

Supplementary Information for

Acetic Acid from CO₂, CH₃I and H₂
by Means of a Water-Soluble Electron Storage Catalyst

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Experimental Section

Materials and Methods. All experiments were carried out under an N₂ atmosphere using standard Schlenk techniques and a glovebox. Acetonitrile was distilled over CaH₂ under an N₂ atmosphere. Methanol was distilled over Mg/I₂ prior to use. H₂ (99.9999%) and CO₂ (99.99%) were purchased from Sumitomo Seika Chemical Co., Ltd., ultra-pure water, CH₃I and KPF₆ were purchased from FUJIFILM Wako Pure Chemical Corporation, NaCF₃SO₃ was purchased from Tokyo Chemical Industry Co and DMSO-*d*₆ and ¹³CH₃I were purchased from Cambridge Isotope Laboratories, Inc. These reagents were used without further purification. 2,2':6',2'':6'',2'''-quaterpyridine (qpy) was prepared by the method described in the literature.¹

Electrospray ionization-mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100LC AccuTOF. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker Avance III 600 FT-NMR spectrometer. Chemical shifts in DMSO-*d*₆ were referenced to tetramethylsilane (TMS) for ¹H NMR. Ultraviolet-visible-near-infrared (UV-vis-NIR) spectra were recorded on a JASCO V-670 UV-visible-NIR spectrophotometer. Gas chromatography mass spectrometry (GC-MS) data were recorded on an Agilent 7890B GC coupled to a 5977B MSD. High performance liquid chromatography (HPLC) was performed by using an Agilent 1260 HPLC infinity system equipped with a reverse phase C18 column (TSK-GEL ODS-100 V 4.6 mm x 250 mm, particle size 5 mm). Gas chromatography (GC) analyses were conducted using a Shimadzu GC-2014 (Ar carrier) instrument with an activated charcoal column equipped with a thermal conductivity detector. X-ray photoelectron spectroscopy (XPS) was performed by using an ULVAC PHI 5000 VersaProbe II system with an Al anode X-ray source. The binding energies were corrected by assuming the C 1s binding energy of the carbon atoms of the ligand to be 284.5 eV.² Elemental analysis were performed using a Yanaco CHN-coder MT-5.

[Rh^{III}(qpy)Cl₂](Cl) {[1](Cl)}. An ethanol solution (20 mL) of Rh^{III}Cl₃ (67 mg, 0.32 mmol) and qpy (100 mg, 0.32 mmol) was refluxed for 5 h. After the resulting solution was cooled to room temperature, light-brown solid was collected by filtration, washed by diethyl ether and dried in vacuo {yield: 62% based on Rh^{III}Cl₃}. ¹H NMR (600 MHz, in DMSO-*d*₆, referenced to TMS): δ 8.09 (t, 2H, C-H), 8.54 (t, 2H, C-H), 8.70 (t, 2H, C-H), 8.90 (d, 2H, C-H), 8.94 (dd, 4H, C-H), 9.66 (d, 2H, C-H). ESI-MS (in methanol): *m/z*

483.1 {[1]⁺, relative intensity(*I*) = 100% in the range of *m/z* 200 to 2000}. Anal. Calcd for 1·3.5H₂O: C₂₀H₂₁Cl₃N₄O_{3.5}Rh: C, 41.23; H, 3.63; N, 9.62%. Found: C, 41.26; H, 3.38; N, 9.61%.

[Rh^I(ppy)](CF₃SO₃) {[2](CF₃SO₃)}. An aqueous suspension (pH 2.0–10, 6 mL) of [1](Cl) (20 mg, 38.5 μmol) was stirred under an H₂ atmosphere (0.1–0.6 MPa) for 12 h at room temperature to form [2](Cl). Aqueous solution of NaCF₃SO₃ (9.9 mg, 57.5 μmol) was added to the resulting solution. The black solid was collected by filtration, washed by water and dried in vacuo {yield: 72% based on 1}. ESI-MS (in methanol): *m/z* 413.0 {[2]⁺, *I* = 100% in the range of *m/z* 200 to 2000}. Anal. Calcd for [2](CF₃SO₃) + 0.2NaCF₃SO₃: C_{21.2}H₁₄F_{3.6}N₄Na_{0.2}O_{3.6}RhS_{1.2}: C, 42.67; H, 2.36; N, 9.39%. Found: C, 42.56; H, 2.40; N, 9.35%.

