Electronic Supplementary Information (ESI)

Vapour- and solvent-mediated crystalline transformations in Mo(VI) hydrazone complexes controlled by noncovalent interactions

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1. Crystallographic data

Table S1. Crystallographic data for compounds $[MoO_2(L)]_n$ (**1**), $[MoO_2(L)(MeOH)]$ (**2α**, **2β**, and **2γ**), and $[MoO_2(L)(H_2O)]$ (**2w-α**).

Compound	**1**	**2α**	**2β**	**2γ**	**2w-α**
Formula	$C_{14}H_{11}MoN_3O_5$	$C_{15}H_{15}MoN_3O_6$	$C_{15}H_{15}MoN_3O_6$	$C_{15}H_{15}MoN_3O_6$	$C_{14}H_{13}MoN_3O_6$
Formula weight	397.20	429.24	429.24	429.24	415.21
Space group	*P bca*	*P* -1	*P* -1	*P* -1	*P* -1
a/Å	8.0702(3)	6.6351(3)	7.2390(3)	7.6639(4)	6.6377(4)
b/Å	10.9452(4)	7.6159(3)	10.6694(4)	9.7687(4)	10.1622(6)
c/Å	31.8143(12)	16.3967(8)	11.8410(4)	11.6636(4)	11.6931(6)
α/°	90	91.525(3)	106.795(3)	76.424(3)	97.524(5)
β/°	90	93.644(4)	95.133(3)	76.154(4)	94.078(4)
γ/°	90	95.790(3)	104.217(3)	89.268(6)	93.698(5)
V/Å^3	2810.16(18)	822.21(6)	835.94(6)	823.28(6)	777.80(8)
D_{calc}/g cm^{-3}	1.878	1.734	1.705	1.732	1.773
μ/mm^{-1}	0.965	0.836	0.822	0.835	0.880
F(000)	1584	432	432	432	416
Θ range/°	4.2-27.0	4.3-27.0	4.2-27.0	4.2-27.0	4.2-27.0
T/K	150	293	150	150	293
Radiation wavelength	0.71073	0.71073	0.71073	0.71073	0.71073
Range of *h*, *k*, *l*	-10-8, -13-12,-39-40	-8-8, -9-9, -20-20	-9-9, -13-13, -15-15	-9-9, -12-12, -14-14	-8-8, -12-12, -14-14
Reflections collected	10923	7686	14008	13777	12804
Independent	3048	3576	3630	3580	3364
Observed reflections	2522	3318	3290	3246	2794
R_{int}	0.034	0.028	0.029	0.039	0.071
R^a, $wR^b[I \geq 2\sigma(I)]$	0.0298, 0.0714	0.0301, 0.0749	0.0231, 0.0559	0.0246, 0.0612	0.0565, 0.1319
Goodness-of-fit, S^c	1.06	1.04	1.05	1.07	1.13
No. of parameters	208	230	227	231	223
No. of restraints	0	0	0	0	0
$\Delta\rho_{min}$, $\Delta\rho_{max}$	-0.34, 0.48	-0.73, 0.79	-0.32, 0.23	-0.38, 0.56	-0.68, 0.93

[a] $R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$; [b] $wR = [\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; [c] $S = \Sigma[w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$

Table S2. Crystallographic data for compounds $[MoO_2(HL)(MeOH)]Cl$ (**3**), $[MoO_2(HL)(MeOH)]Br$ (**4**), $[MoO_2(HL)(MeOH)]NO_3 \cdot MeOH$ (**5·MeOH**), and $[MoO_2(HL)(MeOH)]MeOSO_3$ (**6**).

Compound	**3**	**4**	**5·MeOH**	**6**
Formula	$C_{15}H_{16}MoN_3O_6,Cl$	$C_{15}H_{16}MoN_3O_6,Br$	$C_{15}H_{16}MoN_3O_6$, NO_3, CH_4O	$C_{15}H_{16}MoN_3O_6$, CH_3OSO_3
Formula weight	465.70	510.15	524.30	541.34
Space group	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1$	$P\,2_1$
a/Å	8.9395(4)	8.9754(2)	7.6699(2)	7.2340(3)
b/Å	12.0713(4)	12.0144(9)	13.2183(3)	13.8890(6)
c/Å	16.8359(6)	16.8807(6)	10.0377(2)	10.4510(5)
α/°	90	90	90	90
β/°	95.768(4)	96.192(3)	92.579(2)	100.841(4)
γ/°	90	90	90	90
V/Å^3	1807.59(12)	1809.69(16)	1016.62(4)	1031.30(8)
D_{calc}/g cm^{-3}	1.711	1.872	1.713	1.743
μ/mm^{-1}	0.910	2.970	0.708	0.797
F(000)	936	1008	532	548
Θ range/°	3.9-27.0	4.2-29.0	4.5-27.0	4.2-27.0
T/K		150	150	150
Radiation wavelength	0.71073	0.71073	0.71073	0.71073
Range of h, k, l	-8-11, -15-15, -21-21	-12-11, -16-14, -22-13	-9-9, -16-16, -12-12	-9-9, -17-17, -13-13
Reflections collected	15313	10292	4901	7173
Independent reflections	3928	4235	3476	4281
Observed reflections ($I \geq 2\sigma$)	2601	3747	3402	4216
R_{int}	0.041	0.022	0.016	0.017
R^a, $wR^b[I \geq 2\sigma(I)]$	0.0289, 0.0530	0.0260, 0.0562	0.0204, 0.0507	0.0207, 0.0511
Goodness-of-fit, S^c	0.84	1.04	1.08	1.05
No. of parameters	243	239	289	290
No. of restraints	0	0	0	0
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	-0.26, 0.29	-0.41, 0.45	-0.54, 0.26	-0.26, 0.78

[a] $R = \Sigma \left|\left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$; [b] $wR = [\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; [c] $S = \Sigma[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$

Table S3. Selected bond lengths (Å) and angles (°) for compounds **1**, **2α**, **2β**, **2γ**, and **2w-α.**

	1	**2α**	**2β**	**2γ**	**2w-α**
Mo1−O1	1.7037(17)	1.7053(18)	1.6856(16)	1.7039(15)	1.701(3)
Mo1−O2	1.690(2)	1.6982(17)	1.6990(16)	1.6967(16)	1.687(4)
Mo1−O3	1.9252(18)	1.9394(16)	1.9263(14)	1.9165(15)	1.917(4)
Mo1−O4	2.0258(17)	2.0122(17)	2.0140(14)	2.0123(15)	1.998(4)
Mo1−O6	-	2.3387(17)	2.3594(15)	2.3775(15)	2.322(4)
Mo1−N1	2.241(2)	2.219(2)	2.2459(15)	2.2464(17)	2.213(4)
Mo1−N3^{i}	2.459(2)	-	-	-	-
C1–N1	1.300(3)	1.284(3)	1.284(3)	1.298(3)	1.266(6)
C2–N2	1.291(3)	1.290(3)	1.293(3)	1.305(3)	1.286(7)
N1–N2	1.413(3)	1.399(3)	1.397(2)	1.400(2)	1.411(6)
O1−Mo1−O2	105.79(9)	105.25(9)	104.99(8)	106.13(7)	105.55(16)
O1−Mo1−O3	104.28(9)	100.82(7)	100.24(8)	103.05(7)	101.15(17)
O1−Mo1−O4	95.99(9)	98.32(8)	97.17(7)	96.16(7)	98.30(17)
O1−Mo1−O6	-	84.26(7)	171.02(7)	84.36(6)	85.09(16)
O1−Mo1−N1	159.57(10)	157.88(7)	94.65(7)	156.50(7)	159.25(17)
O1−Mo1−N3^{i}	83.24(9)	-	-	-	-
O2−Mo1−O3	99.59(9)	99.24(8)	104.33(7)	101.00(7)	98.38(17)
O2−Mo1−O4	98.27(8)	95.96(8)	95.39(7)	96.32(7)	95.67(17)
O2−Mo1−O6	-	170.29(8)	83.59(6)	168.77(7)	169.27(16)
O2−Mo1−N1	92.44(8)	95.78(8)	157.95(7)	95.53(7)	94.11(17)
O2−Mo1−N3^{i}	170.25(8)	-	-	-	-
O3−Mo1−O4	148.07(7)	151.40(7)	149.18(6)	149.27(6)	151.92(14)
O3−Mo1−O6	-	80.54(6)	79.78(6)	80.03(6)	80.63(15)
O3−Mo1−N1	81.12(7)	82.14(6)	81.45(6)	81.14(6)	82.10(15)
O3−Mo1−N3^{i}	81.32(7)	-	-	-	-
O4−Mo1−O6	-	80.46(6)	79.15(6)	78.23(6)	81.07(14)
O4−Mo1−N1	71.85(7)	72.31(7)	71.92(6)	72.03(6)	72.73(15)
O4−Mo1−N3^{i}	76.80(7)	-	-	-	-
N1−Mo1−N3^{i}	78.07(8)	-	-	-	-
O6−Mo1−N1	-	74.55(6)	76.44(5)	73.50(6)	75.16(16)

^{i} 2-*x*,1/2+*y*,1/2-*z*

Table S4. Selected bond lengths (Å) and angles (°) for compounds **3**, **4**, **5·MeOH**, and **6**.

	3	**4**	**5·MeOH**	**6**
Mo1−O1	1.6847(18)	1.6926(17)	1.694(2)	1.709(2)
Mo1−O2	1.7030(16)	1.7113(16)	1.708(2)	1.695(2)
Mo1−O3	1.9220(17)	1.9245(17)	1.926(2)	1.920(2)
Mo1−O4	2.0132(16)	2.0100(16)	2.025(2)	2.011(2)
Mo1−O6	2.3216(18)	2.3301(17)	2.329(2)	2.302(3)
Mo1−N1	2.2275(19)	2.2277(18)	2.228(3)	2.244(3)
C1–N1	1.296(3)	1.297(3)	1.294(4)	1.298(4)
C2–N2	1.293(3)	1.293(3)	1.297(4)	1.289(4)
N1–N2	1.397(3)	1.399(3)	1.396(4)	1.404(4)
O1−Mo1−O2	105.87(8)	106.01(8)	106.32(11)	105.10(11)
O1−Mo1−O3	100.54(8)	101.02(8)	99.50(10)	103.75(10)
O1−Mo1−O4	94.74(8)	94.75(8)	97.12(9)	96.76(9)
O1−Mo1−O6	170.09(8)	170.44(7)	170.88(10)	81.86(10)
O1−Mo1−N1	93.95(8)	94.20(8)	95.16(10)	154.95(11)
O2−Mo1−O3	102.23(8)	102.22(7)	103.95(9)	99.15(13)
O2−Mo1−O4	97.26(7)	97.04(7)	95.21(9)	95.08(12)
O2−Mo1−O6	82.96(8)	82.41(7)	82.02(10)	171.99(11)
O2−Mo1−N1	158.47(8)	158.04(7)	156.38(10)	98.29(11)
O3−Mo1−O4	150.78(7)	150.53(7)	149.83(9)	150.93(9)
O3−Mo1−O6	81.58(7)	81.21(7)	81.67(10)	82.75(11)
O3−Mo1−N1	81.87(7)	81.79(7)	81.54(10)	80.90(10)
O4−Mo1−O6	79.42(6)	79.46(6)	78.14(10)	79.97(10)
O4−Mo1−N1	72.30(7)	72.30(7)	72.01(10)	72.01(10)
O6−Mo1−N1	76.70(7)	76.84(6)	76.01(9)	74.25(10)

Table S5. Angle between phenyl and pyridyl moieties, φ (°), angle between the five and six-membered chelate rings, ψ (°), and dihedral angle C14–O5–C11–C12, ϕ (°), for investigated compounds.

