Electronic Supporting Information

Novel self-adaptive boat-shaped complexes with a tetraphosphine ligand: synthesis, derivatization and investigations of encapsulating organic anions. DFT calculations on intramolecular CH···π interactions

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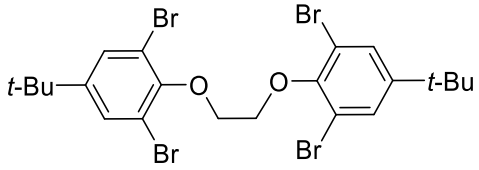
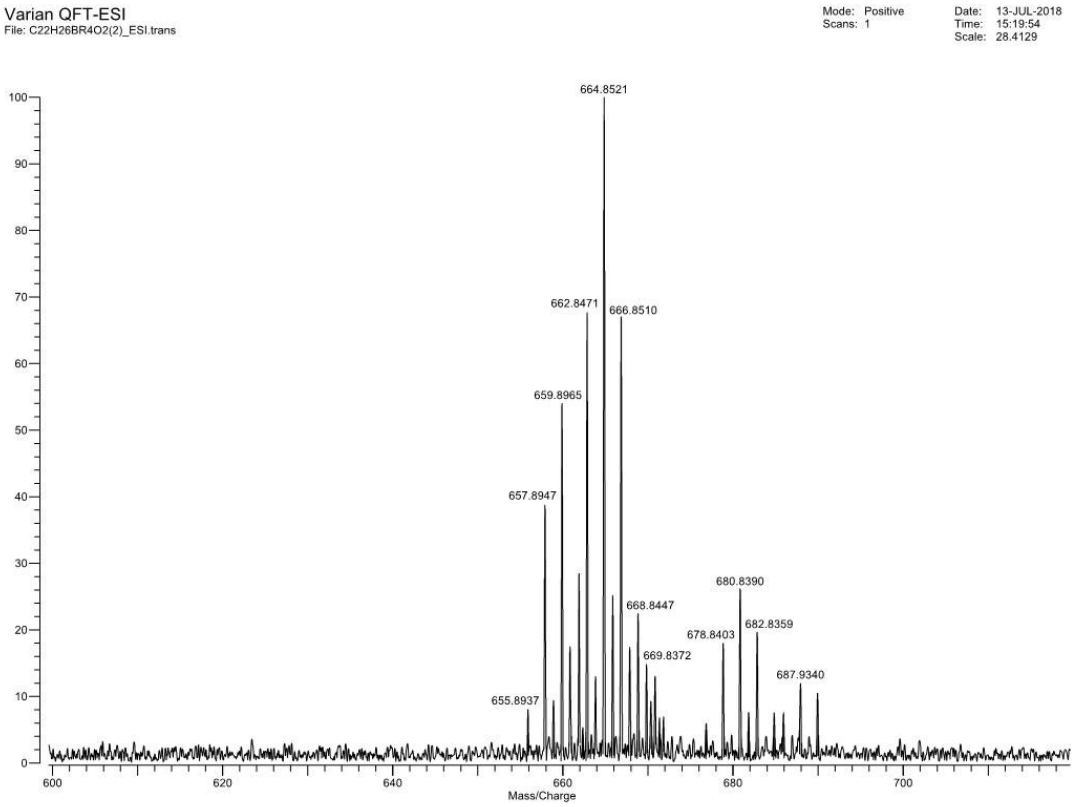
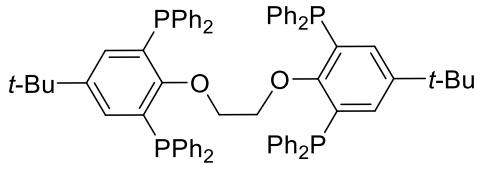
1. HR-MS(ESI) of Compound c





2. NMR spectra



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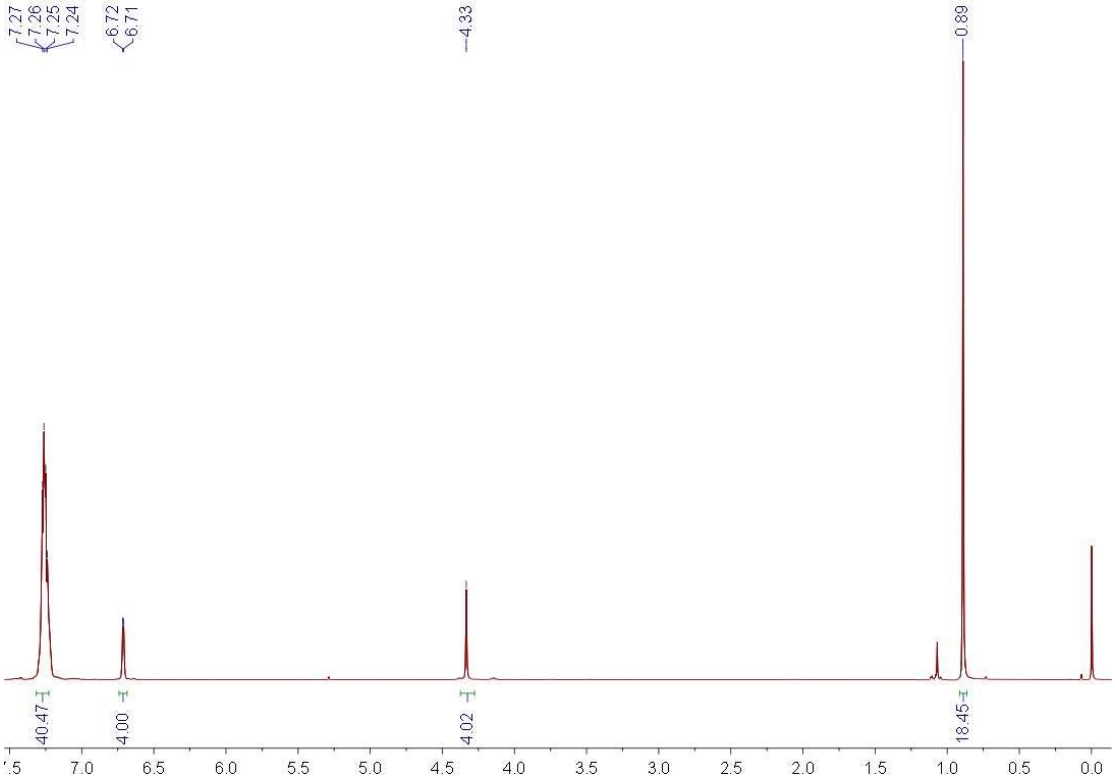


Fig. S1. 400 MHz ^{1}H NMR spectrum of Ligand **L** in $CDCl_3$ solution.

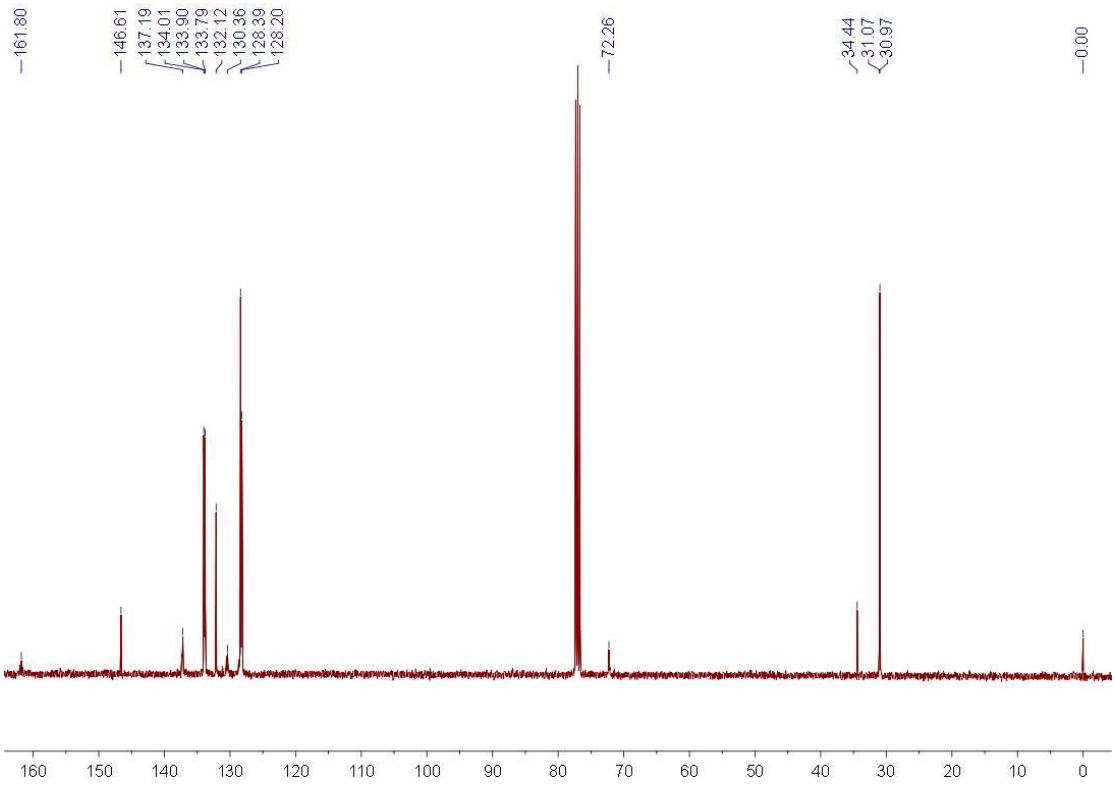


Fig. S2. 101 MHz ^{13}C NMR spectrum of Ligand **L** in $CDCl_3$ solution.

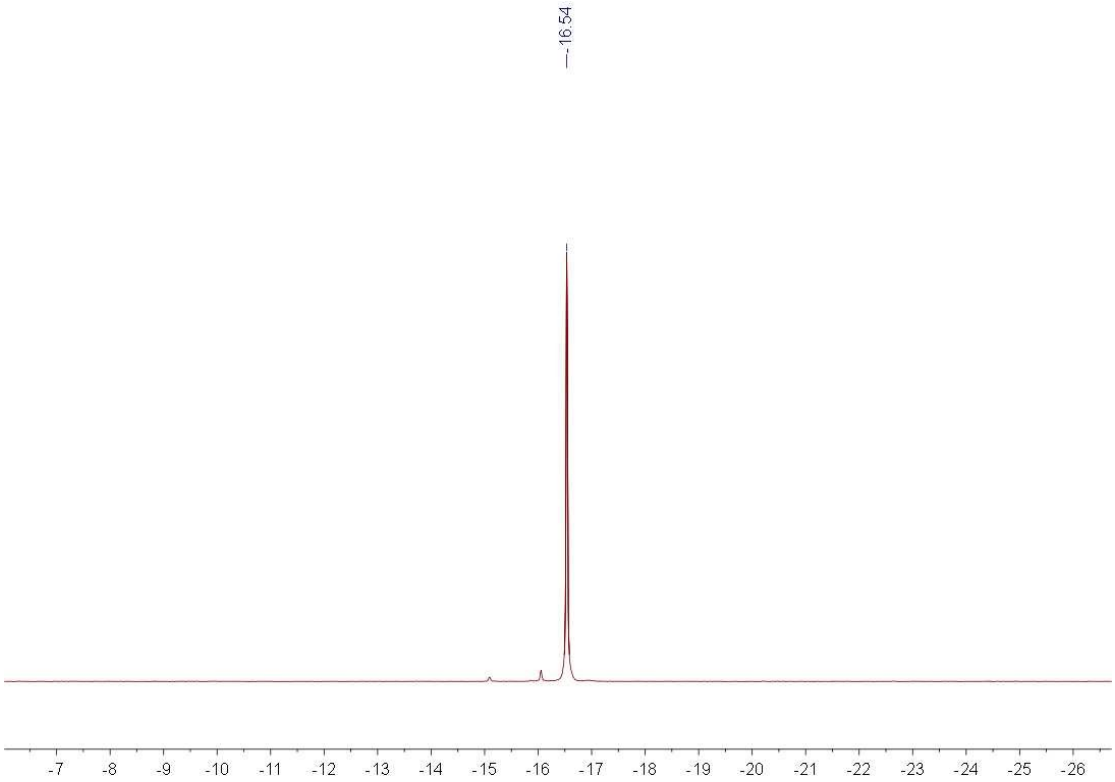
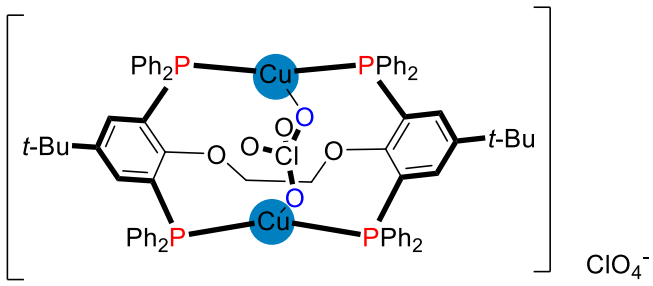


Fig. S3. 162 MHz ^{31}P NMR spectrum of Ligand **L** in $CDCl_3$ solution.



