Electronic Supplementary Material (ESI) for Dalton Transactions.

Non-redox reactivity of V(II) and Fe(II) formamidinates towards CO_2 resulting in the formation of novel M(II) carbamates

Krzesimir Korona,[a] Arkadiusz Kornowicz,[b] Iwona Justyniak,[b] Michał Terlecki,[a] Artur Błachowski,[c] and Janusz Lewiński[a,b]*

[a] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
[b] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
[c] AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Kraków, Poland
*lewin@ch.pw.edu.pl

Table of contents

1. Fourier-Transform Infrared attenuated total reflectance (FTIR-ATR) data for 1-6

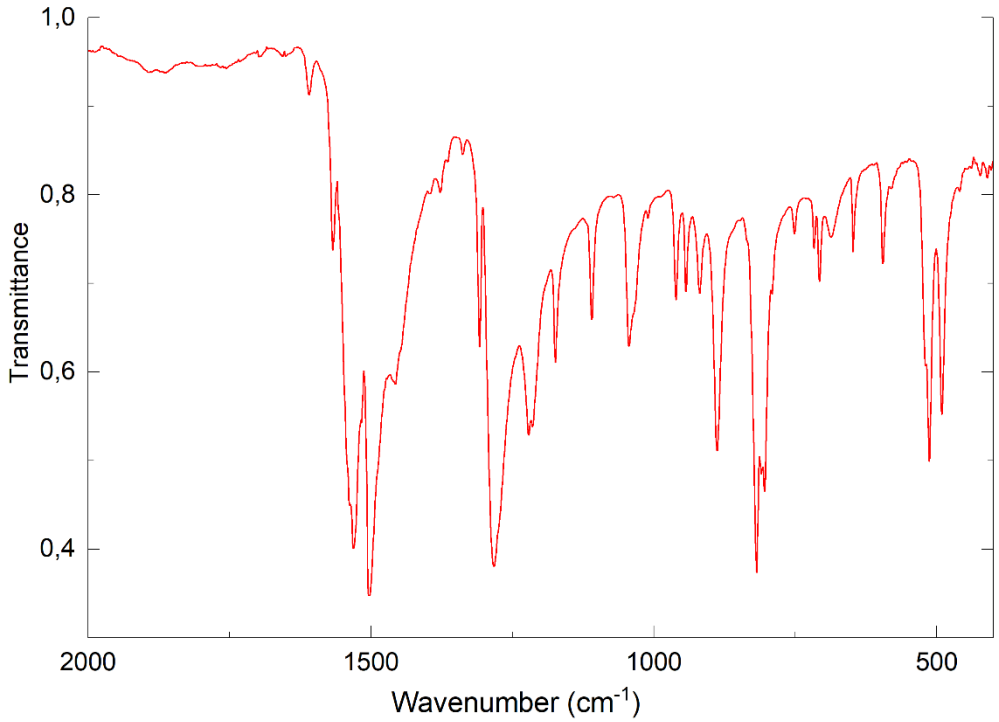

Fig. S1. FTIR spectrum of **1** shown in a range of 2000-400 cm^{-1}.

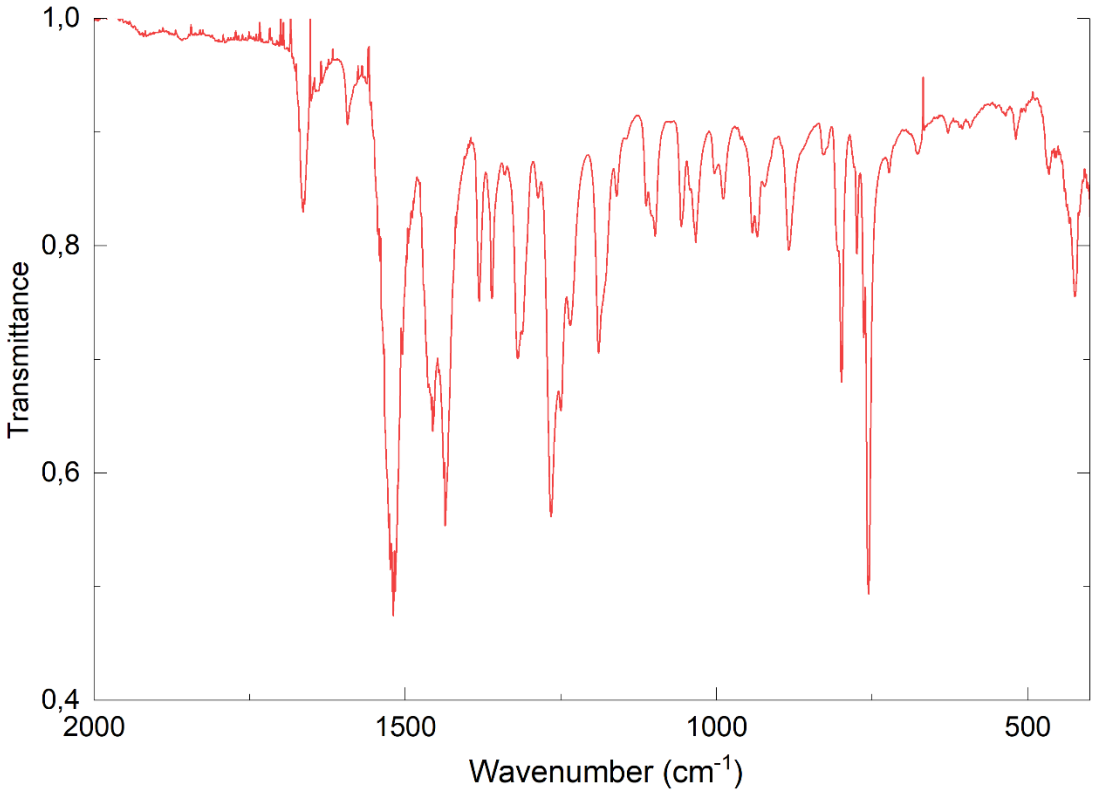

Fig. S2. FTIR spectrum of **2** shown in a range of 2000-400 cm^{-1}.

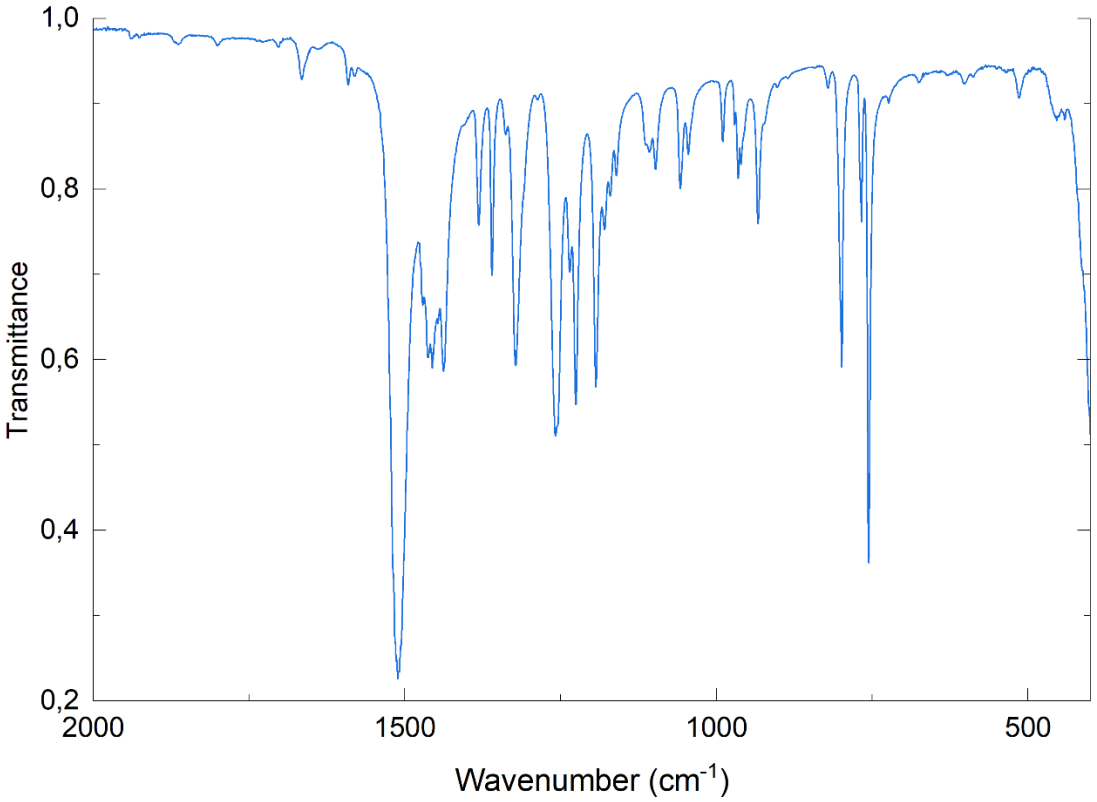

Fig. S3. FTIR spectrum of **3** shown in a range of 2000-400 cm^{-1}.

