MS-TOF Study of the Formation of Thiolato bridged Rhodium Oligomers

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Keywords: Rhodium / Thiolato ligands / MS-TOF / Oligomerisation / Inorganic clusters

Complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl was used as starting material to synthesize various oligomeric materials of general formula [Cp*Rh(μ-SPh)$_x$(μ-Cl)$_{3-x}$(Rh(μ-SPh)$_3$)$_n$RhCp*] (x = 1 to 3; n = 1 to 4), which are formally formed by insertion of n Rh(SPh)$_3$ into one μ-Rh-SPh bond. The insertion of Ir(SPh)$_3$ was also observed to generate the heterotrimetallic species. All complexes were observed using HR-MS-TOF and [Cp*Rh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]Cl **[3$^+$]Cl** was characterized using X-ray crystallography.

((Abstract Text----Continued))

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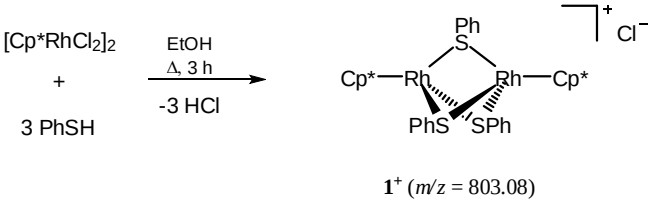
Introduction

Polynuclear thiolato-complexes of transition metals have been widely studied for their structural, chemical, and electronic properties,[1] and as models for active centers in biomolecules.[2] Many μ-thiolato bridged metal oligomers of general formula [M(μ-SR)$_x$]$_n$ have been reported, where x = 1 – 4, with a wide variety of metals, oxidation states, and ancillaries.[3] More specifically, dimeric species [CpRh(μ-*p*-SC$_6$H$_4$Me)$_3$RhCp]$^+$ (Cp = η^5-C$_5$H$_5$)[4] and [Cp*Rh(μ-SR)$_3$RhCp*]$^+$ (Cp* = η^5-C$_5$Me$_5$) have been reported for Rh(III) where R = Ph, *i*-Bu, allyl,[5] Me,[6] H,[7] or fluorinated aromatics.[8] Further functionalization of the bridging thiolato for specific purposes was also accomplished by esterification with R = *p*-C$_6$H$_4$OH[9] or Suzuki coupling with R = *p*-C$_6$H$_4$Br.[10]

While the rhodium centers in each of these complexes are 18-electron saturated species, thiolato ligands can shift from a bridging to a terminal position, giving access to free coordination sites that can become available for incoming ligand coordination. For example, the binding of a substrate can occur in complex CpMo(μ-SMe)$_3$(μ-Cl)MoCp by opening of a chlorido-bridge by controlled redox chemistry.[11] Of course, other factors, such as pH, can modify the coordination mode of the thiolato ligand.[12] It was therefore expected that in the right experimental conditions, the addition of *n* equivalents of [Rh(SPh)$_3$][3a] to triply bridged thiolato binuclear Cp*Rh(III) complexes would yield new thiolato bridges that would form oligomeric clusters with an added *n* [Rh(SPh)$_3$]. Such step-wise control could eventually lead to the formation of hybrid metal-organic polymers if a good control of the insertion process was achieved.[13] In order to gain more insight on the possibility of such transformations, high-resolution MS-TOF (HR-MS) studies were undertaken.[14]

Results and Discussion

Complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl (**[1$^+$]Cl**) was used as substrate and was synthesized by adding thiophenol to a refluxing solution of [Cp*RhCl$_2$]$_2$ in technical grade ethanol, as described by Chérioux and co-workers for the synthesis of [Cp*Rh(μ-*p*-SC$_6$H$_4$OH)$_3$RhCp*]Cl (Scheme 1).[9] The HR-MS spectrum of a solution of **[1$^+$]Cl** in CH$_2$Cl$_2$ shows the single ion [Cp*Rh(μ-SPh)$_3$RhCp*]$^+$ (**1$^+$**) (*m*/*z* = 803.08), as expected. The ^{1}H NMR spectrum in chloroform-*d* exhibits multiplets in the aromatic region corresponding to the *ortho* hydrogen atoms of the thiophenolato ligands at δ 7.82 – 7.77 and to the *meta* and *para* hydrogens at δ 7.40 – 7.33, as well as a singlet at δ 1.34 accounting for the 30 protons of the two Cp* ligands. This is in perfect accordance with the ^{1}H NMR data for complex **1$^+$** which has previously been characterized as the triflate salt **[1$^+$]OTf**.[5]



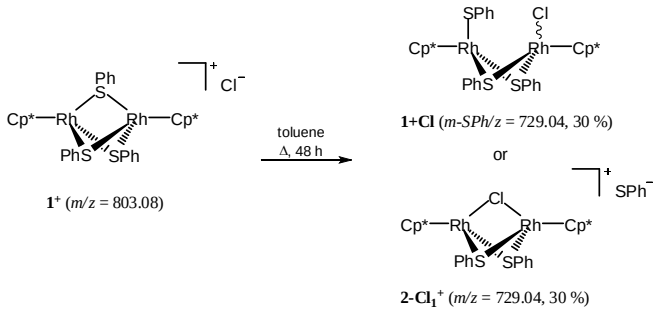
1$^+$ (*m*/*z* = 803.08)

Scheme 1. Synthesis of dinuclear complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl (**[1$^+$]Cl**)

The ethanol solution proves perfectly adequate in order to obtain **[1$^+$]Cl** cleanly, as only **1$^+$** was observed (*m*/*z* = 803.08; 100%) by HR-MS after refluxing **[1$^+$]Cl** for 48 hours with RhCl$_3$.xH$_2$O (x = 2 or 3) and three equivalents of PhSH. However, heating a solution **[1$^+$]Cl** by reflux in toluene, where the salt is not totally soluble, and then dissolving the residues in methylene chloride, affords by HR-MS species [Cp*Rh(Cl)(μ-SPh)$_2$RhCp*]$^+$ (**2-Cl$_1^+$**) (*m*/*z* = 729.04, 30 %) in addition to **1$^+$** (*m*/*z* = 803.08; 70%) (Scheme 2). The low

dielectric constant of toluene compared to ethanol suggests that the neutral complex [Cp*Rh(Cl)(μ-SPh)$_2$Rh(SPh)Cp*] **1+Cl** is favoured in toluene and could show as the [m-SPh]/z in the mass spectrum. Similar neutral binuclear rhodium(III) Cp* complexes are know in which the rhodium centers are bridged by two thiolato ligands and each contains one non-bridging chlorido ligand either in a *syn*[6b] or *anti* conformation.[7] In addition, the cationic binuclear analogue [CpRh(μ-*p*-SC$_6$H$_4$Me)$_2$(μ-Cl)RhCp]$^+$ has been reported with the weakly coordination $SbCl_6$ counteranion.[4a] It should be noted, however, that if the species observed (*m/z* = 729.04) corresponds to a cationic complex, it has to contain a phenylthiolato counteranion. While it is much less likely to observe a phenylthiolato counteranion rather than chlorido or $SbCl_6$, the formation of a cationic analogue of **[1$^+$]Cl** having a bridging chloride ligand and thiophenolato anion [Cp*Rh(μ-Cl)(μ-SPh)$_2$RhCp*]SPh **[2-Cl$_1^+$]SPh** cannot be discarded since a few transition metal complexes are known to have such phenylthiolato counterions.[15]

A similar solvent effect was observed by Maitlis and co-workers where the position of the equilibrium between the ionic [Cp*Rh(μ-SAr$_f$)$_3$RhCp*][Cp*Rh(SAr$_f$)$_3$] (Ar$_f$ = C$_6$F$_5$) and neutral Cp*Rh(SAr$_f$)$_2$ complexes depended on the polarity of the solvent.[8] The implication of these observations is that in non-polar solvents, one of the thiolato bridge opens, thus leaving one coordination site available for further bonding interactions with the chloride counteranion or other nucleophiles in its environment. Therefore, it should be possible to observe chain growing of an inorganic precursor *via* the controlled addition of [Rh(SR)$_3$]$_n$ units.

