

Supplementary Information

for

Oxido- and Mixed-Ligand Peroxido Complexes of Niobium(V) as Potent Phosphatase Inhibitors and Efficient Catalysts for Eco-Friendly Styrene Epoxidation

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Characterization of the synthesized complexes

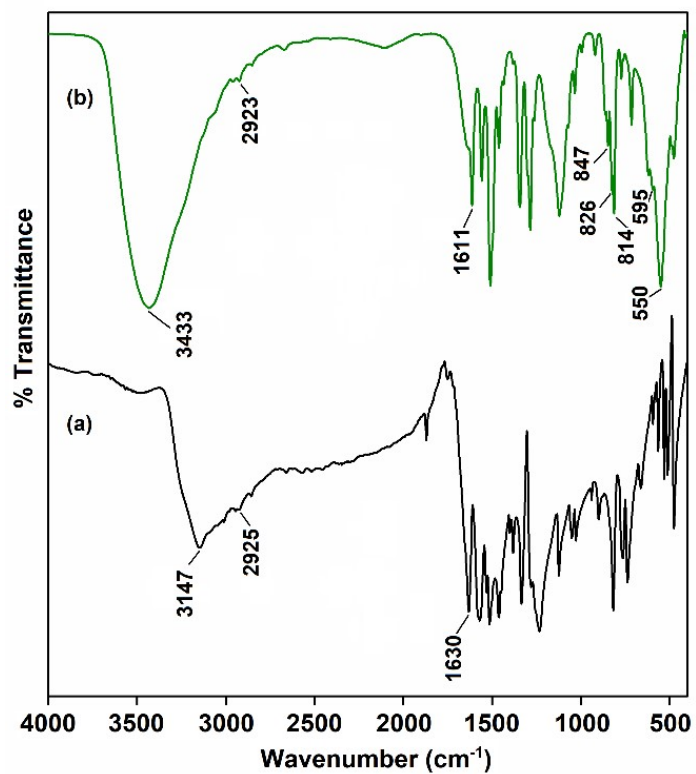


Fig. S1 FTIR spectra of (a) Deferiprone and (b) complex 3.

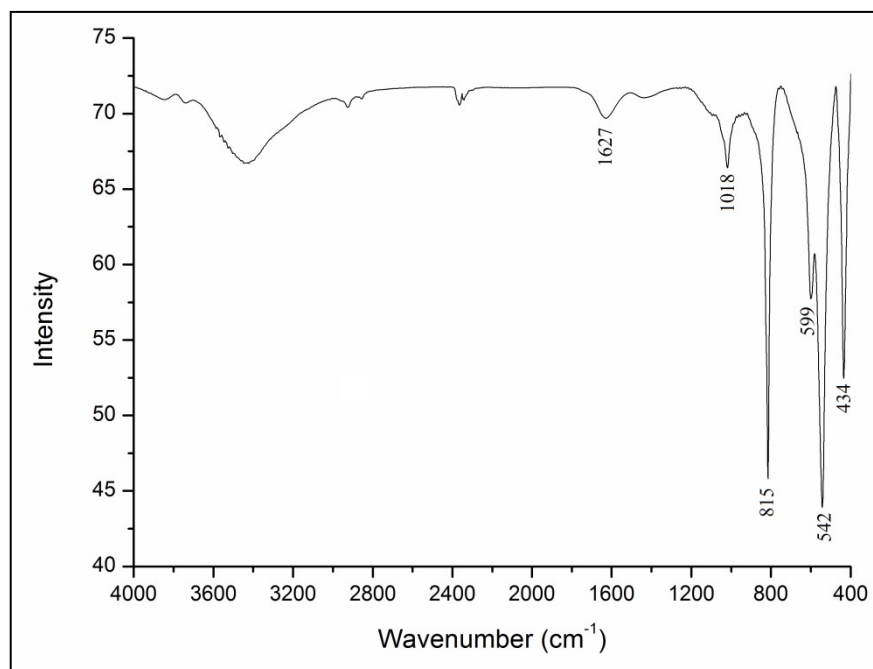
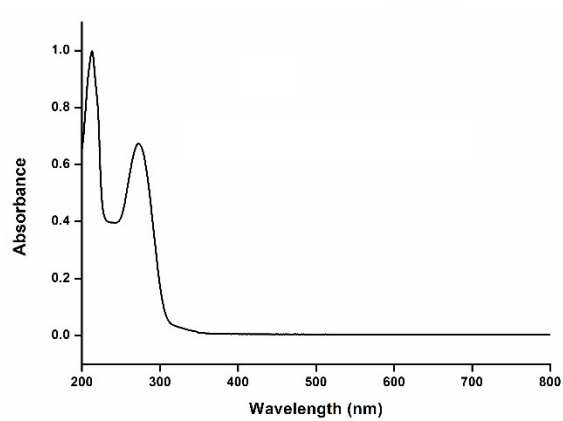
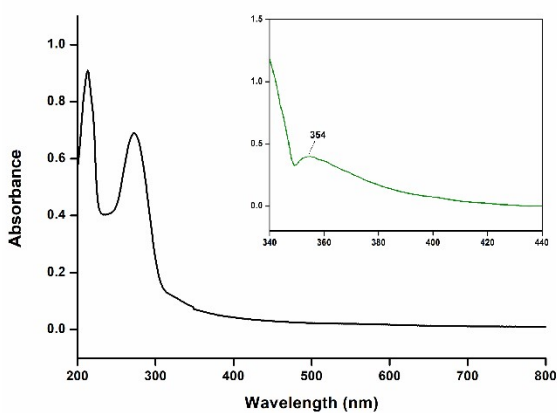


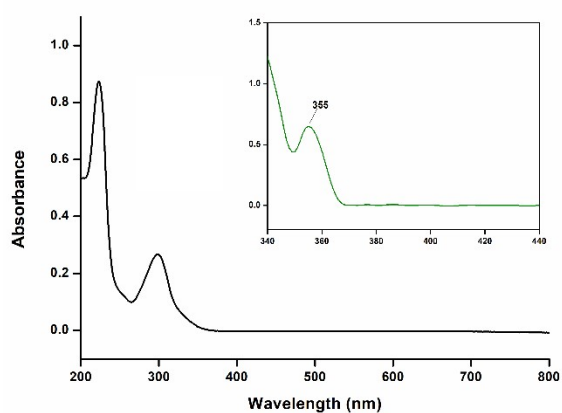
Fig. S2 IR spectrum of complex 4.



(a)



(b)



(c)

Fig. S3 UV-Vis absorption spectra of (a) **1** (conc.: 2.5×10^{-5} M), (b) **2** (conc.: 2.5×10^{-5} M; Inset conc.: 2.0×10^{-2} M) and (b) **3** (conc.: 2.5×10^{-5} M; Inset conc.: 2.0×10^{-2} M) in H_2O .

