Supporting Information

Constructing a chemoenzymatic strategy for enhancing the efficiency of selectively transforming 5-hydroxymethylfurfural to furan carboxylic acid

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1. General Materials and Methods

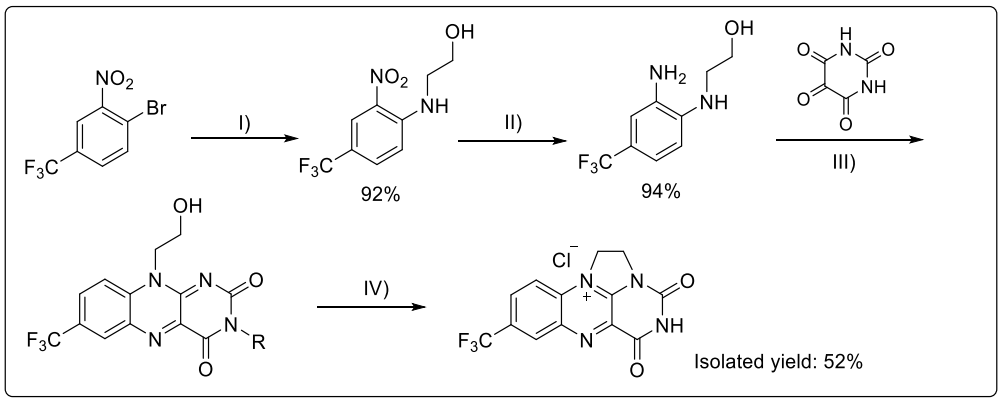
1.1 Materials

The nature flavin cofactor mimic catalysts (NFCMs) was synthesized according to our previous report.[1] Other reagents including NAD(P) $^{+}$, HMF, HMFCA, FFCA, sodium alginate , methacrylic anhydride, N-Ethyl-N'-(3-dimethylaminopropyl)-carbodiimide (EDAC) and N-Hydroxysuccinimide (NHS) were purchased from Aladdin. Galactose oxidase was purchased from Sigma.

1.2 General equipment

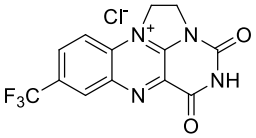
NMR spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer at ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz). HPLC (Waters) was equipped with a Aminex HPX-87H column (300 mm × 7.8 μm) or for product quantification.

1.3 Preparation and characterization of the artificial cofactors.



Scheme S1. General procedure for the synthesis of NFCM [1]. I) 2-aminoethanol, K_2CO_3, EtOH, reflux, 8 h; II) $HCOONH_4$, Pd/C, MeOH, 0 ℃, 1h; III) alloxan monohydrate or N-methyl alloxan monohydrate, $B(OH)_3$, AcOH, 50 ℃, overnight; IV) $SOCl_2$, 50 ℃, 20 h.

7-(Trifluoromethyl)-1,10-ethyleneisoalloxazinium chloride



The catalyst 7-(trifluoromethyl)-1,10-ethyleneisoalloxazinium chloride was synthesized from 4-bromo-3-nitrobenzotrifluoride according to Scheme S1, isolated as yellow solid; ^{1}H NMR (400 MHz, CF_3COOD) δ 9.30 (s, 1H), 8.99 (d, J = 8.6 Hz, 1H), 8.70 (d, J = 8.8 Hz, 1H), 6.10 (t, J = 8.4 Hz, 2H), 5.48 (t, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, CF_3COOD) δ 158.7, 146.2, 144.9, 140.9, 136.7, 135.5 (q, J = 36 Hz, C_7-F), 133.5,

131.4, 131.1, 122.2 (d, J = 271 Hz, CF_3), 118.5, 51.9, 45.9.

1.4. Enzyme preparation, purification and assay

The evolved unspecific peroxygenase from Agrocybe aegerita (rA*ae*UPO) (EC 1.11.2.1) was expressed in *Pichia. pastoris* and purified as described previously.[1] The yeast culture containing rA*ae*UPO was clarified by centrifugation at 10000 rpm for 1 hour at 4 ℃. The supernatant was filtered through a 20 μm filter and concentrated and dialyzed against 100 mM sodium phosphate, pH 7.0. Then the saturated ammonium sulfate solution was slowly added to give a 40% saturated solution at 4 ℃. The suspension was again centrifuged at 12000 rpm for 30 min at 4 ℃ to discard precipitated protein. The supernatant was concentrated with 30 kDa ultrafiltration tubes and then washed with 50 mM sodium phosphate buffer, pH 7.0 and stored at -80 ℃. The activity of rA*ae*UPO was 270 ±5 U mg^{-1} (pH 5.0 in Kpi buffer). One unit of the enzyme activity was defined as the amount of the enzyme catalyzing the oxidation of 1 μmol of ABTs per minute.

The preparation, purification and assay of alcohol dehydrogenase (ADH) (gene ID: 100034242) from horse liver was conducted according to our previous report [2]. The protein concentration was determined by the Bradford method using bovine serum albumin as standard.

1.5 Hydrogel preparation

Firstly, 1 g sodium alginate was dissolved in 50 mL deionized water and followed by 7.14 mL methacrylic anhydride. The pH of the mixture was adjusted to 8.0 with 5 mol/L NaOH solution, and then the reaction solution was stirred at 0℃ for 24 h (600 rpm/min). When the reaction was over, the polymer product was washed with ethanol, and then dried in vacuum at 40℃ for 6 h to obtain double-bond sodium alginate (SA-MA). Finally, the hydrogel material was obtained by adding 2 mg of photoinitiator lithium phenyl phosphate to 5% w/v sodium alginate solution, and then irradiating the solution with 405 nm blue light for 3 min.

1.6 Enzyme immobilization

The enzyme hydrogel preparation process has been reported in our previous work.[2] Before the enzyme immobilizing, the synthetic hydrogel material was activated by using the mixture solution of EDAC (1 g/L) and NHS (2 g/L) for 2 h. Then, 1 g hydrogel material was washed in water for three times and added into 5 mL of 2 g/L enzyme solution. The mixture was shaken thoroughly and left to rest for 2 hours. Finally, the enzyme is smoothly fixed to the material,

and then washed and preserved in n-hexane.

1.7 Calculation of enzyme immobilization efficiency

The detailed calculation formula is as follows:

$$\text{Immobilization efficiency (\%)} = \frac{c\ (\text{initial}) - c\ (\text{free})}{c\ (\text{initial})}$$

The *c (initial)* was defined as the initial concentration of enzyme.

