Electronic Supplementary Information (ESI)

for

Accessing bimetallic complexes through a variable bridging ligand strategy

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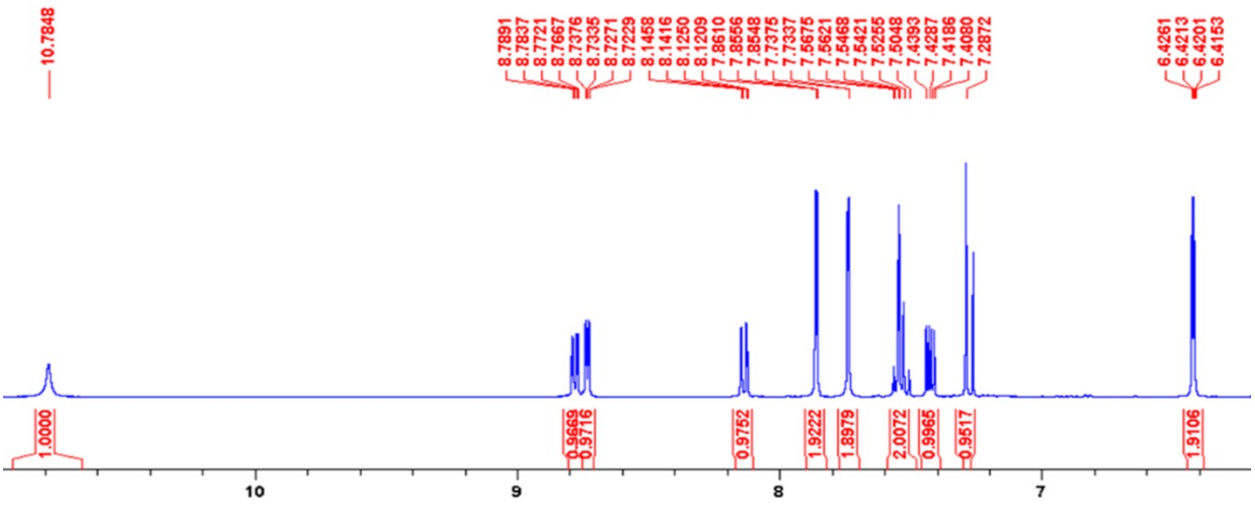


Figure S1. The ^{1}H-NMR spectrum of the **HL^{Q}2Pz** ligand.

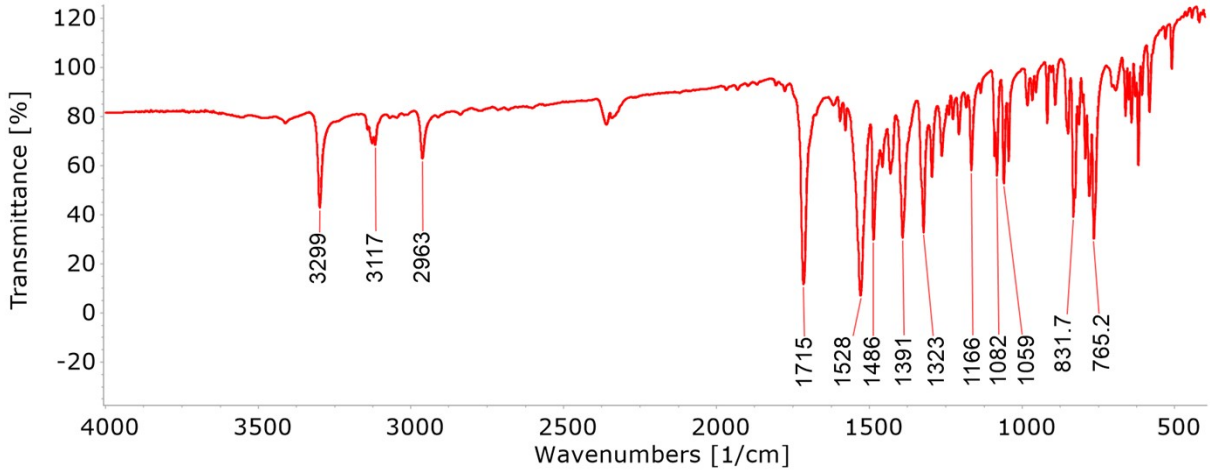


Figure S2. The IR spectrum of the **HL^{Q}2Pz** ligand in KBr matrix.

Table S1. Summary of the IR and UV-Visible spectroscopic data for **(L^{Q}2Pz)Cu(OAc) · H$_2$O**, **(L^{Q}2Pz)Cu(BF$_4$)**, and **(L^{Q}2Pz)Cu(ClO$_4$) · MeCN**.

Compound	$\tilde{\nu}_{NH}$ cm^{-1}	$\tilde{\nu}_{CO}$ cm^{-1}	$\tilde{\nu}_{pz}$ cm^{-1}	$\tilde{\nu}_{as\ COO}$ cm^{-1}	$\tilde{\nu}_{s\ COO}$ cm^{-1}	Δ cm^{-1}	λ_{max}/nm (ε/M^{-1}cm^{-1})
HL^{Q}2Pz	3299	1715	1528	-	-	-	-
(L^{Q}2Pz)Cu(OAc) · H$_2$O	-	1632	1500	1582	1387	195	258 (72.2 x 10^3), 368 (5.7 x 10^3), 634 (99)
(L^{Q}2Pz)Cu(BF$_4$)	-	1608	1505	-	-	-	260 (42.3 x 10^3), 368 (4.7 x 10^3), 670 (125)
(L^{Q}2Pz)Cu(ClO$_4$) · MeCN	-	1620	1504	-	-	-	259 (59.4 x 10^3), 368 (5.7 x 10^3), 667 (134)

Table S2. Crystal data collection and refinement parameters for **(L^{Q}2Pz)Cu(OAc)**, **(L^{Q}2Pz)Cu(BF_4)**, and **[(L^{Q}2Pz)Cu(NCMe)]ClO_4** complexes.

