Supporting Information

Cation/Ligand-Induced Solvent-Assisted Transformations of Zn(II) and Cu(II) Complexes Featuring Single-Pocket Multidentate Chelating Members

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Content

Single-Crystal X-ray Crystallography (SCXRD)

Single crystals of **L1H**–**L3H** and **mbac** were picked under the microscope, leapt in paratone oil and mounted in a nylon loop, and all geometric and intensity data were taken from one single crystal. Datasets were collected on a Bruker D8 VENTURE APEX-IV AXS area detector diffractometer,[1] equipped with a graphite monochromator and a Mo-Kα (λ = 0.71073 Å, fine-focus sealed tube operated at 2.0 kW (50 kV, 40 mA). All reflections were emerged and integrated with the Bruker SAINT and XPREP software packages, respectively.[2] Data were collected for absorption effects using the multi-scan techniques SADABS,[3] and the structures were solved by the direct methods package SHELXT and refined using X-Seed[4] software incorporating SHELXL.[5,6] The final anisotropic full-matrix least-squares refinement was done on F^2. The methyl and aromatic protons were placed in geometrically idealised positions (C–H = 0.93–0.98 Å) and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eqv}(C). SHELX constraints and restraints were used to model structures. The non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data for all the ligands are given in Table S1.

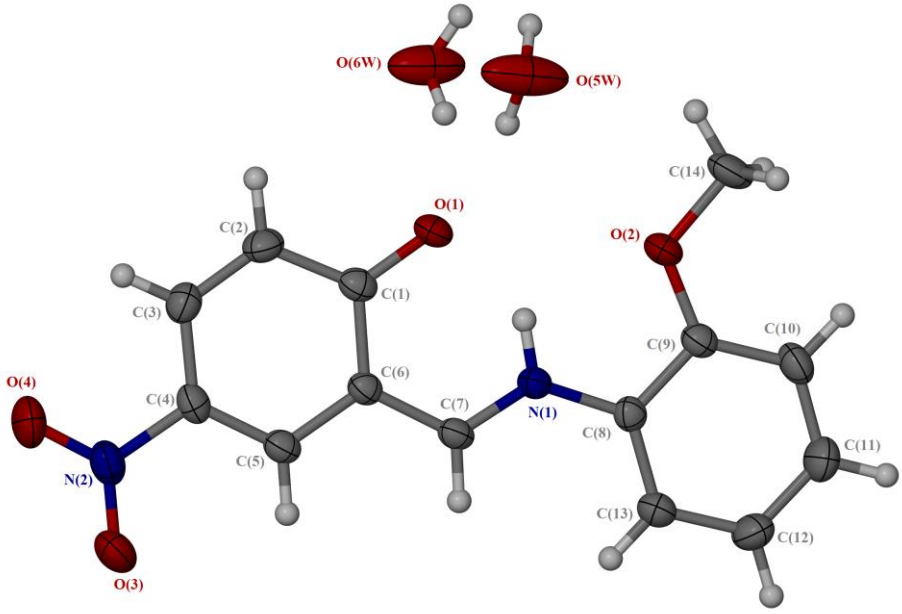

Figure S1a. ORTEP View and Atom Numbering Scheme of **L1H** with Displacement Ellipsoids Drawn at 50% Probability Level. Hydrogen Atoms are Shown as Off-white Spheres with 0.2 Å radius.

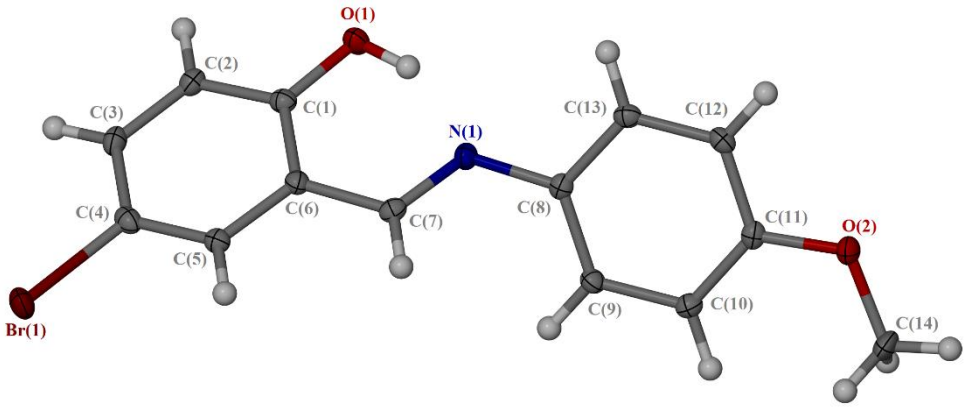

Figure S1b. ORTEP View and Atom Numbering Scheme of **L2H** with Displacement Ellipsoids Drawn at 50% Probability Level. Hydrogen Atoms are Shown as Off-white Spheres with 0.2 Å radius.

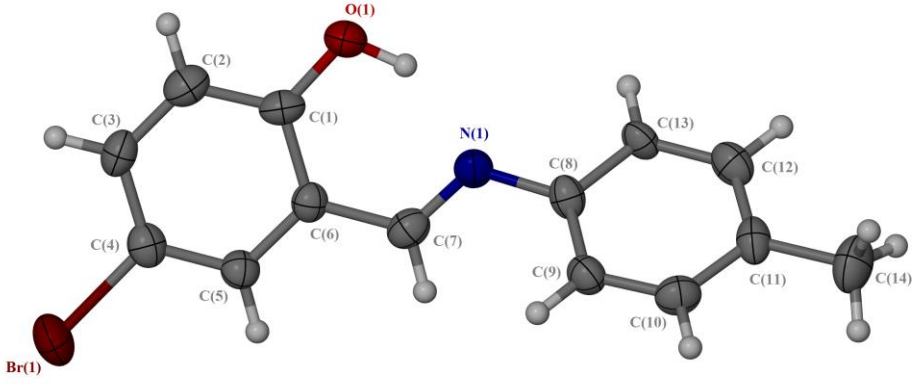

Figure S1c. ORTEP View and Atom Numbering Scheme of **L3H** with Displacement Ellipsoids Drawn at 50% Probability Level. Hydrogen Atoms are Shown as Off-white Spheres with 0.2 Å radius.

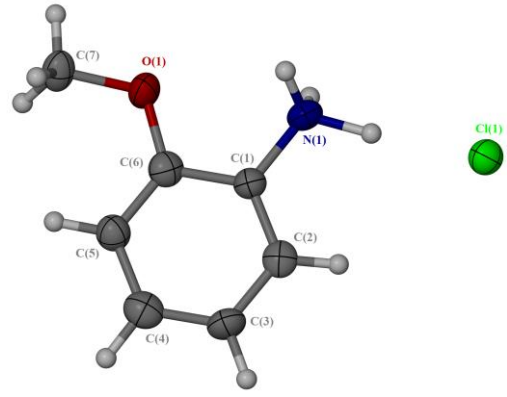

Figure S1d. ORTEP View and Atom Numbering Scheme of **mbac** with Displacement Ellipsoids Drawn at 50% Probability Level. Hydrogen Atoms are Shown as Off-white Spheres with 0.2 Å radius.

Table S1. Crystal Data Parameters of **L1H**–**L3H** and **mbac**.

Compound	**L1H**	**L2H**	**L3H**	**mbac**
Empirical Formula	$C_{14}H_{12}N_2O_4$, H_2O	$C_{14}H_{12}NBrO_2$	$C_{14}H_{12}NBrO$	$C_7H_{10}ClNO$
F. W. ($g.mol^{-1}$)	290.27	306.16	290.16	159.61
T (K)	100(2)	100(2)	300(2)	100(2)
Crystal size (mm^3)	0.375 x 0.263 x 0.115	0.218 x 0.155 x 0.125	0.411 x 0.203 x 0.187	0.249 x 0.196 x 0.060
Crystal colour	Orange	Green	Green	Colourless
Lattice	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c* (No. 15)	*Pc* (No. 7)	*Pc* (No. 7)	$P2_1/c$ (No. 14)
a (Å)	26.0472(18)	14.1564(11)	14.0399(10)	5.3543(7)
b (Å)	6.9006(4)	6.8759(5)	7.0073(5)	13.7595(17)
c (Å)	15.7484(12)	6.2553(5)	6.1969(4)	10.7185(16)
β (º)	111.814(3)	91.004(3)	96.953(2)	98.524(4)
Vol. ($Å^3$)	2627.9(3)	608.79(8)	605.18(7)	780.94(18)
Z	8	2	2	4
$D_{calcd.}$ ($g.cm^{-3}$)	1.467	1.670	1.592	1.358
F(000)	1208.0	308.0	292.0	336.0
μ (mm^{-1})	0.113	3.368	3.378	0.418
No. reflns.	38550	9387	15534	13494
Data/ restr. / par.	2699 / 13 / 201	2174 / 2 / 168	2015/ 2/ 160	1152 / 0 / 93
R(int) / R(sigma)	0.1278 / 0.0366	0.0427 / 0.0444	0.0495 / 0.0137	0.1571 / 0.0611
GOF[a]	1.224	1.082	1.040	1.236
R_1 / wR_2 ($I > 2\sigma(I)$)[b]	0.0843 / 0.2160	0.0243 / 0.0531	0.0206 / 0.0460	0.0716 / 0.1729
R_1 / wR_2 [all data][c]	0.1367 / 0.2988	0.0265 / 0.0538	0.0247 / 0.0476	0.1471 / 0.2619
Completeness (%)	100	100	100	100
Flack parameter	–	0.050(8)	–	–

[a] $GOF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$
[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
[c] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2+bP]$, $P = (F_o^2+2F_c^2)/3$

Table S2. Selected Bond Lengths [Å] and Angles [°] for **L1H**.

Bond Length					
O1–C1	1.290(4)	C3–C4	1.405(5)	C3–H3	0.9500
O2–N2	1.242(4)	C4–C5	1.366(5)	O5W–H5WA^{i}	0.9400
O3–N2	1.229(4)	C5–C6	1.402(5)	C11–H11	0.9500
O4–C9	1.360(4)	C6–C7	1.420(5)	C12–H12	0.9500
O4–C14	1.439(5)	C8–C13	1.389(5)	C13–H13	0.9500
N1–C7	1.306(5)	C8–C9	1.400(5)	C14–H14A	0.9800
N1–C8	1.406(4)	C9–C10	1.399(5)	C14–H14B	0.9800
N2–C4	1.441(5)	C10C11	1.386(5)	C14–H14C	0.9800
C1–C2	1.426(5)	C11–C12	1.384(6)	O6W–H6WA^{i}	1.0100
C1–C6	1.447(5)	C12–C13	1.388(5)		
C2–C3	1.358(5)	C2–H2	0.9500		
Bond Angle					
C9–O4–C14	117.9(3)	C1–C6–C5	120.3(1)	H5WA–O5W–H5WA^{i}	111.00
C7–N1–C8	129.0(3)	N1–C7–C6	120.8(3)	N1–C7–H7	120.00
O2–N2–O3	121.8(3)	C9–C8–C13	120.3(3)	C6–C7–H7	120.00
O2–N2–C4	118.1(3)	N1–C8–C9	115.0(3)	C11–C10–H10	121.00
O3–N2–C4	120.1(3)	N1–C8–C13	124.7(3)	C9–C10–H10	121.00
O1–C1–C2	121.8(3)	C8–C9–C10	120.2(3)	C10–C11–H11	120.00
O1–C1–C6	121.3(3)	O4–C9–C8	115.0(3)	C12–C11–H11	120.00
C2–C1–C6	116.9(3)	O4–C9–C10	124.8(3)	C13–C12–H12	120.00
C8–N1–H1	118.00	C9–C10–C11	118.8(4)	C11–C12–H12	120.00
C7–N1–H1	113.00	C10–C11–C12	120.9(4)	C8–C13–H13	120.00
C1–C2–C3	121.7(3)	C11–C12–C13	120.6(4)	C12–C13–H13	120.00
C2–C3–C4	119.7(3)	C8–C13–C12	119.2(3)	O4–C14–H14A	109.00
C3–C4–C5	121.9(3)	C1–C2–H2	119.00	O4–C14–H14B	109.00
N2–C4–C3	118.7(3)	C3–C2–H2	119.00	O4–C14–H14C	109.00
N2–C4–C5	119.4(3)	C2–C3–H3	120.00	H14A–C14–H14B	109.00
C4–C5–C6	119.5(3)	C4–C3–H3	120.00	H14B–C14–H14C	109.00
C5–C6–C7	118.9(3)	C4–C5–H5	120.00	H14A–C14–H14C	109.00
C1–C6–C7	120.8(3)	C6–C5–H5	120.00	H6WA–O6W–H6WA^{i}	103.00

Symmetry code: (i) –x, y, 1/2–z

Table S3. Selected Bond Lengths [Å] and Angles [°] for **L2H**.

Bond Length					
Br1–C4	1.907(5)	C4–C5	1.362(7)	C3–H3	0.9500
O1–C1	1.353(5)	C5–C6	1.413(9)	C5–H5	0.9500
O2–C11	1.360(7)	C6–C7	1.442(9)	C7–H7	0.9500
O2–C14	1.435(9)	C8–C13	1.401(7)	C9–H9	0.9500
N1–C7	1.289(6)	C8–C9	1.400(8)	C10–H10	0.9500
N1–C8	1.409(7)	C9–C10	1.396(7)	C12–H12	0.9500
C1–C6	1.418(9)	C10–C11	1.395(8)	C13–H13	0.9500
C1–C2	1.383(9)	C11–C12	1.402(8)	C14–H14A	0.9800
C2–C3	1.383(9)	C12–C13	1.374(7)	C14–H14B	0.9800
C3–C4	1.396(7)	C2–H2	0.9500	C14–H14C	0.9800
Bond Angle					
C11–O2–C14	118.0(5)	N1–C8–C13	117.8(4)	N1–C7–H7	120.00
C7–N1–C8	121.7(5)	C9–C8–C13	118.9(5)	C6–C7–H7	120.00
C1–O1–H1	99.00(5)	N1–C8–C9	123.1(5)	C8–C9–H9	120.00
O1–C1–C2	118.7(5)	C8–C9–C10	120.6(5)	C10–C9–H9	120.00
C2–C1–C6	119.7(5)	C9–C10–C11	119.8(5)	C9–C10–H10	120.00
O1–C1–C6	121.5(5)	O2–C11–C10	125.5(6)	C11–C10–H10	120.00
C1–C2–C3	121.4(6)	O2–C11–C12	115.2(5)	C11–C12–H12	120.00
C2–C3–C4	118.6(5)	C10–C11–C12	119.3(5)	C13–C12–H12	120.00
Br1–C4–C5	120.0(4)	C11–C12–C13	120.7(4)	C8–C13–H13	120.00
C3–C4–C5	121.7(4)	C8–C13–C12	120.5(4)	C12–C13–H13	120.00
Br1–C4–C3	118.2(4)	C1–C2–H2	119.00	O2–C14–H14A	110.00
C4–C5–C6	120.2(5)	C3–C2–H2	119.00	O2–C14–H14B	109.00
C1–C6–C7	121.2(6)	C2–C3–H3	121.00	O2–C14–H14C	109.00
C5–C6–C7	120.4(6)	C4–C3–H3	121.00	H14A–C14–H14B	109.00
C1–C6–C5	118.3(6)	C4–C5–H5	120.00	H14A–C14–H14C	109.00
N1–C7–C6	120.8(5)	C6–C5–H5	120.00	H14B–C14–H14C	109.00

Table S4. Selected Bond Lengths [Å] and Angles [°] for **L3H**.

Bond Length					
Br1–C4	1.900(4)	C5–C6	1.392(8)	C3–H3	0.9300
O1–C1	1.342(10)	C6–C7	1.452(11)	C7–H7	0.9300
N1–C7	1.271(10)	C8–C13	1.386(8)	C10–H10	0.9300
N1–C8	1.416(9)	C8–C9	1.383(10)	C13–H13	0.9300
C1–C6	1.424(9)	C9–C10	1.381(11)	C14–H14A	0.9600
C1–C2	1.389(11)	C10–C11	1.369(10)	C14–H14B	0.9600
C2–C3	1.369(9)	C11–C14	1.507(11)	C14–H14C	0.9600
C3–C4	1.389(6)	C11–C12	1.394(11)		
C4–C5	1.369(6)	C12–H13	1.372(9)		
Bond Angle					
C7–N1–C8	121.2(6)	C9–C8–C13	119.4(6)	C6–C7–H7	119.00
C1–O1–H1	108.0(4)	N1–C8–C9	118.7(6)	C8–C9–H9	120.00
O1–C1–C2	119.2(6)	C8–C9–C10	119.5(6)	C10–C9–H9	120.00
C2–C1–C6	119.0(7)	C9–C10–C11	122.4(7	C9–C10–H10	119.00
O1–C1–C6	121.8(7)	C10–C11–C12	117.1(7)	C11–C10–H10	119.00
C1–C2–C3	121.3(6)	C10–C11–C14	122.5(7)	C11–C12–H12	119.00
C2–C3–C4	119.4(5)	C12–C11–C14	120.4(7)	C13–C12–H12	119.00
Br1–C4–C5	119.4(3)	C11–C12–C13	122.0(6)	C8–C13–H13	120.00
C3–C4–C5	121.2(4)	C8–C13–C12	119.6(5)	C12–C13–H13	120.00
Br1–C4–C3	119.5(3)	C1–C2–H2	119.00	C11–C14–H14A	109.00
C4–C5–C6	120.4(4)	C3–C2–H2	119.00	C11–C14–H14B	109.00
C1–C6–C7	120.0(7)	C2–C3–H3	120.00	C11–C14–H14C	109.00
C5–C6–C7	121.0(6)	C4–C3–H3	120.00	H14A–C14–H14B	109.00
C1–C6–C5	118.9(6)	C4–C5–H5	120.00	H14A–C14–H14C	110.00
N1–C7–C6	122.4(6)	C6–C5–H5	120.00	H14B–C14–H14C	110.00
N1–C8–C13	121.6(6)	N1–C7–H7	119.00		

Table S5. Selected Bond Lengths [Å] and Angles [°] for **mbac**.

Bond Length					
O1–C6	1.372(9)	C2–C3	1.398(12)	C3–H3	0.9800(7)
O1–C7	1.451(10)	C3–C4	1.374(12)	C4–H4	1.010(8)
N1–C1	1.456(10)	C4–C5	1.386(12)	C7–H7B	1.010(7)
C1–C2	1.364(11)	C5–C6	1.379(11)	C7–H7C	1.020(7)
C1–C6	1.395(10)	C2–H2	0.9600(7)		
Bond Angle					
C6–O1–C7	116.5(6)	C2–C3–C4	118.9(7)	C5–C4–H4	121.0(4)
N1–C1–C2	120.5(7)	C3–C4–C5	121.1(8)	C4–C5–H5	122.0(3)
N1–C1–C6	118.1(6)	C4–C5–C6	120.0(8	C6–C5–H5	118.0(3)
C2–C1–C6	121.4(7)	C1–C6–C5	118.7(7)	O1–C7–H7A	103.0(5)
C1–N1–H1A	108.0(4)	O1–C6–C1	115.3(6)	O1–C7–H7B	113.0(4)
C1–N1–H1B	118.0(6)	O1–C6–C5	126.0(7)	O1–C7–H7C	114.0(4)
C1–N1–H1C	111.0(4)	C1–C2–H2	116.0(4)	H7A–C7–H7B	108.0(6)
H1A–N1–H1B	106.0(7)	C3–C2–H2	124.0(4)	H7A–C7–H7C	110.0(7)
H1A–N1–H1C	116.0(6)	C2–C3–H3	121.0(4)	H7B–C7–H7C	108.0(6)
H1B–N1–H1C	98.00(7)	C4–C3–H3	120.0(4)		
C1–C2–C3	119.9(7)	C3–C4–H4	118.0(4)		

Table S6: List of Hydrogen Bonds for **L1H**–**L3H** and **mbac**.

