Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information for:

Novel copper(II) complexes with *NNO*-Schiff base-like ligand – structures, magnetic properties and anticancer activity

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Table S1. Crystallographic data for the ligands and complexes presented in this paper.

	HL1	**HL4**	**HL5**	**HL6**	**1-OAc**	**1-NO_3**	**1-Cl**	**1-I**
CCDC	1566611	1566612	1566613	1566614	1566615	1566619	1566623	1566633
formula	HL1	HL4	HL5	HL6	[(μ–1,1–OAc)$_2$(CuL1)$_2$]	[(μ–1,1–NO_3)(μ–1,3–NO_3)(CuL1)$_2$]	[(μ–Cl)$_2$(CuL1)$_2$]	[(μ–I)$_2$(CuL1)$_2$]
sum formula	$C_{13}H_{16}N_2O_3$	$C_{12}H_{13}N_3O_2$	$C_{18}H_{18}N_3O_3$	$C_{12}H_{14}N_2O_3$	$C_{30}H_{36}Cu_2N_4O_{10}$	$C_{26}H_{30}Cu_2N_6O_{12}$	$C_{26}H_{30}Cl_2Cu_2N_4O_6$	$C_{26}H_{30}I_2Cu_2N_4O_6$
M/ g mol^{-1}	248.28	231.25	310.34	234.25	739.70	745.64	692.54	875.44
crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/a$	P–1	P–1	$C2/c$	$P2_1/c$	$C2/c$	P–1	$P2_1/C$
crystal description	colourless block	colourless block	colourless block	colourless block	blue block	blue block	blue block	green block
a/ Å	7.339(5)	6.0280(4)	5.5863(5)	25.029(5)	7.5927(5)	12.7796(5)	7.3859(5)	7.8179(3)
b/ Å	14.815(5)	9.2207(6)	11.6567(11)	4.211(5)	23.9283(12)	13.8977(8)	9.1298(7)	14.6683(6)
c/ Å	11.777(5)	11.3737(7)	13.2094(12)	28.823(5)	8.5927(5)	16.9969(6)	10.3252(7)	13.0905(4)
α/ °	90	74.653(5)	71.808(7)	90	90	90	94.110(6)	90
β/ °	97.495(5)	75.243(5)	79.534(7)	129.016(5)	93.078(5)	105.798(3)	96.016(6)	92.391(3)
γ/ °	90	87.728(5)	77.545(7)	90	90	90	105.895(6)	90
V/ Å^3	1269.5(11)	589.26(7)	791.86(13)	2360(3)	1558.87(16)	2904.7(2)	662.26(8)	1499.85(10)
Z	4	2	2	8	2	4	1	4
ρ_{calcd}/ g cm^{-3}	1.299	1.303	1.302	1.319	1.576	1.705	1.736	1.938
μ/ mm^{-1}	0.093	0.092	0.090	0.096	1.428	1.540	1.858	3.522
crystal size/ mm	0.149×0.128×0.230	0.266×0.182×0.137	0.162×0.137×0.362	0.186×0.210×0.203	0.135×0.115×0.097	0.118×0.093×0.088	0.120×0.105×0.093	0.101×0.077×0.063
F(000)	528	244	328	992	764	1528	354	852
T/ K	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)
λ/ Å	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073	Mo-K$_\alpha$ 0.71073
Θ range/ °	1.7-28.0	1.92–28.42	1.9-28.1	1.7-28.0	1.70–27.98	2.22–26.62	2.00–28.40	2.08–27.62
Reflns. collected	7264	6744	6984	7104	3530	9232	6277	3516
Indep. reflns.(R_{int})	2852 (0.112)	2762 (0.031)	3448 (0.037)	2682 (0.083)	2653 (0.0403)	3429 (0.0237)	3054 (0.0820)	2940 (0.0314)
Parameters	163	154	208	154	208	210	181	181
R1 (all data)	0.0757	0.0421 (0.0560)	0.0512	0.0620	0.0307 (0.0483)	0.0251 (0.0335)	0.0609 (0.0701)	0.0205 (0.0273)
wR2	0.2103	0.1172	0.1397	0.2176	0.0618	0.0766	0.1742	0.0458
GooF	0.92	1.029	0.96	1.04	0.909	1.076	1.069	0.936

Table S1 (continued). Crystallographic data for the ligands and complexes presented in this paper.

	1-NCS	**1-N_3**	**2-NO_3**	**2-Cl**	**2-NCS**	**2-N_3**	**2-SO_4**	**3-OAc**
CCDC	1566635	1566638	1566620	1566624	1566636	1566639	1566640	1566616
formula	[(μ–1,3–NCS)(CuL1)]$_n$	[(μ–1,1–N_3)$_2$(CuL1)$_2$]	[CuL2(NO_3)(H_2O)]·H_2O	[(μ–Cl)$_2$(CuL2)$_2$]	[CuL2(SCN)(MeOH)]	[(μ–1,1–N_3)$_2$(CuL2)$_2$]	[(CuL2)$_2SO_4$]·MeOH	[(μ–1,1–OAc)$_2$(CuL3)$_2$]
sum formula	$C_{14}H_{15}CuN_3O_3S$	$C_{26}H_{30}Cu_2N_{10}O_6$	$C_{12}H_{15}CuN_3O_6$, H_2O	$C_{24}H_{26}Cl_2Cu_2N_4O_4$	$C_{14}H_{17}CuN_3O_3S$	$C_{24}H_{26}Cu_2N_{10}O_4$, 2($H_2O$)	$C_{25}H_{30}Cu_2N_4O_9S$, CH_4O	$C_{32}H_{40}Cu_2N_4O_{10}$, 2($H_2O$)
M/ g mol^{-1}	368.89	705.68	378.82	632.46	370.90	681.66	721.71	835.78
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
crystal description	blue block	blue needle	blue hexagon	blue block	blue block	blue block	blue green block	blue block
a/ Å	5.9027(5)	20.5772(11)	8.7846(4)	7.6352(5)	9.8474(5)	7.3993(4)	12.7600(18)	8.8660(6)
b/ Å	16.4411(12)	19.5249(15)	18.8515(6)	9.0924(6)	15.5449(6)	9.3862(5)	16.897(3)	8.8511(6)
c/ Å	15.7542(13)	7.1596(4)	9.0280(4)	9.5031(6)	10.2348(6)	10.6959(5)	13.781(2)	12.7620(8)
α/ °	90	90	90	91.652(5)	90	105.369(4)	90	94.241(5)
β/ °	98.344(6)	94.083(4)	99.363(3)	98.150(5)	92.590(4)	99.166(4)	102.639(11)	104.942(5)
γ/ °	90	90	90	107.858(5)	90	97.860(4)	90	108.277(5)
V/ Å^3	1512.7(2)	2869.2(3)	1475.14(11)	619.77(7)	1565.11(14)	694.52(6)	2899.3(7)	905.63(11)
Z	4	4	4	1	4	1	4	1
ρ_{calcd}/ g cm^{-3}	1.620	1.634	1.706	1.695	1.574	1.630	1.653	1.532
μ/ mm^{-1}	1.597	1.543	1.523	1.971	1.544	1.590	1.603	1.247
crystal size/ mm	0.112×0.051×0.045	0.145×0.071×0.068	0.145×0.103×0.096	0.124×0.074×0.043	0.155×0.102×0.067	0.098×0.091×0.059	0.170×0.115×0.114	0.169×0.107×0.080
F(000)	756	1448	780	322	764	350	1488	434
T/ K	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)
λ/ Å	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073
Θ range/ °	1.82–28.49	1.99–28.36	2.16–27.65	2.17–28.08	2.39–28.46	2.02–26.62	1.76–26.00	1.68–26.61
Reflns. collected	3520	3421	3572	2769	3689	3289	6861	4267
Indep. reflns.(R_{int})	2615 (0.0386)	2681 (0.0335)	3105 (0.0452)	2197 (0.0792)	3020 (0.1146)	2967 (0.0168)	4686 (0.0615)	3604 (0.0366)
Parameters	199	199	224	163	200	190	390	243
R1 (all data)	0.0313 (0.0517)	0.0277 (0.0413)	0.0250 (0.0311)	0.0454 (0.0563)	0.0746 (0.0659)	0.0256 (0.0294)	0.0468 (0.0742)	0.0309 (0.0397)
wR2	0.0632	0.0606	0.0639	0.1123	0.1957	0.0672	0.1030	0.0867
GooF	0.894	0.934	1.030	0.962	1.067	1.084	0.909	1.140

Table S1 (continued). Crystallographic data for the ligands and complexes presented in this paper.

