Electronic Supplementary Information

Activity and degradation pathways of penthamethyl-cyclopentadienyl-iridium catalysts for water oxidation

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Table 1S Clark electrode results for [Cp*Ir(bpy)Cl]Cl (**1**).

C_{cat} (μM)	$10^7 \cdot k_{obs}(Ms^{-1})$[a]	$TOF(min^{-1})$[b]
0.5	0.6	7.6
1.0	1.2	7.3
1.5	2.1	8.4
1.5	2.2	8.6
2.0	2.4	7.2
2.5	2.7	6.6
3.1	3.7	7.2
3.7	4.4	7.2
5.0	5.5	6.8

[a]From the $[O_2]$ *versus* t trends ($[Ce^{+4}]_0$=10 mM). [b]From the k_{obs}/C_{cat} ratio

Table 2S Volumetric results for [Cp*Ir(bpy)Cl]Cl (**1**).

C_{cat} (μM)	Initial $TOF(min^{-1})$[a]	Mean $TOF(min^{-1})$[b]	TON
3.1	5.1	3.7	1240
6.9	3.0	1.6	470
7.1	3.0	1.8	690
14.6	3.3	1.6	415

[a]From the number of cycles *versus* t trends ($[Ce^{+4}]_0$= 28 mM). [b]From the TON/total time ratio

Table 3S UV-Vis spectrophotometric results for [Cp*Ir(bpy)Cl]Cl (**1**).

C_{cat} (μM)	$10^5 \cdot k_{obs}(s^{-1})$[a]	TOF(min^{-1})[b]
1.8	7.5	2.5
2.0	6.4	1.9
2.4	9.4	2.8
3.0	10.6	2.2
4.0	12.9	1.9
4.0	15.6	2.4
4.5	15.8	2.1
5.0	16.8	2.0
10.0	37.8	2.3

[a]From the $\ln(A_t/A_0)$ *versus* -4t trends ($[Ce^{+4}]_0$=1 mM). [b]From the $k_{obs}*[Ce^{+4}]_0/C_{cat}$ ratio

Table 4S Clark electrode results for [Cp*Ir(bzpy)NO_3] (**2**).

C_{cat} (μM)	$10^7 \cdot k_{obs}(Ms^{-1})$[a]	$TOF(min^{-1})$[b]
1.3	2.7	12.5
1.3	2.8	12.9
1.3	2.5	11.7
2.0	3.2	9.6
3.0	8.4	16.8

[a]From the [O_2] *versus* t trends ([Ce^{+4}]$_0$=10 mM). [b]From the k_{obs}/C_{cat} ratio

Table 5S Volumetric results for [Cp*Ir(bzpy)NO_3] (**2**).

C_{cat} (μM)	Initial $TOF(min^{-1})$[a]	Mean $TOF(min^{-1})$[b]	TON
3.1	10.6	5.9	514
7.1	14.4	3.9	375
15.0	7.1	2.4	252

[a]From the number of cycles *versus* t trends ([Ce^{+4}]$_0$= 28 mM). [b]From the TON/total time ratio

Table 6S UV-Vis spectrophotometric results for [Cp*Ir(bzpy)NO_3] (**2**).

C_{cat} (μM)	$10^7 \cdot k_{obs}(Ms^{-1})$[a]	TOF(min^{-1})[b]
1.0	1.2	7.4
1.1	1.4	7.9
1.5	2.1	8.5
1.5	2.0	8.0
2.0	2.8	8.3
2.5	3.5	8.3
2.6	4.2	9.8
3.0	4.4	8.8
3.5	5.1	8.8
4.0	5.3	8.0
4.5	6.7	8.9
5.0	6.8	8.2
5.5	7.4	8.0

[a]From the (A_t/A_0) versus $-4t/[Ce^{+4}]_0$ trends ($[Ce^{+4}]_0$=1 mM). [b]From the k_{obs}/C_{cat} ratio

Table 7S Clark electrode results for $[Cp^*Ir(H_2O)_3](NO_3)_2$ (**3**).

C_{cat} (μM)	$10^7 \cdot k_{obs}(Ms^{-1})^a$	$TOF(min^{-1})^b$
1.0	0.8	4.9
1.0	1.0	5.8
2.0	2.6	8.0
3.0	5.3	11
4.8	15.2	19
10.0	63.3	38

[a]From the $[O_2]$ *versus* t trends ($[Ce^{+4}]_0$=10 mM). [b]From the k_{obs}/C_{cat} ratio

Table 8S Volumetric results for $[Cp^*Ir(H_2O)_3](NO_3)_2$ (**3**).

C_{cat} (μM)	Initial $TOF(min^{-1})^a$	Mean $TOF(min^{-1})^b$	TON
3.1	4.7	3.1	524
4.6	10.7	5.7	701
7.0	18.6	15.8	983
15.0	47.6	26.4	454
15.0	50.4	36.1	454
6.9[c]	12.8	9.0	2034
7.0[d]	8.2	9.6	4042

[a]From the number of cycles *versus* t trends ($[Ce^{+4}]_0$= 28 mM). [b]From the TON/total time ratio. [c]$[Ce^{+4}]_0$= 56 mM. [d]$[Ce^{+4}]_0$= 0.11 M.

Table 9S UV-Vis spectrophotometric results for $[Cp^*Ir(H_2O)_3](NO_3)_2$ (**3**).

C_{cat} (μM)	$10^7 \cdot k_{obs}(Ms^{-1})$[a]	TOF(min^{-1})[b]
0.5	0.6	6.7
0.5	0.6	6.8
1.0	2.0	12.0
1.0	2.2	13.3
1.1	2.7	14.6
1.1	2.5	13.8
1.5	4.1	16.3
1.5	4.2	16.8
1.5	4.3	17.2
2.0	6.5	19.3
2.0	7.1	21.2
2.5	8.6	20.5
2.5	8.8	21.1
3.0	11.1	22.2
3.0	10.6	21.1
3.0	11.1	22.3
3.5	13.0	22.2
3.5	12.2	20.9
3.6	13.0	21.7
4.0	16.1	24.2
4.0	14.7	22.0
4.0	15.9	23.8
4.0	14.7	22.1
4.1	15.6	22.8
4.1	16.5	24.2

4.5	17.2	22.9
4.5	15.0	20.0
4.5	18.0	23.9
5.0	20.3	24.4
5.0	17.9	21.4

[a]From the $\ln(A_t/A_0)$ versus -4t trends ($[Ce^{+4}]_0$=1 mM). [b]From the $k_{obs}*[Ce^{+4}]_0/C_{cat}$ ratio

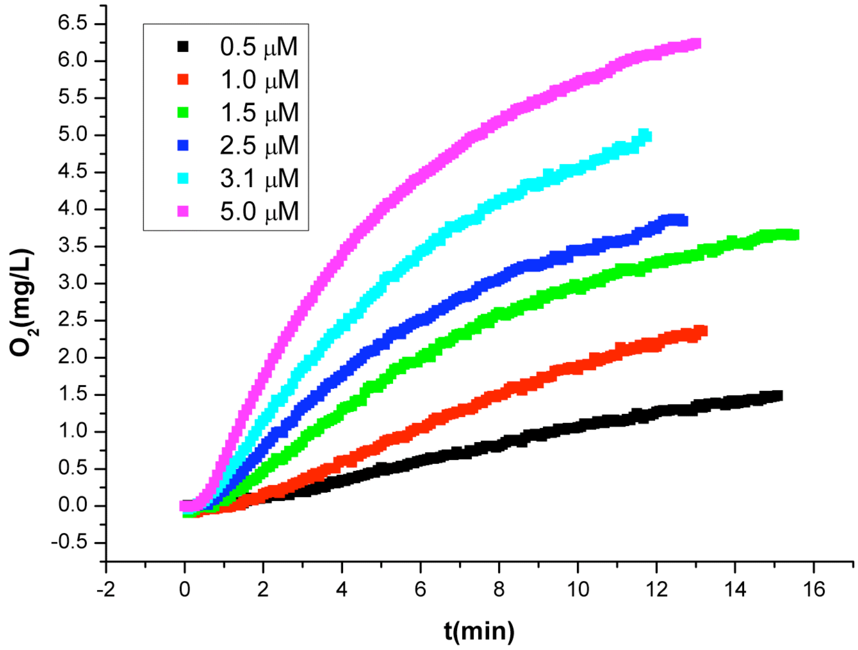

Fig. 1S Oxygen evolution with time detected by the Clark Electrode for catalyst **1**

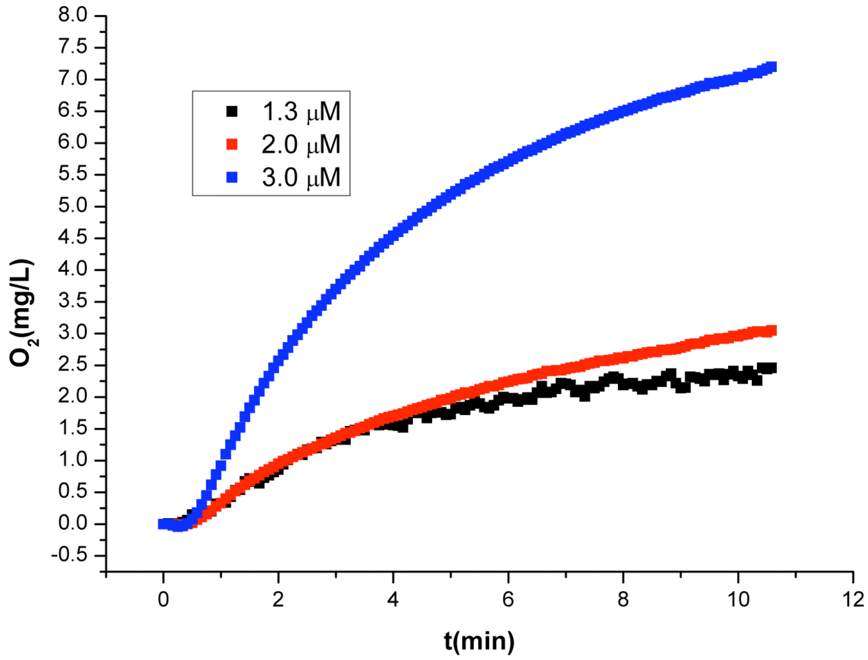

Fig. 2S Oxygen evolution with time detected by the Clark Electrode for catalyst **2**

