Supporting Information

Effect of non-covalent self-dimerization on the spectroscopic and electrochemical properties of mixed Cu(I) complexes.

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I.- Syntheses of complexes

General procedures

The new series of [Cu(NN'-R)(PPh_3)Br] complexes were synthesized by the template condensation method from equimolar amounts of reagents.

To a dichloromethane/methanol (10:1) mixture solution of CuBr, a DCM/MeOH (8:2) solution of pyridine-2-carbaldehyde was added at room temperature, and after continuous stirring for 20 min, corresponding 4-substituted-aniline in the same solvent's mixture was added, and the solution mixture was stirred for 30 min. Subsequently, a solution of triphenylphosphine (PPh_3) was added dropwise and stirred for one more hour at room temperature, forming a coloured solution. The volume of solution was reduced in a rotary evaporator and the concentrate was precipitate with diethyl ether and washed with 3x5 mL of diethyl ether. The slow evaporation from a relatively concentrated solution of dichloromethane/methanol (8:2) yield pure crystals of complexes ranging from orange to purple red color. However, for some complexes, adequate crystals for crystallographic studies were obtained by diffusion of diethyl ether vapor into a concentrated compound in dichloromethane solutions.

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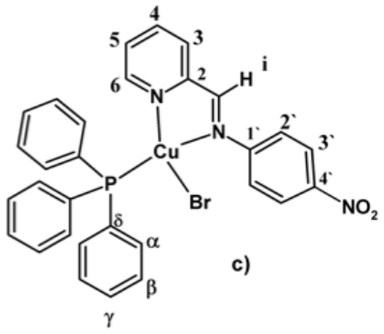


Structure of the [Cu(NN`-R)(PPh_3)Br] complexes with the labels used in the NMR assignments

1.1- [Cu(NN'-NO_2)(PPh_3)Br]. This complex was previously reported. (Jara H. D., Lemus L., Farías L., Freire E., Baggio R., Guerrero J., Eur. J. Inorg. Chem. 2012, 1579–1583)

Yield: 71 %. (Found: C, 57.0; H, 3.9; N, 6.2. Calc. for $C_{30}H_{24}BrCuN_3O_2P$: C, 56.9; H, 3.8; N, 6.6%) ^{1}H-NMR ($CDCl_3$, 10 mM, 298 K): δ/ppm = 8.73 (d, 1H, $J_{H6,5}$ = 4.10 Hz, H_6), 8.59 (s, 1H, H_i), 8.12 (d, 2H, $J_{H3',2'}$ = 8.86 Hz, $H_{3'}$), 7.91 (overlapping with H_3, H_4), 7.86 (overlapping with H_4, H_3), 7.62 (d, 2H, $J_{2',3'}$ = 8,86 Hz, $H_{2'}$), 7.52 (m, 1H, H_5), 7.36 (st, 6H, H_α), 7.32 (t, 3H, $J_{H\gamma,\beta}$ = 7.1 Hz, H_γ), 7.24 (st, 6H, $J_{H\beta,\gamma}$ = 7.1 Hz, $J_{H\beta,\alpha}$ = 8.60 Hz, H_β). ^{13}C {^{1}H} NMR ($CDCl_3$, 10 mM, 298 K): δ/ppm = 158.7 (C_i), 153.6 ($C_{1'}$), 150.4 (C_6), 149.4 (C_2), 146.8 ($C_{4'}$), 137.5 (C_4), 133.7 (C_α), 129.9 (C_γ), 126.7 (C_β), 127.98 (C_5), 128.0 (C_3), 124.9 ($C_{3'}$), 123.2 ($C_{2'}$). ^{31}P {^{1}H} NMR (10 mM, $CDCl_3$): δ/ppm = -1.3.

1.2- [Cu(NN'-$COCH_3$)(PPh_3)Br]. CuBr (0.11 g, 0.79 mmol), pyridine-2-carbaldehyde (0.11 g, 0.79 mmol), 4-aminoacetophenone (0.08 g, 0.79 mmol), PPh_3 (0.21 g, 0.79 mmol). The slow evaporation of DCM/MeOH of solution gave red crystals. Yield: 87%. (Found: C, 61.2; H, 4.4; N, 4.6. Calc. for $C_{32}H_{27}BrCuN_2OP$: C, 61.1; H, 4.3; N, 4,45%). ^{1}H-NMR ($CDCl_3$, 8 mM, 298 K): δ/ppm = 8.66 (d, 1H, $J_{H6,5}$ =4.57 Hz, H_6), 8.52 (s, 1H, H_i), 7.88 (t, overlap with $H_{3'}$, H_4), 7.87 (d, 2H, $J_{H3',2'}$ =8.42 Hz, $H_{3'}$), 7.79 (d, 1H, $J_{H3,4}$ =7.50 Hz, H_3), 7.59 (d, 2H, $J_{2',3'}$ = 8,42 Hz, $H_{2'}$), 7.46 (t, 1H, $J_{H5,6}$ = 6.04 Hz, H_5), 7.37 (st, 6H, H_α), 7.32 (t, 3H, $J_{H\gamma,\beta}$ = 7.1 Hz, H_γ), 7.24 (st, 6H, $J_{H\beta,\gamma}$ = 7.1 Hz, $J_{H\beta,\alpha}$ = 8.4 Hz, H_β), 2.60 (s, 3H, H_a). ^{13}C {^{1}H} NMR ($CDCl_3$, 8 mM, 298 K): δ/ppm = 158.5 (C_i), 157.8 ($C_{1'}$), 150.4 (C_6), 148.8 (C_2), 146.7 ($C_{4'}$), 137.4 (C_4), 133.60 (C_γ), 129.8 (C_α), 128.5 (C_β), 127.9 (C_5), 127.5 (C_3), 124.8 ($C_{3'}$), 122.8 ($C_{2'}$). ^{31}P {^{1}H} NMR ($CDCl_3$, 0.02 M, 298 K): δ/ppm= -1.3.

1.3- [Cu(NN'-H)(PPh_3)Br]. This complex was prepared using CuBr (0.24 g, 1.70 mmol), pyridine-2-carbaldehyde (0.18 g, 1.70 mmol), aniline (0.16 g, 1.70 mmol), PPh_3 (0.45 g, 1.70 mmol). The slow evaporation of DCM/MeOH of solution gave dark red crystals. Yield: 91 %. (Found: C, 61.1; H, 4.5; N, 4.6. Calc. for $C_{30}H_{25}BrCuN_2P$: C, 61.3; H, 4.3; N, 4,8%). ^{1}H-NMR ($CDCl_3$,10mM, 298 K): δ/ppm = 8.62 (d, 1H, $J_{H6,5}$ = 4.03 Hz, H_6), 8.49 (s, 1H, H_i), 7.85 (t, 1H, $J_{H4,3}$ = 7.50 Hz, H_4), 7.73 (d, 1H, $J_{H3,4}$ = 7.50 Hz, H_3), 7.60 (d, 2H, $J_{2',3'}$ = 7.14 Hz, $H_{2'}$), 7.42 (overlap with H_α, H_5), 7.29 (overlap with H_γ, $H_{3'}$), 7.23 (overlap with H_β, $H_{4'}$), 7.39 (st, 6H, H_α), 7.32 (t,3H $J_{H\gamma,\beta}$= 7.5 Hz, H_γ), 7.23 (st, 6H, $J_{H\beta,\gamma}$ = 7.5 Hz, $J_{H\beta,\alpha}$ = 8.1 Hz, H_β).^{13}C {^{1}H} NMR ($CDCl_3$, 10 mM, 298 K): δ/ppm = 155.5 (C_i), 150.3 (C_2), 150.0 (C_6), 148.2 ($C_{1'}$), 128.2 ($C_{4'}$), 137.2 (C_4), 129.4 (C_γ), 133.5 (C_α), 128.4 (C_β), 126.9 (C_3), 129.1 ($C_{3'}$), 127.0 (C_5), 126.9 (C_δ), 122.5 ($C_{2'}$). ^{31}P{^{1}H} NMR ($CDCl_3$,0.02 mM, 298 K): δ/ppm=-1.6.

1.4- [Cu(NN'-CH_3)(PPh_3)Br]. This complex was prepared using CuBr (0.24 g, 1.66 mmol), pyridine-2-carbaldehyde (0.18 g, 1.66 mmol), 4-methylaniline (0.18 g, 1.66 mmol), PPh_3 (0.44 g, 1.66 mmol). The slow evaporation of DCM/MeOH of solution gave brick-red crystals. Yield: 89 %. (Found: C, 61.7; H, 4.7; N, 4.6. Calc. for $C_{31}H_{27}BrCuN_2P$: C, 61.85; H, 4.5; N, 4,65%) ^{1}H-NMR ($CDCl_3$, $CDCl_3$,10 mM, 298 K): δ = 8.60 (d, 1H, $J_{H5,6}$ = 4.03 Hz, H_6), 8.49 (s, 1H, H_i), 7.83 (t, 1H, $J_{H4,3}$ = 7.50 Hz, H_4), 7.69 (d, 1H, $J_{H3,4}$ = 7.50 Hz, H_3), 7.53 (d, 2H, $J_{2',3'}$ = 7.87 Hz, $H_{2'}$), 7.39 (overlap with H_α, H_5), 7.39 (st, 6H, H_α), 7.31 (t, 3H, $J_{H\gamma,\beta}$ = 7.3 Hz, H_γ), 7.24 (st, 6H, $J_{H\beta,\gamma}$ = 7.3 Hz, $J_{H\beta,\alpha}$= 7.9 Hz, H_β), 7.08 (d, 2H, $J_{H3',2'}$ = 7.87 Hz, $H_{3'}$), 2.34 (s, 6H, H_a). ^{13}C {^{1}H} NMR (CDCl3, 10 mM, 298 K): δ/ppm = 154.4 (C_i), 150.1 (C_6), 150.0 (C_2), 145.8 ($C_{1'}$), 137.1 (C_4), 133.7 (C_γ), 130.8 ($C_{4'}$), 129.8 (C_3), 129.5 (C_α), 128.4 (C_β), 126.8 (C_5), 126.5 ($C_{3'}$), 122.4 ($C_{2'}$), 21.1 (C_a). ^{31}P{^{1}H} NMR $CDCl_3$,10 mM, 298 K): δ/ppm = -1.6.

1.5- [Cu(NN'-OCH_3)(PPh_3)Br]. This complex was prepared using CuBr (0.23 g, 1.62 mmol), pyridine-2-carbaldehyde (0.17 g, 1.62 mmol), 4-methoxyaniline (0.20 g, 1.62 mmol), PPh_3 (0.42 g, 1.62 mmol). The diffusion of diethyl ether vapor into the concentrated solution gave dark red crystals. Yield: 81 %. (Found: C, 60.4; H, 4.3; N, 4.2. Calc. for $C_{31}H_{27}BrCuN_2OP$: C, 60.25; H, 4.4; N, 4,5%)^{1}H-NMR ($CDCl_3$, $CDCl_3$,10 mM, 298 K): δ = 8.60 (d, 1H, $J_{H5,6}$ = 4.03 Hz, H_6), 8.50 (s, 1H, H_i), 7.80 (t, 1H, $J_{H4,3}$ = 7.50 Hz, H_4), 7.68 (d, 1H, $J_{H3,4}$ = 7.50 Hz, H_3), 7.65 (d, 2H, $J_{2',3'}$ = 7.87 Hz, $H_{2'}$), 7.36 (overlap with H_α, H_5), 7.39 (st, 6H, H_α), 7.31 (t, 3H, $J_{H\gamma,\beta}$ = 7.3 Hz, H_γ), 7.24 (st, 6H, $J_{H\beta,\gamma}$ = 7.3 Hz, $J_{H\beta,\alpha}$ = 7.9 Hz H_β), 6.78 (d, 2H, $J_{H3',2'}$ = 7.87 Hz, $H_{3'}$), 3.80 (s, 6H, H_a). ^{13}C {^{1}H} NMR ($CDCl_3$, 10 mM, 298 K): δ/ppm= 154.4 (C_i), 150.1 (C_6), 150.0 (C_2), 145.8 ($C_{1'}$), 137.1 (C_4), 133.7 (C_γ), 130.8 ($C_{4'}$), 129.8 (C_3), 129.5 (C_α), 128.4 (C_β), 126.8 (C_5), 126.5 ($C_{3'}$), 122.4 ($C_{2'}$), 21.1 (C_a). ^{31}P{^{1}H} NMR ($CDCl_3$, 10 mM, 298 K): δ/ppm = -2.0.

1.6- [Cu(NN'-N(CH_3)$_2$)(PPh_3)Br]. This complex was prepared using CuBr (0.23 g, 1.58 mmol), pyridine-2-carbaldehyde (0.17 g, 1.58 mmol), N,N-dimethylbenzene-1,4-diamine(0.22 g, 1.58 mmol), PPh_3 (0.41 g, 1.58 mmol).Yield: 87 %. (Found: C, 57.2; H, 3.9; N, 6.6. Calc. for $C_{32}H_{30}BrCuN_3P$: C, 57.3; H, 4.0; N, 6,7%) The diffusion of diethyl ether vapor into the concentrated solution gave dark red crystals. ^{1}H-NMR ($CDCl_3$,10 mM, 298 K): δ = 8.53 (d, 1H, $J_{H6,5}$ = 4.57 Hz, H_6), 8.48 (s, 1H, H_i), 7.76 (t, 1H, $J_{H4,3}$ = 7.68 Hz, H_4), 7.68 (d, 2H, $J_{2',3'}$ = 8,97 Hz, $H_{2'}$), 7.60 (d, 1H, $J_{H3,4}$ = 7.68 Hz, H_3), 7.43 (st, 6H, H_α), 7.29 (overlap with H_γ, H_5), 7.31 (t, 3H, $J_{H\gamma,\beta}$ = 7.1 Hz, H_γ), 7.25 (st, 6H, $J_{H\beta,\gamma}$ = 7.1 Hz, $J_{H\beta,\alpha}$ = 8.4 Hz, H_β), 6.56 (d, 2H, $J_{H3',2'}$ = 8.97 Hz, $H_{3'}$), 2.97 (s, 6H, H_a). ^{13}C {^{1}H} NMR ($CDCl_3$, 10 mM, 298 K): δ/ppm= 154.4 (C_i), 150.1 (C_6), 150.0 (C_2), 145.8 ($C_{1'}$), 137.1 (C_4), 133.7 (C_γ), 130.8 ($C_{4'}$), 129.8 (C_3), 129.5 (C_α), 128.4 (C_β), 126.8 (C_5), 126.5($C_{3'}$), 122.4 ($C_{2'}$), 21.1 (C_a). ^{31}P{^{1}H} NMR ($CDCl_3$, 10 mM, 298 K): δ/ppm = -2.6.

1.7- [Cu(NN'-Cl)(PPh_3)Br]. This complex was prepared using CuBr (0.23 g, 1.61 mmol), pyridine-2-carbaldehyde (0.17 g, 1.61 mmol), 4-chloroaniline (0.21 g, 1.61 mmol), PPh_3 (0.42 g, 1.61 mmol), The solid is a brick-red crystal powder. Yield: 89 %. (Found: C, 57.8; H, 3.9; N, 4.6. Calc. for $C_{30}H_{24}BrCuN_2PCl$: C, 57,9; H, 3.9; N, 4,5%) ^{1}H-NMR ($CDCl_3$, 60 mM, 298 K): δ/ppm =), 8.63 (s, 1H, H_i), 8.53 (d, 1H, $J_{H6,5}$ = 3,5 Hz, H_6), 7.79 (d, $J_{H3,4}$ = 7.3 Hz, H_3), 7.71 (dd, 1H, $J_{H3,4}$ = 7.3 Hz, $J_{H4,5}$ = 8,7 Hz H_4),7.54 (d, 2H, $J_{H2',3'}$ = 8.3 Hz, $H_{2'}$), 7.36 (t, 1H, overlap with H_α, H_5),7.38 (st, 6H, H_α),7.31 (t, 3H, $J_{H\gamma,\beta}$ = 7.1 Hz, H_γ),7.23 (st, 6H, $J_{H\beta,\gamma}$ = 7.1 Hz, $J_{H\beta,\alpha}$ = 8.4 Hz, H_β), 7.12 (d, 2H, $J_{3',2'}$ = 8,3 Hz, $H_{3'}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 mM, 298 K): δ/ppm =156.1 (C_i), 150.1 (C_6), 150.0 (C_2), 146.6 ($C_{1'}$), 137.2 (C_4), 133.6 (C_α), 133.3 ($C_{4'}$), 129.6 (C_γ), 129.3 ($C_{3'}$), 128.4 (C_β), 127.2 (C_5), 127.1 (C_3), 123.8 ($C_{2'}$).^{31}P {^{1}H} NMR ($CDCl_3$, 20 mM, 298 K): δ/ppm = -1.7.

II.- Crystallography Information.

Table SI1. Experimental details for all [Cu(NN'-R)(PPh_3)Br] complexes.

	Cu(NN'-NO_2)(PPh_3)Br	Cu(NN'-$COCH_3$)(PPh_3)Br	Cu(NN'-H)(PPh_3)Br	Cu(NN'-CH_3)(PPh_3)Br	Cu(NN'-$0CH_3$)(PPh_3)Br	Cu(NN'-$N(CH_3)_2$)(PPh_3)Br
Chemical formula	$C_{30}H_{24}BrCuN_3O_2P$	$C_{32}H_{27}BrCuN_2OP$	$C_{30}H_{25}BrCuN_2P$	$C_{31}H_{27}BrCuN_2P$	$C_{31}H_{27}BrCuN_2OP$	$C_{32}H_{30}BrCuN_3P$
*M*r	632.94	629.97	587.94	601.96	617.97	631.01
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Triclinic, *P*-1	Monoclinic, *C*2/*c*	Triclinic, *P*-1	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	33.966 (2) 9.1945 (4) 20.1441 (13)	34.8404 (19), 9.2350 (3), 20.3611 (10)	8.8211 (3), 10.3594 (3) 16.2494 (4)	34.1246 (18), 9.3360 (3), 20.2331 (9)	9.8750 (3) 9.9744 (3) 15.7009 (5)	9.36873 (18) 12.5828 (3) 25.2196 (6)
α, β, γ (°)	90, 117.499 (8) 90	90, 118.270 (7), 90	77.816 (2) 84.816 (2) 65.413 (3)	90, 119.101 (7) 90	84.458 (3) 85.700 (3) 63.811 (3)	90 97.584 (2), 90
V (Å^3)	5580.2 (7)	5769.8 (6)	1319.84 (7)	5632.3 (5)	1380.36 (8)	2947.00 (11)
Z	8	8	2	8	2	4
μ (mm^{-1})	2.30	2.23	2.42	2.27	2.32	2.18
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	9502, 5845, 3091	30855, 6893, 3020	19767, 5160, 3527	16074, 5530, 2806	23131, 5396, 2814	25850, 5779, 4150
R_{int}	0.028	0.059	0.028	0.044	0.063	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.664	0.682	0.617	0.617	0.617	0.617
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.104, 0.86	0.069, 0.224, 1.03	0.030, 0.071, 0.92	0.034, 0.069, 0.78	0.036, 0.069, 0.80	0.030, 0.070, 0.96
No. of reflections	5845	6893	5160	5530	5396	5779
No. of parameters	343	344	316	326	335	345
No. of restraints	318	318	0	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.61, -0.34	1.08, -0.56	0.73, -0.43	0.68, -0.34	0.41, -0.29	0.30, -0.33

Table SI2. π...π bonds for [Cu(NN'-R)(PPh_3)Br] complexes.

R		***Cg... Cg***	***ccd(Å)***	***da(º)***	***ipd(Å)***
$-NO_2$	**#1** (i) -*x*+1, -*y*+1, -*z*	Cg2 ... Cg6^{i}	3.739(3)	21(3)	3.48(5)
$-COCH_3$	**#1** (i) 1-x,1-y,1-z	Cg2 ... Cg6^{i}	3.824(6)	10.8(5)	3.48(14)
-H	**#1** (i) 1-x,1-y,1-z	Cg2 ... Cg2^{i}	3.6471(17)	0.00	3.4516(11)
$-CH_3$	**#1** (i) 1-x,-y,1-z	Cg2 ... Cg6^{i}	3.837(3)	20(9)	3.58(18)
$-OCH_3$	**#1** (i) -*x*+2, -*y*+1, -*z*	Cg2 ... Cg6^{i}	3.570(2)	1.89(17)	3.360(15)
$-N(CH_3)_2$	**#1** (i) -*x*+1, -*y*, -*z*+1	Cg2 ... Cg6^{i}	3.8153(14)	18.50(12)	3.5(2)

ccd: center-to-center distance; ***da***: dihedral angle between rings; ***ipd***: interplanar distance, or (mean) distance from one plane to the neighbouring centroid. For details, see Janiak, C. (2000). A critical account on π–π stacking in metal complexes with aromatic nitrogen-containing ligands., J. Chem. Soc., Dalton Trans., (21), 3885-3896.

Ring Codes:

Cg2: N1,C14,C24,C34,C44,C54; Cg6: C15,C25,C35,C45,C55,C65.

Table SI3. Hydrogen bonding geometry for [Cu(NN'-R)(PPh_3)Br] complexes.

R		*D—H···A*	*D—H(Å)*	*H···A(Å)*	*D···A(Å°)*	*D—H···A(°)*
-NO_2	***#2***	C44-H44...Br1[i]	0.93	3.13	3.940(5)	146.1
	#3	C64-H64...Br1[i]	0.93	3.02	3.842(4)	148.3
	#4	C34-H34...Br1[ii]	0.93	2.90	3.664(5)	140.8
	#5	C43-H43...Br1[iii]	0.93	3.04	3.766(4)	136.2
	#6	C35—H35···Cg5[iv]	0.93	2.83	3.673(6)	153
	[i] -x+1, -y+1, -z; [ii] x, y+1, z ; [iii] x, -y+1, z+1/2, [iv] = -x+1,y,-z+1/2,					
-$COCH_3$	***#2***	C44-H44...Br1[i]	0.93	3.198	4.033(10)	150.5
	#3	C64-H64...Br1[i]	0.93	3.145	3.984(9)	151.0
	#4	C34-H34...Br1[ii]	0.93	2.97	3.715(10)	137.7
	#5	C41-H41...Br1[iii]	0.93	3.08	3.815(7)	137.4
	[i] 1-x, 1-y, 1-z; [ii] x, y-1, z; [iii] x, -y+1, z-1/2					
-H	***#2***	C34—H34···Cg4[i]	0.93	2.83	3.348(3)	170
	#3	C32-H32...Br1[ii]	0.93	2.93	3.757(3)	148.7
	#4	C33-H33...Br1[iii]	0.93	2.98	3.728(3)	139.1
	#5	C25-H25...Br1[iv]	0.93	3.04	3.926(3)	158.9
	#6	C61-H61...Br1	0.93	2.87	3.769(2)	162.8
	[i] 1-x,1-y,1-z; [ii] x, y+1, z; [iii] -x, -y+1, -z+1; [iv] x+1, y, z					
-CH_3	***#2***	C64-H64...Br1[i]	0.93	3.18	4.018(5)	150.9
	#3	C34-H34...Br1[ii]	0.93	2.96	3.749(4)	143.4
	#4	C42-H42...Br1[iii]	0.93	3.04	3.806(4)	140.3
	#5	C75-H75B...Br1[iv]	0.96	3.00	3.907(4)	158.8
	#6	C35—H35···Cg4[v]	0.93	2.81	3.645(5)	150
	[i] 1-x, -y, 1-z; [ii] x, y-1, z; [iii] x, -y, z+1/2; [iv] -x+1, -y+1, -z+1; [v] 1-x,y,3/2-z;					
-OCH_3	***#2***	C64-H64...Br1[i]	0.93	3.00	3.873(3)	156.7
	#3	C22-H22...O1[ii]	0.93	2.57	3.328(5)	139.2
	#4	C41-H41...Br1[iii]	0.93	3.200	3.948(4)	138.9
	#5	C32-H32...Br1[iv]	0.93	3.173	4.068(6)	162.2
	[i] -x+2, -y+1, -z; [ii] -x+2, -y, -z; [iii] x,-1+y,z; [iv] 1+x,-1+y,z					
-$N(CH_3)_2$	***#2***	C64-H64...Br1[i]	0.93	3.10	3.870(2)	141.8
	#3	C44-H44...Br1[i]	0.93	3.16	3.921(2)	139.8
	#4	C32-H32...Br1[ii]	0.93	2.85	3.756(3)	166.3
	#5	C34-H34...Br1[iii]	0.93	3.09	3.752(3)	129.6
	#6	C52—H52···Cg3[ii]	0.93	2.79	3.618(3)	148
	#7	C41—H41···Cg6[iv]	0.93	2.91	3.699(4)	144
	[i] -x+1, -y, -z+1 [ii] -x+1, y+1/2, -z+1/2 [iii] x+1, y, z; [iv] 1-x,1-y,1-z					

Ring Codes:

Cg2: N1,C14,C24,C34,C44,C54; Cg3: C11,C21,C31,C41,C51,C61; Cg4: C12,C22,C32,C42,C52,C62;
Cg5: C13,C23,C33,C43,C53,C63; Cg6: C15,C25,C35,C45,C55,C65.

