Supplementary information

Template-free fabrication of magnetic mesoporous poly(ionic liquid)s: efficient interfacial catalysts for hydrogenation reaction and transesterification of soybean oil

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1. Characterization.

All of the chemicals involved were commercially available without further purification and the water was deionized. Fourier transform infrared spectrometer (FTIR, NEXUS-470), Transmission electron microscopy (TEM, 80-200kVJEM-2100PLUS), X-ray diffractometer (XRD, PANalytical X-ray Diffractometer Model X pert3), hysteresis loop test (VSM, PPMS-9), Inductively coupled plasma (ICP), Thermogravimetric analyses (TGA), X-ray photoelectron spectroscopy (XPS), and water contact angle (WCA) were used to feature the morphology and structure of the samples. The surface area and pore size distribution were obtained via the N_2 adsorption-desorption isotherm and calculated by BET and BJH method respectively.

2. Synthesis of terminal alkene modified Fe_3O_4@SiO_2 nanoparticles.

Put the sodium dodecylbenzene sulphonate (SDBS, 26.25 g) and xylene (225 mL) into the beaker to obtain the dissolved SDBS solution completely by ultrasound treatment. Then put the $FeCl_2$ $4H_2O$ (2.235 g), $Fe(NO_3)_3$ $9H_2O$ (9.09 g), and H_2O (11.25 mL) into the beaker to obtain the dissolved mix salt solution completely by ultrasound treatment. Mixing the dissolved salt solution with the SDBS solution and stirring overnight. After that, heated the system to 90 ^oC and kept it for 1 h under the nitrogen atmosphere. Next added hydrazinium hydroxide solution (10.2 mL, 50 wt%) continued reacting 3 h. Then added tetraethyl orthosilicate (TEOS, 30 mL) for another

24 h with stirring vigorously when the system cooled down to 40 ºC to prevent the complete evaporation of water. After the reaction was over, the products were washed successively with H_2O and methanol and separated by external magnetic force and put it in the oven at 80 ºC for 5 h to get Fe_3O_4@SiO_2. Sodium dodecyl sulfate (SDS, 1 g) was dissolved in deionized H_2O (100 mL) to form the SDS solvent, then put it and Fe_3O_4@SiO_2 (1 g) to the round-bottom flask with ultrasound treatment for 20 min. Triethoxyvinylsilane (TEVS, 7 mL) was injected into the mixture solvent under the N_2 atmosphere and vigorous stirring, then the temperature was raised to 50 ºC and kept stirring for 48 h. The final terminal alkene modified Fe_3O_4@SiO_2 were rigorously washed with H_2O and ethanol, then dried at 80 ºC for 6 h.

3. Preparation of functional 1,4-diazabicyclo[2.2.2]octane (FDABCO).

1,4-Diazabicyclo[2.2.2]octane (25 mmol), 2-bromoethyl acrylate (25 mmol), and methanol (20 mL) were added to the flask, heated at 55 ºC for 24 h under the N_2 atmosphere. After the reaction finished, the mixed coarse solvent was concentrated under reduced pressure to obtain the crude product. Then ethyl acetate was added to remove the unreacted compound, the product precipitated out by ultrasonic treatment and repeated the same operation three times.

Table S1. The surface area, pore size, and volume of Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4, p(3TEMPA-FDABCO-2DVB)@Fe_3O_4 in absence of terminal alkene modified Fe_3O_4@SiO_2 nanoparticles and various of p(xTEMPA-yFDABCO-zDVB)@Fe_3O_4.

Entry	Samples	S_{BET} [a] (m^2 g^{-1})	D_{AV} [b] (nm)	V_{total} [c] (cm^3g^{-1})

1	p(TEMPA-FDABCO-DVB) @Fe_3O_4	272.49	4.27	0.5817
2	p(TEMPA-FDABCO-4DVB) @Fe_3O_4	327.86	2.19	0.3597
3	p(2.5TEMPA-2.5FDABCO-DVB)@Fe_3O_4	51.22	6.36	0.1629
4	p(3TEMPA-FDABCO-2DVB)@Fe_3O_4	273.28	3.04	0.4154
5	p(TEMPA-3FDABCO-2DVB)@Fe_3O_4	276.95	2.12	0.2933
6	Pd-p(3TEMPA-FDABCO-2DVB) [d]	3.4669	3.75	0.0819
7	Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4	247.04	3.92	0.4838
8	p(FDABCO-2DVB)@Fe_3O_4	76.24	2.43	0.2167

[a] Brunauer-Emmett-Teller (BET) surface area was calculated over the relative pressure range of 0.05-0.20. [b] Average pore size. [c] Total pore volume. [d] Polymerization reaction in absence of terminal alkene modified Fe_3O_4@SiO_2 nanoparticles.

Table S2. The catalytic effect of different catalysts on styrene hydrogenation.

Entry	**catalyst**	**Reaction time (min)**	**Reaction condition**	**Conv. (%)**	**Ref.**
1	Pd-p(3TEMPA-FDABCO-2DVB) @Fe_3O_4	10	25 °C, 101 kPa	>99	This work
2	[C_4AzoC_2DMEA]Br/Pd@SM	40	25 °C, 101 kPa	>99	Ref.[1]
3	Pd/MSS-C20	35	40 °C, 0.35 MPa	89	Ref.[2]
4	Pd/SN–ON	90	40 °C, 0.35 MPa	>99	Ref.[3]
5	Pd/PEG4000	90	25 °C, 101 kPa	60	Ref.[4]

Table S3. Element distribution on terminal alkene modified of Fe_3O_4@SiO_2 and Pd-p(xTEMPA-yFDABCO-zDVB)@Fe_3O_4.

Entry	Catalytic	Element distribution (%)			TEMPA loading (mmol g^{-1})	FDABCO loading (mmol g^{-1})	Pd (mmol g^{-1})
		C	N	O			
1	terminal alkene modified of Fe_3O_4@SiO_2	6.07	0.05	7.79	0	0	0
2	Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4	58.74	6.13	12.91	0.53	0.19	0.2053
3	Pd-p(TEMPA-FDABCO-DVB)@Fe_3O_4	52.47	5.62	12.63	0.61	0.17	0.1852
4	Pd-p(2.5TEMPA-2.5FDABCO-DVB)@Fe_3O_4	51.23	4.67	12.89	1.02	0.12	0.1241
5	Pd-p(3TEMPA-FDABCO-2DVB) [a]	55.63	4.84	13.69	1.51	0.11	0.1048
6	Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4 [b]	53.62	5.24	12.36	0.51	0.16	0.1733

[a] Pd-p(3TEMPA-FDABCO-2DVB) without terminal alkene modified of Fe_3O_4@SiO_2.

