Supporting Information

Three polymorphic forms of a monomeric Mo(VI) complex: building blocks for two metal-organic supramolecular isomers. Intermolecular interactions and ligand substituent effects

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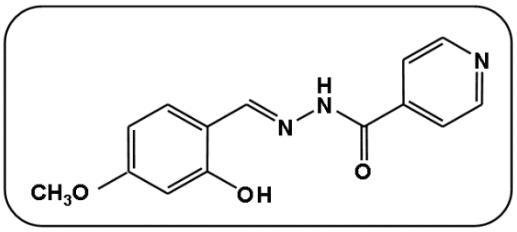
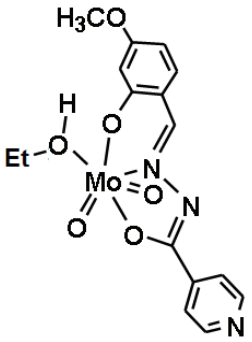
Contents:

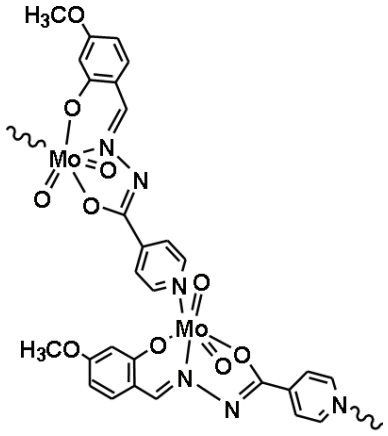
Scheme S1. 4-Methoxy-2-oxybenzaldehyde izonicotinoyl ligand (H_2L); the mononuclear dioxomolybdenum(VI) complex $[MoO_2(L)(EtOH)]$ (**1α**, **1β** and **1γ**); supramolecular isomers: coordination polymer $[MoO_2(L)]_n$ (**2a**) and square molecular host $[MoO_2(L)]_4$ (**2b**).



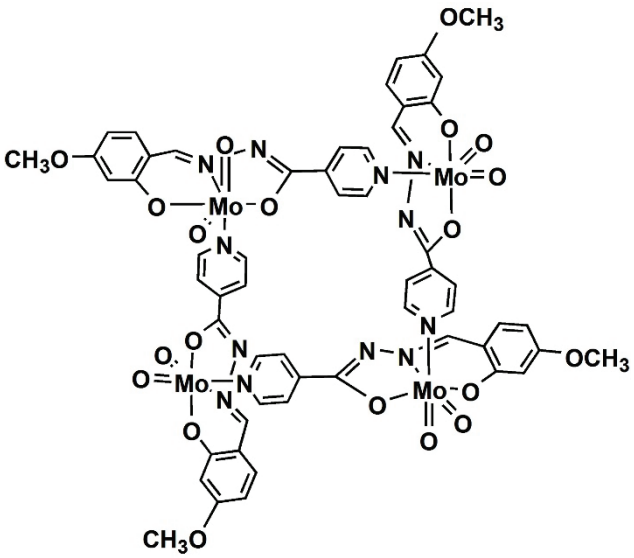
H_2L



$[MoO_2(L)(EtOH)]$ (**1α**, **1β** and **1γ**)

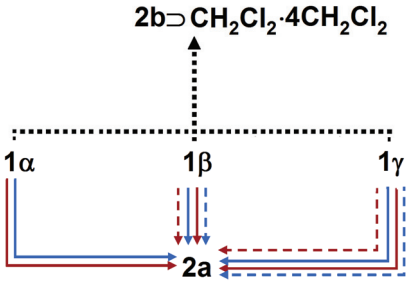


$[MoO_2(L)]_n$ (**2a**)

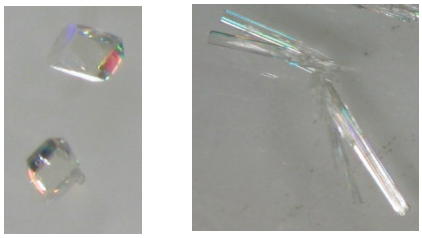


$[MoO_2(L)]_4$ (**2b**)

Scheme S2. Structural conversion: in the solid-state after heating of **1α**, **1β** and **1γ** at 220 °C for 1 h (red solid arrow), upon an exposure of samples (that were obtained by grinding) to ethanol vapours (red dashed arrow); by slurry experiments at room temperature (blue dashed arrow), in refluxing ethanol (blue solid arrow) or in dichloromethane (black dotted arrow).



Spectroscopic and analytical data for H_2L.



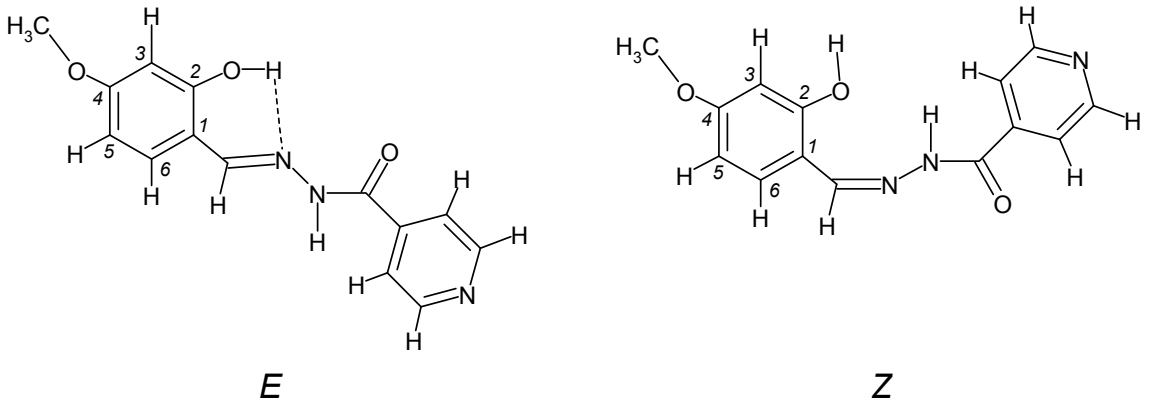
H_2L **$H_2L \cdot H_2O$**

Anal. Calcd. for $C_{14}H_{13}N_3O_3$ (271.271): C, 61.99; H, 4.83; N, 15.49. Found: C, 61.43; H, 4.61; N, 15.18%. DSC melting peak: onset 228.0 °C (174 J/g). Selected IR data (cm^{-1}): 3189 (N−H), 1681 (C=O), 1627 (C=N)py, 1601 (C=N), 1559 (C−O_{phenol}).

^{1}H NMR (dmso-d_6): ***major isomer***: δ (ppm) = 3.78 (s, 3H, OCH_3), 6.51 (s, 1H, H-C3)
6.55 (d, 1H, H-C5), 7.49 (d, 1H, H-C6), 7.83 (d, 2H, H *meta* pyridyl), 8.58 (s, 1H, CH=N), 8.79 (d, 2H, H *ortho* pyridyl), 11.43 (s, 1H, OH), 12.21 (s, 1H, NH).

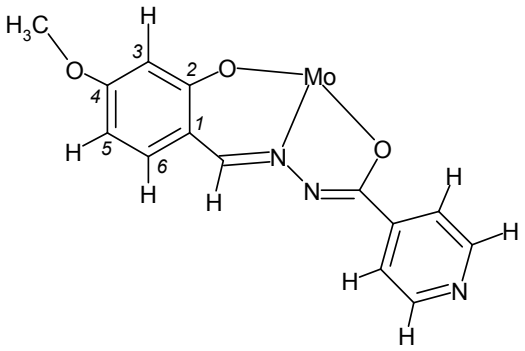
minor isomer: ^{1}H NMR (dmso-d_6): δ (ppm) = 3.71 (s, 3H, OCH_3), 6.40 (s, 1H, H-C3)
6.42 (d, 1H, H-C5), 7.31 (d, 1H, H-C6), 7.61 (d, 2H, H *meta* pyridyl), 8.27 (s, 1H, CH=N), 8.72 (d, 2H, H *ortho* pyridyl), 10.12 (s, 1H, OH), 11.92 (s, 1H, NH).

Scheme S3. Numbering scheme for H_2L



The ^{1}H NMR spectrum of the ligand H_2L was recorded in dmso-d_6. Two sets of signals are present, with integrated intensity ratio of about 1:0.05. Exchange peaks between the signals of the two sets indicate the presence of two isomers, which interconvert slowly on the NMR time scale at R.T... NOE contacts observed in the ROESY experiment are in agreement with an *E* conformation with respect to the C=N bond of the more abundant isomer.

Scheme S4. Numbering scheme for molybdenum compounds



1α (major set), 2a, 2b, 3·γ-pic, 4: ^{1}H NMR (dmso-d_6): δ (ppm) = 3.83 (s, 3H, OCH_3), 6.57 (d, 1H, H-C3), 6.71 (d, 1H, H-C5), 7.67 (d, 1H, H-C6), 7.84 (d, 2H, *meta* pyridyl), 8,74 (d, 2H, *ortho* pyridyl), 8.91 (s, 1H, CH=N).
1α (minor set) ^{1}H NMR (dmso-d_6): δ(ppm) = 3.90 (s, 3H, OCH_3), 6.70 (superimposed signals, 2H, H-C3 and H-C5), 7.70 (d, 1H, H-C6), 7.97 (d, 2H, *meta* pyridyl), 8,79 (d, 2H, *ortho* pyridyl), 9.12 (s, 1H, CH=N).

1α ^{1}H NMR (CD_2Cl_2): δ(ppm) = 1.19 (t, 3H, C*H*$_3$CH$_2$OH), 1.33 (t, 1H, CH$_3$CH$_2$O*H*), 3.65 (m, 2H, CH$_3$C*H*$_2$OH), 3.88 (s, 3H, OCH_3), 6.59 (d, 1H, H-C3), 6.73 (d, 1H, H-C5), 7.48 (d, 1H, H-C6), 7.76 (broad s, 2H, *meta* pyridyl), 8,52 (broad s, 2H, *ortho* pyridyl), 8.66 (s, 1H, CH=N).

Spectoscopic and analytical data for:

[MoO_2(L)(EtOH)] (1α): Anal. Calcd. for $C_{16}H_{17}MoN_3O_6$ (443.26): C, 43.35; H, 3.87; N, 9.48. Found: C, 43.12; H, 3.59; N, 9.21%. TG: CH_3CH_2OH, 10.21% (Calcd. 10.39%); MoO_3, 32.12% (Calcd. 32.47%). Selected IR data (cm^{-1}): 1609 (C=N)py, 1596 (C=N), 1543 ($C-O_{phenolate}$), 1330 ($C-O_{enolate}$), 1042 ($C-O_{EtOH}$), 931 (MoO_{2_asym}), 905 (MoO_{2_sym}). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 215 (18039), 319 (11599) and 409 (6020). UV-Vis ($BaSO_4$): λ/nm: 332, 428, 486.

[MoO_2(L)(EtOH)] (1β): Anal. Calcd. for $C_{16}H_{17}MoN_3O_6$ (443.26): C, 43.35; H, 3.87; N, 9.48. Found: C, 43.01; H, 3.54; N, 9.17%. TG: CH_3CH_2OH, 10.08% (Calcd. 10.39%); MoO_3, 32.16% (Calcd. 32.47%). Selected IR data (cm^{-1}): 1616 (C=N)py, 1597 (C=N), 1542 ($C-O_{phenolate}$), 1332 ($C-O_{enolate}$), 1041 ($C-O_{EtOH}$), 930 (MoO_{2_asym}), 907 (MoO_{2_sym}). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 217 (17926), 318 (11599) and 409 (5693). UV-Vis ($BaSO_4$): λ/nm: 327, 419, 487.

