Electronic Supplementary Information

Synthesis, Characterization and DFT Study of Oxorhenium(V) Complexes Incorporating Quinoline Based Tridentate Ligands†

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Table S1 Frontier Molecular Orbital Composition (%) in the Ground State for $[Re^{V}O(L^{2})Cl_{2}]$, **2**

Orbital	Energy (eV)	Contribution(%)					Main bond type
		Re	Cl	=O	Aromatic system	Imine	
L+5	−1.3962	15	8	1	75	1	$p(Re) + \pi^{*}(L^{1})$
L+4	−1.4411	26	15	2	53	3	$d(Re) + p(Cl) + \pi^{*}(L^{1})$
L+3	−2.3148	6	0	1	82	10	$\pi^{*}(L^{1})$
L+2	−2.8332	53	1	17	26	3	$d(Re) + \pi^{*}(O) + \pi^{*}(L^{1})$
L+1	−3.1146	23	1	8	51	17	$d(Re) + \pi^{*}(L^{1})$
LUMO	−3.5543	46	6	19	19	10	$d(Re) + \pi^{*}(O) + \pi^{*}(L^{1})$
HOMO	−5.8523	35	10	1	53	1	$d(Re) + p(Cl) + \pi(L^{1})$
H-1	−6.5868	22	17	0	59	1	$d(Re) + p(Cl) + \pi(L^{1})$
H-2	−6.7335	2	5	1	81	11	$\pi(L^{1})$
H-3	−7.5923	1	12	0	80	7	$p(Cl) + \pi(L^{1})$
H-4	−7.9101	0	7	0	92	1	$\pi(L^{1})$
H-5	−7.9942	1	78	9	12	1	$p(Cl) + \pi(L^{1})$

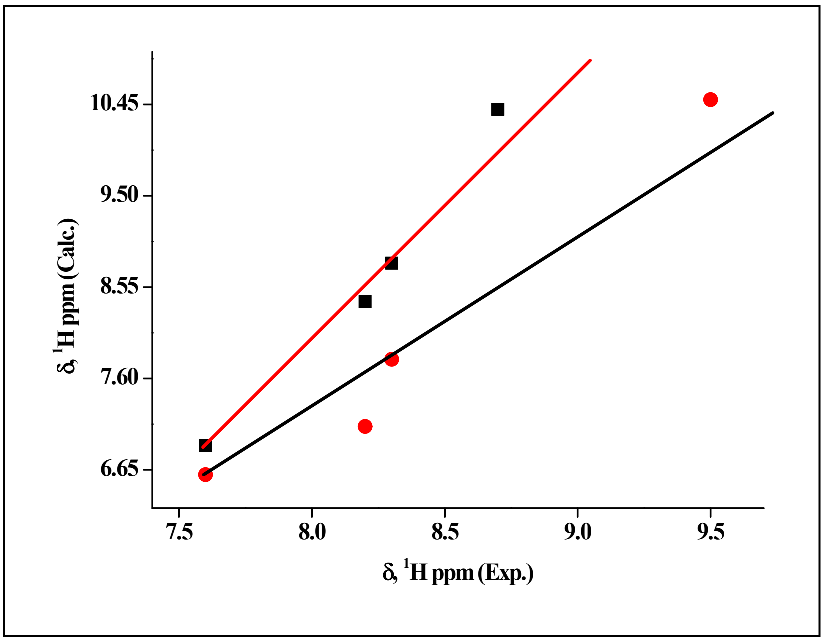
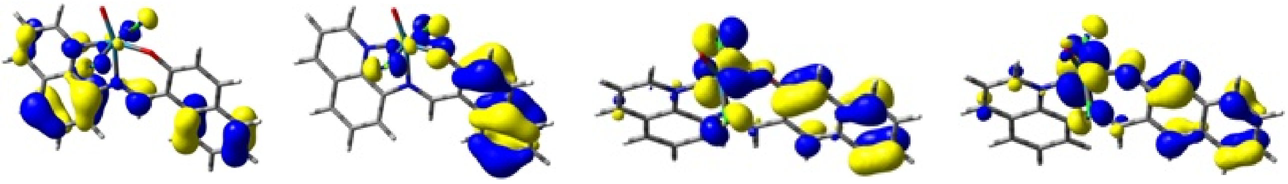


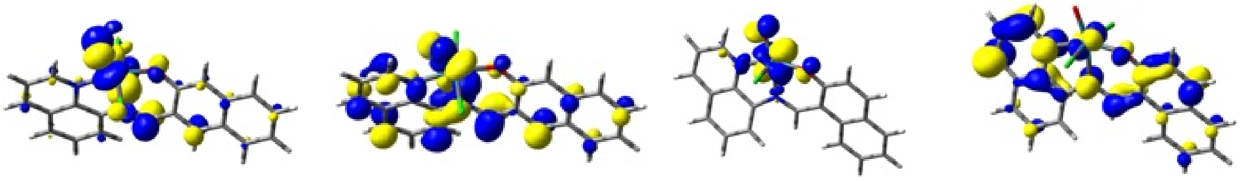
Fig. S1 Linear correlation between the experimental and calculated ^{1}H NMR chemical shifts of **1** (■) and **2** (●).

