Supporting Information

Mechanistic Studies on the pH Controllable Hydrogenation of NAD^+ by H_2 and Generation of H_2 from NADH by a Water Soluble Biomimetic Iridium Complex

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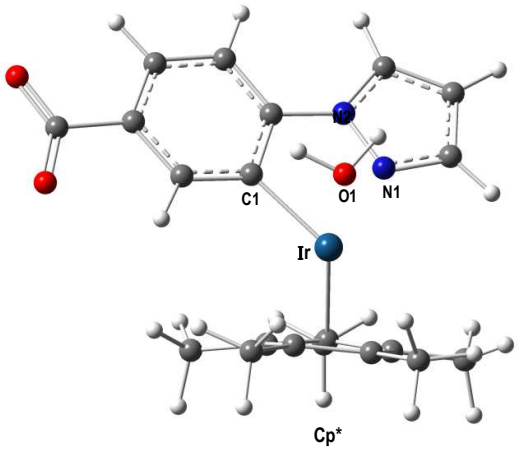
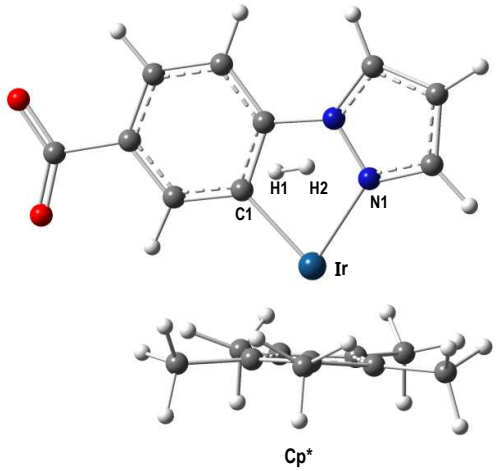


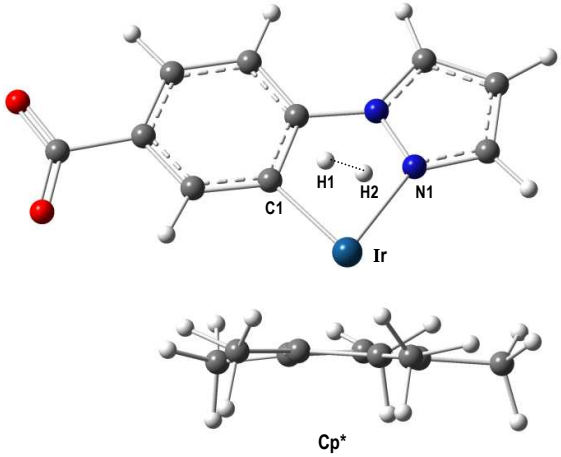
Bond length	
Ir–N1	2.110
Ir–O1	2.302
Ir–C1	2.016
Ir–Cp*	1.835

Compound 2



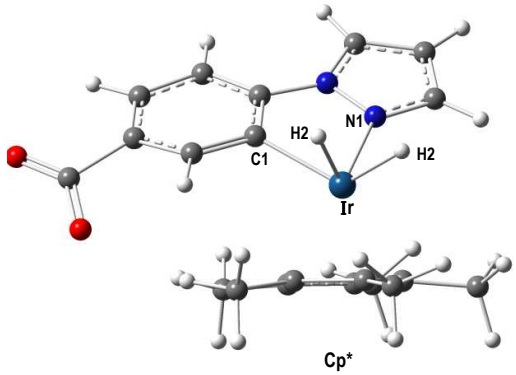
Bond length	
Ir–N1	2.101
Ir–C1	2.007
Ir–Cp*	1.800
Ir–H1	3.494
H1–H2	0.741

P1(E)



Bond length	
Ir–N1	2.107
Ir–C1	2.018
Ir–Cp*	1.821
Ir–H1	2.416
Ir–H2	2.427
H1–H2	0.749

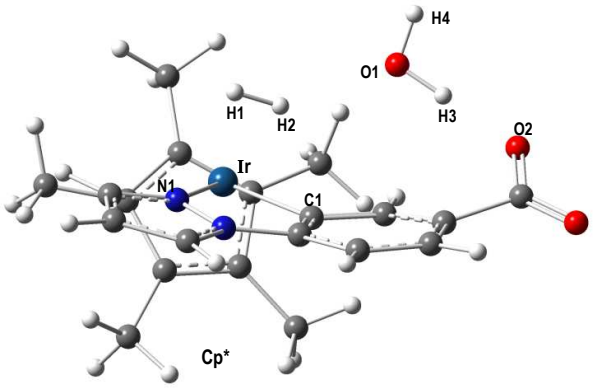
P1(T)



Bond length	
Ir–N1	2.091
Ir–C1	2.062
Ir–Cp*	1.916
Ir–H1	1.570
Ir–H2	1.575
H1–H2	1.712

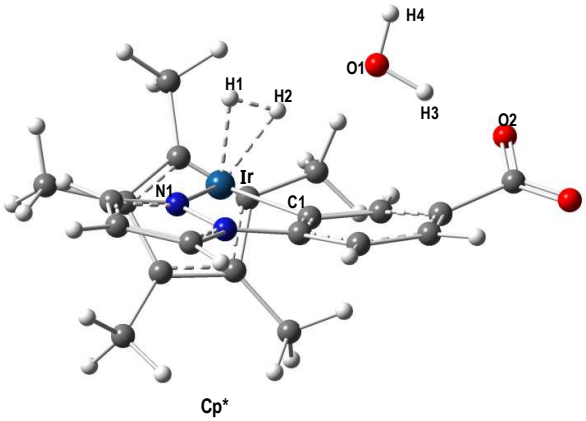
P1(Pr)

Figure S1. Optimized geometries of pathway 1.