Compound	D-H···*A*	d(D-H) (Å)	d(H···A) (Å)	d(D-A) (Å)	∠(D-H···*A*) °	Symmetry
L1H	N1–H1···O1	1.03(4)	1.690(5)	2.560(4)	140(4)	
	N1–H1···O4	1.03(4)	2.120(5)	2.570(4)	104(3)	
	O5W–H5WA···O1	1.02(11)	1.870(12)	2.882(4)	174(14)	x, y, z
	O6W–H6WA···O1	1.07(12)	1.810(12)	2.859(4)	165(10)	1–x, y, 1/2–z
	C5–H5···O6W	0.950	2.540	3.262(5)	133	1–x, –y, 1–z
	C7–H7···O5W	0.950	2.570	3.294(4)	133	1–x, 1–y, 1–z
	C10–H10···O2	0.950	2.370	3.319(5)	175	1/2+x, 1/2+y, z
	π–π stacking			4.955(2)		1–x, –y, 1–z
	π–π stacking			3.695(2)		1–x, 1–y, 1–z
	π–π stacking			4.362(2)		1–x, –y, 1–z
	π–π stacking			5.539(2)		3/2–x, –1/2+y, 3/2–z
L2H	O1–H1···N1	0.870(9)	1.740(9)	2.577(6)	160.0(8)	
	C2–H2···π	0.950	2.770	3.449(6)	129.0	x, –y, –1/2+z
	C5–H5···π	0.950	2.860	3.535(5)	129.0	x, 1–y, 1/2+z
	C10–H10···π	0.950	2.750	3.509(5)	138.0	x, –y, 1/2+z
	C13–H13···π	0.950	2.590	3.327(5)	134.0	x, 1–y, –1/2+z
	π–π stacking			4.606(3)		x, –y, 1/2+z
	π–π stacking			4.738(3)		x, –y, –1/2+z
L3H	O1–H1···N1	0.930(6)	1.760(6)	2.593(7)	147.0(6)	
	C2–H2···π	0.930	2.810	3.480(6)	130.0	x, 1–y, 1/2+z
	C5–H5···π	0.930	2.900	3.565(4)	129.0	x, –y, –1/2+z
	C9–H9···π	0.930	2.800	3.490(6)	132.0	x, –y, 1/2+z
	C12–H12···π	0.930	2.750	3.481(6)	136.0	x, 1–y, –1/2+z
	π–π stacking			4.717(3)		x, –y, 1/2+z
	π–π stacking			4.673(4)		x, 1–y, –1/2+z
mbac	N1–H1A···Cl1	0.960(7)	2.230(7)	3.163(7)	166.0(5)	–x, 1–y, 1–z
	N1–H1B···Cll	0.840(9)	2.330(9)	3.137(8)	161.0(8)	1+x, y, z
	N1–H1C···Cl1	1.130(9)	2.030(9)	3.144(8)	169.0(7)	–x, 1–y, 1–z
	C5–H5···Cl1	0.980(6)	2.790(6)	3.727(9)	161.0(4)	1+x, 1/2–y, –1/2+z
	C7–H7A···Cl1	0.980(9)	2.800(8)	3.753(9)	164.0(6)	1–x, 1–y, 1–z
	C7–H7B···π	0.844(8)	2.870(7)	3.748(9)	146.0(5)	1+x, y, z
	C7–H7C···π	1.132(1)	2.760(8)	3.763(9)	169.0(6)	x, 1/2–y, –1/2+z
	π–π stacking			5.354(5)		–1+x, y, z
	π–π stacking			5.355(5)		1+x, y, z

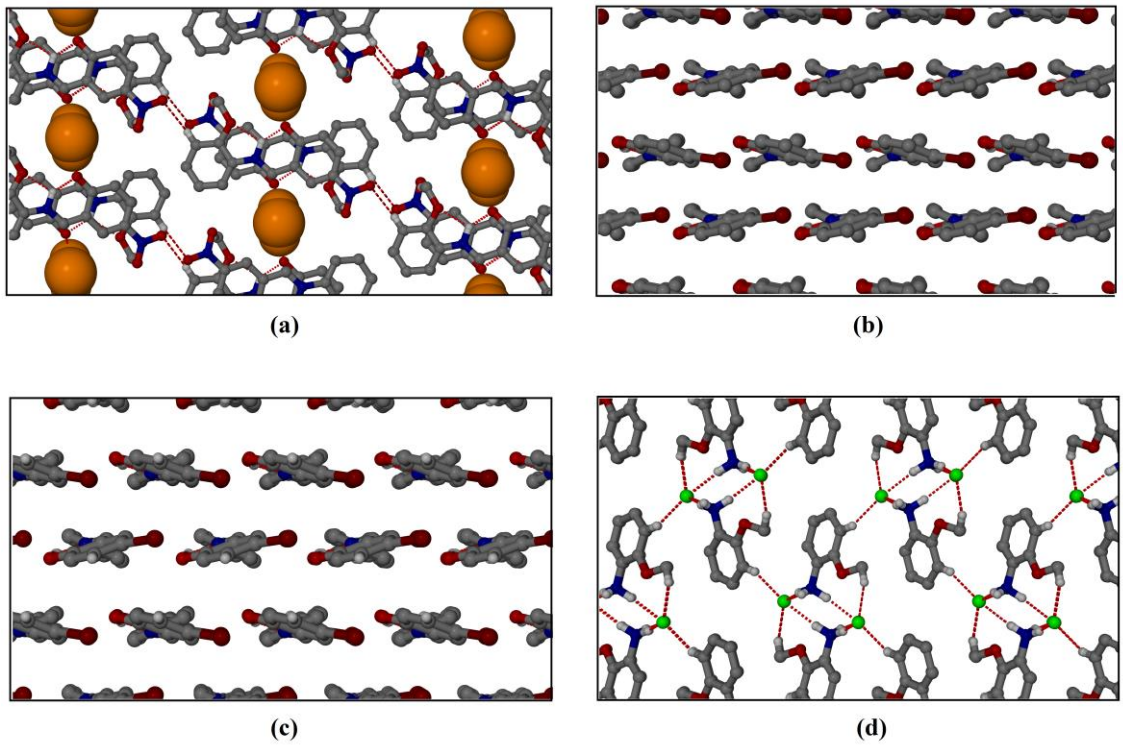

Figure S2. Hydrogen Bonding Properties of (a) **L1H** viewed along the *b*-axis, (b) **L1H** viewed down the *a*-axis, (c) **L2H** viewed along the *a*-axis, (d) **L3H** viewed down the *c*-axis and (e) **mbac** viewed along the *a*-axis Å.

Crystal Packing Features for L1H–L3H and mbac: Hydrogen bonded layers are generated in **L1H** (Figure S2a), including molecular pairs related by a centre of symmetry with O5W–H5W···O1^{i} (1.870(12) Å), O6W–H6W···O1^{ii} (1.810(12) Å), C5–H5···O6W^{iii} (2.540 Å), C7–H7···O5W^{iv} (2.570 Å), and C10–H10···O2^{v} (2.370 Å) hydrogen bonds (symmetry code: (i) x, y, z; (ii) 1–x, y, 1/2–z; (iii) 1–x, –y, 1–z; (iv) 1–x, 1–y, 1–z; (v) 1/2+x, 1/2+y, z) while N1–H1···O1 and N1–H1···O4 form intramolecular hydrogen bonds with short supramolecular distances of 1.690(5) and 2.120(5) Å, respectively. Besides the noticeable hydrogen bonds, there exist π···π (symmetry code: 1–x, –y, 1–z, 1–x, 1–y, 1–z and 3/2–x, –1/2+y, 3/2–z, as well as stacking interactions with centroid–centroid distances ranging from 3.695(2)–5.539(2) Å) (see Table S6).

Likewise, strong O1–H1···N1 intramolecular hydrogen bonds are seen in both **L2H** and **L3H** (Figure S2b–c) with intermolecular distances of 1.740(9) and 1.760(6) Å, respectively. Furthermore, packing properties of **L2H** and **L3H** are both stabilised through weak C2–H2···π$^{iv/v}$, C5–H5···π$^{iv/v}$, C9–H9···π^{vi}/C10–H10···π^{vi} and C12–H12···π^{vii}/C13–H13···π^{vii} intermolecular hydrogen bonding with distances varying from 2.590–2.900 Å, as well as π···π$^{v/vii}$ stacking interactions ranging from 4.559(3) to 4.738(3) Å for **L2H** and 4.637(3) to 4.717(3) Å for **L3H** (symmetry code: (iv) x, –y, 1/2+z; (v) x, 1–y, –1/2+z; (vi) x, –y, 1/2+z; (vii) x, 1–y, –1/2+z).

In the crystal of **mbac** (Figure S2d), chains of molecules are formed along the *a*-axis by five-point Cl1 mediated halogen bonding interactions; N1–H1A···Cl1^{viii}, N1–H1B···Cl1^{ix}, N1–H1C···Cl1^{x}, C5–H5···Cl1^{xi}, C7–H7A···Cl1^{xii} (with distances 2.230(7), 2.330(9), 2.030(9), 2.790(6) and 2.800(8) Å, respectively). Moreover, **mbac** is further stabilised *via* C7–H7B···π^{xiii}, C7–H7C···π^{xiv} hydrogen bonds, and two π–π$^{ix/xv}$ stacking interactions with respective distances of 2.870(7), 2.760(8), and 5.354(5) Å (symmetry code: (viii) –x, 1–y, 1–z; (ix) 1+x, y, z; (x) –x, 1–y, 1–z; (xi) 1+x, 1/2–y, –1/2+z; (xii) 1–x, 1–y, 1–z; (xiii) 1+x, y, z; (xiv) x, 1/2–y, –1/2+z; (xv) –1+x, y, z).

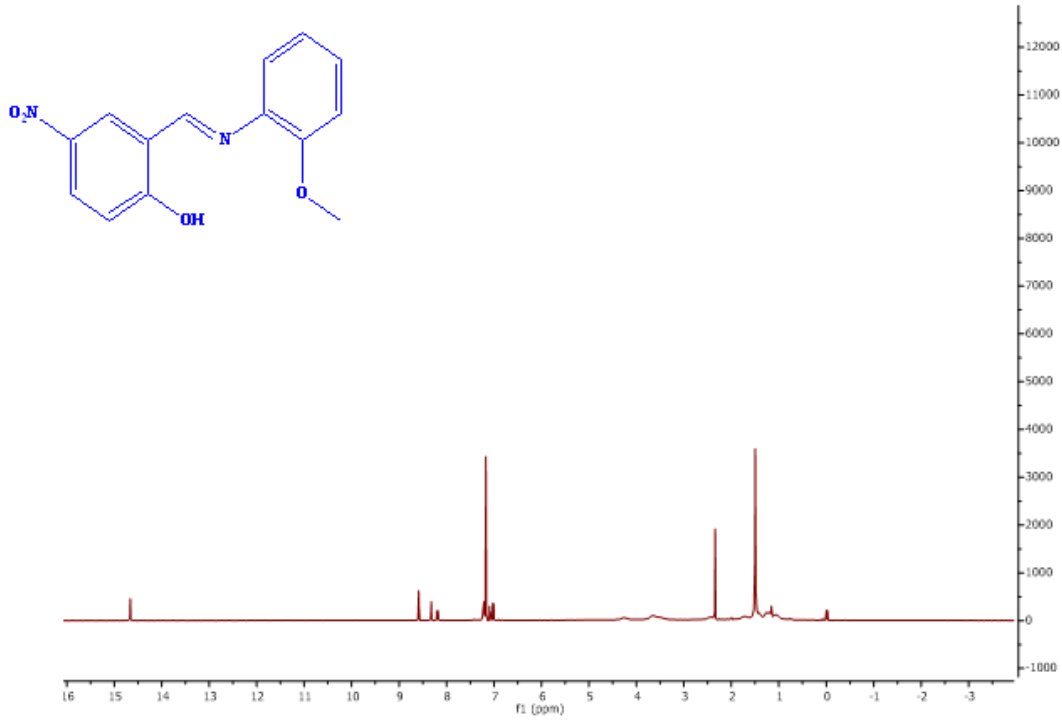

Figure S3(a). ^{1}H NMR Spectrum of Compound **L1H** in $CDCl_3$ at 298 K.

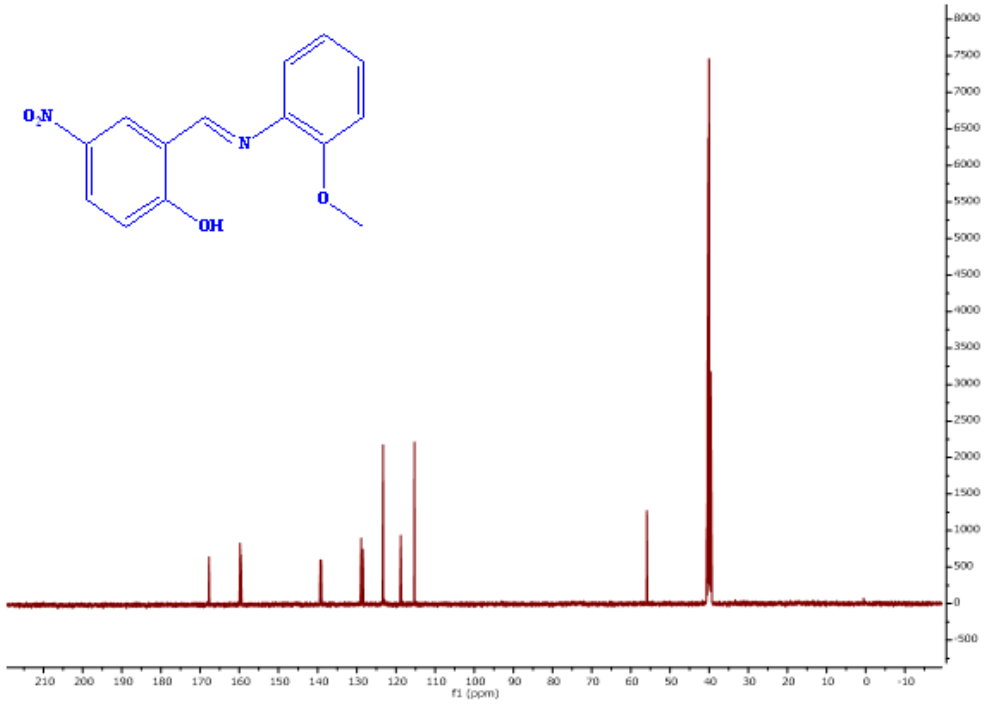

Figure S3(b). ^{13}C NMR Spectrum of Compound **L1H** in DMSO-d_6 at 298 K.

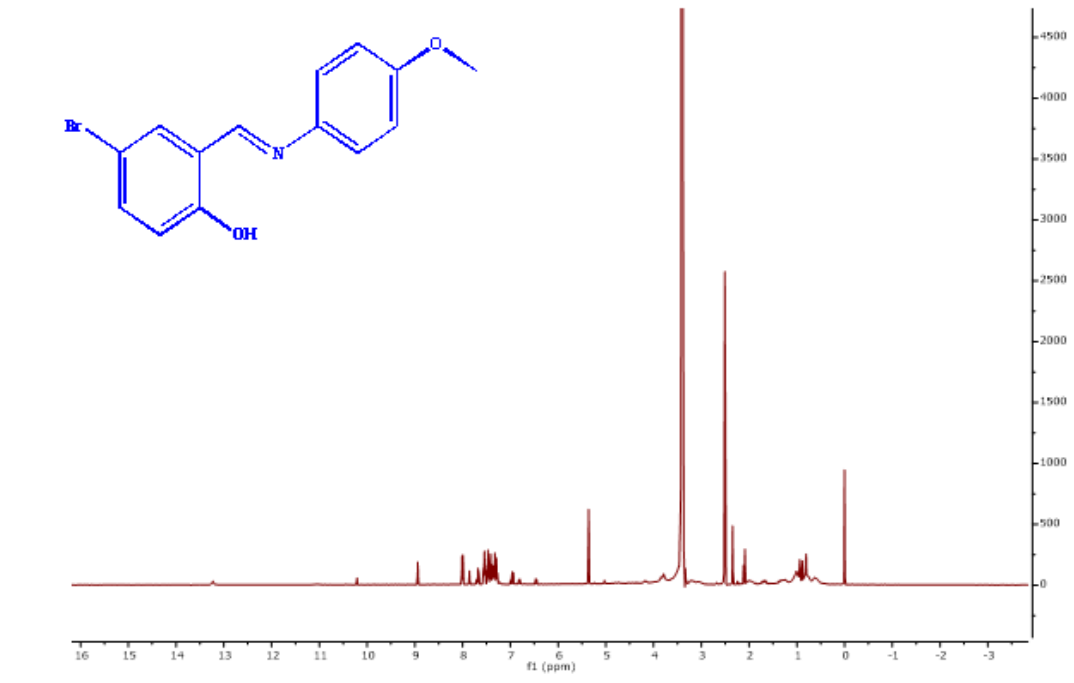

Figure S3(c). ^{1}H NMR Spectrum of Compound **L2H** in $CDCl_3$ at 298 K.

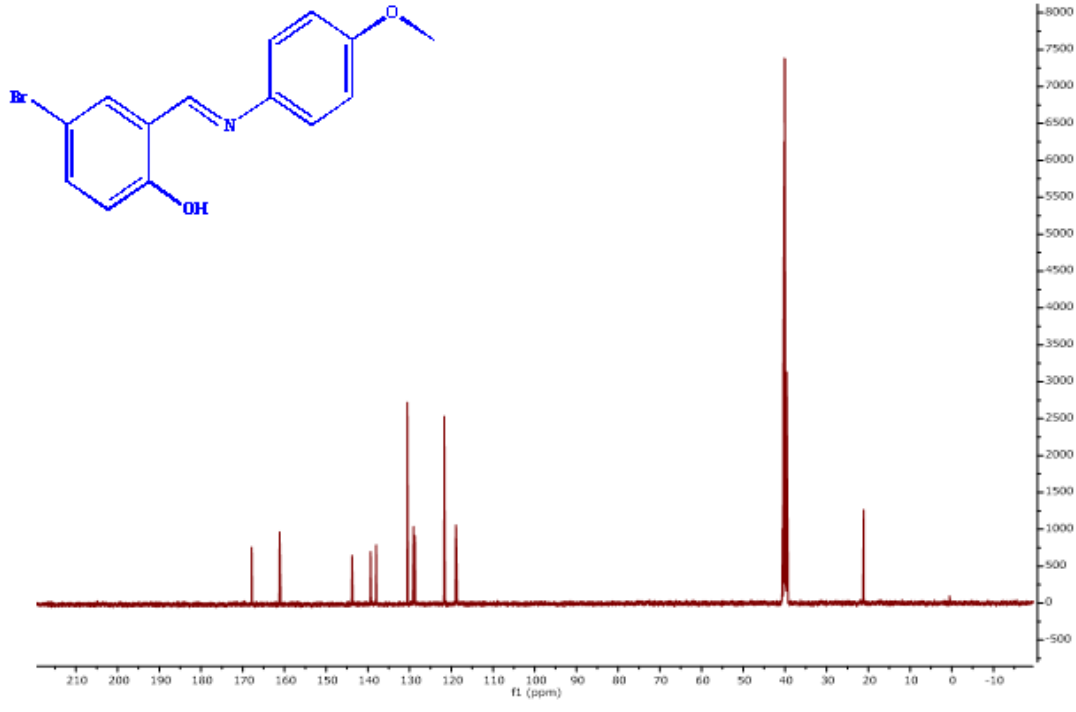

Figure S3(d). ^{13}C NMR Spectrum of Compound **L2H** in DMSO-d_6 at 298 K.

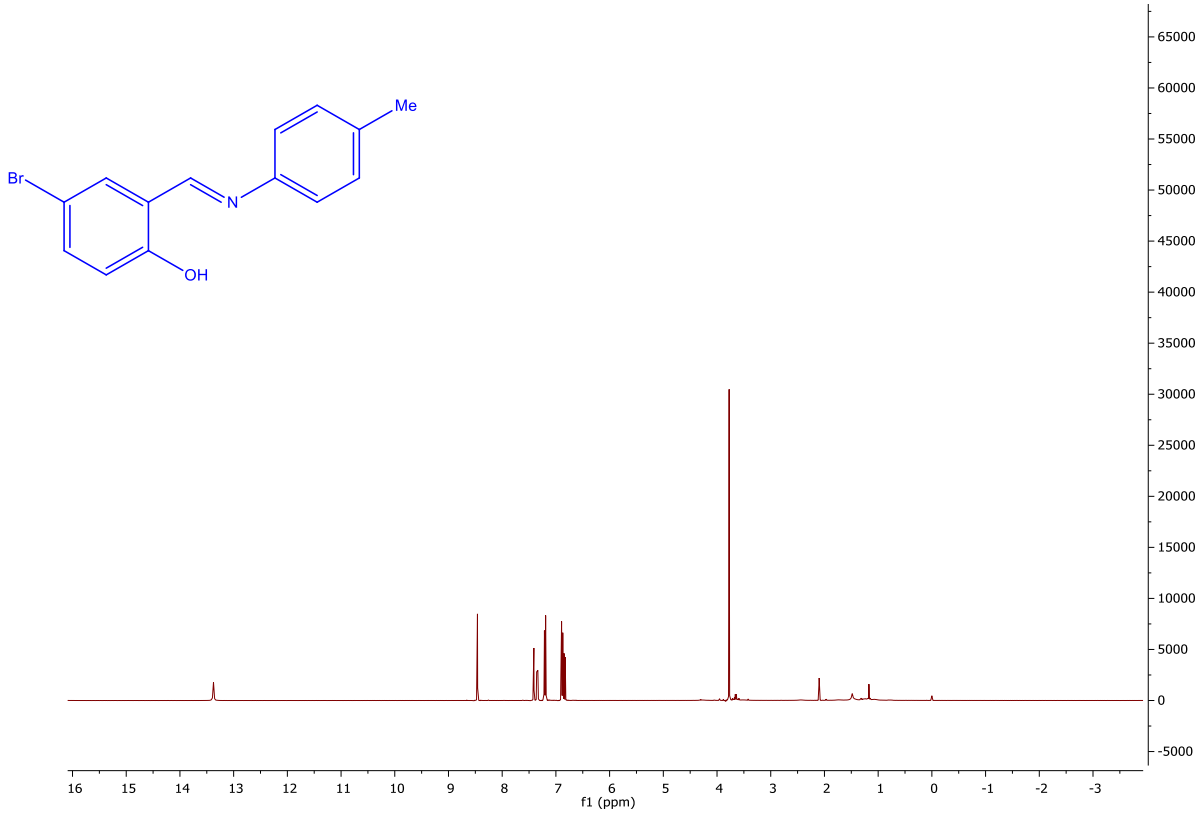

Figure S3(e). ^{1}H NMR Spectrum of Compound **L3H** in $CDCl_3$ at 298 K.

