Supporting Information

Highly Efficient and Recycling Acid-Catalysis using High-Temperature Resistant O/W Emulsion Stabilized by Dodecyl Phosphonic Acid

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1. Experimental

1.1 Materials and instruments

All the experiments used tap water. DPA is purchased from Shanghai Bidd Pharmaceutical Technology Co., LTD. Toluene (99%), Malonitrile (99%), p-methoxybenzaldehyde (99%), p-methylbenzaldehyde (99%), p-hydroxybenzaldehyde (99%), p-aminobenzaldehyde (98%), p-dimethylaminobenzaldehyde (99%) is procured from Sahn Chemical Technology (Shanghai) Co., LTD. All chemicals are analytical grade and can be used without further purification. The particle size of the emulsion was measured by dynamic light scattering technique (DLS) (Malvern Zetasizer Nano Zs). The surface morphology of O/W emulsions was studied by optical microscopy (microscope system (VHX-1000, keyence)) and field emission scanning electron microscopy (MAIA3 LMH). The surface tension was measured by the hanging drop method using an optical contact angle measuring instrument (DSA100). Record pH values using a Mettler Toledo digital pH meter. ^{1}H NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz and referenced internally to the corresponding solvent resonances, 31P NMR spectra were recorded at 162 MHz, Chemical shifts for phosphorus are reported in parts per million downfield from the

external 85% H_3PO_4 signal at 0.0 ppm as a standard. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad).

1.2 Stability Test

The stability of O/W emulsions was investigated by DLS, optical micrographs, and visual observations.

1.3 Droplet size measurement

The emulsion particle size after dilution was measured at room temperature, and the emulsion particle size was calculated by DLS method. To reduce error, the measurements were repeated three times. The Stokes-Einstein equation is then used to calculate the Z-mean diameter (Dz) of the droplets, assuming that all droplets are spherical.

1.4 Morphology

O/W emulsion samples were taken for morphological study. The morphology was observed by optical microscope.

1.5 Preparation of O/W emulsion

In a standard procedure, 3 wt.% DPA was introduced into a glass vial along with 12ml of water, followed by the addition of 3ml of toluene. The mixture was subjected to ultrasound treatment (700 W) for 15 minutes to achieve emulsion stabilization. All parameters for emulsification were held constant unless specified otherwise for particular experiments.

1.6 pH adjustment emulsion stabilization/re-stabilization

The O/W emulsion prepared previously is transferred into a small bottle along with a suitable volume of NaOH solution (1 mol/L). The mixture is stirred at 25°C, and the entire dynamic process, from emulsification to phase separation, is carefully observed and documented. The reversibility of pH alteration is accomplished by adding an appropriate volume of HCl (1 mol/L).

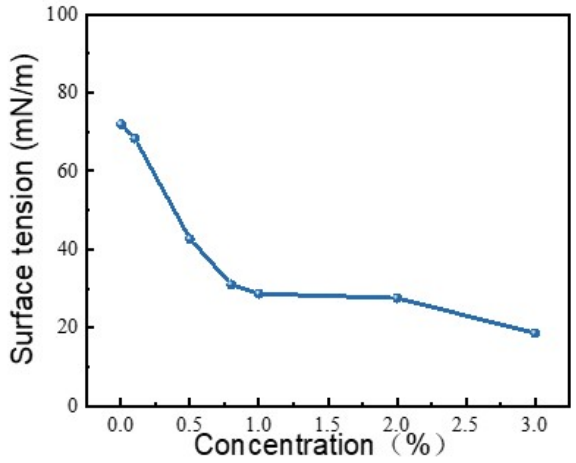


Figure S1: Curve of surface tension of emulsion with DPA concentration.

