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Electronic Influence of Substitution on the Pyridine Ring within NNN Pincer-Type Molecules

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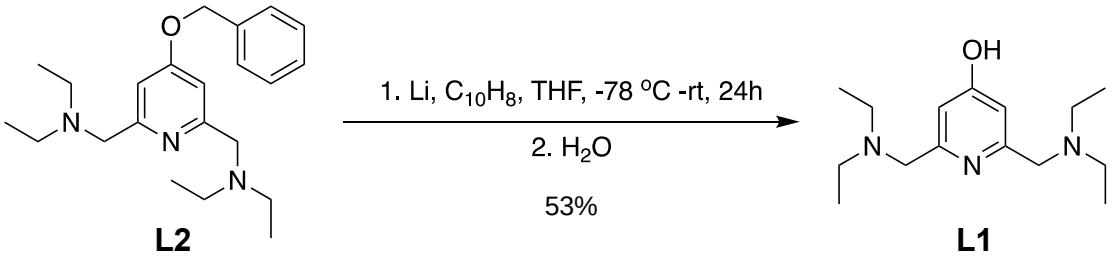
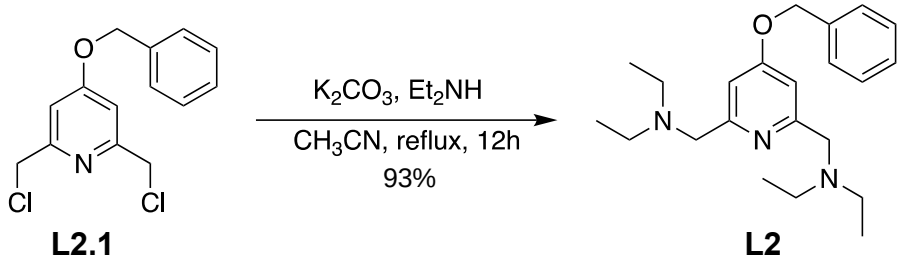
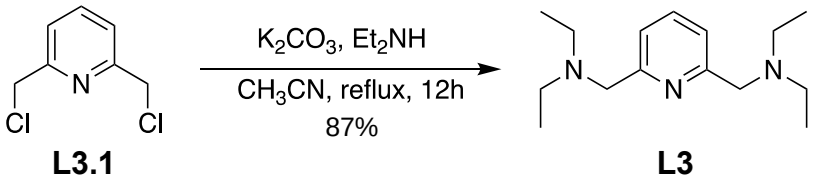


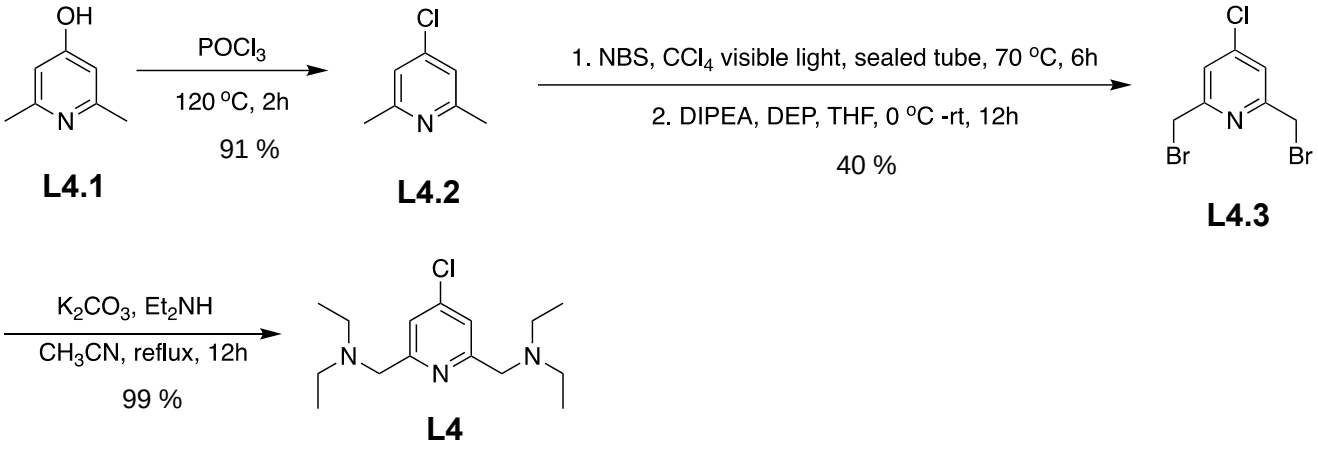
Scheme S1. Synthetic pathway of **L1**.[1, 2]



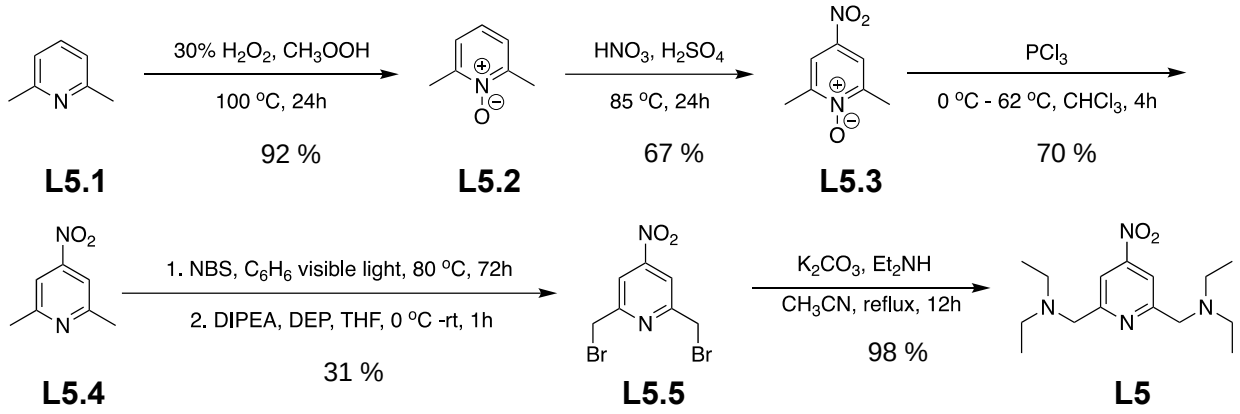
Scheme S2. Synthetic pathway of **L2**. **L2.1** was synthesized using modified methods from 3.



Scheme S3. Synthetic pathway of **L3**. This is based on previous work where OTs groups were used in the place of Cl groups within **L3.1**.[4]



Scheme S4. Synthetic pathway of **L4** based on ref. [5]



Scheme S5. Synthetic pathway of **L5** based on ref.[5]

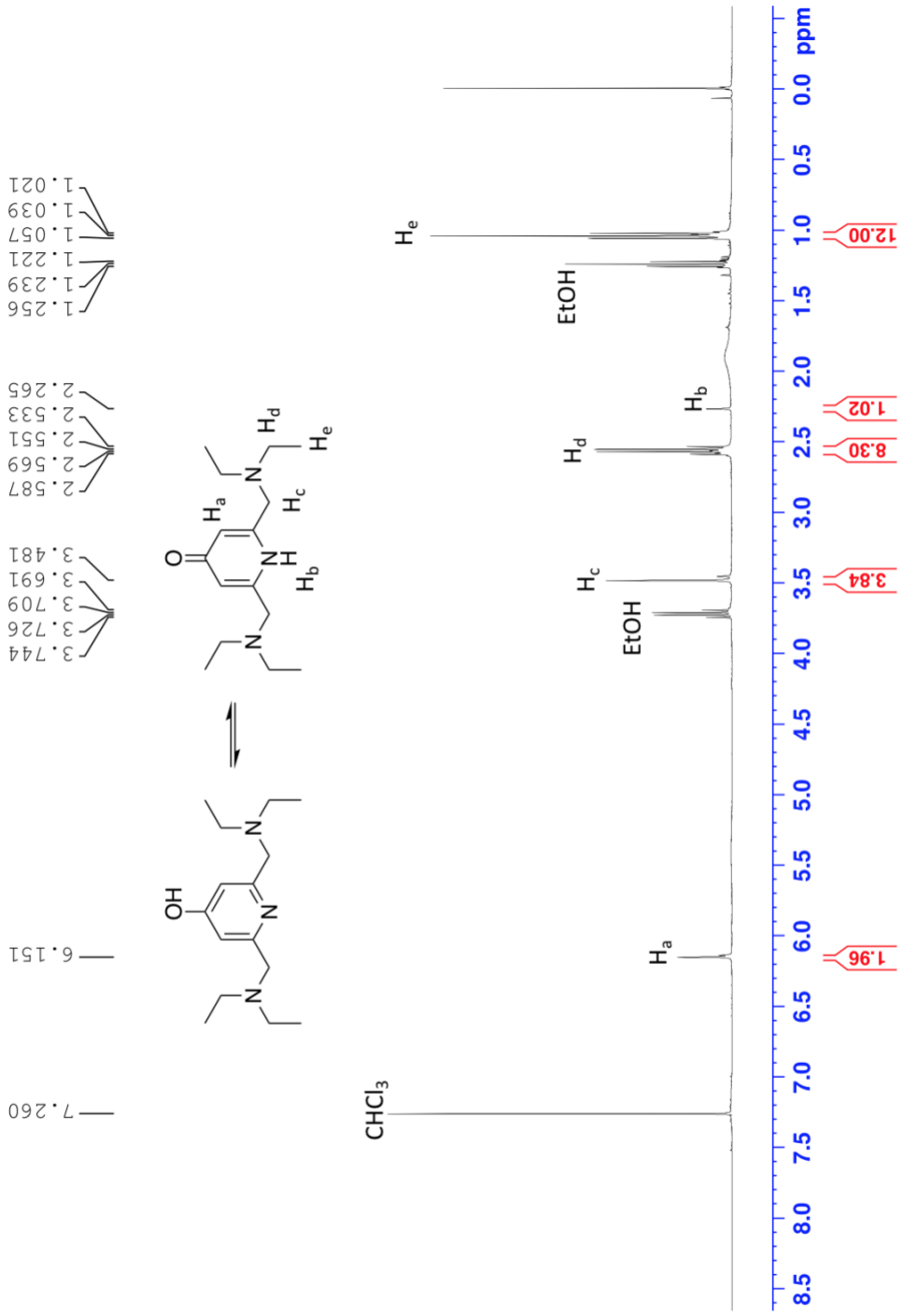


Figure S1. ^{1}H NMR of **L1** in $CDCl_3$ at 25 °C.

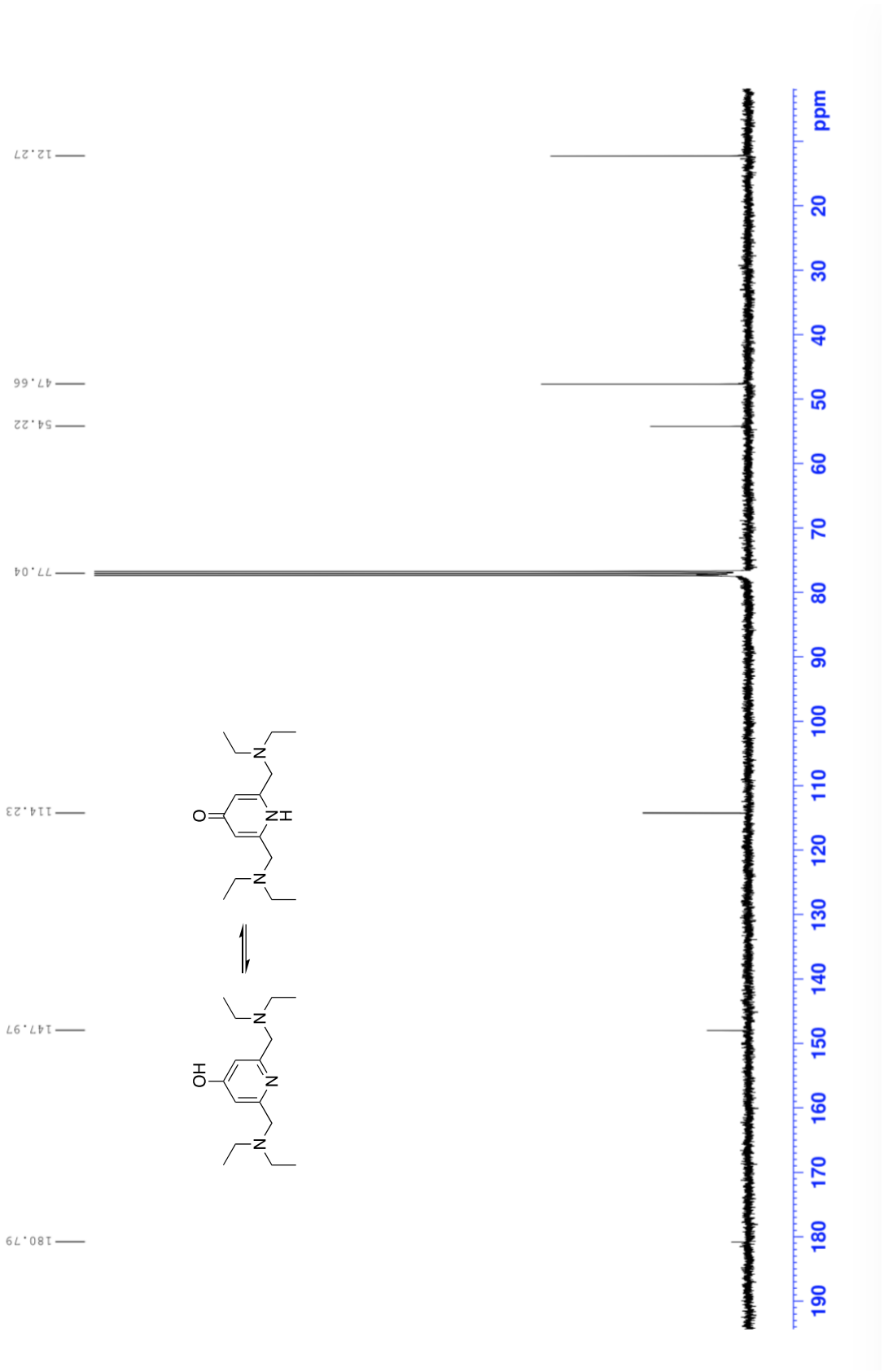


Figure S2. ^{13}C NMR of **L1** in $CDCl_3$ at 25 °C.

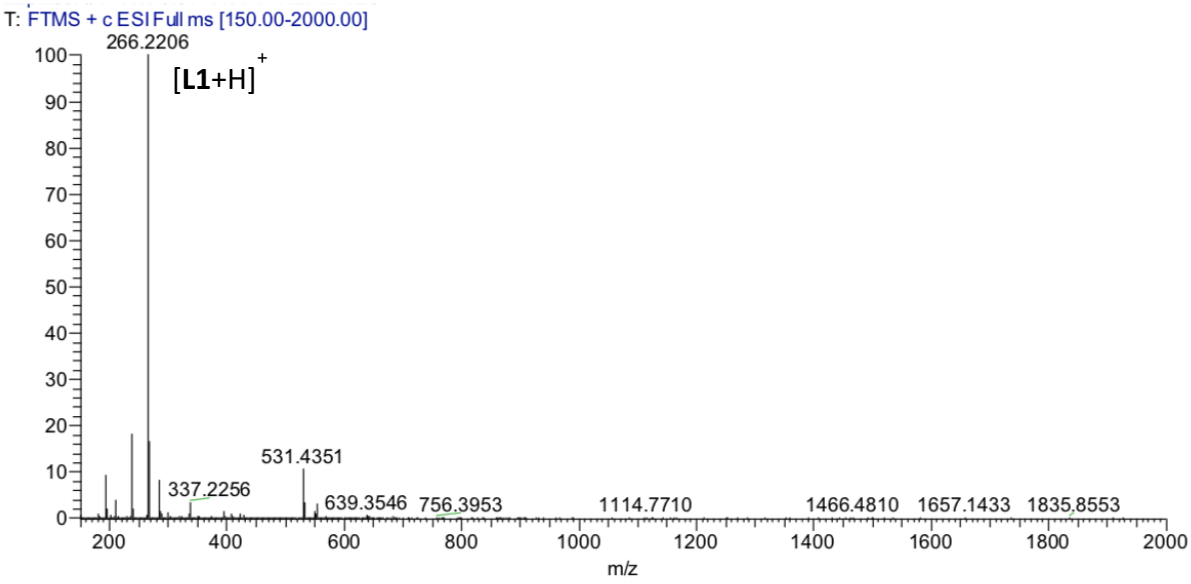


Figure S3. ESI-HRMS Mass Spectrum of **L1**.