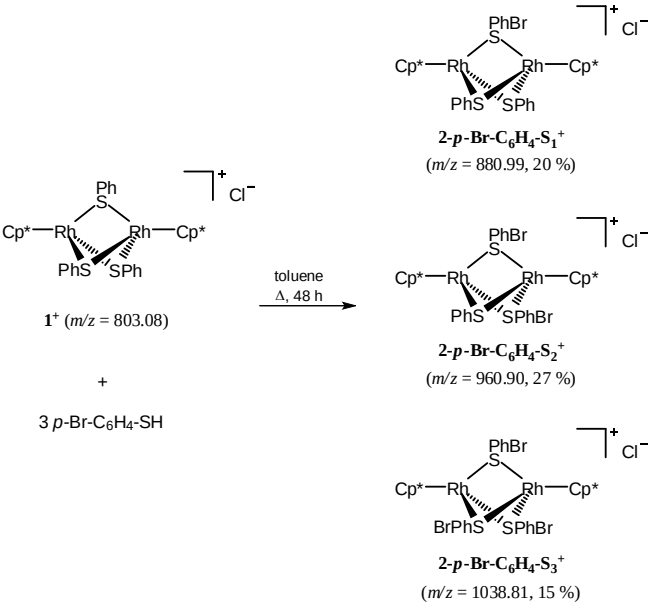


Scheme 2. Formation of neutral complex **1+Cl** or cationic complex **2-Cl$_1^+$**

Ligand exchange

Polar solvents, such as ethanol, water, and DMF, seem to inhibit any ligand exchange or addition reactions. Indeed, after mercaptans or [Rh(SPh)$_3$]$_n$[3a] are added to a solution of **[1$^+$]Cl** and heated 48 hours in refluxing conditions, only (**1**$^+$) was observed when an aliquot of the solution was diluted in CH_2Cl_2 and analyzed by HR-MS (*m/z* = 803.08). Therefore, as stated previously, toluene was chosen as solvent of choice for reactions with **[1$^+$]Cl**. Addition of three equivalents of *t*-BuSH to **[1$^+$]Cl** in toluene resulted in a very slow exchange of thiol. Only trace amounts of [Cp*Rh(μ-S-*t*-Bu)(μ-SPh)$_2$RhCp*]$^+$ (*m/z* = 783.11) (**2-*t*BuS$_1^+$**) were obtained after 48 hours in refluxing toluene.

In the same reaction conditions, however, an exchange between thiophenolate and p-Br-thiophenolate ligands occurs to give a mixture of **[1$^+$]Cl** (30 %), [Cp*Rh(μ-S-*p*-Br-C$_6$H$_4$)(μ-SPh)$_2$RhCp*]$^+$ (*m/z* = 880.99, 20 %) (**2-*p*-Br-C$_6$H$_4$-S$_1^+$**), [Cp*Rh(μ-S-*p*-Br-C$_6$H$_4$)$_2$(μ-SPh)RhCp*]$^+$ (*m/z* = 960.90, 27 %) (**2-*p*-Br-C$_6$H$_4$-S$_2^+$**), and [Cp*Rh(μ-S-*p*-Br-C$_6$H$_4$)$_3$RhCp*]$^+$ (*m/z* = 1038.81, 15 %) (**2-*p*-Br-C$_6$H$_4$-S$_3^+$**) (Scheme 3). The protonation of the phenylthiolato ligand by more acidic *p*-Br-C$_6$H$_4$-SH and the coordination of the conjugate base of the latter mercaptan is therefore favoured, as expected.[12e]



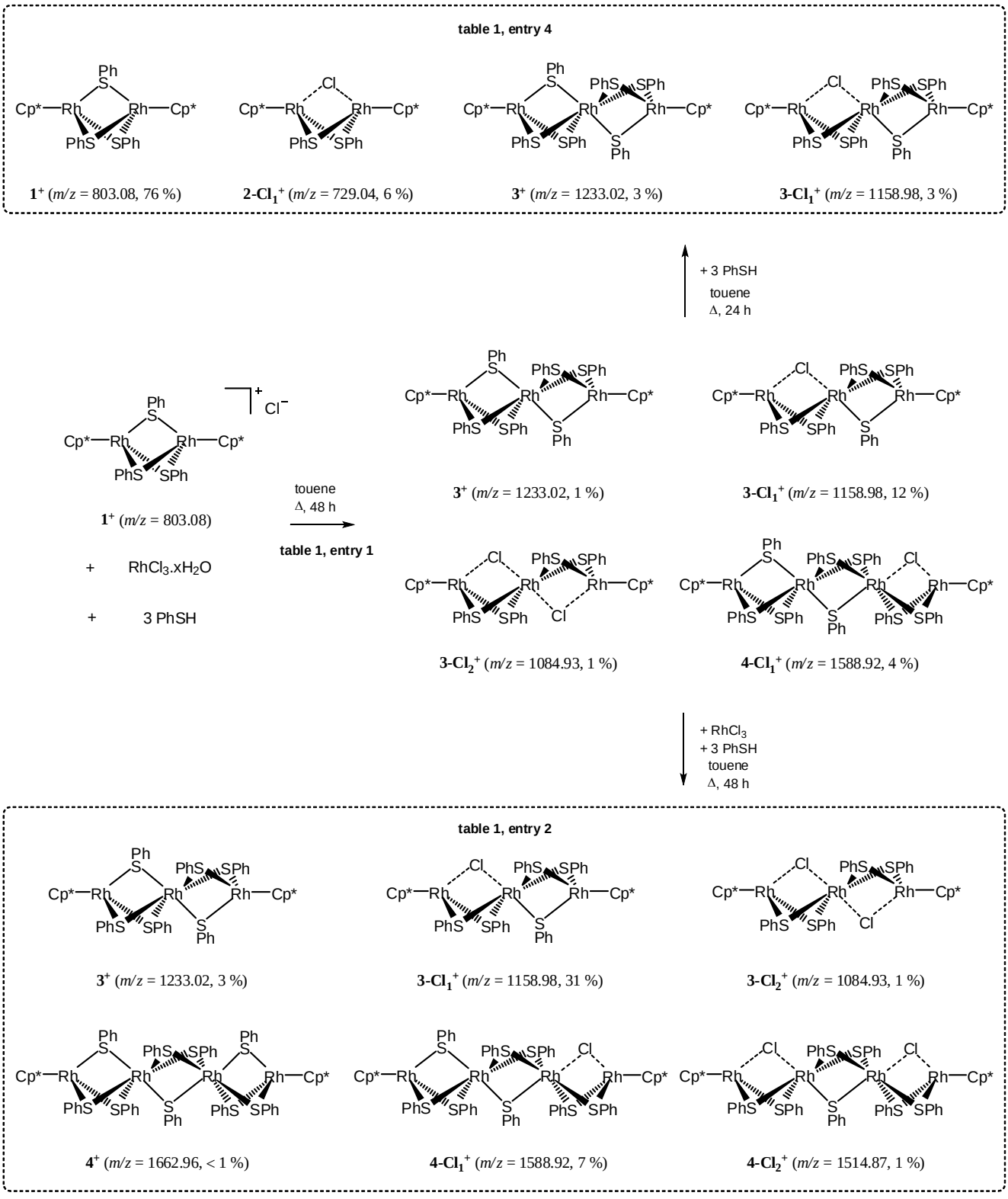
Scheme 3. Ligand exchange of (**[1$^+$]Cl**) with *p*-Br-C$_6$H$_4$-SH to form [Cp*Rh(μ-SPh)$_{3-x}$(μ-S-*p*-Br-C$_6$H$_4$)$_x$RhCp*]Cl, x = 1 (**[2-*p*-Br-C$_6$H$_4$-S$_1^+$]Cl**), x = 2 (**[2-*p*-Br-C$_6$H$_4$-S$_2^+$]Cl**), and x = 3 (**[2-*p*-Br-C$_6$H$_4$-S$_3^+$]Cl**).

