

Supplementary Information

Solid state molecular structure of $(\text{H}_2\text{pz})[\text{AuCl}_4]$

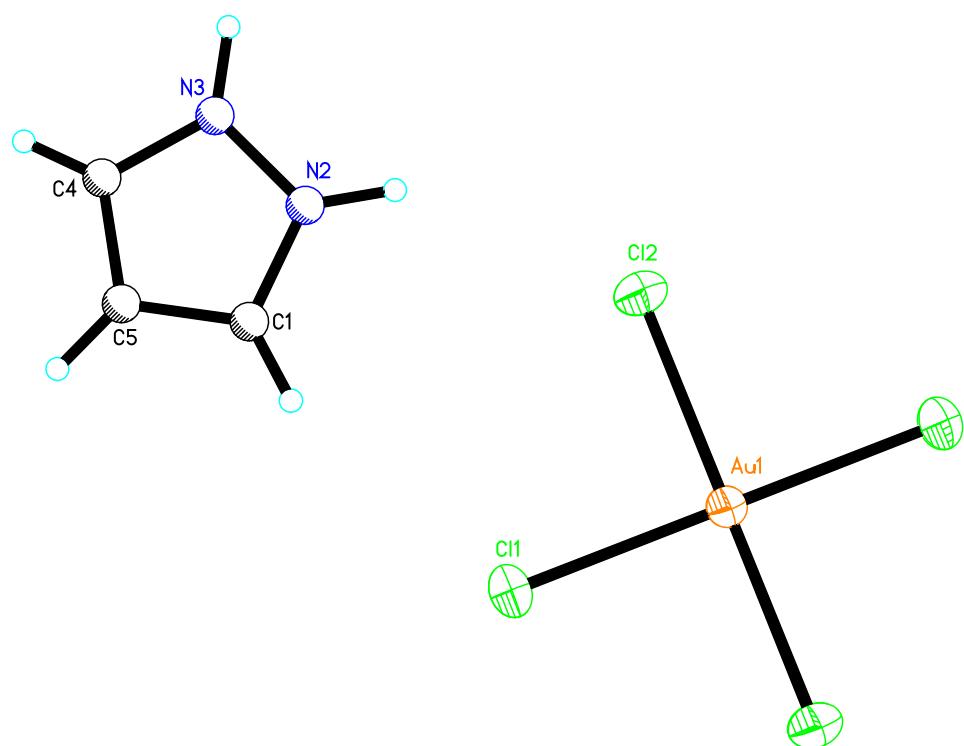


Figure SI1 – Solid state molecular structure of $(\text{H}_2\text{pz})[\text{AuCl}_4]$, the hydrolysis product of **1** (CCDC 951722 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif)

Temperature programmed desorption (TPD) profiles of carbon materials with different surface treatments

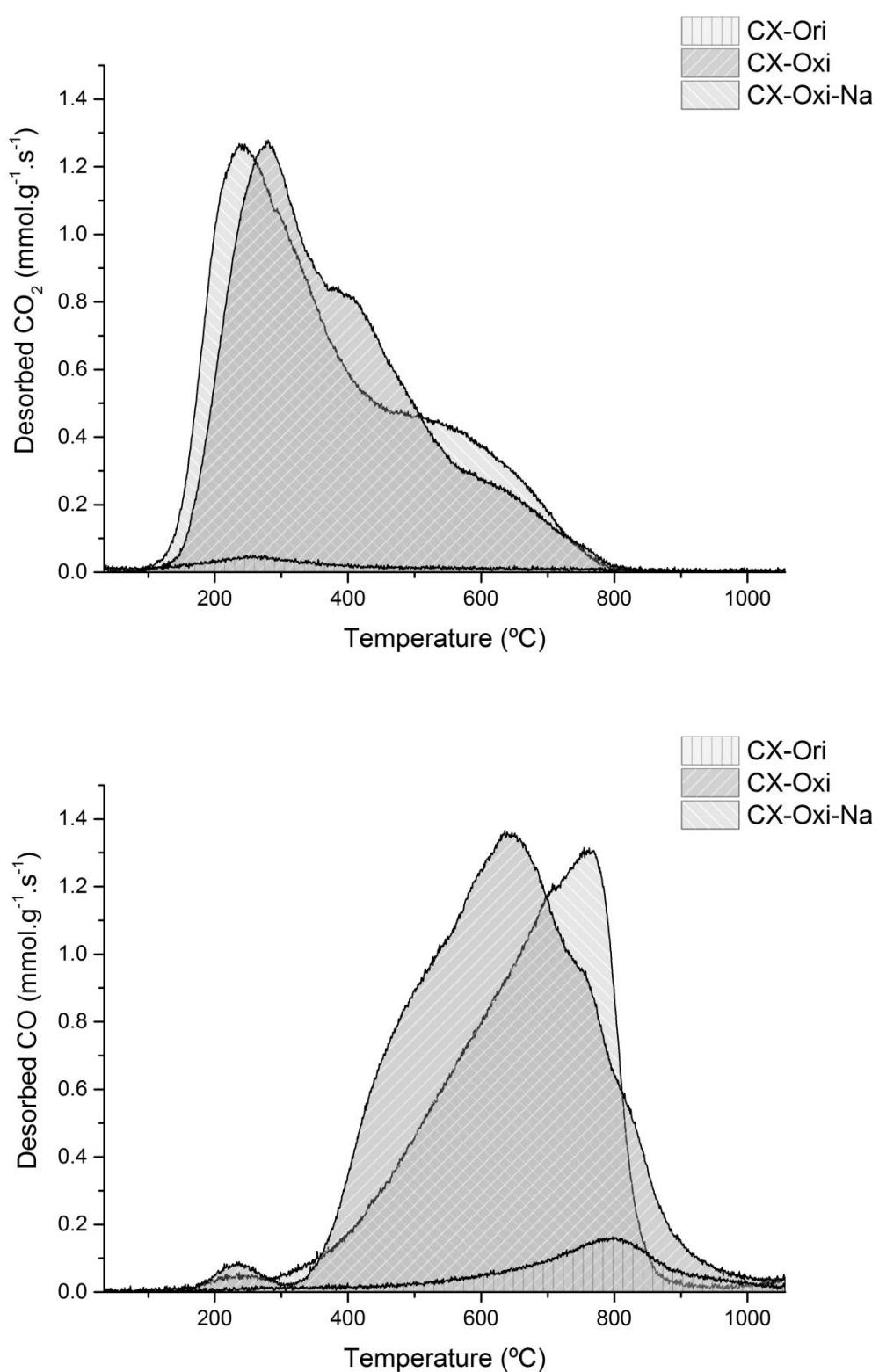


Figure SI2 – TPD profiles for the three CX materials. CO₂ – top and CO – bottom.

