Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

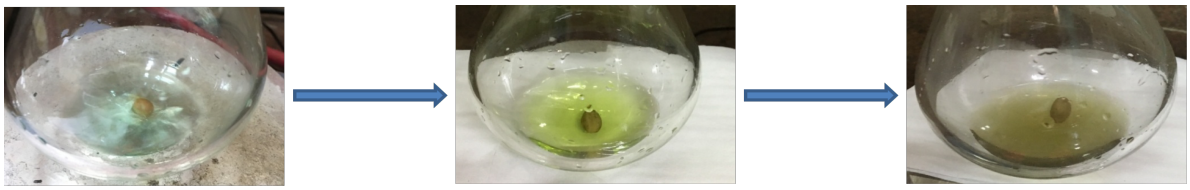
Binding Enabled Catalytic Activation of SO_2 by Copper Koneramine Complexes at Ambient Conditions

Manoj Chahal,[†] Sakthi Raje[,†] Gopichand Kotana[†] and Raja Angamuthu*[,†]*

†Laboratory of Inorganic Synthesis and Bioinspired Catalysis (LISBIC), Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India.

Table of content

The reaction of [Cu(L-OMe)Cl_2] and 2 equivalent ferrocene with SO_2 in CH_3CN



[Cu(L-OMe)Cl_2] (5 mL CH_3CN)

[Cu(L-OMe)Cl_2] + 2 Fc (10 mL CH_3CN)

[Cu(L-OMe)Cl_2] + 2 Fc after purging SO_2 for 15 min

[Cu(L-OMe)Cl_2] (50 mg, 0.083 mmol) was dried under vacuum for 30 minutes in Schlenk flask and dissolved with 5 mL CH_3CN under N_2 atmosphere resulted in a light blue-green solution. It was stirred for 5 minutes and the yellow solution of ferrocene (31 mg, 0.166 mmol) in 5 mL CH_3CN was added at room temperature. The light blue-green solution changed to lime green upon addition of ferrocene solution. The lime green solution was stirred for 5 minutes then SO_2 was purged for 15 minutes at room temperature along with the stirring. The clear lime green solution turned to olive green within 10 minutes of SO_2 purging with little turbidity then the solution was left in open air and sample was analysed by high-resolution ESI-MS.

High resolution ESI-MS (cation mode):

m/z for $C_{10}H_{10}Fe$ = 186.0159 (calcd. 186.0132) = Fc^+

m/z for $C_{11}H_{24}N_7$ = 254.2113 (calcd. 254.2093) = [N^2-(2-aminoethyl)-N^4,N^6-diisopropyl-1,3,5-triazine-2,4,6-triamine + H]

m/z for $C_{17}H_{27}N_8$ = 343.2369 (calcd. 343.2359) = Tim-H

m/z for $C_{17}H_{26}N_8CuCl$ = 440.1289 (calcd. 440.1265) = $[Cu(Tim)Cl]^+$

m/z for $C_{24}H_{33}N_9OCuCl$ = 561.1796 (calcd. 561.1793) = $[Cu(L\text{-}OMe)Cl]^+$

High resolution ESI-MS (anion mode):

m/z for HSO_4 = 96.9595 (calcd. 96.9596) = bisulfate anion

Control reactions:

anhydrous $CuCl_2$ + 2Fc + SO_2 + O_2 ⟶ No activation

anhydrous $CuCl_2$ (14 mg, 0.104 mmol) was dried under vacuum for 30 minutes in Schlenk flask and added to the stirred 10 mL CH_3CN yellow solution of ferrocene (31 mg, 0.166 mmol) at room temperature. The yellow-brown solution changed to green-brown upon addition of metal salt. The green-brown solution was stirred for 5 minutes then SO_2 was purged for 15 minutes at room temperature along with the stirring. The color of the solution changed to red from green-brown on SO_2 purging. The solution was left in open air and sample was analysed by high-resolution ESI-MS. No bisulfate peak was observed in negative ion mode.

Fc + SO_2 + O_2 ⟶ No activation

Ferrocene (15 mg, 0.08 mmol) was dried under vacuum for 30 minutes in Schlenk flask and then dissolved in 10 mL CH_3CN. SO_2 was purged in yellow solution of ferrocene at room temperature along with the stirring. No change in yellow color of the solution upon SO_2 purging. The solution was left in open air and sample was analysed by high-resolution ESI-MS. No bisulfate peak was observed in negative ion mode.

The reaction of [Cu(L-OMe)Cl_2] and 2 equivalent ferrocene with SO_2 in CH_3CN for 3 days

[Cu(L-OMe)Cl_2] (10 mg, 0.016 mmol) was dried under vacuum for 30 minutes in Schlenk flask and dissolved with 5 mL CH_3CN under N_2 atmosphere resulted in a light blue-green solution. It was stirred for 5 minutes and the yellow solution of ferrocene (6 mg, 0.032 mmol) in 5 mL CH_3CN was added at room temperature. The light blue-green solution changed to lime green upon addition of ferrocene solution. The lime green solution was stirred for 5 minutes then SO_2 was purged for 15 minutes at room temperature along with the stirring. The clear lime green solution turned to olive green within 10 minutes of SO_2 purging with little turbidity, and then the Schlenk flask was left at -20 ^oC for 72 h. The turbid reaction mixture was filtered through the cannula and the filtrate was analysed by high-resolution ESI-MS.

High resolution ESI-MS (cation mode):

m/z for $C_{10}H_{10}Fe$ = 186.0125 (calcd. 186.0131) = Fc^+

m/z for $C_{11}H_{24}N_7$ = 254.2100 (calcd. 254.2093) = [N^2-(2-aminoethyl)-N^4,N^6-diisopropyl-1,3,5-triazine-2,4,6-triamine + H]

m/z for $C_{17}H_{27}N_8$ = 343.2379 (calcd. 343.2359) = Tim-H

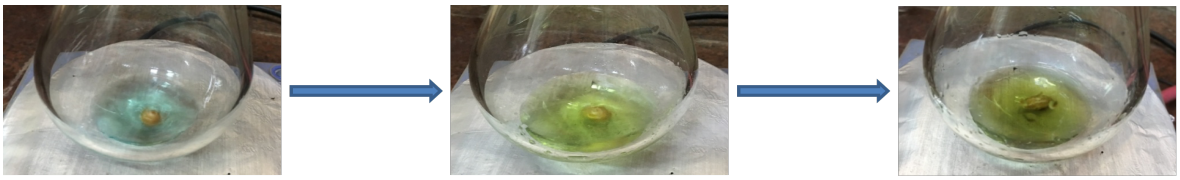
High resolution ESI-MS (anion mode):

m/z for HSO_4 = 96.9589 (calcd. 96.9596) = bisulfate anion

m/z for $2HSO_4 + H$ = 194.9268 (calcd. 194.9269) = $[H(HSO_4)_2]^-$

No peak was observed for $[Cu(L\text{-}OMe)Cl]^+$

The reaction of $[Cu(L\text{-}H)Cl_2]$ and 2 equivalent ferrocene with SO_2 in CH_3CN



$[Cu(L\text{-}H)Cl_2]$ (5 mL CH_3CN)

$[Cu(L\text{-}H)Cl_2]$ + 2 Fc (10 mL CH_3CN)

$[Cu(L\text{-}H)Cl_2]$ + 2 Fc after purging SO_2 for 15 min

$[Cu(L\text{-}H)Cl_2]$ (9 mg, 0.016 mmol) was dried under vacuum for 30 minutes in Schlenk flask and dissolved with 5 mL CH_3CN under N_2 atmosphere resulted in a light blue-green solution. It was stirred for 5 minutes and the yellow solution of ferrocene (6 mg, 0.032 mmol) in 5 mL CH_3CN was added at room temperature. The light blue-green solution changed to lime green upon the addition of ferrocene solution. The lime green solution was stirred for 5 minutes, and SO_2 was purged for 15 minutes at room temperature along with the stirring. The lime green solution turned olive green upon SO_2 purging then, the Schlenk flask was left at -20 ^oC for 70 h. The solution was analysed by high-resolution ESI-MS and evaporated under reduced pressure resulted in green solid. Weight of green solid = 18 mg.

High resolution ESI-MS (cation mode):

m/z for $C_{10}H_{10}Fe$ = 186.0134 (calcd. 186.0131) = Fc^+

m/z for $(C_{23}H_{31}N_9Cu)/2$ = 248.0979 (calcd. 248.0999) = $[Cu(L\text{-}H)]^{2+}$

m/z for $(C_{23}H_{32}N_9CuCl)/2$ = 266.0861 (calcd. 266.0882) = $[Cu(L\text{-}H)+HCl]^{2+}$

m/z for $C_{23}H_{31}N_9CuCl$ = 531.1683 (calcd. 531.1687) = $[Cu(L\text{-}H)Cl]^+$

m/z for $C_{24}H_{32}N_9O_2Cu$ = 541.1991 (calcd. 541.1975) = $[Cu(L\text{-}H)HCOO]^+$

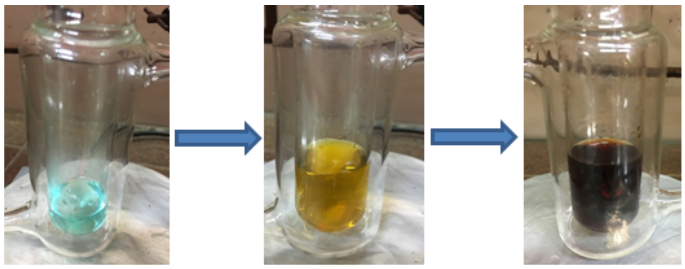
m/z for $C_{23}H_{32}N_9O_4SCu$ = 593.1595 (calcd. 593.1594) = $[Cu(L\text{-}H)HSO_4]^+$

High resolution ESI-MS (anion mode):

m/z for HSO_4 = 96.9606 (calcd. 96.9596) = bisulfate anion

m/z for $2HSO_4 + H$ = 194.9272 (calcd. 194.9269) = $[H(HSO_4)_2]^-$

The reaction of $[Cu(L\text{-}H)Cl_2]$ and 51 equivalent ferrocene with SO_2 in CH_3CN



$[Cu(L\text{-}H)Cl_2]$ (5 mL CH_3CN) | $[Cu(L\text{-}H)Cl_2]$ + 51 Fc (15mL CH_3CN) | $[Cu(L\text{-}H)Cl_2]$ + 51 Fc SO_2 purged - 30 min

$[Cu(L\text{-}H)Cl_2]$ (9 mg, 0.016 mmol) was dried under vacuum for 30 minutes in Schlenk tube and dissolved with 5 mL CH_3CN under N_2 atmosphere resulted in a blue-green solution. It was stirred for 5 minutes and the yellow solution of ferrocene (153 mg, 0.82 mmol) in 10 mL CH_3CN was added at room temperature. The blue-green solution changed to yellow upon the addition of ferrocene. The yellow solution was stirred for 5 minutes, and SO_2 was purged for 30 minutes at room temperature along with the stirring. The yellow solution changed to wine red upon purging SO_2 within 2 minutes. The solution was transferred to 50 mL round bottom flask and evaporated to dryness under reduced pressure resulted in yellow-green solid.

The weight of the yellow-green solid = 180 mg.

High resolution ESI-MS (cation mode):

m/z for $C_{10}H_{10}Fe$ = 186.0169 (calcd. 186.0131) = Fc^+

m/z for $(C_{23}H_{31}N_9Cu)/2$ = 248.0989 (calcd. 248.0999) = $[Cu(L\text{-}H)]^{2+}$

m/z for $(C_{23}H_{32}N_9CuCl)/2$ = 266.0851 (calcd. 266.0882) = $[Cu(L\text{-}H)+HCl]^{2+}$

m/z for $C_{23}H_{32}N_9$ = 434.2739 (calcd. 434.2781) = [(L-H)+H]

m/z for $C_{23}H_{31}N_9CuCl$ = 531.1682 (calcd. 531.1687) = $[Cu(L\text{-}H)Cl]^+$

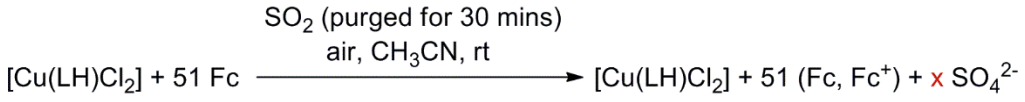
m/z for $C_{24}H_{32}N_9O_2Cu$ = 541.2021 (calcd. 541.1975) = $[Cu(L\text{-}H)HCOO]^+$

High resolution ESI-MS (anion mode):

m/z for HSO_4 = 96.9580 (calcd 96.9596) = bisulfate anion

m/z for $2HSO_4 + H$ = 194.9250 (calcd 194.9269) = $[H(HSO_4)_2]^-$

Calculation for the conversion of SO_2 to sulfate (SO_4^{2-}):



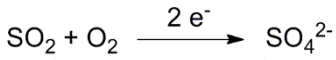
1 equiv. of [Cu(L-H)Cl_2] = 0.016 mmol (9 mg)

51 equiv. of ferrocene = 0.82 mmol (153 mg)

The experimental weight of the reaction mixture after purging SO_2 = 180 mg

The weight of sulfate (SO_4^{2-}) = (the exp. weight of the reaction mixture after purging SO_2) - (the weight of copper complex and ferrocene) = (180 – 162) mg = 18 mg

The moles of sulfate (SO_4^{2-}) formed from the reaction mixture = the weight of sulfate / the molecular weight of sulfate = 18 mg / 96.0626 g/mol = 0.19 mmol

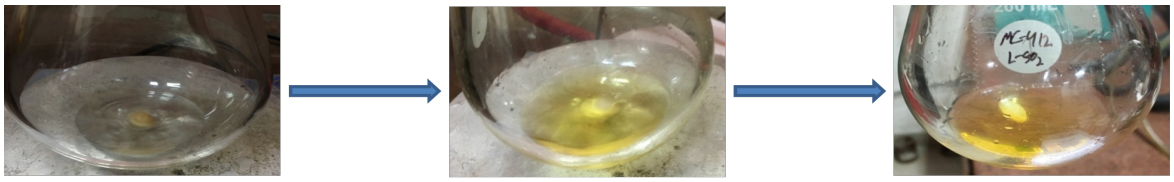


Based on the above reaction, 0.19 mmol of SO_2 was converted to sulfate (SO_4^{2-})

The number of equiv. of SO_2 converted to sulfate (SO_4^{2-}) = the moles of SO_2 reacted / the moles of [Cu(L-H)Cl_2] = 0.19 mmol / 0.016 mmol = **11.8 equivalents**

Therefore, 11.8 equivalents of SO_2 was converted to sulfate (SO_4^{2-}) for a equivalent of [Cu(L-H)Cl_2] and 51 equivalent of ferrocene.

The reaction of [L-H] and 2 equivalent ferrocene with SO_2 in CH_3CN



[L-H]
(5 mL CH_3CN)

[L-H] + 2 Fc
(10 mL CH_3CN)

[L-H] + 2 Fc
after purging SO_2 for 15 min

[L-H] (7 mg, 0.016 mmol) was dried under vacuum for 30 minutes in Schlenk flask and dissolved with 5 mL CH_3CN under N_2 atmosphere. The colourless solution was stirred for 5 minutes and the yellow solution of ferrocene (6 mg, 0.032 mmol) in 5 mL CH_3CN was added at room temperature. The colourless solution changed to light yellow upon the addition of ferrocene solution. The solution was stirred for 5 minutes then SO_2 was purged for 15 minutes at room temperature along with the stirring. The light yellow solution turned deep yellow upon SO_2 purging, and then, the Schlenk flask was left at -20 ^oC for 70 h. The yellow solution was analysed by high-resolution ESI-MS. It was evaporated under reduced pressure resulted in yellow solid.

High resolution ESI-MS (cation mode):

m/z for $(C_{17}H_{30}N_8)/2$ = 173.1266 (calcd. 173.1296) = [N^2,N^4-diisopropyl-N^6-(2-((pyridin-2-ylmethyl)amino)ethyl)-1,3,5-triazine-2,4,6-triamine + 2H]

m/z for $C_{10}H_{10}Fe$ = 186.0118 (calcd. 186.0131) = Fc^+

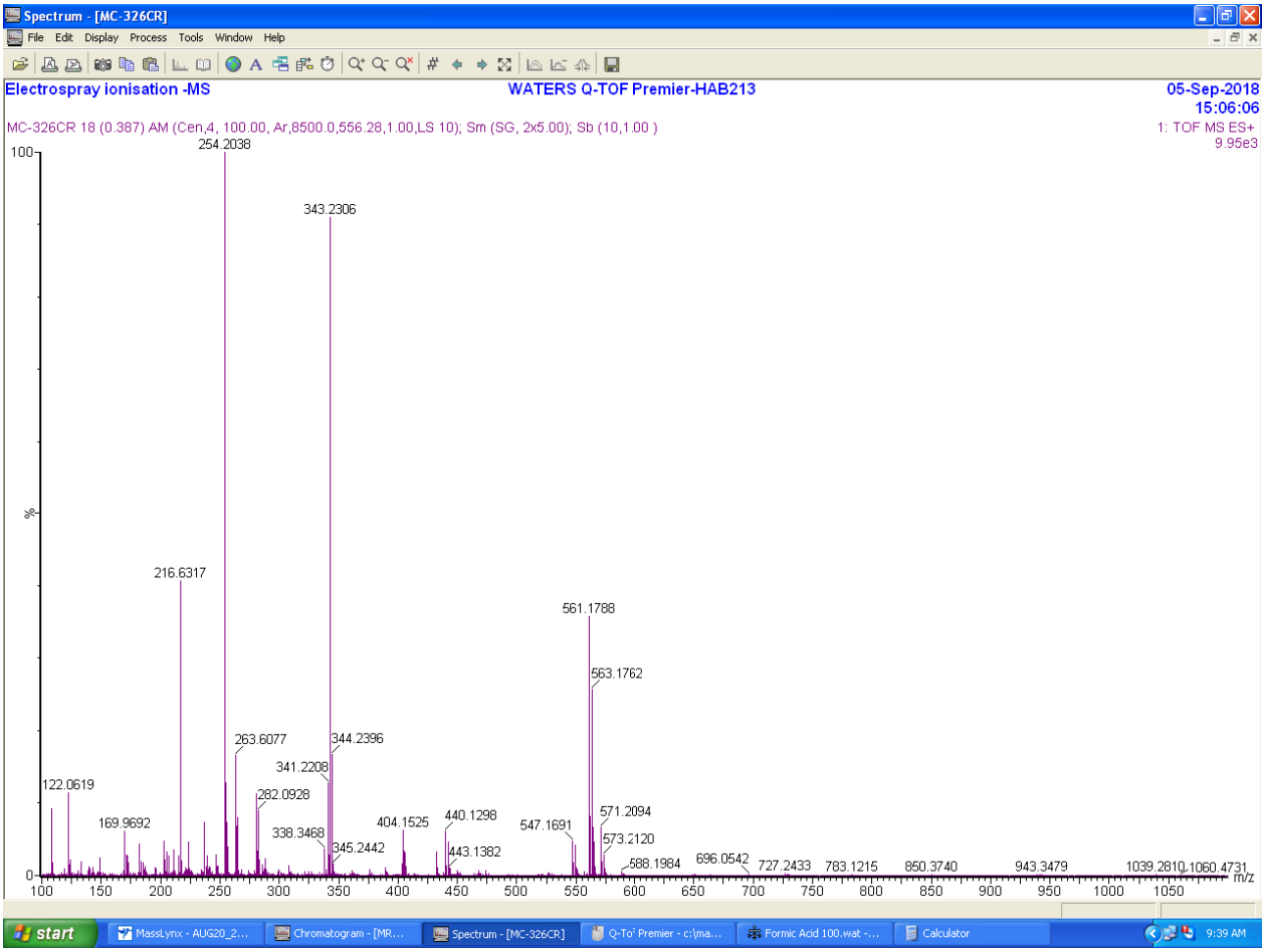
m/z for $C_{17}H_{29}N_8$ = 345.2511 (calcd. 345.2515) = [N^2,N^4-diisopropyl-N^6-(2-((pyridin-2-ylmethyl)amino)ethyl)-1,3,5-triazine-2,4,6-triamine + H]

High resolution ESI-MS (anion mode):

m/z for HSO_4 = 96.9598 (calcd. 96.9596) = bisulfate anion

m/z for $2HSO_4 + H$ = 194.9277 (calcd. 194.9269) = $[H(HSO_4)_2]^-$

Figure S 1. ESI-MS of [Cu(L-OMe)Cl_2].



