Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

“Design of Brønsted acidic ionic liquid functionalized mesoporous organosilica nanospheres for efficient synthesis of ethyl levulinate and levulinic acid from 5-hydroxymethylfurfural”

Catalyst preparation

CTAB-directed [C_3PrIm][OTf]-MONSs catalysts. At first, *CTAB Pr*Cl-MONSs support was fabricated by using a liquid-interface assembly strategy *via* one-pot CTAB-directed sol–gel co-condensation process in oil-in-water (O/W) emulsion. Typically, CTAB (0.3 g) was dissolved in a mixed solution of ammonia (NH_4OH, 2 mL, 25 wt%), water (80 mL) and ethanol (EtOH, 40 mL), and the resulting colloidal solution was stirred at 550 rpm continuously for 20 min at 30 ^{o}C. Additionally, cyclohexane (20 mL) contained 1,2-bis(trimethoxysilyl)ethane (BTMSE, 0.35 mL) and 3-chloropropyltrimethoxysilane (CPTMS, 0.25 mL) mixture was slowly added to the above CTAB-water-EtOH-NH_4OH solution, and the co-hydrolysis and -condensation of BTMSE and CPTMS was lasted for a period of 6, 12 or 24 h at 30 ^{o}C. The resulting mixture was transferred to an autoclave and heated to 120 ^{o}C (ramping rate of 2 ^{o}C min^{-1}) and held for 5 h. Afterwards, the cooled product was collected by centrifugation, and then it was suffered from air drying at 40, 80 and 100 °C for 6 h, successively. The resulting powder was recovered after removing CTAB and keeping the filtrate neutral by water washing for several times at 60 °C and boiling ethanol washing for 3 times. The final product was dried at 100 ^{o}C for 12 h, and it was denoted as *CTAB Pr*Cl-MONSs**x**, where **x** = **6**, **12** and **24**, referring to the hydrolysis time of organosilica precursors of 6, 12 and 24 h. The molar ratios of the aforementioned starting materials were CTAB 0.82: NH_4OH 11.29: cyclohexane 190: EtOH 690: H_2O/water 4444: BTMSE 1.35: CPTMS 1.35.

Subsequently, *CTAB Pr*Cl-MONSs was functionalized by BAILs based on following steps. *CTAB Pr*Cl-MONSs (0.32 g) was dispersed to a mixture of toluene (10 mL) and imidazole (0.092 g), and continuous stirring was applied for 24 h at 110 ^{o}C. Afterwards, the powder was recovered by centrifugation and dried at 100 °C after removing extra imidazole by washing with dichloromethane for five times. The obtained powder (*CTAB Pr*Im-MONSs) was dispersed to toluene solvent (10 mL) again, and 1,3-propanesultone (0.165 g) was added to the suspension, followed by stirring for 8 h at 110 °C. Next, after the suspension was cooled to room temperature, trifluoromethane sulfonic acid (HOTf, 0.092 g) was added, and the mixture thus obtained was stirred for additional 12 h at 60 °C. The final product was obtained after successive treatment including centrifugation, washing with hot toluene and then dichloromethane (to remove completely the adsorbed acidic compounds) followed by drying at 80 and 100 °C for 6 h, respectively. The product was denoted as *CTAB* [C_3PrIm][OTf]-MONSs**x** (**x** = **6, 12** and **24**), where C_3 = *Pr*SO_3H, Im = imidazole and OTf = SO_3CF_3.

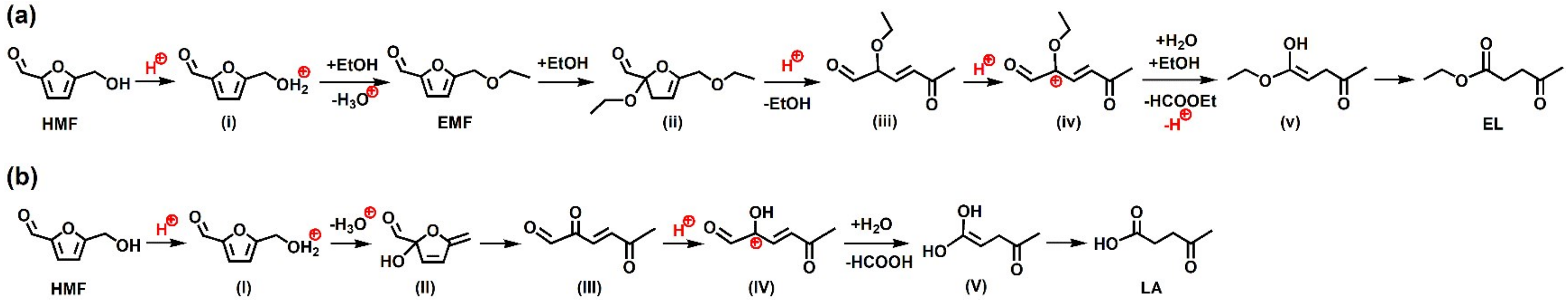
Other surfactant-directed [C_3PrIm][OTf]-MONSs catalysts. The preparation procedure is similar to that of the CTAB-directed [C_3PrIm][OTf]-MONSs**12** catalyst, however, CTAB was replaced by CTAC, CPB or CTATOS (0.82 mmol). The product was denoted as *CTAC* [C_3PrIm][OTf]-MONSs**12**, *CPB* [C_3PrIm][OTf]-MONSs**12** and *CTATOS* [C_3PrIm][OTf]-MONSs**12**, respectively.

***CTAB Pr*SO_3H-MONSs catalyst.** The procedure is similar to that of the *CTAB Pr*Cl-MONSs**12**, however, CPTMS was replaced by 3-mercaptopropyl trimethoxysilane (1.35 mmol, MPTMS). Afterwards, the resulting mercaptopropyl functionalized periodic mesoporous organosilica nanosphere was oxidized by excessive H_2O_2 solution (1.35 mL, 30%). The final product was denoted as *CTAB Pr*SO_3H-MONSs**12**. The composition of the precursor solution was CTAB 0.82: NH_4OH 11.29: cyclohexane 190: EtOH 690: H_2O 4444: BTMSE 1.35: MPTMS 1.35: H_2O_2 13.5 (molar ratio).

Table S1 Contents of nitrogen, sulphur and fluorine elements (At.%) and the corresponding atomic ratios in various [C_3PrIm][OTf]-MONSs catalysts.

