

Electronic supplementary information

for

**Selective catalytic 2e⁻-oxidation of organic substrates by an Fe^{II} complex
having an *N*-heterocyclic carbene ligand in water**

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1. General
2. Synthesis
3. Measurements
4. Supplementary figure

1. General.

NMR measurements were performed on Bruker AVANCE 400 and DPX 400 spectrometers. DSS (= 3-(trimethylsilyl)-propane-sulfonate sodium salt) and sodium acetate were used as an internal standard for ^1H NMR spectroscopy in D_2O . ESI-TOF-MS spectra were obtained on a JEOL JMS-T100CS mass spectrometer. UV-Vis absorption spectra were measured on a Shimadzu UV-2450 spectrophotometer at room temperature. IR spectra were measured on a JASCO FT/IR-550 spectrometer using KBr disks in the range of $400 \sim 4000 \text{ cm}^{-1}$. Cyclic, differential-pulse and square-wave voltammograms (CV, DPV, and SWV, respectively) were recorded on a BAS electrochemical analyser Model 660A. ESR spectroscopy was performed on a Bruker BioSpin EMXPlus 9.5/2.7 spectrometer.

Chemicals and solvents were used as received from Tokyo Chemical Industry (TCI) Co., FUJIFILM Wako Pure Chemical Corp., Nacalai Tesque or Sigma-Aldrich Corp., unless otherwise mentioned. All syntheses were performed under Ar atmosphere.

2. Synthesis.

5,6-Dichloro-1,3-dihydro-1,3-bis(2-pyridyl)methyl-2H-benzimidazolium bromide ($\text{PY}_4\text{Cl}_2\text{Blm-H}\cdot\text{Br}$). 5,6-Dichloro-1,3-*N,N'*-bis(di-pyridylmethyl)-phenylenediamine ($\text{PY}_4\text{Cl}_2\text{BDA}$) was synthesized as a precursor according to the literature procedure.¹ A solution of 4,5-dichloro-1,2-phenylenediamine (200 mg, 1.1 mmol), di-2-pyridylketone (438 mg, 2.4 mmol) and *N,N,N',N'*-tetramethyl-ethylenediamine (2.0 mL, 14 mmol) in toluene (10 mL) was heated at 80°C for 30 min. TiCl_4 (400 mL, 3.4 mmol) was then added dropwise over 20 min, during the temperature increased to 110°C . After stirring at the temperature for 1 d, the reaction mixture was cooled to R.T. and filtered through a Celite pad to remove insoluble materials. The solids on the Celite pad were washed well with AcOEt (30 mL) and CH_2Cl_2 (30 mL), and the combined filtrate was concentrated to dryness. NaBH_4 (300 mg, 7.8 mmol) and dry EtOH (20 mL) were added to the residue and the reaction mixture was stirred at R.T. for 18 h in the dark. After addition of distilled water (50 mL) to quench unreacted NaBH_4 , the reaction mixture was stirred at R.T. for several hours. Then, CH_2Cl_2 (25 mL) and distilled water (25 mL) were added to the reaction mixture, and the organic layer was separated, washed with water (30 mL) three times, dried over Na_2SO_4 . By removing the volatile with a rotary evaporator under reduced pressure, crude $\text{PY}_4\text{Cl}_2\text{BDA}$ was obtained and used for the next reaction without purification. The crude $\text{PY}_4\text{Cl}_2\text{BDA}$ was dissolved into $\text{CH}(\text{OMe})_3$ (15 mL, 137 mmol), and NH_4PF_6 (0.52 g, 3.19 mmol) in MeOH (5 mL) and a drop of 12 M HCl were added to the solution. The reaction mixture was stirred at 40°C for 24 h in the dark. After neutralization by adding a saturated aqueous solution of NaHCO_3 , CH_2Cl_2 (15 mL) and distilled water (30 mL) were added to the reaction mixture. The organic layer was separated, washed with water (30 mL) three times, dried over Na_2SO_4 , and then the volatile was evaporated under reduced pressure. The crude mixture obtained was dissolved into MeCN (5 mL), and the solution of LiBr (2.37 g, 27.2 mmol) in MeCN was added. After stirring for an hour, the reaction mixture was filtered through membrane to obtain white-yellow crystals (292.4 mg, 0.48 mmol) of $\text{PY}_4\text{Cl}_2\text{Blm-H}\cdot\text{Br}$ in 54% yield for the three steps. ^1H NMR (CD_3CN ; Fig. S14): δ 7.37 (s, 2H), 7.39 (ddd, $J = 8, 5, 1 \text{ Hz}$, 4H), 7.62 (d, $J = 8 \text{ Hz}$, 4H), 7.88 (td, $J = 8, 2 \text{ Hz}$, 4H), 8.28 (s, 2H), 8.55 (ddd, $J = 8, 5, 1 \text{ Hz}$, 4H), 10.64 (s, 1H). ESI-TOF-MS: $m/z = 523.12$ (sim for $[\text{M} - \text{Br}]^+$: $m/z = 523.12$).

$[\text{Fe}^{\text{II}}(\text{PY}_4\text{Cl}_2\text{Blm})(\text{MeCN})](\text{PF}_6)_2$. To a suspension of iron(II) acetate (305 mg, 1.6 mmol) in DMSO (10.0 mL), $\text{PY}_4\text{Cl}_2\text{Blm-H}\cdot\text{Br}$

H·Br (101 mg, 0.16 mmol) was added and the mixture was stirred at 50 °C for 24 h in the dark. After addition of KPF₆ (351 mg, 1.9 mmol) and distilled water (20 mL), the reaction mixture was filtered through membrane to obtain red solid. The crude product was recrystallized from MeCN/Et₂O and pale-red crystals of [Fe^{II}(PY₄Cl₂BIm)(MeCN)](PF₆)₂ (100 mg, 0.13 mmol) were obtained in 81% yield. ¹H NMR (CD₃CN; Fig. S15): δ 7.36 (ddd, *J* = 8, 5, 1 Hz, 4H), 7.58 (s, 2H), 7.82 (td, *J* = 8, 1 Hz, 4H), 7.88 (dd, *J* = 8, 1 Hz, 4H), 8.31 (s, 2H), 9.41 (d, *J* = 5 Hz, 4H). UV-Vis (CH₃CN): λ_{max} [nm] = 340, 396, 448. ESI-TOF-MS (CH₃CN): *m/z* = 309.49 (sim for [M – 2PF₆]²⁺: *m/z* = 309.54). IR (KBr): ν [cm⁻¹] = 566 (PF₆), 856 (PF₆), 1447 (C=C). Anal. Calcd. for C₃₁H₂₃Cl₂N₇Fe·2PF₆·2H₂O: H 2.88, C 39.35, N 10.36; Found: H 2.91, C 38.62, N 10.58.

[Fe^{II}(PY₄Cl₂BIm)(OH₂)](NO₃)₂ (1·(NO₃)₂). A saturated solution of KNO₃ in acetone (2 mL) was added to a solution of [Fe^{II}(PY₄Cl₂BIm)(MeCN)](PF₆)₂ (17.0 mg, 26.3 mmol) in acetone to obtain a red solution. After stirring overnight, the reaction mixture was filtered through membrane to obtain red powder of 1·(NO₃)₂ (13 mg, 20.1 mmol) in 76% yield. ¹H NMR (D₂O): δ 7.49 (dd, *J* = 8, 5 Hz, 4H), 7.82 (s, 2H), 7.93 (dd, *J* = 8, 5 Hz, 4H), 8.02 (d, *J* = 8 Hz, 4H), 8.12 (s, 2H), 9.61 (d, *J* = 5 Hz, 4H). IR (KBr): ν [cm⁻¹] = 1391 (NO₃), 1447 (C=C), 3408 (OH₂). Anal. Calcd. for C₂₉H₂₂Cl₂N₆OFe·2NO₃·H₂O: H 3.27, C 47.11, N 15.16; Found: H 3.20, C 47.05, N 15.20.

