Electronic Supplementary Information

Hydrogen Peroxide Production from Oxygen and Formic Acid by Homogeneous Ir-Ni Catalyst

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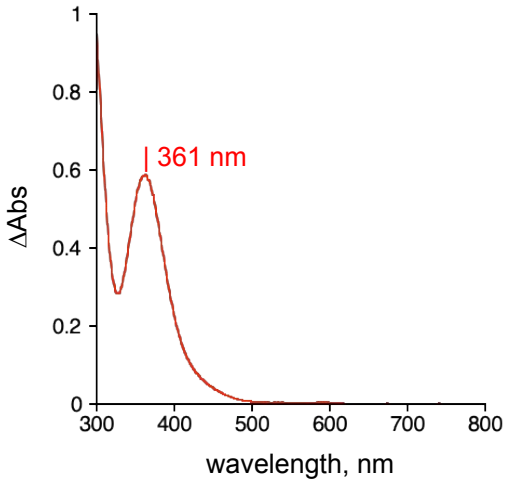

Fig. S1 An absorption difference of UV-Vis spectra before and after the addition of reaction mixture (30 μL) into MeCN (3.0 mL, [$HClO_4$] = 0.5 mM, [NaI] = 0.5 M) at RT. The reaction conditions: [**1**] = 0.10 mM, [HCOOH] = 0.20 M, solvent: ethylene glycol (1.0 mL), reaction time: 15 h, reaction temp.: 313 K, under air.

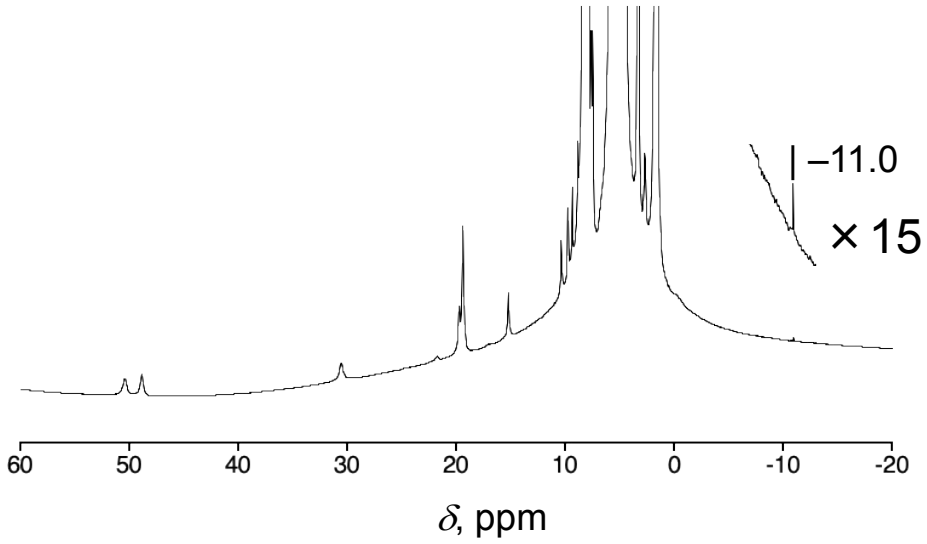

Fig. S2 ^{1}H NMR spectrum of **1** in methanol-d_4 in the presence of 0.80 M HCOOH at 298 K.

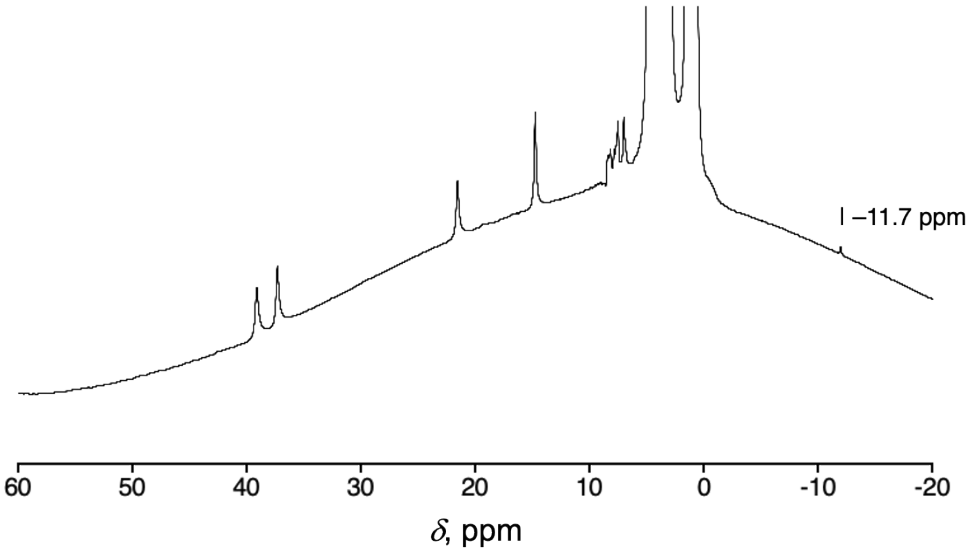

Fig. S3 ^{1}H NMR spectrum of **1** in methanol-d_4 in the presence of $NaBH_4$ (3.0 mM) at 298 K.

