Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Three Pd-Decavanadates with Controllable Molar Ratio of Pd to Decavanadate and their Heterogeneous Aerobic Oxidation of Benzylic C-H Bonds

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

1	**V site**	V1	V2	V3	V4	V5
	BVS	4.96	5.02	4.96	4.97	4.99
	assigned O.S.	5	5	5	5	5
2	**V site**	V1	V2	V3	V4	V5
	BVS	4.73	4.91	4.80	4.77	4.91
	assigned O.S.	5	5	5	5	5
3	**V site**	V1	V2	V3	V4	V5
	BVS	5.09	5.14	5.11	5.09	5.10
	assigned O.S.	5	5	5	5	5
4	**V site**	V1	V2	V3	V4	V5
	BVS	5.03	5.08	4.89	5.07	4.98
	assigned O.S.	5	5	5	5	5
	V site	V6	V7	V8	V9	V10
	BVS	5.00	4.99	5.04	5.08	5.09
	assigned O.S.	5	5	5	5	5

[a] The calculations were performed twice for each individual vanadium atom using bond-valence parameters presented by Brese and O'Keeffe[1]. 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 [º] for compounds **1–4**.

Compound **1**

Pd(1)-N(4)	2.038(4)	Pd(1)-N(3)	2.035(4)
Pd(1)-N(1)	2.043(4)	Pd(2)-N(6)#1	2.044(4)
Pd(2)-N(6)	2.044(4)	Pd(2)-N(5)#1	2.046(4)
Pd(2)-N(5)	2.046(4)	Pd(1)-N(2)	2.046(4)
V(1)-O(5)	1.939(3)	V(1)-O(3)	2.124(3)
V(2)-O(9)	1.603(3)	V(3)-O(10)	1.807(3)
V(2)-O(8)	1.845(3)	V(3)-O(6)	1.830(3)
V(2)-O(6)	1.877(3)	V(3)-O(2)	2.024(3)
V(2)-O(7)	1.878(3)	V(4)-O(13)	1.625(3)
V(2)-O(1)	2.046(3)	V(4)-O(12)	1.820(3)
V(3)-O(11)	1.629(3)	V(4)-O(2)	2.016(3)
V(4)-O(3)	2.233(3)	V(5)-O(4)	2.057(3)
V(5)-O(14)	1.608(3)	V(5)-O(3)	2.311(3)
V(5)-O(12)	1.884(3)	N(4)-Pd(1)-N(3)	90.81(15)
N(4)-Pd(1)-N(1)	89.06(15)	N(1)-Pd(1)-N(2)	90.49(16)
N(3)-Pd(1)-N(1)	179.70(15)	N(6)#1-Pd(2)-N(6)	180.0(2)
N(4)-Pd(1)-N(2)	179.07(16)	N(6)#1-Pd(2)-N(5)#1	89.46(17)
N(3)-Pd(1)-N(2)	89.64(16)	N(6)-Pd(2)-N(5)#1	90.51(17)
N(5)#1-Pd(2)-N(5)	180.0(2)	N(6)#1-Pd(2)-N(5)	90.51(17)
N(6)-Pd(2)-N(5)	89.49(17)	O(4)-V(1)-O(1)	106.08(14)
O(4)-V(1)-O(5)	96.43(13)	O(4)-V(1)-O(2)	97.96(13)
O(1)-V(1)-O(5)	96.50(13)	O(1)-V(1)-O(2)	98.20(13)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z #2 -x+2,-y+1,-z

Compound **2**

Pd(1)-N(2)	2.034(9)	V(1)-O(4)	1.701(6)
Pd(1)-N(3)	2.045(9)	V(1)-O(2)	1.716(7)
Pd(1)-N(1)	2.052(8)	V(1)-O(1)	1.921(5)
Pd(1)-O(15)	2.082(9)	V(1)-O(3)	1.964(6)
V(1)-O(14)	2.095(6)	V(2)-O(8)	1.939(6)
V(1)-O(14)#1	2.153(5)	V(2)-O(2)	2.040(6)
V(2)-O(6)	1.618(8)	V(2)-O(14)#1	2.351(6)
V(2)-O(7)	1.858(6)	V(2)-V(5)#1	3.097(3)
V(2)-O(5)	1.873(6)	V(3)-O(10)	1.618(6)
N(2)-Pd(1)-N(3)	85.5(4)	O(4)-V(1)-O(2)	107.3(3)
N(2)-Pd(1)-N(1)	84.2(3)	O(4)-V(1)-O(1)	99.2(3)
N(3)-Pd(1)-N(1)	169.5(4)	O(2)-V(1)-O(1)	97.3(3)
N(2)-Pd(1)-O(15)	176.7(3)	O(4)-V(1)-O(3)	95.5(2)
N(3)-Pd(1)-O(15)	95.3(4)	O(2)-V(1)-O(3)	95.8(3)
N(1)-Pd(1)-O(15)	94.8(3)	O(1)-V(1)-O(3)	156.4(3)
O(1)-V(1)-O(14)	81.6(2)	O(4)-V(1)-O(14)	87.8(3)

O(3)-V(1)-O(14)	80.6(3)	O(2)-V(1)-O(14)	164.8(3)
O(2)-V(1)-O(14)#1	86.3(3)	O(3)-V(1)-O(14)#1	80.4(2)
O(4)-V(1)-O(14)#1	166.2(3)	O(1)-V(1)-O(14)#1	81.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1