Formation of Oligomers

After addition of one equivalent of rhodium(III) chloride and three equivalents of thiophenol to a solution of [Cp*Rh(μ-SPh)$_3$RhCp*]Cl **[1$^+$]Cl** in toluene, the reaction mixture was heated under reflux for 48 hours. It should be noted that in most of these reactions, an aliquot of the toluene solution was taken and diluted in methylene choride for HR-MS analysis. Unless stated otherwise, the products exhibit poor solubility and a solid residue is present in the reaction flask, which can account for more than 70% of the overall yield of material. However, when dissolving the residual solid in methylene chloride, the product distribution observed by HR-MS does not differ significantly from the one in the original aliquot of the toluene solution. (See ESI for HRMS data supporting this statement) NMR spectroscopy proves to be unreliable to get chemical information on this system for two reasons. First, the low solubility of the solids in usual NMR solvents in most of the experiments makes difficult the acquisition of good data and the isolation of each species. Also, the solutions obtained contain complex mixtures of many species that all have very similar signatures as starting materials. This results in very broad resonances in the ^{1}H NMR spectra and very weak or absent resonances in the ^{13}C{^{1}H} NMR spectra, even with over 8000 acquisitions (^{1}H and ^{13}C{^{1}H} NMR spectra for a typical oligomerization reaction along with the corresponding HR-MS spectrum are given in ESI). The only species that could be identified by ^{1}H NMR is **[3$^+$]Cl** which has a single resonance for the Cp* region at a chemical shift of δ = 1.27.

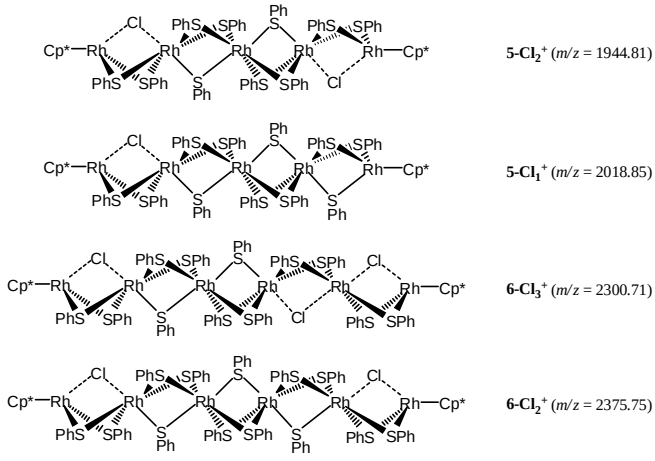
The HR-MS spectrum in CH_2Cl_2 of the previously mentioned reaction reveals many new species, among which the anticipated compound [Cp*Rh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]Cl **[3$^+$]Cl** as the cationic ion [Cp*Rh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]$^+$ (**3**$^+$, *m/z* =

1233.02) in a 1 % yield only (Table 1, entry 1). The species containing one or two chlorido ligands, **[3-Cl$_1^+$]** (*m/z* = 1158.98) and **[3-Cl$_2^+$]** (*m/z* = 1084.93) were also observed in 12 and 1 % yields, respectively, as well as the tetrameric complex with one chlorido ligand, [Cp*Rh(μ-SPh)$_2$ClRh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]$^+$ **[4-Cl$_1^+$]** (*m/z* = 1588.92) in 4 % yield (Scheme 4). Addition of one more equivalent of $RhCl_3$ and three equivalents of thiophenol to this reaction mixture shifts the equilibrium towards tri-, tetra- and pentanuclear rhodium species after heating for another 24 hours in refluxing conditions (entry 2). It shows the possibility of controlling the oligomer distribution by stepwise addition of reagents. The yields in tri- and tetranuclear compounds after 48 hours refluxing are higher if $RhCl_3$ and PhSH are stirred in methanol under reflux for two hours and dried to give an orange powder of oligomeric $[Rh(SPh)_3]_x$ [3a] before adding to the solution thiophenol (three equivalents) in this last reaction mixture does not have the effect of replacing the chlorido ligands by thiolato ligands as predicted. Instead it shifts the product distribution towards the binuclear species (entry 4).



Scheme 4. Formation of oligomers by stepwise insertion of $Rh(SPh)_{3-x}Cl_x$ units in dinuclear cation **1**$^+$ The chlorido containing species are depicted as cationic species bearing bridging chlorido ligands, however, as previously discussed they may also exist in their neutral form containing an additional chlorido or phenylthiolato ligand, in which case the species observed by HR-MS would be *m-Cl/z* or *m-SPh/z*, respectively.

Just like the coordinating solvents inhibit the chain growing process, excess thiol or coordinating bases, such as NEt_3, also prevent the insertion of RhX_3 (X = Cl or SR) species (entry 5, NEt_3) even after refluxing for 12 days (entry 6). The addition of three equivalents of HCl (2% in Et_2O), on the other hand, favours the insertion and greatly helps increasing the solubility of the resulting mixture. Indeed, a clean red solution is obtained after 48 hours in refluxing toluene. The HR-MS spectrum of this solution reveals di-, tri- and tetra-rhohium species **[2-Cl$_2$,$^+$], [3-Cl$_{0,1,2,3}^+$]** and **[4-Cl$_{0,1,2,3}^+$]**, most of which were separated by HPLC and identified with the coupled HR-MS all with errors under 5 ppm. (See ESI for HPLC chromatogram and HR-MS data) Trace amounts of compounds were also observed which *m/z* ratios correspond to the penta- and hexanuclear thiolato bridged rhodium analogues of **3**$^+$ each containing two Cp* ligands, and, respectively, one or two chlorido ligands, **[5-Cl$_{1,2}^+$]**, and two or three chlorido ligands, **[6-Cl$_{2,3}^+$]**, (entry 7). Possible structures of these complexes are depicted in scheme 5, although the exact structures, particularly the position of the chloride ligands, cannot be deducted from HR-MS data. It can be speculated that the acid protonates the thiphenolato ligand, therefore helping opening a coordination site for chloride coordination to form the neutral analogue, which should have a better solubility in toluene. Dilution of this reaction mixture in excess ethanol (10 x the volume) once again resulted in the displacement of the product distribution towards the dimeric species (entry 8), putting forward the dynamic process at hand. When the reaction was carried out in a biphasic system (1:1 toluene and water) with NBu_4Br as a phase transfer agent, a distribution where the thiolate ligands are favoured over the chloride ligands was observed (entry 9). Finally, high yields in trinuclear compounds (50 %) can be obtained by heating under reflux **[1**$^+$**]Cl**, $RhCl_3$, and thiophenol in xylene, however a large amount of decomposition to unidentifiable compounds of mass ranging from 600 to 2000 is obtained (34 %) (entry 10).



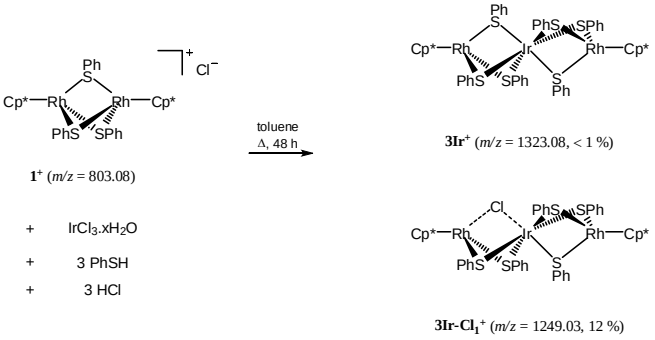
Scheme 5. Putative structure of penta- and hexanuclear complexes **[5-Cl$_{1,2}^+$]**, and **[6-Cl$_{2,3}^+$]**. The exact position of the chlorido ligands on the chain is unkown as well as its bridging or terminal position since these complexes were identified based on HRMS results.

According to the proposed reaction scheme, it could be possible to form heterometallic complexes using the same strategy. Indeed, the addition of one equivalent of $IrCl_3$ and three equivalents of PhSH to a solution of **[1**$^+$**]Cl** in toluene with HCl gave the insertion of the Ir(III) fragment to give [Cp*Rh(μ-SPh)$_3$Ir(μ-SPh)$_3$RhCp*]$^+$ **[3Ir**$^+$**]** (*m/z* = 1323.08, < 1 %) as well as the chloride containing **[3Ir-Cl$_1^+$]** (*m/z* = 1249.03, 12 %), albeit in low yields (Scheme 6). It should be noted, however, that the addition of iron(III) chloride did not yield any insertion product.

