Supplementary information

A Noble-metal-free Electrocatalytic System for Direct Synthesis of α,β-Unsaturated Carbonyl Solids in Aqueous Solution

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Experimental Procedures

Note S1. Preparation of anode electrocatalysts.

All chemicals are analytical grade and used without further purification.

Synthesis of c-NiFe-LDH powder: Typically, 1.5 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 1.5 mmol $Fe(NO_3)_3 \cdot 9H_2O$, 2 mmol NH_4F, 5 mmol $CO(NH_2)_2$ were dissolved completely in 50 mL of deionized water and stirred at room temperature for 5 minutes. Then the mixed solution was placed in a 100 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 120 °C for 8 h and cooled to room temperature naturally. Next, the mixture in the autoclave was transferred to a 50 ml centrifuge tube. The tubes were put into the centrifuge at 12000 rpm for 3 min. The waste liquid was drained and the left powder was washed by DI water and ethanol, and finally dried in a vacuum oven at 60 °C for 10 h to yield the NiFe-LDH precursor. Finally, the precursor is subjected to calcination at 350 °C for 2 hours under air atmosphere to yield c-NiFe-LDH. The atomic ratios of nickel to iron were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis (Table S1).

Synthesis of c-Ni$_2$Fe-LDH powder: The preparation process was same as that of c-NiFe-LDH, except that 2 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 1 mmol $Fe(NO_3)_3 \cdot 9H_2O$ were added.

Synthesis of c-NiFe$_2$-LDH powder: The preparation process was same as that of c-NiFe-LDH, except that 1 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 2 mmol $Fe(NO_3)_3 \cdot 9H_2O$ were added.

Synthesis of c-Ni(OH)$_2$ powder: The preparation process was same as that of c-NiFe-LDH, except that 3 mmol $Ni(NO_3)_2 \cdot 6H_2O$ were added.

Synthesis of c-Fe(OH)$_3$ powder: The preparation process was same as that of c-NiFe-LDH, except that 3 mmol $Fe(NO_3)_3 \cdot 9H_2O$ were added.

Synthesis of NiMo-LDH powder: The preparation process was same as that of c-NiFe-LDH, except that 1.4 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 0.2 mmol $(NH4)_6Mo_7O_{24} \cdot 4H_2O$ were added without calcination.

Synthesis of CuCoO powder: The preparation process was same as that of c-NiFe-LDH, except that 1 mmol $Cu(NO_3)_2 \cdot 3H_2O$, 2 mmol $Co(NO_3)_2 \cdot 6H_2O$, 3 mmol NH_4F, 6 mmol $CO(NH_2)_2$ were added.

Synthesis of Ni-MOF/NF electrode: Ni sponge (NF) was purchased from Jiangsu AKX Materials Technology Co., Ltd. Ni-MOF was deposited on the Ni sponge by solvothermal process. A piece of Ni sponge (2.0 × 1.0 cm^2) was cleaned with 1 M HCl and acetone under ultrasonication for 30 min to remove the surface oxide layer followed by rinsing with deionized (DI) water. Meanwhile, 0.24 mmol $Ni(CH_3COO)_2 \cdot 4H_2O$, and 0.32 mmol benzene-1,4-dicarboxylate (BDC, $C_8H_6O_4$) were dissolved in 50 mL of DI water and transferred into the autoclave with cleaned NF. The autoclave was sealed and maintained at 150 °C for 20 h. After cooled down to room temperature (RT) naturally, the material was washed by DI water and ethanol for three times, and finally dried in a vacuum oven at 60 °C for 10 h to yield the electrocatalyst.[1]

Synthesis of Fe-MOF/NF electrode: The preparation process was same as that of Ni-MOF/NF except that 0.24 $Fe(NO_3)_3 \cdot 9H_2O$ was added.

Synthesis of NiCo-MOF/NF electrode: The preparation process of NiCo-MOF/NF was same as that of Ni-MOF/NF, except that 0.12 mmol $CoCl_2 \cdot 6H_2O$ and 0.12 mmol $Ni(CH_3COO)_2 \cdot 4H_2O$ was added.

Note S2. Materials characterizations.

1. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis

1 mg c-Ni_xFe_yOH catalyst was dissolved in a mixed solution of 1 mL HNO_3, 0.5 mL HCl, 0.5 mL H_2O_2, 18 mL deionized water. Then the solution was diluted 10 times. The mass concentration of catalysts in sample solution is 5 mg•L^{-1}.

2. High Resolution Transmission Electron Microscope (HRTEM)

The morphology of samples was obtained by using a Titan Themis Cubed G2 300. The powder samples were dispersed into ethanol and dropped on the Cu grid for analysis.

3. Powder X-ray Diffraction (PXRD)

The XRD patterns were recorded using an X-ray diffractometer diffractometer (Bruker D8 Advance) with a Cu-Kα radiation source (40 kV, 40 mA) with a step size of 0.02°, a scan rate of 0.1°·s-1, and a scan range of 5° to 80°.

4. Confocal Raman spectroscopy (Raman)

Raman spectra were collected with a Raman spectrometer (Horiba Jobin Yvon HR Evolution) using a 633 nm laser excitation source.