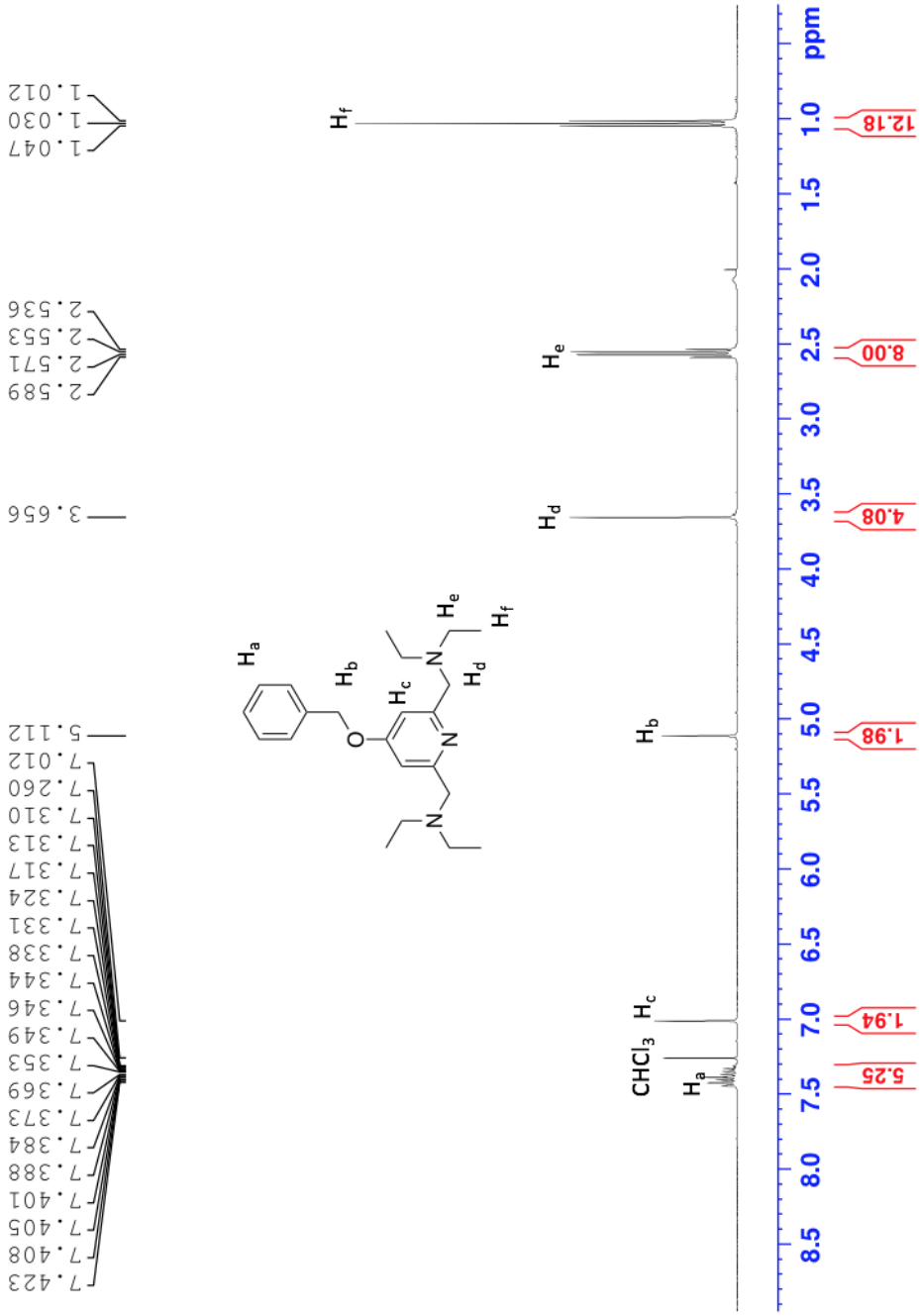


Figure S4. ^{1}H NMR of **L2** in $CDCl_3$.

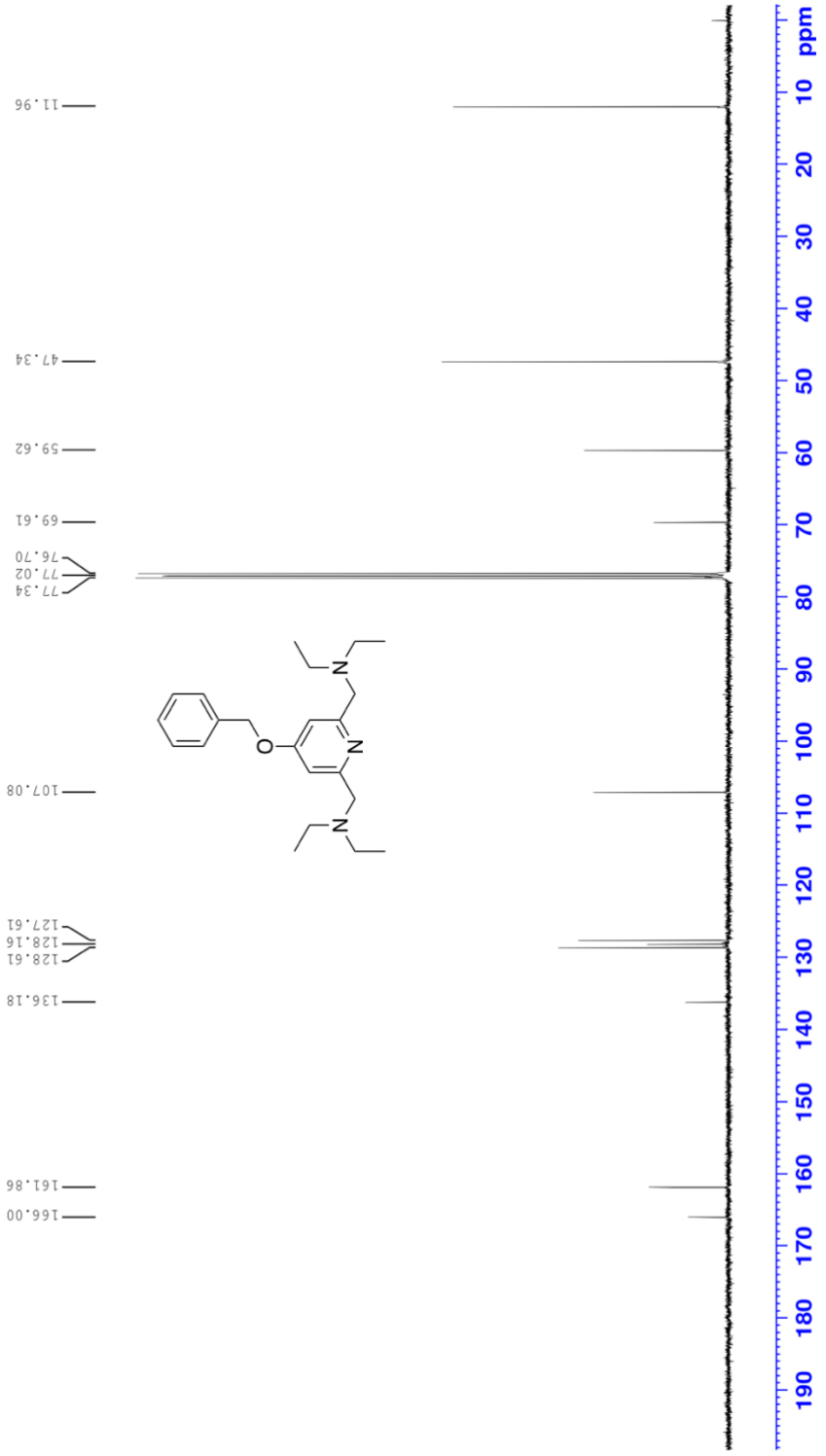


Figure S5: ^{13}C NMR of **L2** in $CDCl_3$.

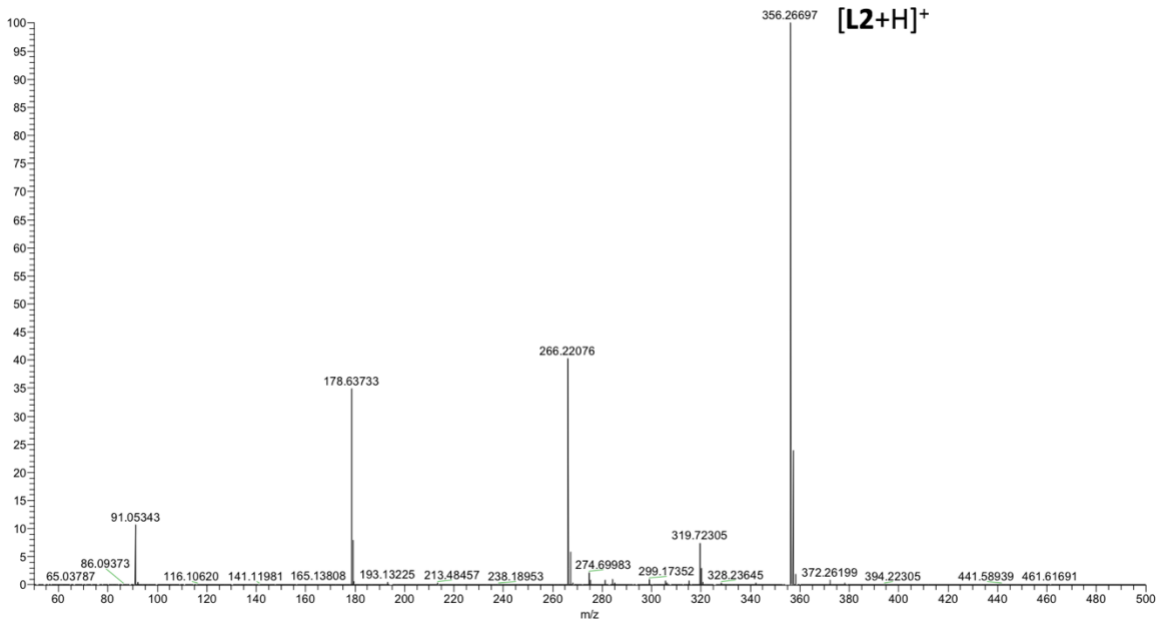


Figure S6. ESI-HRMS Mass Spectrum of **L2**.

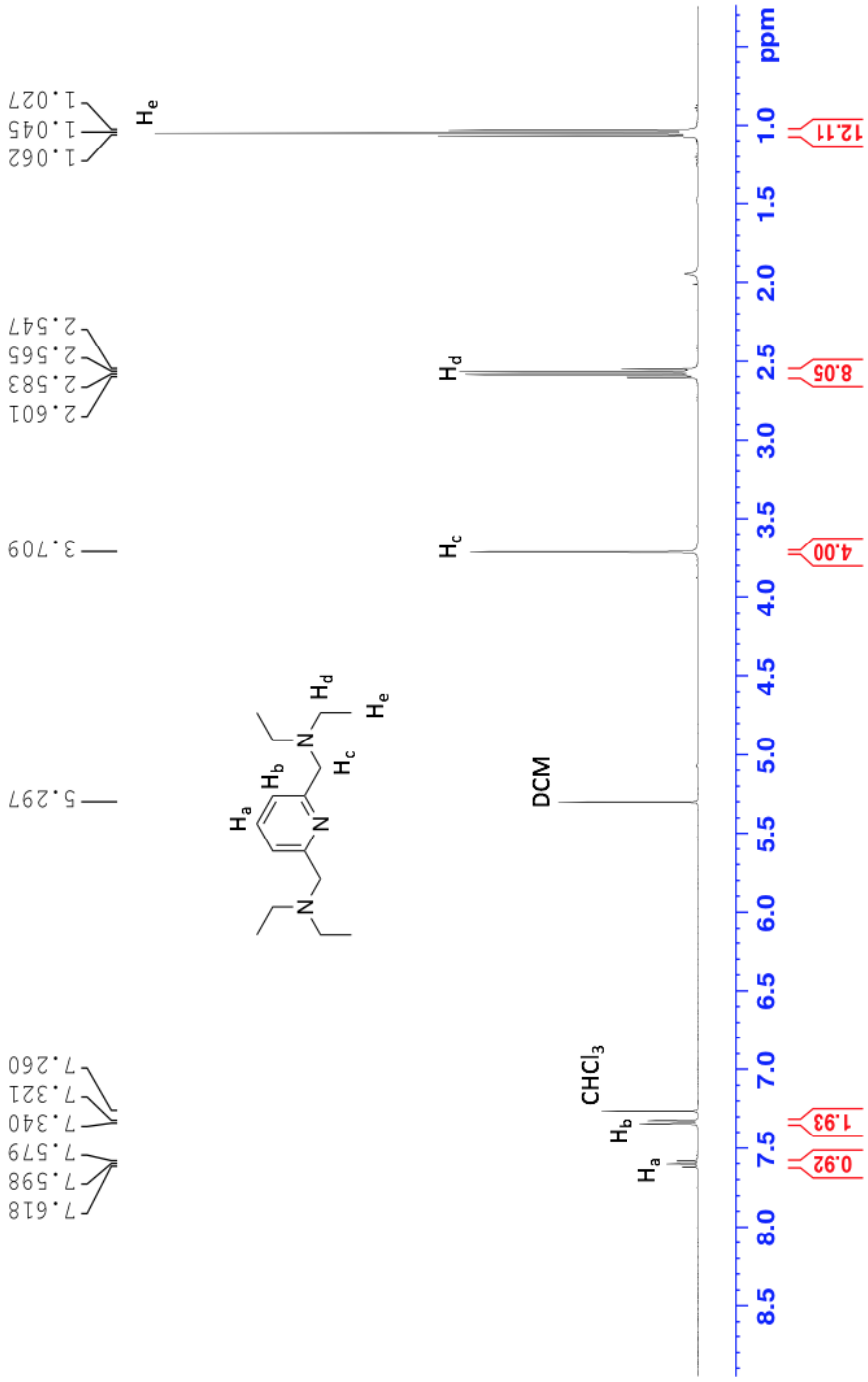


Figure S7. ^{1}H NMR of **L3** in $CDCl_3$.

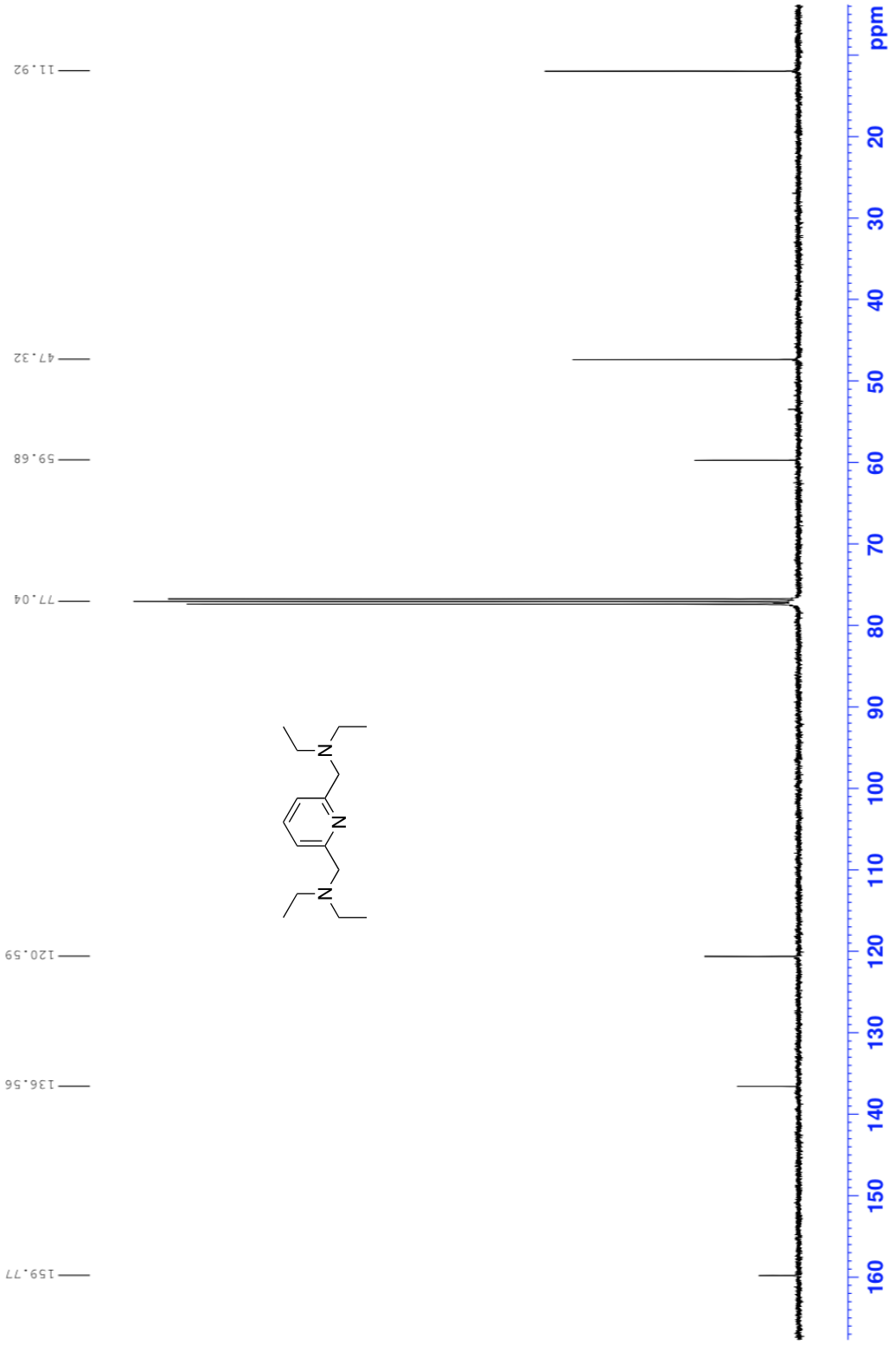


Figure S8. ^{13}C NMR of **L3** in $CDCl_3$.

