

Supporting information for

Four Alkoxohexavanadate-Based Pd-Polyoxovanadates as Robust Heterogeneous Catalysts for Oxidation of Benzyl-Alkanes

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Table S1. Bond valance sum calculations for compound **1-4**.^[a]

Compound	V ^{IV}	V ^V		Bond-valence sums					
				V ₁	V ₂	V ₃	V ₄	V ₅	V ₆
1	0	6	V ^{IV}	4.92	4.93	4.90	—	—	—
			V ^V	5.18	5.19	5.16	—	—	—
2	2	4	V ^{IV}	5.08	4.78	4.31	—	—	—
			V ^V	5.35	5.03	4.53	—	—	—
3	2	4	V ^{IV}	4.87	4.25	4.97	5.06	4.21	4.87
			V ^V	5.13	4.47	5.23	5.34	4.44	5.12
4	2	4	V ^{IV}	4.72	4.25	4.84	—	—	—
			V ^V	4.97	4.47	5.10	—	—	—

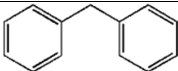
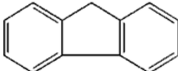
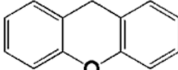
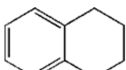
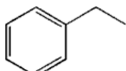
[a] The calculations were performed twice for each individual vanadium atom using bond-valence parameters presented by Brese and O’Keeffe. The oxidation state of atom *i* is given by $\sum v_{ij}=V$ with $v_{ij}=\exp[(R_{ij}-d_{ij})/b]$. Here *b* is taken to be a ‘universal’ constant equal to 0.37 Å, *v_{ij}* is the valence of a bond between two atoms *i* and *j*, *R_{ij}* is the empirical parameter, and *d_{ij}* is the observed bond length.

Table S2. Selected Bond lengths [Å] and angles [deg] for compounds **1–5**.

Compound 1			
Pd(1)-O(12)	1.963(6)	Pd(1)-O(11)	1.965(7)
Pd(1)-N(3)	1.987(7)	Pd(1)-N(1)	2.007(7)
V(1)-O(2)	1.591(5)	V(1)-O(5)	1.781(6)
V(1)-O(6)	1.880(6)	V(1)-O(3)	1.975(6)
V(1)-O(4)	1.995(6)	V(1)-O(1)	2.2318(14)
V(2)-O(7)	1.604(7)	V(2)-O(6)	1.807(6)
V(2)-O(9)	1.872(7)	V(2)-O(8)	1.924(7)
V(2)-O(3)#1	1.980(6)	V(2)-O(1)	2.2276(15)
V(3)-O(10)	1.582(7)	V(3)-O(5)	1.848(6)
V(3)-O(9)	1.887(7)	V(3)-O(8)#1	1.937(7)
V(3)-O(4)#1	1.969(6)	V(3)-O(1)	2.2223(16)
O(12)-Pd(1)-(11)	92.9(3)	O(12)-Pd(1)-N(3)	87.9(3)
O(11)-Pd(1)-N(3)	178.8(2)	O(12)-Pd(1)-N(1)	177.1(3)
O(11)-Pd(1)-N(1)	88.6(3)	N(3)-Pd(1)-N(1)	90.5(3)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z			
Compound 2			
Pd(1)-O(12)	2.001(9)	Pd(1)-N(1)	2.008(9)
Pd(1)-O(11)	2.015(9)	Pd(1)-N(2)	2.050(10)
V(1)-O(1)	1.579(10)	V(1)-O(4)	1.782(8)
V(1)-O(2)	1.872(10)	V(1)-O(3)	1.928(9)
V(1)-O(10)#1	1.981(9)	V(1)-O(6)	2.244(2)
V(2)-O(5)	1.586(10)	V(2)-O(7)	1.847(8)
V(2)-O(2)	1.930(10)	V(2)-O(3)#1	1.954(10)
V(2)-O(8)#1	1.954(8)	V(2)-O(6)	2.234(2)
V(3)-O(9)	1.622(8)	V(3)-O(7)	1.822(9)
V(3)-O(4)	1.948(8)	V(3)-O(10)	2.046(9)
V(3)-O(8)	2.085(9)	V(3)-O(6)	2.243(2)
O(12)-Pd(1)-N(1)	179.1(4)	O(12)-Pd(1)-(11)	92.7(4)
N(1)-Pd(1)-O(11)	86.7(4)	O(12)-Pd(1)-N(2)	89.8(4)
N(1)-Pd(1)-N(2)	90.8(4)	O(11)-Pd(1)-N(2)	176.2(4)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+2,-z			
Compound 3			
Pd(1)-O(21)	1.978(9)	Pd(1)-O(20)	1.985(9)
Pd(1)-N(1)	2.020(11)	Pd(1)-N(2)	2.028(11)
V(1)-O(1)	1.608(10)	V(1)-O(5)	1.748(9)
V(1)-O(4)	1.909(9)	V(1)-O(2)	1.918(9)
V(1)-O(3)	2.065(10)	V(1)-O(19)	2.243(10)
V(2)-O(6)	1.608(10)	V(2)-O(9)	1.848(9)
V(2)-O(5)	2.001(9)	V(2)-O(8)	2.008(10)
V(2)-O(7)	2.072(9)	V(2)-O(19)	2.308(9)
V(3)-O(10)	1.579(10)	V(3)-O(12)	1.792(10)
V(3)-O(7)	1.938(10)	V(3)-O(11)	1.949(10)
V(3)-O(2)	2.015(10)	V(3)-O(19)	2.160(9)
V(4)-O(13)	1.591(11)	V(4)-O(14)	1.697(10)
V(4)-O(3)	1.932(10)	V(4)-O(15)	1.946(11)
V(4)-O(11)	2.065(10)	V(4)-O(19)	2.180(9)
V(5)-O(16)	1.615(10)	V(5)-O(9)	1.876(9)
V(5)-O(4)	1.968(9)	V(5)-O(18)	2.003(10)
V(5)-O(14)	2.064(9)	V(5)-O(19)	2.327(9)
V(6)-O(17)	1.611(12)	V(6)-O(8)	1.762(11)
V(6)-O(12)	1.908(11)	V(6)-O(18)	1.928(11)
V(6)-O(15)	2.012(11)	V(6)-O(19)	2.260(10)
O(21)-Pd(1)-(20)	90.4(4)	O(21)-Pd(1)-N(1)	89.3(4)

