The high-valent vanadium chemistry of isoindoline chelates

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Supplementary Information

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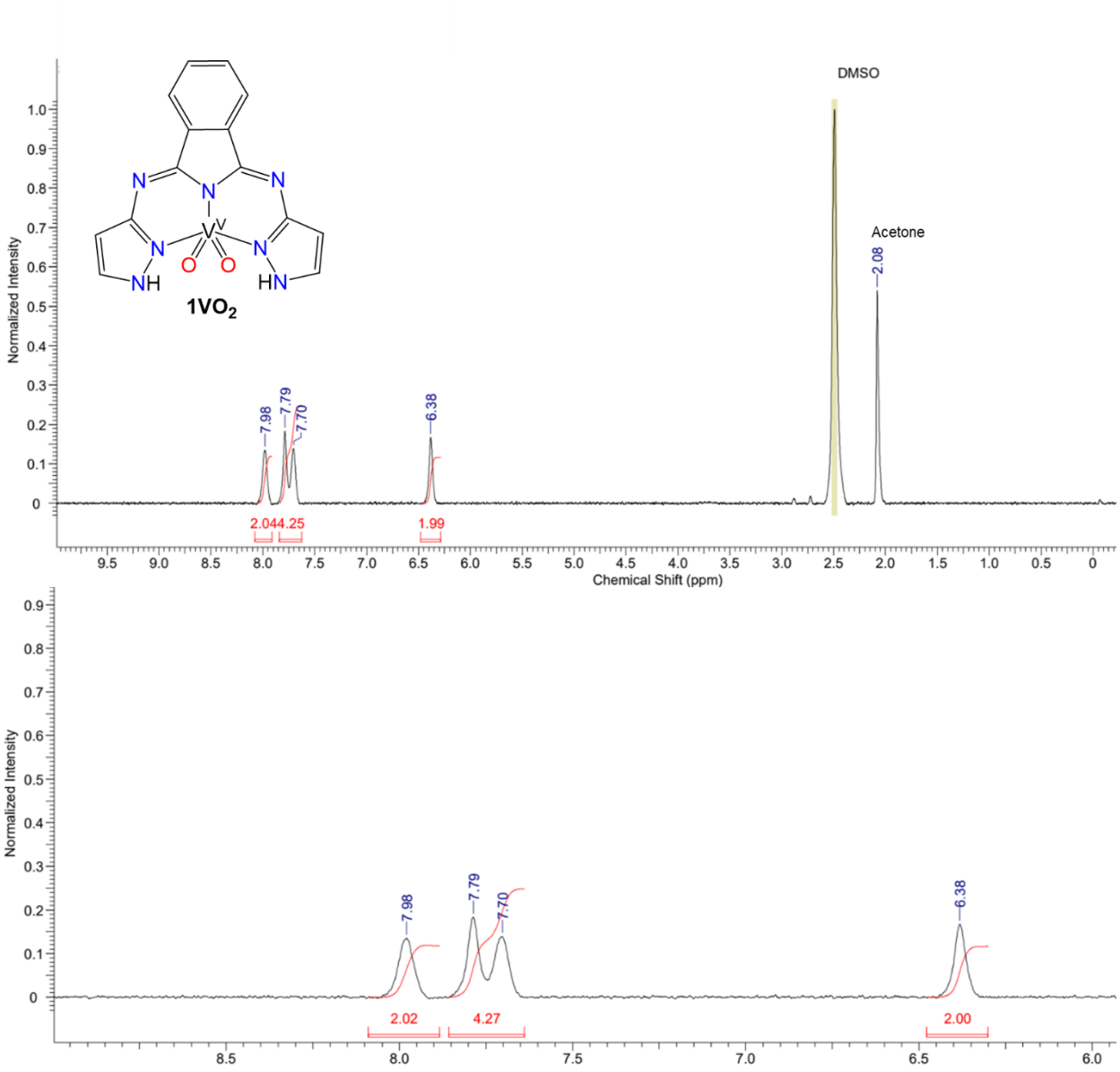

Figure S1: ^{1}H NMR (300 MHz) of **1VO$_2$** in d6-DMSO. Full spectrum on the top, zoomed in spectrum on the bottom.

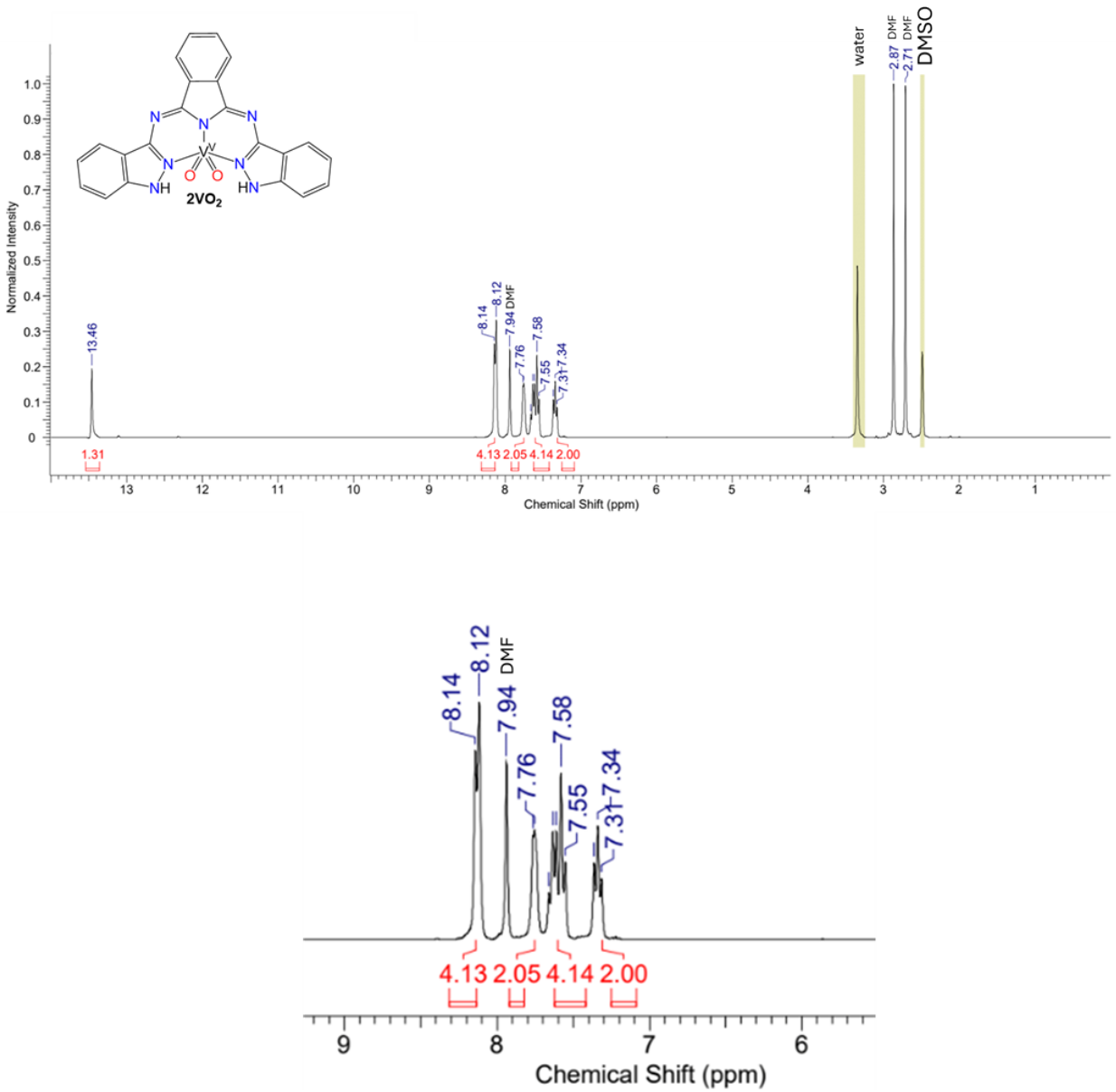

Figure S2: ^{1}H NMR (300 MHz) of **$2VO_2$** in d6-DMSO. Full spectrum on the top, zoomed in spectrum on the bottom.

