Electronic Supplementary Material (ESI) for Dalton Transactions.

Phosphate and polyphosphate anions recognition by a dinuclear copper(II) complex of an unsymmetrical squaramide

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Electronic Supplementary Information (ESI)

Table S1. Overall (β_i^H) and stepwise (K_i^H) protonation constants of the 2-aminoethylphosphonic acid (H_2aep) in aqueous solution at 298.2±0.1 K in 0.10±0.01 M KNO_3.

Equilibrium Reaction[a]	log β_i^H
$aep^{2-} + H^+ \rightleftarrows Haep^-$	11.056(2)
$aep^{2-} + 2\ H^+ \rightleftarrows H_2aep$	17.327(3)
	log K_i^H
$aep^{2-} + H^+ \rightleftarrows Haep^-$	11.056(2)
$Haep^- + H^+ \rightleftarrows H_2aep$	6.271(3)

Table S2. Overall ($\beta_{Cu_mH_hA}$) and stepwise ($K_{Cu_mH_hA}$) stability constants of the copper(II) complexes of the studied anions in aqueous solution at 298.2±0.1 K in 0.10±0.01 M KNO_3.

Equilibrium reaction[a]	PPi^{4-}	ATP^{4-}	ADP^{3-}	AMP^{2-}	PhP^{2-}	aep^{2-}
			log $\beta_{Cu_mH_hA}$			
$Cu^{2+} + H^+ + A^i \rightleftarrows [CuHA]^{3+i}$	13.56(6)	9.99(2)	8.76(9)			13.86(4)
$Cu^{2+} + A^i \rightleftarrows [CuA]^{2+i}$	7.46(9)	6.40(1)	5.91(1)	3.07(6)	2.77(3)	8.53(1)
$Cu^{2+} + A^i \rightleftarrows [CuAH_{-1}]^{1+i} + H^+$	−1.5(1)	−0.14(1)	−0.59(1)			1.20(2)
$Cu^{2+} + A^i \rightleftarrows [CuAH_{-2}]^i + 2\ H^+$		−7.33(1)	−8.86(2)			−7.8(8)
$Cu^{2+} + A^i \rightleftarrows [CuAH_{-3}]^{i-1} + 3\ H^+$		−16.67(6)				
			log $K_{Cu_mH_hA}$			
$Cu^{2+} + HA^{i+1} \rightleftarrows [CuHA]^{3+i}$	6.10(8)	3.59(2)	2.85(5)			5.33(3)
$Cu^{2+} + A^i \rightleftarrows [CuA]^{2+i}$	7.46(9)	6.40(1)	5.91(1)	3.07(6)	2.77(3)[l]	8.53(1)
$[CuAH_{-1}]^{1+i} + H^+ \rightleftarrows [CuA]^{2+i}$	8.96(5)	6.54(1)	6.50(1)			7.33(1)
$[CuAH_{-2}]^i + H^+ \rightleftarrows [CuAH_{-1}]^{1+i}$		7.19(1)	8.27(2)			9.0(4)
$[CuAH_{-3}]^{i-1} + H^+ \rightleftarrows [CuAH_{-2}]^i$		9.34(4)				

[a] A denotes the anion in general; i denotes the charge of the anion which can take the values −2, −3, or −4; values in parenthesis are standard deviations in the last significant figures.

Table S3. Overall association constants (β_{H_hLA}) of PPi^{4-} and aep^{2-} with protonated forms of the **L** in aqueous solution at 298.2±0.1 K in 0.10±0.01 M KNO_3.

Equilibrium reaction[a]	PPi^{4-}	aep^{2-}
$5\ H^+ + L + A^i \rightleftarrows H_5LA^{5+i}$	32.96(3)	34.92(9)
$4\ H^+ + L + A^i \rightleftarrows H_4LA^{4+i}$	30.07(3)	32.53(4)
$3\ H^+ + L + A^i \rightleftarrows H_3LA^{3+i}$	26.56(2)	28.85(5)
$2\ H^+ + L + A^i \rightleftarrows H_2LA^{2+i}$	20.24(2)	22.31(7)
$H^+ + L + A^i \rightleftarrows HLA^{1+i}$	11.34(5)	13.12(9)
$L + A^i \rightleftarrows LA^i$	–	2.09(9)

[a] A denotes the anion; i denotes the charge of A (−2 or −4); values in parenthesis are standard deviations in the last significant figures.

Table S4. Overall ($\beta_{Cu_mH_hLA}$) association constants of the copper(II) complexes of **L** with the anions under study at 298.2±0.1 K and I = 0.10±0.01 M KNO_3 in aqueous solution.

Equilibrium reaction[a]	$\beta_{Cu_mH_hLA}$
$2\ Cu^{2+} + H^+ + \mathbf{L} + PhP^{2-} \rightleftarrows [Cu_2H\mathbf{L}(PhP)]^{3+}$	22.0(1)
$2\ Cu^{2+} + \mathbf{L} + PhP^{2-} \rightleftarrows [Cu_2\mathbf{L}(PhP)]^{2+}$	18.57(3)
$2\ Cu^{2+} + \mathbf{L} + PhP^{2-} \rightleftarrows [Cu_2\mathbf{L}H_{-1}(PhP)]^{+} + H^+$	12.69(4)
$2\ Cu^{2+} + 3\ H^+ + \mathbf{L} + aep^{2-} \rightleftarrows [Cu_2H_3\mathbf{L}(aep)]^{5+}$	40.51(3)
$2\ Cu^{2+} + 2\ H^+ + \mathbf{L} + aep^{2-} \rightleftarrows [Cu_2H_2\mathbf{L}(aep)]^{4+}$	36.50(2)
$2\ Cu^{2+} + H^+ + \mathbf{L} + aep^{2-} \rightleftarrows [Cu_2H\mathbf{L}(aep)]^{3+}$	30.97(3)
$2\ Cu^{2+} + \mathbf{L} + aep^{2-} \rightleftarrows [Cu_2\mathbf{L}(aep)]^{2+}$	25.01(2)
$2\ Cu^{2+} + \mathbf{L} + aep^{2-} \rightleftarrows [Cu_2\mathbf{L}H_{-1}(aep)]^{+} + H^+$	17.38(2)
$2\ Cu^{2+} + H^+ + \mathbf{L} + AMP^{2-} \rightleftarrows [Cu_2H\mathbf{L}(AMP)]^{4+}$	23.28(3)
$2\ Cu^{2+} + \mathbf{L} + AMP^{2-} \rightleftarrows [Cu_2\mathbf{L}(AMP)]^{3+}$	19.37(1)
$2\ Cu^{2+} + \mathbf{L} + AMP^{2-} \rightleftarrows [Cu_2\mathbf{L}H_{-1}(AMP)]^{2+} + H^+$	13.42(2)
$2\ Cu^{2+} + \mathbf{L} + AMP^{2-} \rightleftarrows [Cu_2\mathbf{L}H_{-2}(AMP)]^{+} + 2\ H^+$	5.79(4)
$2\ Cu^{2+} + 2\ H^+ + \mathbf{L} + ADP^{3-} \rightleftarrows [Cu_2H_2\mathbf{L}(ADP)]^{3+}$	27.35(6)
$2\ Cu^{2+} + H^+ + \mathbf{L} + ADP^{3-} \rightleftarrows [Cu_2H\mathbf{L}(ADP)]^{2+}$	23.89(7)
$2\ Cu^{2+} + \mathbf{L} + ADP^{3-} \rightleftarrows [Cu_2\mathbf{L}(ADP)]^{+}$	19.75(9)
$2\ Cu^{2+} + \mathbf{L} + ADP^{3-} \rightleftarrows [Cu_2\mathbf{L}H_{-1}(ADP)] + H^+$	14.63(3)
$2\ Cu^{2+} + H^+ + \mathbf{L} + ATP^{4-} \rightleftarrows [Cu_2H\mathbf{L}(ATP)]^{+}$	25.13(6)
$2\ Cu^{2+} + \mathbf{L} + ATP^{4-} \rightleftarrows [Cu_2\mathbf{L}(ATP)]$	21.60(3)
$2\ Cu^{2+} + \mathbf{L} + ATP^{4-} \rightleftarrows [Cu_2\mathbf{L}H_{-1}(ATP)]^{-} + H^+$	16.49(2)
$2\ Cu^{2+} + \mathbf{L} + ATP^{4-} \rightleftarrows [Cu_2\mathbf{L}H_{-2}(ATP)]^{2-} + 2\ H^+$	7.89(4)
$2\ Cu^{2+} + 3\ H^+ + \mathbf{L} + PPi^{4-} \rightleftarrows [Cu_2H_3\mathbf{L}(PPi)]^{3+}$	35.80(3)
$2\ Cu^{2+} + 2\ H^+ + \mathbf{L} + PPi^{4-} \rightleftarrows [Cu_2H_2\mathbf{L}(PPi)]^{2+}$	32.11(5)
$2\ Cu^{2+} + H^+ + \mathbf{L} + PPi^{4-} \rightleftarrows [Cu_2H\mathbf{L}(PPi)]^{+}$	26.95(9)
$2\ Cu^{2+} + \mathbf{L} + PPi^{4-} \rightleftarrows [Cu_2\mathbf{L}(PPi)]$	22.48(5)
$2\ Cu^{2+} + \mathbf{L} + PPi^{4-} \rightleftarrows [Cu_2\mathbf{L}H_{-1}(PPi)]^{-} + H^+$	16.82(2)
$2\ Cu^{2+} + \mathbf{L} + PPi^{4-} \rightleftarrows [Cu_2\mathbf{L}H_{-2}(PPi)]^{2-} + 2H^+$	8.95(4)

[a] Values in parenthesis are standard deviations in the last significant figures; L denotes the ligand and A the anion in general.

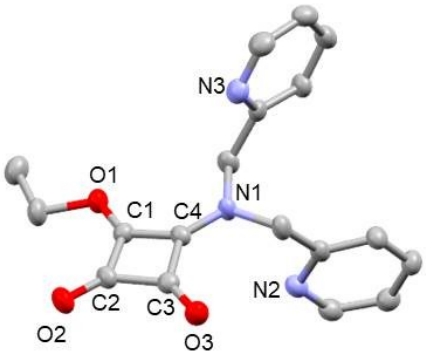

Fig. S1. View of the crystal structure of **smdpa** determined from single crystal X-ray diffraction data. Hydrogen atoms bound to carbon atoms are omitted for clarity. The ORTEP plots are at 50% probability level.

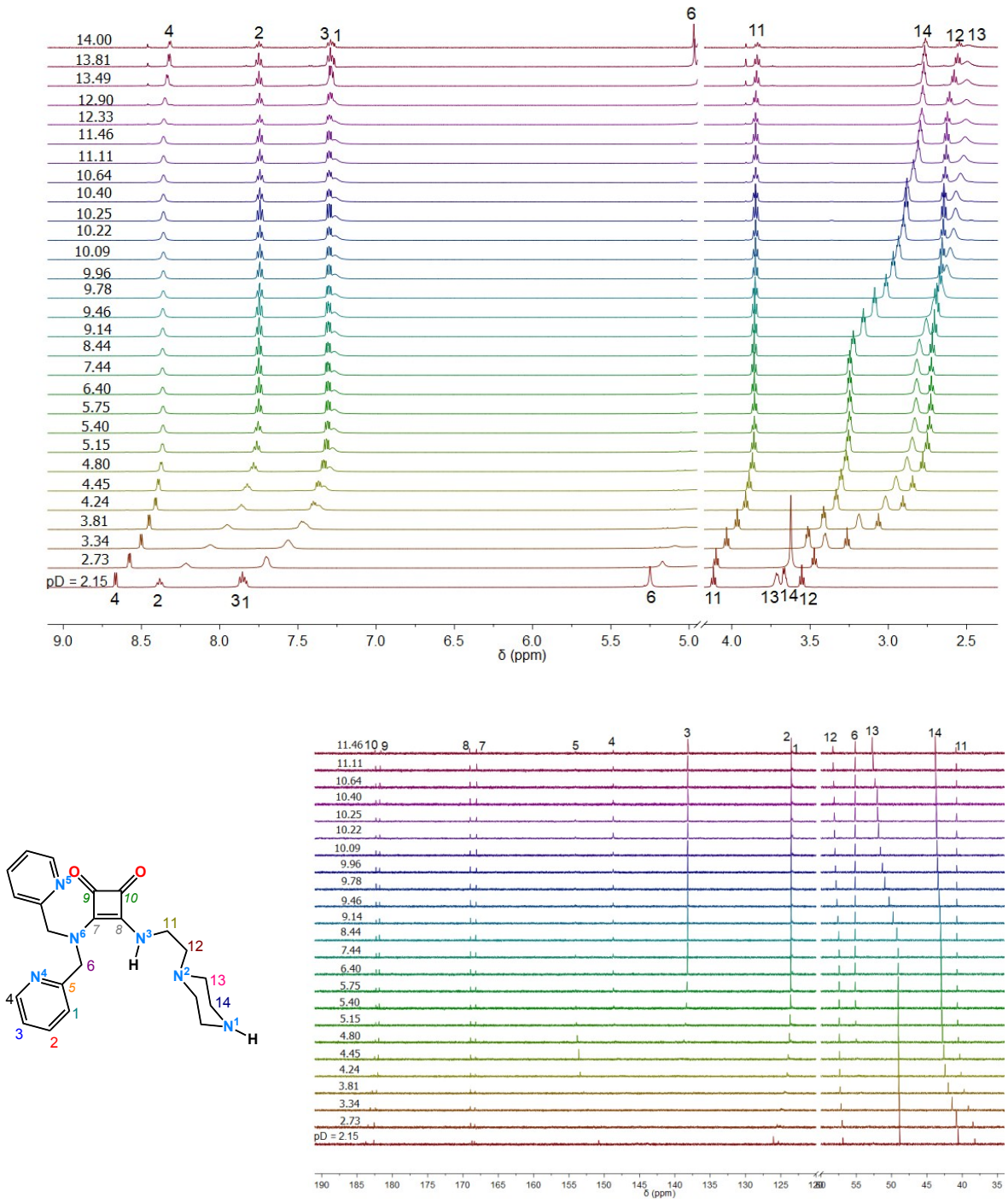

Fig. S2. The experimental chemical shifts at different pD values following the titration of L with DCl or NaOD in D_2O at 298.2 K. The ^{1}H (top), the ^{13}C (bottom) NMR spectra and the structure of the compound with numbering of atoms (bottom).

