

Counter anion effects on the formation and structural transformations of Mo(VI)-hydrazone coordination assemblies: salts, solvates, co-crystals, and neutral complexes

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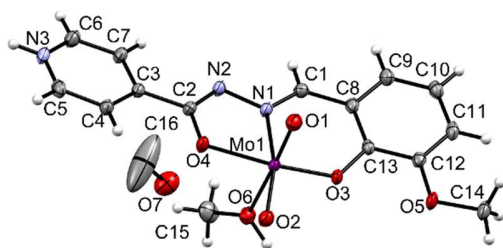
Supplementary Materials

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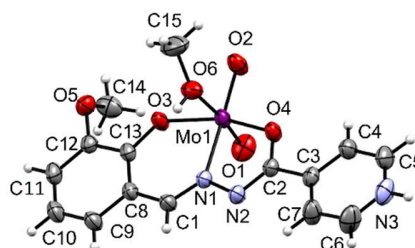
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1. Single crystal and powder X-ray diffraction

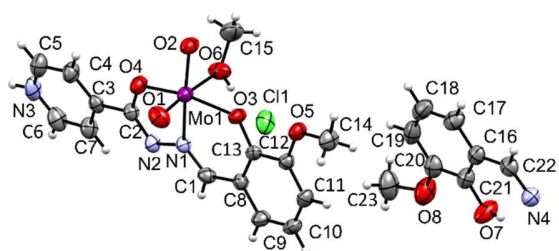
1.1. The asymmetric units of compounds



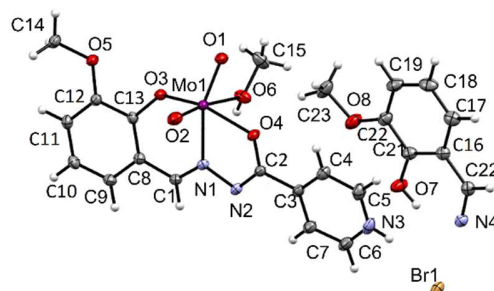
Cl1
[1H]Cl·MeOH



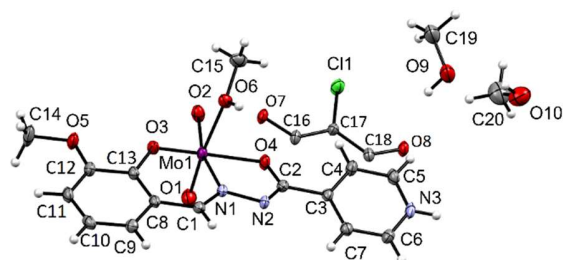
Br1
[1H]Br



[1H]Cl·0.5VA



[1H]Br·0.5VA



[1H](ClA)_{0.5}·2MeOH

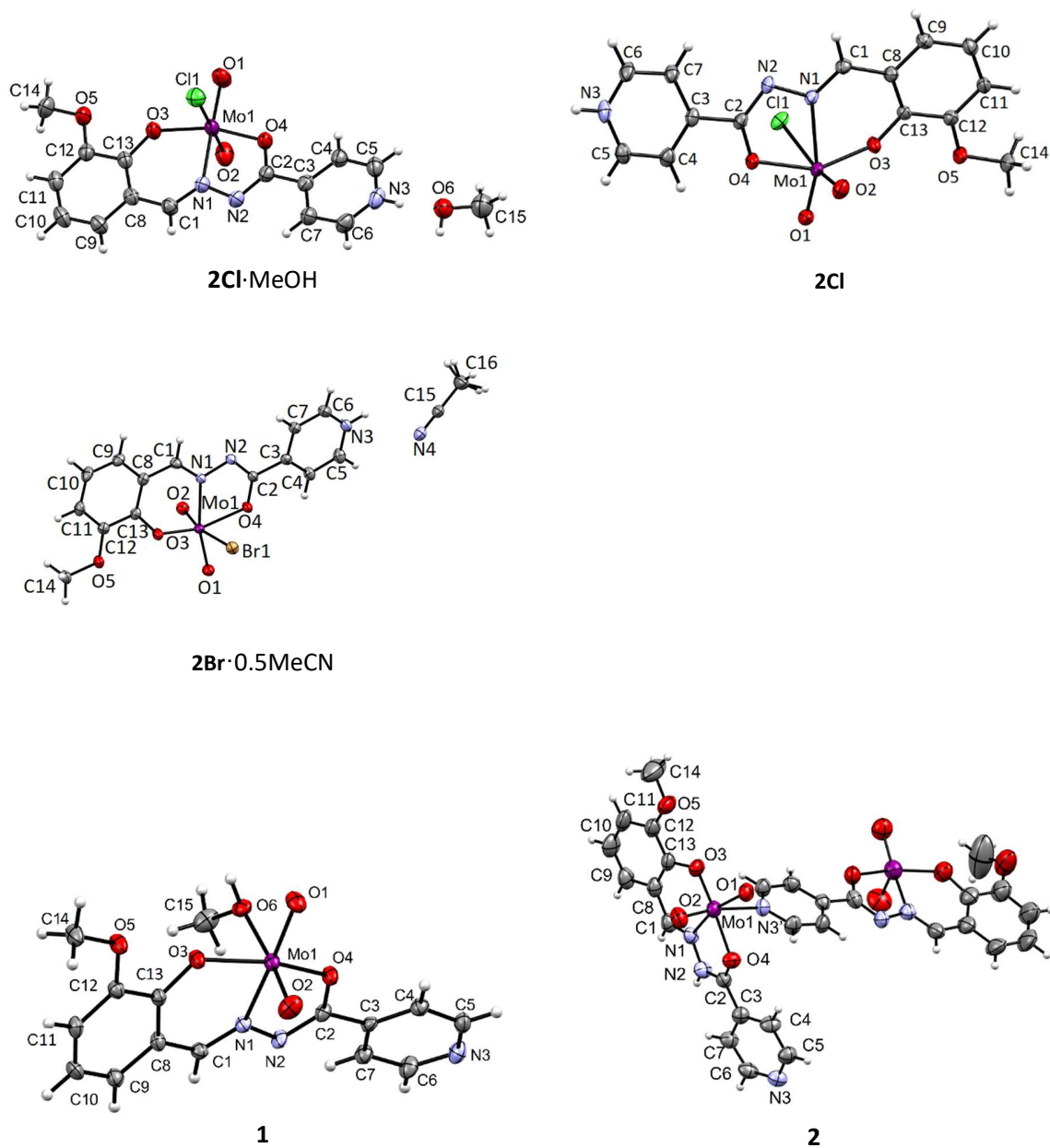


Figure S1. The asymmetric units of $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl} \cdot \text{MeOH}$ (**[1H]Cl·MeOH**), $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Br}$ (**[1H]Br**), $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl} \cdot 0.5\text{VA}$ (**[1H]Cl·0.5VA**), $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Br} \cdot 0.5\text{VA}$ (**[1H]Br·0.5VA**), $[\text{MoO}_2(\text{HL})(\text{MeOH})](\text{ClA})_{0.5} \cdot 2\text{MeOH}$ (**[1H](ClA)_{0.5}·2MeOH**), $[\text{MoO}_2(\text{HL})\text{Cl}] \cdot \text{MeOH}$ (**2Cl·MeOH**), $[\text{MoO}_2(\text{HL})\text{Cl}]$ (**2Cl**), $[\text{MoO}_2(\text{HL})\text{Br}] \cdot 0.5\text{MeCN}$ (**2Br·0.5MeCN**), $[\text{MoO}_2(\text{L})(\text{MeOH})]$ (**1**) and $[\text{MoO}_2(\text{L})]_n$ (**2**). Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are depicted as sphere of arbitrary radii.

1.2. Crystallographic data and structure refinement data

Table S1. Crystallographic data and structure refinement data for compounds: **[1H]Cl·MeOH**, **[1H]Br**, **[1H]Cl·0.5VA**, **[1H]Br·0.5VA** and **[1H](ClA)_{0.5}·2MeOH**.

Compound	[MoO ₂ (HL)(MeOH)]Cl·MeOH ([1H]Cl·MeOH)	[MoO ₂ (HL)(MeOH)]Br ([1H]Br)	[MoO ₂ (HL)(MeOH)]Cl·0.5VA ([1H]Cl·0.5VA)	[MoO ₂ (HVIH)(MeOH)]Br·0.5VA ([1H]Br·0.5VA)	[MoO ₂ (HL)(MeOH)]·0.5ClA ·2MeOH ([1H](ClA) _{0.5} ·2MeOH)
Formula	C ₁₅ H ₁₆ MoN ₃ O ₆ , Cl, CH ₄ O	C ₁₅ H ₁₆ MoN ₃ O ₆ , Br	C ₁₅ H ₁₆ MoN ₃ O ₆ , 0.5(C ₁₆ H ₁₆ N ₂ O ₄), Cl	C ₁₅ H ₁₆ MoN ₃ O ₆ , 0.5(C ₁₆ H ₁₆ N ₂ O ₄), Br	C ₁₅ H ₁₆ MoN ₃ O ₆ , C ₃ ClO ₂ , 2(CH ₄ O)
Formula weight	497.74	510.15	615.85	660.30	597.81
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> /Å	19.5865(10)	7.7808(3)	10.2441(3)	10.2544(2)	9.0075(4)
<i>b</i> /Å	7.3199(4)	8.7660(3)	18.6524(3)	18.8197(3)	11.9859(5)
<i>c</i> /Å	25.7421(14)	13.9414(3)	13.6683(3)	13.5337(2)	12.5361(7)
<i>α</i> /°	90	90.693(2)	90	90	66.790(5)
<i>β</i> /°	99.207(5)	105.309(2)	103.818(2)	104.976(2)	72.504(4)
<i>γ</i> /°	90	99.391(3)	90	90	77.916(4)
<i>V</i> /Å ³	3643.1(3)	903.34(5)	2536.11(10)	2523.09(8)	1179.96(11)
<i>D</i> _{calc} /g cm ⁻³	1.749	1.875	1.613	1.738	1.683
<i>μ</i> /mm ⁻¹	0.908	2.975	0.678	2.159	0.730
<i>F</i> (000)	1928	504	1252	1324	608.0
<i>θ</i> range/°	4.2-30.0	4.4-29.0	3.8-29.0	2.5-29.0	4.1-32.9
<i>T</i> /K	150	295	295	150	150
Radiation	0.71073	0.71073	0.71073	0.71073	0.71073
wavelength					
Range of <i>h</i> , <i>k</i> , <i>l</i>	-27-27, -10-10, -36-35	-10-10, -11-11, -19:-19	-13-13, -25-24, -18-17	-13-13, -25-25, -18-18	-13-13, -17-18, -18-19
Reflections collected	18429	19126	27991	25267	14736
Independent reflections	5311	4774	6064	6667	7681
Observed reflections (<i>I</i> ≥ 2σ)	4208	4349	3695	5868	5411
<i>R</i> _{int}	0.039	0.021	0.052	0.031	0.061
<i>R</i> ^a , <i>wR</i> ^b [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0350, 0.0956	0.0231, 0.0537	0.0345, 0.0601	0.0255, 0.0563	0.0512, 0.0968
Goodness-of-fit, <i>S</i> ^c	1.09	1.04	0.86	1.05	1.00
No. of parameters	251	239	349	345	329
No. of restraints	0	0	0	0	3
<i>Δρ</i> _{min} , <i>Δρ</i> _{max} (e Å ⁻³)	-0.55, 0.98	-0.60, 0.48	-0.35-0.45	-0.44, 0.40	0.79/-0.73

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

Table S2. Crystallographic data and structure refinement data for compounds: [MoO₂(HL)Cl]·MeOH (**2Cl**·MeOH), [MoO₂(HL)Cl] (**2Cl**), [MoO₂(HL)Br]·0.5MeCN (**2Br**·0.5MeCN), [MoO₂(L)(MeOH)] (**1**) and [MoO₂(L)]_n (**2**).

