Electronic Supplementary Information

Article

Vanadium Complexes with Methyl-substituted 8-Hydroxyquinolines: Catalytic Potential in the Oxidation of Hydrocarbons and Alcohols with Peroxides and Biological Activity

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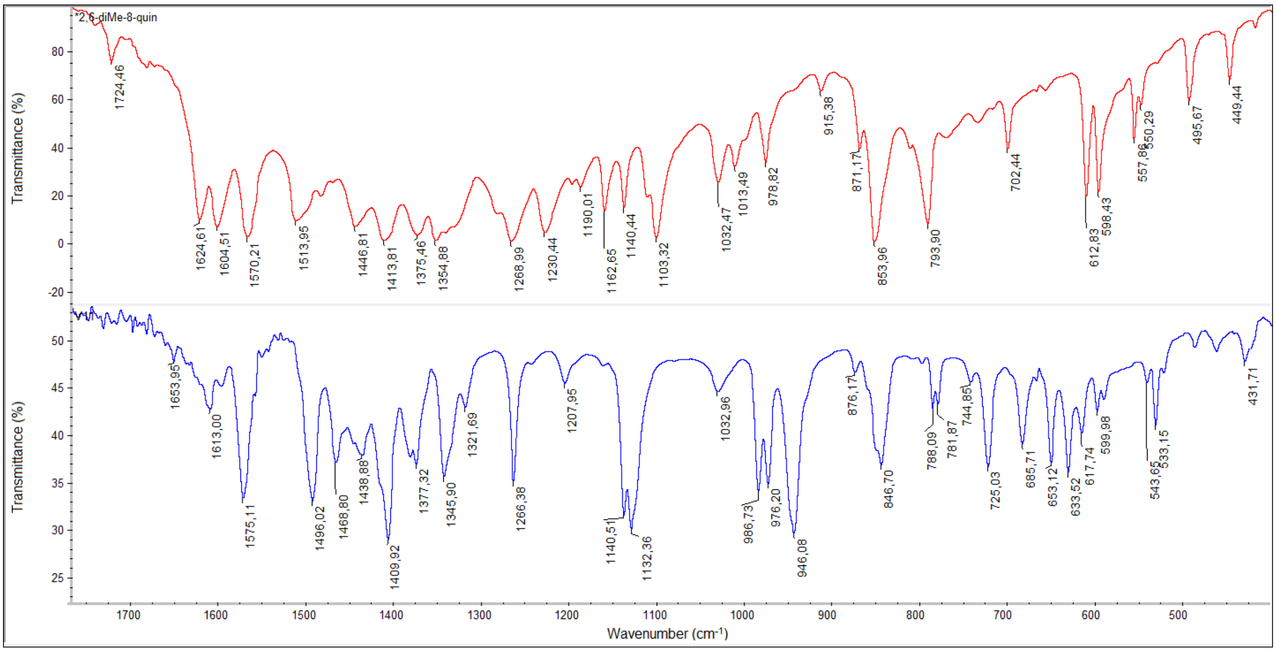
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1446,81
1413,81
1375,46
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1190,01
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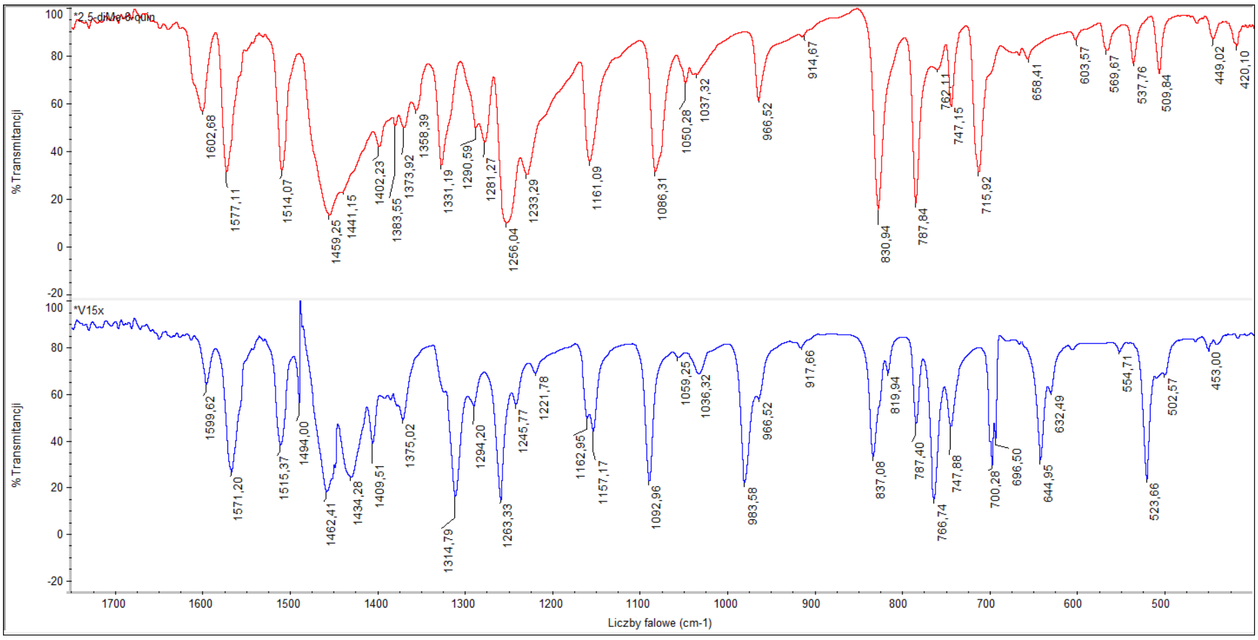
(a)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*V15x
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Liczby falowe (cm-1)
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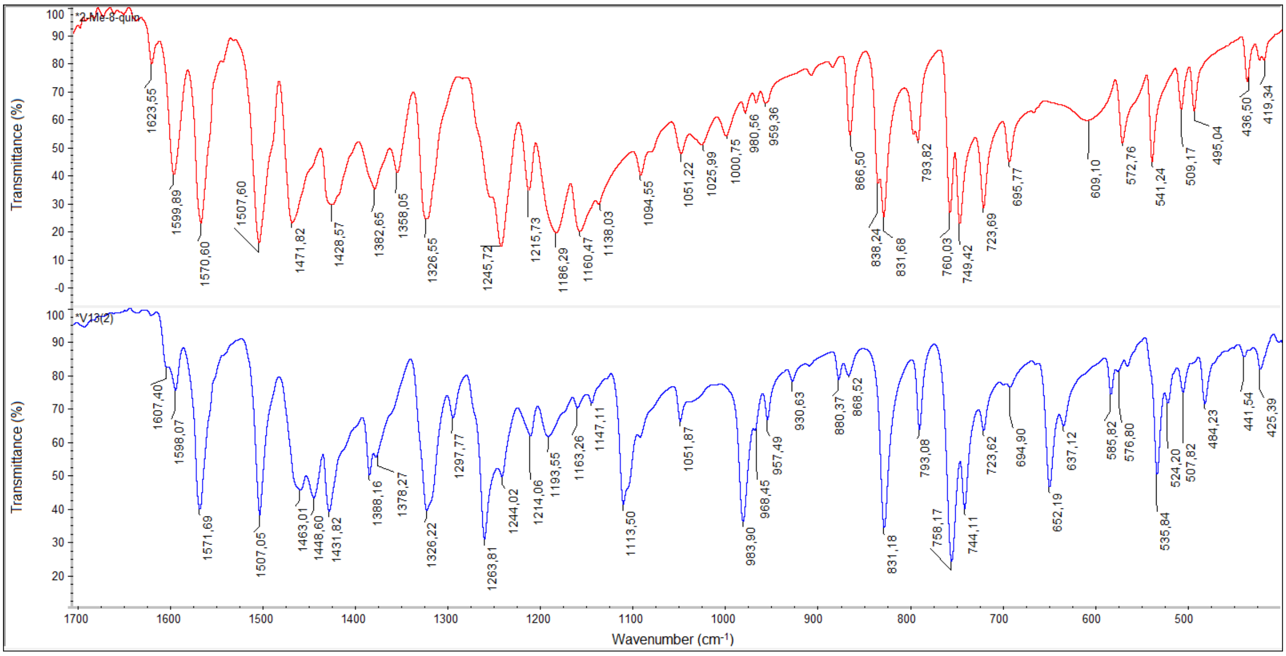
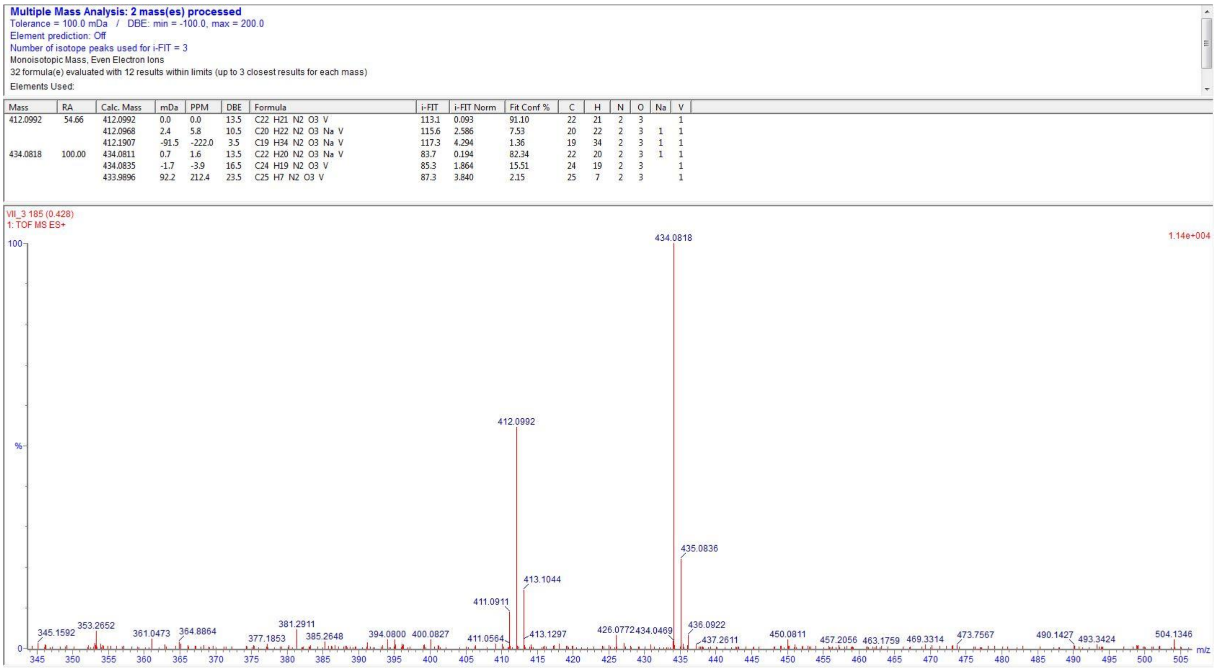
453,00