Compound **3**

Pd(1)-N(3)	2.017(5)	V(1)-O(5)	1.781(4)
Pd(1)-N(3)#1	2.017(5)	V(1)-O(4)	1.822(4)
Pd(1)-N(2)	2.021(5)	V(1)-O(2)	2.007(4)
Pd(1)-N(2)#1	2.021(5)	V(1)-O(8)#2	2.075(4)
V(1)-O(3)	1.600(4)	V(2)-O(13)#2	1.830(5)
V(1)-O(1)#2	2.251(4)	V(2)-O(5)	1.923(4)
V(2)-O(6)	1.602(5)	V(2)-O(7)	2.030(4)
V(2)-O(10)#2	1.813(4)	V(2)-O(1)#2	2.338(4)
V(3)-O(7)	1.677(4)	V(4)-O(9)	1.601(4)
V(3)-O(11)	1.684(4)	V(4)-O(12)	1.747(4)
V(3)-O(2)	1.859(4)	V(4)-O(10)	1.850(4)
V(3)-O(8)	2.038(4)	V(4)-O(2)	1.983(4)
V(3)-O(1)	2.082(4)	V(4)-O(8)#2	2.095(4)
V(3)-O(1)#2	2.086(4)	V(4)-O(1)	2.281(4)
V(5)-O(14)	1.592(5)	V(5)-O(12)	1.920(4)
V(5)-O(13)	1.823(5)	V(5)-O(11)	2.059(4)
V(5)-O(4)#2	1.838(4)	V(5)-O(1)	2.348(4)
N(3)-Pd(1)-N(3)#1	180.0(3)	N(2)-Pd(1)-N(2)#1	180.0(3)
N(3)-Pd(1)-N(2)	94.4(2)	O(3)-V(1)-O(5)	104.8(2)
N(3)#1-Pd(1)-N(2)	85.6(2)	O(3)-V(1)-O(4)	102.3(2)
N(3)-Pd(1)-N(2)#1	85.6(2)	O(5)-V(1)-O(4)	96.8(2)
N(3)#1-Pd(1)-N(2)#1	94.4(2)	O(3)-V(1)-O(2)	99.5(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z #2 -x,-y,-z+1

Compound **4**

V(1)-O(23)	1.682(6)	V(4)-O(2)	1.625(6)
V(1)-O(10)	1.711(6)	V(4)-O(9)	1.771(6)
V(1)-O(13)	1.819(6)	V(4)-O(27)	1.824(6)
V(2)-O(15)	1.652(6)	V(5)-O(1)	1.610(6)
V(2)-O(24)	1.706(6)	V(5)-O(25)	1.750(6)
V(2)-O(8)	1.903(6)	V(5)-O(17)	1.919(6)
V(2)-O(21)	2.161(6)	V(5)-O(21)	2.249(5)
V(3)-O(3)	1.618(6)	V(6)-O(6)	1.610(6)
V(3)-O(12)	1.796(6)	V(6)-O(26)	1.796(7)
V(3)-O(5)	1.905(6)	V(6)-O(14)	1.813(6)
V(3)-O(8)	1.960(6)	V(6)-O(8)	2.017(6)
V(8)-O(11)	1.829(7)	V(7)-O(18)	1.625(6)
V(8)-O(14)	1.845(6)	V(7)-O(5)	1.785(6)
V(8)-O(9)	1.892(6)	V(7)-O(20)	1.838(6)
V(8)-O(15)	2.055(6)	V(7)-O(4)	2.009(6)
V(8)-O(22)	2.393(6)	V(8)-O(16)	1.598(6)
V(9)-O(19)	1.601(6)	V(10)-O(11)	1.802(6)
V(9)-O(20)	1.825(6)	V(10)-O(27)	1.867(6)
V(9)-O(12)	1.846(6)	V(10)-O(26)	1.888(6)
V(9)-O(25)	1.936(6)	V(10)-O(23)	2.074(6)
V(10)-O(28)	1.600(6)	V(10)-O(22)	2.325(6)
O(23)-V(1)-O(10)	106.1(3)	O(15)-V(2)-O(24)	109.0(3)
O(23)-V(1)-O(13)	100.5(3)	O(15)-V(2)-O(8)	97.9(3)
O(10)-V(1)-O(13)	100.0(3)	O(24)-V(2)-O(8)	96.6(3)
O(23)-V(1)-O(22)	87.4(3)	O(15)-V(2)-O(17)	97.0(3)
O(3)-V(3)-O(12)	103.1(3)	O(2)-V(4)-O(9)	104.6(3)
O(3)-V(3)-O(5)	101.6(3)	O(2)-V(4)-O(27)	102.6(3)
O(12)-V(3)-O(5)	92.3(3)	O(9)-V(4)-O(27)	96.2(3)
O(3)-V(3)-O(8)	102.6(3)	O(2)-V(4)-O(17)	101.0(3)
O(1)-V(5)-O(17)	102.6(3)	O(6)-V(6)-O(14)	103.5(3)
O(25)-V(5)-O(17)	97.0(3)	O(26)-V(6)-O(14)	95.3(3)
O(18)-V(7)-O(5)	104.0(3)	O(16)-V(8)-O(11)	104.5(3)
O(5)-V(7)-O(20)	94.5(3)	O(11)-V(8)-O(14)	92.0(3)
O(18)-V(7)-O(4)	96.7(3)	O(16)-V(8)-O(9)	102.4(3)
O(19)-V(9)-O(12)	102.8(3)	O(28)-V(10)-O(27)	102.5(3)
O(20)-V(9)-O(12)	91.4(3)	O(11)-V(10)-O(27)	91.4(3)
O(19)-V(9)-O(25)	100.5(3)	O(28)-V(10)-O(26)	102.4(3)

Figure S1. The FT-IR spectra of compound **1**.

