

Electronic Supplementary Information

Endo- versus Exocyclic Coordination in Copper complexes with Methylthiazolylcarboxylate tacn derivatives

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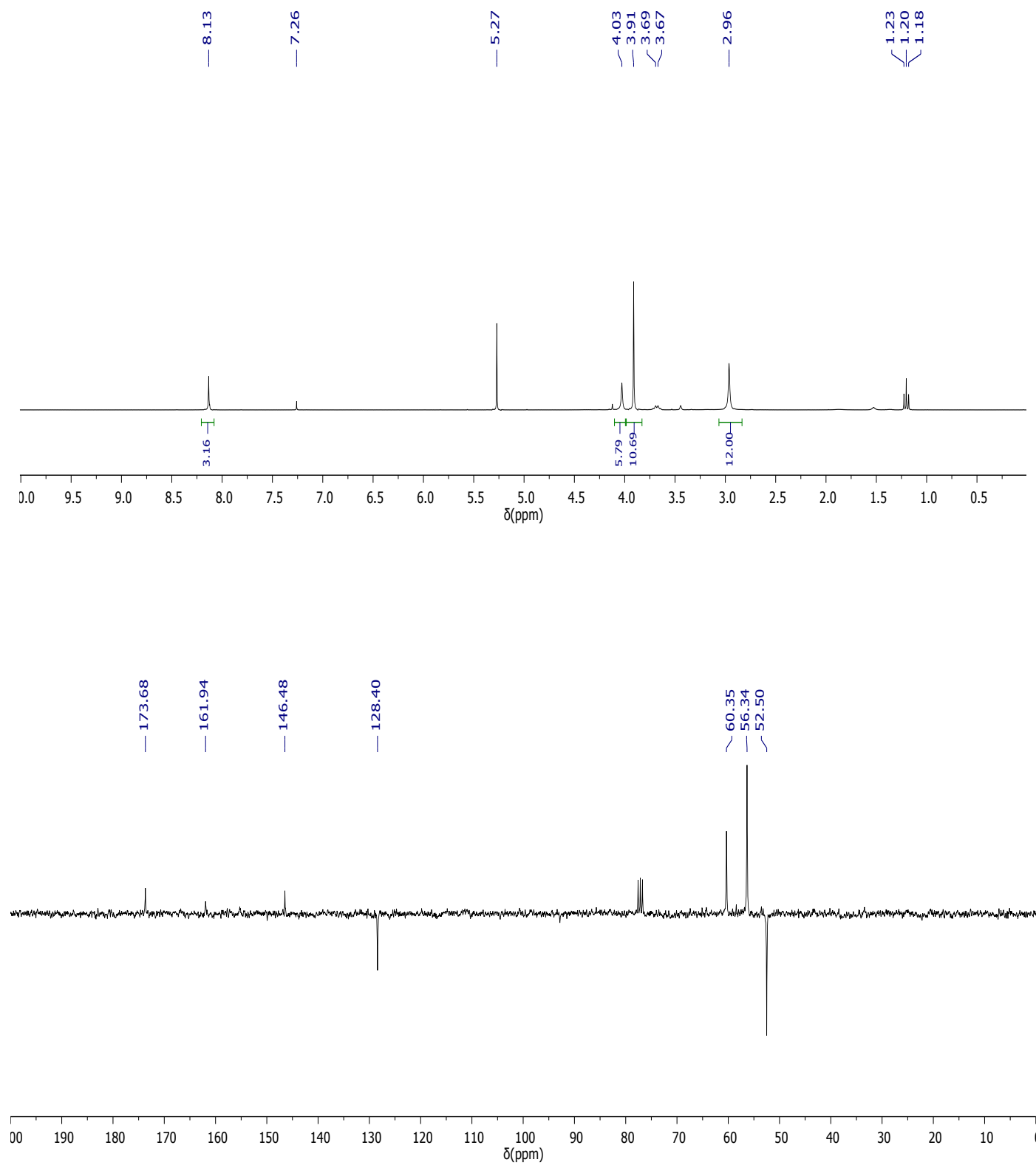


Figure S1. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra of **1 (no3tha ester)** (298 K, CDCl_3)

Analysis Info

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Analysis Name **X035654CYC.d**

Acquisition Date

11/07/2017 21:29:33

Instrument / Ser#

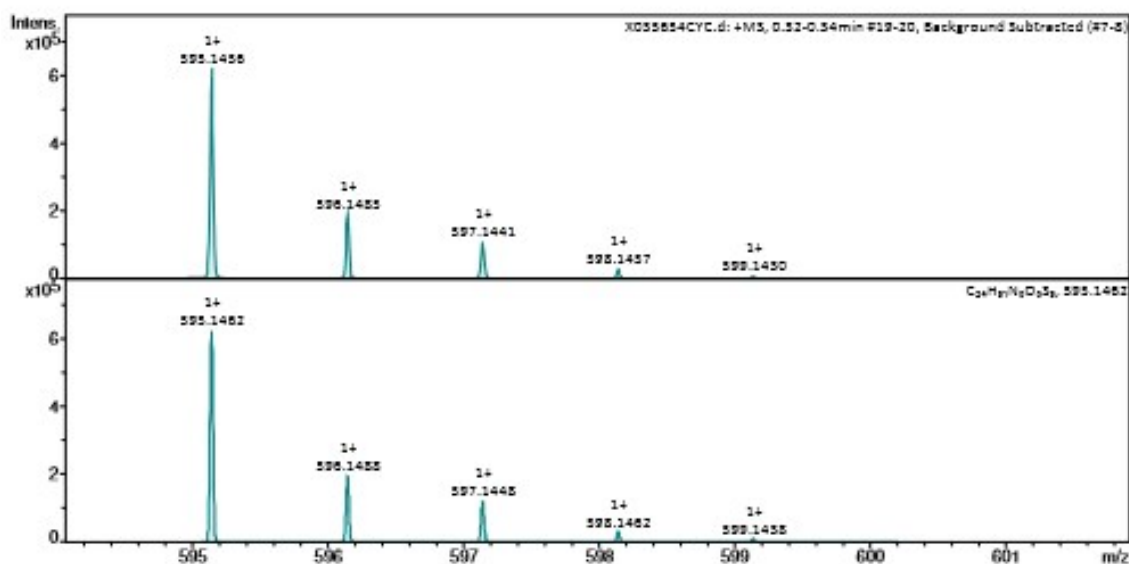
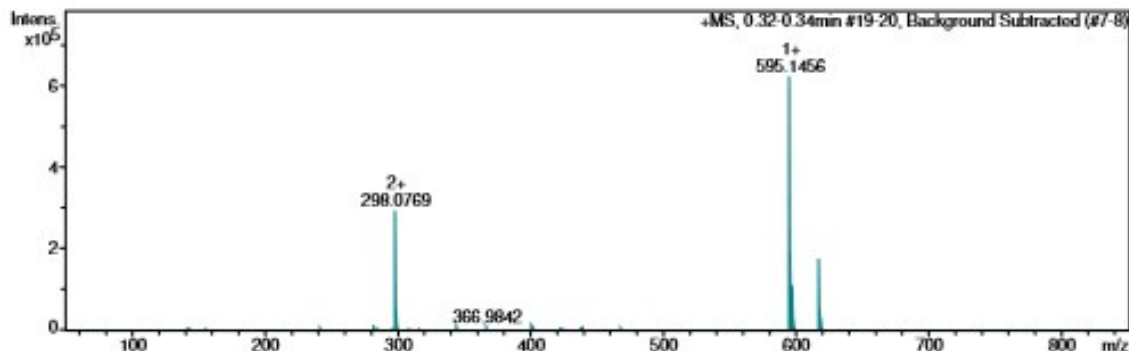
maXis 255552.00086

Method

Positil.m

Acquisition Parameter

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Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻	Conf
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595.145573	1+	1	C24H31N6O6S3	595.146172	1.0	7.4	13.0	even	
	1+	2	C23H35N2O10S3	595.144835	-1.2	12.3	8.0	even	
617.127463	1+	1	C24H30N6NaO6S3	617.128116	1.1	5.9	13.0	even	
	1+	2	C23H34N2NaO10S3	617.126779	-1.1	11.3	8.0	even	

Figure S2. HRMS of 1 (no3tha ester)

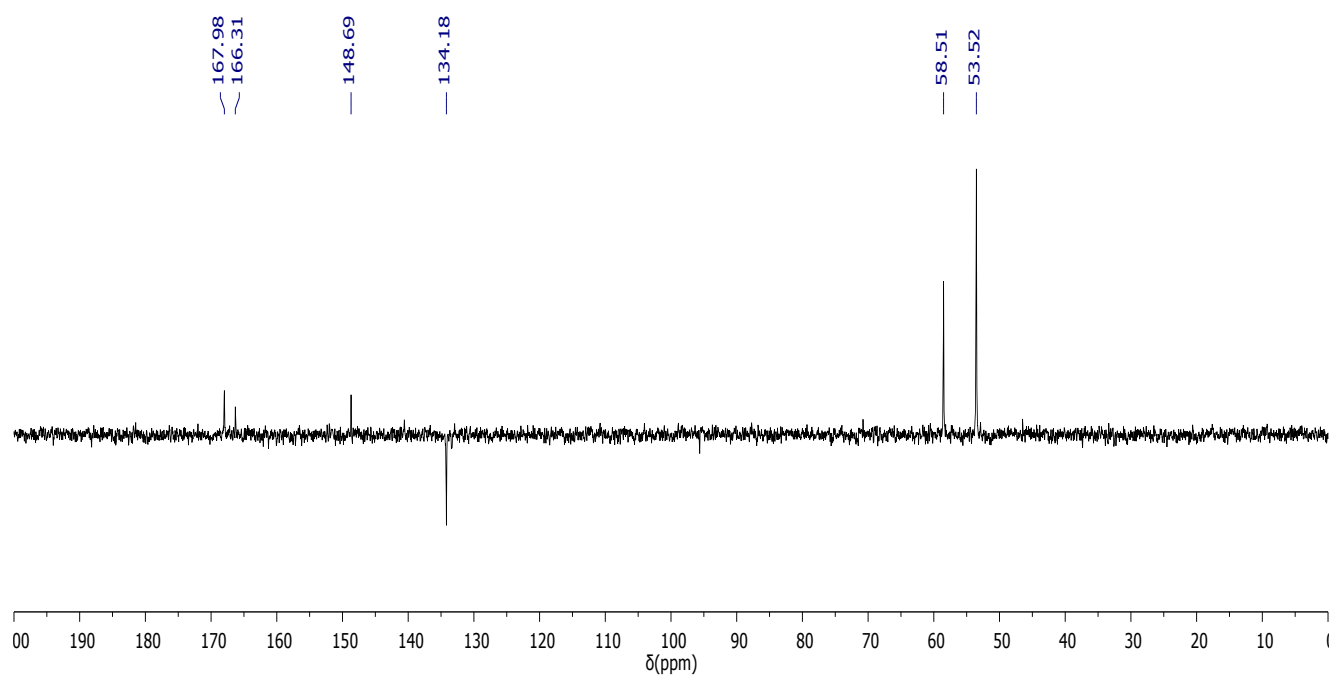
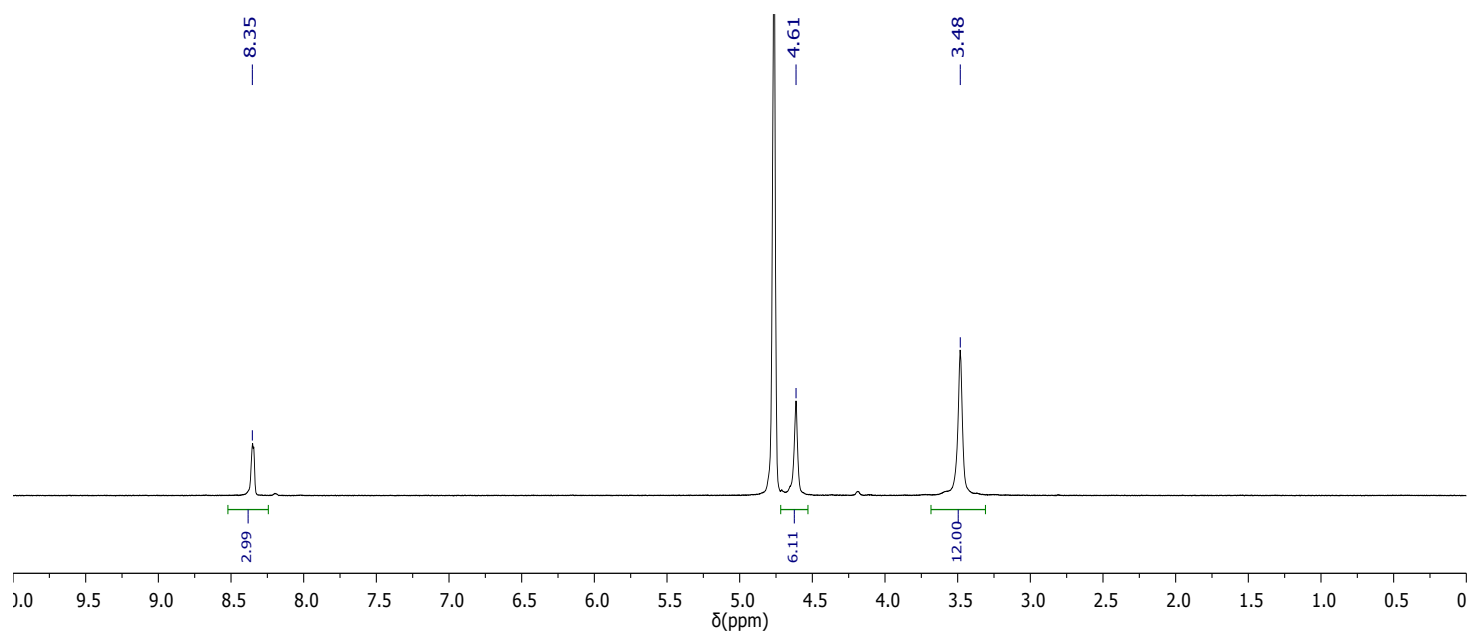


Figure S3. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of **2** ($\text{H}_3\text{no3tha}$, 3HCl) (298 K, D_2O)



