Supporting Information

Oxidovanadium(IV) and dioxidovanadium(V) complexes of hydrazones of 2-benzoylpyridine and their catalytic applications

Mannar R. Maurya, Nikita Chaudhary, Fernando Avecilla, Pedro Adão and J. Costa Pessoa

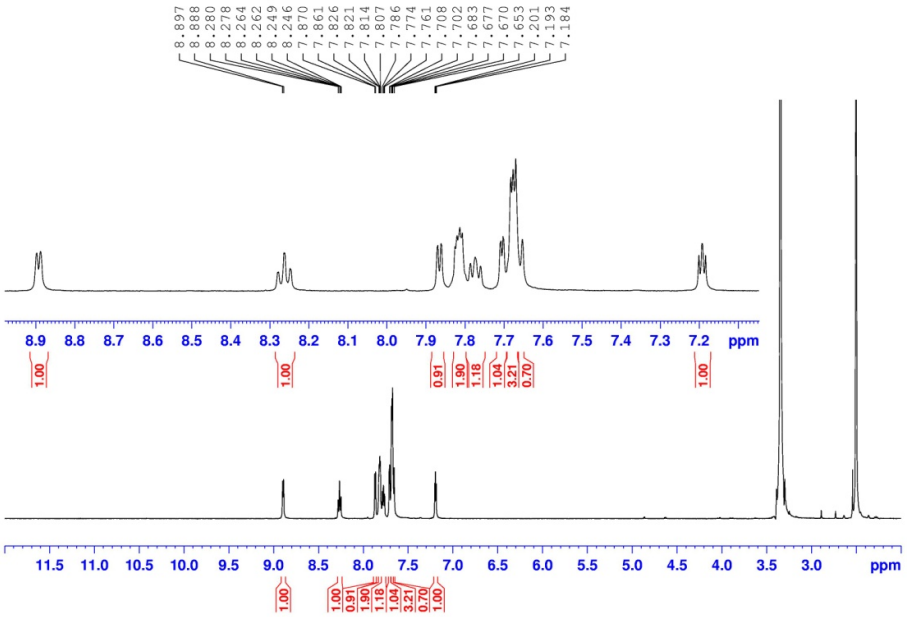

Figure SI-1. ^{1}H NMR spectrum of [{$V^{V}O$(bzpy-tch)}$_2$(μ-O)$_2$] (**3**).

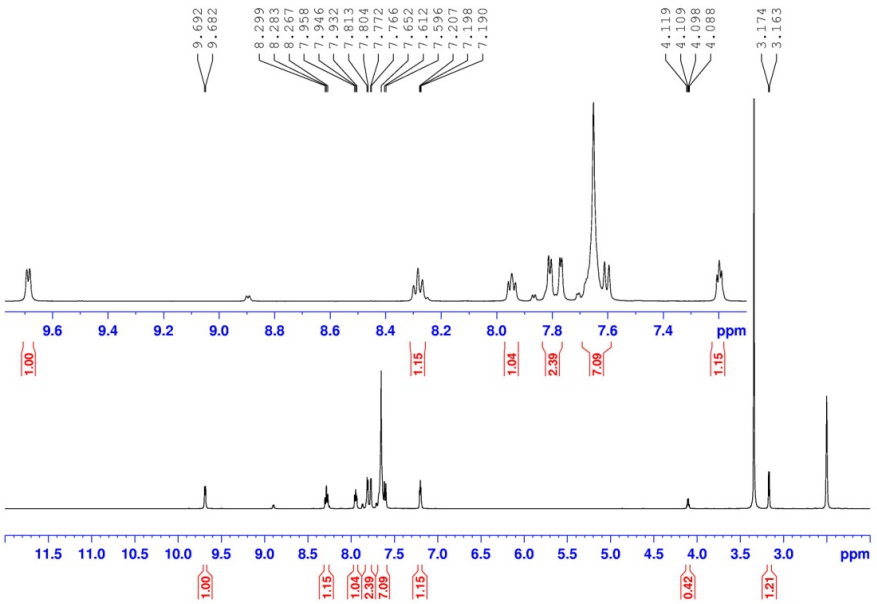

Figure SI-2. ^{1}H NMR spectrum of [$V^{V}O(O_2)$(bzpy-tch)] (**6**).