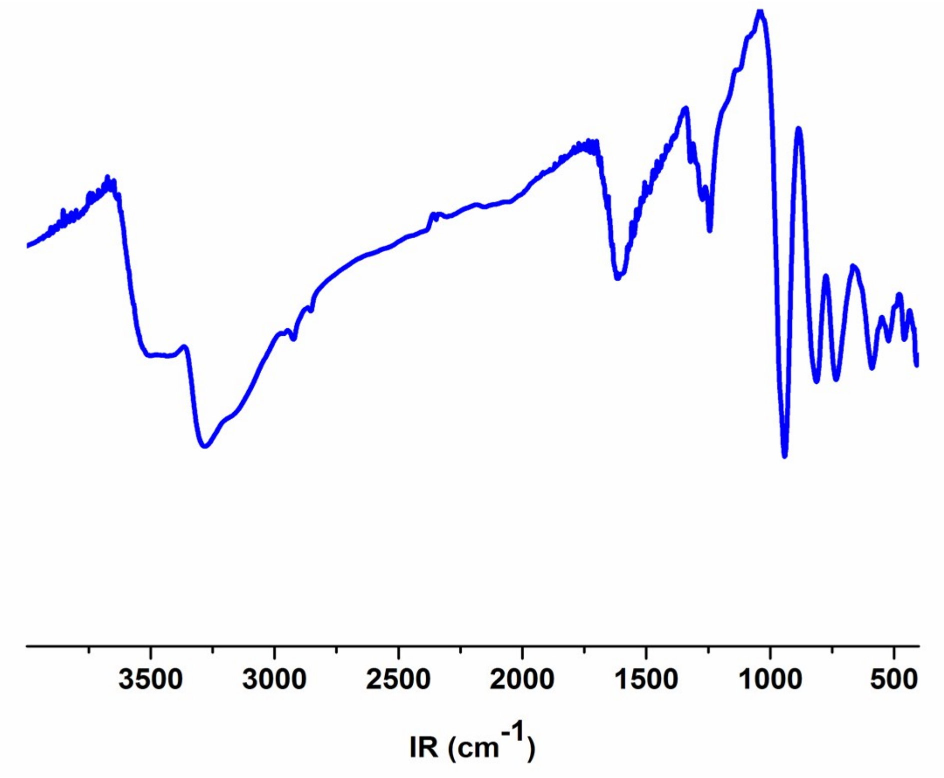


Figure S2. The FT-IR spectra of compound **2**.

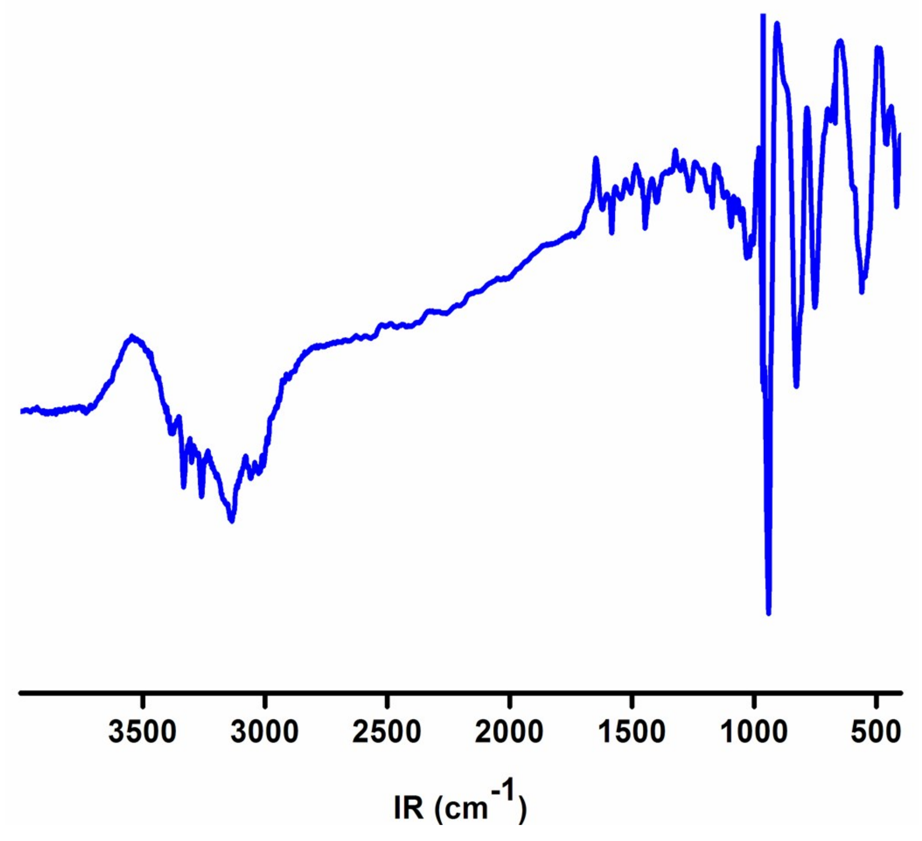


Figure S3. The FT-IR spectra of compound **3**.

