

**ELECTRONIC SUPPLEMENTARY INFORMATION FOR**

**Elucidating the Intimate Mechanism of NAD<sup>+</sup> hydrogenation with Phosphonic Acid  
Catalysed by Cp\*Ir(Pyridine-2-sulfonamidate) Complexes**

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## Materials and methods

All reagents and the organic solvents were purchased from Sigma-Aldrich and used as received. Water was purified using a Milli-QUltrapure water purification system.  $[\text{Cp}^*\text{IrCl}_2]_2$ ,<sup>1</sup>  $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3](\text{NO}_3)_2$ , **1**, and **2** were prepared according to the literature.<sup>1,2</sup>

NMR spectra were recorded on a Bruker Avance III 400 spectrometer equipped with a smartprobe (400 MHz for  $^1\text{H}$ ) with a z gradient coil. Residual solvent resonances were used for referencing; reported chemical shifts are relative to external TMS.

## Catalytic and kinetic measurements

**Hydrogenation of NAD<sup>+</sup> with phosphonic acid: Uv-Vis.** The reaction was monitored by UV-Vis spectroscopy, following the formation of the absorption band of NADH centered at 340 nm ( $\epsilon = 6220 \text{ M}^{-1} \text{ cm}^{-1}$ ), using a diode array spectrometer (HP 8453). In a typical experiment, 3 mL of a solution of NAD<sup>+</sup> in phosphite buffer at pH = 6.58 were transferred inside a cuvette. The system was allowed to equilibrate under stirring for 10 min at 313 K; after the background correction, 15-30  $\mu\text{L}$  of a solution of the catalyst was injected and acquisition started.

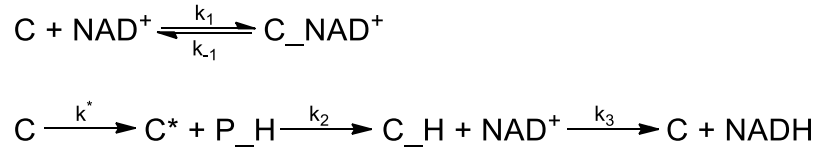
**Table S1.** Kinetic data for the hydrogenation of NAD<sup>+</sup> with phosphonic acid at different concentration of cofactor and reducing agent acid catalysed by complex 2.

Entry	[Cat] ( $\mu\text{M}$ )	[H <sub>2</sub> PO <sub>3</sub> <sup>-</sup> + HPO <sub>3</sub> <sup>2-</sup> ] (M)	[NAD <sup>+</sup> ] (mM)	TOF <sub>ini</sub> (h <sup>-1</sup> )	r <sub>NADH</sub> (10 <sup>-7</sup> M s <sup>-1</sup> )
1	5	0.4	0.25	770 ± 50	10.7 ± 0.7
2	5	0.4	0.5	1453 ± 94	20 ± 1
3	5	0.4	1.00	2473 ± 160	34 ± 2
4	5	0.4	1.25	2814 ± 183	39 ± 3
5	5	0.4	1.50	3050 ± 198	42 ± 3
6	5	0.4	3.00	3731 ± 243	52 ± 3
7	5	0.4	6.00	3366 ± 219	47 ± 3
8	5	0.4	10.00	3038 ± 197	42 ± 3
9	5	0.8	0.25	874 ± 57	12.1 ± 0.8
10	5	0.8	0.50	1452 ± 94	20 ± 1
11	5	0.8	1.00	2538 ± 165	35 ± 2
12	5	0.8	1.25	2827 ± 183	39 ± 3
13	5	0.8	1.50	3136 ± 204	44 ± 3
14	5	0.8	3.00	3947 ± 257	55 ± 4
15	5	0.8	6.00	3709 ± 241	52 ± 3
16	5	0.8	10.00	3060 ± 199	43 ± 3
17	5	0.1	6.00	2005 ± 130	28 ± 2
18	5	0.2	6.00	2735 ± 178	38 ± 2
19	5	0.6	6.00	3599 ± 233	50 ± 3
20	5	1.0	6.00	3822 ± 248	53 ± 3

## Reaction mechanism and kinetic equations

### Equation 1)

Assuming that the hydrogenation of  $\text{NAD}^+$  with  $\text{H-P(O)(OH)}_2$  occur through the following mechanism:



where  $\text{P\_H} = \text{H-P(O)(OH)}_2$ ,  $\text{C} = \text{Catalyst}$ ,  $\text{C\_H} = \text{Catalyst in its hydride form}$ ,  $\text{C\_NAD}^+ = \text{Catalyst/NAD}^+$  inactive adduct,  $\text{C}^* = \text{Catalyst in its activated form}$ .

Consequently, the reaction rate, evaluated in the initial stage,  $r_{\text{NADH}}$  can be expressed as:

$$r_{\text{NADH}} = \frac{d[\text{NADH}]}{dt} = k_3[\text{C\_H}][\text{NAD}^+] \quad 1$$

Applying the steady-state approximation at  $\text{C\_H}$ ,  $\text{C}^*$  and  $\text{C\_NAD}^+$  leads to the following equations:

$$\frac{d[\text{C\_H}]}{dt} = k_2[\text{C}^*][\text{P\_H}] - k_3[\text{C\_H}][\text{NAD}^+] = 0 \rightarrow [\text{C}^*] = \frac{k_3[\text{C\_H}][\text{NAD}^+]}{k_2[\text{P\_H}]} \quad 2$$

$$\frac{d[\text{C}^*]}{dt} = k^*[\text{C}] - k_2[\text{C}^*][\text{P\_H}] = 0 \rightarrow [\text{C}] = \frac{k_2[\text{C}^*][\text{P\_H}]}{k^*} \quad 3$$

$$\frac{d[\text{C\_NAD}^+]}{dt} = k_1[\text{C}][\text{NAD}^+] - k_{-1}[\text{C\_NAD}^+] = 0 \rightarrow [\text{C\_NAD}^+] = \frac{k_1}{k_{-1}}[\text{C}][\text{NAD}^+] \quad 4$$

Combining 2 and 3 and 3 and 4:

$$[\text{C}] = \frac{k_2[\text{C}^*][\text{P\_H}]}{k^*} = \frac{k_3[\text{C\_H}][\text{NAD}^+]}{k^*} \quad 5$$

$$[\text{C\_NAD}^+] = \frac{k_1}{k_{-1}}[\text{C}][\text{NAD}^+] = \frac{k_1}{k_{-1}} \frac{k_3[\text{C\_H}][\text{NAD}^+]}{k^*} [\text{NAD}^+] \quad 6$$

According to the conservation of mass:

$$C_{0_{CAT}} = [C] + [C_{-H}] + [C_{NAD^+}] + [C^*] \quad 7$$

$$C_{0_{CAT}} = [C_{-H}] \left( \frac{k_3[NAD^+]}{k^*} + 1 + \frac{k_1}{k_{-1}} \frac{k_3[NAD^+]^2}{k^*} + \frac{k_3[NAD^+]}{k_2[P_{-H}]} \right) \quad 8$$