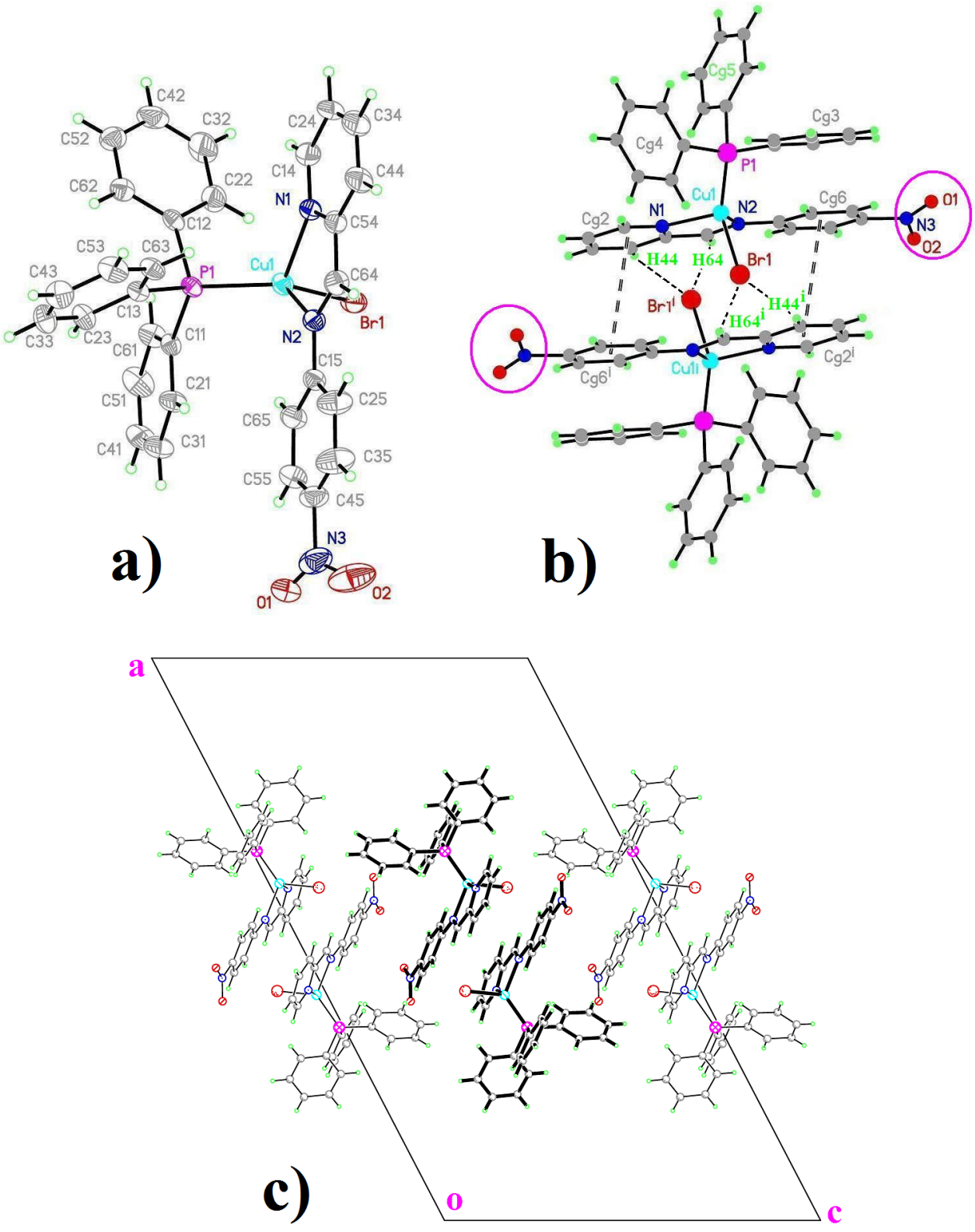


Figure SI1. Molecular (a), dimeric (b) and packing (c) diagrams for **Cu(NN'-NO_2)(PPh_3)Br**. (a) Displacement ellipsoids drawn at a 30% level. (b) Bold dashed lines represent π-π bonds; simple gashed lines, C-H···Br bonds. Encircled, the NO_2 substituent. (c) One of the (100) planes in the structure. The [010] columnar arrays viewed in projection (the central one highlighted, for clarity). Non-covalent interactions are omitted for clarity. For details, see Jara H. D., Lemus L., Farías L., Freire E., Baggio R., Guerrero J., Eur. J. Inorg. Chem. 2012, 1579–1583

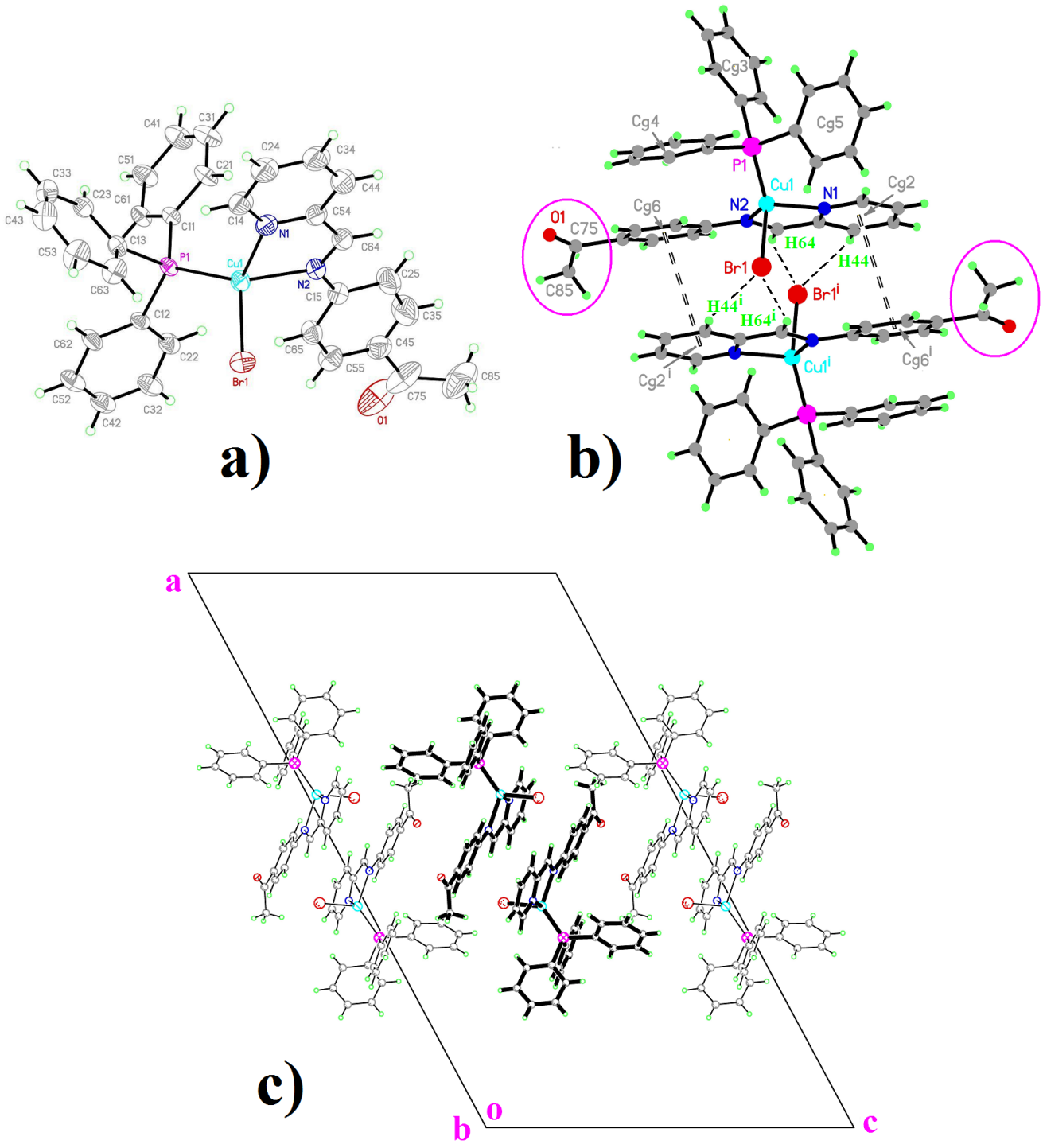


Figure SI2. Molecular (a), dimeric (b) and packing (c) diagrams for **Cu(NN'-$COCH_3$)(PPh_3)Br**. (a) Displacement ellipsoids drawn at a 30% level. (b) Bold dashed lines represent π-π bonds; simple dashed lines, C-H···Br bonds. Encircled, the $COCH_3$ substituent. (c) One of the (100) planes in the structure. The [010] columnar arrays viewed in projection (the central one highlighted, for clarity). Non-covalent interactions are omitted for clarity.

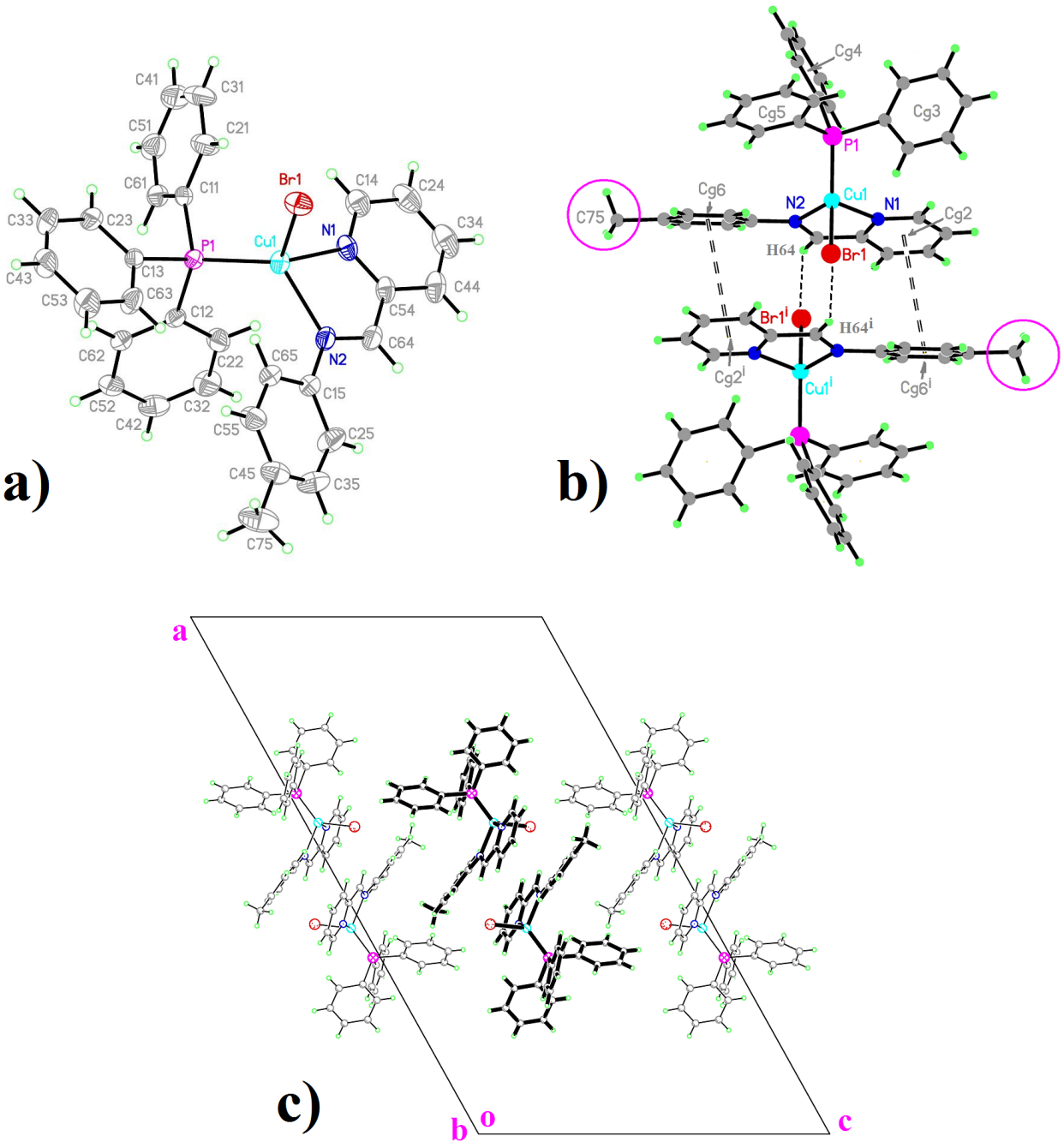


Figure SI3. Molecular (a), dimeric (b) and packing (c) diagrams for 4. **Cu(NN'-CH_3)(PPh_3)Br**. (a) Displacement ellipsoids drawn at a 30% level. (b) Bold dashed lines represent π-π bonds; simple dashed lines, C-H···Br bonds. Encircled, the CH_3 substituent. (c) One of the (100) planes in the structure. The [010] columnar arrays viewed in projection (the central one highlighted, for clarity). Non-covalent interactions are omitted for clarity.

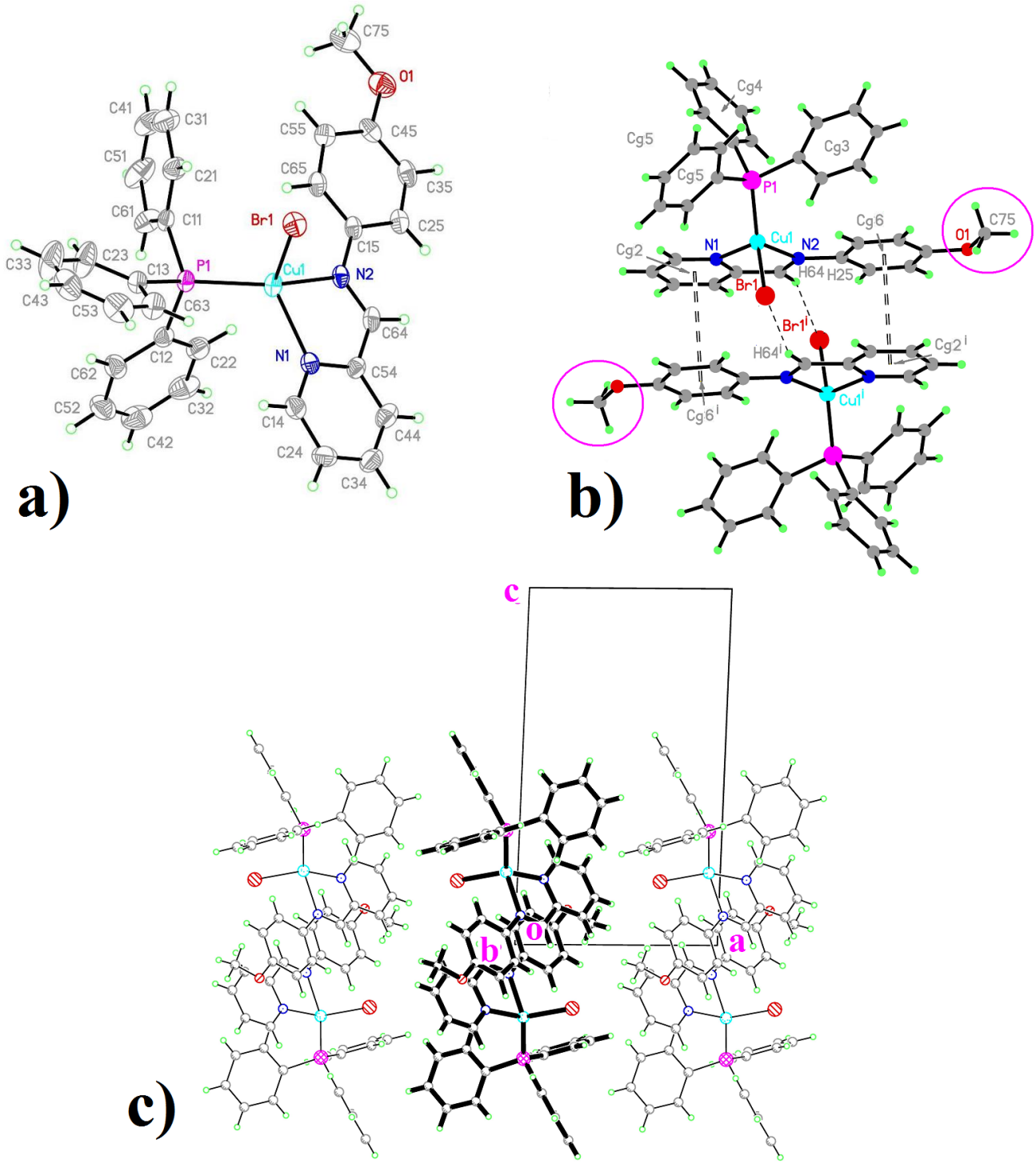


Figure SI4. Molecular (a), dimeric (b), and packing (c) diagrams for 5. **Cu(NN'-OCH_3)(PPh_3)Br**. (a) Displacement ellipsoids drawn at a 30% level. (b) Bold dashed lines represent π-π bonds; simple dashed lines, C-H···Br bonds. Encircled, the OCH_3 substituent. (c) One of the (001) planes in the structure. The [010] columnar arrays viewed in projection (the central one highlighted, for clarity). Non-covalent interactions are omitted for clarity.

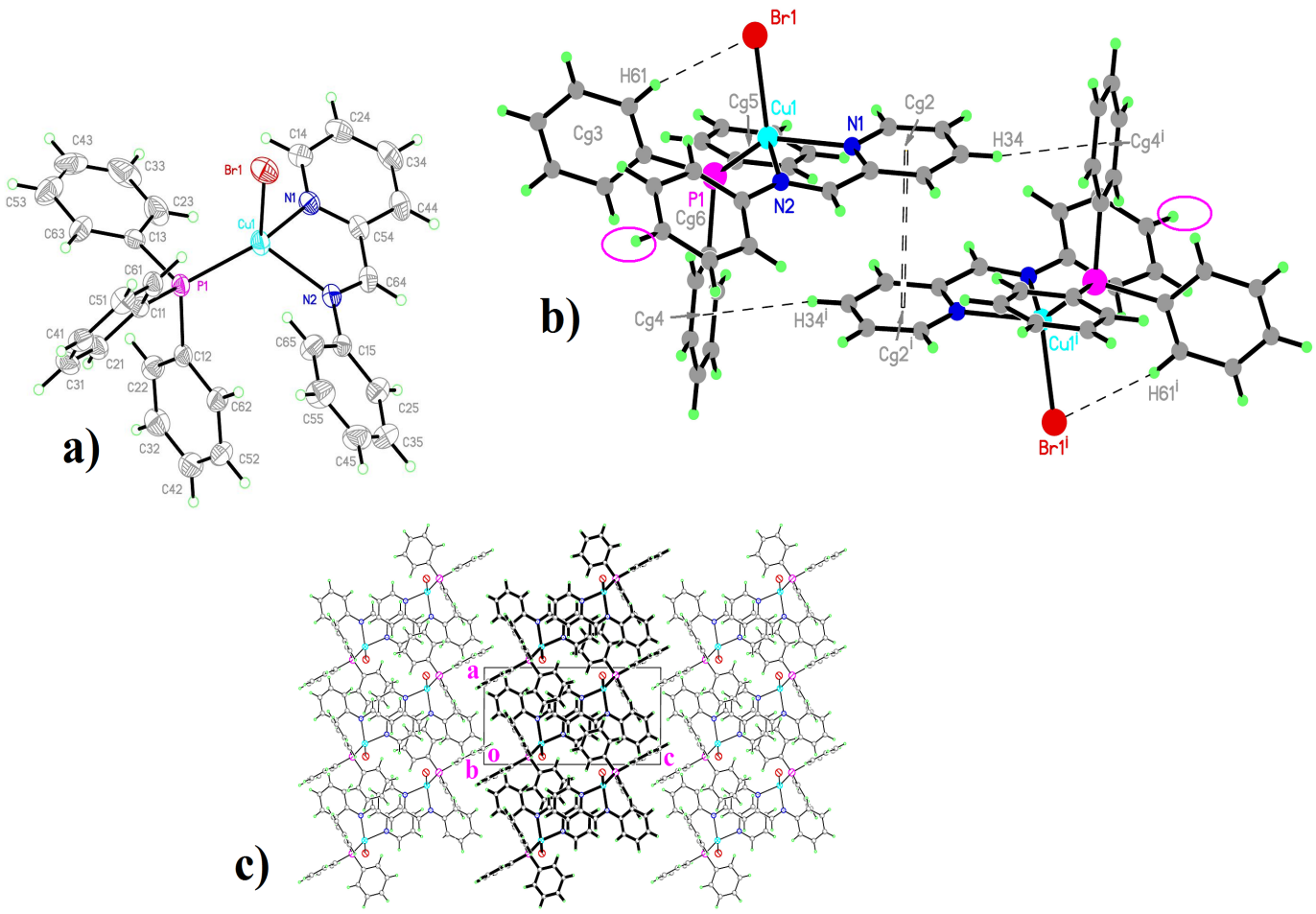


Figure SI5. Molecular (a), dimeric (b), and packing (c) diagrams for 3. **Cu(NN'-H)(PPh$_3$)Br.** (a) Displacement ellipsoids drawn at a 30% level. (b) Bold dashed lines represent π-π bonds; simple dashed lines, C-H···Br and C-H···π bonds. Encircled, the unsubstituted H site. (c) One of the (100) planes in the structure. The [010] columnar arrays viewed in projection (the central one highlighted, for clarity). Note the different columnar width as compared with the remaining structures, due to differences in dimer shape. Non-covalent interactions are omitted for clarity.

