

Supplementary Information for

Highly Efficient Electrosynthesis of Oximes from Nitrates and Carbonyl Compounds in Acidic Media

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Experimental Section

Chemicals

K₂HPO₄ (99.8%), KH₂PO₄ (99%), citric acid (98%), KNO₃ (99%), K¹⁵NO₃ (99.8%), Zn(NO₃)₂·6H₂O (99%), Zn(OAc)₂ (98%), ZnSO₄ (98%), ZnCl₂ (99.888%), ZnBr₂ (98%), ZnI₂ (99%), ZnCO₃ (99%) and Zn(CF₃SO₂)₂ (99.9%) were purchased from Aladdin Ltd (Shanghai, China). Phenylacetaldehyde (99%), cinnamaldehyde (98%), perillaldehyde (99%), indole-3-acetaldehyde (99%) and pivalaldehyde (98%) were obtained from Energy Chemical Ltd (Shanghai, China). Butyraldehyde (98%), acetone (98%), pinacolone (98%), butanone (98%), cyclohexanone (99%), acetophenone (99%) and benzophenone (98%) were provided by Bide Ltd (Shanghai, China). Monolithic metal foils of Pb, Ni, Cu, Ti, and Zn were obtained from Zhengying Metal Materials (Hefei, China). Deionized water was used in all the experimental processes.

Electrochemical measurements

The electrochemical measurements were carried out on a HY3005B DC power supply with a two-electrode setup, with the platinum grid as the counter electrode and the catalyst as the working electrode. The working electrode used was 1.1×1.5 cm² and the counter electrode size was 1×1 cm². A Nafion117 proton exchange membrane was applied to separate the anode and cathode compartments of the H-type cell. Each compartment has 5 mL of electrolyte solution. Typically, 5 mL of 1 M phosphate buffer solution (PBS, pH = 5.8) and 0.4 mmol of phenylacetaldehyde and 0.4 M KNO₃ were used as the electrolytes (all substrates were dissolved directly in PBS except for phenylacetaldehyde which was first dissolved in 1 mL of acetonitrile and then added to 4 mL of PBS. In the constant-current electrolysis test, the current density was set to −3 to −30 mA cm^{−2}.

Modified-Zn electrodes preparation

Firstly, Zn foil (99.994%, 0.2 mm in thick) was mechanical polished with sandpaper (400 grit) followed by sonication treatment in acetone and water. The multilayered Zn nanosheets (M-ZnNSs) electrodes were prepared using a modified electrochemical Zn deposition procedure. In a typical experiment, 0.5 mol of ZnCl₂ was dissolved in 5 M KOH solution to form a precursor solution for Zn deposition. The electrodeposition was

performed by applying a constant current of -90 mA cm^{-2} for 2 min at ambient temperature. Upon completion of deposition, the electrodes were rinsed with deionized water and immediately used for electrochemical testing to prevent oxidation of the Zn electrodes. The prepared electrodes were used in electrolysis testing immediately or undergo relevant structural characterization to minimize exposure to the atmosphere and prevent oxidation as much as possible.

When depositing different Zn salt precursors electrochemically, only the substitution of ZnCl_2 was required.

Characterizations

Scanning electron microscopy (SEM, HITACHI S-4800) was used to characterize the morphology of the samples. The catalysts were also assessed on an X-ray diffractometer (XRD, Rigaku Ultima VI) and an X-ray photoelectron spectroscopy (XPS, AXIS Supra). Synchrotron X-ray absorption spectroscopy (XAS) was performed at the Shanghai Synchrotron Radiation Facility with the BL13SSW beamline. The Zn K-edge X-ray absorption spectra of M-ZnNSs electrodes were obtained, and Zn foil, ZnO were used as references. The Bruker Dektak XT was used to measure deposit thickness of catalyst. In situ ATR-FTIR testing was performed using a PerkinElmer Spectrum-3 at Hefei in situ technology Co. The background spectrum of the catalyst electrode was acquired before each electrochemical measurement, and the measured current was 7 mA.

Online DEMS measurement.

A mass spectrometer (QAS 100) and an electrochemical workstation (Chenhua, Shanghai) were used for online differential electrochemical mass spectrometry (DEMS) measurements. 1 M PBS containing 0.4 M KNO_3 was used as the electrolyte. M-ZnNSs and Pt wire electrodes were used as the working electrode, counter electrode respectively. A constant current test of -12 mA cm^{-2} was performed, and the corresponding mass signals could be detected during this period. After the electrochemical test was finished and the quality signal returned to the baseline, the next cycle was started under the same test conditions to avoid unexpected errors in the DEMS measurement. The measurement was completed after six cycles.

Buffer Preparation

The pH was controlled at 3.2, 4.0, and 5.0 using a citric acid- Na_2HPO_4 buffer system, and at 5.8, 6.5, and 7.0 using a NaH_2PO_4 - Na_2HPO_4 buffer system.

Products identification and quantification

After electrolysis, the reaction solution was extracted by dichloromethane to obtain an organic solution, and the separation was confirmed by gas chromatography-mass spectrometry (GC-MS) and H nuclear magnetic resonance spectra (^1H NMR) for product confirmation. Tetradecane was added to the organic solution as an internal standard during post-conditional screening and quantitatively analyzed by GC. The substrate expansions were all isolated yields.

The PAH conversion and products yield were obtained by the following equations:

$$\text{PAH conversion (\%)} = (n_0 - n_1) / n_0 \times 100\%$$

$$\text{Alcohol yield (\%)} = n_2 / n_3 \times 100\%$$

$$\text{Phenylacetaldehyde oxime yield (\%)} = n_4 / n_5 \times 100\%$$

$$\text{Faraday efficiency (\%)} = n_4 * \alpha * F / Q \times 100\%$$

Where n_0 : moles of PAH added before the reaction;

n_1 : moles of PAH remaining after the reaction;

n_2 : moles of alcohol produced in the reaction;

n_3 : theoretically producing moles of alcohol;

n_4 : moles of phenylacetaldehyde oxime in the reaction;

n_5 : theoretically producing moles of phenylacetaldehyde oxime;

Q is the charge in the electrolysis, α is the amount of electrons transferred for the products, and F is Faraday constant (96485 C mol^{-1}).

Supplementary Figures

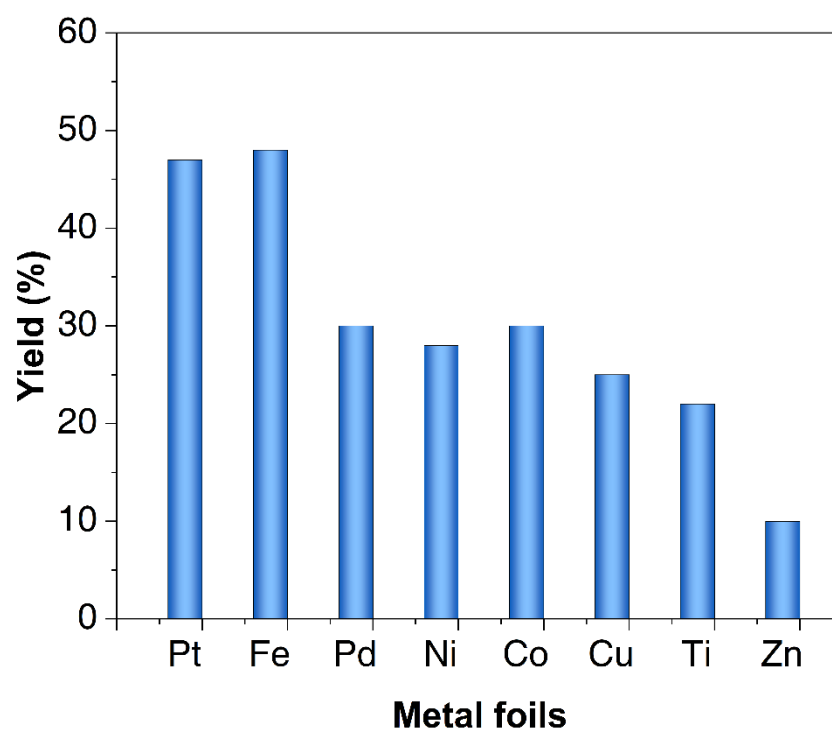


Figure S1 Yield of phenylethanol over different electrodes.