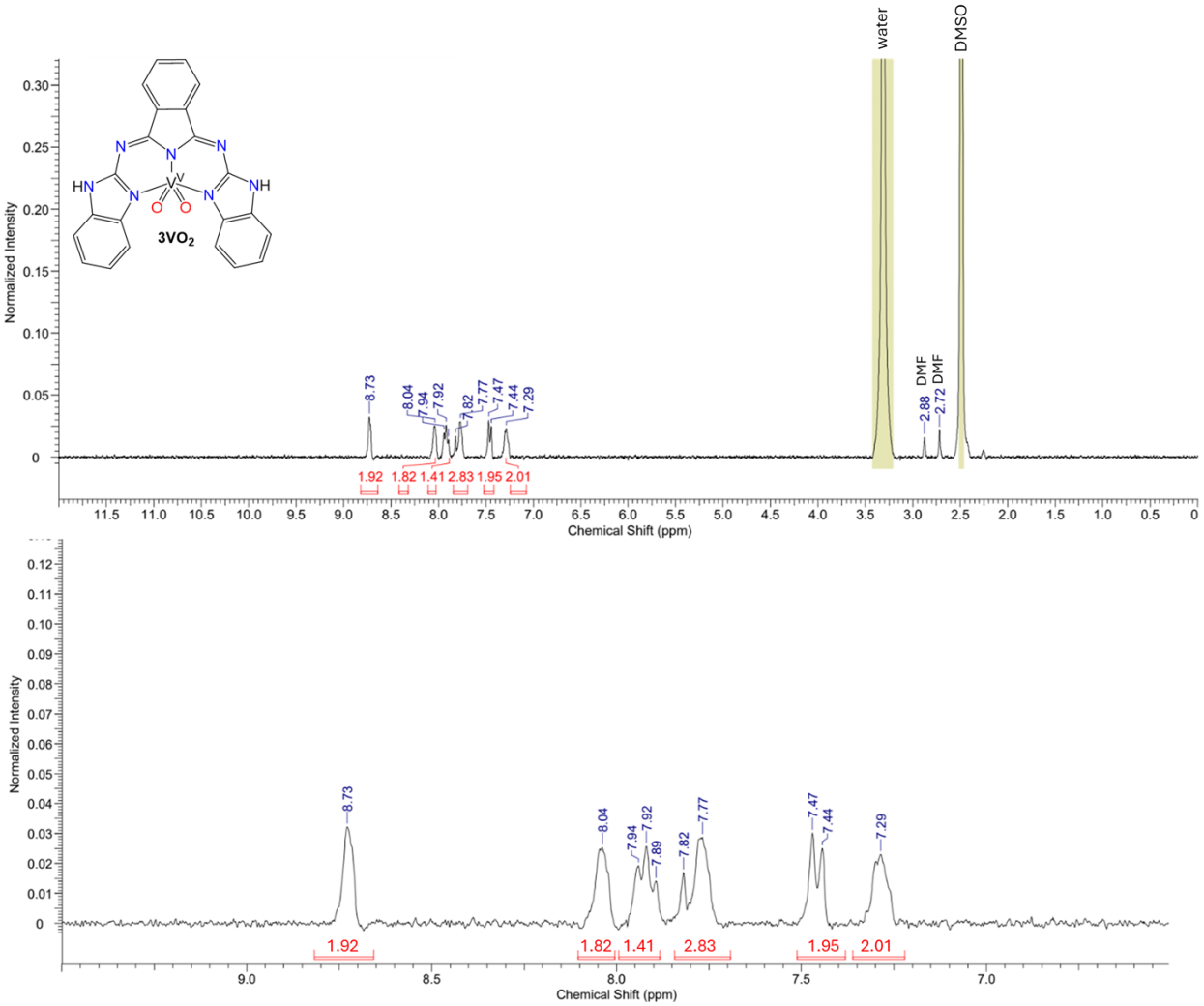

Figure S3: ^{1}H NMR (300 MHz) of **$3VO_2$** in d6-DMSO. Full spectrum on the top, zoomed in spectrum on the bottom.