(b)



(c)

Figure S1. IR spectra of the complexes **1–3** (blue) and free ligands (red) (a-c).



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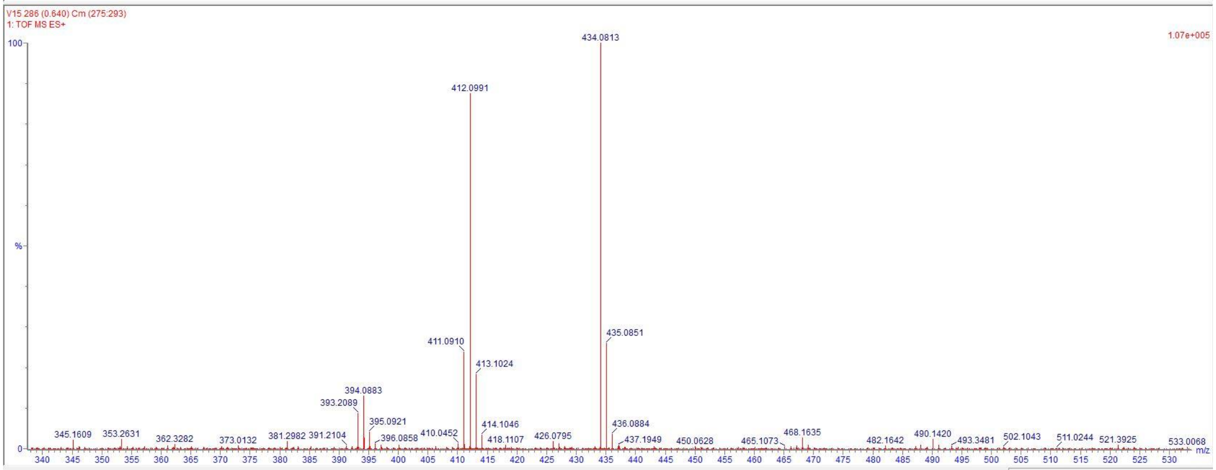
412.0992	54.66	412.0992	0.0	0.0	13.5	C22 H21 N2 O3 V	113.1	0.093	91.10	22	21	2	3		1
		412.0968	2.4	5.8	10.5	C20 H22 N2 O3 Na V	115.6	2.586	7.53	20	22	2	3	1	1
		412.1907	-91.5	-222.0	3.5	C19 H34 N2 O3 Na V	117.3	4.294	1.36	19	34	2	3	1	1
434.0818	100.00	434.0811	0.7	1.6	13.5	C22 H20 N2 O3 Na V	83.7	0.194	82.34	22	20	2	3	1	1
		434.0835	-1.7	-3.9	16.5	C24 H19 N2 O3 V	85.3	1.864	15.51	24	19	2	3		1
		433.9896	92.2	212.4	23.5	C25 H7 N2 O3 V	87.3	3.840	2.15	25	7	2	3		1

(a)

HRMS (ESI): calcd for $C_{22}H_{20}N_2O_3NaV^+$ $[M+Na]^+$ 434.0811 found 434.0818.

Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 100.0 mDa / DBE: min = -100.0, max = 200.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 12 results within limits (up to 3 closest results for each mass)
Elements Used:

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	Na	V
412.0991	87.55	412.0992	-0.1	-0.2	13.5	C22 H21 N2 O3 V	322.1	2.942	5.27	22	21	2	3		1
		412.0968	2.3	5.6	10.5	C20 H22 N2 O3 Na V	319.7	0.596	55.09	20	22	2	3	1	1
		412.1907	-91.6	-222.3	3.5	C19 H34 N2 O3 Na V	320.1	0.925	39.64	19	34	2	3	1	1
434.0813	100.00	434.0811	0.2	0.5	13.5	C22 H20 N2 O3 Na V	290.5	0.677	50.81	22	20	2	3	1	1
		434.0835	-2.2	-5.1	16.5	C24 H19 N2 O3 V	290.5	0.730	48.20	24	19	2	3		1
		433.9896	91.7	211.3	23.5	C25 H7 N2 O3 V	294.4	4.613	0.99	25	7	2	3		1

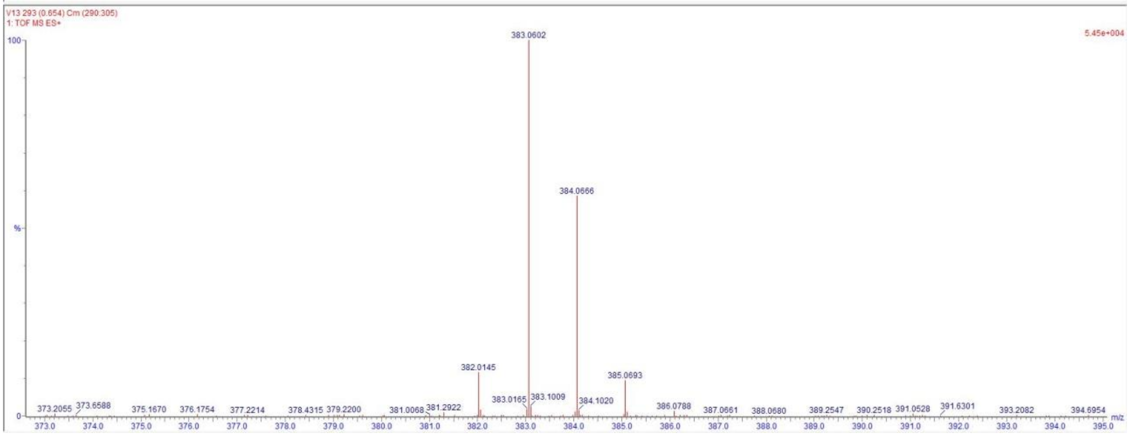


(b)

HRMS (ESI): calcd for $C_{22}H_{20}N_2O_3NaV^+$ $[M+Na]^+$ 434.0811 found 434.0813.

Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 50.0 mDa / DBE: min = -100.0, max = 200.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
36 formula(e) evaluated with 4 results within limits (up to 3 closest results for each mass)
Elements Used:

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	V
383.0602	100.00	383.0601	0.1	0.3	14.0	C20 H16 N2 O3 V	239.2	0.591	55.36	20	16	2	3	1
		383.0237	36.5	95.3	15.0	C19 H12 N2 O4 V	239.5	0.806	44.64	19	12	2	4	1
384.0666	58.54	384.0679	-1.3	-3.4	13.5	C20 H17 N2 O3 V	181.6	0.280	75.57	20	17	2	3	1
		384.0315	35.1	91.4	14.5	C19 H13 N2 O4 V	182.7	1.410	24.43	19	13	2	4	1



(c)

HRMS (ESI): calcd for $C_{20}H_{16}N_2O_3V$ $[M]^+$ 383.0601 found 383.0602.