[Rh^{III}(ppy)(CH₃)I](I) {[3](I)}. Under dark conditions, CH₃I (12 μL, 193 μmol) was added to an aqueous solution of [2](Cl) (6.4 mM, 3 mL) at pH 2.0–10. The resulting mixture was stirred for 6 h to form yellow particulates, which were collected by filtration, washed with small amount of water and dried in vacuo. The yellow powder was dissolved to acetonitrile/DMF (1/4), and insoluble materials were removed by filtration. Recrystallisation was conducted by the slow vapor diffusion of diethyl ether to the filtrate. Orange crystals were collected by filtration and dried in vacuo {yield: 32% based on 2}. ¹H NMR (600 MHz, in DMSO-*d*₆, referenced to TMS): δ 0.79 (d, 3H, Rh-CH₃), 7.96 (t, 2H, C-H), 8.43 (t, 2H, C-H), 8.54 (t, 2H, C-H), 8.77–8.80 (m, 6H, C-H), 9.43 (d, 2H, C-H). ESI-MS (in methanol): *m/z* 554.9 {[3]⁺, *I* = 100% in the range of *m/z* 200 to 2000}. Anal. Calcd for [3](I)·0.5(CH₃)₂NCHO: C_{22.5}H_{20.5}I₂N_{4.5}O_{0.5}Rh: C, 37.60; H, 2.88; N, 8.77%. Found: C, 37.73; H, 2.72; N, 8.53%.

Stepwise Reaction of 3 with CO₂. An aqueous solution (1.5 mL) of [3](I) (3.0 mg, 4.39 μmol) was stirred for 12 h at 80 °C under CO₂ atmosphere (0.8 MPa) at pH 2.0. After cooling at room temperature, a portion (800 μL) of the resulting solution was passed through a short silica column to remove complex(es). The amount of acetic acid was quantified with HPLC. The mobile phase was H₂O/CH₃CN (98/2) with phosphoric acid (0.1v/v%) and a flow rate was 1.0 mL min⁻¹. The yield of acetic acid was determined as 12 % based on [3](I).

Catalytic Production of Acetic Acid. A H₂O/CH₃OH (1/1) solution (3.9 mL) of [1](Cl) (1.0 mg, 1.92 μmol) and CH₃I (6.7 μL, 108 μmol) was stirred for 24 h at 80 °C

under an H₂ (0.15 MPa) and CO₂ (0.8 MPa) atmosphere in presence of LiBr (54 mg, 0.62 mmol) at pH 2.0. After cooling at room temperature, a portion (800 μL) of the resulting solution was passed through a short silica column to remove complex(es). The amount of acetic acid was quantified with HPLC. The mobile phase was H₂O/CH₃CN (98/2) with phosphoric acid (0.1v/v%) and a flow rate was 1.0 mL min⁻¹. Turnover number of acetic acid production was determined as 1 by HPLC (TON = mol of acetic acid/mol of **1**). No catalytic production of acetic acid was occurred without **1**, H₂, CO₂ or CH₃I, which was confirmed by HPLC as blank experiment.

Qualitative Analysis of Acetic Acid by GC-MS. A H₂O/CH₃OH (1/1) solution (3.9 mL) of [**1**](Cl) (1.0 mg, 1.92 μmol) and CH₃I (6.7 μL, 108 μmol) was stirred for 24 h at 80 °C under an H₂ (0.15 MPa) and CO₂ (0.8 MPa) atmosphere in presence of LiBr (54 mg, 0.62 mmol) at pH 2.0. A portion (350 μL) of the reaction solution was added to diethyl ether (1.4 mL) and stirred for 30 min at 30 °C. The organic phase was concentrated to 500 μL, and acetic acid in the solution was detected by GC-MS.

¹³C-labelled Experiment for Catalytic Reaction. The procedure was the same as that of the above CH₃I experiment except ¹³CH₃I (6.7 μL, 108 μmol) was used. The produced ¹³CH₃COOH was detected by GC-MS.

pH Adjustment. pH of aqueous solutions were adjusted by using 1.0 M HNO₃ solution. The pH values of the solutions were determined by a pH meter (IQ Scientific Instruments, Inc., IQ200) equipped with a stainless steel micro pH probe (IQ Scientific Instruments, Inc., PH15-SS).