	φ (°)	ψ (°)	ϕ (°)
1	58.06(12)	11.06(9)	-175.9(2)
2α	5.53(11)	8.43(8)	-8.0(3)
2β	7.54(10)	8.21(7)	179.83(18)
2γ	22.97(11)	7.13(8)	4.5(3)
2w-α	3.2(3)	6.75(18)	6.9(9)
3	8.13(12)	5.39(9)	0.5(4)
4	10.35(11)	6.14(8)	1.6(3)
5·MeOH	3.55(15)	6.91(11)	-5.8(5)
6	4.41(16)	5.62(12)	2.9(5)

Table S6. Geometry of intermolecular hydrogen bonds (Å, °) and π···π interactions involved in the formation of dimers and between neighbouring dimer for compounds **2α**, **2β**, **2γ**, and **2w-α**.

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A(°)
	O6−H61···N3[a]	0.84(2)	1.88(2)	2.715(3)	173.2(17)
	C1−H1···O2[b]	0.93	2.34	3.263(3	171
2α	C5−H5···O1[c]	0.93	2.38	3.282(3)	162
	C10−H10···O2[d]	0.93	2.50	3.242(3)	137
	C14−H14a···O1[e]	0.96	2.52	3.374(5)	148
	π···π	Cg3···Cg3[a] /Å	Slipage		
		3.6539(14)	1.360		
		Cg4···Cg4[d]Å	Slipage		
		3.6063(13)	1.225		
		Cg2···Cg4[d]Å	Slipage		
		3.8719(12)	1.874		
	O6−H61···N3[f]	0.827(13)	1.891(15)	2.715(2)	174(2)
2β	C6−H6···O5[f]	0.93	2.59	3.370(2)	141
	C14−H14a···O2[h]	0.96	2.49	3.149(3)	126
	π···π	Cg3···Cg3[i] /Å	Slipage		
		3.7510(11)	1.718		
		Cg3···Cg4[c]/Å			
		3.8209(12)			
	O6−H6···N3[j]	0.830(14)	1.884(14)	2.708(2)	172.1(16)
2γ	C10−H10···O5[k]	0.93	2.56	3.461(3)	163
	O6−H1w···N3[l]	0.85	1.90	2.730(7)	166
	O6−H2w···O1[m]	0.85(6)	1.96(6)	2.792(6)	169(5)
	C1−H1···O2[n]	0.93	2.28	3.203(6)	170
	C10−H10···O2[i]	0.93	2.55	3.328(7)	142
2w-α	π···π	Cg3···Cg3[l] /Å	Slipage		
		3.595(4)	1.286		
		Cg3···Cg4[o] /Å	Slipage		
		3.606(3)	1.120		
		Cg4···Cg3[o] /Å	Slipage		
		3.606(3)[l]	1.214		
		Cg4···Cg4[m]	Slipage		
		3.687(3)	1.336		

[a]1-x,1-y,-z; [b]1+x,y,z; [c]-x,1-y,-z; [d]1-x,1-y,1-z; [e]-x,-y,1-z; [f]-1-x,-y,-z; [g]-1+x,-1+y,-1+z; [i] 1-x,1-y,-z ; [j] x,1+y,z; [k] 2-x,2-y,-z; [l]x, 1+y,z; [m]1-x,-y,1-z; [m] 2-x,1-y,1-z;[n]-1+x,y,z; [o] x,-1+y,z

Table S7. Geometry of intermolecular hydrogen bonds (Å, °) and π···π interactions for compounds **3**, **4**, **5·MeOH** and **6.**

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A(°)
	N3−H3···Cl1	0.86	2.16	2.970(2)	158
	O6−H61···Cl1[a]	0.825(17)	2.236(17)	3.0550(19)	171.7(15)
	C4−H4···O4	0.93	2.46	2.774(3)	100.00
3	C5−H5···O5[b]	0.93	2.45	3.354(3)	165
	C6−H6···O2[c]	0.93	2.47	3.119(3)	127
	C10−H10···Cl1[d]	0.93	2.76	3.596(3)	151
	C14−H14b···Cl1[e]	0.96	2.68	3.638(3)	174
	C15−H15c···O1[f]	0.96	2.56	2.971(3)	106
	π···π	Cg3···Cg3[a] /Å	Slippage		
		3.7814(15)	1.844		
	N3−H3···Br1[a]	0.86	2.32	3.128(2)	156
	O6−H61···Br1	0.83(2)	2.38(2)	3.2053(16)	169.7(18)
	C1−H1···O1[g]	0.93	2.60	3.268(3)	130
	C4−H4···O3[h]	0.93	2.58	3.387(3)	145
	C5−H5···O5[b]	0.93	2.44	3.339(3)	162
4	C6−H6···O2[i]	0.93	2.40	3.092(3)	131
	C10−H10···Br1[j]	0.93	2.84	3.644(3)	145
	C14−H14a···O2[h]	0.96	2.55	3.493(3)	168
	C14−H14b···Br1[k]	0.96	2.75	3.693(2)	168
	π···π	Cg3···Cg3[i] /Å	Slippage		
		3.8141(12)	1.936		
	N3−H3···O8[m]	0.86	1.87	2.729(4)	175
	N3−H3···O10[m]	0.86	2.58	3.175(4)	128
	O6−H61···O8	0.85(2)	1.86(3)	2.685(3)	166(4)
	O7−H71···O9[n]	0.85(3)	1.98(3)	2.825(4)	174(4)
5·MeOH	C1−H1···O7	0.93	2.46	3.165(4)	132
	C5−H5···O9[o]	0.93	2.56	3.166(4)	123
	C6−H6···O1[p]	0.93	2.58	3.238(4)	128
	C10−H10···O2[r]	0.93	2.43	3.228(4)	144
	π···π	Cg3···Cg4[m]/Å	Slipage		
		3.4807(18)	1.218		
	π···π	Cg4···Cg3[s]/Å	Slipage		
		3.4807(18)	1.076		
	N3−H3···O7[t]	0.86	1.83	2.682(4)	172
	O6−H61···O7[u]	0.84(3)	1.79(3)	2.620(4)	171(2)
	C1−H1···O9[v]	0.93	2.55	3.327(4)	141

	C4−H4···O4	0.93	2.41	2.737(4)	100
	C5−H5···O10[ii]	0.93	2.46	3.208(5)	138
6	C6−H6···O2ii[i]	0.93	2.53	3.173(4)	126
	C10−H10···O1[iv]	0.93	2.47	3.271(4)	145
	C12−H12···O9[v]	0.93	2.44	3.260(4)	146
	C15−H15b···O2[v]	0.96	2.53	2.996(5)	110
	C16−H16b···O1[vi]	0.96	2.58	3.454(5)	151
	C16−H16c···O9[vi]	0.96	2.49	2.849(6)	102
	π···π	Cg3···Cg4[s] /Å	Slipage		
		3.6237(19)	1.363		
		Cg4···Cg3[m] /Å	Slipage		
		3.6236(19)	1.254		

[a]2-x,1-y,1-z; [b]-1+x,1+y,z;[c]x,1/2-y,-1/2+z; [d]1+x,-1+y,z; [e]1+x,1/2-y,1/2+z; [f]2-x,1/2+y,3/2-z; [g]2-x,-y,-z; [h]2-x,1/2+y,1/2-z; [i]x,1/2-y,-1/2+z;[j]3-x,-y,-z; [k] 3-x,-1/2+y,1/2-z; [l] 2-X,1-Y,-Z; [m]x,y,-1+z; [n]-1+x,y,z; [o] 1-x,-1/2+y,-z; [p] 1-x,-1/2+y,-z; [r] -x,1/2+y,1-z; [s] x, y, 1+z; [t] x,1+y,1+z; [u]x,1+y,1+z; [v]-1+x,1+y,z; [ii]1-x,1/2+y,1-z; [iii] -x,1/2+y,1-z; [iv]-x,1/2+y,-z ; [v]1-x,1/2+y,-z; [vi]1+x,y,z ; [vii] 1-x,-1/2+y,1-z

Polymer 1 and polymorphic forms 2α, 2β, and 2γ

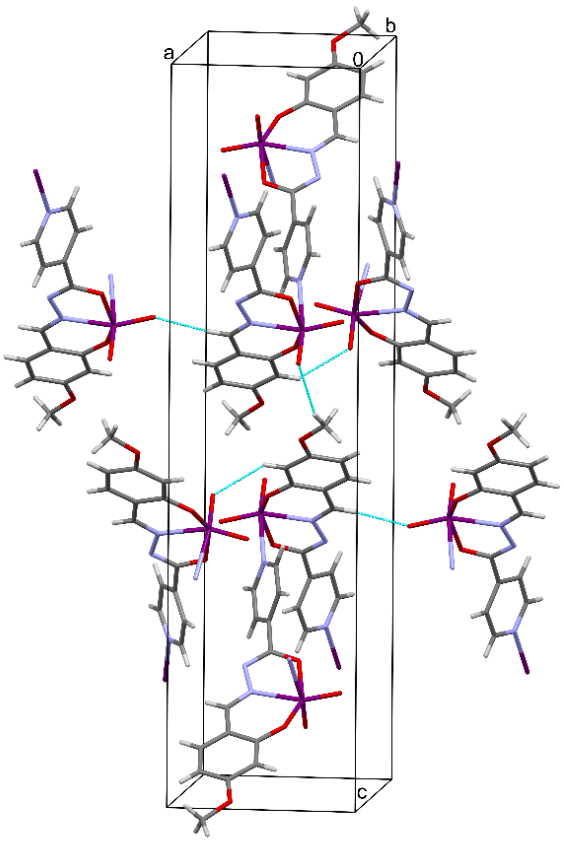


Fig. S1 Packing arrangement in the unit cell of **1**. Hydrogen bonds between chains are shown as blue dashed lines.

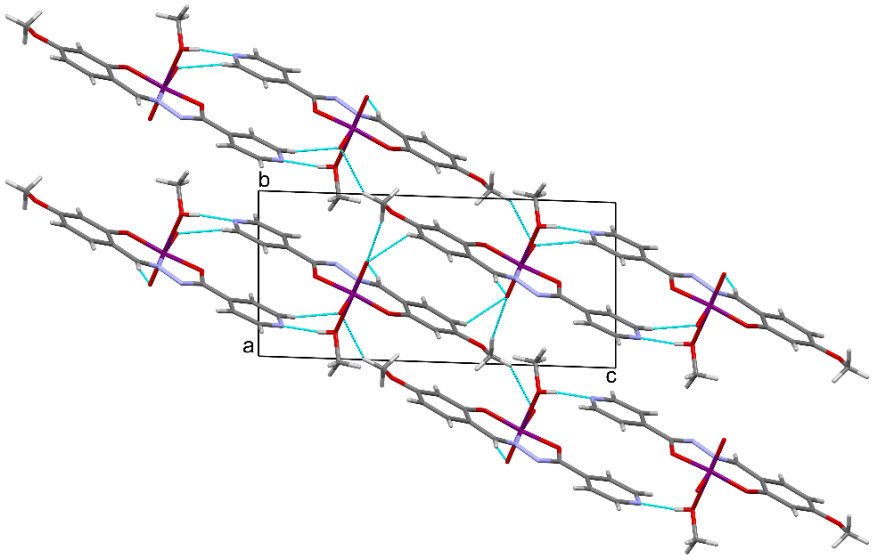


Fig. S2 Packing arrangement in the unit cell of **2α.** Hydrogen bonds are shown as blue dashed lines.

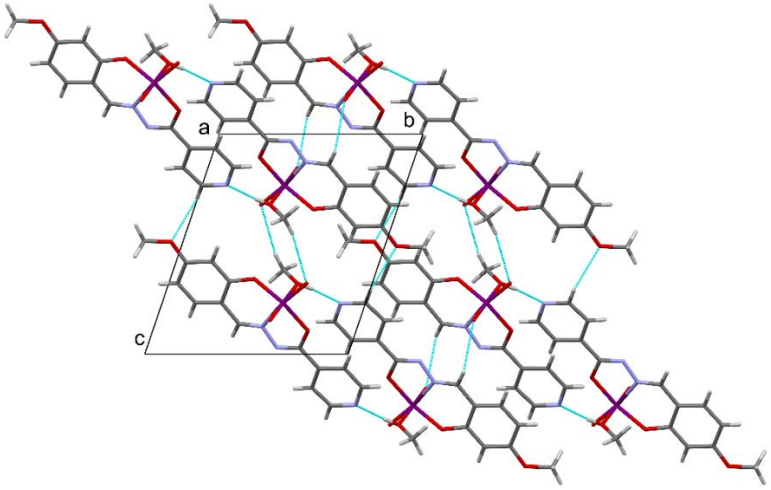


Fig. S3 Packing arrangement in the unit cell of **2β.** Hydrogen bonds are shown as blue dashed lines.

