Discovery of thirteen cobalt(II) and copper(II) salicylaldehyde Schiff-bases complexes that induces apoptosis and autophagy in human lung adenocarcinoma A549/DDP cells, overcoming cisplatin-resistant *in vitro* and *in vivo*

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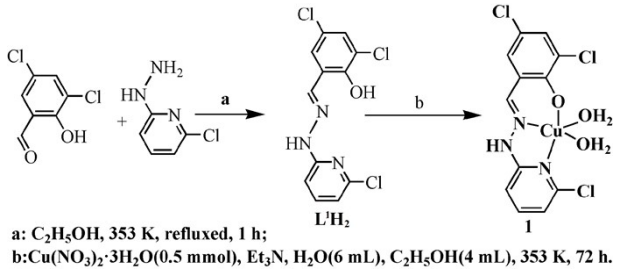
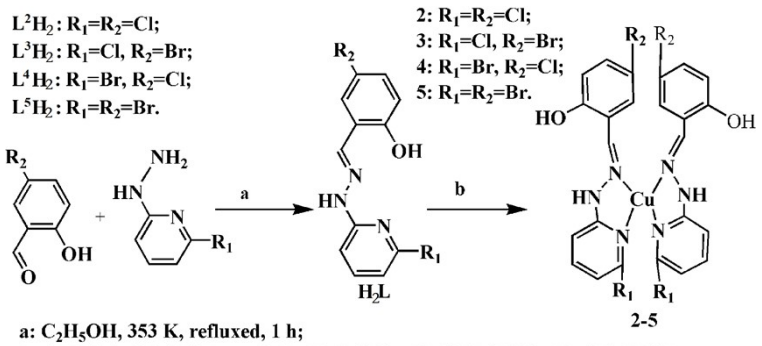
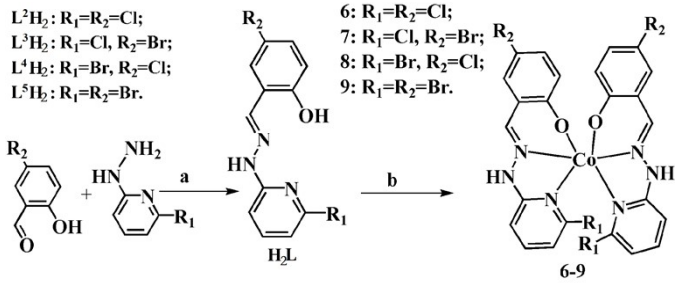


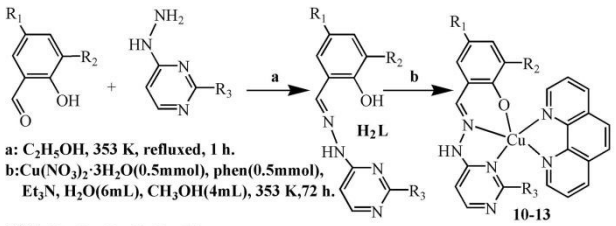
Scheme S1. Synthesis routes for **1**.



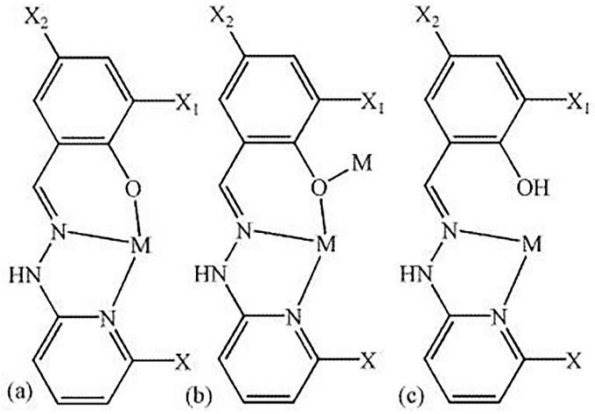
Scheme S2. Synthesis routes for **2**–**5**.



Scheme S3. Synthesis routes for **6**–**9**.



Scheme S4. Synthesis routes for **10**–**13**.



Scheme S5. Coordination modes of the Schiff base ligands.

Table S1. Crystallographic data for **1-9.**

Complexes	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Chemical Formula	$C_{12}H_{13}Cl_3CuN_4O_7$	$C_{24}H_{22}Cl_4CuN_7O_7$	$C_{24}H_{22}Br_2Cl_2CuN_7O_7$	$C_{24}H_{22}Br_2Cl_2CuN_7O_7$	$C_{24}H_{22}Br_4CuN_7O_7$	$C_{48}H_{33}Cl_8Co_2N_{12}O_{4.5}$	$C_{48}H_{33}Br_4Cl_4Co_2N_{12}O_{4.5}$	$C_{97}H_{68}Br_8Cl_8Co_4N_{24}O_9$	$C_{97}H_{68}Br_{16}Co_4N_{24}O_9$
MW ($g \cdot mol^{-1}$)	495.16	725.84	814.74	814.74	903.64	1251.32	1429.12	2872.27	3227.87
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	*C*2/*c*	*I*2	*I*2	*C*2	*C*2	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$
a (Å)	20.398(2)	21.242(1)	22.667(1)	23.057(3)	23.291(2)	10.090(1)	10.067(1)	10.247(1)	10.305(1)
b (Å)	14.198(1)	7.120(1)	7.210(1)	7.219(1)	7.289(1)	12.348(1)	12.285(1)	13.434(1)	13.617(1)
c (Å)	13.639(1)	22.406(1)	21.144(1)	22.309(2)	22.583(2)	13.279(1)	13.517(1)	20.930(1)	21.171(1)
α (°)	90.00	90.00	90.00	90.00	90.00	63.24(1)	63.38(1)	88.404(4)	89.131(4)
β (°)	113.84(1)	115.88(1)	115.48(1)	123.60(2)	124.60(1)	71.90(1)	71.62(1)	80.376(4)	80.042(4)
γ (°)	90.00	90.00	90.00	90.00	90.00	78.89(1)	79.00(1)	79.353(4)	78.773(5)
V ($Å^3$)	3612.8(4)	3049.1(3)	3119.3(3)	3092.9(8)	3155.9(5)	1401.4(2)	1415.7(2)	2791.8(2)	2869.5(3)
F(000)	1992	1472	1616	1616	1760	631	703	1414	1558
Z	8	4	4	4	4	1	1	1	1
D_c ($g\ cm^{-3}$)	1.821	1.581	1.735	1.750	1.902	1.483	1.676	1.708	1.868
μ (mm^{-1})	1.698	1.121	3.487	3.516	5.809	1.027	3.650	3.703	6.202
θ range (°)	3.34-25.01	3.40-26.50	3.36-25.10	3.36-25.10	3.29-25.01	3.37-25.10	3.49-25.10	3.34-25.10	3.33-25.01
Ref. meas. / indep.	12202, 3178	10307, 5920	10066, 5079	9684, 4880	10157, 4447	8796, 4975	9727, 4941	18233, 9651	18226, 10024
Obs. ref.[$I > 2\sigma(I)$]	2683	3929	3710	3065	3499	4294	3815	7293	6983
R_{int}	0.0329	0.0334	0.0325	0.0473	0.0294	0.0136	0.0269	0.0251	0.0298
R_1 [$I \geq 2\sigma(I)$] [a]	0.0361	0.0586	0.0439	0.0661	0.0544	0.0521	0.0544	0.0426	0.0482
ωR_2(all data)[b]	0.1188	0.1462	0.1021	0.2065	0.1592	0.1418	0.1380	0.1179	0.1197
Goof	1.007	1.056	1.007	1.003	1.007	1.001	0.991	1.001	1.005

$\Delta\rho$(max, min)(e Å^{-3})	0.403, -0.422	0.665, -0.597	0.529, -0.545	0.902, -0.826	0.935, -0.576	1.462, -0.803	1.936, -1.464	0.902, -0.503	1.485, -0.682

Table S2. Crystallographic data for **10-13.**

Complexes	**10**	**11**	**12**	**13**
Chemical Formula	$C_{93}H_{62}Br_4Cl_2Cu_4N_{24}O_5$	$C_{100}H_{98}Cu_4N_{24}O_{21}$	$C_{103.94}H_{99.82}Cl_{1.06}Cu_4N_{24}O_{17.44}$	$C_{70}H_{63}Cl_3Cu_3N_{18}O_{11}$
M_W (g·mol^{-1})	2240.37	2226.22	2256.00	1629.38
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P2_1/c$
a (Å)	12.923(1)	16.369(1)	10.256(1)	20.591(1)
b (Å)	13.303(1)	19.839(1)	15.040(1)	12.324(1)
c (Å)	14.076(1)	17.318(1)	17.018(1)	28.485(1)
α (°)	85.644(4)	90.00	88.110(4)	90.00
β (°)	71.862(7)	117.660(4)	87.004(4)	106.204(2)
γ (°)	72.048(6)	90.00	83.153(4)	90.00
V (Å^3)	2187.2(3)	4981.2(3)	2601.7(2)	6941.1(3)
F(000)	1118	2300	1165	3340
Z	1	2	1	4
D_c (g cm^{-3})	1.701	1.484	1.440	1.559
μ (mm^{-1})	2.918	0.927	0.912	6.011
θ range (°)	3.37-25.01	3.36-25.00	3.41-25.00	2.936-60.65
Ref. meas. / indep.	15472, 7677	33470, 16474	17108, 9123	55337, 15483
Obs. ref.[$I > 2\sigma(I)$]	4205	12519	5485	11304
R_{int}	0.0557	0.0329	0.0372	0.0413
R_1 [$I \geq 2\sigma(I)$] [a]	0.0633	0.0431	0.0689	0.0504
ωR_2(all data)[b]	0.1783	0.1122	0.1867	0.1319
Goof	1.018	1.005	1.006	1.017
Δρ(max,min)(eÅ^{-3})	1.050, -0.744	0.354, -0.339	0.772, -0.557	1.085, -0.761

Table S3. Selected bond lengths (Å) and bond angles (°) for **1-13**.