O(20)-Pd(1)-N(1)	176.5(4)	O(21)-Pd(1)-N(2)	175.7(4)
O(20)-Pd(1)-N(2)	88.5(4)	N(1)-Pd(1)-N(2)	92.0(4)
Compound 4			
Pd(1)-O(1)	2.00(5)	Pd(1)-O(2)	2.00(5)
Pd(1)-N(1)	2.01(6)	Pd(1)-N(3)	2.03(6)
V(1)-O(4)	1.60(5)	V(1)-O(8)	1.85(5)
V(1)-O(11)#1	1.91(5)	V(1)-O(12)	1.92(5)
V(1)-O(5)	1.98(5)	V(1)-O(3)	2.236(12)
V(2)-O(6)	1.65(5)	V(2)-O(8)	1.85(5)
V(2)-O(7)	1.93(5)	V(2)-O(9)	2.04(5)
(2)-O(5)#1	2.03(5)	V(2)-O(3)	2.245(11)
V(3)-O(10)	1.60(5)	V(3)-O(7)#1	1.77(5)
V(3)-O(12)	1.92(5)	V(3)-O(9)	2.02(5)
V(3)-O(11)	1.94(5)	V(3)-O(3)	2.254(12)
O(1)-Pd(1)-O(2)	93(2)	O(1)-Pd(1)-N(1)	179(2)
O(2)-Pd(1)-N(1)	85(2)	O(1)-Pd(1)-N(3)	89(2)
O(2)-Pd(1)-N(3)	178(2)	N(1)-Pd(1)-N(3)	93(2)
Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+2			
Compound 5			
V(1)-O(2)	1.598(2)	V(1)-O(6)	1.786(2)
V(1)-O(5)	1.886(2)	V(1)-O(4)	1.9525(19)
V(1)-O(3)	2.0352(19)	V(1)-O(1)	2.2376(5)
V(2)-O(7)	1.600(2)	V(2)-O(9)	1.764(2)
V(2)-O(6)	1.912(2)	V(2)-O(3)#1	1.9695(19)
V(2)-O(8)	2.042(2)	V(2)-O(1)	2.2427(5)
V(3)-O(10)	1.597(2)	V(3)-O(5)	1.767(2)
V(3)-O(9)	1.906(2)	V(3)-O(8)#1	1.962(2)
V(3)-O(4)#1	2.0478(19)	V(3)-O(1)	2.2360(5)
Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z			

Table S3. The benzyl C-H bond energies of some substrates.

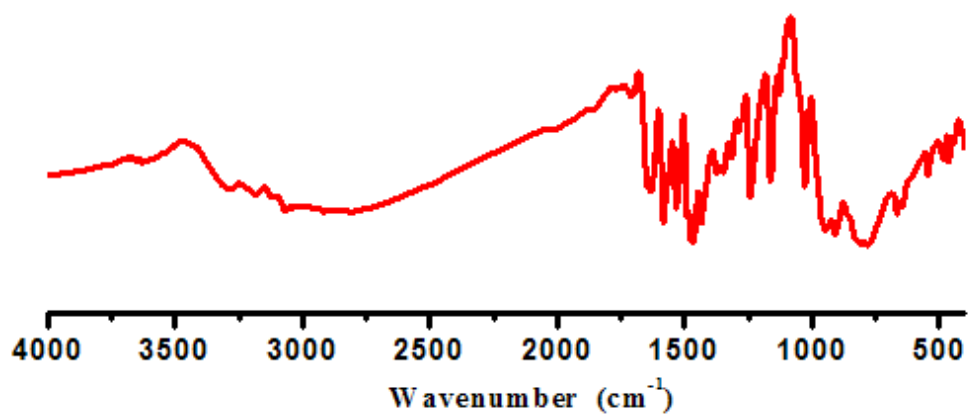
Substrates	BDE ^[a] (kcal/mol)	Ref.
	82±1	[1]
	80±2	[1a], [2]
	75±1	[2]
	85±1	[3]
	85±1	[3], [4]

[a] BDE: C-H bond dissociation energy.

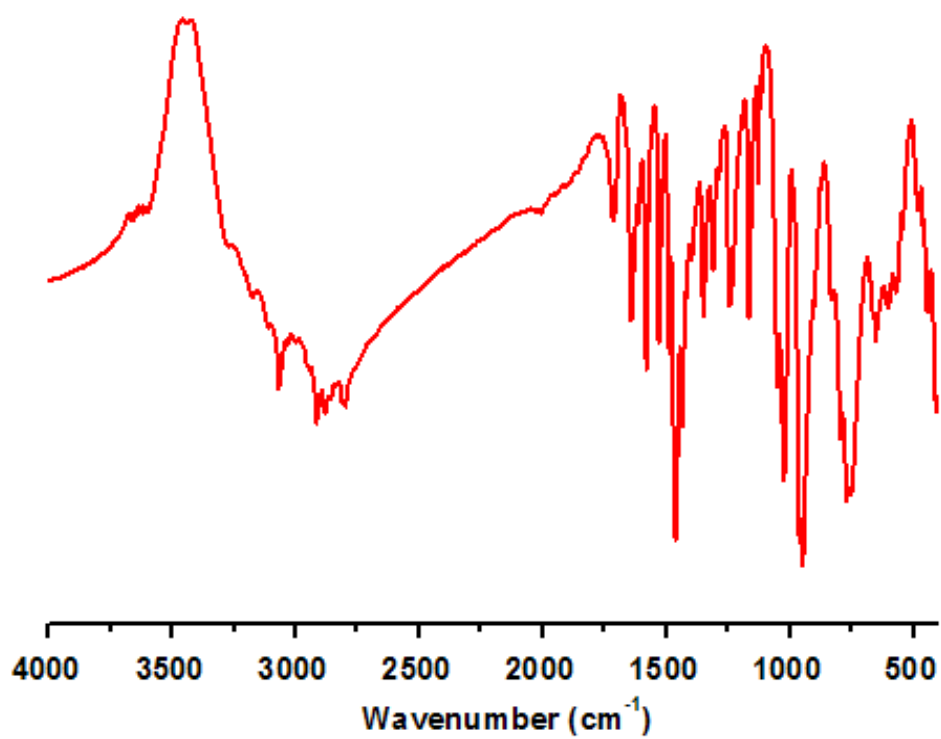
Table S4. Effect of radical trap on the oxidation of diphenylmethane catalyzed by **1**.^[a]

Entry	Radical trap	mmol	Conv. (%)
1	-	-	95.8
2	Ph ₂ NH	0.125	4.5
3	Ph ₂ NH	0.250	N.D.
4	TEMPO	0.250	88.5
5	TEMPO	0.500	80.8
6	TEMPO	1.000	56.5

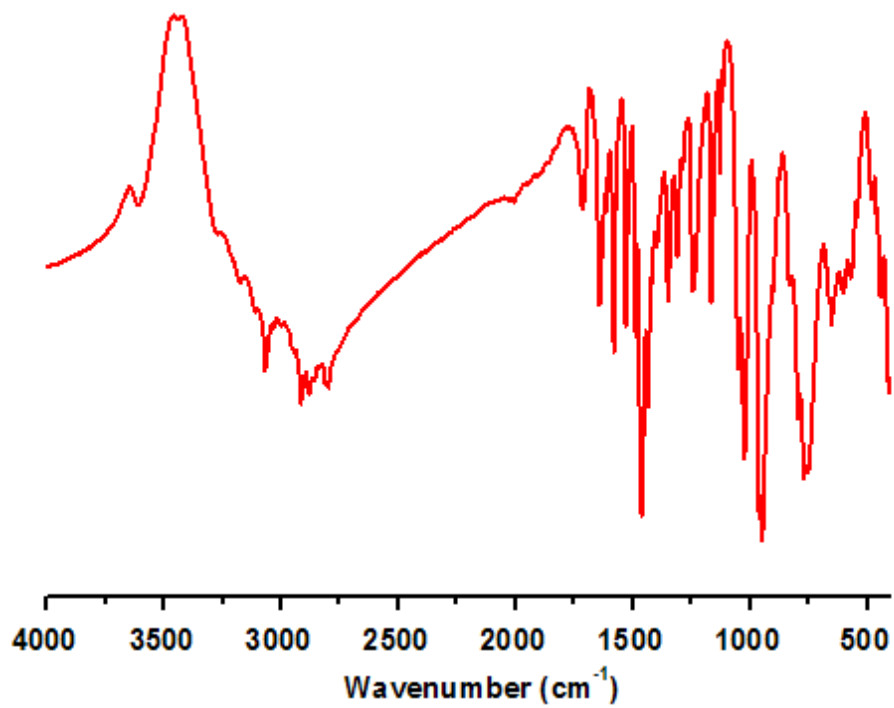
[a] Reaction conditions: diphenylmethane (0.25 mmol, 1 equiv), catalyst (3.75 μ mol, 1.5 mol %), TBHP (2.5 equiv), chlorobenzene (1 mL), 65 °C, 16 h.



