Supplementary Materials: Imidazo-Phenanthroline Ligands as a Convenient Modular Platform for the Preparation of Heteroleptic Cu(I) Photosensitizers

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1. NMR Spectra of the Complexes C1–C4

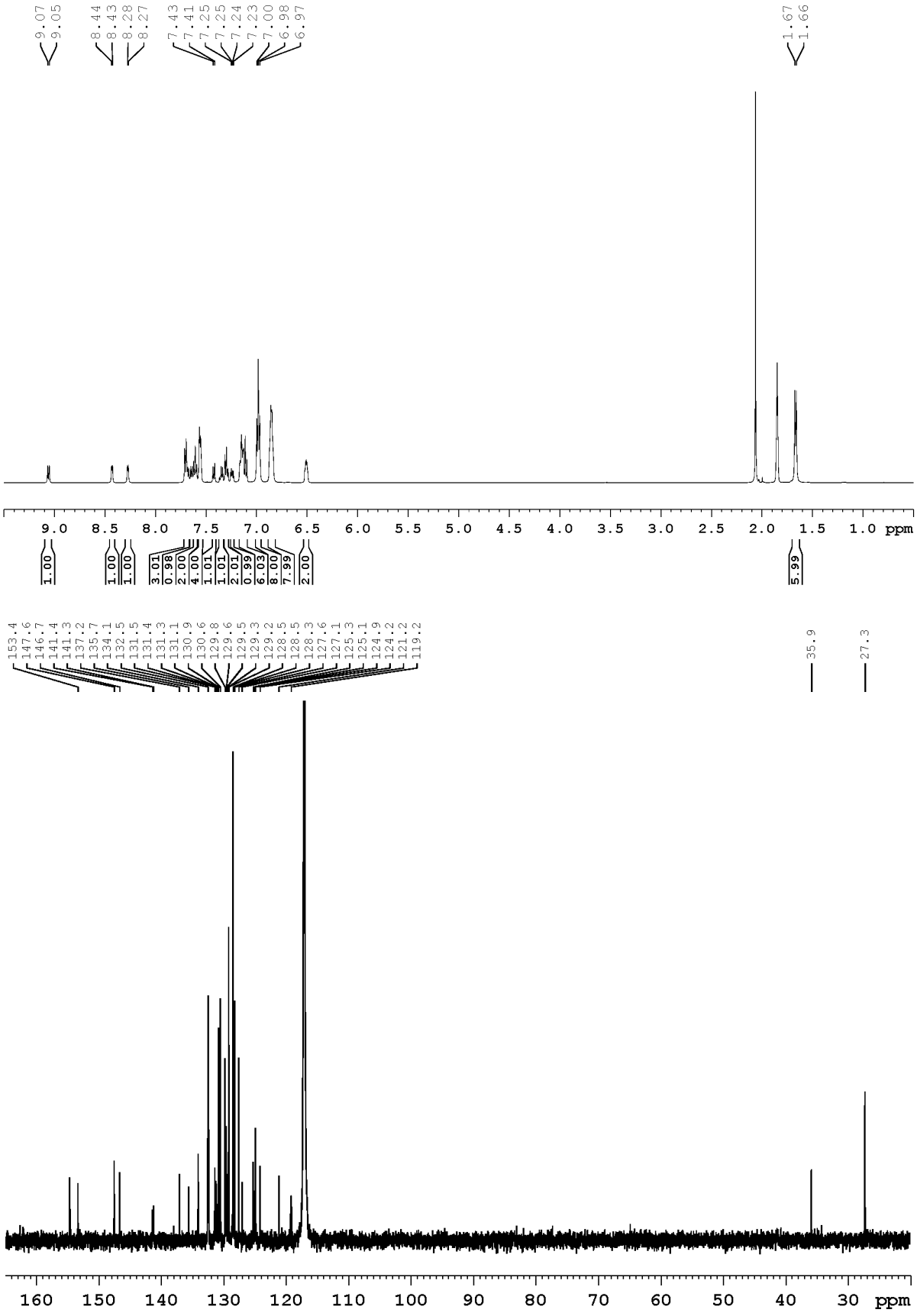


Figure S1. Presentation of the ^{1}H-NMR (top, 500 MHz) and ^{13}C-NMR (bottom, 126 MHz) spectra of **C1** in CD_3CN.