1	Cu1−O1	1.914(2)	O1−Cu1−O3	87.34(11)
	Cu1−N1	1.950(2)	N1−Cu1−N3	80.90(10)
	Cu1−N3	2.038(3)	N1−Cu1−O2	119.26(10)
	Cu1−O2	2.183(2)	N1−Cu1−O3	141.12(10)
	Cu1−O3	2.017(2)	N3−Cu1−O3	100.13(10)
	O1−Cu1−N1	91.36(9)	O2−Cu1−N3	93.50(10)
	O1−Cu1−N3	171.92(10)	O2−Cu1−O3	99.55(10)
	O1−Cu1−O2	88.26(10)		
2	Cu1−N3	2.075(7)	N4−Cu1−N6	80.9(3)
	Cu1−N4	2.020(6)	N1−Cu1−N3	81.0(3)
	Cu1−N1	2.015(7)	N1−Cu1−N4	126.4(3)
	Cu1−N6	2.071(7)	N1−Cu1−N6	130.2(3)
	N4−Cu1−N3	136.4(3)	N6−Cu1−N3	108.0(3)
3	Cu1−N6	2.034(6)	N6−Cu1−N4	81.3(3)
	Cu1−N3	2.081(6)	N1−Cu1−N6	126.1(3)

	Cu1−N1	2.009(7)	N1−Cu1−N3	80.5(3)
	Cu1−N4	2.071(7)	N1−Cu1−N4	130.6(3)
	N6−Cu1−N3	136.1(3)	N4−Cu1−N3	108.4(2)
	Cu1−N3	2.088(12)	N6−Cu1−N4	81.2(5)
	Cu1−N6	2.023(10)	N6−Cu1−N1	125.6(5)
4	Cu1−N4	2.084(13)	N4−Cu1−N3	107.5(4)
	Cu1−N1	2.037(13)	N1−Cu1−N3	80.7(5)
	N6−Cu1−N3	137.9(5)	N1−Cu1−N4	130.3(5)
	Cu1−N3	2.034(10)	N6−Cu1−N4	80.9(4)
	Cu1−N6	2.084(10)	N6−Cu1−N1	108.4(4)
5	Cu1−N4	2.032(11)	N4−Cu1−N3	126.0(4)
	Cu1−N1	2.078(10)	N1−Cu1−N3	81.1(4)
	N6−Cu1−N3	136.3(5)	N1−Cu1−N4	130.4(4)
	Co1−O2	2.046(3)	N3−Co1−N6	106.64(14)
	Co1−N4	2.070(3)	N3−Co1−N1	76.01(14)
	Co1−N3	2.075(3)	O1−Co1−N4	88.63(13)
	Co1−O1	2.054(3)	O1−Co1−N3	86.66(13)
	Co1−N6	2.237(4)	O1−Co1−N6	90.04(14)
6	Co1−N1	2.209(4)	O1−Co1−N1	160.29(13)
	O2−Co1−N4	86.81(13)	N1−Co1−N6	86.08(13)
	O2−Co1−N3	91.52(13)	N4−Co1−N3	174.61(15)
	O2−Co1−O1	101.11(14)	N4−Co1−N6	75.96(13)
	O2−Co1−N6	159.29(13)	N4−Co1−N1	109.05(14)
	O2−Co1−N1	88.84(13)		
	Co1−O2	2.031(3)	N6−Co1−N3	108.47(16)
	Co1−N6	2.062(4)	N6−Co1−N4	76.14(15)
	Co1−O1	2.045(4)	O1−Co1−N6	89.20(15)
	Co1−N1	2.063(4)	O1−Co1−N1	86.68(15)
	Co1−N3	2.203(4)	O1−Co1−N3	160.40(15)
7	Co1−N4	2.222(4)	O1−Co1−N4	90.21(16)
	O2−Co1−N6	86.71(14)	N1−Co1−N6	175.01(18)
	O2−Co1−O1	100.81(16)	N1−Co1−N3	76.03(16)
	O2−Co1−N1	91.29(15)	N1−Co1−N4	106.66(16)
	O2−Co1−N3	88.92(15)	N3−Co1−N4	86.04(16)
	O2−Co1−N4	159.52(15)		
	Co1−O1	2.036(3)	N4−Co1−N6	75.93(13)
	Co1−O2	2.049(3)	N4−Co1−N3	109.14(12)
	Co1−N4	2.081(3)	N1−Co1−N4	172.54(13)
8	Co1−N1	2.066(3)	N1−Co1−N6	110.20(13)
	Co1−N6	2.228(3)	N1−Co1−N3	76.14(12)
	Co1−N3	2.256(3)	N6−Co1−N3	85.44(12)

	Co2−O4	2.044(3)	O4−Co2−N9	91.35(11)
	Co2−N9	2.070(3)	O4−Co2−N10	86.88(11)
	Co2−N10	2.070(3)	O4−Co2−O3	103.30(12)
	Co2−O3	2.052(3)	O4−Co2−N7	87.21(12)
	Co2−N7	2.220(3)	O4−Co2−N12	157.65(12)
	Co2−N12	2.267(3)	N9−Co2−N10	173.39(13)
	O1−Co1−O2	102.83(12)	N9−Co2−N7	76.27(13)
	O1−Co1−N4	89.26(11)	N9−Co2−N12	107.30(12)
	O1−Co1−N1	86.53(11)	N10−Co2−N7	109.97(13)
	O1−Co1−N6	89.97(11)	N10−Co2−N12	75.90(12)
	O1−Co1−N3	159.22(12)	O3−Co2−N9	86.11(12)
	O2−Co1−N4	86.17(12)	O3−Co2−N10	88.11(12)
	O2−Co1−N1	88.83(12)	O3−Co2−N7	159.76(12)
	O2−Co1−N6	157.81(12)	O3−Co2−N12	90.45(12)
	O2−Co1−N3	88.15(12)	N7−Co2−N12	85.46(12)
	Co1−O2	2.038(4)	N4−Co1−N6	76.28(17)
	Co1−N6	2.069(4)	N4−Co1−N3	109.64(16)
	Co1−N3	2.072(4)	N1−Co1−N4	85.29(16)
	Co1−N4	2.224(4)	N1−Co1−N6	107.63(17)
	Co1−O1	2.053(4)	N1−Co1−N3	76.17(16)
	Co1−N1	2.263(5)	N6−Co1−N3	173.44(17)
	Co2−O3	2.038(4)	O4−Co2−N9	86.11(16)
	Co2−N7	2.231(5)	O4−Co2−N10	88.27(17)
	Co2−O4	2.052(4)	O4−Co2−O3	102.31(16)
	Co2−N9	2.083(4)	O4−Co2−N7	157.78(16)
9	Co2−N12	2.071(4)	O4−Co2−N12	89.02(16)
	Co2−N10	2.251(5)	N9−Co2−N10	109.63(17)
	O1−Co1−O2	102.72(16)	N9−Co2−N7	76.05(17)
	O1−Co1−N4	159.95(15)	N9−Co2−N12	172.20(18)
	O1−Co1−N1	90.52(16)	N10−Co2−N7	85.43(16)
	O1−Co1−N6	86.39(15)	N10−Co2−N12	76.27(17)
	O1−Co1−N3	88.25(15)	O3−Co2−N9	88.57(15)
	O2−Co1−N4	87.62(15)	O3−Co2−N10	159.70(16)
	O2−Co1−N1	158.38(16)	O3−Co2−N7	90.54(16)
	O2−Co1−N6	90.40(15)	O3−Co2−N12	86.51(15)
	O2−Co1−N3	87.10(15)	N7−Co2−N12	110.02(17)
	Cu1−O1	1.921(5)	O1−Cu1−N4	93.1(2)
	Cu1−N4	1.934(6)	O1−Cu1−N2	166.0(2)
10	Cu1−N2	1.977(6)	N4−Cu1−N2	80.3(3)
	Cu1−N6	2.029(6)	O1−Cu1−N6	87.3(2)
	Cu1−N5	2.344(6)	N4−Cu1−N6	179.5(2)