	3-Cl	**3-SO_4**	**4-OAc**	**4-NO_3**	**5-NO_3**	**5-Cl**	**5-I**
CCDC	1566625	1566641	1566617	1566621	1566622	1566626	1566634
formula	$[CuL3Cl]_2$	$[(CuL3)_2SO_4]\cdot MeOH\cdot H_2O$	$[CuL4(OAc)]_n$	$\{[CuL4(H_2O)]\cdot NO_3\cdot H_2O\}_n$	$[(\mu\text{–}1,1\text{–}NO_3)_2(CuL5)_2]$	$[(\mu\text{–}Cl)(CuL5)]_n$	$[(\mu\text{–}I)_2(CuL5)_2]$
sum formula	$C_{28}H_{34}Cl_2Cu_2N_4O_8$	$C_{28}H_{34}Cu_2N_4O_{10}S$, CH_4O, H_2O	$C_{14}H_{15}CuN_3O_4$, $7(H_2O)$	$C_{12}H_{14}CuN_3O_3$, NO_3, H_2O	$C_{36}H_{34}Cu_2N_6O_{12}$	$C_{18}H_{17}ClCuN_2O_3$	$C_{36}H_{34}Cu_2I_2N_4O_6$
M/ g mol^{-1}	752.56	827.81	478.94	391.83	869.76	408.32	999.55
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\text{–}1$	$P2_1/c$	$P2_1/c$	$P2_1/n$	Cc	$P2_1/n$
crystal description	green block	purple plate	blue plate	blue block	blue block	green block	green plate
a/ Å	10.9871(5)	6.7842(6)	6.8193(4)	9.0597(6)	10.2653(4)	12.9059(7)	10.3415(7)
b/ Å	20.1512(12)	15.8946(15)	11.6812(6)	14.5372(7)	8.8823(4)	18.9389(13)	9.2060(4)
c/ Å	13.9510(6)	15.9754(18)	28.7206(16)	11.8354(8)	20.2634(9)	7.6909(4)	19.3186(14)
α/ °	90	93.458(9)	90	90	90	90	90
β/ °	94.232(3)	96.606(8)	95.047(4)	95.232(5)	97.713(3)	115.017(4)	98.818(5)
γ/ °	90	97.754(8)	90	90	90	90	90
V/ Å^3	3080.4(3)	1690.5(3)	2278.9(2)	1552.26(7)	1830.89(14)	1703.47(18)	1817.5(2)
Z	8	2	4	4	2	4	2
ρ_{calcd}/ g cm^{-3}	1.623	1.622	1.355	1.677	1.578	1.592	1.826
μ/ mm^{-1}	1.610	1.394	1.012	1.452	1.235	1.459	2.919
crystal size/ mm	0.179×0.112×0.094	0.157×0.095×0.086	0.177×0.158×0.132	0.150×0.109×0.083	0.163×0.136×0.134	0.142×0.110×0.090	0.130×0.102×0.075
F(000)	1544	852	948	804	892	836	980
T/ K	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)
λ/ Å	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073
Θrange/ °	1.78–28.59	1.76–28.26	1.49–26.02	2.23–28.52	2.03–28.45	2.05–28.22	2.12–28.50
Reflns. collected	7232	7952	5514	3688	4324	2498	4329
Indep. reflns.(R_{int})	4234 (0.2943)	4466 (0.2163)	3886 (0.0791)	2876 (0.0312)	3240 (0.0405)	2368 (0.0354)	3384 (0.2146)
Parameters	397	451	262	233	253	226	226
$R1$ (all data)	0.0711 (0.1126)	0.1353 (0.1789)	0.0567 (0.0824)	0.0274 (0.0410)	0.0314 (0.0487)	0.0240 (0.0260)	0.1270 (0.1413)
$wR2$	0.1847	0.3285	0.1517	0.057	0.0687	0.0544	0.3393
GooF	0.956	1.137	0.999	0.906	0.913	1.033 (Flack 0.010(12))	1.372

Table S1 (continued). Crystallographic data for the ligands and complexes presented in this paper.

	6-OAc	**6-Cl**	**6-NCS**
CCDC	1566618	1566627	1566637
formula	$[(\mu\text{–}1,1\text{–}OAc)_2(CuL6)_2]\cdot 4H_2O$	$[(\mu\text{–}Cl)_2(CuL6)_2]$	$[(CuL6)SCN]_2$
sum formula	$C_{28}H_{32}Cu_2N_4O_{10}$, $4(H_2O)$	$C_{24}H_{26}Cl_2Cu_2N_4O_6$	$C_{26}H_{26}Cu_2N_6O_6S_2$
M/ g mol^{-1}	783.72	664.46	709.73
crystal system	orthorhombic	triclinic	monoclinic
space group	*P*bca	*P*–1	$P2_1/c$
crystal description	blue needle	green block	blue needle
a/ Å	8.7017(4)	7.5941(5)	12.3364(8)
b/ Å	18.0339(11)	9.0685(6)	13.4022(11)
c/ Å	21.7086(12)	10.0399(6)	8.6223(5)
α/ °	90	90.393(5)	90
β/ °	90	96.377(5)	97.437(5)
γ/ °	90	110.150(5)	90
V/ Å^3	3406.6(3)	644.33(7)	1413.57(17)
Z	4	1	2
ρ_{calcd}/ g cm^{-3}	1.528	1.712	1.668
μ/ mm^{-1}	1.320	1.906	1.705
crystal size/ mm	0.198×0.049×0.048	0.130×0.105×0.082	0.176×0.057×0.051
F(000)	1624	338	724
T/ K	133(2)	133(2)	133(2)
λ/ Å	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073
Θ range/ °	1.88–28.46	2.05–28.44	2.26–27.48
Reflns. collected	4130	3031	3338
Indep. reflns.(R_{int})	1910 (0.0705)	2347 (0.0786)	1756 (0.0997)
Parameters	233	172	190
$R1$ (all data)	0.0343 (0.0985)	0.0470 (0.0606)	0.0551 (0.1126)
$wR2$	0.0531	0.1161	0.1208
GooF	0.728	0.942	0.857

Figure S1. ORTEP drawings of ligands **HL1** (top left), **HL4** (top right), **HL5** (bottom left), and **HL6** (bottom right). Ellipsoids were drawn at 50 % probability level.

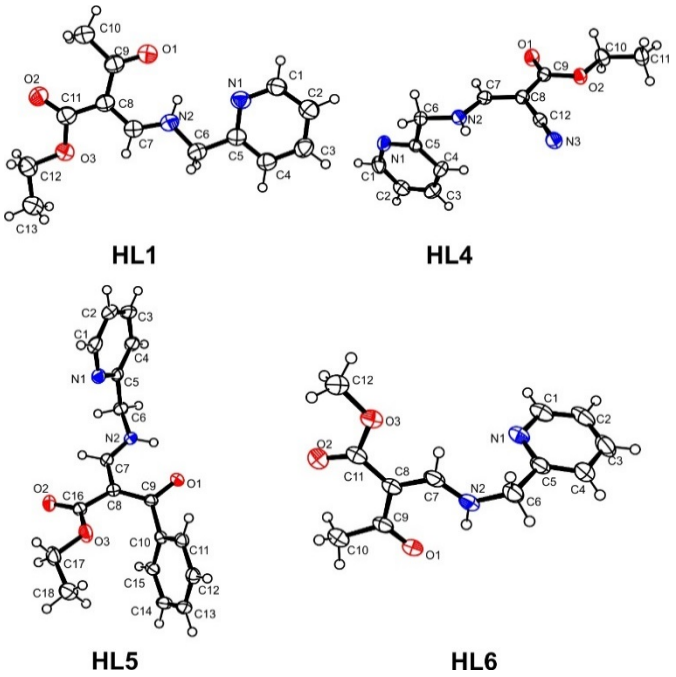

Table S2. Selected bond lengths / Å of the ligands **HL1**, **HL4**, **HL5**, and **HL6**.

	HL1	HL4	HL5	HL6
N2–C7	1.310(5)	1.3147(17)	1.312(2)	1.305(6)
C7–C8	1.391(4)	1.3805(18)	1.392(3)	1.391(4)
C8–C9	1.453(5)	1.4570(18)	1.442(3)	1.451(5)
C9–O1	1.243(4)	1.2155(16)	1.246(2)	1.245(4)

Figure S2. ORTEP drawings of **1-Cl** (top left), **1-I** (top centre), **1-OAc** (top right), **1-NCS** (middle left), **2-N_3** (middle centre), **2-Cl** (middle right), **2-NO_3** (bottom left), **3-SO_4** (bottom centre), and **4-OAc** (bottom right). Ellipsoids are drawn at 50 % probability level. Hydrogen atoms and solvent molecules (**2-N_3**, **3-SO_4**, and **4-OAc**) were omitted for clarity.