III- NMR results.

Table SI3a. ^{1}H-NMR data (δ/ppm) for NN'-NO_2 ligand in [Cu(NN'-NO_2)(PPh_3)Br] complex at several temperatures and concentrations, δ calculated for monomer and dimer and self-association constants.

T/K	298		290		280		270		260	
Proton	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
C/mM	$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$	
2	8.770	7.558	8.765	7.563	8.764	7.569	8.761	7.576	8.758	7.583
	7.960	7.864	7.964	7.856	7.968	7.851	7.972	7.852	7.977	7.856
	8.529	7.601	8.531	7.611	8.536	7.619	8.544	7.626	8.554	7.630
	8.170		8.161		8.155		8.150		8.145	
5	8.753	7.541	8.747	7.543	8.743	7.547	8.739	7.551	8.735	7.555
	7.940	7.860	7.940	7.858	7.940	7.859	7.940	7.860	7.938	7.866
	8.550	7.611	8.560	7.619	8.570	7.626	8.584	7.631	8.600	7.633
	8.145		8.136		8.128		8.120		8.113	
10	8.730	7.519	8.728	7.524	8.723	7.525	8.718	7.527	8.714	7.528
	7.913	7.862	7.914	7.861	7.912	7.861	7.908	7.866	7.903	
	8.585	7.619	8.592	7.625	8.606	7.630	8.624	7.634	8.643	7.635
	8.117		8.112		8.102		8.093		8.084	
15	8.715	7.503	8.711	7.507	8.705	7.507	8.703	7.509	8.699	7.508
	7.895	7.864	7.895		7.890		7.877*		7.875*	
	8.610	7.624	8.621	7.629	8.634	7.633	8.654	7.635	8.675	7.636
	8.098		8.091		8.083		8.072		8.062	
20	8.705	7.494	8.701	7.495	8.696	7.495	8.691	7.494	8.686	7.495
	7.883	7.881	7.878*		7.870		7.860	7.890	7.851	7.895
	8.626	7.628	8.638	7.632	8.656	7.636	8.677	7.638	8.699	7.638
	8.086		8.079		8.068		8.057		8.045	
25	8.697	7.485	8.695	7.489	8.690	7.488	8.684*	7.488	8.681	7.488
	7.870		7.866*		7.859		7.850	7.891	7.842	7.897
	8.641	7.630	8.650	7.633	8.667	7.636	8.688	7.638	8.711	7.637
	8.076		8.071		8.060		8.048		8.037	
30	8.691	7.479	8.688	7.479	8.680*	7.478	8.676	7.477	8.672	7.476
	7.860		7.852	7.889	7.845	7.889	7.836	7.894	7.827	7.901
	8.650	7.631	8.669	7.635	8.686	7.638	8.707	7.639	8.729	7.638
	8.070		8.058		8.048		8.036		8.025	
35	8.690	7.479	8.675	7.477	8.673*	7.475	8.672	7.473	8.668	7.473
	7.858		7.852		7.842		7.832	7.895	7.823	7.902
	8.651	7.631	8.669	7.636	8.688	7.640	8.712	7.641	8.735	7.640
	8.068		8.057		8.044		8.031		8.020	
δ_M	8.789	7.577	8.784	7.582	8.782	7.591	8.781	7.602	8.782	7.613
	7.978		7.980		7.992		8.006		8.017	
	8.503		8.503		8.503		8.499		8.507	
	8.199		8.186		8.180		8.180		8.178	
δ_D	8.561	7.343	8.577	7.361	8.553	7.354	8.562	7.349	8.563	7.347
	7.653		7.650		7.644		7.649		7.632	
	8.902		8.895		8.904		8.917		8.947	
	7.936		7.924		7.903		7.889		7.877	
K_D	23	22	27	26	24	28	29	31	33	35
	15		16		20		28		31	
	16		20		24		31		33	
	33		29		28		31		34	
K_D	21.8±7.2		23.6 ± 5.4		24.8 ± 3.3		30.0 ± 1.4		33.2	± 1.5

Table S13a continued.

T/K	250		240		230		220	
Proton	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
C/mM	$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$	
2	8.756	7.589	8.752	7.596	8.749	7.601	8.7459	7.6082
	7.980	7.864	7.983	7.874	7.985	7.885	7.9863	7.8977
	8.566	7.633	8.581	7.635	8.596	7.636	8.6137	7.6365
	8.141		7.874		7.895		8.1316	
5	8.731	7.558	8.727	7.561	8.723	7.565	8.7184	7.5688
	7.936	7.874	7.933	7.885	7.929	7.895	7.9160*	
	8.619	7.634	8.639	7.634	8.662	7.633	8.6890	7.6306
	8.105		8.098		7.895		8.0831	
10	8.710	7.530	8.706	7.531	8.701	7.534	8.698	7.536
	7.895*		7.887*		7.877	7.913	7.870	7.921
	8.663	7.635	8.685	7.633	8.709	7.630	8.736	7.626
	8.074		8.065		8.055		8.046	
15	8.690*	7.510	8.690	7.510	8.686	7.511	8.683	7.512
	7.863	---	7.854	7.907	7.846	7.915	7.837	7.924
	7.635	7.635	8.721	7.632	8.743	7.628	8.767	7.624
	8.051		8.040		8.031		8.0213	
20	8.682	7.495	8.678	7.495	8.675	7.496	8.671	8.497
	7.842	7.903	7.831	7.912	7.820	7.921	7.809	7.931
	8.723	7.636	8.748	7.632	8.775	7.626	8.804	7.699
	8.034		8.023		7.921		7.999	
25	8.676	7.487	8.672	7.487	8.669	7.488	8.667	7.489
	7.832	7.905	7.821	7.914	7.809	7.923	7.796	7.933
	8.735	7.635	8.760	7.632	8.786	7.626	8.817	7.618
	8.026		8.014		8.002		7.989	
30	8.668	7.476	8.665	7.476	8.662	7.478	8.660	7.479
	7.817	7.909	7.806	7.917	7.796	7.924	7.787	7.930
	8.752	7.636	8.776	7.632	8.798	7.626	8.816	7.621
	8.014		8.003		7.992		7.984	
35	8.665	7.473	8.662	7.473	8.660	7.475	8.658	7.477
	7.813	7.910	7.801	7.919	7.790	7.927	7.778	7.935
	8.758	7.637	8.782	7.631	8.806	8.624	8.833	7.616
	8.009		7.998		7.987		7.975	
δ_M	8.785	7.624	8.780	7.637	8.783	7.647	8.781	7.662
	8.027		8.047		8.062		8.080	
	8.508		8.514		8.511		8.511	
	8.180		8.182		8.189		8.196	
δ_D	8.573	7.348	8.567	7.353	8.578	7.355	8.581	7.362
	7.631		7.626		7.617		7.612	
	8.960		8.979		8.984		8.999	
	7.870		7.859		7.853		7.844	
K_D	44.5	40	42	48	56	53	63	64
	39		51		61		76	
	41		48	-	65		83	
	40		46		56		66	
K_D	40.9 ± 2.1		47.0 ± 3.3		58.2 ± 4.8		70.4 ± 8.7	

* Assigned by COSY

See Jara H. D., Lemus L., Farías L., Freire E., Baggio R., Guerrero J., Eur. J. Inorg. Chem. 2012, 1579–1583

Table SI3b. ^{1}H-NMR data (δ/ppm) for NN'-$COCH_3$ ligand in [Cu(NN'-$COCH_3$)(PPh_3)Br] complex at several temperatures and concentrations, δ calculated for monomer and dimer and self-association constants.

T/K	220		235		250		265		280		298	
Proton / C/mM	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a
2	8.615	7.509	8.558	7.507	8.646	7.502	8.658	7.497	8.671	7.494	8.686	7.489
	7.914	7.832*	7.917	7.816	7.915	7.799	7.912	7.787	7.908*	7.783	7.908*	7.794
	8.582	7.615	8.558	7.616	8.539	7.615	8.524	7.613	8.514	7.604	8.510	7.592
	7.856*	2.627	7.864	2.621	7.870	2.613	7.876	2.606	7.884	2.601	7.895*	2.596
8	8.581	7.451	8.600	7.451	8.613	7.454	8.626	7.455	8.640	7.456	8.657	7.463
	7.846*		7.848*	---	7.859	7.837**	7.864	7.806*	7.871*	7.810	7.882*	---
	8.639	7.602	8.605	7.602	8.583	7.608	8.559	7.607	8.543	7.602	8.531	7.588
	7.801	2.605	7.813	2.599	7.826	2.596	7.838	2.591	7.851*	2.588	7.872*	2.586
14	8.559	7.415	8.575	7.418	8.590	7.422	8.604*	7.426	8.620	7.432	8.636	7.435
	7.789*	7.881	7.801*	7.864	7.828*	7.824**	7.836*	7.806*	7.840*	---	7.858*	---
	8.675	7.594	8.641	7.600	8.613	7.604	8.588	7.605	8.569	7.605	8.551	7.596
	7.766	2.592	7.784	2.588	7.799	2.584	7.815	2.581	7.832*	2.580	7.847*	2.578
20	8.547	7.396	8.560	7.398	8.576	7.403	8.588*	7.407	8.606	7.412	8.622	7.418
	7.760*	7.890	7.767*	7.872	7.793*	7.857	7.805	---	7.820*	---	7.835*	---
	8.695	7.590	8.659	7.595	8.631	7.601	8.603	7.604	8.584	7.603	8.564	7.595
	7.748	2.584	7.764	2.579	7.781	2.577	7.796	2.575	7.812*	2.574	7.832*	2.573
26	8.534	7.375	8.547	7.378	8.563	7.384	8.575	7.388	8.593	7.396	8.603	7.406*
	7.729*	7.899	7.749*	7.884	7.774*	7.868	7.781*	7.850	7.797*	---	7.820*	---
	8.715	7.585	8.680	7.592	8.650	7.600	8.621	7.602	8.598	7.603	8.581	7.597
	7.726	2.576	7.749*	2.572	7.771*	2.570	7.780	2.568	7.800*	2.568	7.819*	2.567
34	8.523	7.358	8.535	7.359	8.551	7.368	8.564	7.372	8.579	7.382*	8.593	7.398*
	7.706*	7.909	7.729*	7.893	7.754*	7.880	7.760*	7.861	7.779*	7.848	7.804*	---
	8.735	7.582	8.698	7.589	8.668	7.598	8.639	7.601	8.615	7.603	8.551	7.596
	7.709*	2.570	7.729*	2.565	7.754*	2.565	7.767*	2.562	7.786*	2.562	7.847*	2.578
δ_M	8.632	7.542	8.650	7.535	8.662	7.527	8.673	7.516	8.684	7.511	8.699	7.505
	7.950		7.958	---	7.950	---	7.929	---	7.924	---	7.920	---
	8.553		8.650	---	8.518	---	8.509	---	8.684	---	8.501	---
	7.884	2.639	7.889	2.485	7.893	2.622	7.894	2.613	7.898	2.475	7.907	2.600
δ_D	8.380	7.155	8.365	7.140	8.388	7.155	8.388	7.129	8.395	7.153	8.363	7.210
	7.329		7.461	---	7.520	---	7.323	---	7.407	---	7.424	---
	8.962		8.946	---	8.904	---	8.916	---	8.878	---	8.938	---
	7.490	2.491	7.532	2.485	7.581	2.487	7.565	2.481	7.578	2.475	7.546	2.452
K_D	21	24.5	17	21	17	18.5	15	14	13	13	10	14
	16		24	---	23	---	8	---	8	---	14	---
	21.5		16	---	14.5	---	10	---	13	---	5	---
	21.5	24	21	22	22	19	15	15	12	11	8	7
K_D	21.4 ± 3.0		20.2 ± 3.1		19.0± 3.1		12.8 ± 3.0		11.7 ± 2.0		9.7 ± 3.7	

* Assigned by COSY

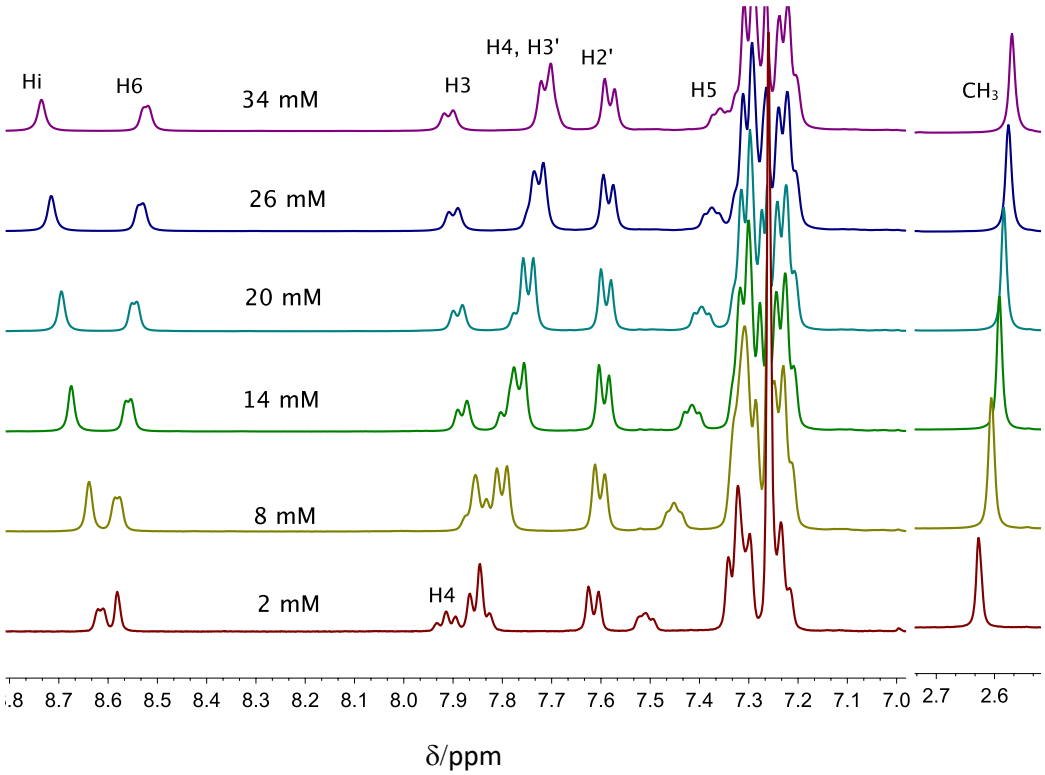


Figure SI6 a). ^{1}H-NMR spectra of [Cu(NN'-$COCH_3$)(PPh_3)Br] at 220 K to several concentration used for calculating self-association constants. Proton assignments are included. Similar behaviour is observed at all temperatures used in this study.

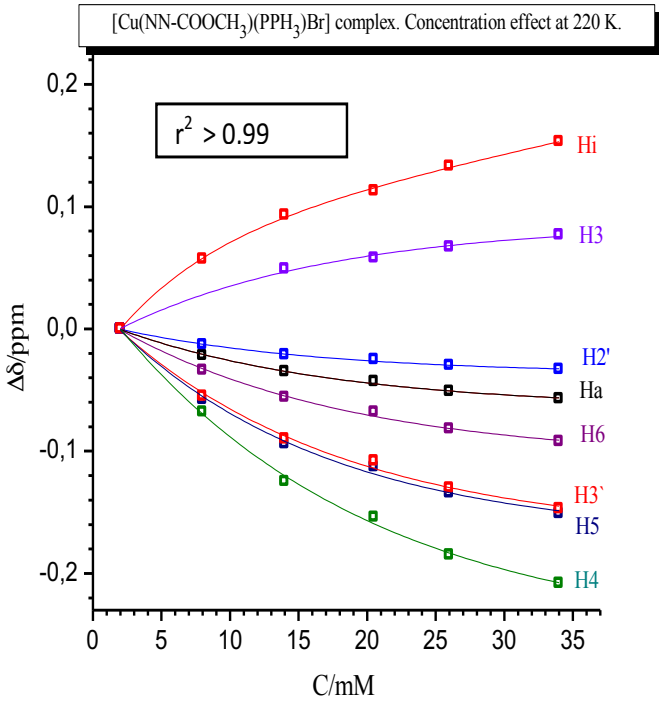


Figure SI6 b) Concentration effect on NN`-$COCH_3$ ligand protons chemical shifts of [Cu(NN'-$COCH_3$)(PPh_3)Br] at 220 K.

Table SI3c. ^{1}H-NMR data (δ/ppm) for NN'-H ligand in [Cu(NN'-H)(PPh$_3$)Br] complex at several temperatures and concentrations, δ calculated for monomer and dimer and self-association constants.

T/K	220		235		250		265		280		298	
Proton	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
C/mM	$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$	
2	8.563	7.461	8.580	7.454	8.597	7.450	8.614	7.447	8.629	7.442	8.646	7.438
	7.893	7.777	7.887	7.752	7.884	7.735	7.881	7.724	7.875	7.719	7.870	7.724
	8.542	7.615	8.520	7.611	8.507	7.607	8.498	7.603	7.875	7.600	8.492	7.591
	7.293*		7.288*		7.294*		7.300*		7.306*		7.299*	
10	8.533	7.409	8.552*	7.410	8.570	7.413	8.590	7.415	8.606	7.416	8.623	7.416*
	7.833*	7.789*	7.841	7.771	7.847	7.752	7.850	7.739	7.852	7.731	7.853	7.728
	8.554	7.605	8.533	7.604	8.515	7.602	8.504	7.603	7.852	7.601	8.493	7.596
	7.259*		7.269*		7.271*		7.279*		7.288*		7.286*	
20	8.502	7.358*	8.522	7.366*	8.541*	7.368*	8.562	7.379*	8.577	7.385*	8.597	7.384*
	7.771	7.815	7.791*	7.791*	7.798*	7.773*	7.817	7.758	7.819	7.744	7.826	7.737
	8.570	7.597	8.544	7.598	8.525	7.600	8.512	7.601	7.819	7.597	8.494	7.593
	7.230*		7.239*		7.250*		7.263*		7.272*		7.276*	
30	8.486	7.328*	8.503	7.336*	8.523*	7.345*	8.543	7.349*	8.560	7.361*	8.579	7.364*
	7.740	7.820	7.759	7.805*	7.772*	7.782*	7.789	----	7.801	7.752	7.810	7.744
	8.579	7.595	8.550	7.595	8.531	7.597	8.516	7.599	7.801	7.596	8.495	7.592
	7.215*		7.224*		7.238*		7.246*		7.254*		7.261*	
40	8.470	7.302*	8.486	7.311*	8.509	7.318*	8.531*	7.334*	8.545	7.341*	8.565	7.345*
	7.710	7.833	7.735	7.812	7.748	7.800	7.774*	----	7.786	7.762	7.798	7.754
	8.586	7.591	8.558	7.593	8.509	7.595	8.522	7.599	7.786	7.596	8.501	7.594
	7.200*		7.208*		7.221*		7.236*		7.246*		7.253*	
50	8.459	7.284*	8.474	7.291*	8.496	7.306*	8.513*	7.313*	8.530	7.322*	8.552	7.332*
	7.687	7.841	7.713	7.822	7.736	7.806	7.755	7.789	7.768*	7.769*	7.784*	7.767*
	8.594	7.587	8.563	7.589	8.542	7.595	8.525	7.597	7.768*	7.594	8.502	7.592
	7.191*		7.196*		7.213*		7.223*		7.233*		7.244	
δ_M	8.574	7.480	8.589	7.468	8.607	7.465	8.622	7.458	8.638	7.450	8.654	7.447
	7.915	----	7.904	7.745	7.900	----	7.384	----	7.883	7.715	7.877	----
	8.538	----	8.516	----	8.504	----	8.496	----	8.491	----	----	----
	7.306		7.296		7.302		7.303				7.032	
δ_D	8.257	6.940	8.199	6.872	8.264	6.964	8.221	6.918	8.241	6.794	8.275	6.953
	7.290	----	7.312	7.968	7.382	----	7.384	----	7.396	7.942	7.481	----
	8.747	----	8.659	----	8.666	----	8.621	----	8.728	----	----	----
	7.036		6.870		7.023		6.892		6.975		7.010	
K_D	9	9	6	6	7	7	5	5	5	3	5	4
	9		7	8	7	----	5	----	4	4	4	----
	5		7	----	4	----	4	----		----	----	----
	13		4		7		4		4		3	
K_D	9.0 ± 2.8		6.3 ± 1.4		6.4 ± 1.3		4.6 ± 0.5		4.0 ± 0.7		4.0 ± 0.8	

* Assigned by COSY

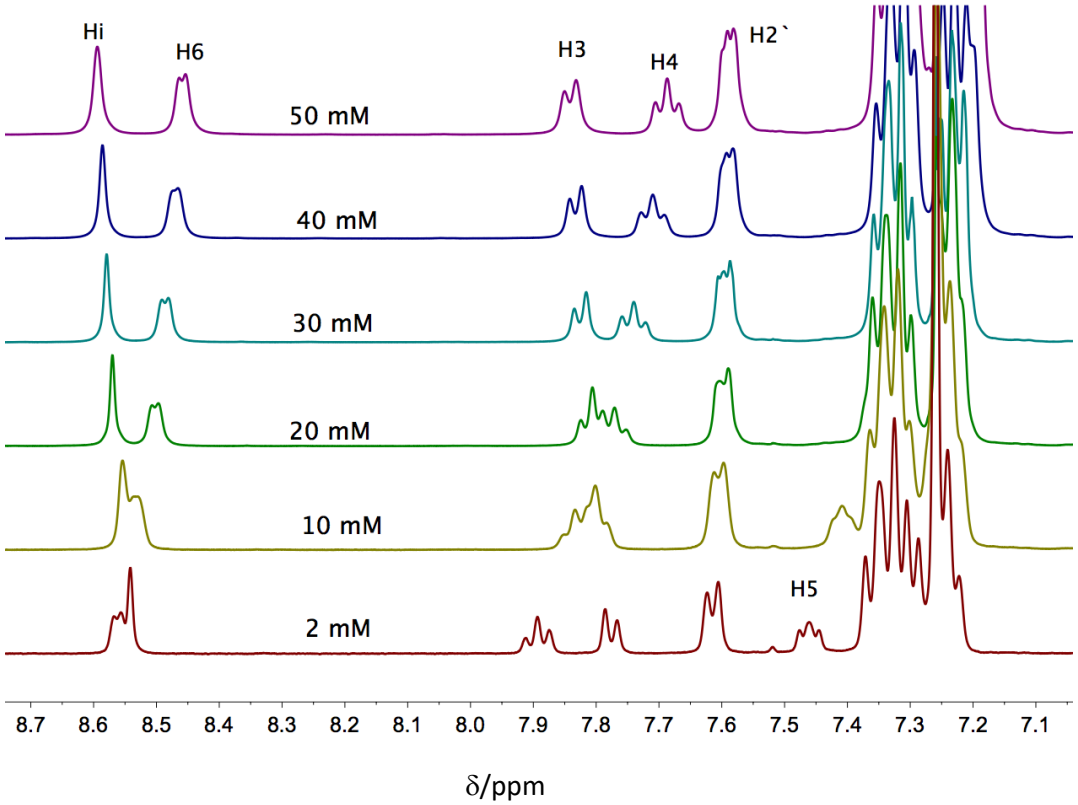


Figure SI7 a). ^{1}H-NMR spectra of [Cu(NN'-H)(PPh_3)Br] at 220K to several concentration used for calculated self-association constants. Proton assignments are included. Similar behavior is observed at all temperatures used in this study.