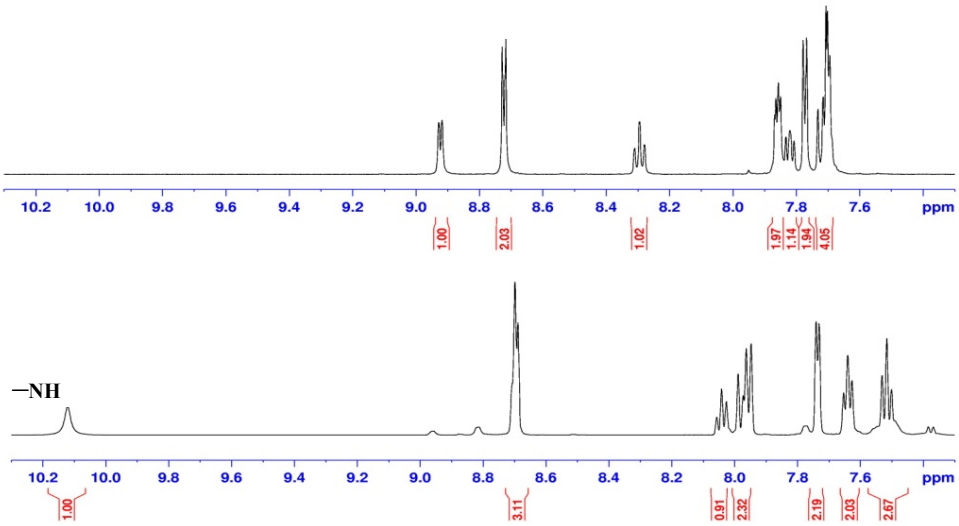

Figure SI-3. ^{1}H NMR spectra of (Hbzpy-inh) (**II**) and [{$V^{V}O$(bzpy-inh)}$_2$(μ-O)$_2$] (**4**).

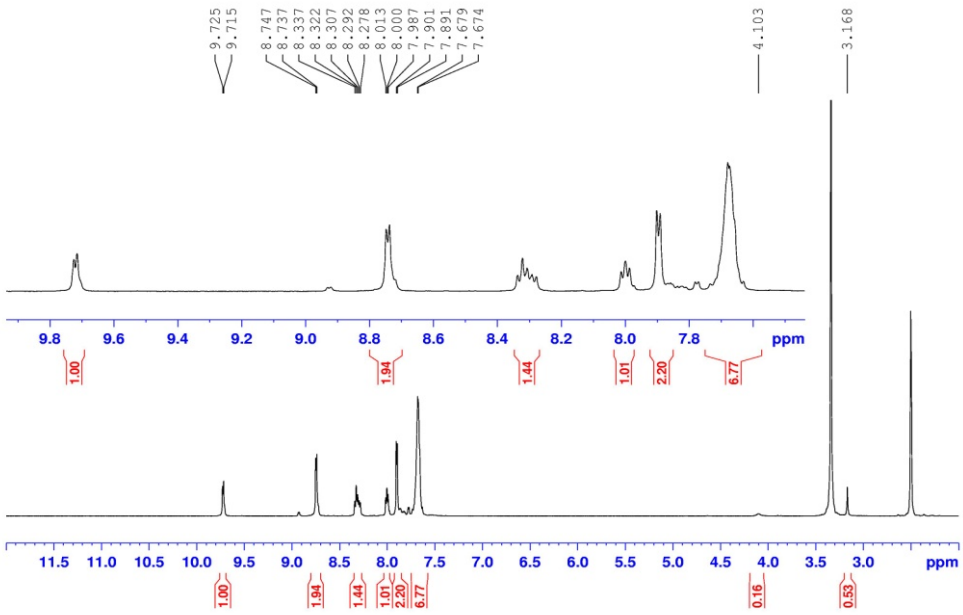

Figure SI-4. ^{1}H NMR spectra of [$V^{V}O(O_2)$(bzpy-inh)] (**6**).

