SUPPORTING INFORMATION

Versatile coordination behaviour of chloro-tetrazine-picolylamine ligand: mixed-valence binuclear Cu(I)/Cu(II) complexes†

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Ligand HL^1 1

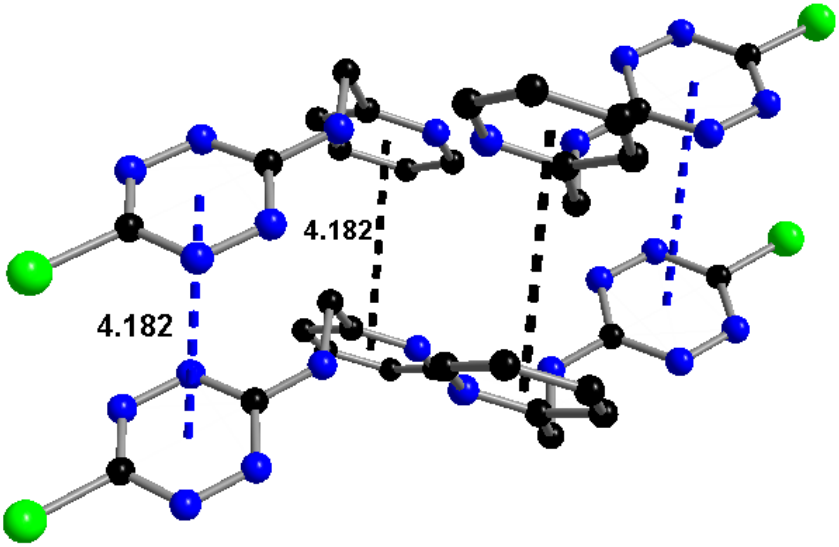
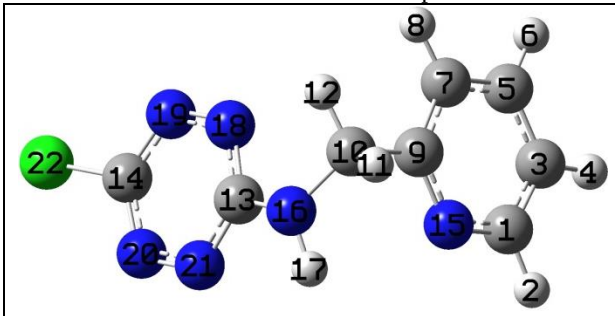


Figure **S1**. Interaction between tetrazine (blue line) and pyridine (black line) rings in **HL^1**. Hydrogen atoms were omitted.

Table S1. Hydrogen bonds parameters for **HL^1**

d(A···H), Å	**d(A···D) , Å**	**∠ (A-H-D), °**
N(1)···H(2) = 2.07	N(1)···N(2) = 2.90	162
Cl(1)···H(4) = 2.94	Cl(1)···C(4) = 3.82	159

Table S2. Distance matrix for the optimized structure



The geometry of the optimized structure M11L/6-311G(d,p)
E_{ZPC} -1097.521719 a.u.

		1	2	3	4	5
1	C	0.000000				
2	H	1.094981	0.000000			
3	C	1.381600	2.151195	0.000000		
4	H	2.148979	2.482422	1.089661	0.000000	
5	C	2.367759	3.367727	1.378270	2.157537	0.000000
6	H	3.369150	4.287175	2.152039	2.505690	1.091753
7	C	2.691057	3.785636	2.371139	3.373327	1.379062
8	H	3.780177	4.874170	3.373809	4.298738	2.158871
9	C	2.254540	3.230559	2.696142	3.784752	2.371545
10	C	3.593289	4.420416	4.194517	5.281748	3.770087
11	H	3.960053	4.682073	4.660933	5.720364	4.336643
12	H	4.396817	5.323187	4.736547	5.817469	4.008196
13	C	4.571550	5.189289	5.256031	6.241345	4.988943
14	C	6.419518	6.986665	6.856886	7.692476	6.500284
15	N	1.316819	2.046961	2.382797	3.354250	2.771432

		6	7	8	9	10
6	H	0.000000				
7	C	2.150991	0.000000			
8	H	2.504131	1.090402	0.000000		
9	C	3.371196	1.382256	2.147918	0.000000	
10	C	4.669680	2.524076	2.748687	1.500362	0.000000
11	H	5.243901	3.168135	3.402801	2.134593	1.100620
12	H	4.723822	2.637579	2.404320	2.151785	1.096755
13	C	5.831379	3.957237	4.144259	3.095690	2.397823
14	C	7.106123	5.661114	5.644126	5.205287	4.728937
15	N	3.863130	2.384271	3.356764	1.323507	2.373712
16	N	5.645790	3.588216	3.890793	2.434236	1.430155
17	H	6.040647	4.077431	4.580623	2.764196	2.076049
18	N	5.362338	3.650632	3.544794	3.249920	2.713296
19	N	6.131036	4.693868	4.513143	4.451920	4.012221
20	N	7.423285	5.863063	6.054813	5.129867	4.631452
21	N	6.819366	5.083248	5.387773	4.146082	3.578734
22	Cl	8.355330	7.131295	7.025981	6.820922	6.390512

		11	12	13	14	15
11	H	0.000000				
12	H	1.771188	0.000000			
13	C	3.268655	2.621173	0.000000		
14	C	5.672644	4.602031	2.479758	0.000000	
15	N	2.738433	3.298920	3.506352	5.631622	0.000000
16	N	2.049659	2.068633	1.335870	3.807997	2.791498
17	H	2.375672	2.953567	1.964937	4.317242	2.633148
18	N	3.732541	2.441476	1.332882	2.221591	4.016758
19	N	5.020746	3.672279	2.238618	1.314243	5.138003
20	N	5.461968	4.789622	2.239181	1.324211	5.277310
21	N	4.319438	3.938325	1.340923	2.220078	4.208670

16	N	4.047429	4.659078	4.889329	5.930372	4.697366
17	H	3.860593	4.252963	4.928808	5.908565	5.012929
18	N	4.935829	5.726876	5.283550	6.254015	4.713209
19	N	5.927705	6.663458	6.184485	7.065015	5.610405
20	N	6.105774	6.503907	6.784011	7.612255	6.667964
21	N	5.163924	5.554516	5.990880	6.882648	5.950064
22	Cl	7.937192	8.473095	8.267057	9.017517	7.876619

22	Cl	7.340427	6.162483	4.176189	1.698744	7.252312

		16	17	18	19	20
16	N	0.000000				
17	H	1.010712	0.000000			
18	N	2.293652	3.140899	0.000000		
19	N	3.453997	4.196553	1.299253	0.000000	
20	N	3.432240	3.647874	2.701833	2.364497	0.000000
21	N	2.270145	2.365689	2.376798	2.699721	1.288673
22	Cl	5.499119	5.986850	3.770522	2.569269	2.572868