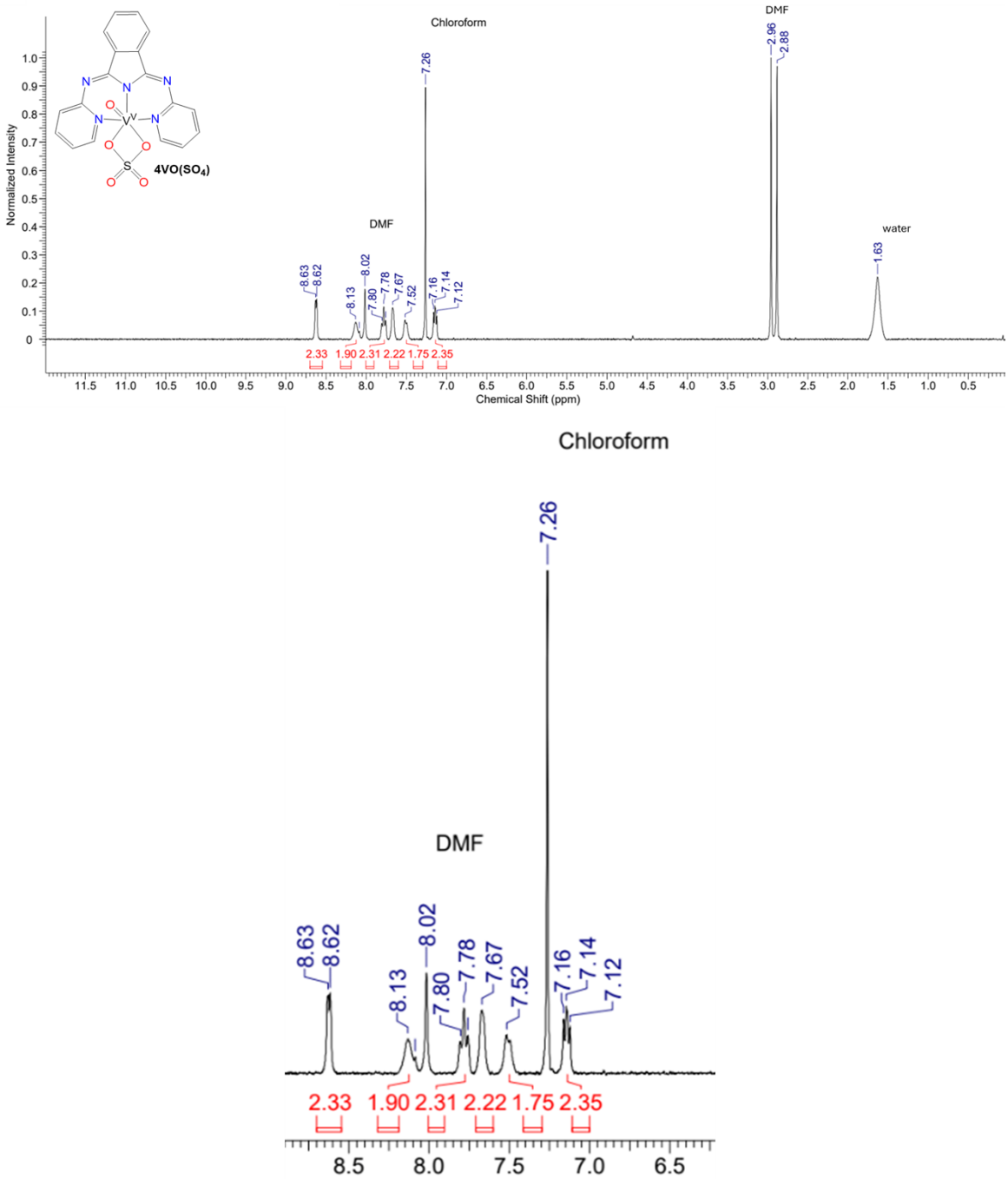

Figure S4: ^{1}H NMR (300 MHz) of **4VO(SO$_4$)** in $CDCl_3$. Full spectrum on the top, zoomed in spectrum on the bottom.

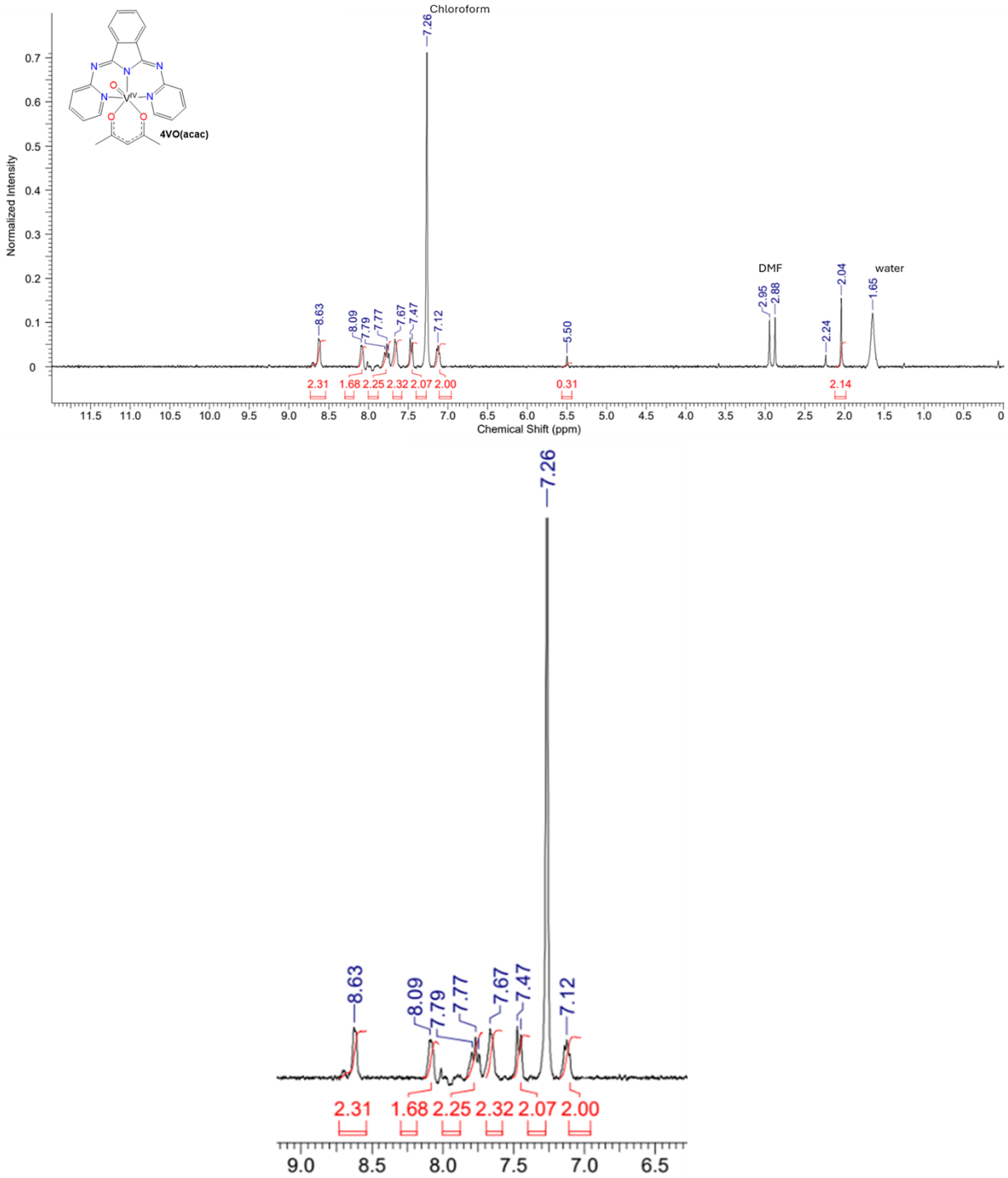

Figure S5: ^{1}H NMR (300 MHz) of **4VO(acac)** in $CDCl_3$. Full spectrum on the top, zoomed in spectrum on the bottom.

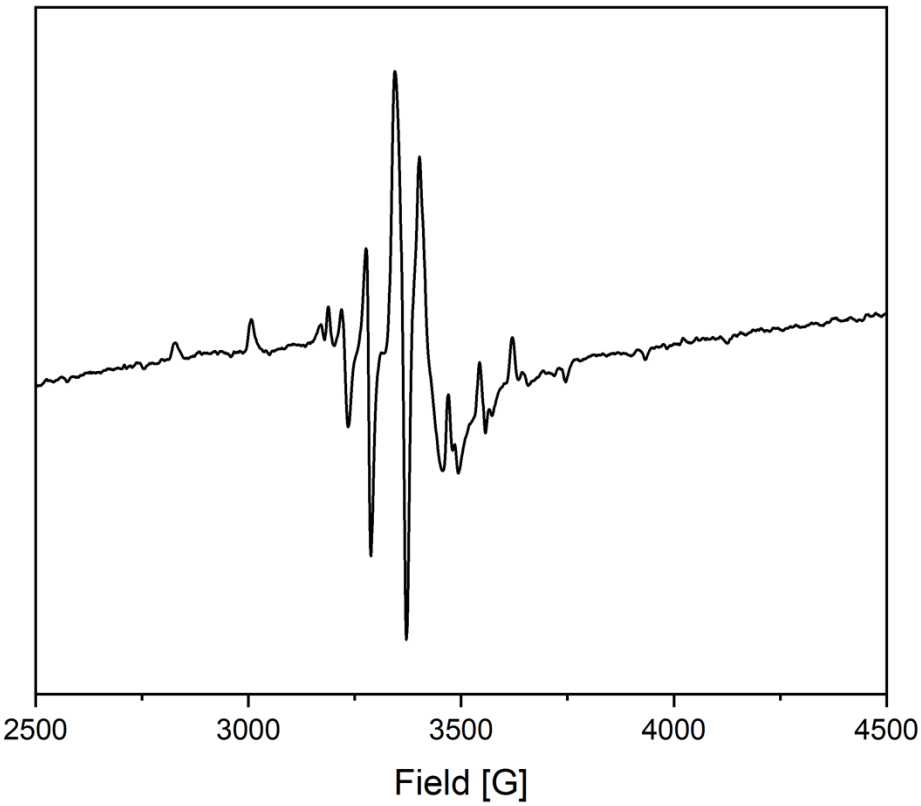

Figure S6: EPR spectrum of **4VO(acac)** in DMF at 130 K.