	(L^{Q}2Pz)Cu(OAc)	**(L^{Q}2Pz)Cu(BF_4)**	**[(L^{Q}2Pz)Cu(NCMe)]ClO_4**
Crystal data			
Chemical formula	0.28(H_2O)·0.229(O)· 2($C_{19}H_{16}CuN_6O_3$)	$C_{17}H_{13}BCuF_4N_6O$	$C_{19}H_{16}CuN_7O{\cdot}ClO_4$
Mr	888.56	467.68	521.38
Crystal system, space group	Triclinic, P	Monoclinic, P21/n	Monoclinic, C2/c
Temperature (K)	100	100	100
a, b, c (Å)	9.6542 (6) 13.8554 (8) 16.0283 (9)	9.1850 (4) 17.3019 (6) 12.1405 (4)	29.990 (3) 8.1215 (8) 17.9630 (16)
α, β, γ (°)	114.194 (3) 93.294 (3) 103.183 (3)	90.977(2)	104.213(4)
V (Å^3)	1876.4 (2)	1929.06 (12)	4241.2 (7)
Z	2	4	8
Radiation type	Cu Kα	Cu Kα	Cu Kα
μ (mm^{-1})	1.97	2.15	3.05
Crystal size (mm)	0.29 × 0.12 × 0.11	0.17 × 0.16 × 0.08	0.28 × 0.17 × 0.13
Data collection			
Diffractometer	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture
Absorption correction	Multi-scan SADABS 2016/2	Multi-scan SADABS 2016/2	Multi-scan SADABS 2016/2
Tmin, Tmax	0.615, 0.753	0.671, 0.753	0.591, 0.753
No. of measured, independent and observed [I > 2σ(I)] reflections	42460, 6721, 6029	28188, 3488, 2940	45384, 3891, 3683
Rint	0.040	0.052	0.051
(sin θ/λ)max (Å^{-1})	0.602	0.602	0.602
Refinement			
R[F2 > 2σ(F2)], wR(F2), S	0.038, 0.099, 1.12	0.045, 0.167, 1.06	0.035, 0.090, 1.06
No. of reflections	6721	3488	3891
No. of parameters	578	271	309
No. of restraints	56		69
Δρmax, Δρmin (e Å^{-3})	0.41, −0.44	0.96, −0.81	0.93, −0.53

Table S3. Selected bond lengths (Å) and angles (°) for **(L^{O}2pz)Cu(OAc)**.

Atoms		Bond lengths	Atoms			Bond Angles
Cu1A	O2A	1.9420(19)	O2A	Cu1A	N1A	95.10(9)
Cu1A	N1A	2.002(2)	O2A	Cu1A	N2A	177.10(9)
Cu1A	N2A	1.969(2)	O2A	Cu1A	N3A	93.35(9)
Cu1A	N3A	2.035(2)	O2A	Cu1A	N5A	95.35(8)
Cu1A	N5A	2.329(2)	N1A	Cu1A	N3A	155.34(9)
			N1A	Cu1A	N5A	117.12(8)
			N2A	Cu1A	N1A	82.20(9)
			N2A	Cu1A	N3A	89.55(9)
			N2A	Cu1A	N5A	84.97(9)
			N3A	Cu1A	N5A	85.01(9)
Cu1B	O2B	1.944(8)	O2B	Cu1B	N1B	91.4(4)
Cu1B	N1B	2.006(2)	O2B	Cu1B	N2B	168.3(3)
Cu1B	N2B	1.973(2)	O2B	Cu1B	N3B	104.2(4)
Cu1B	N3B	2.088(3)	O2B	Cu1B	N5B	87.6(4)
Cu1B	N5B	2.236(2)	N1B	Cu1B	N3B	144.95(10)
			N1B	Cu1B	N5B	127.71(10)
			N2B	Cu1B	N1B	81.96(10)
			N2B	Cu1B	N3B	86.61(10)
			N2B	Cu1B	N5B	88.77(9)
			N3B	Cu1B	N5B	84.78(9)

Table S4. Selected bond lengths (Å) and angles (°) for **(L^{O}2Pz)CuBF$_4$**.

Atoms		Bond lengths	Atoms			Bond Angles
Cu1	F1	1.975(2)	F1	Cu1	N1	176.93(11)
Cu1	N1	1.986(3)	F1	Cu1	N3	94.40(10)
Cu1	N3	2.194(3)	F1	Cu1	N5	93.16(11)
Cu1	N5	2.070(3)	F1	Cu1	N6	94.71(11)
Cu1	N6	2.003(3)	N1	Cu1	N3	86.67(10)
			N1	Cu1	N5	89.76(11)
			N1	Cu1	N6	82.33(11)
			N5	Cu1	N3	86.81(11)
			N6	Cu1	N3	125.10(12)
			N6	Cu1	N5	146.25(12)

Table S5. Selected bond lengths (Å) and angles (°) for **[(L^Q2Pz)Cu(NCCH$_3$)]ClO$_4$**.

Atoms		Bond lengths	Atoms			Bond Angles
Cu1	N1	2.0034(18)	N1	Cu1	N4	123.75(8)
Cu1	N2	1.9606(18)	N1	Cu1	N6	149.32(7)
Cu1	N4	2.1960(19)	N2	Cu1	N1	82.40(8)
Cu1	N6	2.0881(19)	N2	Cu1	N4	87.14(7)
Cu1	N7	1.961(2)	N2	Cu1	N6	89.67(8)
			N2	Cu1	N7	177.18(8)
			N6	Cu1	N4	85.11(7)
			N7	Cu1	N1	95.00(8)
			N7	Cu1	N4	95.23(8)
			N7	Cu1	N6	92.05(8)

Table S6. Selected IR and UV-Visible spectroscopic data for **(L^Q2Pz)Cu[O$_2$CCH(pz)$_2$]** and **(L^Q2Pz)Cu[O$_2$CCH(CH$_2$pz)$_2$]**.

Compound	$\tilde{\nu}_{CO}$ cm^{-1}	$\tilde{\nu}_{pz}$ cm^{-1}	$\tilde{\nu}_{as\ COO}$ cm^{-1}	$\tilde{\nu}_{s\ COO}$ cm^{-1}	Δ cm^{-1}	λ_{max}/nm (ε/M^{-1}cm^{-1})
(L^Q2Pz)Cu[O$_2$CCH(pz)$_2$]	1654	1502	1626	1391	235	259 (76.8 x 103), 368 (6.9 x 103), 669 (144.9)
(L^Q2Pz)Cu[O$_2$CCH(CH$_2$pz)$_2$]	1626	1504	1612	1401	211	259 (73.6 x 103), 365 (6.7 x 103), 637 (130)

Table S7. Crystal data collection and refinement parameters for **(L^Q2Pz)Cu[O$_2$CCH(pz)$_2$]** and **(L^Q2Pz)Cu[O$_2$CCH(CH$_2$pz)$_2$]** metalloligands.