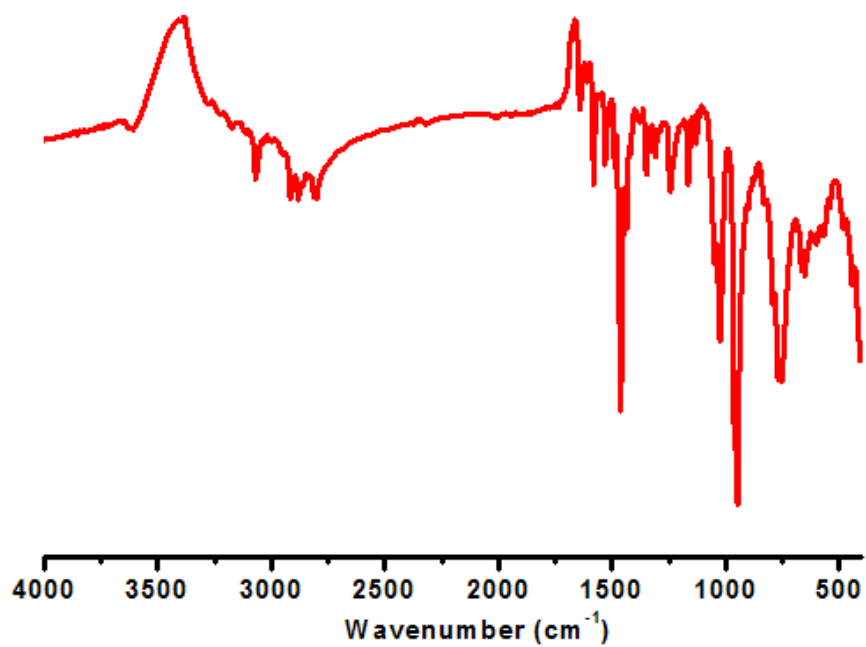
Compound 1



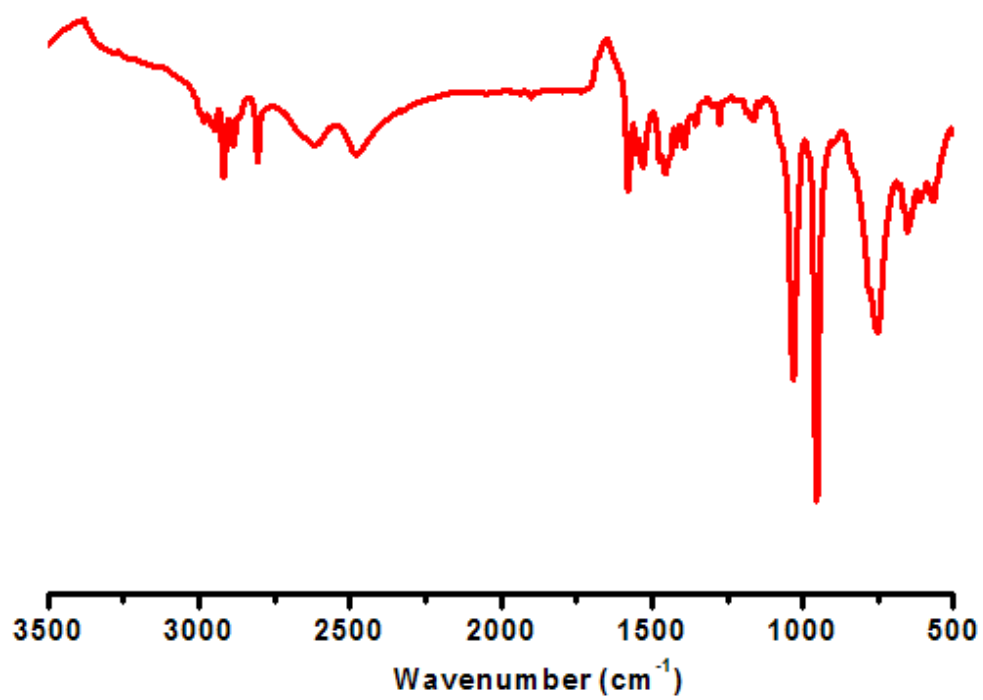
Compound 2



Compound 3

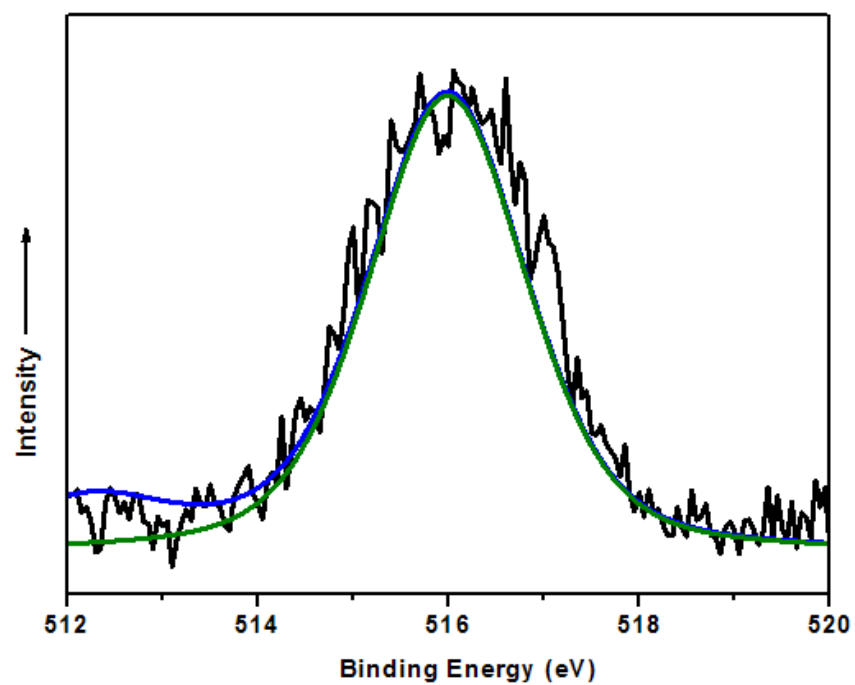


Compound 4

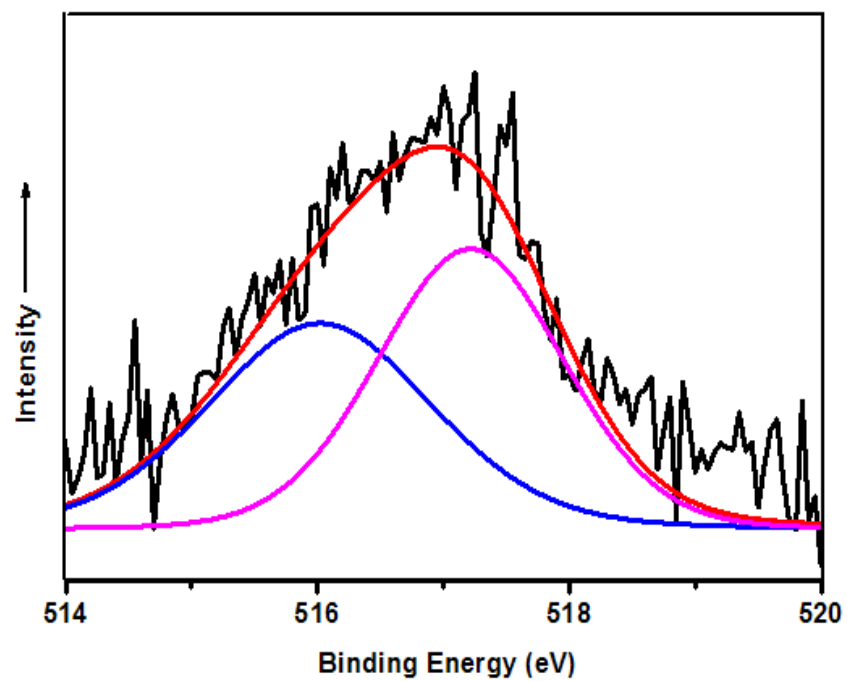


Compound 5

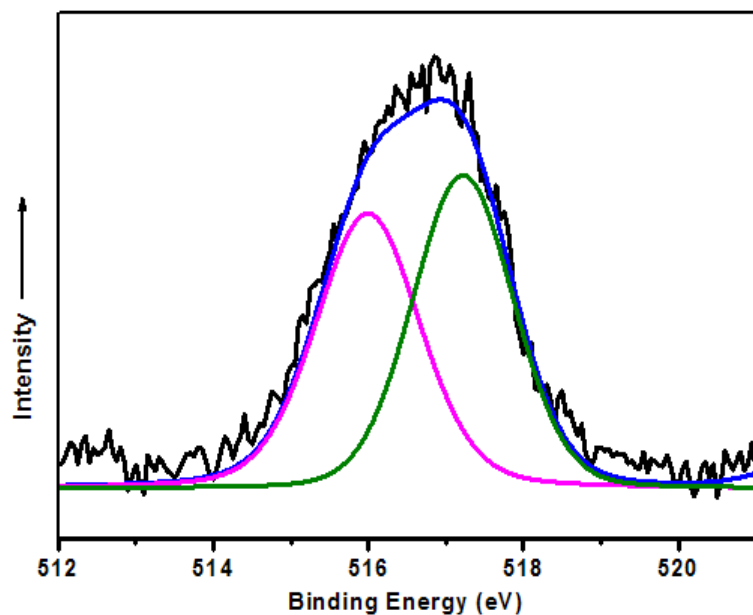
Figure S1. The FT-IR spectra of compounds 1–5.