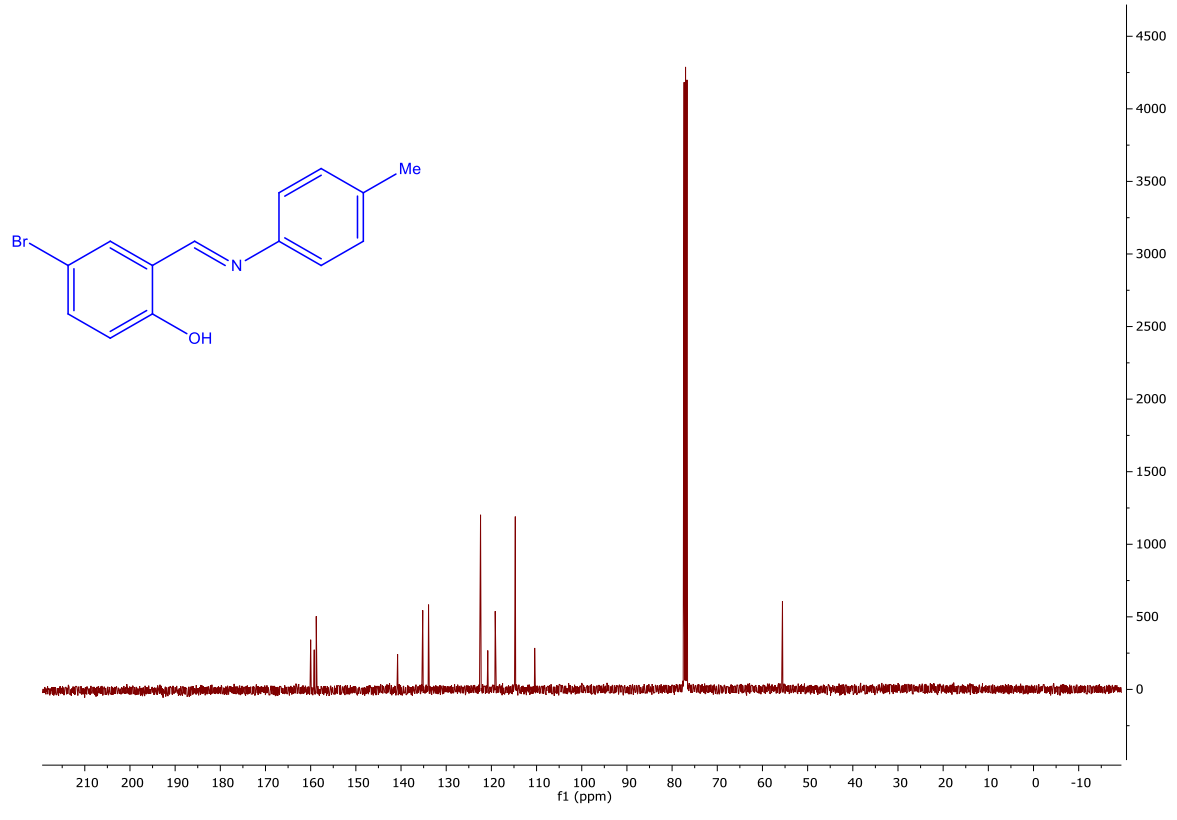

Figure S3(f). ^{13}C NMR Spectrum of Compound **L3H** in $CDCl_3$ at 298 K.

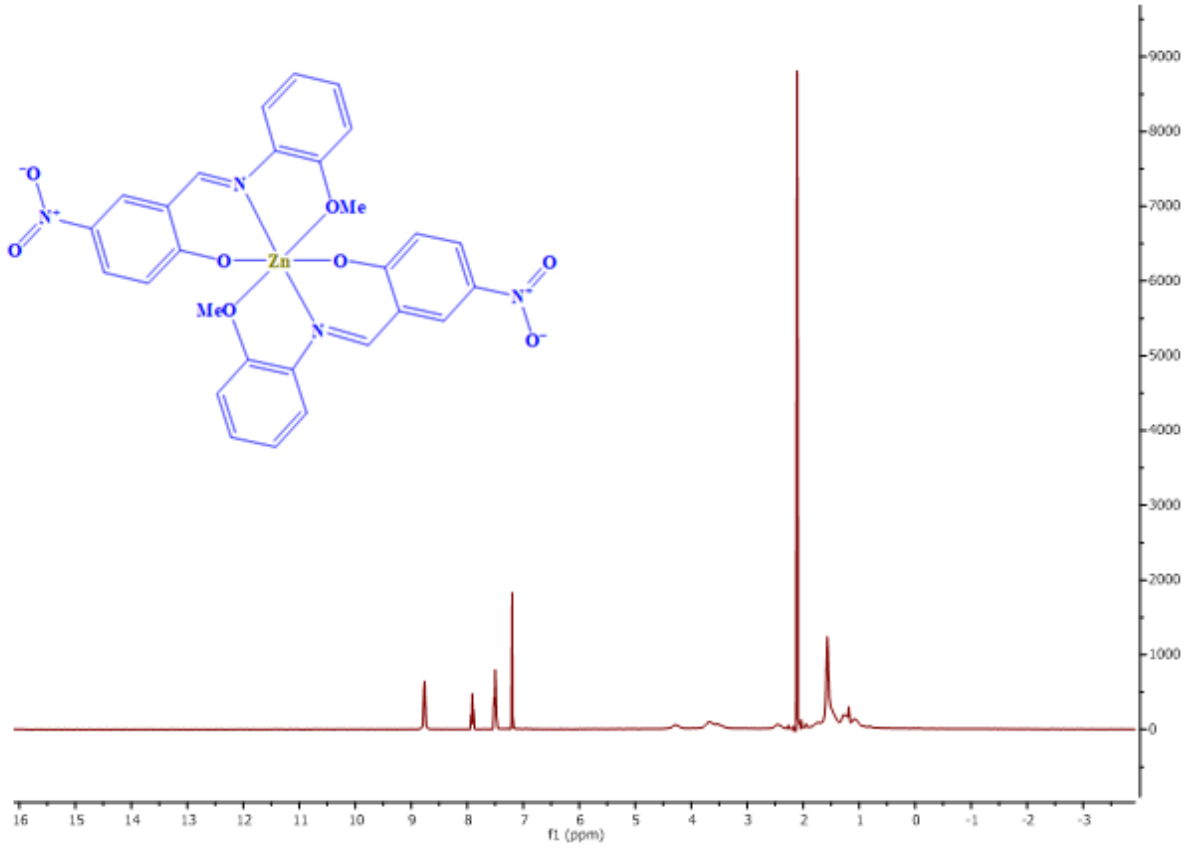

Figure S3(f). ^{1}H NMR Spectrum of Compound **1a** in $CDCl_3$ at 298 K.

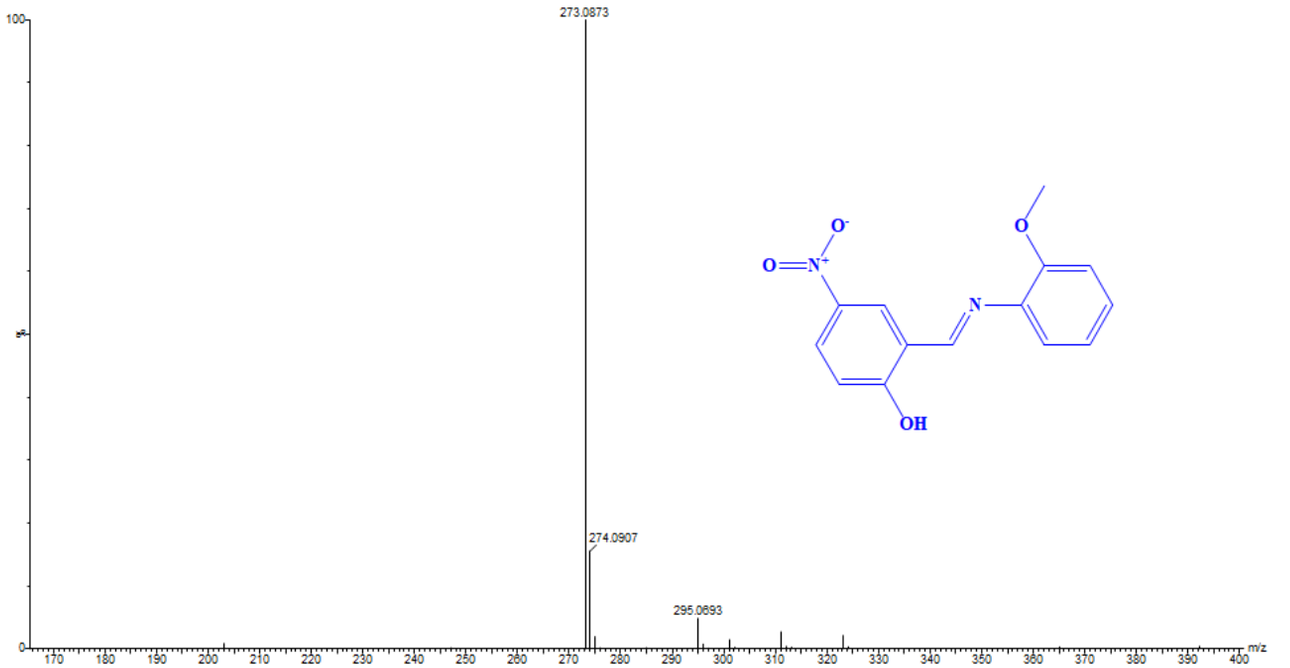

Figure S4(a). Mass Spectrum (positive mode, ESI-MS) of **L1H**.

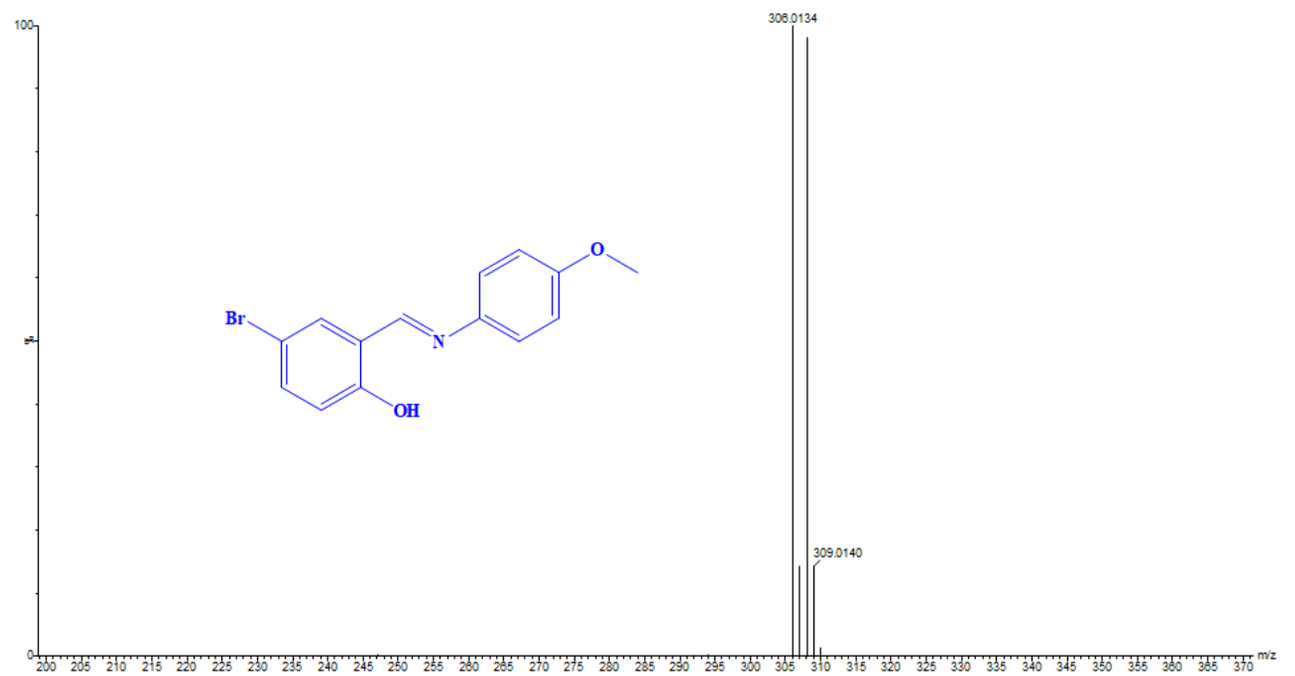

Figure S4(b). Mass Spectrum (positive mode, ESI-MS) of **L2H**.

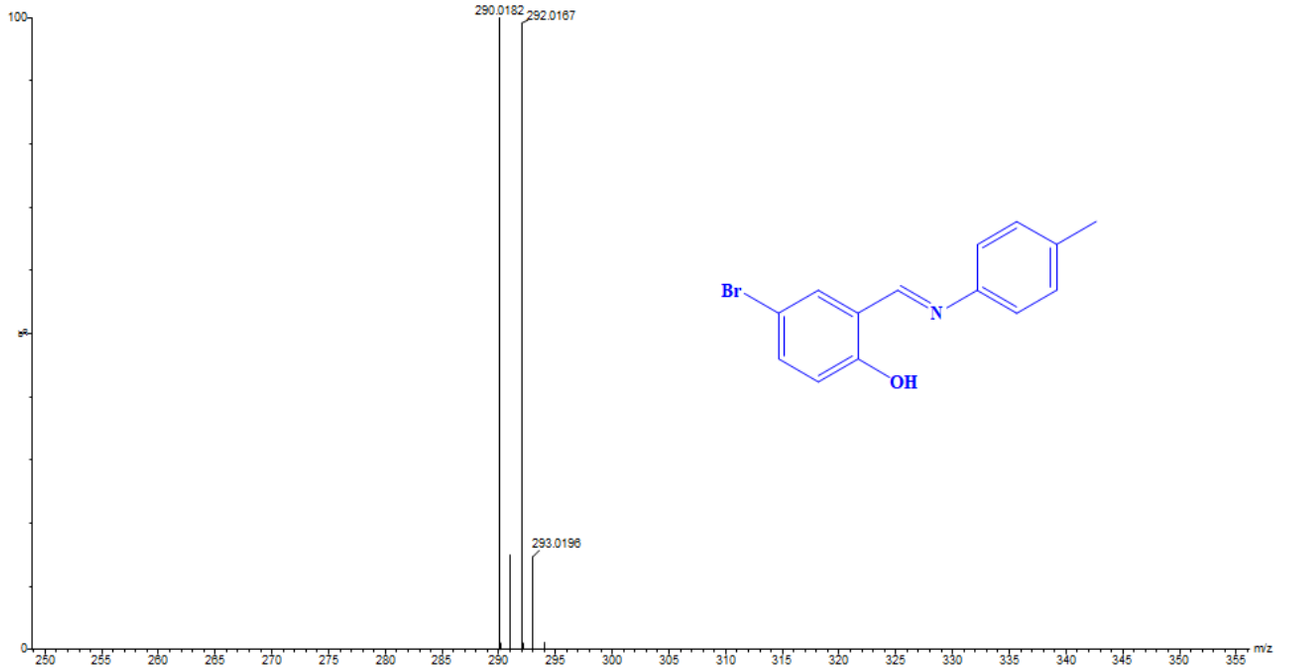

Figure S4(c). Mass Spectrum (positive mode, ESI-MS) of **L3H**.

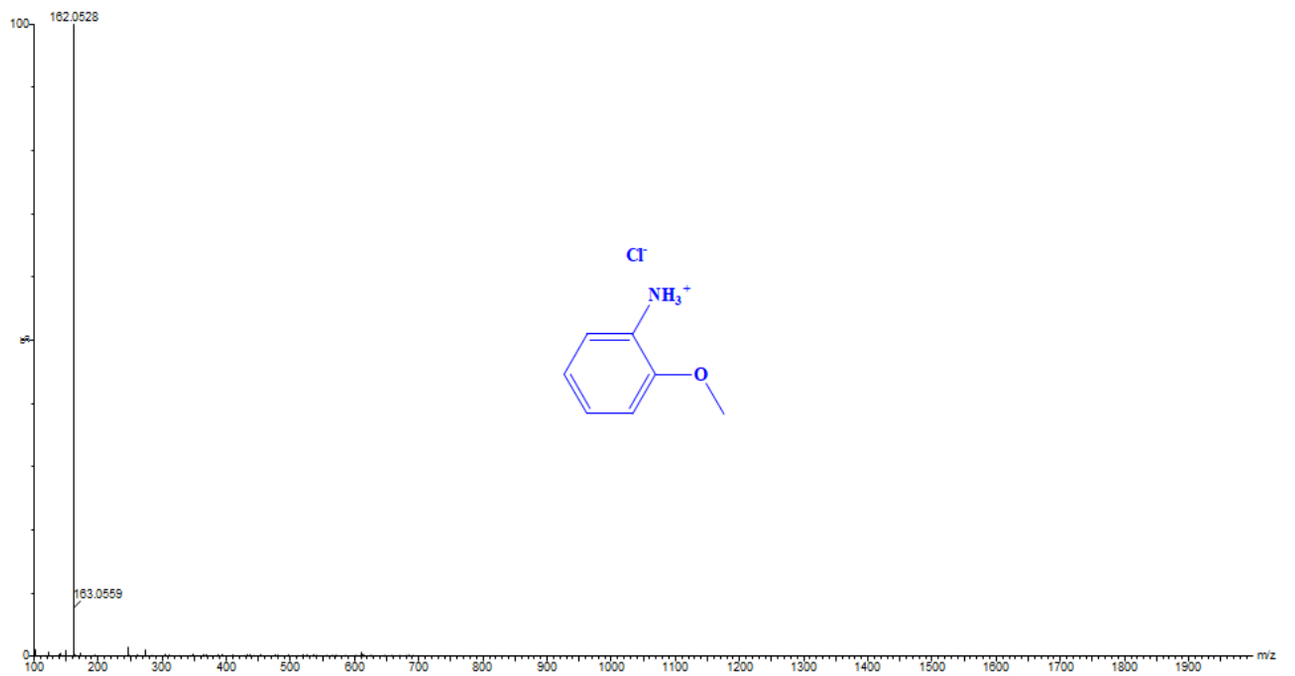

Figure S4(d). Mass Spectrum (positive mode, ESI-MS) of **mbac**.