Figure S2. HRMS spectra of the complexes **1–3** (a-c)

X-Ray studies

Table S1. Selected bond lengths (Å) and angles (deg) for **1**.

Bond lengths		Bond angles	
V(1)–O(1)	1.9210(14)	O(1)a–V(1)–O(1)	125.26(9)
V(1)–O(2)	1.590(2)	O(1)–V(1)–O(2)	117.37(5)
V(1)–N(1)	2.1239(15)	O(1)–V(1)–N(1)	80.51(6)
		O(1)a–V(1)–N(1)	89.93(6)
		O(2)–V(1)–N(1)	100.40(4)
		N(1)–V(1)–N(1)a	159.19(9)

[a]Symmetry transformations used to generate equivalent atoms: (a) = *-x,y,1/2-z*

Table S2. Selected bond lengths (Å) and angles (deg) for **2**.

Bond lengths		Bond angles	
V(1)–O(1)	1.924(2)	O(1)–V(1)–O(2)	126.96(11)
V(1)–O(2)	1.917(2)	O(1)–V(1)–O(3)	116.84(11)
V(1)–O(3)	1.595(3)	O(2)–V(1)–O(3)	116.20(12)
V(1)–N(1)	2.122(2)	O(1)–V(1)–N(1)	80.07(9)
V(1)–N(2)	2.125(2)	O(2)–V(1)–N(1)	91.91(9)
		O(3)–V(1)–N(1)	98.56(11)
		O(1)-V(1)-N(2)	90.18(9)
		O(2)-V(1)-N(2)	80.51(10)
		O(3)–V(1)–N(2)	100.85(11)
		N(1)–V(1)–N(2)	160.56(11)

Table S3. Selected bond lengths (Å) and angles (deg) for **3**.

Bond lengths		Bond angles	
V(1)–O(1)	1.9139(13)	O(1)[a]–V(1)–O(1)	127.03(9)
V(1)–O(2)	1.588(2)	O(1)–V(1)–O(2)	116.48(5)
V(1)–N(1)	2.1308(16)	O(1)–V(1)–N(1)	80.31(6)
		O(1)[a]–V(1)–N(1)	91.33(6)
		O(2)–V(1)–N(1)	99.36(4)
		N(1)–V(1)–N(1)[a]	161.29(9)

Table S4. Short intra- and intermolecular hydrogen bonds.

D–H•••A	D–H [Å]	H•••A [Å]	D–A [Å]	D–H•••A [°]
1				
C(10)–H(10A)•••O(1)[a]	0.96	2.56	3.237(3)	128.0
C(2)–H(2)•••O(2)[b]	0.93	2.66	3.142(3)	112.9
2				
C(10)–H(10C)•••O(2)	0.96	2.50	3.084(4)	119.0
C(21)–H(21C)•••O(1)	0.96	2.36	3.185(5)	144.0
C(22)–H(22A)•••O(3)[c]	0.96	2.49	3.399(5)	158.0
3				
C(10)–H(10C)•••O(1)	0.96	2.33	3.503(15)	145.2

Symmetry codes: (a) = *–x,y,*1/2*–z;* (b) = *–x,*1*-y,–z;* (c) = 2*–x,*1*–y,*2*–z;* (d) = 1–x,y,1/2–z

Table S5. Short π•••π interactions.

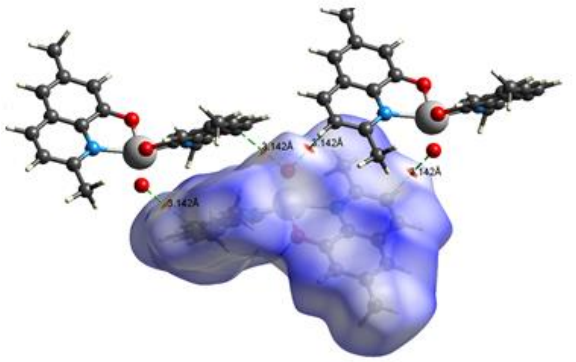
Cg(I)•••Cg(J)	Cg(I)•••Cg(J) [Å]	α [°]	β [°]	γ [°]	Cg(I)-Perp [Å]	Cg(J)-Perp [Å]
1						
Cg(1)•••Cg(1)[a]	3.5193(12)	0	12.33	12.33	3.4381(8)	3.4381(8)
Cg(1)•••Cg(2)[a]	3.9845(13)	0.42(10)	30.38	30.36	3.4382(8)	3.4375(9)
2						
Cg(1)•••Cg(2)[b]	3.8928(18)	0.94(15)	29.2	29.1	3.4024(13)	3.3991(13)
Cg(3)•••Cg(3)[c]	3.8328(19)	0.00(15)	6.4	6.4	3.8091(13)	3.8090(13)
Cg(2)•••Cg(2)[b]	3.7055(19)	0.02(15)	23.9	23.9	3.3885(13)	3.3885(13)
3						
Cg(4)•••Cg(4)[b]	3.6285(12)	0	10.77	10.77	3.5645(8)	3.5645(8)

α = dihedral angle between *Cg*(I) and *Cg*(J); *Cg*(I)-Perp = Perpendicular distance of *Cg*(I) on ring J; *Cg*(J)-Perp = perpendicular distance of *Cg*(J) on ring I; β = angle *Cg*(I)→*Cg*(J) vector and normal to ring I; γ = angle *Cg*(I) →*Cg*(J) vector and normal to plane J;
Cg1 is the centroid of atoms N(1)/C(1)/C(2)/C(3)/C(4)/C(9); Cg2 is the centroid of atoms C(4)/C(5)/C(6)/C(7)/C(8)/C(9); Cg3 is the centroid of atoms N(2)/C(12)/C(13)/C(14)/C(15)/C(16); Cg4 is the centroid of atoms N(1)/C(1)/C(2)/C(3)/C(4)/C(5);
Symmetry codes: (a) = -*x*,2-*y*,-*z*; (b) = 1-*x*,1-*y*,1-*z*; (c) = 2-*x*,1-*y*,2-*z*

Table S6. X—Y•••Cg(J)(π-ring) interactions.

Y-X(I)•••Cg(J)	X(I)•••Cg(J) [Å]	X-Perp [Å]	γ [°]	Y-X(I)•••Cg(J) [°]
1				
C(10)–H(10C)•••Cg(1)a	2.91	-2.86	9.70	140.0
2				
C(10)–H(10B)•••Cg(3)b	2.98	-2.89	14.41	136.0
3				
C(10)–H(10A)•••Cg(3)c	2.78	-2.73	11.42	165.0

γ = angle X(I)→Cg(J) vector and normal to plane J.
Cg1 is the centroid of atoms N(1)/C(1)/C(2)/C(3)/C(4)/C(9); Cg3 is the centroid of atoms N(1)/C(1)/C(2)/C(3)/C(4)/C(5);
Symmetry codes: (a) = -*x*,*1-y*,-*z*; (b) = 1-*x*,1/2+*y*,3/2-*z;* (c) = 1-*x*,–*y*,1-*z*;



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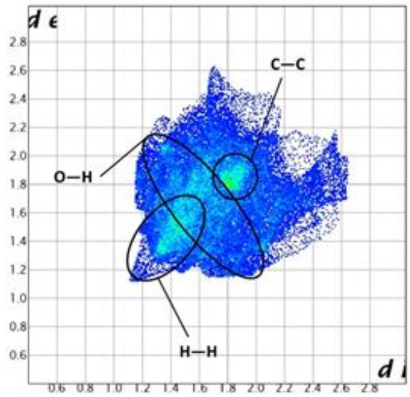

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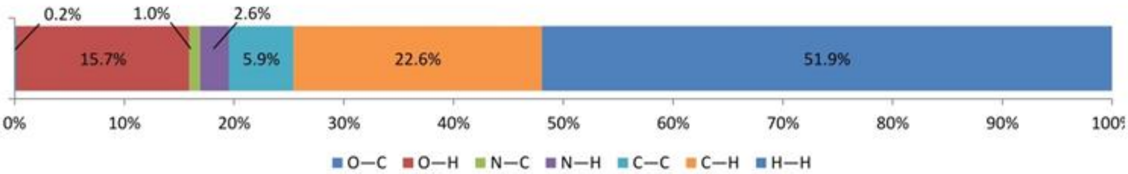
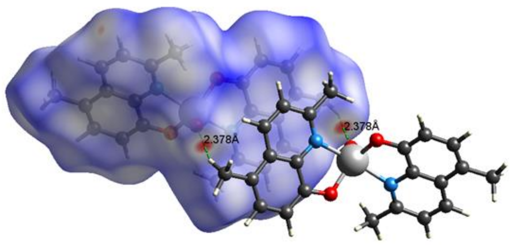


(c)

Figure S3. Hirshfeld surface mapped with d_{norm} along with intermolecular hydrogen bonds (a), and 2D fingerprint plot (b) for **1**, together with the relative contributions of various intermolecular interactions to the Hirshfeld surface (c).