Table 1. Distribution of oligomers formed by addition of $[RhCl_x(SPh)_{3-x}]$ units to **[1**$^+$**]Cl**

Entry[a]	**1**$^+$ (%)	Rh_2[b] (%)	**3**$^+$ (%)	Rh_3 (%)	**4**$^+$ (%)	Rh_4 (%)	other[c] (%)
1	35	77	1	14	0	4	5
2	13	37	3	35	< 1	8	20
3	3	3	15	76	1	18	3
4	76	82	3	6	0	2	10
5	78	96	0	2	0	0	2
6	44	70	2	17	0	2	11
7	0	19	6	50	1	24	7
8	0	65	1	20	0	4	11
9	74	74	6	6	3	4	16
10	10	10	0	50	0	6	34

[a] See ESI for complete distribution of products and detailed reaction conditions. [b] Rh_x: Content of species containing x rhodium atoms, including the parent X^+ species. [c] Other species include Rh_5 and Rh_6 species as well as unidentified compounds with *m/z* ranging from 600 to 2000 amu.



Scheme 6. Formation of [Cp*Rh(μ-SPh)$_3$Ir(μ-SPh)$_3$RhCp*]$^+$ **[3Ir**$^+$**]** and [Cp*Rh(μ-SPh)$_2$ClIr(μ-SPh)$_3$RhCp*]$^+$ **[3Ir-Cl$_1^+$]** by insertion of an Ir fragment in **[1**$^+$**]Cl**.

Structure of [3$^+$]Cl

It was possible to isolate single crystals of complex **[3**$^+$**]Cl** which were analysed by X-ray crystallography.[16] The ORTEP is shown in Figure 1. The complex crystallizes in the $P2_1/c$ space group with Z=4, but with 2 independent molecules. For each of the molecules, the central rhodium atoms are located on inversion centers. The trimetallic structure has all Rh atoms aligned (the Rh-Rh-Rh angle is 180º), where the two terminal metal centers have piano-stool conformation and with the central atom adopting a pseudo-

octahedral geometry. The Rh-S distances on the terminal rhodium atoms vary between 2.377(3) to 2.420(3) Å, whereas the central rhodium atoms have Rh-S distances that vary between 2.350(3) and 2.385(3) Å. The phenyl rings of bridging thiophenolato ligands are rotated in an average angle of 29.4º from the plane formed by the three sulfur atoms in *fac* position of the terminal Rh atoms. Interestingly, there is no significant π-stacking between the thiophenolato ligands within a molecule.

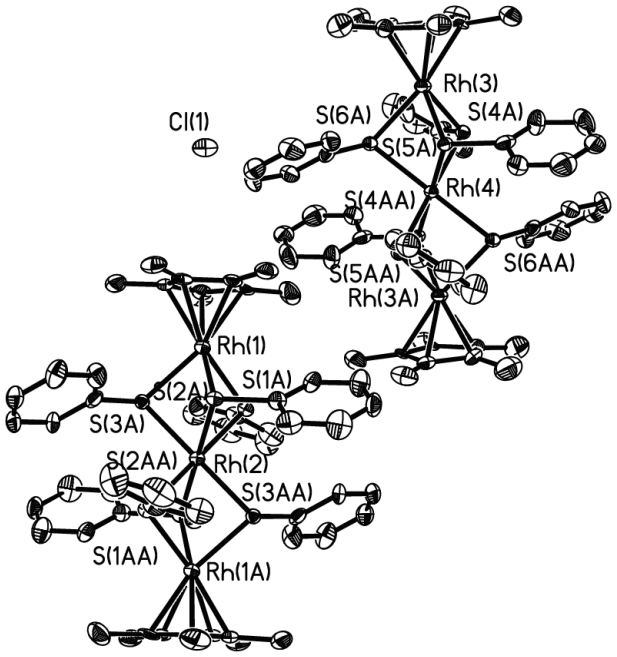


Figure 1. ORTEP view of **[3⁺]Cl** showing the numbering scheme adopted. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms were removed for clarity. The symmetry transformation used to generate equivalent atoms is –x, –y, –z.

Two types of disorder were observed in this crystal structure, accounting for the relatively high R factor (5.96%). First, on one of the complex, the Cp* has rotational disorder. Additionally, it was possible to observe in the Fourier map the presence of large Q peaks in proximity of the rhodium centers that were attributed to sulfur atoms. The refinement of the occupation gave respectively ratios of 85:15 and 90:10 for the two independent molecules between the sulfur of the thiophenolato ligands that were originally assigned and the residual Q peaks. Although no new phenyl ring was assigned to the minor sulfur components, the orientation of the phenyl ring suggest that in some of the molecules, the thiophenolato adopt a counter clockwise orientation relative to the major component (Figure 2). Therefore, no good model for the phenyl rings of the minor components was found to resist the structure refinements.

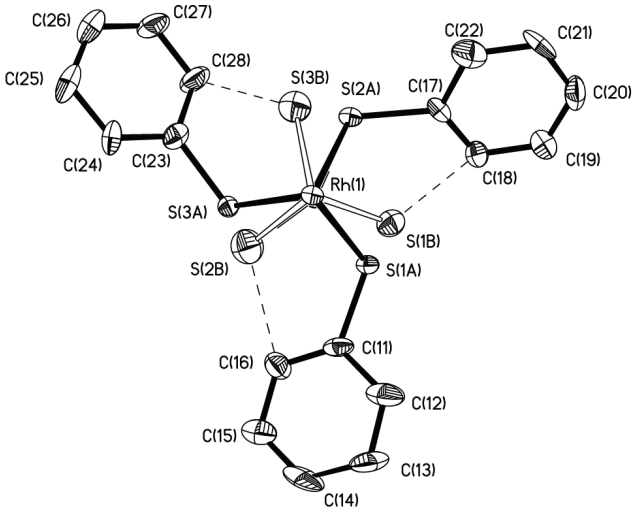


Figure 2. ORTEP view of one of the $Rh(SPh)_3$ fragment of **[3⁺]Cl** in *fac* conformation. The Q peaks that were labelled as sulphur atom show a possible disorder where the thiophenolate are in a counter-clockwise orientation compared to the original model.

Conclusions

Complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl do show a propensity to open up a coordination site in non polar solvents and in acidic conditions to favour the insertion of *n* $Rh(SPh_3)_3$ to form [Cp*[Rh(μ-SPh)$_3$]$_n$RhCp*]Cl and its chlorido derivatives. The oligomeric material formed, which consists of species having up to 6 rhodium atoms, were observed using HR-MS-TOF. Although the isolation and the purification of these complex mixtures proves to be quite difficult on the scale the reactions were carried out, it is nevertheless possible using HPLC to observed them individually. The crystal structure of **[3⁺]Cl** confirms that we have a linear trimeric species. Although similar coordination environments could be obtained with species having more than three metal atoms, no structural proofs could be obtained in our hands that similar arrangement is present in higher rhodium-containing clusters. Current studies are aiming at the isolation of larger species in order to confirm their solid state structures and at increasing the selectivity in product distribution.

Experimental Section

Complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl, **[1⁺]Cl** was prepared according to the literature procedure for [Cp*Rh(μ-*p*-$SC_6H_4OH)_3$RhCp*]Cl.[9] The HR-MS analyses were made on an Agilent 6210 Time of flight LC/MS with an electrospray ion source. Samples for HR-MS analysis were prepared by taking a 10 μL aliquot of the desired solution and diluting it in one mL of methylene chloride, or by dissolving a few milligrams of solid material in one mL of methylene chloride, after which the solutions were filtered (0.2 μm) for direct injection. ^{1}H NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer at 400.0 MHz.

For the ligand exchange reactions, three equivalents of thiol were added to **[1⁺]Cl** (10 mg, 0.012 mmol) in the in a round bottom flask in 10 mL of the

appropriate solvent, after which the solution was heated to refluxing conditions and samples were taken for HR-MS analysis at 24 hours intervals.

