Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Three Si-substituted polyoxovanadates as efficient catalysts for Knoevenagel condensation and selective oxidation of styrene to benzaldehyde

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Fig. S17. ^{1}H NMR spectra of the products from the Knoevenagel condensation reactions.

Fig. S18. The EDS spectra of compound **1**.

Materials and methods.

All chemicals were used as purchased without purification. Hydrothermal synthesis was carried out with a 23 mL Teflon-lined autoclave under autogenous pressure, the reaction vessels were filled to approximately 25% of their volume capacity. FI-IR spectra were recorded in KBr pellets with FTIR-8900 IR spectrometer in the range of 4000-500 cm^{-1}. Powder X-ray diffraction (PXRD) was performed on a Bruker AXS D8 Advance diffractometer. TGA analyses were performed on a Perkin-Elmer Pyris Diamond TG/DTA instrument in following N_2 with a heating rate of 10 ℃ min^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 X-ray photoelectron spectrometer. The reaction products were analyzed by GC (Agilent, GC-7980B with an FID detector equipped with a DB-FFAP capillary column). ^{1}H NMR spectra were measured on a Bruker 500 MHz spectrometer.

Table S1. BVS values of V and Si atoms of compounds **1-3.**

Compound **1**

elements	valence state	elements	valence state	elements	valence state
V1	4.047	V5	4.024	Si1	4.008
V2	4.133	V6	4.066	Si2	4.017

V3	3.973	V7	4.122	Si3	3.925
V4	4.144	V8	4.105		

Compound **2**

elements	valence state	elements	valence state	elements	valence state
V1	4.113	V5	4.079	Si1	4.008
V2	4.110	V6	4.068	Si2	3.946
V3	4.093	V7	4.129		
V4	4.148	V8	4.086		

Compound **3**

elements	valence state	elements	valence state	elements	valence state
V1	4.132	V5	4.151	Si1	3.997
V2	3.994	V6	4.059	Si2	3.957
V3	4.145	V7	4.086		
V4	4.062	V8	4.103		

Table S2. The select bonds and angles of compounds **1-3**.

Compound **1**

Bonds	Å	Bonds	Å	Bonds	Å
Cd(1)-O(42)	2.188(11)	Si(1)-O(10)	1.626(10)	V(4)-O(14)	1.606(11)
Cd(1)-O(43)	2.235(10)	Si(1)#3-O(43)	1.590(11)	V(4)-O(38)	1.933(10)
Cd(1)-N(4)	2.25(2)	Si(2)-O(7)	1.618(10)	V(4)-O(48)	1.947(10)
Cd(1)-N(5)	2.40(3)	Si(2)-O(9)	1.607(11)	V(4)-O(33)	1.965(10)
Cd(1)-N(6)	2.27(6)	Si(2)-O(2)	1.644(12)	V(4)-O(35)	1.972(11)
Cd(2)-O(42)	2.231(11)	Si(2)-O(1)	1.621(12)	V(5)-O(28)	1.925(10)
Cd(2)-O(43)	2.263(10)	Si(3)-O(34)	1.636(11)	V(5)-O(23)	1.998(10)
Cd(2)-N(3)	2.296(17)	Si(3)-O(35)	1.662(11)	V(5)-O(19)	1.994(11)
Cd(2)-N(2)	2.413(17)	Si(3)-O(36)	1.644(11)	V(5)-O(48)	1.919(10)
Cd(2)-N(1)	2.251(15)	Si(3)-O(42)	1.586(10)	V(5)-O(13)	1.629(12)
Cd(3)-O(24)	2.207(12)	V(1)-O(38)	1.935(11)	V(6)-O(5)	1.933(10)
Cd(3)-O(24)#1	2.231(12)	V(1)-O(23)	2.020(11)	V(6)-O(7)	2.009(10)
Cd(3)-N(8)	2.367(19)	V(1)-O(37)	2.021(11)	V(6)-O(6)	2.003(10)
Cd(3)-N(9)	2.274(18)	V(1)-O(33)	1.915(11)	V(6)-O(49)	1.909(10)
Cd(3)-N(7)	2.282(18)	V(1)-O(27)	1.604(10)	V(6)-O(3)	1.613(11)
Cd(4)-O(41)	2.434(11)	V(2)-O(5)	1.936(10)	V(7)-O(5)	1.935(11)
Cd(4)-O(44)	2.520(11)	V(2)-O(38)	1.939(10)	V(7)-O(6)	2.023(11)
Cd(4)-N(14)	2.278(18)	V(2)-O(49)	1.914(10)	V(7)-O(26)	1.989(11)
Cd(4)-N(10)	2.291(18)	V(2)-O(37)	2.034(10)	V(7)-O(4)	1.593(12)
Cd(4)-N(11)	2.373(17)	V(2)-O(44)#2	1.610(10)	V(7)-O(11)	1.927(11)

Cd(4')-N(15)	1.938(10)	V(3)-O(28)	1.940(11)	V(8)-O(29)	1.912(11)
Cd(4')-N(14)	2.52(2)	V(3)-O(49)	1.955(10)	V(8)-O(9)	2.024(10)
Cd(4')-O(41)	2.092(14)	V(3)-O(7)	2.034(9)	V(8)-O(18)	1.911(11)
Si(1)-O(6)	1.630(11)	V(3)-O(48)	1.940(10)	V(8)-O(10)	2.018(12)
Si(1)-O(2)	1.649(12)	V(3)-O(12)	1.628(12)	V(8)-O(8)	1.602(10)

Angles	°	Angles	°
O(42)-Cd(1)-Cd(2)	39.8(3)	N(1)-Cd(2)-N(2)	76.5(6)
O(42)-Cd(1)-O(43)	80.5(4)	O(24)-Cd(3)-Cd(3)#1	40.5(3)
O(42)-Cd(1)-N(6)	113.3(7)	O(24)#1-Cd(3)-Cd(3)#1	40.0(3)
O(42)-Cd(1)-N(5)	111.8(7)	O(24)-Cd(3)-O(24)#1	80.6(4)
O(42)-Cd(1)-N(4)	99.0(7)	O(24)#1-Cd(3)-N(8)	100.7(5)
O(43)-Cd(1)-Cd(2)	40.8(3)	O(24)-Cd(3)-N(8)	173.0(6)
O(43)-Cd(1)-N(6)	95.3(7)	O(24)#1-Cd(3)-N(9)	113.5(6)
O(43)-Cd(1)-N(5)	167.5(7)	O(24)-Cd(3)-N(9)	96.3(6)
N(6)-Cd(1)-Cd(2)	107.5(7)	O(24)-Cd(3)-N(7)	109.9(6)
N(6)-Cd(1)-N(5)	78.4(9)	O(24)#1-Cd(3)-N(7)	94.2(5)
N(5)-Cd(1)-Cd(2)	151.4(6)	N(8)-Cd(3)-Cd(3)#1	140.3(5)
N(4)-Cd(1)-Cd(2)	105.5(7)	N(9)-Cd(3)-Cd(3)#1	109.5(5)
N(4)-Cd(1)-O(43)	102.7(7)	N(9)-Cd(3)-N(8)	76.9(7)
N(4)-Cd(1)-N(6)	145.3(1)	N(9)-Cd(3)-N(7)	144.7(7)
N(4)-Cd(1)-N(5)	77.9(9)	N(7)-Cd(3)-Cd(3)#1	105.7(5)
O(42)-Cd(2)-Cd(1)	38.8(3)	N(7)-Cd(3)-N(8)	77.0(7)
O(42)-Cd(2)-O(43)	79.0(4)	O(41)-Cd(4)-O(44)	175.4(4)
O(42)-Cd(2)-N(3)	98.8(5)	N(14)-Cd(4)-O(41)	101.1(5)
O(42)-Cd(2)-N(2)	173.3(5)	N(14)-Cd(4)-O(44)	82.8(5)
O(42)-Cd(2)-N(1)	108.8(5)	N(14)-Cd(4)-N(10)	94.4(7)
O(43)-Cd(2)-Cd(1)	40.2(3)	N(14)-Cd(4)-N(11)	169.7(7)
O(43)-Cd(2)-N(3)	107.6(5)	N(14)-Cd(4')-N(15)	88.4(9)
O(43)-Cd(2)-N(2)	104.6(5)	N(10)-Cd(4)-O(41)	95.3(5)
N(3)-Cd(2)-Cd(1)	108.3(5)	N(10)-Cd(4)-O(44)	86.9(5)
N(3)-Cd(2)-N(2)	74.8(6)	N(10)-Cd(4)-N(11)	79.1(6)
N(2)-Cd(2)-Cd(1)	144.7(4)	N(11)-Cd(4)-O(41)	87.5(5)
N(1)-Cd(2)-Cd(1)	105.9(4)	N(11)-Cd(4)-O(44)	88.9(5)
N(1)-Cd(2)-O(43)	97.4(5)	N(15)-Cd(4')-O(41)	144.2(1)
N(1)-Cd(2)-N(3)	145.8(6)	N(14)-Cd(4')-O(41)	103.9(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,-z #2 x+1/2,y+1/2,z #3 x-1/2,y+1/2,z #4 x+1/2,y-1/2,z #5 x-1/2,y-1/2,z

Compound **2**

Bonds	Å	Bonds	Å	Bonds	Å
Co(1)-O(18)	2.130(3)	Si(2)-O(3)	1.636(4)	V(4)-O(10)	1.939(3)