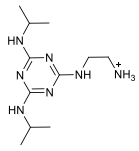
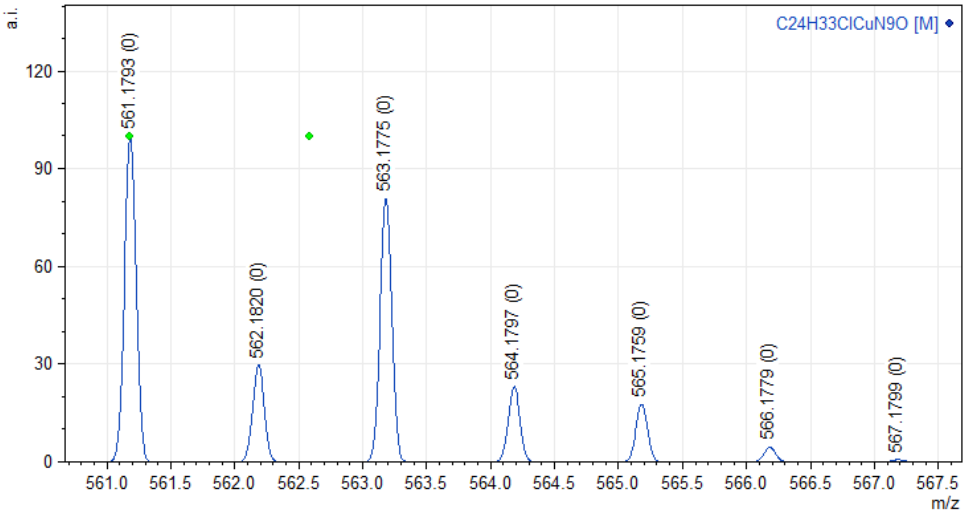
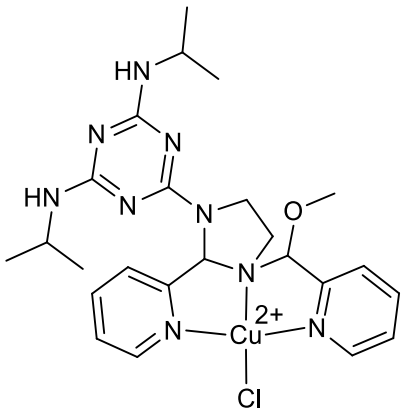
Observed envelope	Observed for	Calculated *m/z*
254.2038		254.2093
343.2306	Imd-H	343.2359
561.1788	$[Cu(L\text{-}OMe)Cl]^+$	561.1793
571.2094	$[Cu(L\text{-}OMe)HCOO]^+$	571.2081

Figure S 2. Simulated ESI-MS of $[Cu(L\text{-}OMe)Cl]^+$ cation.





$[Cu(L\text{-}OMe)Cl]^+$

Figure S 3. ORTEP of *syn*-[Cu(L-OMe)Cl_2] drawn at 50% probability level.

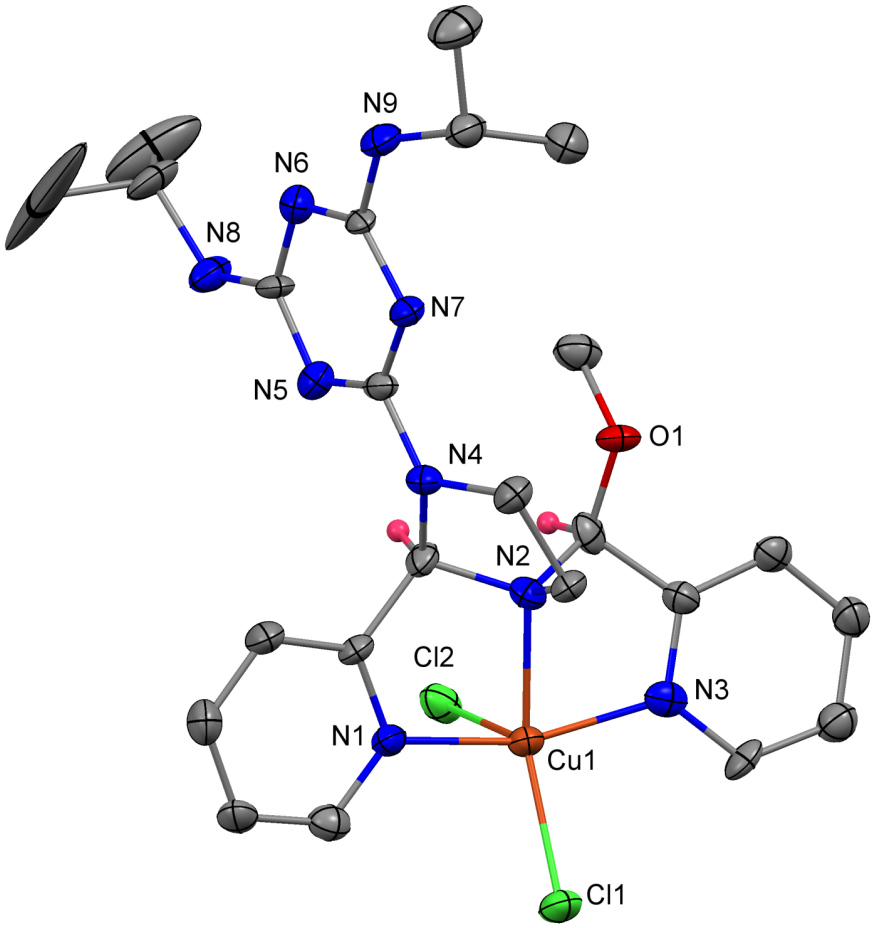
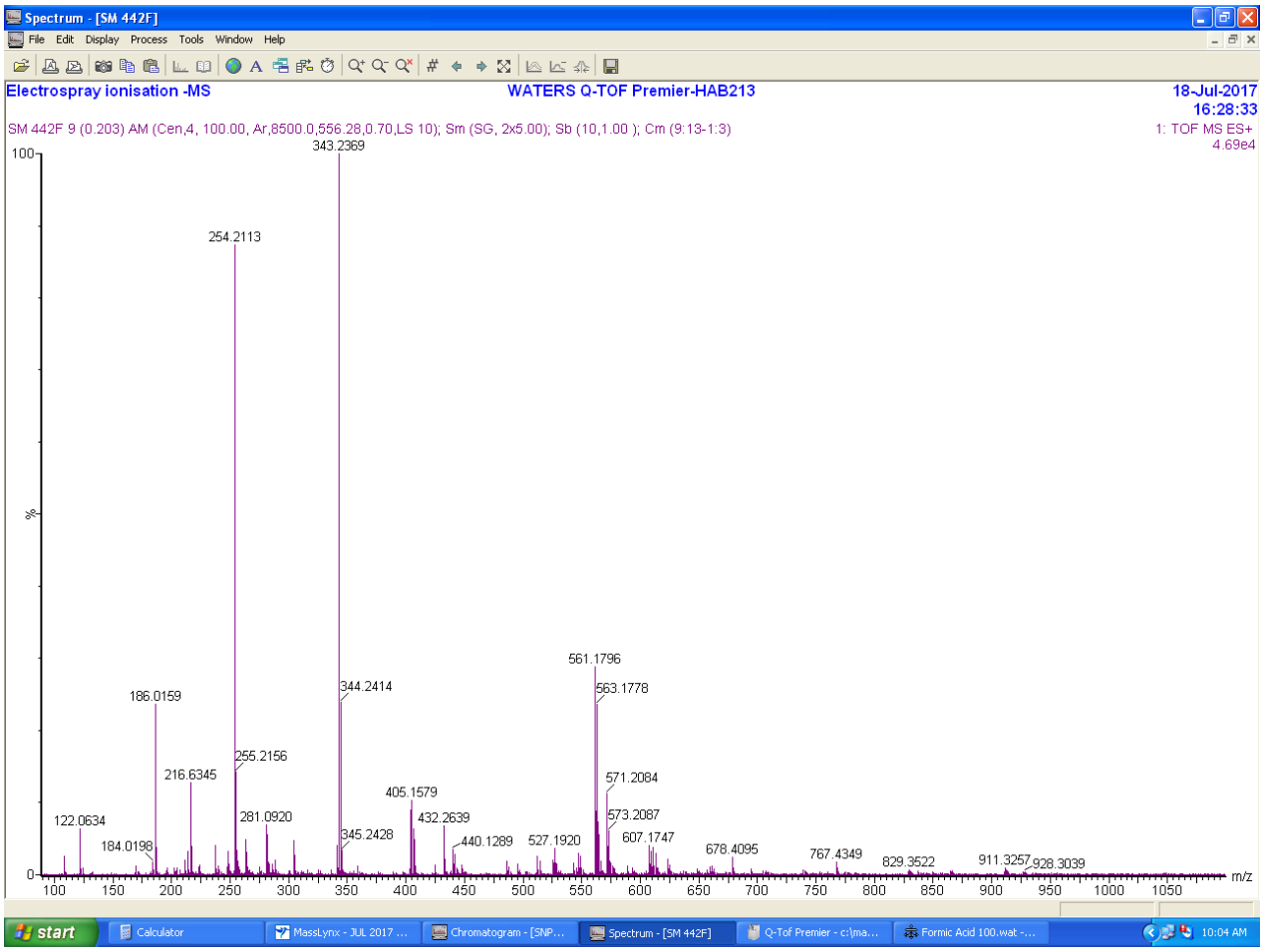


Figure S 4. ESI-MS of the solution containing [Cu(L-OMe)Cl_2] and 2 equivalent ferrocene after purging SO_2 (Positive ion mode) in CH_3CN



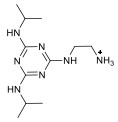
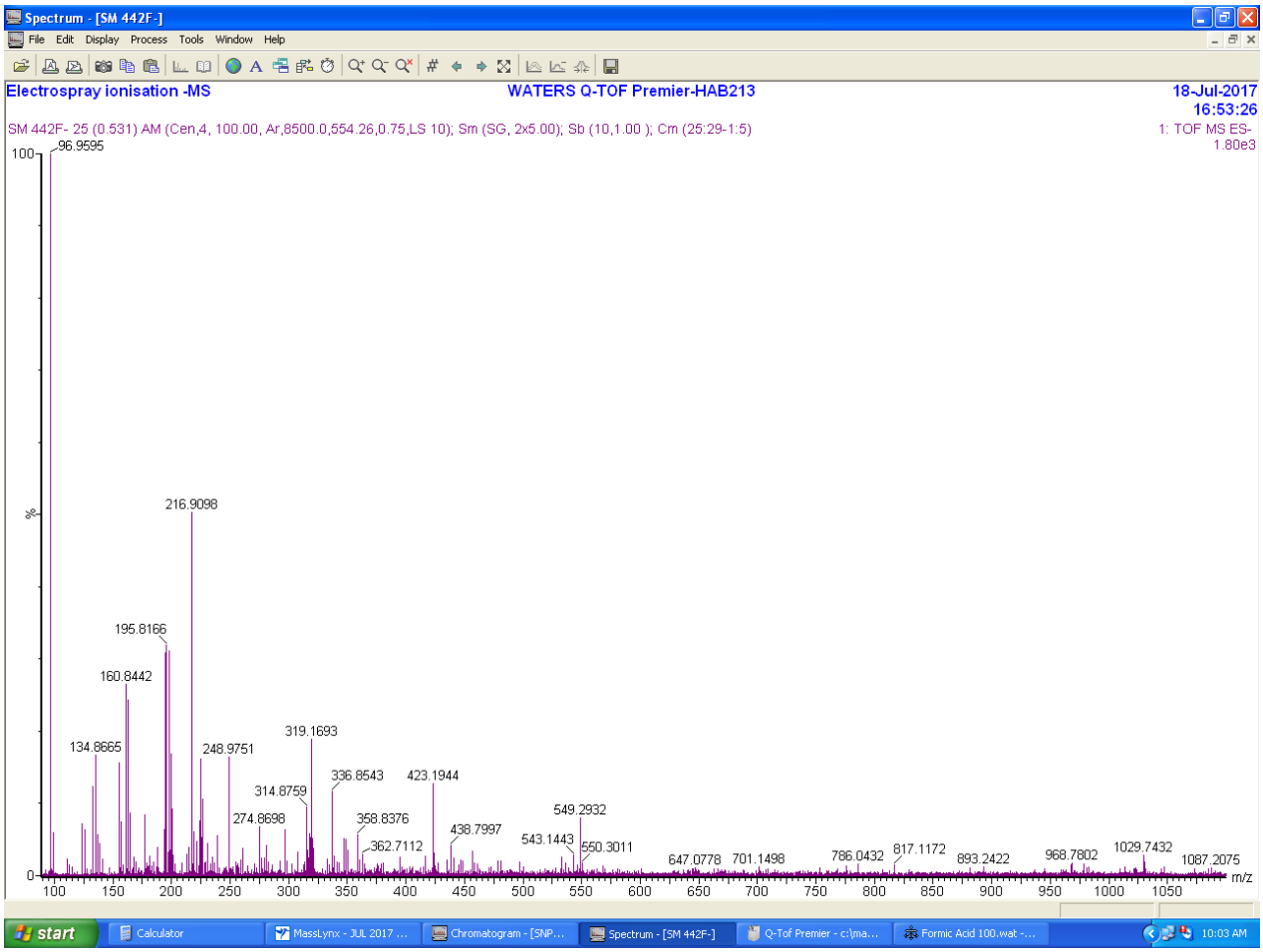
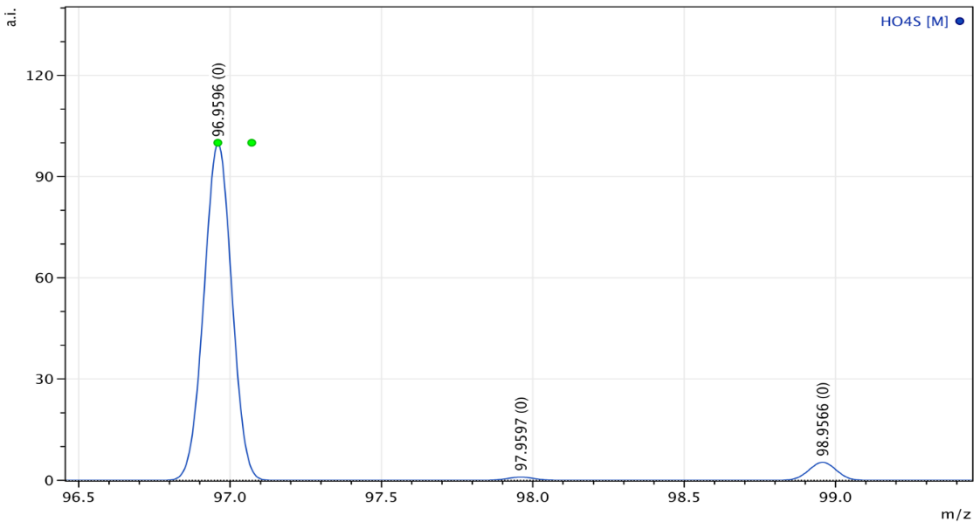
Observed envelope	Observed for	Calculated *m/z*
186.0159	Ferrocenium ion	186.0132
254.2113		254.2093
343.2369	Imd-H	343.2359
440.1289	$[Cu(Imd)Cl]^+$	440.1265
561.1796	$[Cu(L\text{-}OMe)Cl]^+$	561.1793

Figure S 5. ESI-MS of the solution containing [Cu(L-OMe)Cl_2] and 2 equivalent ferrocene after purging SO_2 (Negative ion mode) in CH_3CN



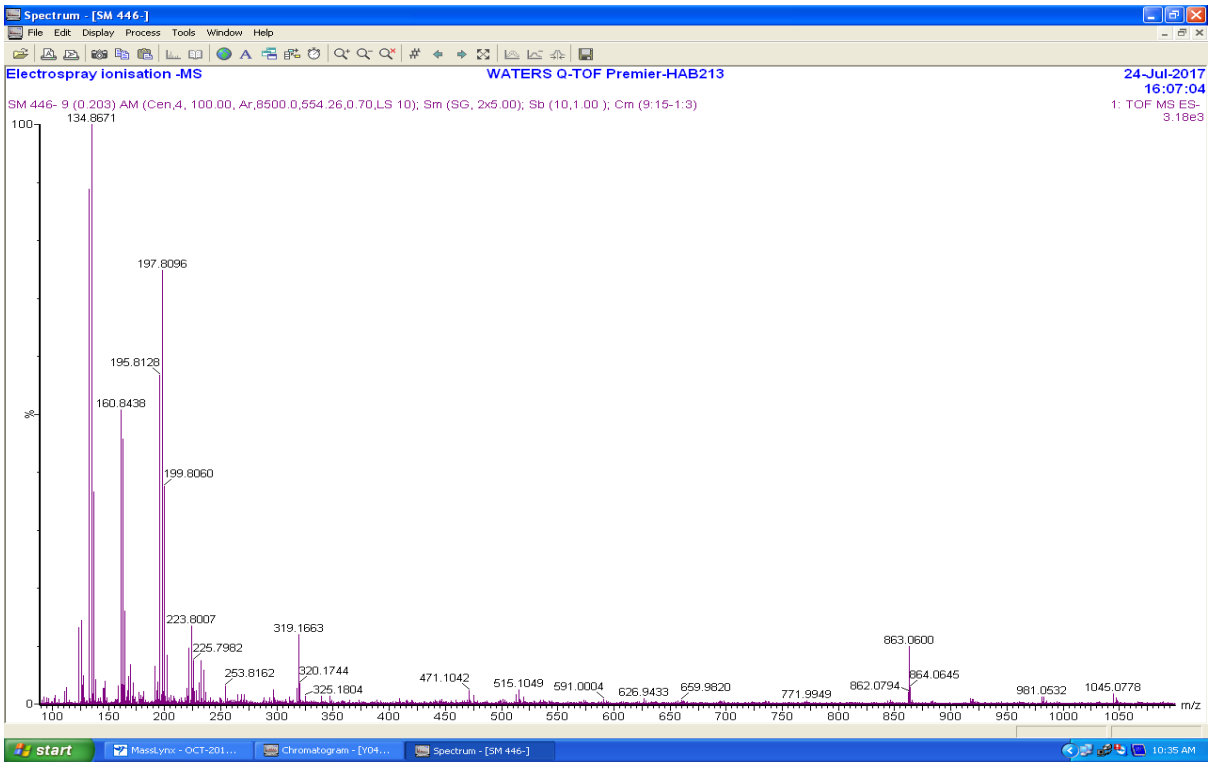
Observed envelope	Observed for	Calculated *m/z*
96.9595	HSO_4^-	96.9596

Figure S 6. Simulated ESI-MS for HSO_4^- anion



HSO_4^-

Figure S 7. ESI-MS of the solution containing anhydrous $CuCl_2$ and 2 equivalent ferrocene after purging SO_2 (Negative ion mode) showing no formation of SO_2 activated products.