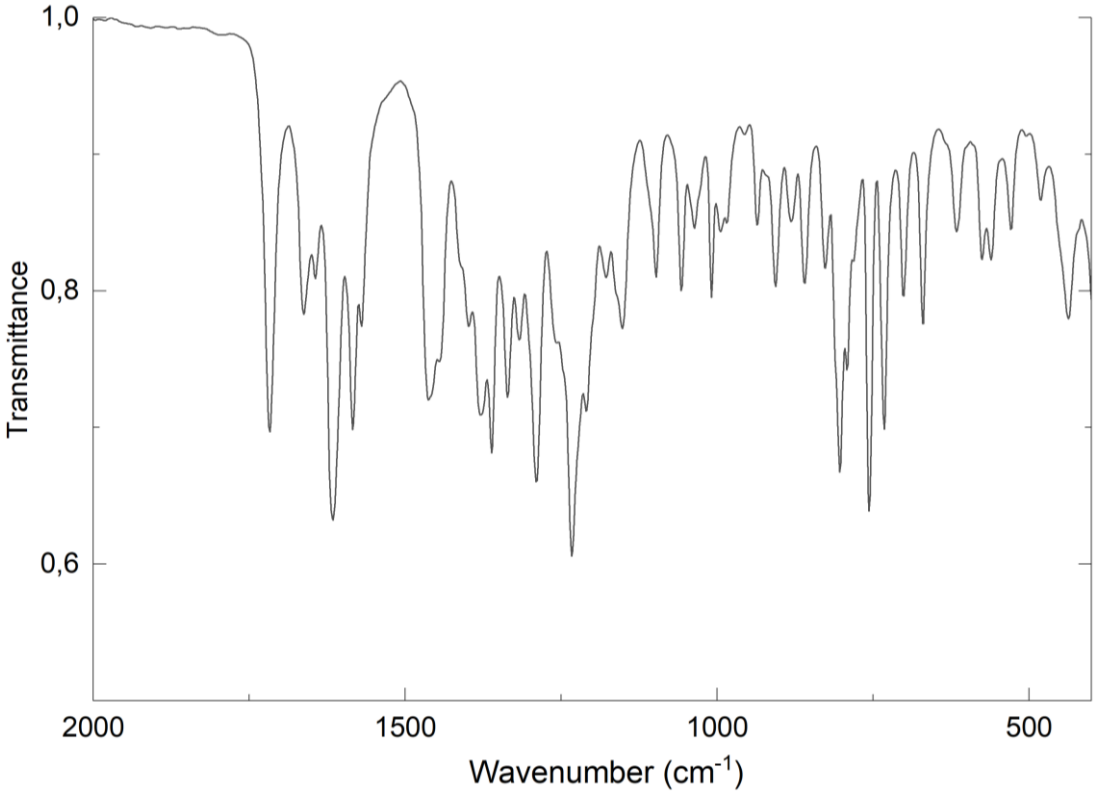

Fig. S4. FTIR spectrum of **4** shown in a range of 2000-400 cm^{-1}.

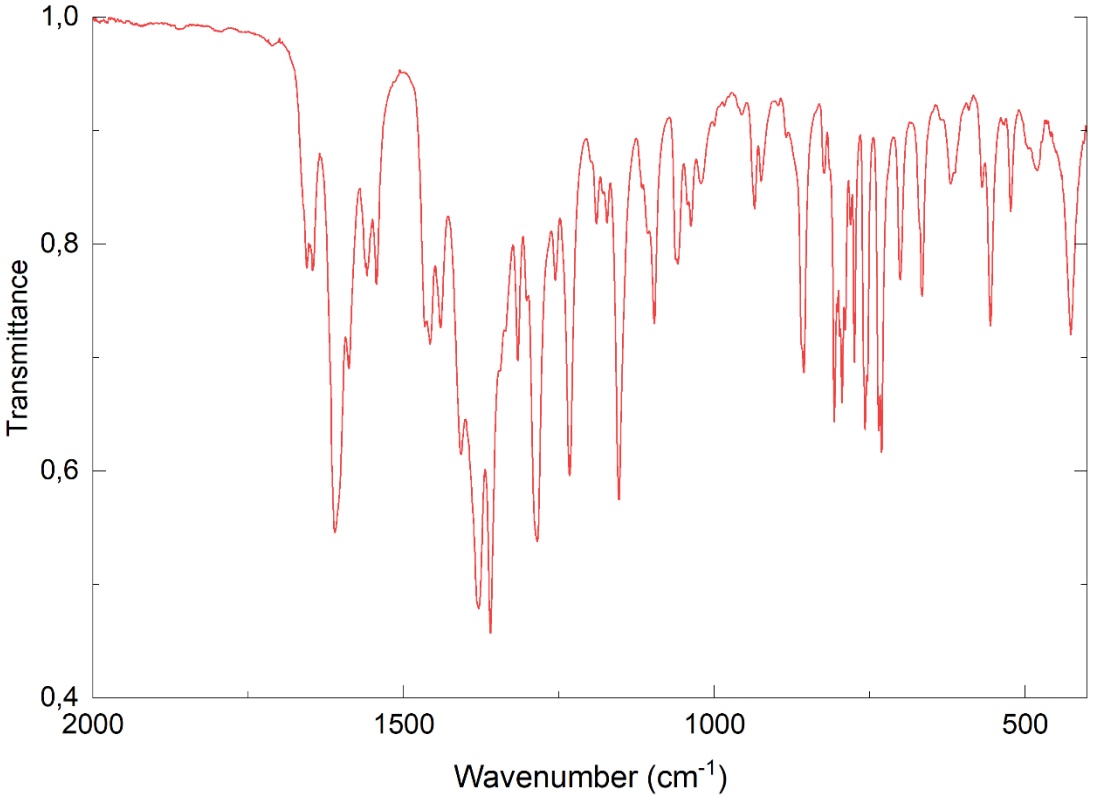

Fig. S5. FTIR spectrum of **5** shown in a range of 2000-400 cm^{-1}.

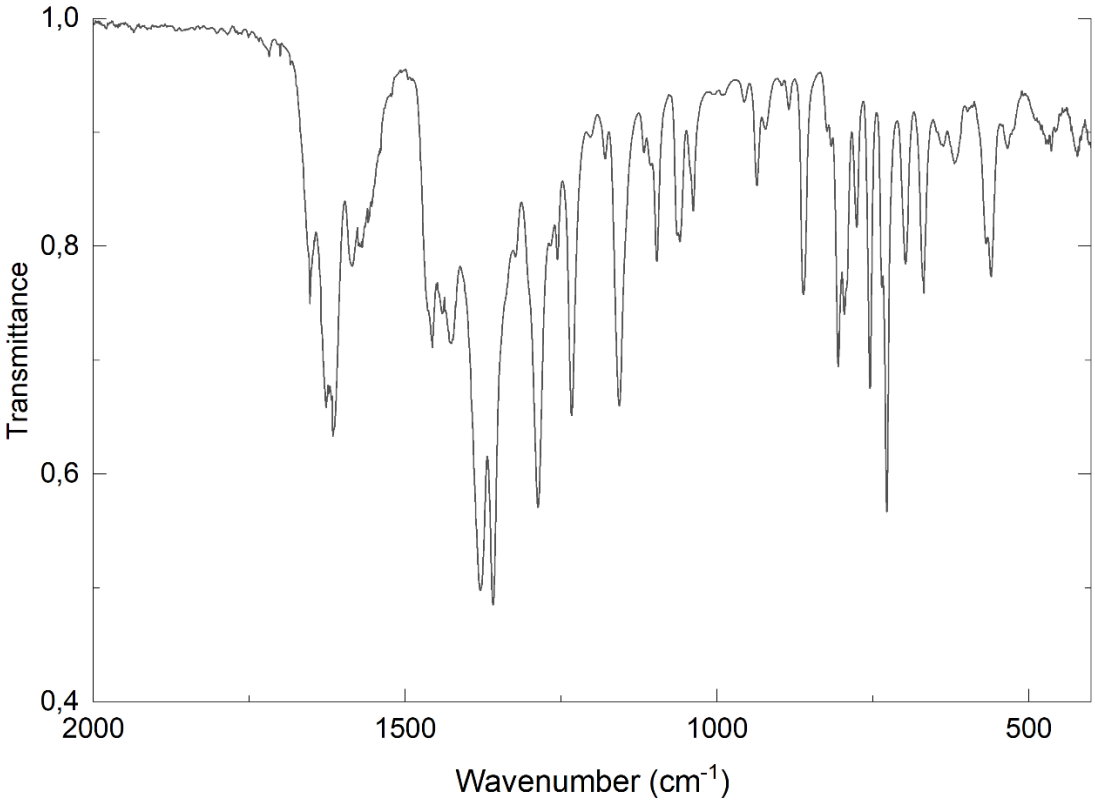

Fig. S6. FTIR spectrum of **6** shown in a range of 2000-400 cm^{-1}.

2. ^{1}H NMR spectra for 4-6.