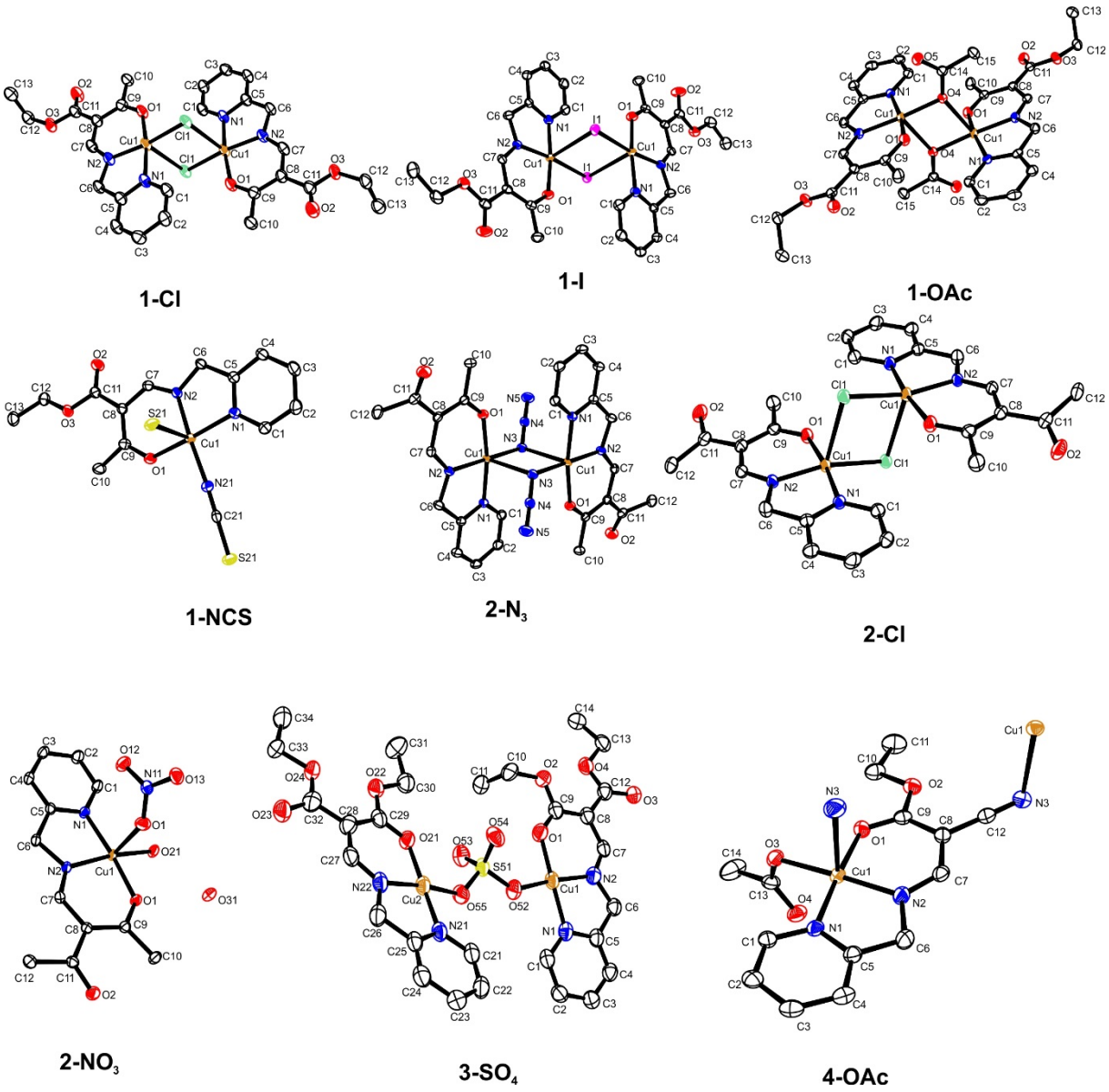

Figure S3. ORTEP drawings of **5-NO_3** (top left), **5-I** (top right), **6-OAc** (bottom left), and **6-Cl** (bottom right). Ellipsoids are drawn at 50 % probability level. Hydrogen atoms and solvent molecules (**6-OAc**) were omitted for clarity.

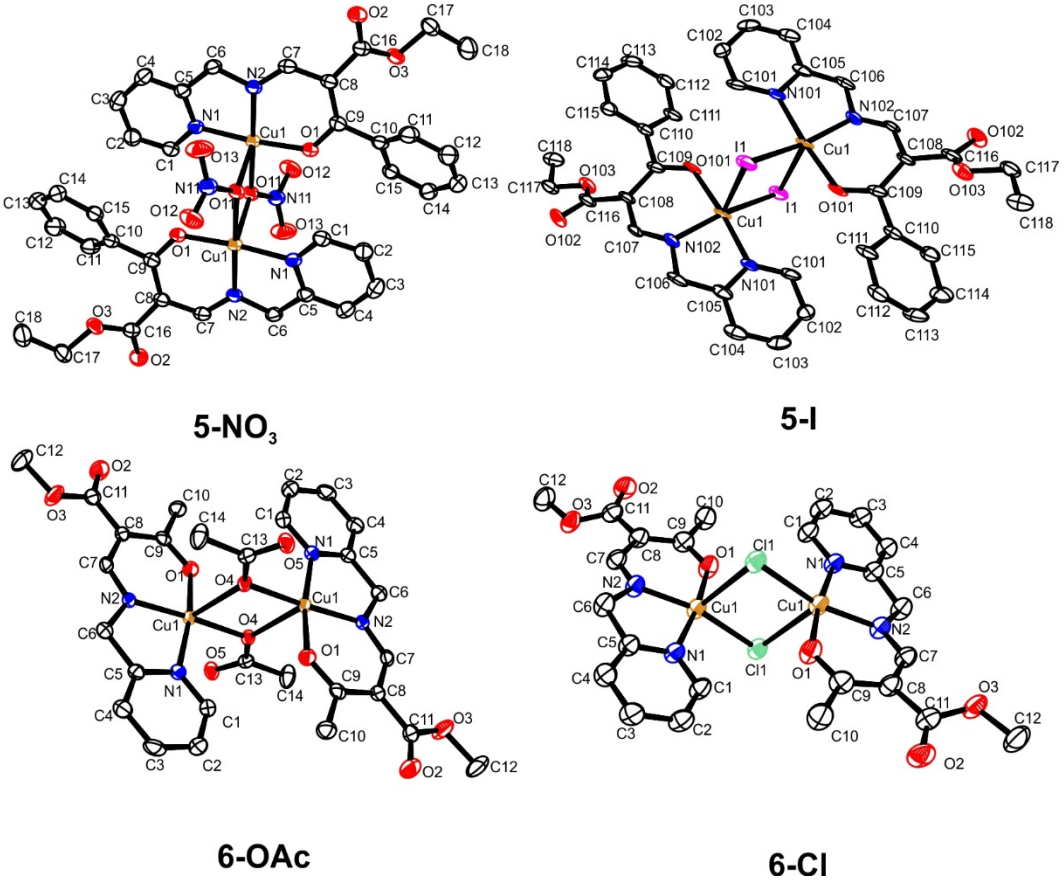

Table S3. Bond lengths/Å and angles/° of the coordination sphere of the complexes discussed in this work.