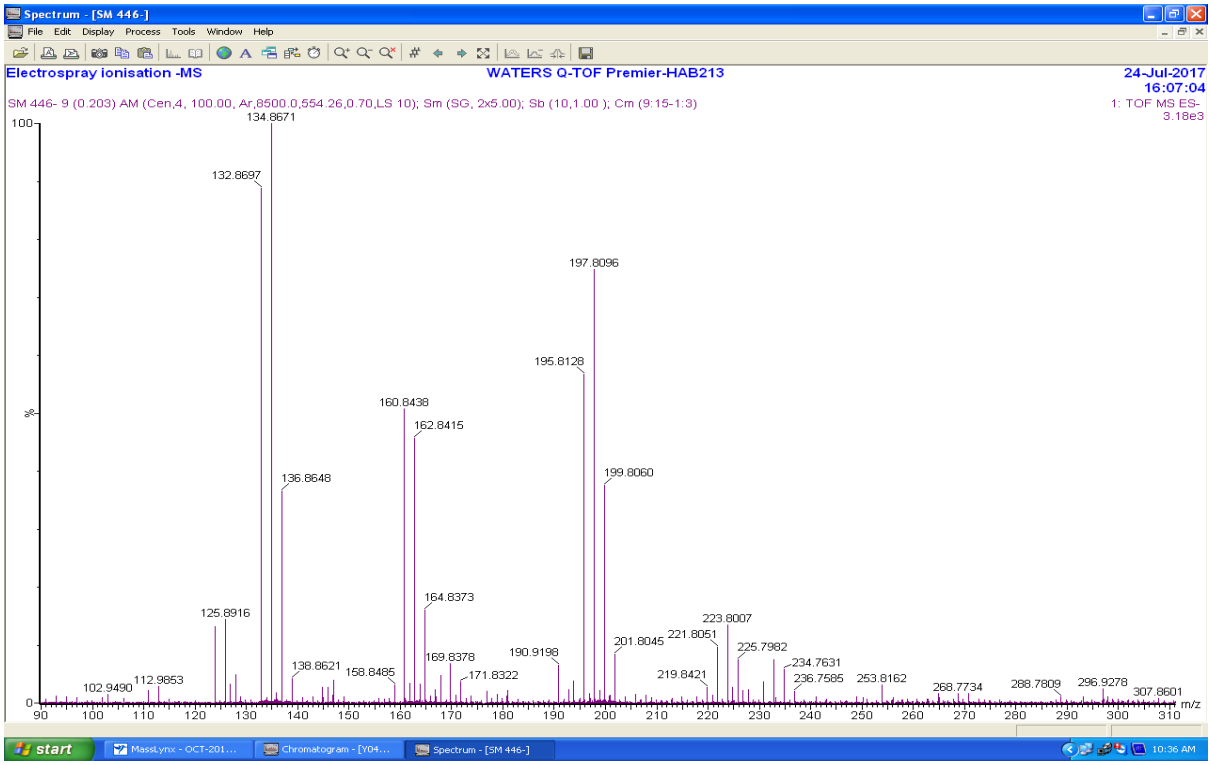


Figure S 8. ESI-MS of the ferrocene solution after purging SO_2 (Negative ion mode) showing no formation of SO_2 activated products.

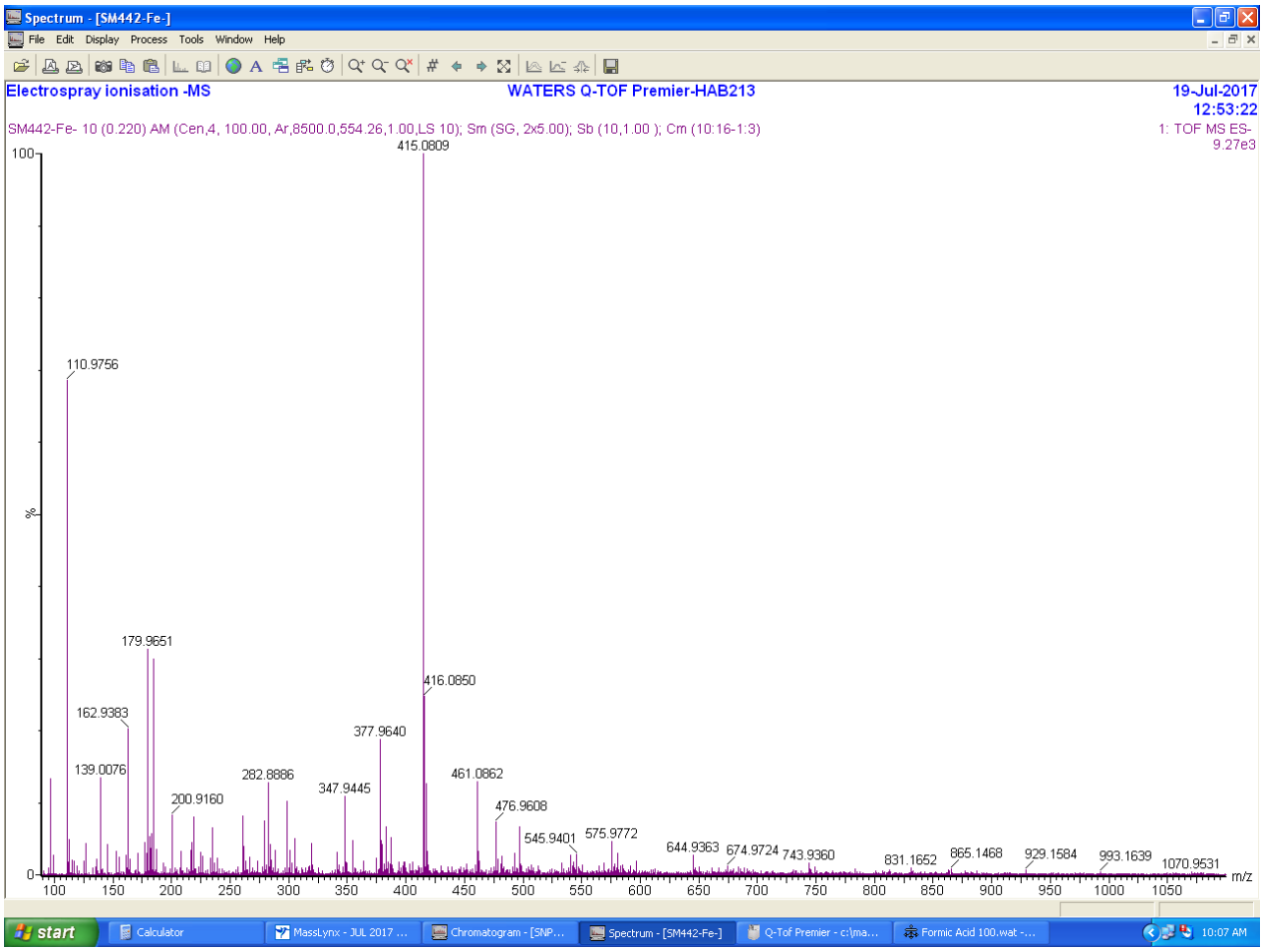
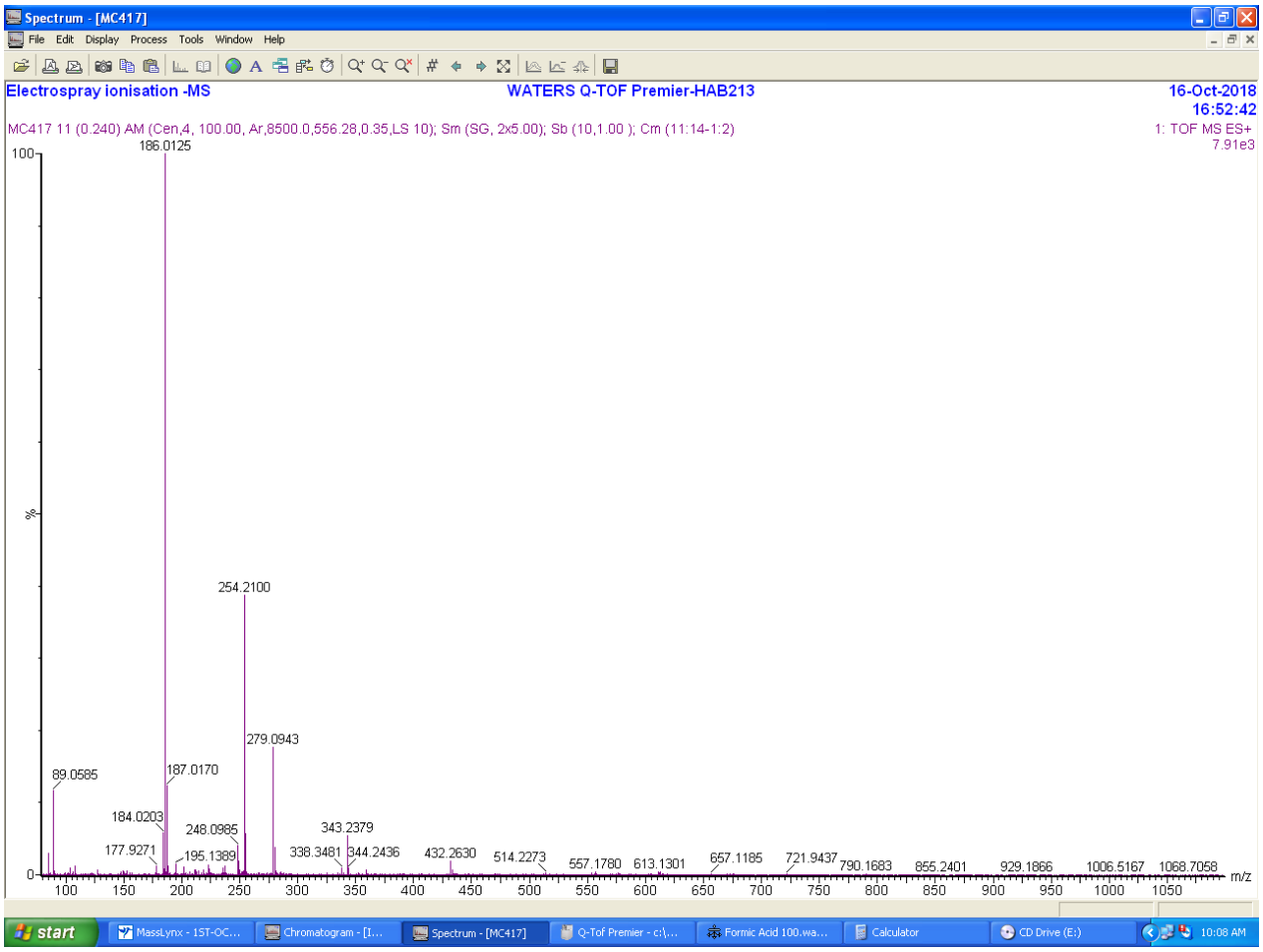


Figure S 9. ESI-MS of the solution containing [Cu(L-OMe)Cl_2] and 2 equivalent ferrocene after purging SO_2 (Positive ion mode) in CH_3CN after 3 days showing no peaks for $[Cu(L\text{-}OMe)Cl]^+$



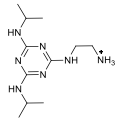
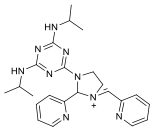
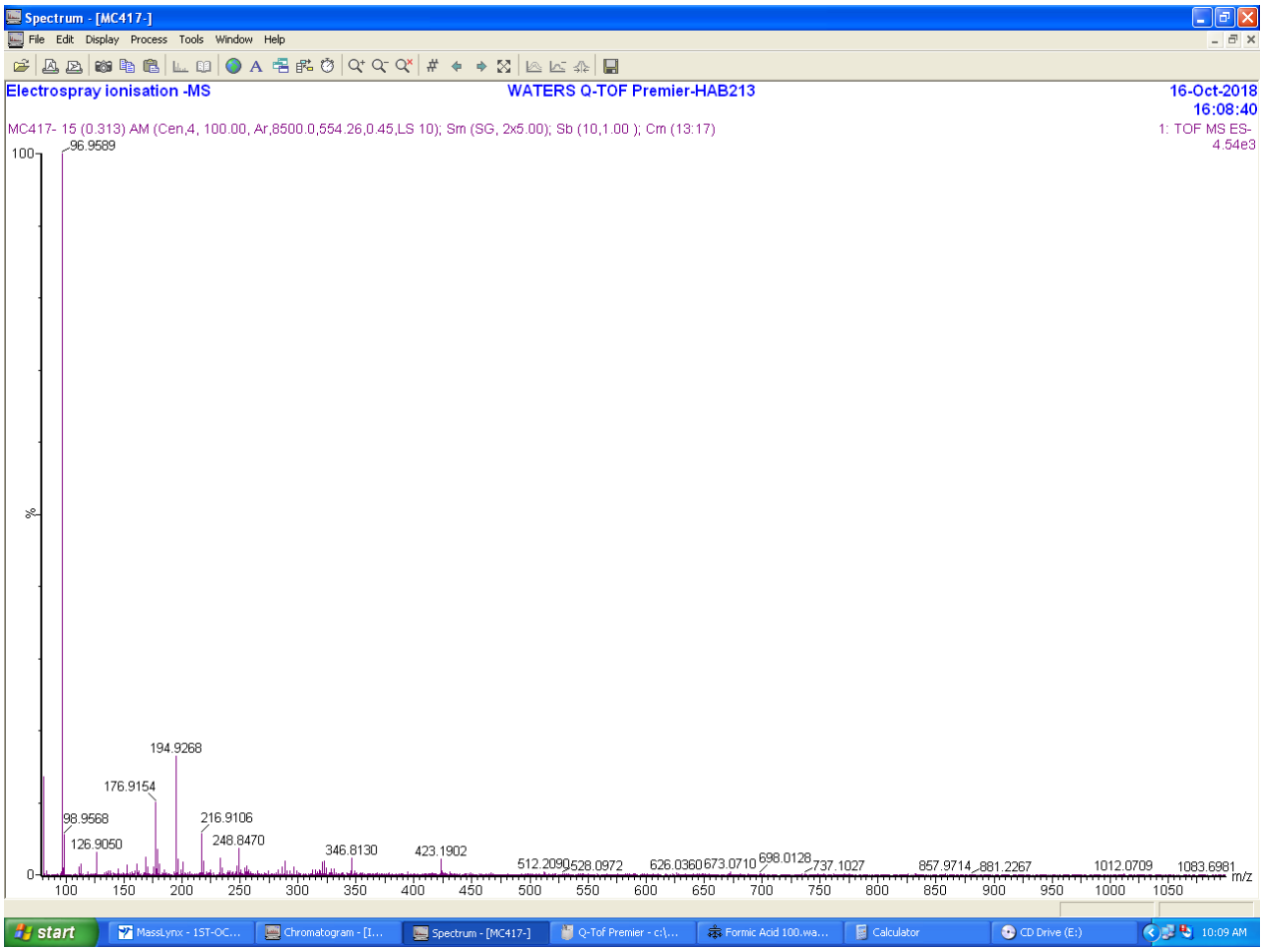
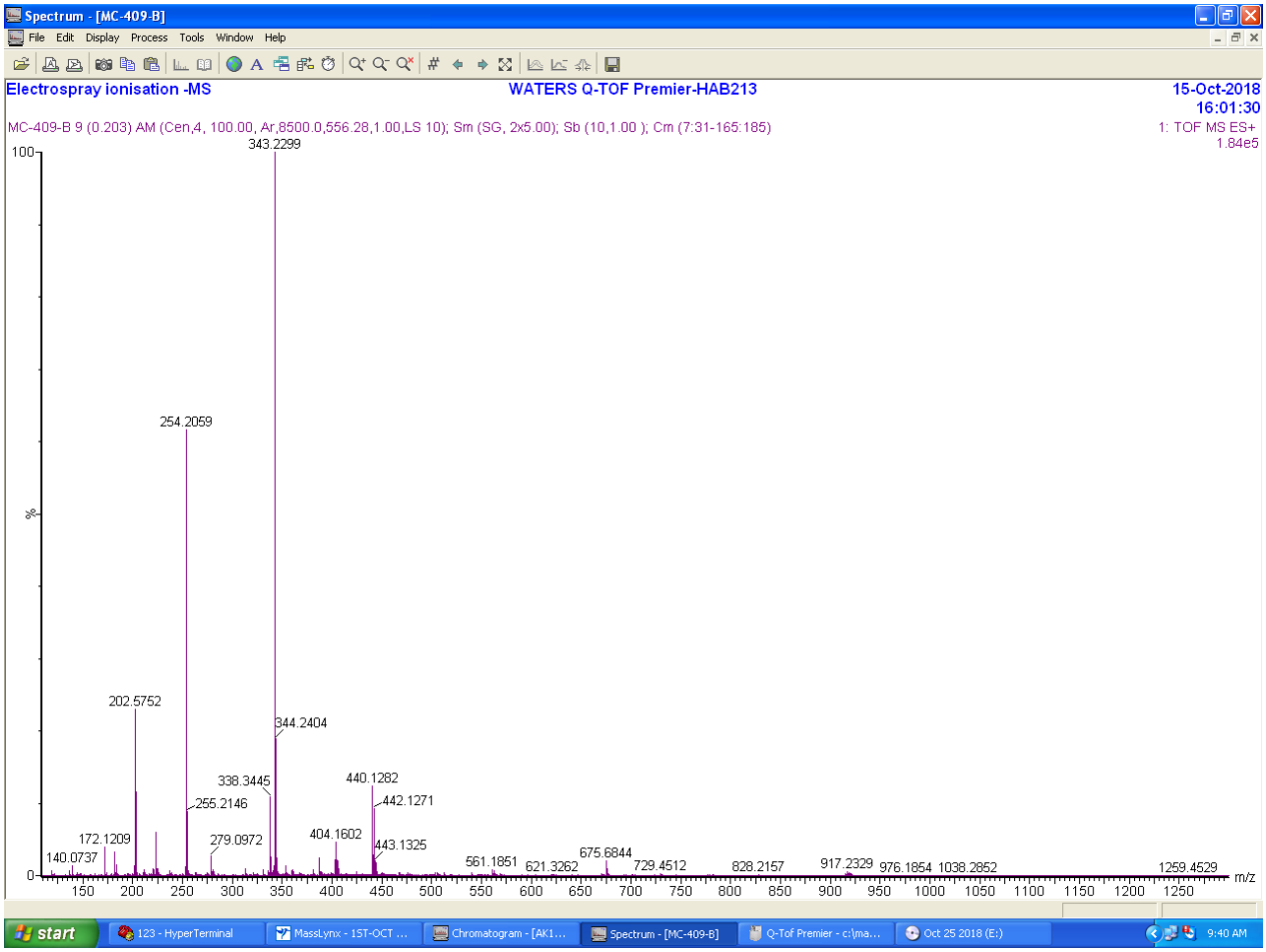
Observed envelope	Observed for	Calculated *m/z*
186.0125	Ferrocenium ion	186.0131
254.2100		254.2093
343.2379	Imd-H	343.2359
432.2630		432.2624

Figure S 10. ESI-MS of the solution containing [Cu(L-OMe)Cl_2] and 2 equivalent ferrocene after purging SO_2 (Negative ion mode) in CH_3CN after 3 days



Observed envelope	Observed for	Calculated *m/z*
96.9589	HSO_4^-	96.9596
194.9268	$[H(HSO_4)_2]^-$	194.9269

Figure S 11. ESI-MS of [Cu(Tim-H)(H_2O)Cl_2](OTf)