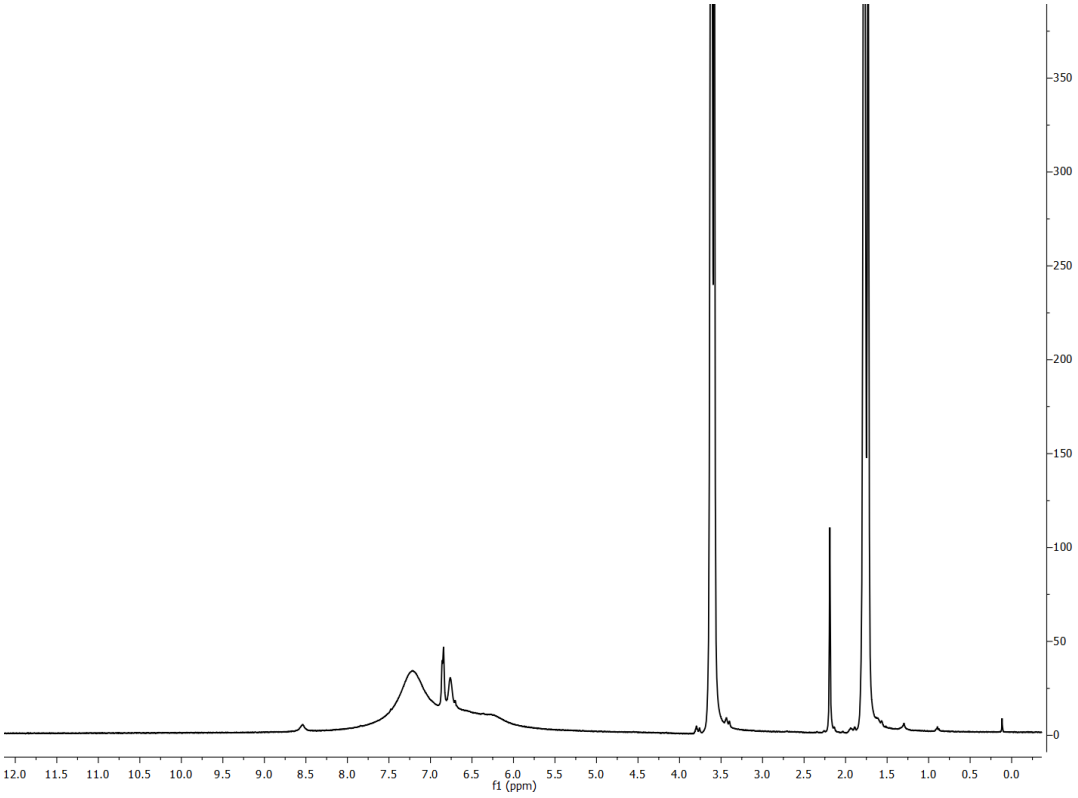

Fig. S7. ^{1}H NMR spectrum of **1** in THF-d_8. The signals from solvent residuals are marked by asterisks.

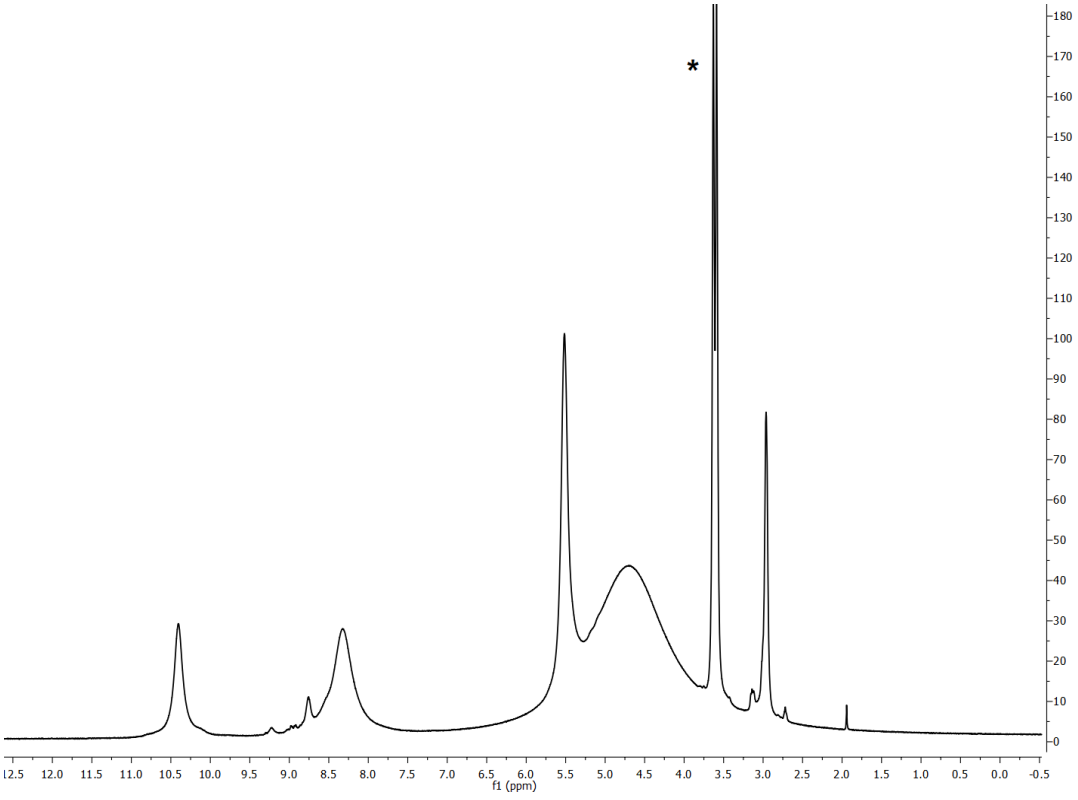

Fig. S8. ^{1}H NMR spectrum of **2** in THF-d_8. The signals from solvent residuals are marked by asterisks.

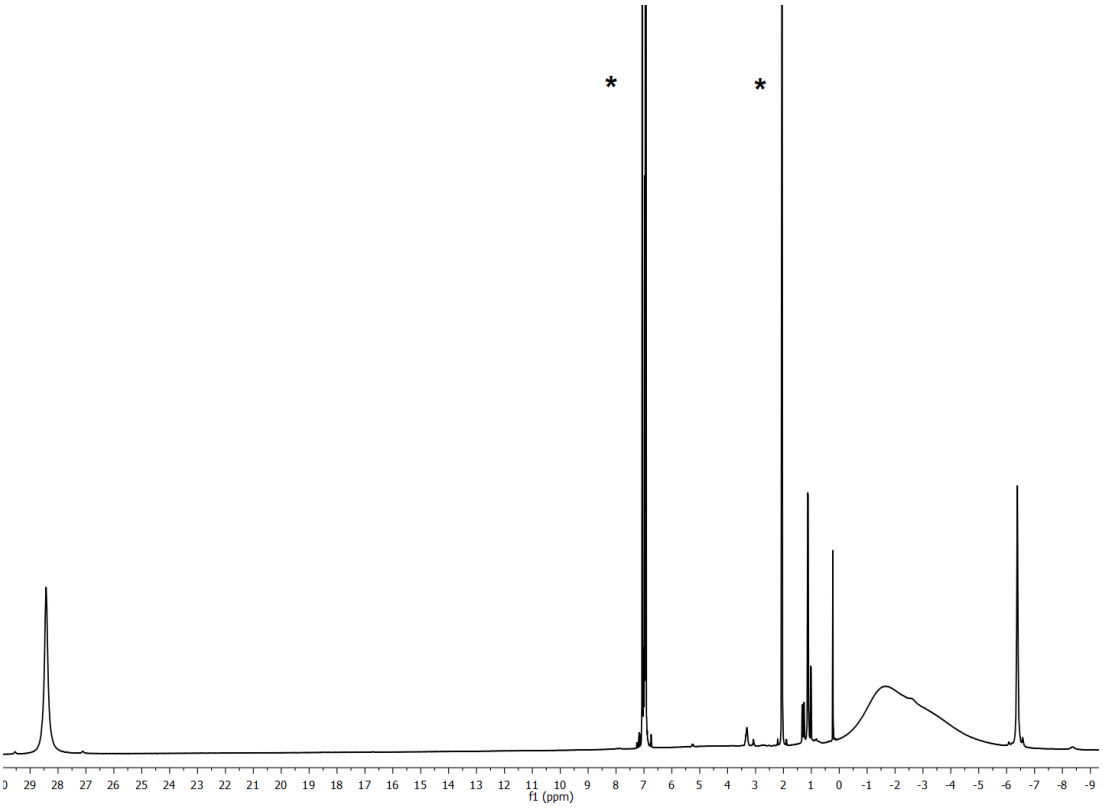

Fig. S9. ^{1}H NMR spectrum of **3** in toluene-d_8. The signals from solvent residuals are marked by asterisks.