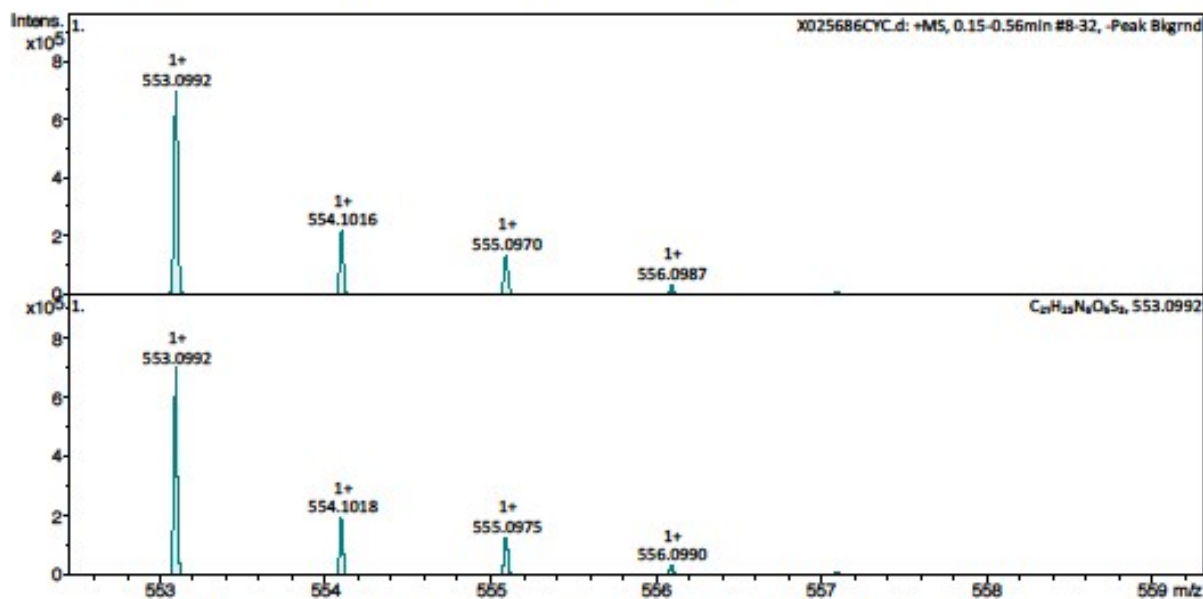
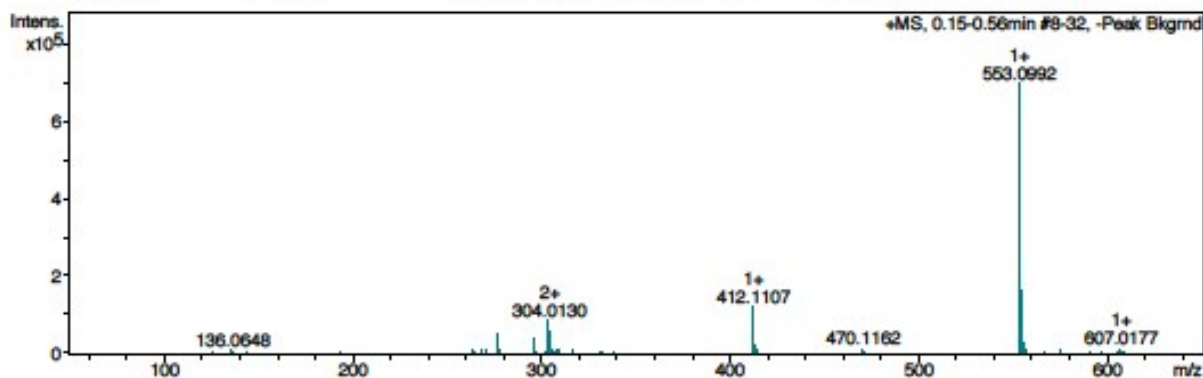
Analysis Info

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Analysis Name X025686CYC.d

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Method Positif.m

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Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e ⁻	Conf
277.053326	2+	1	C21H26N8O6S3	277.053249	-0.3	10.9	13.0	even	
296.026935	2+	1	C21H24CaN8O6S3	296.026720	-0.7	10.4	14.0	even	
412.110707	1+	1	C16H22N5O4S2	412.110773	0.2	7.0	9.0	even	
	1+	2	C24H18N3O2S	412.111424	1.7	33.8	18.0	even	
	1+	3	C15H18N5O9	412.109904	-1.9	44.7	10.0	even	
553.099248	1+	1	C21H25N8O6S3	553.099222	-0.0	17.1	13.0	even	

Figure S4. HRMS of 2 (H₃no3tha, 3HCl)

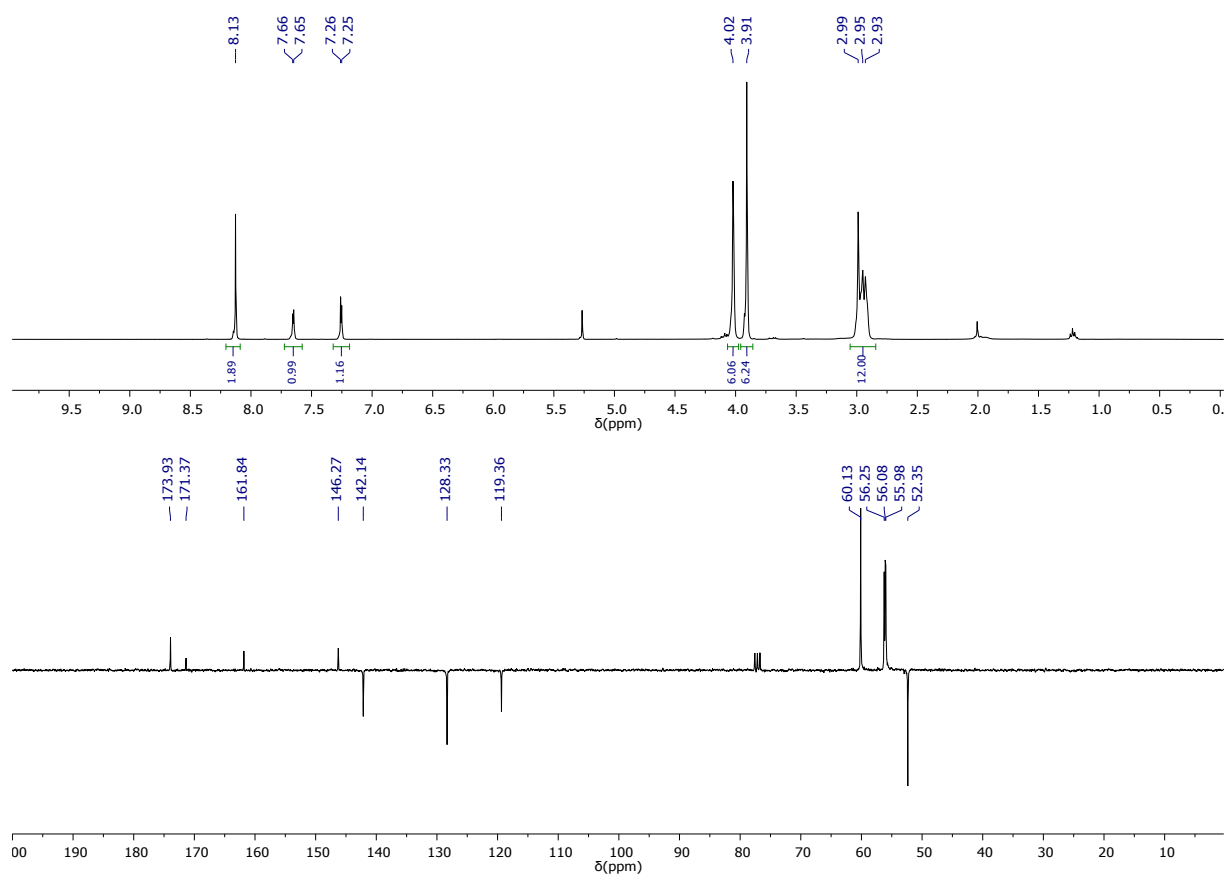


Figure S5. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra of **6** (no1th2tha ester) (298 K, CDCl_3)



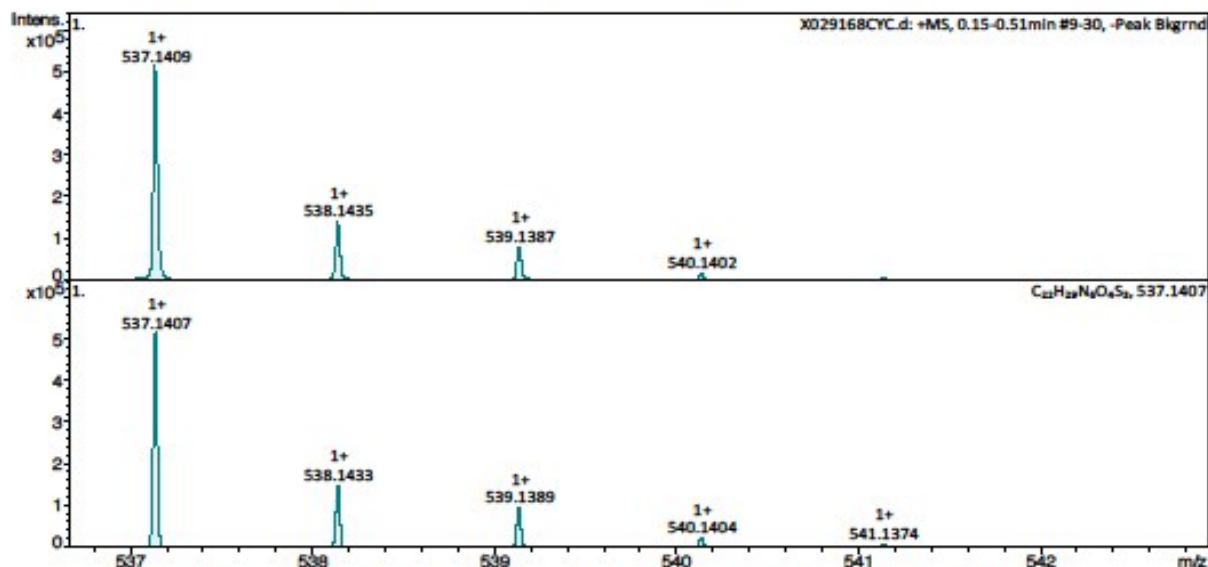
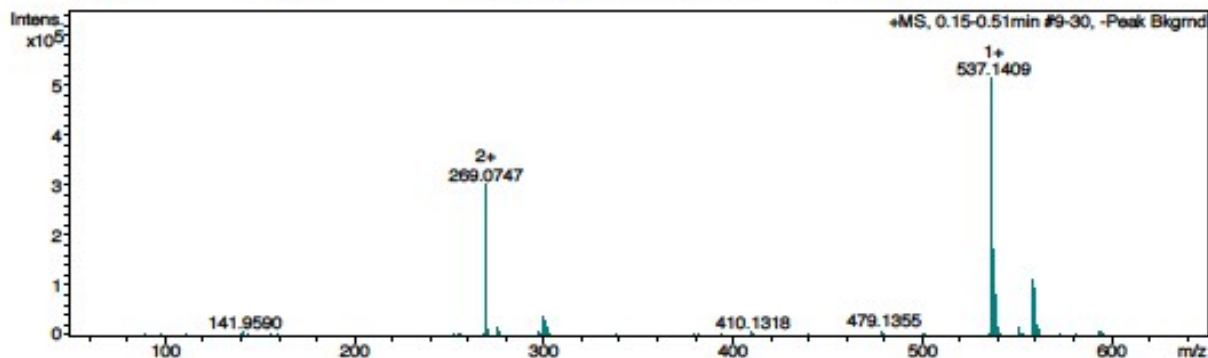
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Analysis Name X029168CYC.d

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Method Positif.m

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Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻	Conf
269.074676	2+	1	C22H30N6O4S3	269.073985	-2.6	8.7	12.0	even	
	2+	2	C26H34O6S3	269.075327	2.4	19.0	11.0	even	
537.140677	1+	1	C22H29N6O4S3	537.140693	-0.3	12.8	12.0	even	
559.122755	1+	1	C22H28N6NaO4S3	559.122637	-0.2	12.2	12.0	even	

Figure S6. HRMS of 6 (no1th2tha ester)

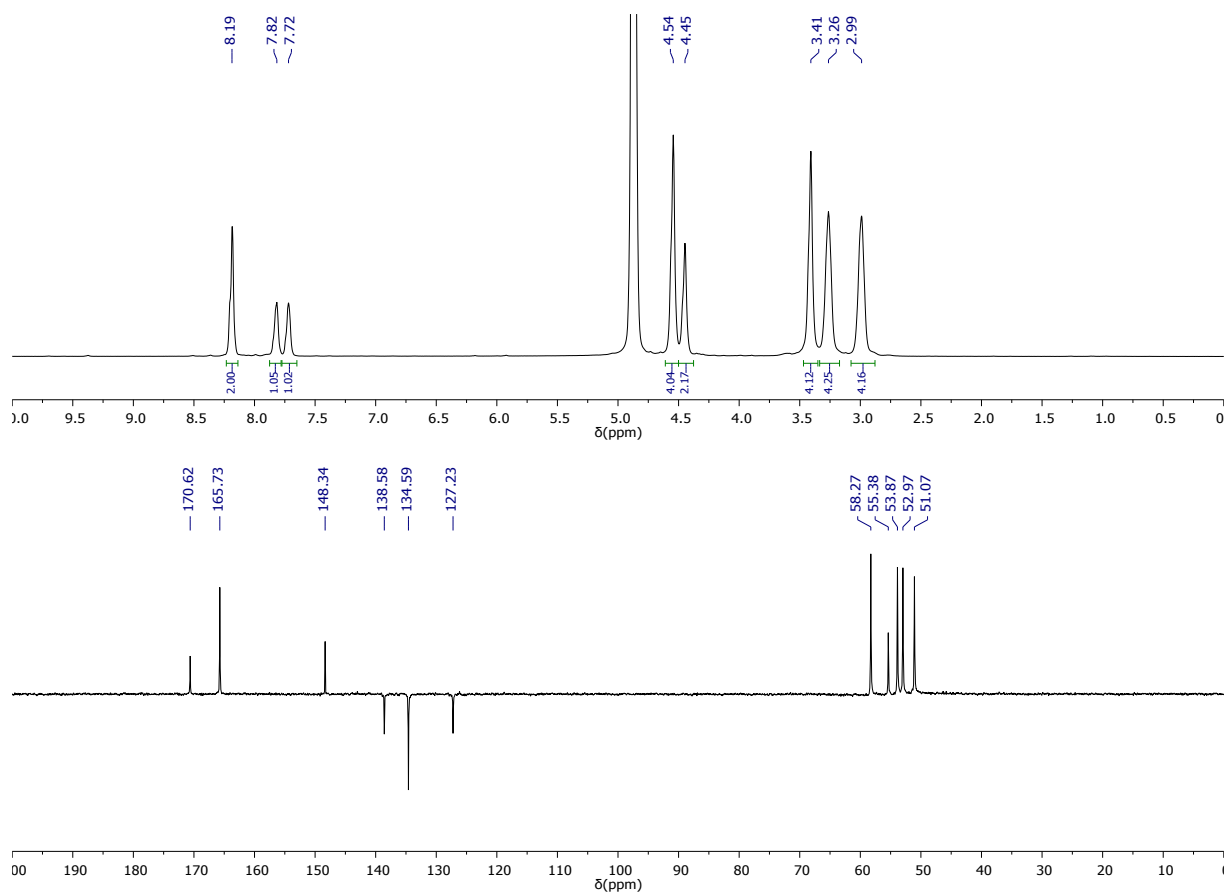


Figure S7. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of **7** ($\text{H}_2\text{no1th2tha}$, 3HCl) (298 K, D_2O)



