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SUPPORTING INFORMATION

Recognition of Phosphopeptides by a Dinuclear Copper(II) Macrocyclic Complex in Water:Methanol 50:50 v/v Solution

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Table S1 Overall protonation constants (β_i^H) of L and overall stability constants ($\beta_{Cu_mH_hL_l}$) of its copper(II) complexes in water/methanol (50:50 v/v) solution.[a]

Equilibrium reaction	log β_i^{H} [b]	Equilibrium reaction	log $\beta_{Cu_mH_hL_l}$ [c]
$L + H^+ \rightleftharpoons HL^+$	8.36(1)	$Cu^{2+} + 2\ H^+ + L \rightleftharpoons [CuH_2L]^{4+}$	24.19(1)
$L + 2\ H^+ \rightleftharpoons H_2L^{2+}$	15.88(1)	$Cu^{2+} + H^+ + L \rightleftharpoons [CuHL]^{3+}$	18.34(2)
$L + 3\ H^+ \rightleftharpoons H_3L^{3+}$	22.39(1)	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	11.24(3)
$L + 4\ H^+ \rightleftharpoons H_4L^{4+}$	28.18(1)	$Cu^{2+} + L \rightleftharpoons [CuL(OH)]^+ + H^+$	2.86(2)
		$2\ Cu^{2+} + L \rightleftharpoons [Cu_2L]^{4+}$	18.30(1)
		$2\ Cu^{2+} + L \rightleftharpoons [Cu_2L(OH)]^{3+} + H^+$	13.87(1)

[a] $T = 298.2 \pm 0.1$ K; $I = 0.10 \pm 0.01$ M in KNO_3. [b] Values in parenthesis are standard deviations in the last significant figures.

Table S2 Overall (β_i^H) and stepwise (K_i^H) protonation constants of the studied substrates in water/methanol (50:50 v/v) solution.[a]

Equilibrium reaction [b]	log β_i^{H} [c]				Equilibrium reaction[b]	log K_i^H			
	PO_4^{3-}	$PhPO_4^{2-}$	$pST3^{2-}$	$pST1^{3-}$		PO_4^{3-}	$PhPO_4^{2-}$	$pST3^{2-}$	$pST1^{3-}$
$S + H^+ \rightleftharpoons HS$	11.91(1)	6.81(3)	10.69(1)	10.81(1)	$S + H^+ \rightleftharpoons HS$	11.91	6.81	10.69	10.81
$S + 2\ H^+ \rightleftharpoons H_2S$	19.42(1)	-	20.45(1)	17.35(3)	$HS + H^+ \rightleftharpoons H_2S$	7.51	–	9.76	6.54
$S + 2\ H^+ \rightleftharpoons H_3S$	22.23(1)	-	26.64(1)	22.36(3)	$H_2S + H^+ \rightleftharpoons H_3S$	2.81	–	6.19	5.01

[a] $T = 298.2 \pm 0.1$ K; $I = 0.10 \pm 0.01$ M in KNO_3. The value for acetate was also determined in the same conditions: log $K_1^H = 5.24(1)$. [b] S denotes the substrate; charges of the substrates were omitted for simplicity. [c] Values in parenthesis are standard deviations in the last significant figures.

Table S3 Overall (log $\beta_{CuH_hS_s}$) stability constants of the copper(II) complexes of the studied substrates in water/methanol (50:50 v/v) solution.[a]

Equilibrium reaction[b,c]	log $\beta_{CuH_hS_s}$ [d]			
	PO_4^{3-}	$PhPO_4^{2-}$	$pST3^{2-}$	$pST1^{3-}$
$Cu^{2+} + 2\ H^+ + S \rightleftharpoons [CuH_2S]$	–	–	23.89(5)	20.63(4)
$Cu^{2+} + H^+ + S \rightleftharpoons [CuHS]$	16.76(2)	–	17.38(6)	16.04(1)
$Cu^{2+} + S \rightleftharpoons [CuS]$	–	4.12(5)	11.11(3)	–

[a] $T = 298.2 \pm 0.1$ K; $I = 0.10 \pm 0.01$ M in KNO_3. [b] S denotes the substrate. [c] Charges of the substrates and complexes were omitted for simplicity. [d] Values in parenthesis are standard deviations in the last significant figures.

Table S4 Overall ($\beta_{Cu_mH_hL_lS_s}$) association constants between the copper(II) complexes of L with the anions in water/methanol (50:50 v/v).[a]

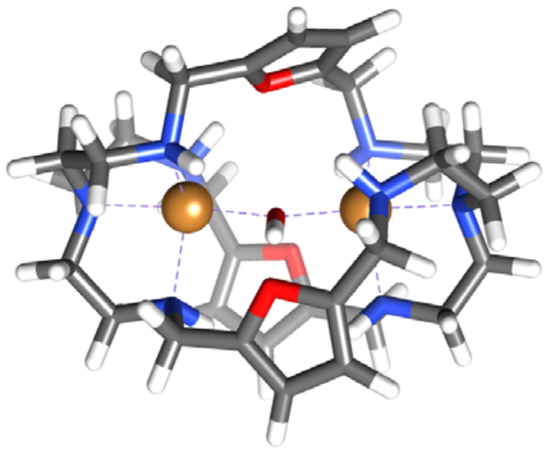
Equilibrium reaction[b,c]	log $\beta_{Cu_mH_hL_lS_s}$ [d]			
	PO_4^{3-}	$PhPO_4^{2-}$	$pST3^{2-}$	$pST1^{3-}$
$2\ Cu^{2+} + L + S \rightleftharpoons [Cu_2L(S)]$	–	25.84(1)	–	–
$2\ Cu^{2+} + H^+ + L + S \rightleftharpoons [Cu_2HL(S)]$	37.80(2)	–	–	36.57(1)
$2\ Cu^{2+} + 2\ H^+ + L + S \rightleftharpoons [Cu_2H_2L(S)]$	41.80(3)	–	45.38(1)	41.28(1)
$2\ Cu^{2+} + 3\ H^+ + L + S \rightleftharpoons [Cu_2H_3L(S)]$	–	–	48.89(7)	45.27(3)

[a] T = (298.2±0.1) K; I = (0.10±0.01) M in KNO_3. [b] Charges of the complex species were omitted for simplicity. [c] S denotes the substrate. [d] Values in parenthesis are standard deviations in the last significant figures.

Table S5 Hydrogen bond details for the main interactions in $[Cu_2L(\mu\text{-}PhPO_4)][Cu_2L(\mu\text{-}PhPO_4)(NO_3)]3NO_3\cdot 24H_2O$.

Sym. Op.	*D–H···A*	*d(H···A)* (Å)	*d(D···A)* (Å)	*(DĤA)* (°)
x, y, z	O15W···O4A	n/a	2.782(9)	n/a
x, y, z	O16W···O4A	n/a	2.649(8)	n/a
-1+x, -1+y, z	O11W···O4B	n/a	2.574(8)	n/a
-1+x, -1+y, z	O17W···O4B	n/a	2.622(8)	n/a
x, y, z	N1A–H···O16W	1.95	2.916(8)	160
–1+x, y, z	N10A–H···O9W	2.16	2.857(10)	125
–1+x, –1+y, z	N1B–H···O11W	2.02	2.932(8)	151
x, y, z	N19B–H···O2C	2.14	2.912(10)	133
x, y, z	N19B–H···O2D	2.29	3.080(10)	135
x, y, z	N19A–H···O3C	2.28	3.059(10)	134
x, y, z	N19A–H···O3D	2.08	2.929(10)	142
x, –1+y, z	N10B–H···O6	2.17	2.963(10)	134
–1+x, –1+y, z	N28B–H···O17W	2.07	2.994(8)	153
x, y, z	N28A–H···O4A	2.43	3.244(8)	138
x, y, z	N28A–H···O15W	2.46	3.317(10)	144

Table S6 Exchange coupling constants J_{iso} ($H = J_{iso}\, S_1 \bullet S_2$) calculated by DFT using different functionals and basis sets for the cryptate reported in reference 24b.



	J_{iso} (cm^{-1})	Cu-Cu (Å)	Cu-O-Cu (º)
M06/TZVP	1190	3.895	165.4
B3LYP/TZVP	1104	3.895	165.4
B3LYP/6-311G(d)^{a}	1094	3.895	165.4
B3LYP/6-311G(d)^{b}	898	3.929	164.9
Exp.	865 $\pm$ 50	3.900	174.0

^{a} Structures optimized at the M06/TZVP level. ^{b} Structures optimized at the B3LYP/6-311G(d) level.

Table S7 Experimental (X-ray) and calculated (DFT) bond distances (Å) and angles (º) of the coordination spheres of the $[Cu_2L(\mu\text{-}PhPO_4)]^{2+}$ and $[Cu_2L(\mu\text{-}PhPO_4)(NO_3)]^{+}$ cation complexes.

	$[Cu_2L(\mu\text{-}PhPO_4)]^{2+}$			$[Cu_2L(\mu\text{-}PhPO_4)(NO_3)]^{+}$	
	X-ray	**M06/TZVP**[a]	**B3LYP/6-311G(d)**[b]	**X-ray**	**B3LYP/6-311G(d)**[b]
Distances / Å					
N1–Cu1	2.068(6)	2.071	2.082	2.072(7)	2.075
N10–Cu1	2.092(8)	2.093	2.106	2.077(5)	2.109
N8–Cu1	1.925(6)	1.927	1.929	1.921(6)	1.937
O1–Cu1	1.872(4)	1.864	1.855	1.875(6)	1.833
O1C–Cu2	–			2.393(8)	2.264
N19–Cu2	2.083(6)	2.089	2.102	2.084(6)	2.119
N26–Cu2	1.929(6)	1.931	1.925	1.924(6)	1.946
N28–Cu2	2.073(6)	2.076	2.079	2.063(6)	2.134
O3–Cu2	1.862(6)	1.881	1.847	1.859(6)	1.864
Cu1···Cu2	5.812(1)	4.480	5.556	5.811(1)	5.664
Angles / º					
N1–Cu1–N10	164.4(2)	163.6	162.3	162.3(2)	162.5
N8–Cu1–O1	171.5(2)	172.7	155.5	164.6(3)	155.2
O1C–Cu2–N19	–			94.1(3)	100.2
O1C–Cu2–N28	–			90.1(3)	85.0
O1C–Cu2–N26	–			86.2(3)	84.1
O1C–Cu2–O3	–			100.9(3)	99.1
N19–Cu2–N28	160.9(2)	161.2	164.7	162.1(2)	161.6
N26–Cu2–O3	173.5(2)	150.8	173.2	173.6(3)	176.8

[a] Bulk solvent effects (water) included using polarized continuum model. [b] Optimizations in the gas phase.

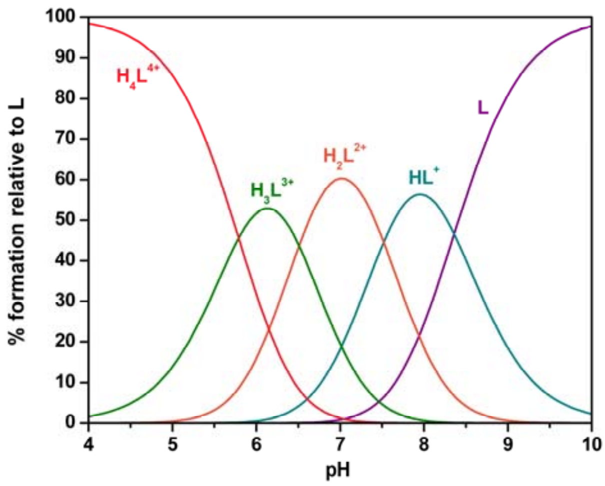


Fig. S1 Species distribution diagram of the protonation of L. $C_L = 1.0\times10^{-3}$ M.

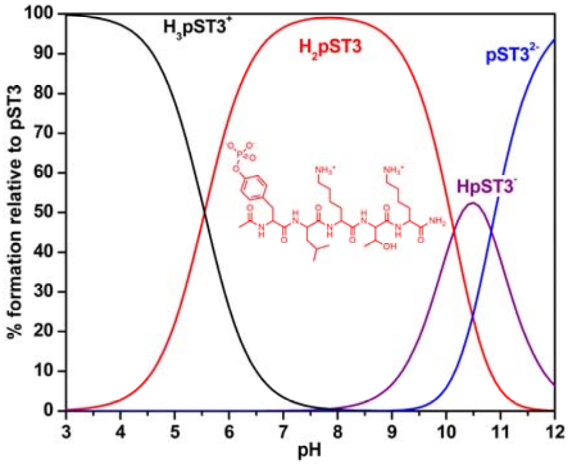


Fig. S2 Species distribution diagram of the protonation of H_2pST3. $C_{peptide} = 1.0\times10^{-3}$ M.

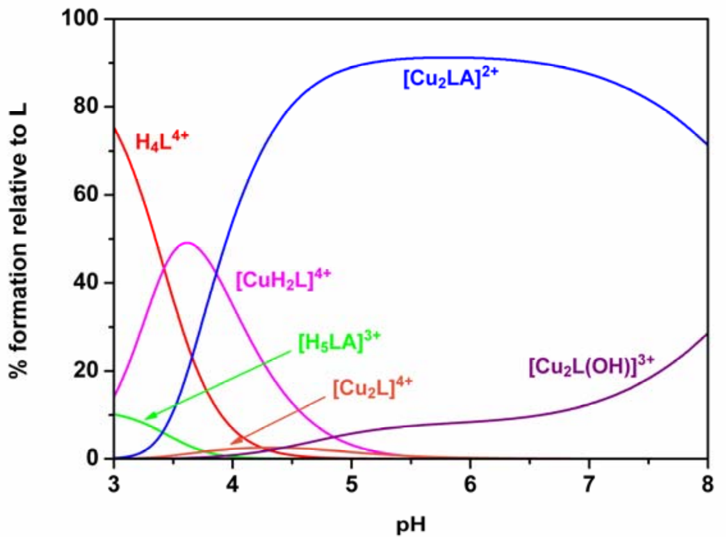


Fig. S3 Species distribution diagram calculated for the complexes of Cu^{2+} with L in presence of the $PhPO_4^{2-}$ anion (A = $PhPO_4^{2-}$). $C_{Cu} = 2\times C_L = 2\times C_A = 2.0\times10^{-3}$ M.

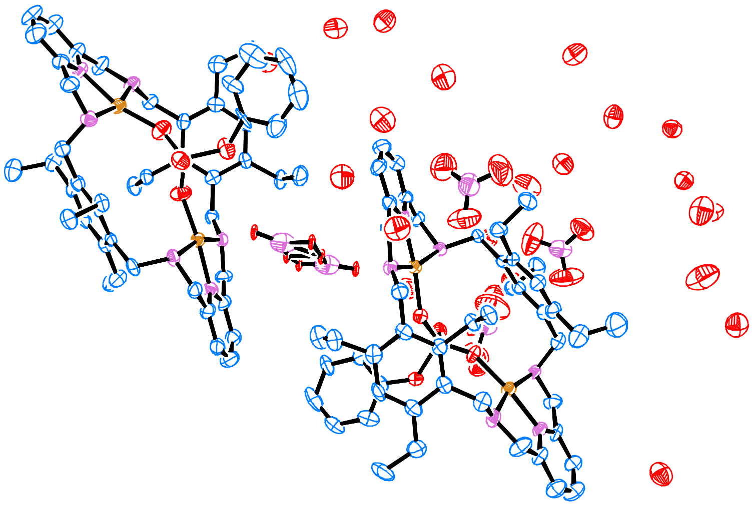


Fig. S4 Thermal ellipsoid plot (ellipsoids set at 50% probability) for the $[Cu_2L(\mu\text{-}PhPO_4)][Cu_2L(\mu\text{-}PhPO_4)(NO_3)]3NO_3{\cdot}24H_2O$ asymmetric unit, depicting all the water molecules and anions. Hydrogen atoms were omitted for clarity.

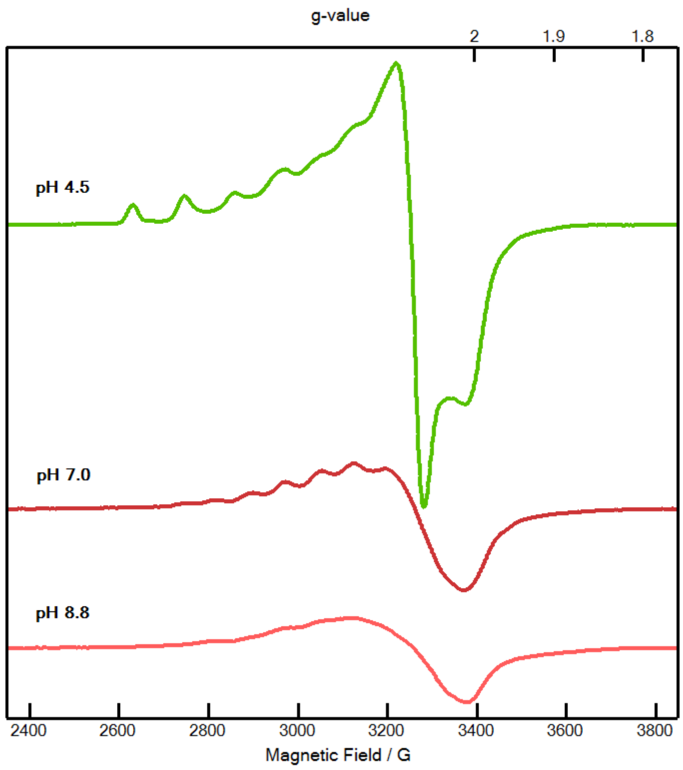


Fig. S5 X-band EPR spectra of copper(II) complexes (Cu^{2+}:L 2:1) at three different pH values. All spectra recorded at 135 K, 2.0 mW microwave power, 1.0 mT modulation amplitude, and frequency (υ) of 9.5 GHz. All samples in H_2O:MeOH (50:50 v/v) solution.