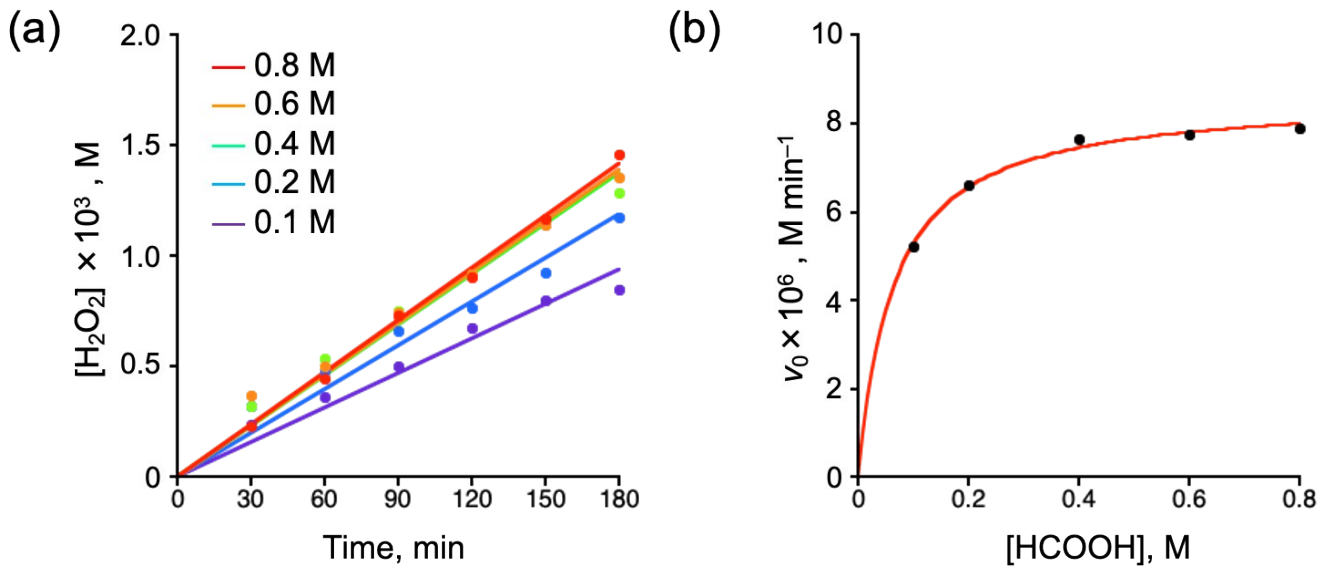

Fig. S4 (a) Time profiles of the H_2O_2 production by **1** at various HCOOH concentrations. (b) Michaelis-Menten analysis of the initial rates of H_2O_2 production. Reaction conditions: [**1**] = 0.10 mM, [HCOOH] = 0.10 – 0.80 M, solvent: ethylene glycol (1.0 mL), temperature: 313 K, under air. The parameters (V_{max}, K_M) were determined from the curve-fitting analysis based on the following equation.