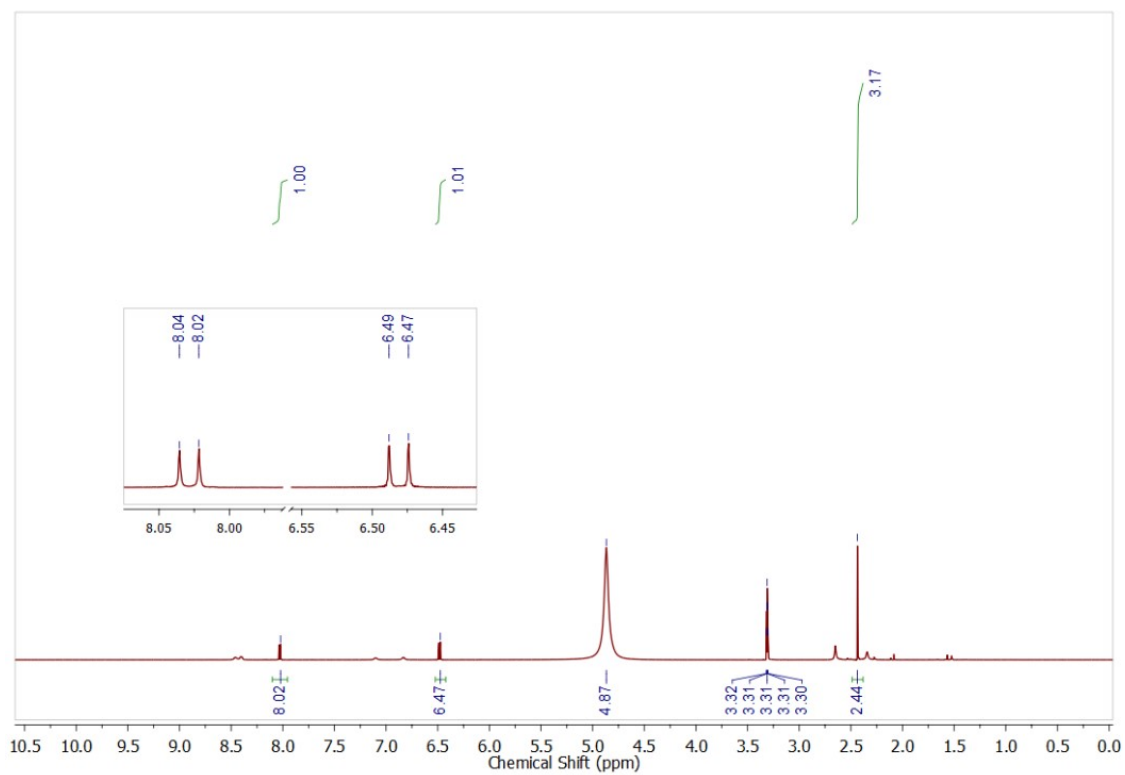


Fig. S4 ¹H NMR spectrum of **1** in Methanol-*d*₄.

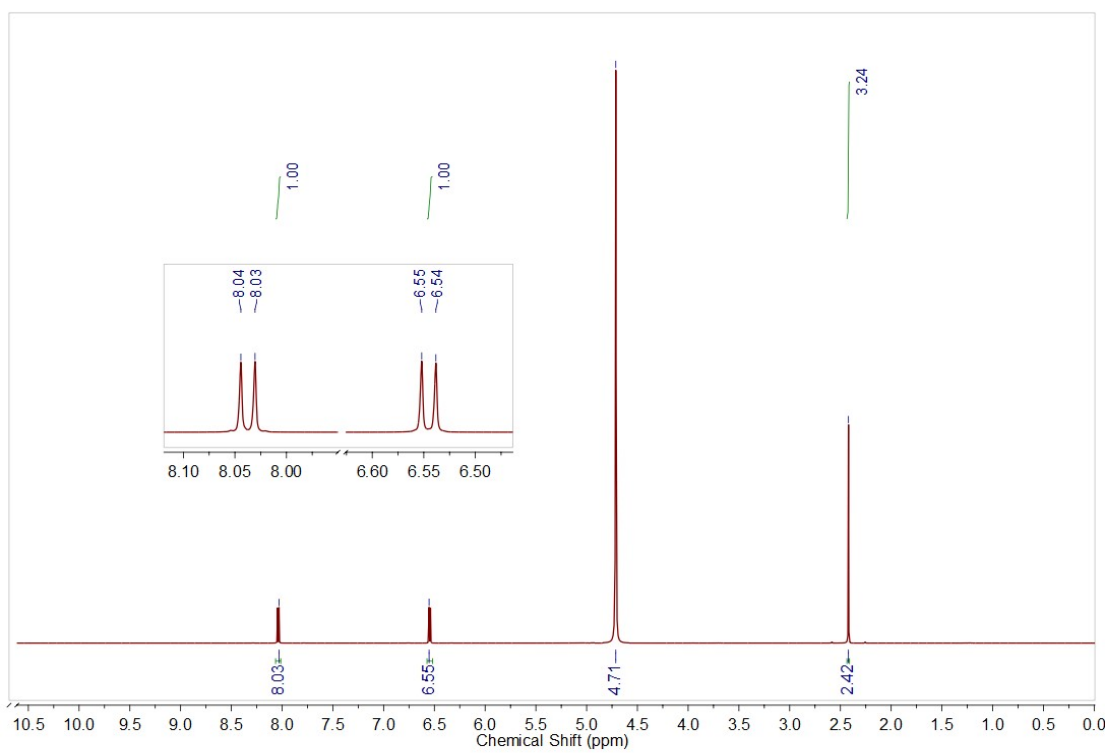


Fig. S5 ¹H NMR spectrum of **2** in D₂O.

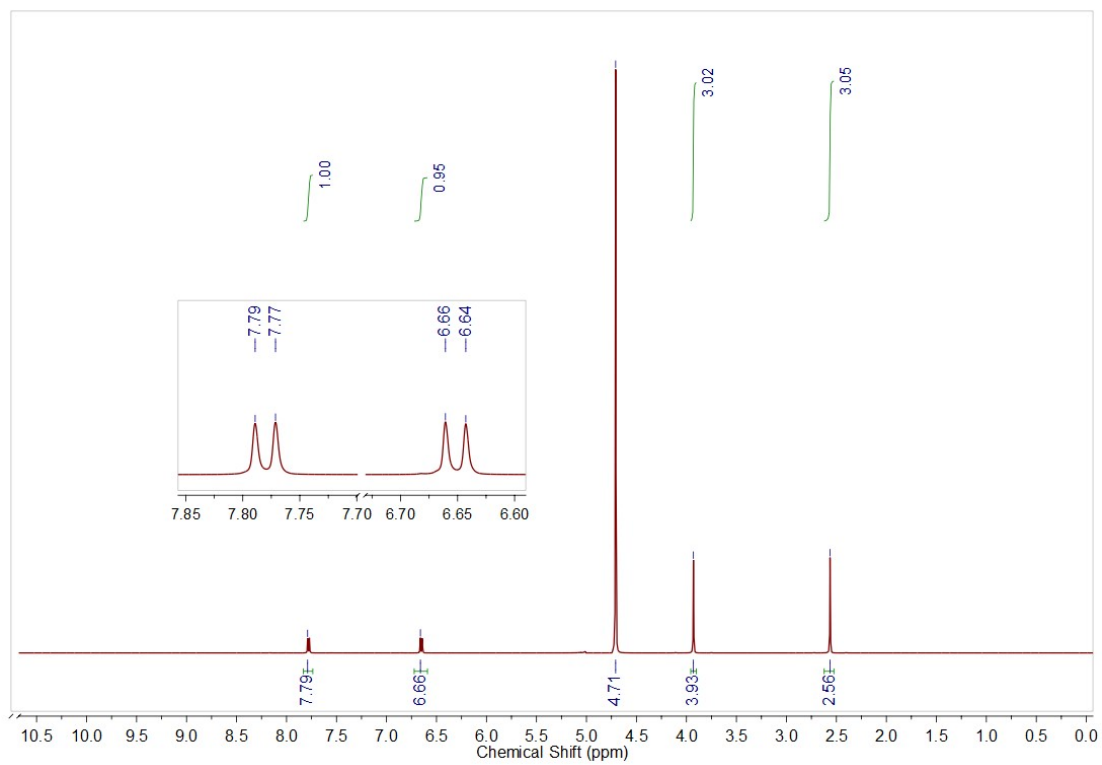


Fig. S6 ^1H NMR spectrum of **3** in D_2O .