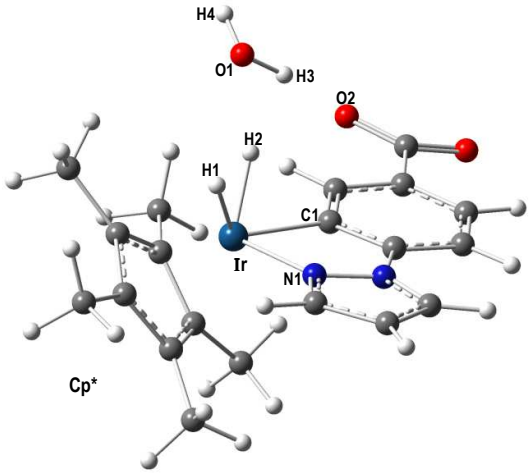
Bond length	
Ir–N1	2.109
Ir–C1	2.033
Ir–Cp*	1.703
Ir–H1	1.722
Ir–H2	0.898
H1–H2	0.970
H2–O1	2.295
H3–O2	1.651

P2(E)



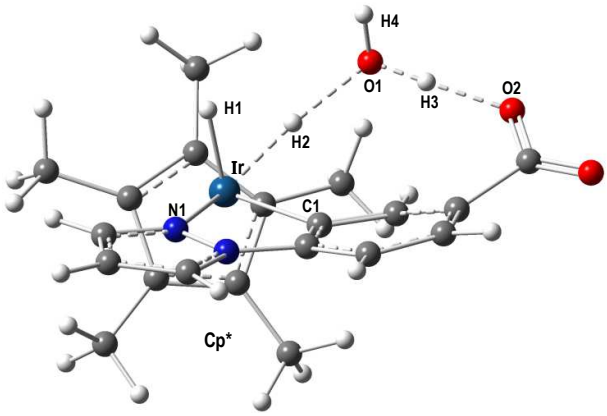
Bond length	
Ir–N1	2.106
Ir–C1	2.032
Ir–Cp*	1.868
Ir–H1	1.678
Ir–H2	1.711
H1–H2	0.970
H2–O1	2.059
H3–O2	1.676

P2(T1)



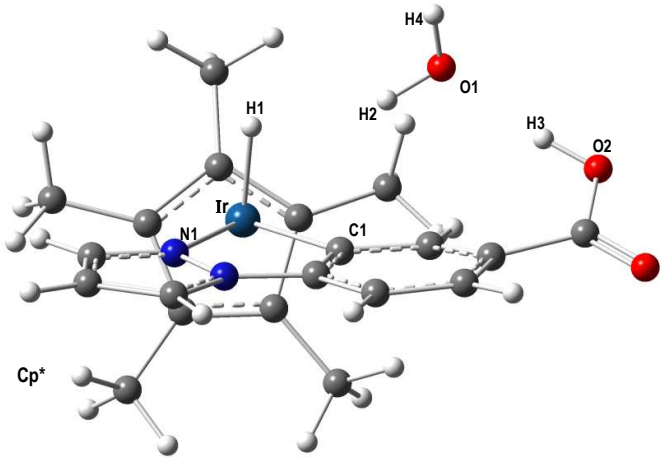
Bond length	
Ir–N1	2.089
Ir–C1	2.065
Ir–Cp*	1.912
Ir–H1	1.575
Ir–H2	1.567
H1–H2	1.677
H2–O1	3.466
H3–O2	1.689

P2(IM1)



Bond length	
Ir–N1	2.103
Ir–C1	2.038
Ir–Cp*	1.914
Ir–H1	1.573
Ir–H2	1.654
H1–H2	1.605
H2–O1	1.694
O1–H3	1.042
H3–O2	1.568

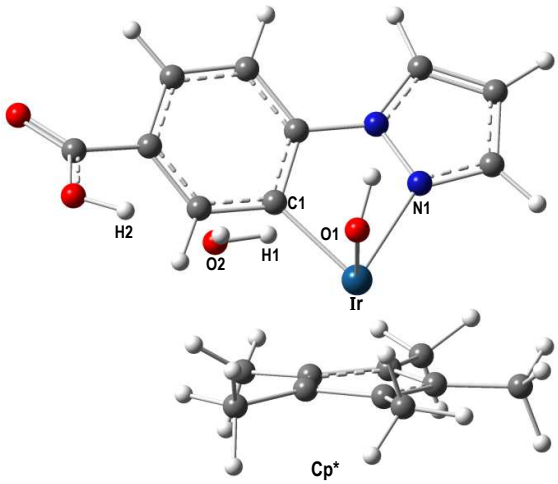
P2(T2)



Bond length	
Ir–N1	2.094
Ir–C1	2.016
Ir–Cp*	1.906
Ir–H1	1.581
H1–H2	2.141
O1–H3	1.969

