Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Three water-soluble copper(II) *N*-heterocyclic carbene complexes: Toward copper-catalyzed ketone reduction under sustainable conditions

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Table of Contents

Instrumental details

Mass spectra were obtained using a Bruker microTOF-QII High Resolution MS system with an ESI ionization source operating in positive mode. UV/vis spectra were obtained using an OLIS modernized HP 8452 UV/vis spectrophotometer. IR spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR. UV-Vis titrations were carried out for DNA binding studies employing the procedure reported previously. [1,2] NMR spectra were obtained using a Bruker AVANCE III 500 MHz spectrometer at room temperature. ^{1}H chemical shifts are reported vs TMS and are referenced to the residual solvent peaks. An EmStat3 potentiostat (PalmSens Compact Electrochemical Interfaces) was used to acquire cyclic voltammetry data at a glassy carbon working electrode. A three-electrode cell with a graphite auxiliary and a KCl saturated calomel reference (SCE) or Ag wire quasi-reference electrode (Ag QRE) was used in an aqueous electrolyte solution or non-aqueous electrolyte solution, respectively. A concentration of 1.0 mM of ligand **1a**, **2a**, **3a** and complexes **1b**, **2b**, **3b** was used in all experiments. 100 mM of tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte in acetonitrile electrolyte, and a ferrocene/ferrocenium couple was added as an internal reference potential standard. In acetonitrile, the potential was scanned between -1.8 V to 1.5 V vs the Ag QRE starting from the open circuit potential OCP. In an aqueous solution ($HClO_4$), the potential was scanned between -0.5 V to 0.5 V vs SCE. The anhydrous acetonitrile solutions were purged with ultra-high purity (UHP) Ar for at least 20 min prior to the electrochemical measurements and Ar was passed over the solution during CV collection. All data were acquired at room temperature. The aqueous CV potentials are reported versus the normal hydrogen electrode (NHE).

The X-ray intensity data was measured at low temperature (T = 100 K), using a three circles goniometer, platform with a fixed Kappa angle at = 54.74 deg Bruker AXS D8 Venture, equipped with a Photon 100 CMOS active pixel sensor detector. A monochromatized copper X-ray radiation (λ = 1.54178 Å) was selected for the measurement. The structure was solved in a centrosymmetric monoclinic unit cell; Space group: P 1 2(1)/n 1, with Z = 4 for the formula unit, $C_{24}H_{26}CuF_6N_5O_3P$. Crystal data and structure refinement details for the complexes **2b** has been reported.[3] X-ray data for **1b** and **3b** are listed in Supplementary Information section Crystal Structure report for **1b** and **3b**. CCDC 2263164 and 2263165 have been deposited for complexes **1b** and **3b**, respectively. Further supplementary crystallographic data for these complexes can be found in the supporting information sections of this paper (cf. Tables SI1b1-SI1b8 for **1b** and Tables SI3b1-3b8 for **3b**). The GC-MS was recorded in a Shimadzu QP-2010S GC-MS and the LC data was recorded in an Agilent HPLC 1200 Series equipped with Chiralpak IB N-5 (4.6x250mm, 5mic) analytical column. The molecular structures of compounds **1b**, **2b** and **3b** were determined unambiguously by measuring X-ray intensity data at low temperature (T = 100 K), using a three-circle goniometer platform with a fixed Kappa angle at = 54.74 deg Bruker AXS D8 Venture, equipped with a Photon 100 CMOS active pixel sensor detector. Monochromatized copper X-ray radiation (λ = 1.54178 Å) was selected for the measurement.

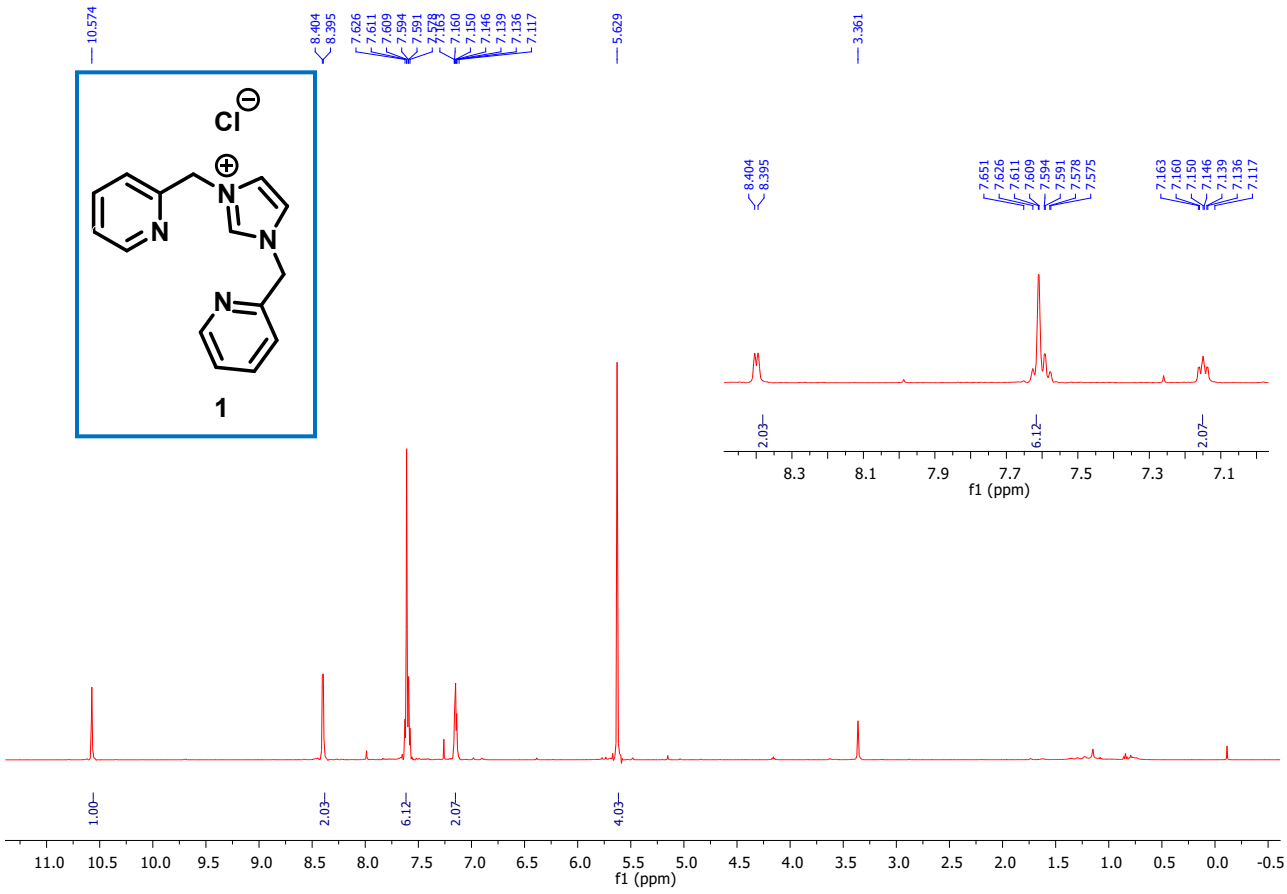


Figure S1: ^{1}H NMR of compound **1**.

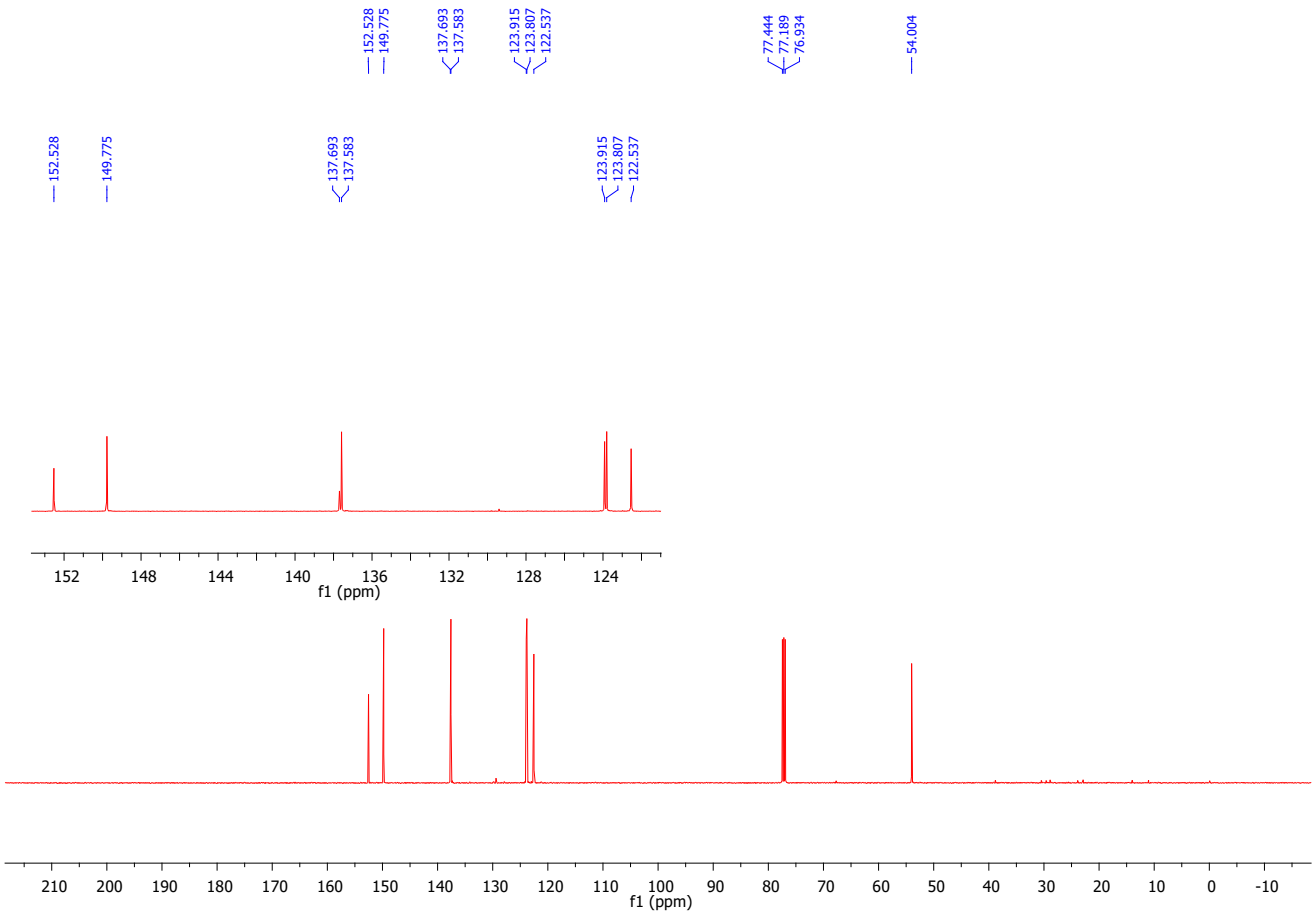


Figure S2: ^{13}C NMR of compound **1**.

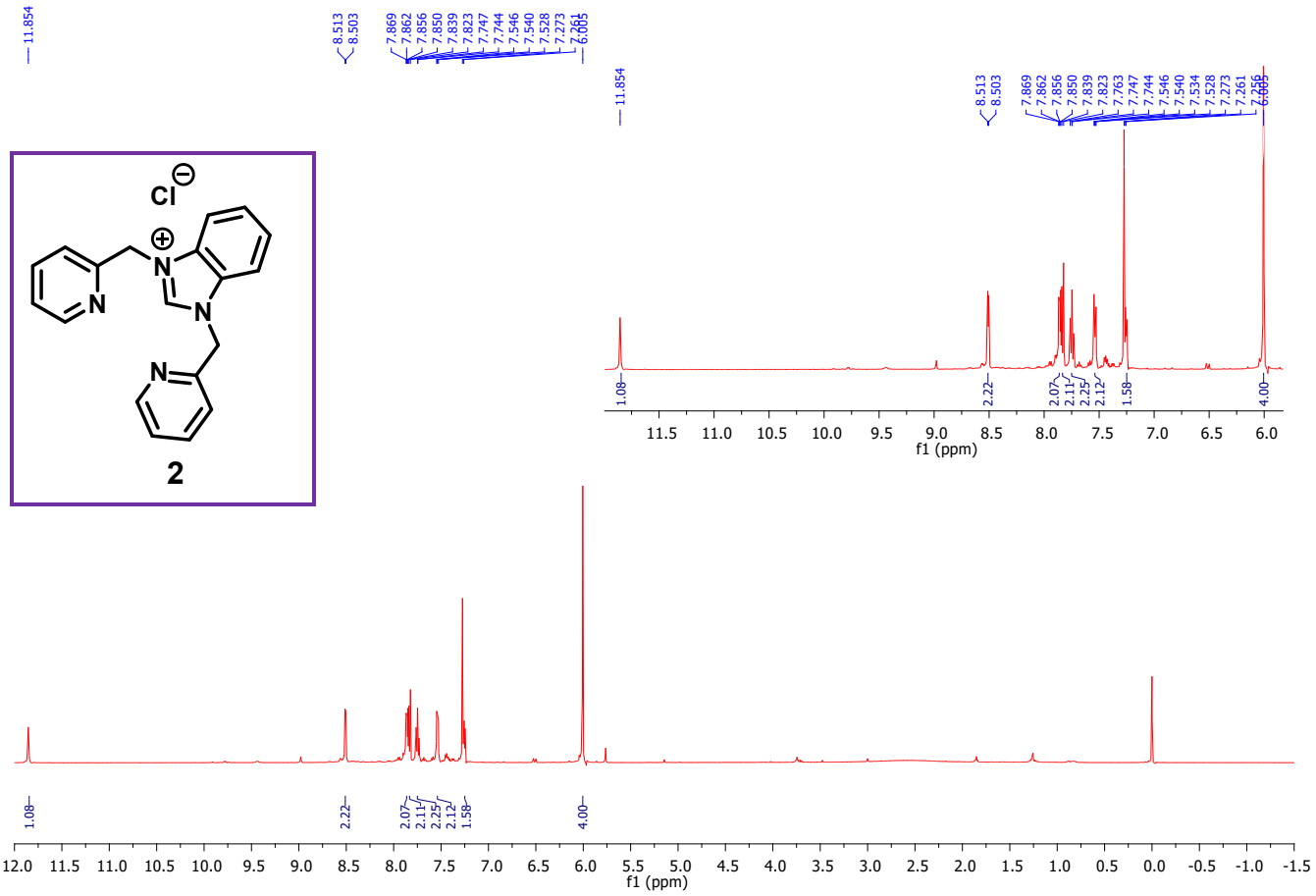


Figure S3: ^{1}H NMR of compound **2**.

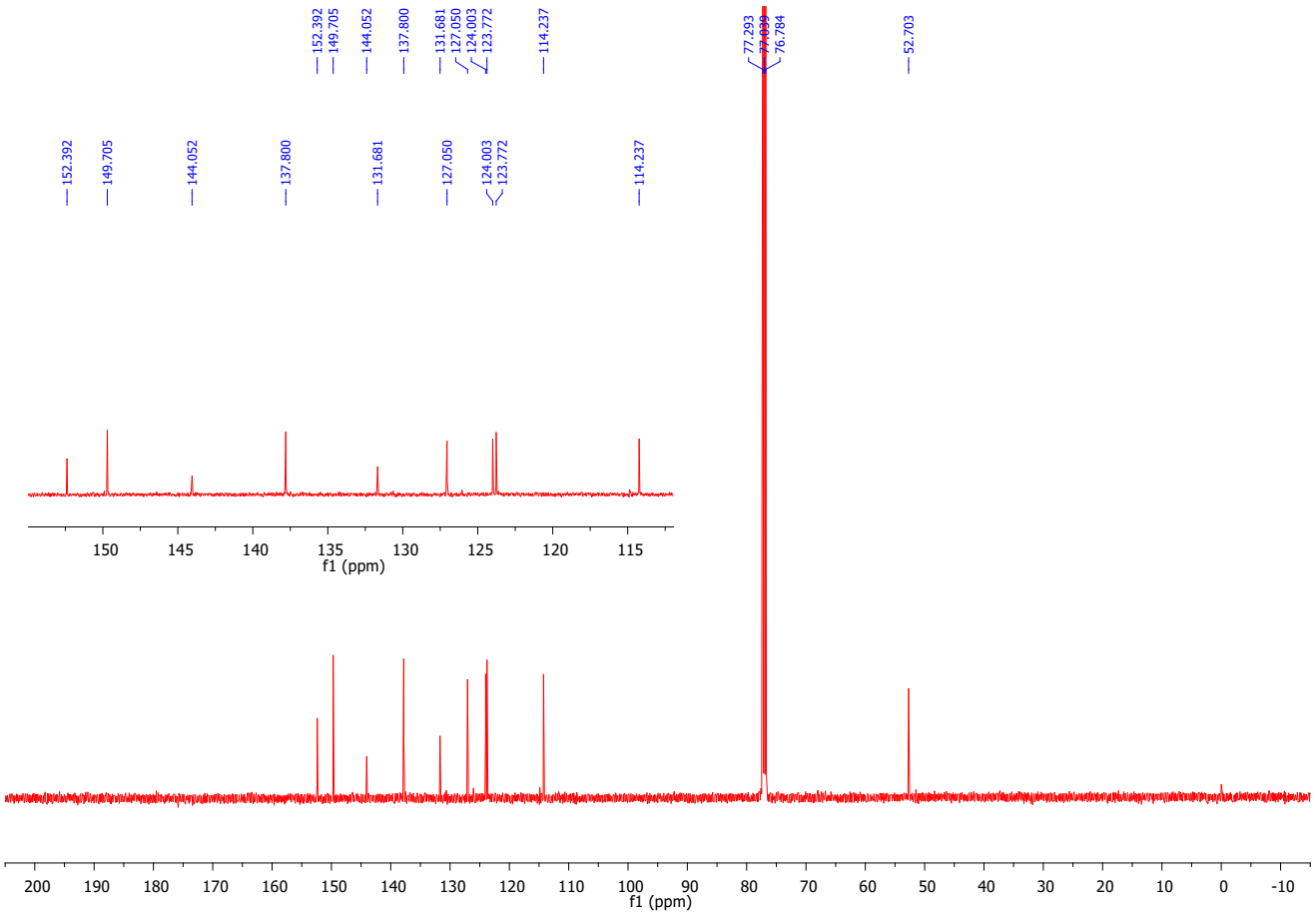


Figure S4: ^{13}C NMR of compound **2**.

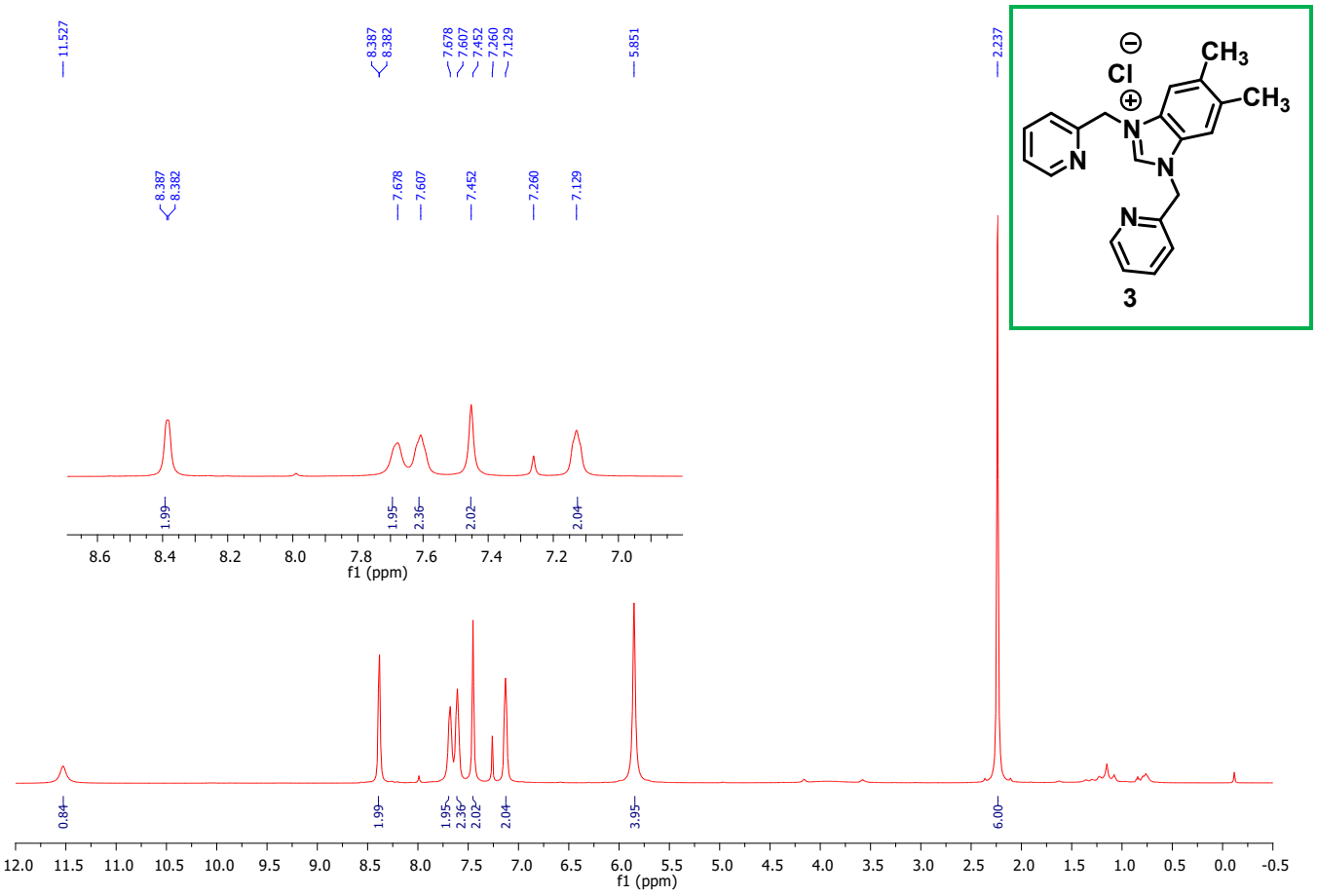


Figure S5: ^{1}H NMR of compound **3**.