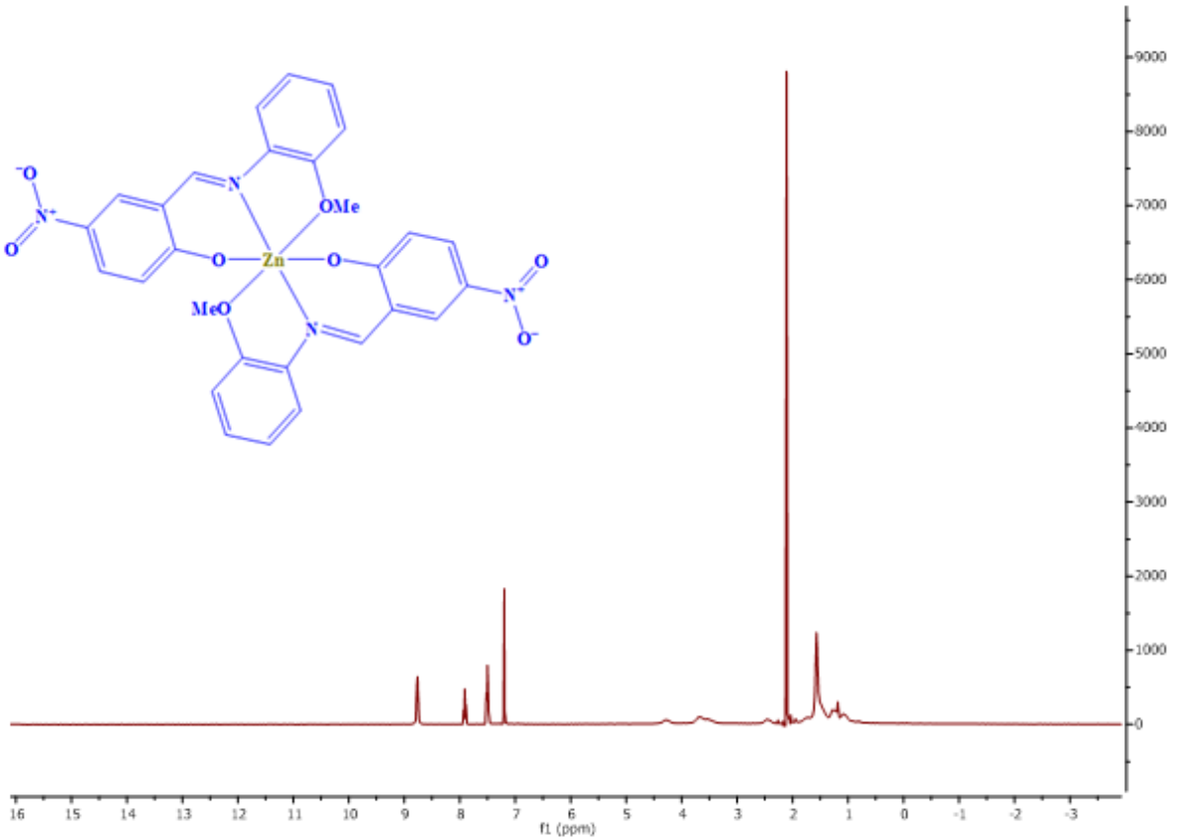

Figure S4(e). Mass Spectrum (negative mode, ESI-MS) of **1a**.

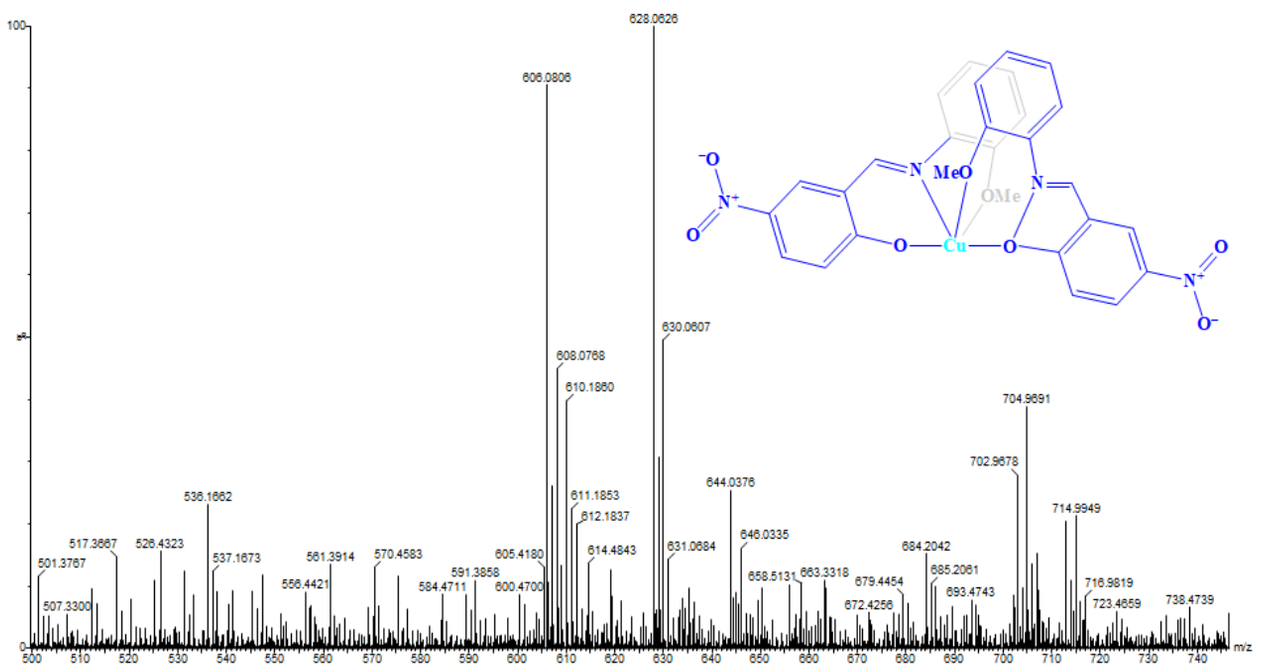

Figure S4(f). Mass Spectrum (positive mode, ESI-MS) of **1b**.

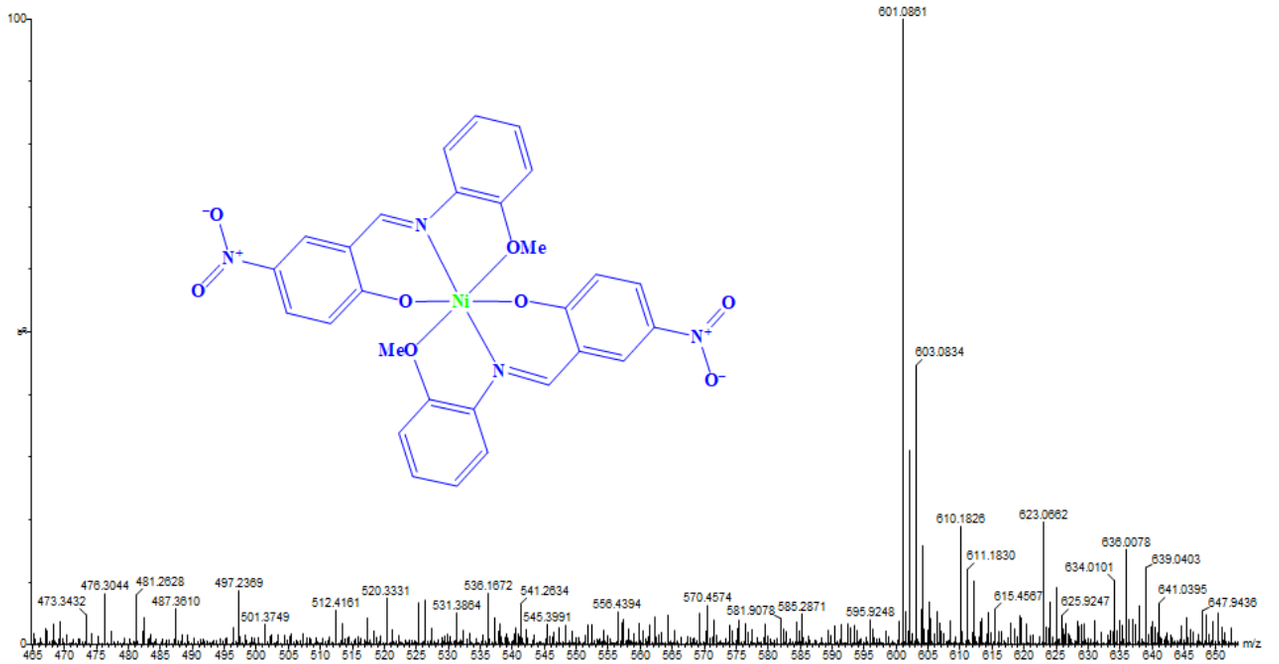

Figure S4(g). Mass Spectrum (positive mode, ESI-MS) of **1c**.

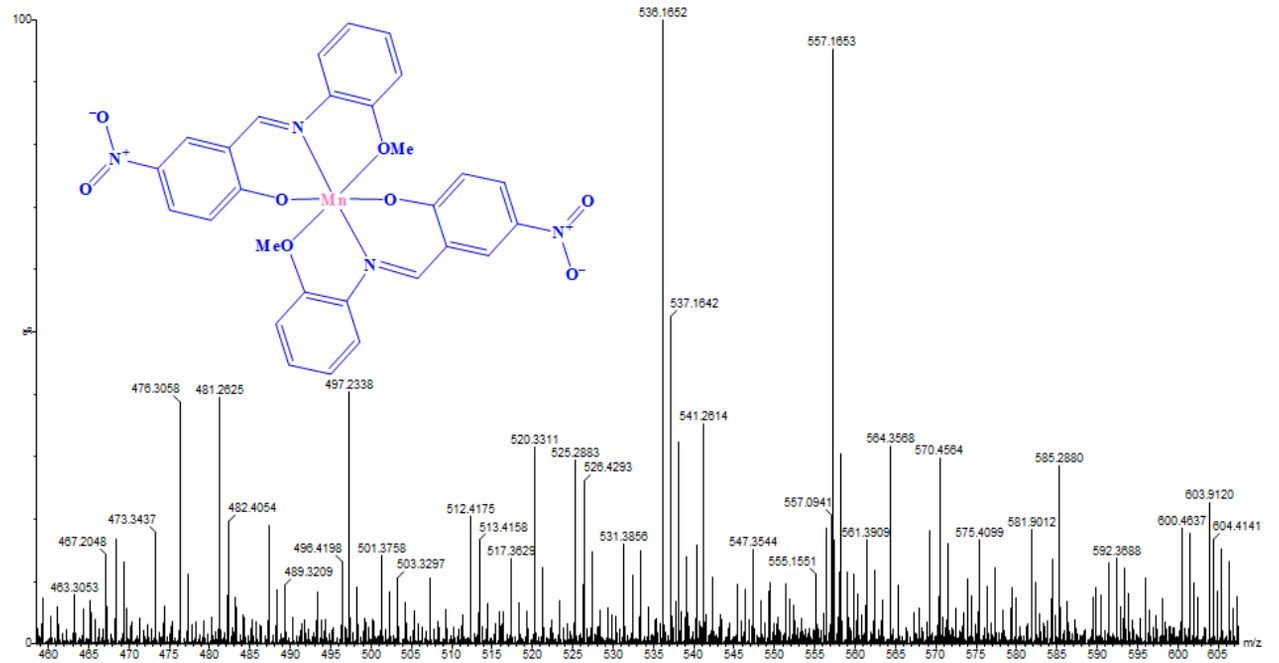

Figure S4(h). Mass Spectrum (positive mode, ESI-MS) of **1d**.

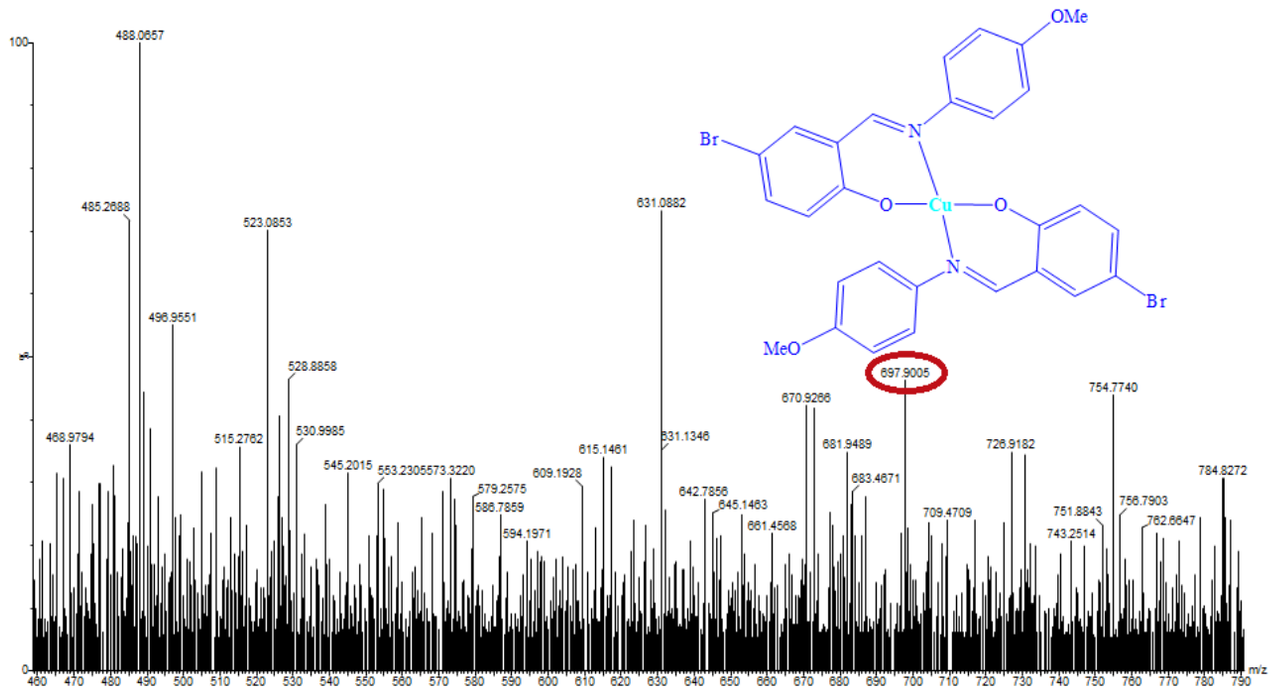

Figure S4(i). Mass Spectrum (negative mode, ESI-MS) of **2a**.

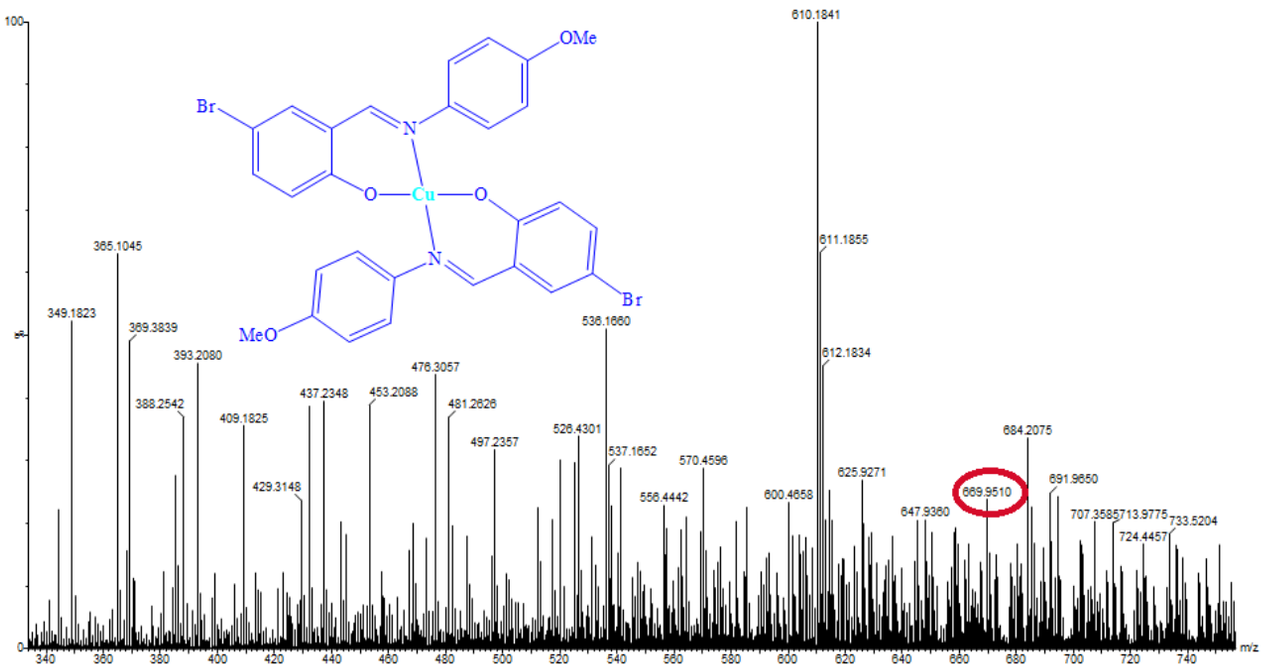

Figure S4(j). Mass Spectrum (positive mode, ESI-MS) of **2a'**.

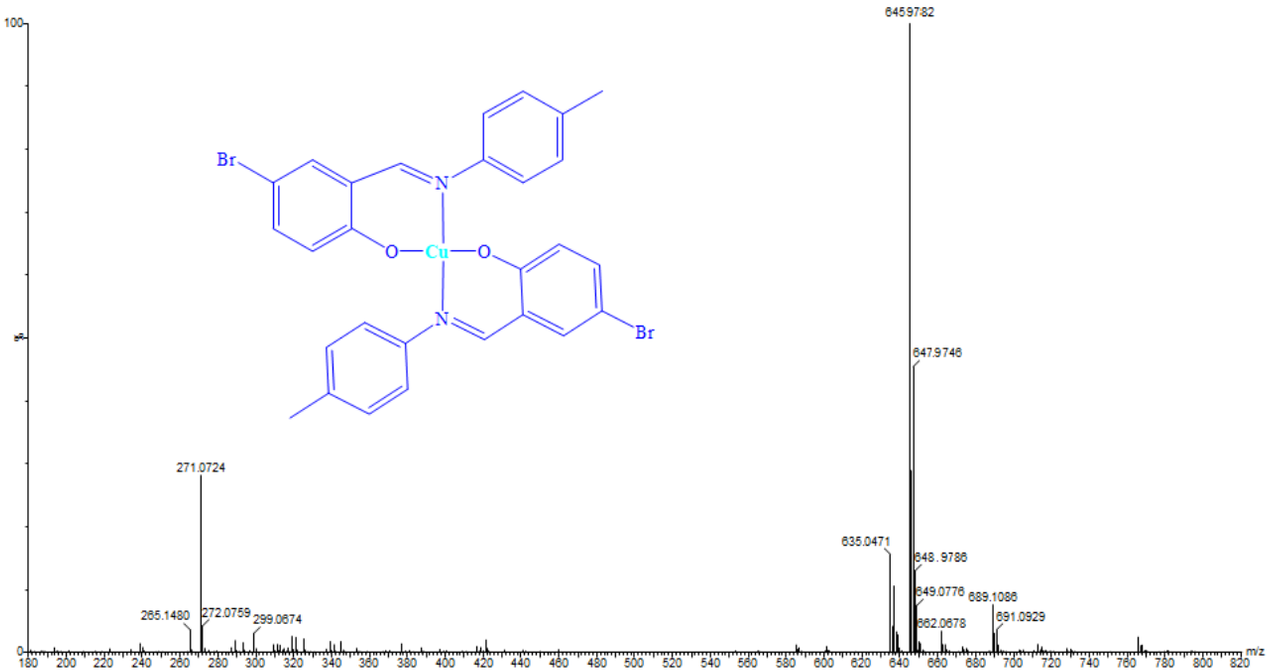

Figure S4(k). Mass Spectrum (positive mode, ESI-MS) of **2b**.

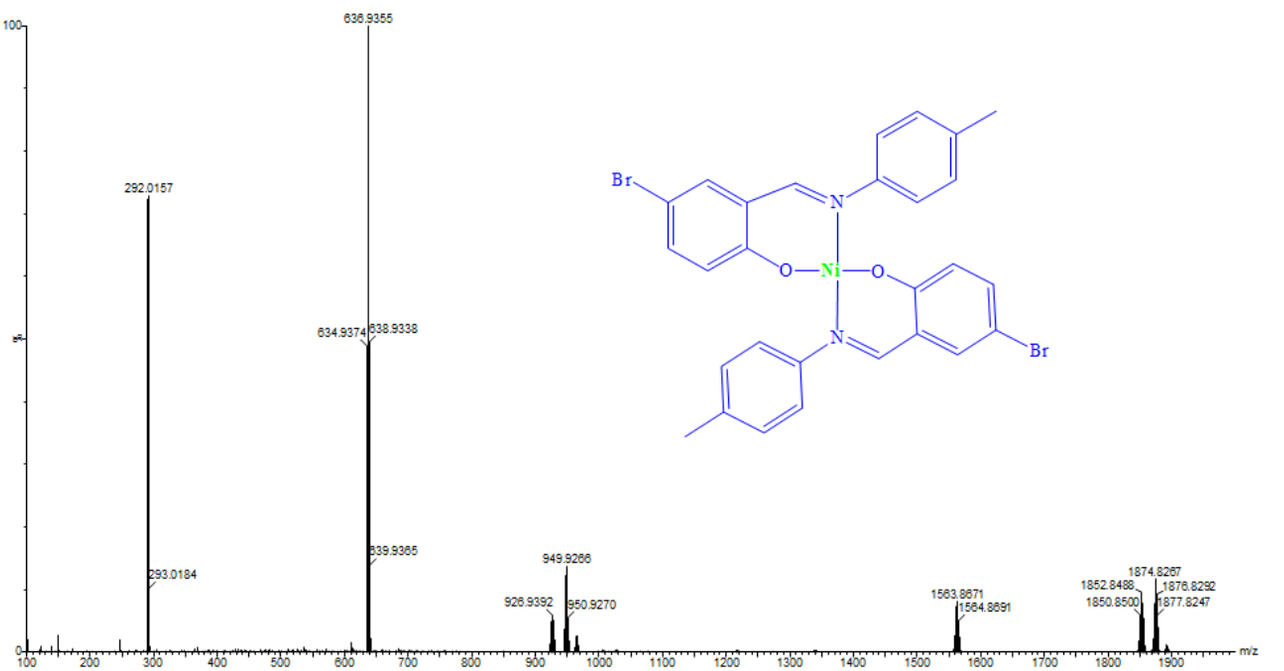

Figure S4(l). Mass Spectrum (positive mode, ESI-MS) of **2c**.