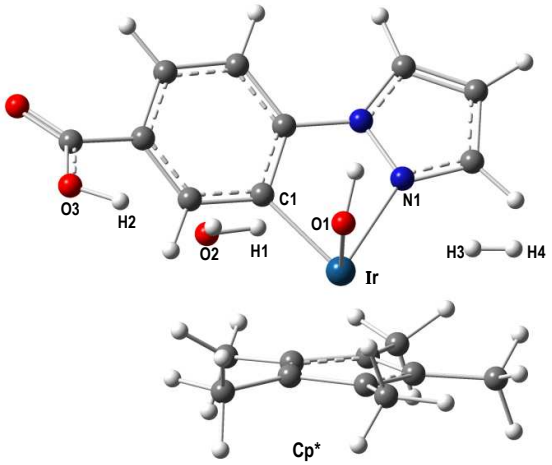
P2(Pr)

Figure S2. Optimized geometries of pathway 2.



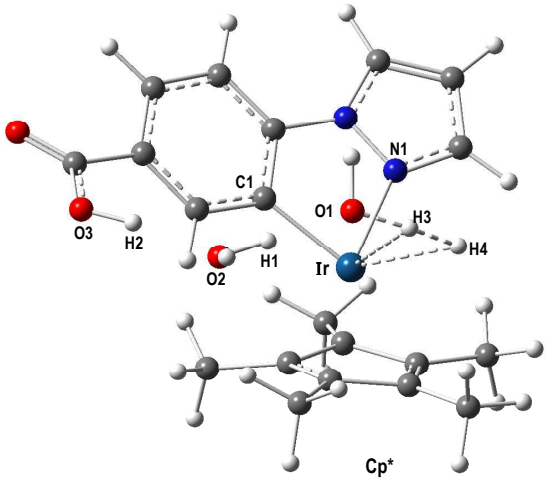
P3(S2)

Bond length	
Ir–N1	2.137
Ir–C1	2.013
Ir–Cp*	1.835
Ir–O1	2.091
O1–H1	1.661
O2–H2	1.809



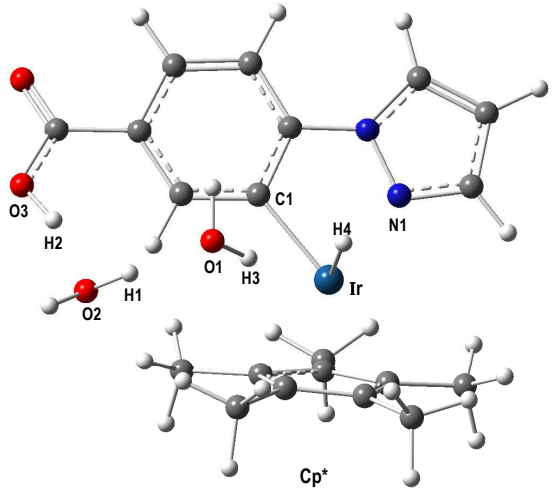
P3(E)

Bond length	
Ir–N1	2.138
Ir–C1	2.012
Ir–Cp*	1.837
Ir–O1	2.096
H3–H4	0.744
O1–H3	2.387
O1–H1	1.665
O2–H2	1.813



P3(T)

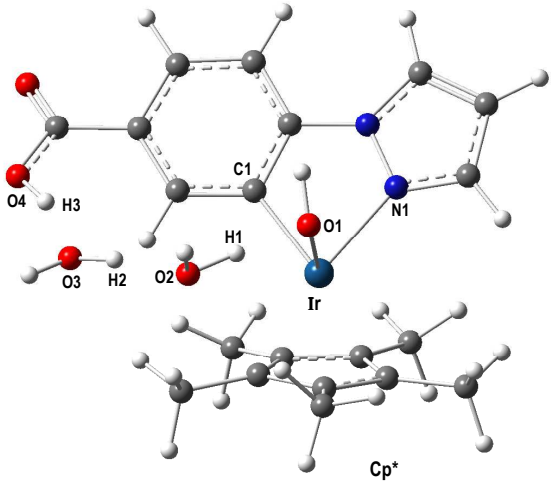
Bond length	
Ir–N1	2.126
Ir–C1	2.005
Ir–Cp*	1.863
Ir–O1	2.587
Ir–H4	2.422
H3–H4	1.138
O1–H3	2.387
O1–H1	1.665
O2–H2	1.813



Bond length	
Ir–N1	2.085
Ir–C1	2.029
Ir–Cp*	1.909
Ir–H4	1.584
H3–H4	2.422
H3–H4	1.876
O1–H1	1.714
O2–H2	1.754

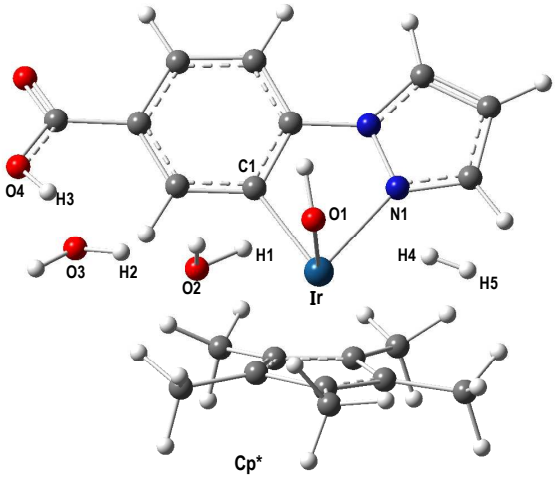
P3(Pr)

Figure S3. Optimized geometries of pathway 3.