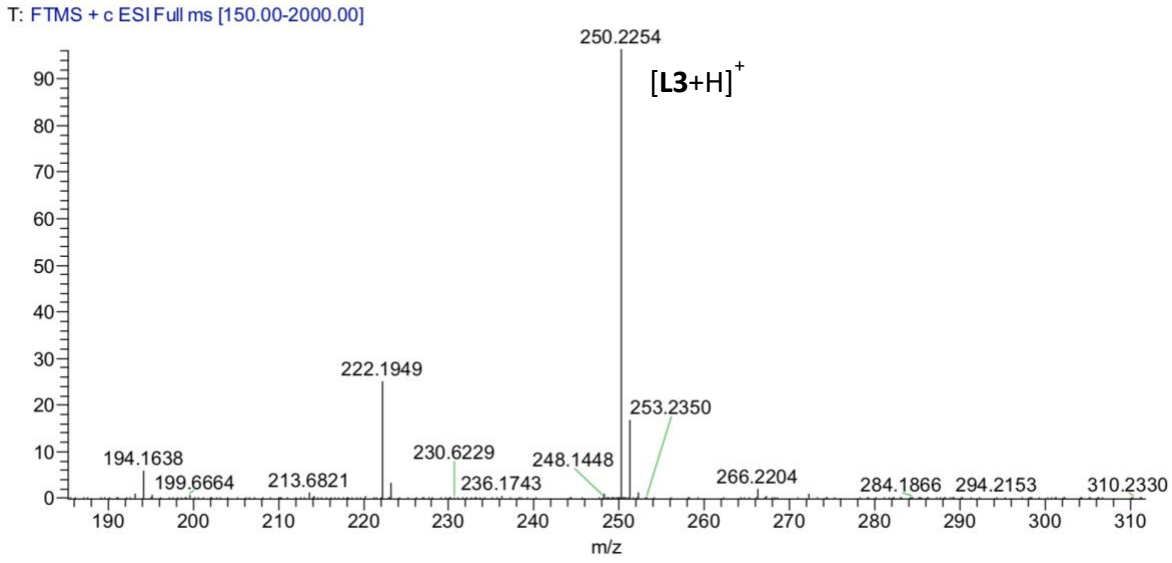


Figure S9. ESI-HRMS Mass Spectrum of **L3**.

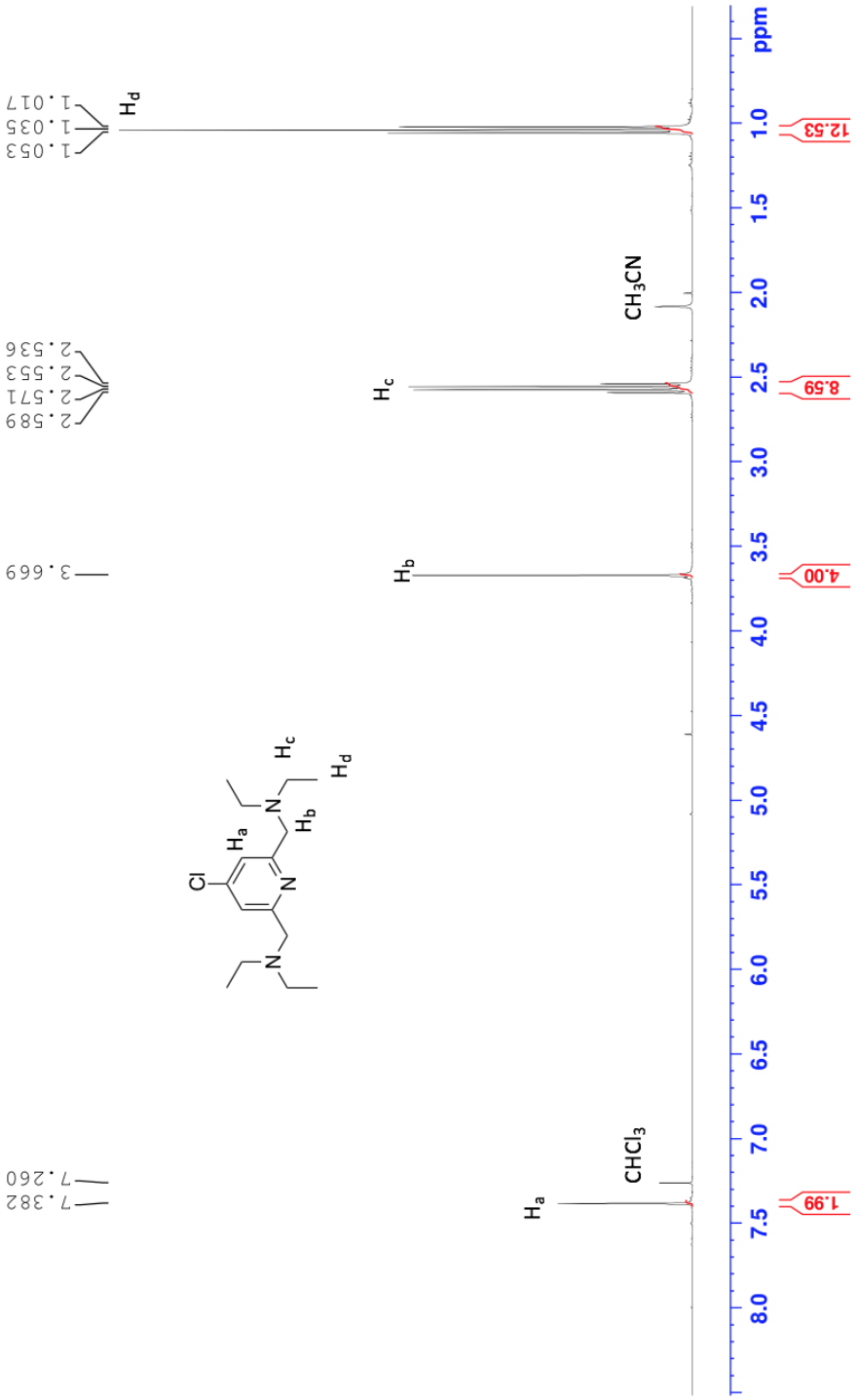


Figure S10. ^{1}H NMR of **L4** in $CDCl_3$.

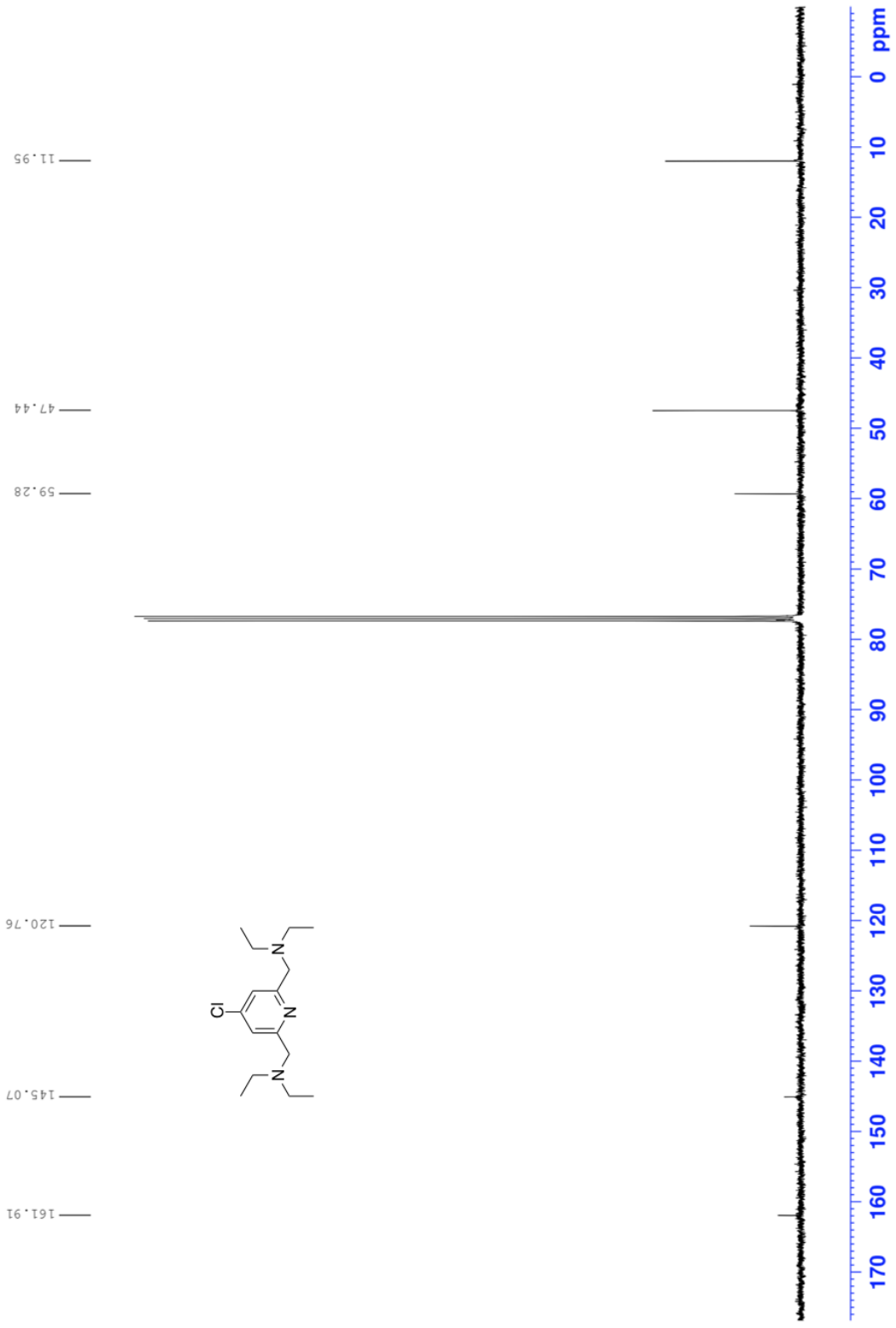


Figure S11. ^{13}C NMR of **L4** in $CDCl_3$.

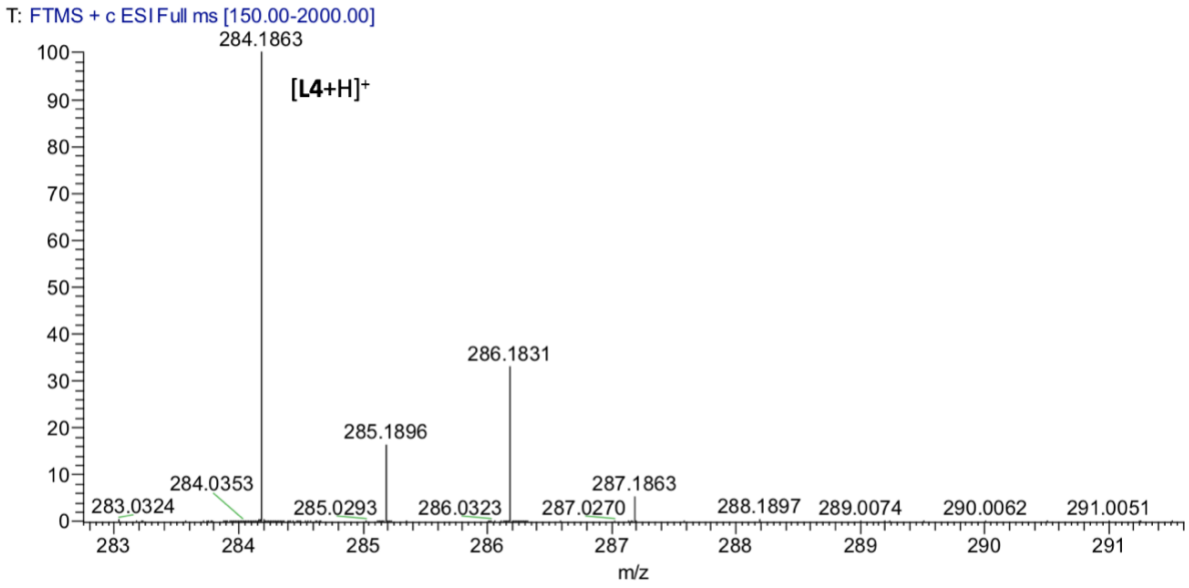


Figure S12. ESI-HRMS Mass Spectrum of **L4**.

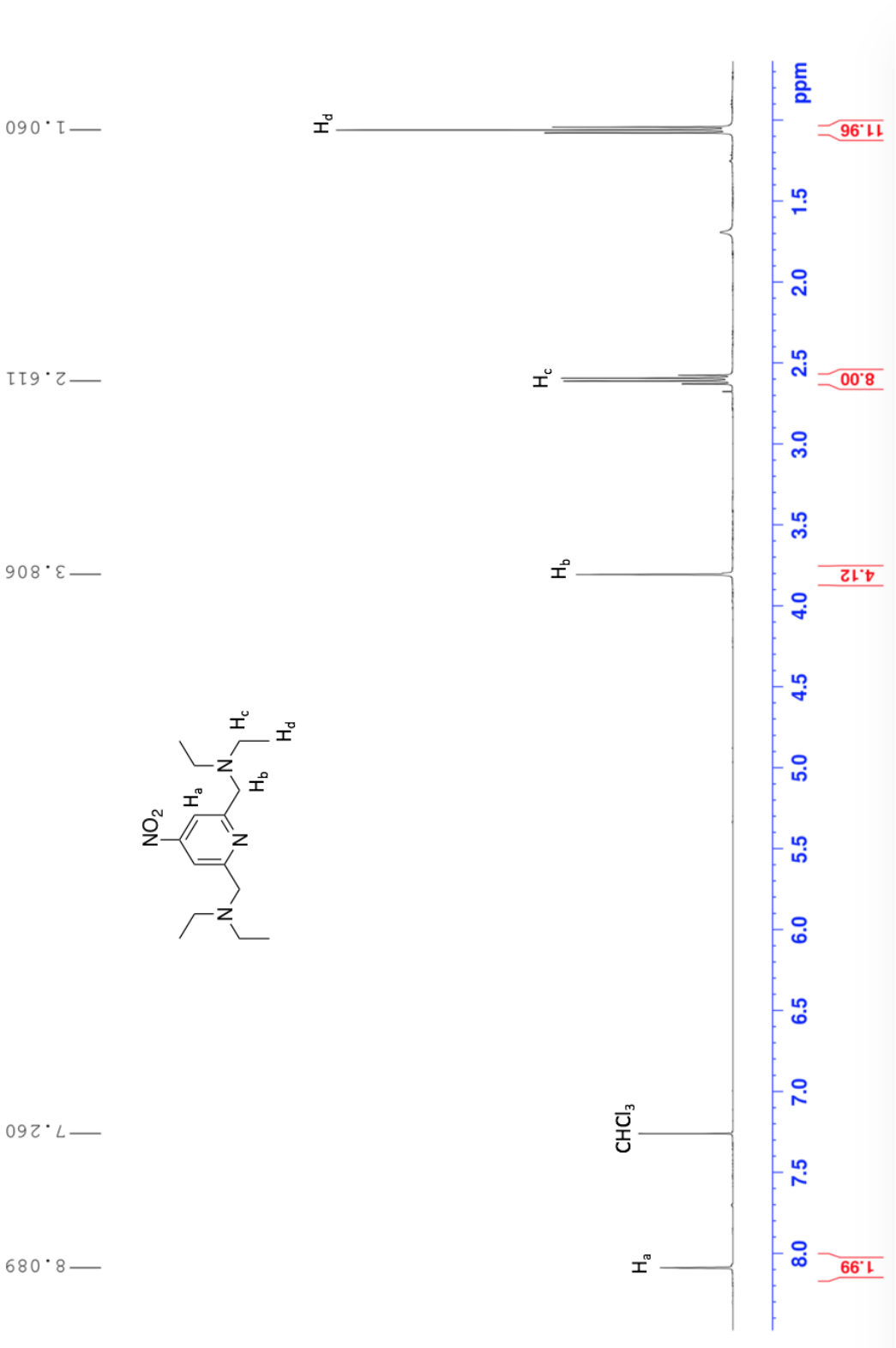


Figure S13. ^{1}H NMR of **L5** in $CDCl_3$.