The *c (free)* was defined as the concentration of free enzyme after immobilization.

1.8 Quantification of the components in the reaction solution

The detailed calculation formula is as follows:

$$\text{Pecentage (\%)} = \frac{c\ (\text{compound})}{c\ (\text{initial})}$$

The *c* (compound) was defined as the concentration of corresponding compound.

The *c* (initial) was defined as the initial concentration of substrate.

1.9 TON of enzymes

The detailed calculation formula is as follows:

$$\text{TON} = \frac{c\ (\text{product})}{c\ (\text{enzyme})}$$

The *c* (product) was defined as the final concentration of target product in the reaction.

The *c* (enzyme) was defined as the total concentration of enzymes used in the reaction.

1.10 The detection method for reaction

Conditions: HPLC (waters) was equipped with a Aminex HPX-87H column (300 mm × 7.8 μm) for product quantification. The injection volume was 10 μL with an autosampler. Mobile phase: 5 mM H_2SO_4 aqueous solution, Flow rate = 0.5 mL/min. The temperature is 50 ℃. The UV detection wavelength is 268 nm.

Substrate	Retention time (min)
HMF	30.8
DFF	38.3
HMFCA	20.8
FFCA	21.4
FDCA	15.3

1.11 Methods for detection of H_2O_2

Electrochemical method:

A self-assembled Prussian Blue (PB) modified electrode was used according to previous literature[1]. The 30 μL aliquots were taken at periodic intervals and added into vessel of electrochemical workstation. The concentration of H_2O_2 was determined according to the fluctuation of the electrical signal.

1.12 The oxidation of HMF and its derivatives by HLADH-NFCM system

0.1 mM NAD^+, 0.02 mM NFCM, 10 mM HMF, 2 μM HLADH were added into 1 mL phosphate buffer (50 mM, pH 7.0) in turn and shaken for 2 h at 30 ℃. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was s further identified by HPLC.

1.13 The oxidation of HMF and its derivatives by UPO-NFCM system

10 mM NADH, 0.1 mM NFCM, 10 mM substrate, 1 μM rA*ae*UPO were added into 1 mL phosphate buffer (50 mM, pH 7.0) in turn and shaken for 2 h at 30 ℃. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was s further identified by HPLC.

1.14 The selectivity oxidation of HMF catalyzed by chemoenzymatic system.

Condition for HMFCA: 0.1 mM NAD^+, 0.02 mM NFCM, 10 mM HMF, 2 μM HLADH and 1 μM rA*ae*UPO were added into 1 mL phosphate buffer (50 mM, pH 7.0) in turn and stirred (800 rpm) for 2 h at 30 ℃. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was s further identified by HPLC.

Condition for FFCA: The one-pot, two-step method was applied. A mixture of HMF (10 mM), NAD^+ (0.1 mM), NFCM (0.02 mM) and were prepared in 50 mM phosphate buffer (pH 7.0). The reactions were initiated by the addition of HLADH solution (80 nM) and rA*ae*UPO solution (100 nM) in a total of 1 mL of aqueous medium. After HMF was completely transformed, HLADH and UPO were inactivated at high temperature, and then GOase (5 μM) was added. Reaction mixtures (1 mL) were shaken at 300 rpm in 2 mL centrifuge tube vessels at 30 °C. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was s further identified by HPLC.

Condition for FDCA: The one-pot, two-step method was applied. A mixture of HMF (10 mM), NAD^+ (0.1 mM), NFCM (0.02 mM) and were prepared in 50 mM phosphate buffer (pH 7.0). The reactions were initiated by the addition of HLADH solution (80 nM) and rA*ae*UPO solution (100 nM) in a total of 1 mL of aqueous medium. After HMF was completely transformed, the GOase (5 μM) was added. Reaction mixtures (1 mL) were shaken at 300 rpm in 2 mL centrifuge tube vessels at 30 °C. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was s further identified by HPLC.

1.15 The selective oxidation of HMF catalyzed by immobilized enzymes.

Condition for HMFCA: 0.1 mM NAD^+, 0.02 mM NFCM, 10 mM HMF were added into 2 mL phosphate buffer (50 mM, pH 7.0) in turn. The reactions were initiated by the addition of immobilized HLADH (160 nM) and rA*ae*UPO (200 nM), the mixture was stirred for 2 h at 30 ℃. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was further identified by HPLC.

Condition for FFCA: The one-pot, two-step method was applied. A mixture of HMF (10 mM), NAD^+ (0.1 mM), NFCM (0.02 mM) were added into 2 mL phosphate buffer (50 mM, pH 7.0) in turn. The reactions were initiated by the addition of immobilized HLADH (160 nM) and rA*ae*UPO (200 nM), the mixture was stirred at 30 ℃. After HMF was completely transformed, immobilized HLADH and rA*ae*UPO were taken out and washed for next batch, and the immobilized GOase (2 μM) was added. Reaction mixtures (2 mL) were shaken at 300 rpm in 5 mL centrifuge tube vessels at 30 °C. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was s further identified by HPLC. When the reaction is over, the enzymes are removed and washed to be used in another batch.

Condition for FDCA: The one-pot, two-step method was applied. A mixture of HMF (10 mM), NAD^+ (0.1 mM), NFCM (0.02 mM) were added into 2 mL phosphate buffer (50 mM, pH 7.0) in turn. The reactions were initiated by the addition of immobilized HLADH (320 nM) and rA*ae*UPO (300 nM), the mixture was stirred for 2 h at 30 ℃. After HMF was completely transformed, the GOase (3 μM) was added. Reaction mixtures (1 mL) were shaken at 300 rpm in 5 mL centrifuge tube vessels at 30 °C. Aliquots (100 μL) were taken at intervals and was diluted to 400 μL with water. The sample was s further identified by HPLC. When the reaction is over, the enzymes are removed and washed to be used in another batch.