For the formation of oligomers (table 1), unless stated otherwise, $RhCl_3.xH_2O$ (3.0 mg, 0.012 mmol) and HSPh (3,6 µL, 0.036 mmol) were added to **[1$^+$]Cl** (10 mg, 0.012 mmol) in toluene (10 mL) in a round bottom flask, which were heated at 110 ºC for 48 hours. An aliquot of the solution was dissolved in CH_2Cl_2 for HR-MS analysis. The percentage given represents the HR-MS intensity of one fragment compared to the summation of the intensity for all fragments observed. In some of the entries, the solvent was removed under reduced pressure and extracted using CH_2Cl_2. An aliquot was taken to confirm that the species observed in the toluene solution were the same than on the bulk sample (ESI). ^{1}H and ^{13}C{^{1}H} NMR spectra were taken on some of the samples, but yielded very little information other than the identification of **[1$^+$]** which has been previously characterized as the triflate salt[5] and **[3$^+$]Cl** which has a ^{1}H chemical shift for the Cp* of 1.27 ppm. Typical NMR spectra are shown in the ESI.

Supporting Information (see footnote on the first page of this article): Reaction conditions, product distributions and corresponding mass spectra for the ligand exchange and oligomer formation reactions. Results of HPLC separation of the complexes and their characterization with relative errors Crystallographic details for **[3$^+$]Cl**. .

Acknowledgments

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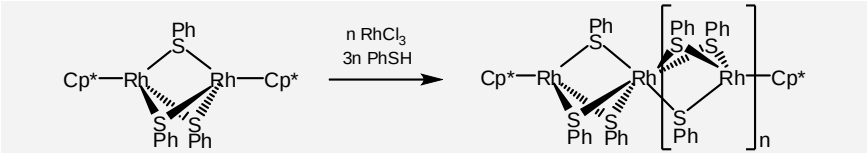
Entry for the Table of Contents

Rhodium thiolato oligomers



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MS-TOF Study of the Formation of Thiolato bridged Rhodium Oligomers

Keywords: Rhodium / Thiolates / MS-TOF / Oligomerisation / Inorganic oligomers

Ligand exchange and coordination studies were done on the dinuclear thiolato-briged complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl. Oligomeric materials of general formula [Cp*Rh(μ-SPh)$_x$(μ-Cl)$_{3-x}$(Rh(μ-SPh)$_3$)$_n$RhCp*] (x = 1 to 3; n = 1 to 4) were formed by insertion of [Rh(SPh)$_3$] units when the bridging coordination mode of the thiophenolato ligands was altered.

Supporting Information for

MS-TOF Study of the Formation of Thiolato bridged Rhodium Oligomers

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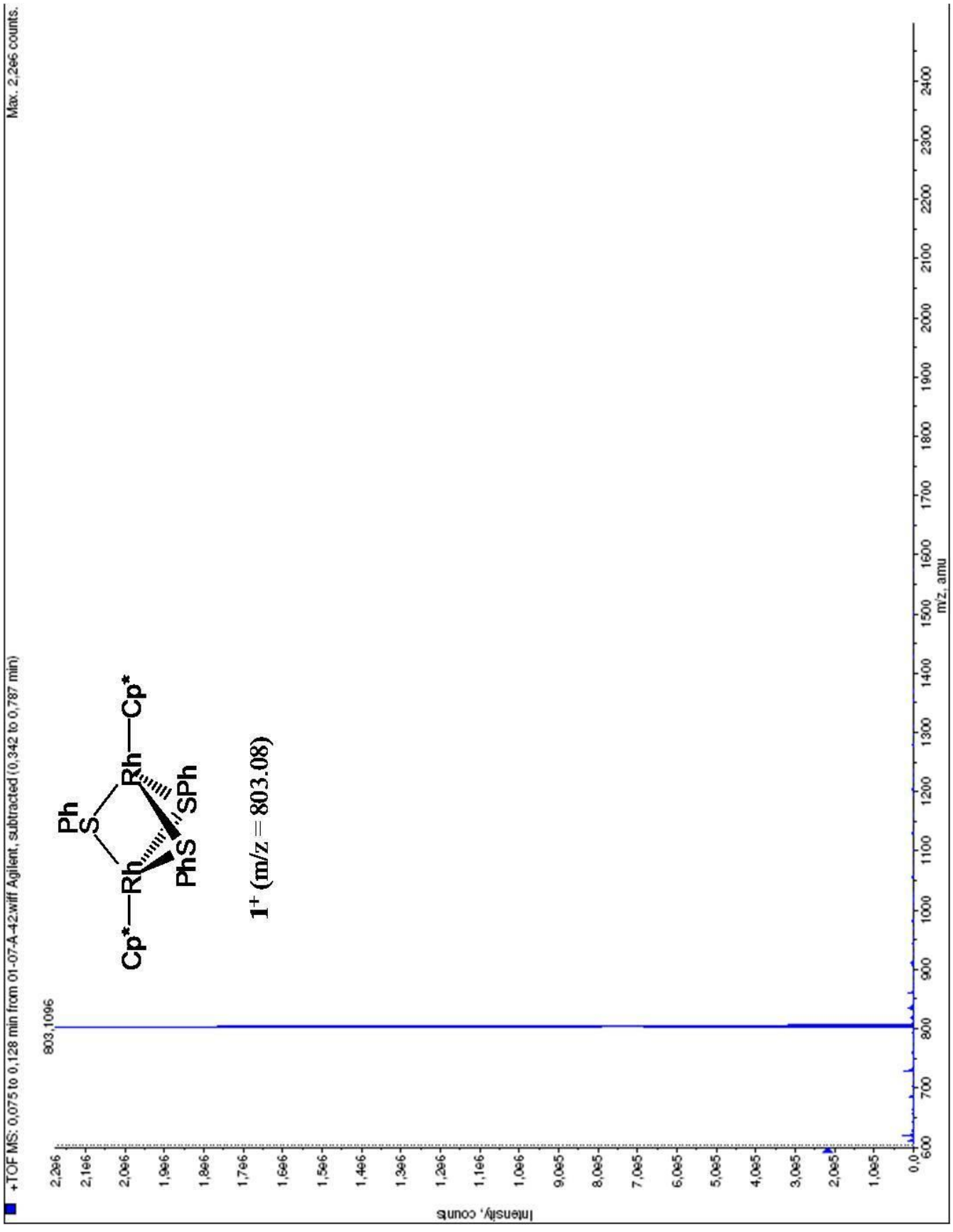
1. HR-MS characterization of [1$^+$]Cl (*m/z* = 803.08)