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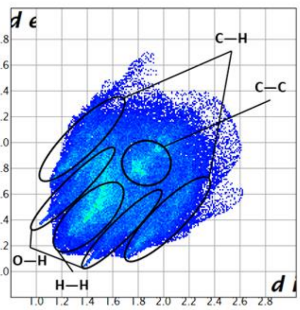

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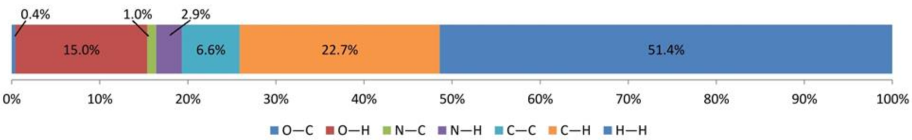
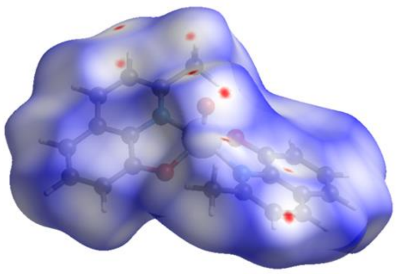


(c)

Figure S4. Hirshfeld surface mapped with d_{norm} along with intermolecular hydrogen bonds (a), and 2D fingerprint plot (b) for **2**, together with the relative contributions of various intermolecular interactions to the Hirshfeld surface (c).



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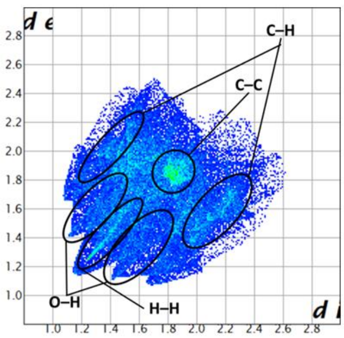

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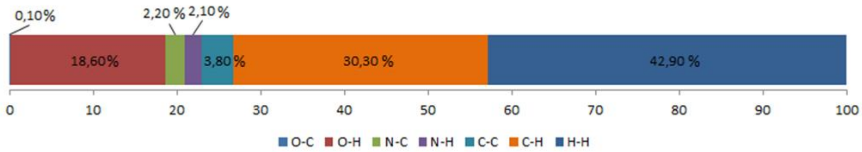
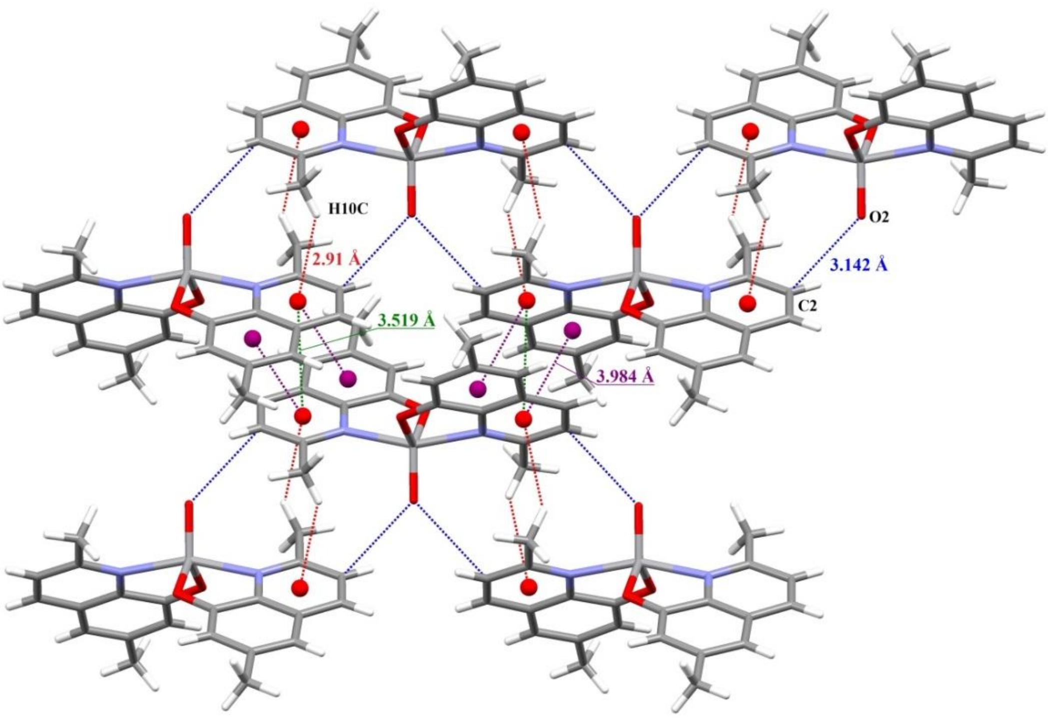


(c)

Figure S5. Hirshfeld surface mapped with dnorm along with intermolecular hydrogen bonds (a), and 2D fingerprint plot (b) for 3, together with the relative contributions of various intermolecular interactions to the Hirshfeld surface (c).



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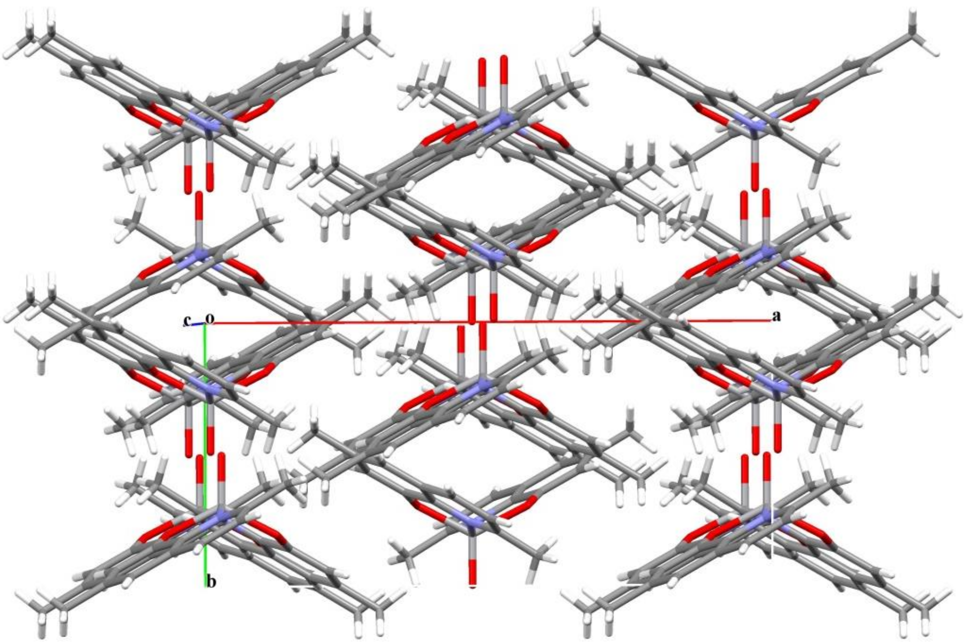
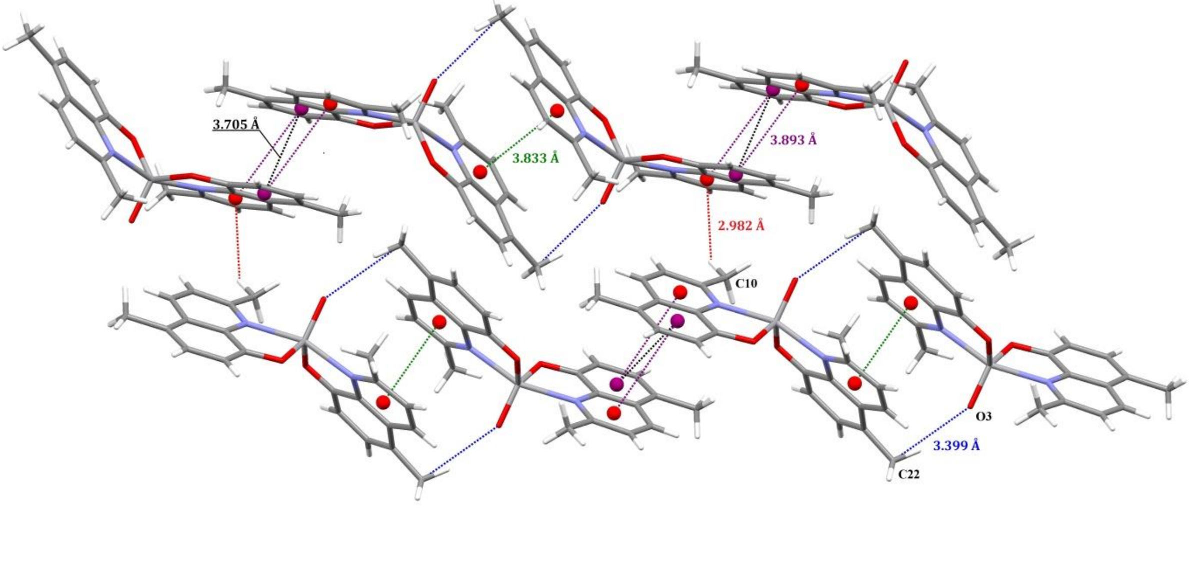


(b)

Figure S6. View of the intermolecular interactions (π•••π, C–H•••π and C–H•••O) in 1 (a), view of the supramolecular packing of 1 alongside c (b).