Co(1)-O(23)	2.068(3)	Si(2)#1-O(11)	1.642(3)	V(4)#3-O(23)	1.649(3)
Co(1)-N(3)	2.123(6)	Si(2)-O(14)	1.650(3)	V(5)-O(7)	1.949(3)
Co(1)-N(4)	2.131(5)	Si(2)-O(16)	1.590(3)	V(5)-O(8)	1.907(3)
Co(1)-N(5)	2.168(7)	V(1)-O(2)	1.926(3)	V(5)-O(9)	2.011(3)
Co(1)-N(6)	2.144(6)	V(1)-O(3)	2.036(3)	V(5)-O(13)	1.929(3)
Co(2)-O(17)	2.161(3)	V(1)#1-O(8)	1.931(3)	V(5)-O(18)	1.632(3)
Co(2)-N(7)	2.141(9)	V(1)#1-O(10)	1.942(3)	V(5)-V(7)#1	3.0317(10)
Co(2)-N(8)	2.126(8)	V(1)-O(24)	1.609(3)	V(6)-O(6)	1.951(3)
Co(3)-O(16)	2.040(4)	V(1)-V(2)	3.0299(11)	V(6)-O(10)	1.949(3)
Co(3)#2-O(16)	2.029(4)	V(2)-O(2)	1.910(3)	V(6)-O(11)	2.031(3)
Co(3')-O(16)	2.185(7)	V(2)-O(3)	2.001(3)	V(6)-O(12)	1.938(3)
Co(3')#2-O(16)	2.298(7)	V(2)-O(4)	1.929(3)	V(6)-O(20)	1.605(4)
Co(3)-O(25W)	1.893(10)	V(2)-O(5)	1.995(3)	V(7)#1-O(9)	2.001(3)
Co(3')-N(1)	1.525(9)	V(2)-O(21)	1.609(3)	V(7)-O(11)	1.996(3)
Co(3)-N(1)	2.166(8)	V(3)-O(4)	1.926(3)	V(7)-O(12)	1.913(3)
Co(3)-N(2)	2.231(10)	V(3)-O(5)	2.020(3)	V(7)#1-O(13)	1.914(3)
Co(3')-N(2)	2.242(11)	V(3)-O(6)	1.935(3)	V(7)-O(22)	1.611(4)
Co(3')-Co(3)	0.873(6)	V(3)-O(7)	1.940(3)	V(8)-O(2)	1.937(3)
Si(1)-O(5)	1.637(4)	V(3)-O(19)	1.618(3)	V(8)-O(4)	1.941(3)
Si(1)-O(9)	1.625(3)	V(4)-O(6)	1.922(3)	V(8)-O(12)	1.950(3)
Si(1)-O(14)	1.631(4)	V(4)-O(7)	1.933(3)	V(8)#1-O(13)	1.952(3)
Si(1)-O(15)	1.620(3)	V(4)-O(8)	1.918(3)	V(8)-O(17)	1.634(3)

Angles	°	Angles	°
O(23)-Co(1)-N(3)	95.82(17)	N(7)-Co(2)-O(17)	90.0(2)
O(23)-Co(1)-O(18)	86.58(13)	N(8)#4-Co(2)-O(17)#4	88.2(2)
N(3)-Co(1)-O(18)	87.65(18)	N(8)-Co(2)-O(17)#4	91.8(2)
O(23)-Co(1)-N(4)	177.4(2)	N(7)#4-Co(2)-O(17)#4	90.0(2)
N(3)-Co(1)-N(4)	81.7(2)	N(7)-Co(2)-O(17)#4	90.0(2)
O(18)-Co(1)-N(4)	93.98(18)	O(17)-Co(2)-O(17)#4	180.00(8)
O(23)-Co(1)-N(6)	88.0(2)	Co(3')-Co(3)-O(25W)	155.8(5)
N(3)-Co(1)-N(6)	175.6(2)	Co(3')-Co(3)-O(16)#2	96.6(4)
O(18)-Co(1)-N(6)	90.5(2)	O(25W)-Co(3)-O(16)#2	102.1(3)
N(4)-Co(1)-N(6)	94.6(3)	O(25W)-Co(3)-O(16)	111.0(3)
N(8)#4-Co(2)-N(8)	180.0	O(16)#2-Co(3)-O(16)	83.62(14)
N(8)#4-Co(2)-N(7)#4	82.1(5)	O(25W)-Co(3)-N(1)	126.3(4)
N(8)-Co(2)-N(7)#4	97.9(5)	O(16)#2-Co(3)-N(1)	94.7(3)
N(8)#4-Co(2)-N(7)	97.9(5)	O(16)-Co(3)-N(1)	121.4(2)
N(8)-Co(2)-N(7)	82.1(5)	Co(3')-Co(3)-N(2)	79.4(5)
N(7)#4-Co(2)-N(7)	180.0	O(25W)-Co(3)-N(2)	81.3(4)
N(8)#4-Co(2)-O(17)	91.8(2)	O(16)#2-Co(3)-N(2)	175.7(3)

N(8)-Co(2)-O(17)	88.2(2)	O(16)-Co(3)-N(2)	97.7(3)
N(7)#4-Co(2)-O(17)	90.0(2)	N(1)-Co(3)-N(2)	81.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+2 #2 -x,-y,-z+1 #3 -x-1,-y,-z+2 #4 -x,-y-1,-z+2

Compound **3**

Bond	Å	Bonds	Å	Bonds	Å
Co(1)-O(2)	2.093(3)	V(1)-O(3)	1.617(3)	V(5)-O(8)	1.917(3)
Co(1)#4-O(22)	2.087(4)	V(1)-O(12)	1.988(3)	V(5)-O(9)	1.934(3)
Co(1)-N(1)	2.137(4)	V(1)-O(13)	1.908(3)	V(5)-O(11)	1.918(3)
Co(1)-N(2)	2.166(5)	V(1)-O(19)	1.997(3)	V(5)-O(10)	2.009(3)
Co(1)-N(3)	2.172(5)	V(1)-O(24)	1.910(3)	V(5)-O(22)	1.622(3)
Co(1)-N(4)	2.147(4)	V(2)-O(9)	1.962(3)	V(6)-O(10)	1.936(3)
Co(2)-O(3)	2.109(3)	V(2)-O(12)	2.108(3)	V(6)-O(11)	2.002(3)
Co(2)-O(18)	2.084(3)	V(2)-O(13)	1.942(3)	V(6)-O(14)	1.931(3)
Co(2)-N(5)	2.162(4)	V(2)#3-O(16)	1.947(3)	V(6)-O(15)	1.999(3)
Co(2)-N(6)	2.127(5)	V(2)-O(5)	1.595(3)	V(6)-O(21)	1.607(3)
Co(2)-N(7)	2.147(4)	V(3)-O(2)	1.652(3)	V(7)-O(7)	1.603(3)
Co(2)-N(8)	2.135(4)	V(3)-O(8)	1.911(3)	V(7)-O(14)	1.941(3)
Si(1)-O(6)	1.620(3)	V(3)-O(9)	1.931(3)	V(7)-O(15)	2.034(3)
Si(1)-O(15)	1.621(3)	V(3)#3-O(16)	1.921(3)	V(7)-O(16)	1.931(3)
Si(1)-O(19)	1.631(3)	V(3)#3-O(17)	1.945(3)	V(7)-O(17)	1.959(3)
Si(1)-O(20)	1.624(3)	V(4)-O(4)	1.614(3)	V(8)#1-O(10)	1.936(3)
Si(2)-O(11)	1.624(3)	V(4)-O(8)	1.949(3)	V(8)#2-O(13)	1.946(3)
Si(2)-O(12)	1.627(3)	V(4)#3-O(17)	1.940(3)	V(8)#1-O(14)	1.951(3)
Si(2)-O(20)	1.640(3)	V(4)#3-O(19)	2.029(3)	V(8)-O(18)	1.629(3)
Si(2)-O(23)	1.620(3)	V(4)#3-O(24)	1.932(3)	V(8)#2-O(24)	1.949(3)

Angles	°	Angles	°
O(22)#4-Co(1)-O(2)	89.98(14)	O(18)-Co(2)-O(3)	94.09(13)
O(22)#4-Co(1)-N(1)	86.02(17)	O(18)-Co(2)-N(6)	87.73(17)
O(2)-Co(1)-N(1)	91.55(15)	O(3)-Co(2)-N(6)	88.02(19)
O(22)#4-Co(1)-N(4)	89.10(17)	O(18)-Co(2)-N(8)	87.34(16)
O(2)-Co(1)-N(4)	86.23(17)	O(3)-Co(2)-N(8)	89.63(15)
N(1)-Co(1)-N(4)	174.6(2)	N(6)-Co(2)-N(8)	174.37(18)
O(22)#4-Co(1)-N(2)	94.12(17)	O(18)-Co(2)-N(7)	96.17(16)
O(2)-Co(1)-N(2)	171.28(17)	O(3)-Co(2)-N(7)	166.05(15)
N(1)-Co(1)-N(2)	81.09(19)	N(6)-Co(2)-N(7)	101.8(2)
N(4)-Co(1)-N(2)	101.5(2)	N(8)-Co(2)-N(7)	81.45(18)
O(22)#4-Co(1)-N(3)	168.09(15)	O(18)-Co(2)-N(5)	167.50(16)
O(2)-Co(1)-N(3)	95.42(16)	O(3)-Co(2)-N(5)	90.28(16)
N(1)-Co(1)-N(3)	104.40(19)	N(6)-Co(2)-N(5)	80.71(19)

N(4)-Co(1)-N(3)	80.69(19)	N(8)-Co(2)-N(5)	104.42(18)
N(2)-Co(1)-N(3)	82.0(2)	N(7)-Co(2)-N(5)	81.66(18)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 -x-1,-y,-z+2 #3 -x,-y,-z+2 #4 -x,-y+1,-z+2 #5 x-1,y,z

Table S3. Selective oxidation of styrene to benzaldehyde with different catalysts[a]

Entry	Catalyst	Time	Conv.[b] (%)	Sele.[b] (%)
1	**1**	15 min	97.6	100
2	**2**	2.5 h	98.8	100
3	**3**	3 h	96.6	96.17
4	blank	1h	0	0
5	TEOS	1h	0	0
6	$CdCl_2$	1h	11.5	100
7	V_2O_5	1h	100	16.3

[a]Reaction conditions: styrene (0.40 mmol), 30% H_2O_2 (1 mmol), catalyst (20 mg), solvent (2 mL) at 80 ℃. [b]Determined by GC analysis.

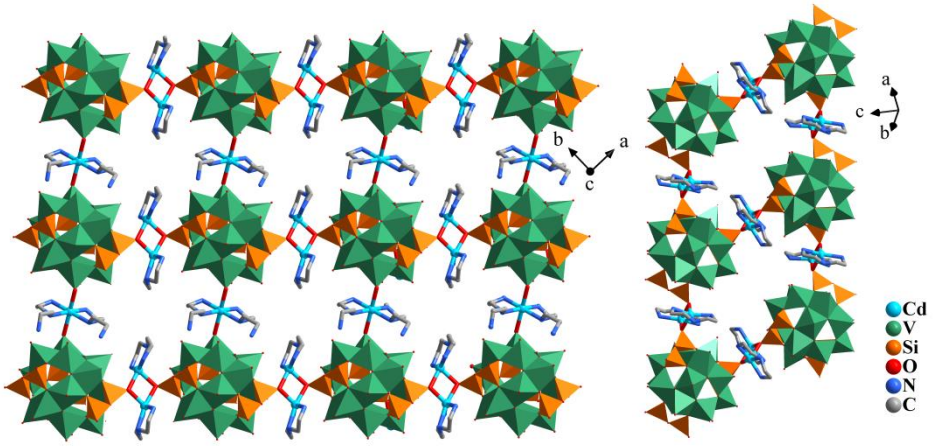


Fig. S1. The 2D bilayer structure of compound **1**.