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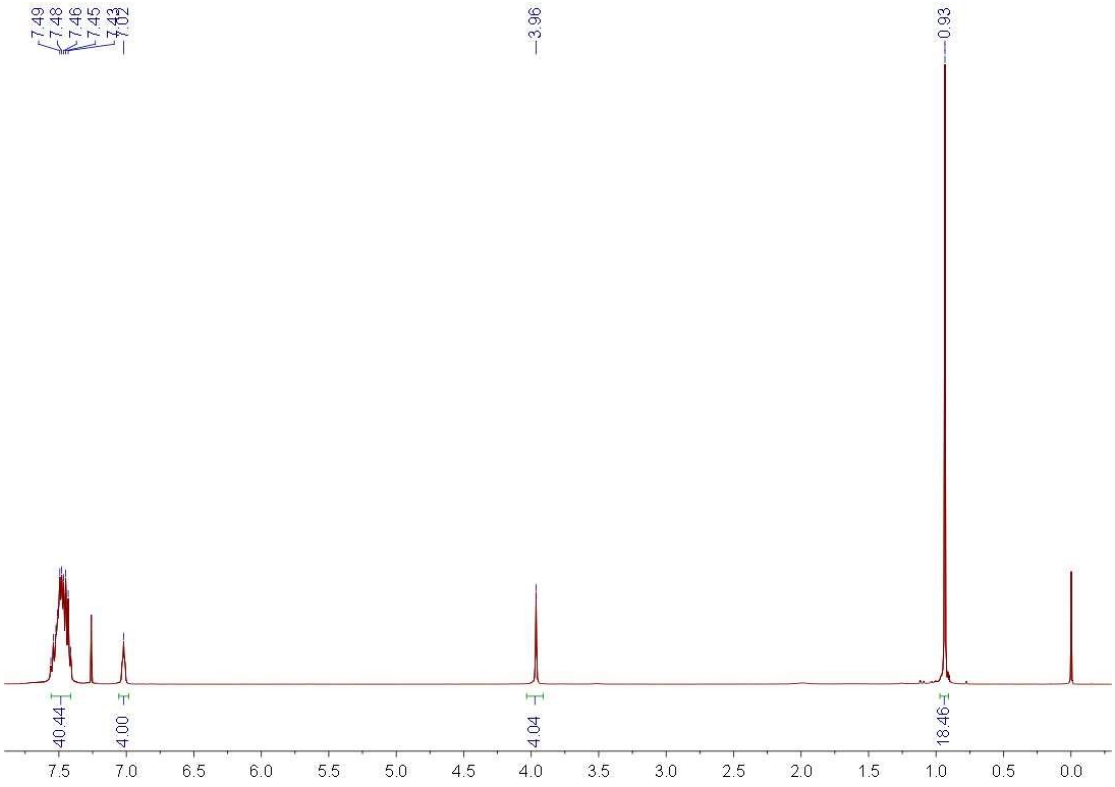


Fig. S4. 400 MHz ^{1}H NMR spectrum of complex **1** in $CDCl_3$ solution.

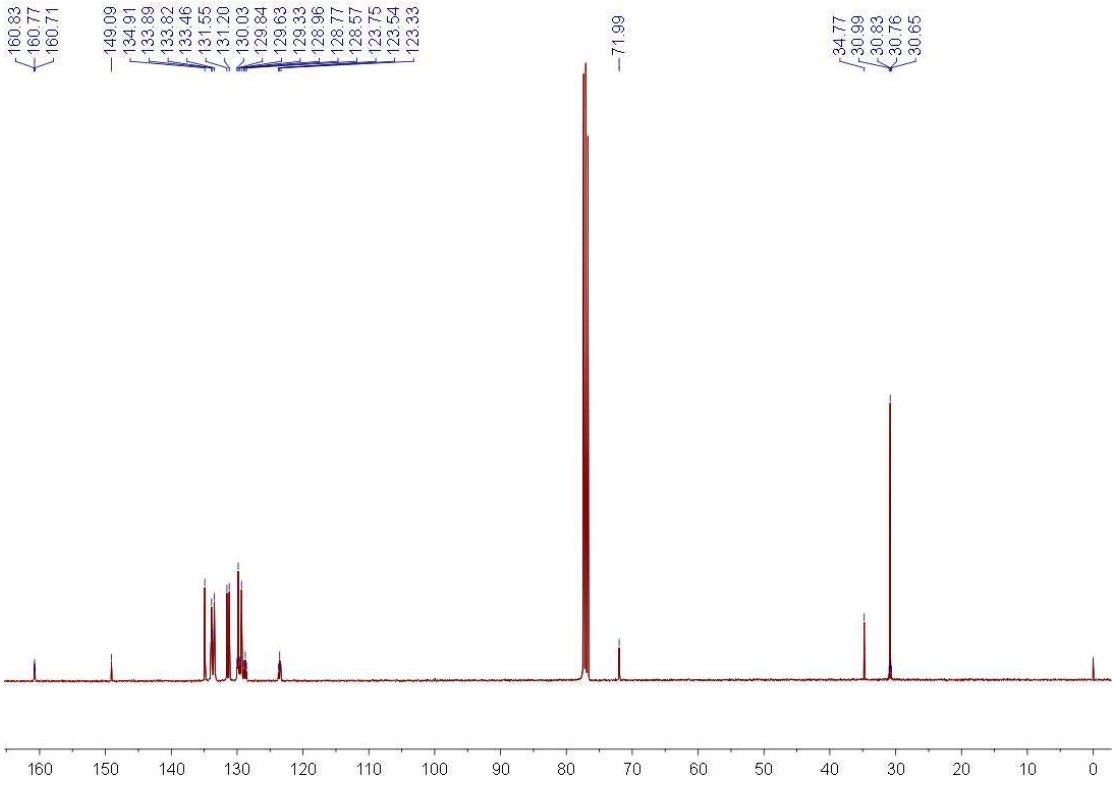


Fig. S5. 101 MHz ^{13}C NMR spectrum of complex **1** in $CDCl_3$ solution.

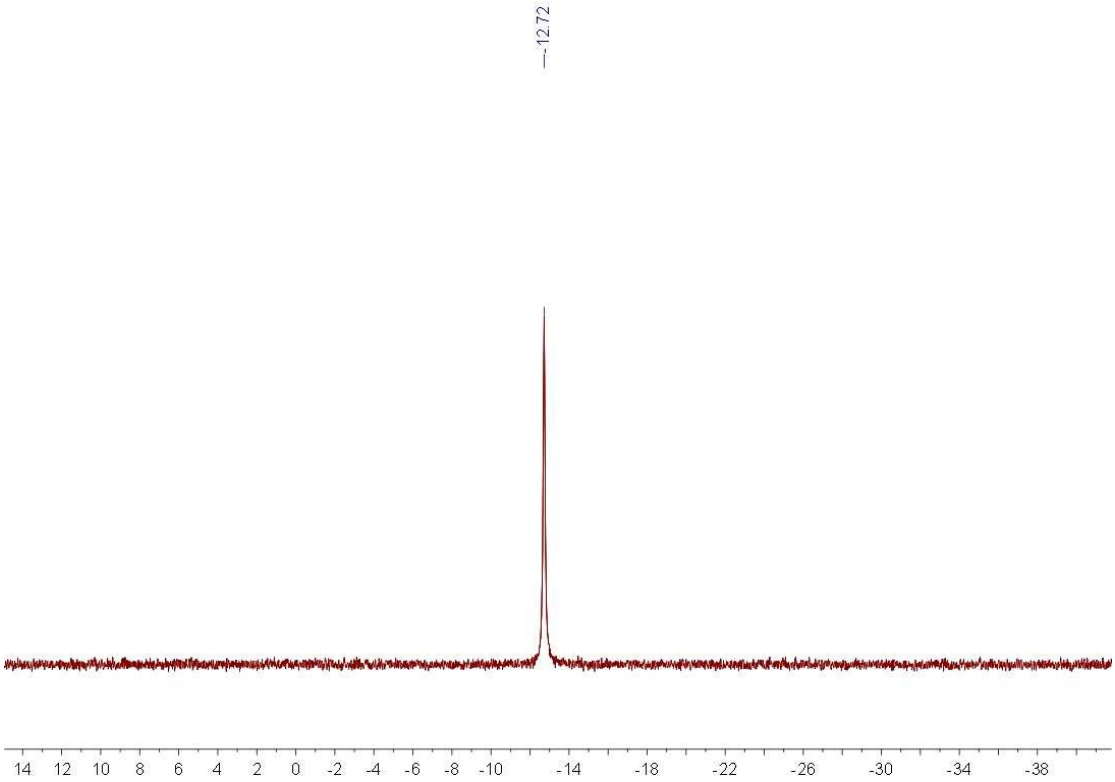
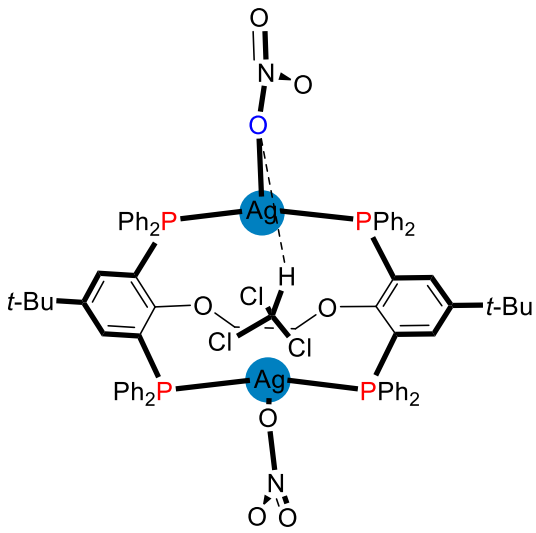


Fig. S6. 162 MHz ^{31}P NMR spectrum of complex **1** in $CDCl_3$ solution.



