

Electronic Supplementary Information (ESI) for

**pH-dependent isotope exchange and hydrogenation
catalysed by water-soluble NiRu complexes as functional
models for [NiFe]hydrogenases**

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This PDF file includes:

Figs. S1 to S5

A Table of Contents

Fig. S1, ESI mass spectra of 2	page 3
Fig. S2, IR spectra of 2	page 4
Fig. S3, ¹ H NMR spectrum of 4 in H ₂ O at pH 9 at 23 °C	page 5
Fig. S4, pH-dependent profile of TOFs for the hydrogenation of glyoxylic acid	page 6
Fig. S5, XPS of 1 , 2 , and 3	page 7

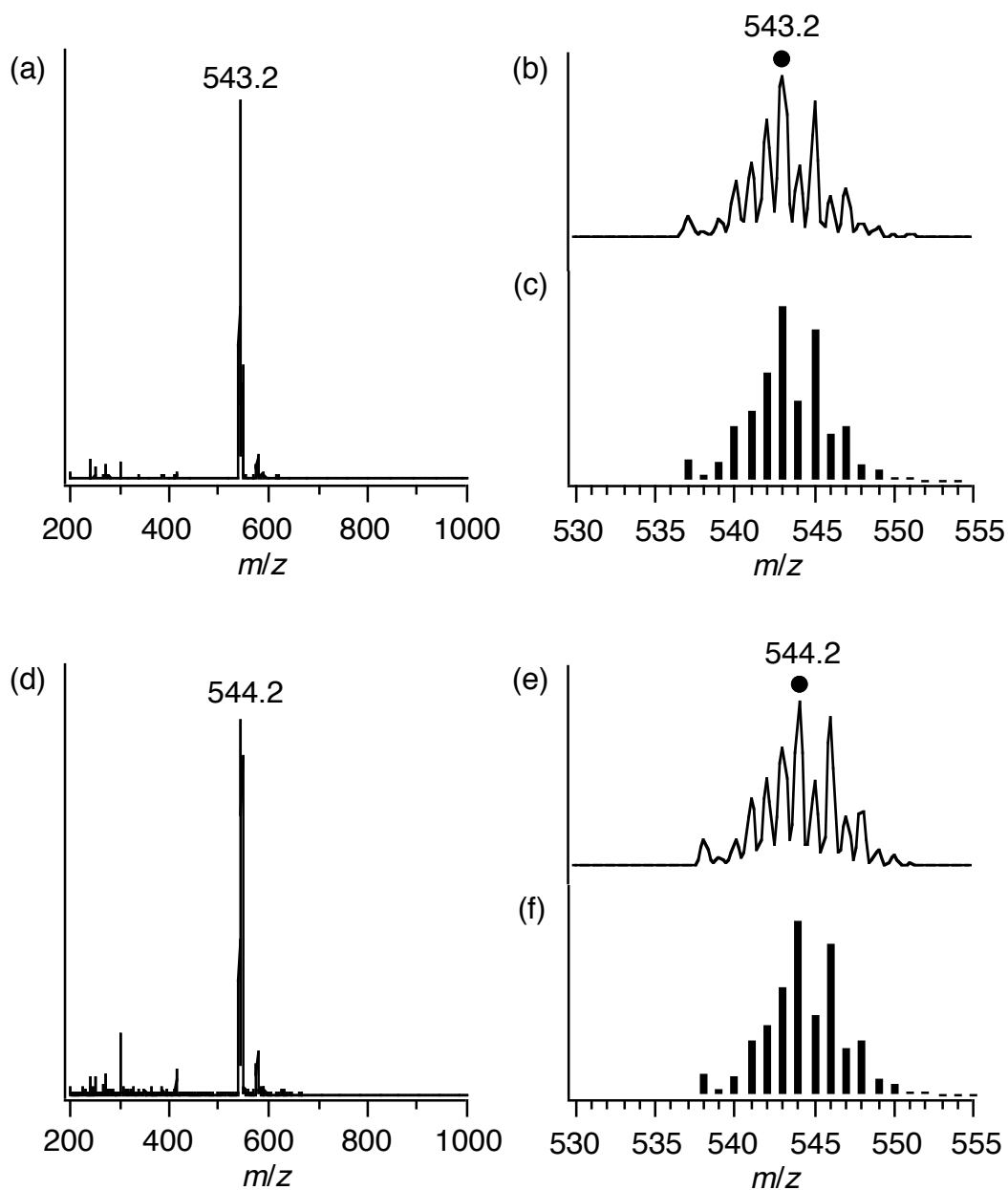


Fig. S1. (a) Positive-ion ESI mass spectrum of $[2](NO_3)$ in H_2O (pH 5). (b) Signal at m/z 543.2 for $[2 - H_2O]^+$. (c) Calculated isotopic distribution for $[2 - H_2O]^+$. (d) Positive-ion ESI mass spectrum of $[D\text{-labeled } 2](NO_3)$ in D_2O (pD 5). (e) The signal at m/z 544.2 for $[D\text{-labeled } 2 - D_2O]^+$. (f) Calculated isotopic distribution for $[D\text{-labeled } 2 - D_2O]^+$.