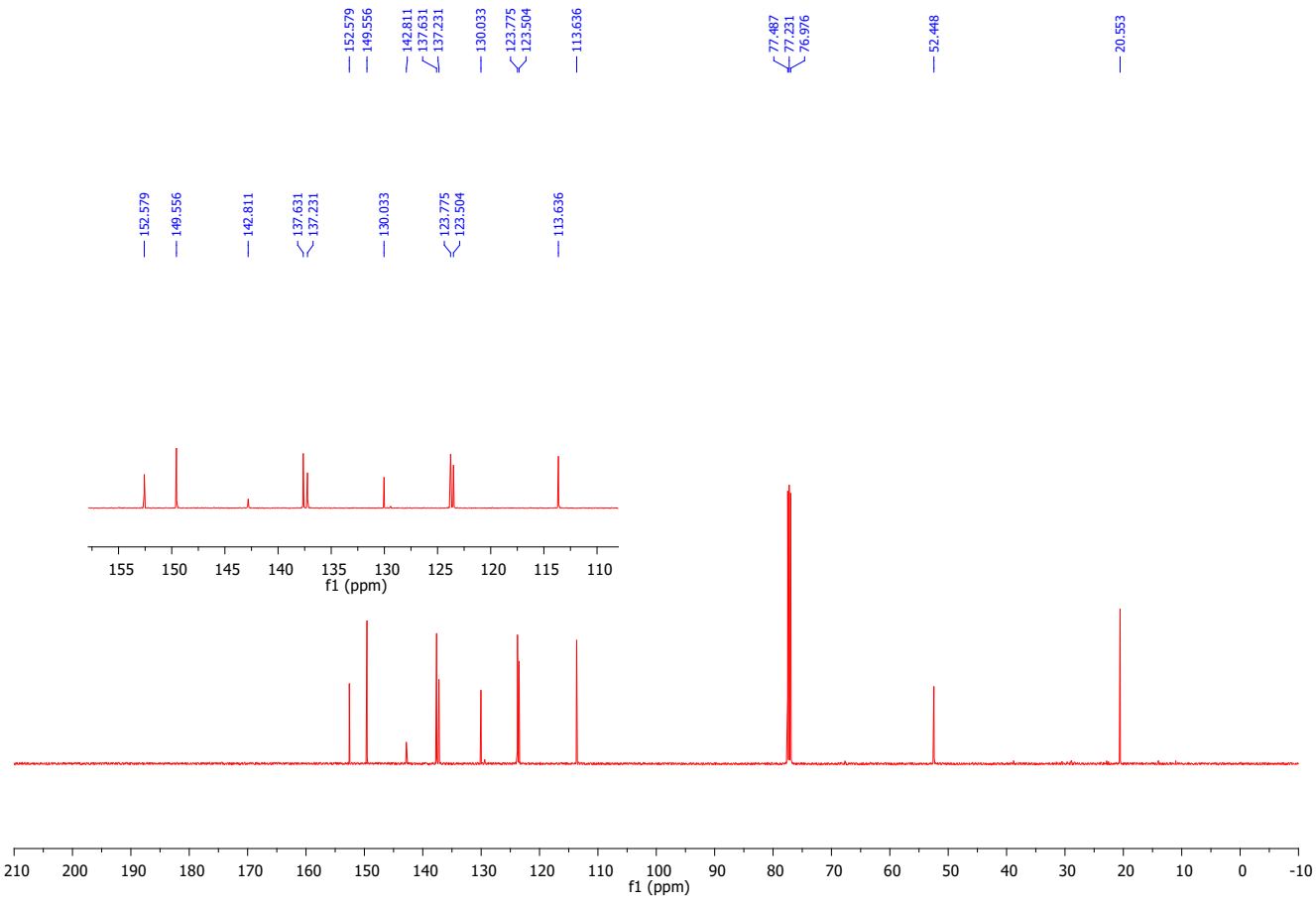


Figure S6: ^{13}C NMR of compound **3**.