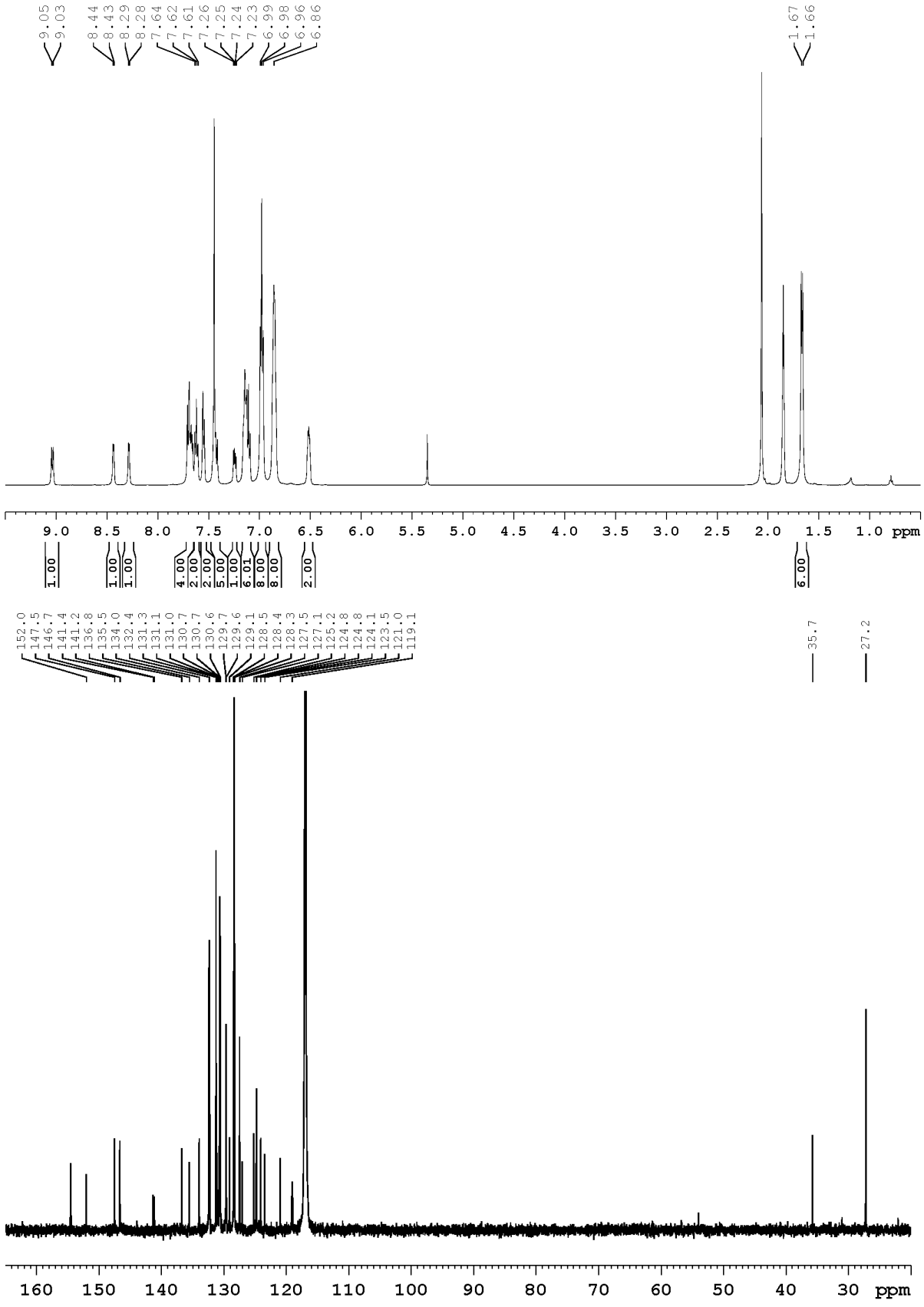


Figure S2. Presentation of the ^{1}H-NMR (top, 500 MHz) and ^{13}C-NMR (bottom, 126 MHz) spectra of **C2** in CD_3CN.