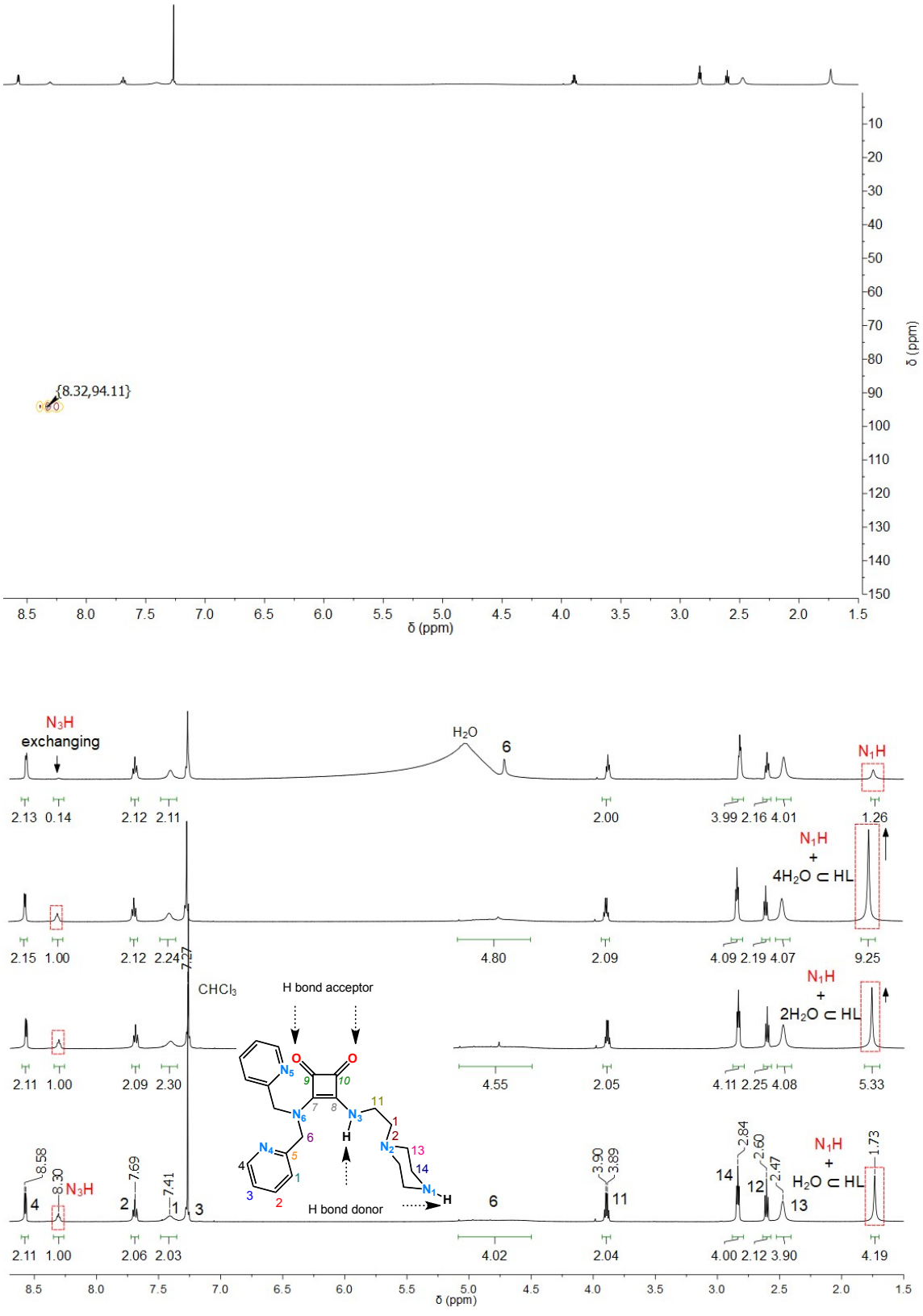

Fig. S3. ^{1}H-^{15}N HSQC spectrum of **L** in $CDCl_3$ (top) and the changes observed in the ^{1}H NMR experimental chemical shifts also in $CDCl_3$ upon addition of increasing amounts of water at 298.2 K (bottom).

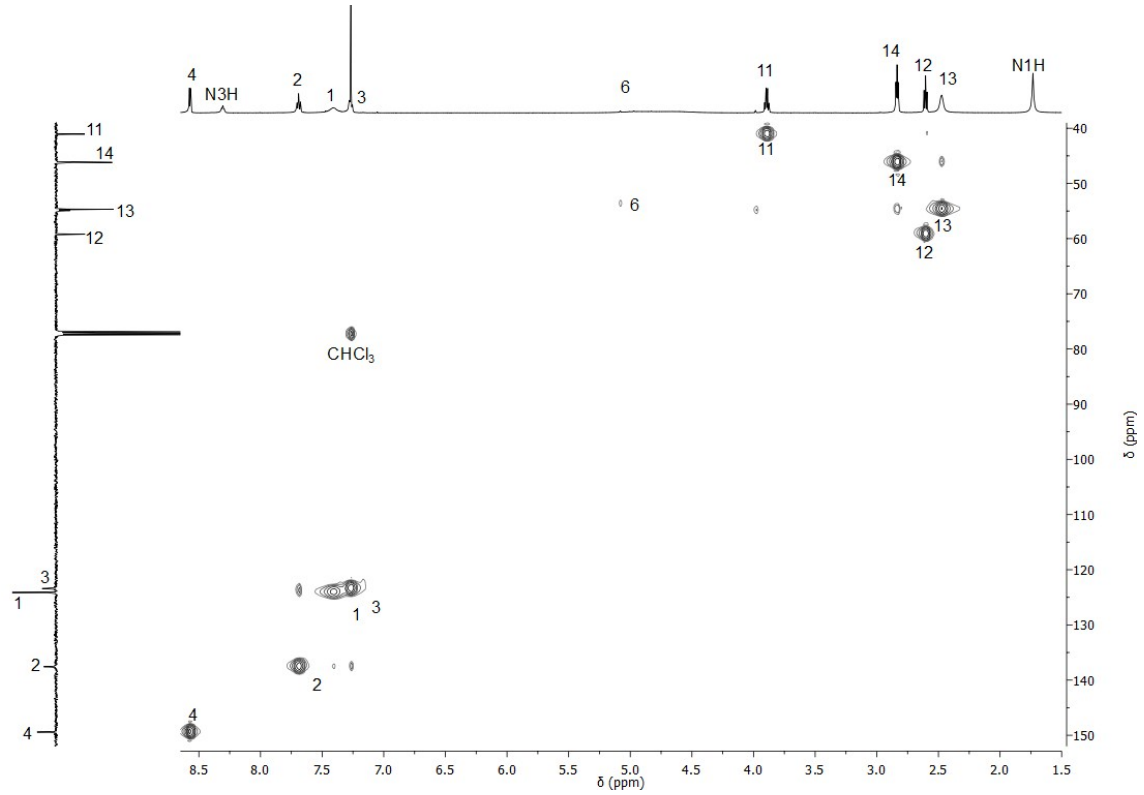

Fig. S4. HSQC spectrum of **L** in $CDCl_3$.

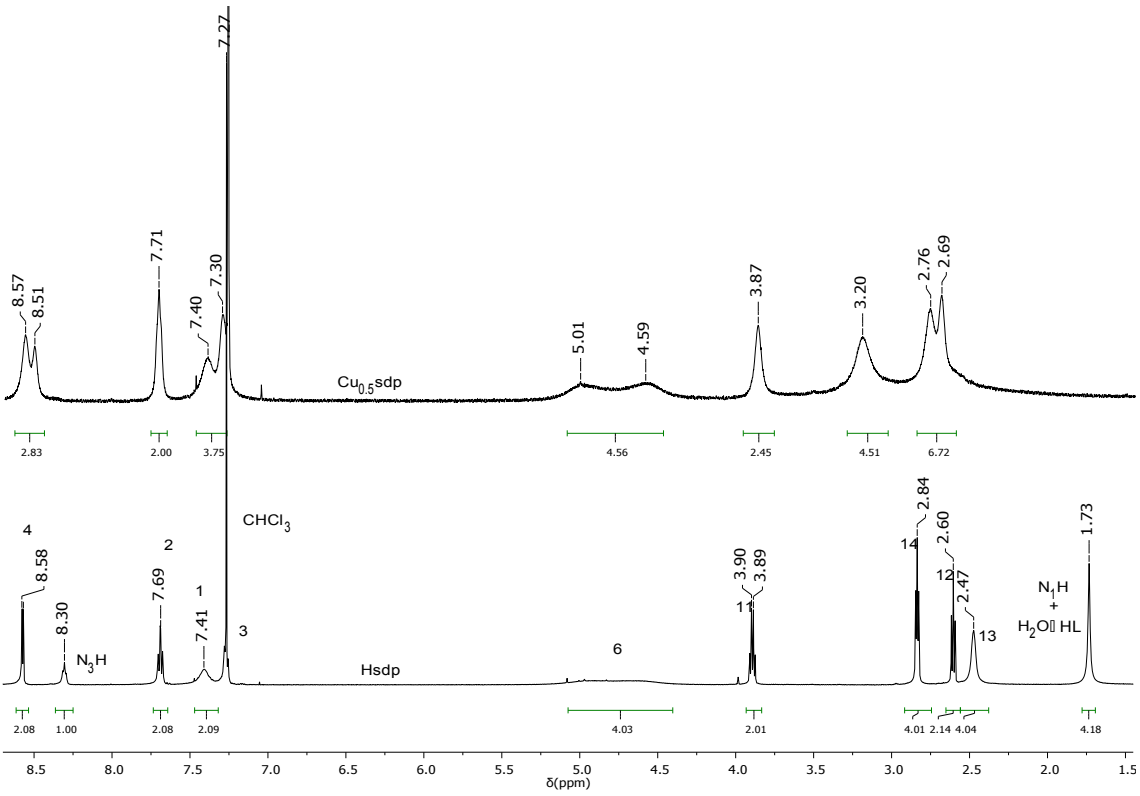

Fig. S5. ^1H NMR spectra of **L** and in the presence of 0.5 equiv. of copper(II) in $CDCl_3$.

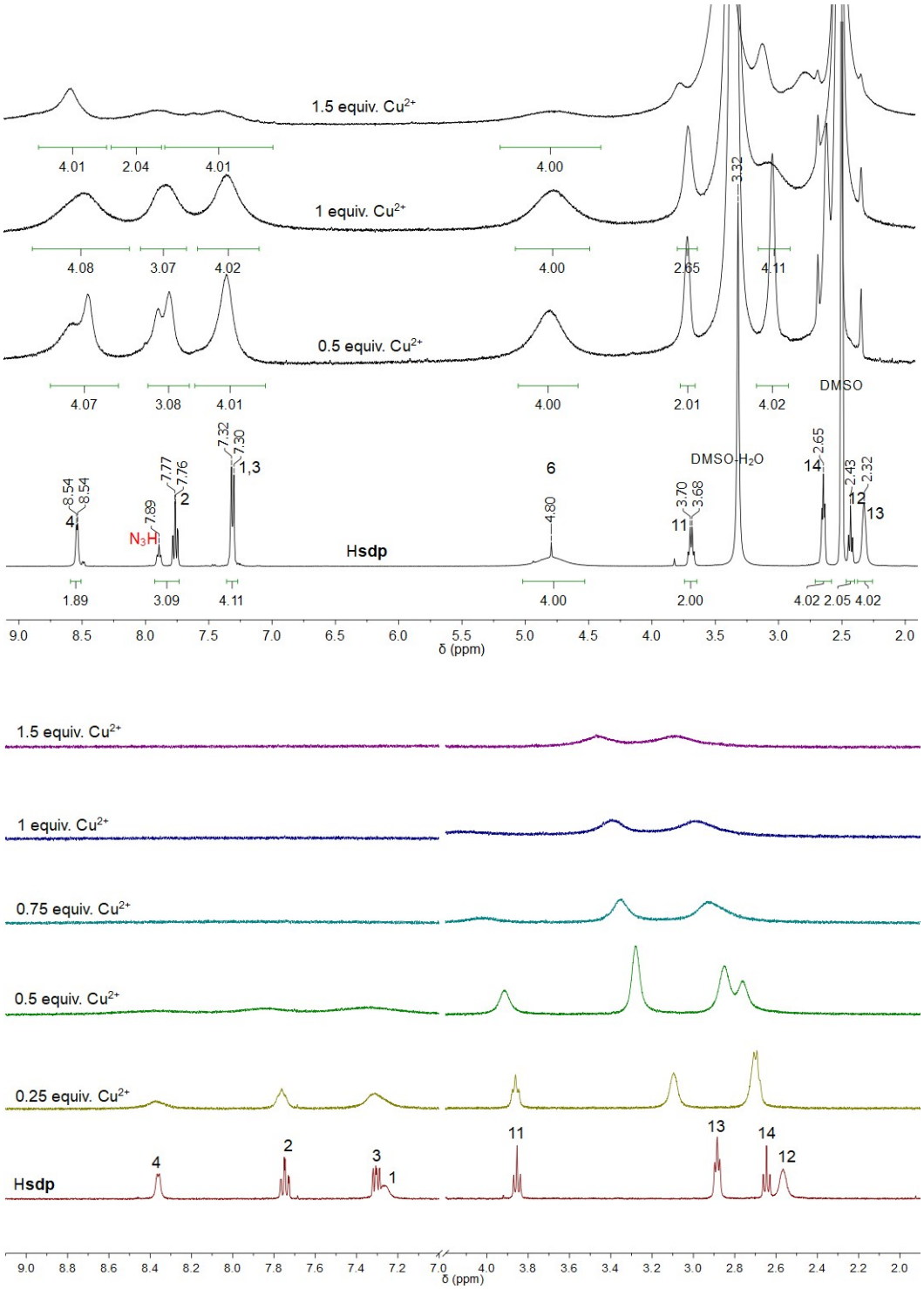

Fig. S6. ^{1}H NMR experimental chemical shifts of **L** with increasing amounts of Cu^{2+} cation, in DMSO-d_6 at 298.2 K (top spectra); and in H_2O/D_2O 9:1 v/v at pH 7.4 (bottom spectra).