	Cu–N_{py}	Cu–N	Cu–O	Cu–X	Cu–Y	Cu–X–Cu	X–Cu–X
1-OAc	2.0052(17)	1.9255(16)	1.9411(17)	1.9549(15) 2.3542(14)	/	102.65(6)	77.35(5)
1-NO_3	1.9883(16)	1.9130(14)	1.9245(13)	2.3258(14) 2.6745(14)	/	143.39(9) 137.40(12) 121.7(2) (O–N–O)	84.54(6)
1-Cl	2.014(3)	1.925(4)	1.938(3)	2.2786(11) 2.7766(12)	/	92.81(4)	97.19(4)
1-I	2.001(2)	1.9296(18)	1.9189(18)	2.6187(4) 3.2212(4)	/	82.48(1)	97.52(1)
1-N_3	1.9918(16)	1.9278(17)	1.9103(14)	1.9745(17) 2.6005(15)	/	95.45(6)	84.55(6)
1-NCS	1.9995(18)	1.9162(19)	1.9296(16)	1.9420(19) (N) 2.9063(7) (S)	/	/	/
2-NO_3	1.9795(13)	1.9191(13)	1.9136(11)	2.3620(13)	1.9690(12) (H_2O)	/	/
2-Cl	1.999(3)	1.926(3)	1.929(3)	2.2907(9) 2.7953(10)	/	92.79(3)	87.21(3)
2-N_3	1.9973(14)	1.9233(15)	1.9266(12)	1.9868(15) 2.5097(15)	/	96.16(6)	83.84(6)
2-NCS	2.001(3)	1.920(3)	1.936(3)	1.944(4)	2.358(3) (MeOH)	/	/
2-SO_4	1.998(3) 1.990(3)	1.901(3) 1.920(3)	1.910(3) 1.926(3)	1.928(2) 1.955(3)	2.409(3) (Cu2, MeOH)	/	/
3-OAc	2.0084(18)	1.9213(18)	1.9562(15)	1.9436(17) 2.3516(17)	/	104.07(8)	75.93(7)
4-OAc	1.985(3)	1.919(3)	1.950(2)	1.962(2)	2.668(3) (–CN)	/	/
4-NO_3	1.9964(15)	1.9366(15)	1.9725(13)	/	2.2064(14) (H_2O) 1.9828(15) (–CN)	/	/
5-NO_3	1.9764(17)	1.9112(16)	1.9081(14)	1.9836(14) 2.3997(15)	/	104.59(6)	75.41(5)
5-Cl	2.030(3)	1.930(3)	1.944(2)	2.2539(8) 2.8230(9)	/	101.41(3)	102.43(3)
6-OAc	1.996(3)	1.920(3)	1.941(2)	1.9560(18) 2.3814(17)	/	105.93(8)	74.07(7)
6-Cl	2.004(3)	1.926(3)	1.932(2)	2.2844(9) 2.7709(11)	/	93.44(3)	86.56(3)
6-NCS	1.998(4)	1.916(4)	1.944(3)	1.940(5)	2.692(4) (–COOMe)	/	/

Table S4. Summary of the C–H···π / X–Y···π interactions of the ligands and complexes presented in this work.

		C_g	H···C_g/Å Y···C_g/Å	X–H···C_g/° X–Y···C_g/°	X···C_g/Å
HL1	C3–H3	N1–C1–C2–C3–C4–C5[a]	2.96	106	3.345(4)
HL5	C4–H4	C10–C11–C12–C13–C14–C15[b]	2.70	134	3.4289(3)
	C12–H12	N1–C1–C2–C3–C4–C5[c]	2.87	130	3.5592(3)
1-OAc	C6–H6A	Cu1–O1–C9–C8–C7–N2[d]	2.96	104	3.012(2)
1-NO_3	C6–H6A	Cu1–O1–C9–C8–C7–N2[e]	2.62	145	3.4855(18)
	C12–H12B	Cu1–O1–C9–C8–C7–N2[f]	2.59	154	3.513(2)
1-N_3	C12–H12A	N1–C1–C2–C3–C4–C5[g]	2.89	166	3.855(2)
1-NCS	C6–H6B	Cu1–O1–C9–C8–C7–N2[h]	2.65	150	3.549(3)
	C11–O2	N1–C1–C2–C3–C4–C5[h]	3.306(2)	96.01(14)	3.642(3)
2-Cl	C12–H12C	Cu1–O1–C9–C8–C7–N2[i]	2.93	139	3.725(4)
2-N_3	C10–H10B	Cu1–O1–C9–C8–C7–N2[j]	2.73	129	3.424(2)
2-NCS	C10–H10B	N1–C1–C2–C3–C4–C5[k]	2.77	91	2.917(3)
2-SO_4	C20–H20B	N11–C11–C12–C13–C14–C15[l]	2.61	137	3.391(4)
	C20–H20C	Cu2–O31–C39–C38–C37–N32[m]	2.69	118	3.260(4)
	C36–H36B	Cu1–O11–C19–C18–C17–N12[m]	2.70	123	3.349(4)
5-NO_3	C2–H2	C10–C11–C12–C13–C14–C15[n]	2.97	114	3.464(3)
5-Cl	C2–H2	C10–C11–C12–C13–C14–C15[o]	2.85	142	3.641(4)
	C11–H11	N1–C1–C2–C3–C4–C5[p]	2.61	129	3.288(4)
6-OAc	C6–H6A	Cu1–O1–C9–C8–C7–N2[q]	2.82	129	3.526(3)
	C12–H12C	Cu1–O1–C9–C8–C7–N2[r]	2.69	140	3.504(3)
6-NCS	C12–H12B	N1–C1–C2–C3–C4–C5[s]	2.83	130	3.520(7)

a: −1/2+x, 1/2−y, z; b: 2−x, −y, 1−z; c: 1−x, −y, 1−z; d: 2−x, 2−y, 1−z; e: −x, −y, −z; f: 1/2−x, 1/2−y, −z; g: 1/2−x, 1/2−y, 1−z; h: 1−x, −y, 1−z; i: 2−x, 1−y, 3−z; j: 2−x, 2−y, 1−z; k: 1/2−x, −1/2+y, 3/2−z; l: −x, −y, 1−z; m: x, y, z; n: −x, 1−y, 1−z; o: −1/2+x, 1/2+y, −1+z; p: x, −y, 1/2+z; q: 1−x, −y, −z; r: 1−x, 1−y, 1−z; s: 1−x, −1/2+y, −1/2−z.

Table S5. Selected distances and angles of the π– π and M– π interactions of the ligands and complexes presented in this work. $C_g(I)$ is the centroid of the ring number I, α is the dihedral angle between the rings, β is the angle between the vector $C_g(I) \rightarrow C_g(J)$ and the normal to ring I, γ is the angle between the vector $C_g(I) \rightarrow C_g(J)$ and the normal to ring J.

	$C_g(I)$	$C_g(J)$	C_g–C_g/Å	α/°	β/°	γ/°
HL4	N1–C1–C2–C3–C4–C5	N1–C1–C2–C3–C4–C5[a]	3.8849(9)	0.03(7)	19.2	19.2
1-Cl	Cu1–O1–C9–C8–C7–N2	Cu[b]	3.988	0	12.05	0
1-I	Cu1–O1–C9–C8–C7–N2	Cu[c]	3.621	0	17.21	0
1-N_3	Cu1–O1–C9–C8–C7–N2	Cu1–O1–C9–C8–C7–N2[d]	3.9849(9)	0.00(6)	31.4	31.4
	Cu1–O1–C9–C8–C7–N2	Cu[d]	3.505	0	6.47	0
2-NO_3	Cu1–O1–C9–C8–C7–N2	Cu[e]	3.481	0	10.58	0
2-Cl	N1–C1–C2–C3–C4–C5	N1–C1–C2–C3–C4–C5[f]	3.673(2)	0.00(18)	22.9	22.9
	Cu1–O1–C9–C8–C7–N2	N1–C1–C2–C3–C4–C5[g]	3.923(2)	1.75(15)	28.7	27.4
2-N_3	Cu1–O1–C9–C8–C7–N2	Cu1–O1–C9–C8–C7–N2[h]	3.8157(9)	0.02(6)	24.5	24.5
	Cu1–O1–C9–C8–C7–N2	Cu[h]	3.544	0	7.16	0
2-NCS	Cu1–O1–C9–C8–C7–N2	Cu[i]	3.560	0	28.35	0
2-SO_4	Cu1–O11–C19–C18–C17–N12	Cu2–N31–C35–C36–N32[i]	3.3578(19)	14.64(14)	9.8	22.8
	Cu1–O11–C19–C18–C17–N12	Cu1[j]	3.234	0	3.84	0
	N31–C31–C32–C33–C34–C35	Cu1[i]	3.461	0	27.33	0
3-OAc	N1–C1–C2–C3–C4–C5	Cu1–O1–C9–C8–C7–N2[k]	3.7700(14)	10.90(11)	30.5	21.4
4-NO_3	N1–C1–C2–C3–C4–C5	Cu[l]	3.823	0	19.87	0
5-NO_3	Cu1–N1–C5–C6–N2	N1–C1–C2–C3–C4–C5[m]	3.5718(11)	1.19(9)	10.2	9.5
5-Cl	Cu1–O1–C9–C8–C7–N2	Cu1–O1–C9–C8–C7–N2[n]	3.8568(17)	11.24(13)	27.7	25.8
	Cu1–O1–C9–C8–C7–N2	Cu[n]	3.493	0	2.29	0
6-NCS	N1–C1–C2–C3–C4–C5	N1–C1–C2–C3–C4–C5[o]	3.599(3)	0.0(2)	25.9	25.9

a: −x, −y, 1−z; b: −x, −y, 1−z; c: 2−x, 1−y, 1−z; d: 1/2−x, 1/2−y, 1−z; e: 1−x, −y, 1−z; f: 1−x, −y, 2−z; g: 2−x, 1−y, 2−z; h: 2−x, 2−y, 1−z; i: x, y, z; j: −x, −y, 1−z; k: 1−x, −y, 1−z; l: −x, −y, 1−z; m: −x, −y, 1−z; n: x, −y, 1/2+z; o: −x, −y, −1−z.