5. X-ray Photoelectron Spectroscopy (XPS)

The chemical compositions of the elements were analyzed by X-ray photoelectron spectroscopy (XPS) using an Escalab 250Xi spectrometer (Thermo Fisher Scientific) equipped with a monochromatic Al Kα X-ray source. Survey scans were measured from 1500 to -10 eV using a pass energy of 160 eV with a step size of 1 eV and a dwell time of 0.1 s, whereas the spectra of C 1s, O 1s and Ni 2p and Fe 2p were collected in the desired energy regions using a pass energy of 30 eV with a step size of 0.05 eV and a dwell time of 0.5 s. The C 1s binding energy of adventitious carbon (284.6 eV) was used for calibration.

Note S3. Preparation of anode electrodes.

Preparation of c-Ni_xFe_yOH electrode: 8 mg of c-Ni_xFe_yOH powder and 2 ml acetylene black were mixed in a mixed solution of 0.94 mL ethanol and 0.06 mL Nafion solution. Then the solution after half an hour of ultrasound was coated on carbon papers (1cm*1cm) and further dried. The loading of catalyst was 1.6 mg•cm^{-2}. The preparation of CuFe-LDH/NF was referred to our previous work.[2] For reusability test, the substrate was replaced with stainless steel mesh. The loading of catalyst was the same as mentioned.

Preparation of NiMo-LDH electrode: The preparation process was same as that of c-Ni_xFe_yOH electrode, except that 8 mg NiMo-LDH was added.

Preparation of CuCoO electrode: The preparation process was same as that of c-Ni_xFe_yOH electrode, except that 8 mg CuCoO was added.

Preparation of c-Ni(OH)$_2$ electrode: The preparation process was same as that of c-NiFe-LDH, except that 3 mmol Ni(NO$_3$)$_2$·6H$_2$O were added.

Preparation of c-Fe(OH)$_3$ electrode: The preparation process was same as that of c-NiFe-LDH, except that 3 mmol Fe(NO$_3$)$_3$·9H$_2$O were added.

Note S4. Electrochemical experiment and Faradaic efficiency calculation.

50 mM benzyl alcohol (BA) and 1 M isopropanol (IPA) were added in 30 mL 1 M KOH aqueous solution in 50 ml electrolytic cell under the two-electrode system at 1.6 V for 24 h. The c-NiFe-LDH coated on carbon paper (CP) and CuFe-LDH were used as anode and cathode, respectively. The bias was applied using a programmable DC power supply (LANHE-CT2001A). After the reaction finished, the solid products were collected by centrifugation and dissolved in ethyl acetate and the liquid was extracted using ethyl acetate. All the resulted solution was analyzed by gas chromatography (GC).

To calculate the faradaic efficiency, we first obtained the total charge (Q) passed through the LANHE-CT2001A system. Next, the faradaic efficiency was calculated using Faraday's law:

$$\text{Faradic efficiency (FE)} = \frac{nFm}{Q}$$

where n is the number of electrons involved in the reaction for oxidation of BA and IPA (n = 6), F is Faraday's constant (96485 A•s•mol^{-1}), m is the moles of solid product **3a**.

Linear sweep voltammetry (LSV) scans were recorded at a scan rate of 5 mV·s^{-1} using an electrochemical workstation (DH7000C, Donghua). The c-NiFe-LDH coated on CP was used as the working electrode. The Hg/HgO (1 M KOH) was used as the reference electrode. Graphite rod was used as the counter electrode (CE). All the measured potentials were converted to reversible hydrogen electrode (RHE) scale using the Nernst equation.

$$E \, (vs. \text{RHE}) = 0.098 + 0.0591 \times pH + E \, (vs. \, Hg/HgO)$$

All the measured currents were converted to current density according to the electrode area.

Note S5. Gram scale of synthesis of Dibenzylideneacetone (3a).

8 mg of c-NiFe-LDH and 2 ml acetylene black were mixed in a mixed solution of 0.94 ml ethanol and 0.06 ml Nafion. Then the solution after half an hour of ultrasound was coated on carbon paper (2 cm*2 cm). The loading of the catalyst is 2 mg•cm^{-2}. CuFe-LDH (2 cm*2 cm) was used as cathode. A 90 mL of the substrate containing solution (100 mM BA and 1 M IPA in 1 M KOH) was reacted under a two-electrode system at 1.6 V for 144 h. The solid product was collected through centrifugation followed by further wash and dry.
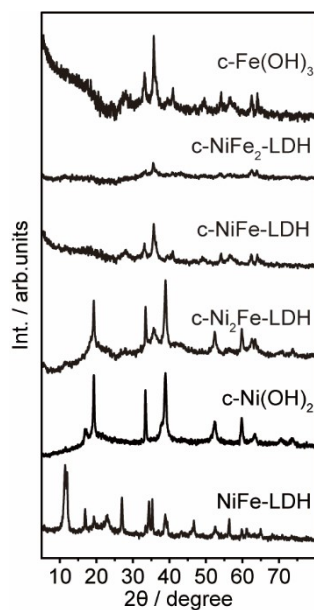
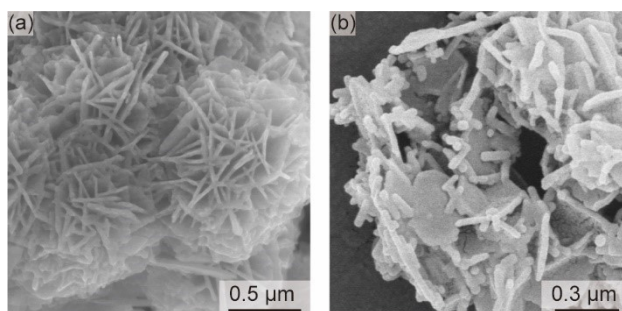**Figure S1.** XRD patterns of NiFe-LDH and c-Ni$_x$Fe$_y$OH powder.

