Reductive Silylation of Polyoxovanadate Surfaces using Mashima's Reagent

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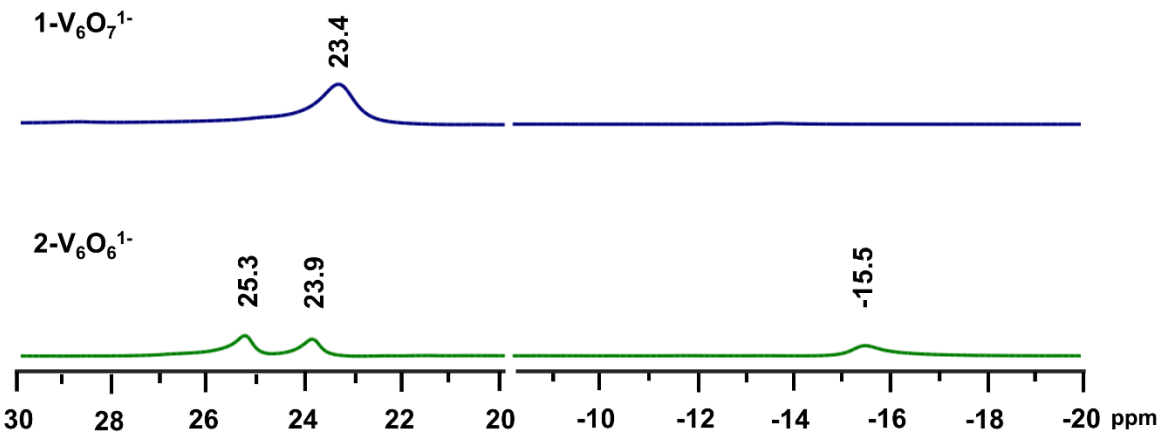

Fig. S1. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectra of **1-$V_6O_7^{1-}$** and **2-$V_6O_6^{1-}$**.