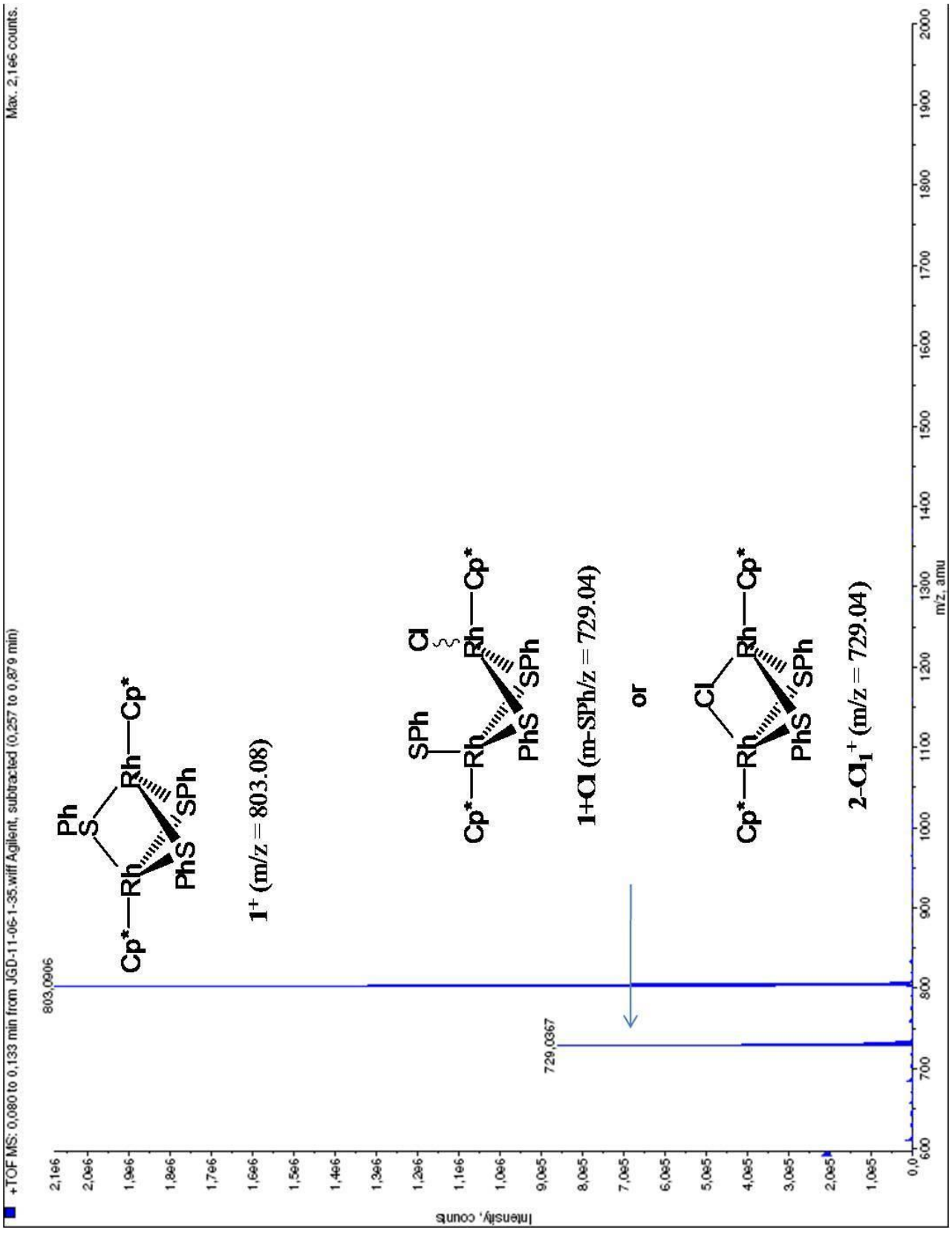


2. [2$^+$]SPh or 1+Cl

2.1 Experimental

[1$^+$]Cl (10 mg, 0.012 mmol) was refluxed in 10 mL toluene in a round bottom flask during 48 hours. HR-MS reveals **2**$^+$ (*m/z* = 729.04) or **1+Cl** (m-SPh/z = 729.04) in a 30 % yield.

2.2 HR-MS characterization

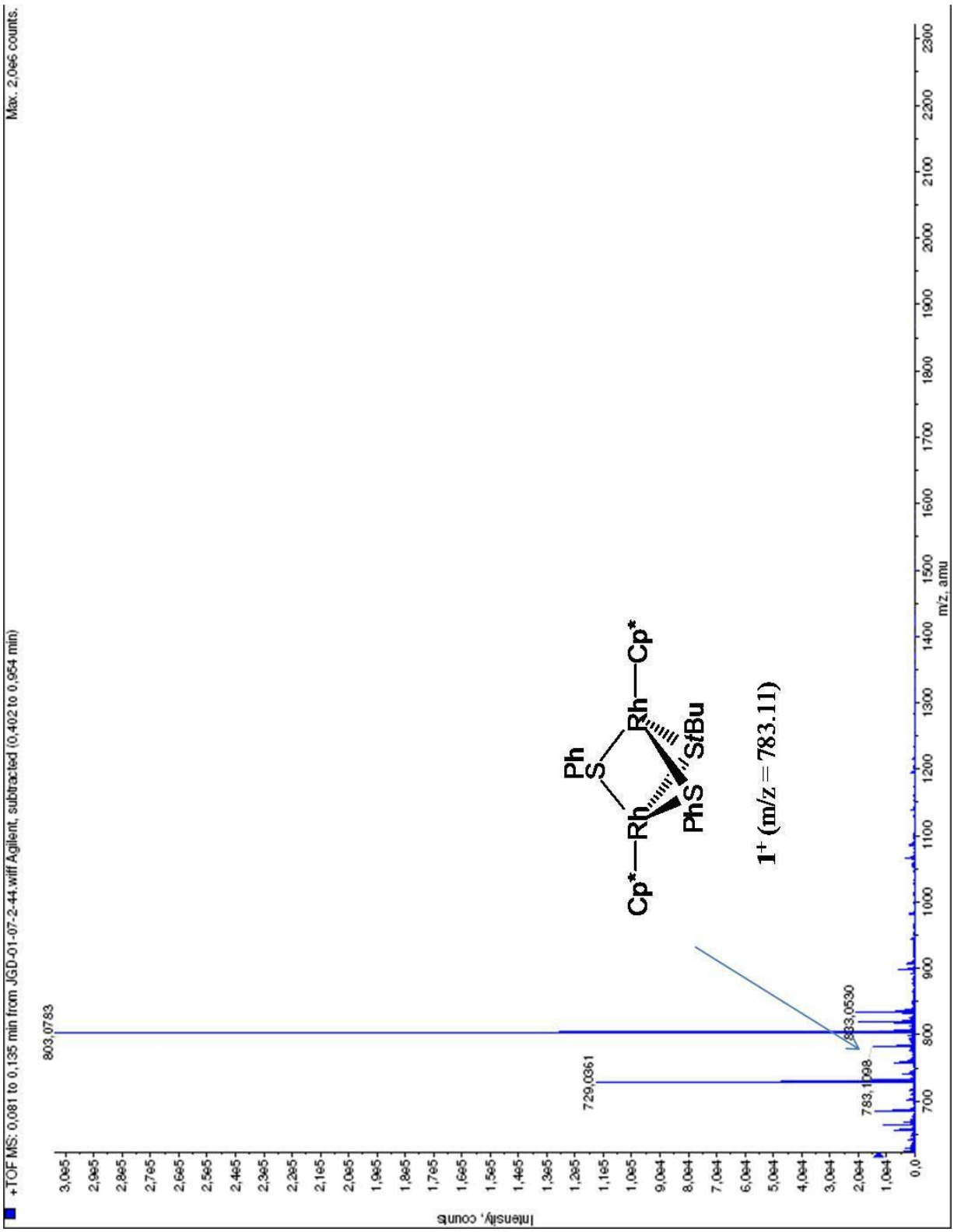


3. Ligand exchange with *t*BuSH and [1$^+$]Cl

3.1 Experimental

Three equivalents of *t*BuSH (4,1 µL, 0.036 mmol) were added to **[1$^+$]Cl** (10 mg, 0.012 mmol) in the in a round bottom flask in 10 mL of toluene, after which the solution was heated to refluxing conditions and samples were taken for HR-MS analysis at 24 hours intervals. After 48 hours, a trace amount of Cp*Rh(μ-SPh)$_2$(μ-S*t*Bu)RhCp*]Cl, **2-*t*BuS$_1$$^+$** was observed by HR-MS (*m/z* = 783.11).