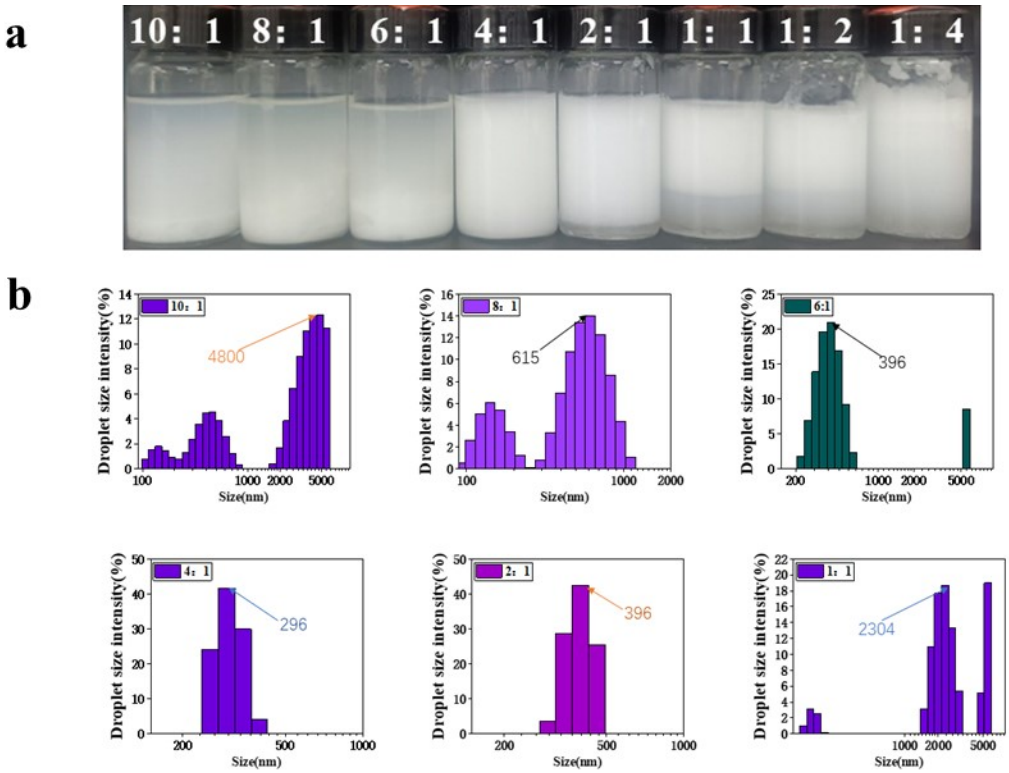


Figure S2: (a) Digital photos, (b)droplet size distributions of O/W emulsions stabilized by 1.0 wt.% DPA with different water-oil ratios, taken after 24 h of preparation.

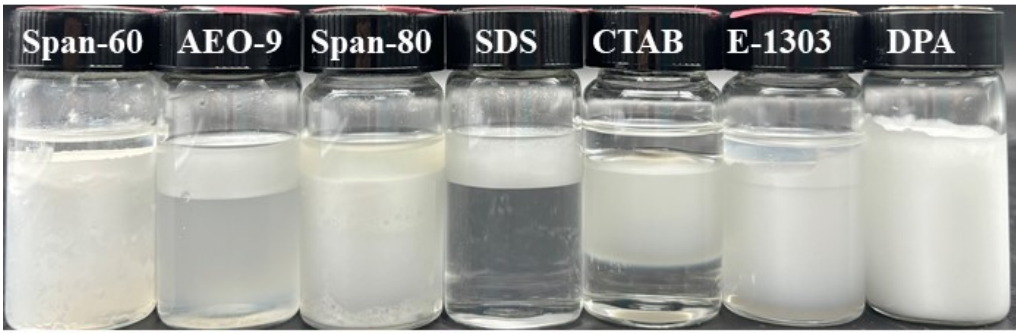


Figure. S3：O/W emulsions stabilized by different surfactants

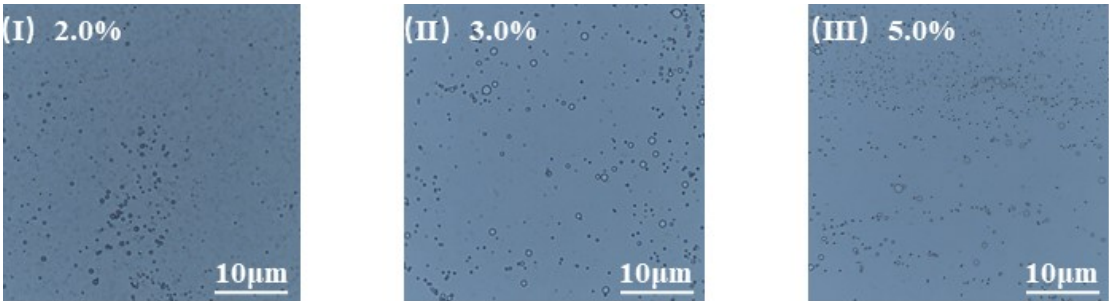


Figure S4: Digital photos of O/W emulsion stabilized by 1.0 wt.% DPA at different concentrations. taken after 24 h of preparation.

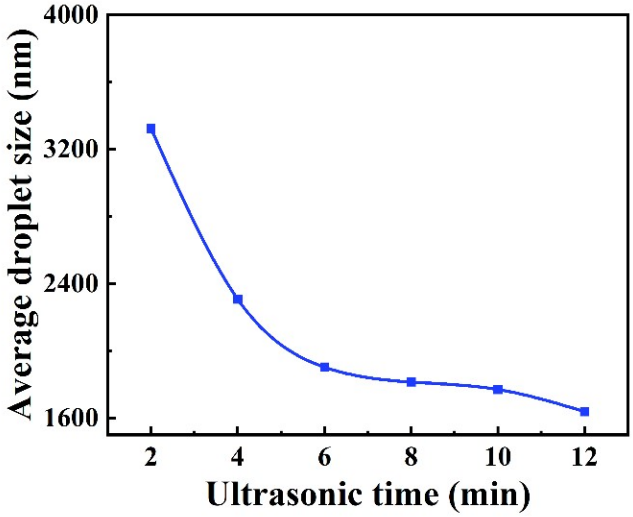


Figure S5: The curve of average particle size of O/W emulsion changing with ultrasonic time.