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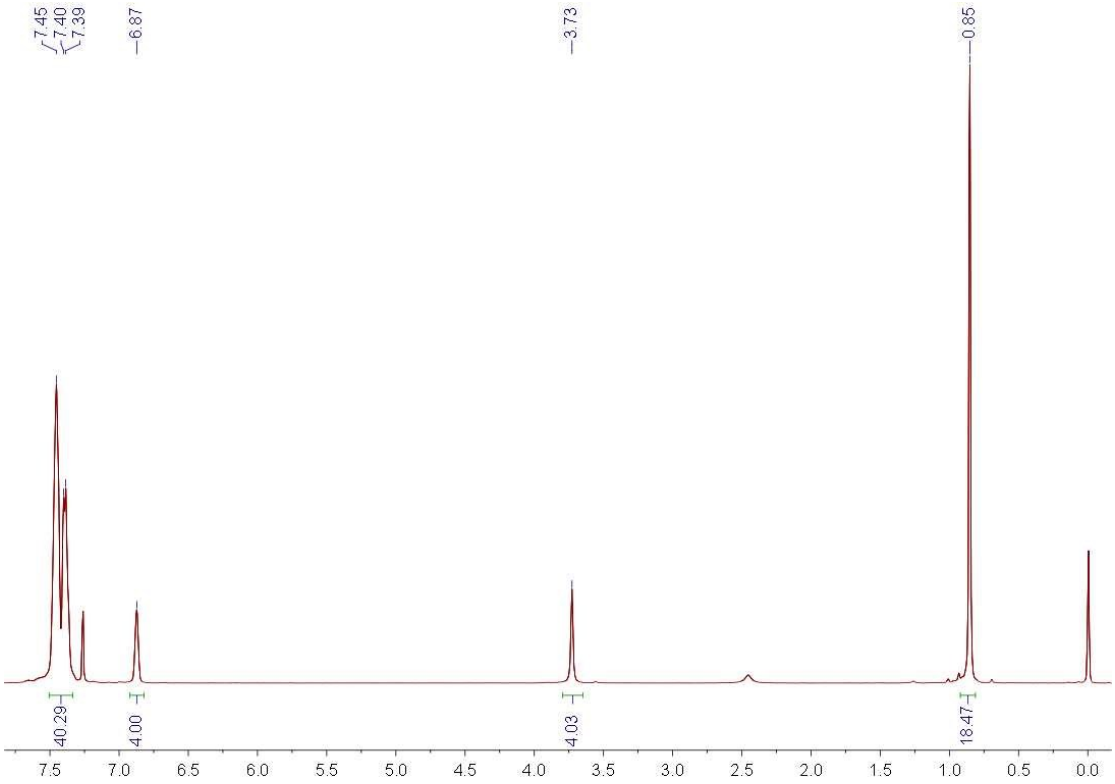


Fig. S7. 400 MHz ^{1}H NMR spectrum of complex **2** in $CDCl_3$ solution.

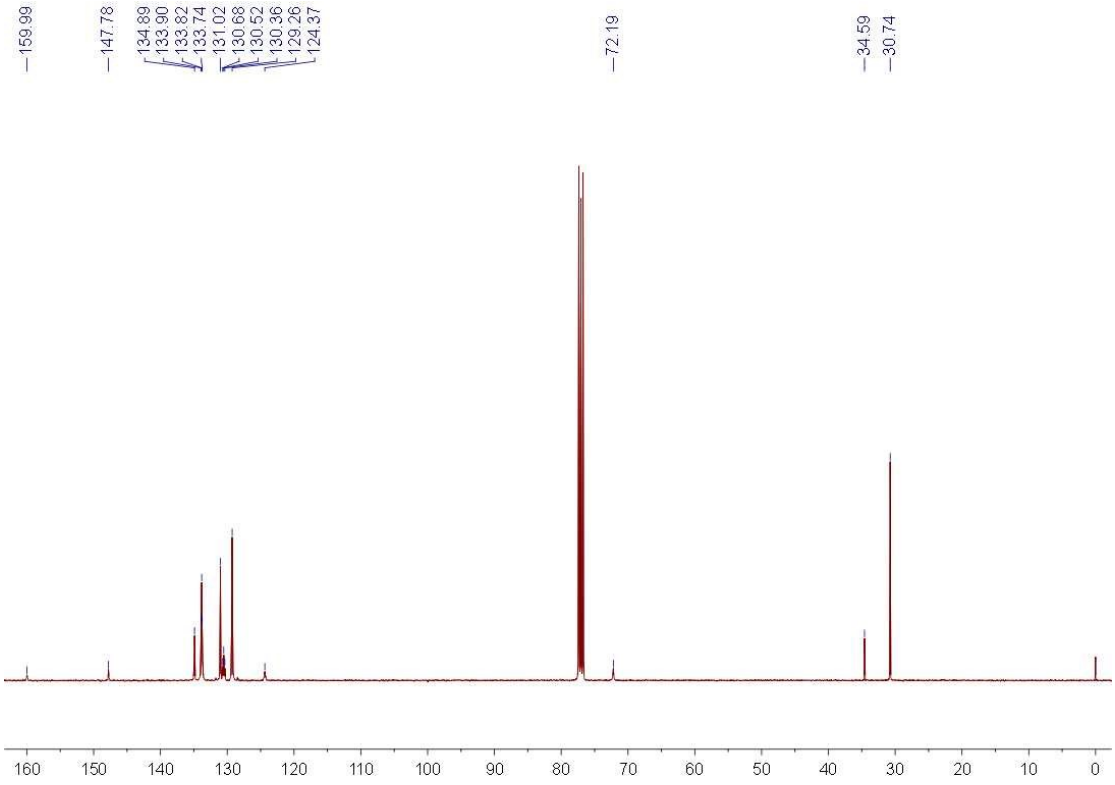


Fig. S8. 101 MHz ^{13}C NMR spectrum of complex **2** in $CDCl_3$ solution.

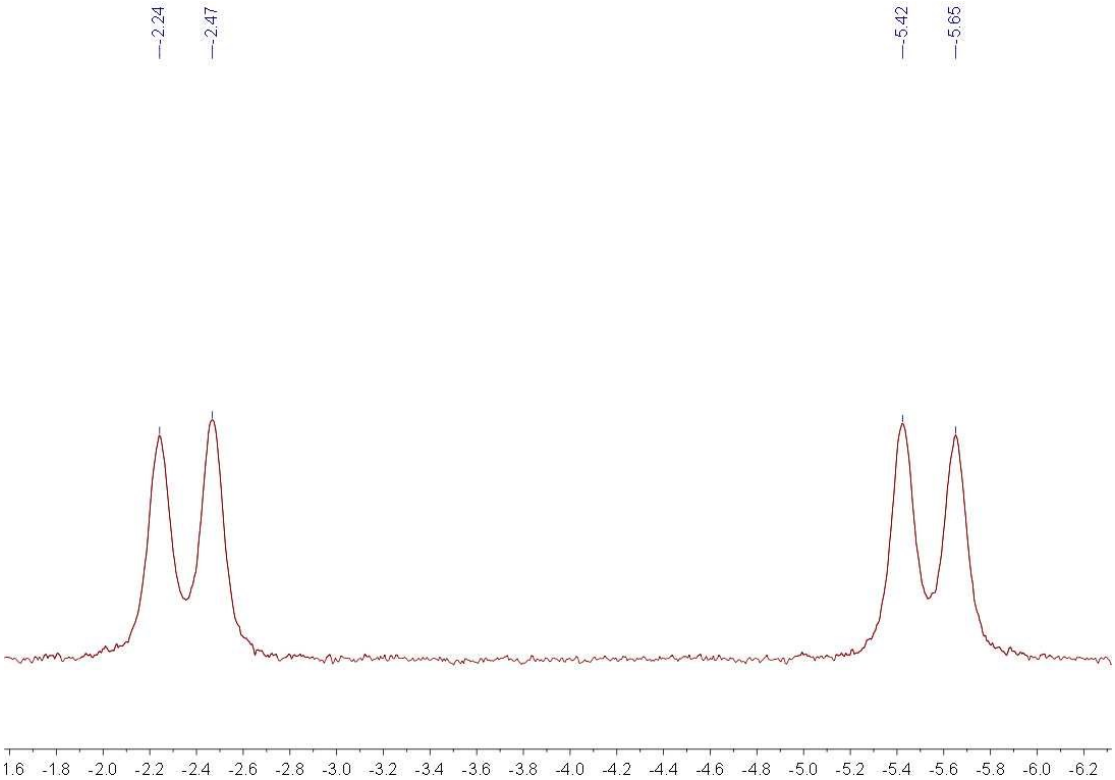
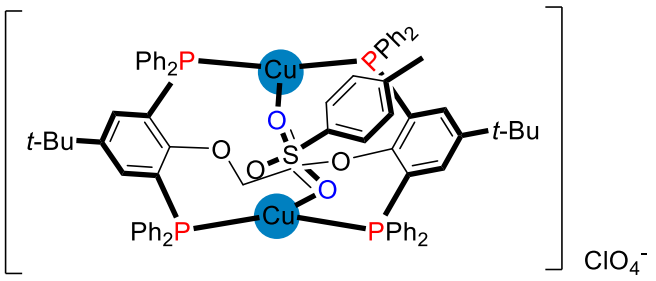


Fig. S9. 162 MHz ^{31}P NMR spectrum of complex **2** in $CDCl_3$ solution.



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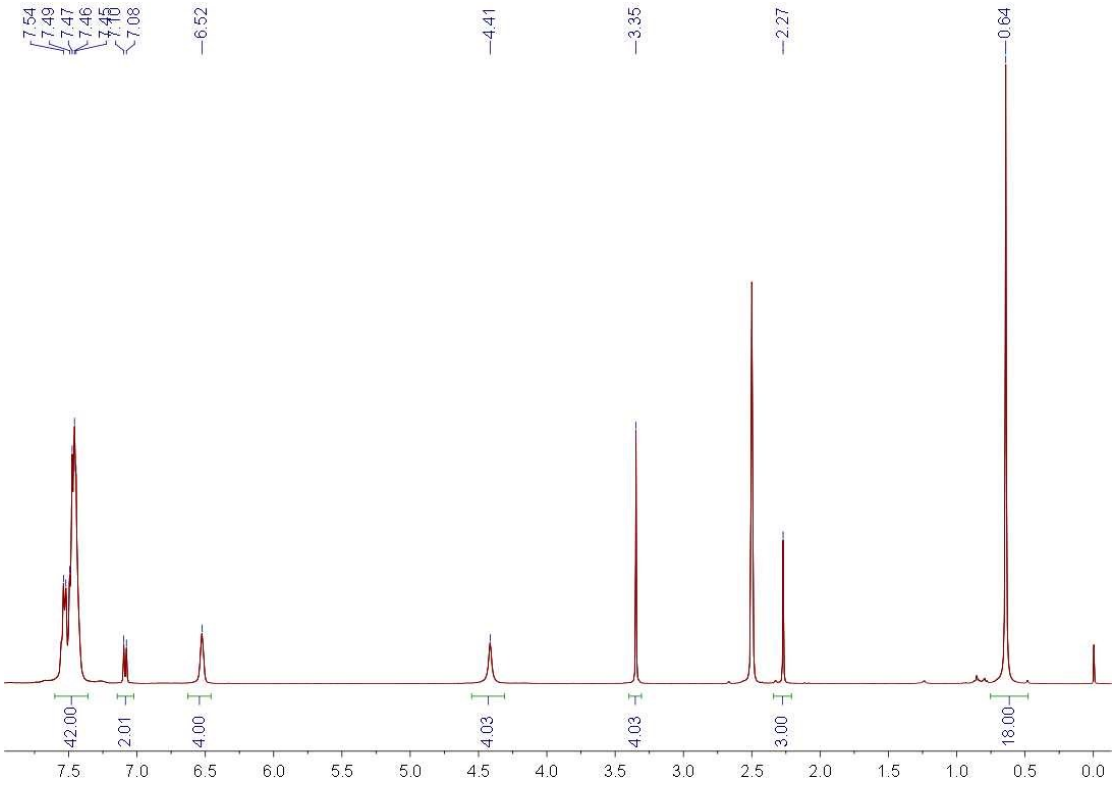


Fig. S10. 400 MHz ^{1}H NMR spectrum of complex **3** in DMSO solution.