Catalyst	N	S	F	N: S: F (atomic ratio)
CTAB [C_3PrIm][OTf]-MONSs**12**	3.21	3.54	5.35	2.00: 2.20: 3.33
CTAC [C_3PrIm][OTf]-MONSs**12**	3.01	2.79	4.24	2.00: 1.85: 2.82
CPB [C_3PrIm][OTf]-MONSs**12**	3.33	3.36	5.00	2.00: 2.02: 3.00
CTATOS [C_3PrIm][OTf]-MONSs**12**	3.82	3.93	5.21	2.00: 2.06: 2.72

Scheme S1 Reaction mechanisms of the synthesis of (a) EL from the ethanolysis of HMF and (b) LA from hydrolysis of HMF catalyzed by the [C_3PrIm[OTf]-MONSs.



Scheme S2 Carbon balances in the ethanolysis (a) and hydrolysis (b) of HMF catalyzed by *CTATOS* [C$_3$PrIm][OTf]-MONSs**12** under the conditions of n_{EtOH}: n_{HMF} molar ratio of 248, 120 ^{o}C and 240 min (a) and n_{H2O}: n_{HMF} molar ratio of 417, 140 ^{o}C and 240 min (b).

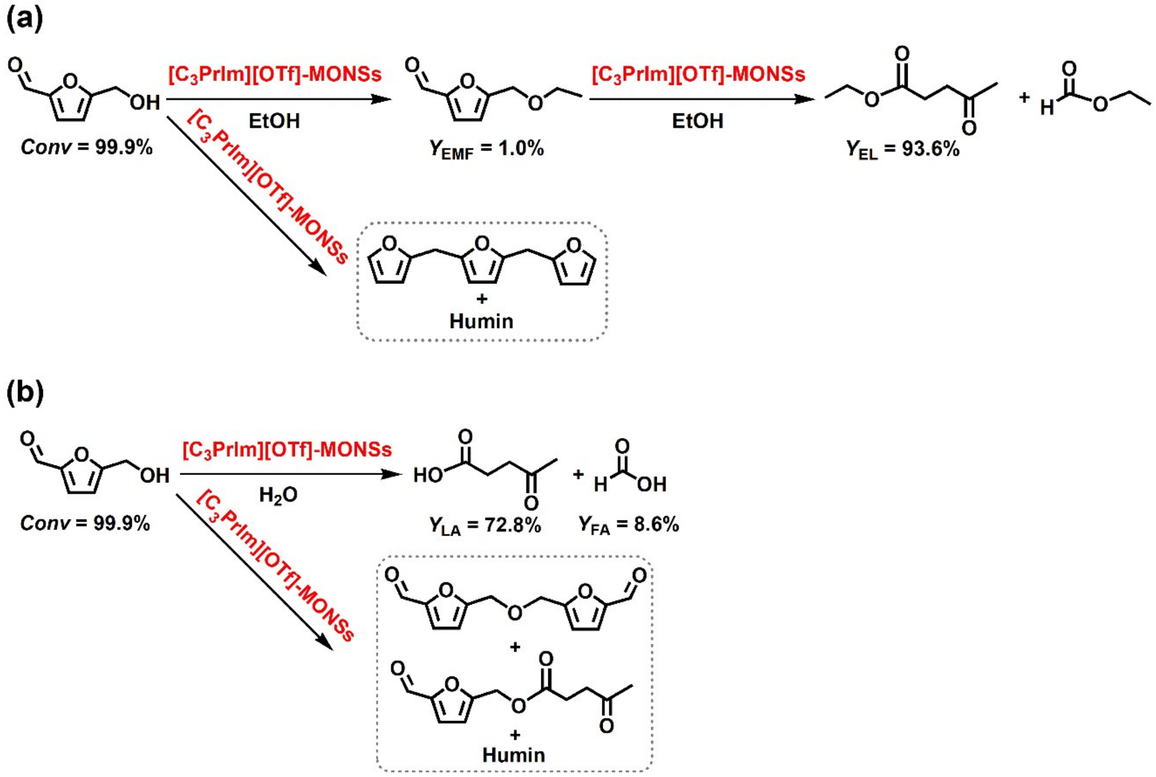


Fig. S1 FESEM images and particle size distributions of *CTAB* [C_3PrIm][OTf]-MONSs**12** (a and a’), *CTAC* [C_3PrIm][OTf]-MONSs**12** (b and b’), *CPB* [C_3PrIm][OTf]-MONSs**12** (c and c’) and *CTATOS* [C_3PrIm][OTf]-MONSs**12** (d and d’).

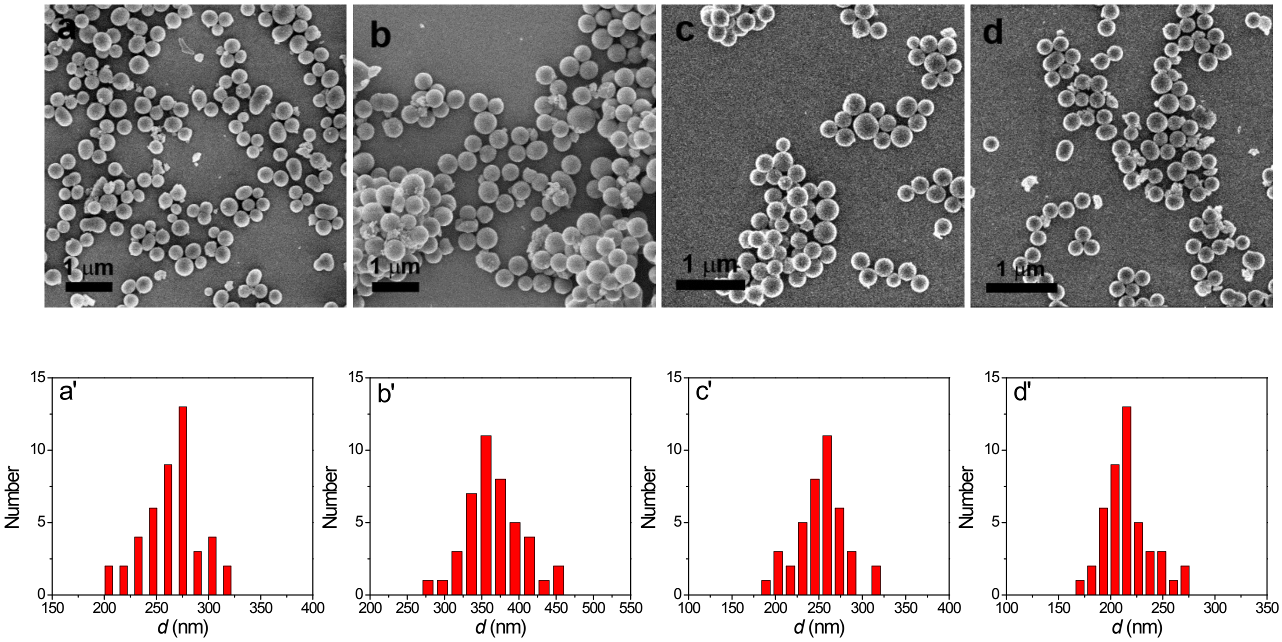


Fig. S2 Nitrogen gas adsorption-desorption isotherms (a and c) and pore size distribution curves (b and d) of *CTAB Pr*Cl-MONSs**12** support, various [C_3PrIm][OTf]-MONSs catalysts and *CTAB Pr*SO_3H-MONSs**12**.