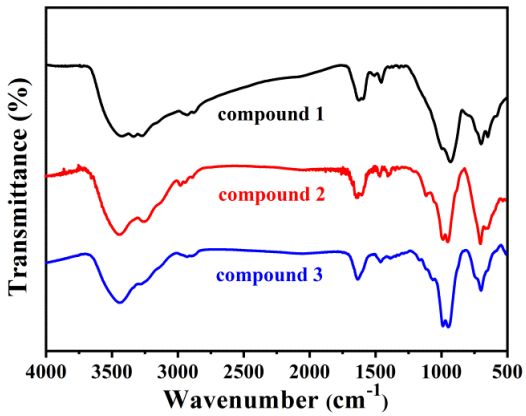


Fig. S2. FT-IR spectra of compounds **1-3**.

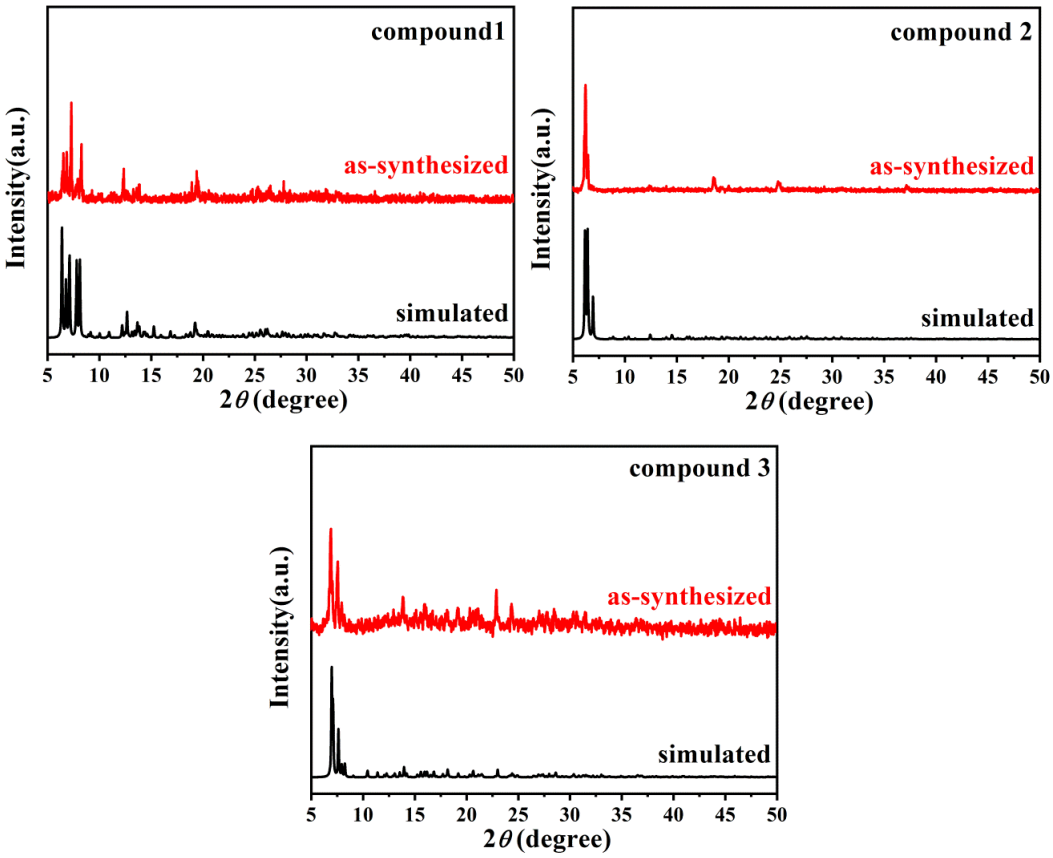


Fig. S3. Simulated and experimental PXRD patterns of compounds **1-3**.

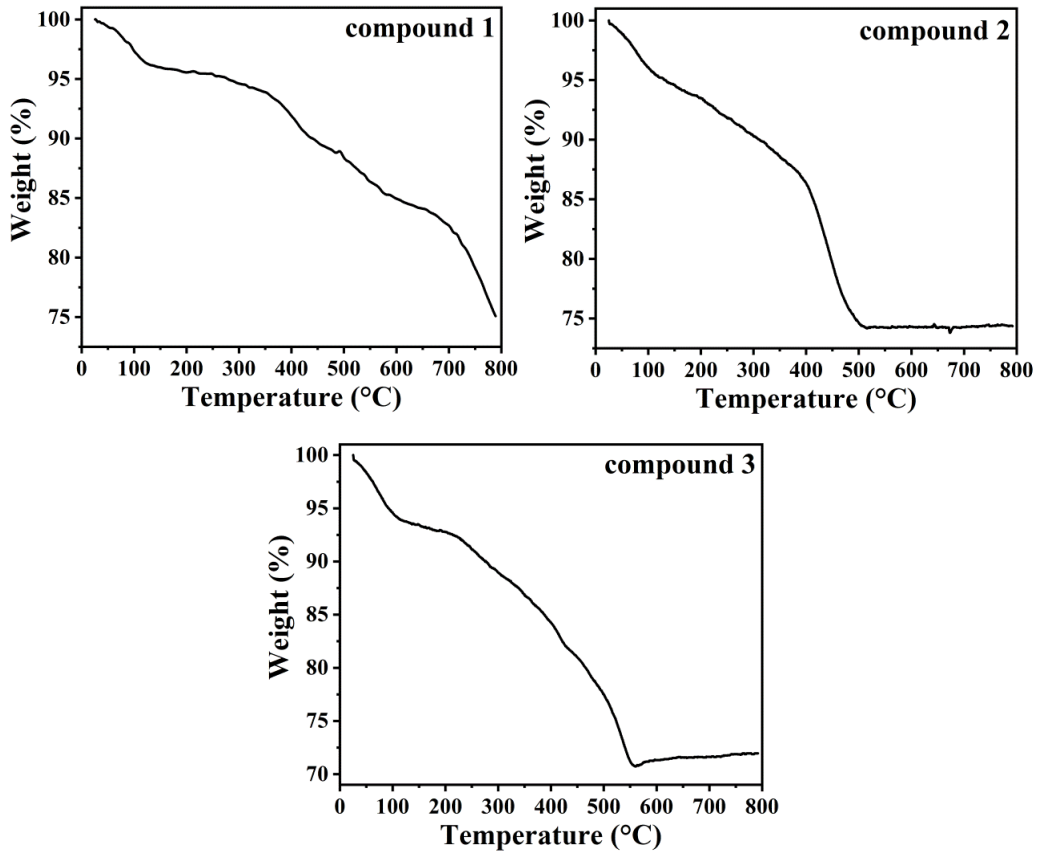


Fig. S4. TG curves of compounds **1-3**.

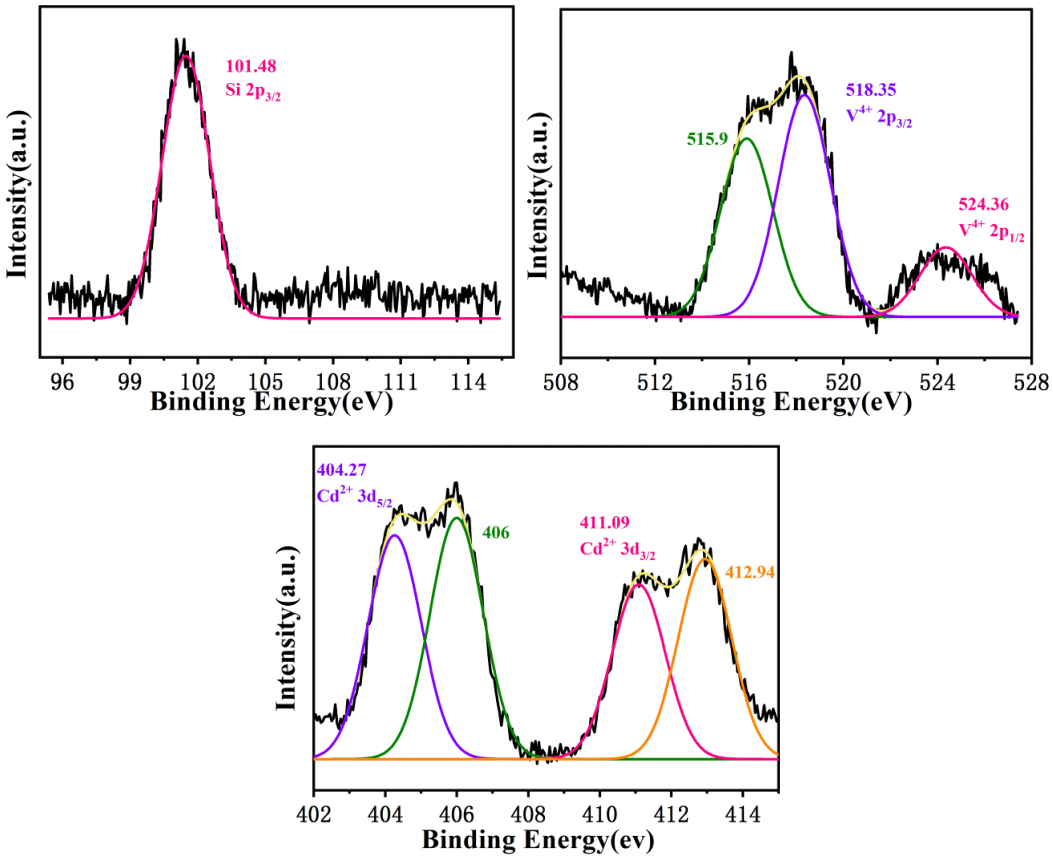


Fig. S5. XPS spectra of compound **1**: Si, V, Cd.