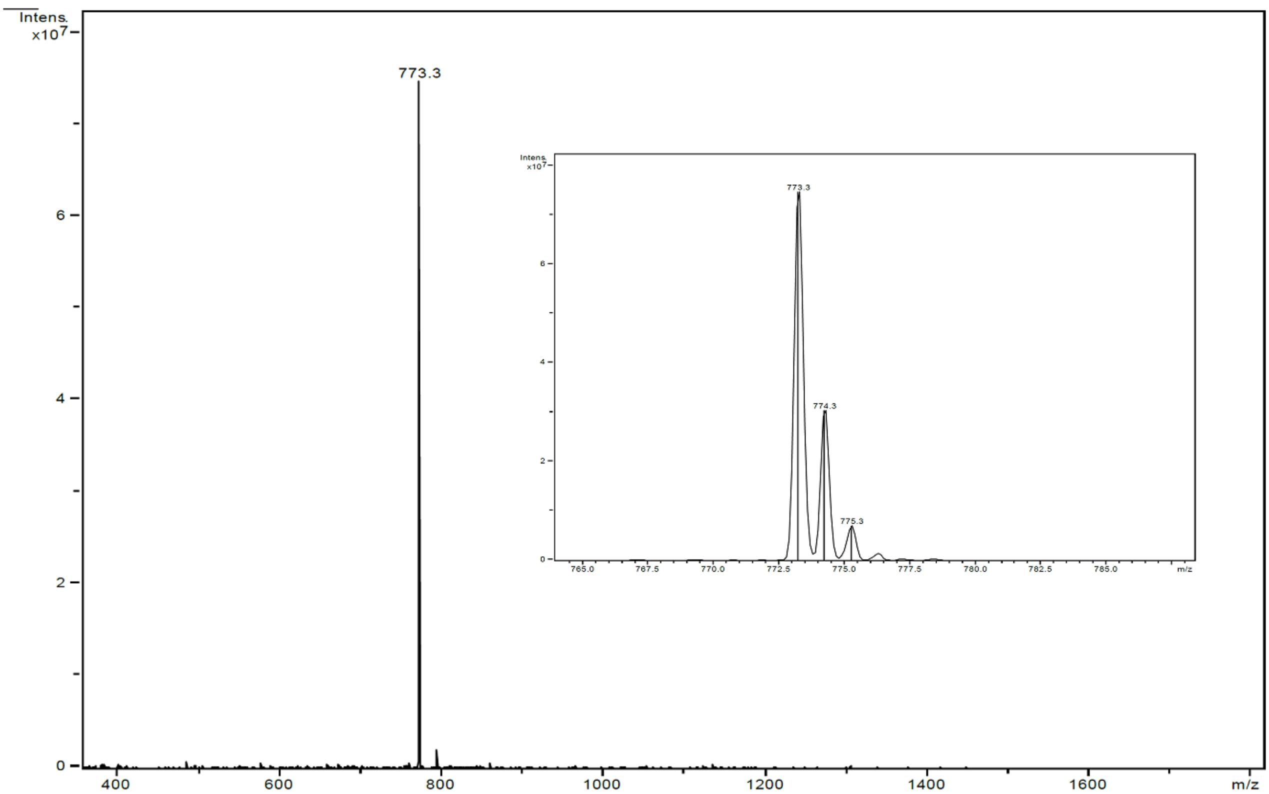


Fig. S6 ESI mass spectrum of H_2pST3, recorded in positive ion mode.

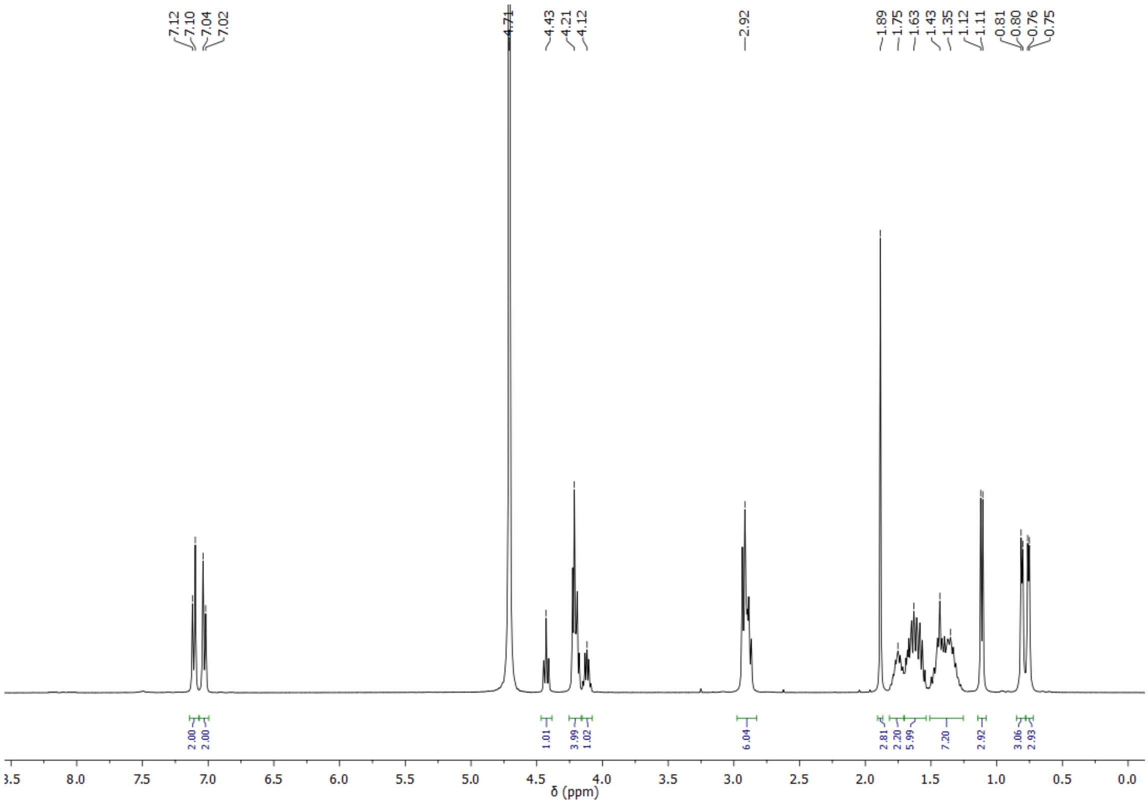


Fig. S7 ^{1}H NMR spectrum of H_2pST3 in D_2O.

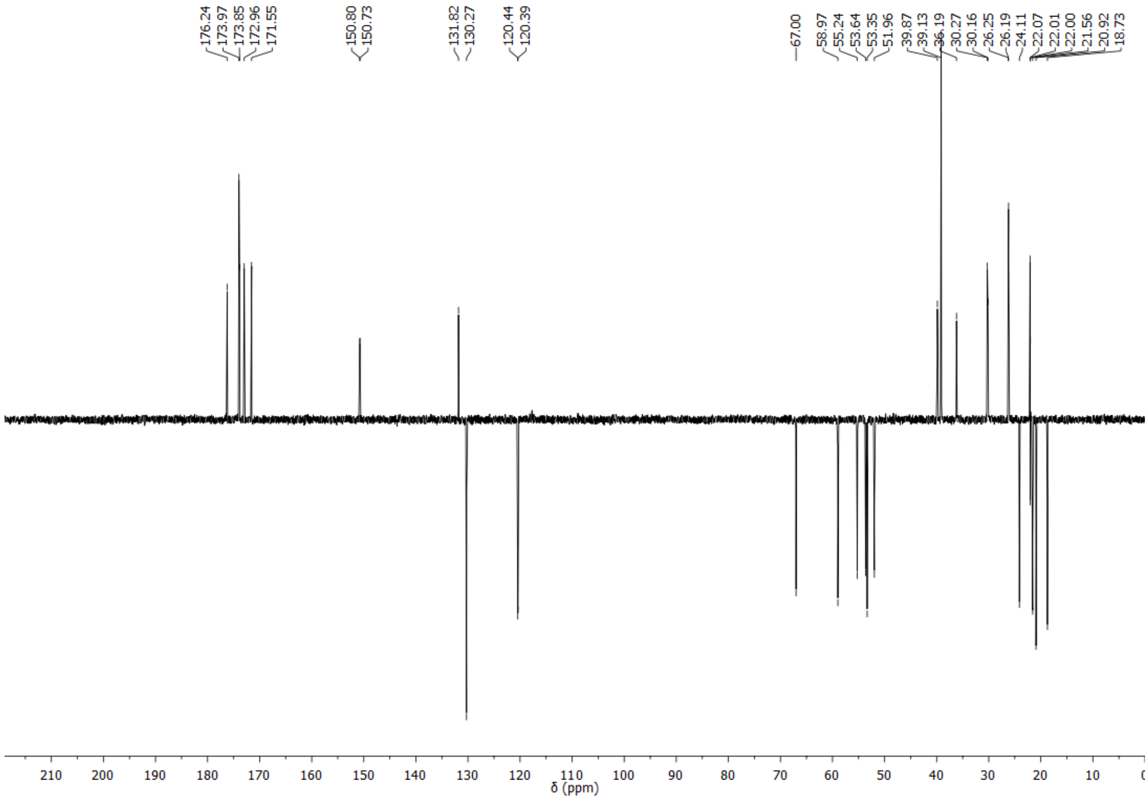


Fig. S8 APT NMR spectrum of H_2pST3 in D_2O.

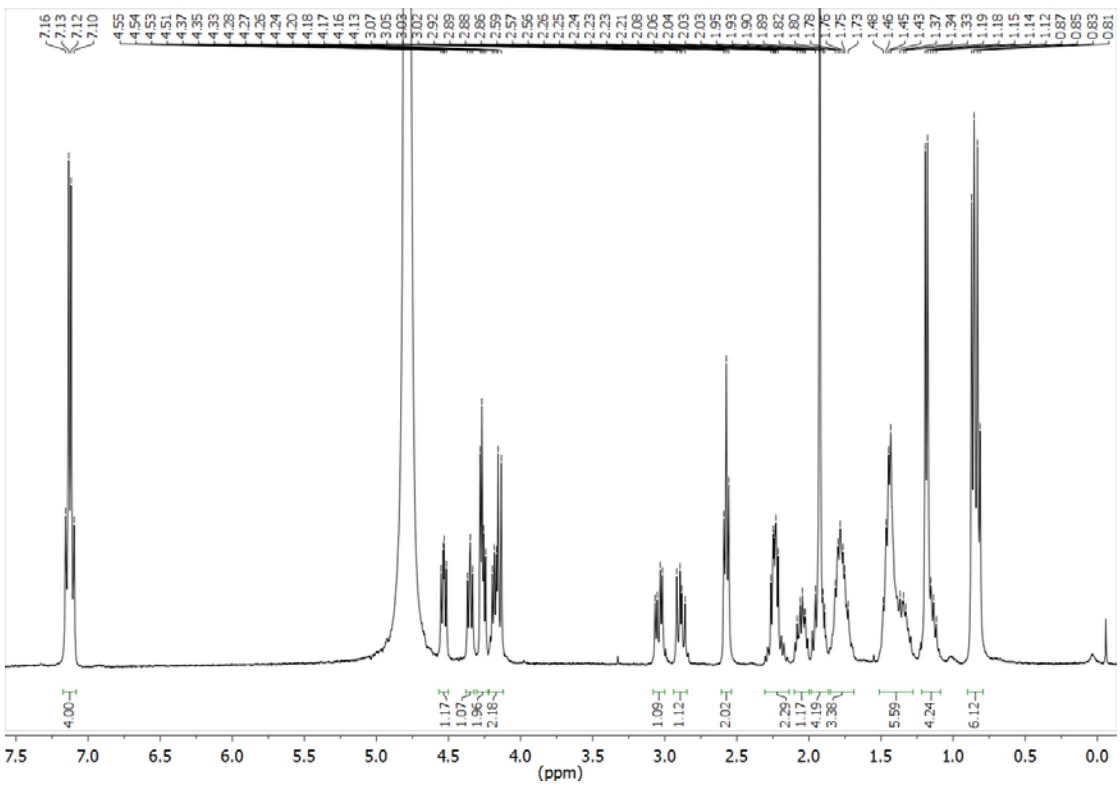


Fig. S9 ^{1}H NMR spectrum of H_3pST1 in D_2O.

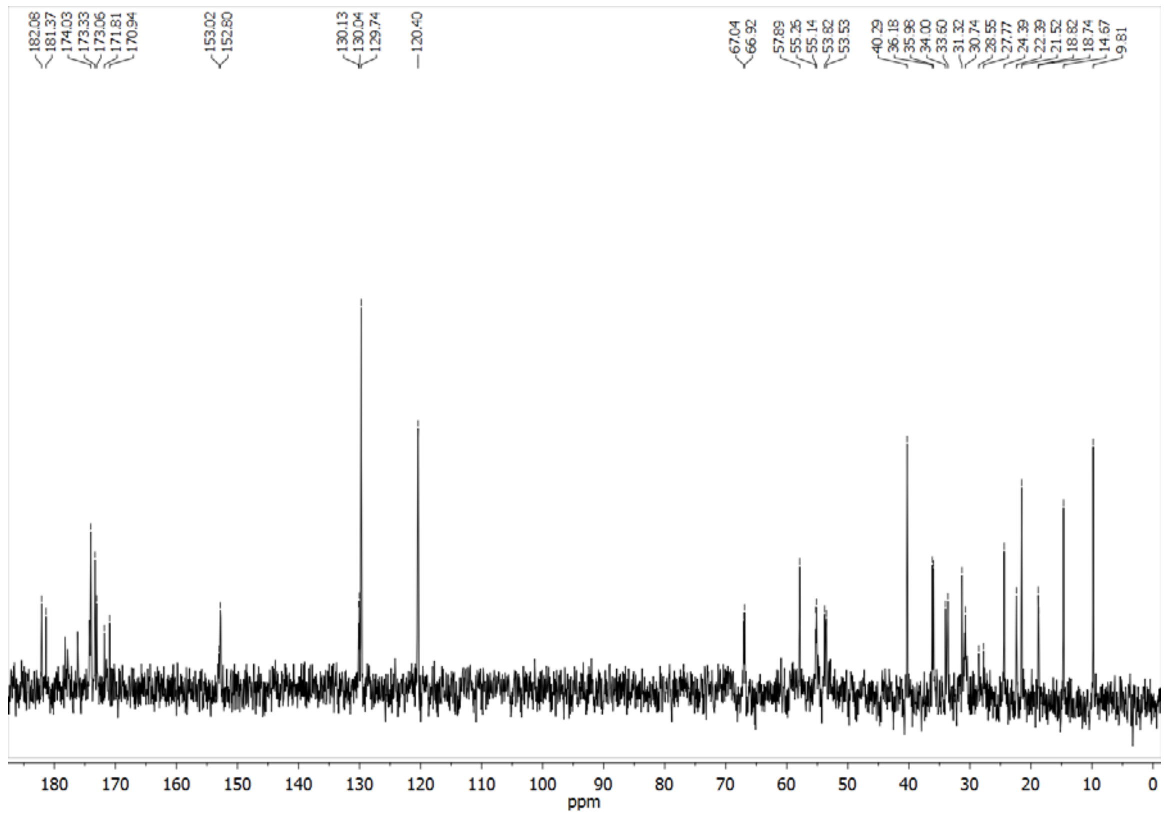


Fig. S10 ^{13}C NMR spectrum of H_3pST1 in D_2O.