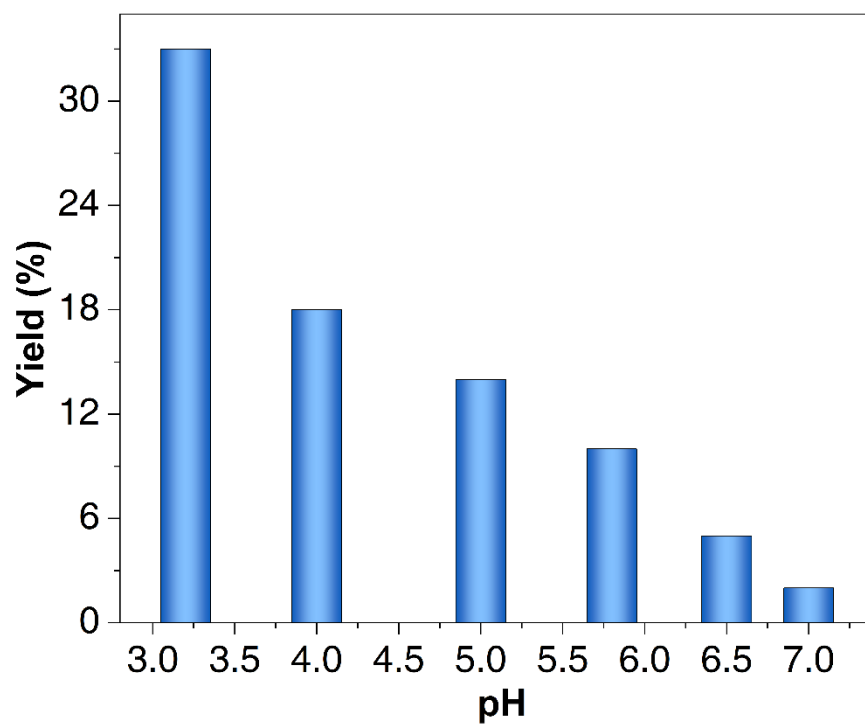


Figure S2 Yield of phenylethanol with different pH on Zn Foil

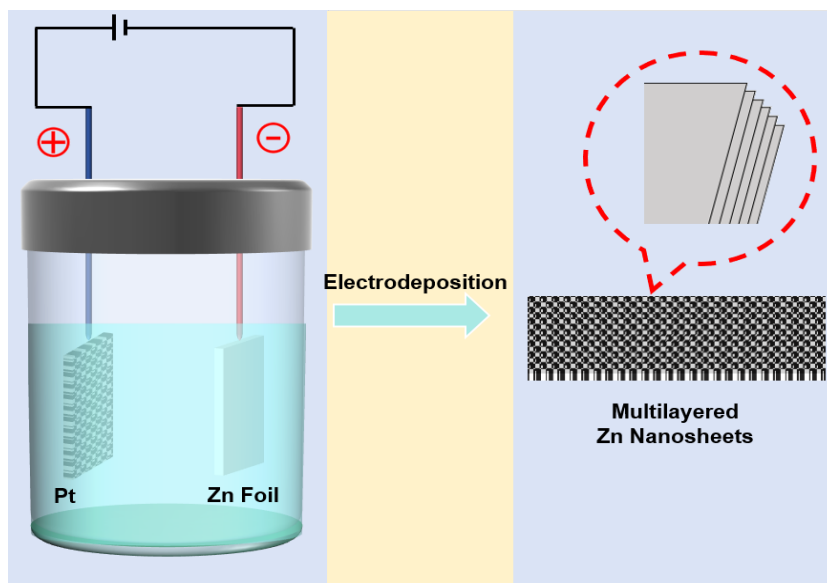


Figure S3 Schematic diagram of Zn-base catalyst preparation.

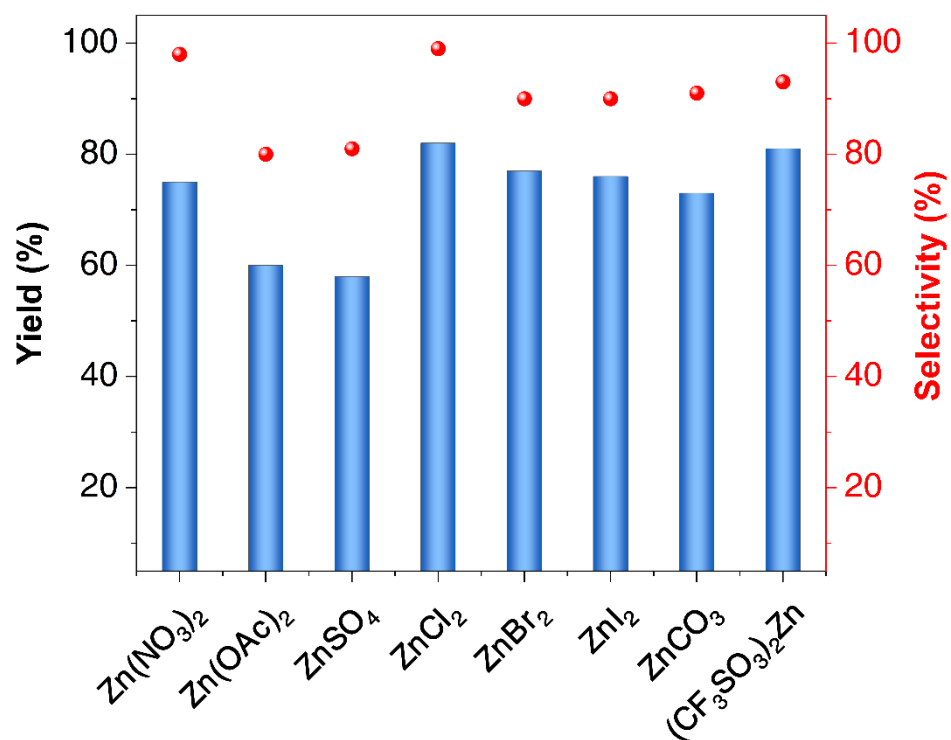


Figure S4 The performance of electrode obtained with different Zn salt precursors for C–N coupling.

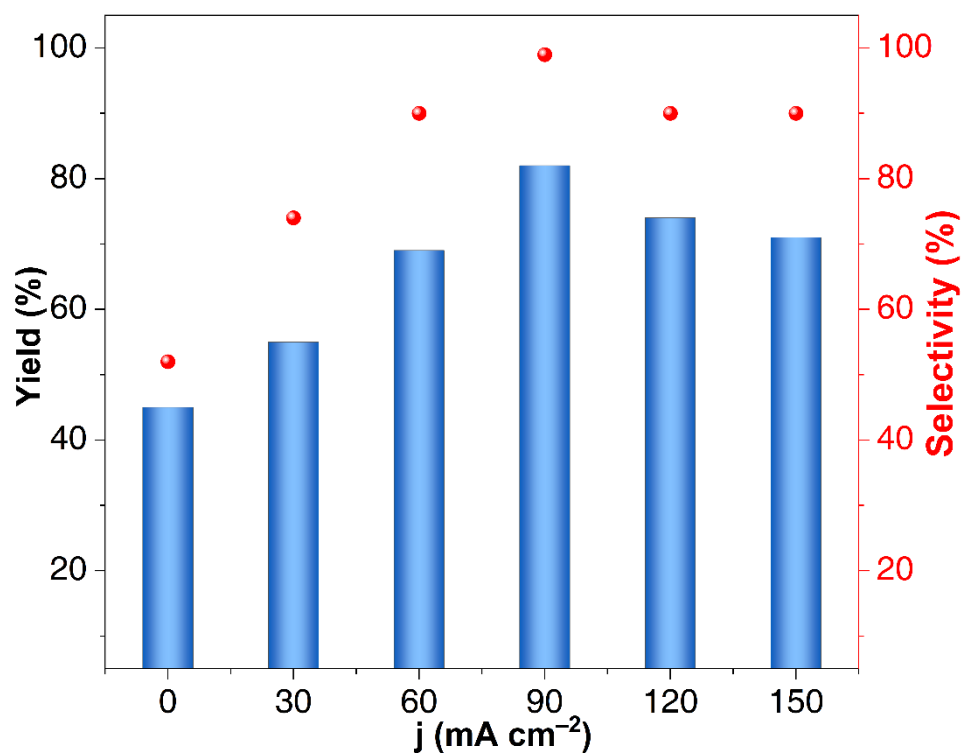


Figure S5 The performance of electrode obtained with ZnCl_2 precursor solutions in 2 min with different deposition currents density for C–N coupling.