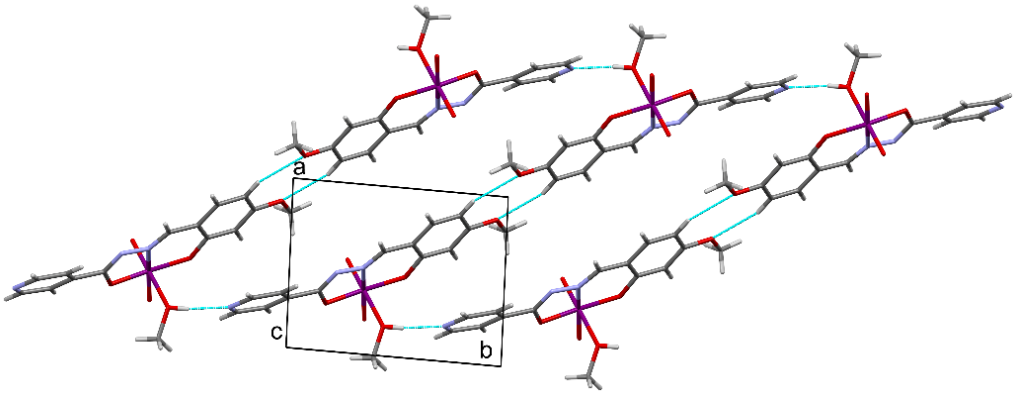
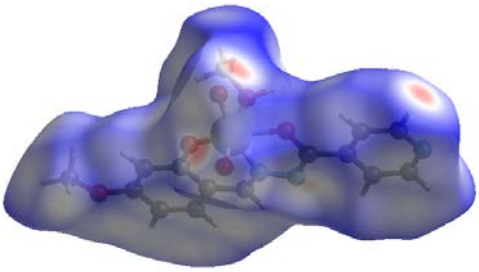
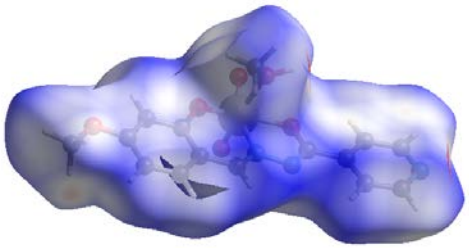


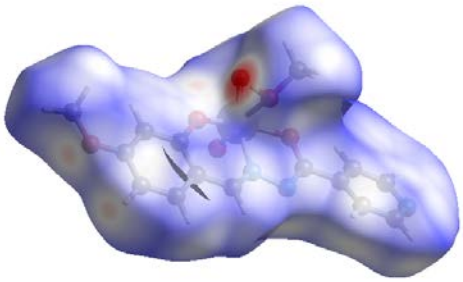
Fig. S4 Packing arrangement in the unit cell of **2γ.** Hydrogen bonds are shown as blue dashed lines.



2α



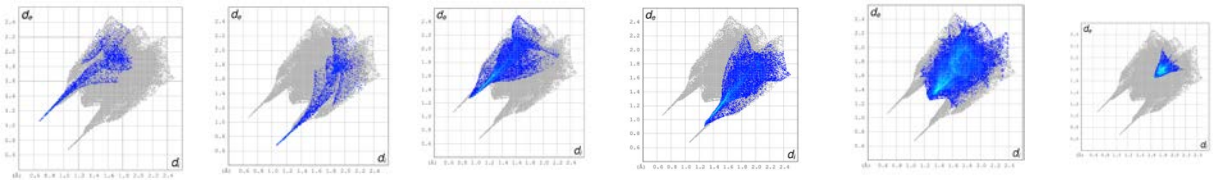
2β



2γ

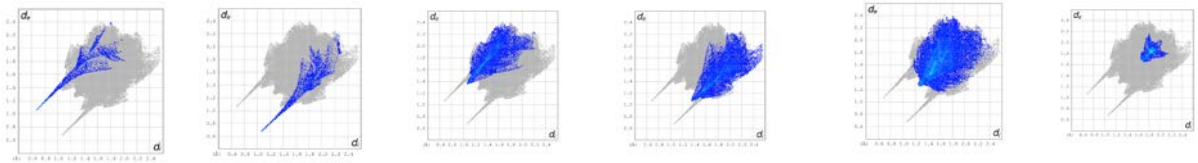
Fig. S5 Graphical presentation of the Hirshfeld surfaces (with mapped d_{norm} property) of **2α**, **2β**, and **2γ**.

2α



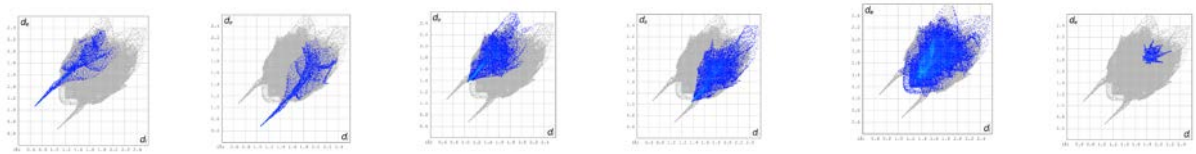
H···N 3.3% N···H 3.9% H···O 13.2% O···H 15.7% H···H 39.2% C···C 7.6 %

2β



H···N 3.2% N···H 4.0% H···O 4.9% O···H 18.3% H···H 5.7% C···C 6.1%

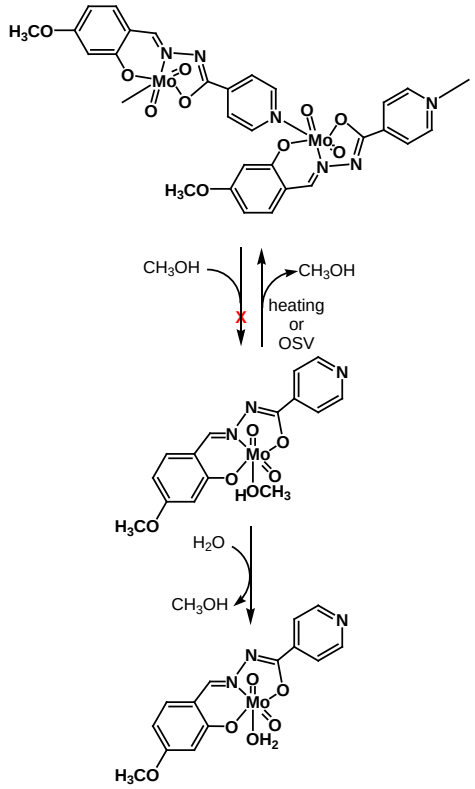
2γ



H··· N 4.5% N···H 5.2% H···O 2.5% O···H 14.9% H···H 33.9% C···C 1.6%

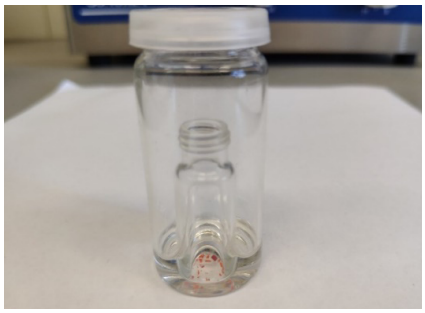
Fig. S6 Hirshfeld fingerprint plot with decomposition of the dominant types of intermolecular contacts in **2α**, **2β**, and **2γ**.

3. Vapour-mediated solid-state transformation



Scheme S1 Organic solvent vapour (OSV) mediated solid-state structural transformation and humidity induced SC-SC interconversion.

(a)



(b)

Fig. S7 Experimental setup for exposing solid materials to: (a) polar organic solvent vapour; (b) non-polar organic vapour – a glass vial of 3.3 cm height and 1.2 cm diameter was placed inside a glass bottle of 5.2 cm height and 2.3 cm diameter. Dry apparatus was assembled as quickly as possible to prevent intrusion of atmospheric moisture and then it was filled with Ar.

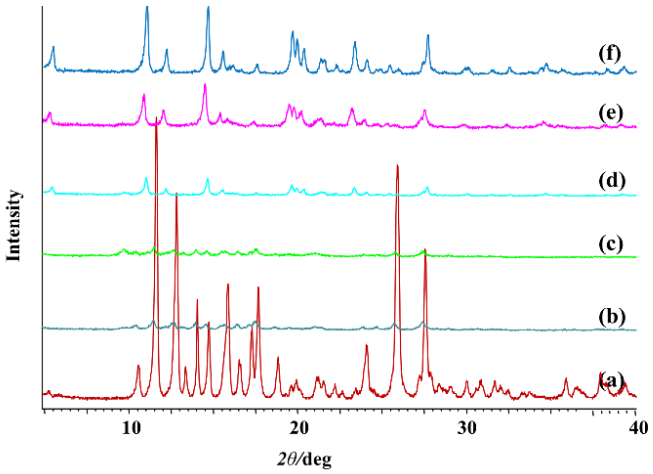
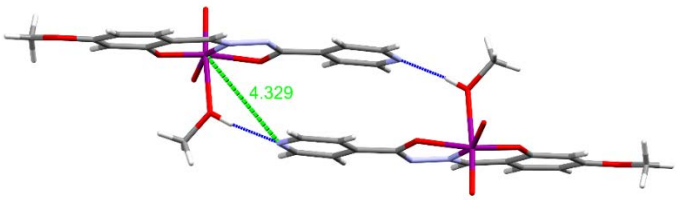
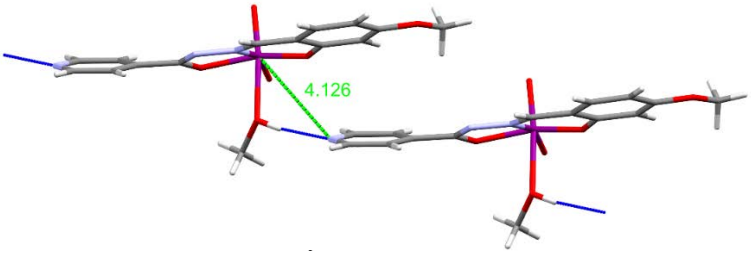


Fig. S8 Powder X-ray diffraction patterns of (a) **2α**; (b-f) samples obtained when crystals of **2α** were exposed to CH_3CN vapour for 1 h (b), 3 h (c), 6 h (d), 7 h (e), and 9 h (f).

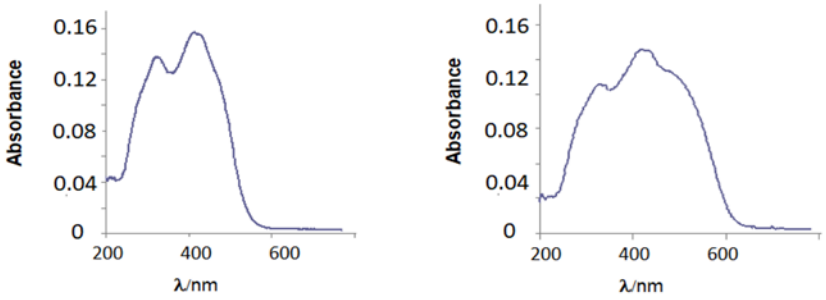


(a)



(b)

Fig. S9 Drawing represents the shorthest Mo···N (Å) distance in polymorphs **2α** (a) and **2γ** (b). Mo and N atoms from neighbouring molecules are connected by green dashed lines.



(a) (b)

Fig. S10 Solid state UV-Vis spectra of (a) **1** and (b) **2α**.