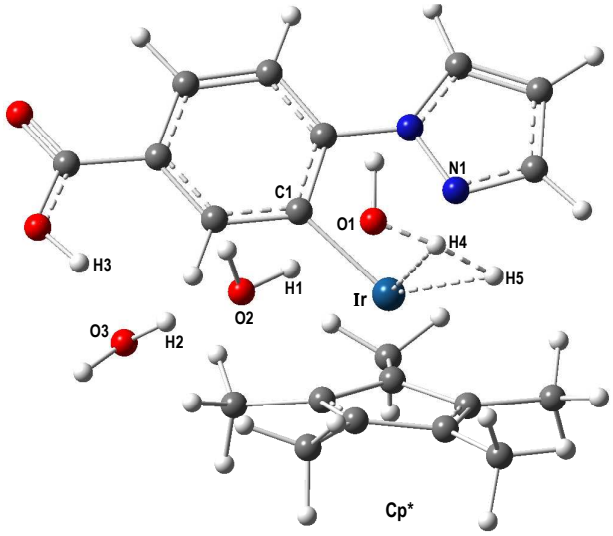
Bond length	
Ir–N1	2.129
Ir–C1	2.029
Ir–Cp*	1.832
Ir–O1	2.094
O1–H1	1.517
O2–H2	1.685
O3–H3	1.697

P4(S2)



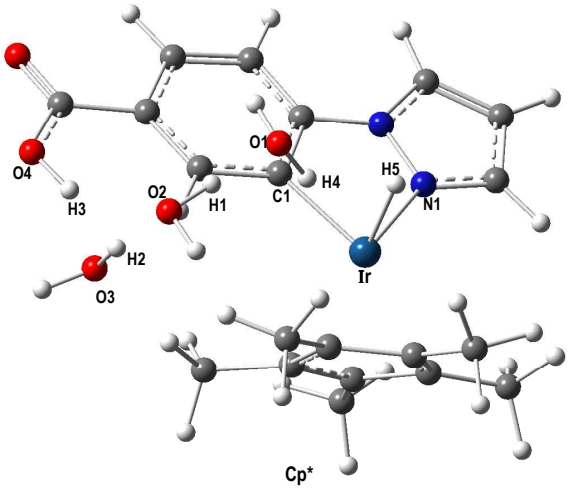
Bond length	
Ir–N1	2.132
Ir–C1	2.027
Ir–Cp*	1.838
Ir–O1	2.097
H4–H5	0.745
O1–H4	2.287
O1–H1	.523
O2–H2	1.685
O3–H3	1.705

P4(E)



Bond length	
Ir–N1	2.115
Ir–C1	2.016
Ir–Cp*	1.871
Ir–O1	2.615
Ir–H5	2.393
H4–H5	1.174
O1–H4	1.099
O1–H1	1.679
O2–H2	1.648
O3–H3	1.739

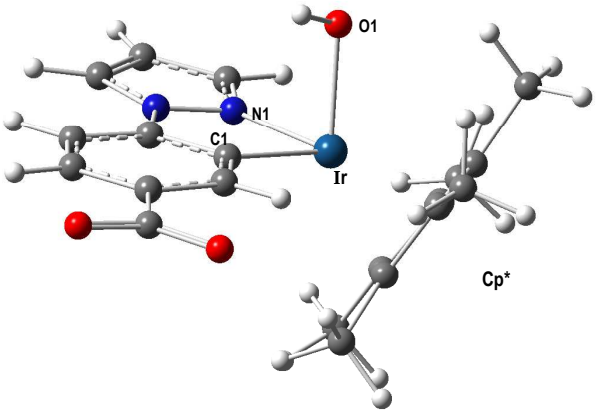
P4(T)



Bond length	
Ir–N1	2.082
Ir–C1	2.030
Ir–Cp*	1.911
Ir–H5	1.581
H4–H5	1.862
O1–H1	1.730
O2–H2	1.675
O3–H3	1.756

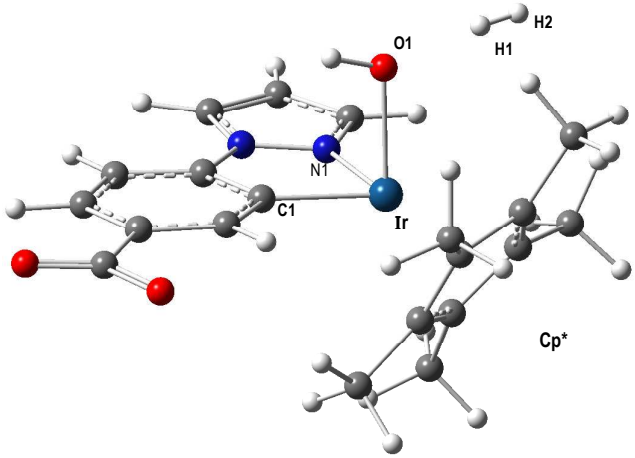
P4((Pr)

Figure S4. Optimized geometries of pathway 4.