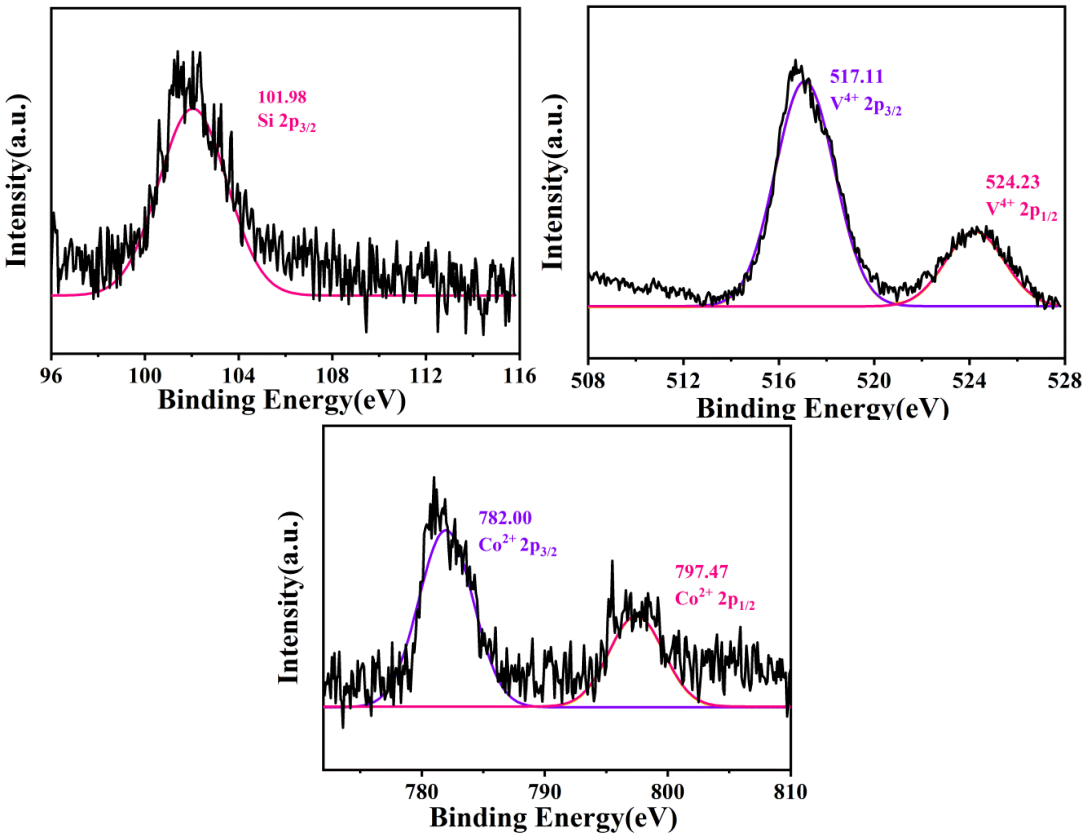


Fig. S6. XPS spectra of compound **2**: Si, V, Co.

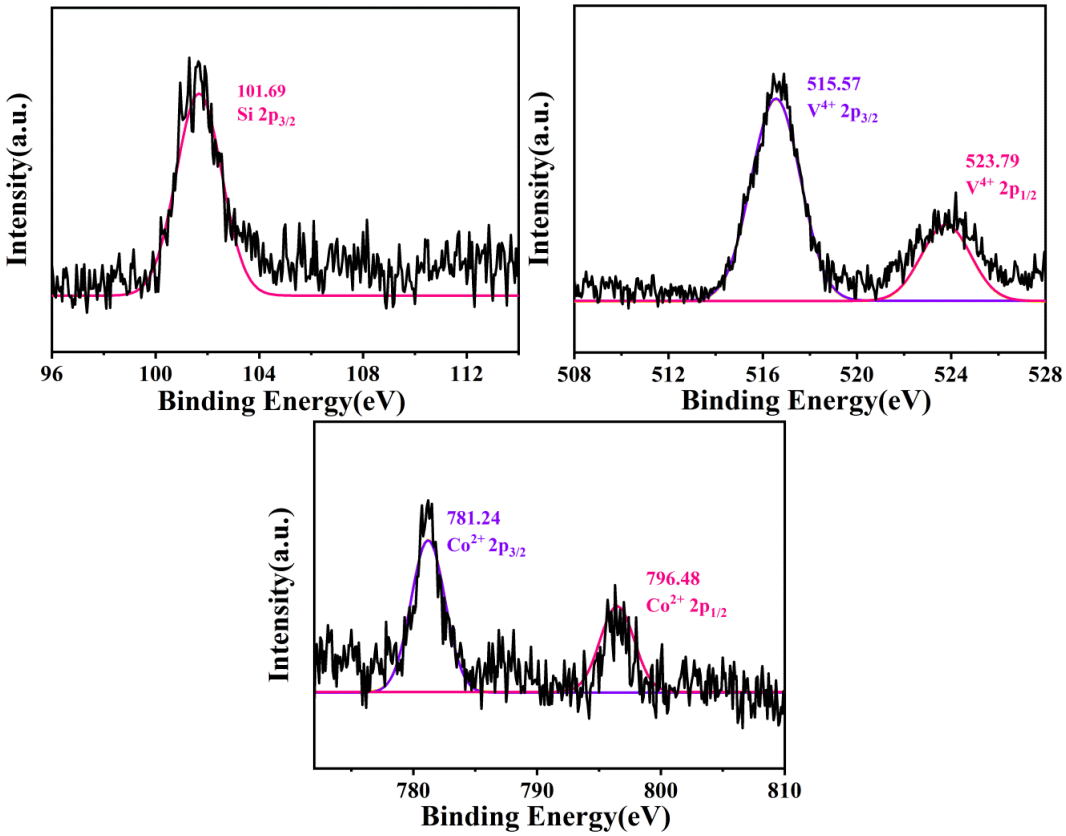


Fig. S7. XPS spectra of compound **3**: Si, V, Co.

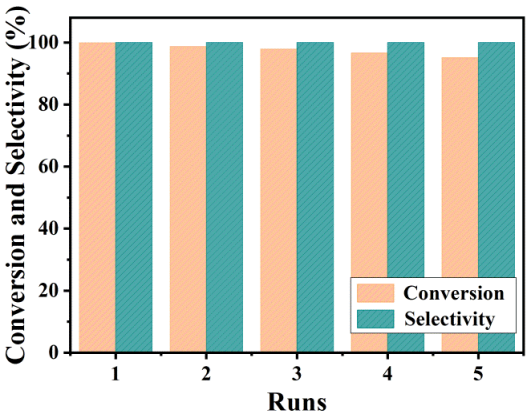


Fig. S8. Recycling of compound **1** for Knoevenagel condensation.

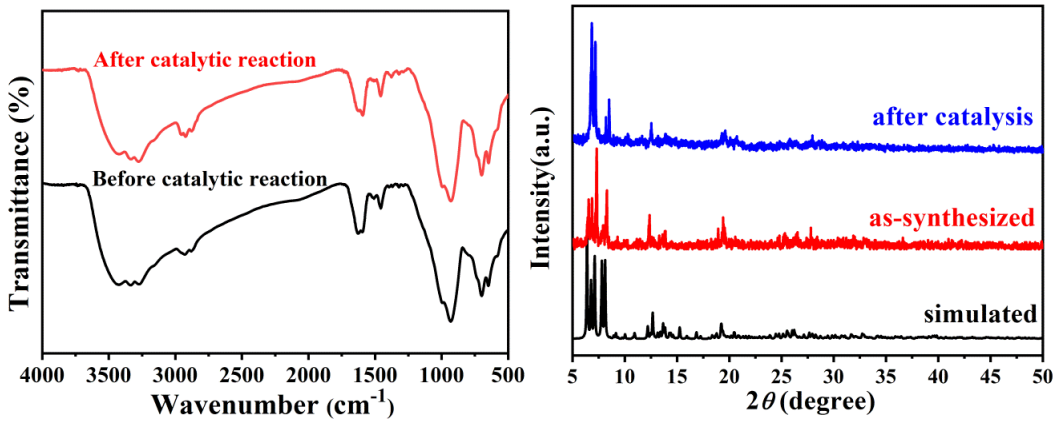


Fig. S9. The FT-IR spectra and PXRD patterns of the reused compound **1** in the Knoevenagel condensation**.**

As shown in Fig. S10, SEM images (Fig. S10 a, b and c) revealed that compounds **1-3** are block crystals. Fig. S10 d, e and f shows the powder images of compounds **1-3** with irregular laminations, respectively.

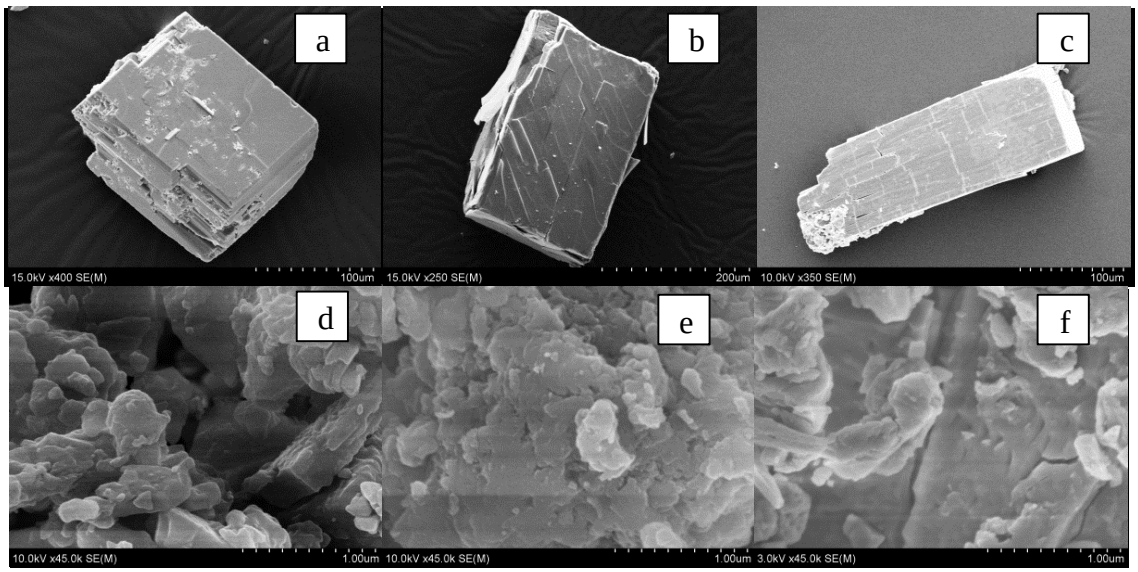


Fig. S10. SEM images of crystal and powder in compounds **1-3**.

The measured BET specific surface areas and pore size of the catalyst powder are shown in Fig. S11 and Table S4. The specific surface area and pore size of compound **1** is slightly higher than that of compound **2** and **3**. It is explained that compound **1** had better catalytic activity than compound **2** and **3**. Compounds **1-3** are mesoporous with an average pore diameter of 35 nm for 1 , 32.5 nm for **2** and 22.96 nm for **3**, respectively.