Table S6. Hydrogen bonds and angles of ligands and complexes presented in this work.

	Donor	Acceptor	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
HL1	N2–H2	O1	0.88	1.98	2.622(4)	129
	N2–H2	N1	0.88	2.28	2.677(5)	107
	C2–H2A	O1[a]	0.95	2.53	3.236(5)	131
	C4–H4	O2[b]	0.95	2.44	3.266(5)	145
HL4	N2–H2A	N3[c]	0.88	2.14	2.9884(16)	162
	C4–H4	N2	0.95	2.56	2.884(2)	100
	C6–H6A	O1[d]	0.99	2.48	3.2701(16)	137
	C7–H7	O1[d]	0.95	2.38	3.2656(17)	155
HL5	N2–H2A	O1	0.88	2.04	2.6730(3)	128
	N2–H2A	O1[e]	0.88	2.24	2.9878(3)	143
	C2–H2B	O2[f]	0.95	2.46	3.3505(3)	156
	C11–H11	O1[g]	0.95	2.48	3.4256(3)	172
HL6	N2–H2	O1	0.88	2.02	2.650(4)	128
	N2–H2	O1[h]	0.88	2.28	3.012(5)	141
	C6–H6A	O1[i]	0.99	2.53	3.340(6)	139
	C6–H6B	N1[j]	0.99	2.58	3.414(6)	142
1-OAc	C2–H2	O2[k]	0.95	2.34	3.279(3)	115
	C6–H6A	O5[k]	0.99	2.52	3.305(2)	168
	C6–H6B	O5[l]	0.99	2.48	3.280(3)	137
	C7–H7	O5[k]	0.95	2.56	3.349(2)	141
1-NO_3	C6–H6A	O12[m]	0.99	2.56	3.179(2)	121
	C7–H7	O12[m]	0.95	2.37	3.179(2)	142
1-Cl	C3–H3	Cl[n]	0.95	2.73	3.535(5)	143
	C6–H6A	Cl[o]	0.99	2.71	3.552(5)	143
	C12–H12B	Cl[p]	0.99	2.81	3.406(4)	119
1-I	C4–H4	O2[q]	0.95	2.55	3.317(3)	138
	C6–H6A	O2[q]	0.99	2.57	3.321(3)	133
1-N_3	C6–H6B	N5[r]	0.99	2.59	3.497(3)	153
	C13–H13B	N5[s]	0.98	2.60	3.516(3)	155
1-NCS	C4–H4	O2[t]	0.95	2.44	3.255(3)	143
	C13–H13C	S21[u]	0.98	2.82	3.580(3)	135

a: −x, 1−y, −z; b: 1/2−x, −1/2+y, 1−z; c: 1−x, 1−y, −z; d: 1−x, 1−y, 1−z; e: 2−x, −y, 1−z; f: 1−x, −y, 1−z; g: 1−x, 1−y, 1−z; h: 3/2−x, 3/2−y, 1−z; i: 3/2−x, 1/2−y, 1−z; j: x, −1+y, z; k: 2−x, 1/2+y, 1/2−z; l: −1+x, y, z; m: −x, −y, −z; n: x, 1+y, z; o: −x, −y, 1−z; p: −1+x, y, −1+z; q: 2−x, −1/2+y, 3/2−z; r: 1/2−x, 1/2−y, 1−z; s: −1/2+x, 1/2−y, 1−z; t: 2−x, −y, 1−z; u: 3/2+x, 1/2−y, −1/2+z.

Table S7. Hydrogen bonds and angles of complexes presented in this work.

	Donor	Acceptor	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
2-NO_3	O21–H21A	O31	0.775(19)	1.865(19)	2.6366(18)	173(3)
	O21–H21B	O2[a]	0.79(3)	1.93(3)	2.7355(16)	167(3)
	O31–H31A	O13[b]	0.75(3)	2.06(3)	2.8033(19)	170(2)
	O31–H31B	O11[c]	0.82(3)	2.06(3)	2.8385(18)	160(3)
	C1–H1	O2[a]	0.95	2.48	3.430(2)	177
	C6–H6A	O12[d]	0.99	2.56	3.2213(19)	124
	C7–H7	O12[d]	0.95	2.48	3.3396(19)	150
2-Cl	C2–H2	O2[e]	0.95	2.45	3.242(5)	140
	C3–H3	Cl1[f]	0.95	2.79	3.542(4)	137
	C6–H6A	O2[g]	0.99	2.82	3.350(5)	143
	C6–H6B	Cl1[h]	0.99	2.82	3.668(4)	144
2-N_3	C3–H3	O2[i]	0.95	2.53	3.266(2)	134
	C4–H4	N5[j]	0.95	2.55	3.251(2)	131
	C6–H6B	O2[k]	0.99	2.51	3.405(2)	151
2-NCS	O21–H21	O2[l]	0.84	1.91	2.742(4)	173
2-SO_4	O60–H60	O54[m]	0.84	1.85	2.682(5)	171
	O70–H70	O53[n]	0.84	1.95	2.765(6)	164
	C11–H11	O70[o]	0.95	2.33	3.190(6)	150
	C13–H13	O12[p]	0.95	2.41	3.320(6)	159
	C14–H14	O31[n]	0.95	2.58	3.522(4)	171
	C16–H16A	O52[n]	0.99	2.33	3.275(4)	159
	C22–H22C	O70	0.98	2.42	3.294(9)	148
	C32–H32	O32[p]	0.95	2.49	3.382(5)	156
	C34–H34	O54[n]	0.95	2.57	3.511(5)	116
3-OAc	O31–H31A	O22	0.75(5)	2.12(5)	2.857(3)	167(5)
	O31–H31B	O3[q]	0.76(5)	2.25(5)	2.983(3)	164(5)
	C6–H6B	O22[r]	0.99	2.52	3.297(3)	135
	C10–H10A	O3[s]	0.99	2.53	3.335(3)	138

a: 1−x, 1/2+y, 1/2−z; b: −1+x, y, z; c: 1−x, −y, −z; d: 2−x, −y, 1−z; e: −1+x, −1+y, −1+z; f: x, −1+y−1+z; g: 2−x, 1−y, 3−z; h: 2−x, 1−y, 2−z; i: −1+x, −1+y, −1+z; j: x, y, −1+z; k: 2−x, 3−x, 1−z; l: 1/2−x, 1/2+y, 3/2−z; m: x, 1/2−y, 1/2+z; n: −x, −1/2+y, 3/2−z; o: −x, 1/2+y, 3/2−z; p: −1+x, y, z; q: 1+x, y, z; r: 1−x, −y, 1−z; s: 1−x, 1−y, 2−z.

Table S8. Hydrogen bonds and angles of complexes presented in this work.

	Donor	Acceptor	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
4-OAc	C2–H2	N3[a]	0.95	2.53	3.248(5)	133
	C3–H3	O22	0.95	2.45	3.274(5)	145
4-NO_3	O31–H31A	O32	0.76(3)	2.01(3)	2.745(2)	164(3)
	O31–H31B	O22[b]	0.75(3)	2.08(3)	2.818(2)	170(3)
	O32–H32A	O22[c]	0.79(3)	2.09(3)	2.879(3)	171(3)
	O32–H32B	O23	0.79(3)	2.14(3)	2.881(3)	158(3)
	C2–H2	O22[d]	0.95	2.55	3.426(3)	153
5-NO_3	C4–H4	O12[e]	0.95	2.54	3.325(3)	140
	C6–H6B	O2[f]	0.99	2.59	3.405(2)	140
	C7–H7	O2[f]	0.95	2.48	3.338(2)	150
5-Cl	C3–H3	O2[g]	0.95	2.31	3.050(4)	135
	C13–H13	Cl1[h]	0.95	2.82	3.682(4)	151
6-OAc	O21–H21A	O2[i]	0.73(5)	2.12(5)	2.845(4)	173(5)
	O21–H21B	O31[j]	0.78(5)	1.95(5)	2.729(4)	175(5)
	O31–H31A	O21[k]	0.72(3)	2.07(4)	2.781(4)	170(4)
	O31–H31B	O5	0.80(4)	2.01(4)	2.800(3)	174(4)
	C2–H2	O21	0.95	2.52	3.460(4)	168
	C3–H3	O5[l]	0.95	2.40	3.319(4)	163
	C7–H7	O5[m]	0.95	2.46	3.281(3)	145
6-Cl	C3–H3	Cl1[n]	0.95	2.75	3.500(4)	137
	C6–H6B	Cl1[o]	0.99	2.67	3.546(4)	148

a: x, 1+y, z; b: 1−x, −1/2+y, 3/2−z; c: x, 1/2−y, 1/2+z; d: 1−x, −y, 1−z; e: −x, −y, 1−z; f: 1−x, −y, 1−z; g: −1/2+x, 1/2+y, −1+z; h: 1/2+x, −1/2−y, 1/2+z; i: 1/2−x, −y, −1/2+z; j: −x, 1/2+y, −1/2−z; k: 1/2−x, −1/2+y, z; l: 1/2−x, 1/2+y, z; m: 1−x, −y, −z; n: x, −1+y, z; o: 2−x, 1−y, −z.