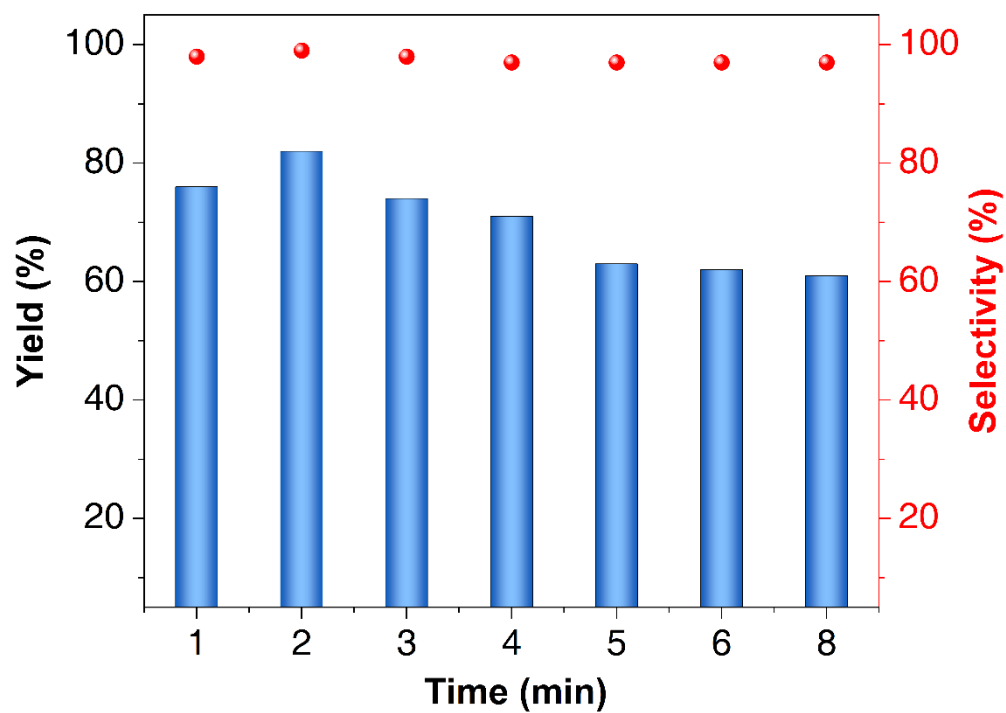


Figure S6 The performance of electrodes obtained with different deposition time using ZnCl_2 precursor solutions at -90 mA cm^{-2} for C-N coupling.

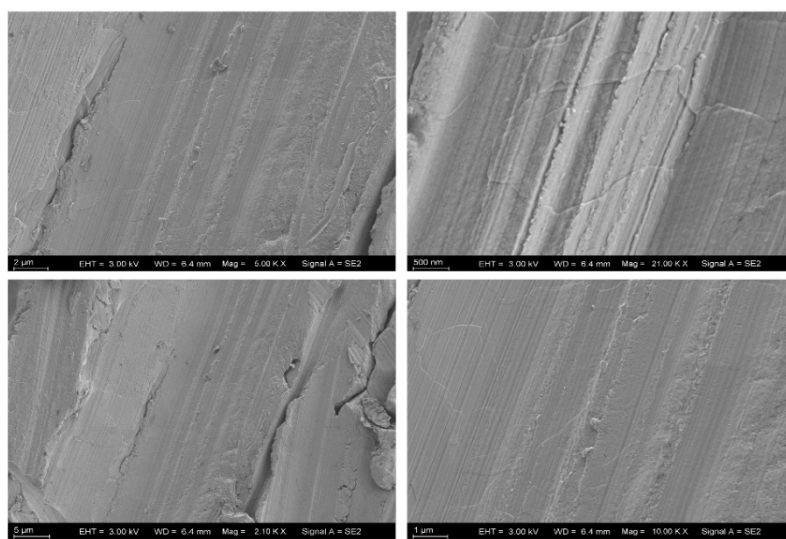


Figure S7 SEM of Zn foil.

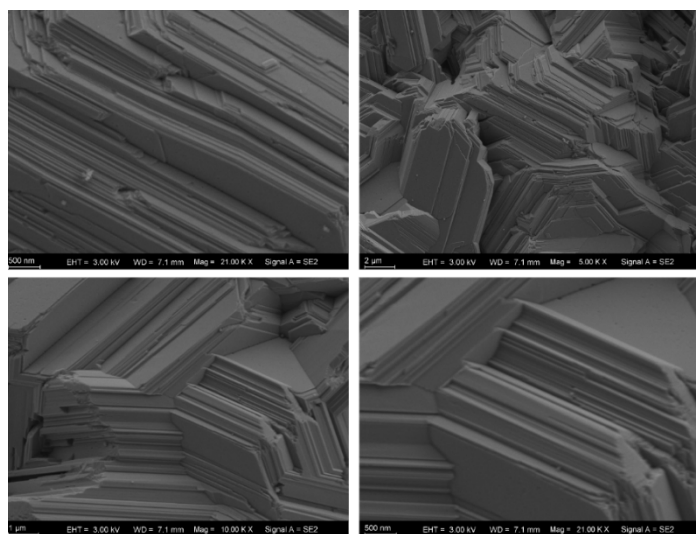


Figure S8 SEM of M-ZnNSs.

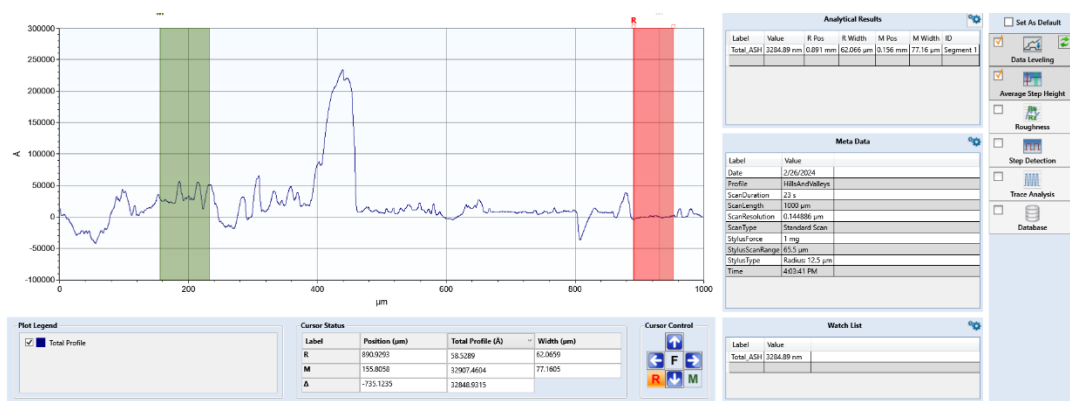


Figure S9 Thickness measurement of M-ZnNSs.

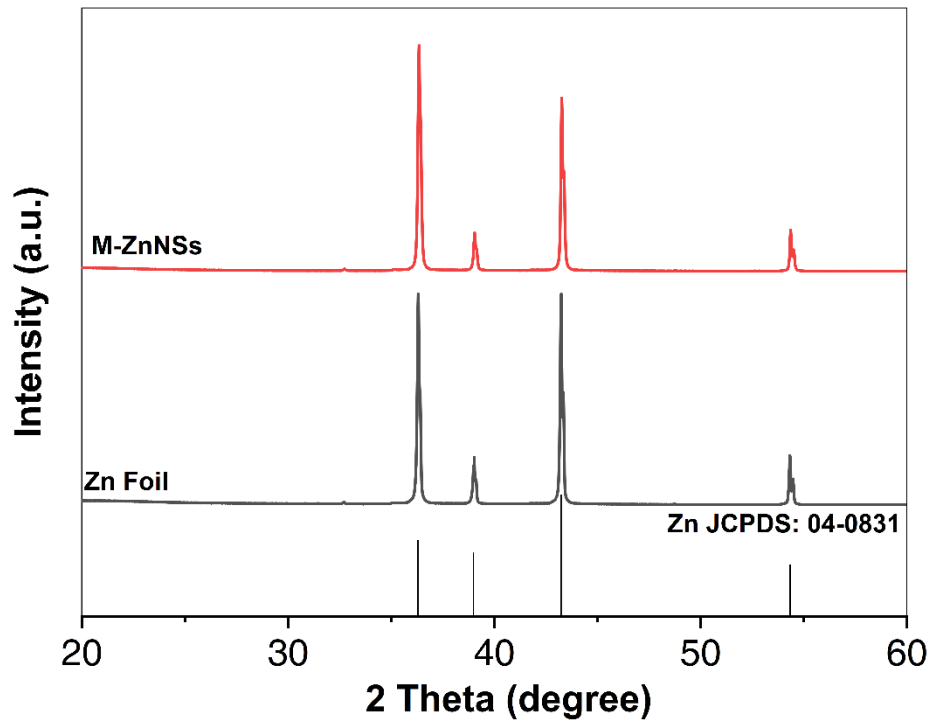


Figure S10 XRD patterns of M-ZnNSs and Zn Foil.