[Fe^{II}(PY₄Cl₂BIm)(OH₂)](ClO₄)₂ (1·(ClO₄)₂). A saturation solution of NaClO₄ in water (2 mL) was added to a solution of 1 (17.0 mg, 26.3 mmol) in water to obtain a red solution. After stirring overnight, the reaction mixture was filtered through a membrane filter to obtain red powder of 1·(ClO₄)₂ (10 mg, 16 mmol) was obtained in 59% yield. ¹H NMR (D₂O): δ 7.49 (dd, *J* = 8, 5 Hz, 4H), 7.82 (s, 2H), 7.93 (dd, *J* = 8, 5 Hz, 4H), 8.02 (d, *J* = 8 Hz, 4H), 8.12 (s, 2H), 9.61 (d, *J* = 5 Hz, 4H). IR (KBr): ν [cm⁻¹] = 1100 (ClO₄), 1447 (C=C), 3530 (OH₂). Anal. Calcd. For C₂₉H₂₂Cl₂N₆OFe·2ClO₄·H₂O: H 2.97, C 42.78, N 10.34; Found: H 2.91, C 42.90, N 10.33.

3. Measurements.

Kinetic analysis on catalytic oxidations of EtPS, CumS, DPMS, TPMS, BnOH and 2-PrOH. Concentrations of the oxidation products were determined by ¹H NMR spectroscopy using DSS or NaOAc as an internal standard. The product amounts were plotted against the reaction time to obtain time profiles of the product formation. Least-square linear fitting was conducted for the plots between 0 to ca. 60 min. The slope of the fitting line obtained was used to determine the initial velocity of the EtPhS, CumS, DPMS, TPMS, BnOH and 2-PrOH oxidation (Table S3).

X-ray crystallography.

Single crystals suitable for X-ray crystallography were obtained by recrystallization from an MeCN solution of [Fe^{II}(PY₄Cl₂BIm)(MeCN)](PF₆)₂ with vapour diffusion of DME, and from an EtOH/water = 2 : 1 (v/v) solution of 1·(ClO₄)₂ with vapour diffusion of AcOEt. The single crystals obtained were mounted using a mounting loop. All diffraction data were collected on a Bruker APEXII diffractometer at 120 K with a graphite-monochromated Mo *K*α radiation source (λ = 0.71073 Å) by the 2θ scan. All structural refinements were performed using the Yadokari-XG crystallographic software package.² The structures were solved by a direct method using SHELX-2017.³ Crystallographic data for [Fe^{II}(PY₄Cl₂BIm)(MeCN)](PF₆)₂ (Fig. S16) and 1·(ClO₄)₂ (Fig. 1) are summarized in Table S5. In the structural refinements of [Fe^{II}(PY₄Cl₂BIm)(MeCN)](PF₆)₂, contributions of the solvent molecules of crystallization were subtracted from the diffraction data by the “Squeeze” program.⁴ CCDC-2002361 for

[Fe^{II}(PY₄Cl₂Blm)(MeCN)](PF₆)₂ and CCDC-2002362 for **1**·(ClO₄)₂ contain the supplementary crystallographic data.

DFT calculations.

DFT calculations for [Fe(O)(PY₄Cl₂Blm)]²⁺ interacting with two water molecules at the oxygen ligand in the singlet, triplet, and quintet states were carried out using the B3LYP functional⁶ implemented in the Gaussian 16 program package.⁷ For the Fe atom, the (14s9p5d)/[9s5p3d] primitive set of Wachters-Hay^{8,9} with one polarization f-function was used, and for the H, C, N, O and Cl atoms, the 6-311+G** basis set¹⁰ was used.

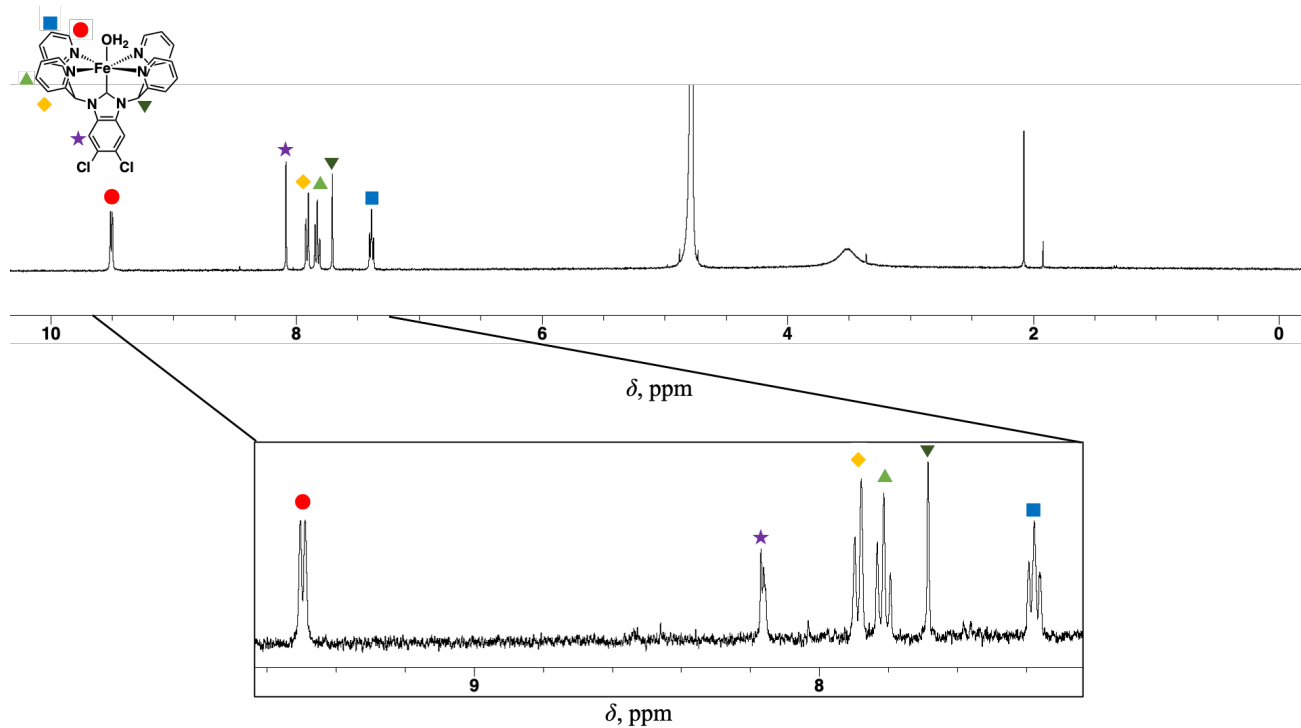


Fig. S1 A ^1H NMR spectrum of **1**·(NO_3) $_2$ in D_2O .

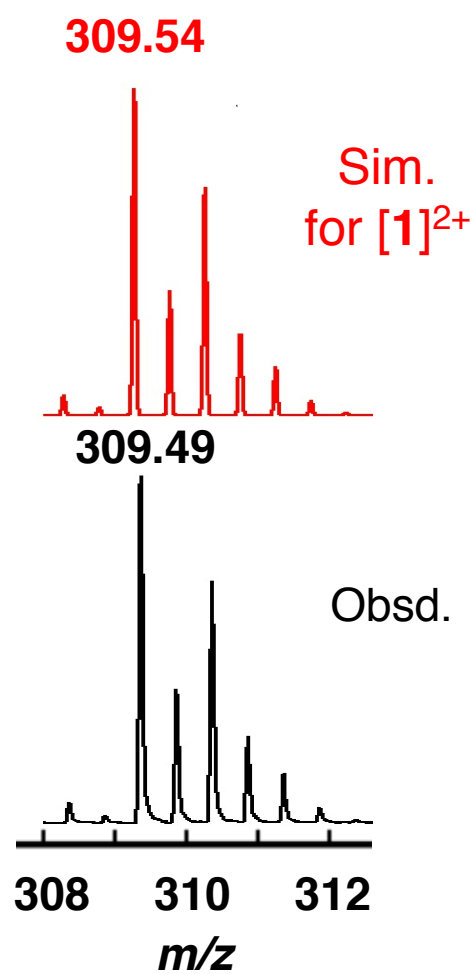


Fig. S2 ESI-TOF-MS spectrum of $1 \cdot (\text{NO}_3)_2$ in acetonitrile: Observed (bottom) and simulated (upper) spectra.