$$v_0 = V_{max}[\mathrm{HCOOH}]/(K_M + [\mathrm{HCOOH}]).$$

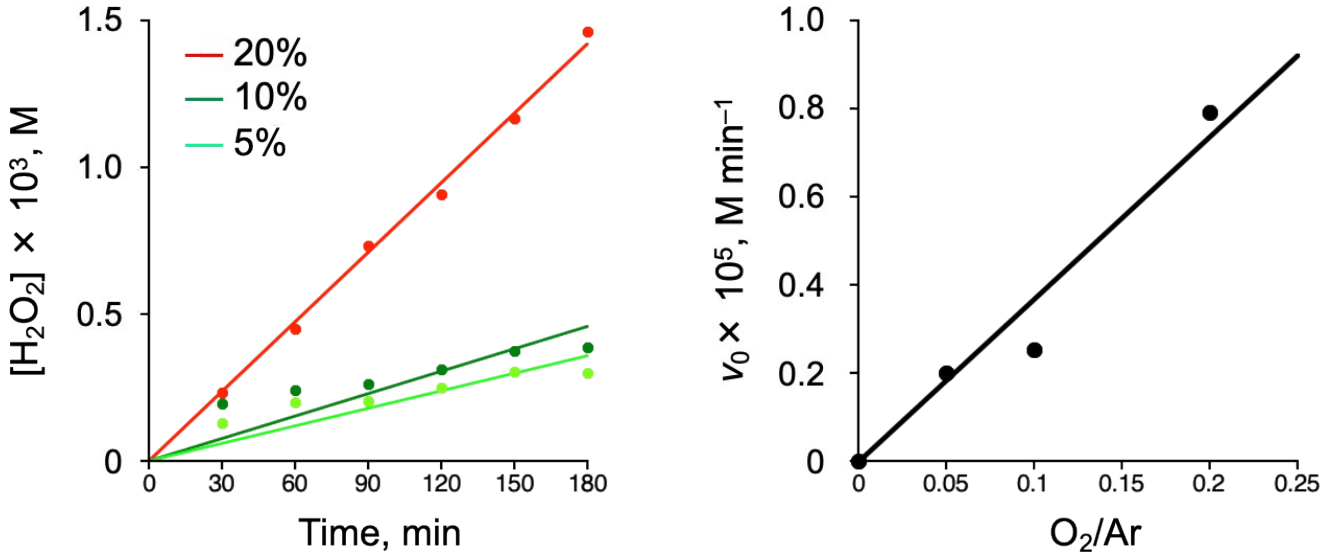

Fig. S5 (a) Time profiles of the H_2O_2 production by **1** at various oxygen concentrations (5, 10 and 20%). (b) Concentration dependence of oxygen on the initial rates of H_2O_2 production. Reaction conditions: [**1**] = 0.10 mM, [HCOOH] = 0.80 M, solvent: ethylene glycol (1.0 mL), temperature: 313 K. O_2 concentration was adjusted by the flow rate ratio between air and Ar balance gas during the gas purging.

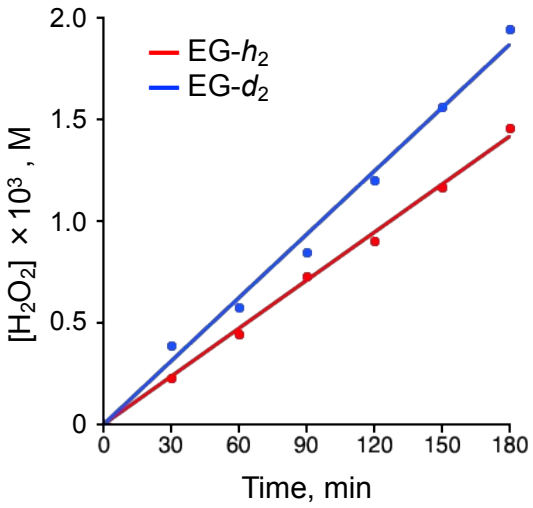

Fig. S6 Time profiles of H_2O_2 production by **1** in EG-h_2 (red) and EG-d_2 (blue). The kinetic isotope effect (KIE, v_0^H/v_0^D) was determined to be 0.76.

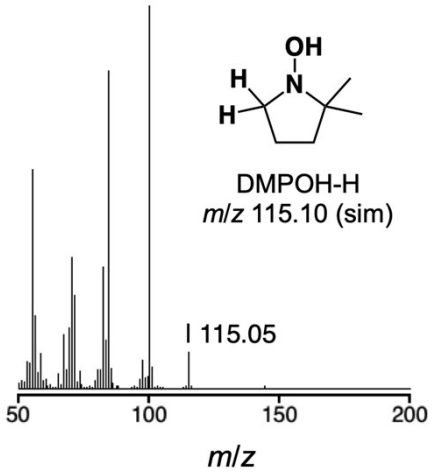

Fig. S7 GC-MS spectrum observed from the H_2O_2 production by **1** in EG in the presence of 0.80 M HCOOH and 10 mM DMPO. The reaction solution (100 μL) was diluted in MeCN (900 μL) to submit the GC-MS measurements.