	Cu2−O2	1.934(5)	N2−Cu1−N6	99.4(2)
	Cu2−N10	1.939(6)	O1−Cu1−N5	99.2(2)
	Cu2−N8	2.000(6)	N4−Cu1−N5	103.3(2)
	Cu2−N11	2.017(6)	N2−Cu1−N5	94.3(2)
	Cu2−N12	2.322(6)	N6−Cu1−N5	76.4(2)
	O2−Cu2−N10	92.5(2)	O2−Cu2−N8	163.7(2)
	N10−Cu2−N8	79.8(2)	O2−Cu2−N11	89.5(2)
	N10−Cu2−N11	176.4(2)	N8−Cu2−N11	99.0(2)
	O2−Cu2−N12	106.8(2)	N10−Cu2−N12	99.8(2)
	N8−Cu2−N12	88.8(2)	N11−Cu2−N12	76.8(2)
11	Cu1−O2	1.925(5)	O2−Cu1−N4	91.6(2)
	Cu1−N4	1.948(6)	O2−Cu1−N5	88.4(2)
	Cu1−N5	2.007(6)	N4−Cu1−N5	175.5(3)
	Cu1−N2	2.011(6)	O2−Cu1−N2	156.8(2)
	Cu1−N6	2.283(7)	N4−Cu1−N2	80.2(3)
	Cu2−O5	1.926(5)	N5−Cu1−N2	101.5(2)
	Cu2−N10	1.936(6)	O2−Cu1−N6	106.9(2)
	Cu2−N12	2.003(6)	N4−Cu1−N6	97.9(3)
	Cu2−N8	2.020(6)	N5−Cu1−N6	77.9(2)
	Cu2−N11	2.306(6)	N2−Cu1−N6	95.7(2)
	Cu3−O8	1.922(5)	O5−Cu2−N10	91.8(2)
	Cu3−N16	1.950(6)	O5−Cu2−N12	90.8(2)
	Cu3−N14	2.013(6)	N10−Cu2−N12	174.3(3)
	Cu3−N18	2.018(6)	O5−Cu2−N8	154.7(2)
	Cu3−N17	2.266(7)	N10−Cu2−N8	79.2(3)
	Cu4−O11	1.904(5)	N12−Cu2−N8	100.6(2)
	Cu4−N22	1.936(6)	O5−Cu2−N11	105.6(2)
	Cu4−N20	2.010(6)	N10−Cu2−N11	97.0(2)
	Cu4−N23	2.020(5)	N12−Cu2−N11	77.3(2)
	Cu4−N24	2.285(6)	N8−Cu2−N11	99.0(2)
	O8−Cu3−N16	91.6(3)	O11−Cu4−N22	92.6(3)
	O8−Cu3−N14	157.5(2)	O11−Cu4−N20	156.3(2)
	N16−Cu3−N14	80.1(3)	N22−Cu4−N20	79.8(3)
	O8−Cu3−N18	88.9(2)	O11−Cu4−N23	89.3(2)
	N16−Cu3−N18	176.3(3)	N22−Cu4−N23	173.2(3)
	N14−Cu3−N18	100.8(3)	N20−Cu4−N23	100.8(2)
	O8−Cu3−N17	103.9(2)	O11−Cu4−N24	105.7(2)
	N16−Cu3−N17	98.2(3)	N22−Cu4−N24	96.1(2)
	N14−Cu3−N17	97.9(3)	N20−Cu4−N24	97.5(2)
	N18−Cu3−N17	78.2(3)	N23−Cu4−N24	77.2(2)
12	Cu1−N4	1.921(5)	N4−Cu1−O1	92.6(2)

	Cu1−O1	1.925(3)	N4−Cu1−N6	174.9(2)
	Cu1−N6	2.001(5)	O1−Cu1−N6	88.5(2)
	Cu1−N2	2.028(5)	N4−Cu1−N2	79.9(2)
	Cu1−N5	2.295(4)	O1−Cu1−N2	155.5(2)
	Cu2−O3	1.915(4)	N6−Cu1−N2	101.2(2)
	Cu2−N10	1.953(6)	N4−Cu1−N5	97.0(2)
	Cu2−N8	2.002(6)	O1−Cu1−N5	108.4(2)
	Cu2−N12	2.022(5)	N6−Cu1−N5	78.0(2)
	Cu2−N11	2.290(5)	N2−Cu1−N5	95.7(2)
	O3−Cu2−N10	91.4(2)	O3−Cu2−N8	151.2(2)
	N10−Cu2−N8	79.9(3)	O3−Cu2−N12	90.5(2)
	N10−Cu2−N12	171.3(2)	N8−Cu2−N12	102.3(2)
	O3−Cu2−N11	115.0(2)	N10−Cu2−N11	94.2(2)
	N8−Cu2−N11	93.2(2)	N12−Cu2−N11	77.3(2)
	Cu1−O1	1.940(3)	O1−Cu1−N6	92.7(1)
	Cu1−N4	2.079(3)	O1−Cu1−N1	87.6(1)
	Cu1−N1	2.014(3)	N6−Cu1−N1	171.6(1)
	Cu1−N2	2.315(3)	O1−Cu1−N4	165.4(1)
	Cu1−N6	1.946(3)	N6−Cu1−N4	79.8(1)
	Cu2−O2	1.942(2)	N1−Cu1−N4	101.6(1)
	Cu2−N10	2.059(3)	O1−Cu1−N2	103.4(1)
	Cu2−N12	1.938(3)	N6−Cu1−N2	94.8(1)
	Cu2−N8	2.009(3)	N1−Cu1−N2	77.0(1)
	Cu2−N7	2.251(3)	N4−Cu1−N2	89.8(1)
	Cu3−O3	1.939(2)	O2−Cu2−N12	91.9(1)
13	Cu3−N16	2.045(3)	N8−Cu2−N12	178.4(1)
	Cu3−N13	2.252(3)	N8−Cu2−O2	177.0(5)
	Cu3−N14	2.014(2)	O2−Cu2−N8	86.9(1)
	Cu3−N18	1.939(3)	N12−Cu2−N10	80.4(1)
	O2−Cu2−N7	99.1(1)	O2−Cu2−N10	162.8(1)
	N8−Cu2−N7	78.6(1)	N8−Cu2−N10	101.0(1)
	N10−Cu2−N7	97.5(1)	N14−Cu3−N16	102.7(1)
	N18−Cu3−N14	173.0(1)	N18−Cu3−N13	94.9(1)
	O3−Cu3−N18	92.3(1)	O3−Cu3−N13	102.4(1)
	O3−Cu3−N14	86.6(1)	N14−Cu3−N13	78.7(1)
	N16−Cu3−N18	80.5(1)	N16−Cu3−N13	95.7(1)
	O3−Cu3−N16	161.1(1)		

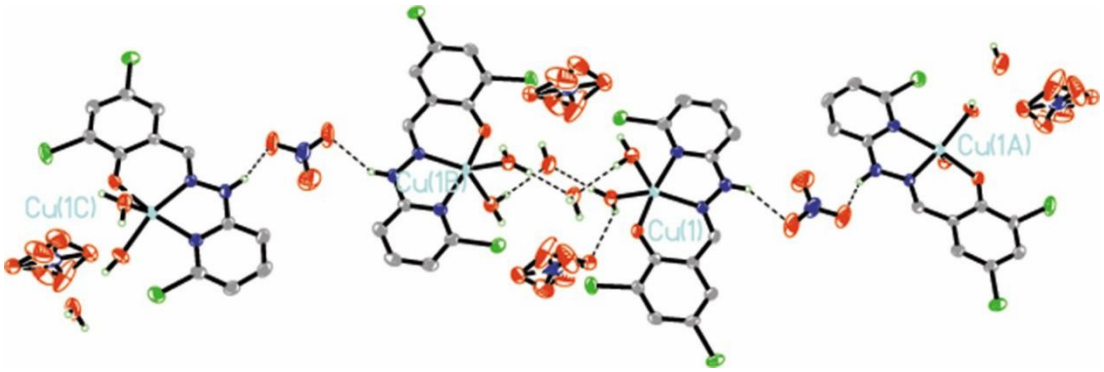


Figure S1. 1D chain of **1,** part H atoms were omitted for clarity.

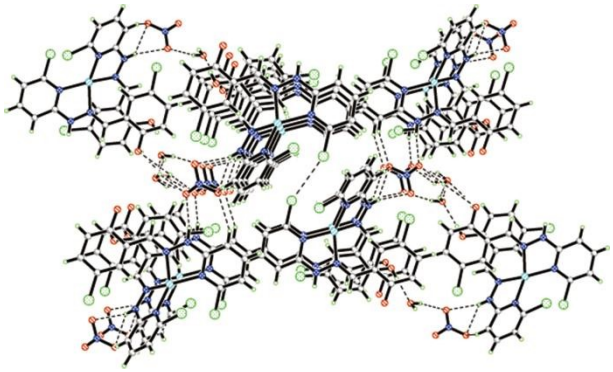


Figure S2. 3D network of **2**.