Figure S2. SEM images of (a) NiFe-LDH and (b) c-NiFe-LDH powder.
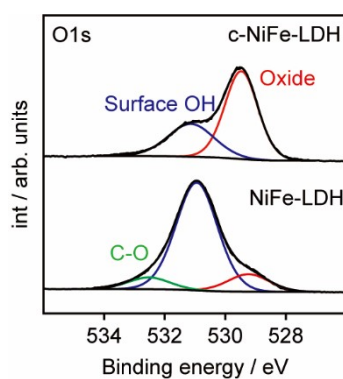

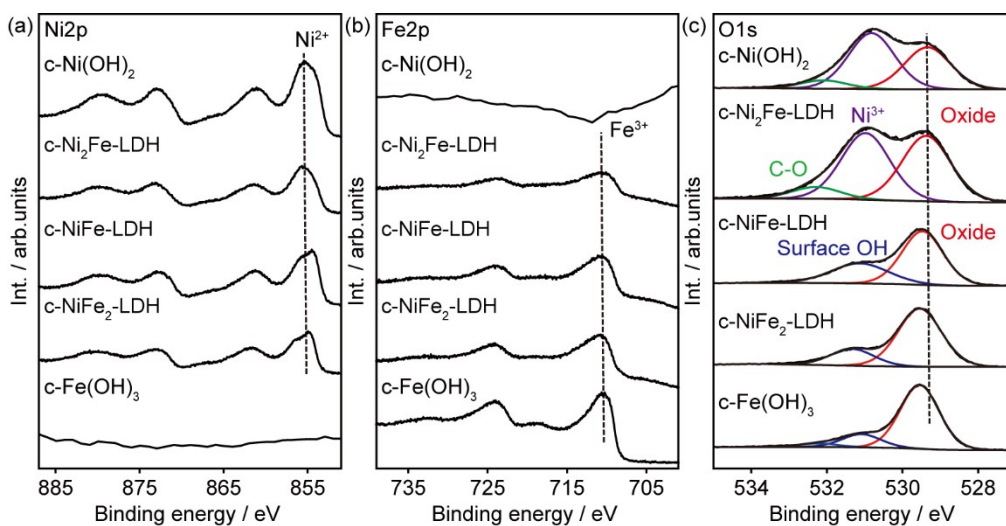**Figure S3.** O 1s XPS spectra of c-NiFe-LDH and NiFe-LDH.

Figure S4. (a) Ni2p, (b) Fe2p and (c) O1s XPS spectra of c-Ni_xFe_yOH powder, respectively.
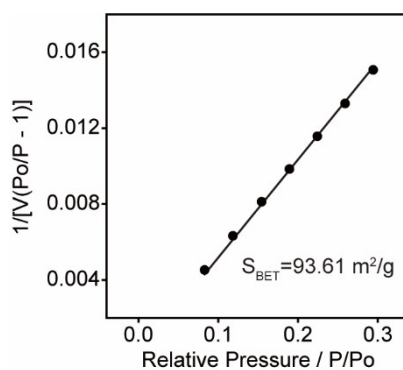

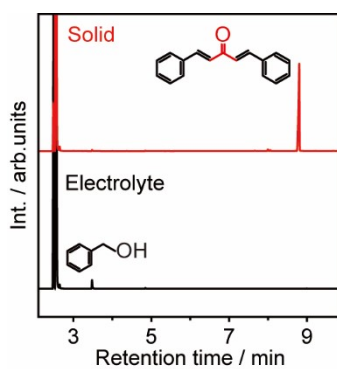**Figure S5.** BET plot of the N_2 adsorption isotherm of c-NiFe-LDH.