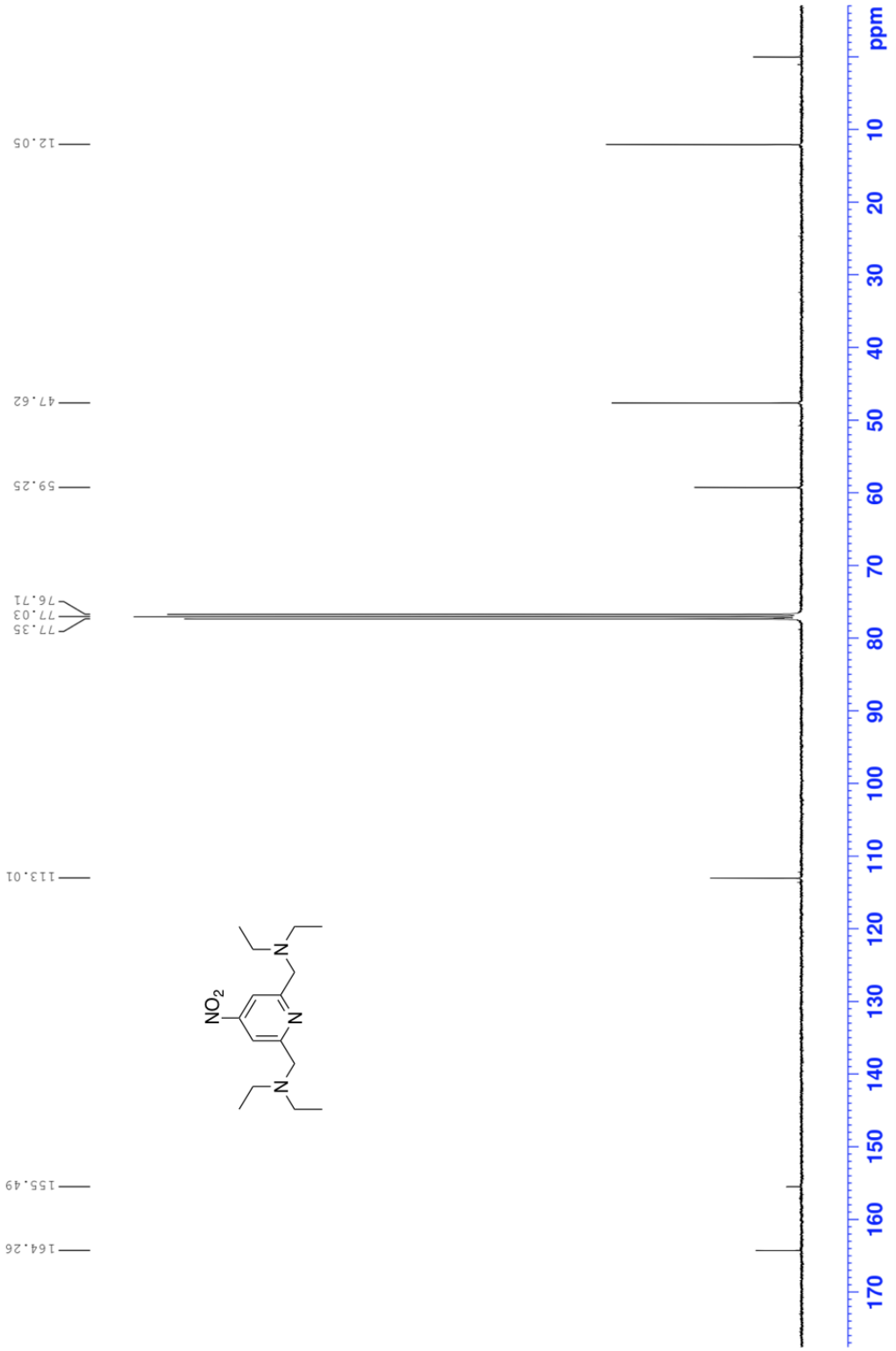


Figure S14. ^{13}C NMR of **L5** in $CDCl_3$.

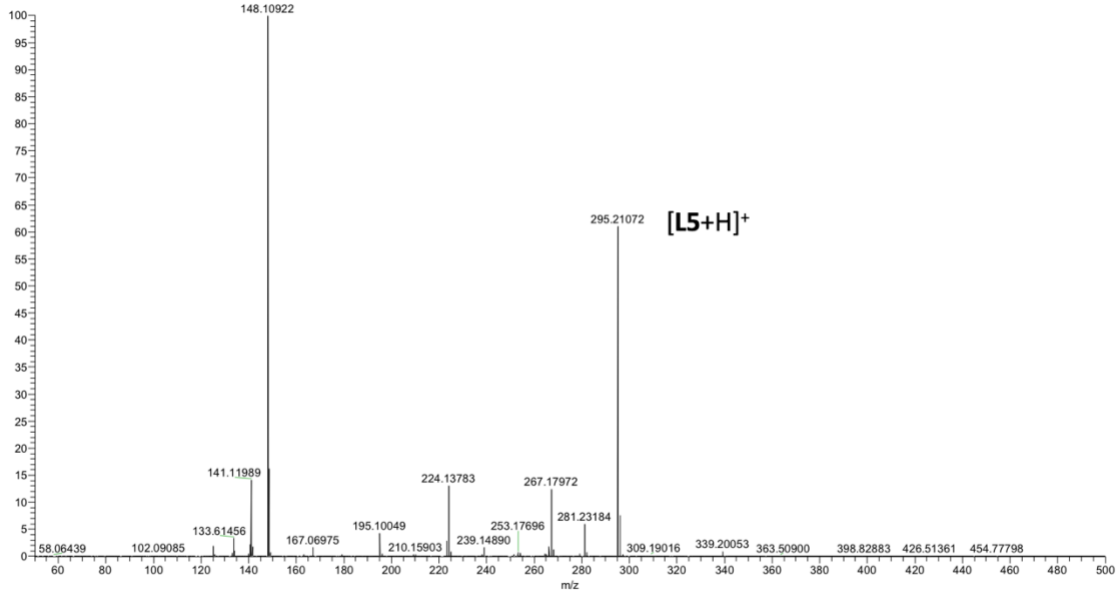


Figure S15. ESI-HRMS Mass Spectrum of **L5**.

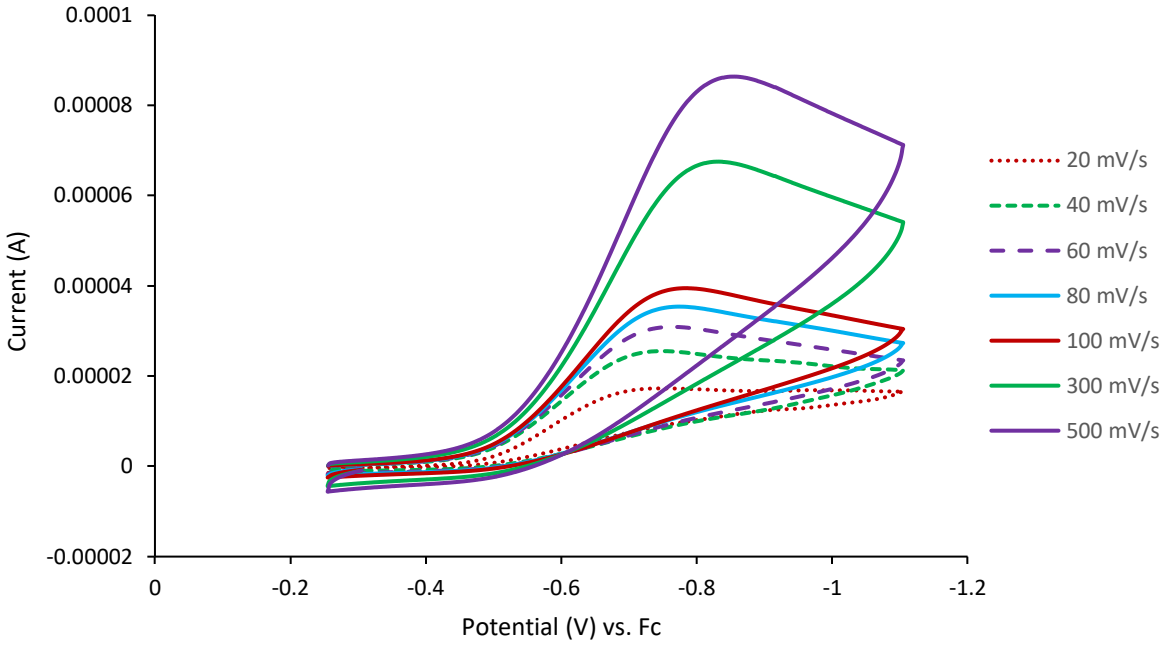


Figure S16. CV of [Cu**L1**Cl_2] where R = OH using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc) at scan rates ranging from 20 mV/s to 500 mV/s.

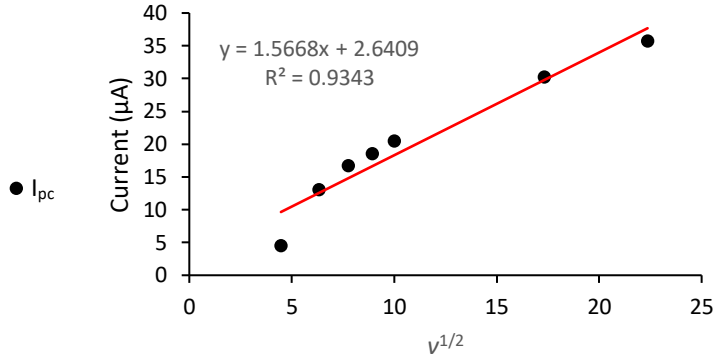


Figure S17. I_{pc} data vs $v^{1/2}$ of [Cu**L1**Cl_2] where R = OH from figure **S16**.

Table S1. Electrochemical data for [Cu**L1**Cl_2] where R = OH using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc).

v (mV/s)	E_{pc} (mV)	I_{pc} (µA)
20	-747	4.4892
40	-747	13.0861
60	-762	16.7361
80	-775	18.5946
100	-786	20.4532
300	-833	30.2770
500	-856	35.7549

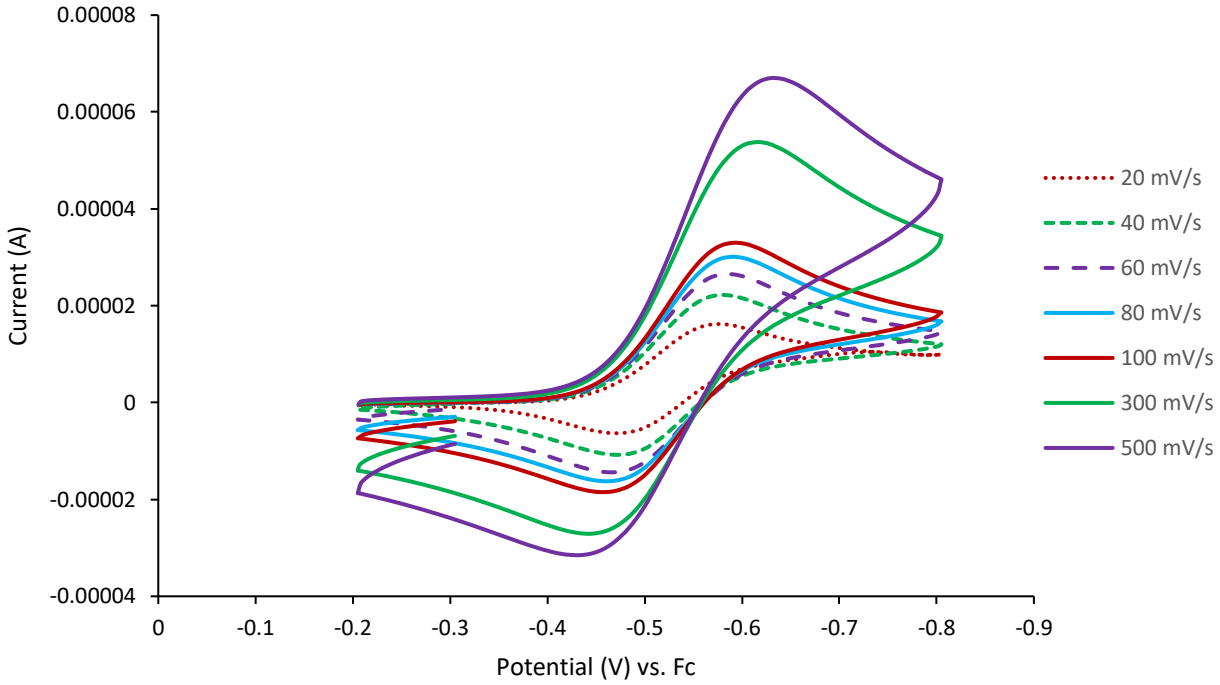


Figure S18. CV of [Cu**L2**Cl_2] where R = OBn using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc) at scan rates ranging from 20 mV/s to 500 mV/s.

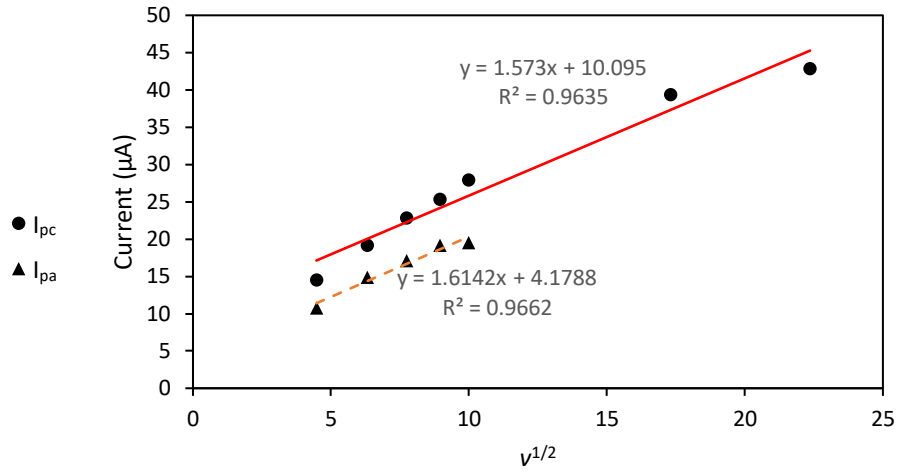


Figure S19. I_{pc} and I_{pa} data vs $v^{1/2}$ of [Cu**L2**Cl_2] where R = OBn from figure **S18**.

Table S2. Electrochemical data for [Cu**L2**Cl_2] where R = OBn using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc).

v (mV/s)	E_{pa} (mV)	E_{pc} (mV)	I_{pa} (mA)	I_{pc} (mA)	$E_{1/2}$ (mV)	ΔE	I_{pa}/I_{pc}
20	-576	14.5541	-473	10.8034	-525	103	0.7423
40	-579	19.1745	-472	14.8745	-526	107	0.7757
60	-587	22.8489	-466	17.1023	-527	121	0.7485
80	-590	25.2995	-461	19.1348	-526	129	0.7563
100	-594	27.9515	-457	19.4888	-526	137	0.6972
300	-615	39.3561	-444	21.3443	-530	171	0.5423
500	-632	42.8656	-430	16.4370	-531	202	0.3835

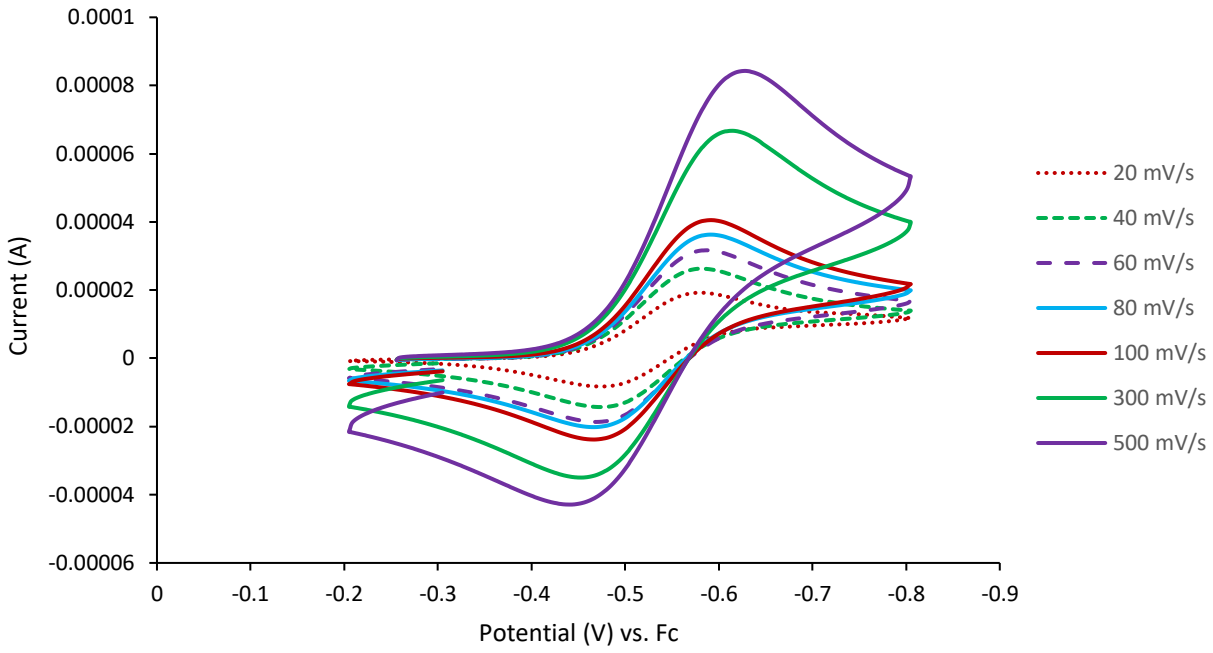


Figure S20. CV of [Cu**L3**Cl_2] where R = H using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc) at scan rates ranging from 20 mV/s to 500 mV/s.

