Electronic Supplementary Information for

Photophysical properties of three-coordinate heteroleptic Cu(I) β-diketiminate triarylphosphine complexes

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Table S1. Crystallographic summary for **Cu1** and **Cu2**.

	Cu(PhNacNac^{Me})(PPh_3) (**Cu1**)	Cu(PhNacNac^{Me})(PPh_3^{F3}) (**Cu2**)
CCDC	2382410	2382411
Crystal data		
Chemical formula	$C_{35}H_{32}CuN_2P$	$C_{35}H_{29}CuF_3N_2P$
M_r	575.13	629.11
Crystal system, space group	Triclinic, $P\overline{1}$	Orthorhombic, *Pbca*
Temperature (K)	123	123
a, b, c (Å)	8.7263 (9), 12.4897 (12), 13.9463 (14)	16.709 (4), 17.529 (4), 20.332 (5)
α, β, γ (°)	98.878 (1), 107.371 (1), 92.195 (1)	90, 90, 90
V (Å^3)	1427.5 (2)	5955 (2)
Z	2	8
μ (mm^{-1})	0.85	0.83
Crystal size (mm)	0.47 × 0.40 × 0.25	0.45 × 0.37 × 0.29
Data collection		
T_{min}, T_{max}	0.629, 0.746	0.646, 0.746
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	20264, 6557, 5861	35583, 6819, 5734
R_{int}	0.027	0.052
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.075, 1.06	0.032, 0.084, 1.06
No. of reflections	6557	6819
No. of parameters	354	381
No. of restraints	0	0
	w = $1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.5015P]$ where $P = (F_o^2 + 2F_c^2)/3$	w = $1/[\sigma^2(F_o^2) + (0.0366P)^2 + 1.6659P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.39	0.35, −0.39

Table S2. Crystallographic summary for **Cu3** and **Cu4**.

	Cu(PhNacNac^{Me})(PPh^{OMe3}) (**Cu3**)	Cu(CyNacNac^{Me})(PPh$_3$) (**Cu4**)
CCDC	2382412	2382413
Crystal data		
Chemical formula	$C_{38}H_{38}CuN_2O_3P$	$C_{35}H_{44}CuN_2P$
M_r	665.21	587.23
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $P2_12_12_1$
Temperature (K)	123	123
a, b, c (Å)	11.3887 (16), 26.548 (4), 11.0375 (15)	11.642 (2), 14.434 (3), 21.728 (4)
α, β, γ (°)	90, 100.983 (2), 90	90, 90, 90
V (Å^3)	3276.0 (8)	3651.5 (11)
Z	4	4
μ (mm^{-1})	0.76	0.66
Crystal size (mm)	0.48 × 0.46 × 0.21	0.41 × 0.19 × 0.18
Data collection		
T_{min}, T_{max}	0.628, 0.746	0.859, 1.000
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	16937, 5776, 5234	21094, 7444, 7075
R_{int}	0.025	0.026
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595	0.626
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.071, 1.05	0.021, 0.051, 1.02
No. of reflections	5776	7444
No. of parameters	411	354
No. of restraints	0	0
	w = $1/[\sigma^2(F_o^2) + (0.0318P)^2 + 1.6905P]$ where P = $(F_o^2 + 2F_c^2)/3$	w = $1/[\sigma^2(F_o^2) + (0.0223P)^2]$ where P = $(F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.36	0.25, −0.18

Table S3. Crystallographic summary for **Cu5** and **Cu6**.

	$Cu(PhNacNac^{CF3})(PPh_3)$ (**Cu5**)	$Cu(dmpNacNac^{Me})(PPh_3)$ (**Cu6**)
CCDC	2382415	2382416
Crystal data		
Chemical formula	$C_{35}H_{26}CuF_6N_2P$	$C_{39}H_{40}CuN_2P$
M_r	683.09	631.24
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	123	183
a, b, c (Å)	8.8151 (15), 12.675 (2), 14.113 (2)	10.5139 (14), 20.262 (3), 16.342 (2)
α, β, γ (°)	98.290 (2), 108.137 (2), 92.018 (2)	90, 104.617 (2), 90
V (Å^3)	1477.5 (4)	3368.6 (8)
Z	2	4
μ (mm^{-1})	0.86	0.73
Crystal size (mm)	0.45 × 0.42 × 0.39	0.48 × 0.46 × 0.08
Data collection		
T_{min}, T_{max}	0.609, 0.746	0.663, 0.746
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	21107, 6845, 6277	21049, 7717, 6142
R_{int}	0.026	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.652	0.651
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.078, 1.05	0.035, 0.090, 1.06
No. of reflections	6845	7717
No. of parameters	406	394
No. of restraints	0	0
	$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.6812P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.4856P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.63	0.25, −0.36

Table S4. Crystallographic summary for **Cu7** and **Cu8**.

	Cu(dmpNacNac^{Me})(PPh^{OMe3})•Et_2O (**Cu7**•Et_2O)	Cu(dippNacNac^{Me})(PPh_3) (**Cu8**)
CCDC	2382417	2382418
Crystal data		
Chemical formula	$C_{44}H_{51}CuN_2O_{3.50}P$	$C_{47}H_{56}CuN_2P$
M_r	758.37	743.44
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	123	123
a, b, c (Å)	9.7777 (16), 42.541 (7), 10.8917 (18)	23.339 (3), 15.8665 (19), 24.171 (3)
α, β, γ (°)	113.821 (2)	111.832 (2)
V (Å^3)	4144.5 (12)	8308.5 (17)
Z	4	8
μ (mm^{-1})	0.61	0.60
Crystal size (mm)	0.39 × 0.23 × 0.08	0.40 × 0.16 × 0.10
Data collection		
T_{min}, T_{max}	0.612, 0.746	0.689, 0.746
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	22454, 8781, 6947	49826, 18268, 12937
R_{int}	0.056	0.039
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.633	0.641
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.115, 0.261, 1.25	0.039, 0.099, 1.03
No. of reflections	8781	18268
No. of parameters	496	939
No. of restraints	34	0
	w = 1/[s^2(F_o^2) + (0.0316P)^2 + 45.0264P] where P = (F_o^2 + 2F_c^2)/3	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, -1.55	0.36, -0.36

Table S5. Crystallographic summary for **Cu9**.

	Cu(dippNacNac^{Me})(PPh^{OMe3}) •0.5C_6H_{14} (**Cu9**•0.5C_6H_{14})
CCDC	2382419
Crystal data	
Chemical formula	$C_{53}H_{68}CuN_2O_3P$
M_r	875.60
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	123
a, b, c (Å)	11.644 (5), 13.759 (5), 16.739 (6)
α, β, γ (°)	104.706 (5), 90.348 (5), 101.897 (5)
V (Å^3)	2533.3 (17)
Z	2
μ (mm^{-1})	0.50
Crystal size (mm)	0.42 × 0.40 × 0.23
Data collection	
T_{min}, T_{max}	0.687, 0.746
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	34092, 10746, 8533
R_{int}	0.053
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.633
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.148, 1.05
No. of reflections	10746
No. of parameters	582
No. of restraints	55
	$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 1.4460P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.27, −0.38

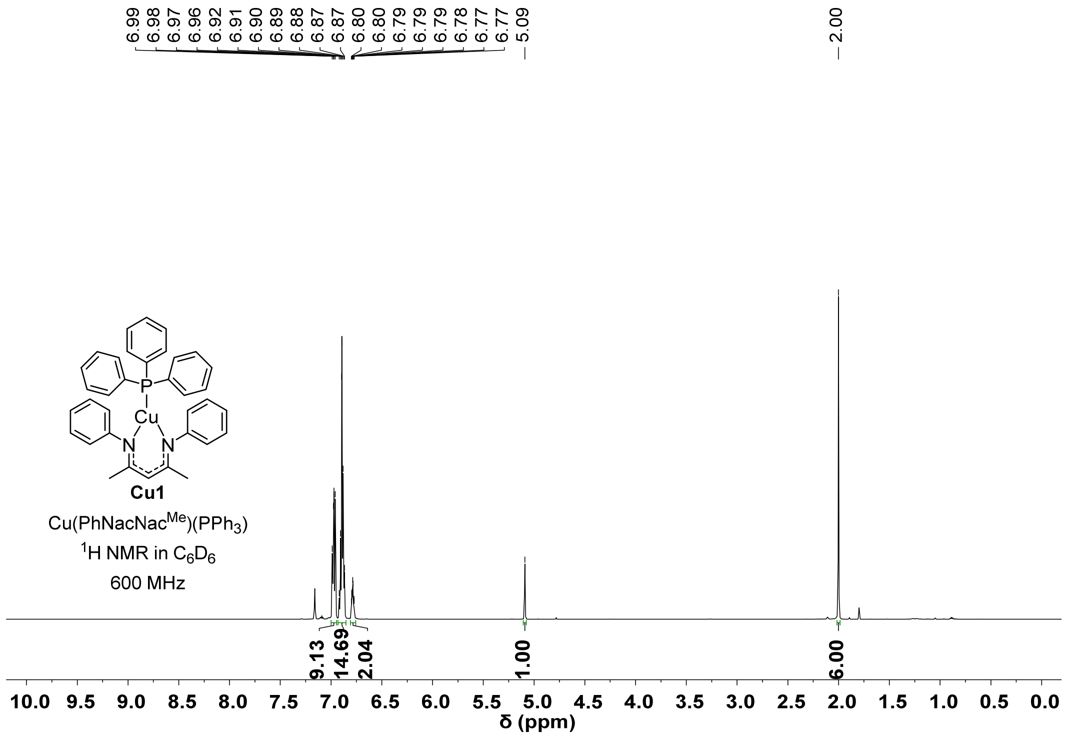


Fig. S1. ^{1}H NMR spectrum of complex **Cu1**, recorded at 600 MHz in C_6D_6.

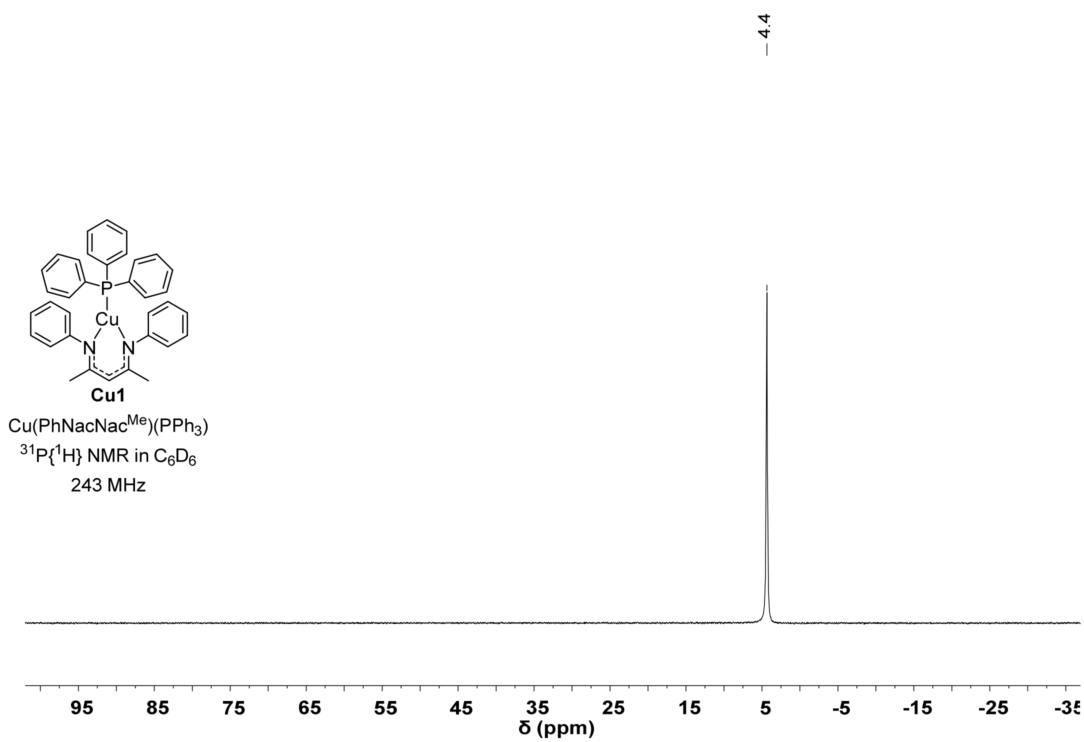


Fig. S2. $^{31}P\{^1H\}$ NMR spectrum of complex **Cu1**, recorded at 243 MHz in C_6D_6.