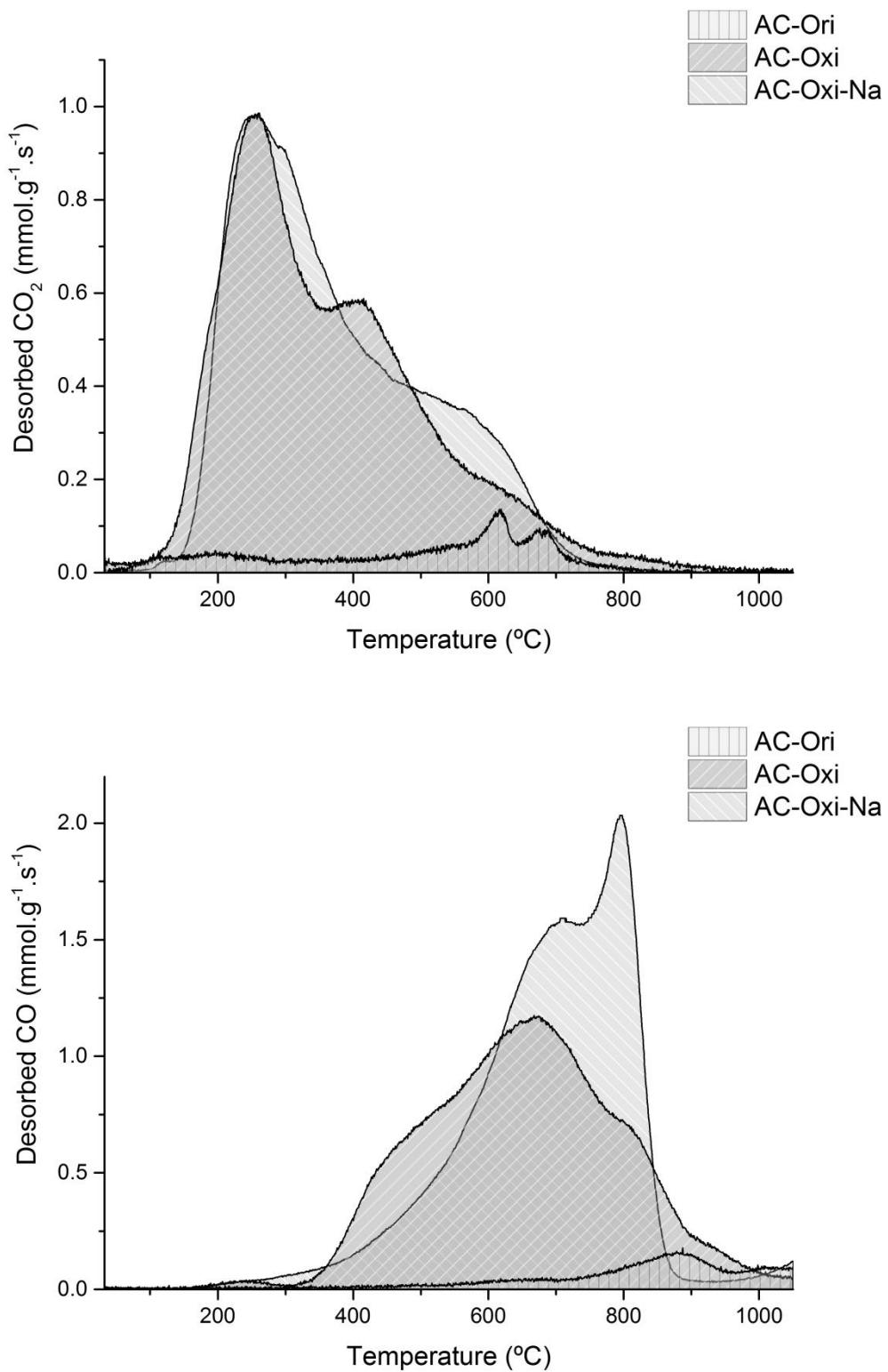


Figure SI3 – TPD profiles for the three AC materials. CO_2 – top and CO – bottom.

Heterogenisation UV-Vis profiles for the twenty-seven combinations of gold Au C-scorpionate and carbon materials

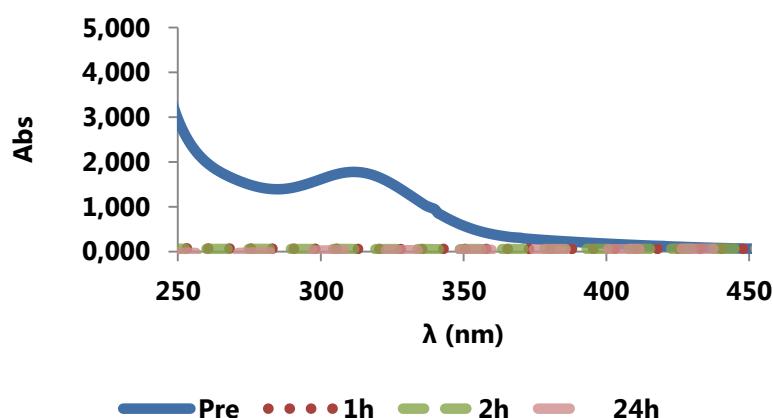


Figure SI4 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on AC-Ori, taken at different times.

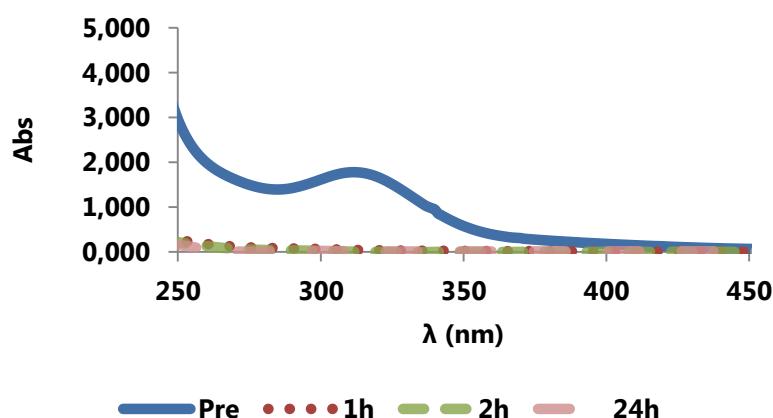


Figure SI5 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on AC-Oxi, taken at different times.

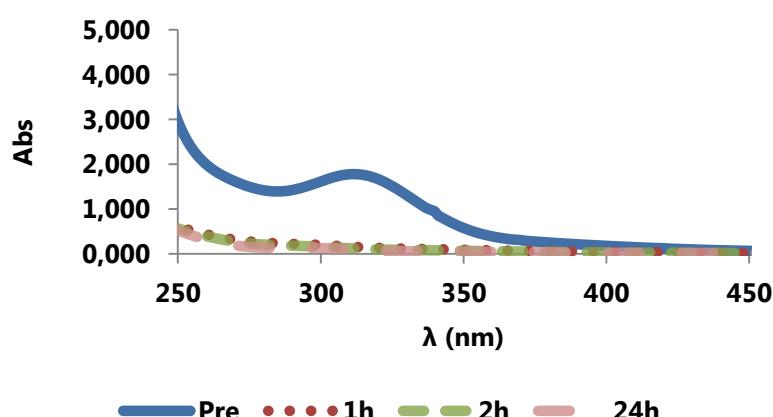


Figure SI6 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on AC-Oxi-Na, taken at different times.

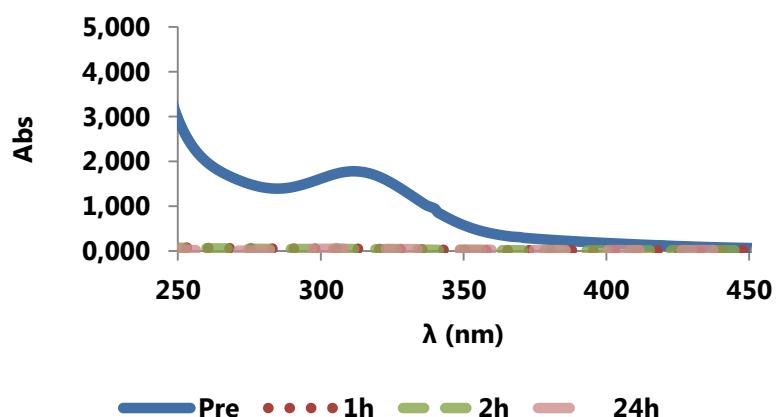


Figure SI7 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on CNT-Ori, taken at different times.

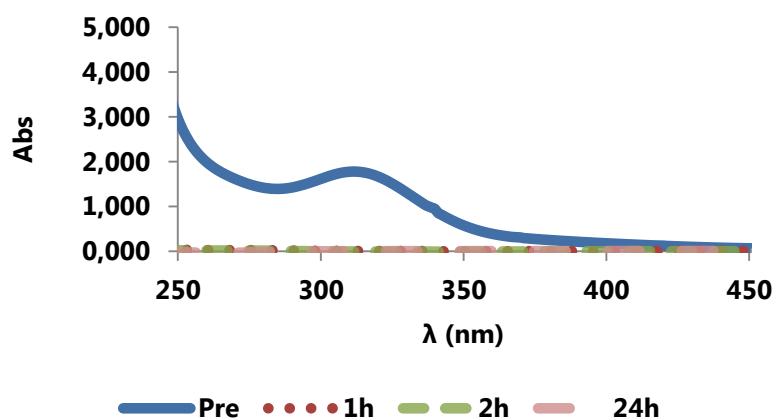


Figure SI8 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on CNT-Oxi, taken at different times.