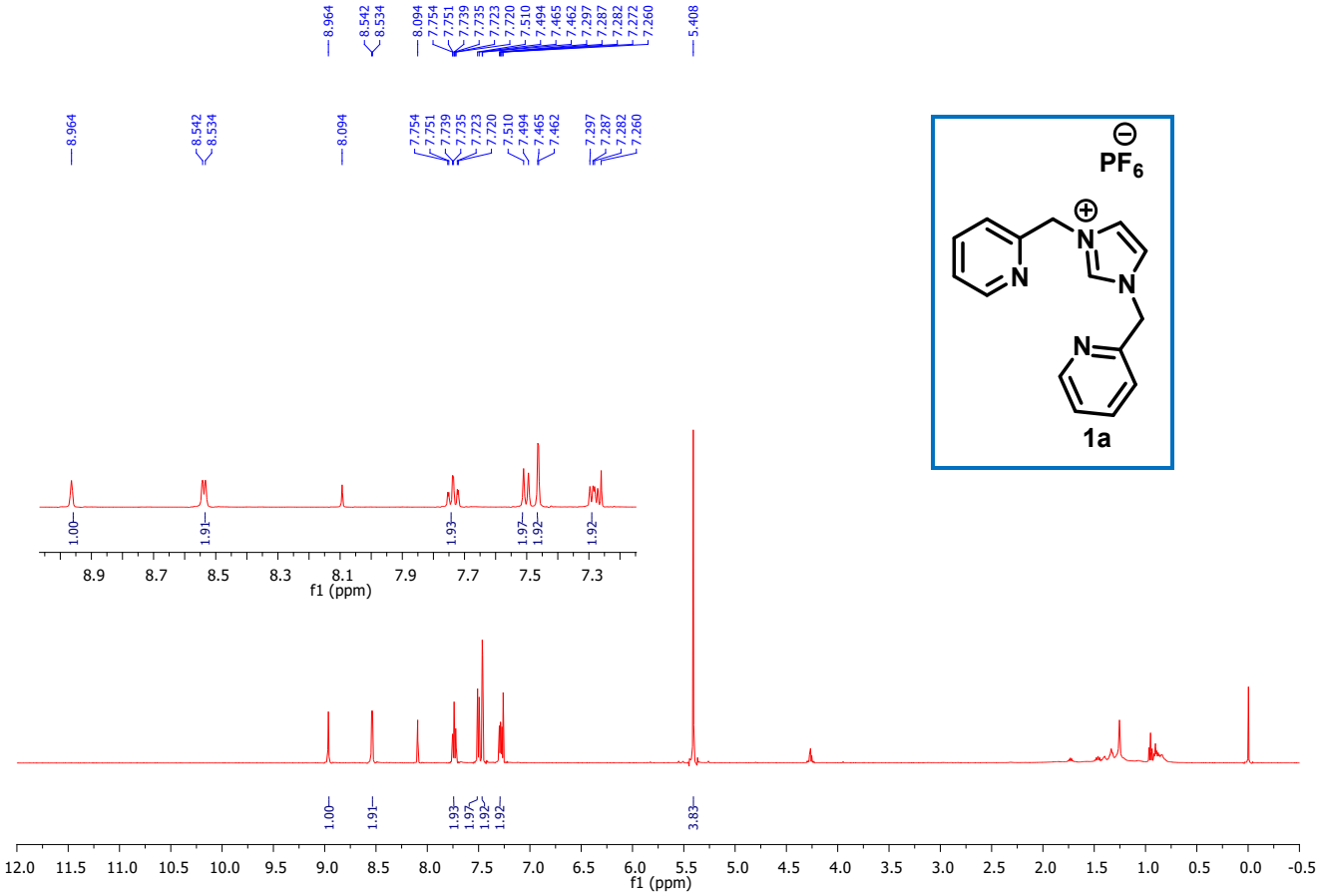


Figure S7: ^{1}H NMR of compound **1a**

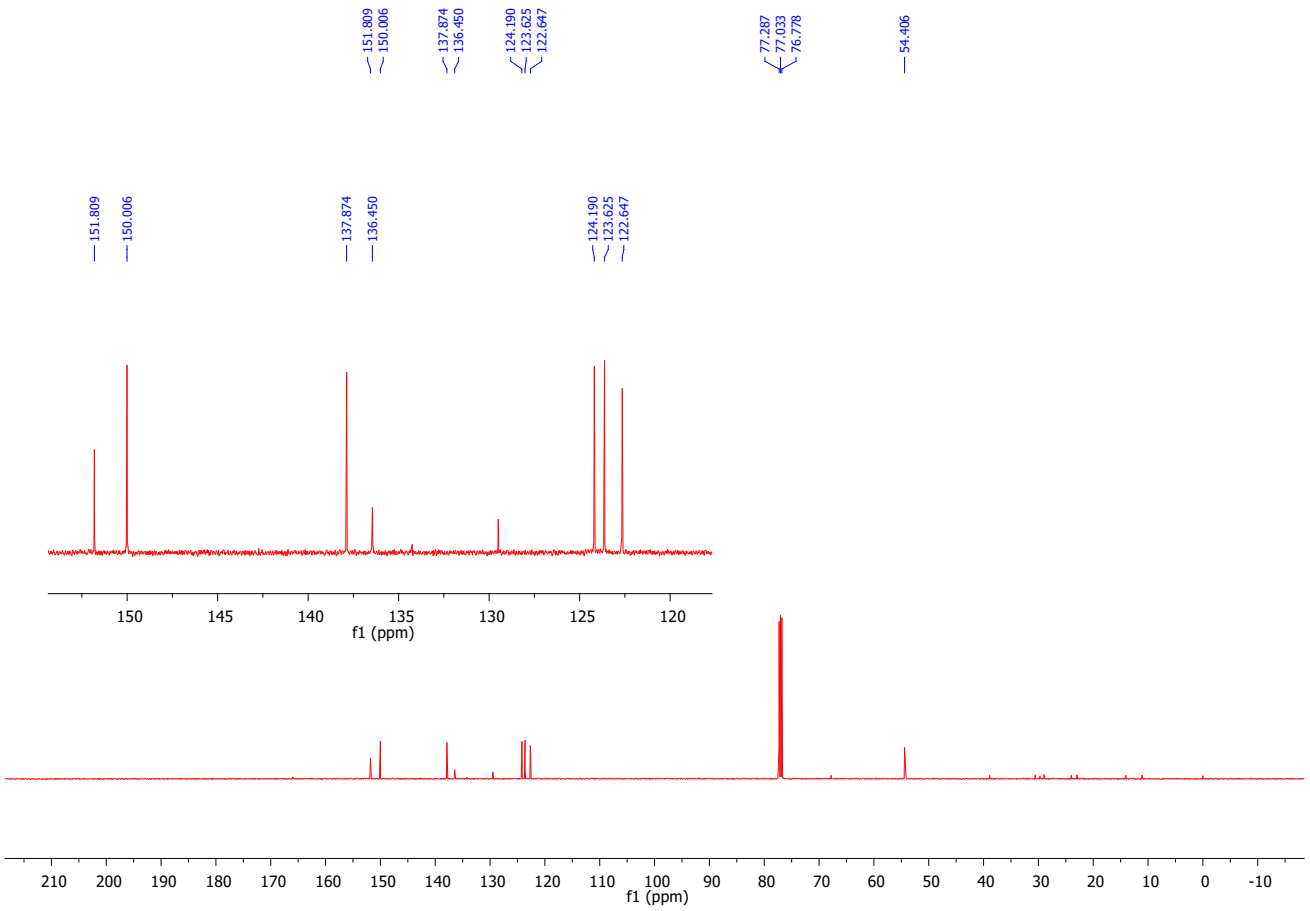


Figure S8: ^{13}C NMR of compound **1a**

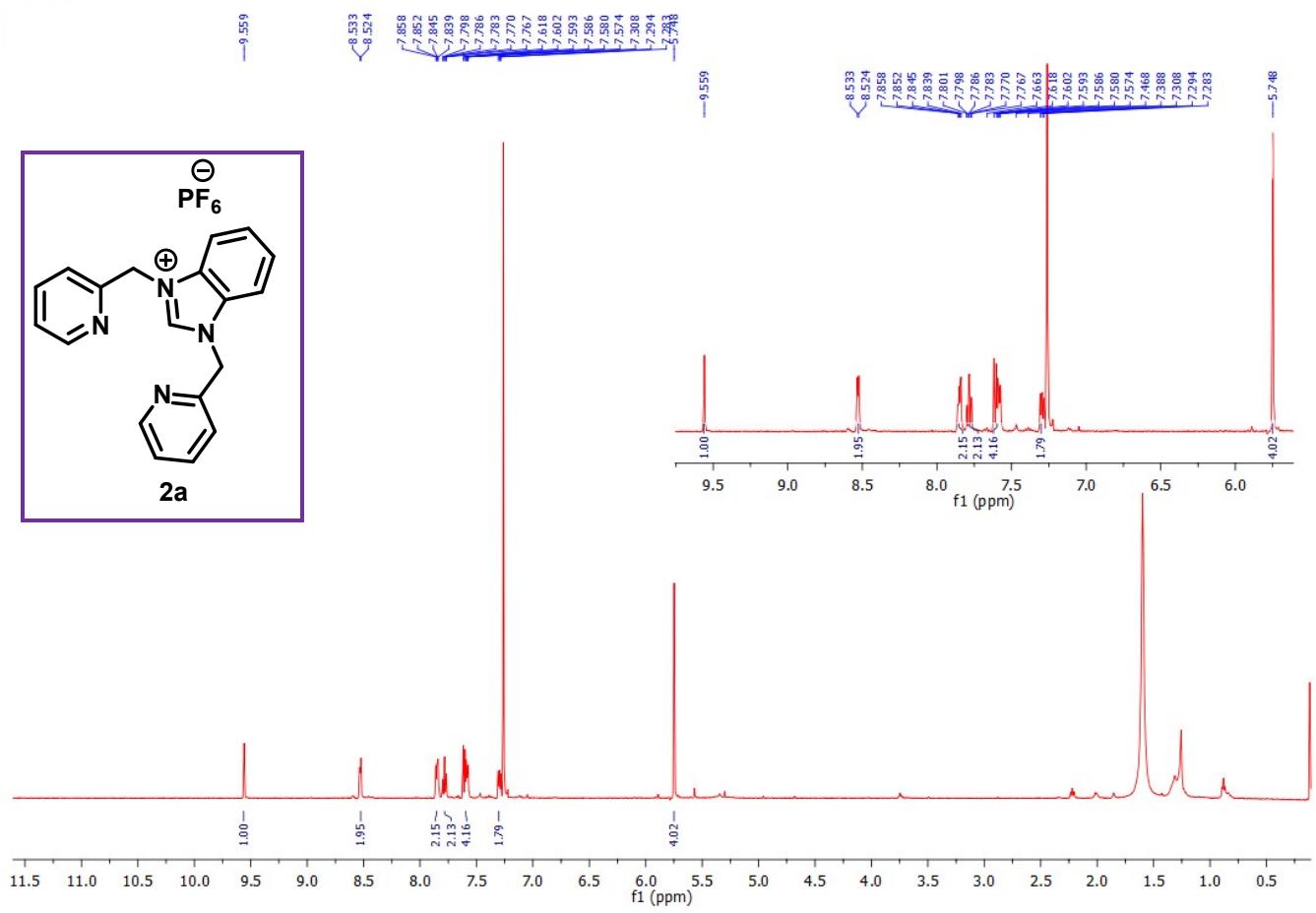


Figure S9: ^{1}H NMR of compound **2a**

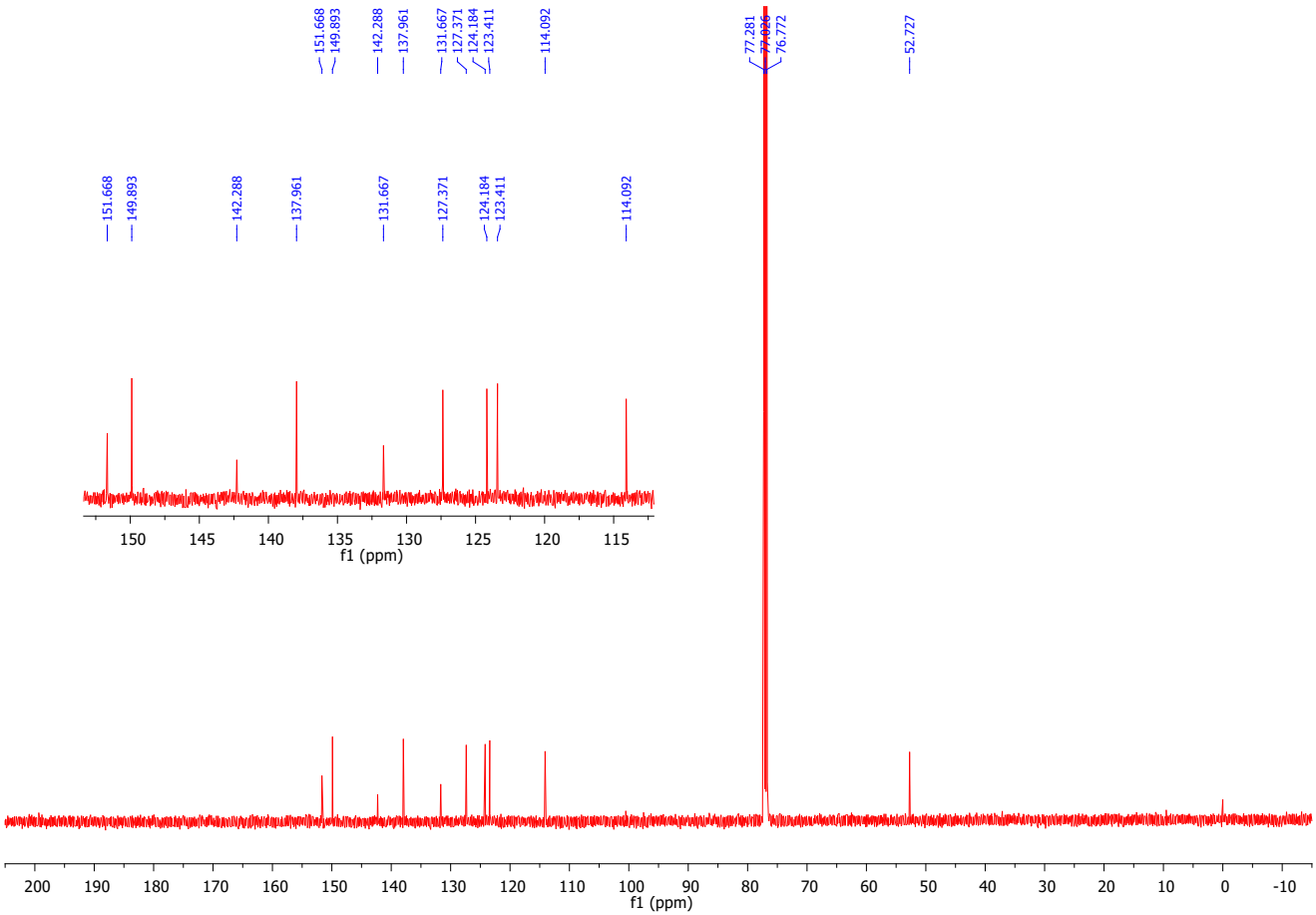


Figure S10: ^{13}C NMR of compound **2a**

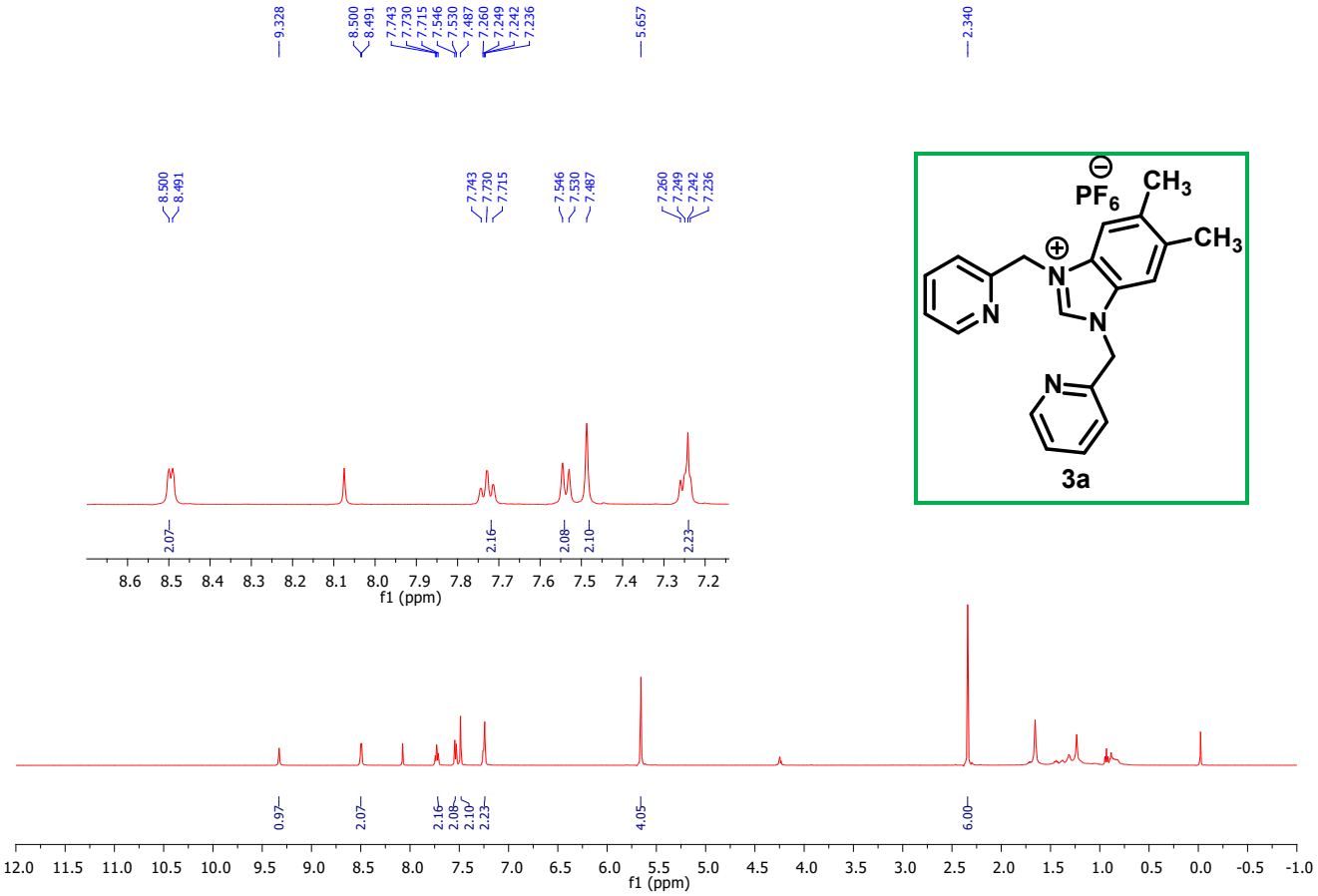


Figure S11: ^{1}H NMR of compound **3a**

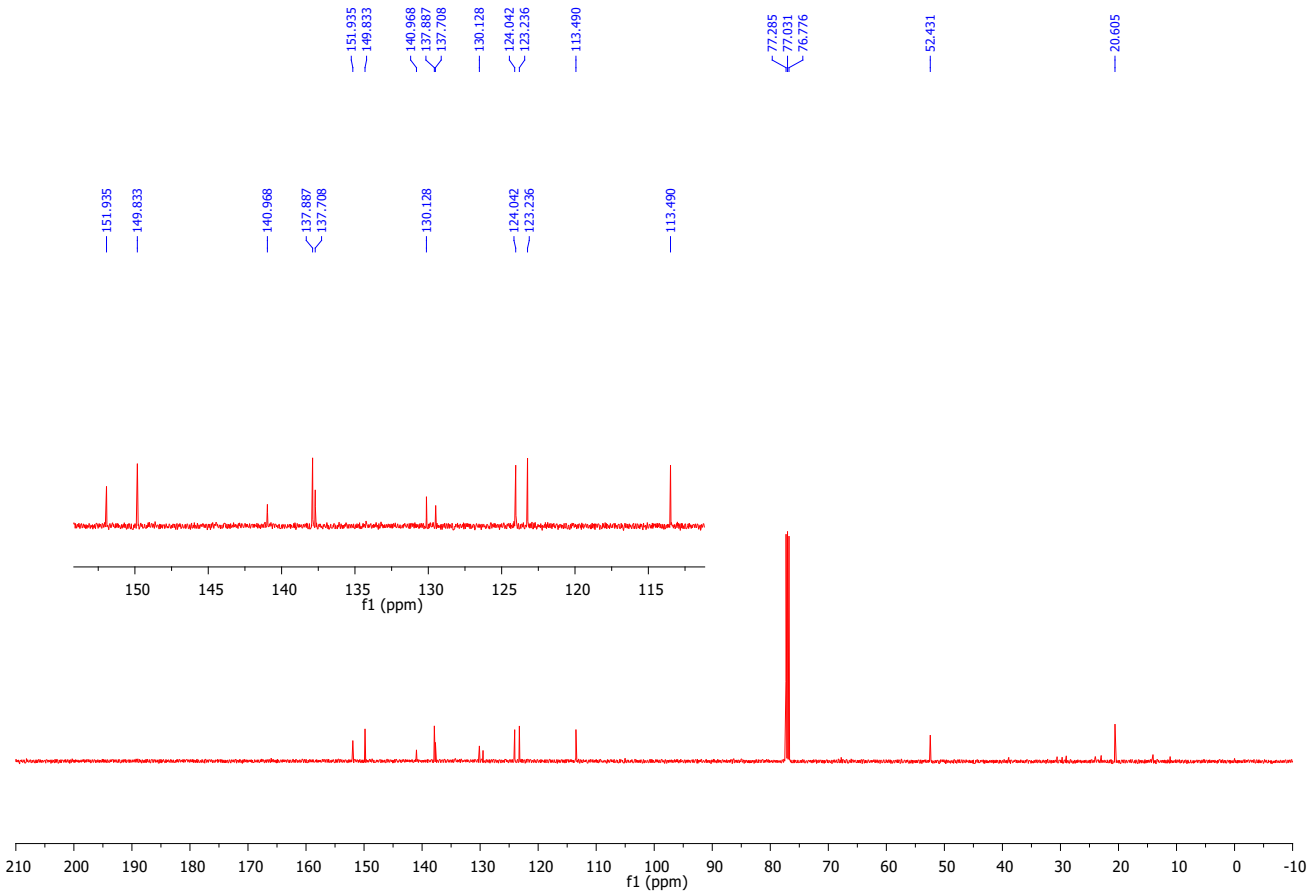


Figure S12: ^{13}C NMR of compound **3a**

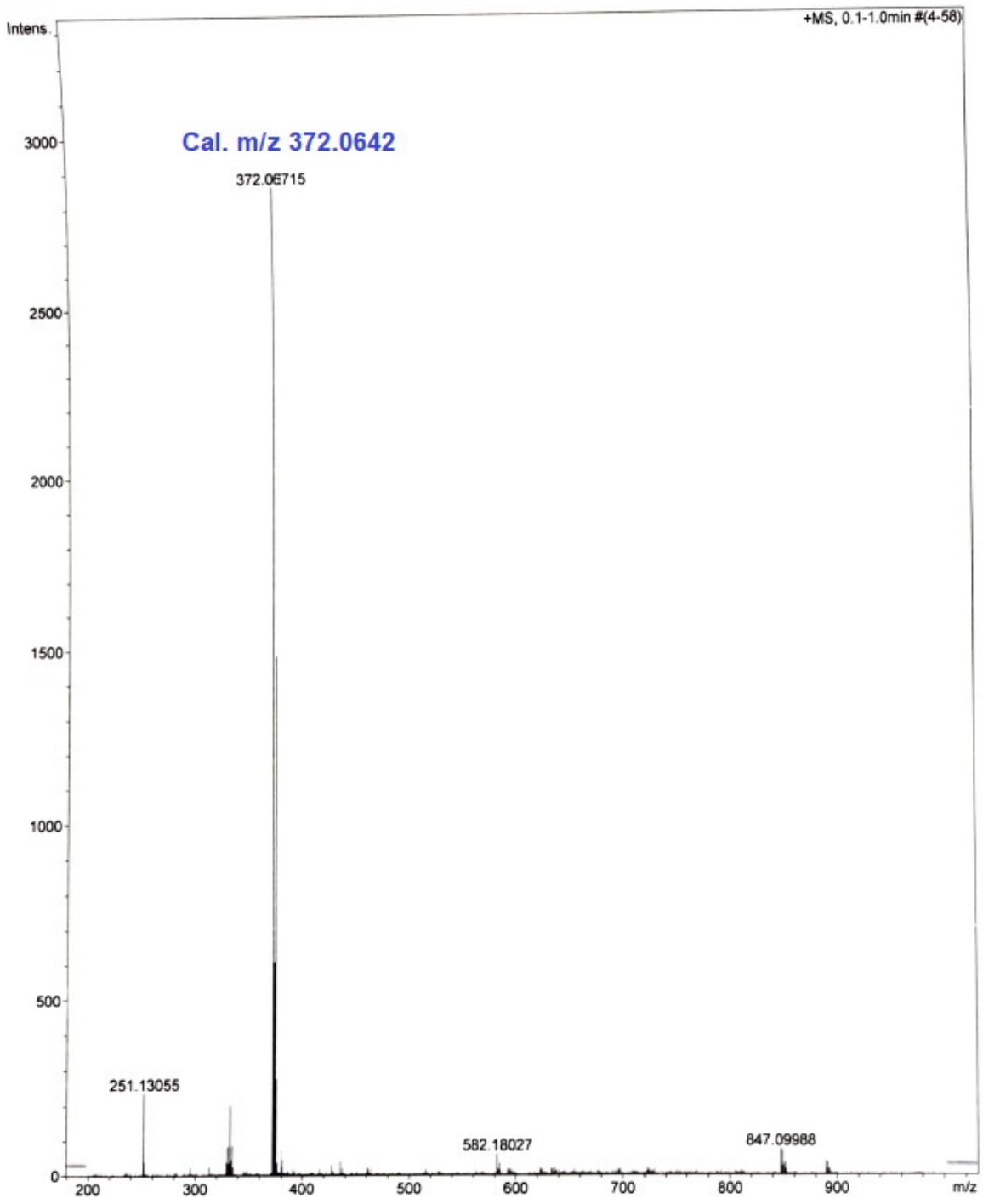


Figure S13: ESI-MS of complex **1b** in CH_3CN solution (TNHC1= tridentate ligand **1** moiety).

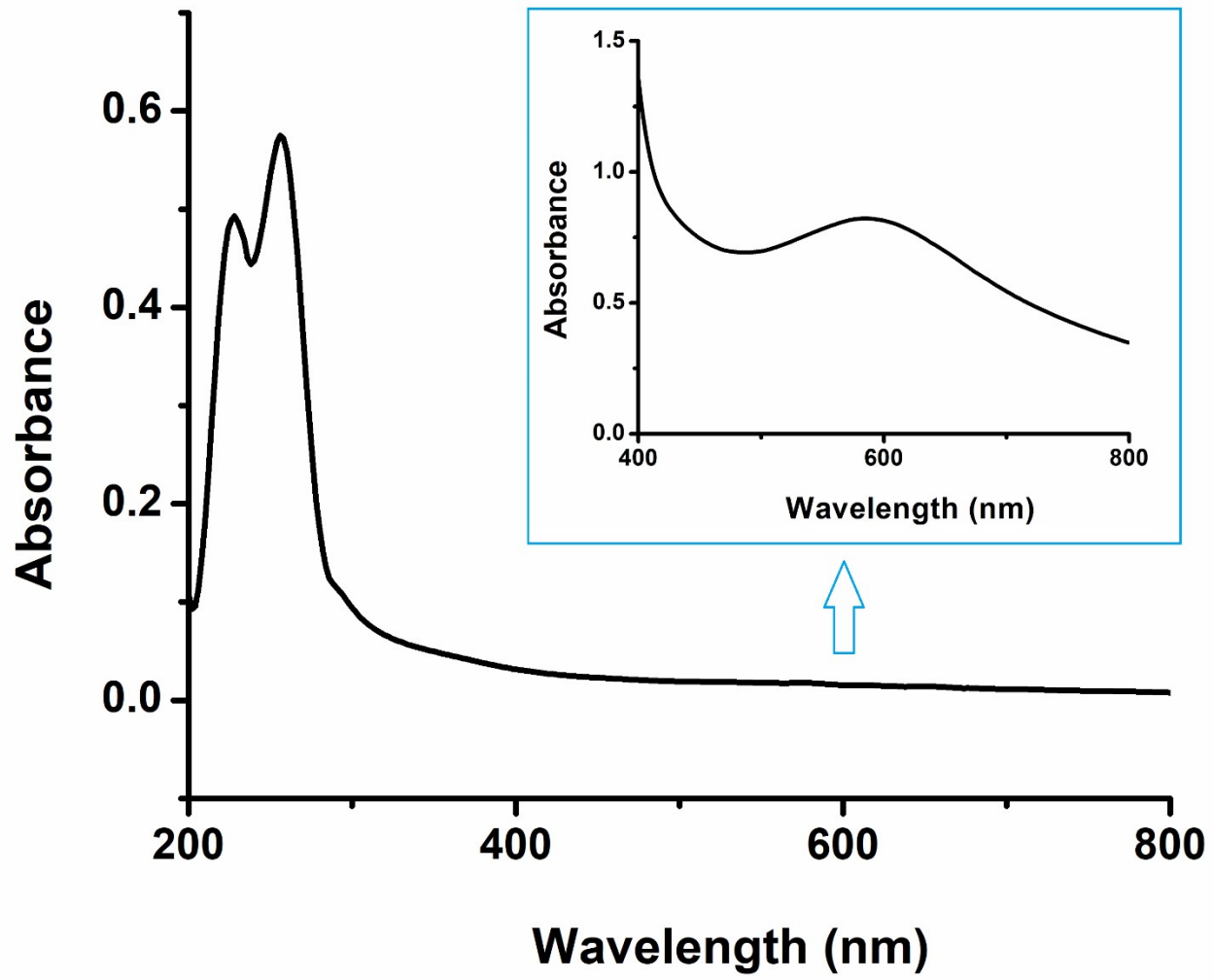


Figure S14: UV–Vis absorption spectra of complex **1b** in CH_3CN. (conc: 5×10^{-5} M; Inset conc: 5×10^{-3} M).

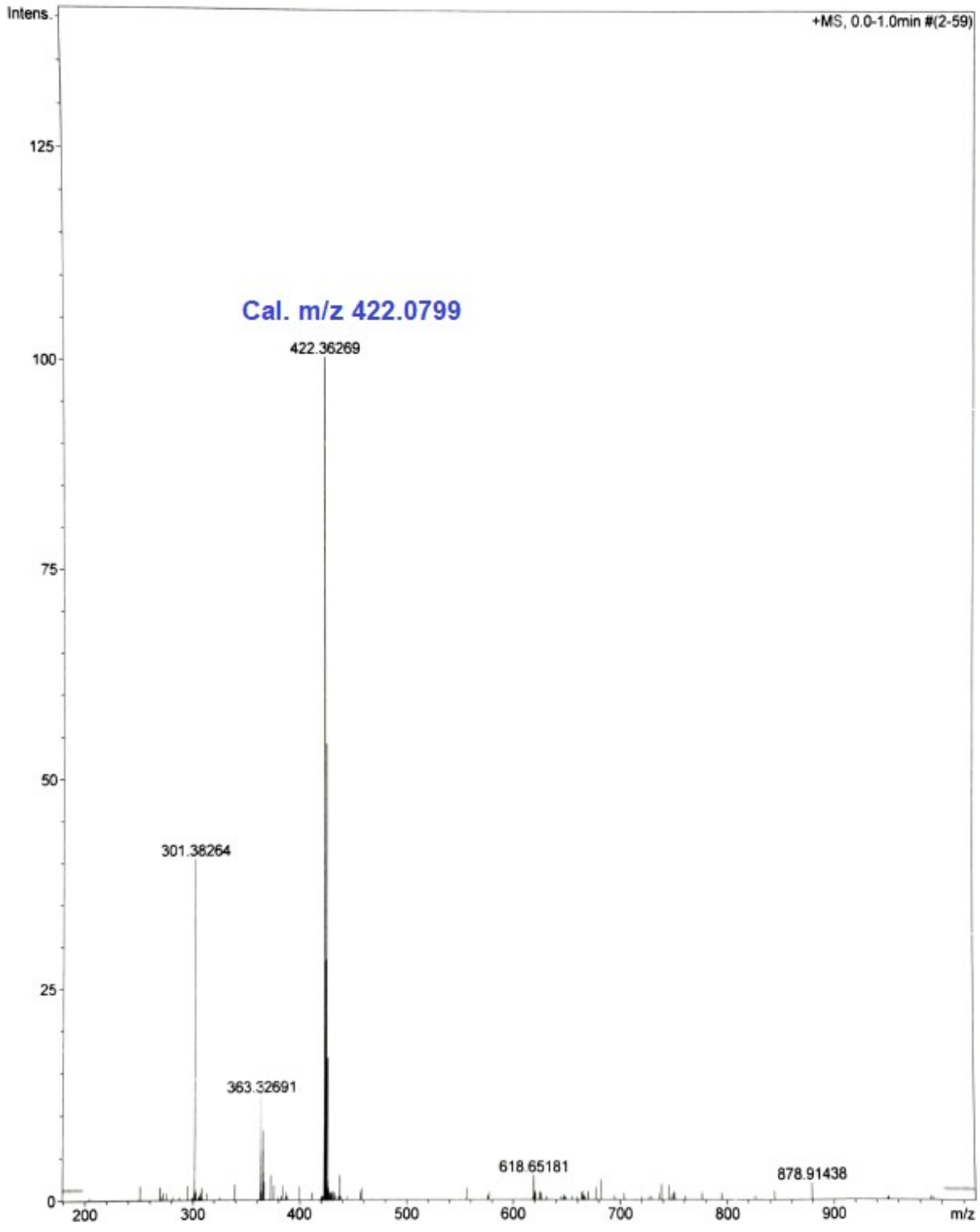


Figure S15: ESI-MS of complex **2b** in CH_3CN solution (TNHC2= tridentate ligand **2** moiety).