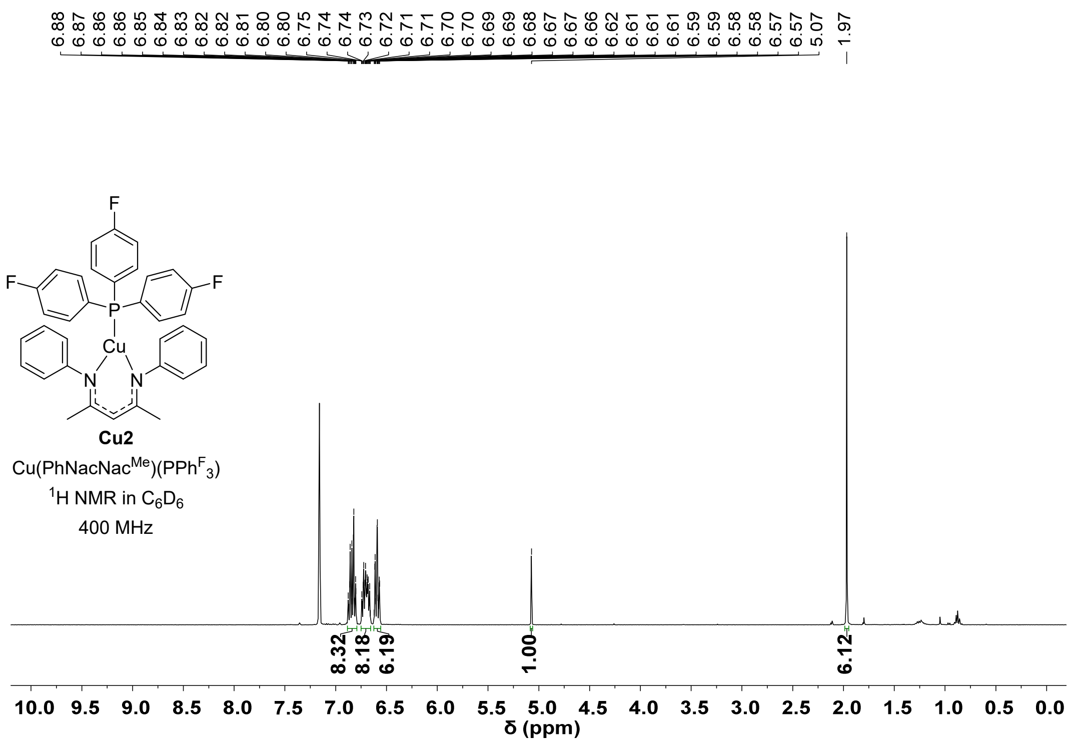


Fig. S3. ^{1}H NMR spectrum of complex **Cu2**, recorded at 400 MHz in C_6D_6.

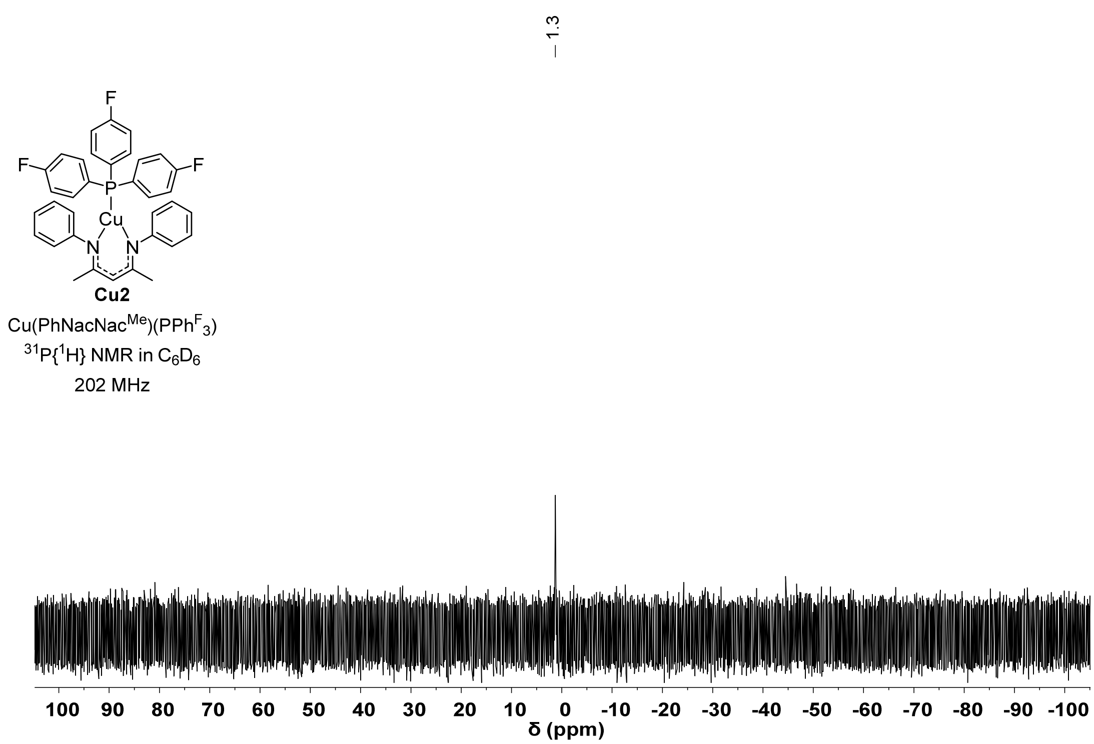


Fig. S4. ^{31}P{^{1}H} NMR spectrum of complex **Cu2,** recorded at 202 MHz in C_6D_6.

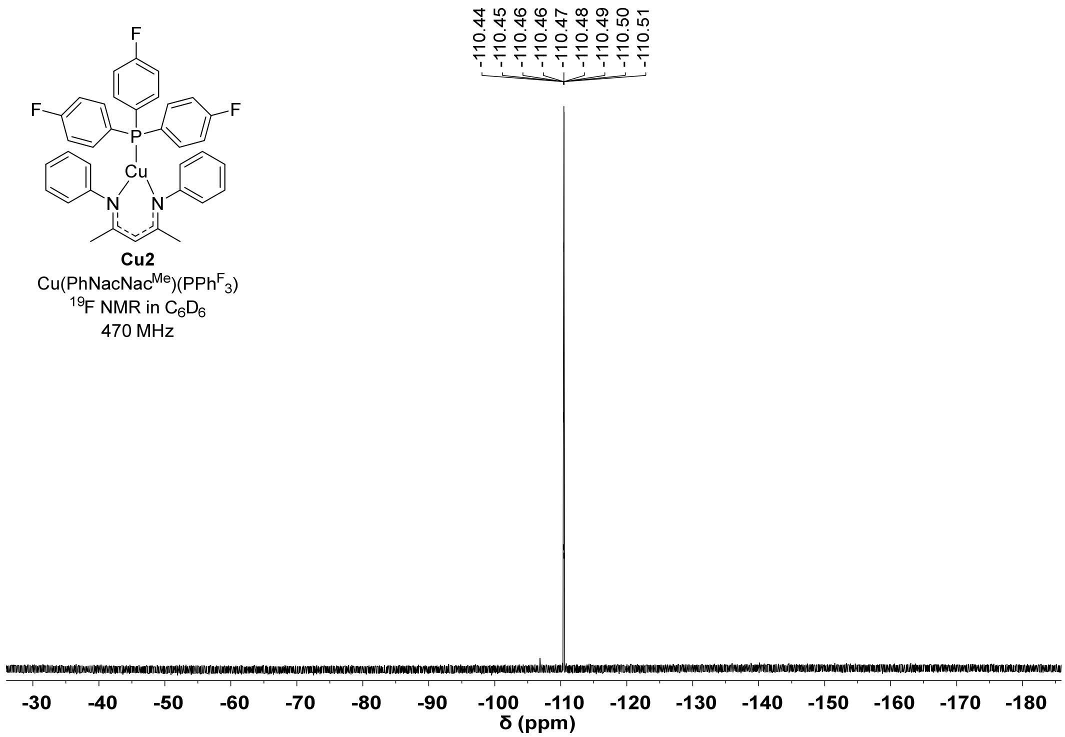


Fig. S5. ^{19}F NMR spectrum of complex **Cu2,** recorded at 470 MHz in C_6D_6.

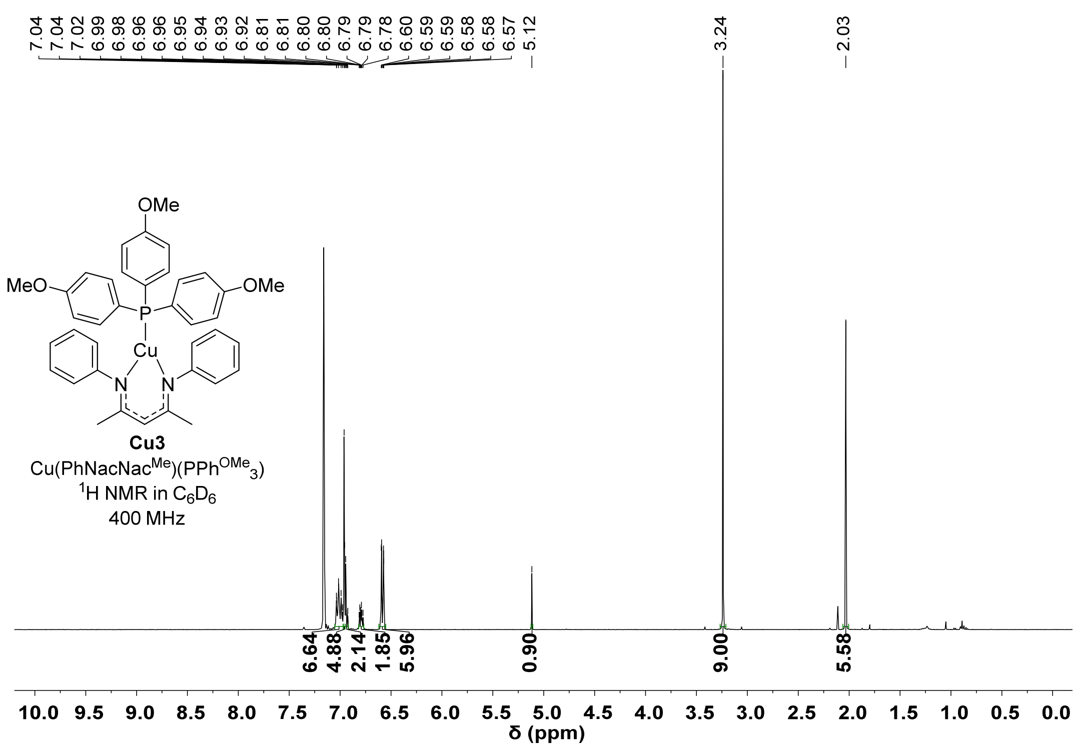


Fig. S6. ^{1}H NMR spectrum of complex **Cu3,** recorded at 400 MHz in C_6D_6.