[MoO_2(L)(EtOH)] (1γ): Anal. Calcd. for $C_{16}H_{17}MoN_3O_6$ (443.26): C, 43.35; H, 3.87; N, 9.48. Found: C, 43.09; H, 3.56; N, 9.17%. TG: CH_3CH_2OH, 10.18% (Calcd. 10.39%); MoO_3, 32.23% (Calcd. 32.47%). Selected IR data (cm^{-1}): 1611 (C=N)py, 1597 (C=N), 1542 ($C-O_{phenolate}$), 1338 ($C-O_{enolate}$), 1035 ($C-O_{EtOH}$), 941 (MoO_{2_asym}), 908 (MoO_{2_sym}). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 216 (17469), 317 (11493) and 409 (5592). UV-Vis ($BaSO_4$): λ/nm: 328, 418.

[MoO_2(L)]$_n$ (2a): Anal. Calcd. for $C_{14}H_{11}MoN_3O_5$ (397.194): C, 42.33; H, 2.79; N, 10.58. Found: C, 42.13; H, 2.53; N, 10.33%. TG: MoO_3, 35.94% (Calcd. 36.23%). Selected IR data (cm^{-1}): 1595 (C=N), 1541 ($C-O_{phenolate}$), 1340 ($C-O_{enolate}$), 935 (MoO_{2_asym}), 911 (MoO_{2_sym}). UV-Vis (EtOH): 215 (17466), 318 (11473) and 410 (5519). UV-Vis ($BaSO_4$): λ/nm: 328, 420.

[MoO_2(L)]$_4$⊃CH_2Cl_2·4CH_2Cl_2 (2b⊃CH_2Cl_2·4CH_2Cl_2): Crystals of **2b⊃CH_2Cl_2·4CH_2Cl_2** easily loose dichlomethane molecules at room temperature. They were left in a dessicator up to constant weight and analyzed as **2b·2CH_2Cl_2.** Anal. Calcd. for $C_{58}H_{48}Cl_4Mo_4N_{12}O_{20}$ (1758.64): C, 39.61; H, 2.75; N, 9.56. Found: C, 39.39; H, 2.85; N, 9.21%. TG: MoO_3, 32.47% (Calcd. 32.74%). Selected IR data (cm^{-1}): 1602 (C=N), 1544 ($C-O_{phenolate}$), 1337 ($C-O_{enolate}$), 927 (MoO_{2_asym}), 900 (MoO_{2_sym}). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 216 (17489), 318 (11495) and 410 (5528). UV-Vis ($BaSO_4$): λ/nm: 328, 419.

[MoO_2(L)(γ-pic)]·γ-pic (3·γ-pic): Anal. Calcd. for $C_{26}H_{25}MoN_5O_5$ (583.447): C, 53.52; H, 4.32; N, 12.00. Found: C, 53.45; H, 4.20; N, 11.99. TG: C_6H_7N, 31.57% (Calcd. 31.92%); MoO_3, 24.45 % (Calcd. 24.67 %). Selected IR data (cm^{-1}): 1616, 1603 (C=N), 1589 (C=N), 1545 ($C-O_{phenolate}$), 1333 ($C-O_{enolate}$), 930 (MoO_{2_asym}), 902 (MoO_{2_sym}). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 217 (20400), 327 (13860) and 416 (3840).

[MoO_2(L)(py)] (4): Anal. Calcd. for $C_{19}H_{16}MoN_4O_5$ (476.294): C, 47.91; H, 3.39; N, 11.76. Found: C, 48.13; H, 3.35; N, 11.79. TG: C_5H_5N, 16.81% (Calcd. 16.61%); MoO_3, 29.89% (Calcd. 30.22%). Selected IR data (cm^{-1}): 1615, 1593 (C=N), 1542 ($C-O_{phenolate}$), 1334 ($C-O_{enolate}$), 932 (MoO_{2_asym}), 908 (MoO_{2_sym}). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 217 (20840), 327 (15100) and 416 (4720).

[MoO_2(L)(dmso)] (5): Anal. Calcd. for $C_{16}H_{17}MoN_3O_6S$ (475.32): C, 40.43; H, 3.60; N, 8.84. Found: C, 40.28; H, 3.53; N, 9.17. TG: C_2H_6OS, 16.12 % (Calcd. 16.44 %); MoO_3, 29.86% (Calcd. 30.28%). Selected IR data (cm^{-1}): 1616, 1593 (C=N), 1544 ($C-O_{phenolate}$), 1343 ($C-O_{enolate}$), 920 (MoO_{2_asym}), 892 (MoO_{2_sym}). UV-Vis (EtOH): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 217 (22250), 318 (13780) and 402 (7040).

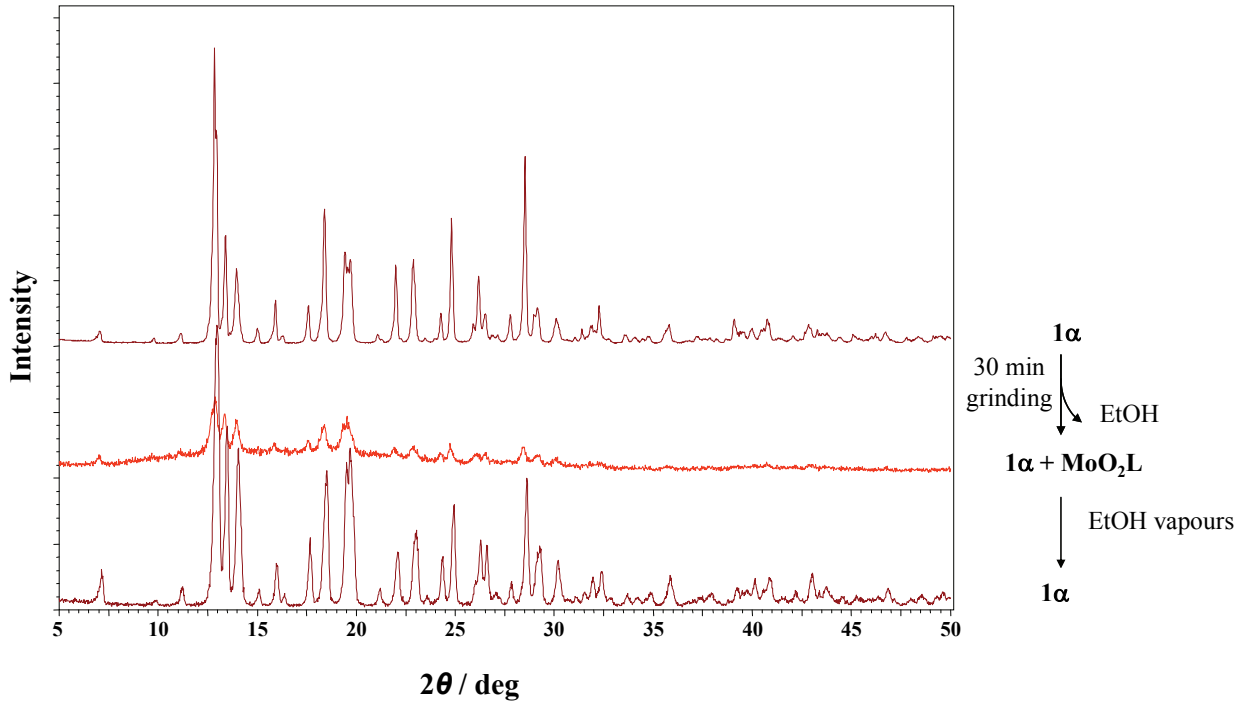


Figure S1. Powder X-ray diffraction patterns of: sample obtained after initial grinding of **1α** (top); sample obtained after 30 min grinding of **1α** (middle) and sample obtained upon an exposure of the second sample to ethanol vapours (bottom).

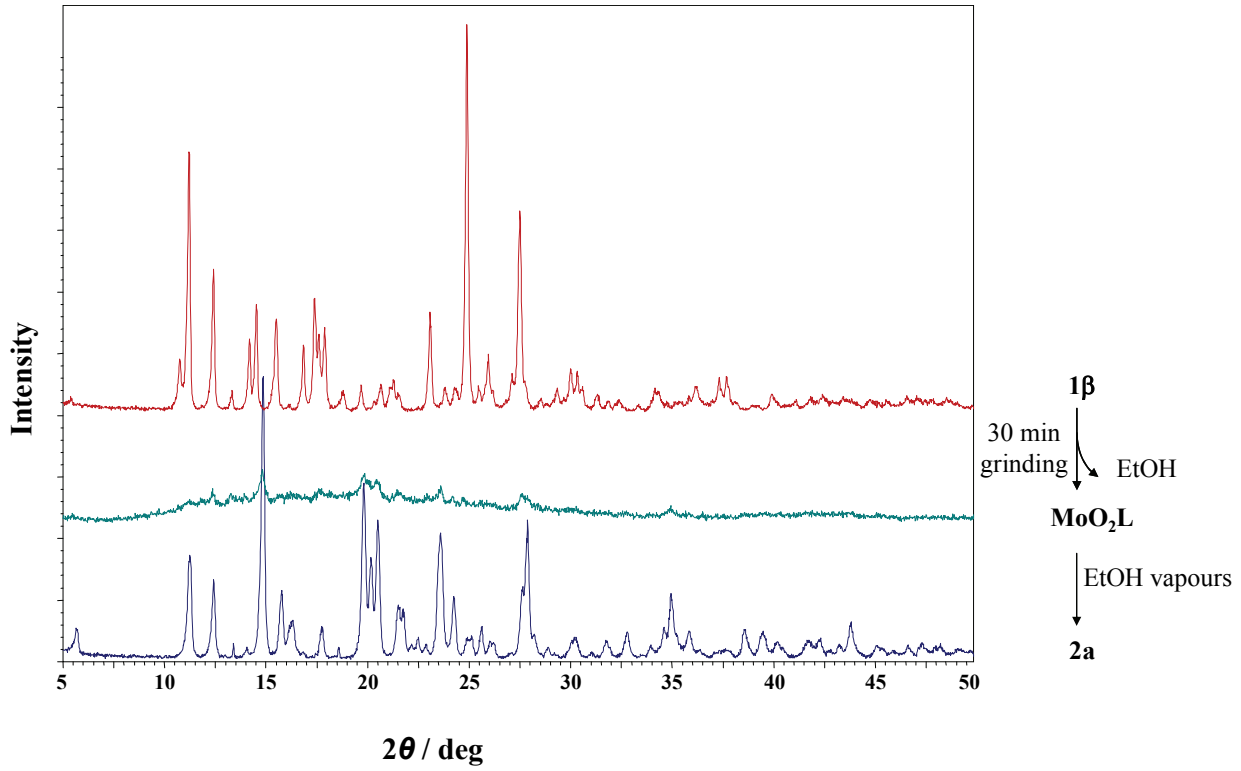


Figure. S2. Powder X-ray diffraction patterns of: sample obtained after initial grinding of **1β** (top); sample obtained after 30 min grinding of **1β** (middle) and sample obtained upon an exposure of MoO_2L sample to ethanol vapours (bottom).