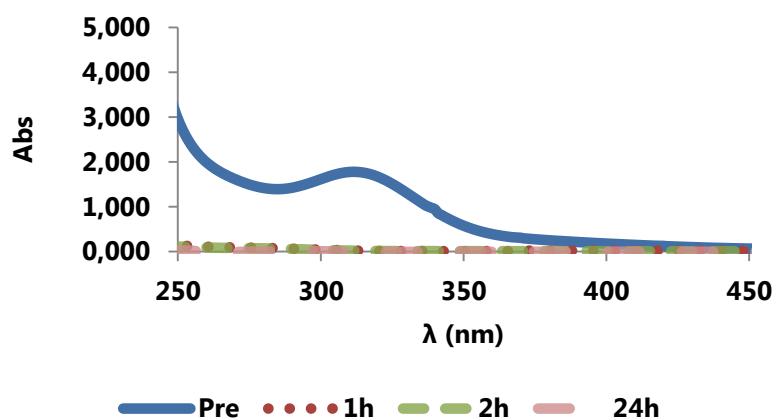


Figure SI9 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on CNT-Oxi-Na, taken at different times.

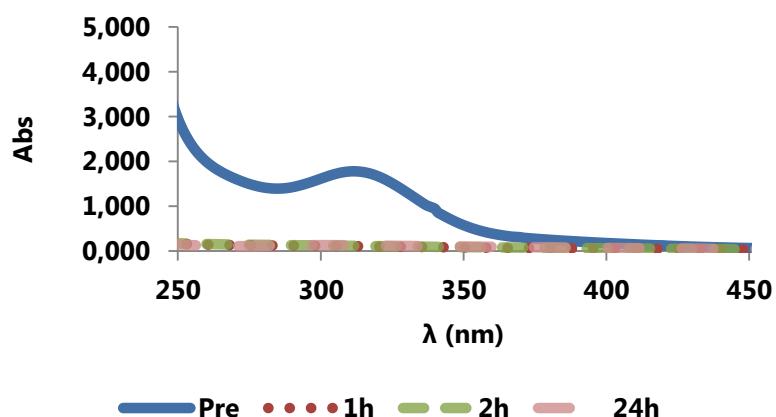


Figure SI10 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on CX-Ori, taken at different times.

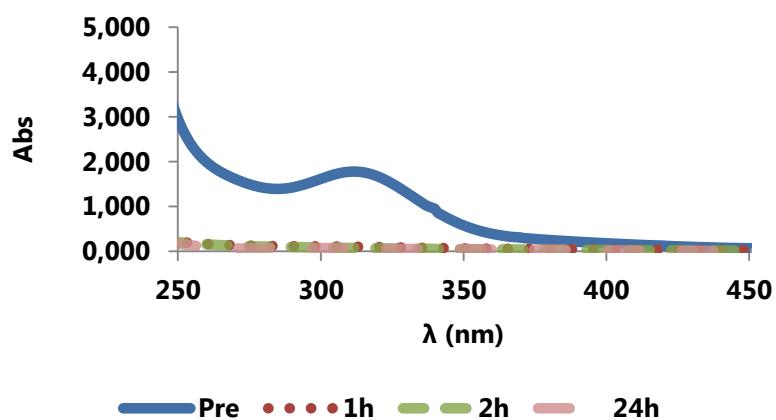


Figure SI11 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on CX-Oxi, taken at different times.

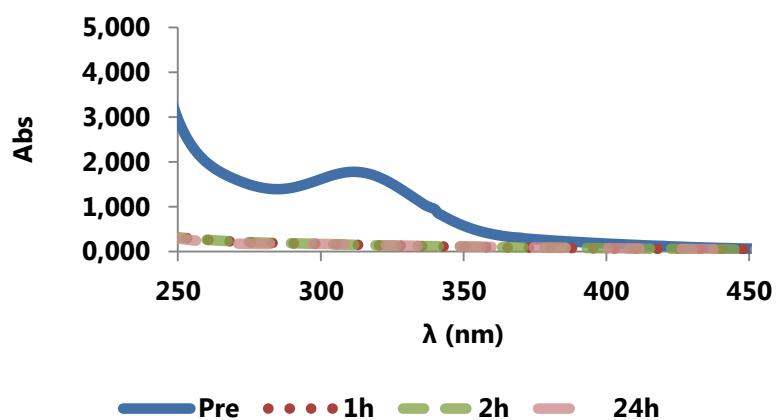


Figure SI12 – Heterogenisation UV-Vis profiles of the supernatant from complex **1** on CX-Oxi-Na, taken at different times.

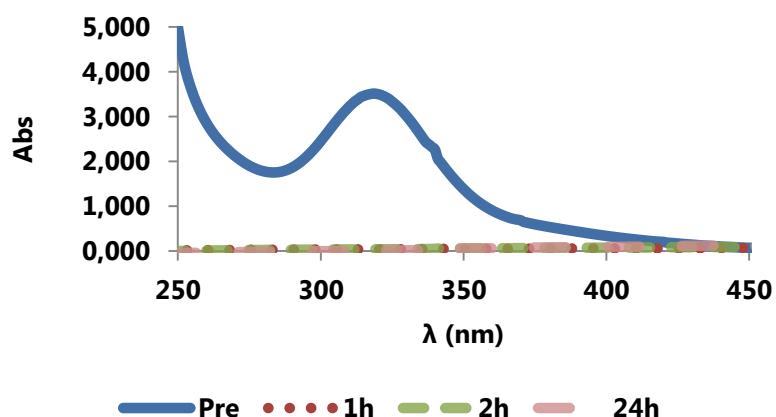


Figure SI13 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on AC-Ori, taken at different times.

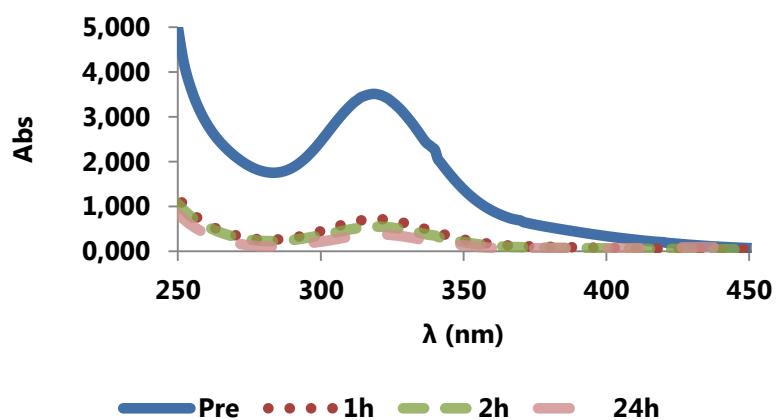


Figure SI14 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on AC-Oxi, taken at different times.

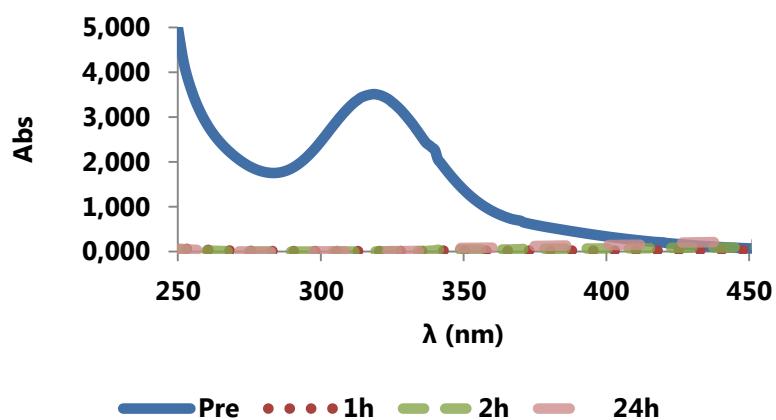


Figure SI15 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on AC-Oxi-Na, taken at different times.

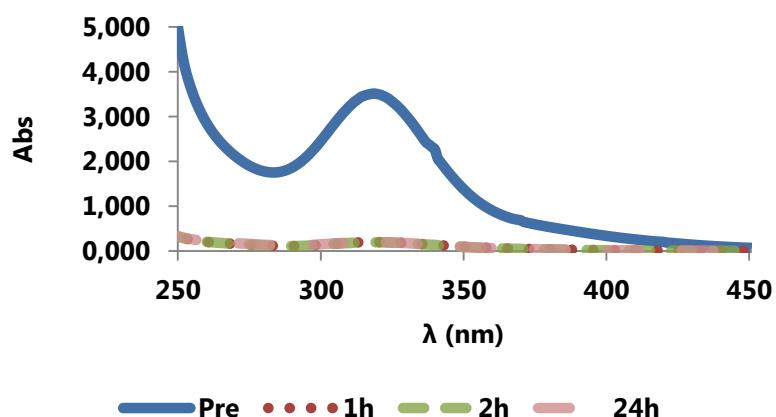


Figure SI16 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on CNT-Ori, taken at different times.