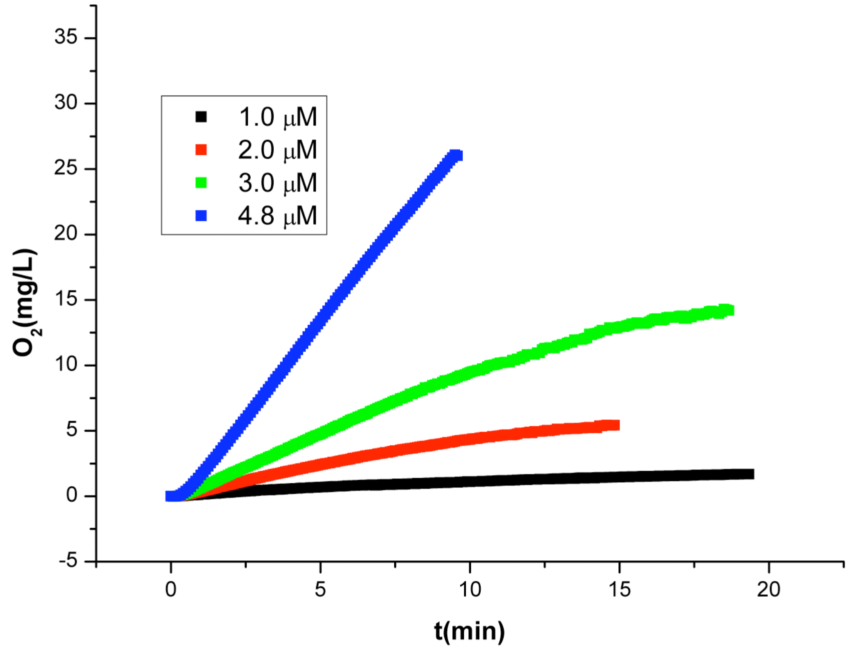

Fig. 3S Oxygen evolution with time detected by the Clark Electrode for catalyst **3**

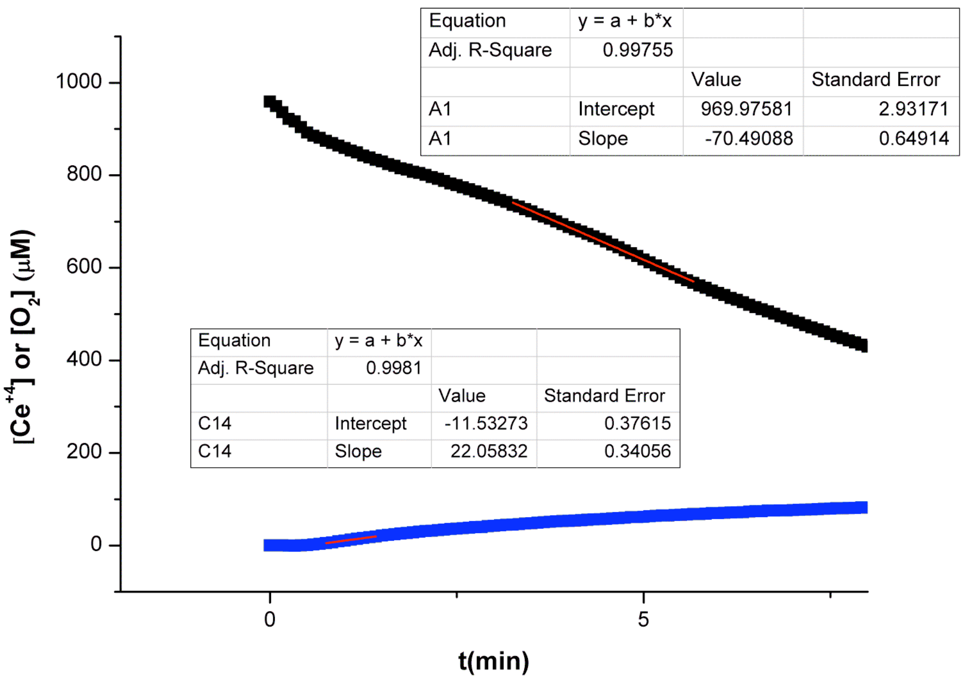

Fig. 4S Rate of oxygen evolution (measured with Clark electrode (■), CAN concentration = 10mM) and Ce^{+4} disappearing (measured by UV-Vis (■), CAN concentration = 1 mM) for catalysts **2** (2.0 μM)

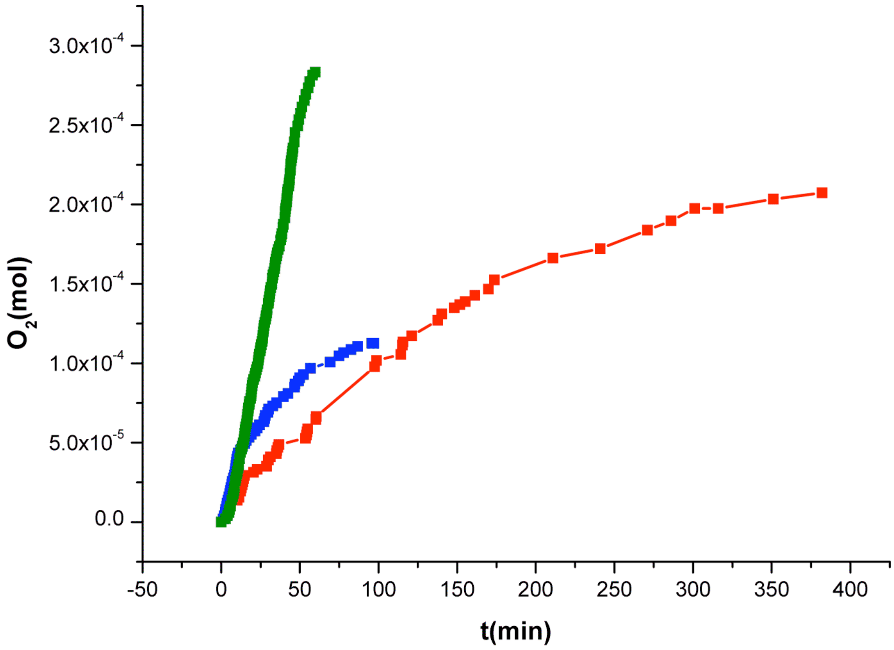

Fig. 5S Evolved oxygen, measured volumetrically, from 28 mM solutions of CAN (pH = 1 by HNO_3) containing catalysts **1** (■ 7.1μM), **2** (■ 7.1μM) and **3** (■ 7.0μM)

Electronic Supplementary Material (ESI) for Green Chemistry

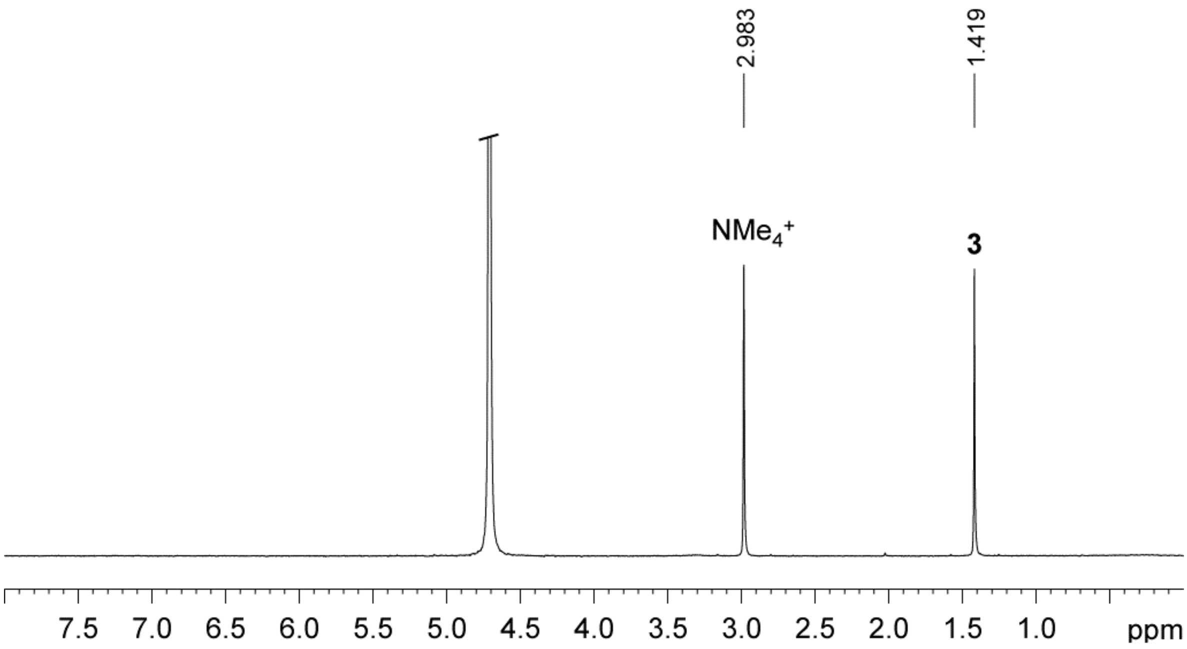

Fig. 6S [1]H NMR spectrum of the mixture of **3** and NMe_4BF_4 in D_2O (pH=1 by HNO_3) before the addition of CAN

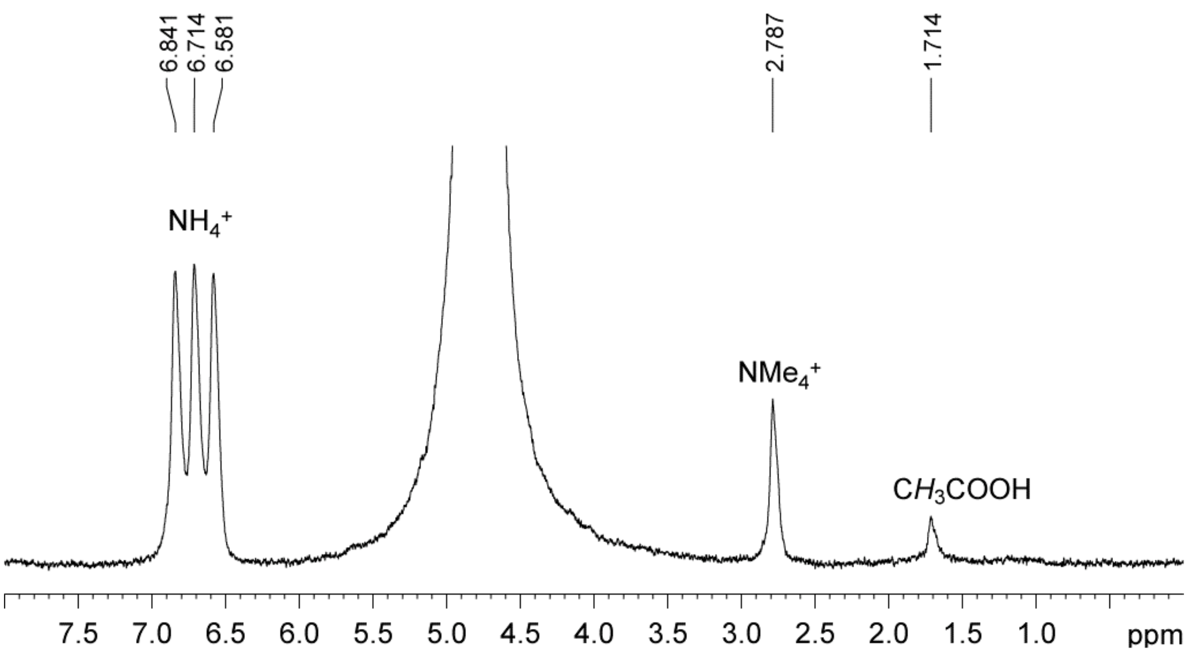

Fig. 7S [1]H NMR spectrum of the mixture of **3** and NMe_4BF_4 in D_2O (pH=1 by HNO_3) recorded 5-10 minutes after the addition of 470 equivalents of CAN.