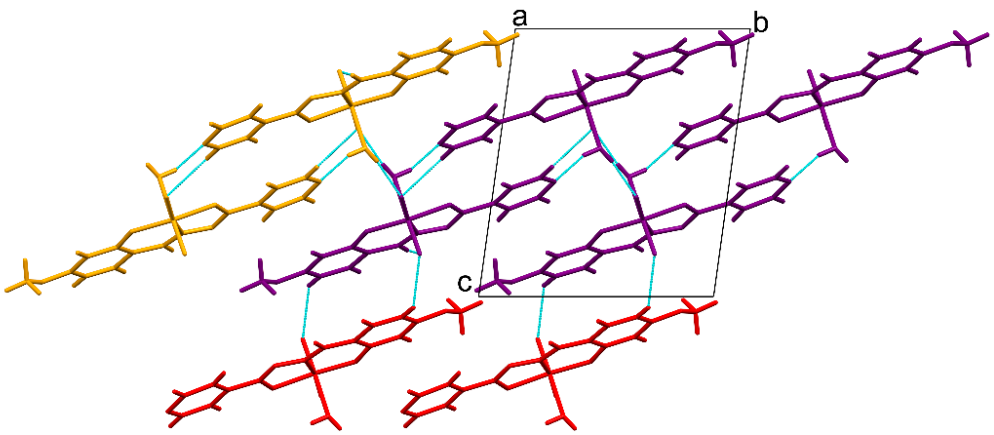
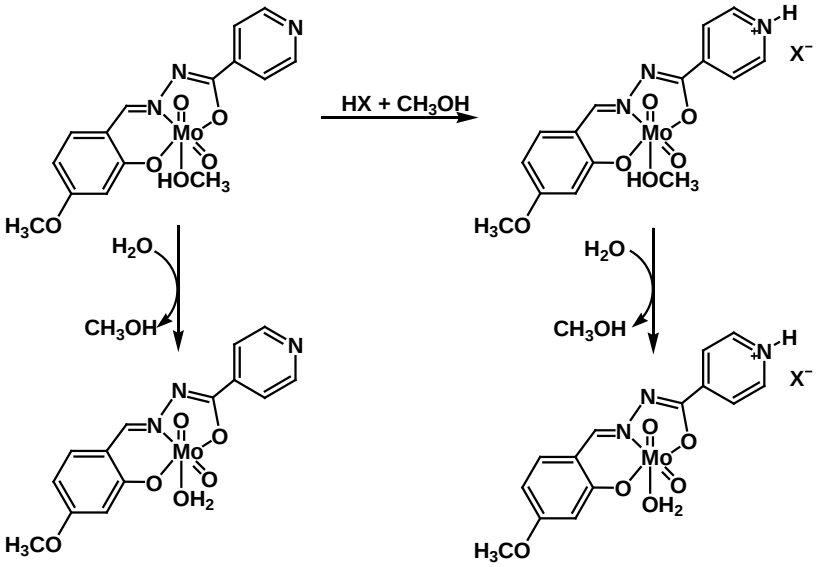


Fig. S11 Packing arrangement in the unit cell of **2w-α**. Hydrogen bonds are shown as blue dashed lines.

Humidity-driven transformations



Scheme S2 Experiments involving exposure of materials to moisture.

Spectroscopic and analytical data:

[MoO_2(L)(H_2O)] (2w-α). Selected IR data (cm^{-1}): 1618 $(C=N)_{py}$, 1595 (C=N), 1332 $(C-O_{phenolate})$, 1224 $(C-O_{izo})$, 926 (MoO_2), 888 (O=Mo−O). Anal. Calcd. for $C_{14}H_{13}MoN_3O_6$ (415.224): C, 40.49; H, 3.16; N, 10.12%. Found: C, 40.23 H, 3.05; N, 9.93%. TG: calcd. for MoO_3, 34.67%, found: 34.28%; calcd. for H_2O, 4.34%, found: 4.19%.

[MoO_2(L)(H_2O)] (2w-γ). Selected IR data (cm^{-1}): 1620 $(C=N)_{py}$, 1596 (C=N), 1336 $(C-O_{phenolate})$, 1227 $(C-O_{izo})$, 932 (MoO_2), 894 (O=Mo−O). Anal. Calcd. for $C_{14}H_{13}MoN_3O_6$ (415.224): C, 40.49; H, 3.16; N, 10.12%. Found: C, 40.19 H, 2.95; N, 9.87%. TG: calcd. for MoO_3, 34.67%, found: 34.33%; calcd. for H_2O, 4.34%, found: 4.15%.

[MoO_2(HL)(H_2O)]Cl (3w). Anal. Calcd. for $C_{14}H_{14}MoN_3O_6Cl$ (451.674): C, 37.22; H, 3.12; N, 9.30%. Found: C, 36.95; H, 3.19; N, 8.95%. TG: calcd. for MoO_3, 31.87%, found: 31.63%; calcd. for H_2O, 3.99%, found: 3.76%. Selected IR data (cm^{-1}): 1638 $(C=N)_{py}$, 1597 (C=N), 1334 $(C-O_{phenolate})$, 1238 $(C-O_{izo})$, 937 (MoO_2), 895 (O=Mo−O).

[MoO_2(HL)(H_2O)]Br (4w). Anal. Calcd. for $C_{14}H_{14}MoN_3O_6Br$ (496.124): C, 33.89; H, 2.84; N, 8.46%. Found: C, 33.51; H, 2.74; N, 8.33%. TG: calcd. for MoO_3, 29.01%, found: 28.82%; calcd. for H_2O, 3.63%, found: 3.35%. Selected IR data (cm^{-1}): 1638 $(C=N)_{py}$, 1596 (C=N), 1334 $(C-O_{phenolate})$, 1238 $(C-O_{izo})$, 938 (MoO_2), 894 (O=Mo−O).

[MoO_2(HL)(H_2O)]NO_3 (5w). Anal. Calcd. for $C_{14}H_{14}MoN_4O_9$ (478.232): C, 35.16; H, 2.95; N, 11.72%. Found: C, 35.45; H, 2.61; N, 11.80%. TG: calcd. for MoO_3, 30.10%, found: 30.31%; calcd. for H_2O, 3.77%, found: 6.65%. Selected IR data (cm^{-1}): 1638 $(C=N)_{py}$, 1594 (C=N), 1326 $(C-O_{phenolate})$, 1224 $(C-O_{izo})$, 931 (MoO_2), 905 (O=Mo−O).

[MoO_2(HL)(H_2O)]$MeOSO_3$ (6w). Anal. Calcd. for $C_{15}H_{17}MoN_3O_{10}S$ (527.323): C, 34.16; H, 3.25; N, 7.97%. Found: C, 34.04; H, 2.98; N, 8.15%. TG: calcd. for MoO_3, 27.30%, found: 27.05%; calcd. for H_2O, 3.42%, found: 3.20%. Selected IR data (cm^{-1}): 1640 $(C=N)_{py}$, 1591 (C=N), 1331 $(C-O_{phenolate})$, 1224 $(C-O_{izo})$, 931 (MoO_2), 901 (O=Mo−O).

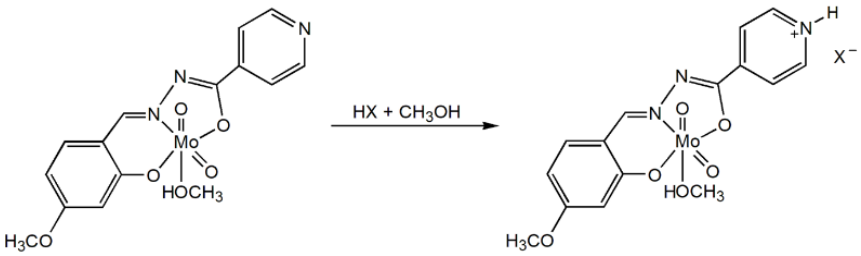
4. Protonation reactions of molybdenum complexes with mineral acids

METHOD A

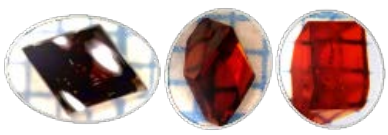
$$[MoO_2(acac)_2] + H_2L \xrightarrow{HX/MeOH} [MoO_2(HL)(MeOH)]X \text{ (3-5)}$$

METHOD B

$$[MoO_2(L)(MeOH)] \xrightarrow{HX/MeOH} [MoO_2(HL)(MeOH)]X \text{ (3-6)}$$



Scheme S3 Synthesis of compounds [MoO_2(HL)(MeOH)]Cl (**3**), [MoO_2(HL)(MeOH)]Br (**4**), [MoO_2(HL)(MeOH)]NO_3·MeOH (**5·MeOH**) and [MoO_2(HL)(MeOH)]$MeOSO_3$ (**6**)



3 **4** **5·MeOH**

Fig. S12. Photos of single crystals of **3**, **4** and **5·MeOH** obtained by Method A.

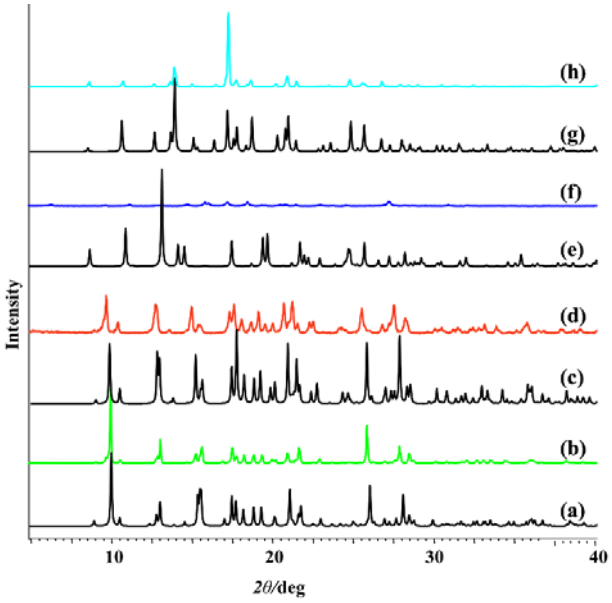


Fig. S13 Powder X-ray diffraction patterns of **3** (a and b); **4** (c and d), **5** (e and f), **6** (g and h). The coloured lines indicate patterns obtained by powder diffraction, CuK_α radiation, while the black lines indicate patterns calculated from the X-ray single-crystal structures of the corresponding compounds.

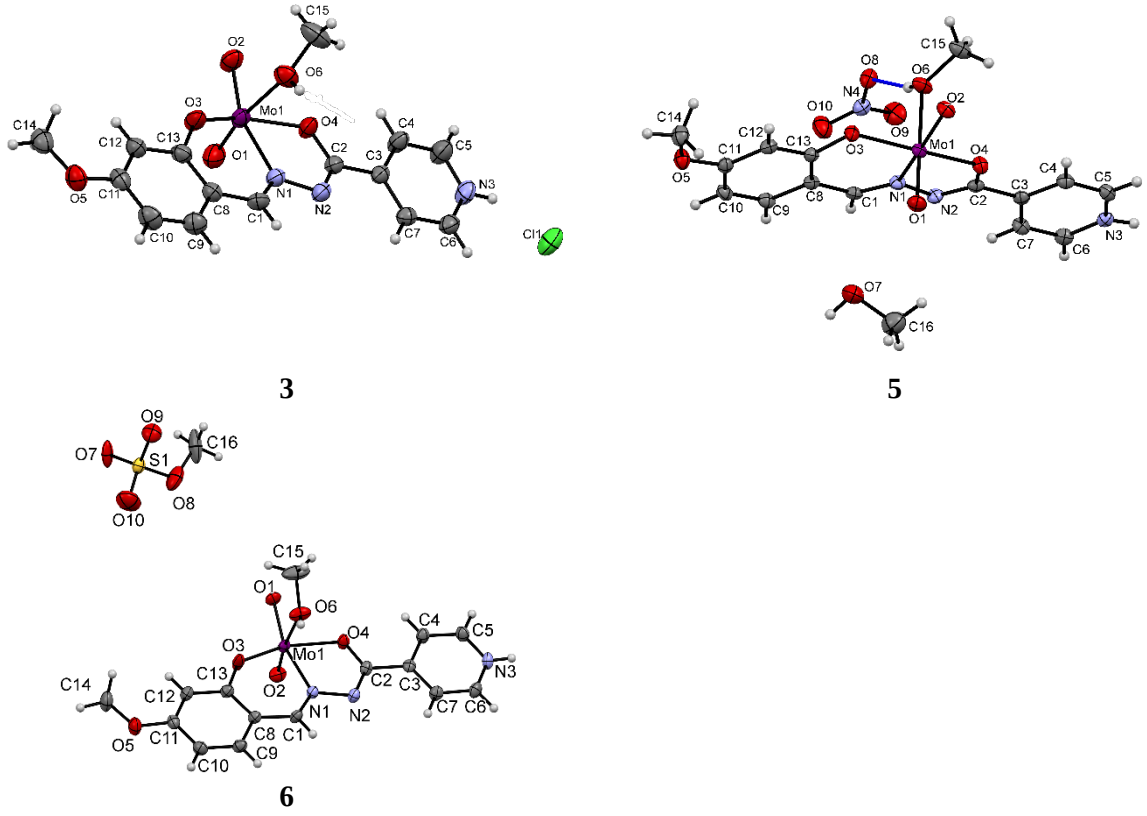


Fig. S14 ORTEP plot of [MoO_2(HL)(MeOH)]Cl (**3**), [MoO_2(HL)(MeOH)]NO_3·MeOH (**5·MeOH**) and [MoO_2(HL)(MeOH)]$MeOSO_3$ (**6**). Displacement ellipsoids of non-hydrogen atoms are drawn at the 50% probability level.

