DT-ART-07-2024-002030.R4

Electronic Supplementary Information

New $V^{V}O_2$, $V^{V}O$, $V^{V}OV^{V}O$ and electrogenerated $V^{IV}OV^{V}O$ systems of valproic acid hydrazones : Study of catalytic activity

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Table S1 Crystallographic data for ligands H_2L^{1-2} complexes **1**, **3**.

	H_2L^1	H_2L^2	Complex 1	Complex 3
Empirical formula	$C_{15}H_{22}N_2O_2$	$C_{19}H_{24}N_2O_2$	$C_{15}H_{21}N_2O_4V$	$C_{17}H_{27}N_2O_5V$
Formula weight	262.35	312.40	344.28	390.35
Temperature /K	293	293	293	293
Space group	P21/c	P21 21 21	P21/n	P21/c
a/Å	9.0199(16)	4.9108(7)	9.7598(12)	12.966(3)
b/Å	19.834(3)	11.4224(14)	13.8657(17)	16.279(3)
c/Å	9.7259(15)	30.400(4)	13.1083(14)	10.330(2)
α/°	90	90	90	90
β/°	115.716(5)	90	111.86(01)	112.488(5)
γ/°	90	90	90	90
Volume/Å^3	1567.7(4)	1705.2(4)	1646.4(3)	2014.6(7)
Z	4	4	4	4
ρ_{calc}g/cm^3	1.112	1.217	1.389	1.287
μ/mm^{-1}	0.074	0.079	0.621	0.519
F(000)	568	672	720.0	824
Radiation	MoKα (λ=0.71073)	MoKα (λ=0.71073)	MoKα (λ=0.71073)	MoKα (λ=0.71073)
GOF	1.029	1.094	1.051	1.05
R_1	0.0523	0.0483	0.0416	0.0720
wR_2	0.1469	0.1373	0.1002	0.1837

Table S2 Selected bond lengths (Å) and bond angles (°) for H_2L^1

H_2L^1					
Bond Length (Å)			**Bond Angle (°)**		
O1	-C1	1.346(2)	O1	-C1 -C2	122.40(15)
O2	-C4	1.220(17)	O1	-C1 -C15	117.90(17)
N1	-N2	1.372(17)	O2	-C4 -C5	122.83(14)
N1	-C3	1.274(18)	O2	-C4 -N2	121.90(15)
N2	-C4	1.347(18)	N1	-N2 -C4	119.95(12)
			N2	-N1 -C3	117.49(12)
			C2–C3–N1–N2		-176.25(13)
			C3–N1–N2–C4		177.43(14)
			O2–C4–N2–N1		2.9(4)

Table S3. Selected bond lengths (Å) and bond angles (°) for H_2L^2

H_2L^1	
Bond Length (Å)	**Bond Angle (°)**
O1 -C7 1.353(4)	C10 -N1 -N2 118.0(3)
O2 -C6 1.225(5)	C6 -N2- N1 118.3(3)
N1 -N2 1.379(4)	N2 -C6 -O2 122.1(3)
N1 -C10 1.295(4)	C9 -C6 -O2 121.9(4)
N2 -C6 1.346(5)	O2 -C6 -N2- N1 -7.2(4)
	N1 -N2 -C6 -C9 171.4(3)
	O1 -C7 -C19 -C4 -175.8(3)
	O1 -C7- C20 -C12 176.2(3)

Table S4. Selected bond lengths (Å) and bond angles (°) for complex **1**

Complex 1							
Bond Length (Å)			**Bond Angle (°)**			
V1	-O1	1.8932(16)	O1	-V1	-O2	153.10(6)
V1	-O2	2.0392(16)	O1	-V1	-O3	103.08(8)
V1	-O3	1.6318(15)	O1	-V1	-O4	98.95(9)
V1	-O4	1.6069(17)	O1	-V1	-N1	80.90(6)
V1	-N1	2.1664(16)	O2	-V1	-O3	96.24(8)
O1	-C1	1.319(3)	O2	-V1	-O4	92.17(8)
O2	-C4	1.260(2)	O2	-V1	-N1	73.36(6)
N1	-N2	1.389(3)	O3	-V1	-O4	108.91(8)
N1	-C3	1.299(3)	O3	-V1	-N1	119.05(7)
N2	-C4	1.322(3)	O4	-V1	-N1	130.85(8)

Table S5. Selected bond lengths (Å) and bond angles (°) for complex **3**

Complex 3							
Bond Length (Å)			Bond Angle (°)			
V1	-O1	1.853(4)	O1	-V1	-O2	152.4(2)
V1	-O2	1.945(4)	O1	-V1	-O3	100.0(2)
V1	-O3	1.590(7)	O1	-V1	-O4	100.44(19)
V1	-O4	1.766(5)	O1	-V1	-O5	81.73(18)
V1	-O5	2.352(5)	O1	-V1	-N1	83.8(2)
V1	-N1	2.121(6)	O2	-V1	-O3	98.9(2)
O1	-C1	1.326(8)	O2	-V1	-O4	95.0(2)
O2	-C4	1.288(9)	O2	-V1	-O5	77.87(18)
N1	-N2	1.373(7)	O2	-V1	-N1	74.2(2)
N1	-C3	1.271(8)	O3	-V1	-O4	102.1(2)
N2	-C4	1.295(9)	O3	-V1	-O5	174.9(2)
			O3	-V1	-N1	96.4(2)
			O4	-V1	-O5	81.73(18)
			O4	-V1	-N1	159.9(3)
			O5	-V1	-N1	79.2(2)

The quality of crystal data

of complex 2 and complex 6 were not crystallographically publishable. We give here it only to visualize the bond connectivity.

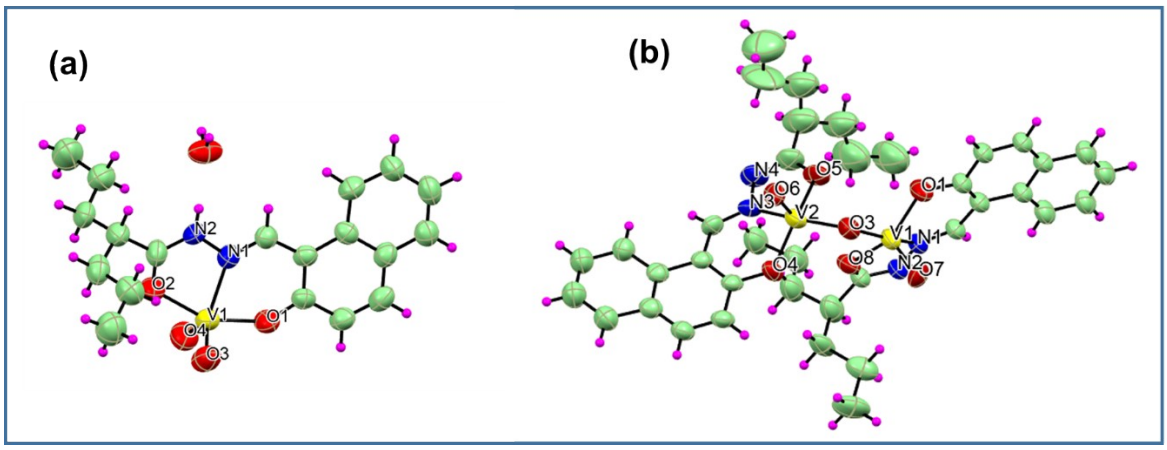
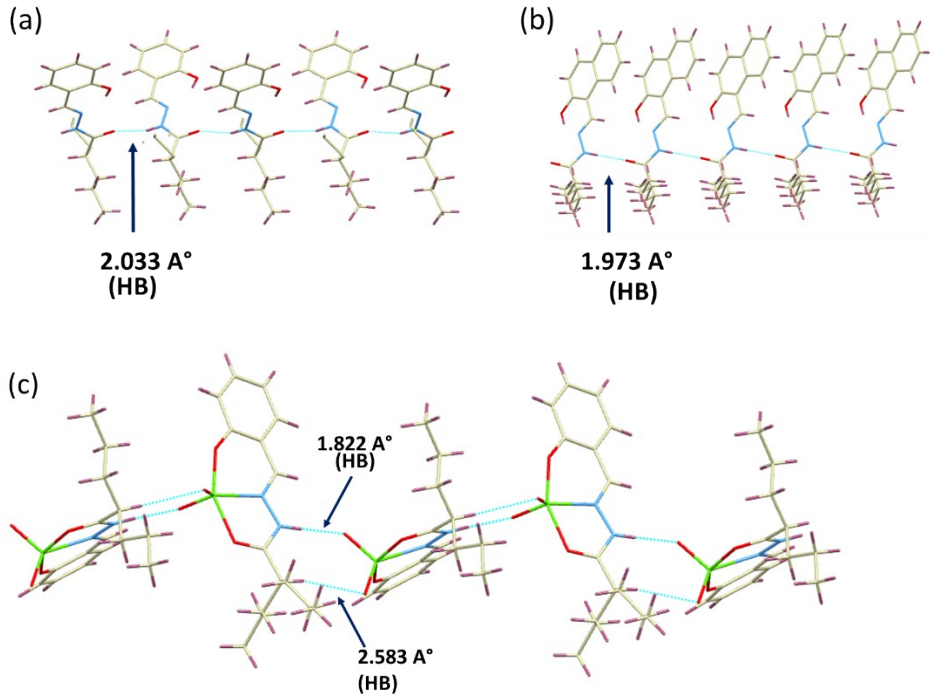


Figure S1. Crystal structure image of a) complex 2 b) complex 6



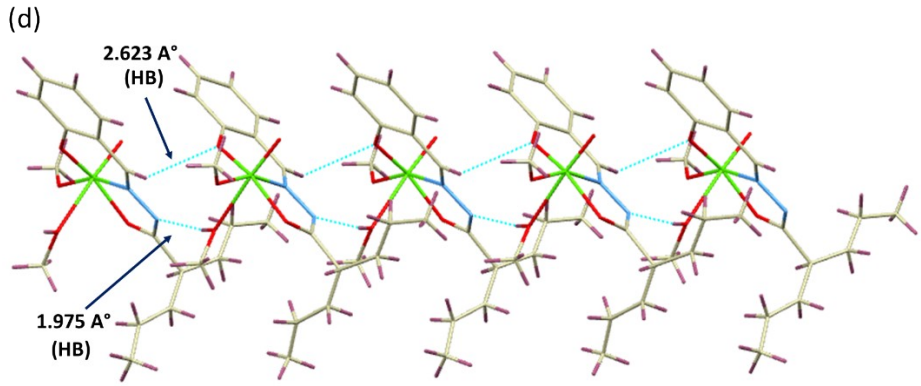


Figure S2. Supramolecular architecture of the complexes (a) **HL^1,1,** (b) **HL^2, 2**, (c) **1**, (d).**3**

Table S6. Absorption parameters of the ligands

Ligands	λ_{max}(nm)[ε($M^{-1}cm^{-1}$)]
H_2L^1	280 (38700), 290 (37000), 322 (18900)
H_2L^2	308 (17800), 321 (24500), 356 (19000), 368 (17700)

Table S7. Absorption parameters of the complexes

Complexes	λ_{max}(nm)[ε($M^{-1}cm^{-1}$)]
1	281 (45500), 320 (26800), 380 (7500)
2	293 (35000), 336 (19500), 412 (6700)
3	282 (42000), 320 (22450), 382 (7350)
4	295 (31750), 333 (19700), 411 (6850)
5	282 (51000), 321 (16100), 384 (4600)
6	295 (48500), 339 (14400), 414 (8150)

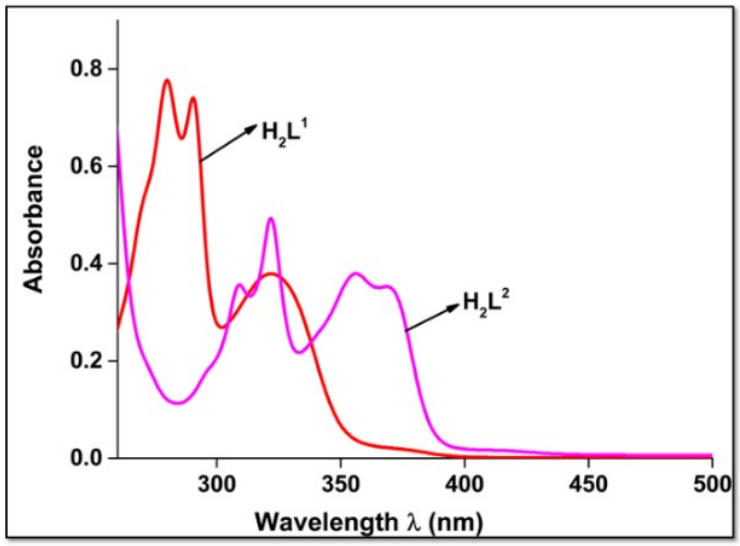


Figure S3. Absorption spectra of ligands in CH_2Cl_2 at room temperature

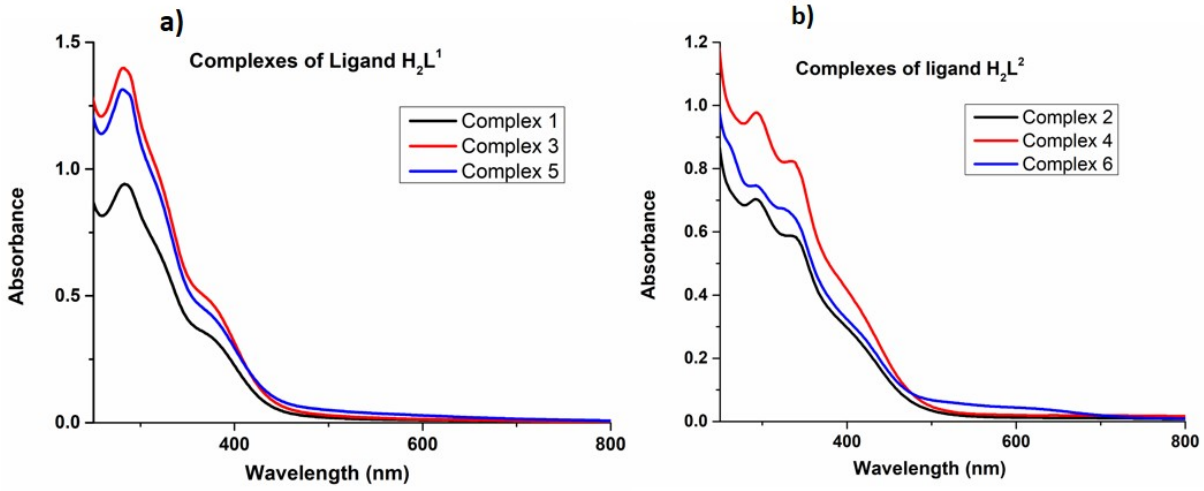


Figure S4. Absorption spectra for a) complexes of H_2L^1 and b) complexes of H_2L^2in CH_2Cl_2 at room temperature.

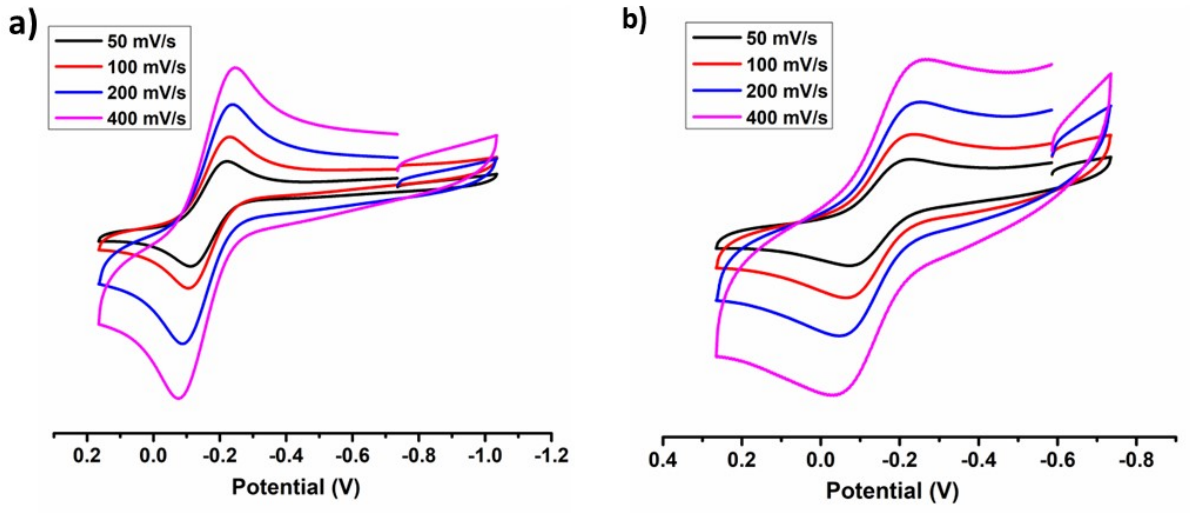


Figure S5 Cyclic voltammogram of (a) complex **1** and (b) complex **2** at different scan rates.

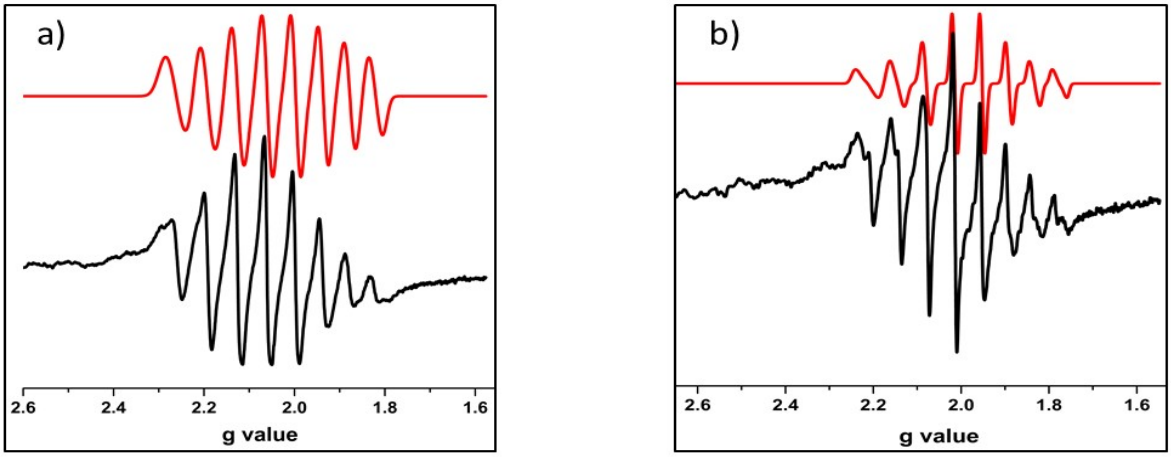


Figure S6. X-band EPR spectra of (a) **5a**, (b) **6a** at RT (black-experimental; red-simulated)

Table S8. X-band EPR Spectral parameter of complexes **5a** and **6a**.