		21	22
21	N	0.000000	
22	Cl	3.763556	0.000000

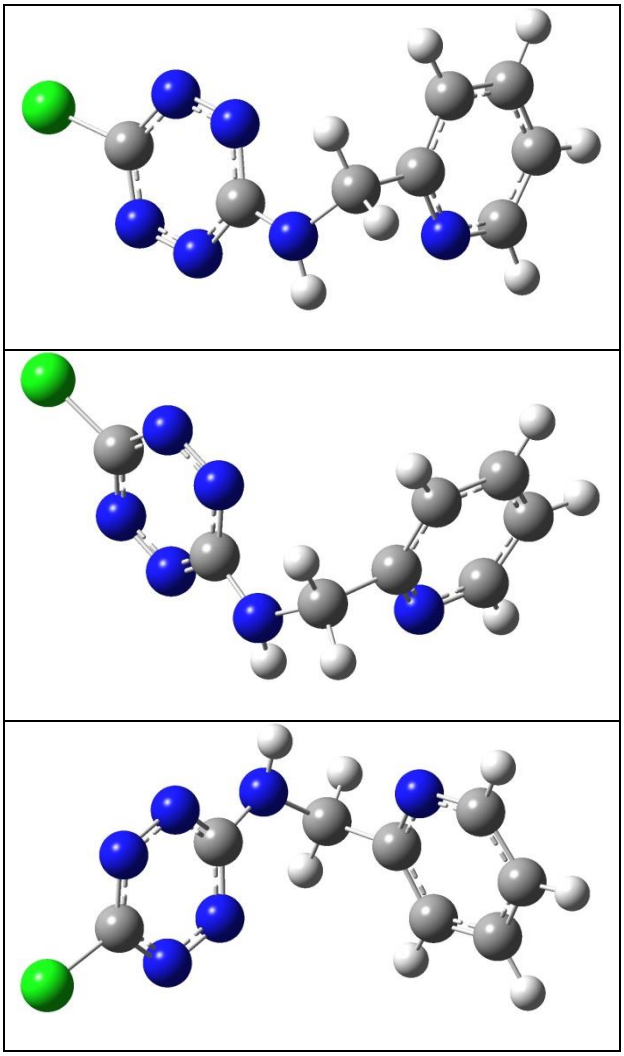
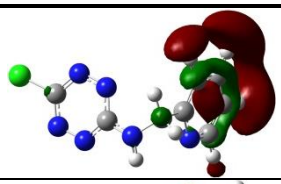
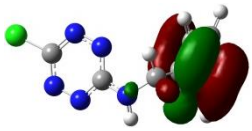
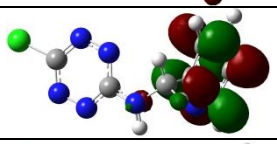
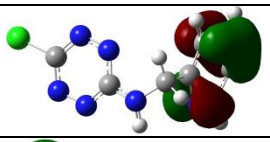
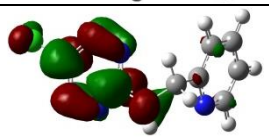
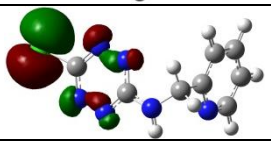
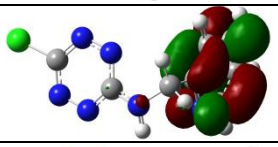
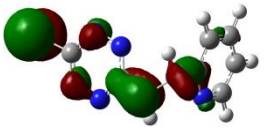
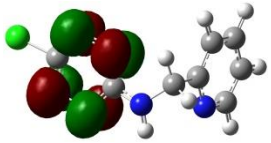
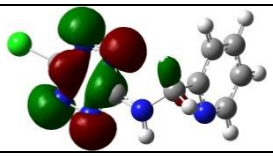
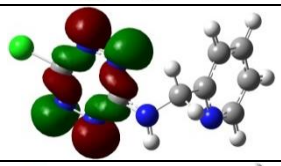
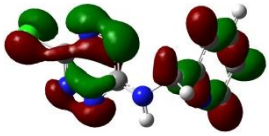
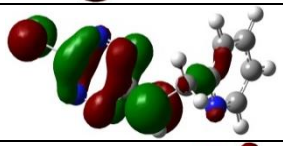
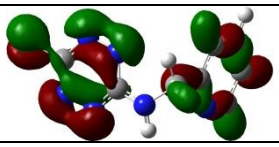
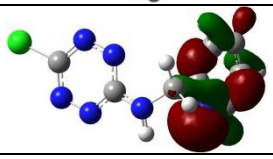
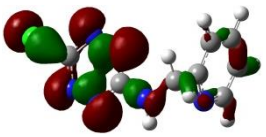


Figure **S2**. Different views of the optimized geometry of **HL**[1].

Table S3. Molecular orbitals for the ligand **HL[1]** (orbital energies in eV); isovalue 0.04

	62 LUMO+4 0.2865		54 HOMO-3 -7.1250
	61 LUMO+3 -1.6443		53 HOMO-4 -7.8851
	60 LUMO+2 -1.8849		52 HOMO-5 -8.2512
	59 LUMO+1 -2.0871		51 HOMO-6 -8.3292
	**58 LUMO** **-3.7406**		50 HOMO-7 -8.6462
	**57 HOMO** **-6.0707**		49 HOMO-8 -9.5432
	56 HOMO-1 -6.4733		48 HOMO-9 -9.5936
	55 HOMO-2 -7.0297		47 HOMO-10 -9.8647

UV-visible spectroscopy of compounds 1-3

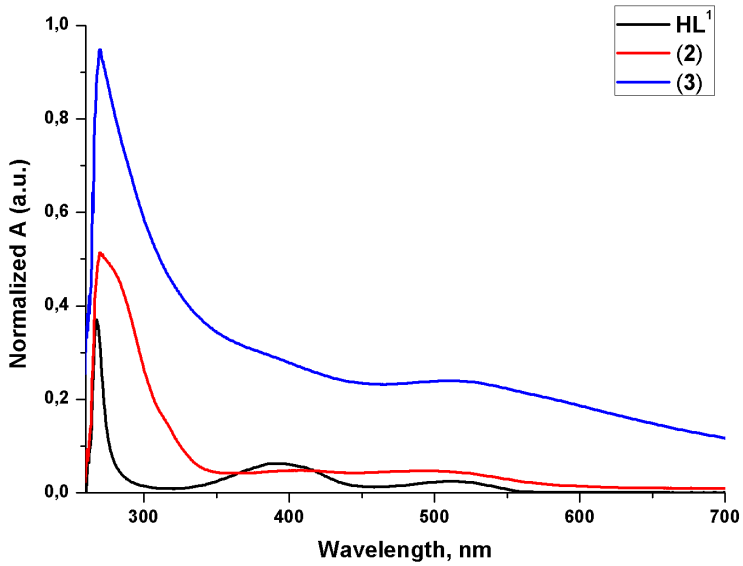


Figure **S3**. UV-visible absorption spectra of compounds **HL[1]** **1** (c = 7·10^{-5} M, black line), **2** (c = 4.88·10^{-5} M, red line) and **3** (c = 4.83·10^{-5} M, blue line) in methanol.

Table S4. UV-visible absorption bands of HL[1] **1**, **2** and **3**

Name	**Transition**	
	λ, nm	ε, L·mol^{-1}·cm^{-1}, 10^4
HL[1]	267	0.529
	392	0.086
	512	0.036
2	270	1.045
	406	0.098
	500	0.096
3	270	1.946
	512	0.497

Complex 2

Table S5. Selected bond lengths and angles for complex **2**

Bond lengths	Å
Cu1–N1	2.0614(18)
Cu1–N2	1.9329(17)
Cu2–N6	1.9404(17)
Cu1–N7	1.9618(17)
Cu2–N11	1.9163(17)
Cu2–N12	2.0139(18)
Cu1–Cl3	2.4853(6)
Cu2–Cl3	2.4575(6)
Cu1–Cu2	2.4313(4)
Angles	º
N2—Cu1—Cl3	102.24(5)
N2—Cu1—Cu2	86.86(5)
N2—Cu1—N1	82.91(7)
N2—Cu1—N7	155.72(7)
N5—N6—Cu2	119.43(13)
N6—Cu2—Cl3	101.69(5)
N6—Cu2—Cu1	88.90(5)
N6—Cu2—N12	103.53(7)
N7—Cu1—Cl3	94.53(5)
N7—Cu1—Cu2	86.50(5)
N7—Cu1—N1	105.83(7)
N11—Cu2—Cl3	106.05(5)
N11—Cu2—Cu1	88.31(5)
N11—Cu2—N12	84.01(7)
N11—Cu2—N6	146.48(7)
N12—Cu2—Cl3	110.64(5)
N12—Cu2—Cu1	166.62(5)
Cu1—Cu2—Cl3	61.108(15)
Cu2—Cl3—Cu1	58.926(14)
Cu2—Cu1—Cl3	59.967(15)

Table S6. Hydrogen bonds and anion-π interactions parameters for **2**

d(A···H), Å	**d(A···D) , Å**	**∠ (A-H-D), °**
Cl(3)···H(11) 2.94	Cl(3)···C(11) 3.44	115
Cl(2)···H(4) 2.86	Cl(2)···C(4) 3.69	150
d(Cl···TTZ), Å		
Cl(1)···TTZ 3.76		
Cl(3)···TTZ 3.45		

Complex 3

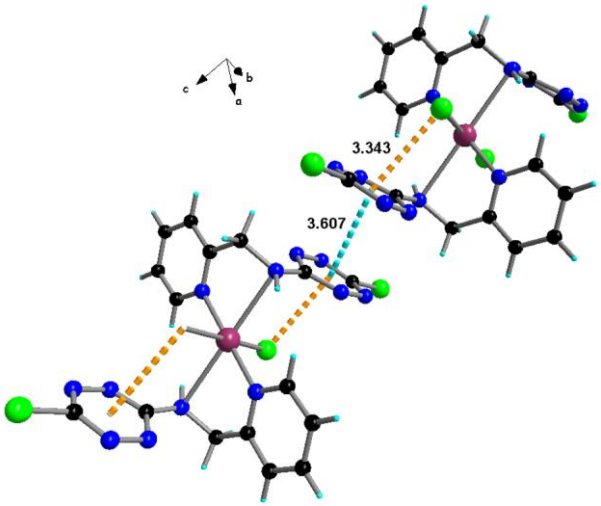


Figure S4. Crystal packing in the structure of **3** with an emphasis on the intramolecular Cl···TTZ (3.343 Å) and intermolecular TTZ···TTZ (3.607 Å) interactions highlighted in dotted orange and blue lines, respectively.