1.16 Preparative procedure for furan carboxylic acid.

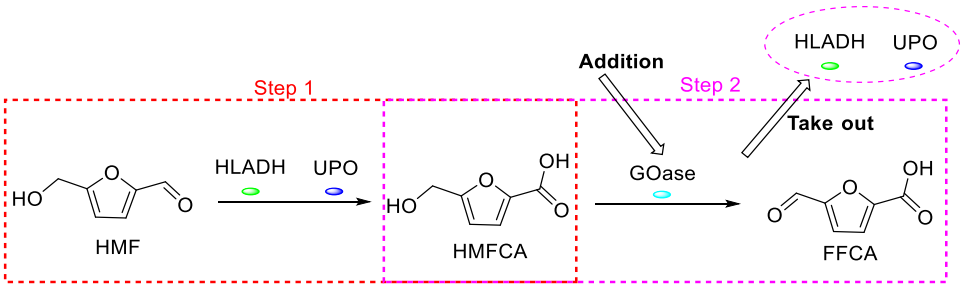
The method for the isolation of HMFCA and FFCA is according to a protocol from the reported literature [17]. The reaction mixture was heated to 80 °C for 10 min and then frozen to -80 °C. The solid sample was freeze-dried with vacuum dryer to get solid mixture. The solid mixture is dissolved with 50 ml deionized water and centrifuged to remove the enzymes. The supernatant was cooled to 4 °C. The pH of supernatant was adjusted to 1.0 by adding of 50% H_2SO_4, followed by extraction 4 times with ethyl acetate. The organic solvent was removed through evaporation, thereby affording the product. The identity of products was confirmed by HPLC.

The method for the isolation of FDCA is according to a protocol from the reported literature [18]. The reaction mixture was heated to 80 °C for 10 min and then frozen to -80 °C. The solid sample was freeze-dried with vacuum dryer to get solid mixture. The solid mixture is dissolved with 50 mL deionized water and centrifuged to remove the enzymes. The supernatant was cooled to 0 °C and FDCA was precipitated by adding 50% H_2SO_4 for adjusting the pH value to 1.0 at 2°C. The precipitate was obtained by filtration and washed once with ice-cold water. After air dry, the precipitate was re-dissolved in 100 ml of ethyl acetate. Then, the solvent was evaporated, then a dry powder was obtained. The identity of products was confirmed by HPLC.

2. Supplementary Figures and Tables

Supplementary Tables

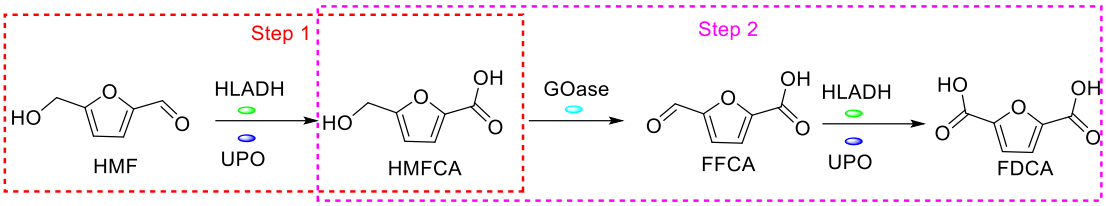
Table S1. The production of FFCA from HMF by immobilized enzymes.



Batch	Time [h]	Yield [%]
1	8	>99
2	8	>99
3	8	98
4	8	>99
5	10	>99
6	10	98

Reaction conditions: 10 mM HMF, 0.02 mM NFCM, 0.1 mM NAD^+, hydrogel containing 400 nM rA*ae*UPO and 320 nM rA*ae*UPO or 3 μM GOase were added into 2 mL phosphate buffer (50 mM, pH 7.0, 40% acetonitrile v/v) in turn and shaken for 2 h at 30 ℃. After HMF was completely transformed, HLADH and rA*ae*UPO were taken out and washed for next batch. The yield of FFCA was quantified by HPLC, which was equipped with a Aminex HPX-87H column (300 mm × 7.8μm). The injection volume was 10 μL with an autosampler. Mobile phase: 5 mM H_2SO_4 aqueous solution, Flow rate = 0.5 mL/min. The temperature is 50 ℃. The UV detection wavelength is 268 nm.

Table S2. The production of FDCA from HMF by immobilized enzymes.



Batch	Time [h]	Yield [%]
1	28	98
2	28	>99
3	30	98
4	30	98
5	36	98
6	40	97
7	42	63

Reaction conditions: 10 mM HMF, 0.02 mM NFCM, 0.1 mM NAD^+, hydrogel containing 600 nM rA*ae*UPO and 480 nM rA*ae*UPO or 3 μM GOase were added into 2 mL phosphate buffer (50 mM, pH 7.0, 40% acetonitrile v/v) in turn and shaken for 2 h at 30 ℃. The yield of FFCA was quantified by HPLC, which was equipped with a Aminex HPX-87H column (300 mm × 7.8μm). The injection volume was 10 μL with an autosampler. Mobile phase: 5 mM H_2SO_4 aqueous solution, Flow rate = 0.5 mL/min. The temperature is 50 ℃. The UV detection wavelength is 268 nm.

Table S3. The comparison of synthesis of HMFCA from HMF catalyzed by different enzymatic systems

Entry	Enzyme	TON	$c_{(enzyme)}$ [μM]	Space-time yield [$g_{product}$ L^{-1} d^{-1}]	Atom efficiency [%][a]	Selectivity [%]	E-factor[b]	ref
1	HLADH	5333	2	0.51	88	81	7.2	3
2	ScCR	4167	33	3.15	89	96	4.7	4
3	Cal-B	126	250	5.04	88	80	6.65	5
4	BovALDH/*E* *c*ALDH, NOX	1600	15	2.29	89	91	3.2	6
5	HLADH, rA*ae*UPO	**55000**	**0.18**	**2.52**	**100**	**99**	**2.7**	**This work**

[a]The atom efficiency (%) was calculated according to the following formula [13,14]:

$$Atom\ \ efficiency\ (\%) = \frac{Weight\ of\ atom\ utilited}{Weight\ of\ reatants\ used\ in\ the\ reaction}$$

[b]The E factor was determined as weight of the waste per kg of product according to the reported literature [15,16].

$$E\text{-factor} = \frac{\sum m(catalysts) - m(product)}{\sum m(product)}$$

Table S4. The comparison of synthesis of FFCA from HMF catalyzed by different enzymatic systems

Entry	Enzyme	TON	$C_{(enzyme)}$ [μM]	Space-time yield [$g_{product}$ L^{-1} d^{-1}]	Atom efficiency [%][a]	Selectivity [%]	E-factor[b]	ref
1	laccase	461	40	3	89	82	2.2	7
2	CotA-TJ102	6500	-	2.66	89	98	3.3	8
3	*Pe*AAO	600	5	2.52	70	98	15	9
4	SADH, HRP, scopoletin	1385	69	6.86	89	97	-[c]	4
5	HLADH, rA*ae*UPO, GOase	8250	**1.2**	**1.35**	**80**	**99**	**2.9**	**This work**

[a]The atom efficiency (%) was calculated according to the following formula [13,14]:

$$Atom\ \ efficiency\ (\%) = \frac{Weight\ of\ atom\ utilited}{Weight\ of\ reatants\ used\ in\ the\ reaction}$$

[b]The E-factor was determined as weight of the waste per kg of product according to the reported literature. [15,16]

$$E\text{-factor} = \frac{\sum m(catalysts) - m(product)}{\sum m(product)}$$

[c]Incalculable due to unknown products.