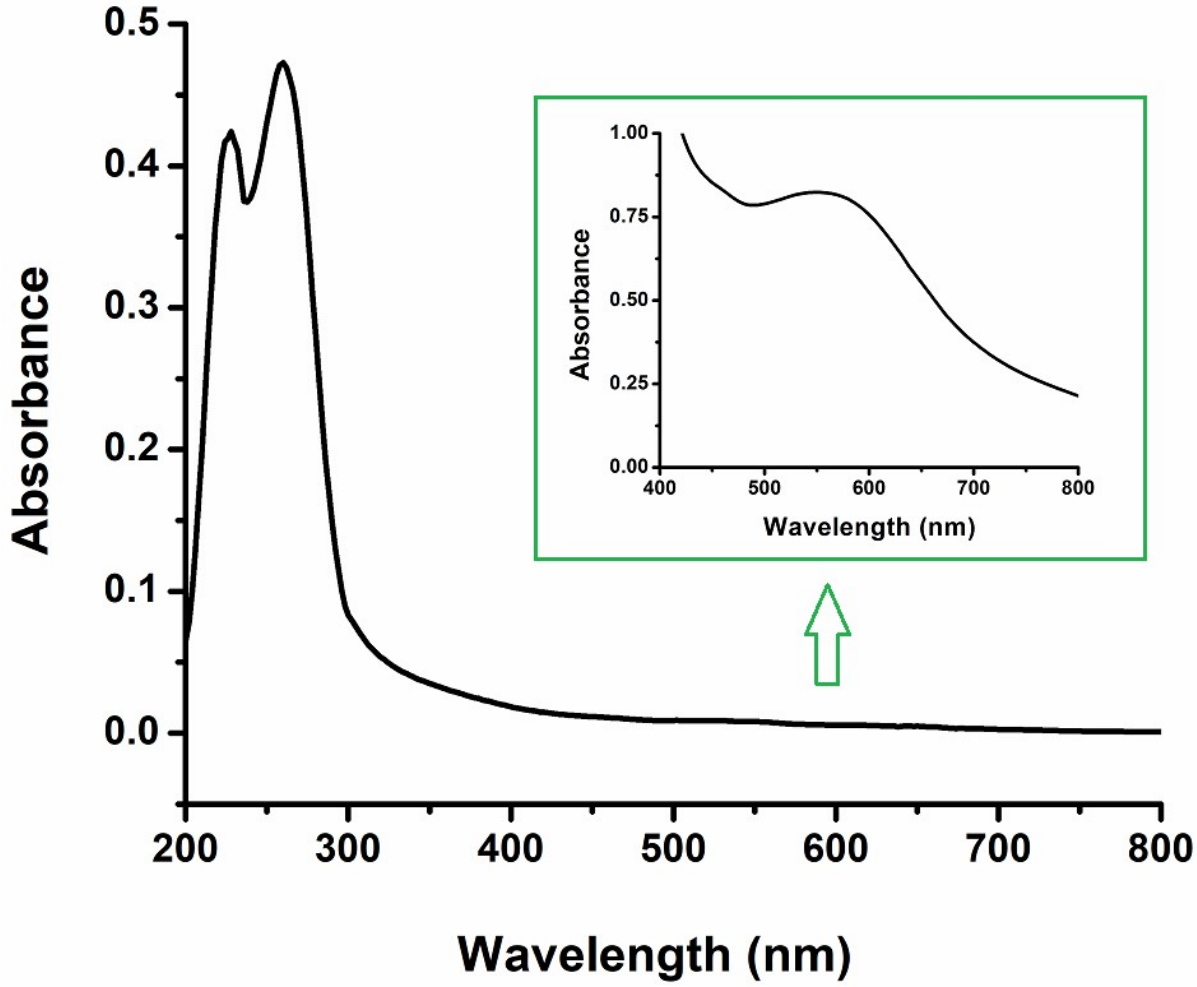


Figure S16: UV–Vis absorption spectra of complex **2b** in CH_3CN. (conc: 5×10^{-5} M; Inset conc: 5×10^{-3} M).

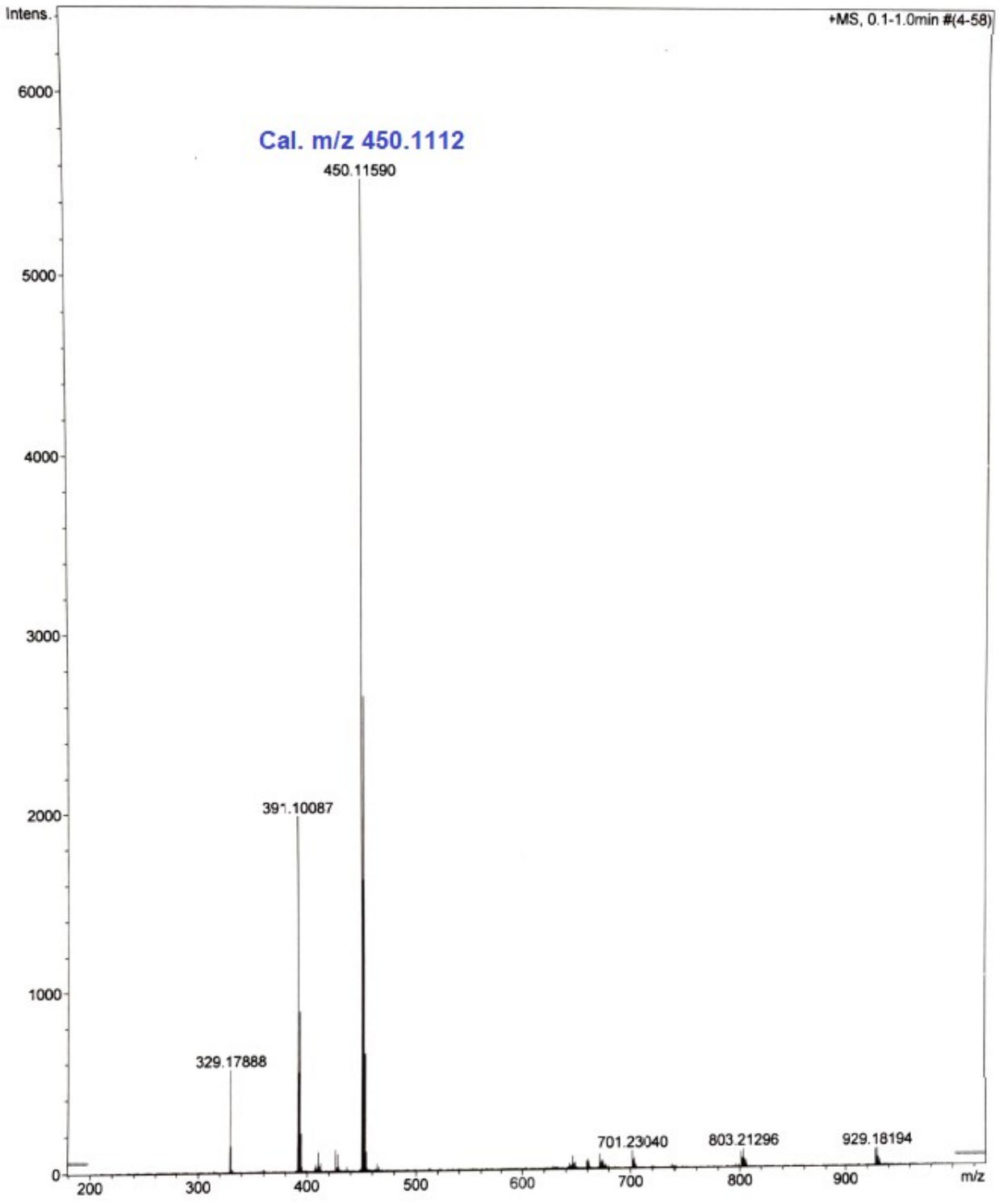


Figure S17: ESI-MS of complex **3b** in CH_3CN solution (TNHC3= tridentate ligand **3** moiety).

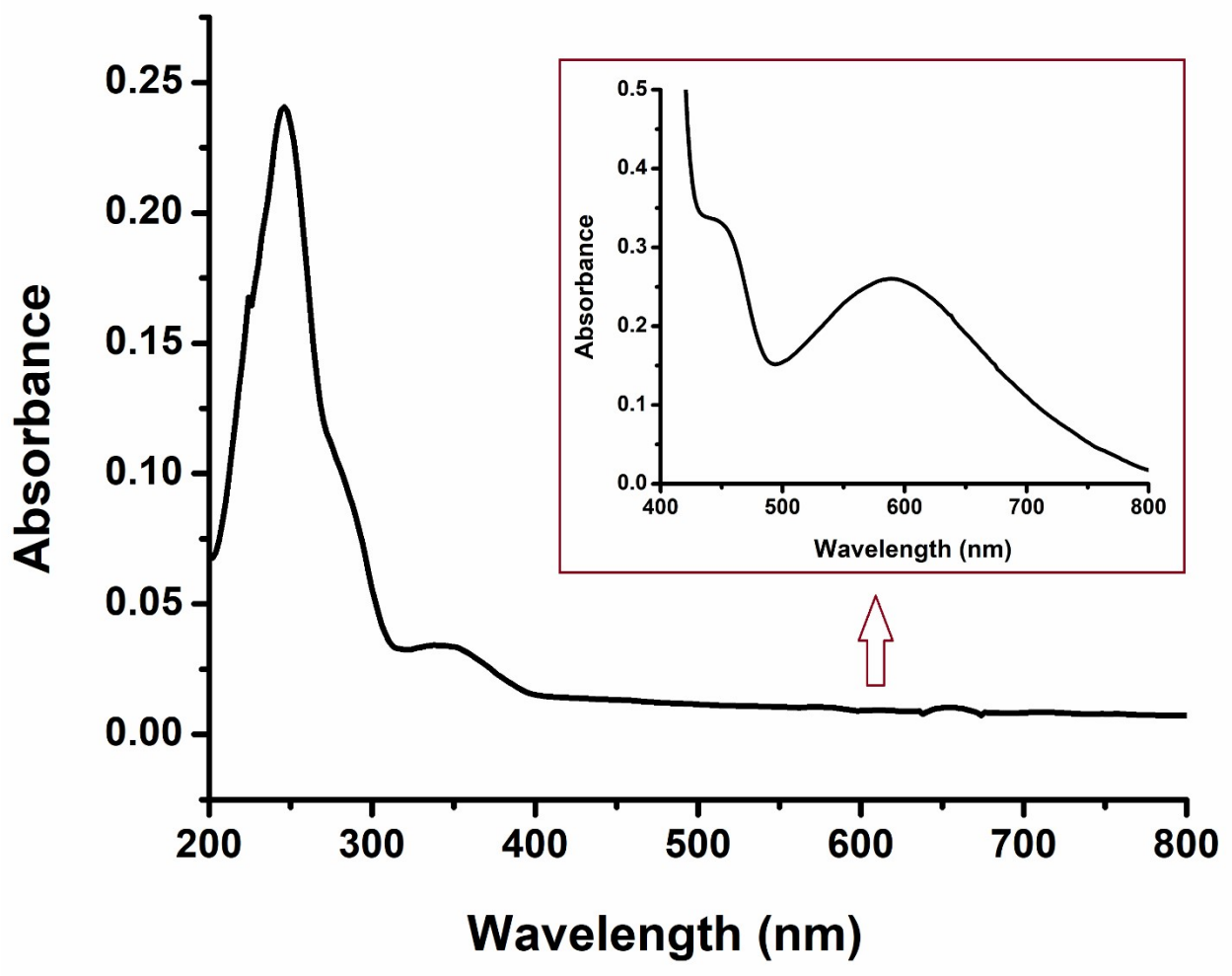


Figure S18: UV–Vis absorption spectra of complex **3b** in CH_3CN. (conc: 5×10^{-5} M; Inset conc: 5×10^{-3} M).

Crystal Structure Report for 1b

A green platelet like single crystal of $C_{17}H_{17}CuF_6N_4O_2P$, approximate dimensions (0.022 x 0.043 x 0.080) mm^3, was selected for the X-ray crystallographic analysis and mounted on a cryoloop using an oil cryoprotectant. The X-ray intensity data was measured at low temperature (T = 100K), using a three circles goniometer Kappa geometry with a fixed Kappa angle at = 54.74 deg Bruker AXS D8 Venture, equipped with a Photon 100 CMOS active pixel sensor detector. A monochromatized Cu X-ray radiation (λ = 1.54178 Å) was selected for the measurement. All frames were integrated with the aid of the Bruker SAINT software[S4] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 23796 reflections to a maximum θ angle of 74.49° (0.80 Å resolution), of which 4057 were independent (average redundancy 5.865, completeness = 99.5%, R_{int} = 8.17%, R_{sig} = 4.72%) and 3172 (78.19%) were greater than 2σ (F^2). The final cell constants of a = 13.0314(3) Å, b = 17.4564(4) Å, c = 9.0216(2) Å, β = 103.6770(14) °, volume = 1994.05(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 1866 reflections above 20 σ (I) with 6.981° < 2θ < 157.6°. Data were corrected for absorption effects using the Multi-Scan method: (SADABS). [5] The ratio of minimum to maximum apparent transmission was 0.832. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7930 and 0.9360. Structure was solved in a monoclinic unit cell; Space group: P 1 2(1)/c 1, with Z = 4 for the formula unit, $C_{17}H_{17}CuF_6N_4O_2P$. Using the Bruker SHELXT Software Package, [6] refinement of the structure was carried out by least squares procedures on weighted F^2 values using the SHELXTL-2018/3 [7] included in the APEX4 v2021, 4.0, AXS Bruker program.[S8] Hydrogen atoms were localized on difference Fourier maps but then introduced in the refinement as fixed contributors in idealized geometry with an isotropic thermal parameters fixed at 20 % higher than those carbons atoms they were connected. The final anisotropic full-matrix least-squares refinement on F^2 with 282 variables converged at R1 = 5.68%, for the observed data and wR2 = 11.26% for all data. The goodness-of-fit: GOF was 1.099. The largest peak in the final difference electron density synthesis was 0.738 $e^-/Å^3$ and the largest hole was -0.403 $e^-/Å^3$ with an RMS deviation of 0.095 $e^-/Å^3$. Based on the final model, the calculated density was 1.725 g/cm^3 and F (000), 1044 e^-. Graphics were performed using softwares: Mercury V.4.2.0: (https://www.ccdc.cam.ac.uk/) and POV-Ray v 3.7: (The Persistence of Vision Raytracer, high quality, Free Software tool).