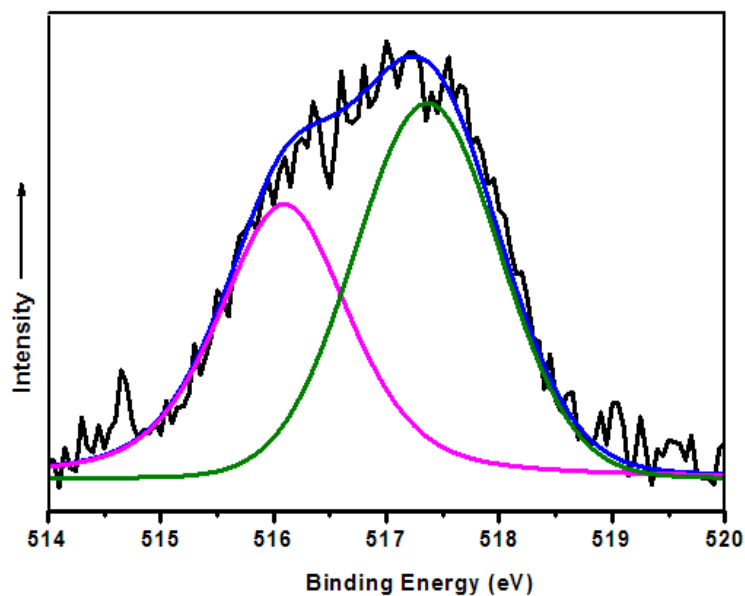
Compound 1



Compound 2

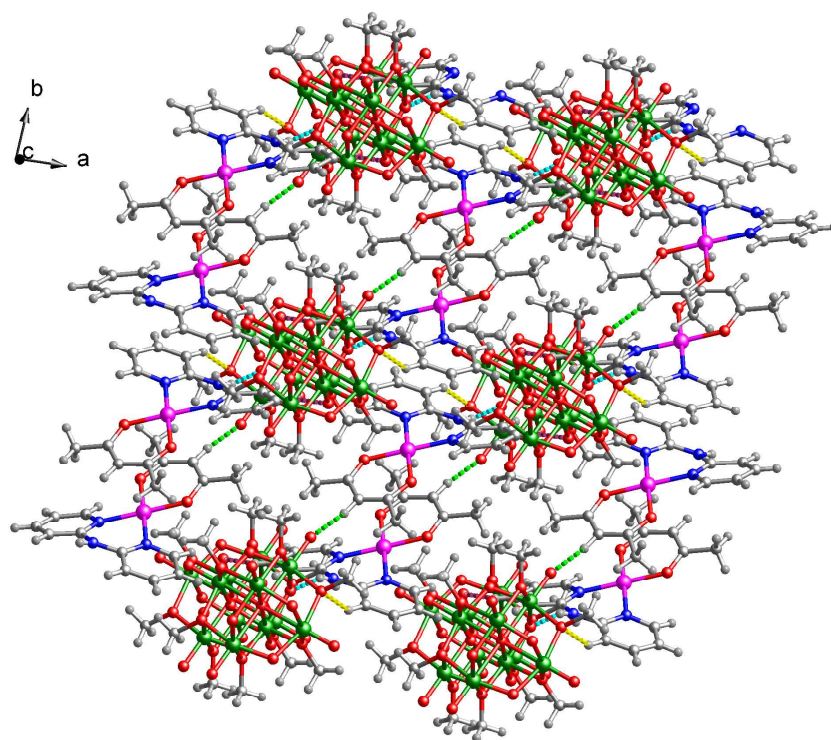


Compound 3

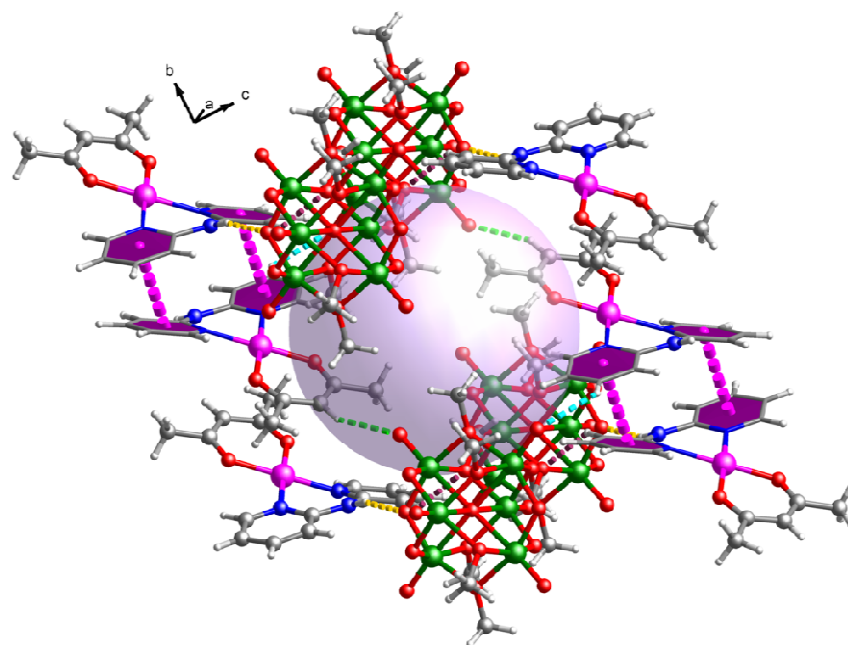


Compound 4

Figure S2. The XPS spectra for V in compounds **1-4**. The single peak with binding energies of 516.2 eV matches the value of $V^{5+} 2p_{3/2}$ for **1**; The two peaks with binding energies of 517.4, 516eV (**2**); 517.5, 516.1eV (**3**) and 517.6, 516.2eV (**4**) just match the values of $V^{5+} 2p_{3/2}$ and $V^{4+} 2p_{3/2}$, respectively.