Table S5. The comparison of synthesis of FDCA from HMF catalyzed by different enzymatic systems

Entry	Enzyme	TON	$c_{(enzyme)}$ [μM]	Space-time yield [$g_{product}$ L^{-1} d^{-1}]	Atom efficiency [%][a]	Selectivity [%]	E factor[b]	ref
1	PeAAO I500M/F501W, CAT	400	0.5	0.2	60	50	5.7	10
2	*Pe*AAO, *Aa*UPO	300	5.65	0.08	78	90	13	9
3	GO M_{3-5}, HRP, CAT, PaoABC	112	42	46.8	75	99	0.6	11
4	DdGO, HLADH, HRP, scopoletin	1696	55	0.6	82	95	-[c]	4
5	GO, *Pe*AAO, *Aa*UPO	400	17	1	78	80	5.2	12
6	HLADH, rA*ae*UPO, GOase	**8250**	**1.2**	**1.4**	**89**	**99**	**2.58**	**This work**

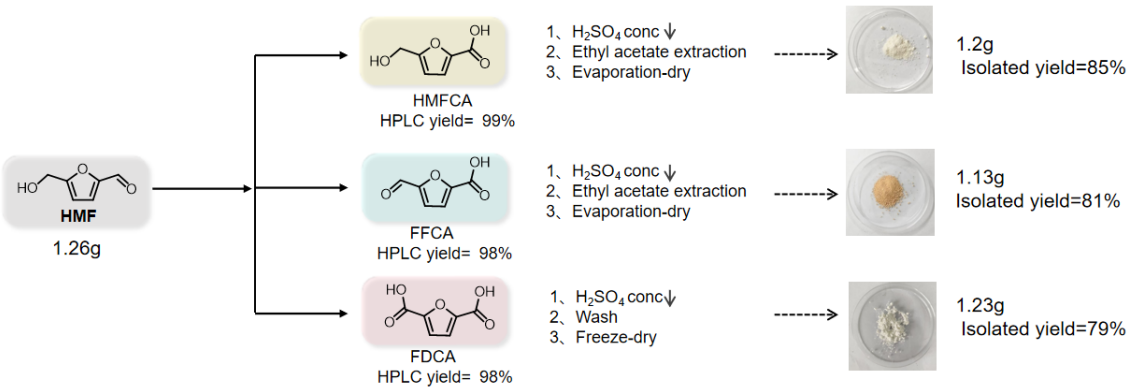
[a]The atom efficiency (%) was calculated according to the following formula [13,14]:

$$Atom\ \ efficiency\ (\%) = \frac{Weight\ of\ atom\ utilited}{Weight\ of\ reatants\ used\ in\ the\ reaction}$$

[b]The E-factor was determined as weight of the waste per kg of product according to the reported literature. [15,16]

[c] Incalculable due to unknown products.

Table S6. Semi-preparative systhesis of furan carboxylic acids from HMF



Entry	Substrate	Product	HPLC yield [%]	Isolated yield [g] (%)
1[a]	HMF	HFMCA	99%	1.2 (85)
2[b]	HMF	FFCA	98%	1.13 (81)
3[c]	HMF	FDCA	98%	1.23 (79)

[a]For HMFCA. Reaction conditions: 0.1 mM NAD^+, 0.02 mM NFCM, 10 mM HMF, 0.16 μM HLADH and 0.2 μM rA*ae*UPO were added into 1 L phosphate buffer (50 mM, pH 7.0) in turn.

[b]For FFCA. After HMF was completely transformed, HLADH and rA*ae*UPO were taken out and 2 μM GOase was added, the mixture was shaken at 30 ℃ (300 rpm).

[c]For FDCA. Reaction conditions: 0.24 μM HLADH and 0.3 μM rA*ae*UPO were used.

Supplementary Figures

2.1 The effect of the continuous addition of H_2O_2 on reactions

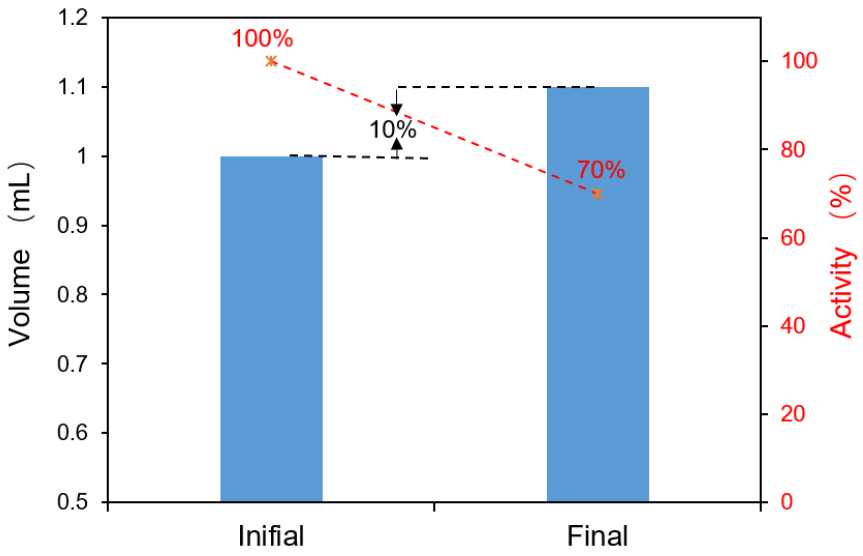


Figure S1. The effect of the continuous addition of H_2O_2 on reactions.