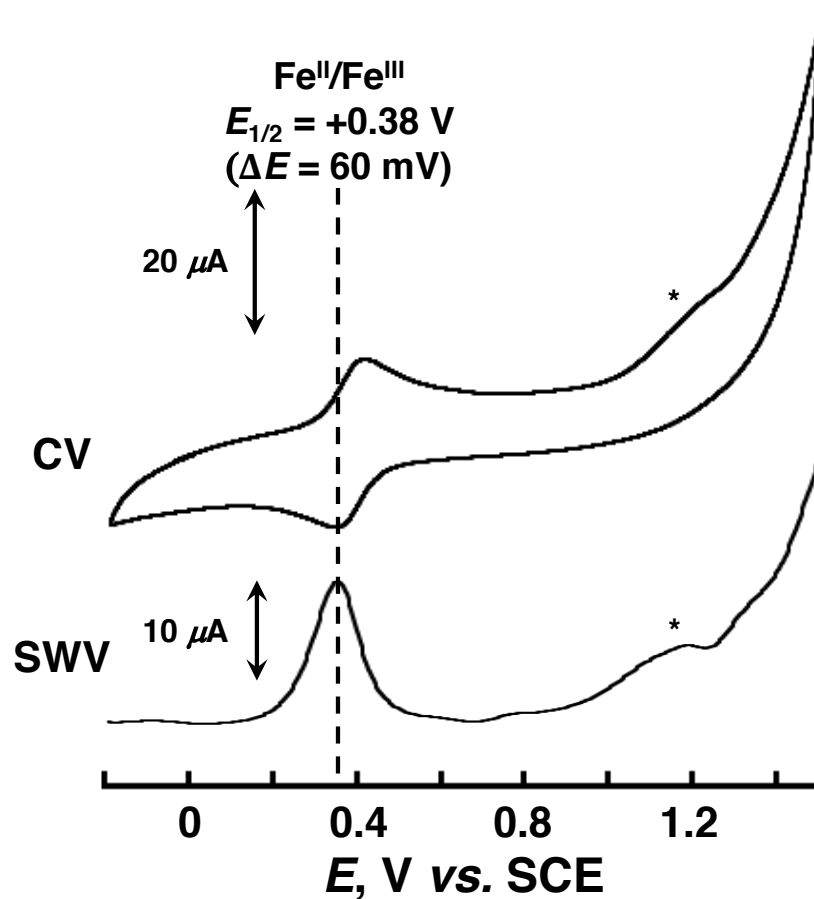


Fig. S3 Cyclic and square-wave voltammograms (CV and SWV) of $1 \cdot (\text{NO}_3)_2$ in H_2O (pH 7.2) at room temperature. Sample concentration: 0.5 mM, working electrode: GC disk, counter electrode: Pt wire, reference electrode: Ag/AgCl, electrolyte: 0.1 M KNO_3 , scan rate: 100 mV/s. *: impurity.

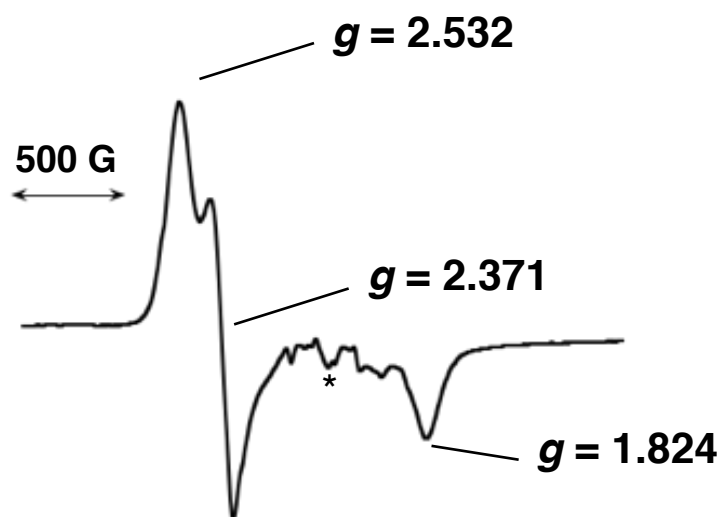


Fig. S4 An ESR spectrum after reaction of $1 \cdot (\text{NO}_3)_2$ (2.0 mM) with cerium(IV) ammonium nitrate (CAN; 2.4 mM) in water measured at 5 K. Microwave frequency: 9.572 GHz, microwave power: 10 mW, modulation frequency: 100.00 Hz, modulation amplitude: 10.00 G. *: impurity.

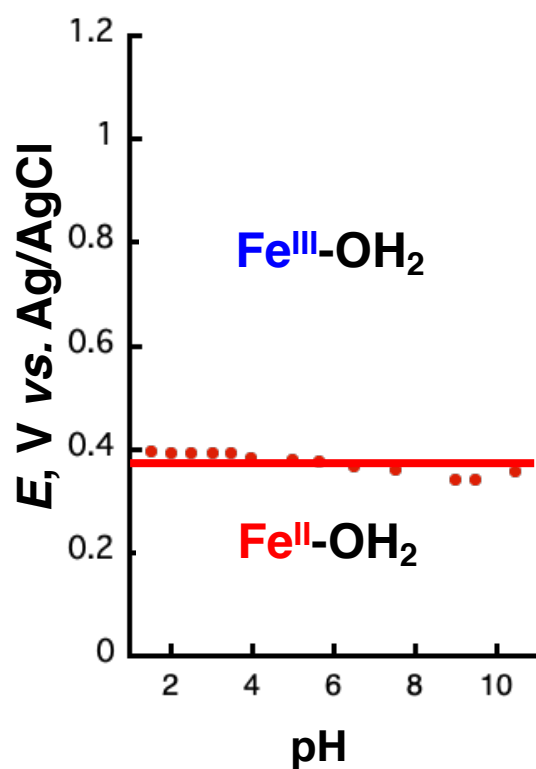


Fig. S5 A Pourbaix diagram of $1\cdot(\text{NO}_3)_2$ in pH-controlled aqueous solutions at room temperature. The oxidation potentials of $1\cdot(\text{NO}_3)_2$ were determined by SWV. Sample concentration: 0.5 mM, working electrode: GC disk, counter electrode: Pt wire, reference electrode: Ag/AgCl, electrolyte: 0.05 M KNO_3 , scan rate: 100 mV/s.

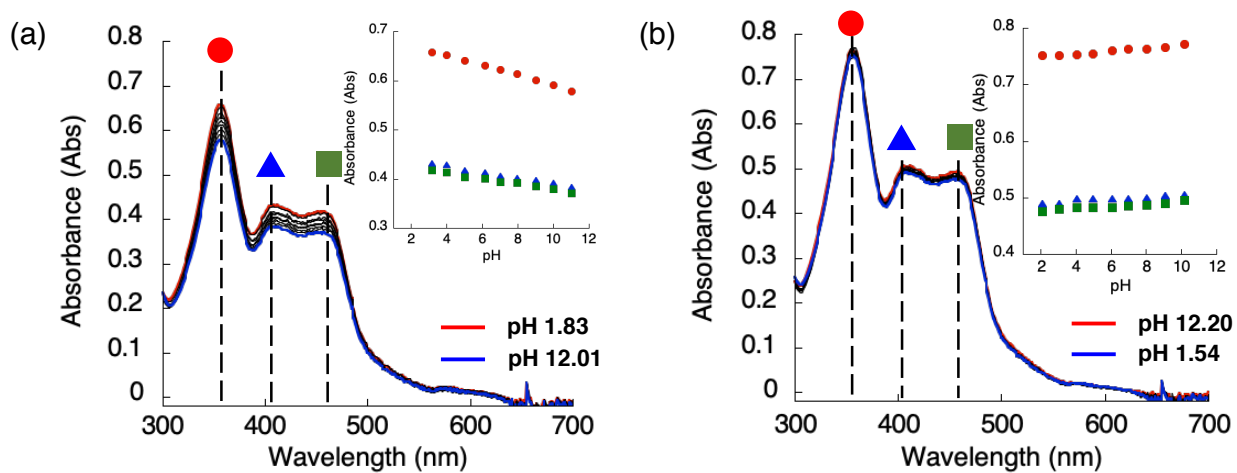


Fig. S6 UV-Vis spectral changes of $1 \cdot (\text{NO}_3)_2$ in the course of pH titration; (inset) absorbance change at 355, 410 and 460 nm against the solution pH at room temperature: (a) pH adjusted from 1.83 to 12.01 by addition of aliquots of 3 M NaOH aq, (b) pH adjusted from 12.20 to 1.54 by addition of aliquots of 3 M HCl aq. [$1 \cdot (\text{NO}_3)_2$]: 1 mM, solvent: H_2O .