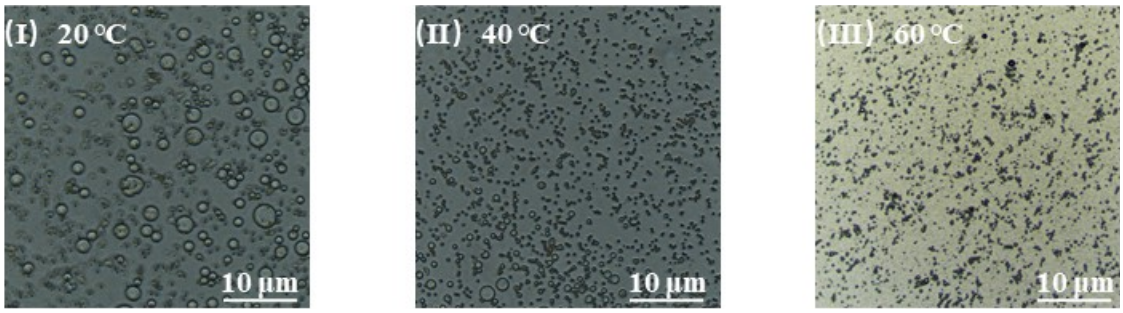
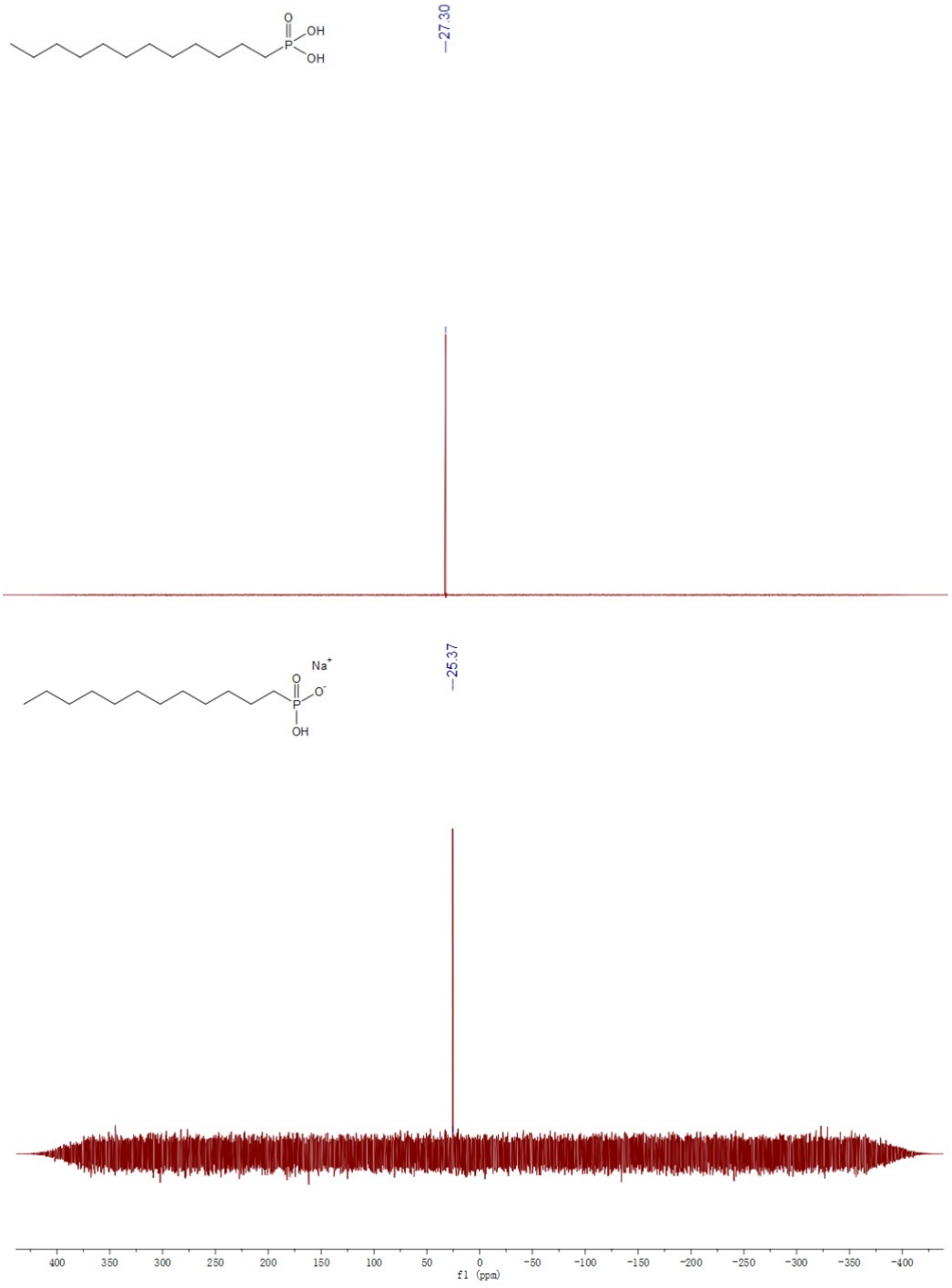


Figure S6: Digital photos of O/W emulsions stabilized at different temperatures with 1.0 wt.% DPA. Take the preparation 24 hours later.

^{31}P Spectra Copies


27.30
25.37
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
f1 (ppm)