2.2 The influence of pH on the efficiency of the chemoenzymatic reaction

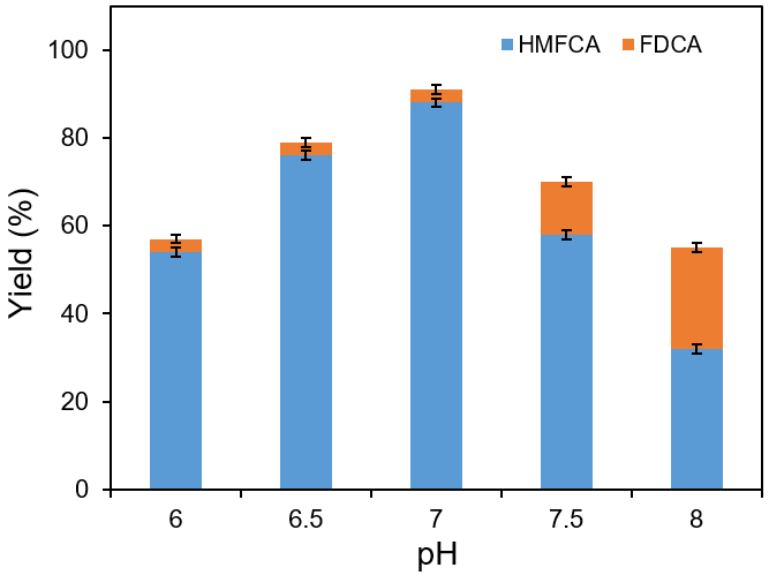


Figure S2. Reaction conditions: 10 mM HMF, 0.02 mM NFCM, 0.1 mM NAD^+, 2μM HLADH and 1 μM rA*ae*UPO were added into 2 mL phosphate buffer (50 mM, pH 6.0, 6.5, 7.0, 7.5,8.0) in turn and shaken for 2 h at 30 ℃.

2.3 The influence of concentration of rA*ae*UPO on the efficiency of the chemoenzymatic reaction

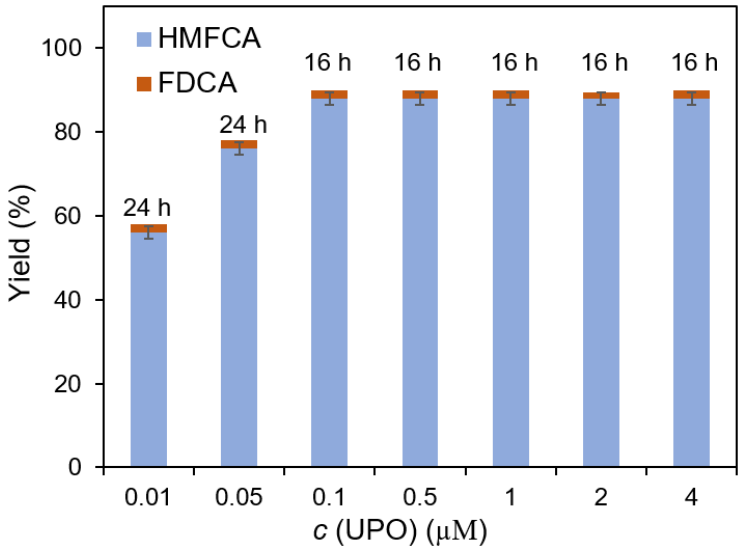


Figure S3. Reaction conditions: 10 mM HMF, 0.02 mM NFCM, 0.1 mM NAD^+, 2μM HLADH and 0.01-4 μM rA*ae*UPO were added into 2 mL phosphate buffer (50 mM, pH 7.0) in turn and shaken for 2 h at 30 ℃.

2.4 The influence of concentration of HLADH on the efficiency of the chemoenzymatic reaction

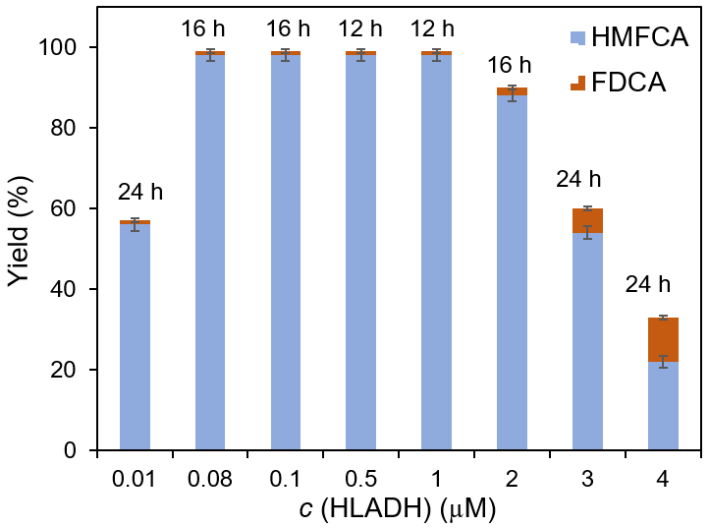


Figure S4. Reaction conditions: 10 mM HMF, 0.02 mM NFCM, 0.1 mM NAD^+, 0.01-4μM HLADH and 0.1 μM rA*ae*UPO were added into 2 mL phosphate buffer (50 mM, pH 7.0) in turn and shaken for 2 h at 30 ℃.

2.5 The influence of concentration of NFCM on the efficiency of the chemoenzymatic reaction

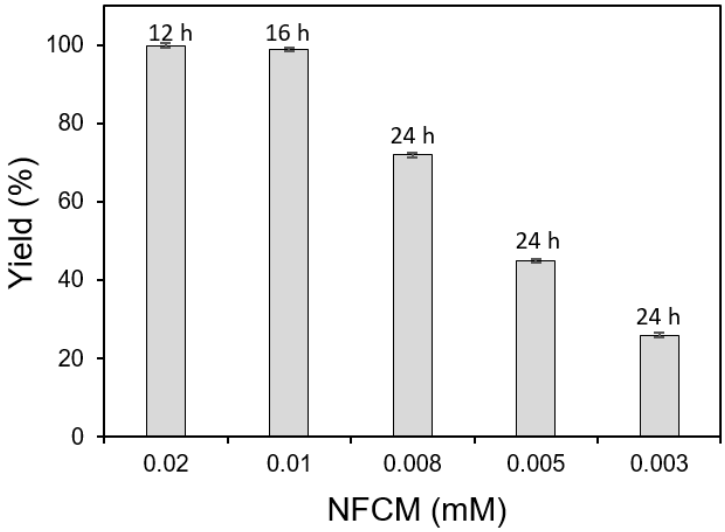


Figure S5. Reaction conditions: 10 mM HMF, 0.003-0.02 mM NFCM, 0.1 mM NAD^+, 0.08 μM HLADH and 0.1 μM rA*ae*UPO were added into 2 mL phosphate buffer (50 mM, pH 7.0) in turn and shaken for 2 h at 30 ℃.