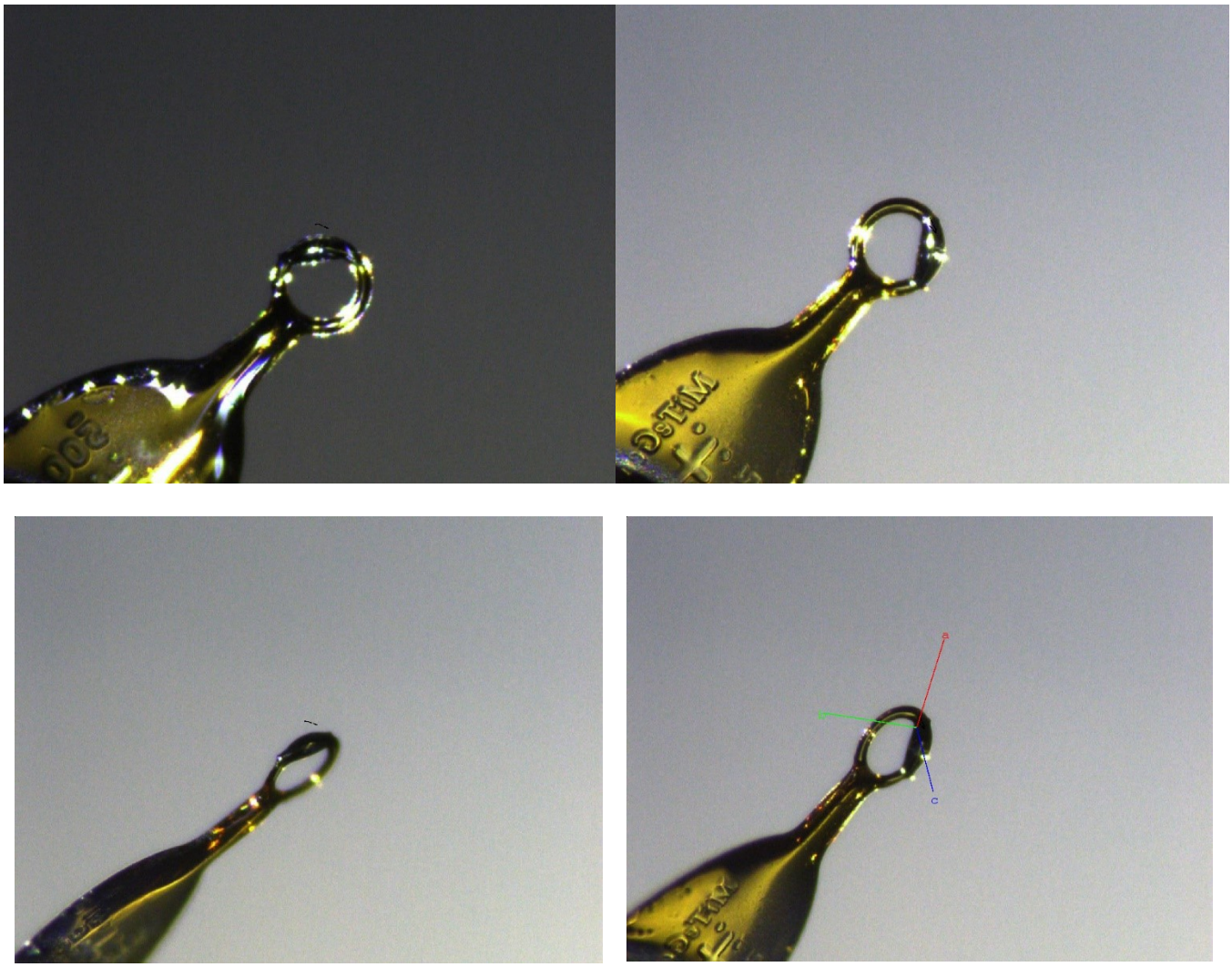


Figure - Crystal views

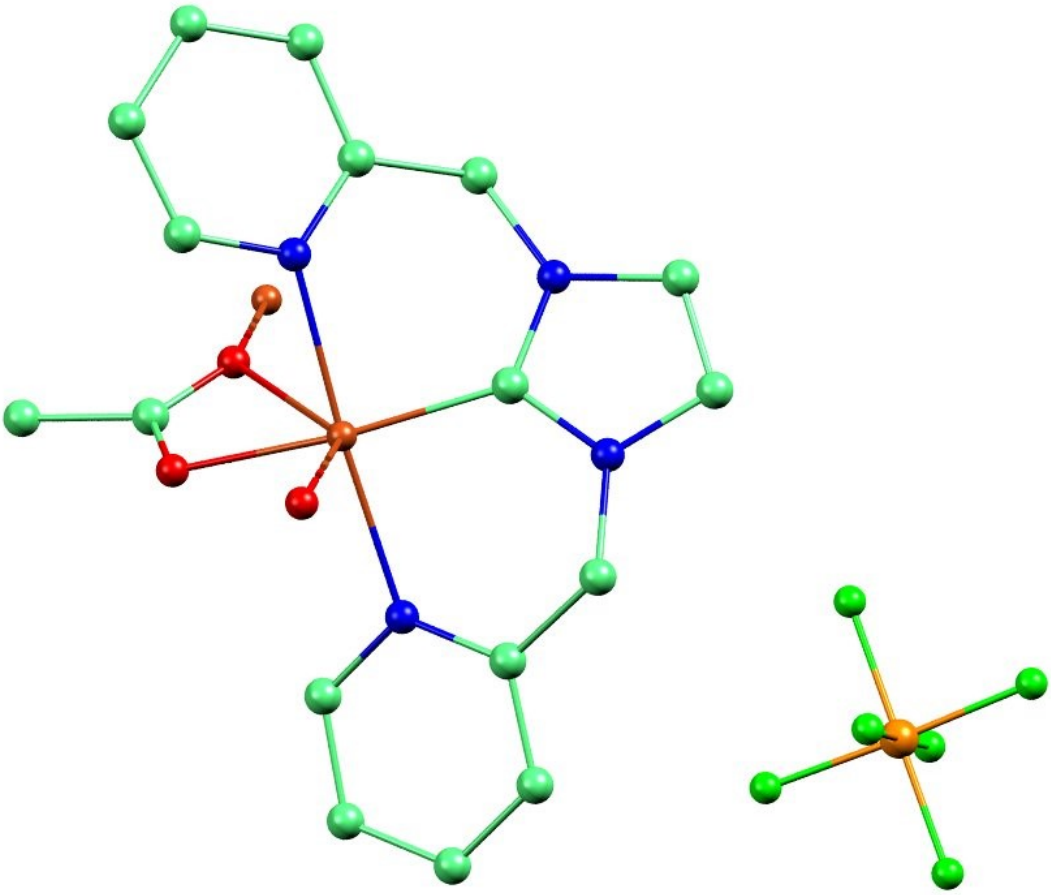


Figure - Asymmetric unit

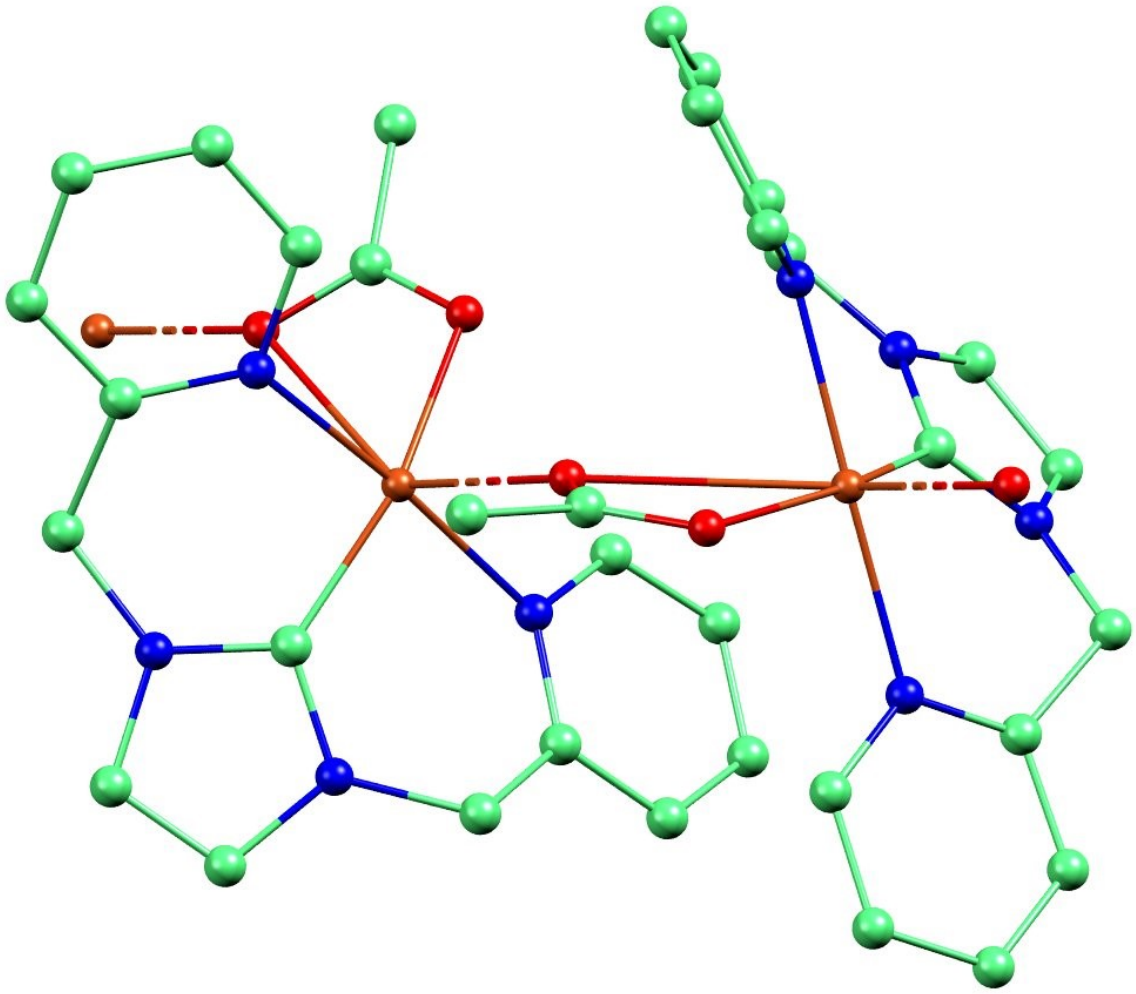


Figure - Acetate bridge

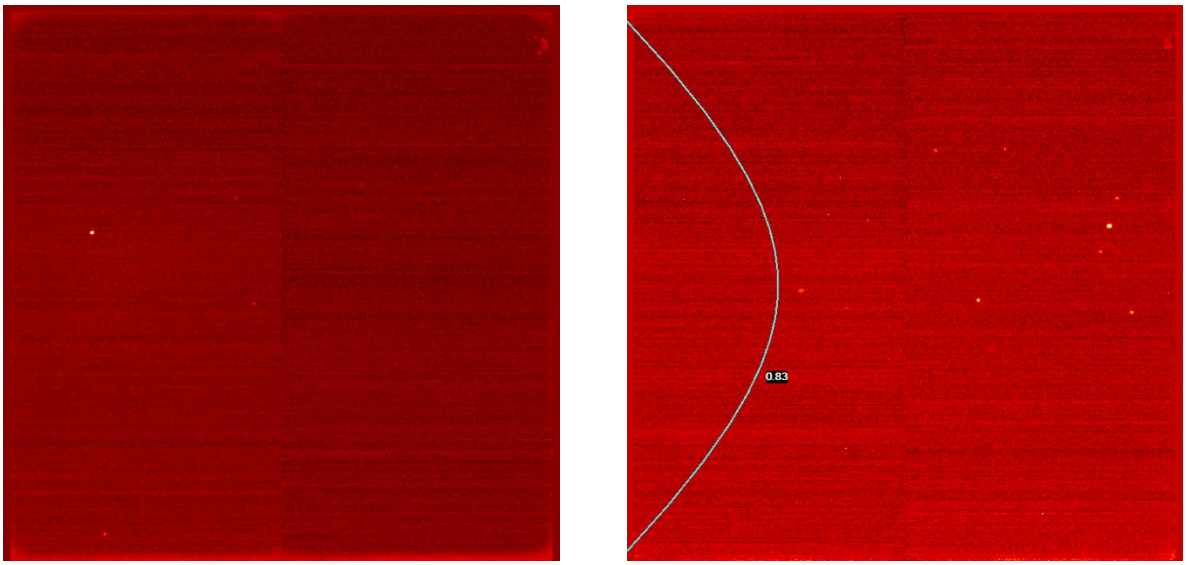


Figure- Frames:

Table S1. Sample and crystal data for 1b.

Identification code	1b	
Chemical formula	$C_{17}H_{17}CuF_6N_4O_2P$	
Formula weight	517.85 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	(0.022 x 0.043 x 0.080) mm^3	
Crystal system	monoclinic	
Space group	P 1 2(1)/c 1	
Unit cell dimensions	a = 13.0314(3) Å	α = 90°
	b = 17.4564(4) Å	β = 103.6770(14)°
	c = 9.0216(2) Å	γ = 90°
Volume	1994.05(8) $Å^3$	
Z	4	
Density (calculated)	1.725 g/cm^3	
Absorption coefficient	3.045 mm^{-1}	

F(000)	1044

Table S2. Data collection and structure refinement for 1b.

Theta range for data collection	3.49 to 74.49°	
Index ranges	-16<=h<=16, -21<=k<=21, -10<=l<=11	
Reflections collected	23796	
Independent reflections	4057 [R(int) = 0.0817]	
Coverage of independent reflections	99.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9360 and 0.7930	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4057 / 0 / 282	
Goodness-of-fit on F^2	1.099	
Final R indices	3172 data; I>2σ(I)	R1 = 0.0568, wR2 = 0.1017
	all data	R1 = 0.0814, wR2 = 0.1126
Weighting scheme	$w=1/[\sigma^2(F_o^2)+8.2561P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.738 and -0.403 eÅ^{-3}	
R.M.S. deviation from mean	0.095 eÅ^{-3}	

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 1b.

U(eq) is defined as one third of the trace of the

orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Cu1	0.18235(4)	0.28742(3)	0.67082(6)	0.01494(16)
N1	0.0410(2)	0.33250(18)	0.5469(3)	0.0175(7)
N2	0.2175(3)	0.43563(18)	0.5398(3)	0.0167(7)
N3	0.3315(3)	0.24788(19)	0.7925(4)	0.0186(7)
N4	0.3335(2)	0.41344(18)	0.7458(4)	0.0179(7)
C1	0.9524(3)	0.2961(2)	0.5619(5)	0.0203(8)
C2	0.8556(3)	0.3079(2)	0.4635(5)	0.0254(9)
C3	0.8481(3)	0.3599(3)	0.3461(5)	0.0272(9)
C4	0.9369(3)	0.3998(2)	0.3345(5)	0.0232(9)
C5	0.0331(3)	0.3851(2)	0.4357(4)	0.0170(8)
C6	0.1298(3)	0.4247(2)	0.4073(4)	0.0191(8)
C7	0.2882(3)	0.4959(2)	0.5590(5)	0.0204(8)
C8	0.3611(3)	0.4824(2)	0.6903(5)	0.0228(9)
C9	0.2460(3)	0.3853(2)	0.6543(4)	0.0178(8)
C10	0.3836(3)	0.3784(2)	0.8918(4)	0.0234(9)
C11	0.4024(3)	0.2930(2)	0.8846(4)	0.0201(8)
C12	0.4915(3)	0.2629(3)	0.9836(5)	0.0291(10)
C13	0.5087(4)	0.1849(3)	0.9870(6)	0.0357(11)
C14	0.4378(3)	0.1387(3)	0.8905(5)	0.0301(10)
C15	0.3504(3)	0.1717(2)	0.7937(5)	0.0214(8)
O1	0.1252(2)	0.18312(14)	0.6229(3)	0.0166(5)
O2	0.1438(2)	0.21544(16)	0.3936(3)	0.0200(6)
C16	0.1124(3)	0.1693(2)	0.4800(4)	0.0161(8)
C17	0.0559(3)	0.0973(2)	0.4195(5)	0.0225(8)
P1	0.70589(8)	0.42517(6)	0.87247(12)	0.0235(2)
F1	0.6039(2)	0.44425(18)	0.7386(4)	0.0486(8)
F2	0.6397(3)	0.4436(2)	0.9958(4)	0.0592(10)
F3	0.8071(2)	0.4058(2)	0.0014(3)	0.0585(9)
F4	0.7705(2)	0.40664(19)	0.7471(3)	0.0474(8)
F5	0.7399(3)	0.51221(18)	0.8692(5)	0.0651(10)
F6	0.6688(3)	0.33882(17)	0.8676(4)	0.0556(9)

Table S4. Bond lengths (Å) for 1b.

Cu1-C9	1.920(4)	Cu1-O1	1.976(3)
Cu1-N1	2.071(3)	Cu1-N3	2.109(3)
Cu1-O2#1	2.184(2)	N1-C5	1.346(5)
N1-C1	1.352(5)	N2-C9	1.340(5)
N2-C7	1.383(5)	N2-C6	1.457(5)
N3-C11	1.342(5)	N3-C15	1.351(5)
N4-C9	1.333(5)	N4-C8	1.384(5)
N4-C10	1.459(5)	C1-C2	1.376(6)
C1-H1	0.950000	C2-C3	1.381(6)
C2-H2	0.950000	C3-C4	1.375(6)
C3-H3	0.950000	C4-C5	1.388(5)
C4-H4	0.950000	C5-C6	1.512(5)
C6-H6A	0.990000	C6-H6B	0.990000
C7-C8	1.352(6)	C7-H7	0.950000
C8-H8	0.950000	C10-C11	1.516(6)
C10-H10A	0.990000	C10-H10B	0.990000
C11-C12	1.390(6)	C12-C13	1.379(7)
C12-H12	0.950000	C13-C14	1.372(7)
C13-H13	0.950000	C14-C15	1.386(6)
C14-H14	0.950000	C15-H15	0.950000
O1-C16	1.283(4)	O2-C16	1.254(4)
C16-C17	1.493(5)	C17-H17A	0.980000
C17-H17B	0.980000	C17-H17C	0.980000
P1-F3	1.576(3)	P1-F6	1.580(3)
P1-F5	1.585(3)	P1-F2	1.594(3)
P1-F4	1.594(3)	P1-F1	1.605(3)

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+1/2, z+1/2

Table S5. Bond angles (°) for 1b.

C9-Cu1-O1	161.83(13)	C9-Cu1-N1	88.03(15)
O1-Cu1-N1	89.46(12)	C9-Cu1-N3	88.26(15)
O1-Cu1-N3	93.77(12)	N1-Cu1-N3	176.17(13)
C9-Cu1-O2#2	106.82(13)	O1-Cu1-O2#2	91.34(10)
N1-Cu1-O2#2	97.85(11)	N3-Cu1-O2#2	84.14(11)
C5-N1-C1	118.6(3)	C5-N1-Cu1	124.3(3)
C1-N1-Cu1	116.0(3)	C9-N2-C7	110.3(3)
C9-N2-C6	124.6(3)	C7-N2-C6	124.9(3)
C11-N3-C15	118.3(4)	C11-N3-Cu1	123.0(3)
C15-N3-Cu1	118.0(3)	C9-N4-C8	110.8(3)
C9-N4-C10	122.6(3)	C8-N4-C10	126.3(3)
N1-C1-C2	122.6(4)	N1-C1-H1	118.700000
C2-C1-H1	118.700000	C1-C2-C3	118.7(4)
C1-C2-H2	120.600000	C3-C2-H2	120.600000
C4-C3-C2	118.9(4)	C4-C3-H3	120.600000
C2-C3-H3	120.600000	C3-C4-C5	120.1(4)
C3-C4-H4	119.900000	C5-C4-H4	119.900000
N1-C5-C4	120.9(4)	N1-C5-C6	121.2(3)
C4-C5-C6	117.6(3)	N2-C6-C5	116.4(3)
N2-C6-H6A	108.200000	C5-C6-H6A	108.200000
N2-C6-H6B	108.200000	C5-C6-H6B	108.200000
H6A-C6-H6B	107.300000	C8-C7-N2	106.6(3)
C8-C7-H7	126.700000	N2-C7-H7	126.700000
C7-C8-N4	106.2(3)	C7-C8-H8	126.900000
N4-C8-H8	126.900000	N4-C9-N2	106.0(3)
N4-C9-Cu1	127.0(3)	N2-C9-Cu1	126.7(3)
N4-C10-C11	114.6(3)	N4-C10-H10A	108.600000
C11-C10-H10A	108.600000	N4-C10-H10B	108.600000
C11-C10-H10B	108.600000	H10A-C10-H10B	107.600000
N3-C11-C12	121.7(4)	N3-C11-C10	120.6(3)
C12-C11-C10	117.6(4)	C13-C12-C11	119.6(4)

C13-C12-H12	120.200000	C11-C12-H12	120.200000
C14-C13-C12	119.0(4)	C14-C13-H13	120.500000
C12-C13-H13	120.500000	C13-C14-C15	119.1(4)
C13-C14-H14	120.500000	C15-C14-H14	120.500000
N3-C15-C14	122.3(4)	N3-C15-H15	118.800000
C14-C15-H15	118.800000	C16-O1-Cu1	110.2(2)
C16-O2-Cu1#1	137.5(2)	O2-C16-O1	121.3(3)
O2-C16-C17	121.2(3)	O1-C16-C17	117.4(3)
C16-C17-H17A	109.500000	C16-C17-H17B	109.500000
H17A-C17-H17B	109.500000	C16-C17-H17C	109.500000
H17A-C17-H17C	109.500000	H17B-C17-H17C	109.500000
F3-P1-F6	90.7(2)	F3-P1-F5	91.8(2)
F6-P1-F5	177.3(2)	F3-P1-F2	91.40(19)
F6-P1-F2	89.98(19)	F5-P1-F2	91.1(2)
F3-P1-F4	89.43(17)	F6-P1-F4	89.75(18)
F5-P1-F4	89.10(19)	F2-P1-F4	179.13(18)
F3-P1-F1	178.86(19)	F6-P1-F1	89.08(18)
F5-P1-F1	88.42(19)	F2-P1-F1	89.72(18)
F4-P1-F1	89.45(16)		

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+1/2, z-1/2

#2 x, -y+1/2, z+1/2

Table S6. Torsion angles (°) for 1b.

C5-N1-C1-C2	3.3(6)	Cu1-N1-C1-C2	-165.2(3)
N1-C1-C2-C3	-1.1(6)	C1-C2-C3-C4	-2.0(6)
C2-C3-C4-C5	2.8(6)	C1-N1-C5-C4	-2.5(5)
Cu1-N1-C5-C4	165.0(3)	C1-N1-C5-C6	-176.6(3)
Cu1-N1-C5-C6	-9.1(5)	C3-C4-C5-N1	-0.6(6)

C3-C4-C5-C6	173.8(4)	C9-N2-C6-C5	36.7(5)
C7-N2-C6-C5	-149.2(3)	N1-C5-C6-N2	-30.6(5)
C4-C5-C6-N2	155.0(3)	C9-N2-C7-C8	-0.9(4)
C6-N2-C7-C8	-175.8(3)	N2-C7-C8-N4	1.0(4)
C9-N4-C8-C7	-0.8(4)	C10-N4-C8-C7	-174.4(3)
C8-N4-C9-N2	0.2(4)	C10-N4-C9-N2	174.1(3)
C8-N4-C9-Cu1	174.2(3)	C10-N4-C9-Cu1	-12.0(5)
C7-N2-C9-N4	0.4(4)	C6-N2-C9-N4	175.3(3)
C7-N2-C9-Cu1	-173.5(3)	C6-N2-C9-Cu1	1.3(5)
C9-N4-C10-C11	50.2(5)	C8-N4-C10-C11	-137.0(4)
C15-N3-C11-C12	-2.4(5)	Cu1-N3-C11-C12	168.4(3)
C15-N3-C11-C10	-178.0(3)	Cu1-N3-C11-C10	-7.3(5)
N4-C10-C11-N3	-37.5(5)	N4-C10-C11-C12	146.7(4)
N3-C11-C12-C13	0.7(6)	C10-C11-C12-C13	176.5(4)
C11-C12-C13-C14	0.8(7)	C12-C13-C14-C15	-0.6(7)
C11-N3-C15-C14	2.6(6)	Cu1-N3-C15-C14	-168.6(3)
C13-C14-C15-N3	-1.1(6)	Cu1#1-O2-C16-O1	159.8(3)
Cu1#1-O2-C16-C17	-22.0(6)	Cu1-O1-C16-O2	6.5(4)
Cu1-O1-C16-C17	-171.7(3)		

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+1/2, z-1/2

Table S7. Anisotropic atomic displacement parameters (Å^2) for 1b.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

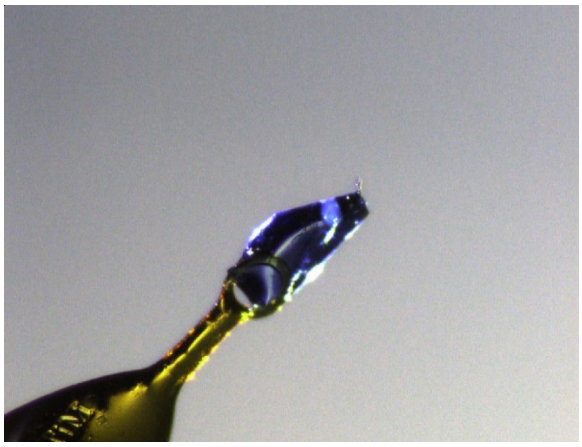
	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Cu1	0.0176(3)	0.0163(3)	0.0113(3)	0.0022(2)	0.0042(2)	0.0008(2)
N1	0.0203(16)	0.0198(16)	0.0139(15)	0.0001(13)	0.0068(13)	0.0027(13)