Table 10S Formation of CH_3COOH and disappearance of catalysts as a function of the number of the equivalents of CAN.

Equivalents of CAN	(I_{cat}/I_{cat}^{0})x100	$(I_{CH_3COOH}/I_{cat}^{0})$x100	$[(I_{CH_3COOH}/(I_{cat}^{0}-I_{cat})]$x100
		[**1**]$_0$=0.13 mM	
4	98.54	0.77	53.05
8	93.64	1.51	23.78
12	85.97	2.68	19.10
16	77.12	4.08	17.85
20	70.64	5.29	18.00
24	64.28	6.56	18.37
32	49.49	9.16	18.14
40	38.33	11.35	18.41
60	24.87	17.66	23.51
80	12.31	20.44	23.31
100	8.42	24.58	26.84
300	-	38.39	38.39
		[**2**]$_0$=0.13 mM	
4	20.20	1.98	2.48
8	8.79	9.40	10.30
12	4.71	12.67	13.28
16	3.67	16.87	17.51
20	2.67	21.53	22.12
24	1.84	26.82	27.32
28	1.01	31.20	31.52
32	-	32.80	32.80
40	-	39.02	39.02
60	-	49.26	49.26
100	-	55.76	55.76
200	-	60.41	60.41
400	-	64.93	64.93
		[**3**]$_0$=0.1 mM	
4	89.50	1.69	16.11
8	72.22	2.56	9.23
12	53.10	5.51	11.76
16	34.31	7.32	11.14
20	21.07	8.82	11.18
24	12.14	10.75	12.24
28	4.95	13.15	13.83
32	1.67	14.43	14.67
40	-	17.12	17.12

60	-	23.45	23.45
100	-	28.27	28.27
200	-	32.00	32.00
400	-	37.04	37.04
600	-	41.04	41.04
1200	-	47.33	47.33
2400	-	50.25	50.25
3600	-	49.52	49.52
6000	-	52.98	52.98

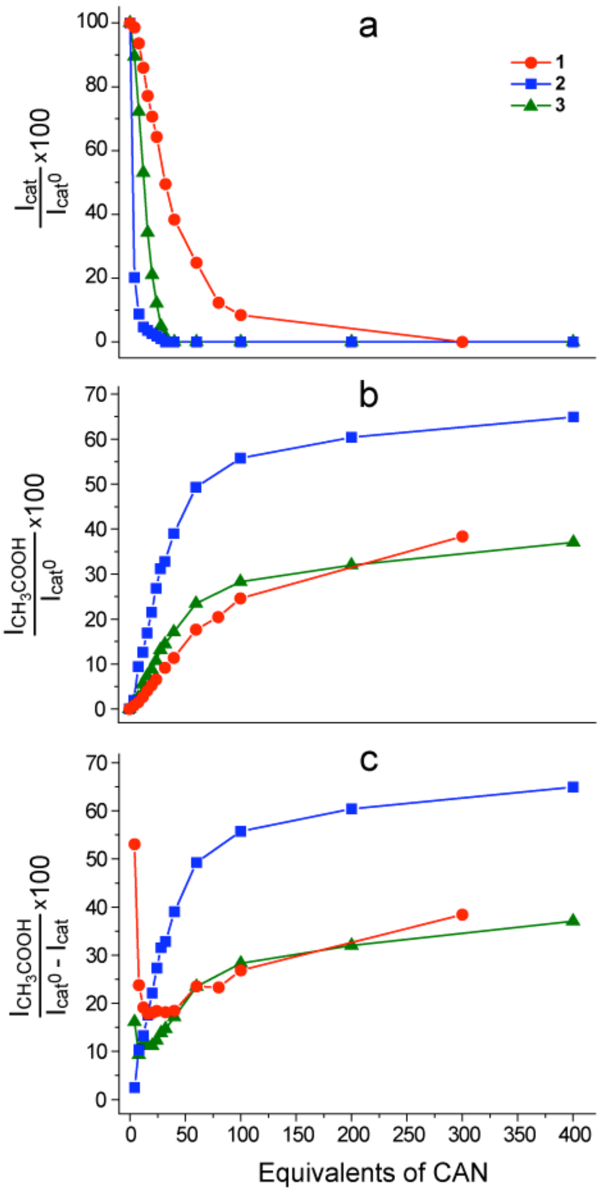

Fig. 8S (a) Trends of consumed catalyst; (b) trends of formed acetic acid; (c) ratio between the amounts of acetic acid formed over that of catalyst entered in the cycle

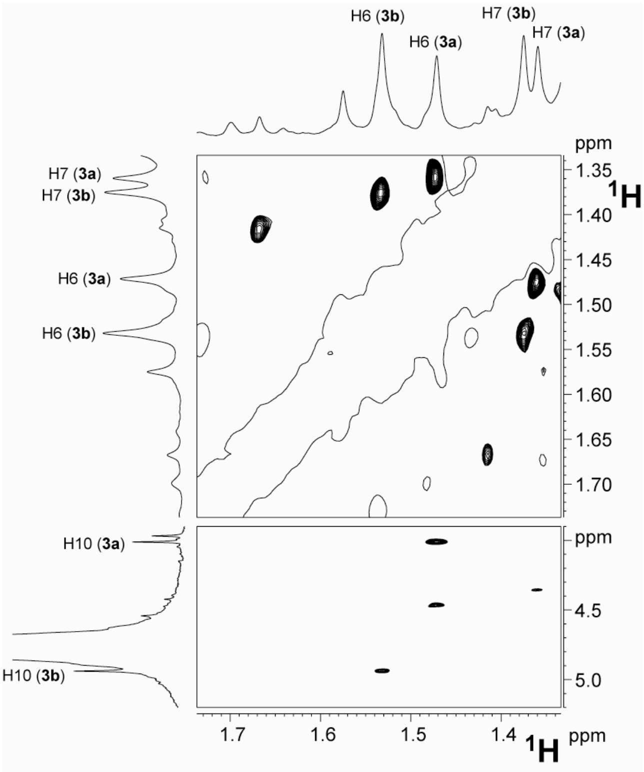

Fig. 9S Two sections of the ^{1}H NOESY NMR spectrum of the mixture obtained after the addition of 12 equivalents of CAN to **3** in D_2O (pH=1 by HNO_3).

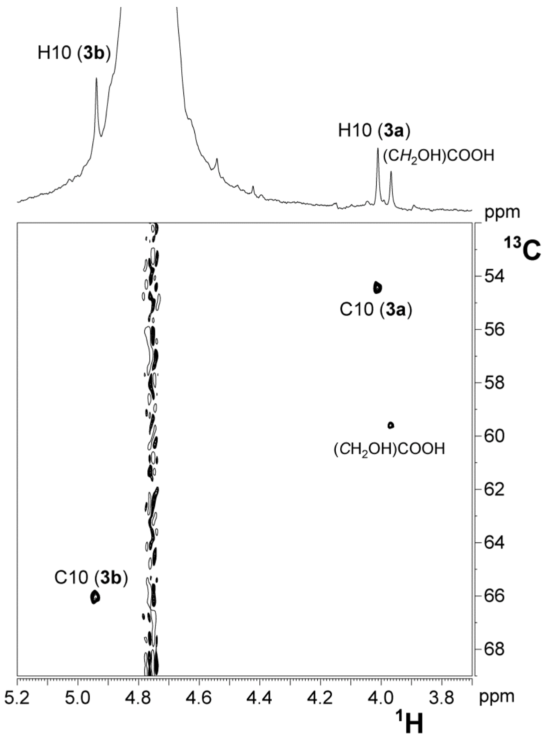

Fig. 10S A section of the $^{1}H,^{13}C$ HMQC NMR spectrum of the mixture obtained after the addition of 12 equivalents of CAN to **3** in D_2O (pH=1 by HNO_3).

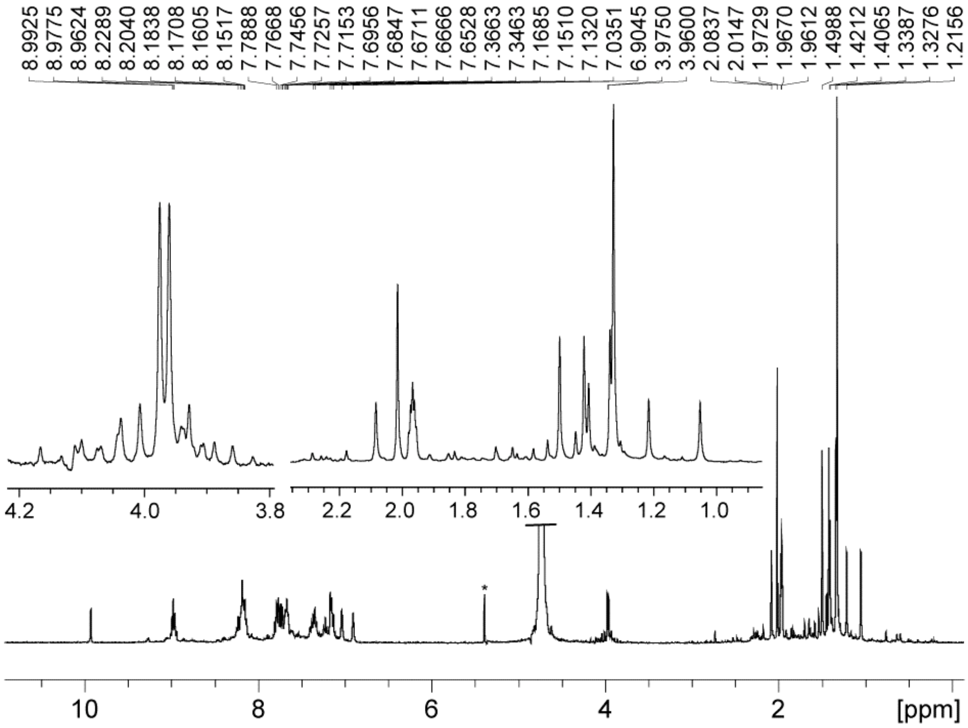

Fig. 11S ^{1}H NMR spectrum of the mixture obtained after the addition of 6 equivalents of CAN to **2** in CD_3CN/D_2O (pH=1 by HNO_3). The asterisk indicates a residual amount of CH_2Cl_2 coming from the synthesis.