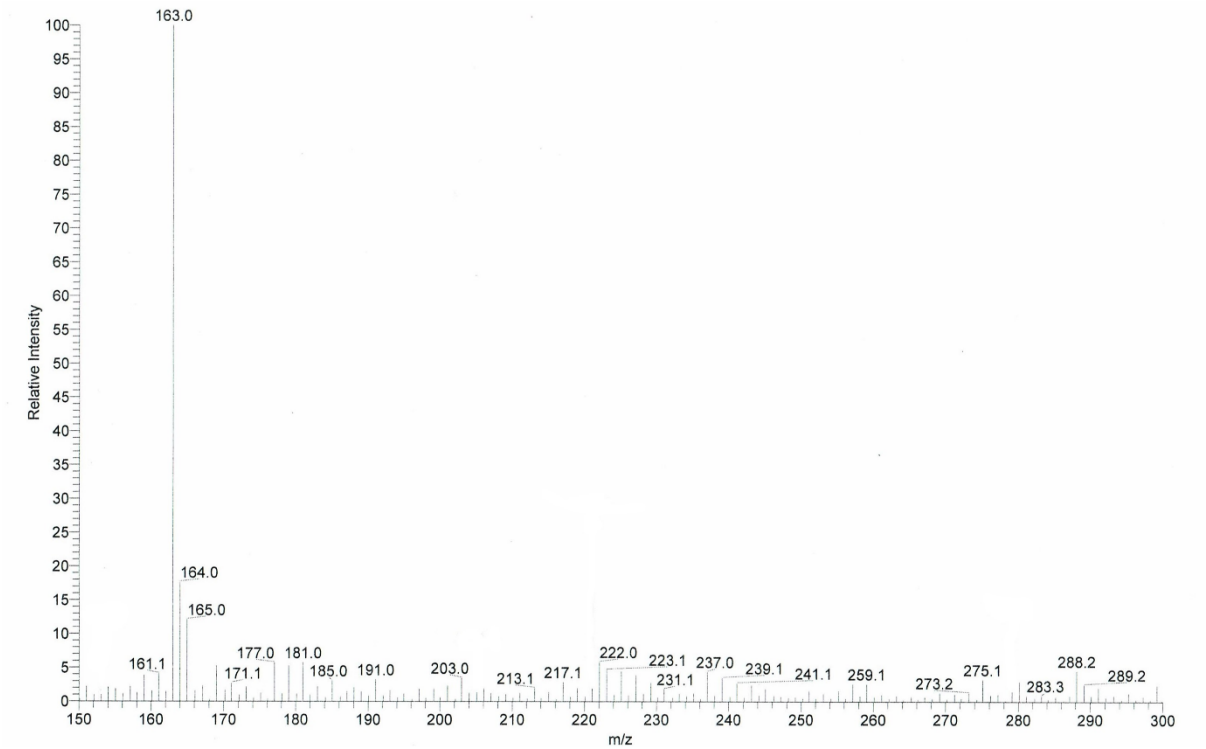

Fig. S2. LC-MS of pentane wash of the reaction of **1-$V_6O_7^{1-}$** with 1equiv $Pyz(SiMe_3)_2$ in dichloromethane. The peak at m/z = 163 ($M+H^+$) amu corresponds to $(Me_3Si)_2O$.

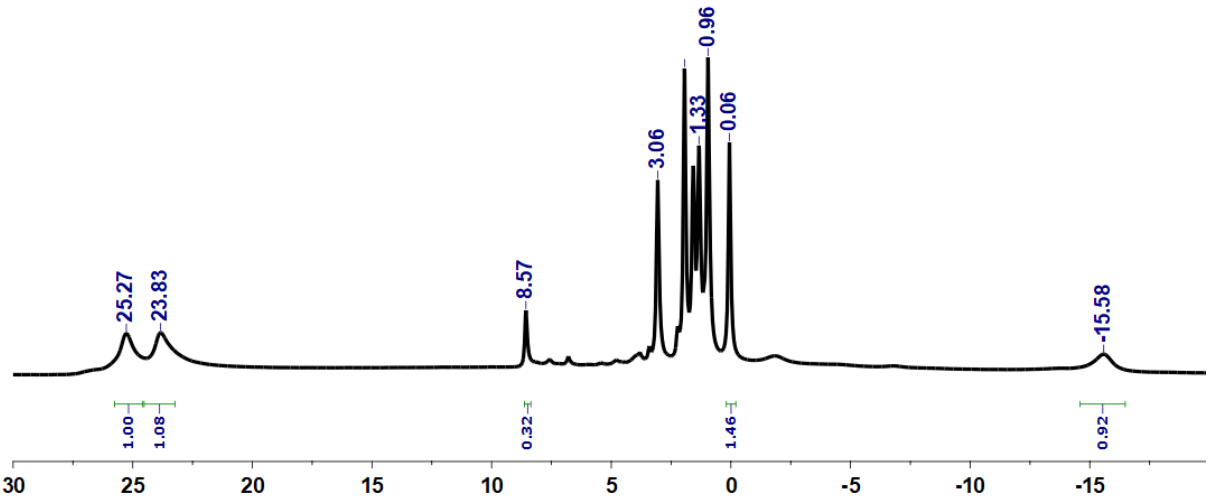

Fig. S3. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of the crude reaction mixture following the addition of 1 equiv of $Pyz(SiMe_3)_2$ to **1-$V_6O_7^{1-}$** in dichloromethane to form **2-$V_6O_6^{1-}$**. The peak integration for 36 protons of **2-$V_6O_6^{1-}$** correspond to 3, *i.e.* integration for each proton is 0.083. The integration of 8.57 ppm (for pyrazine) stands for 4 protons and the integration of 0.06 ppm (TMS_2O) stands for 18 protons. This represents formation of one equivalent of pyrazine and TMS_2O.