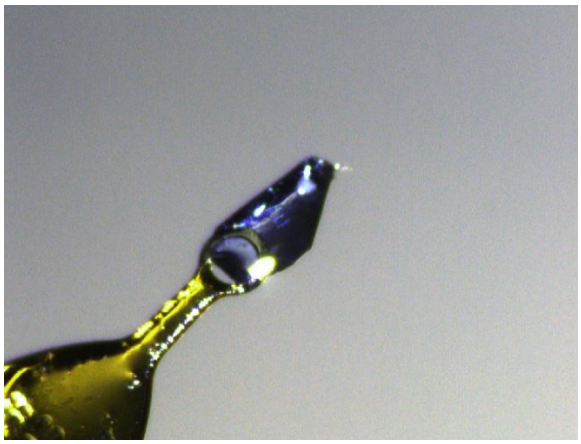
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	0.0231(17)	0.0159(15)	0.0119(15)	0.0000(12)	0.0059(13)	-0.0008(13)
N3	0.0198(16)	0.0223(17)	0.0157(16)	0.0042(13)	0.0081(13)	0.0019(13)
N4	0.0198(16)	0.0200(16)	0.0143(16)	-0.0004(13)	0.0048(13)	-0.0024(13)
C1	0.0203(19)	0.0202(19)	0.022(2)	0.0012(16)	0.0081(16)	0.0037(16)
C2	0.019(2)	0.032(2)	0.026(2)	-0.0033(18)	0.0056(17)	0.0022(17)
C3	0.022(2)	0.034(2)	0.024(2)	-0.0031(18)	0.0018(17)	0.0083(18)
C4	0.030(2)	0.022(2)	0.0155(19)	0.0010(16)	0.0017(16)	0.0063(17)
C5	0.024(2)	0.0165(18)	0.0110(18)	-0.0049(14)	0.0047(15)	0.0024(15)
C6	0.026(2)	0.0192(19)	0.0113(18)	-0.0008(15)	0.0035(15)	0.0005(16)
C7	0.028(2)	0.0156(18)	0.021(2)	-0.0019(15)	0.0106(17)	-0.0012(16)
C8	0.025(2)	0.022(2)	0.023(2)	-0.0026(16)	0.0108(17)	-0.0050(17)
C9	0.0209(19)	0.0202(19)	0.0140(18)	-0.0007(15)	0.0075(15)	0.0022(15)
C10	0.025(2)	0.031(2)	0.0144(19)	0.0019(17)	0.0040(16)	-0.0004(17)
C11	0.0194(19)	0.029(2)	0.0142(18)	0.0041(16)	0.0081(15)	0.0033(17)
C12	0.024(2)	0.034(2)	0.027(2)	0.0060(19)	0.0023(18)	-0.0026(18)
C13	0.023(2)	0.049(3)	0.034(3)	0.017(2)	0.0035(19)	0.006(2)
C14	0.026(2)	0.032(2)	0.034(2)	0.015(2)	0.0119(19)	0.0074(19)
C15	0.021(2)	0.023(2)	0.024(2)	0.0030(16)	0.0125(17)	0.0026(16)
O1	0.0194(13)	0.0185(13)	0.0123(13)	0.0003(10)	0.0048(10)	0.0012(10)
O2	0.0266(14)	0.0235(14)	0.0125(12)	0.0002(11)	0.0095(11)	-0.0055(12)
C16	0.0160(18)	0.0178(18)	0.0150(18)	0.0009(15)	0.0048(14)	0.0038(14)
C17	0.027(2)	0.023(2)	0.019(2)	0.0000(16)	0.0064(17)	-0.0030(17)
P1	0.0212(5)	0.0273(6)	0.0220(5)	0.0002(4)	0.0052(4)	-0.0015(4)
F1	0.0338(16)	0.0546(19)	0.0494(18)	-0.0064(15)	-0.0063(13)	0.0116(14)
F2	0.0518(19)	0.088(3)	0.0458(18)	-0.0311(18)	0.0283(15)	-0.0130(18)
F3	0.0373(17)	0.103(3)	0.0270(16)	0.0141(17)	-0.0080(13)	-0.0046(17)
F4	0.0438(17)	0.073(2)	0.0301(15)	0.0142(14)	0.0175(13)	0.0242(15)
F5	0.061(2)	0.0356(17)	0.099(3)	-0.0048(18)	0.020(2)	-0.0171(16)
F6	0.059(2)	0.0284(15)	0.082(2)	0.0021(16)	0.0223(18)	-0.0069(14)

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for 1b.

	x/a	y/b	z/c	U(eq)
H1	-0.0428	0.2610	0.6437	0.024000
H2	-0.2050	0.2807	0.4761	0.031000
H3	-0.2173	0.3680	0.2745	0.033000
H4	-0.0676	0.4374	0.2572	0.028000
H6A	0.1557	0.3947	0.3305	0.023000
H6B	0.1082	0.4756	0.3621	0.023000
H7	0.2861	0.5385	0.4928	0.025000
H8	0.4196	0.5139	0.7353	0.027000
H10A	0.3386	0.3879	0.9644	0.028000
H10B	0.4522	0.4040	0.9327	0.028000
H12	0.5402	0.2959	1.0486	0.035000
H13	0.5688	0.1635	1.0551	0.043000
H14	0.4484	0.0849	0.8901	0.036000
H15	0.3021	0.1397	0.7257	0.026000
H17A	-0.0204	0.1068	0.3927	0.034000
H17B	0.0723	0.0572	0.4976	0.034000
H17C	0.0787	0.0808	0.3285	0.034000

A blue prism like single crystal of $C_{24}H_{27}CuF_6N_4O_3P$, approximate dimensions (0.107 x 0.250 x 0.636) mm^3, was selected for the X-ray crystallographic analysis and mounted on a cryoloop using an oil cryoprotectant. The X-ray intensity data was measured at low temperature (T = 200K), using a three circles goniometer Kappa geometry with a fixed Kappa angle at = 54.74 deg Bruker AXS D8 Venture, equipped with a Photon 100 CMOS active pixel sensor detector. A monochromatized Cu X-ray radiation (λ = 1.54178 Å) was selected for the measurement. All frames were integrated with the aid of the Bruker SAINT software[S1] using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 29336 reflections to a maximum θ angle of 68.24° (0.83 Å resolution), of which 4812 were independent (average redundancy 6.096, completeness = 99.0%, R_{int} = 3.77%, R_{sig} = 2.57%) and 4349 (90.38%) were greater than 2σ (F^2). The final cell constants of a = 9.4890(14) Å, b = 10.9068(16) Å, c = 14.481(2) Å, α = 111.242(6) °, β = 103.332(6) °, γ = 96.766(5) °, volume = 1325.3(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 1302 reflections above 20 σ (I) with 6.854° < 2θ < 150.3°. Data were corrected for absorption effects using the Multi-Scan method: (SADABS). [S2] The ratio of minimum to maximum apparent transmission was 0.787. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3070 and 0.7810. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{24}H_{26.5}CuF_6N_4O_3P$. Using the Bruker SHELXT Software Package, [S3] refinement of the structure was carried out by least squares procedures on weighted F^2 values using the SHELXTL-2018/3 [4] included in the APEX4 v2021, 4.0, AXS Bruker program.[S5]. Hydrogen atoms were localized on difference Fourier maps but then introduced in the refinement as fixed contributors in idealized geometry with an isotropic thermal parameters fixed at 20 % higher than those carbons atoms they were connected. A molecule of Methanol: CH_3OH and Acetate: CH_3COO^- were found coordinated on a Copper center and found statistically disordered on two sites. A counter anion: PF_6^- was also depicted crystallized with the Copper complex statistically distributed on two positions. All were anisotropically refined with a ratio of occupancy equal to 50%. Restraints were put on interatomic lengths and angles and constraints were added on ADP's parameters in order to get a chemically reasonable refined model. The final anisotropic full-matrix least-squares refinement on $F^2$with 474 variables converged at R1 = 3.63%, for the observed data and wR2 = 9.44% for all data. The goodness-of-fit: GOF was 1.061. The largest peak in the final difference electron density synthesis was 0.511 $e^-/Å^3$ and the largest hole was -0.369 $e^-/Å^3$ with an RMS deviation of 0.057 $e^-/Å^3$. Based on the final model, the calculated density was 1.574 g/cm^3 and F (000), 642 e^-. Graphics were performed using softwares: Mercury V.4.2.0: (https://www.ccdc.cam.ac.uk/) and POV-Ray v 3.7: (The Persistence of Vision Raytracer, high quality, Free Software tool).





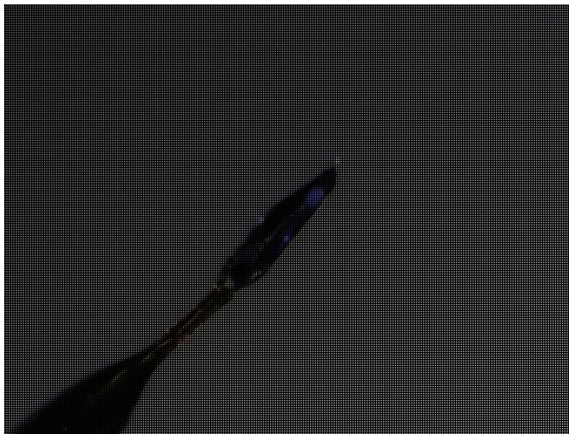


Figure - Crystal views

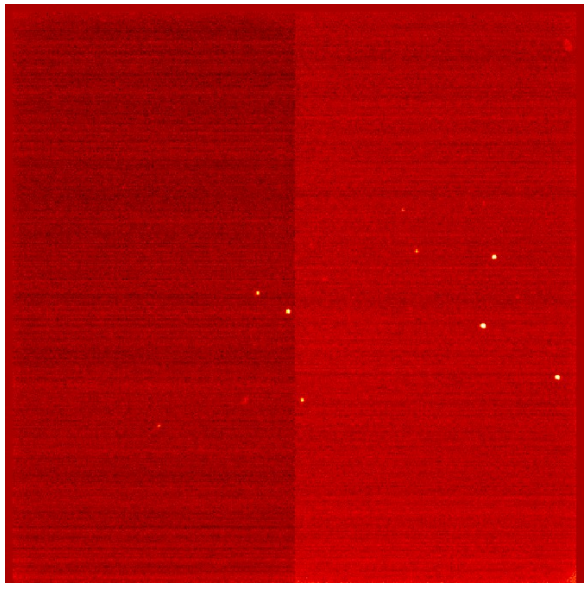


Figure - Frames views

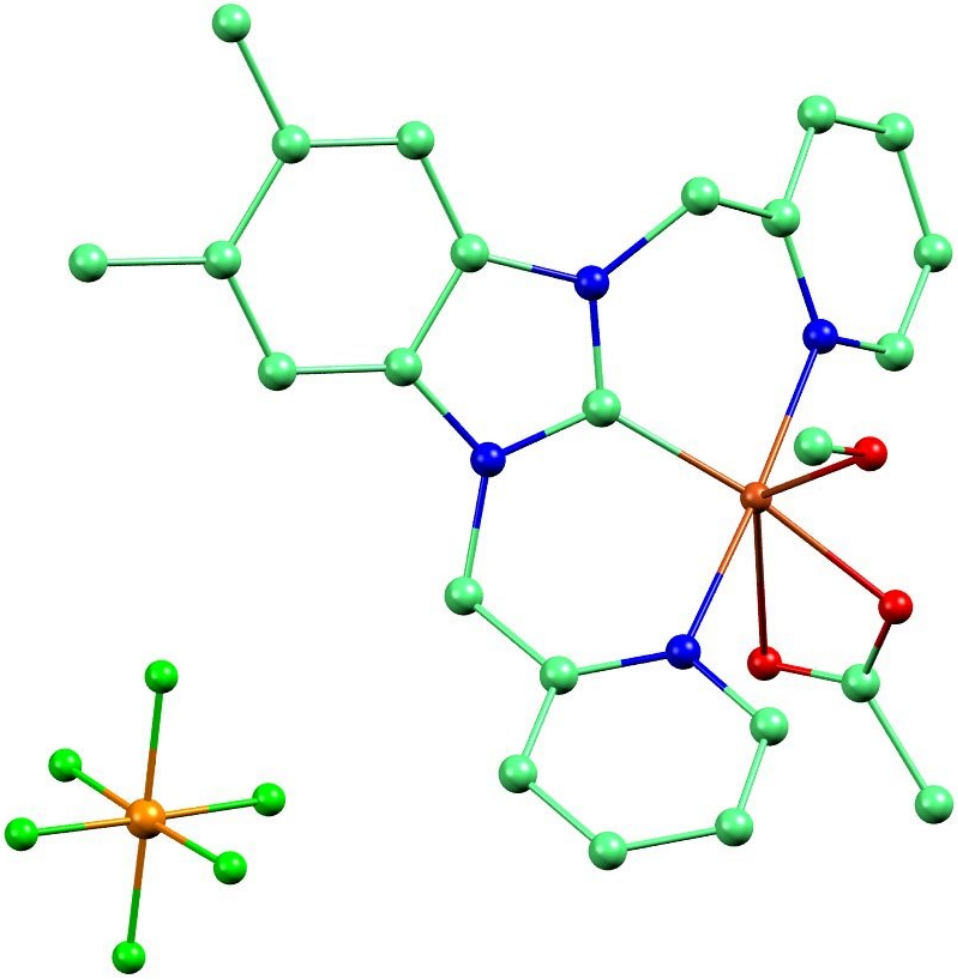


Figure - Asymmetric unit

Table S9. Sample and crystal data for 3b.

Identification code	Cu_C_JM_001	
Chemical formula	$C_{24}H_{27}CuF_6N_4O_3P$	
Formula weight	628.00 g/mol	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal size	(0.107 x 0.250 x 0.636) mm^3	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4890(14) Å	α = 111.242(6)°
	b = 10.9068(16) Å	β = 103.332(6)°
	c = 14.481(2) Å	γ = 96.766(5)°
Volume	1325.3(3) $Å^3$	
Z	2	
Density (calculated)	1.572 g/cm^3	
Absorption coefficient	2.432 mm^{-1}	
F(000)	642	

Table S10. Data collection and structure refinement for 3b.

Theta range for data collection	3.43 to 68.24°
Index ranges	-11<=h<=11, -13<=k<=13, -17<=l<=17
Reflections collected	29336
Independent reflections	4812 [R(int) = 0.0377]
Coverage of independent reflections	99.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7810 and 0.3070
Structure solution technique	direct methods

Structure solution program	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4812 / 183 / 474
Goodness-of-fit on F^2	1.061
Δ/σ_{max}	0.001
Final R indices	4349 data; I>2σ(I) R1 = 0.0363, wR2 = 0.0898
	all data R1 = 0.0414, wR2 = 0.0944
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0322P)^2+1.3940P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0026(2)
Largest diff. peak and hole	0.511 and -0.369 eÅ^{-3}
R.M.S. deviation from mean	0.057 eÅ^{-3}

Table S11. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 3b.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Cu	0.50974(4)	0.23824(3)	0.15753(2)	0.03451(13)
N1	0.6944(2)	0.1813(2)	0.22635(15)	0.0362(4)
N2	0.3143(2)	0.2917(2)	0.09503(15)	0.0399(5)
N3	0.4834(2)	0.22838(19)	0.35155(14)	0.0325(4)
N4	0.3756(2)	0.37723(19)	0.31818(15)	0.0337(4)
C1	0.8188(3)	0.1983(3)	0.1989(2)	0.0436(6)
C2	0.9504(3)	0.1748(3)	0.2455(2)	0.0510(7)
C3	0.9566(3)	0.1328(3)	0.3243(2)	0.0539(7)

	x/a	y/b	z/c	U(eq)
C4	0.8294(3)	0.1160(3)	0.3547(2)	0.0470(6)
C5	0.6999(3)	0.1410(2)	0.30462(18)	0.0360(5)
C6	0.5609(3)	0.1169(2)	0.33583(19)	0.0383(5)
C7	0.4585(3)	0.2883(2)	0.28538(17)	0.0326(5)
C8	0.3430(2)	0.3734(2)	0.40657(17)	0.0315(5)
C9	0.2604(3)	0.4416(2)	0.46775(18)	0.0353(5)
C10	0.2435(3)	0.4071(2)	0.54832(18)	0.0367(5)
C11	0.3128(3)	0.3077(2)	0.56906(18)	0.0366(5)
C12	0.3985(3)	0.2431(2)	0.50923(18)	0.0345(5)
C13	0.4116(2)	0.2768(2)	0.42772(17)	0.0309(5)
C14	0.3282(3)	0.4626(2)	0.26427(19)	0.0401(6)
C15	0.2488(3)	0.3819(2)	0.15093(19)	0.0373(5)
C16	0.1154(3)	0.4059(3)	0.1055(2)	0.0491(7)
C17	0.0501(3)	0.3366(3)	0.9996(3)	0.0622(8)
C18	0.1168(3)	0.2452(3)	0.9428(2)	0.0610(8)
C19	0.2475(3)	0.2236(3)	0.9924(2)	0.0515(7)
C20	0.1473(3)	0.4739(3)	0.6126(2)	0.0514(7)
C21	0.2924(3)	0.2687(3)	0.6559(2)	0.0507(7)
O1A	0.5554(18)	0.2115(12)	0.0297(12)	0.036(2)
C22A	0.609(3)	0.3265(14)	0.0308(10)	0.059(6)
C23A	0.594(2)	0.3320(18)	0.9272(10)	0.070(5)
O2A	0.6563(14)	0.4289(13)	0.1119(10)	0.073(3)
O1S	0.3638(15)	0.0178(13)	0.0711(8)	0.041(2)
C1S	0.220(3)	0.979(2)	0.0797(18)	0.052(4)
P1A	0.20075(14)	0.82657(13)	0.34538(14)	0.0312(15)
F1A	0.2060(10)	0.7199(7)	0.3980(6)	0.067(4)
F2A	0.1989(10)	0.9338(7)	0.2954(7)	0.082(3)
F3A	0.0878(8)	0.7151(6)	0.2446(5)	0.120(3)
F4A	0.0734(6)	0.8744(7)	0.3911(6)	0.093(2)
F5A	0.3325(7)	0.7799(8)	0.3027(6)	0.096(3)
F6A	0.3179(6)	0.9338(6)	0.4461(4)	0.081(2)
O1B	0.5814(18)	0.2222(11)	0.0348(12)	0.035(2)
C22B	0.6073(19)	0.3434(10)	0.0397(7)	0.032(3)

	x/a	y/b	z/c	U(eq)
C23B	0.622(2)	0.3586(17)	0.9435(10)	0.059(3)
O2B	0.6192(13)	0.4418(12)	0.1196(9)	0.057(2)
O1T	0.3827(15)	0.0137(13)	0.0943(8)	0.040(2)
C1T	0.236(3)	0.980(3)	0.0961(19)	0.061(5)
P1B	0.200300	0.826621	0.341208	0.054(2)
F1B	0.2209(10)	0.7347(7)	0.4065(6)	0.059(3)
F2B	0.1804(10)	0.9184(7)	0.2783(6)	0.075(3)
F3B	0.0467(6)	0.7285(8)	0.2714(5)	0.106(3)
F4B	0.1212(7)	0.9134(7)	0.4181(4)	0.085(2)
F5B	0.2796(8)	0.7391(6)	0.2669(5)	0.090(2)
F6B	0.3518(5)	0.9227(6)	0.4143(5)	0.087(2)

Table S12. Bond lengths (Å) for 3b.

Cu-O1A	1.925(16)	Cu-C7	1.925(2)
Cu-O1B	2.002(15)	Cu-N1	2.086(2)
Cu-N2	2.112(2)	Cu-O1T	2.337(13)
Cu-O1S	2.346(13)	N1-C1	1.343(3)
N1-C5	1.349(3)	N2-C15	1.345(3)
N2-C19	1.348(3)	N3-C7	1.337(3)
N3-C13	1.403(3)	N3-C6	1.469(3)
N4-C7	1.343(3)	N4-C8	1.398(3)
N4-C14	1.463(3)	C1-C2	1.375(4)
C1-H1	0.950000	C2-C3	1.367(4)
C2-H2	0.950000	C3-C4	1.391(4)
C3-H3	0.950000	C4-C5	1.386(3)
C4-H4	0.950000	C5-C6	1.514(3)
C6-H6A	0.990000	C6-H6B	0.990000
C8-C13	1.390(3)	C8-C9	1.390(3)
C9-C10	1.385(3)	C9-H9	0.950000

C10-C11	1.418(4)	C10-C20	1.512(3)
C11-C12	1.388(3)	C11-C21	1.510(3)
C12-C13	1.384(3)	C12-H12	0.950000
C14-C15	1.504(4)	C14-H14A	0.990000
C14-H14B	0.990000	C15-C16	1.386(4)
C16-C17	1.385(4)	C16-H16	0.950000
C17-C18	1.366(5)	C17-H17	0.950000
C18-C19	1.375(4)	C18-H18	0.950000
C19-H19	0.950000	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	O1A-C22A	1.289(7)
C22A-O2A	1.232(8)	C22A-C23A	1.499(7)
C23A-H23A	0.980000	C23A-H23B	0.980000
C23A-H23C	0.980000	O1S-C1S	1.43(3)
O1S-H1S	1.040(15)	C1S-H1S1	0.980000
C1S-H1S2	0.980000	C1S-H1S3	0.980000
P1A-F4A	1.561(3)	P1A-F6A	1.562(3)
P1A-F3A	1.563(4)	P1A-F5A	1.575(3)
P1A-F2A	1.583(3)	P1A-F1A	1.605(3)
O1B-C22B	1.288(7)	C22B-O2B	1.230(8)
C22B-C23B	1.497(6)	C23B-H23D	0.980000
C23B-H23E	0.980000	C23B-H23F	0.980000
O1T-C1T	1.40(3)	O1T-H1T	1.033(14)
C1T-H1T1	0.980000	C1T-H1T2	0.980000
C1T-H1T3	0.980000	P1B-F6B	1.558(3)
P1B-F5B	1.560(3)	P1B-F3B	1.569(4)
P1B-F4B	1.578(3)	P1B-F2B	1.579(3)
P1B-F1B	1.608(3)		

Table S13. Bond angles (°) for 3b.