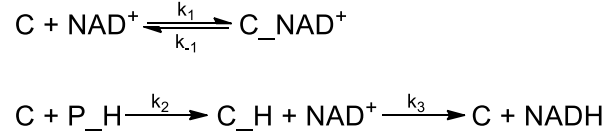
$$[C_{-H}] = \frac{k_2 k^* C_{0_{CAT}} [P_{-H}]}{k_3 k_2 [NAD^+] [P_{-H}] + k_3 k^* [NAD^+] + k_2 k^* [P_{-H}] + \frac{k_1}{k_{-1}} k_3 k_2 [NAD^+]^2 [P_{-H}]} \quad 9$$

Finally, introducing equation 9 in 1, a mathematical equation relating  $r_{NADH}$  to the concentration of  $NAD^+$  is obtained:

$$\frac{d[NADH]}{dt} = \frac{k_3 k_2 k^* C_{0_{CAT}} [NAD^+] [P_{-H}]}{k_3 k_2 [NAD^+] [P_{-H}] + k_3 k^* [NAD^+] + k_2 k^* [P_{-H}] + \frac{k_1}{k_{-1}} k_3 k_2 [NAD^+]^2 [P_{-H}]} \quad \text{Eq.1}$$

## Equation 2)

Assuming that the hydrogenation of  $\text{NAD}^+$  with  $\text{H-P(O)(OH)}_2$  occur through the following mechanism:



where  $\text{P\_H} = \text{H-P(O)(OH)}_2$ ,  $\text{C} = \text{Catalyst}$ ,  $\text{C\_H} = \text{Catalyst in its hydride form}$ ,  $\text{C\_NAD}^+ = \text{Catalyst/NAD}^+ \text{ inactive adduct}$ .

Consequently, the reaction rate, evaluated in the initial stage,  $r_{\text{NADH}}$  can be expressed as:

$$r_{\text{NADH}} = \frac{d[\text{NADH}]}{dt} = k_3[\text{C\_H}][\text{NAD}^+] \quad 10$$

Applying the steady-state approximation at  $\text{C\_H}$  and  $\text{C\_NAD}^+$  leads to the following equations:

$$\frac{d[\text{C\_H}]}{dt} = k_2[\text{C}][\text{P\_H}] - k_3[\text{C\_H}][\text{NAD}^+] = 0 \rightarrow [\text{C}] = \frac{k_3[\text{C\_H}][\text{NAD}^+]}{k_2[\text{P\_H}]} \quad 11$$

$$\frac{d[\text{C\_NAD}^+]}{dt} = k_1[\text{C}][\text{NAD}^+] - k_{-1}[\text{C\_NAD}^+] = 0 \rightarrow [\text{C\_NAD}^+] = \frac{k_1}{k_{-1}}[\text{C}][\text{NAD}^+] \quad 12$$

Combining 11 and 12:

$$[\text{C\_NAD}^+] = \frac{k_1}{k_{-1}}[\text{C}][\text{NAD}^+] = \frac{k_1}{k_{-1}} \left( \frac{k_3[\text{C\_H}][\text{NAD}^+]}{k_2[\text{P\_H}]} \right) [\text{NAD}^+] \quad 13$$

According to the conservation of mass:

$$C_{0\text{CAT}} = [\text{C}] + [\text{C\_H}] + [\text{C\_NAD}^+] \quad 14$$

$$C_{0\text{CAT}} = [\text{C\_H}] \left( \frac{k_3[\text{NAD}^+]}{k_2[\text{P\_H}]} + 1 + \frac{k_1}{k_{-1}} \frac{k_3[\text{NAD}^+]^2}{k_2[\text{P\_H}]} \right) \quad 15$$

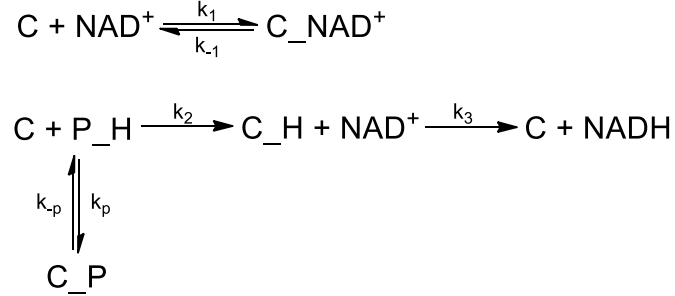
$$\frac{d[NADH]}{dt} = \frac{k_2 C_{0CAT} [P-H]}{k_3 [NAD^+] + k_2 [P-H] + \frac{k_1}{k_{-1}} k_3 [NAD^+]^2} \quad 16$$

Finally, introducing equation 16 in 10, a mathematical equation relating  $r_{NADH}$  to the concentrations of the reagents is obtained:

$$r_{NADH} = \frac{d[NADH]}{dt} = \frac{k_3 k_2 C_{0CAT} [NAD^+] [P-H]}{k_3 [NAD^+] + k_2 [P-H] + \frac{k_1}{k_{-1}} k_3 [NAD^+]^2} \quad \text{Eq. 2}$$

**Equation 3)**

Assuming that the hydrogenation of  $\text{NAD}^+$  with  $\text{H-P(O)(OH)}_2$  occur through the following mechanism:



where  $\text{P\_H} = \text{H-P(O)(OH)}_2$ ,  $\text{C} = \text{Catalyst}$ ,  $\text{C\_H} = \text{Catalyst in its hydride form}$ ,  $\text{C\_NAD}^+ = \text{Catalyst/NAD}^+$  inactive adduct,  $\text{C\_P} = \text{Catalyst/phosphite inactive adduct}$ .