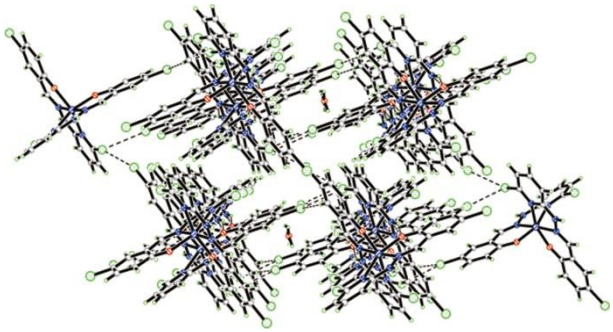


Figure S3. 3D network of **6**.

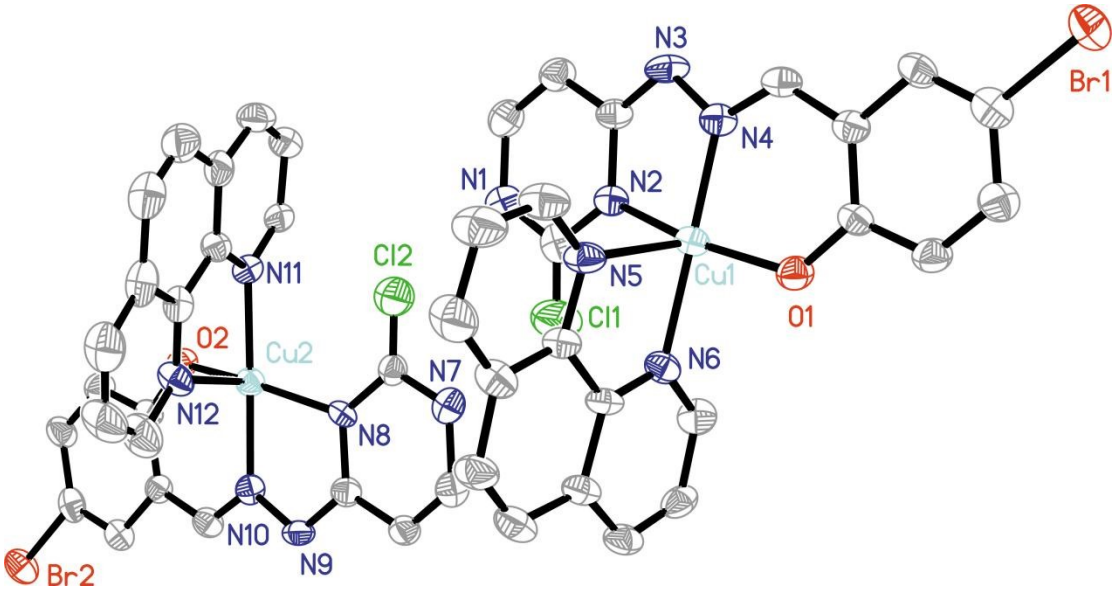


Figure S4. The molecular structure of **10**, with the H atoms, and lattice solvent molecules were omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

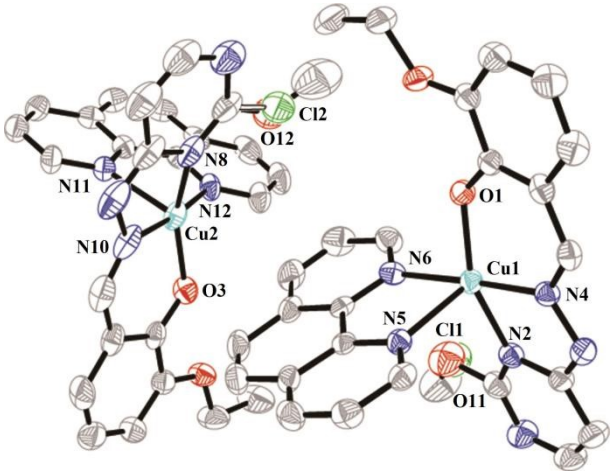


Figure S5. The molecular structure of **12**, with the H atoms, and solvent molecules were omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

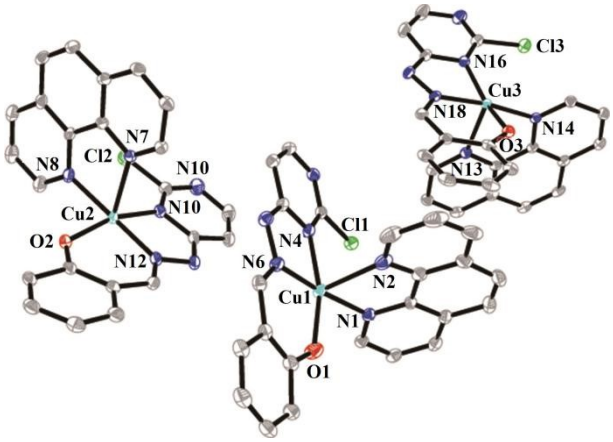


Figure S6. The molecular structure of **13**, with the H atoms, and solvent molecules were omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

Table S4. Hydrogen bond lengths (Å) and angles (°) for **11**.

D - H···*A*	*D* - H	H···*A*	*D*···*A*	*D* - H···*A*
O18-H18A···N15	0.850	2.040	2.868	164.44
O18-H18B···N9	0.850	2.022	2.863	169.90
O19-H19A···O7	0.850	2.054	2.819	149.44
O19-H19B···N19	0.850	2.063	2.852	154.24
O17-H17A···O18	0.850	2.014	2.763	146.51
O17-H17B···O20^{i}	0.850	1.999	2.836	168.23
O14-H14A···O3	0.881	2.236	3.0003	145.50
O14-H14B···O2	0.883	2.441	3.221	147.52
O16-H16A···O17	0.850	2.031	2.803	150.61
O16-H16B···O19^{ii}	0.850	1.970	2.817	178.81
O15-H15A···O13	0.850	2.098	2.816	142.00
O15-H15B···O14	0.850	2.343	2.882	121.62
O1W-H1WA···O16^{iii}	0.850	2.159	2.812	133.52
O13-H13F···N3^{iii}	0.850	2.040	2.876	167.63
O13-H13G···N21^{iv}	0.850	2.056	2.886	164.99
O20-H20A···O5	0.842	2.195	2.921	144.38
O20-H20B···O6	0.844	2.199	2.842	133.00

Symmetry codes: (i) $1-x$, $y-1/2$, $1-z$; (ii) $1-x$, $y-1/2$, $2-z$; (iii) $-x$, $y-1/2$, $1-z$; (iv) $x-1$, $y-1$, $z-1$.

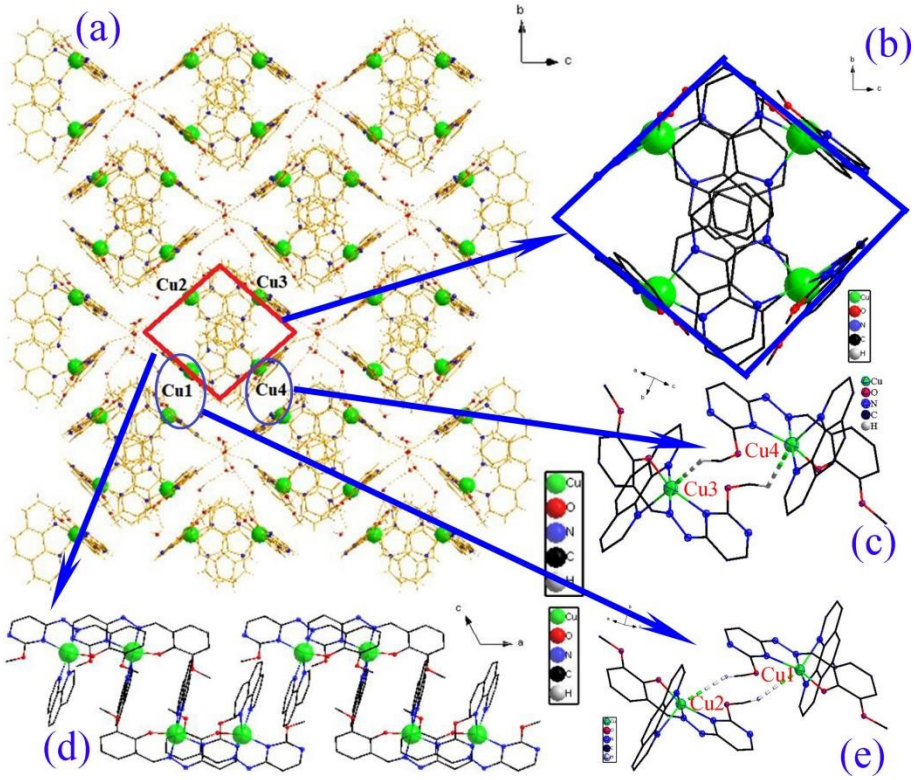


Figure S7. 3D network of **11** (a); 1D chain of **11** in a direction (b);1D chain of **11** in b direction (d); Cu···H interaction of **11** (c,e).