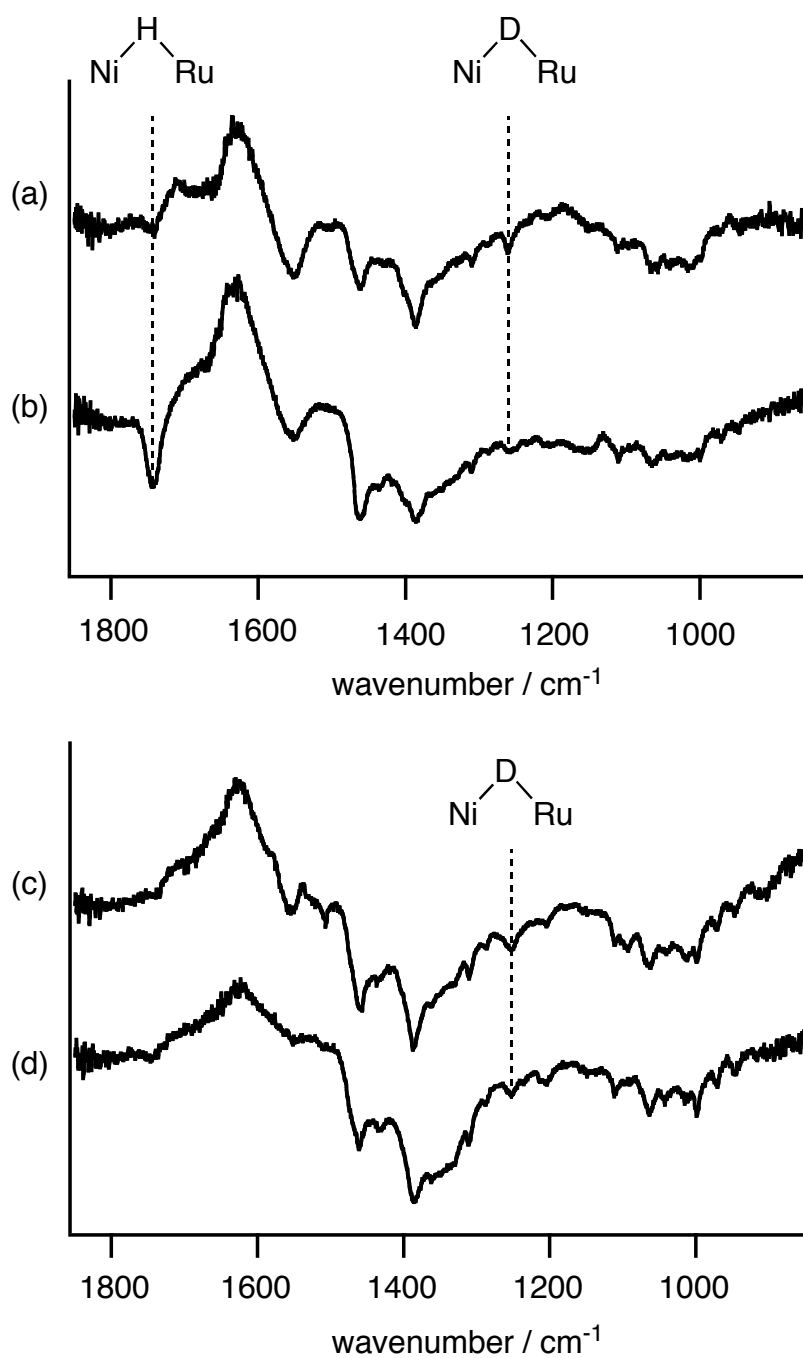


Fig. S2. IR spectrum of D-labeled **2** (50 mM) in H₂O at pH 4.0 at 23 °C for (a) 0 h and (b) 1 h. The spectrum of H₂O (pH 4.0 at 23 °C) was measured as the background. IR spectrum of D-labeled **2** (50 mM) in H₂O at pH 8.0 at 23 °C for (c) 0 h and (d) 1 h. The spectrum