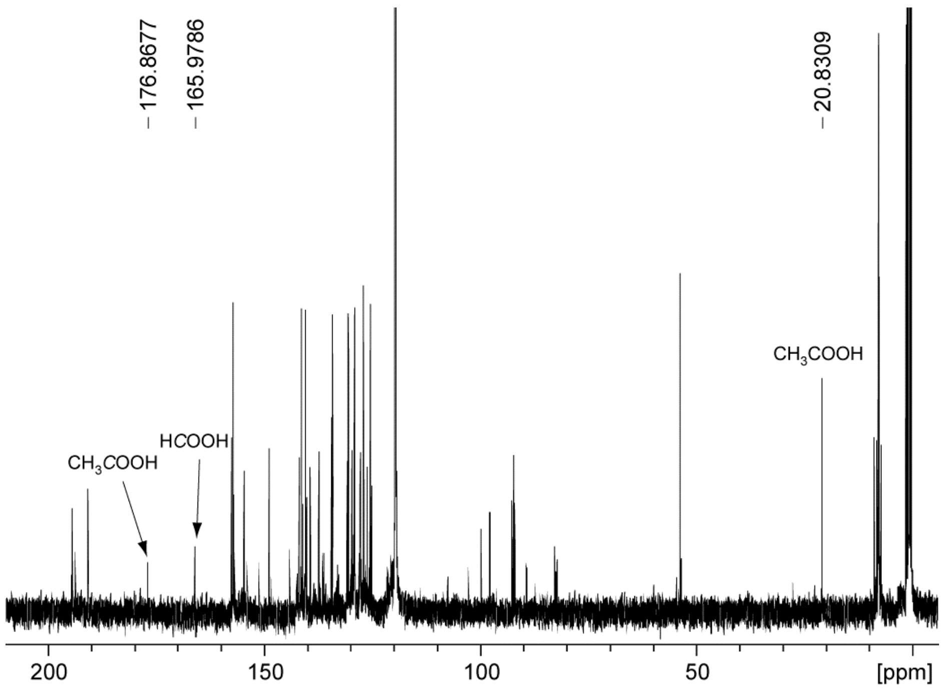

Fig. 12S $^{13}C\{^{1}H\}$ NMR spectrum of the mixture obtained after the addition of 6 equivalents of CAN to **2** in CD_3CN/D_2O (pH=1 by HNO_3).

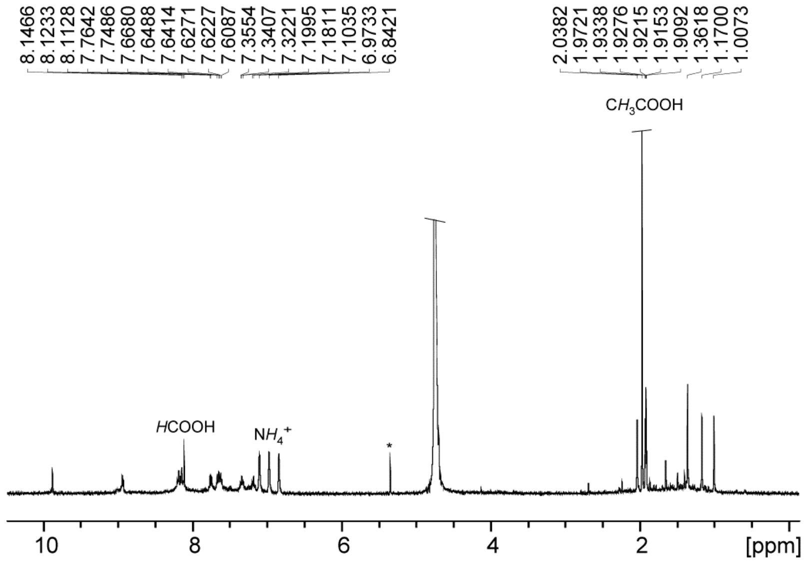

Fig. 13S ^{1}H NMR spectrum of the mixture obtained after the addition of 10 equivalents of CAN to **2** in CD_3CN/D_2O (pH=1 by HNO_3). The major organometallic species is **2b**. The asterisk indicates a residual amount of CH_2Cl_2 coming from the synthesis.

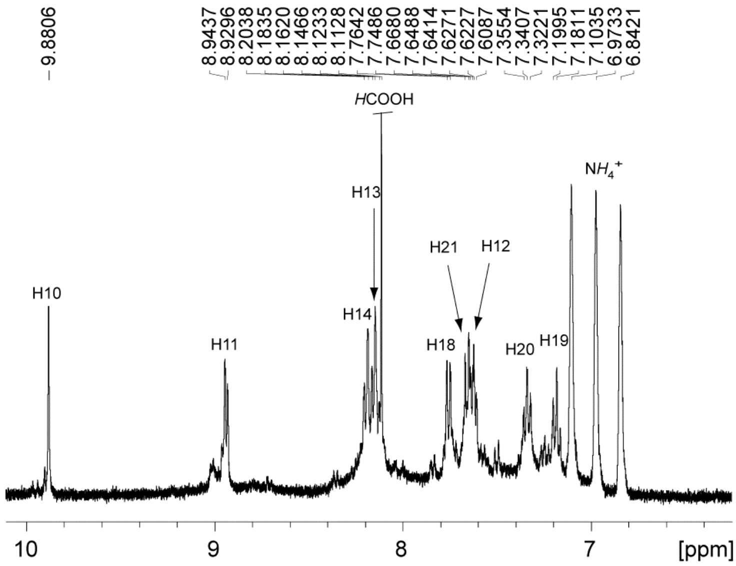

Fig. 14S Aromatic region of the ^{1}H NMR spectrum of the mixture obtained after the addition of 10 equivalents of CAN to **2** in CD_3CN/D_2O (pH=1 by HNO_3). The major organometallic species is **2b**.

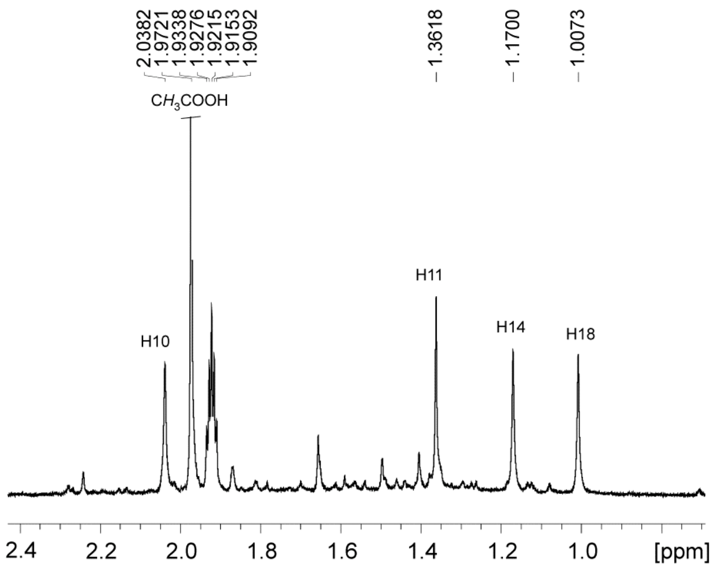

Fig. 15S Aliphatic region of the ^{1}H NMR spectrum of the mixture obtained after the addition of 10 equivalents of CAN to **2** in CD_3CN/D_2O (pH=1 by HNO_3). The major organometallic species is **2b**.

Table 11S Summary of PGSE diffusion NMR data.

Species	D_t (10^{-10} m^2 s^{-1})	V_H (Å^3)
3	4.42	484
NMe_4^+	9.73	119
NH_4^+	15.42	69
NMe_4^+	8.94	133
CH_3COOH	9.84	116
HCOOH	12.40	87
NH_4^+	15.60	68
CH_3COOH	9.68	119
3	4.61	440
3a	4.35	503
3b	4.27	525

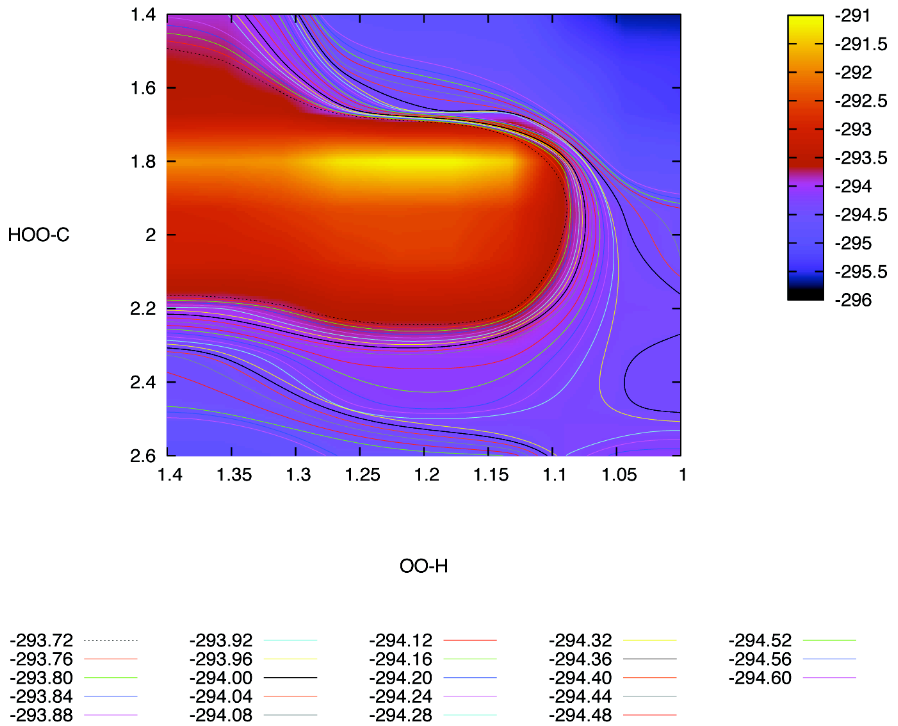

Fig. 16S Two-dimensional cut through the energy hypersurface for mechanism B for complex **1_oxo**. The surface is constructed by calculating the energy at various OO-H and HOO-C distances, optimizing all other geometrical parameters at each point.

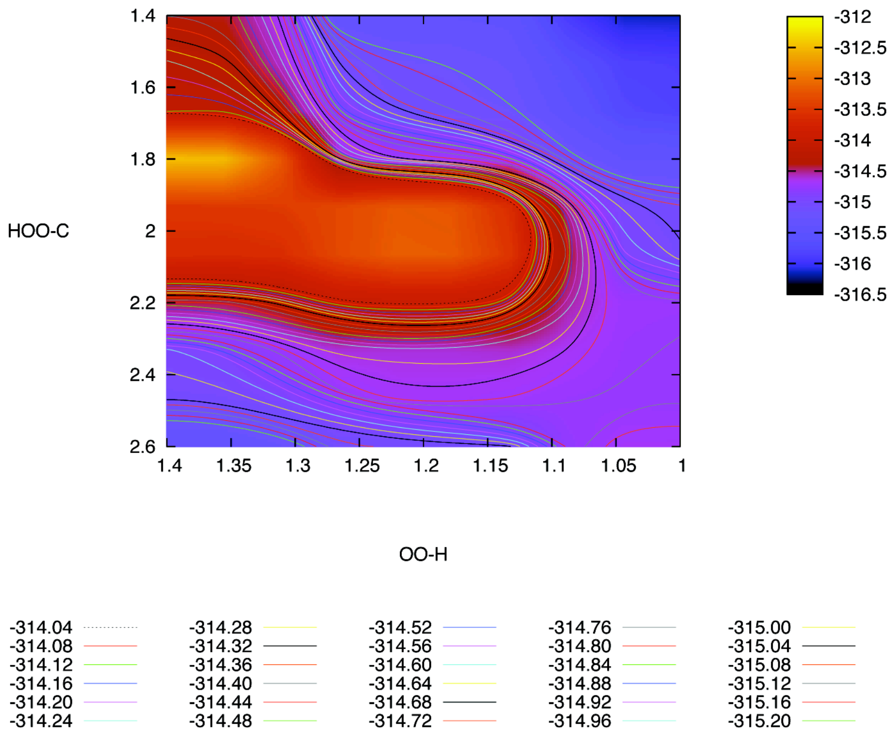

Fig. 17S Two-dimensional cut through the energy hypersurface for mechanism B for complex **2_oxo**. The surface is constructed by calculating the energy at various OO-H and HOO-C distances, optimizing all other geometrical parameters at each point