X-ray Crystallographic Analyses of **1, **2** and **3**.** A single crystal of [**1**](Cl) was obtained from its ethanol solution at room temperature. A single crystal of [**2**](CF₃SO₃) was obtained from the DMF solution diffused with acetone at room temperature. A single crystal of [**3**](PF₆) was obtained from the acetonitrile solution of **3** diffused with diethyl ether at room temperature in presence of KPF₆. Measurements were made on a Rigaku XtaLAB P200 with confocal monochromated Mo-Kα radiation (λ = 0.7107 Å). Data were collected and processed using the CrystalClear program. All calculations were performed using the CrystalStructure crystallographic software package. Crystallographic data for **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 2054176 (**1**), 2054177 (**2**) and 2054178 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge

CB2 1EZ, UK {fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk}.

Table S1. Characterisation of Rh complexes **1**, **2** and **3**

	1	2	3
X-ray	Fig. 1	Fig. 2	Fig. 3
ESI-MS	Fig. S1	Fig. S3	Fig. S6
¹ H NMR	Fig. S2	-	Fig. S7
UV-vis	-	Fig. S4	Fig. S8
XPS	Fig. S5	Fig. S5	-

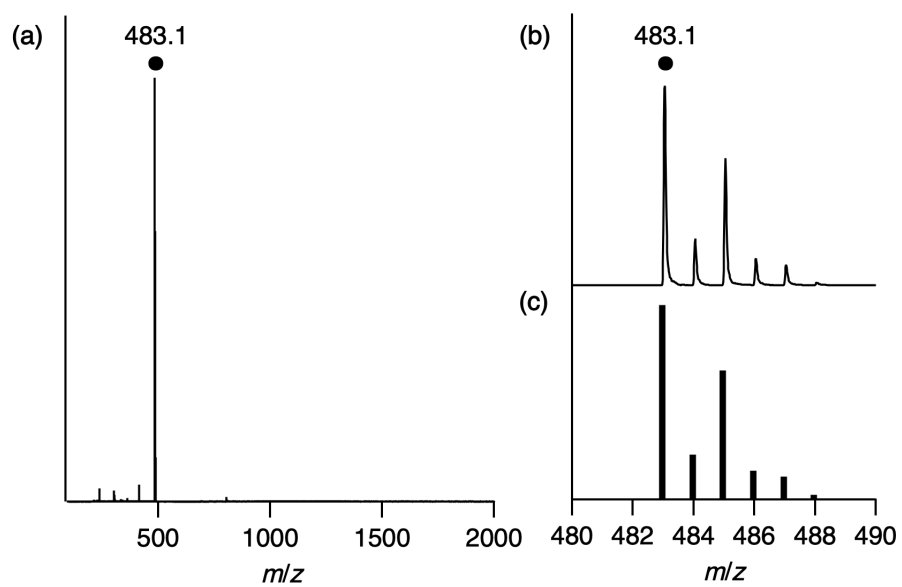


Fig. S1 (a) A positive-ion ESI mass spectrum of [1](Cl) in methanol. The signal at m/z 483.1 corresponds to [1]⁺. (b) The signal at m/z 483.1 for [1]⁺. (c) The calculated isotopic distribution for [1]⁺.