Complex	**Matrix**	**g**	**A** (G)	**lw** (mT)
5a	CH_2Cl_2, 300 K	1.96775	284.98	3.8
6a	CH_2Cl_2, 300 K	1.9678	294.40	2.0

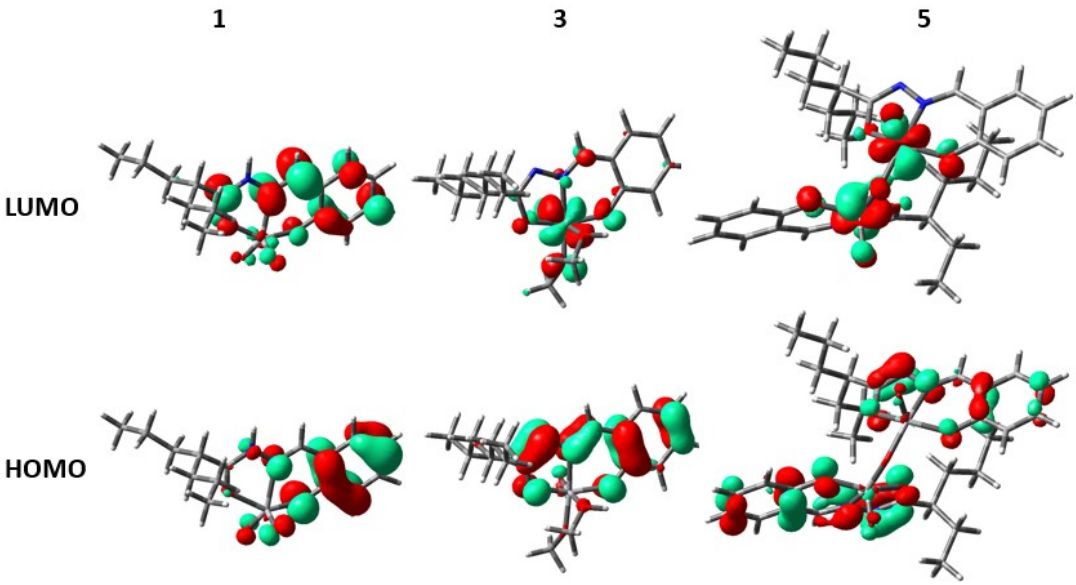


Figure S7 Isodensity plot of selected frontier orbitals of complexes **1,3** and **5**

Table S9 X-band EPR Spectral parameter of complex **1**$^{-}$ and **2**$^{-}$

Complex	**Matrix**	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}$ (G)	$A_{\perp}$(G)	A_{av} (G)	**lw** (mT)
1^{-}	CH_2Cl_2, 300 K	1.9525	1.9643	1.9564	262.05	204.73	223.84	1.6
2^{-}	CH_2Cl_2, 300 K	1.9338	1.9646	1.9492	280.00	235.647	257.82	1.6

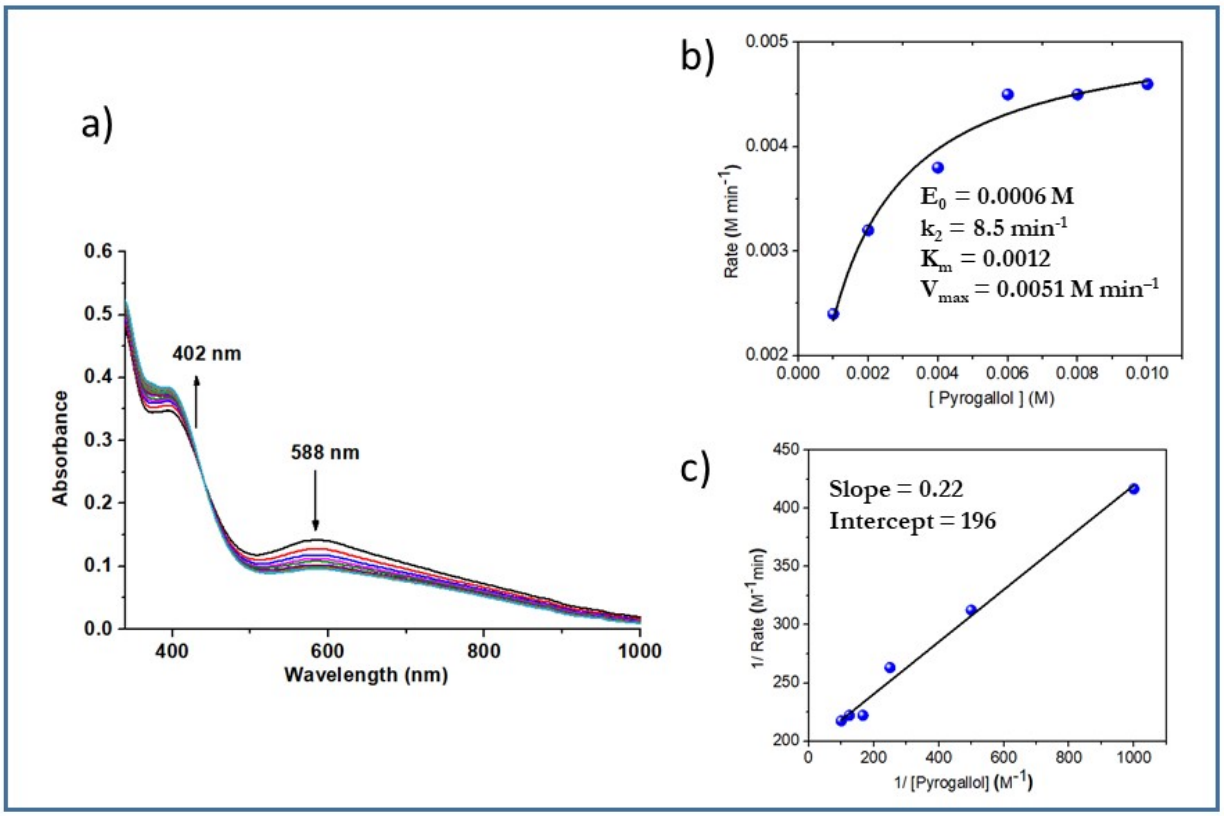


Figure S8 (a) Absorption spectra of a solution containing 6×10^{-4} M of complex **2** and 0.006 M of Pyrogallol, recorded at the interval of 5 min in methanol. (b) Plot of rate versus concentration of Pyrogallol for the oxidation reaction catalyzed by complex**2**. (c) Lineweaver−Burk plot.

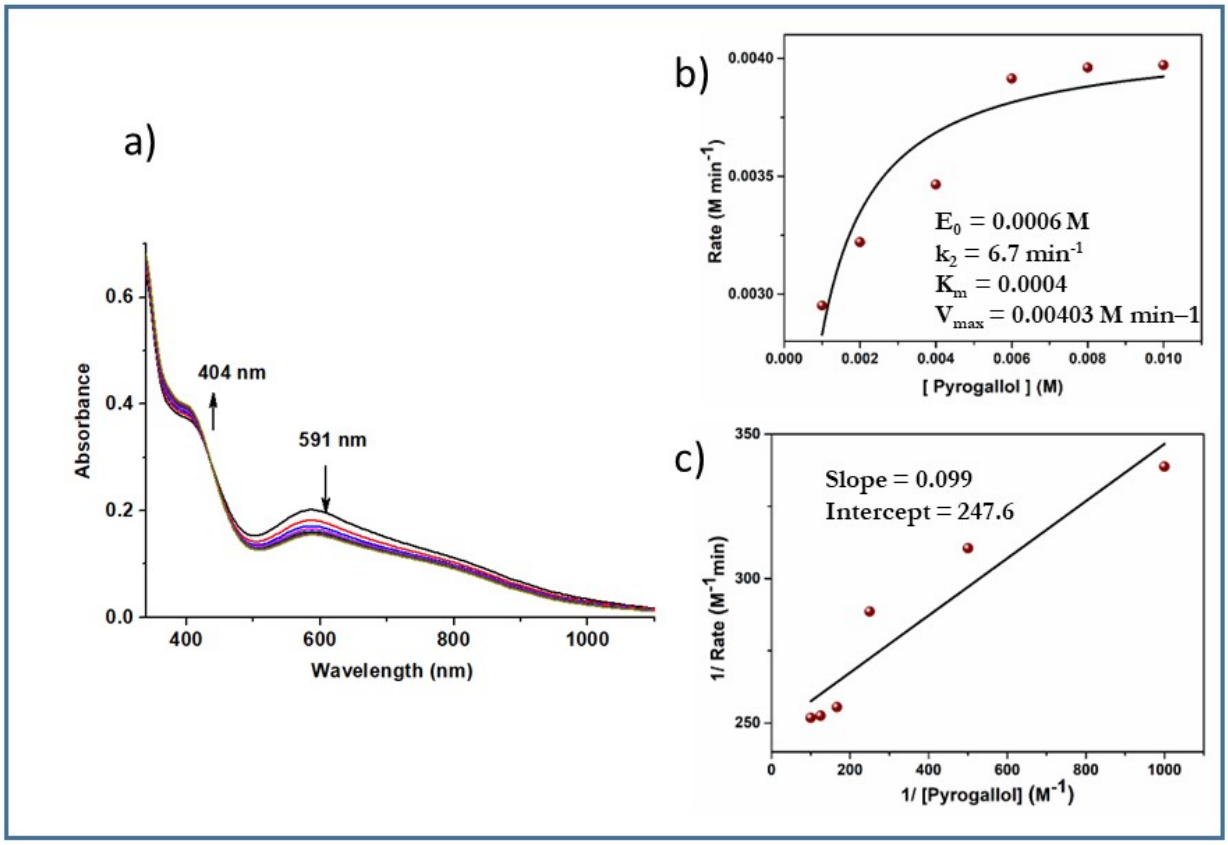


Figure S9 (a) Absorption spectra of a solution containing 6×10^{-4} M of complex **4** and 0.006 M of Pyrogallol at the interval of 5 min in methanol. (b) Plot of rate versus concentration of Pyrogallol for the oxidation reaction catalyzed by complex.**4**(c) Lineweaver−Burk plot.

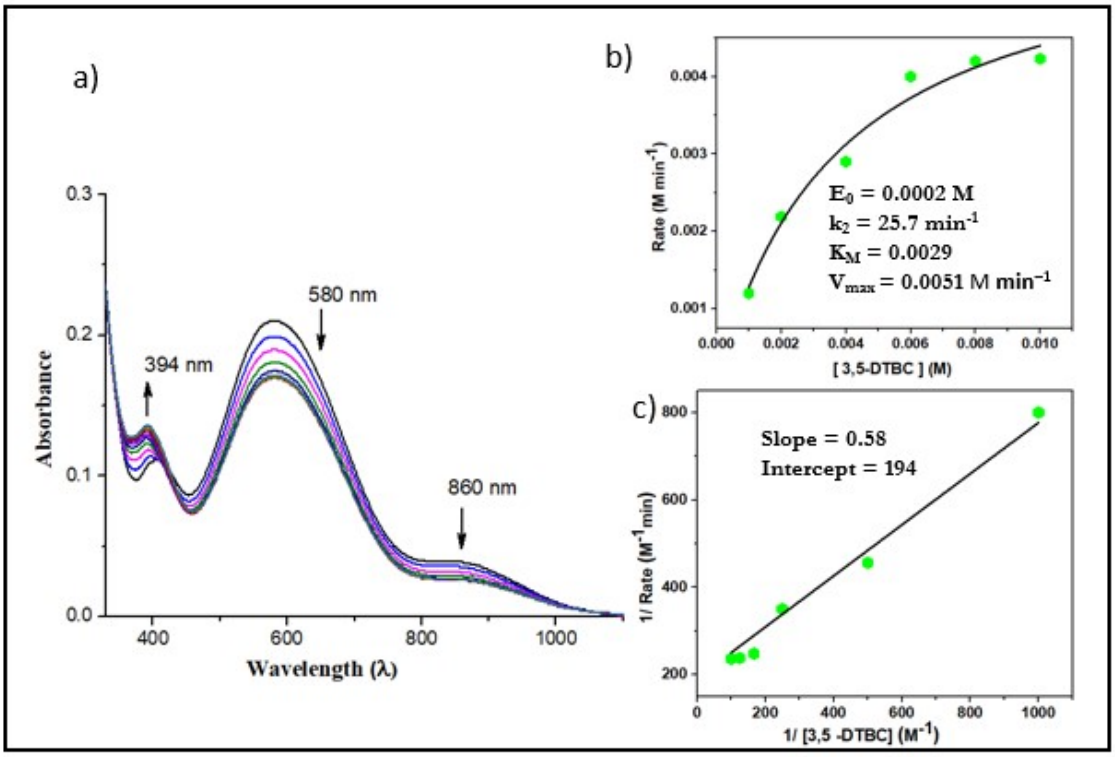


Figure S10 (a) Absorption spectra of a solution containing 2×10^{-4} M of complex **3** and 0.004 M of 3,5-DTBC, recorded at the interval of 5 min in methanol. (b) Plot of rate versus concentration of 3, 5-DTBC for the oxidation reaction catalysed by complex**3**. (c) Lineweaver−Burk plot.

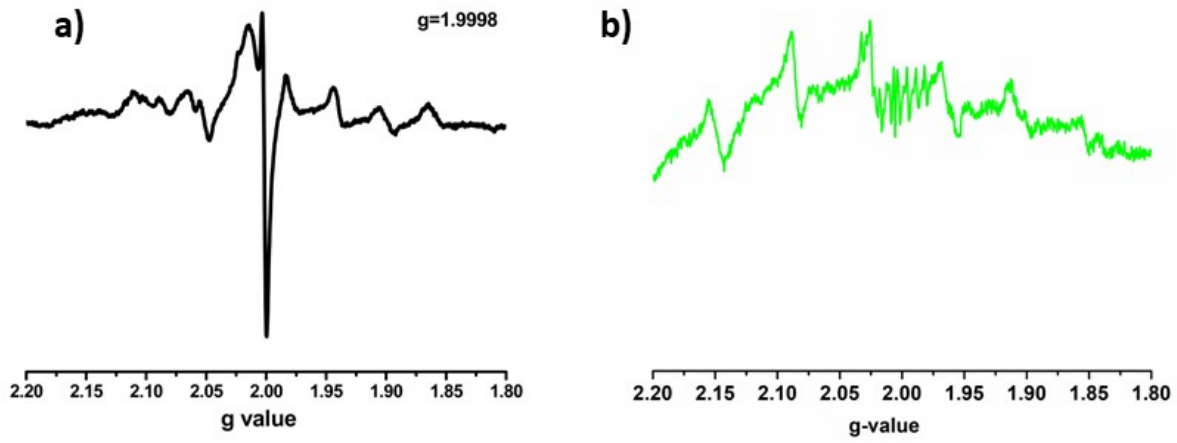


Figure S11. X-band EPR spectra of the reaction of 3, 5- DTBC with complex **3** a) intermediate **III** ($\mathbf{3_{cat}}$) b) $\mathbf{3_{cat}}$ with TEMPO for complex **3**.

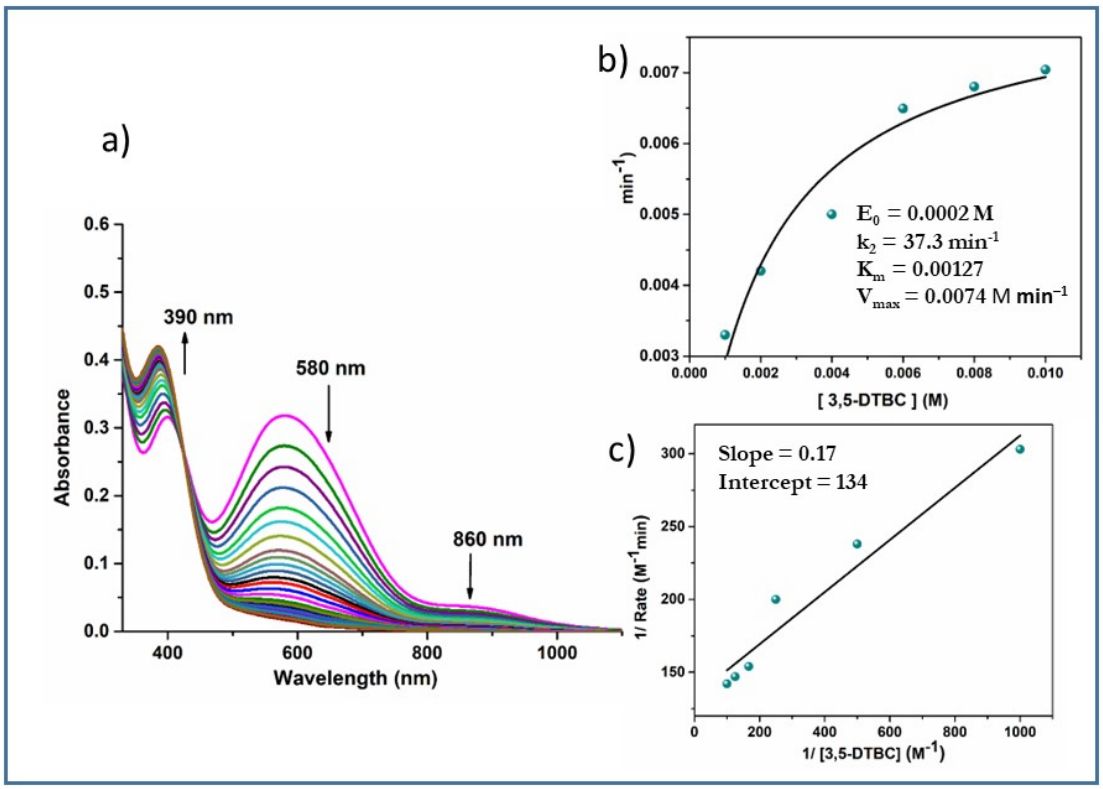


Figure S12(a) Absorption spectra of a solution containing 2×10^{-4} M of complex **1** and 0.004 M of 3,5-DTBC in presence of one drop portion of H_2O_2 (10^{-2} M) recorded at the interval of 5 min in methanol. (b) Plot of rate versus concentration of 3, 5-DTBC for the oxidation reaction catalysed by complex**3**. (c) Lineweaver−Burk plot.

Table S10 Kinetic Data for Catecholase-like Activity of Different Mono- and Dinuclear vanadium a Complexes

Catalyst	Solvent	k_{cat}	Ref
Mononuclear V(V)	MeOH	2.063×10^3 h^{-1}	18b
Dinuclear V(V) breaks down to Mononuclear V(V)	MeOH	1.737×10^3 h^{-1}	18c
Oxovanadium(V)	MeOH	3.24 h^{-1}	21b

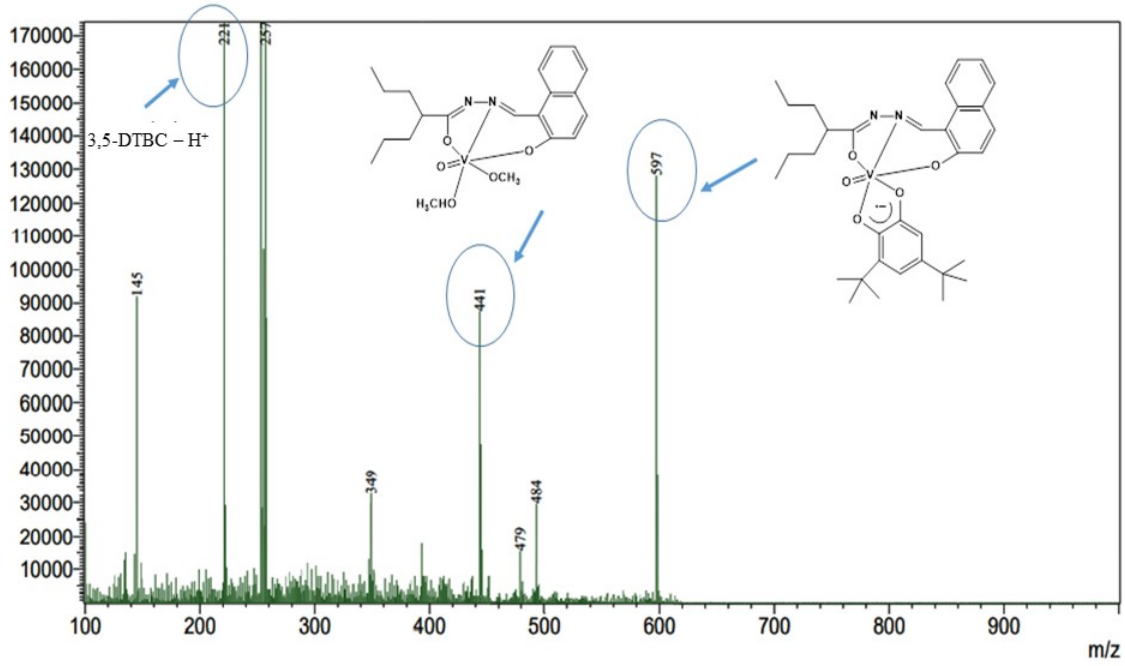


Figure S13. (-Ve) ESI-MS spectra of [Complex **4** + 3,5-DTBC] system

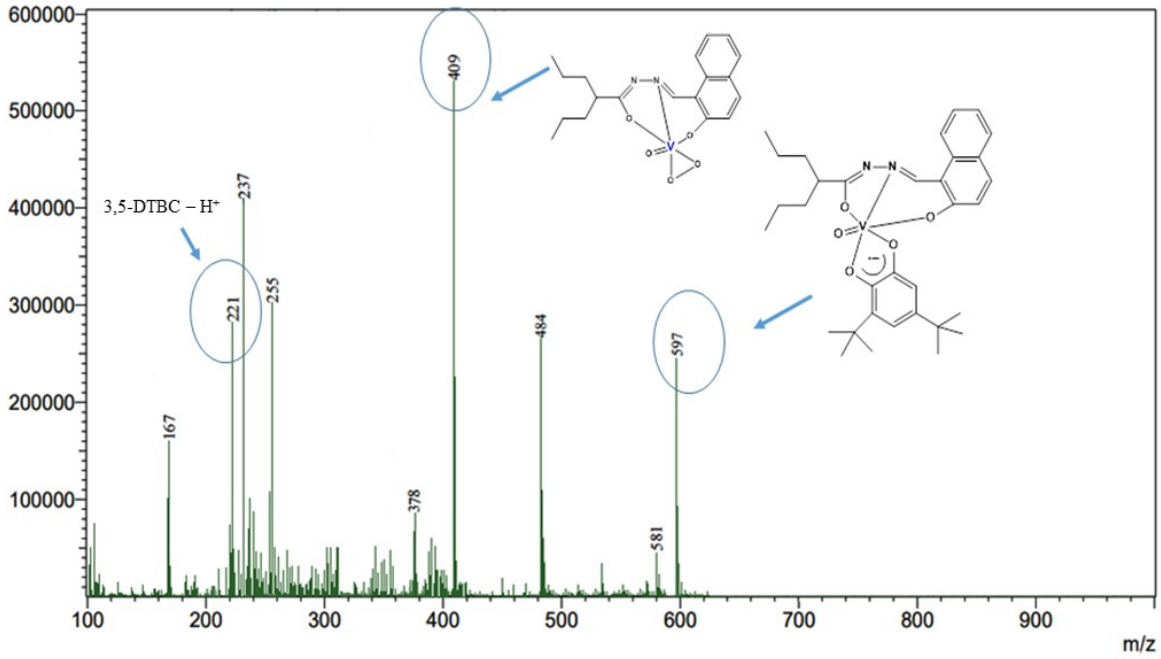


Figure S14. (-Ve) ESI-MS spectra of [Complex **2** + 3,5-DTBC] system.