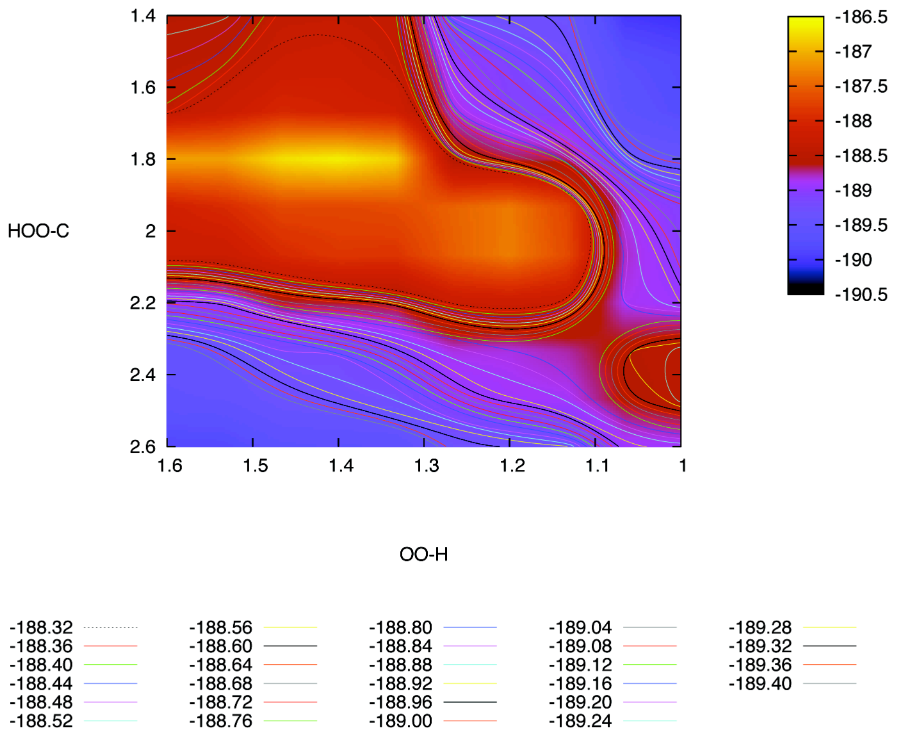

Fig. 18S Two-dimensional cut through the energy hypersurface for mechanism B for complex **3_oxo**. The surface is constructed by calculating the energy at various OO-H and HOO-C distances, optimizing all other geometrical parameters at each point

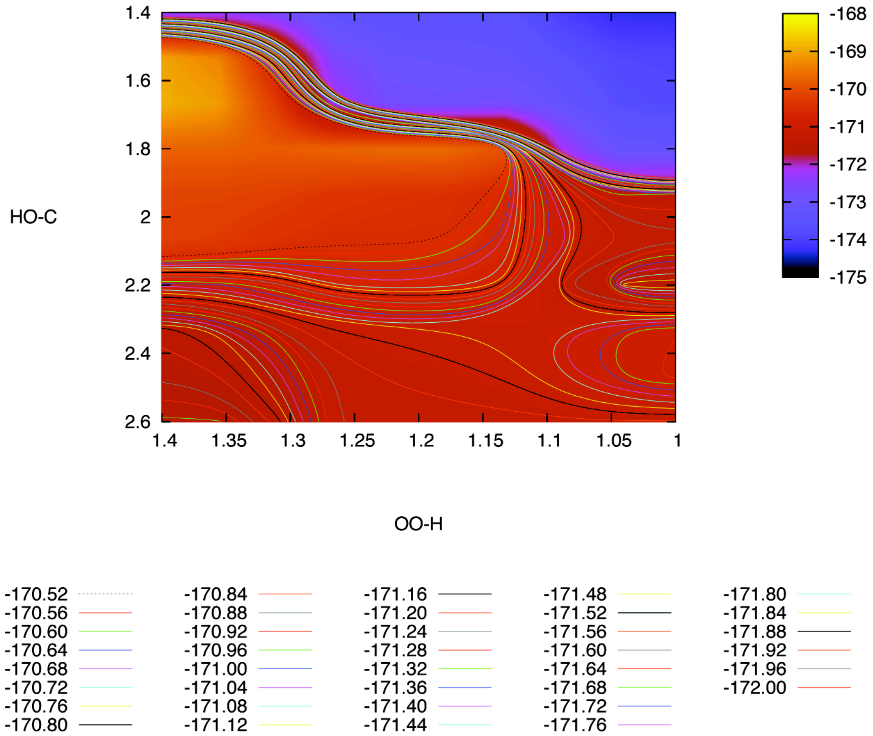

Fig. 19S Two-dimensional cut through the energy hypersurface for mechanism B for complex **4_oxo**. The surface is constructed by calculating the energy at various OO-H and HO-C distances, optimizing all other geometrical parameters at each point

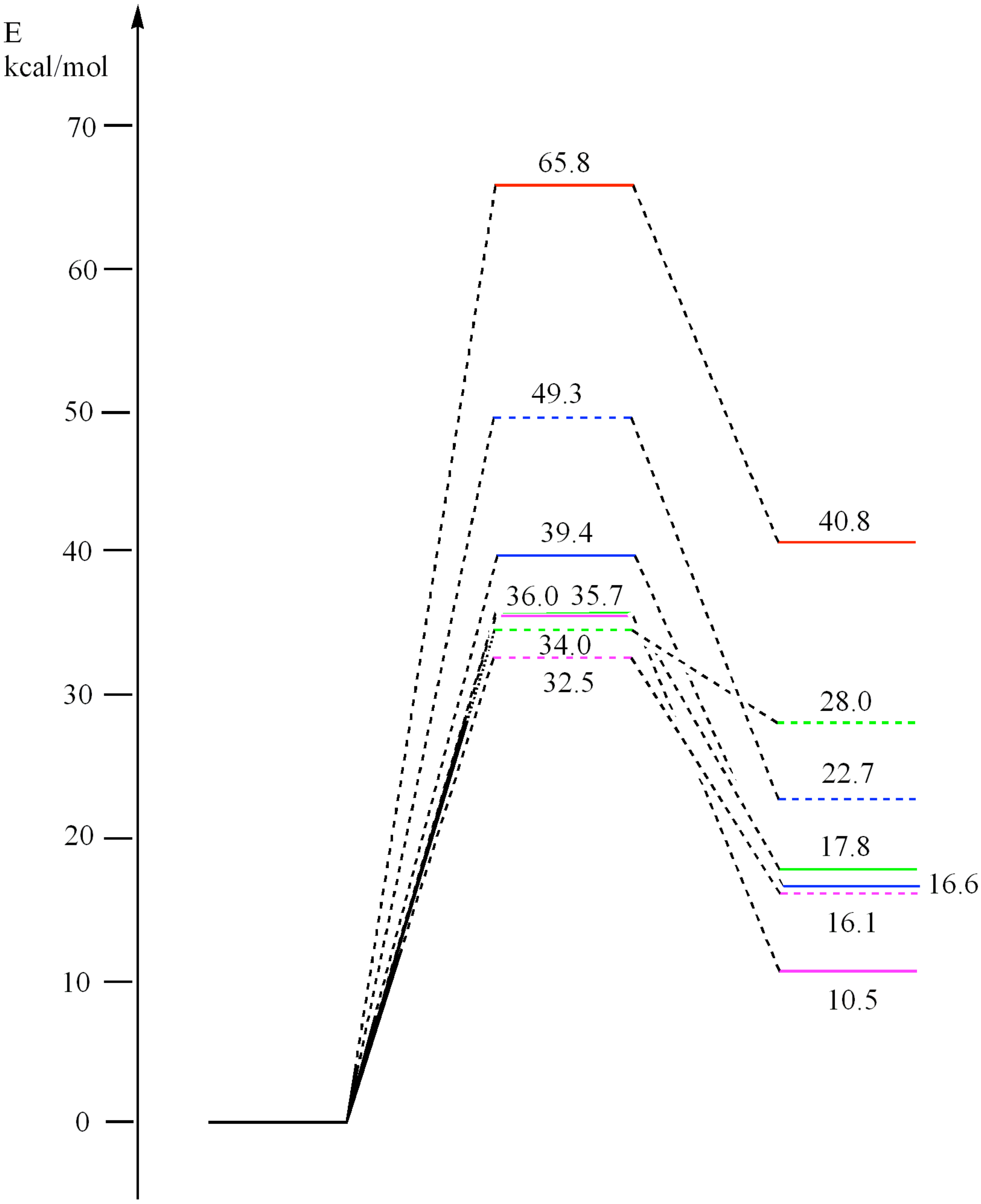

Fig. 20S Energy profile (in kcal/mol) for mechanism A and A'. Reactant energy is set to zero. Green line stands for complex **1_oxo**, pink line for complex **2_oxo**, blue line for complex **3_oxo** and red line for complex **4_oxo**. Activation energy barriers and reaction energies are indicated.