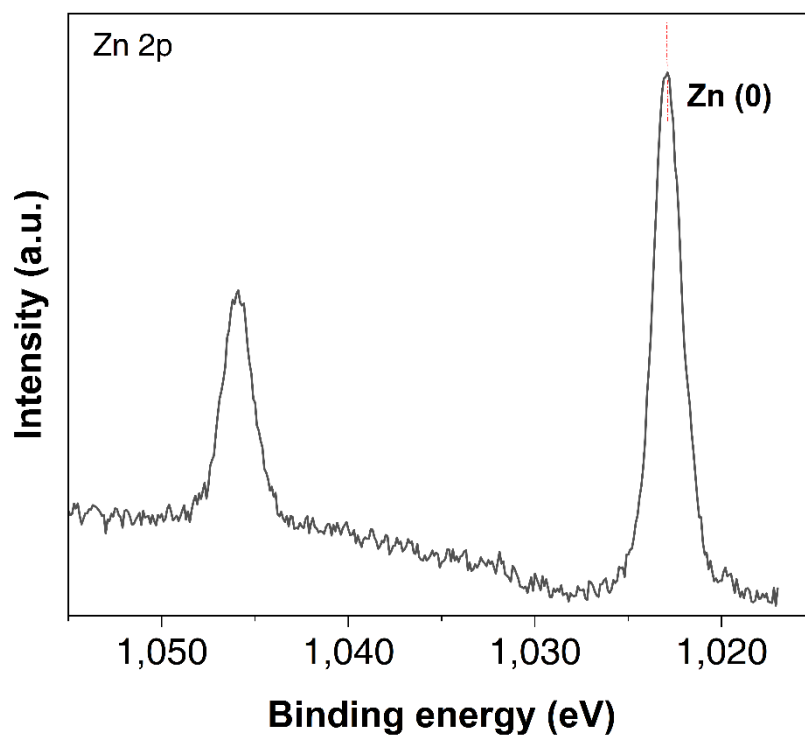


Figure S11 XPS spectrum of M-ZnNSs.

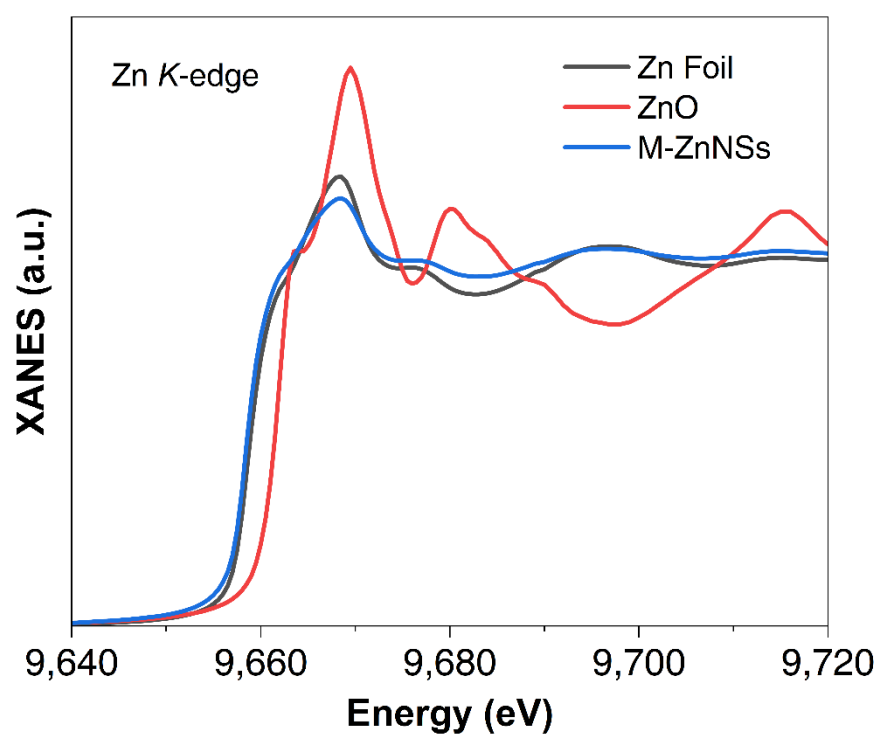


Figure S12 Normalized Zn Kedge XANES spectra of M-ZnNSs, referenced with Zn foil, ZnO.

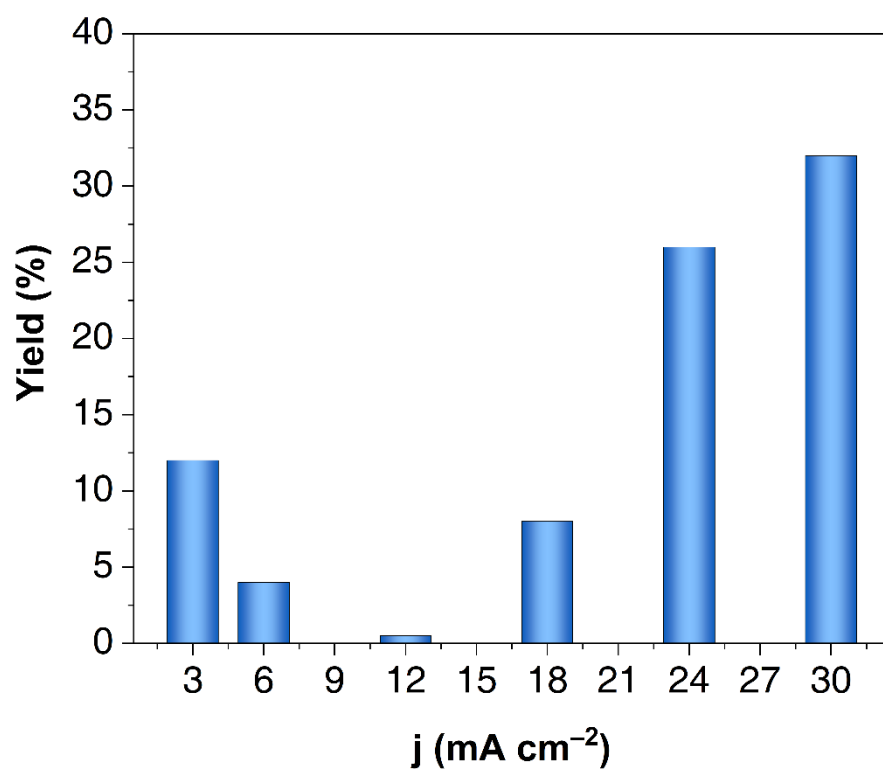


Figure S13 Phenylethanol yield at different current densities on M-ZnNSs.

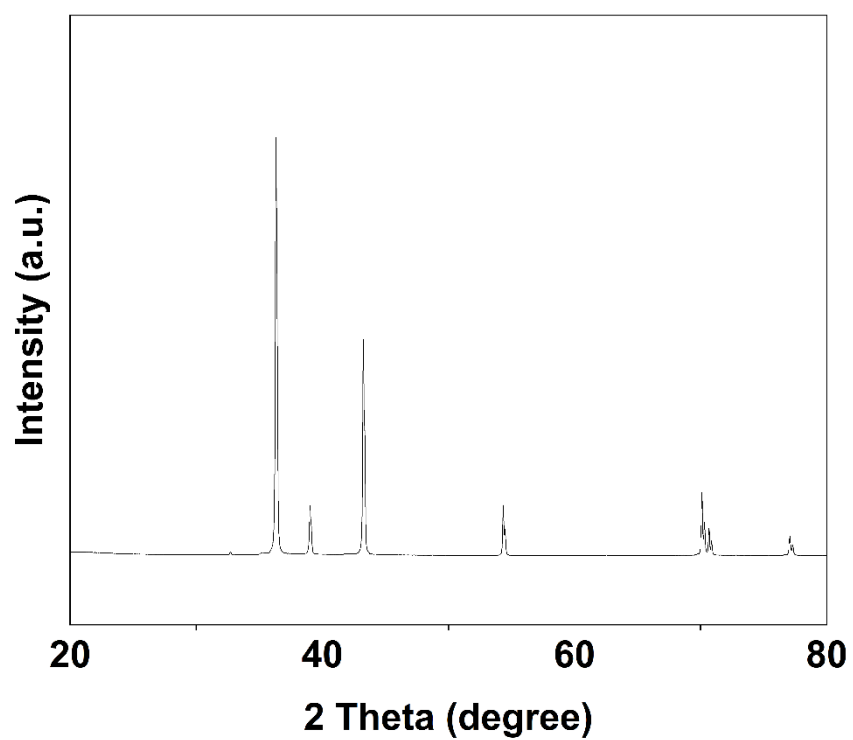


Figure S14 XRD pattern of M-ZnNSs after reaction for 100 h.