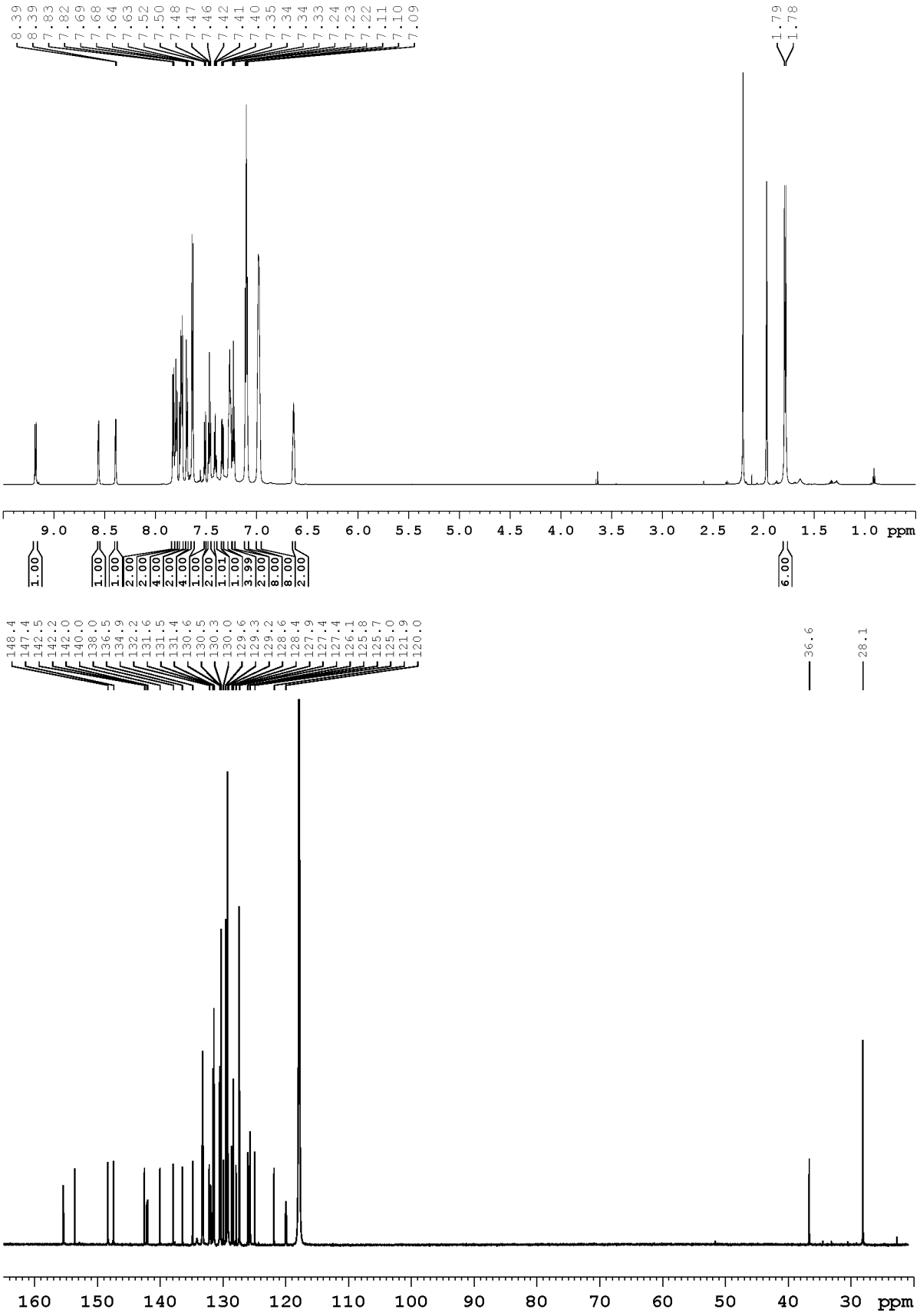


Figure S3. Presentation of the ^{1}H-NMR (top, 700 MHz) and ^{13}C-NMR (bottom, 176 MHz) spectra of **C3** in CD_3CN.

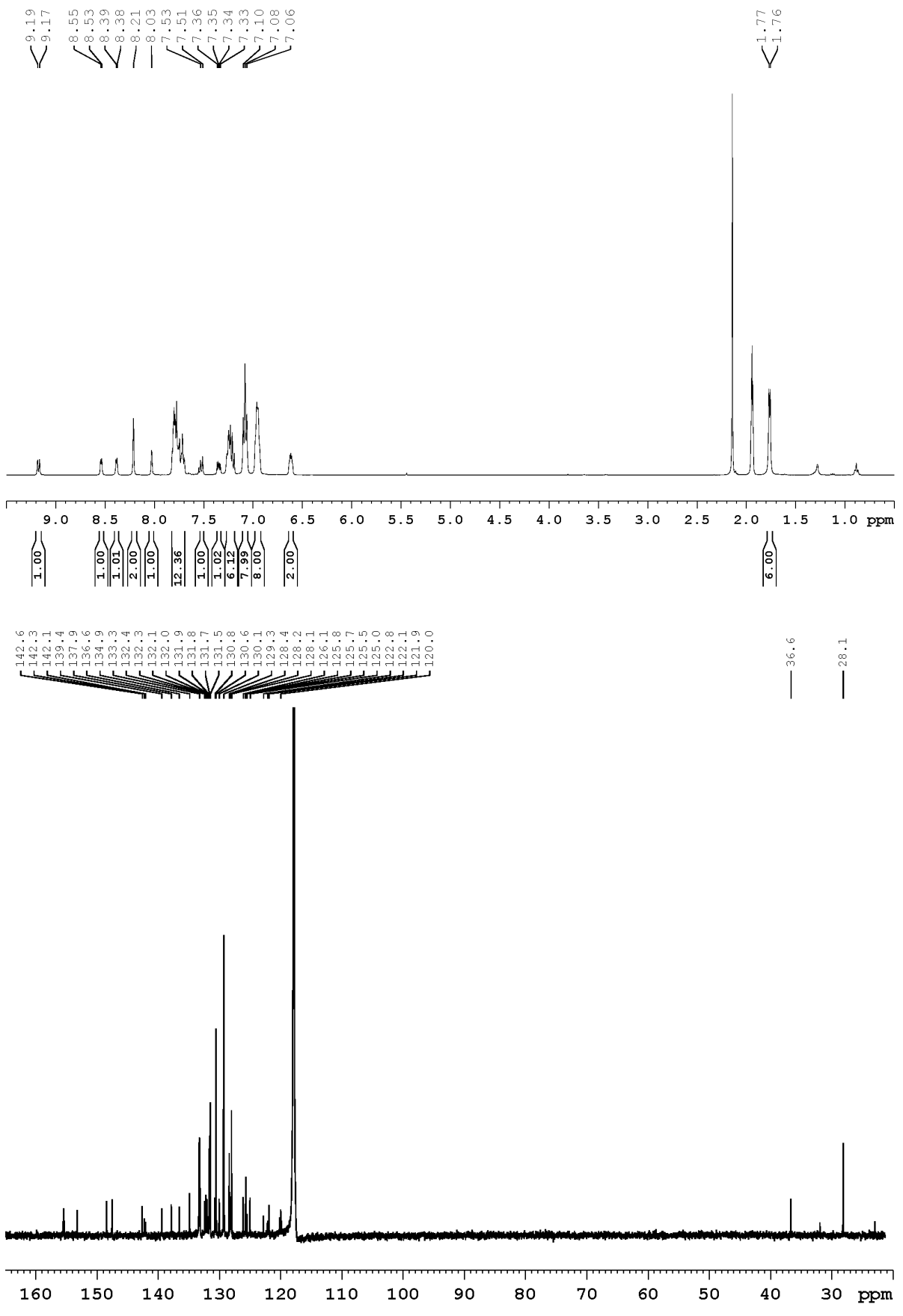


Figure S4. Presentation of the ^{1}H-NMR (top, 400 MHz) and ^{13}C-NMR (bottom, 101 MHz) spectra of **C4** in CD_3CN.