3.1 HR-MS characterization

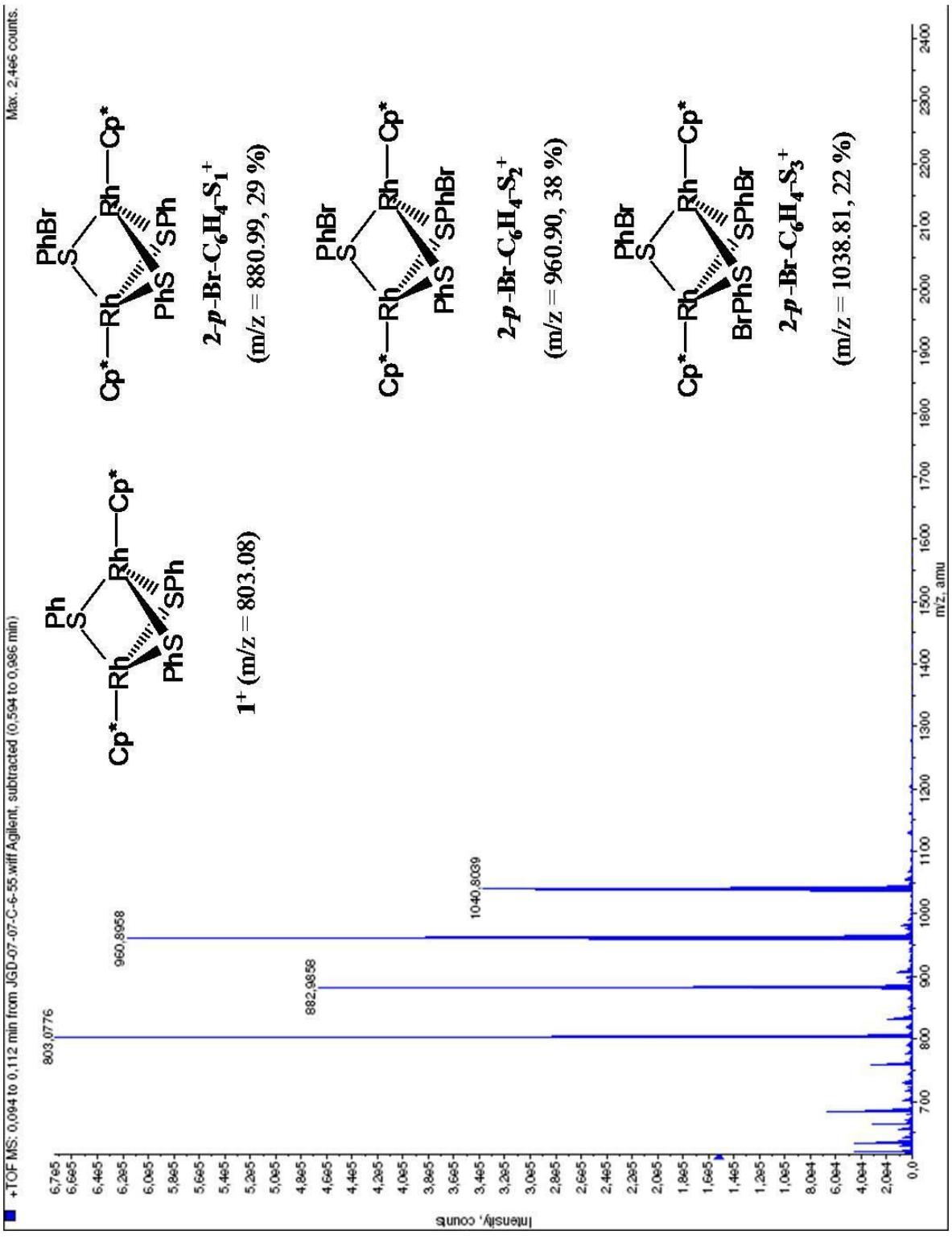


4. Ligand exchange with *p*-Br-C_6H_4SH and [1^+]Cl

4.1 Experimental

Three equivalents of *p*-Br-C_6H_4SH (6.8 mg, 0.036 mmol) were added to **[1^+]Cl** (10 mg, 0.012 mmol) in the in a round bottom flask in 10 mL of toluene, after which the solution was heated to refluxing conditions and samples were taken for HR-MS analysis at 24 hours intervals. After 24 hours, a mixture of **[1^+]Cl** (30 %), [Cp*Rh(μ-S-*p*-Br-C_6H_4)(μ-SPh)$_2$RhCp*]$^+$ (*m/z* = 880.99, 20 %) (**2-*p*-Br-C_6H_4-S_1^+**), [Cp*Rh(μ-S-*p*-Br-C_6H_4)$_2$(μ-SPh)RhCp*]$^+$ (*m/z* = 960.90, 27 %) (**2-*p*-Br-C_6H_4-S_2^+**), and [Cp*Rh(μ-S-*p*-Br-C_6H_4)$_3$RhCp*]$^+$ (*m/z* = 1038.81, 15 %) (**2-*p*-Br-C_6H_4-S_3^+**) was observed by HR-MS.

4.2 HR-MS characterization



5. Formation of homonuclear (Rh) oligomers

5.1 Product distribution and experimental

Table S1 - Distribution of oligomers formed by addition of $[RhCl_x(SPh)_{3-x}]$ units to $[1^+]Cl$

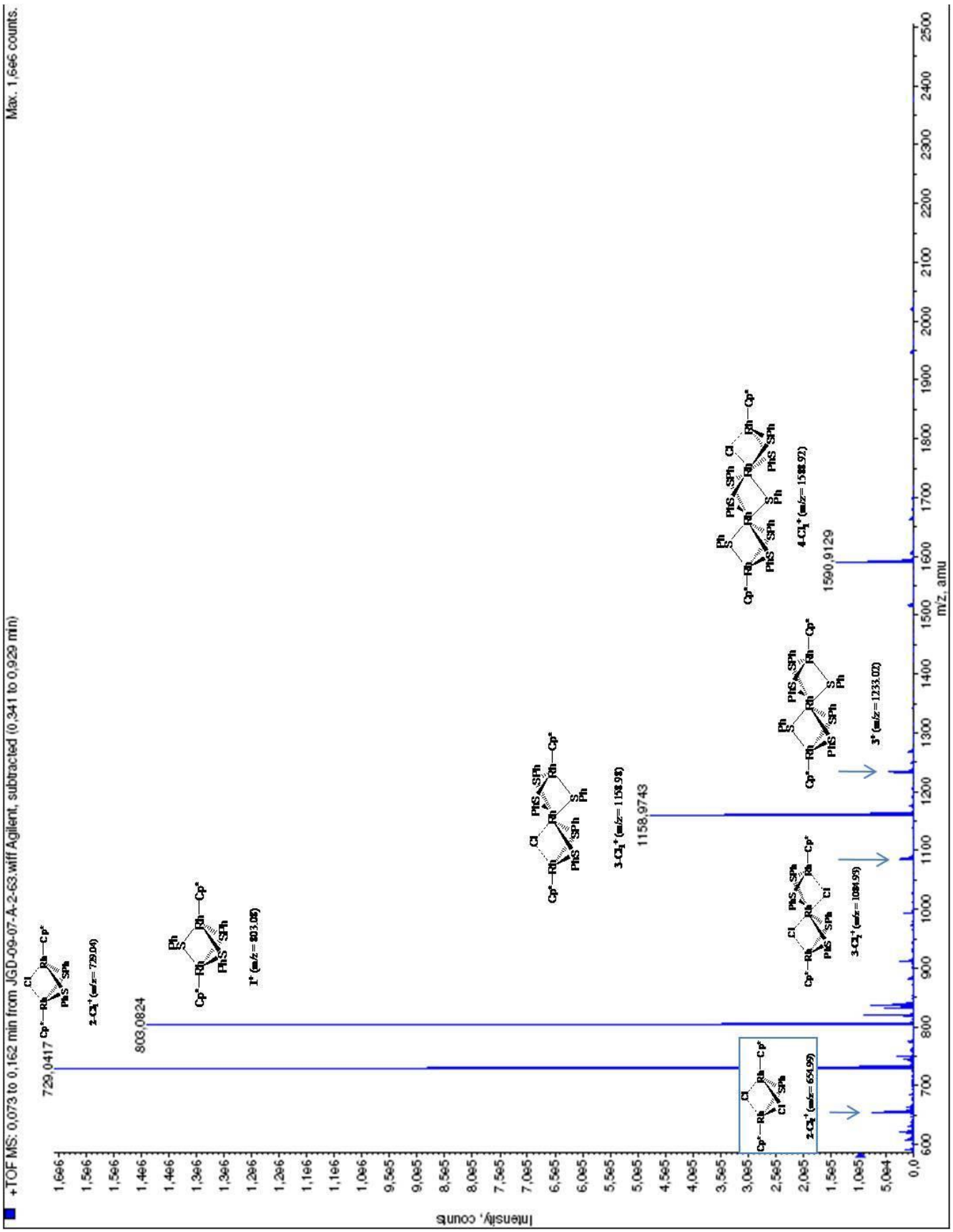
Entry	Dimetallicr			Trimetallic					
Species	$[2\text{-}Cl_2^+]$	$[2\text{-}Cl_1^+]$	$[1^+]$	**Sum Rh_2**	$[3\text{-}Cl_3^+]$	$[3\text{-}Cl_2^+]$	$[3\text{-}Cl_1^+]$	$[3^+]$	**Sum Rh_3**
Exact Mass	654.99	729.04	803.08		1010.89	1084.93	1158.98	1233.02	
1[a]	2	40	35	**77**	-	1	12	1	**14**
2[a,b]	14	10	13	**37**	-	1	31	3	**35**
3[c]	-	-	3	**3**	2	6	53	15	**76**
4[c,d]	-	6	76	**82**	-	-	3	3	**6**
5[a,e]	-	18	78	**96**	-	-	2	-	**2**
6[a,e,f]	8	18	44	**70**	-	-	15	2	**17**
7[a,g]	19	-	-	**19**	3	6	35	6	**50**
8[a,g,h]	53	12	-	**65**	2	10	7	1	**20**
9[a,i]	-	-	74	**74**	-	-	-	6	**6**
10[j]	-	-	10	**10**	9	18	23	-	**50**