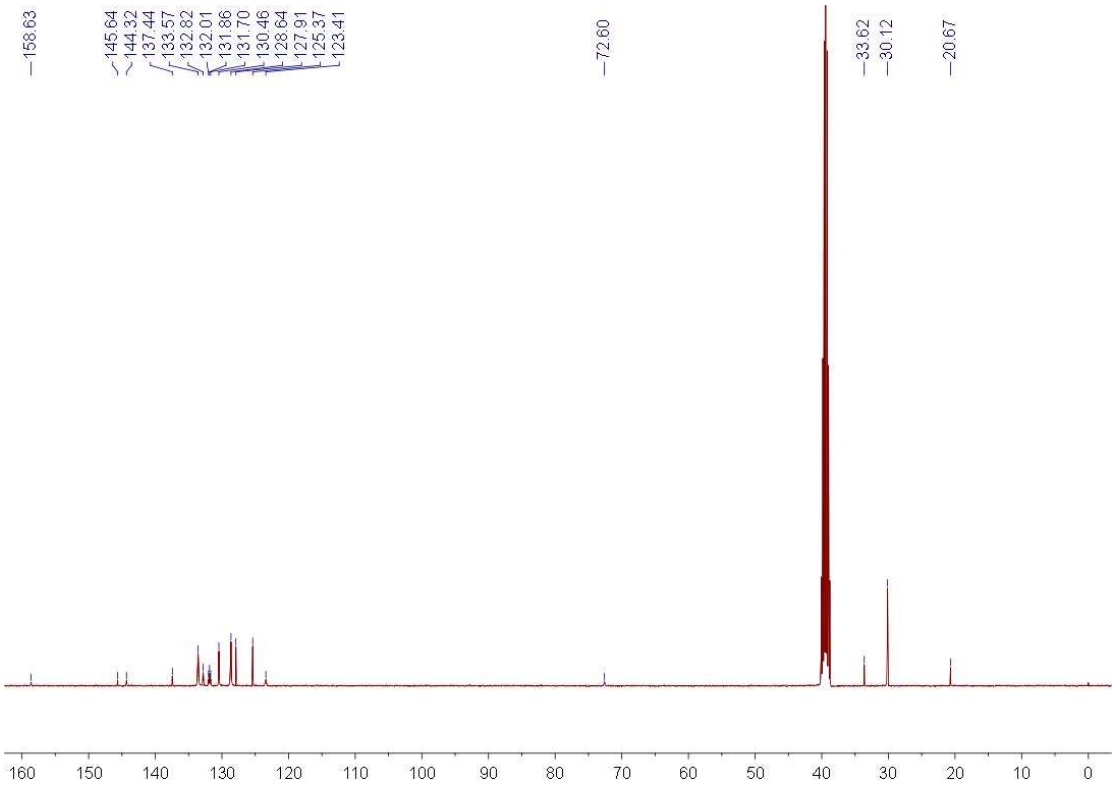


Fig. S11. 101 MHz ^{13}C NMR spectrum of complex **3** in DMSO solution.

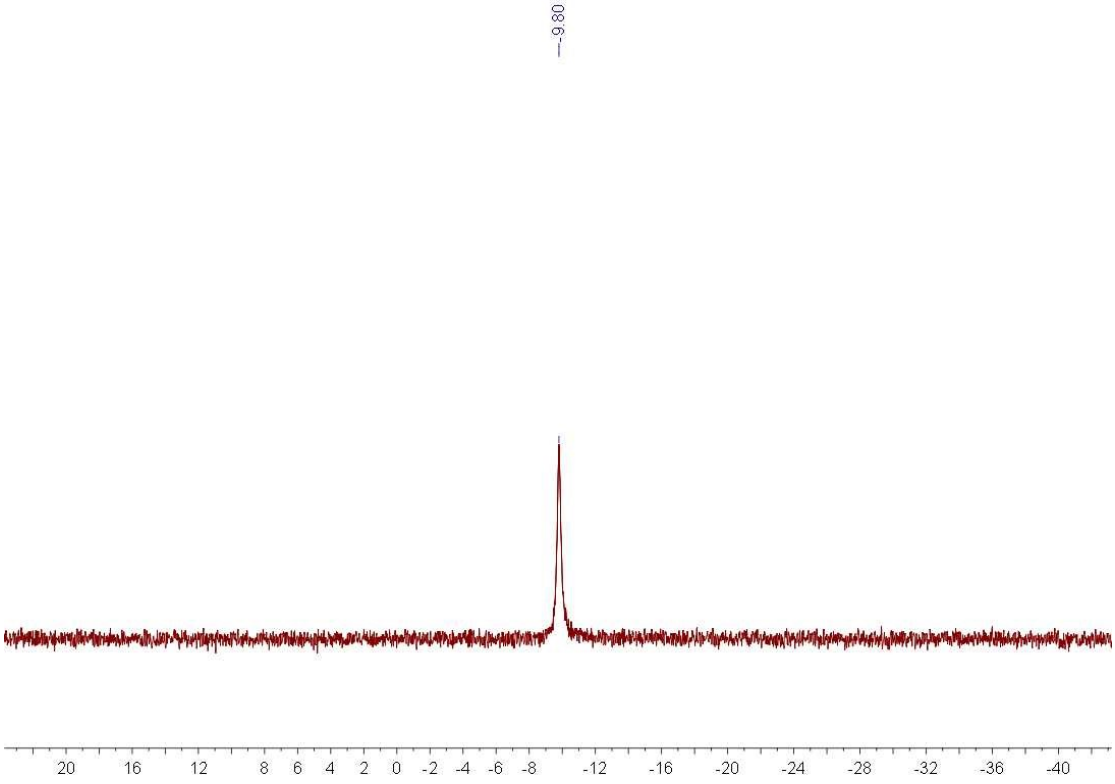
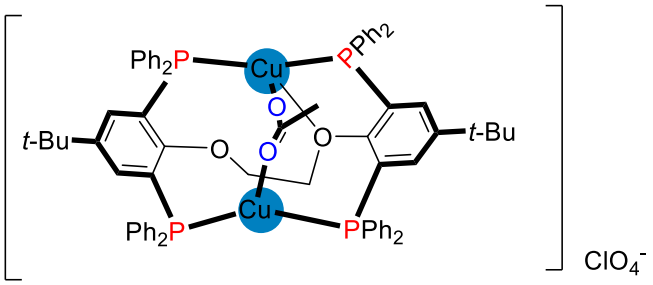


Fig. S12. 162 MHz ^{31}P NMR spectrum of complex **3** in DMSO solution.



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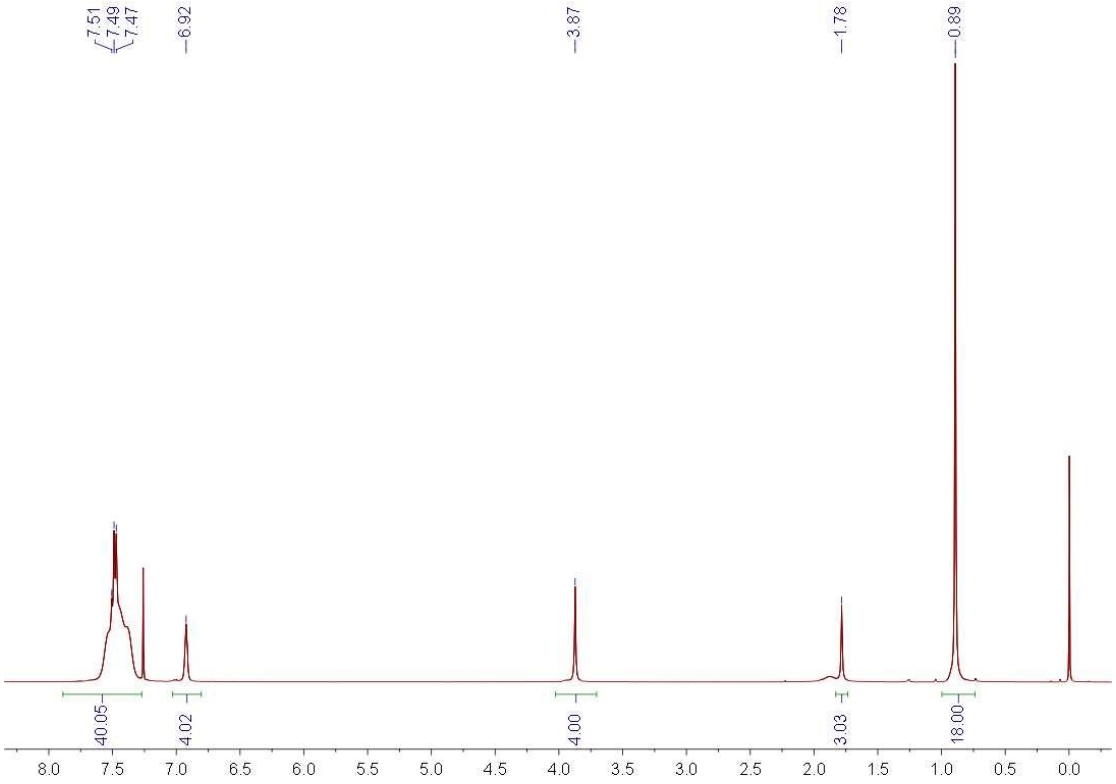


Fig. S13. 400 MHz ^{1}H NMR spectrum of complex **4** in $CDCl_3$ solution.

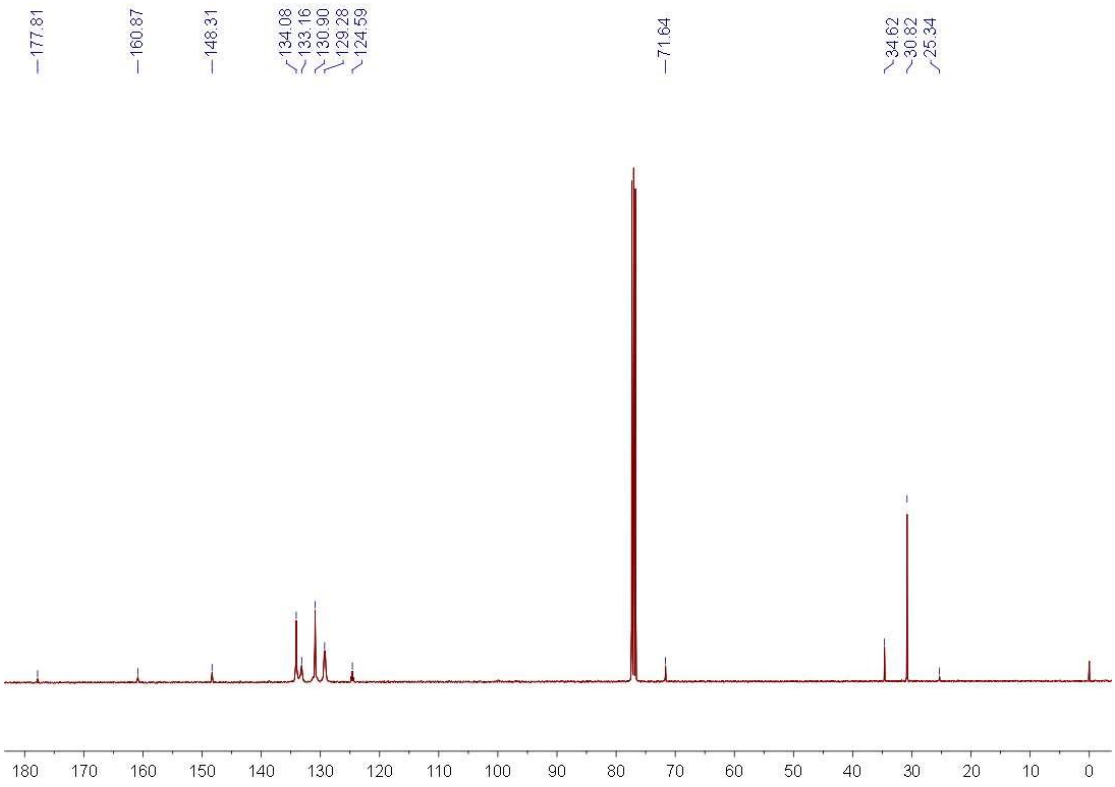


Fig. S14. 101 MHz ^{13}C NMR spectrum of complex **4** in $CDCl_3$ solution.