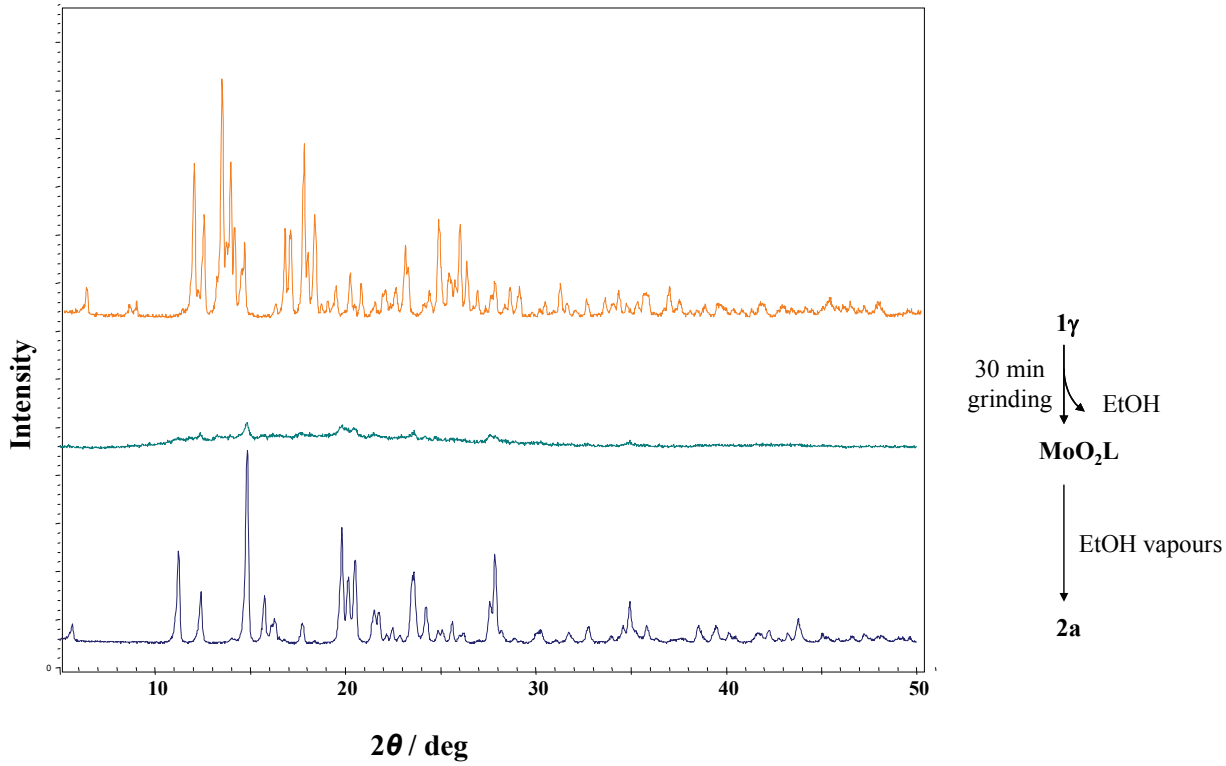


Figure S3. Powder X-ray diffraction patterns of: sample obtained after initial grinding of **1γ** (top); sample obtained after 30 min grinding of **1γ** (middle) and sample obtained upon an exposure of MoO_2L to ethanol vapours (bottom).

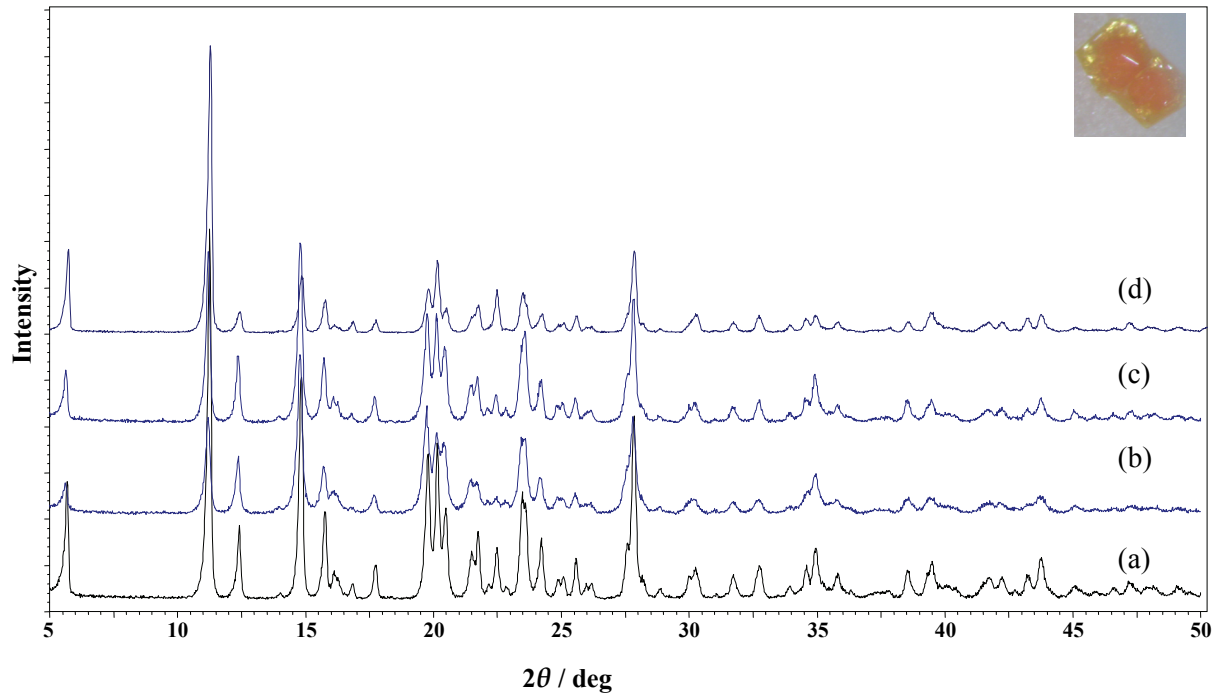


Figure S4. Powder X-ray diffraction patterns of (a) **2a** obtained upon reaction of $[MoO_2(acac)_2]$ with H_2L in C_2H_5OH; (b–d) samples obtained upon heating of the crystalline sample of **1α**, **1β**, or **1γ** for 1 hour at 220 °C, respectively.

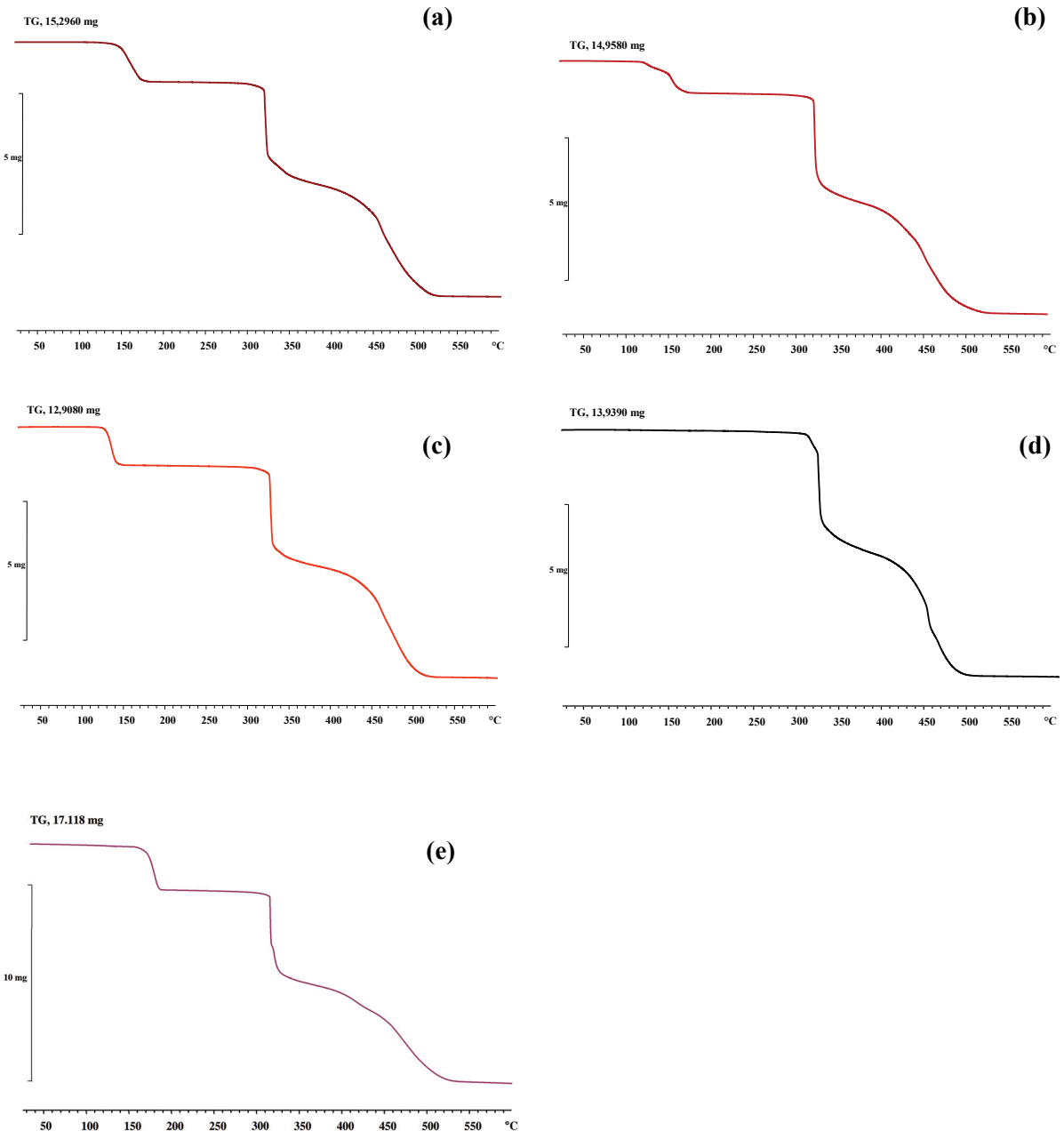


Figure S5. TG curves of (a) form **1α**; (b) form **1β**; (c) form **1γ** and (d) coordination polymer **2a** and (e) molecular square **2b·2CH$_2$Cl$_2$** under the O_2 atmosphere. Experiments were recorded with a heating rate of 5 °C min^{-1} in a dynamic atmosphere with a flow rate of 200 cm^3 min^{-1}.