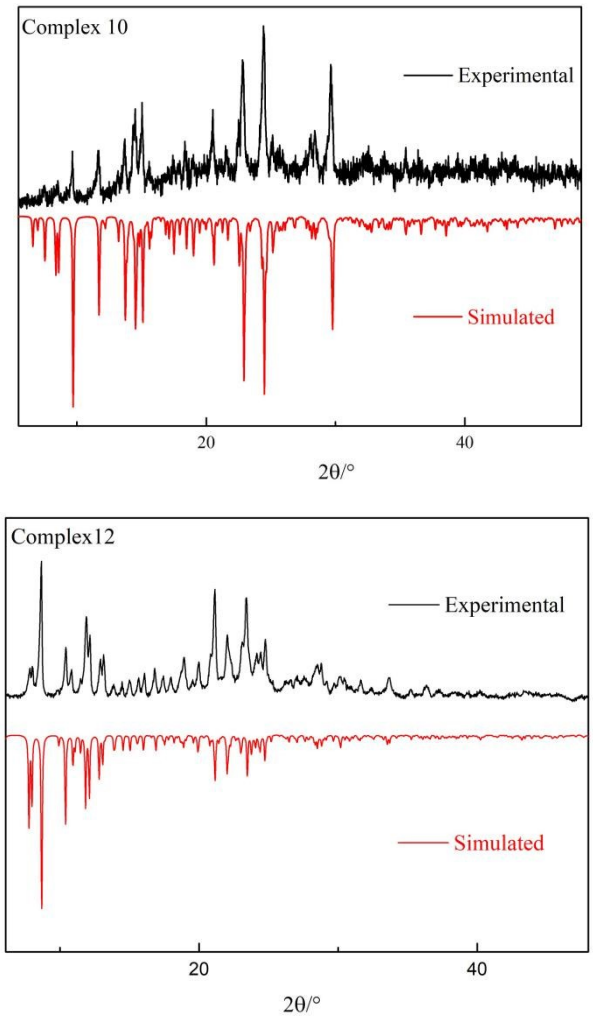


Figure S8. XRD of the complexes **10** and **12**.

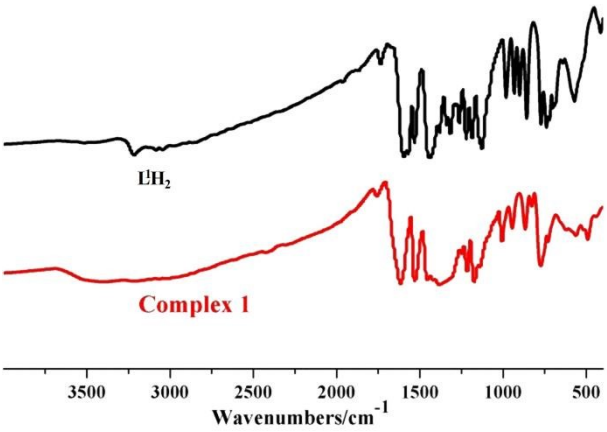


Figure S9. IR (KBr) spectra of **1** and L^1H_2.

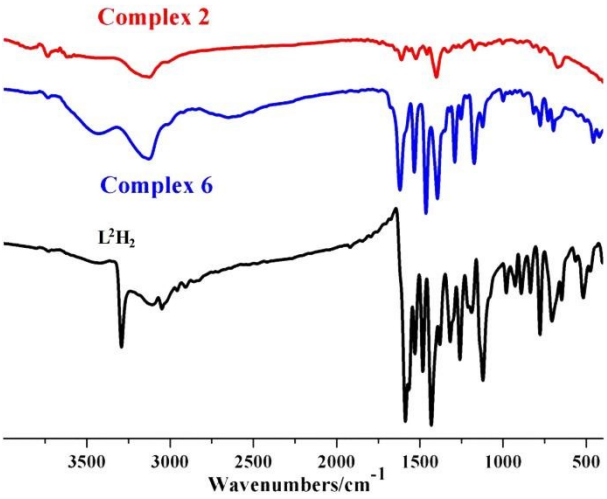


Figure S10. IR (KBr) spectra of **2, 6** and **L^2H_2.**

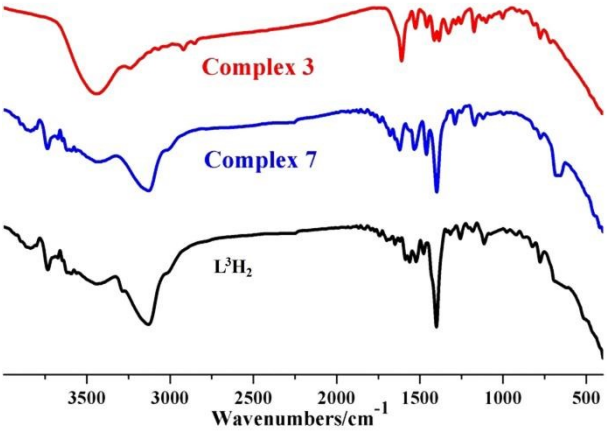


Figure S11. IR (KBr) spectra of **3,7** and L^3H_2**.**

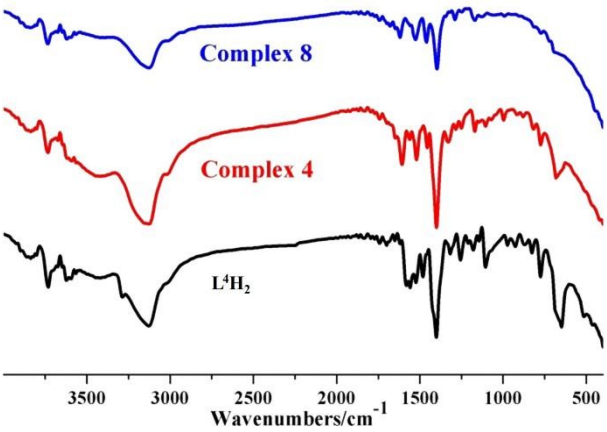


Figure S12. IR (KBr) spectra of **4,8** and L^4H_2**.**

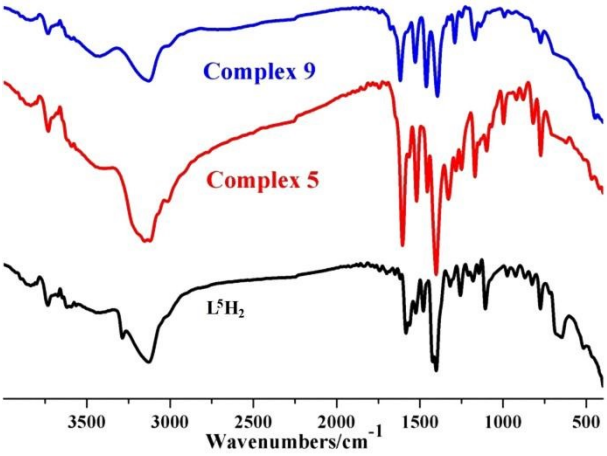


Figure S13. IR (KBr) spectra of **5,9** and L^5H_2.

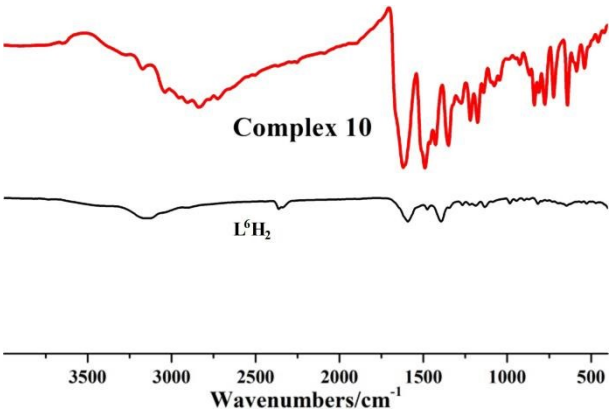


Figure S14. IR (KBr) spectra of **10** and L^6H_2.

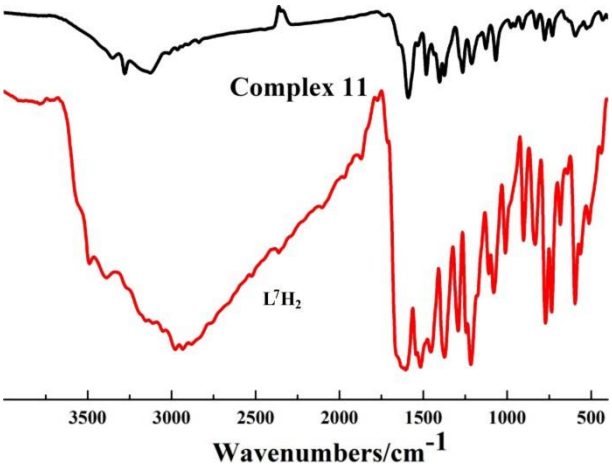


Figure S15. IR (KBr) spectra of **11** and L^7H_2.

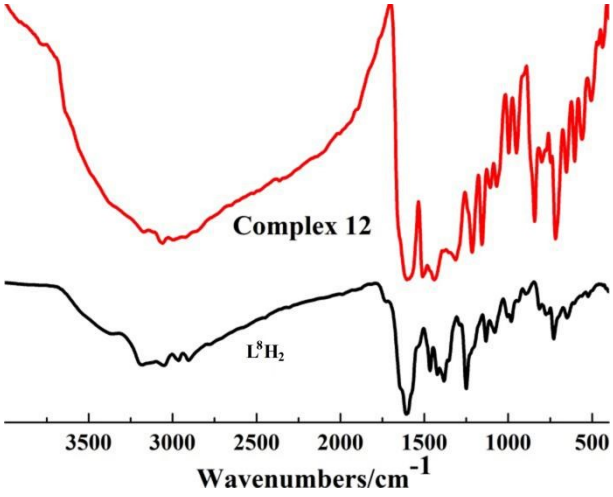


Figure S16. IR (KBr) spectra of **12** and L^8H_2.