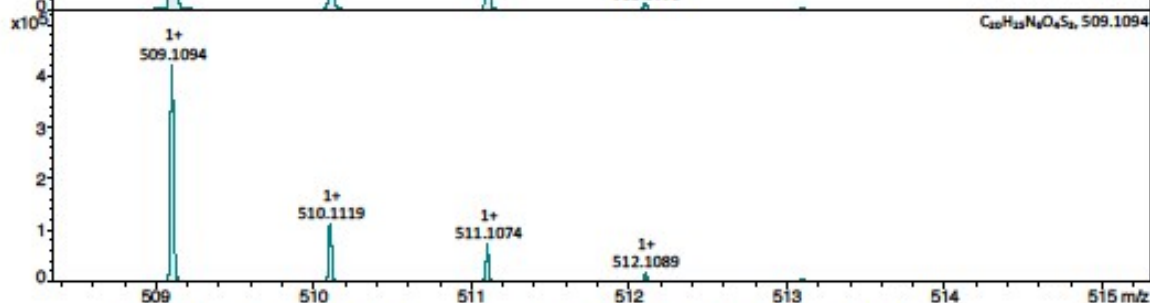
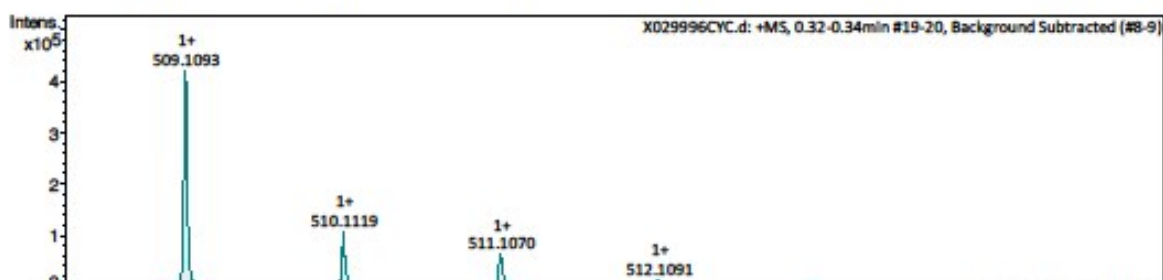
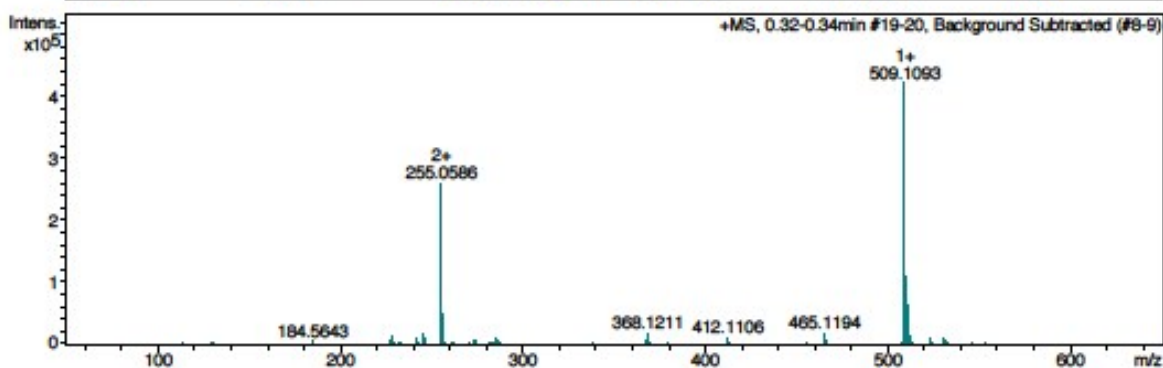
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Instrument / Ser# maXis 255552.00086
Method Positif.m

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Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻	Conf
255.058594	2+	1	C22H28N3O5S3	255.059006	1.6	2.9	11.5	odd	
	2+	2	C20H26N8O4S3	255.058335	-1.0	3.9	12.0	even	
509.109337	1+	1	C20H25N8O4S3	509.109393	0.1	10.4	12.0	even	

Figure S8. HRMS of 7 (H₂no1th2tha)

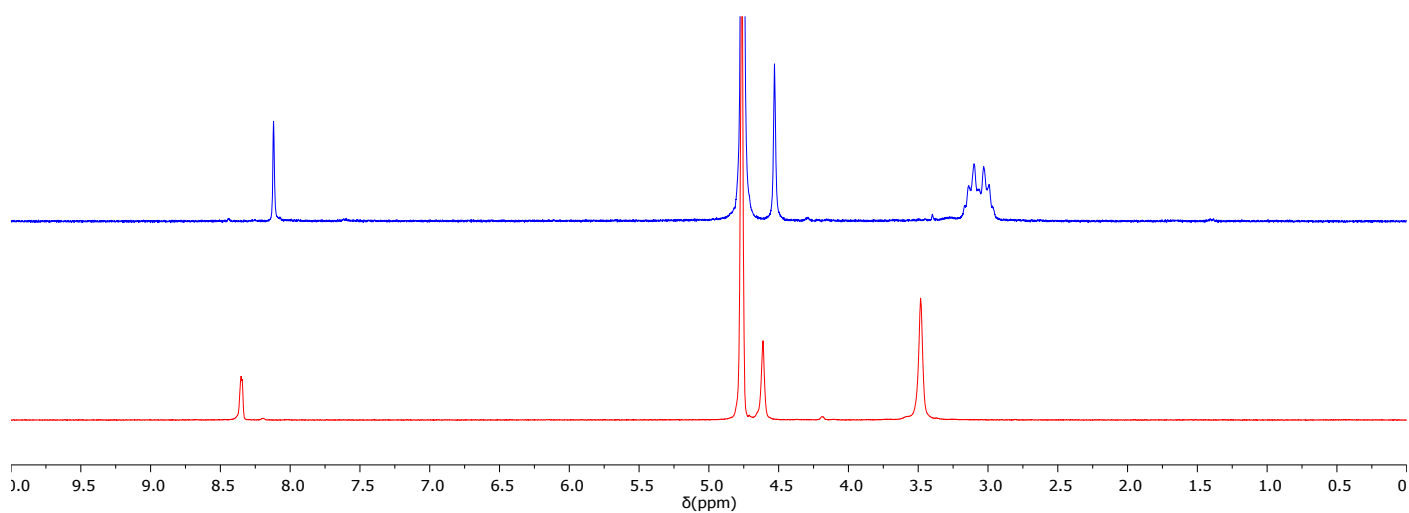


Figure S9. ^1H NMR (300 MHz, 298 K, D_2O) spectra of $[\text{Zn}(\text{Hno3tha})]$ (blue) and Hno3tha (red)



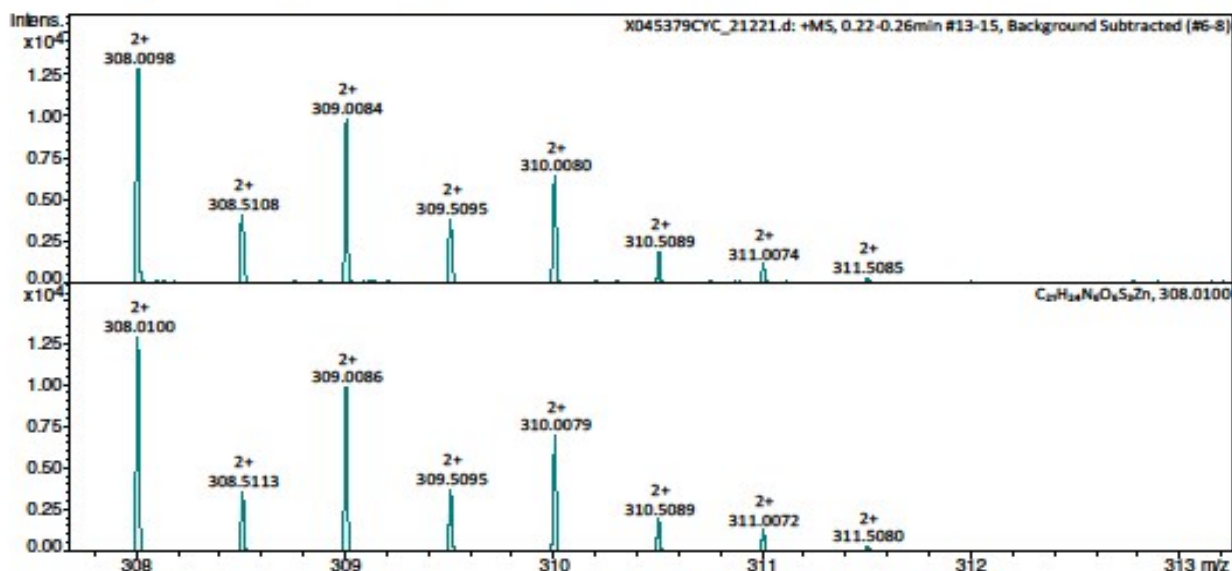
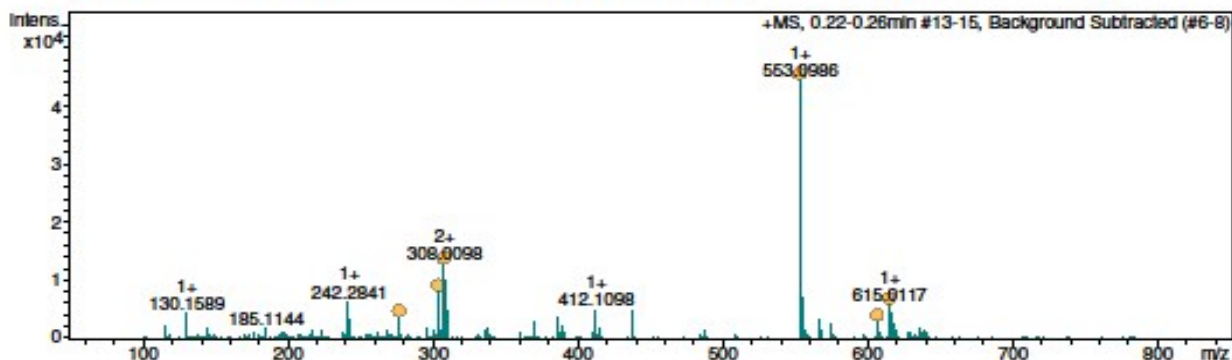
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Acquisition Date 24/10/2018 16:02:30
Instrument / Ser# maXis 255552.00086
Method Positif.m

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Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻ Conf
277.053072	2+	1	C21H26N8O6S3	277.053249	0.6	20.7	13.0	even
	2+	2	C20H30N2O10S3	277.052581	-1.8	23.4	8.0	even
304.012824	2+	1	C21H24FeN8O6S3	304.012893	0.3	9.6	14.0	even
	2+	2	C20H28FeN2O10S3	304.012224	-1.9	12.2	9.0	even
308.009837	2+	1	C21H24N8O6S3Zn	308.009995	0.5	21.8	14.0	even
	2+	2	C20H28N2O10S3Zn	308.009327	-1.7	29.2	9.0	even
553.098553	1+	1	C21H25N8O6S3	553.099222	1.2	11.3	13.0	even
	1+	2	C20H29N2O10S3	553.097885	-1.2	12.4	8.0	even

Figure S10. HRMS of [Zn(Hno3tha)]



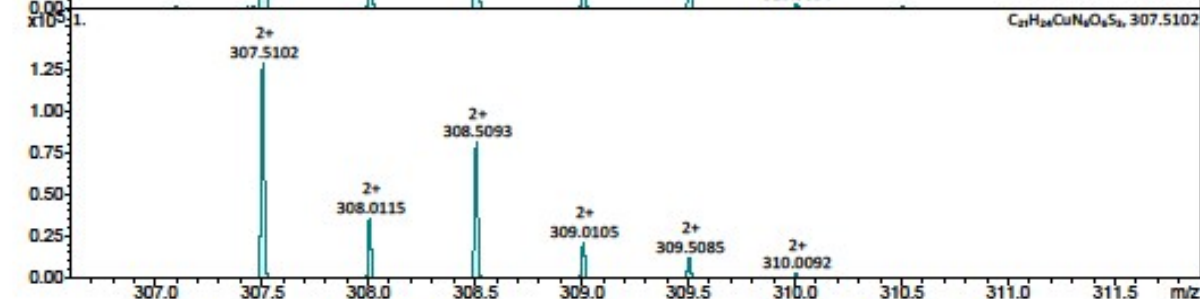
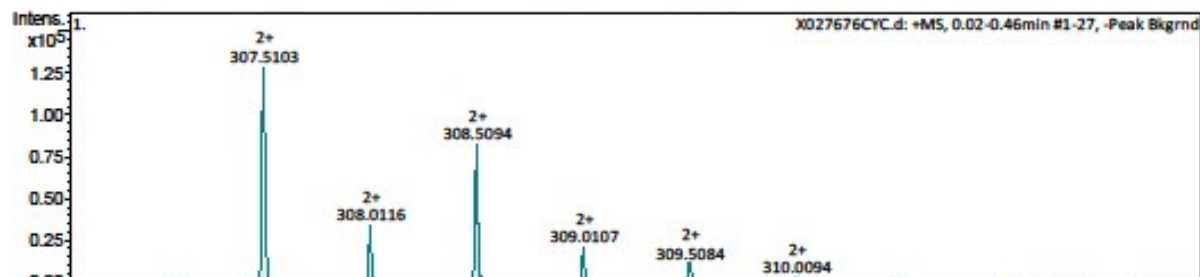
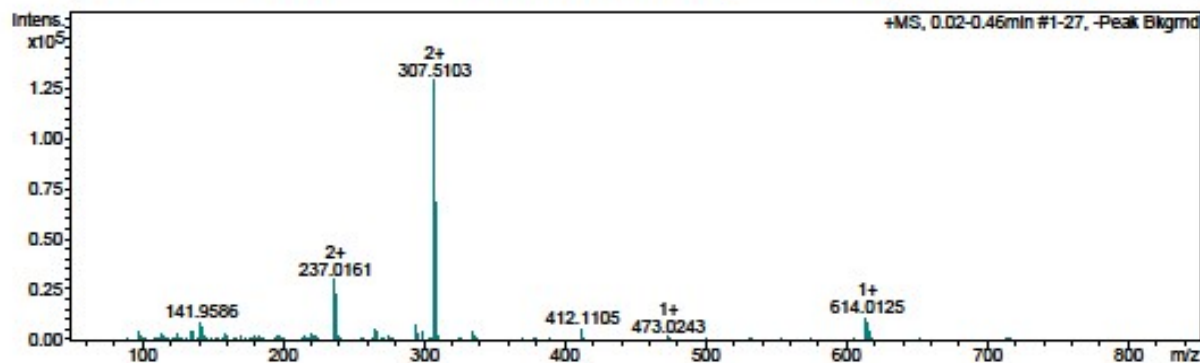
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Analysis Name X027676CYC.d

Acquisition Date 29/06/2016 14:35:52
Instrument / Ser# maXis 255552.00086
Method Positif.m

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Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻ Conf
237.016088	2+	1	C16H21CuN5O4S2	237.015998	-0.4	19.1	9.5	odd
	2+	2	C24H17CuN3O2S	237.016324	1.0	42.8	18.5	odd
307.510285	2+	1	C21H24CuN6O6S3	307.510223	-0.2	6.9	13.5	odd
614.012479	1+	1	C21H23CuN6O6S3	614.013169	1.1	10.8	13.5	odd

Figure S11. HRMS of [Cu(Hno3tha)]

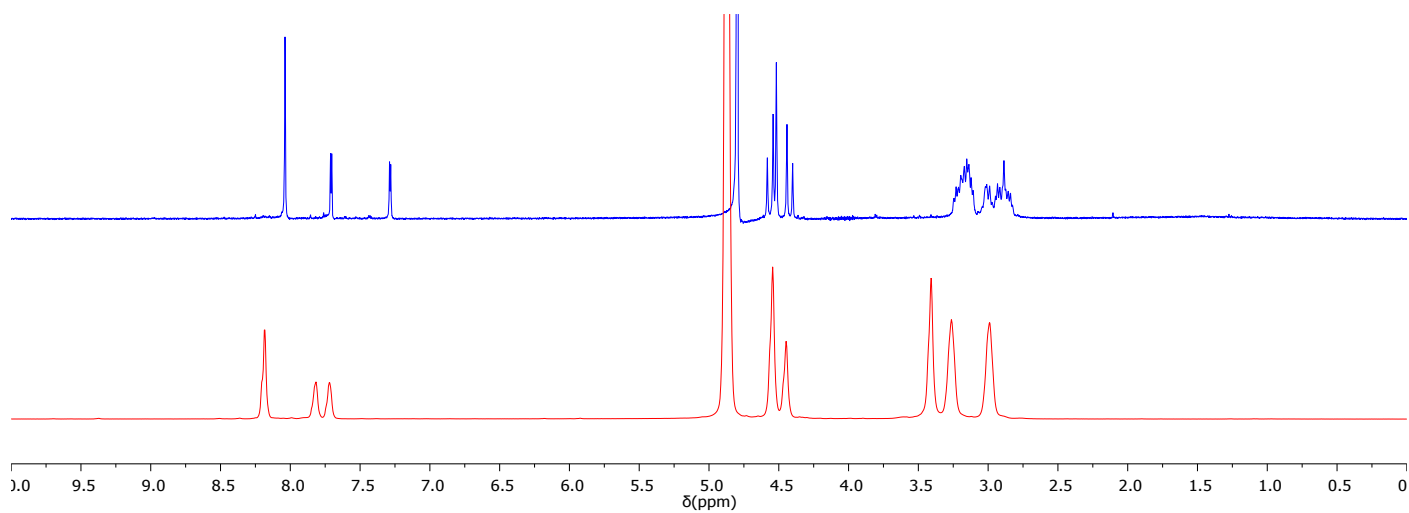


Figure S12. ^1H NMR (300 MHz, 298 K, D_2O) spectra of $[\text{Zn}(\text{no1th2tha})]$ (blue) and Hno1th2tha (red)