	(L^Q2Pz)Cu[O$_2$CCH(pz)$_2$]	**(L^Q2Pz)Cu[O$_2$CCH(CH$_2$pz)$_2$]**
Crystal data		
Chemical formula	$C_{25}H_{20}CuN_{10}O_3$	$C_{27}H_{24}CuN_{10}O_3 \cdot 0.566(CH_2Cl_2)$
Mr	572.05	648.08
Crystal system, space group	Monoclinic, P21	Triclinic, P
Temperature (K)	100	173
a, b, c (Å)	8.8835 (3) 15.2234 (5) 9.6987 (3)	7.9593 (6) 12.0730 (9) 15.9301 (11)
α, β, γ (°)	β = 112.045 (2)	69.659 (4) 81.772 (4) 89.586 (4)
V (Å^3)	1215.73 (7)	1419.04 (18)
Z	2	2
Radiation type	Cu Kα	Cu Kα
μ (mm^{-1})	1.71	2.49
Crystal size (mm)	0.43 × 0.41 × 0.07	0.26 × 0.13 × 0.12

Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEX-II CCD
Absorption correction	Multi-scan SADABS 2016/2	Multi-scan SADABS 2016/2
Tmin, Tmax	0.596, 0.753	0.205, 0.272
No. of measured, independent and observed [I > 2σ(I)] reflections	14511, 4250, 4183	30909, 5069, 4408
Rint	0.030	0.067
(sin θ/λ)max (Å^{-1})	0.602	0.604
Refinement		
R[F2 > 2σ(F2)], wR(F2), S	0.024, 0.060, 1.05	0.038, 0.109, 1.09
No. of reflections	4250	5069
No. of parameters	353	534
No. of restraints	1	300
Δρmax, Δρmin (e Å−3)	0.26, −0.22	0.49, −0.52

Table S8. Selected bond lengths (Å) and angles (°) for **(L^{O}2Pz)Cu[$O_2CCH(pz)_2$]**.

Atoms		Bond lengths	Atoms			Bond Angles
Cu1	O2	1.9436(18)	O2	Cu1	N1	97.14(9)
Cu1	N1	1.992(2)	O2	Cu1	N2	175.18(10)
Cu1	N2	1.973(2)	O2	Cu1	N4	89.33(8)
Cu1	N4	2.126(2)	O2	Cu1	N6	95.55(8)
Cu1	N6	2.152(2)	N1	Cu1	N4	138.08(11)
			N1	Cu1	N6	134.59(10)
			N2	Cu1	N1	82.50(10)
			N2	Cu1	N4	87.77(9)
			N2	Cu1	N6	88.05(10)
			N4	Cu1	N6	85.32(10)

Table S9. Selected bond lengths (Å) and angles (°) for **(L^{O}2Pz)Cu[$O_2CCH(CH_2pz)_2$]**.

Atoms		Bond lengths	Atoms			Bond Angles
Cu1	N1	2.009(2)	N1	Cu1	N4	127.70(7)
Cu1	N2	1.9927(19)	N1	Cu1	N6A	148.0(6)
Cu1	N4	2.377(2)	N2	Cu1	N1	82.21(8)
Cu1	N6	1.998(13)	N2	Cu1	N4	84.24(7)
Cu1	N6A	2.174(19)	N2	Cu1	N6	92.2(4)
Cu1	O2	1.9432(16)	N2	Cu1	N6A	86.6(6)
			N6	Cu1	N1	144.8(4)
			N6	Cu1	N4	85.8(4)
			N6A	Cu1	N4	80.4(6)
			O2	Cu1	N1	96.09(8)
			O2	Cu1	N2	170.09(8)
			O2	Cu1	N4	89.17(7)
			O2	Cu1	N6	94.7(4)
			O2	Cu1	N6A	99.6(6)

Table S10. Selected IR and UV-Visible spectroscopic data for **{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2Cu^{I}(PPh_3)_2$]}$NO_3$** and **{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2$]}$_2Cu^{I}(PF_6)$**.

Compound	$\tilde{\nu}_{CO}$ cm^{-1}	$\tilde{\nu}_{pz}$ cm^{-1}	$\tilde{\nu}_{as\ COO}$ cm^{-1}	$\tilde{\nu}_{s\ COO}$ cm^{-1}	Δ cm^{-1}	λ_{max}/nm (ε/$M^{-1}cm^{-1}$)
{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2Cu^{I}(PPh_3)_2$]}$NO_3$	1625	1502	1607	1383	224	259 (66.8 x 10^3), 368 (6.7 x 10^3), 655 (134.7)
{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2$]}$_2Cu^{I}$ (PF_6)	1624	1503	1612	1385	227	259 (84.4 x 10^3), 368 (6.2 x 10^3), 669 (141.3)

Table S11. Crystal data collection and refinement parameters for **{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2Cu^{I}(PPh_3)_2$]}$NO_3$** and **{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2$]}$_2Cu^{I}(PF_6)$**

	{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2Cu^{I}(PPh_3)_2$]} NO_3	**{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2$]}$_2$ $Cu^{I}(PF_6)$**
Crystal data		
Chemical formula	$C_{63}H_{54}Cu_2N_{10}O_3P_2 \cdot CH_2Cl_2 \cdot NO_3 \cdot 2[CH_2Cl_2]$	$C_{54}H_{48}Cu_3N_{20}O_6 \cdot PF_6$
Mr	1504.97	1408.71
Crystal system, space group	Triclinic, P	Monoclinic, C2/c
Temperature (K)	100	100
a, b, c (Å)	13.4052 (7), 14.3404 (7), 19.2792 (9)	25.722 (4) 15.807 (2) 34.480 (6)
α, β, γ (°)	77.040 (3), 70.484 (3), 81.514 (3)	95.155 (10)
V (Å^3)	3393.6 (3)	13962 (4)
Z	2	8
Radiation type	Cu Kα	Cu Kα
μ (mm^{-1})	3.88	1.92
Crystal size (mm)	0.49 × 0.20 × 0.11	0.36 × 0.11 × 0.04
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEX-II CCD
Absorption correction	Multi-scan SADABS 2016/2	Multi-scan SADABS 2016/2
Tmin, Tmax	0.499, 0.753	0.631, 0.753
No. of measured, independent and observed [I > 2σ(I)] reflections	73975, 12076, 10259	71301, 8255, 5035
Rint	0.055	0.247
(sin θ/λ)max ($Å^{-1}$)	0.603	0.521
Refinement		
R[F2 > 2σ(F2)], wR(F2), S	0.041, 0.119, 1.06	0.070, 0.200, 1.01
No. of reflections	12076	8255
No. of parameters	788	812
Δρmax, Δρmin (e $Å^{-3}$)	1.11, −0.57	0.48, −0.59