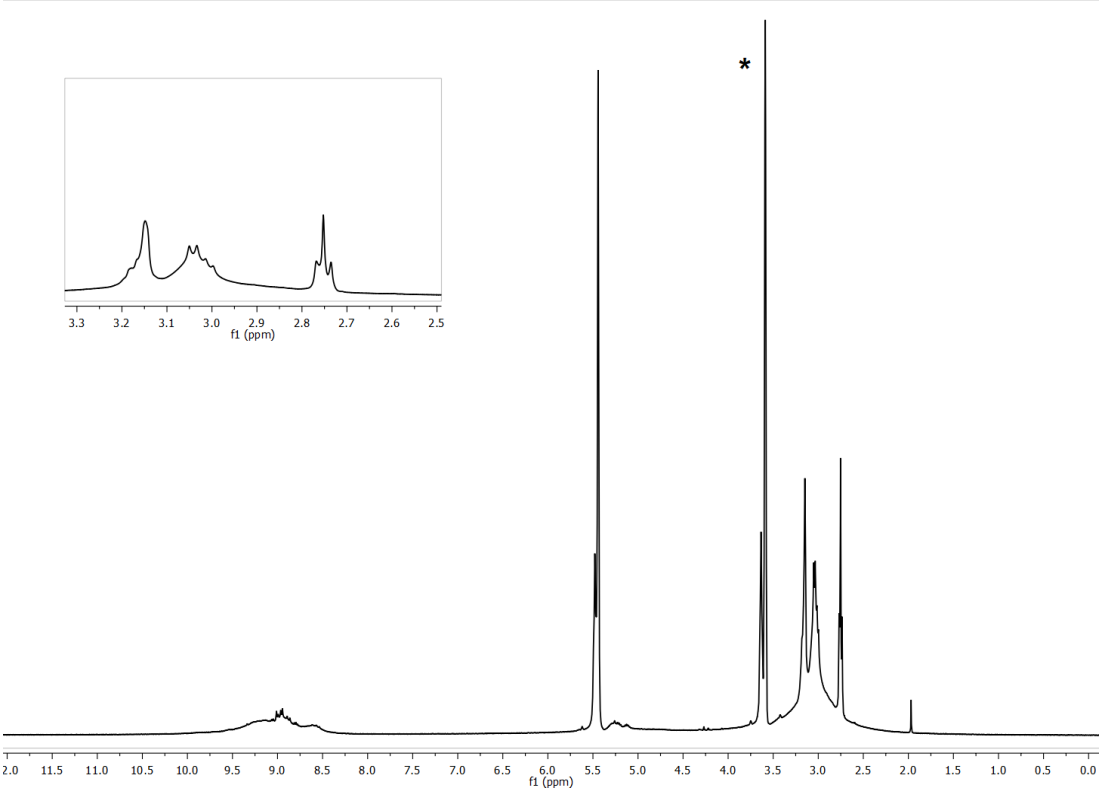

Fig. S10. ^{1}H NMR spectrum of **4** in THF-d_8. The signals from solvent residuals are marked by asterisks.

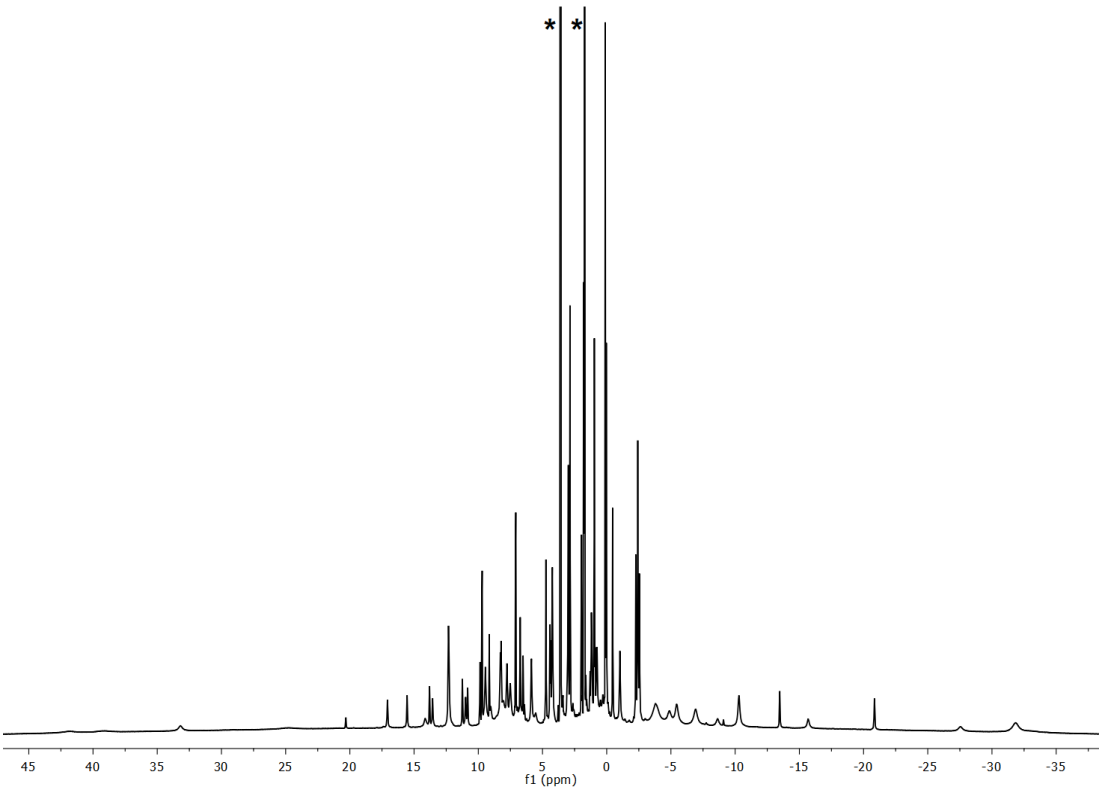

Fig. S11. ^{1}H NMR spectrum of **5** in THF-d_8. The signals from solvent residuals are marked by asterisks.

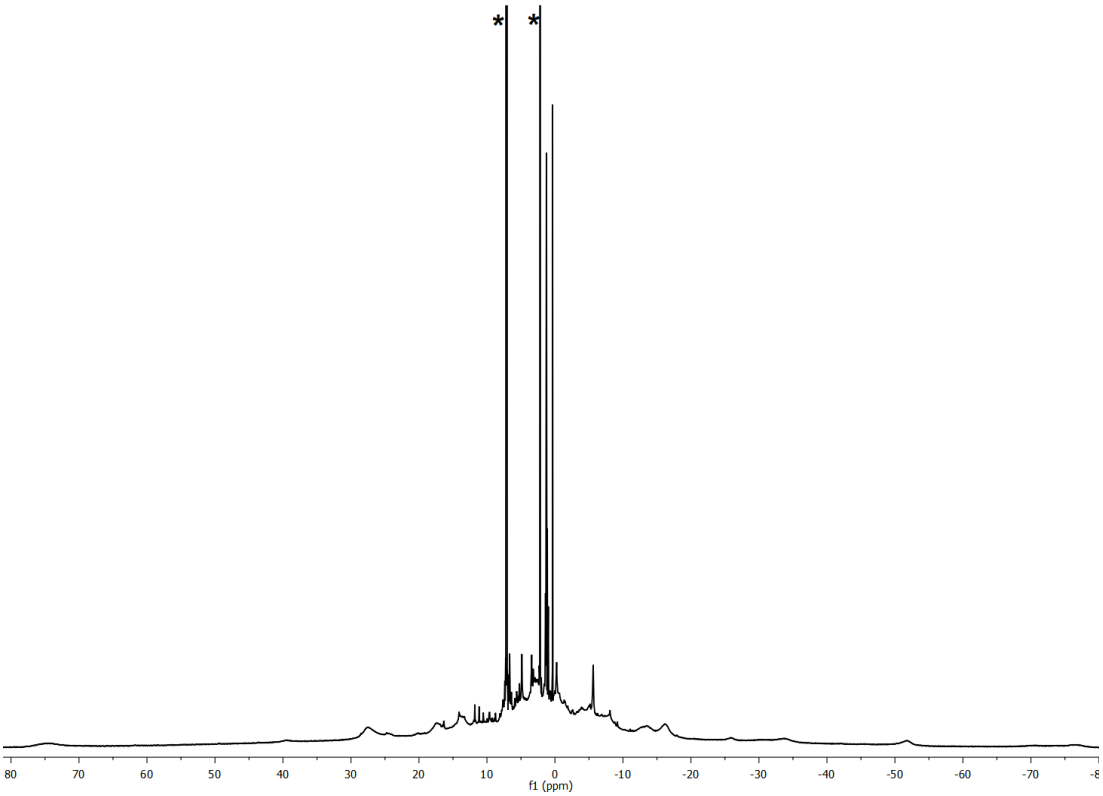

Fig. S12. ^{1}H NMR spectrum of **6** in toluene-d_8. The signals from solvent residuals are marked by asterisks.

3. X-Ray crystallographic data

3.1. Complex 1

Table S1. Crystal data and structure refinement for **1** (CCDC- 2175762).