[b] Pd-p(3TEMPA$_3$-FDABCO-2DVB)@Fe_3O_4 after 5 runs.

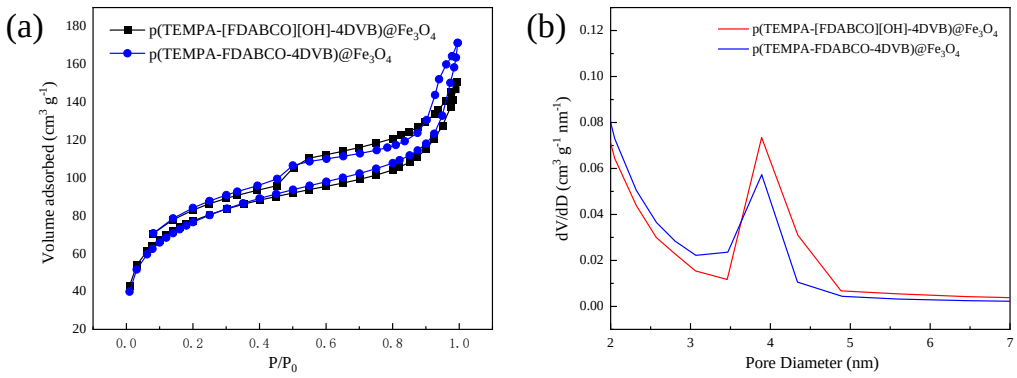

Fig. S1. N_2 adsorption/desorption isotherms (a) and the pore size distributions (b) of p(TEMPA-[FDABCO][OH]-4DVB)@Fe_3O_4 and p(TEMPA-FDABCO-4DVB)@Fe_3O_4.

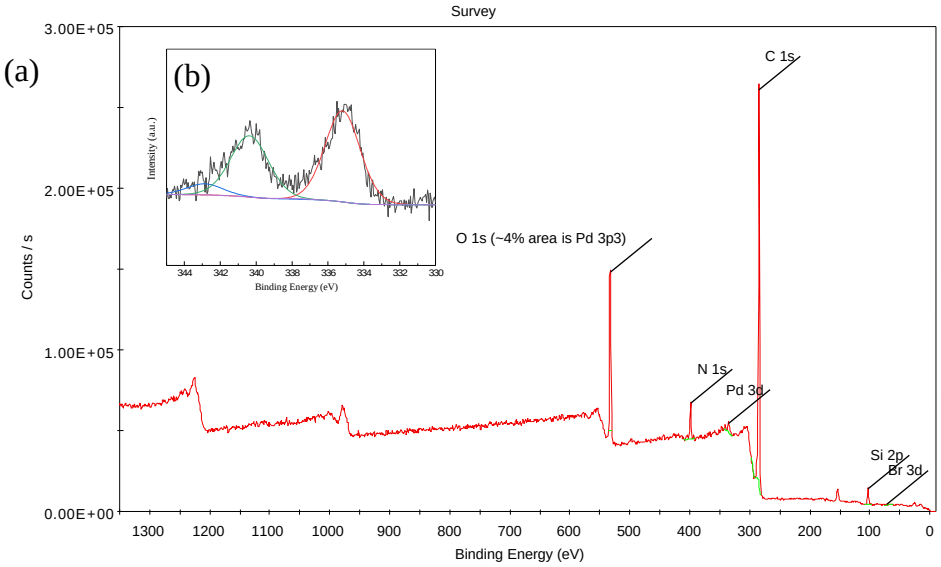

Fig. S2. (a) Full-range XPS spectrum; (b) Pd 3d spectrum of Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4.

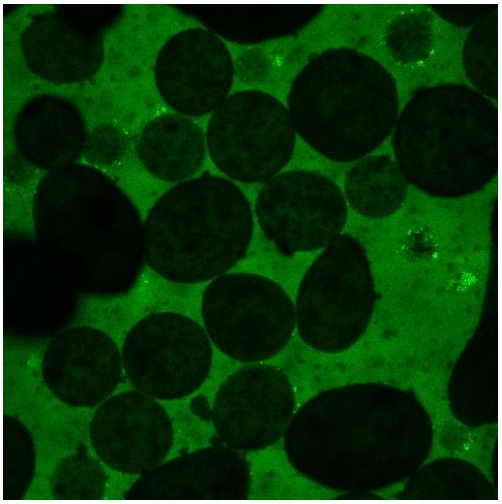

Fig. S3. Visual and confocal microscopy images of 20 mg Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4-stabilized Pickering emulsions with the volume ratio of water to *n*-octane (2:1).

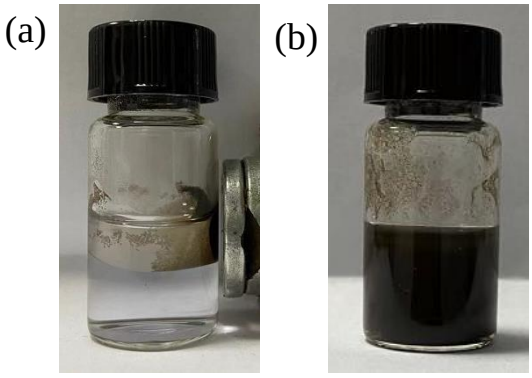

Fig. S4. The demulsification under magnetic and CO_2 (a); the Pickering emulsion with 20 mg Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4, *n*-octane/water (1 mL/2 mL) (b).