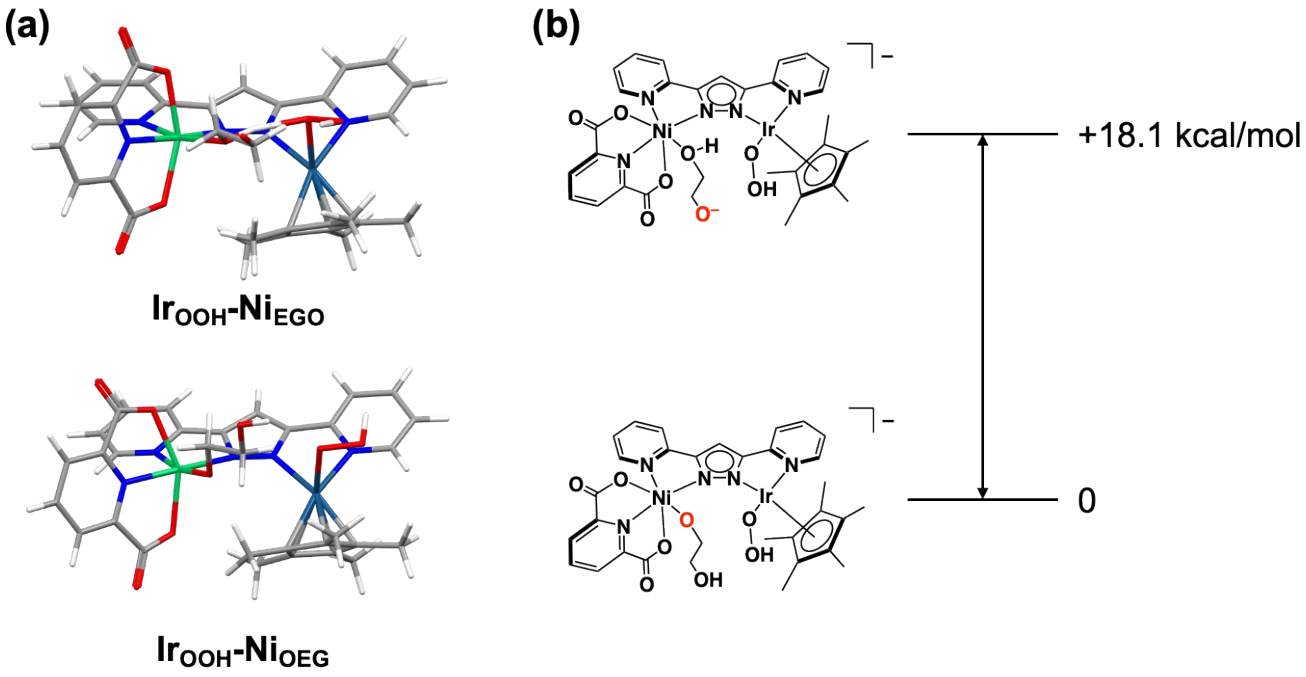

Fig. S8. (a) DFT-optimized structures of $\mathbf{Ir_{OOH}\text{-}Ni_{EGO}}$ (top) and $\mathbf{Ir_{OOH}\text{-}Ni_{OEG}}$ (bottom) calculated at UB3LYP/SDD (Ir, Ni), 6-311G(d,p) (others) level of theory. (b) An energy diagram of $\mathbf{Ir_{OOH}\text{-}Ni_{EGO}}$ and $\mathbf{Ir_{OOH}\text{-}Ni_{OEG}}$.

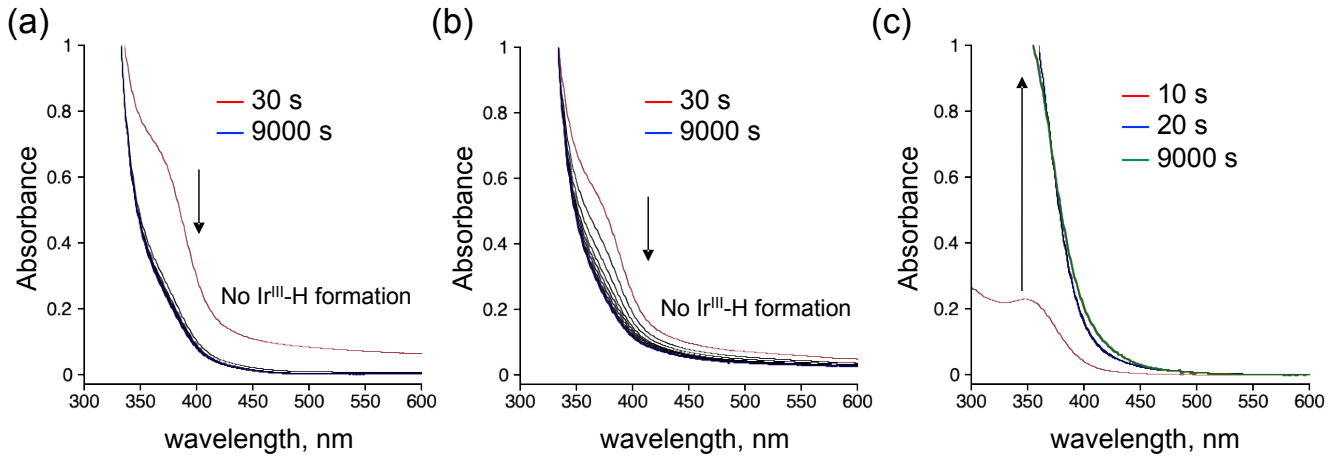

Fig. S9 UV-Vis spectral changes of **1** in 2-propanol (a), *tert*-butanol (b) and water (c). The reaction conditions: [**1**] = 0.10 mM, [HCOOH] = 0.20 M, reaction temp.: 298 K, under air.