2. Mass Spectra of the Complexes C1–C4

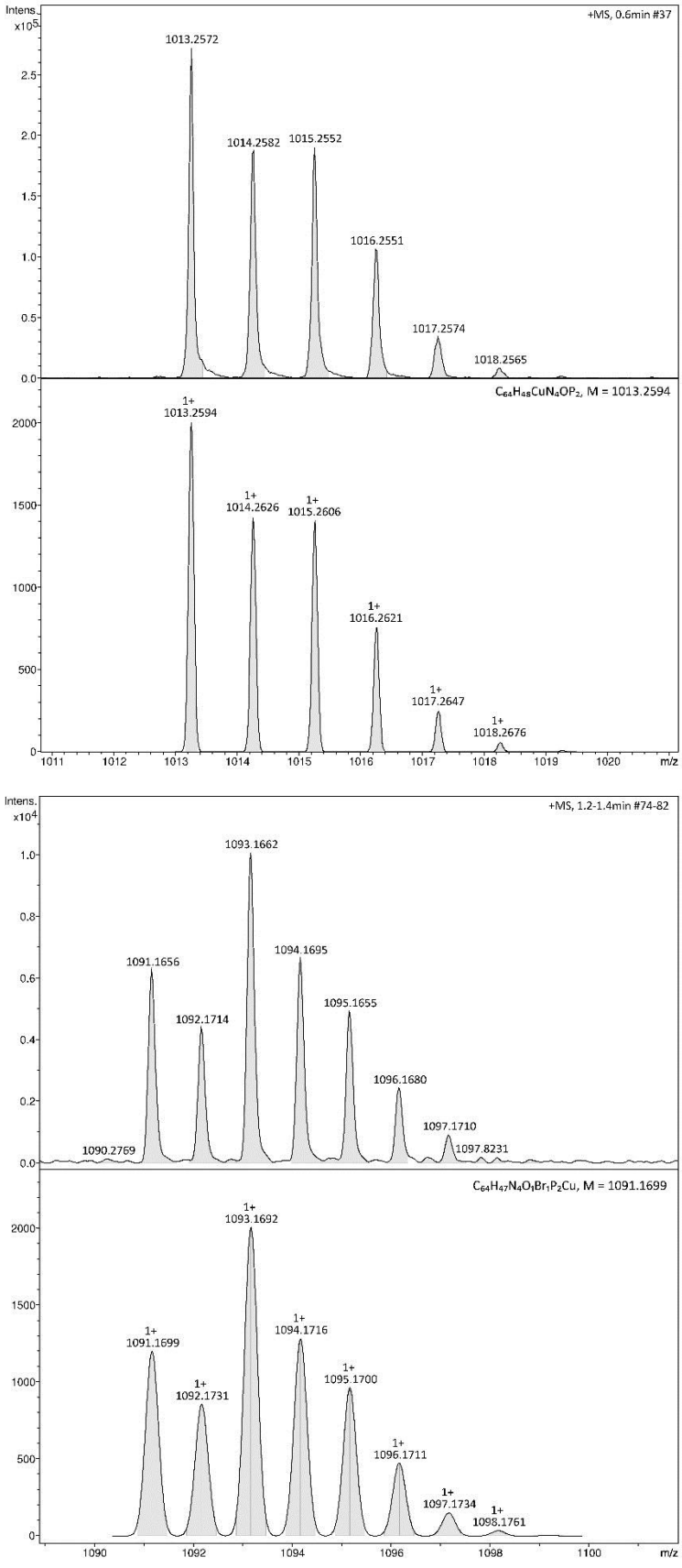


Figure S5. High resolution ESI mass spectra of the complexes **C1** (top) and C**2** (bottom) with matching isotopic pattern.