Consequently, the reaction rate, evaluated in the initial stage,  $r_{\text{NADH}}$  can be expressed as:

$$r_{\text{NADH}} = \frac{d[\text{NADH}]}{dt} = k_3[\text{C\_H}][\text{NAD}^+] \quad 17$$

Applying the steady-state approximation at  $\text{C\_H}$ ,  $\text{C\_NAD}^+$  and  $\text{C\_P}$  leads to the following equations:

$$\frac{d[\text{C\_H}]}{dt} = k_2[\text{C}][\text{P\_H}] - k_3[\text{C\_H}][\text{NAD}^+] = 0 \rightarrow [\text{C}] = \frac{k_3[\text{C\_H}][\text{NAD}^+]}{k_2[\text{P\_H}]} \quad 18$$

$$\frac{d[\text{C\_NAD}^+]}{dt} = k_1[\text{C}][\text{NAD}^+] - k_{-1}[\text{C\_NAD}^+] = 0 \rightarrow [\text{C\_NAD}^+] = \frac{k_1}{k_{-1}}[\text{C}][\text{NAD}^+] \quad 19$$

$$\frac{d[\text{C\_P}]}{dt} = k_p[\text{C}][\text{P\_H}] - k_{-p}[\text{C\_P}] = 0 \rightarrow [\text{C\_P}] = \frac{k_p}{k_{-p}}[\text{C}][\text{P\_H}] \quad 20$$

Combining 18 and 19 and 18 and 20:

$$[\text{C\_NAD}^+] = \frac{k_1}{k_{-1}}[\text{C}][\text{NAD}^+] = \frac{k_1}{k_{-1}} \left( \frac{k_3[\text{C\_H}][\text{NAD}^+]}{k_2[\text{P\_H}]} \right) [\text{NAD}^+] \quad 21$$



$$[C_{-P}] = \frac{k_p}{k_{-p}} [C][P_{-H}] = \frac{k_9}{k_{-p}} \left( \frac{k_3 [C_{-H}] [NAD^+]}{k_2 [P_{-H}]} \right) [P_{-H}] \quad 22$$

According to the conservation of mass:

$$C_{0_{CAT}} = [C] + [C_{-H}] + [C_{-NAD^+}] + [C_{-P}] \quad 23$$

$$C_{0_{CAT}} = [C_{-H}] \left( \frac{k_3 [NAD^+]}{k_2 [P_{-H}]} + 1 + \frac{k_1}{k_{-1}} \frac{k_3 [NAD^+]^2}{k_2 [P_{-H}]} + \frac{k_p}{k_{-p}} \frac{k_3 [NAD^+]}{k_2} \right) \quad 24$$

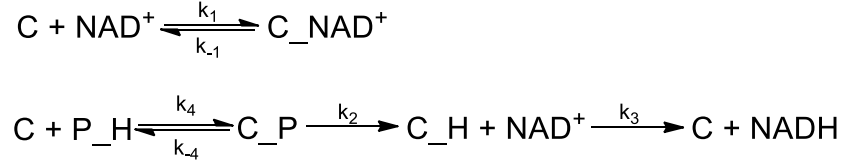
$$[C_{-H}] = \frac{k_2 C_{0_{CAT}} [P_{-H}]}{k_3 [NAD^+] + k_2 [P_{-H}] + \frac{k_p}{k_{-p}} k_3 [NAD^+] [P_{-H}] + \frac{k_1}{k_{-1}} k_3 [NAD^+]^2} \quad 25$$

Finally, introducing equation 25 in 17, a mathematical equation relating  $r_{NADH}$  to the concentrations of the reagents is obtained:

$$\frac{d[NADH]}{dt} = \frac{k_3 k_2 C_{0_{CAT}} [NAD^+] [P_{-H}]}{k_3 [NAD^+] + k_2 [P_{-H}] + \frac{k_p}{k_{-p}} k_3 [NAD^+] [P_{-H}] + \frac{k_1}{k_{-1}} k_3 [NAD^+]^2} \quad \text{Eq. 3}$$

**Equation 4)**

Assuming that the hydrogenation of  $NAD^+$  with  $H-P(O)(OH)_2$  occur through the following mechanism:



where  $P\_H = H-P(O)(OH)_2$ ,  $C =$  Catalyst,  $C\_H =$  Catalyst in its hydride form,  $C\_NAD^+ =$  Catalyst/ $NAD^+$  inactive adduct,  $C\_P =$  Catalyst/phosphite complex.

Consequently, the reaction rate, evaluated in the initial stage,  $r_{NADH}$  can be expressed as:

$$r_{NADH} = \frac{d[NADH]}{dt} = k_3[C\_H][NAD^+] \quad 26$$

Applying the steady-state approximation at  $C\_H$ ,  $C\_P$  and  $C\_NAD^+$  leads to the following equations:

$$\frac{d[C\_H]}{dt} = k_2[C\_P] - k_3[C\_H][NAD^+] = 0 \rightarrow [C\_P] = \frac{k_3[C\_H][NAD^+]}{k_2} \quad 27$$

$$\frac{d[C\_P]}{dt} = k_4[C][P\_H] - k_{-4}[C\_P] - k_2[C\_P] = 0 \rightarrow [C] = \frac{(k_{-4} + k_2)[C\_P]}{k_4[P\_H]} \quad 28$$

$$\frac{d[C\_NAD^+]}{dt} = k_1[C][NAD^+] - k_{-1}[C\_NAD^+] = 0 \rightarrow [C\_NAD^+] = \frac{k_1}{k_{-1}}[C][NAD^+] \quad 29$$

Combining 27 and 28 and 28 and 29:

$$[C] = \frac{(k_{-4} + k_2)[C\_P]}{k_4[P\_H]} = \frac{(k_{-4} + k_2)k_3[C\_H][NAD^+]}{k_2k_4[P\_H]} \quad 30$$

$$[C\_NAD^+] = \frac{k_1}{k_{-1}}[C][NAD^+] = \frac{k_1}{k_{-1}} \frac{(k_{-4} + k_2)k_3[C\_H][NAD^+]^2}{k_2k_4[P\_H]} \quad 31$$

According to the conservation of mass:

$$C_{0_{CAT}} = [C] + [C_{-H}] + [C_{-NAD^+}] + [C_{-P}] \quad 32$$

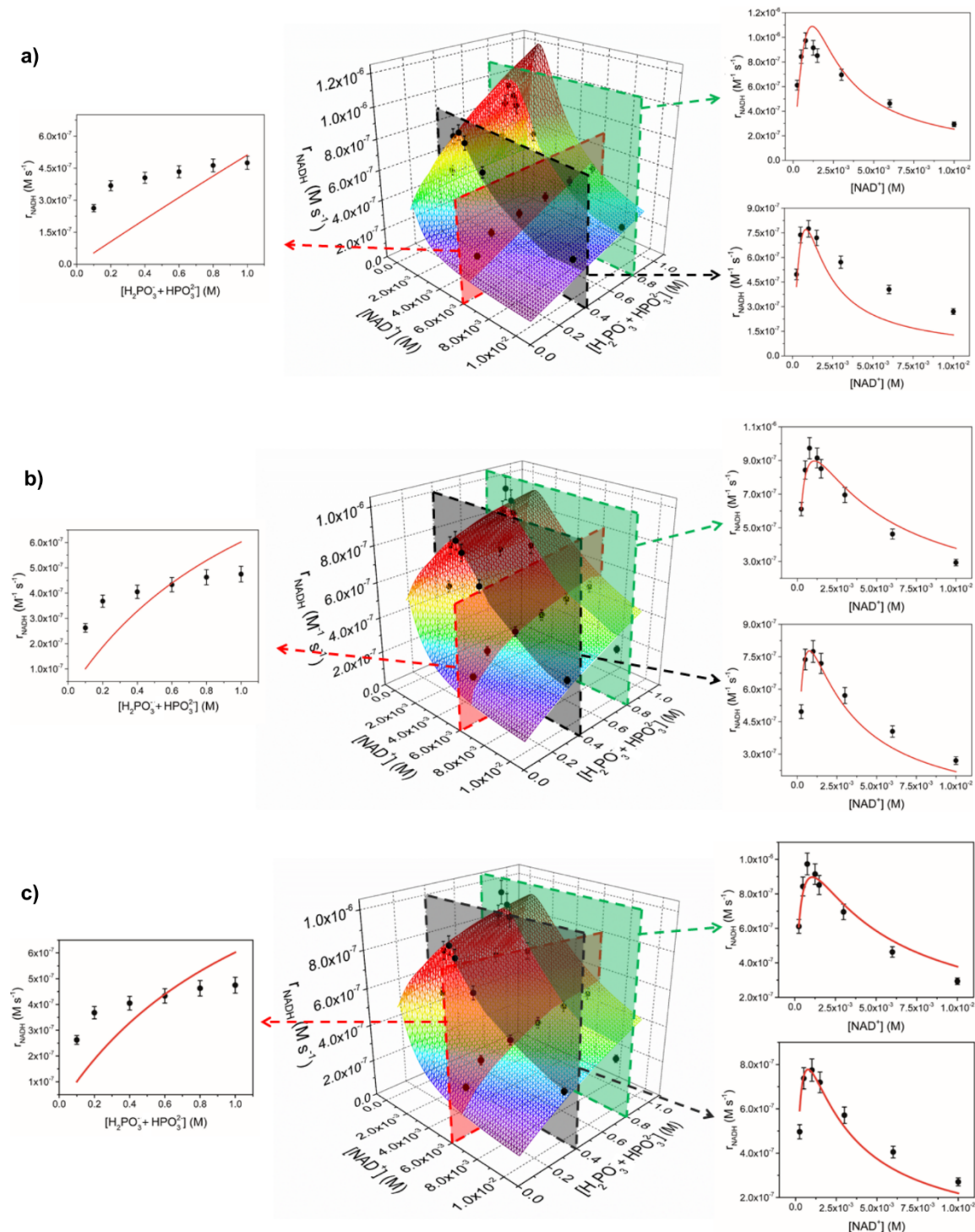
$$C_{0_{CAT}} = [C_{-H}] \left( \frac{(k_{-4} + k_2)k_3[NAD^+]}{k_2k_4[P_{-H}]} + 1 + \frac{k_1}{k_{-1}} \frac{(k_{-4} + k_2)k_3[NAD^+]^2}{k_2k_4[P_{-H}]} + \frac{k_3[NAD^+]}{k_2} \right) \quad 33$$

$$[C_{-H}] = \frac{k_3k_2k_4C_{0_{CAT}}[NAD^+][P_{-H}]}{k_3k_{-4}[NAD^+] + k_3k_2[NAD^+] + k_3k_4[NAD^+][P_{-H}] + k_2k_4[P_{-H}] + \frac{k_1}{k_{-1}}k_3k_{-4}[NAD^+]^2 + \frac{k_1}{k_{-1}}k_3k_2[NAD^+]^2} \quad 34$$

Finally, introducing equation 34 in 26, a mathematical equation relating  $r_{NADH}$  to the concentration of  $NAD^+$  is obtained:

$$r_{NADH} = \frac{k_3k_2k_4C_{0_{CAT}}[NAD^+][P_{-H}]}{k_3k_{-4}[NAD^+] + k_3k_2[NAD^+] + k_3k_4[NAD^+][P_{-H}] + k_2k_4[P_{-H}] + \frac{k_1}{k_{-1}}k_3k_{-4}[NAD^+]^2 + \frac{k_1}{k_{-1}}k_3k_2[NAD^+]^2} \quad \text{Eq. 4}$$

## Fitting Results



**Figure S1.** Global fittings of 3D and 2D trends of initial rate of reaction ( $r_{\text{NADH}}$ ,  $\text{M s}^{-1}$ ) vs concentration of reactants ( $\text{NAD}^+$  on the right and phosphonic acid on the left) for the NADH regeneration with phosphonic acid mediated by **1** (Experimental conditions:  $T = 313 \text{ K}$ ,  $[\mathbf{1}] = 5 \text{ mM}$ ,  $\text{pH} = 6.58$ ). The fitting of the data was made with Eq.2 (Part a, top), Eq.3 (Part b, middle), and Eq.4 (Part c, bottom).

**Table S2.** Kinetic parameter values for the proposed reaction mechanisms obtained through the fitting of the experimental data with Eqs 1-4. Numbers reported in red have unrealistically high error intervals arising from the application of an unsuitable rate law.

Equation	Fitting Parameters	1	2
Eq. 1	$k_1/k_{-1}$	$900 \pm 200 \text{ M}^{-1}$	$260 \pm 60 \text{ M}^{-1}$
	$k^*$	$0.7 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$	$3.7 \pm 0.6 \text{ M}^{-1} \text{ s}^{-1}$
	$k_2$	$1.0 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$	$12 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$
	$k_3$	$780 \pm 50 \text{ M}^{-1} \text{ s}^{-1}$	$1040 \pm 60 \text{ M}^{-1} \text{ s}^{-1}$
	$R^2$	0.98	0.99
Eq. 2	$k_1/k_{-1}$	$8 \times 10^{13} \pm 6 \times 10^{15} \text{ M}^{-1}$	$9 \times 10^{10} \pm 9 \times 10^{12} \text{ M}^{-1}$
	$k_2$	$5 \times 10^{10} \pm 4 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$	$1 \times 10^9 \pm 1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$
	$k_3$	$370 \pm 70 \text{ M}^{-1} \text{ s}^{-1}$	$700 \pm 100 \text{ M}^{-1} \text{ s}^{-1}$
	$R^2$	0.63	0.49
Eq. 3	$k_1/k_{-1}$	$1 \times 10^9 \pm 2 \times 10^{11} \text{ M}^{-1}$	$6 \times 10^4 \pm 6 \times 10^6 \text{ M}^{-1}$
	$k_p/k_{-p}$	$6 \times 10^6 \pm 9 \times 10^8 \text{ M}^{-1}$	$2 \times 10^3 \pm 2 \times 10^5 \text{ M}^{-1}$
	$k_2$	$2 \times 10^6 \pm 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	$2 \times 10^3 \pm 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
	$k_3$	$900 \pm 400 \text{ M}^{-1} \text{ s}^{-1}$	$1400 \pm 300 \text{ M}^{-1} \text{ s}^{-1}$
	$R^2$	0.87	0.95
Eq. 4	$k_1/k_{-1}$	$3 \times 10^9 \pm 7 \times 10^{15} \text{ M}^{-1}$	$8 \times 10^{20} \pm 1 \times 10^{26} \text{ M}^{-1}$
	$k_4$	$2 \times 10^{12} \pm 2 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$	$4 \times 10^{19} \pm 6 \times 10^{24} \text{ M}^{-1} \text{ s}^{-1}$
	$k_{-4}$	$1 \times 10^5 \pm 2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$	$1 \times 10^{-5} \pm 4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
	$k_2$	$0.3 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$	$1.5 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$
	$k_3$	$900 \pm 400 \text{ M}^{-1} \text{ s}^{-1}$	$1400 \pm 200 \text{ M}^{-1} \text{ s}^{-1}$
	$R^2$	0.87	0.95