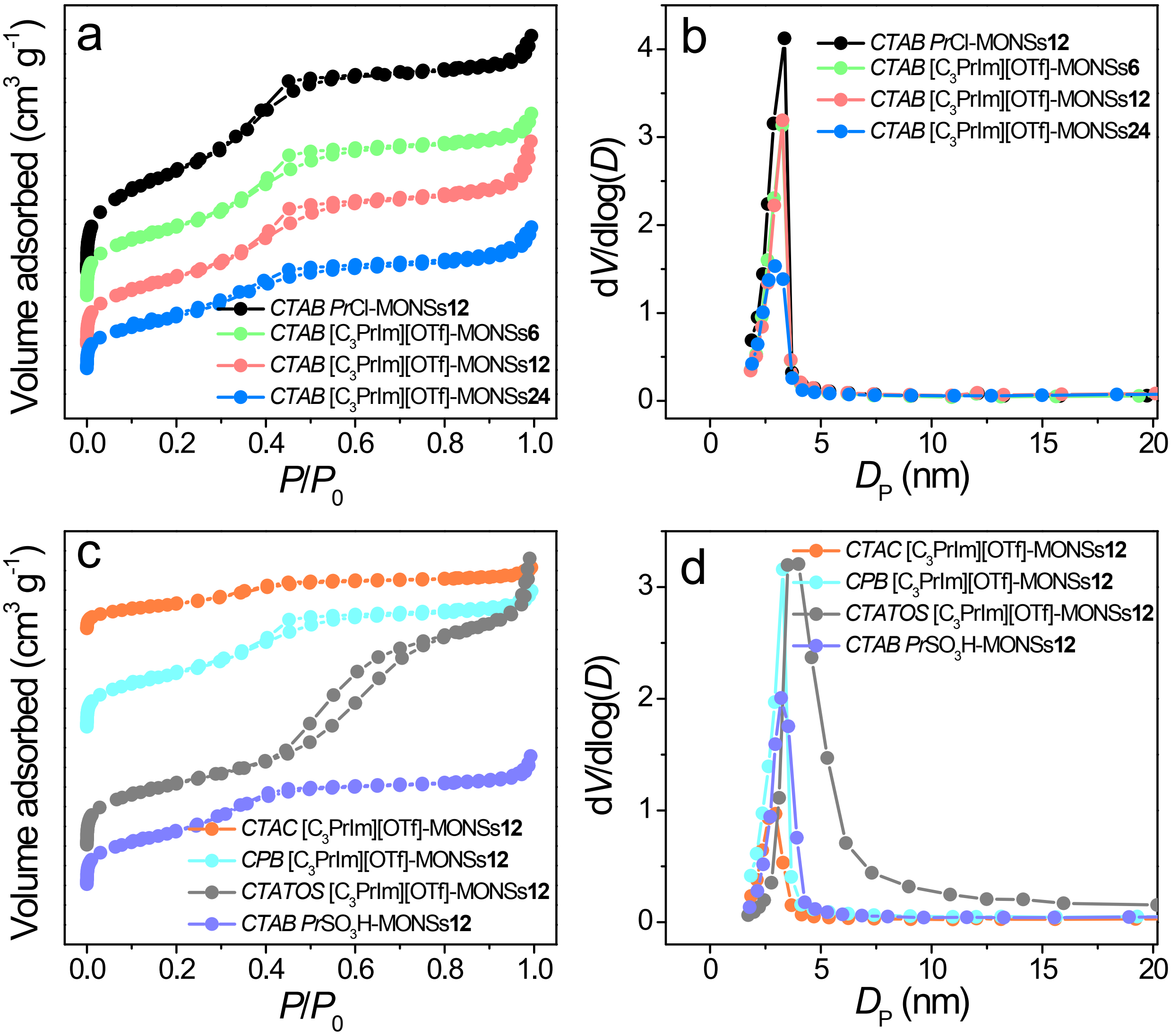


Fig. S3 XPS whole spectra of *CTAB* [C_3PrIm][OTf]-MONSs**12** (a), *CTAC* [C_3PrIm][OTf]-MONSs**12** (b), *CPB* [C_3PrIm][OTf]-MONSs**12** (c) and *CTATOS* [C_3PrIm][OTf]-MONSs**12** (d).