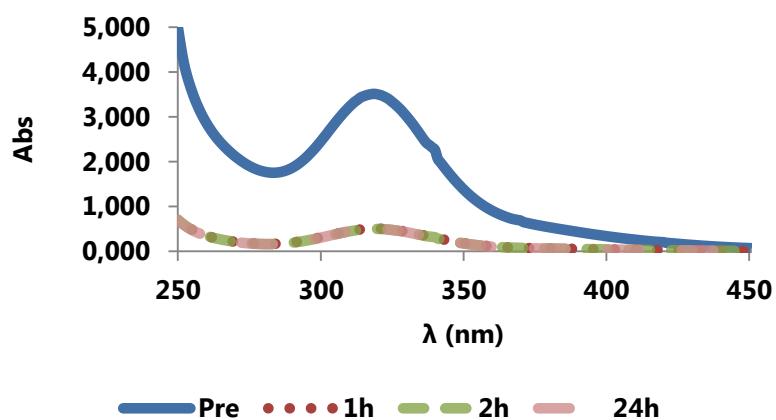


Figure SI17 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on CNT-Oxi, taken at different times.

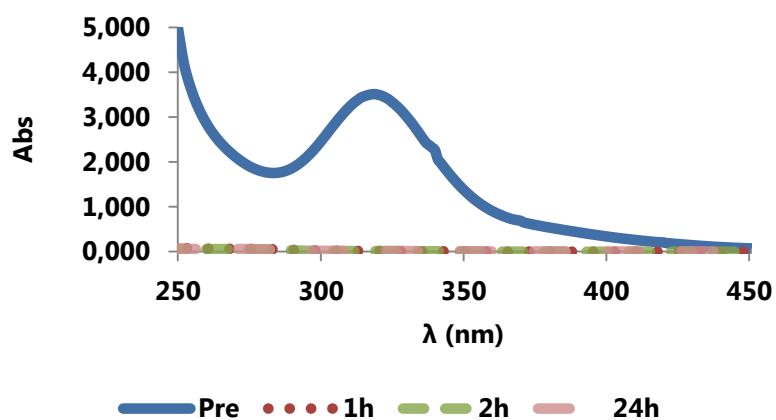


Figure SI18 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on CNT-Oxi-Na, taken at different times.

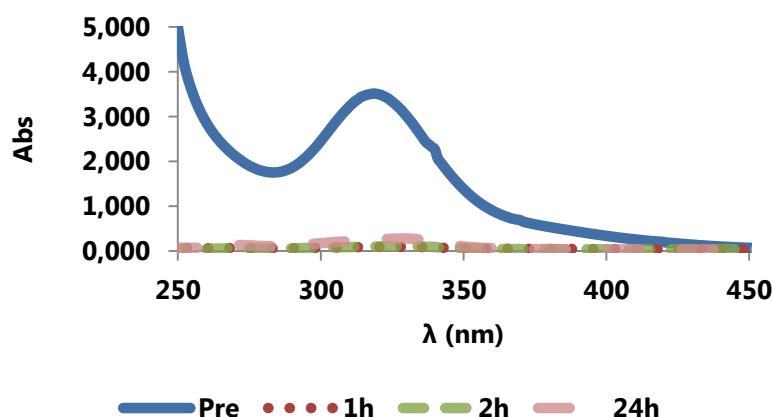


Figure SI19 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on CX-Ori, taken at different times.

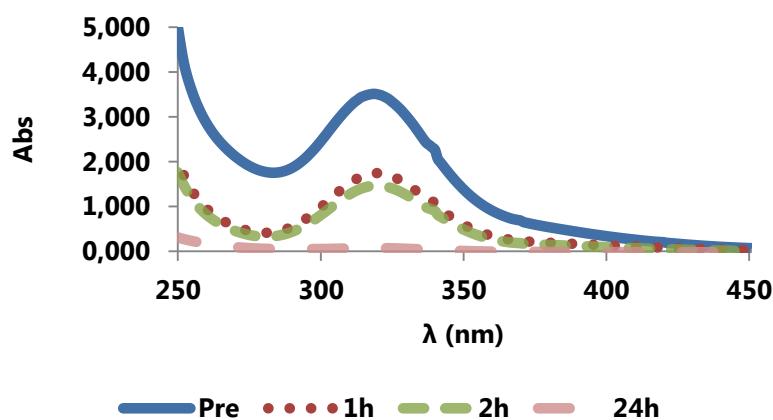


Figure SI20 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on CX-Oxi, taken at different times.

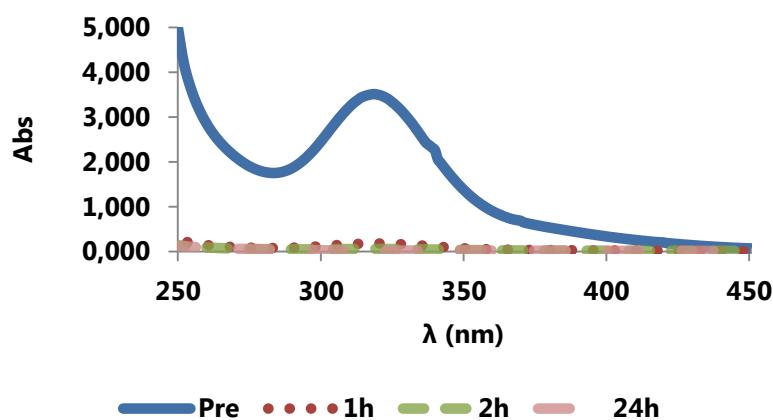


Figure SI21 – Heterogenisation UV-Vis profiles of the supernatant from complex **2** on CX-Oxi-Na, taken at different times.

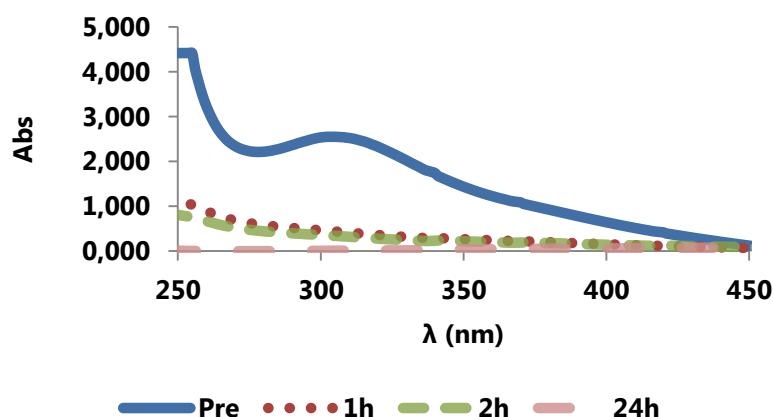


Figure SI22 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on AC-Ori, taken at different times.

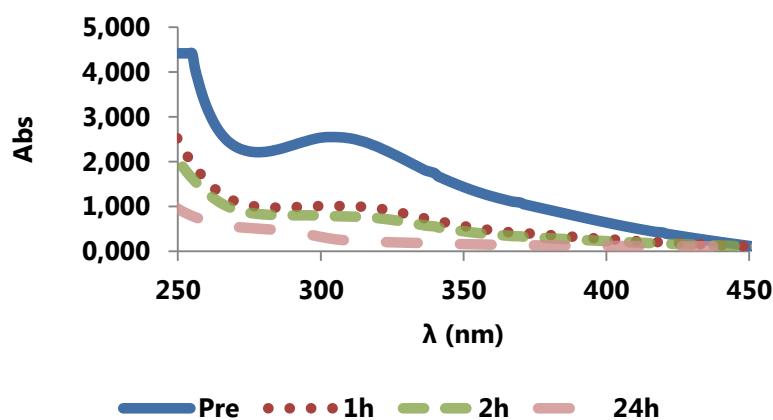


Figure SI23 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on AC-Oxi, taken at different times.