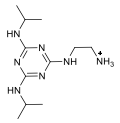
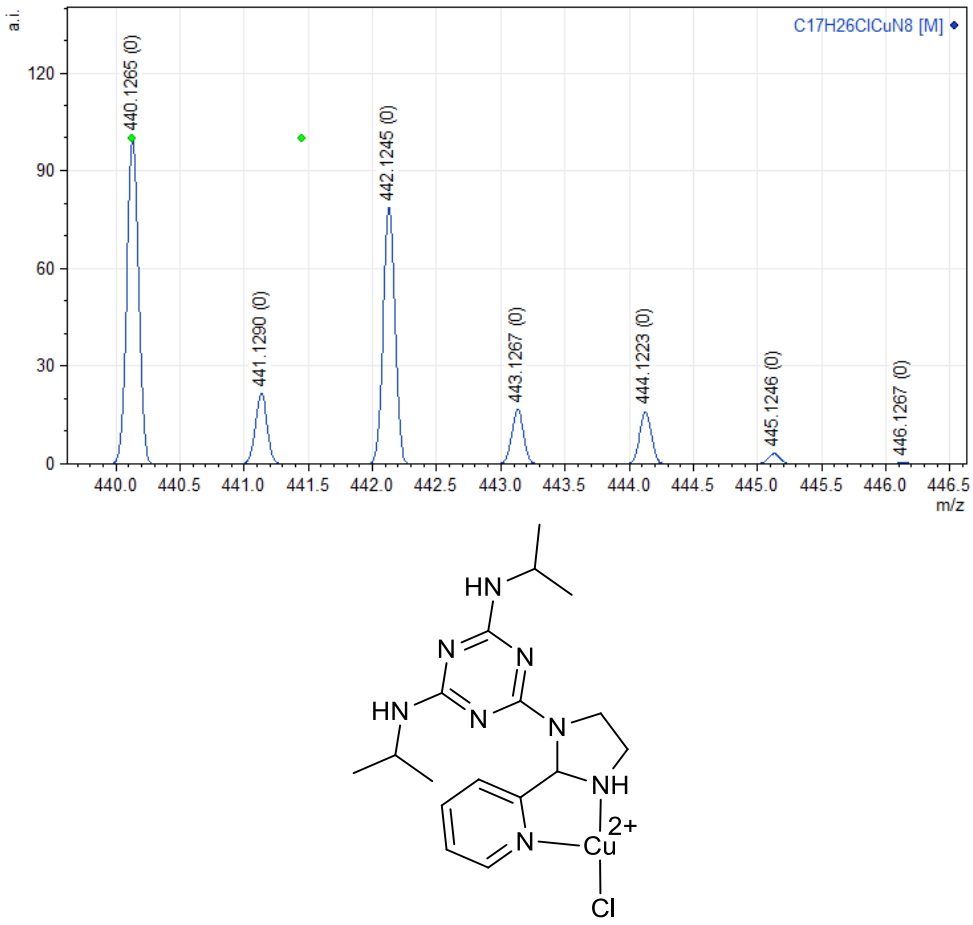
Observed envelope	Observed for	Calculated *m/z*
254.2059		254.2093
343.2299	Tim-H	343.2359
440.1282	$[Cu(Tim)Cl]^+$	440.1265

Figure S 12. Simulated ESI-MS of [Cu(Tim-H)(H_2O)Cl_2](OTf) for $[Cu(Tim)Cl]^+$



$[Cu(Tim)Cl]^+$

Figure S 13. ORTEP of [Cu(Tim-H)(H_2O)Cl_2](OTf) drawn at 50% probability level

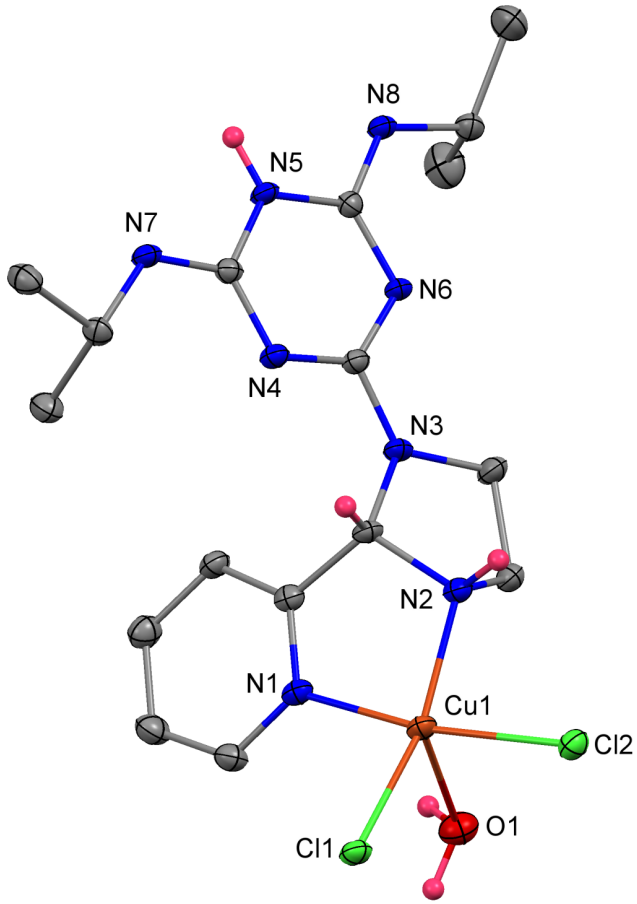


Figure S 14. One-dimensional hydrogen-bonded chain of [Cu(Tim-H)(H_2O)Cl_2](OTf)

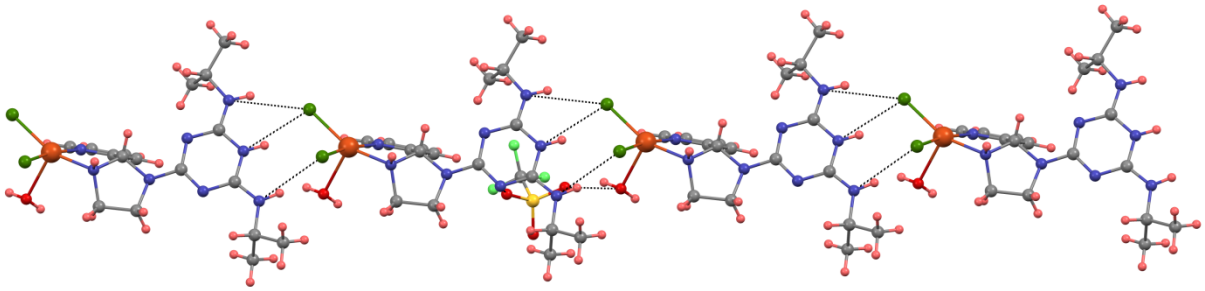
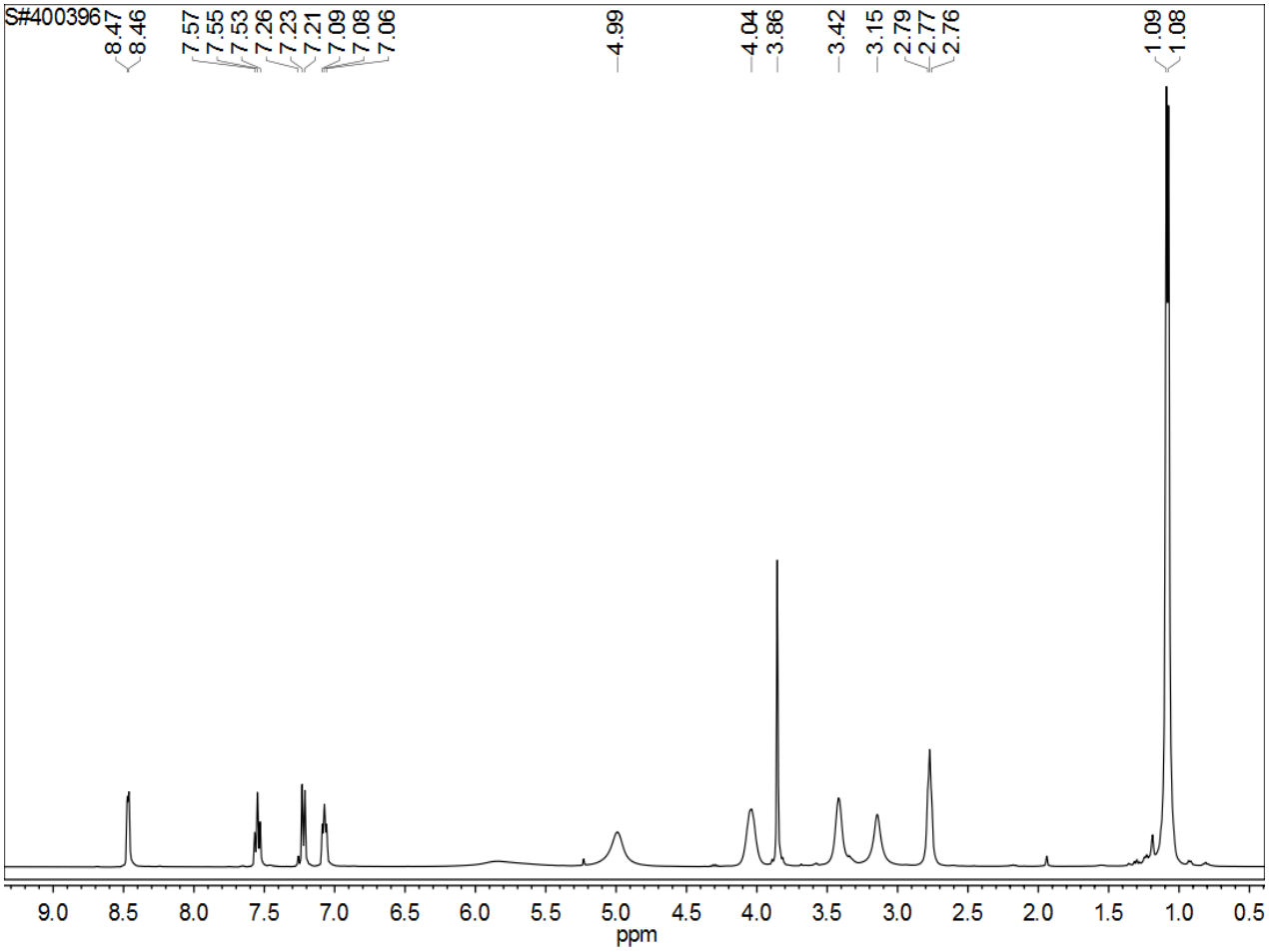


Figure S 15. ^{1}H NMR of N^{2},N^{4}-diisopropyl-N^{6}-(2-((pyridin-2-ylmethyl)amino)ethyl)-1,3,5-triazine-2,4,6-triamine in $CDCl_3$.



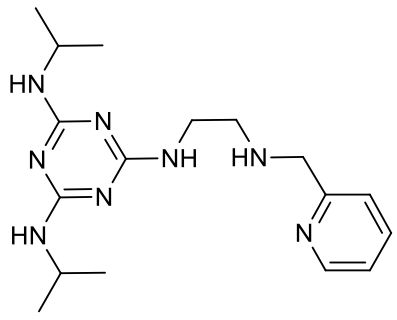
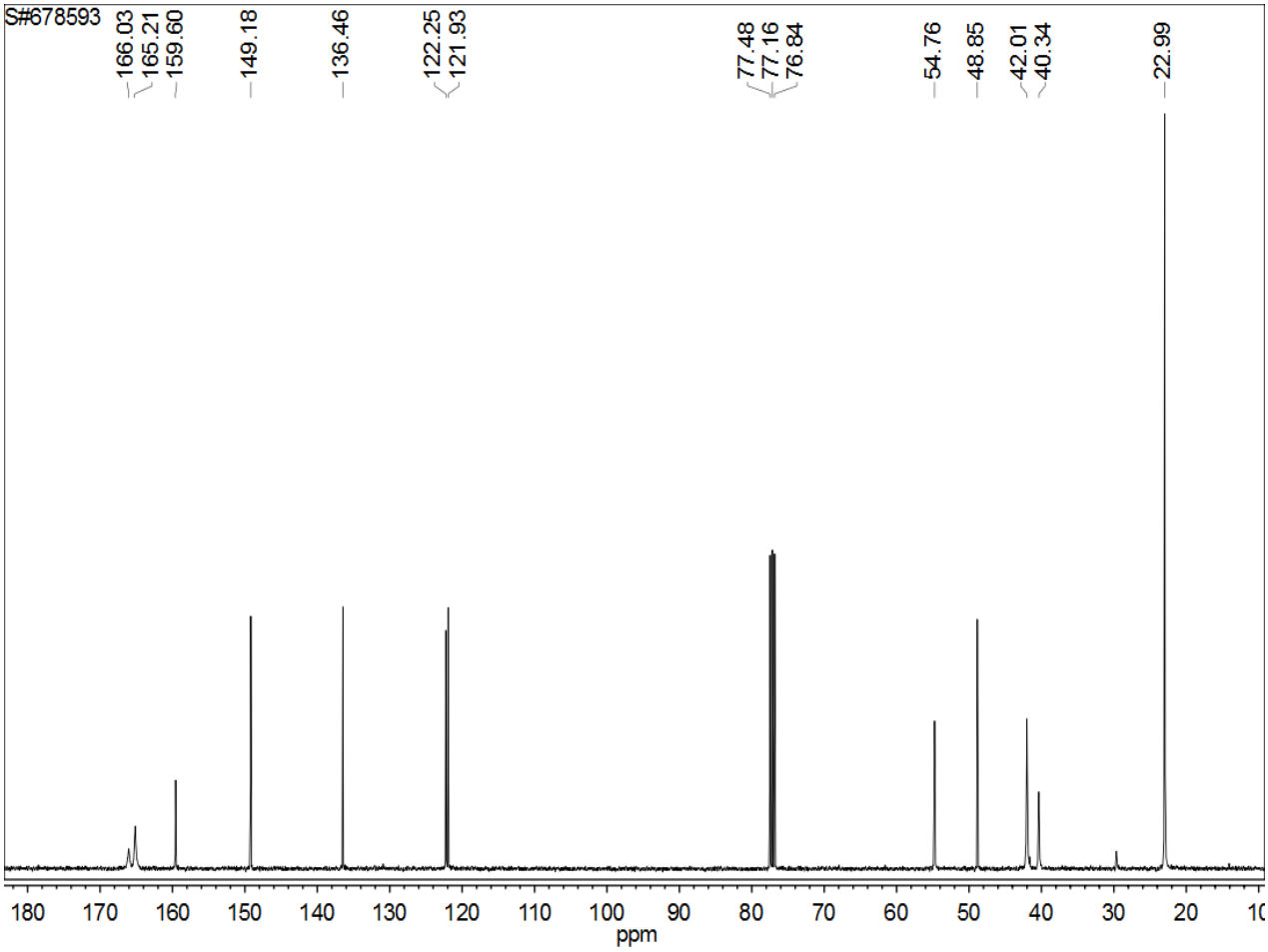


Figure S 16. ^{13}C NMR of N^2,N^4-diisopropyl-N^6-(2-((pyridin-2-ylmethyl)amino)ethyl)-1,3,5-triazine-2,4,6-triamine in $CDCl_3$.



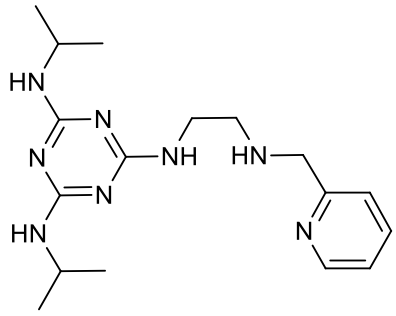
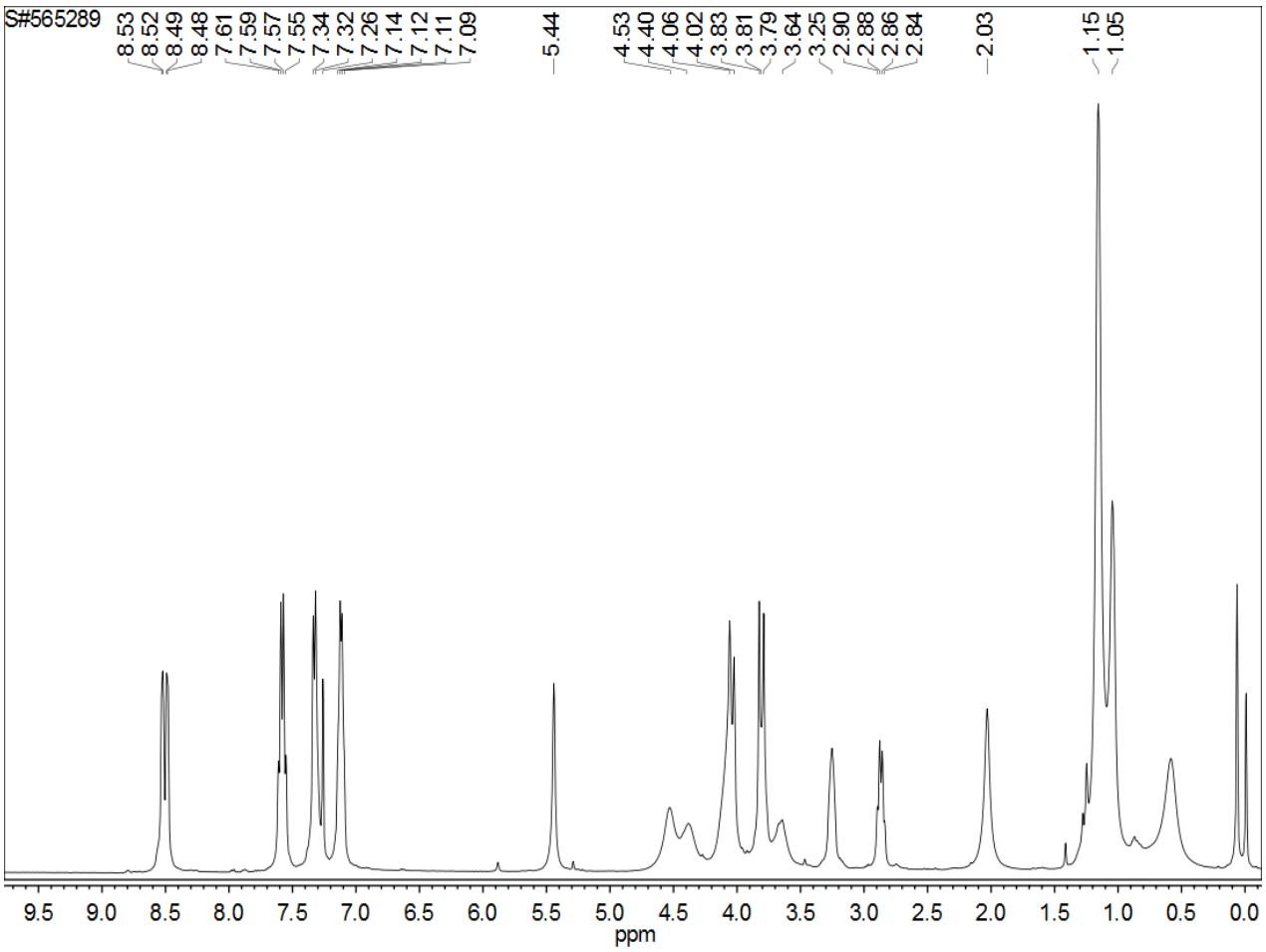