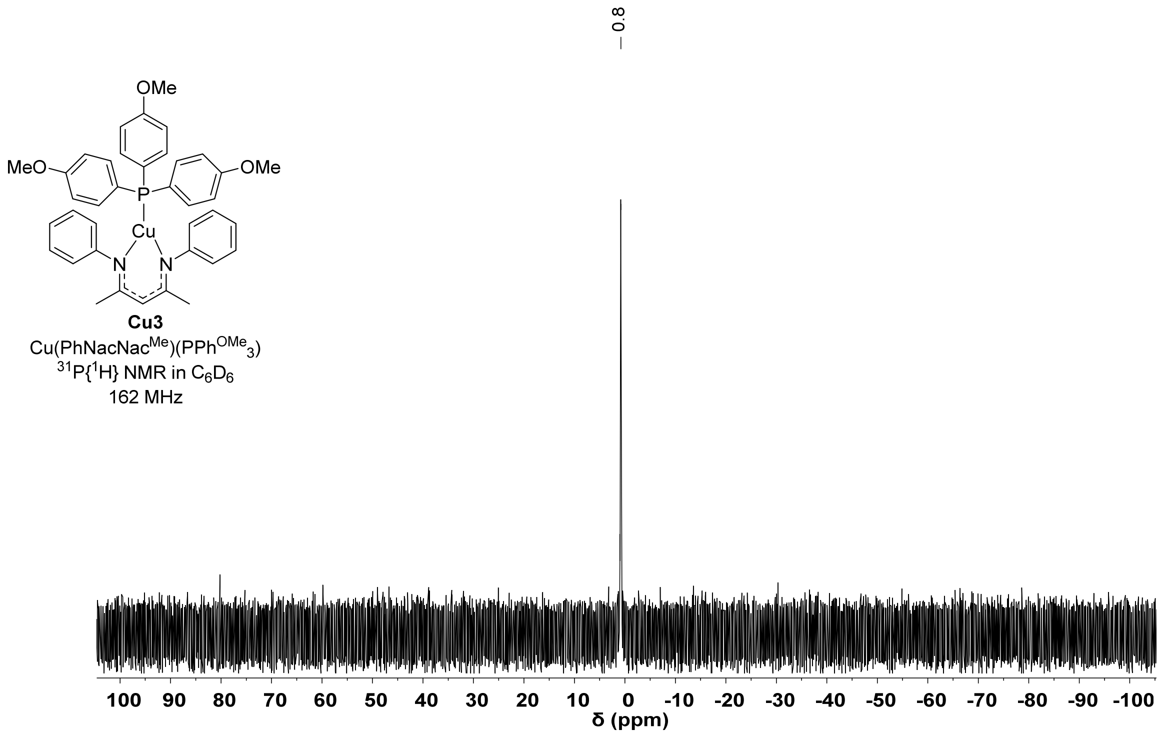


Fig. S7. ^{31}P{^{1}H} NMR spectrum of complex **Cu3,** recorded at 162 MHz in C_6D_6.

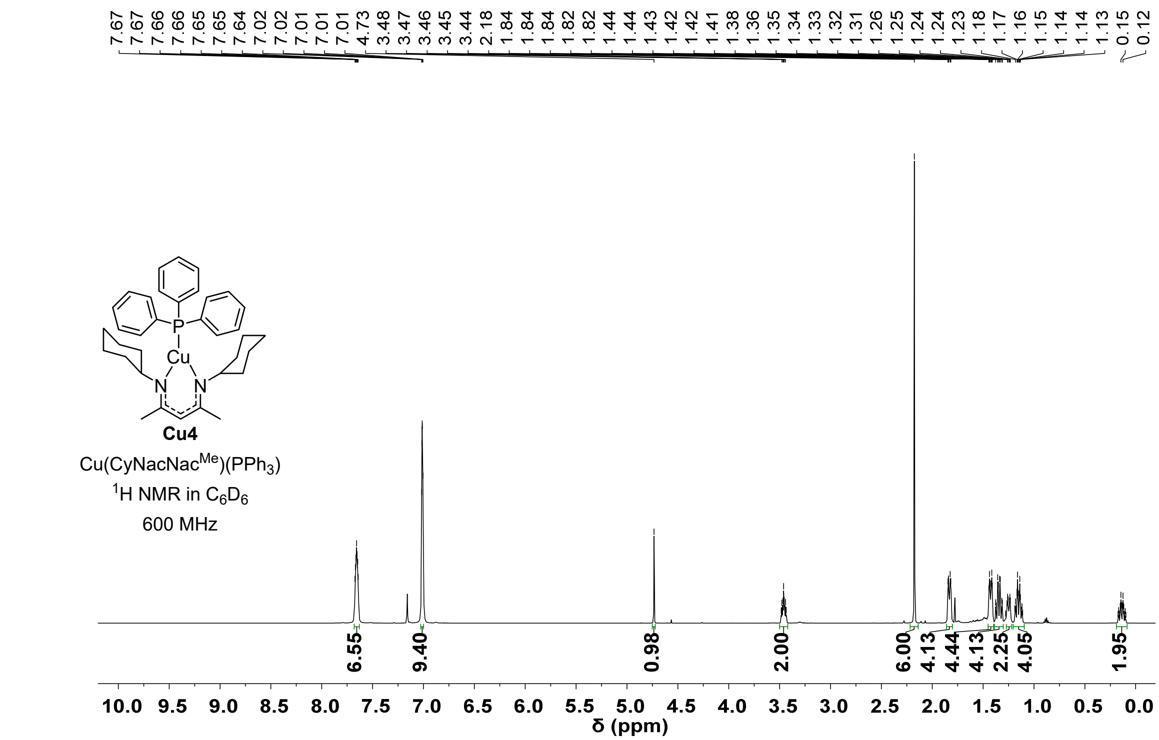


Fig. S8. ^{1}H NMR spectrum of complex **Cu4**, recorded at 600 MHz in C_6D_6.

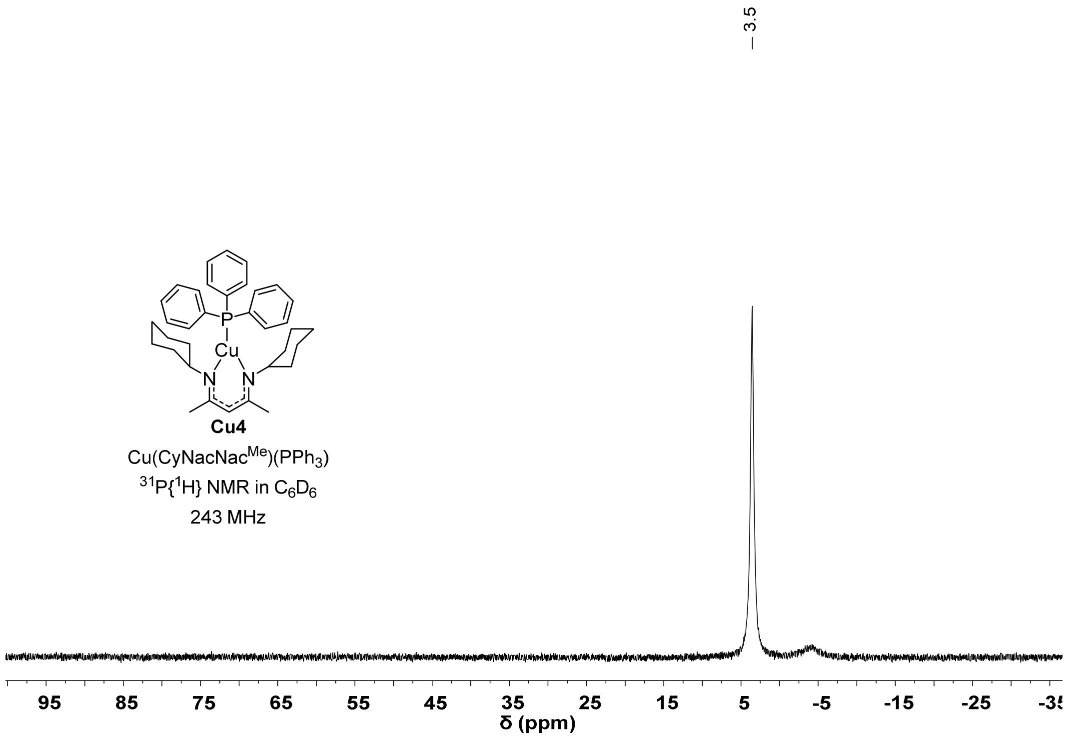


Fig. S9. $^{31}P\{^{1}H\}$ NMR spectrum of complex **Cu4**, recorded at 243 MHz in C_6D_6.

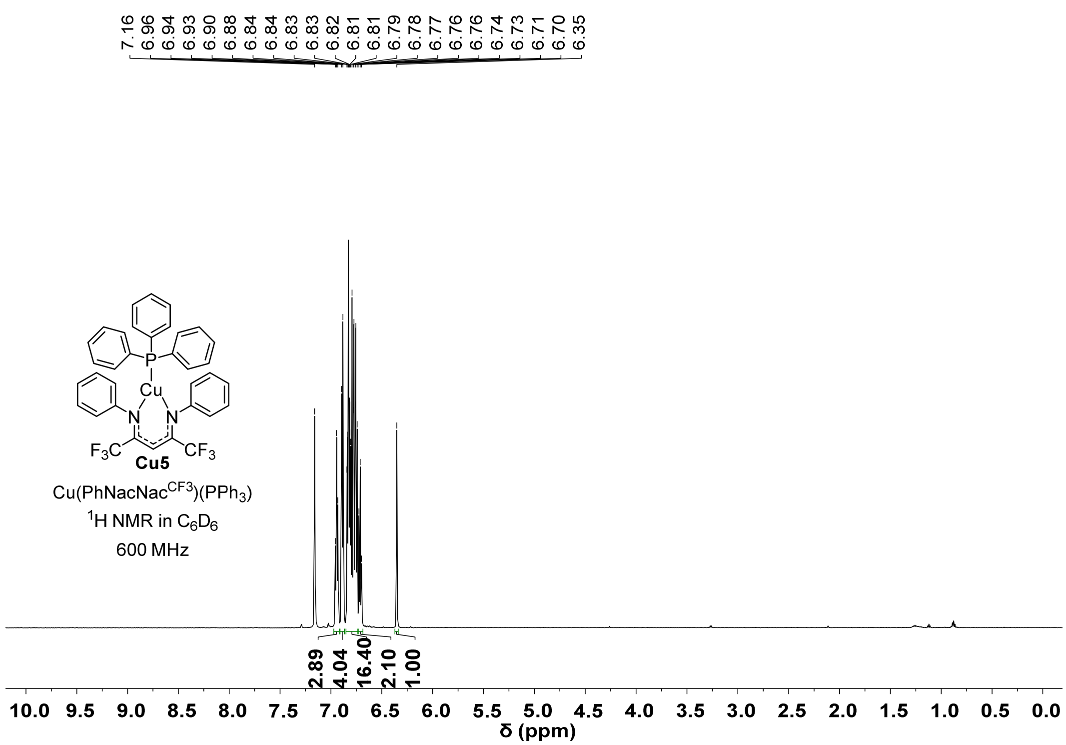


Fig. S10. ^{1}H NMR spectrum of complex **Cu5**, recorded at 600 MHz in C_6D_6.