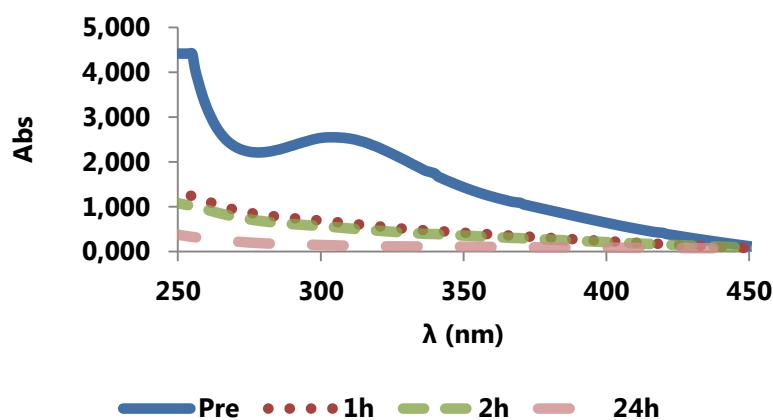


Figure SI24 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on AC-Oxi-Na, taken at different times.

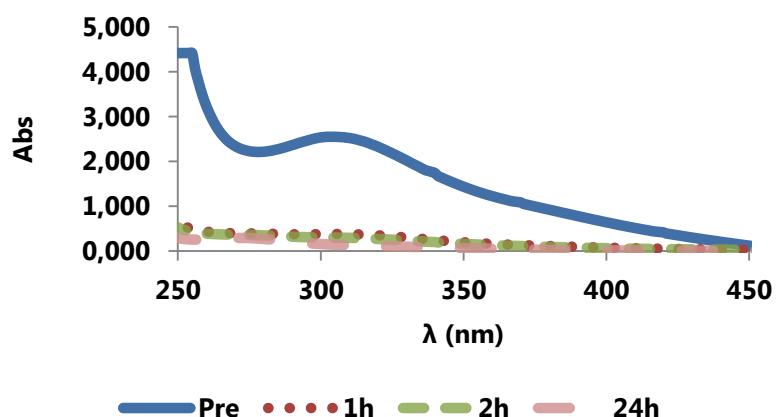


Figure SI25 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on CNT-Ori, taken at different times.

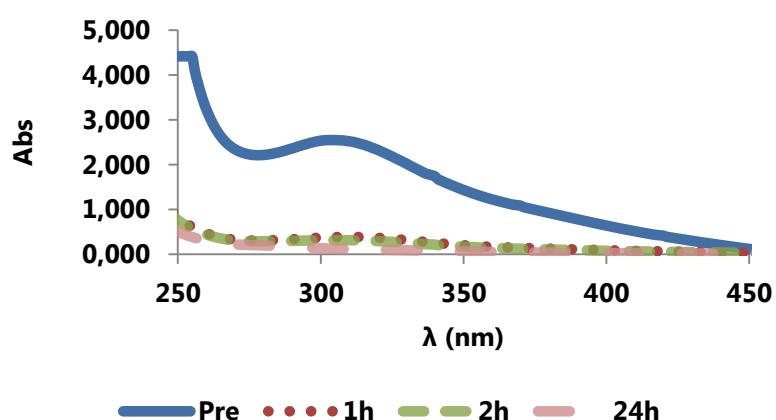


Figure SI26 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on CNT-Oxi, taken at different times.

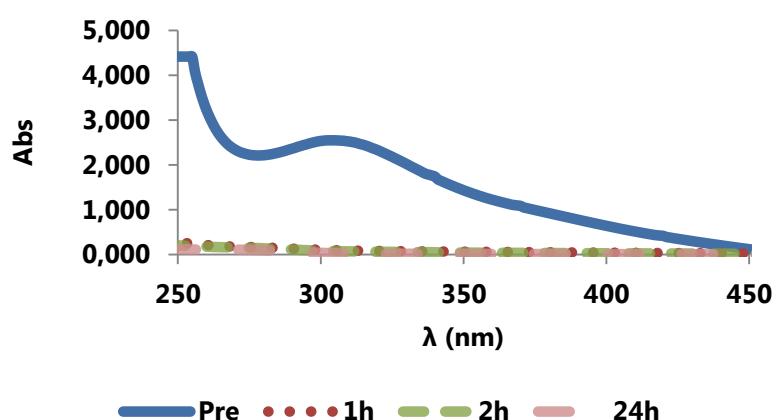


Figure SI27 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on CNT-Oxi-Na, taken at different times.

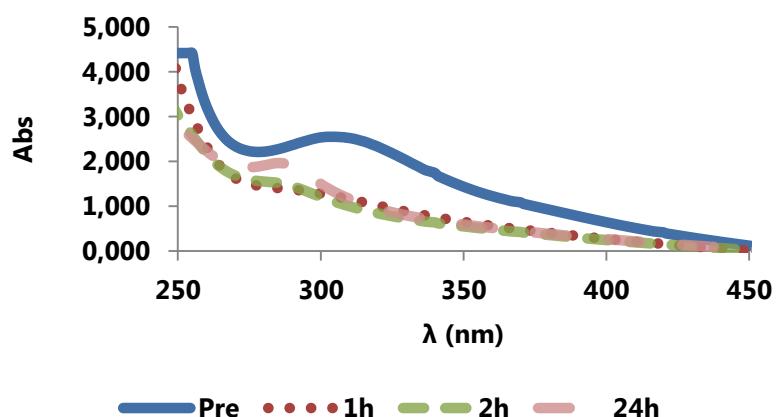


Figure SI28 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on CX-Ori, taken at different times.

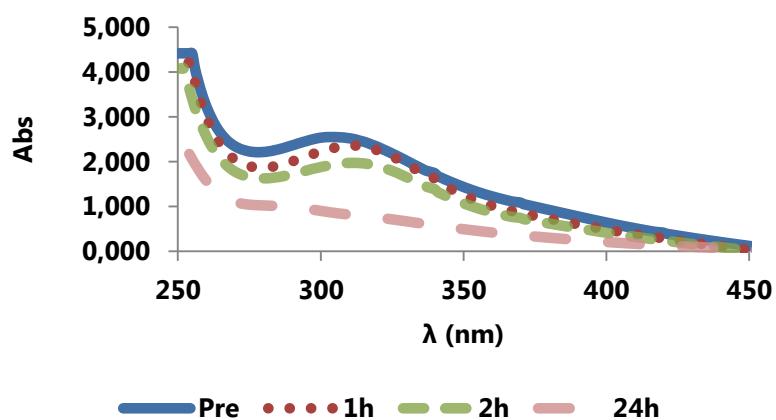


Figure SI29 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on CX-Oxi, taken at different times.

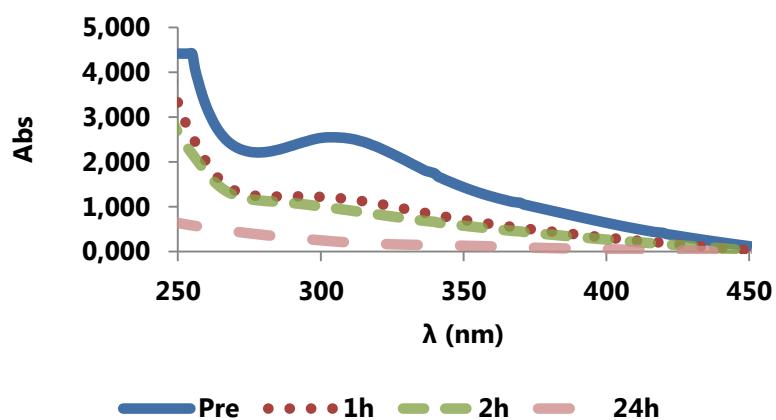


Figure SI30 – Heterogenisation UV-Vis profiles of the supernatant from complex **3** on CX-Oxi-Na, taken at different times.