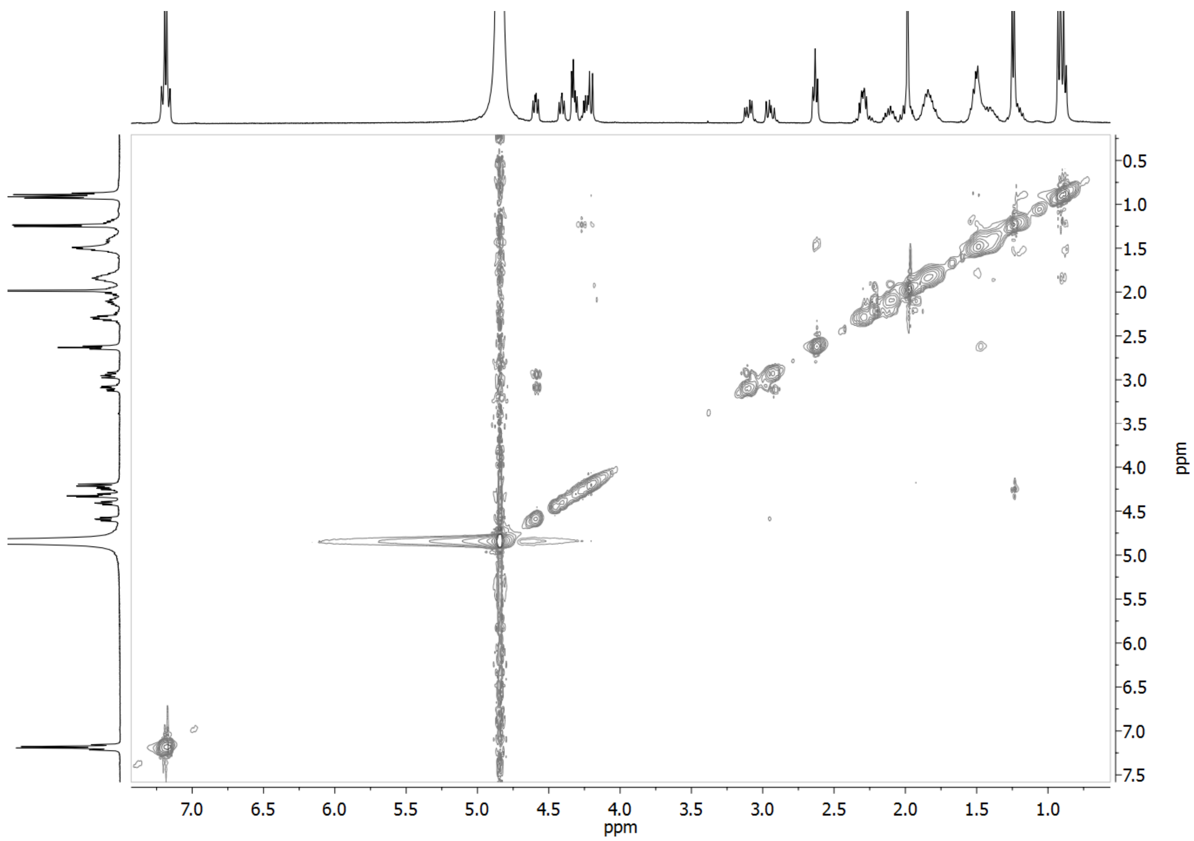


Fig. S11 COSY spectrum of H_3pST1 in D_2O.

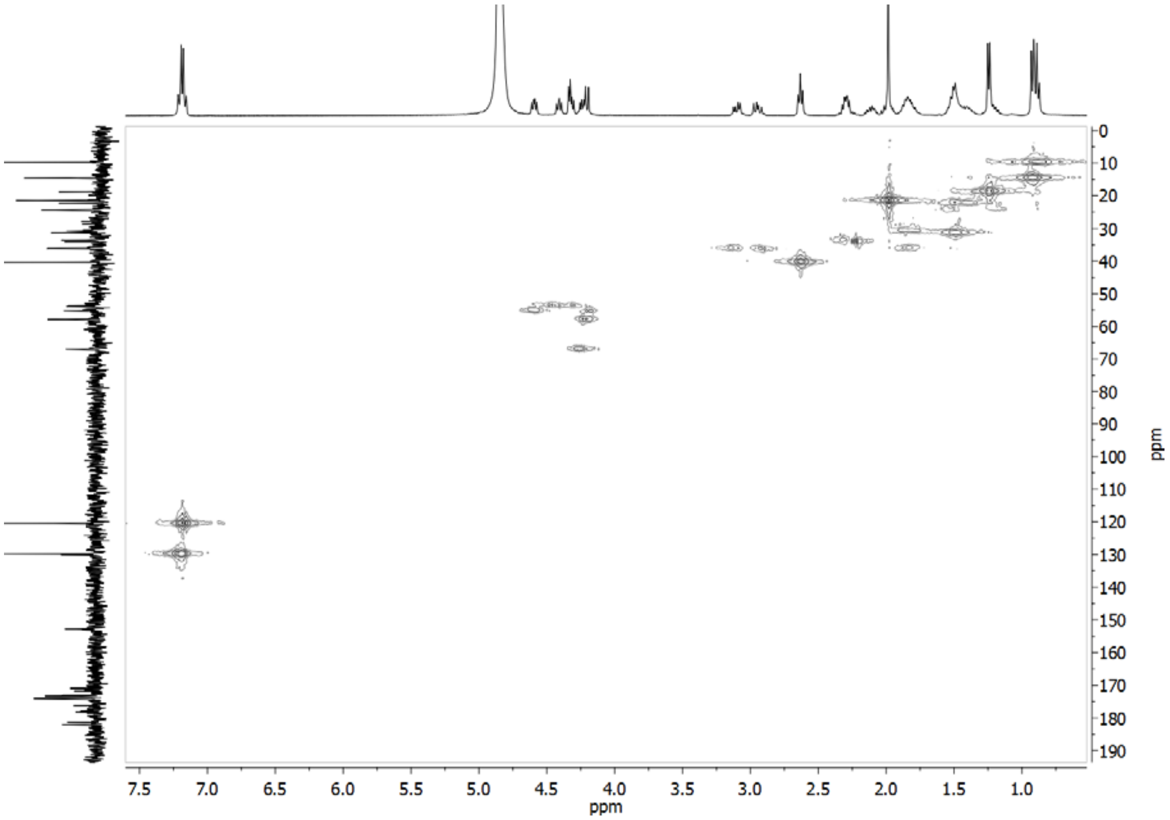


Fig. S12 HMQC spectrum of H_3pST1 in D_2O.

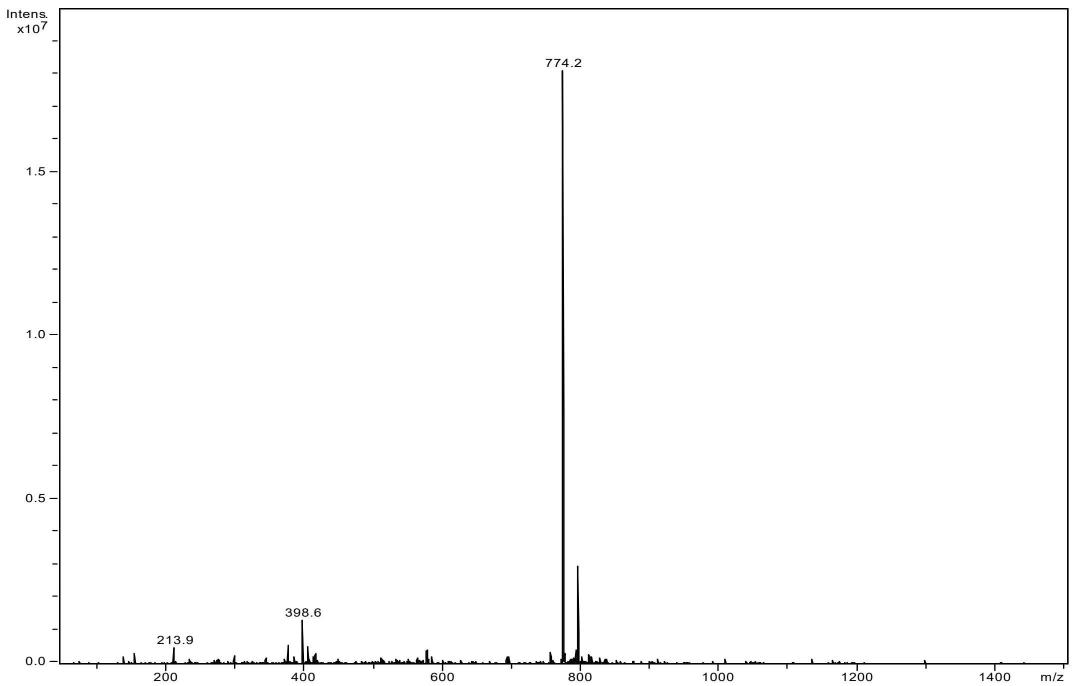


Fig. S13 ESI mass spectrum of H_3pST1 in H_2O/MeOH, recorded in positive ion mode.

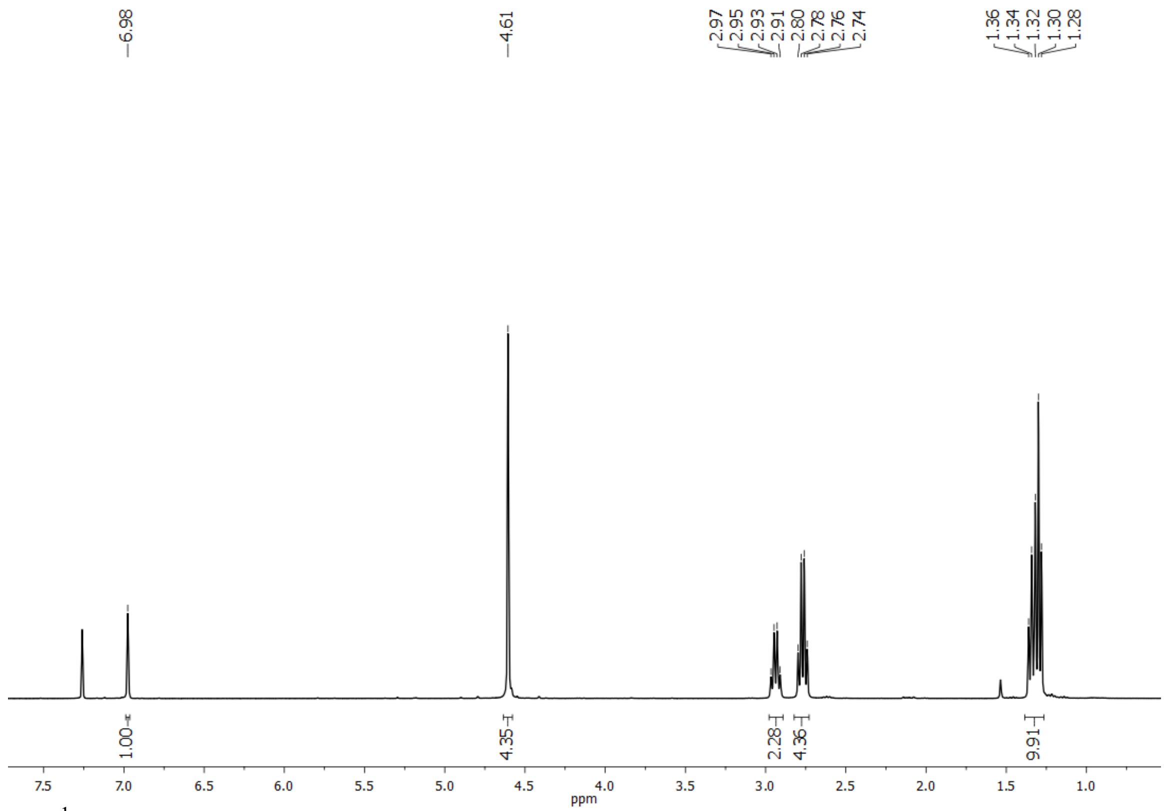


Fig. S14 [1]H NMR spectrum of 2,4-bis(bromomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

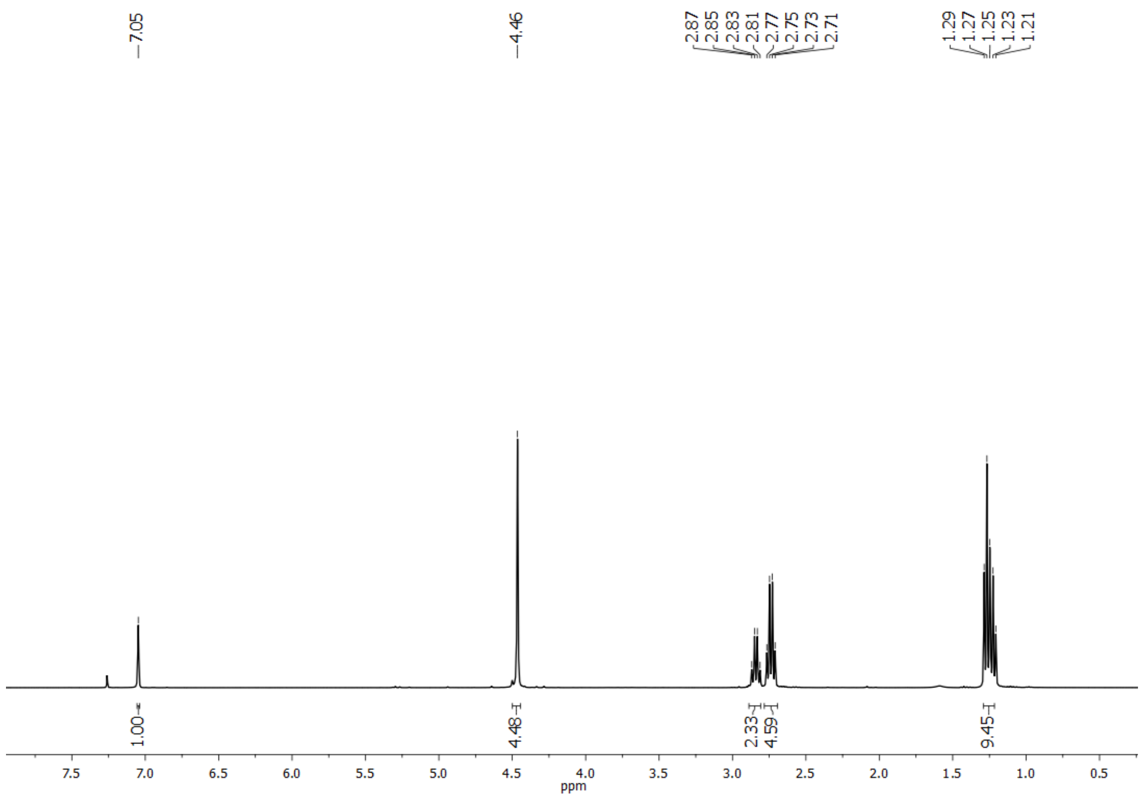


Fig. S15 [1]H NMR spectrum of 2,4-bis(azidomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

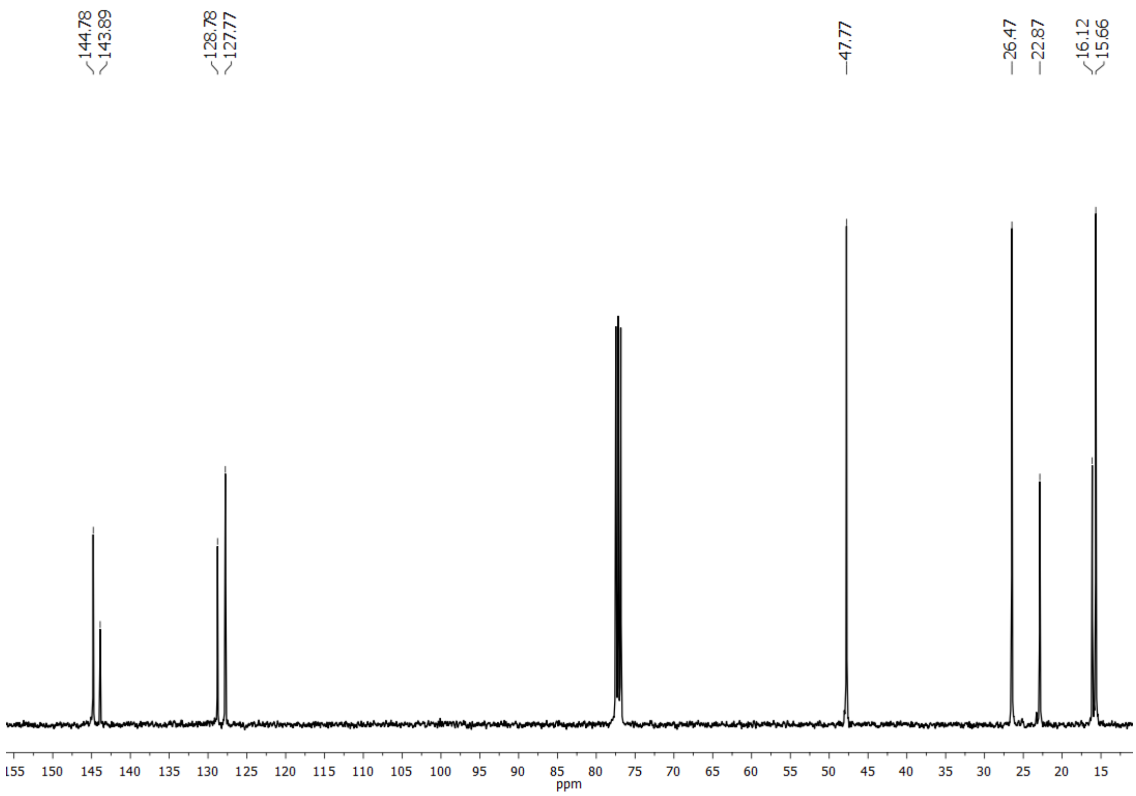


Fig. S16 ^{13}C NMR spectrum of 2,4-bis(azidomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