Table S1 Catalytic H_2O_2 production by 1 in EG for a prolonged time. [a]

Entry	[**1**], mM	H_2O_2	
		Concentration, mM	TON
1	0.1	6.0	60
2	0.01	2.8	280
3	0.001	0.52	520

[a] Reaction conditions: [**1**] = 0.1 – 0.001 mM, [HCOOH] = 0.80 M, solvent: EG, reaction temp.: 313 K, reaction time: 86 h, under air.

Table S2 Catalytic H_2O_2 production by 1 in EG in the presence of different electron donors. [a]

Entry	Electron donor	H_2O_2	
		Concentration, mM	TON
1	Sodium formate (HCOONa)	<0.1	<1
2	Ammonium formate ($HCOONH_4$)	<0.1	<1
3	Methyl formate (HCOOMe)	0.1	1
4	L(+)-Ascorbic acid	0.2	2

[a] Reaction conditions: [**1**] = 0.10 mM, [electron donor] = 0.20 M, solvent: EG, reaction temp.: 313 K, reaction time: 15 h, under air.

Table S3 Dielectric constants, initial rates of H_2 evolution, Ir-H formation rates and H_2O_2 concentrations for the H_2O_2 production by 1 at various protic solvents.

Solvent	Dielectric constant [a]	H_2 evolution rate (μmol min^{-1}) [b]	Ir-H formation rate (s^{-1}) [c]	H_2O_2 conc. (mM) [d]
Water	78.5 [S1]	4.2×10^{-1}	n. d. [e]	0.1
Methanol	31.5 [S1]	7.3×10^{-4}	1.2×10^{-3}	3.2
Ethanol	24.3 [S1]	1.2×10^{-2}	6.0×10^{-4}	2.0
2-Propanol	18.0 [S1]	7.4×10^{-6}	n. d. [f]	0.8
tert-Butanol	9.9 [S1]	2.1×10^{-5}	n. d. [f]	0.2
Ethylene glycol (EG)	37.7 [S1]	5.9×10^{-3}	6.0×10^{-3}	3.7
1,2-Propanediol	28 [S2]	5.4×10^{-4}	7.9×10^{-4}	1.4
1,3-Propanediol	34.9 [S3]	1.3×10^{-3}	1.7×10^{-3}	2.5
Glycerol	40.1 [S1]	1.7×10^{-2}	n. d. [g]	0.2

[a] The dielectric constant values are determined at 298 K (ref. S1–S3). [b] Reaction conditions: [**1**] = 0.10 mM, [HCOOH] = 0.20 M, reaction temp.: 298 K, under Ar. [c] Reaction conditions: [**1**] = 0.10 mM, [HCOOH] = 0.20 M, reaction temp.: 298 K, under Ar. [d] Reaction conditions: [**1**] = 0.10 mM, [HCOOH] = 0.20 M, reaction temp.: 313 K, reaction time: 15 h, under air. [e] Too fast to be determined. [f] The Ir-H species was not observed probably due to the slow formation in the time scale. [g] It was not able to measure the absorption changes due to the high viscosity of glycerol.

Reference

S1 G. Åkerlöf, *J. Am. Chem. Soc.* 1932, **54**, 4125–4139.

S2 Y. Kato, *YAKUGAKU ZASSHI* 1958, **78**, 565–567

S3 F. Wang, R. Pottel, U. Kaatze, *J. Phys. Chem. B* 1997, **101**, 922–929.