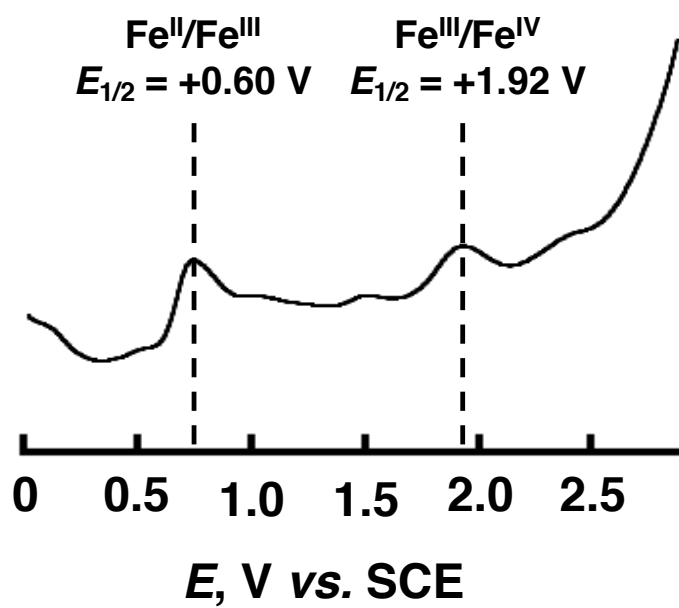


Fig. S7 A SWV of $\mathbf{1} \cdot (\text{NO}_3)_2$ in CH_2Cl_2 at room temperature. [$\mathbf{1} \cdot (\text{NO}_3)_2$]: 1.0 mM, working electrode: GC disk, counter electrode: Pt wire, reference electrode: Ag/AgCl, electrolyte: 0.1 M $n\text{-Bu}_4\text{N} \cdot \text{PF}_6$.

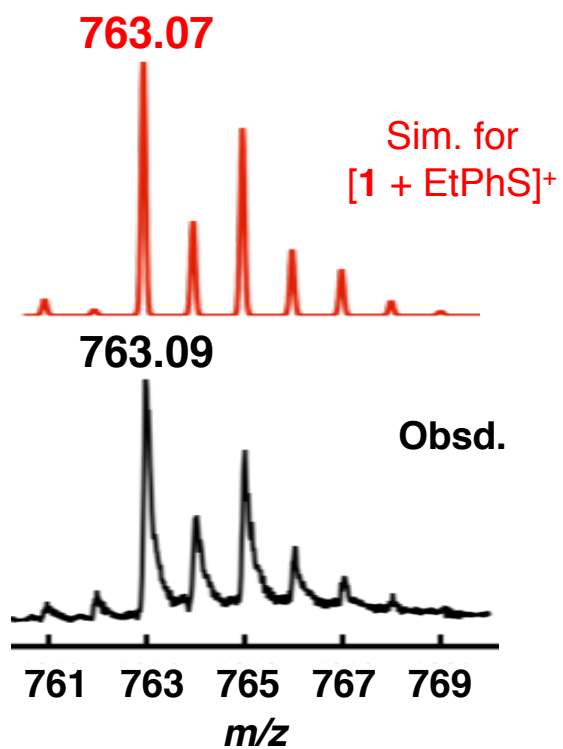


Fig. S8 ESI-TOF-MS spectrum of the reaction mixture after the catalytic oxidation of EtPhS catalysed by **1**·(NO₃)₂ in the presence of Na₂S₂O₈ in acetonitrile: Observed (bottom) and simulated (upper) spectra.

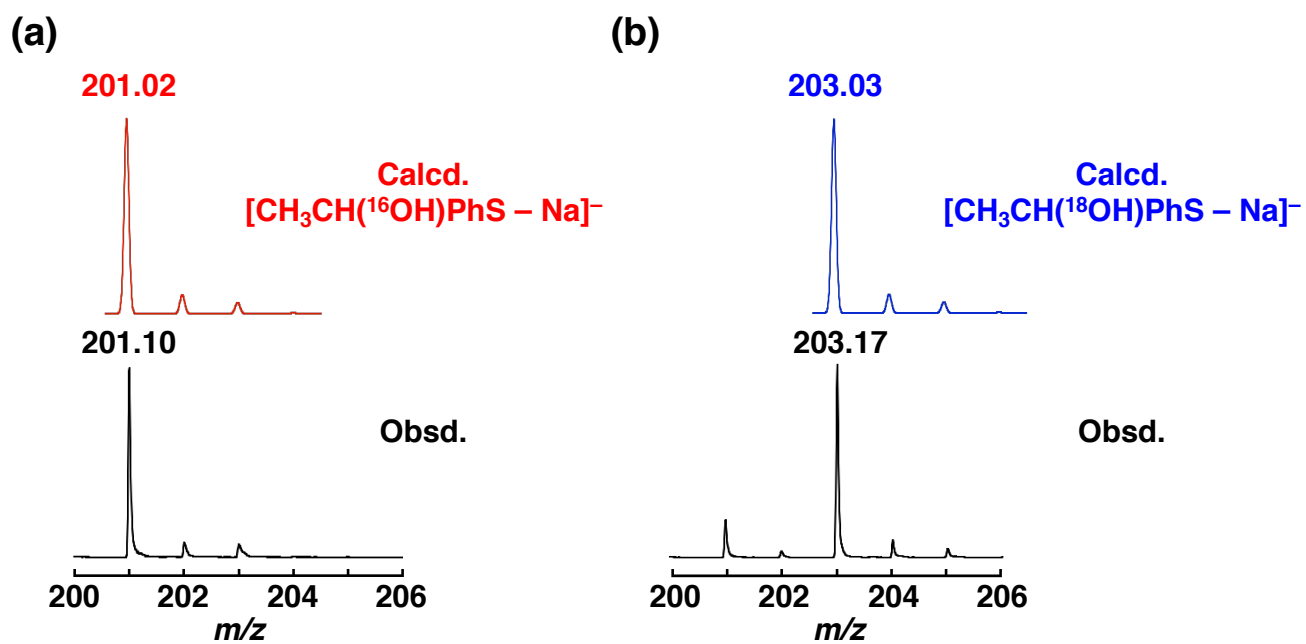


Fig. S9 ESI-TOF-MS spectra (bottom) of the reaction mixture performed in MeCN in H_2^{16}O (a), and that in MeCN in H_2^{18}O (b) and their simulation (top). Reaction conditions are as follows: $[\mathbf{1} \cdot (\text{NO}_3)_2] = 0.1 \text{ mM}$, $[\text{Na}_2\text{S}_2\text{O}_8] = 50 \text{ mM}$, $T = 323 \text{ K}$, reaction time = 3 h.