Empirical formula	$C_{38}H_{46}N_4O_2V$	
Formula weight	641.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 9.479(5) Å	α = 108.573(5)°.
	b = 12.620(5) Å	β = 92.537(5)°.
	c = 15.960(5) Å	γ = 107.338(5)°.
Volume	1707.0(12) $Å^3$	
Z	2	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.329 mm^{-1}	
F(000)	682	
Crystal size	0.18 x 0.11 x 0.07 mm^3	
Theta range for data collection	2.278 to 26.994°.	
Index ranges	-11<=h<=12, -13<=k<=15, -20<=l<=18	
Reflections collected	13170	
Independent reflections	7355 [R(int) = 0.0220]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7355 / 0 / 412	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R_1[a] = 0.0376, wR_2[b] = 0.0867	
R indices (all data)	R1 = 0.0462, wR2 = 0.0926	
Largest diff. peak and hole	0.436 and -0.303 $e.Å^{-3}$	

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

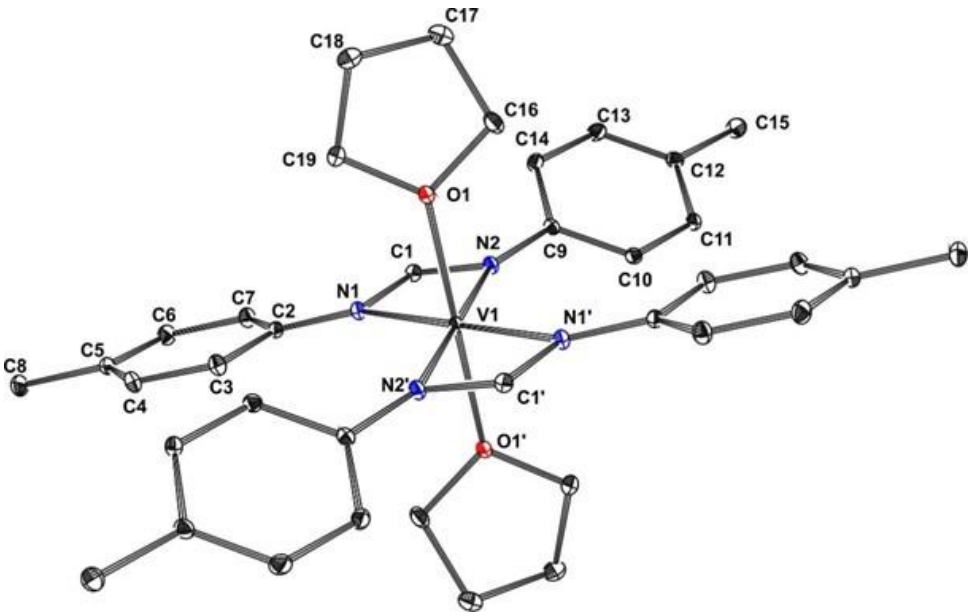

Fig. S13. The molecular structure of **1** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: (*-x+1,-y+1,-z+2*), (*x,-y+1,-z+1*).

Table S2. Selected intermolecular bond lengths [Å] and angles [°] for **1**.

V1-N1	2.1953(13)	N1-V1-N2	61.23(5)
V1-N2	2.1933(14)	N1-V1-O1	87.70(5)
V1-O1	2.1352(14)	N2-V1-O1	90.17(5)
N1-C1	1.324(2)	N1-V1-N1’	180.00(7)
N1-C2	1.4013(19)	N1-V1-N2’	118.77(5)
N2-C1	1.322(2)	N2-V1-N2’	180.00(7)
N2-C9	1.4039(19)	N2-V1-N1’	118.77(5)

3.2. Complex 2

Table S3. Crystal data and structure refinement for **2** (CCDC-2161489).

Empirical formula	$C_{54}H_{78}N_4OV_2$	
Formula weight	850.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 15.2867(3) Å	α = 90°.
	b = 14.7719(2) Å	β = 107.502(2)°.
	c = 25.4469(4) Å	γ = 90°.
Volume	5480.24(17) $Å^3$	
Z	4	
Density (calculated)	1.0304 Mg/m^3	
Absorption coefficient	0.218 mm^{-1}	
F(000)	1846	
Crystal size	0.19 x 0.13 x 0.05 mm^3	
Theta range for data collection	2.17 to 26.497°.	
Index ranges	-20<=h<=16, -20<=k<=19, -35<=l<=35	
Reflections collected	49808	
Independent reflections	11308 [R(int) = 0.0257]	
Completeness to theta = 25.242°	99.9 %	
Data / restraints / parameters	11308 / 0 / 557	
Goodness-of-fit on F^2	0.8625	
Final R indices [I>2sigma(I)]	R_1 = 0.0388, wR_2 = 0.1132	
R indices (all data)	R_1 = 0.0461, wR_2 = 0.1218	
Largest diff. peak and hole	0.552 and -0.310 $e.Å^{-3}$	

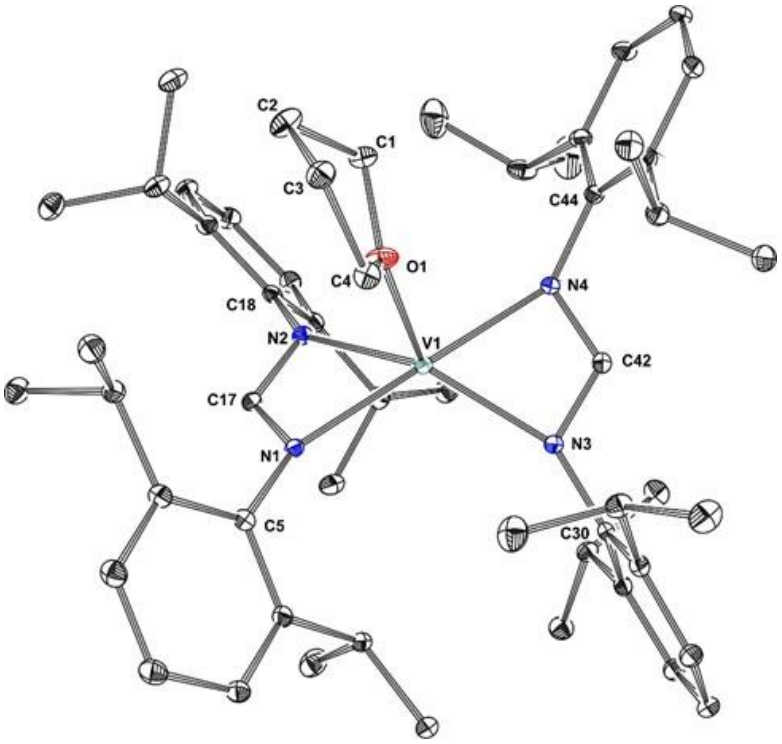

Fig. S14. The molecular structure of **2** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S4. Selected intermolecular bond lengths [Å] and angles [°] for **2**.

V1-O1	2.1242(11)	O1-V1-N1	90.10(5)
V1-N1	2.1601(12)	O1-V1-N2	126.97(5)
V1-N2	2.1332(12)	O1-V1-N3	92.24(5)
V1-N3	2.1638(12)	O1-V1-N4	91.36(5)
V1-N4	2.1628(11)	N1-V1-N2	63.36(4)
N1-C5	1.4209(17)	N1-V1-N3	117.06(5)
N1-C17	1.3176(18)	N1-V1-N4	178.45(4)
N2-C17	1.3371(18)	N2-V1-N3	140.26(5)
N2-C18	1.4277(17)	N2-V1-N4	116.03(4)
N3-C30	1.4276(18)	N3-V1-N4	62.37(4)
N3-C42	1.3257(18)		
N4-C42	1.3210(18)		
N4-C43	1.4190(17)		

3.3. Complex 3

Table S5. Crystal data and structure refinement for **3** (CCDC-2161490).

Formula weight	782.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 12.2223(8) Å	α = 90°.
	b = 16.0549(9) Å	β = 107.628(7)°.
	c = 12.3894(9) Å	γ = 90°.
Volume	2317.0(3) $Å^3$	
Z	2	
Density (calculated)	1.122 Mg/m^3	
Absorption coefficient	0.361 mm^{-1}	
F(000)	848	
Crystal size	0.14 x 0.09 x 0.03 mm^3	
Theta range for data collection	2.411 to 26.999°.	
Index ranges	-15<=h<=14, -19<=k<=19, -15<=l<=15	
Reflections collected	11640	
Independent reflections	7617 [R(int) = 0.0324]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7617 / 19 / 516	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R_1[a] = 0.0674, wR_2[b] = 0.1686	
R indices (all data)	R_1 = 0.0730, wR_2 = 0.1759	
Largest diff. peak and hole	1.493 and -0.718 e.$Å^{-3}$	

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

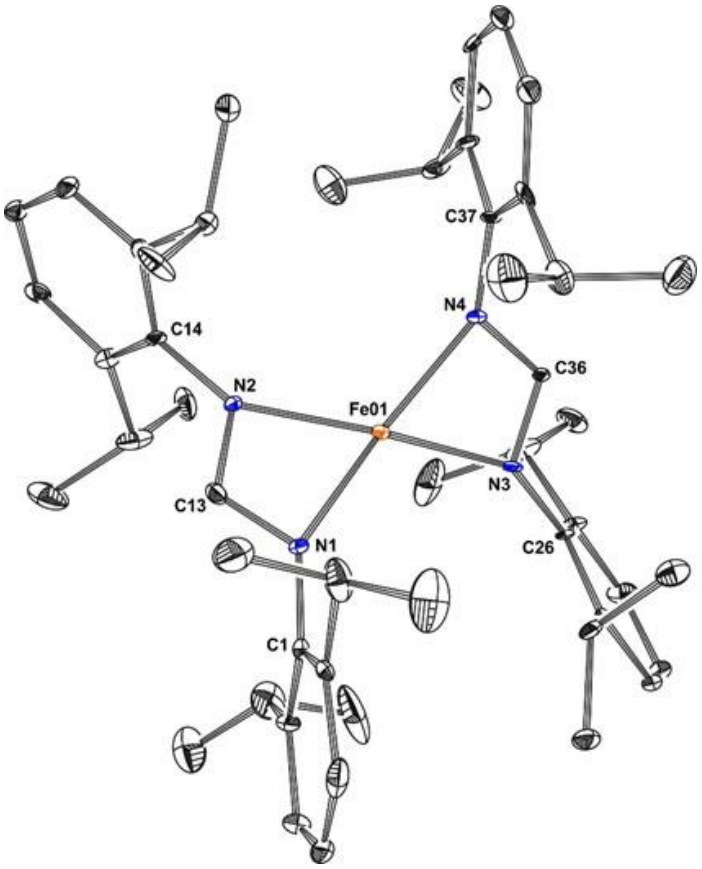

Fig. S15. The molecular structure of **3** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S6. Selected intermolecular bond lengths [Å] and angles [°] for **3**.