Compound	[MoO ₂ (HL)Cl]·MeOH (2Cl ·MeOH)	[MoO ₂ (HL)Cl] (2Cl)	[MoO ₂ (HL)Br]·0.5 CH ₃ CN (2Br ·0.5MeCN)	[MoO ₂ (L)(MeOH)] (1)	[MoO ₂ (L)] _n (2)
Formula	C ₁₄ H ₁₂ ClMoN ₃ O ₅ , CH ₄ O	C ₁₄ H ₁₂ ClMoN ₃ O ₅	C ₁₄ H ₁₂ BrMoN ₃ O ₅ * 0.5 (CH ₃ CN)	C ₁₅ H ₁₅ MoN ₃ O ₆	C ₂₈ H ₂₂ Mo ₂ N ₆ O ₁₀
Formula weight	465.70	433.66	498.64	429.24	794.39
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>	C2/c
<i>a</i> /Å	7.4772(2)	9.9104(2)	11.9498(3)	10.0868(16)	30.4098(14)
<i>b</i> /Å	8.9766(3)	12.8572(2)	10.0809(2)	12.596(2)	10.1021(4)
<i>c</i> /Å	13.9858(4)	12.9601(3)	28.4503(6)	13.206(2)	21.7234(12)
<i>α</i> /°	89.486(2)	90	90	90	90
<i>β</i> /°	79.735(2)	109.353(2)	93.341(2)	110.462(14)	90.095(5)
<i>γ</i> /°	74.303(2)	90	90	90	90
<i>V</i> /Å ³	888.49(5)	1558.06(6)	3421.43(13)	1572.0(4)	6673.5(5)
<i>D</i> _{calc} /g cm ⁻³	1.741	1.849	1.9361(1)	1.814	1.583
<i>μ</i> /mm ⁻¹	0.926	8.766	9.325	0.874	0.813
<i>F</i> (000)	468	864.0	1960.0	864	3176.0
<i>θ</i> range/°	4.2-27.5	4.9 - 77.9	3.11 - 77.2470	4.3-28.6	4.1-27.0
<i>T</i> /K	295	170.12(11)	169.98(10)	150	298
Radiation wavelength	0.71073	1.54184	1.54184	0.71073	0.71073
Range of <i>h</i> , <i>k</i> , <i>l</i>	-9-9, -11-11, -18-18	-11-12, -15-16, -16-16	-15-14, -12-12, -35-35	-12-11, -15-14, -16-15	-38-38, -12-12, -27-25
Reflections collected	14677	13156	15038	6030	32276
Independent reflections	4058	3269	3589	3446	7266
Observed reflections (<i>I</i> ≥ 2σ)	3687	3093	3408	2862	4573
<i>R</i> _{int}	0.032	0.055	0.0375	0.047	0.105
<i>R</i> ^a , <i>wR</i> ^b [≥2σ(<i>I</i>)]	0.0268, 0.0632	0.0357, 0.0975	0.0268, 0.0749	0.0325, 0.0836	0.0549, 0.1525
Goodness-of-fit, <i>S</i> ^c	1.06	1.062	1.141	1.07	1.04
No. of parameters	238	219	235	230	417
No. of restraints	0	0	0	0	0
<i>Δρ</i> _{min} , <i>Δρ</i> _{max} (e Å ⁻³)	-0.35, 0.42	0.87/-1.10	-0.59, 0.53	-0.98, 0.69	1.06/-0.41

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

1.3. Selected bond lengths and angles

Table S3. Selected bond lengths (Å) and angles (°) for compounds **[1H]Cl·MeOH**, **[1H]Br** and **[1H]ClA_{0.5}·2MeOH**.

	[1H]Cl·MeOH	[1H]Br	[1H](ClA)_{0.5}·2MeOH
Mo1–O1	1.7049(19)	1.6825(17)	1.694(2)
Mo1–O2	1.6999(16)	1.6970(14)	1.700(2)
Mo1–O3	1.9329(18)	1.9286(14)	1.925(2)
Mo1–O4	2.0188(17)	2.0196(12)	2.028(2)
Mo1–O6	2.3503(16)	2.3173(16)	2.317(2)
Mo1–N1	2.236(2)	2.2467(15)	2.249(2)
C1–N1	1.295(3)	1.289(2)	1.293(4)
C2–N2	1.299(3)	1.295(2)	1.302(4)
N1–N2	1.396(3)	1.403(2)	1.403(3)
C2–O4	1.321(3)	1.306(2)	1.312(4)
Cl1–C17	—	—	1.738(3)
O7–C16	—	—	1.261(4)
O8–C18	—	—	1.249(3)
C16–C17	—	—	1.378(4)
C16–C18_a	—	—	1.538(5)
C17–C18	—	—	1.410(5)
O1–Mo1–O2	105.49(9)	106.41(8)	106.15(11)
O1–Mo1–O3	102.37(8)	98.86(7)	99.19(9)
O1–Mo1–O4	97.71(8)	95.63(7)	96.34(9)
O1–Mo1–O6	82.23(9)	170.06(7)	170.32(10)
O1–Mo1–N1	159.49(9)	94.66(7)	91.69(10)
O2–Mo1–O3	98.45(9)	105.11(7)	103.65(9)
O2–Mo1–O4	98.10(8)	94.77(6)	98.20(9)
O2–Mo1–O6	172.27(7)	83.14(6)	83.07(9)
O2–Mo1–N1	93.56(8)	156.09(7)	160.55(9)
O3–Mo1–O4	149.43(8)	150.83(6)	148.36(9)
O3–Mo1–O6	79.98(8)	80.88(6)	81.10(8)
O3–Mo1–N1	81.85(8)	82.11(6)	80.48(8)
O4–Mo1–O6	80.17(6)	80.55(6)	79.13(7)
O4–Mo1–N1	71.63(7)	71.56(5)	71.64(8)
O6–Mo1–N1	78.74(7)	75.44(6)	78.79(8)

Table S4. Selected bond lengths (Å) and angles (°) for compounds [1H]Cl·0.5VA and [1H]Br·0.5VA.

	[1H]Cl·0.5VA	[1H]Br·0.5VA
Mo1–O1	1.6750(18)	1.7069(12)
Mo1–O2	1.6967(16)	1.6874(15)
Mo1–O3	1.9180(15)	1.9254(13)
Mo1–O4	2.0184(15)	2.0212(12)
Mo1–O6	2.372(2)	2.3750(15)
Mo1–N1	2.2221(19)	2.2325(15)
C1–N1	1.291(3)	1.289(2)
C2–N2	1.286(3)	1.287(2)
N1–N2	1.403(2)	1.4023(19)
C2–O4	1.320(3)	1.323(2)
O1–Mo1–O2	105.77(9)	105.86(7)
O1–Mo1–O3	99.66(8)	103.59(6)
O1–Mo1–O4	97.02(8)	95.35(6)
O1–Mo1–O6	171.47(8)	82.16(6)
O1–Mo1–N1	97.14(8)	154.58(6)
O2–Mo1–O3	103.58(7)	99.35(6)
O2–Mo1–O4	95.27(7)	97.09(6)
O2–Mo1–O6	82.47(8)	171.49(6)
O2–Mo1–N1	155.10(8)	97.67(6)
O3–Mo1–O4	150.26(7)	150.35(6)
O3–Mo1–O6	80.15(7)	81.15(6)
O3–Mo1–N1	81.60(7)	81.48(5)
O4–Mo1–O6	79.77(7)	79.06(6)
O4–Mo1–N1	72.00(7)	71.96(5)
O6–Mo1–N1	74.37(7)	73.95(5)

Table S5. Selected bond lengths (Å) and angles (°) for compounds **2Cl**·MeOH, **2Cl** and **2Br**.

	2Cl ·MeOH	2Cl	2Br
Mo1–O1	1.6991(16)	1.707(2)	1.711(2)
Mo1–O2	1.6947(17)	1.699(3)	1.707(2)
Mo1–O3	1.9206(14)	1.941(2)	1.916(2)
Mo1–O4	2.0290(14)	2.015(2)	2.043(2)
Mo1–X1*	2.7086(6)	2.6542(8)	2.8265(7)
Mo1–N1	2.227(2)	2.247(3)	2.248(2)
C1–N1	1.289(3)	1.282(4)	1.285(3)
C2–N2	1.298(3)	1.305(5)	1.295(3)
N1–N2	1.394(3)	1.400(4)	1.393(3)
C2–O4	1.305(3)	1.302(4)	1.313(3)
O1–Mo1–O2	105.31(10)	106.39(13)	105.39(10)
O1–Mo1–O3	102.71(7)	103.21(12)	103.22(9)
O1–Mo1–O4	98.17(7)	97.27(12)	98.87(9)
O1–Mo1–X	83.07(6)	85.99(9)	85.39(8)
O1–Mo1–N1	159.99(8)	160.55(12)	162.21(10)
O2–Mo1–O3	99.18(8)	96.63(12)	99.90(10)
O2–Mo1–O4	94.23(7)	96.14(12)	92.51(9)
O2–Mo1–X1	170.06(7)	167.53(9)	167.43(7)
O2–Mo1–N1	93.04(9)	91.17(11)	90.65(9)
O3–Mo1–O4	151.13(7)	151.65(9)	150.66(8)
O3–Mo1–X1	83.87(5)	81.59(7)	83.52(7)
O3–Mo1–N1	81.71(6)	82.48(10)	81.03(8)
O4–Mo1–X1	79.07(5)	80.50(7)	79.23(6)
O4–Mo1–N1	72.10(6)	72.06(10)	72.28(8)
X1–Mo1–N1	77.97(5)	76.36(7)	77.87(6)

*X= Cl for 2Cl and Br for 2Br

Table S6. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

	1	2
Mo1–O1	1.703(2)	1.693(3)
Mo1–O2	1.682(2)	1.687(4)
Mo1–O3	1.930(2)	1.926(3)
Mo1–O4	2.008(2)	2.030(3)
Mo1–O6	2.339(2)	-
Mo1–N1	2.241(2)	2.247(4)
Mo1–N3'	-	2.451(4)
C1–N1	1.286(4)	1.274(7)
C2–N2	1.299(4)	1.299(6)
N1–N2	1.396(3)	1.377(6)
C2–O4	1.311(3)	1.309(6)
O1–Mo1–O2	106.25(11)	106.17(19)
O1–Mo1–O3	104.41(10)	103.04(16)
O1–Mo1–O4	95.75(9)	97.46(15)
O1–Mo1–O6	80.70(9)	-
O1–Mo1–N1	157.94(10)	156.31(17)
O1–Mo1–N3'	-	80.60(16)
O2–Mo1–O3	98.45(10)	100.74(17)
O2–Mo1–O4	98.09(10)	95.22(17)
O2–Mo1–O6	173.04(10)	-
O2–Mo1–N1	93.74(10)	158.3(2)
O2–Mo1–N3'	-	169.90(17)
O3–Mo1–O4	149.09(9)	149.21(15)
O3–Mo1–O6	79.90(8)	-
O3–Mo1–N1	81.20(9)	80.13(15)
O3–Mo1–N3'	-	84.66(15)
O4–Mo1–O6	80.54(8)	-
O4–Mo1–N1	71.81(8)	72.09(14)
O4–Mo1–N3'	-	76.24(14)
O6–Mo1–N1	79.33(8)	-
N1–Mo1–N3'	-	76.30(15)

1.4. Geometry of hydrogen bonds and π -stacking interactions

Table S7. Geometry of intermolecular hydrogen bonds (\AA , $^\circ$) and π -stacking interactions for compounds **[1H]Br**, **[1H]Cl·MeOH** and **[1H](ClA)_{0.5}·2MeOH**.

	D-H...A	D-H / \AA	H...A / \AA	D...A / \AA	D-H...A / $^\circ$
[1H]Br	O6-H61...Br1 ^a	0.86	2.37	3.2040(14)	163
	N3-H3...Br1 ^b	0.86	2.30	3.1604(18)	175
	C4-H4...O4	0.93	2.42	2.731(2)	100
	C6-H6...Br1 ^c	0.93	2.91	3.644(3)	137
	$\pi \cdots \pi$	Cg3...Cg4 ^d / \AA	Slipage / \AA		
		3.8960(15)	1.430		
		Cg3...Cg4 ^b / \AA	Slipage / \AA		
		3.9110(15)	0.825		
		Cg4...Cg3 ^e / \AA	Slipage / \AA		
		3.9110(15)	0.932		
[1H]Cl·MeOH		Cg4...Cg3 ^f / \AA	Slipage / \AA		
		3.8960(15)	1.512		
	N3-H3...Cl1 ^g	0.86	2.29	3.071(2)	151
	N3-H3...O1 ^h	0.86	2.51	3.037(3)	121
	O6-H61...Cl1	0.93	2.29	3.0034(19)	133
	C1-H1...O2 ⁱ	0.93	2.45	3.005(3)	118
	C4-H4...O7 ^g	0.93	2.49	3.235(5)	137
	C6-H6...O1 ^h	0.93	2.44	3.011(3)	120
[1H](ClA)_{0.5}·2MeOH	C10-H10...Cl1 ^j	0.93	2.77	3.573(3)	145
	N3-H3...O7 ^k	0.86(4)	1.99(4)	2.730(3)	144(3)
	N3-H3...O8 ^l	0.86(4)	2.21(4)	2.893(3)	136(3)
	O6-H6...O7	0.857(16)	1.785(16)	2.640(3)	175(3)
	O9-H9A...O8	0.84	2.0700	2.834(3)	151
	O9-H9A...Cl1	0.84	2.92	3.559(4)	134
	C14-H14B...Cl1 ^m	0.98	2.95	3.793(3)	145
	O10-H1A...O9	0.84	2.1100	2.893(4)	154
	C6-H6A...O10 ^l	0.95	2.5700	3.207(4)	125
	C14-H14C...O ^a	0.98	2.5400	3.438(4)	153
	C19-H19B...O1 ⁿ	0.98	2.6000	3.428(4)	142
	$\pi \cdots \pi$	Cg3...Cg4 ^k / \AA	Slipage / \AA		
		3.6660(15)	0.859		
		Cg4...Cg3 ^a / \AA	Slipage / \AA		
		3.6659(15)	0.847		

^a1+x,y,z; ^bx,-1+y,z; ^c1-x,-y,z; ^d-1+x,-1+y,z; ^ex,1+y,z; ^f1+x,1+y,z; ^g-x,y,1/2-z; ^h-1/2+x,-1/2+y,z; ⁱ-x,-y,-z; ^j1/2-x,-1/2-y,-z; ^k-1+x,y,z; ^l-x,2-y,1-z; ^m2-x,1-y,1-z; ⁿ-1+x,y,1+z

Cg3 is centre of gravity of the pyridyl ring and Cg4 is centre of gravity of the phenyl ring.