Figure S4. Powder X-ray diffraction spectra of **1-OAc**, **1-NO$_3$**, **1-Cl**, **2-Cl**, and **3-OAc**. Spectra were recorded at room temperature, the calculated spectra were obtained from the crystal data (133 K).

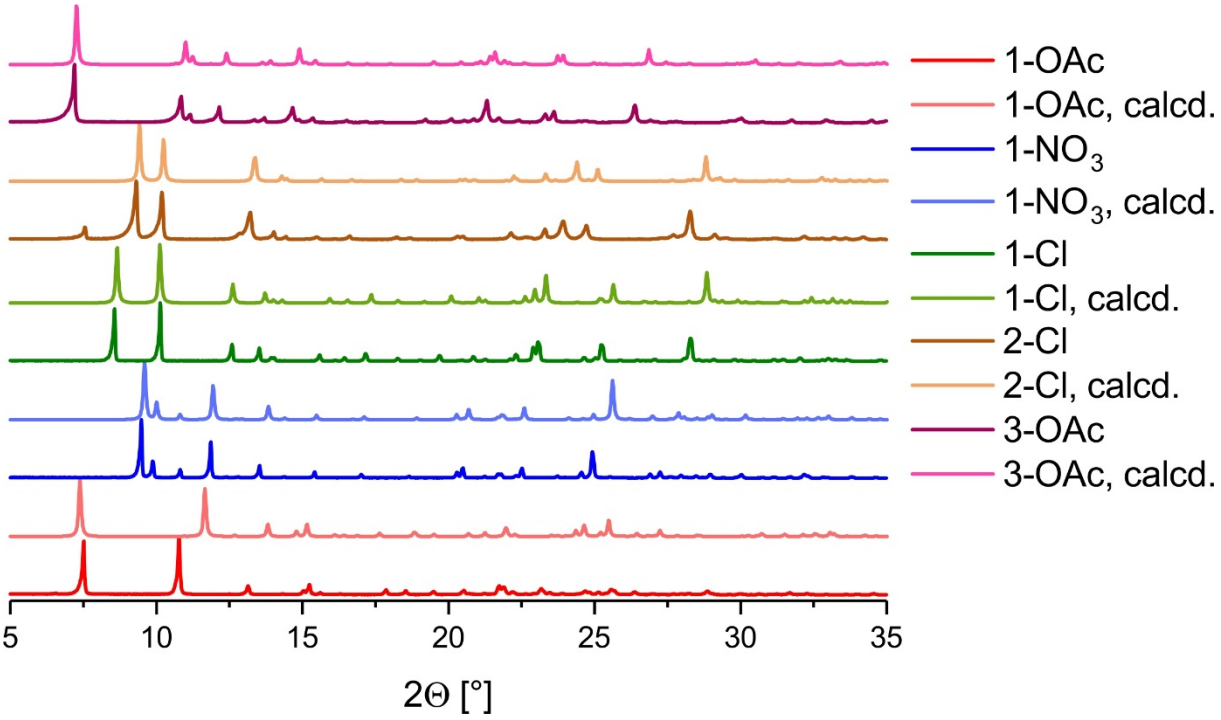

Figure S5. Powder X-ray diffraction spectra **5-NO$_3$**, **5-Cl**, **5-I**, **6-OAc**, and **6-Cl**. Spectra were recorded at room temperature, the calculated spectra were obtained from the crystal data (133 K).

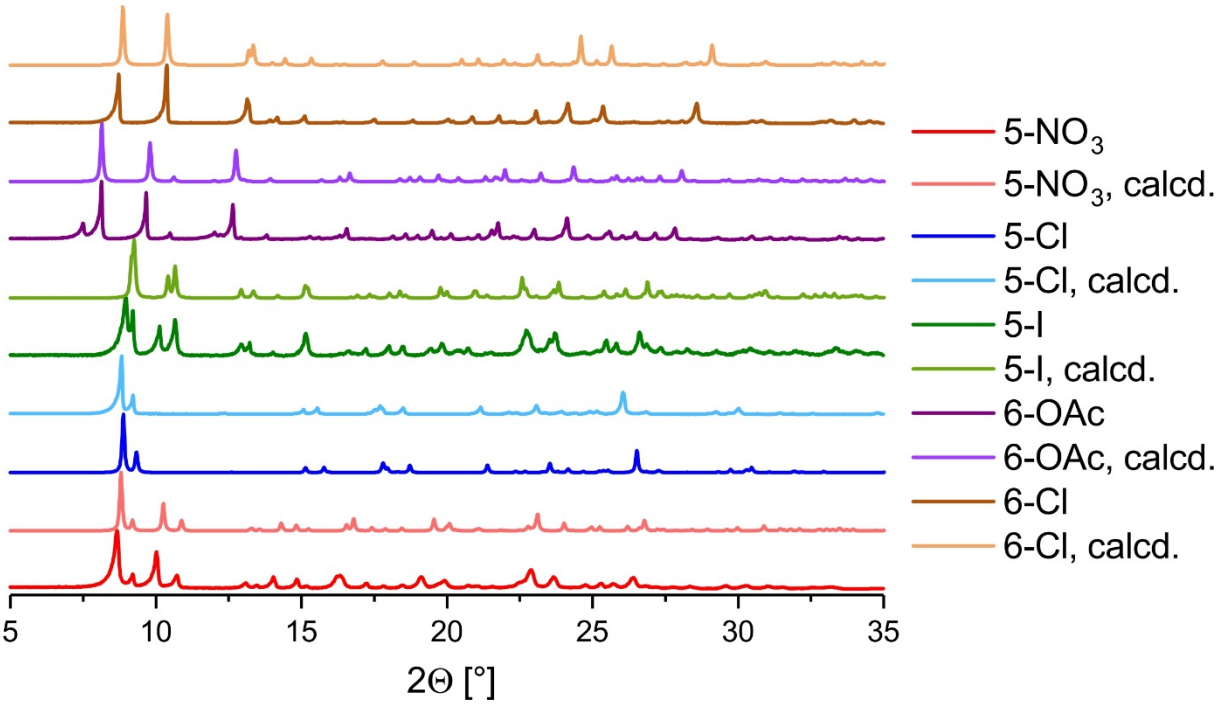

Table S9. Data of the magnetic measurements with μ_{eff} at 300 K, and $\chi_M T$ at 300 K, 50 K, and, if measured, 2 K.

	μ_{eff} [μ_B] (300 K)	$\chi_M T$ [$cm^3K^{-1}mol^{-1}$] (300 K)	$\chi_M T$ [$cm^3K^{-1}mol^{-1}$] (50 K)	$\chi_M T$ [$cm^3K^{-1}mol^{-1}$] (2 K)
1-OAc	2.95	1.09	0.88	0.39
1-NO_3	2.71	0.92	0.16	0.01
1-Cl	2.95	1.08	0.91	0.68
1-NCS	2.00	0.50	0.42	
2-OAc	2.07	0.54	0.40	
2-NO_3	2.23	0.62	0.50	
2-Cl	2.89	1.05	0.89	0.78
2-NCS	2.12	0.56	0.46	
3-OAc	3.18	1.27	0.95	0.20
3-NO_3	2.13	0.57	0.45	
3-Cl	2.92	1.06	0.92	
3-NCS	2.02	0.51	0.43	
4-OAc	2.17	0.59	0.47	
4-NO_3	2.10	0.55	0.44	0.41
4-Cl	2.03	0.51	0.44	
4-NCS	2.05	0.53	0.44	
5-OAc	2.07	0.53	0.43	
5-NO_3	2.81	0.99	0.88	1.01
5-Cl	2.04	0.52	0.46	0.69
5-I	3.18	1.26	0.86	0.14
5-NCS	2.15	0.58	0.45	
6-OAc	2.99	1.12	0.91	0.40
6-NO_3	2.17	0.59	0.48	
6-Cl	2.84	1.01	0.89	1.08
6-NCS	2.88	1.03	0.87	

Figure S6. Plots of the $\chi_M T$ product *vs*. *T* for complexes **1-OAc** (top left), **1-Cl** (top right), **1-NCS** (middle left), **2-OAc** (middle right), **2-NO_3** (bottom left), and **2-Cl** (bottom right). The data points are black squares, the red line corresponds to the fit.