Figure S6. GC spectra of the electrolyte (black line) and solid phase (red line) after electrochemical reaction under standard reaction conditions.
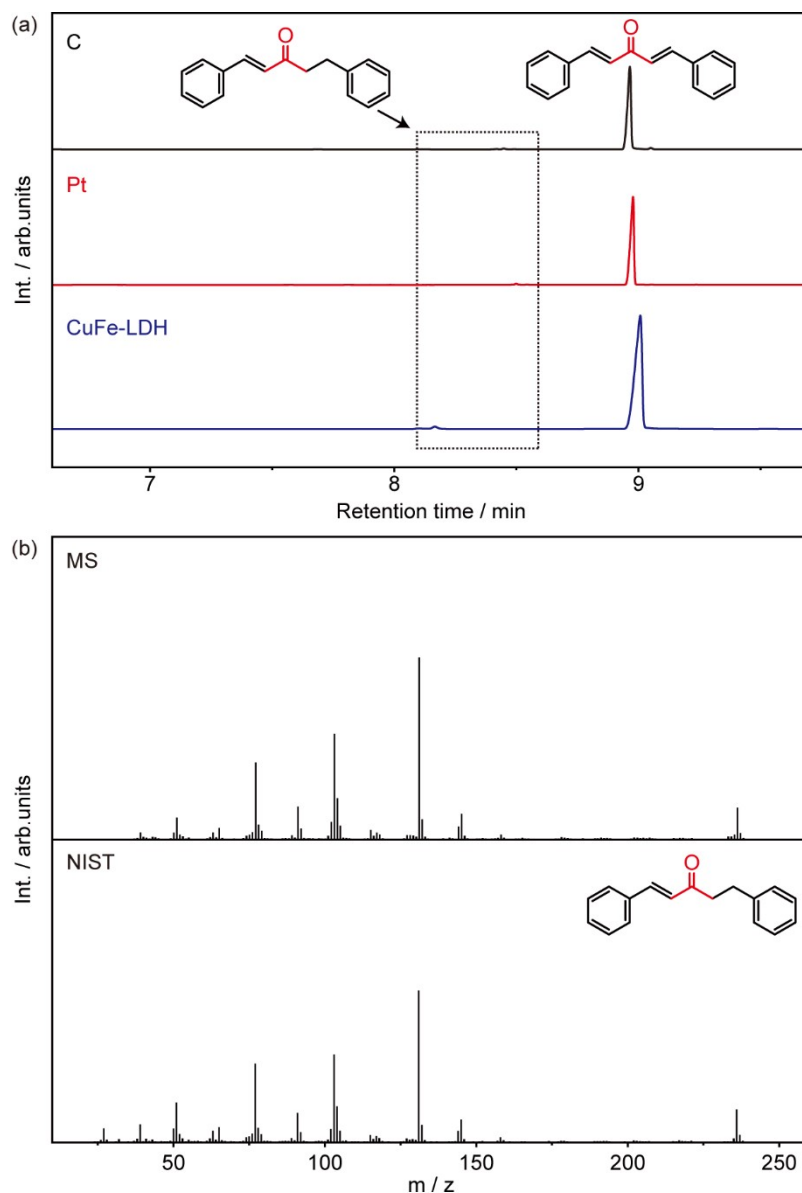
Figure S7. (a) GC spectra of solid phase after electrochemical reaction using CuFe-LDH, Pt and C as the cathode. (b) MS spectrum of the possible hydrogenation product from GC-MS (above) and the standard MS spectrum from the National Institute of Standards and Technology (NIST) database (below).
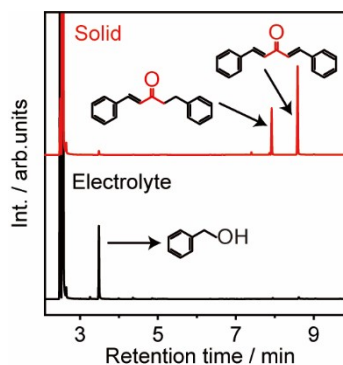
Figure S8. GC spectra of the electrolyte (black line) and the solid phase (red line) after electrochemical reaction using Pd as the cathode.
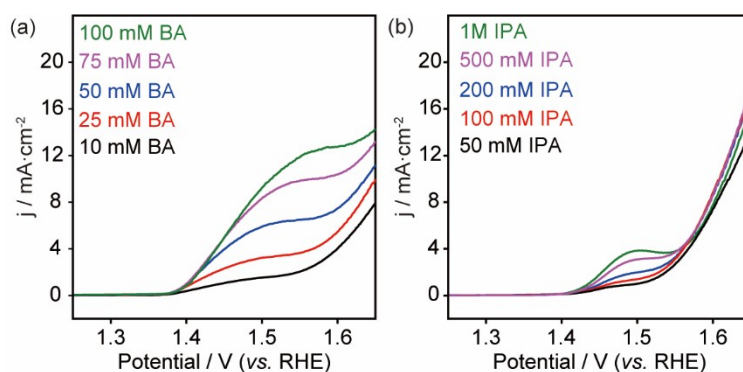

Figure S9. LSV of different concentration of (a) BA, (b) IPA in 1 M KOH. Reaction condition: c-NiFe-LDH coated on carbon paper as working electrode, graphite sheet as counter electrode, Hg/HgO as reference electrode.
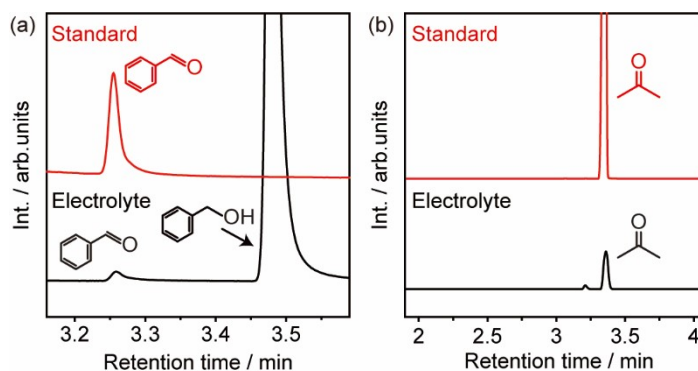