Table S8. Geometry of intermolecular hydrogen bonds (Å, °) and π -stacking interactions for compounds [MoO₂(HL)(MeOH)]Cl·0.5VA ([**1H**]Cl·0.5VA) and [MoO₂(HL)(MeOH)]Br·0.5VA ([**1H**]Br·0.5VA).

	D–H...A	D–H / Å	H...A / Å	D...A / Å	D–H...A / °
[1H]Cl·0.5VA	N3–H3...Cl1 ^a	0.86	2.16	2.995(2)	163
	O6–H61...Cl1	0.89(2)	2.13(2)	3.013(2)	172(2)
	O7–H71...N4	0.72(3)	1.99(3)	2.615(4)	145(3)
	C4–H4...O4	0.93	2.46	2.776(3)	100
	C5–H5...O7 ^b	0.93	2.41	3.194(4)	142
	C10–H10...O5 ^c	0.93	2.59	3.477(3)	159
	C11–H11...O2 ^c	0.93	2.33	3.229(3)	162
	C15–H15A...O2 ^d	0.96	2.44	3.360(3)	159
	C19–H19...O1 ^e	0.93	2.52	3.388(3)	155
	π ... π	Cg3...Cg4 ^a / Å	Slipage / Å		
		3.9653(15)	1.787		
		Cg4...Cg3 ^f / Å	Slipage / Å		
		3.9653(15)	1.939		
		Cg3...Cg5 ^g / Å	Slipage / Å		
		3.4952(17)	0.912		
		Cg4...Cg5 ^h / Å	Slipage / Å		
		3.8038(16)	1.462		
		Cg5...Cg3 ⁱ / Å	Slipage / Å		
		3.4952(17)	0.987		
[1H]Br·0.5VA	N3–H3...Br1	0.80(3)	2.37(3)	3.1496(17)	165(2)
	O6–H61...Br1 ^a	0.89(2)	2.30(2)	3.1805(14)	171.9(19)
	O7–H70...N4	0.86	1.86	2.608(2)	145
	C5–H5...O7	0.95	2.33	3.156(3)	145
	C10–H10...O5 ^b	0.95	2.51	3.398(2)	156
	C11–H11...O1 ^b	0.95	2.33	3.240(2)	160
	C15–H15B...O1	0.98	2.53	3.062(3)	114
	C19–H19...O2 ^j	0.95	2.48	3.362(2)	154
	π ... π	Cg3...Cg4 ^f / Å	Slipage / Å		
		3.9161(11)	1.889		
		Cg4...Cg3 ^a / Å	Slipage / Å		

3.9162(11)	1.810
Cg3...Cg5 ^k / Å	Slipage / Å
3.4410(12)	0.939
Cg4...Cg5 ^l / Å	Slipage / Å
3.7689(11)	1.319
Cg5...Cg3 ^m / Å	Slipage / Å
3.4410(12)	0.915
Cg5...Cg4 ⁿ / Å	Slipage / Å
3.7688(11)	0.901

^a1-x,1/2+y,1/2-z; ^bx,3/2-y,-1/2+z; ^cx,3/2-y,1/2+z; ^d1-x,2-y,-z; ^e2-x,-1/2+y,1/2-z; ^f1-x,-1/2+y,1/2-z; ^gx,1+y,z; ^h2-x,1-y,1-z; ⁱx,-1+y,z; ^j-x, 1-y, 1-z; ^kx,1/2-y,-1/2+z; ^l-x,1/2+y,1/2-z; ^mx,1/2-y,1/2+z; ⁿ-x,-1/2+y,1/2-z

Cg3 is centre of gravity of the pyridyl ring

Cg4 is center of gravity of the phenyl ring

Cg5 is center of gravity of vanillin azine molecule ring C16-C21

Table S9. Geometry of intermolecular hydrogen bonds (Å, °) and π -stacking interactions for compounds **2Cl**·MeOH, **2Cl** and **2Br**·0.5CH₃CN.

	D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / °
2Cl ·MeOH	N3–H3···O6	0.86	1.88	2.730(3)	169
	O6–H6A···Cl1 ^a	0.82	2.46	3.227(2)	157
	C1–H1···O1 ^b	0.93	2.28	3.049(3)	140
	C5–H5···Cl1 ^c	0.93	2.70	3.601(3)	164
	C14–H14C···O2 ^d	0.96	2.58	3.401(3)	143
	π ··· π	Cg3···Cg4 ^c / Å	Slipage / Å		
		3.7230(13)	1.711		
		Cg4···Cg3 ^d / Å	Slipage / Å		
		3.7231(13)	1.178		
		Cg4···Cg4 ^e / Å	Slipage / Å		
		3.5657(13)	0.840		
2Cl	N3–H3···O2 ^f	0.8800	2.4800	2.955(4)	115
	N3–H3···Cl1 ^g	0.8800	2.2500	3.062(3)	154
	C6–H6···O2 ^f	0.9500	2.5600	3.006(5)	109
	C14–H14B···Cl1 ^e	0.9800	2.9200	3.794(4)	149
	C10–H10···O5 ^h	0.9500	2.4500	3.369(5)	162
	C11–H11···O1 ^h	0.9500	2.3500	3.242(4)	156
	π ··· π	Cg3···Cg4 ⁱ / Å	Slipage / Å		
		3.753(2)	1.783		
		Cg4···Cg3 ^j / Å	Slipage / Å		
		3.753(2)	1.680		
2Br ·0.5MeCN	N3–H3···O1 ^c	0.8800	2.4600	3.038(4)	124
	N3–H3···N4	0.8800	2.4000	3.057(3)	132
	C6–H6···Br1 ^c	0.9500	2.8700	3.538(3)	128
	C14–H14A···O2 ^k	0.9800	2.5800	3.441(4)	147
	N3–H3···Br1 ^c	0.8800	2.967	3.574(3)	128
	π ··· π	Cg4···Cg4 ^l / Å	Slipage / Å		
		3.7838(18)	1.675		

^a-1+x,1+y,z; ^b-1+x,y,z; ^cx,1+y,z; ^dx,-1+y,z; ^e1-x,1-y,2-z; ^f1+x,y,z; ^g1/2+x,1/2-y,-1/2+z; ^h1/2-x,1/2+y,3/2-z; ⁱ3/2-x,-1/2+y,3/2-z; ^j3/2-x,1/2+y,3/2-z; ^k1-x,-1/2+y,1/2-z; ^l1/2-x,1/2-y,1/2-z

Cg3 is center of gravity of the pyridyl ring and Cg4 is center of gravity of the phenyl ring.

Table S10. Geometry of intermolecular hydrogen bonds (Å, °) and π -stacking interactions for compounds **1** and **2**.

	D–H...A	D–H / Å	H...A / Å	D...A / Å	D–H...A / °
1	O6–H61...N3 ^a	0.88(3)	1.83(4)	2.702(4)	170(4)
	C10–H10...O5 ^b	0.93	2.51	3.384(3)	157
	C14–H14C...O1 ^b	0.96	2.55	3.197(4)	125
	π ... π	Cg3...Cg3' ^c / Å	Slipage / Å		
		3.9287(16)	2.034		
		Cg3'...Cg3 ^d / Å	Slipage / Å		
		3.9287(16)	1.733		
2	C1–H1...O2 ^e	0.93	2.57	3.227(7)	128
	C4'–H4'...O5 ^f	0.93	2.55	3.145(7)	122
	C5–H5...O2 ^g	0.93	2.57	3.392(7)	148
	C5'–H5'...O5 ^f	0.93	2.55	3.154(7)	123
	C6'–H6'...O4	0.93	2.51	2.953(7)	109
	C10–H10...O1 ^h	0.93	2.52	3.371(7)	152
	C14'–H14E...O3'	0.96	2.44	2.851(13)	106
	π ... π	Cg1...Cg4' / Å			
		3.754(3)			
		Cg2...Cg4 ⁱ / Å			
		3.881(3)			

^a-1/2+x,-1/2-y,1/2+z; ^b1/2-x,1/2+y,3/2-z; ^c3/2-x,-1/2+y,3/2-z; ^d3/2-x,1/2+y,3/2-z; ^e1-x,-y,1-z; ^f1-x,y,1/2-z;
^g1-x,1-y,1-z; ^hx,-1+y,z; ⁱx,1-y,-1/2+z

Cg1 and Cg2 are centers of gravity of five membered chelate rings

Cg3 and Cg3' are centers of gravity of the pyridyl rings

Cg4 and Cg4' are centers of gravity of the phenyl rings.

1.5. Crystal structure

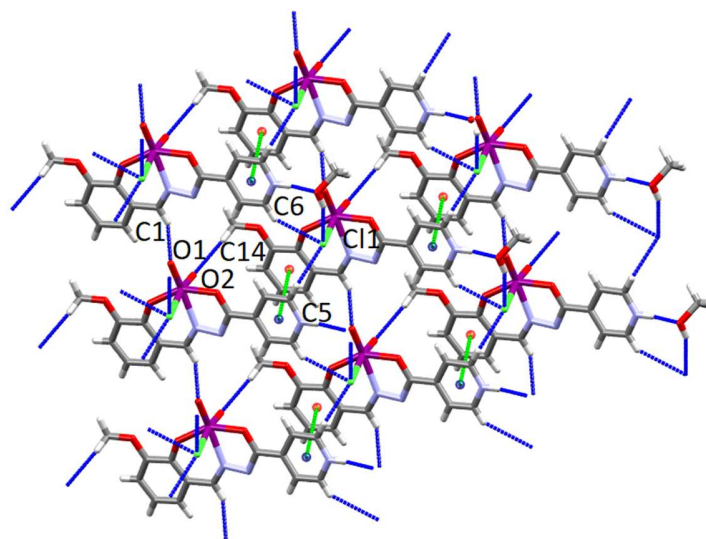


Figure S2. 2D network in 2Cl·MeOH formed through the C-H...Cl, C-H...O interactions (shown by blue dotted lines) and π -stacking interactions between the pyridyl and the phenyl ring (shown by green dashed lines; Cg3 is centre of gravity of the pyridyl ring - blue spheres and Cg4 is centre of gravity of the phenyl ring - red spheres).

2. Characterization - analytical data for compounds

2.1.1. [MoO₂(HL)(MeOH)]Cl·MeOH ([1H]Cl·MeOH)

The sample of [1H]Cl·MeOH was sensitive to traces of moisture and was kept in a dry atmosphere at –15 °C prior to analysis. Anal. Calcd. for C₁₆H₂₀ClMoN₃O₇ ([1H]Cl·MeOH, 497.74): C, 38.61; H, 4.05; N, 8.44%. Found: C, 38.78; H, 3.79; N, 8.78 %. TG: calcd. for CH₃OH and HCl, 20.20%, found: 19.53%, calcd. for MoO₃, 28.92%, found 28.87%. Selected ATR-IR data (cm⁻¹): 1608 (C=N), 1346 (C–O_{phen}), 1261 (C–O_{iso}), 945, 920 (MoO₂²⁺).

2.1.2. [MoO₂(HL)(MeOH)]Br ([1H]Br)

The sample of [1H]Br was sensitive to traces of moisture and was kept in a dry atmosphere at –15 °C prior to analysis. Anal. Calcd. for C₁₅H₁₆BrMoN₃O₆ ([1H]Br, 510.15): C, 35.32; H, 3.16; N, 8.24%. Found: C, 35.08; H, 2.89; N, 7.89%. TG: calcd. for CH₃OH 6.28%, found: 6.23%; calcd. for MoO₃, 28.22%, found: 27.85%. Selected ATR-IR data (cm⁻¹): 1603 (C=N), 1342 (C–O_{phen}), 1258 (C–O_{iso}), 971, 925 (MoO₂²⁺).

2.1.3. [MoO₂(HL)(MeOH)](ClA)_{0.5}·2MeOH ([1H](ClA)_{0.5}·2MeOH)

The sample for elemental analysis was desolvated at room temperature until constant weight and was analysed as [1H](ClA)_{0.5}. Anal. Calcd. for C₁₈H₁₆ClMoN₃O₈ ([1H](ClA)_{0.5}, 533.73): C, 40.51; H, 3.02; N, 7.87%. Found: C, 40.26; H, 2.75; N, 7.52%. TG for [1H](ClA)_{0.5}·2MeOH (597.81): calcd. for CH₃OH, 16.08%, found: 15.21%; calcd. for MoO₃, 24.08%, found: 24.14%. Selected ATR-IR data (cm⁻¹): 1603 (C=N), 1494 (C[≡]O)_{ClA}, 1339 (C–O_{phen}), 1263 (C–O_{iso}), 938, 913 (MoO₂²⁺).