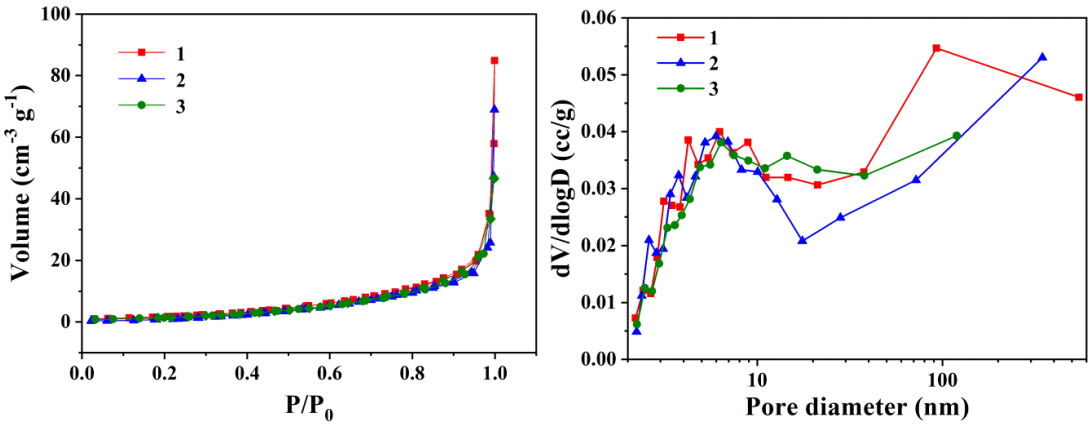


Fig. S11. N_2 adsorptionedesorption isotherm and pore-size distribution of compounds **1-3**.

Table S4. The parameters of BET surface area and pore size of compounds **1-3**.

Compound	BET surface area [m^2 g^{-1}]	Pore size [nm]
1	7.5049	35

2	6.5638	32.5
3	6.2756	22.96

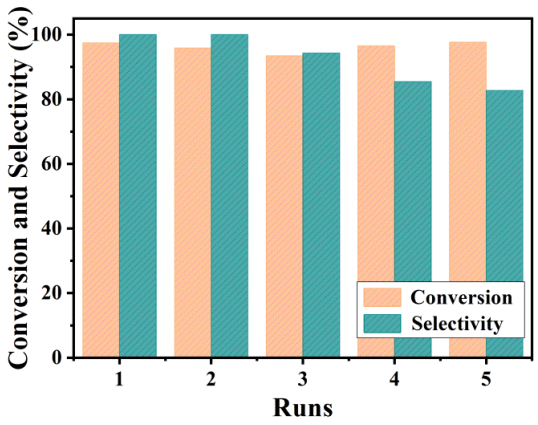


Fig. S12. Recycling of compound **1** for catalytic oxidation of styrene.

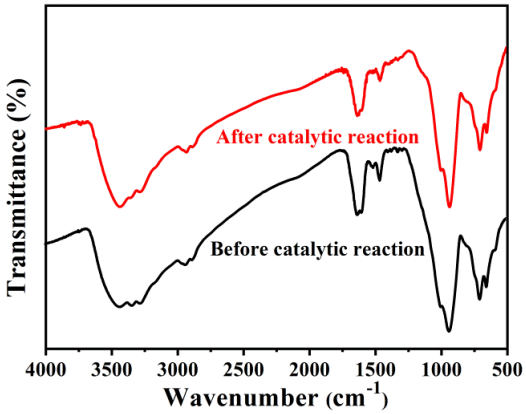


Fig. S13. The FT-IR spectra of the reused compound **1** in the catalytic oxidation of styrene.

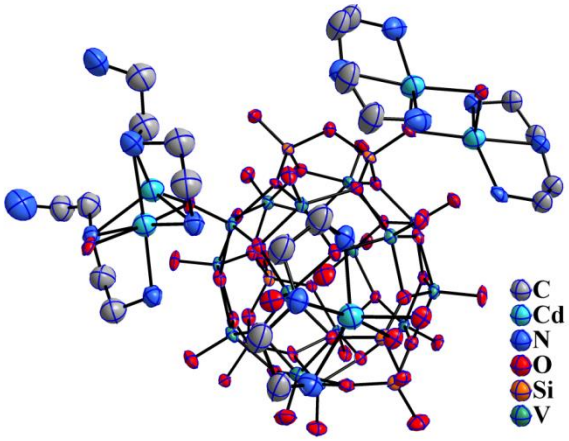


Fig. S14. Diagram showing anisotropic displacement parameters (ADPs) of compound **1**, with the thermal ellipsoids shown at a 30% probability level. All hydrogen atoms are omitted for clarity.

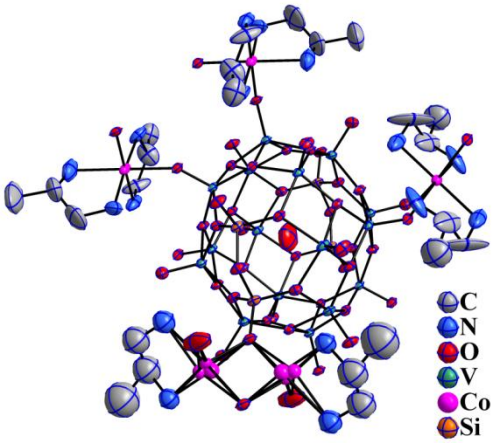


Fig. S15. Diagram showing anisotropic displacement parameters (ADPs) of compound **2**, with the thermal ellipsoids shown at a 30% probability level. All hydrogen atoms are omitted for clarity.

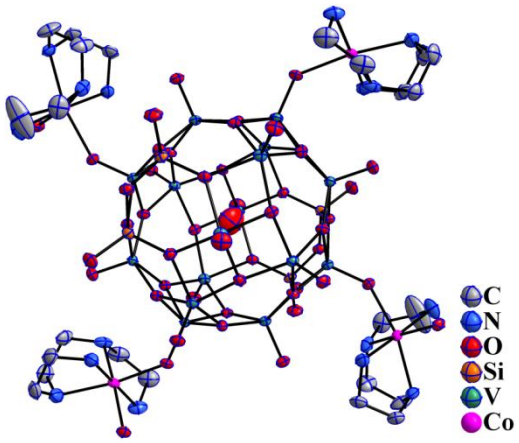
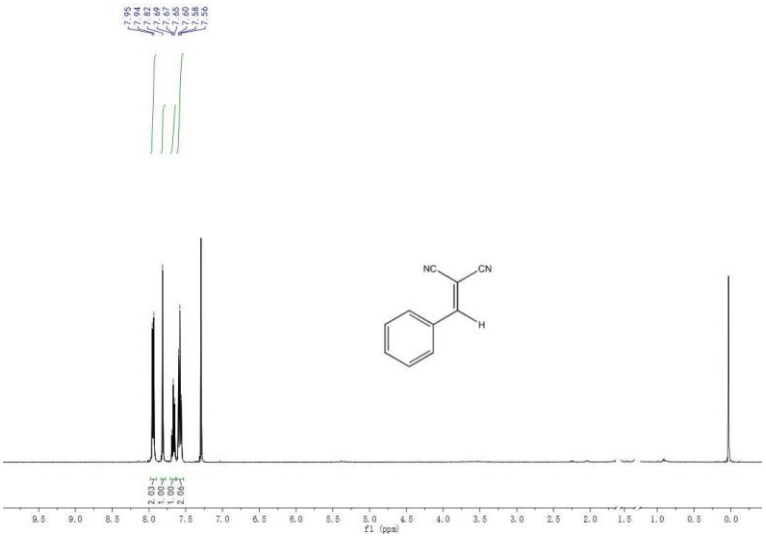
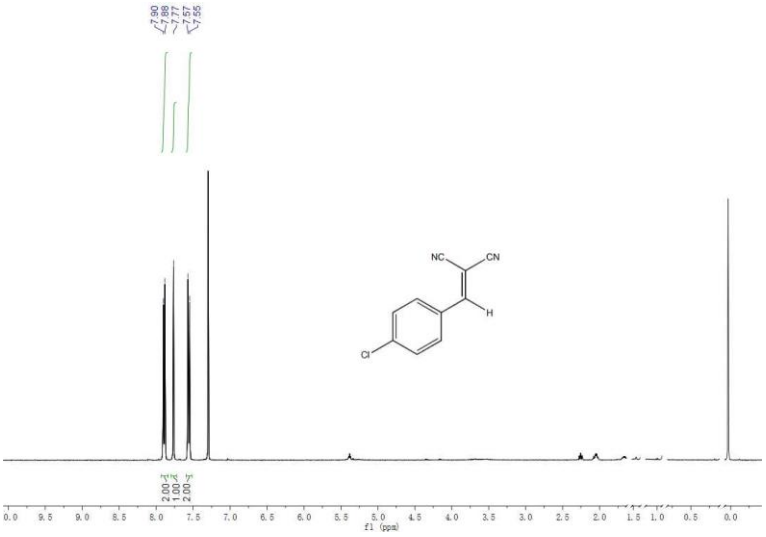


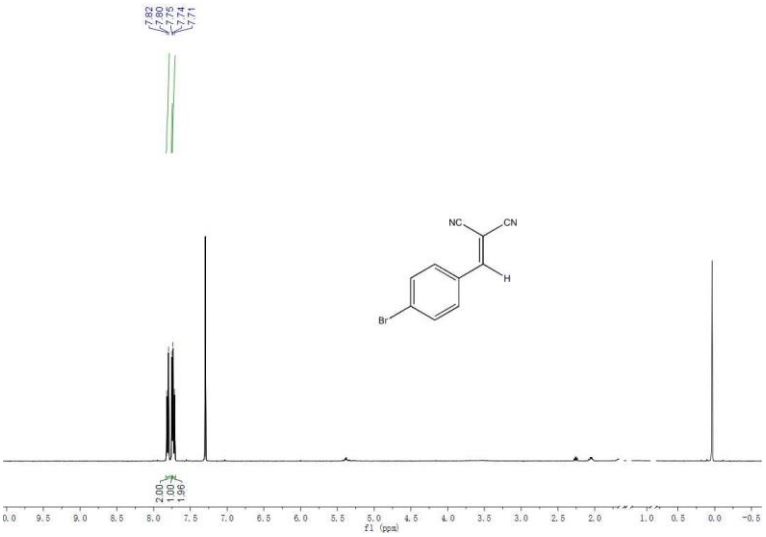
Fig. S16. Diagram showing anisotropic displacement parameters (ADPs) of compound **3**, with the thermal ellipsoids shown at a 30% probability level. All hydrogen atoms are omitted for clarity.