(a)



(b)

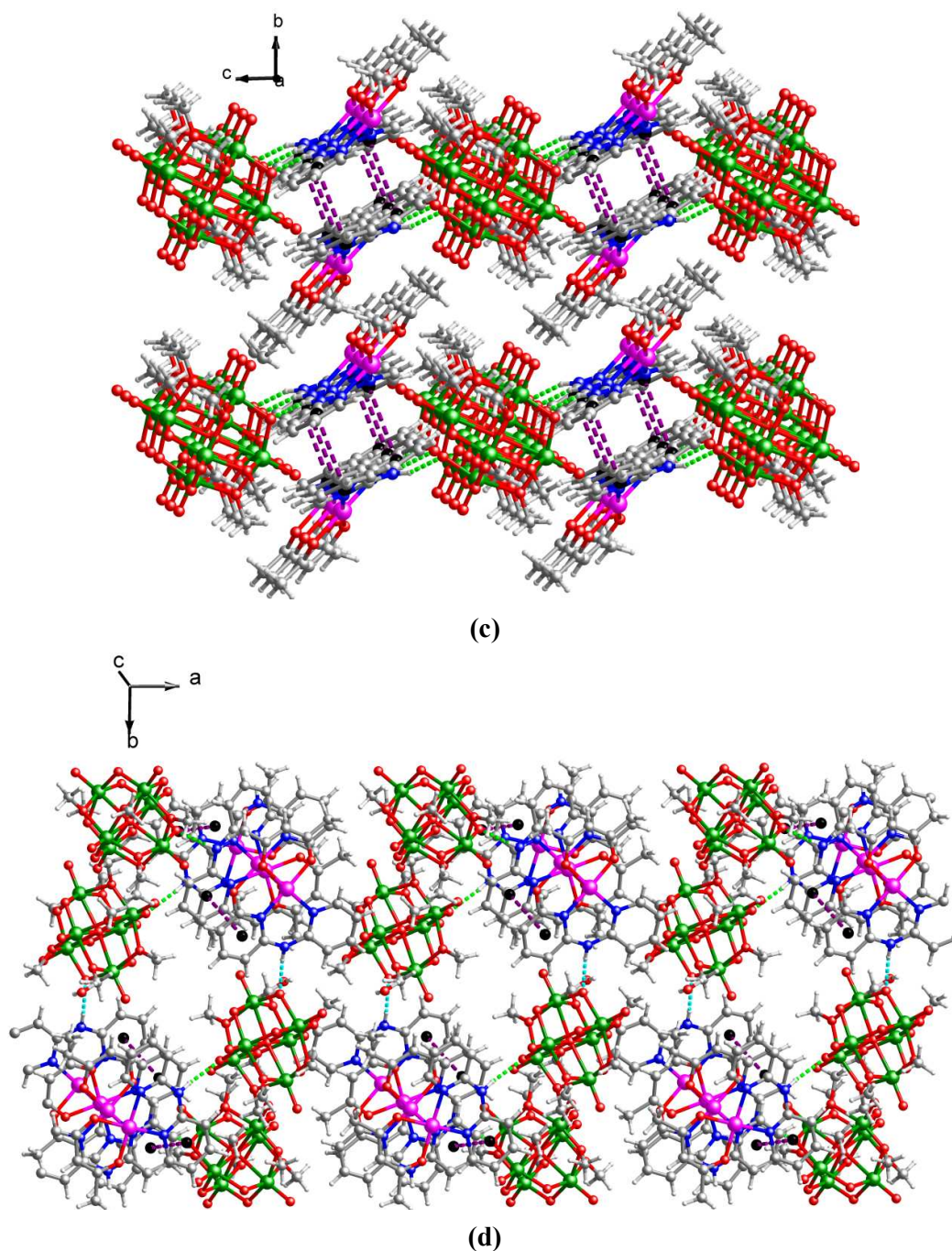
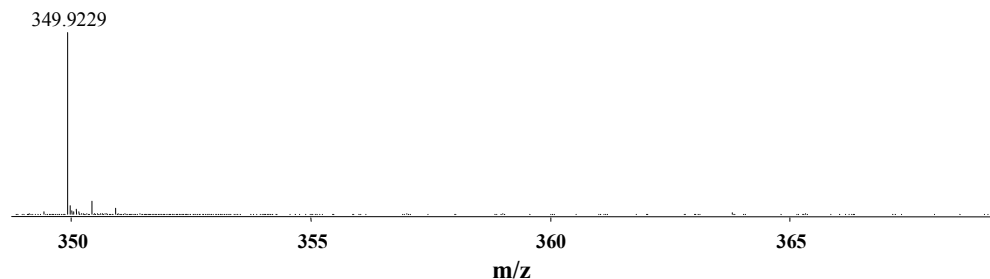
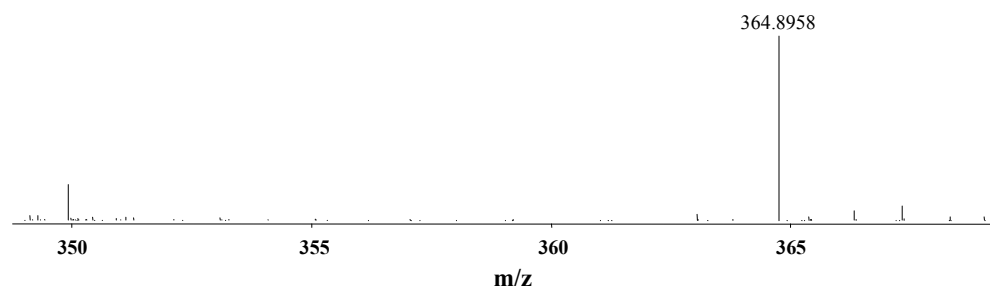


Figure S3. The 3D supramolecular structure of **1** (a). The hydrogen bondings and $\pi \cdots \pi$ interactions in **1** (b) and the 3D supramolecular structure of **2** (c) and **3** (d) formed by hydrogen bondings and $\pi \cdots \pi$ interactions. The lattice water molecules in **3** were omitted for clarity.