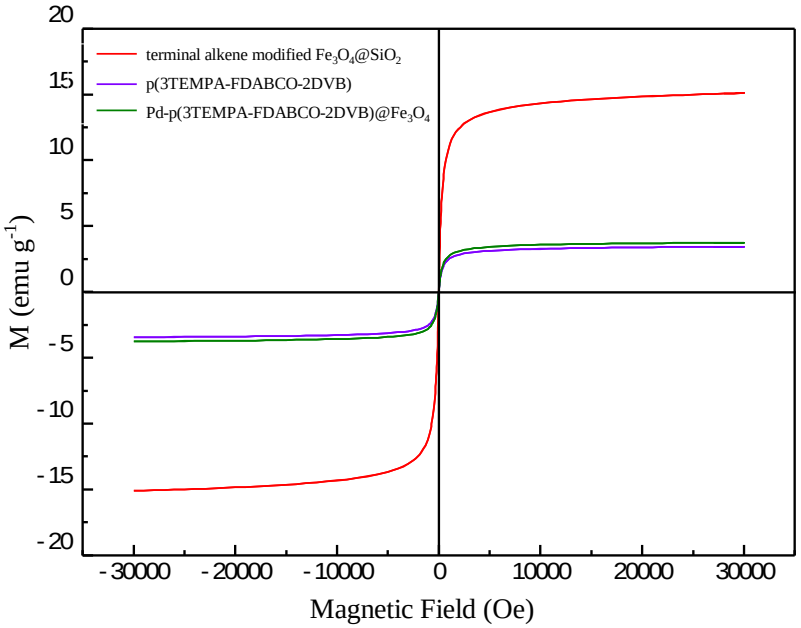

Fig. S5. Magnetization curves of terminal alkene modified Fe_3O_4@SiO_2, p(3TEMPA-FDABCO-2DVB)@Fe_3O_4, and Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4.

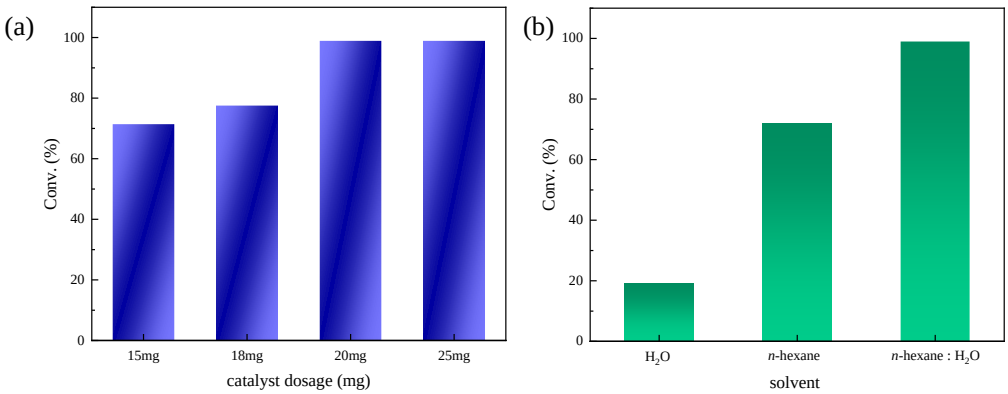

Fig. S6. Hydrogenation conversion rate of styrene with different catalyst dosage of Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4 (a) and different solvents (b). Reaction condition: 25 °C, 101 kPa, and mixture solvent ($V_{n\text{-hexane}}$: V_{H_2O} = 1 : 2).

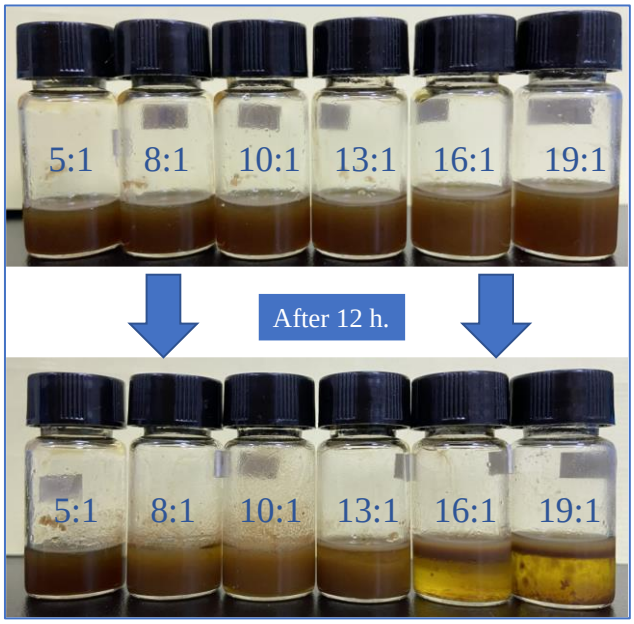

Fig. S7. The stability of the system with p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 under different ratios of ethanol/soybean oil.

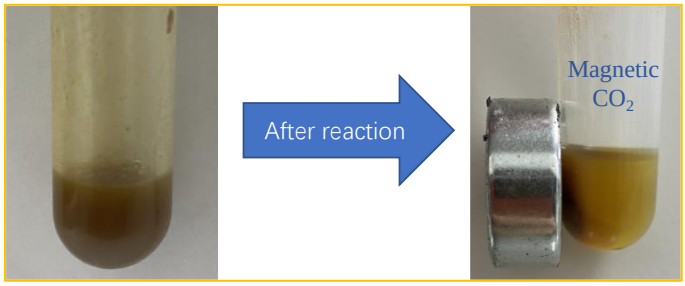

Fig. S8. Demulsification operation after transesterification reaction with dual-stimuli of the magnetic and CO_2.

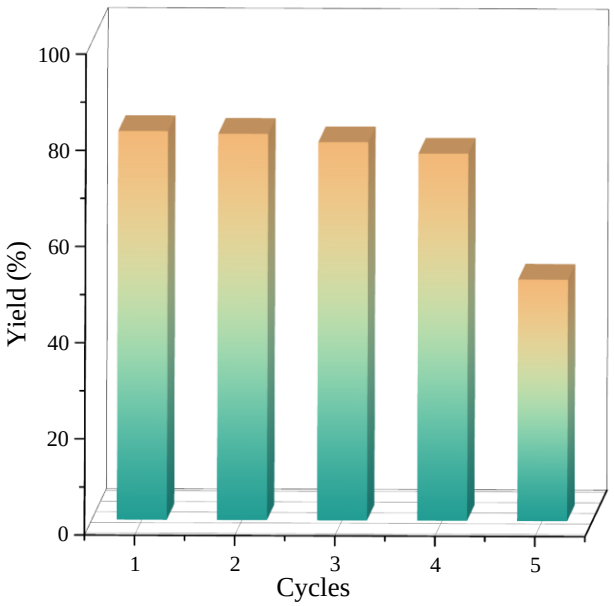

Fig. S9. Recycling test of transesterification catalytic by the p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4.