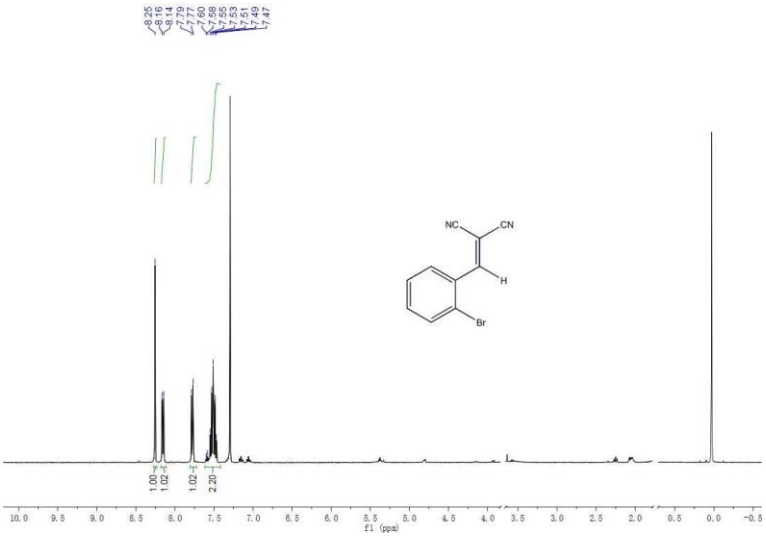
(a) ^{1}H NMR spectrum of 2-benzylidenemalononitrile in $CDCl_3$.



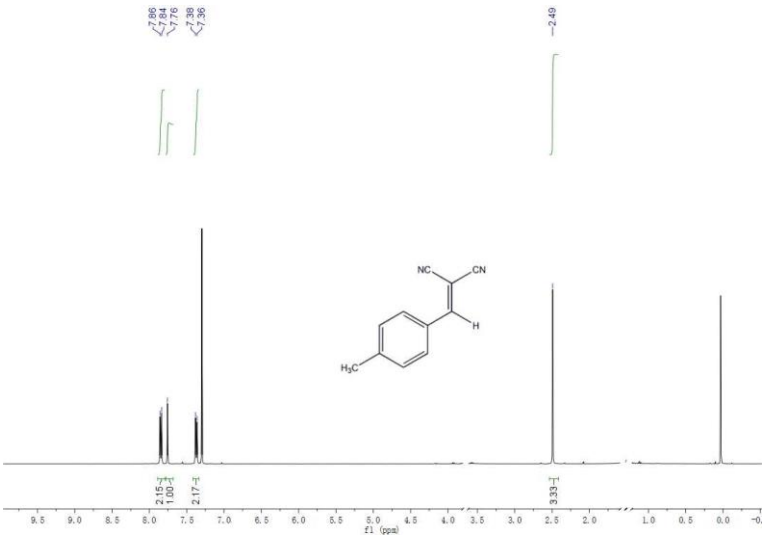
(b) ^{1}H NMR spectrum of 2-(4-chlorobenzylidene)malononitrile in $CDCl_3$.



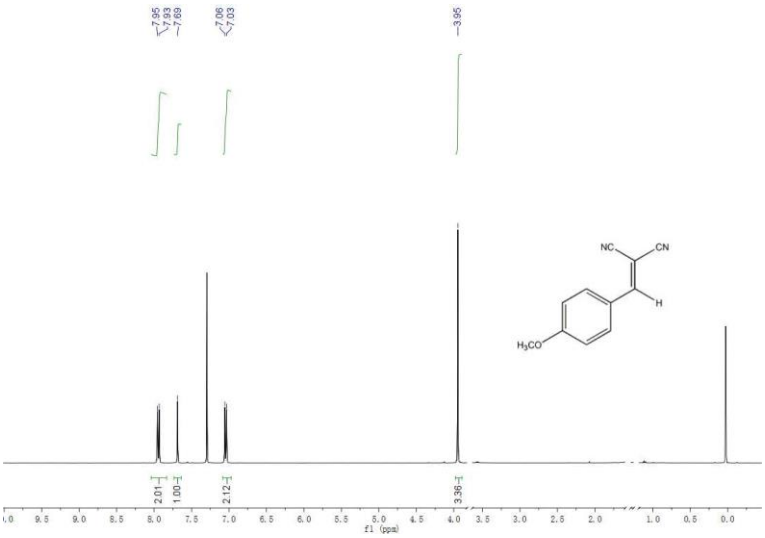
(c) ^{1}H NMR spectrum of 2-(4-bromobenzylidene)malononitrile in $CDCl_3$.



(d) ^{1}H NMR spectrum of 2-(2-bromobenzylidene)malononitrile in $CDCl_3$.



(e) ^{1}H NMR spectrum of 2-(4-methylbenzylidene)malononitrile in $CDCl_3$.



(f) ^{1}H NMR spectrum of 2-(4-methoxybenzylidene)malononitrile in $CDCl_3$.

Fig. S17. ^{1}H NMR spectra of the products from the Knoevenagel condensation reactions.

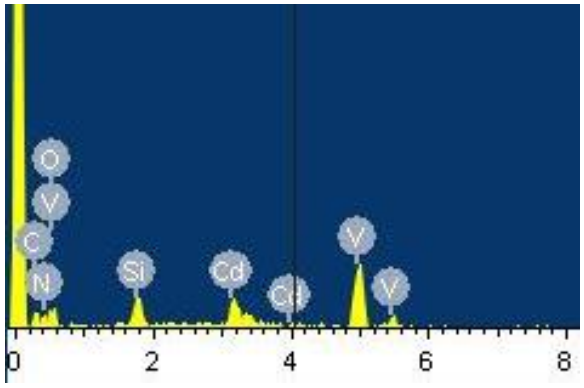
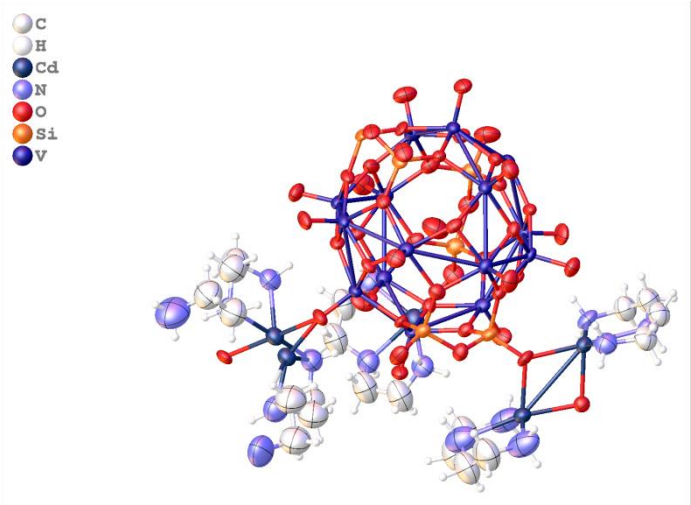


Fig. S18. The EDS spectra of compound **1**.

R_1=10.91%

Crystal Data and Experimental



Experimental. Single brown block-shaped-shaped crystals of **1** were used as supplied. A suitable crystal with dimensions 0.15 × 0.13 × 0.10 mm³ was selected and mounted on a CCD area detector diffractometer. The crystal was kept at a steady T = 296(2) K during data collection. The structure was solved with the **ShelXL-2018/3** (Sheldrick, 2018) solution program using ? and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL-2018/3** (Sheldrick, 2018) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{20}H_{85}Cd_4N_{15}O_{56}Si_6V_{15}$, M_r = 2814.27, monoclinic, $C2/c$ (No. 15), a = 20.788(4) Å, b = 19.333(3) Å, c = 44.011(8) Å, β = 98.456(3)°, α = γ = 90°, V = 17495(5) Å³, T = 296(2) K, Z = 8, Z' = 1, μ(MoK$_\alpha$) = 2.651, 42993 reflections measured, 15385 unique (R_{int} = 0.0419) which were used in all calculations. The final wR_2 was 0.2612 (all data) and R_1 was 0.1091 (I≥2 σ(I)).

Compound	**1**
Formula	$C_{20}H_{85}Cd_4N_{15}O_{56}Si_6V_{15}$
$D_{calc.}$/ g cm^{-3}	2.137
μ/mm^{-1}	2.651
Formula Weight	2814.27
Colour	brown
Shape	block-shaped-shaped
Size/mm^3	0.15×0.13×0.10
T/K	296(2)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	20.788(4)
b/Å	19.333(3)
c/Å	44.011(8)
α/°	90
β/°	98.456(3)
γ/°	90
V/Å^3	17495(5)
Z	8
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.446
Θ_{max}/°	25.000
Measured Refl's.	42993
Indep't Refl's	15385
Refl's I≥2 σ(I)	11750
R_{int}	0.0419
Parameters	986
Restraints	258
Largest Peak	4.195
Deepest Hole	-3.168
GooF	1.084
wR_2 (all data)	0.2612
wR_2	0.2530
R_1 (all data)	0.1329
R_1	0.1091

Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=50.0° 0.84	I/σ(I) CIF 19.5	Rint CIF 4.19%	Full 50.0° CIF 99.8
Refinement:	Shift CIF 0.011	Max Peak CIF 4.2	Min Peak CIF -3.2	GooF CIF 1.084

A brown block-shaped-shaped-shaped crystal with dimensions 0.15 × 0.13 × 0.10 mm^3 was mounted. Data were collected using a CCD area detector diffractometer operating at T = 296(2) K.

Data were measured ? (d, runs) with MoK_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program SAINT v7.68A (Bruker, 2009). The maximum resolution that was achieved was Θ= 25.000° (0.84 Å).

The unit cell was refined using Bruker ShelXTL on 9994 reflections, 23% of the observed reflections.

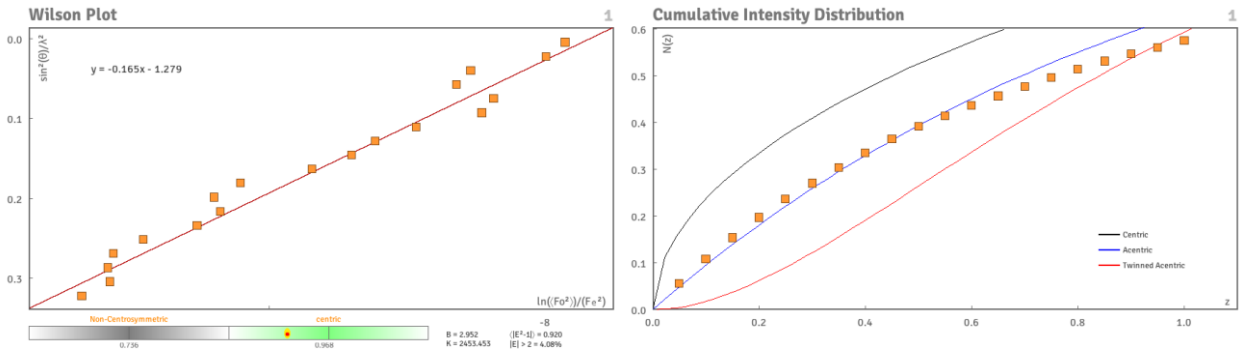
Data reduction, scaling and absorption corrections were performed using Bruker ShelXTL. The final completeness is 99.80 % out to 25.000° in Θ. SADABS (Bruker, 2009). The absorption coefficient μ of this material is 2.651 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.679 and 0.768.