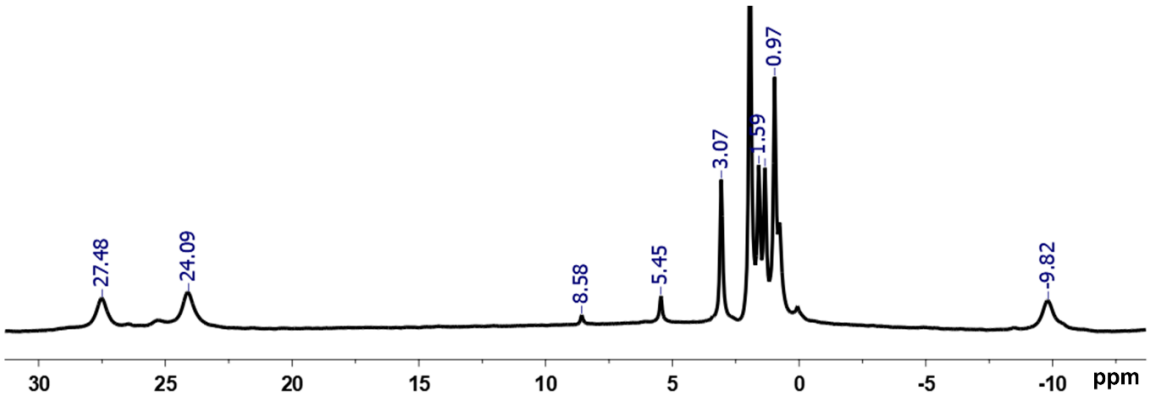

Fig. S4.. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of the crude reaction mixture of **3-$V_6O_6(OSiMe_3)^{1-}$**. The peak at 8.58 ppm (CD_3CN, 21ºC) signifies the formation of pyrazine.

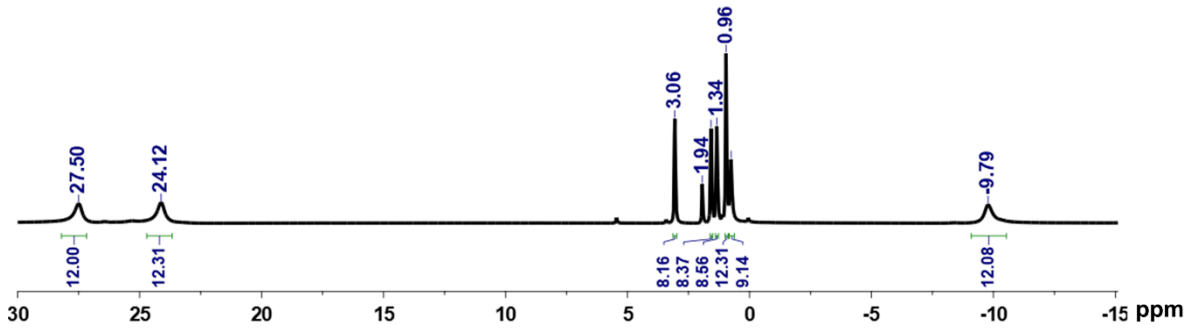

Fig. S5. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of **3-$V_6O_6(OSiMe_3)^{1-}$**.