Figure S10. (a) and (b) GC spectra of electrolyte (black line) and standard chemicals (red line) measured at ramping rates of 30 K·min^{-1} and 4 K·min^{-1}, respectively.
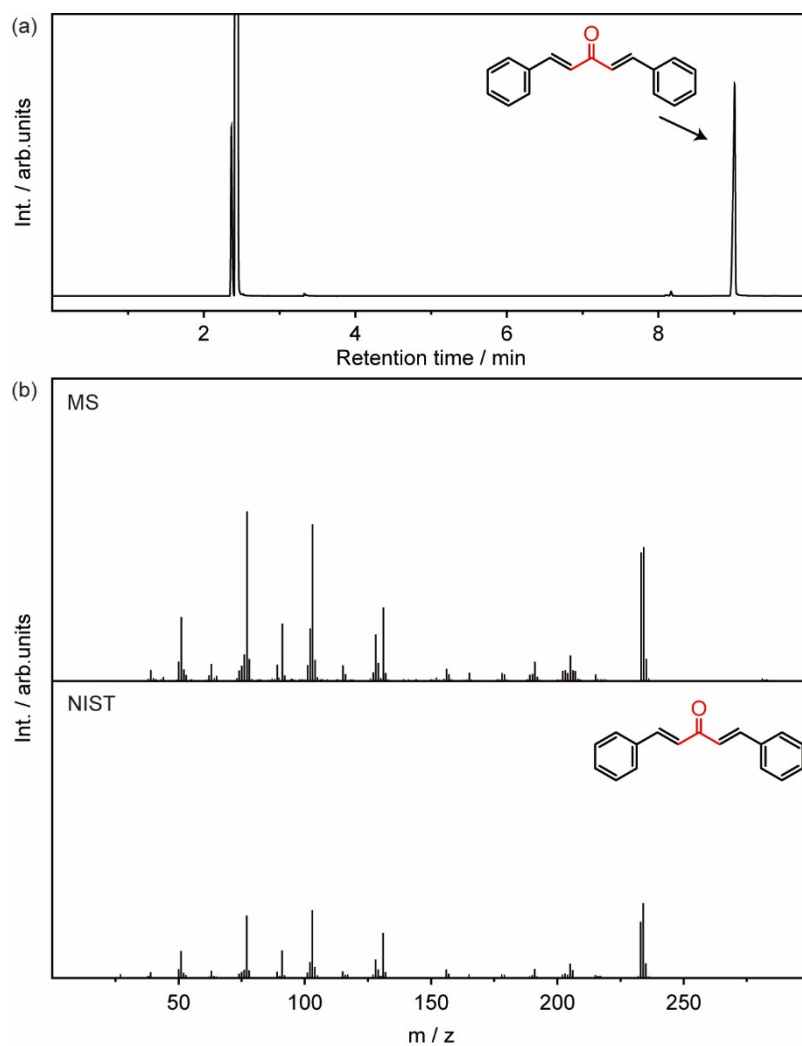
Figure S11.Benzyl alcohol as primary alcohol substrate, **3a**. (a) GC spectrum. (b) MS spectrum from GC-MS (above) and the standard MS spectrum from the National Institute of Standards and Technology (NIST) database (below).
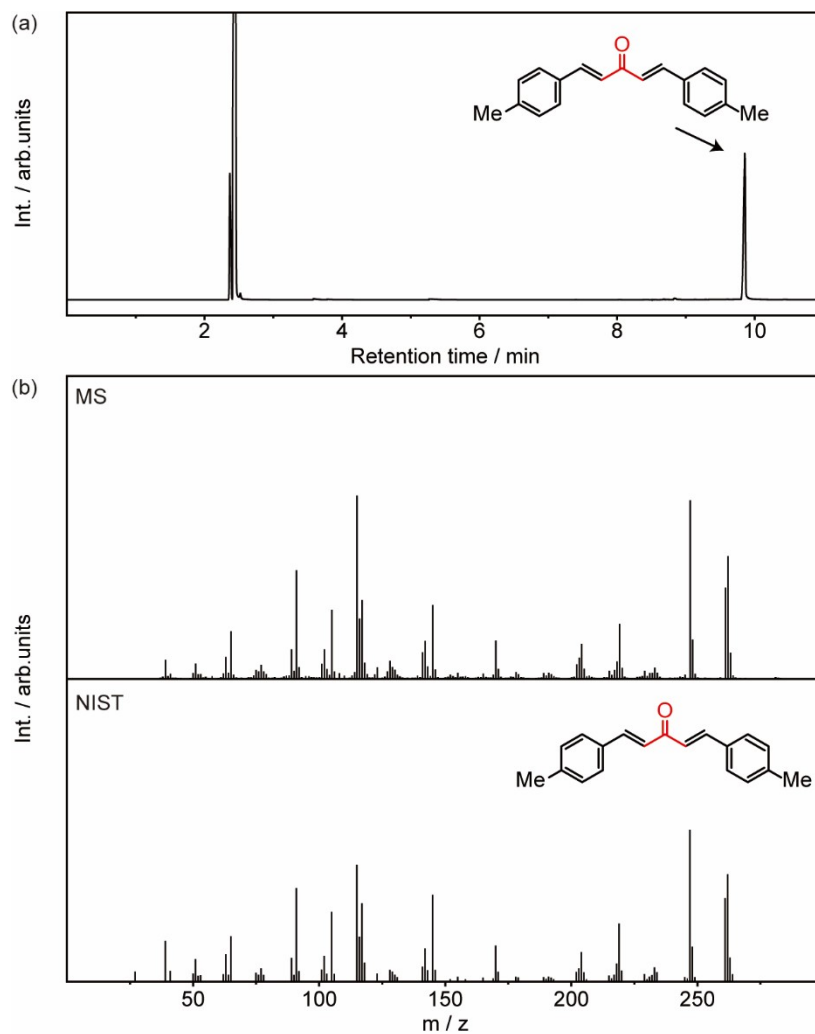
Figure S12. 4-methyl benzyl alcohol as primary alcohol substrate, **3b**. (a) GC spectrum. (b) MS spectrum from GC-MS (above) and the standard MS spectrum from the National Institute of Standards and Technology (NIST) database (below).