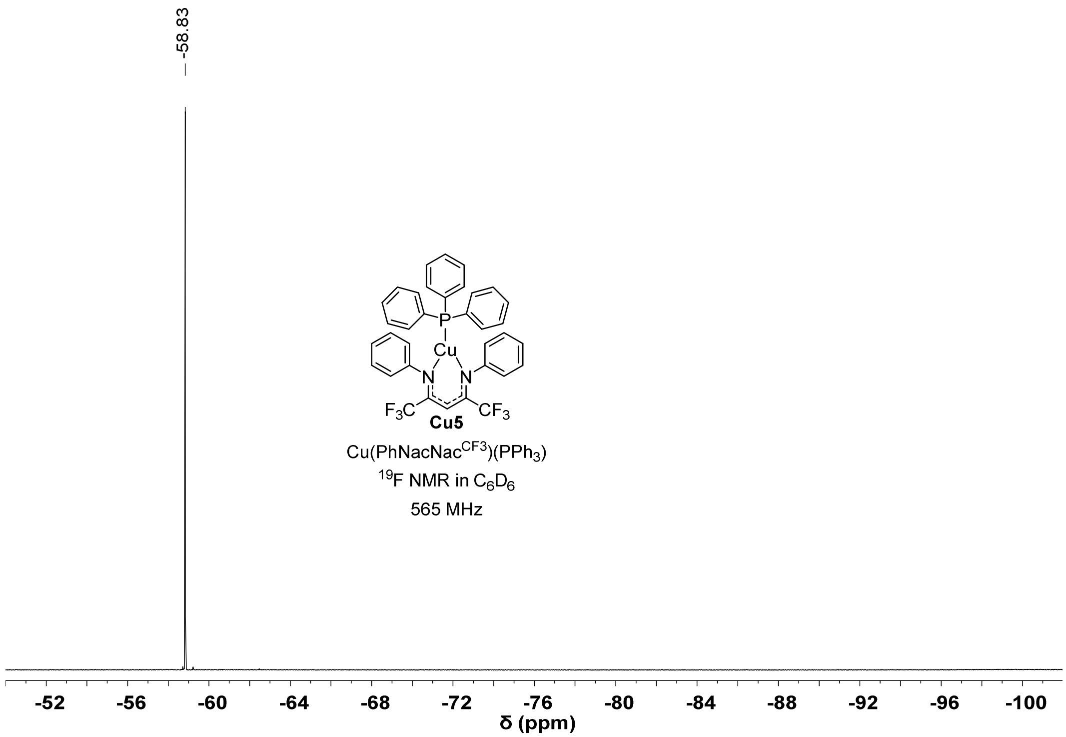


Fig. S11. ^{19}F NMR spectrum of complex **Cu5**, recorded at 565 MHz in C_6D_6.

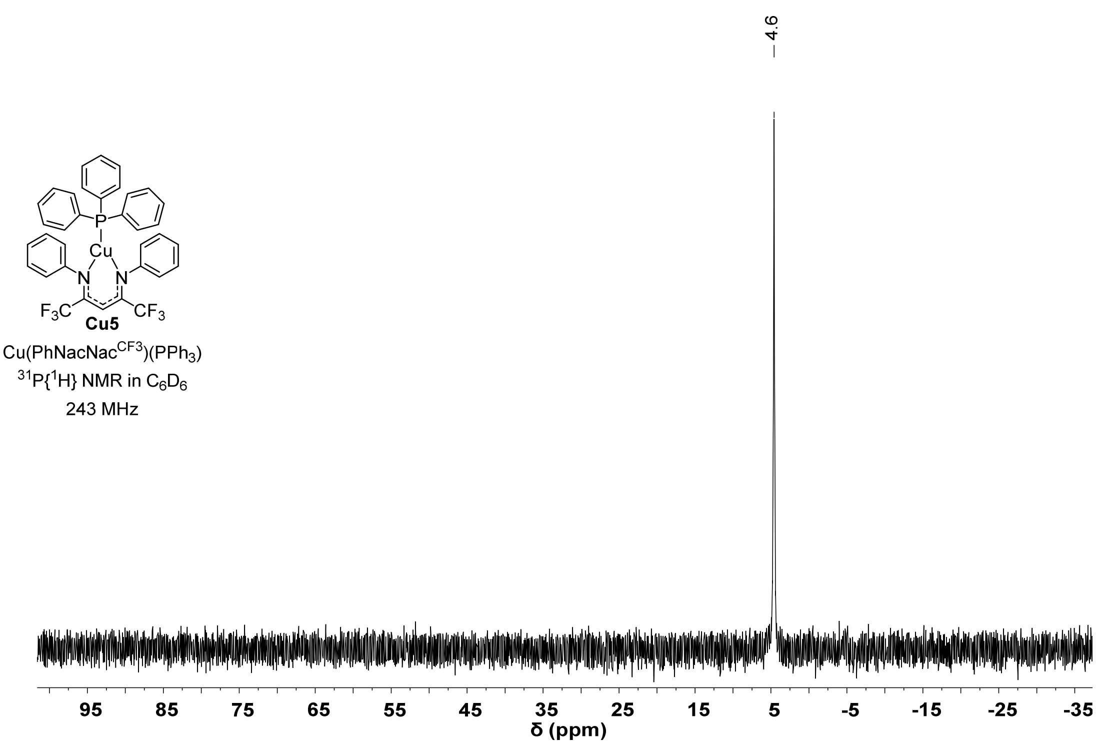


Fig. S12. ^{31}P{^{1}H} NMR spectrum of complex **Cu5**, recorded at 243 MHz in C_6D_6.

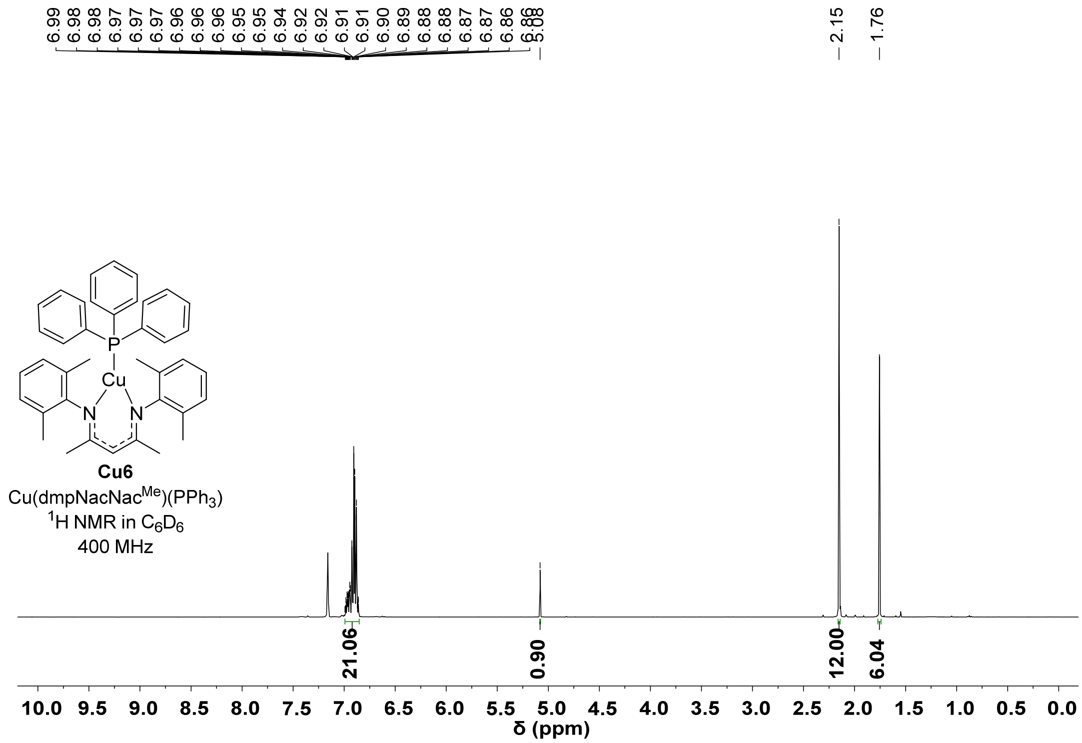


Fig. S13. ^{1}H NMR spectrum of complex **Cu6,** recorded at 400 MHz in C_6D_6.

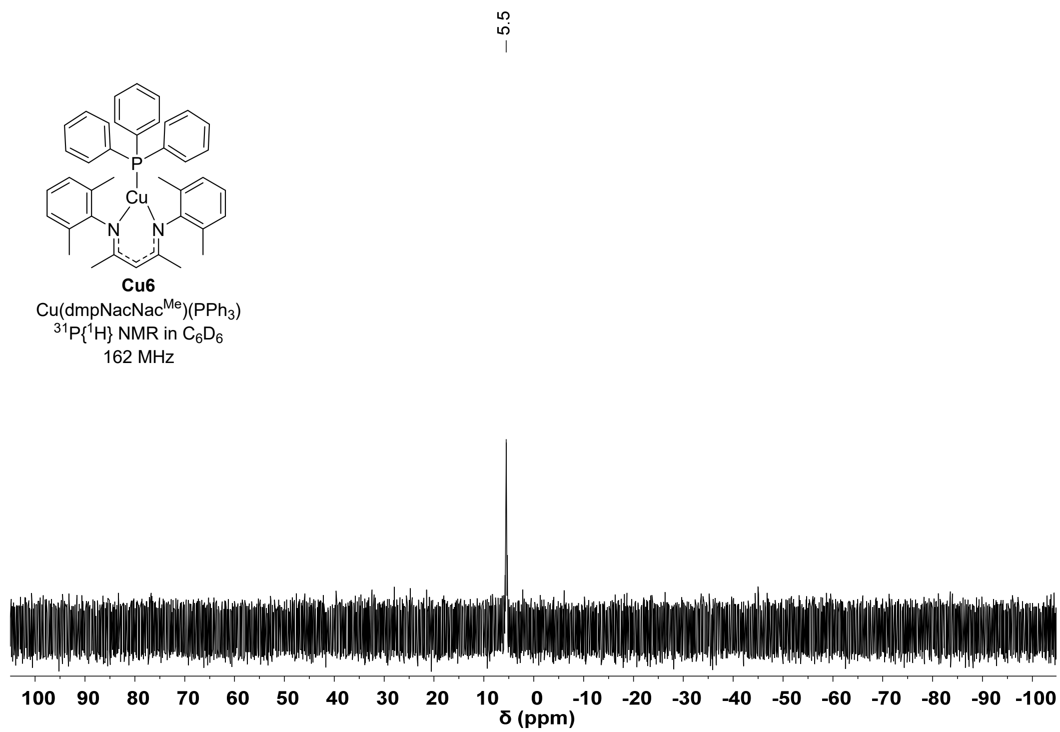


Fig. S14. ^{31}P {^{1}H} NMR spectrum of complex **Cu6,** recorded at 162 MHz in C_6D_6.