Figure S 17. ^{1}H NMR of [L-H] in $CDCl_3$



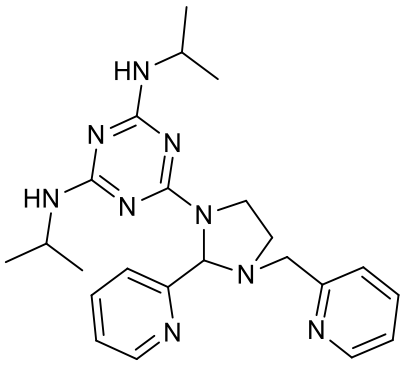
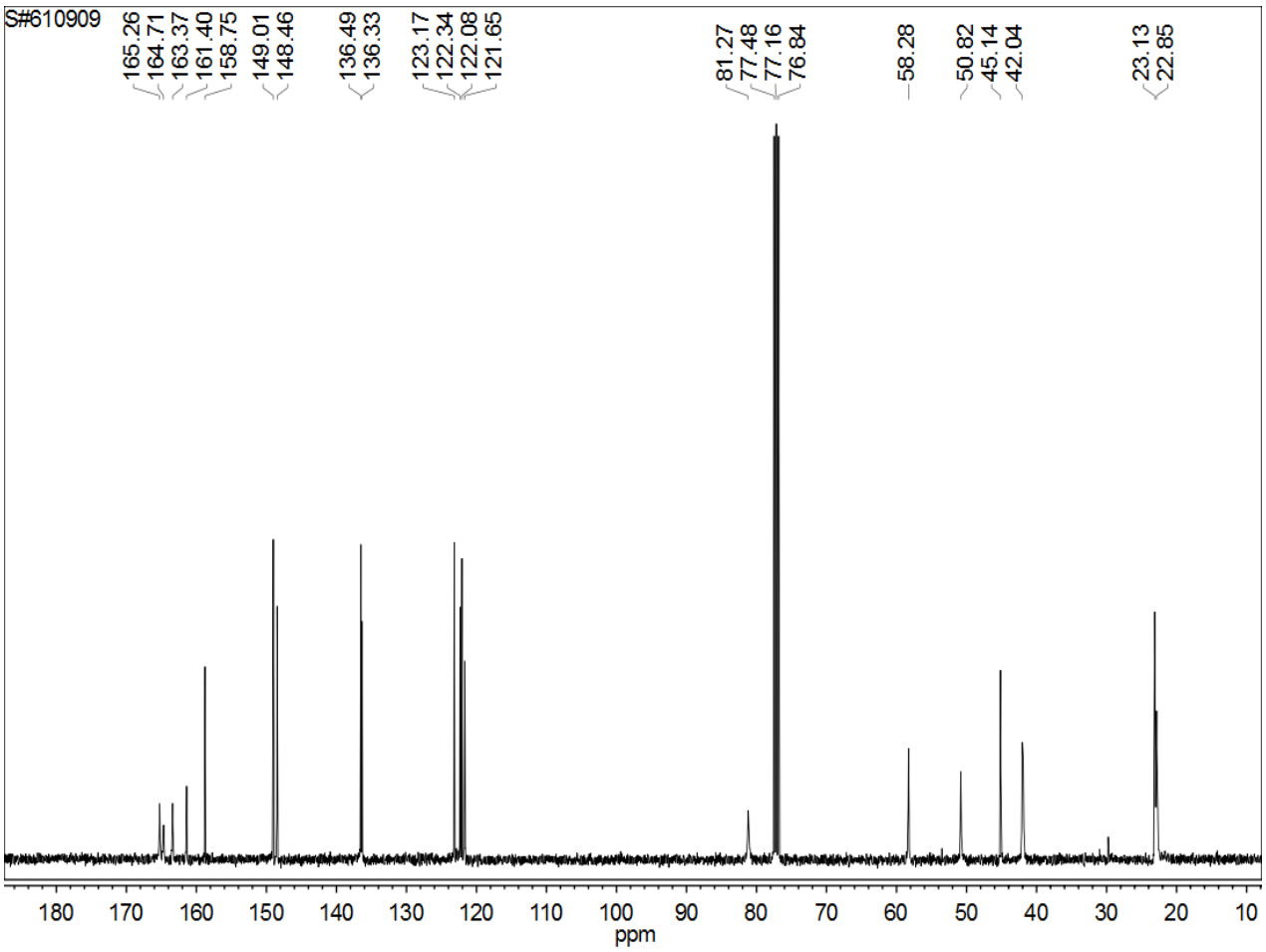


Figure S 18. ^{13}C NMR of [L-H] in $CDCl_3$



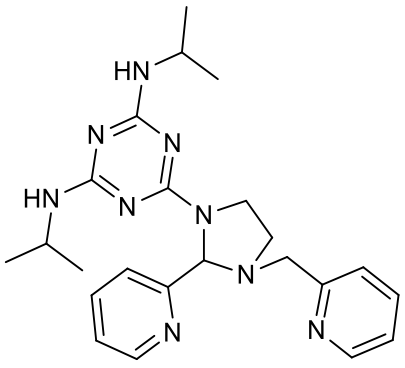
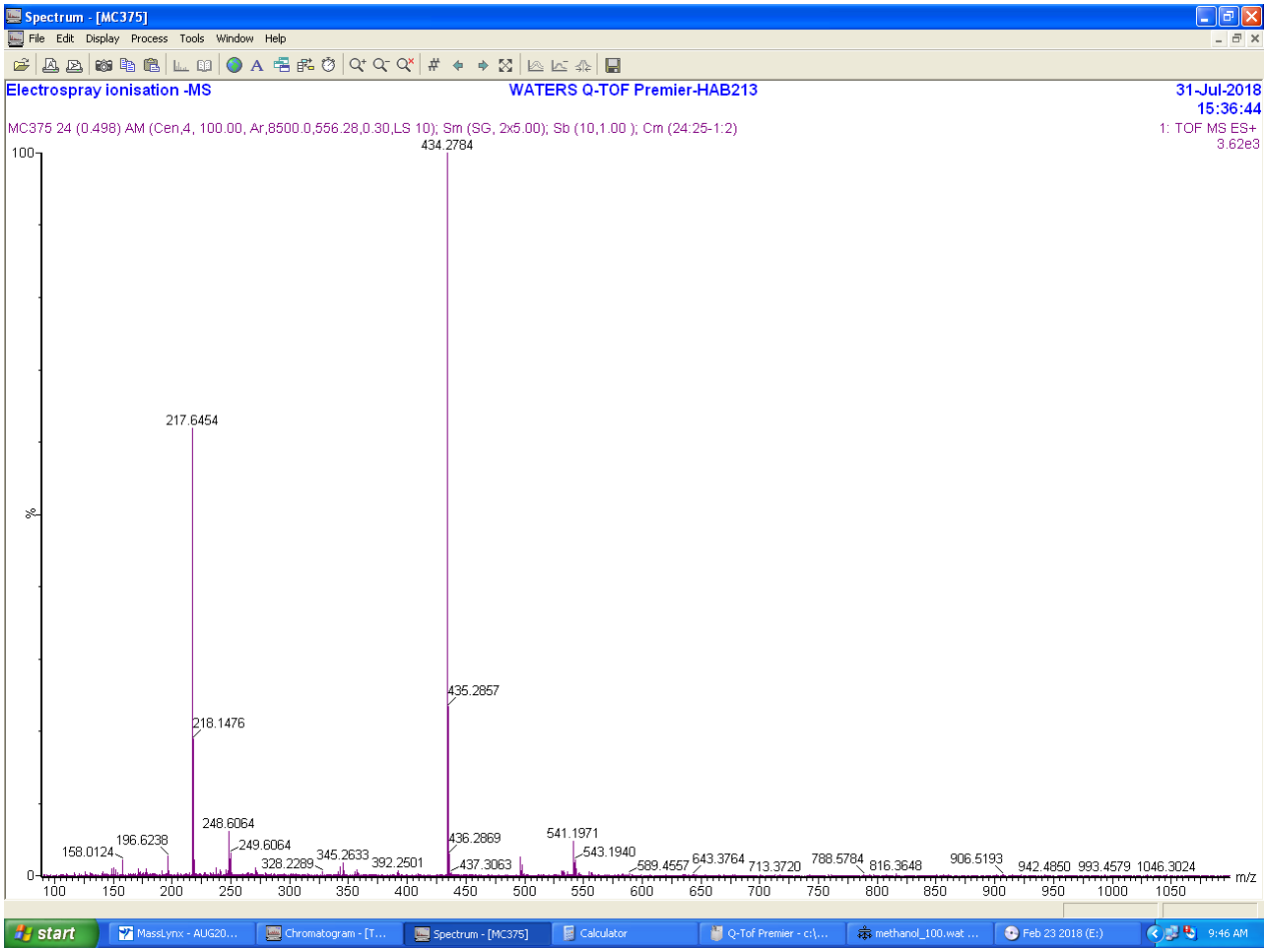
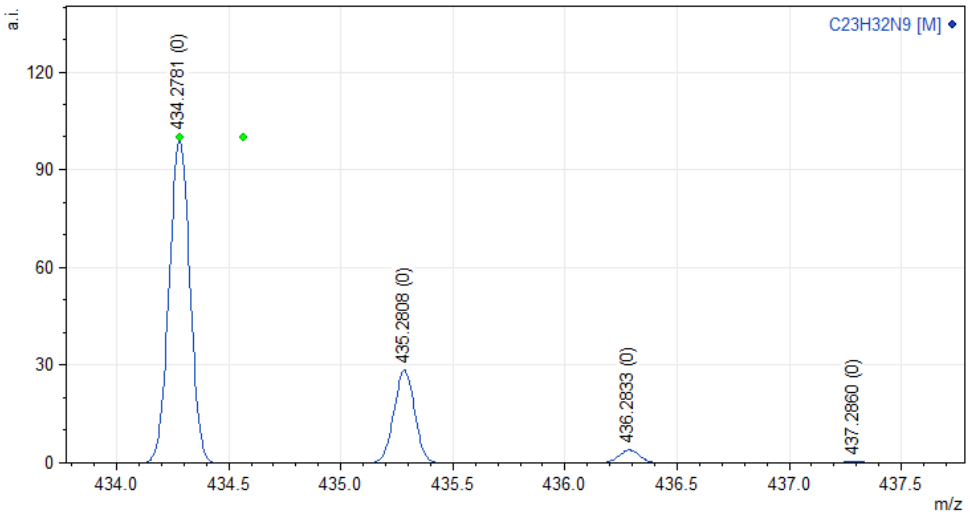


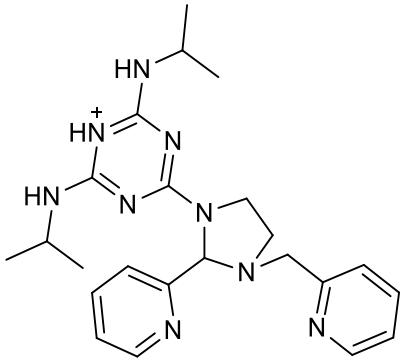
Figure S 19. ESI-MS of [L-H]



Observed envelope	Observed for	Calculated *m/z*
217.6454	[L-H]+ 2H	217.6429
434.2784	[L-H]+ H	434.2781

Figure S 20. Simulated ESI-MS of [L-H] for [(L-H)+H]





[(L-H)+H]

Figure S 21. ORTEP of [L-H] drawn at 50% probability level

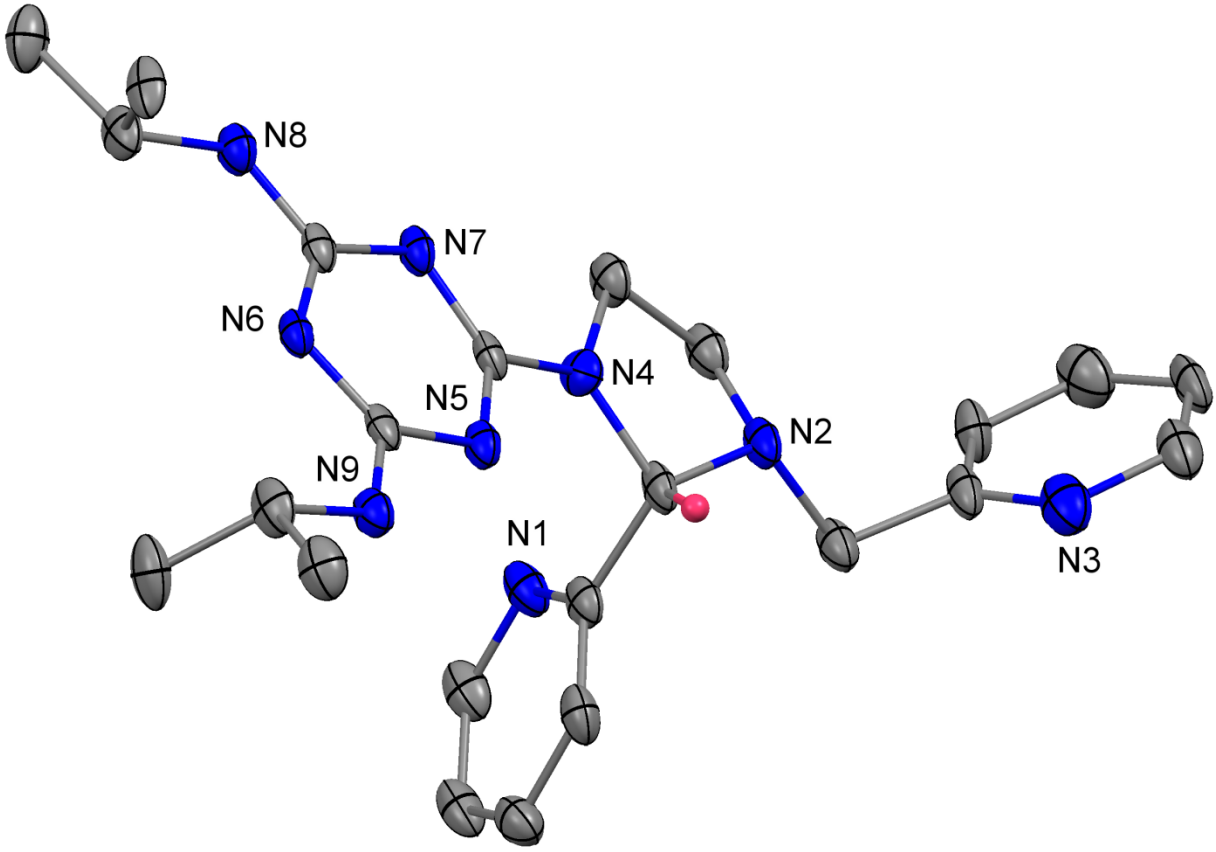
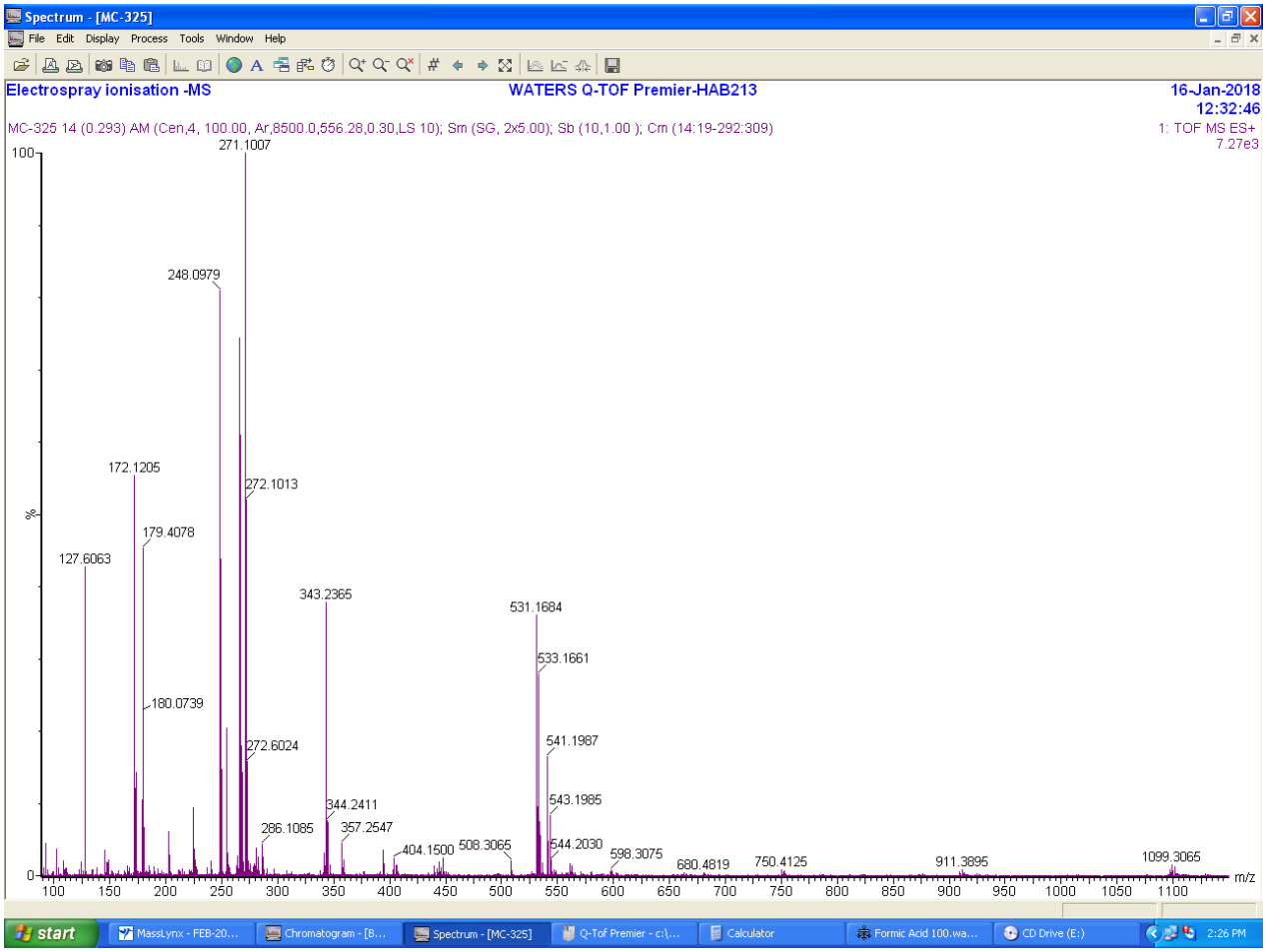
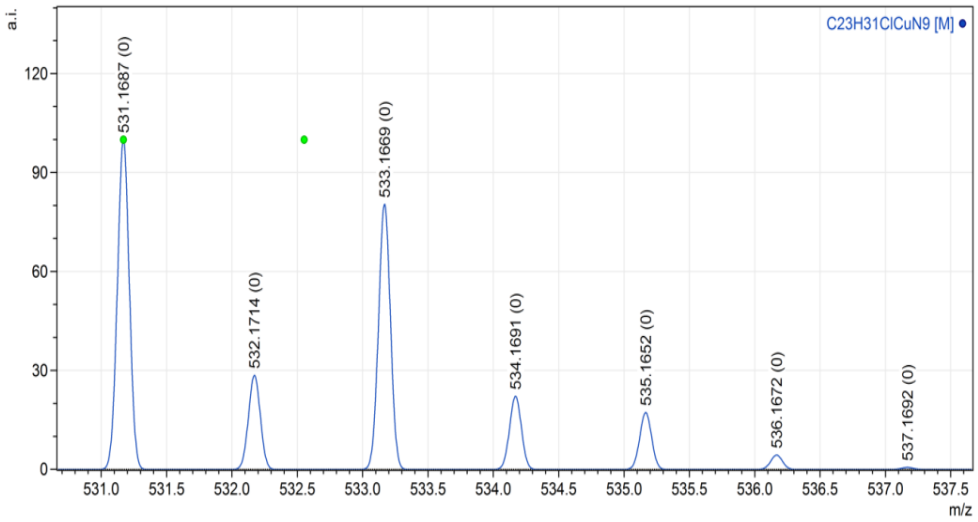


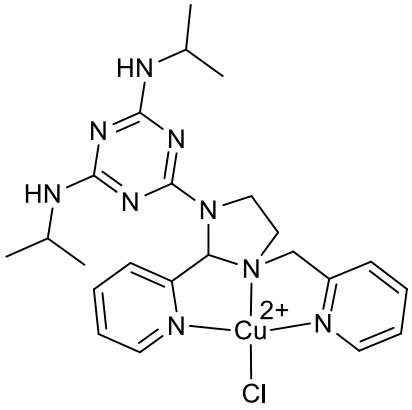
Figure S 22. ESI-MS of $[Cu(L\text{-}H)Cl_2]$



Observed envelope	Observed for	Calculated *m/z*
248.0979	$[Cu(L\text{-}H)]^{2+}$	248.0999
266.0863	$[Cu(L\text{-}H)+HCl]^{2+}$	266.0882
271.1007	$[Cu(L\text{-}H)+HCOOH]^{2+}$	271.1026
531.1684	$[Cu(L\text{-}H)Cl]^{+}$	531.1687
541.1987	$[Cu(L\text{-}H)(HCOO)]^{+}$	541.1975