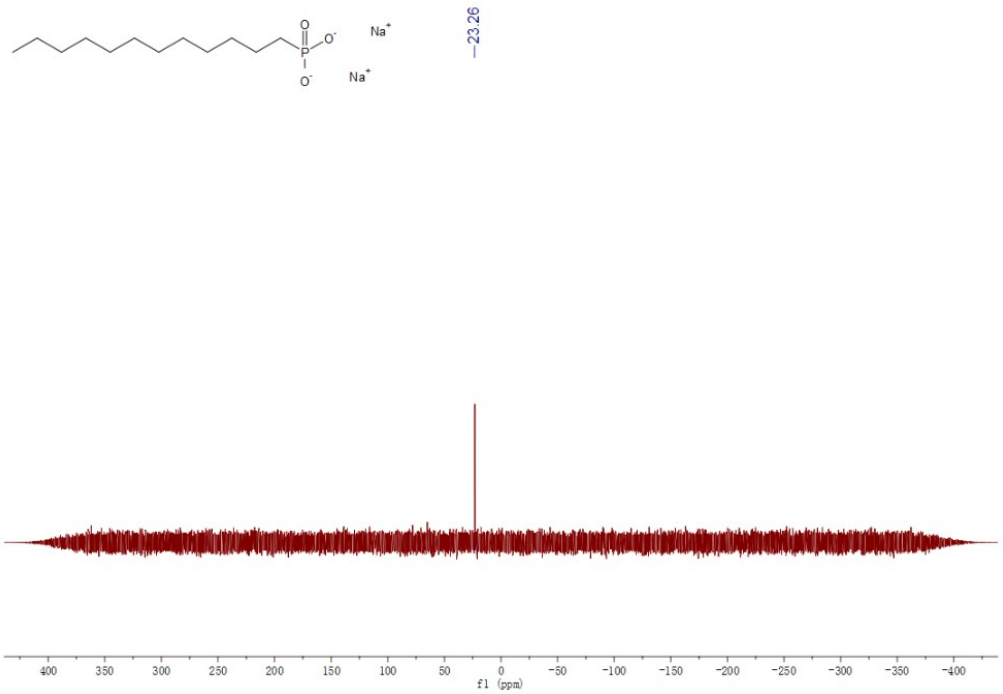


Figure S7

^{31}P Spectra Copies

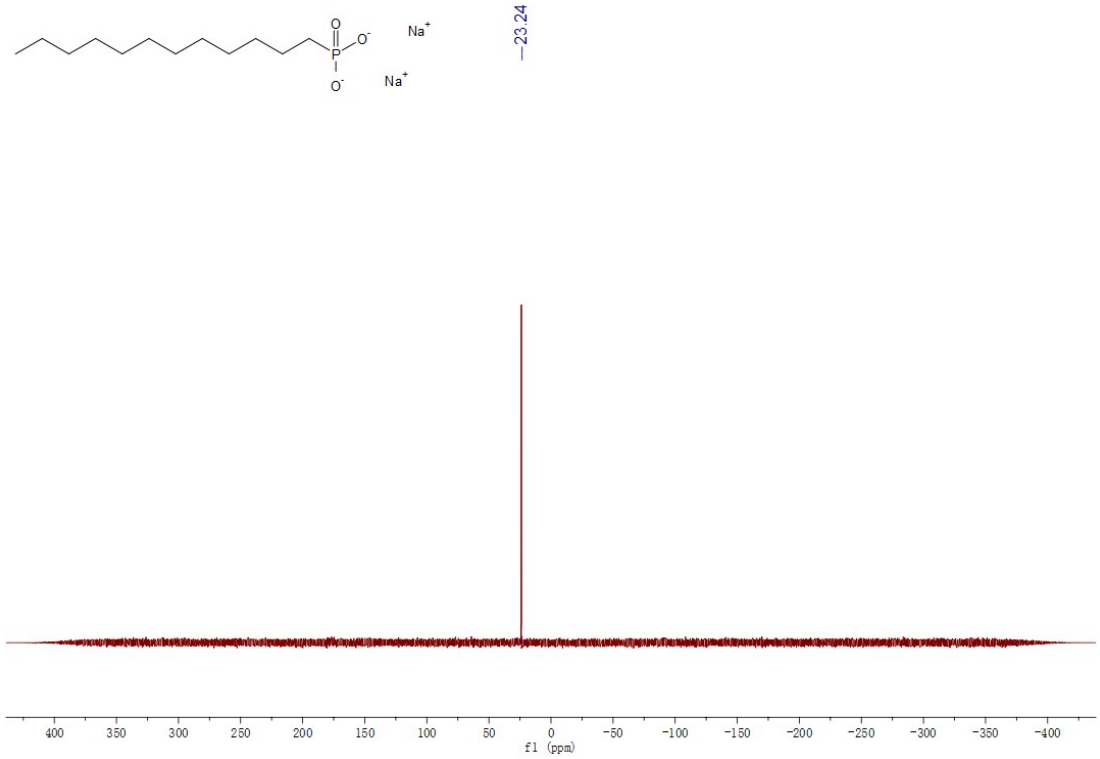


Figure S8

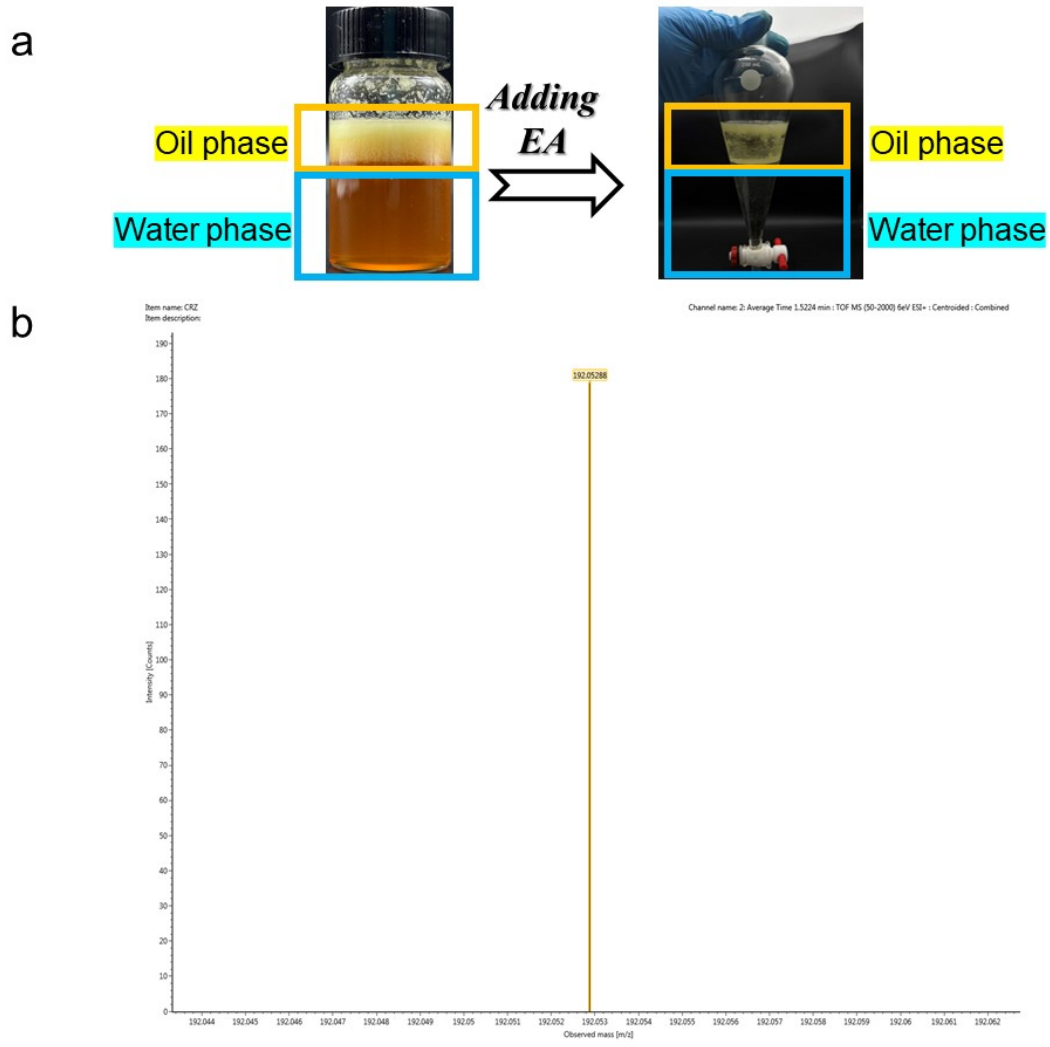


Figure. S9. (a) Digital photos before and after