## Thermodynamic study of dimerization reaction

4 mg of complex **2** (ca. 0.007 mmol) were dissolved in 0.6 mL of D<sub>2</sub>O and transferred to an NMR tube. The formation of complexes **2-H<sub>2</sub>O** and **2-Dimer** were observed as described in the text. Detection of <sup>13</sup>C NMR peaks of **2-Dimer** were hampered by the broadening of the signals.

NMR data for **2-H<sub>2</sub>O**:

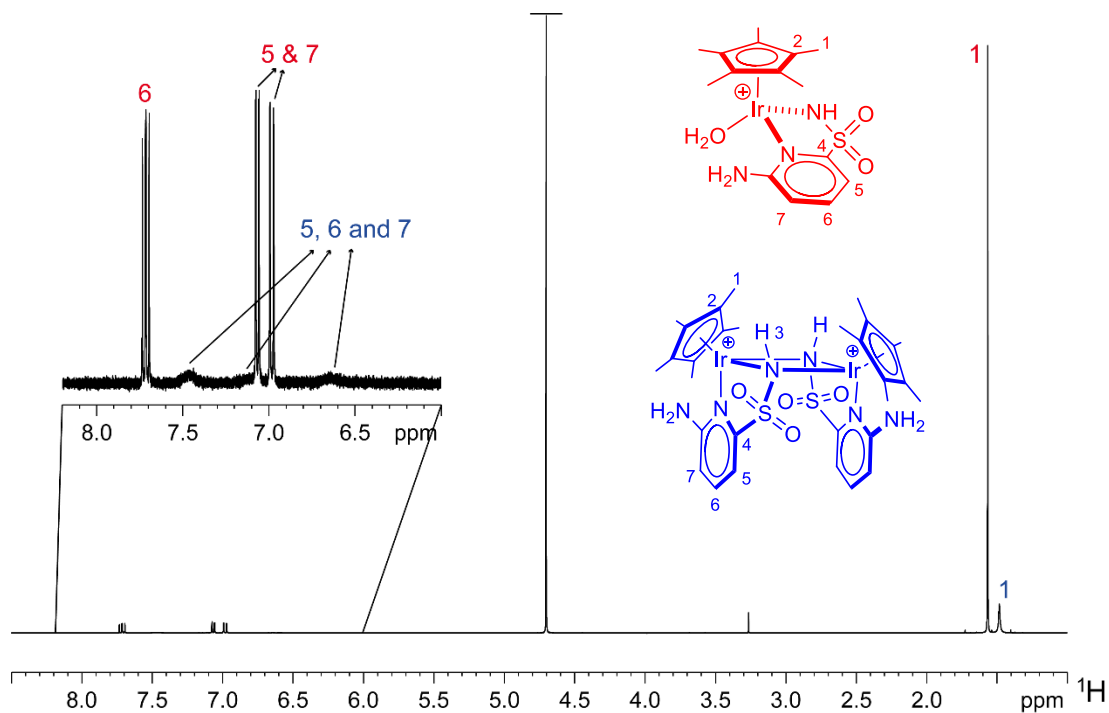
<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 298 K,  $\delta$  in ppm):  $\delta$  = 7.79 (dd, H6), 7.15 (d, H5 or H7), 7.06 (d, H5 or H7), 1.64 (s, H1).

<sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, D<sub>2</sub>O, 298 K,  $\delta$  in ppm):  $\delta$  = 158.1 (s, C8 or C4), 154.2 (s, C8 or C4), 141.1 (s, C6), 114.4 (s, C7 or C5), 110.4 (s, C7 or C5), 87.9 (s, C2), 8.4 (s, C1).

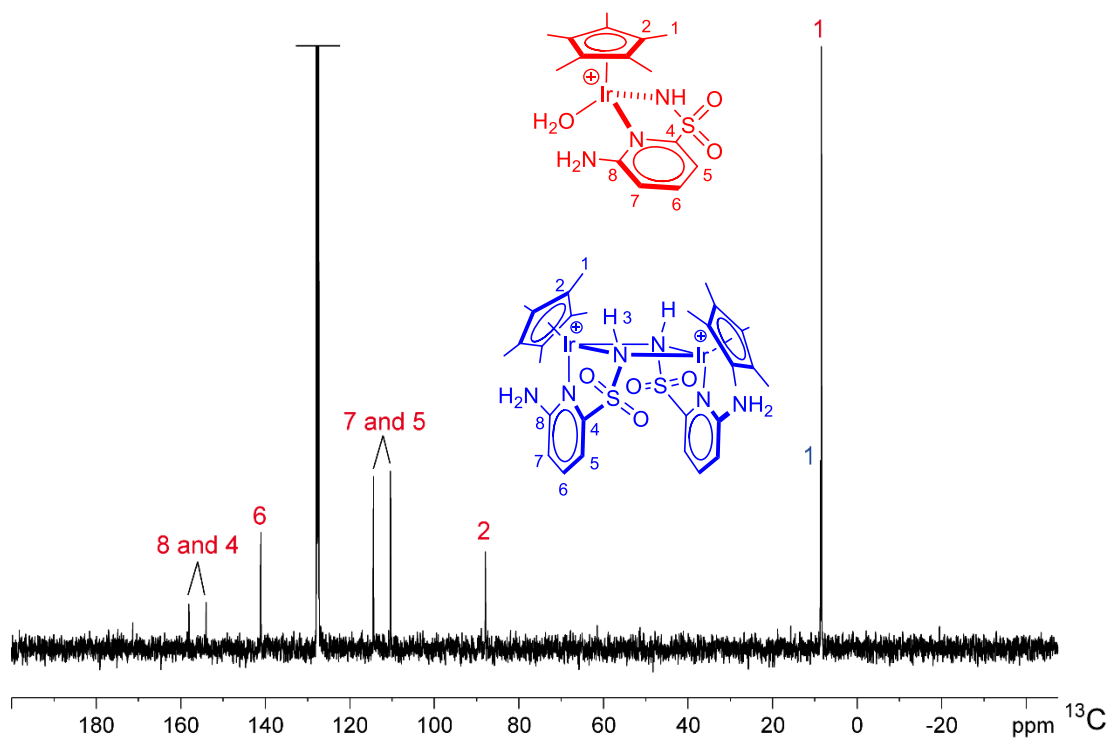
NMR data for **2-Dimer**:

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 298 K,  $\delta$  in ppm):  $\delta$  = 7.54 (b, H5 or H6 or H7), 7.18 (b, H5 or H6 or H7), 6.71 (b, H5 or H6 or H7), 1.56 (s, H1).

<sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, D<sub>2</sub>O, 298 K,  $\delta$  in ppm):  $\delta$  = 8.6 (s, C1).



**Figure S2.** <sup>1</sup>H NMR spectrum relative to the reaction mixture of **2-H<sub>2</sub>O** (red) and **2-Dimer** (blue) (D<sub>2</sub>O, 298 K).



**Figure S3.**  $^{13}\text{C}$  NMR spectrum relative to the reaction mixture of **2-H<sub>2</sub>O** (red) and **2-Dimer** (blue) ( $\text{D}_2\text{O}$ , 298 K).

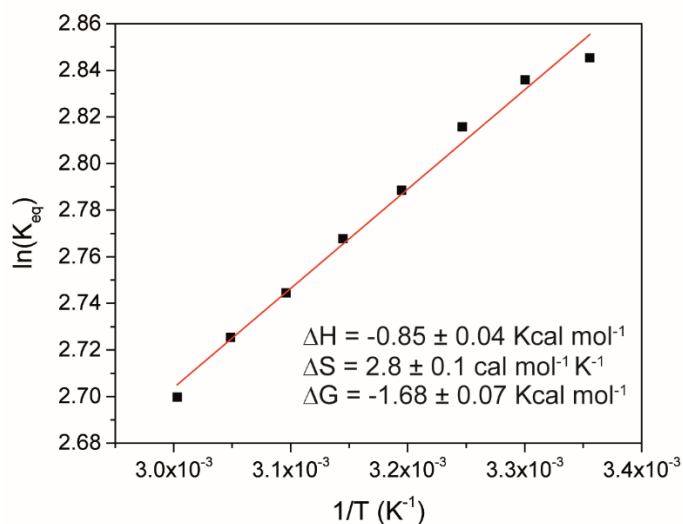
## Van'T Hoff plots of dimerization reaction

The concentration of the reagent(s) and the product(s) were estimated by quantitative  $^1\text{H}$  NMR spectra using an external standard. The equilibrium constant of the dimerization reactions of **1** and **2** were calculated as shown in Equation 35. Thermodynamic parameters were estimated from the corresponding Van'T Hoff plots; errors on enthalpy and entropy of formation were determined from the quality of linear fitting and computed at 95% confidence interval.

$$K_{Eq} = \frac{[\mathbf{2} - \text{Dimer}]}{[\mathbf{2} - \text{H}_2\text{O}]^2} \quad 35$$

**Table S3.** Equilibrium constant ( $K_{eq}$ ) relative to the dimerization reaction of **2** in  $\text{D}_2\text{O}$  at different temperature.

T (K)	[ <b>2</b> - $\text{H}_2\text{O}$ ] (mM)	[ <b>2</b> -Dimer] (mM)	$K_{eq}$ (M)
298	9.17	1.45	17.21
303	9.19	1.44	17.04
308	9.22	1.42	16.70
313	9.27	1.40	16.26
318	9.31	1.38	15.92
323	9.35	1.36	15.56
328	9.37	1.34	15.26
333	9.42	1.32	14.88

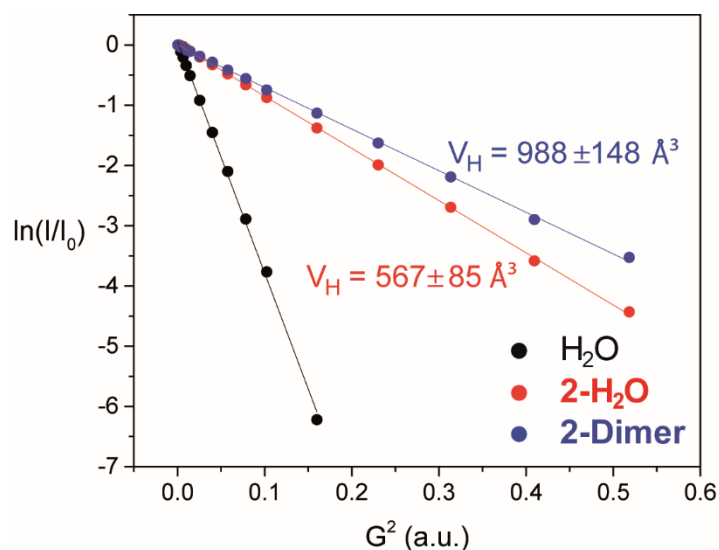


**Figure S4.** Van'T Hoff plot relative to the dimerization reaction of **2** in  $\text{D}_2\text{O}$ . (linear fit; intercept =  $1.43 \pm 0.06$ , slope =  $430 \pm 20$ ,  $R = 0.995$ ).



## PGSE NMR Diffusion experiments

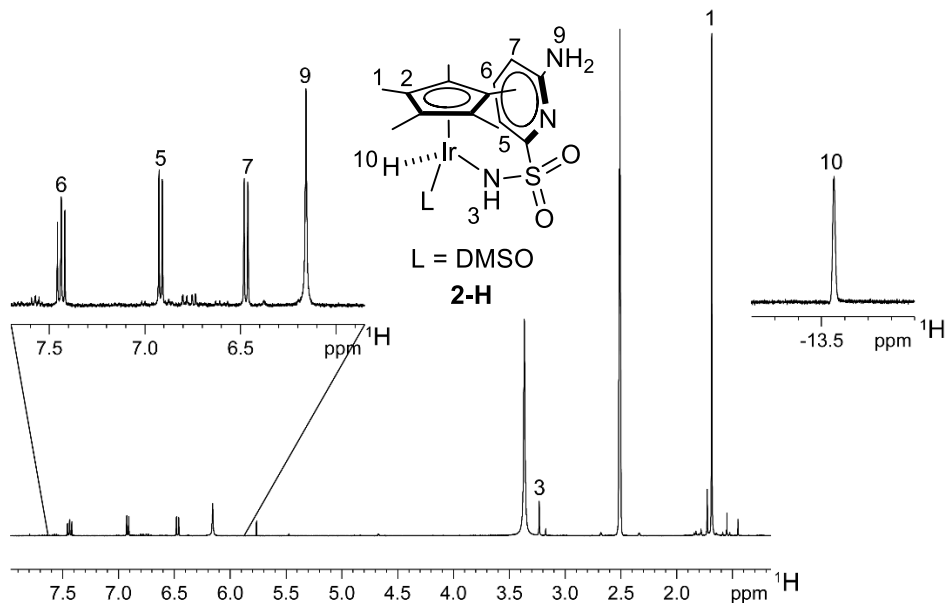
$^1\text{H}$  PGSE NMR measurements were performed on a Bruker Avance III HD 400 spectrometer equipped with a smart probe with a z gradient coil, by using the standard double-stimulated echo pulse sequence without spinning.<sup>1</sup> The shape of the gradients was rectangular, their duration ( $\delta$ ) was 4 ms, and their strength ( $G$ ) was varied during the experiments. All the spectra were acquired using 32k points, 16 scans and were processed with a line broadening of 1.0 Hz. The experiments were carried out with a total recycle delay of ca. 10 s. The semilogarithmic plots of  $\ln(I/I_0)$  versus  $G^2$  (a.u.) were fitted using a standard linear regression algorithm. Self-diffusion coefficients ( $D_t$ ), proportional to the slope of linear fittings, were calculated using the diffusion coefficient of residual solvent resonance as internal reference standard.