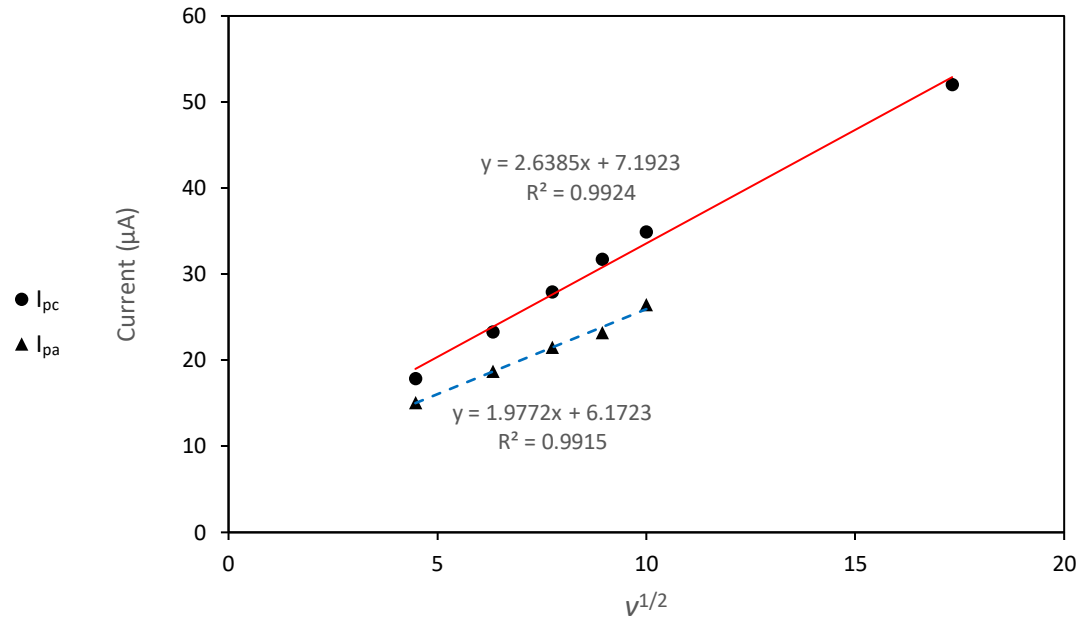


Figure S21. I_{pc} and I_{pa} data vs $v^{1/2}$ of [Cu**L3**Cl_2] where R = H from Figure **S20**.

Table S3. Electrochemical data for [Cu**L3**Cl_2] where R = H using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc).

v (mV/s)	E_{pa} (mV)	E_{pc} (mV)	I_{pa} (mA)	I_{pc} (mA)	$E_{1/2}$ (mV)	ΔE	I_{pa}/I_{pc}
20	-580	17.8683	-475	15.0820	-528	105	0.8441
40	-581	23.2853	-475	18.7472	-528	106	0.8051
60	-587	27.9515	-469	21.5030	-528	118	0.7693
80	-591	31.7418	-467	23.2242	-529	124	0.7317
100	-592	34.9340	-467	26.4225	-530	125	0.7564
300	-614	51.9814	-453	29.0654	-534	161	0.5592
500	-628	61.1063	-441	24.6403	-535	187	0.4032

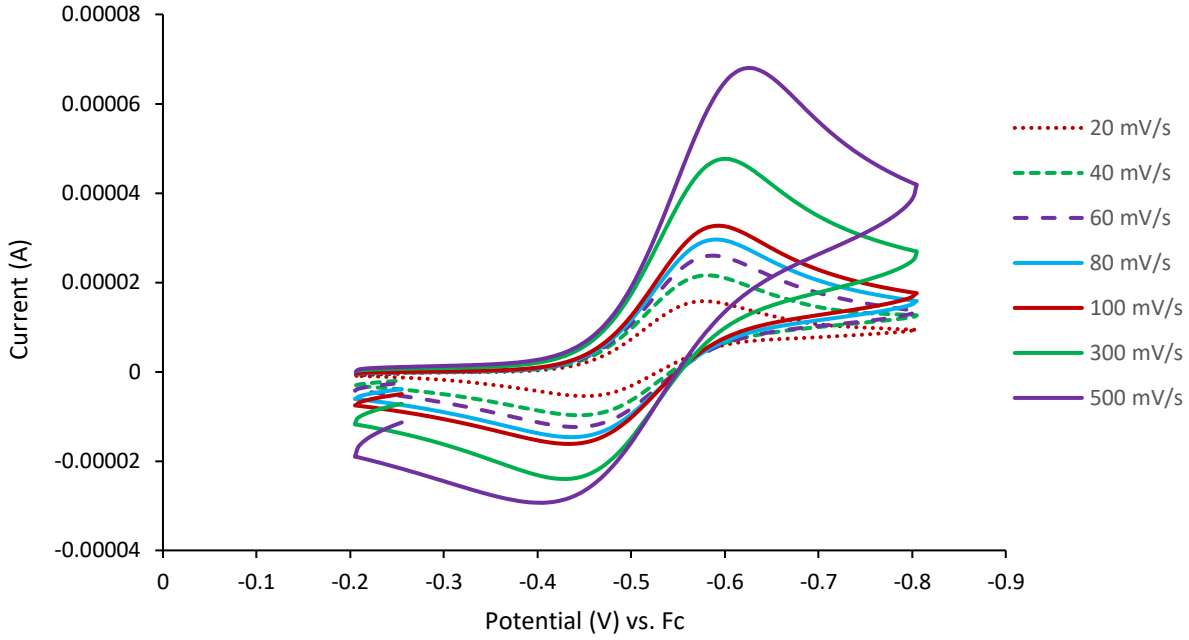


Figure S22. CV of [Cu**L4**Cl_2] where R = Cl using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc) at scan rates ranging from 20 mV/s to 500 mV/s.

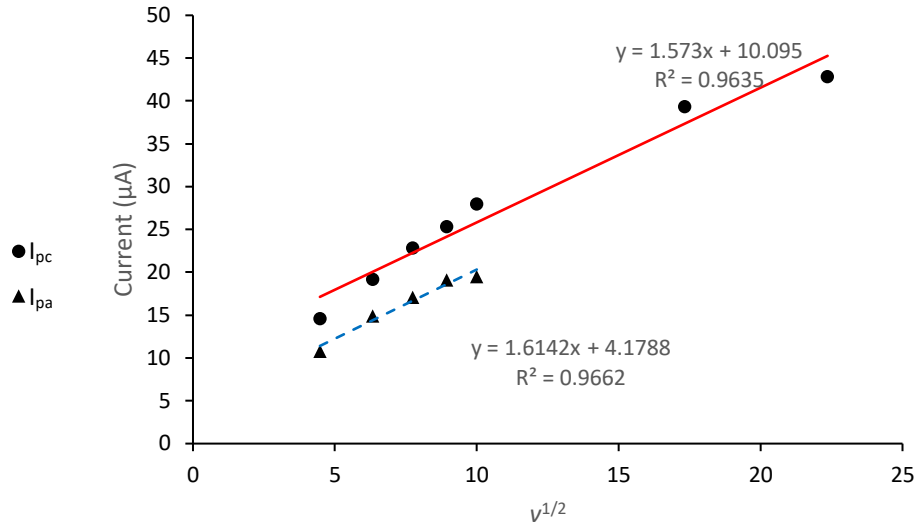


Figure S23. I_{pc} and I_{pa} data vs $v^{1/2}$ of [Cu**L4**Cl_2] where R = Cl from Figure **S22**.

Table S4. Electrochemical data for [Cu**L4**Cl_2] where R = Cl using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc).

v (mV/s)	E_{pa} (mV)	E_{pc} (mV)	I_{pa} (mA)	I_{pc} (mA)	$E_{1/2}$ (mV)	ΔE	I_{pa}/I_{pc}
20	-579	14.5541	-451	10.8034	-515	128	0.7423
40	-581	19.1745	-442	14.8745	-512	139	0.7757
60	-587	22.8489	-441	17.1023	-514	146	0.7485
80	-591	25.2995	-435	19.1348	-513	156	0.7563
100	-593	27.9515	-434	19.4888	-514	159	0.6972
300	-600	39.3561	-429	21.3443	-515	171	0.5423
500	-625	42.8656	-403	16.4370	-514	222	0.3835

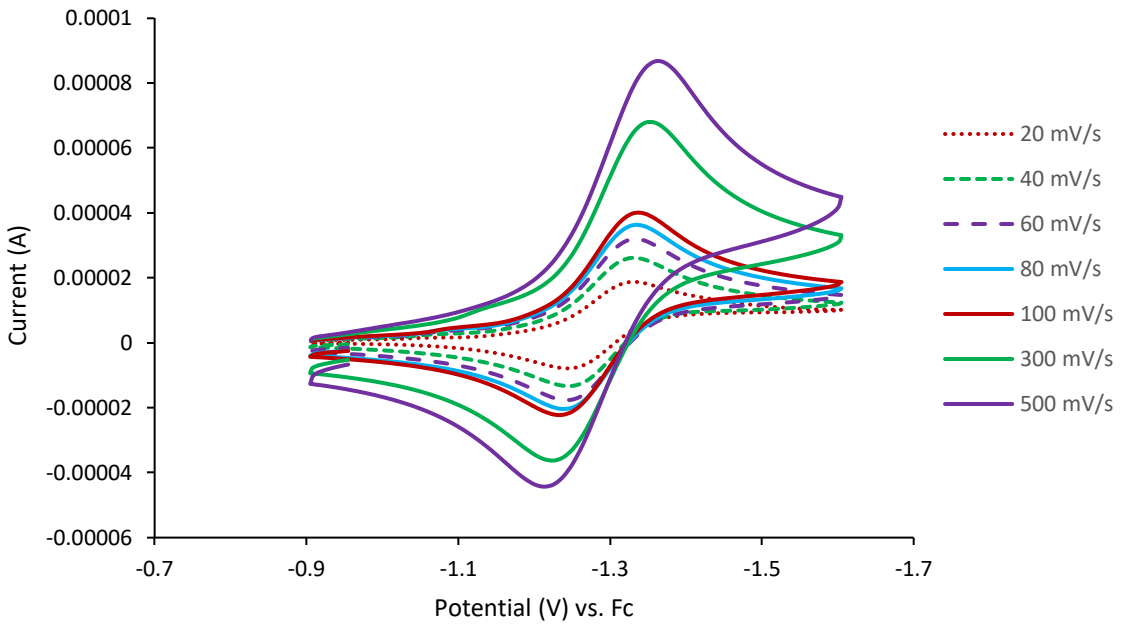


Figure S24. CV of free ligand **L5** where R = NO_2 using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc) at scan rates ranging from 20 mV/s to 500 mV/s.

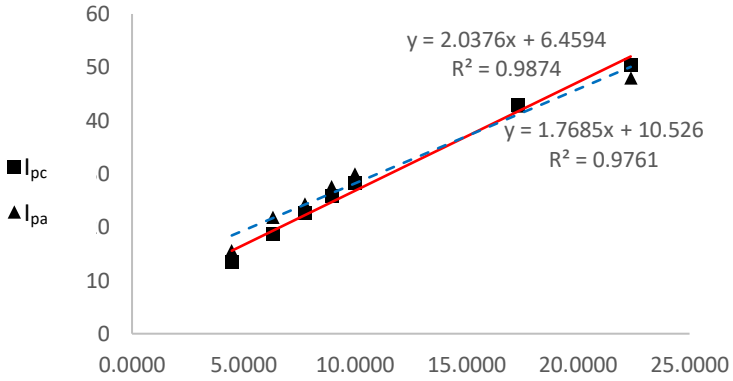


Figure S25. I_{pc} and I_{pa} data vs $v^{1/2}$ of free ligand **L5** where R = NO_2 from Figure **S24**.

Table S5. Electrochemical data for free ligand **L5** where R = NO_2 using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc).

v (mV/s)	E_{pa} (mV)	E_{pc} (mV)	I_{pa} (mA)	I_{pc} (mA)	$E_{1/2}$ (mV)	ΔE	I_{pa}/I_{pc}
20	-1330	13.4249	-1244	15.6161	-1287	86	1.1632
40	-1332	18.735	-1248	21.8845	-1290	84	1.1681
60	-1333	22.7176	-1243	24.3809	-1288	90	1.0732
80	-1335	25.8976	-1239	27.5517	-1287	96	1.0639
100	-1337	28.3635	-1233	29.9168	-1285	104	1.0548
300	-1354	42.9572	-1224	42.7649	-1289	130	0.9955
500	-1363	50.3548	-1214	48.0415	-1289	149	0.9541

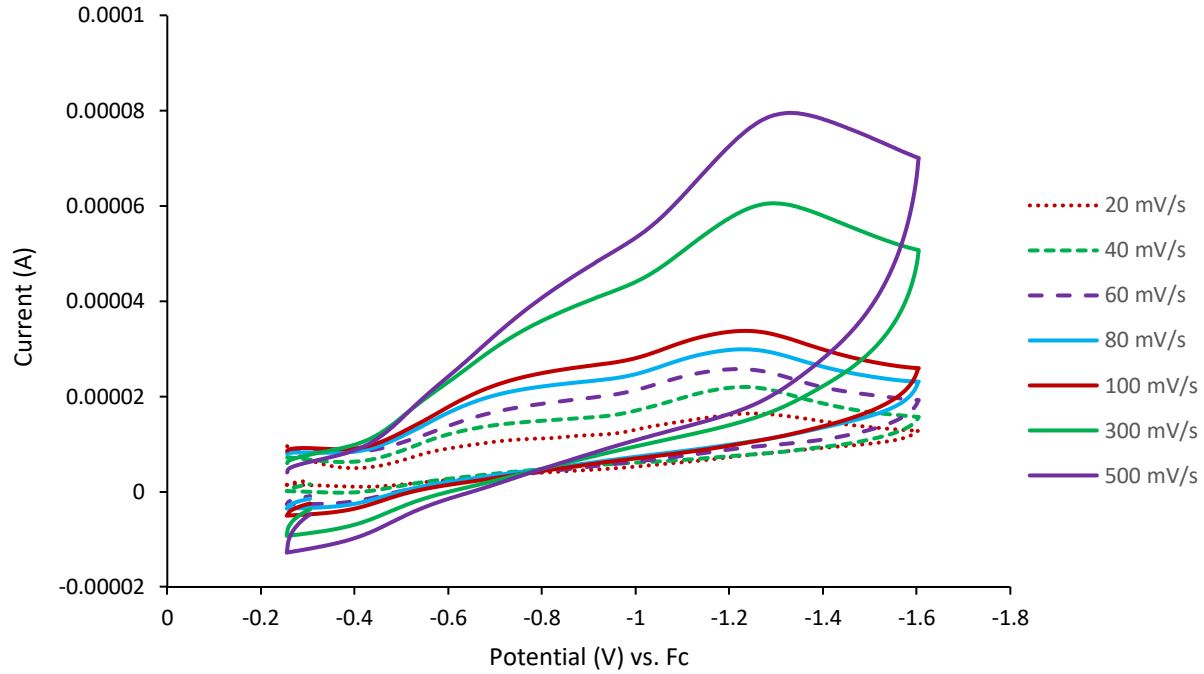


Figure S26. CV of [Cu**L5**Cl_2] (NO_2) where R = NO_2 using a glassy carbon working electrode, platinum auxiliary electrode, and Ag wire quasi reference electrode (CH_3CN, TBAP, vs. Fc) at scan rates ranging from 20 mV/s to 500 mV/s.