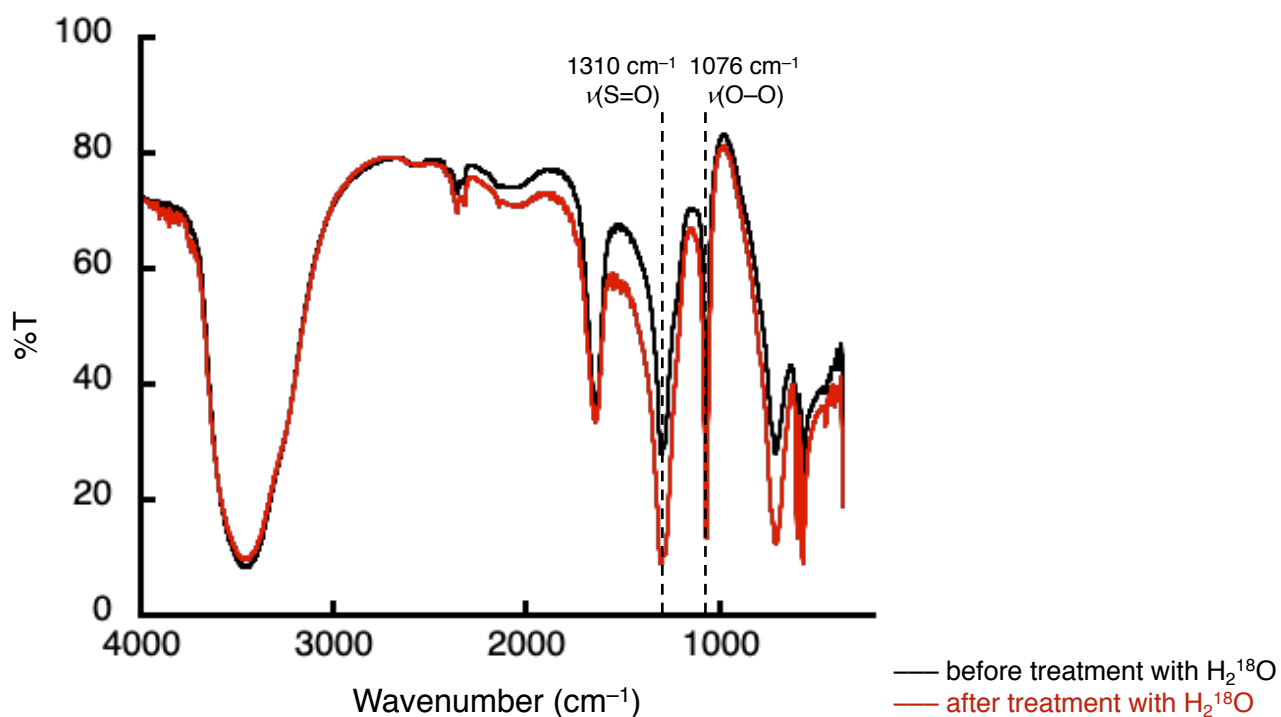


Fig. S10 IR spectra of $\text{Na}_2\text{S}_2\text{O}_8$ in KBr pellet were measured before (black line) and after treatment with H_2^{18}O (red line). The treatment with H_2^{18}O was performed as follows; $\text{Na}_2\text{S}_2\text{O}_8$ was dissolved in H_2^{18}O and kept for several hours, and then the solution was concentrated and dried *in vacuo*.

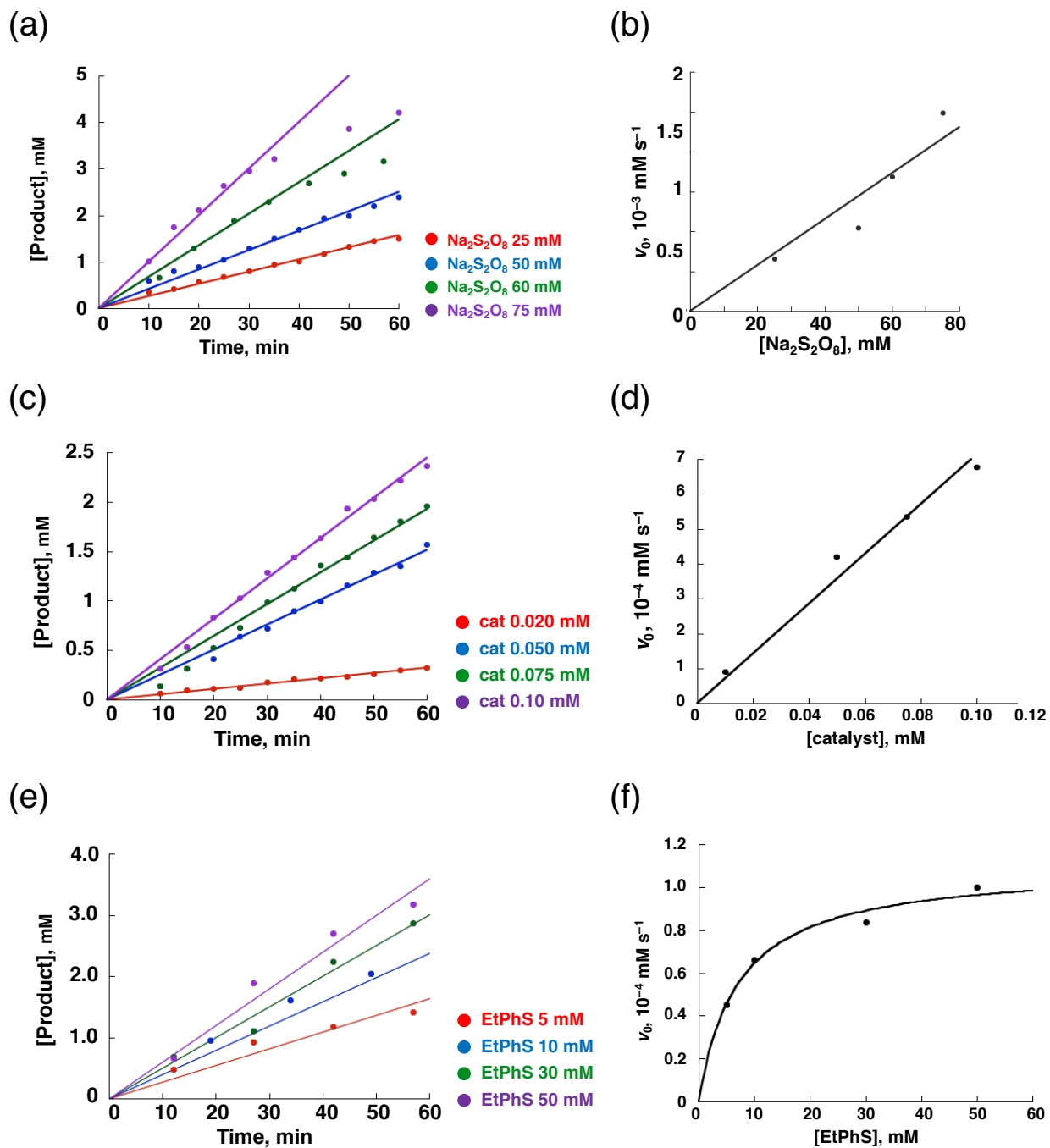


Fig. S11 (a) Time profiles of EtPhS oxidation catalysed by $1 \cdot (\text{NO}_3)_2$ with various $[\text{Na}_2\text{S}_2\text{O}_8]$; (b) initial rate dependence on $[\text{Na}_2\text{S}_2\text{O}_8]$; (c) time profiles of EtPhS oxidation catalysed by $1 \cdot (\text{NO}_3)_2$ with various [catalyst]; (d) initial rate dependence on [catalyst]; (e) time profiles of EtPhS oxidation catalysed by $1 \cdot (\text{NO}_3)_2$ with various $[\text{EtPhS}]$; (f) initial rate dependence on $[\text{EtPhS}]$.