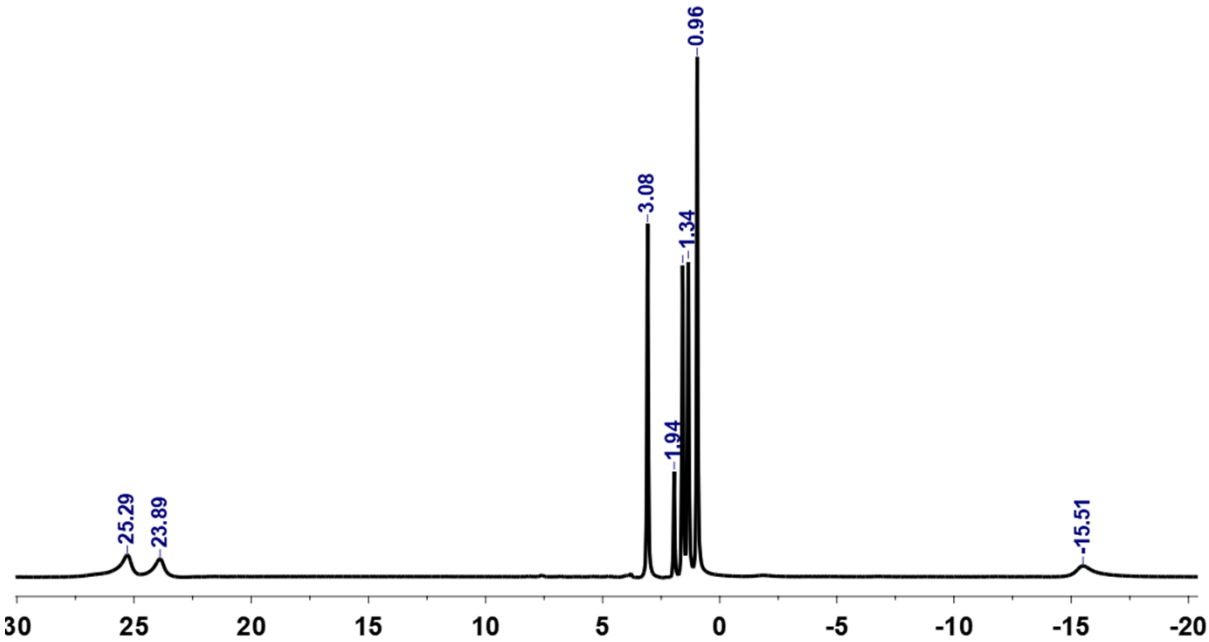

Fig. S6. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of **2-$V_6O_6^{1-}$** formed as a product of the reaction between **3-$V_6O_6(OSiMe_3)^{1-}$** and 0.5 equiv. $Pyz(SiMe_3)_2$ in dichloromethane at low temperature.