extraction. (b) HR-MS spectra of the product in the aqueous phase.

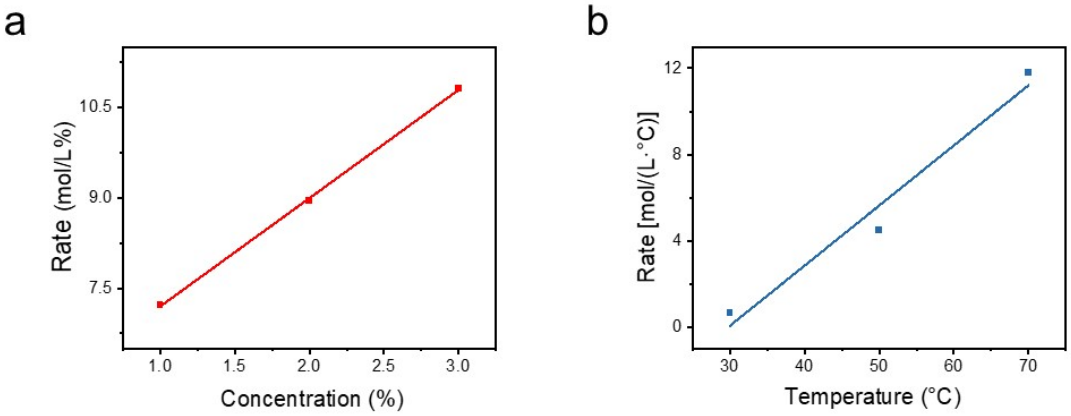
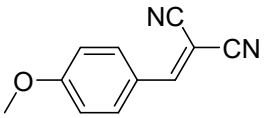
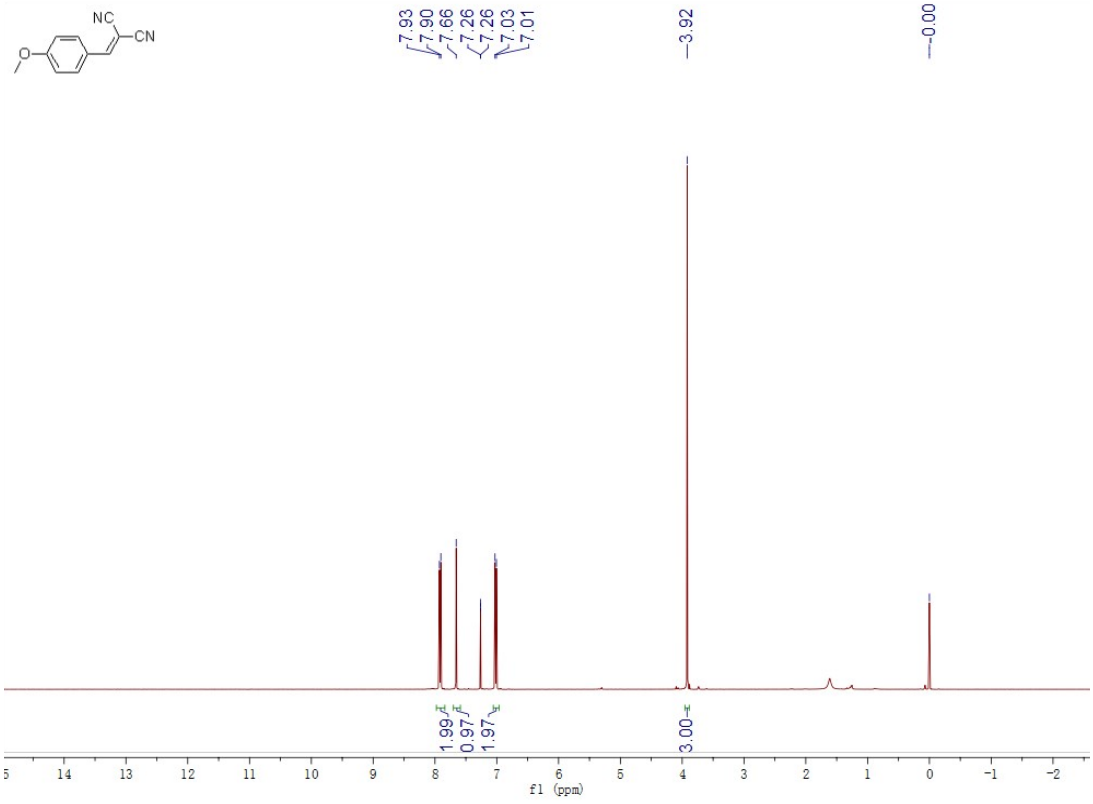
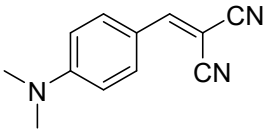