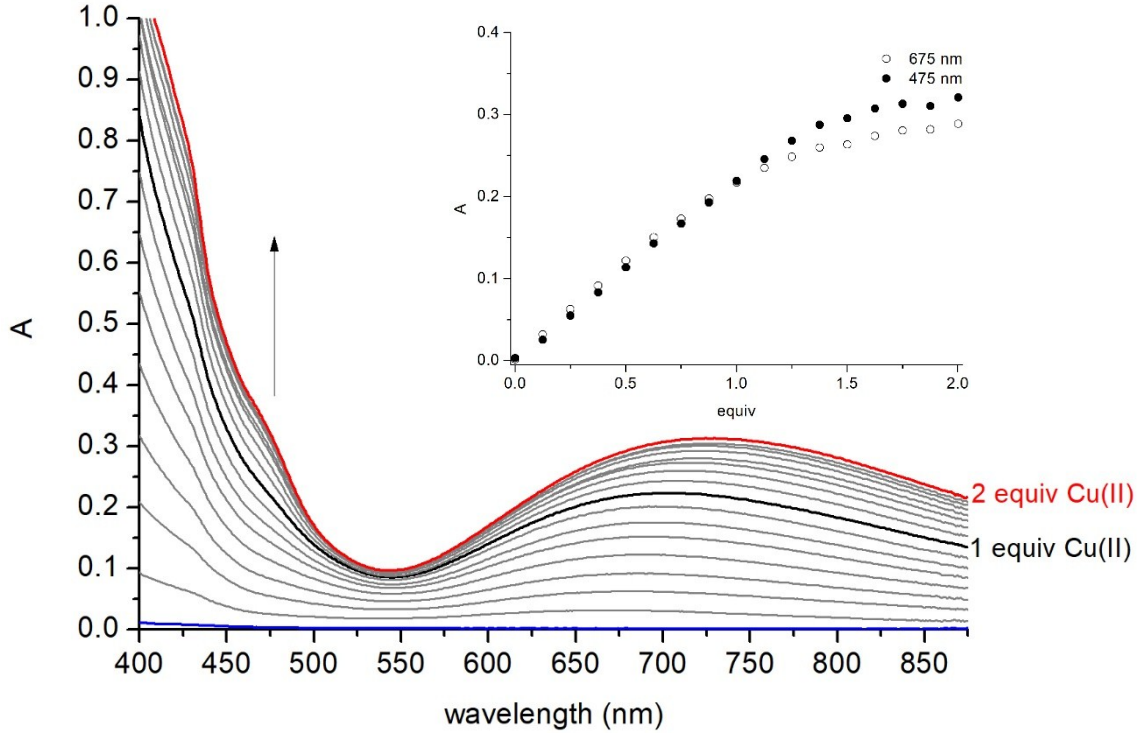

Fig. S7. Vis batch titration of **L** (2.89×10^{-5} M) with $Cu(NO_3)_2$ in buffered aqueous solution ([MOPS] = 2.5×10^{-2} M, pH = 7.4). In the inset is shown the spectral variations at the two selected wavelengths.

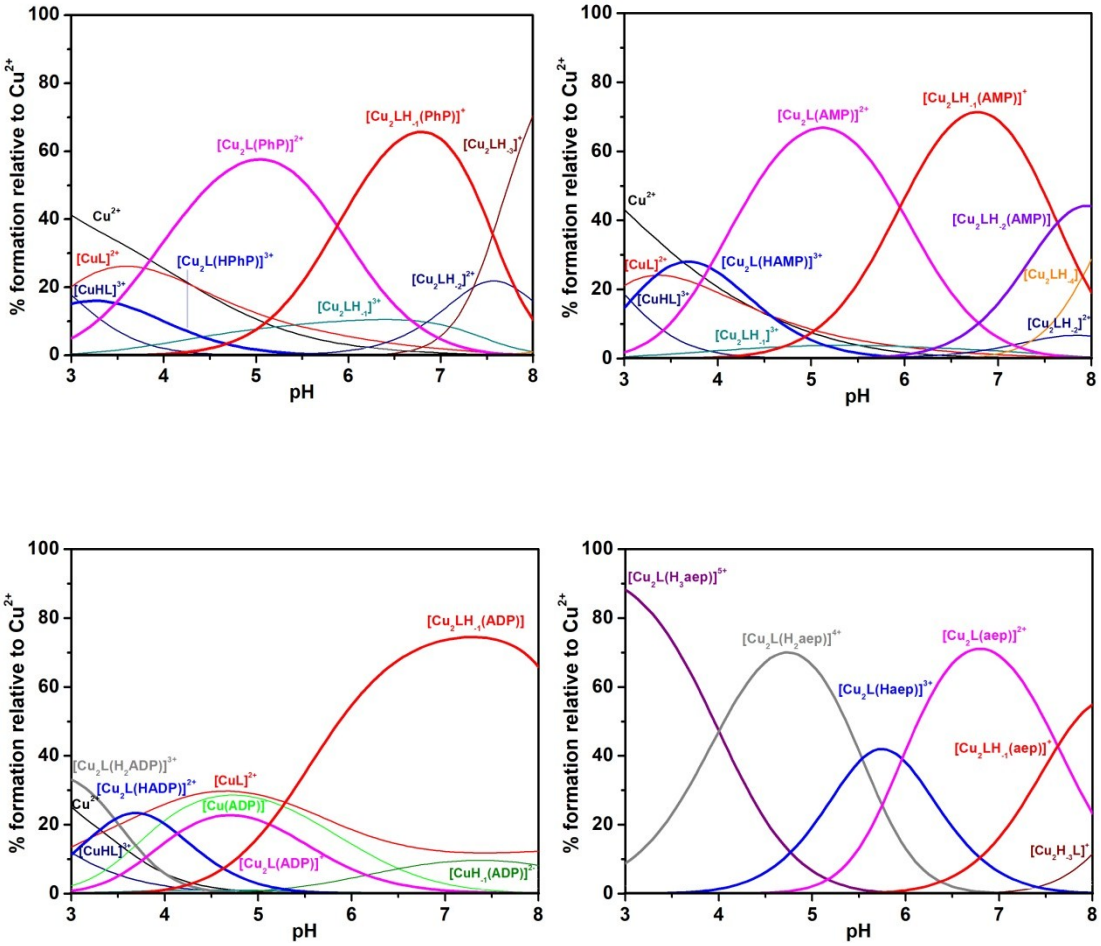

Fig. S8. Species distribution diagrams calculated for the cascade species formed between the copper(II) complexes of **L** and PhP^{2-}, AMP^{2-}, aep^{2-} and ADP^{3-} anions at 2:1:3 $Cu^{2+}/L/A^{i-}$ stoichiometry. $C_{Cu} = 2\ C_L = 1/3\ C_A = 2.0\times10^{-3}$ M; L denotes the ligand and A the anion.

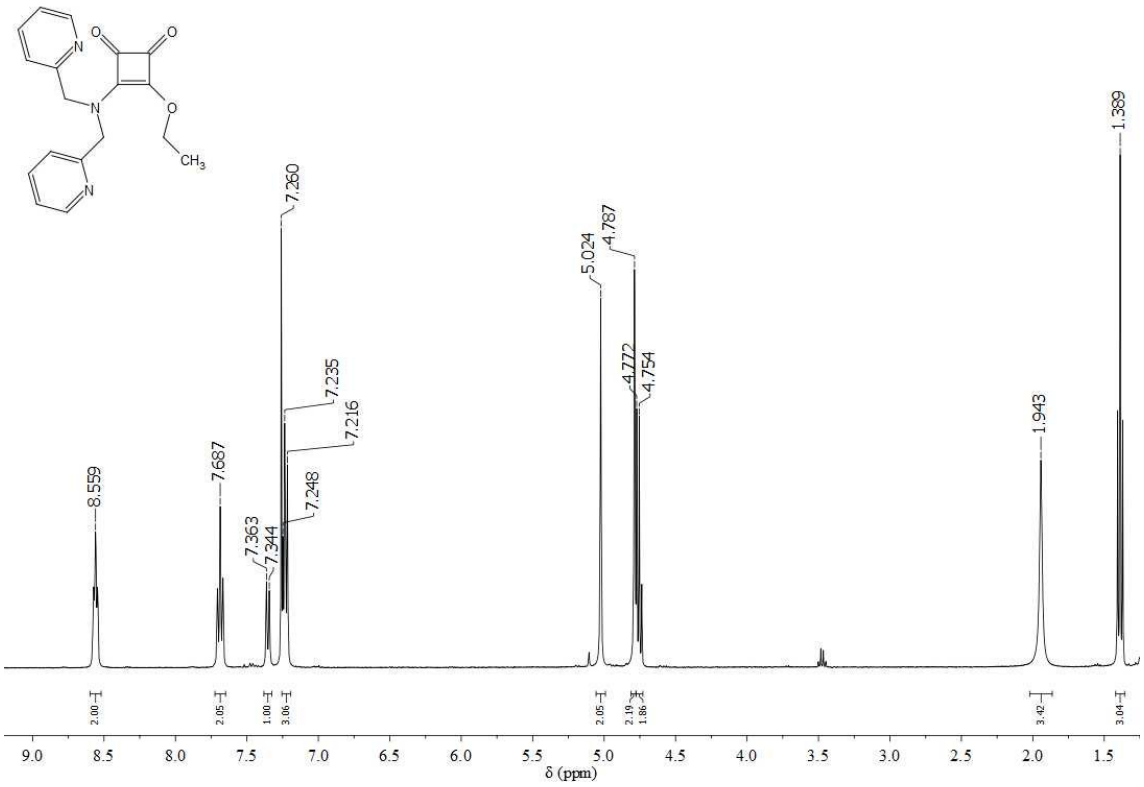

Fig. S9. ^{1}H NMR spectrum of **smdpa** in $CDCl_3$.

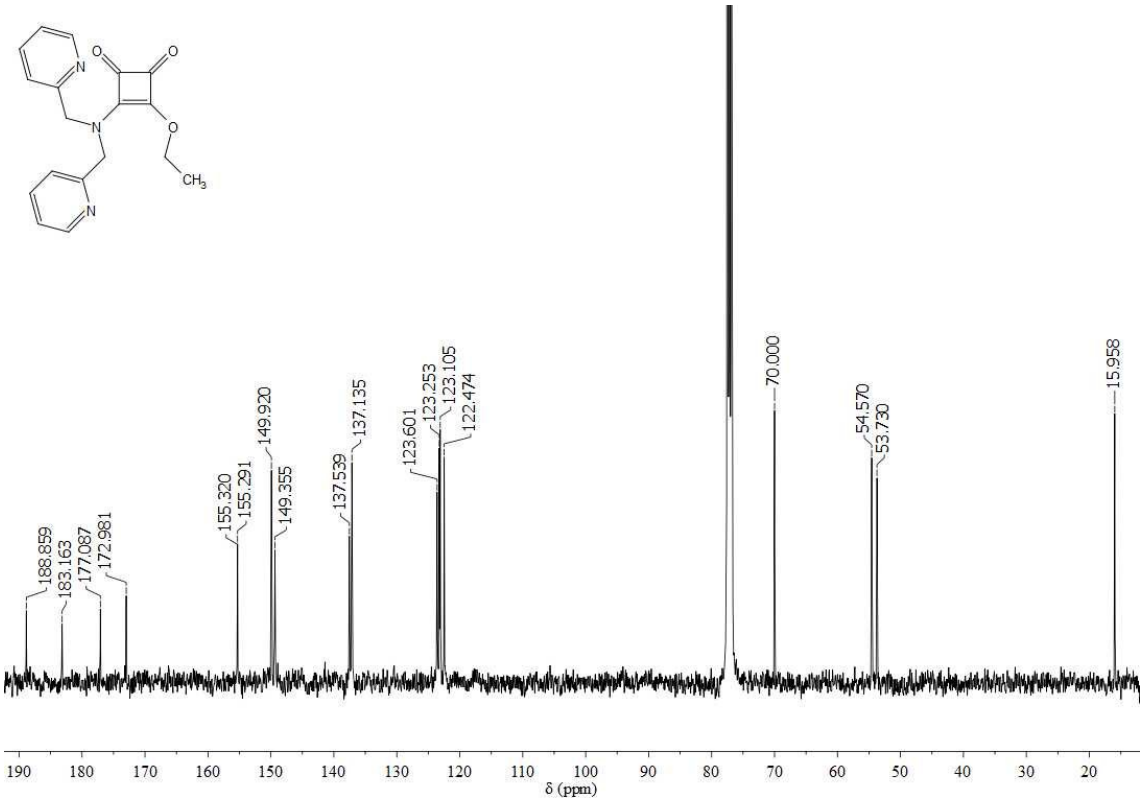

Fig. S10. ^{13}C NMR spectrum of **smdpa** in $CDCl_3$.