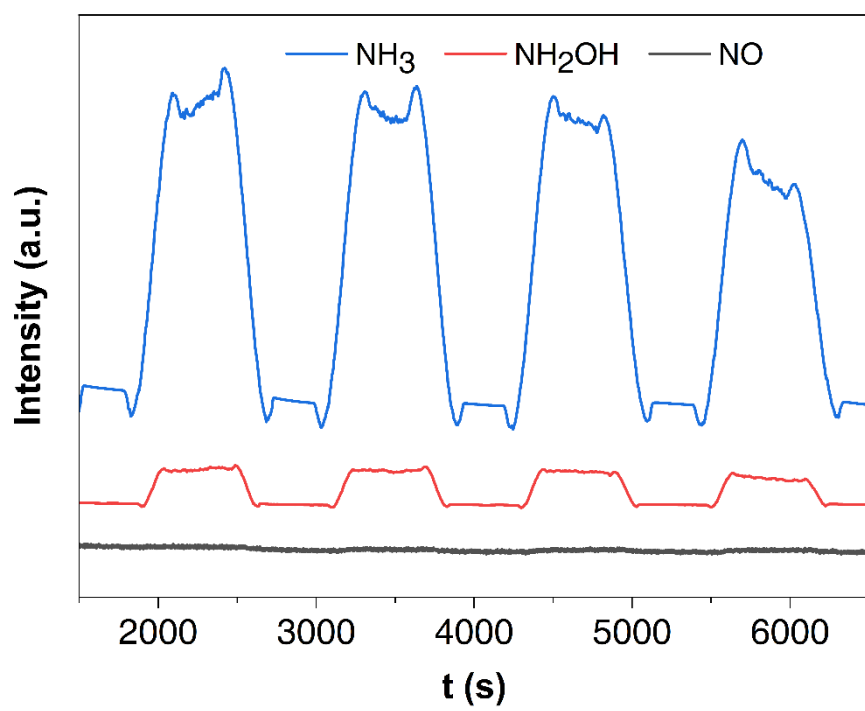


Figure S15 Online DEMS measurements for the NO_3RR over the M-ZnNSs electrode.

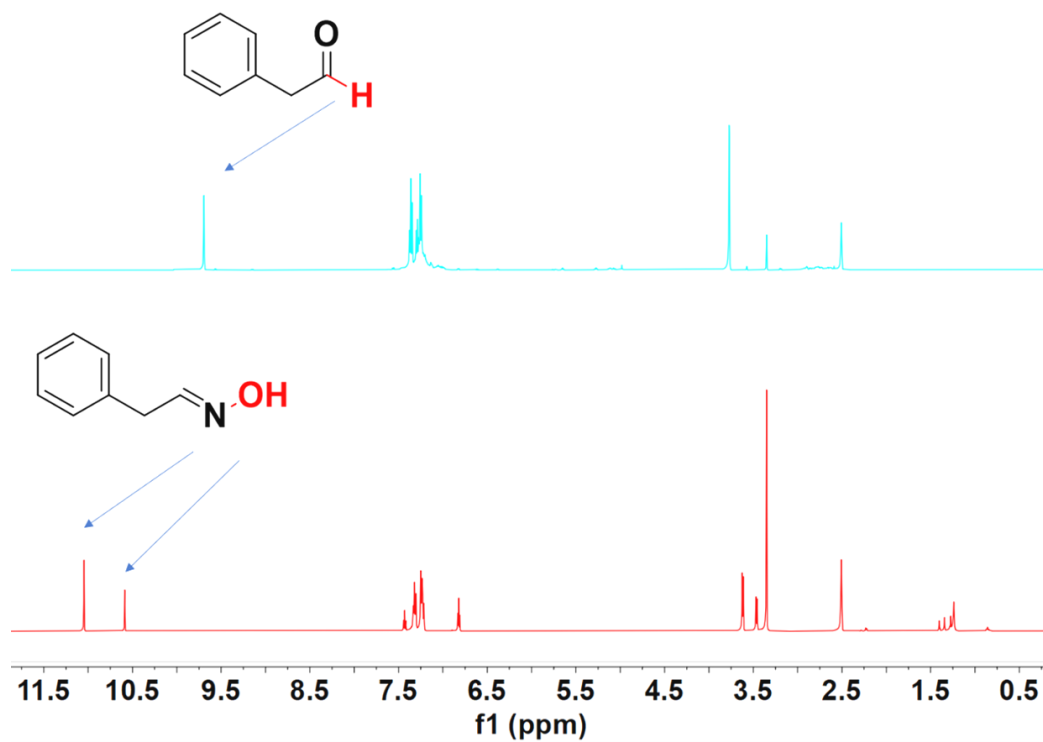


Figure S16 ^1H NMR of phenylacetaldehyde oxime product obtained over the M-ZnNSs electrode.

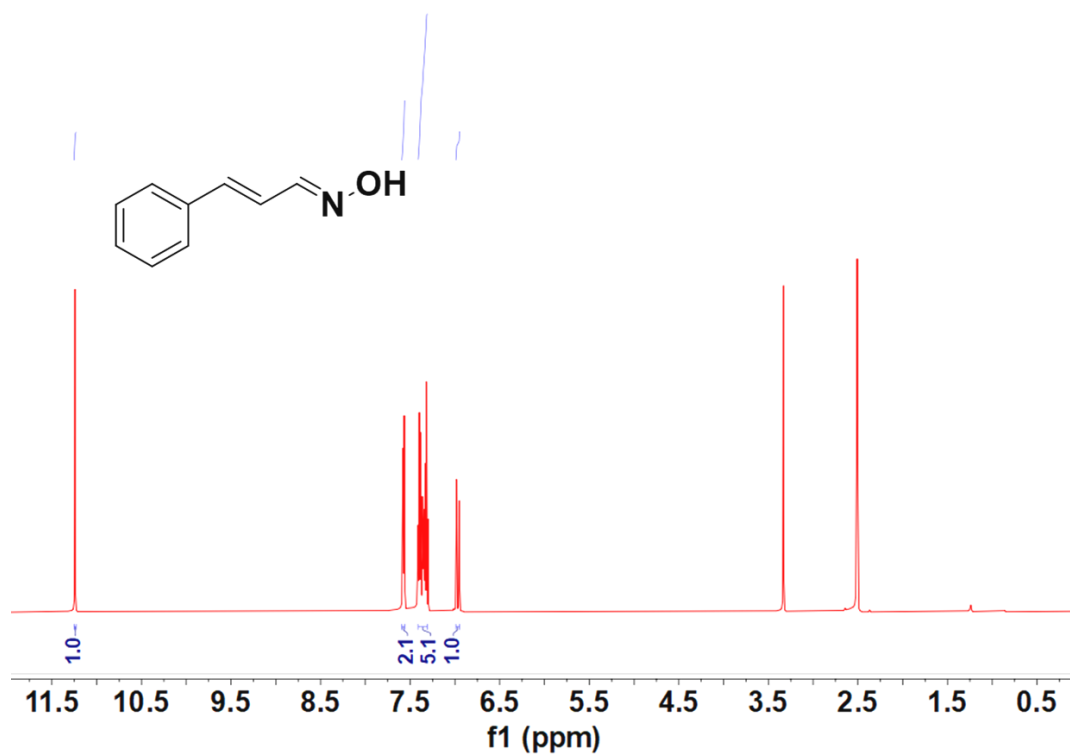


Figure S17 ^1H NMR of cinnamaldehyde oxime product obtained over the M-ZnNSs electrode.

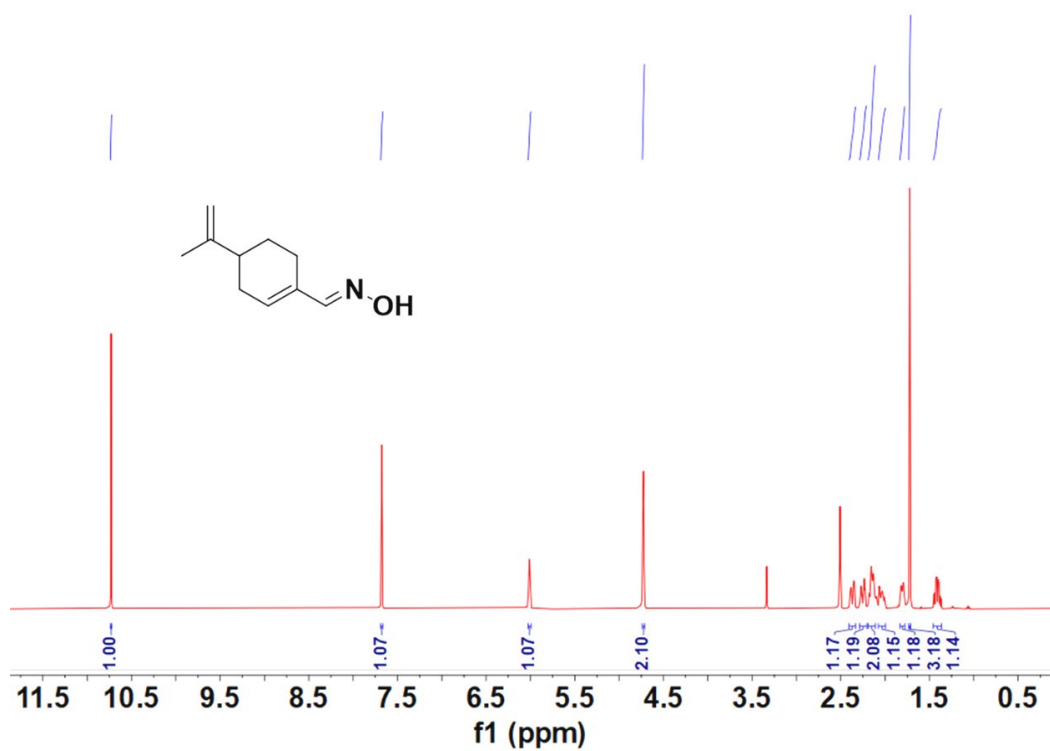


Figure S18 ^1H NMR of perillartine product obtained over the M-ZnNSs electrode.