2.1.4. [MoO₂(HL)(MeOH)](BrA)_{0.5}·2MeOH ([1H](BrA)_{0.5}·2MeOH)

The sample for elemental analysis was desolvated at room temperature until constant weight and was analysed as [1H](BrA)_{0.5}. Anal. Calcd. for C₁₈H₁₆BrMoN₃O₈ ([1H](BrA)_{0.5}, 578.17): C, 37.39; H, 2.79; N, 7.27%. Found: C, 37.12; H, 3.00; N, 6.94%. TG for [1H](BrA)_{0.5}·2MeOH (642.26): calcd. for CH₃OH, 14.97%, found: 13.83% calcd. for MoO₃, 22.41%, found: 23.12%. Selected ATR-IR data (cm⁻¹): 1604 (C=N), 1497 (C[≡]O)_{BrA}, 1343 (C–O_{phen}), 1263 (C–O_{iso}), 937, 909 (MoO₂²⁺).

2.1.5. [MoO₂(HL)(MeOH)]Cl·0.5VA ([1H]Cl·0.5VA)

Anal. Calcd. for C₂₃H₂₄ClMoN₄O₈ ([1H]Cl·0.5VA, 615.85): C, 44.86; H, 3.93; N, 9.10%. Found: C, 44.75; H, 3.72; N, 9.49%. TG: calcd. for CH₃OH, 5.20%, found: 5.02%; calcd. for MoO₃, 23.37%, found: 23.78%. Selected ATR-IR data (cm⁻¹): 1623, 1599 (C=N), 1336 (C–O_{phen}), 1264 (C–O_{iso}), 947, 922 (MoO₂²⁺).

2.1.6 [MoO₂(HL)(MeOH)]Br·0.5VA ([1H]Br·0.5VA)

Anal. Calcd. for C₂₃H₂₄BrMoN₄O₈ ([1H]Br·0.5VA, 660.30): C, 41.84; H, 3.66; N, 8.49%. Found: C, 41.63; H, 3.53; N, 8.54%. TG: calcd. for CH₃OH, 4.85%, found: 4.73; calcd. for MoO₃, 21.80%, found 22.02%. Selected ATR-IR data (cm⁻¹): 1622, 1598 (C=N), 1329 (C–O_{phen}), 1266 (C–O_{iso}), 938, 908 (MoO₂²⁺).

2.1.7. [MoO₂(HL)Cl]·MeOH (2Cl·MeOH)

Anal. Calcd. for C₁₅H₁₆ClMoN₃O₆ (2Cl·MeOH, 465.70): C, 38.69; H, 3.46; N, 9.02%. Found: 38.46; H, 3.12; N, 9.32%. TG: calcd. for CH₃OH 6.88%, found: 6.65%; calcd. for MoO₃, 30.91%, found: 32.49%. Selected ATR-IR data (cm⁻¹): 1604, 1593 (C=N), 1342 (C–O_{phen}), 1260 (C–O_{iso}), 928, 917, 900 (MoO₂²⁺).

2.1.8. [MoO₂(HL)Cl] (**2Cl**)

Anal. Calcd. for C₁₄H₁₂ClMoN₃O₅ (**2Cl**, 433.66): C, 38.77; H, 2.79; N, 9.69%. Found: C, 38.64; H, 2.54; N, 9.42%. TG: calcd. for MoO₃, 33.19%, found: 32.82%. Selected ATR-IR data (cm⁻¹): 1616 (C=N), 1337 (C–O_{phen}), 1259 (C–O_{iso}), 919, 894 (MoO₂²⁺).

2.1.9. [MoO₂(HL)Br]·0.5MeCN (**2Br**·0.5MeCN)

Anal. Calcd. for C₁₅H_{13.5}BrMoN_{3.5}O₅ (**2Br**·0.5MeCN, 498.64): C, 36.13; H, 2.73; N, 9.83%. Found: C, 35.85; H, 2.34; N, 9.72%. TG: calcd. for CH₃CN 4.11%, found: 3.73%; calcd. for MoO₃, 28.87%, found 29.11%. Selected ATR-IR data (cm⁻¹): 1612 (C=N), 1346 (C–O_{phen}), 1259 (C–O_{iso}), 911, 891 (MoO₂²⁺).

2.1.10. [MoO₂(L)(MeOH)] (**1**)

Anal. Calcd. for C₁₅H₁₅MoN₃O₆ (**1**, 429.24): C, 41.97; H, 3.52; N, 9.79%. Found: C, 41.66; H, 3.24; N, 9.46%. TG: calcd. for CH₃OH, 7.46%, found: 7.57%. calcd. for MoO₃, 33.53%, found: 33.10%. Selected ATR-IR data (cm⁻¹): 1621, 1600 (C=N), 1347 (C–O_{phen}), 1263 (C–O_{iso}), 942, 918, 908 (MoO₂²⁺).

2.1.11. [MoO₂(L)]_n (**2**)

Anal. Calcd. for C₁₄H₁₁MoN₃O₅ (**2**, 397.190): C, 42.33; H, 2.79; N, 10.58%. Found: C, 42.06; H, 2.58; N, 10.23%. Selected ATR-IR data (cm⁻¹): 1621, 1600 (C=N), 1347 (C–O_{phen}), 1263 (C–O_{iso}), 942, 918, 894 (MoO₂²⁺).

3. IR-ATR spectra

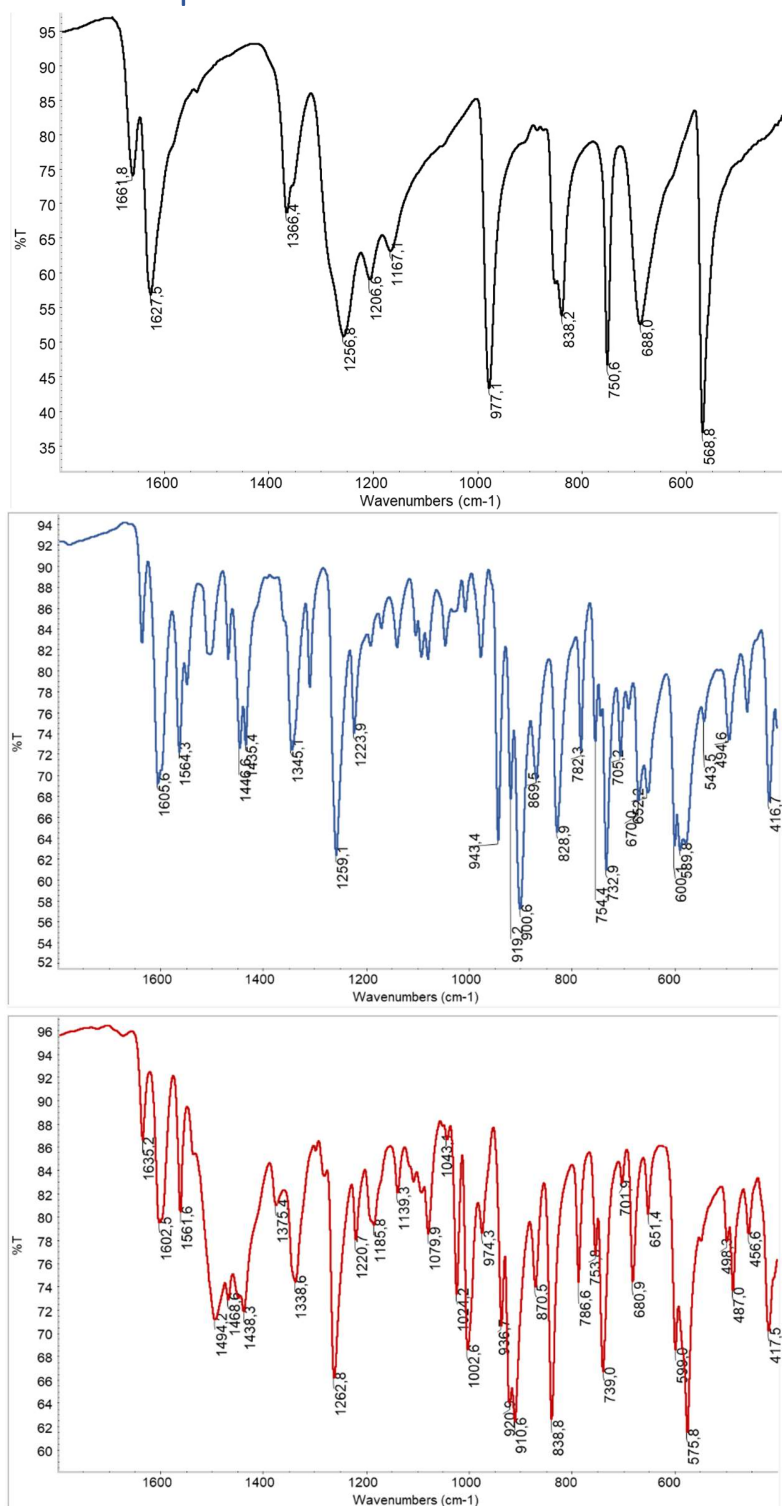


Figure S3. Comparison of IR-ATR spectra of: H₂CIA (top), [1H]Cl·MeOH (middle), and [1H](CIA)_{0.5}·2MeOH (bottom).

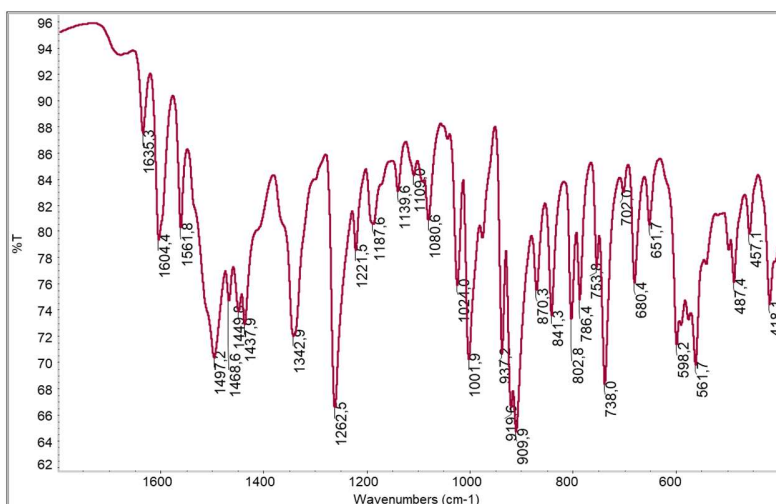
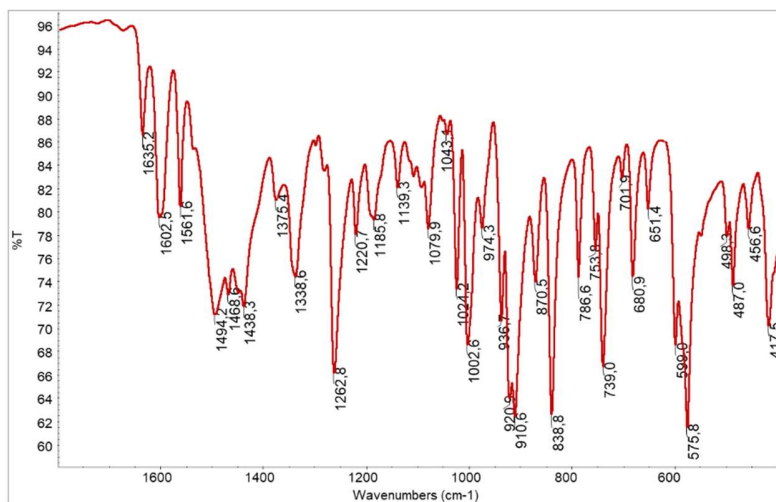


Figure S4. Comparison of IR-ATR spectra of: $[1H](ClA)_{0.5} \cdot 2MeOH$ (top) and $[1H](BrA)_{0.5} \cdot 2MeOH$ (bottom).