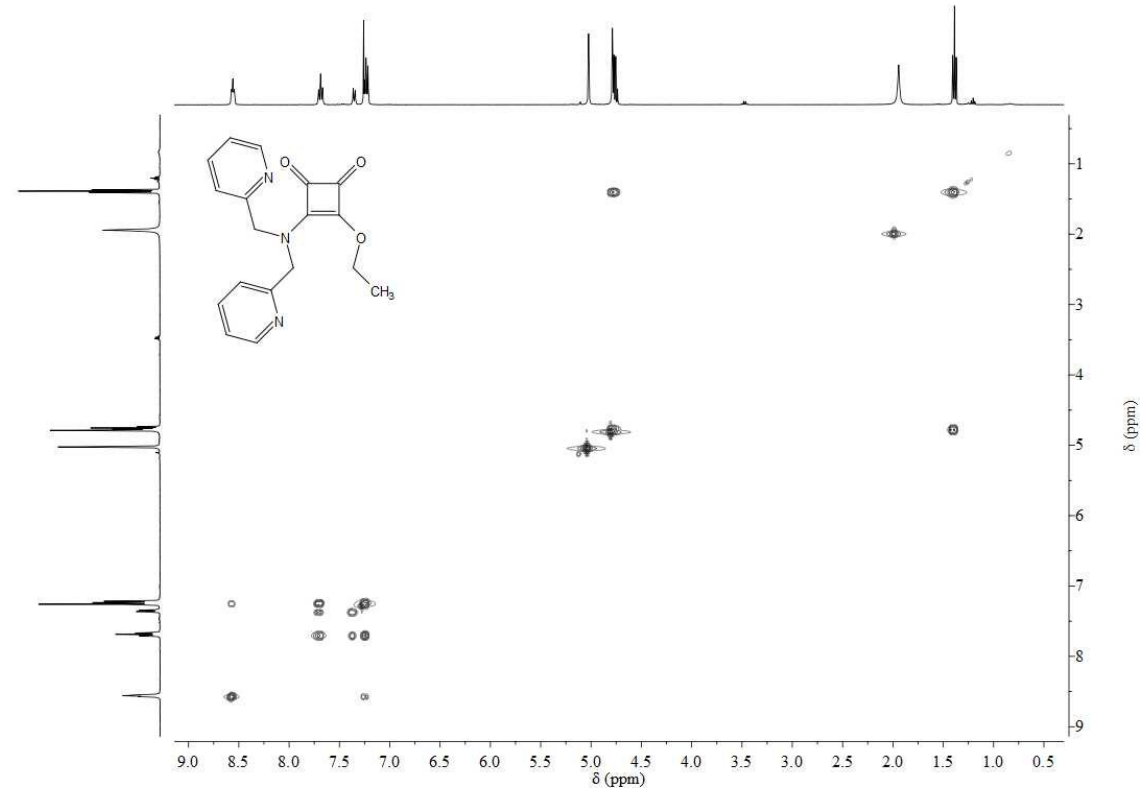

Fig. S11. COSY spectrum of **smdpa** in $CDCl_3$.

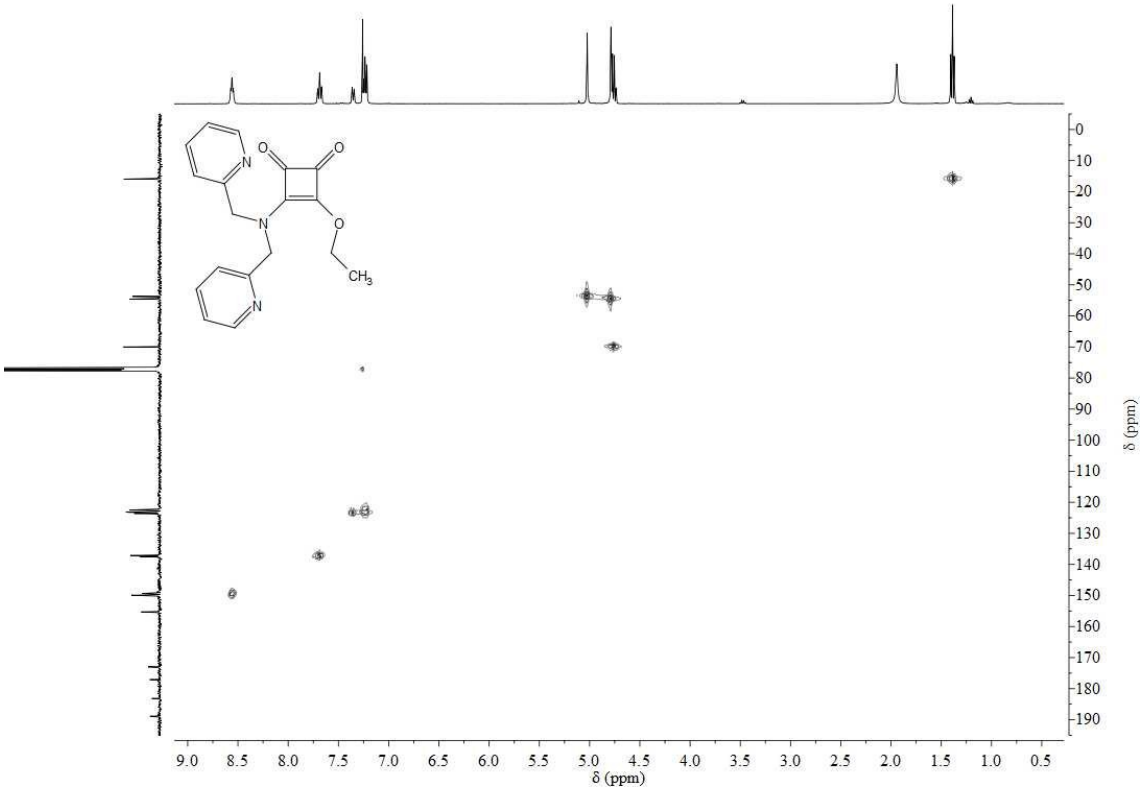

Fig. S12. HMQC spectrum of **smdpa** in $CDCl_3$.

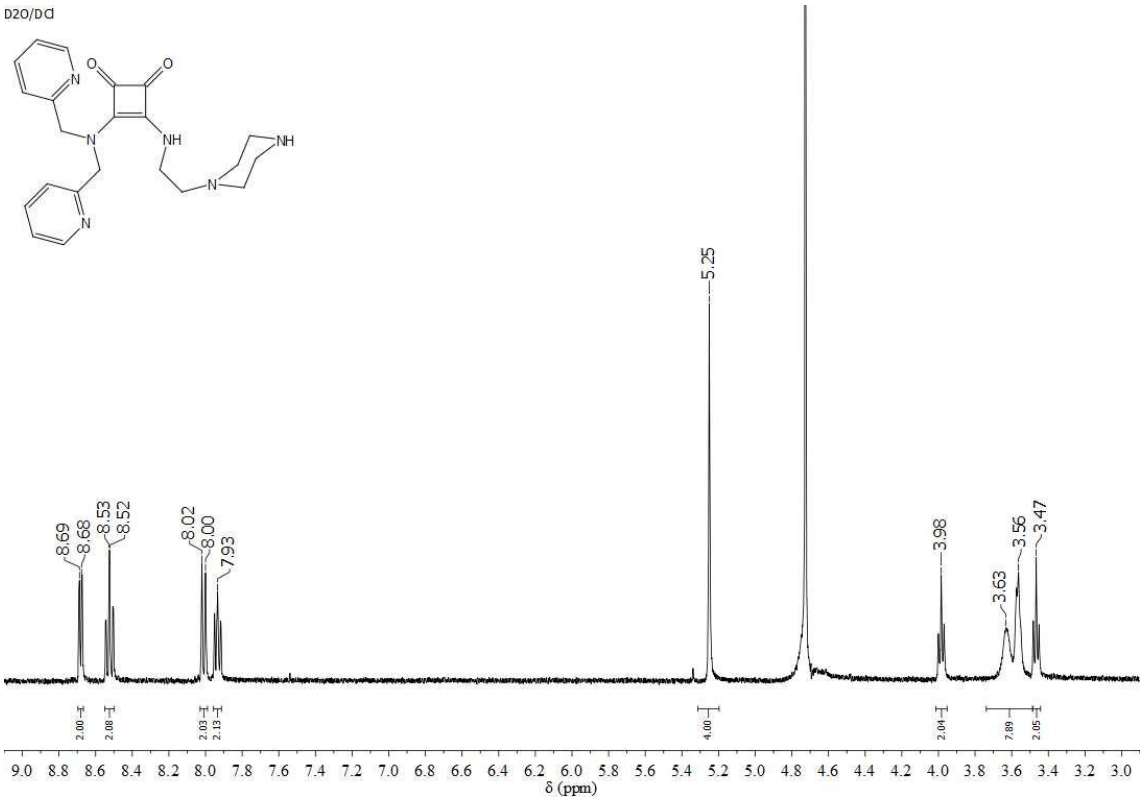

Fig. S13. ^{1}H NMR spectrum of **L** in D_2O/DCl at pD < 1.

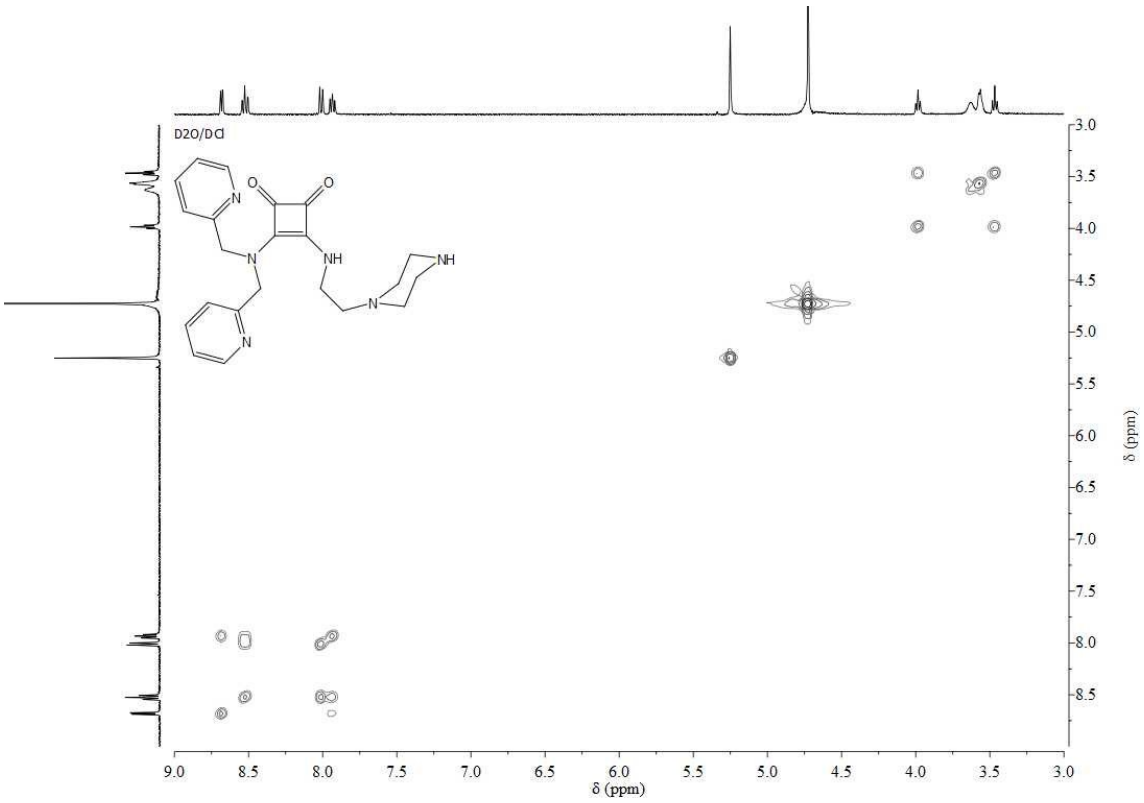

Fig. S14. COSY spectrum of **L** in D_2O/DCl at pD < 1.

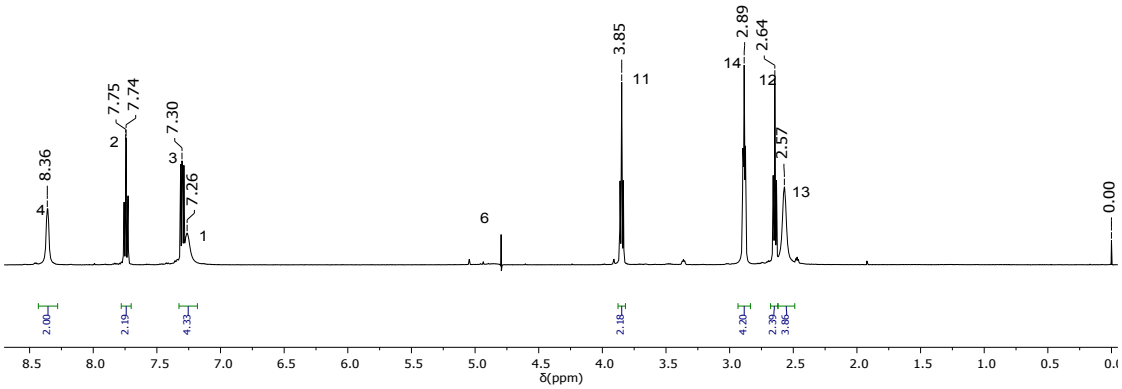

Fig. S15. ^{1}H NMR spectrum of **L** in D_2O at pD 10.24.