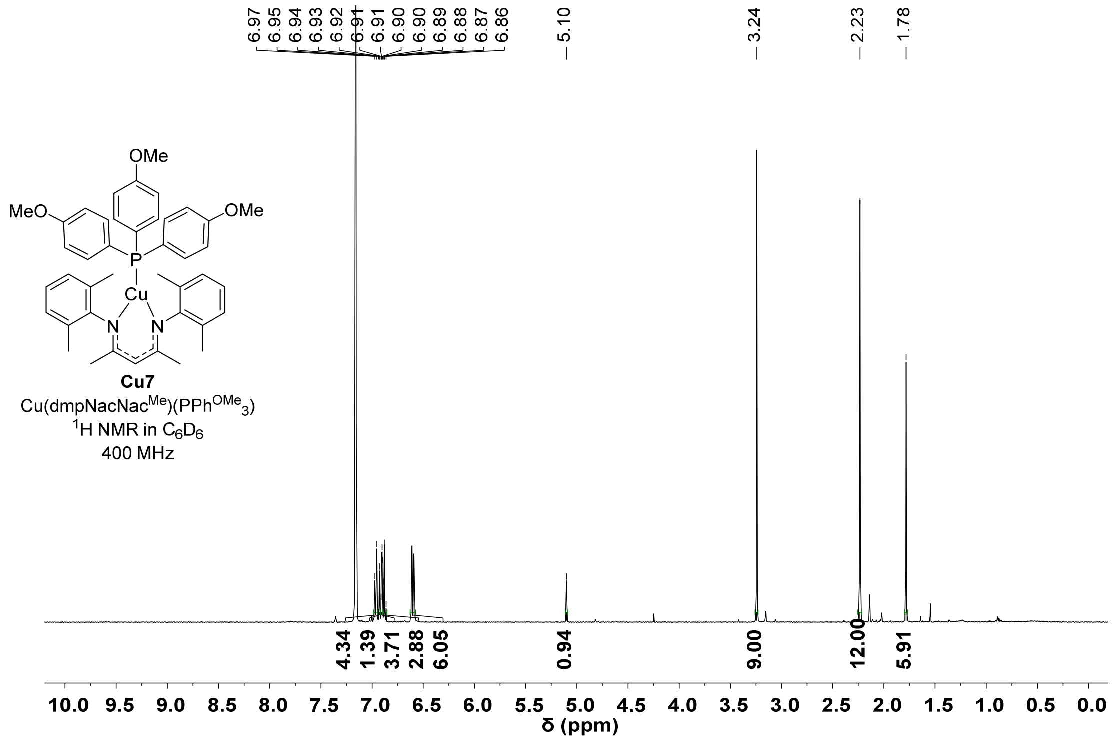


Fig. S15. ^{1}H NMR spectrum of complex **Cu7,** recorded at 400 MHz in C_6D_6.

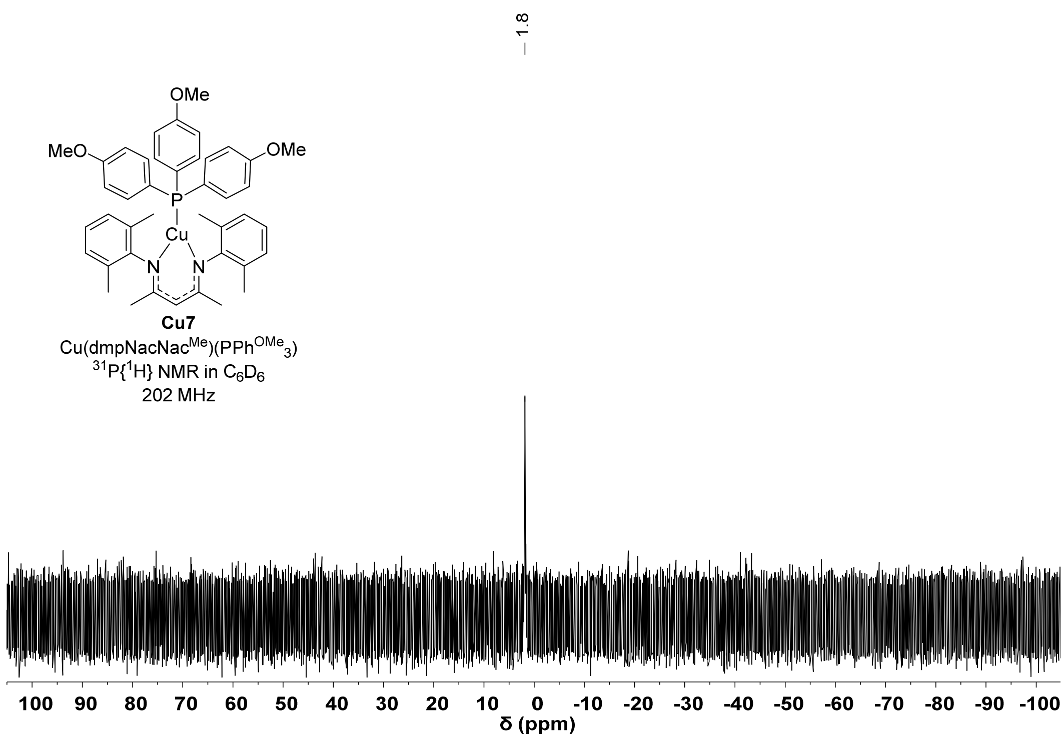


Fig. S16. ^{31}P $\{^{1}H\}$ NMR spectrum of complex **Cu7,** recorded at 202 MHz in C_6D_6.

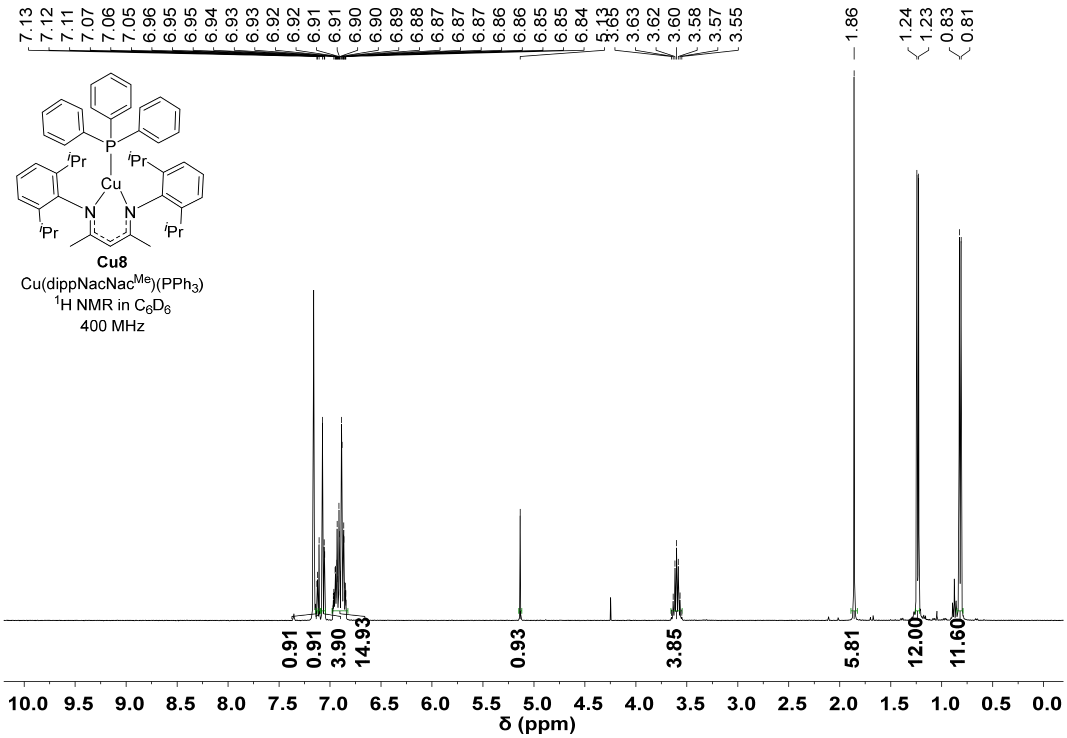


Fig. S17. ^{1}H NMR spectrum of complex **Cu8,** recorded at 400 MHz in C_6D_6.

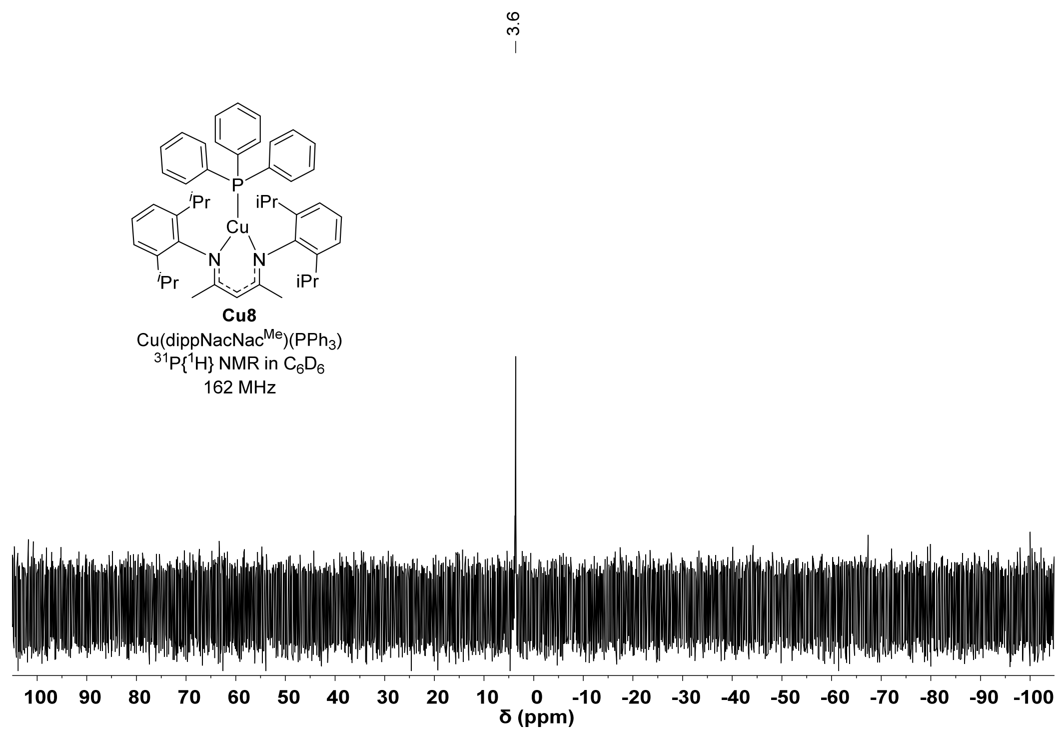


Fig. S18. ^{31}P{^{1}H} NMR spectrum of complex **Cu8,** recorded at 162 MHz in C_6D_6.