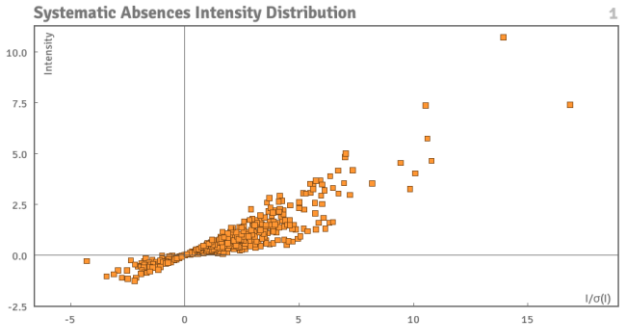
The structure was solved and the space group $C2/c$ (# 15) determined by the ShelXL-2018/3 (Sheldrick, 2018) structure solution program using using ? and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL-2018/3** (Sheldrick, 2018). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

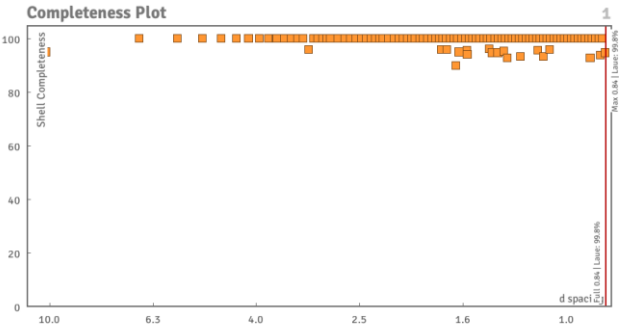
_exptl_absorpt_process_details: SADABS (Bruker, 2009)

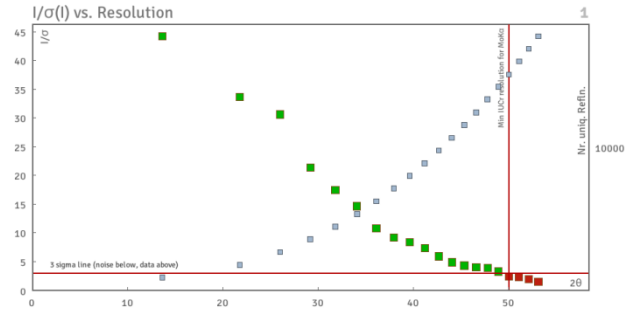
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

Data Plots: Diffraction Data

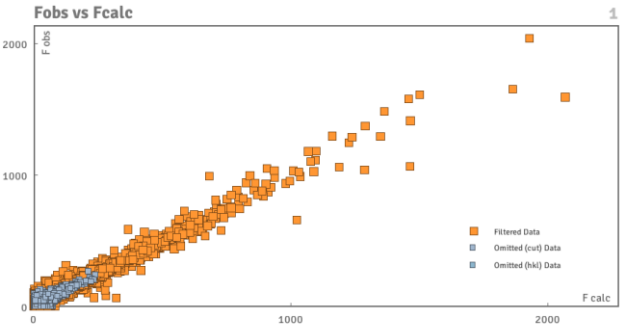


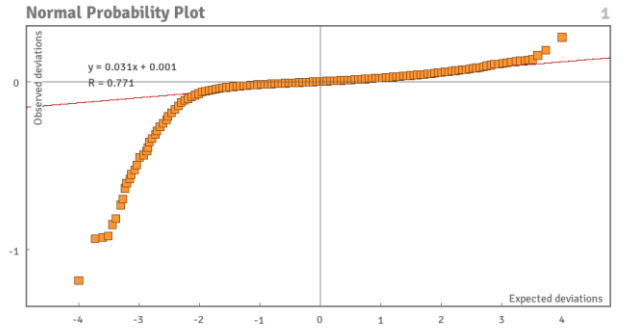






Data Plots: Refinement and Data





Citations

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

SADABS, Bruker axs, Madison, WI (?).

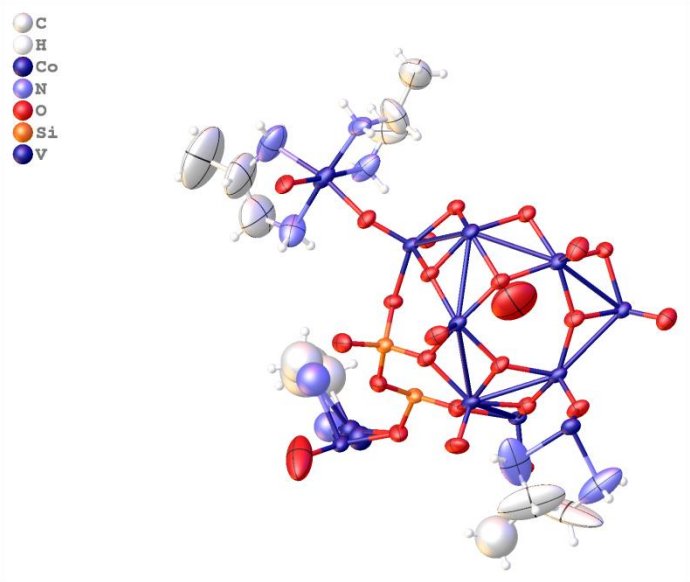
ShelXTL, Bruker axs, Madison, WI (?).

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

R_1=4.89%

Crystal Data and Experimental



Experimental. Single brown strip-shaped crystals of **2** were used as supplied. A suitable crystal with dimensions 0.11 × 0.09 × 0.04 mm^3 was selected and mounted on a CCD area detector diffractometer. The crystal was kept at a steady T = 296(2) K during data collection. The structure was solved with the **ShelXL-2018/3** (Sheldrick, 2018) solution program using ? and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL-2018/3** (Sheldrick, 2018) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{24}H_{100}N_{16}O_{54}V_{16}Co_5Si_4$, M_r = 2699.24, triclinic, P-1 (No. 2), a = 12.9632(9) Å, b = 13.8288(10) Å, c = 14.4745(11) Å, α = 91.7840(10)°, β = 98.7650(10)°, γ = 96.3390(10)°, V = 2545.8(3) Å^3, T = 296(2) K, Z = 1, Z' = 0.5, μ(MoK$_\alpha$) = 2.314, 12882 reflections measured, 8858 unique (R_{int} = 0.0174) which were used in all calculations. The final wR_2 was 0.1458 (all data) and R_1 was 0.0489 (I≥2 σ(I)).

Compound	**2**
Formula	$C_{24}H_{100}N_{16}O_{54}V_{16}Co_5Si_4$
$D_{calc.}$/ g cm^{-3}	1.761
μ/mm^{-1}	2.314
Formula Weight	2699.24
Colour	brown
Shape	strip-shaped
Size/mm^3	0.11×0.09×0.04
T/K	296(2)
Crystal System	triclinic
Space Group	P-1
a/Å	12.9632(9)
b/Å	13.8288(10)
c/Å	14.4745(11)
α/°	91.7840(10)
β/°	98.7650(10)
γ/°	96.3390(10)
V/Å^3	2545.8(3)
Z	1
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	1.483
Θ_{max}/°	24.999
Measured Refl's.	12882
Indep't Refl's	8858
Refl's I≥2 σ(I)	7173
R_{int}	0.0174
Parameters	495
Restraints	2
Largest Peak	1.584
Deepest Hole	-0.916
GooF	1.019
wR_2 (all data)	0.1458
wR_2	0.1393
R_1 (all data)	0.0583
R_1	0.0489

Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=50.0° 0.84	I/σ(I) CIF 28.5	Rint CIF 1.74%	Full 50.0° 98.7
Refinement:	Shift CIF 0.012	Max Peak CIF 1.6	Min Peak CIF -0.9	GooF CIF 1.019

A brown strip-shaped-shaped crystal with dimensions 0.11 × 0.09 × 0.04 mm^3 was mounted. Data were collected using a CCD area detector diffractometer operating at T = 296(2) K.

Data were measured ? (d, runs) with MoK_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program SAINT v7.68A (Bruker, 2009). The maximum resolution that was achieved was Θ= 24.999° (0.84 Å).

The unit cell was refined using Bruker ShelXTL on 15841 reflections, 123% of the observed reflections.

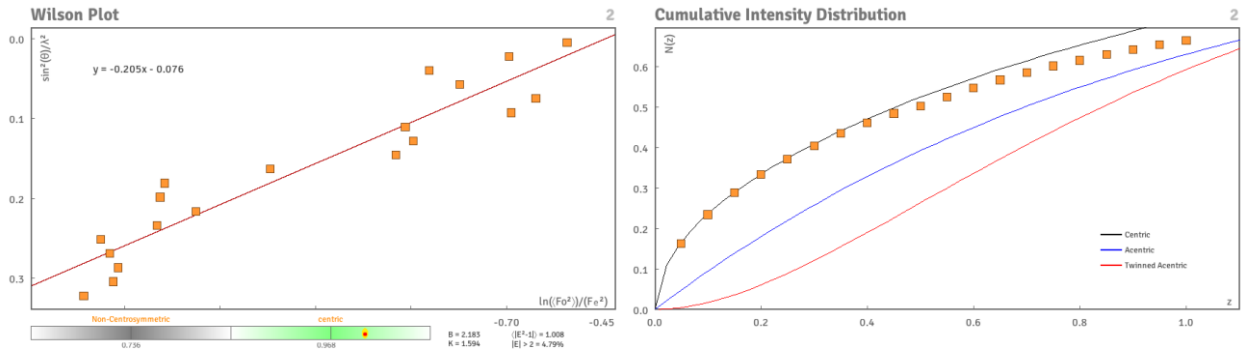
Data reduction, scaling and absorption corrections were performed using Bruker ShelXTL. The final completeness is 98.70 % out to 24.999° in Θ. SADABS (Bruker, 2009). The absorption coefficient μ of this material is 2.314 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.779 and 0.912.