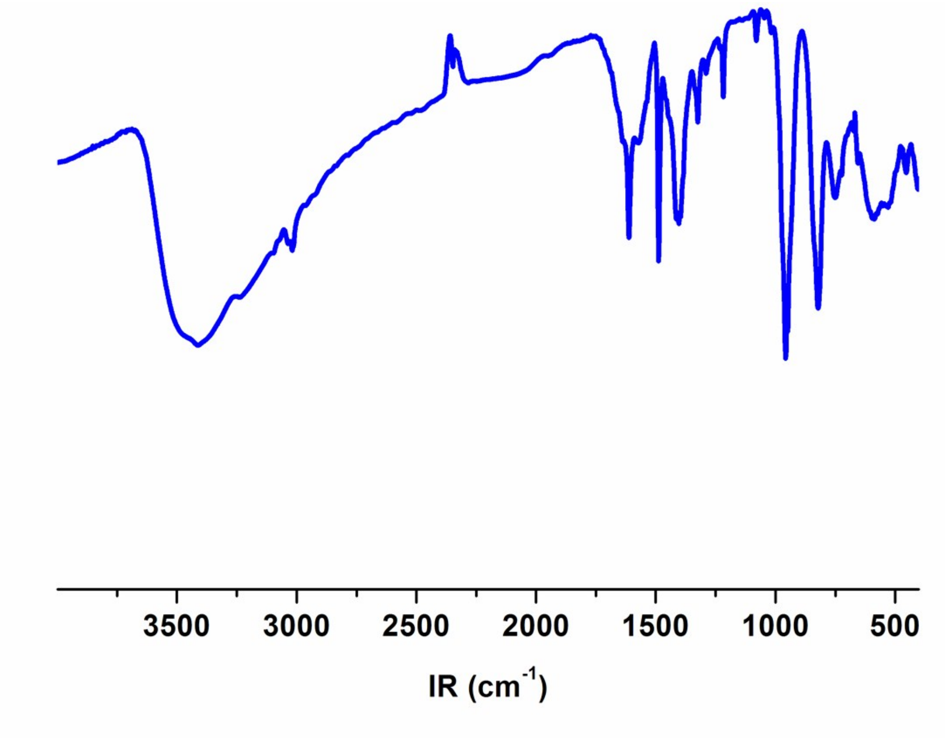


Figure S4. The FT-IR spectra of compound **4**.

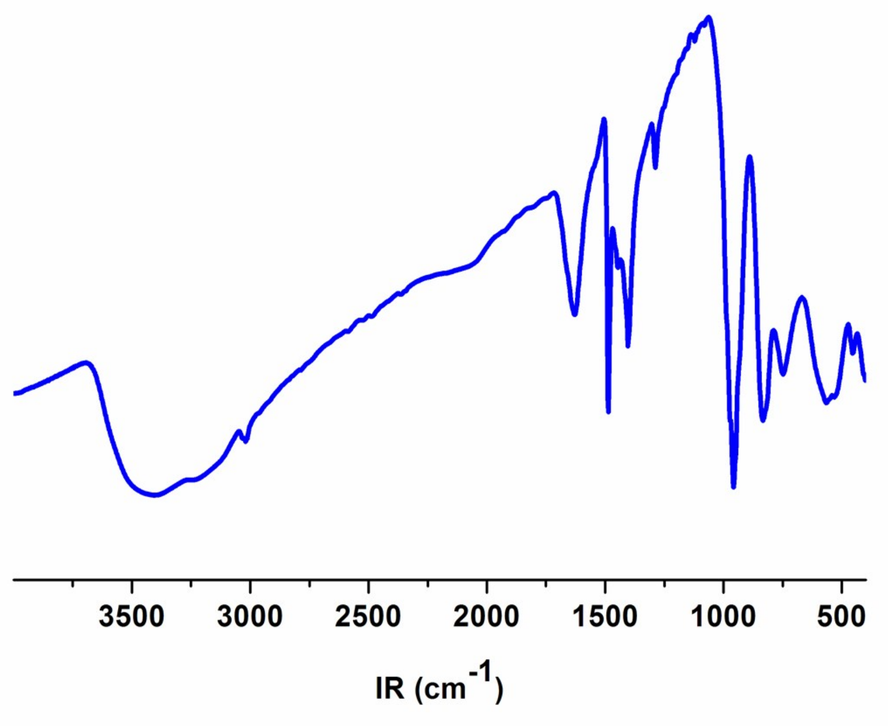


Figure S5. The simulated (black) and experimental (red) PXRD patterns of compound **1**. Simulation based on the SXRD data.

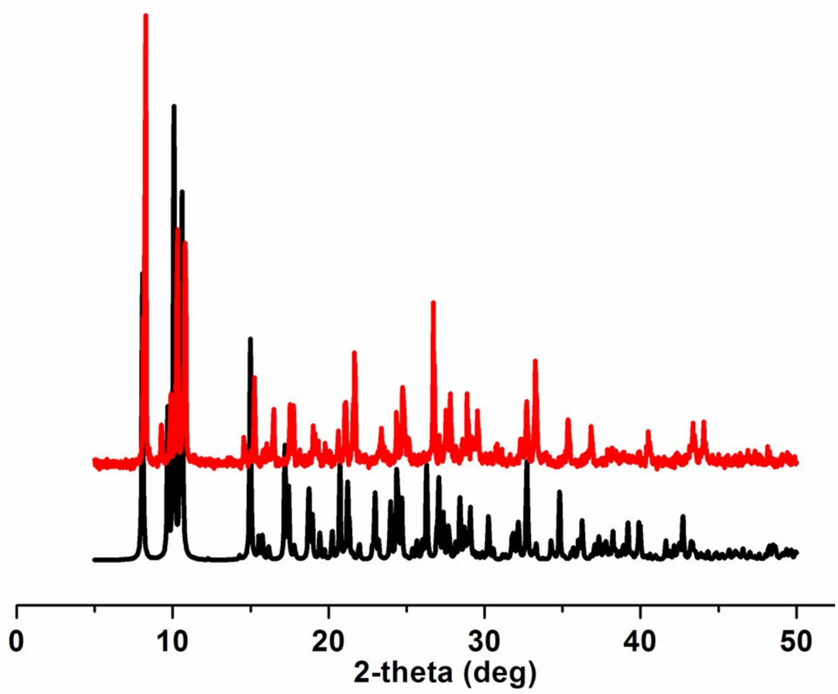


Figure S6. The simulated (black) and experimental (red) PXRD patterns of compound **2**. Simulation based on the SXRD data.