Table S2 Main calculated optical transition for the complex $[Re^{V}O(L^{2})Cl_{2}]$, **2** with composition in terms of molecular orbital contribution of the transition, vertical excitation energies, and oscillator strength in acetonitrile

Excitation	Composition	E (eV)	Oscillator strength (f)	λ_{theo} (nm)	Assign	λ_{exp} (nm)
1	HOMO – 1 → LUMO (2%) HOMO – 1 → LUMO + 1 (13%) HOMO → LUMO + 2 (79%)	2.6569	0.0709	466.65	d–d/ILCT/LLCT d–d/ILCT/LLCT d–d/ILCT/LLCT	456
2	HOMO → LUMO + 2 (69%) HOMO → LUMO + 4 (21%)	3.3512	0.0612	369.96	d–d /ILCT/LLCT d–d /ILCT/LLCT	375
3	HOMO – 8 → LUMO (3%) HOMO – 7 → LUMO (39%) HOMO – 5 → LUMO (10%) HOMO – 4 → LUMO (32%)	3.7666	0.0221	329.16	LMCT/ILCT/LLCT LMCT/ILCT/LLCT LMCT/ILCT/LLCT LMCT/ILCT/LLCT	318
4	HOMO – 10 → LUMO + 2 (55%) HOMO – 9 → LUMO + 1 (10%) HOMO – 9 → LUMO + 2 (8%) HOMO → LUMO + 7 (5%) HOMO → LUMO + 9 (5%) HOMO → LUMO + 10 (2%)	4.7511	0.0258	260.96	LMCT/ILCT/LLCT LMCT/ILCT/LLCT LMCT/ILCT/LLCT MLCT/ILCT/LLCT MLCT/ILCT/LLCT MLCT/ILCT/LLCT	256
5	HOMO – 15 → LUMO (3%) HOMO – 14 → LUMO (22%) HOMO – 13 → LUMO (6%) HOMO – 11 → LUMO + 1 (7%) HOMO – 11 → LUMO + 2 (10%) HOMO – 5 → LUMO + 3 (15%) HOMO – 3 → LUMO + 5 (3%)	5.0294	0.0126	246.52	LMCT/ILCT/LLCT LMCT/ILCT/LLCT LMCT/ILCT/LLCT LMCT/ILCT/LLCT LMCT/ILCT/LLCT ILCT/LLCT LMCT/ILCT/LLCT	230



HOMO–3 **HOMO–2** **HOMO–1** **HOMO**



LUMO **LUMO+1** **LUMO+2** **LUMO+3**

Fig. S2 Isodensity plots of frontier orbitals of [Re^{V}O(L^{2})Cl$_2$].

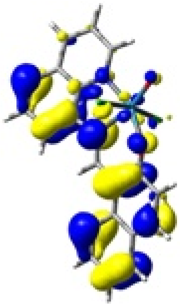
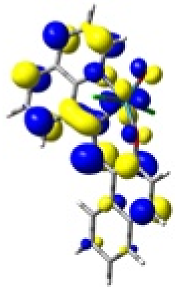
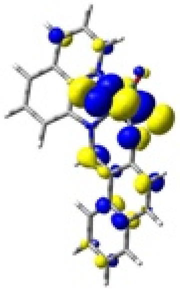
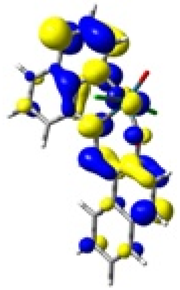
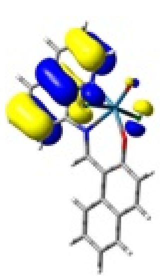
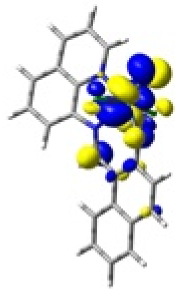
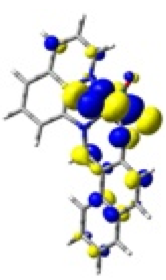
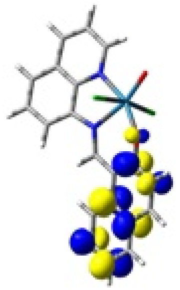
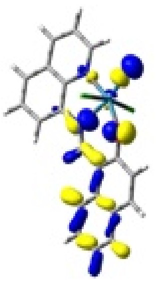
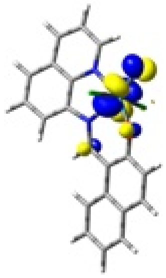
		Hole	Electron
456 nm	S_5 w = 0.79 2.6569 eV f =0.0709		
375 nm	S_{10} w = 0.69 3.3512 eV f = 0.0612		
318 nm	S_{19} w = 0.39 3.7666 eV f = 0.0221		
256 nm	S_{42} w = 0.55 4.7511 eV f = 0.0258		
230 nm	S_{50} w = 0.22 5.0294 eV f = 0.0126		