Figure S10: (a) Reaction kinetics fitting curves at different catalyst concentrations, (b) Reaction kinetics fitting curves at different temperatures.

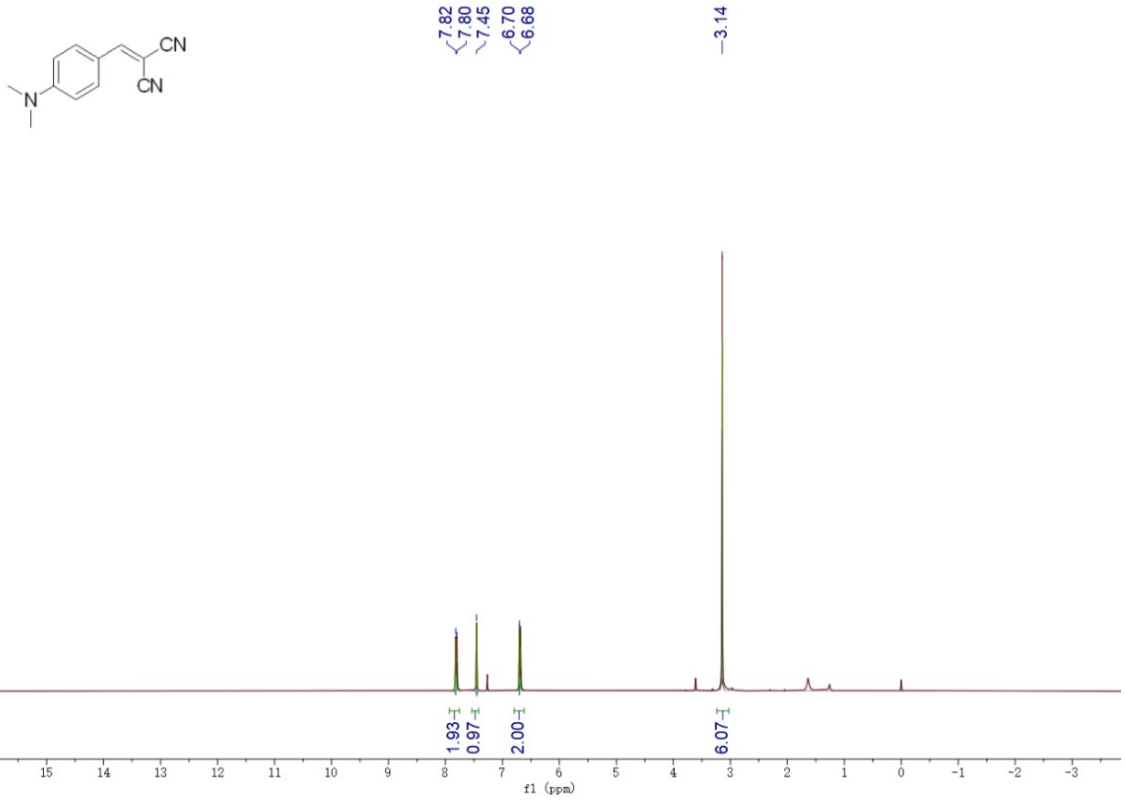


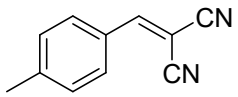
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.66 (s, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H).[[1]]



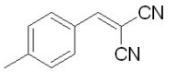


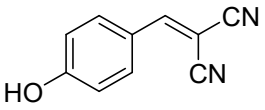
^{1}H NMR (400 MHz,$CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.45 (s, 1H), 6.69 (d, *J* = 8.2 Hz, 2H), 3.14 (s, 6H).[[1]]