O1A-Cu-C7	172.1(4)	C7-Cu-O1B	169.4(3)
O1A-Cu-N1	96.8(5)	C7-Cu-N1	88.74(9)
O1B-Cu-N1	92.2(5)	O1A-Cu-N2	87.2(5)
C7-Cu-N2	87.53(9)	O1B-Cu-N2	91.9(5)
N1-Cu-N2	175.65(8)	C7-Cu-O1T	93.5(3)
O1B-Cu-O1T	97.1(4)	N1-Cu-O1T	87.2(3)
N2-Cu-O1T	90.8(3)	O1A-Cu-O1S	86.4(5)
C7-Cu-O1S	98.8(3)	N1-Cu-O1S	94.4(3)
N2-Cu-O1S	84.0(3)	C1-N1-C5	118.2(2)
C1-N1-Cu	118.51(17)	C5-N1-Cu	122.97(16)
C15-N2-C19	118.6(2)	C15-N2-Cu	124.77(16)
C19-N2-Cu	116.53(18)	C7-N3-C13	110.33(18)
C7-N3-C6	122.62(19)	C13-N3-C6	126.68(19)
C7-N4-C8	110.79(18)	C7-N4-C14	122.12(19)
C8-N4-C14	127.08(19)	N1-C1-C2	123.3(3)
N1-C1-H1	118.300000	C2-C1-H1	118.300000
C3-C2-C1	118.9(3)	C3-C2-H2	120.500000
C1-C2-H2	120.500000	C2-C3-C4	118.6(2)
C2-C3-H3	120.700000	C4-C3-H3	120.700000
C5-C4-C3	119.8(3)	C5-C4-H4	120.100000
C3-C4-H4	120.100000	N1-C5-C4	121.2(2)
N1-C5-C6	119.7(2)	C4-C5-C6	119.1(2)
N3-C6-C5	113.6(2)	N3-C6-H6A	108.900000
C5-C6-H6A	108.900000	N3-C6-H6B	108.900000
C5-C6-H6B	108.900000	H6A-C6-H6B	107.700000
N3-C7-N4	107.10(19)	N3-C7-Cu	125.77(17)
N4-C7-Cu	126.64(17)	C13-C8-C9	121.2(2)
C13-C8-N4	105.58(19)	C9-C8-N4	133.3(2)
C10-C9-C8	118.1(2)	C10-C9-H9	120.900000
C8-C9-H9	120.900000	C9-C10-C11	120.5(2)
C9-C10-C20	119.4(2)	C11-C10-C20	120.1(2)
C12-C11-C10	120.8(2)	C12-C11-C21	118.8(2)
C10-C11-C21	120.4(2)	C13-C12-C11	118.0(2)
C13-C12-H12	121.000000	C11-C12-H12	121.000000

C12-C13-C8	121.4(2)	C12-C13-N3	132.4(2)
C8-C13-N3	106.17(19)	N4-C14-C15	112.33(19)
N4-C14-H14A	109.100000	C15-C14-H14A	109.100000
N4-C14-H14B	109.100000	C15-C14-H14B	109.100000
H14A-C14-H14B	107.900000	N2-C15-C16	121.6(2)
N2-C15-C14	118.1(2)	C16-C15-C14	120.2(2)
C17-C16-C15	118.8(3)	C17-C16-H16	120.600000
C15-C16-H16	120.600000	C18-C17-C16	119.6(3)
C18-C17-H17	120.200000	C16-C17-H17	120.200000
C17-C18-C19	119.0(3)	C17-C18-H18	120.500000
C19-C18-H18	120.500000	N2-C19-C18	122.3(3)
N2-C19-H19	118.800000	C18-C19-H19	118.800000
C10-C20-H20A	109.500000	C10-C20-H20B	109.500000
H20A-C20-H20B	109.500000	C10-C20-H20C	109.500000
H20A-C20-H20C	109.500000	H20B-C20-H20C	109.500000
C11-C21-H21A	109.500000	C11-C21-H21B	109.500000
H21A-C21-H21B	109.500000	C11-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000
C22A-O1A-Cu	109.6(9)	O2A-C22A-O1A	121.8(6)
O2A-C22A-C23A	121.6(7)	O1A-C22A-C23A	116.3(8)
C22A-C23A-H23A	109.500000	C22A-C23A-H23B	109.500000
H23A-C23A-H23B	109.500000	C22A-C23A-H23C	109.500000
H23A-C23A-H23C	109.500000	H23B-C23A-H23C	109.500000
C1S-O1S-Cu	123.7(12)	C1S-O1S-H1S	112.7(14)
Cu-O1S-H1S	121.7(10)	O1S-C1S-H1S1	109.500000
O1S-C1S-H1S2	109.500000	H1S1-C1S-H1S2	109.500000
O1S-C1S-H1S3	109.500000	H1S1-C1S-H1S3	109.500000
H1S2-C1S-H1S3	109.500000	F4A-P1A-F6A	89.8(3)
F4A-P1A-F3A	92.1(4)	F6A-P1A-F3A	177.6(3)
F4A-P1A-F5A	178.3(4)	F6A-P1A-F5A	88.7(4)
F3A-P1A-F5A	89.5(4)	F4A-P1A-F2A	90.5(3)
F6A-P1A-F2A	89.5(3)	F3A-P1A-F2A	92.0(3)
F5A-P1A-F2A	90.2(3)	F4A-P1A-F1A	89.8(3)
F6A-P1A-F1A	89.3(3)	F3A-P1A-F1A	89.2(3)

F5A-P1A-F1A	89.4(3)	F2A-P1A-F1A	178.7(4)
C22B-O1B-Cu	104.7(9)	O2B-C22B-O1B	121.6(5)
O2B-C22B-C23B	121.7(6)	O1B-C22B-C23B	116.8(7)
C22B-C23B-H23D	109.500000	C22B-C23B-H23E	109.500000
H23D-C23B-H23E	109.500000	C22B-C23B-H23F	109.500000
H23D-C23B-H23F	109.500000	H23E-C23B-H23F	109.500000
C1T-O1T-Cu	121.4(14)	C1T-O1T-H1T	111.8(14)
Cu-O1T-H1T	122.8(10)	O1T-C1T-H1T1	109.500000
O1T-C1T-H1T2	109.500000	H1T1-C1T-H1T2	109.500000
O1T-C1T-H1T3	109.500000	H1T1-C1T-H1T3	109.500000
H1T2-C1T-H1T3	109.500000	F6B-P1B-F5B	91.0(4)
F6B-P1B-F3B	177.7(3)	F5B-P1B-F3B	90.2(4)
F6B-P1B-F4B	88.8(3)	F5B-P1B-F4B	178.6(3)
F3B-P1B-F4B	90.0(4)	F6B-P1B-F2B	90.5(3)
F5B-P1B-F2B	91.0(3)	F3B-P1B-F2B	91.5(3)
F4B-P1B-F2B	90.4(3)	F6B-P1B-F1B	89.1(3)
F5B-P1B-F1B	89.6(3)	F3B-P1B-F1B	88.9(3)
F4B-P1B-F1B	89.1(3)	F2B-P1B-F1B	179.3(3)

Table S14. Torsion angles (°) for 3b.

C5-N1-C1-C2	1.0(4)	Cu-N1-C1-C2	174.4(2)
N1-C1-C2-C3	-0.5(4)	C1-C2-C3-C4	-0.3(4)
C2-C3-C4-C5	0.4(4)	C1-N1-C5-C4	-0.8(4)
Cu-N1-C5-C4	-173.92(19)	C1-N1-C5-C6	-178.3(2)
Cu-N1-C5-C6	8.6(3)	C3-C4-C5-N1	0.1(4)
C3-C4-C5-C6	177.6(2)	C7-N3-C6-C5	45.2(3)

C13-N3-C6-C5	-142.4(2)	N1-C5-C6-N3	-49.5(3)
C4-C5-C6-N3	133.0(2)	C13-N3-C7-N4	1.6(3)
C6-N3-C7-N4	175.1(2)	C13-N3-C7-Cu	-170.83(16)
C6-N3-C7-Cu	2.7(3)	C8-N4-C7-N3	-1.2(3)
C14-N4-C7-N3	179.4(2)	C8-N4-C7-Cu	171.12(16)
C14-N4-C7-Cu	-8.3(3)	C7-N4-C8-C13	0.4(3)
C14-N4-C8-C13	179.7(2)	C7-N4-C8-C9	-178.5(2)
C14-N4-C8-C9	0.9(4)	C13-C8-C9-C10	-2.4(3)
N4-C8-C9-C10	176.3(2)	C8-C9-C10-C11	1.9(3)
C8-C9-C10-C20	-176.6(2)	C9-C10-C11-C12	0.0(3)
C20-C10-C11-C12	178.5(2)	C9-C10-C11-C21	-179.1(2)
C20-C10-C11-C21	-0.6(4)	C10-C11-C12-C13	-1.3(3)
C21-C11-C12-C13	177.8(2)	C11-C12-C13-C8	0.8(3)
C11-C12-C13-N3	-177.3(2)	C9-C8-C13-C12	1.1(3)
N4-C8-C13-C12	-177.9(2)	C9-C8-C13-N3	179.6(2)
N4-C8-C13-N3	0.6(2)	C7-N3-C13-C12	176.9(2)
C6-N3-C13-C12	3.7(4)	C7-N3-C13-C8	-1.4(3)
C6-N3-C13-C8	-174.5(2)	C7-N4-C14-C15	54.0(3)
C8-N4-C14-C15	-125.3(2)	C19-N2-C15-C16	0.0(4)
Cu-N2-C15-C16	-175.86(19)	C19-N2-C15-C14	-176.9(2)
Cu-N2-C15-C14	7.3(3)	N4-C14-C15-N2	-50.8(3)
N4-C14-C15-C16	132.3(2)	N2-C15-C16-C17	-1.2(4)
C14-C15-C16-C17	175.6(3)	C15-C16-C17-C18	1.0(5)
C16-C17-C18-C19	0.3(5)	C15-N2-C19-C18	1.4(4)
Cu-N2-C19-C18	177.6(2)	C17-C18-C19-N2	-1.5(5)
Cu-O1A-C22A-O2A	17.(3)	Cu-O1A-C22A-C23A	-156.7(16)
Cu-O1B-C22B-O2B	16.(2)	Cu-O1B-C22B-C23B	-163.6(14)

Table S15. Anisotropic atomic displacement parameters (Å^2) for 3b.

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The anisotropic atomic displacement factor exponent takes the form: -2π^2[

$h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0.0376(2)	0.0418(2)	0.0293(2)	0.01684(15)	0.01206(14)	0.01535(15)
N1	0.0378(10)	0.0406(11)	0.0325(10)	0.0142(9)	0.0122(8)	0.0154(9)
N2	0.0390(11)	0.0472(12)	0.0334(11)	0.0184(9)	0.0061(9)	0.0114(9)
N3	0.0354(10)	0.0368(10)	0.0319(10)	0.0167(8)	0.0132(8)	0.0163(8)
N4	0.0386(10)	0.0358(10)	0.0330(10)	0.0171(8)	0.0128(8)	0.0162(8)
C1	0.0411(14)	0.0524(15)	0.0422(14)	0.0191(12)	0.0176(11)	0.0171(12)
C2	0.0399(14)	0.0621(17)	0.0541(16)	0.0201(14)	0.0201(12)	0.0209(13)
C3	0.0440(15)	0.0656(18)	0.0552(17)	0.0237(15)	0.0121(13)	0.0301(14)
C4	0.0509(15)	0.0550(16)	0.0457(15)	0.0251(13)	0.0170(12)	0.0293(13)
C5	0.0415(13)	0.0353(12)	0.0332(12)	0.0126(10)	0.0124(10)	0.0175(10)
C6	0.0473(14)	0.0398(13)	0.0402(13)	0.0223(11)	0.0188(11)	0.0227(11)
C7	0.0359(12)	0.0351(12)	0.0279(11)	0.0129(9)	0.0087(9)	0.0129(9)
C8	0.0313(11)	0.0321(11)	0.0292(11)	0.0116(9)	0.0067(9)	0.0074(9)
C9	0.0336(12)	0.0325(11)	0.0364(12)	0.0097(10)	0.0094(10)	0.0109(9)
C10	0.0322(12)	0.0373(12)	0.0354(12)	0.0088(10)	0.0107(10)	0.0070(10)
C11	0.0332(12)	0.0399(13)	0.0334(12)	0.0127(10)	0.0095(10)	0.0036(10)
C12	0.0363(12)	0.0341(12)	0.0335(12)	0.0146(10)	0.0091(10)	0.0089(10)
C13	0.0306(11)	0.0315(11)	0.0288(11)	0.0100(9)	0.0085(9)	0.0079(9)
C14	0.0502(14)	0.0360(12)	0.0414(13)	0.0205(11)	0.0145(11)	0.0185(11)
C15	0.0372(12)	0.0379(12)	0.0438(13)	0.0252(11)	0.0101(10)	0.0090(10)
C16	0.0428(14)	0.0477(15)	0.0606(17)	0.0299(14)	0.0071(13)	0.0138(12)
C17	0.0434(16)	0.0647(19)	0.075(2)	0.0396(17)	-0.0068(15)	0.0107(14)
C18	0.0559(18)	0.0665(19)	0.0477(17)	0.0242(15)	-0.0073(14)	0.0078(15)
C19	0.0509(16)	0.0606(17)	0.0386(14)	0.0199(13)	0.0048(12)	0.0135(13)
C20	0.0512(16)	0.0570(17)	0.0495(16)	0.0161(13)	0.0258(13)	0.0211(13)
C21	0.0559(16)	0.0617(17)	0.0453(15)	0.0268(14)	0.0251(13)	0.0147(14)
O1A	0.035(4)	0.041(3)	0.036(3)	0.017(2)	0.014(3)	0.008(2)
C22A	0.059(6)	0.060(7)	0.058(6)	0.020(4)	0.022(4)	0.019(4)
C23A	0.087(9)	0.079(8)	0.071(7)	0.056(6)	0.032(5)	0.017(6)
O2A	0.096(7)	0.052(4)	0.064(5)	0.018(4)	0.020(4)	0.017(4)
O1S	0.040(3)	0.042(3)	0.041(4)	0.016(3)	0.013(3)	0.009(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1S	0.048(6)	0.059(6)	0.051(6)	0.019(5)	0.028(5)	0.006(5)
P1A	0.034(2)	0.035(2)	0.027(2)	0.0130(16)	0.0085(16)	0.0148(18)
F1A	0.091(6)	0.051(4)	0.072(5)	0.031(3)	0.035(4)	0.020(3)
F2A	0.111(6)	0.103(6)	0.082(5)	0.068(4)	0.049(4)	0.061(4)
F3A	0.153(6)	0.079(4)	0.061(3)	0.003(3)	-0.043(4)	0.016(4)
F4A	0.053(2)	0.107(5)	0.151(6)	0.066(4)	0.053(3)	0.044(3)
F5A	0.104(4)	0.143(6)	0.106(5)	0.080(4)	0.069(4)	0.088(4)
F6A	0.110(5)	0.049(3)	0.054(2)	0.017(2)	-0.006(3)	-0.015(3)
O1B	0.038(5)	0.039(4)	0.035(3)	0.018(2)	0.016(3)	0.012(3)
C22B	0.038(4)	0.033(4)	0.031(4)	0.019(3)	0.011(3)	0.008(3)
C23B	0.068(6)	0.064(6)	0.058(5)	0.035(4)	0.028(5)	0.017(5)
O2B	0.066(4)	0.041(3)	0.058(4)	0.012(3)	0.021(3)	0.016(3)
O1T	0.043(4)	0.039(3)	0.037(4)	0.013(3)	0.013(3)	0.008(2)
C1T	0.057(7)	0.060(7)	0.066(9)	0.024(6)	0.020(6)	0.011(5)
P1B	0.057(4)	0.059(4)	0.050(3)	0.027(2)	0.013(2)	0.017(3)
F1B	0.080(5)	0.047(4)	0.057(4)	0.031(3)	0.014(3)	0.017(3)
F2B	0.104(5)	0.087(5)	0.060(3)	0.055(3)	0.022(3)	0.038(4)
F3B	0.060(3)	0.154(6)	0.087(4)	0.063(4)	-0.008(3)	-0.027(3)
F4B	0.135(6)	0.103(4)	0.067(3)	0.054(3)	0.064(3)	0.078(4)
F5B	0.157(6)	0.062(3)	0.088(4)	0.034(3)	0.090(4)	0.044(3)
F6B	0.052(2)	0.071(4)	0.124(5)	0.055(4)	-0.018(3)	-0.005(2)

Table S16. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 3b.

	x/a	y/b	z/c	U(eq)
H1	0.8157	0.2281	0.1446	0.052000
H2	1.0356	0.1876	0.2233	0.061000
H3	1.0459	0.1155	0.3576	0.065000
H4	0.8313	0.0875	0.4096	0.056000

	x/a	y/b	z/c	U(eq)
H6A	0.4921	0.0334	0.2814	0.046000
H6B	0.5881	0.1027	0.4008	0.046000
H9	0.2168	0.5100	0.4547	0.042000
H12	0.4467	0.1778	0.5238	0.041000
H14A	0.4163	0.5277	0.2716	0.048000
H14B	0.2614	0.5146	0.2973	0.048000
H16	0.0696	0.4687	0.1463	0.059000
H17	-0.0404	0.3526	-0.0333	0.075000
H18	0.0735	0.1973	-0.1300	0.073000
H19	0.2923	0.1584	-0.0471	0.062000
H20A	0.1142	0.5440	0.5914	0.077000
H20B	0.2048	0.5148	0.6861	0.077000
H20C	0.0607	0.4063	0.6019	0.077000
H21A	0.1891	0.2220	0.6384	0.076000
H21B	0.3167	0.3501	0.7201	0.076000
H21C	0.3584	0.2088	0.6656	0.076000
H23A	0.6148	0.4263	-0.0641	0.105000
H23B	0.4935	0.2868	-0.1186	0.105000
H23C	0.6659	0.2864	-0.1033	0.105000
H1S	0.4091	-0.0644	0.0397	0.061000
H1S1	0.1442	-0.0087	0.0268	0.077000
H1S2	0.2146	0.0351	0.1487	0.077000
H1S3	0.2010	-0.1160	0.0695	0.077000
H23D	0.5357	0.3877	-0.0865	0.088000
H23E	0.6280	0.2719	-0.1068	0.088000
H23F	0.7127	0.4262	-0.0391	0.088000
H1T	0.4091	-0.0644	0.0397	0.061000
H1T1	0.2026	0.0630	0.1277	0.092000
H1T2	0.2321	-0.0742	0.1369	0.092000
H1T3	0.1712	-0.0715	0.0251	0.092000

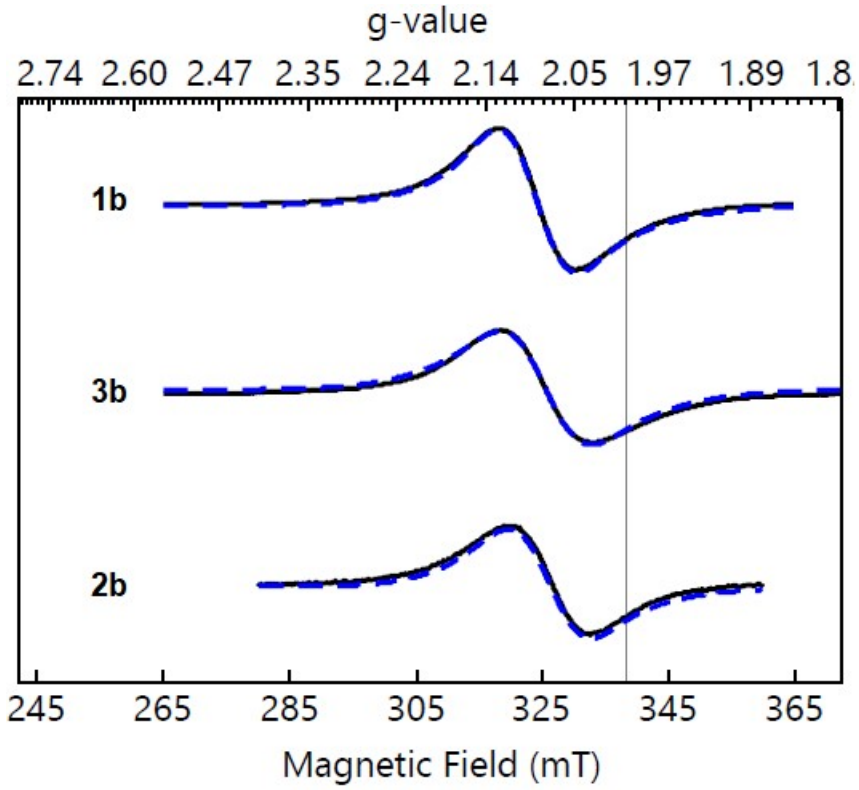


Figure S19: EPR data for complex **1b**, **2b**, and **3b** in acetonitrile at LNT.