The structure was solved and the space group *P*-1 (# 2) determined by the ShelXL-2018/3 (Sheldrick, 2018) structure solution program using using ? and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL-2018/3** (Sheldrick, 2018). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

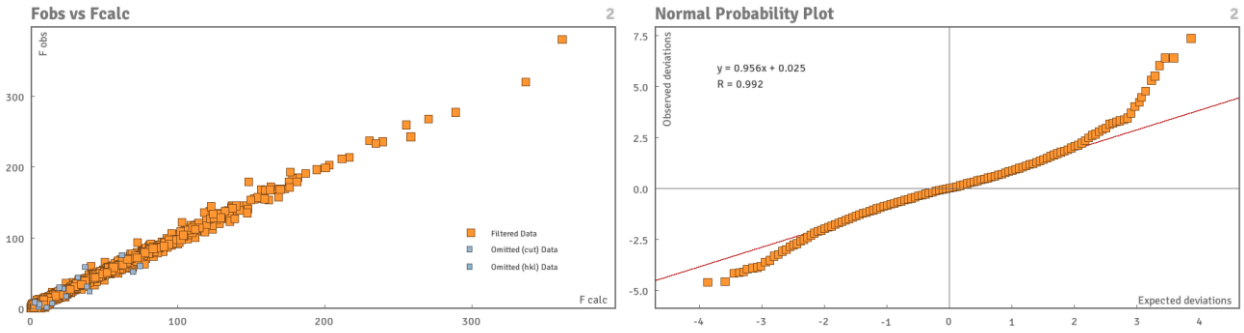
_exptl_absorpt_process_details: SADABS (Bruker, 2009)

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Data Plots: Diffraction Data



Data Plots: Refinement and Data



Citations

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

SADABS, Bruker axs, Madison, WI (?).

ShelXTL, Bruker axs, Madison, WI (?).

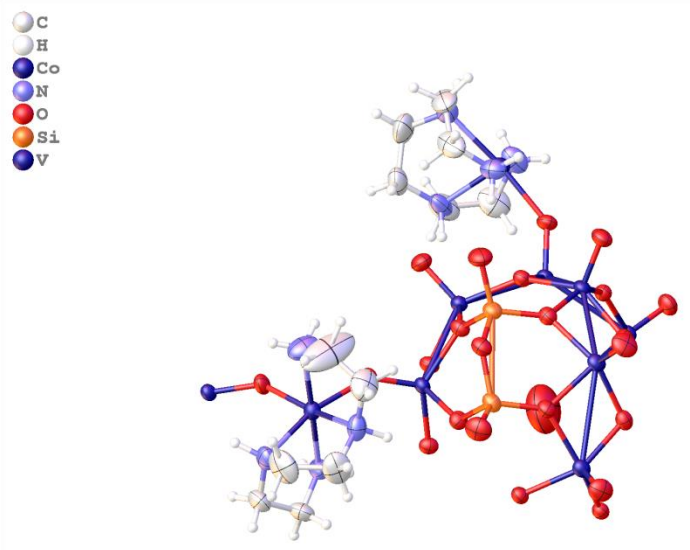
Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

3

R_1=4.63%

Crystal Data and Experimental



Experimental. Single brown strip-shaped crystals of **3** were used as supplied. A suitable crystal with dimensions 0.16 × 0.06 × 0.03 mm³ was selected and mounted on a CCD area detector diffractometer. The crystal was kept at a steady T = 296(2) K during data collection. The structure was solved with the **ShelXL-2018/3** (Sheldrick, 2018) solution program using ? and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL-2018/3** (Sheldrick, 2018) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{24}H_{98}N_{16}O_{57}Si_4V_{16}Co_4$, M_r = 2686.30, triclinic, P-1 (No. 2), a = 12.8549(13) Å, b = 13.2678(13) Å, c = 14.8024(14) Å, α = 69.796(2)°, β = 64.329(2)°, γ = 81.152(2)°, V = 2135.4(4) Å³, T = 296(2) K, Z = 1, Z' = 0.5, μ(MoK$_\alpha$) = 2.575, 13452 reflections measured, 9772 unique (R_{int} = 0.0235) which were used in all calculations. The final wR_2 was 0.1313 (all data) and R_1 was 0.0463 (I≥2 σ(I)).

Compound	**3**
Formula	$C_{24}H_{98}N_{16}O_{57}Si_4V_{16}Co_4$
$D_{calc.}$/ g cm^{-3}	2.083
μ/mm^{-1}	2.575
Formula Weight	2686.30
Colour	brown
Shape	strip-shaped
Size/mm^3	0.16×0.06×0.03
T/K	296(2)
Crystal System	triclinic
Space Group	P-1
a/Å	12.8549(13)
b/Å	13.2678(13)
c/Å	14.8024(14)
α/°	69.796(2)
β/°	64.329(2)
γ/°	81.152(2)
V/Å^3	2135.4(4)
Z	1
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.607
Θ_{max}/°	28.320
Measured Refl's.	13452
Indep't Refl's	9772
Refl's I≥2 σ(I)	6908
R_{int}	0.0235
Parameters	502
Restraints	3
Largest Peak	1.250
Deepest Hole	-0.958
GooF	1.069
wR_2 (all data)	0.1313
wR_2	0.1181
R_1 (all data)	0.0704
R_1	0.0463

Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=56.6° 0.75	I/σ(I) CIF 17.1	Rint CIF 2.35%	Full 50.5° 92% to 56.6° 99.1
Refinement:	Shift CIF 0.001	Max Peak CIF 1.2	Min Peak CIF -1.0	GooF CIF 1.069

A brown strip-shaped-shaped crystal with dimensions 0.16 × 0.06 × 0.03 mm^3 was mounted. Data were collected using a CCD area detector diffractometer operating at T = 296(2) K.

Data were measured ? (d, runs) with MoK_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program SAINT v7.68A (Bruker, 2009). The maximum resolution that was achieved was Θ = 28.320° (0.83 Å).

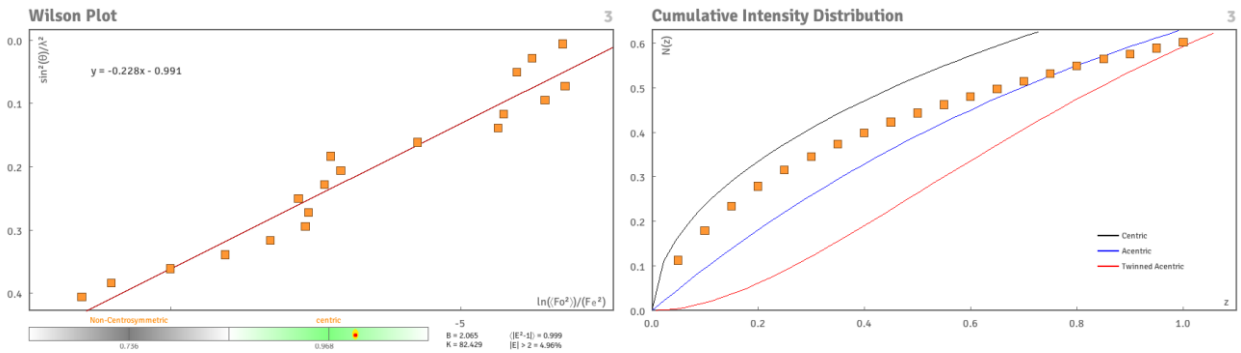
The unit cell was refined using Bruker ShelXTL on 13452 reflections, 100% of the observed reflections.

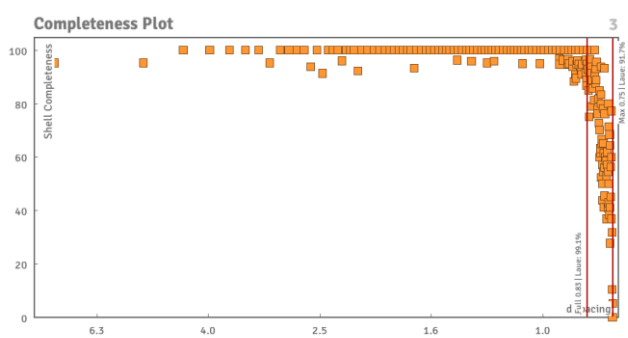
Data reduction, scaling and absorption corrections were performed using Bruker ShelXTL. The final completeness is 99.10 % out to 28.320° in Θ. A multi-scan absorption correction was performed using ?. The absorption coefficient μ of this material is 2.575 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.831 and 0.926.

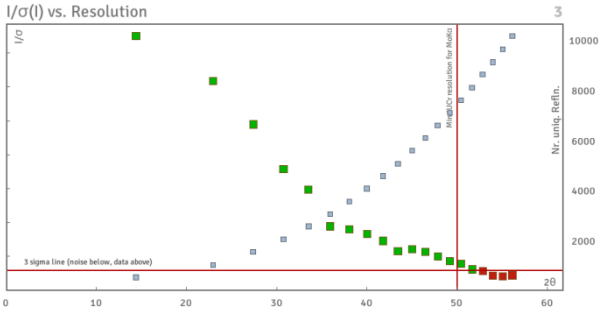
The structure was solved and the space group P-1 (# 2) determined by the ShelXL-2018/3 (Sheldrick, 2018) structure solution program using using ? and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL-2018/3** (Sheldrick, 2018). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

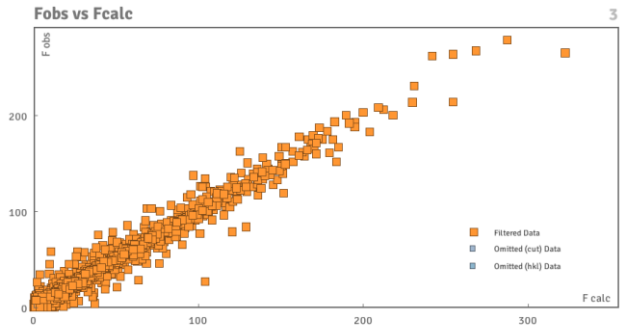
Data Plots: Diffraction Data

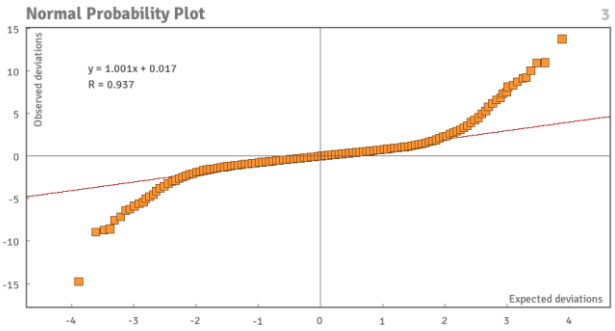






Data Plots: Refinement and Data





Citations

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

ShelXTL, Bruker axs, Madison, WI (?).

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.