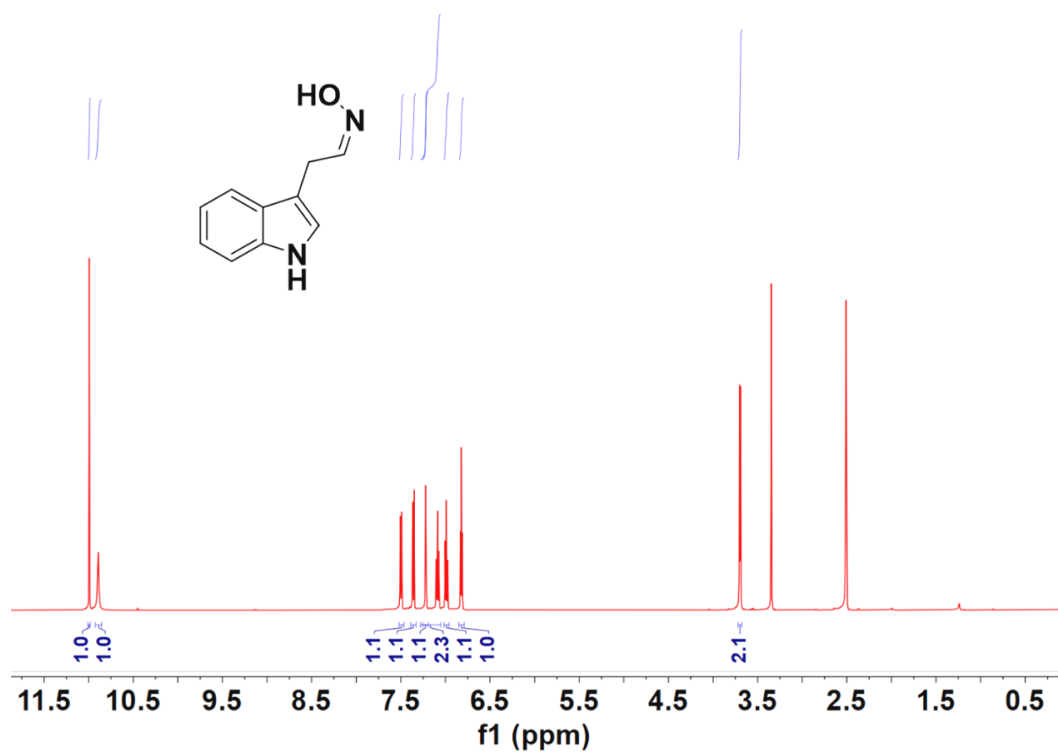


Figure S19 ^1H NMR of indole-3-acetaldehyde oxime product obtained over the M-ZnNSs electrode.

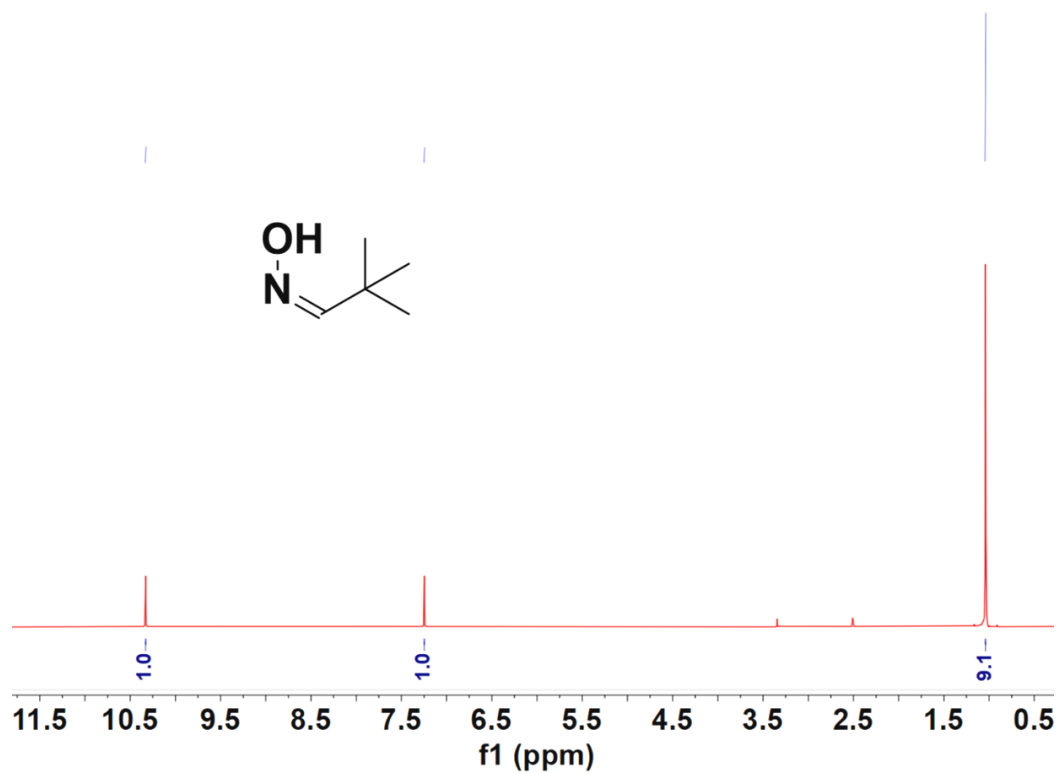


Figure S20 ^1H NMR of pivalaldehyde oxime product obtained over the M-ZnNSs electrode.

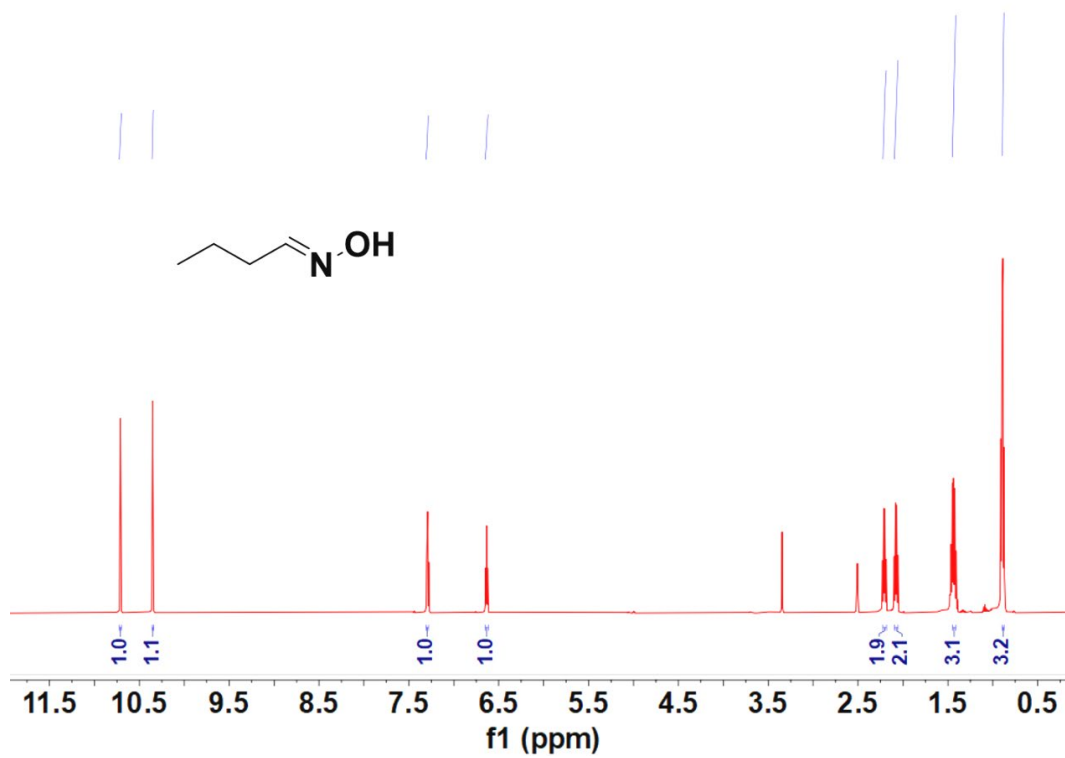


Figure S21 ¹H NMR of butyraldehyde oxime product obtained over the M-ZnNSs electrode.