Table S7. Selected lengths (Å) and angles (º) for **3**

Distances	(Å)		
C1—C2	1.372(4)	C8—Cl2	1.709(3)
C1—N1	1.345(3)	C8—N3	1.332(4)
C2—C3	1.394(4)	C8—N6	1.334(4)
C3—C4	1.381(4)	C9—C10	1.444(4)
C4—C5	1.382(4)	C10—N7	1.130(4)
C5—C6	1.508(3)	N1—Cu1	1.998(2)
C5—N1	1.343(3)	N3—N4	1.331(3)
C6—N2	1.460(3)	N5—N6	1.322(3)
C7—N2	1.360(3)	Cl1—Cu1	2.3080(6)
C7—N4	1.336(4)		
C7—N5	1.362(3)		
Angles	(˚)		
C1—C2—C3	118.1(2)	N(1i)—Cu1—Cl1	90.56(6)
C1—N1—Cu1	118.55(17)	N(1i)—Cu1—Cl(1i)	89.44(6)
C3—C4—C5	119.7(3)	N2—C6—C5	114.4(2)
C4—C3—C2	118.9(2)	N2—C7—N5	115.3(2)
C4—C5—C6	119.9(2)	N3—C8—Cl2	117.8(2)
C5—N1—C1	118.5(2)	N3—C8—N6	126.5(3)
C5—N1—Cu1	122.90(17)	N3—N4—C7	116.6(2)
C7—N2—C6	120.7(2)	N4—C7—N2	119.4(2)
N1—C1—C2	123.3(2)	N4—C7—N5	125.3(2)
N1—C5—C4	121.5(2)	N4—N3—C8	117.1(2)
N1—C5—C6	118.6(2)	N5—N6—C8	116.7(2)
N1—Cu1—Cl1	89.44(6)	N6—C8—Cl2	115.6(2)
N1—Cu1—Cl(1i)	90.56(6)	N6—N5—C7	116.9(2)
N1—Cu1—N1i	180	N7—C10—C9	178.2(4)
		Cl(1i)—Cu1—Cl1	180
(i) 1-*x*, 1-*y*, 1-*z*.			

Complex 4

Table S8. Selected lengths (Å) and angles (°) for **4**

Distances	(Å)		
C1—C2	1.378(4)	C13—F4	1.330(3)
C1—N1	1.344(3)	C13—F5	1.331(3)
C2—C3	1.381(4)	C13—F6	1.325(3)
C3—C4	1.378(4)	C14—C15	1.391(4)
C4—C5	1.391(3)	C14—C18	1.534(3)
C5—C6	1.508(3)	C14—O3	1.258(3)
C5—N1	1.342(3)	C15—C16	1.390(4)
C6—N2	1.463(3)	C16—C17	1.531(4)
C7—N2	1.357(3)	C16—O4	1.262(3)
C7—N3	1.349(3)	C17—F7	1.317(3)
C7—N5	1.345(3)	C17—F8	1.313(3)
C8—Cl1	1.712(3)	C17—F9	1.306(4)
C8—N4	1.327(3)	C18—F10	1.325(3)
C8—N6	1.335(3)	C18—F11	1.334(3)
C9—C10	1.379(4)	C18—F12	1.326(3)
C9—C13	1.519(4)	N3—N4	1.321(3)
C9—O1	1.265(3)	N5—N6	1.319(3)
C10—C11	1.407(4)	N1—Cu1	1.9826(19)
C11—C12	1.540(4)	N2—Cu1	2.5906(21)
C11—O2	1.238(3)	O1—Cu1	1.9599(17)
C12—F1	1.282(4)	O2—Cu1	2.2694(19)
C12—F2	1.254(4)	O3—Cu1	1.9476(17)
C12—F3	1.339(5)	O4—Cu1	1.9526(17)
Angles	(˚)		
C1—C2—C3	118.6(2)	F10—C18—F11	107.7(2)
C1—N1—Cu1	119.04(16)	F10—C18—F12	107.6(2)
C3—C4—C5	119.7(2)	F11—C18—C14	109.8(2)
C4—C3—C2	119.1(2)	F12—C18—C14	111.3(2)
C4—C5—C6	120.7(2)	F12—C18—F11	107.1(2)
C5—N1—C1	119.0(2)	N1—C1—C2	122.6(2)
C5—N1—Cu1	121.91(16)	N1—C5—C4	121.0(2)
C7—N2—C6	119.95(19)	N1—C5—C6	118.2(2)
C9—C10—C11	123.2(2)	N1—Cu1—O2	100.67(8)
C9—O1—Cu1	123.83(15)	N2—C6—C5	113.40(19)
C10—C11—C12	115.9(2)	N3—C7—N2	117.4(2)
C10—C9—C13	118.0(2)	N3—N4—C8	116.8(2)
C11—O2—Cu1	117.15(17)	N4—C8—Cl1	116.84(19)
C14—O3—Cu1	124.68(16)	N4—C8—N6	126.7(2)
C15—C14—C18	120.0(2)	N4—N3—C7	116.8(2)
C15—C16—C17	118.7(2)	N5—C7—N2	117.3(2)
C16—C15—C14	120.3(2)	N5—C7—N3	125.3(2)
C16—O4—Cu1	124.10(16)	N5—N6—C8	116.8(2)
F1—C12—C11	113.3(3)	N6—C8—Cl1	116.44(19)
F1—C12—F3	102.6(3)	N6—N5—C7	116.8(2)
F2—C12—C11	112.2(3)	O1—C9—C10	130.2(2)
F2—C12—F1	112.5(4)	O1—C9—C13	111.7(2)
F2—C12—F3	103.4(4)	O1—Cu1—N1	90.76(7)
F3—C12—C11	112.1(3)	O1—Cu1—O2	87.32(7)
F4—C13—C9	110.9(2)	O2—C11—C10	128.4(2)
F4—C13—F5	106.4(2)	O2—C11—C12	115.7(2)
F5—C13—C9	114.5(2)	O3—C14—C15	128.0(2)
F6—C13—C9	111.1(2)	O3—C14—C18	112.0(2)
F6—C13—F4	105.8(2)	O3—Cu1—N1	170.67(8)
F6—C13—F5	107.7(2)	O3—Cu1—O1	86.44(7)
F7—C17—C16	113.3(2)	O3—Cu1—O2	88.10(7)
F8—C17—C16	111.4(2)	O3—Cu1—O4	91.16(7)

F8—C17—F7	105.8(2)	O4—C16—C15	128.7(2)
F9—C17—C16	110.1(2)	O4—C16—C17	112.6(2)
F9—C17—F7	107.7(3)	O4—Cu1—N1	91.51(7)
F9—C17—F8	108.4(3)	O4—Cu1—O1	177.53(7)
F10—C18—C14	113.1(2)	O4—Cu1—O2	93.21(7)

Complex 5

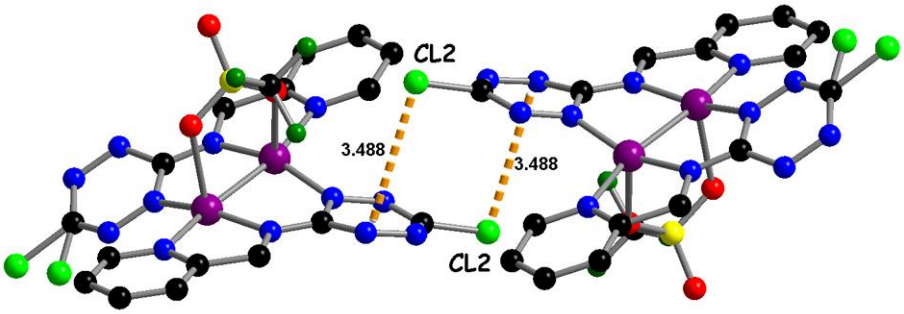


Figure S5. Cl···TTZ interactions in the structure of **5**.