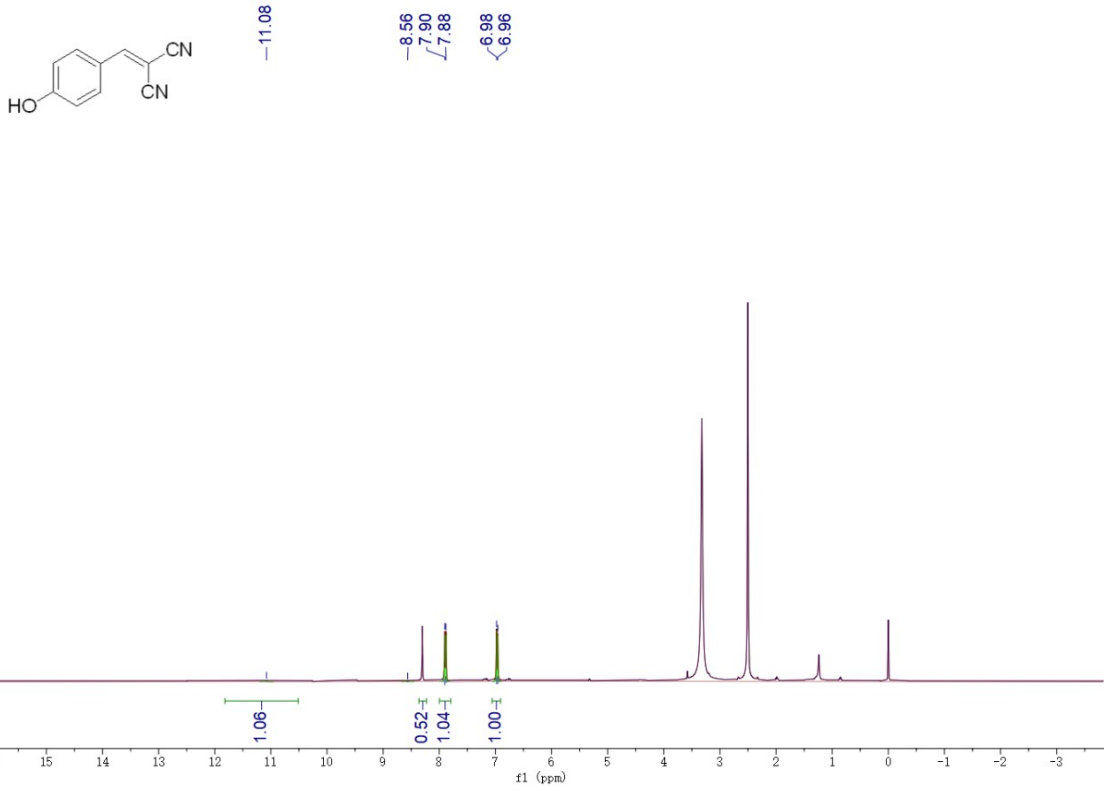


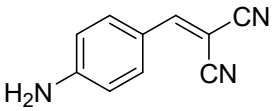
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.72 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.52 (s, 3H).[[2]]



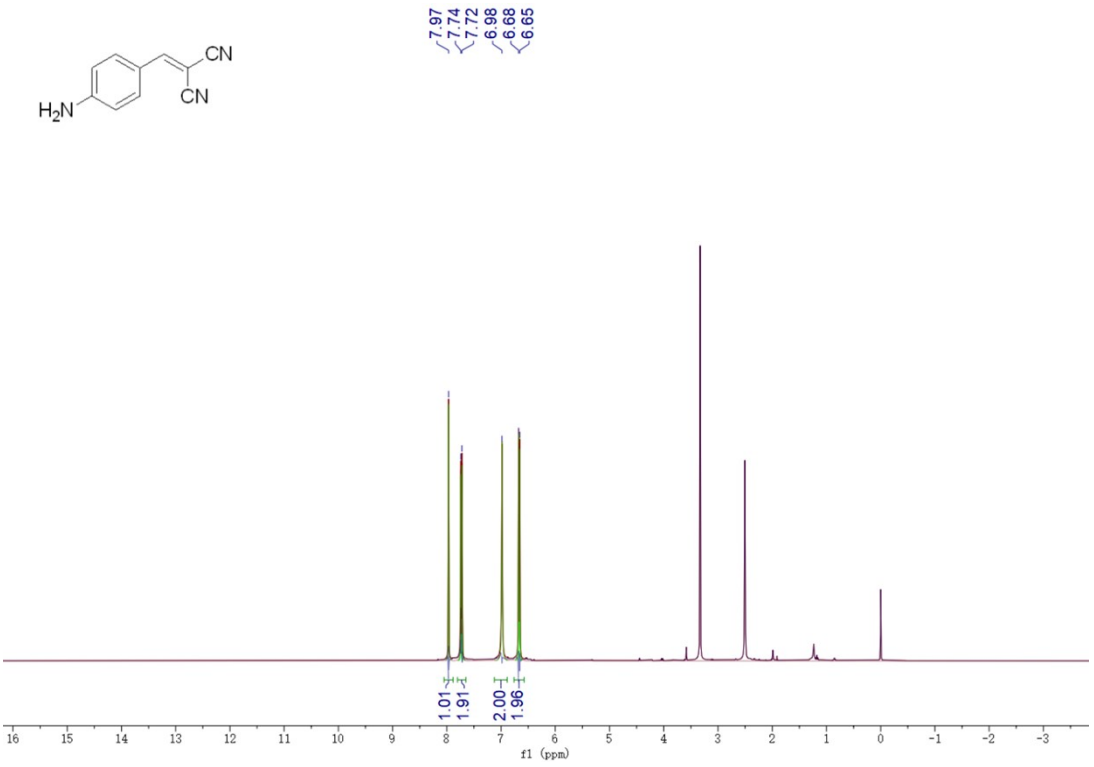


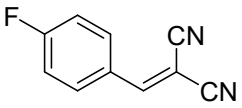
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.08 (s, 1H), 8.30 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 6.97 (d, J = 8.6 Hz, 1H).[[2]]