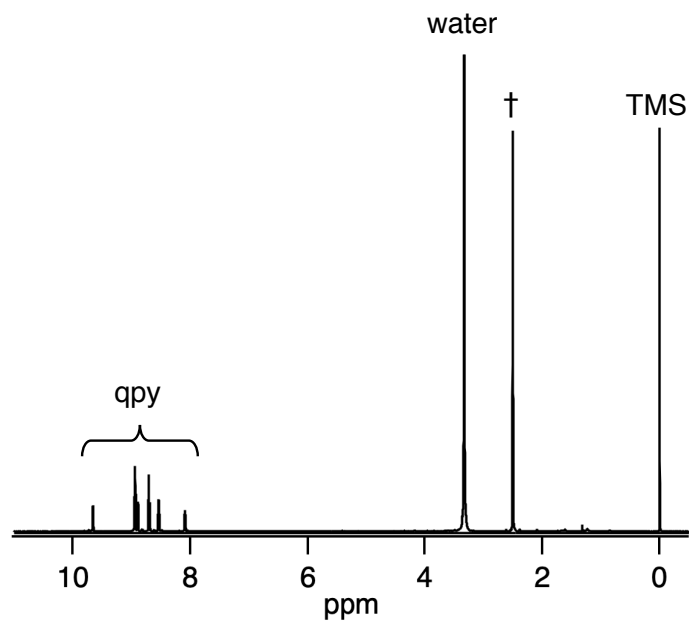


Fig. S2 A ^1H NMR spectrum of $[\mathbf{1}](\text{Cl})$ in $\text{DMSO-}d_6$. Tetramethylsilane (TMS), reference with the methyl proton resonance set at 0.00 ppm. †: The signal of dimethyl sulfoxide contained in $\text{DMSO-}d_6$.

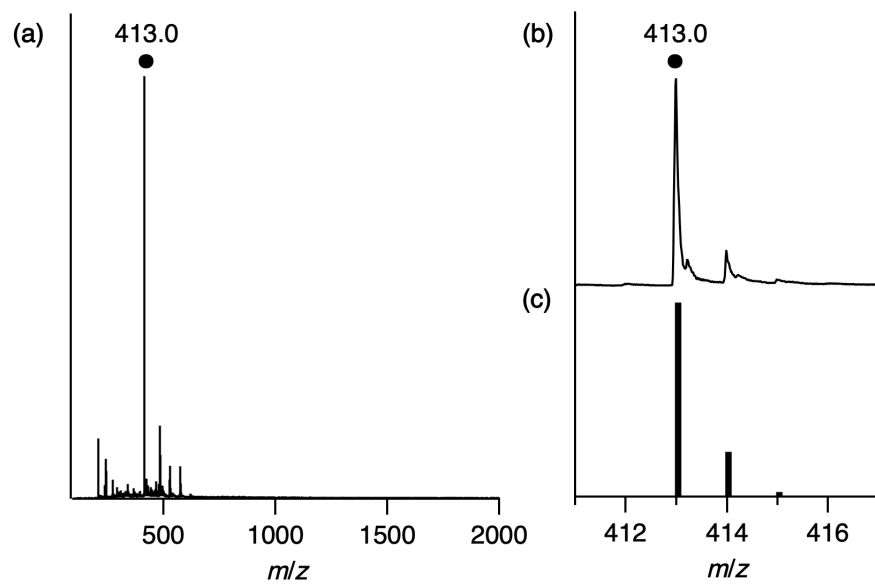


Fig. S3 (a) A positive-ion ESI mass spectrum of [2](Cl) in methanol. The signal at m/z 413.0 corresponds to [2]⁺. (b) The signal at m/z 413.0 for [2]⁺. (c) The calculated isotopic distribution for [2]⁺.

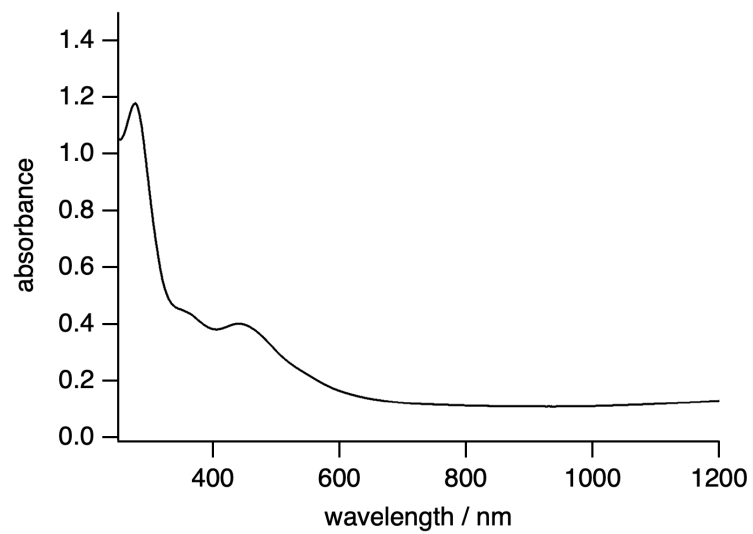


Fig. S4 An UV-vis-NIR absorption spectrum of [2](Cl) obtained from the reaction of [1](Cl) with H₂ (0.6 MPa) at room temperature for 12 h in water (pH 5.5). Light pass length is 0.1 cm.