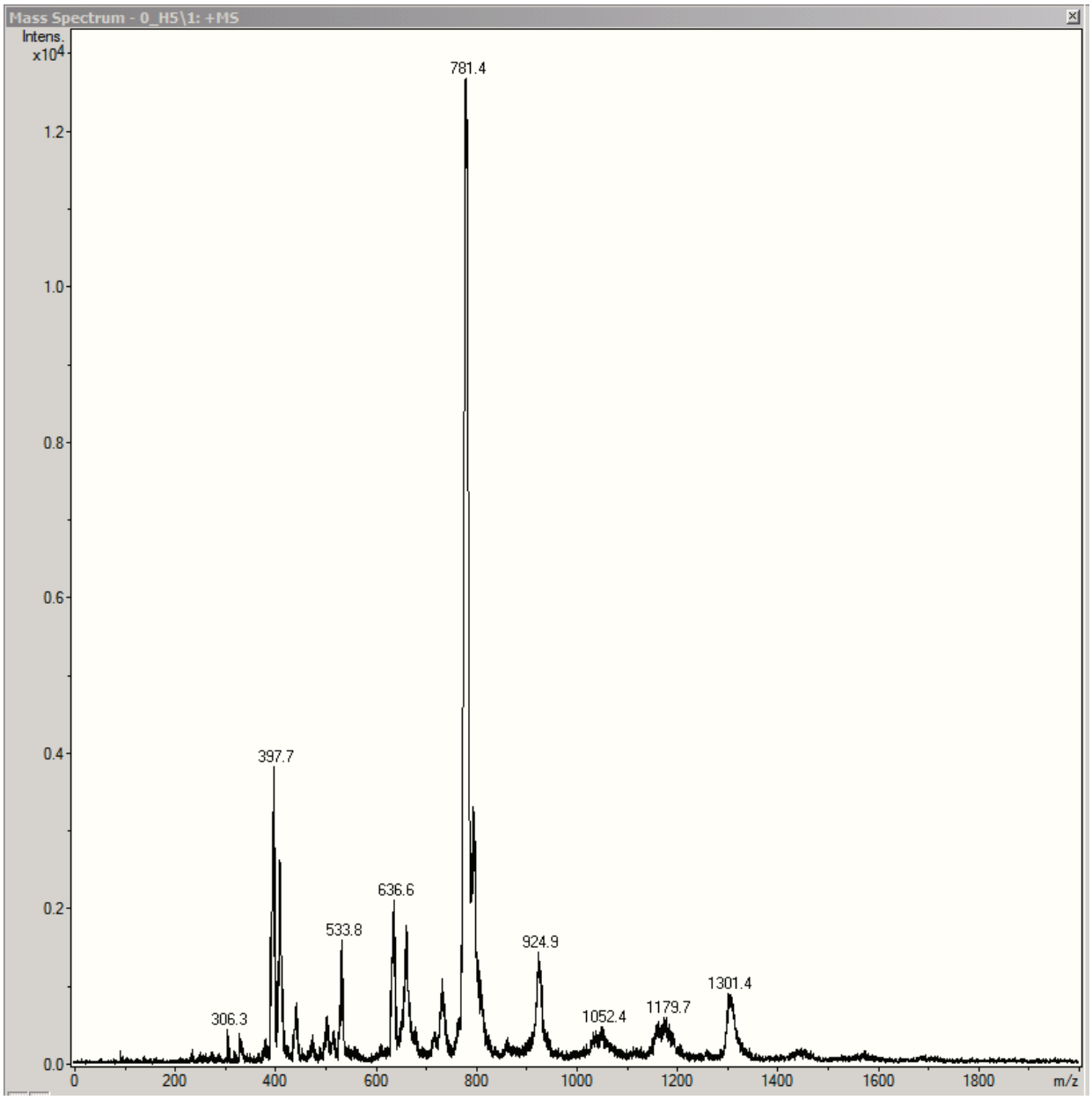
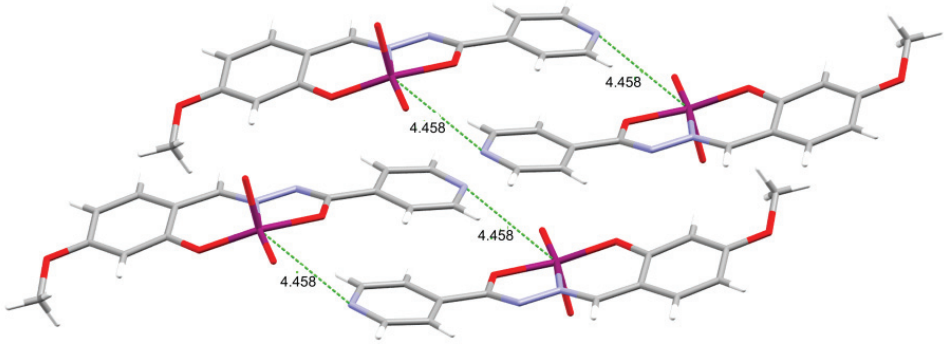
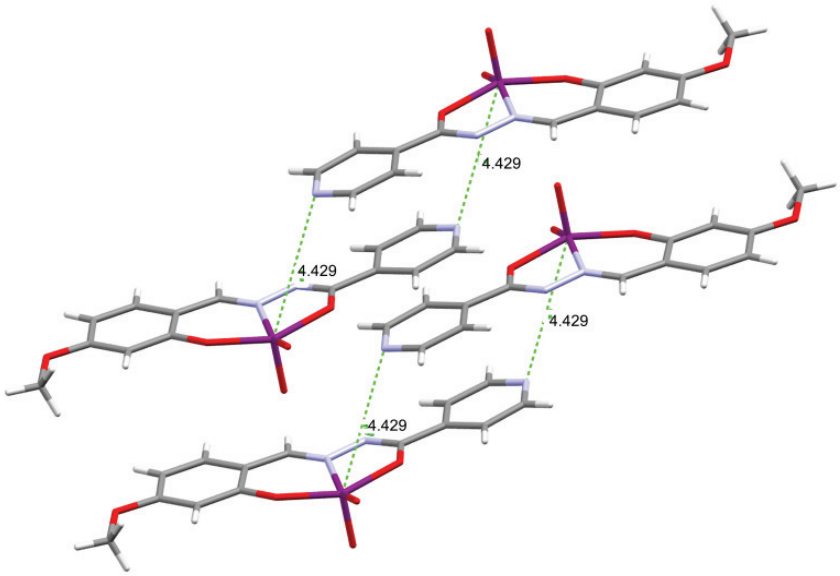


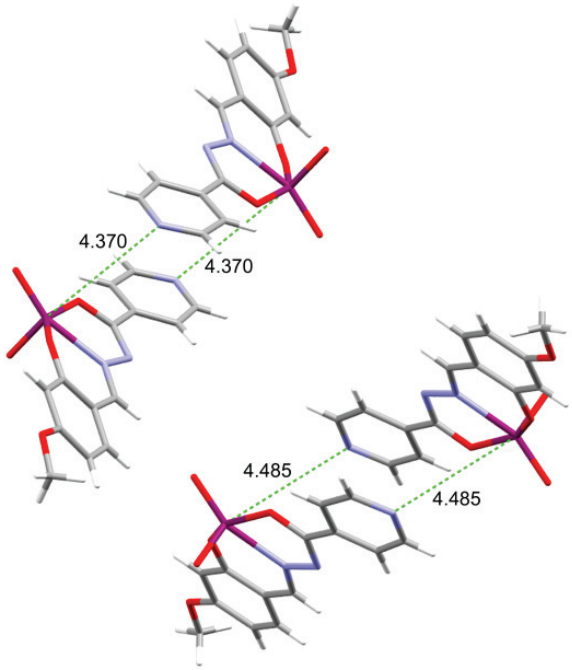
Figure S6. Mass spectra of **2a (**obtained directly from individual crystals).



(a)



(b)



(c)

Figure S7. Drawing represents the shorthes Mo···N (Å) distance in polymorphs **1α** (a), **1β** (b) and **1γ** (c). The molecules are presented with the EtOH moiety deleted. Mo and N atoms from neighboring molecules are connected by green dashed lines.

Table S1. Selected bond lengths (Å) and angles (°) for **1α**, **1β**, **1γ**, **2b⊃CH_2Cl_2·4CH_2Cl_2**, **3·γ-pic**, **4** and **5**

	1α	**1β**	**1γ***	**2b⊃CH_2Cl_2·4CH_2Cl_2**[‡]	**3·γ-pic**	**4**	**5**
Mo1-O1	1.6896(17)	1.6896(16)	1.687(4), 1.682(4)	1.7003(18), 1.7034(17)	1.692(2)	1.6939(18)	1.6892(16)
Mo1-O2	1.700(2)	1.6984(14)	1.689(3), 1.691(3)	1.7027(19), 1.7040(17)	1.703(2)	1.7021(17)	1.7043(17)
Mo1-O3	1.9273(16)	1.9228(14)	1.928(3), 1.937(3)	1.9340(17), 1.9263(17)	1.9437(17)	1.9364(15)	1.9311(14)
Mo1-O4	2.0004(15)	2.0043(14)	2.006(3), 2.007(3)	2.0083(17), 2.0098(17)	2.0171(17)	2.0191(16)	1.9936(15)
Mo1-O6	2.3300(15)	2.3493(18)	2.392(3), 2.394(3)	-	-	-	2.3007(16)
Mo1-N1	2.2223(16)	2.218(2)	2.239(3), 2.242(3)	2.234(2), 2.2405(19)	2.242(2)	2.2319(18)	2.2264(17)
Mo11-N23	-	-	-	2.434(2)	-	-	-
Mo21-N13[i]	-	-	-	2.443(2)	-	-	-
Mo1-N4	-	-	-	-	2.456(2)	2.4285(17)	-
N1-N2	1.401(2)	1.399(2)	1.399(4), 1.399(5)	1.397(3), 1.394(3)	1.404(3)	1.400(3)	1.400(2)
N1-C1	1.284(3)	1.285(3)	1.289(5), 1.291(5)	1.291(3), 1.294(3)	1.286(3)	1.279(3)	1.284(3)
N2-C2	1.287(3)	1.290(3)	1.308(5), 1.281(6)	1.294(4), 1.295(3)	1.299(3)	1.289(3)	1.288(3)
O1-Mo1-O2	104.45(8)	105.02(7)	105.06(15), 105.23(17)	106.88(9), 106.08(8)	106.01(10)	106.01(8)	104.93(8)
O1-Mo1-O3	98.27(8)	99.07(7)	99.69(17), 99.81(18)	98.62(8), 100.26(8)	99.58(9)	97.39(8)	96.79(7)
O1-Mo1-O4	99.81(8)	97.22(7)	96.01(16), 98.79(17)	100.32(8), 97.91(8)	96.45(8)	98.78(8)	97.26(7)
O1-Mo1-O6	169.42(7)	169.86(7)	170.96(13), 170.30(13)	-	-	-	170.11(8)
O1-Mo1-N1	90.31(7)	94.04(6)	95.34(13), 92.59(14)	92.38(8), 94.63(8)	93.99(9)	92.34(8)	94.60(8)
O1-Mo1-N4	-	-	-	-	170.15(8)	170.19(7)	-
O2-Mo1-O3	103.33(8)	101.23(7)	100.77(13),102.64(1)	103.32(8), 102.04(8)	103.13(9)	105.49(7)	102.06(7)
O2-Mo1-O4	97.17(8)	98.06(7)	99.19(13), 97.80(17)	96.27(8), 98.04(7)	97.39(9)	94.79(7)	97.70(7)

O2-Mo1-O6	86.13(7)	85.01(7)	83.73(13), 84.46(15)	-	-	-	84.95(7)
O2-Mo1-N1	163.09(8)	159.68(7)	158.57(14), 160.61(16)	159.11(9), 158.15(8)	158.48(8)	158.80(7)	159.10(7)
O2-Mo1-N4	-	-	-	-	83.03(8)	83.79(7)	-
O3-Mo1-O4	148.22(6)	150.50(6)	150.35(11), 147.55(12)	147.38(7), 147.88(7)	149.23(7)	149.37(6)	151.85(6)
O3-Mo1-O6	79.11(6)	80.07(6)	80.36(12), 78.17(14)	-	-	-	80.40(6)
O3-Mo1-N1	82.23(6)	82.27(6)	81.82(11), 81.30(11)	81.13(7), 80.58(7)	80.77(7)	82.01(6)	82.57(6)
O3-Mo1-N4	-	-	-	-	81.78(7)	80.12(6)	-
O4-Mo1-O6	78.33(6)	79.60(6)	80.27(11), 79.03(14)	-	-	-	81.59(6)
O4-Mo1-N1	71.78(6)	72.16(6)	71.76(11), 71.49(11)	71.80(7), 71.72(7)	72.03(7)	71.51(7)	72.10(6)
O4-Mo1-N4	-	-	-	-	78.19(7)	79.53(6)	-
O6-Mo1-N1	79.20(6)	75.82(6)	75.69(11), 77.73(11)	-	-	-	75.67(6)
N1-Mo1-N4	-	-	-	-	76.54(7)	77.94(6)	-

*The labels in the two independent molecules in **1γ** are: Mo11 and Mo21, N11 and N21, N12 and N22, N13 and N23, O11 and O21, O12 and O22, O13 and O23, O14 and O24, O16 and O26, C11 and C21, C12 and C22

‡The labels in **2b⊃CH_2Cl_2·4CH_2Cl_2** are Mo11 and Mo21, N11 and N21, N12 and N22, N13 and N23, O11 and O21, O12 and O22, O13 and O23, O14 and O24, O16 and O26, C11 and C21, C12 and C22

i=-x, y, 1/2-z

Table S2. Geometry of intermolecular hydrogen bonds (Å,°) and π···π interactions involved in the formation of dimers and between neighbouring dimer molecules for compounds **1α**, **1β** and **1γ**