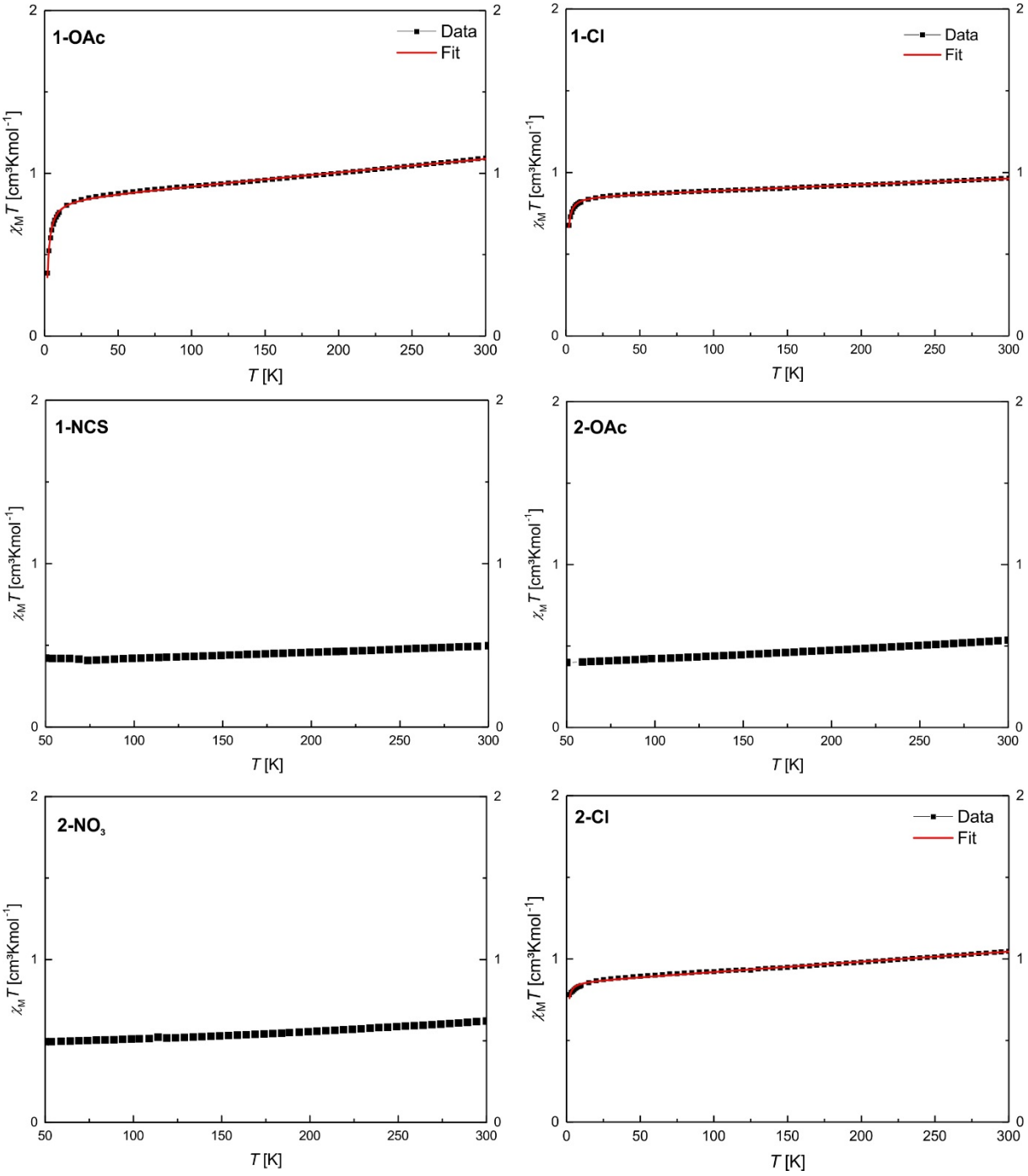

Figure S7. Plots of the $\chi_M T$ product *vs*. *T* for complexes **2-NCS** (top left), **3-OAc** (top right), **3-NO$_3$** (middle left), **3-Cl** (middle right), **3-NCS** (bottom left), and **4-OAc** (bottom right). The data points are black squares, the red line corresponds to the fit.

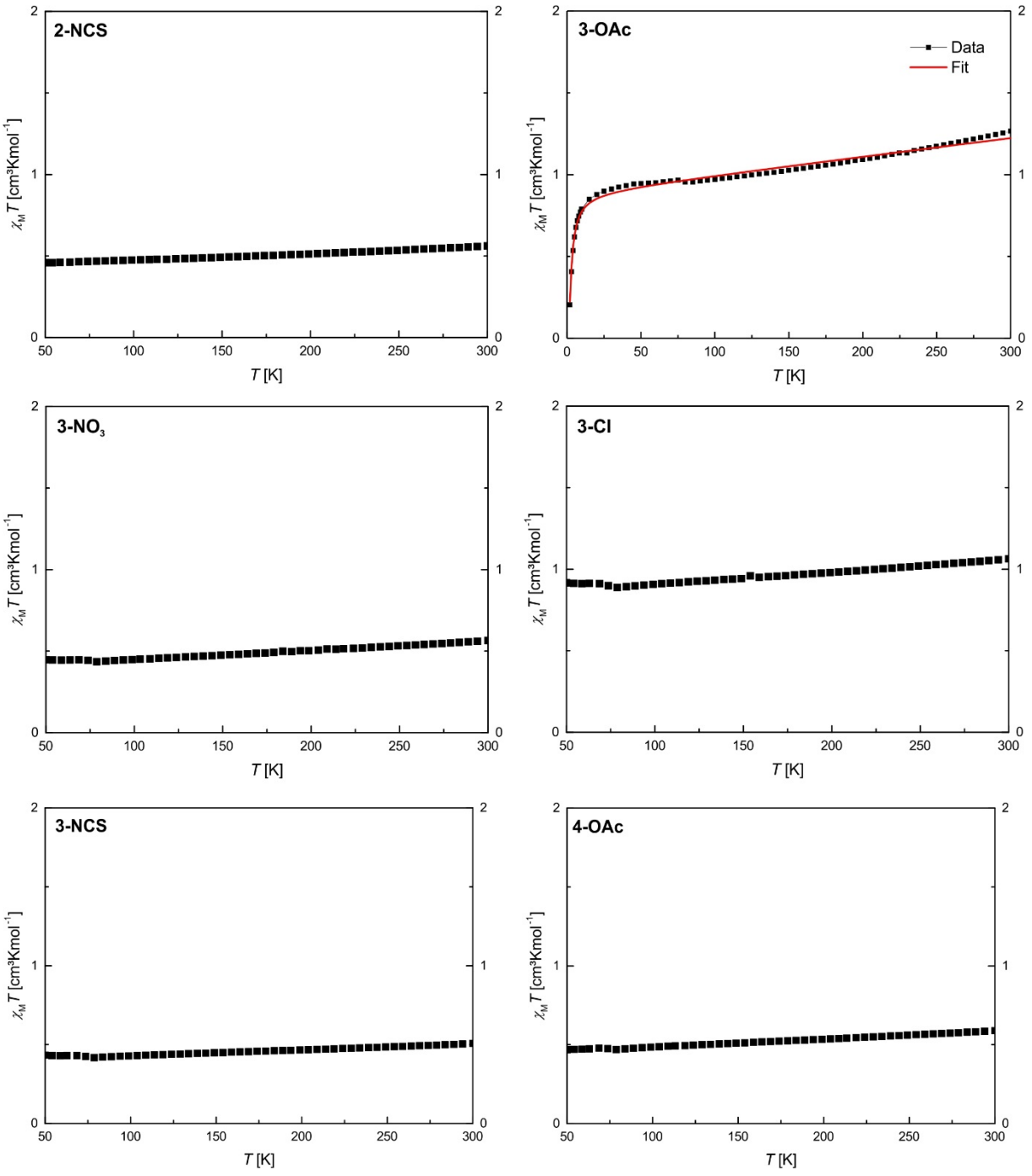

Figure S8. Plots of the $\chi_M T$ product *vs*. *T* for complexes **4-NO$_3$** (top left), **4-Cl** (top right), **4-NCS** (middle left), **5-OAc** (middle right), **5-NO$_3$** (bottom left), and **5-Cl** (bottom right). The data points are black squares, the red lines corresponds to the fit.