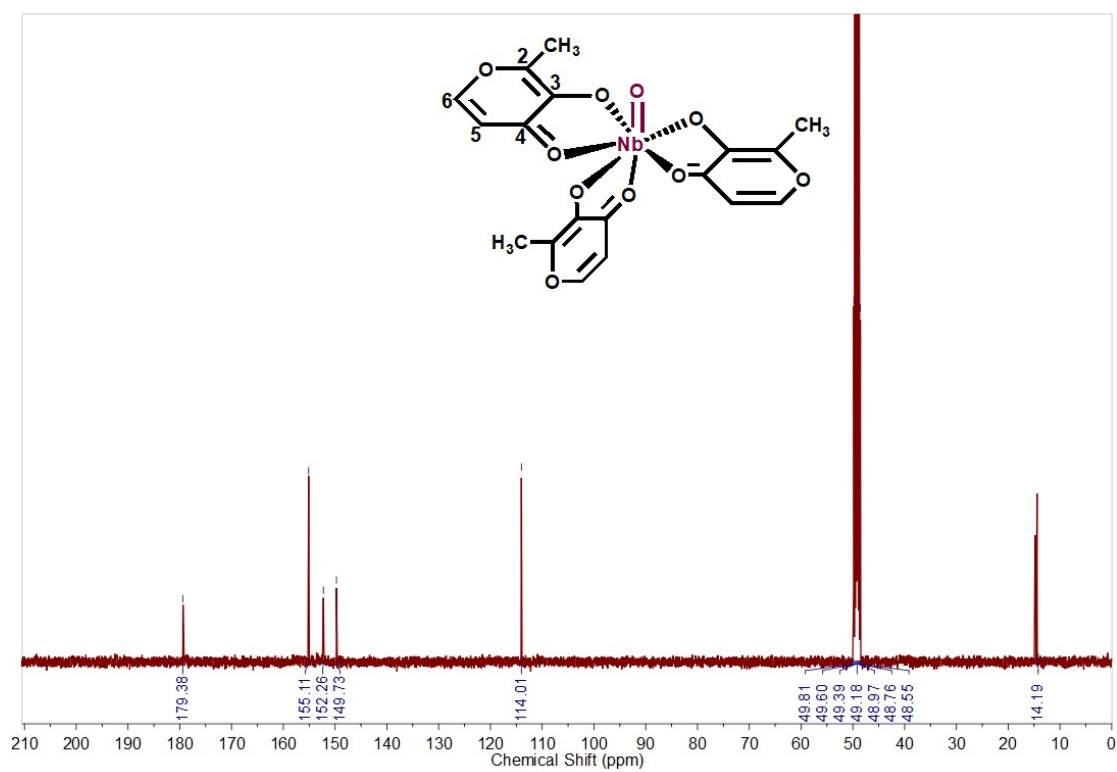
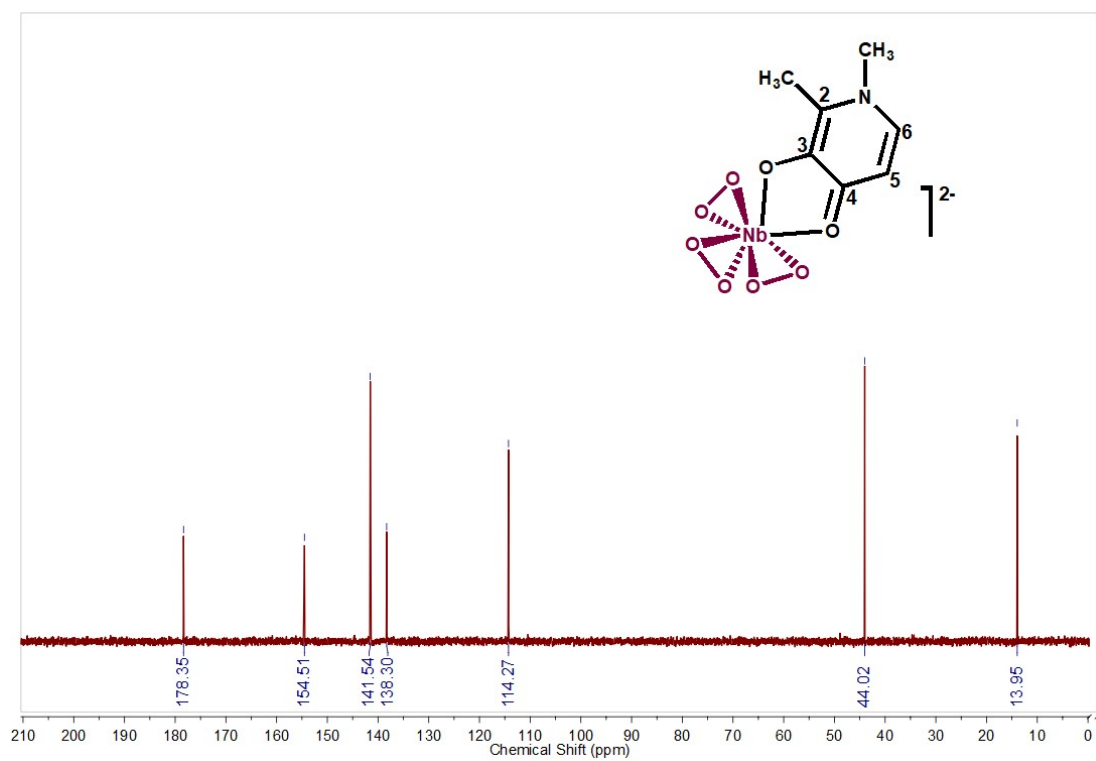
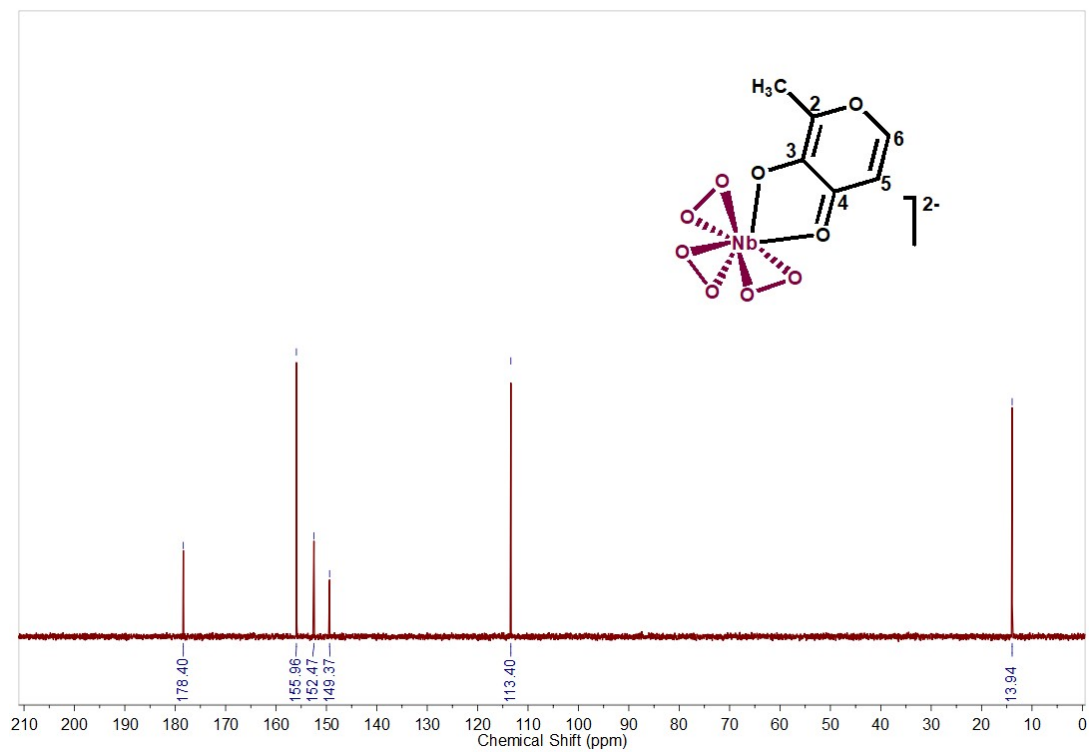