Table S9. Selected lengths (Å) and angles (º) for **5**

Distances	(Å)		
C1—N1	1.350(7)	C15—N9	1.386(7)
C1—C2	1.370(9)	C16—N8	1.327(7)
C2—C3	1.393(9)	C16—N10	1.346(7)
C3—C4	1.389(9)	C16—CL2	1.714(6)
C4—C5	1.389(8)	C17—F1	1.273(9)
C5—N1	1.339(7)	C17—F2	1.317(9)
C5—C6	1.505(7)	C17—F3	1.322(9)
C6—N2	1.459(6)	C17—S1	1.839(7)
C7—N2	1.305(7)	N3—N4	1.327(7)
C7—N5	1.386(8)	N5—N6	1.322(7)
C7—N3	1.391(7)	N7—N8	1.329(6)
C8—N6	1.325(8)	N9—N10	1.308(7)
C8—N4	1.354(8)	O1—S1	1.437(5)
C8—CL1A	1.715(6)	O2—S1	1.450(5)
C9—N12	1.342(7)	O3—S1	1.434(5)
C9—C10	1.375(8)	Cu1—N2	1.892(4)
C10—C11	1.379(9)	Cu1—N7	1.930(5)
C11—C12	1.381(9)	Cu1—N1	2.028(4)
C12—C13	1.386(8)	Cu1—O1	2.372(4)
C13—N12	1.335(7)	Cu1—Cu2	2.5199(11)
C13—C14	1.495(8)	Cu2—N11	1.903(5)
C14—N11	1.468(7)	Cu2—N5	1.923(5)
C15—N11	1.298(7)	Cu2—N12	2.051(4)
C15—N7	1.381(7)	Cu2—O2	2.422(5)
Angles	(˚)		
C1—C2—C3	118.9(6)	N6—C8—CL1A	117.3(5)
C1—C2—H2	120.600	N7—C15—N9	120.0(5)
C1—N1—Cu1	127.8(4)	N8—C16—N10	125.6(5)
C3—C4—C5	118.9(5)	N8—C16—CL2	117.2(4)
C4—C3—C2	118.9(5)	N8—N7—C15	118.5(4)
C4—C5—C6	121.2(5)	N8—N7—Cu1	120.4(3)
C5—N1—C1	119.0(5)	N9—N10—C16	118.0(4)
C5—N1—Cu1	113.2(3)	N10—N9—C15	117.3(5)
C6—N2—Cu1	117.1(3)	N10—C16—CL2	116.8(4)
C7—N2—C6	118.1(4)	N11—C15—N7	117.8(5)
C7—N2—Cu1	124.6(4)	N11—C15—N9	122.0(5)
C7—N5—Cu2	121.1(4)	N11—C14—C13	109.6(4)
C9—C10—C11	118.7(6)	N12—C9—C10	122.4(5)
C9—N12—Cu2	128.6(4)	N12—C13—C12	121.4(5)
C10—C11—C12	119.1(5)	N12—C13—C14	118.0(5)
C11—C12—C13	119.3(5)	O1—S1—O2	113.7(3)
C12—C13—C14	120.6(5)	O1—S1—C17	101.9(3)

C13—N12—C9	119.2(5)	O2—S1—C17	104.1(3)
C13—N12—Cu2	112.1(4)	O3—S1—O1	116.5(3)
C14—N11—Cu2	116.3(3)	O3—S1—O2	115.5(3)
C15—N11—C14	118.0(5)	O3—S1—C17	102.3(3)
C15—N11—Cu2	125.4(4)	S1—O1—Cu1	126.9(3)
C15—N7—Cu1	121.1(3)	S1—O2—Cu2	118.4(3)
C16—N8—N7	116.2(5)	N1—Cu1—O1	93.10(17)
F1—C17—S1	110.7(5)	N1—Cu1—Cu2	168.49(13)
F1—C17—F2	107.0(7)	N2—Cu1—N7	161.1(2)
F1—C17—F3	106.7(6)	N2—Cu1—N1	83.19(18)
F2—C17—S1	112.0(5)	N2—Cu1—Cu2	86.96(13)
F2—C17—F3	109.7(7)	N2—Cu1—O1	108.31(19)
F3—C17—S1	110.5(6)	N5—Cu2—N12	105.3(2)
N1—C1—C2	122.5(5)	N5—Cu2—O2	102.5(2)
N1—C5—C4	121.8(5)	N5—Cu2—Cu1	86.18(15)
N1—C5—C6	117.0(4)	N7—Cu1—N1	105.22(18)
N2—C6—C5	109.4(4)	N7—Cu1—O1	88.44(19)
N2—C7—N5	118.7(5)	N7—Cu1—Cu2	85.96(13)
N2—C7—N3	120.9(5)	N11—Cu2—N5	162.0(2)
N3—N4—C8	117.3(5)	N11—Cu2—N12	83.04(18)
N4—N3—C7	117.0(5)	N11—Cu2—Cu1	86.39(14)
N4—C8—CL1A	116.0(5)	N11—Cu2—O2	94.0(2)
N5—N6—C8	116.2(5)	N12—Cu2—O2	85.31(18)
N5—C7—N3	120.3(5)	N12—Cu2—Cu1	168.44(13)
N6—N5—C7	119.0(5)	O1—Cu1—Cu2	84.33(11)
N6—N5—Cu2	119.9(4)	O2—Cu2—Cu1	90.79(12)
N6—C8—N4	126.2(6)		

EPR measurements of complexes 3 and 4

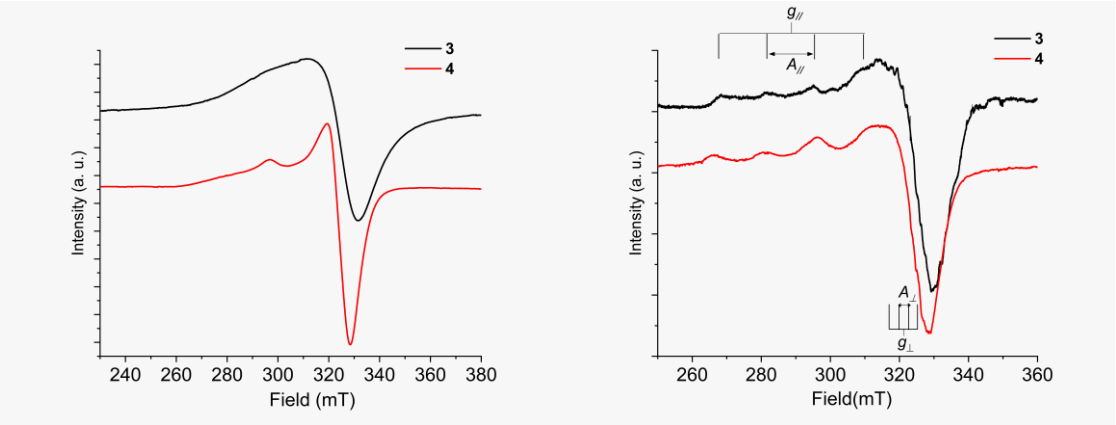


Figure S6. X-Band (ν ca. 9.4 GHz) EPR spectra of **3** and **4** recorded at 50 K on microcrystalline powder (left) and frozen solution (right). See main text for experimental details.

Magnetic measurements of complexes 2 and 5

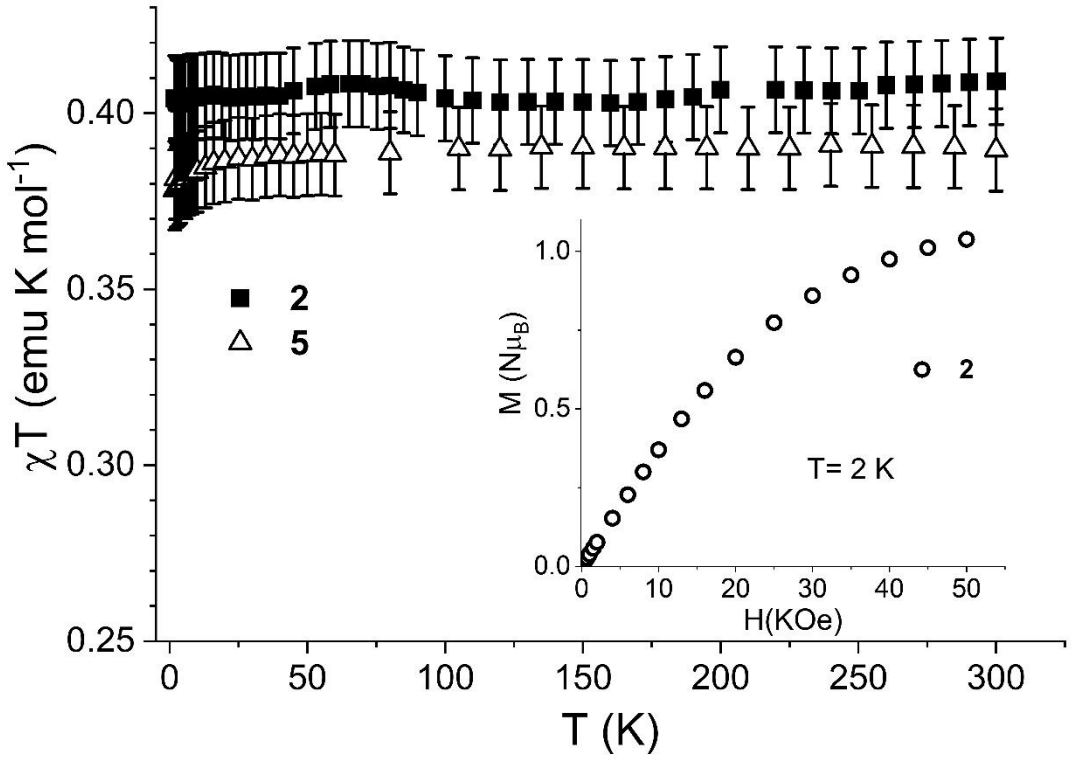
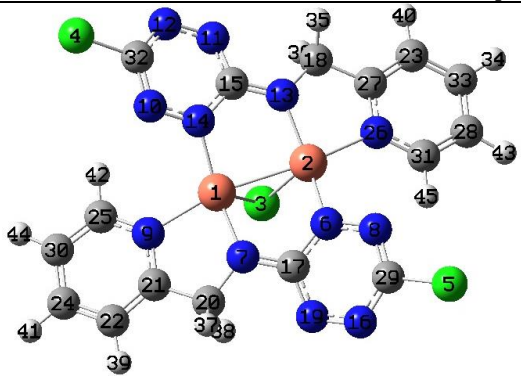


Figure S7. χT vs T product for **2** and **5** (main panel), and isothermal field dependent magnetization measured at 2 K for **2**. Error bars correspond to ± 3 %.