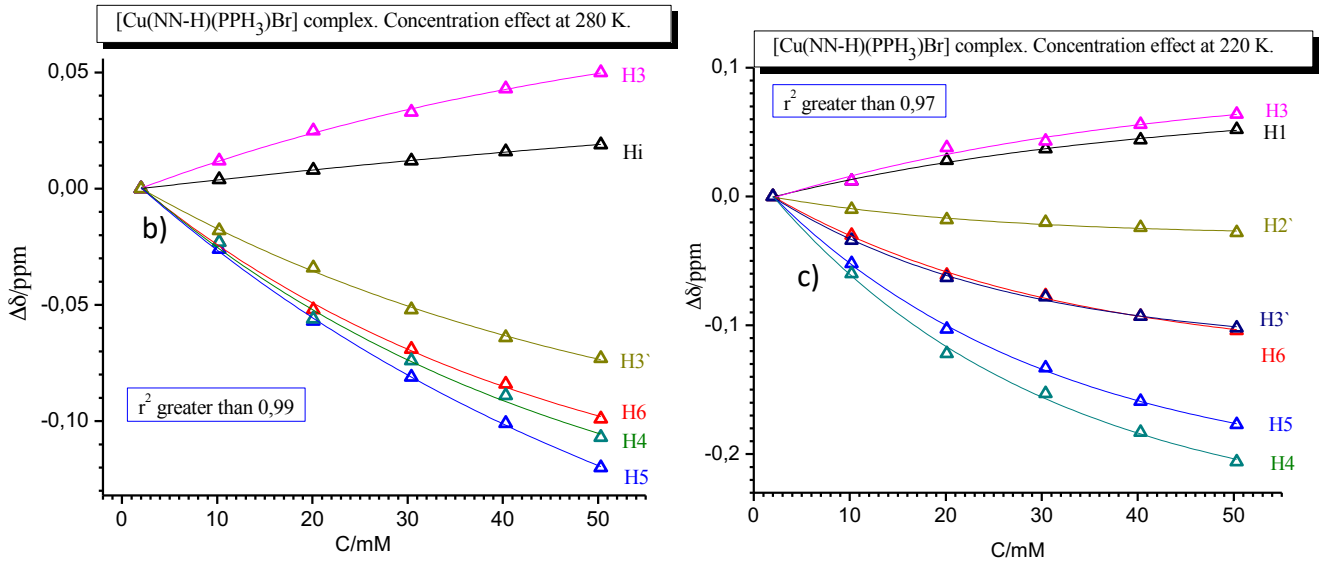


Figure SI7 b) Concentration effect on NN`-H ligand protons chemical shifts of [Cu(NN'-H)(PPh_3)Br] complex at 280 K and **c**) at 220 K**.**

Table SI3d. ^{1}H-NMR data (δ/ppm) for NN'-CH_3 ligand in [Cu(NN'-CH_3)(PPh_3)Br] complex at several temperatures and concentrations, δ calculated for monomer and dimer and self-association constants.

T/K	220		235		250		265		280		298	
Proton	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
C/mM	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a
2	8.538	7.444*	8.555	7.435*	8.571	7.430*	8.590	7.424*	8.607	7.427*	8.627	7.418*
	7.884	7.737	7,877	7.717	7.870	7.699	7.859	7.687	7.863	7.686	7.858	7.689
	8.542	7.551	8.522	7.546	8.506	7.542	8.496	7.540	8.493	7.535	8.490	7.527
	7.084	2.328	7.082	2.330	7.084	2.333	7.090	2.336	7.097	2.342	7.108	2.348
10	8.497	7.373*	8.518	7.378*	8.538	7.379*	8.557	7.385*	8.575	7.384*	8.593	7.389*
	7.812	7.751	7.820	7.734	7.826	7.718	7.828	7.704	7.832	7.696	7.833	7.692
	8.554	7.539	8.532	7.539	8.514	7.536	8.502	7.536	8.494	7.534	8.489	7.527
	7.036	2.305	7.046	2.312	7.055	2.317	7.063	2.324	7.072	2.330	7.082	2.336
20	8.467	7.329*	8.487	7.332*	8.507	7.339*	8.527	7.345*	8.546	7.351*	8.567	7.358*
	7.737	7.766	---	---	7.789	7.732	7.795	7.718	7.802	7.708	7.808	7.702
	8.566	7.533	8.540	7.532	8.521	7.532	8.507	7.532	8.497	7.531	8.490	7.526
	7.004	2.290	7.017	2.298	7.029	2.305	7.040	2.311	7.050	2.318	7.063	2.323
30	8.448	7.296*	8.468	7.301*	8.485	7.313*	8.504	7.322*	8.526	7.328*	8.547	7.335*
	7.716	7.778	---	---	---	---	7.775	7.726	7.781	7.714	7.790	7.707
	8.573	7.528	8.545	7.529	8.525	7.530	8.511	7.530	8.499	7.529	8.491	7.524
	6.984	2.280	7.000	2.289	7.013	2.296	7.025	2.303	7.036	2.310	7.049	2.318
40	8.447	7.295*	8.466	7.295*	8.487	7.307*	8.503	7.317*	8.525	7.327*	8.547	7.333*
	7.711	7.779	---	---	---	---	7.771	7.725	7.780	7.717	7.789	7.708
	8.573	7.528	8.546	7.528	8.526	7.529	8.512	7.530	---	7.529	8.492	7.524
	6.981	2.279	6.996	2.287	7.011	2.295	7.022	2.302	7.035	2.310	7.048	2.317
60	8.446	7.288*	8.463	7.294*	8.482	7.306*	8.500	7.316*	8.521	7.323*	8.544	7.326*
	7.710	7.780	---	---	---	---	7.770	7.728	7.777	7.716	7.789	---
	8.574	7.527	8.547	7.527	8.527	7.528	8.513	7.529	8.499	7.528	8.491	7.523
	6.979	2.278	6.994	2.286	7.007	2.293	7.020	2.300	7.032	2.308	7.047	2.317
δ_M	8.575	7.503	8.585	7.479	8.592	7.467	8.611	7.453	8.630	7.456	8.649	7.434
	7.960	7.727	---	---	---	---	7.882	7.675	7.885	7.678	7.874	---
	8.533	7.563	8.515	7.551	8.499	7.546	8.533	7.542	---	7.536	---	7.528
	7.128	2.348	7.109	2.343	7.105	2.343	7.106	2.344	7.114	2.349	7.126	2.355
δ_D	8.382	7.187	8.392	7.181	8.406	7.207	8.421	7.220	8.453	7.246	8.480	7.226
	7.593	7.823	---	---	---	---	7.687	7.756	7.699	7.747	7.884	---
	8.599	7.514	8.563	7.513	8.540	7.519	8.599	7.519	---	7.515	---	7.510
	6.911	2.246	6.925	2.251	6.943	2.260	6.961	2.267	6.980	2.278	7.001	2.289
K_D	69	68	50	47	34	47	32	38	39	45	42	21
	77	29	---	---	---	---	34	52	31	30	30	---
	43	104	49	45	53	48	43	31	---	7	---	4
	75	74	48	46	40	39	35	28	38	32	46	33
K_D	67.4±22.7		47.5 ± 1.9		43.5 ± 7.0		36.6 ± 7.7		31.7±12.1		29.3 ± 15.3	

* Assigned by COSY

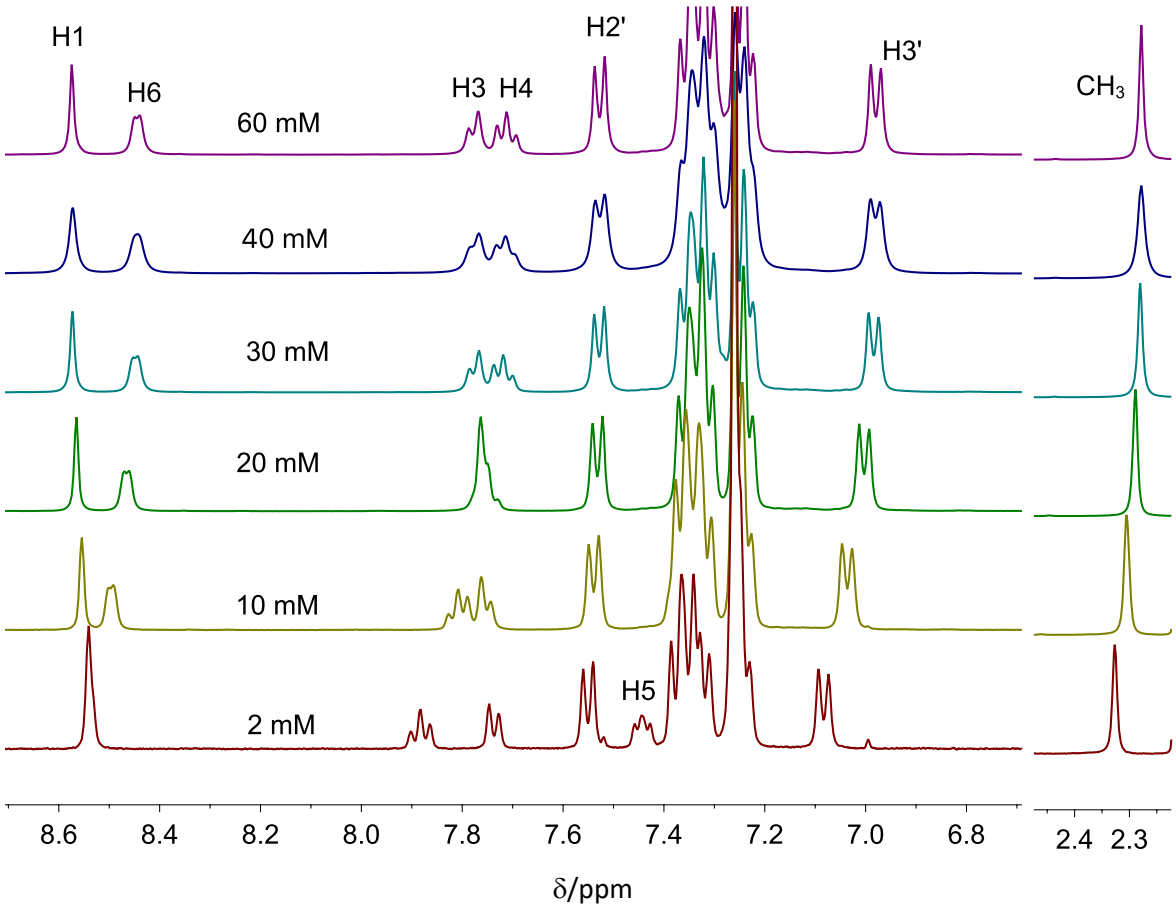


Figure SI8 a) ^{1}H-NMR spectra of [Cu(NN'-CH_3)(PPh_3)Br] at 220 K for several concentrations used for calculating self-association constants. Proton assignments are included. Similar behavior is observed at all temperatures used in this study.

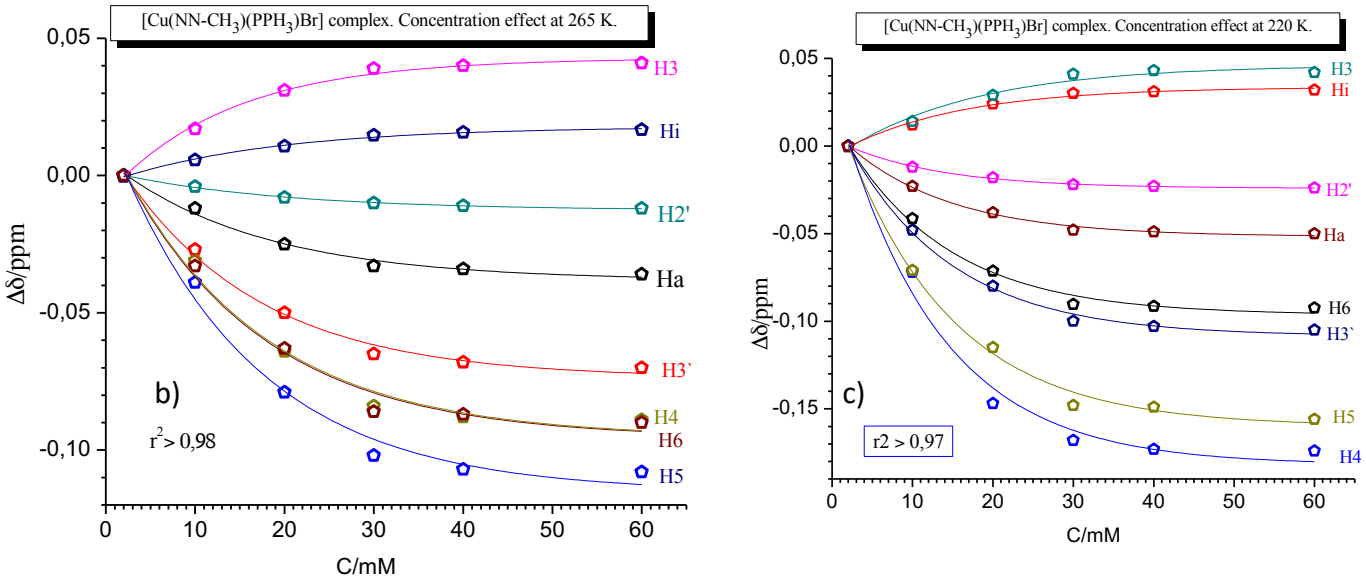


Figure SI8 b) Concentration effect on NN`-CH_3 ligand protons chemical shifts of [Cu(NN'-CH_3)(PPh_3)Br] complex at 265 K and **c)** at 220 K.

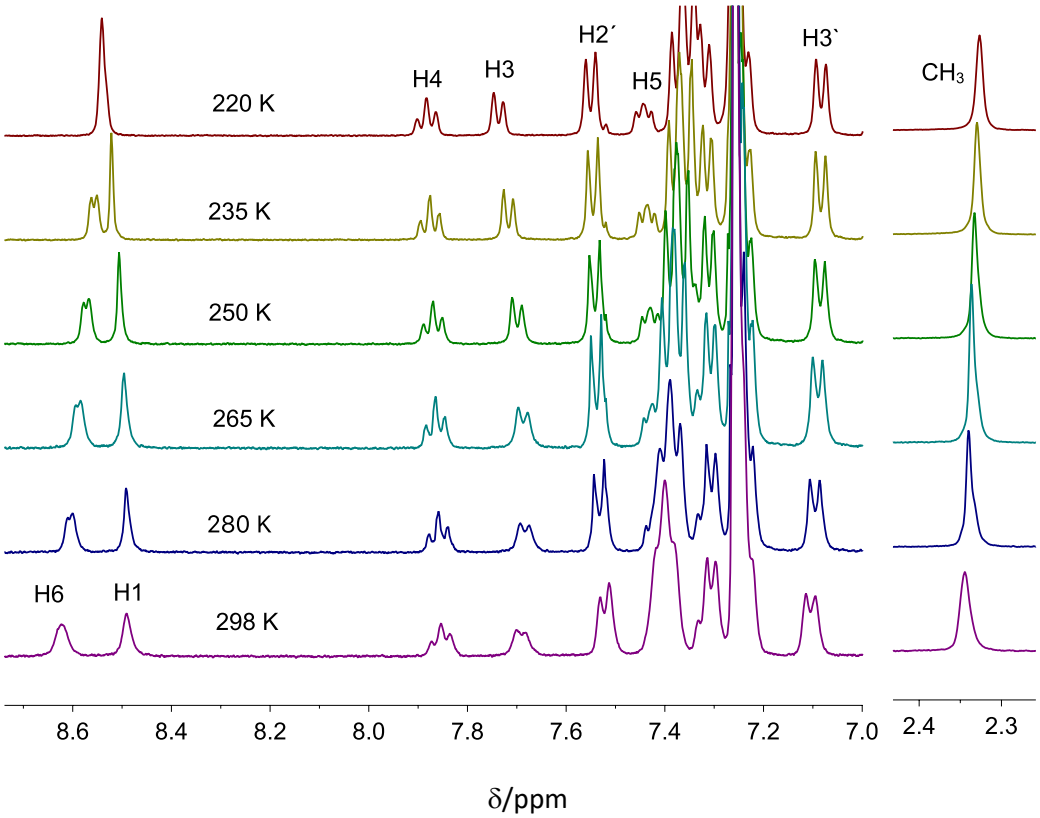


Figure SI9 a).^{1}H-NMR spectra of [Cu(NN'-CH_3)(PPh_3)Br] of 2 mM at several temperatures. Proton assignments are included. Similar behavior is observed at all concentrations used in this study.

Table SI3e. ^{1}H-NMR data (δ/ppm) for NN'-OCH_3 ligand in [Cu(NN'-OCH_3)(PPh_3)Br] complex at several temperatures and concentrations, δ calculated for monomer and dimer and self-association constants.

T/K	220		235		250		265		280		298	
Proton	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
C/mM	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a
2	8.536	7.400*	8.554	7.401*	8.569	7.403*	8.588	7.403*	8.605	7.404*	8.619	7.404*
	7.823	7.725	7.832	7.702	7.837	7.683*	7.838	7.672*	7.839	7.668*	7.837	7.676*
	8.578	7.670	8.541	7.669	8.516	7.668	8.498	7.664	8.489	7.660	8.484	7.651
	6.745	3.794	6.757	3.795	6.769	3.797	6.782	3.799	6.796	3.804	6.809	3.808
10	8.483	7.311*	8.502	7.322*	8.521	7.334*	8.542*	7.340*	8.564	7.353*	8.579	7.359*
	7.696*	7.748	7.729*	----	7.755	7.710	7.772	7.696	7.786	7.686	7.795	7.680
	8.642	7.644	8.599	7.650	8.557	7.651	8.529	7.653	8.511	7.654	8.496	7.648
	6.667	3.769	6.694	3.775	6.716	3.779	6.738	3.783	6.758	3.790	6.775	3.795
20	8.455	7.262*	8.470	7.277*	8.491	7.285*	8.511	7.298*	8.534*	7.316*	8.549	7.322*
	7.633*	7.759	7.670	7.744	7.702*	----	7.723*	----	7.748	7.702	7.762	7.691
	8.684	7.629	8.626	7.639	8.582	7.642	8.550	7.646	8.528	7.649	8.507	7.644
	6.626	3.756	6.656	3.761	6.685	3.767	6.708	3.772	6.732	3.780	6.751	3.785
40	8.424	7.215	8.435	7.220*	8.453	7.237*	8.472	7.252*	8.494	7.265*	8.515*	7.280*
	7.563	7.771	7.605*	7.759	7.643*	7.747	7.668	7.735	7.694*	7.721	7.719*	7.712
	8.723	7.618	8.662	7.628	8.614	7.634	8.578	7.638	8.552	6.642	8.527	7.640
	6.584	3.741	6.616	3.745	6.646	3.752	6.672	3.757	6.697	3.765	6.720	3.771
60	8.410	7.189	8.416	7.197*	8.431	7.207*	8.452	7.225*	8.473	7.241*	8.493	7.263*
	7.532	7.776	7.573	7.766	7.603*	7.757	7.640*	7.744	7.666	7.437	7.695*	7.720
	8.743	7.613	8.680	7.621	8.632	7.630	8.594	7.635	8.568	7.641	8.541	7.639
	6.564	3.733	6.595	3.737	6.626	3.743	6.653	3.748	6.679	3.756	6.703	3.763
80	8.398	7.170	8.405	7.177	8.421	7.191	8.438	7.205*	8.457	7.218*	8.476	7.237*
	7.512	7.778	7.549	7.773	7.603*	7.765	7.617*	7.754	7.648*	7.744	7.671	7.733
	8.745	7.610	8.693	7.618	8.645	7.629	8.609	7.633	8.579	7.638	8.552	7.638
	6.552	3.725	6.580	3.730	6.612	3.736	6.638	3.741	6.665	3.749	6.688	3.756
δ_M	8.559	7.440	8.575	7.432	8.586	7.430	8.604	7.425	8.619	7.419	8.632	7.419
	7.882	----	7.874	----	7.865	----	7.861	----	7.857	7.663	7.849	----
	8.545	7.686	----	7.677	8.504	7.678	8.489	7.669	8.483	----	8.480	----
	6.782	----	6.782	3.802	6.788	3.803	6.797	3.803	6.809	3.807	6.820	3.812
δ_D	8.303	7.017	8.282	6.994	8.277	7.000	8.283	7.018	8.280	6.983	8.308	7.042
	7.311	----	7.334	----	7.343	----	7.389	----	7.416	7.868	7.433	----
	8.865	7.578	----	7.580	8.783	7.607	8.746	7.609	8.723	----	8.754	----
	6.427	----	6.440	3.666	6.472	3.669	6.491	3.663	6.517	3.661	6.546	3.681
K_D	28	30	21	21	16	18	14	16	11	10	11	8
	34	----	24	----	16	----	14	----	11	----	8	----
	32	53	----	25	13	48	10	24	7	7	11	----
	34	----	22	15	18	12	14	9	12	7	3	8
K_D	35.2 ± 9.0		21.3 ± 3.5		20.1 ± 12.5		14.4 ± 4.9		9.3 ± 2.2		8.2 ± 2.9	

* Assigned by COSY

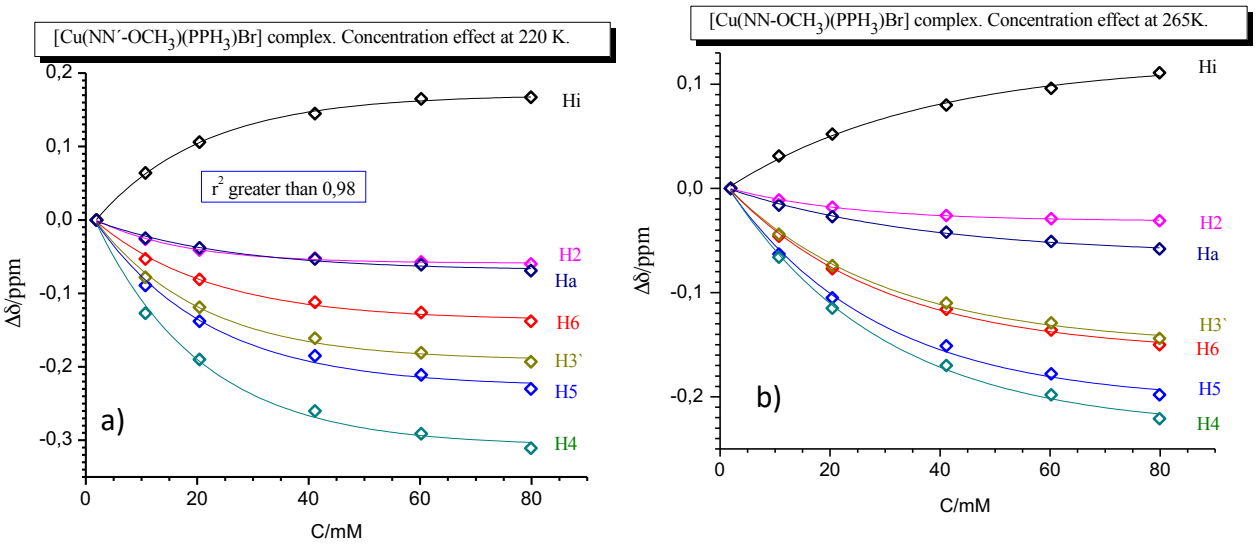


Figure SI10. a) Concentration effect on NN`-OCH_3 ligand protons chemical shifts of [Cu(NN'-OCH_3)(PPh_3)Br] complex at 220 K and **b)** at 265 K**.**

Table SI3f. [1]H-NMR data (δ/ppm) for NN'-N(CH$_3$)$_2$ ligand in [Cu(NN'-N(CH$_3$)$_2$)(PPh$_3$)Br] complex at several temperatures and concentrations, δ calculated for monomer and dimer and self-association constants.

