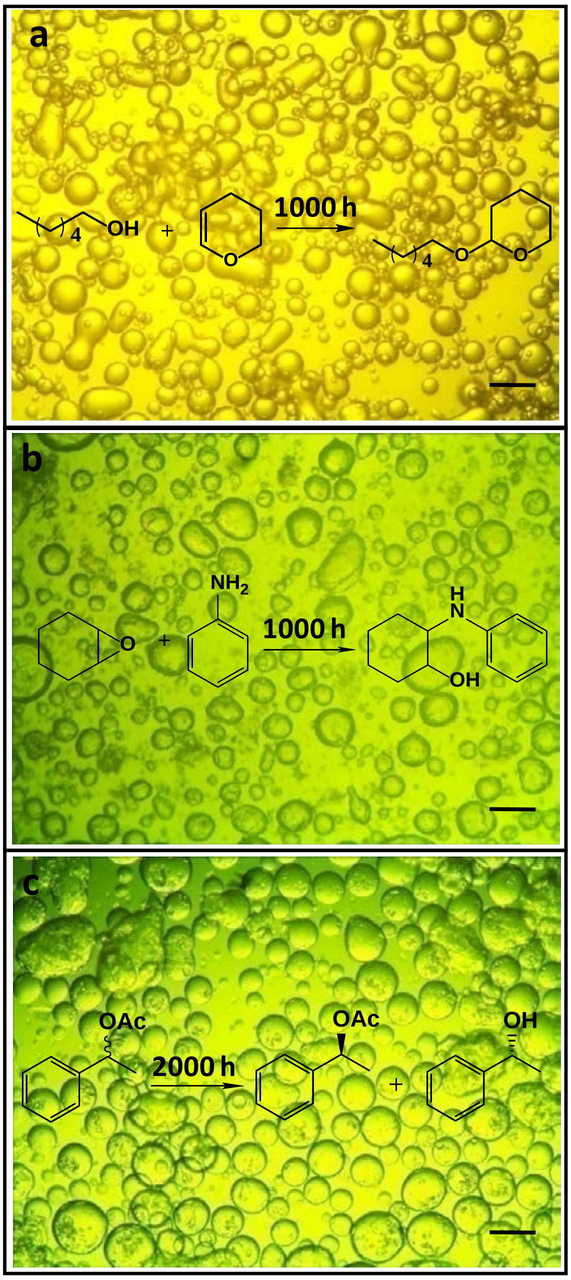

Figure S11. Optical micrographs for Pickering emulsion after reactions (scale bar = 100 μm). (a) H_2SO_4-catalyzed addition reaction of *n*-octanol with 3, 4-dihydro-2*H*-pyran, (b) HPA-catalyzed ring opening reaction of aniline with cyclohexene oxide, (c) CALB-catalyzed kinetic resolution of racemic 1-phenylethyl acetate. The emulsion compositions are included in the Experimental Section.

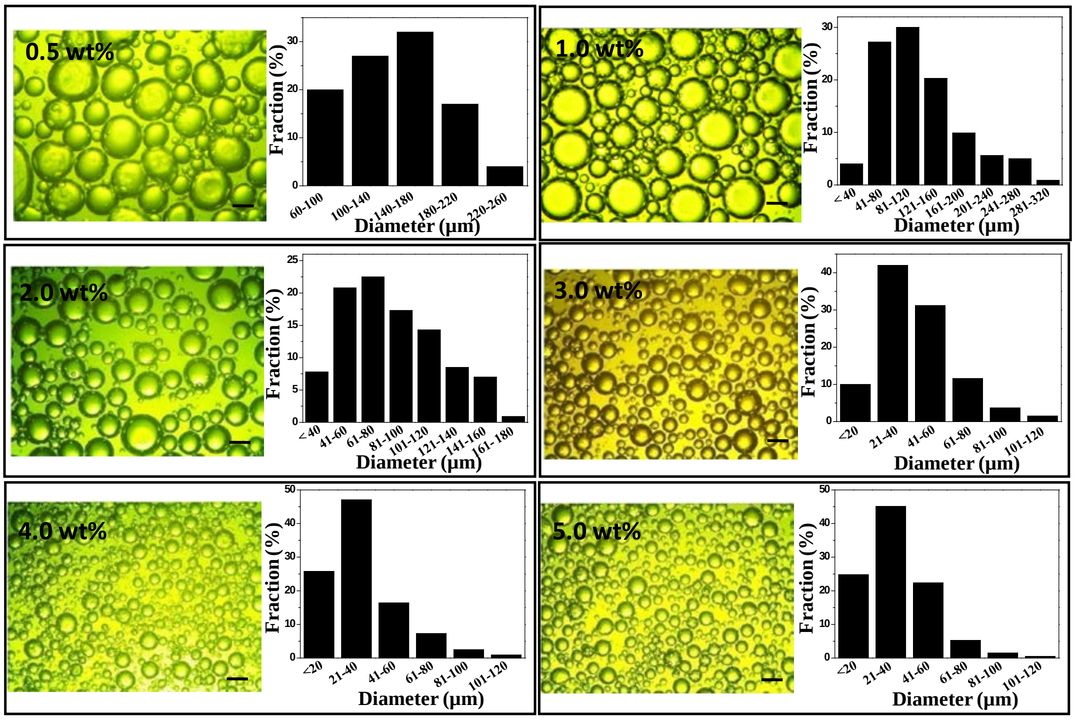

Figure S12. Optical micrographs and droplet size distributions of emulsions for the H_2SO_4-catalyzed addition of *n*-octanol with 3, 4-dihydro-2*H*-pyran using the FPE method with different amounts of emulsifier given (wt.%). The emulsion compositions are included in Experiment Section.