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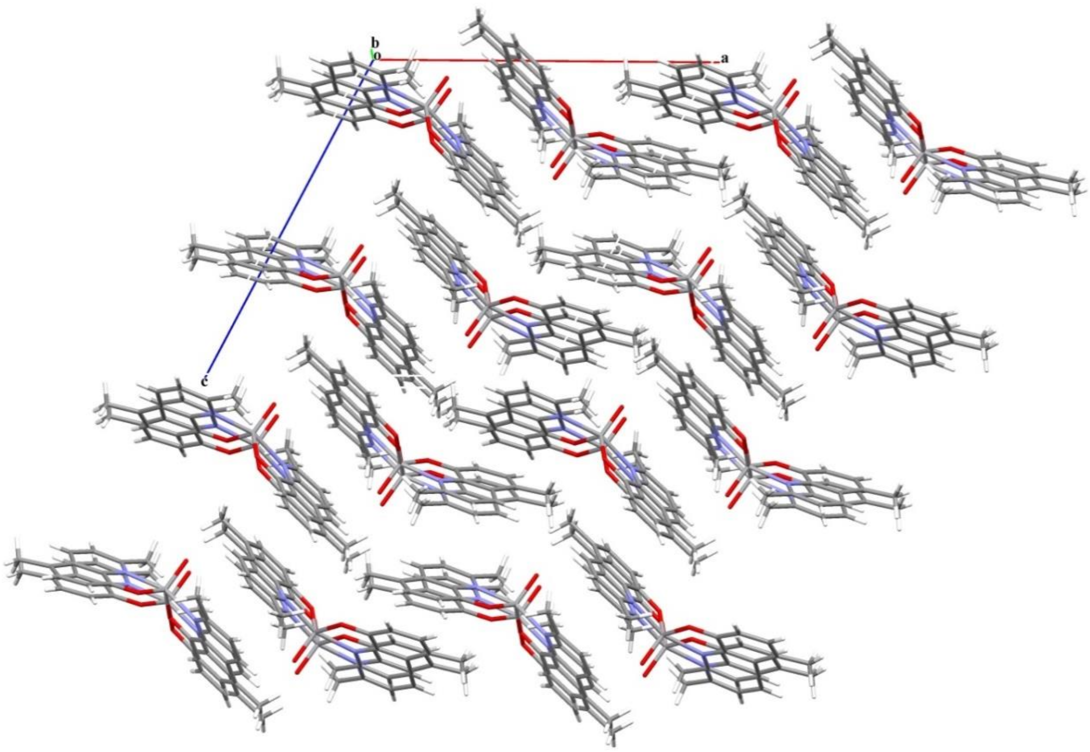
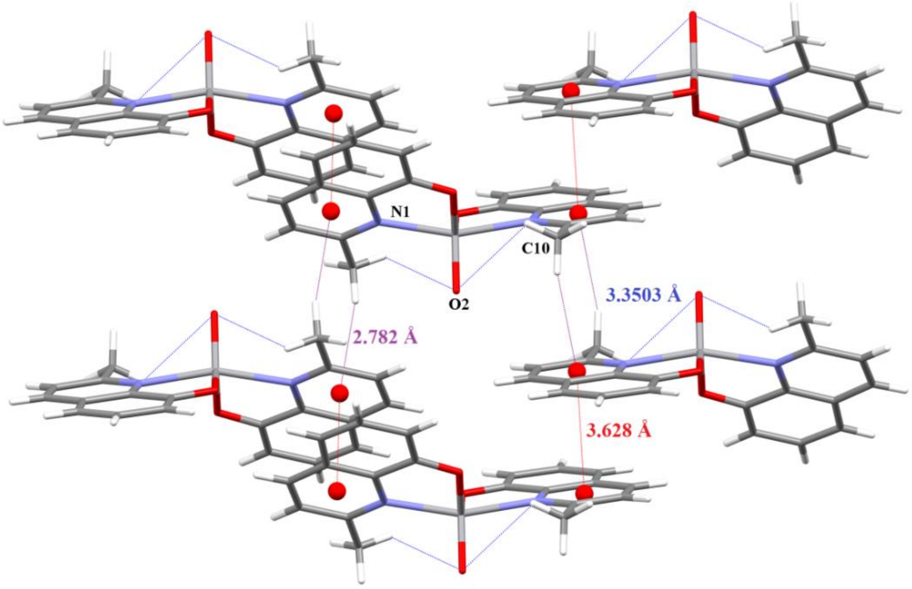


(b)

Figure S7. View of the intermolecular interactions (π•••π, C–H•••π and C–H•••O) in 2 (a), view of the supramolecular packing of 2 alongside *b* (b).



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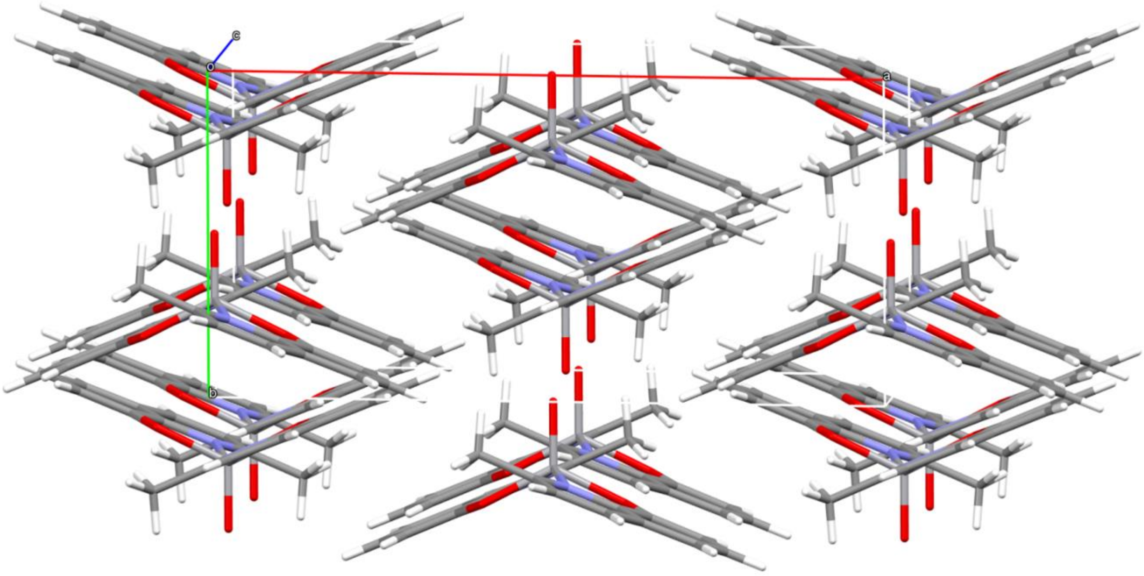


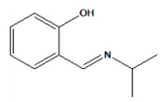
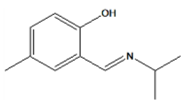
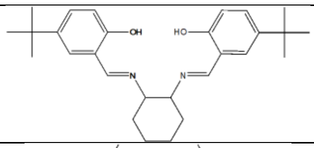
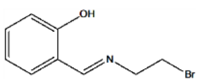
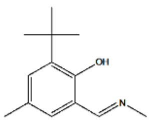
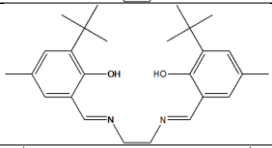
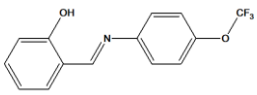
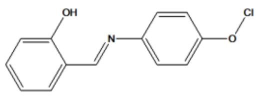
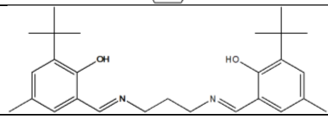
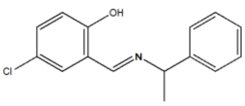
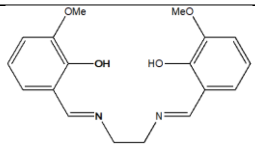
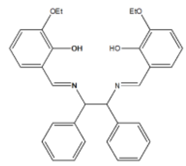
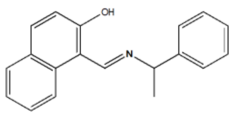
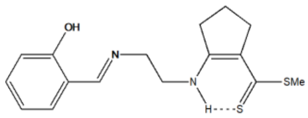
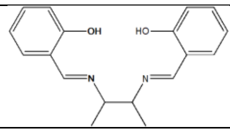
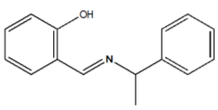
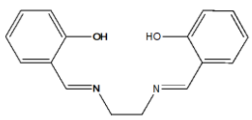
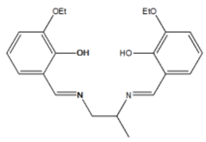
(b)