of H₂O (pH 8.0 at 23 °C) was measured as the background. The IR spectra were recorded on Thermo Nicolet NEXUS 8700 FT-IR instrument (ATR system) from 650 to 4000 cm⁻¹ using 2 cm⁻¹ standard resolution.

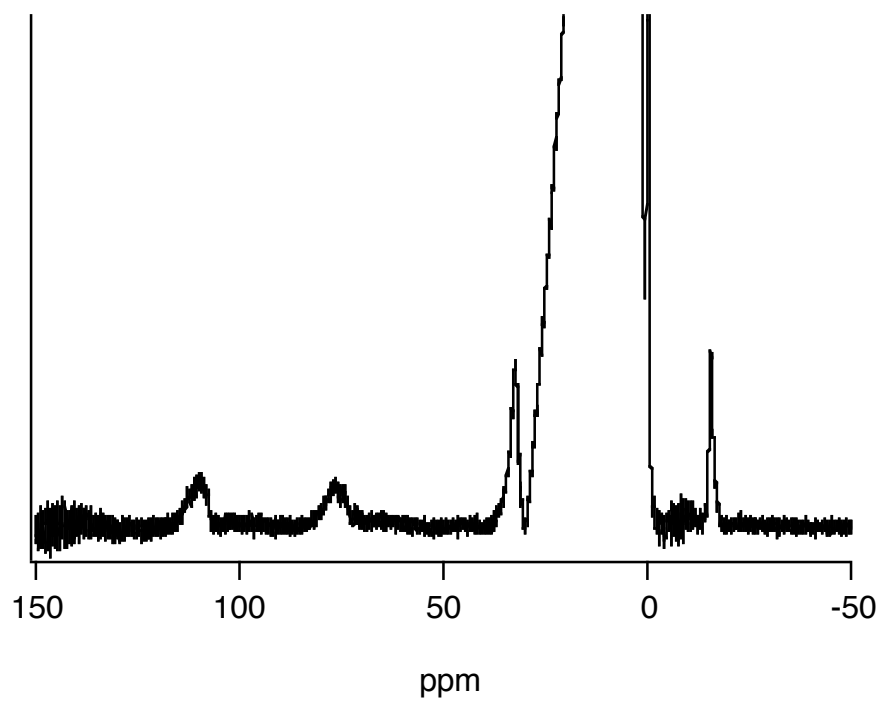


Fig. S3. ^1H NMR spectrum of **4** in H_2O at pH 9 at 23 °C.