Dependence of the turnover numbers on the amount of oxidant for complexes 1 and 3

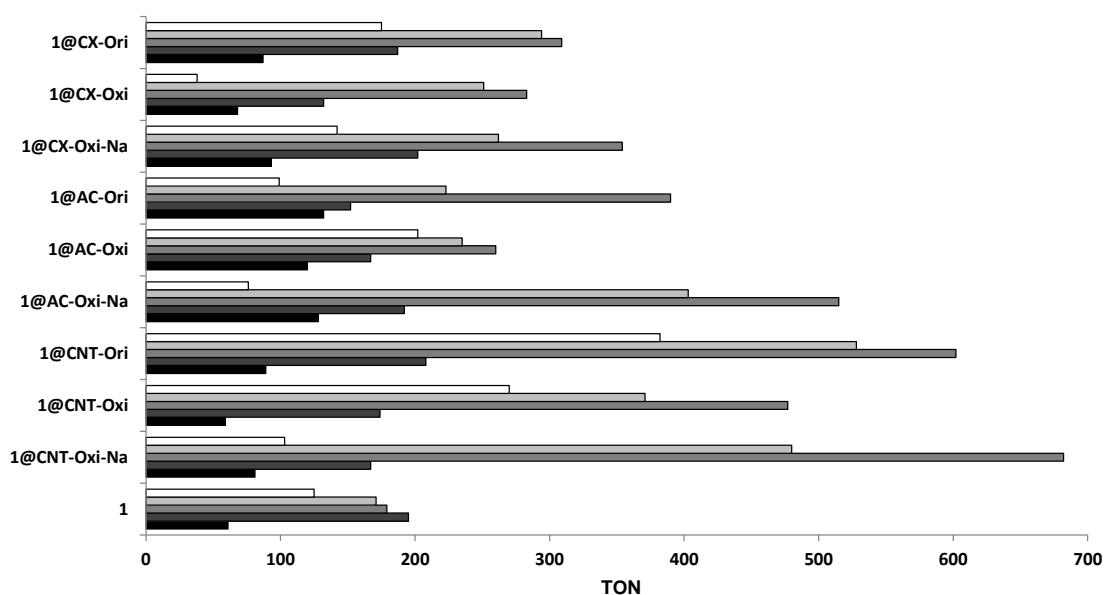


Figure SI31 – Dependence of the overall turnover number (moles of cyclohexanol + cyclohexanone per mole of Au-complex or Au-complex loaded on the carbon material) of the products on the amount of oxidant (H₂O₂, molar ratio relatively to **1** or **1** supported at nine different carbon materials (10² (■), 10³ (■), 5 × 10³ (■), 10⁴ (■), 5 × 10⁴ (□)), in the oxidation of cyclohexane. Reaction conditions: CH₃CN (3.0 mL), cyclohexane (5.0 mmol), 6 h, r.t.

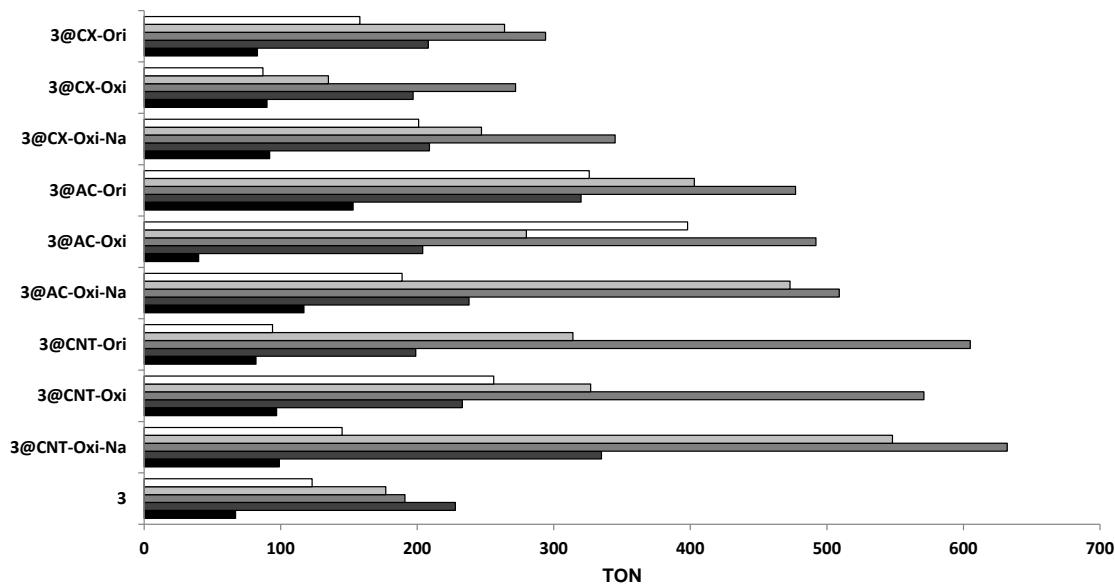


Figure SI32 – Dependence of the overall turnover number (moles of cyclohexanol + cyclohexanone per mole of Au-complex or Au-complex loaded on the carbon material) of the products on the amount of oxidant (H₂O₂, molar ratio relatively to **3** or **3** supported at nine different carbon materials (10² (■), 10³ (■), 5 × 10³ (■), 10⁴ (■), 5 × 10⁴ (□)), in the oxidation of cyclohexane. Reaction conditions: CH₃CN (3.0 mL), cyclohexane (5.0 mmol), 6 h, r.t.

Table SI1 – Metal loading ($\mu\text{mol}_{\text{Au}}/\text{g}_c$) on the 27 prepared catalysts.

Carbon Material	Au C-scorpionate		
	$[\text{AuCl}_2(\eta^2\text{-Tpm})]\text{Cl}$	$[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{OH}})]\text{Cl}$	$[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{Me}2})]\text{Cl}$
CX-Ori	5.2	3.9	5.4
CX-Oxi	5.0	4.1	2.8
CX-Oxi-Na	6.2	6.3	9.8
AC-Ori	11.2	5.8	8.4
AC-Oxi	4.5	5.2	4.3
AC-Oxi-Na	10.4	7.8	21.7
CNT-Ori	4.5	5.7	3.8
CNT-Oxi	3.4	8.6	5.3
CNT-Oxi-Na	5.9	5.6	20.5

Table SI2 – pH values of the 27 supernatants after the heterogenisation process.

Carbon Material	Au C-scorpionate		
	$[\text{AuCl}_2(\eta^2\text{-Tpm})]\text{Cl}$	$[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{OH}})]\text{Cl}$	$[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{Me}2})]\text{Cl}$
CX-Ori	3.1	3.5	4.0
CX-Oxi	2.7	3.0	3.1
CX-Oxi-Na	5.4	5.7	5.3
AC-Ori	7.3	7.2	7.5
AC-Oxi	2.7	2.7	3.0
AC-Oxi-Na	5.5	5.5	5.6
CNT-Ori	2.5	2.5	2.8
CNT-Oxi	2.7	2.7	3.1
CNT-Oxi-Na	5.5	5.5	6.6

Table SI3 – Cyclohexane oxidation to cyclohexanol and cyclohexanone catalysed by complexes $[\text{AuCl}_2(\eta^2\text{-Tpm})]\text{Cl}$ (**1**), $[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{OH}})]\text{Cl}$ (**2**) or $[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{Me}2})]\text{Cl}$ (**3**) heterogeneized at nine different carbon materials.^a

$(n_{\text{oxidant}} / n_{\text{catalyst}}) \times 10^{-3}$			1 st cycle				2 nd cycle			
			Total TON ^b	Yield (%) ^c -ol	Yield (%) ^c -one	Total ^d	Total TON ^b	Yield (%) ^c -ol	Yield (%) ^c -one	Total ^d
$[\text{AuCl}_2(\eta^2\text{-Tpm})]\text{Cl}$	Homogeneous	0.1	61	1.7	1.5	3.2	6	0.1	0.2	0.3
		1	195	4.7	3.4	8.1	31	1.1	0.2	1.3
		5	179	4.2	3.2	7.4	20	0.4	0.4	0.8
		10	171	3.6	3.5	7.1	5	0.2	0	0.2
		50	125	4.0	1.2	5.2	-	-	-	-
		100	83	2.2	1.9	4.1	4	0.2	0	0.2
	@CX-Ori	0.1	87	1.4	0.6	2.0	63	0.9	0.5	1.4
		1	187	2.6	1.7	4.3	160	2.4	1.3	3.7
		5	309	4.3	2.8	7.1	222	3.8	1.3	5.1
		5 ^e	141	2.1	1.1	3.2	-	-	-	-
		10	294	3.6	3.2	6.8	196	2.4	2.1	4.5
		50	175	3.0	1.0	4.0	149	2.0	1.4	3.4
$[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{OH}})]\text{Cl}$	@CX-Oxi	0.1	68	0.7	0.6	1.3	51	0.6	0.4	1.0
		1	132	3.6	1.4	5.0	83	1.1	0.5	1.6
		5	283	3.5	2.0	5.5	210	2.9	1.2	4.1
		5 ^e	163	2.4	1.3	3.7	-	-	-	-
		10	251	3.3	1.6	4.9	151	1.8	1.1	2.9
		50	38	0.5	0.2	0.7	0	0	0	0
	@CX-Oxi-Na	0.1	93	1.7	0.6	2.3	64	1.2	0.4	1.6
		1	202	2.9	2.1	5.0	117	2.1	0.8	2.9
		5	354	5.3	3.5	8.8	258	3.9	2.5	6.4
		5 ^e	165	1.9	1.9	3.8	-	-	-	-
		10	262	5.1	1.4	6.5	198	3.0	1.9	4.9
		50	142	2.4	1.1	3.5	97	1.3	1.1	2.4
$[\text{AuCl}_2(\eta^2\text{-Tpm}^{\text{Me}2})]\text{Cl}$	@AC-Ori	0.1	132	2.0	0.5	2.5	104	1.6	0.4	2.0
		1	152	1.7	1.2	2.9	123	1.3	1.0	2.3
		5	390	4.5	2.8	7.3	290	4.0	1.5	5.5
		5 ^e	233	3.1	2.3	5.4	-	-	-	-
		10	223	3.1	1.1	4.2	131	1.1	1.4	2.5
		50	99	1.1	0.8	1.9	43	0.3	0.5	0.8