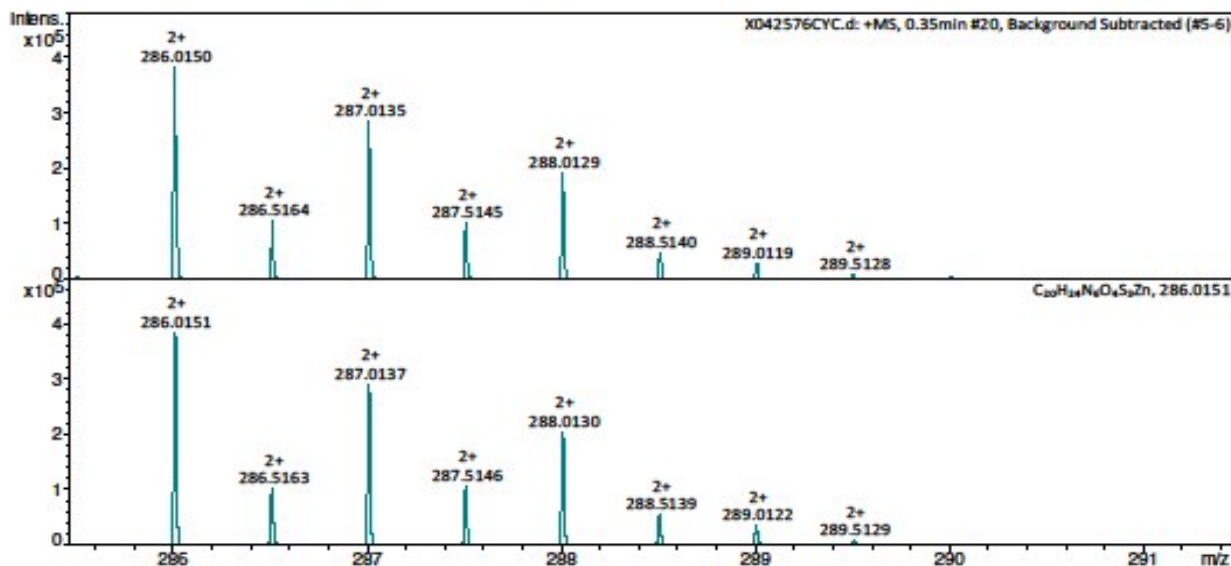
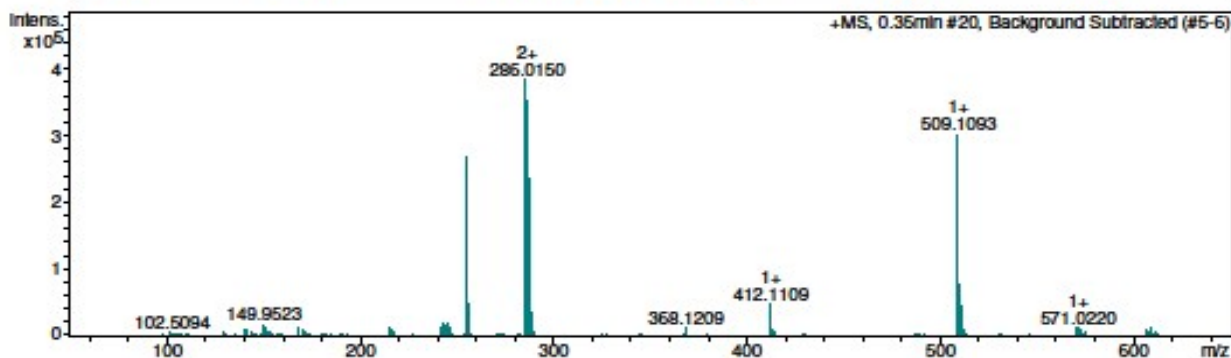
Analysis Info

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Analysis Name X042576CYC.d

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Instrument / Ser# maXis 255552.00086
Method Positif.m

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Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻	Conf
255.058178	2+	1	C20H26N6O4S3	255.058335	0.6	4.7	12.0	even	
	2+	2	C19H30N2O8S3	255.057666	-2.0	5.9	7.0	even	
286.015001	2+	1	C20H24N6O4S3Zn	286.015081	0.3	16.5	13.0	even	
	2+	2	C19H28N2O8S3Zn	286.014412	-2.1	18.5	8.0	even	
412.110923	1+	1	C16H22N5O4S2	412.110773	-0.4	23.1	9.0	even	
	1+	2	C24H18N3O2S	412.111424	1.2	56.4	18.0	even	
509.109300	1+	1	C20H25N6O4S3	509.109393	0.2	13.2	12.0	even	
571.022048	1+	1	C19H27N2O8S3Zn	571.021547	-0.9	22.7	8.0	even	

Figure S13. HRMS of [Zn(no1th2tha)]



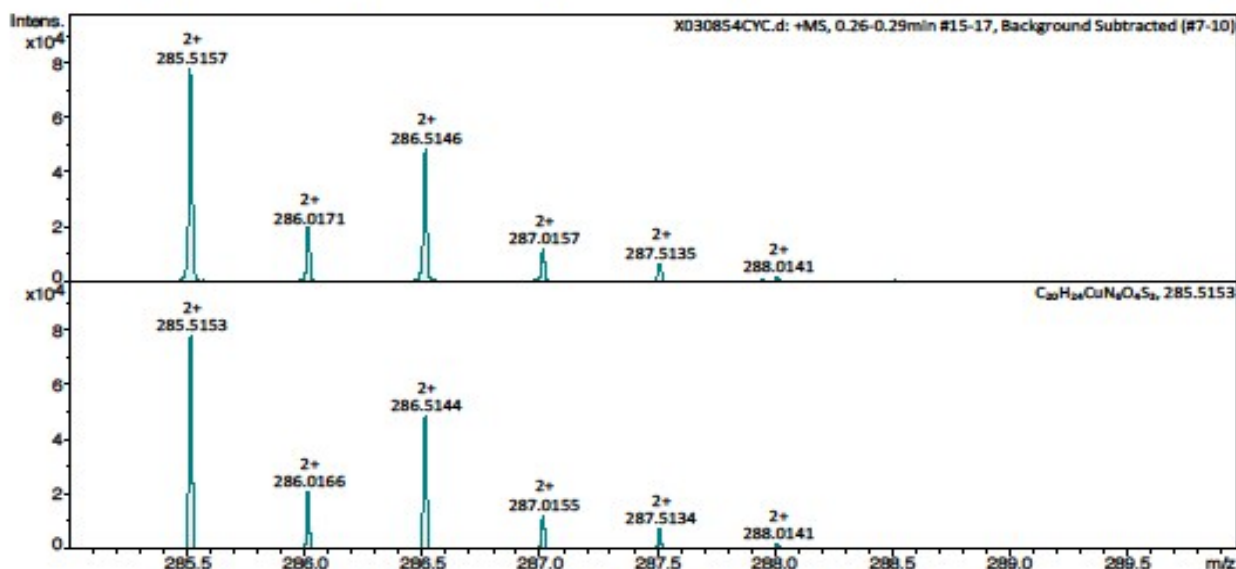
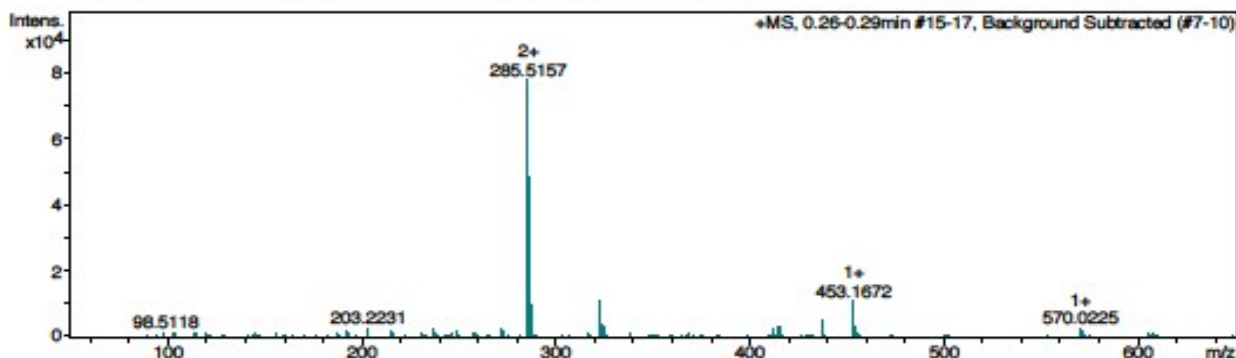
Analysis Info

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Analysis Name X030854CYC.d

Acquisition Date 14/12/2016 14:41:32
Instrument / Ser# maXis 255552.00086
Method Positif.m

Acquisition Parameter

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Scan End 2500 m/z Set Collision Cell RF 1800.0 Vpp Set Dry Gas 7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻	Conf
285.515728	2+	1	C ₂₀ H ₂₄ CuN ₆ O ₄ S ₃	285.515308	-1.5	7.5	12.5	odd	
570.022480	1+	1	C ₂₀ H ₂₃ CuN ₆ O ₄ S ₃	570.023340	1.5	50.9	12.5	odd	
	1+	2	C ₁₉ H ₂₇ CuN ₂ O ₈ S ₃	570.022003	-0.8	54.5	7.5	odd	

Figure S14. HRMS of [Cu(no1th2tha)]

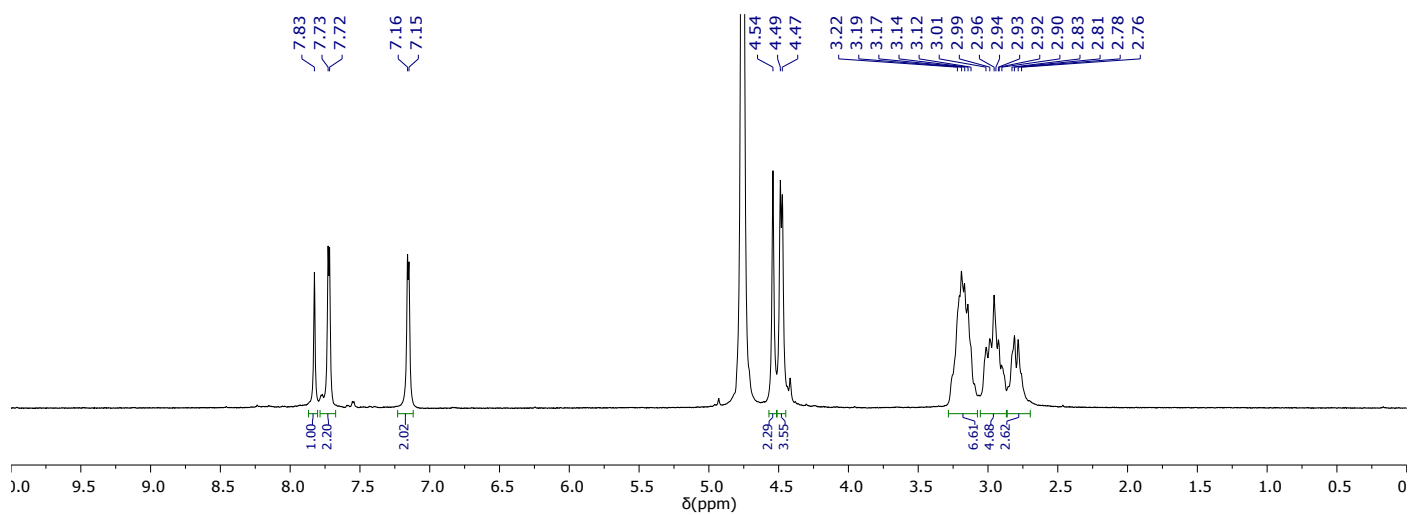


Figure S15. ¹H NMR (300 MHz, 298 K, D₂O) spectrum of [Zn(no2th1tha)]⁺



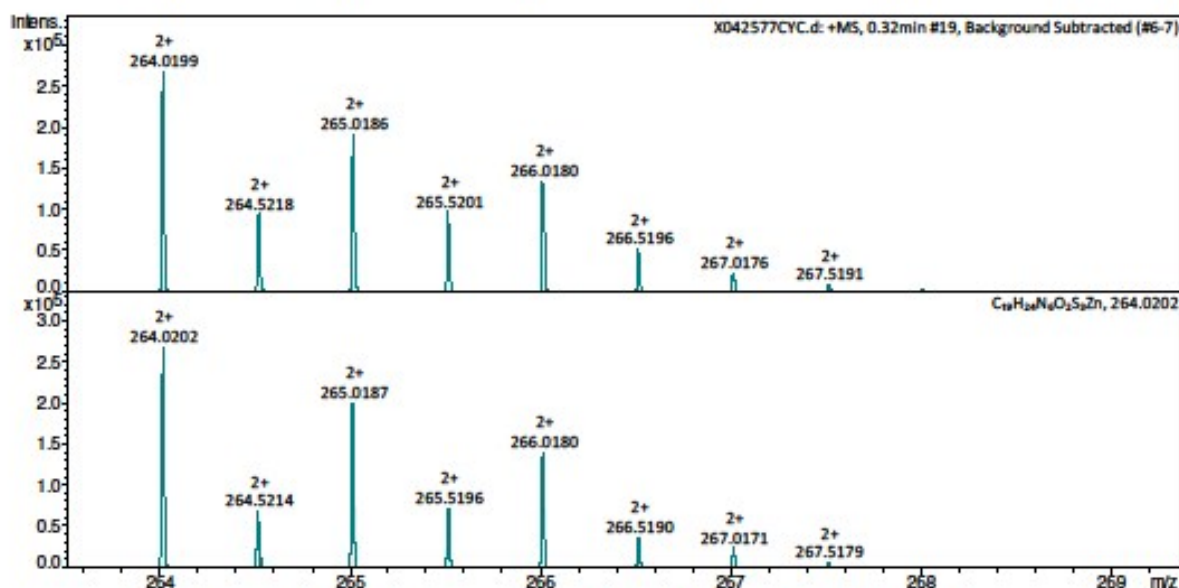
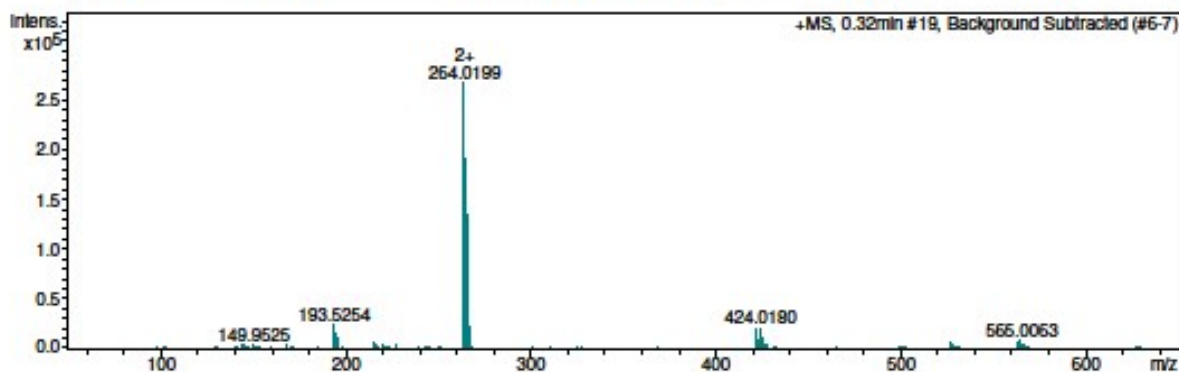
Analysis Info