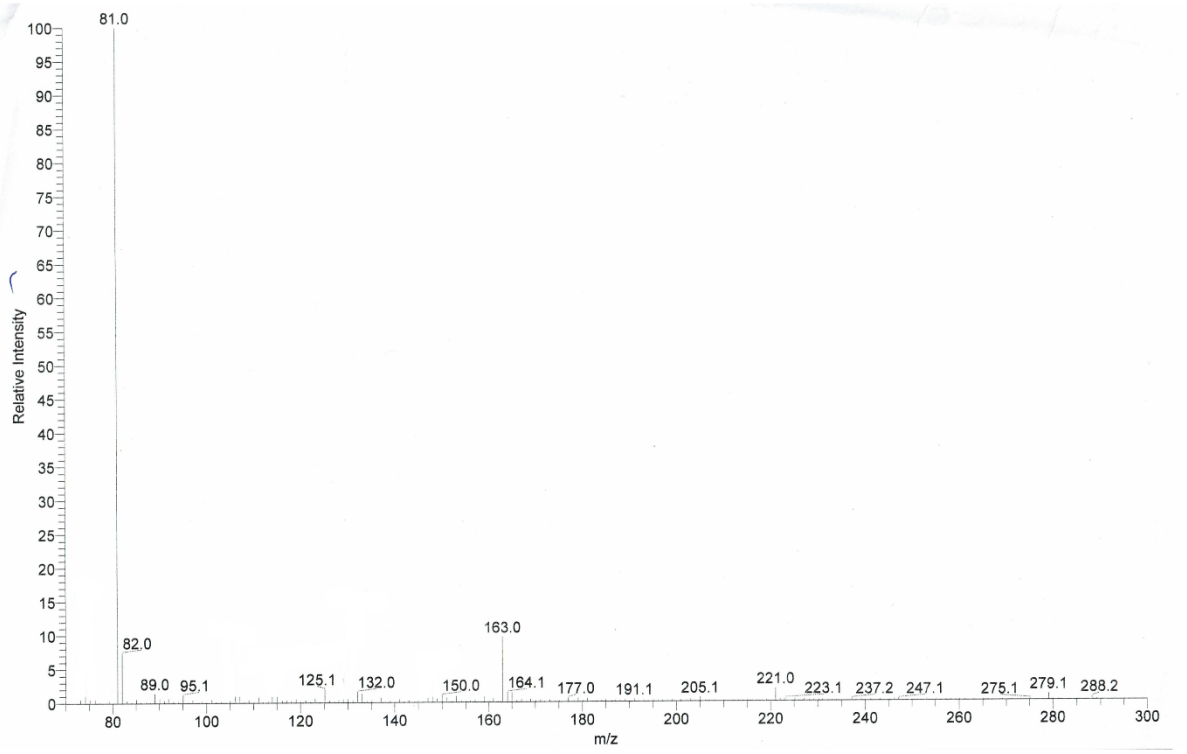

Fig. S7. LC-MS of pentane wash of the reaction of **3-$V_6O_6(OSiMe_3)^{1-}$** with 0.5 eq. $Pyz(SiMe_3)_2$ in dichloromethane. The peak at m/z = 81 ($M+H^+$) amu and m/z = 163 ($M+H^+$) amu correspond to pyrazine and $(Me_3Si)_2O$ respectively.

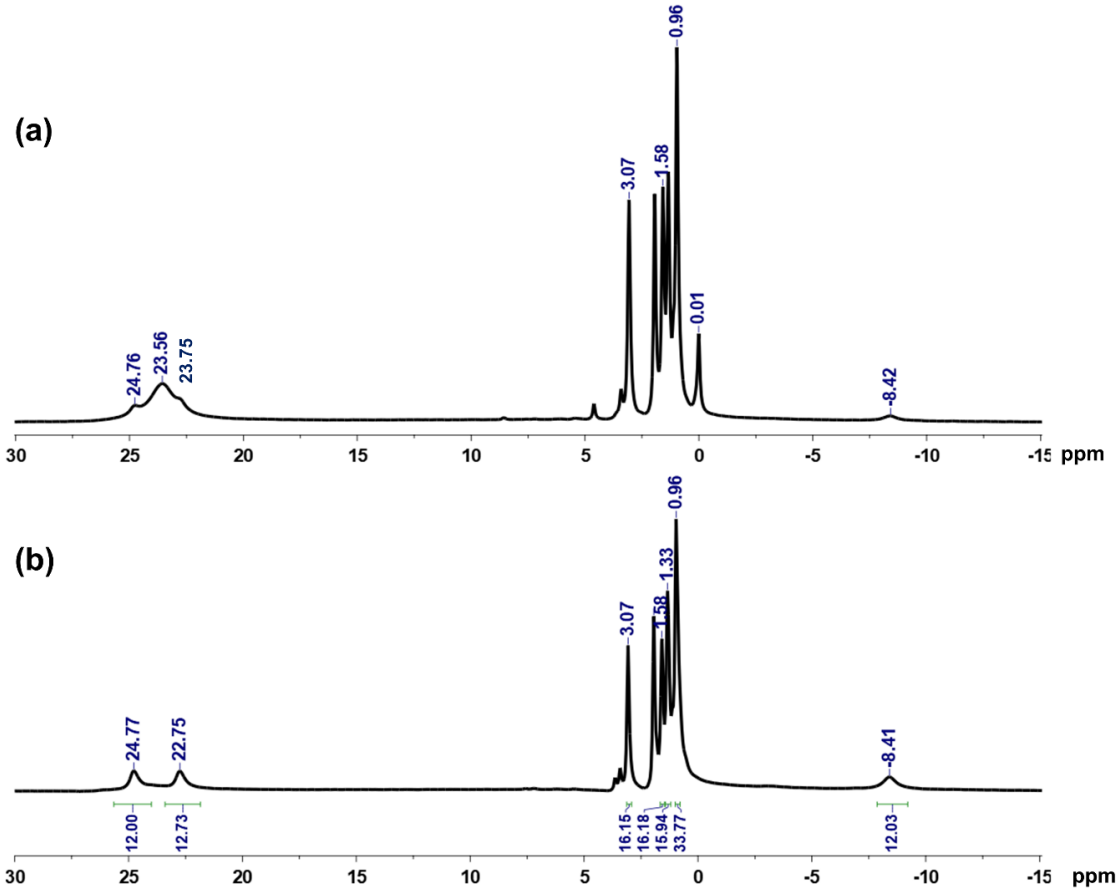

Fig. S8. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of (a) the crude reaction mixture of the synthesis of **5-$V_6O_6(OSiMe_3)^{2-}$**, and (b) **5-$V_6O_6(OSiMe_3)^{2-}$** following work-up.