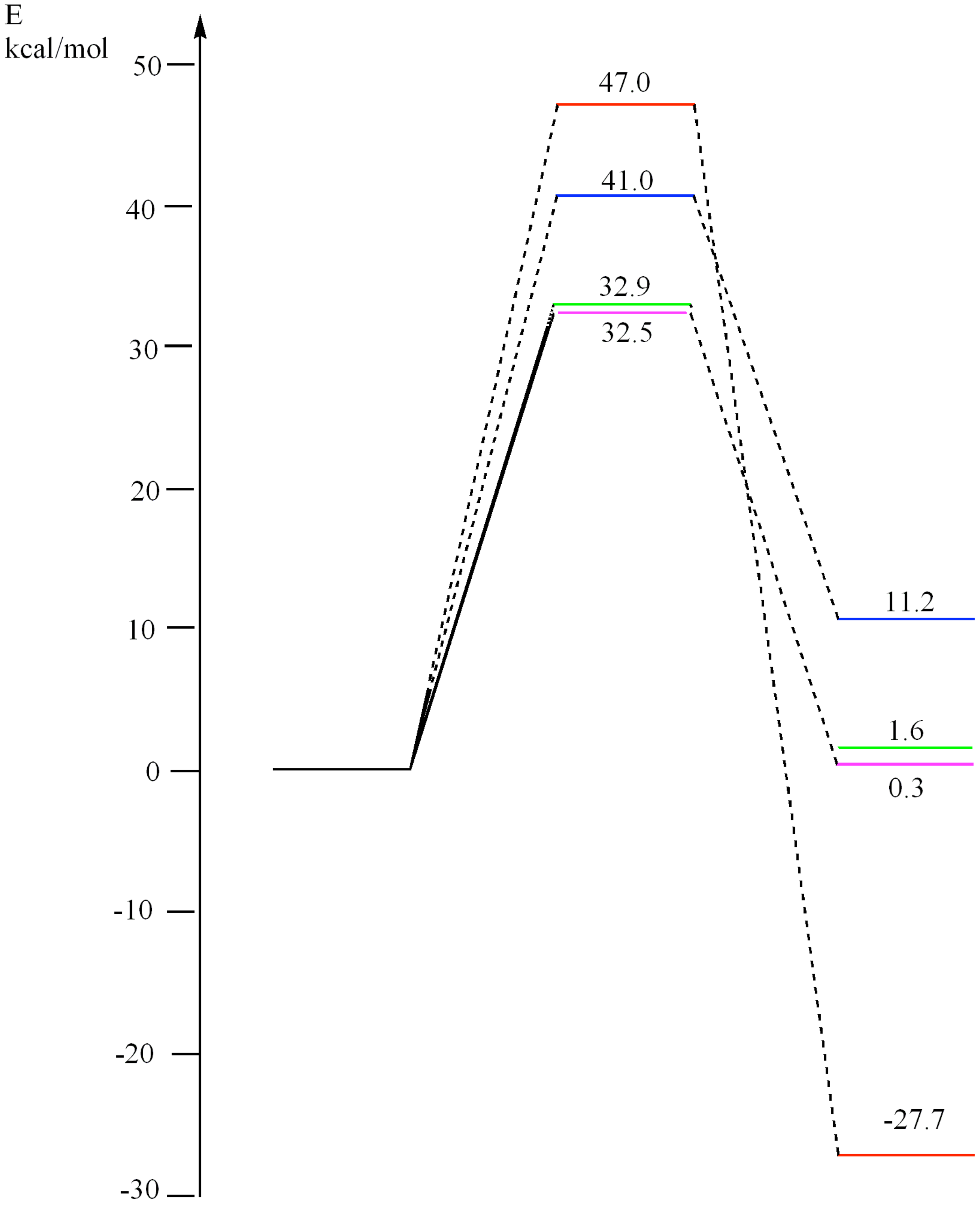

Fig.21S Energy profile (in kcal/mol) for mechanism B. Reactant energy is set to zero. Green line stands for complex **1_oxo**, pink line for complex **2_oxo**, blue line for complex **3_oxo** and red line for complex **4_oxo**. Activation energy barriers and reaction energies are indicated.

Cartesian coordinates for the DFT optimized structures

Complex **1_oxo**

48

C	-1.121936	-0.641238	0.469373
C	-0.016794	-1.154391	1.229059
C	1.173689	-1.061832	0.392705
C	0.779726	-0.536974	-0.879439
C	-0.658116	-0.297079	-0.847261
Ir	-0.276144	-2.397575	-0.522709
N	0.493447	-4.252292	-0.068156
C	-0.045365	-1.449215	2.695300
C	2.572566	-1.341469	0.832327
C	1.697965	-0.169557	-1.997845
C	-1.461061	0.429228	-1.878744
C	-2.507922	-0.443279	0.979619
O	-2.134796	-3.424515	-0.372107
O	-3.055572	-3.084350	-1.179382
H	-2.458276	-0.000715	-2.007545
H	-1.594550	1.475636	-1.574302
H	-0.967273	0.450420	-2.852948
H	-2.772571	-1.159466	1.760425
H	-2.578372	0.563257	1.415733
H	-3.256962	-0.513119	0.188700
H	0.837992	-1.998259	3.029646

H	-0.057084	-0.506535	3.258279
H	-0.934133	-2.012195	2.993906
H	2.631799	-2.154758	1.559873
H	3.227647	-1.594628	-0.003937
H	2.988241	-0.446509	1.315647
H	2.615975	-0.761077	-1.994579
H	1.233194	-0.280481	-2.980587
H	1.986312	0.885742	-1.895490
C	0.783507	-5.075433	-1.110204
C	1.364257	-6.326203	-0.899016
C	1.631825	-6.754852	0.389188
C	1.287954	-5.924654	1.451379
C	0.719578	-4.694333	1.181837
C	0.406277	-4.542591	-2.408526
H	1.600552	-6.967016	-1.741504
H	2.086693	-7.726846	0.563607
H	1.450706	-6.222685	2.483971
H	0.423662	-4.028066	1.981283
C	0.563781	-5.209862	-3.622327
C	0.108997	-4.627807	-4.793519
C	-0.525512	-3.392614	-4.720448
C	-0.650898	-2.775301	-3.489802
N	-0.167756	-3.312051	-2.355844
H	1.033034	-6.187222	-3.651678
H	0.231509	-5.138250	-5.745655
H	-0.929226	-2.906394	-5.604793

H	-1.156114	-1.824575	-3.386854

Complex **2_oxo**

50

C	-0.835238	-0.183429	-1.020556
C	-1.476657	-0.316564	0.242233
C	-0.438495	-0.439422	1.243789
C	0.836915	-0.332713	0.591961
C	0.602064	-0.221975	-0.833360
Ir	-0.153443	-2.122251	-0.166375
N	-1.171740	-3.701122	0.703960
C	-2.947109	-0.191817	0.486190
C	-0.616543	-0.379278	2.729662
C	2.114049	-0.064196	1.325954
C	1.608679	0.083879	-1.895104
C	-1.504238	0.035341	-2.333362
O	-0.781725	-3.223924	-1.825053
O	-0.534820	-2.855837	-3.016651
H	1.306180	-0.333621	-2.858702
H	1.722856	1.170389	-2.019406
H	2.592971	-0.328548	-1.663021
H	-2.586437	-0.097979	-2.275079
H	-1.308886	1.059037	-2.680036
H	-1.118436	-0.654561	-3.091553
H	-3.257713	-0.629663	1.438037

H	-3.240351	0.867131	0.517555
H	-3.538454	-0.672518	-0.297596
H	-1.642287	-0.584776	3.047045
H	0.045636	-1.071772	3.257765
H	-0.383232	0.633325	3.088783
H	2.340130	-0.819401	2.084148
H	2.973802	0.014975	0.657745
H	2.030689	0.903248	1.841070
C	-1.147006	-4.955031	0.191313
C	-2.069709	-5.924596	0.600200
C	-2.990945	-5.649001	1.588723
C	-2.959124	-4.381512	2.168924
C	-2.056172	-3.456190	1.695148
C	-0.067004	-5.418713	-0.741949
H	-2.005595	-6.892359	0.112844
H	-3.705599	-6.401245	1.916950
H	-3.633431	-4.098840	2.974218
H	-2.023682	-2.460310	2.108842
C	1.249819	-4.760871	-0.640352
C	2.345321	-5.610259	-0.873132
C	3.642150	-5.158075	-0.736509
C	3.844730	-3.828262	-0.371448
C	2.764033	-2.983917	-0.168773
C	1.426493	-3.400536	-0.294602
H	2.136167	-6.638267	-1.157697

H	4.484982	-5.825273	-0.907166
H	4.856608	-3.440875	-0.249860
H	2.985401	-1.958051	0.088805
O	-0.253903	-6.451969	-1.377597

Complex **3_oxo**

32

C	-1.318044	-0.615412	0.348028
C	-0.232840	-0.794760	1.283179
C	0.990126	-0.606921	0.536906
C	0.667325	-0.248489	-0.828963
C	-0.779596	-0.255917	-0.948601
Ir	-0.089096	-2.168152	-0.395060
C	-0.352792	-1.036655	2.752612
C	2.368897	-0.695419	1.102994
C	1.617148	0.152447	-1.906040
C	-1.545151	0.140167	-2.165397
C	-2.770090	-0.714308	0.681379
O	0.080959	-3.188597	-2.159349
O	0.179479	-2.548519	-3.270323
H	1.347191	-0.315153	-2.858281
H	1.594399	1.242793	-2.042118
H	2.646735	-0.129694	-1.673451
H	-2.587604	-0.184143	-2.120017
H	-1.542051	1.233950	-2.274026

H	-1.098537	-0.292689	-3.065790
H	-2.960096	-1.435594	1.479983
H	-3.135641	0.265010	1.021345
H	-3.369206	-1.009491	-0.183307
H	-1.256066	-1.598625	3.004762
H	0.499427	-1.595212	3.148793
H	-0.399299	-0.081516	3.296149
H	2.430027	-1.412868	1.924946
H	3.102489	-0.989995	0.348835
H	2.668726	0.287242	1.493852
O	0.917910	-3.956970	0.269295
N	-0.163553	-4.644685	0.356154
O	-0.197014	-5.797054	0.693944
O	-1.208057	-3.955571	0.063318

Complex **4_oxo**

31

C	-0.521284	-0.370530	-1.054345
C	-1.122900	-0.541592	0.237019
C	-0.063132	-0.602406	1.233557
C	1.193305	-0.475481	0.556033
C	0.927512	-0.369827	-0.876137
Ir	0.179817	-2.186896	-0.203689
O	1.461707	-3.710961	-0.657892
O	0.525595	-3.631714	-1.589773

C	-2.587224	-0.552843	0.526396
C	-0.260337	-0.707807	2.708093
C	2.540677	-0.429619	1.191912
C	1.939984	-0.113388	-1.939803
C	-1.235366	-0.173456	-2.348288
O	-0.839818	-3.922970	0.854535
H	3.317470	-0.849715	0.549044
H	2.806254	0.619004	1.385650
H	2.567997	-0.957020	2.147648
H	1.622991	-0.495902	-2.912610
H	2.089162	0.970284	-2.042814
H	2.909357	-0.557703	-1.703645
H	-2.236958	-0.608498	-2.343565
H	-1.345504	0.904251	-2.533115
H	-0.686344	-0.594563	-3.193760
H	-3.175924	-0.936210	-0.310548
H	-2.834621	-1.134795	1.417972
H	-2.923353	0.476168	0.715260
H	-1.155578	-1.276298	2.970755
H	0.591573	-1.173478	3.208220
H	-0.379616	0.300213	3.129040
H	-1.781174	-3.960143	0.644420
H	-0.476301	-4.759068	0.527183

Complex **1_oxo** – product from mechanism A

48

C	-1.612695	-0.749383	0.504958
C	-0.393829	-1.399996	1.158811
C	0.812229	-0.970576	0.499207
C	0.406625	-0.407451	-0.784442
C	-1.009825	-0.535213	-0.885349
Ir	-0.124786	-2.495383	-0.640459
N	0.588885	-4.345049	-0.155148
C	-0.487695	-1.881749	2.573818
C	2.186262	-0.919284	1.083426
C	1.322003	0.251877	-1.763039
C	-1.869500	-0.018277	-1.993501
C	-2.257401	0.450230	1.193261
O	-2.125707	-2.845898	-0.242553
O	-2.632526	-1.738739	0.448889
H	-2.758224	-0.641738	-2.131829
H	-2.221547	0.991929	-1.745078
H	-1.345029	0.070676	-2.947514
H	-2.640826	0.170967	2.179016
H	-1.522515	1.251915	1.316821
H	-3.098824	0.830106	0.606218
H	0.449545	-2.295972	2.952619
H	-0.732439	-1.038846	3.233813
H	-1.282642	-2.623871	2.698170
H	2.361716	-1.725921	1.798581
H	2.966108	-0.971997	0.320300