Fig. S3 Natural transition orbitals (NTOs) for the complex **2** illustrating the nature of optically active singlet excited states in the absorption bands 456, 375, 318, 256 and 230 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 20% to each excited state.

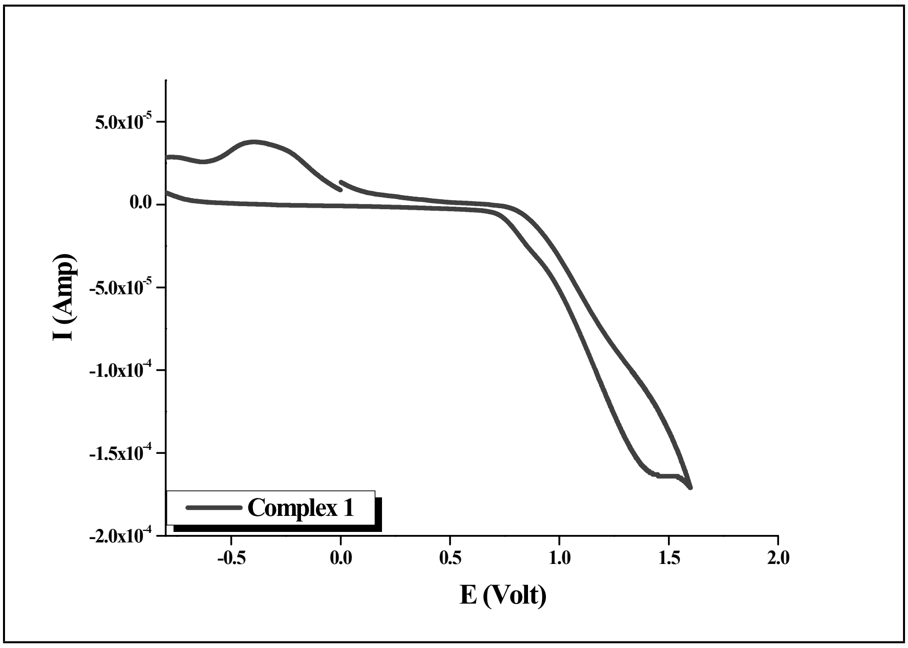


Fig. S4 Cyclic voltammogram of complex **1** in acetonitrile solution (scan rate 50 mV/s)