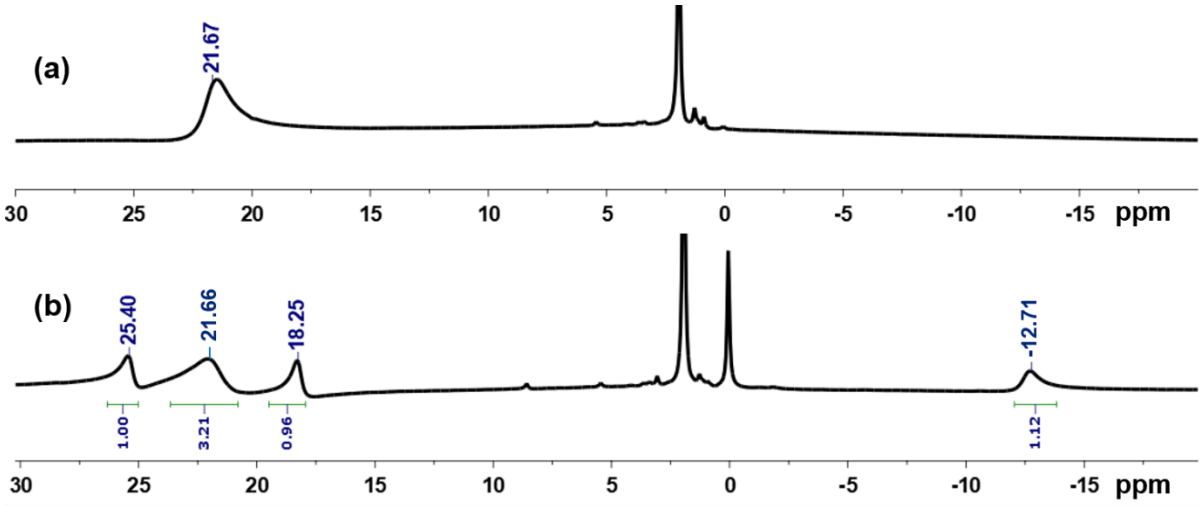

Fig. S9. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of (a) **6-$V_6O_7^0$**, (b) the crude reaction mixture following the addition of 0.5 equiv of $Pyz(SiMe_3)_2$ to **6-$V_6O_7^0$** in acetonitrile.

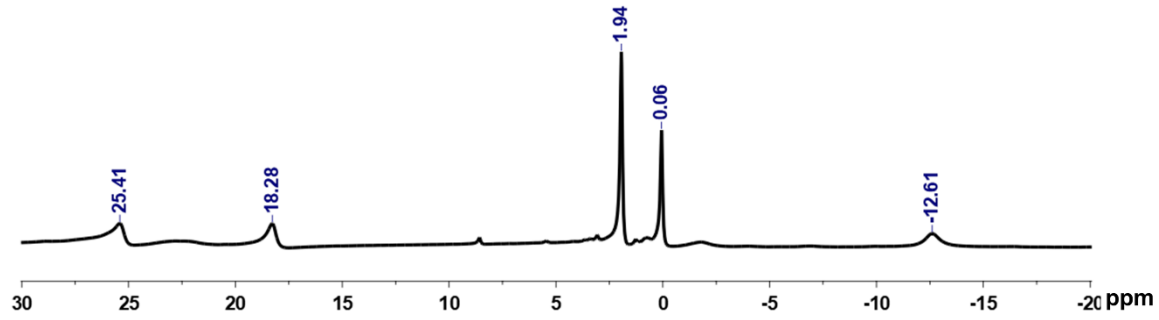

Fig. S10. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of the crude reaction mixture following the addition of 1 equiv of $Pyz(SiMe_3)_2$ to **6-$V_6O_7^0$** in acetonitrile.