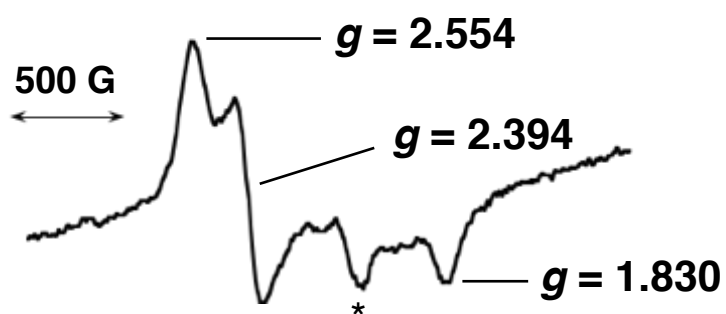


Fig. S12 An ESR spectrum after reaction of $1 \cdot (\text{NO}_3)_2$ (2.0 mM) with $\text{Na}_2\text{S}_2\text{O}_8$ (50 mM) in water measured at 100 K. Microwave frequency: 9.572 GHz, microwave power: 10 mW, modulation frequency: 100.00 Hz, modulation amplitude: 10.00 G. *: impurity.

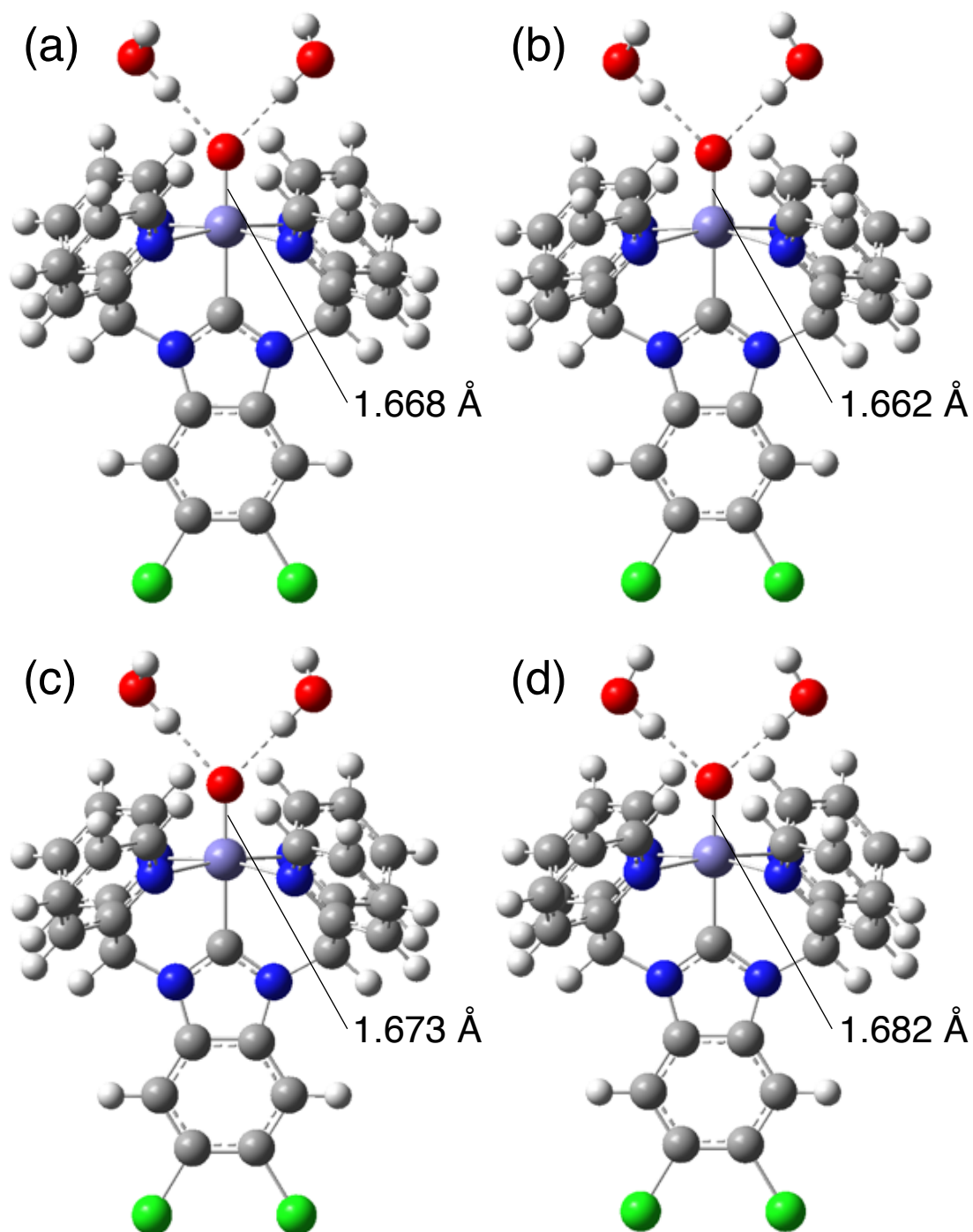


Fig. S13 DFT-optimized structures for $2e^-$ -oxidation product of **1** formulated as $[\text{Fe}(\text{O})(\text{PY}_4\text{Cl}_2\text{Blm})]^{2+}$ with solvation by two water molecules: (a) triplet state of $\text{Fe}^{\text{IV}}=\text{O}$ ($S = 1$), (b) quintet state of $\text{Fe}^{\text{IV}}=\text{O}$ ($S = 2$), (c) open-shell singlet state of $\text{Fe}^{\text{III}}-\text{O}^\bullet$, and (d) closed-shell singlet state of $\text{Fe}^{\text{IV}}=\text{O}$.

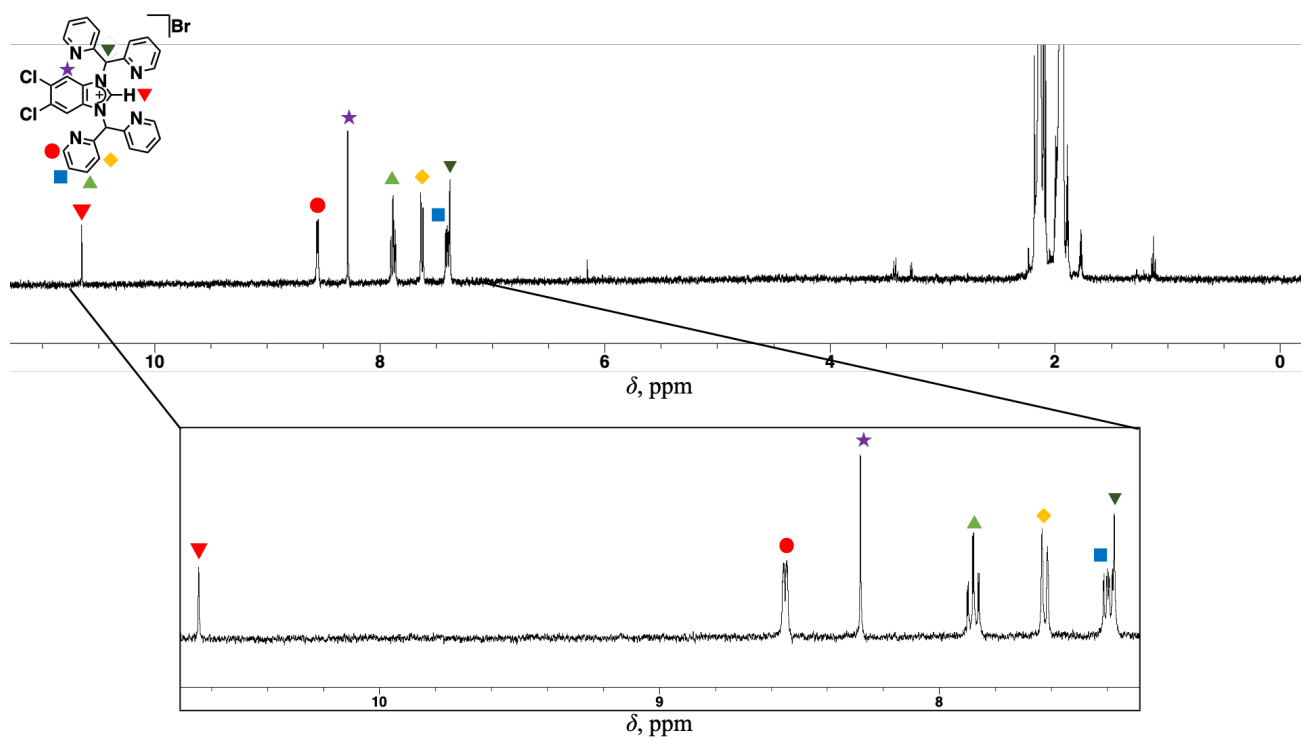


Fig. S14 An ^1H NMR spectrum of $\text{PY}_4\text{Cl}_2\text{Blm-H}\cdot\text{Br}$ in CD_3CN .