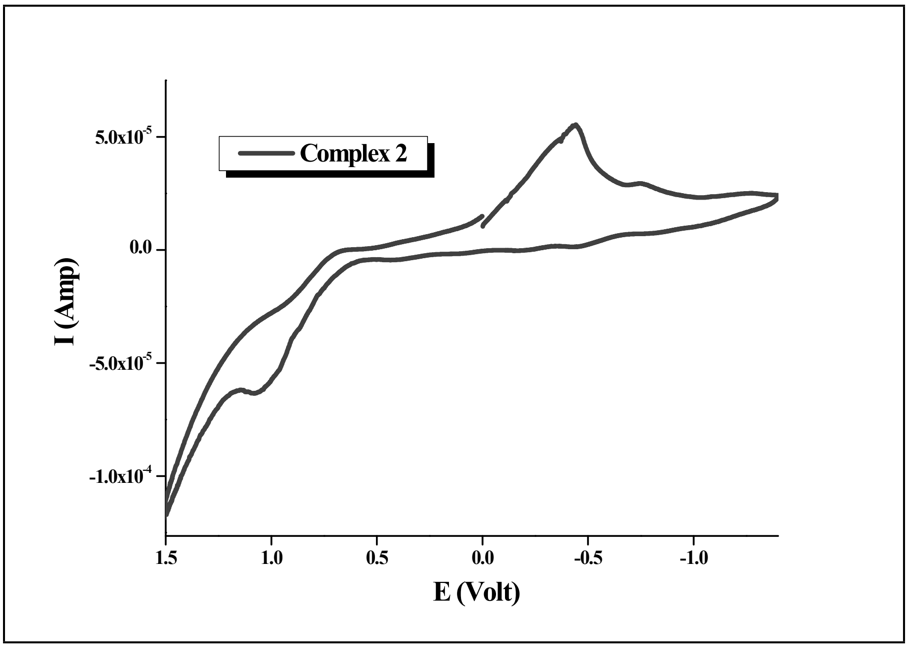


Fig. S5 Cyclic voltammogram of complex **2** in acetonitrile solution (scan rate 50 mV/s)

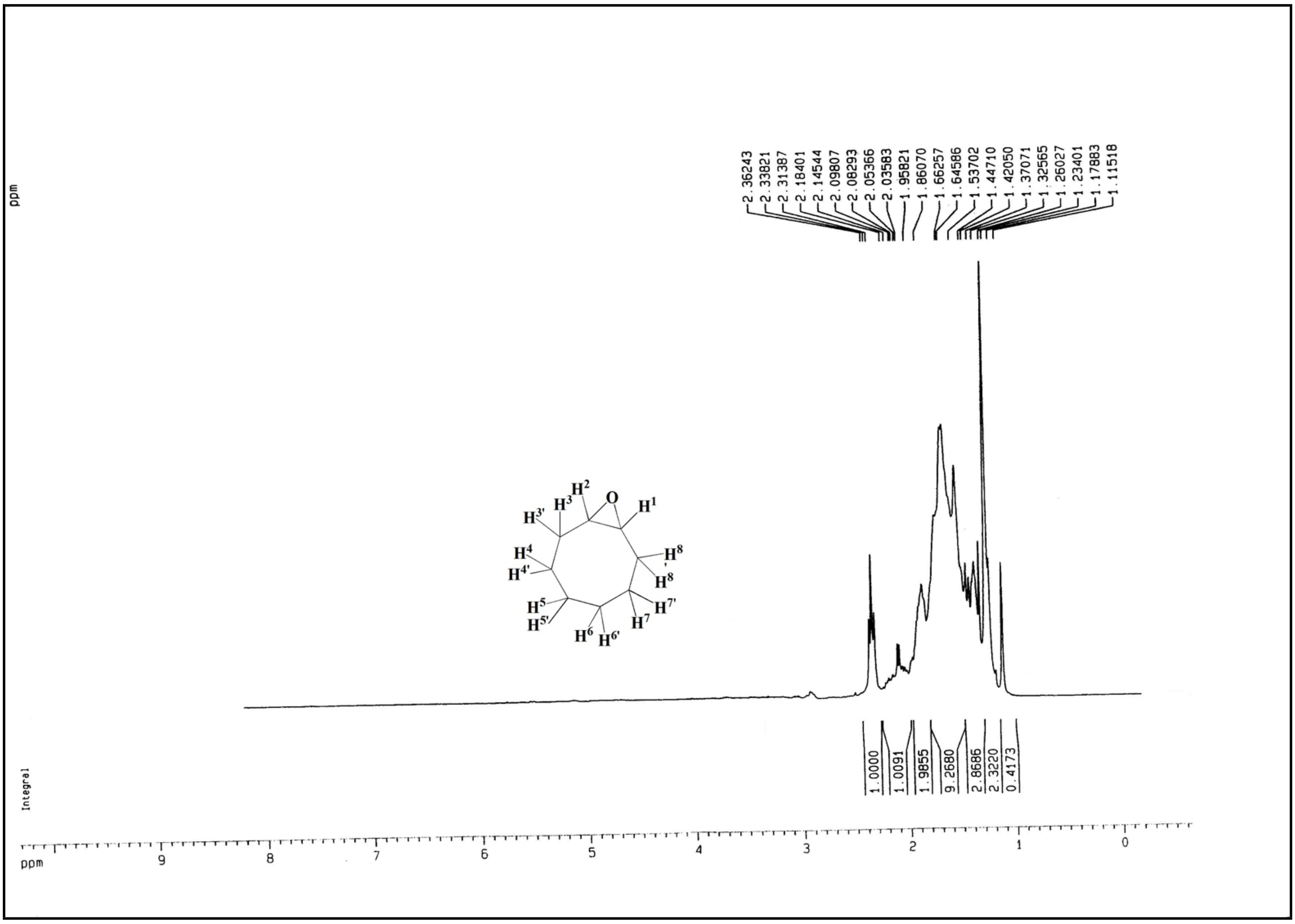


Fig. S6 ^{1}H NMR spectrum (in $CDCl_3$) of catalytic product obtained after column chromatography (using 5% ethylacetate in hexane) of the reaction mixture of *cis*cyclooctene (**R**), catalysts and TBHP (5.0–6.0 M in n-decane).