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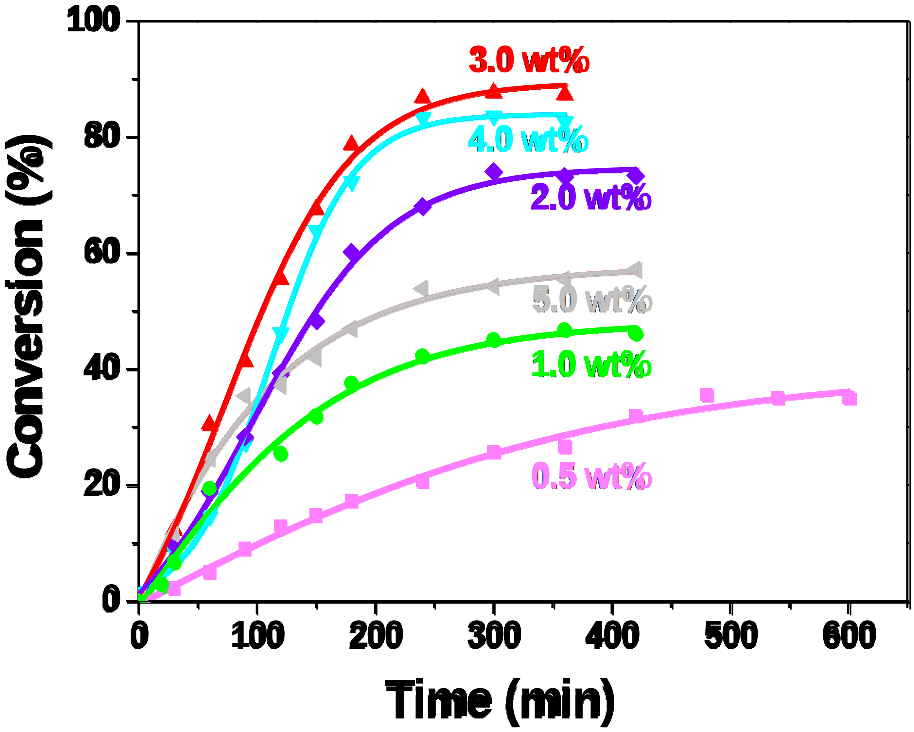


Figure S13. Conversions with time for addition reaction of *n*-octanol with 3, 4-dihydro-2*H*-pyran in the FPE columns using different amounts of emulsifier in the Pickering emulsion. Other reaction conditions are the same as in Figure 6.

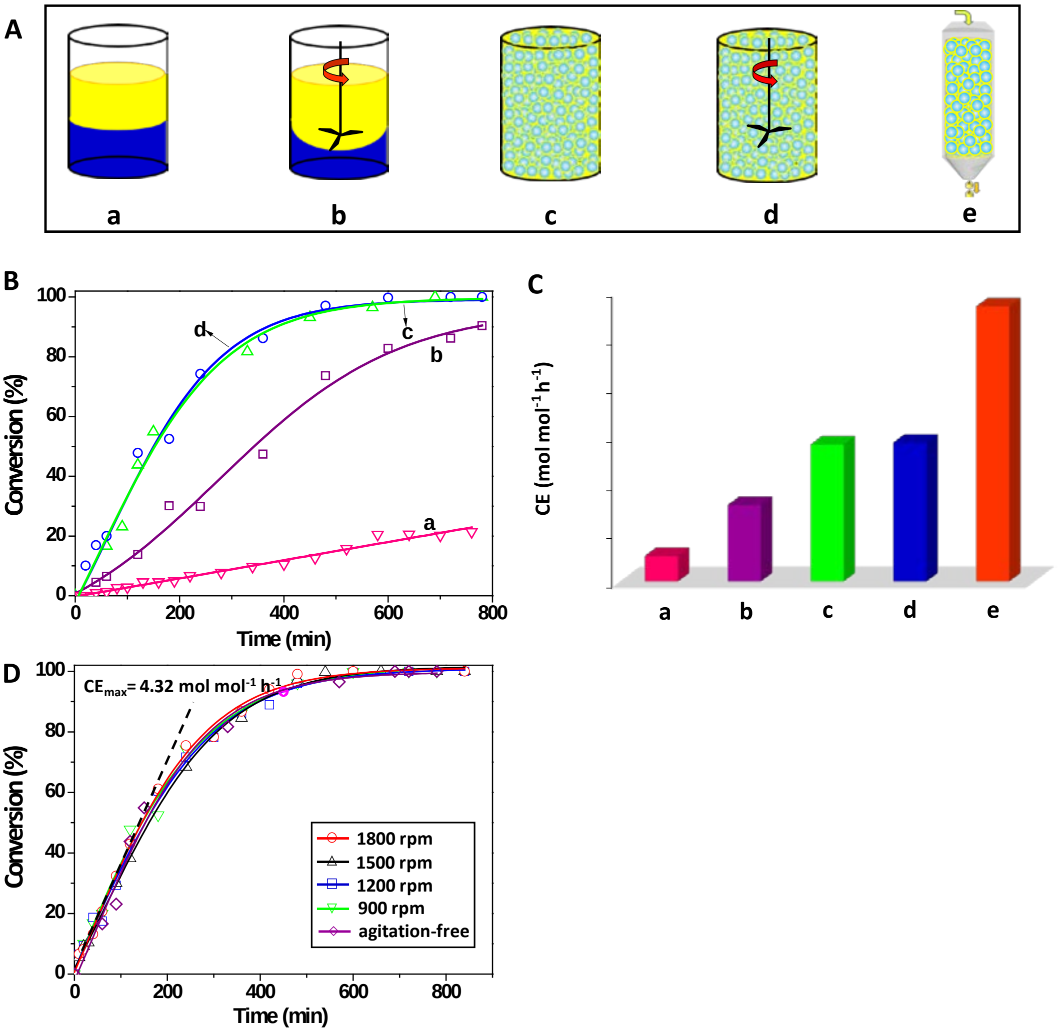


Figure S14. Comparison of the HPA-catalyzed ring-opening of aniline with cyclohexene oxide in the FPE systems with that in batch biphasic reaction systems. (A) Cartoon representation of various reaction systems: a - agitation-free biphasic reaction, b - biphasic reaction with agitation speed of 900 rpm, c - agitation-free Pickering emulsion reaction, d - Pickering emulsion reaction with agitation speed of 900 rpm, e - FPE reaction. (B) Kinetic reaction profile with time for the batch reactions. (C) Catalysis efficiency (CE) of the FPE reaction and the batch reactions. The definition of catalysis efficiency (CE) is included in Figure 9. For the batch reactions, CE is calculated according to the conversion within 360 min. For the FPE reaction, CE is calculated after the conversion levelled off (from 6 to 16 h). (D) Kinetic reaction profiles for the Pickering emulsion systems with different agitation speeds. The maximum catalysis efficiency (CE$_{max}$) is defined at the moles of converted reactants per mole of catalysis per h (mol mol^{-1} h^{-1}) under the mass-transport-limitation-free conditions, which is calculated just at the beginning of reaction. Batch reaction conditions: 10 mL HPA (0.01 M), 5 mL aniline/cyclohexene oxide solution in toluene (0.5 M), 0.2 g emulsifier if needed, 50 °C. The reaction conditions of the FPE system are the same as in Figure 7d.