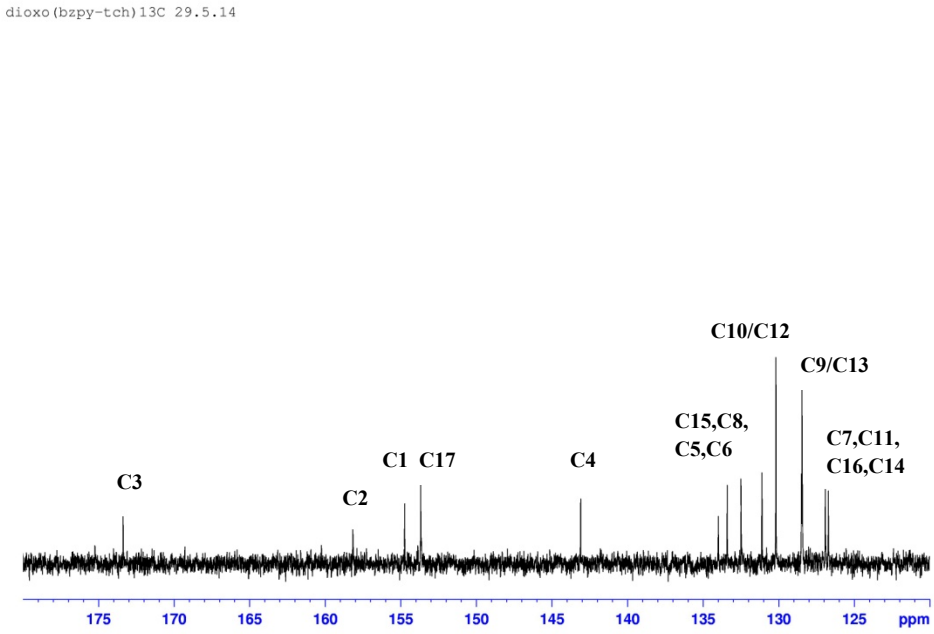

Figure SI-5. ^{13}C NMR spectra of [{$V^{V}O$(bzpy-tch)}$_2$(μ-O)$_2$] (**3**).

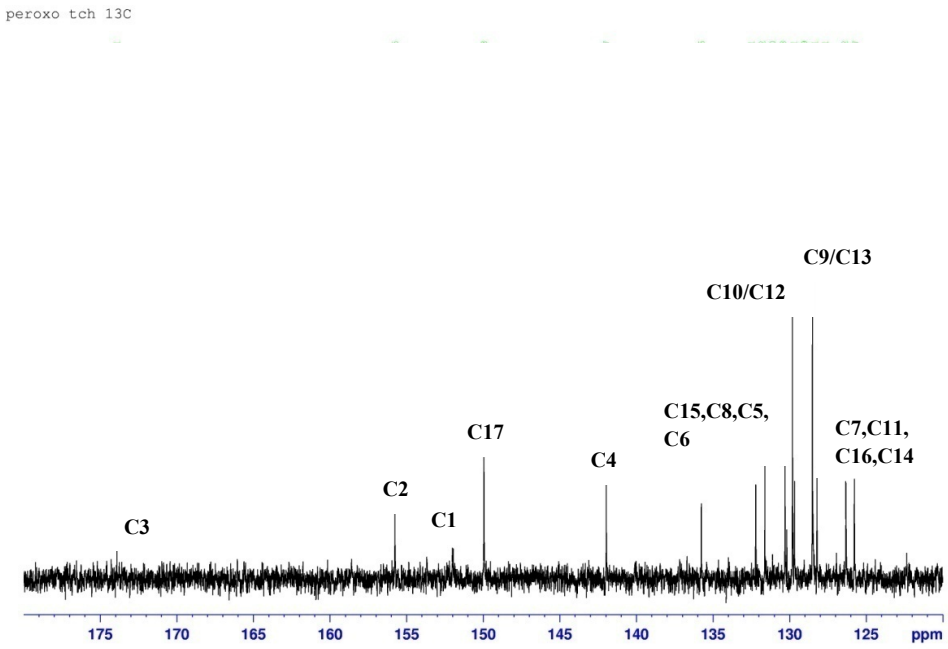

Figure SI-6. ^{13}C NMR spectra of [$V^{V}O(O_2)$(bzpy- tch)] (**5**)

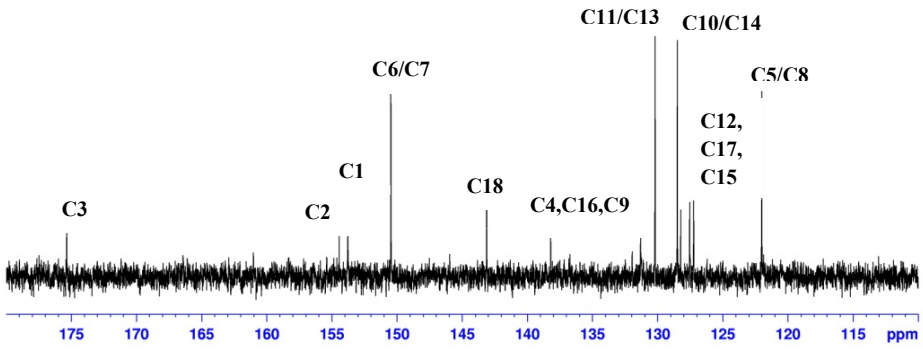

Figure SI-7. ^{13}C NMR spectra of [{$V^{V}O$(bzpy-inh)}$_2$(μ-$O)_2$] (**4**)