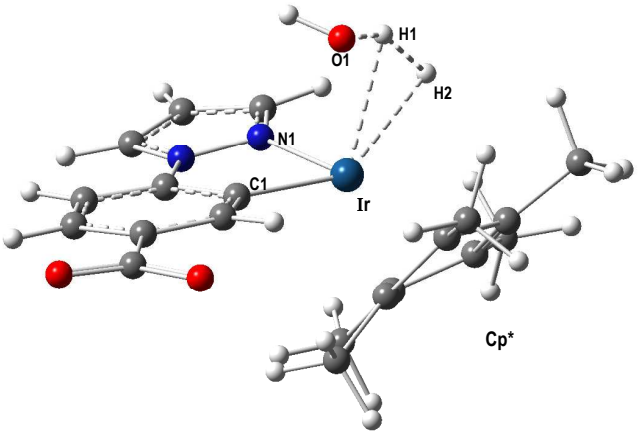
Bond length	
Ir–N1	2.108
Ir–C1	2.015
Ir–Cp*	1.859
Ir–O1	2.052

P5(S1)



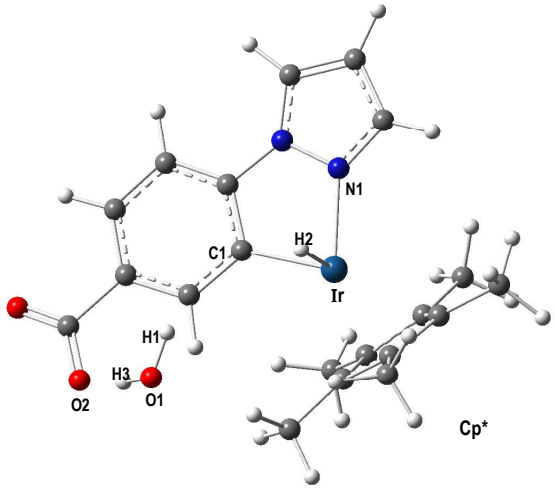
Bond length	
Ir–N1	2.110
Ir–C1	2.016
Ir–Cp*	1.858
Ir–O1	2.056
H1–H2	0.747
O1–H1	2.216

P5(E)



Bond length	
Ir–N1	2.137
Ir–C1	2.000
Ir–Cp*	2.017
Ir–O1	2.279
Ir–H2	2.323
H1–H2	1.353

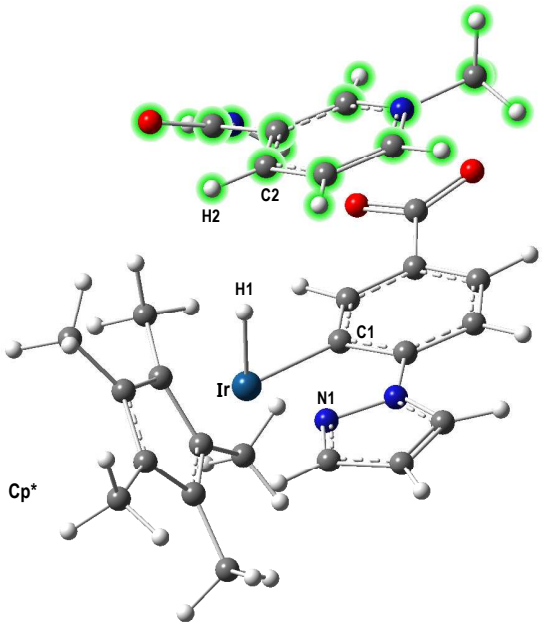
P5(T)



Bond length	
Ir–N1	2.085
Ir–C1	2.015
Ir–Cp*	1.925
Ir–H2	1.570
H1–H2	3.176
O2–H3	1.785

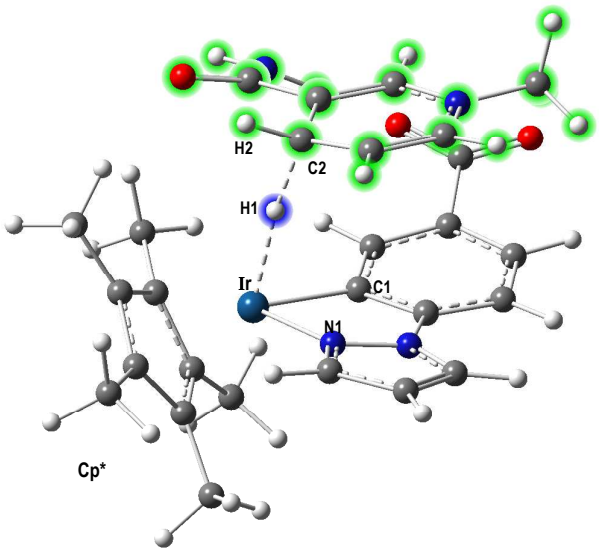
P5(Pr)

Figure S5. Optimized geometries of pathway 5.