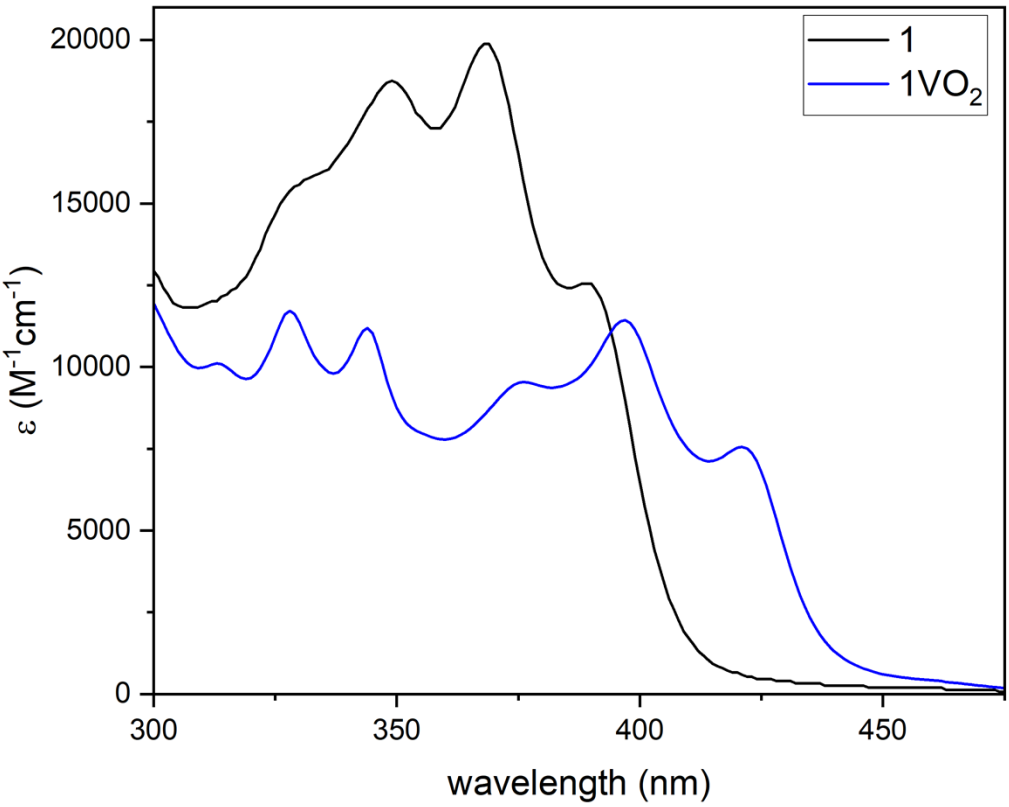

Figure S7: The UV-visible spectra of **1** and **$1VO_2$** in DMF.

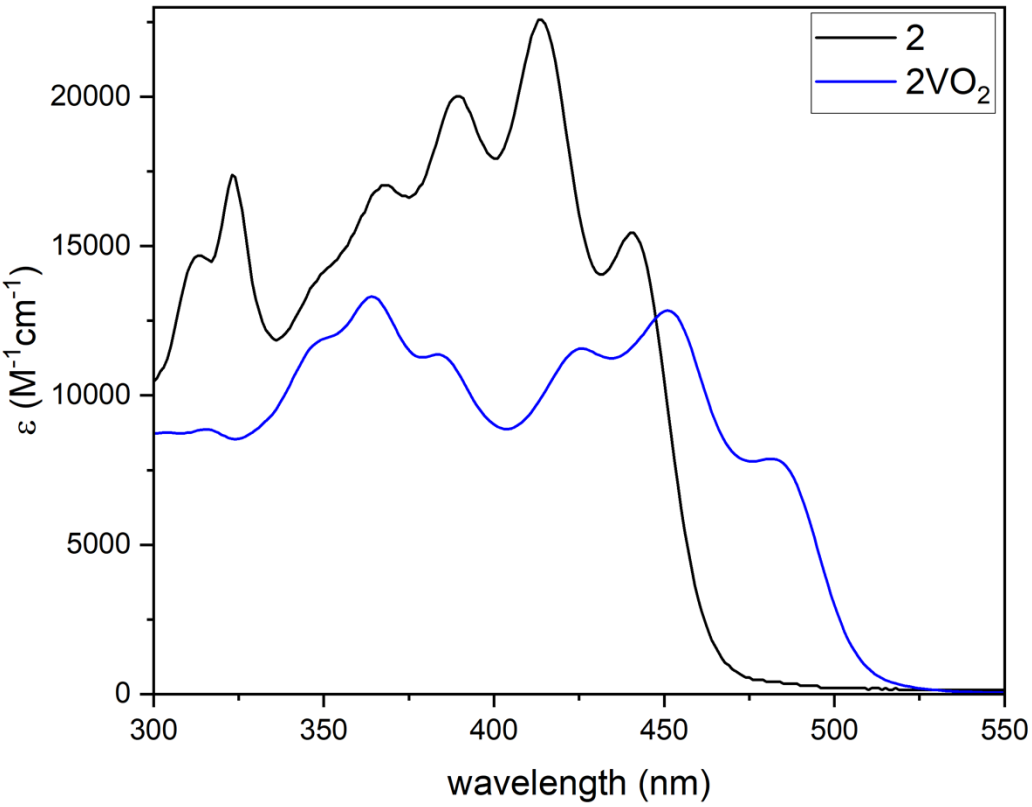

Figure S8: The UV-visible spectra of **2** and **$2VO_2$** in DMF.