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Method Positif.m

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Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e ⁻	Conf
193.525398	2+	1	C14H21N6S2Zn	193.525941	2.8	33.6	8.0	even	
	2+	2	C13H25NO4S2Zn	193.525273	-0.6	43.2	3.0	even	
264.019865	2+	1	C19H24N6O2S3Zn	264.020166	1.1	53.6	12.0	even	
	2+	2	C18H28N2O6S3Zn	264.019497	-1.4	63.9	7.0	even	
422.020831	1+	1	C14H21ClN5S2Zn	422.021284	1.1	33.0	7.0	even	
	1+	2	C13H25ClNO4S2Zn	422.019947	-2.1	37.0	2.0	even	
527.031711	1+	1	C19H23N6O2S3Zn	527.033056	2.6	62.5	12.0	even	
	1+	2	C18H27N2O6S3Zn	527.031718	0.0	72.5	7.0	even	

Figure S16. HRMS of $[\text{Zn}(\text{no2th1tha})]^+$



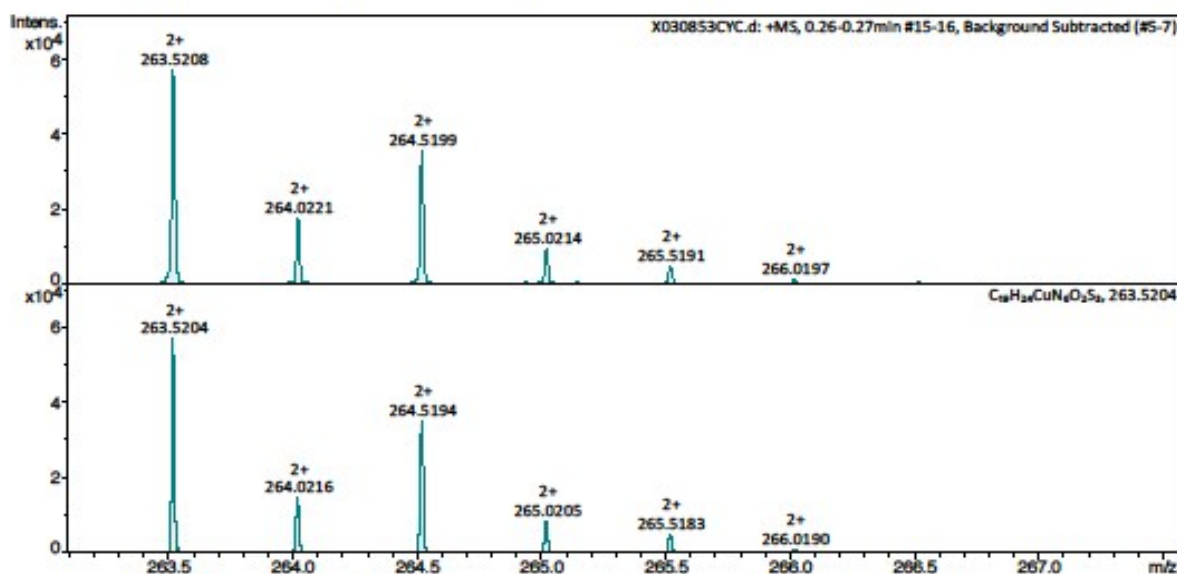
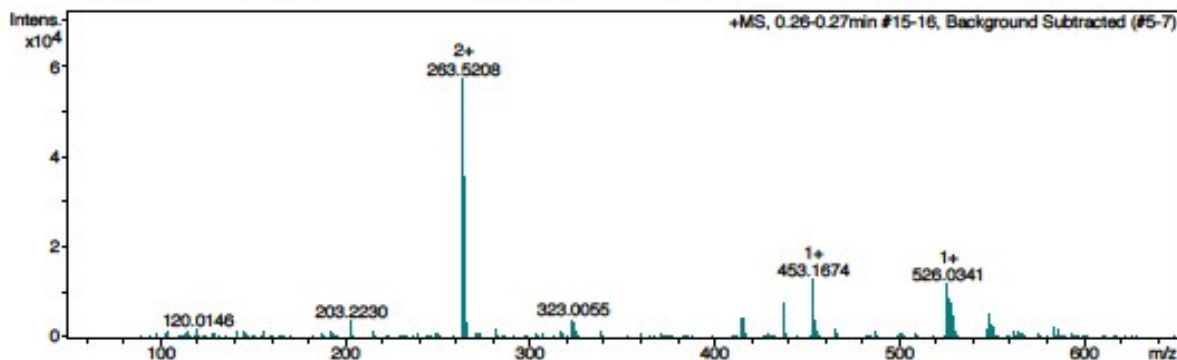
Analysis Info

Sample Name Cute2th1tha
Analysis Name X030853CYC.d

Acquisition Date 14/12/2016 14:40:03
Instrument / Ser# maXis 255552.00086
Method Positif.m

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdB	e ⁻	Conf
263.520768	2+	1	C ₁₉ H ₂₄ CuN ₆ O ₂ S ₃	263.520394	-1.4	23.3	11.5	odd	
526.034052	1+	1	C ₁₉ H ₂₃ CuN ₆ O ₂ S ₃	526.033511	-1.0	223.6	11.5	odd	

Figure S17. HRMS of [Cu(no2th1tha)]⁺

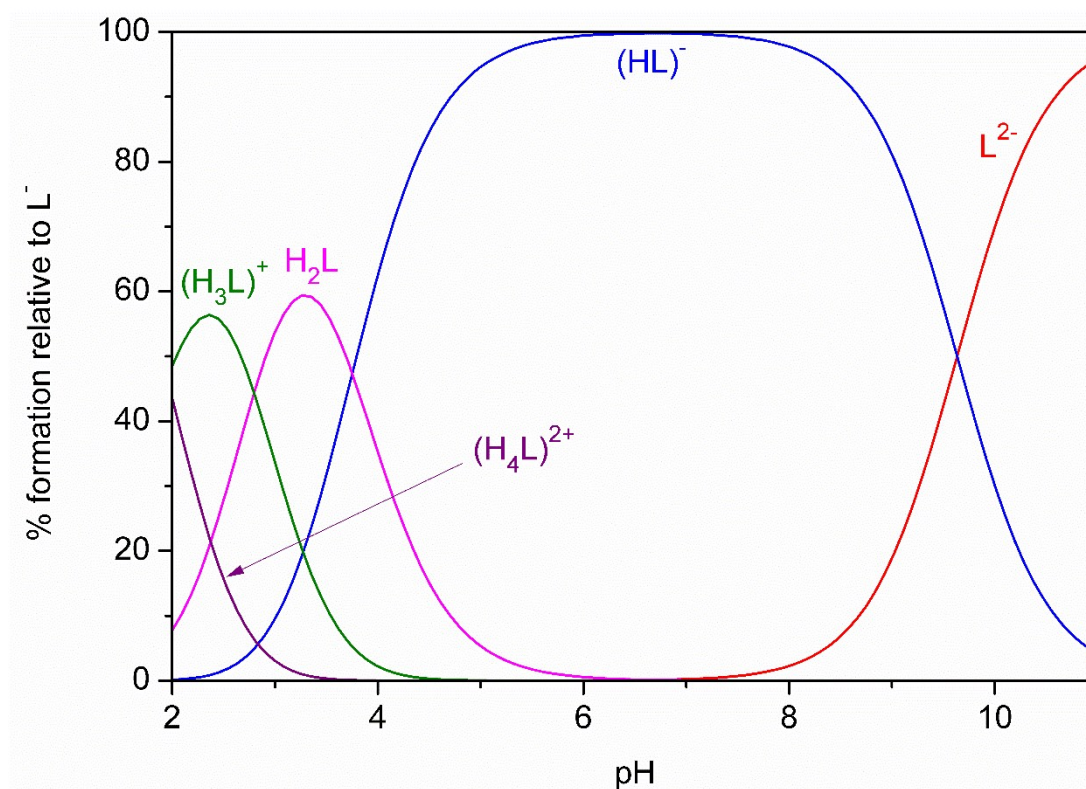


Figure S18. Species distribution diagram for H₂no1th2tha at 1.0 mM of ligand. L denotes the ligand.

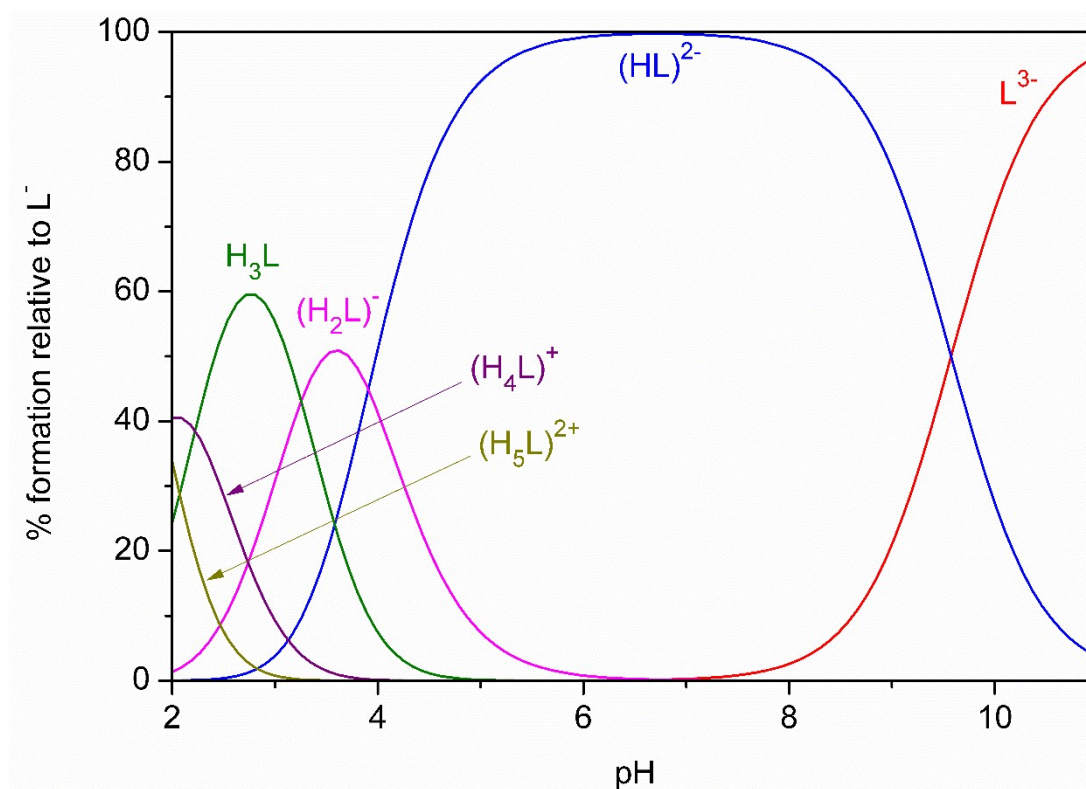


Figure S19. Species distribution diagram for H₃no3tha at 1.0 mM of ligand. L denotes the ligand.

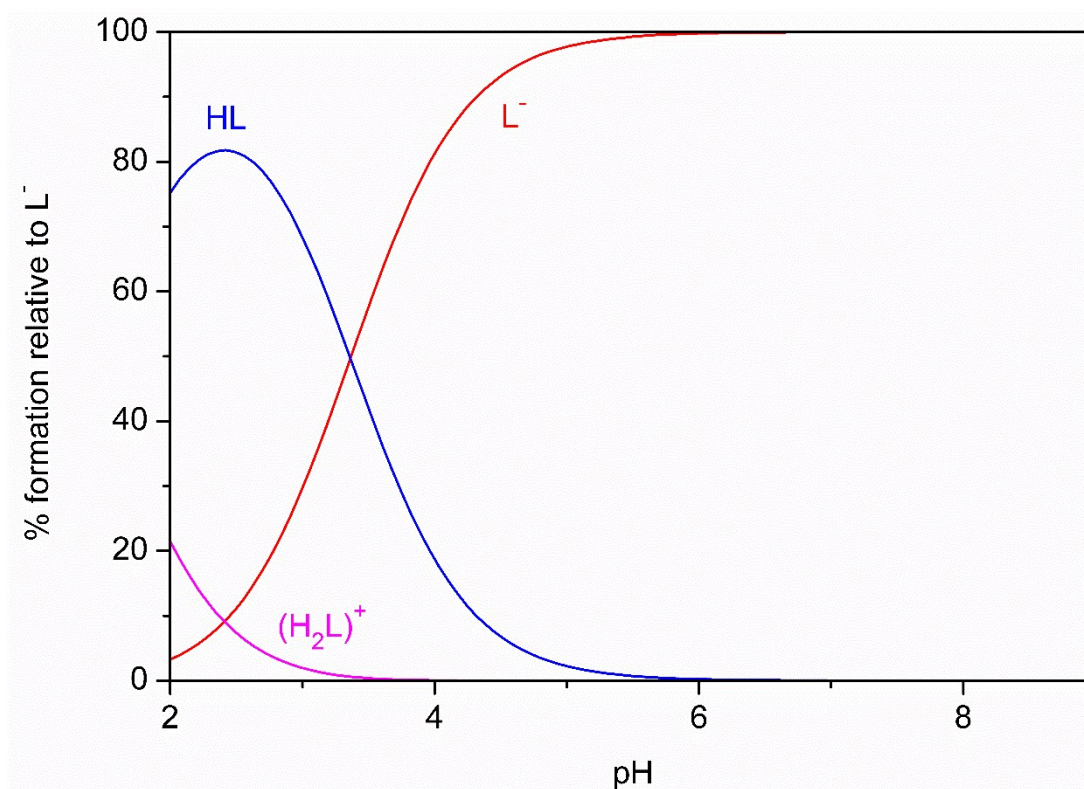


Figure S20. Species distribution diagram for Htha at 1.0 mM of ligand. L denotes the ligand.

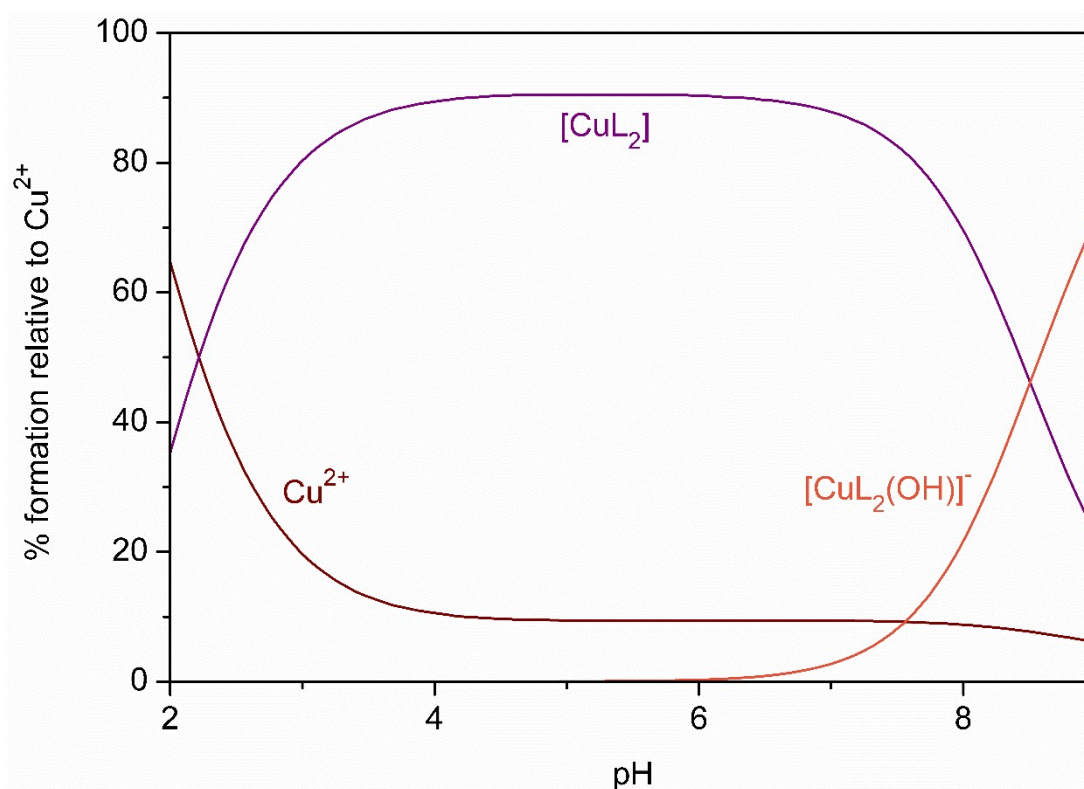


Figure S21. Species distribution diagram for the copper(II) complexes of Htha at 1.0 mM of ligand and 1:2 Cu^{2+}/L ratio. L denotes the ligand.