[AuCl ₂ (η ² -Tp ^m ^{0H})Cl]	@AC-Oxi	0.1	120	1.6	1.2	2.8	73	1.0	0.7	1.7
		1	167	3.6	2.3	5.9	142	1.9	1.4	3.3
		5	260	3.3	2.7	6.0	216	3.2	1.8	5.0
		5 ^e	205	1.9	2.8	4.7	-	-	-	-
		10	235	3.9	1.5	5.4	148	2.1	1.3	3.4
		50	202	1.6	3.1	4.7	137	0.9	2.3	3.2
	@AC-Oxi-Na	0.1	128	2.1	0.7	2.9	100	1.7	0.6	2.3
@CNT-Ori	@CNT-Ori	1	192	2.2	2.2	4.4	113	1.8	0.8	2.6
		5	515	8.3	3.4	11.7	476	7.2	3.7	10.9
		5 ^e	212	2.8	2.1	4.9	-	-	-	-
		10	403	6.7	2.5	9.2	376	6.8	1.8	8.6
		50	76	1.0	0.7	1.7	52	0.4	0.8	1.2
		0.1	89	0.9	0.7	1.6	67	0.7	0.5	1.2
@CNT-Oxi	@CNT-Oxi	1	208	2.2	1.5	3.7	133	1.2	1.2	2.4
		5	602	6.6	4.1	10.7	449	4.3	3.7	8.0
		5 ^e	284	4.8	1.7	6.5	-	-	-	-
		10	528	5.1	4.3	9.4	339	3.2	2.8	6.0
		50	382	2.9	3.9	6.8	176	1.5	1.6	3.1
		0.1	59	0.8	0.6	1.4	47	0.7	0.4	1.1
@CNT-Oxi-Na	@CNT-Oxi-Na	1	174	1.3	2.8	4.1	101	1.0	1.4	2.4
		5	477	7.3	3.9	11.2	401	6.4	3.0	9.4
		5 ^e	321	5.1	2.3	7.4	-	-	-	-
		10	371	4.9	3.8	8.7	315	4.1	3.3	7.4
		50	270	2.8	3.5	6.3	155	1.9	1.7	3.6
		0.1	81	0.9	0.6	1.5	77	1.1	0.3	1.4
Homogeneous	Homogeneous	1	167	1.9	1.2	3.1	122	1.6	0.7	2.3
		5	682	8.3	4.4	12.7	594	6.2	4.9	11.1
		5 ^e	347	4.2	3.8	8.0	-	-	-	-
		10	480	4.8	4.2	9.0	382	3.7	3.4	7.1
		50	103	1.1	0.8	1.9	85	0.9	0.7	1.6
		0.1	131	2.5	1.9	4.4	12	0.3	0.1	0.4
1 ^f	1 ^f	1	300	6.3	4.0	10.3	29	0.9	0.1	1
		1 ^f	119	4.3	3.8	8.1	-	-	-	-
		1 ^g	41	3.9	3.3	7.2	-	-	-	-
		5	242	5.2	3.1	8.3	-	-	-	-
		10	182	3.8	2.4	6.2	0	0	0	0
		50	172	3.3	1.6	4.9	-	-	-	-

		100	138	2.9	1.8	4.7	0	0	0	0
@CX-Ori	0.1	75	1.2	0.3	1.5	49	0.8	0.2	1.0	
	1	161	2.4	0.8	3.2	129	1.1	0.5	2.6	
	5	378	5.0	1.6	7.6	282	4.5	1.1	5.6	
	5 ^e	211	2.1	2.1	4.2	-	-	-	-	
	10	214	2.4	1.9	4.3	135	1.2	1.5	2.7	
	50	160	1.5	1.7	3.2	91	0.8	1.0	1.8	
@CX-Oxi	0.1	82	1.3	0.3	1.6	58	1.0	0.2	1.2	
	1	198	2.2	1.8	4.0	146	1.6	1.3	2.9	
	5	353	4.4	2.7	7.1	280	3.5	2.1	5.6	
	5 ^e	175	2.3	1.2	3.5	-	-	-	-	
	10	322	3.1	3.3	6.4	222	2.5	1.9	4.4	
	50	257	1.9	3.2	5.1	179	1.7	1.9	3.6	
@CX-Oxi-Na	0.1	68	1.1	0.3	1.4	47	0.7	0.2	0.9	
	1	211	3.4	0.8	4.2	149	2.4	0.6	3.0	
	5	399	5.4	2.6	8.0	279	4.5	1.1	5.6	
	5 ^e	237	2.9	1.8	4.7	-	-	-	-	
	10	359	2.8	4.4	7.2	226	1.6	2.9	4.5	
	50	290	1.9	3.9	5.8	183	1.6	2.1	3.7	
@AC-Ori	0.1	101	1.6	0.4	2.0	78	1.3	0.3	1.6	
	1	205	2.9	1.2	4.1	163	1.8	1.5	3.3	
	5	513	6.3	4.0	10.3	410	5.8	2.6	8.4	
	5 ^e	146	1.7	1.2	2.9	-	-	-	-	
	10	477	4.6	4.9	9.5	367	3.8	3.5	7.3	
	50	391	3.6	4.2	7.8	234	1.8	2.9	4.7	
@AC-Oxi	0.1	73	1.2	0.3	1.5	57	0.9	0.2	1.1	
	1	294	4.7	1.2	5.9	214	3.4	0.9	4.3	
	5	539	5.7	4.5	10.2	505	8.1	2.0	10.1	
	5 ^e	334	3.4	3.3	6.7	-	-	-	-	
	10	284	2.6	3.1	5.7	213	1.4	2.9	4.3	
	50	215	1.9	2.4	4.3	147	1.2	1.7	2.9	
@AC-Oxi-Na	0.1	102	1.6	0.4	2.0	79	0.9	0.7	1.6	
	1	302	4.5	1.5	6.0	285	4.4	1.3	5.7	
	5	694	8.1	5.8	13.9	555	5.9	4.2	11.1	
	5 ^e	332	3.7	2.9	6.6	-	-	-	-	
	10	522	5.3	5.1	10.4	407	4.3	3.8	8.1	