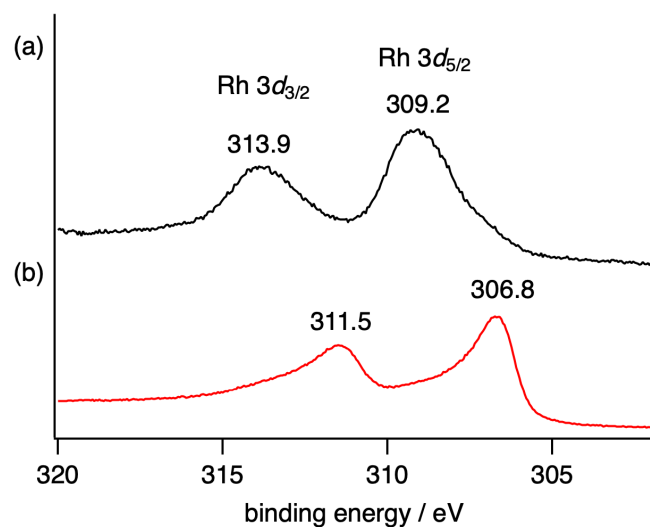


Fig. S5 XPS spectra of the Rh 3d regions for (a) the Rh^{III} complex **[1]**(Cl) and (b) the Rh^I complex **[2]**(CF₃SO₃).

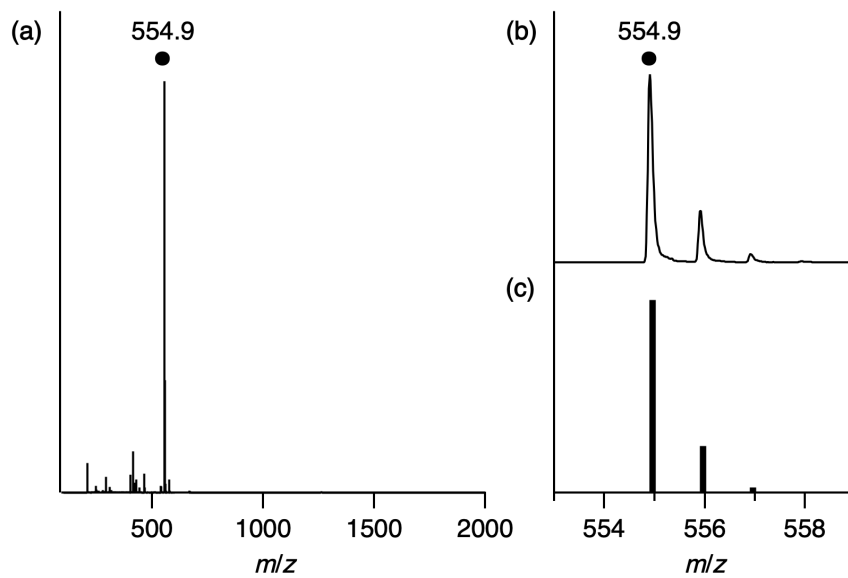


Fig. S6 (a) A positive-ion ESI mass spectrum of [3](I) in methanol. The signal at m/z 554.9 corresponds to [3]⁺. (b) The signal at m/z 554.9 for [3]⁺. (c) The calculated isotopic distribution for [3]⁺.