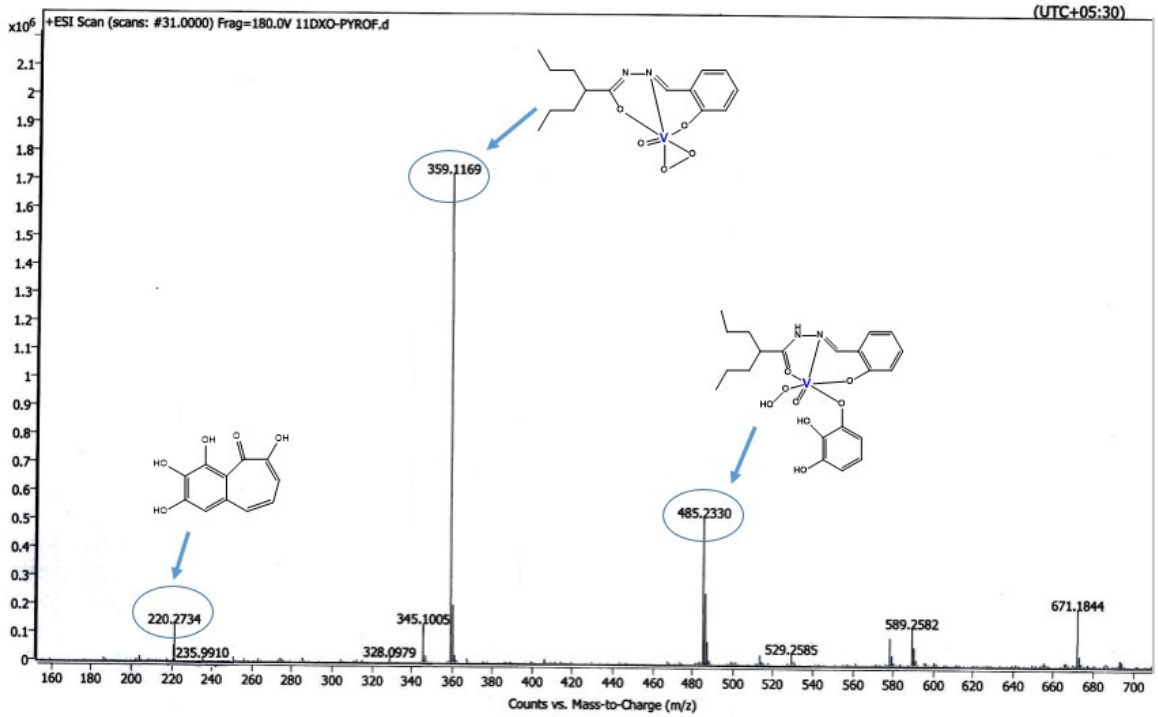


Figure S15.(+Ve) ESI-MS spectra of [Complex **1** + pyrogallol] system.

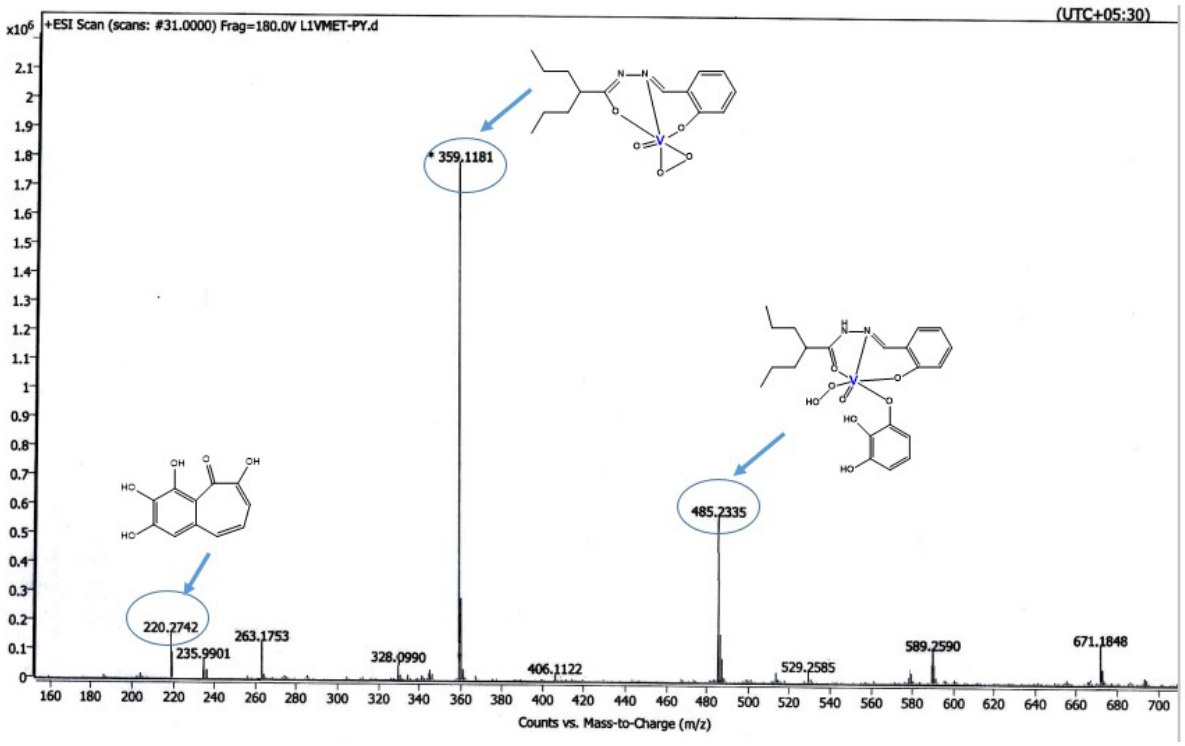


Figure S16. (+Ve) ESI-MSspectra of [Complex **3** + pyrogallol] system

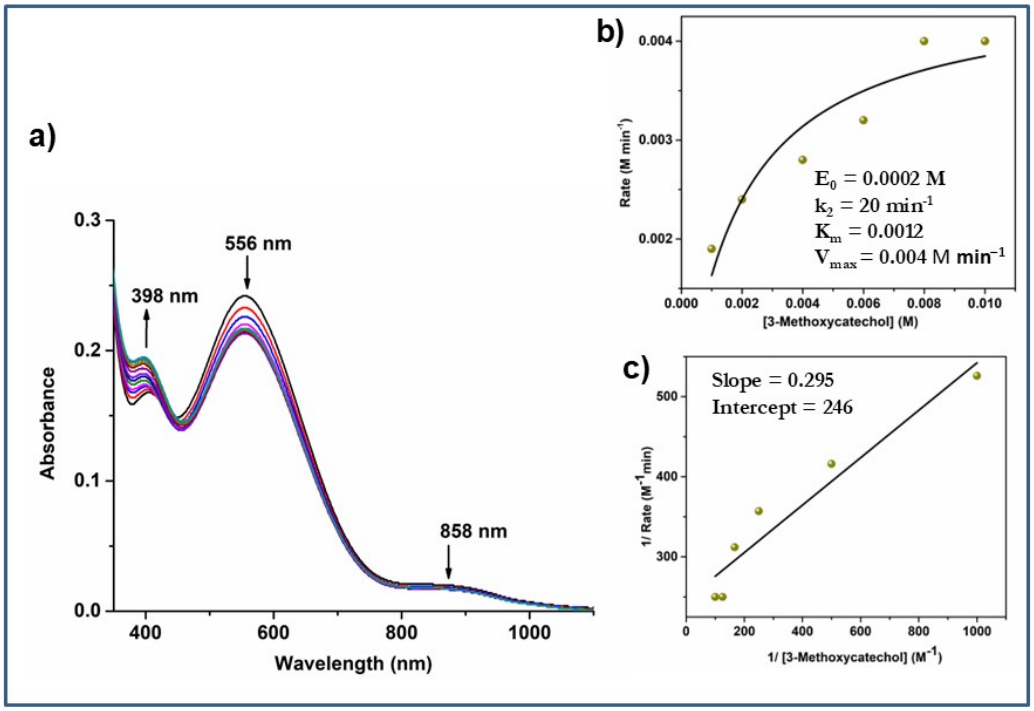


Figure S17(a) Absorption spectra of a solution containing 2×10^{-4} M of complex **3** and 0.004 M of 3-Methoxycatechol recorded at the interval of 5 min in methanol. (b) Plot of rate versus concentration of 3-Methoxycatechol for the oxidation reaction catalysed by complex**3**. (c) Lineweaver–Burk plot

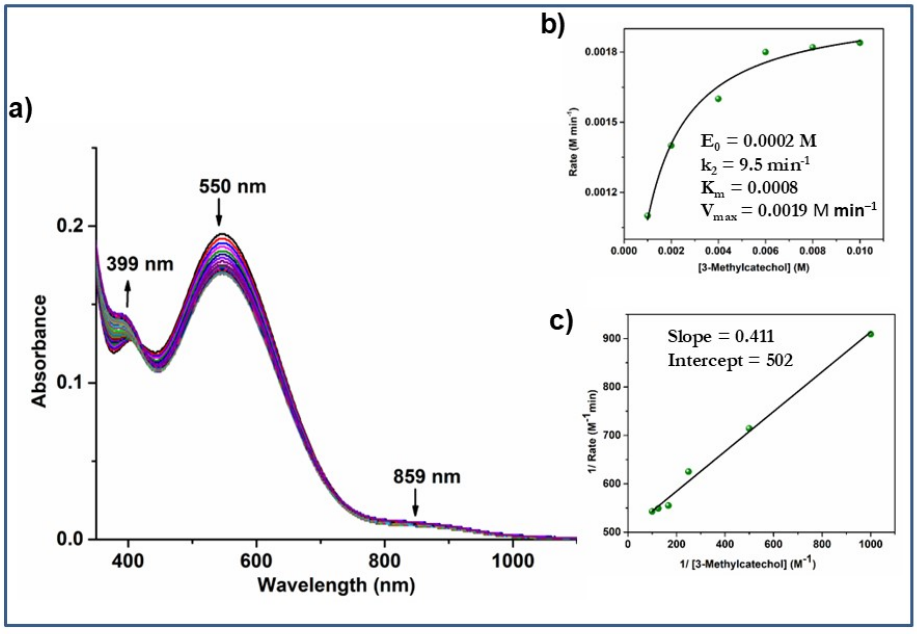


Figure S18(a) Absorption spectra of a solution containing 2×10^{-4} M of complex **3** and 0.004 M of 3-Methylcatechol recorded at the interval of 5 min in methanol. (b) Plot of rate versus concentration of 3-Methylcatechol for the oxidation reaction catalysed by complex **3**. (c) Lineweaver–Burk plot.

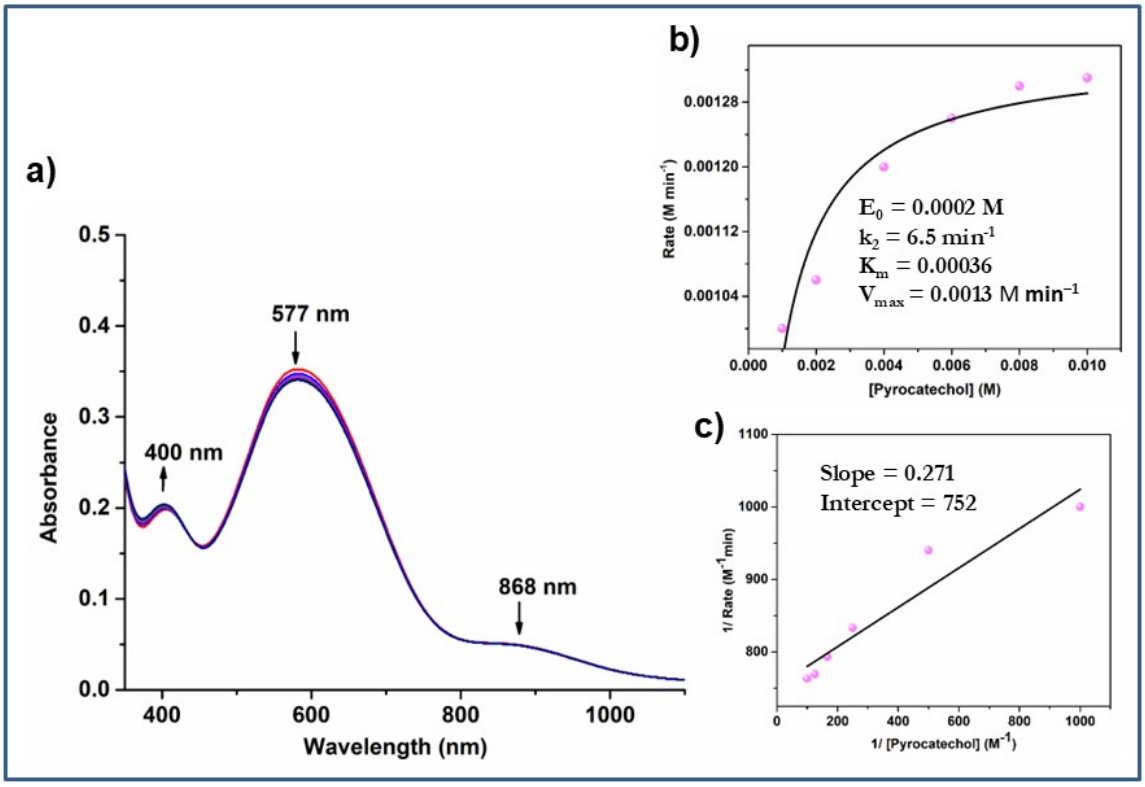


Figure S19(a) Absorption spectra of a solution containing 2×10^{-4} M of complex **3** and 0.004 M of pyrocatechol recorded at the interval of 5 min in methanol. (b) Plot of rate versus concentration of pyrocatechol for the oxidation reaction catalysed by complex **3**. (c) Lineweaver–Burk plot.

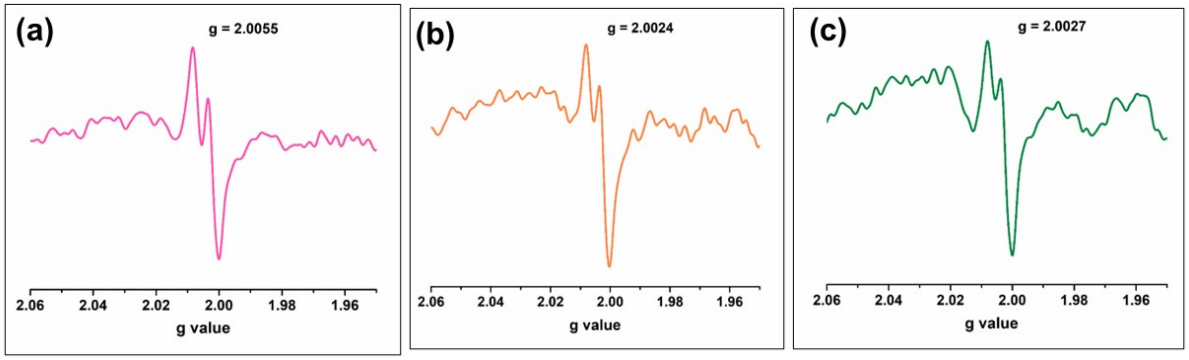


Figure S20. X-band EPR spectra of a) 3-Methoxycatechol with complex **3**, a) 3-Methylcatechol with complex **3**, a) Pyrocatechol with complex **3**

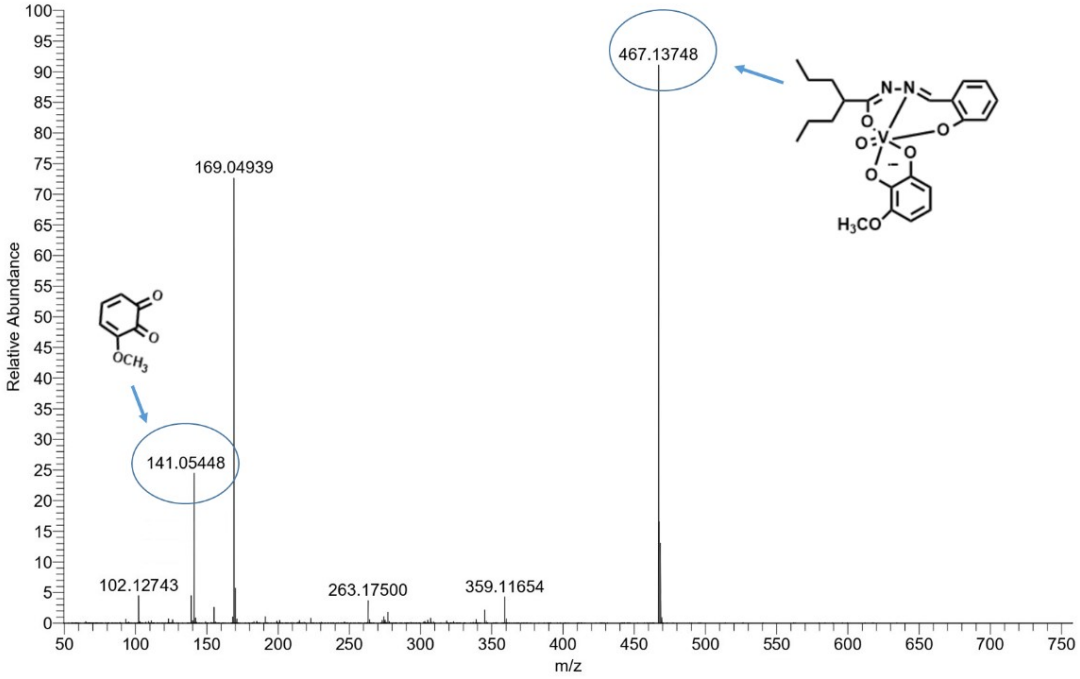


Figure S21. (+Ve) ESI-MS spectra of [Complex **3** + 3-Methoxycatechol] system.