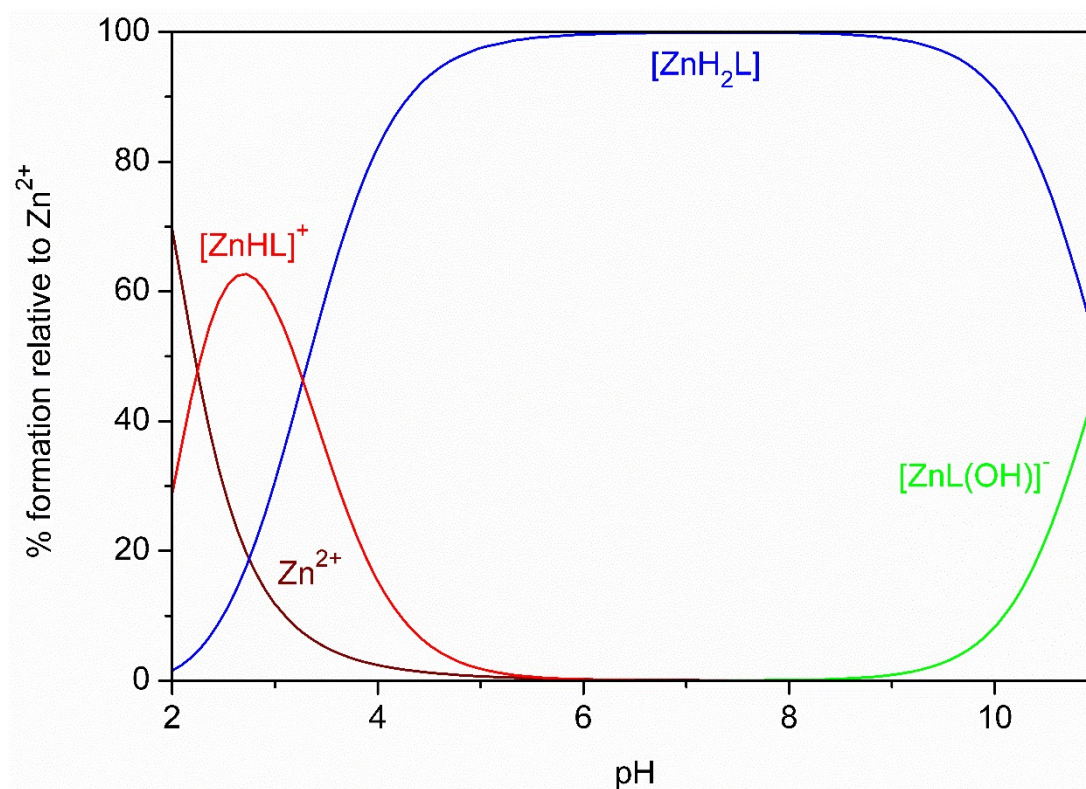


Figure S22. Species distribution diagram for the zinc(II) complexes of H₂no1th2tha at 1.0 mM of ligand and 1:1 Zn²⁺/L ratio. L denotes the ligand.

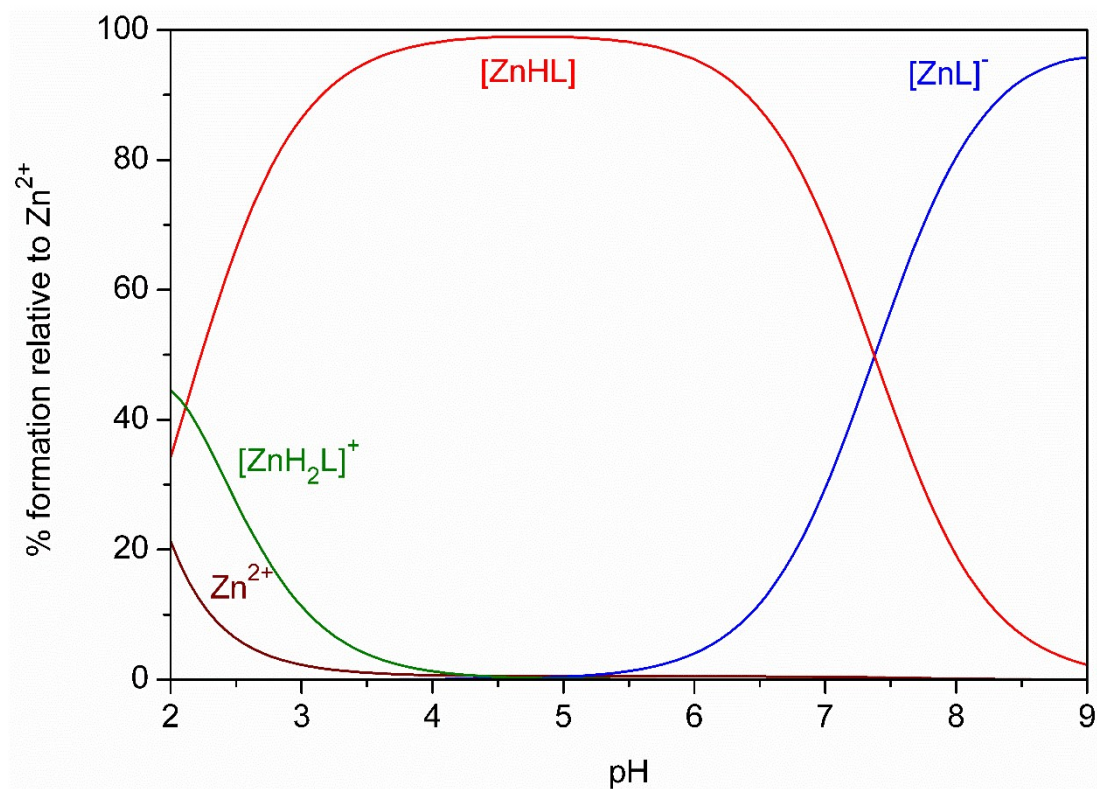


Figure S23. Species distribution diagram for the zinc(II) complexes of H₃no3tha at 1.0 mM of ligand and 1:1 Zn²⁺/L ratio. L denotes the ligand.

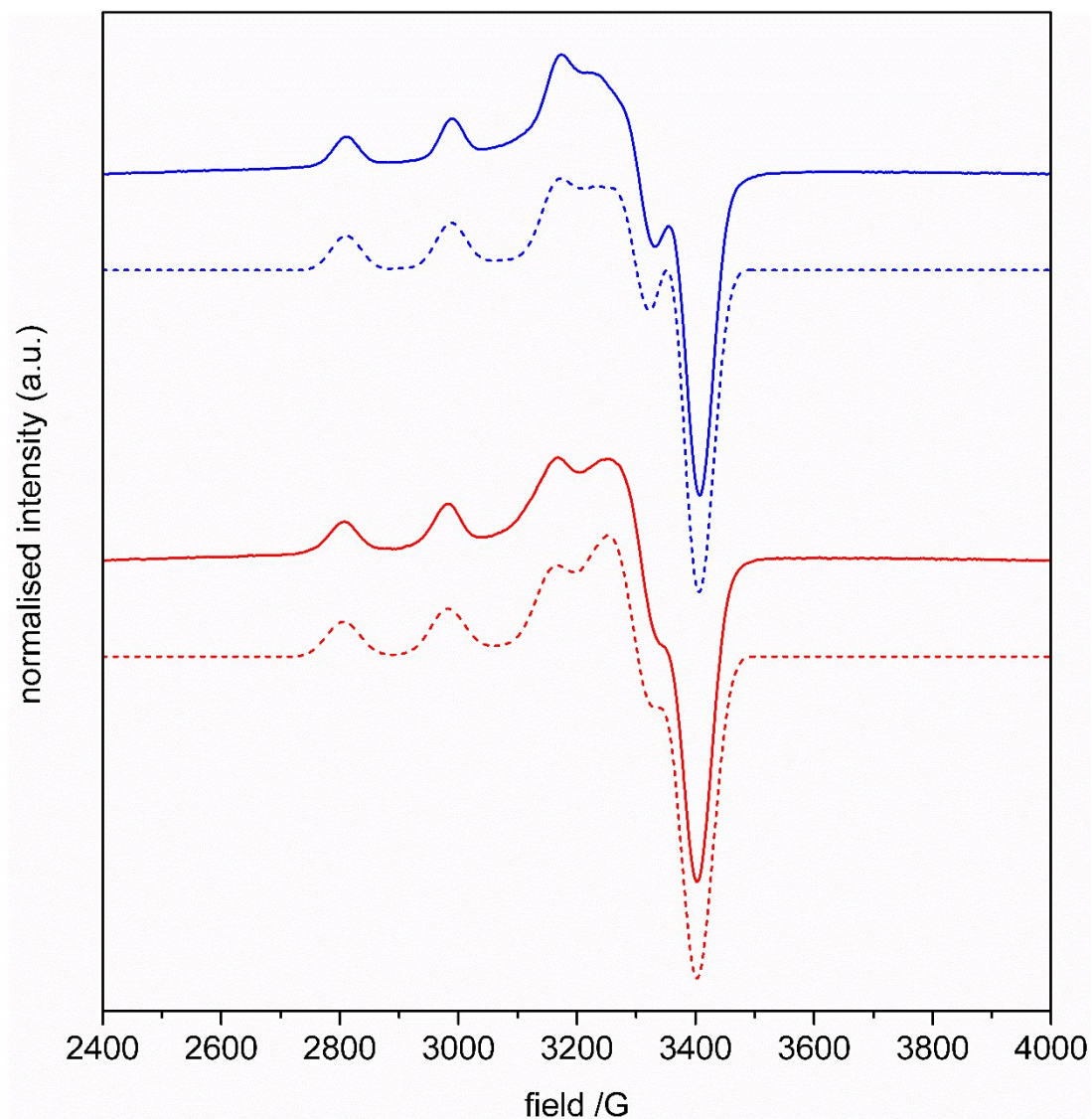


Figure S24. Experimental (solid) and simulated (dotted) EPR spectra for the copper(II) complexes of **Hno2th1tha** at 1:1 (blue) and 3:2 (red) Cu²⁺/L ratios in aqueous solutions at 1 M in NaClO₄ and pH = 7.0.

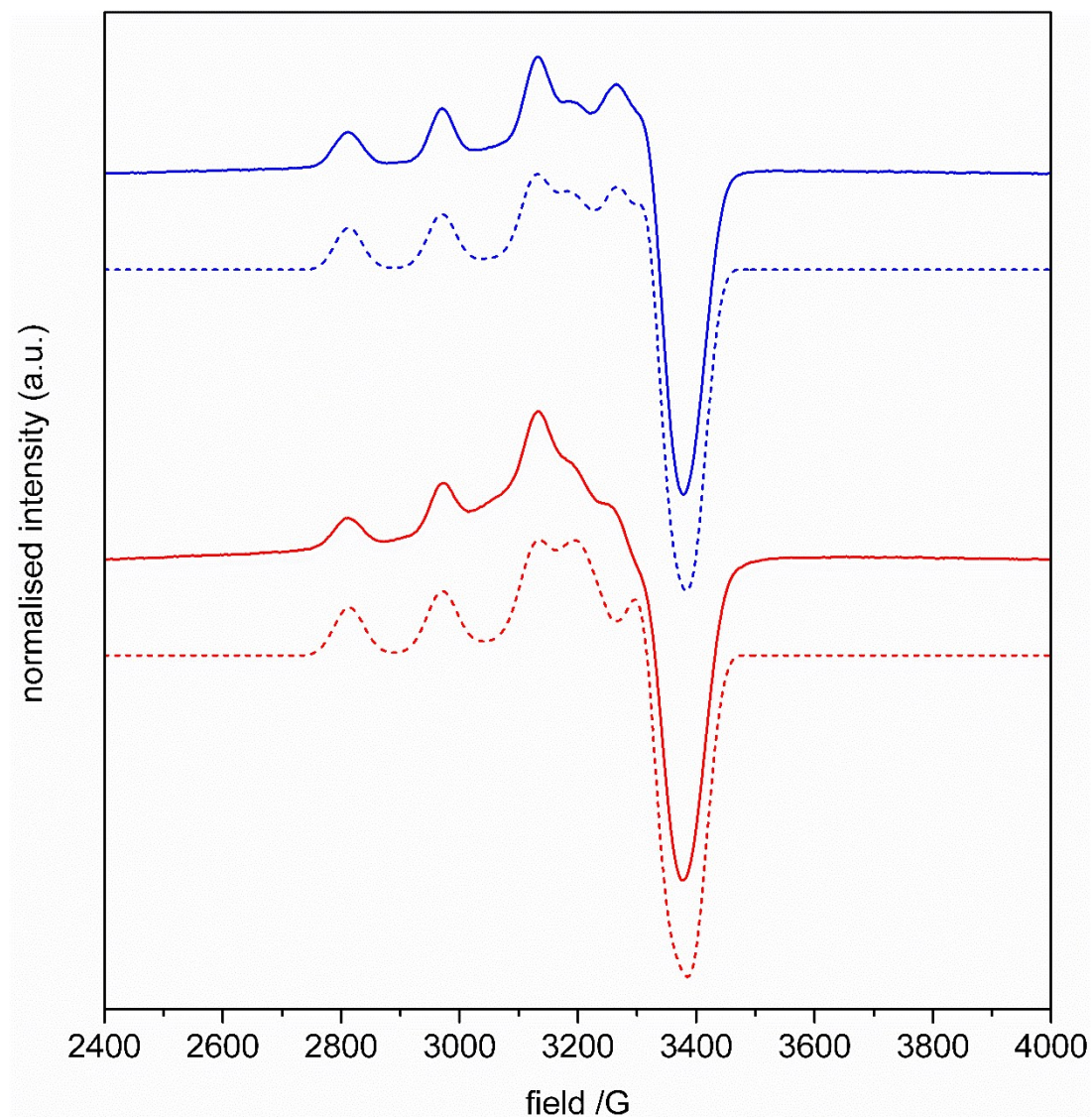


Figure S25. Experimental (solid) and simulated (dotted) EPR spectra for the copper(II) complexes of H₂no1th2tha at 1:1 (blue) and 3:2 (red) Cu²⁺/L ratios in aqueous solutions at 1 M in NaClO₄ and pH = 7.0.