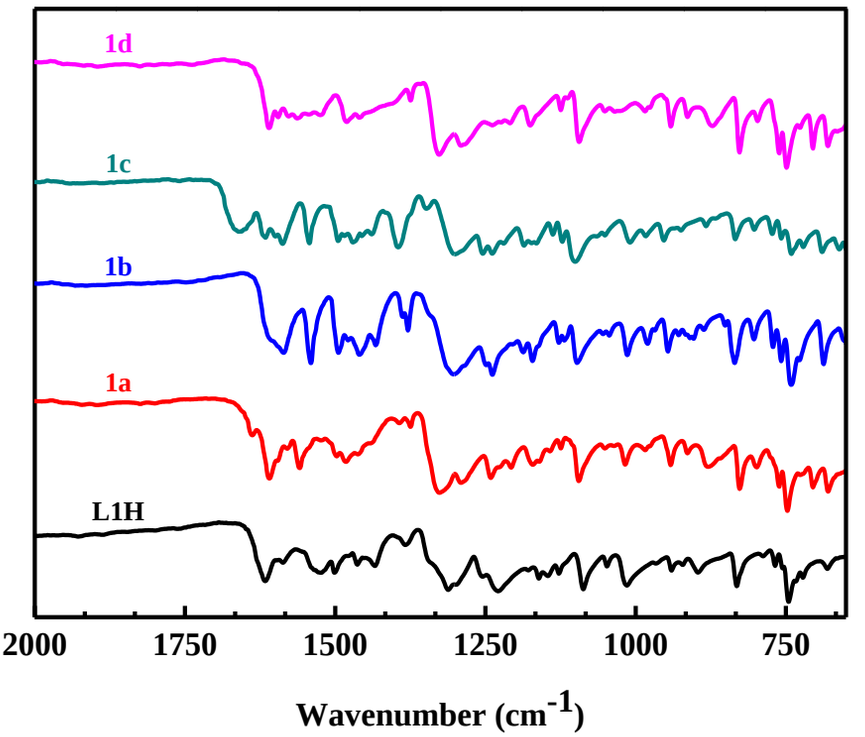

Figure S5(a). IR Spectra (truncated: 2000–650 cm^{-1}) for the Ligand **L1H** and its Complexes **1a**–**d**.

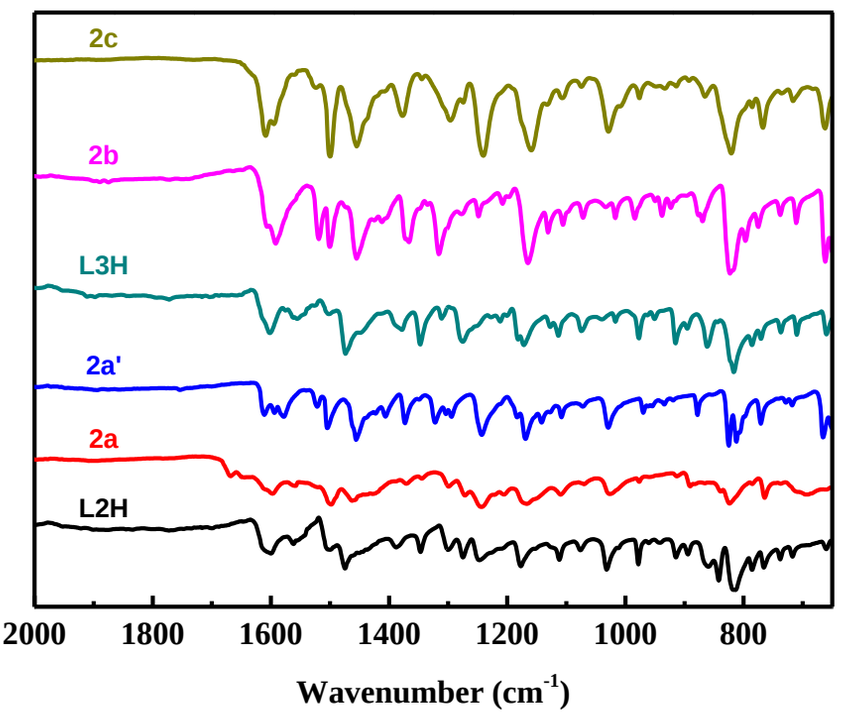

Figure S5(b). IR Spectra (truncated: 2000–6500 cm^{-1}) for the Ligand **L2H/L3H** and their Complexes **2a**–**c**.

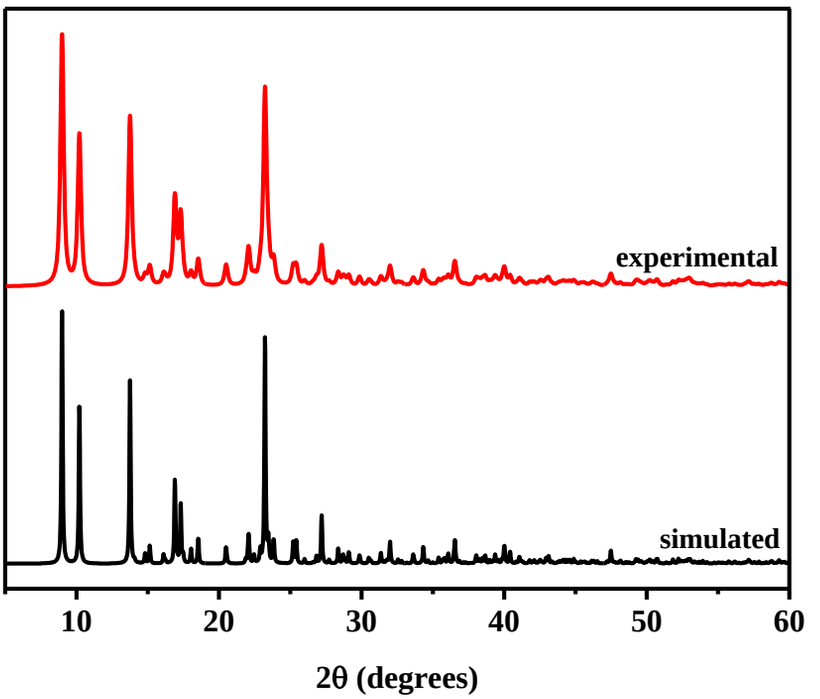

Figure S6(a). Simulated and Experimental PXRD for Complex **1a**.

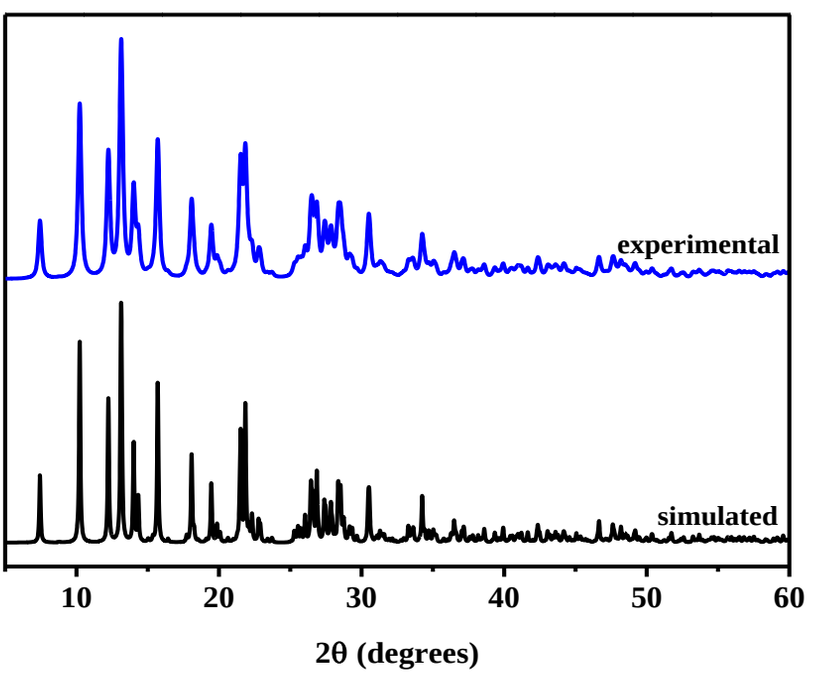

Figure S6(b). Simulated and Experimental PXRD for Complex **1b**.

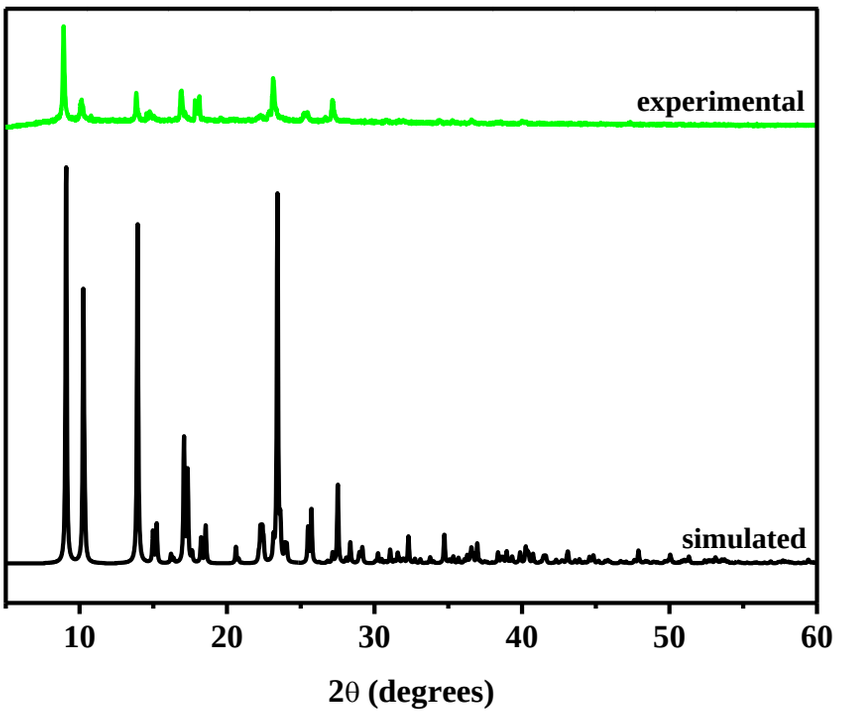

Figure S6(c). Simulated and Experimental PXRD for Complex **1c**.

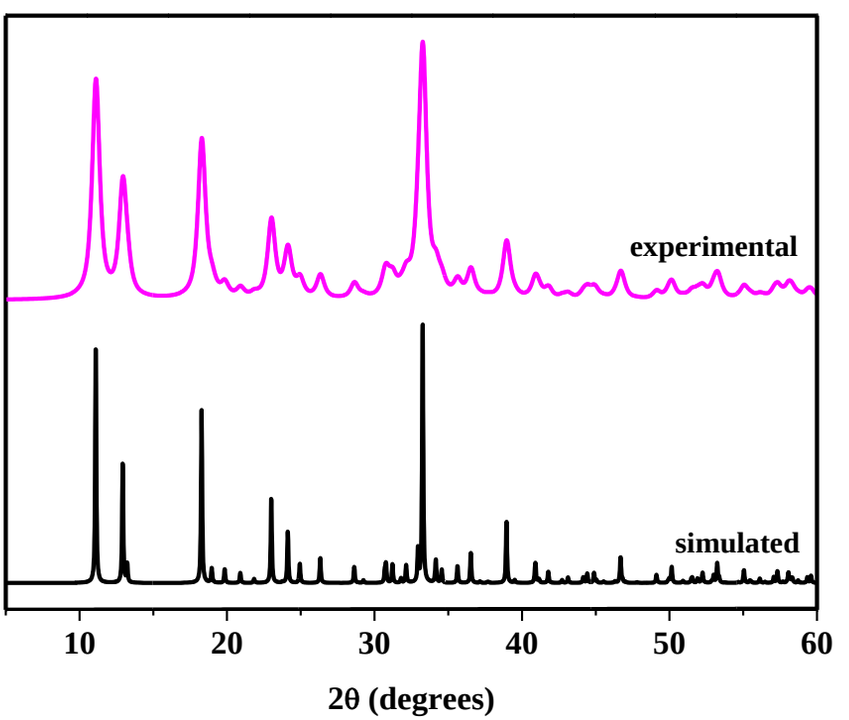

Figure S6(d). Simulated and Experimental PXRD for Complex **1d**.

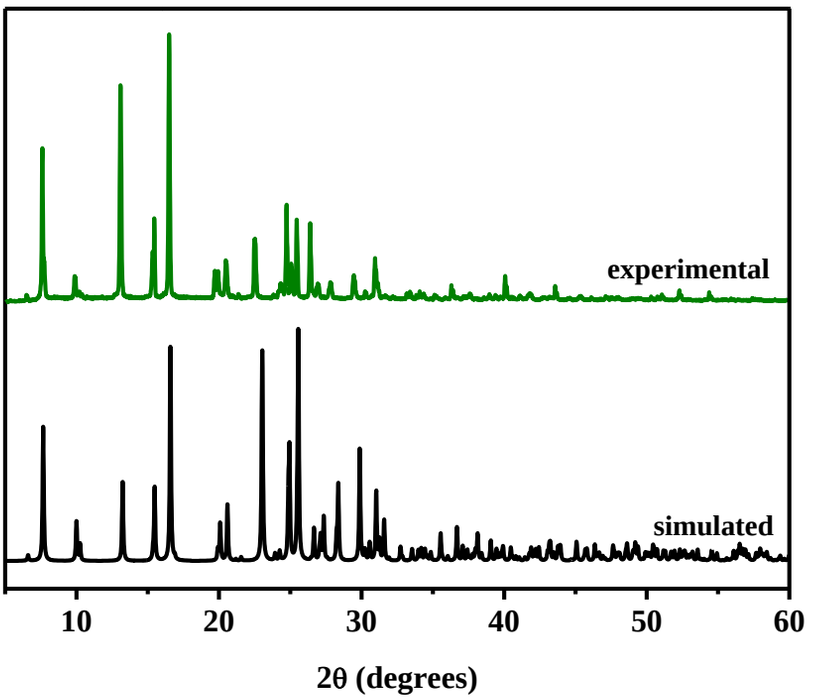

Figure S6(e). Simulated and Experimental PXRD for Complex **2a**.

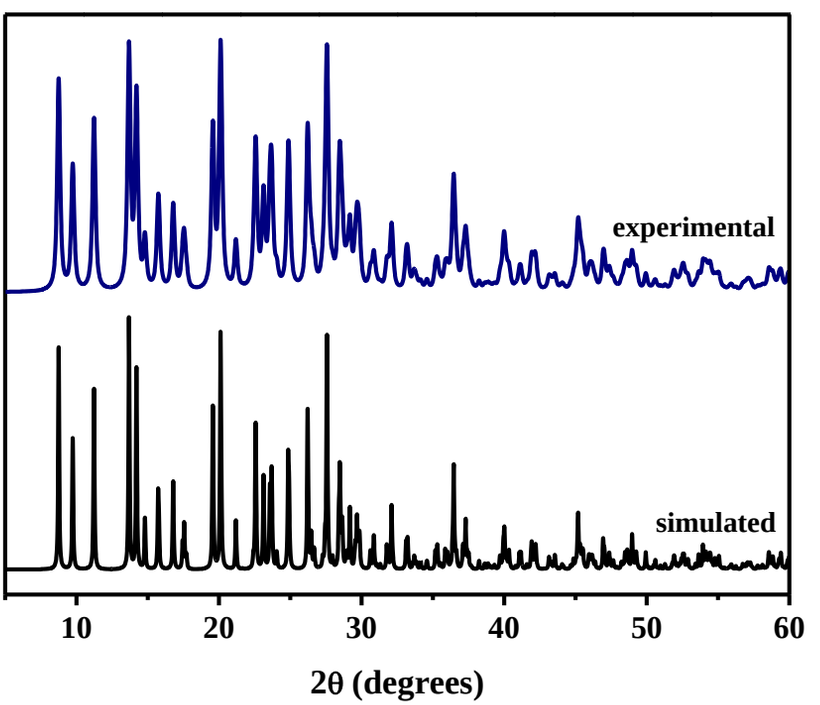

Figure S6(f). Simulated and Experimental PXRD for Complex **2a'**.

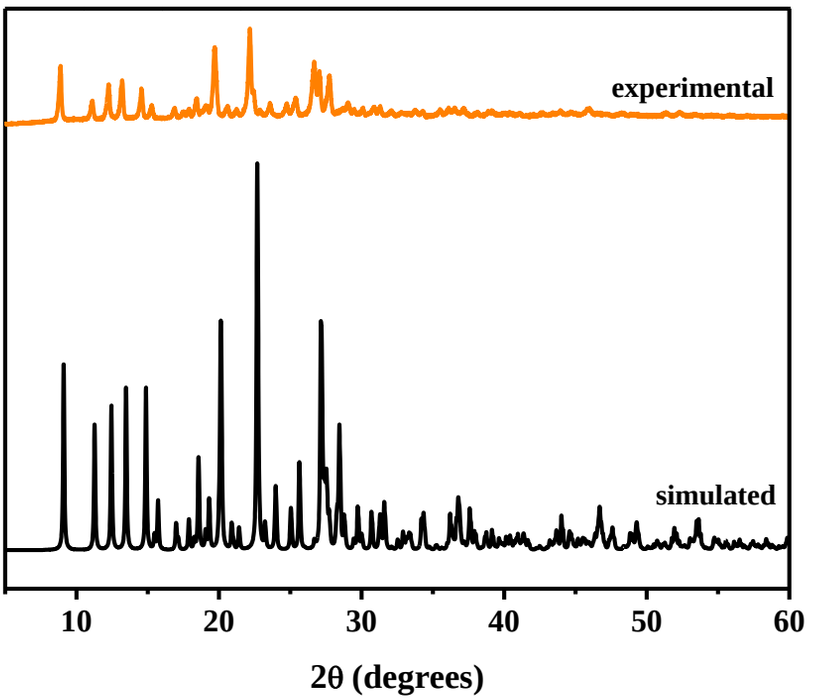

Figure S6(g). Simulated and Experimental PXRD for Complex **2b**.

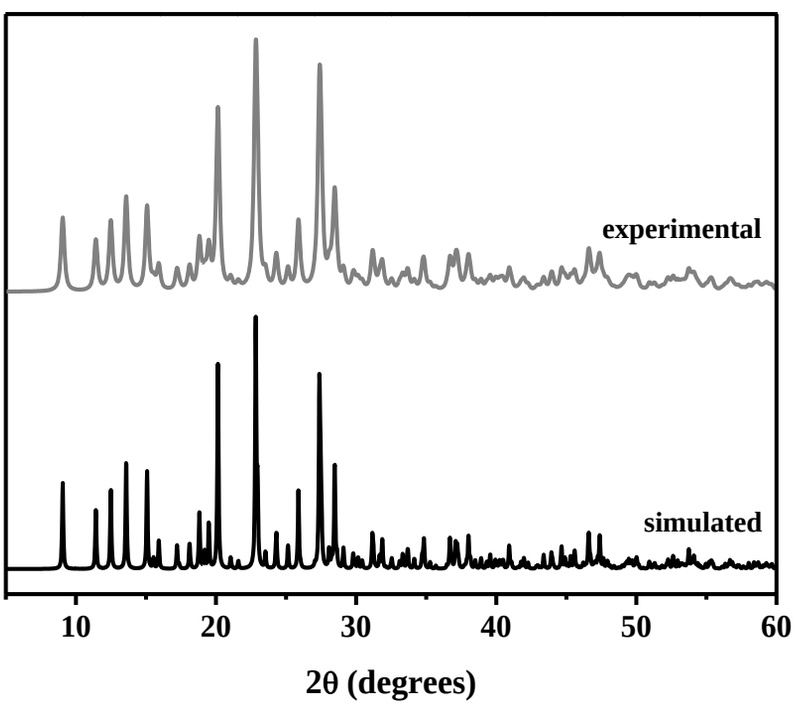

Figure S6(h). Simulated and Experimental PXRD for Complex **2c**.