Table S4. Cartesian coordinates of $\mathbf{Ir_H\text{-}Ni_{EG}}$ at the UB3LYP/SDD(Ir, Ni), 6-311G(d,p) level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
Ir	-2.303000	-0.399400	0.004600
O	2.850000	0.926300	-1.744700
O	4.704900	0.856100	-3.040500
O	2.063400	-1.016800	1.807900
O	3.251100	-2.616900	2.873700
O	0.988100	-1.358700	-1.074700
H	0.045800	-1.226800	-0.868500
N	-3.379900	1.183500	-0.969100
C	-4.594400	1.057100	-1.531000
H	-5.014900	0.061500	-1.528700
N	-0.916600	1.175600	-0.154100
N	0.342100	1.312700	0.241100
N	2.819000	2.011000	0.924200
N	3.833200	-0.788300	-0.065100
C	-5.277200	2.124900	-2.088600
H	-6.254500	1.966300	-2.525300
C	-4.675300	3.384500	-2.080300
H	-5.181500	4.241000	-2.509400
C	-3.411000	3.520200	-1.534200
H	-2.899300	4.473800	-1.536300
C	-2.769900	2.402500	-0.987700
C	-1.429600	2.398900	-0.459500
C	-0.458700	3.372800	-0.210800
H	-0.536500	4.438200	-0.350500
C	0.639500	2.638600	0.237400
C	1.968300	3.032800	0.701500
C	2.341100	4.356800	0.945700
H	1.641100	5.161500	0.760400
C	3.614400	4.617600	1.433500
H	3.926100	5.637600	1.626900
C	4.481100	3.555300	1.675800
H	5.480000	3.715900	2.060300
C	4.037400	2.266700	1.401100
H	4.676600	1.406000	1.559800
C	-1.722000	-2.120500	1.298500
C	-2.976900	-2.412300	0.633800
C	-3.942100	-1.458900	1.089700
C	-3.317700	-0.613700	2.102000
C	-1.966200	-1.022700	2.222900
C	-0.521500	-3.019000	1.330300
H	-0.666900	-3.789000	2.098000
H	0.388800	-2.472100	1.574100
H	-0.369900	-3.527500	0.377600
C	-3.239600	-3.593200	-0.252400
H	-2.349300	-3.867900	-0.817900
H	-4.040900	-3.395900	-0.965600
H	-3.530700	-4.459700	0.352400
C	-5.408000	-1.473700	0.776100

H	-5.943100	-2.048800	1.540400
H	-5.613400	-1.944200	-0.186800
H	-5.837900	-0.470400	0.768200
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H	-4.753700	0.983900	2.325800
H	-3.315700	1.149900	3.333700
H	-4.557500	-0.027700	3.757200
C	-0.944100	-0.469300	3.165600
H	-0.984300	-1.029600	4.107500
H	-1.133300	0.580500	3.396600
H	0.070100	-0.568900	2.773900
C	4.025800	0.523800	-2.076800
C	4.614900	-0.519600	-1.108600
C	5.838900	-1.170600	-1.238700
H	6.467400	-0.942400	-2.089700
C	6.201000	-2.097000	-0.258200
H	7.147800	-2.621100	-0.335600
C	5.351900	-2.356200	0.821200
H	5.595400	-3.069000	1.598400
C	4.146700	-1.664400	0.887900
C	3.075200	-1.802000	1.977500
H	-1.892100	-0.843000	-1.478900
C	1.119500	-1.530600	-2.495900
H	2.175600	-1.441100	-2.734900
H	0.588600	-0.740200	-3.032600
C	0.602200	-2.900500	-2.910200
H	-0.451400	-3.006200	-2.609000
H	1.185600	-3.674900	-2.394900
O	0.741400	-2.984200	-4.324300
H	0.573400	-3.891500	-4.591400
Ni	2.097200	0.162000	0.073800

Table S5. Cartesian coordinates of $\mathbf{Ir_{OOH}\text{-}Ni_{EG}}$ at the UB3LYP/SDD(Ir, Ni), 6-311G(d,p) level of theory.

Atom	Coordinates (Angstroms) X	Y	Z
Ir	-2.296800	-0.311600	0.179200
O	2.847000	0.896500	-1.749900
O	4.737900	0.876600	-2.994600
O	2.098300	-0.903900	1.891900
O	3.346800	-2.385400	3.055500
O	1.064100	-1.391600	-1.010700
H	0.132100	-1.165800	-1.257600
N	-3.365700	1.190200	-0.969500
C	-4.560400	1.008600	-1.550600
H	-4.987700	0.019500	-1.458300
N	-0.917100	1.247000	-0.095600
N	0.350100	1.391400	0.263500
N	2.848100	2.106500	0.834900
N	3.877000	-0.693500	0.025200
C	-5.220100	2.017700	-2.234600
H	-6.184300	1.821200	-2.684700
C	-4.610700	3.269400	-2.327200
H	-5.099000	4.082200	-2.851900
C	-3.362200	3.456500	-1.757600
H	-2.846900	4.404700	-1.837900
C	-2.743300	2.394300	-1.089600
C	-1.409200	2.433200	-0.538000
C	-0.414400	3.405500	-0.412100
H	-0.466700	4.448000	-0.678400
C	0.675100	2.700200	0.104600
C	2.017700	3.115900	0.507700
C	2.418000	4.450700	0.597200
H	1.732700	5.243800	0.326500
C	3.701400	4.738400	1.042400
H	4.036400	5.766700	1.115000
C	4.547300	3.691800	1.397500
H	5.553300	3.873000	1.753600
C	4.074900	2.389700	1.272400
H	4.700000	1.540100	1.521700
C	-1.743500	-1.984500	1.514600
C	-3.047500	-2.273300	0.934600
C	-3.949400	-1.245100	1.337400
C	-3.227300	-0.301100	2.181200
C	-1.881900	-0.791000	2.314700
C	-0.558900	-2.898000	1.485400
H	-0.662300	-3.652300	2.275100
H	0.371500	-2.355900	1.652100
H	-0.483600	-3.417600	0.530100
C	-3.374400	-3.500500	0.143300
H	-2.609100	-3.700000	-0.605000
H	-4.328700	-3.407900	-0.375500