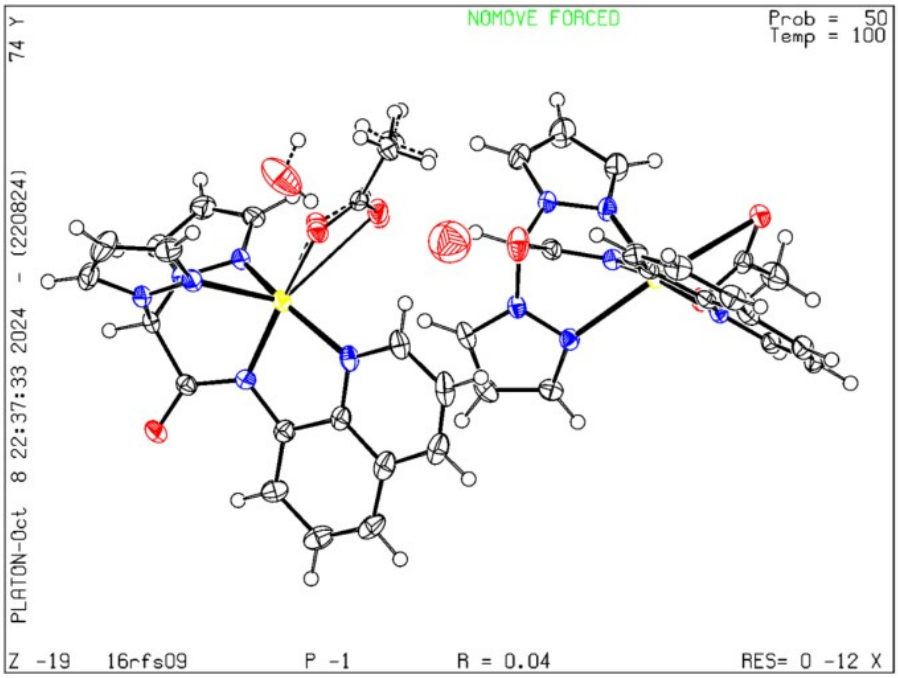
Table S12. Selected bond lengths (Å) and angles (°) for **{(L^{Q}2Pz)Cu^{II}[O_2CCH(CH_2pz)$_2$$Cu^{I}$($PPh_3$)$_2$]}$NO_3$**

Atoms		Bond lengths	Atoms			Bond Angles
Cu1	O2	1.9360(19)	O2	Cu1	N1	93.24(9)
Cu1	N1	2.020(2)	O2	Cu1	N2	170.48(10)
Cu1	N2	1.991(2)	O2	Cu1	N4	89.68(10)
Cu1	N4	2.129(3)	O2	Cu1	N6	103.11(9)
Cu1	N6	2.174(2)	N1	Cu1	N4	142.53(10)
			N1	Cu1	N6	130.54(10)
			N2	Cu1	N1	82.03(10)
			N2	Cu1	N4	89.12(10)
			N2	Cu1	N6	86.18(9)
			N4	Cu1	N6	84.63(10)
Cu2	P1	2.3187(7)	P2	Cu2	P1	122.25(3)
Cu2	P2	2.3037(7)	N8	Cu2	P1	106.99(6)
Cu2	N8	2.094(2)	N8	Cu2	P2	105.40(6)
Cu2	N10	2.082(2)	N10	Cu2	P1	102.73(6)
			N10	Cu2	P2	108.87(7)
			N10	Cu2	N8	110.40(8)

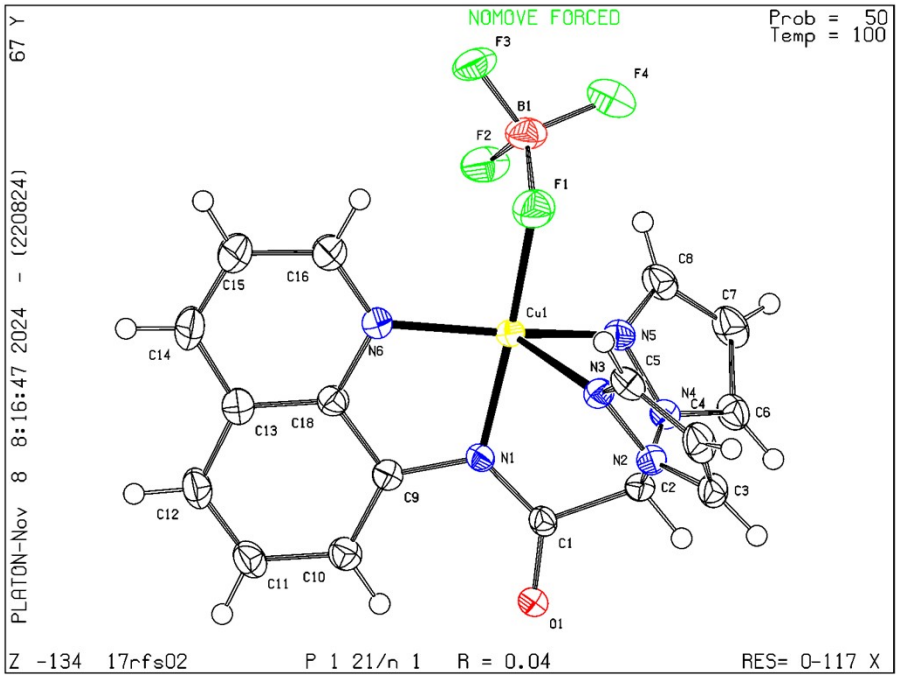
Table S13. Selected bond lengths (Å) and angles (°) for **{(L^{Q}2Pz)Cu^{II}[O_2CCH(CH_2pz)$_2$]}$_2$$Cu^{I}$($PF_6$)**