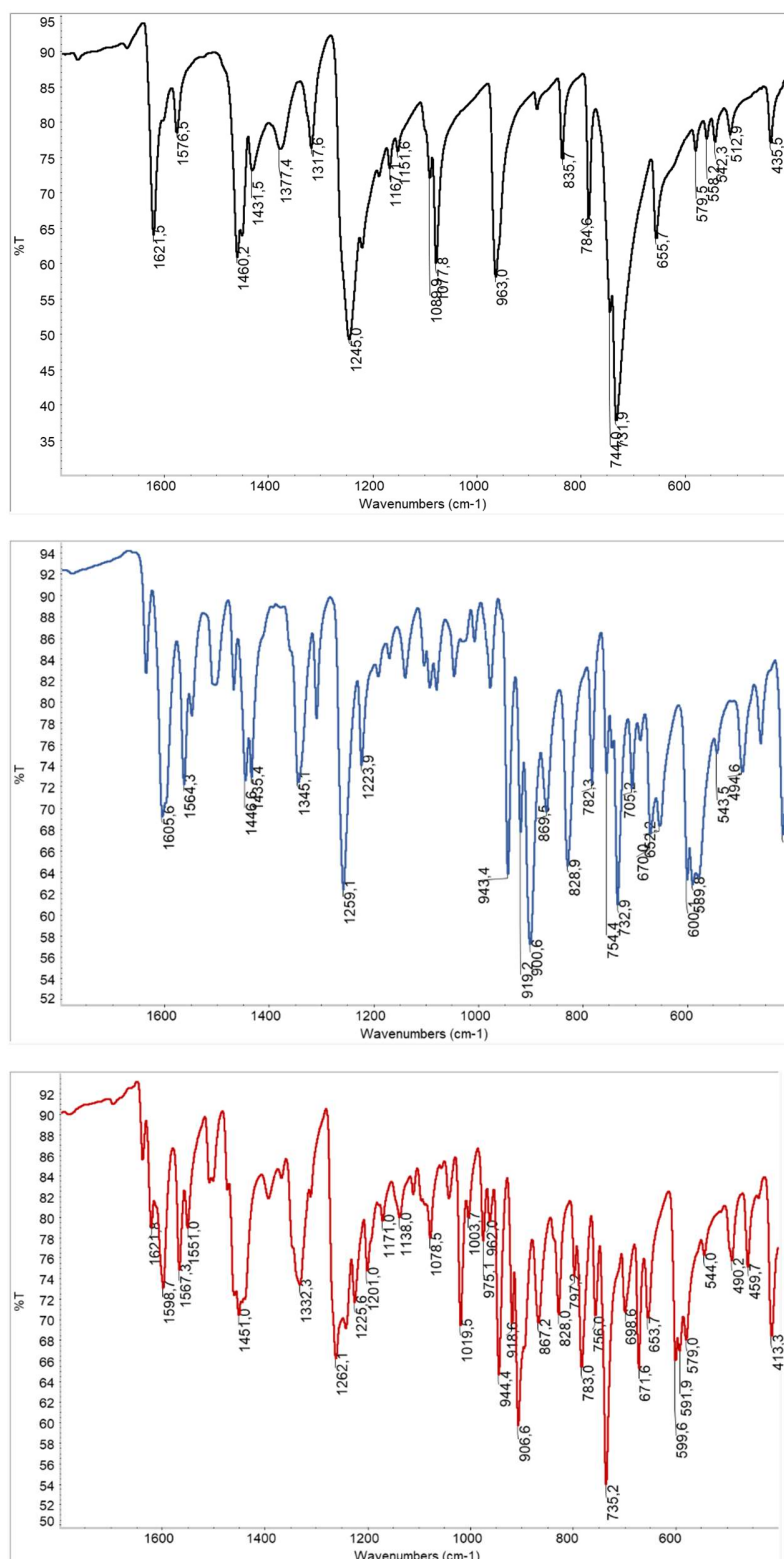
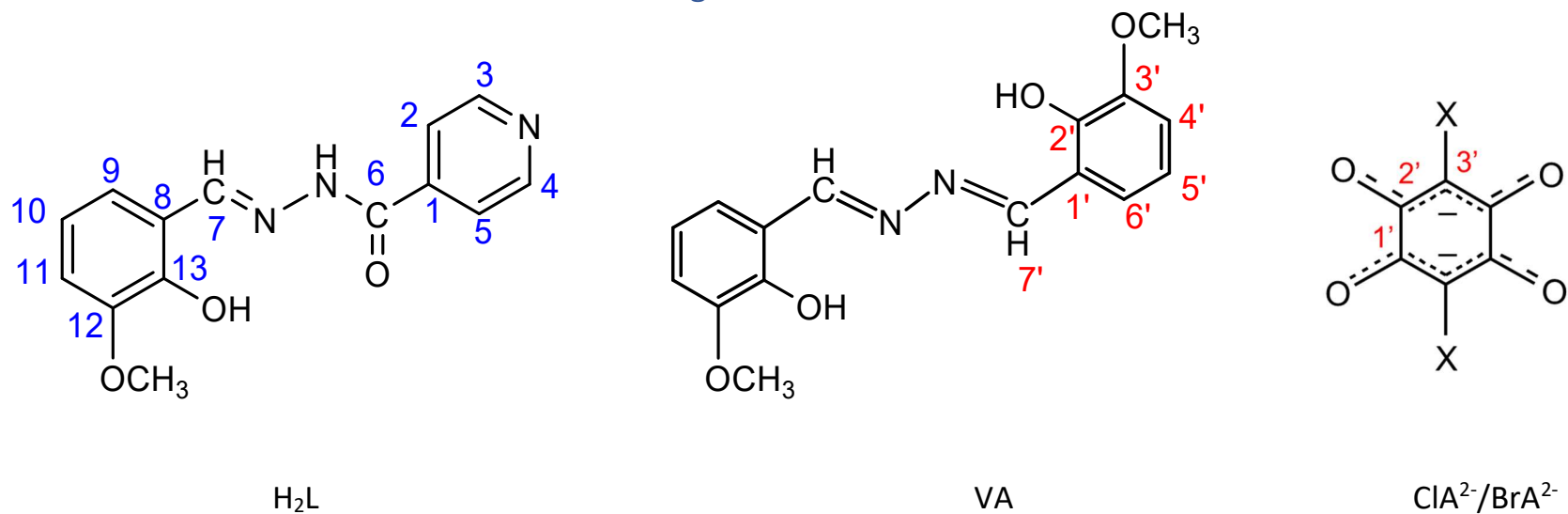


Figure S5. Comparison of IR-ATR spectra of: **VA** (top), **[1H]Cl-MeOH** (middle), and **[1H]Cl-VA** (bottom).

4. NMR spectroscopy

4.1. Structure and the NMR numbering scheme



Scheme S1. Structure and the NMR numbering scheme in 3-methoxysalicylaldehyde isonicotinoyl hydrazone (H₂L), *o*-vanillin azine (VA), chloranilate, CIA²⁻ (X = Cl) /bromanilate, BrA²⁻ (X = Br).

4.2. ^1H and ^{13}C chemical shifts of compounds in $\text{dms}\text{-}d_6$

Table S8. ^1H and ^{13}C chemical shifts of $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl}$ (**[1H]Cl**), $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Br}$ (**[1H]Br**), $[\text{MoO}_2(\text{HL})(\text{MeOH})](\text{ClA})_{0.5}$ (**[1H]ClA**), and $[\text{MoO}_2(\text{HL})(\text{MeOH})](\text{BrA})_{0.5}$ (**[1H]BrA**) in $\text{dms}\text{-}d_6$.

Atom	[1H]Cl		[1H]Br		[1H]ClA		[1H]BrA	
	δ / ppm (^1H)	δ / ppm (^{13}C)	δ / ppm (^1H)	δ / ppm (^{13}C)	δ / ppm (^1H)	δ / ppm (^{13}C)	δ / ppm (^1H)	δ / ppm (^{13}C)
1	-	141.83	-	143.70	-	142.60	-	147.12
2,5	8.21	123.77	8.31	124.44	7.97	122.97	8.26	124.35
3,4	8.94	159.14	9.00	159.46	8.82	149.50	8.75	146.28
6	-	166.31	-	165.71	-	-	-	-
7	9.07	159.14	9.11	159.45	9.03	148.92	9.05	149.75
8	-	120.70	-	120.69	-	119.46	-	118.83
9	7.38	126.20	7.32	126.44	7.36	126.24	7.28	122.39
10	7.07	122.67	7.10	122.43	7.07	119.71	6.90	119.76
11	7.31	118.21	7.42	118.43	7.31	118.21	7.10	115.90
12	-	149.98	-	149.95	-	147.74	-	147.78
13	-	149.10	-	148.82	-	148.45	-	148.46
NH	6.63		5.60				5.23	
CH ₃ O	3.84	56.16	3.87	56.65	3.84	56.29	3.81	56.29
1'	-	-	-	-	-	161.09	-	167.01
2'	-	-	-	-	-	161.09	-	167.21
3'	-	-	-	-	-	*	-	119.48

* not detected

Table S9. ^1H and ^{13}C chemical shifts of $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl}\cdot 0.5\text{VA}$ (**[1H]Cl·0.5VA**) and $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl}\cdot 0.5\text{VA}$ (**[1H]Br·0.5VA**) in $\text{dms}\text{-}d_6$.

Atom	[1H]Cl·0.5VA		[1H]Br·0.5VA	
	δ / ppm (^1H)	δ / ppm (^{13}C)	δ / ppm (^1H)	δ / ppm (^{13}C)
1	-	148.46	-	142.06
2,5	8.15	123.3	8.21	123.47
3,4	8.99	163.24	8.99	162.74
6	-	166.8	-	165.69
7	9.07	159.06	9.09	158.62
8	-	120.73	-	120.22
9	7.39	126.14	7.39	125.84
10	7.07	119.76	6.90	119.27
11	7.31	118.22	7.28	117.86
12	-	149.86	-	149.34
13	-	148.94	-	148.48
NH	5.13		4.75	
CH ₃ O	3.84	56.47	3.84	55.91
1'	-	118.83	-	118.31
2'	-	148.94	-	148.48
3'	-	148.09	-	147.85
4'	7.28	115.75	7.13	115.25
5'	6.91	122.33	7.08	121.84
6'	7.31	122.52	7.31	121.98
7'	9.00	147.62	8.99	146.52

Table S10. ^1H and ^{13}C chemical shifts (ppm) of $[\text{MoO}_2(\text{HL})\text{Cl}] \cdot \text{MeOH}$ (**2Cl**·MeOH), $[\text{MoO}_2(\text{L})(\text{MeOH})]$ (**1**), and $[\text{MoO}_2(\text{L})]_n$ (**2**) in $\text{dmsO}-d_6$.

Atom	2Cl ·MeOH		2Br ·0.5MeCN		1		2	
	δ / ppm (^1H)	δ / ppm (^{13}C)	δ / ppm (^1H)	δ / ppm (^{13}C)	δ / ppm (^1H)	δ / ppm (^{13}C)	δ / ppm (^1H)	δ / ppm (^{13}C)
1	-	142.61		142,43	-	137.95	-	137.99
2,5	8.27	124.06	8.2	123,88	7.87	122.20	7.89	122.30
3,4	9.98	158.98	8.93	159,49	8.77	158.08	8.78	158.60
6	-	166.17		166,49	-	168.05	-	167.29
7	9.08	146.64	9.07	147,19	9.02	151.50	9.02	151.22
8	-	120.75		120,85	-	120.75	-	120.79
9	7.40	126.34	7.38	126,21	7.36	126.07	7.35	125.89
10	7.08	122.31	7.08	122,60	7.06	122.00	7.06	121.98
11	7.31	118.24	7.31	118,44	7.28	117.96	7.29	117.95
12	-	150.09		149,90	-	149.91	-	149.71
13	-	149.04		148,93	-	148.91	-	148.77
NH	5.17	-	5.00	-	-	-	-	-
CH ₃ O	3.84	56.41	3.83	56.26	3.82	56.41	3.82	56.33

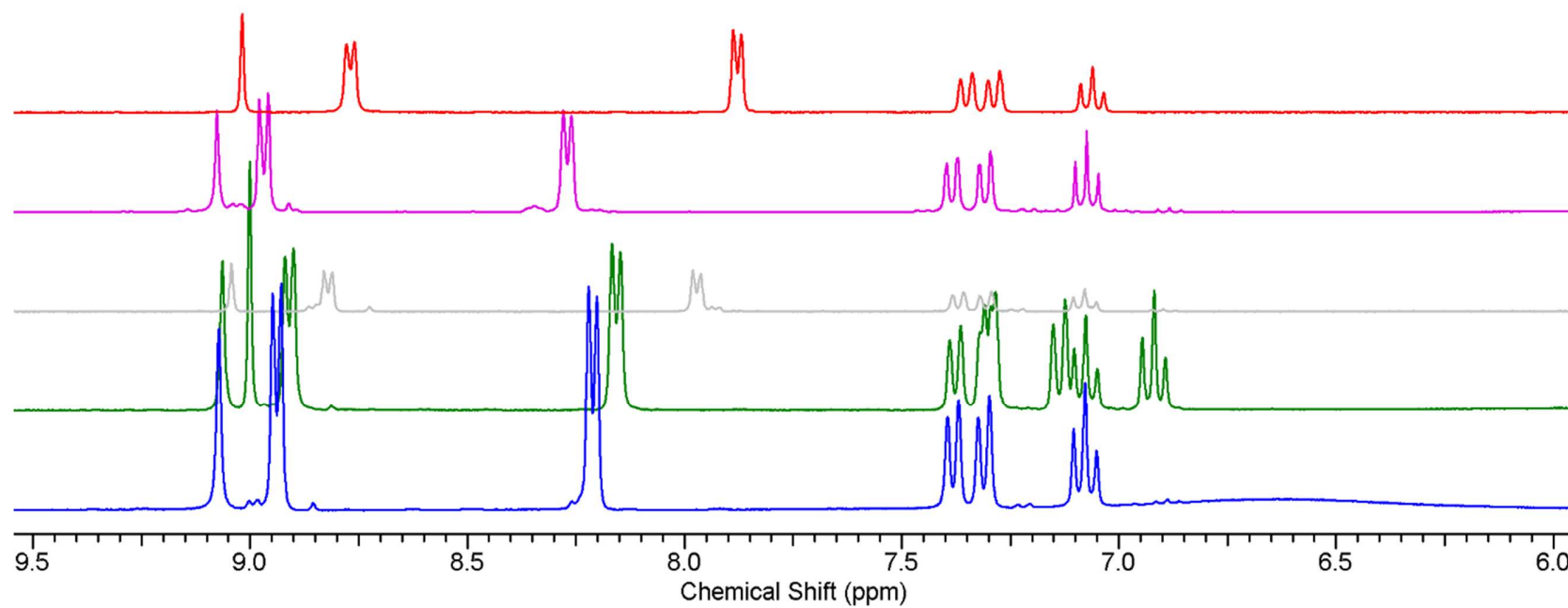


Figure S6. A portion of the ^1H NMR spectra of $[\mathbf{1H}]\text{Cl}\cdot\text{MeOH}$, $[\mathbf{1H}]\text{Cl}\cdot\mathbf{0.5VA}$, $[\mathbf{1H}](\text{ClA})_{0.5}\cdot\mathbf{2MeOH}$, and $\mathbf{2Cl}\cdot\text{MeOH}$, and $\mathbf{1}$ (from bottom to top).