H	-3.436100	-4.362700	0.816800
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H	-5.963500	-1.671700	1.889000
H	-5.682300	-1.736700	0.150300
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H	-0.912600	0.888300	3.246300
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C	4.669600	-0.422800	-1.010300
C	5.934400	-1.000900	-1.078900
H	6.570000	-0.772800	-1.924600
C	6.326500	-1.856300	-0.046900
H	7.305000	-2.324100	-0.077400
C	5.468600	-2.114100	1.025700
H	5.736400	-2.769200	1.844500
C	4.221700	-1.496500	1.030700
C	3.142400	-1.631000	2.113400
C	1.668000	-2.015100	-2.152000
H	2.727700	-2.139800	-1.939200
H	1.573000	-1.377800	-3.034800
C	1.046900	-3.381100	-2.409100
H	-0.027000	-3.269200	-2.605300
H	1.175700	-4.006400	-1.514400
O	1.728800	-3.936400	-3.533800
H	1.364600	-4.809300	-3.700900
Ni	2.095700	0.184400	0.095000
O	-1.479100	-0.802200	-1.691100
O	-2.175200	-1.929900	-2.311900
H	-2.285300	-1.578200	-3.205000

Table S6. Cartesian coordinates of $\mathbf{Ir_{OOH}\text{-}Ni_{EGO}}$ at the UB3LYP/SDD(Ir, Ni), 6-311G(d,p) level of theory.

Atom	Coordinates (Angstroms) X	Y	Z
Ir	2.264000	-0.304200	-0.146800
O	-2.820200	0.879900	1.851700
O	-4.658100	0.763100	3.169700
O	-2.216200	-0.766800	-1.921000
O	-3.568100	-2.122000	-3.125800
O	-1.008200	-1.383800	0.948600
H	-0.172400	-1.081800	1.364400
N	3.379400	1.251000	0.859800
C	4.584400	1.093100	1.431800
H	4.989400	0.090800	1.414000
N	0.895000	1.276700	0.084600
N	-0.385300	1.412200	-0.234200
N	-2.904400	2.126500	-0.735000
N	-3.878000	-0.694000	0.071100
C	5.275200	2.135000	2.025000
H	6.244100	1.949800	2.470700
C	4.686700	3.407000	2.048100
H	5.199100	4.246300	2.503500
C	3.419700	3.566100	1.508000
H	2.911500	4.521500	1.547700
C	2.767800	2.472700	0.932200
C	1.413200	2.483500	0.438900
C	0.418200	3.454700	0.297900
H	0.487900	4.510000	0.504000
C	-0.695900	2.729900	-0.131500
C	-2.050600	3.138000	-0.486700
C	-2.449000	4.474100	-0.605400
H	-1.744300	5.269800	-0.398900
C	-3.750600	4.755600	-0.994300
H	-4.081900	5.784100	-1.088400
C	-4.622200	3.703700	-1.265000
H	-5.645000	3.879400	-1.573600
C	-4.149900	2.403800	-1.116800
H	-4.791300	1.549600	-1.301900
C	1.616000	-1.957200	-1.507600
C	2.830500	-2.363700	-0.836900
C	3.864500	-1.437700	-1.172500
C	3.310400	-0.448600	-2.095300
C	1.933500	-0.781100	-2.295400
C	0.358800	-2.759600	-1.608400
H	0.490100	-3.535900	-2.373900
H	-0.493700	-2.141700	-1.886500
H	0.115800	-3.245700	-0.664300
C	2.985900	-3.576000	0.025900
H	2.015300	-3.960300	0.338900
H	3.551100	-3.345300	0.929200
H	3.504900	-4.365900	-0.530100