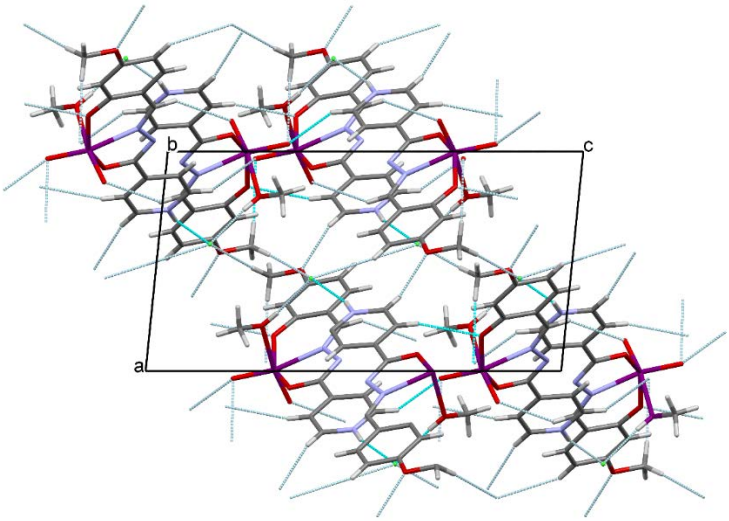


Fig. S15 Packing arrangement in the unit cell of **3**. Hydrogen bonds are shown as blue dashed lines.

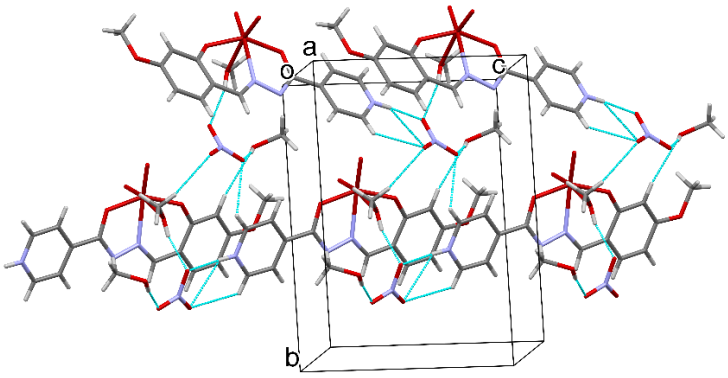


Fig. S16 Packing arrangement in the unit cell of **5·MeOH**. Hydrogen bonds are shown as blue dashed lines.

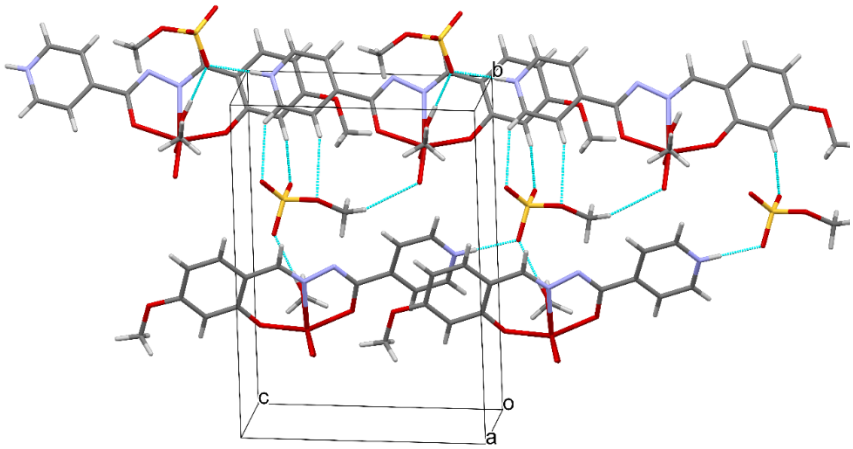


Fig. S17 Packing arrangement in the unit cell of **6**. Hydrogen bonds are shown as blue dashed lines.

5. Characterisation

IR spectroscopy

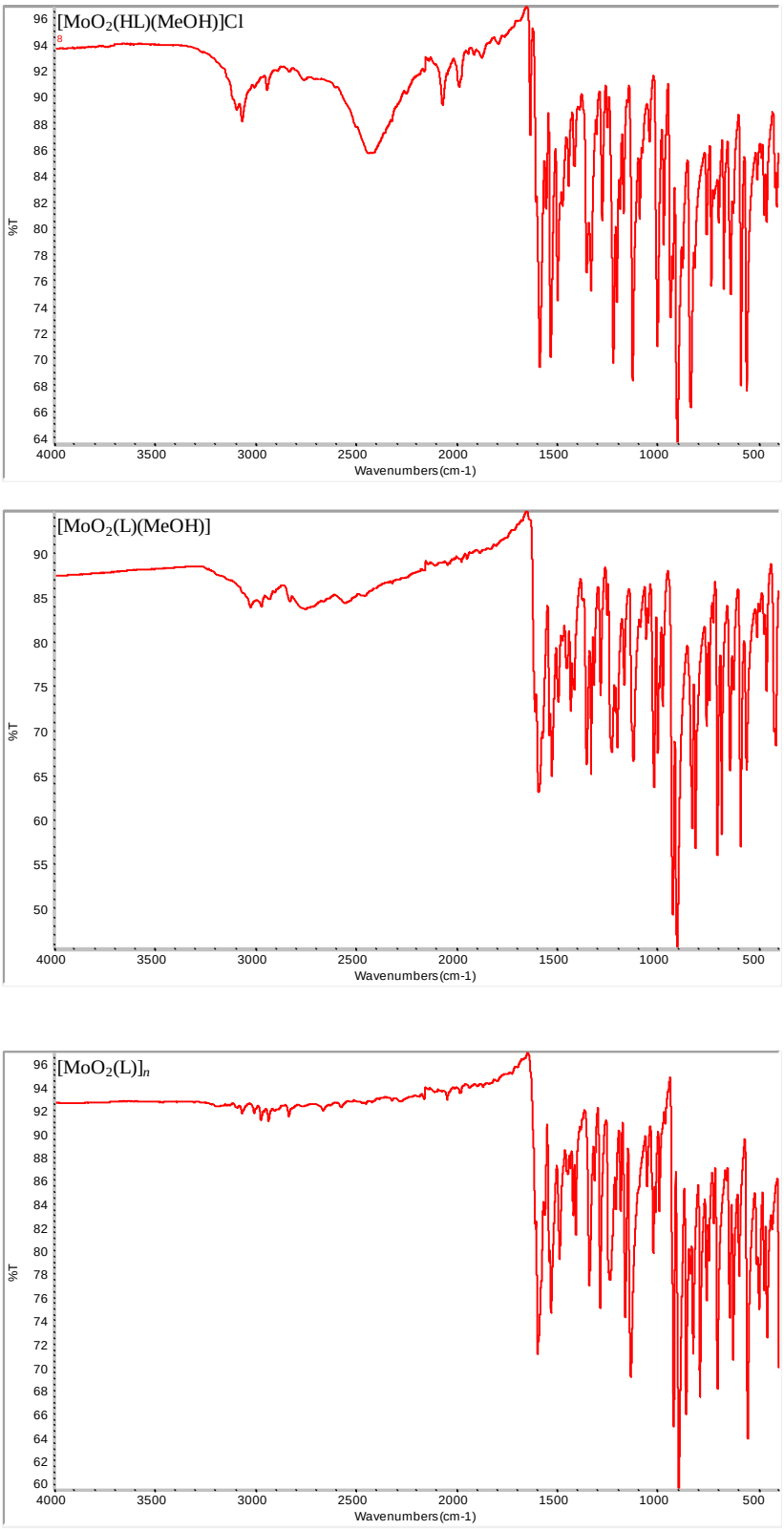


Fig. S18 IR spectra of [MoO_2(HL)(MeOH)]Cl (**3**), [MoO_2(L)(MeOH)] (**2α**), and [MoO_2(L)]$_n$ (**1**).

Thermogravimetric analysis

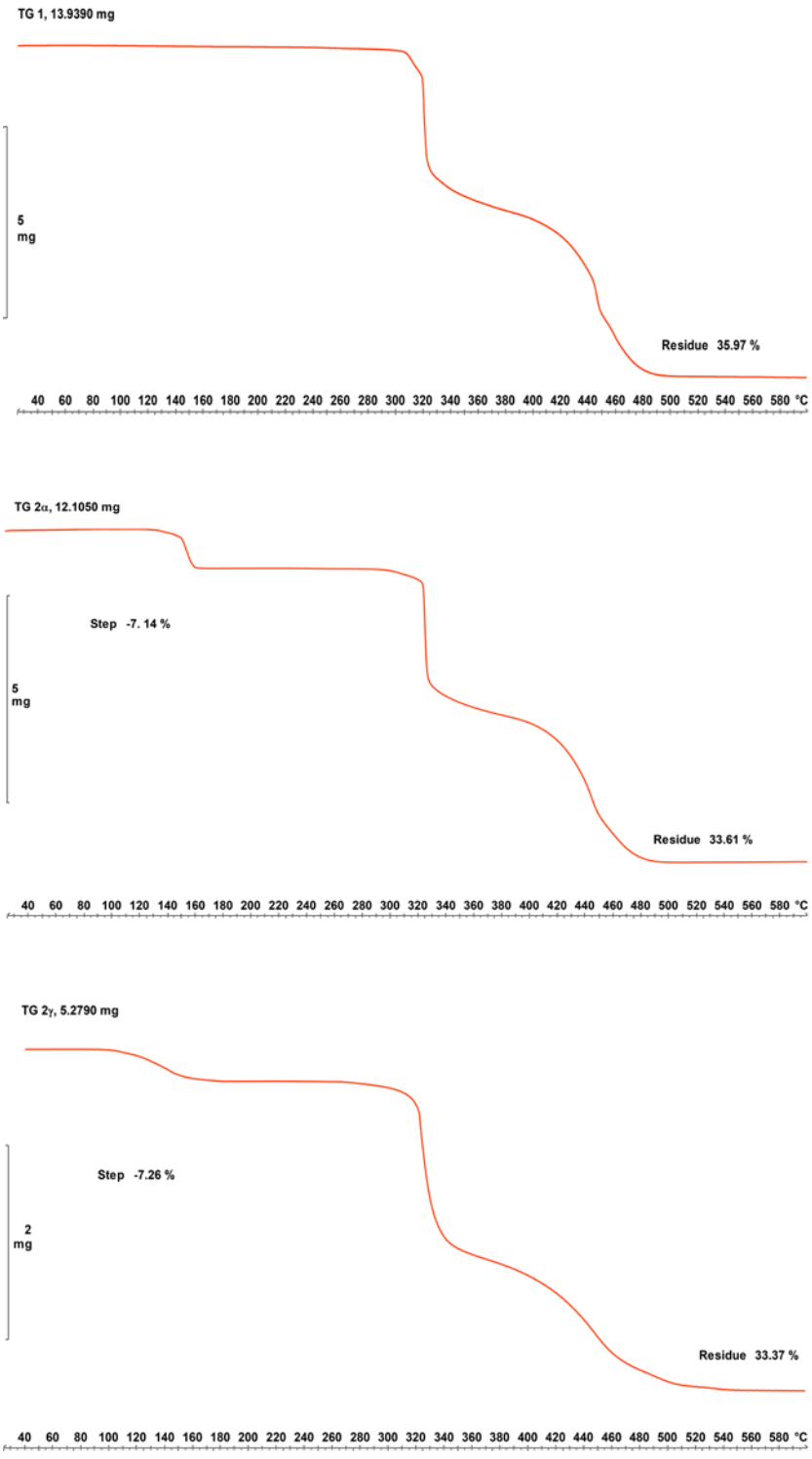


Fig. S19 From top to bottom: TG curves of **1**, **2α**, and **2γ** under the O_2 atmosphere.