Fig. S7 ^{13}C NMR spectrum of **1** in $\text{Methanol-}d_4$.



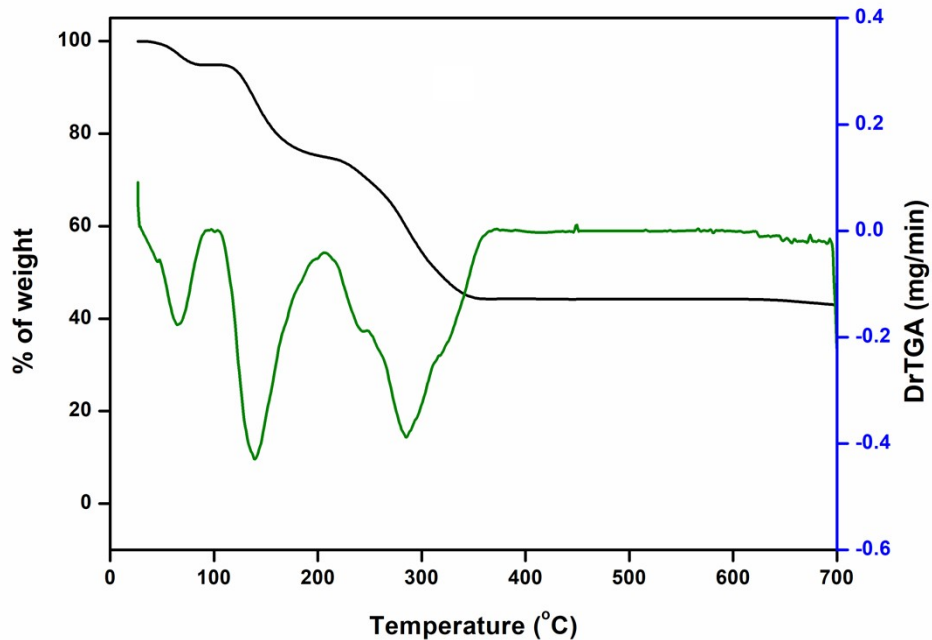


Fig. S10 TGA-DTG plots of complex **2**.

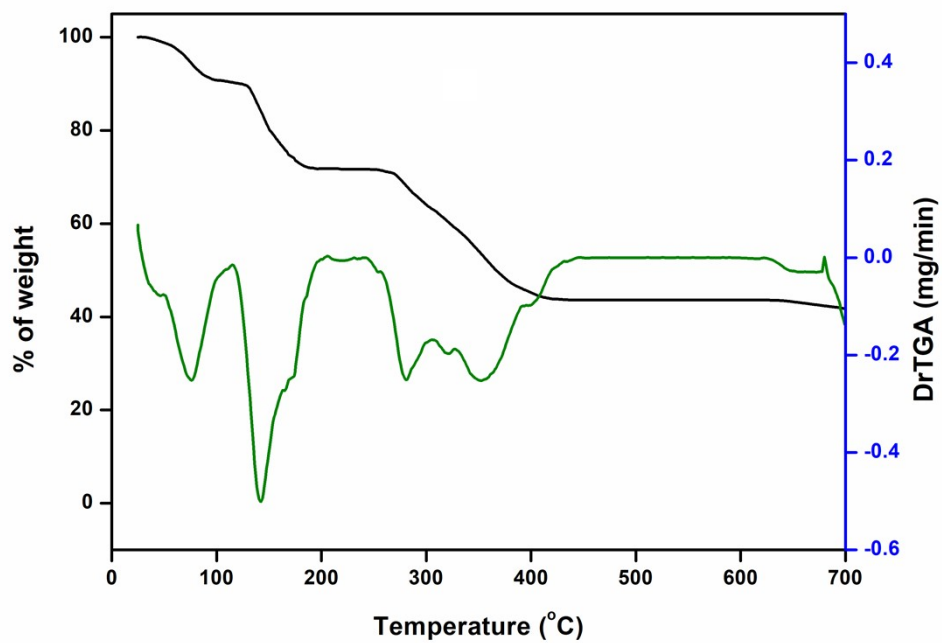


Fig. S11 TGA-DTG plots of complex **3**.

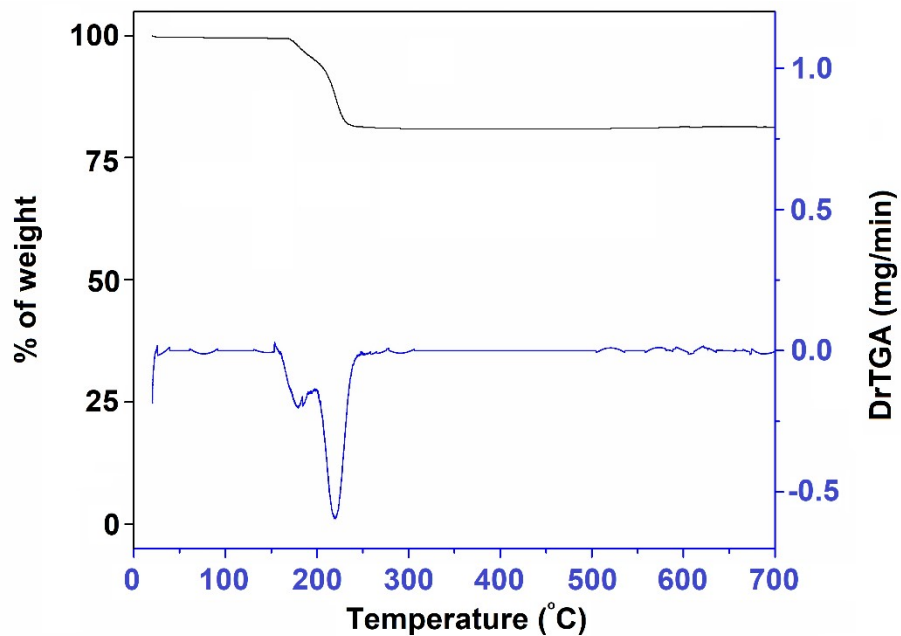


Fig. S12 TGA-DTG plots of complex **4**.