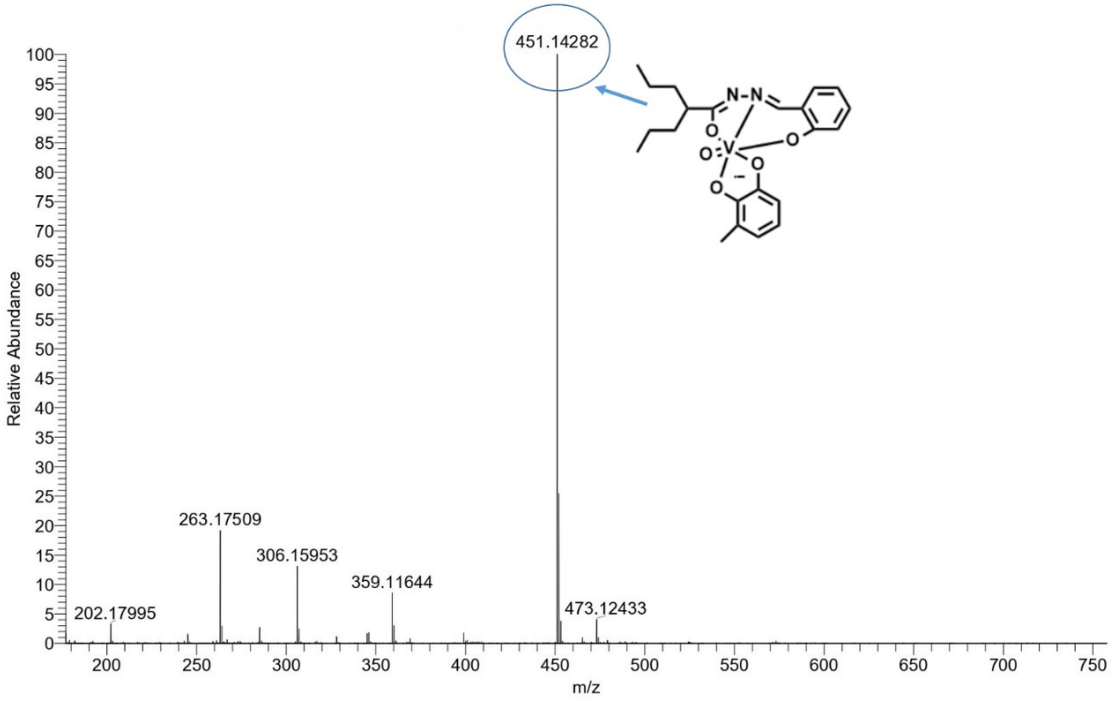


Figure S22. (+Ve) ESI-MS spectra of [Complex **3** + 3-Methylcatechol] system.

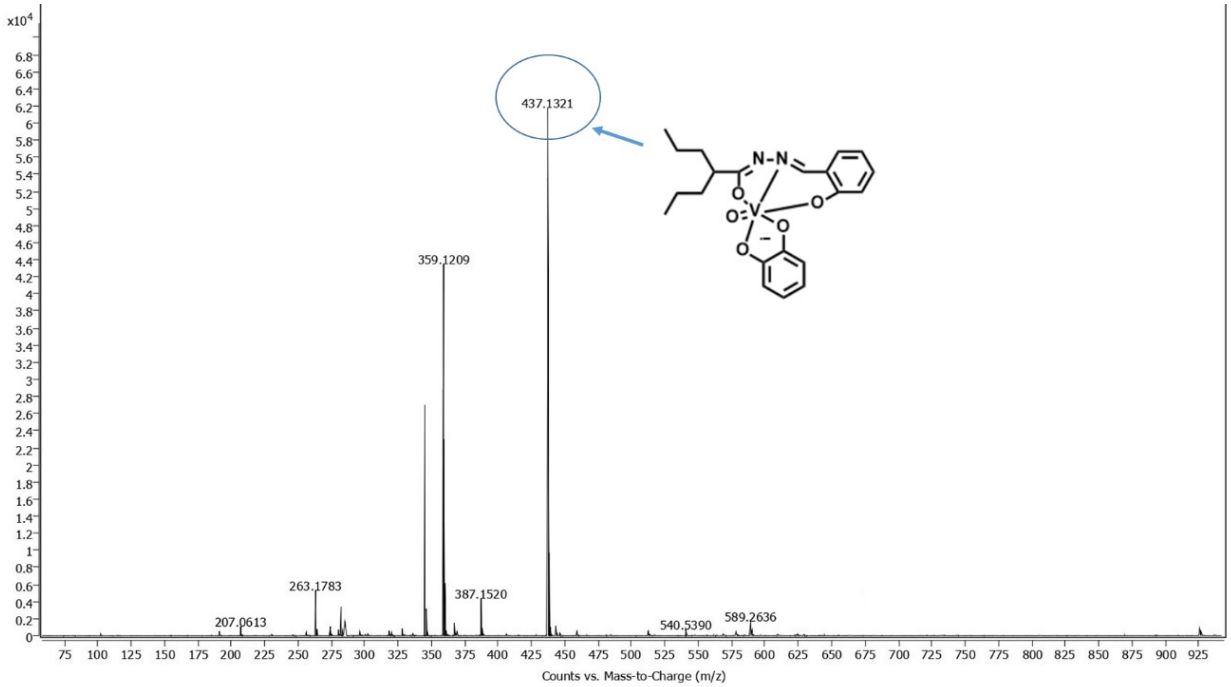


Figure S23. (+Ve) ESI-MS spectra of [Complex **3** + pyrocatechol] system.

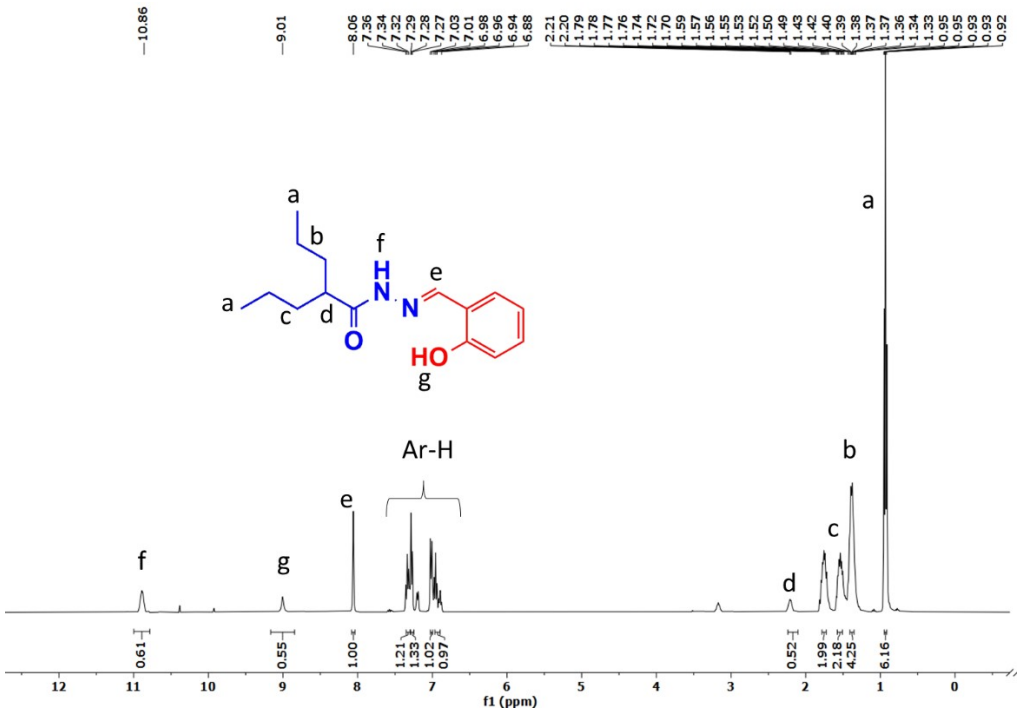


Figure S24. ^{1}H NMR spectra of ligand $\mathbf{H_2L^1}$ in $CDCl_3$.

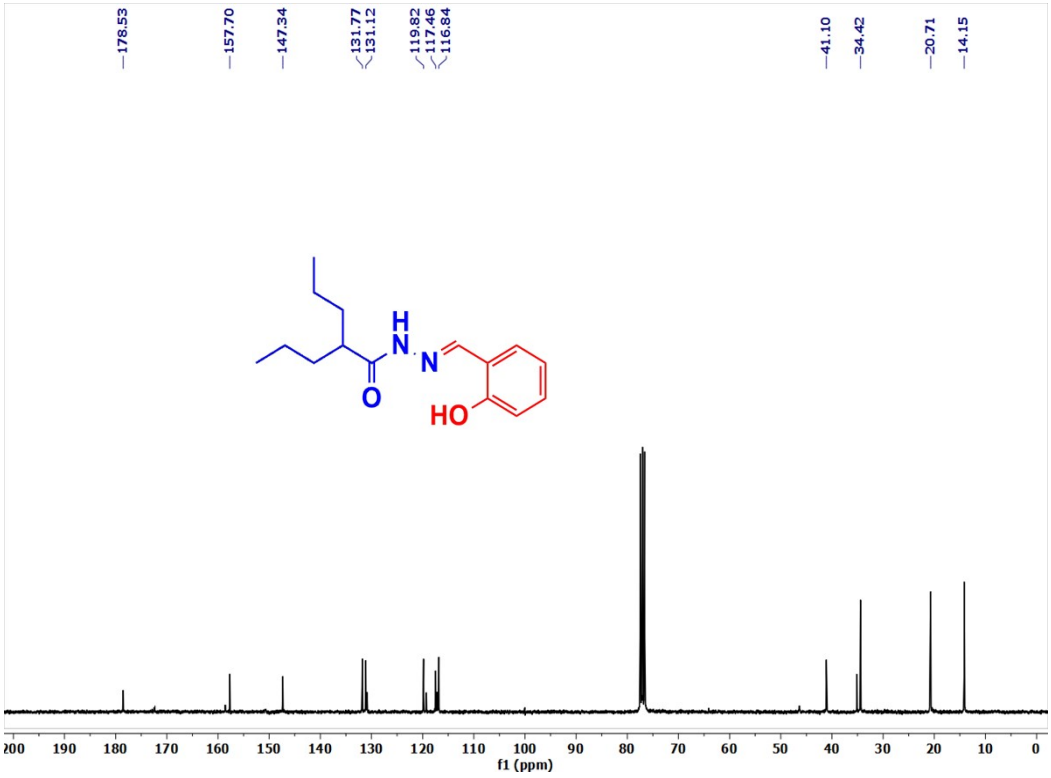


Figure S25. ^{13}C NMR spectra of ligand $\mathbf{H_2L^1}$ in $CDCl_3$.

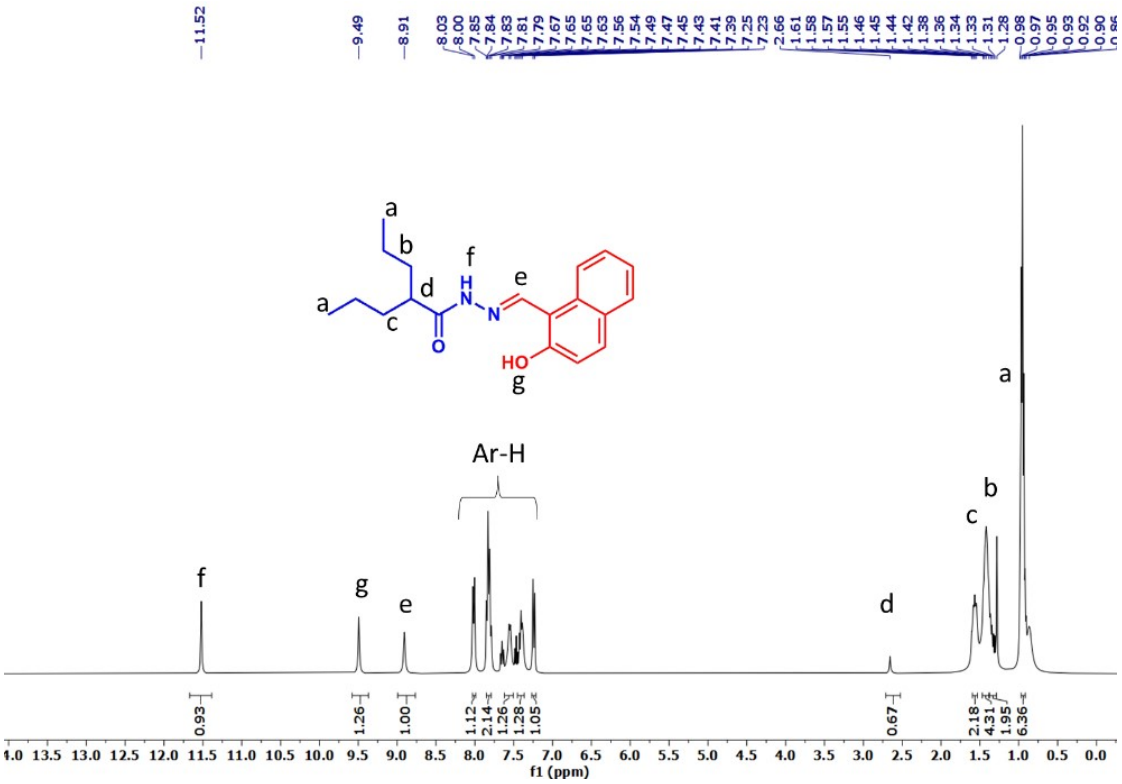


Figure S26. ^{1}H NMR spectra of ligand $\mathbf{H_2L^2}$ in $CDCl_3$.

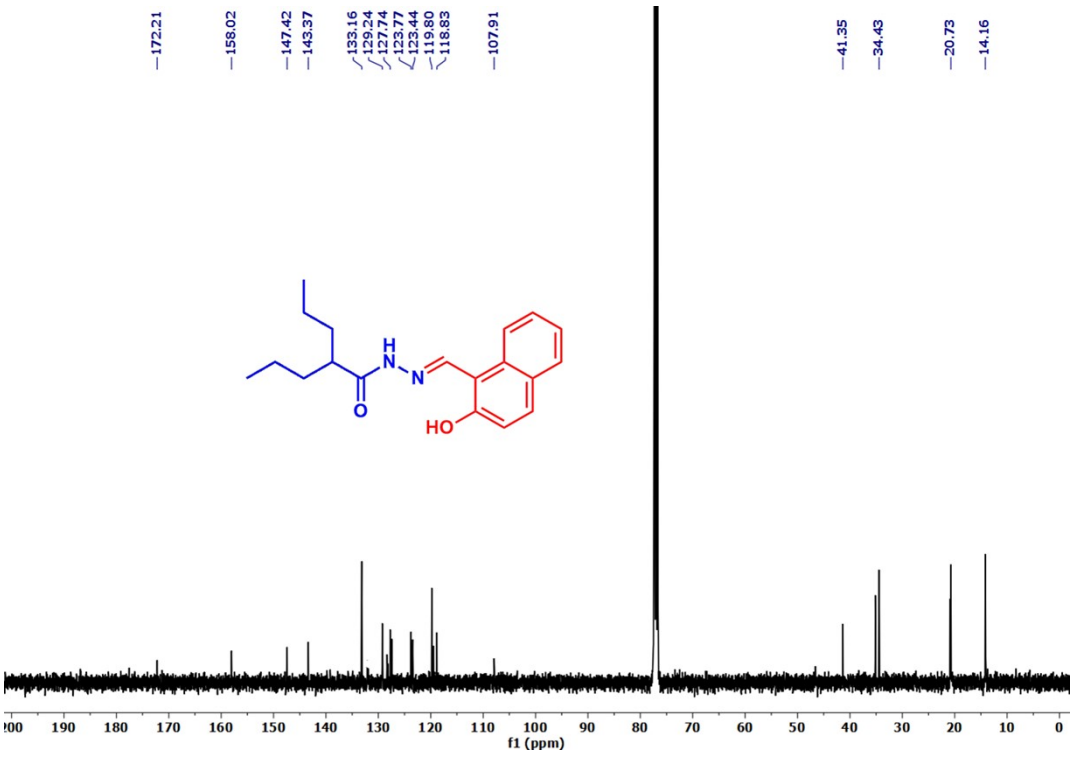


Figure S27. ^{13}C NMR spectra of ligand $\mathbf{H_2L^2}$ in $CDCl_3$.