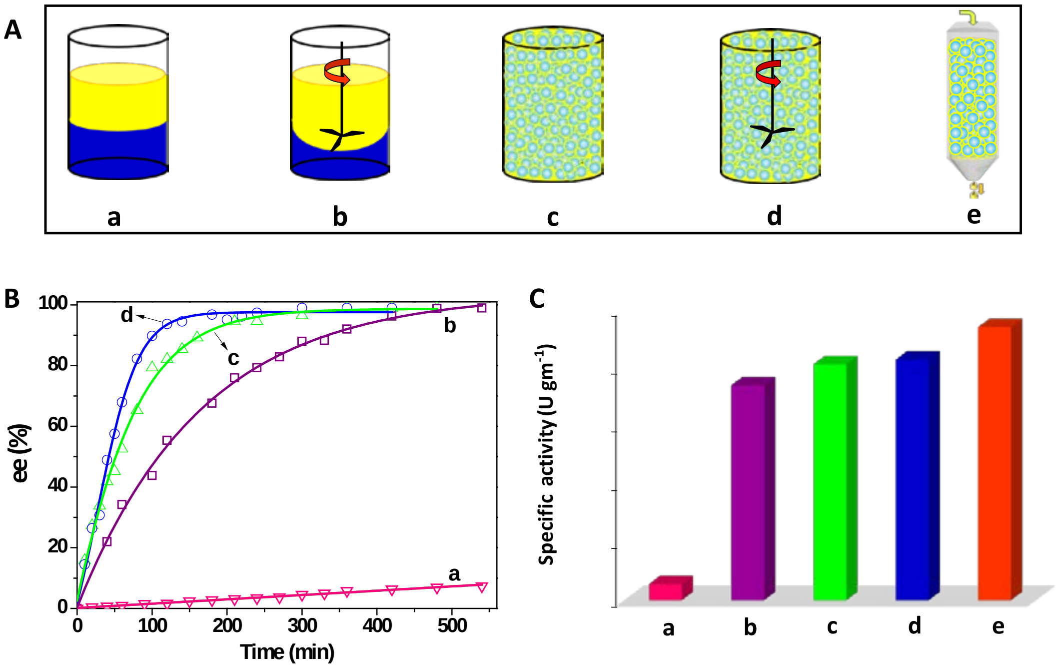
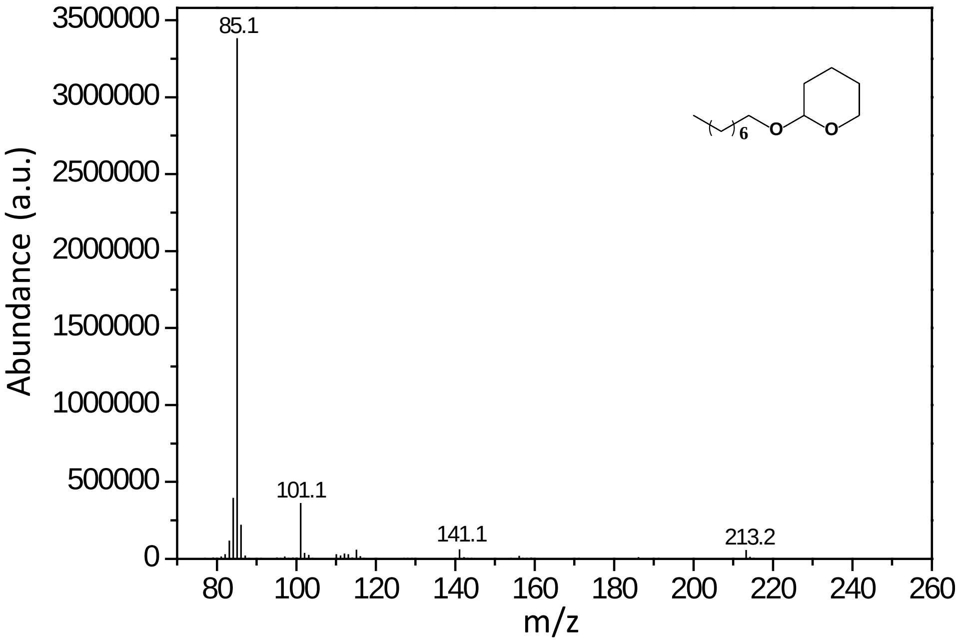
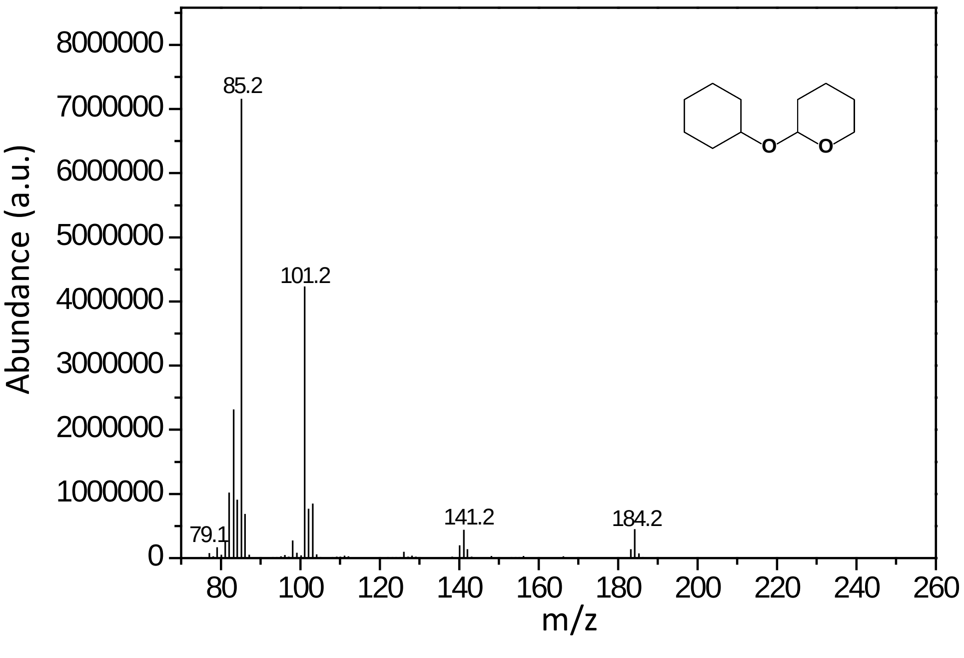
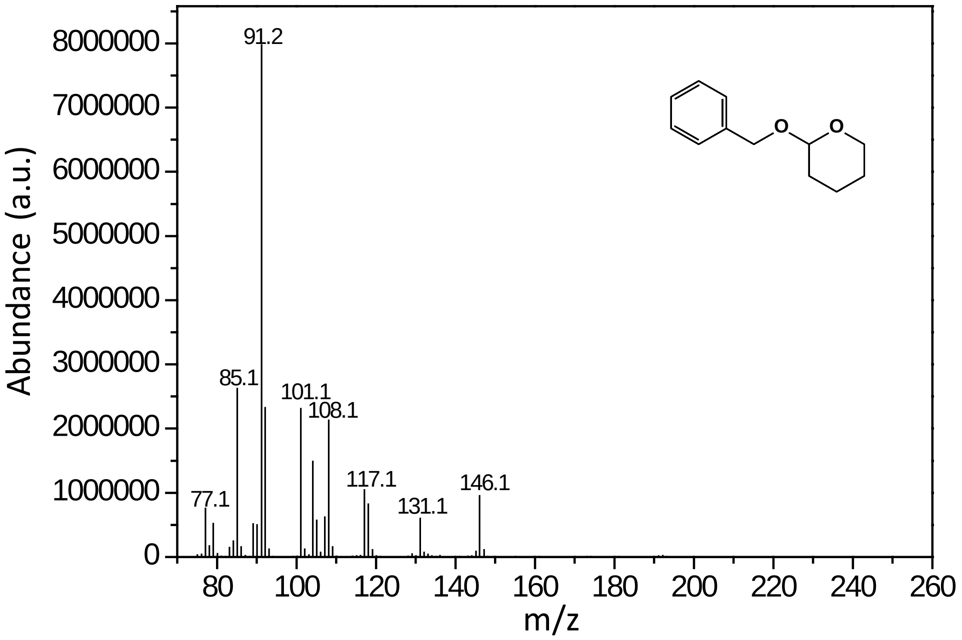