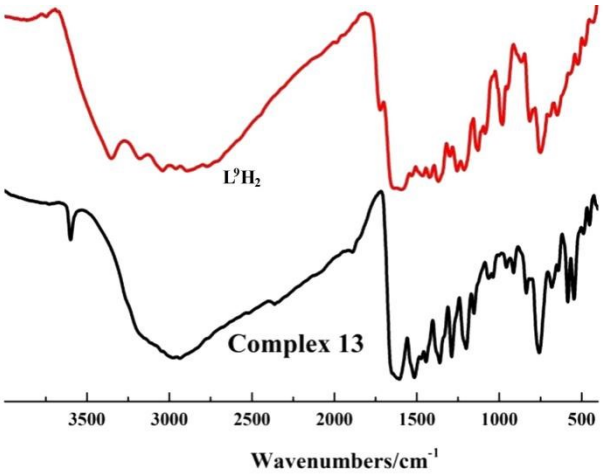


Figure S17. IR (KBr) spectra of **13** and L^9H_2.

Table S5. IC_{50} (μM) values determined by MTT assay of salicylaldehyde Schiff-bases ($L^{1\text{-}9}H_2$) and 1,10-phenanthroline (phen) ligands against A549 and A549/DDP cells for 24 h.

complexes	A549	A549/DDP	HL-7702
L^1H_2	>50	>50	>50
L^2H_2	>50	>50	>50
L^3H_2	>50	>50	>50
L^4H_2	>50	>50	>50
L^5H_2	>50	>50	>50
L^6H_2	>50	>50	>50
L^7H_2	>50	>50	>50
L^8H_2	>50	>50	>50
L^9H_2	>50	>50	>50
phen	>50	>50	>50

$Cu(NO_3)_2 \cdot 3H_2O$	>50	>50	>50

	mg/kg	1day	3d			5d			7d		
		Tumor Volume (mm^3)	Tumor Volume (mm^3)	RTV	T/C%	Tumor Volume (mm^3)	RTV	T/C%	Tumor Volume (mm^3)	RTV	T/C %
control	-	90.6±8.0	164.3±31.0	1.825±0.388	100.0	332.0±45.4	3.692±0.633	100.0	539.5±64.4	5.976±0.733	100.0
11	5.0	91.7±3.2	160.0±9.5	1.748±0.124	97.4	293.6±36.3	3.213±0.477	87.0	426.5±59.0*	4.662±0.720*	79.1
13	5.0	91.4±5.5	157.2±18.7	1.716±0.123	94.0	266.2±24.9*	2.934±0.444*	79.5	369.9±33.9**	4.076±0.619**	68.6

Table S6. The tumor volume in treated and non-treated mice from the date of surgery to the study end point in the A549/DDP xenograft model.

	mg/kg	9d			11d			13d		
		Tumor Volume (mm^3)	RTV	T/C %	Tumor Volume (mm^3)	RTV	T/C%	Tumor Volume (mm^3)	RTV	T/C%
control	-	694.1±75.5	7.683±0.787	100.0	860.1±96.0	9.528±1.099	100.0	1069.0±180.5	11.783±1.462	100.0
11	5.0	471.2±61.4**	5.150±0.754**	67.9	523.3±58.6**	5.723±0.774**	60.8	587.0±62.3**	6.418±0.812**	54.9
13	5.0	434.8±46.2**	4.793±0.787**	62.6	482.2±50.9**	5.315±0.864**	56.1	519.3±59.1**	5.720±0.965**	48.6

	mg/kg	15d		
		Tumor Volume (mm^3)	RTV	T/C%
control	-	1246.9±103.9	13.768±1.522	100.0
11	5.0	631.3±61.4**	6.899±0.780**	50.6
13	5.0	546.4±75.6**	6.022±1.109**	43.8

* p <0.05, ** p <0.01, p *vs* vehicle control (5.0% v/v DMSO/ saline vehicle).

Table S7. Average body weight in treated and non-treated mice from the date of surgery to the study end point in the A549/DDP xenogfart model.

	mg/kg	1 d	3 d	5 d	7 d	9 d	11 d	13 d	15 d
control	-	19.3±0.6	19.4±0.6	19.6±0.6	19.7±0.6	19.9±0.6	20.0±0.5	20.1±0.5	20.2±0.5
11	5.0	19.2±0.5	19.3±0.5	19.5±0.5	19.5±0.5	19.7±0.5	19.9±0.4	20.0±0.4	20.1±0.4
13	5.0	19.3±0.5	19.4±0.5	19.5±0.5	19.7±0.5	19.8±0.5	19.9±0.5	20.0±0.4	20.1±0.4

* p <0.05, ** p <0.01, p *vs* vehicle control (5.0% v/v DMSO/ saline vehicle).

Table S8. In Vivo Anticancer Activity of **11** and **13** toward A549/DDP Tumor Xenograft.

	mg/kg	average tumor weight (mean ± SD, g)	inhibition of tumor growth (%)
control	-	1.303±0.100	—
11	5.0	0.653±0.060**	49.9
13	5.0	0.570±0.105**	56.3

* p <0.05, ** p <0.01, p *vs* vehicle control (5.0% v/v DMSO/ saline vehicle).

Methods

The A549/DDP xenograft mouse models were purchased from Changzhou Cavens Experimental Animal Co., Ltd (Jiangsu, China, Approval No. SCXK 2016-0010). The animal procedures were approved by Changzhou Cavens Experimental Animal Co., Ltd (Jiangsu, China, Approval No. 2017-0040). Further, all the experimental procedures were conducted in accordance with the NIH Guidelines for the Care and Use of Laboratory Animals. Animal experiments were approved by Changzhou Cavens Experimental Animal Co., Ltd ((Jiangsu, China).

Syntheses

4.2 Syntheses of L^nH_2 (n = 1-9)

4.2.1 Syntheses of L^1H_2

A mixture of 3,5-dichloro-2-hydroxy-benzaldehyde (10 mmol, 1.9101 g), (6-chloro-pyridin-2-yl)-hydrazine (Hcph, 10 mmol, 1.4353 g) and ethanol (20 mL) in a 100 mL flask refluxed at 80 °C for 1 h. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 3.0072 g, *ca*. 95 % based on Hcph). *Anal. Calc*. for L^1H_2: $C_{12}H_8Cl_3N_3O$ (M_r = 316.55), *calc*.: C, 45.53; H, 2.55; N, 13.27 %; Found: C, 45.48; H, 2.61; N, 13.32. IR data for L^1H_2 (KBr, cm^{-1}, Fig. S9): 3288 s, 3052 s, 1578 s, 1527 s, 1482 s, 1423 m, 1314 m, 1257 s, 1183 s, 1147 m, 1104 s, 974 m, 875 m, 872 m, 776 m, 646 m, 521 w.

4.2.2 Syntheses of L^2H_2

L^2H_2 was prepared in a similar way to L^1H_2, except that 3,5-dichloro-2-hydroxy-benzaldehyde was replaced by 5-chloro-2-hydroxy-benzaldehyde. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 2.6518 g, *ca*. 94 % based on Hcph). *Anal. Calc*. for L^2H_2: $C_{12}H_9Cl_2N_3O$ (M_r = 282.10), *calc*.: C, 51.09; H, 3.22; N, 14.89 %; Found: C, 51.03; H, 3.29; N, 14.94. IR data for L^2H_2 (KBr, cm^{-1}, Fig. S10): 3288 w, 3052 s, 1578 w, 1527 w, 1482 w, 1423 w, 1314 m, 1257 w,

1183 m, 1194 w, 974 w, 931 s, 875 s, 776 s, 646 w, 521 s.

4.2.3 Syntheses of L^3H_2

L^3H_2 was prepared in a similar way to L^1H_2, except that 3,5-dichloro-2-hydroxy-benzaldehyde was replaced by 5-Bromo-2-hydroxy-benzaldehyde. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 3.0044 g, *ca*. 92 % based on Hcph). *Anal. Calc*. for L^3H_2: $C_{12}H_9BrClN_3O$ (M_r = 326.56), *calc*.: C, 44.14; H, 2.78; N, 12.86 %; Found: C, 44.09; H, 2.82; N, 12.91. IR data for L^3H_2 (KBr, cm^{-1}, Fig. S11): 3288 w, 3052 s, 1578 w, 1527 w, 1482 w, 1423 w, 1314 m, 1257 w, 1183 m, 1147 s, 1104 w, 974 w, 931 s, 875 s, 776 s, 646 w, 521 s.