Table S1 Thermogravimetric data of niobium(V) complexes

Compound	Temperature range (°C)	Observed weight loss (%)	Final residue (%)
1	35-120	14.43	23.02
	135-550	62.55	
2	36-102	5.07	45.01
	112-204	19.66	
	215-373	30.26	
3	35-102	9.10	44.56
	118-212	18.42	
	223-430	27.92	
4	165-255	18.34	81.66

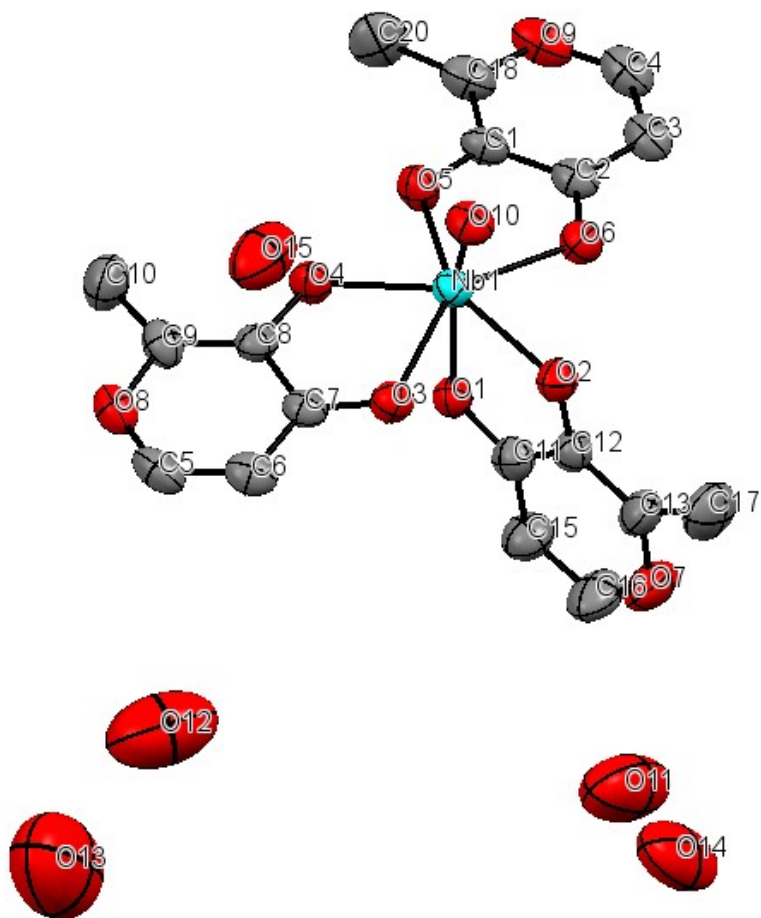


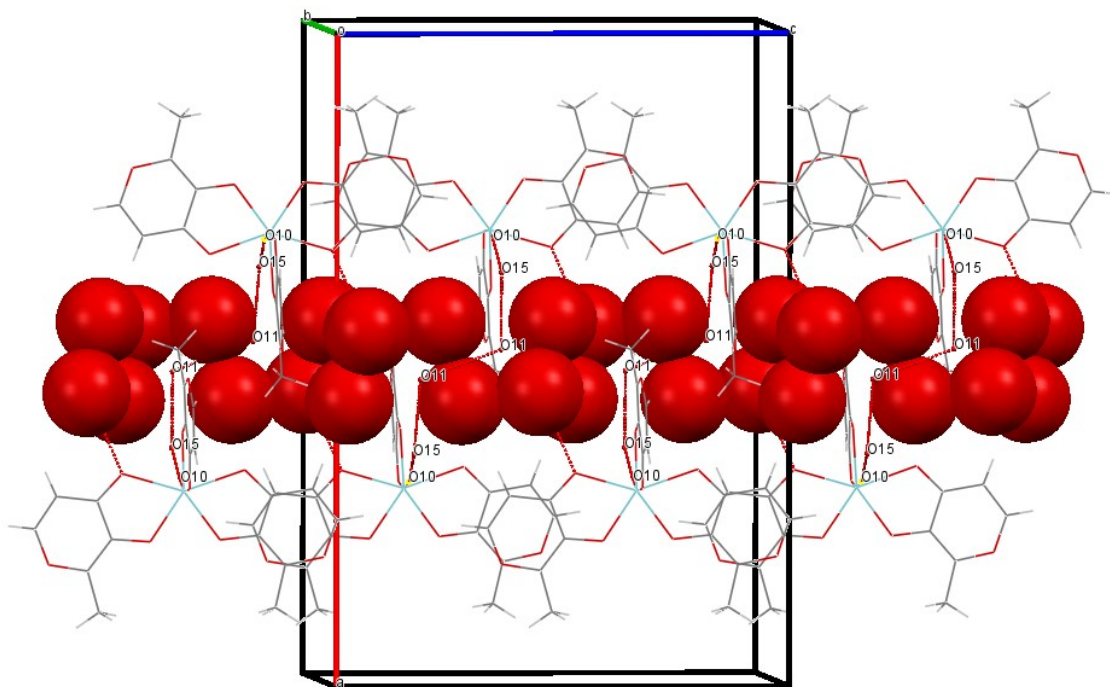
Fig. S13 ORTEP representation of the crystal structure of $[\text{NbO}(\text{malt})_3]_2 \cdot 9\text{H}_2\text{O}$ showing atom numbering scheme of non-hydrogen atoms. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table S2 Selected bond lengths and bond angles of **1** and **4**

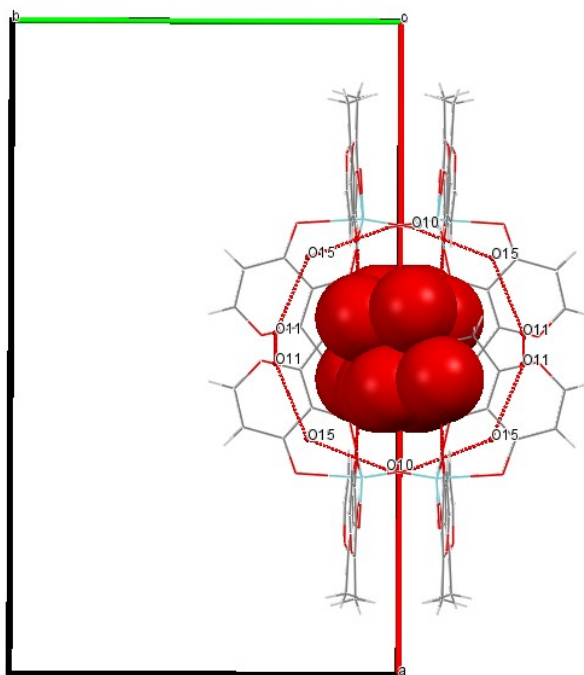
Bond length (Å)				
1		4		
Nb1-O10	1.724(3)	Nb1-O1	1.9992(12)	
Nb1-O1	2.270(3)	Nb1-O2	2.0539(10)	
Nb1-O2	2.079(3)	O1-O2	1.510(2)	
Nb1-O3	2.223(3)	O1-K1	2.6620(5)	
Nb1-O4	2.078(3)	O2-K1	3.0156(14)	
Nb1-O5	2.077(3)	O2-K3	2.7533(10)	
Nb1-O6	2.223(3)	K1-K3	3.90949(9)	
Bond angle (°)				
1		4		
O10-Nb1-O1	166.80(14)	O1-Nb1-O2	93.10(5)	
O10-Nb1-O2	92.98(15)	Nb1-O1-O2	70.06(6)	
O10-Nb1-O3	91.19(12)	Nb1-O1-K1	113.25(3)	
O10-Nb1-O4	102.46(14)	O2-O1-K1	88.06(4)	
O10-Nb1-O5	101.28(14)	Nb1-O2-O1	66.21(6)	
O10-Nb1-O6	93.86(12)	Nb1-O2-K3	172.71(11)	
O2-Nb1-O1	73.98(12)	O1-O2-K1	61.91(5)	