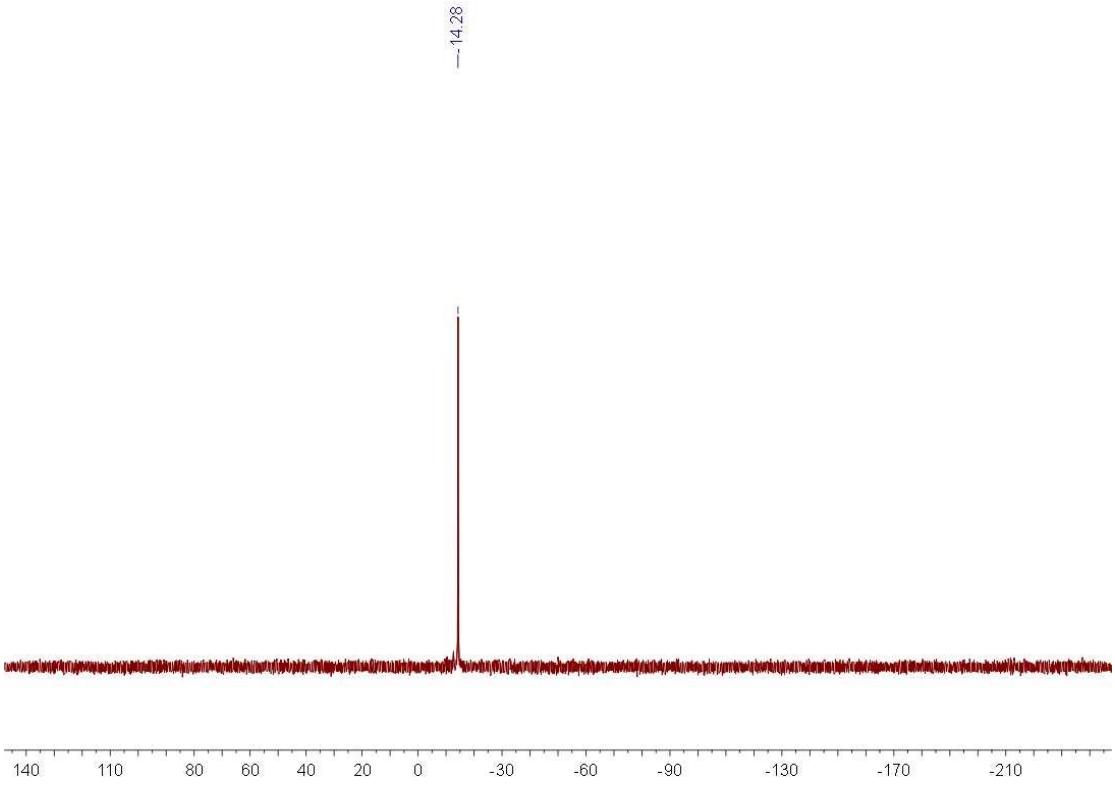
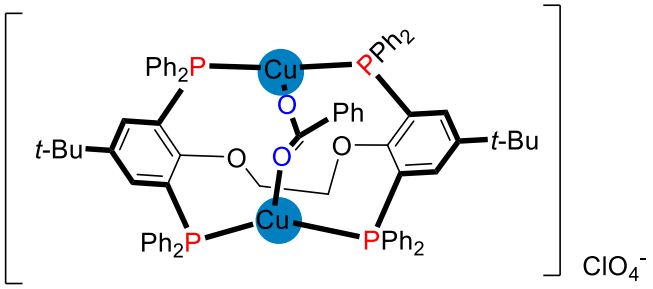


Fig. S15. 162 MHz ^{31}P NMR spectrum of complex **4** in $CDCl_3$ solution.



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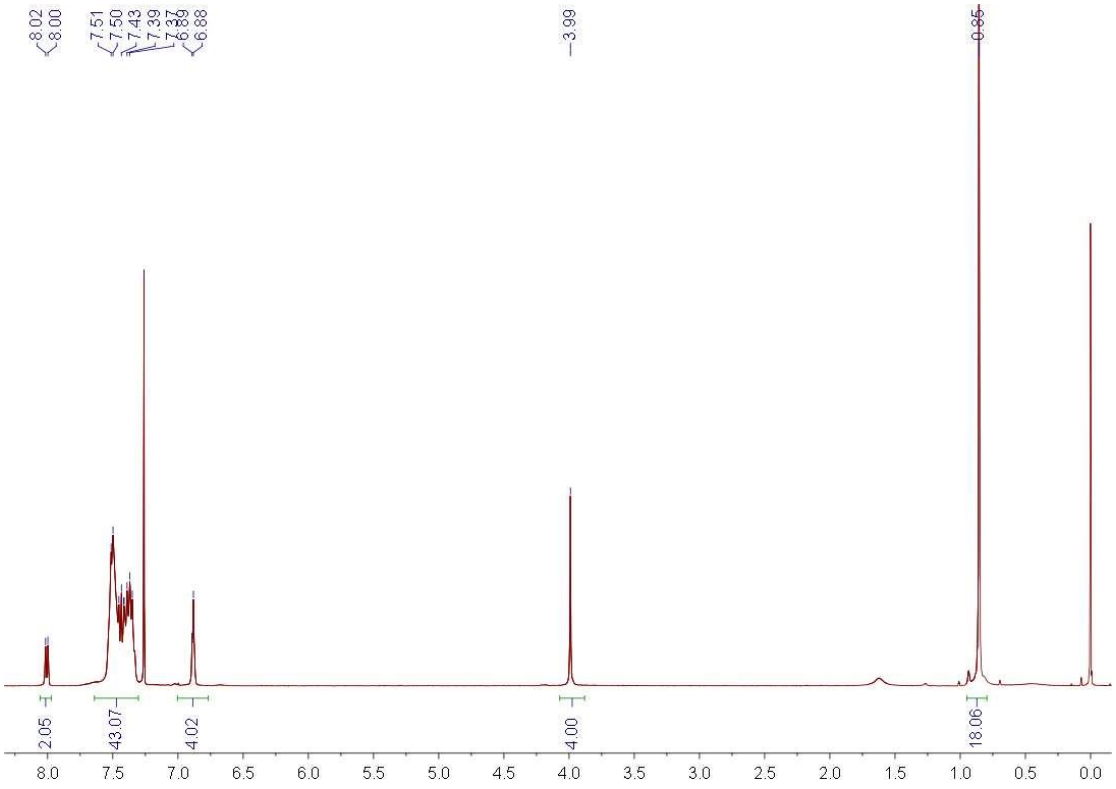

Fig. S16. 400 MHz ^{1}H NMR spectrum of complex **5** in $CDCl_3$ solution.

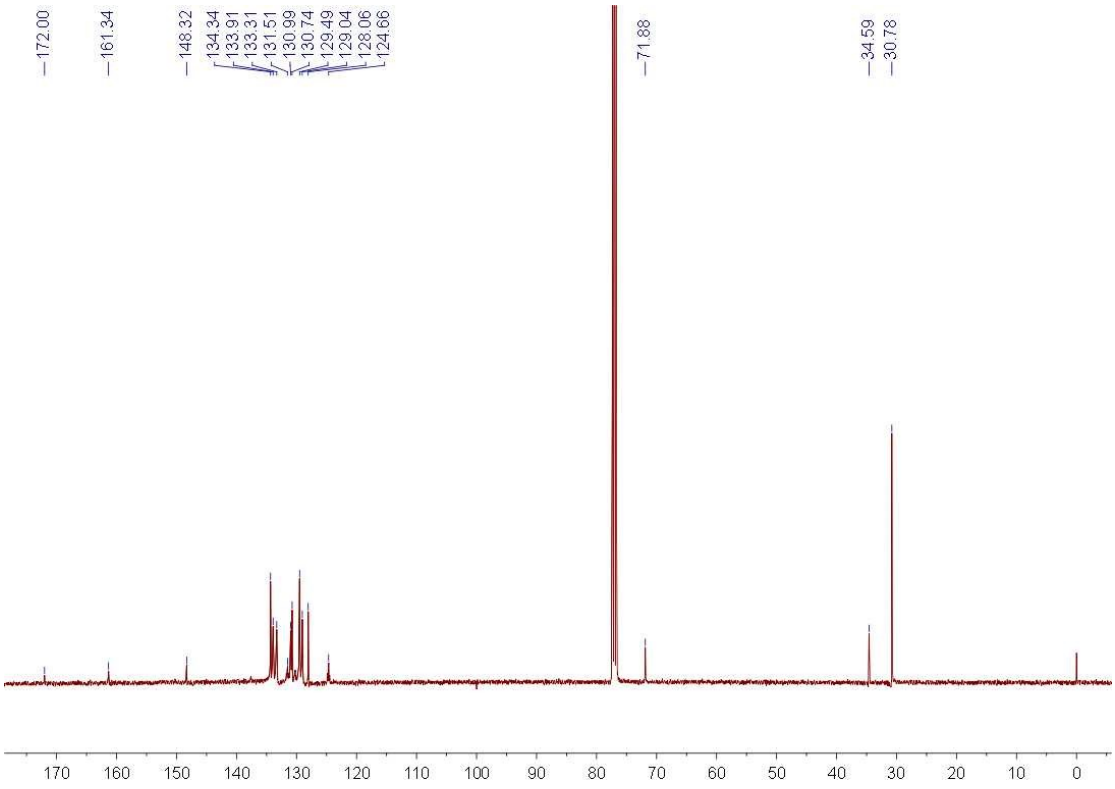

Fig. S17. 101 MHz ^{13}C NMR spectrum of complex **5** in $CDCl_3$ solution.

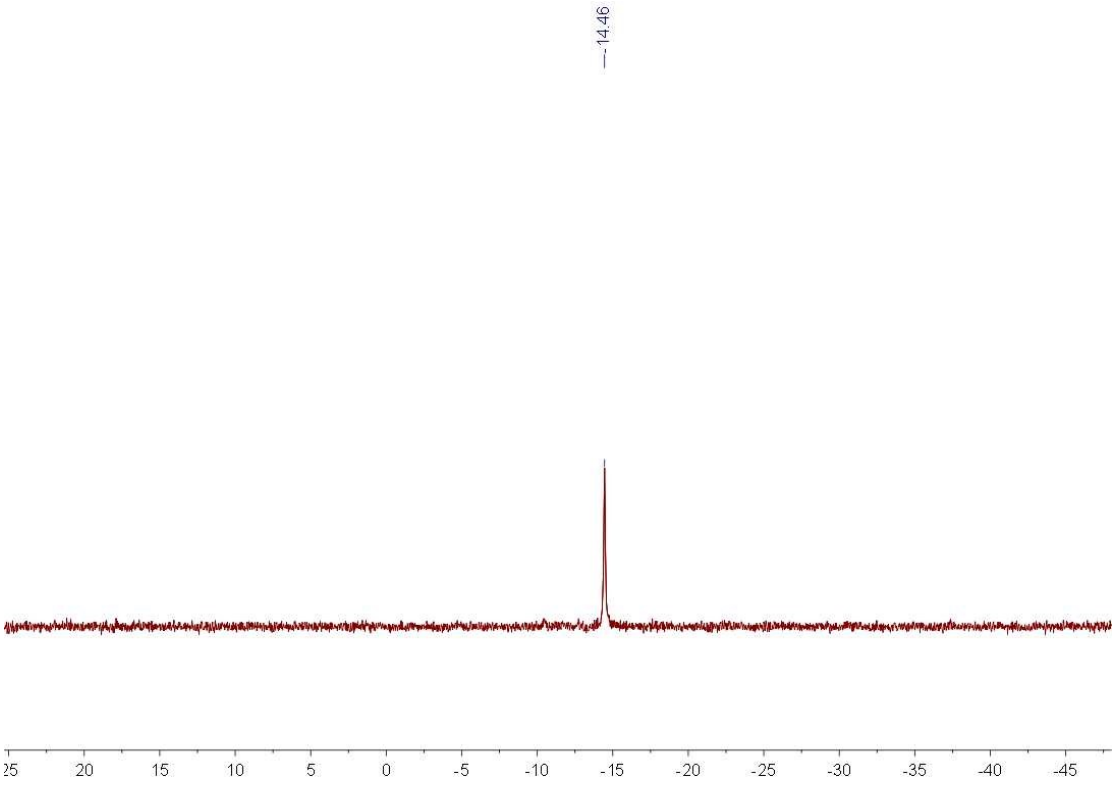

Fig. S18. 162 MHz ^{31}P NMR spectrum of complex **5** in $CDCl_3$ solution.