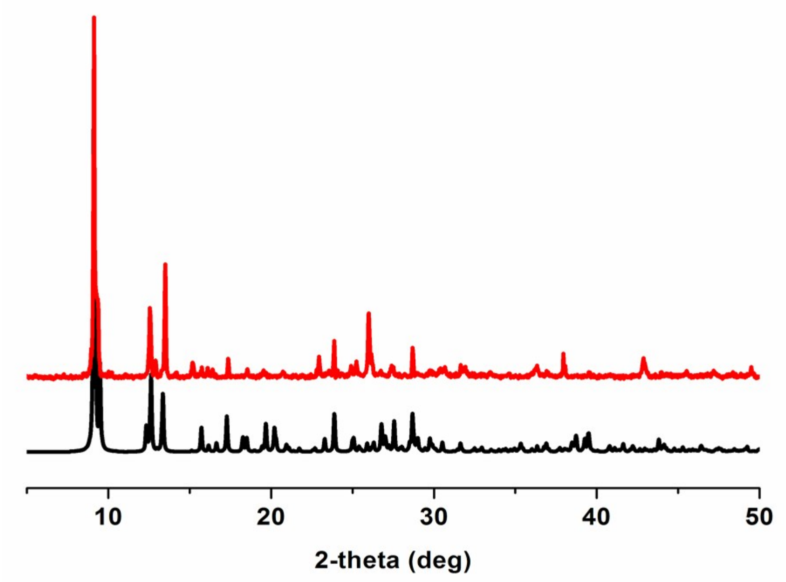


Figure S7. The simulated (black) and experimental (red) PXRD patterns of compound **3**. Simulation based on the SXRD data.

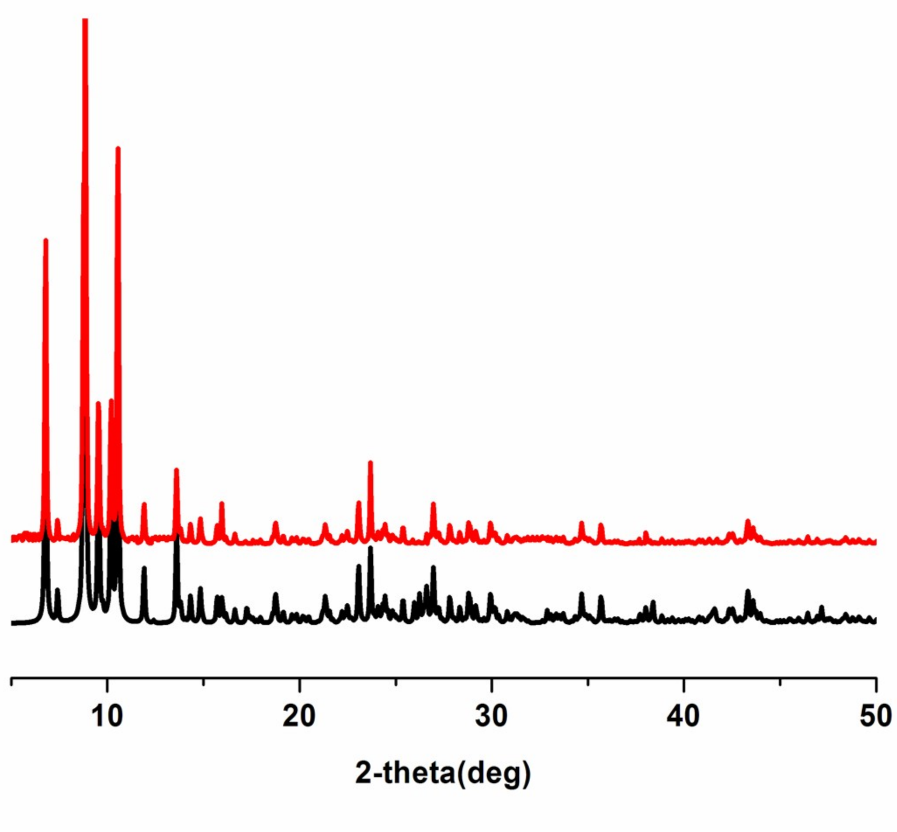


Figure S8. The simulated (black) and experimental (red) PXRD patterns of compound **4**. Simulation based on the SXRD data.

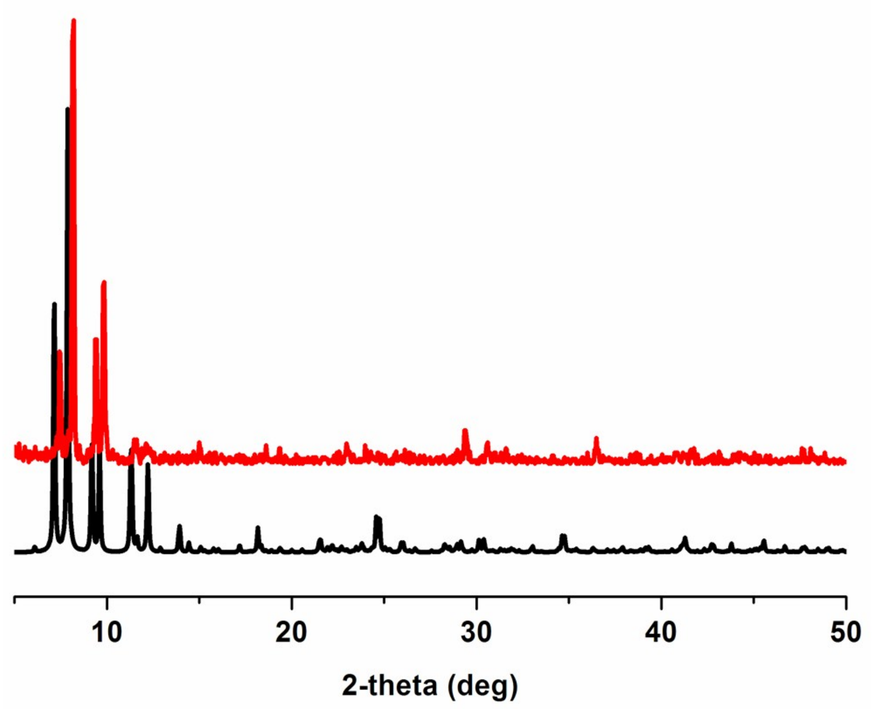


Figure S9. The color change in aerobic oxidation of diphenylmethane with different the amount of N-ligands and $Pd(OAc)_2$.

a) $Pd(OAc)_2$ b) $Pd(OAc)_2$ and NH_4Cl c) $Pd(OAc)_2$ and EDTA d) $Pd(OAc)_2$ and dpa

Figure S10. The powder XRD patterns of compound **1** after each cycle.