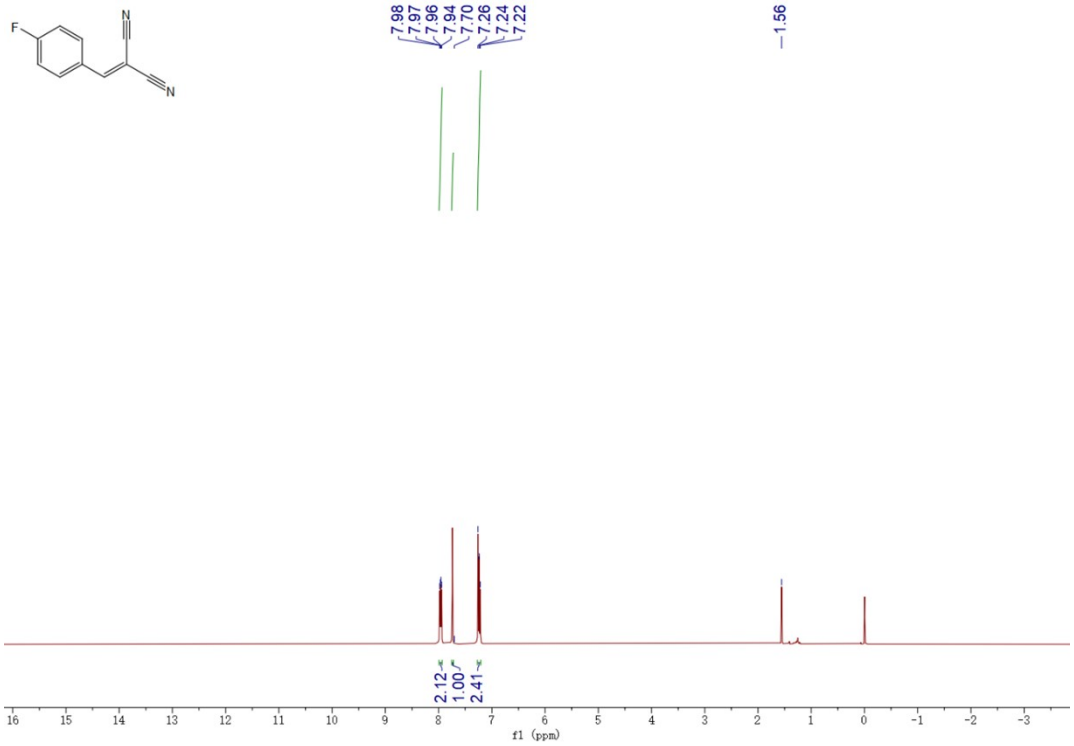


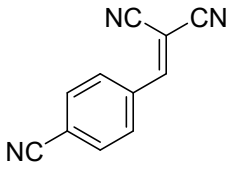
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (s, 1H), 7.73 (d, J = 8.8 Hz, 2H), 6.98 (s, 2H), 6.67 (d, J = 8.6 Hz, 2H).[[3]]



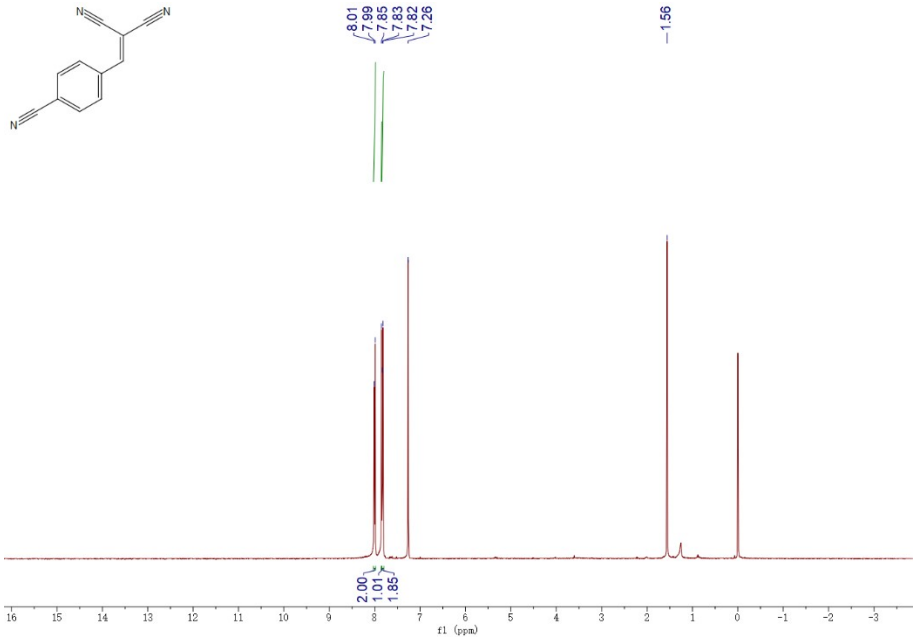


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.9, 5.1 Hz, 1H), 7.74 (s, 1H), 7.28 – 7.19 (m, 1H).





^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.5 Hz, 2H), 7.85 (s, 1H), 7.82 (d, J = 4.2 Hz, 2H).



Reference

[1] S. A. A. Rahman, C. N. Patra, G. K. Kole, S. Peters, T. Sadhukhan, B. Baskar, *New J. Chem.,* 2024, **48**, 3513–3524.

[2] N. Zohreh, M. Tavakolizadeh, S. H. Hosseini, A. Pourjavadi, C. Bennett, *Polymer.,* 2017, **112**, 342–350.

[3] W.-L. Jiang, Q.-J. Fu, B.-J. Yao, L.-G. Ding, C.-X. Liu, Y.-B. Dong, *ACS Appl. Mater. Interfaces.,* 2017, **9**, 36438–36446.