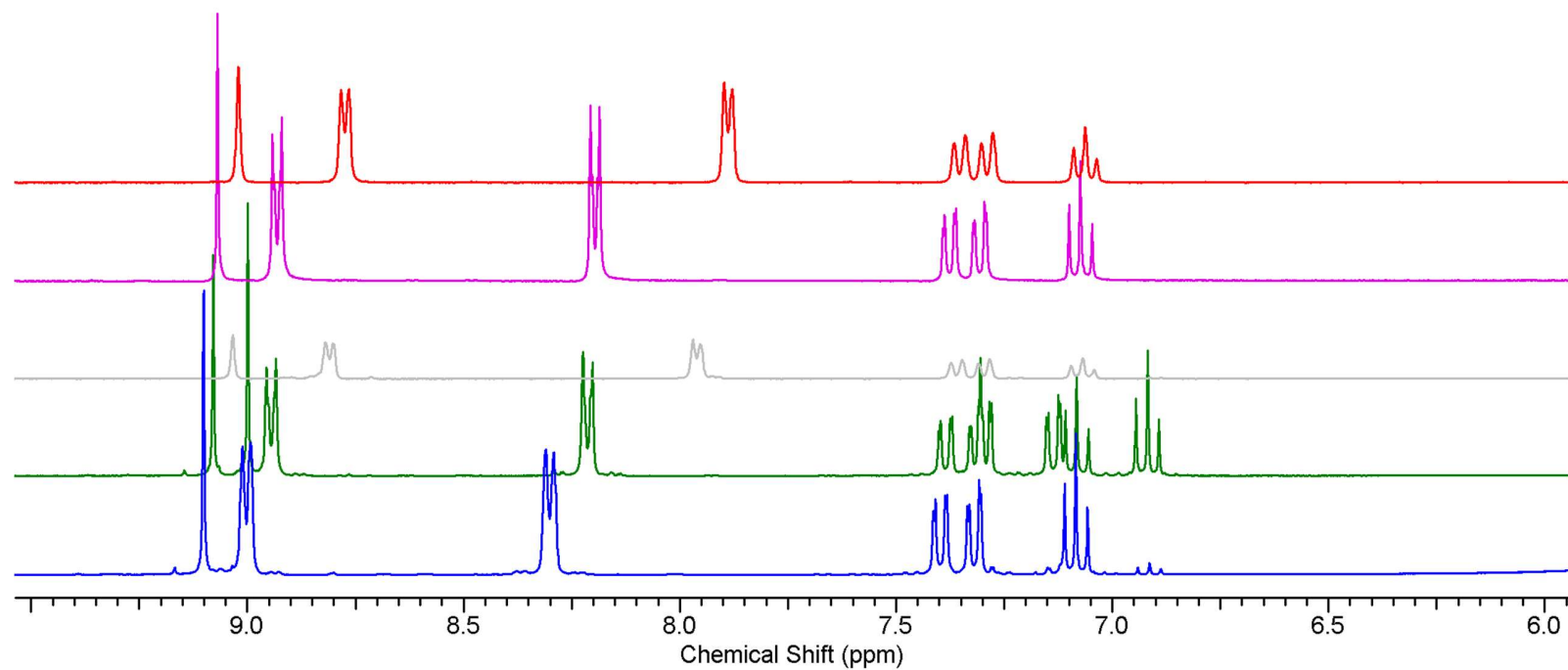


Figure S7. A portion of the ^1H NMR spectra of $[\mathbf{1H}]\text{Br}$, $[\mathbf{1H}]\text{Br}\cdot\mathbf{0.5VA}$, $[\mathbf{1H}](\text{BrA})_{0.5}\cdot 2\text{MeOH}$, and $\mathbf{2Br}\cdot\mathbf{0.5MeCN}$, and $\mathbf{2}$ (from bottom to top).

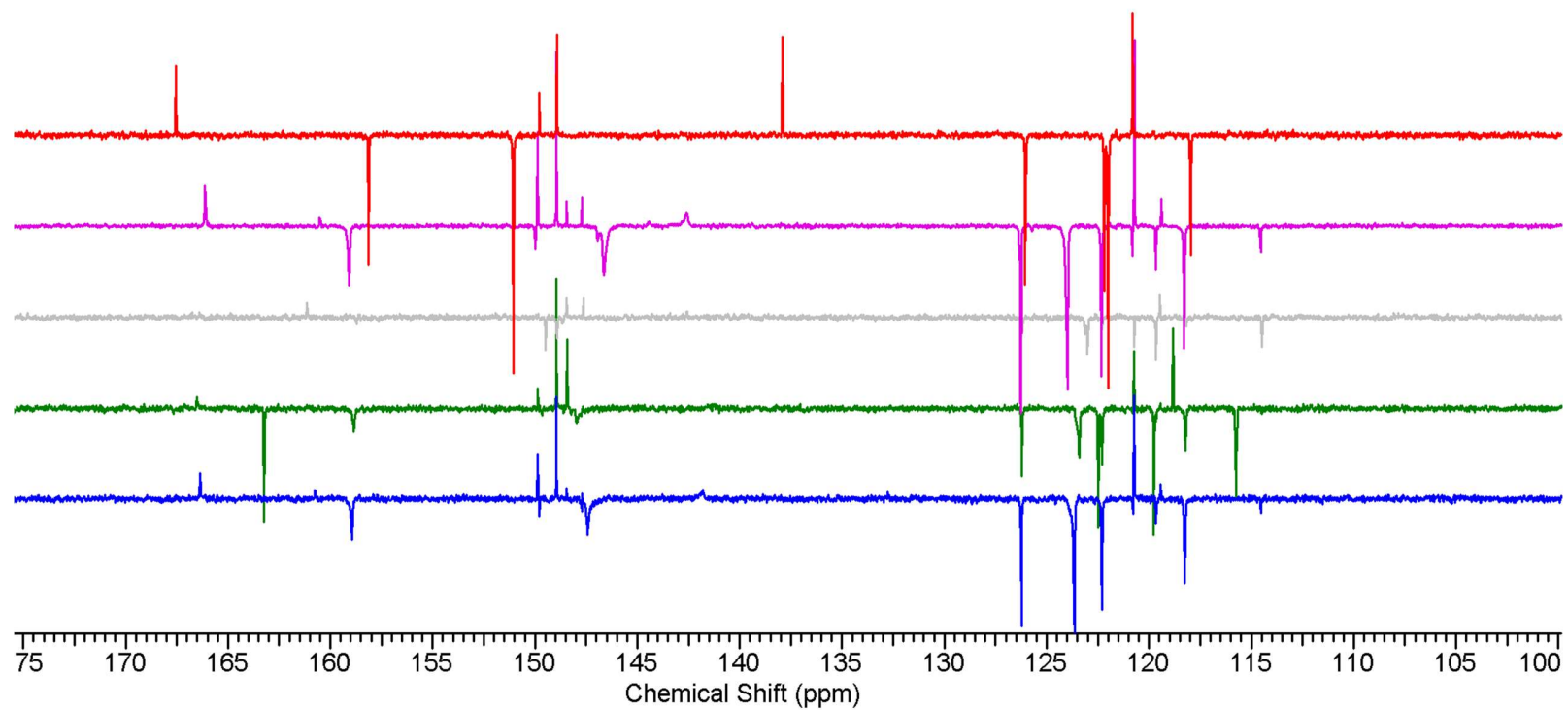


Figure S8. A portion of the ^{13}C NMR spectra of $[\mathbf{1H}]\text{Cl}\cdot\text{MeOH}$, $[\mathbf{1H}]\text{Cl}\cdot\mathbf{0.5VA}$, $[\mathbf{1H}](\text{CIA})_{0.5}\cdot 2\text{MeOH}$, and $\mathbf{2Cl}\cdot\text{MeOH}$, and $\mathbf{1}$ (from bottom to top).

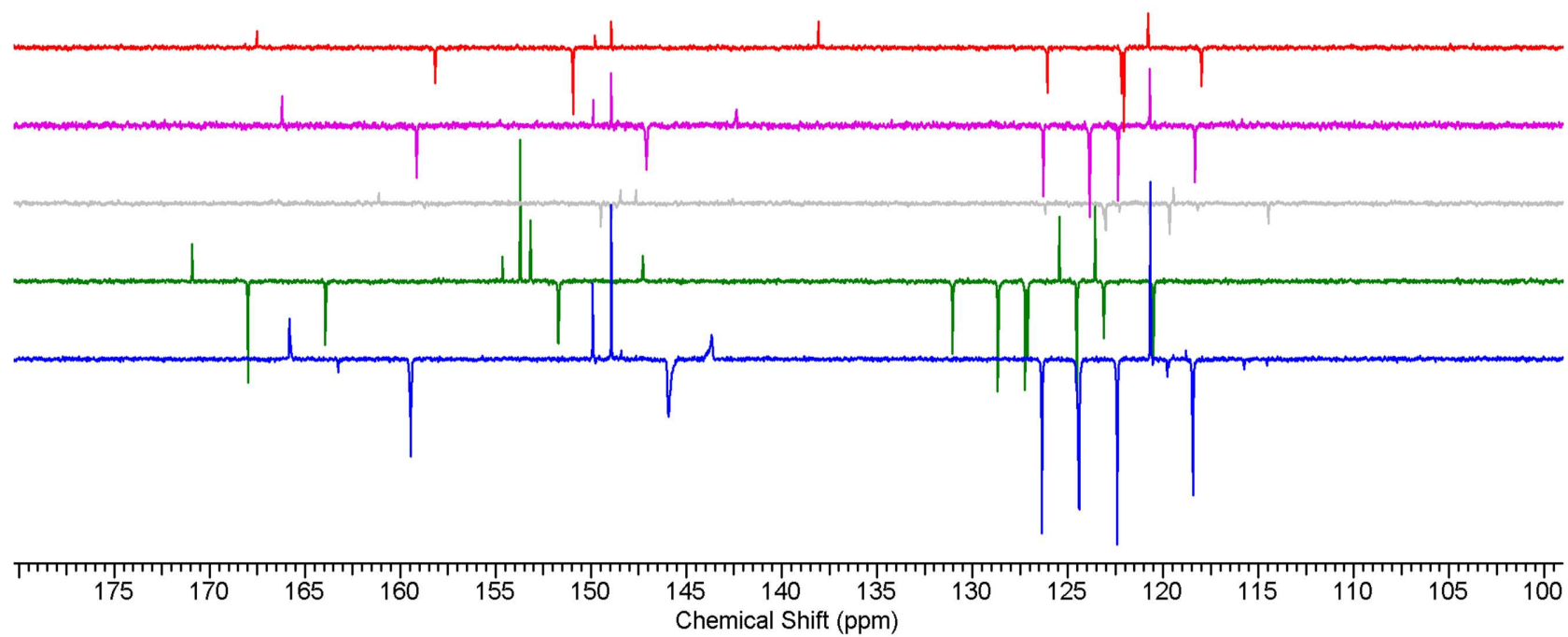


Figure S9. A portion of the ^{13}C NMR spectra of $[1\text{H}]\text{Br}$, $[1\text{H}]\text{Br}\cdot 0.5\text{VA}$, $[1\text{H}](\text{BrA})_{0.5}\cdot 2\text{MeOH}$, and $2\text{Br}\cdot 0.5\text{MeCN}$, and **2** (from bottom to top).