T/K	220		235		250		265		280		298	
Proton	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
C/mM	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a	$H_{3'}$	H_a
2	8.460	7.328*	8.479	7.325*	8.503*	7.328*	8.521	7.330*	8.544	7.331*	8.566	7.333*
	7.782	7.639	7.788	7.618	7.791	7.604	7.794	7.593	7.794	7.595	7.793	7.603
	8.571	7.705	8.534	7.699	8.509	7.698	8.493	7.693	8.487	7.688	8.483	7.680
	6.504	2.977	6.517	2.976	6.532	2.976	6.548	2.978	6.565	2.979	6.585	2.983
10	8.412	7.244*	8.437	7.252*	8.462	7.269*	8.497	7.281*	8.507	7.288*	8.529	7.294*
	7.663*	----	7.701	7.633	7.725	7.619	7.742	7.604	7.752	7.603	7.759	7.600
	8.615	7.676	8.564	7.681	8.528	7.683	8.480	7.680	8.491	7.679	8.479	7.675
	6.439	2.958	6.469	2.960	6.494	2.963	6.515	2.965	6.535	2.968	6.556	2.971
20	8.381	7.182	8.405	7.202	8.431	7.221*	8.456	7.238*	8.480	7.251*	8.503	7.263*
	7.593*	7.667*	7.641*	7.656*	7.676*	7.627	7.702	7.615	7.720	7.612	7.732	7.606
	8.644	7.655	8.584	7.665	8.541	7.669	8.512	7.671	8.497	7.673	8.482	7.669
	6.395	2.945	6.433	2.948	6.463	2.952	6.489	2.955	6.513	2.959	6.535	2.963
35	8.358	7.141	8.379	7.162	8.405	7.183	8.429	7.203	8.454	7.219*	8.479*	7.232*
	7.538	7.655*	7.590	7.662*	7.634*	7.652*	7.669*	----	7.687	7.620	7.705	7.612
	8.667	7.643	8.602	7.653	8.553	7.660	8.520	7.662	8.503	7.666	8.484	7.663
	6.364	2.934	6.403	2.938	6.437	2.942	6.466	2.945	6.492	2.950	6.516	2.953
45	8.346	7.120	8.366	7.140	8.390	7.161	8.417	7.182	8.440	7.201	8.464	7.214*
	7.512	7.653*	7.566	7.654*	7.607	7.628*	7.644*	----	7.669*	7.624	7.691	7.618
	8.678	7.636	8.609	7.649	8.558	7.655	8.526	7.660	8.508	7.663	8.488	7.661
	6.348	2.929	6.388	2.931	6.421	2.934	6.454	2.940	6.479	2.944	6.505	2.948
60	8.334	7.098	8.352	7.118	8.375	7.139	8.399	7.161	8.423	7.180	8.448	7.197
	7.484	7.652*	7.541	7.644*	7.583	7.642*	7.628*	----	7.651*	----	7.675*	7.625
	8.686	7.633	8.618	7.643	8.566	7.650	8.530	7.656	8.513	7.660	8.493	7.658*
	6.332	2.921	6.372	2.925	6.407	2.928	6.438	2.932	6.466	2.937	6.493	2.942
δ_M	8.484	7.372	8.498	7.357	8.519	7.352	8.534	7.350	8.556	7.346	8.579	7.347
	7.845	----	7.828	----	7.815	----	7.814	----	7.808	----	7.805	----
	8.548	7.724	8.521	7.708	8.502	7.705	----	7.699	----	7.691	----	7.682
	6.537	2.985	6.538	2.982	6.547	2.980	6.560	2.982	6.575	2.982	6.596	2.987
δ_D	8.219	6.881	8.203	6.892	8.205	6.887	8.146	6.910	8.235	6.927	8.277	6.967
	7.333	----	7.277	----	7.292	----	7.393	----	7.409	----	7.477	----
	8.793	7.575	8.708	7.580	8.637	7.592	----	7.616	----	7.620	----	7.612
	6.174	2.858	6.201	2.854	6.230	2.832	6.278	2.851	6.312	2.845	6.366	2.868
K_D	25	24	16	18	13	13	7	10	10	9	11	9
	29	----	19	----	12	----	12	----	9	----	9	----
	26	25	16	18	14	16	----	19	----	12	----	7
	25	16	16	12	12	7	11	8	10	6	12	8
K_D	24.3 ± 4.0		16.4 ± 2.3		12.4 ± 2.8		11.2 ± 4.3		9.3 ± 2.0		9.3 ± 1.9	

* Assigned by COSY

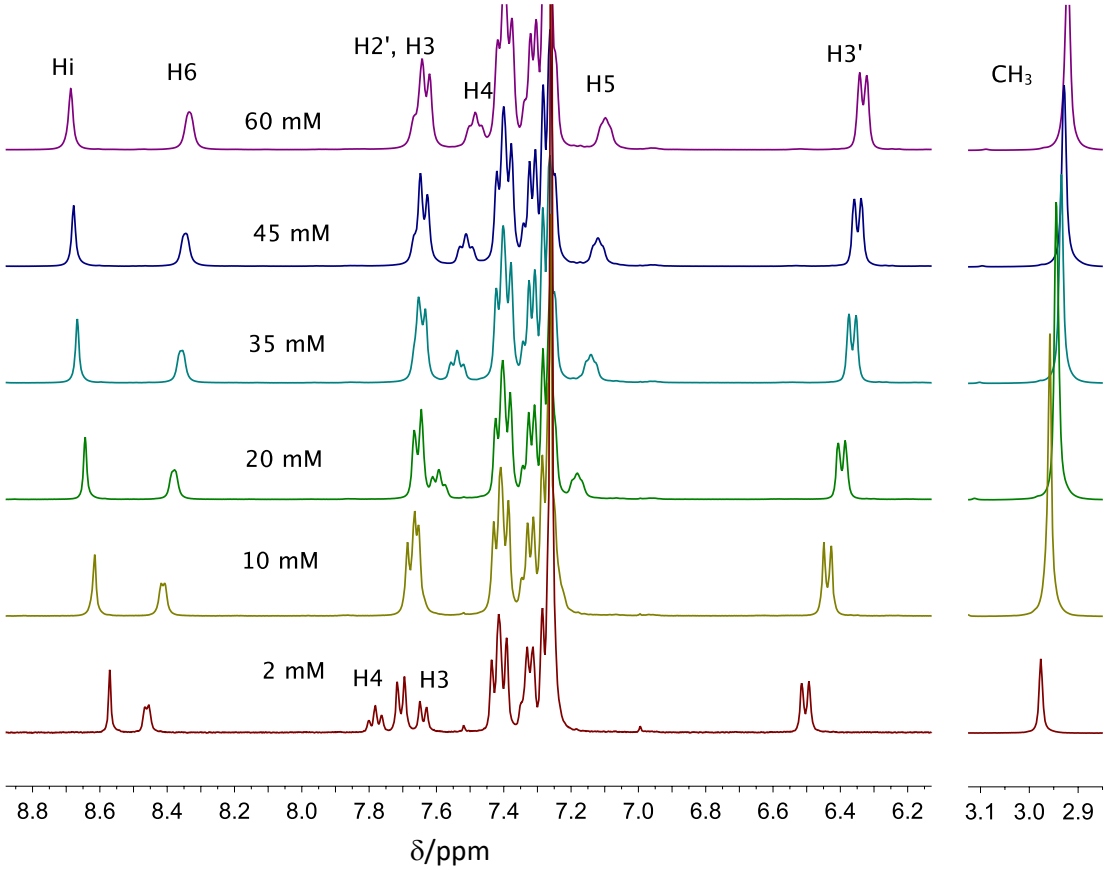


Figure SI11). ^{1}H-NMR spectra of [Cu(NN'-N$(CH_3)_2$)(PPh_3)Br] at 220K at several concentrations used for calculating self-association constants. Proton assignments are included. Similar behavior is observed at all temperatures used in this study.

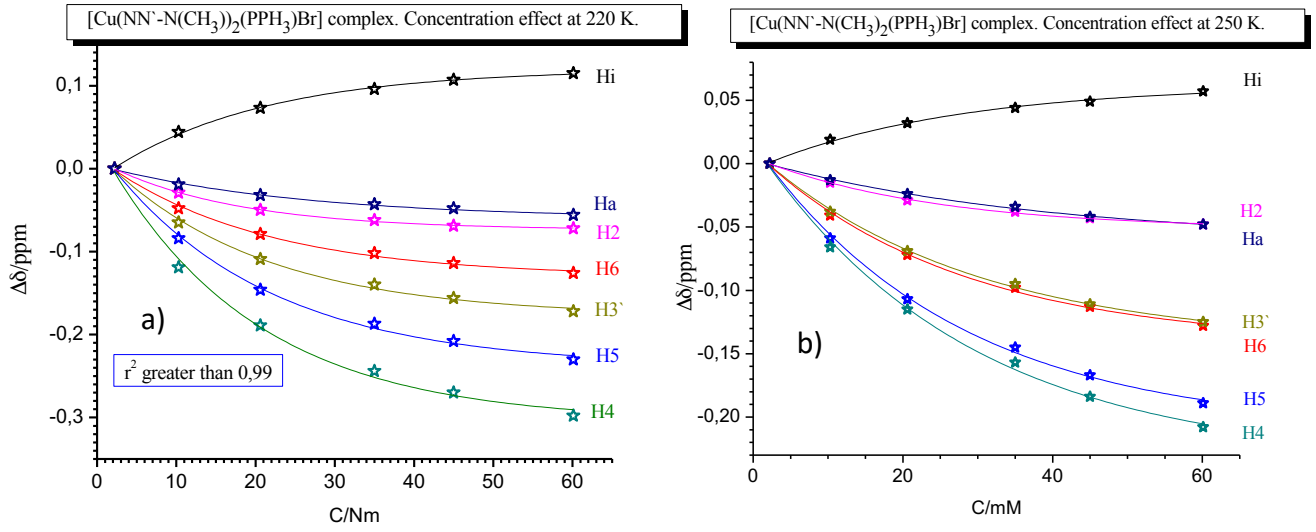


Figure SI11. **a)** Concentration effect on NN`-N$(CH_3)_2$ ligand protons chemical shifts of [Cu(NN'-N$(CH_3)_2(PPh_3)$Br] complex at 220 K, and **b)** at 250 K.

Table SI3g. [1]H-NMR data (δ/ppm) for NN'-Cl ligand in [Cu(NN'-Cl)(PPh_3)Br] complex at several temperatures and concentrations, δ calculated for monomer and dimer and self-association constants.

T/K	220		235		250		265		280		298	
Proton	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5	H_6	H_5
	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3	H_4	H_3
	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$	H_i	$H_{2'}$
C/mM	$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$		$H_{3'}$	
2	8.595*	7.466	8.612	7.465	8.629	7.464	8.644	7.466	8.655	7.464	8.673	7.468
	7.845	7.780	7.858	7.762	7.868	7.748	7.874	7.737	7.876	7.736	7.878	7.745
	8.597	7.547	8.555	7.543	8.525	7.543	8.503	7.542	8.488	7.536	8.483	7.521
	7.171		7.188		7.204*		7.219*		7.234*		7.245*	
20	8.503	7.337*	8.518	7.340*	8.536	7.353*	8.554	7.365*	8.572	7.763*	8.590	7.381*
	7.638	7.795	7.675	7.791	7.710	7.786	7.737	7.778	7.765*	7.763*	7.786	---
	8.767	7.510	8.708	7.521	8.662	7.531	8.622	7.535	8.587	7.537	8.559	7.532
	7.030		7.064		7.096		7.123		7.147		7.175	
40	8.478	7.301*	8.486	7.301*	8.501	7.311*	8.518	7.322*	8.534	7.330*	8.554	7.343*
	7.578	7.800	7.614	7.800	7.650	7.799	7.681	7.794	7.707	7.788	7.734	7.781
	8.821	7.503	8.761	7.515	8.714	7.526	8.671	7.533	8.637	7.538	8.602	7.536
	6.991		7.023		7.055		7.083		7.110		7.138	
60	8.464	7.277*	8.469	7.278*	8.481	7.282*	8.495	7.293*	8.510	7.300*	8.529	7.311*
	7.546	7.802	7.582	7.806	7.616	7.808	7.647	7.802	7.674	7.797	7.705	7.793
	8.848	7.500	8.791	7.513	8.744	7.524	8.701	7.532	8.665	7.536	8.630	7.537
	6.970		7.000		7.031		7.059		7.085		7.116	
80	8.460	7.270*	8.463	7.269*	8.472	7.272*	8.486	7.281*	8.502	7.292*	8.517	7.304*
	7.536*	7.804	7.571	7.807	7.603	7.811	7.633	7.806	7.662	7.803	7.691	7.796
	8.857	7.499	8.802	7.513	8.756	7.524	8.715	7.532	8.679	7.538	8.642	7.537
	6.963		6.993		7.022		7.049		7.077		7.105	
100	8.461	7.269*	8.462	7.267*	8.463	7.265*	8.479	7.275*	8.493	7.281*	8.510	7.293*
	7.534*	7.805	7.565	7.807	7.591	7.812	7.622	7.810	7.650	7.805	7.683	7.800
	8.862	7.499	8.808	7.512	8.764	7.522	8.725	7.532	8.688	7.538	8.649	7.539
	6.962		6.990		7.014		7.042		7.069		7.100	
δ_M	8.646	7.522	8.648	7.514	8.658	7.495	8.668	7.490	8.675	7.485	8.692	7.488
	7.947	-----	7.931	-----	7.918	7.736	7.911	7.724	7.902	-----	7.898	-----
	8.522	-----	8.501	-----	8.482	-----	8.471	-----	8.465	-----	8.468	-----
	7.236		7.23		7.238		7.244		7.256		7.260	
δ_D	8.402	7.171	8.379	7.162	8.368	7.132	8.366	7.123	8.365	7.133	8.377	7.148
	7.390	-----	7.413	-----	7.428	7.852	7.450	7.851	7.458	-----	7.493	-----
	8.990	-----	8.950	-----	8.910	-----	8.878	-----	8.858	-----	8.827	-----
	6.862		6.884		6.900		6.916		6.948		6.958	
K_D	87	60	47	49	32	27	25	20	19	18	18	17
	72	-----	50	-----	33	32	25	-----	17	-----	14	-----
	60	-----	41	-----	32	-----	24	-----	17	-----	12	-----
	68		48		32		33		22		14	
K_D	69.4 ± 11.1		47.0 ± 3.5		31.3 ± 2.2		25.4 ± 4.7		18.6 ± 2.1		15.0 ± 2.4	

* Assigned by COSY. The association constants calculated do not include the data obtained at the concentration of 100 mM.

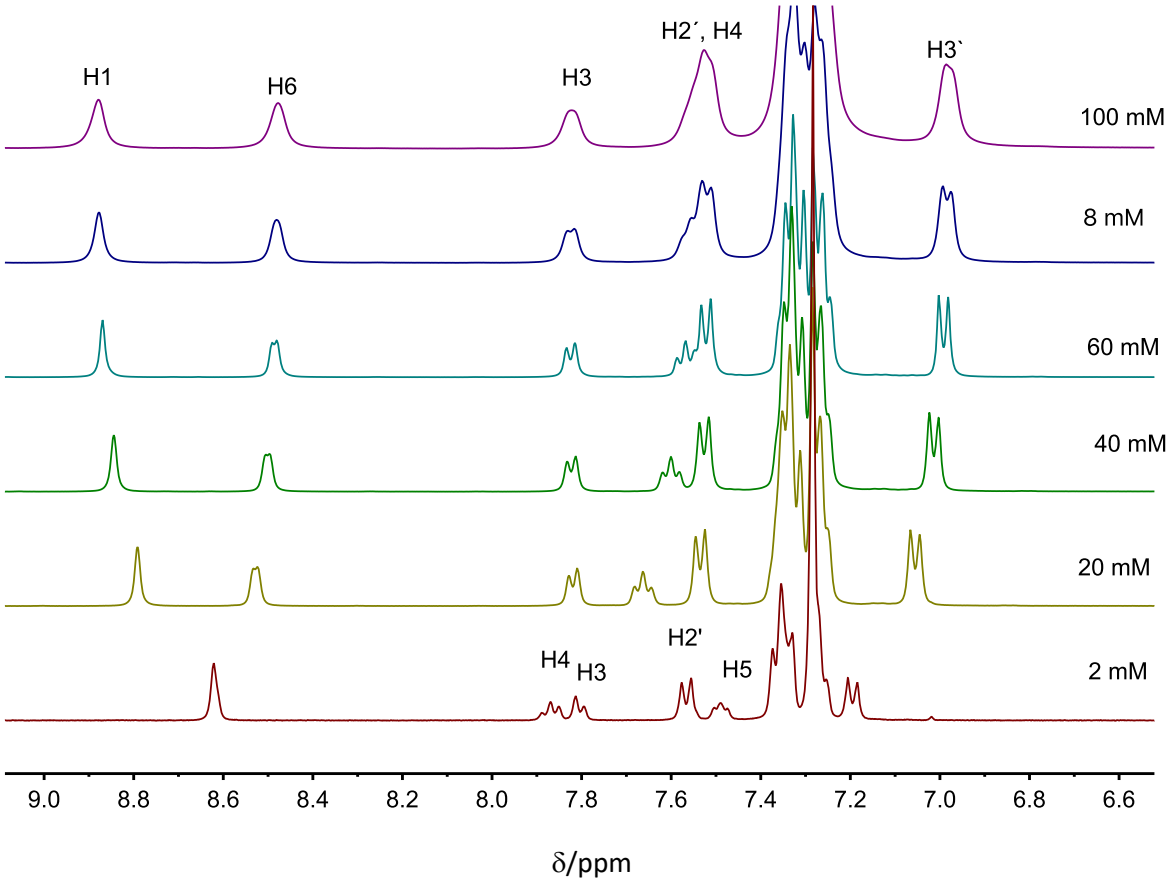


Figure SI12a.[1]H-NMR spectra of [Cu(NN'-Cl)(PPh_3)Br] at 220K at several concentration used for calculating self-association constants. Proton assignments are included. Similar behavior is observed at all temperatures used in this study.

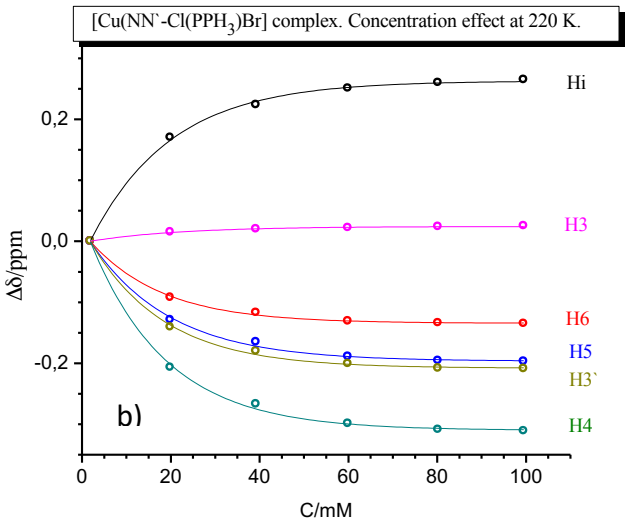


Figure 7 b) Concentration effect on **NN`-Cl** ligand protons chemical shifts of [Cu(NN'-Cl)(PPh_3)Br] complex at 220 K.

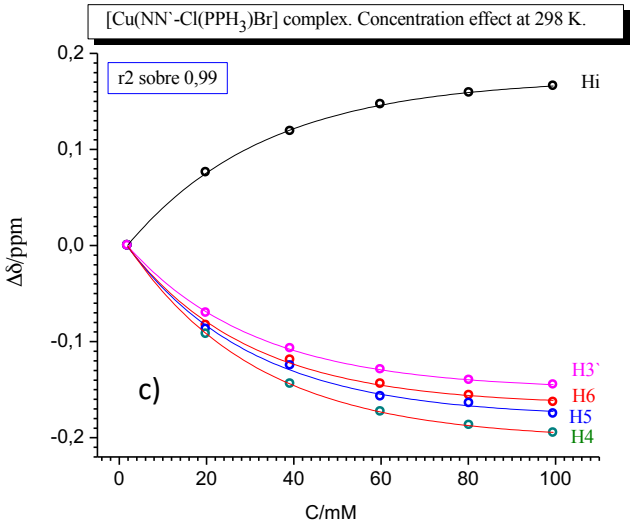


Figure SI12 c). Concentration effect on **NN`-Cl** ligand protons chemical shifts of [Cu(NN'-Cl(PPh_3)Br] complex at 250 K**.**

The next **figures SI13**, are examples of COSY and NOESY spectra for [Cu(NN'-R)(PPh_3)Br] complexes.

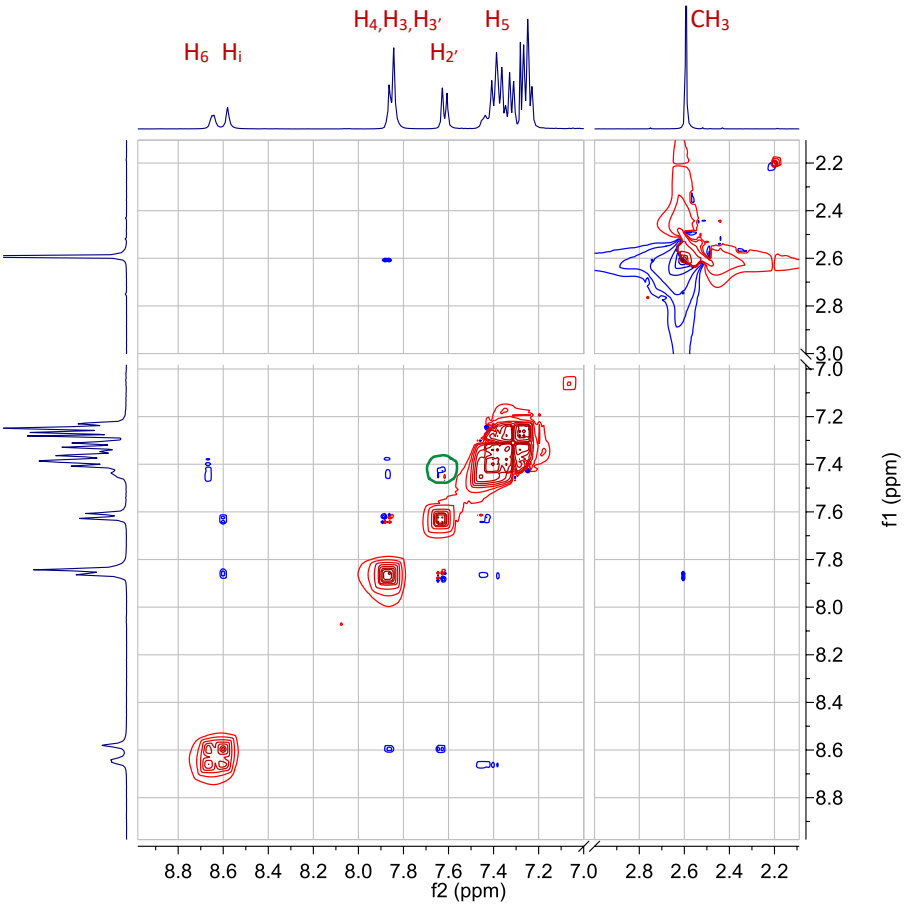


Figure SI13 a. NOESY spectrum for [Cu(NN'-$COCH_3$)(PPh_3)Br], 20 mM solution at 298 K.