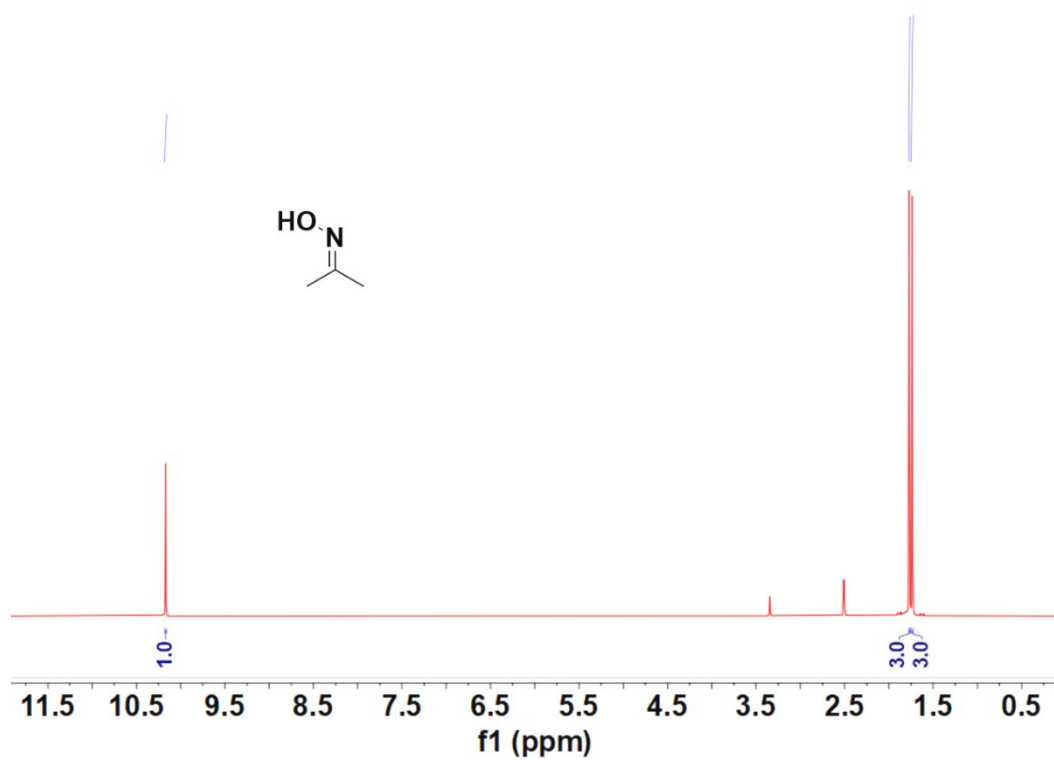


Figure S22 ^1H NMR of acetone oxime product obtained over the M-ZnNSs electrode.

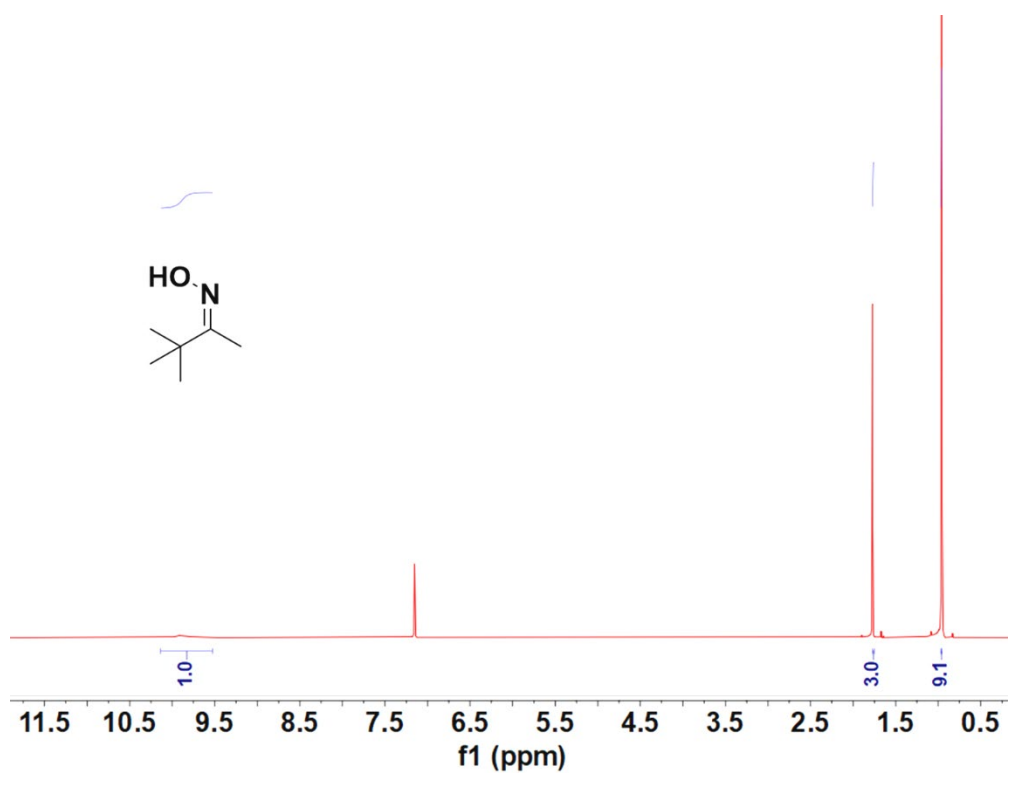


Figure S23 ¹H NMR of pinacolone oxime product obtained over the M-ZnNSs electrode.

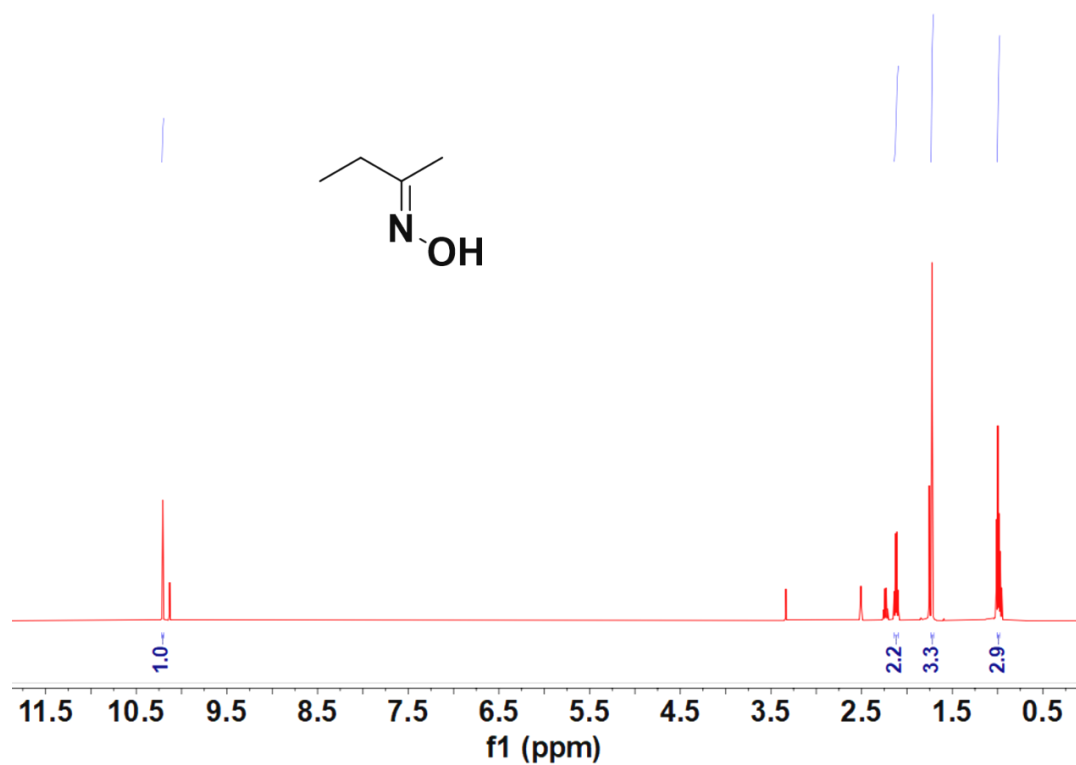


Figure S24 ¹H NMR of butanone oxime product obtained over the M-ZnNSs electrode.