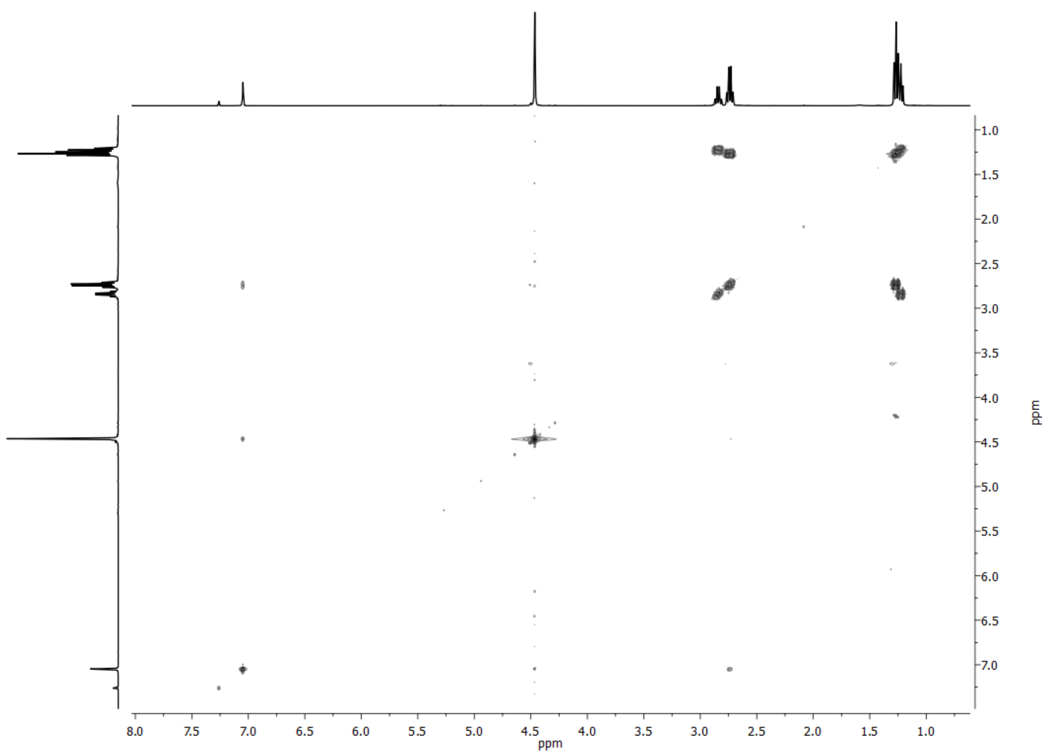


Fig. S17 COSY spectrum of 2,4-bis(azidomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

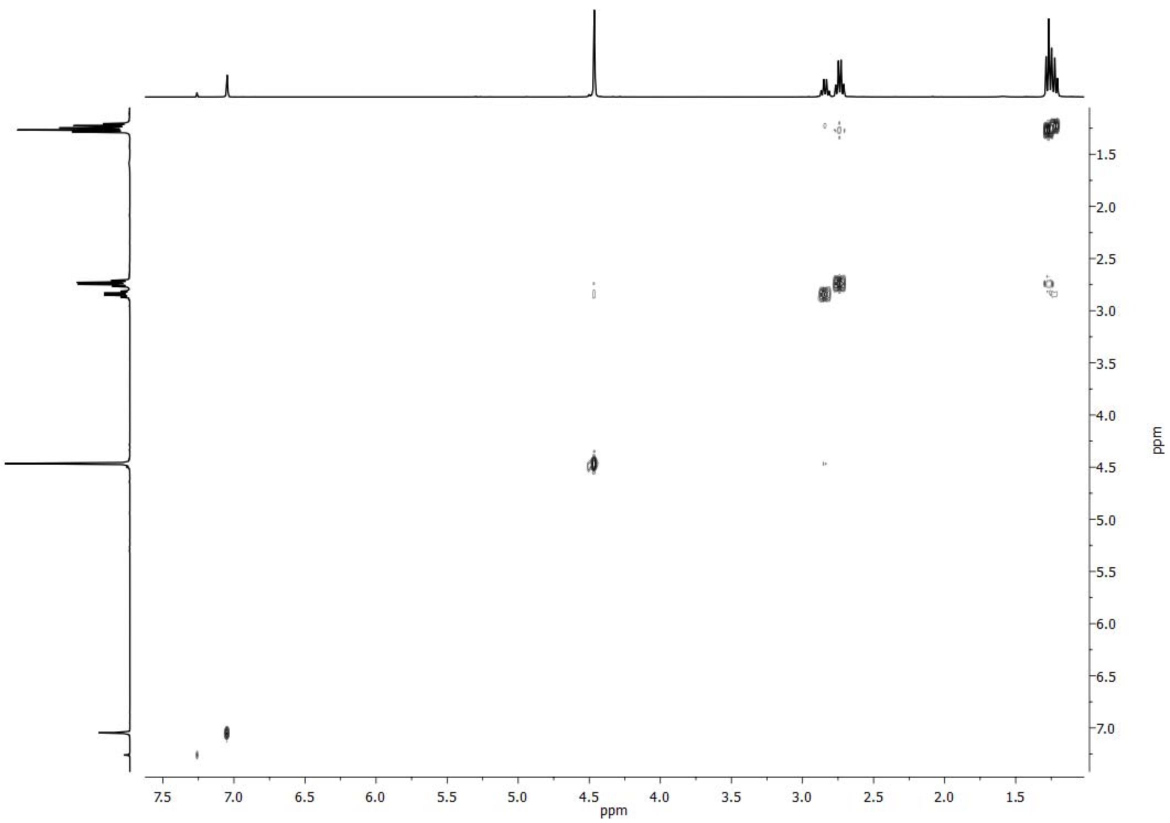


Fig. S18 NOESY spectrum of 2,4-bis(azidomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

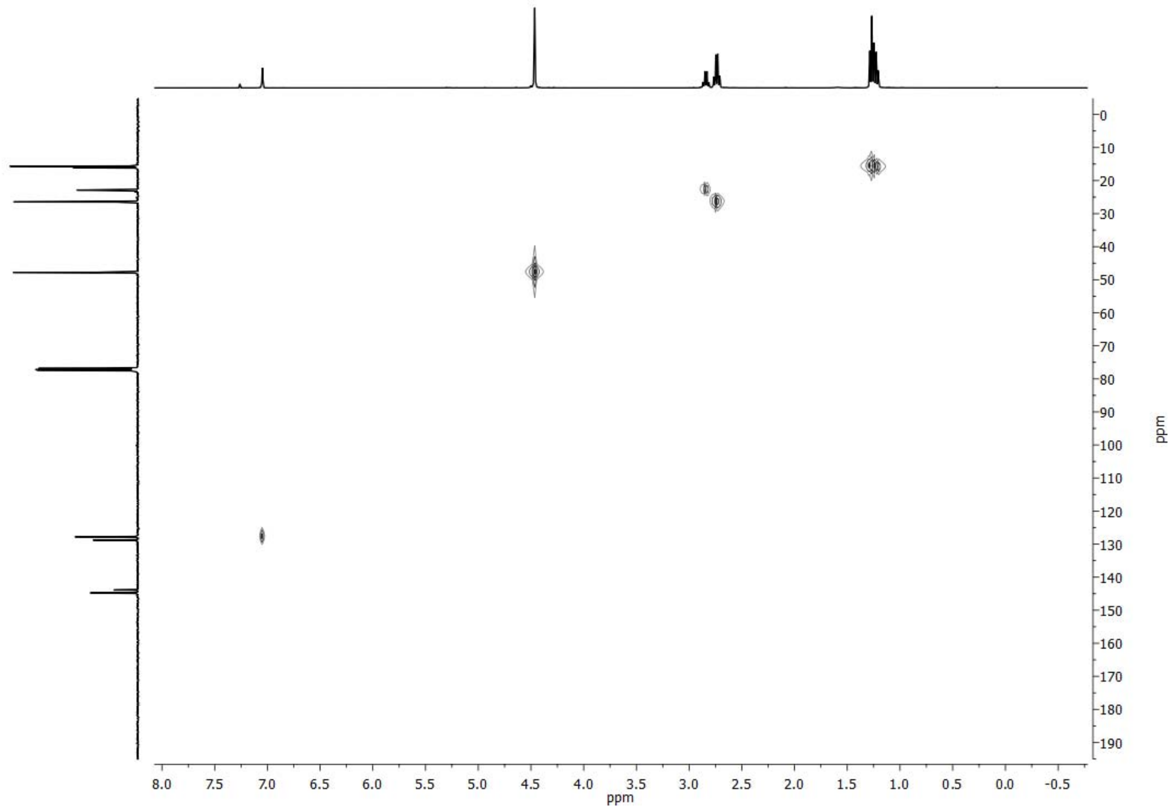


Fig. S19 HMQC spectrum of 2,4-bis(azidomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

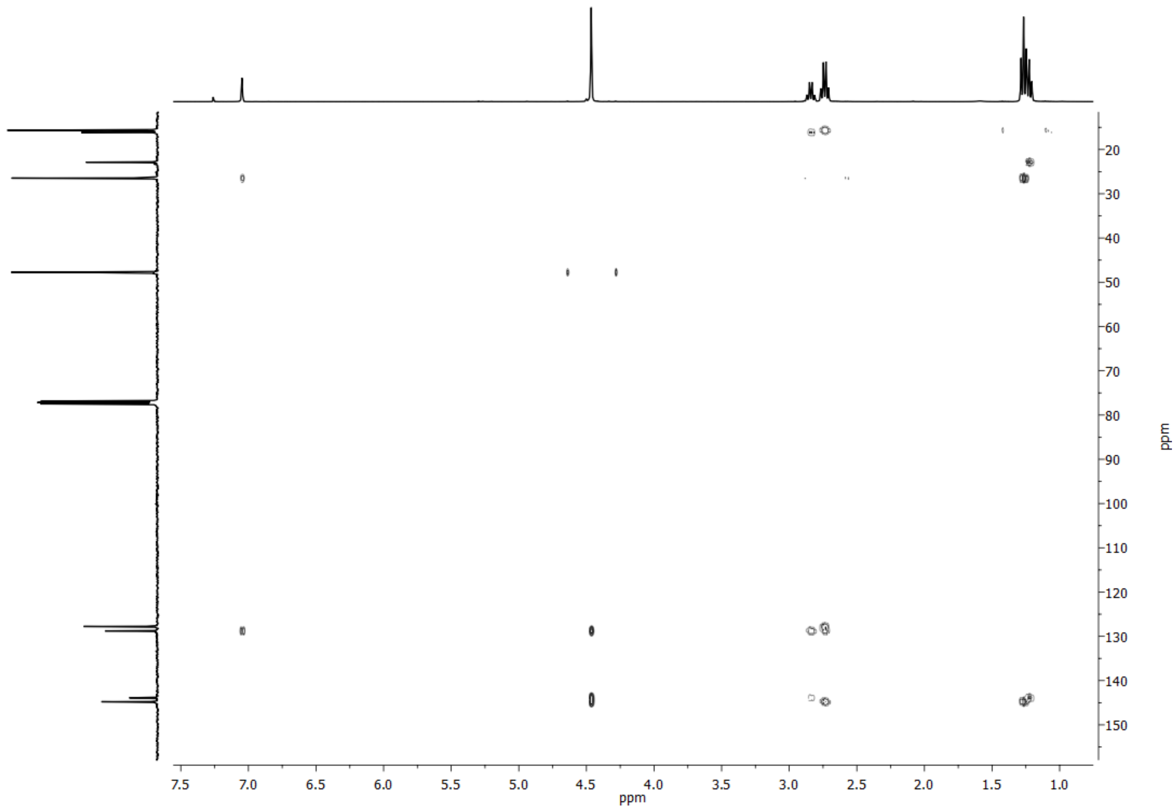


Fig. S20 HMBC spectrum of 2,4-bis(azidomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

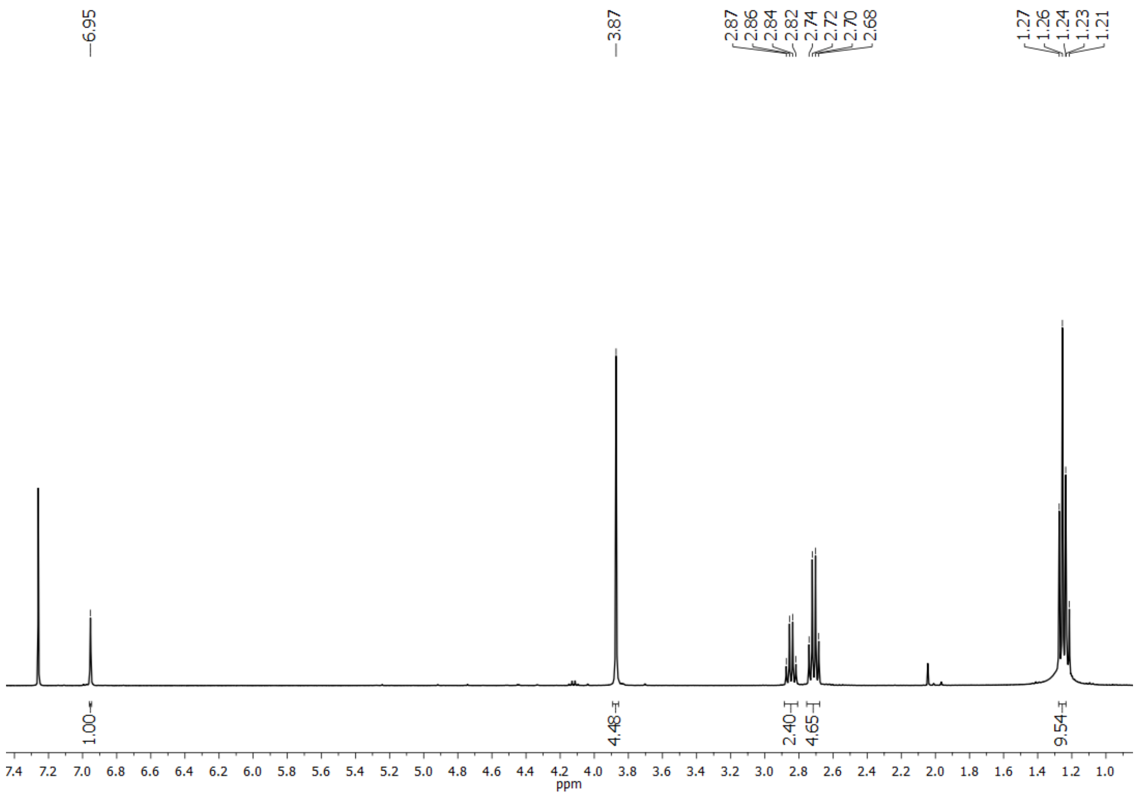


Fig. S21 ^{1}H NMR spectrum of 2,4-bis(aminomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

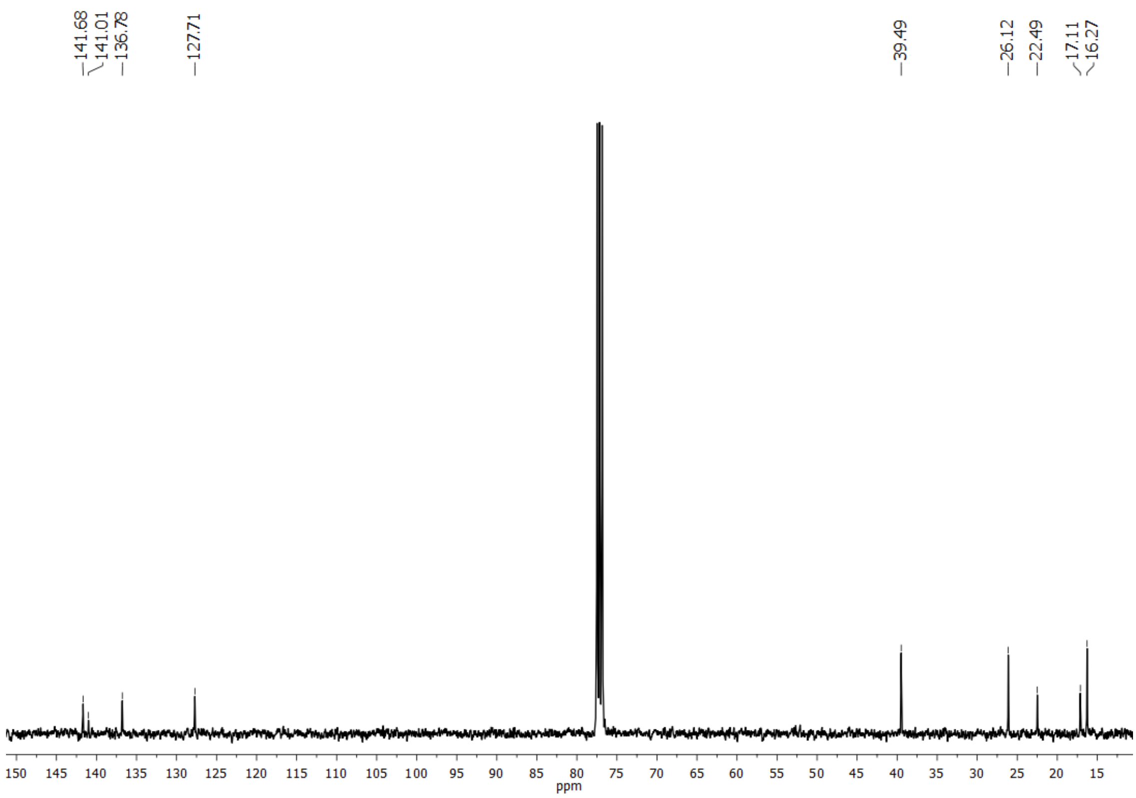


Fig. S22 ^{13}C NMR spectrum of 2,4-bis(aminomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