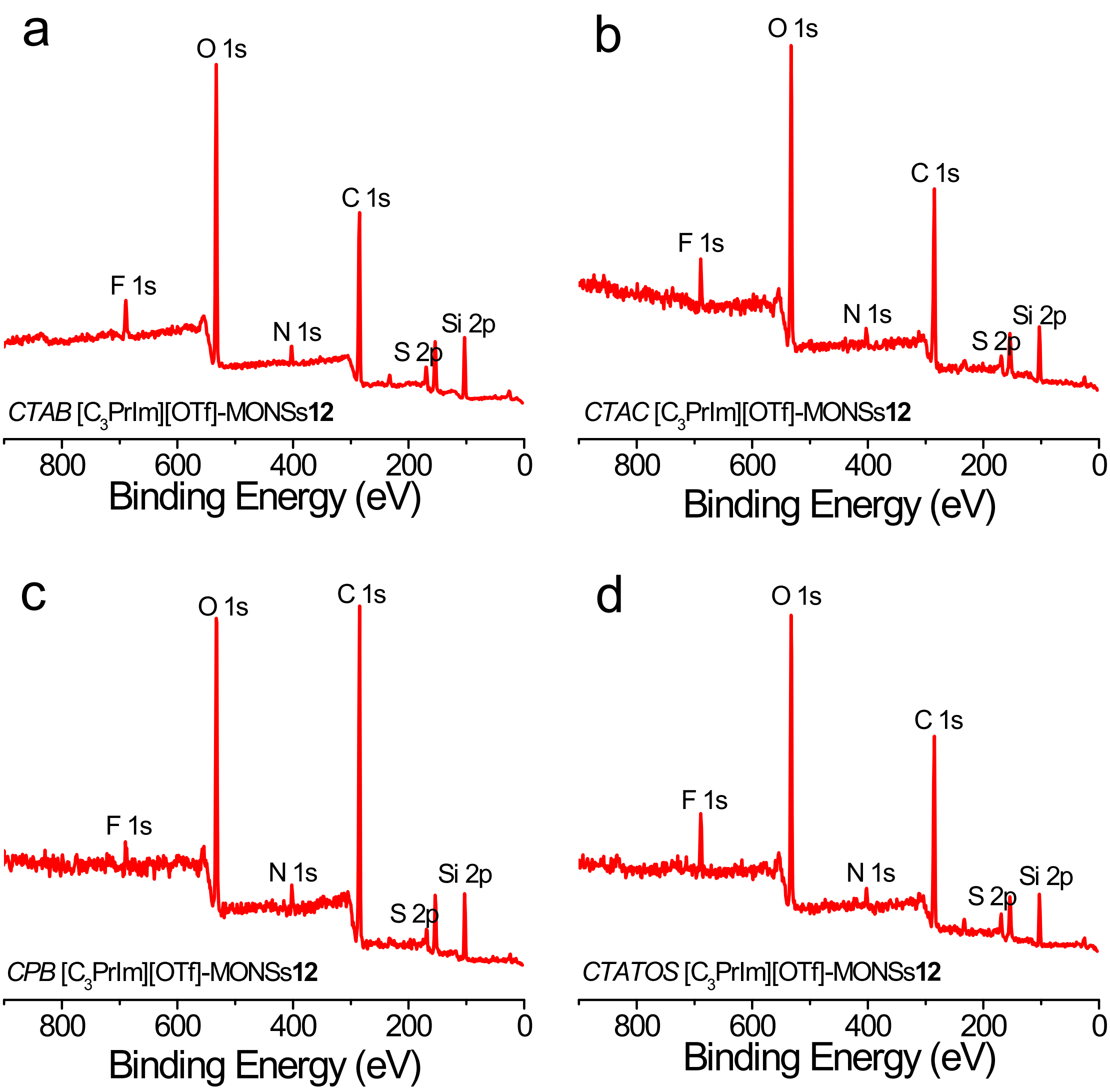
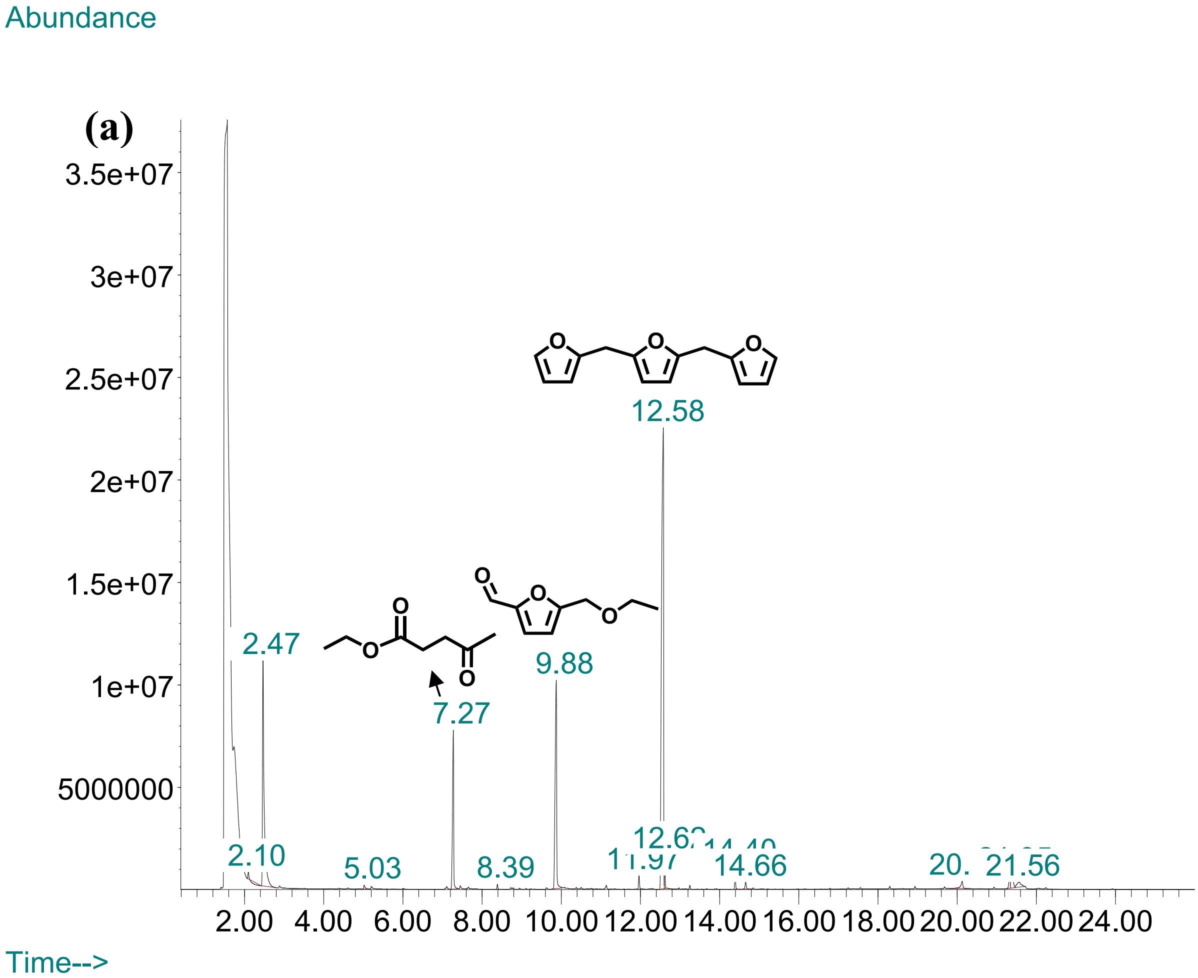