Figure S15. Comparison of the CALB-catalyzed hydrolysis kinetic resolution of racemic 1-phenylethyl acetate in the FPE reaction and that in batch biphasic reactions.(A)Cartoon representation of various reaction systems, as described in Figure S13A. (B) Kinetic reaction profile with time for the batch biphasic reactions. (C) Catalysis efficiency (CE) of the FPE reaction and the batch reactions. For the batch reactions, CE is calculated according to the conversion within 240 min. For the FPE reaction, CE is calculated after the conversion levelled off (from 1 to 11 h). Batch reaction conditions: 10 mL enzyme solution (0.1 mgmL^{-1}), 5 mL *n*-octane (*R, S*)-1-phenylethyl acetate solution in *n*-octane (0.25 M), 0.3 g emulsifier if needed, 35 °C. The reaction conditions of the FPE system are the same as in Figure 8d.

For H_2SO_4-catalyzed addition reactions:



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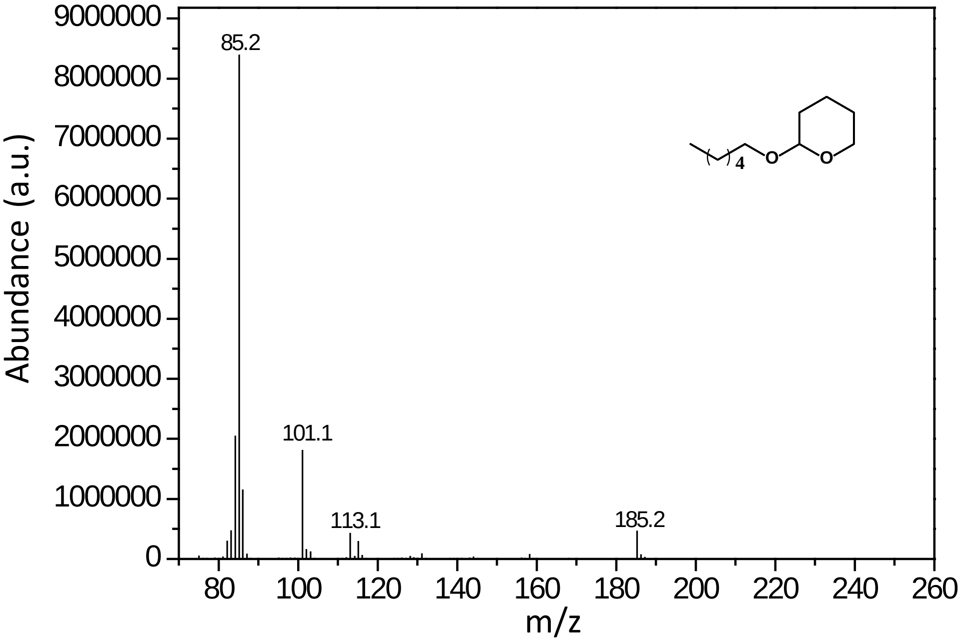
101.1
108.1
77.1
117.1
131.1
146.1
O
O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113.1
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( )4
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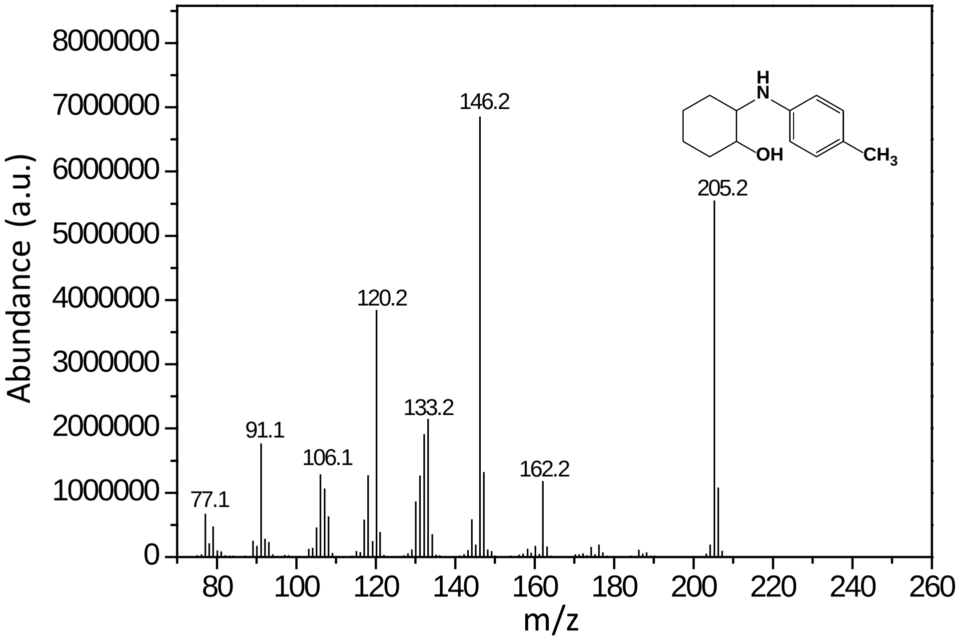
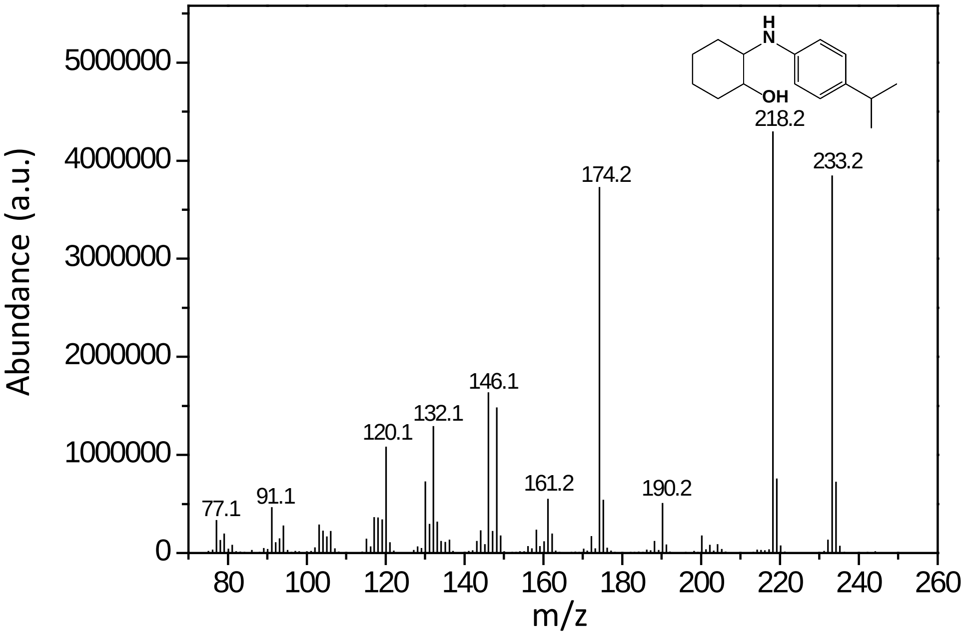
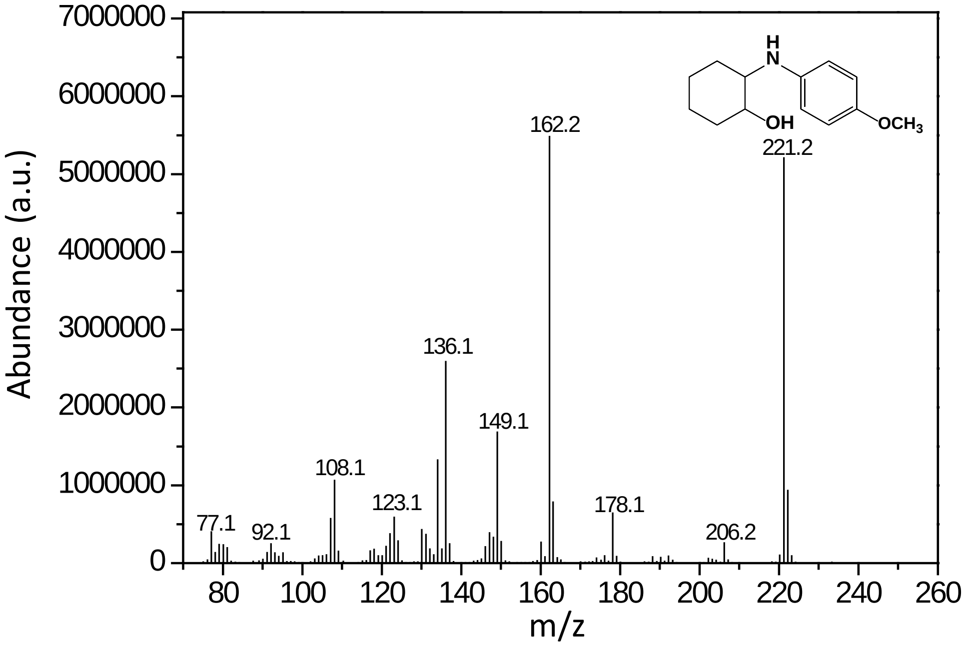
O

For HPA-catalyzed ringopening reactions:







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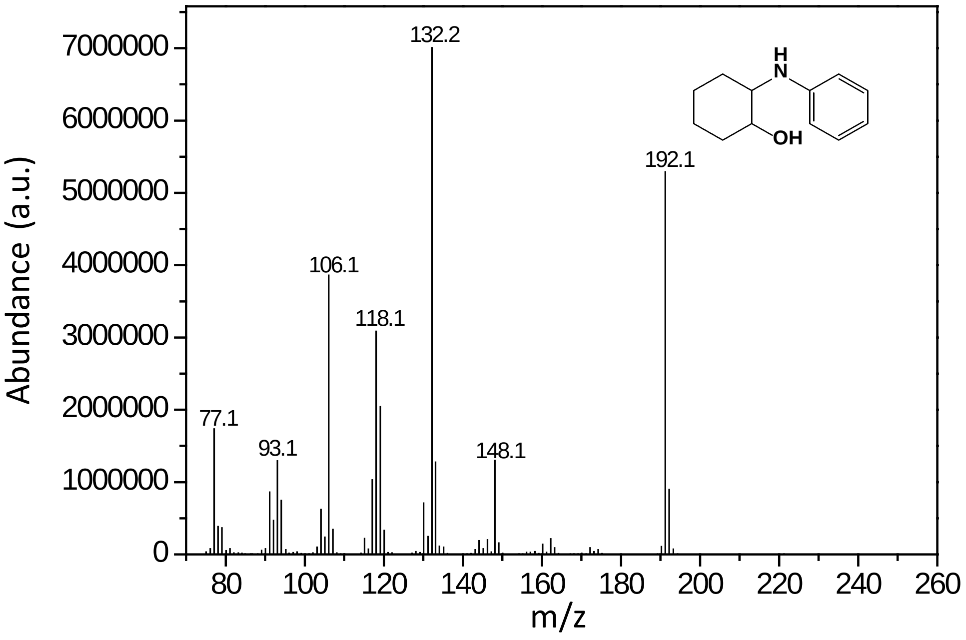
OH
OCH3



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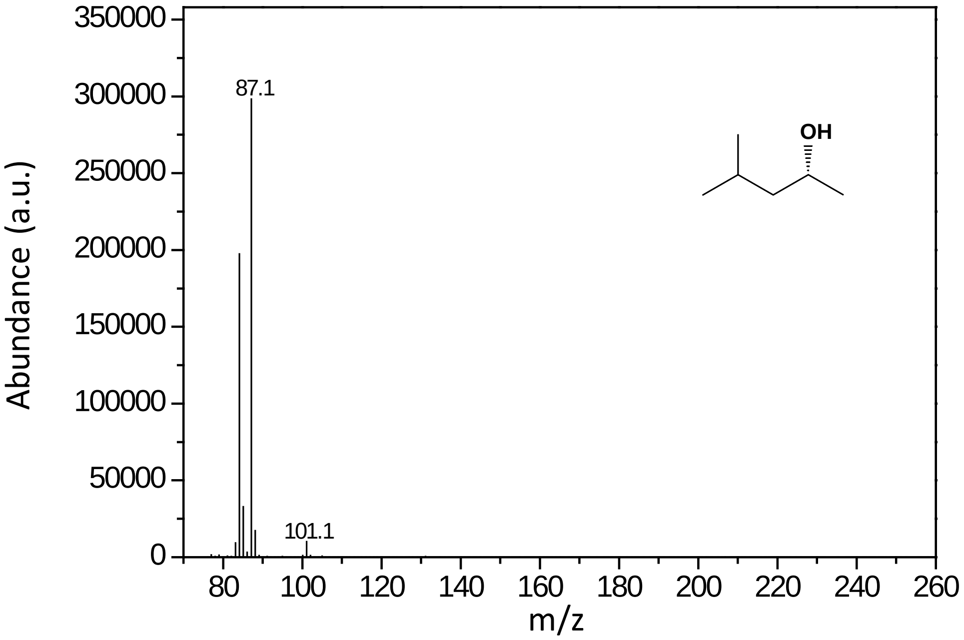
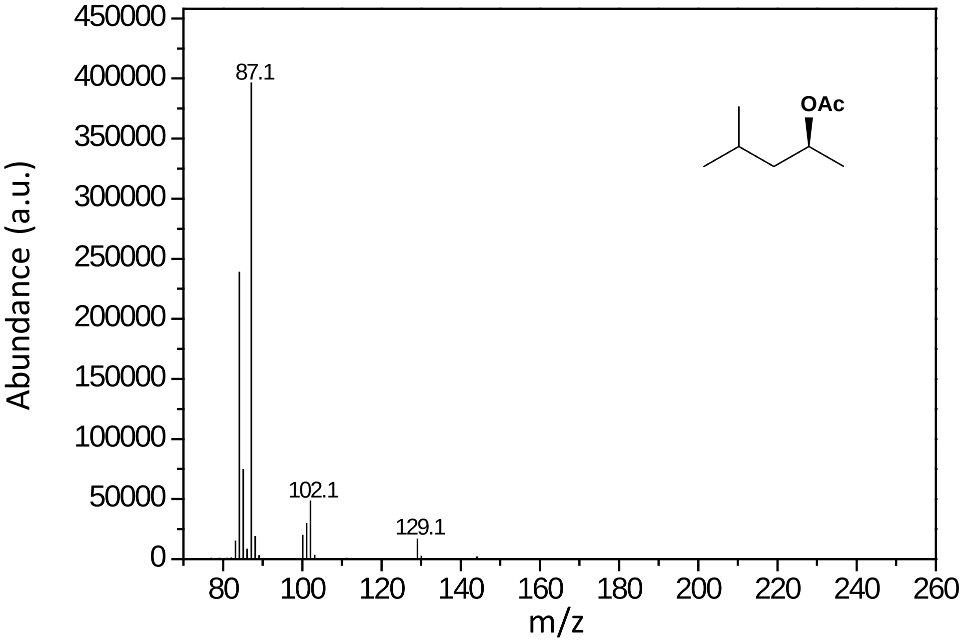
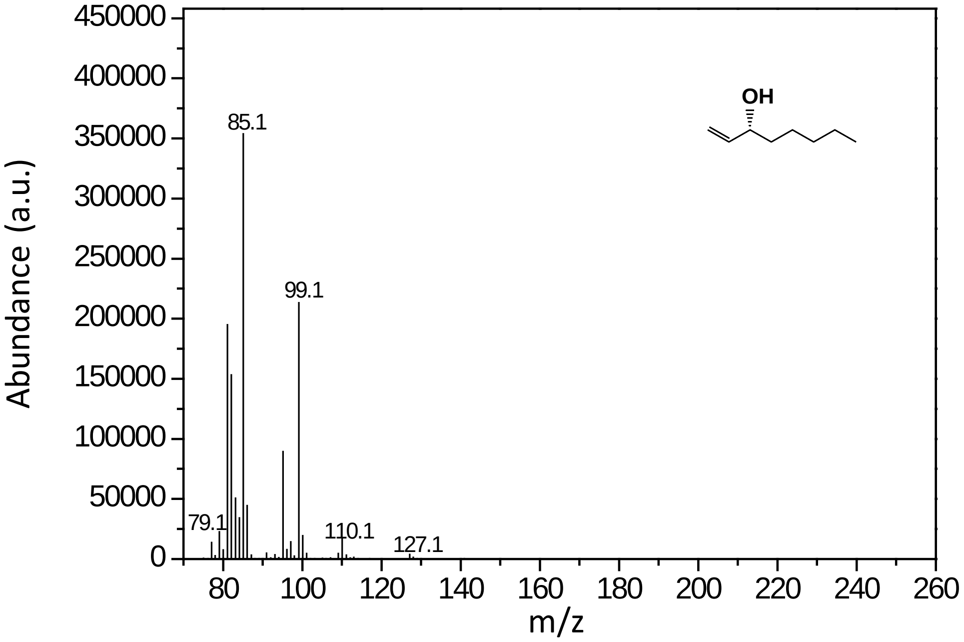
N
OH