(a)



(b)

Figure S4. The negative ion mass spectra of $[\text{Pd}(\text{dpa})(\text{acac})]_2[\text{V}_6\text{O}_{13}(\text{OMe})_6]$ **1** (a) and $[\text{Pd}(\text{dpa})(\text{acac})]_2[\text{V}_6\text{O}_{11}(\text{OMe})_8]$ **2** (b). For the observed main peaks, $m/z = 349.92$ in **1** and $m/z = 364.89$ in **2** could be assigned to $[\text{V}_6\text{O}_{13}(\text{OMe})_6]^{2-}$ and $[\text{V}_6\text{O}_{11}(\text{OMe})_8]^{2-}$, respectively, which are consistent with the polyanions determined by single crystal X-ray diffraction.

Mass spectra were recorded on an Agilent 6520 Q-TOF LC/MS in the negative ion mode. The dual-spray electrospray ionization source condition was as follows: V_{cap} : 3500 V; skimmer: 65 V; OCT R_fV : 750 V; drying and nebulizer gas: N_2 ; nebulizer: 30 psi; drying gas flow: 10 L/min; drying gas temperature: 300 °C; fragmentator: 80 V; scan range 100-3000 m/z . The sample solutions were made to approximately 10^{-3} M in a mixture of DMF and MeCN with the volume ratio of 1:10 and analyzed by direct injection using an automatic sampler with a flow rate of 0.2 mL/min. Data were accumulated for 500 ms per spectrum.

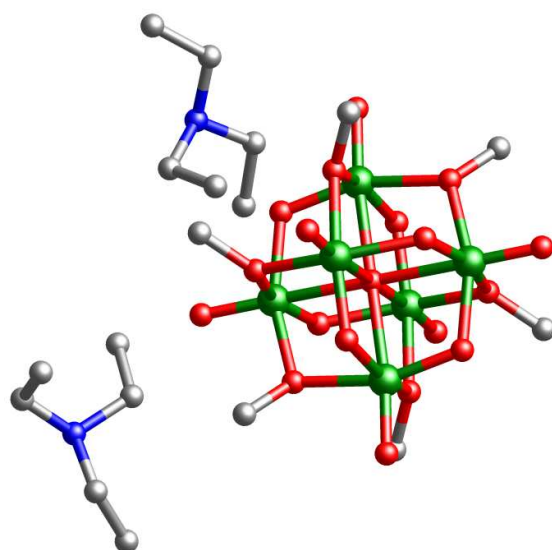


Figure S5. Molecular structure of compound 5.

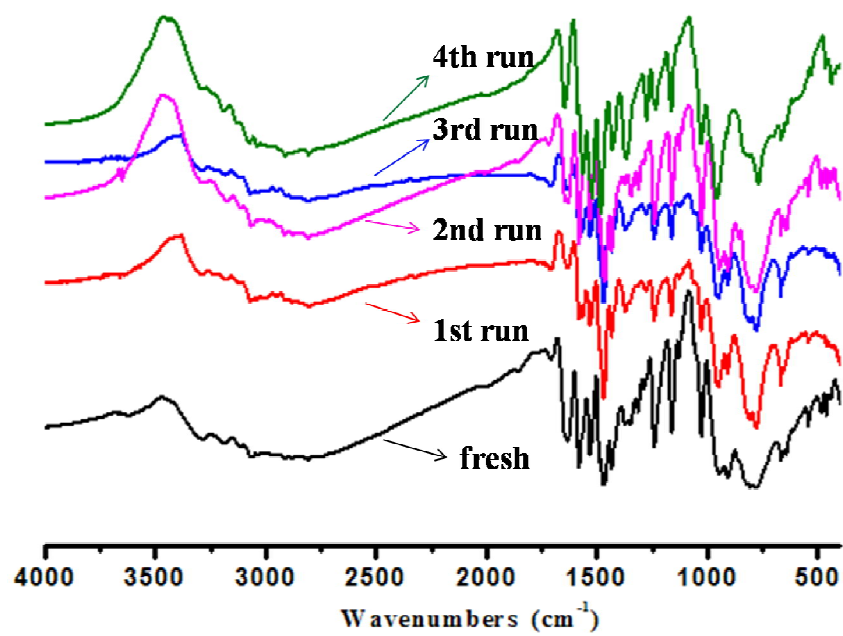


Figure S6. The FT-IR spectra of compound 1 after each catalytic cycle.

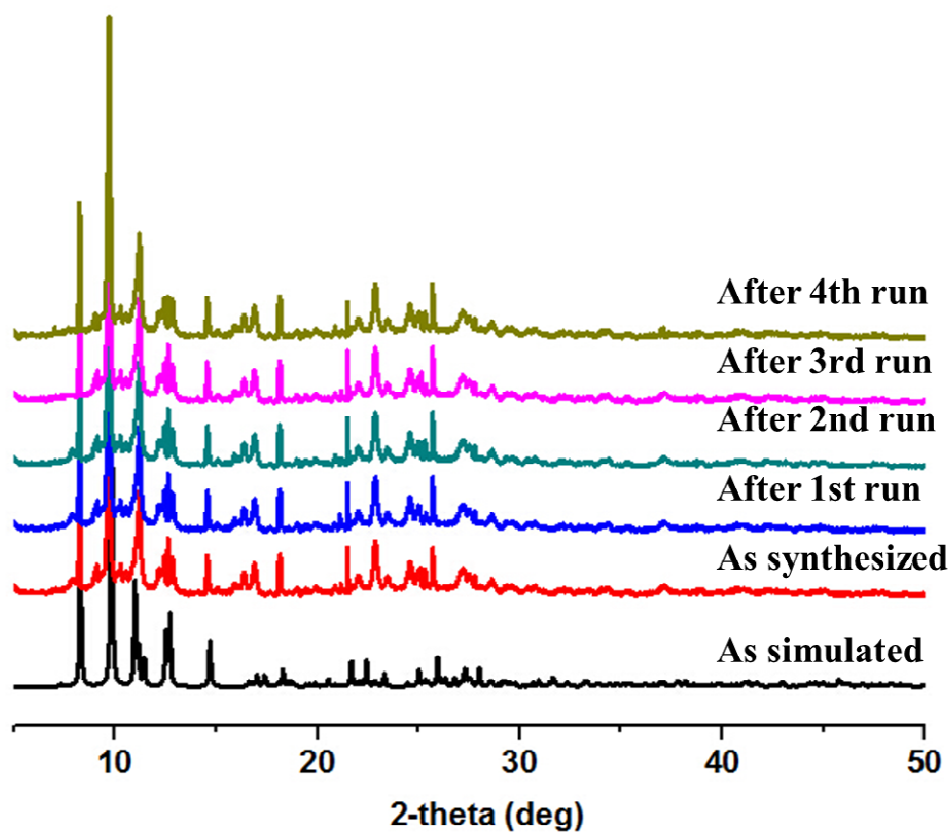


Figure S7. The simulated and experimental PXRD pattern of recovered compound 1.