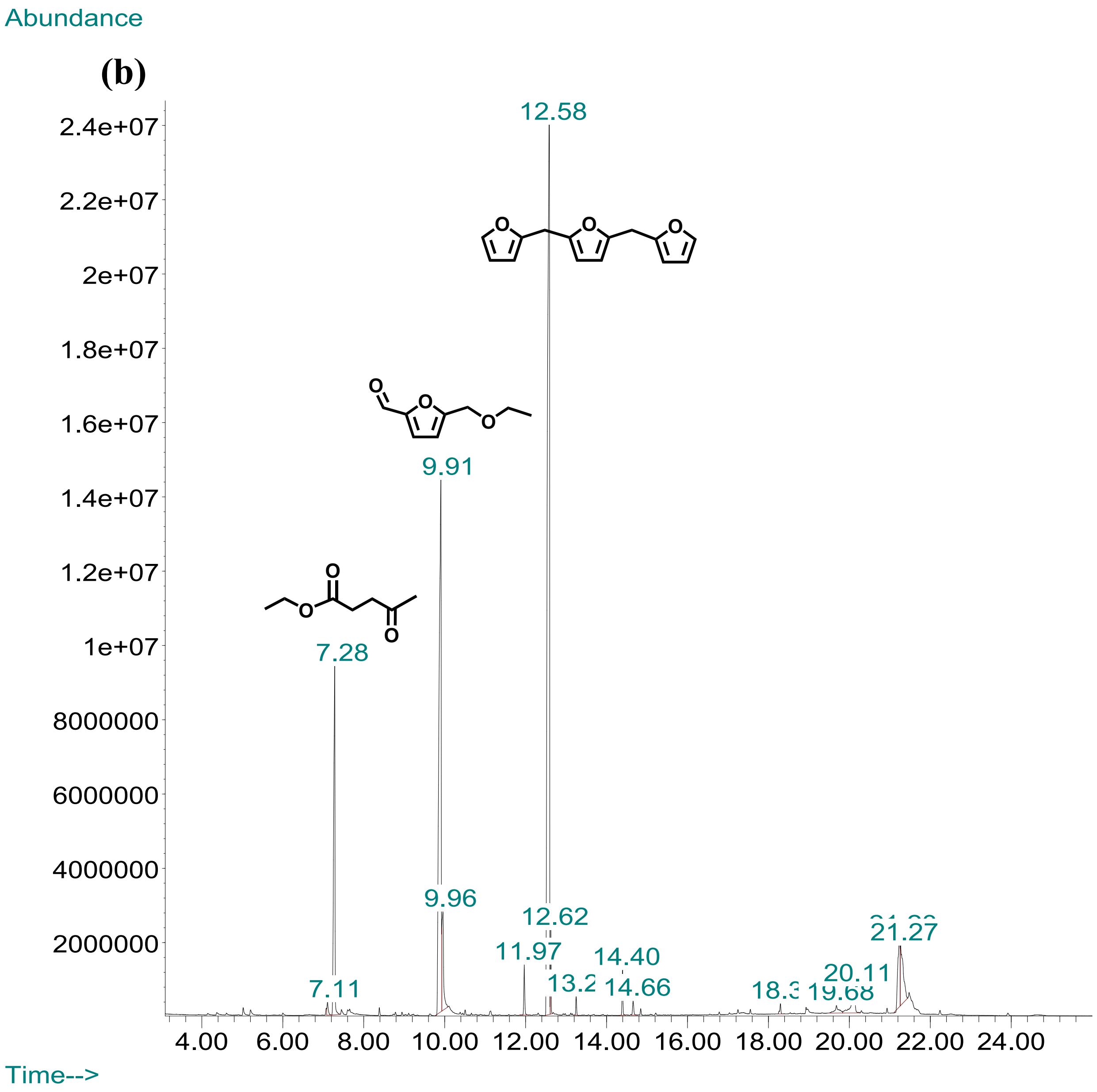
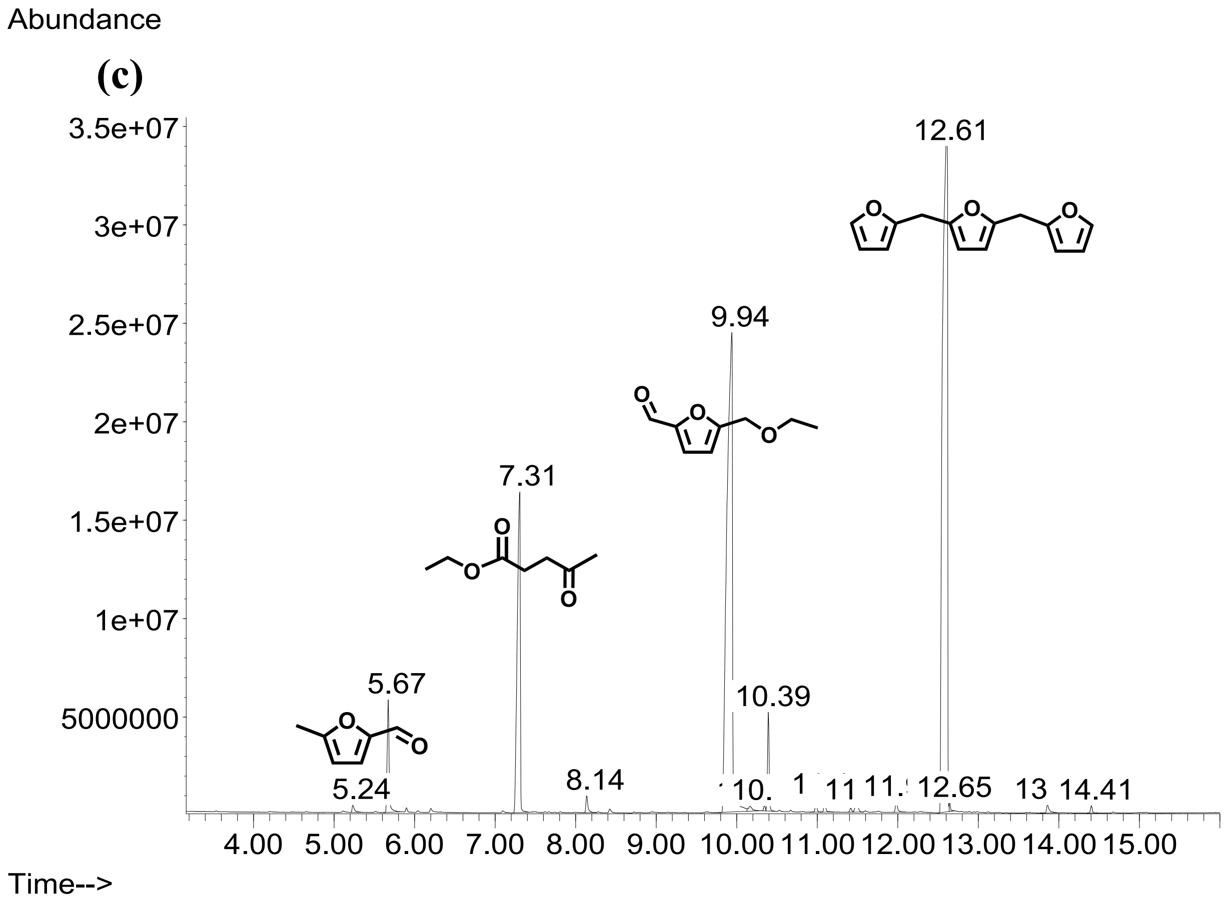