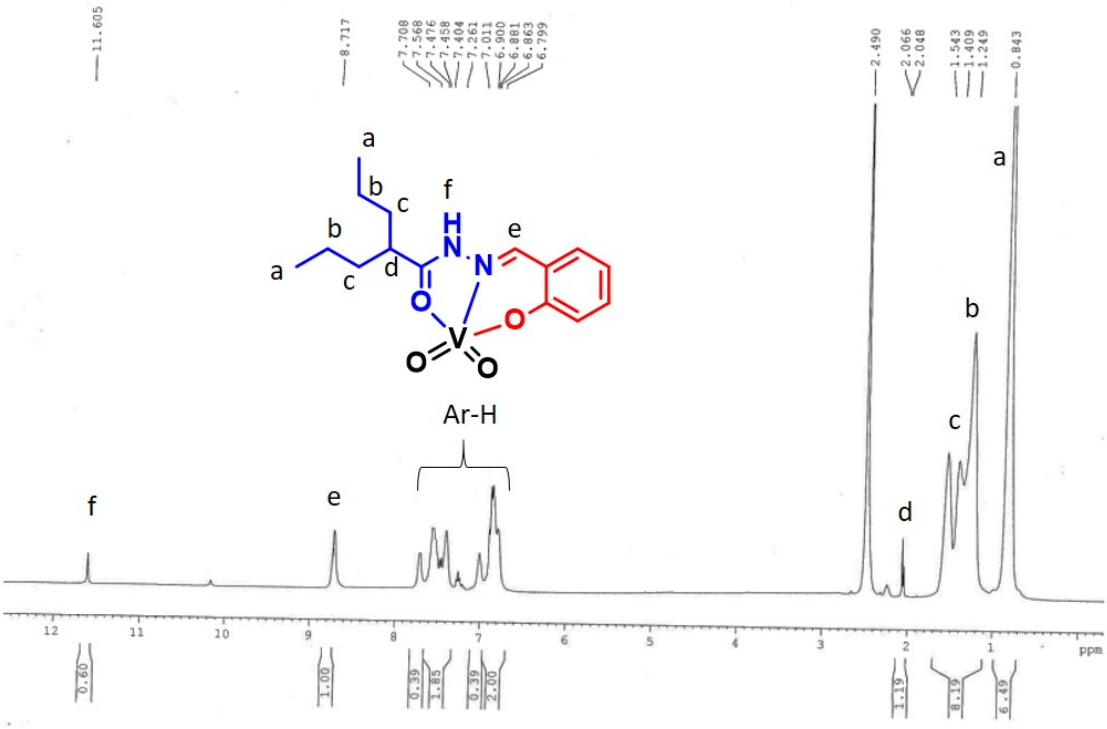


Figure S28. ^{1}H NMR spectra of Complex **1** in DMSO-D6

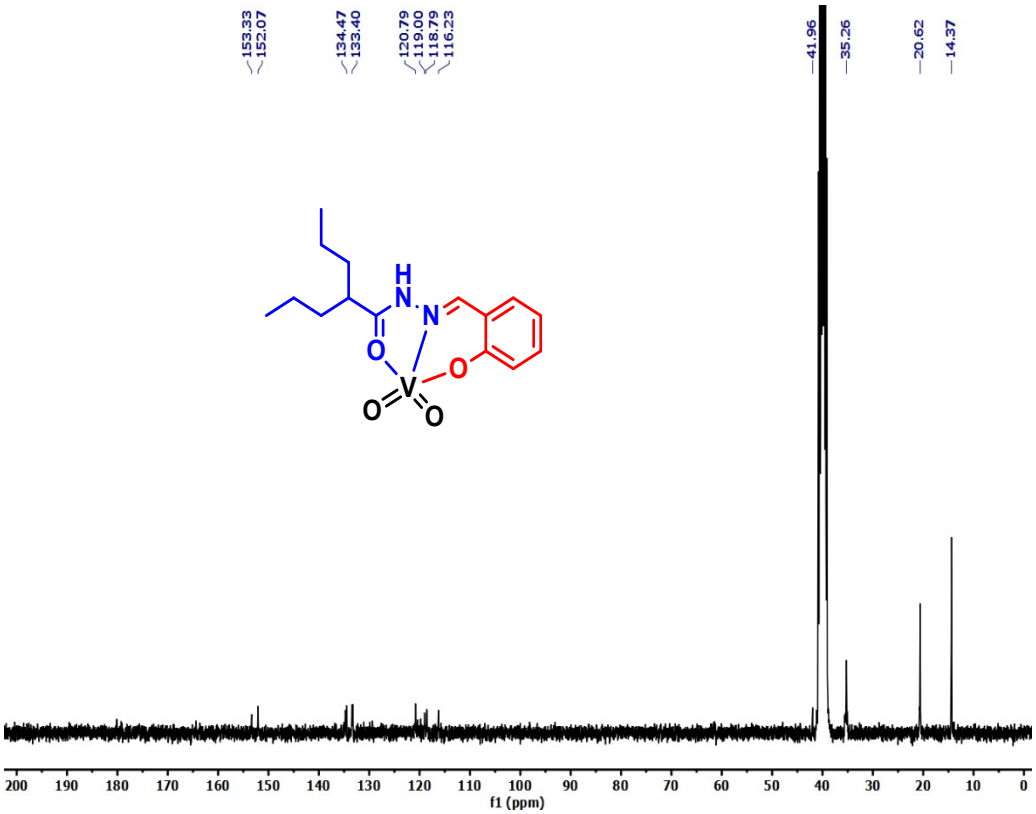


Figure S29. ^{13}C NMR spectra of Complex **1** in DMSO-D6

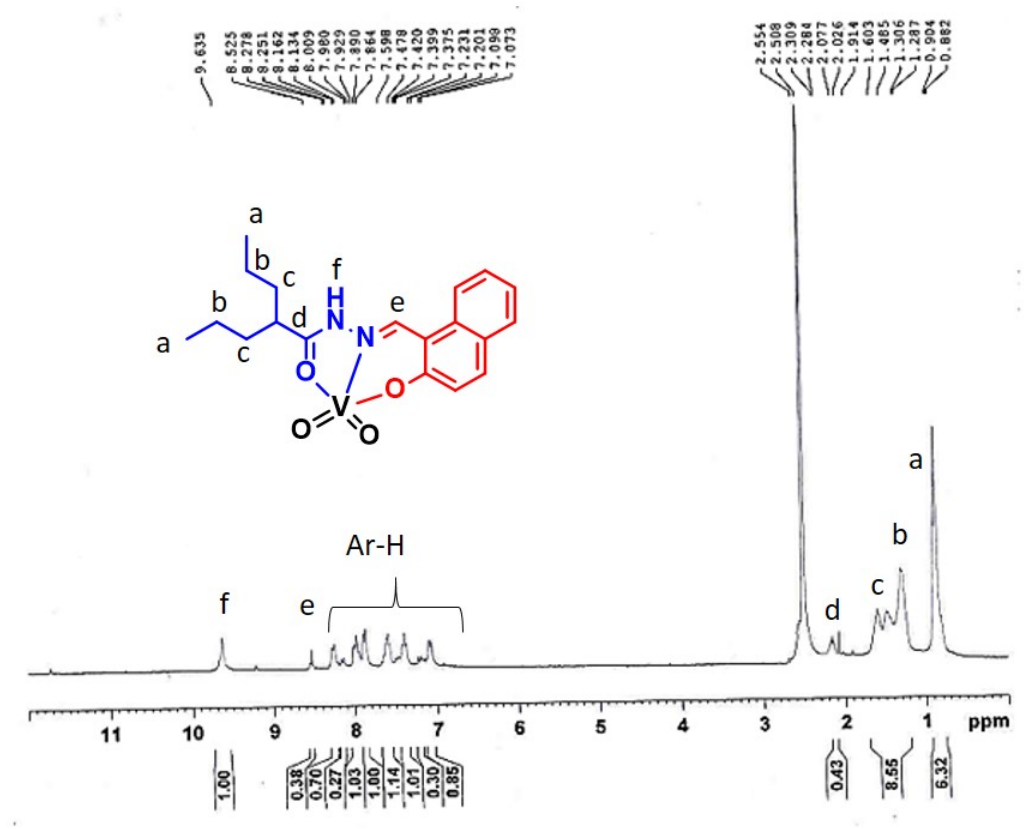


Figure S30. [1]H NMR spectra of Complex **2** in DMSO-D6

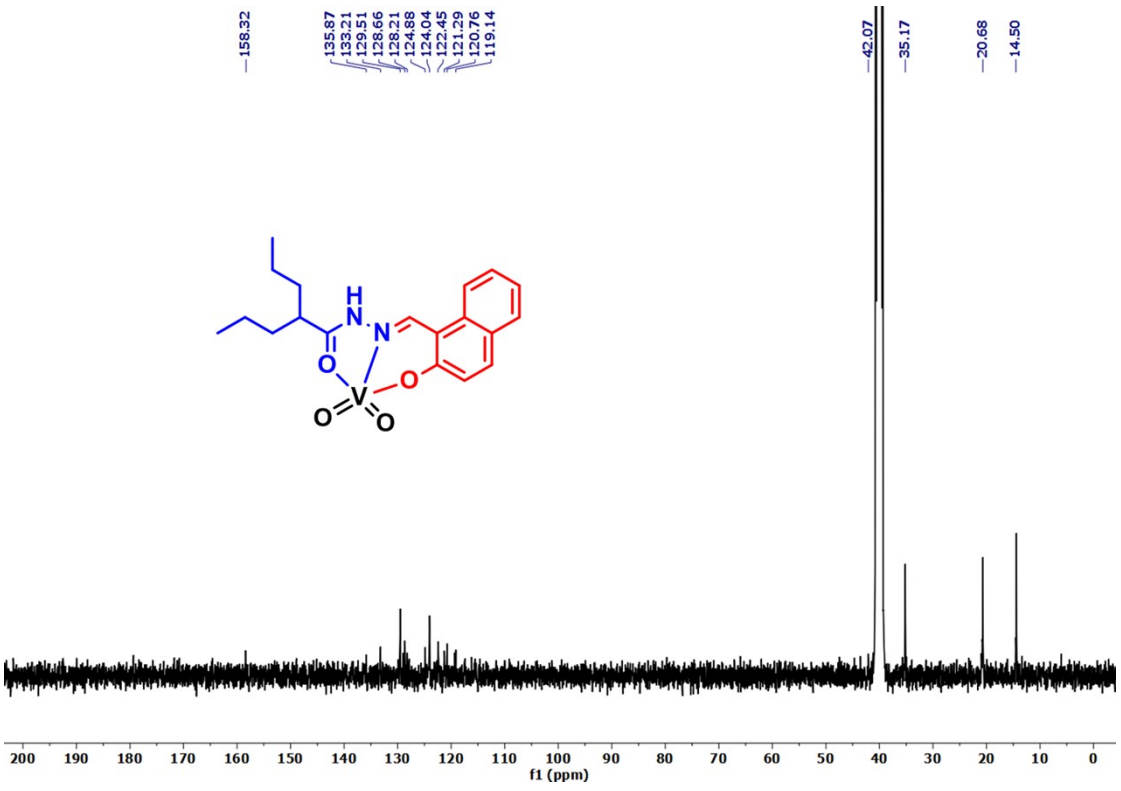


Figure S31. [13]C NMR spectra of Complex **2** in DMSO-D6

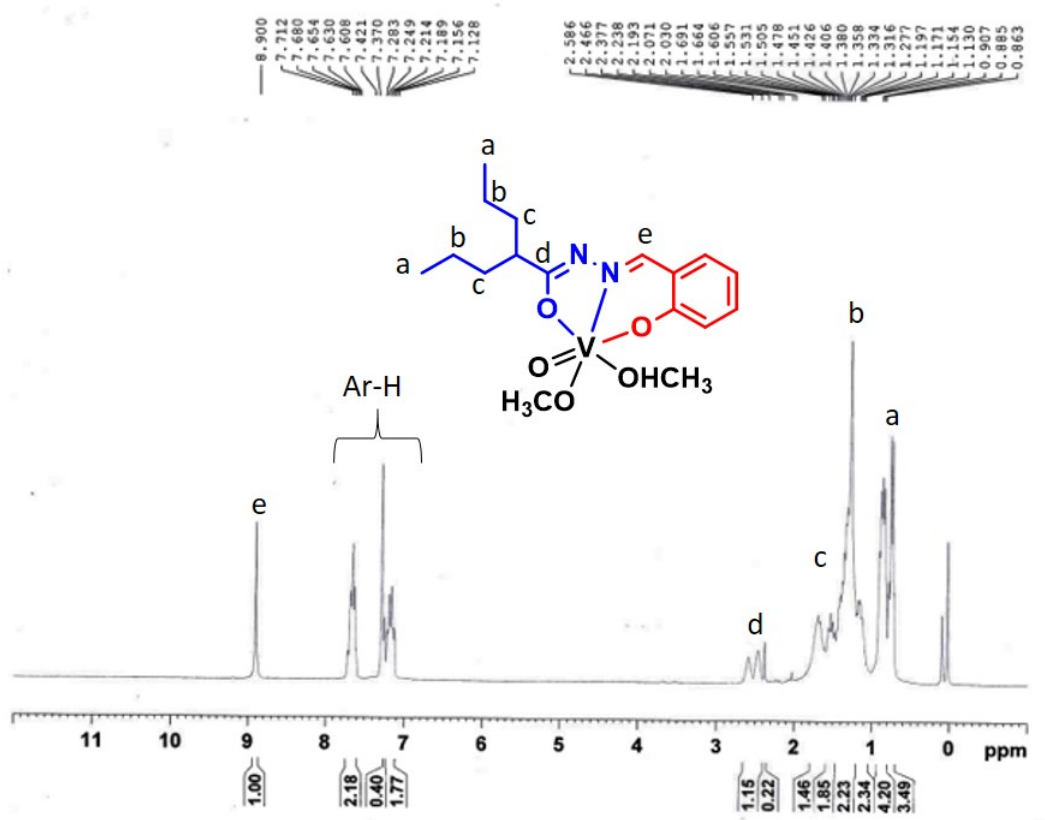


Figure S32. ^{1}H NMR spectra of complex **3** in $CDCl_3$

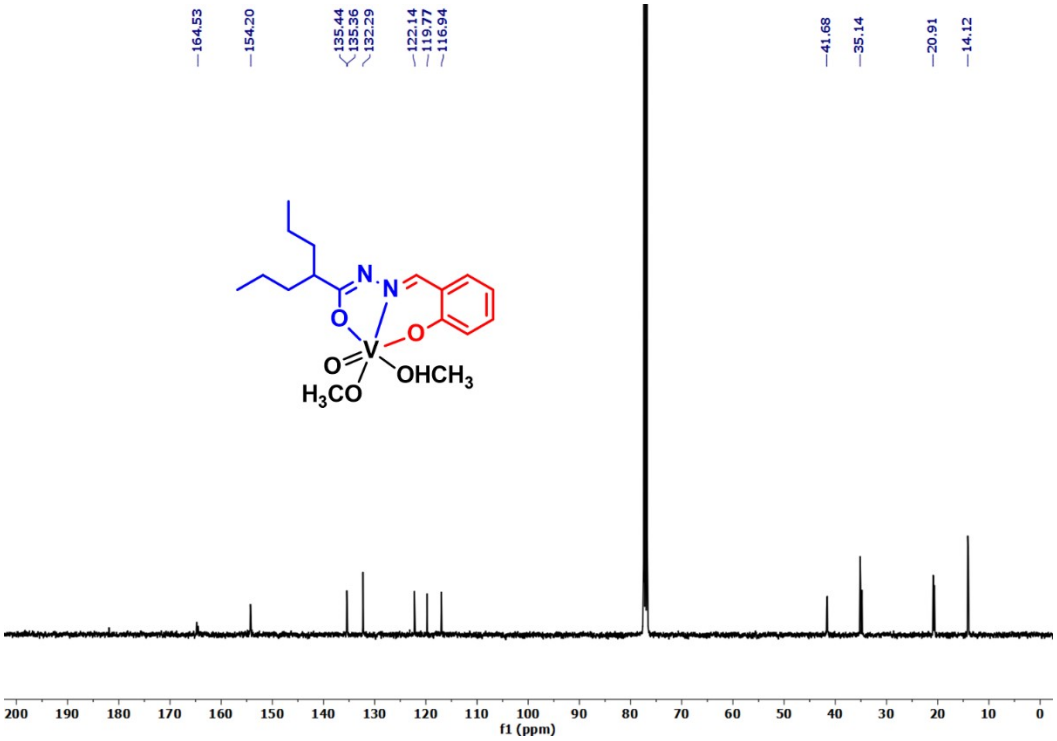


Figure S33. ^{13}C NMR spectra of Complex **3** in $CDCl_3$

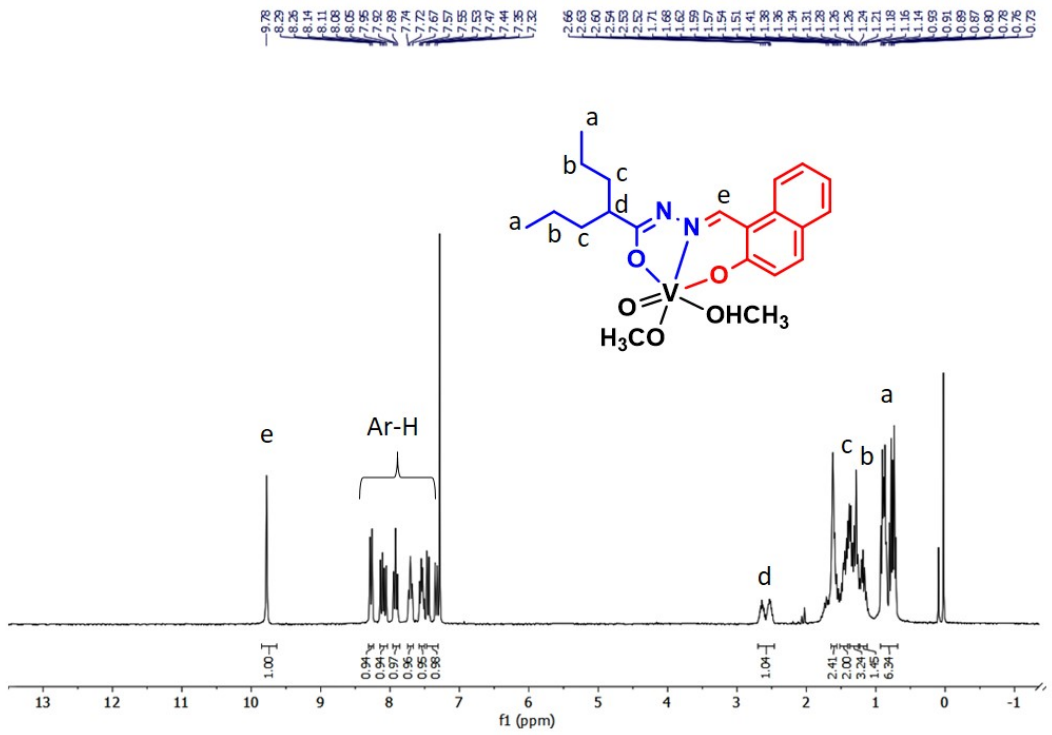


Figure S34. ^{1}H NMR spectra of complex **4** in $CDCl_3$

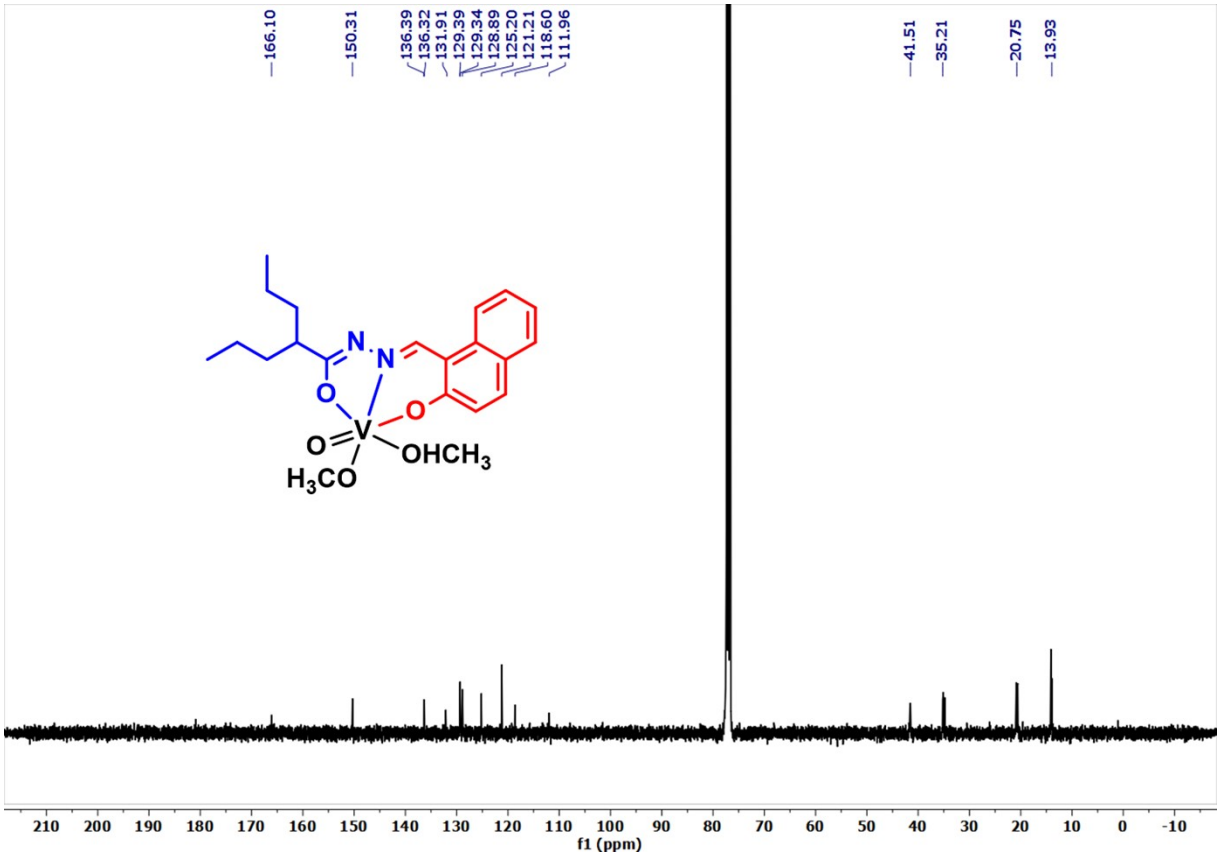


Figure S35. ^{13}C NMR spectra of Complex **4** in $CDCl_3$

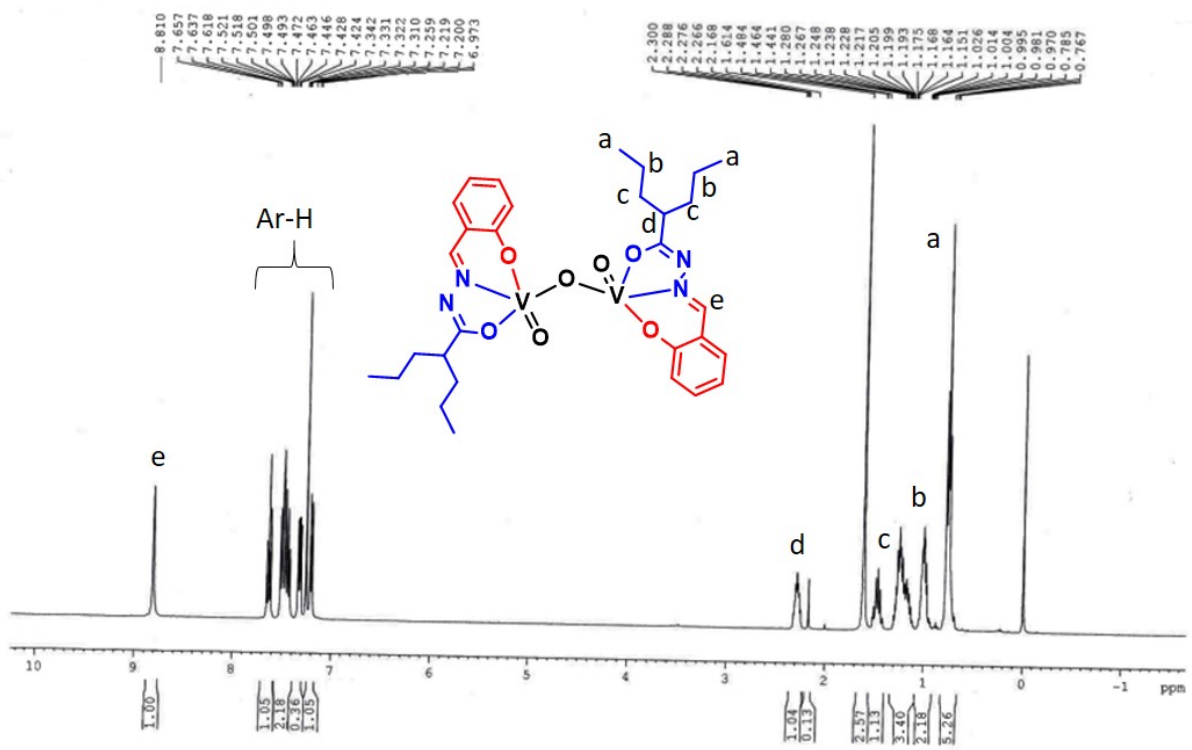


Figure S36. ^{1}H NMR spectra of complex **5** in $CDCl_3$

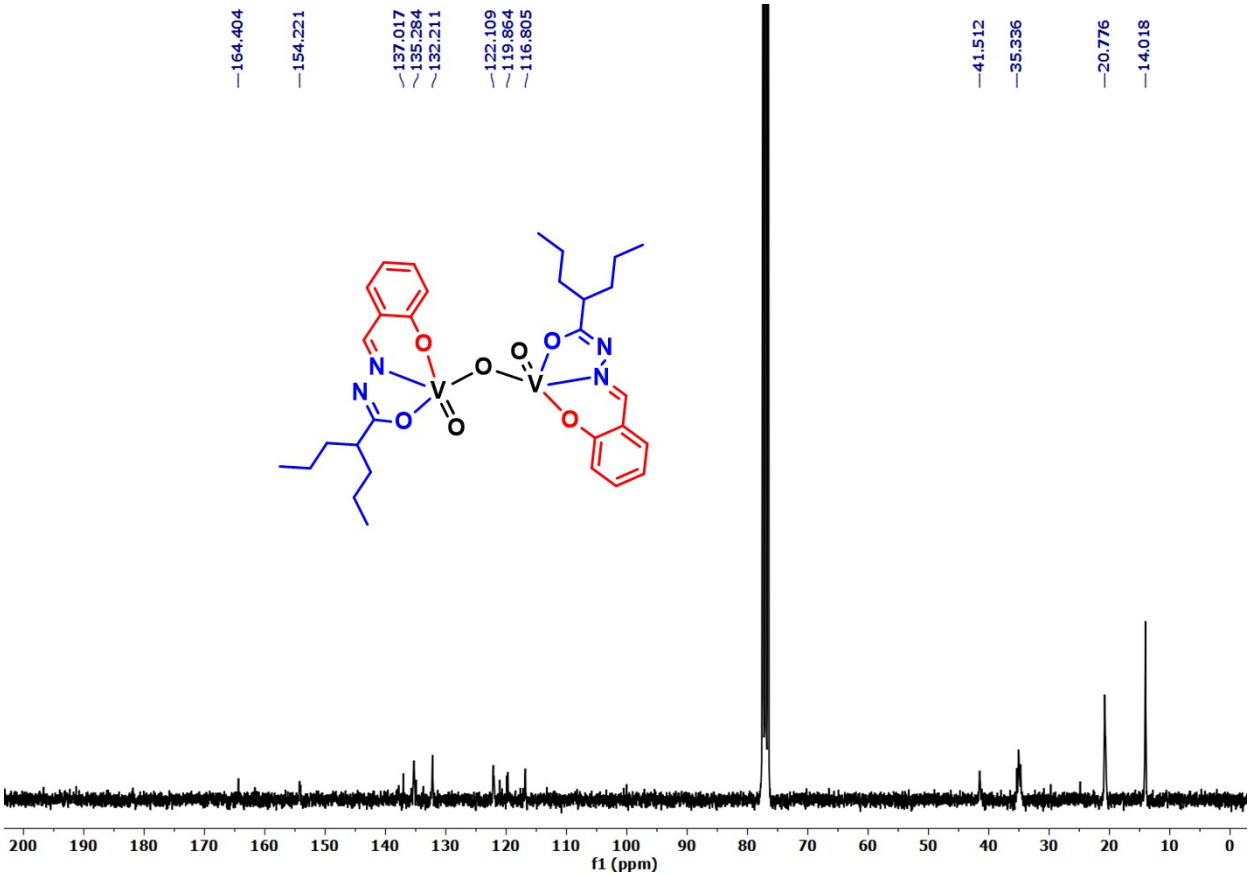


Figure S37. ^{13}C NMR spectra of Complex **5** in $CDCl_3$

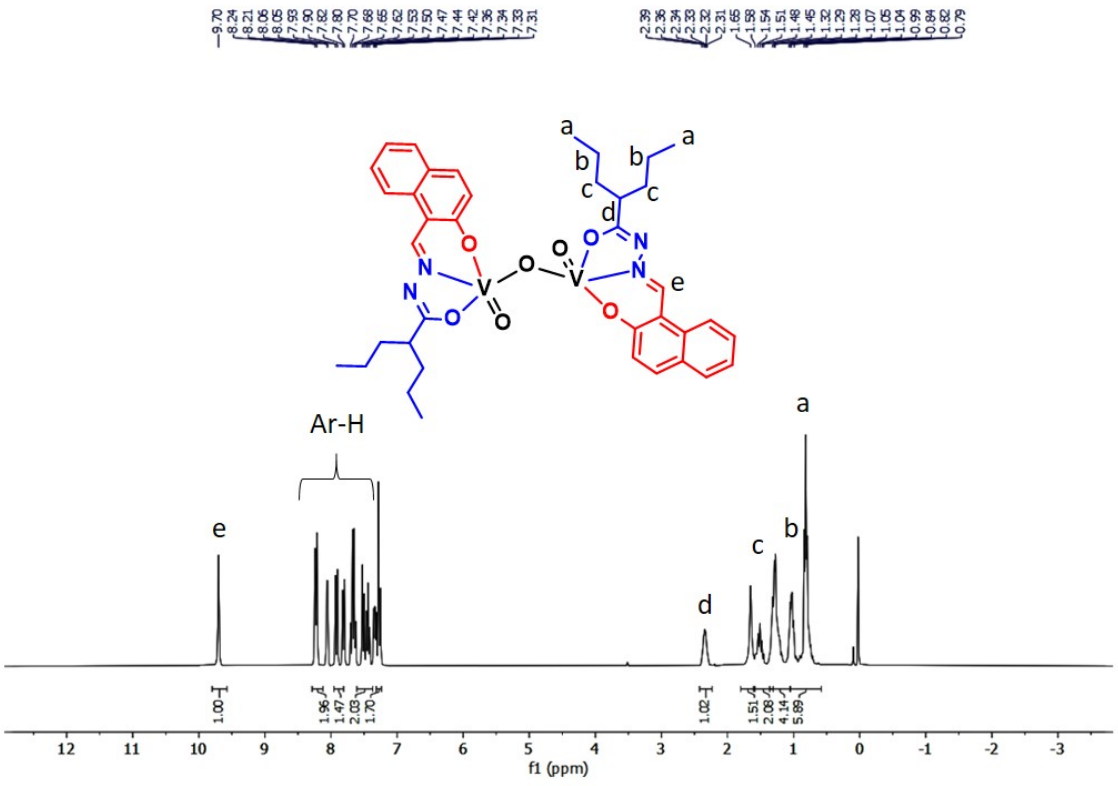


Figure S38. ^{1}H NMR spectra of complex **6** in $CDCl_3$

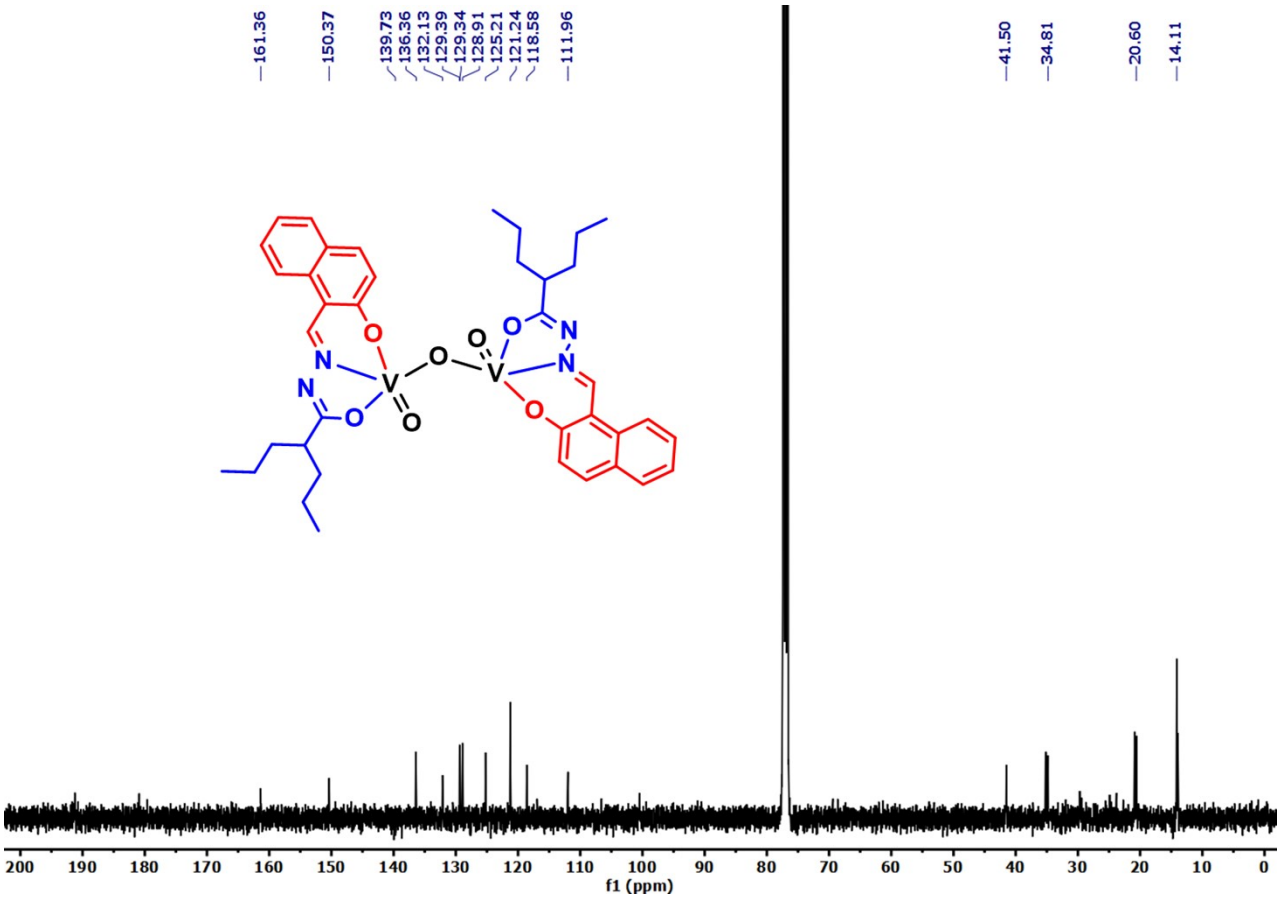


Figure S39. ^{13}C NMR spectra of Complex **6** in $CDCl_3$

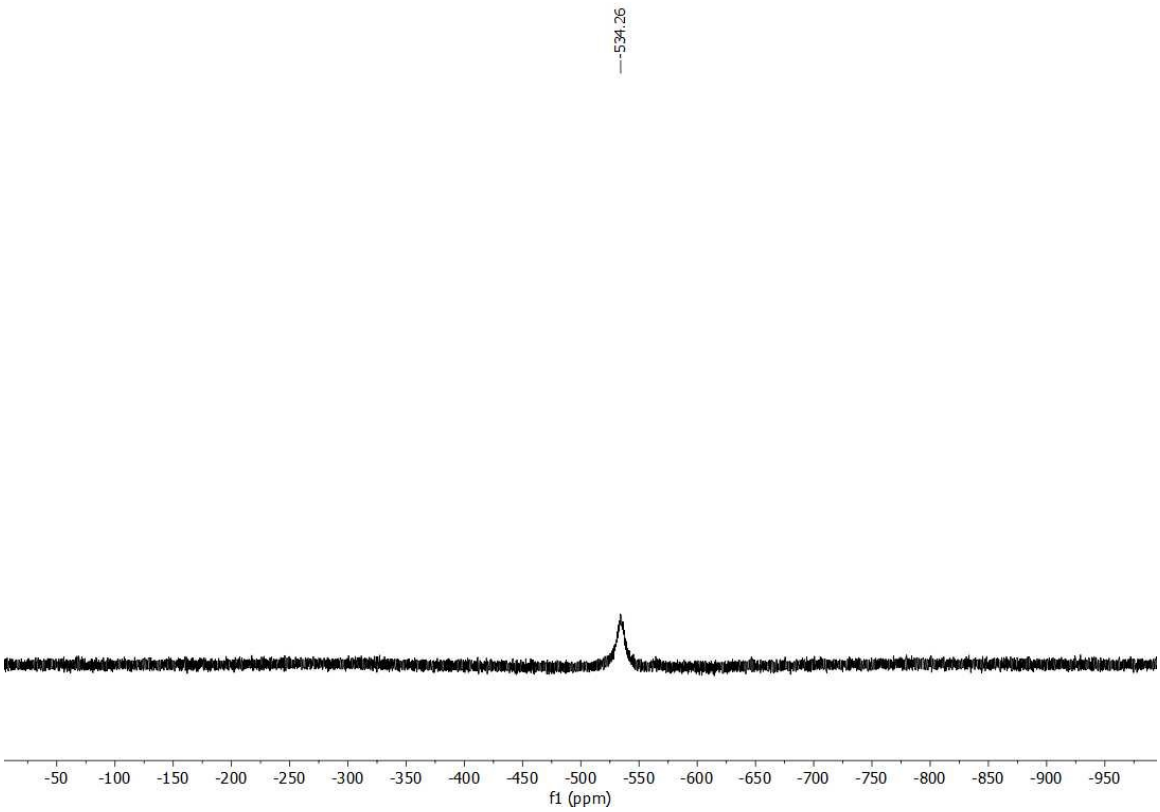


Figure S40. ^{51}V NMR spectra of complex **4** in $CDCl_3$.

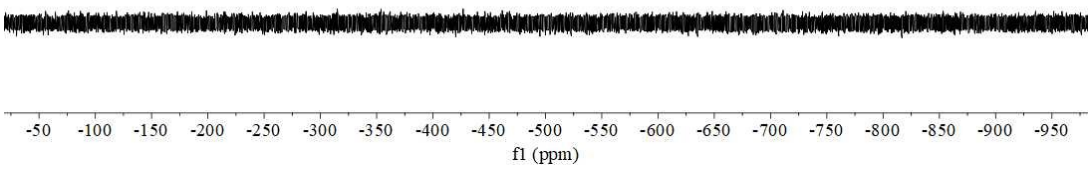


Figure S41. ^{51}V NMR spectra of [Complex **4**+ 3,5-DTBC] in $CDCl_3$.

Computational simulation details

Table S11 Methods and Parameters for Simulation Calculations

Method	DFT
Functional	B3LYP
Basis Set	6-31+G (H) 6-311 +G (C, N, O, V)
Job Type	Optimization
Solvation	Gas Phase
Convergence	SCF (Self Consistent Field Model)

Table S12 Gas Phase Optimized Coordinates of **1** (Singlet Spin State)

Centre Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	23	0.830416	0.71125	1.359265
2	8	2.639132	0.099143	1.246826
3	8	-1.18743	0.286681	0.902801
4	8	0.842526	2.252028	0.926814
5	7	0.756678	-0.47114	-0.56009
6	7	-0.53097	-0.66945	-1.0067
7	8	0.559003	0.580136	2.927354
8	6	3.502698	-0.2029	0.315077
9	6	3.116023	-0.68059	-0.9805
10	6	1.740738	-0.82892	-1.33213
11	1	1.516274	-1.26819	-2.3111
12	6	-1.51098	-0.23212	-0.18638
13	6	-2.95309	-0.40397	-0.60171
14	1	-2.9686	-0.83444	-1.61529
15	6	-3.62962	-1.40989	0.368258
16	1	-2.99132	-2.30104	0.455722
17	1	-3.66463	-0.95879	1.3677