Fe1-N1	2.054(6)	N1-Fe1-N2	66.2(2)
Fe1-N2	2.034(5)	N1-Fe1-N3	117.2(2)
Fe1-N3	2.047(6)	N1-Fe1-N4	159.3(2)
Fe1-N4	2.044(6)	N2-Fe1-N3	158.9(2)
N1-C1	1.426(10)	N2-Fe1-N4	119.0(2)
N1-C13	1.325(9)	N3-Fe1-N4	66.0(2)
N2-C13	1.323(9)		
N2-C14	1.435(8)		
N3-C26	1.426(8)		
N3-C36	1.343(9)		
N4-C36	1.309(9)		
N4-C37	1.424(9)		

3.4. Complex 4

Table S7. Crystal data and structure refinement for **4** (CCDC-2161491).

Empirical formula	$C_{229}H_{324}N_{16}O_{20}V_4$	
Formula weight	3824.78	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 15.3254(4) Å	α = 90°.
	b = 48.4643(15) Å	β = 90.021(2)°.
	c = 15.4889(2) Å	γ = 90°.
Volume	11504.1(5) $Å^3$	
Z	2	
Density (calculated)	1.104 Mg/m^3	
Absorption coefficient	0.219 mm^{-1}	
F(000)	4124	
Crystal size	0.18 x 0.11 x 0.07 mm^3	
Theta range for data collection	2.479 to 26.499°.	
Index ranges	-12<=h<=16, -60<=k<=36, -19<=l<=5	
Reflections collected	25402	
Independent reflections	18423 [R(int) = 0.0285]	
Completeness to theta = 25.242°	77.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18423 / 36 / 1305	
Goodness-of-fit on F^2	1.108	
Final R indices [I>2sigma(I)]	R_1[a] = 0.0723, wR_2[b] = 0.1644	
R indices (all data)	R_1 = 0.0930, wR_2 = 0.1759	
Largest diff. peak and hole	0.621 and -0.452 $e.Å^{-3}$	

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

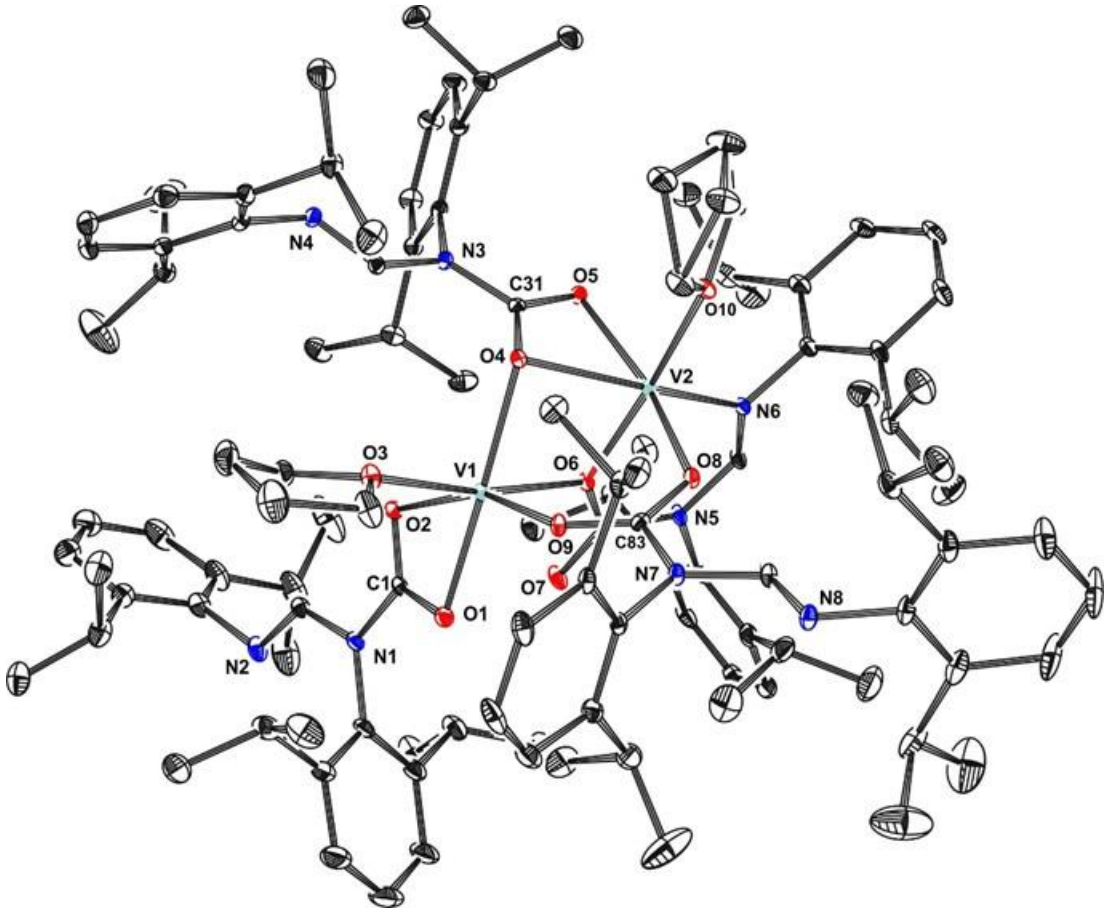

Fig. S16. The molecular structure of **4** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S8. Selected intermolecular bond lengths [Å] and angles [°] for **4**.

V1-O1	2.168(2)	O1-V1-O2	61.60(9)
V1-O2	2.126(2)	O1-V1-O3	86.75(9)
V1-O3	2.177(2)	O1-V1-O4	114.72(9)
V1-O4	2.203(2)	O1-V1-O6	94.26(8)
V1-O6	2.146(2)	O1-V1-O9	157.55(10)
V1-O9	2.087(2)	O2-V1-O3	90.70(10)
V2-O4	2.214(2)	O2-V1-O4	176.07(9)
V2-O5	2.153(2)	O2-V1-O6	99.10(9)
V2-O8	2.093(2)	O2-V1-O9	96.34(10)
V2-N6	2.102(3)	O3-V1-O4	90.42(9)
		O3-V1-O6	169.36(10)
		O3-V1-O9	89.58(9)
		O4-V1-O6	79.53(8)
		O4-V1-O9	87.43(9)

	O6-V1-O9	93.40(9)
	O4-V2-O5	60.90(9)
	O4-V2-O8	102.50(9)
	O4-V2-O10	92.64(8)
	O4-V2-N6	155.42(9)
	O5-V2-O8	163.01(9)
	O5-V2-O10	89.28(9)
	O5-V2-N6	98.82(10)
	O6-V2-O4	81.06(8)
	O6-V2-O5	91.39(9)
	O6-V2-O8	89.25(9)
	O6-V2-O10	172.36(9)
	O6-V2-N6	86.07(9)
	O8-V2-O10	87.90(9)
	O8-V2-N6	98.16(11)

3.5. Complex 5

Table S9. Crystal data and structure refinement for **5** (CCDC- 2161492).