H	2.315000	0.027528	1.626914
H	2.312505	-0.208781	-1.784596
H	0.921862	0.249521	-2.779016
H	1.454407	1.303500	-1.472591
C	0.812858	-5.221827	-1.179394
C	1.295742	-6.508872	-0.937673
C	1.534097	-6.932380	0.356265
C	1.260567	-6.050007	1.398577
C	0.790514	-4.787757	1.104203
C	0.483369	-4.706850	-2.493673
H	1.479414	-7.183020	-1.766863
H	1.912341	-7.932599	0.551284
H	1.406237	-6.333286	2.437885
H	0.559763	-4.085845	1.891187
C	0.602432	-5.429587	-3.683191
C	0.226042	-4.855174	-4.882689
C	-0.283666	-3.558464	-4.871809
C	-0.380850	-2.893514	-3.667492
N	0.007336	-3.430475	-2.494238
H	0.984893	-6.444080	-3.669447
H	0.318356	-5.411140	-5.812559
H	-0.605629	-3.064621	-5.784880
H	-0.784215	-1.891945	-3.617209

Complex **2_oxo** – product from mechanism A

50

C	1.495510	-3.502428	-0.219673
C	1.246323	-4.788822	-0.749096
C	2.299730	-5.639929	-1.123857
C	3.614201	-5.272253	-0.906982
C	3.881144	-4.039456	-0.310053
C	2.844480	-3.174214	0.007152
C	-0.109813	-5.364409	-0.861028
O	-0.386341	-6.288078	-1.616743
Ir	-0.022317	-2.214818	0.071128
O	-0.818549	-2.672025	-1.785658
O	-1.226927	-1.440517	-2.437459
C	-1.586187	-0.596861	-0.206877
C	-0.904366	-0.400454	-1.559435
C	0.553992	-0.519494	-1.103615
C	0.656609	-0.214529	0.285682
C	-0.704484	-0.281473	0.844808
C	-1.275197	0.884195	-2.305621
C	-3.067061	-0.761946	-0.120865
C	-1.065549	0.097792	2.248237
C	1.854303	0.313759	1.011692
C	1.658069	-0.481393	-2.110102
N	-1.062496	-3.793822	0.849759
C	-1.135392	-4.965028	0.169852

C	-2.106435	-5.917976	0.489509
C	-2.960783	-5.719296	1.556127
C	-2.818768	-4.550011	2.303462
C	-1.878371	-3.622195	1.911888
H	1.408350	-1.121996	-2.960875
H	1.800482	0.541162	-2.488866
H	2.613251	-0.821346	-1.705440
H	-2.342026	0.892317	-2.551634
H	-1.048219	1.757678	-1.685531
H	-0.714248	0.957483	-3.242791
H	-3.400033	-1.155133	0.843495
H	-3.578148	0.200627	-0.270029
H	-3.415751	-1.442650	-0.903521
H	-2.070614	-0.235799	2.518228
H	-0.360720	-0.295639	2.987854
H	-1.061103	1.192904	2.348500
H	1.945531	-0.084886	2.026726
H	2.781172	0.099794	0.475777
H	1.778235	1.407991	1.093923
H	-2.137759	-6.814495	-0.121485
H	-3.709920	-6.463867	1.818300
H	-3.434196	-4.348703	3.177299
H	-1.751928	-2.691537	2.451454
H	2.052915	-6.602409	-1.564967
H	4.427264	-5.942279	-1.180585
H	4.910379	-3.747232	-0.100492

H	3.097723	-2.216308	0.452942

Complex **3_oxo** – product from mechanism A

32

C	-0.806928	-0.654359	-1.227198
C	-1.154742	-0.499782	0.160495
C	0.100909	-0.559008	0.911024
C	1.146611	-0.746509	-0.059459
C	0.673204	-0.334384	-1.456496
Ir	-0.204594	-2.334819	-0.146077
O	-1.324359	-4.103217	-0.502543
N	-0.471493	-4.862486	0.100162
O	-0.585262	-6.050847	0.196321
C	-2.515691	-0.238095	0.720681
C	0.267515	-0.369453	2.384396
C	2.599154	-0.917020	0.243840
C	1.039443	1.059131	-1.959087
O	1.192194	-1.235226	-2.395803
O	0.840805	-2.568286	-1.913315
C	-1.769737	-0.710910	-2.367707
O	0.513122	-4.190254	0.595892
H	0.606894	1.237256	-2.949182
H	0.662797	1.821163	-1.268574
H	2.126214	1.165413	-2.041190

H	-2.670320	-1.282395	-2.125666
H	-2.084590	0.301098	-2.661708
H	-1.290630	-1.179988	-3.231882
H	-2.629938	-0.621582	1.738296
H	-2.699128	0.846327	0.751556
H	-3.298684	-0.682533	0.100995
H	-0.599931	-0.717936	2.951632
H	1.150746	-0.892032	2.760453
H	0.401436	0.700016	2.605443
H	2.770894	-1.538942	1.126983
H	3.100782	-1.387314	-0.606789
H	3.076281	0.057645	0.423049

Complex **4_oxo** – product from mechanism A

31

C	-0.245718	-0.734750	-1.293414
C	-0.880694	-0.363502	-0.050875
C	0.110823	-0.517598	1.005591
C	1.326660	-0.983282	0.339110
C	1.282495	-0.678723	-1.169653
Ir	-0.176378	-2.344886	0.014742
O	1.838854	-1.777656	-1.859121
O	1.122364	-2.966769	-1.393516
C	-2.279528	0.127746	0.118665

C	-0.027535	-0.142447	2.441748
C	2.604368	-1.323893	1.021206
C	2.011846	0.557750	-1.678213
C	-0.910532	-0.780824	-2.627031
O	0.442291	-4.246819	0.968910
H	3.246439	-1.916732	0.364364
H	3.141183	-0.391575	1.252025
H	2.458487	-1.854731	1.965287
H	1.850394	0.680960	-2.753265
H	1.645140	1.450861	-1.161894
H	3.088467	0.466783	-1.504709
H	-1.925275	-1.185389	-2.583416
H	-0.982672	0.237439	-3.036006
H	-0.322717	-1.380512	-3.326708
H	-2.945520	-0.247371	-0.661646
H	-2.702478	-0.130449	1.092790
H	-2.278778	1.224752	0.041822
H	-1.056750	-0.225750	2.798688
H	0.613769	-0.745951	3.088639
H	0.280140	0.906345	2.568004
H	-0.194925	-4.974469	0.993020
H	1.169082	-4.547142	0.399047

Complex **1_oxo** – product from mechanism A'

48

C	-1.563595	-0.935471	0.414428
C	-0.375373	-1.575273	1.113695
C	0.826430	-0.993348	0.599387
C	0.489785	-0.430625	-0.714212
C	-0.901652	-0.687627	-0.933137
Ir	0.223987	-2.504548	-0.717393
N	0.952344	-4.383805	-0.258195
C	-0.543024	-2.188406	2.470396
C	2.144308	-0.844896	1.285625
C	1.423848	0.356674	-1.572052
C	-1.698183	-0.181745	-2.096358
C	-2.224020	0.248267	1.101831
O	-2.564936	-2.048765	0.281434
O	-3.729295	-1.664499	-0.155500
H	-2.477655	-0.885559	-2.401363
H	-2.208159	0.749500	-1.818630
H	-1.077834	0.056453	-2.964032
H	-2.605878	-0.038484	2.086848
H	-1.499961	1.060582	1.228081
H	-3.068100	0.613262	0.511920
H	0.390774	-2.565994	2.892064
H	-0.915169	-1.433184	3.175260
H	-1.273673	-3.002953	2.458998
H	2.269092	-1.548139	2.112243
H	2.985894	-0.974358	0.599283

H	2.221886	0.164405	1.714287
H	2.441311	-0.043161	-1.548314
H	1.101187	0.396361	-2.614931
H	1.468104	1.394153	-1.210634
C	0.834011	-5.324897	-1.231825
C	1.185133	-6.653573	-0.999570
C	1.704569	-7.023166	0.230316
C	1.870553	-6.046707	1.204910
C	1.473551	-4.752490	0.923625
C	0.396396	-4.802076	-2.526049
H	1.067094	-7.397776	-1.779256
H	1.985613	-8.056147	0.420934
H	2.291676	-6.279192	2.179588
H	1.567225	-3.968802	1.662348
C	0.233706	-5.575555	-3.673869
C	-0.073371	-4.962719	-4.877841
C	-0.205041	-3.579995	-4.910711
C	-0.065528	-2.871938	-3.731021
N	0.215714	-3.455219	-2.554805
H	0.351200	-6.652671	-3.632828
H	-0.201400	-5.556892	-5.779569
H	-0.428583	-3.049417	-5.832521
H	-0.187717	-1.797989	-3.706813

Complex **2_oxo** – product from mechanism A'

50

C	-0.946995	-0.567633	-1.626944
C	-1.600395	-0.799544	-0.279342
C	-0.735997	-0.320918	0.737806
C	0.617183	-0.254117	0.159075
C	0.503753	-0.715673	-1.192925
Ir	0.018195	-2.247805	0.220810
N	-1.000023	-3.797703	1.028948
C	-3.082007	-0.979977	-0.151104
C	-1.110842	0.168580	2.099911
C	1.808547	0.359330	0.820449
C	1.616266	-0.742702	-2.194528
C	-1.323249	0.707433	-2.366180
O	-1.347522	-1.751363	-2.460549
O	-1.137338	-1.605260	-3.738052
H	1.431869	-1.491333	-2.969632
H	1.710100	0.231126	-2.695547
H	2.577531	-0.976274	-1.731881
H	-2.397091	0.730580	-2.581048
H	-1.070075	1.574883	-1.746131
H	-0.789423	0.780279	-3.316752
H	-3.374478	-1.315361	0.847532
H	-3.613854	-0.036793	-0.343926
H	-3.455207	-1.715680	-0.869940
H	-2.083366	-0.214178	2.420749

H	-0.368848	-0.107466	2.856521
H	-1.184645	1.266221	2.102136
H	1.899548	0.059467	1.869438
H	2.736720	0.092658	0.310577
H	1.729187	1.456247	0.796012
C	-1.124365	-4.893573	0.241460
C	-2.126846	-5.836526	0.486998
C	-2.925803	-5.721470	1.608715
C	-2.708683	-4.648916	2.474052
C	-1.759736	-3.705663	2.139911
C	-0.128903	-5.208321	-0.851829
H	-2.224622	-6.658147	-0.215654
H	-3.694382	-6.461943	1.822436
H	-3.281948	-4.529039	3.390526
H	-1.590162	-2.828577	2.754491
C	1.257701	-4.721939	-0.686135
C	2.276778	-5.567812	-1.157097
C	3.600958	-5.272485	-0.893433
C	3.913042	-4.119366	-0.167712
C	2.913353	-3.245933	0.231709
C	1.554733	-3.502341	-0.031885
H	2.000392	-6.464027	-1.707169
H	4.391359	-5.939512	-1.233168
H	4.952915	-3.896890	0.072900
H	3.197873	-2.343171	0.767384