2.6 The characterization of hydrogel material

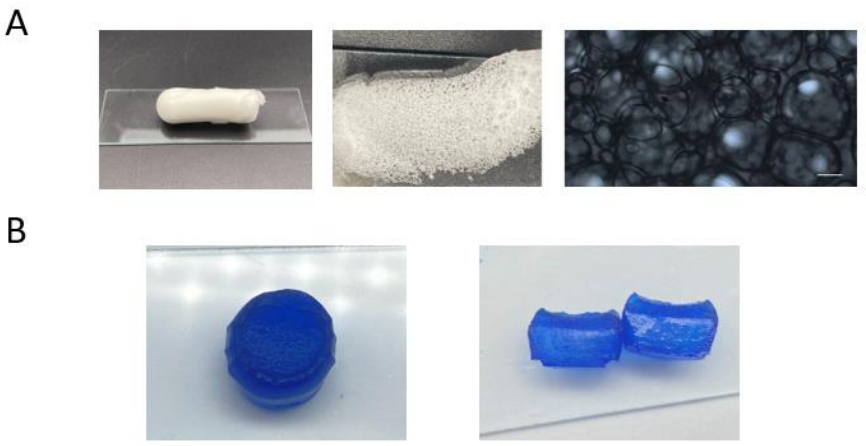


Figure S6. A) Microscopic structure of hydrogel material before immobilization; B) hydrogel material after enzyme immobilization and coomassie blue staining.

2.7 The oxidation of HMFCA catalyzed by GOase.

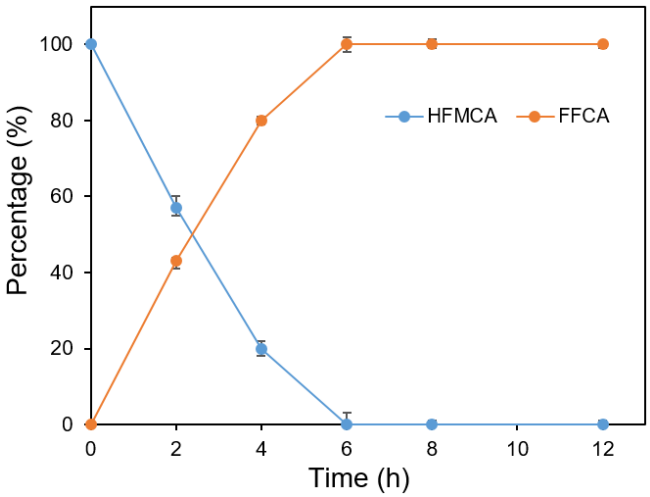


Figure S7. The oxidation of HMFCA catalyzed by GOase. Reaction conditions: 10 mM HMFCA, 5 μM GOase were added into 2 mL phosphate buffer (50 mM, pH 7.0) in turn and shaken for 12 h at 30 ℃.

2.8 Leaching retention ratio of immobilized enzyme from the hydrogel

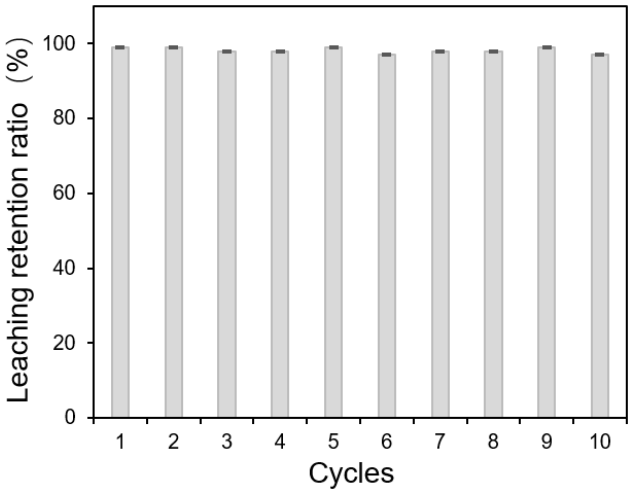


Figure S8. The leaching retention ratio of immobilized enzyme from the hydrogel. Conditions: 1 g of immobilized enzyme was soaked in 2 ml PBS buffer and left for 1 h to determine the amount of leached enzyme in the solution.

$$\text{Leaching retention ratio (\%)} = (E_1\text{-}E_2) / E_1$$

E_1 : The initial amount of enzyme contained in 1g of immobilized enzyme;
E_2 : The amount of free enzyme leached in solution.

2.9 The expansion and reuse of soluable rA*ae*UPO-HLADH system.

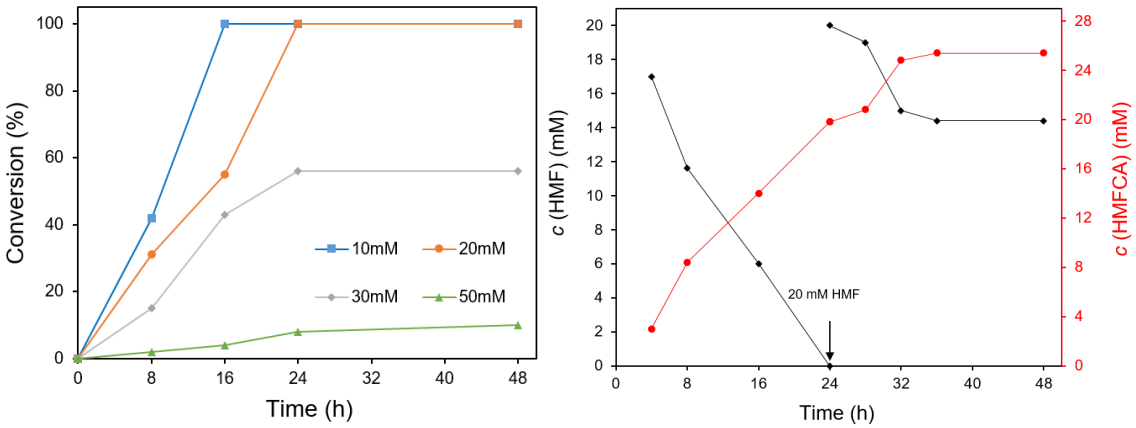


Figure S9. The the recyclability of soluable rA*ae*UPO-HLADH system.