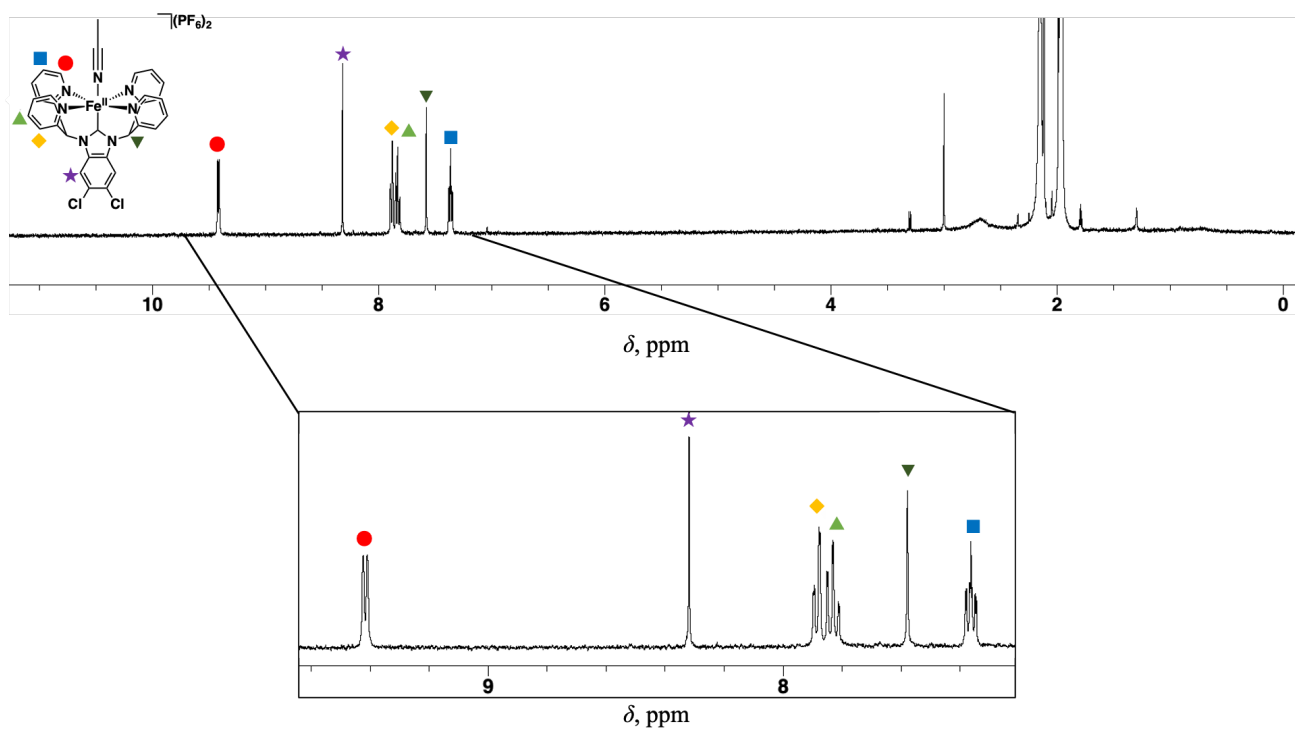


Fig. S15 An ^1H NMR spectrum of $[\text{Fe}^{\text{II}}(\text{PY}_4\text{Cl}_2\text{Blm})(\text{MeCN})](\text{PF}_6)_2$ in CD_3CN .

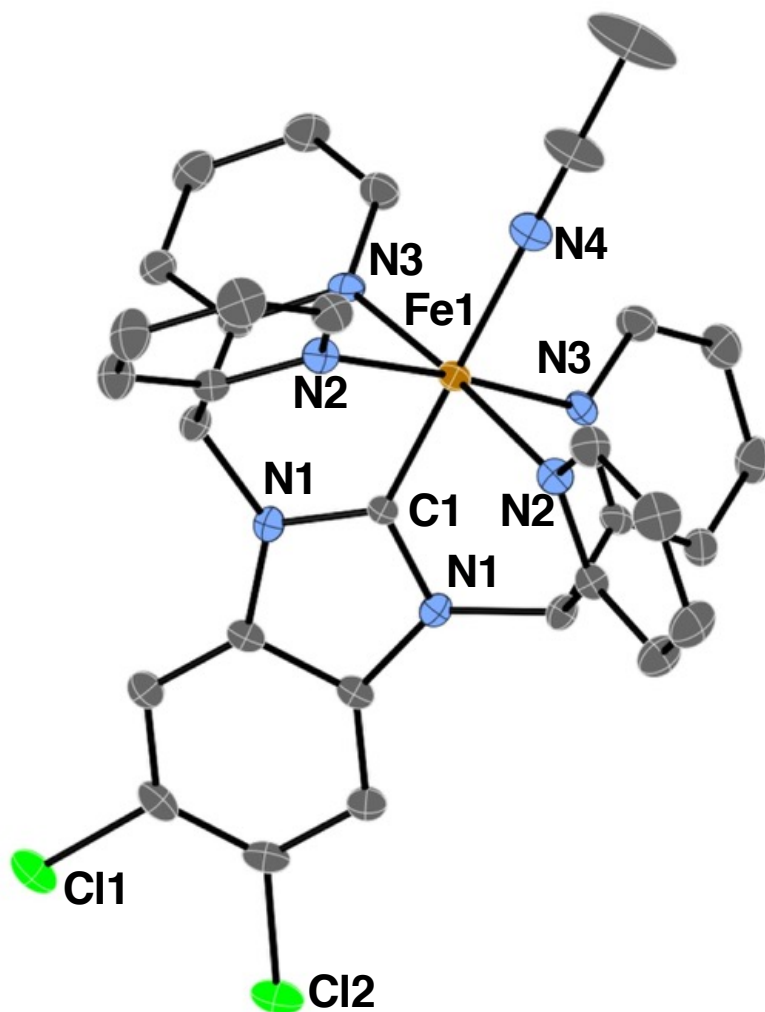
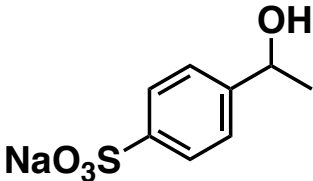
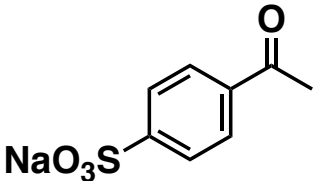


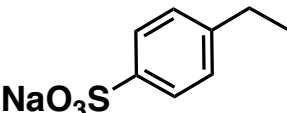
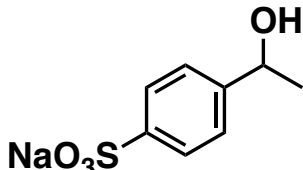
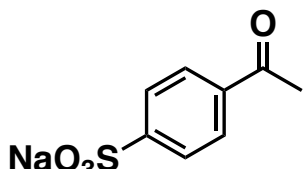
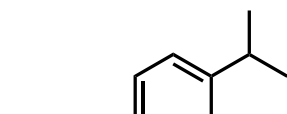
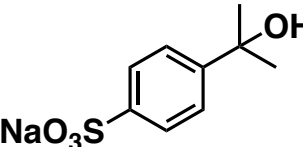
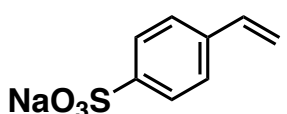
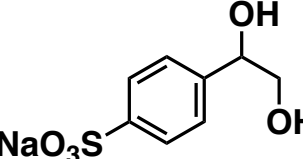
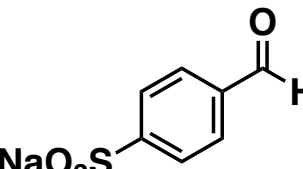
Fig. S16 ORTEP drawing for the crystal structure of $[\text{Fe}^{\text{II}}(\text{PY}_4\text{Cl}_2\text{Blm})(\text{MeCN})](\text{PF}_6)_2$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and two PF_6^- ions are omitted for clarity.