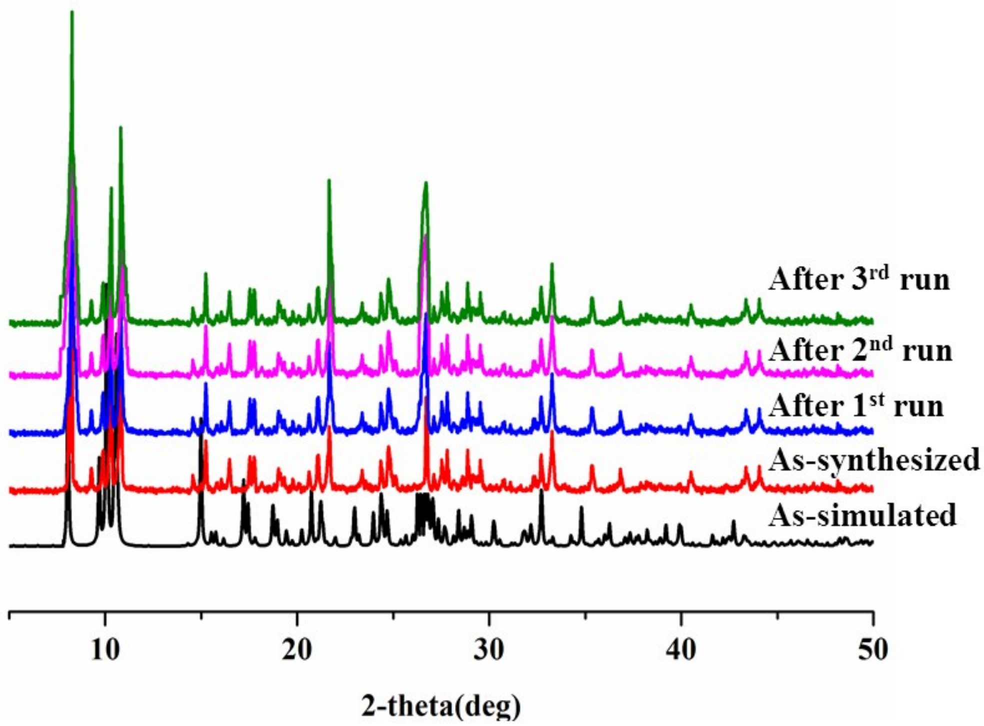


Figure S11. The relevance of turnover number (TON) of catalysts **1-4** and Pd atom number per decavanadates unit in the aerobic oxidation of diphenylmethane.

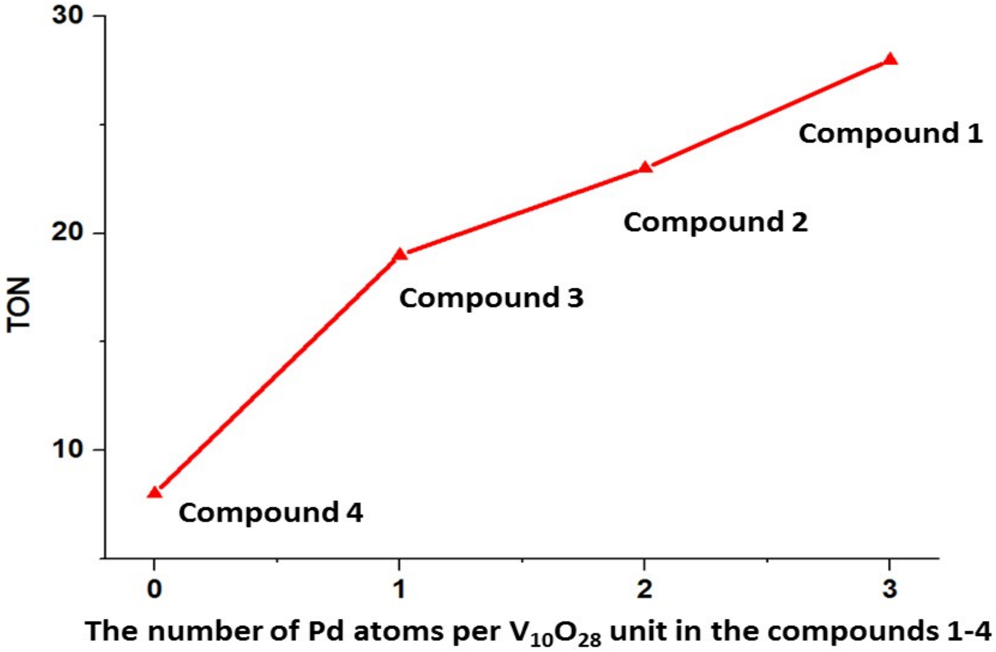


Figure S12. Conversion of diphenylmethane with different oxygen pessure. Reaction conditions: diphenylmethane (10 mmol), catalyst **1** (8 mol%), 90 ºC, O_2, 36 h.