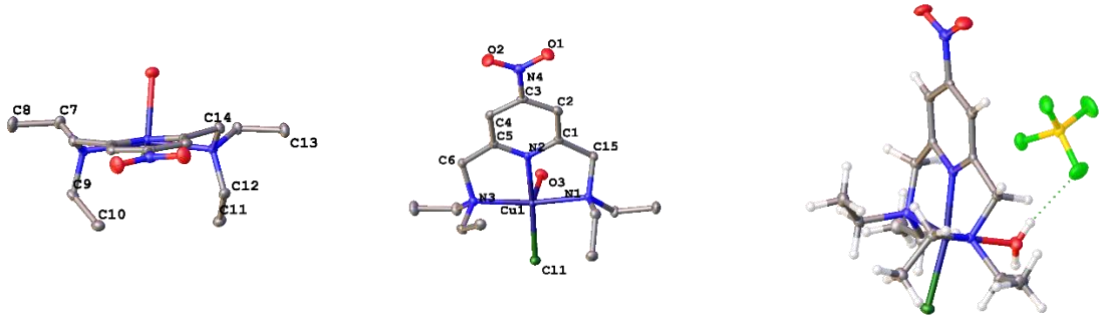


Figure S27. Crystal structure of [Cu**L5**(OH_2)Cl][BF_4] with labeling scheme. The hydrogen bonding between the bound water ligand and BF_4 counterion is shown on the right.

Table S6. Crystal data and structure parameters for [Cu**L5**(OH_2)Cl][BF_4] Deposition Number 1958460.

Identification code	[Cu**L5**OH_2Cl][BF_4]
Empirical formula	$C_{15}H_{28}BClCuF_4N_4O_3$
Formula weight	498.21
Temperature/K	100.78
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.572(12)
b/Å	8.044(7)
c/Å	22.68(4)
α/°	90
β/°	101.16(6)
γ/°	90
Volume/Å^3	2071(4)
Z	4
ρ_{calc}g/cm^3	1.598
μ/mm^{-1}	1.243
F(000)	1028.0
Crystal size/mm^3	2.859 × 0.988 × 0.583
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.95 to 55.98
Index ranges	-14 ≤ h ≤ 15, -10 ≤ k ≤ 10, -29 ≤ l ≤ 29
Reflections collected	68134
Independent reflections	4918 [R_{int} = 0.0364, R_{sigma} = 0.0191]
Data/restraints/parameters	4918/0/267
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0353, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0430, wR_2 = 0.0796
Largest diff. peak/hole / e Å^{-3}	0.66/-0.76

Table S7. Bond lengths for [Cu**L5**(OH_2)Cl][BF_4].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl1	2.222(2)	N2	C5	1.340(3)
Cu1	O3	2.248(3)	N3	C6	1.490(3)
Cu1	N1	2.128(3)	N3	C7	1.498(3)
Cu1	N2	1.945(2)	N3	C9	1.492(3)
Cu1	N3	2.126(3)	N4	C3	1.483(3)
F3	B1	1.393(3)	C15	C1	1.515(3)
F4	B1	1.382(3)	C1	C2	1.385(3)
F1	B1	1.410(3)	C6	C5	1.499(3)
F2	B1	1.377(3)	C4	C3	1.379(3)
O2	N4	1.230(3)	C4	C5	1.386(3)
O1	N4	1.220(3)	C3	C2	1.386(3)
N1	C15	1.493(3)	C7	C8	1.524(3)
N1	C12	1.501(3)	C9	C10	1.512(3)
N1	C14	1.505(3)	C11	C12	1.516(3)
N2	C1	1.335(3)	C14	C13	1.524(3)

Table S8. Bond angles for [Cu**L5**(OH_2)Cl][BF_4].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl1	Cu1	O3	95.59(5)	O1	N4	O2	124.84(18)
N1	Cu1	Cl1	98.25(10)	O1	N4	C3	117.09(18)
N1	Cu1	O3	93.54(7)	N1	C15	C1	109.14(17)
N2	Cu1	Cl1	170.68(5)	N2	C1	C15	112.87(17)
N2	Cu1	O3	93.71(6)	N2	C1	C2	120.54(19)
N2	Cu1	N1	81.78(11)	C2	C1	C15	126.55(19)
N2	Cu1	N3	81.15(12)	N3	C6	C5	110.85(16)
N3	Cu1	Cl1	96.22(11)	C3	C4	C5	116.10(19)
N3	Cu1	O3	102.28(6)	C4	C3	N4	117.46(18)
N3	Cu1	N1	157.37(7)	C4	C3	C2	123.59(19)
C15	N1	Cu1	103.46(14)	C2	C3	N4	118.94(19)
C15	N1	C12	107.02(15)	N2	C5	C6	114.56(18)
C15	N1	C14	110.21(16)	N2	C5	C4	120.9(2)
C12	N1	Cu1	111.95(12)	C4	C5	C6	124.49(18)
C12	N1	C14	112.57(16)	N3	C7	C8	115.52(18)
C14	N1	Cu1	111.15(13)	C1	C2	C3	116.4(2)
C1	N2	Cu1	117.63(15)	N3	C9	C10	113.40(18)
C1	N2	C5	122.36(18)	N1	C12	C11	115.06(17)
C5	N2	Cu1	119.48(16)	N1	C14	C13	115.69(17)
C6	N3	Cu1	108.86(14)	F3	B1	F1	107.70(18)
C6	N3	C7	110.05(16)	F4	B1	F3	109.6(2)
C6	N3	C9	109.99(15)	F4	B1	F1	108.64(19)
C7	N3	Cu1	108.54(14)	F2	B1	F3	109.75(19)
C9	N3	Cu1	108.42(12)	F2	B1	F4	110.22(19)
C9	N3	C7	110.92(17)	F2	B1	F1	110.8(2)
O2	N4	C3	118.07(19)				

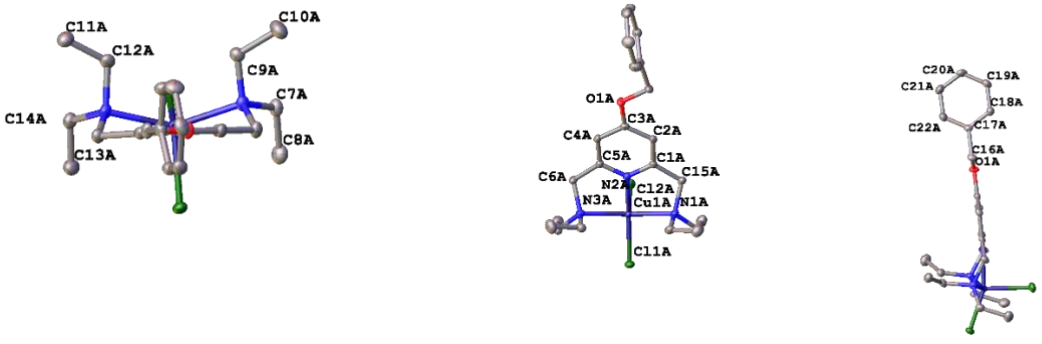


Figure S28. Crystal structure of ethyl arm orientation a of [Cu**L2**Cl_2] with corresponding labeling scheme.

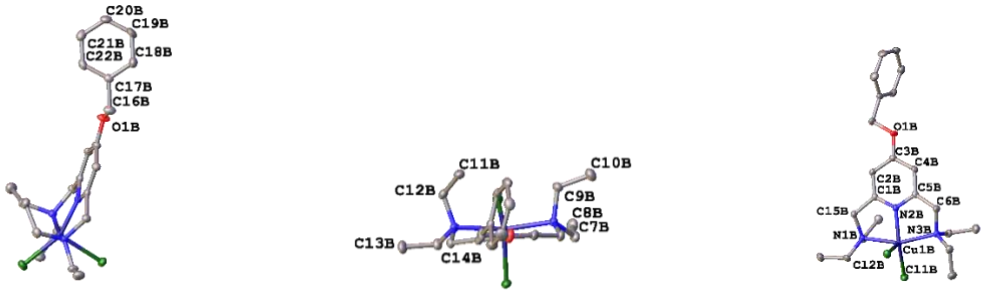


Figure S29. Crystal structure of ethyl arm orientation a of [Cu**L2**Cl_2] with corresponding labeling scheme.

Table S9. Crystal data and structure parameters for [Cu**L2**Cl_2] Deposition Number 1958458.

Identification code	[Cu**L2**Cl_2]
Empirical formula	$C_{22}H_{33}Cl_2CuN_3O$
Formula weight	489.95
Temperature/K	237.13
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.8714(6)
b/Å	29.123(2)
c/Å	20.2519(16)
α/°	90
β/°	97.706(4)
γ/°	90
Volume/Å^3	4600.5(6)
Z	8
ρ_{calc}g/cm^3	1.415
μ/mm^{-1}	1.200
F(000)	2056.0
Crystal size/mm^3	0.24 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.926 to 52.744
Index ranges	-9 ≤ h ≤ 9, -35 ≤ k ≤ 36, -25 ≤ l ≤ 25
Reflections collected	45376
Independent reflections	9345 [R_{int} = 0.0493, R_{sigma} = 0.0417]
Data/restraints/parameters	9345/0/531
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0737
Final R indexes [all data]	R_1 = 0.0469, wR_2 = 0.0808
Largest diff. peak/hole / e Å^{-3}	0.49/-0.50

Table S10. Bond lengths for [Cu**L2**Cl_2].

Atom	Atom	Length/Å	Atom	Atom
Cu1A	Cl1A	2.2447(6)	C5B	C4B
Cu1A	Cl2A	2.4394(6)	C5B	C6B
Cu1A	N2A	1.9473(19)	C5A	C4A
Cu1A	N1A	2.156(2)	C5A	C6A
Cu1A	N3A	2.184(2)	C4B	C3B
Cu1B	Cl2B	2.4350(6)	C2A	C3A
Cu1B	Cl1B	2.2548(6)	C4A	C3A
Cu1B	N2B	1.9532(19)	C1B	C15B
Cu1B	N3B	2.176(2)	C1B	C2B
Cu1B	N1B	2.1751(19)	C3B	C2B
O1A	C3A	1.357(3)	C9B	C10B
O1A	C16A	1.457(3)	C17B	C22B
O1B	C3B	1.353(3)	C17B	C16B
O1B	C16B	1.455(3)	C17B	C18B
N2A	C1A	1.339(3)	C12A	C11A
N2A	C5A	1.341(3)	C17A	C16A
N2B	C5B	1.346(3)	C17A	C18A
N2B	C1B	1.338(3)	C17A	C22A
N3B	C9B	1.497(3)	C18A	C19A
N3B	C6B	1.498(3)	C14B	C13B
N3B	C7B	1.496(3)	C22B	C21B
N1A	C12A	1.520(3)	C7A	C8A
N1A	C15A	1.490(3)	C20A	C19A
N1A	C14A	1.486(3)	C20A	C21A
N1B	C15B	1.484(3)	C9A	C10A
N1B	C14B	1.494(3)	C14A	C13A
N1B	C12B	1.493(3)	C12B	C11B
N3A	C6A	1.483(3)	C21B	C20B
N3A	C7A	1.484(3)	C7B	C8B
N3A	C9A	1.503(3)	C20B	C19B
C1A	C2A	1.380(3)	C18B	C19B
C1A	C15A	1.503(3)	C21A	C22A

Table S11. Bond angles for [Cu**L2**Cl_2].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl1A	Cu1A	Cl2A	108.89(2)	N2A	C1A	C2A	121.5(2)
N2A	Cu1A	Cl1A	160.65(6)	N2A	C1A	C15A	113.5(2)
N2A	Cu1A	Cl2A	90.46(6)	C2A	C1A	C15A	125.0(2)
N2A	Cu1A	N1A	79.52(8)	N2B	C5B	C4B	121.5(2)
N2A	Cu1A	N3A	78.67(8)	N2B	C5B	C6B	113.9(2)
N1A	Cu1A	Cl1A	94.59(5)	C4B	C5B	C6B	124.5(2)
N1A	Cu1A	Cl2A	107.07(6)	N2A	C5A	C4A	121.5(2)
N1A	Cu1A	N3A	140.95(8)	N2A	C5A	C6A	112.8(2)
N3A	Cu1A	Cl1A	95.41(5)	C4A	C5A	C6A	125.7(2)
N3A	Cu1A	Cl2A	105.10(6)	C5B	C4B	C3B	118.8(2)
Cl1B	Cu1B	Cl2B	108.26(2)	C1A	C2A	C3A	117.9(2)
N2B	Cu1B	Cl2B	98.26(6)	C5A	C4A	C3A	118.2(2)
N2B	Cu1B	Cl1B	153.18(6)	N2B	C1B	C15B	114.1(2)
N2B	Cu1B	N3B	80.57(8)	N2B	C1B	C2B	122.0(2)
N2B	Cu1B	N1B	80.40(8)	C2B	C1B	C15B	123.8(2)
N3B	Cu1B	Cl2B	98.38(5)	O1A	C3A	C2A	124.5(2)
N3B	Cu1B	Cl1B	99.00(5)	O1A	C3A	C4A	115.5(2)
N1B	Cu1B	Cl2B	98.21(5)	C2A	C3A	C4A	120.0(2)
N1B	Cu1B	Cl1B	91.70(5)	O1B	C3B	C4B	116.2(2)
N1B	Cu1B	N3B	156.30(7)	O1B	C3B	C2B	124.4(2)
C3A	O1A	C16A	116.26(17)	C2B	C3B	C4B	119.4(2)
C3B	O1B	C16B	117.54(18)	N3B	C9B	C10B	117.0(2)
C1A	N2A	Cu1A	119.53(15)	C5B	C6B	N3B	111.41(19)
C1A	N2A	C5A	120.8(2)	N1B	C15B	C1B	111.05(18)
C5A	N2A	Cu1A	119.57(15)	C22B	C17B	C16B	119.6(2)
C5B	N2B	Cu1B	120.02(15)	C18B	C17B	C22B	118.8(2)
C1B	N2B	Cu1B	119.77(16)	C18B	C17B	C16B	121.6(2)
C1B	N2B	C5B	119.9(2)	C11A	C12A	N1A	116.8(2)
C9B	N3B	Cu1B	105.59(14)	N3A	C6A	C5A	108.57(19)
C9B	N3B	C6B	109.40(18)	C1B	C2B	C3B	118.3(2)
C6B	N3B	Cu1B	106.37(13)	C18A	C17A	C16A	121.0(2)
C7B	N3B	Cu1B	116.09(15)	C22A	C17A	C16A	120.4(2)
C7B	N3B	C9B	112.66(18)	C22A	C17A	C18A	118.5(2)
C7B	N3B	C6B	106.48(18)	N1A	C15A	C1A	109.07(18)
C12A	N1A	Cu1A	101.98(14)	O1A	C16A	C17A	107.96(18)
C15A	N1A	Cu1A	104.96(14)	C19A	C18A	C17A	120.6(2)
C15A	N1A	C12A	110.00(19)	N1B	C14B	C13B	116.0(2)
C14A	N1A	Cu1A	117.85(15)	C21B	C22B	C17B	120.9(2)
C14A	N1A	C12A	108.97(18)	N3A	C7A	C8A	114.8(2)
C14A	N1A	C15A	112.47(18)	C21A	C20A	C19A	119.7(2)
C15B	N1B	Cu1B	106.13(13)	N3A	C9A	C10A	117.2(2)
C15B	N1B	C14B	110.82(18)	N1A	C14A	C13A	114.6(2)
C15B	N1B	C12B	110.92(18)	N1B	C12B	C11B	114.4(2)
C14B	N1B	Cu1B	107.69(14)	C22B	C21B	C20B	119.8(2)
C12B	N1B	Cu1B	111.56(14)	N3B	C7B	C8B	115.4(2)
C12B	N1B	C14B	109.63(18)	O1B	C16B	C17B	106.68(19)
C6A	N3A	Cu1A	103.18(14)	C20A	C19A	C18A	120.3(2)
C6A	N3A	C7A	111.19(19)	C19B	C20B	C21B	119.8(2)
C6A	N3A	C9A	110.81(19)	C17B	C18B	C19B	120.2(2)

C7A	N3A	Cu1A	118.20(15)	C20A	C21A	C22A	119.9(2)
C7A	N3A	C9A	109.14(19)	C17A	C22A	C21A	120.9(2)
C9A	N3A	Cu1A	103.97(14)	C20B	C19B	C18B	120.5(2)

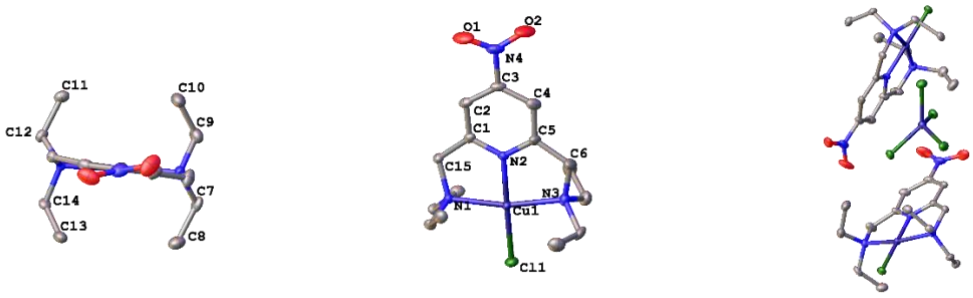


Figure S30. Crystal structure of [Cu**L5**Cl]$_2$[CuCl$_4$] with corresponding labeling scheme. The full unit cell is displayed on the right.