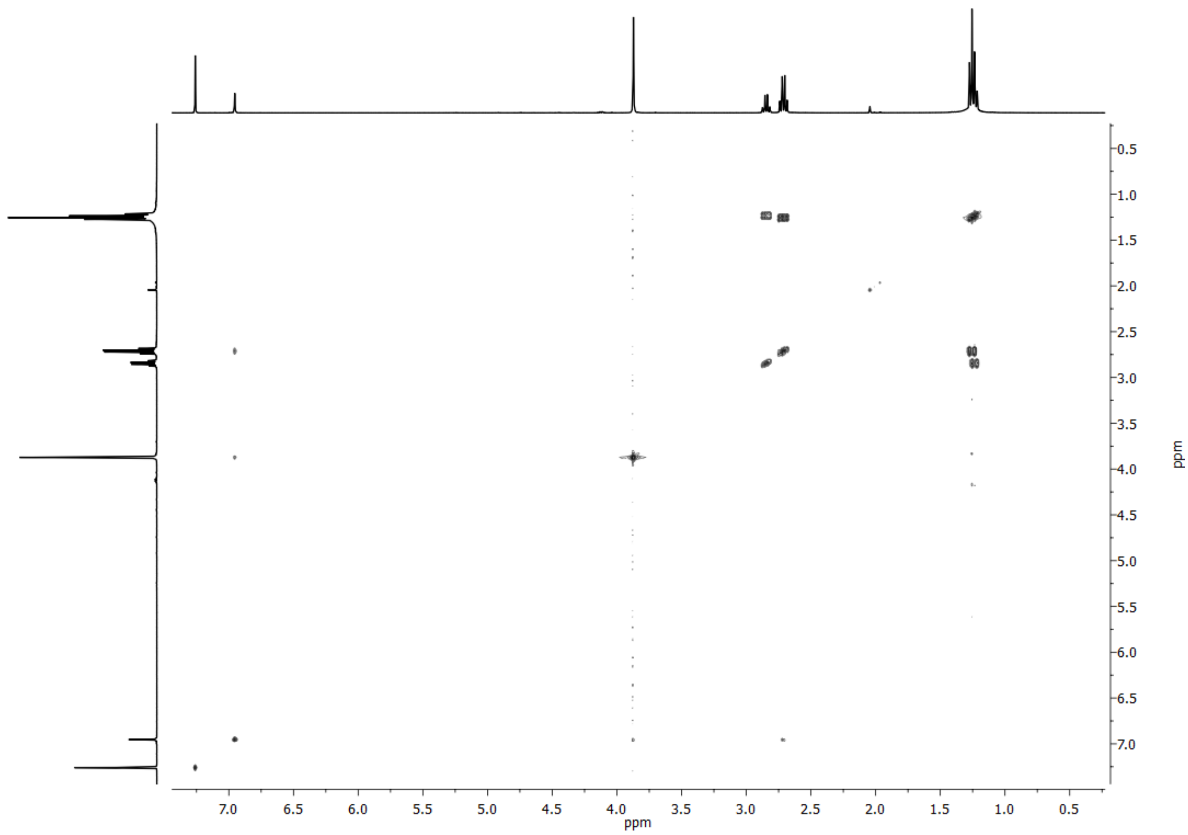


Fig. S23 COSY spectrum of 2,4-bis(aminomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

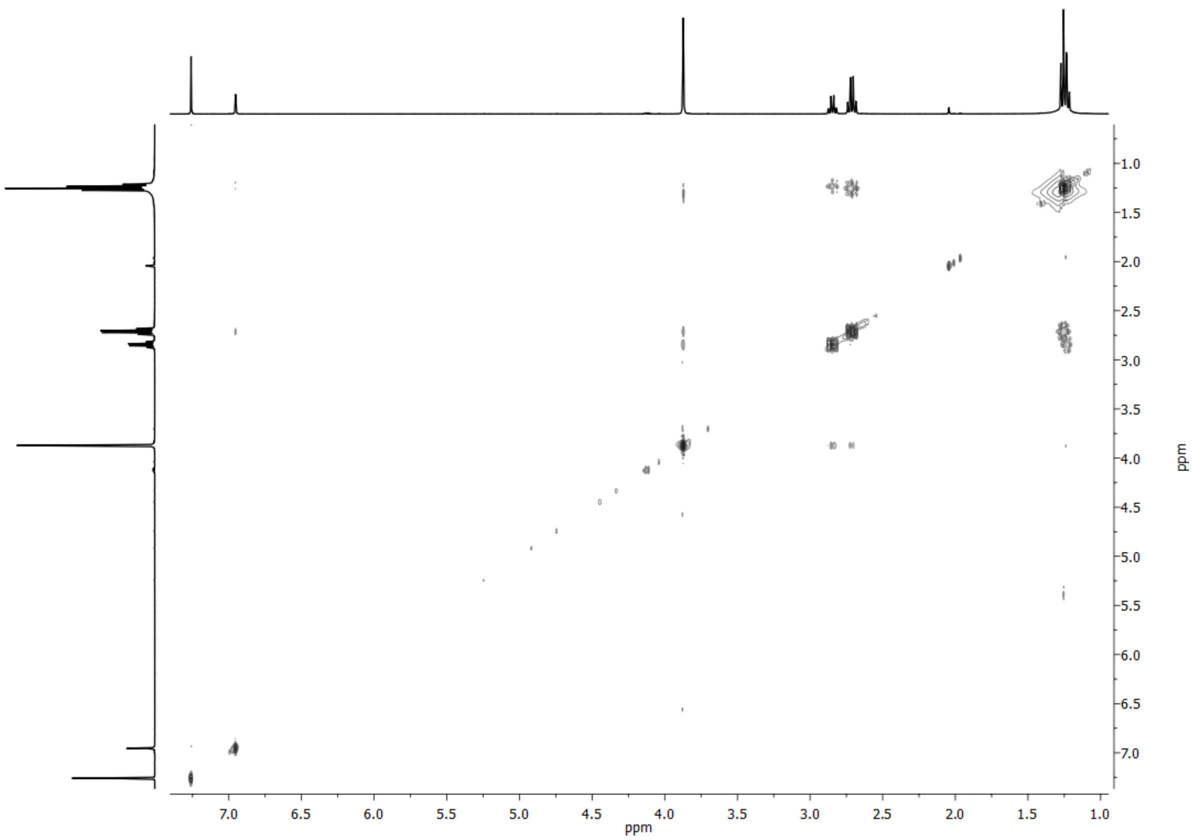


Fig. S24 NOESY spectrum of 2,4-bis(aminomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

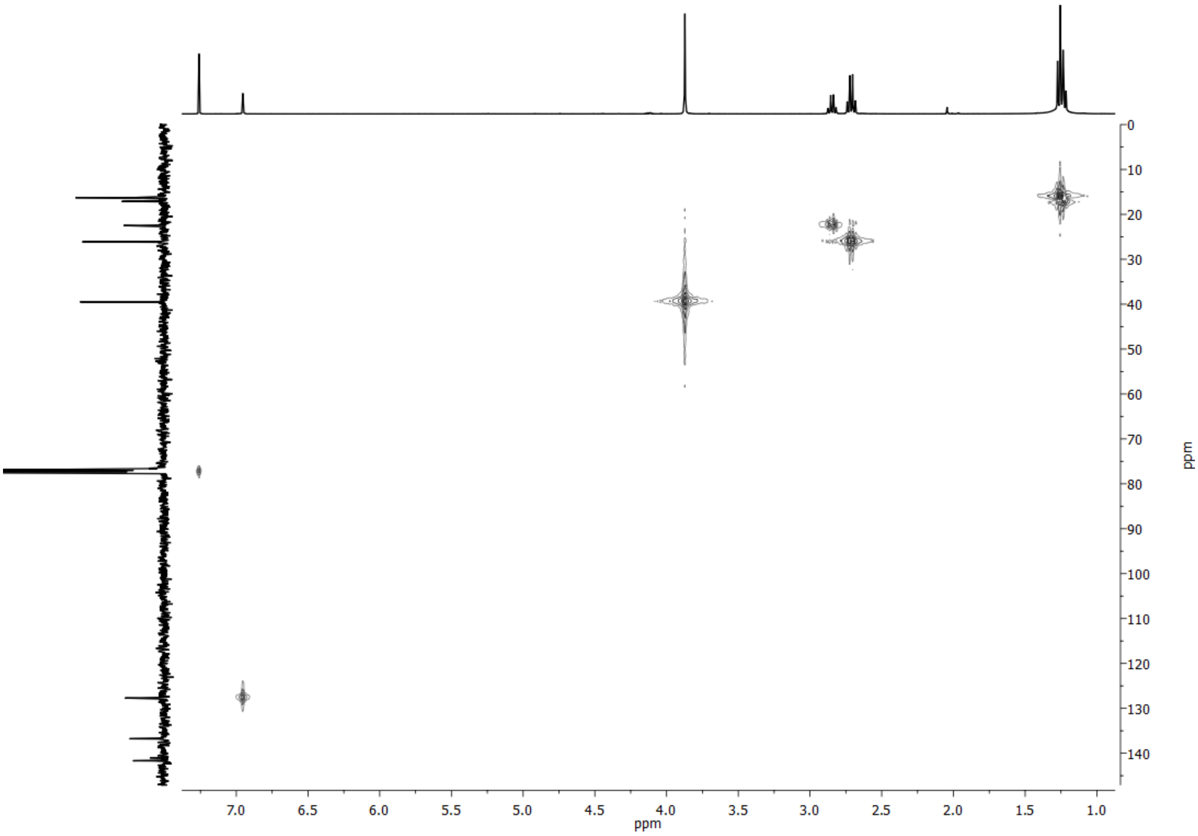


Fig. S25 HMQC spectrum of 2,4-bis(aminomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

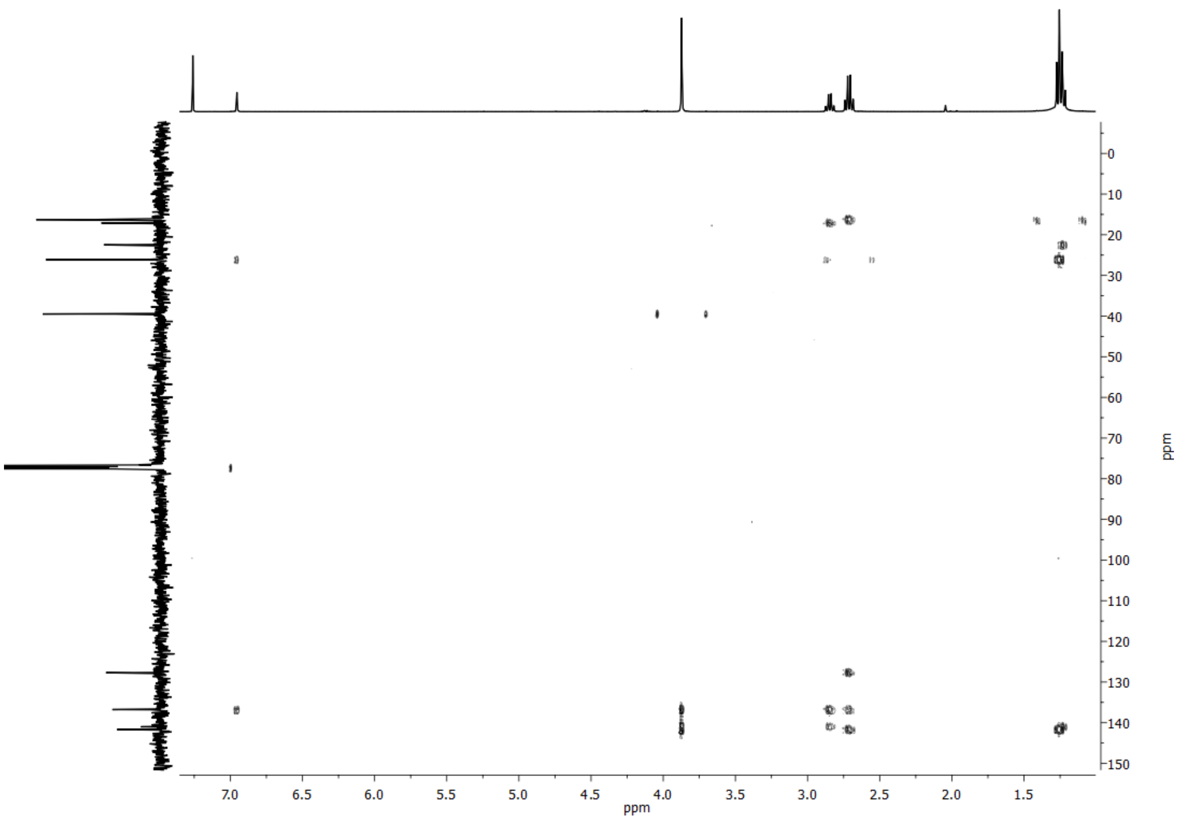


Fig. S26 HMBC spectrum of 2,4-bis(aminomethyl)-1,3,5-triethylbenzene in $CDCl_3$.

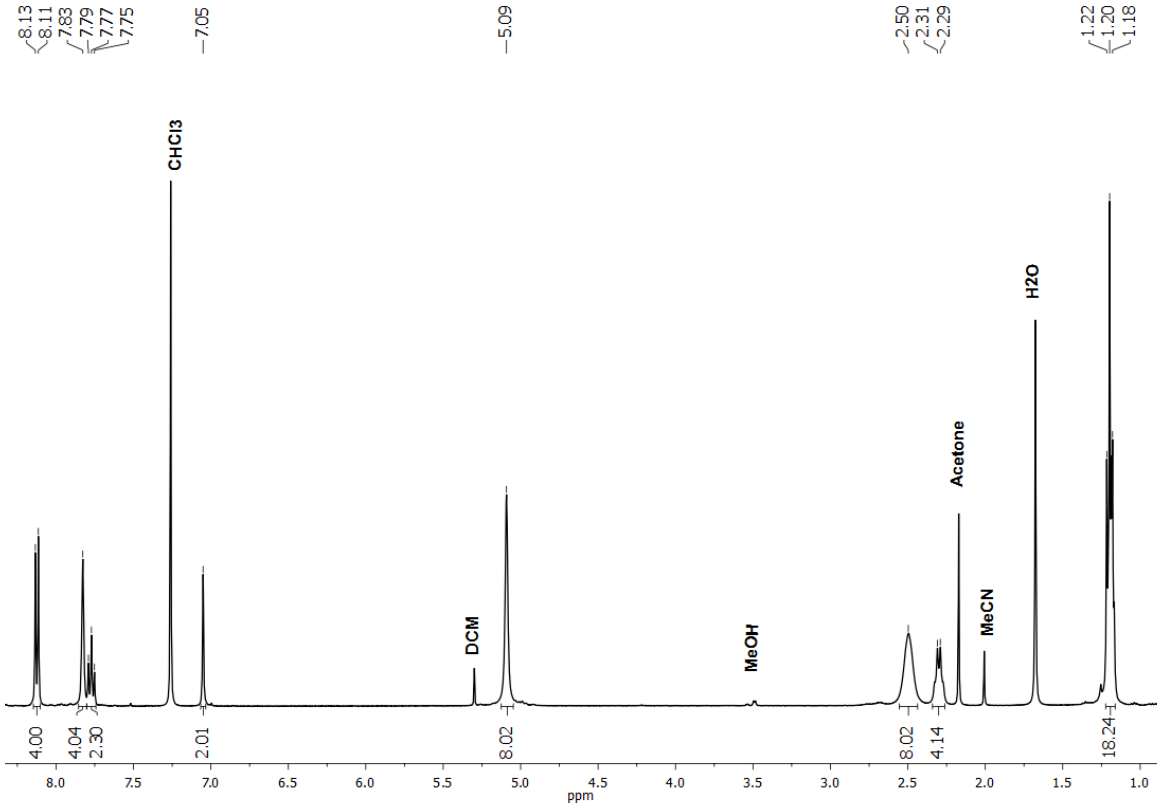


Fig. S27 [1]H NMR spectrum of L(imine) in $CDCl_3$.