Table S3 Potential hydrogen bonds in the complex $[\text{NbO}(\text{malt})_3]_2 \cdot 9\text{H}_2\text{O}$ (**1**)

Entry	Donor-H...Acceptor	H...A (Å)	D-H...A (°)
1	C ₄ -H ₄ ...O ₁	2.52	130
2	C ₄ -H ₄ ...O ₁₀	2.58	131
3	C ₅ -H ₅ ...O ₁₀	2.51	133
4	C ₁₆ -H ₁₆ ...O ₁₁	2.59	179



(a)



(b)

Fig. S14 (a), (b) Water tap through O–H···O hydrogen bonding along the crystallographic axis [001] connecting the host molecules in $[\text{NbO}(\text{malt})_3]_2 \cdot 9\text{H}_2\text{O}$.

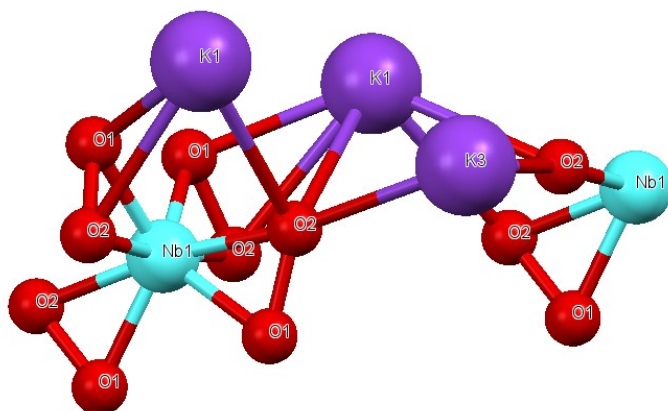


Fig. S15 Ball and stick representation of $K_3[Nb(O_2)_4]$ showing the connectivity between two $[Nb(O_2)_4]^{3-}$ units.

Table S4 Bond lengths (Å) and bond angles (°) of the pNb complexes (a) **2** and (b) **3** corresponding to the central metal atom Nb connected to the surrounding oxygen atoms of the ligands obtained at the M06-2X/def2-TZVPP level of theory.

Structural index^a	2	3
Nb1-O2	1.97945	1.98143
Nb1-O3	1.94981	1.95288
Nb1-O4	1.97663	1.98113
Nb1-O5	1.97664	1.97905
Nb1-O6	1.98068	1.97953
Nb1-O7	2.34255	2.31100
Nb1-O8	1.97946	1.98057
Nb1-O9	2.41861	2.42149
O2-O4	1.46055	1.46020
O5-O8	1.46054	1.46089
O3-O6	1.45903	1.45921
∠O3-Nb1-O6	43.572	43.557
∠O2-Nb1-O4	43.331	43.246
∠O5-Nb1-O8	43.331	43.301
∠O7-Nb1-O9	68.358	68.436

See **Fig. 6** for atom numbering

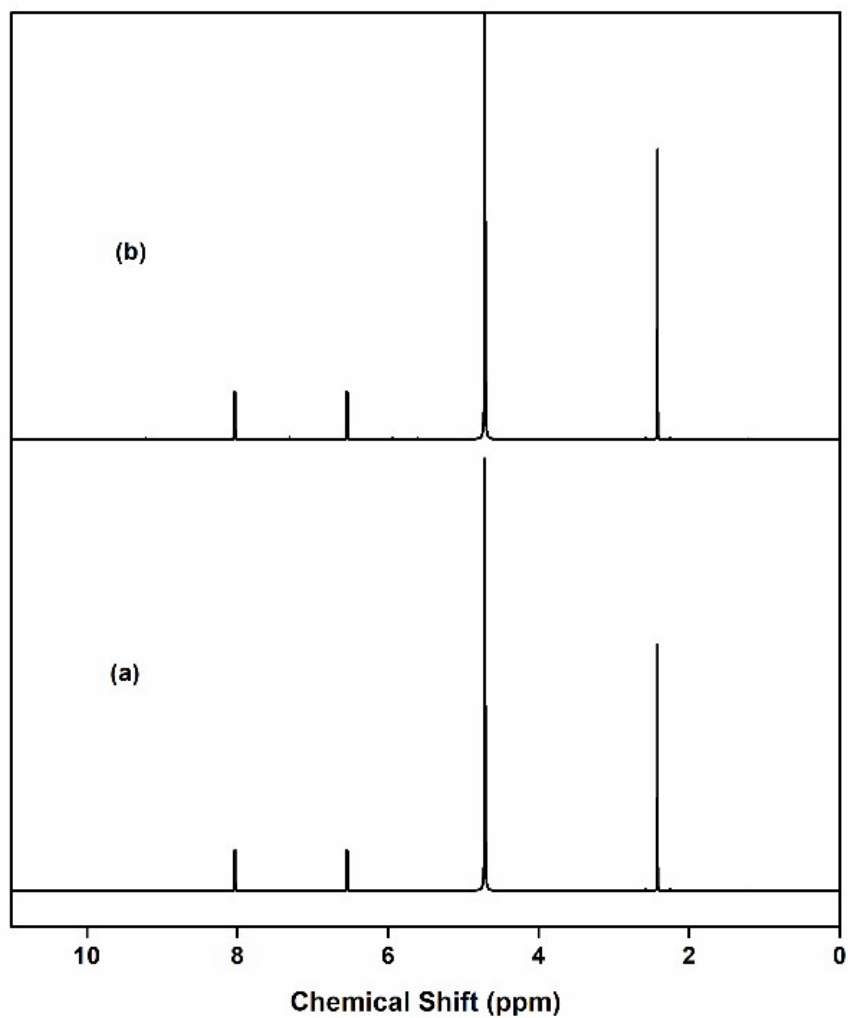


Fig. S16 ¹H NMR spectra of complex **2** in D₂O. The spectra were recorded as follows: (a) solution of **2** immediately after preparation and (b) solution of (a) after 12 h.