Figure S 23. Simulated ESI-MS of $[Cu(L\text{-}H)Cl_2]$ for $[Cu(L\text{-}H)Cl]^+$





$[Cu(L\text{-}H)Cl]^+$

Figure S 24. ORTEP of [Cu(L-H)Cl_2] drawn at 50% probability level

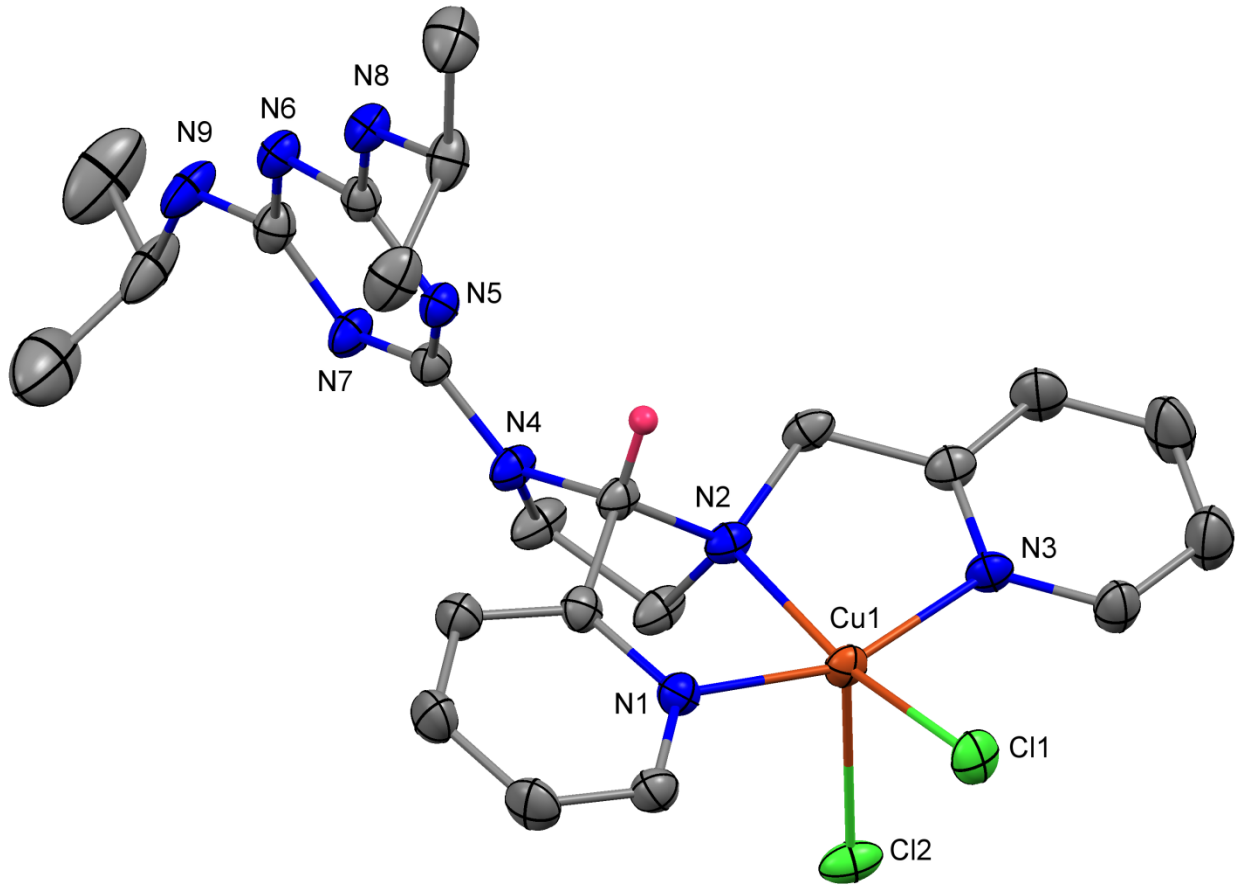
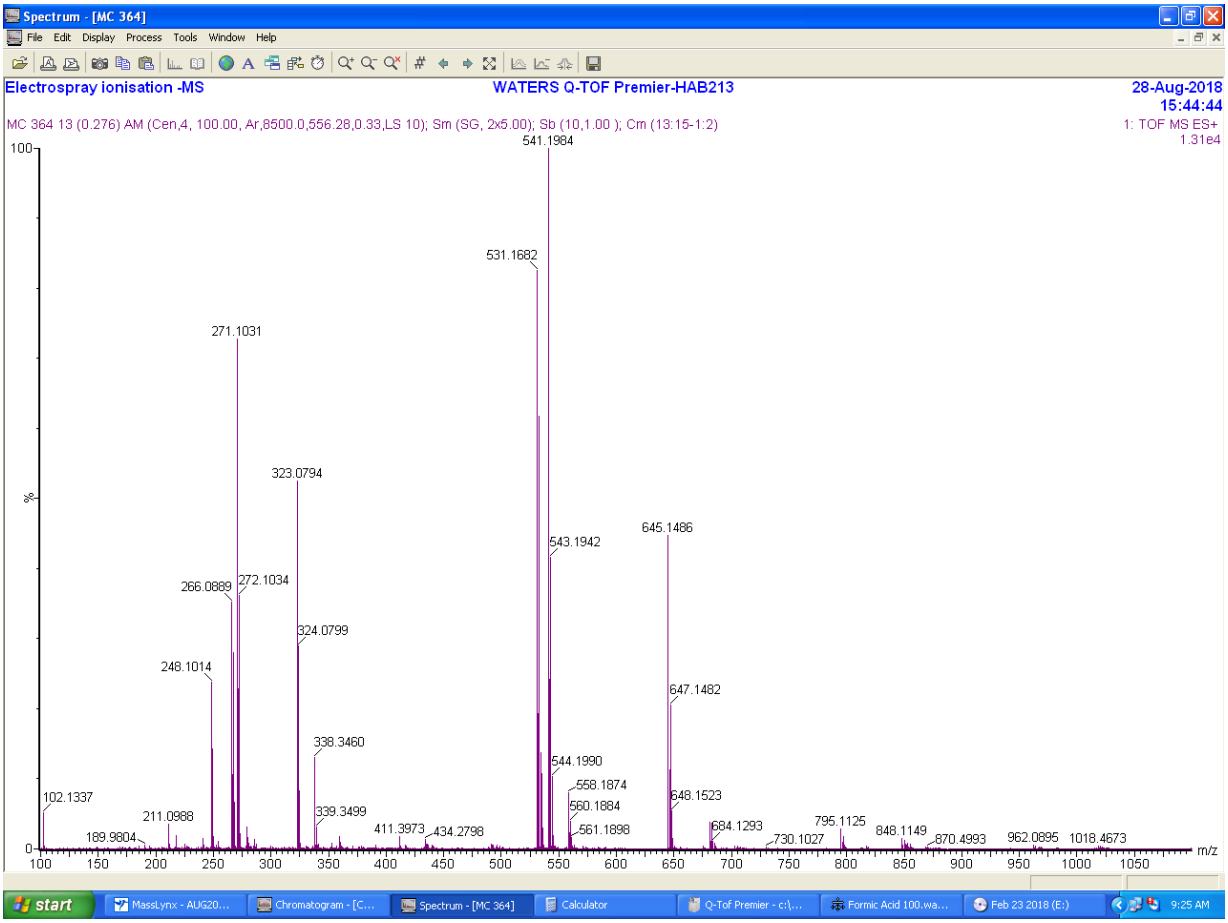
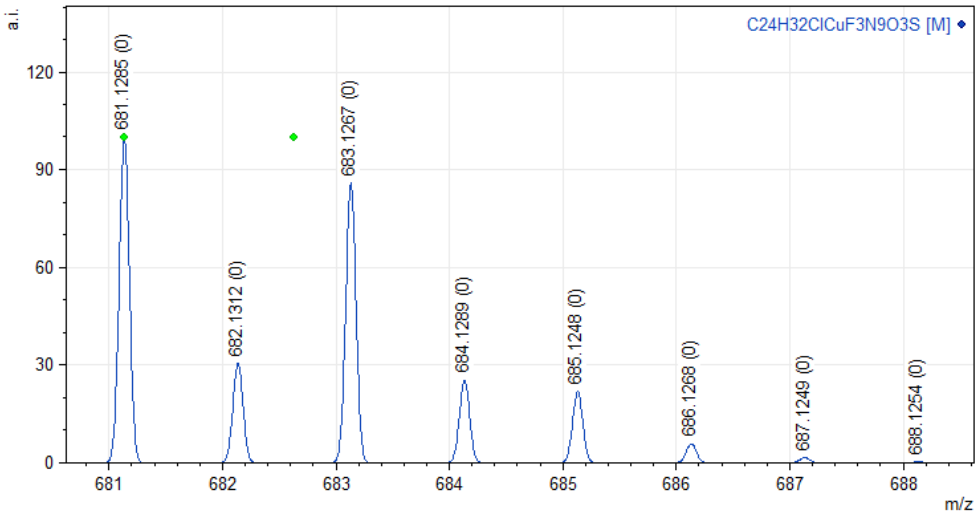


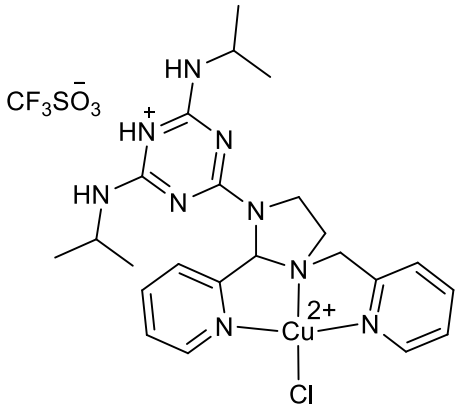
Figure S 25. ESI-MS of [Cu(L-H)(H^+)(OTf)(Cl)](OTf)



Observed envelope	Observed for	Calculated *m/z*
248.1014	$[Cu(L-H)]^{2+}$	248.0999
266.0889	$[Cu(L-H)+HCl]^{2+}$	266.0882
271.1031	$[Cu((L-H)+HCOOH]^{2+}$	271.1026
323.0794	$[Cu(L-H)+CF_3SO_3H]^{2+}$	323.0798
531.1682	$[Cu(L-H)Cl]^{+}$	531.1687
541.1984	$[Cu(L-H)(HCOO)]^{+}$	541.1975
645.1486	$[Cu(L-H)(CF_3SO_3)]^{+}$	645.1519
681.1262	$[Cu(L-H)Cl+CF_3SO_3H]^{+}$	681.1285
795.1125	$[Cu(L-H)(CF_3SO_3)+CF_3SO_3H]^{+}$	795.1117

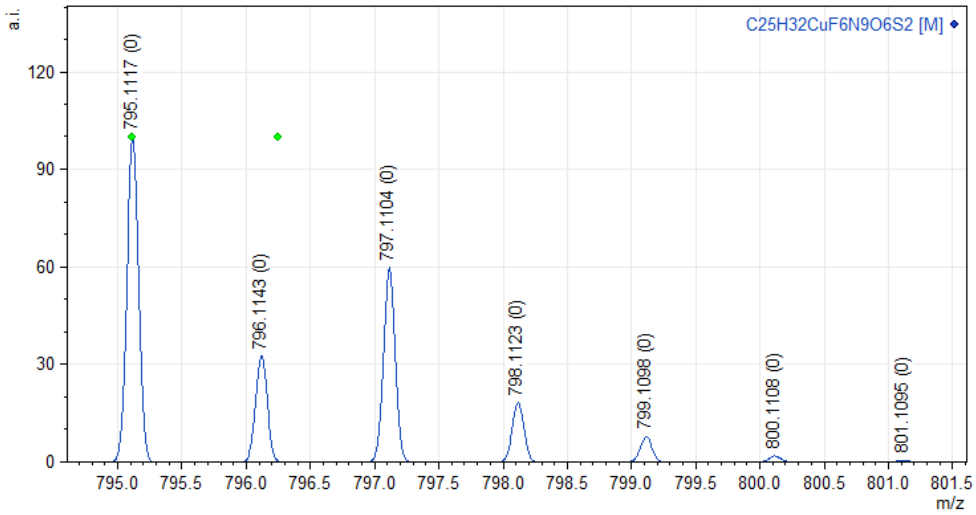
Figure S 26. Simulated ESI-MS of [Cu(L-H)(H$^+$)(OTf)(Cl)](OTf) for [Cu(L-H)Cl+CF_3SO_3H]$^+$

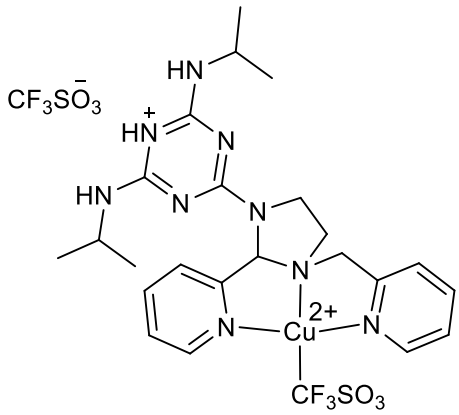




[Cu(L-H)Cl+CF_3SO_3H]$^+$

Figure S 27. Simulated ESI-MS of [Cu((L-H)(H^+)(OTf)Cl](OTf) for [Cu(L-H)(CF_3SO_3)+CF_3SO_3H]$^+$





[Cu(L-H)(CF_3SO_3)+CF_3SO_3H]$^+$

Figure S 28. ORTEP of [Cu(L-H)(H^+)(OTf)Cl](OTf) drawn at 50% probability level

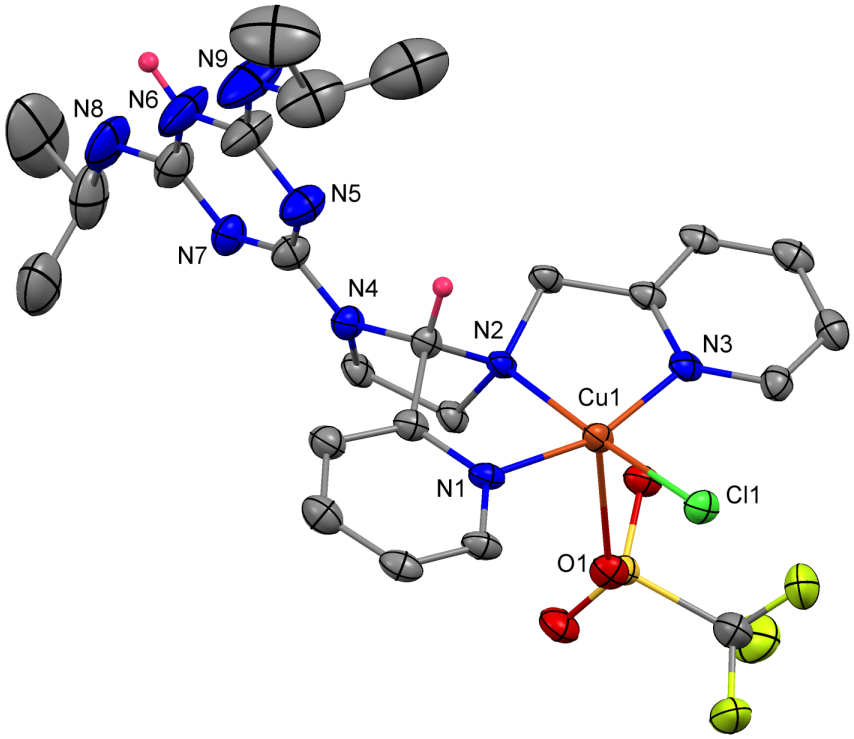
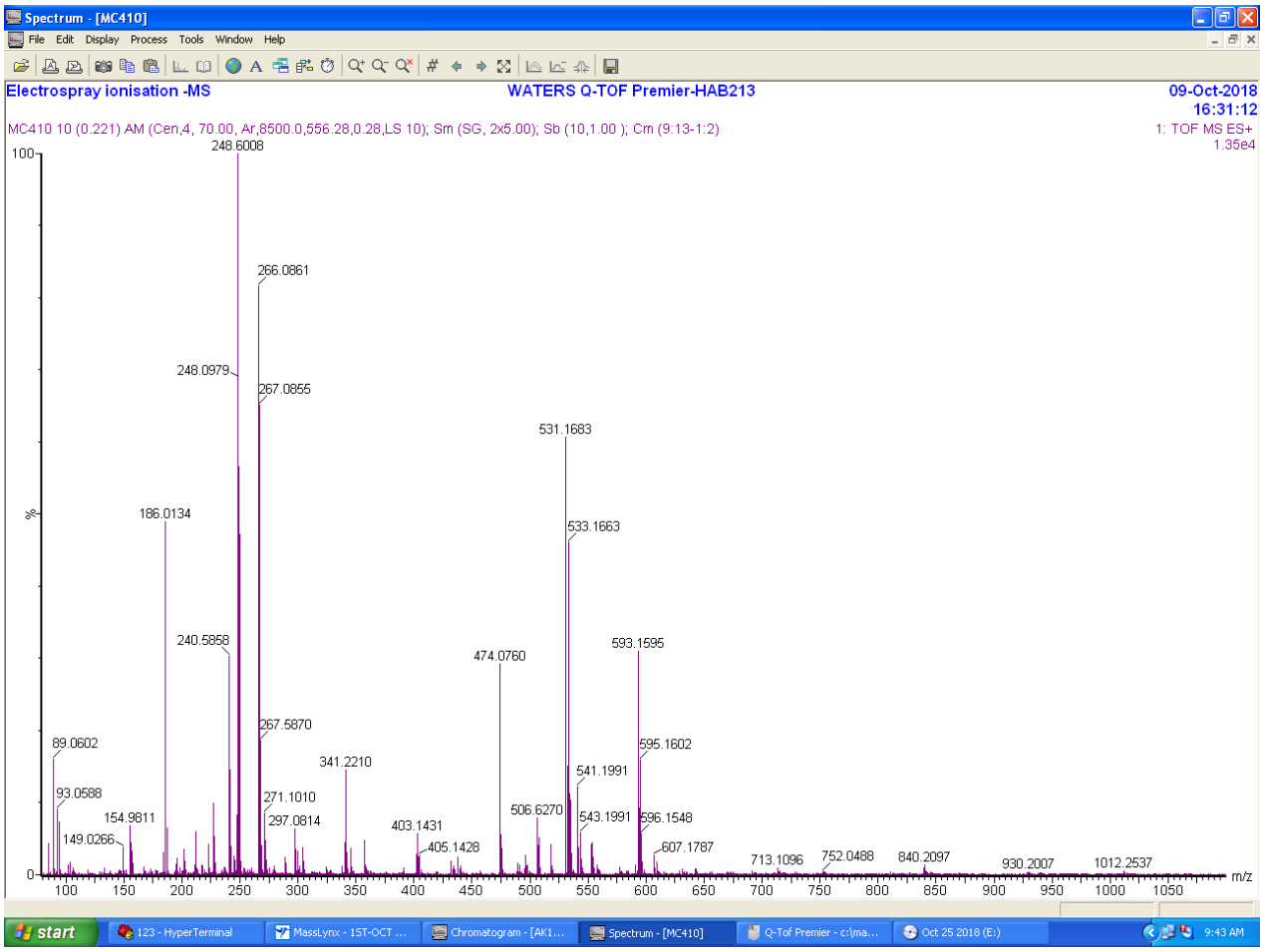
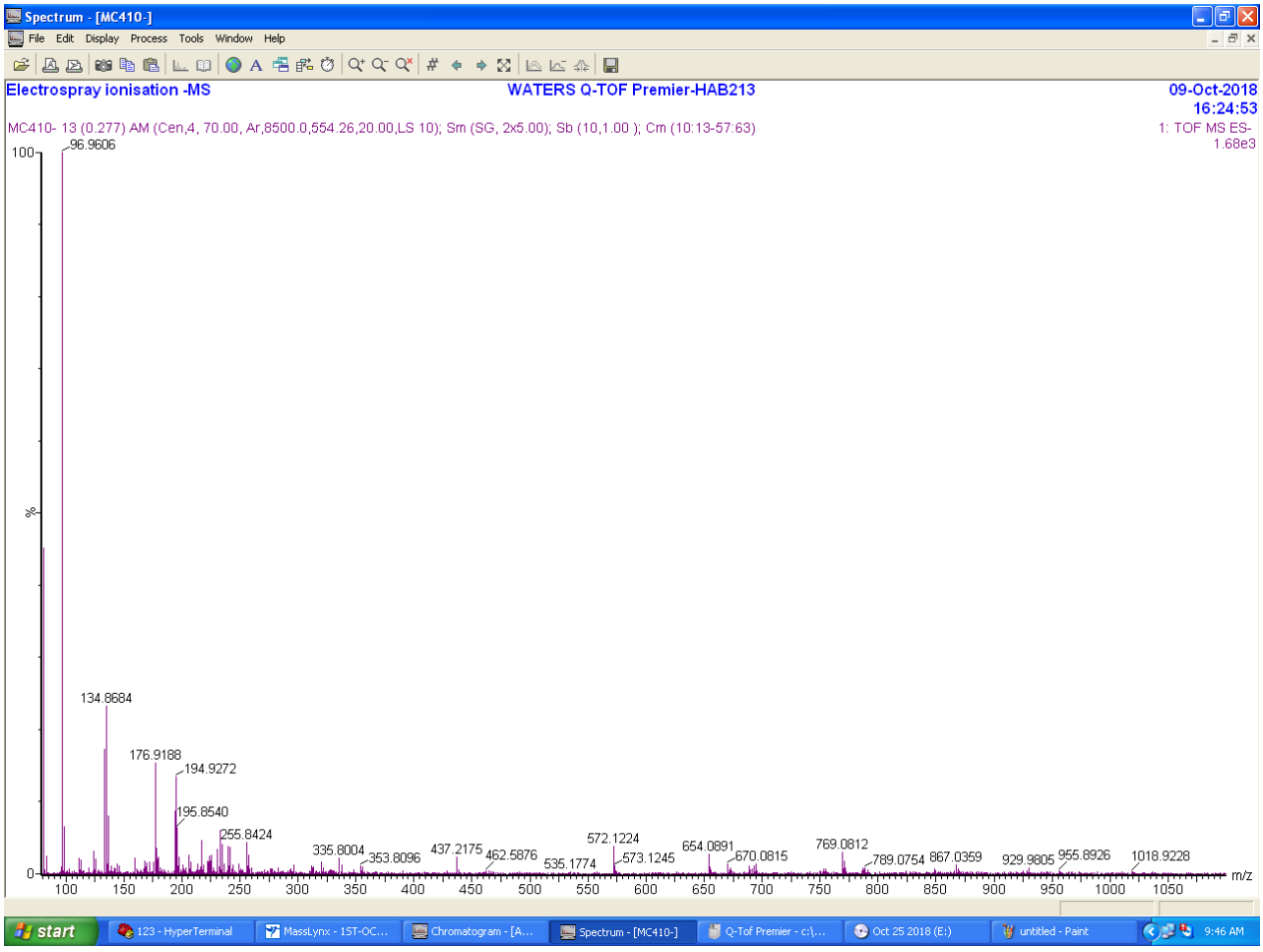