18	6	-5.03435	-1.85606	-0.06299
19	1	-4.99286	-2.25807	-1.08643
20	1	-5.71179	-0.99383	-0.09607
21	6	-5.61923	-2.91682	0.878556
22	1	-4.98994	-3.81536	0.906888
23	1	-6.62198	-3.22083	0.556526
24	1	-5.69894	-2.53495	1.903856
25	6	-3.64937	0.976946	-0.63898

26	1	-3.62938	1.400084	0.373355
27	1	-4.70256	0.819692	-0.90063
28	6	-3.02864	1.974127	-1.62895
29	1	-1.98563	2.176644	-1.3504
30	1	-3.00688	1.525971	-2.63435
31	6	-3.79564	3.301151	-1.68059
32	1	-4.83796	3.14751	-1.98874
33	1	-3.33493	3.996538	-2.39149
34	1	-3.80408	3.787853	-0.69785
35	6	4.110156	-1.04515	-1.92503
36	1	3.795417	-1.41181	-2.90068
37	6	5.45388	-0.93471	-1.62559
38	1	6.207379	-1.2092	-2.35747
39	6	5.834753	-0.4597	-0.35047
40	1	6.89083	-0.37061	-0.10698
41	6	4.88975	-0.10656	0.59758
42	1	5.176497	0.253246	1.580701
43	1	-0.71282	-1.09784	-1.91004

Table S13 Gas Phase Optimized Coordinates of **1**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	23	0.866537	-0.11425	1.520081
2	8	2.699865	-0.44111	1.156962
3	8	-1.22959	-0.02244	0.997394
4	8	0.840799	1.34516	2.212225
5	7	0.743968	-0.22284	-0.60311
6	7	-0.53286	-0.1618	-1.11073
7	8	0.546847	-1.26969	2.603506
8	6	3.557168	-0.26261	0.165397
9	6	3.114883	-0.11582	-1.20132
10	6	1.739416	-0.11124	-1.52822
11	1	1.449958	0.024848	-2.57432
12	6	-1.53163	-0.07165	-0.22578
13	6	-2.9679	-0.0455	-0.70505
14	1	-2.96057	-0.0049	-1.80715
15	6	-3.67798	-1.35586	-0.27735
16	1	-3.04198	-2.20426	-0.56744
17	1	-3.73278	-1.38016	0.818683
18	6	-5.07399	-1.55995	-0.88346
19	1	-5.01219	-1.47223	-1.97938

20	1	-5.75407	-0.76532	-0.54966
21	6	-5.68052	-2.92168	-0.51803
22	1	-5.04836	-3.74556	-0.87383
23	1	-6.67736	-3.04865	-0.95983
24	1	-5.77979	-3.03007	0.569637
25	6	-3.6751	1.22132	-0.17145
26	1	-3.65866	1.181913	0.925599
27	1	-4.72897	1.199811	-0.48109
28	6	-3.04326	2.539535	-0.64073
29	1	-2.00128	2.586347	-0.30124
30	1	-3.01695	2.561874	-1.74146
31	6	-3.79762	3.771298	-0.12459
32	1	-4.84208	3.774796	-0.46674
33	1	-3.32806	4.700234	-0.47148
34	1	-3.8052	3.793436	0.972449
35	6	4.108541	0.027243	-2.21209
36	1	3.779608	0.13681	-3.24616
37	6	5.467189	0.029957	-1.91597
38	1	6.197146	0.142542	-2.71598
39	6	5.888619	-0.11032	-0.58181
40	1	6.948989	-0.10758	-0.33593
41	6	4.936515	-0.2537	0.436566
42	1	5.23862	-0.36627	1.474981
43	1	-0.68352	-0.23886	-2.11223

Table S14 Gas Phase Spin densities of **1**$^{-}$(Doublet Spin State)