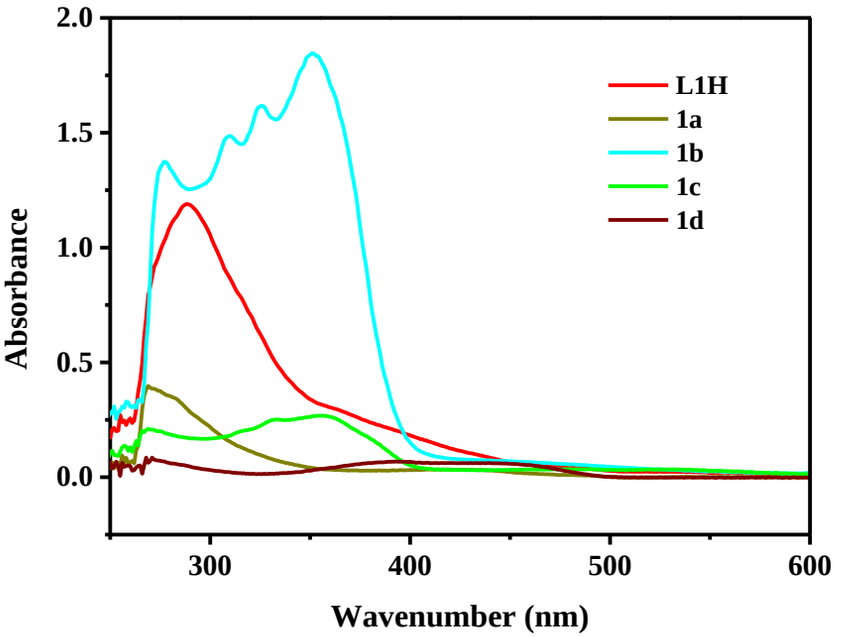

Figure S7(a). Solution Ultraviolet-visible (UV-vis) Spectra of Compounds **L1H**, **1a–1d** at 298 K.

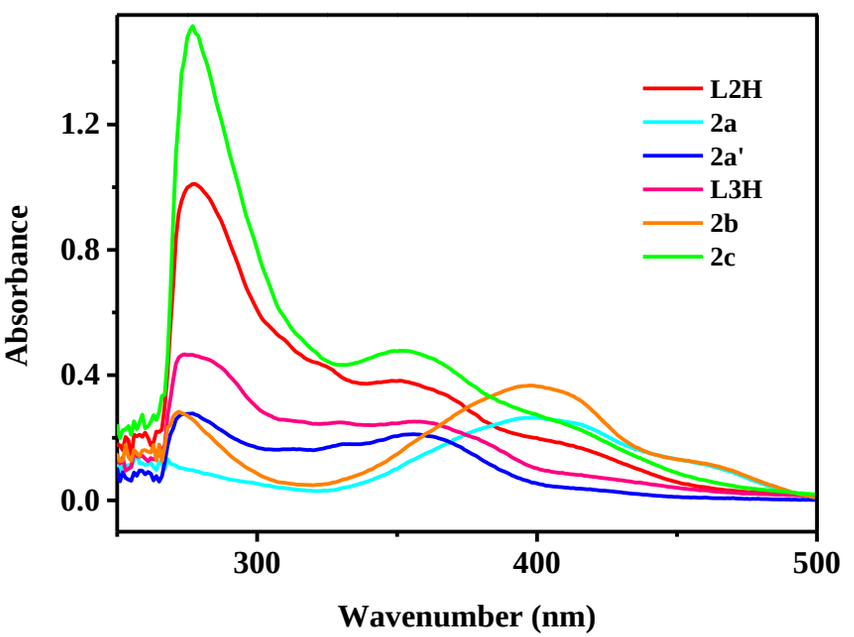

Figure S7(b). Solution Ultraviolet-visible (UV-vis) Spectra of Compounds **L2H–L3H**, **2a–2c** at 298 K.

Table S7. Selected Bond Lengths [Å] and Angles [°] for **1a**.

Bond Length			
Zn1–O2	2.2853(15)	C1–C6	1.430(2)
Zn1–O1	1.9760(14)	C2–C3	1.356(3)
Zn1–N1	2.0763(13)	C3–C4	1.382(3)
O1–C1	1.282(2)	C4–C5	1.356(3)
O2–C13	1.359(2)	C5–C6	1.400(2)
O2–C14	1.427(3)	C6–C7	1.430(2)
O3–N2	1.211(3)	C8–C9	1.380(3)
O4–N2	1.205(3)	C8–C13	1.394(3)
N1–C7	1.293(2)	C9–C10	1.379(4)
N1–C8	1.419(2)	C10–C11	1.362(4)
N2–C4	1.452(2)	C11–C12	1.360(4)
C1–C2	1.419(3)	C12–C13	1.381(3)
Bond Angles			
O1–Zn1–O2	163.64(6)	O4–N2–C4	118.4(19)
O1–Zn1–N1	92.68(5)	O1–C1–C2	119.40(17)
O1–Zn1–O1*	101.64(11)	O1–C1–C6	124.02(16)
O1–Zn1–O2*	89.50(8)	C2–C1–C6	116.59(16)
O1–Zn1–N1*	99.23(5)	C1–C2–C3	122.6(2)
O2–Zn1–N1	73.55(5)	C2–C3–C4	119.3(2)
O2–Zn1–O1*	89.50(8)	N2–C4–C3	119.16(19)
O2–Zn1–O2*	82.39(11)	N2–C4–C5	119.53(18)
O2–Zn1–N1*	92.09(5)	C3–C4–C5	121.31(18)
N1–Zn1–O1*	99.23(5)	C4–C5–C6	121.00(17)
N1–Zn1–O2*	92.09(6)	C1–C6–C5	119.00(16)
N1–Zn1–N1*	161.14(8)	C1–C6–C7	125.31(15)
O1*–Zn1–O2*	163.64(6)	C5–C6–C7	115.64(15)
O1*–Zn1–N1*	92.68(5)	N1–C7–C6	127.61(15)
O2*–Zn1–N1*	73.55(5)	N1–C8–C9	125.26(18)
Zn1–O1–C1	127.80(12)	N1–C8–C13	116.97(15)
Zn1–O2–C13	115.07(11)	C9–C8–C13	117.77(18)
Zn1–O2–C14	125.44(15)	C8–C9–C10	120.70(2)
C13–O2–C14	119.16(18)	C9–C10–C11	120.30(3)
Zn1–N1–C7	121.24(11)	C10–C11–C12	120.70(2)
Zn1–N1–C8	119.10(11)	C11–C12–C13	119.40(2)
C7–N1–C8	119.49(14)	O2–C13–C8	115.23(16)
O3–N2–O4	122.7(2)	O2–C13–C12	123.60(19)
O3–N2–C4	118.9(2)	C8–C13–C12	121.17(19)

Table S8. Selected Bond Lengths [Å] and Angles [°] for **1b**.

Bond Length					
Cu1–O1	1.9135(13)	O3–N2	1.224(3)	C8–C13	1.403(3)
Cu1–O2	2.7102(14)	O6–C28	1.431(2)	C12–C13	1.385(3)
Cu1–O5	1.8974(13)	N1–C8	1.426(2)	C17–C18	1.393(3)
Cu1–O6	2.6769(14)	N4–C18	1.454(2)	C22–C23	1.385(3)
Cu1–N1	1.9959(15)	C3–C4	1.392(3)	C25–C26	1.382(4)
Cu1–N3	1.9703(15)	C8–C9	1.388(3)	O2–C13	1.363(2)
O2–C14	1.434(2)	C11–C12	1.378(4)	O5–C15	1.290(2)
O6–C27	1.358(2)	C16–C17	1.364(3)	O8–N4	1.228(2)
N1–C7	1.291(2)	C20–C21	1.443(2)	N3–C21	1.291(2)
N3–C22	1.430(2)	C24–C25	1.377(4)	C1–C6	1.428(3)
C2–C3	1.364(3)	O1–C1	1.290(2)	C5–C6	1.398(2)
C6–C7	1.438(3)	O4–N2	1.231(3)	C9–C10	1.378(3)
C10–C11	1.371(4)	O7–N4	1.216(2)	C15–C16	1.420(2)
C15–C20	1.427(3)	N2–C4	1.450(2)	C18–C19	1.370(3)
C19–C20	1.400(2)	C1–C2	1.422(3)	C22–C27	1.398(3)
C23–C24	1.391(3)	C4–C5	1.374(3)	C26–C27	1.396(3)
Bond Angles					
O1–Cu1–O2	127.31(5)	O3–N2–C4	118.90(19)	C18–C19–C20	120.25(17)
O1–Cu1–O5	88.01(6)	O4–N2–C4	118.34(18)	C19–C20–C21	117.19(16)
O1–Cu1–O6	91.23(5)	Cu1–N3–C21	124.32(12)	N3–C22–C27	116.37(16)
O1–Cu1–N1	91.69(6)	Cu1–N3–C22	116.88(11)	C23–C24–C25	119.70(2)
O1–Cu1–N3	154.08(7)	C21–N3–C22	118.80(15)	O6–C27–C22	115.18(16)
O2–Cu1–O5	90.76(6)	O7–N4–O8	123.25(18)	N1–C8–C13	118.88(16)
O2–Cu1–O6	131.20(4)	O7–N4–C18	118.02(18)	C9–C10–C11	119.5(2)
O2–Cu1–N1	68.07(5)	O8–N4–C18	118.71(18)	O2–C13–C8	116.17(16)
O2–Cu1–N3	78.59(5)	O1–C1–C2	119.26(17)	O5–C15–C16	118.23(17)
O5–Cu1–O6	122.95(6)	O1–C1–C6	123.06(16)	C15–C16–C17	121.83(18)
O5–Cu1–N1	152.89(7)	C2–C1–C6	117.66(16)	N4–C18–C19	119.49(18)
O5–Cu1–N3	93.29(6)	C1–C2–C3	121.37(19)	C15–C20–C19	119.40(16)
O6–Cu1–N1	84.17(5)	C2–C3–C4	119.63(18)	N3–C21–C20	125.06(16)
O6–Cu1–N3	66.44(5)	N2–C4–C3	119.28(18)	C23–C22–C27	120.82(18)
N1–Cu1–N3	98.57(6)	N2–C4–C5	119.27(19)	C24–C25–C26	121.50(2)
Cu1–O1–C1	122.71(11)	C3–C4–C5	121.44(17)	O6–C27–C26	125.60(2)
Cu1–O2–C13	99.02(10)	C4–C5–C6	119.90(18)	C9–C8–C13	119.34(18)
Cu1–O2–C14	126.97(12)	C1–C6–C5	119.80(17)	C10–C11–C12	120.80(2)
C13–O2–C14	117.27(17)	C1–C6–C7	122.51(15)	O2–C13–C12	124.87(19)
Cu1–O5–C15	127.02(12)	C5–C6–C7	117.68(16)	O5–C15–C20	124.02(16)
Cu1–O6–C27	98.79(10)	N1–C7–C6	125.47(16)	C16–C17–C18	119.11(18)
Cu1–O6–C28	134.38(14)	N1–C8–C9	121.51(17)	C17–C18–C19	121.62(17)
C27–O6–C28	118.06(17)	C8–C9–C10	120.80(2)	C15–C20–C21	123.37(16)
Cu1–N1–C7	122.19(12)	C11–C12–C13	120.50(2)	N3–C22–C23	122.74(18)
Cu1–N1–C8	118.75(11)	C8–C13–C12	119.00(2)	C22–C23–C24	119.40(2)
C7–N1–C8	118.83(15)	C16–C15–C20	117.75(16)	C25–C26–C27	119.30(2)
O3–N2–O4	122.77(18)	N4–C18–C17	118.85(17)	C22–C27–C26	119.20(2)

Table S9. Selected Bond Lengths [Å] and Angles [°] for **1c**.

Bond Length			
Ni1–O2	2.132(5)	C1–C6	1.437(11)
Ni1–O1	1.977(5)	C2–C3	1.354(12)
Ni1–N1	2.026(6)	C3–C4	1.391(11)
O1–C1	1.287(9)	C4–C5	1.363(11)
O2–C13	1.390(9)	C5–C6	1.399(11)
O2–C14	1.435(10)	C6–C7	1.429(10)
O3–N2	1.183(8)	C8–C9	1.385(11)
O4–N2	1.219(8)	C8–C13	1.403(12)
N1–C7	1.290(9)	C9–C10	1.380(12)
N1–C8	1.430(9)	C10–C11	1.380(13)
N2–C4	1.477(10)	C11–C12	1.372(13)
C1–C2	1.445(11)	C12–C13	1.376(11)
Bond Angles			
O1–Ni1–O2	170.1(2)	O4–N2–C4	115.9(7)
O1–Ni1–N1	93.1(2)	O1–C1–C2	118.9(8)
O1–Ni1–O1*	95.9(3)	O1–C1–C6	125.5(9)
O1–Ni1–O2*	89.3(2)	C2–C1–C6	115.6(7)
O1–Ni1–N1*	93.4(2)	C1–C2–C3	122.7(9)
O2–Ni1–N1	78.1(2)	C2–C3–C4	119.8(9)
O2–Ni1–O1*	89.3(2)	N2–C4–C3	119.4(8)
O2–Ni1–O2*	86.8(3)	N2–C4–C5	120.4(7)
O2–Ni1–N1*	94.8(2)	C3–C4–C5	120.3(8)
N1–Ni1–O1*	93.4(2)	C4–C5–C6	122.0(8)
N1–Ni1–O2*	94.8(2)	C1–C6–C5	119.5(8)
N1–Ni1–N1*	170.3(3)	C1–C6–C7	125.0(7)
O1*–Ni1–O2*	170.1(2)	C5–C6–C7	115.4(7)
O1*–Ni1–N1*	93.1(2)	N1–C7–C6	125.4(7)
O2*–Ni1–N1*	78.1(2)	N1–C8–C9	116.3(7)
Ni1–O1–C1	125.6(5)	N1–C8–C13	125.7(7)
Ni1–O2–C13	114.7(5)	C9–C8–C13	118.0(8)
Ni1–O2–C14	126.9(5)	C8–C9–C10	115.3(8)
C13–O2–C14	118.0(6)	C9–C10–C11	123.8(8)
Ni1–N1–C7	124.2(5)	C10–C11–C12	120.9(8)
Ni1–N1–C8	116.1(5)	C11–C12–C13	119.9(9)
C7–N1–C8	119.6(6)	O2–C13–C8	120.0(10)
O3–N2–O4	125.7(8)	O2–C13–C12	120.3(9)
O3–N2–C4	118.4(7)	C8–C13–C12	120.7(8)

Table S10. Selected Bond Lengths [Å] and Angles [°] for **1d**.

Bond Length			
Mn1–O2	2.2660(18)	C1–C6	1.4329(1)
Mn1–O1	2.0353(1)	C2–C3	1.3581(1)
Mn1–N1	2.2244(15)	C3–C4	1.3848(1)
O1–C1	1.2760(1)	C4–C5	1.3677(1)
O2–C13	1.3648(1)	C5–C6	1.3956(1)
O2–C14	1.4353(1)	C6–C7	1.4401(1)
O3–N1	1.2152(1)	C8–C9	1.3788(1)
O4–N1	1.2207(1)	C8–C13	1.3921(1)
N1–C4	1.4403(1)	C9–C10	1.3831(1)
N2–C7	1.2895(1)	C10–C11	1.3608(1)
N2–C8	1.4171(1)	C11–C12	1.3691(1)
C1–C2	1.4196(1)	C12–C13	1.3850(1)
Bond Angles			
O1–Mn1–O2	157.01(6)	C7–N2–C8	119.16(1)
O1–Mn1–N1	86.28(1)	O1–C1–C2	119.55(1)
O1–Mn1–O1*	100.15(8)	O1–C1–C6	123.99(1)
O1–Mn1–O2*	91.34(1)	C2–C1–C6	116.46(1)
O1–Mn1–N1*	104.56(1)	C1–C2–C3	122.97(1)
O2–Mn1–N1	71.51(1)	C2–C3–C4	119.09(1)
O2–Mn1–O1*	91.34(1)	N2–C4–C3	119.00(1)
O2–Mn1–O2*	85.30(1)	N2–C4–C5	120.07(1)
O2–Mn1–N1*	95.94(1)	C3–C4–C5	120.93(1)
N1–Mn1–O1*	104.56(1)	C4–C5–C6	121.17(1)
N1–Mn1–O2*	95.94(1)	C1–C6–C5	119.18(1)
N1–Mn1–N1*	163.29(1)	C1–C6–C7	124.74(1)
O1*–Mn1–O2*	157.01(6)	C5–C6–C7	116.05(1)
O1*–Mn1–N1*	86.28(1)	N1–C7–C6	127.52(1)
O2*–Mn1–N1*	71.51(1)	N1–C8–C9	125.37(1)
Mn1–O1–C1	132.90(1)	N1–C8–C13	117.04(1)
Mn1–O2–C13	118.67(1)	C9–C8–C13	117.56(1)
Mn1–O2–C14	122.52(1)	C8–C9–C10	120.39(1)
C13–O2–C14	118.80(1)	C9–C10–C11	120.99(1)
O3–N1–O4	122.48(1)	C10–C11–C12	120.31(1)
O3–N1–C4	118.29(1)	C11–C12–C13	118.77(1)
O4–N1–C4	119.23(1)	O2–C13–C8	115.49(1)
Mn1–N2–C7	123.31(1)	O2–C13–C12	122.53(1)
Mn1–N2–C8	117.28(1)	C8–C13–C12	121.98(1)

Table S11. Selected Bond Lengths [Å] and Angles [°] for **2a**.

Bond Length			
Cu1–O1	1.8834(12)	C4–C5	1.374(3)
Cu1–N1	2.004(3)	C4–C3*	1.400(4)
O1–C1	1.301(3)	C5–C6	1.402(3)
O2–C11	1.373(3)	C6–C7	1.433(3)
O2–C14	1.432(2)	C6–C1*	1.418(4)
N1–O7	1.292(3)	C8–C9	1.390(3)
N1–O8	1.431(3)	C8–C13	1.407(4)
C1–C2	1.424(3)	C9–C10	1.385(3)
C1–C6*	1.418(4)	C10–C11	1.388(4)
C2–C3	1.364(3)	C11–C12	1.392(3)
C3–C4*	1.400(4)	C12–C13	1.369(4)
Br1–C4	1.898(2)		
Bond Angles			
O1–Cu1–N1	94.38(8)	Br1–C4–C5	120.3(2)
O1–Cu1–O1*	149.49(5)	Br1–C4–C3*	119.52(15)
O1–Cu1–N1*	93.07(8)	C5–C4–C3*	120.1(2)
N1–Cu1–O1*	93.07(8)	C4–C5–C6	119.9(3)
N1–Cu1–N1*	151.43(7)	C5–C6–C7	117.2(2)
O1*–Cu1–N1*	94.38(8)	C5–C6–C1*	120.9(2)
Cu1–O1–C1	126.88(15)	C7–C6–C1*	121.8(2)
Cu1–N1–C7	120.44(19)	N1–C7–C6	128.6(3)
Cu1–N1–C8	123.60(15)	N1–C8–C9	122.3(2)
C11–O2–C14	117.46(19)	N1–C8–C13	119.16(18)
C7–N1–C8	115.9(3)	C9–C8–C13	118.5(2)
O1–C1–C2	118.7(2)	O2–C11–C12	114.8(2)
O1–C1–C6*	124.10(19)	C10–C11–C12	119.5(2)
C2–C1–C6*	117.2(2)	C11–C12–C13	120.4(3)
C1–C2–C3	121.1(3)	C8–C13–C12	120.72(19)
C2–C3–C4*	120.8(2)		

Table S12. Selected Bond Lengths [Å] and Angles [°] for **2a'**.