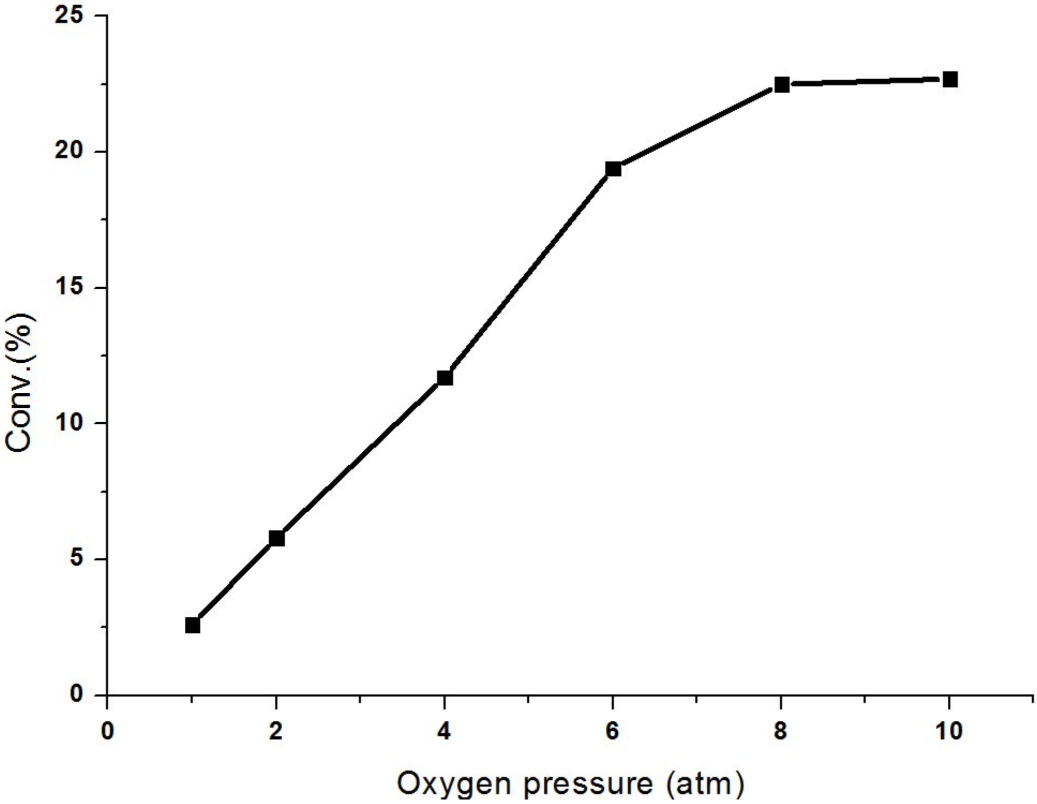


Figure S13. Conversion of diphenylmethane with different the amount of catalyst. Reaction conditions: diphenylmethane (10mmol), catalyst **1**, 90 ºC, O_2(8atm), 36 h.

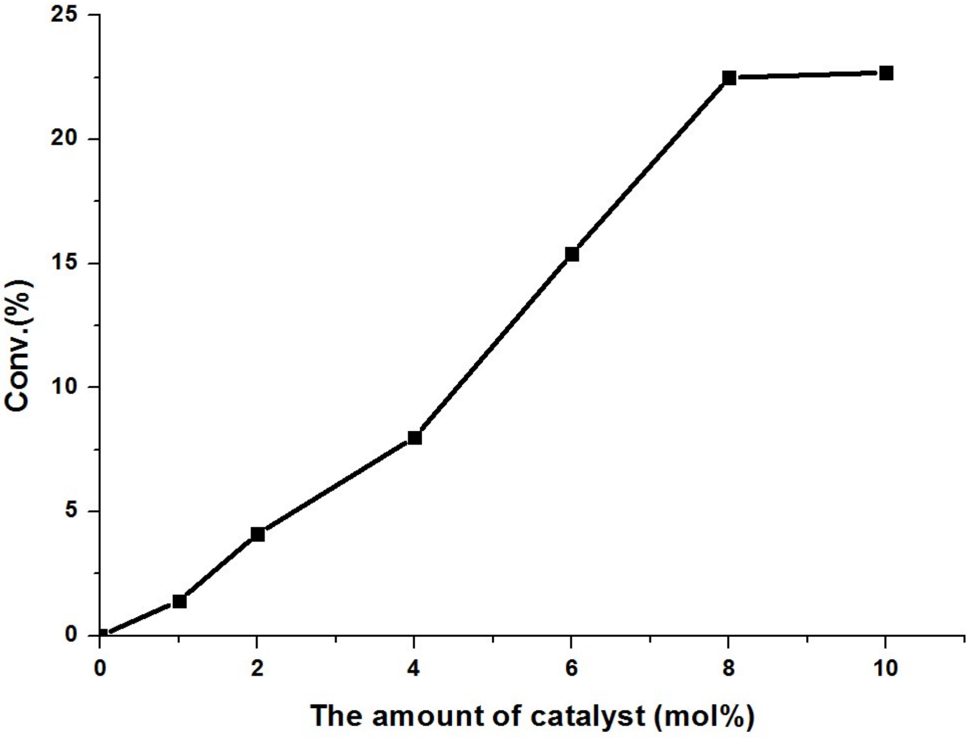
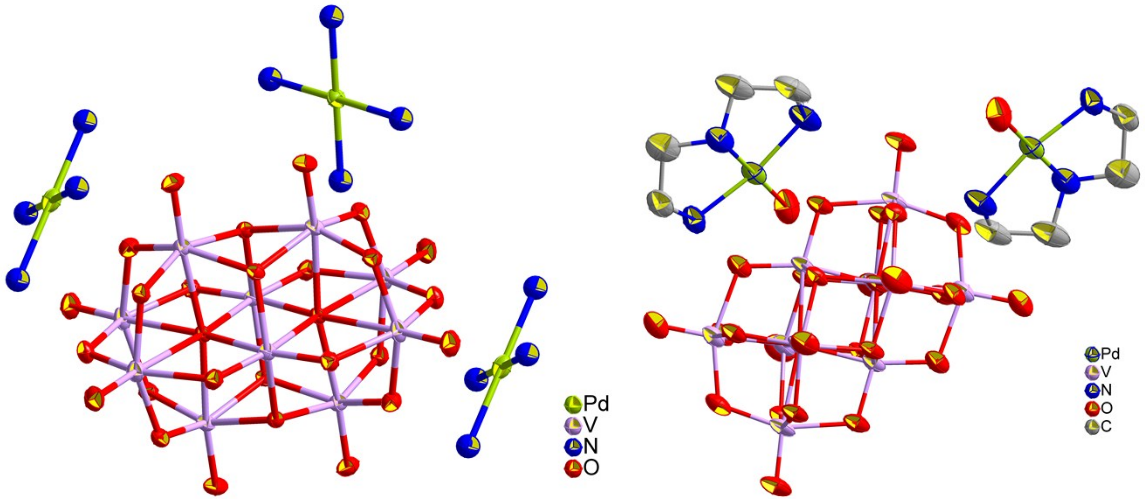
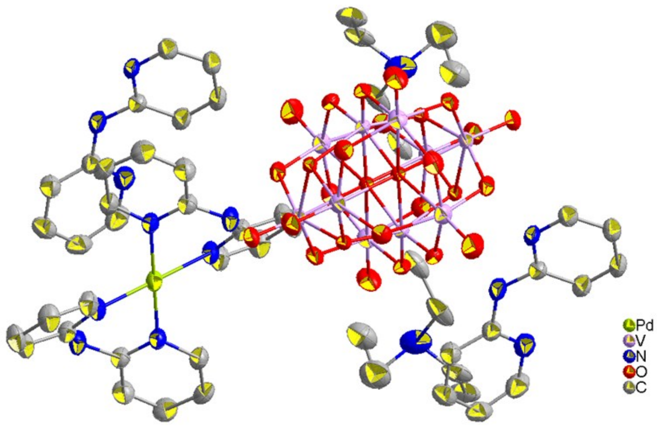