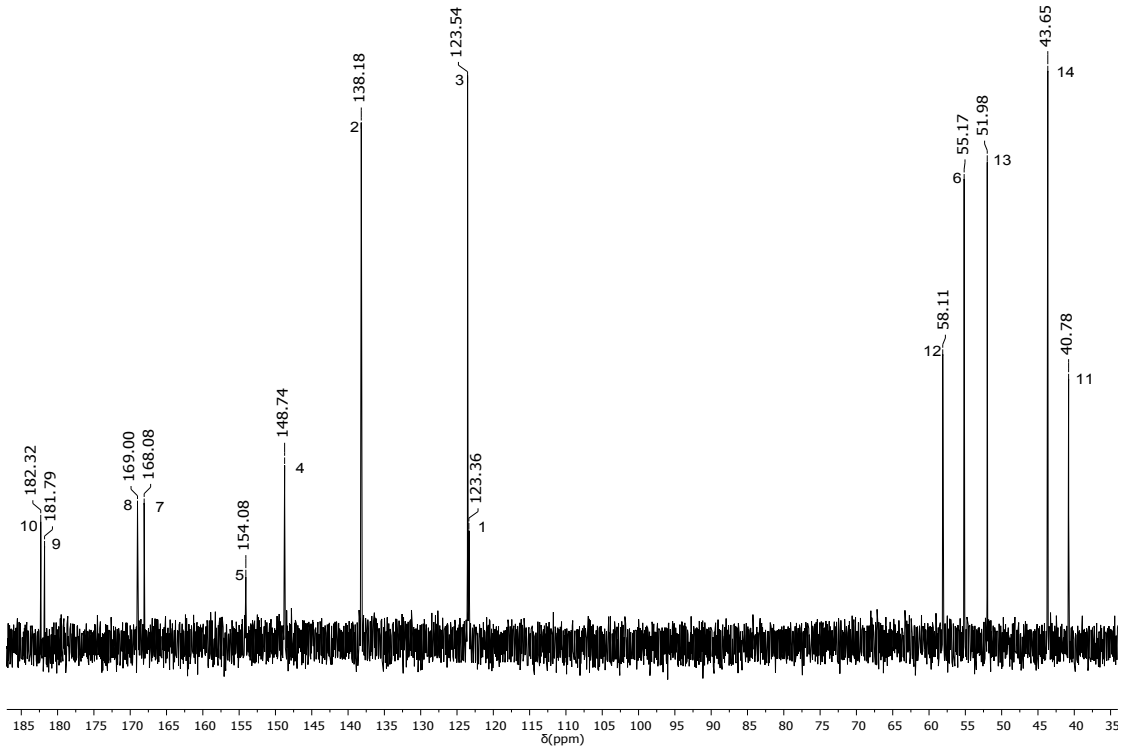

Fig. S16. ^{13}C NMR spectrum of **L** in D_2O at pD 10.24.

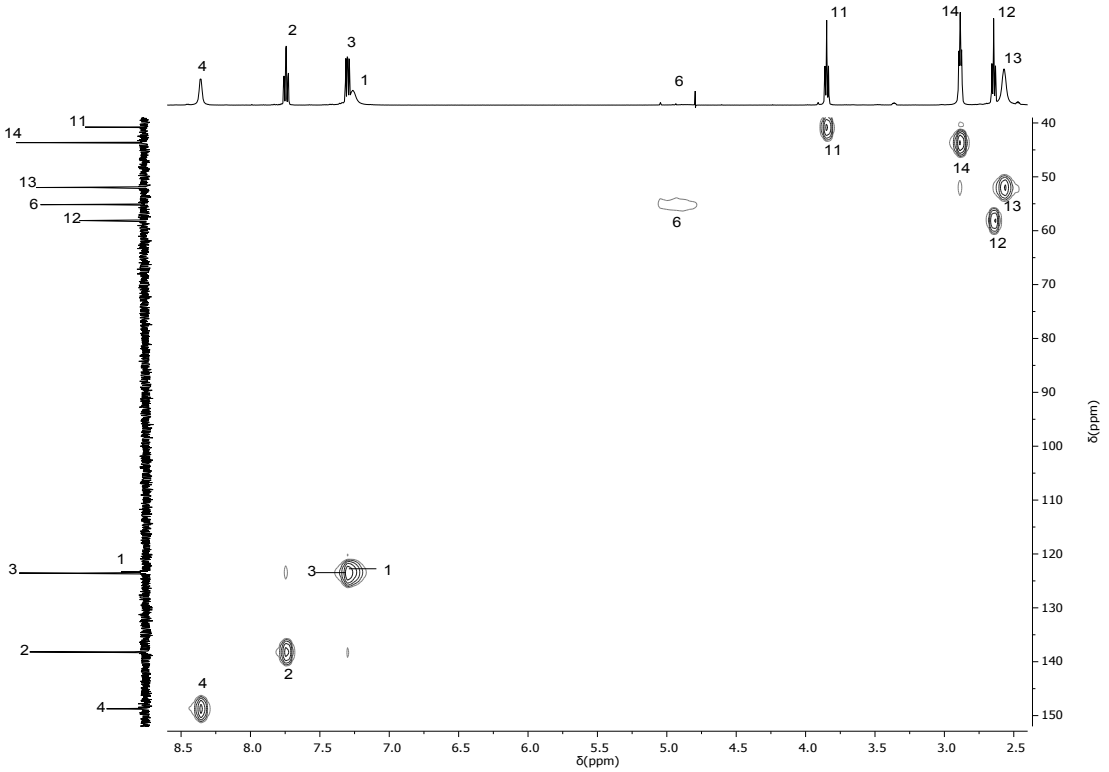

Fig. S17. HSQC spectrum of **L** in D_2O at pD 10.24.

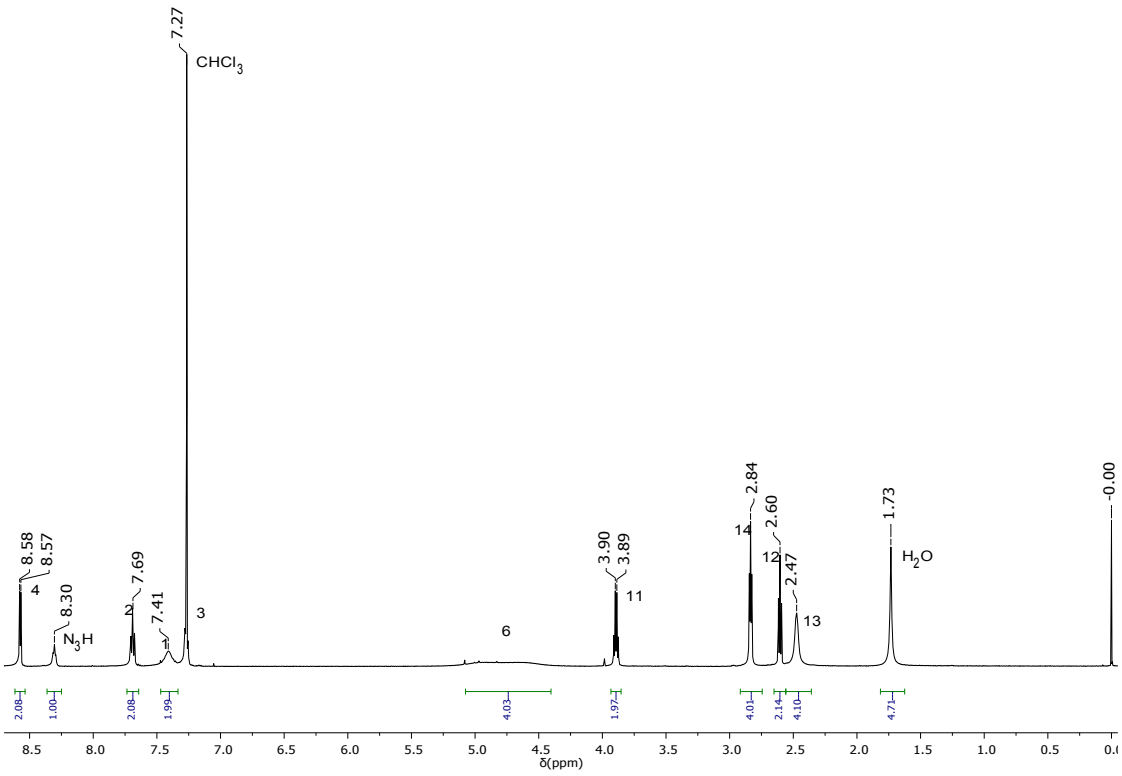

Fig. S18. ^{1}H NMR spectrum of **L** in $CDCl_3$.

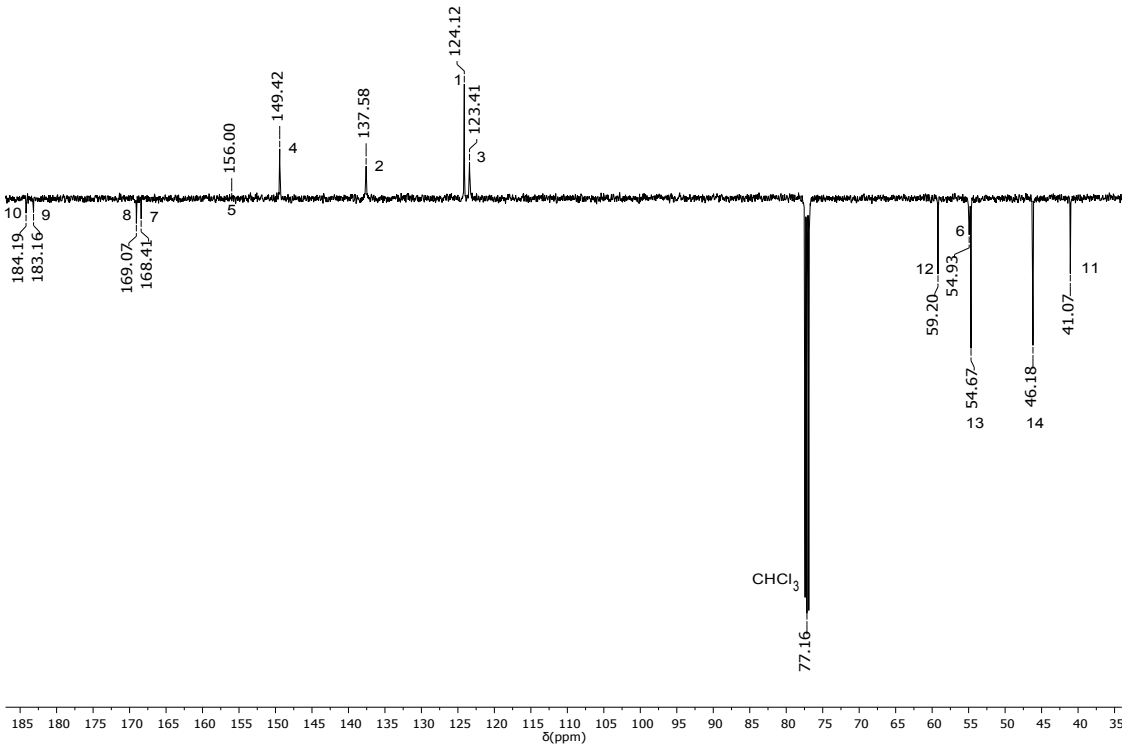

Fig. S19. ^{13}C APT spectrum of **L** in $CDCl_3$.

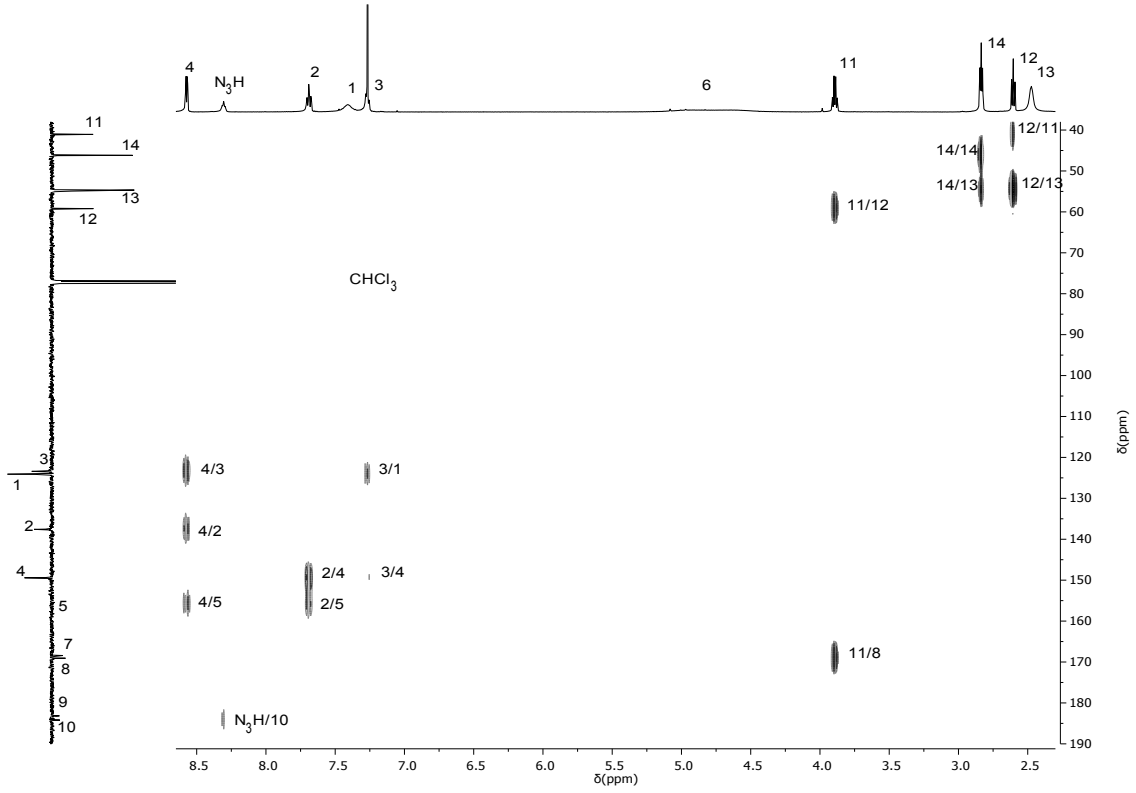

Fig. S20. HMBC spectrum of **L** in $CDCl_3$.