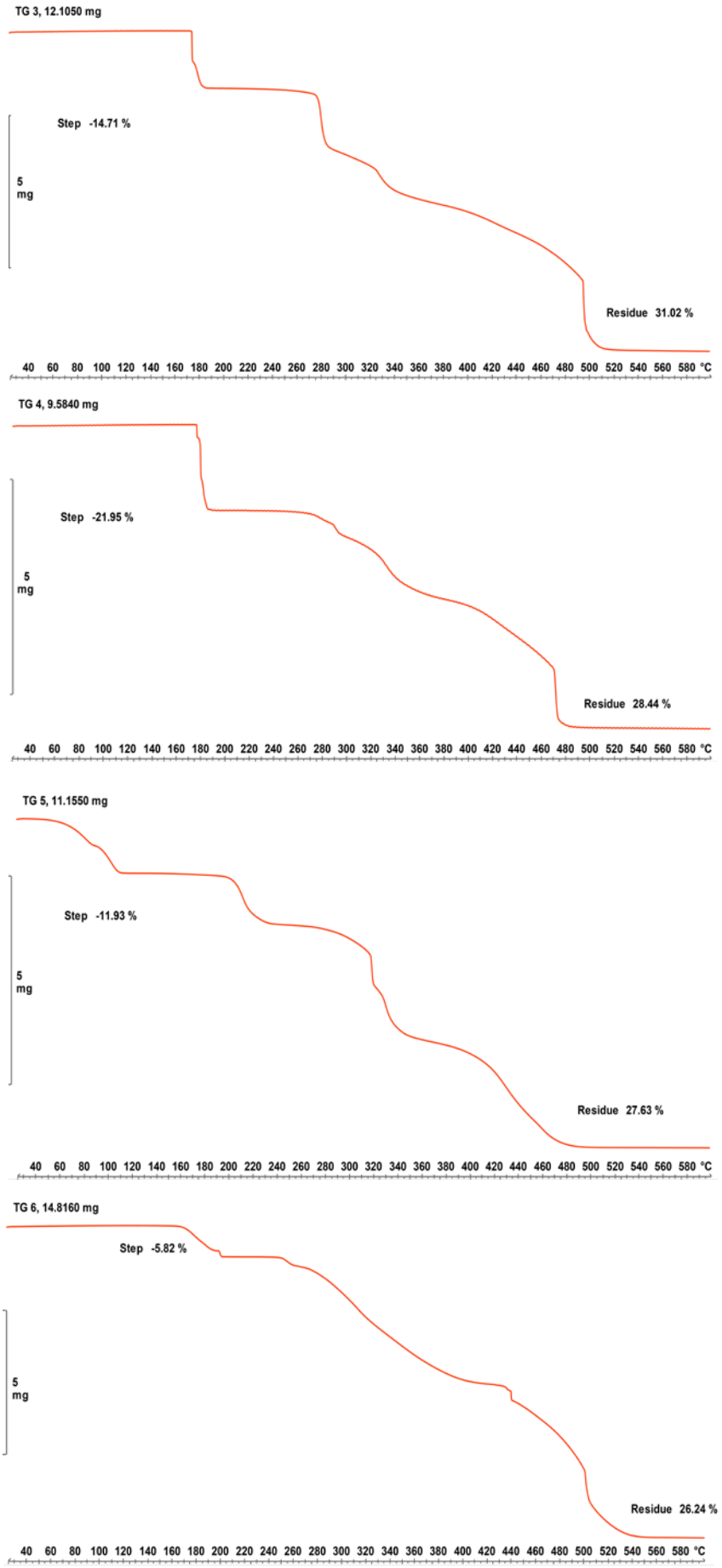


Fig. S20 From top to bottom: TG curves of salts **3**, **4**, **5·MeOH** and **6** under the O_2 atmosphere.

NMR spectroscopy

[MoO_2(L)(dmso)]: Anal. Calcd. for $C_{16}H_{17}MoN_3O_6S$ (475.32): C, 40.43; H, 3.60; N, 8.84. Found: C, 40.21; H, 3.48; N, 9.20. TG: C_2H_6OS, 16.18 % (Calcd. 16.44 %); MoO_3, 29.89% (Calcd. 30.28%). Selected IR data (cm^{-1}): 1616 $(C{=}N)_{py}$, 1593 (C=N), 1343 $(C{-}O_{phenolate})$, 1217 $(C{-}O_{enolate})$, 920 (MoO_2), 892 (O=Mo−O). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 217 (22250), 318 (13780) and 402 (7040).

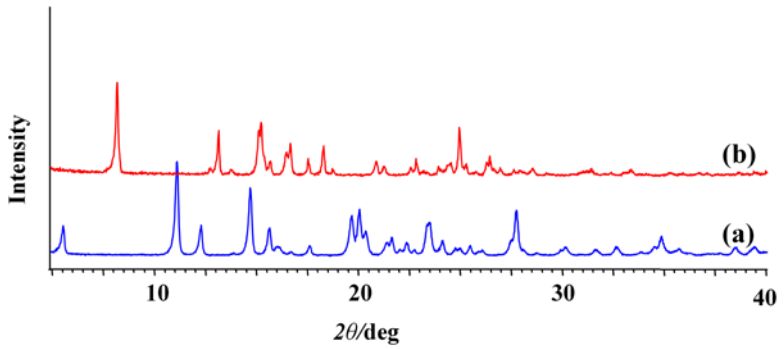
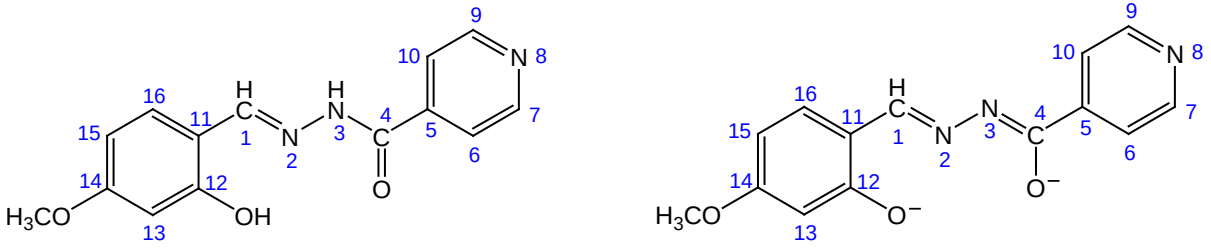


Fig. S21 Powder X-ray diffraction patterns of (a) **1** and (b) [MoO_2(L)(dmso)].

Table S8 ^{1}H and ^{13}C chemical shifts (ppm) of **H_2L**, **1** and **3–6**

Atom	**H_2L**		**1**		**3**		**4**		**5**		**6**	
	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)
1	8.58	150.01	8.92	157.61	8.93	143.07	8.98	143.94	8.97	144.16	8.87	141.75
4	–	161.52	–	166.26	–	164.76	–	164.54	–	164.54	–	165.20
5	–	140.50	–	137.99	–	146.57	–	145.70	–	145.70	–	148.11
6, 10	7.84	121.92	7.85	121.87	8.21	124.01	8.30	124.66	8.29	124.23	8.13	123.57
7, 9	8.80	150.83	8.76	150.99	8.98	158.62	9.01	159.28	8.99	159.28	8.97	157.97
11	–	112.16	–	113.87	–	113.93	–	113.71	–	113.49	–	114.19
12	–	159.90	–	161.98	–	162.13	–	162.35	–	162.13	–	161.91
13	6.54	101.62	6.59	103.56	6.61	103.85	6.61	103.41	6.61	103.41	6.61	103.41
14	–	162.80	–	166.16	–	166.73	–	166.73	–	166.29	–	166.51
15	6.51	107.09	6.72	110.17	7.73	110.42	7.75	110.20	7.72	110.42	7.73	110.64
16	7.49	131.47	7.68	136.28	6.74	136.71	6.74	136.49	6.75	136.71	6.72	136.93
OH	11.42	–	–	–	–	–	–	–	–	–	–	–
NH	12.19	–	–	–	12.86	–	12.52	–	12.44	–	12.34	–
OMe	3.78	55.81	–	56.39	3.86	56.53	3.86	56.74	3.85	56.53	3.83	56.53



Scheme S4. Structure and the NMR numbering scheme in H_2L and in the deprotonated ligand L^{2-}

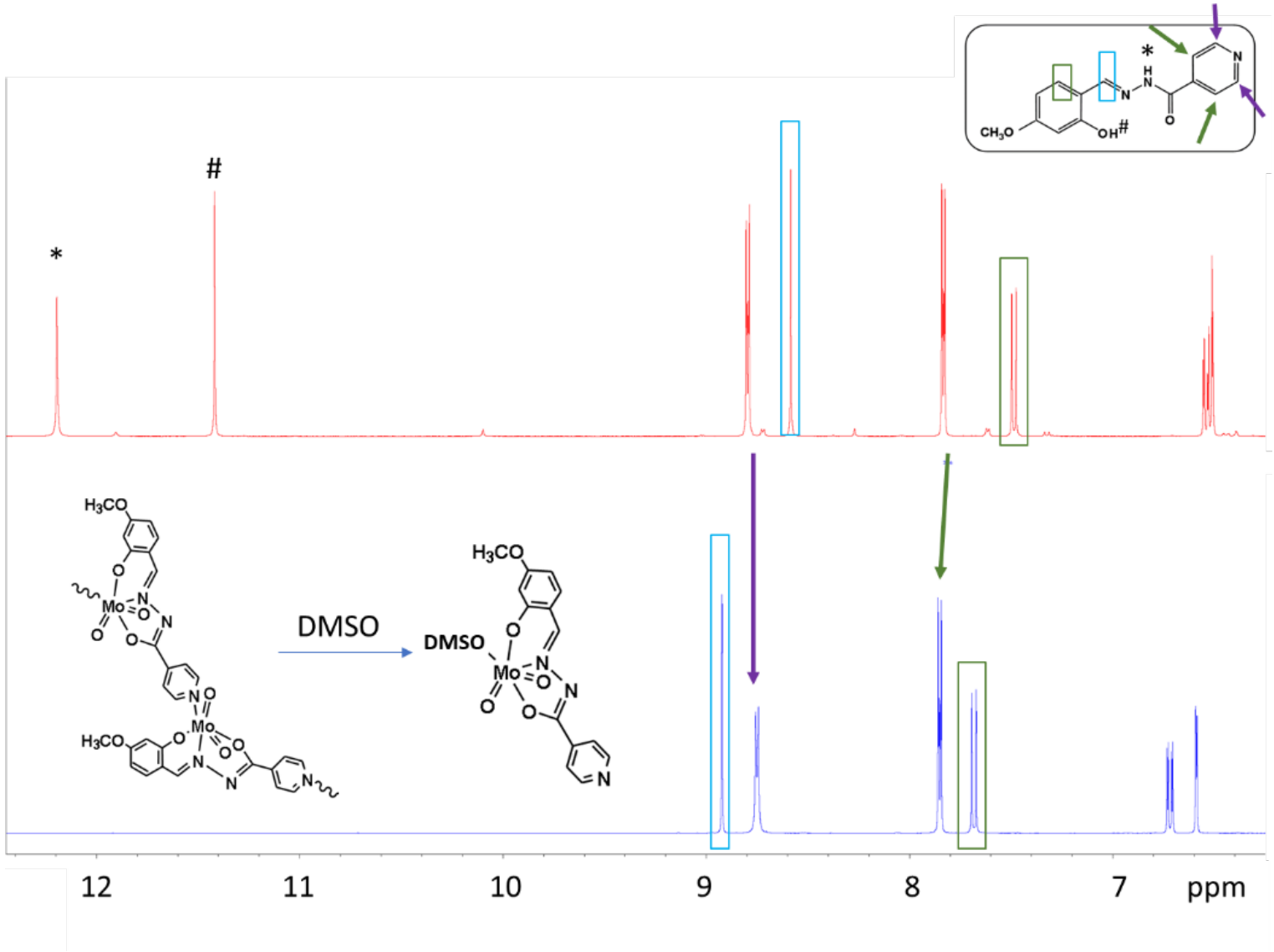


Fig. S22 A portion of the ^{1}H NMR spectra in dmso-d_6 of: H_2L (the red line), $[MoO_2(L)]_n$ (**1**) (the blue line).