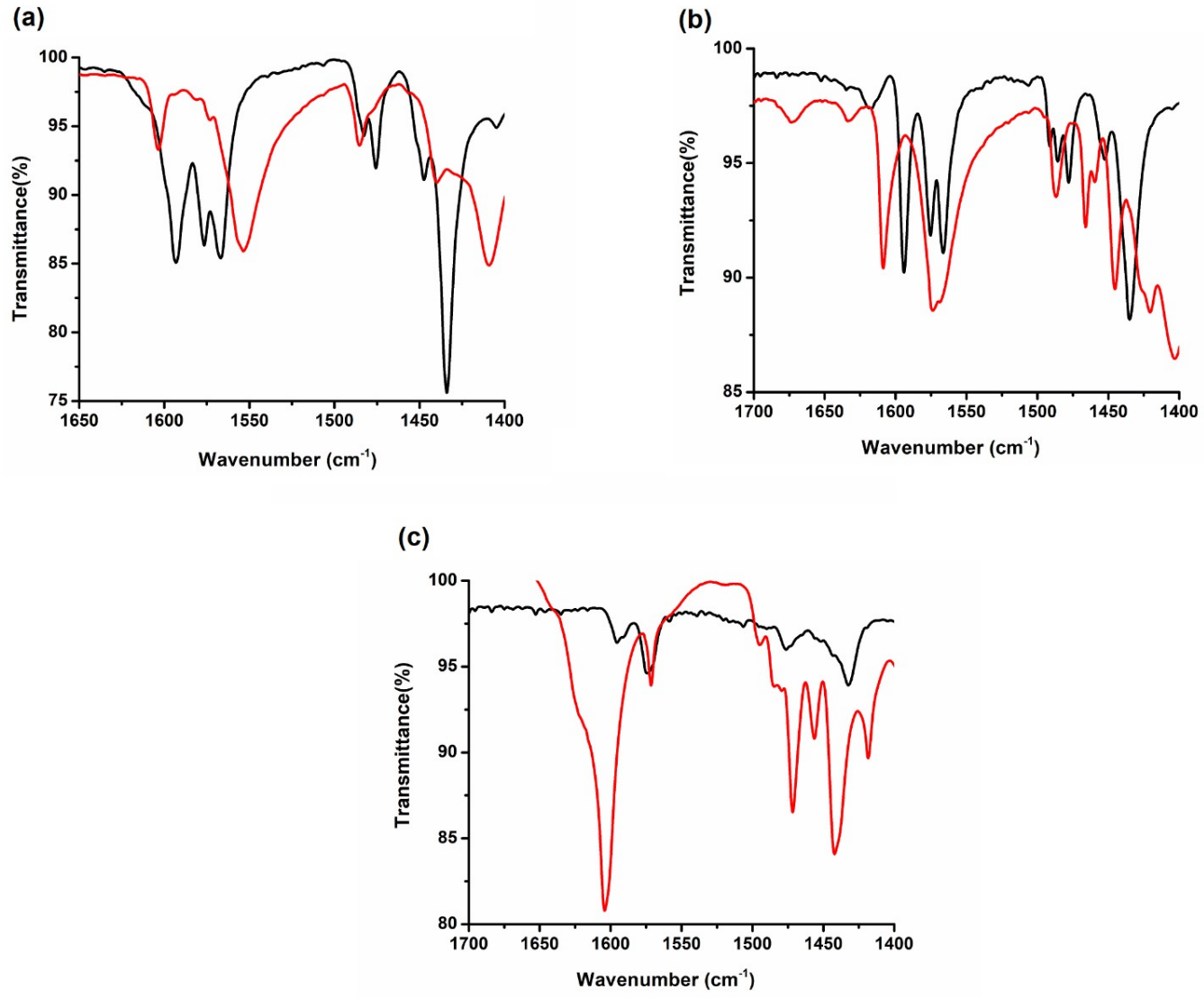


Figure S20: FT-IR spectra of (a) Comparison of compound **1a** (black) and complex **1b** (red), (b) Comparison of compound **2a** (black) and complex **2b** (red), (c) Comparison of compound **3a** (black) and complex **3b** (red).

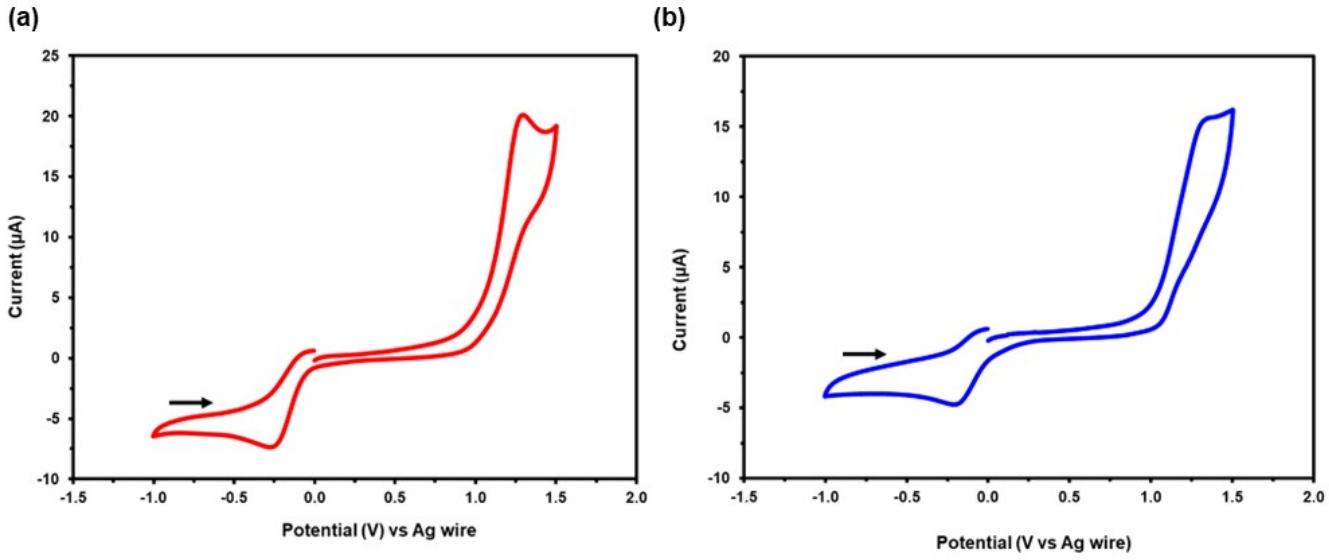


Figure S21: Cyclic voltammograms of (**a**) **1b** (red), and (**b**) **3b** (blue) in the absence of Fc.

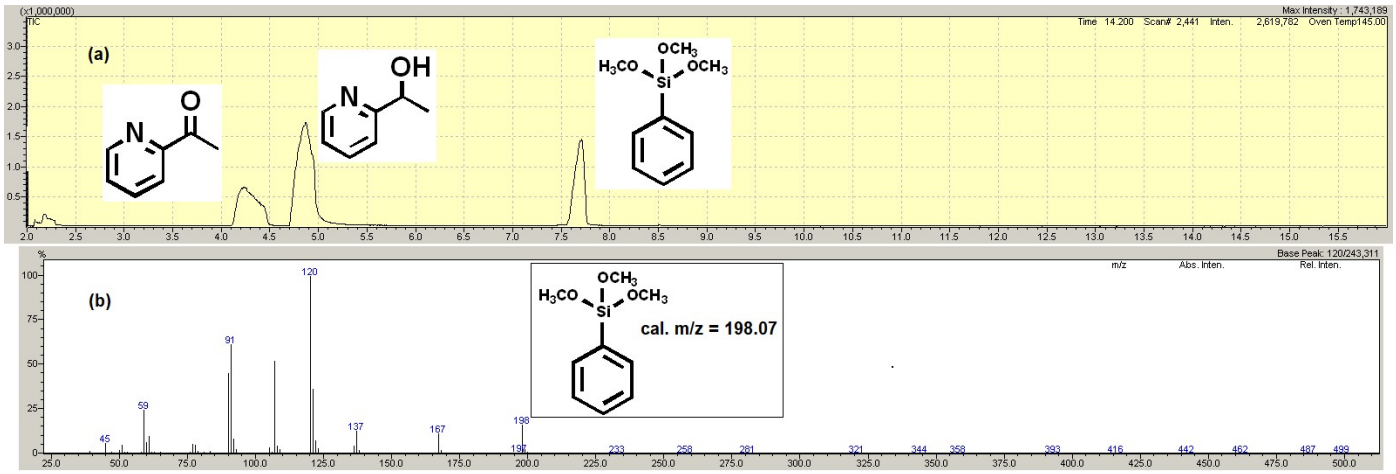


Figure S22: (a) GC for the hydrogenation of ketone in methanol as solvent, showing 2-acetylpyridine, 1-(pyridin-2-yl)ethan-1-ol and silylated byproduct containing the -OCH_3 moieties. (b) Mass spectrum obtained from GC showing the formation of the methoxysilyl byproduct at 198 m/z.

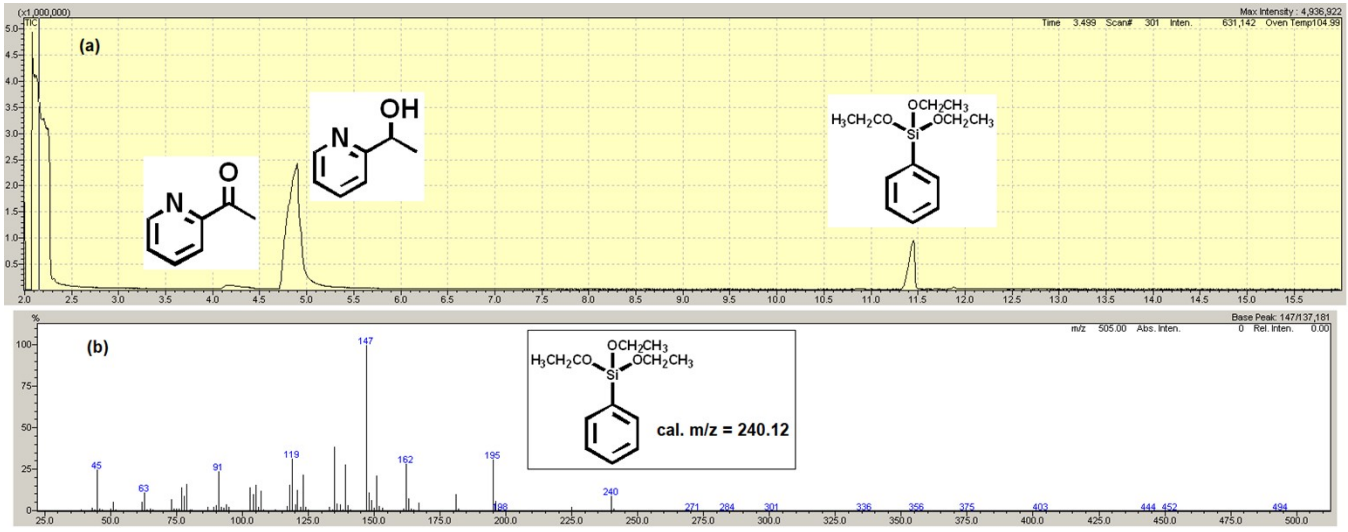
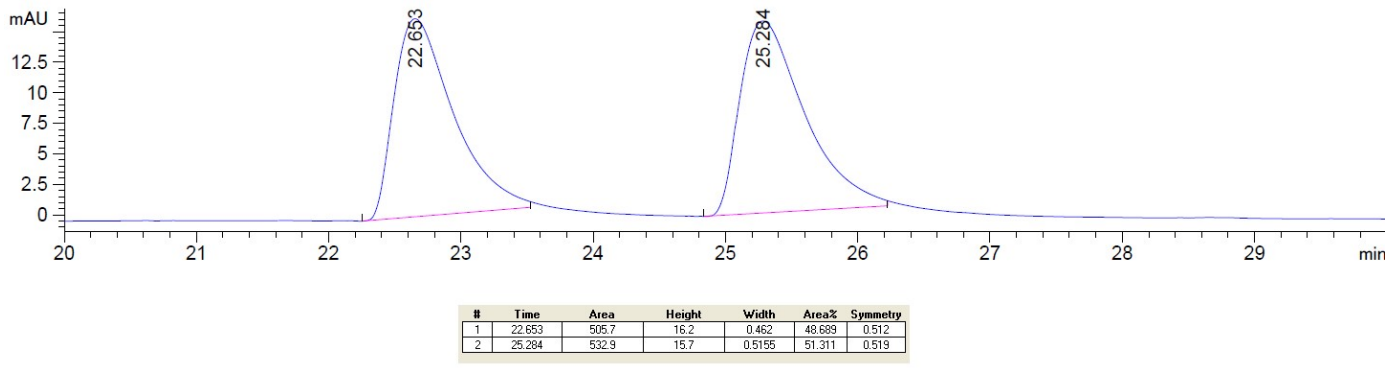


Figure S23: (a) GC for the hydrogenation of ketone in ethanol as solvent, showing 2-acetylpyridine, 1-(pyridin-2-yl)ethan-1-ol and silylated byproduct containing the -OCH_2CH_3 moieties. (b) Mass spectrum obtained from GC showing the formation of the ethoxysilyl byproduct at 240 m/z.



#	Time	Area	Height	Width	Area%	Symmetry
1	22.653	505.7	16.2	0.462	48.689	0.512
2	25.284	532.9	15.7	0.5155	51.311	0.519

Figure S24: LC-MS data showing the *R*- and *S*- isomer alcohol products of 2-acetylpyridine hydrogenation using a Chiralpak IB N-5 analytical column.

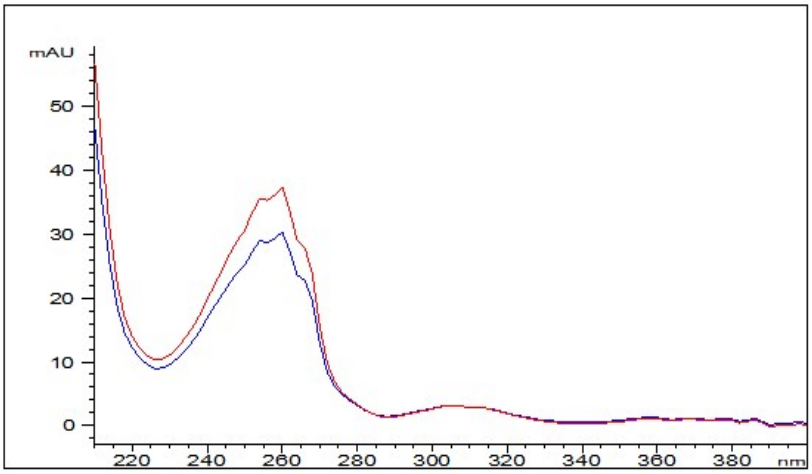


Figure S25: UV-vis data of the *R*- and *S*-isomer alcohol product of 2-acetylpyridine hydrogenation obtained from LC-MS.

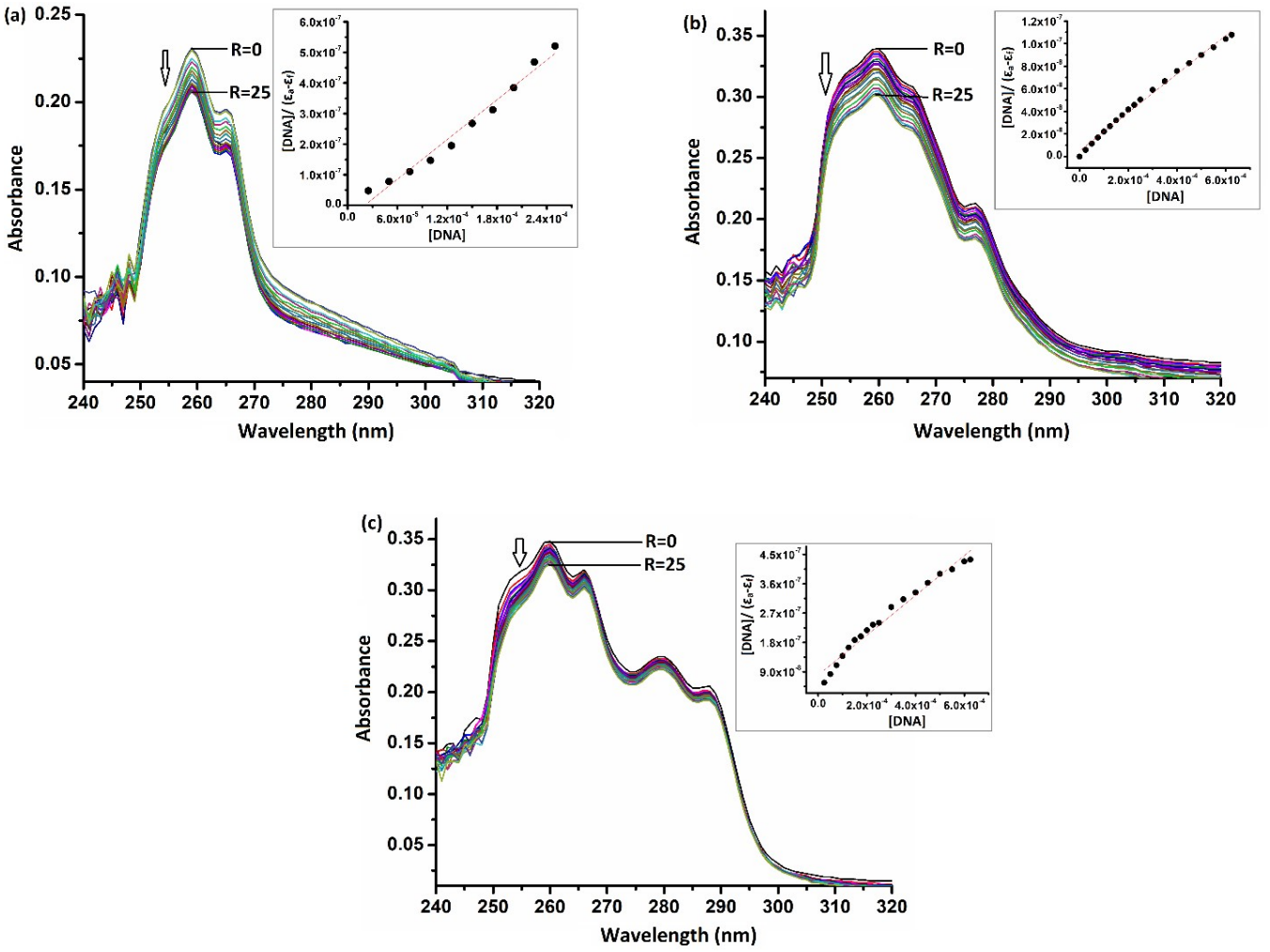


Figure S26: Absorption spectra of (a) **1b**, (b) **2b**, and (c) **3b** in 5 mM Tris-HCl buffer at pH 7.1, in the absence (R = 0) and presence (R = 1–25) of increasing amounts of CT DNA. Insets: the plot of [DNA] vs. [DNA]/(εa − εf) at R = 25 of the complex **1b**, **2b**, and **3b**.

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