Atoms		Bond lengths	Atoms			Bond Angles
Cu1	O2	1.932(5)	O2	Cu1	N1	178.6(3)
Cu1	N1	1.954(7)	O2	Cu1	N2	96.6(3)
Cu1	N2	2.001(7)	O2	Cu1	N4	89.8(2)
Cu1	N4	2.020(7)	O2	Cu1	N6	97.0(2)
Cu1	N6	2.353(7)	N4	Cu1	N6	84.4(3)
Cu2	N7	2.044(7)	N9	Cu2	N7	113.2(3)
Cu2	N9	2.008(7)	N13	Cu2	N7	113.2(3)
Cu2	N11	2.078(6)	N13	Cu2	N9	113.5(3)
Cu2	N13	2.008(7)	N13	Cu2	N11	115.1(2)
Cu3	O4	1.935(5)	O4	Cu3	N15	167.2(3)
Cu3	N15	1.976(6)	O4	Cu3	N16	93.8(2)
Cu3	N16	1.993(7)	O4	Cu3	N17	101.6(2)
Cu3	N17	2.131(7)	O4	Cu3	N19	89.0(2)
Cu3	N19	2.212(7)	N17	Cu3	N19	84.7(3)

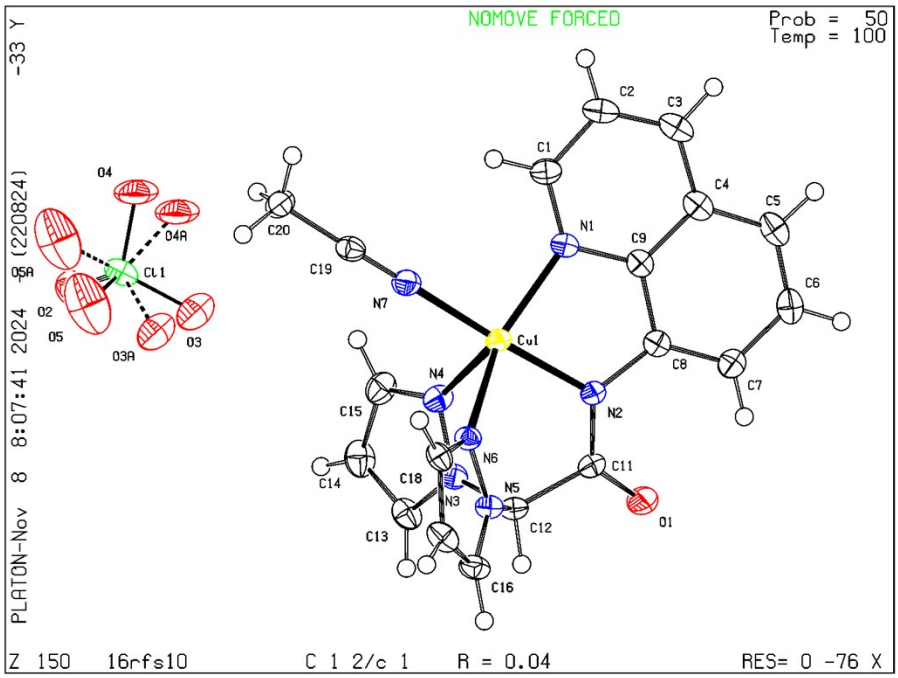
ORTEP Figures



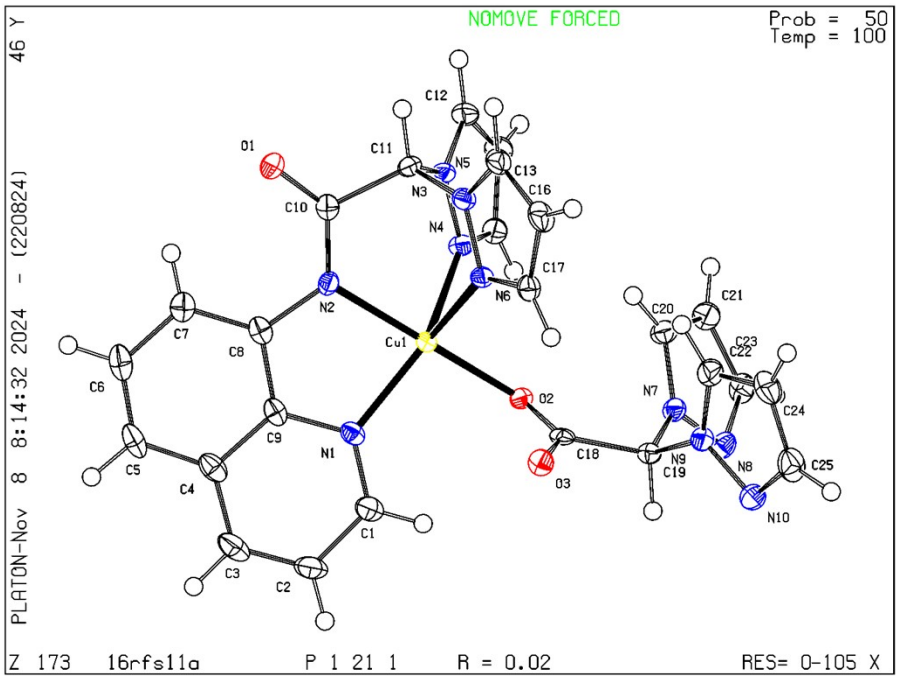
ORTEP of **(L^{Q}2Pz)Cu(OAc)**.



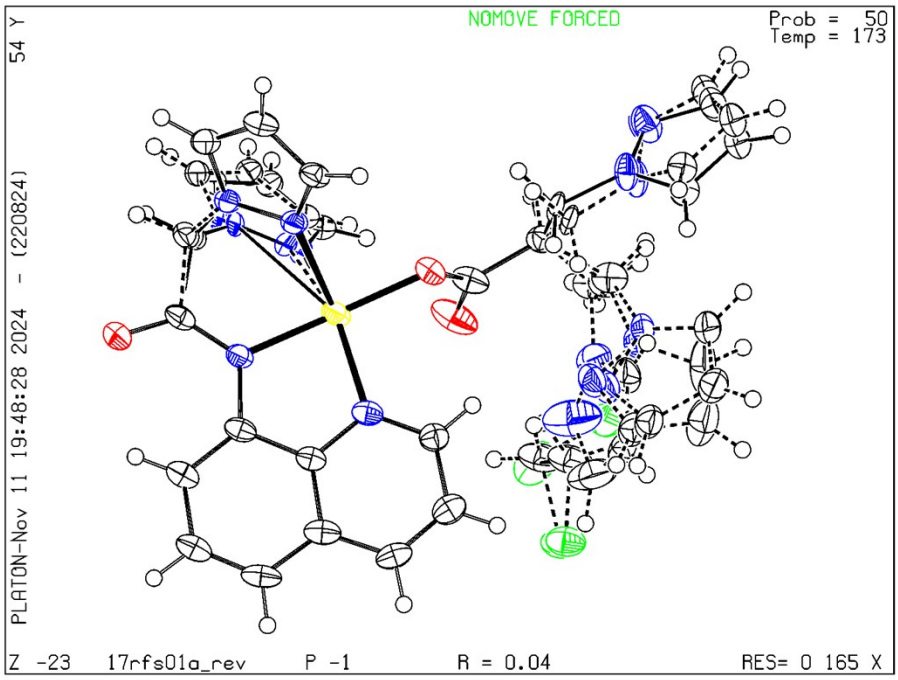
ORTEP of **(L^{Q}2Pz)Cu(BF$_4$)**.