Bond Length			
Cu1–O1	1.8915(4)	Br1–C4	1.909(6)
Cu1–N1	2.001(4)	C4–C5	1.362(10)
O1–C1	1.302(6)	C5–C6	1.406(8)
O2–C11	1.374(7)	C6–C7	1.437(7)
O2–C14	1.411(8)	C8–C9	1.380(7)
N1–O7	1.293(7)	C8–C13	1.389(8)
N1–O8	1.441(8)	C9–C10	1.394(10)
C1–C2	1.423(7)	C10–C11	1.386(9)
C1–C6	1.414(7)	C11–C12	1.376(8)
C2–C3	1.372(7)	C12–C13	1.386(9)
C3–C4	1.399(7)		
Bond Angles			
O1–Cu1–N1	91.30(18)	Br1–C4–C3	119.1(5)
O1–Cu1–O1*	180.00	C3–C4–C5	121.1(5)
O1–Cu1–N1*	88.71(18)	C4–C5–C6	120.5(5)
N1–Cu1–O1*	88.71(18)	C1–C6–C5	119.9(5)
N1–Cu1–N1*	180.00	C1–C6–C7	122.2(4)
O1*–Cu1–N1*	91.30(18)	C5–C6–C7	118.0(5)
Cu1–O1–C1	127.9(4)	N1–C7–C6	126.5(5)
Cu1–N1–C7	123.9(4)	N1–C8–C9	120.2(6)
Cu1–N1–C8	119.2(3)	N1–C8–C13	119.6(4)
C11–O2–C14	118.1(5)	C9–C8–C13	120.1(6)
C7–N1–C8	116.5(4)	C8–C9–C10	120.4(6)
O1–C1–C2	118.5(5)	C9–C10–C11	119.2(5)
O1–C1–C6	123.8(5)	O2–C11–C10	124.6(5)
C2–C1–C6	117.7(4)	O2–C11–C12	115.2(5)
C1–C2–C3	121.5(5)	C10–C11–C12	120.2(5)
C2–C3–C4	119.4(5)	C11–C12–C13	120.7(6)
Br1–C4–C5	119.8(4)	C8–C13–C12	119.3(5)

Table S13. Selected Bond Lengths [Å] and Angles [°] for **2b**.

Bond Length			
Cu1–O1	1.8883(16)	C4–C5	1.372(3)
Cu1–N1	2.0047(18)	C5–C6	1.409(3)
Cu1–O1*	1.8883(16)	Br1–C4	1.904(2)
Cu1–N1*	2.0047(18)	C6–C7	1.438(3)
O1–C1	1.303(3)	C8–C9	1.385(3)
N1–C7	1.294(3)	C8–C13	1.393(3)
N1–C8	1.439(3)	C9–C10	1.387(3)
C1–C2	1.416(3)	C10–C11	1.394(3)
C1–C6	1.420(3)	C11–C12	1.386(3)
C2–C3	1.378(3)	C11–C14	1.504(4)
C3–C4	1.397(3)	C12–C13	1.388(3)
Bond Angles			
O1–Cu1–N1	91.31(7)	C3–C4–C5	121.3(2)
O1–Cu1–O1*	180.00	C4–C5–C6	119.66(19)
O1–Cu1–N1*	88.69(7)	C1–C6–C5	120.47(19)
N1–Cu1–O1*	88.69(7)	C1–C6–C7	122.29(19)
N1–Cu1–N1*	180.00	C5–C6–C7	117.21(19)
O1*–Cu1–N1*	91.31(7)	N1–C7–C6	126.47(19)
Cu1–O1–C1	127.16(14)	N1–C8–C9	119.78(18)
Cu1–N1–C7	122.95(15)	N1–C8–C13	120.47(19)
Cu1–N1–C8	120.22(14)	C9–C8–C13	119.73(19)
C7–N1–C8	116.03(18)	C8–C9–C10	119.90(19)
O1–C1–C2	119.16(19)	C9–C10–C11	121.41(19)
O1–C1–C6	123.40(19)	C10–C11–C12	117.67(19)
O2–C1–C6	117.43(19)	C10–C11–C14	120.2(2)
C1–C2–C3	121.69(19)	C12–C11–C14	122.1(2)
C2–C3–C4	119.47(19)	C11–C12–C13	121.89(19)
Br1–C4–C3	119.56(16)	C8–C13–C12	119.40(19)
Br1–C4–C5	119.16(16)		

Table S14. Selected Bond Lengths [Å] and Angles [°] for **2c**.

Bond Length			
Ni1–O1	1.8349(17)	C4–C5	1.371(3)
Ni1–N1	1.9132(18)	C5–C6	1.410(3)
Ni1–O1*	1.8349(17)	Br1–C4	1.903(2)
Ni1–N1*	1.9132(18)	C6–C7	1.430(3)
O1–C1	1.305(3)	C8–C9	1.387(3)
N1–C7	1.300(3)	C8–C13	1.391(3)
N1–C8	1.445(3)	C9–C10	1.387(3)
C1–C2	1.422(3)	C10–C11	1.397(3)
C1–O6	1.413(3)	C11–C12	1.394(3)
C2–C3	1.377(3)	C11–C14	1.507(4)
C3–C4	1.400(3)	C12–C13	1.388(3)
Bond Angles			
O1–Ni1–N1	92.54(7)	C3–C4–C5	121.2(2)
O1–Ni1–O1*	180.00	C4–C5–C6	119.71(19)
O1–Ni1–N1*	87.46(7)	C1–C6–C5	120.35(19)
N1–Ni1–O1*	87.46(7)	C1–C6–C7	120.80(19)
N1–Ni1–N1*	180.00	C5–C6–C7	118.79(19)
O1*–Ni1–N1*	92.54(7)	N1–C7–C6	125.70(19)
Ni1–O1–C1	127.04(14)	N1–C8–C9	119.52(18)
Ni1–N1–C7	124.34(15)	N1–C8–C13	120.50(18)
Ni1–N1–C8	120.18(14)	C9–C8–C13	119.97(19)
C7–N1–C8	115.15(18)	C8–C9–C10	119.68(19)
O1–C1–C2	118.56(19)	C9–C10–C11	121.59(19)
O1–C1–C6	123.42(19)	C10–C11–C12	117.55(19)
C2–C1–C6	118.00(19)	C10–C11–C14	120.3(2)
C1–C2–C3	120.99(19)	C12–C11–C14	122.1(2)
C2–C3–C4	119.8(2)	C11–C12–C13	121.67(19)
Br1–C4–C3	119.48(16)	C8–C13–C12	119.53(19)
Br1–C4–C5	119.35(16)		

Table S15: List of Hydrogen Bonds for **1a**–**2c**.

Complex	D-H···*A*	d(D-H) (Å)	d(H···A) (Å)	d(D-A) (Å)	∠(D-H···*A*) °	Symmetry
1a	C5–H5···O1	0.930	2.47	3.347(2)	158	1/2+x, 1–y, z
	C14–H14B···O4	0.960	2.51	2.987(3)	111	–1/2+x, 1/2+y, 1/2+z
	C14–H14B···π	0.960	2.87	3.416(4)	117	1/2–x, y, 1–z
1b	C21–H21···O8	0.950	2.43	3.107(2)	129	3/2–x, 1/2+y, 3/2–z
	C25–H25···O1	0.950	2.38	3.268(2)	155	x, 1+y, z
	C28–H28A···O7	0.980	2.56	3.159(3)	120	–1/2+x, 3/2–y, –1/2+z
	C28–H28C···π	0.980	2.93	3.866(3)	160	1–x, 2–y, 1–z
1c	C5–H5···O1	0.950	2.43	3.339(11)	160	x, 1–y, –1/2+z
	C14–H14A···O4	0.980	2.56	3.326(12)	135	1–x, 1–y, 1–z
	C14–H14B···O4	0.980	2.44	2.924(10)	110	1/2+x, 1/2+y, 1+z
	C14–H14B···π	0.980	2.83	3.335(10)	113	1–x, y, 3/2–z
1d	C5–H5···O1	0.950	2.41	3.303(3)	157	1/2+x, 1–y, z
	C14–H14C···O3	0.980	2.52	3.027(3)	112	–1/2+x, 1/2+y, 1/2+z
	C14–H14C···π	0.960	2.87	3.499(4)	123	x, y, z
	C14–H14C···π	0.960	3.00	3.398(3)	106	1/2–x, y, 1–z
2a	C13–H13···O1	0.950	2.44	3.301(5)	151	x, 1+y, z
	C14–H14A···O2	0.980	2.53	3.456(5)	157	x, 1+y, z
2a'	C5–H5···O1	0.950	2.48	3.318(7)	147	3/2–x, 1/2+y, 1/2–z
2b	C13–H13···π	0.930(3)	2.92	3.543(2)	125	x, 1/2–y, –1/2+z
2c	C9–H9···π	0.950	2.88	3.557(2)	129	x, 3/2–y, –1/2+z

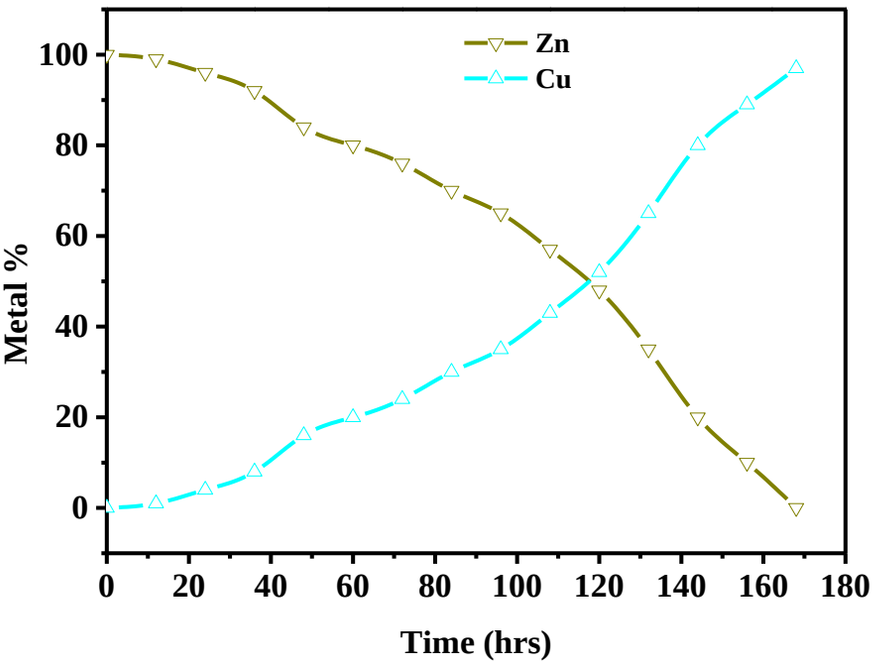

Figure S8(a). Kinetics for **1a** → **1b** or Zinc-to-Copper ion Exchange (%) per 12-hr intervals.

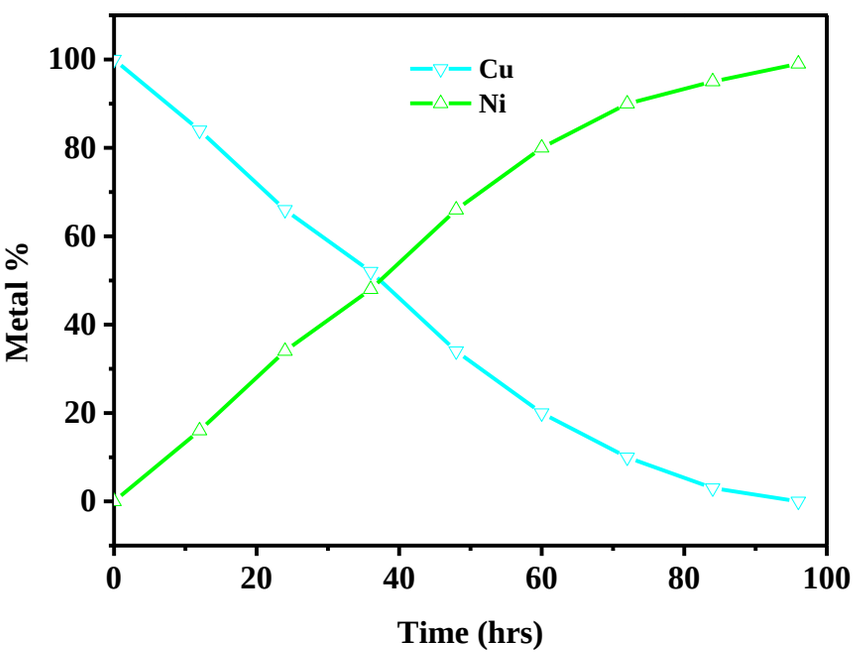

Figure S8(b). Kinetics for **1b** → **1c** or Copper-to-Nickel ion Exchange (%) per 12-hr intervals.

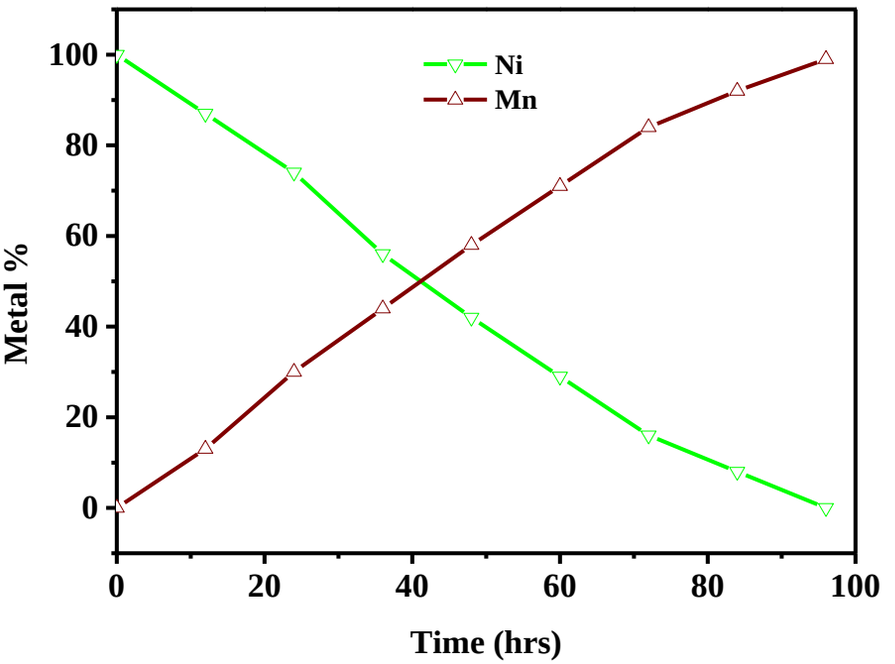

Figure S8(c). Kinetics for **1c** → **1d** or Nickel-to-Manganese ion Exchange (%) per 12-hr intervals.

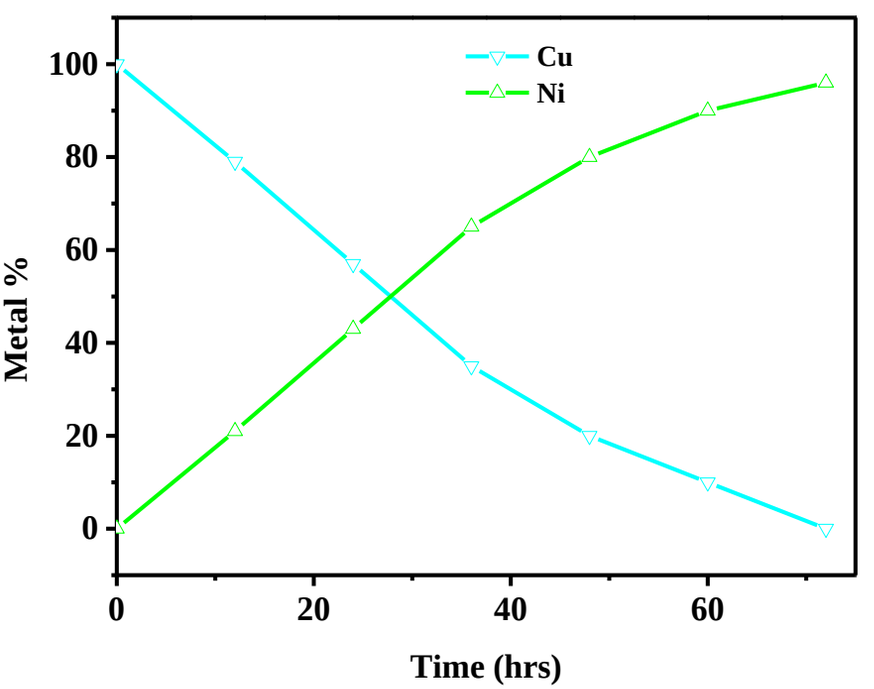

Figure S8(d). Kinetics for **2a** → **2c** or Copper-to-Nickel ion Exchange (%) per 12-hr intervals.

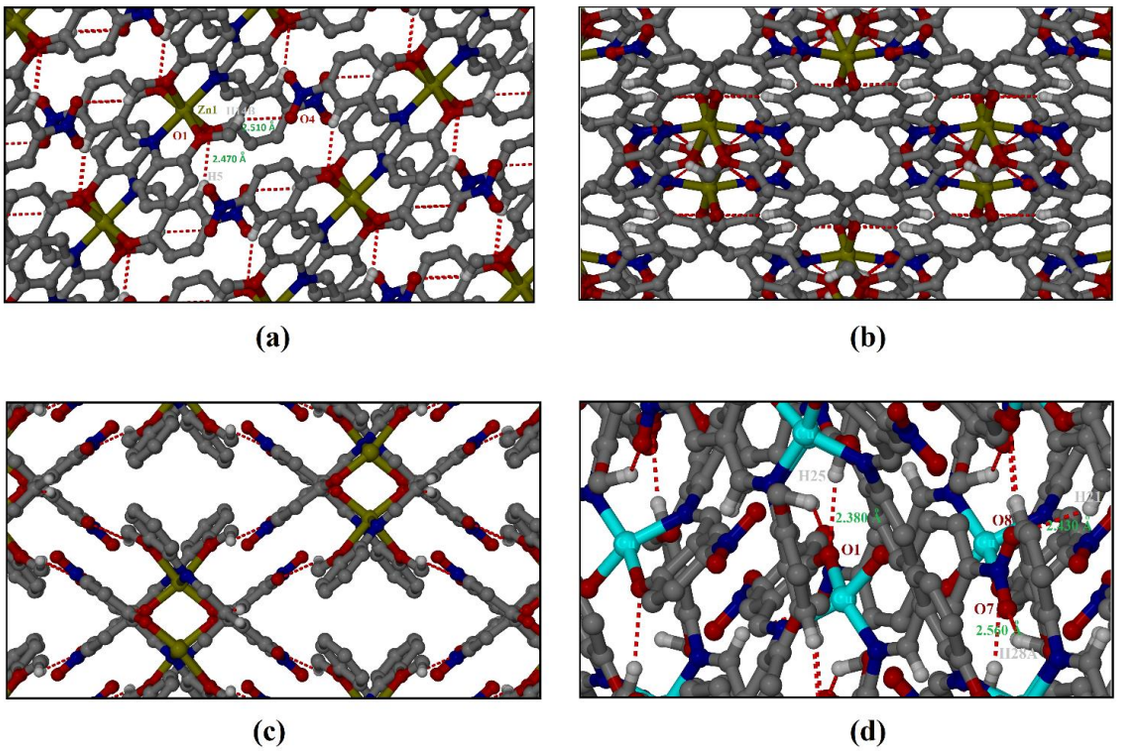

Figure S9. Hydrogen Bonding Features of (a) **1a** viewed along the *b*-axis, (b) **1a** viewed down the *c*-axis, (c) **1a** viewed along the *a*-axis, and (d) **1b** viewed along the *c*-axis.

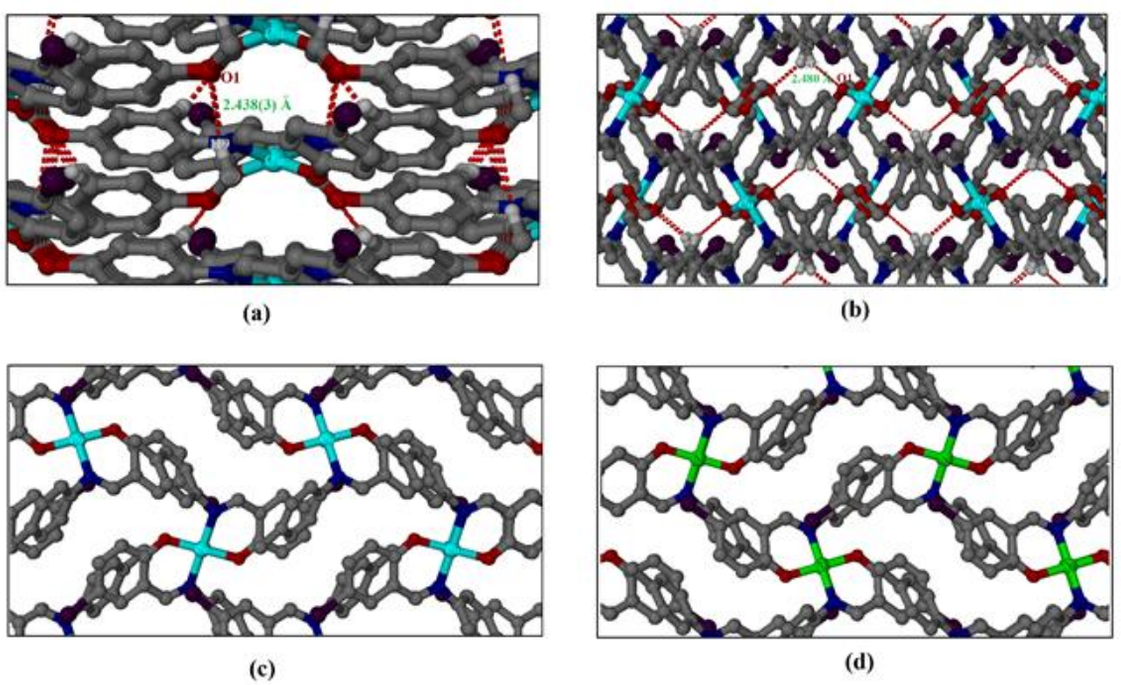

Figure S10. Hydrogen Bonding Properties of (a) **2a** viewed down the *c*-axis, (b) **2a'** viewed down the *a*-axis, (c) **2b** viewed along the *a*-axis, and (d) **2c** viewed down the *a*-axis.