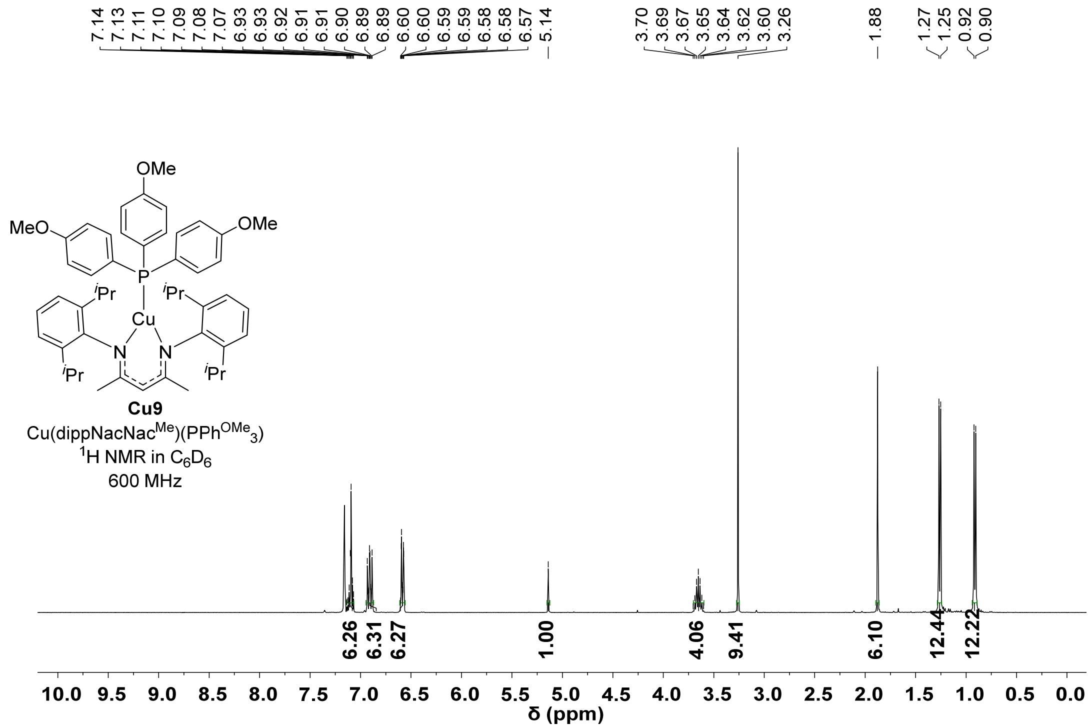


Fig. S19. ^{1}H NMR spectrum of complex **Cu9,** recorded at 600 MHz in C_6D_6.

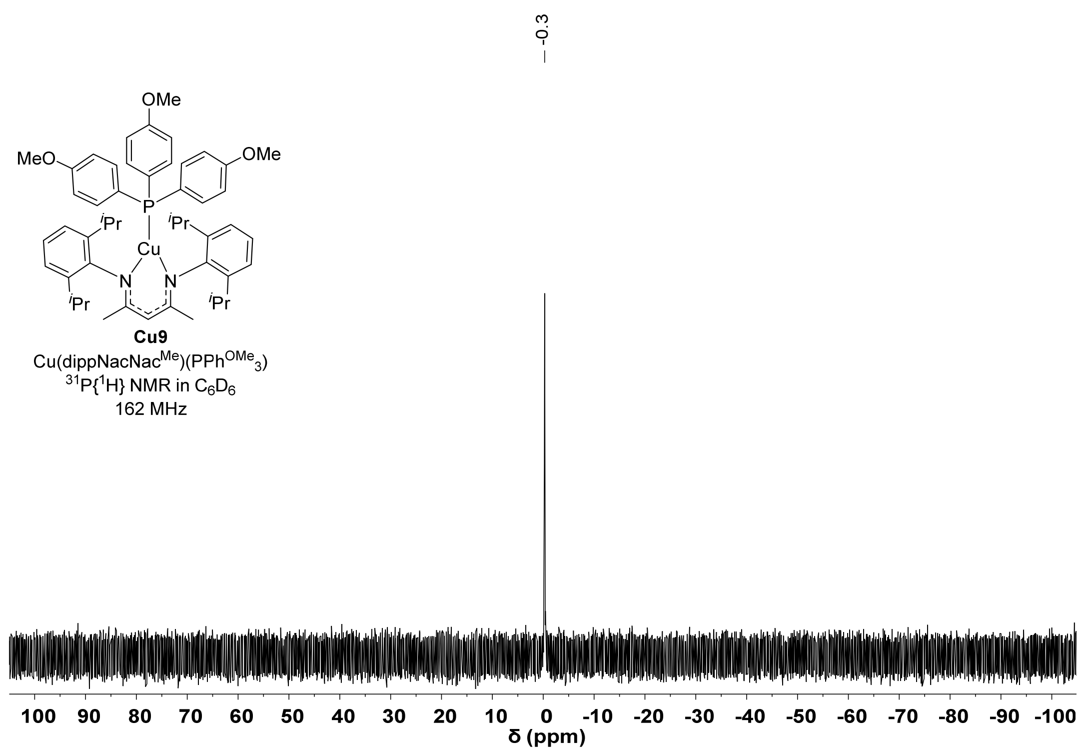


Fig. S20. ^{31}P {^{1}H} NMR spectrum of complex **Cu9,** recorded at 162 MHz in C_6D_6.

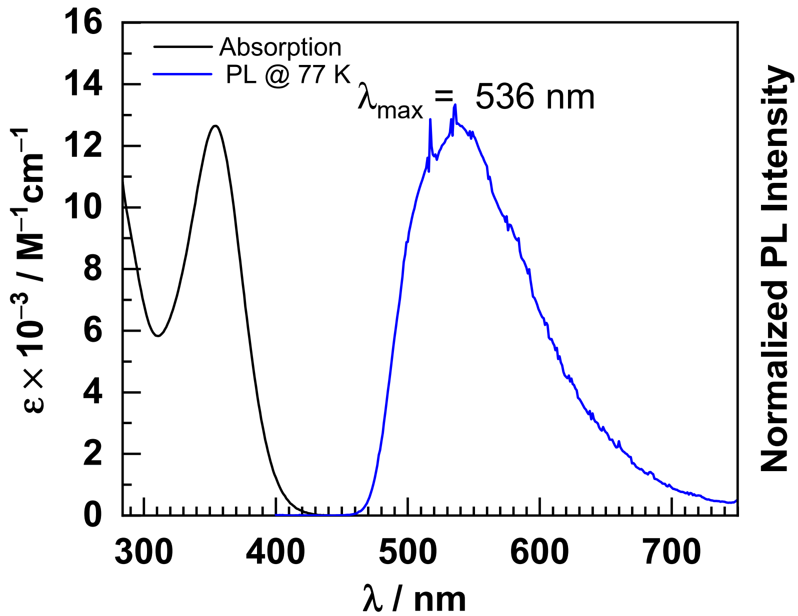


Fig. S21. UV–vis absorption (solid black line, 298 K) and photoluminescence (solid blue line, 77 K) spectra of **Cu1**, recorded in toluene.

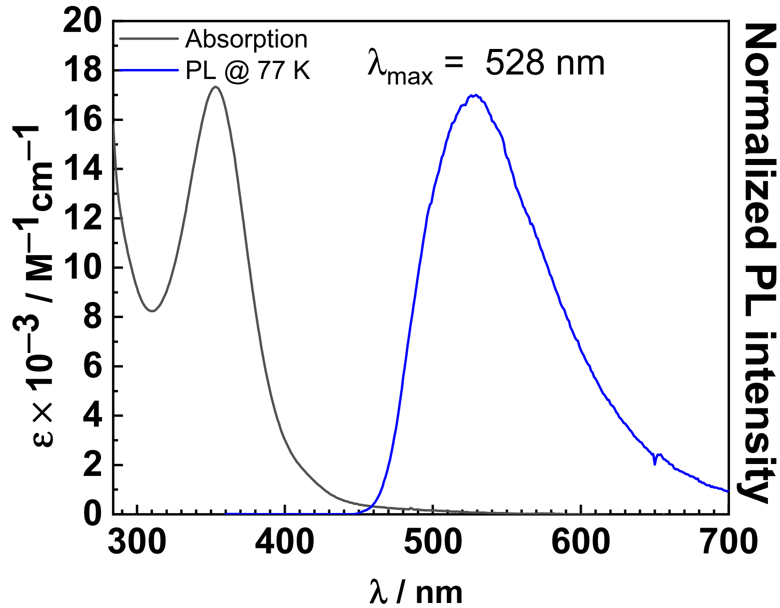


Fig. S22. UV–vis absorption (solid black line, 298 K) and photoluminescence (solid blue line, 77 K) spectra of **Cu2**, recorded at 298 K in toluene.

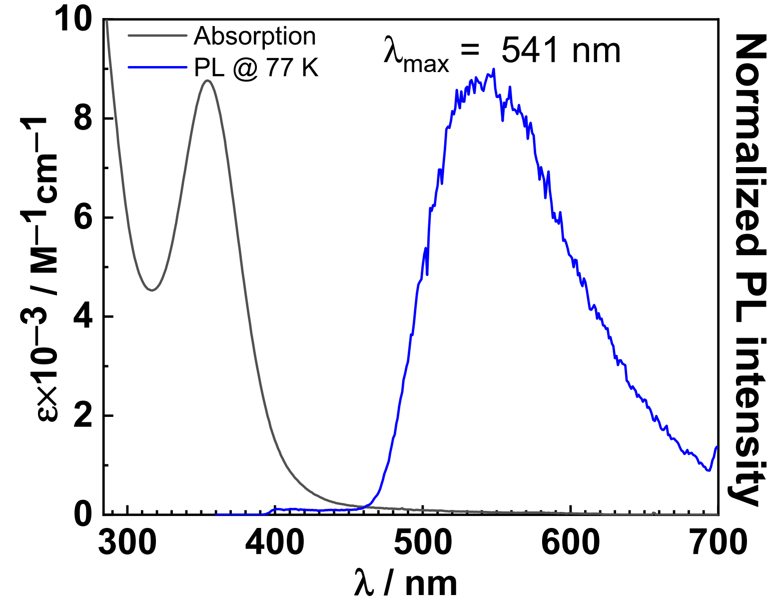


Fig. S23. UV–vis absorption (solid black line, 298 K) and photoluminescence (solid blue line, 77 K) spectra of **Cu3**, recorded in toluene. recorded at 298 K in toluene.

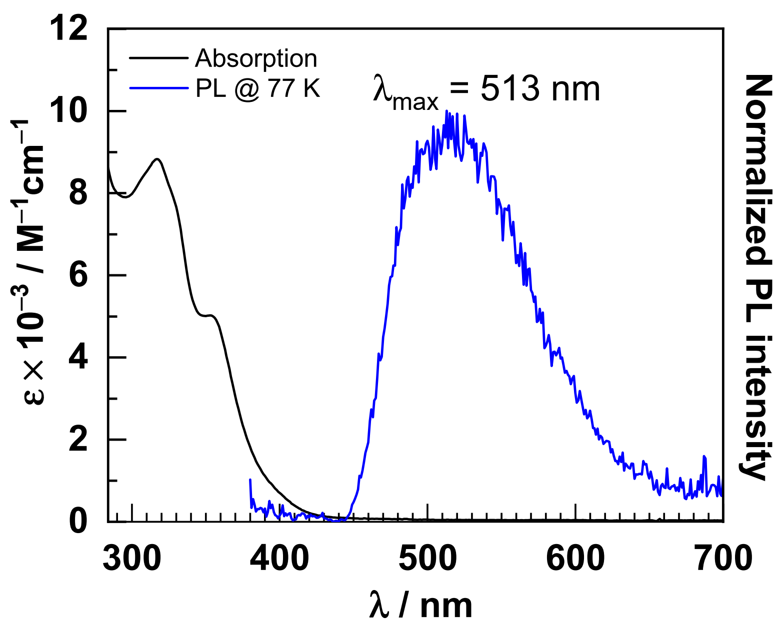


Fig. S24. UV–vis absorption (solid black line, 298 K) and photoluminescence (solid blue line, 77 K) spectra of **Cu4**, recorded in toluene.