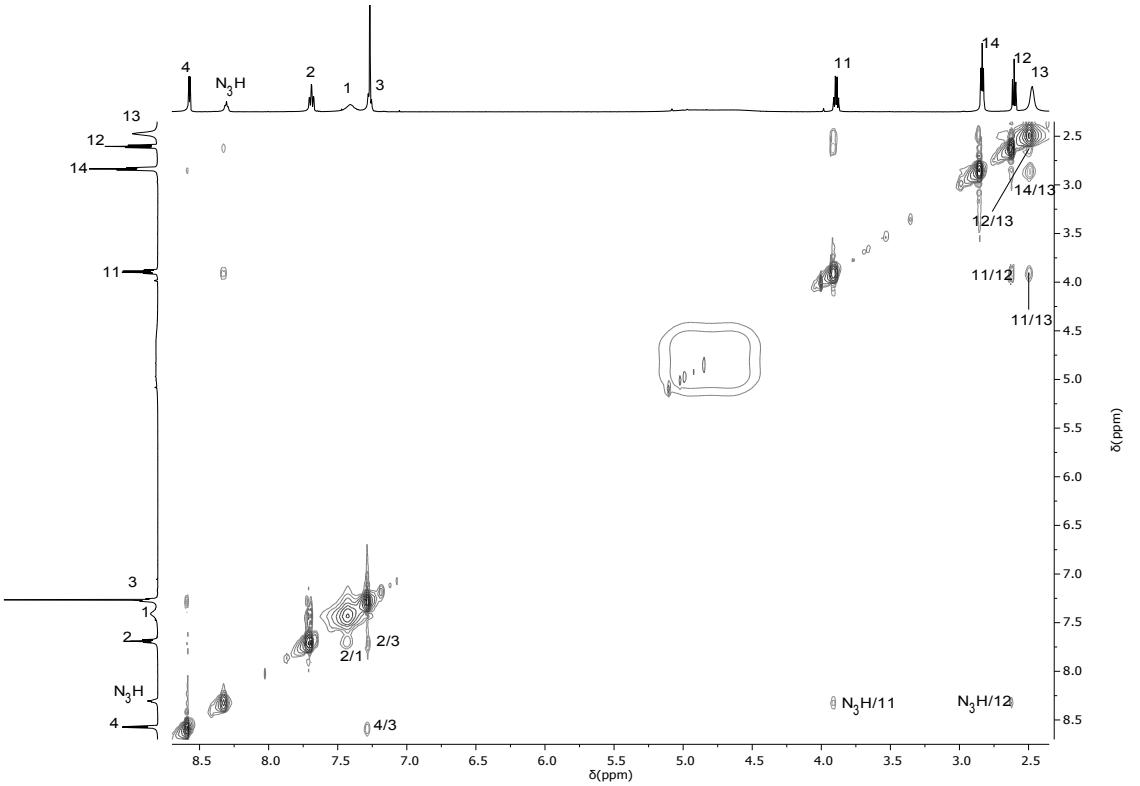

Fig. S21. NOESY spectrum of **L** in $CDCl_3$.

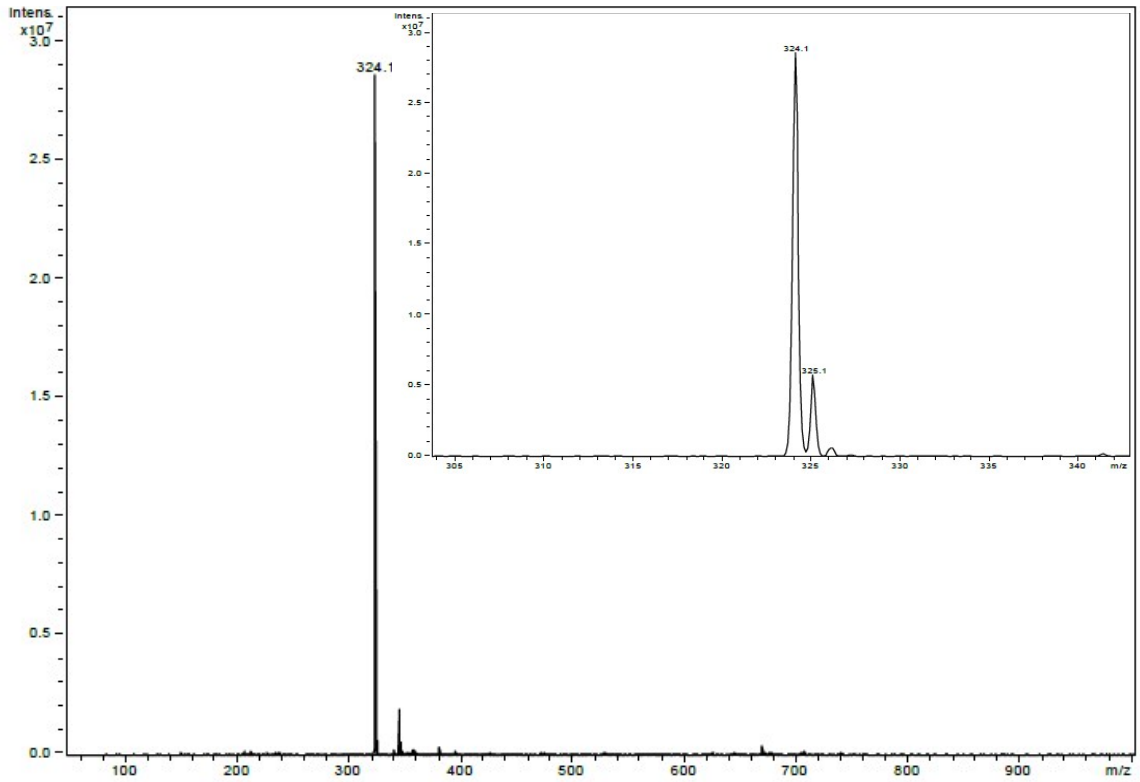

Fig. S22. ESI mass spectrum of **smdpa** in MeOH acquired in positive mode. The inset represents the isotopic peak m/z 324.1.

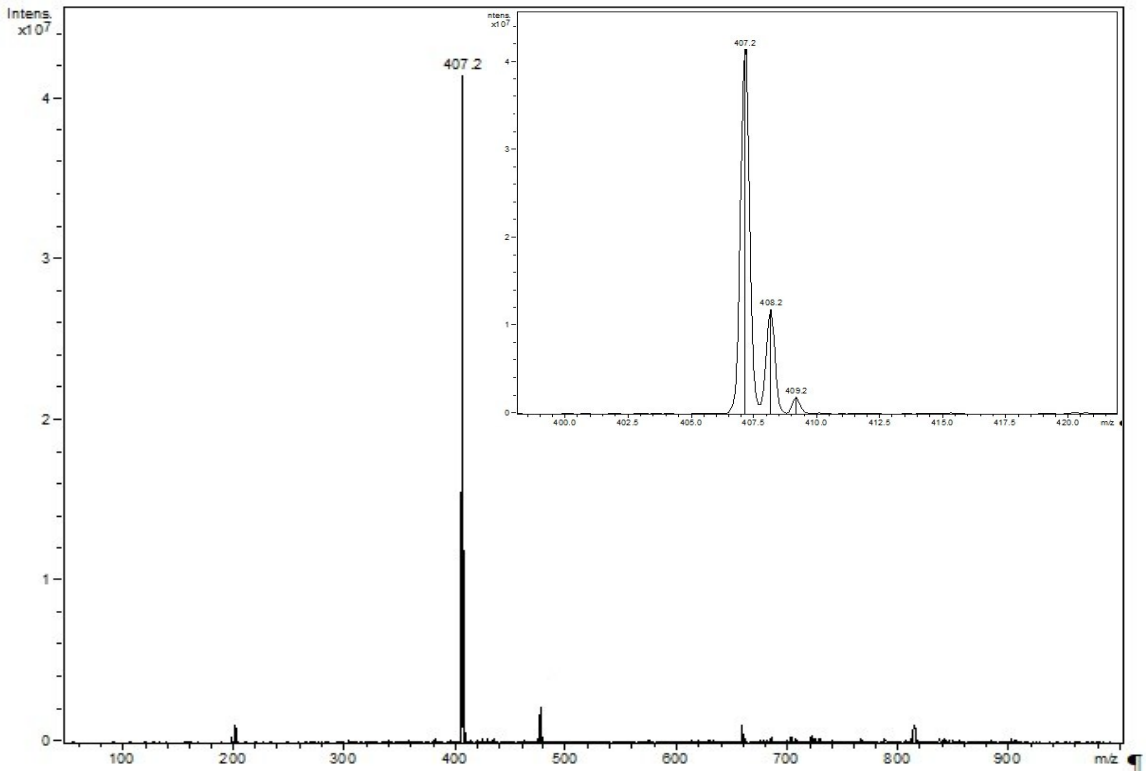

Fig. S23. ESI mass spectrum of **L** in MeOH acquired in positive mode. The inset represents the isotopic peak m/z 407.2.

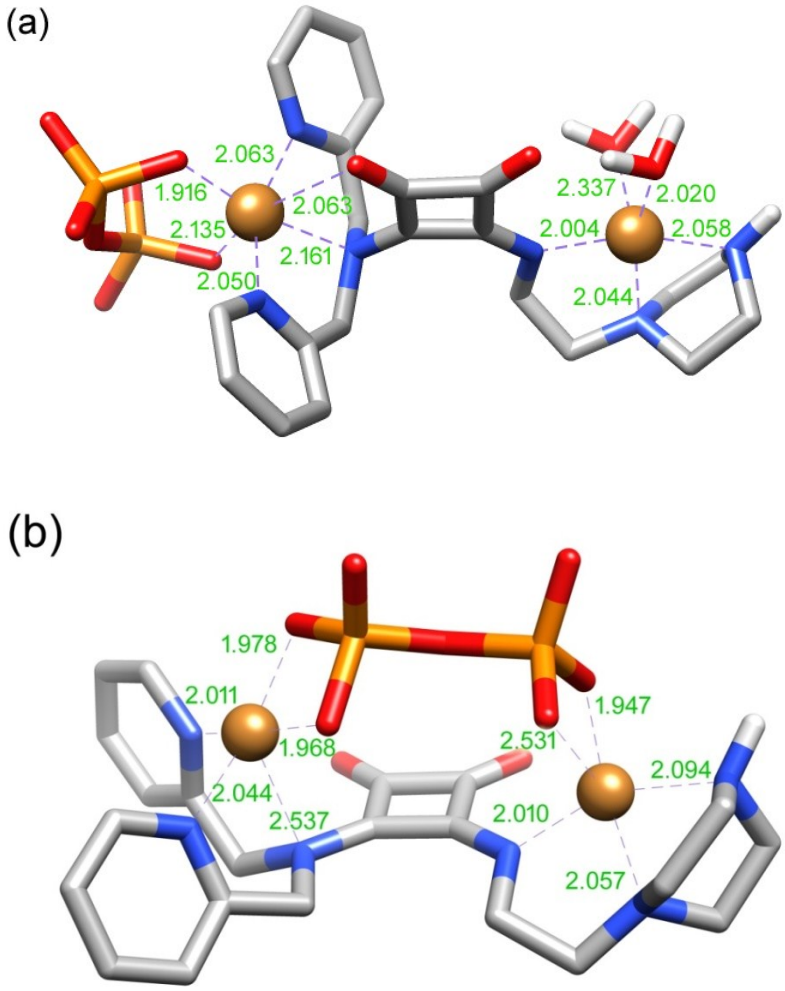

Fig. S24. Structures of the $[Cu_2\mathbf{L}H_{-1}(PPi)(H_2O)_2]^-$ (a) and $[Cu_2\mathbf{L}H_{-1}(\mu_2\kappa^4\text{-}PPi))]^-$ (b) complexes obtained with DFT calculations. The numbers indicate the calculated bond distances in Å.