Packing Properties of the Complexes 1a–2c. The packing of the molecules in **1a**, **1c** and **1d** (Figure S8) are mainly dominated by C–H···O hydrogen bonds with the participation of the nitro group oxygen atoms. The intermolecular C5–H5···O1$^{i/ii/iii}$ and C14–H14A···O4$^{iv/v/vii}$/ C14–H14B···O4$^{iv/v/vii}$ / C14–H14C···O4$^{iv/v/vii}$ interactions with distances ranging from 2.380–2.560 Å (Table S15) stabilised the mononuclear complexes (symmetry code: (i) 1/2+x, 1–y, z; (ii) x, 1–y, –1/2+z; (iii) 1/2+x, 1–y, z; (iv) –1/2+x, 1/2+y, 1/2+z; (v) 1–x, 1–y, 1–z; (vi) –1/2+x, 1/2+y, 1/2+z; (vii) 1/2+x, 1/2+y, 1+z). Furthermore, there exist C14–H14B···$\pi^{vii/ix}$ / C14–H14C···$\pi^{vii/ix}$ hydrogen bond interactions with 2.870, 2.830 and 3.000 Å intermolecular distances (symmetry code: (vii) 1/2–x, y, 1–z; (viii) 1–x, y, 3/2–z; (ix) 1/2–x, y, 1–z). Similarly, the packing arrangements observed in the crystal structure of **1b** is generated by strong and weak C21–H21···O8^{xi}, C25–H25···O1^{xii}, C28–H28A···O7^{xiii} and C28–H28C···π^{xiv} hydrogen bond interactions with distances 2.430, 2.380, 2.560 and 2.930 Å, respectively (symmetry code: (xi) 3/2–x, 1/2+y, 3/2–z; (xii) x, 1+y, z; (xiii) –1/2+x, 3/2–y, –1/2+z; (xiv) 1–x, 2–y, 1–z).

By the same token, **2a** and **2a'** assemble through C13–H13···O1^{xv} and C5–H5···O1^{xvi} (Figure S9a–b) while **2a** is further supported by an additional C14–H14A···O2^{xv} with their respective distances 2.440 and 2.480 Å, and 2.530 Å, (symmetry code: (xv) x, 1+y, z; (xvi) 3/2–x, 1/2+y, 1/2–z). There are similarities in the packing arrangements of complexes **2b** and **2c** (compare Figures S9c–d), as they exhibit C13–H13···π^{xvii} and C9–H9···π^{xviii} (Table S15) hydrogen bond interactions with distances 2.920 and 2.880 Å, respectively (symmetry code: (xvii) x, 1/2–y, –1/2+z; (xviii) x, 3/2–y, –1/2+z).

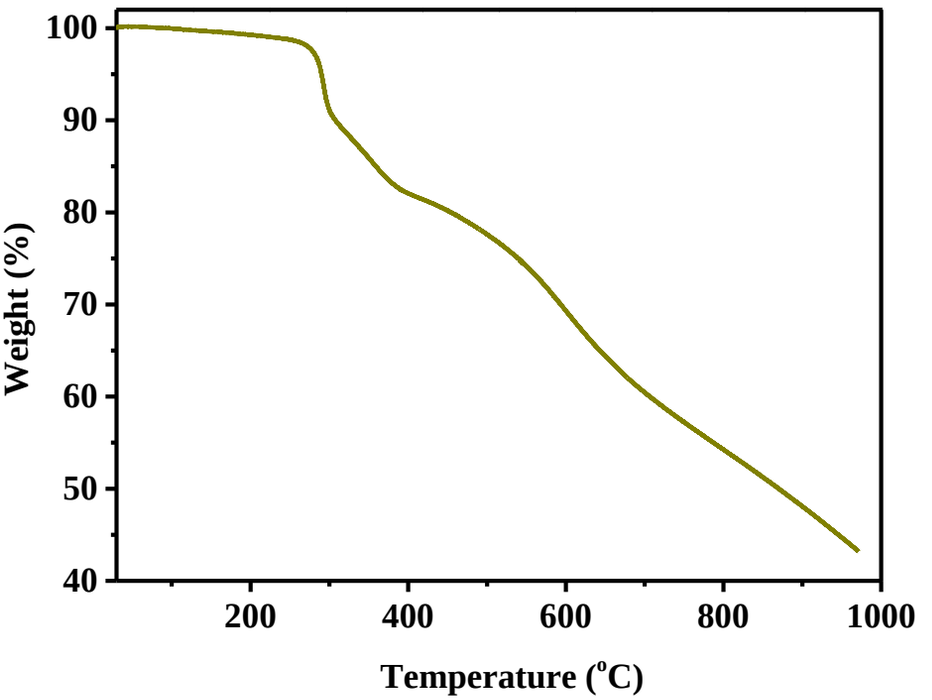

Figure S11(a). TG Measurement for the Mononuclear Complex **1a**.

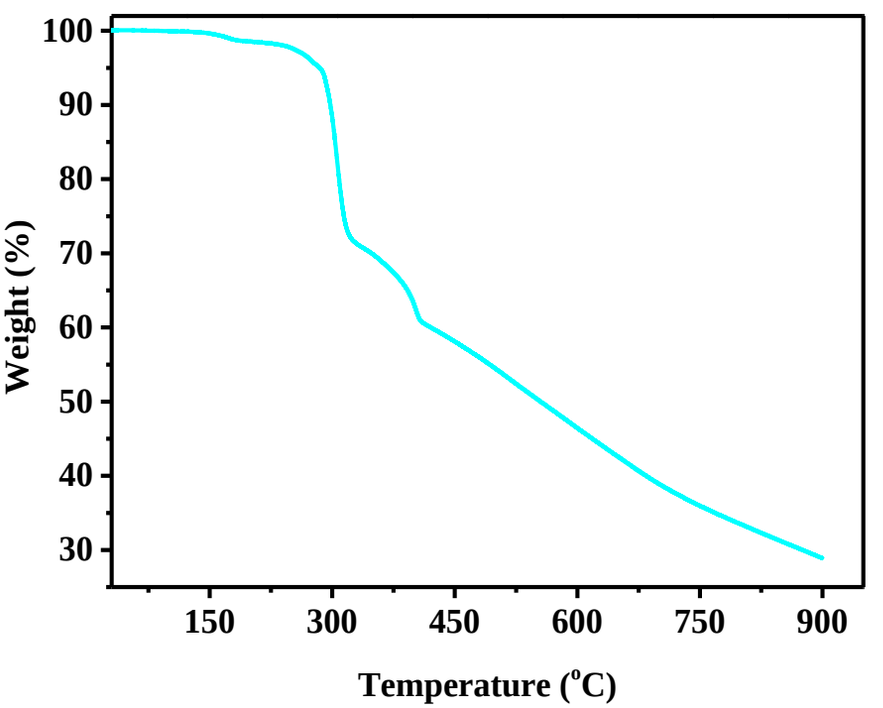

Figure S11(b). TG Measurement for the Mononuclear Complex **1b**.

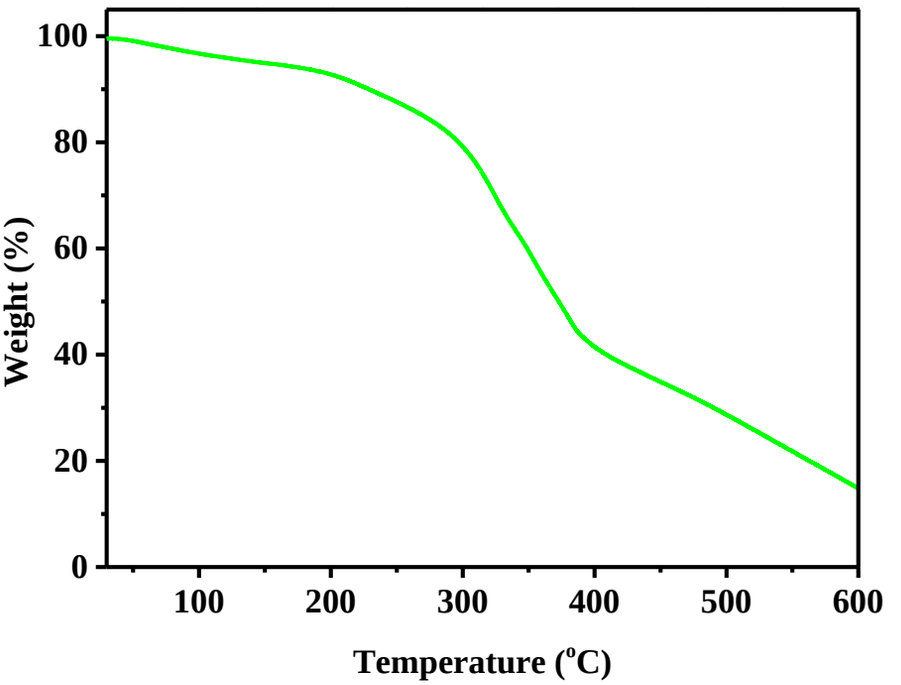

Figure S11(c). TG Measurement for the Mononuclear Complex **1c**.

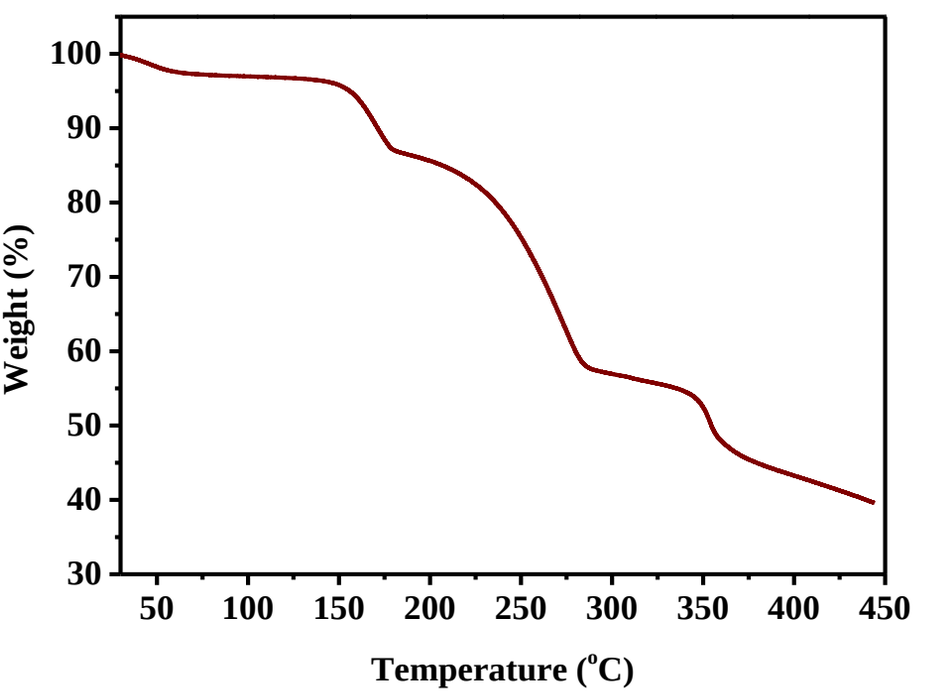

Figure S11(d). TG Measurement for the Mononuclear Complex **1d**.

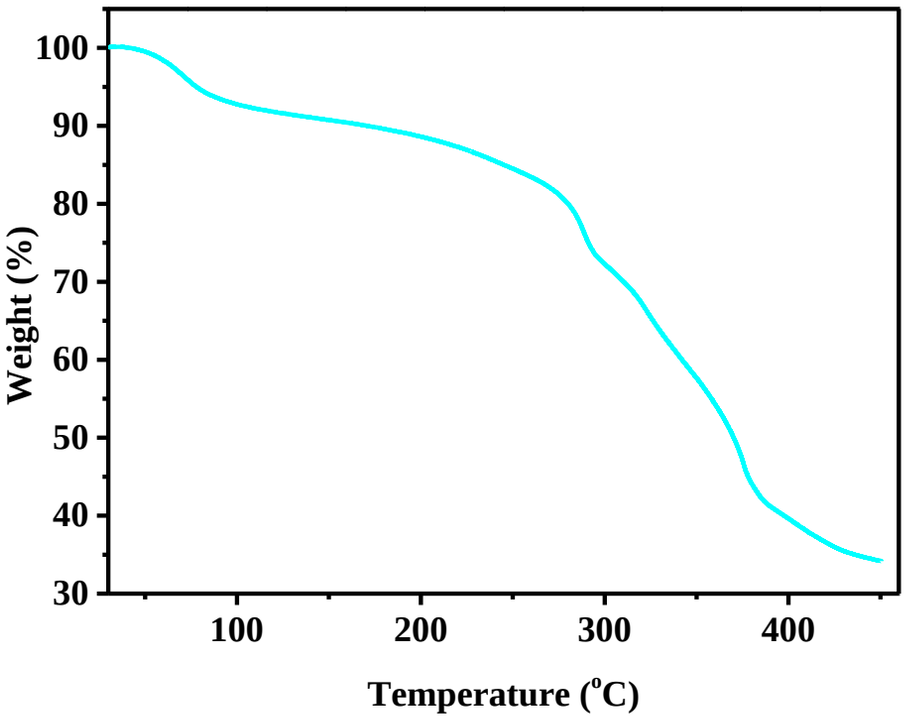

Figure S11(e). TG Measurement for the Mononuclear Complex **2a**.

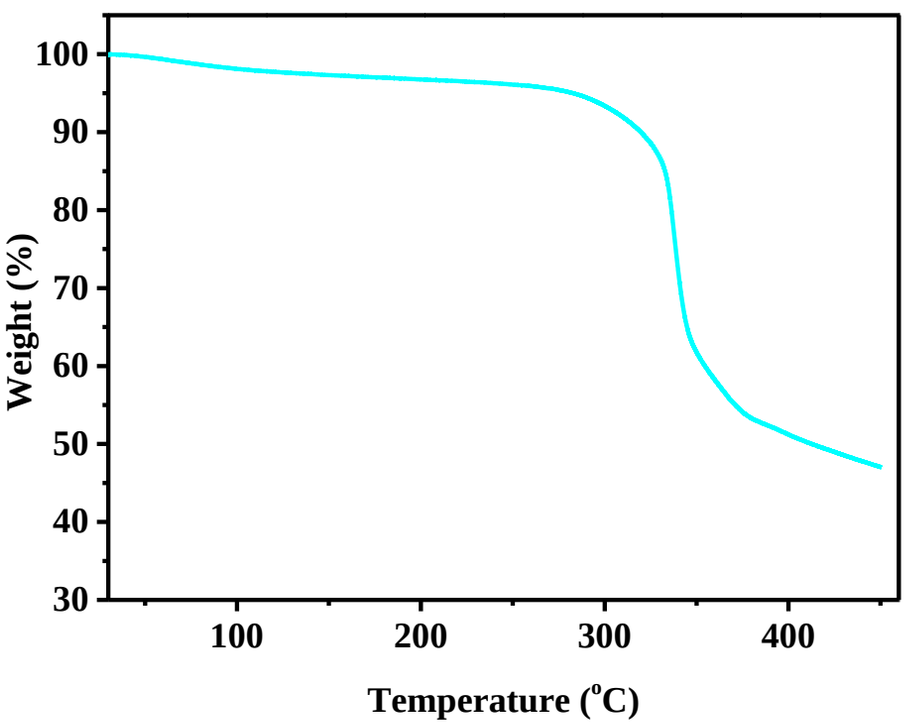

Figure S11(f). TG Measurement for the Mononuclear Complex **2a'**.

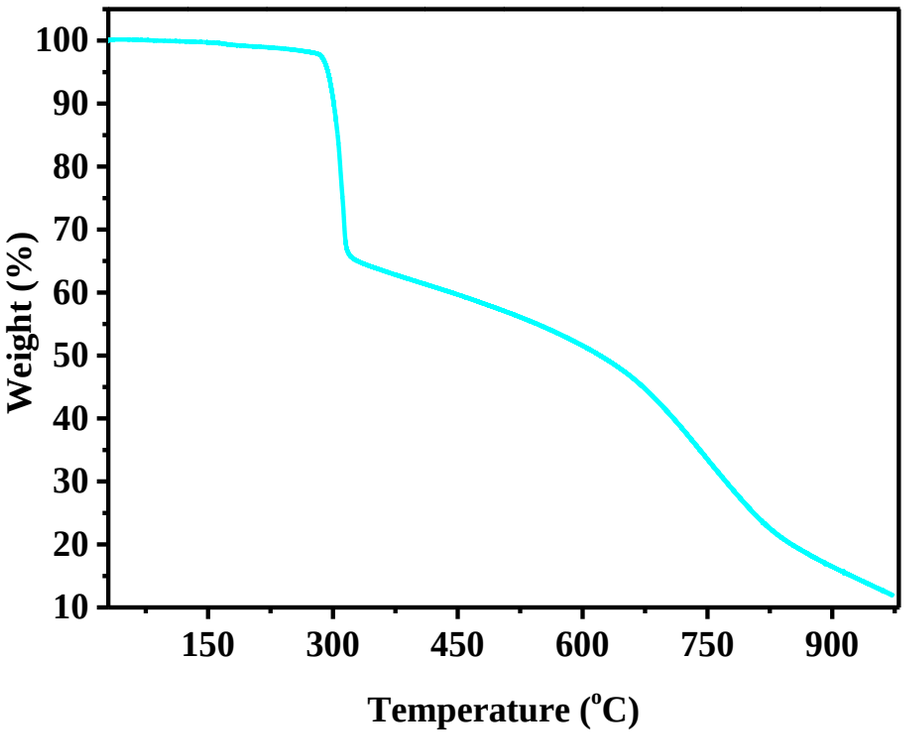

Figure S11(g). TG Measurement for the Mononuclear Complex **2b**.

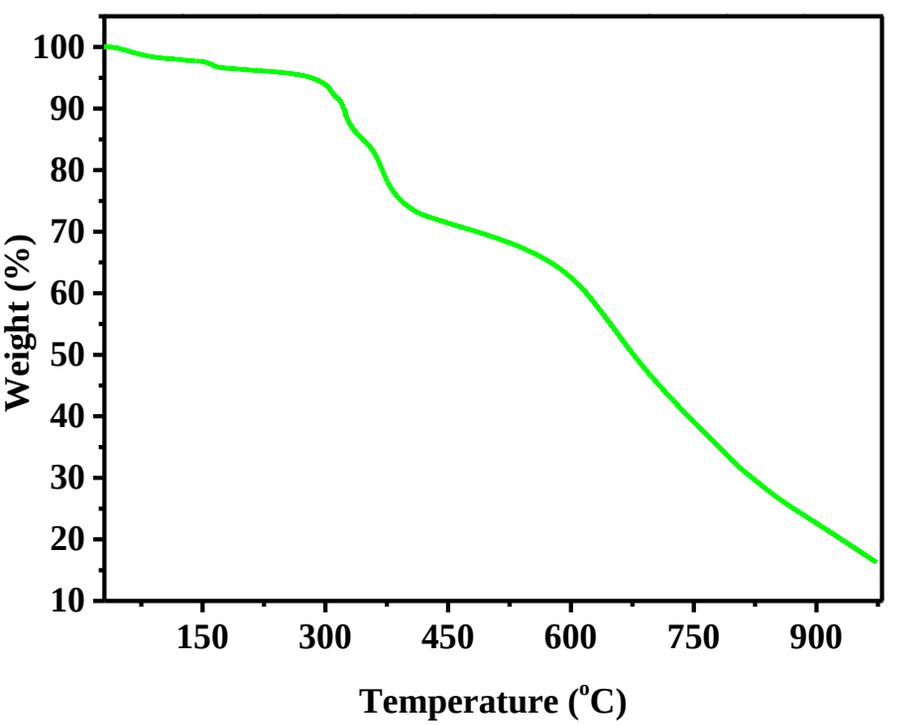

Figure S11(h). TG Measurement for the Mononuclear Complex **2c**.

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