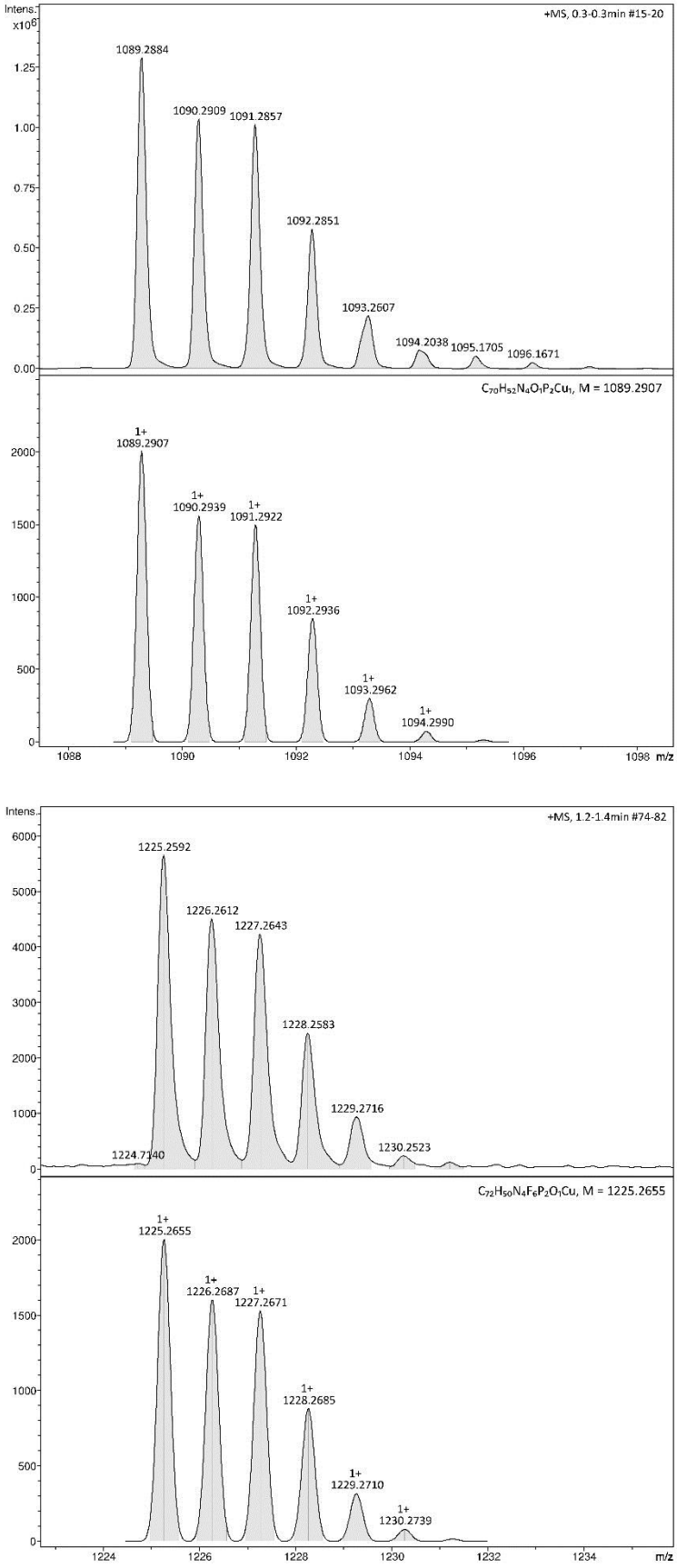


Figure S6. High resolution ESI mass spectra of the complexes **C3** (top) and C**4** (bottom) with matching isotopic pattern.

3. Crystallographic Data and Structures of C1 and C2

Table S1. Crystallographic data and refinement details of the heteroleptic copper complexes **C1** and **C2**.

Compound	C1	C2
CCDC number [#]	187 5532	187 5530
Empirical formula	$C_{65}H_{50}Cl_2CuF_6N_4OP_3$	$C_{65}H_{49}BrCl_2CuF_6N_4OP_3$
Formula weight (g mol^{-1})	1244.44	1323.34
Temperature (K)	130(2)	130(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, P2(1)/n	Monoclinic, P 21/c
Unit cell dimensions (Å, °)		
a	12.1254(10)	9.8687(8)
b	13.9304(12)	27.521(2)
c	40.007(3)	21.7494(17)
α	90	90
β	93.564(4)	95.369(2)
γ	90	90
Volume (Å^3)	6744.6(10)	5881.2(8)
Z, calculated density (Mg m^{-3})	4, 1.226	4, 1.495
Absorption coefficient (mm^{-1})	0.532	1.290
F(000)	2552	2688
Crystal size (mm)	0.306 x 0.212 x 0.188	0.22 x 0.05 x 0.05
Theta range for data collection (°)	1.548 to 25.473	1.48 to 25.07
Limiting indices	-14<=h<=14, -16<=k<=15, -45<=l<=48	-11<=h<=11, -32<=k<=24, -22<=l<=25
Reflections collected / unique	39834 / 12284 [R(int) = 0.0732]	40422 / 10384 [R(int) = 0.1441]
Completeness to theta = 25.242 (%)	98.9	99.4
Absorption correction	Numerical	Semi-empirical from equivalents
Max. and min. transmission	0.7277 and 0.4801	0.7452 and 0.6284
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	12284 / 54 / 741	10384 / 0 / 751
Goodness-of-fit on F^2	1.047	1.036
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.1232, wR2 = 0.2599	R1 = 0.0700, wR2 = 0.0918
R indices (all data)	R1 = 0.1986, wR2 = 0.2824	R1 = 0.1811, wR2 = 0.1047
Largest diff. peak and hole (e.Å^{-3})	0.749 and -0.869	0.690 and -0.675

[#] CCDC 1875532 (**C1**) and 1875530 (**C2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge by the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html

