The processing details of the reactions in Table 3

Reactions were conducted in 50 mL or 250 mL stainless steel pressure vessels (from kemi company) equipped with a glass liner. All the materials needed for the reaction are weighed and added to the glass liner. After the reaction, all the remaining substances in the reaction vessel and the pressure gauge channel are washed out using ultrapure water and collected. Then the reaction solution volume was adjusted with ultrapure water to 250 mL, and analyzed by UPLC.

The way to calculate the conversion and yield is as follows:

$$w_{LA} = \left(1 - \frac{C_{LA} \times V}{M_{LA} \times n_{LA}}\right) \times 100\%$$

$$w_{PA} = \frac{C_{PA} \times V - m_{PA}}{M_{PA} \times n_{LA}} \times 100\%$$

w_{LA}: conversion of LA
C_{LA} or C_{PA}: LA or PA concentration after reaction (g/L)
V: solvent volume (L)
n_{LA}: initial mole mass of LA (mol)
w_{PA}: yield of PA
m_{PA}: initial PA feed (g)
M_{LA} or M_{PA}: LA or PA molecular mass (g/mol)

The process for purifying PA from I- solution

After the reaction in Table 3 entry 10, the total propionic acid was determined to be 8.9 g (8.0 g solvent + 0.9 g product). An equal volume of cyclohexane (8 mL) was used to extract PA. After standing still, most PA was extracted into cyclohexane, and the aqueous phase with remaining PA was separated for the next cycle. Cyclohexane in the organic phase was evaporated at 45ºC for 20 min, and the residue was dissolved with ultrapure water (final solution). The final solution was analyzed by UPLC (Fig. S3). It was found that 8.2 g propionic acid was extracted (the extraction rate reached 92%). And no NaI was detected. Therefore, PA can be separated through this simple method.

Two-step process description for the preparation of PA from cellulose

The conversion of cellulose to lactic acid was referred to Dong's work[1]. After the reaction, the reaction solution was directly evaporated to dryness at 45°C. Subsequently, 10 mL of acetic acid was added to dissolve the lactic acid (solution A). After measuring the concentration of lactic acid, 8 mL solution A and 1eq. NaI were put into the reactor for the second step using the condition as shown in Scheme 7 (the second step). After the reaction, UPLC was used to determine the final yield of propionic acid.

Table S1 The concentration of metal ions in the reaction solution

Elem	Conc.(ppm)
Ir2242	0.02792
Al1670	0.5851
As1890	-0.03936
B_2497	0.3411
Ba4554	0.5621
Be3130	-0.001093
Bi2230	0.1450
Cd2288	0.1384
Co2286	0.07062
Cr2835	0.07184
Cu3247	0.02564
Fe2599	0.8339
Ga2943	-0.09403
Li6707	0.02166
Mg2795	0.6136
Mn2576	0.08055
Ni2216	0.9558
Pb2203	0.05893
Pd3404	0.009119
Pt2144	-0.01072
Rh3434	-0.05374
Ru2678	0.09911
Sb2068	0.03085
Sn1899	3.212
Sr4077	0.04939
Ti3349	0.2804
Tl1908	-0.3288
V_3093	0.1525
Zn2138	0.1731

Table S2 Conversion of LA by adding $SnCl_2$

Catalyst	Conversion (%)	Yield of AOPA (%)	Yield of PA (%)
$SnCl_2$	92.4	31.3	57.4

Reaction condition: LA 2 mmol, 400 psi H_2, 500 rpm, 1 h, 2 mmol NaI, 0.01 g $SnCl_2$(2.3% eq), 8 ml HAc.

Table S3 PA recovery experiment

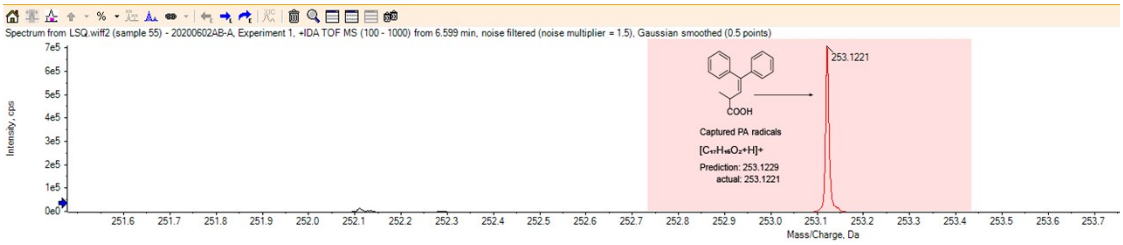
Entry	PA recovery /%
1	99.0
2	100.1
3	99.5

Rection condition: 8 g Propionic acid, 2 mmol NaI, 220^{o}C, 1 h, 400 psi H_2, 500 rpm.