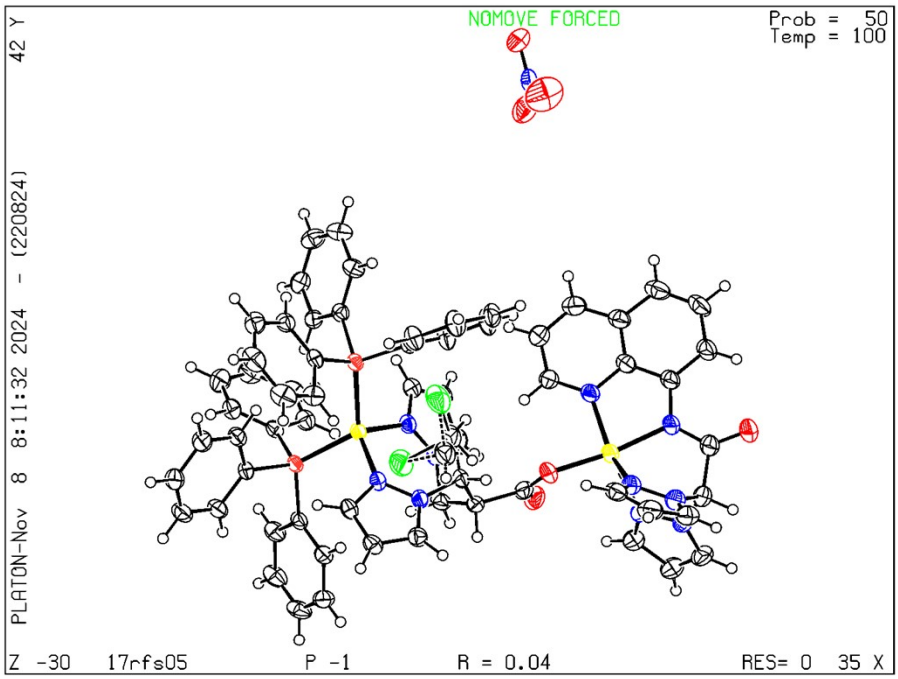
ORTEP of **[(L^{Q}2Pz)Cu(NCMe)]ClO$_4$**.



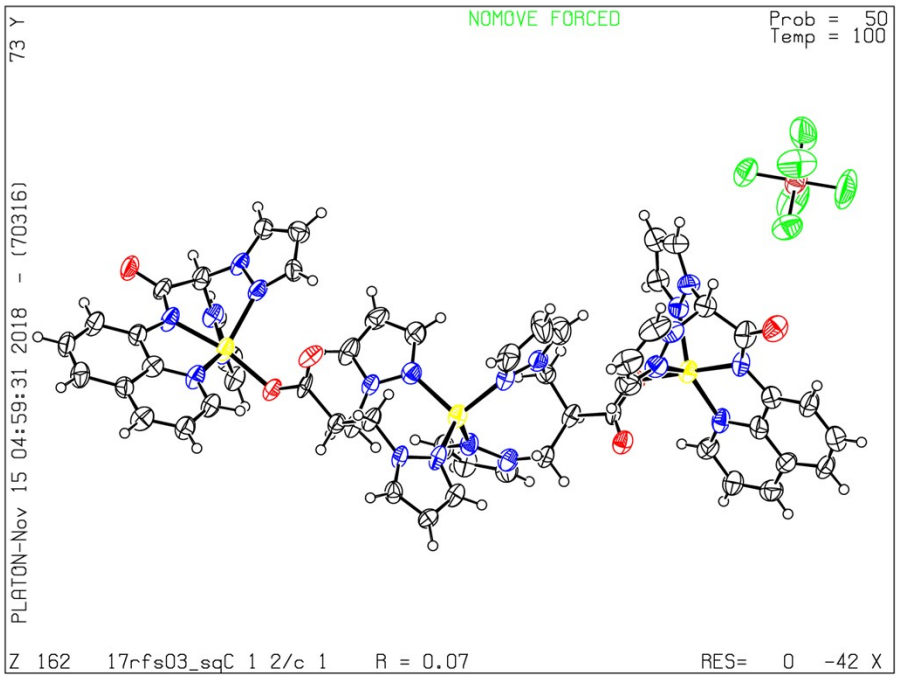
ORTEP of **(L^{Q}2Pz)Cu[O$_2$CCH(pz)$_2$]**.



ORTEP of **$(L^{Q}2Pz)Cu[O_2CCH(CH_2pz)_2]$**.

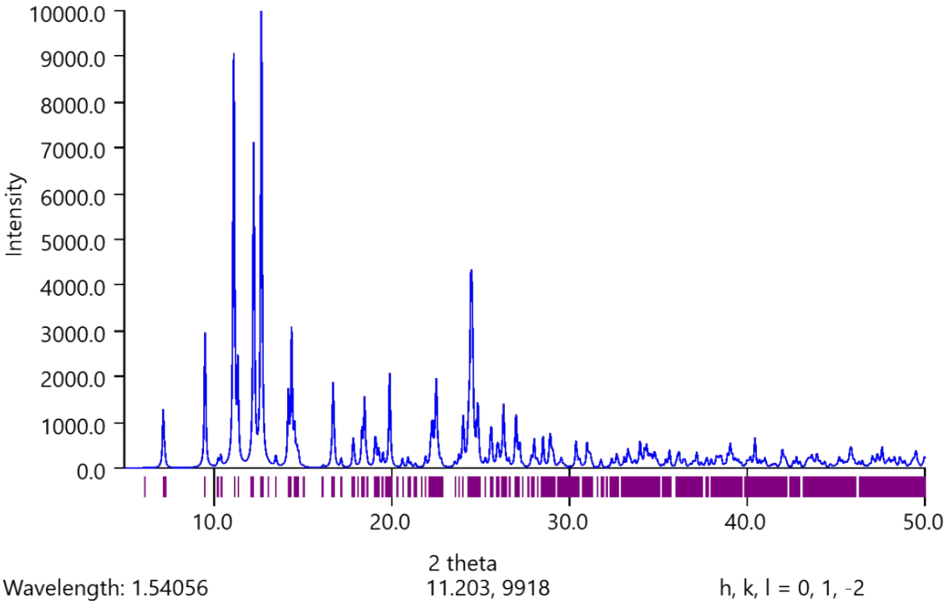


ORTEP of **$\{(L^{Q}2Pz)Cu^{II}[O_2CCH(CH_2pz)_2Cu^{I}(PPh_3)_2]\}NO_3$**.