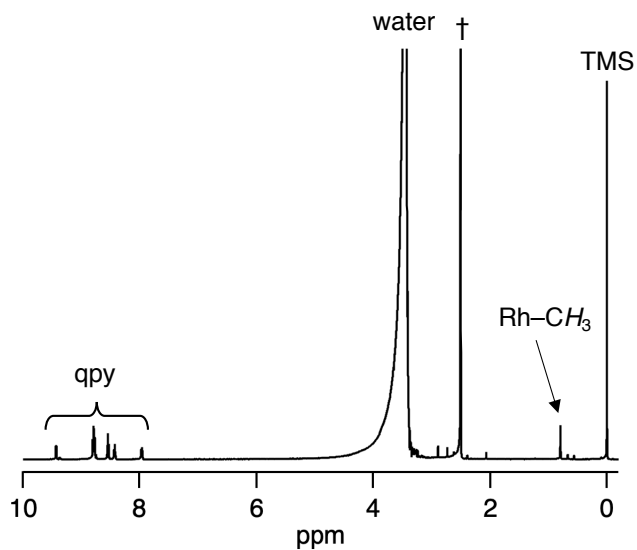


Fig. S7 A ^1H NMR spectrum of [3](I) in $\text{DMSO-}d_6$. Tetramethylsilane (TMS), reference with the methyl proton resonance set at 0.00 ppm. †: The signal of dimethyl sulfoxide contained in $\text{DMSO-}d_6$.

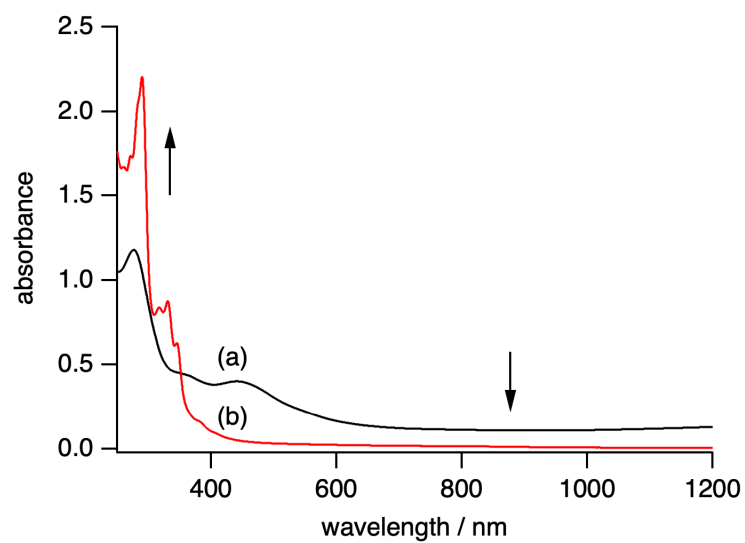


Fig. S8 UV-vis-NIR absorption spectra of (a) aqueous solution of [2](Cl) and (b) aqueous solution 30 min after the reaction of [2](Cl) with 5 equivalents of CH₃I at room temperature. Light pass length is 0.1 cm.

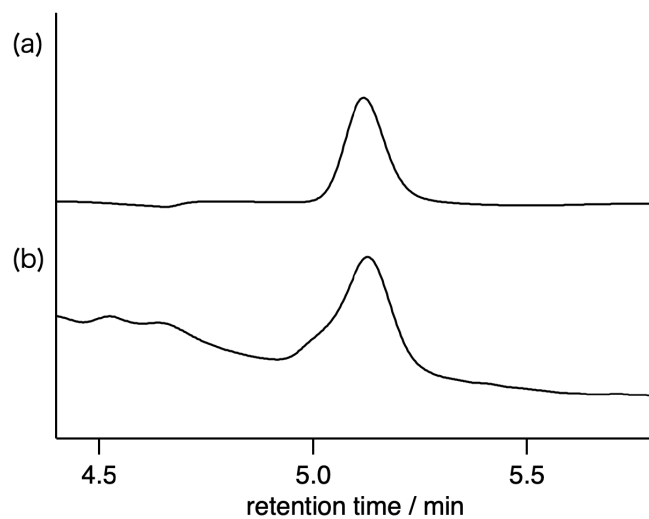


Fig. S9 Liquid chromatograms of (a) authentic acetic acid in H₂O/CH₃CN (98/2) with phosphoric acid (0.1v/v%) and (b) the *in-situ* solution of [3](I) with CO₂ in H₂O /CH₃CN (98/2) with phosphoric acid (0.1v/v%).