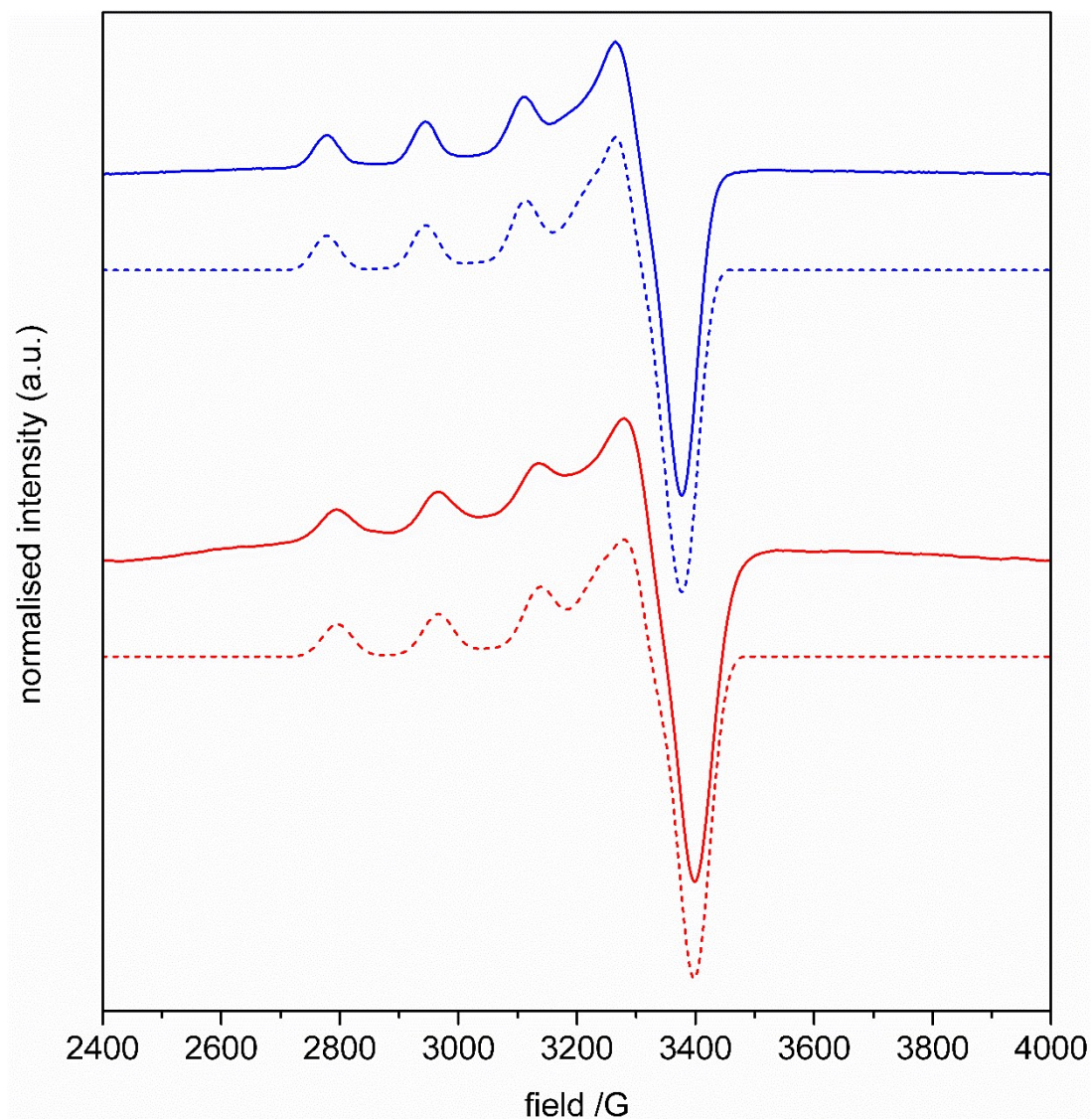


Figure S26. Experimental (solid) and simulated (dotted) EPR spectra for the copper(II) complexes of H₃no3tha at 1:1 (blue) and 3:2 (red) Cu²⁺/L ratios in aqueous solutions at 1 M in NaClO₄ and pH = 7.0.

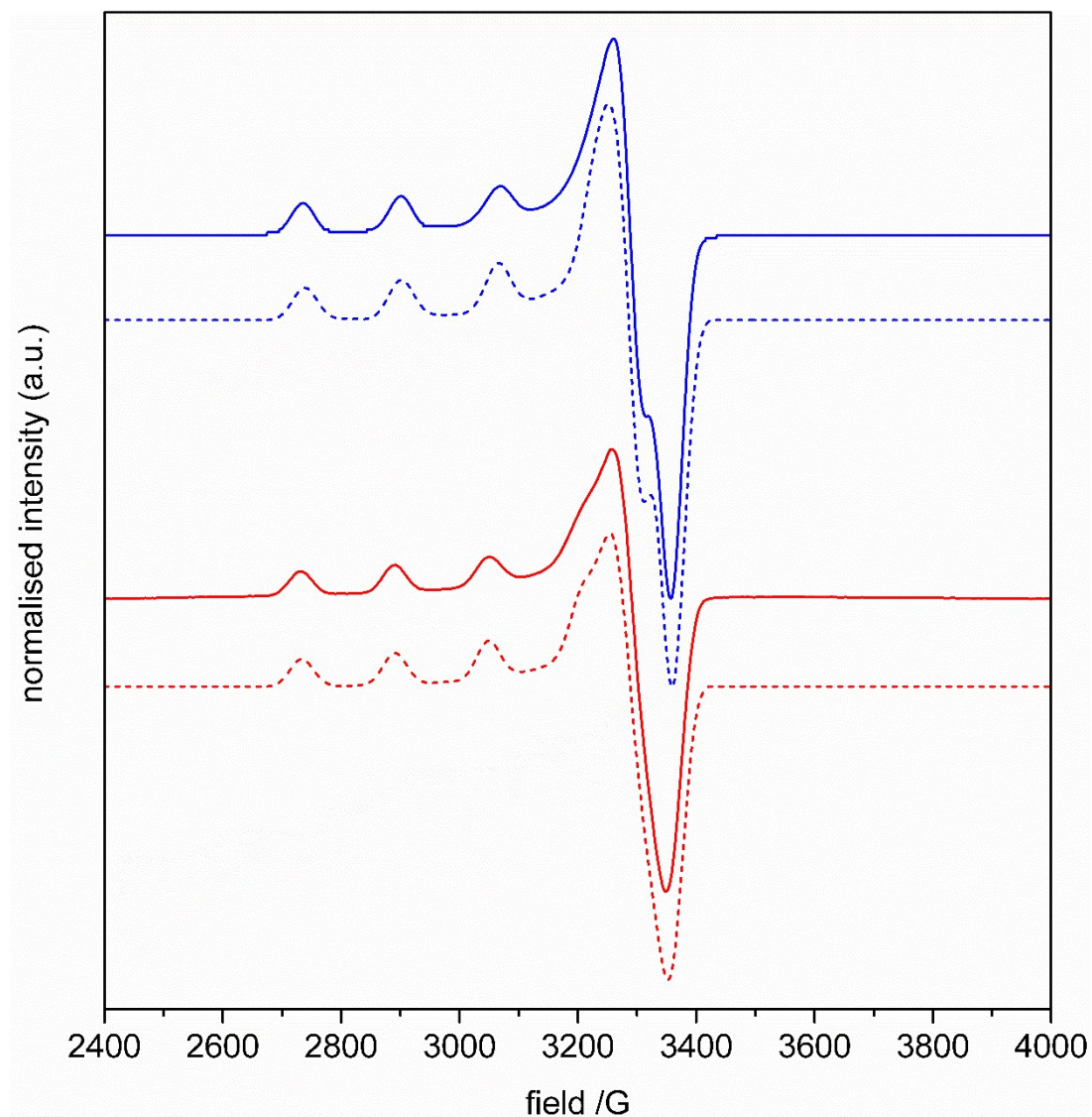
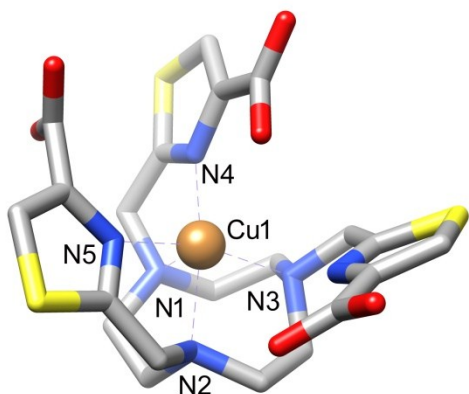
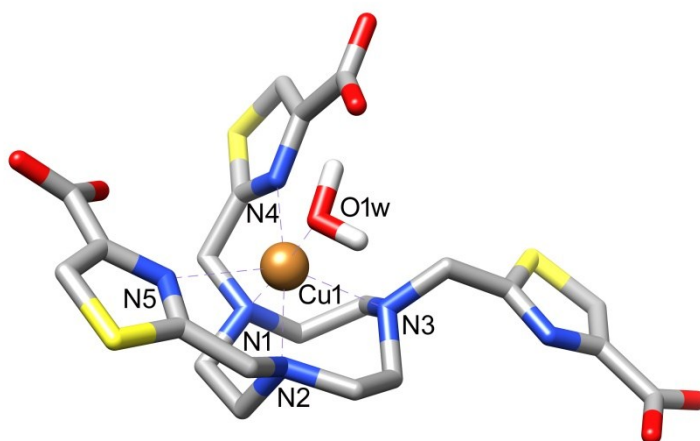


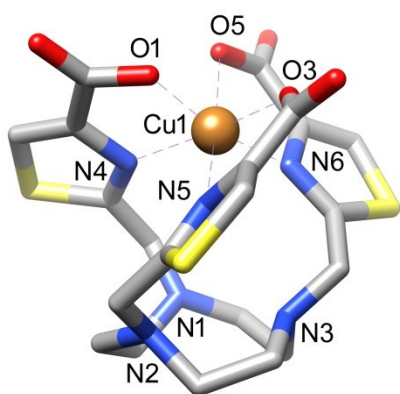
Figure S27. Experimental (solid) and simulated (dotted) EPR spectra for the copper(II) complexes of Htha at 1:2 (blue) and 1:3 (red) Cu²⁺/L ratios in aqueous solutions at 1 M in NaClO₄ and pH = 7.0.



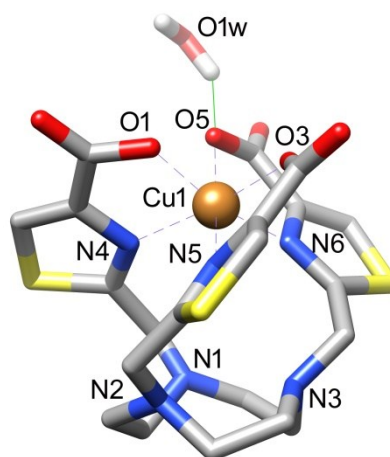
endo-[Cu(**no3tha**)]⁻



endo-[Cu(**no3tha**)(H₂O)]⁻



exo-[Cu(**no3tha**)]⁻



exo-[Cu(**no3tha**)(H₂O)]⁻

Figure S28. Structures of the copper complexes obtained with DFT calculations.

Table S1. Overall ($\log \beta_i^H$) protonation constants^a of the studied ligands in aqueous solution at 25.0 ± 0.1 °C and $I = 0.10 \pm 0.01$ M in KNO₃.

Equilibrium reaction ^b	Hno2th1tha ^c	H ₂ no1th2tha	H ₃ no3tha	no2th ^d	Htha
L + H ⁺ $\rightleftharpoons$ HL	9.47(1)	9.63(1)	9.58(1)	11.03	3.36(1)
L + 2 H ⁺ $\rightleftharpoons$ H ₂ L	12.65(2)	13.38(2)	13.48(1)	13.48	4.82(3)
L + 3 H ⁺ $\rightleftharpoons$ H ₃ L	14.47(2)	16.18(2)	16.74(1)	–	–
L + 4 H ⁺ $\rightleftharpoons$ H ₄ L	–	18.14(3)	18.96(1)	–	–
L + 5 H ⁺ $\rightleftharpoons$ H ₅ L	–	–	20.88(2)	–	–

^a Values in parenthesis are the standard deviations in the last significant figures. ^b L denotes each ligand in general; the charges of ligand containing species are omitted for clarity. ^c From ref. 24. ^d From ref. 23.

Table S2. Overall ($\log \beta_{M_mH_hL_l}$) stability constants^a for the metal complexes of the studied ligands in aqueous solution at 25.0 ± 0.1 °C and $I = 0.10 \pm 0.01$ M in KNO₃.

Equilibrium reaction ^b	Hno2th1tha ^c	H ₂ no1th2tha	H ₃ no3tha	no2th ^d	Htha
Cu ²⁺ + 2 L $\rightleftharpoons$ CuL ₂	–	–	–	–	9.09(2)
Cu ²⁺ + 2 L $\rightleftharpoons$ CuL ₂ H ₋₁ + H ⁺	–	–	–	–	0.58(4)
Cu ²⁺ + L $\rightleftharpoons$ CuL	19.8	18.0(1) ^e	16.6(1) ^e	20.77	–
Cu ²⁺ + L + H ⁺ $\rightleftharpoons$ CuHL	22.76	21.65(4)	20.98(4)	23.60	–
Cu ²⁺ + L $\rightleftharpoons$ CuLH ₋₁ + H ⁺	8.86	7.65(5)	6.79(3)	11.59	–
3 Cu ²⁺ + 2 L $\rightleftharpoons$ Cu ₃ L ₂	46.53	44.17(9)	42.48(9)	–	–
3 Cu ²⁺ + 2 L $\rightleftharpoons$ Cu ₃ L ₂ H ₋₁ + H ⁺	–	37.2(1)	36.8(1)	–	–
3 Cu ²⁺ + 2 L $\rightleftharpoons$ Cu ₃ L ₂ H ₋₂ + 2 H ⁺	33.24	28.9(1)	28.8(1)	–	–
Zn ²⁺ + L $\rightleftharpoons$ ZnL	16.0	12.0(1) ^e	9.85(6)	16.28	–
Zn ²⁺ + L + H ⁺ $\rightleftharpoons$ ZnHL	18.56	15.27(4)	17.23(6)	18.30	–
Zn ²⁺ + L + 2 H ⁺ $\rightleftharpoons$ ZnH ₂ L	–	–	19.34(7)	–	–
Zn ²⁺ + L $\rightleftharpoons$ ZnLH ₋₁ + H ⁺	4.85	0.96(6)	–1.19(9)	5.75	–

^a Values in parenthesis are the standard deviations in the last significant figures. ^b L denotes each ligand in general; the charges of ligand containing species are omitted for clarity. ^c From ref. 24. ^d From ref. 23. ^e Values determined from competition titrations with K₂H₂edta.

Table S3. EPR parameters^a obtained from simulation of the experimental spectra of the copper(II) complexes studied in this work at non stoichiometric Cu²⁺/L ratio.

	g_x	g_y	g_z	A_x	A_y	A_z
Hno2th1tha ^b	2.040	2.069	2.212	2	20	182
H₂no1th2tha ^b	2.043	2.087	2.228	37	29	164
H₃no3tha ^b	2.035	2.064	2.226	10	24	177
Htha ^c	2.058	2.073	2.284	1	5	172

^a A_i given in 10^{-4} cm⁻¹. ^b At 1.5:1 Cu²⁺/L ratio. ^c At 1:3 Cu²⁺/L ratio.

Table S4. g-values obtained with DFT calculations for the copper(II) complexes investigated in this work and their breakdown into relativistic mass correction (RMC), the diamagnetic spin-orbit term (DSO) and the paramagnetic spin-orbit (PSO) term.

ligand		g_x	g_y	g_z
Hno2th1tha	g_{el}	2.0023193	2.0023193	2.0023193
	g_{RMC}	-0.0011083	-0.0011083	-0.0011083
	$g_{DSO(tot)}$	0.0004135	0.0004333	0.0005931
	$g_{PSO(tot)}$	0.0613173	0.0831981	0.2157740
	$g(tot)$	2.0629419	2.0848425	2.2175782
H₃no3tha ^a	g_{el}	2.0023193	2.0023193	2.0023193
	g_{RMC}	-0.0010580	-0.0010465	-0.0010465
	$g_{DSO(tot)}$	0.0003684	0.0003792	0.0005568
	$g_{PSO(tot)}$	0.0586321	0.0648581	0.1853924
	$g(tot)$	2.0602734	2.0665102	2.1872221
H₃no3tha ^b	g_{el}	2.0023193	2.0023193	2.0023193
	g_{RMC}	-0.0010580	-0.0010580	-0.0010580
	$g_{DSO(tot)}$	0.0003664	0.0004022	0.0005682
	$g_{PSO(tot)}$	0.0434251	0.0692263	0.1748304
	$g(tot)$	2.0450528	2.0708898	2.1766599
H₃no3tha ^c	g_{el}	2.0023193	2.0023193	2.0023193
	g_{RMC}	-0.0010457	-0.0010457	-0.0010457
	$g_{DSO(tot)}$	0.0003559	0.0003898	0.0005570
	$g_{PSO(tot)}$	0.0454897	0.0725765	0.1827629
	$g(tot)$	2.0471192	2.0742399	2.1845934

^a Calculated for the exocyclic [Cu(**no3tha**)]⁻ complex. ^d Calculated for the endocyclic [Cu(**no3tha**)(H₂O)]⁻ complex. ^e Calculated for the endocyclic [Cu(**no3tha**)]⁻ complex.