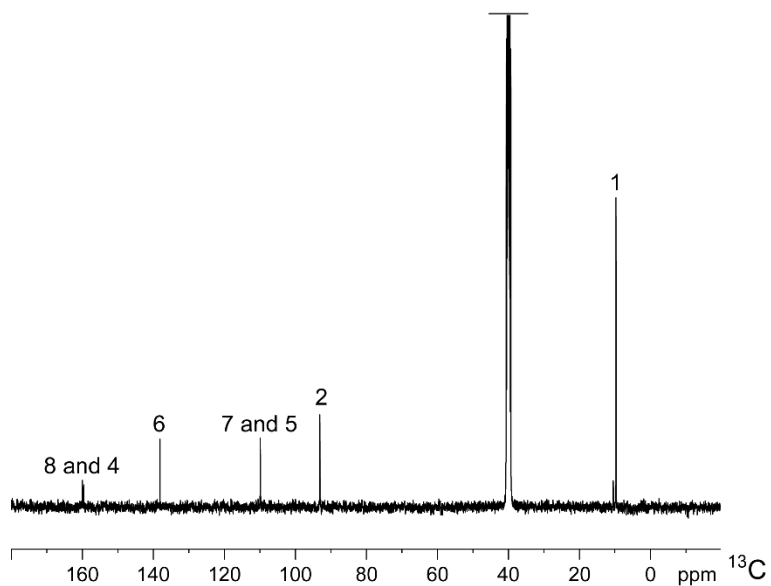
**Figure S5.** Semilogarithmic plots of  $\ln(I/I_0)$  vs  $G^2$  (a.u.) of  $2\text{-H}_2\text{O}$  (red dots),  $2\text{-Dimer}$  (blue dots) and  $\text{H}_2\text{O}$  (black dots) at 298K.

## NMR Characterization of 2-H

**2-H**:  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ , 298K,  $\delta$  in ppm, J in Hz):  $\delta$  = 7.43 (d,  $^3J_{\text{HH}}$  = 7.7, H6), 6.91 (d,  $^3J_{\text{HH}}$  = 7.2, H5), 6.47 (d,  $^3J_{\text{HH}}$  = 8.4, H7), 6.16 (b, H9), 3.23 (s, H3), 1.67 (d,  $^4J_{\text{HH}}$  = 0.85, H1), -13.56 (s, H10).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $(\text{CD}_3)_2\text{SO}$ , 298K,  $\delta$  in ppm):  $\delta$  = 160.0 (s, C8 or C4), 159.6 (s, C8 or C4), 138.2 (s, C6), 109.9 (s, C5), 109.8 (s, C7), 93.0 (s, C2), 9.6 (s, C1).



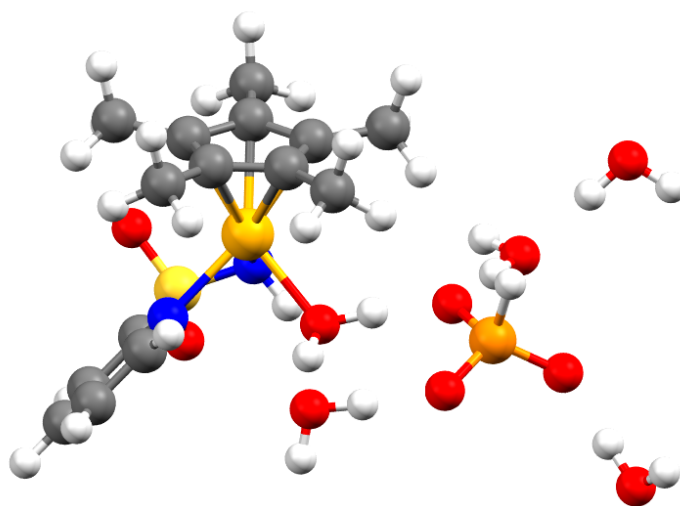
**Figure S6.**  $^1\text{H}$  NMR spectrum of complex **2-H** ( $(\text{CD}_3)_2\text{SO}$ , 298 K).



**Figure S7.**  $^{13}\text{C}$  NMR spectrum of complex **2-H** ( $(\text{CD}_3)_2\text{SO}$ , 298 K).

## Computational details

All calculations were performed without symmetry restrictions. All calculations were done with the Gaussian09 (Revision D.01) program package. Geometry optimizations were performed using density functional theory (DFT) with the B3LYP functional together with 6-311++G\*\* (for all nonmetal atoms) and sdd (for Ir). The vibrational frequency analyses showed no imaginary frequencies for the ground states and one imaginary frequency for the transition states, corresponding to the expected translational motion of the transition states.



**Figure S8.** Computed structure of **1-H<sub>2</sub>O** showing the orientation of water molecules after calculations.

### Coordinates for optimized geometries

#### **1-H<sub>2</sub>O**

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**1-TS<sub>i</sub>**

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**1-TP-OH**

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## 1-TS<sub>II</sub>

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### 1-HPO<sub>3</sub><sup>-</sup>

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H 1.4408250000 -3.6755010000 -1.2552560000  
H 0.0394910000 -3.5504270000 0.5634540000  
H 0.9839870000 -3.8626810000 2.0296650000  
H -0.3066380000 -2.6591210000 2.0557930000  
H 0.7583670000 0.1457810000 -2.7844110000  
H -4.2729330000 0.9715200000 -0.6848350000  
H -4.1020710000 2.2182500000 -1.5839010000  
H 0.4042180000 4.1591270000 2.2623690000  
H -1.0029090000 4.0041510000 2.8238910000  
H -3.2158820000 3.6835800000 1.5997670000  
H -1.9426390000 3.0282690000 0.9960280000  
H -2.0250070000 3.0992880000 -1.7379300000  
H -2.4426740000 2.9230120000 -3.2267130000  
H 1.4849460000 1.4469080000 -2.2805060000