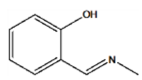
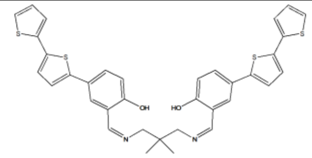
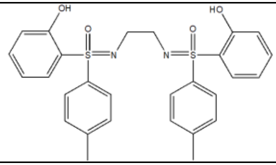
Figure S8. View of the intermolecular interactions (π•••π, C–H•••π and C–H•••O) in **3** (a), view of the supramolecular packing of **3** alongside *c* (b).

Table S7. The selected structural parameters of five-coordinated vanadium(IV) complexes $[VO(N^{\cap}O)_2]$ and $[VO(O^{\cap}N^{\cap}N^{\cap}O)]$.

Compound	V=O [Å]	V–O [Å]	V–N [Å]	τ	Ref.
$[VO(N^{\cap}O)_2]$					
[VO(2,6-(Me)$_2$-quin)$_2$] (1)	1.590(2)	1.9210(14)	2.1239(15)	0.57	this work
[VO(2,5-(Me)$_2$-quin)$_2$] (2)	1.595(3)	1.924(2); 1.917(2)	2.122(2); 2.125(2)	0.56	this work
[VO(2-Me-quin)$_2$)]	1.600(8)	1.921(5)	2.136(6)	0.56	1
[VO(2-Me-5-SMe-quin)$_2$)]	1.576(6)	1.934(6); 1.923(6)	2.106; 2.122(8)	0.50	2
[VO(n-Pr-sal)$_2$]	1.5945(18)	1.9042(16); 1.8976(19)	2.126(2); 2.107(2)	0.53	3
[VO(L^1)$_2$]	1.587(4)	1.901 (4); 1.914 (3)	2.087 (4); 2.088 (4)	0.58	4
[VO(2-OC$_6$H$_4$CHNH)$_2$]	1.589(4)	1.917 (4); 1.919(4)	2.056(6); 2.058(6)	0.22	5
[VO(L^2)$_2$]	1.5987(16)	1.9038(16); 1.9194(17)	2.1088(19); 2.1095(18)	0.37	6
[VO(L^3)$_2$]	1.589 (2)	1.891(2); 1.904(2)	2.110(2); 2.121(2)	0.42	7
[VO{(S)-Clsal-am}$_2$]·C$_7$H$_8$	1.592(5)	1.912(4); 1.915(4)	2.076(6); 2.085(6)	0.62	8
[VO{(S)-naph-am}$_2$]	1.611(2)	1.900(3); 1.904(3)	2.065(3); 2.085(3)	0.75	
[VO{(R)-sal-am}$_2$]·C$_7$H$_8$	1.592(2)	1.905(2); 1.910(2)	2.112(3); 2.100(3)	0.44	
[VO(L^4)$_2$]	1.590(4)	1.893(3)	2.097(3)	0.55	9
[VO(L^5)$_2$]	1.5988(18)	1.9117(16); 1.9149(16)	2.096(2); 2.098(2)	0.58	
[VO(L^6)$_2$]	1.601(2)	1.9005(17);	2.076(2); 2.089(2)	0.70	

		1.9027(16)			
[VO(L^7)$_2$]	1.615(8)	1.902(7); 1.900(8)	2.153(9); 2.145(9)	0.43	10
[VO(O⌒N⌒N⌒O)]					
[VO(3-MeOsalen)] ·$H_3N(CH_2)_2NH_2Cl$	1.5938(18)	1.9228(16); 1.9287(17)	2.047(2); 2.051(2)	0.13	11
syn-[VO(HL^8)$_2$]	1.596(6)	1.914(4)	2.100(4)	0.55	12
anti-[VO(HL^8)$_2$]	1.577(4)	1.763(3); 1.896(3)	2.064(3); 2.189(3)	0.06	
[VO(salen)]·MeOH	1.6070 (17)	1.9155 (17); 1.9429 (16)	2.051 (2); 2.0597 (19)	0.20	13
[VOL^9]·MeCN	1.610(5)	1.961(5); 1.972(5)	2.091(6); 2.093(6)	0.03	14
[VOL^{10}]·$CHCl_3$	1.606(2)	1.921(2); 1.922(2)	2.060(3); 2.072(3)	0.29	15
[VOL^{11}]·$CHCl_3$	1.5913(13)	1.9226(12); 1.9351(12)	2.0589(15); 2.0710(15)	0.26	9
[VOL^{12}]	1.581(3)	1.937(3); 1.954(3)	2.095(3); 2.100(3)	0.30	
[VO(3-EtOsal-*meso*-stien)]·H_2O	1.597(3)	1.925(3); 1.934(2)	2.065(3); 2.072(3)	0.05	16
[VO(sal-*meso*-bn)]	1.595(2)	1.937(2); 1.948(2)	2.061(2); 2.068(2)	0.04	17
[VO(salen)]ClO_4	1.576(3)	1.795(3); 1.813(3)	2.074(3), 2.083(3)	0.01	18
[VO{3-EtOsal-(R)-pn}]	1.598(3)	1.918(3); 1.938(3)	2.066(4); 2.053(4)	0.11	19
[VOL^{13}]	1.585(3)	1.924(3); 1.938(3)	2.050(3); 2.055(3)	0.12	20
[VO(salen)BF4]	1.577(2)	1.794(2); 1.814(2)	2.067(2); 2.085(2)	0.01	21

HL^1		HL^5		H_2L^{10}	
HL^2		HL^6		H_2L^{11}	
HL^3		HL^7		H_2L^{12}	
(S)-Clsal-am		3-MeOsalenH$_2$		3-EtOsal-*meso*-stienH$_2$	
(S)-naph-am		H_2L^8		sal-*meso*-bnH$_2$	
(R)-sal-am		H$_2$salen		3-EtOsal-(R)-pnH$_2$	

HL^4		H_2L^9		H_2L^{13}	

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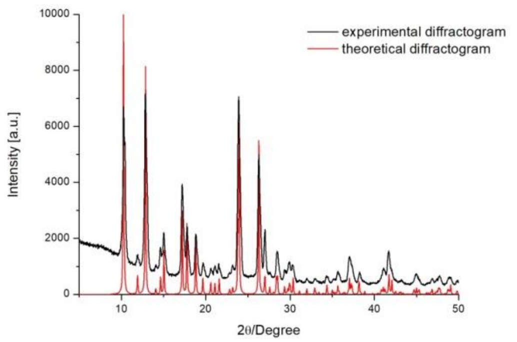

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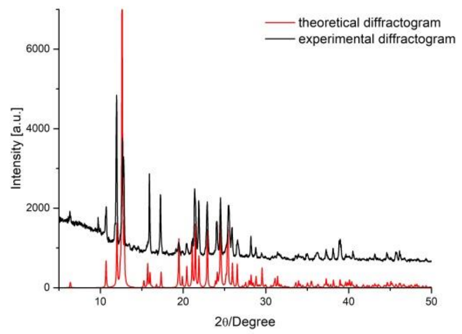

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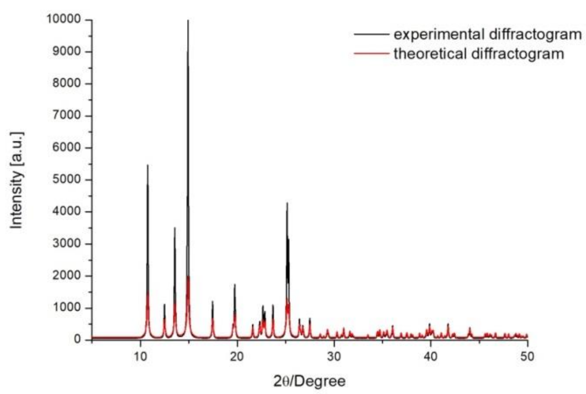


3

Figure S9. X–ray powder diffraction pattern of **1–3** together with the calculated pattern from the single crystal data.