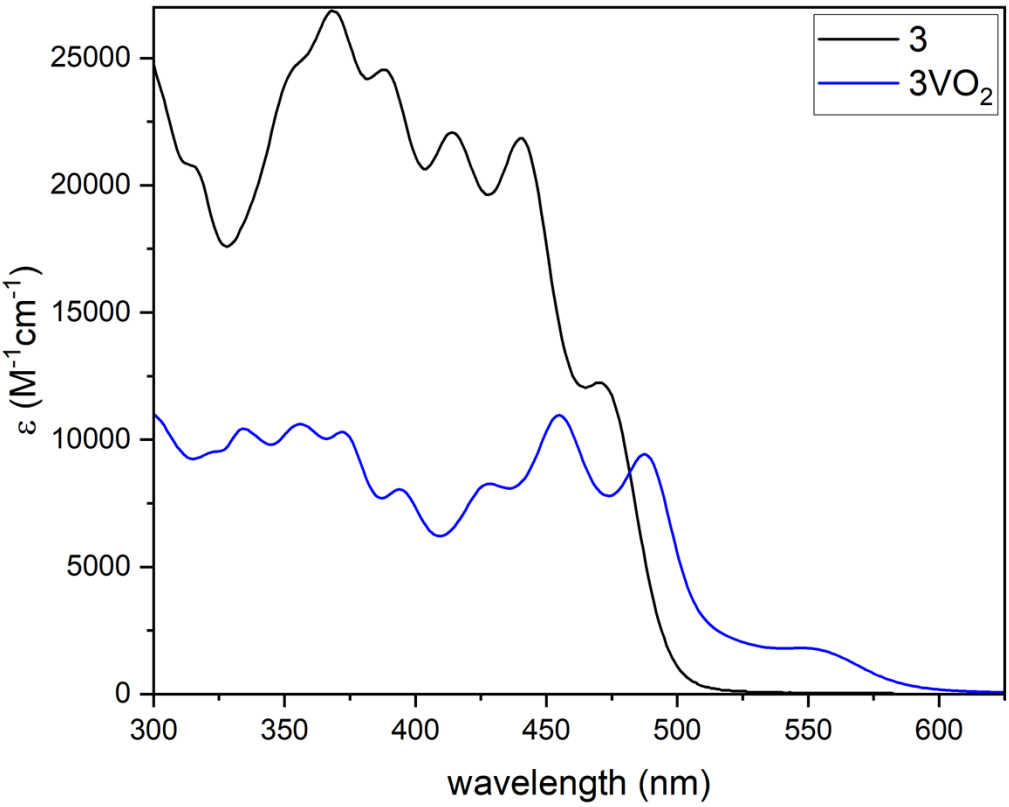

Figure S9: The UV-visible spectra of **3** and **$3VO_2$** in DMF.

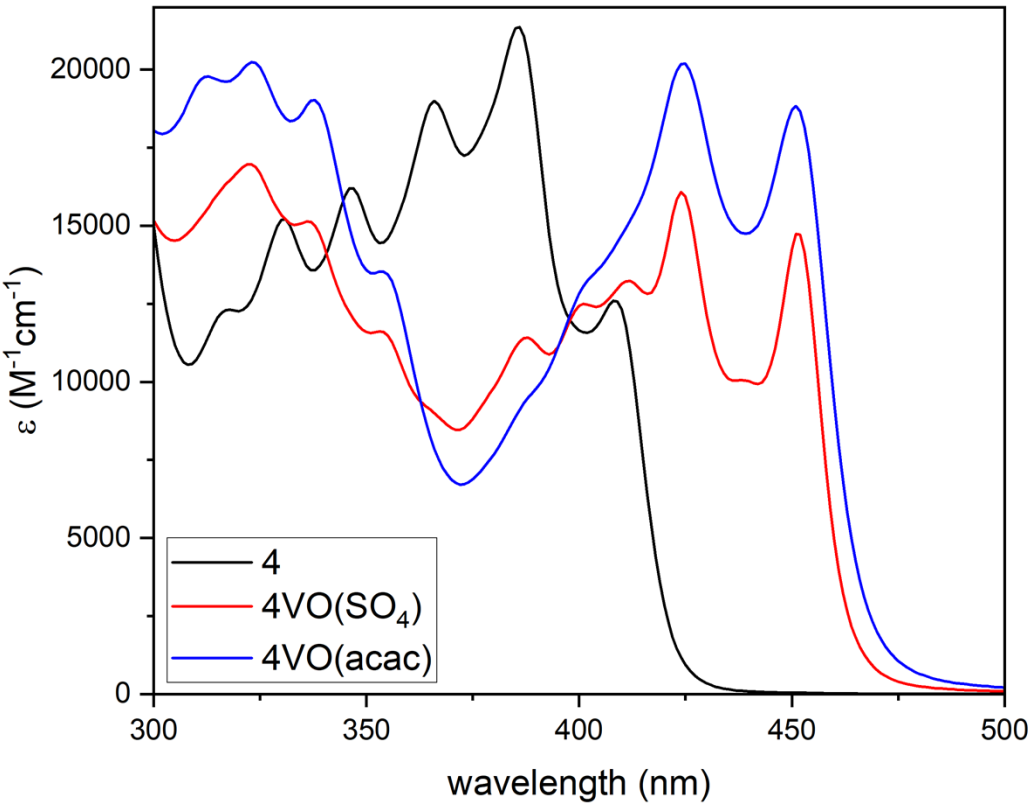

Figure S10: The UV-visible spectra of **4, 4VO(acac)** and **1VO(SO_4)** in DMF.

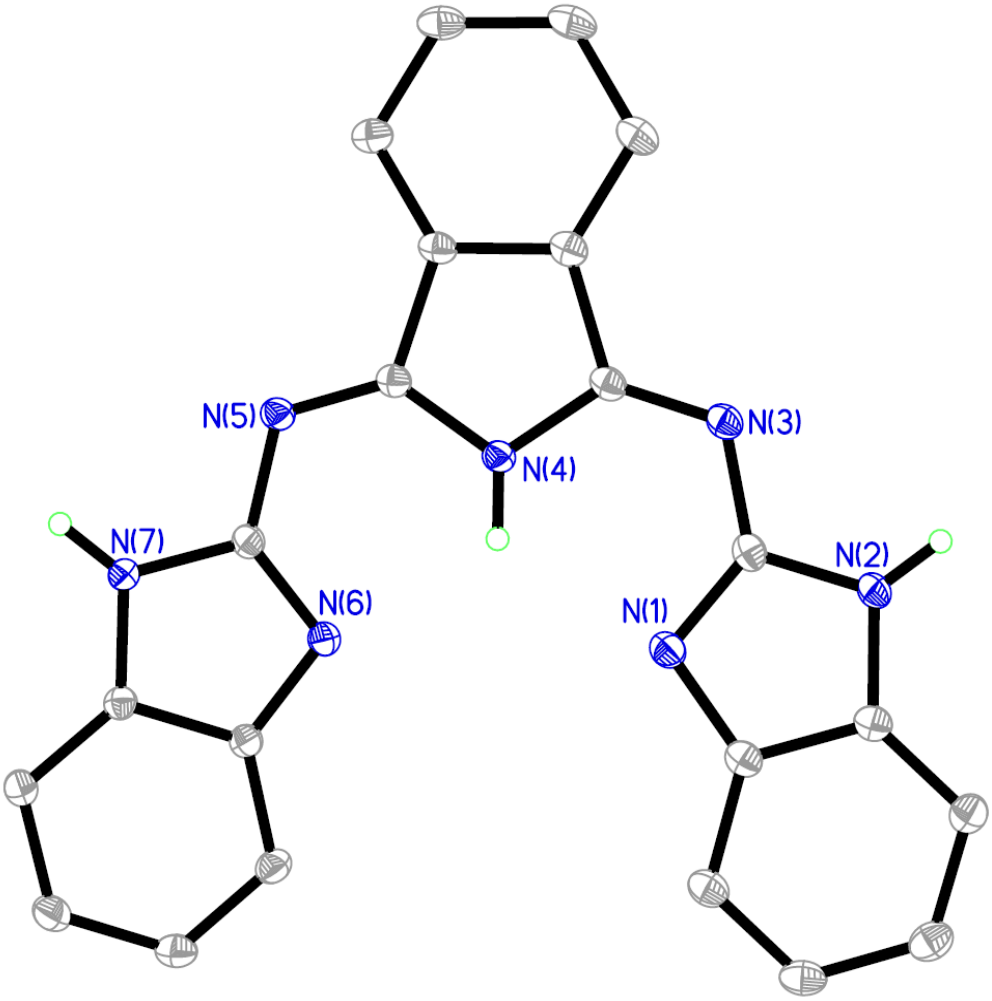

Figure S11: Structure of compound **3**, with 35% probability ellipsoids.