DFT calculations

Complex 2

Table S10. Distance matrix for the optimized structure



		1	2	3	4	5
1	Cu	0.000000				
2	Cu	2.419266	0.000000			
3	Cl	2.532603	2.532610	0.000000		
4	Cl	5.293653	6.664014	6.824287	0.000000	
5	Cl	6.664007	5.293656	6.824315	11.379132	0.000000
6	N	2.950647	1.850888	3.407137	7.853382	3.766324
7	N	1.855744	3.000061	3.224350	6.939546	5.469299
8	N	4.236572	2.742834	4.475441	8.954729	2.565964
9	N	2.007144	4.381977	3.618447	5.305536	8.027956
10	N	2.742834	4.236572	4.475418	2.565963	8.954723
11	N	4.030717	4.036739	4.464129	3.767045	9.202970
12	N	4.492811	5.034923	5.298885	2.583311	10.144601
13	N	3.000074	1.855744	3.224396	5.469310	6.939525
14	N	1.850893	2.950644	3.407130	3.766327	7.853372
15	C	2.814809	2.779858	3.516906	4.206913	7.941495
16	N	5.034923	4.492793	5.298859	10.144621	2.583309
17	C	2.779861	2.814794	3.516875	7.941515	4.206906
18	C	4.356451	2.806232	3.960546	6.291577	7.453382
19	N	4.036741	4.030693	4.464076	9.202996	3.767046
20	C	2.806228	4.356425	3.960455	7.453412	6.291567
21	C	2.796654	4.933460	4.139454	6.546668	7.697707
22	C	4.141507	6.303313	5.279082	7.214625	8.777507
23	C	6.303297	4.141493	5.279053	8.777527	7.214636
24	C	4.751588	7.066019	5.864021	6.763424	10.038307
25	C	3.021169	5.376833	4.382109	4.690495	9.338005
26	N	4.381953	2.007129	3.618393	8.027964	5.305573
27	C	4.933454	2.796646	4.139455	7.697721	6.546672
28	C	6.663471	4.299403	5.471165	10.296460	5.511896
29	C	5.036059	3.929395	5.286367	9.942761	1.701513
30	C	4.299428	6.663525	5.471308	5.511792	10.296448
31	C	5.376782	3.021144	4.381978	9.338011	4.690593
32	C	3.929401	5.036062	5.286358	1.701513	9.942753
33	C	7.065980	4.751565	5.863924	10.038324	6.763477

		6	7	8	9	10
6	N	0.000000				
7	N	2.261545	0.000000			
8	N	1.302074	3.426140	0.000000		
9	N	4.561536	2.568713	5.836857	0.000000	
10	N	5.336284	4.449348	6.493436	3.213285	0.000000

		11	12	13	14	15
11	N	0.000000				
12	N	1.282763	0.000000			
13	N	2.313842	3.443601	0.000000		
14	N	2.364286	2.683995	2.261547	0.000000	
15	C	1.352728	2.258926	1.293633	1.361287	0.000000
16	N	8.397423	9.194982	6.325798	6.622293	7.059903
17	C	6.361896	7.059914	4.519084	4.431574	5.022308
18	C	2.652596	3.921809	1.423016	3.553366	2.312972
19	N	7.695781	8.397433	5.809965	5.758552	6.361892
20	C	6.822643	7.183893	5.620524	4.584369	5.618144
21	C	6.477576	6.609011	5.780932	4.255783	5.450760
22	C	7.605744	7.600060	7.103809	5.451110	6.681822
23	C	5.085761	6.348305	3.684368	5.927384	4.785482
24	C	7.658016	7.453284	7.567035	5.690424	6.935243
25	C	5.311233	5.093234	5.472789	3.464235	4.680424
26	N	4.738784	5.958086	2.568710	4.561521	3.844168
27	C	4.119940	5.390722	2.381188	4.619258	3.572972
28	C	6.802627	8.071244	4.837857	6.921925	6.106297
29	C	7.900062	8.787514	5.699850	6.364836	6.589773
30	C	6.593349	6.266166	6.838669	4.829826	6.038528
31	C	6.052343	7.279820	3.890519	5.804053	5.160774
32	C	2.222826	1.330798	3.787115	2.210513	2.511942
33	C	6.382296	7.655637	4.751887	6.973269	5.945417

		16	17	18	19	20
16	N	0.000000				
17	C	2.258922	0.000000			
18	C	7.183865	5.618136	0.000000		
19	N	1.282765	1.352727	6.822622	0.000000	
20	C	3.921808	2.312969	6.895585	2.652595	0.000000
21	C	5.390728	3.572978	7.095548	4.119950	1.486809
22	C	6.348309	4.785488	8.403164	5.085771	2.502753
23	C	7.600000	6.681777	2.502752	7.605672	8.403095
24	C	7.655649	5.945431	8.837330	6.382315	3.752335
25	C	7.279837	5.160793	6.716689	6.052365	3.620066
26	N	5.306020	4.321886	2.394591	5.247056	6.164210
27	C	6.608966	5.450727	1.486809	6.477524	7.095500
28	C	6.266091	6.038453	4.195853	6.593235	8.064819
29	C	1.330797	2.511937	6.417260	2.222828	4.650615
30	C	8.071259	6.106314	8.064953	6.802648	4.195850
31	C	5.093170	4.680354	3.620067	5.311131	6.716568
32	C	8.787525	6.589789	4.650622	7.900080	6.417288
33	C	7.453210	6.935179	3.752333	7.657916	8.837221

		21	22	23	24	25
21	C	0.000000				
22	C	1.383160	0.000000			
23	C	8.904066	10.226608	0.000000		
24	C	2.376921	1.374024	10.828540	0.000000	
25	C	2.279695	2.694832	8.893628	2.366425	0.000000
26	N	6.840217	8.184547	2.371820	8.950081	7.233039
27	C	7.567846	8.904081	1.383157	9.514885	7.584516
28	C	8.910177	10.207773	2.370633	11.055674	9.478883
29	C	6.031618	7.150722	6.635328	8.385471	7.656091

11	N	5.758544	5.809982	6.689475	5.247120	2.698345
12	N	6.622290	6.325818	7.628791	5.306065	2.356896
13	N	3.650171	4.352040	4.449327	4.847917	3.426141
14	N	4.190288	3.650184	5.336279	3.088064	1.302074
15	C	4.431565	4.519092	5.408420	4.321929	2.281899
16	N	2.683989	3.443600	2.356894	5.958097	7.628805
17	C	1.361286	1.293634	2.281899	3.844181	5.408437
18	C	4.584353	5.620529	5.130100	6.164281	4.593356
19	N	2.364282	2.313844	2.698348	4.738799	6.689497
20	C	3.553361	1.423016	4.593353	2.394592	5.130129
21	C	4.619266	2.381187	5.797196	1.327138	4.476807
22	C	5.927394	3.684367	7.054773	2.371826	5.463939
23	C	5.451086	7.103769	5.463927	8.184565	7.054768
24	C	6.973290	4.751889	8.170418	2.757863	5.430026
25	C	5.804080	3.890523	7.093894	1.325503	3.142123
26	N	3.088050	4.847874	3.213299	6.308066	5.836847
27	C	4.255764	5.780905	4.476796	6.840245	5.797192
28	C	4.829806	6.838589	4.390244	8.520452	8.189816
29	C	2.210510	3.787108	1.305202	6.344565	7.456450
30	C	6.921951	4.837858	8.189834	2.374366	4.390205
31	C	3.464218	5.472713	3.142171	7.232998	7.093874
32	C	6.364841	5.699870	7.456448	4.424122	1.305201
33	C	5.690398	7.566970	5.430034	8.950062	8.170404

30	C	2.710582	2.370630	10.207855	1.381197	1.373976
31	C	7.584440	8.893557	2.694832	9.773267	8.247241
32	C	5.720365	6.635348	7.150729	6.444111	4.132601
33	C	9.514827	10.828492	1.374024	11.548505	9.773300

		26	27	28	29	30
26	N	0.000000				
27	C	1.327137	0.000000			
28	C	2.374363	2.710586	0.000000		
29	C	4.424123	5.720348	5.267248	0.000000	
30	C	8.520496	8.910263	10.718130	8.613198	0.000000
31	C	1.325503	2.279698	1.373974	4.132622	9.478882
32	C	6.344563	6.031622	8.613195	8.510401	5.267232
33	C	2.757854	2.376918	1.381197	6.444104	11.055712