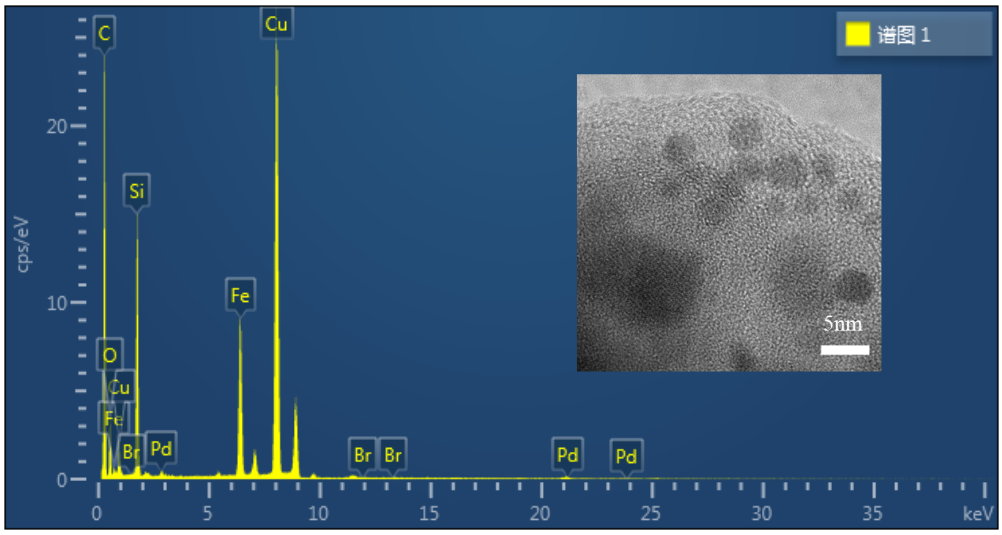

Fig. S10. The EDS spectrum of the Pd-p(3TEMPA-FDABCO-2DVB)@Fe_3O_4.

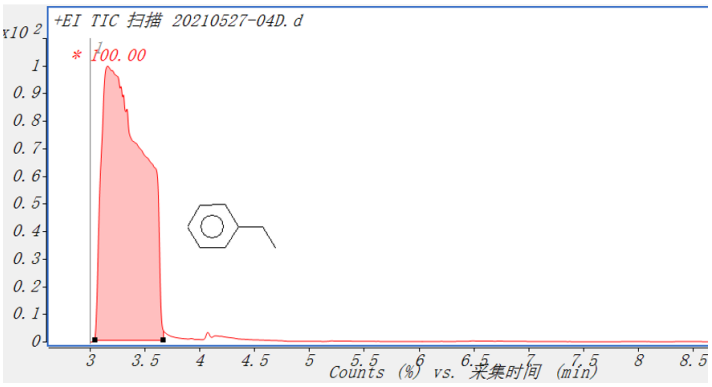

Fig. S11. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 1).

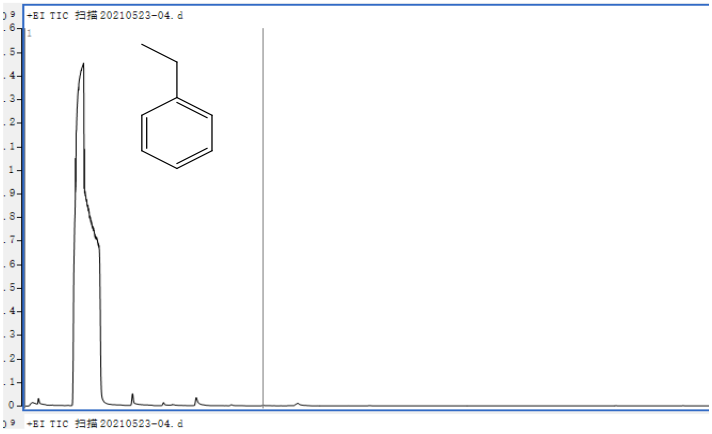

Fig. S12. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 2).

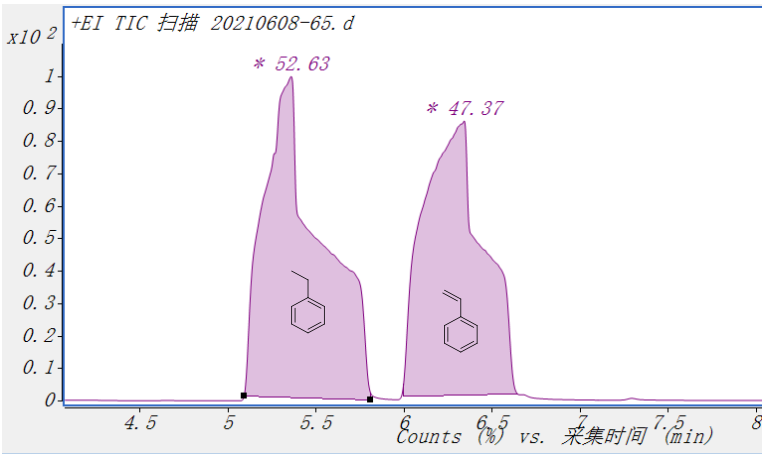

Fig. S13. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 3).

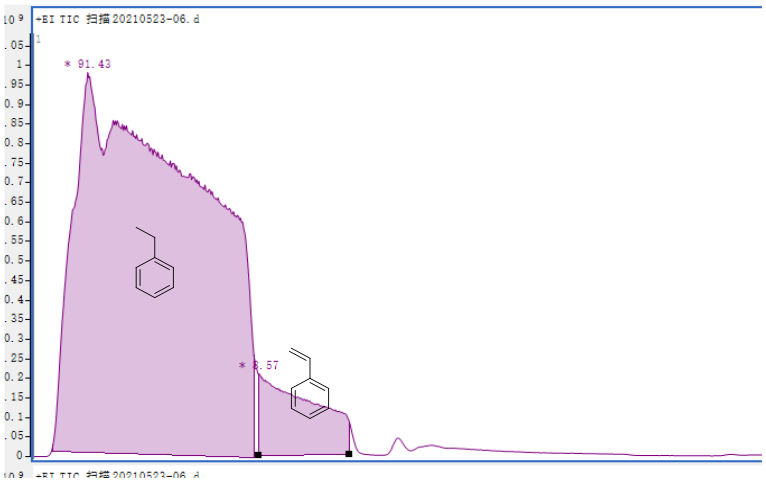

Fig. S14. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 4).