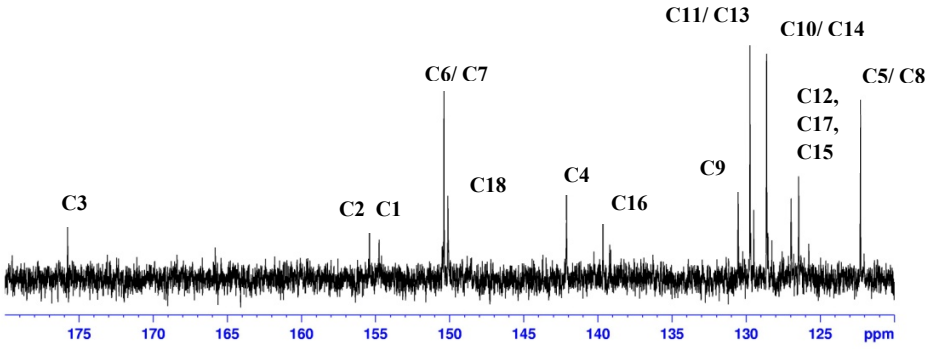

Figure SI-8. ^{13}C NMR spectra of $[V^{V}O(O_2)(bzpy\text{- }inh)]$ (**6**)

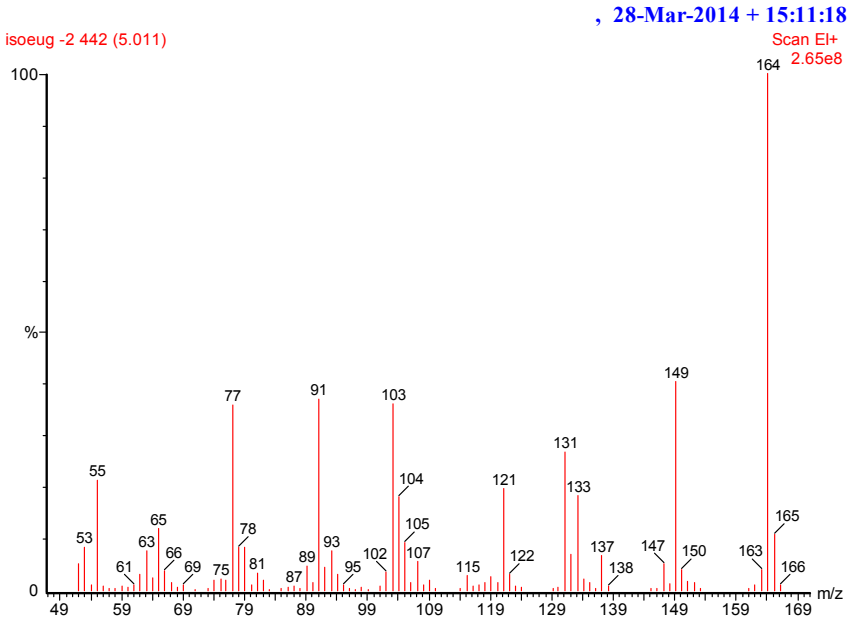

Fig. SI-9. Mass spectrum of isoeugenol.