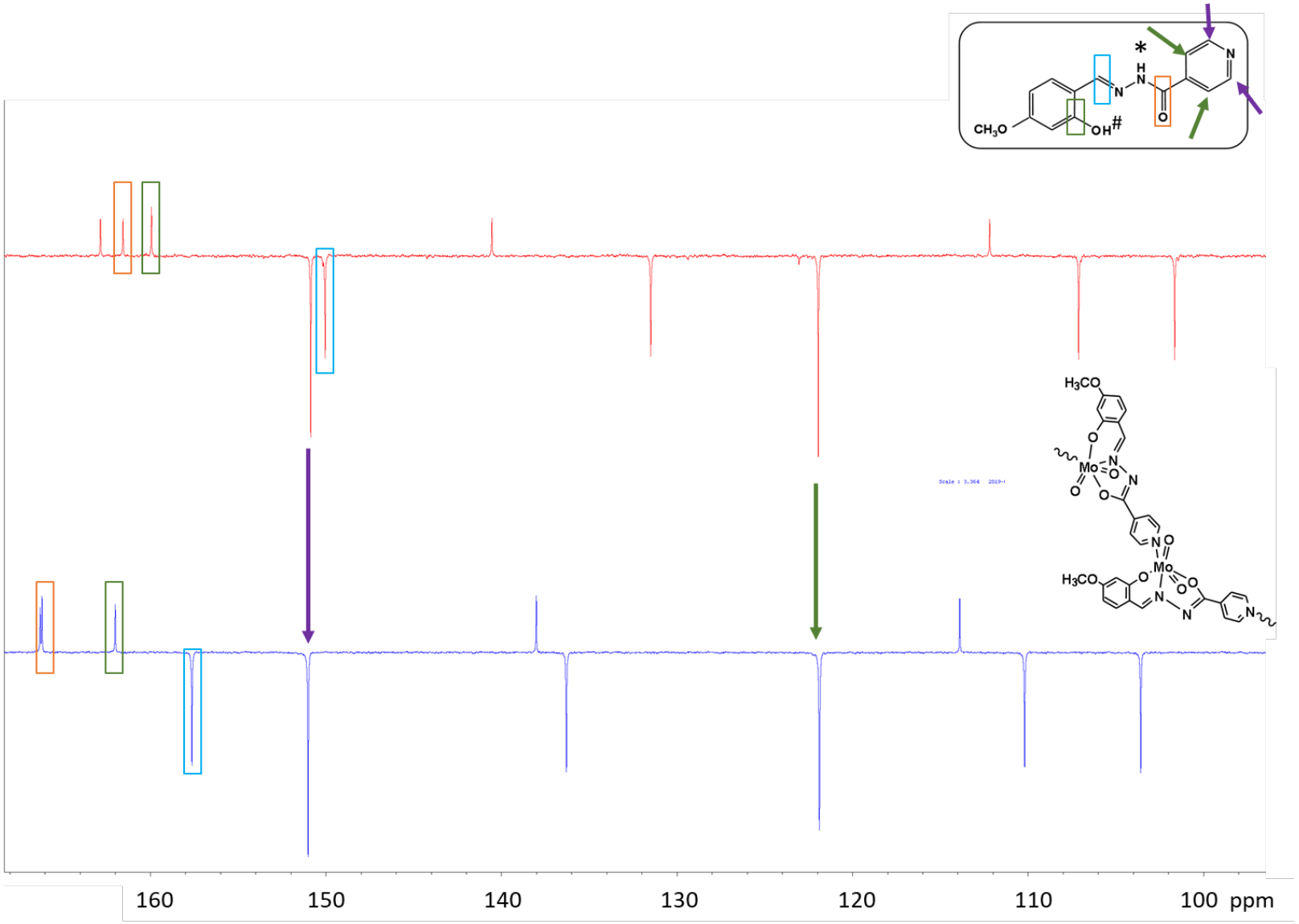


Fig. S23 A portion of the ^{13}C NMR spectra in dmso-d_6 of: H_2L (the red line), $[MoO_2(L)]_n$ (**1**) (the blue line).

Table S9 Tentative assignment of ^{13}C CP-MAS spectra

	1	**3**	**4**	**5**	**6**
Atom	δ /ppm	δ / ppm	δ / ppm	δ / ppm	δ / ppm
1	162.14	164.59	161.22	162.70	160.16
4	171.31	168.46-170.74	169.45	168.03	167.31-169.31
5	140.92-142.01	138.00-148.57	137.66-149.58	145.01-149.30	143.30-149.86
7,9	140.92-142.01	138.00-148.57	137.66-149.58	145.01-149.30	143.30-149.86
6,10	124.39-127.62	125.68-129.13	126.31-129.15	127.73	127.84-130.41
11	116.48	104.74-117.06	103.89-116.94	103.80-115.52	104.96-117.26
12	164.47	164.59	165.47	165.48	165.59
13,15	109-47-110.91	104.74-117.06	103.89-116.94	103.80-115.52	104.96-117.26
14	169.51	168-46-170.74	169.45	168.03	167.31-169.31
16	140.92-142.01	138.00-148.57	137.66-149.58	137.38	136.70-138.14
OMe	58.24	59.04, 54.50	59.321, 55,097	61.31, 54.78	59.04, 54.50

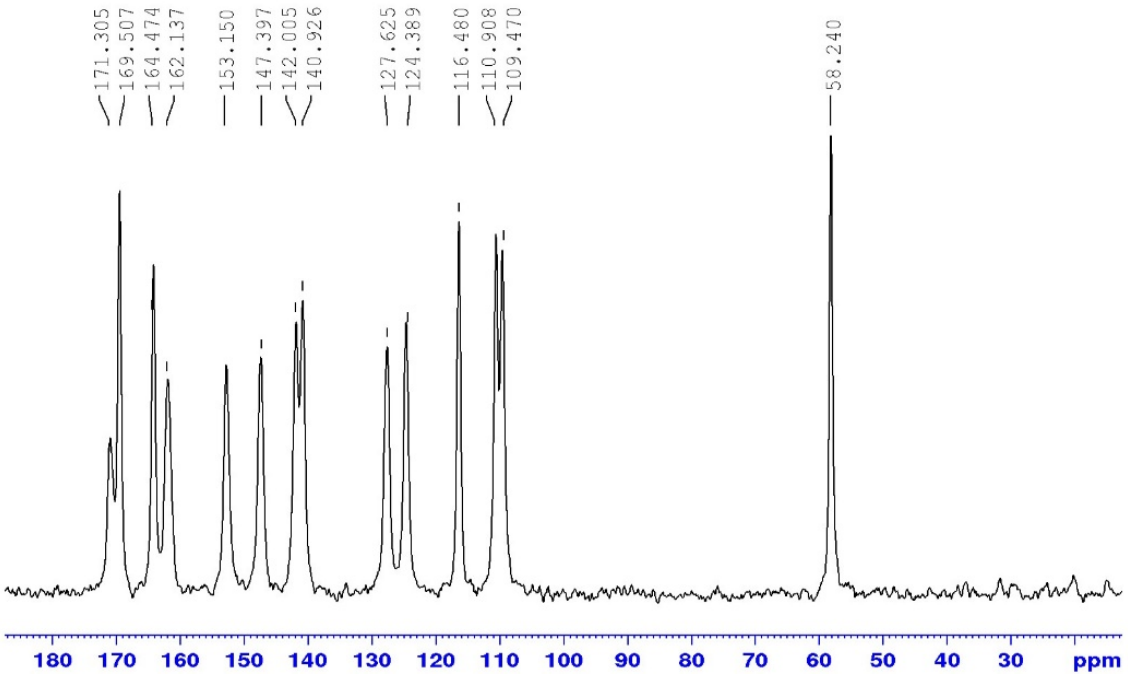


Fig. S24 ^{13}C CP-MAS spectrum of **1**.

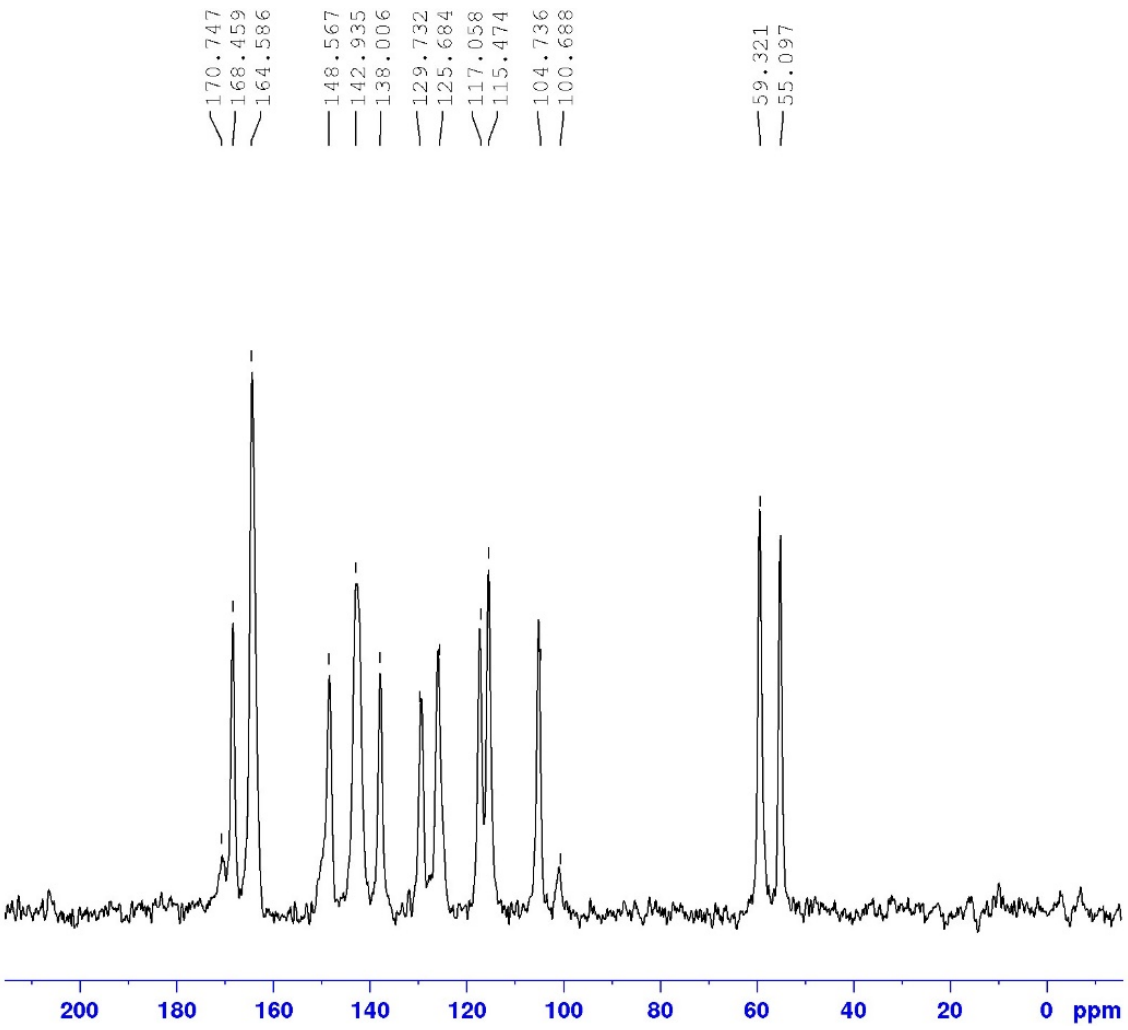


Fig. S25 ^{13}C CP-MAS spectrum of **3**.