4.2.4 Syntheses of L^4H_2

L^4H_2 was prepared in a similar way to L^2H_2, except that 6-Bromo-pyridin-2-yl)-hydrazine (Hbph) was replaced by (6-Chloro-pyridin- 2-yl)-hydrazine. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 3.1350 g, *ca*. 96 % based on Hbph). *Anal. Calc*. for L^4H_2: $C_{12}H_9BrClN_3O$ (M_r = 326.56), *calc*.: C, 44.14; H, 2.78; N, 12.86 %; Found: C, 44.02; H, 2.86; N, 12.93. IR data for L^4H_2 (KBr, cm^{-1}, Fig. S12): 3444s, 3288s, 3052s, 1578w, 1527w, 1482w, 1423w, 1314w, 1257s, 1183s, 1147s, 1104s, 974s, 931s, 875s, 827s, 776s, 646s, 521s.

4.2.5 Syntheses of L^5H_2

L^5H_2 was prepared in a similar way to L^4H_2, except that 5-Chloro-2-hydroxy-benzaldehyde was replaced by 5-Bromo-2-hydroxy- benzaldehyde. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 3.3391 g, *ca*. 93 % based on Hbph). *Anal. Calc*. for L^5H_2: $C_{12}H_9Br_2N_3O$ (M_r = 371.01), *calc*.: C, 38.85; H, 2.41; N, 11.29 %; Found: C, 38.81; H, 2.43; N, 11.32. IR data for L^5H_2 (KBr, cm^{-1}, Fig. S13): 3444 s, 3288 m, 3052 s, 1578 w, 1482 w, 1482 s, 1423 w, 1314 w, 1257 s, 1183 w, 1147 s, 1104 w, 974 s, 875 s, 827 s, 776 s, 646 s, 521 s.

4.2.6 Syntheses of L^6H_2

L^6H_2 was prepared in a similar way to L^3H_2, except that (6-chloro-pyridin-2-yl)- hydrazine

was replaced by (2-Chloro-pyrimidin-4-yl)-hydrazine(Hcpmh). Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 3.1118 g, *ca*. 95 % based on Hcpmh). *Anal. Calc*. for L^6H_2: $C_{11}H_8BrClN_4O$ (M_r = 327.56), *calc*.: C, 40.33; H, 2.46; N, 17.10 %; Found: C, 40.26; H, 2.54; N, 17.19. IR data for L^6H_2 (KBr, cm^{-1}, Fig. S14): 3166 w, 2833 w, 1709 w, 1619 s, 1426 w, 1347 m, 1137 s, 1039 s, 984 w, 774 m, 643 s, 532 w.

4.2.7 Syntheses of L^7H_2

L^7H_2 was prepared in a similar way to L^6H_2, except that 5-Bromo-2-hydroxy- benzaldehyde was replaced by 2-Hydroxy-3-methoxy-benzaldehyde. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 2.6754 g, *ca*. 96 % based on Hcpmh). *Anal. Calc*. for L^7H_2: $C_{12}H_{11}ClN_4O_2$ (M_r = 278.69), *calc*.: C, 51.72; H, 3.98; N, 20.10 %; Found: C, 57.66; H, 4.07; N, 20.16. IR data for L^7H_2 (KBr, cm^{-1}, Fig. S15): 3390 w, 2976 w, 31603 m, 1456 w, 1371 m, 1290 m, 1217 s, 1075 w, 1009 m, 902 s, 834 m, 773 s, 732 m, 594 s, 511 w.

4.2.8 Syntheses of L^8H_2

L^8H_2 was prepared in a similar way to L^6H_2, except that 5-bromo-2-hydroxy- benzaldehyde was replaced by 3-ethoxy-2-hydroxy-benzaldehyde. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 2.7516 g, *ca*. 94 % based on Hcpmh). *Anal. Calc*. for L^8H_2: $C_{12}H_{11}ClN_4O_2$ (M_r = 292.72), *calc*.: C, 53.34; H, 4.48; N, 19.14 %; Found: C, 53.25; H, 4.55; N, 19.21. IR data for L^8H_2 (KBr, cm^{-1}, Fig. S16): 3191 w, 2911 w, 1609 m, 1420 w, 1384 w, 1249 m, 1136 w, 1084 w, 983 w, 929 w, 816 w, 727 s, 648 w, 520 w.

4.2.9 Syntheses of L^9H_2

L^9H_2 was prepared in a similar way to L^6H_2, except that 5-bromo-2-hydroxy- benzaldehyde was replaced by 2-hydroxy-benzaldehyde. Beige precipitate appeared and then was rinsed three times with fresh ethanol (10 mL × 3) and dried at 50 °C for 24 h (yield: 2.2629 g, *ca*. 91 % based on Hcpmh). *Anal. Calc*. for L^9H_2: $C_{12}H_{11}ClN_4O_2$ (M_r = 248.67), *calc*.: C, 53.13; H, 3.65; N, 22.53 %; Found: C, 53.08; H, 3.72; N, 22.61. IR data for L^9H_2 (KBr, cm^{-1}, Fig. S17): 3351

s, 3288 m, 3037 s, 1578 w, 1482 w, 1423 w, 1363 s, 1257 s, 1208 w, 1147 s, 1121 s, 974 s, 875 s, 736 s, 646 s, 521 s.

4.3 Syntheses of 1-13

4.3.1 Syntheses of $[Cu(L^1H)(H_2O)_2]\cdot NO_3\cdot(H_2O)$ (1)

A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.5 mmol, 0.121 g), L^1H_2 (0.5 mmol, 0.158 g), ethanol (4 mL) and deionized water (6 mL) with a pH adjusted to 6 by the addition of trimethylamine was stirred for 10 min at room temperature. The mixture was poured into a Teflon-lined autoclave (20 mL) and then heated at 80 °C for 72 h. Blue block crystals of **1** were collected by filtration, washed with deionized water (10 mL × 3) and dried in air (yield: 179 mg, *ca*. 72.3 % based on L^1H_2). *Anal. Calc*. for **1**: $C_{12}H_{13}N_4Cl_3O_7Cu$ (M_r = 495.16), *calc*.: C, 29.11; H, 2.65; N, 11.31. Found: C, 29.02; H, 2.71; N, 11.36. IR data for **1** (KBr, cm^{-1}, Fig. S9): 3403 w, 1616 s, 1529 w, 1381 w, 1216 w, 1173 w, 1006 s, 945 s, 896 s, 773 w, 592 w, 490 w.

4.3.2 Syntheses of $[Cu(L^2H_2)_2]\cdot(NO_3)\cdot(H_2O)_2$ (2)

Complex **2** was obtained by the similar route to **1**, except that L^1H_2 was replaced by L^2H_2. Blue crystals of **2** were obtained (yield: 135.6 mg, *ca*. 74.73 % based on L^2H_2). *Anal. Calc*. for **2**: $C_{24}H_{22}Cl_4CuN_7O_7$ (M_r = 725.83), *calc*.: C, 39.72; H, 3.06; N, 13.50. Found: C, 39.65; H, 3.12; N, 13.56. IR data for **2** (KBr, cm^{-1}, Fig. S10): 3444 s, 3288 w, 3052 s, 1578 s, 1527 w, 1482 w, 1423 w, 1314 m, 1257 w, 1183 m, 1147 s, 1104 s, 974 w, 931 s, 875 s, 776 s, 646 w, 521 w.

4.3.3 Syntheses of $[Cu(L^3H_2)_2]\cdot(NO_3)\cdot(H_2O)_2$ (3)

Complex **3** was obtained by the similar route to **1**, except that L^1H_2 was replaced by L^3H_2. Blue crystals of **3** were obtained (yield: 155.45 mg, *ca*. 76.32 % based on L^3H_2). *Anal. Calc*. for **3**: $C_{24}H_{22}Br_2Cl_2CuN_7O_7$ (M_r = 814.75), *calc*.: C, 35.38; H, 2.72; N, 12.03. Found: C, 35.33; H, 2.79; N, 12.14. IR data for **3** (KBr, cm^{-1}, Fig. S11): 3444 s, 3288 s, 3052 m, 1578 s, 1527 s, 1482 w, 1423 w, 1314 m, 1257 w, 1183 m, 1147 m, 1104 m, 974 w, 931 m, 875 w, 776 w, 646 w, 521 w.

4.3.4 Syntheses of $[Cu(L^4H_2)_2]\cdot(NO_3)\cdot(H_2O)_2$ (4)

Complex **4** was obtained by the similar route to **1**, except that L^1H_2 was replaced by L^4H_2. Blue crystals of **4** were obtained (yield: 154.07 mg, *ca*. 75.64 % based on L^4H_2). *Anal. Calc*. for **4**: $C_{24}H_{22}Br_2Cl_2CuN_7O_7$ (M_r = 814.75), *calc*.: C, 35.38; H, 2.72; N, 12.03. Found: C, 35.31; H, 2.77; N, 12.11. IR data for **4** (KBr, cm^{-1}, Fig. S12): 3440 w, 3288 m, 3052 m, 1665 s, 1525 s, 1456 m, 1293 s, 1175 m, 1124 m, 1108 m, 977 w, 935 m, 873 w, 778 w, 648 w, 523 w.