Figure S 29. ESI-MS of the solution containing [Cu(L-H)Cl_2] and 2 equivalent ferrocene after purging SO_2 (Positive ion mode) in CH_3CN



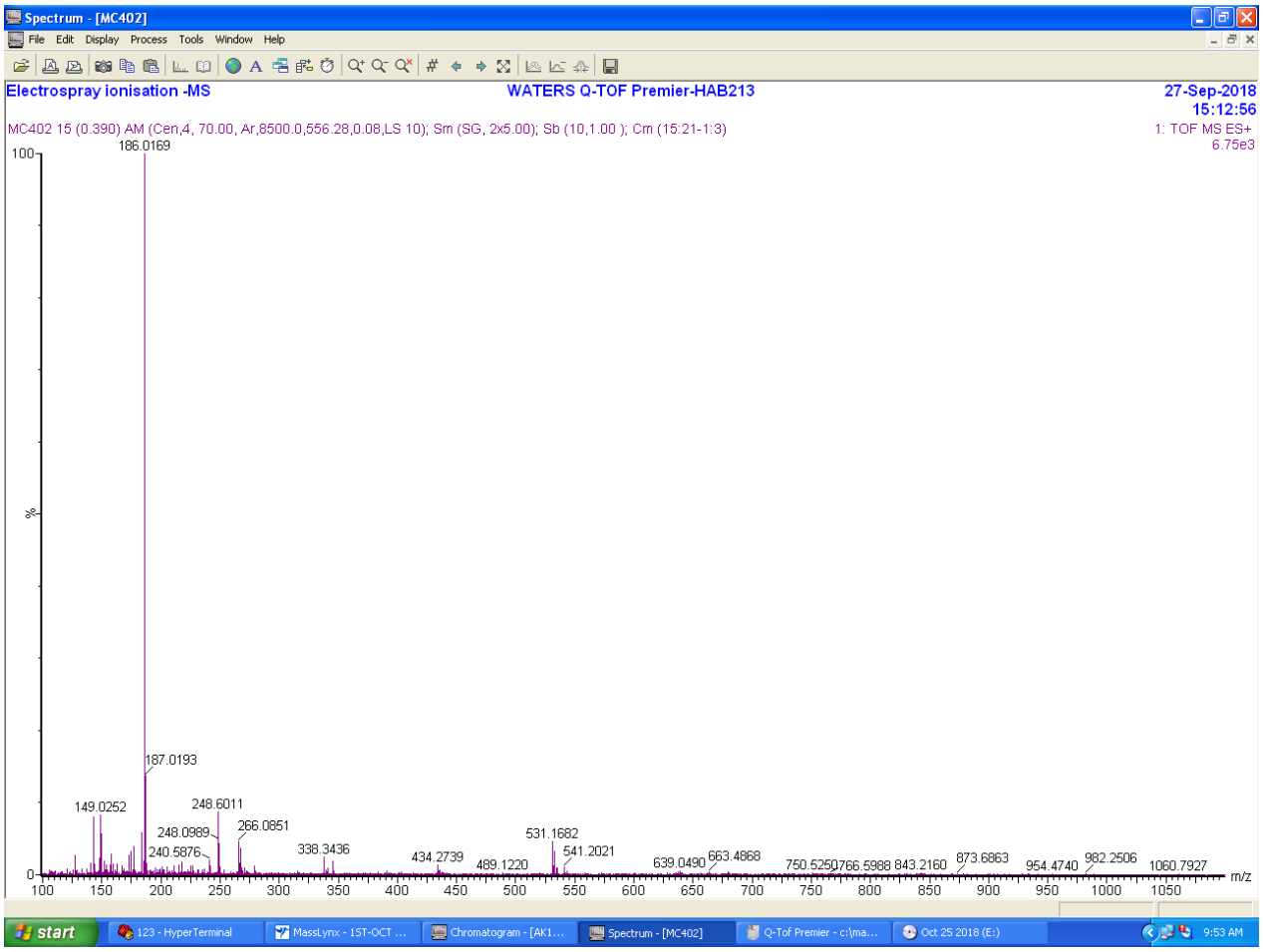
Observed envelope	Observed for	Calculated *m/z*
186.0134	Ferrocenium ion	186.0131
248.0979	$[Cu(L-H)]^{2+}$	248.0999
266.0861	$[Cu(L-H)+HCl]^{2+}$	266.0882
271.1010	$[Cu(L-H)+HCOOH]^{2+}$	271.1026
531.1683	$[Cu(L-H)Cl]^{+}$	531.1687
541.1991	$[Cu(L-H)(HCOO)]^{+}$	541.1975
593.1595	$[Cu(L-H)(HSO_4)]^{+}$	593.1595

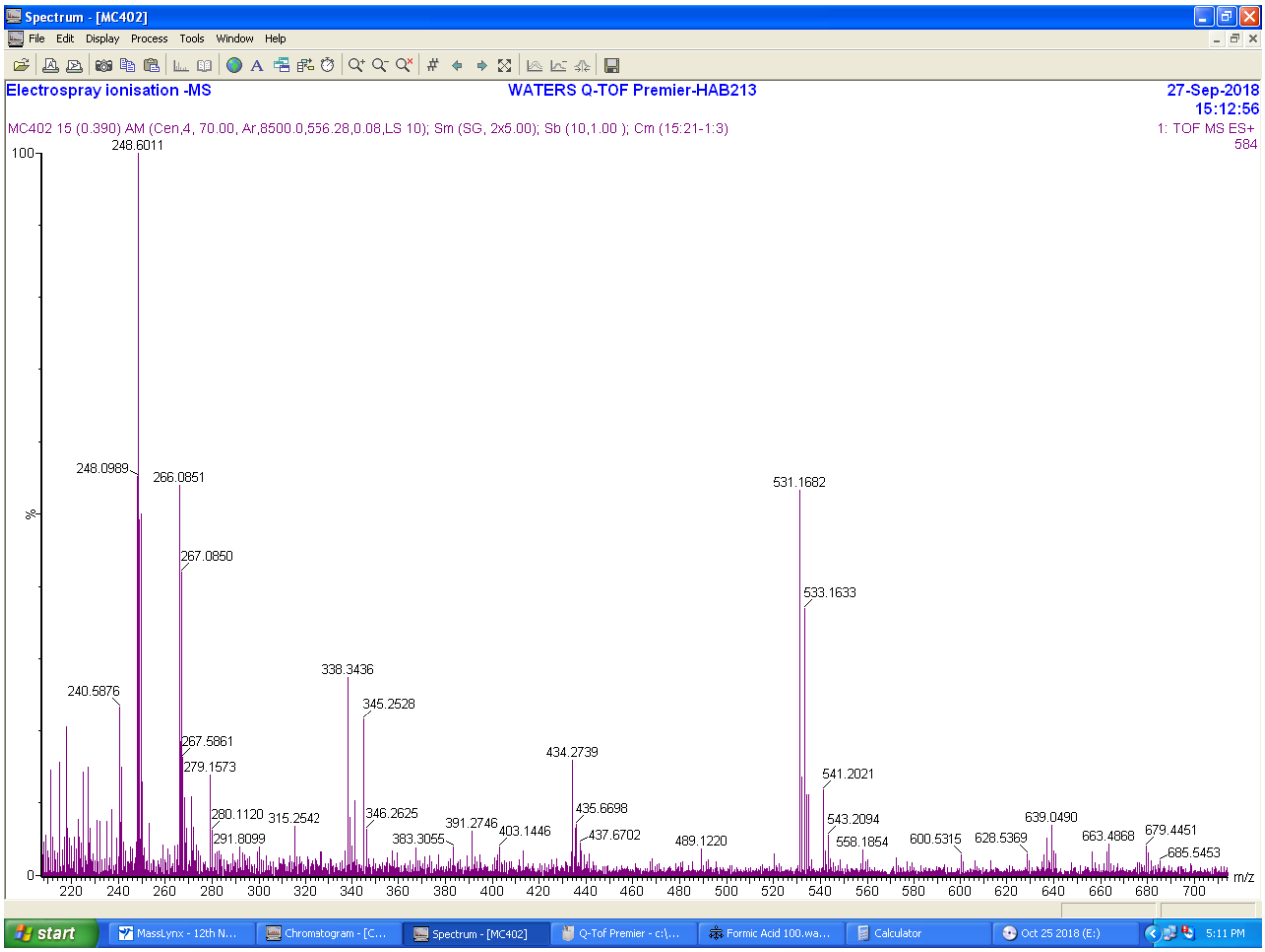
Figure S 30. ESI-MS of the solution containing $[Cu(L\text{-}H)Cl_2]$ and 2 equivalent ferrocene after purging SO_2 (Negative ion mode) in CH_3CN



Observed envelope	Observed for	Calculated *m/z*
96.9606	HSO_4^-	96.9596
194.9272	$[H(HSO_4)_2]^-$	194.9269

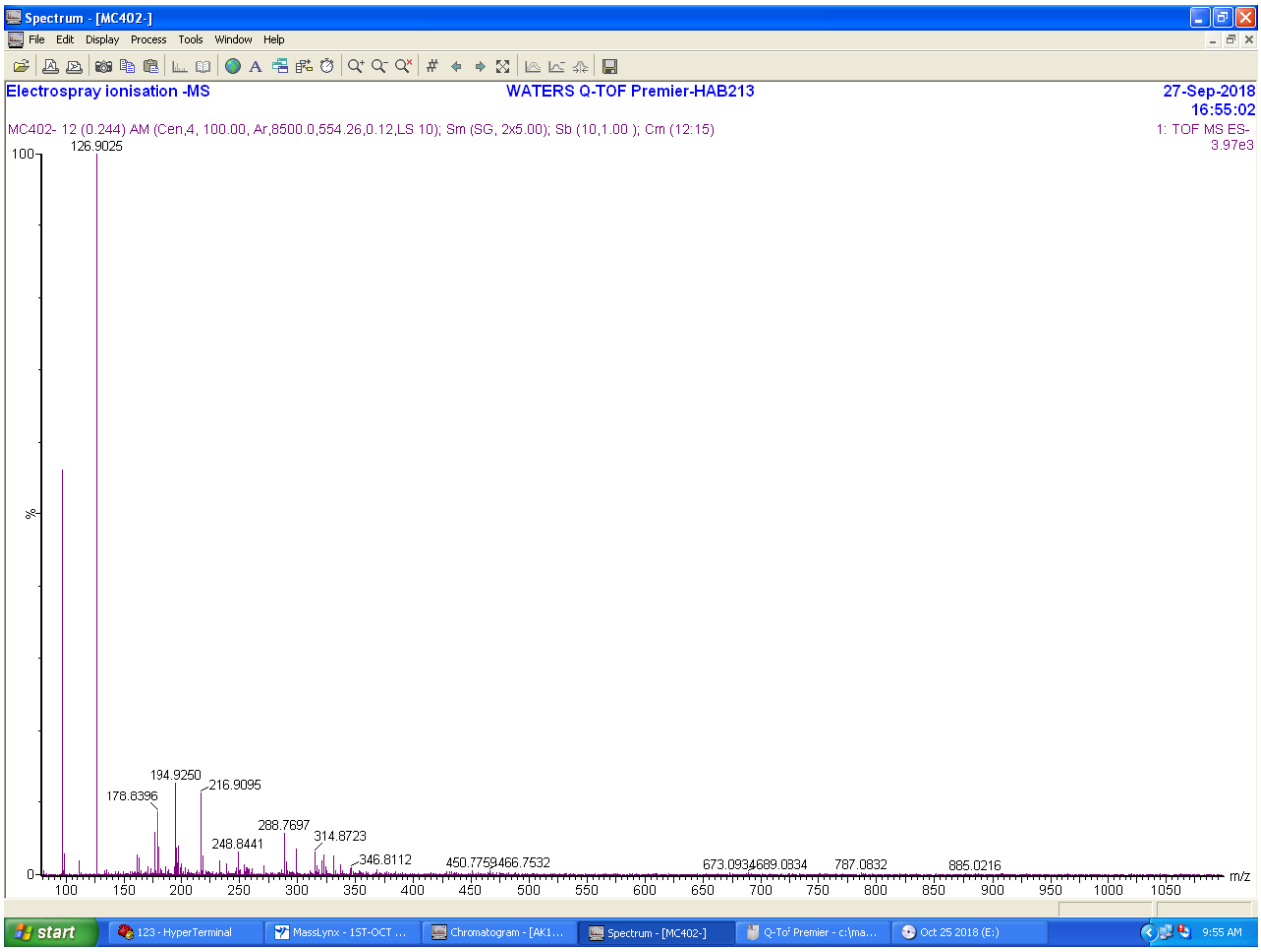
Figure S 31. ESI-MS of the solution containing [Cu(L-H)Cl_2] and 51 equivalent ferrocene after purging SO_2 (Positive ion mode) in CH_3CN

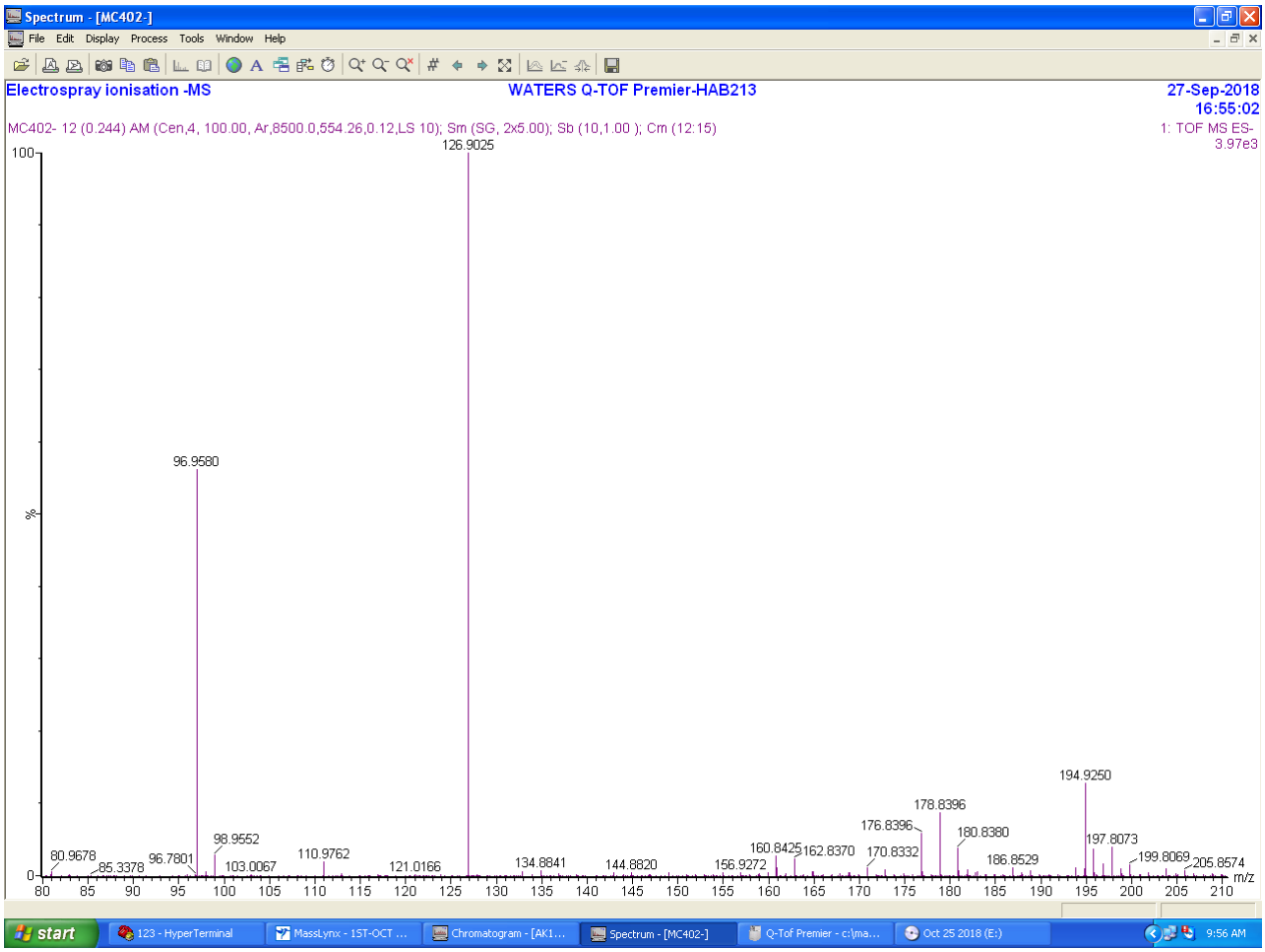




Observed envelope	Observed for	Calculated *m/z*
186.0169	Ferrocenium ion	186.0131
248.0989	$[Cu(L-H)]^{2+}$	248.0999
266.0851	$[Cu(L-H)+HCl]^{2+}$	266.0882
434.2739	$[(L-H)+H^{+}]$	434.27881
531.1682	$[Cu(L-H)Cl]^{+}$	531.1687
541.2021	$[Cu(L-H)(HCOO)]^{+}$	541.1975