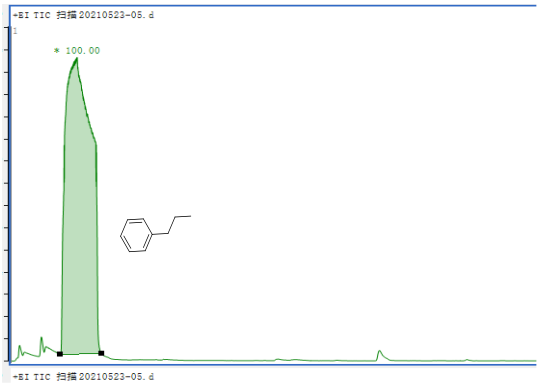

Fig. S15. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 5).

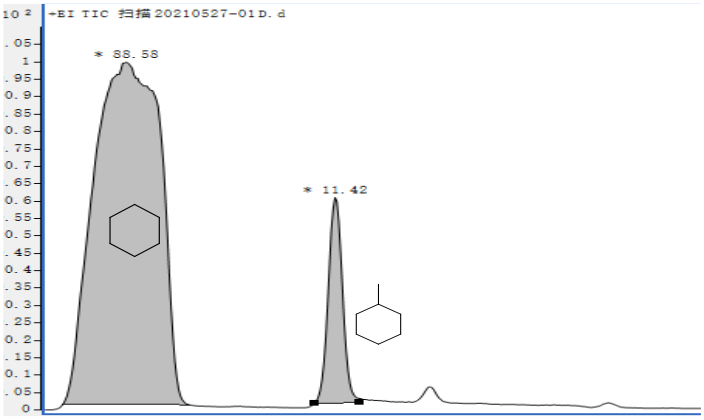

Fig. S16. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 6).

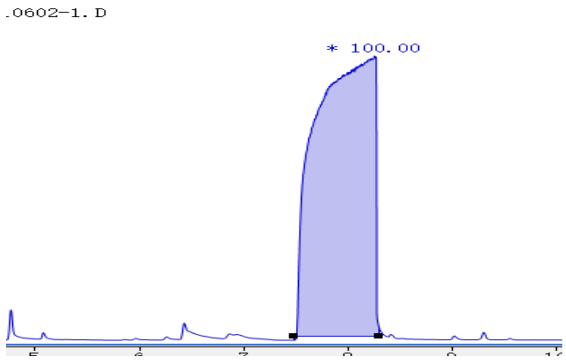

Fig. S17. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 7).

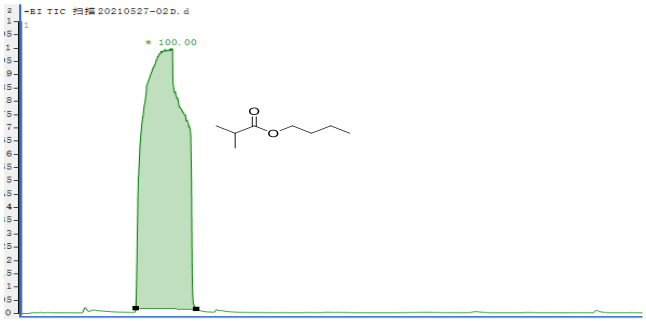

Fig. S18. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 8).

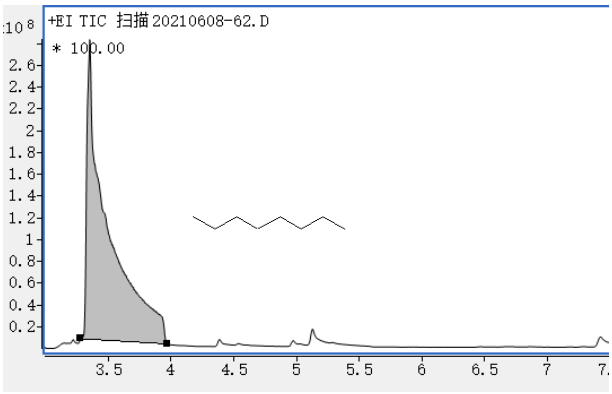

Fig. S19. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 9).

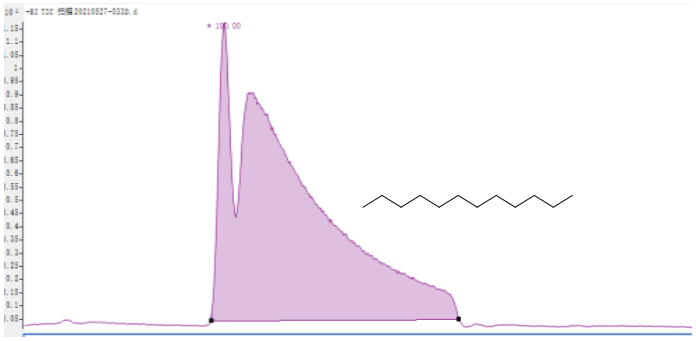

Fig. S20. The GC-MS spectrum of the hydrogenation (table 1 of main text, entry 10).

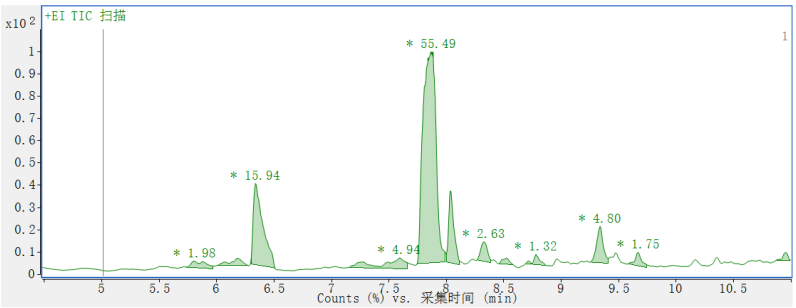

Fig. S21. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4.

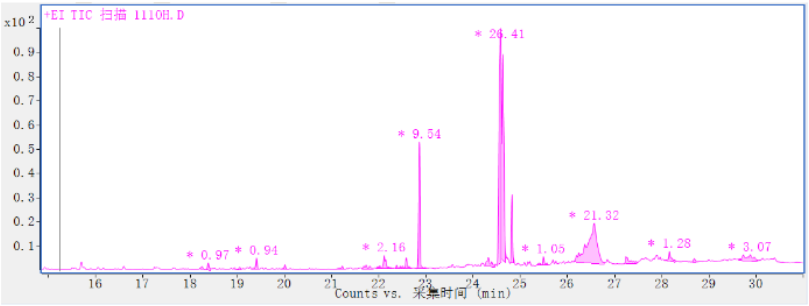

Fig. S22. The GC-MS spectrum of transesterification catalytic by p(TEMPA-[FDABCO][OH]-DVB)@Fe_3O_4.