Table S1 Catalytic substrate oxidation by **1**·(NO₃)₂ with various oxidants in water

Oxidant	Product, TON ^{a,b}			
				
	R.T.	323 K	R.T.	323 K
H ₂ O ₂	N.D.	N.D.	N.D.	N.D.
Oxone [®]	N.D.	N.D.	N.D.	N.D.
TBHP	N.D.	N.D.	N.D.	N.D.
NaIO ₄	N.D.	N.D.	N.D.	N.D.
Na ₂ S ₂ O ₈	N.D.	42 (2)	N.D.	7 (8)
CAN	N.D.	2 (2)	N.D.	10 (8)

^a Yields = [Product]/[Substrate]₀. Conditions: [**1**·(NO₃)₂] = 0.1 mM, [Oxidant] = 50 mM, [EtPhS] = 10 mM, 323 K, and reaction time = 3 h. ^b Numbers in parentheses are product yields for the reactions without the catalyst. TBHP: *tert*-butyl hydroperoxide, CAN: cerium ammonium nitrate.

Table S2 Substrate oxidation in the absence of catalyst **1**·(NO₃)₂

Substrate	Product	Yields, % ^a	Alcohol /ketone	Conversion, %
 EtPhS		2	0.25	10
		8		
 CumS		1	–	1
 StyS		0	–	4
		2		
	HCOOH	2		

^a Yields = [Product]/[Substrate]₀. Conditions: [Na₂S₂O₈] = 50 mM, [Substrate] = 10 mM, 323 K, and reaction time = 3 h.

Table S3 Summary for the first-order rate constants, k , and the equilibrium constants, K , for oxidation of EtPhS, DPMS, TPMS, TPMS- d_1 , CumS, BnOH and 2-PrOH and their BDE values of C-H bonds to be cleaved

Substrates	BDE ^a , kcal mol ⁻¹	k , s ⁻¹	K , M ⁻¹
EtPhS	85.4	$(7.9 \pm 0.4) \times 10^{-3}$	$(1.3 \pm 0.2) \times 10^2$
DPMS	82.0	$(8.4 \pm 0.1) \times 10^{-3}$	$(1.8 \pm 0.4) \times 10^2$
TPMS	79.0	$(4.4 \pm 0.1) \times 10^{-3}$	$(1.9 \pm 0.3) \times 10^2$
TPMS- d_1	—	$(1.2 \pm 0.5) \times 10^{-3}$	46 ± 5
CumS	83.5	$(2.5 \pm 0.3) \times 10^{-3}$	28 ± 7
BnOH	87.5	$(2.6 \pm 0.4) \times 10^{-4}$	50 ± 6
2-PrOH	90.0	$(8.0 \pm 0.9) \times 10^{-6}$	56 ± 5

^a BDE values are obtained from ref. 5.

Table S4 Summary of the DFT calculations on [Fe(O)(PY₄Cl₂Blm)]²⁺

	T	Q	OSS	CSS
Spin quantum number, <i>S</i>	1	2	0	0
Relative energy, kcal mol ⁻¹	0	2.6	9.0	26.1
Spin density on Fe	1.26	3.09	0.19	0.00
Spin density on O	0.85	0.76	-0.17	0.00
Fe-O, Å	1.668	1.662	1.673	1.682
$\nu(\text{Fe-O})$, cm ⁻¹	845	862	784	817
bond order of Fe-O	1.83	1.98	1.82	2.58

T: Triplet, Q: Quintet, OSS: Open-Shell Singlet, CSS: Closed-Shell Singlet

Table S5 Crystallographic data for [Fe^{II}(PY₄Cl₂Blm)(MeCN)](PF₆)₂ and **1**·(ClO₄)₂

Compound	[Fe ^{II} (PY ₄ Cl ₂ Blm)(MeCN)](PF ₆) ₂	1 ·(ClO ₄) ₂
MW	910.25	938.33
Formula	C ₃₁ H ₂₃ N ₇ P ₂ Cl ₂ F ₁₂ Fe	C ₃₃ H ₃₆ N ₆ O ₁₄ Cl ₄ Fe
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pmna</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.5092(14)	12.005(6)
<i>b</i> , Å	10.5574(12)	14.781(7)
<i>c</i> , Å	35.527(4)	23.238(11)
α , deg	90	85.501(6)
β , deg	90	87.116(6)
γ , deg	90	73.751(6)
<i>V</i> , Å ³	4316.8(9)	3945(3)
<i>Z</i>	4	4
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>)), %	6.87	9.84
<i>wR</i> 2 (all data), %	13.75	25.59
GOF	1.126	1.021

Table S6 Cartesian coordinates of $[\text{Fe}^{\text{IV}}(\text{O})(\text{PY}_4\text{Cl}_2\text{Blm})]^{2+}$ in the $S = 1$ (T) state including two water molecules interacting with the oxo ligand. Units are in Angstrom.

C	10.64156	2.00176	11.12888
N	10.90207	2.26875	12.41868
C	11.09321	1.20269	13.2361
C	11.02417	-0.10816	12.79844
C	10.76059	-0.34737	11.4577
C	10.57782	0.70357	10.62639
Fe	10.99274	4.11293	13.19233
C	12.36204	3.54161	14.21097
N	13.47491	4.25211	14.54188
C	14.21264	3.591	15.51467
C	13.54697	2.36366	15.72771
N	12.44971	2.38753	14.88019
C	13.99901	1.45991	16.65858
C	15.11338	1.82417	17.39032
C	15.76183	3.03068	17.20507
C	15.32701	3.94265	16.24872
C	13.52479	5.5892	13.95625
C	12.35191	6.41266	14.42633
N	11.12513	5.93686	14.06161
C	10.08351	6.72791	14.34528
C	10.18897	7.90659	15.03302
C	11.4237	8.33119	15.43825
C	12.5378	7.5661	15.1187
C	11.28449	1.4965	14.71346
C	10.04878	2.20925	15.20438
N	9.72478	3.33241	14.56063
C	8.5844	3.93459	14.90566
C	7.79229	3.48865	15.93379
C	8.1432	2.35096	16.61459
C	9.29047	1.67454	16.22093
Cl	17.09973	3.47215	18.20704
Cl	15.66903	0.71993	18.60834
O	9.43662	4.74135	12.06902
N	12.33971	4.91695	11.93703
C	13.45468	5.50039	12.44647

C	14.42458	6.06077	11.66379
C	14.26078	6.05716	10.28136
C	13.11568	5.51646	9.7534
C	12.19587	4.94783	10.60323
O	7.34821	3.129	11.13154
O	9.65506	7.24233	10.82911
H	15.77512	4.76911	16.11001
H	13.56565	0.62411	16.79139
H	14.37689	6.03958	14.22484
H	15.1985	6.44522	12.05828
H	14.92945	6.42351	9.71505
H	12.96156	5.53319	8.81729
H	11.4171	4.55687	10.22609
H	13.40875	7.84161	15.3796
H	11.51803	9.13918	15.92944
H	9.41391	8.42093	15.22728
H	9.22197	6.45568	14.05342
H	11.42165	0.64722	15.22221
H	9.54704	0.86391	16.64472
H	7.61372	2.03295	17.33597
H	7.00484	3.96407	16.17145
H	8.30947	4.70204	14.41748
H	11.15385	-0.82985	13.40231
H	10.70933	-1.23749	11.12839
H	10.40548	0.55735	9.70299
H	10.4956	2.72803	10.53488
H	6.74323	3.65657	10.62908
H	8.86646	7.42005	10.33582
H	8.05677	3.67605	11.44962
H	9.58094	6.39378	11.24979

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