Figure S14. The crystal structures of compounds 1-4 with 50% ellipsoid. Color codes: Pd, lime; V, lavender; C, gray-40%; O, red; N, blue. All H atoms and lattice solvent molecules are omitted for clarity.

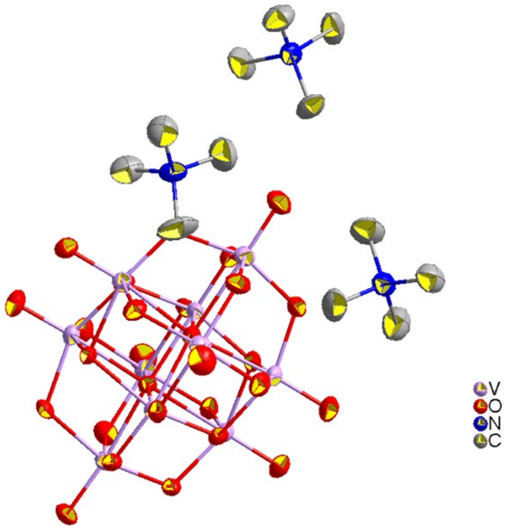


Compound 1

Compound 2

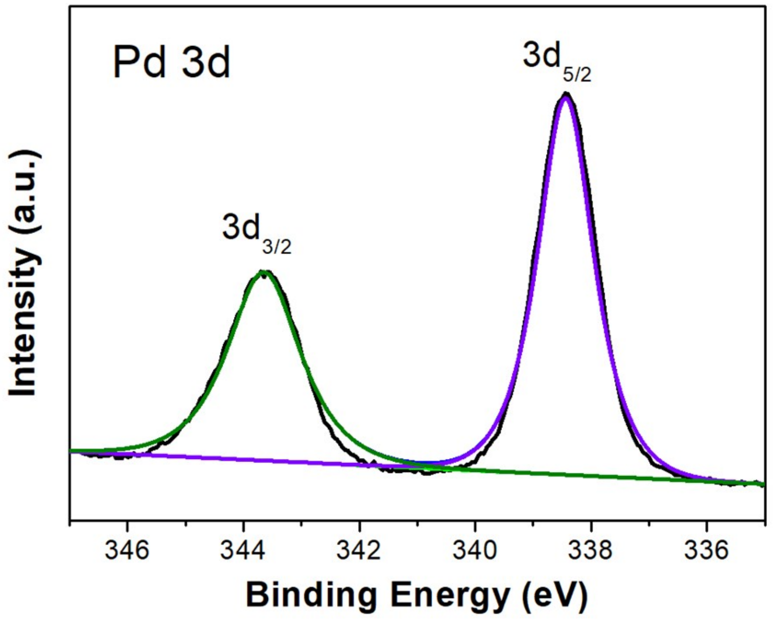


Compound 3



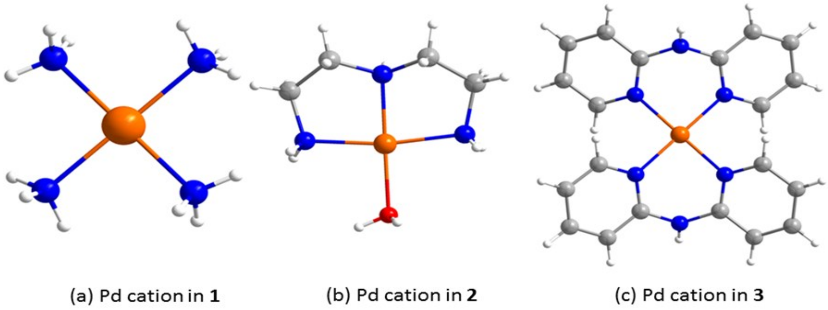
Compound 4

Figure S15. The XPS spectrum for Pd in compound 1



In order to further confirm the oxidation state of Pd, XPS of compound **1** were performed where the peaks at 343.6 eV and 338.4eV are attributed to $Pd_{3d3/2}$ and $Pd_{3d5/2}$, respectively. These results further confirm the valences of Pd [2].

Figure S16. The coordination mode of Pd centers in compounds **1-3**. Color codes: Pd, orange; C, gray-40%; O, red; N, blue, H, white.


(a) Pd cation in **1**
(b) Pd cation in **2**
(c) Pd cation in **3**

Reference:

[1] N. E. Brese and M. O'Keeffe, *Acta Cryst. Sect. B,* 1991, **47**, 192.

[2] K. R. Priolkar, P. Bera, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro and N. P. Lalla, *Chem. Mater.* 2002**, 14***,* 2120.