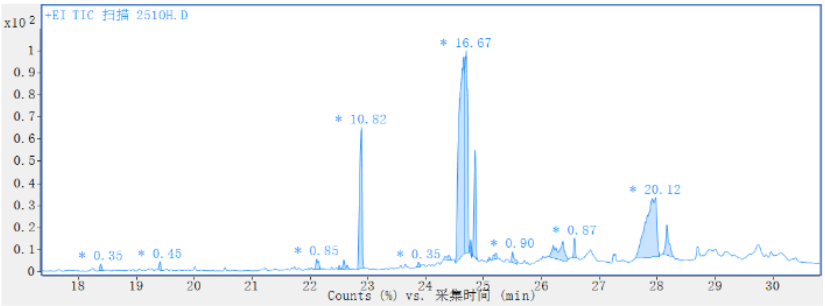

Fig. S23. The GC-MS spectrum of transesterification catalytic by p(2.5TEMPA-2.5[FDABCO][OH]-DVB)@Fe_3O_4.

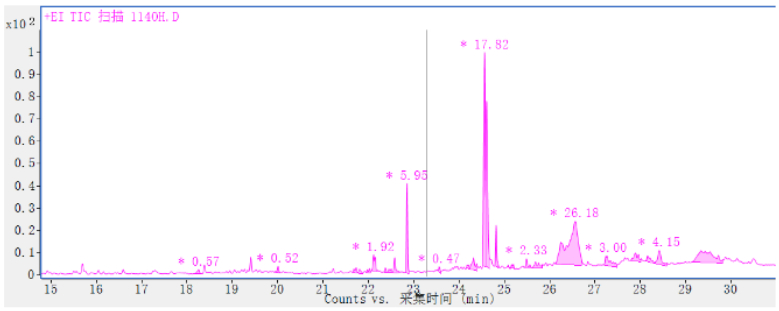

Fig. S24. The GC-MS spectrum of transesterification catalytic by p(TEMPA-[FDABCO][OH]-4DVB)@Fe_3O_4.

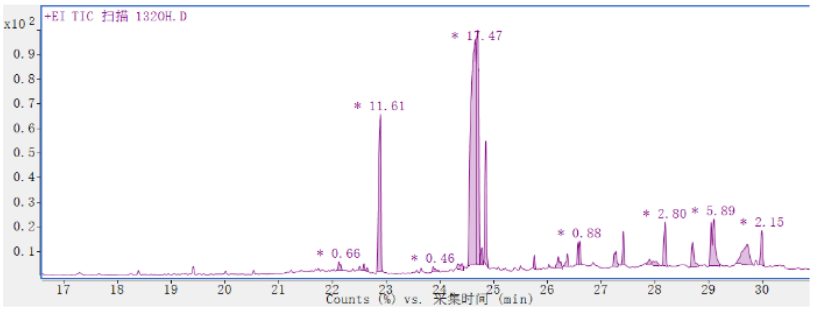

Fig. S25. The GC-MS spectrum of transesterification catalytic by p(TEMPA-3[FDABCO][OH]-2DVB)@Fe_3O_4.

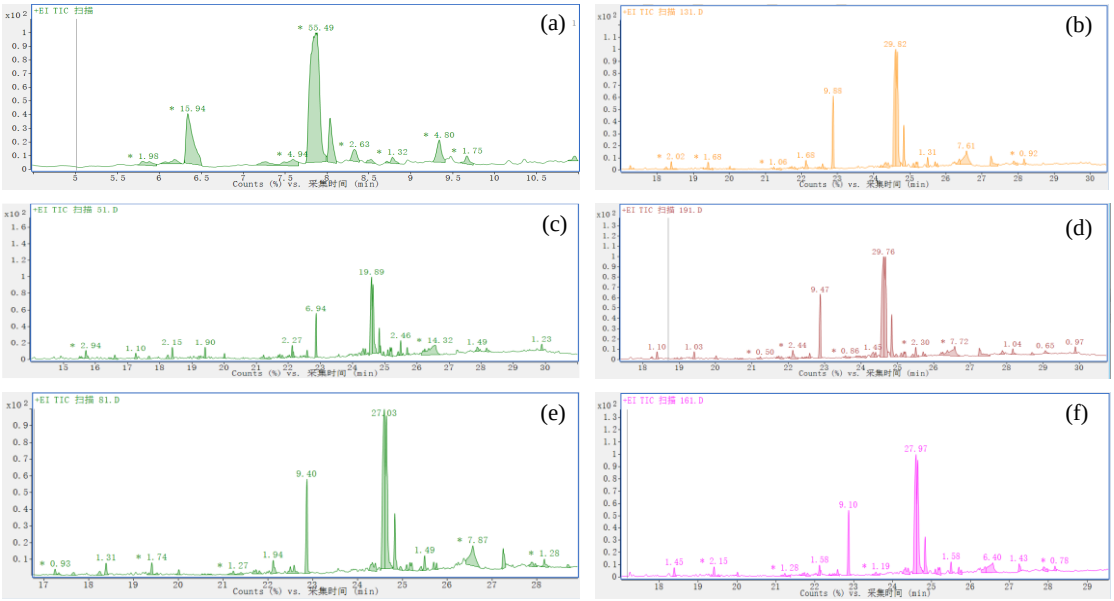

Fig. S26. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 and different molar ratio of ethanol/soybean oil (a = 10:1; b = 13:1; c = 5:1; d = 19:1; e = 8:1; f = 16:1).

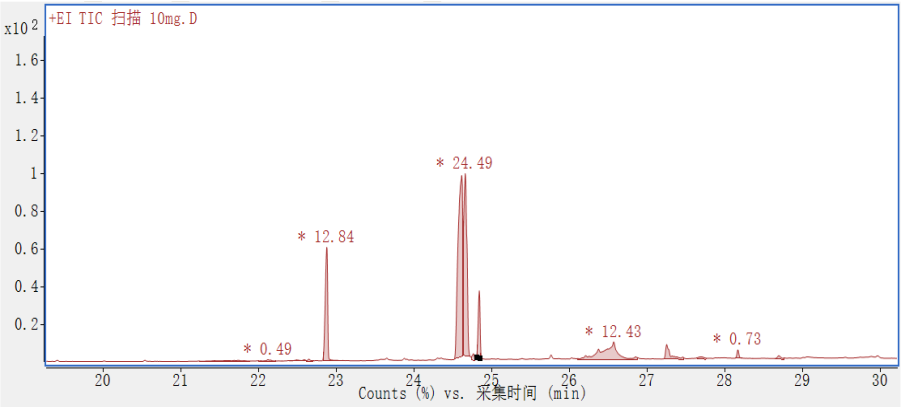

Fig. S27. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 (10 mg).