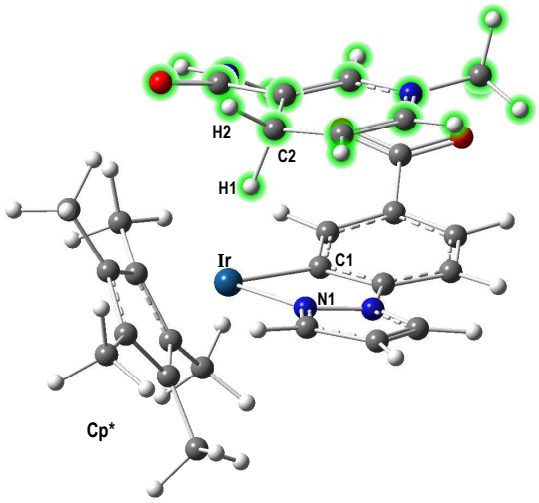
Bond length	
Ir–N1	2.093
Ir–C1	2.016
Ir–Cp*	1.912
Ir–H1	1.577
H1–C2	2.912
C2–H2	1.086

R(E)



Bond length	
Ir–N1	2.099
Ir–C1	2.019
Ir–Cp*	1.848
Ir–H1	1.760
H1–C2	1.332
C2–H2	1.091

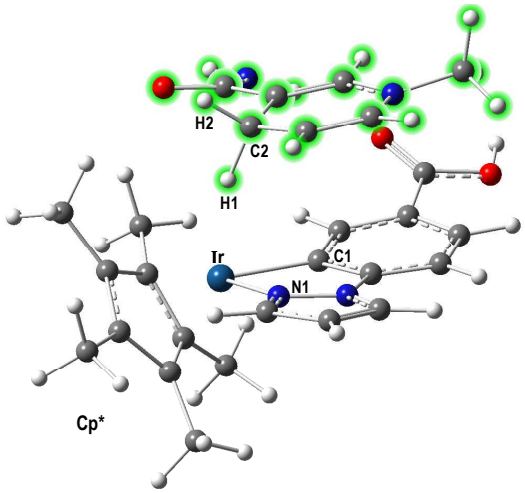
R(T)



Bond length	
Ir–N1	2.102
Ir–C1	2.021
Ir–Cp*	1.827
Ir–H1	1.941
H1–C2	1.190
C2–H2	1.095

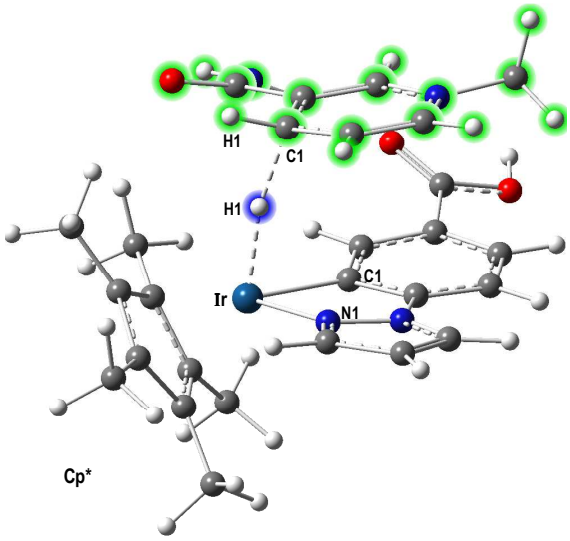
R(Pr)

Figure S6. Optimized geometries of NAD^+ oxidation.



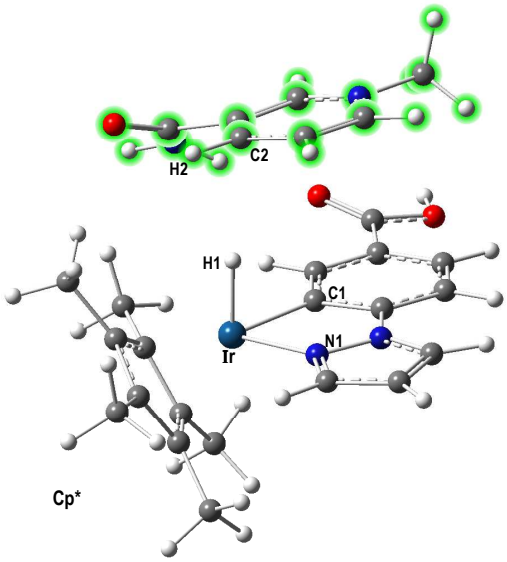
Bond length	
Ir–N1	2.115
Ir–C1	2.038
Ir–Cp*	1.809
Ir–H1	2.030
H1–C2	1.151
C2–H2	1.094

O(E)



Bond length	
Ir–N1	2.111
Ir–C1	2.022
Ir–Cp*	1.853
Ir–H1	1.668
H1–C2	1.505
C2–H2	1.085

O(T)



Bond length	
Ir–N1	2.102
Ir–C1	2.020
Ir–Cp*	1.898
Ir–H1	1.569
H1–C2	2.656
C2–H2	1.083

O(Pr)

Figure S7. Optimized geometries of NADH oxidation.