Figure S13. 4-methoxy benzyl alcohol as primary alcohol substrate, **3c**. (a) GC spectrum. (b) MS spectrum from GC-MS (above) and the standard MS spectrum from the National Institute of Standards and Technology (NIST) database (below).
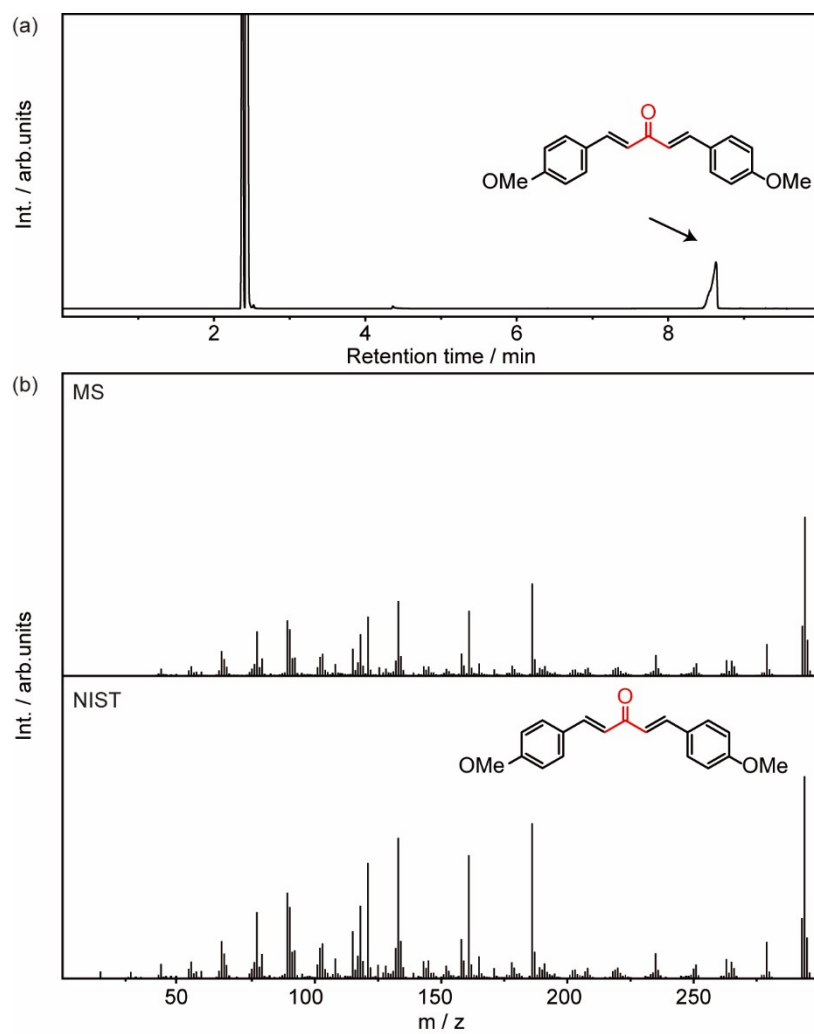
Figure S14. 2-thiophenemethanol as primary alcohol substrate, **3d**. (a) GC spectrum. (b) MS spectrum from GC-MS.