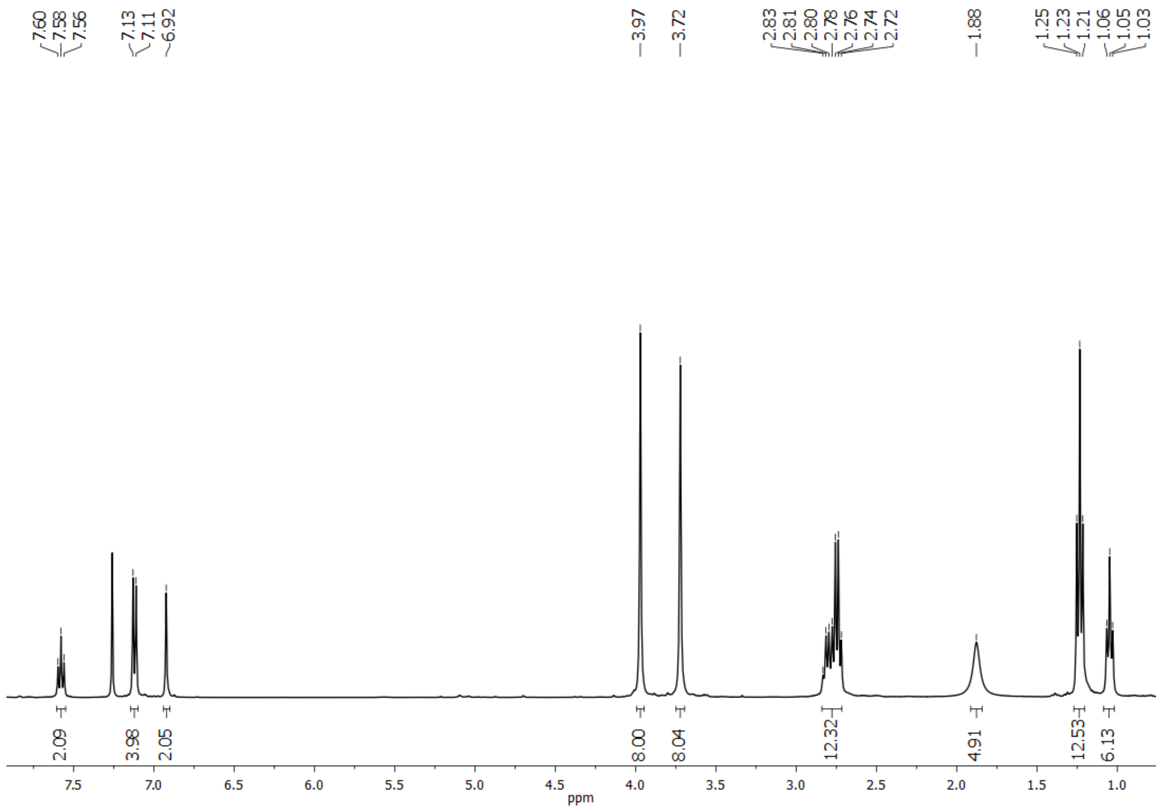


Fig. S28 [1]H NMR spectrum of L in $CDCl_3$.

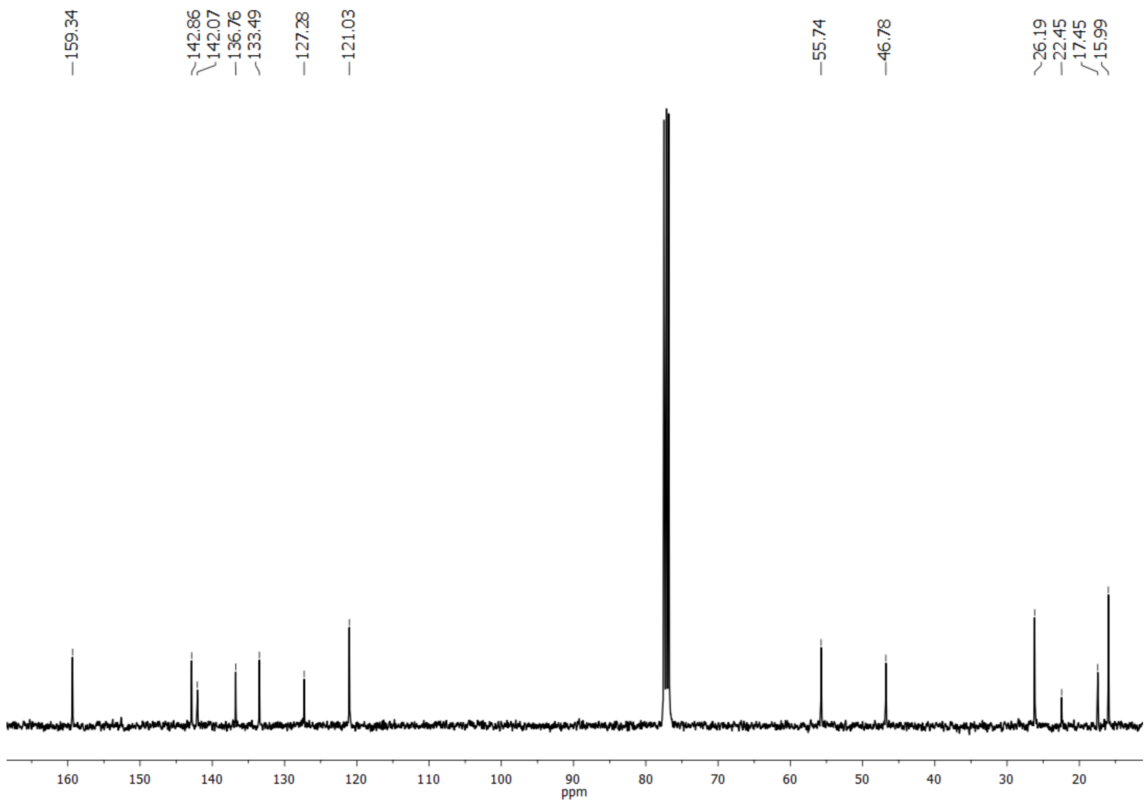


Fig. S29 ^{13}C NMR spectrum of L in $CDCl_3$

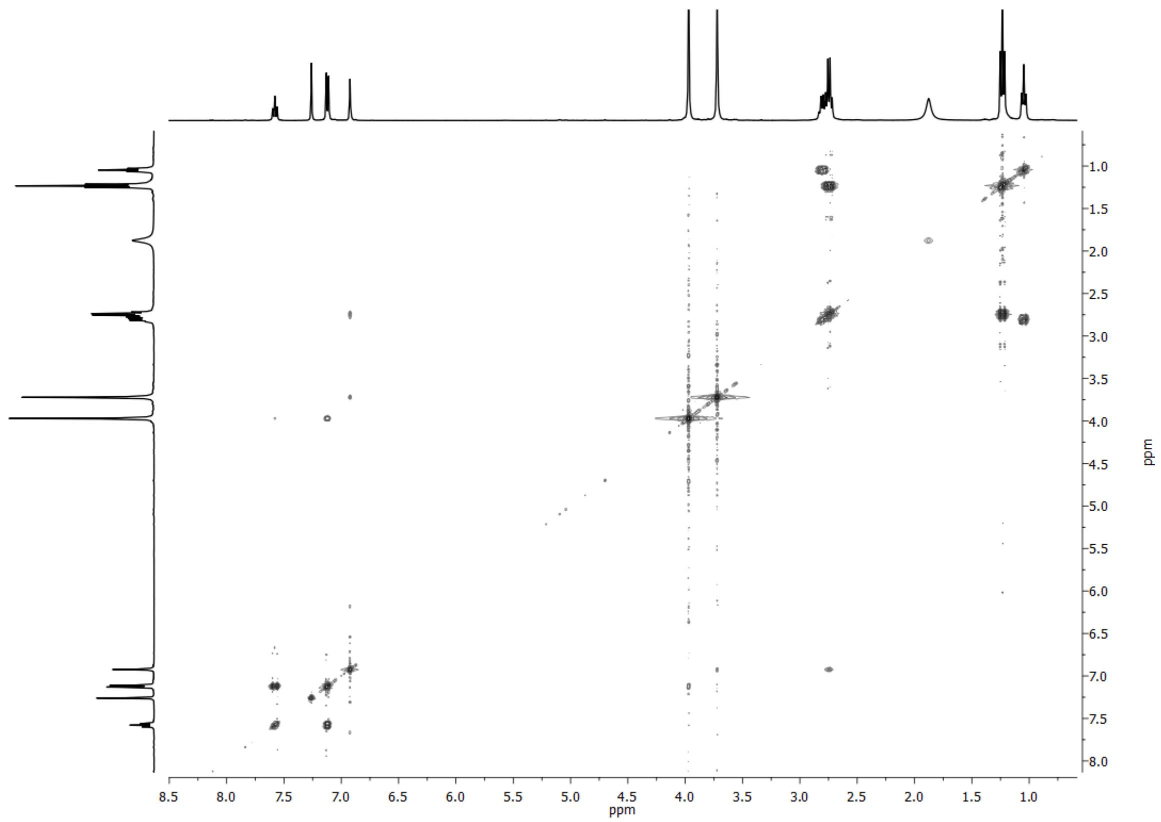


Fig. S30 COSY spectrum of L in $CDCl_3$.

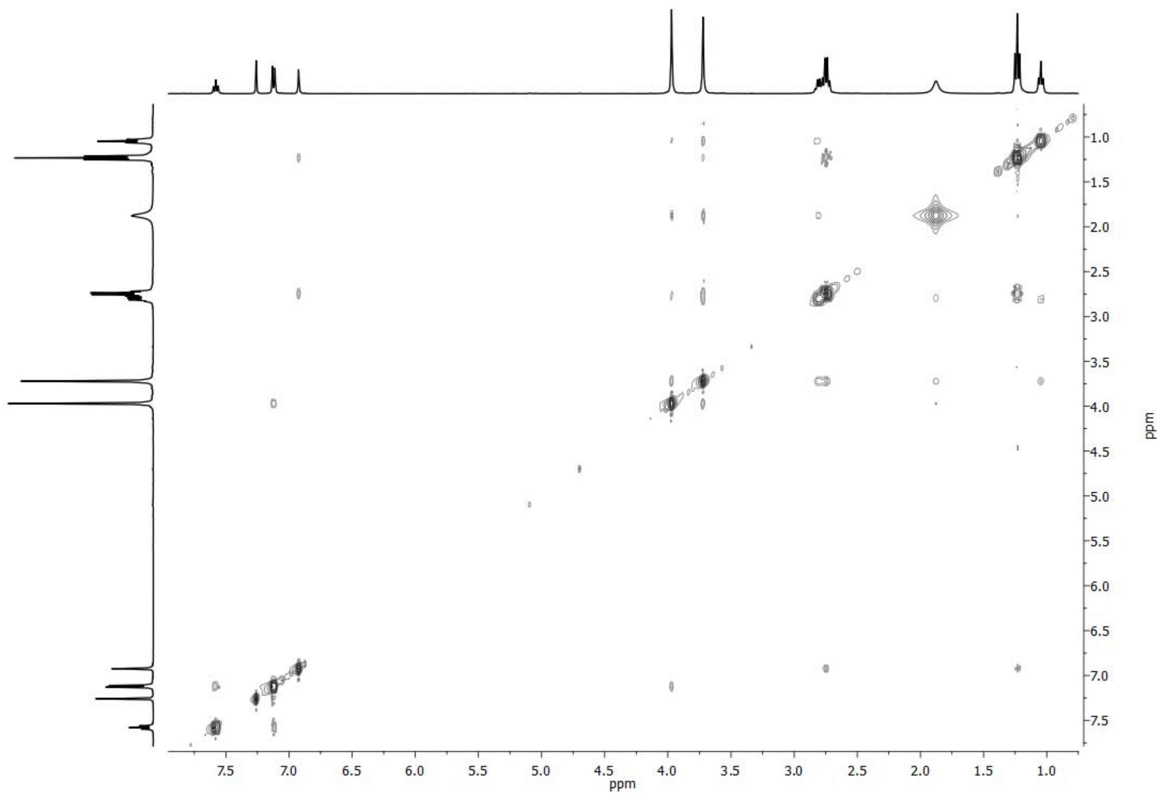


Fig. S31 NOESY spectrum of L in $CDCl_3$.

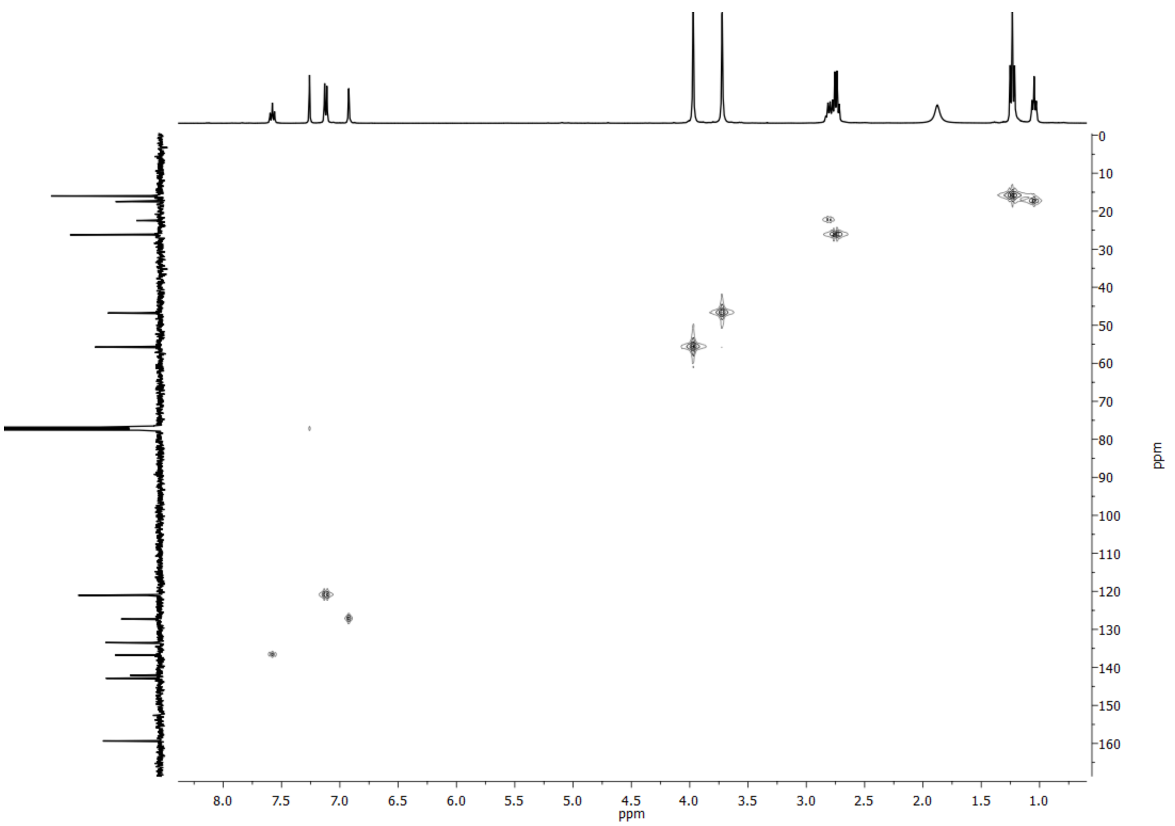


Fig. S32 HMQC spectrum of L in $CDCl_3$.