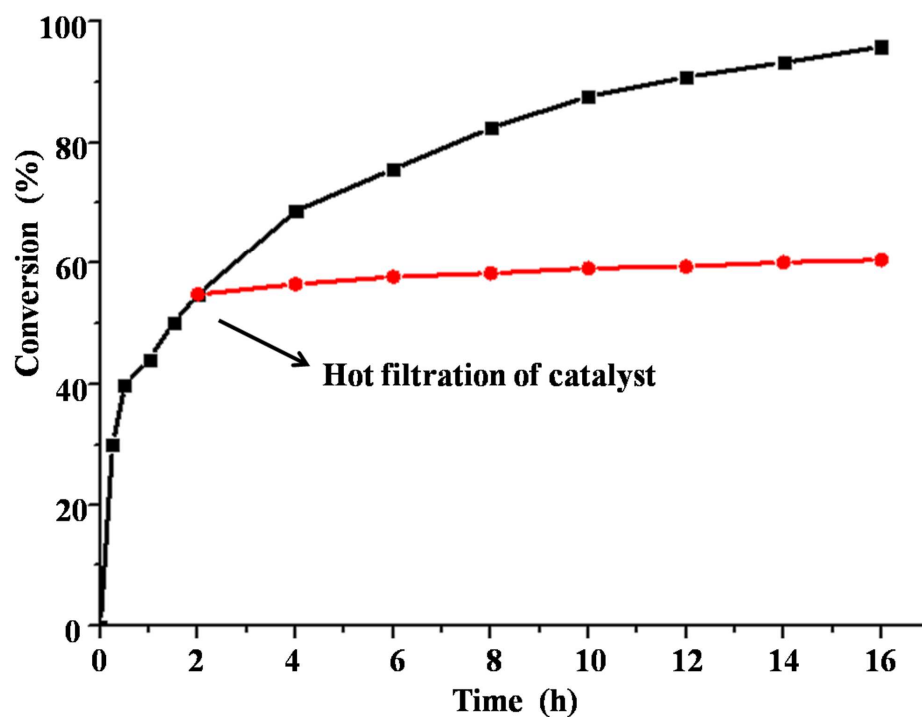
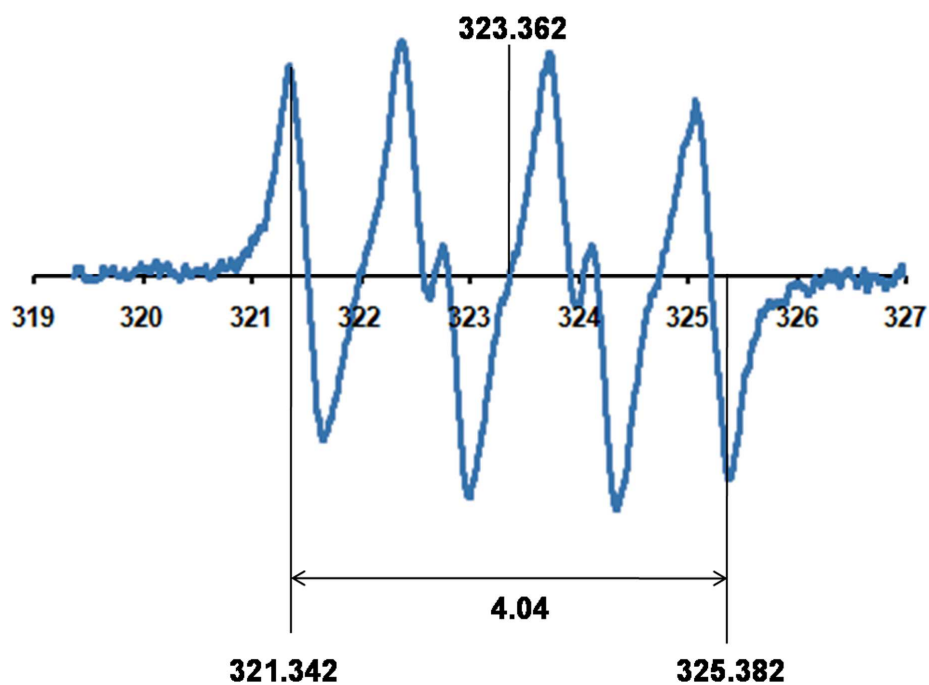


Figure S8. Kinetics of diphenylmethane oxidation using hot filtration technique: (black) with catalyst **1**, (red) catalyst filtration off after 2 h reaction. Reaction conditions: diphenylmethane (0.25 mmol, 1 equiv), catalyst (3.75 μ mol, 1.5 mol %), TBHP (2.5 equiv), chlorobenzene (1 mL), 65 $^{\circ}$ C, 16h.

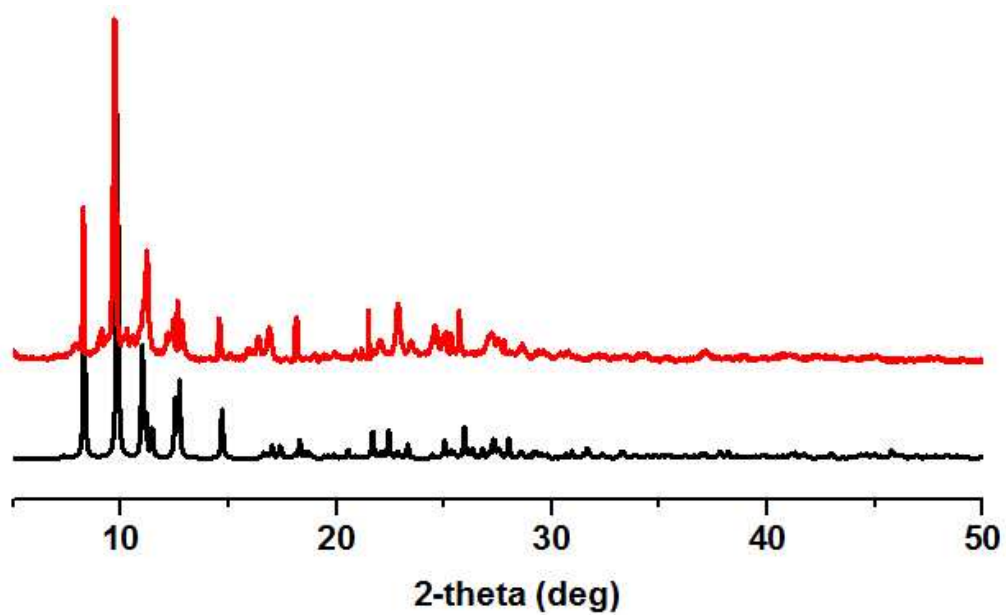
S9. Atomic absorption analysis of product solution after four catalytic cycles

The detection limit of the inductively coupled plasma (ICP) analyzer (ICP-6000) is 1 mg/L and analysis results of palladium and vanadium ions are both below the detection limit.