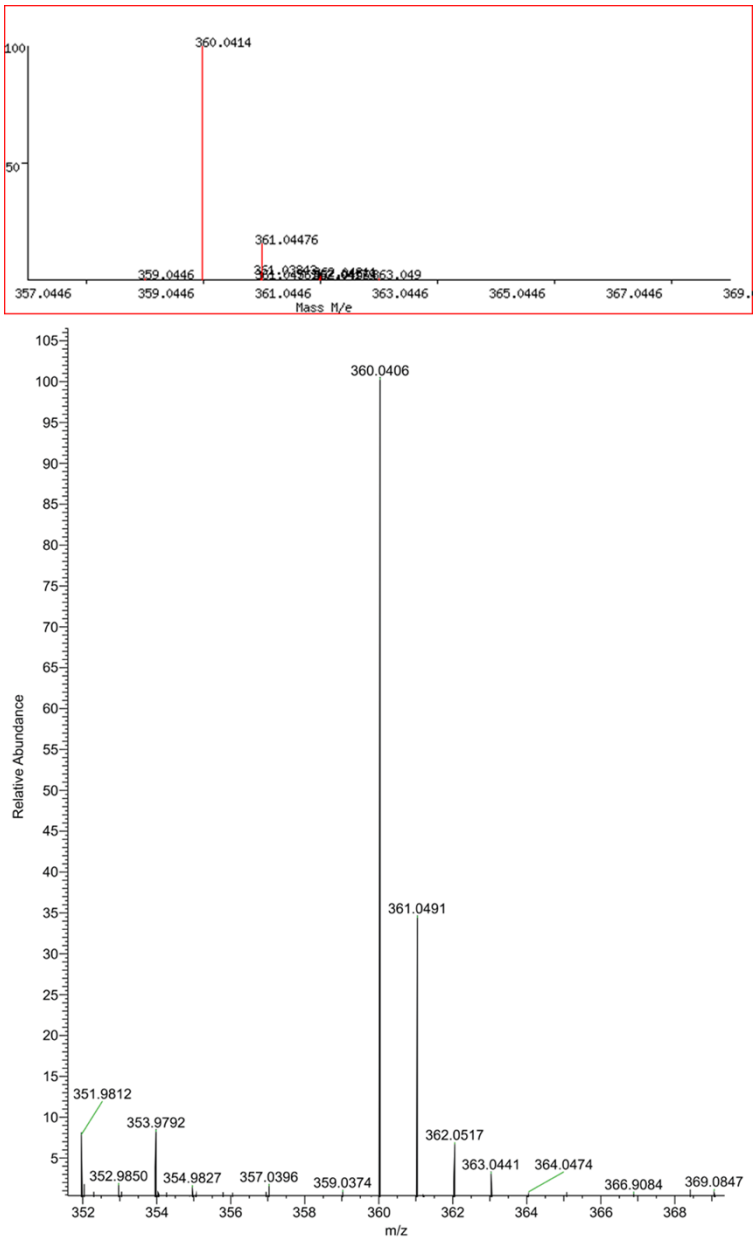

Figure S12: High-resolution ESI mass spectra of **1VO$_2$**. Top: calculated spectrum. Bottom: experimental spectrum.

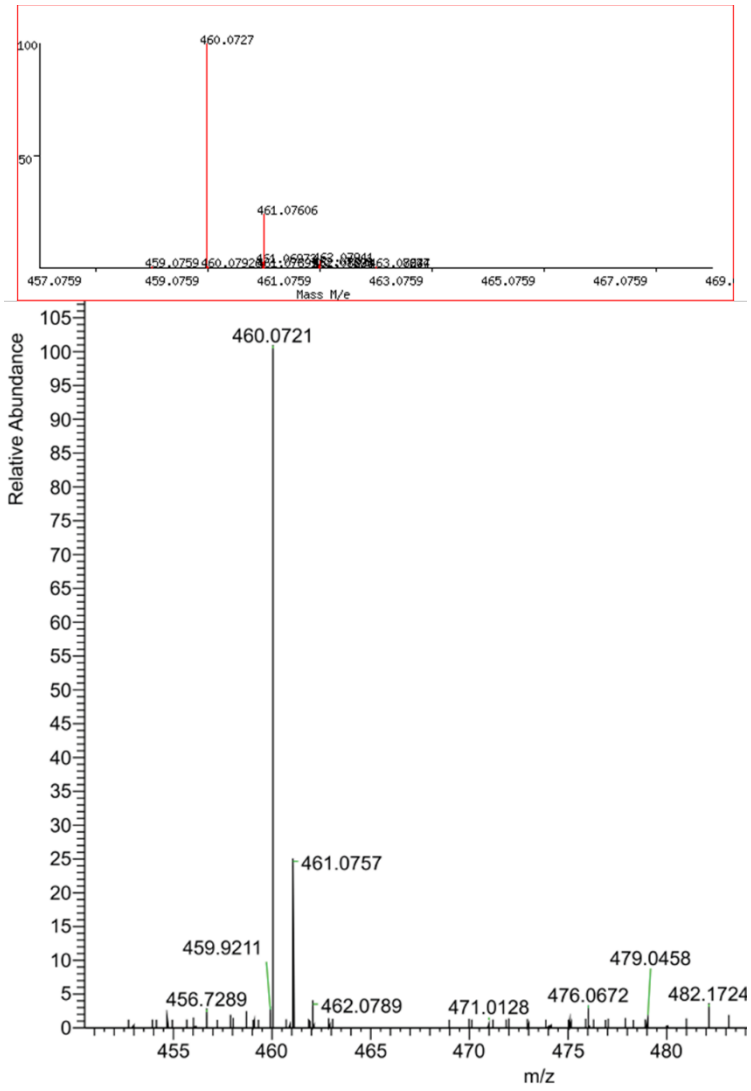

Figure S13: High-resolution ESI mass spectra of **$2VO_2$**. Top: calculated spectrum. Bottom: experimental spectrum.