Fig. S4 GC-MS analysis results of ethanolysis of HMF to produce EL catalyzed by the *CTATOS* [C_3PrIm][OTf]-MONSs**12** under different conditions (a and b), *CATB Pr*SO_3H-MONSs**12** (c) and HY zeolite (d). Reaction conditions: (a) 140 °C, n_{EtOH}: n_{HMF} = 248, 120 min; (b) 120 °C, n_{EtOH}: n_{HMF} = 124, 120 min; (c, d) 120 °C, n_{EtOH}: n_{HMF} = 248, 120 min.

HP6890GC-5973MSD was equipped with HP-5MS capillary column (30 m length, 0.25 mm *i.d.,* 0.25 μm film thickness). The GC injector and MS ion source temperatures were 250 °C and 230 °C, respectively. The MS detector was operated in the EI mode at 70 eV with a scanning range of m/z 20–500.




Abundance
(b)
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
12.58
9.91
7.28
9.96
12.62
11.97
14.40
13.2
14.66
7.11
18.3
20.11
19.68
21.27
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
Time-->


Abundance
(c)
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
12.61
9.94
7.31
5.67
10.39
5.24
8.14
10.
1
11
11.
12.65
13
14.41
O
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
Time-->

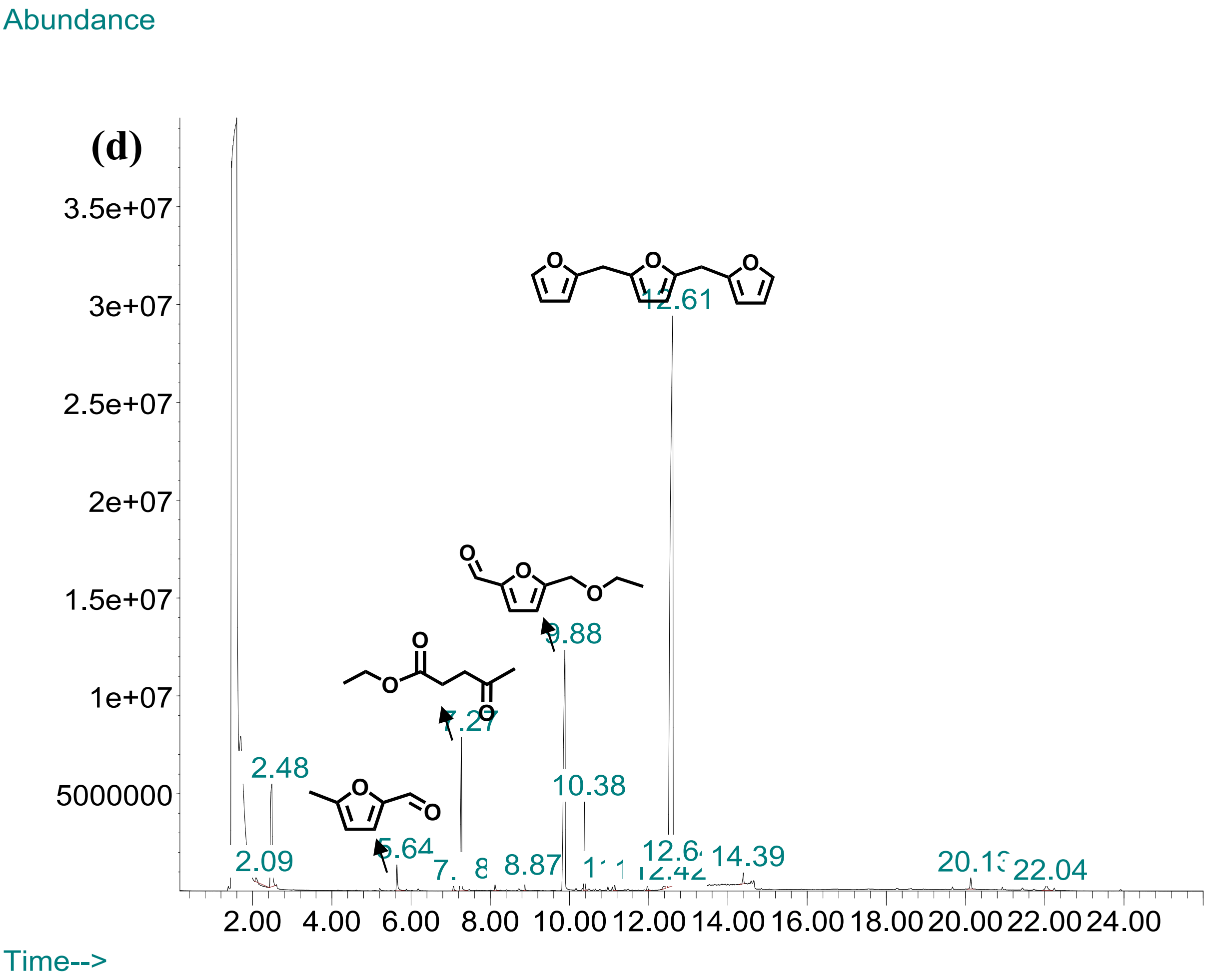

(d)
Abundance
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
12.61
9.88
7.27
2.48
10.38
5.64
2.09
8.87
12.6
12.42
14.39
20.1
22.04
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
Time-->

Fig. S5 Arrhenius plot to determine the activation energy in *CTAB* [C_3PrIm][OTf]-MONSs**12**-catalyzed ethanolysis reaction of HMF. 0.278 mmol HMF, 69 mmol EtOH, n_{EtOH}: n_{HMF} = 248, 120 min.