2.10 Characterization and analysis of oxidation of HMF catalysed by rA*ae*UPO-NFCM system

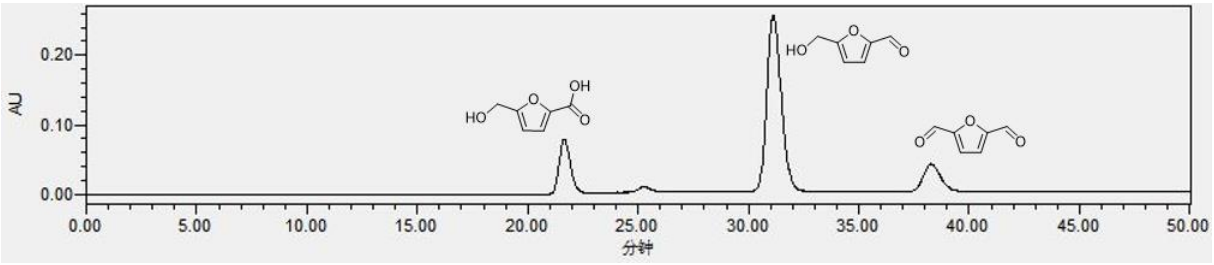


Figure S10. The reaction mixtures were identified by HPLC spectrum after 2 h.

2.11 Characterization and analysis of oxidation of HMF catalysed by rA*ae*UPO-HLADH system

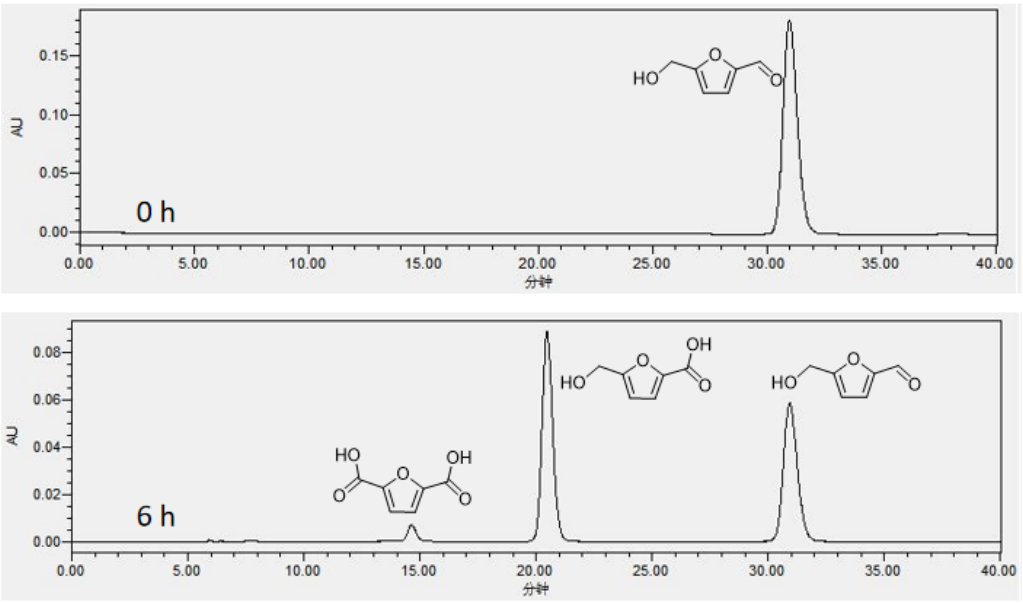


Figure S11. The reaction mixtures were identified by HPLC spectrum.

2.12 Characterization and analysis of oxidation of HMFCA catalysed by GOase

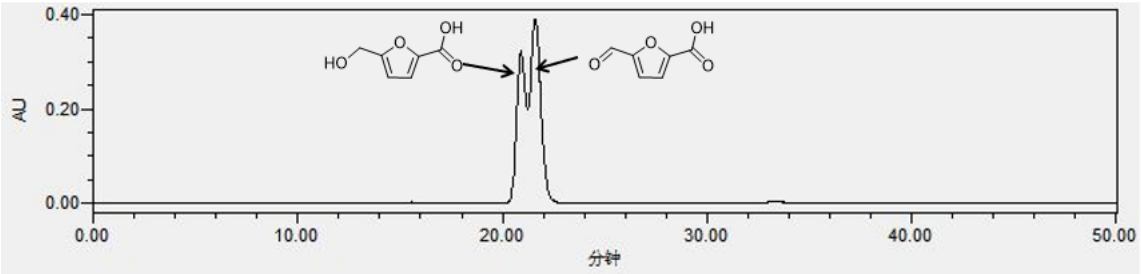


Figure S12. HPLC spectrum of reaction mixture of GOase-catalysed system after 2 h**.**

2.13 Characterization and analysis of oxidation of FFCA catalysed by rA*ae*UPO-HLADH system

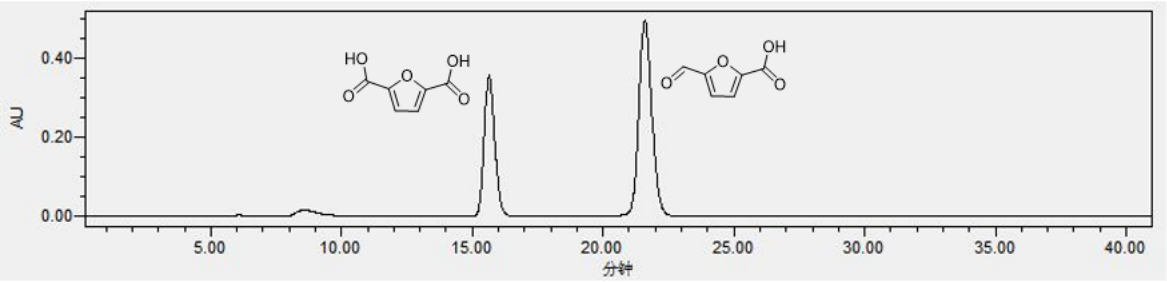


Figure S13. HPLC spectrum of reaction mixture of rA*ae*UPO-HLADH system after 4 h**.**