Figure S15. 3-methyl-2-butano as secondary alcohol substrate, **4a**. (a) GC spectrum. (b) MS spectrum from GC-MS (above) and the standard MS spectrum from the National Institute of Standards and Technology (NIST) database (below).
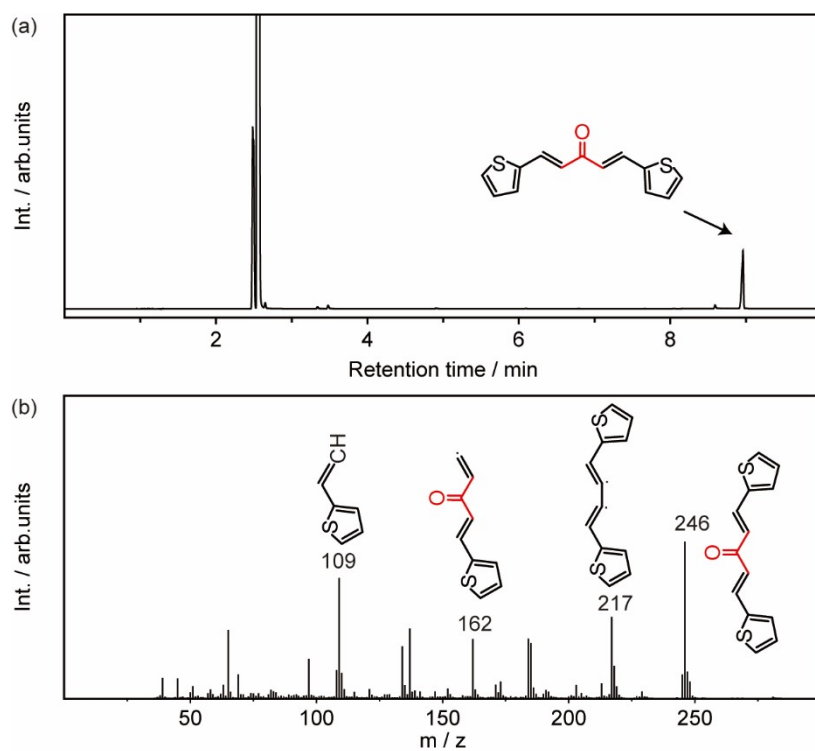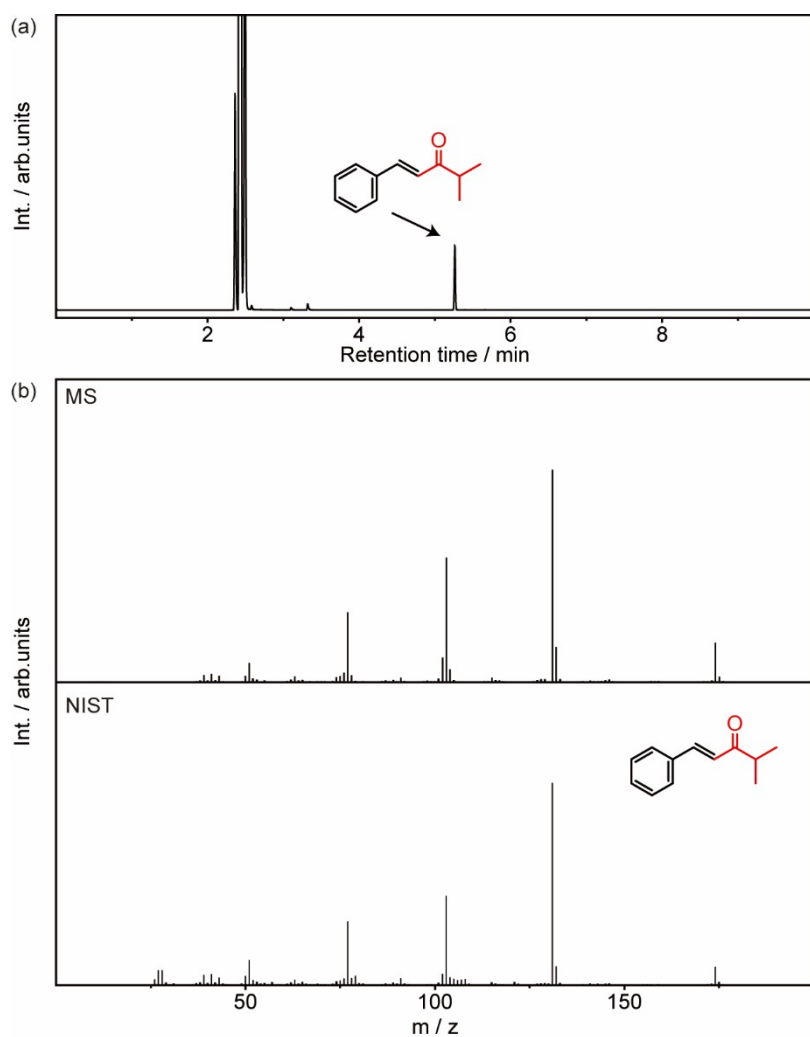
Figure S16. 4-methyl-2-pentanol as secondary alcohol substrate, **4b**. (a) GC spectrum. (b) MS spectrum from GC-MS (above) and the standard MS spectrum from the National Institute of Standards and Technology (NIST) database (below).
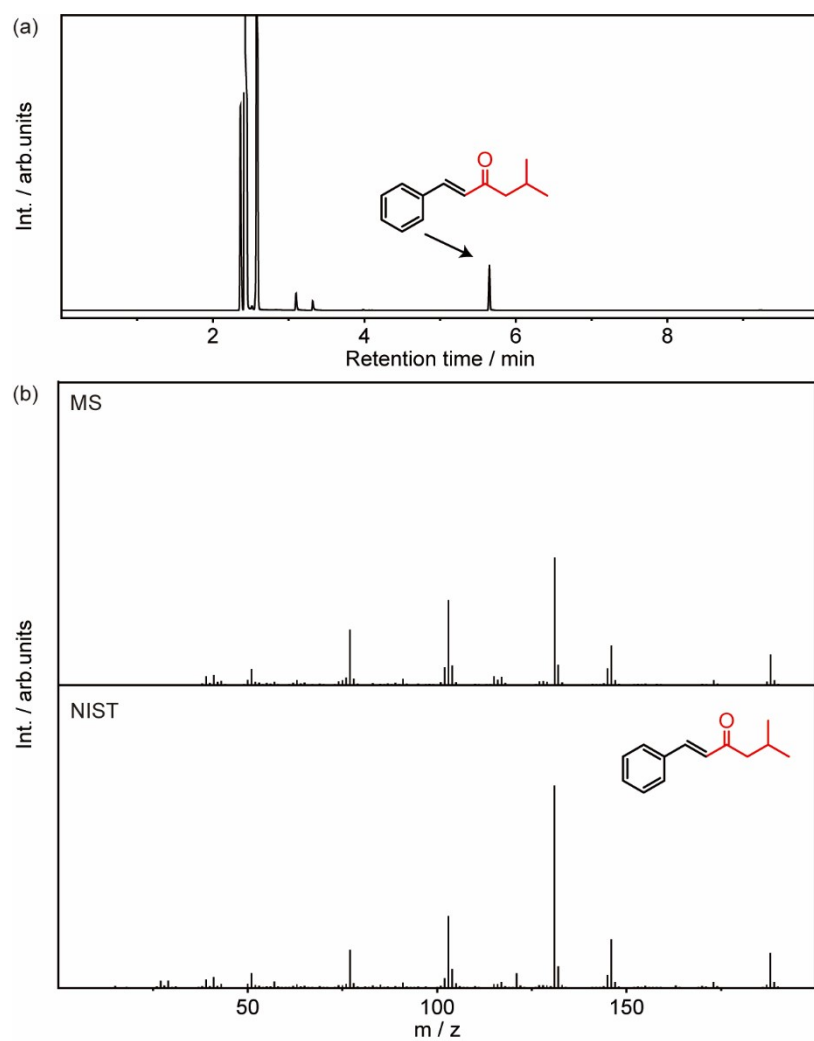
Supporting Tables