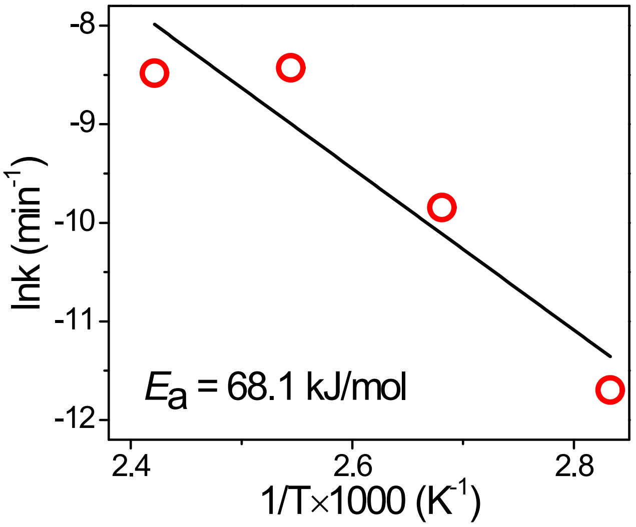
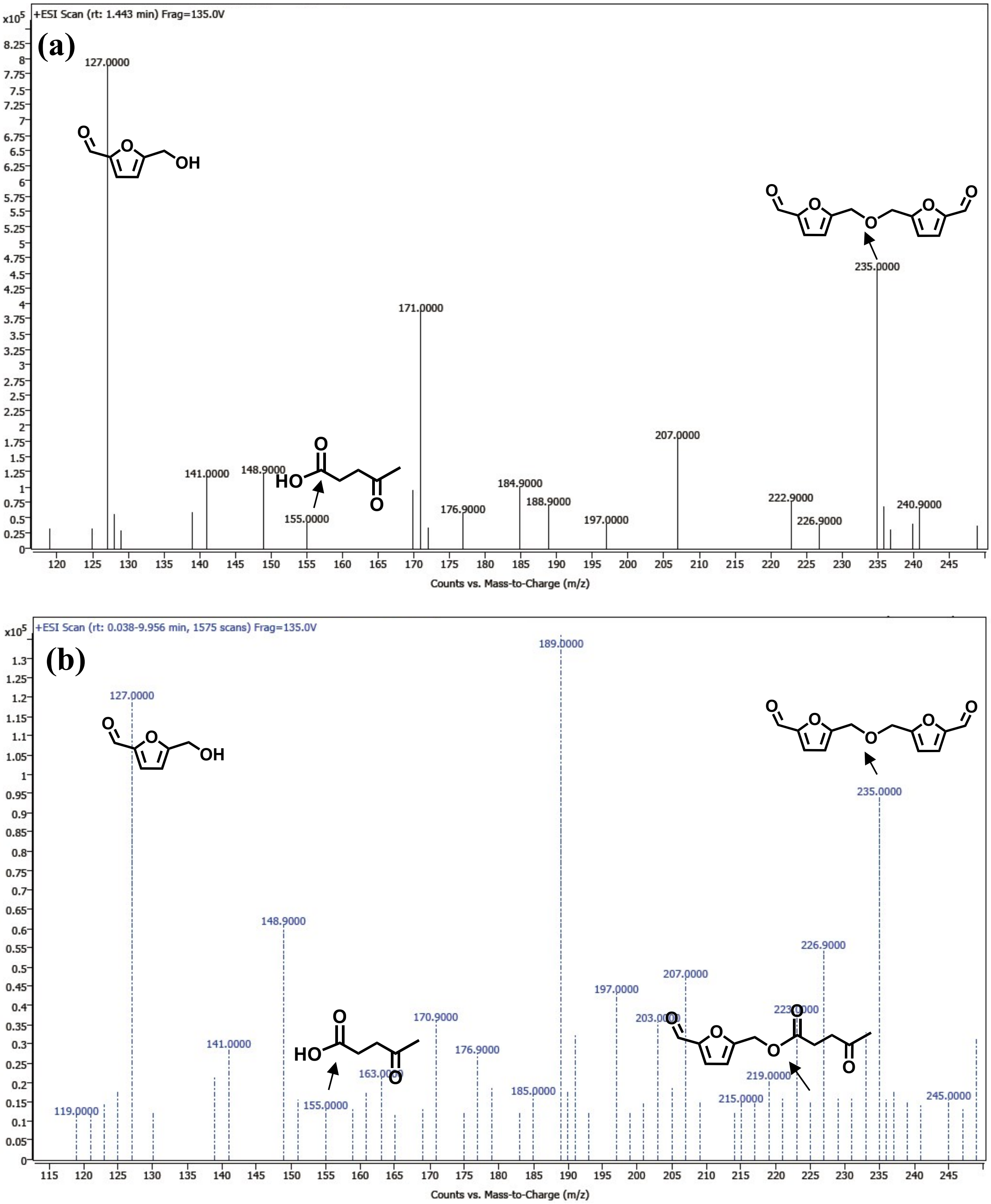
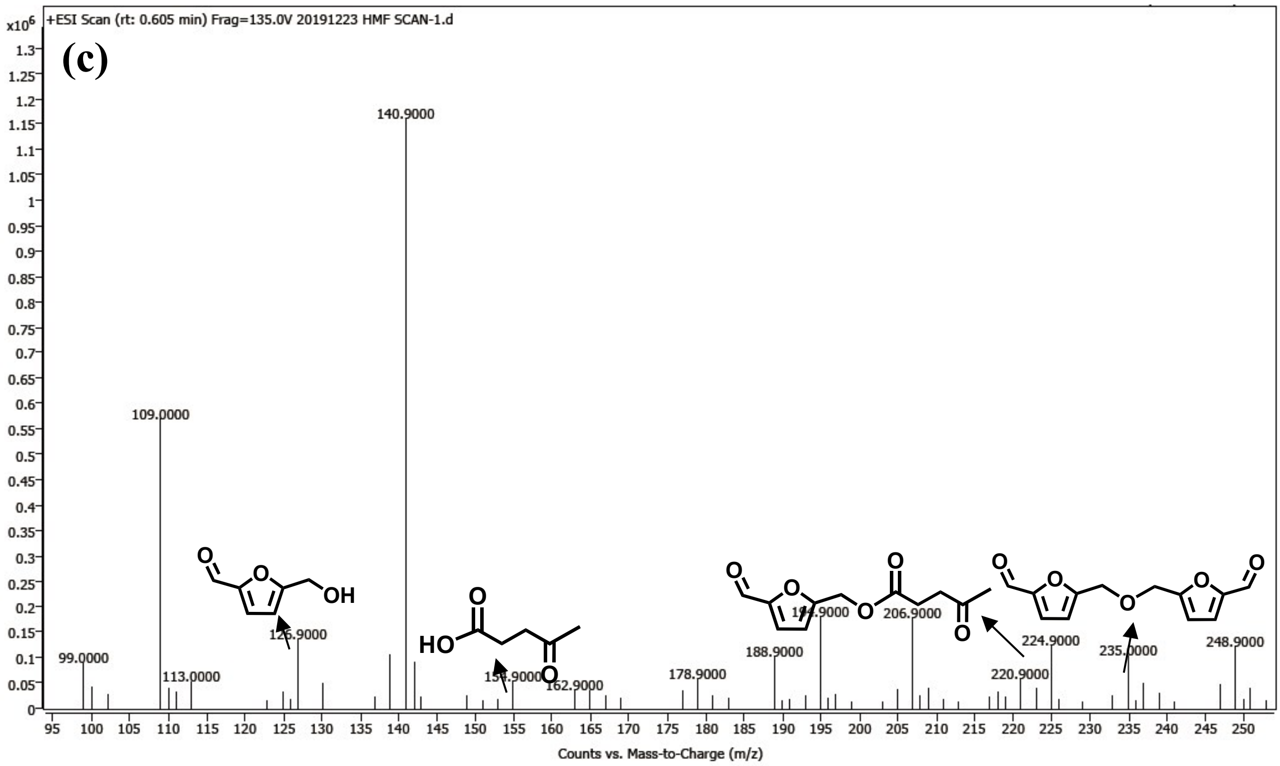
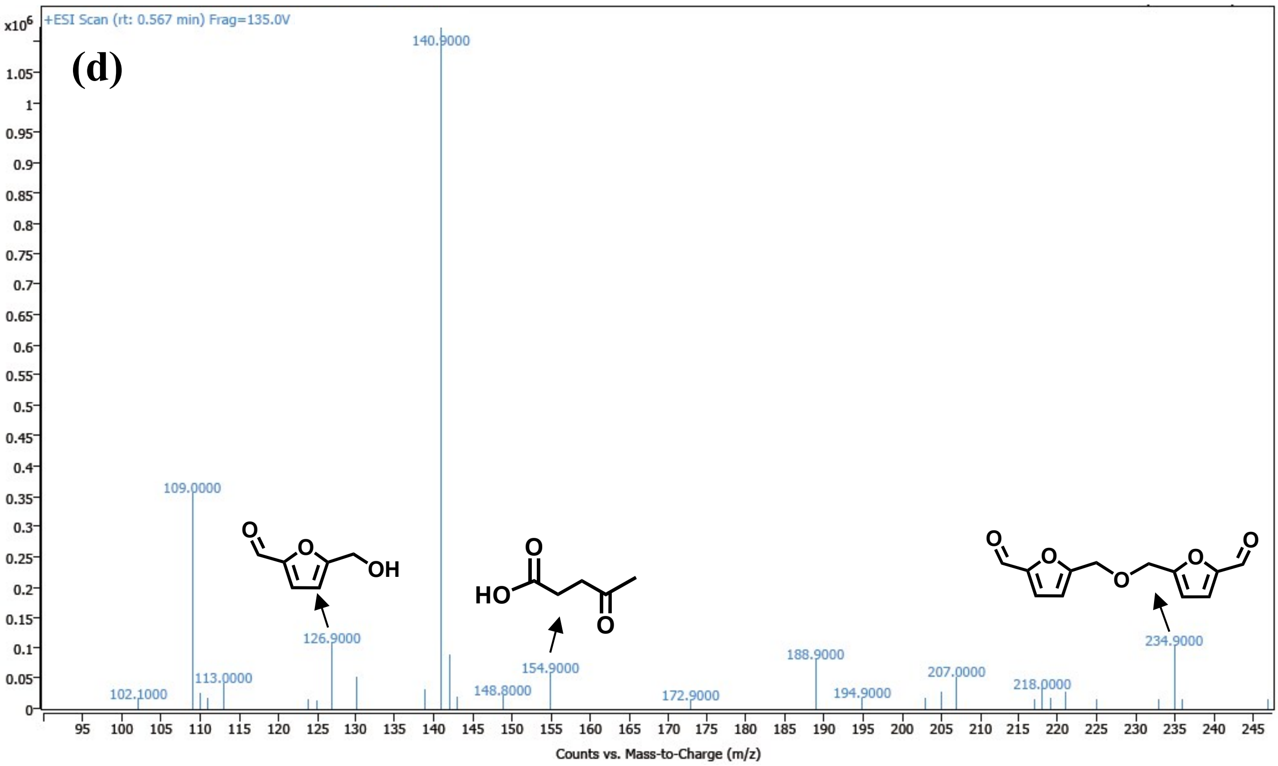