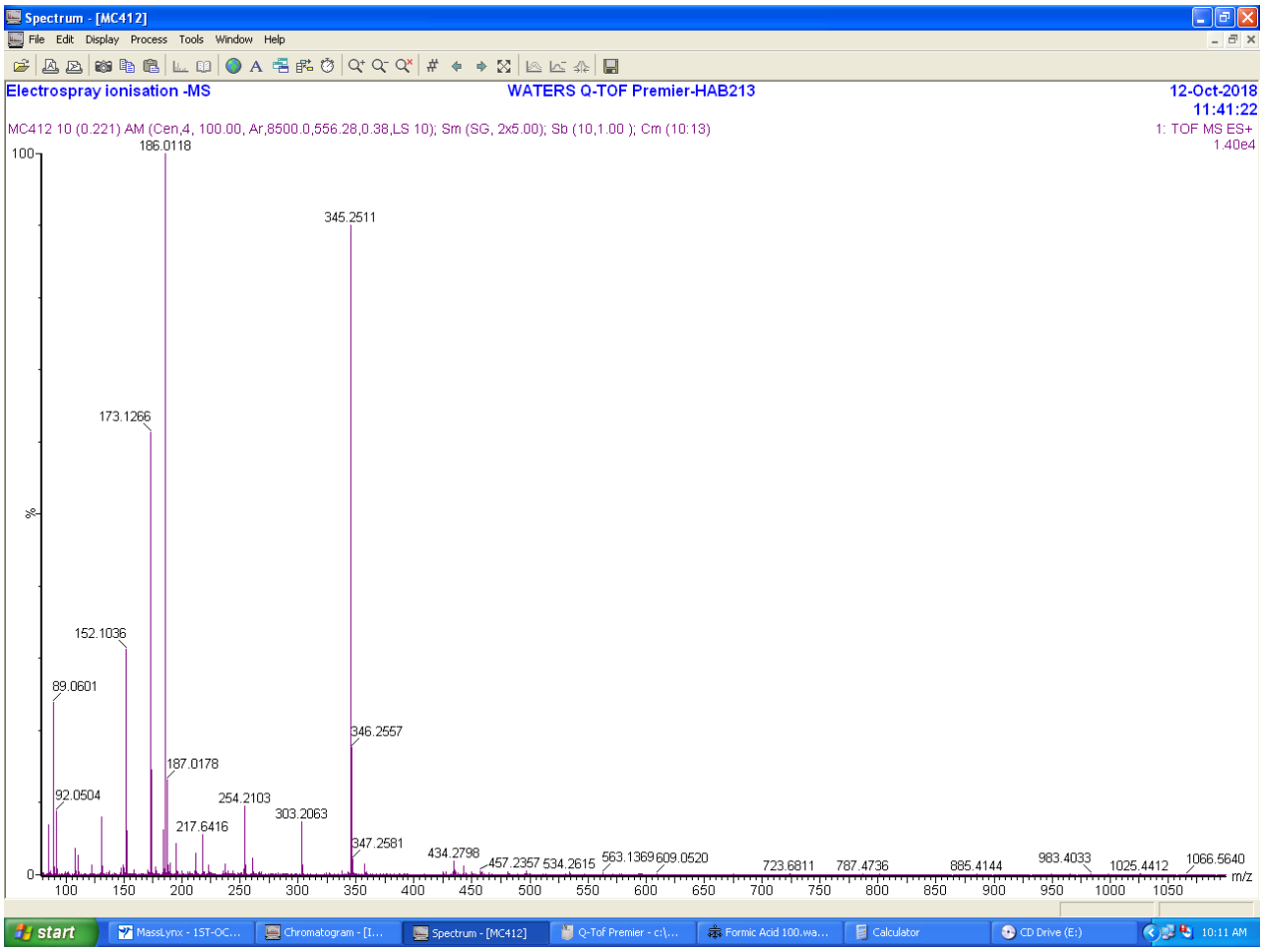
Figure S 32. ESI-MS of the solution containing [Cu(L-H)Cl_2] and 51 equivalent ferrocene after purging SO_2 (Negative ion mode) in CH_3CN





Observed envelope	Observed for	Calculated *m/z*
96.9580	HSO_4^-	96.9596
194.9250	$[H(HSO_4)_2]^-$	194.9269

Figure S 33. ESI-MS of the solution containing [L-H] and 2 equivalent ferrocene after purging SO_2 (Positive ion mode) in CH_3CN



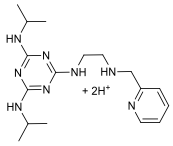
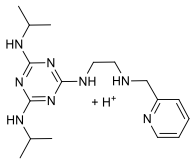
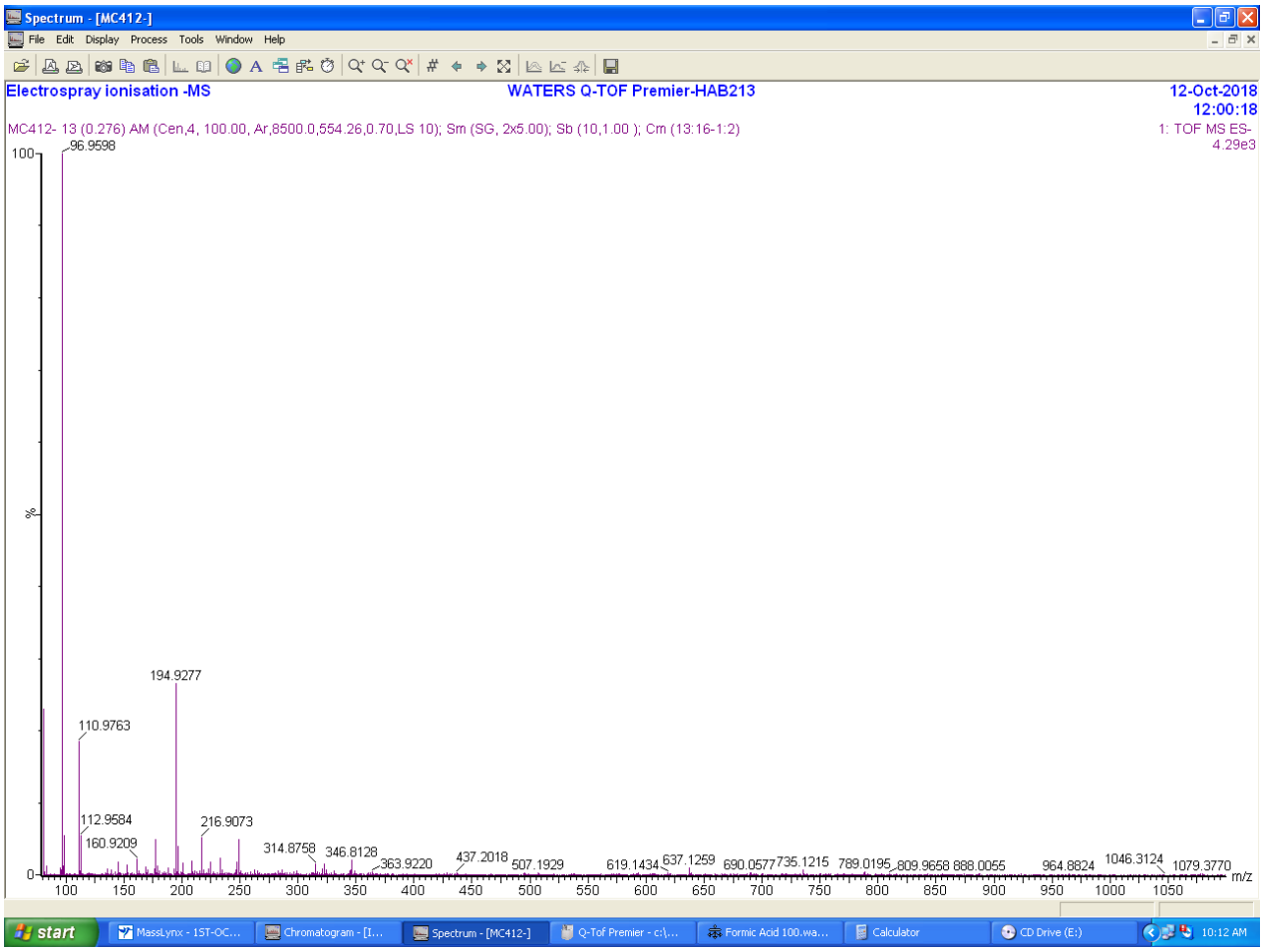
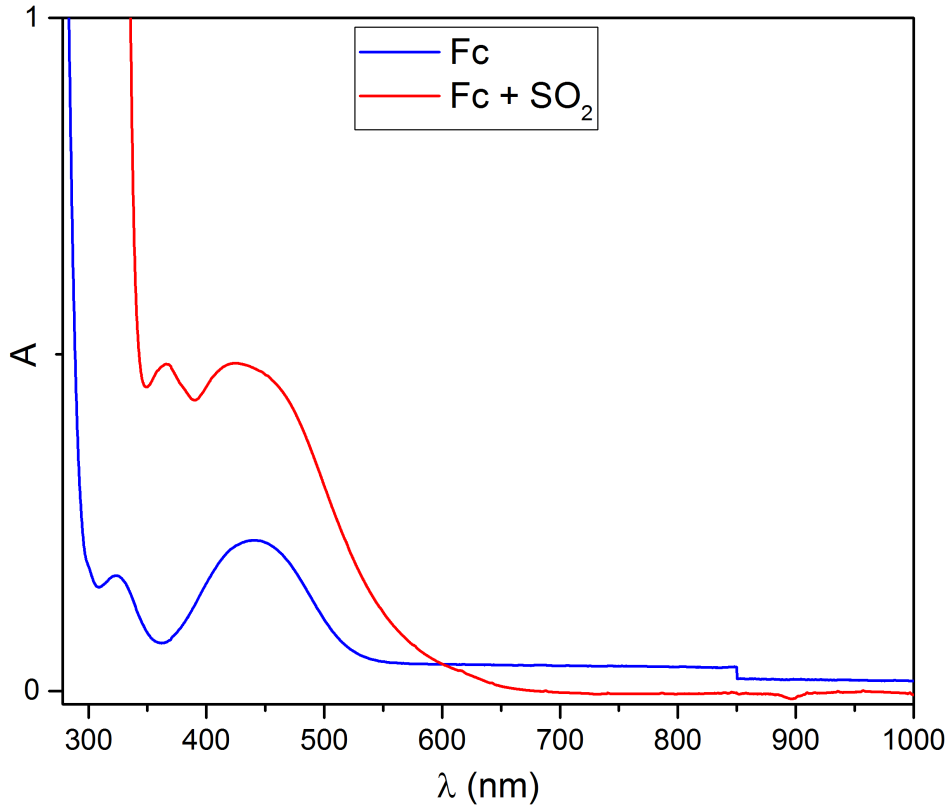
Observed envelope	Observed for	Calculated *m/z*
173.1266		173.1296
186.0118	Ferrocenium ion	186.0132
345.2511		345.2515

Figure S 34. ESI-MS of the solution containing [L-H] and 2 equivalent ferrocene after purging SO_2 (Negative ion mode) in CH_3CN



Observed envelope	Observed for	Calculated *m/z*
96.9598	HSO_4^-	96.9596
194.9277	$[H(HSO_4)_2]^-$	194.9269

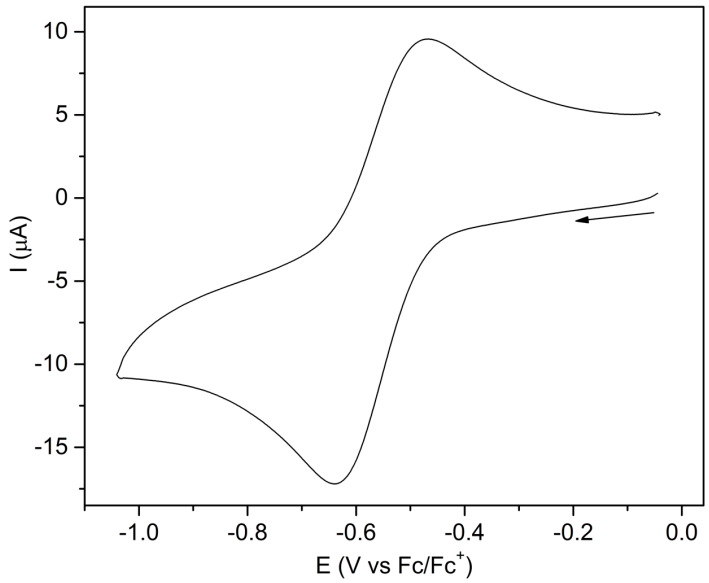
Figure S 35. UV-Vis of ferrocene in acetonitrile and in SO_2-purged acetonitrile.



Blue line: Ferrocene solution in acetonitrile (323nm and 445 nm)

Red line: After purging SO_2; change in absorbance is due to solvent evaporation

Figure S 36. CV of [Cu(L-H)Cl_2] in acetonitrile.



Cyclic voltammogram of 1mM acetonitrile solution of [Cu(L-H)Cl_2] containing 0.1 M Bu_4NPF_6 recorded on a static glassy carbon disc working electrode with a Pt wire auxiliary electrode and Ag/AgCl reference electrode (with internal ferrocene) at 25 °C with a scan rate of 200 mV s^{-1}; E_{pc} = –0.64 V; E_{pa} = –0.45 V *vs* $Fc^{0/+}$

Table S 1. Crystal data for [Cu(L-OMe)Cl_2]

Identification code	CCDC-1454816	
Empirical formula	C26 H36 Cl2 Cu N10 O	
Formula weight	639.09	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 27.313(8) Å	α = 90°.
	b = 9.409(3) Å	β = 107.956(4)°.
	c = 24.649(7) Å	γ = 90°.
Volume	6026(3) $Å^3$	
Z	8	
Density (calculated)	1.409 Mg/m^3	
Absorption coefficient	0.941 mm^{-1}	
F(000)	2664	
Crystal size	0.25 x 0.17 x 0.11 mm^3	
Theta range for data collection	1.567 to 28.431°.	
Index ranges	-36<=h<=27, -12<=k<=11, -29<=l<=32	
Reflections collected	18469	
Independent reflections	7153 [R(int) = 0.0605]	
Completeness to theta = 25.500°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.856 and 0.768	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7153 / 51 / 393	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1358	
R indices (all data)	R1 = 0.1146, wR2 = 0.1876	
Largest diff. peak and hole	0.917 and -0.853 e.$Å^{-3}$	

Table S 2. Crystal data for [Cu(Tim-H)(H_2O)Cl_2](OTf)

Identification code	CCDC-1895745	
Empirical formula	$C_{18}H_{31}Cl_2CuF_3N_8O_5S$	
Formula weight	663.01	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.9180(10) Å	α = 90°
	b = 11.9455(8) Å	β = 110.940(2)°
	c = 16.2476(11) Å	γ = 90°
Volume	2704.1(3) $Å^3$	
Z	4	
Density (calculated)	1.629 g/cm^3	
Absorption coefficient	1.149 mm^{-1}	
F(000)	1364.0	
Crystal size	0.22 × 0.2 × 0.18 mm^3	
Theta range for data collection	4.34 to 56.586	
Index ranges	$-19 \leq h \leq 19$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$	
Reflections collected	41974	
Independent reflections	6713 [R_{int} = 0.0654, R_{sigma} = 0.0435]	
Completeness to theta = 28.293°	100 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.746 and 0.701	
Data / restraints / parameters	6713/0/358	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R_1 = 0.0471, wR_2 = 0.1280	
R indices (all data)	R_1 = 0.0742, wR_2 = 0.1610	
Largest diff. peak and hole	1.06 and -1.02 $e.Å^{-3}$	

Table S 3. Crystal data for [L-H]

Identification code	CCDC-1895746	
Empirical formula	$C_{23}H_{31}N_9$	
Formula weight	433.57	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Iba2	
Unit cell dimensions	a = 21.678(2) Å	α = 90°
	b = 11.7948(13) Å	β = 90°
	c = 17.695(3) Å	γ = 90°
Volume	4524.4(10) $Å^3$	
Z	8	
Density (calculated)	1.273 g/cm^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	1856.0	
Crystal size	0.08 × 0.06 × 0.05 mm^3	
Theta range for data collection	5.944 to 50.246	
Index ranges	$-25 \leq h \leq 25$, $-14 \leq k \leq 14$, $-21 \leq l \leq 21$	
Reflections collected	25154	
Independent reflections	4016 [R_{int} = 0.0762, R_{sigma} = 0.0495]	
Completeness to theta = 25.123°	100 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.746 and 0.569	
Data / restraints / parameters	4016/7/314	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R_1 = 0.0469, wR_2 = 0.1038	
R indices (all data)	R_1 = 0.0604, wR_2 = 0.1129	
Largest diff. peak and hole	0.22 and -0.22 e. $Å^{-3}$	

Table S 4. Crystal data for $[Cu(L\text{-}H)Cl_2]$

Identification code	CCDC-1895747	
Empirical formula	$C_{25}H_{39}Cl_2CuN_9O_2$	
Formula weight	632.09	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.1817(3) Å	α = 90°
	b = 15.7088(7) Å	β = 95.9210(10)°
	c = 24.5591(11) Å	γ = 90°
Volume	3139.6(2)Å^3	
Z	4	
Density (calculated)	1.337 g/cm^3	
Absorption coefficient	0.903 mm^{-1}	
F(000)	1324.0	
Crystal size	0.2 × 0.18 × 0.16 mm^3	
Theta range for data collection	4.224 to 56.542	
Index ranges	$-10 \le h \le 10$, $-20 \le k \le 20$, $-32 \le l \le 32$	
Reflections collected	48948	
Independent reflections	7778 [R_{int} = 0.0631, R_{sigma} = 0.0430]	
Completeness to theta = 28.271°	99.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.746 and 0.690	
Data / restraints / parameters	7778/0/360	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R_1 = 0.0486, wR_2 = 0.1375	
R indices (all data)	R_1 = 0.0667, wR_2 = 0.1548	
Largest diff. peak and hole	0.59 and -0.82e.Å^{-3}	

Table S 5. Crystal data for [Cu(L-H)(H^+)(OTf)Cl](OTf)

Identification code	CCDC-1895748	
Empirical formula	$C_{25}H_{32}ClCuF_6N_9O_6S_2$	
Formula weight	831.70	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4954(8)Å	α = 100.763(2)°
	b = 11.7314(11)Å	β = 99.350(2)°
	c = 19.2810(18)Å	γ = 108.877(2)°
Volume	1734.2(3)$Å^3$	
Z	2	
Density (calculated)	1.593g/cm^3	
Absorption coefficient	0.912 mm^{-1}	
F(000)	850.0	
Crystal size	0.24 × 0.22 × 0.2 mm^3	
Theta range for data collection	4.43 to 56.676	
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-25 \leq l \leq 25$	
Reflections collected	21482	
Independent reflections	8622 [R_{int} = 0.0452, R_{sigma} = 0.0680]	
Completeness to theta = 28.338°	99.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.746 and 0.679	
Data / restraints / parameters	8622/43/455	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R_1 = 0.0819, wR_2 = 0.2246	
R indices (all data)	R_1 = 0.1196, wR_2 = 0.2612	
Largest diff. peak and hole	1.59 and -1.19 e.$Å^{-3}$	

Reference

(1) Mehrotra, S.; Raje, S.; Jain, A. K.; Jain, A.; Kandasamy, P.; Butcher, R. J.; Angamuthu, R. *ChemistrySelect***2018**, *3*, 4844.