		50	403	3.8	4.3	8.1	321	3.3	3.1	6.4
@CNT-Ori	0.1	68	1.1	0.3	1.4	56	0.9	0.2	1.1	
	1	283	4.4	1.3	5.7	207	3.0	1.1	4.1	
	5	704	7.4	6.7	14.1	570	7.1	4.3	11.4	
	5 ^e	376	3.9	3.6	7.5	-	-	-	-	
	10	553	4.9	6.2	11.1	409	4.6	3.6	8.2	
	50	386	3.8	3.9	7.7	301	2.7	3.3	6.0	
@CNT-Oxi	0.1	103	1.4	0.6	2.1	60	1.0	0.2	1.2	
	1	297	3.3	2.6	5.9	219	3.2	1.2	4.4	
	5	671	8.6	4.8	13.4	540	7.6	3.2	10.8	
	5 ^e	420	4.3	4.1	8.4	-	-	-	-	
	10	556	5.8	5.3	11.1	467	5.4	3.9	9.3	
	50	429	4.1	4.5	8.6	363	3.7	3.6	7.3	
@CNT-Oxi-Na	0.1	83	0.9	0.8	1.7	69	1.1	0.3	1.4	
	1	310	4.8	1.4	6.2	254	4.1	1.0	5.1	
	5	808	9.0	7.2	16.2	744	9.0	5.9	14.9	
	5 ^e	248	2.6	2.4	5.0	-	-	-	-	
	5 ^f	62	0.5	0.7	1.2	-	-	-	-	
	5 ^g	56	0.8	0.3	1.1	-	-	-	-	
	10	763	8.7	6.6	15.3	612	5.8	6.4	12.2	
	50	696	8.1	5.8	13.9	563	7.0	4.3	11.3	
[AuCl ₂ (η ² -Tpmp ^{NMe₂})Cl]	Homogeneous	0.1	67	2.3	1.6	3.9	2	0.1	0	0.1
		1	228	5.7	3.2	8.9	23	0.7	0.2	0.9
		5	191	4.6	2.9	7.5	10	0.3	0.1	0.4
		10	177	4.9	2.0	6.9	4	0.1	0.1	0.2
		50	123	3.1	1.7	4.8	-	-	-	-
		100	90	2.7	0.8	3.5	3	0.1	0	0.1
@CX-Ori	@CX-Ori	0.1	83	1.4	0.3	1.7	57	0.9	0.2	1.1
		1	208	2.1	2.1	4.2	182	2.8	0.8	3.6
		5	294	3.7	2.2	5.9	212	2.5	1.7	4.2
		5 ^e	201	2.1	1.9	4.0	-	-	-	-
		10	264	2.0	3.1	5.3	177	0.8	2.7	3.5
		50	158	1.9	1.3	3.2	94	0.8	1.1	1.9
@CX-Oxi	@CX-Oxi	0.1	90	1.4	0.4	1.8	60	0.9	0.3	1.2
		1	197	2.5	1.4	3.9	143	1.9	1.0	2.9
		5	272	2.8	2.6	5.4	200	2.3	1.7	4.0

		5 ^e	146	1.6	1.3	2.9	-	-	-	-
		10	135	1.2	1.5	2.7	102	1.0	1.0	2.0
		50	87	0.6	1.1	1.7	56	0.3	0.7	1.1
@CX-Oxi-Na	0.1	92	1.3	0.5	1.8	73	1.1	0.4	1.5	
	1	209	3.1	1.1	4.2	175	2.8	0.7	3.5	
	5	345	3.7	3.2	6.9	207	2.3	1.8	4.1	
	5 ^e	221	2.4	2.0	4.4	-	-	-	-	
	10	247	3.0	1.9	4.9	174	1.8	1.7	3.5	
	50	201	1.7	2.3	4.0	159	1.3	1.9	3.2	
@AC-Ori	0.1	153	1.7	1.4	3.1	116	1.4	0.9	2.3	
	1	320	3.3	3.1	6.4	269	3.3	2.1	5.4	
	5	477	4.9	4.6	9.5	391	4.2	3.6	7.8	
	5 ^e	277	2.8	2.7	5.5	-	-	-	-	
	10	403	4.5	3.6	8.1	310	3.8	2.4	6.2	
	50	326	2.5	4.0	6.5	271	2.7	2.7	5.4	
@AC-Oxi	0.1	40	0.6	0.2	0.8	26	0.3	0.2	0.5	
	1	204	2.9	1.2	4.1	140	1.8	1.0	2.8	
	5	492	6.7	3.1	9.8	404	4.5	3.6	8.1	
	5 ^e	299	3.2	2.8	6.0	-	-	-	-	
	10	398	5.4	2.6	8.0	310	4.0	2.2	6.2	
	50	280	2.3	3.3	5.6	186	1.6	2.1	3.7	
@AC-Oxi-Na	0.1	117	1.7	0.6	2.3	86	1.2	0.5	1.7	
	1	238	3.6	1.2	4.8	159	2.2	1.0	3.2	
	5	509	6.1	4.1	10.2	457	6.5	2.6	9.1	
	5 ^e	295	3.2	2.7	5.9	-	-	-	-	
	10	473	4.9	4.6	9.5	377	4.3	3.2	7.5	
	50	189	2.2	1.6	3.8	93	1.1	0.8	1.9	
@CNT-Ori	0.1	82	0.8	0.8	1.6	71	0.9	0.5	1.4	
	1	199	2.4	1.6	4.0	112	1.3	0.9	2.2	
	5	605	6.6	5.5	12.1	494	6.1	3.8	9.9	
	5 ^e	345	3.7	3.2	6.9	-	-	-	-	
	10	314	3.2	3.1	6.3	244	3.5	1.4	4.9	
	50	94	0.8	1.1	1.9	52	0.3	0.7	1.0	
@CN-T-Oxi	0.1	97	1.2	0.7	1.9	53	0.9	0.2	1.1	
	1	233	2.9	1.7	4.6	159	1.8	1.4	3.2	

		5	571	6.7	4.7	11.4	483	6.5	3.2	9.7
		5 ^e	401	4.1	3.9	8.0	-	-	-	-
		10	327	2.8	3.7	6.5	266	2.9	2.4	5.3
		50	256	2.2	2.9	5.1	128	0.9	1.7	2.6
@CNT-Oxi-Na	0.1	99	1.2	0.8	2.0	65	0.7	0.6	1.3	
	1	335	4.6	2.1	6.7	223	2.8	1.7	4.5	
	5	632	6.7	5.9	12.6	601	7.5	4.5	12.0	
	5 ^e	333	3.9	2.8	6.7	-	-	-	-	
	10	548	4.3	6.7	11.0	467	5.0	4.3	9.3	
	50	145	0.5	2.4	2.9	32	0.1	0.9	1.0	

^a Reaction conditions (unless stated otherwise): acetonitrile (3.0 mL), cyclohexane (5.0 mmol), 6 h, r.t., under dinitrogen; 0.1–11 µmol of **1** – **3** supported on carbon xerogel (**CX**), activated carbon (**AC**) or multi-walled carbon nanotubes (**CNT**), used in their original forms (-Ori), oxidised with nitric acid (-Oxi) or oxidised with nitric acid and subsequently treated with sodium hydroxide (-Oxi-Na); H₂O₂ (1:100 to 100000:1 molar ratio of oxidant to Au catalyst). Percentage of yield, TON determined by GC analysis (upon treatment with PPh₃). ^b Turnover number (moles of product per mol of Au catalyst). ^c Molar yield (%) based on substrate, i.e. moles of products (cyclohexanol and cyclohexanone) per 100 mol of cyclohexane. ^d Moles of cyclohexanol + cyclohexanone per 100 moles of cyclohexane. ^e Reaction in the presence of pyrazine carboxylic acid (Hpca, molar ratio 1 catalyst :50 acid). ^f Reaction in the presence of CBrCl₃. ^g Reaction in the presence of Ph₂NH.

Table SI4 – Cyclohexane oxidation to cyclohexanol and cyclohexanone catalysed by [ⁿBu₄N][AuCl₄] (**4**) heterogeneized at nine different carbon materials.^a

Carbon Material	Total TON ^b	Yield (%) ^c		
		-ol	-one	total ^d
CX-Ori	68	13.4	0.3	13.7
CX-Oxi	84	12.4	0	12.4
CX-Oxi-Na	66	12.9	0	12.9
AC-Ori	65	13.0	0	13.0
AC-Oxi	85	13.5	0	13.5
AC-Oxi-Na	63	12.5	0	12.5
CNT-Ori	67	12.3	0	12.3
CNT-Oxi	84	14.2	0	14.2
CNT-Oxi-Na	51	9.6	0	9.6

^a Reaction conditions (unless stated otherwise): acetonitrile (3.0 mL), cyclohexane (5.0 mmol), 24 h, r.t., under dinitrogen; 7.4–10 µmol of **4** supported on carbon xerogel (**CX**), activated carbon (**AC**) or multi-walled carbon nanotubes (**CNT**), used in their original forms (-Ori), oxidised with nitric acid (-Oxi) or oxidised with nitric acid and subsequently treated with sodium hydroxide (-Oxi-Na); H₂O₂ (1:1000 molar ratio of oxidant to Au catalyst). Percentage of yield, TON determined by GC analysis (upon treatment with PPh₃). ^b Turnover number (moles of product per mol of Au catalyst). ^c Molar yield (%) based on substrate,

i.e. moles of products (cyclohexanol and cyclohexanone) per 100 mol of cyclohexane. ^d Moles of cyclohexanol + cyclohexanone per 100 moles of cyclohexane.