Atom Number	Atom Type	Mullikan Charges	Spin Densities
1	V	1.235778	-0.0054
2	O	-0.54858	0.026677
3	O	-0.36911	0.021666
4	O	-0.40229	0.02411
5	N	0.023317	0.135699
6	N	-0.21279	-0.03091
7	O	-0.43597	0.03419
8	C	-0.25185	0.164019
9	C	2.785987	-0.14694
10	C	-1.77412	0.460604
12	C	-0.34029	0.071476
13	C	0.756852	0.03525
15	C	-0.13886	-0.01151
18	C	0.264373	0.014696

21	C	-0.37398	-0.00318
25	C	-0.21764	-0.00815
28	C	0.494796	0.009259
31	C	-0.40529	-0.00737
35	C	-1.15827	0.172248
37	C	0.108466	-0.12303
39	C	-0.18973	0.228426
41	C	0.14919	-0.06183

Table S15 Gas Phase Optimized Coordinates of **2** (Singlet Spin State)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	23	-0.57398	-1.89055	-0.5013
2	8	1.35574	-1.95216	-0.65803
3	8	-2.35115	-0.79699	-0.34491
4	7	-0.01559	0.183386	-0.00298
5	7	-1.13863	0.995127	0.243033
6	1	-1.02978	1.948138	0.560647
7	8	-0.8813	-2.86001	0.753596
8	6	3.668275	0.820605	0.204591
9	8	-1.0121	-2.57607	-1.89348
10	6	2.415813	0.104643	-0.01836
11	6	2.446172	-1.26178	-0.42514
12	6	1.169673	0.74728	0.164446
13	1	1.181386	1.7899	0.470115
14	6	4.901866	0.122653	0.007824
15	6	4.873855	-1.2524	-0.39916
16	1	5.819285	-1.7615	-0.54082
17	6	3.745911	2.17793	0.607563
18	1	2.846828	2.755216	0.771789
19	6	3.704403	-1.91913	-0.60836
20	1	3.674416	-2.95337	-0.91621
21	6	-4.44781	1.31767	-0.94832
22	1	-4.69611	0.318398	-1.31398
23	1	-5.38937	1.802501	-0.67451
24	6	6.172331	2.113165	0.607597
25	1	7.118368	2.612879	0.763117
26	6	-2.33811	0.410136	0.056979
27	6	6.132964	0.789194	0.215158
28	1	7.051629	0.23756	0.059254
29	6	4.96366	2.807641	0.803964
30	1	4.983598	3.844745	1.111746
31	6	-4.40044	0.430548	1.457656
32	1	-4.71862	-0.53768	1.064261

33	1	-5.30526	1.012679	1.656127
34	6	-3.60644	1.165712	0.344754
35	1	-3.33934	2.165655	0.708326
36	6	-3.76115	2.121221	-2.06561
37	1	-3.46869	3.105332	-1.68039
38	1	-2.83828	1.615518	-2.36742
39	6	-3.62171	0.217658	2.767356
40	1	-2.75538	-0.42358	2.577561
41	1	-3.23404	1.179213	3.125138
42	6	-4.65827	2.301726	-3.29914
43	1	-5.57861	2.8329	-3.04411
44	1	-4.9372	1.33531	-3.72421
45	6	-4.48343	-0.42497	3.864378
46	1	-5.34349	0.202364	4.112306
47	1	-3.90669	-0.57795	4.777955
48	1	-4.85967	-1.39861	3.543762
49	1	-4.14881	2.87225	-4.07756

Table S16 Gas Phase Optimized Coordinates of **2**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Coordinates (Angstrom)		
		X	Y	Z
1	23	0.496235	1.847532	0.642002
2	8	-1.36721	2.064053	0.360144
3	8	2.36986	0.812787	0.409732
4	7	0.050757	-0.05507	-0.1878
5	7	1.151745	-0.85222	-0.42035
6	1	1.039796	-1.75243	-0.87666
7	8	0.683399	1.996804	2.238769
8	6	-3.65307	-0.79276	-0.29882
9	8	1.0935	3.133682	-0.1324
10	6	-2.39567	-0.06412	-0.13808
11	6	-2.45372	1.325986	0.229917
12	6	-1.14922	-0.68088	-0.33748
13	1	-1.10818	-1.7341	-0.61501
14	6	-4.905	-0.11074	-0.09106
15	6	-4.9012	1.264211	0.271923
16	1	-5.85136	1.771589	0.428888
17	6	-3.71602	-2.16334	-0.6557
18	1	-2.7978	-2.72023	-0.8188
19	6	-3.7061	1.949063	0.425737
20	1	-3.69159	3.000262	0.701877
21	6	4.510079	-0.37919	-1.37173

22	1	4.771801	0.59461	-0.93802
23	1	5.447151	-0.94603	-1.48011
24	6	-6.14132	-2.16476	-0.60373
25	1	-7.08702	-2.69061	-0.72062
26	6	2.343446	-0.33882	-0.10166
27	6	-6.12118	-0.82758	-0.25215
28	1	-7.05575	-0.29146	-0.08965
29	6	-4.91853	-2.84026	-0.80749
30	1	-4.91393	-3.89329	-1.08256
31	6	4.358643	-1.389	0.963638
32	1	4.618312	-0.41812	1.404995
33	1	5.304702	-1.89899	0.727338
34	6	3.608507	-1.12866	-0.36313
35	1	3.326435	-2.09983	-0.80181
36	6	3.880458	-0.16626	-2.75511
37	1	3.578677	-1.13885	-3.17448
38	1	2.963881	0.42813	-2.65239
39	6	3.573772	-2.21908	1.988404
40	1	2.643874	-1.69673	2.245914
41	1	3.279137	-3.1786	1.535451
42	6	4.829167	0.537445	-3.73365
43	1	5.751852	-0.04039	-3.88247
44	1	5.112549	1.528893	-3.35864
45	6	4.373722	-2.48538	3.269712
46	1	5.30166	-3.03386	3.056339
47	1	3.791623	-3.07788	3.98643
48	1	4.64781	-1.54414	3.76257
49	1	4.358401	0.67593	-4.71488

Table S17 Gas Phase Spin densities of **2**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Mullikan Charges	Spin Densities
1	V	1.216883	-0.00483
2	O	-0.52968	0.043746
3	O	-0.35903	0.01699
4	N	0.113014	0.12897
5	N	-0.35079	-0.02994
7	O	-0.39749	0.025149
8	C	0.461455	0.105446
9	O	-0.42829	0.034718
10	C	1.160457	-0.12292
11	C	-0.37769	0.203808

12	C	-1.11405	0.358855
14	C	0.266829	-0.08092
15	C	0.037598	0.253399
17	C	-0.14118	-0.06559
19	C	-0.16933	-0.04464
21	C	-0.40151	-0.00682
24	C	-0.35006	-0.05877
26	C	0.33809	0.068368
27	C	0.19239	0.063088
29	C	-0.35867	0.089383
31	C	-0.4615	-0.00537
34	C	0.451509	0.036643
36	C	0.542106	0.003768
39	C	0.53908	0.004207
42	C	-0.44109	-0.00842
45	C	-0.43905	-0.00832

Table S18 Gas Phase Optimized Coordinates of **3** (Singlet Spin State)

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	23	0.6924	-1.16117	0.371921
2	8	2.442683	-0.50379	0.611706
3	8	0.60032	0.042001	2.35245
4	1	1.532972	0.200867	2.574733
5	8	-1.22483	-0.82715	0.422624
6	7	0.407614	0.784992	-0.53242
7	8	0.827115	-1.89611	-1.04218
8	6	0.349317	-3.95628	1.277678
9	1	-0.71415	-4.15085	1.431014
10	1	0.926993	-4.53243	2.001479
11	1	0.627219	-4.24833	0.26216
12	7	-0.94144	1.176289	-0.69874
13	6	1.312765	1.583506	-1.01458
14	1	0.968813	2.478415	-1.52484
15	8	0.60801	-2.5571	1.487184
16	6	3.25974	0.295391	-0.12199
17	6	-3.95843	3.599772	1.88698
18	1	-3.48327	4.35486	1.255927
19	1	-3.75079	3.857636	2.927791
20	1	-5.03869	3.672977	1.735684
21	6	2.732082	1.345449	-0.91835
22	6	-3.69932	-0.0347	-1.70484

23	1	-4.78645	0.093739	-1.74364
24	6	5.002166	1.999761	-1.52617
25	1	5.675692	2.650927	-2.06513
26	6	-1.725	0.259594	-0.18247
27	6	5.508316	0.951875	-0.73975
28	1	6.576872	0.795765	-0.67316
29	6	-3.34575	-1.4777	-2.10326
30	1	-3.75769	-2.16714	-1.35873
31	6	-3.44237	2.193801	1.545065
32	1	-2.36589	2.147676	1.733966
33	6	-3.71675	1.796736	0.08529
34	1	-4.7945	1.84354	-0.10464
35	6	4.648265	0.109558	-0.04267
36	1	5.02044	-0.69865	0.569752
37	6	3.629923	2.19121	-1.60649
38	1	3.22777	2.995389	-2.21024
39	6	-0.20583	-0.36217	3.501002
40	1	-0.21606	0.430415	4.250057
41	1	0.167885	-1.29289	3.925892
42	1	-1.2053	-0.51913	3.112936
43	6	-3.22509	0.378485	-0.28421
44	6	-3.8724	-1.84965	-3.49761
45	1	-3.45124	-1.19447	-4.26441
46	1	-4.96119	-1.76211	-3.54759
47	1	-3.60871	-2.87664	-3.75829
48	1	-2.26174	-1.61607	-2.07588
49	1	-3.26989	0.664069	-2.4293
50	1	-3.23997	2.517519	-0.58348
51	1	-3.90927	1.460783	2.2128
52	1	-3.63453	-0.33865	0.432989

Table S19 Gas Phase Optimized Coordinates of **3**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	23	0.560888	-0.96539	0.09404
2	8	2.330661	-0.10897	0.416994
3	8	4.291737	-1.92125	1.184115
4	1	3.50041	-1.33307	1.191369
5	8	-1.41734	-0.951	0.543426
6	7	-0.06953	1.024892	-0.27217
7	8	0.679266	-1.73265	-1.32563
8	6	0.109291	-3.22983	1.924898

9	1	-0.95596	-2.97278	1.948645
10	1	0.409454	-3.5553	2.928595
11	1	0.233519	-4.08378	1.242996
12	7	-1.48117	1.222728	-0.28623
13	6	0.65776	2.061005	-0.58306
14	1	0.12771	2.973037	-0.85143
15	8	0.914436	-2.1196	1.522362
16	6	2.881495	0.993593	-0.09878
17	6	-4.71989	3.033943	2.417599
18	1	-4.37431	3.873383	1.808458
19	1	-4.52177	3.278458	3.464366
20	1	-5.80443	2.957667	2.29224
21	6	2.096115	2.086922	-0.58579
22	6	-4.04878	-0.38274	-1.32555
23	1	-5.14565	-0.42123	-1.33226
24	6	4.134534	3.346072	-1.07857
25	1	4.617689	4.240668	-1.44972
26	6	-2.07824	0.121205	0.136948
27	6	4.902311	2.260359	-0.60967
28	1	5.98425	2.321947	-0.62384
29	6	-3.49133	-1.735	-1.80458
30	1	-3.79144	-2.51661	-1.09859
31	6	-4.0182	1.731488	2.002807
32	1	-2.94192	1.831665	2.161704
33	6	-4.26966	1.357475	0.533102
34	1	-5.35004	1.263882	0.364959
35	6	4.294247	1.111931	-0.12928
36	1	4.864245	0.265125	0.227685
37	6	2.752933	3.248416	-1.06057
38	1	2.145098	4.072462	-1.41882
39	6	3.948471	-3.13332	0.467824
40	1	3.345293	-2.9235	-0.41862
41	1	3.385168	-3.82468	1.10155
42	1	4.883578	-3.6083	0.166215
43	6	-3.58951	0.042603	0.096843
44	6	-3.97422	-2.1017	-3.21634
45	1	-3.6537	-1.35302	-3.94616
46	1	-5.06646	-2.16452	-3.26235
47	1	-3.5692	-3.06559	-3.53301
48	1	-2.40003	-1.71906	-1.78235
49	1	-3.7537	0.403715	-2.02824
50	1	-3.90765	2.163639	-0.1097
51	1	-4.35446	0.912995	2.649453
52	1	-3.86527	-0.75334	0.795453

Table S20 Gas Phase Spin densities of **3**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Mullikan Charges	Spin Densities
1	V	1.5843	1.09302
2	O	-0.74517	0.007158
3	O	-0.23448	0.001573
5	O	-0.64359	-0.0006
6	N	-0.51953	-0.010598
7	O	-0.60461	-0.12895
8	C	0.168503	0.009857
12	N	-0.27579	0.00136
13	C	0.265188	0.008287
15	O	-0.7056	0.010039
16	C	0.369201	0.00486
17	C	-0.03763	-0.000001
21	C	-0.10351	-0.003031
22	C	-0.00488	0.000271
24	C	-0.07304	-0.002146
26	C	0.456502	0.004824
27	C	0.01326	0.003222
29	C	0.037146	-0.000077
31	C	0.018431	0.000046
33	C	0.012153	-0.000106
35	C	-0.04605	-0.002281
37	C	-0.00707	0.002945
39	C	0.186024	0.000343
43	C	-0.07038	-0.000009
44	C	-0.0394	-0.000007

Table S21. Gas Phase Optimized Coordinates of **4** (Singlet Spin State)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	23	-0.44104	1.636608	0.247857
2	8	1.329892	1.803294	-0.39495
3	8	-0.63876	1.588394	-2.07177
4	1	0.237345	1.867455	-2.38662
5	8	-2.15398	0.734695	0.116813
6	7	0.025562	-0.44653	0.007257
7	8	-0.19197	1.619004	1.827209

8	6	-1.66529	4.240502	0.944142
9	1	-2.74908	4.118775	0.999175
10	1	-1.43613	5.241916	0.577622
11	1	-1.23562	4.100754	1.939003
12	7	-1.09309	-1.31385	-0.03252
13	6	1.198835	-1.01414	-0.03507
14	1	1.197611	-2.09583	-0.08027
15	8	-1.12772	3.275237	0.02344
16	6	2.467521	1.091886	-0.22215
17	6	-3.81483	-2.92768	-3.46481
18	1	-3.02657	-3.67939	-3.37662
19	1	-3.77498	-2.52132	-4.47779
20	1	-4.77459	-3.43815	-3.34872
21	6	2.449408	-0.30259	-0.03582
22	6	-3.78978	-1.85308	1.53517
23	1	-4.76916	-2.34392	1.529741
24	6	4.934328	-0.27263	0.017702
25	6	-2.19243	-0.60567	0.052205
26	6	4.886087	1.13891	-0.18218
27	1	5.819083	1.685758	-0.23792
28	6	-3.74993	-0.81485	2.669141
29	1	-4.48405	-0.02859	2.46381
30	6	-3.64191	-1.82306	-2.41142
31	1	-2.68513	-1.31691	-2.56979
32	6	-3.69796	-2.36037	-0.97165
33	1	-4.65644	-2.86611	-0.81258
34	6	3.69415	1.802851	-0.29714
35	1	3.644969	2.871605	-0.44454
36	6	3.707178	-1.01168	0.09648
37	6	-1.73693	2.229341	-2.79047
38	1	-1.70389	1.957965	-3.84628
39	1	-1.69953	3.310607	-2.66568
40	1	-2.64369	1.846713	-2.33724
41	6	-3.54335	-1.27256	0.115693
42	6	-4.03081	-1.43549	4.04598
43	1	-3.28939	-2.20026	4.290993
44	1	-5.01675	-1.90739	4.075272
45	1	-3.99988	-0.67978	4.833444
46	1	-2.77473	-0.32087	2.686121
47	1	-3.04439	-2.63207	1.723014
48	1	-2.91257	-3.10745	-0.83192
49	1	-4.42267	-1.06564	-2.54524
50	1	-4.27835	-0.48266	-0.06297
51	6	3.797283	-2.41378	0.316093

52	6	6.174757	-0.95077	0.144438
53	6	5.019748	-3.04589	0.434594
54	6	6.223841	-2.31329	0.346668
55	1	2.900078	-3.00802	0.404746
56	1	5.053758	-4.11431	0.601674
57	1	7.174129	-2.82043	0.442706
58	1	7.088208	-0.37239	0.081398

Table S22. Gas Phase Optimized Coordinates of **4**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	23	-0.55422	1.445065	0.685001
2	8	1.349565	1.750742	0.229037
3	8	0.319395	4.361984	-2.00824
4	1	-0.02505	3.967692	-1.15445
5	8	-2.28329	0.675137	-0.01172
6	7	-0.07426	-0.53047	0.138901
7	8	-0.68992	1.48729	2.291486
8	6	-2.28802	3.730682	-0.07101
9	1	-3.05737	2.988406	-0.30021
10	1	-2.31258	4.516896	-0.83187
11	1	-2.51663	4.178353	0.904121
12	7	-1.19571	-1.37714	-0.11542
13	6	1.095759	-1.11258	0.071436
14	1	1.073167	-2.17577	-0.14085
15	8	-0.97746	3.138357	-0.06716
16	6	2.416197	0.972674	0.249359
17	6	-3.32502	-3.43408	-3.59621
18	1	-2.57192	-4.15966	-3.27763
19	1	-3.10885	-3.16331	-4.63282
20	1	-4.29752	-3.93551	-3.57784
21	6	2.358816	-0.44867	0.210714
22	6	-4.14582	-1.73018	1.146245
23	1	-5.11513	-2.23121	1.027174
24	6	4.849801	-0.52587	0.267881
25	6	-2.29396	-0.64539	-0.14717
26	6	4.856796	0.905206	0.274532
27	1	5.813521	1.415277	0.28887
28	6	-4.29682	-0.56692	2.142216
29	1	-4.9879	0.174068	1.726616
30	6	-3.31766	-2.20027	-2.68037
31	1	-2.34232	-1.71139	-2.7364

32	6	-3.61655	-2.54603	-1.21247
33	1	-4.59025	-3.04815	-1.1524
34	6	3.696254	1.621158	0.267617
35	1	3.683026	2.701584	0.275144
36	6	3.590685	-1.21471	0.241238
37	6	0.564972	3.28289	-2.9287
38	1	-0.23127	2.528946	-2.90003
39	1	1.513886	2.771012	-2.72465
40	1	0.610968	3.700462	-3.93724
41	6	-3.63933	-1.32645	-0.26767
42	6	-4.8048	-1.03414	3.51497
43	1	-4.1108	-1.74863	3.966282
44	1	-5.78117	-1.52338	3.435922
45	1	-4.9061	-0.19253	4.203977
46	1	-3.34316	-0.04969	2.260491
47	1	-3.45305	-2.47323	1.555797
48	1	-2.86416	-3.25093	-0.85023
49	1	-4.05402	-1.47288	-3.0407
50	1	-4.3227	-0.5721	-0.67006
51	6	3.631515	-2.63767	0.259994
52	6	6.059083	-1.26328	0.292521
53	6	4.827606	-3.33158	0.284108
54	6	6.059877	-2.6446	0.297245
55	1	2.710293	-3.20143	0.270015
56	1	4.815287	-4.41454	0.299387
57	1	6.991465	-3.19561	0.317421
58	1	6.994466	-0.7153	0.310669

Table S23. Gas Phase Spin densities of **4**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Mullikan Charges	Spin Densities
1	V	1.605001	1.101839
2	O	-0.6758	0.010501
3	O	-0.23919	0.002259
5	O	-0.64888	-0.00087
6	N	-0.53962	-0.01175
7	O	-0.5909	-0.13141
8	C	0.193685	0.009036
12	N	-0.26672	0.001143
13	C	0.290113	0.007666
15	O	-0.76223	0.00235
16	C	0.351942	0.004982

17	C	-0.03633	-1E-06
21	C	-0.10157	-0.00313
22	C	-0.00424	0.000285
24	C	-0.09242	-0.00145
25	C	0.453853	0.005107
26	C	0.058793	0.002955
28	C	0.034309	-1.8E-05
30	C	0.017397	0.000039
32	C	0.013647	-9.7E-05
34	C	-0.04756	-0.00124
36	C	0.000972	0.001625
37	C	0.152924	0.000129
41	C	-0.06986	-0.0001
42	C	-0.03828	-1.4E-05
51	C	0.035558	-0.00081
52	C	-0.03446	0.000892
53	C	-0.03377	0.000904
54	C	-0.02636	-0.00083