2.14 Characterization and analysis of oxidation of HMFCA catalysed by rA*ae*UPO-HLADH-GOase system

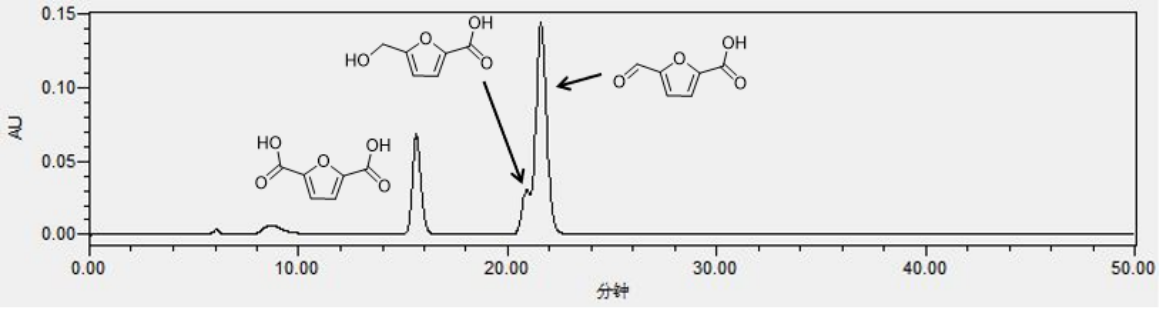
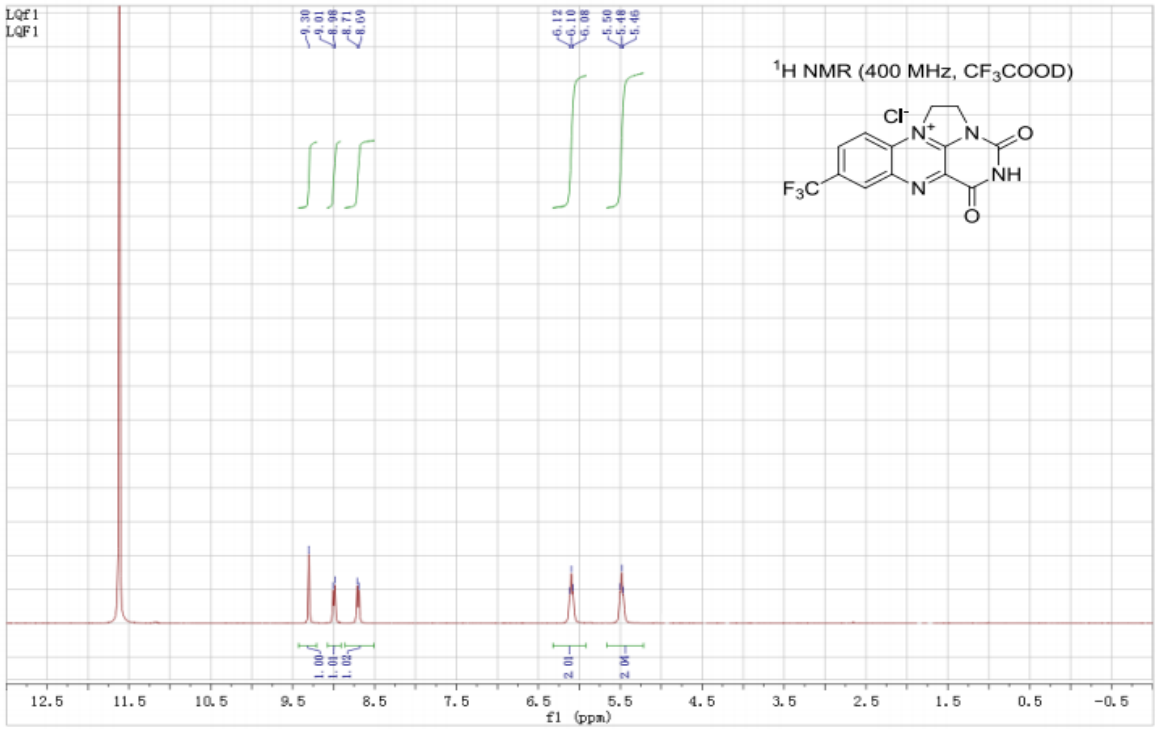


Figure S14. HPLC spectrum of reaction mixture of rA*ae*UPO-HLADH-GOase system after 4 h**.**

3. Spectrum



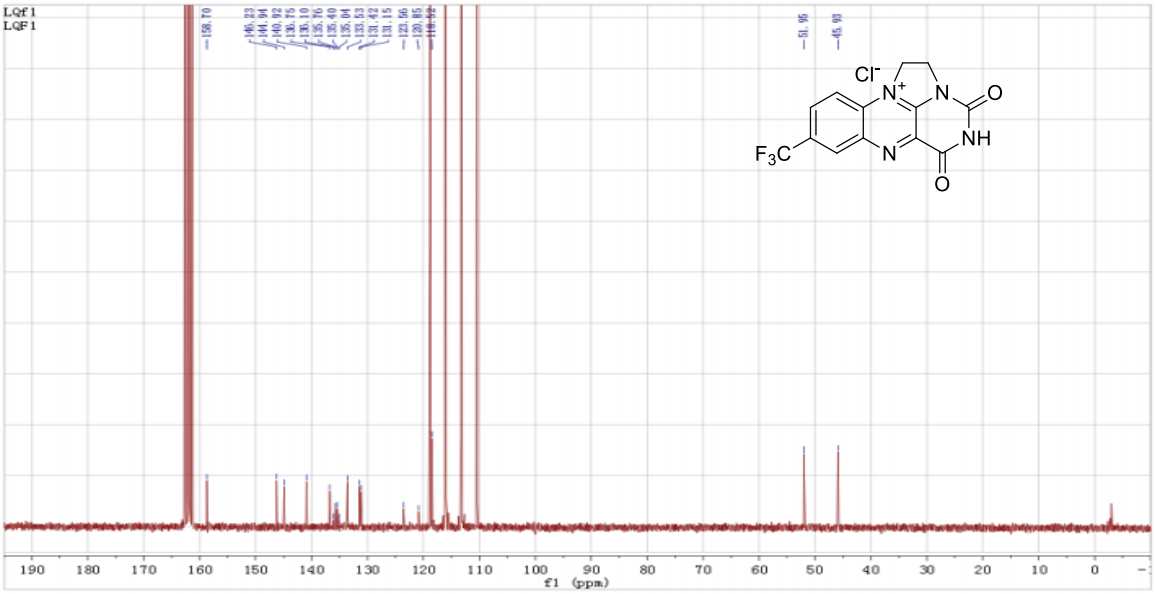


Figure S15. ^{1}H, ^{13}C of NFCM.

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