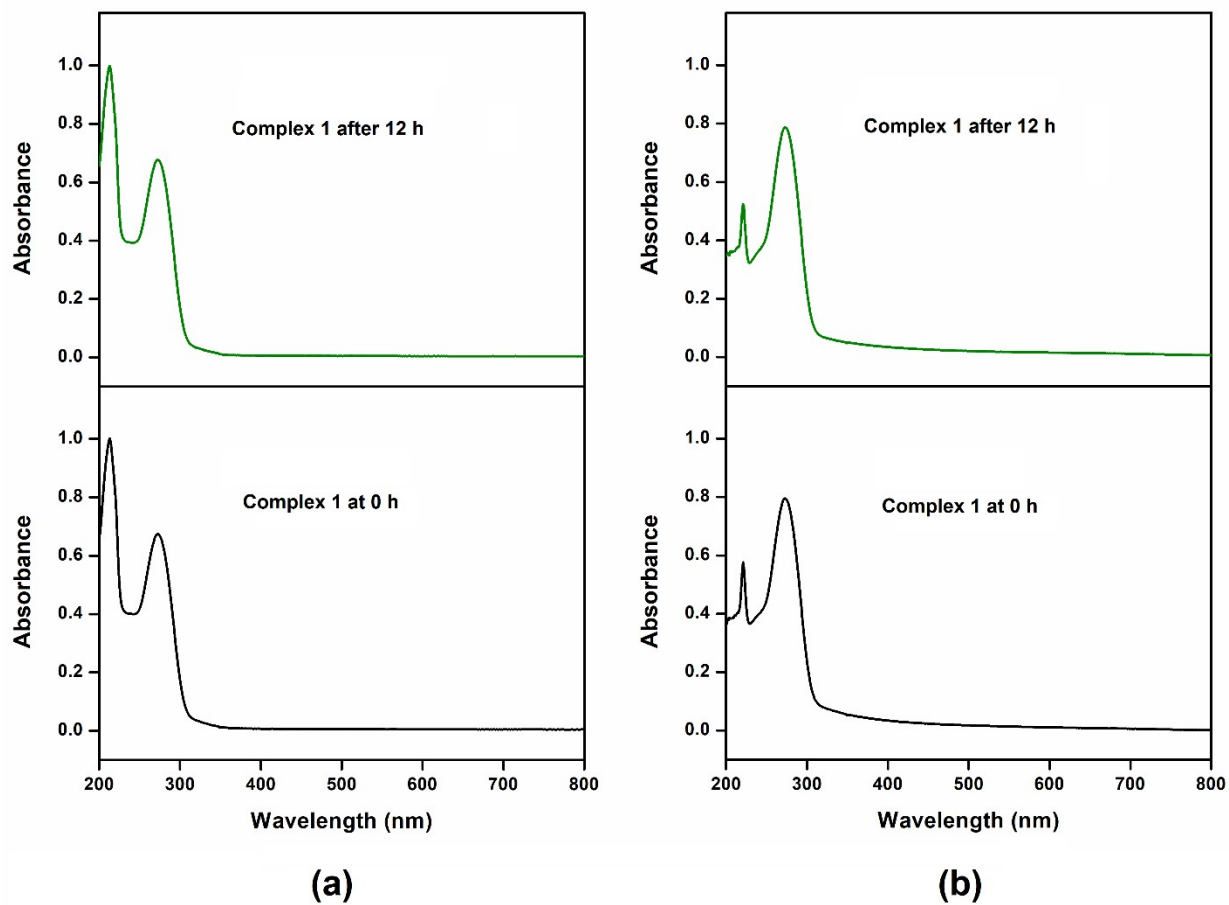


Fig. S17 UV-visible spectra of complex **1** recorded immediately after preparation and 12 h later (a) at natural pH (5.2) of the complex and (b) at pH = 4.6.

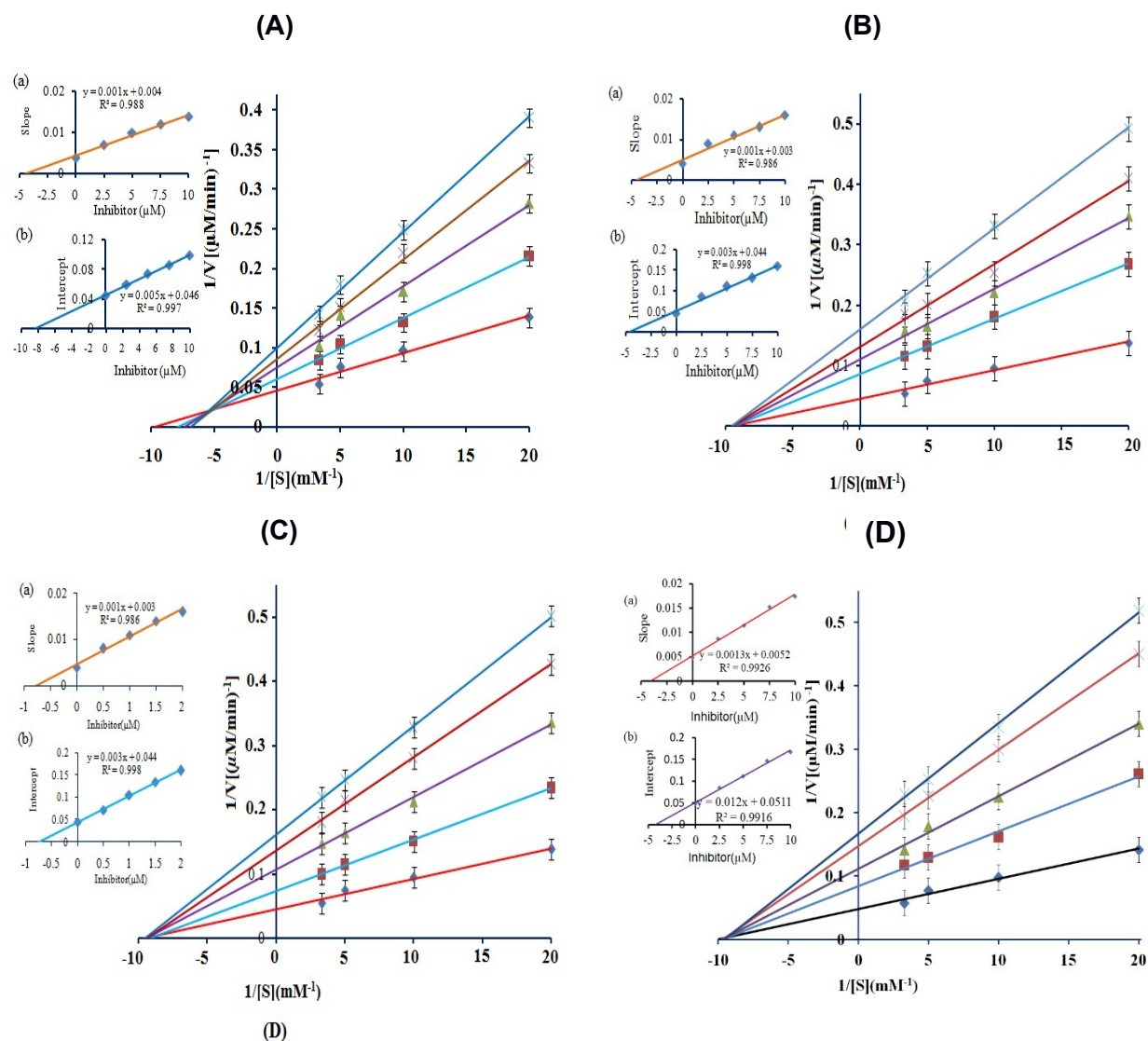
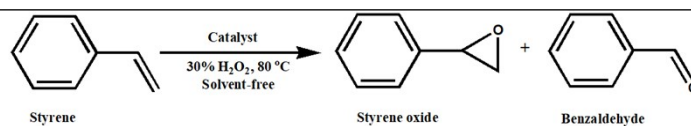


Fig. S18 L-B plots for the ACP inhibition in the absence and presence of \blacklozenge $0 \mu\text{M}$, \blacksquare $2.5 \mu\text{M}$, \blacktriangle $5 \mu\text{M}$, \times $7.5 \mu\text{M}$, ж $10 \mu\text{M}$ concentrations of (A) **4**, (B) **6**, (C) **5** and (D) **7**. The reaction started with the addition of ACP ($18.38 \mu\text{g mL}^{-1}$) to the pre-incubated reaction solution of 0.1 M acetate buffer (pH 4.6) and *p*-NPP ($50\text{-}300 \mu\text{M}$) and then the rates of hydrolysis were determined. The results are expressed as means \pm SE ($n = 3$) from independent experiments. Inset: (a) secondary plot of slopes versus $[I]$, where x -intercept defines the K_i value. (b) secondary plot of y -intercepts against $[I]$, where x -intercept refers to K_{ii} value.