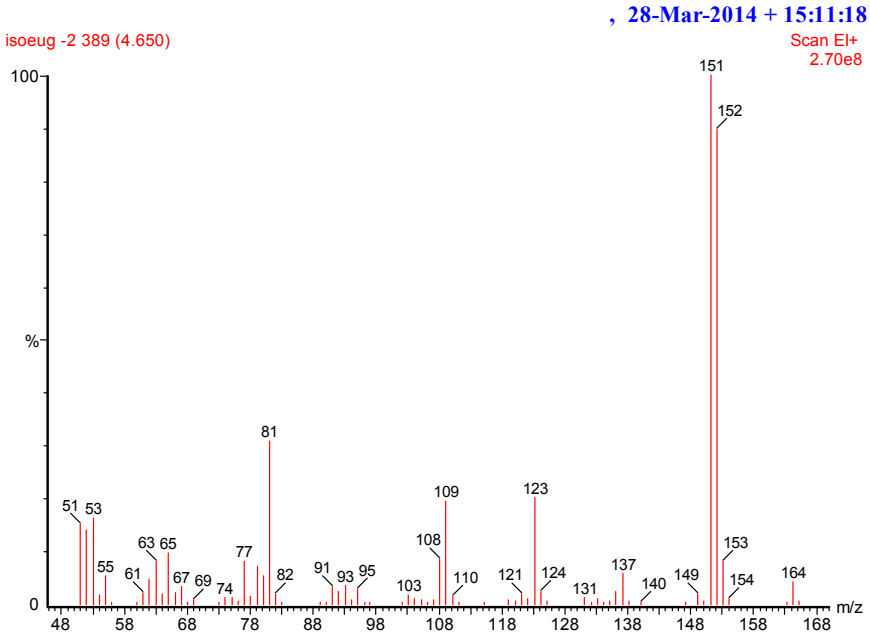

Fig. SI-10. Mass spectrum of vanillin.

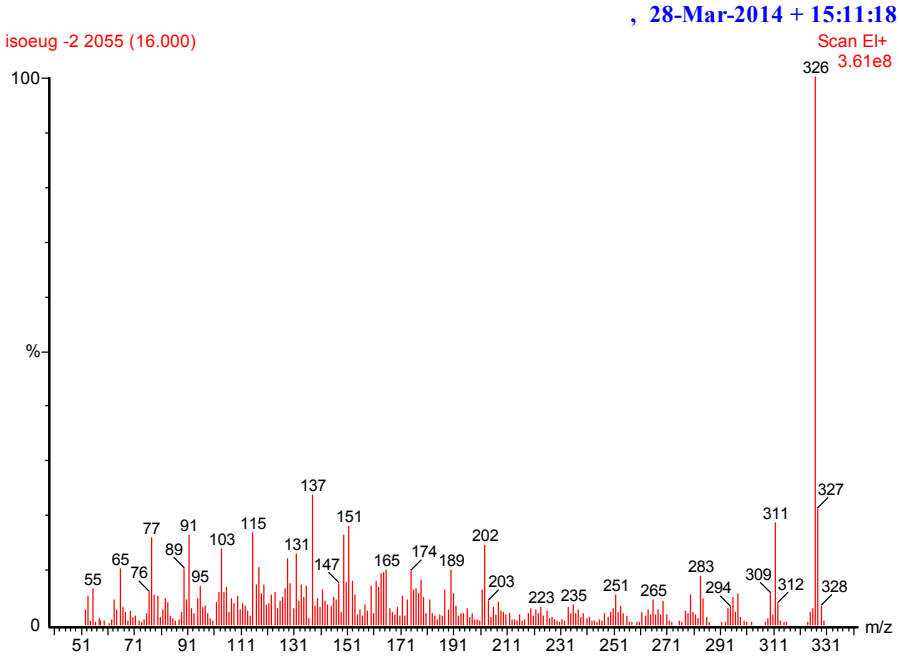

Fig. SI-11. Mass spectrum of dehydrodiisoeugenol (DDI)

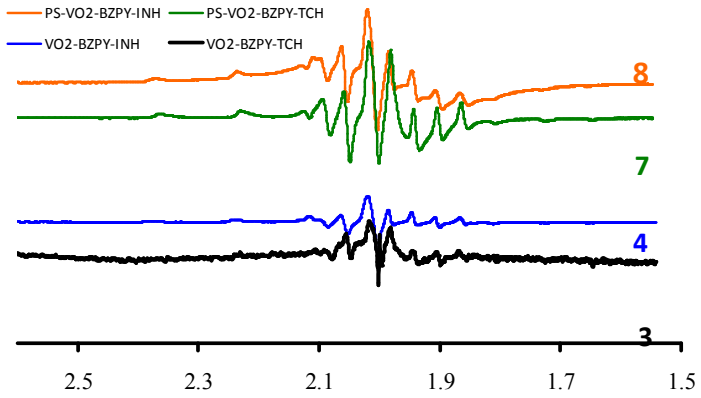

Figure SI-12. EPR signals of the V^{IV}-impurities found in some samples of compounds **3, 4** at 77 K and of **7** and **8** at room temperature.

Table SI-1. Spin Hamiltonian parameters obtained from the EPR signals of the V^{IV}-impurities found in some samples of compounds **4, 7** and **8** dissolved in DMF.