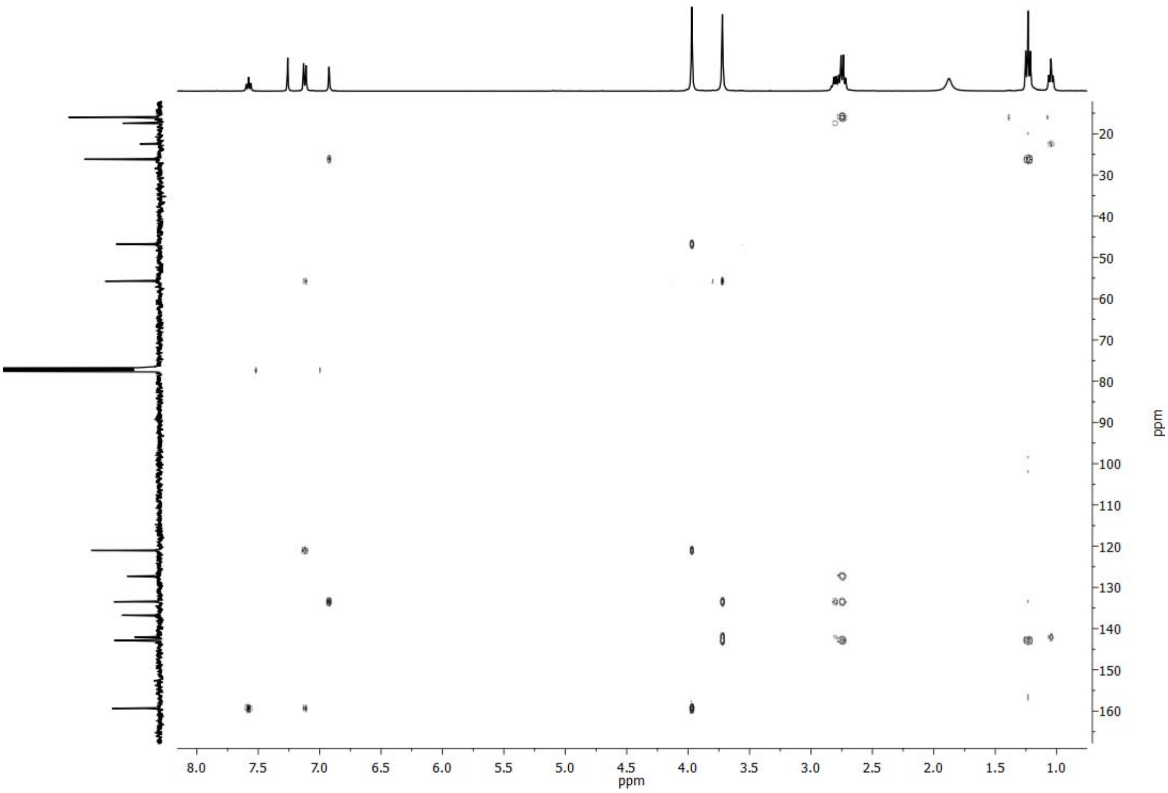


Fig. S33 HMBC spectrum of L in $CDCl_3$

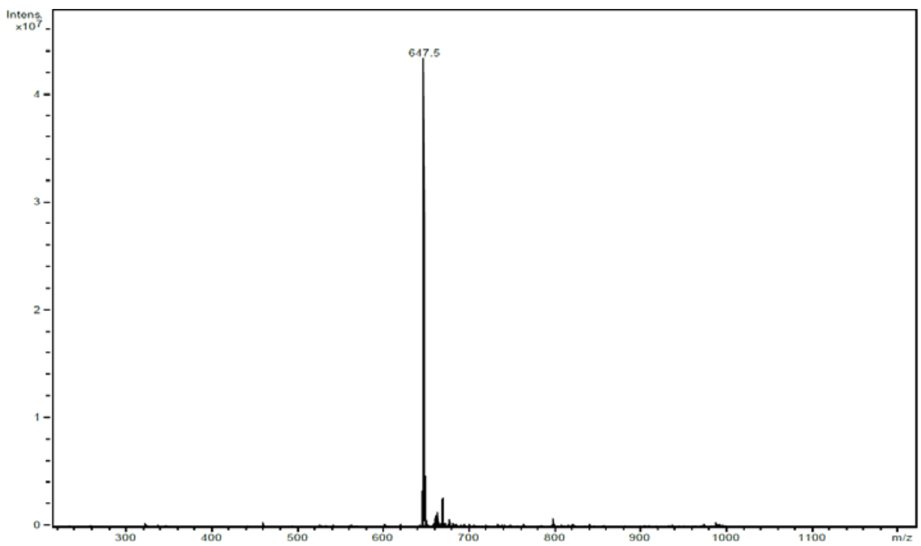


Fig. S34 ESI mass spectrum of L in H_2O/MeOH, recorded in positive ion mode.

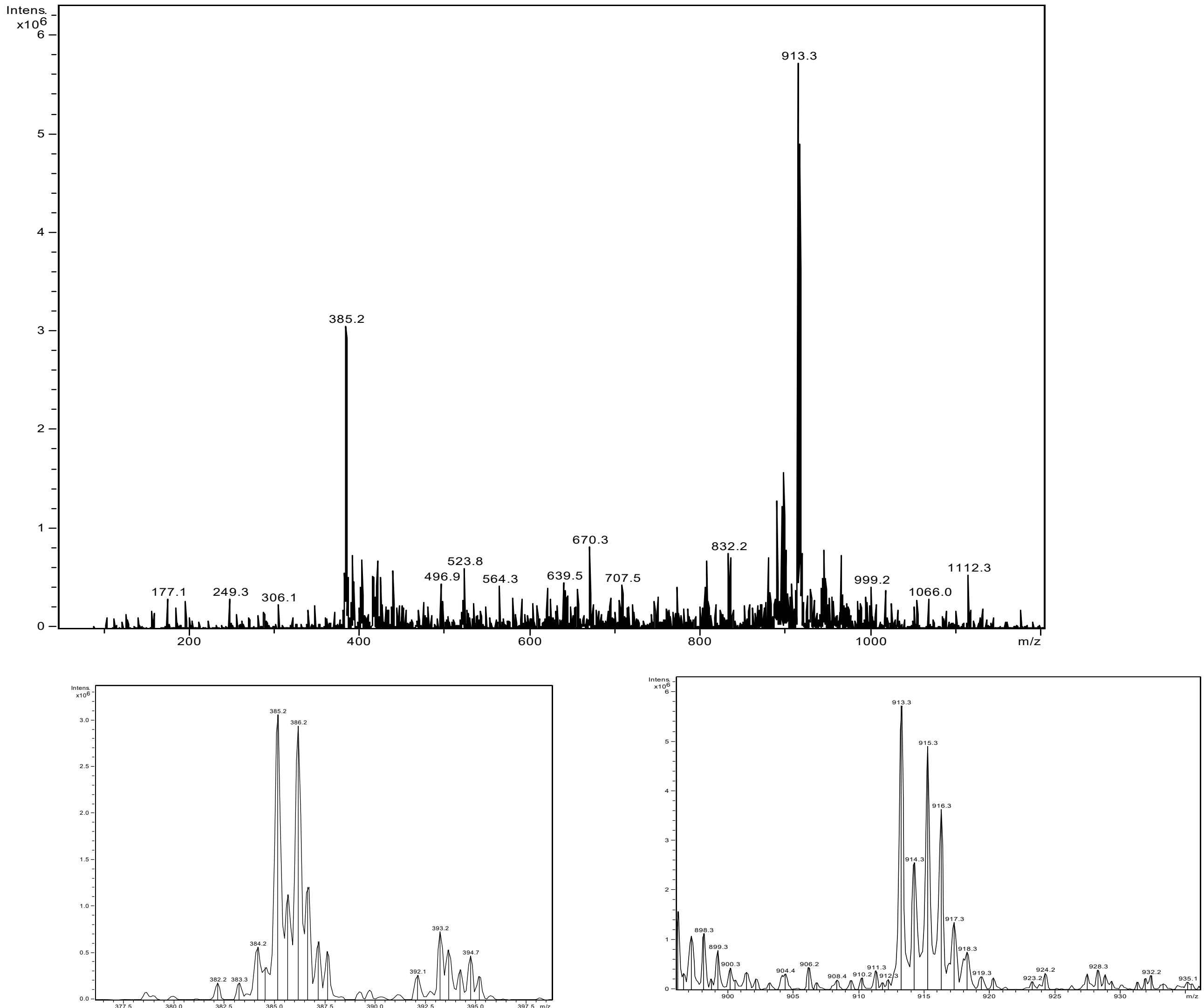


Fig. S35 ESI mass spectrum of a solution of the dicopper(II) complex of L at pH = 6.5 in H_2O/MeOH, and the zoom range of the isotopic series of peaks *m/z* 385 and 913, recorded in positive ion mode.

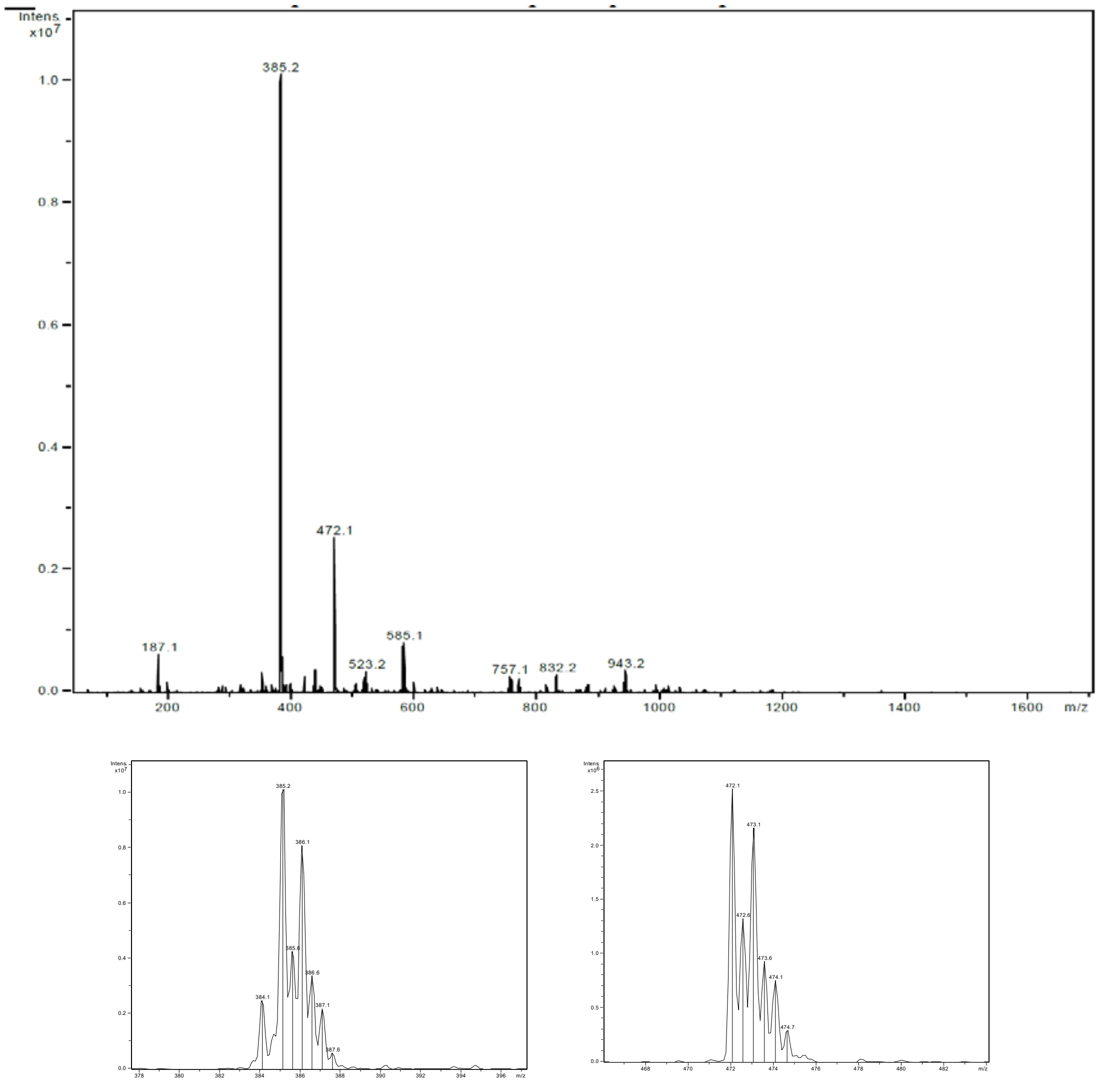


Fig. S36 ESI mass spectrum of crystals of $[Cu_2L(\mu\text{-}PhPO_4)][Cu_2L(\mu\text{-}PhPO_4)(NO_3)]3NO_3{\cdot}24H_2O$ dissolved in MeOH, and the zoom range of the isotopic series of peaks *m/z* 385 and 472, recorded in positive ion mode.

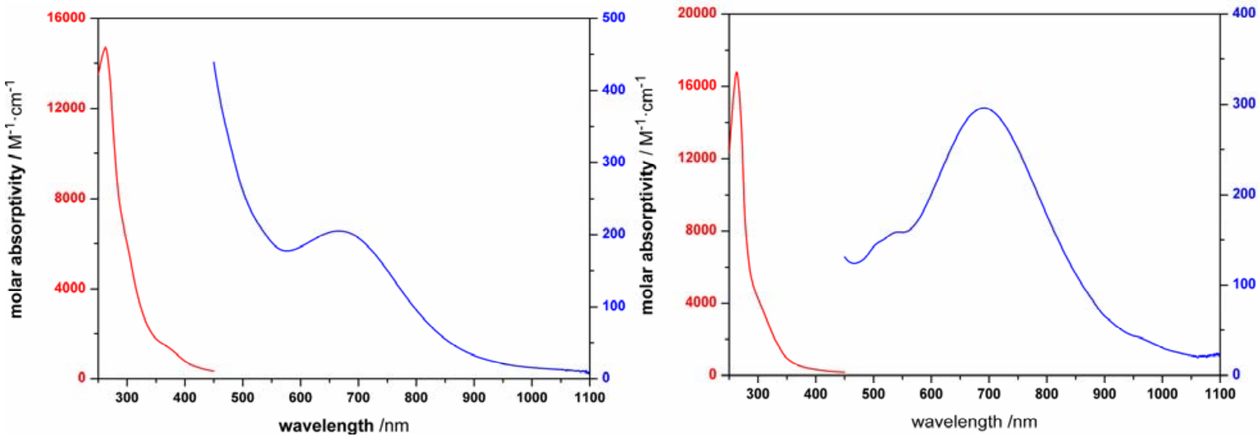


Fig. S37 UV-vis spectra of the dicopper complex of L at pH 7.0 (left), and of this complex in presence of $PhPO_4^{2-}$ at pH 5.8 and Cu^{2+}:L:$HPhPO_4^{-}$ 2:1:1 ratio (right).

Table S8 Coordinates of the cryptate reported by Nelson (reference 24 in the main text) optimized at the B3LYP/6-311G(d) level.

Atom	Coordinates in Å		
	X	Y	Z
Cu	4.939706	13.934508	3.780555
Cu	4.498767	13.819864	7.671916
O	4.569814	14.081113	5.714299
N	5.132066	13.954538	1.691375
N	4.321994	13.866320	9.759705
C	5.957259	12.768759	1.302519
C	6.984989	12.467632	2.381355
N	6.300893	12.296823	3.695599
C	5.785769	10.896509	3.855789
C	5.200128	10.632828	5.191510
C	5.575108	9.825137	6.222446
C	4.575091	9.976303	7.235920
C	3.669467	10.876595	6.760126
O	4.024485	11.263224	5.496282
C	2.426132	11.454452	7.328538
N	2.543905	12.908210	7.732571
C	2.037584	13.159658	9.110977
C	3.171566	12.976317	10.109272
C	5.814257	15.225622	1.293254
C	5.315249	16.393136	2.131314
N	5.544378	16.102306	3.572548
C	6.907443	16.563714	4.033518
C	7.645812	15.562477	4.842742
C	8.754157	14.808710	4.597980
C	8.974789	14.012605	5.767376
C	7.990640	14.345156	6.648592
O	7.185383	15.309843	6.105995
C	7.668255	13.875157	8.015959
N	6.436708	13.017376	8.064337
C	6.267303	12.378247	9.401887
C	5.596776	13.353402	10.354609
C	3.769414	13.876398	1.069197
C	2.800162	13.146949	1.986036
N	2.779288	13.799706	3.323569
C	1.840558	14.968250	3.368545
C	1.558268	15.434374	4.750521
C	0.451265	15.388722	5.535984
C	0.808138	15.977839	6.795933
C	2.112383	16.347296	6.705669
O	2.586294	16.045886	5.445207
C	3.071885	16.973228	7.655679
N	4.287143	16.130743	7.930746

C	4.762757	16.284167	9.331197
C	4.062215	15.269081	10.222431
H	6.442258	12.940981	0.336920
H	5.289015	11.917465	1.166520
H	7.690291	13.291772	2.487841
H	7.565743	11.579415	2.113614
H	6.995831	12.448873	4.424292
H	6.600008	10.185182	3.688066
H	5.041989	10.716423	3.076654
H	6.432220	9.168027	6.247092
H	4.521906	9.443966	8.174588
H	2.152492	10.866972	8.205296
H	1.598222	11.356068	6.621557
H	1.969879	13.449287	7.093332
H	1.202561	12.499556	9.362851
H	1.648847	14.178044	9.141409
H	2.833580	13.173412	11.131627
H	3.523583	11.943268	10.084160
H	5.664648	15.414035	0.225373
H	6.887520	15.097501	1.443689
H	4.246184	16.552719	1.981195
H	5.809041	17.317351	1.816168
H	4.856536	16.626890	4.102584
H	6.796226	17.500556	4.587000
H	7.514509	16.798596	3.158818
H	9.374797	14.844050	3.714379
H	9.784648	13.318320	5.938476
H	7.525386	14.723225	8.687867
H	8.522410	13.307153	8.396797
H	6.574437	12.268369	7.388144
H	7.226142	12.045654	9.811980
H	5.652379	11.489476	9.259371
H	5.403367	12.884763	11.323821
H	6.251930	14.203189	10.547270
H	3.828929	13.385591	0.093712
H	3.414533	14.889117	0.879519
H	3.111876	12.109951	2.131396
H	1.804757	13.116055	1.530227
H	2.437046	13.118259	3.995316
H	0.885837	14.698871	2.905459
H	2.262148	15.778790	2.770554
H	-0.518963	15.005902	5.254459
H	0.153680	16.132269	7.641510
H	2.538361	17.143521	8.591048
H	3.384800	17.961033	7.300011
H	5.030766	16.458080	7.322203

H	4.595103	17.295343	9.716225
H	5.843379	16.127838	9.340273
H	4.374364	15.379879	11.265165
H	2.986757	15.445849	10.202402
H	4.026592	14.877564	5.670831

Table S9 Coordinates of $[Cu_2L(\mu\text{-OH})]^{3+}$ optimized at the B3LYP/6-311G(d) level.