EPR spectra

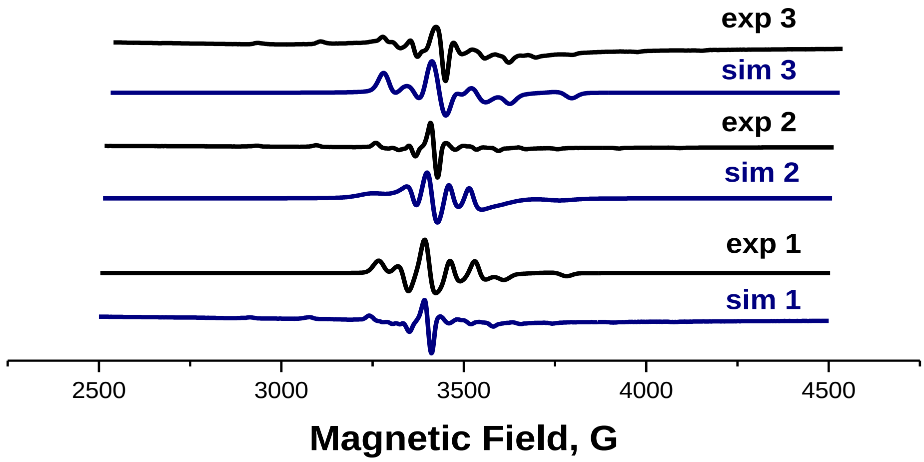
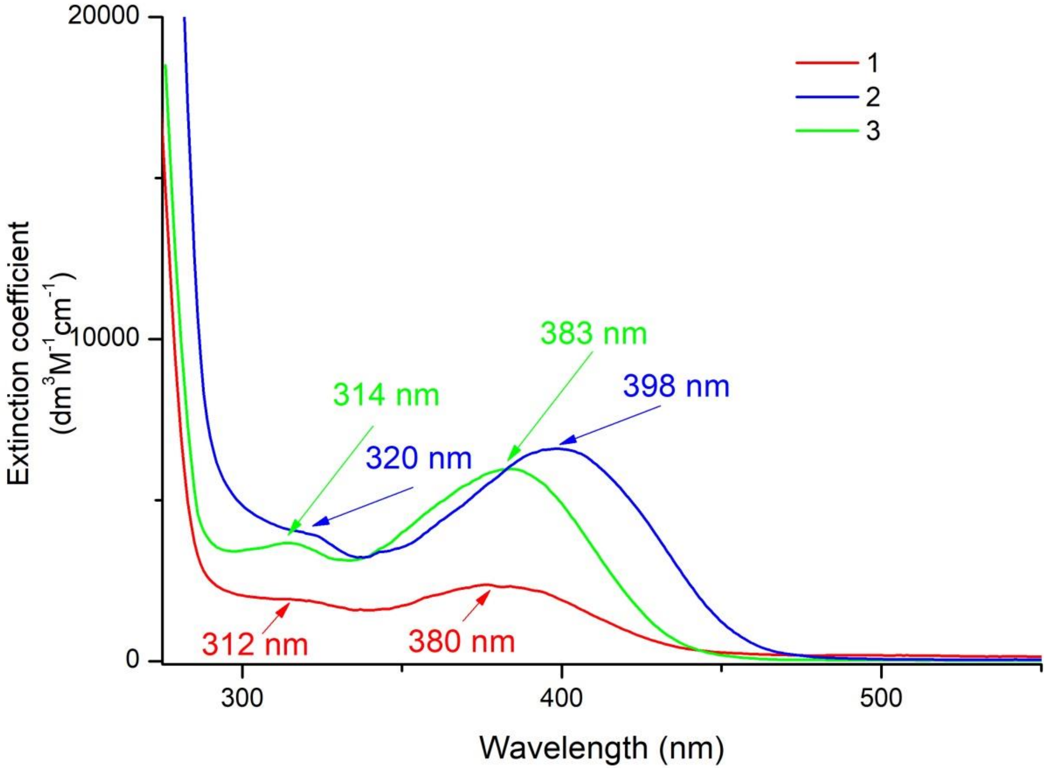
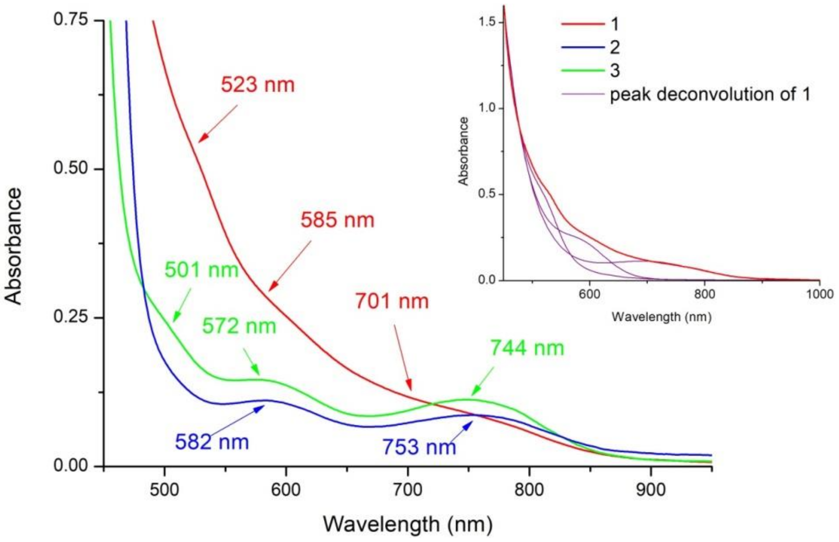


Figure S10. EPR frozen solution spectra (at 77 K) of compounds **1–3**; in acetonitrile solvent together with the theoretical spectrum calculated using the parameters: $g_x = g_y$ =1.980, g_z = 1.942, $A_x = A_y$ = 65 G, A_z = 181 G for **1** and $g_x = g_y$ =1.979, g_z = 1.957, $A_x = A_y$ = 53 G, A_z = 169 G for **2;** $g_x = g_y$ =1.978, g_z = 1.959, $A_x = A_y$ = 55 G, A_z = 168 G for **3**

Absorption spectroscopy



(a)



(b)

Figure S11. UV-Vis spectra of **1–3** in DMSO full scale ($5\cdot10^{-5}$ M) (a), close-up of the 500–900 nm region (concentrated solutions in DMSO) (b), insert: peak deconvolution of **1** calculated using deconvolution formula implemented in the OriginPro 9.1 software

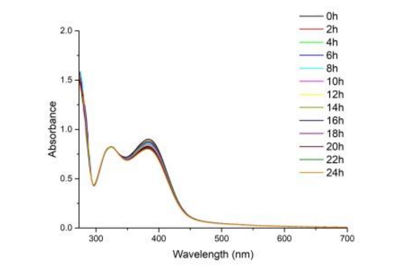
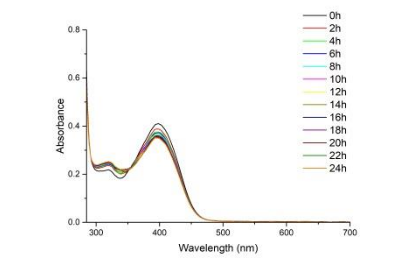
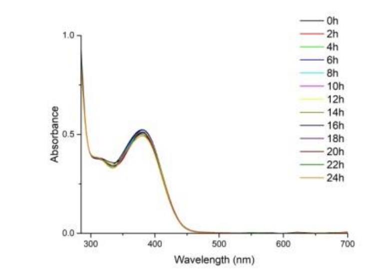
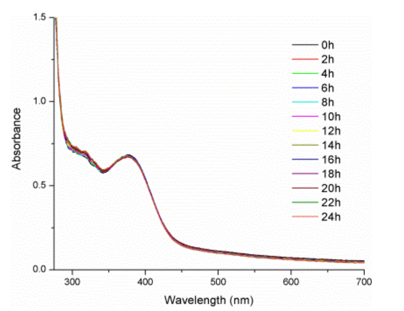
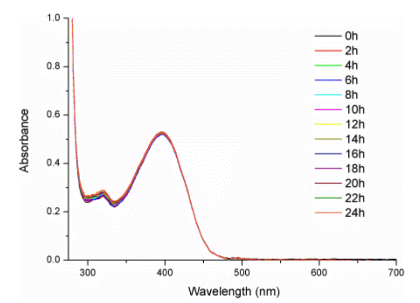
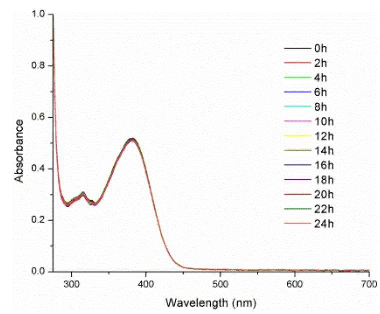
		
(a)	**(b)**	**(c)**
		
(d)	**(e)**	**(f)**

Figure S12. UV-Vis stability spectra for compounds **1–3** in DMSO (10^{-4} M) (a-c) and CH_3CN (d-f). Spectra were recorded every 2 hours for 24h.