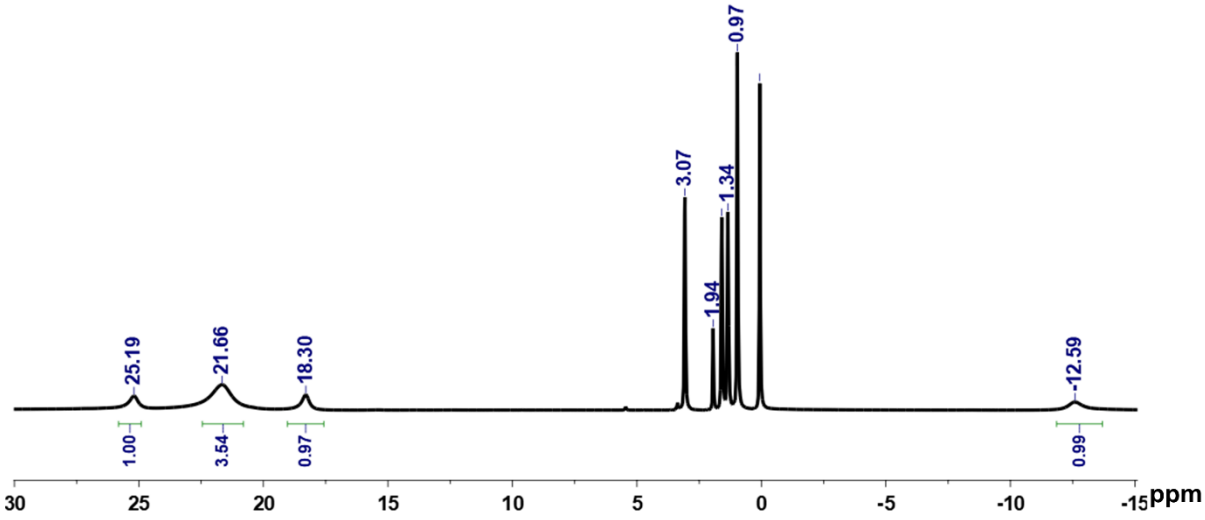

Fig. S11. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectrum of the oxidation of **3-$V_6O_6OSiMe_3^{1-}$** with 1.0 equiv of AgOTf ($E_{1/2}$ = +0.65 V vs. $Fc^{+/0}$) in dichloromethane.

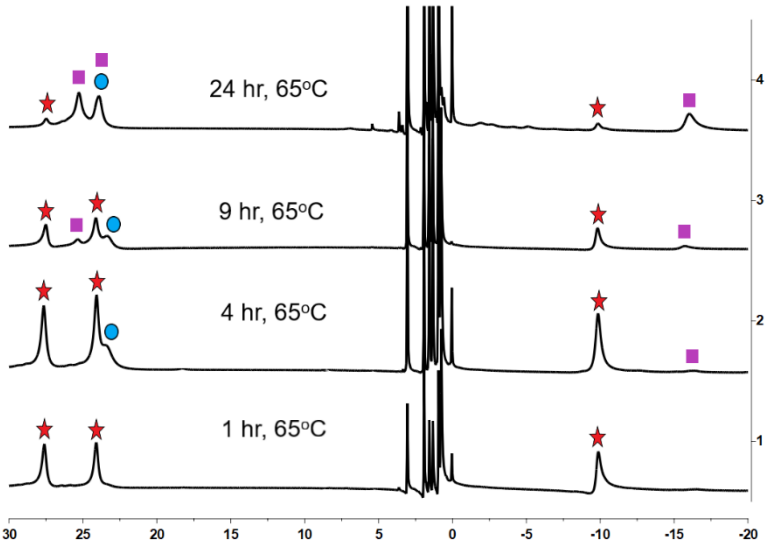

Fig. S12. ^{1}H NMR (500 MHz, CD_3CN, 21 ºC) spectra of the thermal degradation of **3-$V_6O_6OSiMe_3^{1-}$** in CD_3CN, 65ºC. The red stars represent **3-$V_6O_6OSiMe_3^{1-}$**, blue circles stand for **1-$V_6O_7^{1-}$** and the pink squares denote **2-$V_6O_6^{1-}$**.