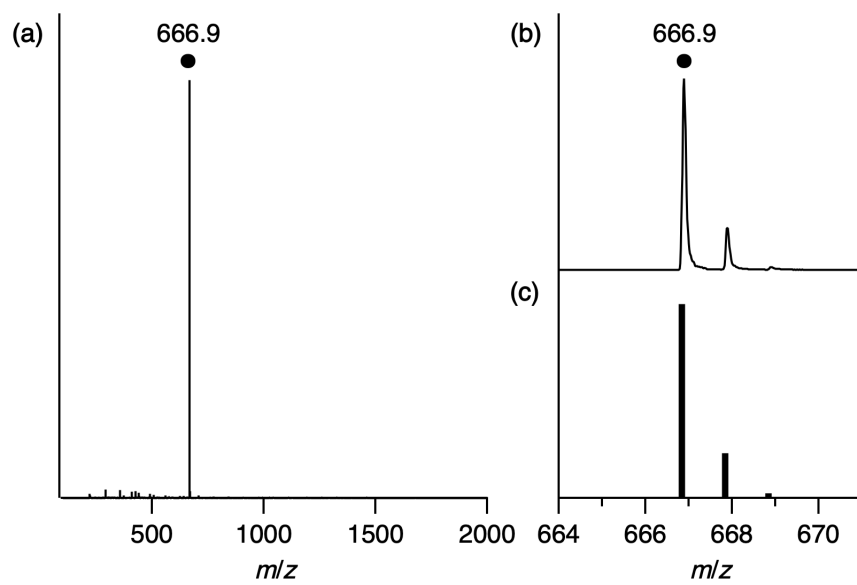


Fig. S10 (a) A positive-ion ESI mass spectrum of **4** in methanol. The signal at m/z 666.9 corresponds to $[\mathbf{4}]^+$. (b) The signal at m/z 666.9 for $[\mathbf{4}]^+$. (c) The calculated isotopic distribution for $[\mathbf{4}]^+$.

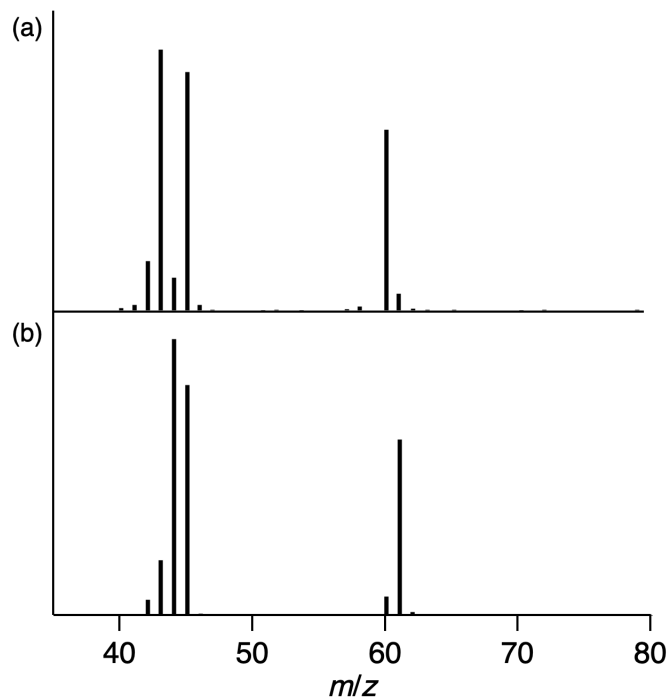


Fig. S11 Positive-ion GC mass spectra of (a) acetic acid obtained from the catalytic reaction solution of **[1]**(Cl) and CH_3I stirring for 24 h at 80 °C under an H_2 (0.15 MPa) and CO_2 (0.8 MPa) atmosphere in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1/1) solution in the presence of LiBr and (b) $^{13}\text{CH}_3\text{COOH}$ obtained from the reaction of **[1]**(Cl) with $^{13}\text{CH}_3\text{I}$ stirring for 24 h at 80 °C under an H_2 (0.15 MPa) and CO_2 (0.8 MPa) atmosphere in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1/1) solution in the presence of LiBr. The detailed procedures are described in the experimental section.

References

- 1 W. Muramatsu, T. Hattori, H. Yamamoto, *J. Am. Chem. Soc.* 2019, **141**, 12288–12295.
- 2 J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, In *Handbook of X-ray Photoelectron Spectroscopy*; Chastin, J., King, R. C., Jr., Eds.; Physical Electronics, Inc.: Eden Prairie, MN, 1995; pp 40– 41.