		31	32	33
31	C	0.000000		
32	C	7.656084	0.000000	
33	C	2.366420	8.385471	0.000000

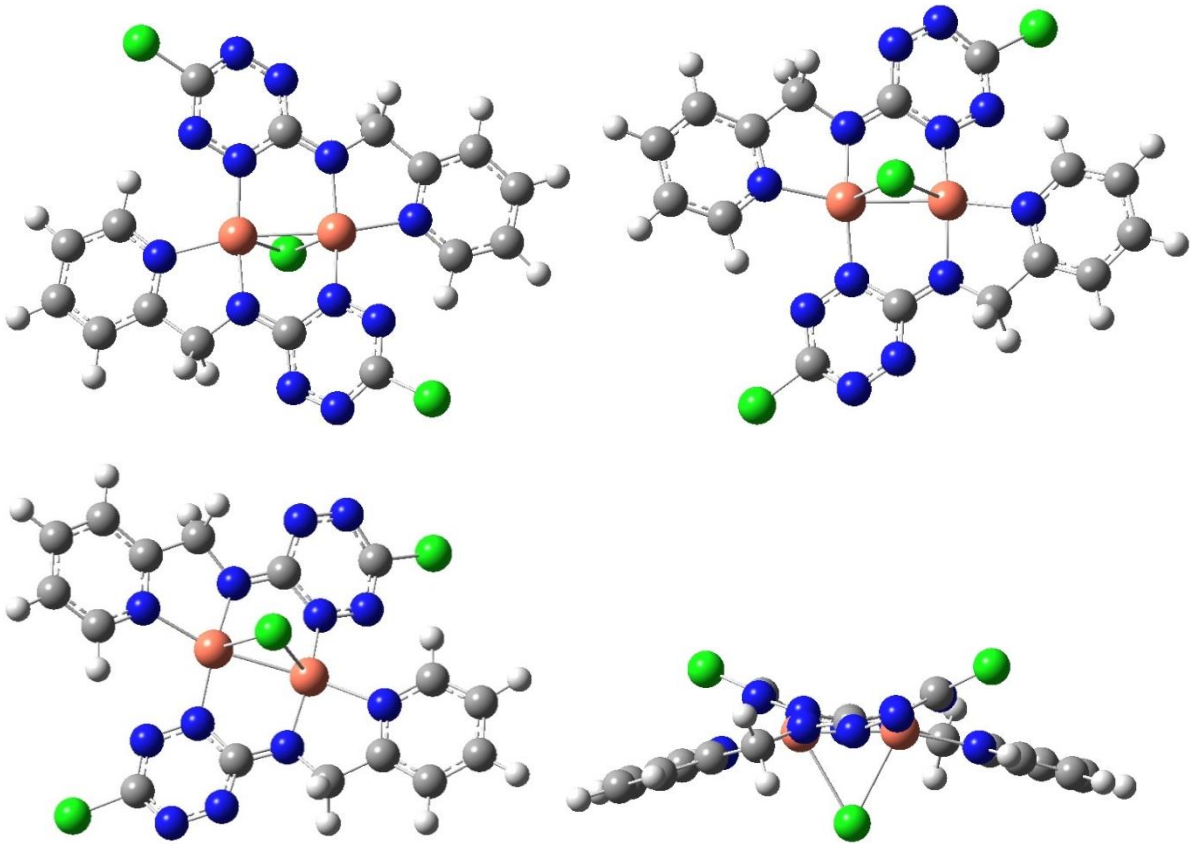


Figure S8. Different views of the optimized geometry of **2**.

Table S11. Molecular orbitals for the complex **2** (orbital energies in eV); isovalue 0.04

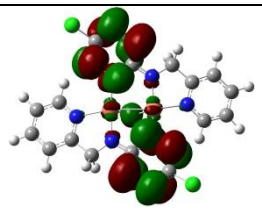
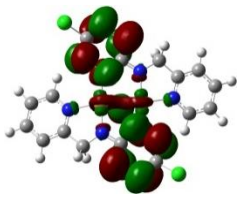
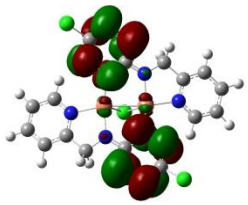
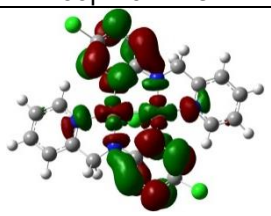
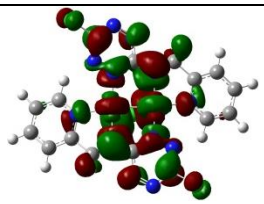
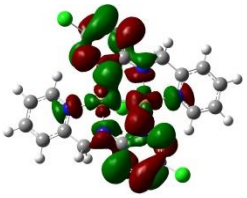
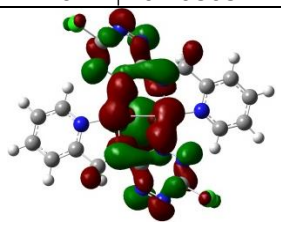
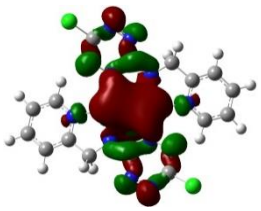
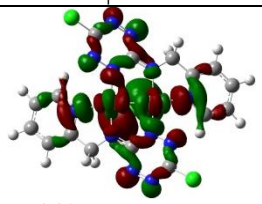
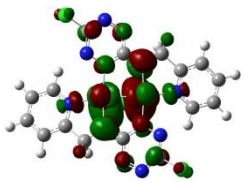
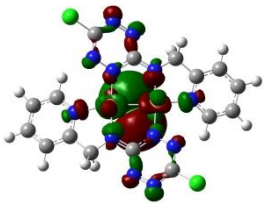
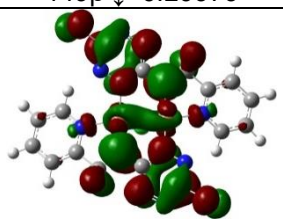
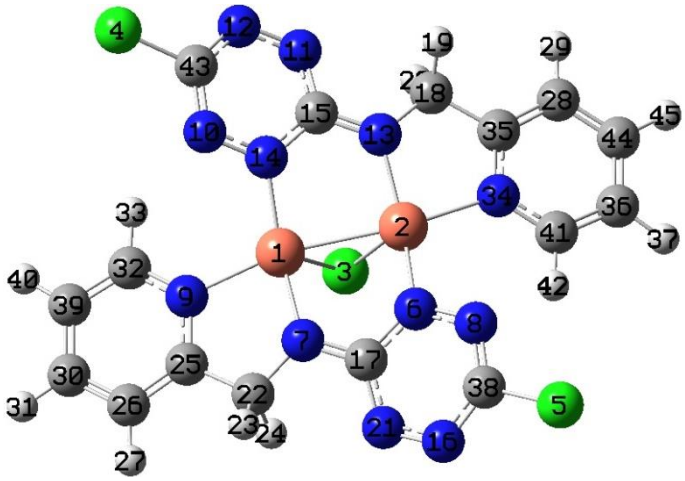
 153α -0.14357	 153β -0.14152
 152α -0.14440	 152β -0.14213
 151α ↑ -0.20363	 151β -0.14869
 150α ↑ -0.20726	 150β ↓ -0.18998
 149α ↑ -0.21938	 149β ↓ -0.20676
 148α ↑ -0.22227	 148β ↓ -0.21625

Table S12. Calculated Mulliken charge and spin density for the complex **2**

		Mulliken charge	Spin density
1	Cu	1.078548	0.384634
2	Cu	1.078548	0.384628
3	Cl	-0.759923	0.020911
4	Cl	-0.050523	0.001541
5	Cl	-0.050522	0.001541
6	N	-0.625289	0.024236
7	N	-0.845749	0.059242
8	N	-0.174409	-0.018427
9	N	-0.764105	0.041982
10	N	-0.174414	-0.018428
11	N	-0.301150	0.007689
12	N	-0.195304	-0.021227
13	N	-0.845754	0.059238
14	N	-0.625287	0.024237
15	C	0.866198	-0.009210
16	N	-0.195307	-0.021225
17	C	0.866192	-0.009210
18	C	0.025621	-0.001020
19	H	0.160309	0.003008
20	H	0.188563	0.000074
21	N	-0.301148	0.007686
22	C	0.025621	-0.001020
23	H	0.160309	0.003009
24	H	0.188564	0.000074
25	C	0.376086	-0.001117
26	C	-0.255494	0.002739
27	H	0.122129	0.001049
28	C	-0.255498	0.002739
29	H	0.122128	0.001049
30	C	0.067060	-0.003835
31	H	0.127695	0.000253
32	C	0.227133	-0.004101
33	H	0.157998	0.002220
34	N	-0.764108	0.041983
35	C	0.376092	-0.001117
36	C	-0.263837	0.004572
37	H	0.125442	0.000710
38	C	0.333042	0.014538
39	C	-0.263836	0.004572
40	H	0.125442	0.000710
41	C	0.227143	-0.004101
42	H	0.157989	0.002220
43	C	0.333047	0.014540
44	C	0.067061	-0.003835
45	H	0.127696	0.000253