Compound	g_z	$A_z \times 10^4$ cm^{-1}	Suggested Donor atom set
4[a]	1.95	163	N_{imine}, N_{pyr}, O_{DMF}, O_{ArO}
7[b]	1.946	162.6	N_{imine}, N_{pyr}, O_{DMF}, O_{ArO}
8[b]	1.95	161.2	N_{imine}, N_{pyr}, O_{DMF}, O_{ArO}

[a] Spectrum measured from a DMF solution at 77 K.

[b] Spectrum measured from the neat solid at room temperature.

Some samples of the V^{V} compounds exhibited V^{IV} signals, confirming the incomplete oxidation of the respective $V^{IV}O$ precursor compounds. In the case of **4**, **7** and **8**, the $V^{IV}O$ signal was strong enough to allow the estimation of the respective spin Hamiltonian parameters. The *z*-component parameters are in agreement with a [N_{imine}, N_{pyr}, O_{DMF}, O_{ArO}] donor atom sets for the V^{IV}-impurities present in these samples. The [N_{imine}, N_{pyr}, O_{acac}, O_{ArO}] donor atom set cannot be ruled out, particularly for **7** and **8**, where a negative charge must be present to compensate charges of the V^{IV}-species. If it is DMF that binds, then some Cl^- must be present.

Upon their purification, the V^{V}-compounds gave no EPR signals, either in solution or in the powder form.

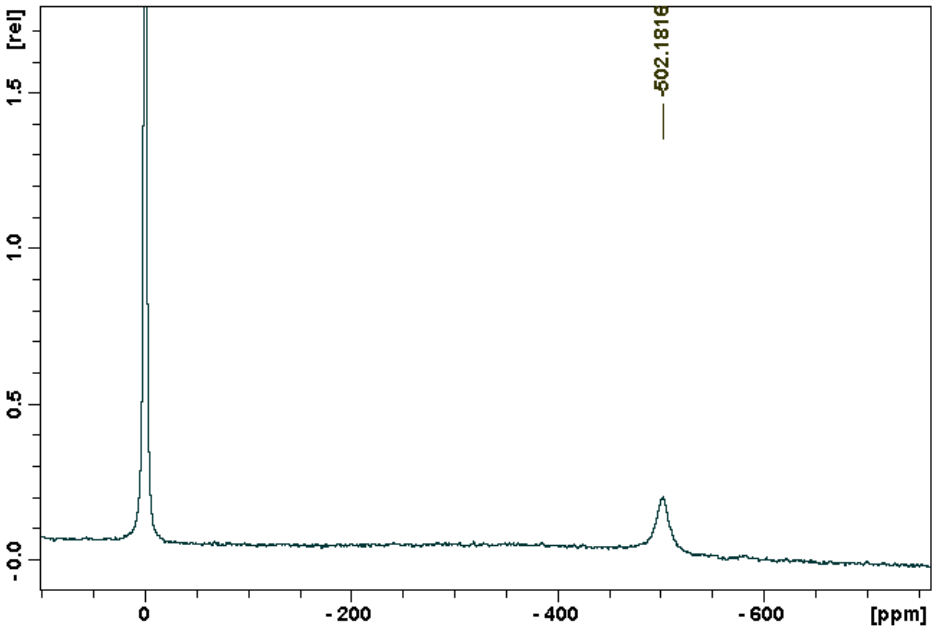

Figure SI-13. ^{51}V NMR of [{$V^{V}O$(bzpy-tch)}μ-O_2] (**3**) in DMSO-d_6.