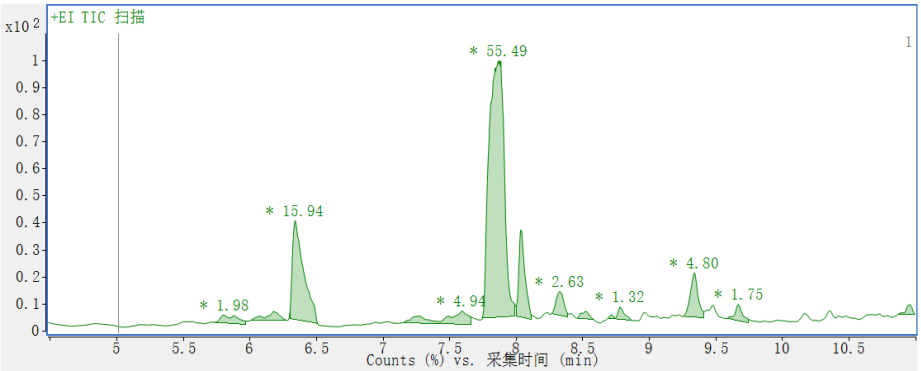

Fig. S28. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 (20 mg).

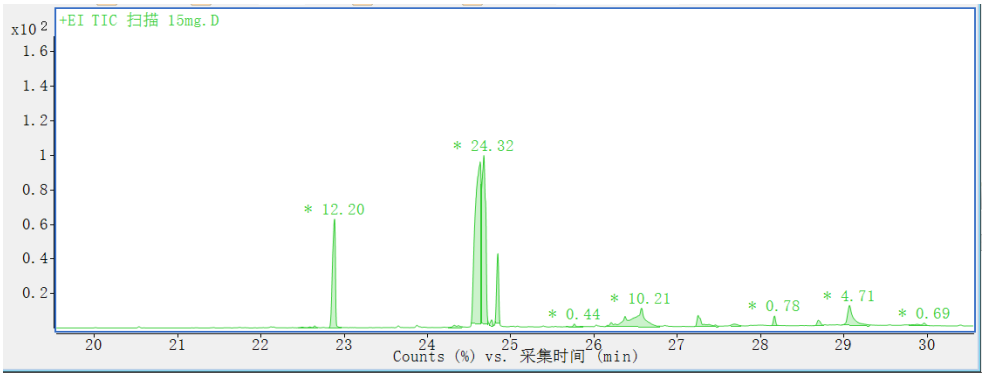

Fig. S29. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 (15 mg).

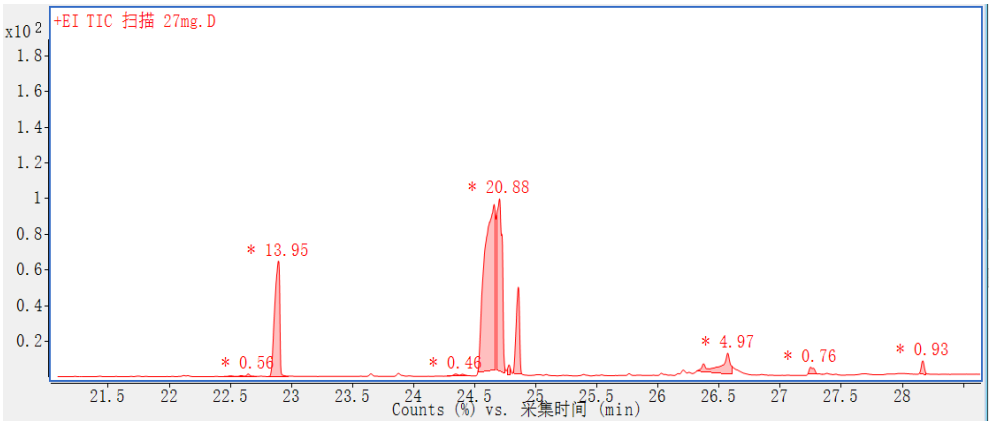

Fig. S30. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 (27 mg).

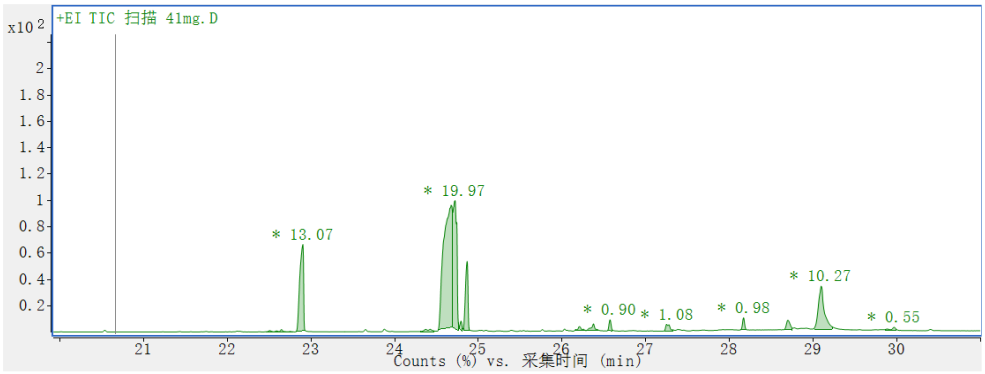

Fig. S31. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 (41 mg).

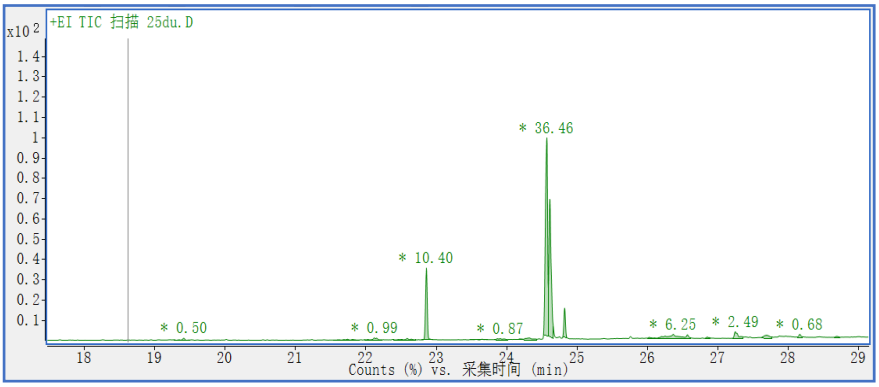

Fig. S32. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 under 25 ºC.