DFT calculations

Complex 5

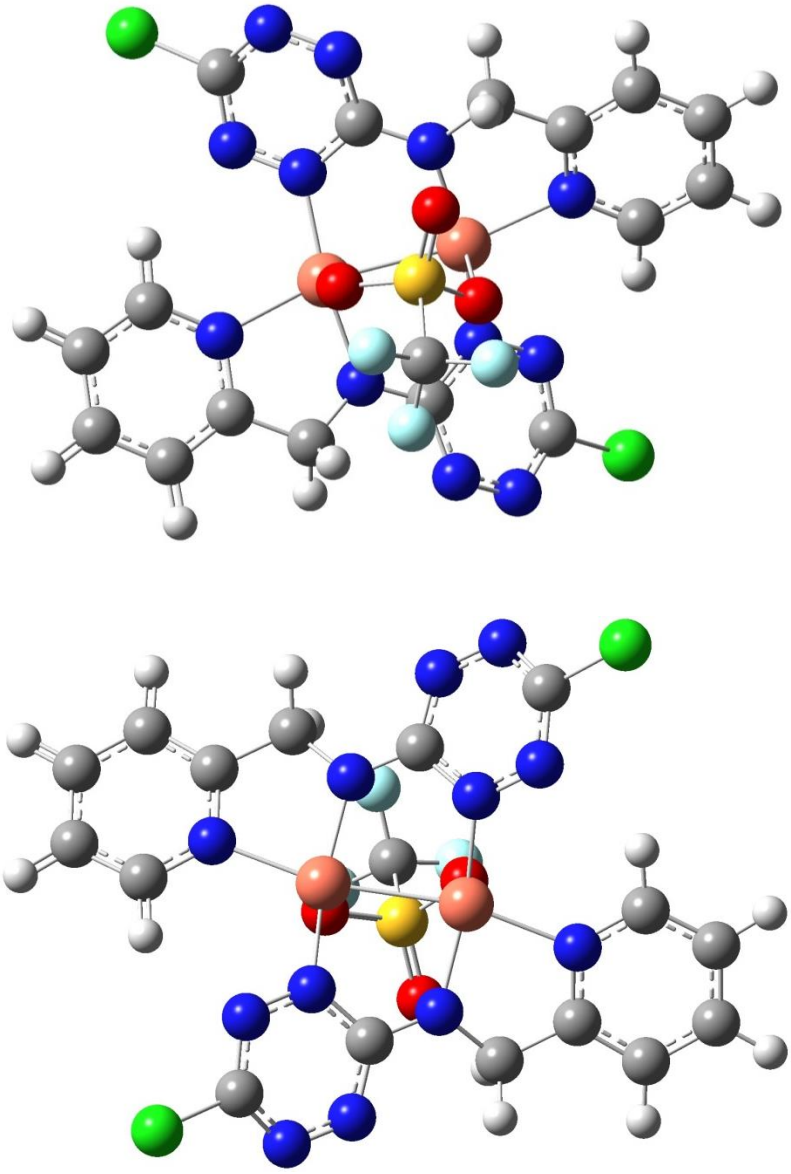
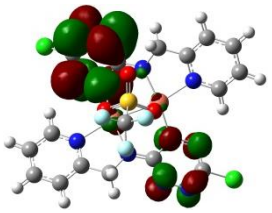
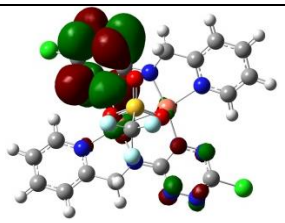
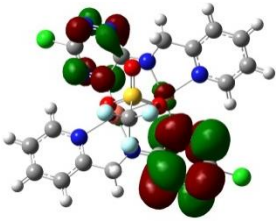
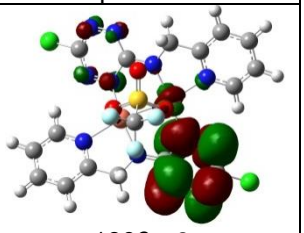
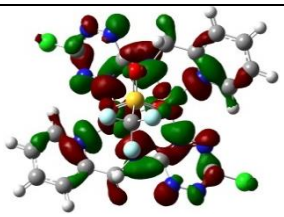
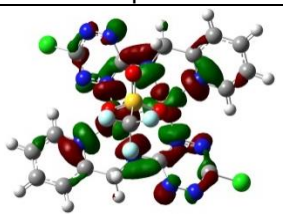
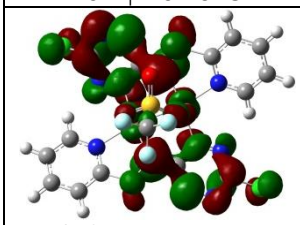
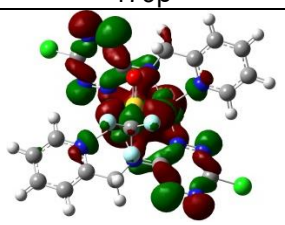
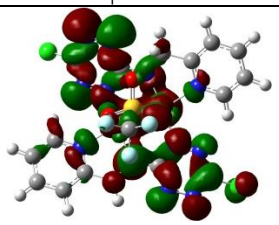
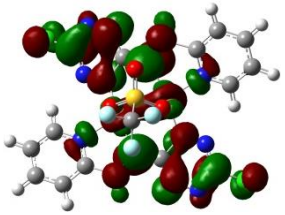
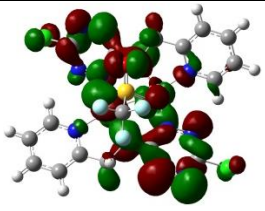
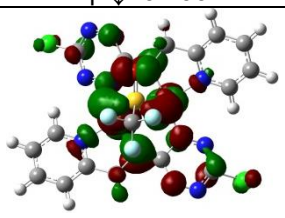


Figure S9. Different views of the optimized geometry of **5**.

Table S13. Molecular orbitals for the complex **5** (orbital energies in eV); isovalue 0.04

 181α -0.14251	 181β -0.14174
 180α -0.14393	 180β -0.
 179α ↑ -0.19734	 179β
 178α ↑ -0.21088	 178β ↓
 177α ↑ -0.21719	 177β ↓ -0.20627
 176α ↑ -0.21831	 176β ↓ -0.20998

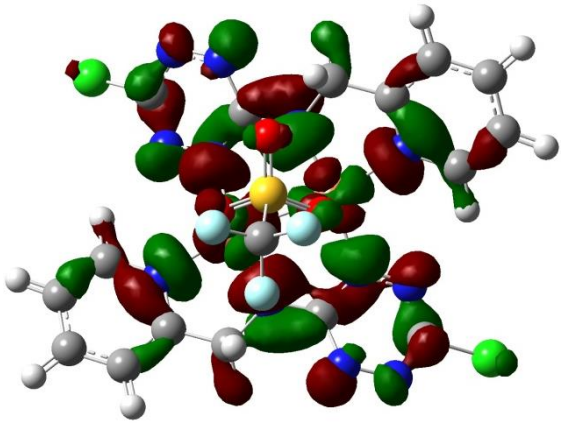


Figure S10. Graphical representation of the singly occupied molecular orbital (SOMO, orbital 179α) of complex **5** at the M11L/6-311G(d,p) level of theory.

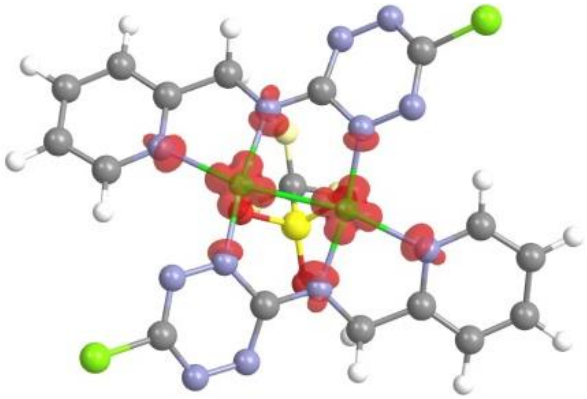


Figure S11. Spin density map in complex **5** (isovalue 0.005). The spin density value on each Cu equals 0.3749 (Cu1) and 0.3659 (Cu2).

DFT calculations

Complex 3

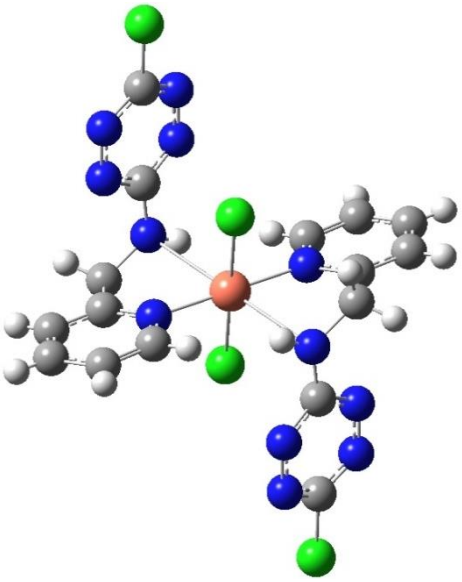


Figure S12. Optimized geometry of **3**.