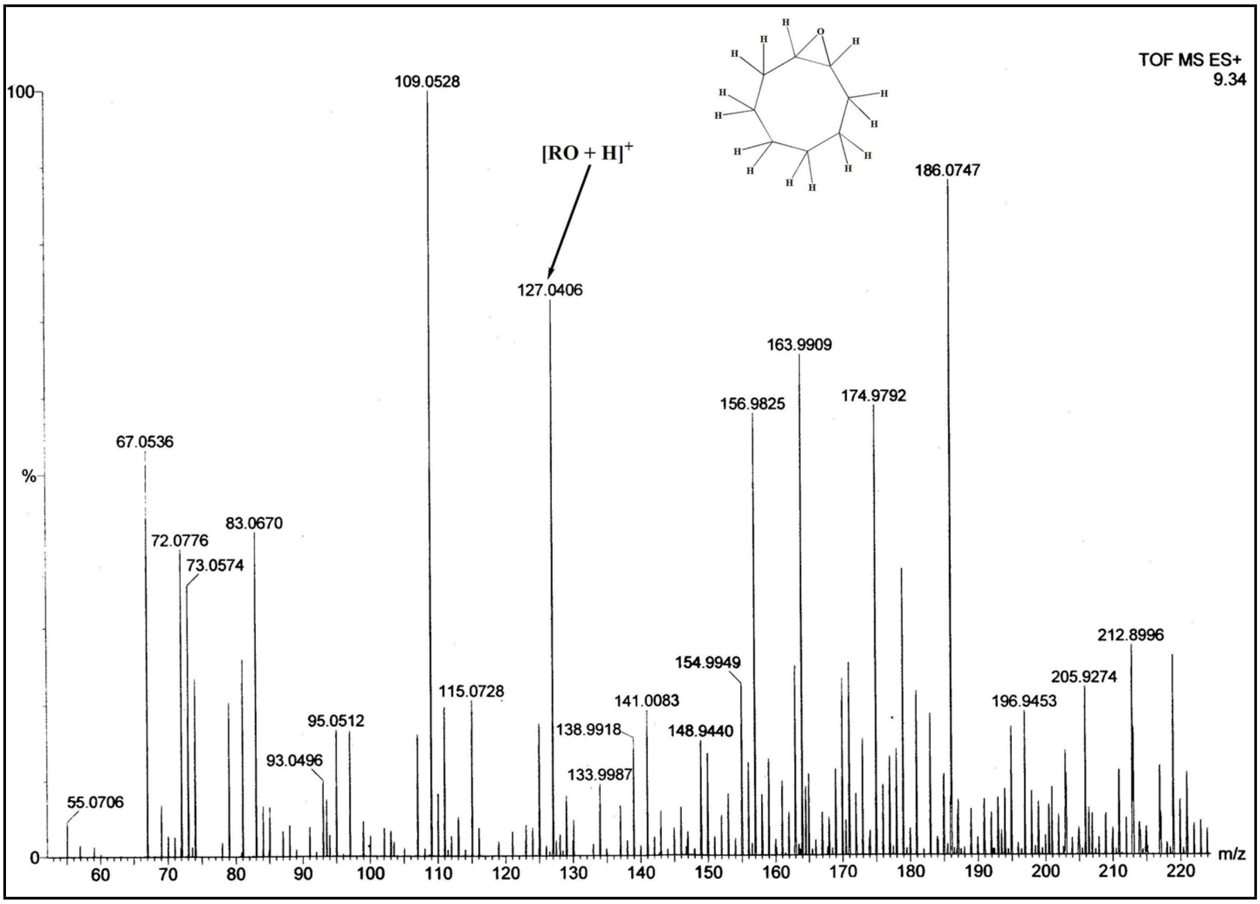


Fig. S7 ESI mass spectrum (in $CDCl_3$) of catalytic product obtained after column chromatography (using 5% ethylacetate in hexane) of the reaction mixture of *cis*cyclooctene (**R**), catalysts and TBHP (5.0–6.0 M in n-decane).