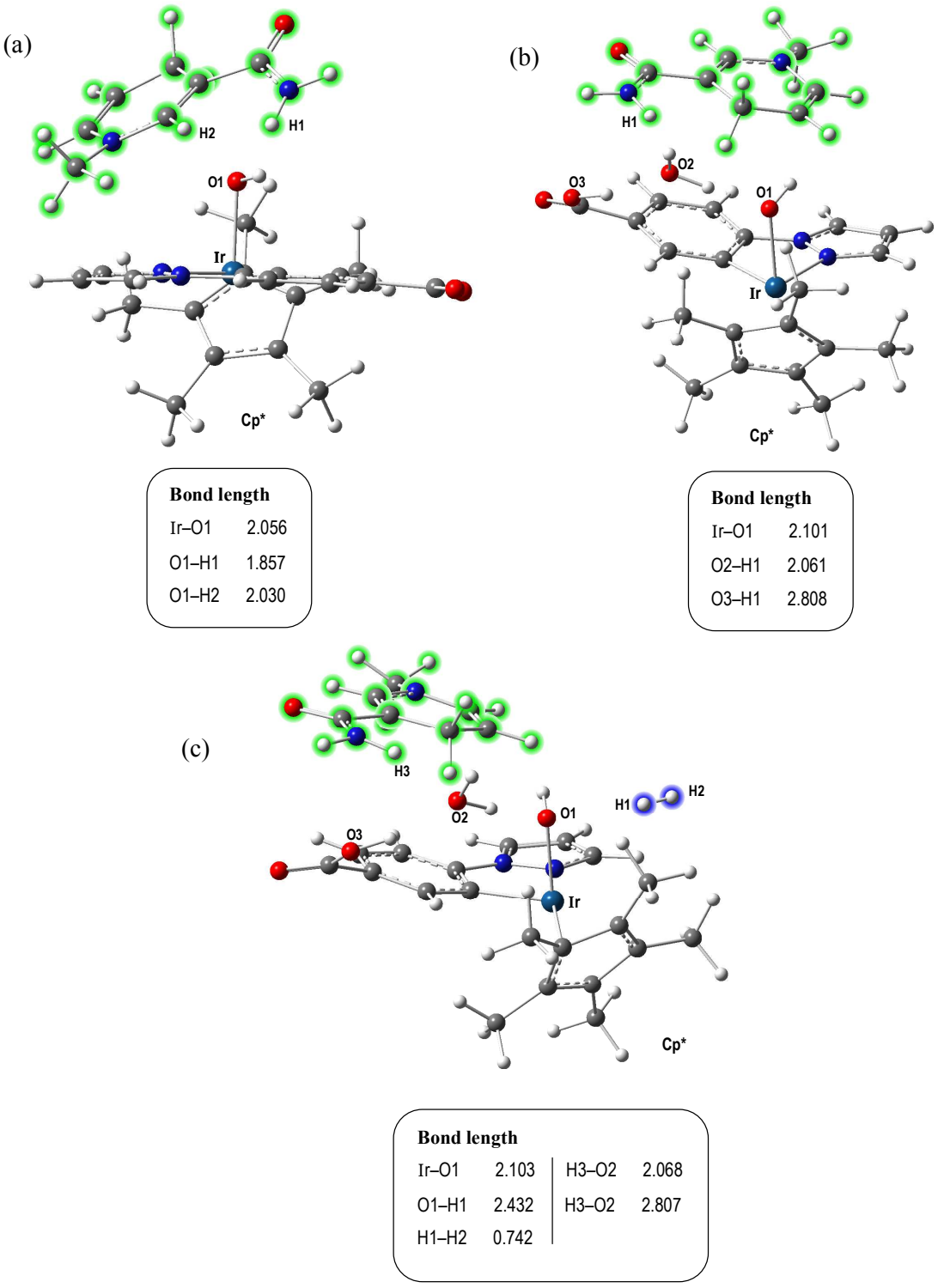


Figure S8. Optimized geometries of inhibition of (a) P5(S) and (b) P3(S2) by NADH.

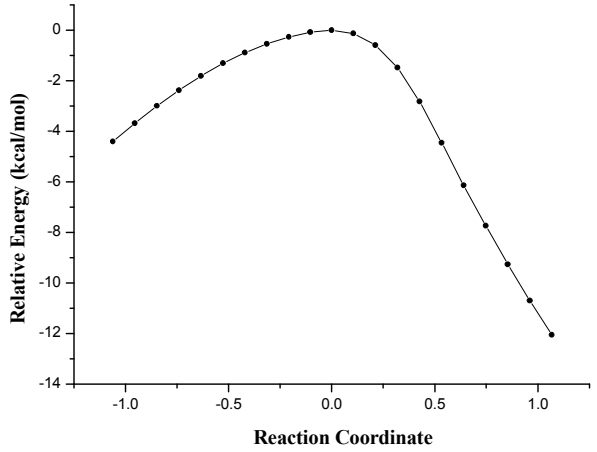


Figure S9. Relative energy profile of IRC path for pathway 3.

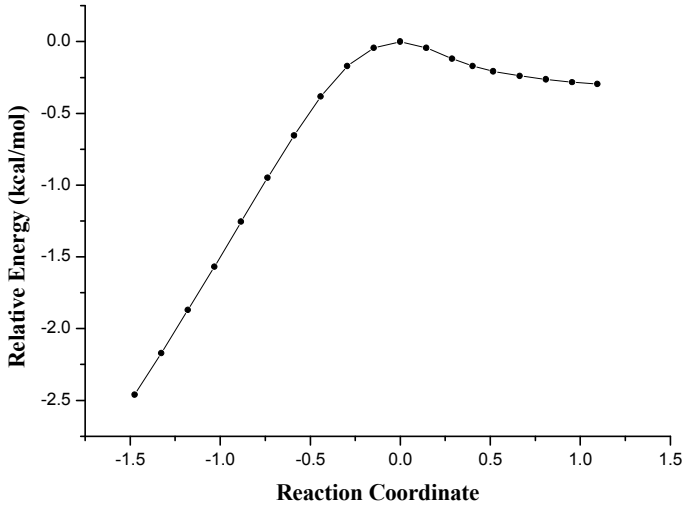


Figure S10. Relative energy profile of IRC path for the reduction of NAD^+.