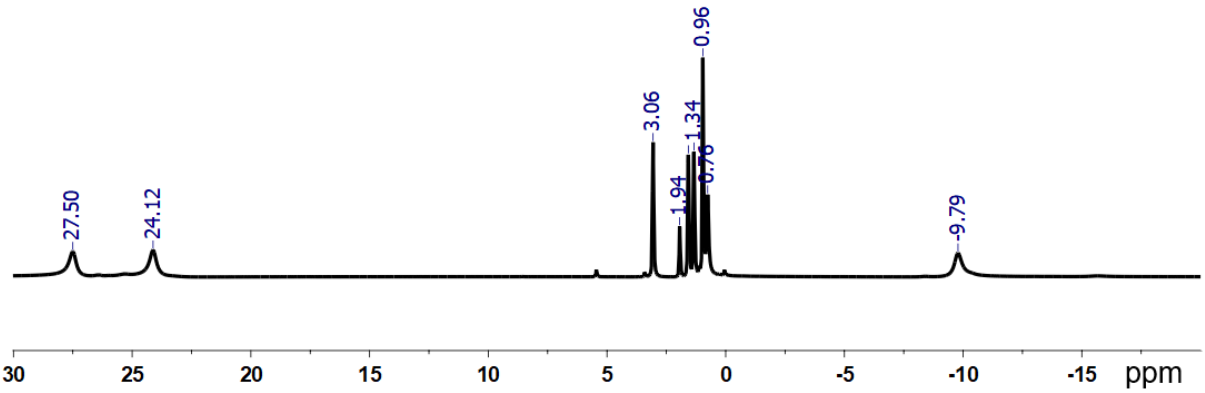

Fig. S13. ^{1}H-NMR (500 MHz, CD_3CN, 21 ºC) spectrum of the reaction following the addition of 0.5 equiv of $Pyz(SiMe_3)_2$ to **1-$V_6O_7^{1-}$** in acetonitrile.

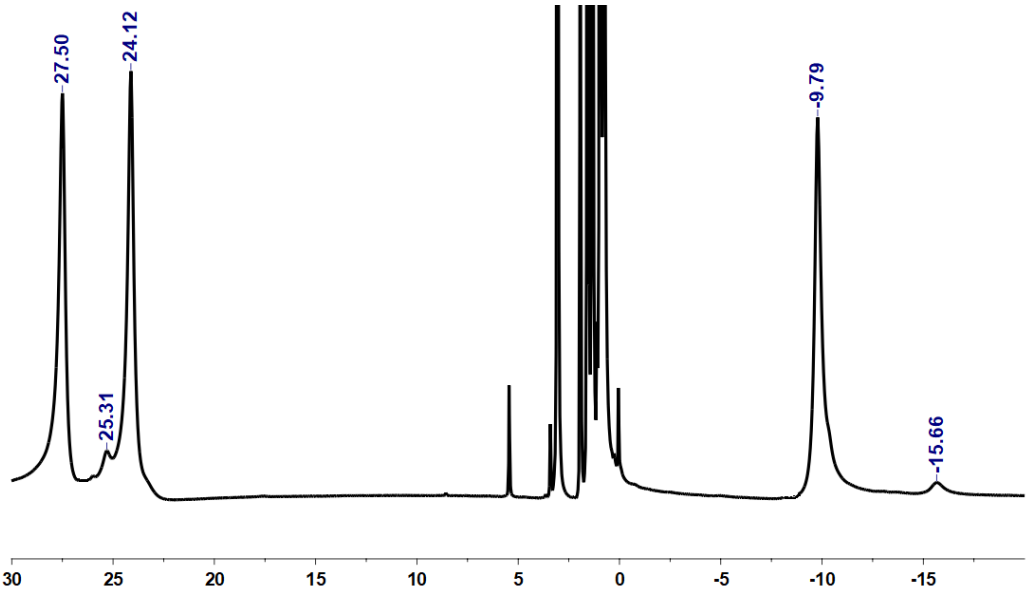

Fig. S14 ^{1}H-NMR (500 MHz, CD_3CN, 21 ºC) spectrum of the reaction following the addition of 0.55 equiv of $Pyz(SiMe_3)_2$ to **1-$V_6O_7^{1-}$** in dichloromethane.