For CALB -catalyzed kinetic resolution reactions:







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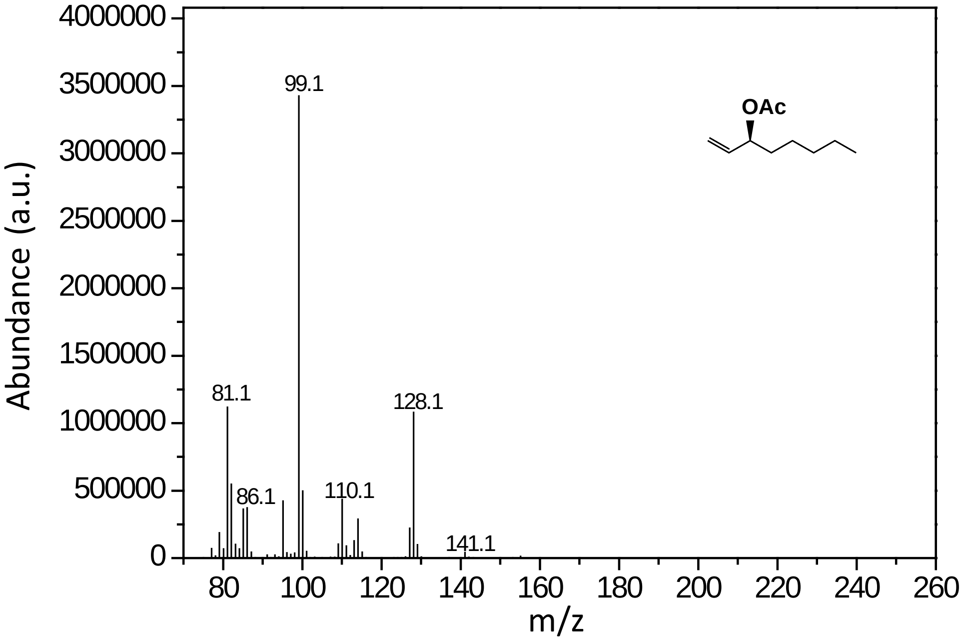