4.3. Tentative assignment of ^{13}C CP-MAS spectra

Table S11. Tentative assignment of ^{13}C CP-MAS spectra $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl}$ (**[1H]Cl**), $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Br}$ (**[1H]Br**), $[\text{MoO}_2(\text{HL})(\text{MeOH})](\text{CIA})_{0.5}$ (**[1H](CIA)_{0.5}**), and $[\text{MoO}_2(\text{HL})(\text{MeOH})](\text{BrA})_{0.5}$ (**[1H](BrA)_{0.5}**).

Atom	[1H]Cl	[1H]Br	[1H]CIA	[1H]BrA
	δ / ppm	δ / ppm	δ / ppm	δ / ppm
1	146.39	145.98	147.82-154.62	146.93-150.95
2.5	127.36	119.57-129.98	118.52-130.99	114.45-128.06
3.4	164,14	166.04	167.10	166.11-176.63
6	167.96	170.10	175.23-177.68	166.11-176.63
7	164,14	166.04	167.10	166.11-176.63
8	121.27 – 123.56	119.57-129.98	118.52-130.99	114.45-128.06
9	127.36	135.32	118.52-130.99	114.45-128.06
10	121.27 – 123.56	119.57-129.98	118.52-130.99	114.45-128.06
11	121.27 – 123.56	119.57-129.98	118.52-130.99	114.45-128.06
12	149.68	151.34	147.82-154.62	146.93-150.95
13	151.97	151.34	147.82-154.62	146.93-150.95
OCH3	54.80	56.91	58.60	59.70
1'	-	-	175.23-177.68	166.11-176.63
2'	-	-	175.23-177.68	175.23-177.63
3'	-	-	118.52-130.99	114.45-128.06

Table S12. Tentative assignment of ^{13}C CP-MAS spectra of $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl}\cdot 0.5\text{VA}$ (**[1H]Cl-0.5VA**) and $[\text{MoO}_2(\text{HL})(\text{MeOH})]\text{Cl}\cdot 0.5\text{VA}$ (**[1H]Br-0.5VA**).

Atom	[1H]Cl-0.5VA	[1H]Br-0.5VA
	δ /ppm	δ /ppm
1	140.55-144.61	139.80-144.36
2.5	121.02-127.11	121.01-127.10
3.4	168.00	167.70
6	170.24	170.24
7	166.18	165.92
8	121.02-127.11	121.01-127.10
9	131.17	130.65
10	121.02-127.11	121.01-127.10
11	121.02-127.11	121.01-127.10
12	148.41 – 150.70	148.67-150.70
13	148.41 – 150.70	148.67-150.70
OCH3	58.33	58.33
1'	121.02-127.11	121.01-127.10
2'	148.41-127.11	148.67-150.70
3'	148.41 – 150.70	148.67-150.70
4'	117,46	117.47
5'	121.02-127.11	121.01-127.10
6'	121.02-127.11	121.01-127.10
7'	140.55-144.61	139.80-144.36

Table S13. Tentative assignment of ^{13}C CP-MAS spectra $[\text{MoO}_2(\text{HL})\text{Cl}] \cdot \text{MeOH}$ (**2Cl**·MeOH), $[\text{MoO}_2(\text{HL})\text{Br}] \cdot 0.5\text{MeCN}$ (**2Br**·0.5MeCN), and $[\text{MoO}_2(\text{L})(\text{MeOH})]$ (**1**).

Atom	2Cl ·MeOH	2Br ·0.5MeCN	1
	δ /ppm	δ /ppm	δ /ppm
1	146.30	141.50-143.12	142.58
2.5	128.30	127.11 – 128.46	126.60
3.4	149.80 – 151.80	159.40	153.24
6	167.60	164.91	169.98
7	146.30	141.50–143.12	153.24
8	120.90 – 124.00	121.60–122.40	122.54 – 124.53
9	128.30	127.11–128.46	130.40
10	120.90 – 124.00	121.60–122.40	122.54 – 124.57
11	120.90 – 124.00	115.28	122.54 – 124.57
12	164.00	147.29–149.04	164.91
13	149.80 – 151.80	147.29–149.04	153.24
OCH ₃	54.20	57.51	55.81

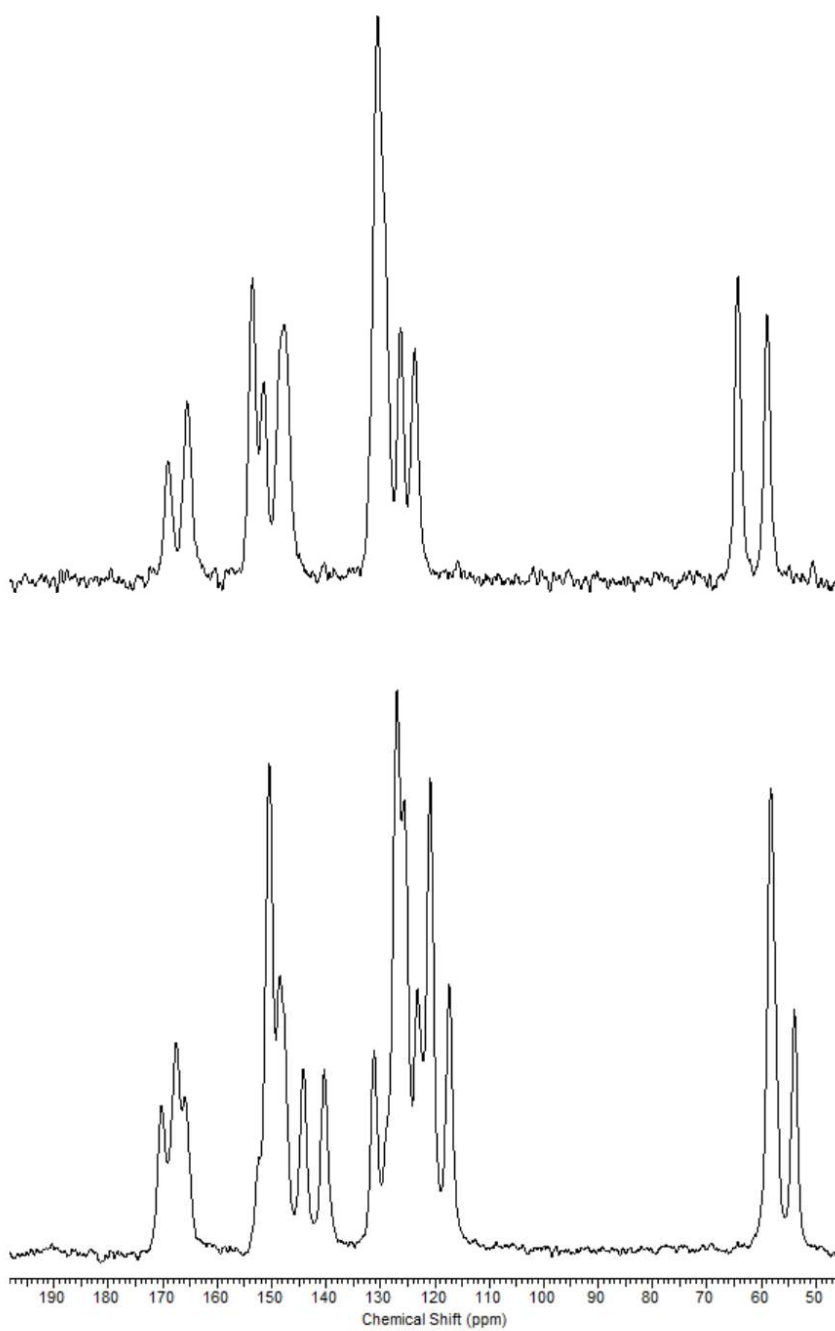


Figure S10. ^{13}C CP-MAS spectra of $[\text{1H}]\text{Cl}\cdot\text{MeOH}$ (top) and $[\text{1H}]\text{Cl}\cdot 0.5\text{VA}$ (bottom).

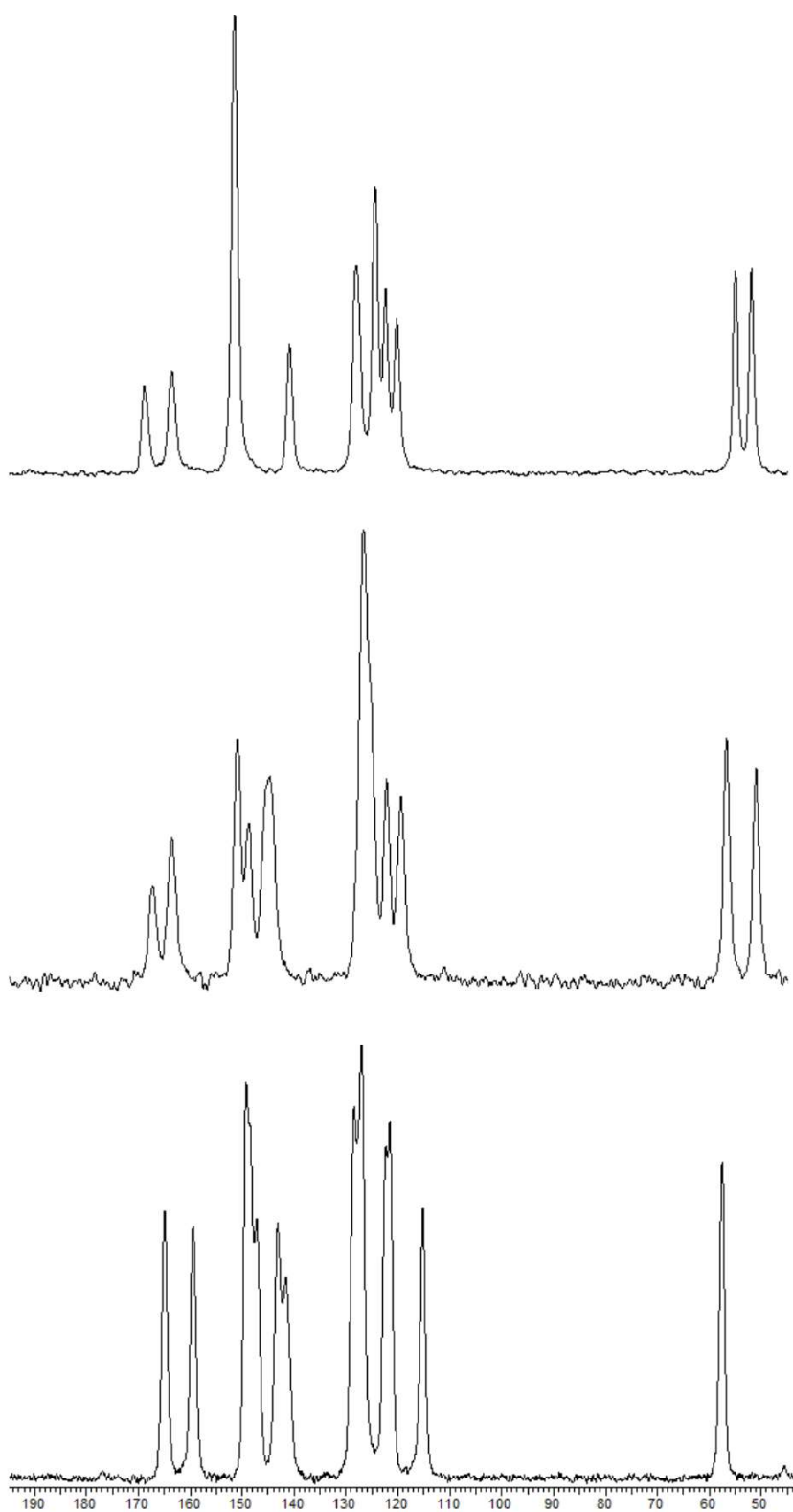


Figure S11. ^{13}C CP-MAS spectra of **1**, **2Cl**·MeOH and **2Br**·0.5MeCN (from top to bottom).