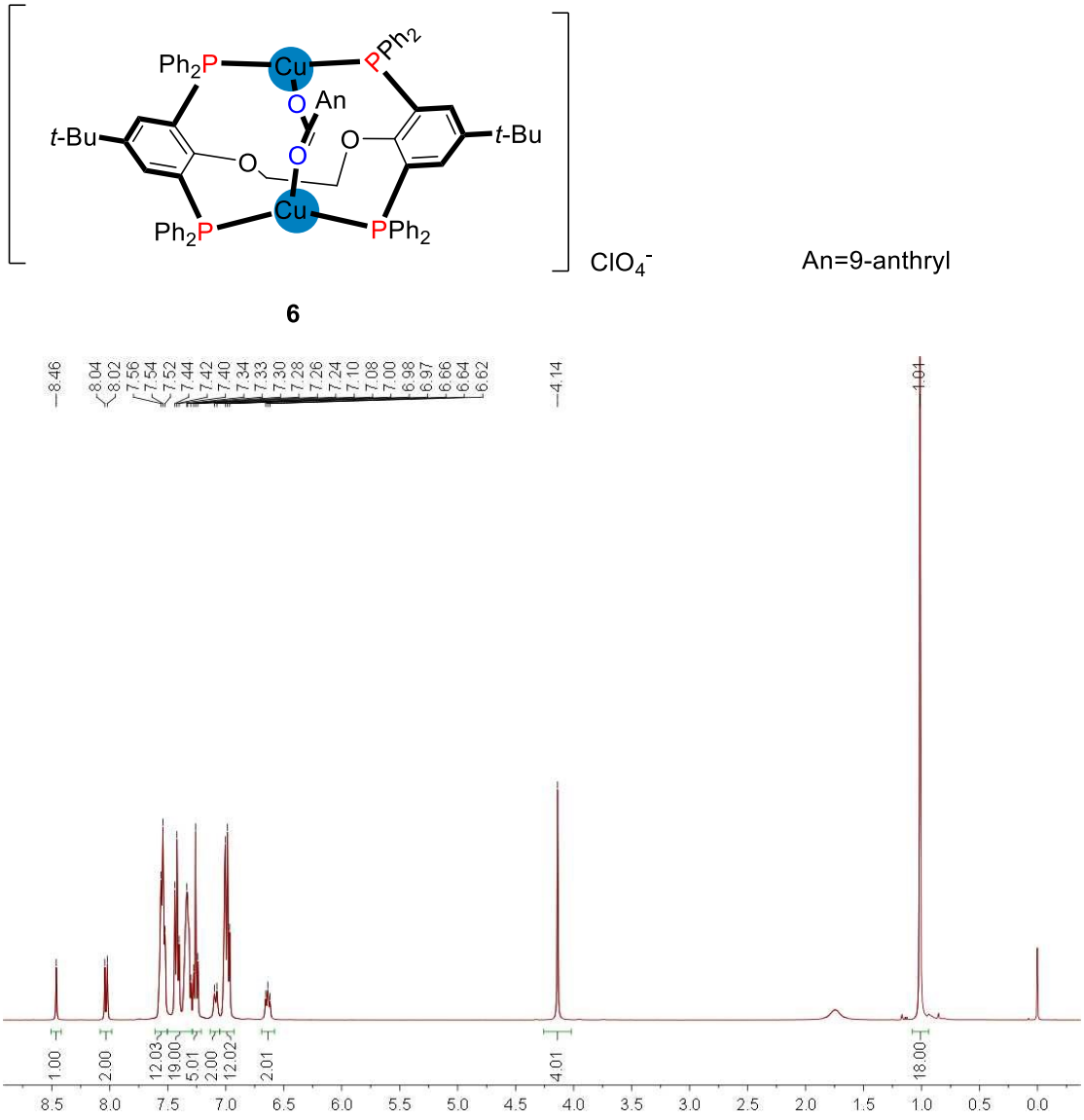

Fig. S19. 400 MHz ^{1}H NMR spectrum of complex **6** in $CDCl_3$ solution.

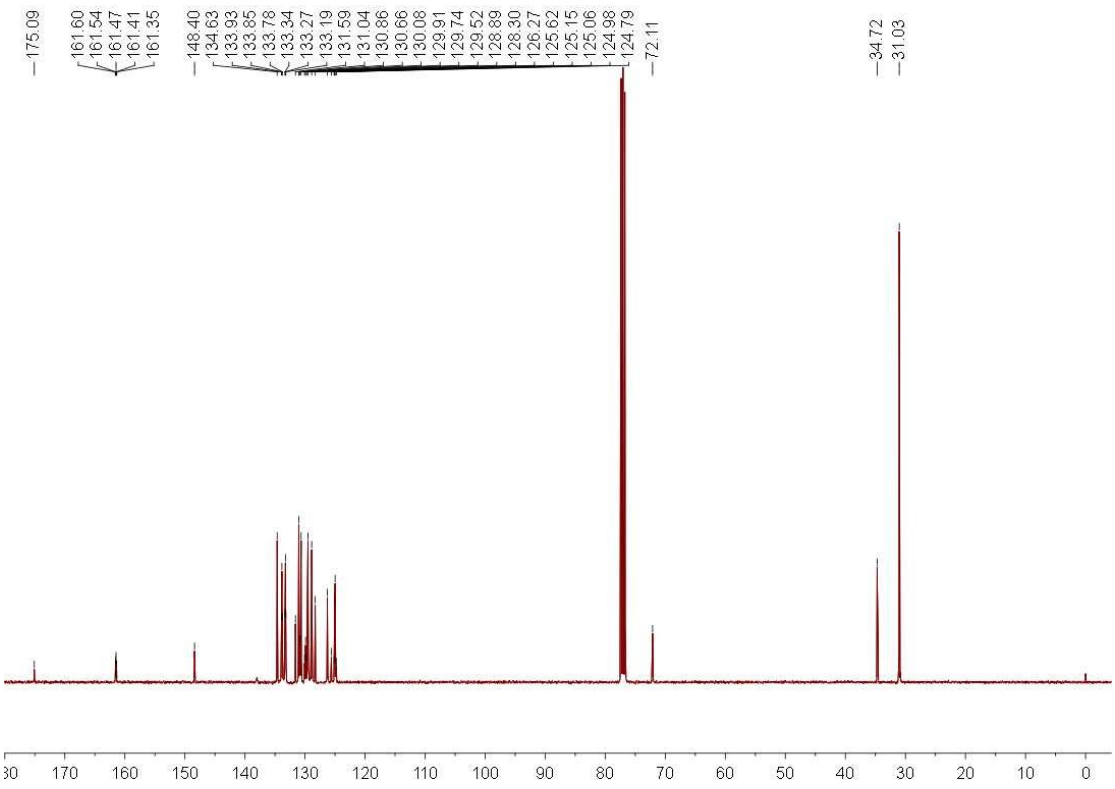

Fig. S20. 101 MHz ^{13}C NMR spectrum of complex **6** in $CDCl_3$ solution.

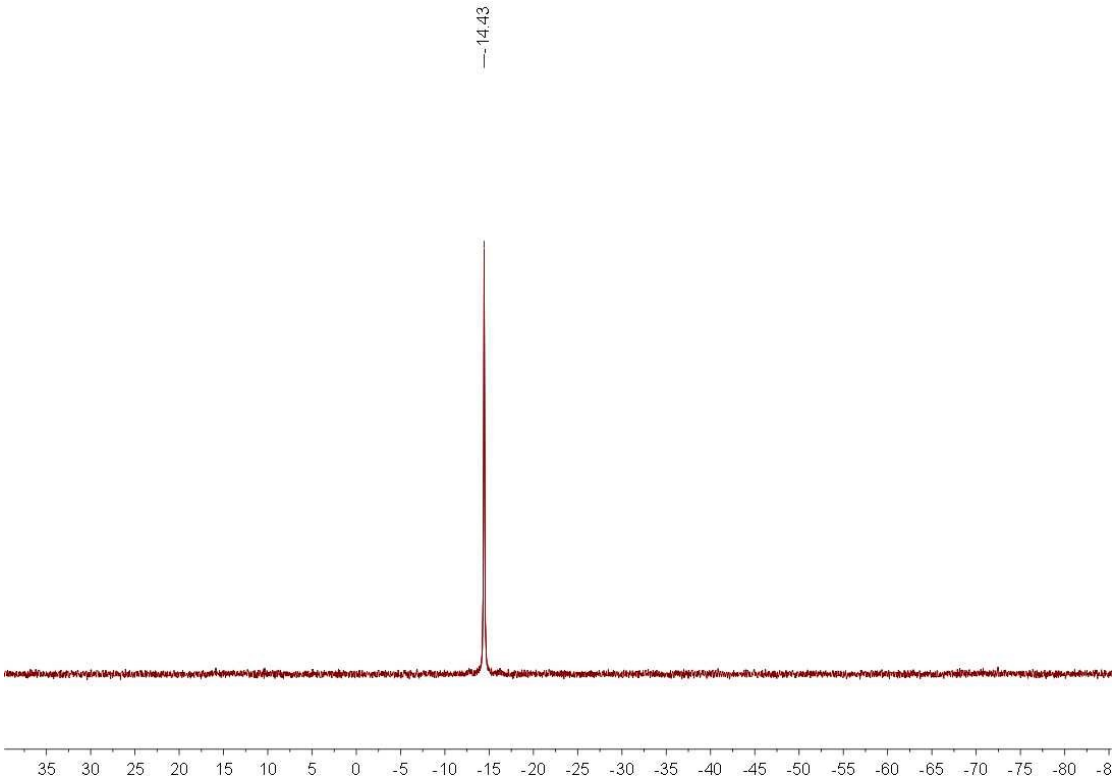

Fig. S21. 162 MHz ^{31}P NMR spectrum of complex **6** in $CDCl_3$ solution.

3. Crystallographic structures

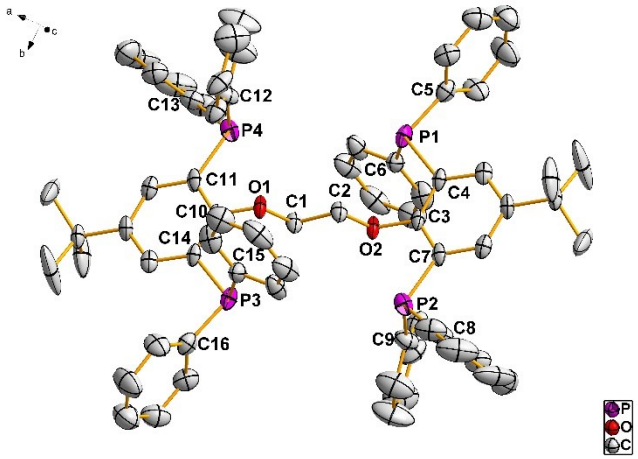

Fig. S22. Molecular views of the X-ray crystal structures of the ligand **L.** Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

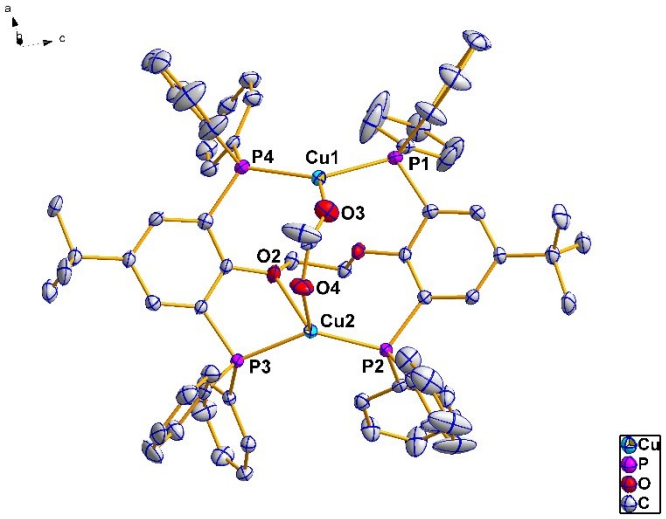

Fig. S23. Molecular views of the X-ray crystal structures of the Cu(I) complex **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, one perchlorate anion and solvent molecules are omitted for clarity.