Table S12. Crystal data and structure parameters for [Cu**L5**Cl]$_2$[CuCl$_4$] Deposition Number 1958461.

Identification code	[Cu**L5**Cl]$_2$[CuCl$_4$]
Empirical formula	$C_{15}H_{26}Cl_3Cu_{1.5}N_4O_2$
Formula weight	496.06
Temperature/K	191.49
Crystal system	monoclinic
Space group	C2/c
a/Å	27.845(3)
b/Å	9.7687(9)
c/Å	14.6761(11)
α/°	90
β/°	98.652(4)
γ/°	90
Volume/Å^3	3946.7(6)
Z	8
ρ_{calc}g/cm^3	1.670
μ/mm^{-1}	2.055
F(000)	2036.0
Crystal size/mm^3	0.155 × 0.099 × 0.052
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.92 to 52.738
Index ranges	-34 ≤ h ≤ 34, -12 ≤ k ≤ 12, -18 ≤ l ≤ 13
Reflections collected	20089
Independent reflections	3996 [R_{int} = 0.0583, R_{sigma} = 0.0488]
Data/restraints/parameters	3996/0/235
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.1101
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.1231
Largest diff. peak/hole / e Å^{-3}	1.35/-0.84

Table S13. Bond lengths for [Cu**L5**Cl]$_2$[CuCl$_4$].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl1	2.1909(10)	N3	C6	1.490(5)
Cu1	N1	2.067(3)	N3	C9	1.518(5)
Cu1	N2	1.920(3)	O2	N4	1.224(5)
Cu1	N3	2.092(3)	N4	C3	1.483(5)
Cu2	Cl3^1	2.2456(10)	C1	C15	1.496(5)
Cu2	Cl3	2.2456(10)	C1	C2	1.384(5)
Cu2	Cl2	2.2514(11)	C14	C13	1.505(6)
Cu2	Cl2^1	2.2513(11)	C2	C3	1.372(6)
N1	C15	1.499(4)	C5	C4	1.386(5)
N1	C14	1.500(5)	C5	C6	1.509(6)
N1	C12	1.503(5)	C3	C4	1.385(6)
N2	C1	1.343(5)	C12	C11	1.514(6)
N2	C5	1.344(5)	C7	C8	1.513(6)
O1	N4	1.224(5)	C9	C10	1.507(6)
N3	C7	1.495(5)			

Table S14. Bond angles for [Cu**L5**Cl]$_2$[CuCl$_4$].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	Cu1	Cl1	97.89(9)	C6	N3	C7	110.3(3)
N1	Cu1	N3	166.27(12)	C6	N3	C9	112.9(3)
N2	Cu1	Cl1	178.96(10)	C9	N3	Cu1	106.2(2)
N2	Cu1	N1	83.10(12)	O1	N4	C3	117.3(4)
N2	Cu1	N3	83.19(13)	O2	N4	O1	124.8(4)
N3	Cu1	Cl1	95.82(9)	O2	N4	C3	117.9(4)
Cl3^1	Cu2	Cl3	98.05(6)	N2	C1	C15	115.2(3)
Cl3^1	Cu2	Cl2^1	99.97(4)	N2	C1	C2	120.3(4)
Cl3	Cu2	Cl2	99.97(4)	C2	C1	C15	124.4(3)
Cl3	Cu2	Cl2^1	133.25(4)	C1	C15	N1	111.7(3)
Cl3^1	Cu2	Cl2	133.25(4)	N1	C14	C13	114.1(3)
Cl2^1	Cu2	Cl2	98.24(6)	C3	C2	C1	116.7(4)
C15	N1	Cu1	109.0(2)	N2	C5	C4	120.7(4)
C15	N1	C14	110.4(3)	N2	C5	C6	115.4(3)
C15	N1	C12	108.8(3)	C4	C5	C6	123.9(4)
C14	N1	Cu1	107.0(2)	C2	C3	N4	118.4(4)
C14	N1	C12	108.1(3)	C2	C3	C4	124.0(4)
C12	N1	Cu1	113.6(2)	C4	C3	N4	117.6(4)
C1	N2	Cu1	118.6(3)	N1	C12	C11	113.1(3)
C1	N2	C5	122.4(3)	C3	C4	C5	115.9(4)
C5	N2	Cu1	119.0(3)	N3	C7	C8	113.9(3)
C7	N3	Cu1	112.2(3)	N3	C6	C5	112.5(3)
C7	N3	C9	106.1(3)	C10	C9	N3	112.3(3)
C6	N3	Cu1	109.1(2)				

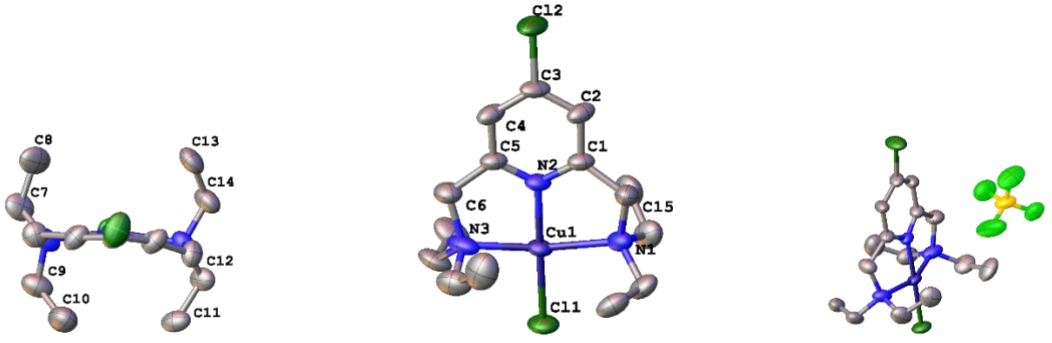


Figure S31. Crystal structure of [Cu**L4**Cl][BF$_4$] with corresponding labeling scheme. Hydrogen atoms have been removed for clarity. This figure shows the full pincer ligand for clarity.

Table S15. Crystal data and structure parameters for [Cu**L4**Cl][BF_4] Deposition Number 1958465.

Identification code	[Cu**L4**Cl][BF_4]
Empirical formula	$C_{15}H_{26}BCl_2CuF_4N_3$
Formula weight	450.44
Temperature/K	107.42
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	8.3793(4)
b/Å	10.1329(5)
c/Å	11.8915(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1009.67(8)
Z	2.1
ρ_{calc}g/cm^3	1.556
μ/mm^{-1}	1.388
F(000)	485.0
Crystal size/mm^3	3.328 × 1.687 × 0.887
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.852 to 69.132
Index ranges	-13 ≤ h ≤ 12, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	91714
Independent reflections	4279 [R_{int} = 0.0480, R_{sigma} = 0.0222]
Data/restraints/parameters	4279/188/226
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1168
Final R indexes [all data]	R_1 = 0.0553, wR_2 = 0.1248
Largest diff. peak/hole / e Å^{-3}	0.79/-0.60
Flack parameter	0.052(6)

Table S16. Bond lengths for [Cu**L4**Cl][BF_4].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl1	2.1953(13)	N3	C9	1.492(13)
Cu1	N2	1.908(3)	N3	C7	1.496(12)
Cu1	N3	2.037(10)	C9	C10	1.470(17)
Cu1	N1	2.155(9)	C7	C8	1.479(15)
Cl2	C3	1.732(7)	C15	N1	1.504(10)
N2	C5	1.326(15)	N1	C14	1.507(12)
N2	C1	1.339(15)	N1	C12	1.511(11)
C5	C4	1.367(9)	C14	C13	1.507(16)
C5	C6	1.517(12)	C12	C11	1.496(13)
C4	C3	1.368(14)	B1	F1	1.334(11)
C3	C2	1.364(14)	B1	F4	1.383(9)
C2	C1	1.393(11)	B1	F2	1.373(12)
C1	C15	1.499(11)	B1	F3	1.391(14)
C6	N3	1.492(10)			

Table S17. Bond angles for [Cu**L4**Cl][BF_4].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N2	Cu1	Cl1	178.5(13)	C6	N3	C9	111.6(8)
N2	Cu1	N3	83.3(7)	C6	N3	C7	110.4(8)
N2	Cu1	N1	82.3(7)	C9	N3	Cu1	103.2(8)
N3	Cu1	Cl1	97.4(4)	C9	N3	C7	109.5(8)
N3	Cu1	N1	159.6(3)	C7	N3	Cu1	111.9(6)
N1	Cu1	Cl1	96.7(3)	C10	C9	N3	112.9(10)
C5	N2	Cu1	119.7(11)	C8	C7	N3	113.3(7)
C5	N2	C1	119.9(7)	C1	C15	N1	111.1(7)
C1	N2	Cu1	119.5(11)	C15	N1	Cu1	107.7(5)
N2	C5	C4	121.2(8)	C15	N1	C14	110.0(8)
N2	C5	C6	114.2(8)	C15	N1	C12	109.1(7)
C4	C5	C6	124.6(9)	C14	N1	Cu1	108.7(7)
C5	C4	C3	118.4(8)	C14	N1	C12	106.0(7)
C4	C3	Cl2	119.0(10)	C12	N1	Cu1	115.2(6)
C2	C3	Cl2	120.4(10)	N1	C14	C13	113.1(8)
C2	C3	C4	120.6(5)	C11	C12	N1	112.7(7)
C3	C2	C1	117.5(8)	F1	B1	F4	112.1(9)
N2	C1	C2	120.6(8)	F1	B1	F2	109.6(7)
N2	C1	C15	116.8(9)	F1	B1	F3	109.0(13)
C2	C1	C15	122.3(9)	F4	B1	F3	108.2(7)
N3	C6	C5	111.5(8)	F2	B1	F4	110.1(11)
C6	N3	Cu1	110.0(6)	F2	B1	F3	107.6(7)

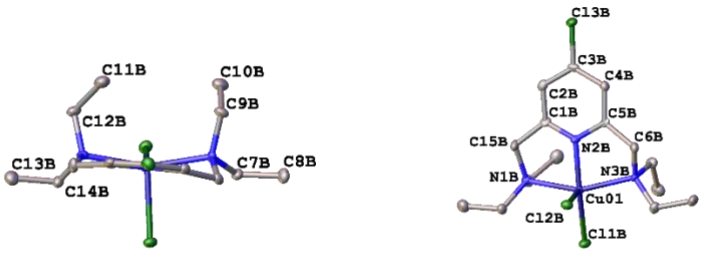


Figure S32. Crystal structure of ligand b of [Cu**L4**Cl_2] with corresponding labeling scheme. Hydrogen atoms have been removed for clarity. The other pincer in the asymmetric unit cell can be found in **Figure S33**.

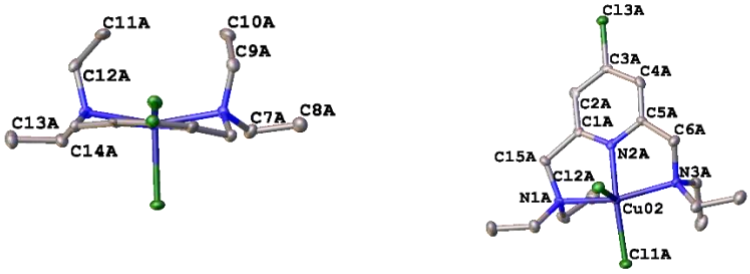


Figure S33. Crystal structure of ligand b of [Cu**L4**Cl_2] with corresponding labeling scheme. Hydrogen atoms have been removed for clarity. The other pincer in the asymmetric unit cell can be found in **Figure S32**.

Table S18. Crystal data and structure parameters for [Cu**L4**Cl_2] Deposition Number 1958462.

Identification code	[Cu**L4**Cl_2]
Empirical formula	$C_{15}H_{26}Cl_3CuN_3$
Formula weight	418.28
Temperature/K	249.19
Crystal system	triclinic
Space group	P-1
a/Å	10.9290(14)
b/Å	12.3008(15)
c/Å	13.8638(17)
α/°	90.396(5)
β/°	90.024(5)
γ/°	95.321(5)
Volume/Å^3	1855.7(4)
Z	4
ρ_{calc}g/cm^3	1.497
μ/mm^{-1}	1.608
F(000)	868.0
Crystal size/mm^3	0.078 × 0.073 × 0.069
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.594 to 52.742
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	19027
Independent reflections	7472 [R_{int} = 0.0556, R_{sigma} = 0.0764]
Data/restraints/parameters	7472/0/406
Goodness-of-fit on F^2	1.101
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.0915
Final R indexes [all data]	R_1 = 0.0741, wR_2 = 0.1053
Largest diff. peak/hole / e Å^{-3}	0.66/-0.78

Table S19. Bond lengths for [Cu**L4**Cl_2].

Atom	Atom	Length/Å	Atom	Atom
Cu01	Cl2B	2.4761(16)	N1B	C12B
Cu01	Cl1B	2.2561(16)	N1A	C15A
Cu01	N2B	1.949(5)	N1A	C14A
Cu01	N3B	2.159(5)	N1A	C12A
Cu01	N1B	2.155(5)	C1A	C15A
Cu02	Cl2A	2.4699(16)	C1A	C2A
Cu02	Cl1A	2.2406(16)	C4B	C5B
Cu02	N2A	1.953(5)	C4B	C3B
Cu02	N3A	2.151(5)	C5A	C4A
Cu02	N1A	2.143(5)	C5A	C6A
Cl3B	C3B	1.728(6)	C1B	C2B
Cl3A	C3A	1.730(6)	C1B	C15B
N2A	C1A	1.323(7)	C2B	C3B
N2A	C5A	1.344(7)	C5B	C6B
N2B	C1B	1.328(7)	C2A	C3A
N2B	C5B	1.364(7)	C3A	C4A
N3B	C6B	1.487(7)	C14A	C13A
N3B	C7B	1.481(7)	C12A	C11A
N3B	C9B	1.501(7)	C7B	C8B
N3A	C6A	1.485(7)	C14B	C13B
N3A	C7A	1.494(7)	C9B	C10B
N3A	C9A	1.497(7)	C7A	C8A
N1B	C15B	1.484(7)	C9A	C10A
N1B	C14B	1.498(7)	C11B	C12B