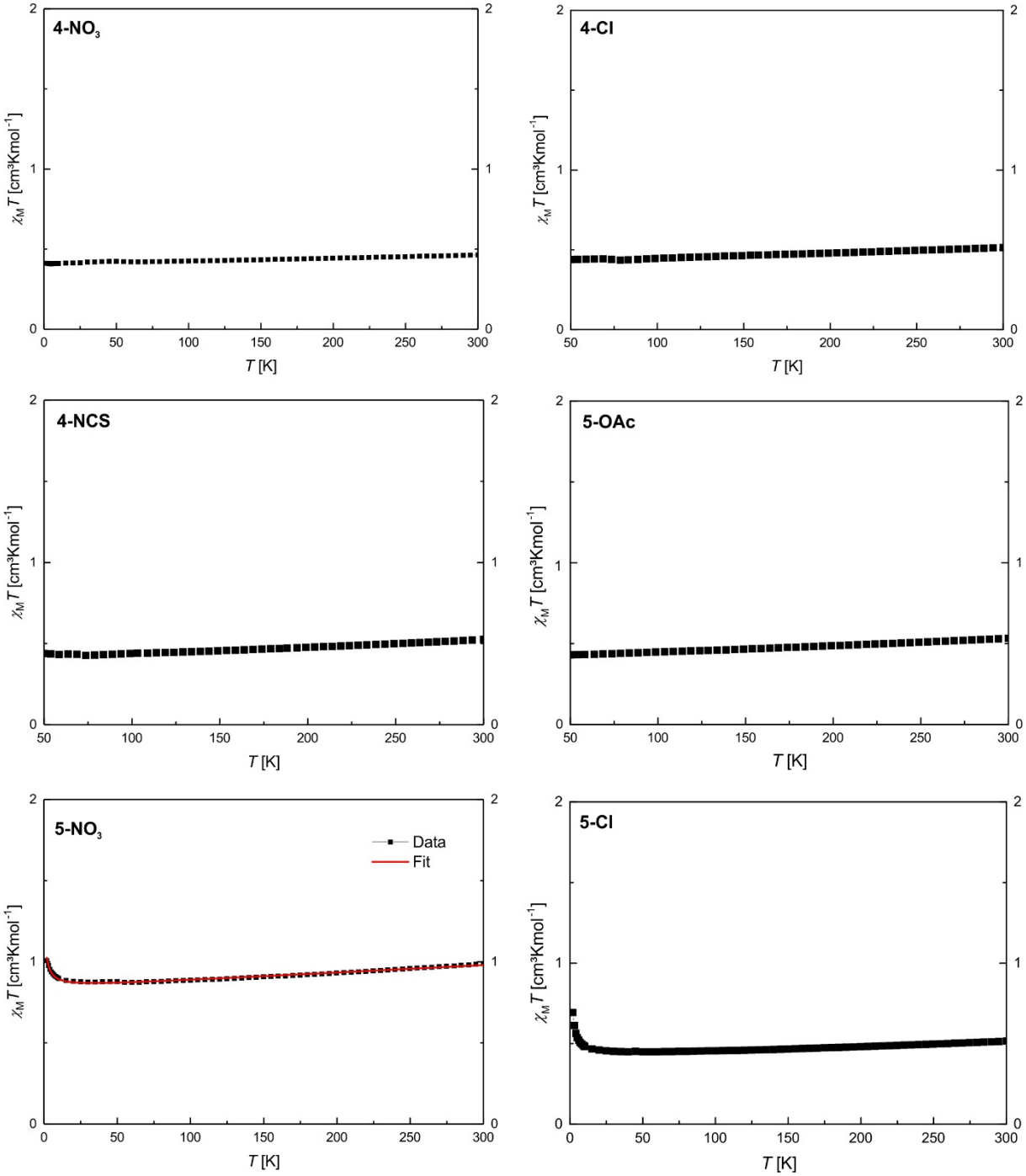

Figure S9. Plots of the $\chi_M T$ product *vs*. *T* for complexes **5-I** (top left), **5-NCS** (top right), **6-OAc** (middle left), **6-NO_3** (middle right), **6-CL** (bottom left), and **6-NCS** (bottom right). The data points are black squares, the red line corresponds to the fit.

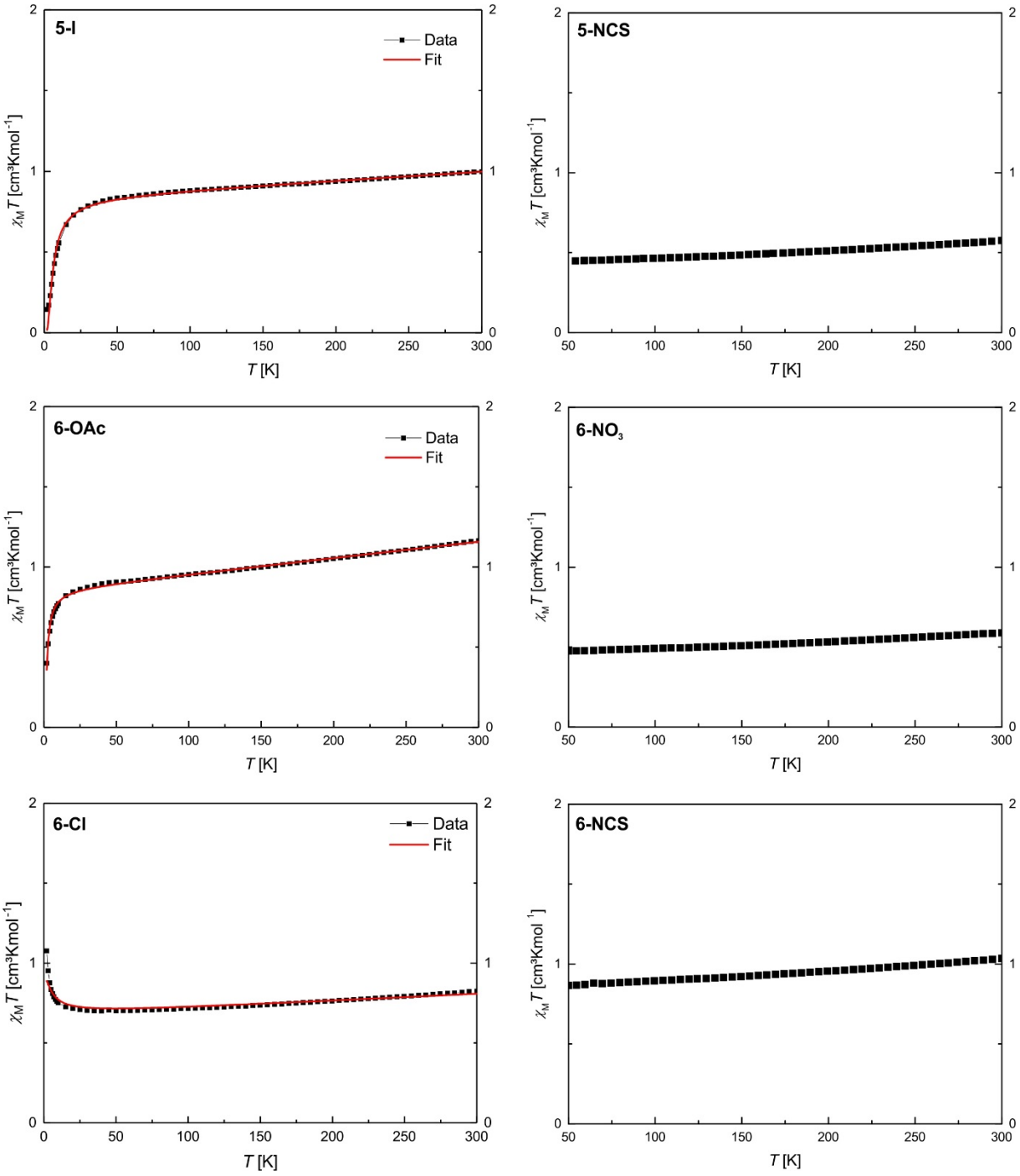

Figure S10. Curie-plot of **4-NO_3**.