C	5.309200	-1.568700	-0.796100
H	5.838100	-2.174400	-1.542000
H	5.425100	-2.063000	0.170200
H	5.809300	-0.599400	-0.750300
C	4.088300	0.621800	-2.800800
H	4.854900	1.054800	-2.154500
H	3.435400	1.431600	-3.129600
H	4.590900	0.218700	-3.688900
C	0.965600	-0.087300	-3.203200
H	0.994300	-0.560800	-4.192000
H	1.215600	0.967700	-3.329300
H	-0.058500	-0.165300	-2.833400
C	-3.986800	0.468400	2.183800
C	-4.614600	-0.499400	1.162700
C	-5.854200	-1.123000	1.278700
H	-6.439200	-0.957600	2.174000
C	-6.284800	-1.938100	0.230900
H	-7.241500	-2.446300	0.300300
C	-5.493900	-2.101600	-0.909200
H	-5.794700	-2.714800	-1.748700
C	-4.267700	-1.446000	-0.957100
C	-3.273400	-1.469800	-2.128300
C	-1.627000	-2.382800	1.813300
H	-2.480600	-2.779000	1.264000
H	-1.988500	-1.906200	2.728900
C	-0.720400	-3.584600	2.190600
H	0.203100	-3.134500	2.718200
H	-0.282200	-3.973900	1.219100
O	-1.354900	-4.486300	2.907900
Ni	-2.093800	0.185700	-0.022100
O	1.590400	-0.638700	1.794100
O	2.329900	-1.700600	2.449200
H	1.614800	-2.354700	2.599700

Table S7. Cartesian coordinates of $\mathbf{Ir_{OOH}\text{-}Ni_{OEG}}$ at the UB3LYP/SDD(Ir, Ni), 6-311G(d,p) level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
Ir	2.343900	-0.356500	-0.144900
O	-3.322100	0.929000	1.785300
O	-5.308500	0.760400	2.863000
O	-2.250000	-0.802200	-1.920900
O	-3.367300	-2.357900	-3.122700
O	-1.396300	-1.369200	0.974400
N	3.521400	1.331300	0.487700
C	4.827600	1.269500	0.790000
H	5.291300	0.300900	0.679300
N	0.920400	1.204900	0.120900
N	-0.370000	1.324400	-0.147200
N	-2.893800	2.082100	-0.750800
N	-4.095000	-0.734300	-0.081000
C	5.545600	2.368000	1.235200
H	6.600500	2.266900	1.456200
C	4.874700	3.583100	1.398200
H	5.403300	4.461700	1.750900
C	3.521700	3.647300	1.122000
H	2.961800	4.562300	1.265400
C	2.850600	2.500800	0.668800
C	1.448500	2.438000	0.374000
C	0.445600	3.398700	0.239400
H	0.528200	4.466000	0.363500
C	-0.679400	2.648700	-0.103900
C	-2.026800	3.071800	-0.477600
C	-2.395800	4.418200	-0.592300
H	-1.682300	5.198700	-0.359400
C	-3.681300	4.731500	-1.007600
H	-3.989400	5.767700	-1.097900
C	-4.567500	3.699400	-1.306000
H	-5.580500	3.898000	-1.633400
C	-4.125200	2.389800	-1.154700
H	-4.780700	1.549500	-1.351500
C	1.452400	-2.129600	-1.240100
C	2.682800	-2.504200	-0.598200
C	3.751900	-1.709300	-1.132800
C	3.172300	-0.826300	-2.147300
C	1.769200	-1.080100	-2.197500
C	0.143200	-2.835000	-1.097900
H	-0.458800	-2.716000	-1.998900
H	-0.453300	-2.429600	-0.260500
H	0.316400	-3.902900	-0.930200
C	2.808300	-3.562200	0.452500
H	1.879500	-3.650600	1.014800
H	3.604500	-3.328200	1.159500
H	3.023400	-4.530600	-0.015900
C	5.212700	-1.916100	-0.865400

H	5.605000	-2.735000	-1.480700
H	5.388600	-2.171500	0.181300
H	5.798800	-1.025800	-1.104500
C	3.945200	0.089400	-3.047800
H	4.782700	0.559900	-2.527200
H	3.308200	0.881700	-3.442900
H	4.356000	-0.465600	-3.900200
C	0.776400	-0.460300	-3.130300
H	0.751500	-1.036000	-4.064200
H	1.044400	0.568900	-3.378900
H	-0.235100	-0.476200	-2.716000
C	-4.496600	0.473600	1.979800
C	-4.949300	-0.556300	0.924800
C	-6.155200	-1.254700	0.944900
H	-6.835800	-1.087300	1.769700
C	-6.428000	-2.137800	-0.099900
H	-7.356800	-2.700900	-0.105200
C	-5.510300	-2.299600	-1.140200
H	-5.677100	-2.969500	-1.973900
C	-4.329300	-1.564200	-1.097600
C	-3.220500	-1.599000	-2.161600
C	-1.640300	-1.649500	2.314800
H	-2.627200	-2.126600	2.484100
H	-1.628000	-0.750000	2.950600
C	-0.567000	-2.603800	2.835200
H	0.407100	-2.112000	2.743900
H	-0.562600	-3.513200	2.213700
O	-0.845400	-2.951900	4.208600
H	-0.006500	-3.193200	4.606800
Ni	-2.272600	0.103700	0.042300
O	3.548700	-0.955500	2.436500
H	3.595000	-0.271400	3.115500
O	2.198700	-0.682900	1.909000