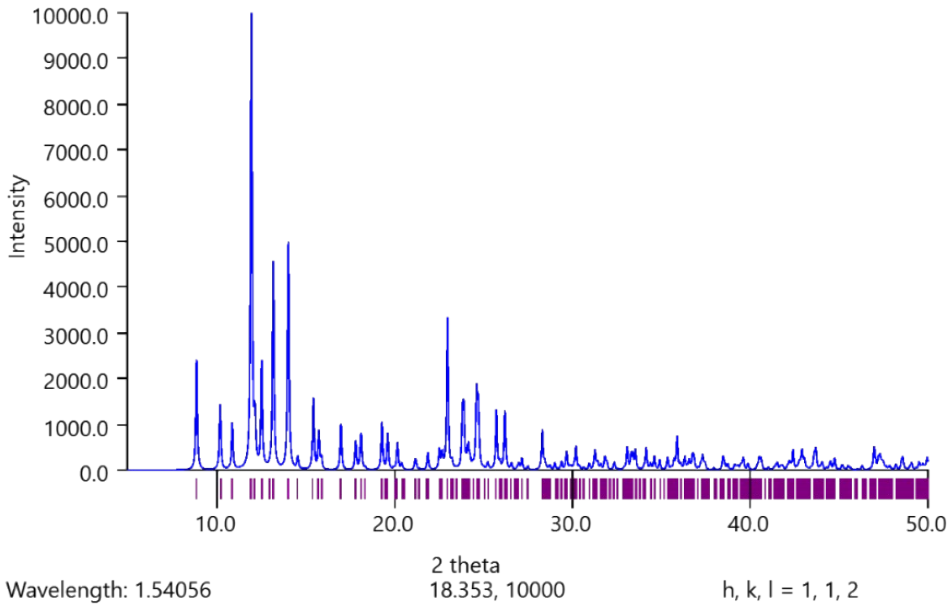


ORTEP of **{(L^{Q}2Pz)Cu^{II}[$O_2CCH(CH_2pz)_2$]}$_2Cu^{I}$}(PF_6)**.

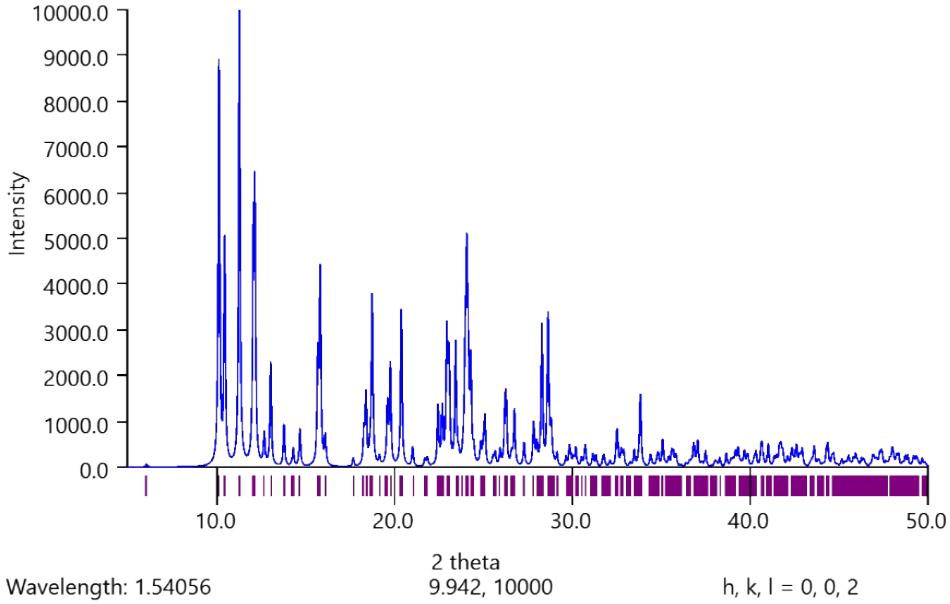
PXRD Figures



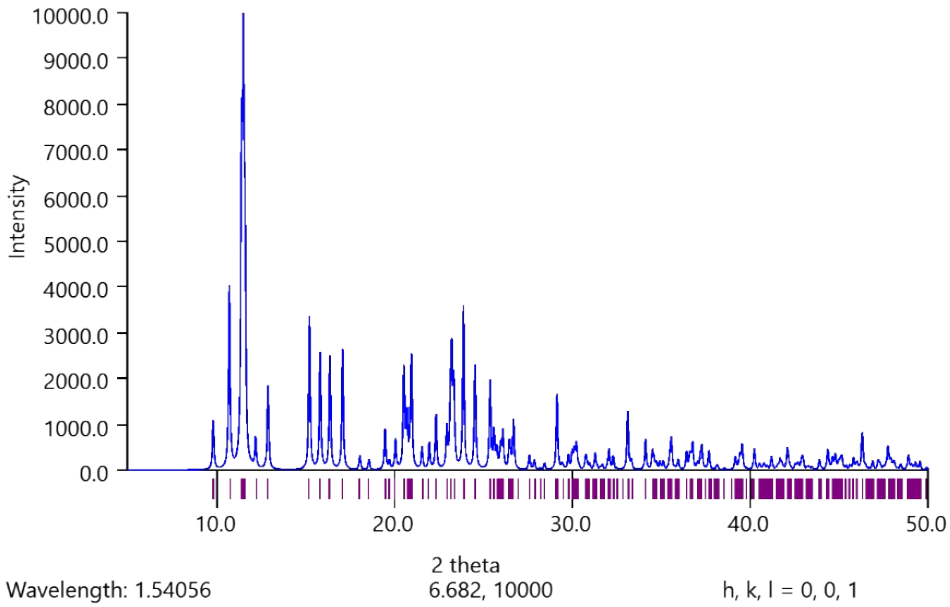
PXRD of **(L^{Q}2Pz)Cu(OAc)**.