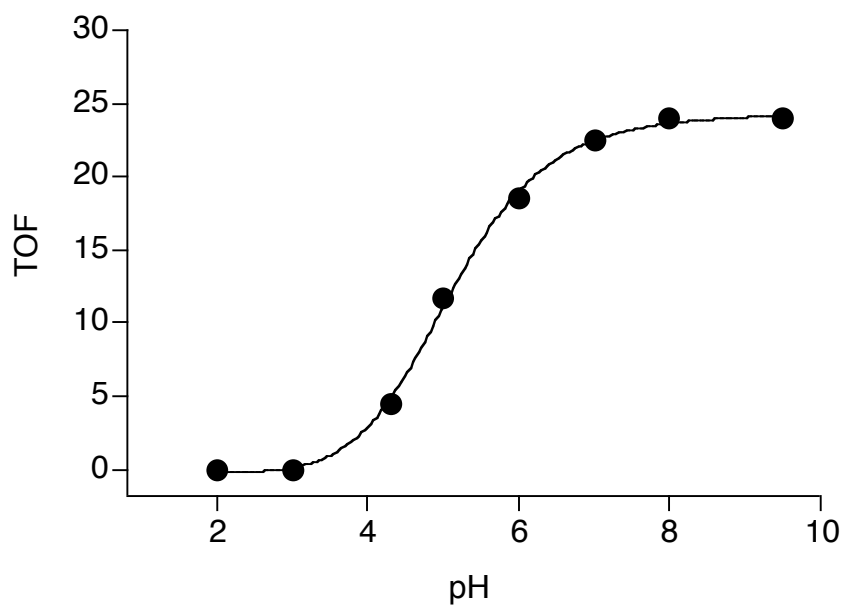


Fig. S4. pH-dependent profile of TOFs for the hydrogenation of glyoxylic acid (250 μmol) with **4** (5 μmol) and H_2 (0.5 MPa) in water (2 mL) at 60 $^\circ\text{C}$ for 1 h.

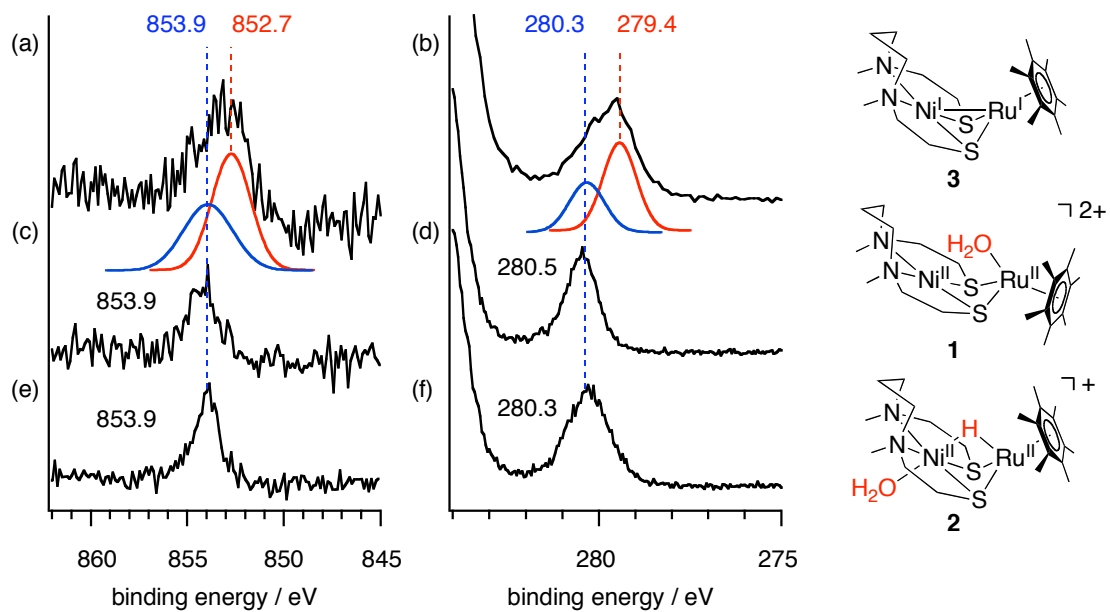


Fig. S5. (a) XPS of Ni 2*p* region for **3**. (b) XPS of Ru 3*d* region for **3**. (c) XPS of Ni 2*p* region for **1**. (d) XPS of Ru 3*d* region for **1**. (e) XPS of Ni 2*p* region for **2**. (f) XPS of Ru 3*d* region for **2**.