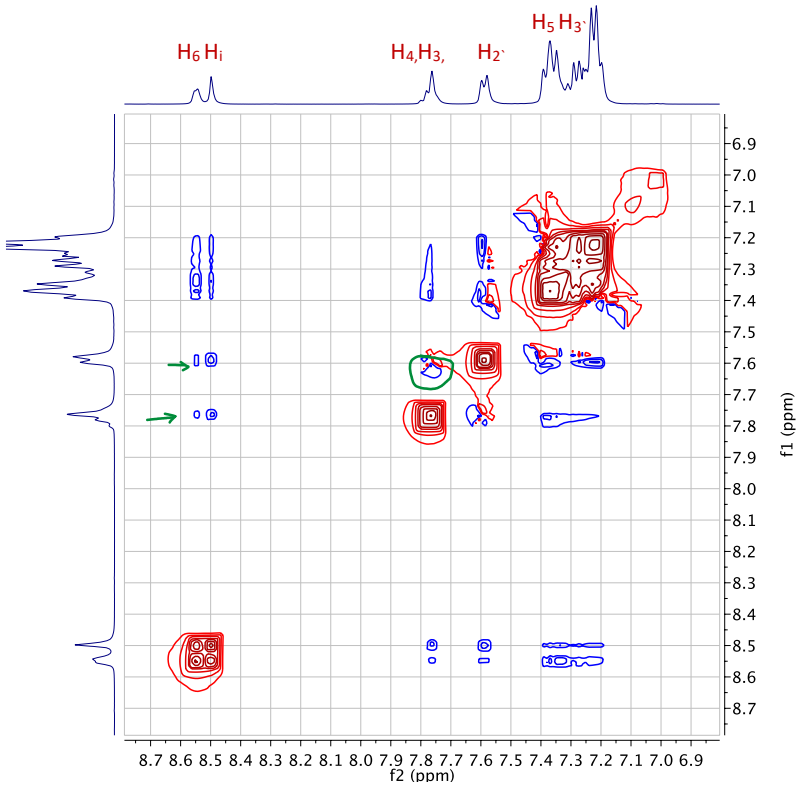


Figure SI13 b. NOESY spectrum for [Cu(NN'-H)(PPh_3)Br], 50 mM solution at 298 K.

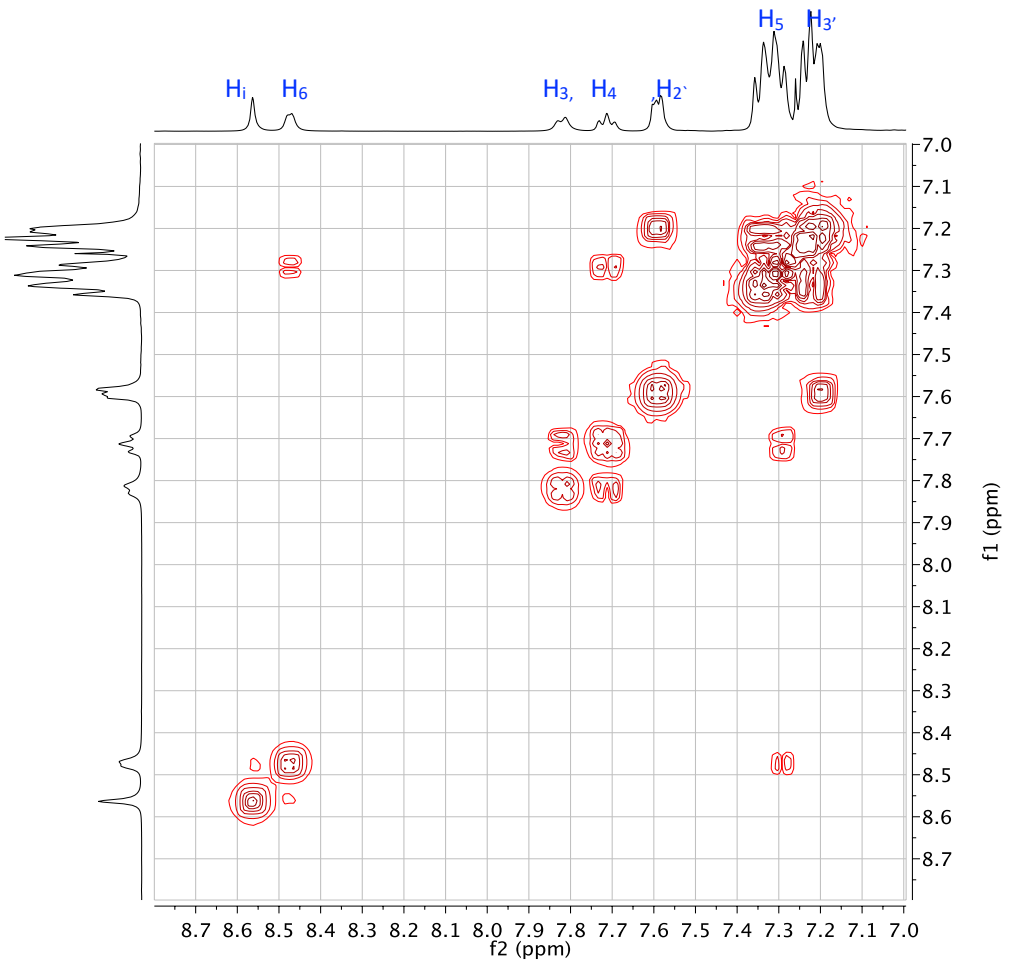


Figure SI13 c. COSY spectrum for [Cu(NN'-H)(PPh_3)Br], 50 mM solution at 235 K.

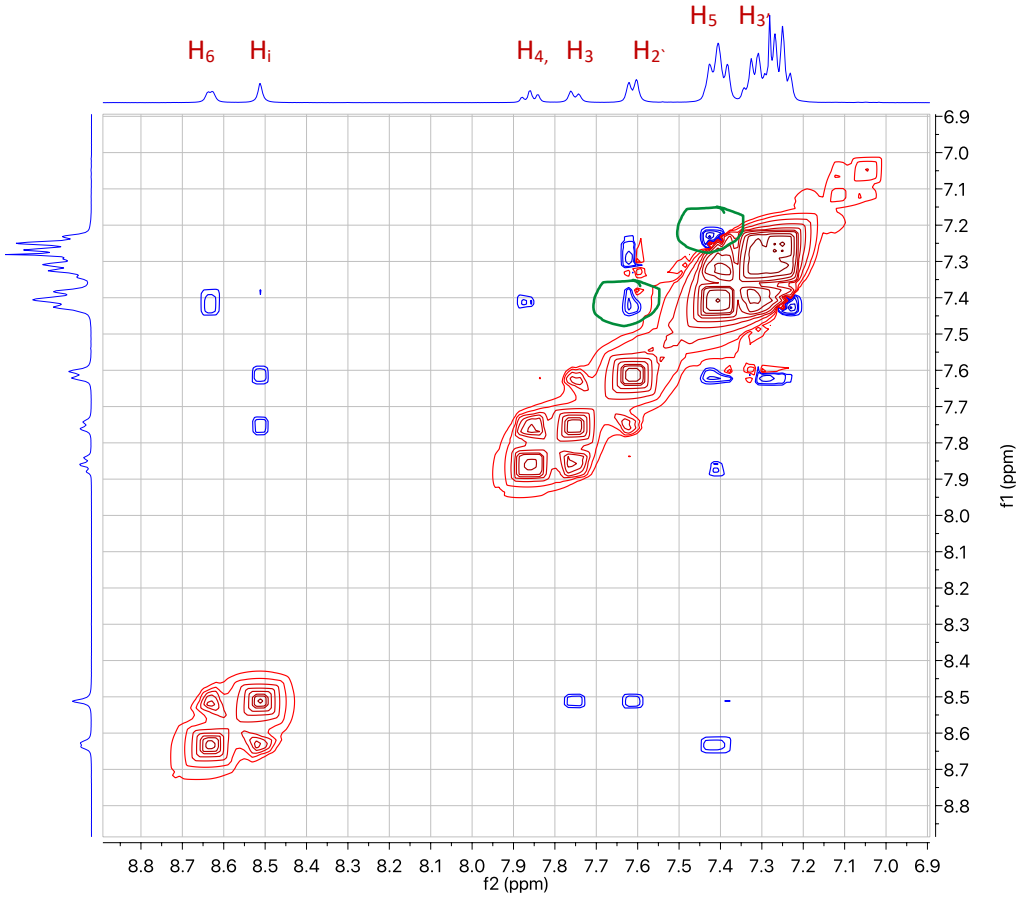


Figure SI13 d. NOESY spectrum for [Cu(NN'-H)(PPh_3)Br], 20 mM solution at 265 K

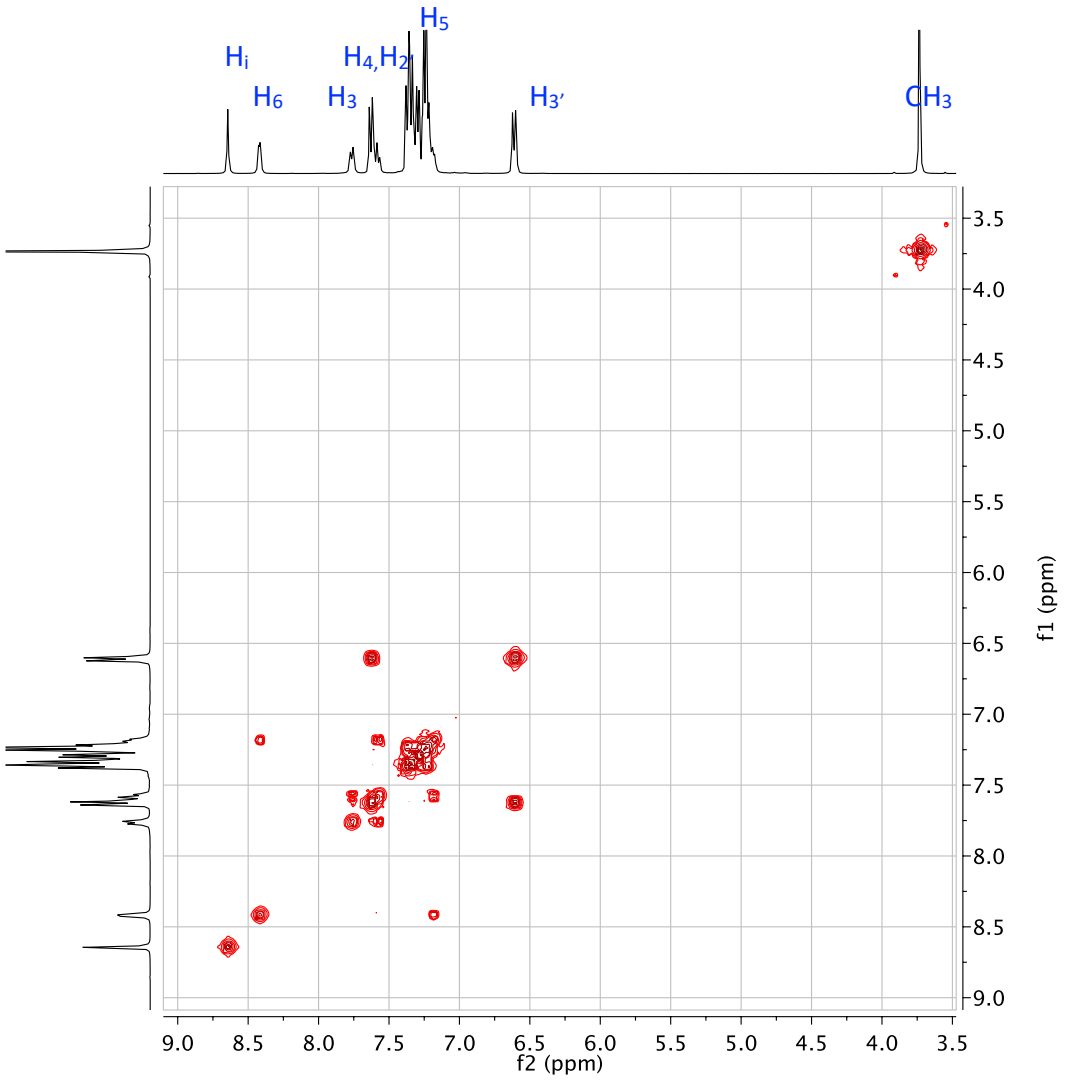


Figure SI13 e. COSY spectrum for [Cu(NN'-OCH_3)(PPh_3)Br], 80 mM solution at 250 K

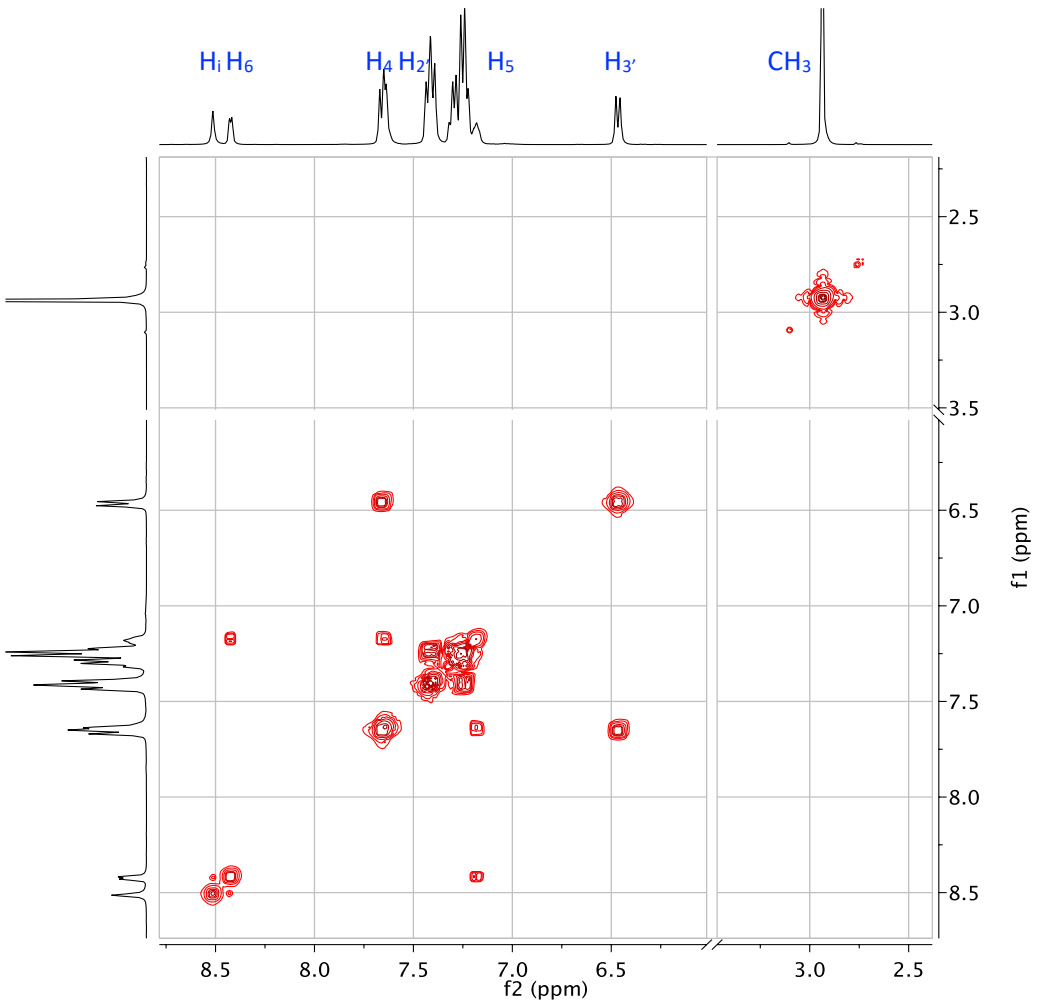


Figure SI13 f. COSY spectrum for [Cu(NN'-N$(CH_3)_2$(PPh_3)Br], 60 mM solution at 280 K

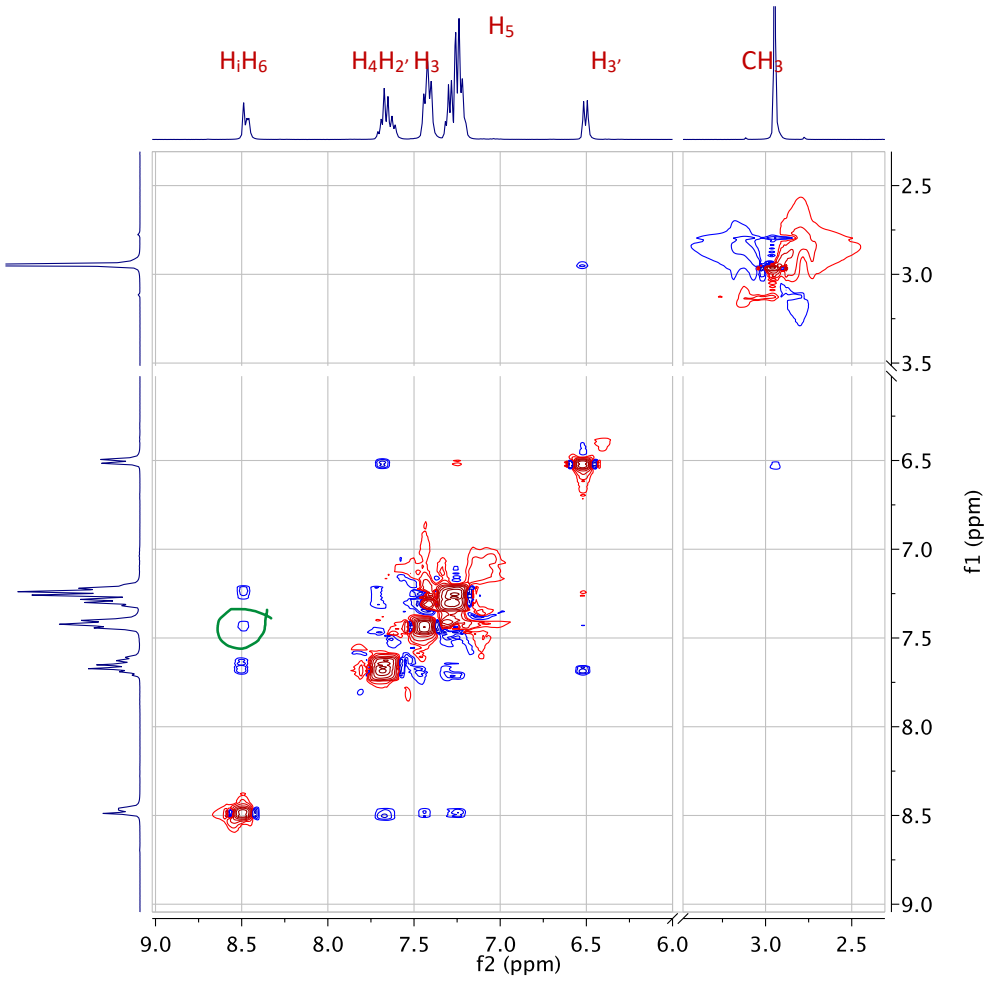


Figure SI13 g. NOESY spectrum for Cu(NN'-N(CH_3)$_2$(PPh_3)Br], 45 mM solution at 298 K

IV- Electrochemical Results.

1.-Instrumental

All measurements were carried out under a nitrogen atmosphere at room temperature with tetrabutylammonium perchlorate (TBAP) 0.1 M as supporting electrolyte, Pt disc as working electrode (CH Instruments, USA), Pt wire as counter electrode, and Ag/AgCl(sat) as reference electrode, in a tree compartment cell using workstation Potentiostat 620E CH Instruments, iR compensation, USA. The cyclic voltammetry (CV) measurements were performed at different scan rates (10, 25, 50, 100, and 200 mV/s); Square wave voltammetry (SWV) was carried out using a frequency of 15 Hz, increasing potential of 4 mV, amplitude potential of 25 mV. Cu(I) complexes were dissolved at different concentrations (1.00, 0.75, 0.50, 0.25, and 0.10 mM of monomer) in freshly distilled CH_2Cl_2 with P_2O_5 (Supelco) and stored in a Shott flask with molecular sieve activated at 573 K. All potentials values were reported as E vs internal reference Fc/Fc^+.

2.- Previous NMR measurements.

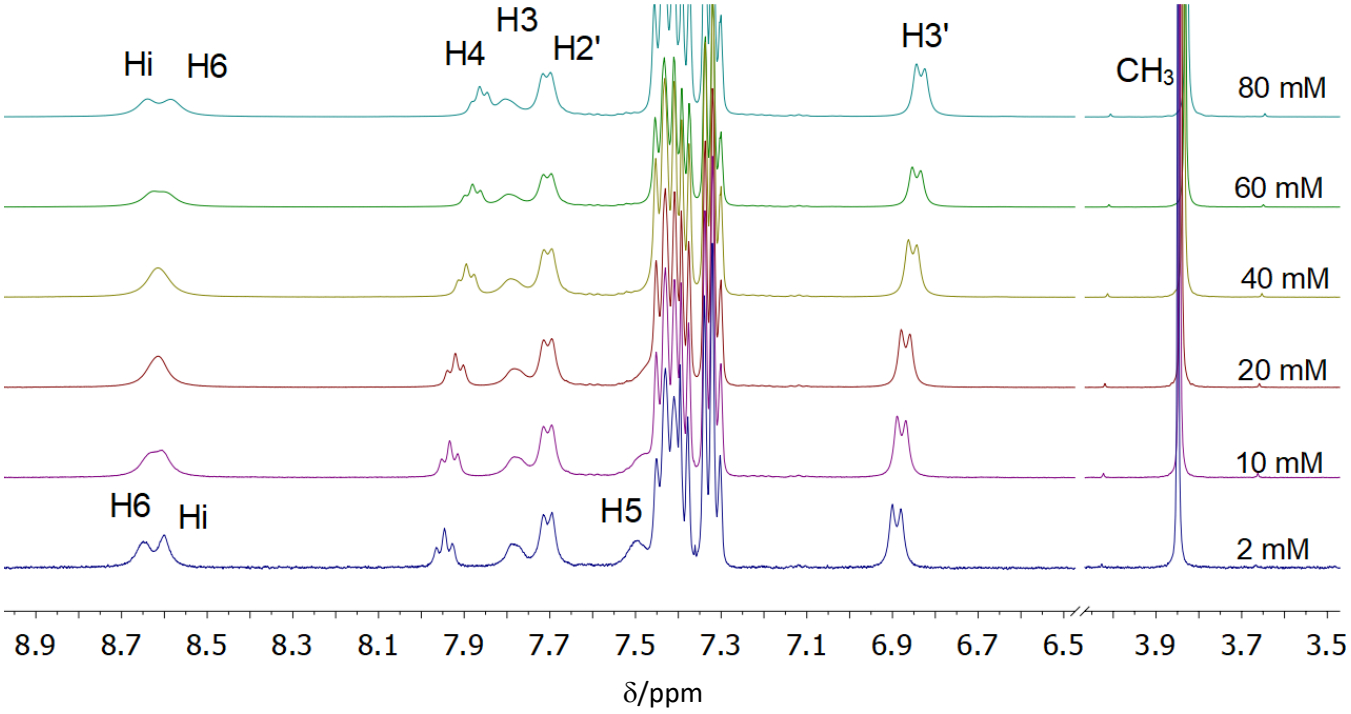


Figure SI13 h. ^{1}H-NMR spectra of [Cu(NN'-OCH_3)(PPh_3)Br] in CD_2Cl_2 at several concentrations. The working temperature was 298 K. Proton assignments are included.