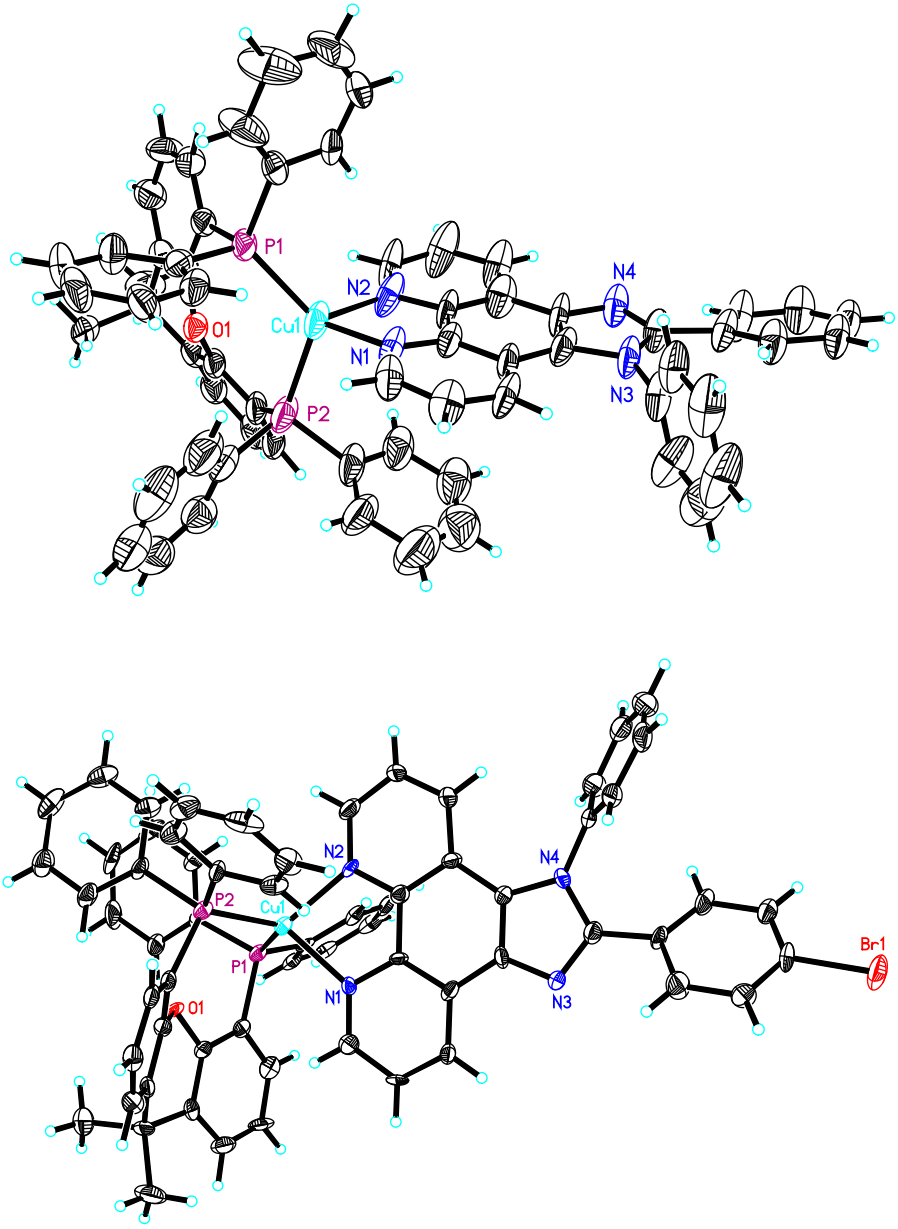


Figure S7. Comparison of the solid-state structures (ORTEP representation) of the complexes **C1** (top) and **C2** (bottom) with thermal ellipsoids at a probability level of 50%. The PF_6^- counter anion is omitted for clarity in both cases. In contrast to Figure 4 of the main text all hydrogen atoms are shown and a different orientation of the molecules are presented.