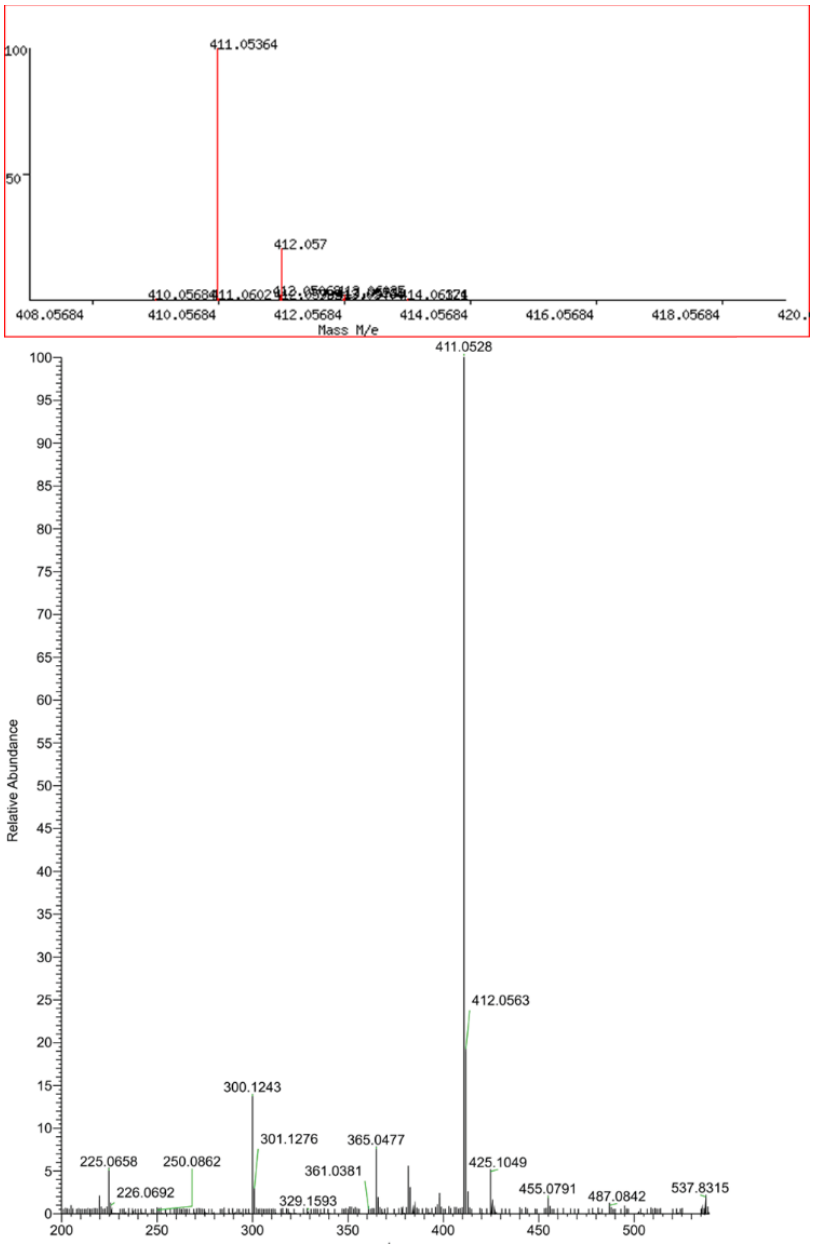

Figure S14: High-resolution ESI mass spectra of **4VO(SO$_4$)**. Top: calculated spectrum. Bottom: experimental spectrum.

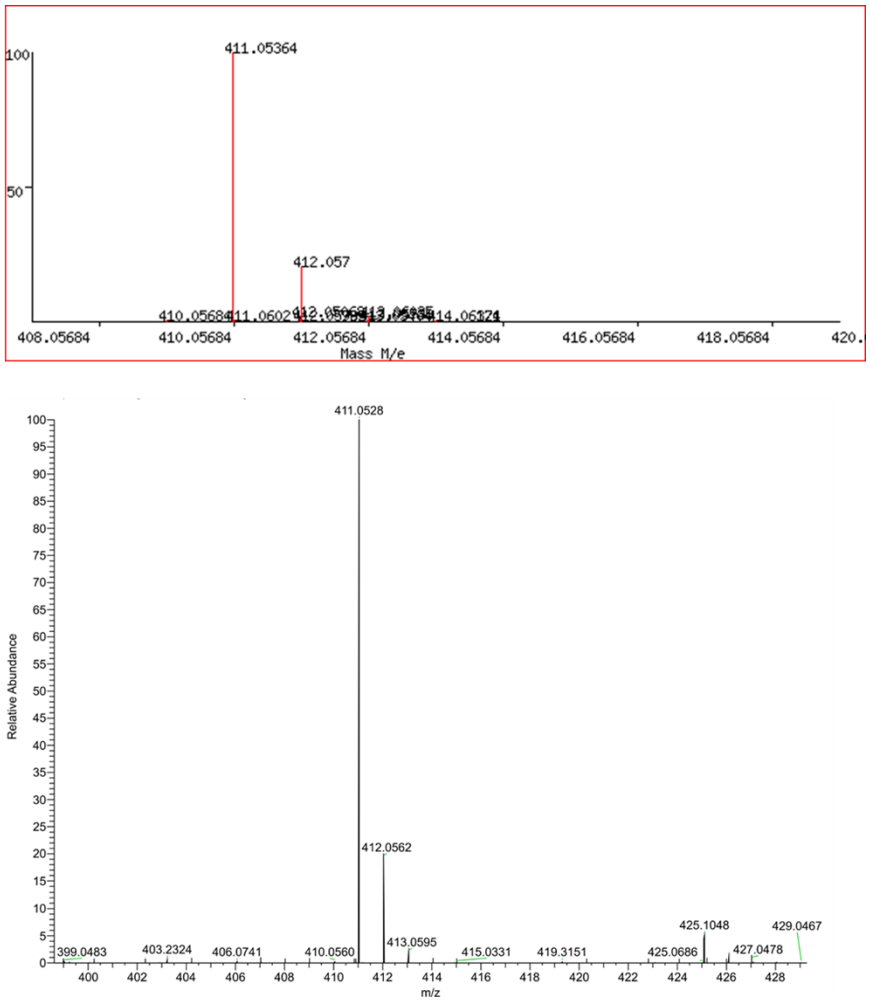

Figure S15: High-resolution ESI mass spectra of **4VO(acac)**. Top: calculated spectrum. Bottom: experimental spectrum.

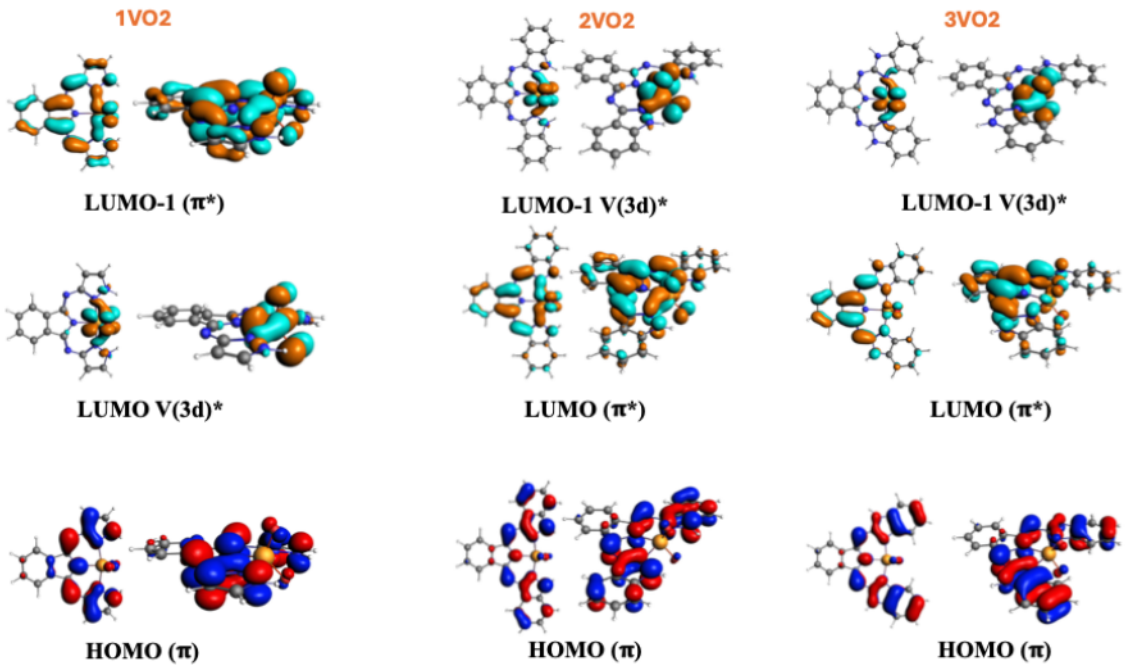

Figure S16: Frontier molecular orbitals for dioxovanadate complexes. Orbitals with significant vanadium 3d character were labeled V(3d)* to represent the unoccupied character.