Table S4 Conversion of LA with HAc as solvent

Conversion (%)	Yield of AOPA (%)	Yield of PA (%)
100.0	0.0	93.3

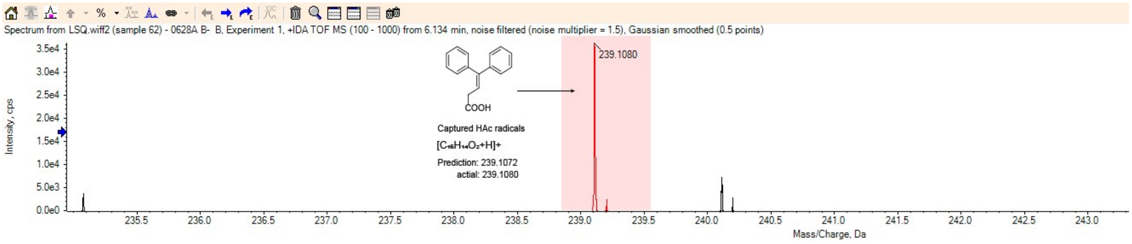
Reaction condition: LA 1.25 g, 1 mmol NaI, 0.3 g H_2O, 400 psi H_2, 8 mL HAc, 220°C, 10 h, 500 rpm.



Spectrum from LSQ.wiff2 (sample 55) - 20200602AB-A, Experiment 1, +IDA TOF MS (100 - 1000) from 6.599 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points)

Fig. S1 MS-QTOF spectrum of the compound formed during the radical capture (Figure S1).

Note: The peak (253.1221) is speculated to be the protonated $C_{17}H_{16}O_2$ ($[C_{17}H_{16}O_2+H]+$), implying that the adduct of $C_3H_6O_2$ and $C_{14}H_{12}$ was generated during the reaction.



Spectrum from LSQ.wiff2 (sample 62) - 0628A B- B, Experiment 1, +IDA TOF MS (100 - 1000) from 6.134 min, noise filtered (noise multiplier = 1.5), Gaussian smoothed (0.5 points)

Fig. S2 MS-QTOF spectrum of the compound formed during the radical capture (Figure S2).

Note: The peak (239.1080) is speculated to be the protonated $C_{16}H_{14}O_2$ ($[C_{16}H_{14}O_2+H]+$), implying that the adduct of $C_2H_4O_2$ and $C_{14}H_{12}$ was generated during the reaction.

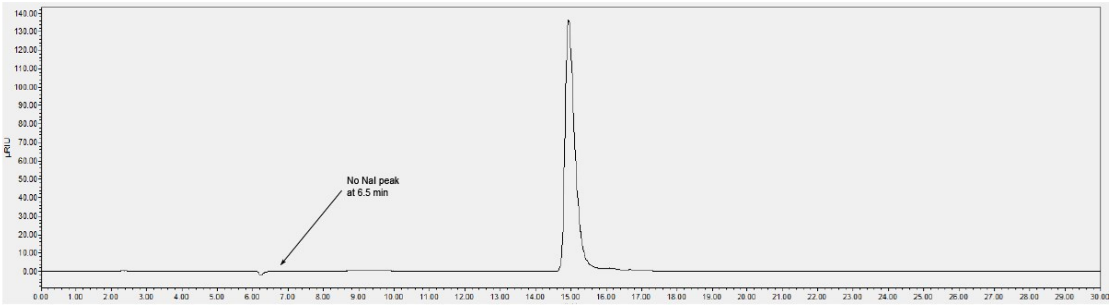


Fig. S3 UPLC spectrum of the aqueous reaction liquid.

Reference:

1. X. Lei, F.-F. Wang, C.-L. Liu, R.-Z. Yang and W.-S. Dong, *Applied Catalysis A: General*, 2014, **482**, 78-83.