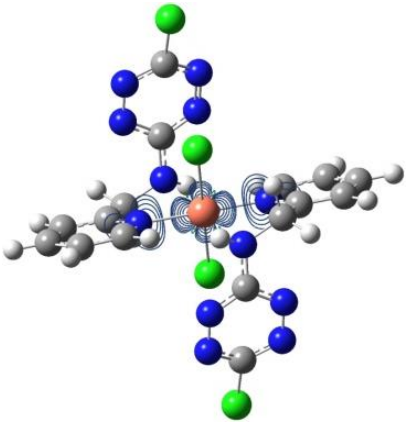


Figure S13. Spin density map in complex **3** (isovalue 0.005). The spin density value on Cu equals 0.6175.

NMR Spectra of HL^1

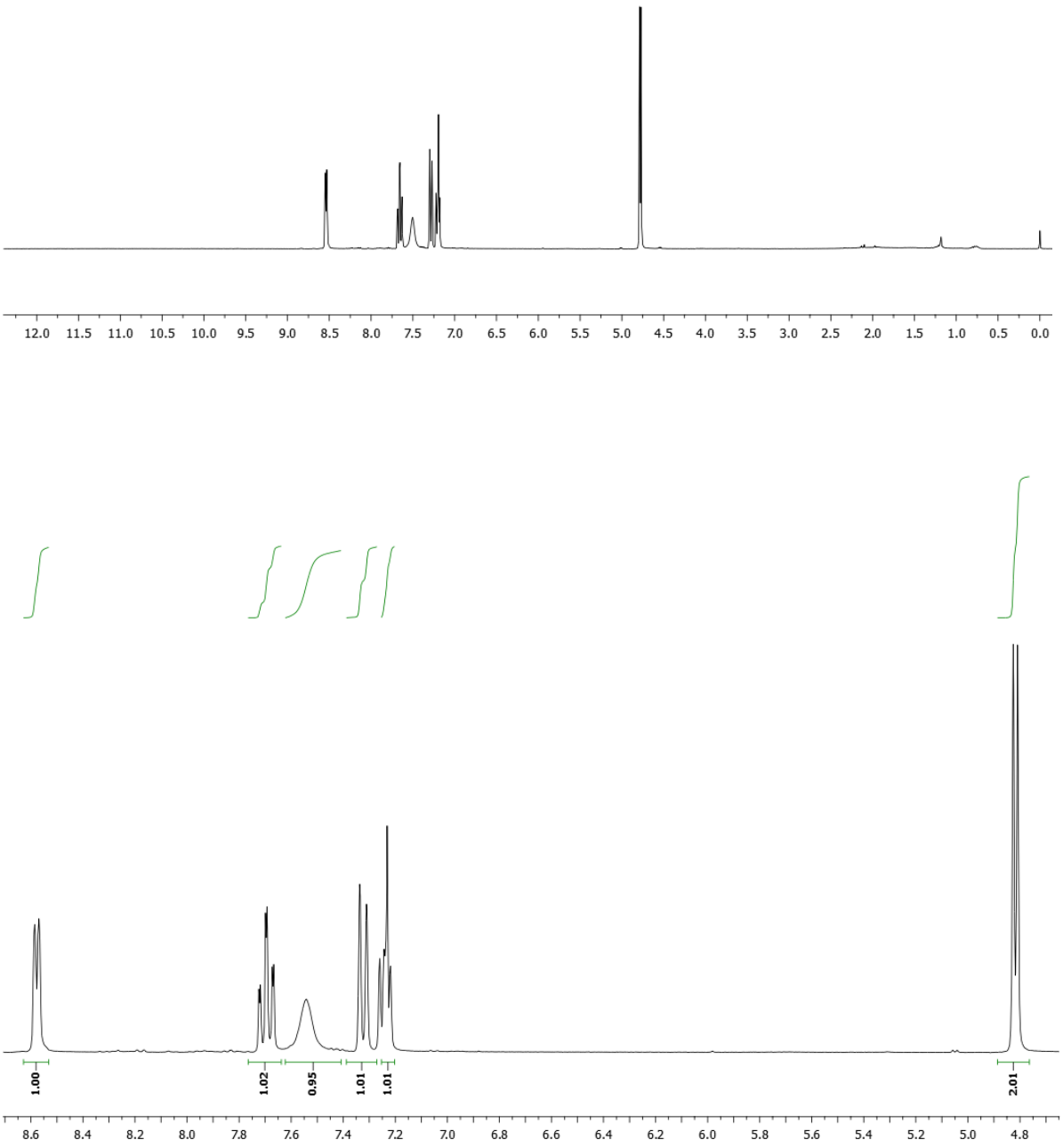


Figure S14. ^{1}H NMR spectrum of **HL^1** in $CDCl_3$

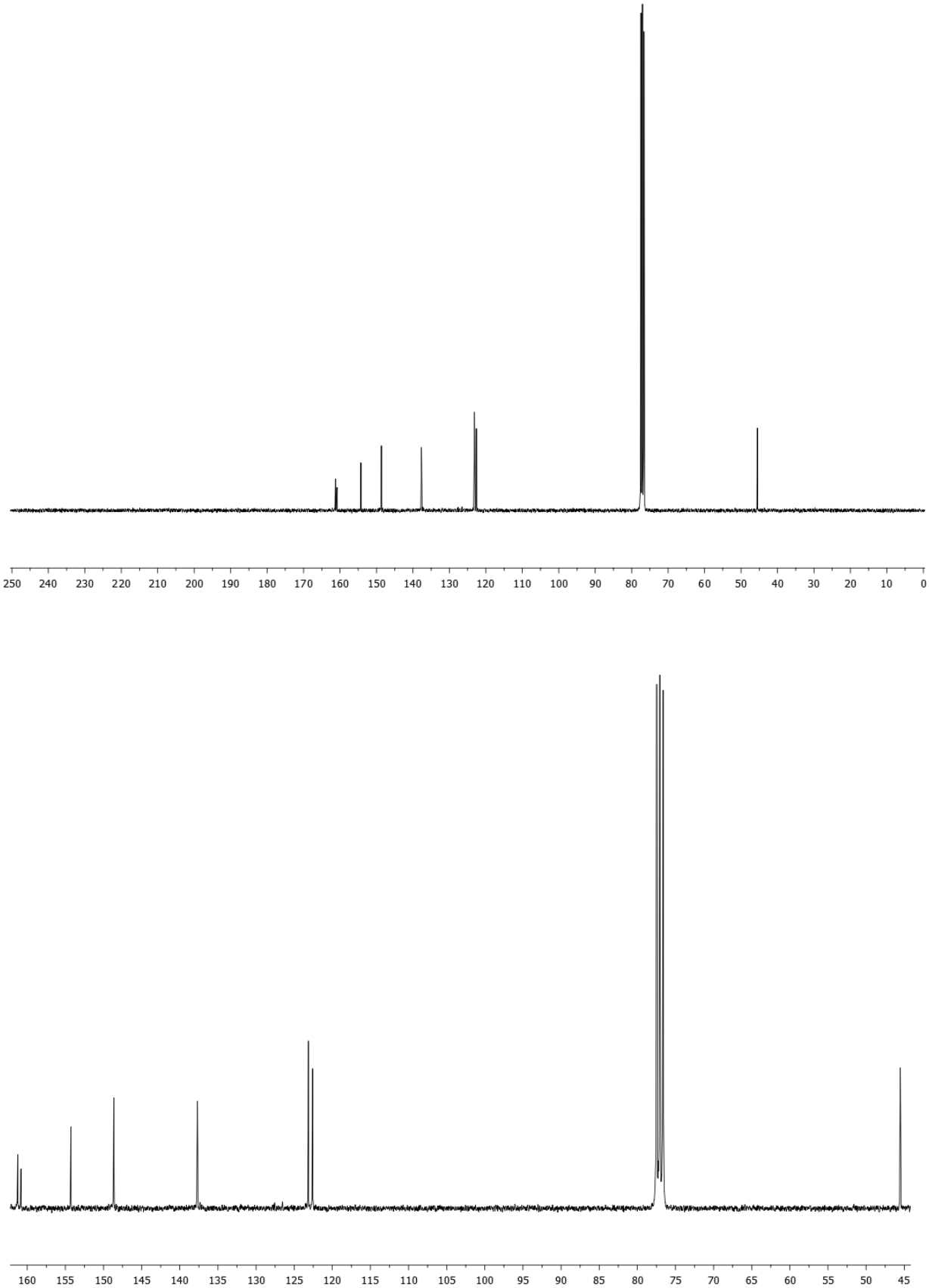


Figure S15. ^{13}C NMR spectrum of **HL^{1}** in $CDCl_3$