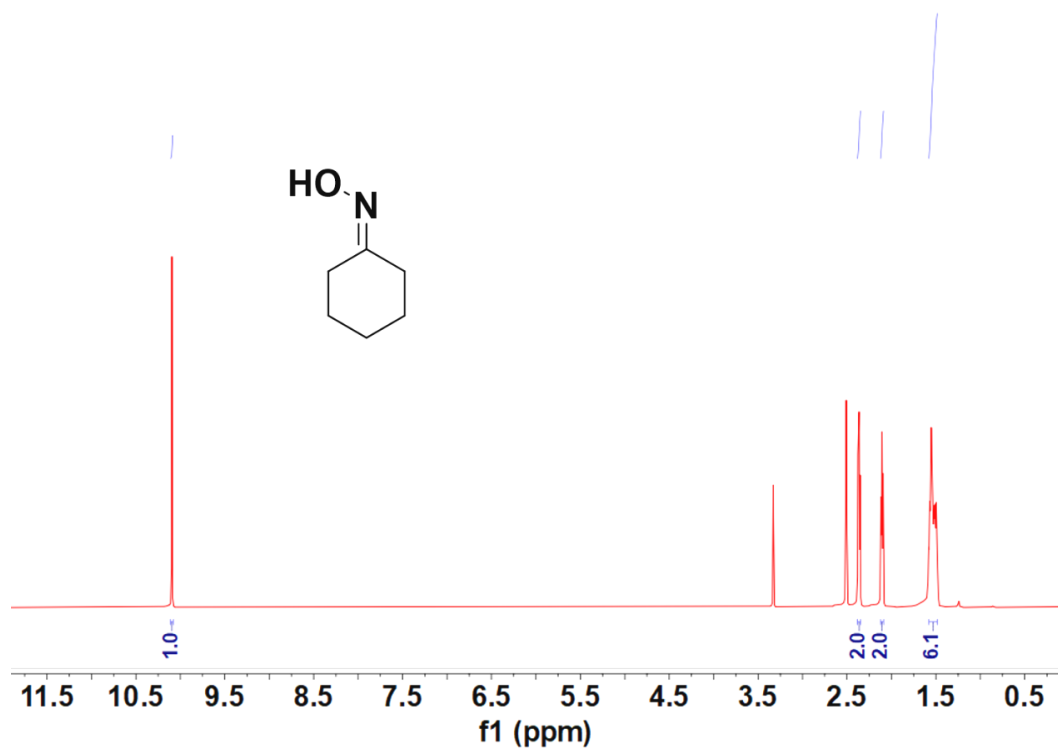


Figure S25 ^1H NMR of cyclohexanone oxime product obtained over the M-ZnNSs electrode.

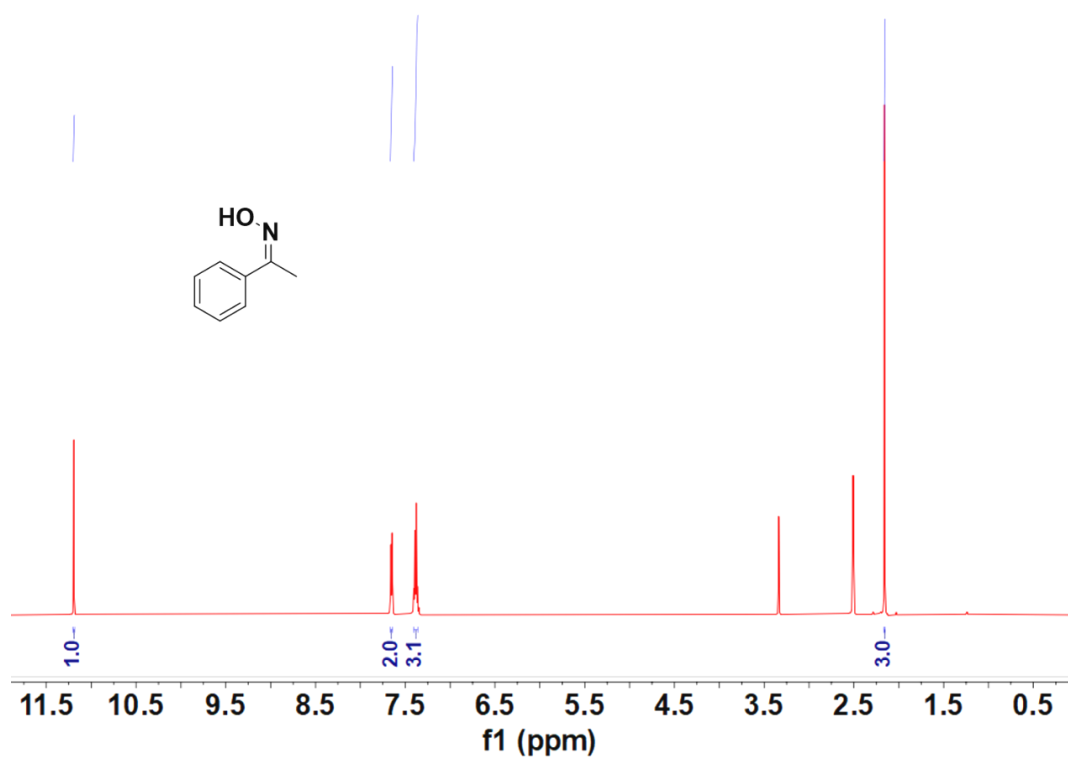


Figure S26 ^1H NMR of acetophenone oxime product obtained over the M-ZnNSs electrode.

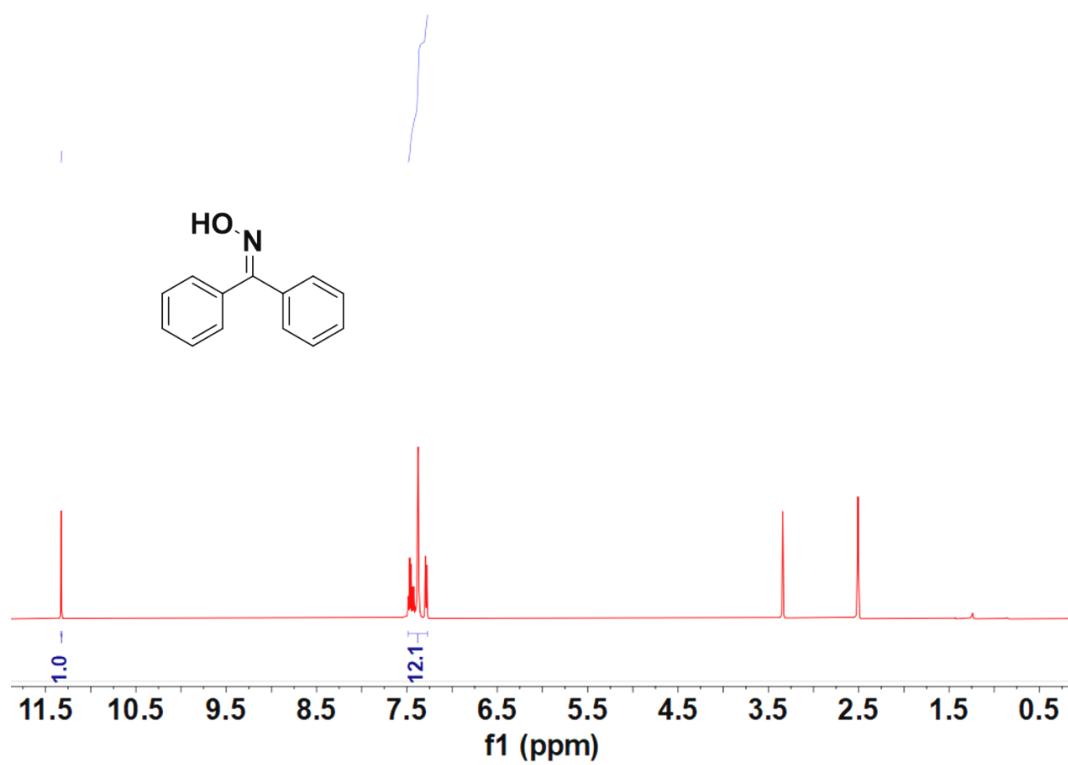


Figure S27 ^1H NMR of benzophenone oxime product obtained over the M-ZnNSs electrode.