1α	D−H···A	D−H /Å	H···A /Å	D···A /Å	D−H···A /°
	O6-H2···N3[i]	0.72(3)	1.99(3)	2.703(3)	174(3)
	π···π	Cg3···Cg3[i] /Å	slippage /Å		
		3.5129(11)	1.12		
		Cg3···Cg3[ii] Å			
		4.0607(12)			
		Cg4···Cg4 [iii] /Å	slippage /Å		
		3.8367(11)	1.74		
1β	D−H···A	D−H /Å	H···A /Å	D···A /Å	D−H···A /°
	O6-H2···N3[iv]	0.70(2)	2.06(3)	2.757(3)	175(4)
	π···π	Cg3···Cg3[i] / Å	slippage /Å		
		3.6467(15)	1.25		
		Cg4···Cg4 [v] /Å	slippage /Å		
		3.6961(14) Å	1.39		
1γ	D−H···A	D−H /Å	H···A /Å	D···A /Å	D−H···A /°
	O16-H33···N13[v]	0.76(4)	1.98(4)	2.733(5)	170(4)
	O26-H34···N23[i]	0.72(5)	2.07(5)	2.775(6)	169(5)
	π···π	Cg3···Cg3[vi] / Å	slippage /Å		
		3.634(3)	1.20		
		Cg7···Cg7[i] / Å	slippage /Å		
		3.762(3)	0.96		
		Cg4···Cg4[vii]			
		4.106(3)	2.01		
		Cg8···Cg8[viii]			
		3.709(3)	1.32		

[i] −*x*,1−*y*,−*z*; [ii] −x,y,1/2-z; [iii]1/2−*x*, 1/2−*y*, −*z*; [iv] −*x*,1−*y*,1−*z*; [v]−*x*, 1−*y*, 2−*z*; [vi]1−*x*, 2−*y*,1−*z*; [vii]−*x*, 1−*y*, 1−*z*; [viii]1−*x*, −*y*, −*z*

Cg3 is the centroid of the ring N3, C3−C7 in **1α** and **1β** and N13, C13−C17 in **1γ**; Cg4 is the centroid of the ring C8 −C13 in **1α** and **1β**, C18-C113 in **1γ**; Cg7 is the centroid of the ring N23, C23−C27 in **1γ**; Cg8 is the centroid of the ring C28 −C213 in **1γ**

Table S3. Geometry of intra- and intermolecular hydrogen bonds (Å, °) for **1α**, **1β**, **1γ**

	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
1α	O6-H2···N3[i]	0.72(3)	1.99(3)	2.703(3)	174(3)
	C5-H5···O5[ii]	0.93	2.50	3.421(3)	173
	C6-H6···O2[iii]	0.93	2.38	3.170(3)	142
	C10-H10···O1[iv]	0.93	2.56	3.461(3)	163
	C14-H14B···O1[v]	0.96	2.45	3.372(3)	161
	C15-H15A···O3	0.96	2.59	3.111(3)	114
1β	O6-H2···N3[vi]	0.70(2)	2.06(3)	2.757(3)	175(4)
	C1-H1···O1[vii]	0.93	2.38	3.298(2)	170
	C5-H5···O2[viii]	0.93	2.46	3.362(3)	163
1γ	O16-H33···N13[ix]	0.76(4)	1.98(4)	2.733(5)	170(4)
	O26-H34···N23[i]	0.72(5)	2.07(5)	2.775(6)	169(5)
	C11-H1···O22[vi]	0.93	2.60	3.459(5)	154
	C14-H2···O23[iii]	0.93	2.55	3.419(5)	155
	C21-H6···O12[x]	0.93	2.48	3.343(5)	154
	C110-H11···O22[i]	0.93	2.54	3.412(6)	156
	C114-H14···O21[vii]	0.96	2.57	3.282(7)	131
	C115-H17···O12	0.97	2.60	3.115(8)	113
	C210-H22···O12[x]	0.93	2.55	3.389(5)	150
	C214-H26···O11[xi]	0.96	2.59	3.121(6)	115

[i] -x,1-y,-z; [ii] -1/2+x,1/2+y, z; [iii] x,1+y,z; [iv] 1/2-x,1/2+y,1/2-z; [v] 1/2-x,-1/2+y,1/2-z; [vi] -x,1-y,1-z; [vii] -1+x,y,z; [viii] 1-x,1-y,1-z; [ix]1-x,2-y,1-z; [x]1-x,1-y,-z; [xi]1+x,-1+y,z

Table S4. Geometry of intra- and intermolecular hydrogen bonds (Å, °) and C-H···π interaction for **3·γ-pic**, **4** and **5**

3·γ-pic	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
	C15- H15···O3	0.93	2.55	3.070(3)	115
	C18-H18···N5[i]	0.93	2.58	3.503(5)	170
	C19-H19···O4	0.93	2.52	2.964(3)	110
	C4-H4···O2[ii]	0.93	2.70	3.582(3)	158
	C-H···π	d(C14···Cg3) (Å)			
	C14-H14a···Cg3[iii]	3.711(4)			
4	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(˚)
	C4-H4···O4	0.93	2.45	2.769(4)	100
	C15-H15···O3	0.93	2.45	2.963(3)	115
	C6-H6···O1[iv]	0.93	2.63	3.256(3)	125
	C7-H7···O1[iv]	0.93	2.66	3.258(3)	123
	C-H···π	d(C1···Cg4) (Å)			
	C1-H1···Cg4[v]	3.847(2)			
5	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(˚)
	C6-H6···O5[vi]	0.93	2.54	3.407(3)	155
	C10-H10···O1[vii]	0.93	2.58	3.072(3)	113
	C15-H15B···O1[viii]	0.96	2.57	3.450(3)	152
	C16-H16C···O1 [viii]	0.96	2.56	3.437(3)	153
	C-H···π	d(C14···Cg4) (Å)			
	C14-H14b···Cg4[vii]	3.711(4)			

[i]-1/2+x,1/2-y,-1/2+z ; [ii]1-x,-y,1-z; [iii]1/2+x,1/2-y,½+z; [iv] x,-1/2-y,1/2+z ; [v]-x, -y, -z; [vi]x,1+y,1+z, [vii]1-x,2-y,-z; [viii]-1+x,y,z

Cg3 is the centroid of the ring N3, C3-C7 in **3·γ-pic**, Cg4 is the centroid of the ring N4, C15-C19 in **4,** Cg3 is the centroid of the ring N4, C15-C19 in **5.**

Table S5. Geometry of intra- and intermolecular hydrogen bonds (Å, °) for **2b⊃CH_2Cl_2·4CH_2Cl_2**

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A(°)
C1A-H1A···O11[i]	0.99	2.51	3.147(6)	122
C1A-H1B···N12[ii]	0.99	2.50	3.485(7)	171
C2B-H2B2···O21	0.99	2.37	3.285(17)	153
C11-H11···O11 [iii]	0.95	2.47	3.051(3)	119
C114-H11B···O25[iv]	0.98	2.59	3.509(4)	156
C21-H21···O21[v]	0.95	2.44	3.238(3)	141
C214-H21B···O13[v]	0.98	2.52	3.080(3)	116
C111-H111···O25[iv]	0.95	2.59	3.152(3)	118

[i] -1/2+x,1/2+y,z; [ii] -x,1+y,1/2-z; [iii] 1/2-x,-1/2+y,1/2-z; [iv] -x,-y,-z ; [v] -x,1-y,-z

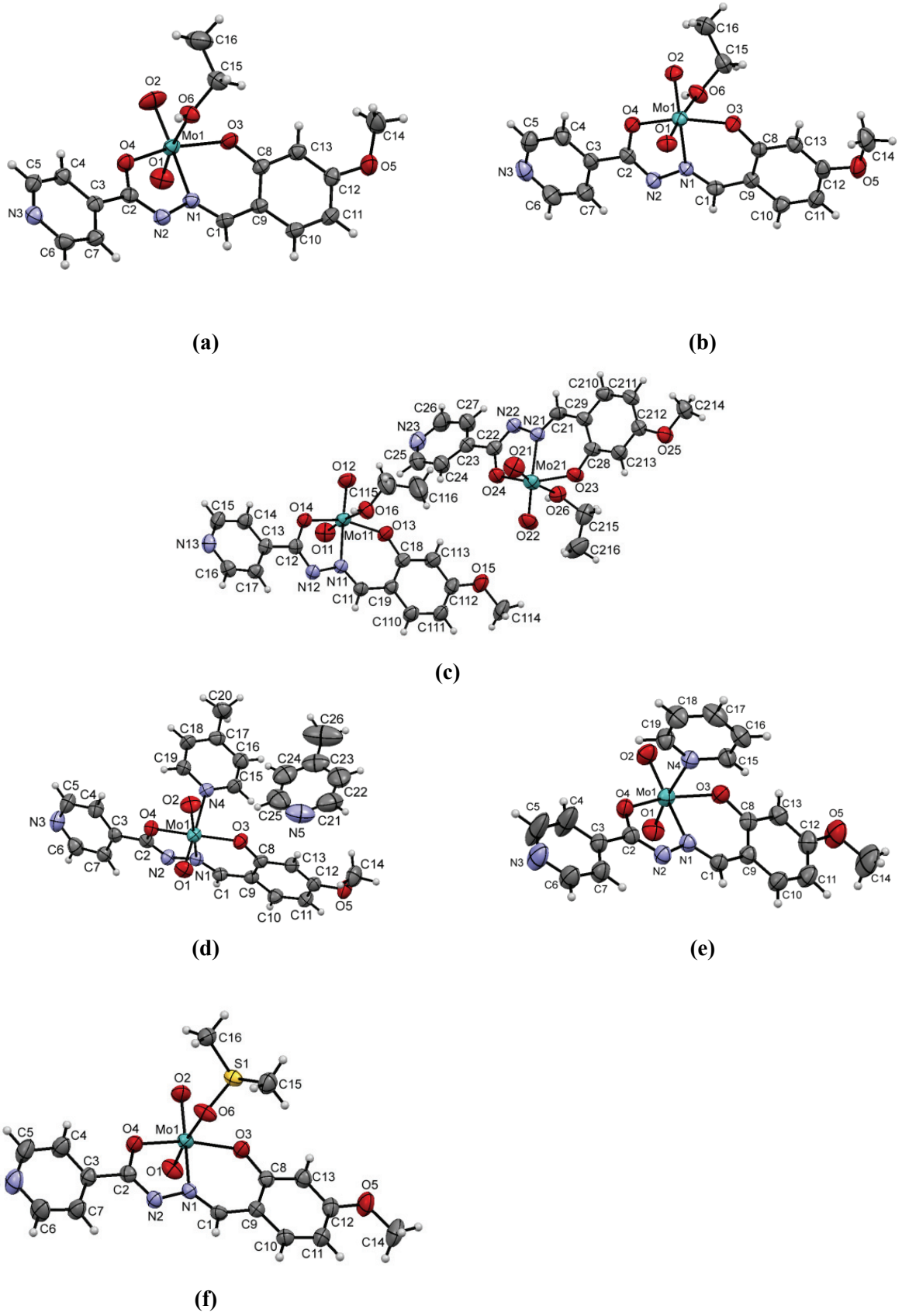


Figure S8. ORTEP plot of **1α** (a), **1β** (b), **1γ** (c), **3·γ-pic** (d), **4** (e) and **5** (f). Displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