Table S24. Gas Phase Optimized Coordinates of **5** (Singlet Spin State)

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	23	1.143792	-1.29563	-1.22146
2	23	-1.32922	0.849546	-1.57892
3	8	-0.10558	-1.46995	0.243223
4	8	-0.10343	-0.35138	-2.09792
5	8	1.230857	-2.74796	-1.86264
6	8	-2.83628	-0.19739	-1.5193
7	8	2.677364	-0.42432	-1.72356
8	8	-1.57819	1.88693	-2.75743
9	8	0.027891	1.690694	-0.4902
10	7	-2.37019	1.894844	-0.0429
11	7	1.585498	-2.15696	1.64582
12	7	2.314253	-1.71169	0.509644
13	6	-4.15563	-0.04367	-1.26555
14	6	-4.5924	0.994811	-0.40393
15	7	-1.58209	2.790742	0.731734
16	6	5.908097	-1.30856	-0.21053
17	6	4.011995	-0.56778	-1.55055
18	6	-5.0827	-0.93424	-1.82502
19	6	4.508703	-1.20498	-0.38465
20	6	-5.97378	1.112688	-0.12606

21	6	3.61367	-1.6911	0.627627
22	1	4.026174	-2.04861	1.56575
23	6	-6.88807	0.236466	-0.68932
24	6	0.306013	-2.0122	1.404521
25	6	-6.4354	-0.78932	-1.53928
26	6	-0.74494	-2.44799	2.384049
27	1	-0.21907	-2.92074	3.217397
28	6	-3.64926	1.879516	0.218679
29	1	-4.00267	2.574185	0.974026
30	6	6.780997	-0.80571	-1.16268
31	6	4.898203	-0.0515	-2.50605
32	6	6.269165	-0.17484	-2.31123
33	6	-0.32293	2.628487	0.405687
34	6	-1.96511	-5.78644	0.639031
35	1	-2.66873	-6.1198	1.406737
36	1	-1.44006	-6.66679	0.263338
37	1	-2.54618	-5.36917	-0.18695
38	6	-1.68769	-3.48916	1.725845
39	1	-2.22473	-3.00284	0.907072
40	1	-2.4338	-3.77771	2.473465
41	6	-0.98042	-4.74897	1.198746
42	1	-0.27035	-4.46977	0.415233
43	1	-0.39075	-5.19931	2.004522
44	6	0.765689	3.479147	0.99274
45	1	0.282172	4.156008	1.702044
46	6	-1.54193	-1.22926	2.918122
47	1	-1.91141	-0.65379	2.064632
48	1	-2.42168	-1.60714	3.448721
49	6	-0.73789	-0.31836	3.860371
50	1	0.175159	0.014526	3.35761
51	1	-0.40976	-0.90264	4.726811
52	6	1.780901	2.588189	1.756791
53	1	2.256113	1.909713	1.042609
54	6	3.753412	2.446849	3.374642
55	1	4.507842	3.018504	3.918944
56	1	4.27518	1.727923	2.73801
57	1	3.17103	1.880975	4.105834
58	6	-1.53736	0.904696	4.334386
59	1	-1.81295	1.545077	3.493282
60	1	-0.95688	1.509222	5.034741
61	1	-2.45652	0.601485	4.843051
62	6	1.436247	4.320181	-0.12777
63	1	1.950309	3.636455	-0.80806
64	1	2.200165	4.949793	0.332972
65	6	0.460005	5.203505	-0.91873

66	1	-0.26209	4.604715	-1.47619
67	1	0.999761	5.821192	-1.63906
68	1	-0.09824	5.870266	-0.25705
69	6	2.851343	3.368515	2.538907
70	1	3.473186	3.946775	1.850855
71	1	4.48776	0.432929	-3.37918
72	1	6.948819	0.220812	-3.05383
73	1	7.848799	-0.89595	-1.02398
74	1	6.289988	-1.79293	0.679315
75	1	-7.14714	-1.47601	-1.97728
76	1	-7.94251	0.338362	-0.47635
77	1	-6.30923	1.903448	0.53309
78	1	-4.7175	-1.71743	-2.47209
79	1	1.226597	1.958815	2.460675
80	1	2.360908	4.093839	3.197623

Table S25. Gas Phase Optimized Coordinates of **5**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	23	-1.3918	1.421612	-0.90481
2	23	1.212312	-0.43876	-1.77708
3	8	-0.10707	1.071392	0.49751
4	8	-0.19736	0.532473	-2.01742
5	8	-1.28755	2.972523	-1.20915
6	8	2.538514	0.87789	-1.58008
7	8	-2.98313	0.850429	-1.51769
8	8	1.607772	-1.13834	-3.14021
9	8	0.141182	-1.89721	-0.951
10	7	2.52391	-1.51212	-0.43443
11	7	-1.67276	1.703758	2.059843
12	7	-2.46395	1.58732	0.887998
13	6	3.81759	0.976474	-1.27143
14	6	4.491178	-0.09741	-0.56418
15	7	2.034304	-2.6615	0.109234
16	6	-6.09558	1.716452	0.228051
17	6	-4.30937	1.080541	-1.29762
18	6	4.527783	2.149834	-1.60517
19	6	-4.71638	1.508417	-0.00897
20	6	5.874044	0.062335	-0.23955
21	6	-3.76046	1.677232	1.044986
22	1	-4.11428	1.872693	2.051569
23	6	6.545743	1.206726	-0.58951

24	6	-0.42791	1.443153	1.767786
25	6	5.862655	2.25564	-1.27627
26	6	0.670376	1.583626	2.780146
27	1	0.195853	1.954927	3.691277
28	6	3.811066	-1.25483	-0.15882
29	1	4.327816	-2.0001	0.435234
30	6	-7.02203	1.513756	-0.78277
31	6	-5.24155	0.866345	-2.31391
32	6	-6.59154	1.087264	-2.05175
33	6	0.711802	-2.81304	-0.22992
34	6	2.217187	5.067461	1.702989
35	1	2.941943	5.170198	2.514369
36	1	1.782242	6.051085	1.520799
37	1	2.763276	4.775766	0.801749
38	6	1.70861	2.634453	2.302791
39	1	2.186588	2.267987	1.388963
40	1	2.487163	2.695179	3.069451
41	6	1.132132	4.038462	2.052391
42	1	0.399624	3.998516	1.241
43	1	0.588173	4.369601	2.94253
44	6	-0.03985	-4.01901	0.210578
45	1	0.631867	-4.59702	0.848042
46	6	1.343248	0.22478	3.097134
47	1	1.708178	-0.21813	2.164805
48	1	2.224349	0.427679	3.713406
49	6	0.43786	-0.77669	3.833074
50	1	-0.44677	-0.99204	3.224592
51	1	0.06415	-0.31268	4.750712
52	6	-1.29404	-3.59421	1.034817
53	1	-1.98199	-3.06162	0.372678
54	6	-3.18797	-4.29743	2.590598
55	1	-3.68428	-5.1441	3.066394
56	1	-3.93425	-3.76833	1.993488
57	1	-2.85091	-3.62286	3.381156
58	6	1.161859	-2.08613	4.180169
59	1	1.535381	-2.5863	3.282099
60	1	0.498519	-2.78054	4.698462
61	1	2.017391	-1.90055	4.833774
62	6	-0.41544	-4.8791	-1.03834
63	1	-1.11169	-4.30324	-1.65252
64	1	-0.95413	-5.75417	-0.67502
65	6	0.787585	-5.33106	-1.87766
66	1	1.302049	-4.48771	-2.34468
67	1	0.461395	-5.99279	-2.68035

68	1	1.514215	-5.87721	-1.27255
69	6	-2.01288	-4.76925	1.719623
70	1	-2.38335	-5.47259	0.970771
71	1	-4.89693	0.536708	-3.28211
72	1	-7.31623	0.928048	-2.8378
73	1	-8.0725	1.682256	-0.59768
74	1	-6.41785	2.042984	1.208011
75	1	6.407149	3.150201	-1.54411
76	1	7.59165	1.322334	-0.3482
77	1	6.38155	-0.73586	0.28449
78	1	4.000059	2.933942	-2.1253
79	1	-0.98306	-2.88162	1.80506
80	1	-1.29785	-5.32041	2.338935

Table S26. Gas Phase Spin denisties of **5**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Mullikan Charges	Spin Densities
1	V	1.655296	0.00107
2	V	1.650205	-0.02134
3	O	-0.71216	0.001737
4	O	-0.70408	-5.2E-05
5	O	-0.38835	-0.00031
6	O	-0.66649	0.076734
7	O	-0.70189	0.000117
8	O	-0.37042	0.036327
9	O	-0.56499	0.106222
10	N	-0.51226	0.153782
11	N	-0.2061	0.00238
12	N	-0.54039	0.000451
13	C	0.446185	0.109614
14	C	-0.13031	0.151978
15	N	-0.1842	0.309909
16	C	0.096181	-0.0001
17	C	0.408409	0.000505
18	C	0.04372	-0.03545
19	C	-0.15926	0.000489
20	C	0.129779	-0.06672
21	C	0.407392	0.000009
23	C	0.042852	0.091379
24	C	0.508913	-0.00042
25	C	0.139418	0.069416

26	C	-0.05279	0.00007
28	C	0.399991	-0.04777
30	C	0.015633	0.000175
31	C	0.027666	-0.00028
32	C	0.093051	0.000533
33	C	0.541176	0.044906
34	C	0.013226	-1.6E-05
38	C	0.027642	-0.00051
41	C	0.023184	0.000027
44	C	-0.06909	-0.00569
46	C	0.014601	-0.00054
49	C	0.01802	-5.5E-05
52	C	0.077319	0.008273
54	C	0.032185	0.001228
58	C	0.011427	0.000699
62	C	0.072422	0.010261
65	C	0.050304	0.000696
69	C	0.016578	0.000249

Table S27. Gas Phase Optimized Coordinates of **6** (Singlet Spin State)

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	23	8.366421	5.358141	12.80011
2	23	7.7261	8.451827	13.78142
3	8	7.15325	6.187602	11.55374
4	8	8.707302	6.982653	13.4805
5	8	9.613361	4.890391	11.93102
6	8	8.19506	9.473107	12.32132
7	8	8.392222	4.328637	14.32629
8	8	8.305768	9.223953	15.04456
9	8	6.333643	7.32593	14.49906
10	7	5.931461	9.540486	13.54149
11	7	6.195415	4.148485	11.09154
12	7	7.026531	3.836332	12.20282
13	6	7.938039	10.69985	11.83049
14	6	6.730991	11.3559	12.13536
15	7	4.787733	9.002096	14.19792
16	6	7.507816	0.732539	14.22628
17	6	8.301752	3.024893	14.65417
18	6	6.853324	-0.26079	13.45101

19	1	6.396433	-0.00087	12.50739
20	6	8.897895	11.28464	10.96595
21	1	9.798482	10.72637	10.76008
22	6	7.594741	2.126335	13.83373
23	6	6.483247	12.67226	11.5784
24	6	6.916348	2.618625	12.67405
25	1	6.228393	1.976468	12.13929
26	6	7.468422	13.24946	10.71163
27	6	7.397794	-1.97215	15.08577
28	1	7.347962	-3.0049	15.40206
29	6	6.346874	5.415104	10.79861
30	6	8.663115	12.52084	10.42601
31	1	9.395913	12.97019	9.7678
32	6	5.668962	6.052831	9.621246
33	1	5.115704	5.259303	9.112494
34	6	5.746655	10.68218	12.92438
35	1	4.752776	11.10093	13.01518
36	6	8.123716	0.323267	15.45437
37	6	5.317406	13.43406	11.85464
38	1	4.559932	13.04748	12.52061
39	6	6.797925	-1.57628	13.87092
40	1	6.29297	-2.31105	13.25831
41	6	8.899337	2.60243	15.86845
42	1	9.416589	3.341932	16.46065
43	6	8.808121	1.290851	16.25118
44	1	9.265806	0.965729	17.17688
45	6	8.050169	-1.03484	15.85845
46	1	8.521204	-1.32374	16.78957
47	6	5.105616	7.835865	14.69806
48	6	8.711282	6.204162	7.089569
49	1	8.175601	6.594694	6.220026
50	1	9.424393	5.457775	6.734157
51	1	9.282429	7.027133	7.526152
52	6	6.729688	6.631112	8.647388
53	1	7.263669	7.438732	9.155494
54	1	6.193603	7.080632	7.805152
55	6	7.741208	5.601431	8.116714
56	1	8.314215	5.187059	8.950969
57	1	7.202397	4.761727	7.664666
58	6	7.24714	14.53542	10.15458
59	1	8.003127	14.95352	9.501878
60	6	6.098481	15.24422	10.43647
61	1	5.939397	16.22391	10.00753
62	6	5.129506	14.68444	11.29669
63	1	4.231111	15.2415	11.52634

64	6	4.142571	7.032342	15.52731
65	1	3.203271	7.588205	15.55123
66	6	4.671641	7.149661	10.07592
67	1	5.198372	7.85127	10.72896
68	1	4.365595	7.713297	9.18857
69	6	3.419535	6.608691	10.78559
70	1	3.712939	6.029236	11.66544
71	1	2.90498	5.91093	10.11559
72	6	3.91378	5.668727	14.90659
73	1	4.815327	5.097943	14.7028
74	6	2.46837	3.787029	14.05406
75	1	1.923804	3.849517	13.10724
76	1	1.86316	3.172082	14.72722
77	1	3.404997	3.260027	13.86699
78	6	2.451505	7.721944	11.21363
79	1	2.918603	8.38858	11.94185
80	1	1.553635	7.306602	11.6763
81	1	2.135566	8.32274	10.35614
82	6	4.683601	6.893398	16.98389
83	1	5.604511	6.306644	16.95314
84	1	3.949179	6.308228	17.54268
85	6	4.940321	8.233443	17.68661
86	1	5.732493	8.79945	17.19358
87	1	5.248504	8.069535	18.72099
88	1	4.042197	8.855606	17.69866
89	6	2.712503	5.152982	14.63342
90	1	1.825535	5.749336	14.8385

Table S28. Gas Phase Optimized Coordinates of **6**$^{-}$(Doublet Spin State)

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	23	8.48569	5.340046	12.74593
2	23	7.816821	8.393829	13.9277
3	8	7.178162	6.348568	11.62085
4	8	8.793564	7.021803	13.69913
5	8	9.788816	4.990968	11.87869
6	8	8.378855	9.422634	12.42233
7	8	8.569587	4.276755	14.39089
8	8	8.358894	9.252647	15.17111
9	8	6.381726	7.304059	14.71246
10	7	5.978196	9.420229	13.48715
11	7	6.233869	4.288184	11.10416

12	7	7.085813	3.908355	12.18763
13	6	8.05903	10.58162	11.85843
14	6	6.792756	11.18569	12.02686
15	7	4.811923	8.892944	14.11841
16	6	7.45042	0.739767	14.11693
17	6	8.372916	2.987604	14.62287
18	6	6.746424	-0.19259	13.30434
19	1	6.310669	0.129353	12.37002
20	6	9.039487	11.1944	11.01943
21	1	9.983062	10.67943	10.91483
22	6	7.605675	2.14199	13.77552
23	6	6.513114	12.44776	11.3708
24	6	6.927624	2.690447	12.6382
25	1	6.189929	2.093833	12.11369
26	6	7.521472	13.04235	10.54124
27	6	7.188626	-1.99933	14.86568
28	1	7.082562	-3.04043	15.1419
29	6	6.379096	5.579445	10.87863
30	6	8.777493	12.37631	10.38753
31	1	9.528835	12.83315	9.754177
32	6	5.658892	6.224079	9.722278
33	1	5.153115	5.421782	9.177547
34	6	5.787207	10.51238	12.79371
35	1	4.773921	10.89557	12.79977
36	6	8.039931	0.239819	15.32546
37	6	5.283833	13.15011	11.50862
38	1	4.502285	12.75072	12.13804
39	6	6.616276	-1.52035	13.6684
40	1	6.073916	-2.19941	13.02235
41	6	8.939431	2.449642	15.82444
42	1	9.497723	3.138983	16.44117
43	6	8.777934	1.137553	16.16013
44	1	9.215751	0.749563	17.07279
45	6	7.890476	-1.12569	15.67265
46	1	8.345081	-1.47509	16.59261
47	6	5.146229	7.791978	14.75308
48	6	8.732259	6.665532	7.266775
49	1	8.190335	7.03342	6.389747
50	1	9.512798	5.98519	6.917743
51	1	9.223897	7.520629	7.737265
52	6	6.687151	6.905217	8.78361
53	1	7.152299	7.730479	9.328888
54	1	6.139432	7.340102	7.938972
55	6	7.786492	5.967742	8.256162

56	1	8.367813	5.584976	9.098456
57	1	7.325864	5.097919	7.774135
58	6	7.262809	14.27512	9.890924
59	1	8.04071	14.70187	9.268587
60	6	6.054344	14.92487	10.04107
61	1	5.869098	15.8656	9.539222
62	6	5.059926	14.35123	10.86199
63	1	4.111608	14.85751	10.99078
64	6	4.137859	7.040245	15.58442
65	1	3.186484	7.569841	15.49969
66	6	4.600753	7.24232	10.21547
67	1	5.083697	7.931703	10.91279
68	1	4.270748	7.83816	9.356191
69	6	3.373805	6.599846	10.8833
70	1	3.697519	5.978597	11.72225
71	1	2.891464	5.922875	10.16799
72	6	3.987219	5.623179	15.0709
73	1	4.921543	5.086592	14.9332
74	6	2.664888	3.617626	14.30743
75	1	2.172819	3.588934	13.33009
76	1	2.051346	3.020968	14.99096
77	1	3.632665	3.124908	14.20668
78	6	2.357402	7.637906	11.38345
79	1	2.802367	8.274205	12.15123
80	1	1.479702	7.153678	11.81988
81	1	2.012196	8.279193	10.56609
82	6	4.58803	7.037799	17.07689
83	1	5.510537	6.458245	17.15109
84	1	3.82289	6.503936	17.6479
85	6	4.810743	8.439719	17.66178
86	1	5.634047	8.949417	17.15926
87	1	5.05875	8.377788	18.72419
88	1	3.917693	9.061933	17.55866
89	6	2.821188	5.031527	14.79857
90	1	1.900182	5.598279	14.92673

Table S29. Gas Phase Spin densities of **6**$^{-}$ **(Doublet Spin State)**

Center Number	Atomic Number	Mullikan Charges	Spin Densities
1	V	1.599661	1.09091
2	V	1.641567	0.061517
3	O	-0.68698	-0.002026
4	O	-0.72349	-0.032805
5	O	-0.54898	-0.137836
6	O	-0.69063	0.00183
7	O	-0.67905	0.012562
8	O	-0.51191	0.005418
9	O	-0.64715	-0.00087
10	N	-0.53448	-0.000945
11	N	-0.26008	0.001063
12	N	-0.55022	-0.014231
13	C	0.38886	0.000112
14	C	-0.1253	0
15	N	-0.26397	-0.000233
16	C	0.003073	0.001786
17	C	0.356235	0.004923
18	C	0.0409	-0.000882
20	C	-0.03814	-0.000023
22	C	-0.1114	-0.003489
23	C	0.005904	0.000065
24	C	0.314429	0.007647
26	C	-0.08683	-0.000082
27	C	-0.01991	-0.000886
29	C	0.466245	0.004071
30	C	0.071947	0.000149
32	C	-0.07919	-0.00058
34	C	0.33139	-0.00017
36	C	-0.09207	-0.001377
37	C	0.054244	-0.00002
39	C	-0.02891	0.000883
41	C	-0.04841	-0.000912
43	C	0.066239	0.002356
45	C	-0.02986	0.00083
47	C	0.494142	0.000412
48	C	-0.0319	0.000009
52	C	0.024515	0.000438
55	C	0.017952	-0.000079
58	C	-0.02814	0.000055
60	C	-0.01166	-0.000042

62	C	-0.02825	0.000038
64	C	-0.1752	-0.000129
66	C	0.025189	0.000483
69	C	0.015151	0.000034
72	C	0.117435	0.00005
74	C	-0.05239	-0.000002
78	C	-0.0318	-0.000004
82	C	0.040502	0.000022
85	C	0.001202	-0.000032
89	C	0.039511	-0.000008