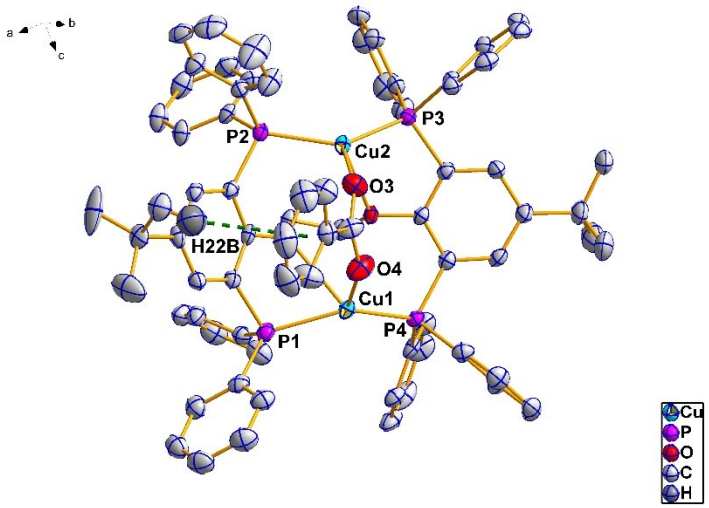

Fig. S24. Molecular views of the X-ray crystal structures of the Cu(I) complex **5**. Thermal ellipsoids are shown at the 50% probability level. Partial hydrogen atoms, one perchlorate anion and solvent molecules are omitted for clarity.

4. Selected bond distances and angles

Ligand **L**			
	Bond Distances (Å)		Bond Angles (º)
O(2)-C(2)	1.442(6)	C(2)-O(2)-C(3)	113.2(4)
O(2)-C(3)	1.397(5)	C(4)-P(1)-C(5)	101.6(2)
P(1)-C(4)	1.838(5)	C(4)-P(1)-C(6)	102.0(3)
P(1)-C(5)	1.822(6)	C(5)-P(1)-C(6)	104.3(3)
P(1)-C(6)	1.827(6)	C(7)-P(2)-C(8)	101.7(2)
P(2)-C(7)	1.842(5)	C(7)-P(2)-C(9)	102.3(3)
P(2)-C(8)	1.825(6)	C(8)-P(2)-C(9)	102.8(3)
P(2)-C(9)	1.836(7)		
Complex **1**			
	Bond Distances (Å)		Bond Angles (º)
Cu(1)-O(3)	2.228(3)	O(3)-Cu(1)-P(1)	121.73(9)
Cu(1)-P(1)	2.2715(13)	O(3)-Cu(1)-P(4)	96.05(9)
Cu(1)-P(4)	2.2787(13)	P(1)-Cu(1)-P(4)	141.89(5)
Cu(2)-O(6)	2.144(3)	O(6)-Cu(2)-P(2)	113.10(9)
Cu(2)-P(2)	2.2496(13)	O(6)-Cu(2)-P(3)	101.27(9)

Cu(2)-P(3)	2.2712(13)	P(2)-Cu(2)-P(3)	144.65(5)
Complex **2**			
	Bond Distances (Å)		Bond Angles (º)
Ag(1)-O(3)	2.445(2)	O(3)-Ag(1)-P(2)	106.79(6)
Ag(1)-P(2)	2.4627(9)	O(3)-Ag(1)-P(1)	105.94(5)
Ag(1)-P(1)	2.4740(10)	P(2)-Ag(1)-P(1)	144.99(3)
N(1)-O(5)	1.242(3)	O(5)-N(1)-O(4)	119.8(3)
N(1)-O(4)	1.261(3)	O(5)-N(1)-O(3)	120.9(3)
N(1)-O(3)	1.264(3)	O(4)-N(1)-O(3)	119.2(2)
Complex **3**			
	Bond Distances (Å)		Bond Angles (º)
Cu(1)-O(3)	2.086(5)	O(3)-Cu(1)-P(1)	122.99(15)
Cu(1)-P(1)	2.2301(18)	O(3)-Cu(1)-P(4)	94.90(15)
Cu(1)-P(4)	2.2881(18)	P(1)-Cu(1)-P(4)	141.86(7)
Cu(2)-O(4)	2.094(4)	O(4)-Cu(2)-P(3)	115.08(15)
Cu(2)-P(3)	2.2332(19)	O(4)-Cu(2)-P(2)	105.22(14)
Cu(2)-P(2)	2.2719(18)	P(3)-Cu(2)-P(2)	139.04(7)
Complex **4**			
	Bond Distances (Å)		Bond Angles (º)
Cu(1)-O(3)	2.015(2)	O(3)-Cu(1)-P(4)	114.55(9)
Cu(1)-P(4)	2.2560(10)	O(3)-Cu(1)-P(1)	105.07(9)

Cu(1)-P(1)	2.3057(10)	P(4)-Cu(1)-P(1)	140.12(3)
Cu(2)-O(4)	2.011(3)	O(4)-Cu(2)-P(2)	113.98(9)
Cu(2)-P(2)	2.2153(9)	O(4)-Cu(2)-P(3)	106.46(8)
Cu(2)-P(3)	2.2673(9)	P(2)-Cu(2)-P(3)	137.33(3)
Cu(2)-O(2)	2.436(2)	O(4)-Cu(2)-O(2)	91.69(10)
		P(2)-Cu(2)-O(2)	116.51(6)
		P(3)-Cu(2)-O(2)	74.01(6)
Complex 5			
	Bond Distances (Å)		Bond Angles (º)
Cu(1)-O(4)	2.041(3)	O(4)-Cu(1)-P(4)	111.14(11)
Cu(1)-P(4)	2.2538(8)	O(4)-Cu(1)-P(1)	108.18(11)
Cu(1)-P(1)	2.2886(8)	P(4)-Cu(1)-P(1)	140.68(3)
Cu(2)-O(3)	2.030(3)	O(3)-Cu(2)-P(3)	117.18(12)
Cu(2)-P(3)	2.2366(8)	O(3)-Cu(2)-P(2)	102.29(11)
Cu(2)-P(2)	2.2509(8)	P(3)-Cu(2)-P(2)	139.40(3)
Complex **6**			
	Bond Distances (Å)		Bond Angles (º)
Cu(1)-O(3)	1.996(2)	O(3)-Cu(1)-P(1)	107.20(7)

Cu(1)-P(1)	2.2349(9)	O(3)-Cu(1)-P(4)	113.75(7)
Cu(1)-P(4)	2.2380(9)	P(1)-Cu(1)-P(4)	138.17(3)
Cu(2)-O(4)	2.001(2)	O(4)-Cu(2)-P(3)	107.30(7)
Cu(2)-P(3)	2.2339(9)	O(4)-Cu(2)-P(2)	111.84(7)
Cu(2)-P(2)	2.2458(9)	P(3)-Cu(2)-P(2)	139.87(3)

5. Crystal Data and Structural Refinement for Complexes.

Table S1. Crystal Data and Structural Refinement for Complexes 1-2

Compound	**1**	**2**
Empirical formula	$C_{70}H_{66}Cl_2Cu_2O_{10}P_4$	$C_{37}H_{35}AgCl_6NO_4P_2$
Formula weight	1389.08	940.17
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/m$
a (Å)	13.292(3)	11.219(2)
b (Å)	28.940(6)	25.594(5)
c (Å)	17.711(4)	14.172(3)
α (º)	90	90
β (º)	106.566(3)	93.92(3)
γ (º)	90	90
V (Å^3)	6530(2)	4060.1(14)
Z	4	4
D_{calcd}(Mg/m^3)	1.413	1.538
Abs coeff (mm^{-1})	0.890	1.009
F (000)	2872	1900
Crystal size	0.180 x 0.160 x 0.140 mm	0.180 x 0.160 x 0.140 mm
Range of θ for data collection	1.391 to 25.018°	1.591 to 25.020°
Reflections collected/ unique	49080 / 11528 [R(int) = 0.0785]	29906 / 7269 [R(int) = 0.0411]
Max. & min. transmission	0.8855 and 0.8562	1.0000 and 0.6742
Final R indices[$I>2\sigma(I)$]	R1 = 0.0667, wR2 = 0.1517	R1 = 0.0373, wR2 = 0.0906

R indices (all data)	R1 = 0.0813, wR2 = 0.1605	R1 = 0.0421, wR2 = 0.0939
Data/restraints/parameters	11528 / 170 / 861	7269 / 354 / 495
Goodness-of-fit on F^2	1.102	1.032

Table S2. Crystal Data and Structural Refinement for Complexes 3-6

Compound	**3**	**4**	**5**	**6**
Empirical formula	$C_{80}H_{76}Cl_{10}Cu_2O_9P_4S$	$C_{74}H_{72}Cl_6Cu_2O_8P_4$	$C_{79}H_{73}Cl_7Cu_2O_8P_4$	$C_{87}H_{77}Cl_7Cu_2O_8P_4$
Formula weight	1818.92	1552.97	1649.48	1749.59
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pna*2$_1$	*P*2$_1$/n	*P*2$_1$/n	*P*2$_1$/n
a (Å)	20.061(4)	13.204(3)	17.962(3)	17.720(4)
b (Å)	23.316(5)	20.254(4)	20.584(3)	20.286(4)
c (Å)	17.798(4)	27.031(5)	21.081(3)	23.057(5)
α (º)	90	90	90	90
β (º)	90	94.95(3)	100.796(3)	90.04(3)
γ (º)	90	90	90	90
V (Å^3)	8325(3)	7202(3)	7656.4(19)	8288(3)
Z	4	4	4	4
D_{calcd}(Mg/m^3)	1.451	1.432	1.431	1.402
Abs coeff (mm^{-1})	0.988	0.957	0.938	0.871
F (000)	3728	3200	3392	3600
Crystal size	0.180 x 0.160 x 0.140 mm	0.180 x 0.160 x 0.140 mm	0.180 x 0.160 x 0.140 mm	0.2000 x 0.1800 x 0.1600 mm
Range of θ for data collection	1.339 to 25.020°	1.816 to 27.869°	1.369 to 25.009°	1.337 to 25.020°
Reflections collected/ unique	60785 / 14685 [R(int) = 0.0520]	78478 / 17101 [R(int) = 0.0497]	79083 / 13500 [R(int) = 0.0417]	68212 / 14638 [R(int) = 0.0585]

Max. & min. transmission	0.8740 and 0.8421	0.8777 and 0.8467	0.8799 and 0.8493	1.0000 and 0.8314
Final R indices[$I>2\sigma(I)$]	R1 = 0.0481, wR2 = 0.1104	R1 = 0.0598, wR2 = 0.1497	R1 = 0.0462, wR2 = 0.1100	R1 = 0.0451, wR2 = 0.1059
R indices (all data)	R1 = 0.0504, wR2 = 0.1116	R1 = 0.0715, wR2 = 0.1598	R1 = 0.0489, wR2 = 0.1119	R1 = 0.0594, wR2 = 0.1141
Data/restraints/parameters	14685 / 109 / 988	17101 / 319 / 937	13500 / 478 / 951	14638 / 0 / 943
Goodness-of-fit on F^2	1.123	0.951	1.081	1.022

6. The optimized ball-and-stick structure of complexes 4-6

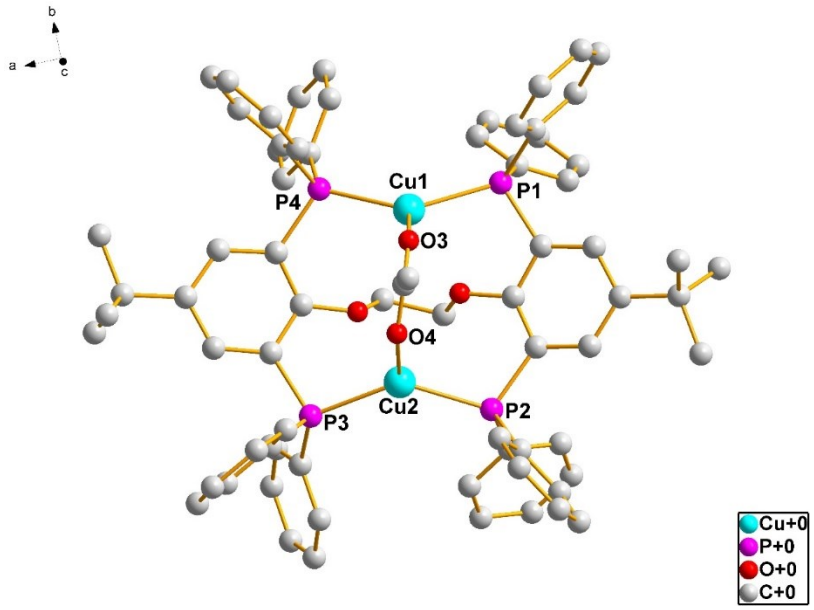

Fig. S25a. The optimized ball-and-stick structure without D3 of the Cu(I) complex **4**. Hydrogen atoms, one perchlorate anion and solvent molecules are omitted.