Table S5 Optimization of reaction conditions for styrene epoxidation using complex **2**^a

Entry	Molar ratio Nb:styrene	30% H ₂ O ₂ (equiv.)	Time (h)	Temperature (°C)	Styrene conversion (%)	Epoxide selectivity (%)	TON ^b
1	1:1000	2	10	RT	9	≥98	90
2	1:1000	2	10	40	28	≥98	280
3	1:1000	2	10	60	66	≥98	660
4	1:1000	2	10	80	99	≥98	990
5	1:1000	1	10	80	90	≥98	900
6	1:1000	3	10	80	96	≥98	960
7	1:1000	4	10	80	93	≥98	930
8	1:1000	5	10	80	89	≥98	890
9	1:1500	2	10	80	94	≥98	1424
10	1:2000	2	10	80	87	≥98	1740
11	1:1000	2	0.5	80	17	≥98	170
12	1:1000	2	1	80	40	≥98	400
13	1:1000	2	2	80	84	≥98	840
14	1:1000	2	3	80	89	≥98	890
15	1:1000	2	4	80	91	≥98	910
16	1:1000	2	5	80	93	≥98	930
17	1:1000	2	6	80	96	≥98	960
18	1:1000	2	8	80	97	≥98	970
19	1:1000	2	12	80	99	≥98	990
20 ^c	1:1000	2	10	80	34	≥96	340
21 ^d	-	2	10	80	8	≥86	-

^a Reaction conditions: 5 mmol (0.52 g) styrene without solvent. ^b TON (turn-over number) = mmol of substrate consumed per mmol of Nb. ^c Reaction with Na₃[Nb(O₂)₄]•13H₂O as catalyst. ^d Blank reaction under catalyst-free condition.

Text S1 Experimental section

S1 Materials and methods

The chemicals used are all reagent-grade products. The sources of chemicals are as follows: *p*-nitrophenyl phosphate (*p*-NPP), maltol (3-Hydroxy-2-methyl-4-pyrone), deferiprone (3-Hydroxy-1,2-dimethylpyridin-4(1H)-one) (TCI Chemicals), hydrogen peroxide [(30%(w/v))], acetone, potassium dihydrogen phosphate, potassium hydrogen phosphate (RANKEM), potassium iodide, sodium-bicarbonate, sodium acetate anhydrous (SRL), sodium thiosulfate, potassium dichromate, sodium hydroxide, methanol, concentrated sulphuric acid (E. Merck, India), boric acid (Emplura), niobium(V) oxide, niobium(V) chloride, acid phosphatase (ACP) from the wheat thylakoid membrane (Sigma-Aldrich Chemical Co., Milwaukee, USA). Solutions were prepared under distilled and deionized water.

The elemental composition of the synthesized compounds was determined by PerkinElmer 2400 series II CHN analyser. The niobium and sodium content were estimated by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in an Avio 220 Max Perkin Elmer spectrometer. Peroxide content in the complexes was estimated volumetrically by iodometric titration (adding a weighted amount of the complex to a cold solution of 1.5% boric acid (w/v) in 0.7 M 100 mL H₂SO₄ and titrated with the standardized sodium thiosulphate solution). The Infrared spectral analyses were carried out in a Perkin-Elmer spectrum 100 FTIR spectrophotometer. An EZRaman-N (Enwaveoptronics), with a diode laser of 350 mW maximum output power and 785 nm excitation wavelength was used to record the Raman spectra. The UV-vis absorption spectra were recorded in solution in a 1 cm quartz cuvette using an Agilent Cary100 Bio spectrophotometer. Thermogravimetric analysis (TGA) was carried out in an aluminium pan with a SHIMADZU TGA-50 system at a heating rate of 10 °C min⁻¹ under an N₂ atmosphere. The ¹H and ¹³C NMR spectra of the compounds were recorded with a Bruker AVANCE NEO, 400 NanoBay 400 MHz FT-NMR spectrometer at a proton frequency of 400.15 MHz, number of scan 256, 4 s of acquisition time and carbon frequency of 100.61 MHz, number of scans 1024, 1.38 s of acquisition time in D₂O (for **2** and **3**) as well as in methanol-*d*₄ (for **1**) as solvents. Magnetic susceptibility of the complexes were measured using the calibrant Hg[Co(NCS)] with the help of the Gouy method.

Table S6 Coordinates of optimized structures of ground state geometries of the Nb compounds (a) **2** and (b) **3** obtained at the M06-2X/def2-TZVPP level of theory.

a) 2

-2 1

Nb	1.48725100	0.04807300	0.00004000
O	1.10599400	0.19788200	-1.93656300
O	3.33112900	-0.58587100	0.00079100
O	1.78739200	1.38426400	-1.42529900
O	1.78628300	1.38365800	1.42619400
O	2.40044700	-1.70952900	0.00008800
O	-0.25721900	-1.51537500	-0.00083100
O	1.10434000	0.19712900	1.93638200
O	-0.67744100	1.12687000	-0.00060900
C	-1.67155300	0.35700700	-0.00034700
C	-1.42060700	-1.09973500	-0.00049700
C	-3.00056400	0.75420200	0.00000800
C	-2.57179600	-1.96400100	-0.00027600
C	-3.81495300	-1.43522900	0.00007800
C	-3.43057500	2.17394200	0.00017800
H	-2.52626000	2.78025300	0.00033200
H	-4.02631800	2.42477800	-0.88424100
H	-4.02649400	2.42449800	0.88455400
O	-4.05344800	-0.13681900	0.00021000
H	-2.43180400	-3.03570200	-0.00035600
H	-4.72594200	-2.01958300	0.00028300

b) 3

-2 1

Nb	-1.75616900	-0.05413100	-0.00919200
O	-1.25928800	-0.17905700	-1.92323900
O	-3.62203000	0.51417500	-0.10583500
O	-1.94556700	-1.38389600	-1.46546400
O	-2.09531300	-1.42684900	1.37546200
O	-2.73171700	1.66812800	-0.03490600
O	-0.07316900	1.52706800	0.08048800
O	-1.47278000	-0.23320400	1.94280400
O	0.43176100	-1.08746300	0.08456200
C	1.40337500	-0.29481900	0.05414500
C	1.11577700	1.15423600	0.05936200
C	2.74807800	-0.69070600	0.02211600
C	2.22711900	2.04297700	0.05117200
C	3.51147800	1.56628000	0.02098500
C	3.08108900	-2.14737300	0.02267300
H	2.12738700	-2.67117400	-0.02817100
H	3.69206700	-2.45422300	-0.83331400
H	3.59869100	-2.47256600	0.93313500
H	2.04513300	3.10842800	0.06527900
H	4.37326600	2.22000000	0.00227600
N	3.77539900	0.24842300	0.00858000
C	5.14236500	-0.20835900	-0.08490700
H	5.32618200	-0.71078600	-1.03789200
H	5.80875600	0.64785000	-0.00545100
H	5.37279300	-0.91175300	0.71667100