Table S5. Bond distances (Å) of the metal coordination environments obtained with DFT calculations.

	[Cu(no3tha)] ^{-a}	[Cu(no3tha)(H ₂ O)] ^{-a}	[Cu(no3tha)] ^{-b}	[Cu(no3tha)(H ₂ O)] ^{-b}
Cu1-N1	2.315	2.050	-	-
Cu1-N2	2.084	2.106	-	-
Cu1-N3	2.146	2.392	-	-
Cu1-N4	2.024	2.081	2.124	2.110
Cu1-N5	2.072	2.628	2.537	2.493
Cu1-N6	-	-	2.070	2.082
Cu1-O1	-	-	1.979	1.985
Cu1-O3	-	-	1.993	1.987
Cu1-O5	-	-	2.292	2.330
Cu1-O1w	-	1.968	-	-

^a Endocyclic coordination. ^b exocyclic coordination.

Table S6. Optimised Cartesian Coordinates (Å) obtained with DFT (TPSSH/def2-TZVPP) for *endo*-[Cu(**no3tha**)]⁻ (0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.953018	1.102575	2.713518
2	1	-2.414166	1.750063	1.968283
3	1	-2.536708	1.189557	3.639838
4	6	-0.530149	1.576201	3.020021
5	1	-0.157770	1.065362	3.907622
6	1	-0.558291	2.640659	3.261184
7	6	1.715332	0.716628	2.483112
8	1	2.495312	0.855262	1.743291
9	1	2.003077	1.215068	3.414344
10	6	1.501628	-0.769510	2.738585
11	1	1.016177	-0.928987	3.700266
12	1	2.473361	-1.263187	2.792226
13	6	-0.429655	-2.215362	2.342921
14	1	-0.916073	-2.808558	1.570407
15	1	0.002283	-2.909194	3.072474
16	6	-1.447317	-1.313687	3.045903
17	1	-2.264762	-1.943431	3.412223
18	1	-1.000861	-0.851408	3.925526
19	6	-3.166185	-0.641623	1.435459
20	1	-3.870221	-1.202019	2.059926
21	1	-3.664779	0.260776	1.073810
22	6	-2.777678	-1.425645	0.213386
23	6	-2.576655	-2.728149	-1.825895
24	1	-2.719322	-3.386653	-2.666129
25	6	-1.505101	-1.926747	-1.565276
26	6	-0.277690	-1.724817	-2.431694
27	6	0.849303	2.582060	1.193882
28	1	0.941590	3.435252	1.871626
29	1	1.822187	2.409839	0.712852
30	6	-0.163258	2.833625	0.129551
31	6	-1.540842	3.600330	-1.699427
32	1	-2.050208	4.174726	-2.455532
33	6	-1.709079	2.282078	-1.399102
34	6	-2.798039	1.427749	-2.045494
35	6	1.441745	-2.370663	0.840883
36	1	1.808133	-3.199604	1.458275
37	1	0.755961	-2.790319	0.101777
38	6	2.595797	-1.717957	0.138927
39	6	4.602526	-1.219592	-1.129211
40	1	5.520235	-1.233360	-1.693596
41	6	3.885476	-0.128762	-0.720480
42	6	4.297370	1.314479	-0.961737
43	7	-1.956395	-0.256993	2.161015
44	7	0.484867	1.345348	1.928919
45	7	0.657702	-1.434056	1.685262
46	7	-1.635422	-1.211635	-0.395740
47	7	-0.897644	1.852874	-0.359222
48	7	2.746538	-0.439639	-0.011578
49	8	0.523653	-0.853017	-2.008420
50	8	-0.197508	-2.427224	-3.465744
51	8	-3.666293	0.999763	-1.248440
52	8	-2.745488	1.306314	-3.290093

53	8	3.631837	2.201559	-0.363463
54	8	5.279846	1.484776	-1.725751
55	16	-3.762385	-2.567248	-0.596736
56	16	-0.403833	4.335166	-0.643357
57	16	3.857141	-2.666000	-0.593095
58	29	-0.352858	0.057985	0.520967

E(UTPSSh) = -4428.8417005 Hartree
Zero-point correction = 0.422846
Thermal correction to Energy = 0.456124
Thermal correction to Enthalpy = 0.457068
Thermal correction to Gibbs Free Energy = 0.356787
Sum of electronic and zero-point Energies = -4428.418854
Sum of electronic and thermal Energies = -4428.385576
Sum of electronic and thermal Enthalpies = -4428.384632
Sum of electronic and thermal Free Energies = -4428.484913

Table S7. Optimised Cartesian Coordinates (Å) obtained with DFT (TPSSh/def2-TZVPP) for *endo*-[Cu(**no3tha**)(H₂O)]⁻ (0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	1.590818	-1.308747	2.389615
2	1	2.629408	-1.220362	2.086289
3	1	1.546925	-1.409804	3.478313
4	6	0.944610	-2.521157	1.728432
5	1	0.009570	-2.777816	2.223831
6	1	1.603711	-3.384379	1.834957
7	6	-0.753256	-2.673907	-0.064050
8	1	-0.849805	-2.602390	-1.148520
9	1	-0.929588	-3.719654	0.209737
10	6	-1.797918	-1.789479	0.611261
11	1	-1.823182	-1.978203	1.683939
12	1	-2.781684	-2.075841	0.232196
13	6	-1.556697	0.467569	1.594709
14	1	-1.425687	1.506572	1.288132
15	1	-2.509771	0.404074	2.134991
16	6	-0.455270	0.058315	2.567590
17	1	-0.415027	0.783438	3.382796
18	1	-0.694200	-0.903129	3.018999
19	6	1.747062	1.134462	2.183938
20	1	1.654757	1.497106	3.210008
21	1	2.790360	0.867262	1.972767
22	6	1.382372	2.179089	1.182536
23	6	1.029340	4.144464	-0.168345
24	1	0.931688	5.138081	-0.570794
25	6	0.829357	2.971419	-0.837782
26	6	0.448053	2.977850	-2.305608
27	6	1.582673	-3.023460	-0.604190
28	1	1.606259	-4.081857	-0.325707
29	1	1.197892	-2.965957	-1.623981
30	6	2.965249	-2.440252	-0.569505
31	6	5.323357	-1.968103	-0.819145
32	1	6.385046	-1.984330	-1.000332
33	6	4.575084	-0.922811	-0.353855
34	6	5.174287	0.416627	0.050659

35	6	-2.402502	0.216907	-0.695843
36	1	-2.048391	1.227693	-0.897781
37	1	-2.253323	-0.377985	-1.597102
38	6	-3.880071	0.232218	-0.403409
39	6	-6.161989	0.745074	0.251140
40	1	-7.087399	1.181109	0.588789
41	6	-5.967409	-0.521753	-0.235490
42	6	-7.082808	-1.554199	-0.370673
43	7	0.905419	-0.063444	1.950999
44	7	0.646404	-2.286140	0.274721
45	7	-1.544425	-0.351369	0.371807
46	7	1.034844	1.848963	-0.045547
47	7	3.228979	-1.210402	-0.225908
48	7	-4.668435	-0.789670	-0.604465
49	8	0.420319	1.873156	-2.942074
50	8	0.201224	4.089499	-2.794957
51	8	4.459403	1.165092	0.764995
52	8	6.343683	0.629622	-0.352646
53	8	-6.763464	-2.692907	-0.791061
54	8	-8.228666	-1.151303	-0.038335
55	8	0.825595	-0.366660	-2.052987
56	16	1.474084	3.862739	1.454062
57	16	4.345981	-3.348896	-1.073224
58	16	-4.696017	1.620481	0.252891
59	29	0.799119	-0.217891	-0.090437
60	1	0.146291	-0.910840	-2.467119
61	1	0.666639	0.628552	-2.418006

E(UTPSSh) = -4505.3263663 Hartree

Zero-point correction = 0.446357

Thermal correction to Energy = 0.481902

Thermal correction to Enthalpy = 0.482846

Thermal correction to Gibbs Free Energy = 0.375174

Sum of electronic and zero-point Energies = -4504.880009

Sum of electronic and thermal Energies = -4504.844464

Sum of electronic and thermal Enthalpies = -4504.843520

Sum of electronic and thermal Free Energies = -4504.951192

Table S9. Optimised Cartesian Coordinates (Å) obtained with DFT (TPSSh/def2-TZVPP) for *exo*-[Cu(**no3tha**)(H₂O)]⁻ (0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.155087	3.492753	1.051683
2	1	-1.995164	3.702927	1.716137
3	1	-0.902673	4.453548	0.576411
4	6	0.054819	3.044062	1.892508
5	1	0.958183	3.083965	1.282816
6	1	0.191578	3.778300	2.705698
7	6	-1.137114	1.466155	3.358760
8	1	-1.711981	2.390723	3.440165
9	1	-0.716383	1.288352	4.360725
10	6	-2.097361	0.301379	3.054126
11	1	-1.562741	-0.644755	3.155601
12	1	-2.871597	0.311265	3.843587

13	6	-3.458212	1.500620	1.370991
14	1	-3.418806	2.206878	2.202744
15	1	-4.519200	1.231046	1.257769
16	6	-3.010869	2.207845	0.079302
17	1	-3.213058	1.561382	-0.775176
18	1	-3.636277	3.109531	-0.047832
19	6	-0.993357	2.611703	-1.237714
20	1	-1.179839	3.588063	-1.720644
21	1	-1.435857	1.843521	-1.874858
22	6	0.499210	2.401500	-1.231441
23	6	2.908829	2.725596	-1.415676
24	1	3.913301	3.085279	-1.561882
25	6	2.522754	1.458408	-1.089792
26	6	3.450497	0.279668	-0.936104
27	6	1.165254	0.994823	2.628607
28	1	1.540408	1.142902	3.656218
29	1	1.921378	1.399230	1.952830
30	6	1.087838	-0.492846	2.390148
31	6	1.142132	-2.918810	2.670353
32	1	1.219856	-3.936738	3.013995
33	6	0.855502	-2.483601	1.411070
34	6	0.593468	-3.336395	0.210677
35	6	-3.155846	-0.923198	1.215985
36	1	-4.217112	-1.095674	1.466684
37	1	-2.585730	-1.728192	1.687320
38	6	-3.000732	-1.069737	-0.280061
39	6	-3.338874	-1.521520	-2.651676
40	1	-3.702342	-1.771477	-3.634668
41	6	-2.078150	-1.125244	-2.297779
42	6	-0.931690	-0.960904	-3.252427
43	7	-1.587256	2.503775	0.076040
44	7	-0.081807	1.679690	2.376470
45	7	-2.652888	0.337260	1.711397
46	7	1.155378	1.289392	-0.979966
47	7	0.829337	-1.112536	1.261030
48	7	-1.904845	-0.872349	-0.959314
49	8	2.900625	-0.849796	-0.875166
50	8	4.681276	0.533926	-0.904417
51	8	0.411170	-2.678790	-0.876861
52	8	0.567987	-4.568424	0.319502
53	8	0.205062	-0.642245	-2.744826
54	8	-1.135656	-1.122957	-4.464800
55	16	1.539381	3.719956	-1.615964
56	16	1.388501	-1.580369	3.696179
57	16	-4.335291	-1.582617	-1.267592
58	29	0.577175	-0.702276	-0.793453
59	8	6.398645	-1.551934	-0.611962
60	1	5.728316	-0.830256	-0.723895
61	1	5.899834	-2.363750	-0.752185

E(UTPSSh) = -4505.3353131 Hartree

Zero-point correction = 0.444307

Thermal correction to Energy = 0.480782

Thermal correction to Enthalpy = 0.481726

Thermal correction to Gibbs Free Energy = 0.374285

Sum of electronic and zero-point Energies = -4504.891006

Sum of electronic and thermal Energies = -4504.854531

Sum of electronic and thermal Enthalpies = -4504.853587

Sum of electronic and thermal Free Energies = -4504.961028

Table S9. Optimised Cartesian Coordinates (Å) obtained with DFT (TPSSH/def2-TZVPP) for *exo*-[Cu(**no3tha**)]⁻ (0 imaginary frequencies).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6		-0.841331	-2.369420	2.740550
2	1		-0.271734	-2.432706	3.669551
3	1		-1.449701	-3.286589	2.700319
4	6		-1.800727	-1.166412	2.816431
5	1		-2.545686	-1.243671	2.023812
6	1		-2.349907	-1.233941	3.772089
7	6		-0.198493	0.470402	3.716488
8	1		-0.121532	-0.379836	4.397184
9	1		-0.602486	1.298512	4.319633
10	6		1.214330	0.883178	3.264715
11	1		1.161510	1.837933	2.738216
12	1		1.803857	1.062349	4.183017
13	6		2.062226	-1.409659	2.882669
14	1		1.610606	-1.477215	3.874470
15	1		3.134786	-1.608651	3.028423
16	6		1.494160	-2.524486	1.986516
17	1		2.062962	-2.565326	1.057097
18	1		1.654894	-3.488332	2.502171
19	6		-0.321571	-2.918478	0.400073
20	1		-0.540806	-3.996231	0.508587
21	1		0.490144	-2.821631	-0.323519
22	6		-1.548429	-2.277329	-0.196284
23	6		-3.808174	-1.849943	-1.008713
24	1		-4.844493	-1.883324	-1.299809
25	6		-2.927141	-0.826655	-1.202090
26	6		-3.229397	0.459820	-1.939511
27	6		-1.936071	1.173015	2.120884
28	1		-2.444685	1.753950	2.909779
29	1		-2.716623	0.732007	1.497900
30	6		-1.167456	2.150746	1.266807
31	6		-0.138860	4.173860	0.364127
32	1		0.221479	5.166651	0.152279
33	6		0.048574	3.043959	-0.374825
34	6		0.800017	2.938301	-1.663645
35	6		2.921754	0.463869	1.562996
36	1		3.905271	0.390124	2.059204
37	1		2.731593	1.527593	1.396997
38	6		3.031691	-0.196848	0.208481
39	6		3.820195	-1.259893	-1.838137
40	1		4.372670	-1.724463	-2.637981
41	6		2.482646	-0.973954	-1.795919
42	6		1.509219	-1.278039	-2.898041
43	7		0.101868	-2.297673	1.635743
44	7		-1.115526	0.104821	2.644392
45	7		1.841810	-0.068315	2.362244
46	7		-1.652805	-1.079191	-0.729656
47	7		-0.538097	1.906986	0.140342
48	7		2.054990	-0.376288	-0.636190
49	8		-2.216332	1.161567	-2.226090
50	8		-4.424049	0.694535	-2.211521
51	8		0.784445	1.769238	-2.194254
52	8		1.371125	3.931854	-2.130025

53	8	0.292908	-0.906667	-2.720316
54	8	1.917477	-1.881127	-3.902544
55	16	-3.026077	-3.161038	-0.249345
56	16	-1.075120	3.808627	1.740619
57	16	4.563944	-0.765498	-0.383830
58	29	-0.279977	0.363295	-1.295521

E(UTPSSh) = -4428.8588601 Hartree

Zero-point correction = 0.420489

Thermal correction to Energy = 0.453608

Thermal correction to Enthalpy = 0.454553

Thermal correction to Gibbs Free Energy = 0.356062

Sum of electronic and zero-point Energies = -4428.438371

Sum of electronic and thermal Energies = -4428.405252

Sum of electronic and thermal Enthalpies = -4428.404307

Sum of electronic and thermal Free Energies = -4428.502798