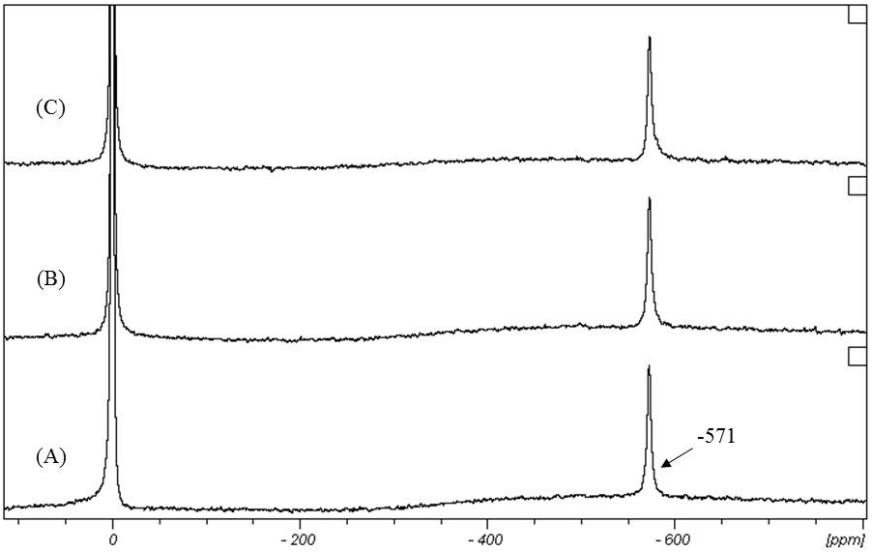

Figure SI-14. ^{51}V NMR spectra of [$V^{V}O(O_2)$(bzpy-tch)] (**5**) (2.5 mM, DMF/acetone-d_6 4:1) in the presence of: A) fresh sample, 1 mole equivalents of H_2O_2 (0.10 M, acetone); B) after the addition of 10 mole equivalents of H_2O_2 (0.10 M, acetone); C) 24 h after addition of oxidant.

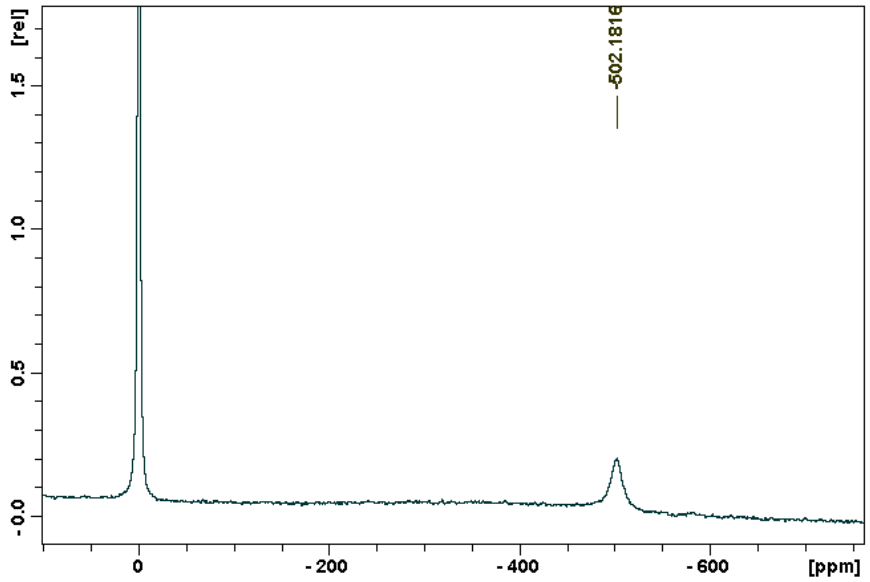

Figure SI-15. ^{51}V NMR of [{$V^{V}O$(bzpy-inh)}μ-O_2] (**4**) in DMSO-d_6.

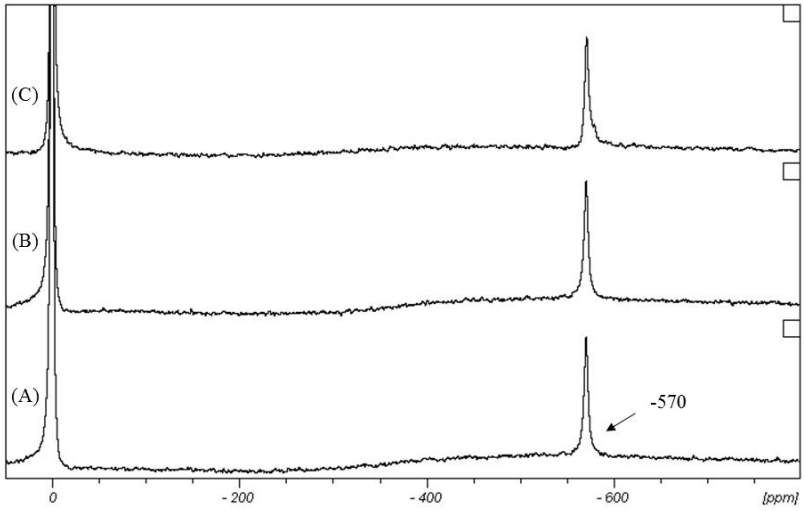

Figure SI-16. ^{51}V NMR spectra of [$V^{V}O(O_2)$(bzpy-inh)] (**6**) (2 mM, DMF/acetone-d_6 4:1) in the presence of: A) fresh sample, 1 mole equivalent of H_2O_2 (0.10 M, acetone); B) after the addition of 10 mole equivalents of H_2O_2 (0.10 M, acetone); C) 24 h after the addition of oxidant.