Empirical formula	$C_{221}H_{304}Fe_4N_{16}O_{14}$	
Formula weight	3632.18	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.00932(15) Å	α = 90°.
	b = 64.6462(8) Å	β = 92.0129(11) °.
	c = 25.1469(3) Å	γ = 90°.
Volume	22760.2(5) $Å^3$	
Z	4	
Density (calculated)	1.060 Mg/m^3	
Absorption coefficient	0.307 mm^{-1}	
F(000)	7832	
Crystal size	021 x 0.13 x 0.07 mm^3	
Theta range for data collection	2.350 to 28.249 °.	
Index ranges	-17<=h<=18, -85<=k<=43, -33<=l<=27	
Reflections collected	96823	
Independent reflections	50059 [R(int) = 0.0405]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	50059 / 87 / 2387	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R_1[a] = 0.0755, wR_2[b] = 0.1411	
R indices (all data)	R_1 = 0.0965, wR_2 = 0.1490	
Largest diff. peak and hole	0.824 and -0.857 $e.Å^{-3}$	

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

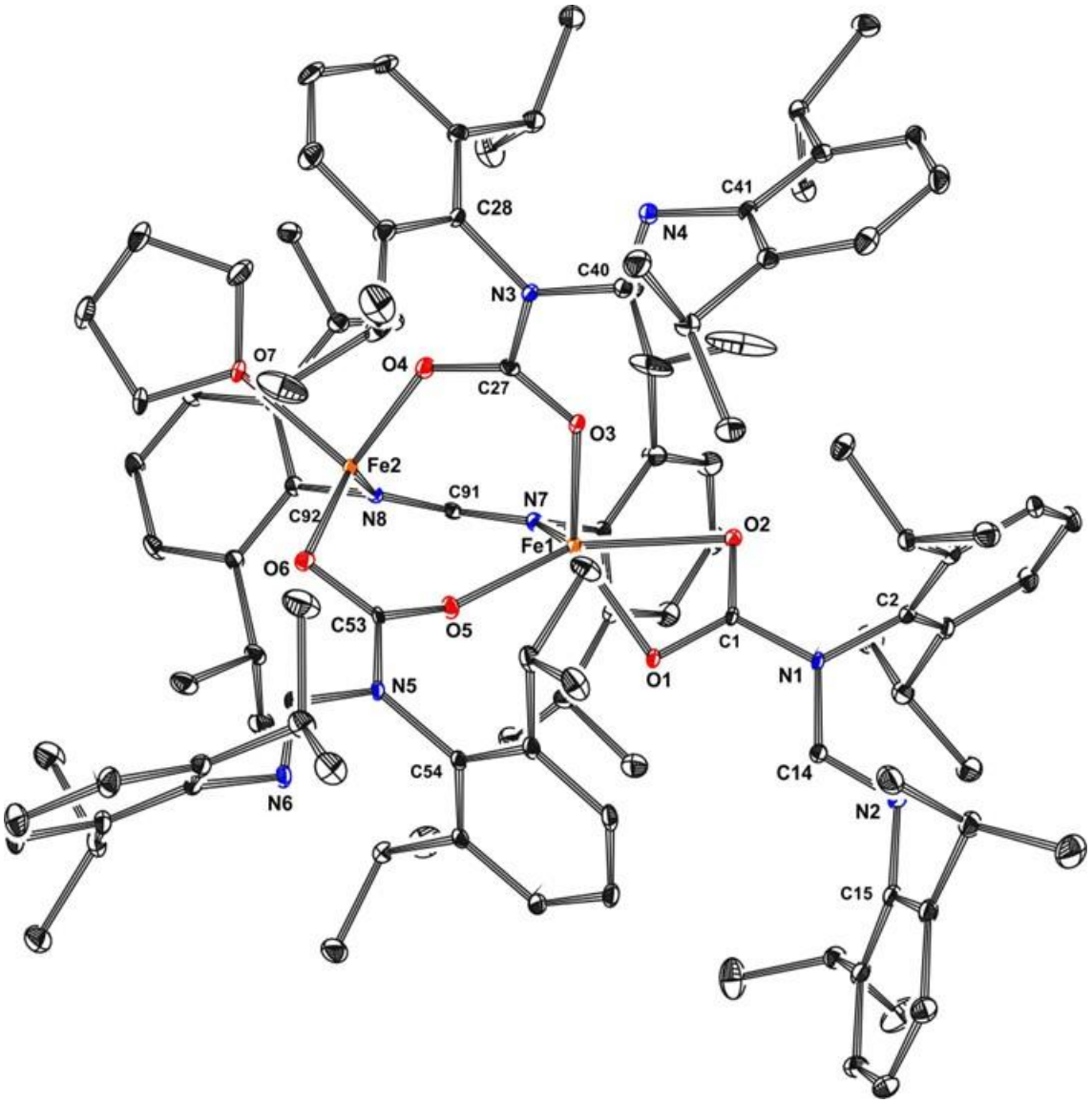

Fig. S17. The molecular structure of **5** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S10. Selected intermolecular bond lengths [Å] and angles [°] for **5**.

Fe1-O1	2.0463(19)	O1-Fe1-O2	61.11(7)
Fe1-O2	2.273(2)	O1-Fe1-O3	116.57(8)
Fe1-O3	2.047(2)	O1-Fe1-O5	89.83(8)
Fe1-O5	2.111(2)	O1-Fe1-N7	125.58(9)
Fe1-N7	2.065(3)	O2-Fe1-O3	89.32(8)
Fe2-O4	1.986(2)	O2-Fe1-O5	149.79(7)
Fe2-O6	2.0227(19)	O2-Fe1-N7	100.82(8)
Fe2-O7	2.090(2)	O3-Fe1-O5	97.48(8)
Fe2-N8	1.993(2)	O3-Fe1-N7	113.70(8)
		O5-Fe1-N7	103.19(9)

	O4-Fe2-O6	105.59(9)
	O4-Fe2-O7	86.71(8)
	O4-Fe2-N8	120.12(9)
	O6-Fe2-O7	101.22(8)
	O6-Fe2-N8	128.10(9)
	O7-Fe2-N8	104.44(9)

3.6. Complex 6

Table S11. Crystal data and structure refinement for **6** (CCDC-2161493).

Empirical formula	$C_{141}H_{204}Fe_2N_{10}O_8$	
Formula weight	2278.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1/n	
Unit cell dimensions	a = 21.550(5) Å	α = 90.000(5)°.
	b = 29.745(5) Å	β = 92.430(5)°.
	c = 22.858(5) Å	γ = 90.000(5)°.
Volume	14639(5) $Å^3$	
Z	4	
Density (calculated)	1.034 Mg/m^3	
Absorption coefficient	0.251 mm^{-1}	
F(000)	4944	
Crystal size	0.16 x 0.11 x 0.08 mm^3	
Theta range for data collection	2.410 to 26.500°.	
Index ranges	-27<=h<=19, -27<=k<=37, -18<=l<=28	
Reflections collected	256608	
Independent reflections	30281 [R(int) = 0.0577]	
Completeness to theta = 25.242°	99.8 %	
Data / restraints / parameters	30281 / 92 / 1494	
Goodness-of-fit on F^2	1.0676	
Final R indices [I>2sigma(I)]	R_1 = 0.0516, wR_2 = 0.1198	
R indices (all data)	R_1 = 0.0736, wR_2 = 0.1356	
Largest diff. peak and hole	0.5997and - 0.6588 e.$Å^{-3}$	