### 1-TS<sub>III</sub>

N -3.1591740000 1.9477030000 0.6123150000  
C -3.4203550000 0.7817440000 0.0262110000  
C -4.4298430000 -0.0870180000 0.4213650000  
C -5.2120470000 0.2892790000 1.5127770000  
C -4.9474710000 1.4975320000 2.1487600000  
C -3.9131690000 2.2951570000 1.6625610000  
S -2.3619050000 0.3738310000 -1.4138390000  
O -2.7146100000 -1.0050260000 -1.7970050000  
N -0.8116760000 0.4297420000 -0.9748300000  
Ir 0.5304460000 -1.0312470000 -0.1848910000  
O 1.2009640000 -0.8110840000 -2.3745630000  
C 1.5708700000 -2.8986710000 0.3075320000  
C 1.4083470000 -2.1005310000 1.4852770000  
C -0.0183920000 -1.9161590000 1.7012830000  
C -0.7176370000 -2.7653870000 0.7329560000  
C 0.2403390000 -3.3323200000 -0.1304980000  
C 2.8627740000 -3.3965790000 -0.2655110000  
C 2.5001920000 -1.6185960000 2.3896280000  
C -0.6442850000 -1.2810490000 2.9062590000  
C -2.1855250000 -3.0470730000 0.7343920000  
C -0.0205300000 -4.2679310000 -1.2687110000  
O -2.6448050000 1.4472660000 -2.3947330000  
O 3.1307450000 1.0119820000 -2.0255190000  
P 3.0393850000 1.6802740000 -0.6823800000  
O 4.0298790000 1.3634150000 0.3937980000  
O 2.1172700000 2.8654770000 -0.5167760000

O 0.2850260000 4.2016590000 -2.0655240000  
O 2.1465910000 4.5062730000 1.7386180000  
O -1.9343350000 4.5086320000 -0.3150480000  
O 4.3418580000 2.9601280000 2.7472640000  
H 1.4164240000 0.3013200000 0.1154220000  
H -4.5938440000 -1.0146140000 -0.1080150000  
H -6.0128840000 -0.3540860000 1.8574250000  
H -5.5289180000 1.8244200000 3.0013470000  
H -0.5345230000 1.4002610000 -0.8623100000  
H -3.6828800000 3.2490390000 2.1252760000  
H 3.6964240000 -2.7446970000 -0.0028020000  
H 2.8162480000 -3.4648110000 -1.3536610000  
H 3.0843180000 -4.3978590000 0.1208460000  
H 3.4362220000 -1.4737030000 1.8507180000  
H 2.2383950000 -0.6769920000 2.8724870000  
H 2.6735360000 -2.3628270000 3.1748500000  
H -0.0126130000 -0.4894070000 3.3106030000  
H -0.7918240000 -2.0282330000 3.6947500000  
H -1.6172660000 -0.8467760000 2.6726540000  
H 0.6371120000 -4.0629160000 -2.1154160000  
H 0.1643980000 -5.3014830000 -0.9541660000  
H -1.0529260000 -4.2036550000 -1.6131570000  
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H -2.3684880000 -3.9832600000 1.2744860000  
H -2.7435830000 -2.2619000000 1.2423910000  
H 0.4510710000 -0.2878950000 -2.6993290000  
H -2.2433070000 3.6126910000 -0.0908190000  
H -1.1940210000 4.3794820000 -0.9368200000  
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H 3.6326120000 3.5972860000 2.5483780000  
H 2.2739900000 5.4181950000 1.4554510000  
H 2.0943900000 3.9797930000 0.9138040000  
H 0.9756660000 3.6770050000 -1.6074960000  
H 0.1391880000 3.7640610000 -2.9111410000  
H 1.9625150000 -0.1817680000 -2.3627380000

**1-H**

C -3.0000640000 -1.6219510000 -1.0751390000  
C -2.7976470000 -2.1511770000 0.2152450000  
C -1.4001920000 -2.5729040000 0.3221340000  
C -0.7863250000 -2.3781240000 -0.9685680000  
C -1.7396430000 -1.7147560000 -1.8155840000  
lr -1.2540620000 -0.4207310000 -0.0776150000  
N -1.3321270000 0.4886570000 1.8786850000  
S -2.3541960000 1.7372860000 1.9243240000  
O -1.9594510000 2.7618200000 2.9120840000  
C -3.8201980000 -2.3105420000 1.2966890000  
C -0.8236930000 -3.3496970000 1.4685120000  
C 0.5630490000 -2.8783670000 -1.3862030000  
C -1.5828930000 -1.4574440000 -3.2850480000  
C -4.2837080000 -1.0982370000 -1.6423180000  
N -1.7150920000 1.6214030000 -0.6607880000

C -1.5546200000 2.0884320000 -1.9143510000  
C -1.8487410000 3.4002870000 -2.2594860000  
C -2.3141750000 4.2752610000 -1.2816260000  
C -2.4748780000 3.8018710000 0.0171700000  
C -2.1694340000 2.4743500000 0.2705150000  
H 0.2721620000 0.0823730000 -0.0903770000  
O -3.7496510000 1.2645840000 1.9875390000  
O 4.0376460000 1.0316900000 1.0753520000  
P 5.1997190000 0.5464740000 0.2386800000  
O 4.5166710000 0.1536340000 -1.2251840000  
O 5.7708640000 -0.8699860000 0.7838760000  
O 6.3916920000 1.4413270000 0.0036110000  
O 1.9347320000 0.8616710000 -2.2387070000  
O 2.0263690000 -0.5009130000 1.9798260000  
O 8.8867700000 0.9958070000 -0.9790610000  
O 3.8327870000 -2.5225660000 1.7535820000  
H -2.8256890000 4.4392310000 0.8181790000  
H -2.5437370000 5.3057180000 -1.5229110000  
H -1.7001040000 3.7243460000 -3.2811280000  
H -0.4301940000 0.8181050000 2.2165830000  
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H -1.9029940000 -2.3353700000 -3.8580740000  
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H -4.9890000000 -0.8219260000 -0.8582810000  
H -4.7582770000 -1.8653560000 -2.2644010000  
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H -4.6394980000 -1.6004880000 1.1874690000  
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H -1.1856750000 -2.9766380000 2.4276280000  
H -1.1104270000 -4.4049420000 1.3933190000  
H 0.2656430000 -3.3007010000 1.4789690000  
H 1.2713000000 0.5346340000 -1.6139450000  
H 2.7913080000 0.6159070000 -1.8472100000  
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H 2.7011200000 0.1345590000 1.6287960000  
H 1.3114810000 -0.5143810000 1.3239700000  
H 5.0785130000 -1.4863480000 1.1327840000  
H 4.0162880000 -2.9511140000 2.5969110000  
H 3.0781880000 -1.9062070000 1.9147070000  
H 5.1726480000 -0.0974480000 -1.8884090000

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