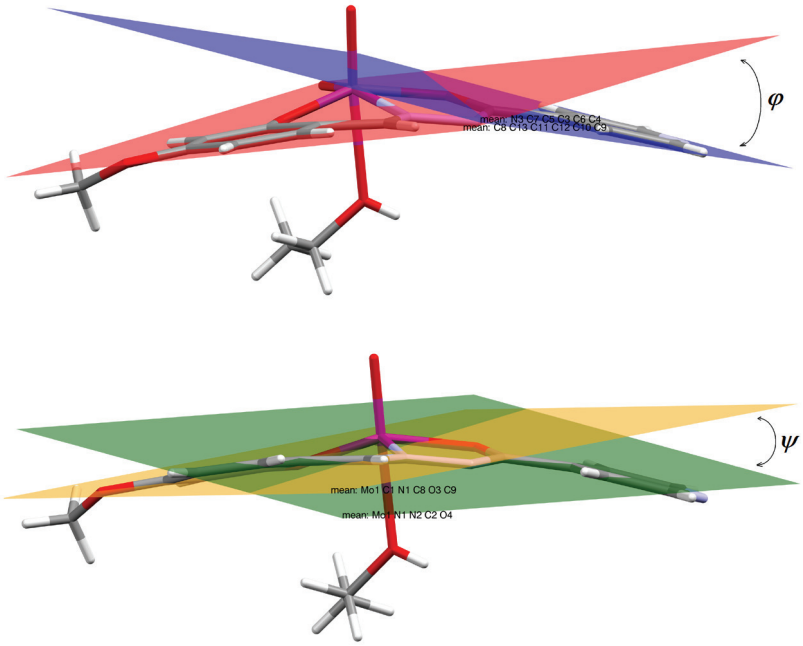
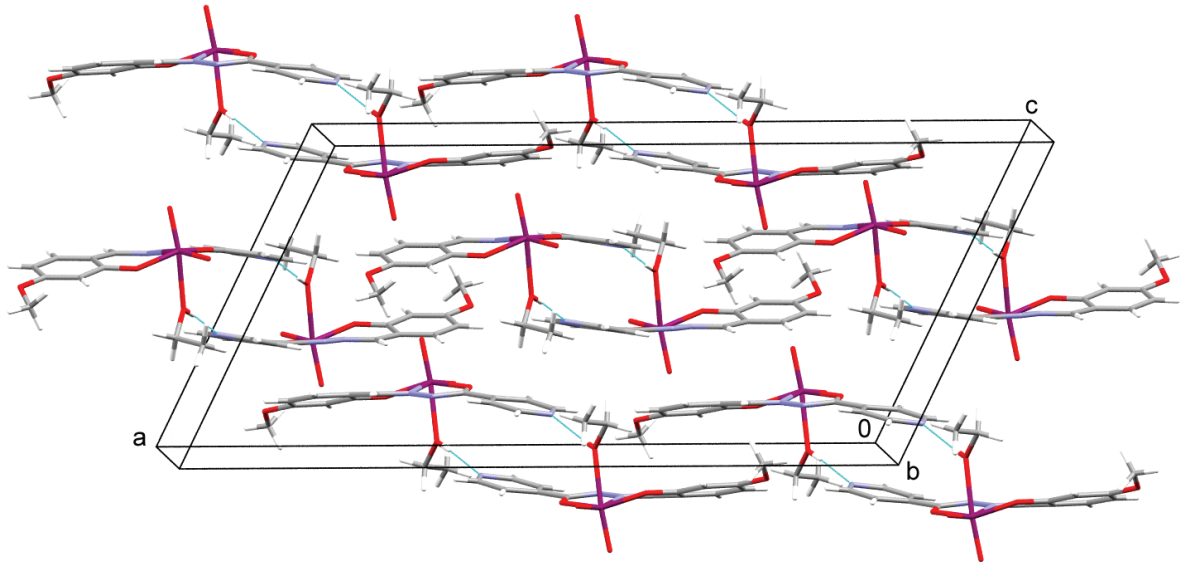
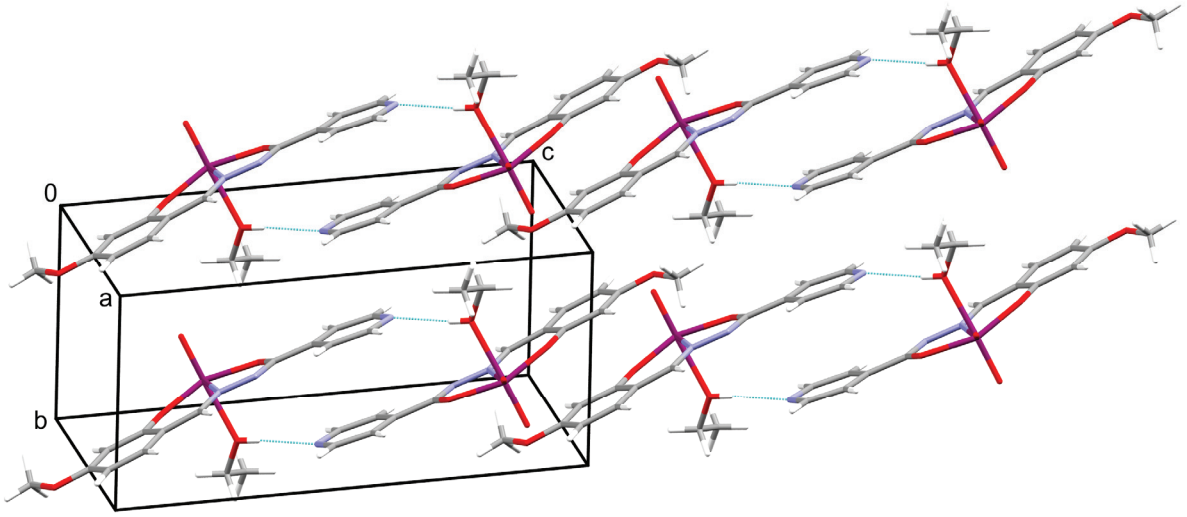


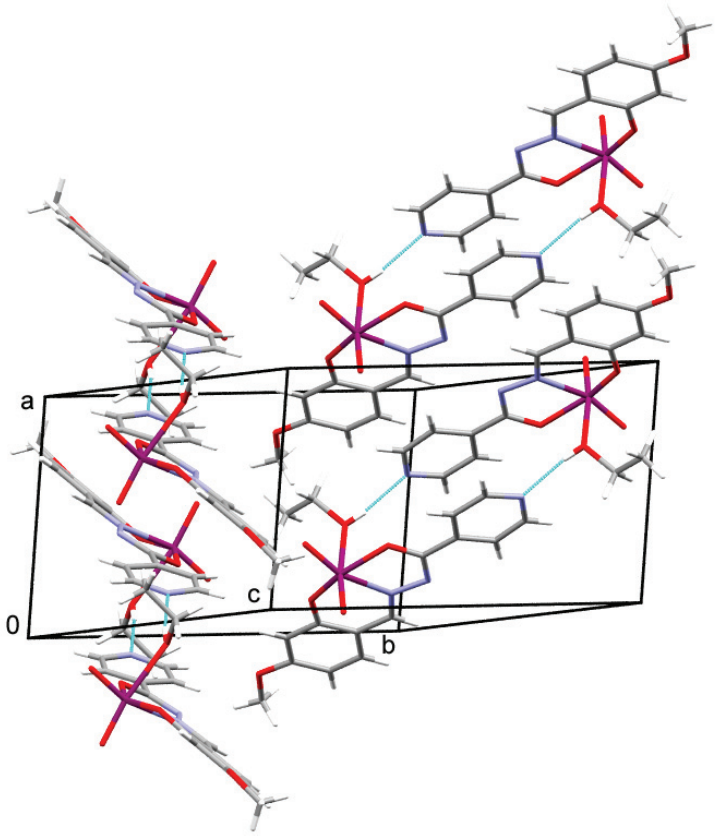
Figure S9. Angle φ between the least-squares planes through the phenyl (red) and the pyridyl rings (blue), and angle ψ between the least-squares planes through the five- (green) and six-membered chelate ring (yellow).



(a)



(b)



(c)

Figure S10. Packing of the molecules of (a)**1α**; (b) **1β**; (c) **1γ** in the unit cell. Hydrogen bonds are shown as blue dashed lines.

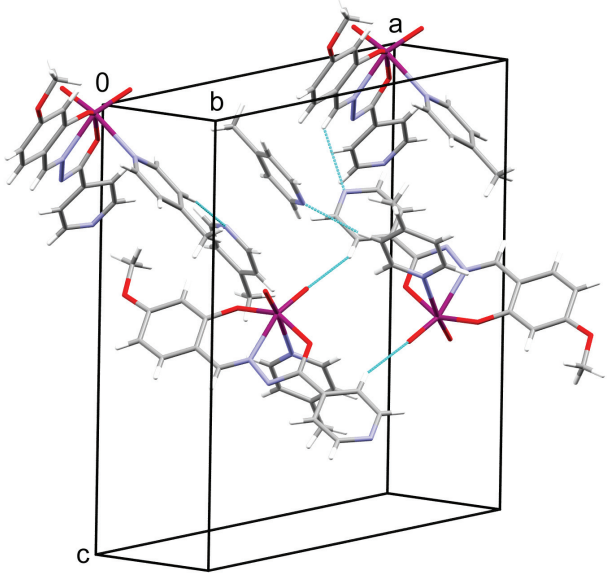


Figure S11. Weak C-H···N and C-H···O hydrogen bonds (C18-H18···N5[-1/2+x,1/2-y,-1/2+z] 3.503(5)Å and C4-H4···O2 [1-x,-y,1-z] 3.582(3) Å) in **3·γ-pic**. Hydrogen bonds are shown as blue dashed lines.

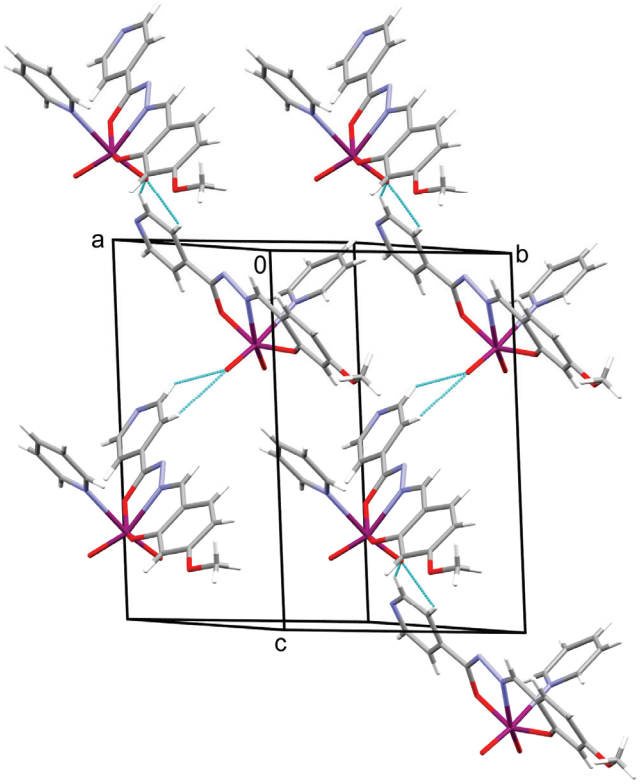


Figure S12. Weak C-H···O hydrogen bonds (C6-H6···O1[x,-1/2-y,1/2+z]) 3.256(3) Å and C7-H7···O1[x,-1/2-y,1/2+z] 3.258(3) Å) in **4.** Hydrogen bonds are shown as blue dashed lines.