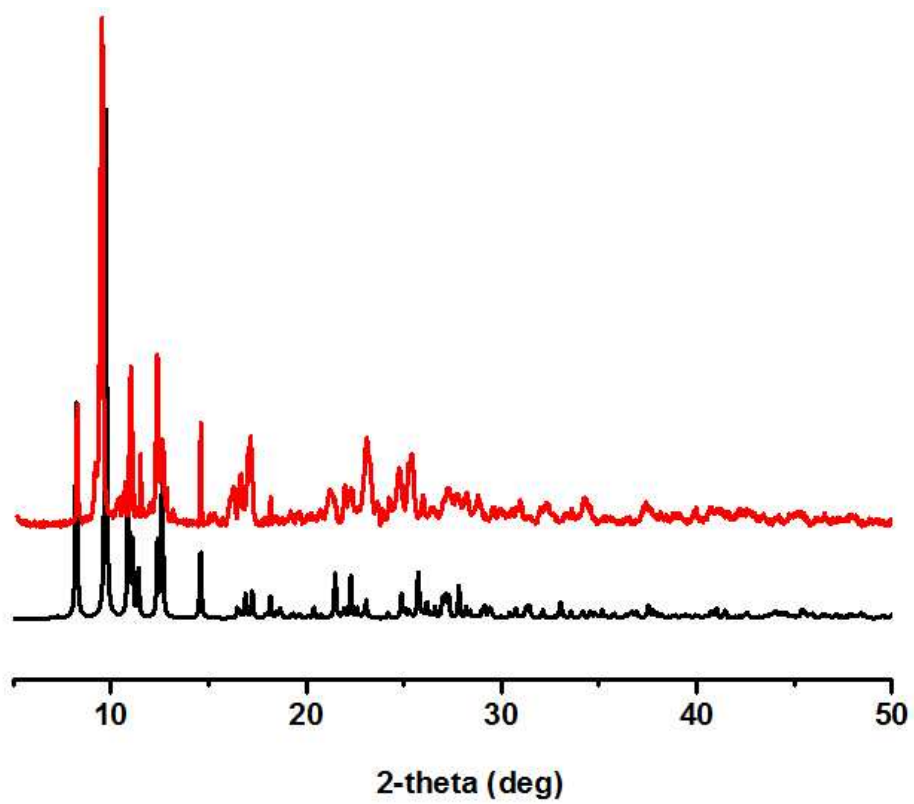


$$g = h\nu/\beta B = \frac{6.626 \times 10^{-26} \times 9.059 \times 10^9}{9.274 \times 10^{-21} \times 323.362 \times 10} = 2.0016$$

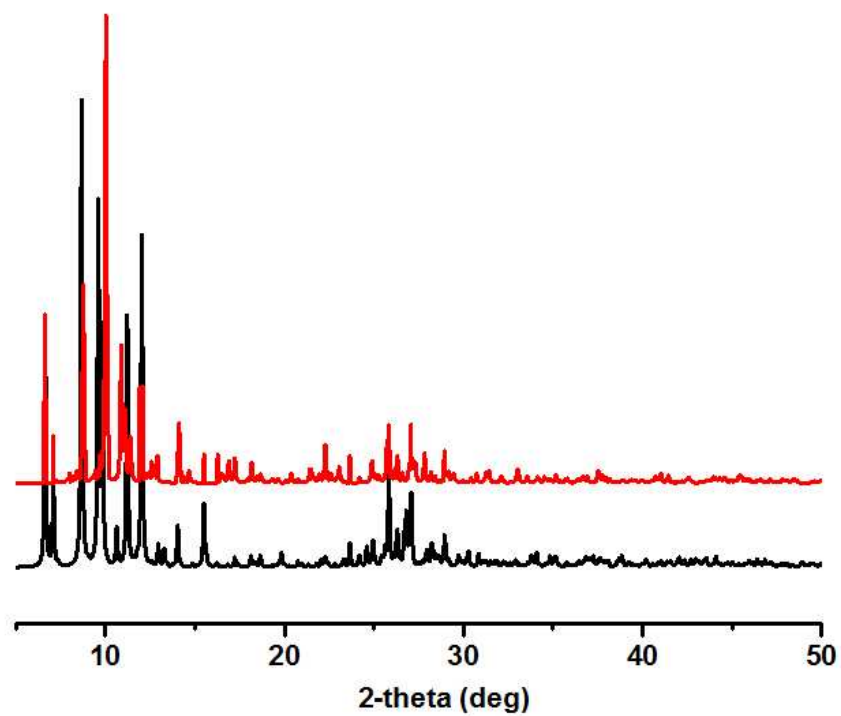
Figure S10. The analysis of EPR spectra of DMPO radical adducts in a Pd-POVs/TBHP system.



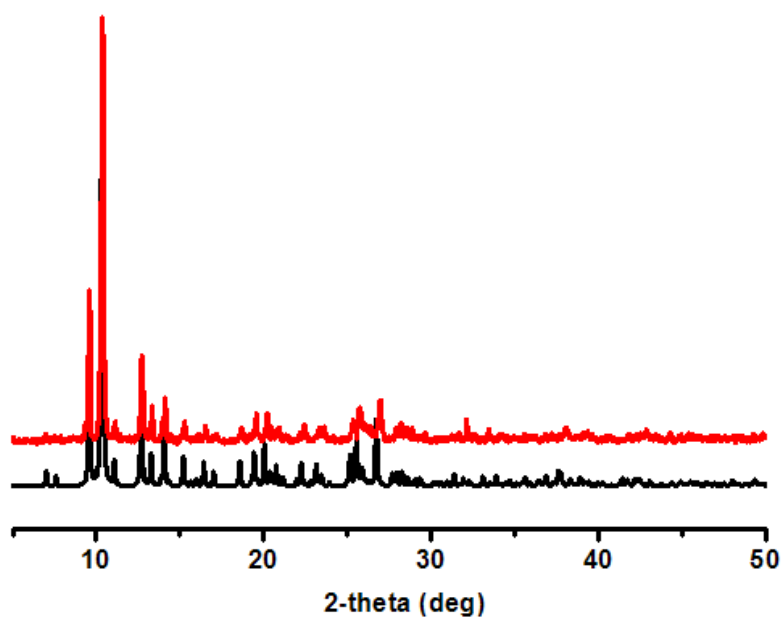
Compound 1



Compound 2



Compound 3



Compound 4

Figure S11. The simulated (black) and experimental (red) PXRD pattern of compounds 1-4. Simulation based on the SXRD data.

References:

- [1] (a) Bordwell, F. G.; Cheng, J. P.; Ji, G. Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790-9795. (b) Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031-5039.
- [2] Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 787-793.
- [3] Arends, I. W. C. E.; Mulder, P.; Clark, K. B.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 8182-8189.
- [4] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.