Table S5. Optimized Cartesian coordinates (Å) obtained for $[CuL(H_2O)_2]^{2+}$ (doublet, 0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	6	0	0.309055	1.332290	-1.221219
2	1	0	-0.730331	1.635816	-1.087337
3	1	0	0.486279	1.166850	-2.285941
4	6	0	1.258371	2.387381	-0.715356
5	6	0	0.935165	3.736691	-0.691632
6	1	0	-0.053141	4.060076	-0.992678
7	6	0	1.896010	4.651837	-0.274416
8	1	0	1.665117	5.709720	-0.247416
9	6	0	3.150734	4.192020	0.111337
10	1	0	3.923988	4.871612	0.444029
11	6	0	3.404158	2.829615	0.075169
12	1	0	4.357459	2.412834	0.370017
13	6	0	0.237854	-1.185607	-1.304511
14	1	0	0.475991	-0.977128	-2.349883
15	1	0	-0.826576	-1.413444	-1.231907
16	6	0	1.080353	-2.335777	-0.818612
17	6	0	0.639817	-3.651257	-0.848544
18	1	0	-0.365070	-3.875364	-1.183057
19	6	0	1.504557	-4.661286	-0.440444
20	1	0	1.181838	-5.695011	-0.456150
21	6	0	2.782485	-4.326058	-0.006677
22	1	0	3.484427	-5.080274	0.323150
23	6	0	3.153419	-2.990744	0.010737
24	1	0	4.132540	-2.682936	0.350671
25	7	0	0.598659	0.039592	-0.530312
26	7	0	2.476765	1.948471	-0.333399
27	7	0	2.322018	-2.015892	-0.391894
28	8	0	4.658818	-0.006723	0.218429
29	8	0	3.082037	-0.019584	-2.620196
30	1	0	3.541454	0.743684	-2.997340
31	1	0	3.481044	-0.795431	-3.038368
32	29	0	2.682277	-0.043695	-0.360502
33	6	0	0.170442	0.010594	0.828252
34	6	0	1.004890	-0.030903	1.999498
35	6	0	-1.052338	0.016609	1.530719
36	6	0	-0.280323	-0.019109	2.848114
37	8	0	2.214266	-0.064307	2.185752
38	8	0	-0.585098	-0.032388	4.010083
39	1	0	5.367238	-0.364473	-0.335442
40	1	0	4.861853	-0.234999	1.137211
41	7	0	-2.326367	0.035686	1.259216
42	1	0	-2.690938	0.040826	0.301350
43	6	0	-3.424178	0.052035	2.237763
44	1	0	-3.679747	1.090729	2.460754
45	1	0	-3.106642	-0.431564	3.159397
46	6	0	-4.601587	-0.690487	1.600495
47	1	0	-4.361407	-1.754800	1.551072
48	1	0	-5.490085	-0.572313	2.237001
49	6	0	-5.496149	-1.221165	-0.604347
50	6	0	-5.547361	1.061590	0.180625
51	6	0	-5.598336	-0.724075	-2.039635
52	1	0	-6.506963	-1.436750	-0.220661
53	1	0	-4.913302	-2.144686	-0.571915
54	6	0	-5.651775	1.549746	-1.257929

55	1	0	-6.558334	0.946389	0.605325
56	1	0	-5.011317	1.801753	0.778859
57	1	0	-6.130889	-1.463066	-2.642604
58	1	0	-4.580541	-0.613476	-2.449646
59	1	0	-6.224588	2.479436	-1.284656
60	1	0	-4.637082	1.759438	-1.635485
61	1	0	-6.436958	0.864707	-3.017318
62	7	0	-4.818533	-0.216839	0.229760
63	7	0	-6.345842	0.537466	-2.059848

E(UTPSSh) = -3126.6438113 Hartree
Zero-point correction = 0.515639
Thermal correction to Energy = 0.549734
Thermal correction to Enthalpy = 0.550679
Thermal correction to Gibbs Free Energy = 0.447044
Sum of electronic and zero-point Energies = -3126.128173
Sum of electronic and thermal Energies = -3126.094077
Sum of electronic and thermal Enthalpies = -3126.093133
Sum of electronic and thermal Free Energies = -3126.196767

Table S6. Optimized Cartesian coordinates (Å) obtained for $[Cu_2\mathbf{L}H_{-1}(H_2O)_4]^{3+}$ (triplet, 0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	6	0	1.647855	-1.361569	1.642178
2	1	0	0.656795	-1.704703	1.942674
3	1	0	2.238280	-1.179812	2.542663
4	6	0	2.339555	-2.397596	0.795276
5	6	0	2.043251	-3.751019	0.872856
6	1	0	1.245814	-4.092353	1.520579
7	6	0	2.782151	-4.646569	0.106668
8	1	0	2.567740	-5.707321	0.151102
9	6	0	3.792664	-4.163761	-0.718208
10	1	0	4.387792	-4.828040	-1.330654
11	6	0	4.028008	-2.797903	-0.758346
12	1	0	4.794094	-2.362238	-1.385211
13	6	0	1.542076	1.156045	1.752980
14	1	0	2.146380	0.945710	2.638021
15	1	0	0.526469	1.386304	2.077032
16	6	0	2.143993	2.316259	1.002866
17	6	0	1.743779	3.628267	1.215325
18	1	0	0.934880	3.839808	1.902939
19	6	0	2.393080	4.651085	0.532461
20	1	0	2.096316	5.681752	0.683230
21	6	0	3.421030	4.332853	-0.348425
22	1	0	3.949494	5.097444	-0.902052
23	6	0	3.763037	3.001119	-0.521921
24	1	0	4.550041	2.704789	-1.201682
25	7	0	1.590888	-0.066947	0.898822
26	7	0	3.317245	-1.936862	-0.013086
27	7	0	3.141662	2.014049	0.143834
28	8	0	5.194224	0.052621	-1.218168
29	8	0	4.653790	0.022269	1.943509
30	1	0	5.239118	-0.727026	2.122157
31	1	0	5.149921	0.807929	2.212797
32	29	0	3.475787	0.053008	-0.057728

33	6	0	0.690690	-0.054766	-0.208347
34	6	0	1.088604	-0.007387	-1.576845
35	6	0	-0.728275	-0.066379	-0.475347
36	6	0	-0.379705	-0.050375	-1.959542
37	8	0	2.176534	0.045830	-2.154086
38	8	0	-1.013553	-0.084430	-2.993475
39	1	0	6.027145	0.405234	-0.873589
40	1	0	5.123233	0.332113	-2.142297
41	7	0	-1.870383	-0.084818	0.125970
42	6	0	-1.934539	-0.069997	1.599997
43	1	0	-2.107074	0.957300	1.935665
44	1	0	-1.006253	-0.417357	2.054616
45	6	0	-3.076186	-0.976554	2.044335
46	1	0	-2.836703	-2.012759	1.806054
47	1	0	-3.250510	-0.895023	3.120412
48	6	0	-5.202931	-1.746510	0.971809
49	6	0	-5.079546	0.514250	1.843668
50	6	0	-6.162918	-1.275978	-0.147381
51	1	0	-5.743413	-2.042844	1.875626
52	1	0	-4.596666	-2.586149	0.636402
53	6	0	-6.058271	0.981728	0.739905
54	1	0	-5.606357	0.179454	2.741936
55	1	0	-4.394614	1.313842	2.121500
56	1	0	-7.208293	-1.339073	0.164363
57	1	0	-6.028937	-1.868454	-1.050674
58	1	0	-7.099300	0.877395	1.055818
59	1	0	-5.875752	2.019553	0.470393
60	1	0	-6.331587	0.473557	-1.252143
61	7	0	-4.291489	-0.613350	1.281013
62	7	0	-5.802271	0.132681	-0.453670
63	29	0	-3.749462	0.078765	-0.567670
64	8	0	-3.618826	-0.342363	-2.567009
65	1	0	-2.679097	-0.236729	-2.869721
66	1	0	-4.164964	0.190668	-3.161239
67	8	0	-3.500759	2.289023	-1.003832
68	1	0	-4.144736	2.808792	-1.504071
69	1	0	-3.137945	2.888486	-0.337555

E(UTPSSh) = -4919.4128006 Hartree
Zero-point correction = 0.558596
Thermal correction to Energy = 0.598353
Thermal correction to Enthalpy = 0.599297
Thermal correction to Gibbs Free Energy = 0.486833
Sum of electronic and zero-point Energies = -4918.854205
Sum of electronic and thermal Energies = -4918.814447
Sum of electronic and thermal Enthalpies = -4918.813503
Sum of electronic and thermal Free Energies = -4918.925968

Table S7. Optimized Cartesian coordinates (Å) obtained for $[Cu_2\mathbf{L}H_{-1}(\kappa^2\text{-}PPi)(H_2O)_2]^-$ (triplet, 0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	6	0	-0.628416	-1.416988	-1.353607
2	1	0	0.328144	-1.784897	-1.730581
3	1	0	-1.274056	-1.139976	-2.190905
4	6	0	-1.328073	-2.473338	-0.537122

5	6	0	-1.005933	-3.822147	-0.604942
6	1	0	-0.177868	-4.151341	-1.220712
7	6	0	-1.762448	-4.729473	0.132496
8	1	0	-1.529183	-5.787318	0.100942
9	6	0	-2.820333	-4.259324	0.902073
10	1	0	-3.438912	-4.935121	1.479218
11	6	0	-3.081119	-2.893452	0.930561
12	1	0	-3.924236	-2.468558	1.470266
13	6	0	-0.363632	1.089467	-1.301690
14	1	0	-1.089914	1.010076	-2.115133
15	1	0	0.636810	1.247073	-1.706540
16	6	0	-0.775581	2.227787	-0.402143
17	6	0	-0.201521	3.492180	-0.446089
18	1	0	0.623707	3.691814	-1.118721
19	6	0	-0.707758	4.485697	0.388134
20	1	0	-0.278125	5.480391	0.373922
21	6	0	-1.768257	4.186186	1.237656
22	1	0	-2.188300	4.933412	1.898709
23	6	0	-2.285532	2.896981	1.229697
24	1	0	-3.116738	2.592404	1.853697
25	7	0	-0.485758	-0.181612	-0.532501
26	7	0	-2.340330	-2.023176	0.229659
27	7	0	-1.793865	1.944340	0.429859
28	6	0	0.457451	-0.287178	0.529792
29	6	0	0.214401	-0.401975	1.949193
30	6	0	1.894221	-0.237832	0.652958
31	6	0	1.715465	-0.308603	2.149129
32	8	0	-0.748089	-0.498429	2.697980
33	8	0	2.460549	-0.255163	3.114040
34	7	0	2.979222	-0.173824	-0.058845
35	6	0	2.922957	-0.173692	-1.531888
36	1	0	3.070397	0.846788	-1.899828
37	1	0	1.963661	-0.528939	-1.907953
38	6	0	4.028764	-1.085739	-2.053495
39	1	0	3.819351	-2.116267	-1.766664
40	1	0	4.108066	-1.032416	-3.142787
41	6	0	6.250713	-1.804241	-1.135545
42	6	0	6.027108	0.421036	-2.074845
43	6	0	7.258665	-1.299009	-0.073935
44	1	0	6.749593	-2.101681	-2.062749
45	1	0	5.682697	-2.652251	-0.758140
46	6	0	7.135025	0.889982	-1.101983
47	1	0	6.438967	0.076051	-3.027831
48	1	0	5.317729	1.224617	-2.266476
49	1	0	8.290901	-1.409644	-0.415470
50	1	0	7.140224	-1.837547	0.865201
51	1	0	8.132360	0.692855	-1.503675
52	1	0	7.044773	1.953489	-0.896020
53	1	0	7.527922	0.510881	0.905681
54	7	0	5.303130	-0.692921	-1.410230
55	7	0	6.943665	0.133637	0.164185
56	29	0	4.903408	0.097332	0.431956
57	8	0	4.947598	0.197506	2.449536
58	1	0	4.028961	0.048673	2.815967
59	1	0	5.268957	1.032763	2.816588
60	8	0	4.619784	2.396522	0.124047
61	1	0	5.148617	3.048259	0.605291
62	1	0	3.700386	2.661576	0.266775
63	29	0	-2.504724	0.020130	0.211934
64	8	0	-4.086130	0.344502	1.244676
65	8	0	-5.875332	-1.542806	1.344193

66	8	0	-6.567150	0.970780	1.287063
67	8	0	-5.576117	-0.235208	-0.812040
68	8	0	-3.218214	0.197230	-1.792392
69	8	0	-4.970444	2.126111	-1.788980
70	8	0	-5.297971	0.034893	-3.319520
71	15	0	-4.722430	0.619968	-2.015222
72	15	0	-5.569172	-0.114777	0.852220

E(UTPSSh) = -5976.8006326 Hartree
Zero-point correction = 0.536516
Thermal correction to Energy = 0.580452
Thermal correction to Enthalpy = 0.581396
Thermal correction to Gibbs Free Energy = 0.457885
Sum of electronic and zero-point Energies = -5976.264117
Sum of electronic and thermal Energies = -5976.220180
Sum of electronic and thermal Enthalpies = -5976.219236
Sum of electronic and thermal Free Energies = -5976.342747

Table S8. Optimized Cartesian coordinates (Å) obtained for $[Cu_2\mathbf{L}H_{-1}(\mu_2\kappa^4\text{-PPi})]^-$ (triplet, 0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	6	0	3.045190	1.323148	1.728436
2	1	0	2.850921	1.535878	2.780536
3	1	0	3.557137	2.195085	1.314762
4	6	0	3.981872	0.134920	1.640858
5	6	0	5.001560	-0.000175	2.581778
6	1	0	5.085617	0.721306	3.385432
7	6	0	5.884178	-1.064592	2.484762
8	1	0	6.681335	-1.182248	3.209093
9	6	0	5.721498	-1.987002	1.452934
10	1	0	6.377807	-2.840853	1.346903
11	6	0	4.687556	-1.794887	0.554321
12	1	0	4.501275	-2.482757	-0.260576
13	6	0	1.473507	2.217505	0.008340
14	1	0	1.252390	3.174798	0.491306
15	1	0	0.598728	1.889356	-0.553474
16	6	0	2.604618	2.399211	-0.973467
17	6	0	3.001758	3.657680	-1.412049
18	1	0	2.526957	4.542806	-1.007359
19	6	0	4.010307	3.754587	-2.364827
20	1	0	4.333933	4.724864	-2.721893
21	6	0	4.601380	2.590506	-2.844576
22	1	0	5.393147	2.620411	-3.581697
23	6	0	4.160877	1.369957	-2.353699
24	1	0	4.594245	0.436123	-2.690157
25	7	0	1.770908	1.169720	0.995517
26	7	0	3.844969	-0.746618	0.638273
27	7	0	3.180924	1.278450	-1.441192
28	6	0	0.748518	0.551554	1.678602
29	6	0	0.848772	-0.424634	2.753666
30	6	0	-0.694387	0.478961	1.637888
31	6	0	-0.650501	-0.527256	2.744445
32	8	0	1.761251	-0.926054	3.417347
33	8	0	-1.490659	-1.121368	3.401973
34	7	0	-1.760511	0.989346	1.075139