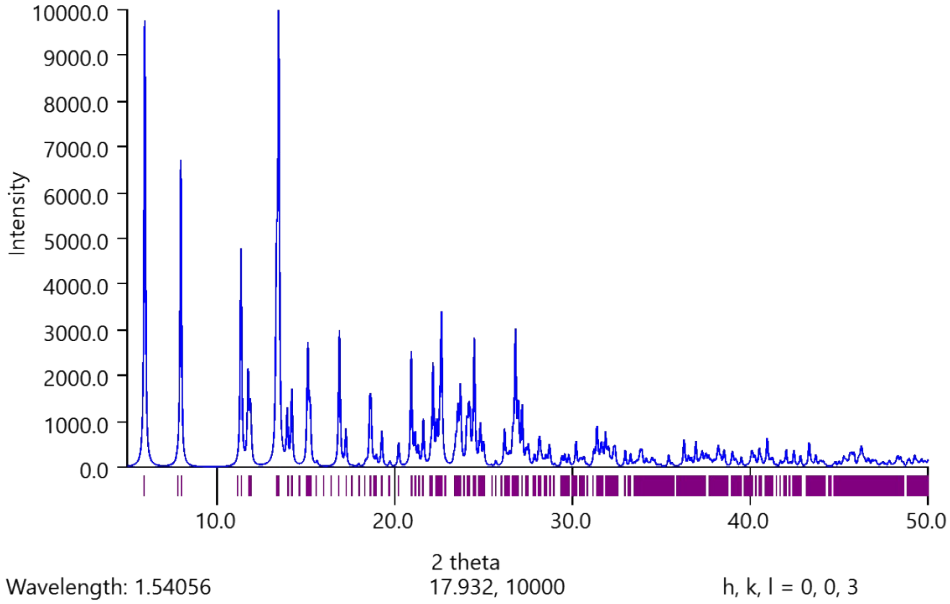
PXRD of **(L^{Q}2Pz)Cu(BF_4)**.



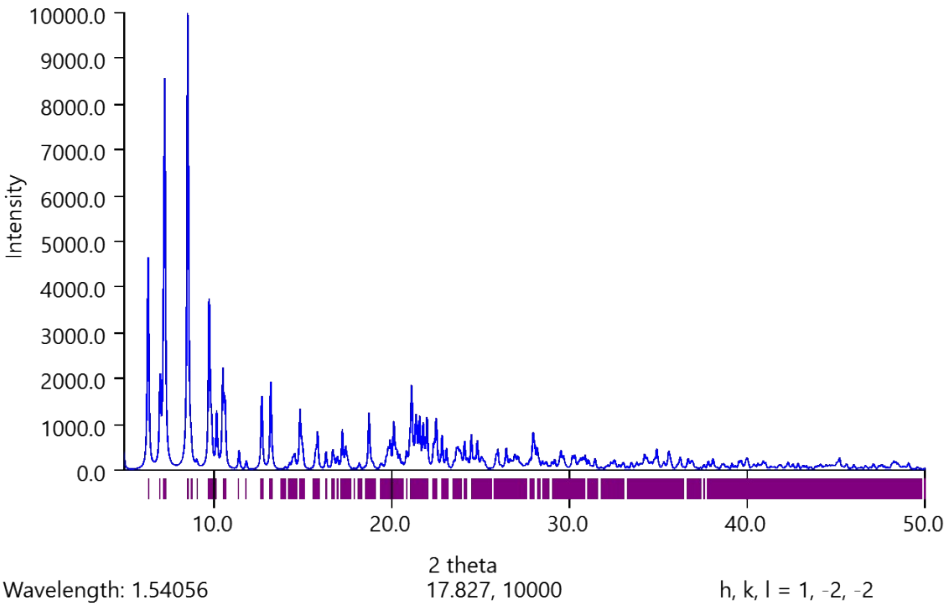
PXRD of **[(L^{Q}2Pz)Cu(NCMe)]ClO_4**.



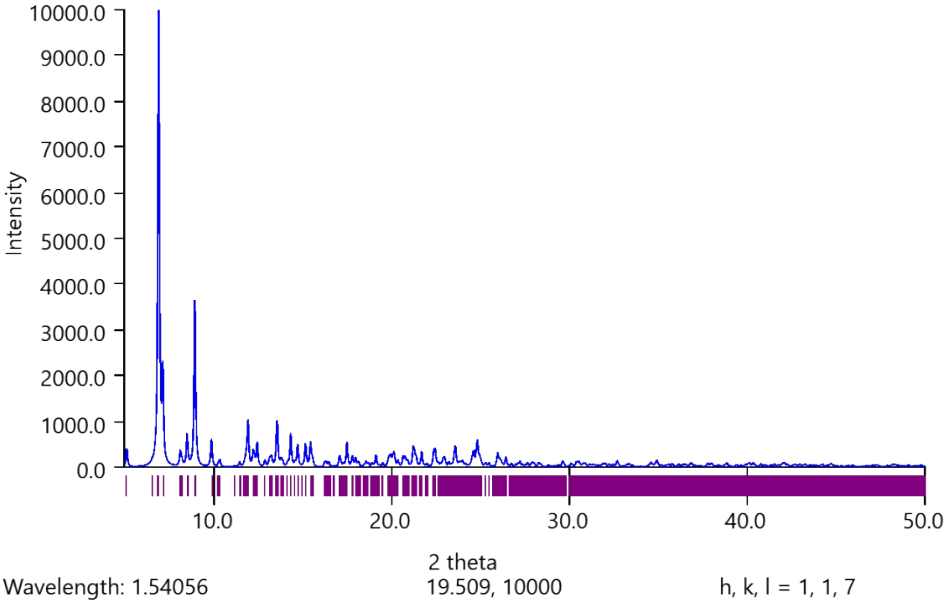
PXRD of **(L^{Q}2Pz)Cu[$O_2CCH(pz)_2$]**.



PXRD of **(L^{Q}2Pz)Cu[$O_2CCH(CH_2pz)_2$]**.



PXRD of **{(L^{Q}2Pz)Cu^{II}[O$_2$CCH(CH$_2$pz)$_2$Cu^{I}(PPh$_3$)$_2$]}NO$_3$.**



PXRD of **{(L^{Q}2Pz)Cu^{II}[O$_2$CCH(CH$_2$pz)$_2$]}$_2$Cu^{I}}(PF$_6$).**