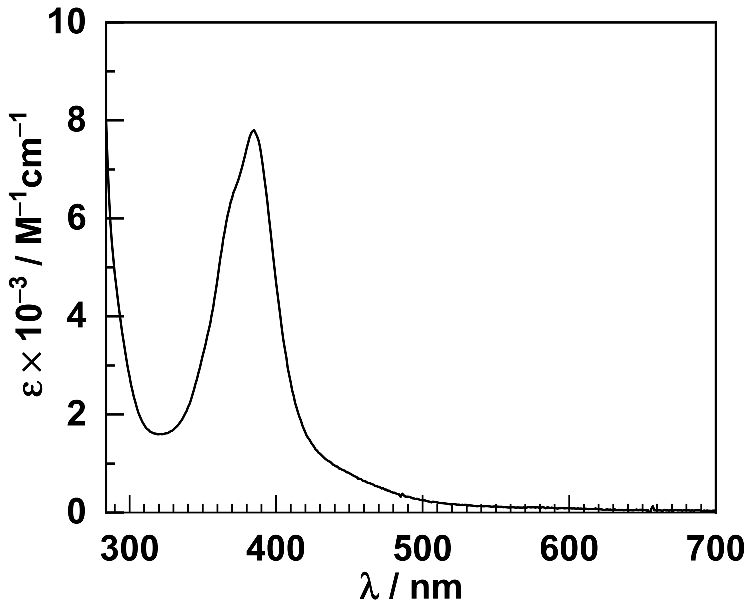


Fig. S25. UV–vis absorption spectrum of **Cu5**, recorded at 298 K in toluene.

Table. S6. Summary of the UV–vis absorption data of complexes **Cu1**–**Cu5**.

	UV-vis absorption, λ / nm (ε ×10^{-3} / M^{-1}cm^{-1})
Cu(PhNacNac^{Me})(PPh_3) (**Cu1**)	354 (13)
Cu(PhNacNac^{Me})($PPh^F{}_3$) (**Cu2**)	353 (17)
Cu(PhNacNac^{Me})($PPh^{OMe}{}_3$) (**Cu3**)	354 (8.8)
Cu(CyNacNac^{Me})(PPh_3) (**Cu4**)	317 (8.8), 353 (5.0)
Cu(PhNacNac^{CF3})(PPh_3) (**Cu5**)	370 (sh) (6.4), 385 (7.8), 448 (sh) (0.82)

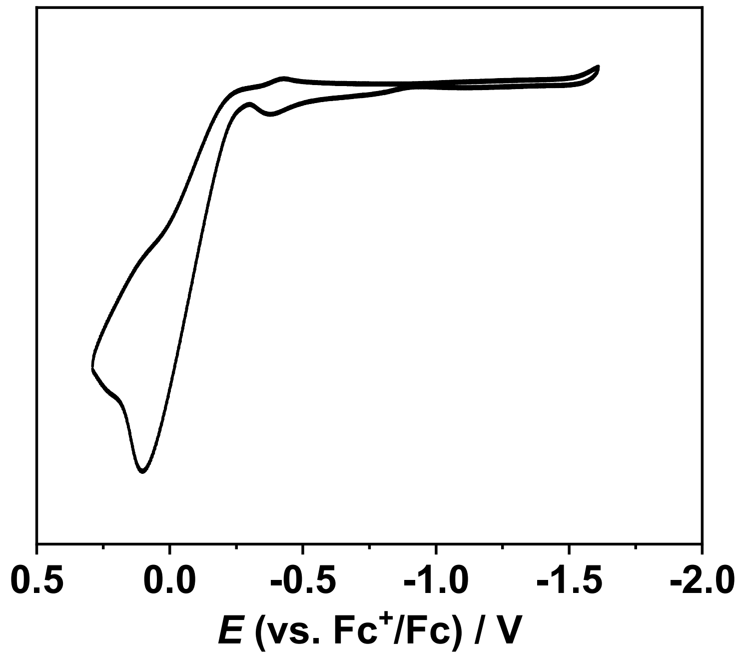


Fig. S26. Cyclic voltammogram of **Cu1** recorded in THF with 0.1 M NBu_4PF_6 as the supporting electrolyte. The potential was referenced against an internal standard of ferrocene.

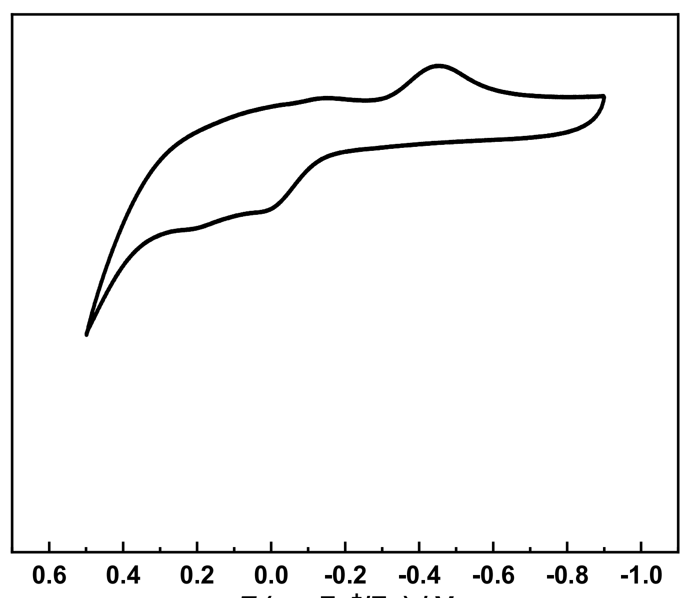


Fig. S27. Cyclic voltammogram of **Cu2** recorded in THF with 0.1 M NBu_4PF_6 as the supporting electrolyte. The potential was referenced against an internal standard of ferrocene.

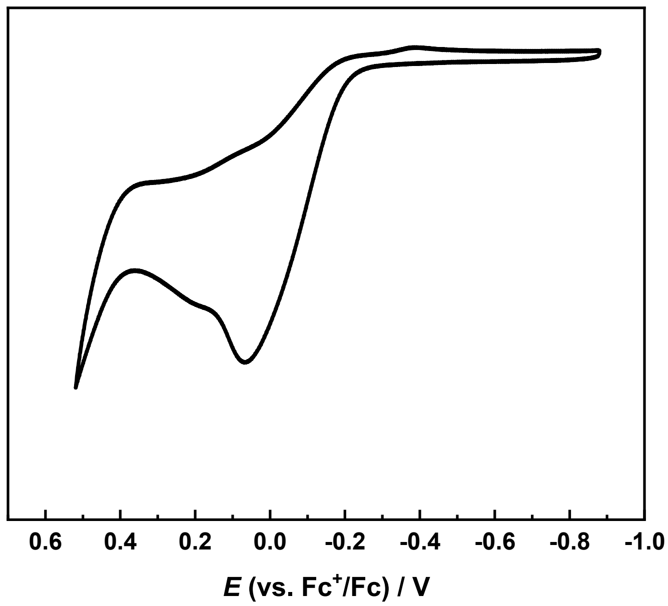


Fig. S28. Cyclic voltammogram of **Cu3** recorded in THF with 0.1 M NBu_4PF_6 as the supporting electrolyte. The potential was referenced against an internal standard of ferrocene.

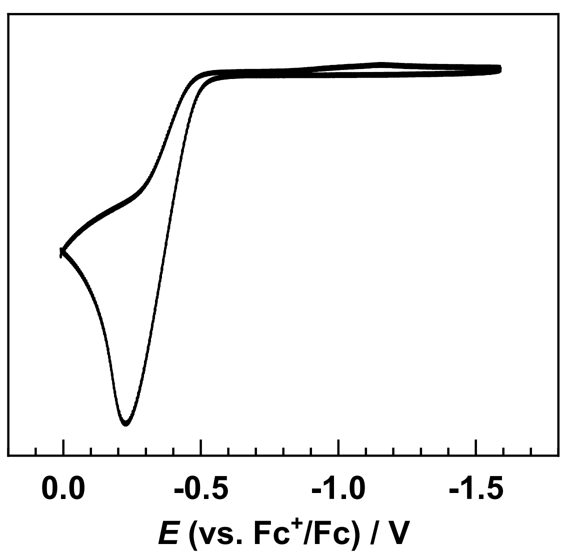


Fig. S29. Cyclic voltammogram of **Cu4** recorded in THF with 0.1 M NBu_4PF_6 as the supporting electrolyte. The potential was referenced against an internal standard of ferrocene.

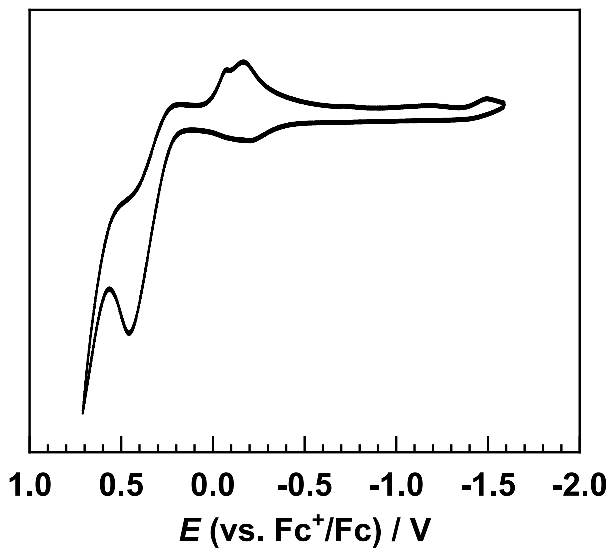
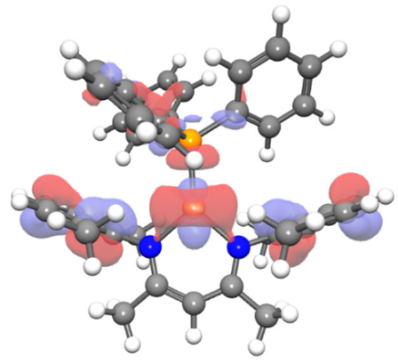


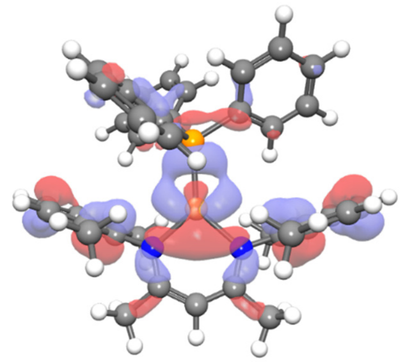
Fig. S30. Cyclic voltammogram of **Cu5** recorded in THF with 0.1 M NBu_4PF_6 as the supporting electrolyte. The potential was referenced against an internal standard of ferrocene.

Table S7. Summary of the electrochemical data of the complexes **Cu1**−**Cu5**. For all of these compounds, there is no reduction wave observed within the solvent electrochemical window. All observed waves are irreversible and potentials are reported as the peak anodic potential, $E_{p,a}$.