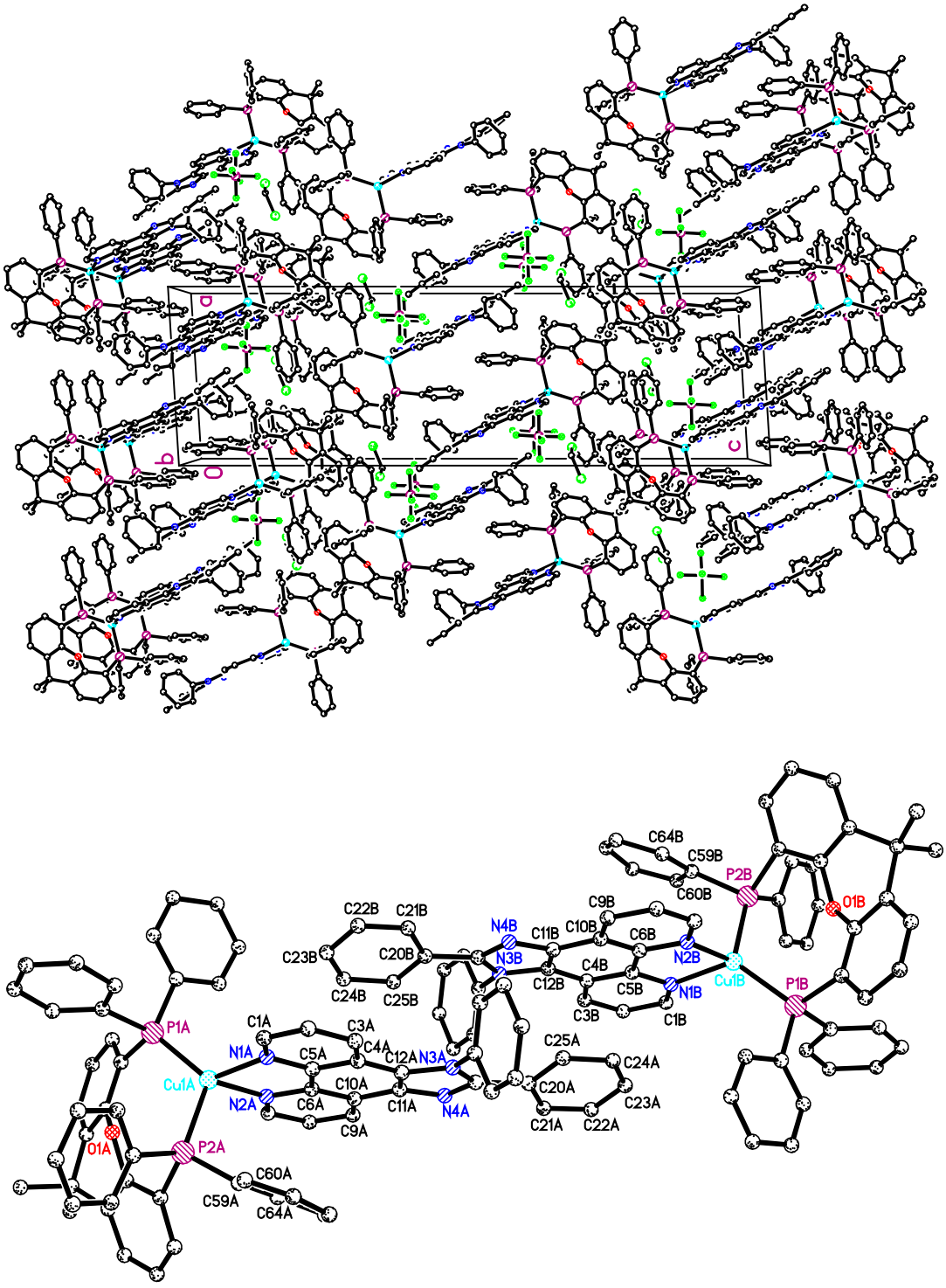
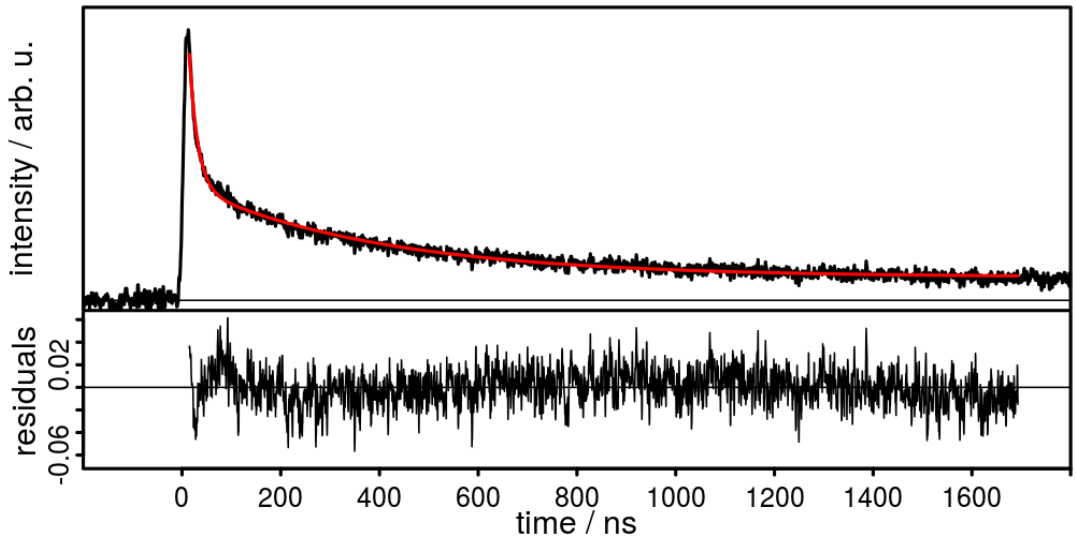
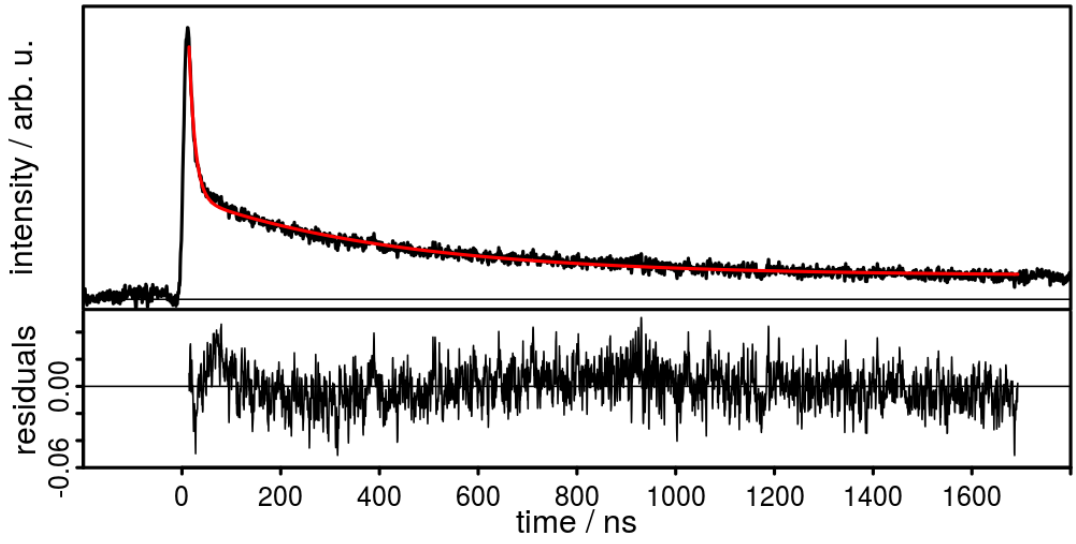


Figure S8. ORTEP representation of the unit cell of complex **C1** (top). The hydrogen atoms and PF_6^- counter ions are omitted for clarity. In the solid state a pairwise stacking of the complex **C1** is found, which is caused by π-π-interactions between the phenyl ring of **L1** of neighboring complexes. The distance between the two neighboring imidazo-phenanthroline ligands is about 3.3 to 3.8 Å. The bottom picture shows an enlargement of the packing situation.