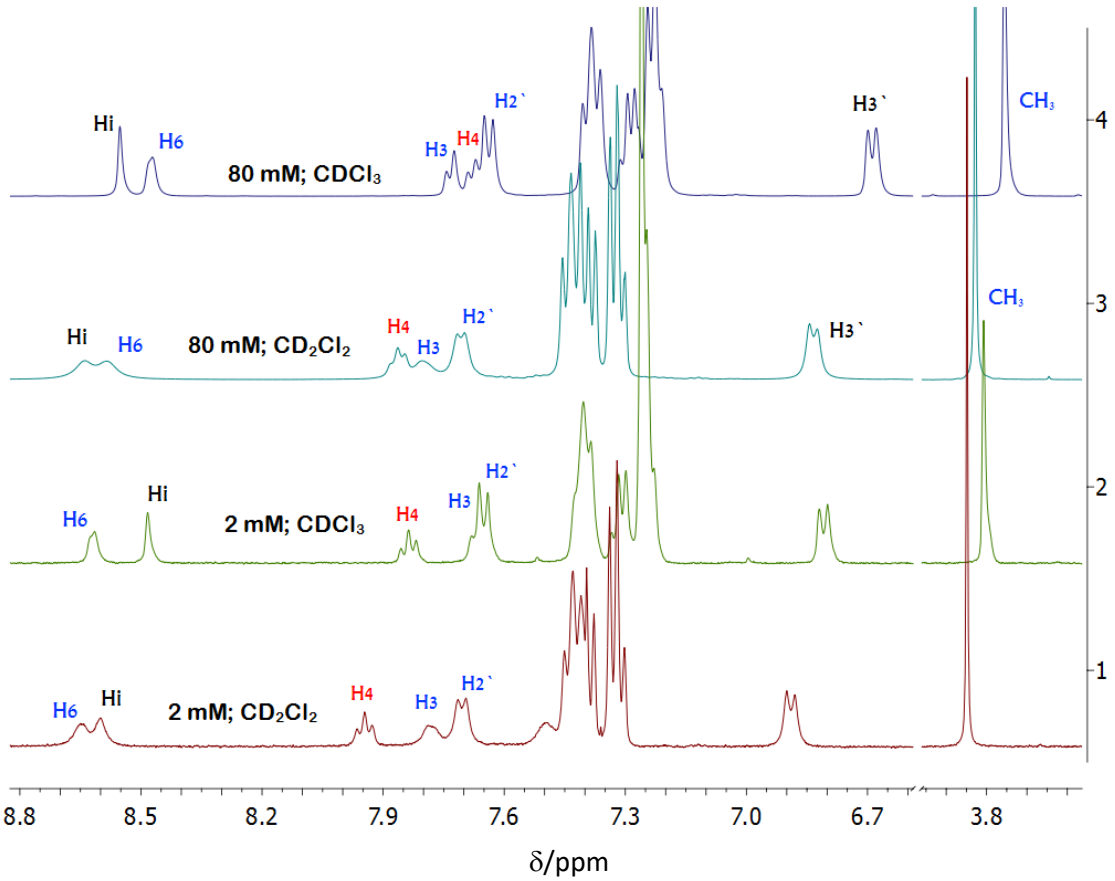


Figure SI13 I. ^{1}H-NMR spectra of [Cu(NN'-OCH_3)(PPh_3)Br]] complex at 298K in $CDCl_3$ and CD_2Cl_2 for 2 and 80 mM concentrations. Proton assignments are included.

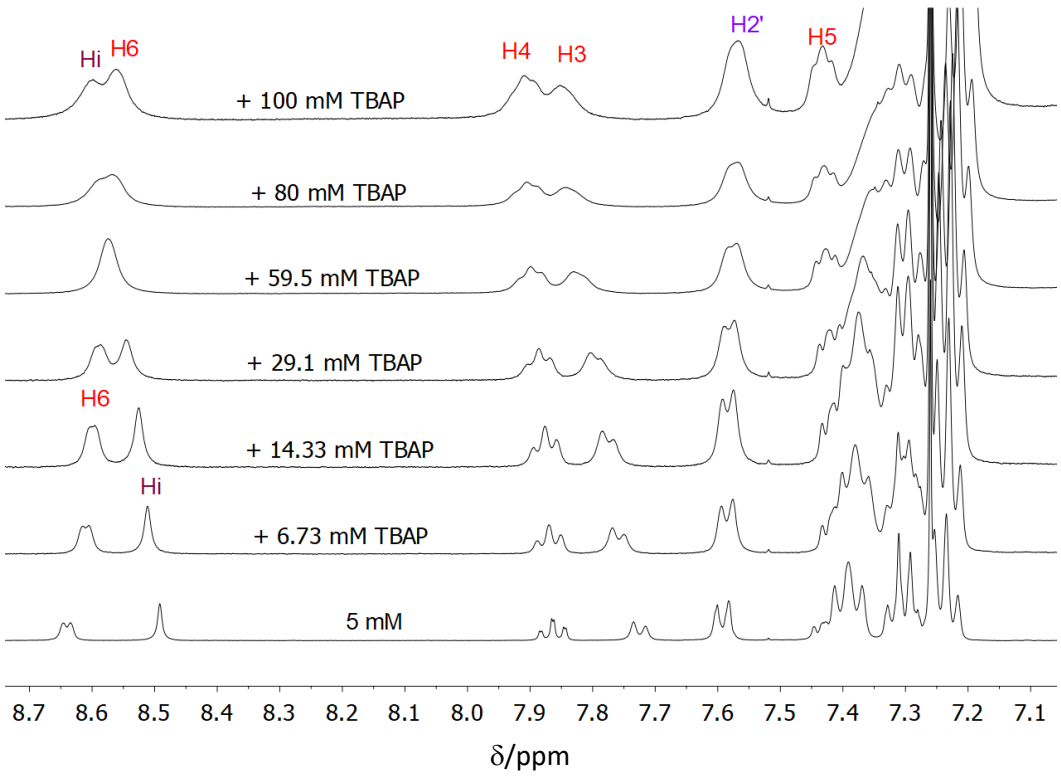


Figure SI13 j ^{1}H-NMR spectra of [Cu(NN'-H)(PPh_3)Br] of 5mM concentration in $CDCl_3$ at 300K, in the presence of increasing amounts of tetrabutylammonium perchlorate (TBAP). Proton assignments are included.

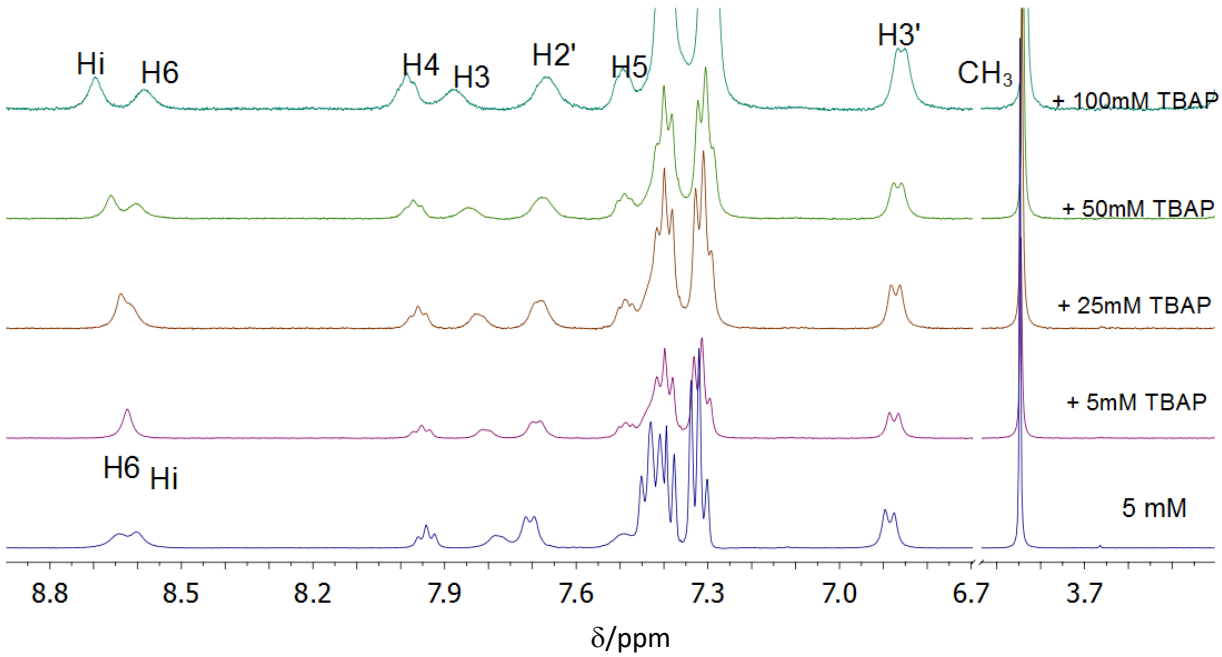
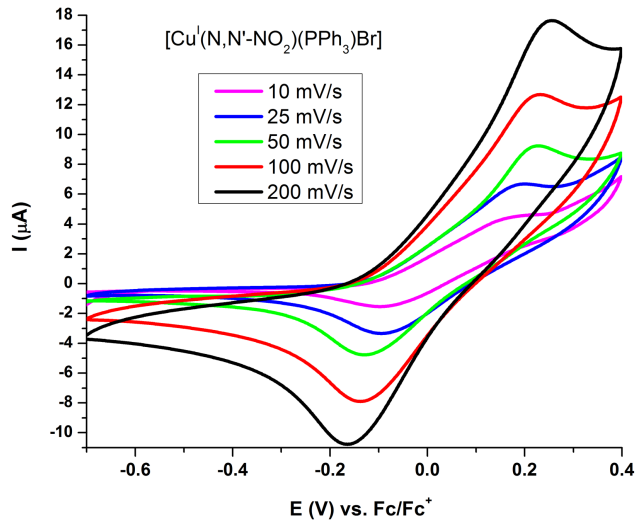
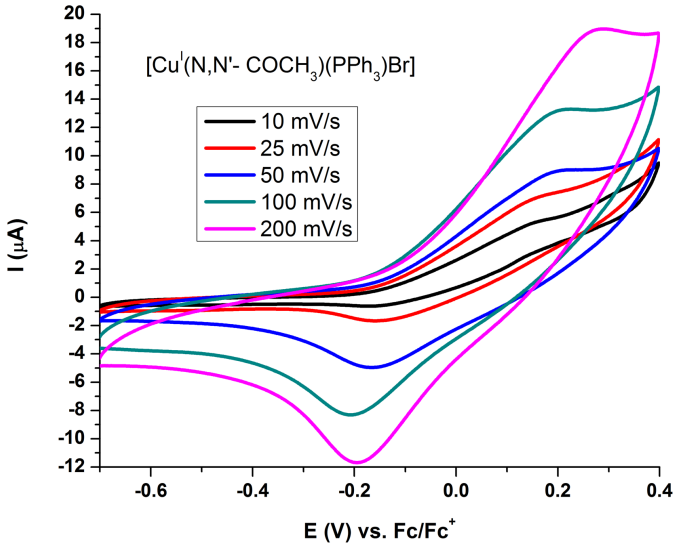
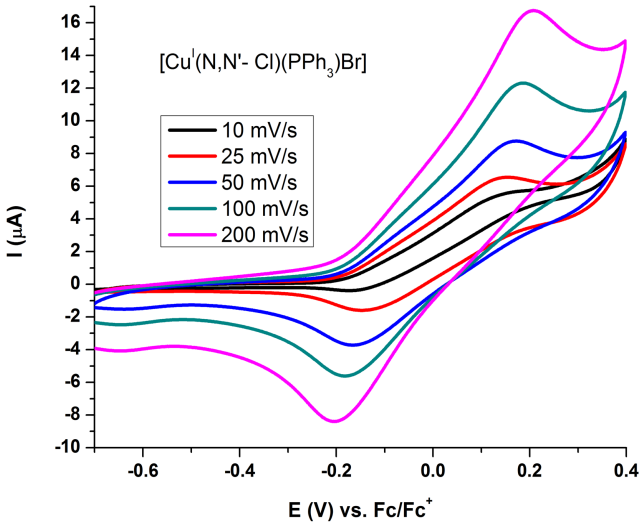


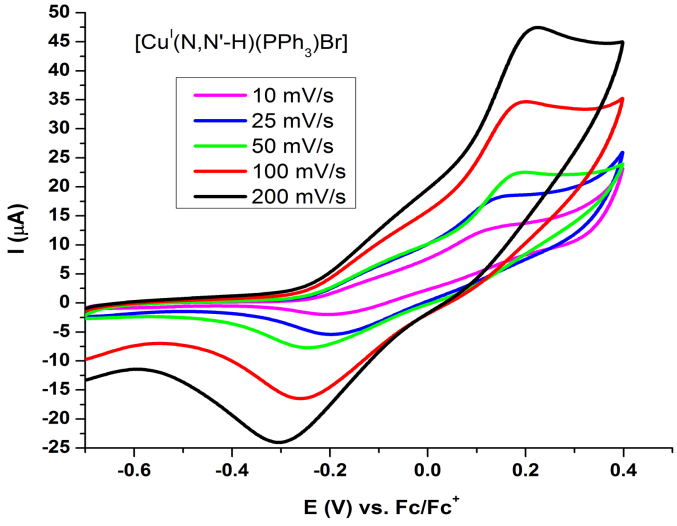
Figure SI13k. ^{1}H-NMR spectra of [Cu(NN'-OCH_3)(PPh_3)Br] of 5mM concentration in CD_2Cl_2 at 298 K, in the presence of increasing amounts of tetrabutylammonium perchlorate (TBAP). Proton assignments are included.

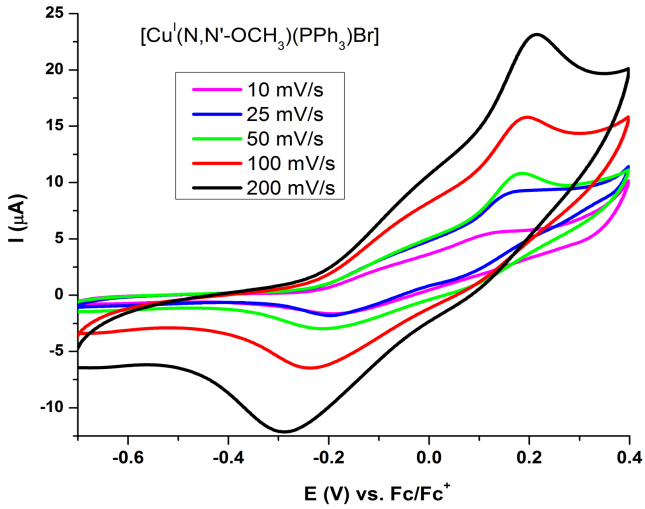
3.- Electrochemical

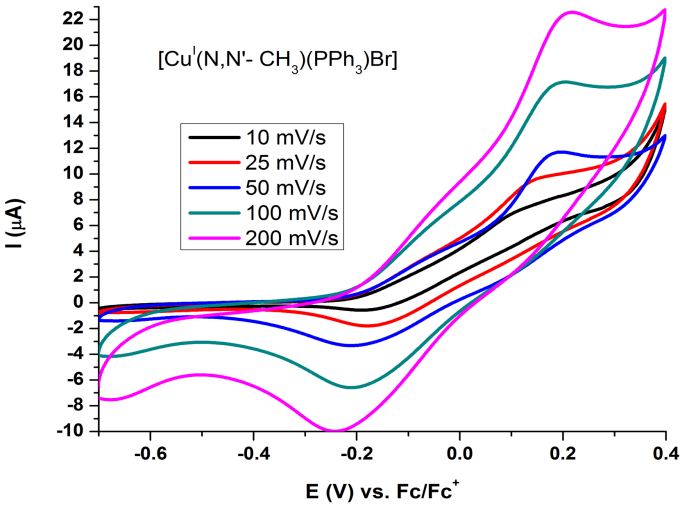












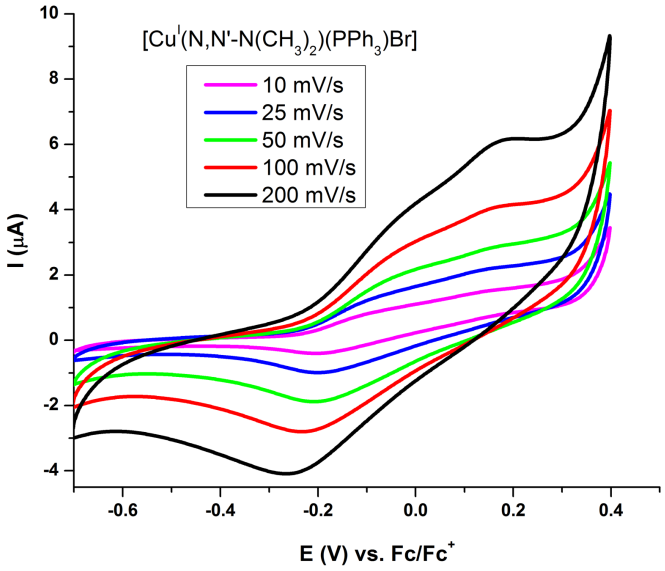


Figure SI14. Voltammetric profile of the different complexes at different scan rates at a concentration of 1 mM CH_2Cl_2 and 0.1 M $[NBu_4]ClO_4$.

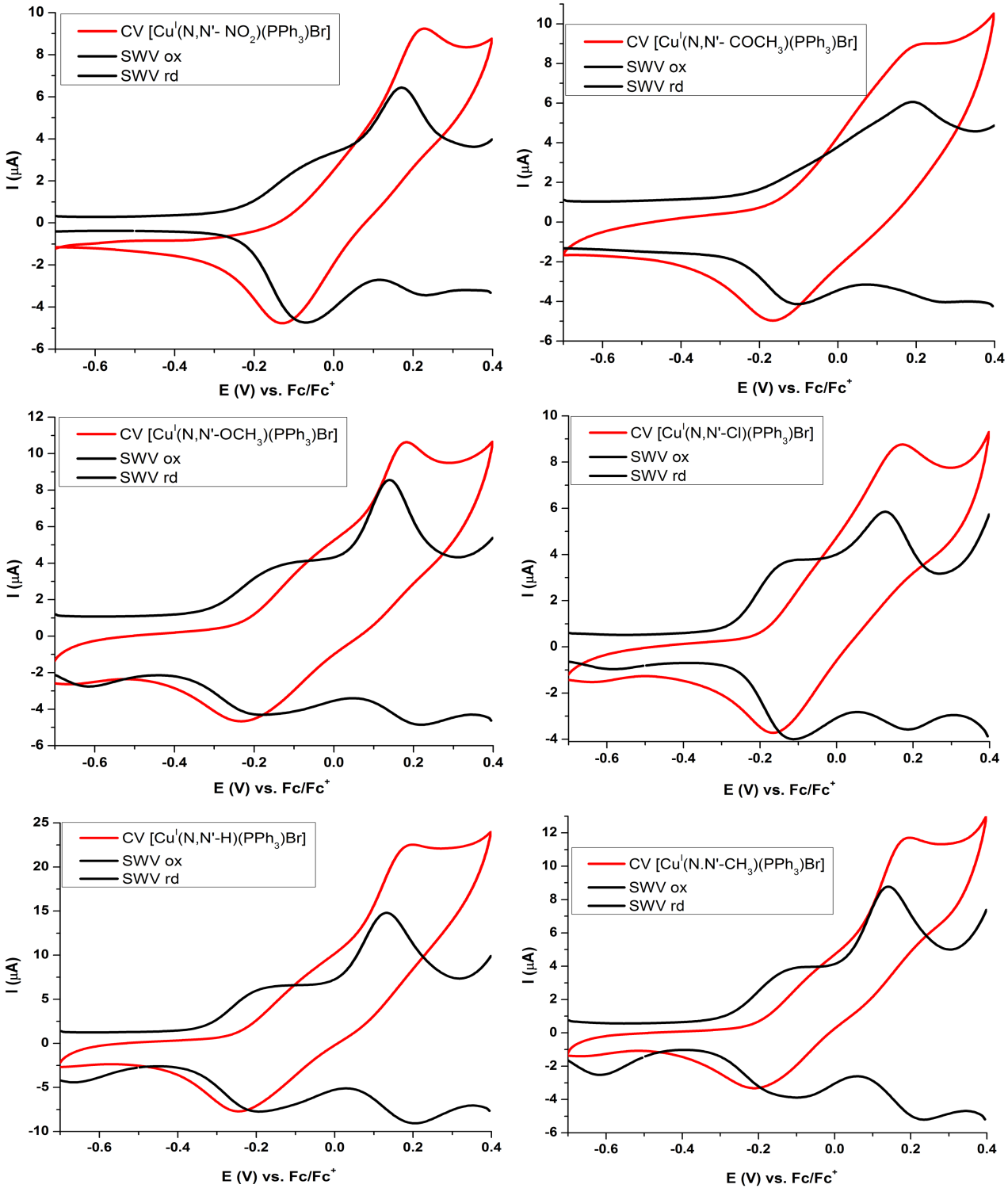
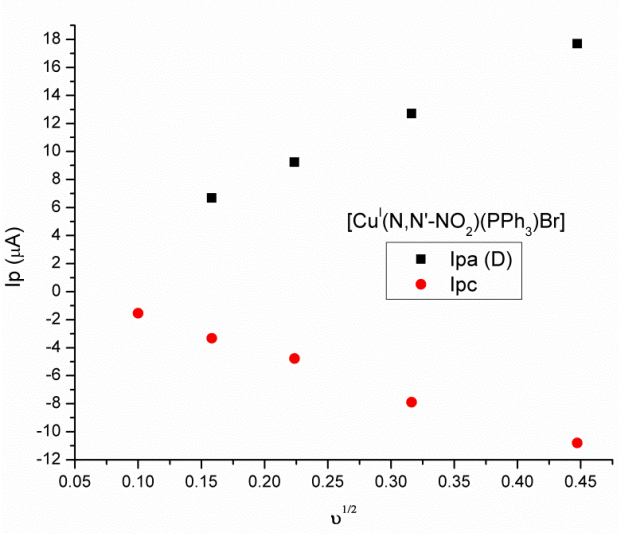
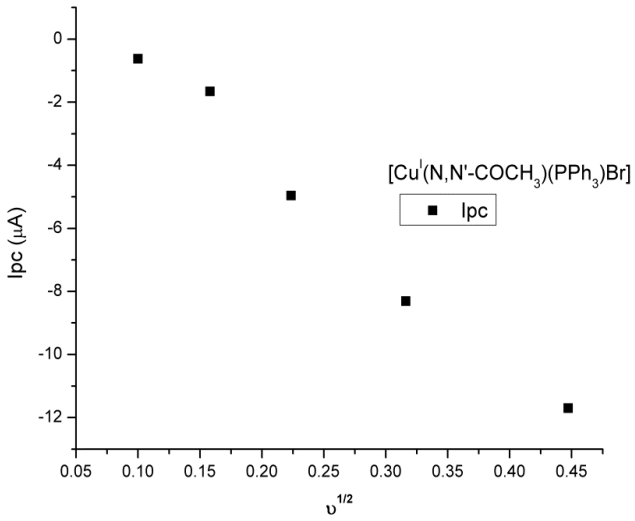
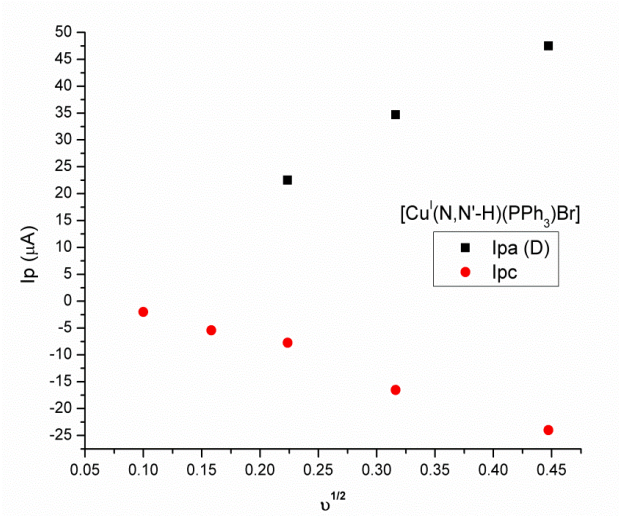
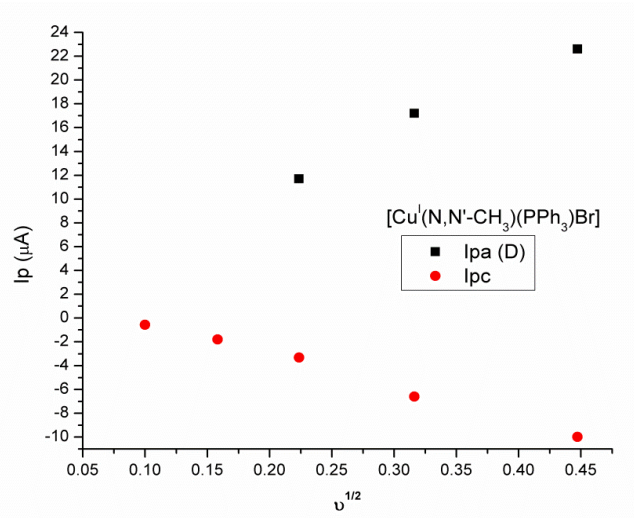