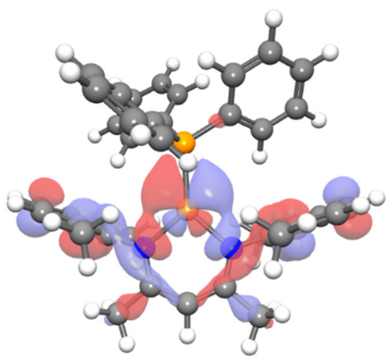
	E^{ox} / V ($[Cu]^+/[Cu]$)
Cu (PhNacNac^{Me})(PPh_3) (**Cu1**)	0.11
Cu(PhNacNac^{Me})($PPh^F{}_3$) (**Cu2**)	0.03
Cu(PhNacNac^{Me})($PPh^{OMe}{}_3$) (**Cu3**)	0.07
Cu(CyNacNac^{Me})(PPh_3) (**Cu4**)	−0.22
Cu(PhNacNac^{CF3})(PPh_3) (**Cu5**)	0.46



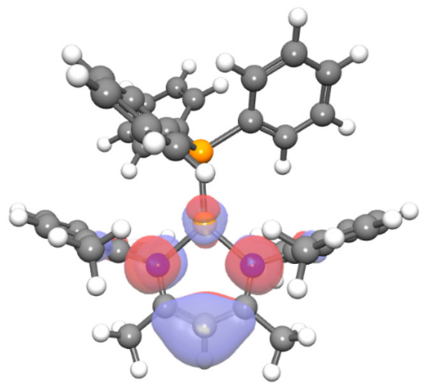
HOMO−3 (−6.18 eV)



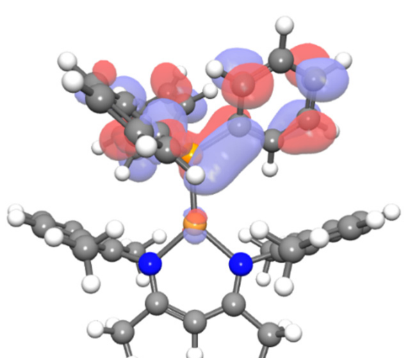
HOMO−2 (−6.04 eV)



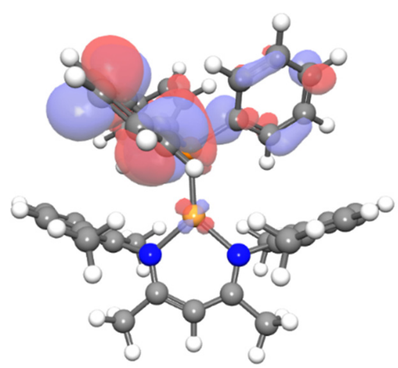
HOMO−1 (−5.11 eV)



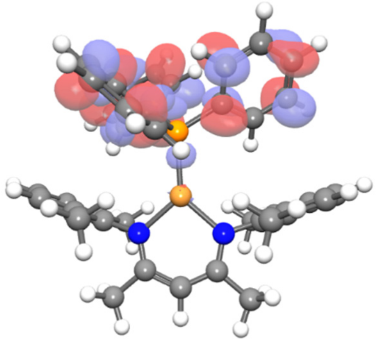
HOMO (−4.87 eV)



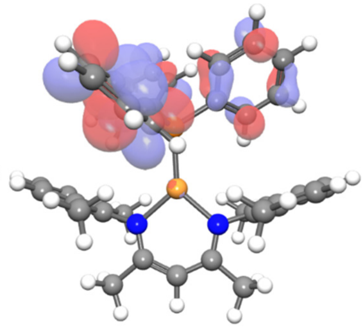
LUMO (−1.12 eV)



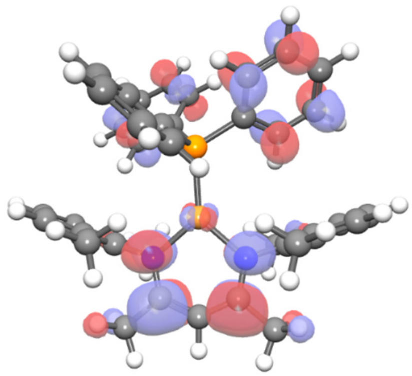
LUMO+1 (−1.06 eV)



LUMO+3 (–0.71 eV)



LUMO+4 (–0.49 eV)



LUMO+6 (–0.38 eV)

Fig. S31. Frontier molecular orbitals (isovalue 0.08) of **Cu6** (at the uB3LYP/6-31+g(d) in toluene) associated with the computed UV–vis absorption transitions.

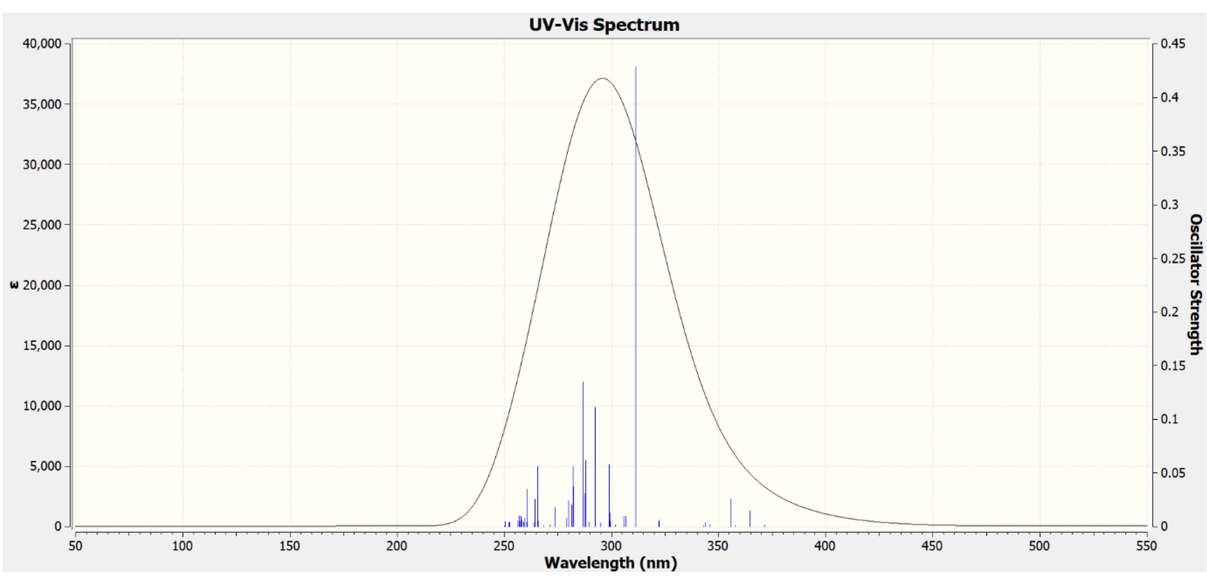


Fig. S32. Simulated UV–vis absorption spectrum of complex **Cu6** obtained by TDDFT calculation at the level of uB3LYP/6-31+g(d) with CPCM solvent model in toluene.

Table S8. Major transition assignments of complex **Cu6**, determined by TDDFT.

λ /nm	Oscillator strength (*f*)	Description
311.41	0.4290	HOMO−1 → LUMO+3 (0.18067)
		HOMO → LUMO+4 (0.63894)
292.53	0.1112	HOMO−3 → LUMO+1 (0.10588)
		HOMO−2 → LUMO+1 (0.67564)
298.91	0.0582	HOMO−2 → LUMO+1 (0.61751)
		HOMO−1 → LUMO+6 (−0.20356)
		HOMO → LUMO+6 (−0.13131)
355.75	0.0262	HOMO−1 → LUMO+1 (0.63937)
		HOMO → LUMO+1 (0.22254)
		HOMO → LUMO (0.11722)
364.68	0.0147	HOMO−1 → LUMO+1 (−0.13219)
		HOMO → LUMO (0.68672)

Table S9. Optimized Cartesian coordinates for **Cu6** in the ground state.

Electronic energy (EE): −58704.626287969 eV

No. of imaginary frequency: 0

Cu	6.8125	9.7106	3.5907
P	5.5812	9.916	5.3652
N	7.3952	10.9257	2.1836
N	7.5602	8.0791	2.809
C	7.0253	12.2966	2.2912
C	7.9072	13.1975	2.8996
C	7.5026	14.5035	3.0926
H	8.0937	15.1218	3.5054
C	6.2534	14.9201	2.6941
H	5.991	15.8233	2.8277
C	5.3835	14.0343	2.103
H	4.5248	14.3341	1.8295
C	5.7421	12.7051	1.899
C	9.2302	12.6982	3.4186
H	9.7076	13.4335	3.8563
H	9.7664	12.3583	2.6723
H	9.0762	11.9779	4.0652
C	4.7735	11.711	1.3131
H	3.9302	12.1629	1.1005
H	4.6064	10.9962	1.9622
H	5.1537	11.3274	0.4953
C	7.2444	6.8398	3.4447
C	7.9444	6.4561	4.5869
C	7.5655	5.2951	5.2503
H	8.0269	5.032	6.038
C	6.5282	4.5211	4.777
H	6.2872	3.7219	5.231
C	5.8454	4.9	3.6579
H	5.1297	4.3582	3.3455
C	6.1723	6.065	2.9605
C	9.0997	7.287	5.076
H	9.3832	6.9652	5.9571
H	8.8216	8.2243	5.1445
H	9.8456	7.2127	4.4451
C	5.4066	6.4869	1.7442
H	5.9468	6.3197	0.9437
H	5.1989	7.4428	1.8042
H	4.5732	5.9743	1.6887
C	8.1428	10.5445	1.158
C	8.6225	9.2417	0.9891
H	9.2205	9.1203	0.261
C	8.3485	8.0882	1.7393
C	8.49	11.5416	0.0685
H	7.6674	11.8457	−0.3698
H	9.0731	11.1138	−0.5923
H	8.9521	12.3099	0.4641
C	8.9934	6.7995	1.2587
H	9.373	6.3191	2.024

H	9.7058	7.0096	0.6191
H	8.3182	6.2389	0.8231
C	5.5931	11.4778	6.3197
C	5.9427	12.6518	5.6722
H	6.1882	12.629	4.7546
C	5.9372	13.861	6.3537
H	6.1873	14.6582	5.9015
C	5.5729	13.9137	7.6763
H	5.5616	14.7451	8.1358
C	5.2226	12.7503	8.3357
H	4.9765	12.7821	9.2528
C	5.2289	11.541	7.6667
H	4.9835	10.7468	8.1265
C	3.8378	9.7485	4.8502
C	2.8769	10.7279	5.0953
H	3.0978	11.4851	5.6247
C	1.5997	10.6017	4.5697
H	0.9544	11.2795	4.7352
C	1.2558	9.5071	3.8119
H	0.3804	9.4315	3.4501
C	2.1932	8.5173	3.5801
H	1.9566	7.7513	3.0702
C	3.4741	8.6391	4.0889
H	4.1138	7.958	3.9171
C	5.7972	8.69	6.7125
C	7.0205	8.6699	7.3721
H	7.7163	9.2538	7.0936
C	7.2319	7.8045	8.432
H	8.0705	7.7993	8.8785
C	6.2314	6.9513	8.8416
H	6.3749	6.3616	9.5723
C	5.0333	6.9592	8.1907
H	4.3458	6.3669	8.471
C	4.8026	7.8195	7.124
H	3.9635	7.8102	6.6781