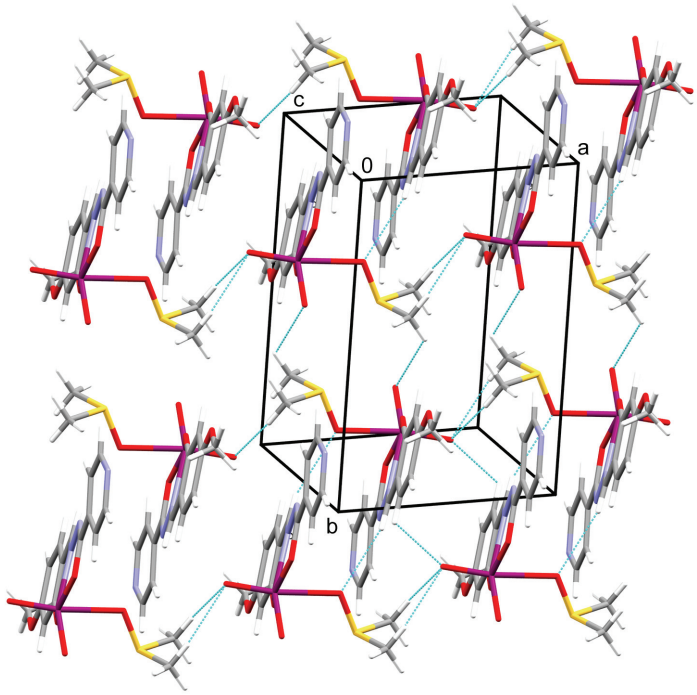
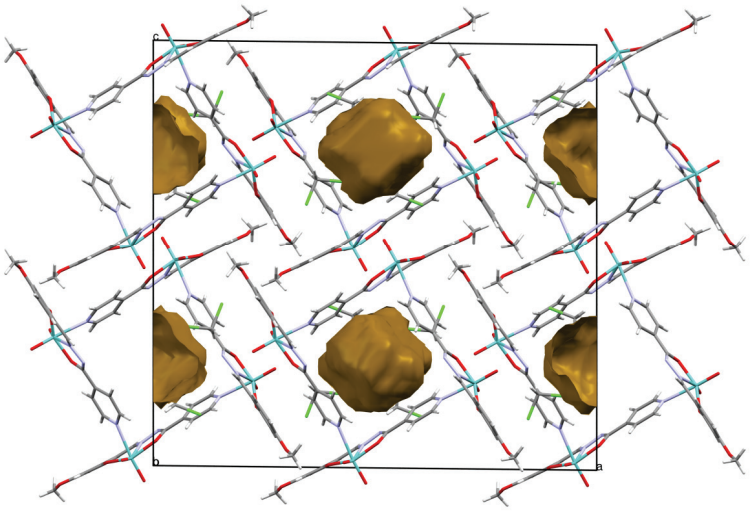
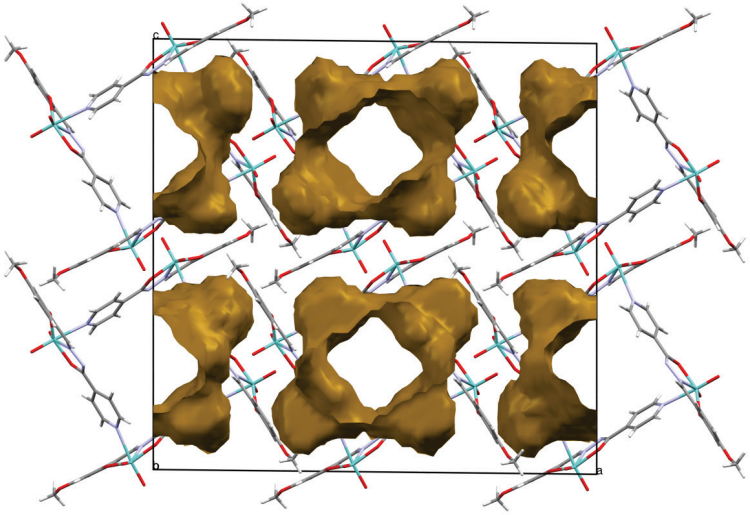


Figure S13. Weak C-H···O hydrogen bonds (C6-H6···O5[x,1+y,1+z] 3.407(3) Å, C10-H10···O1[1-x,2-y,-z] 3.072(3) Å, C15-H15B···O1[-1+x,y,z] 3.450(3) Å and C16-H16C···O1 [-1+x,y,z] 3.437(3) Å) in **5.** Hydrogen bonds are shown as blue dashed lines.



(a)



(b)

Figure S14. (a) Packing of the molecules of **2b⊃CH_2Cl_2·4CH_2Cl_2** along the *b* axis. The solvent accessible area is shown in orange color; (b) Channels extending along the *b*-axis are formed by the stacked molecular squares when all solvent molecules are removed . The probe radius was 1Å.

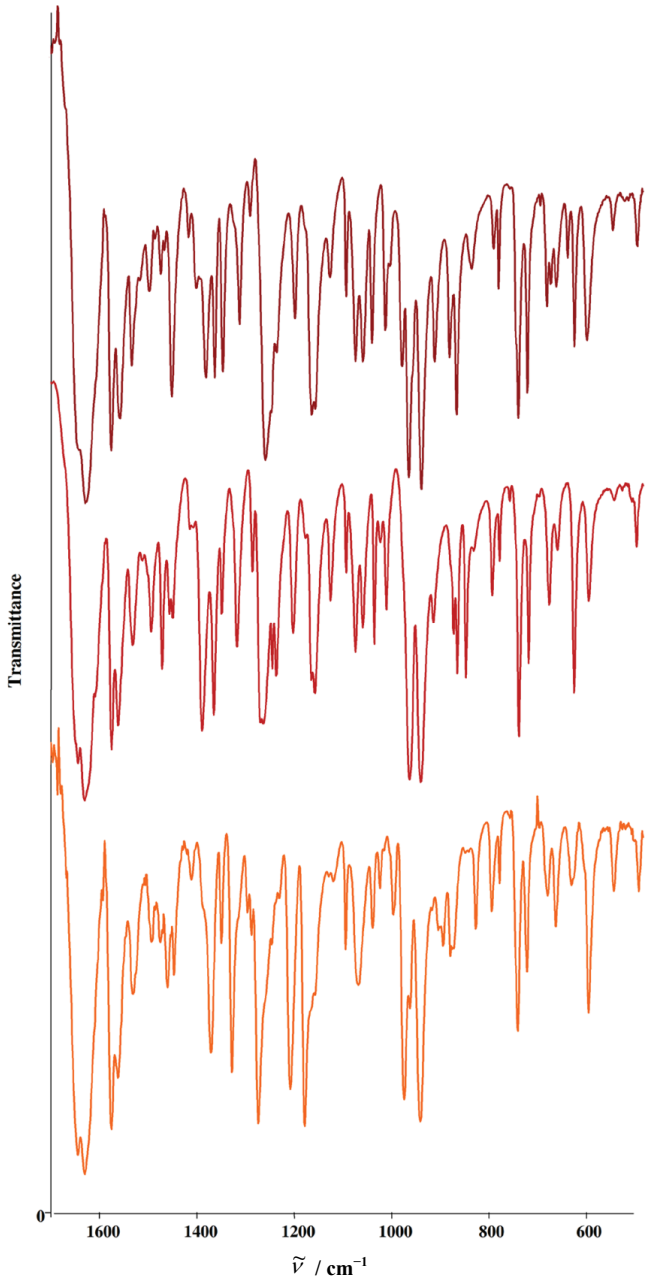


Figure S15. Comparison of FT-IR spectra of polymorphs **1α** (top); **1β** (middle) and **1γ** (bottom).

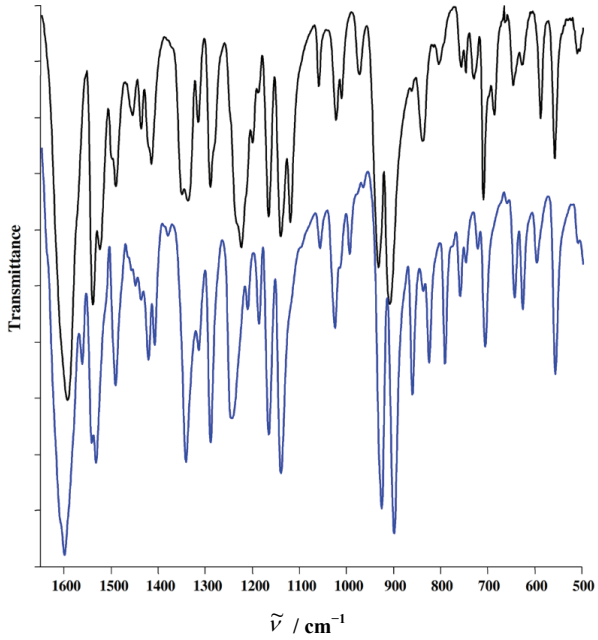


Figure S16. IR spectra of **2a** (blue) and **2b** (black).

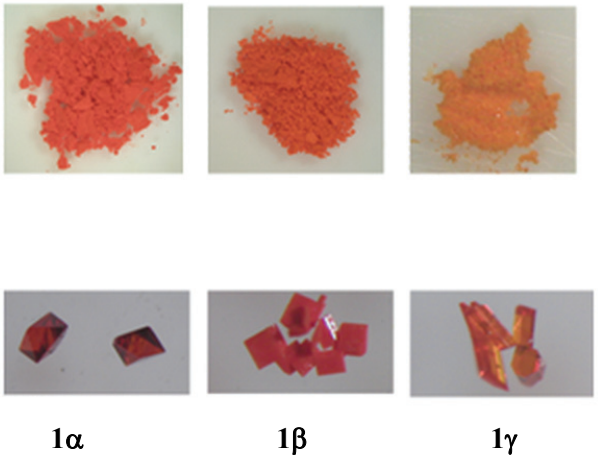


Figure S17. Photos of the powdered (upper part) and crystalline forms (lower part) of **1α**, **1β** and **1γ**.

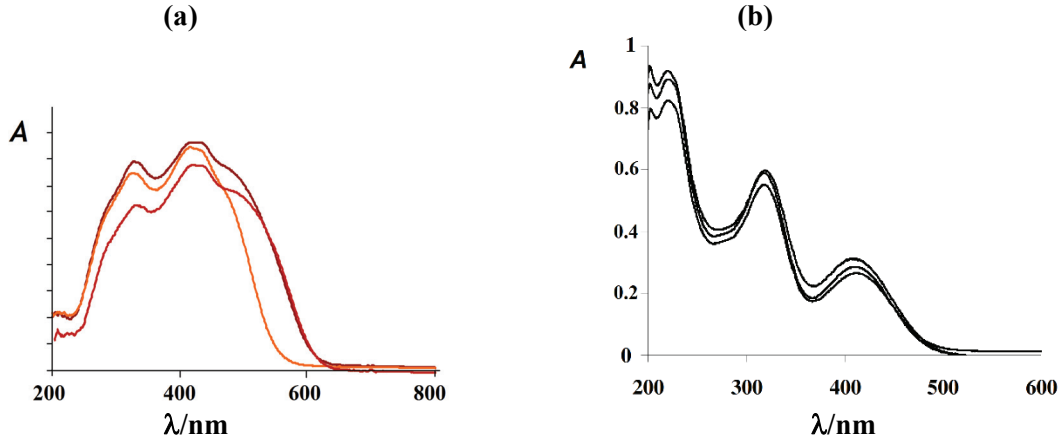


Figure S18. (a) Solid state UV-Vis spectra of **1α** (dark red), **1β** (red) and **1γ** (orange); (b) UV-Vis spectra of **1α**, **1β** and **1γ** in ethanol at 25 °C.