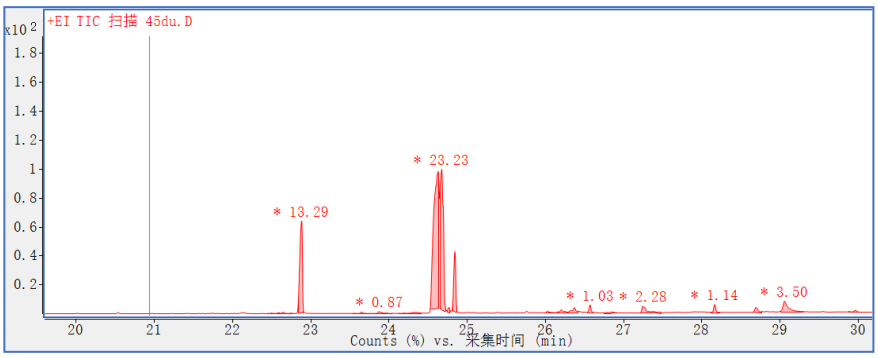

Fig. S33. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 under 45 ºC.

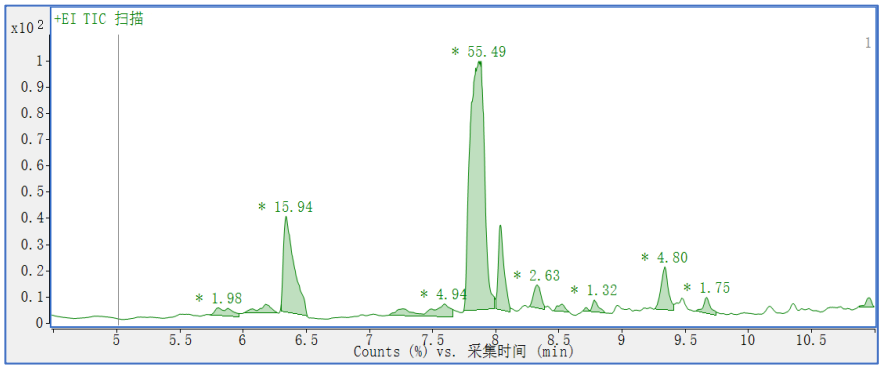

Fig. S34. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 under 65 ºC.

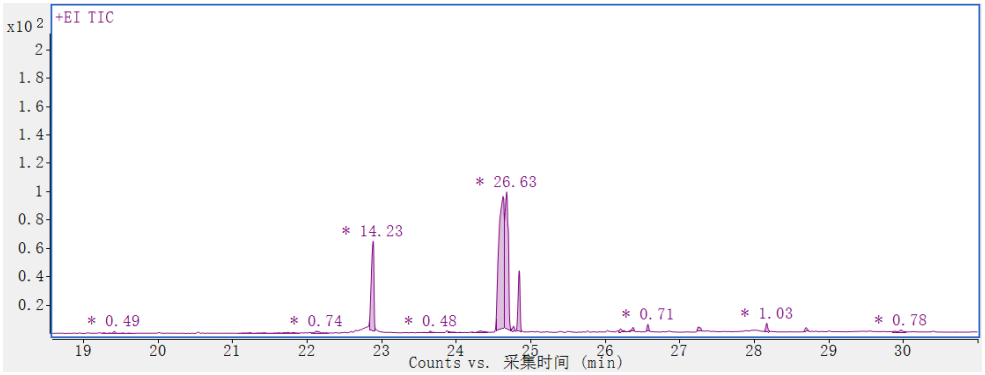

Fig. S35. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 under 90 ºC.

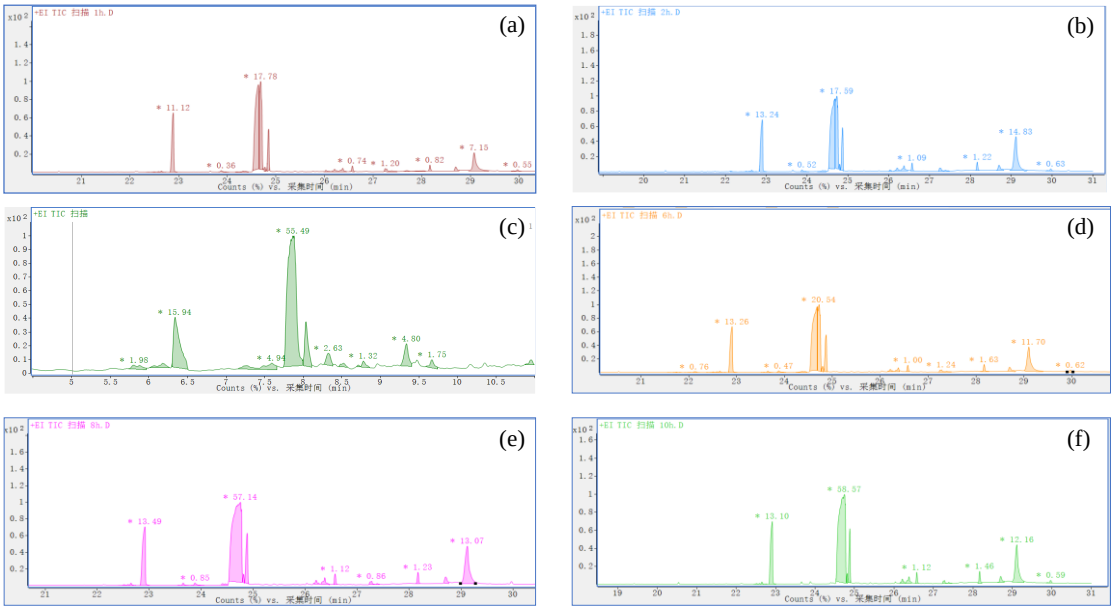

Fig. S36. The GC-MS spectrum of transesterification catalytic by p(3TEMPA-[FDABCO][OH]-2DVB)@Fe_3O_4 for different times (a = 1 h; b = 2 h; c = 4 h; d = 6 h; e = 8 h; f = 10 h).

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