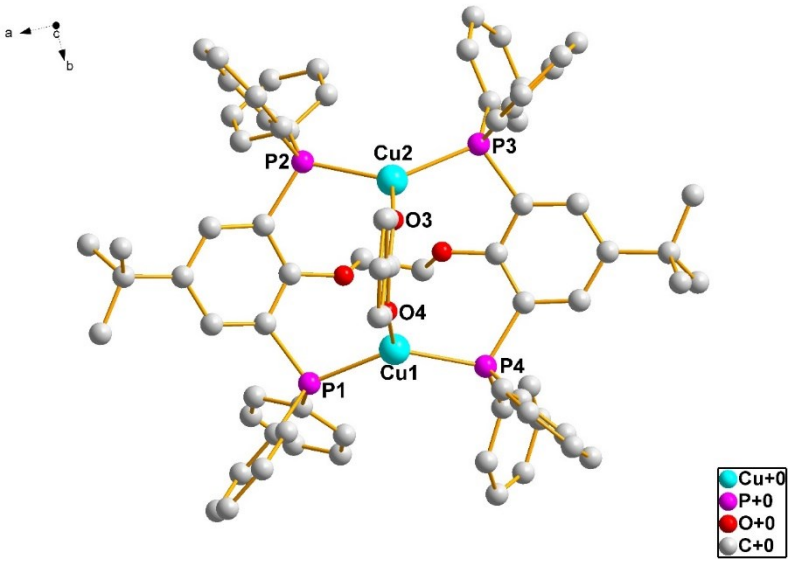

Fig. S25b. The optimized ball-and-stick structure without D3 of the Cu(I) complex **5**. Hydrogen atoms, one perchlorate anion and solvent molecules are omitted.

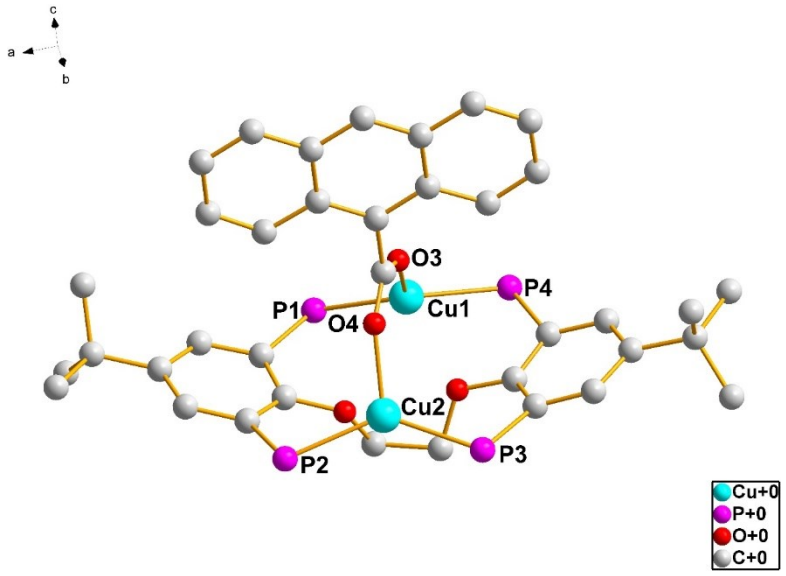

Fig. S25c. The optimized ball-and-stick structure without D3 of the Cu(I) complex **6**. Hydrogen atoms, one perchlorate anion, solvent molecules and phenyl are omitted.

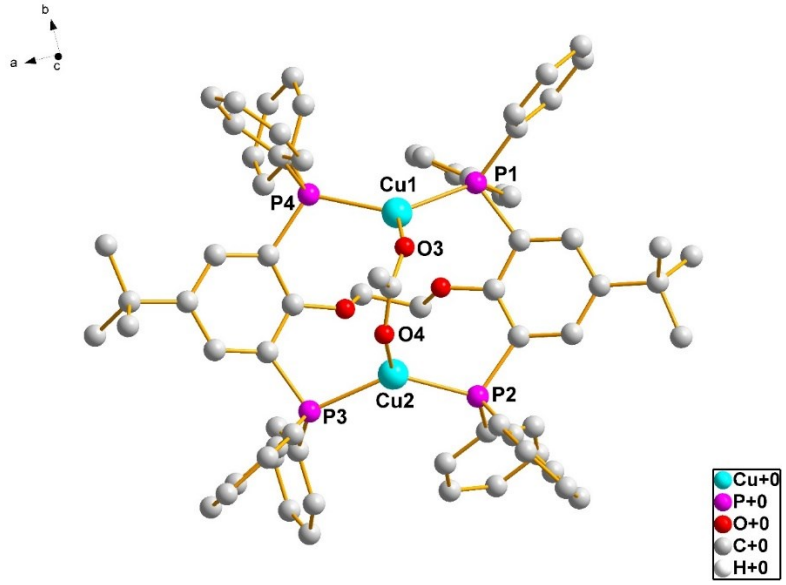

Fig. S26a. The optimized ball-and-stick structure with D3 of the Cu(I) complex **4**. Hydrogen atoms, one perchlorate anion and solvent molecules are omitted.

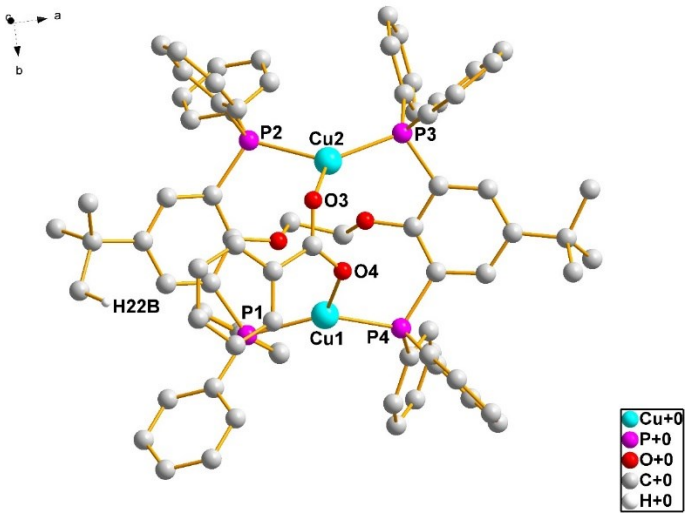

Fig. S26b. The optimized ball-and-stick structure with D3 of the Cu(I) complex **5**. Partial hydrogen atoms, one perchlorate anion and solvent molecules are omitted.

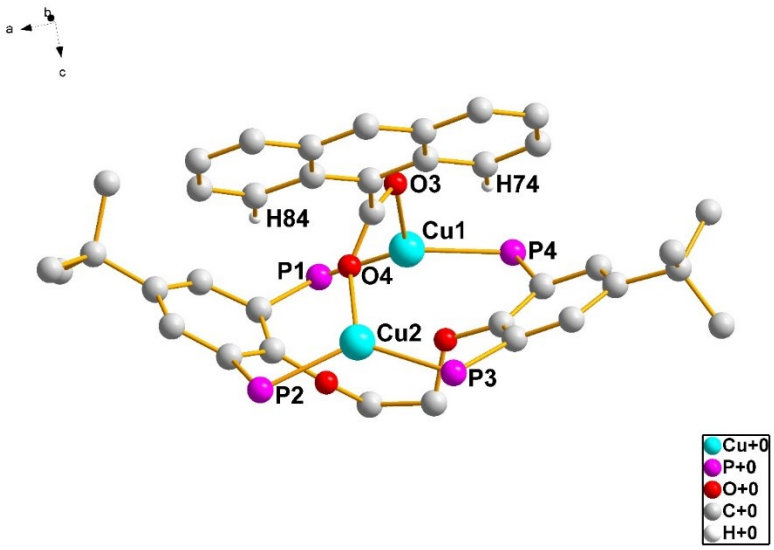

Fig. S26c. The optimized ball-and-stick structure with D3 of the Cu(I) complex **6**. Partial hydrogen atoms, one perchlorate anion, solvent molecules and phenyl are omitted.

7. Comparing diagram of crystal structure (orange) and calculation structure (green) for complex 5.

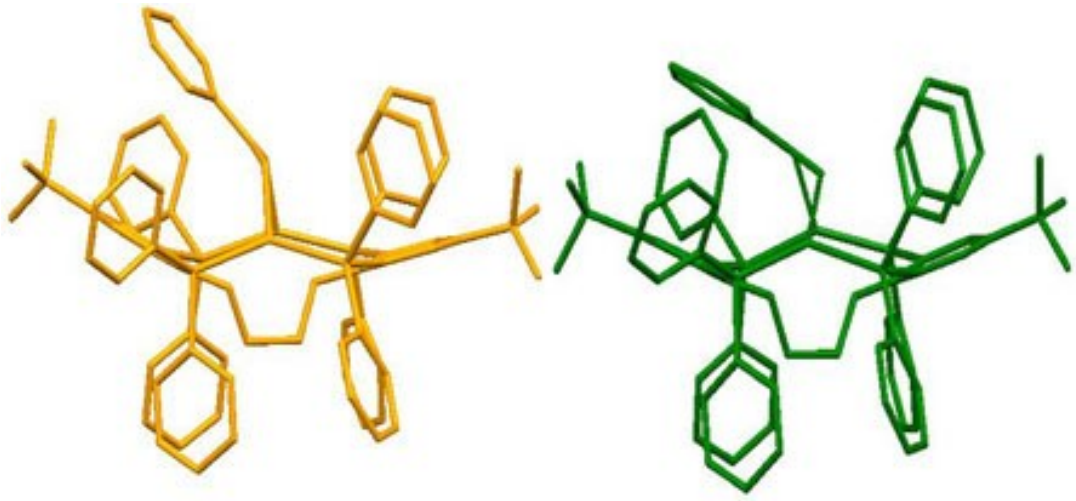

Fig. S27. Comparing diagram of crystal structure (orange) and calculation structure (green) for complex **5**. The structure is displayed in wire model.

8. Calculation information table

Table S3. Details of calculation data collection for complexes 4-6

Calculation (with D3)					
	Dihedral(exp.)	Dihedral(cal)	Gibbs free Energy(A.U.)	Interaction Energy(A.U.)	Interaction Energy(kJ/mol)
host			-4614.606944		
guest 4			-228.5543469		
complex 4	147.96°	142.78°	-4843.262275	-0.100983545	-265.1322974
guest 5			-420.2599563		
complex 5	139.54°	140.69°	-5034.975662	-0.108761619	-285.5536307
guest 6			-727.4469224		
complex 6	133.12°	130.24°	-5342.208723	-0.154856086	-406.5746538
Calculation (NO D3)					
	Dihedral(exp.)	Dihedral(cal)	Gibbs free Energy(A.U.)	Interaction Energy(A.U.)	Interaction Energy(kJ/mol)
host			-4614.161106		
guest 4			-228.5543736		
complex 4	147.96°	147.84°	-4842.778184	-0.06270469	-164.6311636
guest 5			-420.2600786		
complex 5	139.54°	148.97°	-5034.470925	-0.049740727	-130.5942787
guest 6			-727.44722		
complex 6	133.12°	146.88°	-5341.65549	-0.047164471	-123.8303186