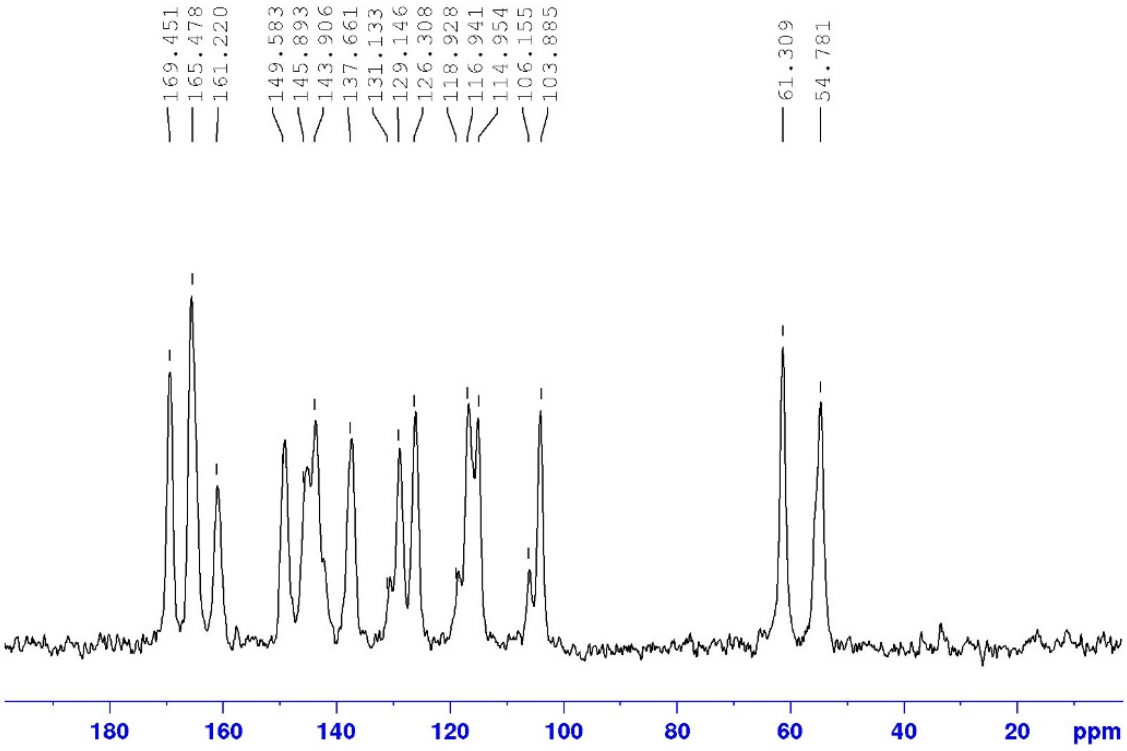


Fig. S26 ^{13}C CP-MAS spectrum of **4**.

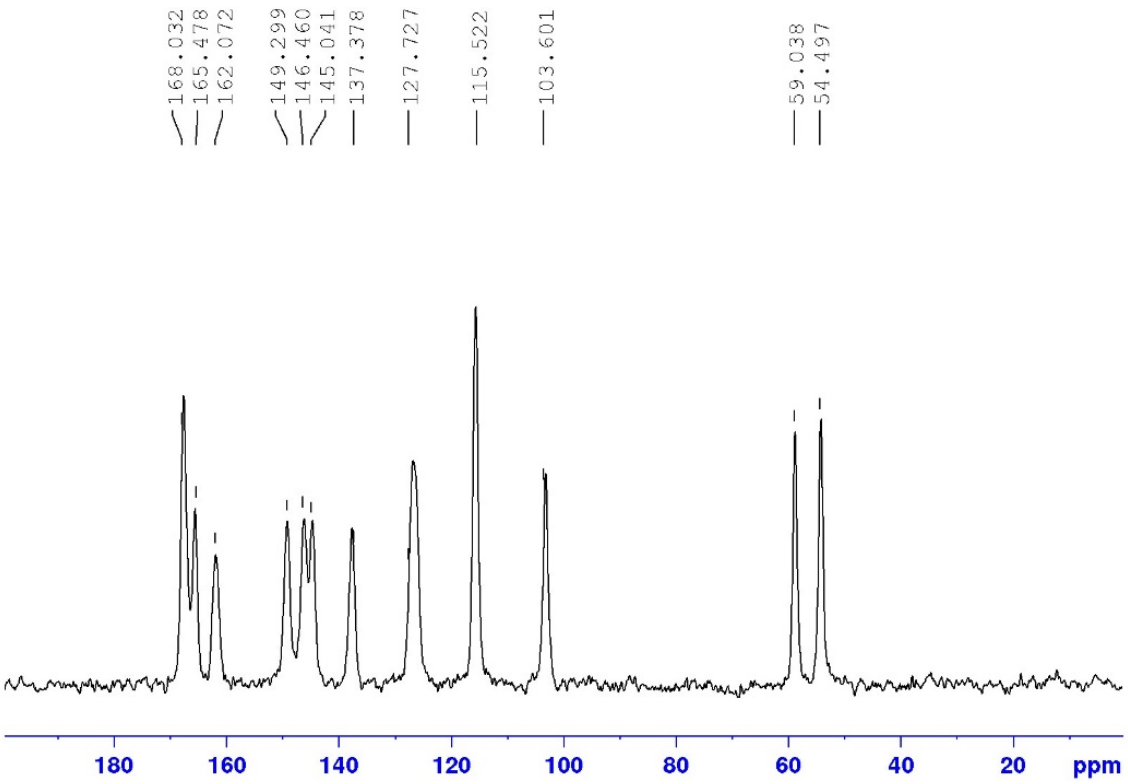


Fig. S27 ^{13}C CP-MAS spectrum of **5**.

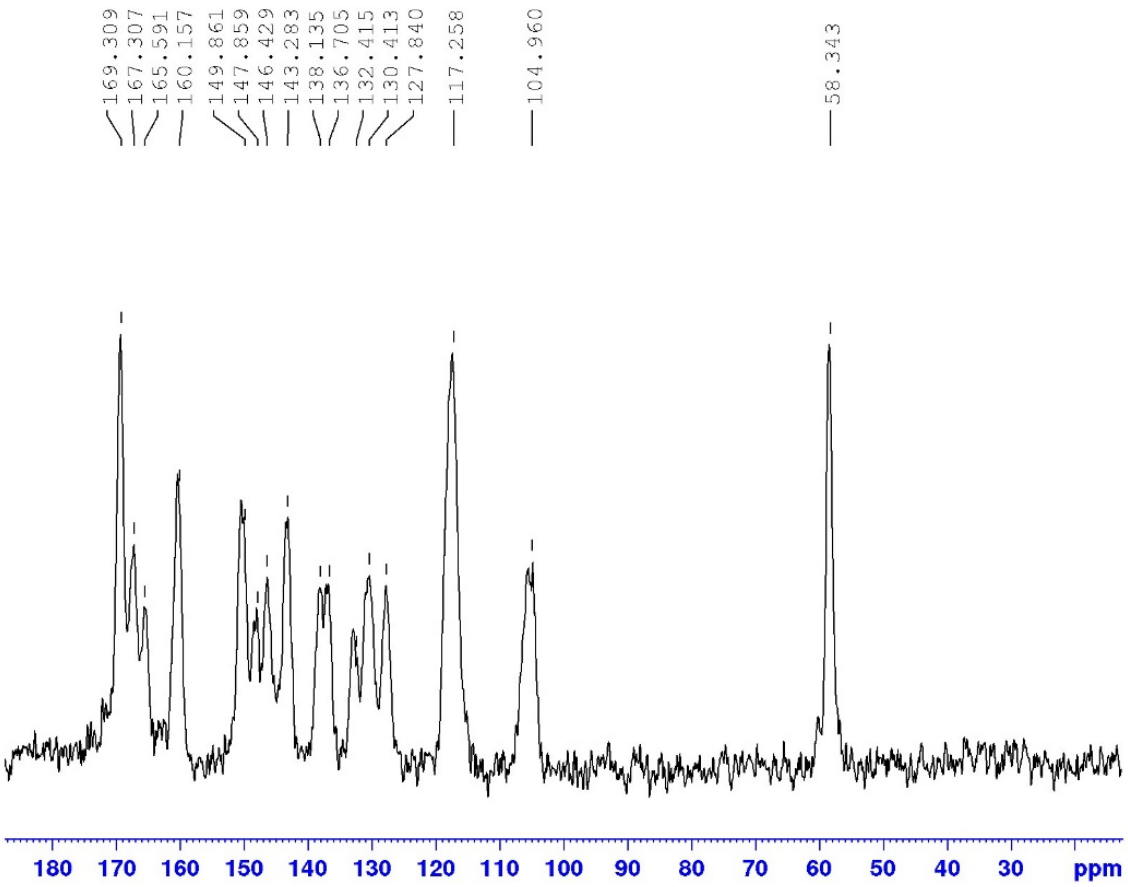


Fig. S28 ^{13}C C P-MAS spectrum of **6**.

6. Antimicrobial activity

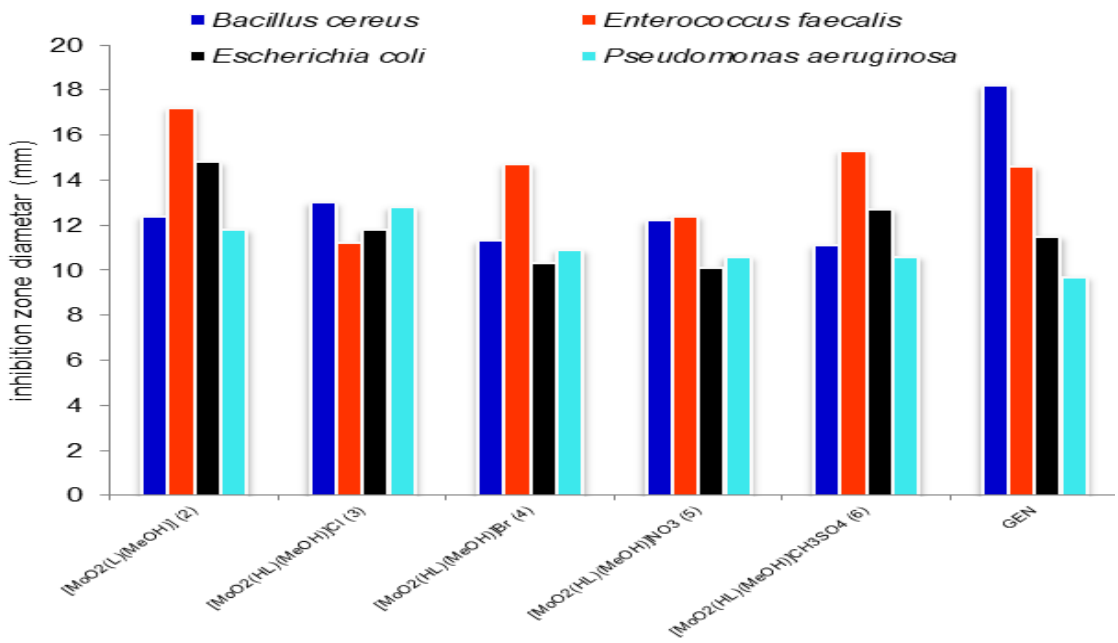


Fig. S29 Antimicrobial activity of dioxomolybdenum(VI) compounds and antibiotic gentamicin (GEN) against Gram-positive and Gram-negative bacteria by disc diffusion assay.