Fig. S6 HPLC-MS analysis result of hydrolysis of HMF to produce LA catalyzed by the *CTATOS* [C_3PrIm][OTf]-MONSs**12** (a-c) and HY zeolite (d). (a) 140 °C, 120 min; (b) 160 °C, 120 min; (c) 140 °C, 240 min; (d) 30 mg HY zeolite, 140 °C, 120 min.





+ESI Scan (rt: 0.605 min) Frag=135.0V 20191223 HMF SCAN-1.d
(c)
x10^6
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
140.9000
109.0000
99.0000
113.0000
126.9000
154.9000
162.9000
178.9000
188.9000
194.9000
206.9000
220.9000
224.9000
235.0000
248.9000
OH
HO
O
95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250
Counts vs. Mass-to-Charge (m/z)



+ESI Scan (rt: 0.567 min) Frag=135.0V
(d)
x10^6
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
140.9000
109.0000
102.1000
113.0000
126.9000
148.8000
154.9000
172.9000
188.9000
194.9000
207.0000
218.0000
234.9000
OH
HO
O
95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245
Counts vs. Mass-to-Charge (m/z)

Fig. S7 Catalytic activity and selectivity of *CTATOS* [C_3PrIm][OTf]-MONSs**12** in ethanolysis (a) and hydrolysis (b) of sugars. (a) 0.278 mmol sugar, 4 mL EtOH, n_{EtOH}: n_{sugar} = 248, 35 mg catalyst, 120 °C, 240 min; (b) 0.4 mmol sugar, 3 mL H_2O, n_{H2O}: n_{sugar} = 417, 50 mg catalyst, 140 °C, 240 min.