Catalytic data

Table S8. Comparative parameters for the oxidation of cyclohexane catalyzed by complexes 1-3 and other vanadium complexes previously published

Catalytic system	Conditions	Vanadium oxidation state	Total yield of oxygenates (%)	Total TON	Ref.
[n-Bu$_4$N][VO$_3$]/pca/H$_2$O$_2$/CH$_3$CN	40 °C, 4 h	V	30	700	1
[n-Bu$_4$N][VO$_2$(pca)$_2$]/H$_2$O$_2$/CH$_3$CN	40 °C, 24 h	V	4.6	215	2
[n-Bu$_4$N][VO$_2$(pca)$_2$]/pca/H$_2$O$_2$/CH$_3$CN	40 °C, 24 h	V	20	900	
[VO(OCH$_3$)(ma)2] Hma – 3-hedroxy-2-methyl-4-pyrone	40°C, 14 h	V	27	2600	3
[VO(tea)] tea – triethanolamine	40 °C, 24 h	V	10	900	4
[VO(OCH3)(5-Cl-quin)$_2$ ·1/2CHCl3/pca/H$_2$O$_2$/CH$_3$CN 5-Cl-quin – 5-chloro-8-hydroxyquinoline	40°C, 6 h	V	39	360	5
[{VO(Oet)(EtOH)}$_2$L]/pca/H$_2$O$_2$/CH$_3$CN H$_4$L – bis(2-hydroxybenzylidene)terephthalohydrazide	50 °C, 24 h	V	30	700	6
[{VO(Oet)(EtOH)}$_2$L]/pca/H$_2$O$_2$/CH$_3$CN H$_4$L – bis(2-hydroxybenzylidene)oxalohydrazonic acid	50 °C, 4 h	V	28.7	2640	7
[VO$_2$(pca)(hmpa)]/pca/H$_2$O$_2$/CH$_3$CN hmpa – hexamethylphosphoramide	40 °C, 24 h	V	29.8	1370	8
[VO$_2$(pycaH)(hmpa)]/pca/H$_2$O$_2$/CH$_3$CN hmpa – hexamethylphosphoramide pycaH$_2$ – pyridine-2,5-dicarboxylic acid	40 °C, 24 h	V	24.8	1140	
[(VO$_2$)$_2$(μ_4-L){Na$_2$(μ-H$_2$O)$_2$(H$_2$O)$_2$}]$_n$/pca/H$_2$O$_2$/CH$_3$CN H$_4$L – bis(salicylaldehyde)-oxaloyldihydrazone	50 °C, 5 h	V	4.8	4400	9
[{V(μ-O)$_2$}$_2$(μ_4-L){K$_2$(μ-H$_2$O)$_2$(H$_2$O)$_2$}]$_n$/pca/H$_2$O$_2$/CH$_3$CN H$_4$L – bis(salicylaldehyde)-oxaloyldihydrazone	50 °C, 5 h	V	5.7	5220	
[{V(μ-O)(μ_3-O)}2(μ_8-L){Cs$_2$(μ-H$_2$O)$_2$(H$_2$O)$_2$}]$_n$ /pca/H$_2$O$_2$/CH$_3$CN H$_4$L – bis(salicylaldehyde)-oxaloyldihydrazone	50 °C, 5 h	V	6.2	5700	
V$_3$O$_3$(Oet)(ashz)$_2$(μ-Oet)]$_2$/pca/H$_2$O$_2$/CH$_3$CN H$_3$ashz – N-acetylsalicylhydrazidate	50 °C, 5 h	mixed IV/V	18.2	8370	10
[(VO)$_4$(hptb)$_2$(H$_2$O)$_2$(μ-O)][ClO$_4$]/pca/H$_2$O$_2$/CH$_3$CN hptbH – N,N,N′,N′-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane	40 °C, 24 h	IV	12.4	570	8
[VOCl$_2$(tmtacn)]/pca/H$_2$O$_2$/CH$_3$CN tmtacn – 1,4,7-trimethyl-1,4,7-triazacyclononane	40 °C, 24 h	IV	6.3	290	
[V(cat)$_3$]$^-$/pca/H$_2$O$_2$/CH$_3$CN catH$_2$ – pyro-cathecol	40 °C, 24 h	IV	21.3	980	
[VOCl$_2$(dpp-bian)]/pca/H$_2$O$_2$/ CH$_3$CN dpp-bian – bis(N-(2,6-diisopropylphenyl)-imino)acenaphthene	50 °C, 5 h	IV	21.5	990	11
VO(acac)$_2$/H$_2$O$_2$/ CH$_3$CN	40°C, 5 h	IV	1.2	23	12,13
1/pca/ H$_2$O$_2$/CH$_3$CN	50 °C, 3 h	IV	30	565	this work
2/pca/ H$_2$O$_2$/CH$_3$CN	50 °C, 2 h	IV	43	870	
3/pca/ H$_2$O$_2$/CH$_3$CN	50 °C, 1.5 h	IV	48	954	

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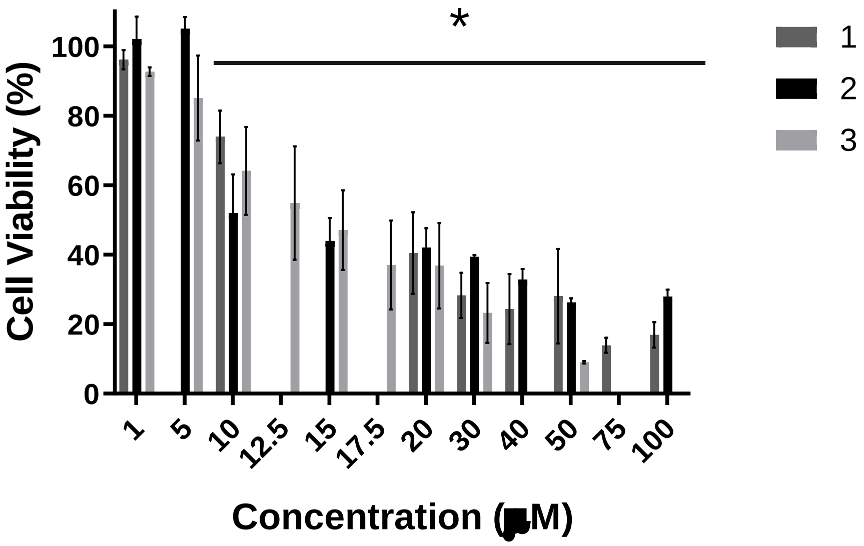

Figure S13. Antiproliferative effect of complexes **1-3** in normal dermal fibroblasts, after 48 h. evaluated by the MTS method. Cell viabilities were normalized to DMSO 0.1% (v/v) (vehicle control). The results presented are mean ± standard deviation of three independent assays. Asterisk indicates a p-values inferior to 0.05

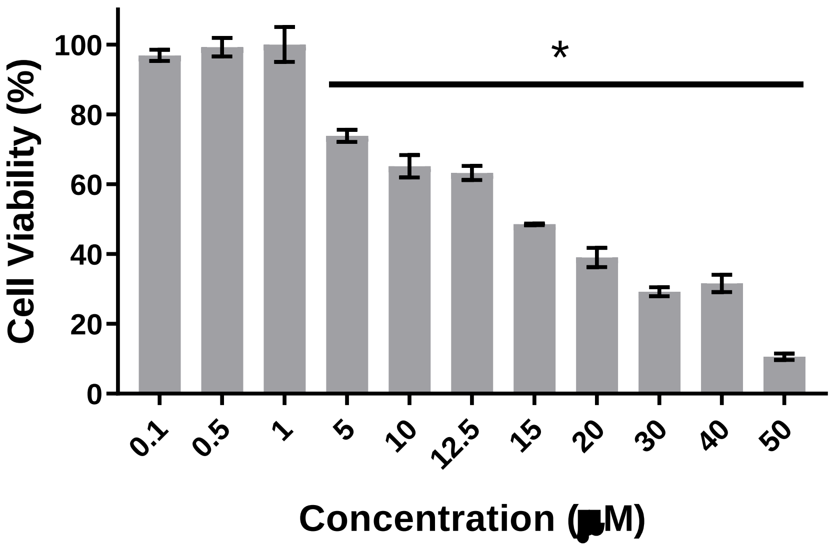

Figure S14. Cell viability of HCT116 cells exposed for 48 h to increasing concentrations of cisplatin. IC_{50} value found is 15.6 ± 5.3 µM.`* $p<0.05$ relative to control.