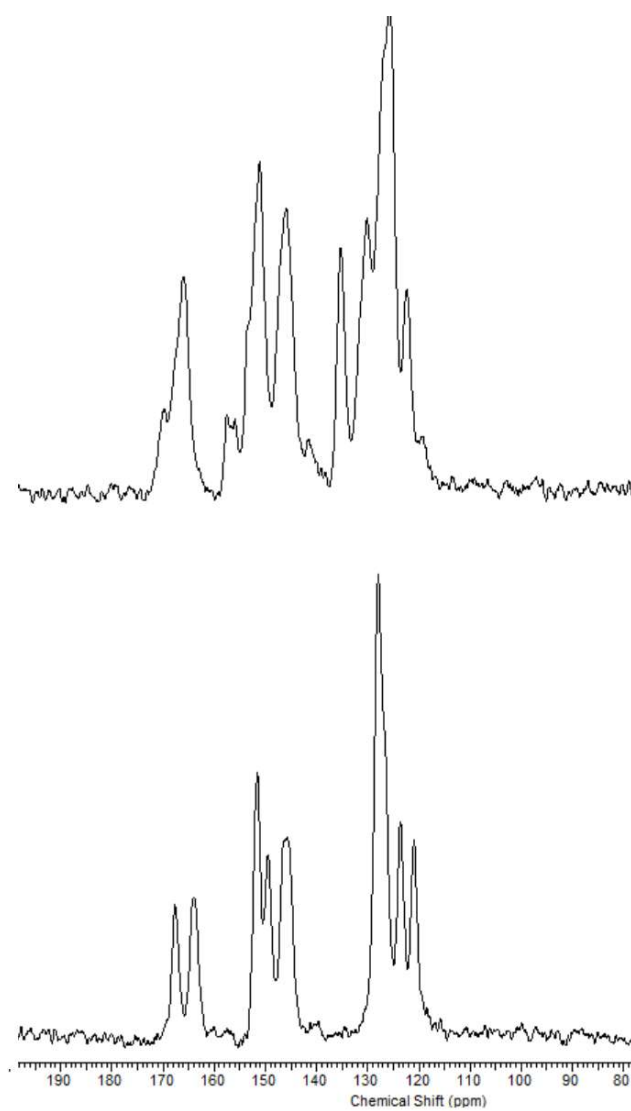
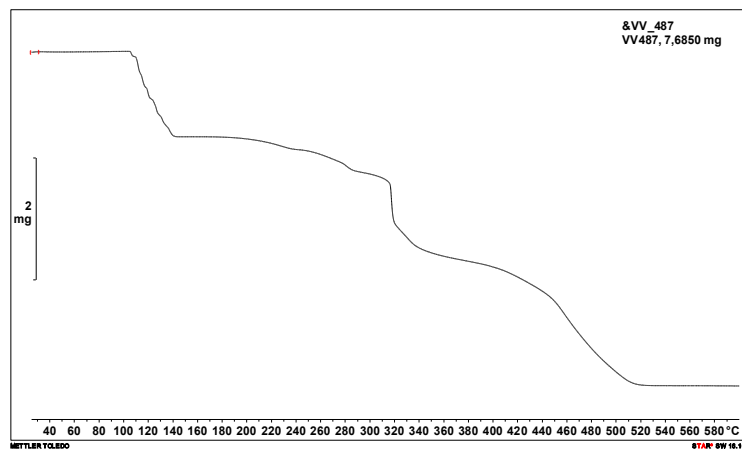
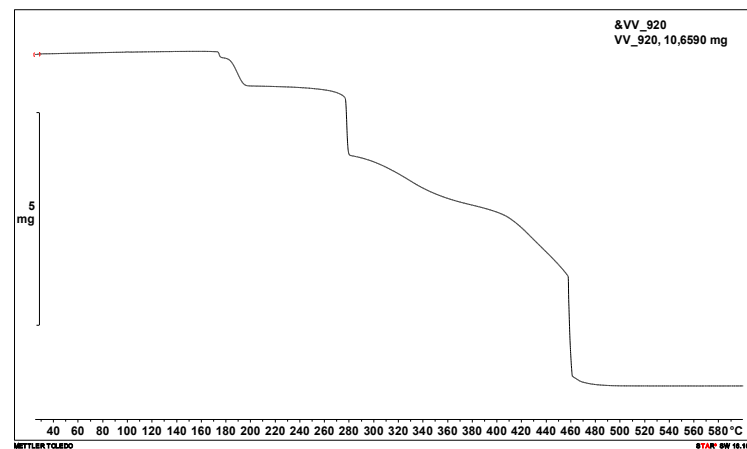


Figure S12. ^{13}C CP-MAS spectra of $[1\text{H}]\text{Br}$ (top) and $[1\text{H}]\text{Cl}\cdot\text{MeOH}$ (bottom).

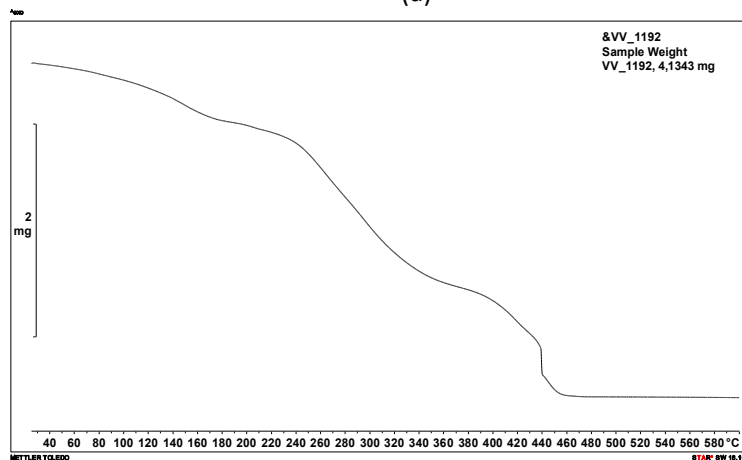
5. Thermogravimetric curves



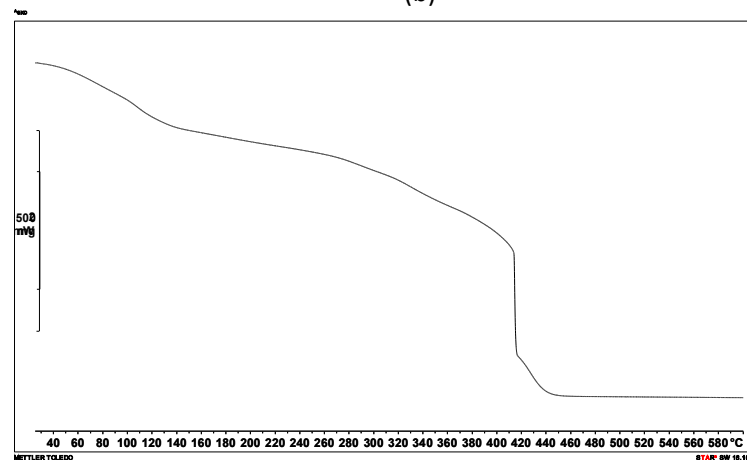
(a)



(b)

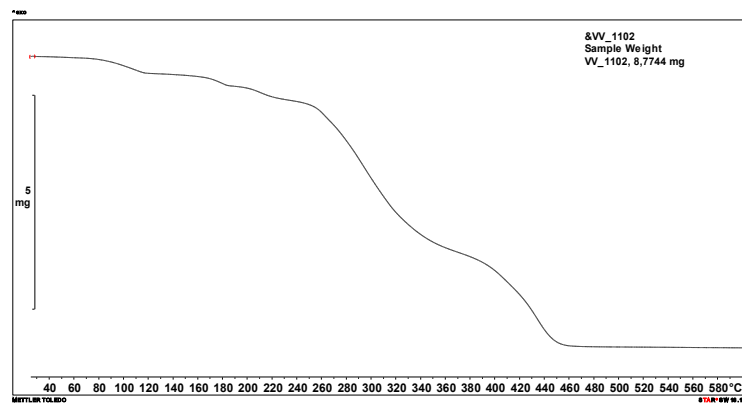


(c)

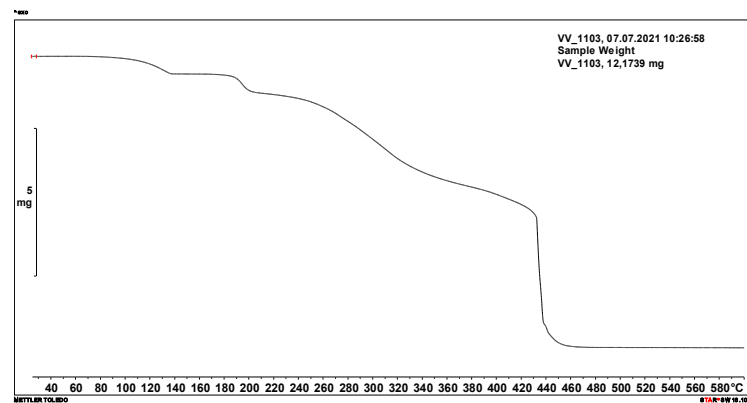


(d)

Figure S13. Thermogravimetric curves of (a) $[1H]Cl \cdot MeOH$, (b) $[1H]Br$, (c) $[1H](ClA)_{0.5} \cdot 2MeOH$, and (d) $[1H](BrA)_{0.5} \cdot 2MeOH$ under the O_2 atmosphere in the range of 25 - 600 °C.

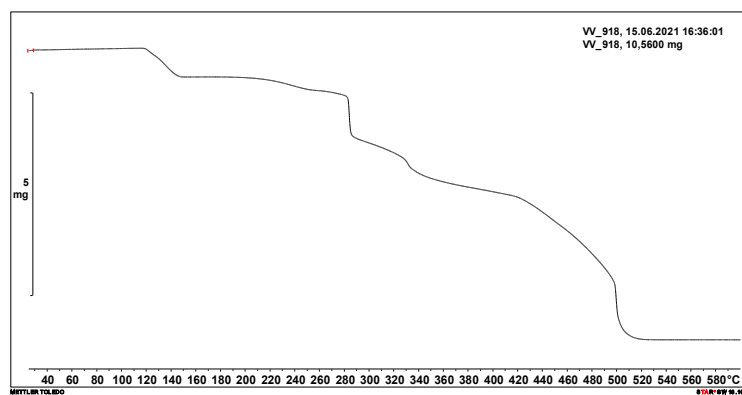


(a)

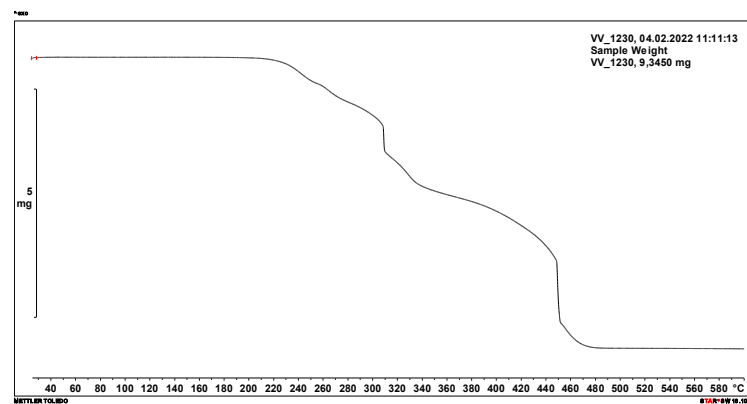


(b)

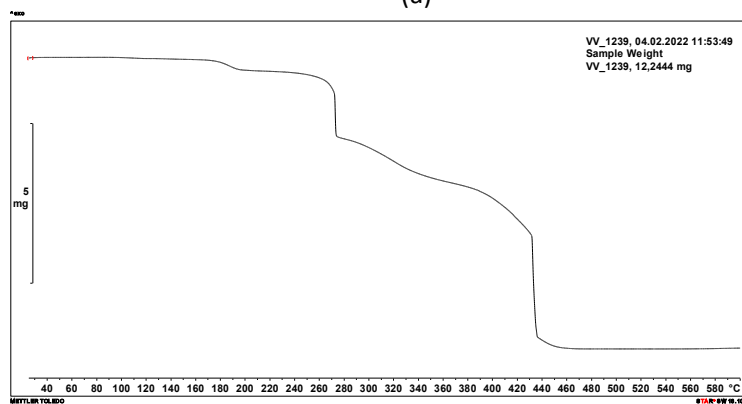
Figure S14. Thermogravimetric curves of (a) $[1H]Cl \cdot 0.5VA$ and (b) $[1H]Br \cdot 0.5VA$ under the O_2 atmosphere in the range of 25 - 600 °C.



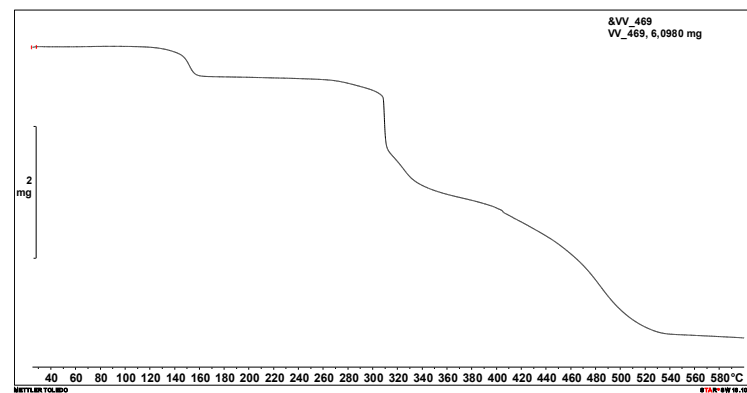
(a)



(b)



(c)



(d)

Figure S15. Thermogravimetric curves of (a) **2Cl**·MeOH, (b) **2Cl**, (c) **2Br**·0.5MeCN, and (d) **1** under the O₂ atmosphere in the range of 25 - 600 °C.