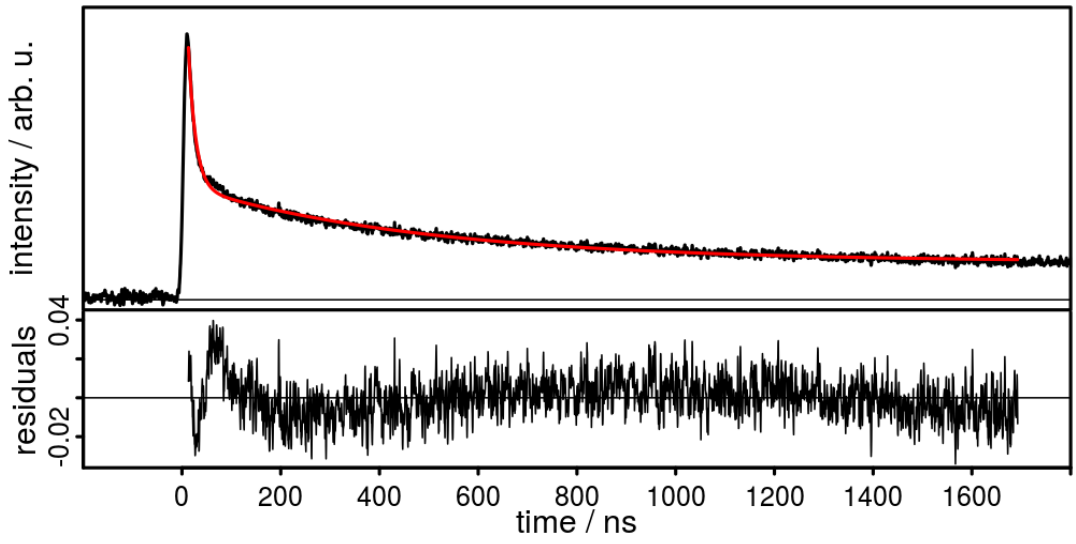
4. Emission Lifetimes of the Complexes C1–C4 and R1



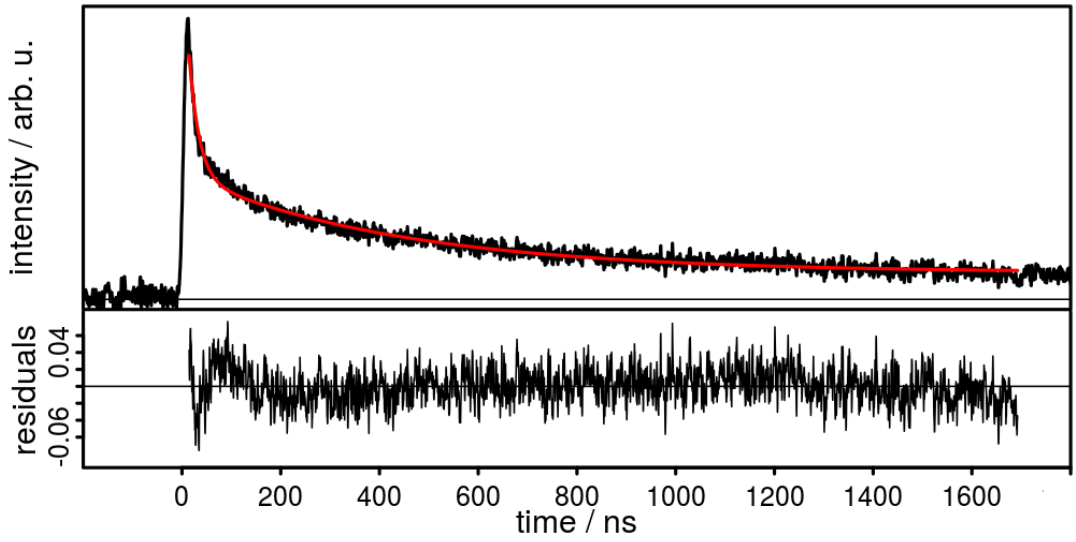
(a)



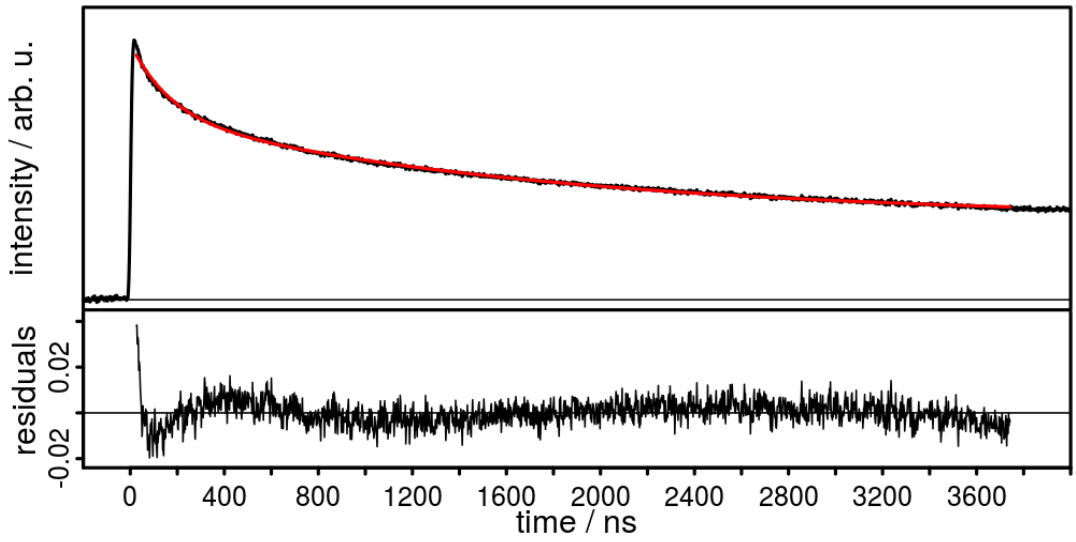
(b)



(c)



(d)



(e)

Figure S9. Emission lifetime measurements of the complexes **C1**-**C4** (panels **(a)**-**(d)**) and the reference **R1** (panel **(e)**). All spectra were detected of the solid samples at room temperature. The black line in the upper part of each panel is the emission intensity decay over time, respectively. The red line represents the double exponential fit of the lifetimes (the corresponding time constants are reported in the main manuscript - Table 2). In the lower half of each panel the residuals of the fit are depicted.