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m/z
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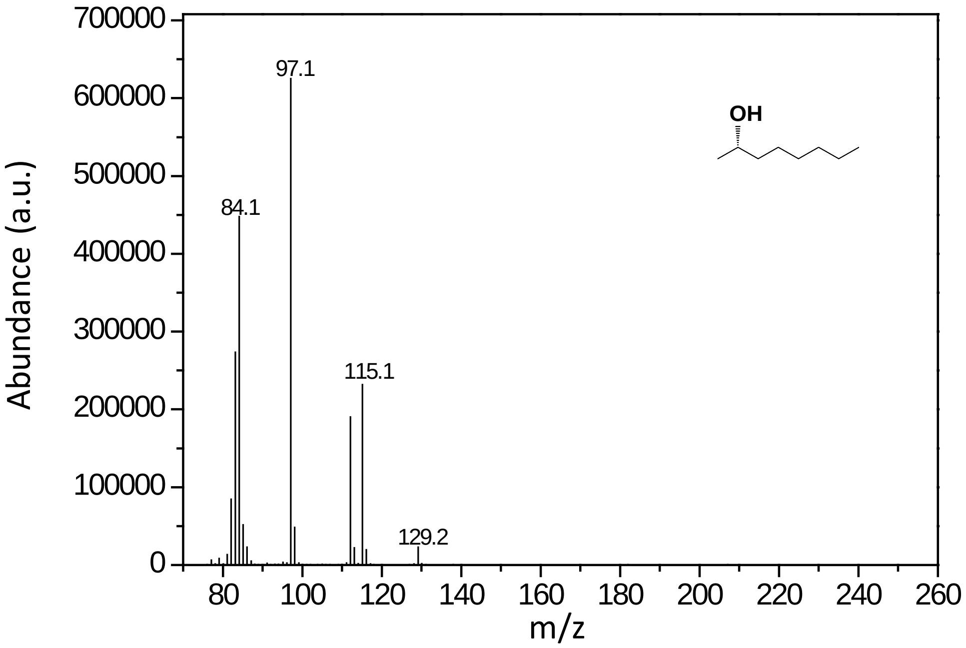
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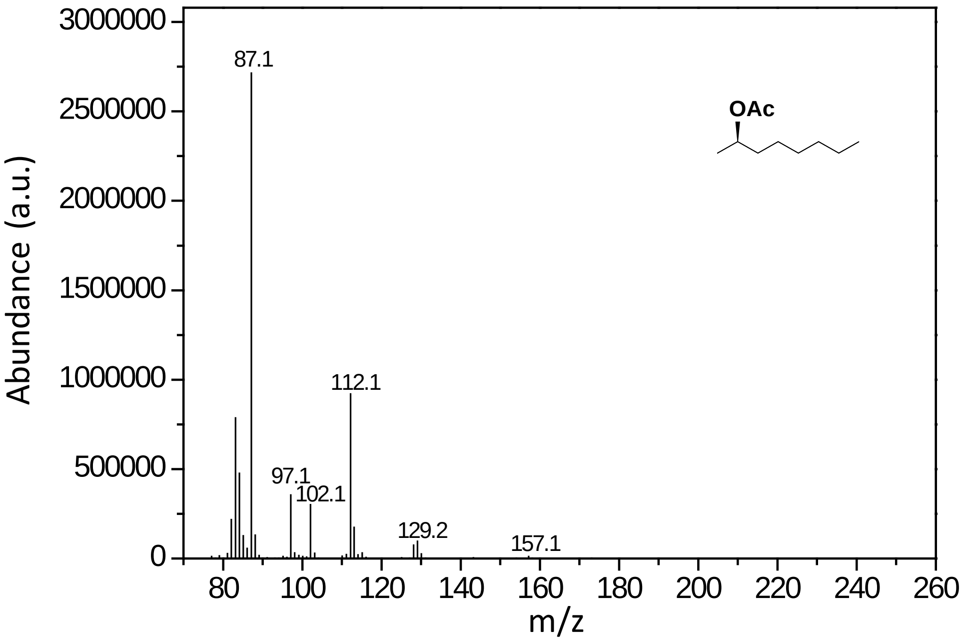
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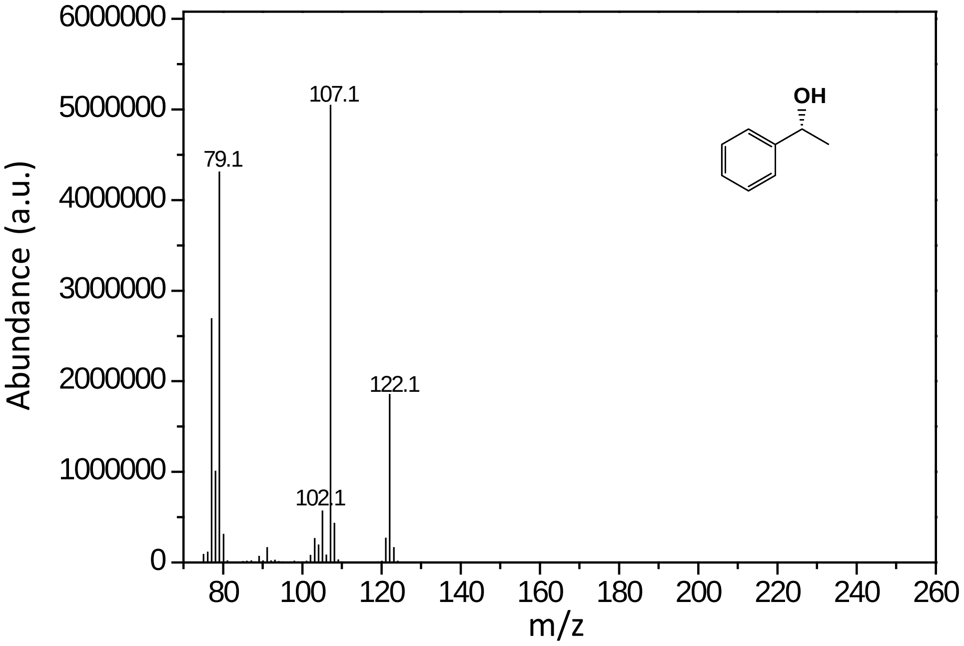
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m/z
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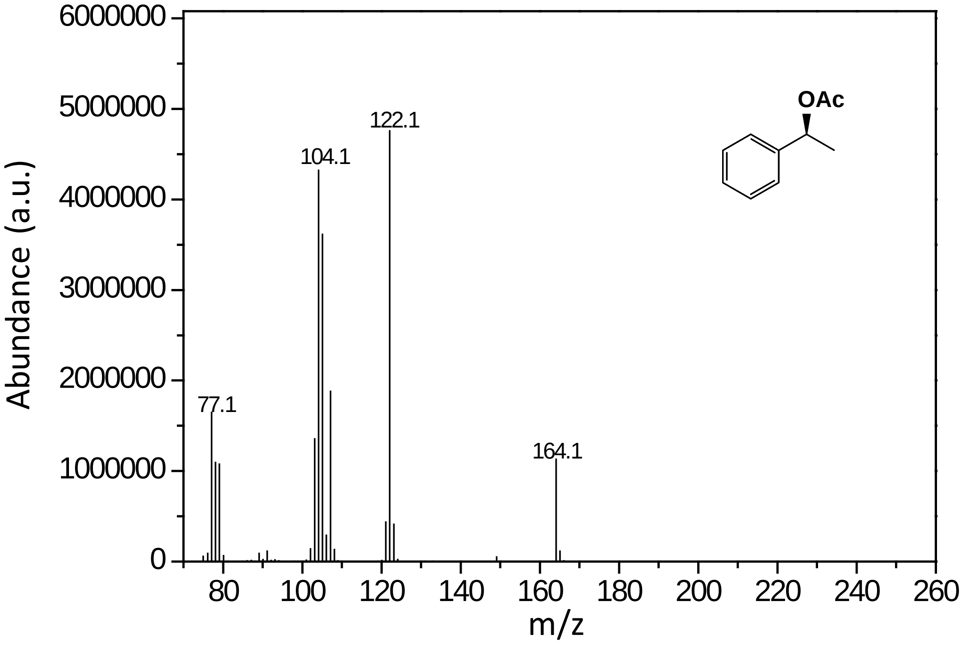
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m/z
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OAc