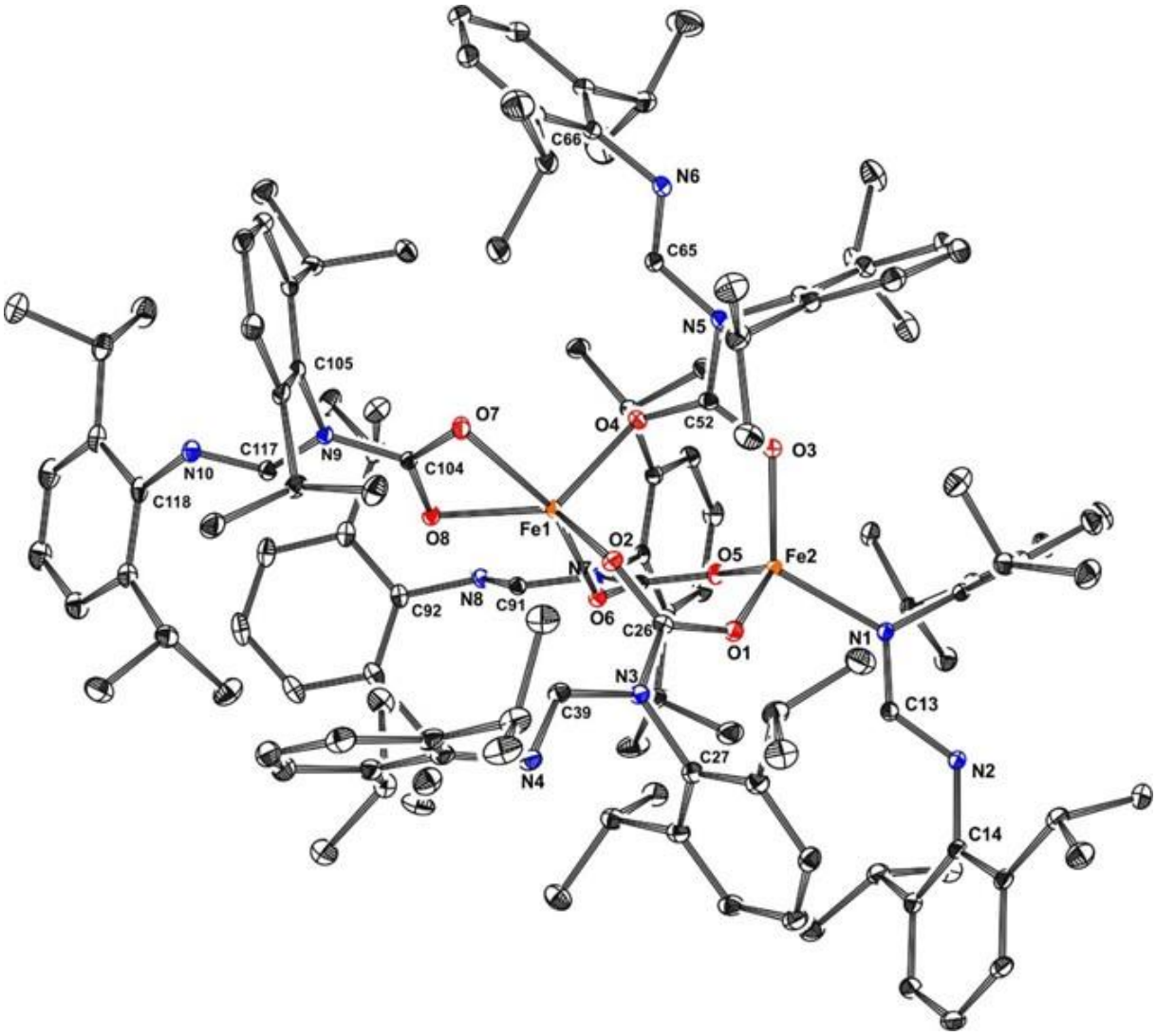

Fig. S18. The molecular structure of **6** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S12. Selected intermolecular bond lengths [Å] and angles [°] for **6**.

Fe1-O2	2.0069(15)	O2-Fe1-O4	99.72(6)
Fe1-O4	2.0242(15)	O2-Fe1-O6	92.94(6)
Fe1-O6	2.0555(15)	O2-Fe1-O7	100.42(6)
Fe1-O7	2.1708(16)	O2-Fe1-O8	131.32(6)
Fe1-O8	2.0721(15)	O4-Fe1-O6	96.76(6)
Fe2-O1	1.9964(15)	O4-Fe1-O7	97.93(6)
Fe2-O3	1.9916(15)	O4-Fe1-O8	126.47(6)
Fe2-O5	2.0055(15)	O6-Fe1-O7	158.14(6)
Fe2-N1	2.0691(17)	O6-Fe1-O8	95.64(6)
		O7-Fe1-O8	62.55(6)
		O1-Fe2-O3	104.05(6)
		O1-Fe2-O5	122.80(6)

	O1-Fe2-N1	93.48(6)
	O3-Fe2-O5	106.97(6)
	O3-Fe2-N1	119.67(7)
	O5-Fe2-N1	110.32(6)

4. Analysis of coordination sphere geometry for 1-6

Table S13. Analysis of the coordination sphere geometry of V(II) centre in **1** using the continuous shape measurement (CShM).

Metal centre	SHAPE (CShM)*				
	Hexagon (D_{6h})	Pentagonal pyramid (C_{5v})	Octahedron (O_h)	Trigonal prism (D_{3h})	Johnson pentagonal pyramid J2 (C_{5v})
V1	23.080	26.938	4.223	16.668	29.107
V2	23.158	26.734	4.074	16.815	28.814

* lower values indicate better fit to given geometry[1–3]

Table S14. Analysis of the coordination sphere geometry of V(II) centre in **2** using the continuous shape measurement (CShM).

Metal centre	SHAPE (CShM)*				
	Pentagon (D_{5h})	Vacant octahedron (C_{4v})	Trigonal bipyramid (D_{3h})	Spherical square pyramid (C_{4v})	Johnson trigonal bipyramid J12 (D_{3h})
V1	22.954	8.813	6.640	8.164	8.808

* lower values indicate better fit to given geometry[1–3]

Table S15. Analysis of the coordination sphere geometry of Fe(II) centre in **3** using the continuous shape measurement (CShM).

Metal centre	SHAPE (CShM)*			
	Square (D_{4h})	Tetrahedron (T_d)	Seesaw (C_{2v})	Vacant trigonal bipyramid (C_{3v})
Fe1	8.524	21.609	13.665	23.868

* lower values indicate better fit to given geometry[1–3]

Table S16. Analysis of the coordination sphere geometry of V(II) centres in **4** using the continuous shape measurement (CShM).

Metal centre	SHAPE (CShM)*				
	Hexagon (D_{6h})	Pentagonal pyramid (C_{5v})	Octahedron (O_h)	Trigonal prism (D_{3h})	Johnson pentagonal pyramid J2 (C_{5v})
V1	27.386	21.592	2.860	12.613	24.988
V2	30.275	21.362	2.310	13.081	25.677

* lower values indicate better fit to given geometry[1–3]

Table S17. Analysis of the coordination sphere geometry of Fe(II) centres in **5** using the continuous shape measurement (CShM).

Metal centre	SHAPE (CShM)*				
	Pentagon (D_{5h})	Vacant octahedron (C_{4v})	Trigonal bipyramid (D_{3h})	Spherical square pyramid (C_{4v})	Johnson trigonal bipyramid J12 (D_{3h})
Fe1	31.151	7.552	3.112	4.531	5.322
Fe3	30.067	7.081	3.550	3.728	5.877
	Square (D_{4h})	Tetrahedron (T_d)	Seesaw (C_{2v})	Vacant trigonal bipyramid (C_{3v})	
Fe2	31.258	1.868	6.826	1.554	
Fe4	32.995	1.575	6.228	1.254	

* lower values indicate better fit to given geometry[1–3]

Table S18. Analysis of the coordination sphere geometry of Fe(II) centres in **6** using the continuous shape measurement (CShM).

Metal centre	SHAPE (CShM)*				
	Pentagon (D_{5h})	Vacant octahedron (C_{4v})	Trigonal bipyramid (D_{3h})	Spherical square pyramid (C_{4v})	Johnson trigonal bipyramid J12 (D_{3h})
Fe1	27.815	6.303	3.683	4.602	5.964
	Square (D_{4h})	Tetrahedron (T_d)	Seesaw (C_{2v})	Vacant trigonal bipyramid (C_{3v})	
Fe2	24.047	1.439	6.591	3.677	

* lower values indicate better fit to given geometry[1–3]

5. TGA measurement and analysis for compound 6.

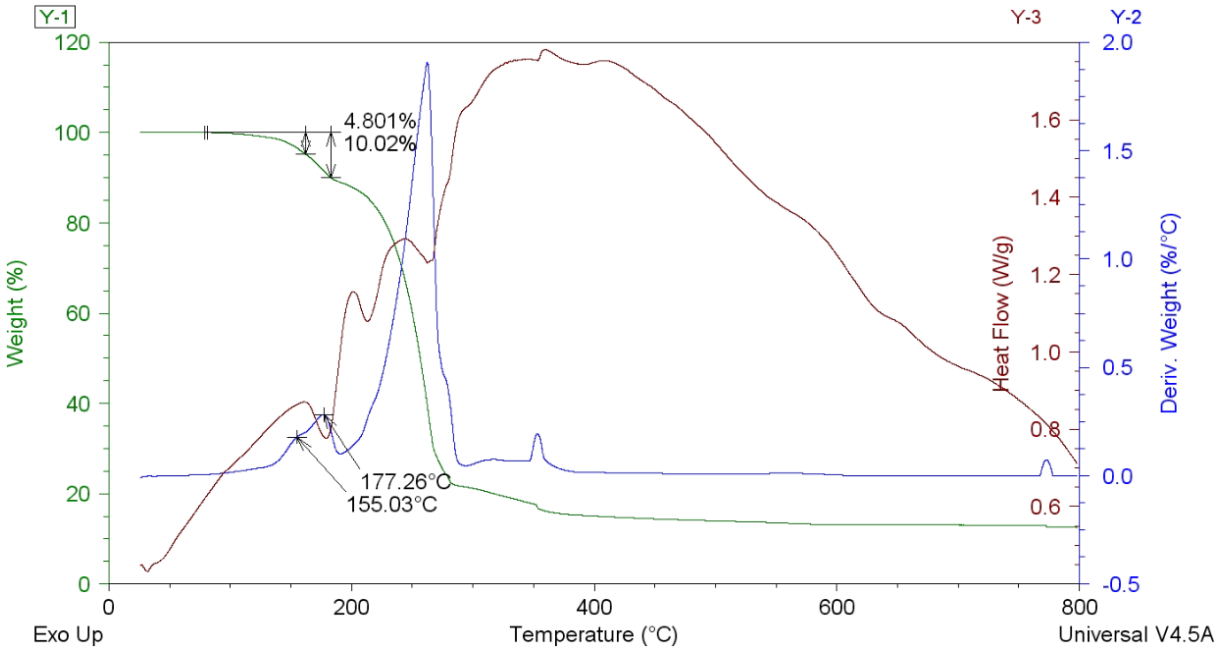

Fig. S19. TGA measurement data and analysis for **6**.

6. References

1 H. Zabrodsky, S. Peleg and D. Avnir, *J. Am. Chem. Soc.*, 1992, **114**, 7843–7851.

2 M. Pinsky and D. Avnir, *Inorg. Chem.*, 1998, **37**, 5575–5582.

3 M. LLunell, D. Casanova, J. Cierera, P. Alemany and S. Alvarez, *SHAPE*, v. 2.1.