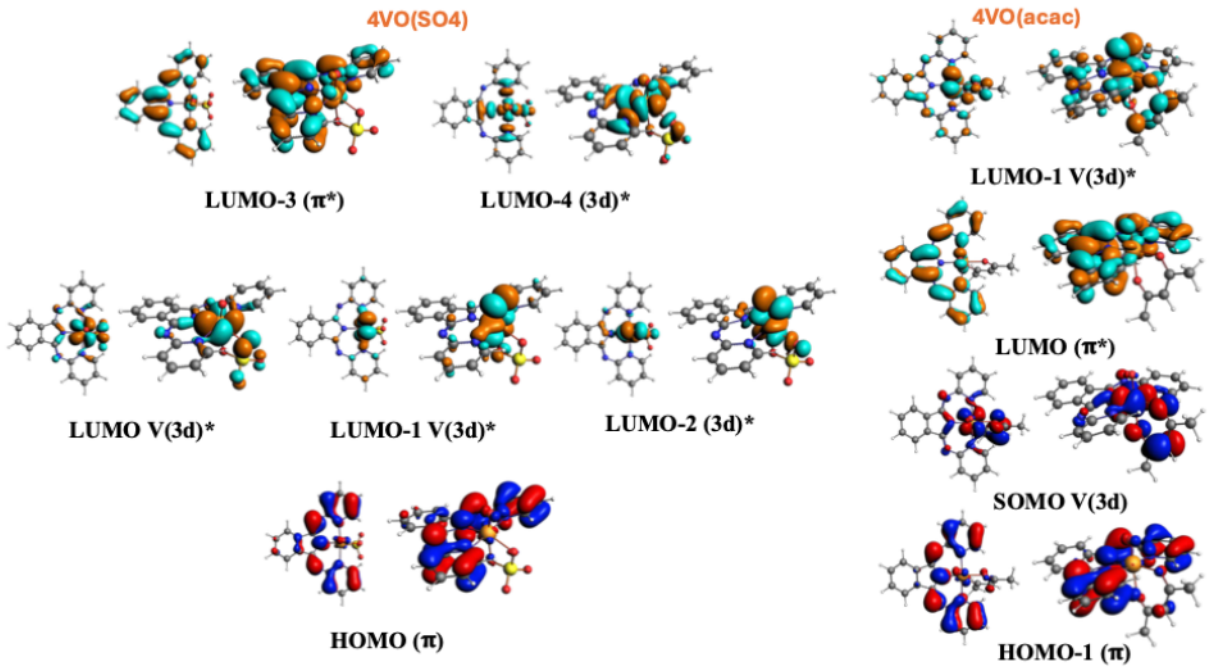

Figure S17: Frontier molecular orbitals for the **4VO(SO$_4$)** and **4VO(acac)** complexes. Orbitals with significant vanadium 3d character were labeled V(3d) and V(3d)* to represent the occupied and unoccupied character, respectively.

Table S1: X-ray crystal data and structure parameters for compounds **3** and **$1VO_2$-$3VO_2$**.

Compound	**3**	**$1VO_2$**	**$2VO_2$**	**$3VO_2$**
CCDC Number	2516084	2516085	2516086	2516089
Empirical formula	$C_{25}H_{22}N_8O$	$C_{17}H_{17}N_8O_3V$	$C_{25}H_{21}N_8O_3V$	$C_{25}H_{21}N_8O_3V$
Formula weight	450.50	432.32	532.44	532.4
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P21/n
a/ Å	7.758(2)	7.625(4)	7.6599(8)	9.9520(6)
b/ Å	17.004(5)	10.356(5)	11.8170(12)	10.4010(5)
c/ Å	17.093(5)	12.502(9)	13.6367(12)	24.4316(12)
α(°)	84.776(10)	80.274(18)	82.479(4)	90
β(°)	81.635(10)	80.55(3)	78.307(4)	93.460(2)
γ(°)	82.344(10)	74.511(11)	80.915(4)	90
Volume ($Å^3$)	2204.8(10)	930.4(9)	1187.3(2)	2524.3(2)
Z	4	2	2	4
Dc (Mg/m^3)	1.357	1.543	1.489	1.401
μ (mm^{-1})	0.089	0.572	0.464	0.437
F(000)	944	444	548	1096
reflns collected	59861	52232	59415	59790
indep. reflns	13630	4595	6076	6271
GOF on F^2	1.049	1.021	1.053	1.096
R1 (on F_o^2, I > 2σ(I))	0.0613	0.0391	0.0576	0.0723
wR2 (on F_o^2, I > 2σ(I))	0.1668	0.0991	0.1487	0.1815
R1 (all data)	0.0827	0.0465	0.0813	0.1081
wR2 (all data)	0.1825	0.1029	0.1630	0.2031

Table S2: X-ray crystal data and structure parameters for compounds **4VO(SO_4)** and **4VO(acac).**

Compound	**4VO(SO_4)**	**4VO(acac)**
CCDC Number	2516088	2516087
Empirical formula	$C_{18}H_{12}N_5O_5SV$	$C_{23}H_{19}N_5O_3V$
Formula weight	461.33	464.37
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
a/ Å	18.4471(18)	8.195(3)
b/ Å	15.3588(18)	9.970(3)
c/ Å	14.4190(17)	14.012(4)
α(°)	90	70.982(9)
β(°)	118.839(3)	73.531(10)
γ(°)	90	74.863(9)
Volume ($Å^3$)	3578.6(7)	1019.8(5)
Z	8	2
Dc (Mg/m^3)	1.713	1.512
μ (mm^{-1})	0.717	0.524
F(000)	1872	478
reflns collected	32962	5527
indep. reflns	3224	4795
GOF on F^2	1.024	1.098
R1 (on F_o^2, I > 2σ(I))	0.0513	0.0606
wR2 (on F_o^2, I > 2σ(I))	0.1106	.01641
R1 (all data)	0.0919	0.0866
wR2 (all data)	0.1311	0.1888

Table S3: Selected bond lengths for **$1VO_2$-$3VO_2$, $4VO(SO_4)$** and **4VO(acac)**.

	$1VO_2$	**$2VO_2$**	**$3VO_2$**	**$4VO(SO_4)$**	**4VO(acac)**
$V\text{-}O_{(V=O)}$	1.6319(17) 1.6221(15)	1.629(2) 1.610(2)	1.612(3) 1.609(3)	1.590(3)	1.607(2)
$V\text{-}N_{(isoindoline)}$	2.0935(18)	2.062(2)	2.123(2)	2.032(3)	2.008(3)
$V\text{-}N_{(aryl)}$	2.0417(17) 2.0492(17)	2.092(2) 2.062(2)	2.057(3) 2.060(3)	2.142(3) 2.132(3)	2.148(3) 2.150(3)
$V\text{-}O_{(SO4)}$	--	--	--	2.027(3) 2.235(3)	--
$V\text{-}O_{(acac)}$	--	--	--	--	2.024(2) 2.166(2)