Table S1. ICP-AES analysis of different ratio of c-NiFe-LDH catalyst.

Catalyst	c(Ni) / mM	c(Fe) / mM
c-Ni(OH)$_2$	14.8	0
c-Ni$_2$Fe-LDH	21.7	10.5
c-NiFe-LDH	6.4	6.3
c-NiFe$_2$-LDH	9.3	17.2
c-Fe(OH)$_3$	0	20.3

Table S2. Screening of catalysts and reaction conditions[a].

Entry	Conditions	Con. / %	n (**3a**) / mmol
1	standard condition	89	0.36
2	no bias	0	0
3[b]	0.5 M Na$_2$SO$_4$	19	0
4[b]	0.1 M PBS	11	0
5[b]	1 M KOH+ 1 M K$_2$CO$_3$	62	0.1
6[b]	0.5 M H$_2$SO$_4$	0	0
7[c]	NiFe-LDH as anode	74	0.26
8[d]	Graphite rod as cathode	71	0.23
9[d]	Pt plate as cathode	76	0.29
10[d]	Pd/CP as cathode	65	0.1
11[e]	divided cell	20	0.01

Reaction conditions. [a] 50 mM benzyl alcohol, 1 M isopropanol in 30 mL 1 M KOH solution, RT, air, 1.6 V, 24 h. The c-NiFe-LDH coated on carbon paper as anode, CuFe-LDH grown on Ni foam as cathode. [b] Using 0.5 M Na$_2$SO$_4$, 0.1 M PBS, 1 M KOH+1 M K$_2$CO$_3$ and 0.5 M H$_2$SO$_4$ instead of 1 M KOH, respectively. [c] Using NiFe-LDH as anode instead of c-NiFe-LDH. [d] Using graphite rod, Pt plate, Pd/CP as cathode instead of CuFe-LDH, respectively. [e] Using divided cell instead.

Supporting References

1   W. Qiao, I. Waseem, G. Shang, D. Wang, Y. Li, F. Besenbacher, H. Niemantsverdriet, C. Yan and R. Su, Paired Electrochemical N–N Coupling Employing a Surface-Hydroxylated Ni_3Fe-MOF-OH Bifunctional Electrocatalyst with Enhanced Adsorption of Nitroarenes and Anilines, *ACS Catal.*, 2021, **11**, 13510-13518.
2   G. Shang, Y. Liu, Y. Li, W. Qiao, C. Wang, Y. Li, D. Zhang, F. Sapountzi, Y. Li, H. Niemantsverdriet, M. H. Rümmeli and R. Su, Copper dendrite stabilized NiFe(OH)x electrocatalyst for durable alkaline hydrogen evolution over 1000 h, *Chem. Commun.*, 2022, **58**, 6024-6027.