O	-0.465665	-6.008131	-1.717036

Complex **3_oxo** – product from mechanism A'

32

C	-1.031212	-0.458057	0.061678
C	0.183382	-0.595178	0.875798
C	1.227468	-0.983031	-0.041184
C	0.855387	-0.466962	-1.425722
C	-0.633805	-0.770337	-1.289564
Ir	-0.314019	-2.379229	-0.001623
C	0.305836	-0.313447	2.337226
C	2.645889	-1.270301	0.348105
C	1.278814	0.942777	-1.800020
C	-1.555017	-0.808646	-2.468314
C	-2.374193	-0.019642	0.545500
O	1.464825	-1.440783	-2.376185
O	1.444532	-1.056546	-3.621400
H	0.911255	1.213198	-2.793051
H	0.877371	1.650089	-1.066173
H	2.371105	1.029408	-1.809211
H	-2.544803	-1.184376	-2.194241
H	-1.682602	0.192989	-2.902932
H	-1.157849	-1.455160	-3.256026
H	-2.578851	-0.371169	1.561418
H	-2.434195	1.078973	0.555599

H	-3.175781	-0.384468	-0.102407
H	-0.607983	-0.570411	2.881449
H	1.131438	-0.869746	2.789589
H	0.500846	0.756796	2.502586
H	2.705015	-1.781240	1.313025
H	3.135480	-1.906369	-0.395579
H	3.230508	-0.342016	0.425494
O	0.288942	-4.277434	0.715956
N	-0.721550	-4.883170	0.186285
O	-0.919941	-6.056958	0.283716
O	-1.490455	-4.074944	-0.465744

Complex **1_oxo** – product from mechanism B

48

C	-1.340689	-1.008721	0.226258
C	-0.363868	-1.361623	1.242726
C	0.929098	-0.976031	0.753129
C	0.759598	-0.412450	-0.571365
C	-0.649095	-0.411050	-0.883227
Ir	0.057923	-2.440952	-0.567146
N	0.947028	-4.215940	-0.185520
C	-0.690710	-1.884613	2.603784
C	2.217935	-0.991901	1.507947
C	1.838872	0.194773	-1.401204
C	-1.271587	0.291575	-2.047543

C	-2.822650	-1.079417	0.433505
O	-3.435571	-1.670553	-0.698875
O	-4.846945	-1.428107	-0.569398
H	-2.279321	-0.068719	-2.260214
H	-1.355443	1.360685	-1.809268
H	-0.666982	0.220014	-2.955625
H	-3.068799	-1.643592	1.342989
H	-3.204267	-0.052763	0.560579
H	-5.167054	-2.330286	-0.415713
H	0.184459	-2.285525	3.118933
H	-1.082529	-1.072927	3.230832
H	-1.447518	-2.673480	2.573232
H	2.175311	-1.608926	2.407669
H	3.057054	-1.338010	0.898325
H	2.452698	0.028672	1.838218
H	2.807888	-0.280089	-1.230168
H	1.619318	0.138113	-2.469977
H	1.943902	1.259235	-1.144921
C	0.952462	-5.144726	-1.195315
C	1.596669	-6.373654	-1.038380
C	2.230883	-6.682466	0.149395
C	2.202786	-5.741204	1.182542
C	1.562999	-4.541627	0.977220
C	0.239189	-4.724179	-2.376047
H	1.598309	-7.090104	-1.852731

H	2.734780	-7.637212	0.275982
H	2.675004	-5.935467	2.142077
H	1.524072	-3.792617	1.755302
C	0.091226	-5.485579	-3.537134
C	-0.635337	-4.993222	-4.603911
C	-1.221909	-3.731171	-4.483180
C	-1.042666	-3.016118	-3.320951
N	-0.315635	-3.473675	-2.274141
H	0.548359	-6.467076	-3.601857
H	-0.750696	-5.579917	-5.511829
H	-1.817029	-3.301641	-5.284865
H	-1.490681	-2.041465	-3.192856

Complex **2_oxo** – product from mechanism B

50

C	-0.686603	-0.551934	-1.221415
C	-1.540038	-0.492218	-0.056195
C	-0.717017	-0.260830	1.081354
C	0.665568	-0.183686	0.633990
C	0.680266	-0.333232	-0.795845
Ir	-0.041248	-2.156416	0.109140
N	-1.092858	-3.723726	0.851082
C	-3.033212	-0.571960	-0.096880
C	-1.172335	0.039196	2.473907
C	1.812008	0.218880	1.503447

C	1.830032	-0.085622	-1.720925
C	-1.175677	-0.530437	-2.647680
O	-1.655684	-1.745698	-3.194154
O	-0.527732	-2.548489	-3.559593
H	1.847292	-0.793585	-2.553316
H	1.755850	0.926824	-2.141696
H	2.795050	-0.149859	-1.215436
H	-2.055165	0.125972	-2.709343
H	-0.407920	-0.114604	-3.311198
H	-0.273891	-2.920037	-2.694336
H	-3.464421	-0.886248	0.857104
H	-3.463778	0.411439	-0.333592
H	-3.376188	-1.275271	-0.860815
H	-2.222300	-0.219704	2.634321
H	-0.575048	-0.475386	3.234239
H	-1.083969	1.116754	2.672782
H	1.785715	-0.279157	2.477106
H	2.778035	-0.003766	1.045938
H	1.784902	1.303443	1.684832
C	-1.106334	-4.987660	0.338499
C	-2.006821	-5.949718	0.805473
C	-2.872415	-5.672433	1.844079
C	-2.817235	-4.394477	2.405430
C	-1.941019	-3.472494	1.884422
C	-0.127332	-5.444020	-0.692139

H	-1.977691	-6.919403	0.318695
H	-3.560522	-6.426238	2.220653
H	-3.449068	-4.106701	3.242931
H	-1.880711	-2.473918	2.292949
C	1.186500	-4.782933	-0.757684
C	2.233504	-5.600411	-1.224829
C	3.541853	-5.164266	-1.203423
C	3.815732	-3.884957	-0.711691
C	2.784009	-3.057994	-0.306212
C	1.424667	-3.449233	-0.328381
H	1.980097	-6.596355	-1.578545
H	4.347088	-5.812991	-1.543491
H	4.845642	-3.532378	-0.652266
H	3.041995	-2.070815	0.061217
O	-0.398365	-6.454103	-1.342104

Complex **3_oxo** – product from mechanism B

32

C	-1.365768	-0.673061	-0.003487
C	-0.413892	-0.463578	1.064981
C	0.905276	-0.401319	0.471537
C	0.757414	-0.549999	-0.960252
C	-0.651760	-0.642642	-1.260870
Ir	0.012680	-2.273593	0.023343
C	-0.744746	-0.249636	2.505470

C	2.183698	-0.125035	1.193448
C	1.853779	-0.487359	-1.975050
C	-1.270517	-0.621678	-2.619918
C	-2.850094	-0.769529	0.149918
O	-0.939705	-1.825560	-3.302981
O	-1.429366	-1.665433	-4.662354
H	1.584176	-1.035033	-2.881628
H	2.054926	0.556819	-2.254662
H	2.787314	-0.910003	-1.593551
H	-2.361461	-0.508776	-2.554179
H	-0.876473	0.233512	-3.192421
H	-2.043866	-2.412699	-4.693410
H	-3.129211	-1.198206	1.115851
H	-3.313084	0.224788	0.082248
H	-3.294889	-1.400206	-0.625045
H	-1.644387	-0.793950	2.804641
H	0.066913	-0.567860	3.165145
H	-0.928135	0.818386	2.697272
H	2.165395	-0.499628	2.220561
H	3.040874	-0.581730	0.691548
H	2.368508	0.958657	1.238149
O	1.186972	-3.956224	-0.169976
N	0.253536	-4.769096	0.241372
O	0.373730	-5.960522	0.357908
O	-0.827117	-4.092169	0.519713

Complex **3_oxo** – product from H abstraction

32

C	-1.312631	-0.681921	0.420111
C	-0.183851	-0.886336	1.285545
C	1.001357	-0.642919	0.497120
C	0.609425	-0.216951	-0.831533
C	-0.852678	-0.099964	-0.852225
Ir	-0.096232	-2.156748	-0.466585
C	-0.225648	-1.249017	2.734527
C	2.406893	-0.743078	0.990862
C	1.515317	0.299227	-1.897324
C	-1.651671	0.374343	-1.885649
C	-2.748784	-0.812882	0.802929
O	0.176482	-3.203121	-2.087126
O	0.400033	-2.471944	-3.295933
H	1.139637	0.052000	-2.892493
H	1.594960	1.392937	-1.820468
H	2.522299	-0.116918	-1.818248
H	-2.733521	0.382391	-1.803238
H	-1.215845	0.754873	-2.803473
H	-0.509828	-2.379996	-3.615768
H	-2.897309	-1.541478	1.602833
H	-3.128393	0.156802	1.154653
H	-3.364448	-1.121663	-0.046329

H	-1.123361	-1.817014	2.991463
H	0.638182	-1.847401	3.035542
H	-0.226797	-0.338573	3.350892
H	2.515591	-1.501264	1.769950
H	3.103475	-0.989557	0.186210
H	2.716118	0.222045	1.416293
O	0.860575	-3.952658	0.435836
N	-0.236378	-4.608976	0.514181
O	-0.303894	-5.722015	0.971885
O	-1.249197	-3.963741	0.078565

Complex **4_oxo** – product from mechanism B

31

C	-0.584230	-0.491494	-1.087815
C	-1.070680	-0.403938	0.254554
C	0.034079	-0.531135	1.151177
C	1.262016	-0.615156	0.365147
C	0.873956	-0.594234	-1.035123
Ir	0.120036	-2.310278	-0.128603
O	2.935629	-1.210234	-2.106773
O	0.864214	-3.850535	-0.468930
C	-2.501883	-0.245417	0.648429
C	-0.021882	-0.468622	2.639702

C	2.639220	-0.593110	0.933863
C	1.745284	-0.483497	-2.251557
C	-1.393342	-0.355413	-2.333274
O	-1.504937	-3.672653	0.770441
H	3.363389	-1.055829	0.264590
H	2.933691	0.456405	1.078544
H	2.685175	-1.082203	1.909280
H	1.175327	-0.812251	-3.132089
H	1.938656	0.599679	-2.379920
H	3.461896	-1.072147	-2.901175
H	-2.446501	-0.590045	-2.168629
H	-1.343387	0.684050	-2.685416
H	-1.026931	-0.993867	-3.140668
H	-3.191823	-0.658619	-0.091336
H	-2.725001	-0.700922	1.615384
H	-2.730522	0.825573	0.733981
H	-0.990116	-0.785411	3.032095
H	0.751199	-1.080122	3.110194
H	0.139945	0.569338	2.961940
H	-2.237290	-3.779339	0.147817
H	-1.067476	-4.538772	0.778552