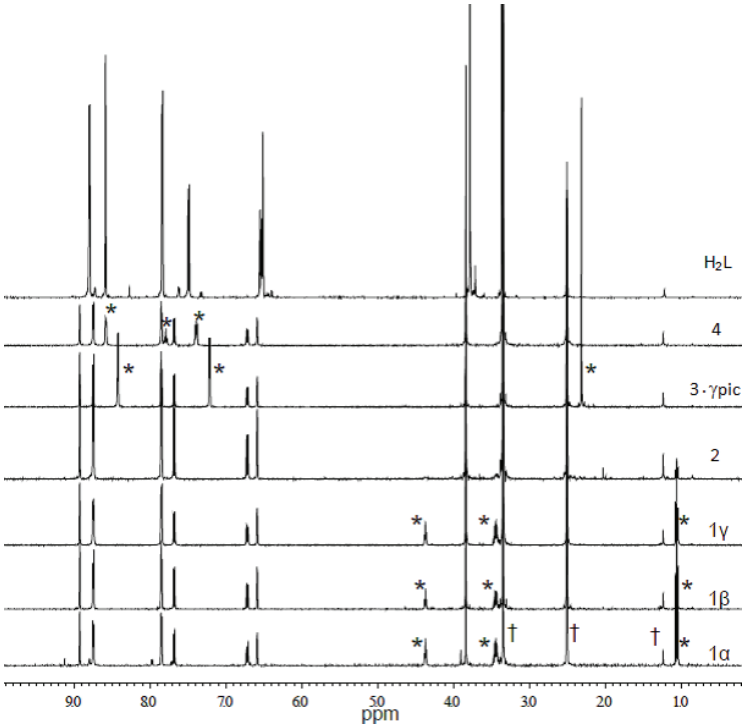


Figure S19. ^{1}H NMR spectra in dmso-d_6 of the complexes **1α**, **1β**, **1γ**, **2**, **3·γ-pic**, **4**, and the ligand H_2L (signals in the range 10–13 ppm of H_2L not shown). The signals of solvent and impurities are marked with a dagger. The resonances of EtOH in the spectra of **1α**, **1β** and **1γ**, and those of pyridine and γ-picoline in the spectra of **3** and **4**, respectively, are marked with an asterisk.

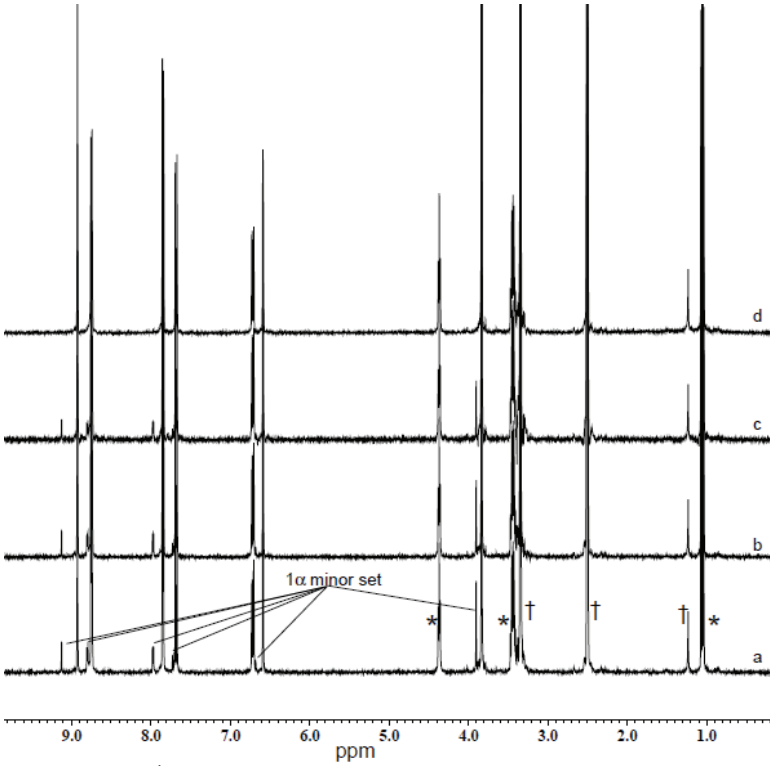


Figure S20. ^{1}H NMR spectra of **1α** in dmso-d_6 recorded immediately after dissolution (a), after about 1h (b), after about 2h (c) and after few days (d). The signals of solvent and impurities are marked with a dagger. The resonances of EtOH are marked with an asterisk.

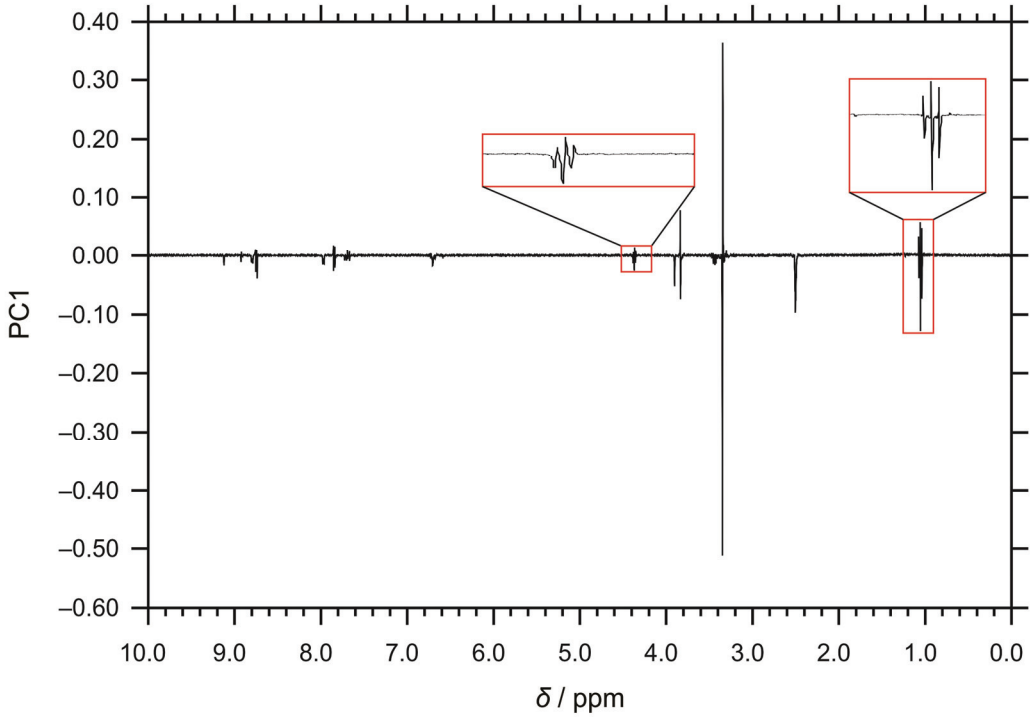


Figure S21. PC1 loadings for a set of 4 time dependent NMR spectra of **1α** dissolved in dmso-d_6.

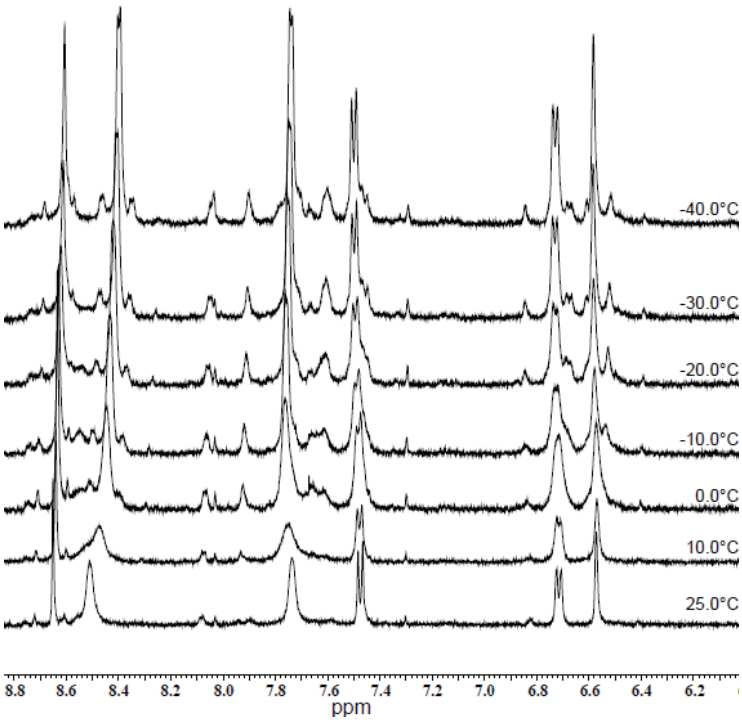


Figure S22. ^{1}H NMR spectra of **1α** in CD_2Cl_2 recorded at different temperatures (aromatic range).

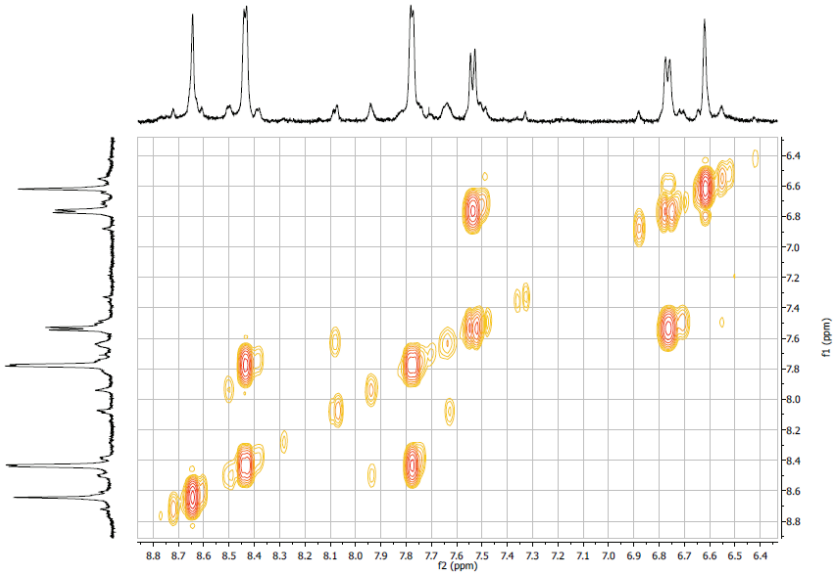


Figure S23. COSY NMR spectrum of **1α** in CD_2Cl_2 recorded at –40.0 °C (aromatic range).

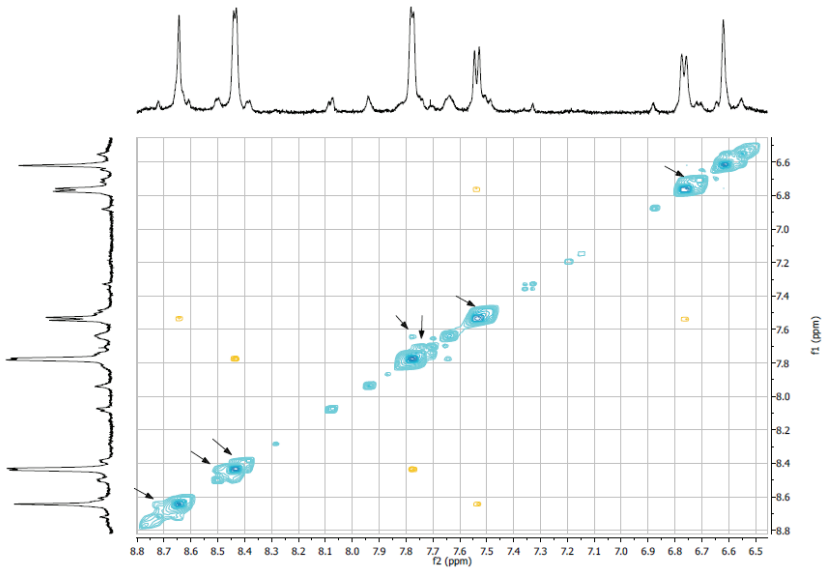


Figure S24. ROESY NMR spectrum of **1α** in CD_2Cl_2 recorded at –40.0 °C (aromatic range). NOE cross-peaks are depicted in orange while chemical exchange cross-peaks are depicted in blue. Some of the latters are marked with arrows.