35	6	0	-1.761990	2.221368	0.285459
36	1	0	-1.605754	2.014079	-0.780878
37	1	0	-0.993609	2.924172	0.616107
38	6	0	-3.128012	2.877820	0.496131
39	1	0	-3.208792	3.205517	1.532945
40	1	0	-3.262297	3.746882	-0.154850
41	6	0	-5.350200	1.954794	1.174053
42	6	0	-4.660987	1.789181	-1.142569
43	6	0	-6.118589	0.611477	1.074596
44	1	0	-5.984043	2.804798	0.899358
45	1	0	-4.978053	2.112951	2.184999
46	6	0	-5.526044	0.510260	-1.266177
47	1	0	-5.225596	2.692252	-1.399208
48	1	0	-3.787109	1.714072	-1.788383
49	1	0	-7.168358	0.775405	0.812095
50	1	0	-6.075291	0.067640	2.017562
51	1	0	-6.568446	0.751911	-1.497159
52	1	0	-5.117966	-0.142703	-2.033351
53	1	0	-5.828021	-1.128449	-0.022556
54	7	0	-4.186428	1.871946	0.260998
55	7	0	-5.437335	-0.193050	0.035994
56	29	0	-3.403848	-0.015344	0.501382
57	29	0	2.442495	-0.510003	-0.782721
58	8	0	1.802495	-2.381535	-0.810726
59	8	0	0.868434	-0.452032	-1.962475
60	8	0	0.418045	-2.817723	-3.026352
61	8	0	-0.714841	-2.163286	-0.769314
62	8	0	-2.914499	-1.898669	0.441063
63	8	0	-2.821069	-3.379426	-1.689854
64	8	0	-2.661556	-0.742940	-1.806769
65	15	0	-2.392946	-2.062994	-1.049452
66	15	0	0.577966	-2.005594	-1.756308

E(UTPSSh) = -5823.8970634 Hartree
Zero-point correction = 0.486820
Thermal correction to Energy = 0.525203
Thermal correction to Enthalpy = 0.526147
Thermal correction to Gibbs Free Energy = 0.415118
Sum of electronic and zero-point Energies = -5823.410244
Sum of electronic and thermal Energies = -5823.371861
Sum of electronic and thermal Enthalpies = -5823.370916
Sum of electronic and thermal Free Energies = -5823.481945

Table S9. Optimized Cartesian coordinates (Å) obtained for $[Cu_2\mathbf{L}H_{-1}(\mu_2\kappa^4\text{-PPi})]^-$ (triplet, 0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	6	0	3.308450	-0.761306	1.852518
2	1	0	3.431781	-1.594082	2.545906
3	1	0	3.895888	0.074827	2.238487
4	6	0	3.876778	-1.174778	0.508084
5	6	0	5.044968	-1.937292	0.475619
6	1	0	5.506966	-2.243788	1.406344
7	6	0	5.589511	-2.303527	-0.745195
8	1	0	6.497072	-2.894074	-0.786190
9	6	0	4.942248	-1.912953	-1.915785
10	1	0	5.320932	-2.185935	-2.892212

11	6	0	3.783575	-1.164773	-1.808391
12	1	0	3.232307	-0.848042	-2.685118
13	6	0	1.626549	1.012068	2.309092
14	1	0	1.795150	1.072266	3.389419
15	1	0	0.578117	1.234832	2.121147
16	6	0	2.472189	2.047495	1.606637
17	6	0	3.055800	3.104610	2.297979
18	1	0	2.935769	3.174123	3.372018
19	6	0	3.789922	4.053128	1.594835
20	1	0	4.252716	4.882936	2.115355
21	6	0	3.926141	3.915473	0.217419
22	1	0	4.492258	4.626862	-0.369594
23	6	0	3.317737	2.835998	-0.405431
24	1	0	3.384266	2.688907	-1.475891
25	7	0	1.903300	-0.336463	1.809047
26	7	0	3.266781	-0.790408	-0.621276
27	7	0	2.608787	1.922334	0.274898
28	6	0	0.956004	-1.316554	1.759327
29	6	0	1.132748	-2.751025	1.544567
30	6	0	-0.479315	-1.408345	1.684416
31	6	0	-0.356027	-2.868425	1.413979
32	8	0	2.087958	-3.534357	1.503089
33	8	0	-1.147615	-3.777965	1.199512
34	7	0	-1.593140	-0.713316	1.762642
35	6	0	-1.707934	0.587124	2.424848
36	1	0	-1.393768	1.407831	1.768596
37	1	0	-1.134969	0.622706	3.358043
38	6	0	-3.197287	0.753181	2.739410
39	1	0	-3.497539	0.015257	3.484112
40	1	0	-3.421972	1.749783	3.128328
41	6	0	-5.090819	-0.455506	1.646060
42	6	0	-4.431470	1.714157	0.792622
43	6	0	-5.555340	-0.865656	0.224471
44	1	0	-5.905006	0.003095	2.218917
45	1	0	-4.722720	-1.320134	2.196576
46	6	0	-4.887822	1.291404	-0.625383
47	1	0	-5.243465	2.183844	1.359734
48	1	0	-3.587694	2.396139	0.721356
49	1	0	-6.601290	-0.588800	0.055125
50	1	0	-5.452526	-1.940102	0.077410
51	1	0	-5.943175	1.531949	-0.792935
52	1	0	-4.277733	1.785587	-1.377691
53	1	0	-4.826504	-0.494107	-1.682389
54	7	0	-3.966581	0.497013	1.495945
55	7	0	-4.668458	-0.168932	-0.733721
56	29	0	-2.747317	-0.435794	0.099495
57	29	0	1.618006	0.455113	-0.757193
58	8	0	0.580711	-1.009376	-1.452128
59	8	0	-0.671754	-2.044604	-3.466061
60	8	0	-1.958512	-1.541182	-1.297597
61	8	0	-1.116283	0.389014	-2.812328
62	8	0	0.554237	1.870054	-1.514213
63	8	0	-1.804977	1.441669	-0.552501
64	8	0	-1.467242	2.917808	-2.693550
65	15	0	-0.996139	1.751784	-1.833389
66	15	0	-0.775293	-1.140397	-2.246498

E(UTPSSh) = -5823.9047593 Hartree
Zero-point correction = 0.486738
Thermal correction to Energy = 0.524877
Thermal correction to Enthalpy = 0.525821

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Thermal correction to Gibbs Free Energy = 0.416285
Sum of electronic and zero-point Energies = -5823.418021
Sum of electronic and thermal Energies = -5823.379882
Sum of electronic and thermal Enthalpies = -5823.378938
Sum of electronic and thermal Free Energies = -5823.488474
```

Table S10. Optimized Cartesian coordinates (Å) obtained for $[Cu_2(\mathbf{L}H_{-1})ATP]^{-}$ (triplet, 0 imaginary frequencies).

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	6	0	-0.301838	3.111773	-2.692799
2	1	0	-0.775623	2.876478	-3.645977
3	1	0	0.180275	4.085600	-2.802625
4	6	0	-1.378262	3.222876	-1.632157
5	6	0	-2.594570	3.817376	-1.965799
6	1	0	-2.761365	4.154481	-2.981510
7	6	0	-3.576161	3.957731	-0.997607
8	1	0	-4.525538	4.418277	-1.242979
9	6	0	-3.327202	3.486137	0.289423
10	1	0	-4.067186	3.560358	1.075323
11	6	0	-2.101897	2.901554	0.550936
12	1	0	-1.863829	2.508320	1.531521
13	6	0	2.124024	2.655748	-2.357747
14	1	0	2.439278	2.984536	-3.352261
15	1	0	2.784924	1.851838	-2.041729
16	6	0	2.257162	3.797889	-1.379673
17	6	0	3.019730	4.921599	-1.678116
18	1	0	3.491787	5.005564	-2.648852
19	6	0	3.160349	5.921665	-0.722620
20	1	0	3.751003	6.803749	-0.937899
21	6	0	2.529290	5.774713	0.507650
22	1	0	2.609597	6.528514	1.279677
23	6	0	1.780602	4.631243	0.738949
24	1	0	1.275602	4.465277	1.681589
25	7	0	0.753827	2.128545	-2.395004
26	7	0	-1.141255	2.782797	-0.388583
27	7	0	1.647769	3.667263	-0.186339
28	6	0	0.490751	0.823401	-2.666938
29	6	0	-0.789767	0.176450	-2.914335
30	6	0	1.193153	-0.439715	-2.623815
31	6	0	-0.086114	-1.138636	-2.912012
32	8	0	-1.964455	0.557299	-3.041774
33	8	0	-0.406374	-2.313144	-3.080675
34	7	0	2.360150	-0.998051	-2.403479
35	6	0	3.658791	-0.330028	-2.532494
36	1	0	3.917858	0.238302	-1.630990
37	1	0	3.689588	0.334277	-3.401347
38	6	0	4.672786	-1.462141	-2.717987
39	1	0	4.475586	-1.976366	-3.658545
40	1	0	5.700419	-1.090441	-2.728591
41	6	0	4.469475	-3.863272	-2.001439
42	6	0	5.393506	-2.238440	-0.457008
43	6	0	3.846226	-4.660029	-0.825020
44	1	0	5.487124	-4.200460	-2.224948
45	1	0	3.863987	-3.963921	-2.900543
46	6	0	4.851387	-3.090384	0.713840

47	1	0	6.410944	-2.528648	-0.740526
48	1	0	5.375872	-1.184090	-0.190669
49	1	0	4.526324	-5.438918	-0.467957
50	1	0	2.907902	-5.125626	-1.124259
51	1	0	5.547772	-3.892669	0.978628
52	1	0	4.684921	-2.460567	1.586179
53	1	0	3.072526	-4.121529	1.026142
54	7	0	4.483164	-2.432608	-1.611846
55	7	0	3.566886	-3.681108	0.255624
56	29	0	2.624090	-2.159706	-0.773520
57	29	0	0.614598	1.989222	0.265292
58	8	0	-0.213733	0.202752	0.324146
59	8	0	-1.094358	-1.711253	1.725429
60	8	0	0.798596	-2.214337	0.058698
61	8	0	1.219232	-0.806159	2.203711
62	8	0	1.961004	1.591223	1.606980
63	8	0	3.215088	-0.452104	0.605962
64	8	0	3.307746	0.105154	3.198793
65	15	0	2.558534	0.168361	1.831914
66	15	0	0.210551	-1.129589	0.970900
67	15	0	5.125166	0.392675	3.523428
68	8	0	5.703250	-1.001736	3.244356
69	8	0	5.455447	1.494215	2.505381
70	8	0	5.029528	0.813123	4.994088
71	6	0	-1.533469	-3.090071	1.587552
72	1	0	-1.842159	-3.404773	2.584185
73	1	0	-0.703916	-3.708448	1.243110
74	6	0	-2.687853	-3.212998	0.609781
75	6	0	-2.463809	-2.504169	-0.737994
76	6	0	-3.504938	-1.357666	-0.703933
77	6	0	-4.601863	-1.969659	0.165535
78	6	0	-6.886209	-1.035849	0.683530
79	6	0	-8.953521	-1.579807	0.130770
80	6	0	-7.315200	0.035121	1.467449
81	1	0	-9.650831	-2.221783	-0.398302
82	6	0	-8.706361	0.247313	1.527136
83	6	0	-5.194271	0.023228	1.620013
84	7	0	-5.509383	-1.028311	0.783940
85	7	0	-6.240996	0.685670	2.050761
86	1	0	-4.171212	0.240028	1.885013
87	7	0	-9.265008	1.263849	2.215962
88	1	0	-10.266458	1.279831	2.332606
89	1	0	-8.702954	1.809600	2.849659
90	7	0	-9.511879	-0.589324	0.840754
91	7	0	-7.659811	-1.880229	-0.010512
92	8	0	-3.886510	-2.646188	1.197514
93	1	0	-2.856625	-4.278889	0.421875
94	1	0	-1.456059	-2.099122	-0.800557
95	1	0	-3.056098	-0.522754	-0.151983
96	8	0	-2.654708	-3.415801	-1.810158
97	1	0	-2.038173	-3.116845	-2.508077
98	8	0	-4.009003	-0.938896	-1.948148
99	1	0	-3.300730	-0.422576	-2.402182
100	1	0	-5.224074	-2.654622	-0.419022

E(UTPSSh) =-7279.1979045 Hartree
Zero-point correction = 0.738388
Thermal correction to Energy = 0.796982
Thermal correction to Enthalpy = 0.797927
Thermal correction to Gibbs Free Energy = 0.641901
Sum of electronic and zero-point Energies = -7278.459516

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Sum of electronic and thermal Energies = -7278.400922
Sum of electronic and thermal Enthalpies = -7278.399978
Sum of electronic and thermal Free Energies = -7278.556003
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