Atom	Coordinates in Å		
	X	Y	Z
Cu	4.884960	11.797291	4.633006
Cu	5.625583	8.133086	6.038966
N	4.336591	13.720156	4.582079
N	5.795369	6.609612	7.322213
N	6.147868	12.653469	6.049971
C	7.458768	13.070328	5.403897
C	8.189493	11.798760	5.052652
C	8.342701	11.356907	3.726254
C	8.748001	10.036314	3.520223
C	8.820629	9.103853	4.557922
C	8.659710	9.571003	5.874603
C	8.383973	8.647031	7.034062
N	6.945510	8.899938	7.454359
N	4.634366	6.533597	4.936994
C	4.545994	6.341518	3.434971
C	3.603701	7.333558	2.818617
C	4.103637	8.577179	2.376100
C	3.199780	9.564070	1.949835
C	3.693075	10.949020	1.645039
N	3.599205	11.830102	2.875352
C	3.496912	13.247189	2.406573
C	3.630310	14.204334	3.549446
C	4.624397	14.494921	5.643975
C	5.424028	13.780846	6.697782
C	4.185631	15.808029	5.714509
C	3.426541	16.313961	4.659214
C	3.145489	15.505931	3.559362
C	1.814323	9.291396	1.854055
C	1.372850	8.027427	2.224910
C	2.226957	7.044672	2.732384
C	1.594980	5.728385	3.149455
C	0.834363	10.326985	1.313504
C	-0.636626	9.913116	1.238681
C	5.606510	8.799367	2.242259
C	6.127474	8.354572	0.865118

C	5.070704	5.228191	5.523290
C	5.418209	5.371098	6.971888
C	6.226000	6.870950	8.570423
C	6.277988	5.877288	9.535329
C	5.863507	4.590962	9.189478
C	5.429504	4.330097	7.891743
C	6.601215	8.311742	8.776959
O	5.012736	9.821469	5.087848
C	8.509441	10.947483	6.125842
C	8.776356	11.520725	7.520258
C	10.256077	11.942996	7.647229
C	9.121440	7.653757	4.229755
C	10.571434	7.246222	4.545459
C	8.140163	12.266699	2.529321
C	9.275390	13.288223	2.339950
C	1.006398	5.737894	4.571799
H	6.379772	11.974579	6.764593
H	8.004104	13.708531	6.103098
H	7.224887	13.679303	4.534427
H	8.935312	9.701299	2.504830
H	9.034059	8.818046	7.895343
H	8.477368	7.596666	6.770562
H	6.835048	9.904573	7.516058
H	3.671652	6.678080	5.244155
H	4.200270	5.322830	3.256881
H	5.555888	6.396035	3.037631
H	4.721157	10.981554	1.295212
H	3.084777	11.408265	0.864525
H	2.699692	11.603220	3.300887
H	2.563283	13.402241	1.859639
H	4.312483	13.418818	1.697064
H	6.114765	14.458362	7.207352
H	4.751258	13.368064	7.456443
H	4.428080	16.425248	6.571774
H	3.063786	17.335186	4.690984
H	2.569032	15.884591	2.723421
H	0.322502	7.784182	2.123236
H	0.785582	5.508886	2.448818
H	2.291709	4.894112	3.042799
H	0.899260	11.244135	1.915885
H	1.160140	10.618904	0.307826
H	-1.229376	10.735085	0.834579
H	-0.786469	9.057829	0.576708
H	-1.050206	9.666374	2.219433
H	6.149376	8.277199	3.030011
H	5.862634	9.844167	2.415985

H	7.204014	8.519159	0.779130
H	5.937496	7.293936	0.685634
H	5.640975	8.903219	0.055515
H	4.302061	4.465996	5.370473
H	5.957162	4.899132	4.971984
H	6.632859	6.097989	10.535302
H	5.886474	3.795596	9.925921
H	5.114659	3.335103	7.599548
H	7.426213	8.415894	9.487116
H	5.746698	8.860547	9.185859
H	8.563026	10.804695	8.316121
H	8.156611	12.390945	7.748775
H	10.451944	12.346469	8.642565
H	10.923562	11.094314	7.487111
H	10.515172	12.708210	6.913153
H	8.433265	6.983018	4.761205
H	8.929914	7.487365	3.166765
H	10.752399	6.209491	4.255546
H	11.279072	7.872513	3.998949
H	10.802938	7.342005	5.609537
H	8.062609	11.651812	1.629013
H	7.182417	12.799388	2.605721
H	9.103617	13.896132	1.449706
H	9.366994	13.963133	3.194958
H	10.235476	12.783469	2.217407
H	0.517092	4.787445	4.792088
H	1.770430	5.892994	5.344827
H	0.262229	6.527977	4.691781
H	4.467049	9.440703	4.384015

Table S10 Coordinates of $[Cu_2L(\mu\text{-}PhPO_4)]^{2+}$ optimized at the B3LYP/6-311G(d) level.

Atom	Coordinates in Å		
	X	Y	Z
Cu	4.657021	12.364886	4.163655
Cu	5.447787	7.218856	6.102633
P	4.176726	10.029577	5.969032
O	4.116731	8.487547	5.861249
N	4.348720	14.222197	3.761165
N	6.214433	5.622553	6.868605
N	5.682267	13.167767	5.783968
C	7.180365	13.210601	5.638294
C	7.746124	11.831255	5.377661
C	8.109788	11.453127	4.072337
C	8.498621	10.135252	3.846897

C	8.460962	9.161745	4.842483
C	8.110116	9.549706	6.149150
C	8.015745	8.513266	7.247105
N	6.598746	8.126633	7.581457
N	4.740999	5.845096	4.671592
C	4.573504	6.172664	3.206083
C	3.622822	7.314837	2.896329
C	4.113794	8.556596	2.432873
C	3.213088	9.580214	2.068492
C	3.717778	10.899991	1.510174
N	3.520890	12.092497	2.415663
C	3.587489	13.372320	1.651250
C	3.794688	14.548452	2.584437
C	4.609638	15.123550	4.720811
C	5.099793	14.514616	6.023666
C	4.347926	16.468726	4.493866
C	3.787187	16.838545	3.270821
C	3.492496	15.874868	2.304994
C	1.820125	9.358568	2.148545
C	1.372486	8.125662	2.611282
C	2.236745	7.100992	2.991910
C	1.611671	5.815090	3.502152
C	0.808803	10.426356	1.747651
C	-0.603493	9.939292	1.405525
C	5.609985	8.769639	2.294975
C	6.167358	8.362566	0.920856
C	5.508410	4.571884	4.835157
C	6.079158	4.451937	6.232990
C	6.677113	5.726817	8.124645
C	7.101341	4.590230	8.799401
C	6.998170	3.358164	8.150231
C	6.470429	3.275620	6.860914
C	6.574216	7.134077	8.688780
C	0.405740	9.933977	6.464949
C	1.658296	10.366230	6.890852
C	1.897887	10.652444	8.233165
C	0.862731	10.491646	9.153622
C	-0.396412	10.061517	8.741002
C	-0.621648	9.784754	7.393543
O	4.750991	10.582603	4.637715
O	4.871961	10.554124	7.208587
C	7.826961	10.902000	6.435183
C	7.715029	11.374004	7.877536
C	9.082548	11.808399	8.437396
C	8.850054	7.742337	4.469014
C	10.325651	7.411978	4.752724

C	8.147989	12.420348	2.902397
C	9.423427	13.279875	2.862655
O	2.626844	10.569046	5.904103
C	1.083212	5.921709	4.945377
H	5.447420	12.523629	6.547299
H	7.599654	13.660485	6.542146
H	7.402250	13.895976	4.822810
H	8.806220	9.846248	2.845948
H	8.491186	8.867342	8.165871
H	8.534938	7.597840	6.970969
H	6.064602	8.971118	7.821670
H	3.804036	5.691952	5.041073
H	4.225062	5.263491	2.705145
H	5.570988	6.363588	2.821677
H	4.777142	10.864586	1.274731
H	3.201851	11.115549	0.568199
H	2.584202	12.012046	2.807114
H	2.698311	13.515614	1.029941
H	4.442324	13.305276	0.970875
H	5.811044	15.176881	6.525477
H	4.240803	14.402231	6.692676
H	4.561403	17.210970	5.254083
H	3.568057	17.881904	3.073347
H	3.039570	16.154683	1.361134
H	0.306905	7.934540	2.661793
H	0.776830	5.547668	2.847573
H	2.307788	4.974278	3.424945
H	0.718040	11.162490	2.560467
H	1.189163	10.981631	0.883643
H	-1.204362	10.771422	1.033173
H	-0.585399	9.170609	0.629710
H	-1.126578	9.533439	2.273577
H	6.132099	8.227597	3.084751
H	5.857006	9.805380	2.512547
H	7.246599	8.530914	0.865473
H	5.985808	7.307856	0.697057
H	5.703866	8.933766	0.111942
H	4.893582	3.701602	4.587262
H	6.333407	4.589403	4.116477
H	7.487058	4.655373	9.809972
H	7.316890	2.455020	8.658533
H	6.364987	2.318258	6.364210
H	7.360850	7.327250	9.423907
H	5.615650	7.227413	9.209112
H	0.253295	9.718980	5.413334
H	2.880274	10.985576	8.542423

H	1.043173	10.714311	10.200147
H	-1.197536	9.946745	9.462582
H	-1.600169	9.452724	7.062941
H	7.288473	10.602437	8.516006
H	7.009339	12.197930	7.973266
H	8.987457	12.143460	9.473043
H	9.807932	10.990934	8.415762
H	9.513474	12.629205	7.858495
H	8.206205	7.015659	4.978190
H	8.662483	7.601439	3.400800
H	10.564669	6.392794	4.439512
H	10.984918	8.090862	4.207821
H	10.573020	7.503664	5.813538
H	8.084732	11.845948	1.973724
H	7.268201	13.075036	2.901692
H	9.420566	13.943060	1.994422
H	9.529261	13.898261	3.757709
H	10.312571	12.649168	2.798249
H	0.680188	4.964228	5.284034
H	1.854596	6.244271	5.652335
H	0.283787	6.661374	5.017843

Table S11 Coordinates of $[Cu_2L(\mu\text{-}PhPO_4)(NO_3)]^+$ optimized at the B3LYP/6-311G(d) level.

Atom	Coordinates in Å		
	X	Y	Z
Cu	4.858249	12.550141	4.057855
Cu	5.756700	7.290285	5.957920
P	4.394830	10.049847	5.951296
O	4.436150	8.519404	5.632717
N	4.962746	14.360646	3.352828
N	6.513021	5.686364	6.738273
N	6.061867	13.437698	5.579836
C	7.552803	13.343752	5.506298
C	8.042381	11.928875	5.268815
C	8.410952	11.525668	3.971814
C	8.780873	10.199483	3.765844
C	8.731457	9.241666	4.774942
C	8.370596	9.649575	6.071788
C	8.269353	8.625593	7.181339
N	6.860153	8.194241	7.465459
N	5.061558	5.903250	4.529714
C	4.891669	6.254682	3.071461
C	3.919242	7.382827	2.781146

C	4.386309	8.642976	2.344684
C	3.474168	9.652391	1.977295
C	3.971439	10.949918	1.358870
N	3.915887	12.190591	2.194716
C	4.137407	13.375418	1.326948
C	4.480273	14.607563	2.132355
C	5.282046	15.335089	4.216276
C	5.598026	14.847141	5.616490
C	5.192332	16.664585	3.826532
C	4.719478	16.950672	2.545462
C	4.341502	15.919290	1.689597
C	2.083971	9.412209	2.061300
C	1.658641	8.168039	2.516584
C	2.538114	7.148187	2.874552
C	1.934264	5.850560	3.380574
C	1.067748	10.474990	1.675298
C	-0.387673	10.018984	1.546734
C	5.878895	8.908747	2.275263
C	6.529017	8.522195	0.936240
C	5.835921	4.640312	4.692529
C	6.386504	4.517041	6.100475
C	6.942584	5.792170	8.004329
C	7.348273	4.654043	8.689992
C	7.258877	3.422611	8.038932
C	6.760603	3.339826	6.737899
C	6.821496	7.201695	8.564418
C	0.585491	9.858585	6.643710
C	1.920473	9.962414	7.033241
C	2.295785	9.683598	8.347891
C	1.323858	9.274313	9.260562
C	-0.009195	9.151346	8.878037
C	-0.373600	9.454199	7.566186
O	4.853358	10.797512	4.692008
O	5.140634	10.389883	7.228974
C	8.084558	11.007090	6.334307
C	7.915846	11.490714	7.766483
C	9.258411	11.912685	8.391123
C	9.109841	7.813853	4.422416
C	10.585905	7.479560	4.696285
C	8.465468	12.471915	2.785898
C	9.771258	13.281763	2.710107
O	2.804079	10.394123	6.063054
C	1.424852	5.943009	4.831752
H	5.730764	12.946956	6.408076
H	7.982283	13.768175	6.419374
H	7.865398	13.999774	4.696265

H	9.082551	9.891952	2.768326
H	8.695737	9.013106	8.111181
H	8.837951	7.728615	6.939365
H	6.272939	9.028255	7.663280
H	4.125623	5.751297	4.901049
H	4.564583	5.347436	2.550827
H	5.886999	6.477648	2.696930
H	5.001378	10.846991	1.024339
H	3.384252	11.138482	0.451364
H	2.979048	12.310019	2.612140
H	3.263481	13.571058	0.696040
H	4.973190	13.154489	0.653146
H	6.318064	15.503215	6.116795
H	4.659202	14.866922	6.174581
H	5.457429	17.460070	4.513304
H	4.625303	17.981801	2.222935
H	3.938354	16.130166	0.705981
H	0.595723	7.966799	2.583046
H	1.092672	5.578017	2.736083
H	2.640333	5.018161	3.288219
H	1.104186	11.289023	2.406723
H	1.367503	10.923920	0.720230
H	-1.004261	10.853092	1.205201
H	-0.504566	9.203216	0.827515
H	-0.802606	9.691087	2.503015
H	6.377055	8.386752	3.094344
H	6.067440	9.955589	2.502024
H	7.602675	8.733931	0.939734
H	6.402747	7.460016	0.707278
H	6.089091	9.071372	0.099610
H	5.237776	3.761914	4.429713
H	6.672805	4.673664	3.987679
H	7.707815	4.719443	9.710251
H	7.563282	2.518946	8.555337
H	6.661923	2.382249	6.240056
H	7.590438	7.395834	9.318808
H	5.850967	7.285717	9.064695
H	0.318126	10.123547	5.627802
H	3.325192	9.827455	8.649266
H	1.614130	9.068505	10.286607
H	-0.759921	8.841767	9.597368
H	-1.412925	9.388048	7.260812
H	7.442695	10.730564	8.383946
H	7.215941	12.323095	7.818378
H	9.115654	12.258234	9.418355
H	9.973725	11.085574	8.413139

H	9.729661	12.723159	7.828844
H	8.467861	7.099323	4.949547
H	8.909933	7.656229	3.358549
H	10.816911	6.451867	4.403073
H	11.242731	8.143948	4.130396
H	10.844282	7.593441	5.752457
H	8.367554	11.883089	1.868973
H	7.608682	13.151791	2.789328
H	9.775495	13.934332	1.833172
H	9.916484	13.908458	3.594013
H	10.636425	12.618338	2.638216
H	1.041028	4.978469	5.175708
H	2.200746	6.279017	5.527159
H	0.618407	6.673218	4.918279
O	1.677229	13.102925	3.609527
O	3.108726	13.363227	5.241921
O	0.976060	13.443291	5.636282
N	1.891384	13.300481	4.847086