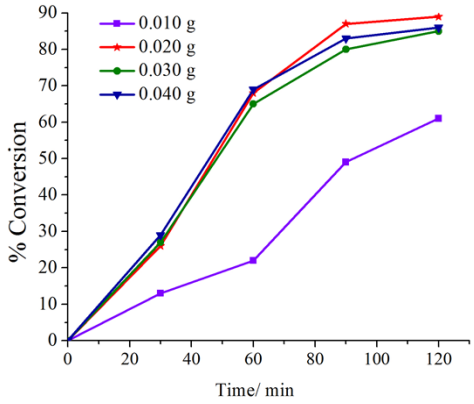

Fig. S17 Effect of the amount of catalyst PS-im[VO_2(bzpy-inh)] on the conversion of isoeugenol. Reaction conditions: isoeugenol (0.82 g, 5.0 mmol), acetonitrile (7.0 mL), 30 % aqueous H_2O_2 (1.13 g, 10 mmol, 1.0 mL), reaction temperature (80 ^oC) and reaction time 2 h.

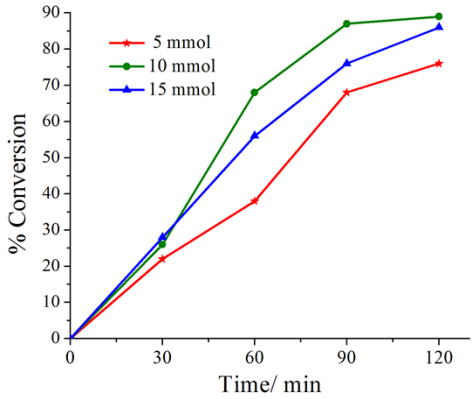

Fig. S18 Effect of the amount of oxidant i.e. 30% aqueous H_2O_2 on the oxidation of isoeugenol. Reaction conditions: isoeugenol (0.82 g, 5.0 mmol), acetonitrile (7.0 mL), PS-im[VO_2(bzpy-inh)] (0.020 g), reaction temperature (80 ^oC) and reaction time 2 h.

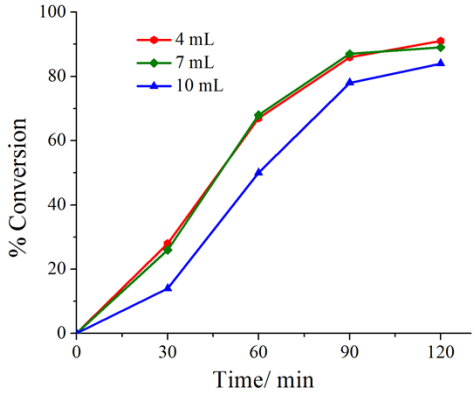

Fig. S19 Effect of the amount of solvent (acetonitrile) on the oxidation of isoeugenol. Reaction conditions: isoeugenol (0.82 g, 5.0 mmol), PS-im[$V^{V}O_2$(bzpy-inh)] (0.020 g), 30 % aqueous H_2O_2 (1.13 g, 10.0 mmol, 1.0 mL), reaction temperature (80 ^{o}C) and reaction time 2 h.

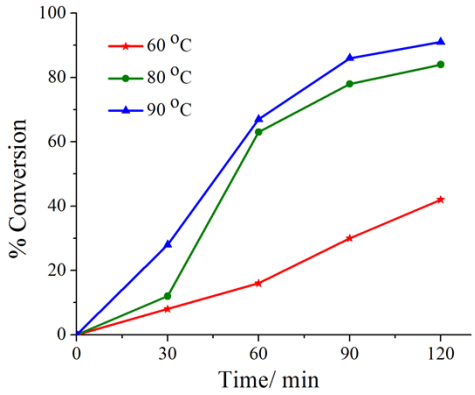

Fig. S20 Effect of the temperature on oxidation of isoeugenol. Reaction conditions: isoeugenol (0.82 g, 5.0 mmol), acetonitrile (4.0 mL), PS-im[$V^{V}O_2$(bzpy-inh)] (0.020 g), 30 % aqueous H_2O_2 (1.13 g, 10.0 mmol, 1.0 mL) for 2 h.