Table S20. Bond angles for [Cu**L4**Cl_2].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl1B	Cu01	Cl2B	104.38(6)	C12B	N1B	Cu01	109.4(3)
N2B	Cu01	Cl2B	91.94(14)	C12B	N1B	C14B	109.5(4)
N2B	Cu01	Cl1B	163.60(14)	C15A	N1A	Cu02	106.8(3)
N2B	Cu01	N3B	79.99(19)	C15A	N1A	C14A	110.4(5)
N2B	Cu01	N1B	80.58(19)	C15A	N1A	C12A	110.8(5)
N3B	Cu01	Cl2B	96.91(13)	C14A	N1A	Cu02	107.6(3)
N3B	Cu01	Cl1B	99.33(13)	C12A	N1A	Cu02	110.8(3)
N1B	Cu01	Cl2B	102.67(13)	C12A	N1A	C14A	110.5(4)
N1B	Cu01	Cl1B	94.00(13)	N2A	C1A	C15A	114.8(5)
N1B	Cu01	N3B	152.74(18)	N2A	C1A	C2A	120.6(5)
Cl1A	Cu02	Cl2A	103.93(6)	C2A	C1A	C15A	124.3(5)
N2A	Cu02	Cl2A	92.25(15)	C5B	C4B	C3B	117.5(6)
N2A	Cu02	Cl1A	163.82(15)	N2A	C5A	C4A	120.6(5)
N2A	Cu02	N3A	79.93(18)	N2A	C5A	C6A	112.0(5)
N2A	Cu02	N1A	81.51(18)	C4A	C5A	C6A	127.2(5)
N3A	Cu02	Cl2A	98.36(14)	N2B	C1B	C2B	121.4(6)
N3A	Cu02	Cl1A	97.54(14)	N2B	C1B	C15B	114.2(5)
N1A	Cu02	Cl2A	101.67(14)	C2B	C1B	C15B	124.2(5)
N1A	Cu02	Cl1A	94.88(13)	C1B	C2B	C3B	117.1(5)
N1A	Cu02	N3A	153.11(18)	N2B	C5B	C4B	120.9(5)
C1A	N2A	Cu02	119.1(4)	N2B	C5B	C6B	113.6(5)
C1A	N2A	C5A	121.9(5)	C4B	C5B	C6B	125.5(5)
C5A	N2A	Cu02	119.0(4)	C4B	C3B	Cl3B	119.4(5)
C1B	N2B	Cu01	120.8(4)	C4B	C3B	C2B	121.4(5)
C1B	N2B	C5B	121.6(5)	C2B	C3B	Cl3B	119.3(4)
C5B	N2B	Cu01	117.6(4)	N1A	C15A	C1A	111.4(5)
C6B	N3B	Cu01	103.4(3)	N1B	C15B	C1B	112.5(5)
C6B	N3B	C9B	106.6(4)	C1A	C2A	C3A	118.3(6)
C7B	N3B	Cu01	110.8(3)	C2A	C3A	Cl3A	119.6(5)
C7B	N3B	C6B	110.2(4)	C2A	C3A	C4A	120.2(6)
C7B	N3B	C9B	112.3(4)	C4A	C3A	Cl3A	120.1(5)
C9B	N3B	Cu01	113.0(3)	N3B	C6B	C5B	108.8(5)
C6A	N3A	Cu02	103.4(3)	C5A	C4A	C3A	118.4(5)
C6A	N3A	C7A	111.1(5)	N3A	C6A	C5A	109.8(5)
C6A	N3A	C9A	106.5(4)	N1A	C14A	C13A	115.4(5)
C7A	N3A	Cu02	109.9(4)	N1A	C12A	C11A	113.7(5)
C7A	N3A	C9A	112.6(5)	N3B	C7B	C8B	116.5(5)
C9A	N3A	Cu02	113.0(3)	N1B	C14B	C13B	116.3(5)
C15B	N1B	Cu01	107.6(3)	N3B	C9B	C10B	115.7(5)
C15B	N1B	C14B	110.2(4)	N3A	C7A	C8A	115.5(5)
C15B	N1B	C12B	110.9(4)	N3A	C9A	C10A	115.5(5)
C14B	N1B	Cu01	109.3(3)	N1B	C12B	C11B	113.2(5)

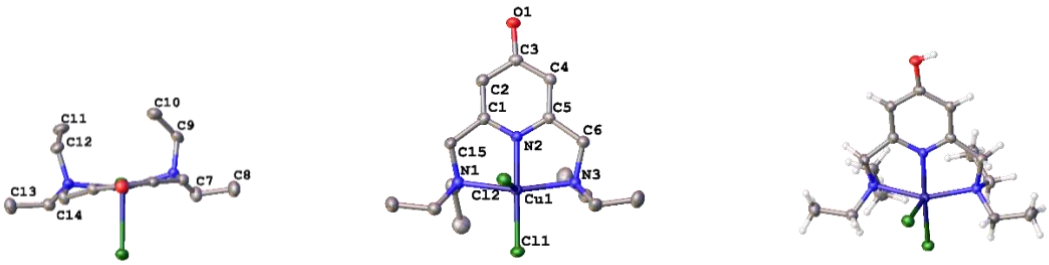


Figure S34. Crystal structure of [Cu**L1**Cl_2] with corresponding labeling scheme. Hydrogen atoms have been added on the right for visualization of the -OH moiety.

Table S21. Crystal data and structure parameters for [Cu**L1**Cl_2] Deposition Number 1958464.

Identification code	[Cu**L1**Cl_2]
Empirical formula	$C_{15}H_{27}Cl_2CuN_3O$
Formula weight	399.83
Temperature/K	170.49
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.0125(5)
b/Å	13.0501(5)
c/Å	13.5828(6)
α/°	90
β/°	110.626(2)
γ/°	90
Volume/Å^3	1826.91(14)
Z	4
ρ_{calc}g/cm^3	1.454
μ/mm^{-1}	1.492
F(000)	836.0
Crystal size/mm^3	0.318 × 0.27 × 0.128
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.41 to 52.74
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	22883
Independent reflections	3722 [R_{int} = 0.0341, R_{sigma} = 0.0247]
Data/restraints/parameters	3722/0/204
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0498, wR_2 = 0.1193
Largest diff. peak/hole / e Å^{-3}	1.54/-0.87

Table S22 Bond lengths for [Cu**L1**Cl_2].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl1	2.2040(8)	N1	C14	1.487(4)
Cu1	Cl2	2.6029(8)	N1	C12	1.498(4)
Cu1	N2	1.926(2)	C5	C4	1.383(4)
Cu1	N3	2.118(2)	C5	C6	1.510(4)
Cu1	N1	2.174(3)	C4	C3	1.406(4)
O1	C3	1.335(4)	C3	C2	1.400(4)
N2	C5	1.339(4)	C1	C15	1.500(4)
N2	C1	1.345(4)	C1	C2	1.370(4)
N3	C7	1.503(4)	C7	C8	1.516(5)
N3	C6	1.494(4)	C14	C13	1.528(4)
N3	C9	1.495(4)	C9	C10	1.504(5)
N1	C15	1.485(4)	C12	C11	1.510(5)

Table S23 Bond angles for [Cu**L1**Cl_2].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl1	Cu1	Cl2	98.07(3)	C15	N1	C12	108.3(2)
N2	Cu1	Cl1	170.98(8)	C14	N1	Cu1	110.39(18)
N2	Cu1	Cl2	90.93(7)	C14	N1	C12	112.6(2)
N2	Cu1	N3	81.65(10)	C12	N1	Cu1	111.3(2)
N2	Cu1	N1	80.74(10)	N2	C5	C4	121.7(3)
N3	Cu1	Cl1	96.37(7)	N2	C5	C6	114.5(3)
N3	Cu1	Cl2	106.20(7)	C4	C5	C6	123.5(3)
N3	Cu1	N1	153.43(10)	C5	C4	C3	117.9(3)
N1	Cu1	Cl1	97.91(7)	O1	C3	C4	123.5(3)
N1	Cu1	Cl2	93.84(7)	O1	C3	C2	117.1(3)
C5	N2	Cu1	119.9(2)	C2	C3	C4	119.4(3)
C5	N2	C1	120.7(3)	N2	C1	C15	113.7(3)
C1	N2	Cu1	119.1(2)	N2	C1	C2	121.2(3)
C7	N3	Cu1	109.36(19)	C2	C1	C15	124.8(3)
C6	N3	Cu1	107.81(17)	N1	C15	C1	111.4(2)
C6	N3	C7	110.0(2)	C1	C2	C3	119.0(3)
C6	N3	C9	110.9(2)	N3	C7	C8	115.5(3)
C9	N3	Cu1	109.33(19)	N3	C6	C5	111.8(2)
C9	N3	C7	109.5(2)	N1	C14	C13	116.1(3)
C15	N1	Cu1	103.41(18)	N3	C9	C10	114.1(3)
C15	N1	C14	110.5(2)	N1	C12	C11	115.1(3)

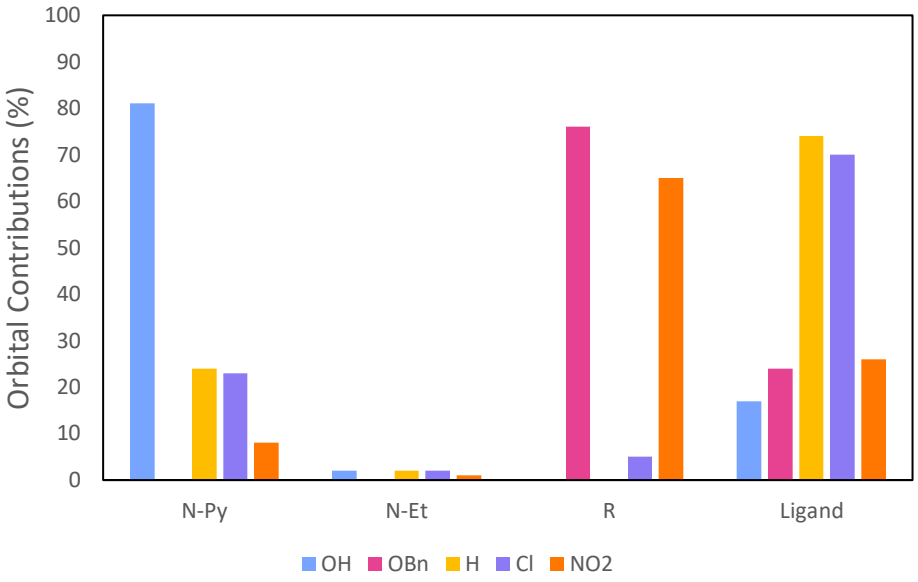


Figure S35. Ligand fragment contributions to the LUMO of **L1-L5**, computed using Chemissian.[6]

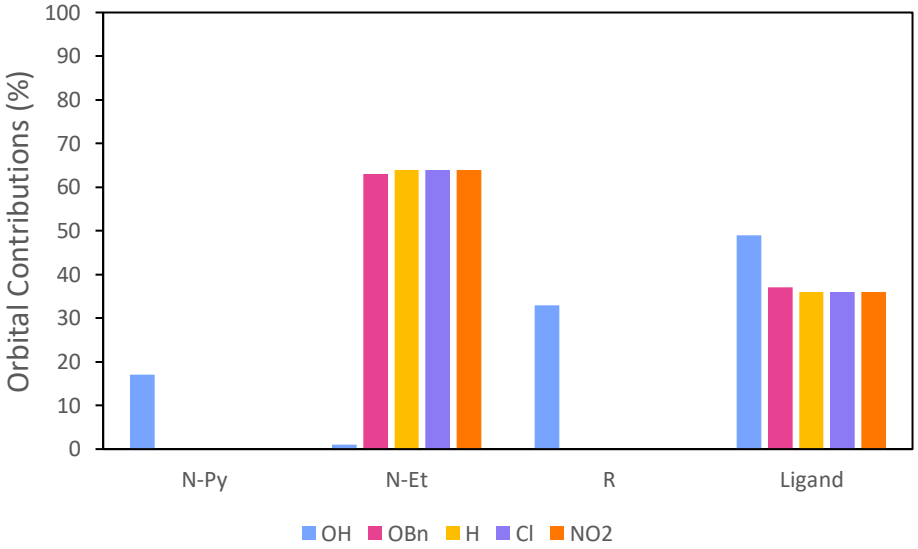


Figure S36. Ligand fragment contributions to the HOMO of **L1-L5** computed using Chemissian.[6]

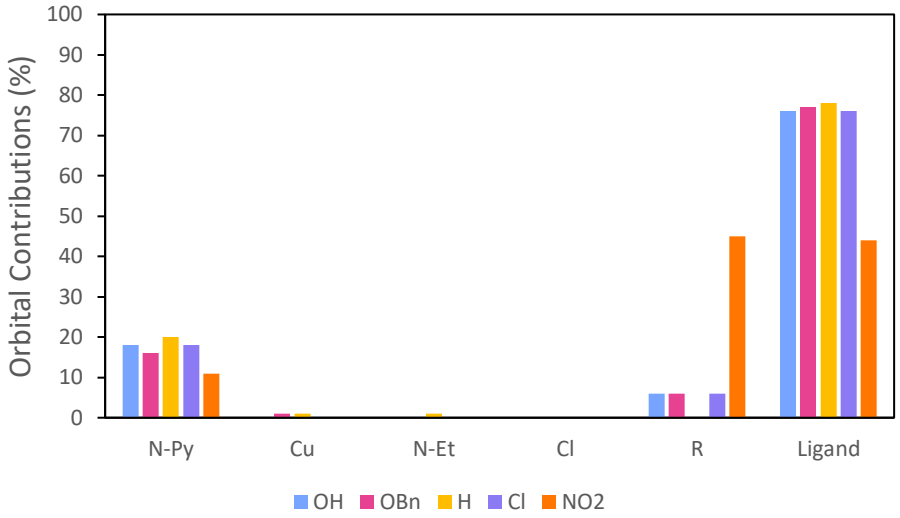


Figure S37. Cu(II) complex fragment contributions to the HOMO of **L1Cu-L5Cu** computed using Chemissian.[6]

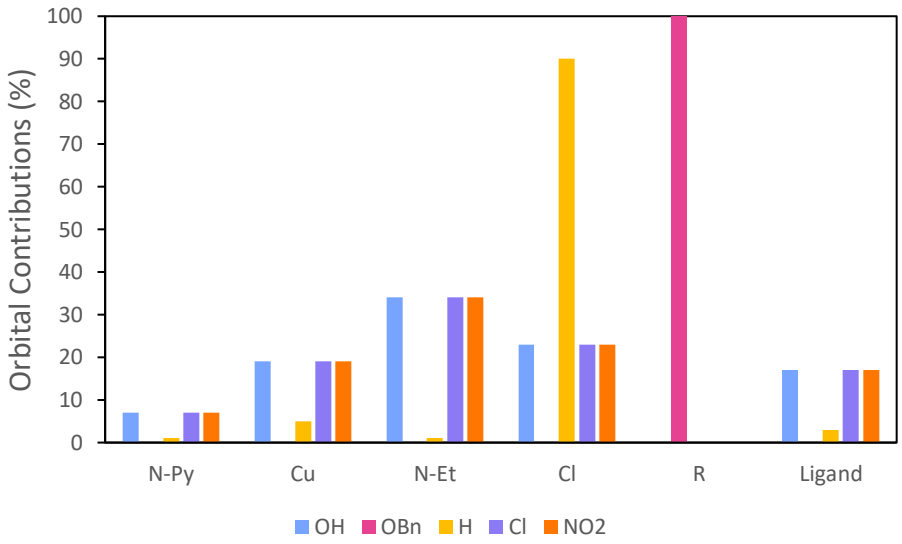


Figure S38. Cu(II) complex fragment contributions to the SOMO of **L1Cu-L5Cu** computed using Chemissian.[6]

Table S24. Partial charge density on the N-pyridine atom.

Species	L1Cu	L2Cu	L3Cu	L4Cu	L5Cu
NBO partial charge	-0.584	-0.591	-0.573	-0.564	-0.543

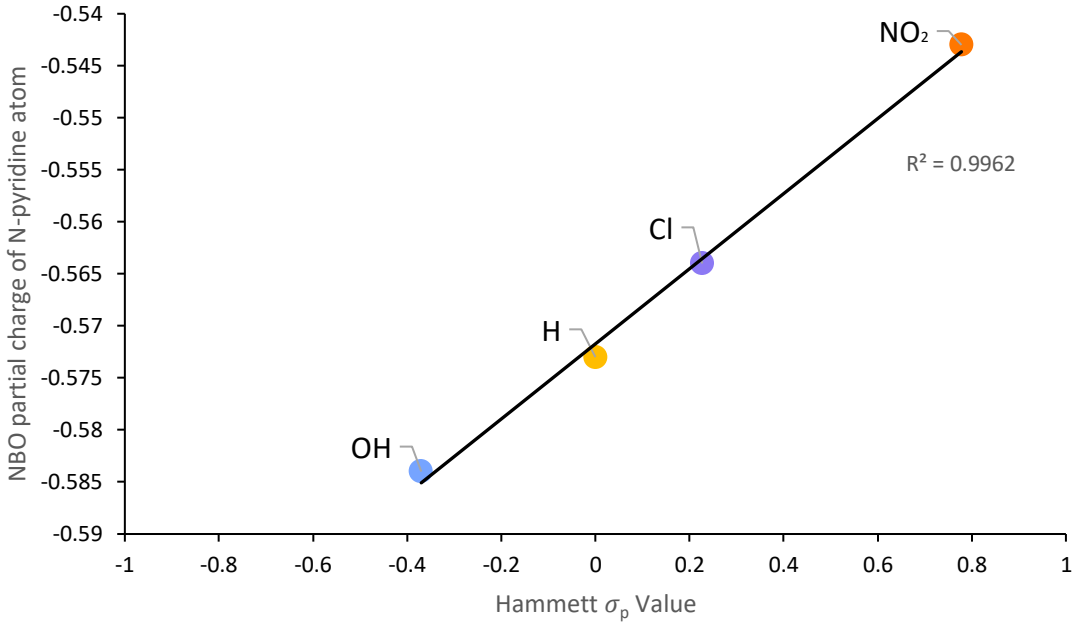


Figure S39. Hammett plot of the partial charge density on the N-pyridine atom with R^2 value.

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