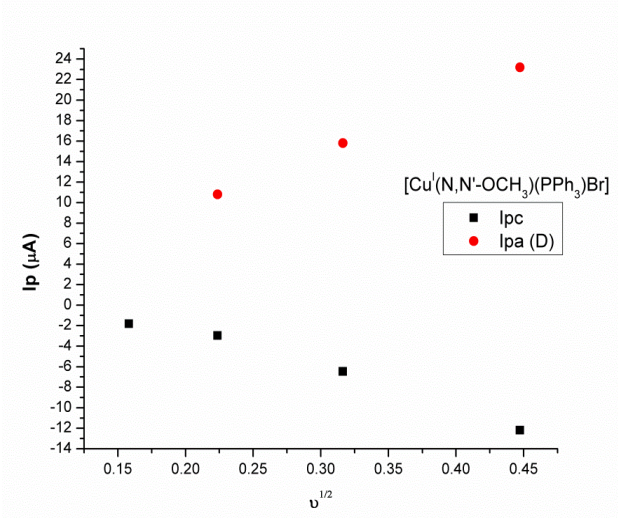
Figure SI15. Cyclic Voltammetry (red) and Square Wave Voltammetry (black) of complexes at 1 mM in CH_2Cl_2, scan rate 50 mV/s to CV and 15 Hz to SWV.

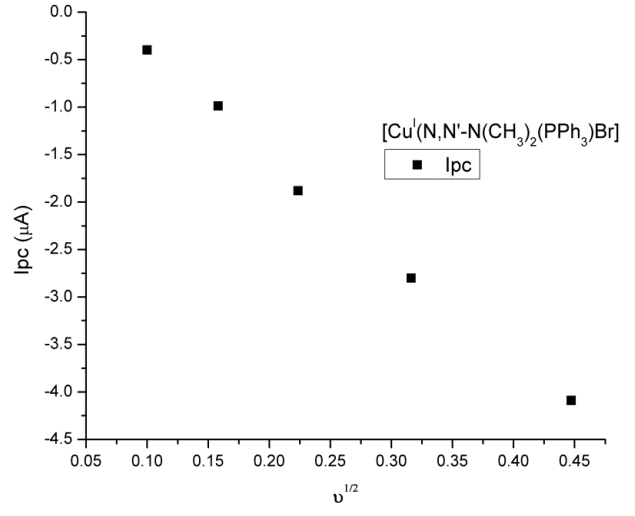

Ip (μA)
υ^1/2
[Cu^I(N,N'-NO2)(PPh3)Br]
Ipa (D)
Ipc


Ipc (μA)
υ^1/2
[Cu^I(N,N'-COCH3)(PPh3)Br]
Ipc


Ip (μA)
υ^1/2
[Cu^I(N,N'-H)(PPh3)Br]
Ipa (D)
Ipc


Ip (μA)
υ^1/2
[Cu^I(N,N'-CH3)(PPh3)Br]
Ipa (D)
Ipc


Ip (μA)
υ^1/2
[Cu^I(N,N'-OCH3)(PPh3)Br]
Ipc
Ipa (D)


Ipc (μA)
υ^1/2
[Cu^I(N,N'-N(CH3)2(PPh3)Br]
Ipc

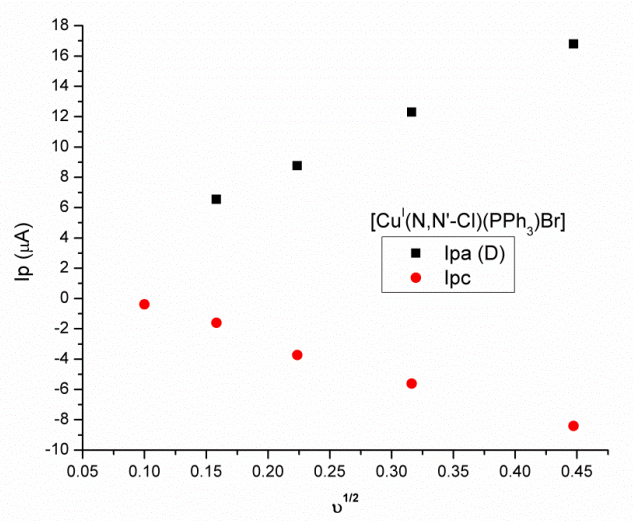


Figure SI16: Ip vs (scan rate)$^{1/2}$ from Cyclic voltammetry.

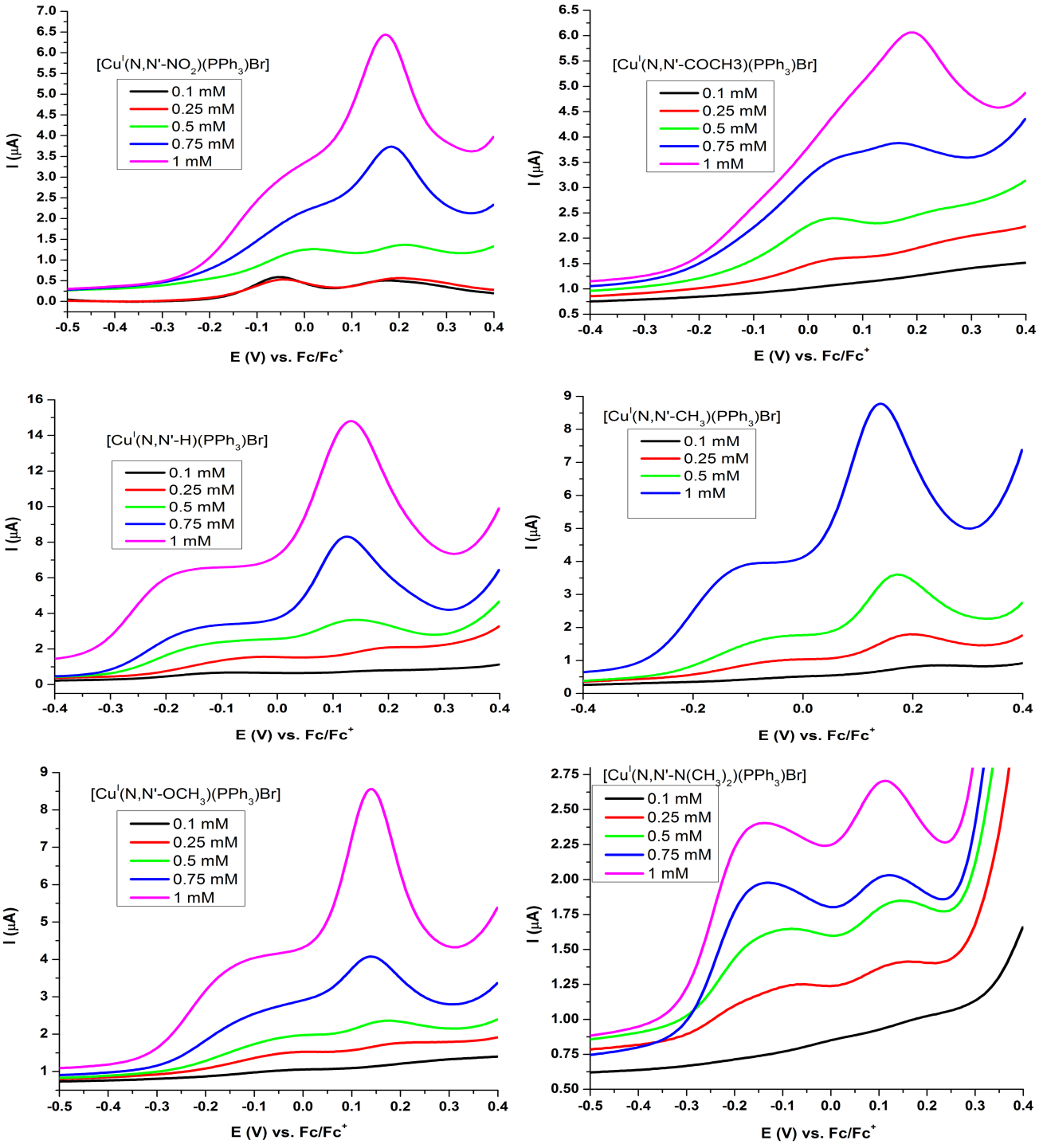


Figure SI17: SWV at different monomer concentrations in CH_2Cl_2, 15 Hz, 4 mV increasing potential.

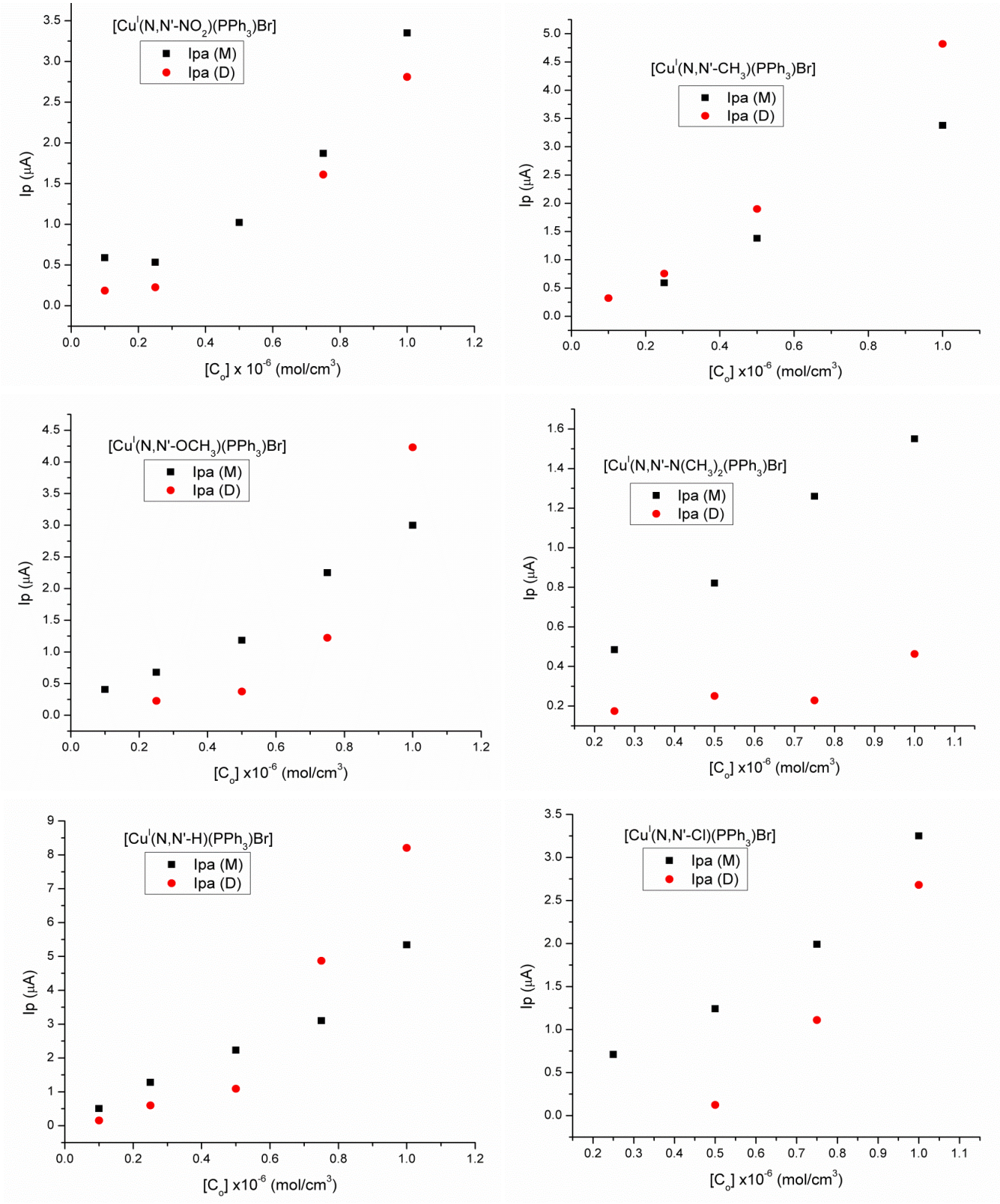


Figure SI18: Change in anodic peak current Ip (monomer (M) and dimer (D)) vs initial monomer concentration from SWV.

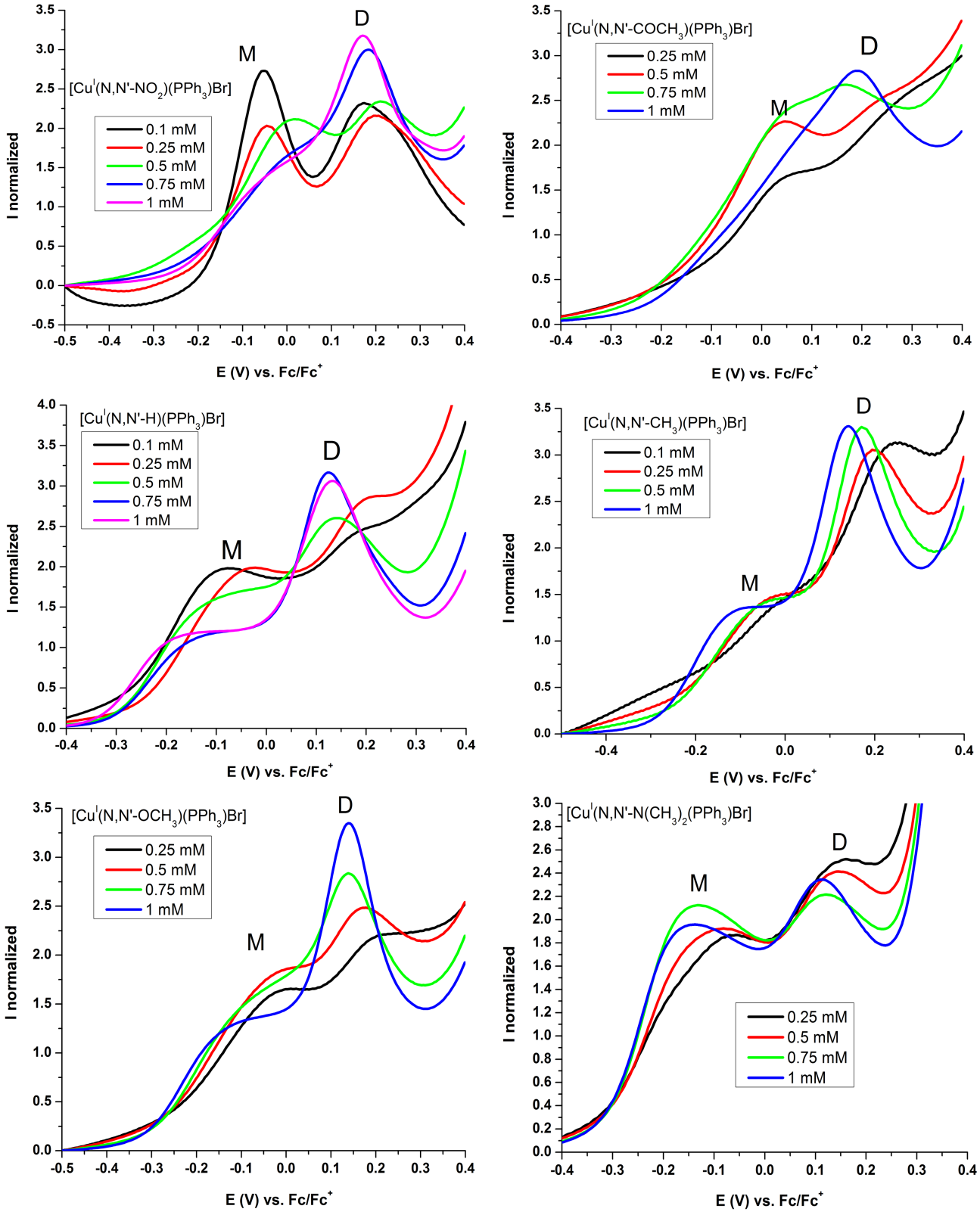


Figure SI19: SWV corrected by absolute area at different concentrations of monomer.

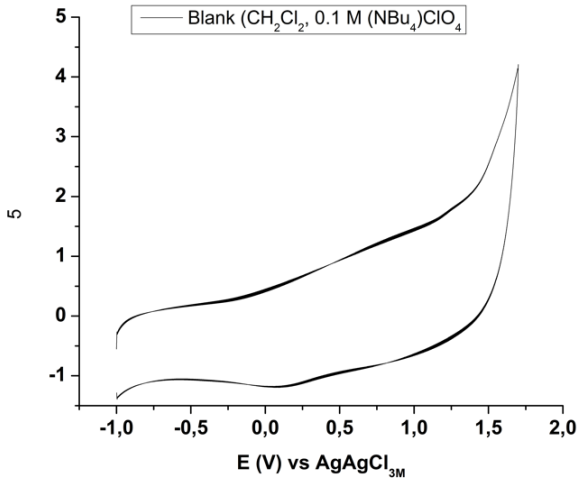


Figure SI20: Pt electrode blank, obtained under N_2, 0.1 M $[NBu_4]ClO_4$ in CH_2Cl_2 at 100 mV/s and 293 K.

The voltammetric profiles of the blanks indeed showed an oxidation process associated to residual water present in CH_2Cl_2 (approximately at 1.3 V (vs $Ag/AgCl_{sat}$)) under the experimental measurement conditions.

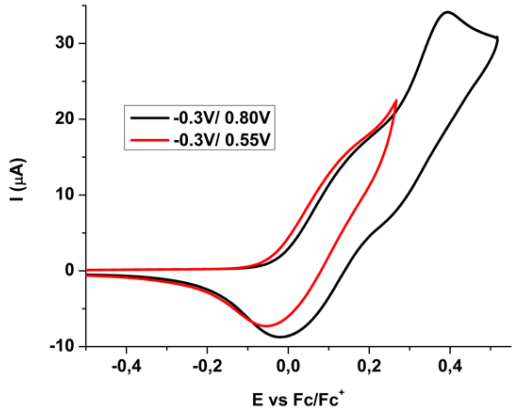


Figure SI21: Cyclic Voltammetry of isolated monomer couple (red), and monomer and dimmer (black), 5mM of $[Cu(N,N´-H)(PPh_3)Br]$ in CH_2Cl_2, 0.1 M of $[NBu_4]ClO_4$, Scan rate: 0.1 V/s.

For the $[Cu(N,N'-H)(PPh_3)Br]$ complex, a study was carried out by varying the potential window in order to isolate the coupling associated with the monomer. The results showed an undefined oxidation peak (shoulder 0.156 V) and a broad reduction peak (-0.051 V) (figure 1 red), with a ΔE peak of approximately 0.104 V, associated with an electrochemically irreversible process. The same figure shows (black) the complete profile with both oxidation processes coupled, evidencing the remarkable current increase in the reduction peak.

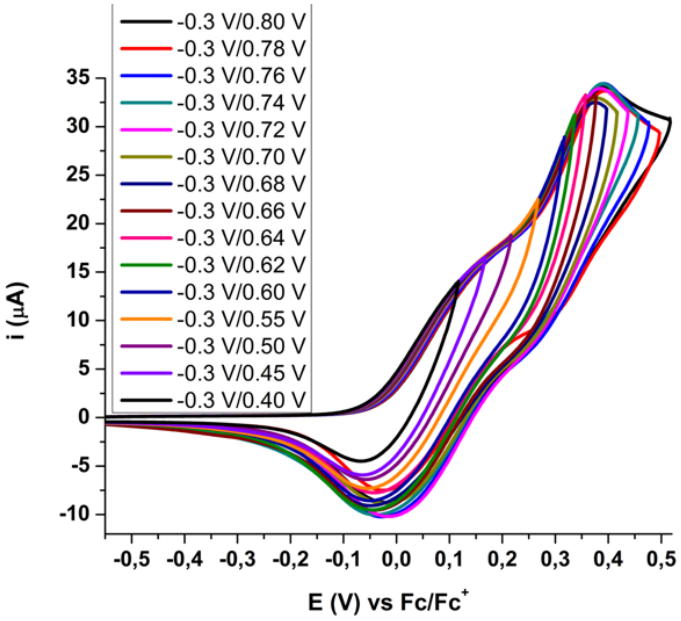


Figure SI22: Cyclic Voltammetry of 5mM solution of [Cu(N,N´-H)(PPh_3)Br] in CH_2Cl_2, 0.1 M of [NBu_4]ClO_4, Scan rate: 0.1 V/s with different potential windows.

In order to demonstrate that oxidation processes are associated with monomer/dimer equilibrium, variable potential window sweeps were performed (figure SI22), showing a remarkable decrease in the reduction peak current intensity as the potential window decreases. This decreasing dependence as the potential window decreases demonstrates a direct relationship between both oxidized species in dynamic equilibrium.