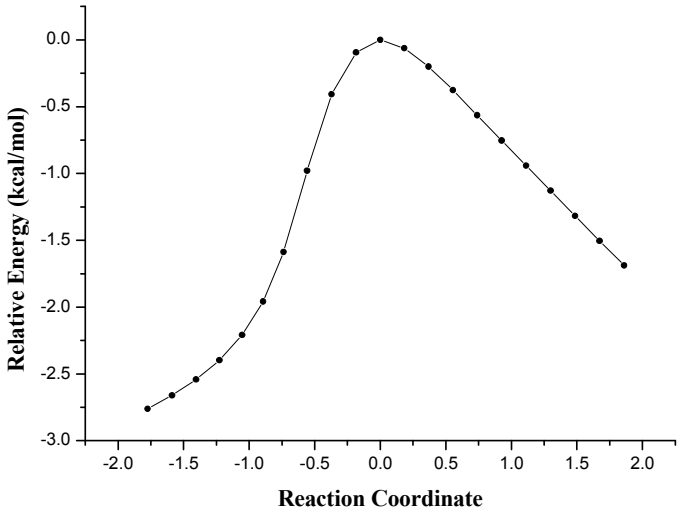


Figure S11. Relative energy profile of IRC path for the oxidation of NADH.

Table S12. NBO charge on the metal and its first coordination sphere for pathway 1, calculated at the level of M06/6-31g* (SDD for Ir)

	Ir	N1	C1	O1	H1	H2
Compound 2	0.26	-0.27	-0.17	-0.87		
P1(E)	0.30	-0.30	-0.24		0.01	-0.01
P1(T)	0.27	-0.28	-0.19		0.07	0.03
P1(Pr)	-0.28	-0.20	-0.07		0.24	0.21

Table S13. NBO charges on the metal and its first coordination sphere for pathway 2, calculated at the level of M06/6-31g* (SDD for Ir)

	Ir	N1	C1	O1	H1	H2
P2(E)	-0.09	-0.22	-0.09	-1.05	0.25	0.16
P2(T1)	-0.13	-0.22	-0.09	-1.04	0.28	0.17
P2(I)	0.28	-0.20	-0.07	-1.04	0.28	0.21
P2(T2)	-0.28	-0.21	-0.09	-1.01	0.37	0.2
P2(Pr)	-0.16	-0.19	-0.11	-0.98	0.52	0.08

Table S14. NBO charges on the metal and its first coordination sphere for pathway 3, calculated at the level of M06/6-31g* (SDD for Ir)

	Ir	N1	C1	O1	H1	H2
P3(S)	0.26	-0.23	-0.11	-0.93		
P3(E)	0.27	-0.23	-0.11	-0.93	0.03	-0.03
P3(T)	0.24	-0.24	-0.11	-1.02	0.37	-0.37
P3(Pr)	-0.18	-0.19	-0.11	-0.98	0.53	0.07

Table S15. NBO charges on the metal and its first coordination sphere for pathway 4, calculated at the level of M06/6-31g* (SDD for Ir)

	Ir	N1	C1	O1	H1	H2
P4(S)	0.26	-0.22	-0.13	-0.93		
P4(E)	0.27	-0.22	-0.13	-0.93	0.05	-0.05
P4(T)	0.22	-0.24	-0.12	-1.02	0.34	-0.34
P4(Pr)	-0.18	-0.19	-0.11	-0.99	0.53	0.08

Table S16. NBO charges on the metal and its first coordination sphere for pathway 5, calculated at the level of M06/6-31g* (SDD for Ir)

	Ir	N1	C1	O1	H1	H2
P5(S)	0.27	-0.20	-0.11	-0.90		
P5(E)	0.28	-0.20	-0.12	-0.91	0.06	-0.07
P5(T)	0.24	-0.25	-0.09	-0.94	0.46	-0.46
P5(Pr)	-0.12	-0.19	-0.09	-1.02	0.47	0.11

Table S17. NBO charges on the metal and its first coordination sphere for reduction of NAD^+, calculated at the level of M06/6-31g* (SDD for Ir)

	Ir	N1	C1	H1	C2	H2
R(E)	-0.13	-0.19	-0.10	0.07	-0.09	0.29
R(T)	0.08	-0.23	-0.14	0.12	-0.28	0.3
R(P)	0.19	-0.25	-0.16	0.14	-0.36	0.28

Table S18. NBO charges on the metal and its first coordination sphere for oxidation of NADH, calculated at the level of M06/6-31g* (SDD for Ir)

	Ir	N1	C1	H1	C2	H2
O(E)	0.22	-0.26	-0.18	0.16	-0.39	0.29
O(T)	-0.02	-0.23	-0.13	0.08	-0.21	0.32
O(P)	-0.15	-0.19	-0.11	0.06	-0.08	0.30