4.3.5 Syntheses of $[Cu(L^5H_2)_2]\cdot(NO_3)\cdot(H_2O)_2$ (5)

Complex **5** was obtained by the similar route to **1**, except that L^1H_2 was replaced by L^5H_2**.** Blue crystals of **5** were obtained (yield: 163.54 mg, *ca*. 75.64 % based on L^5H_2). *Anal. Calc*. for **5**: $C_{24}H_{22}Br_4CuN_7O_7$ (M_r = 903.67), *calc*.: C, 31.90; H, 2.45; N, 10.84. Found: C, 31.82; H, 2.56; N, 10.93. IR data for **5** (KBr, cm^{-1}, Fig. S13): 3444 s, 3288 m, 3052 s, 1578 s, 1527 s, 1482 m, 1423 m, 1314 m, 1257 m, 1183 m, 1147 s, 1104 s, 974 w, 931 s, 875 m, 776 m, 646 m, 521 w.

4.3.6 Syntheses of $[Co(L^2H)_2]_2\cdot(H_2O)_{0.5}$ (6)

A mixture of $Co(NO_3)_2\cdot6H_2O$ (0.5 mmol, 0.145 g), L^2H_2 (0.5 mmol, 0.141 g), ethanol (5 mL) and DMF (5 mL) with a pH adjusted to 6 by the addition of trimethylamine was stirred for 5 min at room temperature. The mixture was poured into a Teflon-lined autoclave (20 mL) and then heated at 80 °C for 72 h. Red block crystals of **6** were collected by filtration, washed with ethanol (10 mL × 3) and dried in air (yield: 138.82 mg, *ca*. 44.38 % based on L^2H_2). *Anal. Calc*. for **6**: $C_{48}H_{33}Cl_8Co_2N_{12}O_{4.5}$ (M_r = 1251.32), *calc*.: C, 46.07; H, 2.66; N, 13.43. Found: C, 45.98; H, 2.75; N, 13.49. IR data for **6** (KBr, cm^{-1}, Fig. S10): 3460 w, 1674 s, 1617 s, 1528 m, 1461 m, 1388 m, 1346 s, 1289 m, 1170 m, 1135 s, 991 s, 814 w, 774 w, 724 w, 686 m, 449 w.

4.3.7 Syntheses of $[Co(L^3H)_2]_2\cdot(H_2O)_{0.5}$ (7)

Complex **7** was obtained by the similar route to **6**, except that L^2H_2 was replaced by L^3H_2 Red crystals of **7** were obtained (yield: 151.26 mg, *ca*. 42.34 % based on L^3H_2). *Anal. Calc*. for **7**: $C_{48}H_{33}Br_4Cl_4Co_2N_{12}O_{4.5}$ (M_r = 1429.12), *calc*.: C, 40.34; H, 2.33; N, 11.76. Found: C, 40.26; H, 2.41; N, 11.84. IR data for **7** (KBr, cm^{-1}, Fig. S11): 3460 w, 1674 s, 1617 m, 1528 s, 1461 m, 1388 s, 1321 s, 1289 s, 1248 s, 1170 s, 1135 s, 991 m, 814 m, 774 w, 724 w, 686 w, 449 w.

4.3.8 Syntheses of $[Co(L^4H)_2]_2\cdot(H_2O)_{0.5}$ (8)

Complex **8** was obtained by the similar route to **6**, except that L^2H_2 was replaced by L^4H_2. Red crystals of **8** were obtained (yield: 153.59 mg, *ca*. 42.99 % based on L^4H_2). *Anal. Calc*. for **8**: $C_{48}H_{33}Br_4Cl_4Co_2N_{12}O_{4.5}$ (M_r = 1429.12), *calc*.: C, 40.34; H, 2.33; N, 11.76. Found: C, 40.29; H, 2.39; N, 11.75. IR data for **8** (KBr, cm^{-1}, Fig. S12): 3420 s, 2928 s, 1657 s, 1617 m, 1581 m, 1534 w, 1461 m, 1417 m, 1388 m, 1303 m, 1255 m, 1215 m, 1170 m, 1147 m, 998 m, 777 m, 724 m, 453 w.

4.3.8 Syntheses of $[Co(L^5H)_2]_2\cdot(H_2O)_{0.5}$ (9)

Complex **9** was obtained by the similar route to **6**, except that L^2H_2 was replaced by L^5H_2. Red crystals of **9** were obtained (yield: 164.53 mg, *ca*. 40.95 % based on L^5H_2). *Anal. Calc*. for **9**: $C_{48}H_{33}Br_8Co_2N_{12}O_{4.5}$ (M_r = 1607.01), *calc*.: C, 35.88; H, 2.07; N, 10.45. Found: C, 35.81; H, 2.12; N, 10.54. IR data for **9** (KBr, cm^{-1}, Fig. S13): 3420 s, 2928 s, 1657 s, 1617 s, 1581 w, 1534 w, 1461 w, 1417 w, 1388 w, 1303 s, 1255 s, 1215 m, 1170 w, 1147 w, 998 m, 777 m, 724 w, 453 w.

4.3.10 Syntheses of $[Cu(L^6)_{0.5}(L^{10}H)_{0.5}(phen)]\cdot(CH_3OH)_{0.25}$ (10)

A mixture of $Cu(NO_3)_2\cdot3H_2O$ (0.5 mmol, 0.121 g), H_2L^6 (0.5 mmol, 0.1638 g), [1,10]phenanthroline (phen, 0.5 mmol, 0.0901 g), methanol (4 mL) and deionized water (6 mL) with a pH adjusted to 6 by the addition of trimethylamine was stirred for 10 min at room temperature. The mixture was poured into a Teflon-lined autoclave (20 mL) and then heated at 80 °C for 72 h. Blue block crystals of **10** were collected by filtration, washed with deionized water (10 mL × 3) and dried in air (yield: 164 mg, *ca*. 58.46 % based on Cu). *Anal. Calc*. for **10**: $C_{23.25}H_{15.5}BrCl_{0.5}CuN_6O_{1.25}$ (M_r = 560.09), *calc*.: C, 49.85; H, 2.79; N, 15.00. Found: C, 49.65; H, 2.88; N, 15.02. IR data for **10** (KBr, cm^{-1}, Fig. S14): 3157 w, 2899 w, 1587 m, 1477 w, 1391 m, 1267 w, 1186 w, 1133 s, 983 s, 943 s, 816 m, 646 s, 527 s.

4.3.11 Syntheses of $[Cu(L^{11}H)(phen)]_4\cdot(H_2O)_9$ (11)

Complex **11** was obtained by the similar route to **10**, except that L^6H_2 was replaced by L^7H_2. The pH of the mixture solvent adjusted to 7.5 by the addition of trimethylamine. Blue crystals

of **11** were obtained (yield: 142.73 mg, *ca*. 51.2 % based on Cu). *Anal. Calc*. for **11**: $C_{100}H_{98}Cu_4N_{24}O_{21}$ (M_r = 2226.22), *calc*.: C, 53.95; H, 4.44; N, 15.10. Found: C, 53.77; H, 4.69; N, 15.17. IR data for **11** (KBr, cm^{-1}, Fig. S15): 3281 w, 2963 w, 1586 m, 1480 w, 1402 m, 1264 w, 1208 m, 1126 w, 1065 m, 907 w, 828 w, 773 m, 727 m, 598 s, 522 w.

4.3.12 Syntheses of $[Cu(L^8)_{0.27}(L^{12}H)_{0.73}(phen)]_4\cdot(H_2O)_{5.5}\cdot(CH_3OH)$ (12)

Complex **12** was obtained by the similar route to **10**, except that L^6H_2 was replaced by L^8H_2. The pH of the mixture solvent adjusted to 7.0 by the addition of trimethylamine. Blue crystals of **12** were obtained (yield: 152.85 mg, *ca*. 54.10 % based on Cu). *Anal. Calc*. for **12**: $C_{103.94}H_{99.82}Cl_{1.06}Cu_4N_{24}O_{17.44}$ (M_r = 2256.00), *calc*.: C, 55.33; H, 4.46; N, 14.89. Found: C, 55.16; H, 4.72; N, 14.92. IR data for **12** (KBr, cm^{-1}, Fig. S16): 3179 w, 1597 m, 1514 w, 1514 w, 1435 w, 1312 w, 1216 m, 1152 m, 1109 w, 1066 w, 999 m, 949 m, 839 s, 713 s, 646 m, 603 m, 560 m, 501 w.

4.3.13 Syntheses of $[Cu(L^9H)(phen)]_3\cdot(H_2O)_7\cdot(CH_3OH)$ (13)

Complex **13** was obtained by the similar route to **10**, except that L^6H_2 was replaced by L^9H_2. Blue crystals of **13** were obtained (yield: 138.58 mg, *ca*. 52.7 % based on Cu). *Anal. Calc*. for **13**: $C_{70}H_{63}Cl_3Cu_3N_{18}O_{11}$ (M_r = 1629.38), *calc*.: C, 51.60; H, 3.90; N, 15.47. Found: C, 51.68; H, 3.88; N, 15.58. IR data for **13** (KBr, cm^{-1}, Fig. S17): 3602 s, 2982 w,1608 m,1516 w, 1442 m, 1361 s, 1289 s, 1202 m, 1151 w, 908 w, 838 m, 751 s, 585 m, 546 m.