	Tetrametallic					Pentametallic			Hexametallic			**Other**
	$[4\text{-}Cl_3^+]$	$[4\text{-}Cl_2^+]$	$[4\text{-}Cl_1^+]$	$[4^+]$	**Sum Rh_4**	$[5\text{-}Cl_2^+]$	$[5\text{-}Cl_1^+]$	**Sum Rh_5**	$[6\text{-}Cl_3^+]$	$[6\text{-}Cl_2^+]$	**Sum Rh_6**	
	1440.83	1514.87	1588.92	1662.96		1944.81	2018.85		2300.71	2375.75		
1	-	-	4	-	**4**	-	-	**-**	-	-	**-**	5
2	-	1	7	trace	**8**	0,5	0,5	**1**	-	-	**-**	19
3	3	4	10	1	**18**	-	-	**-**	-	-	**-**	3
4	-	-	2	-	**2**	-	-	**-**	-	-	**-**	10
5	-	-	-	-	**-**	-	-	**-**	-	-	**-**	2
6	-	-	2	-	**2**	-	-	**-**	-	-	**-**	11
7	1	1	21	1	**24**	1.5	0.5	**2**	0.5	0.5	**1**	4
8	-	1	3	-	**4**	-	-	**-**	-	-	**-**	11
9	-	-	1	3	**4**	-	-	**-**	-	-	**-**	16
10	2	2	2	-	**6**	-	-	**-**	-	-	**-**	34

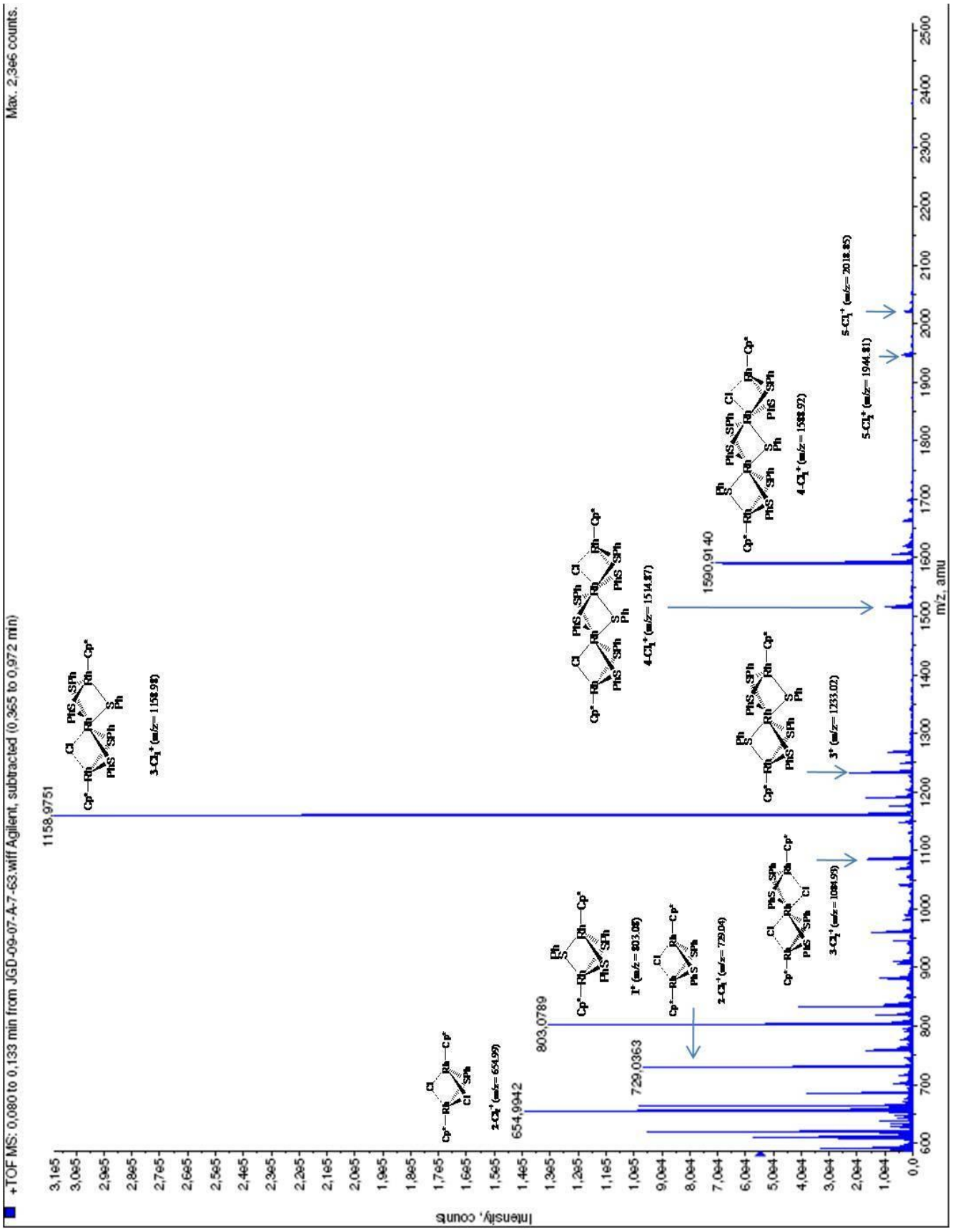
a. $RhCl_3$ (3.0 mg, 0.012 mmol) and HSPh (3.6 μL, 0.012 mmol) were added to **[1^+]Cl** (10 mg, 0.012 mmol) in toluene (10 mL) in a round bottom flask, which was heated at 110 ºC for 48 hours. **b**. After 48 hours reflux, RhCl3 (3.0 mg, 0.012 mmol) and HSPh (3.6 μL, 0.012 mmol) were added and the mixture was refluxed for an additional 24 hours. **c**. RhCl3 (3.0 mg, 0.012 mmol) and HSPh (3.6 μL, 0.012 mmol) were refluxed in methanol for three hours, after which the methanol was evaporated and the resulting orange-brown powder was added to **[1^+]Cl** (10 mg, 0.012 mmol) in toluene (10 mL), and the mixture was heated at 110 ºC for 48 hours. **d**. After 48 hours reflux, HSPh (3.6 μL, 0.012 mmol) was added and mixture was kept in refluxing conditions for an additional 24 hours. **e**. NEt_3 (5.0 μL, 0.036 mmol) was added with the reagents before heating. **f**. An aliquot was taken after 12 days refluxing in toluene. **g**. HCl 2% in ether (65 μL, 0.036 mmol) was added with the reagents before heating. **h**. The solution was diluted in ethanol (10 times the volume). **i**. Water (10 mL) and NBu_4Br (30 mg, 0.093 mmol) were added before heating. **j**. $RhCl_3$ (3.0 mg, 0.012 mmol) and HSPh (3.6 μL, 0.012 mmol) were added to **[1^+]Cl** (10 mg, 0.012 mmol) in *p*-xylene (10 mL) in a round bottom flask, which was heated at 135 ºC for 48 hours.

5.2 Mass spectra for table S1- Entries 1 - 10

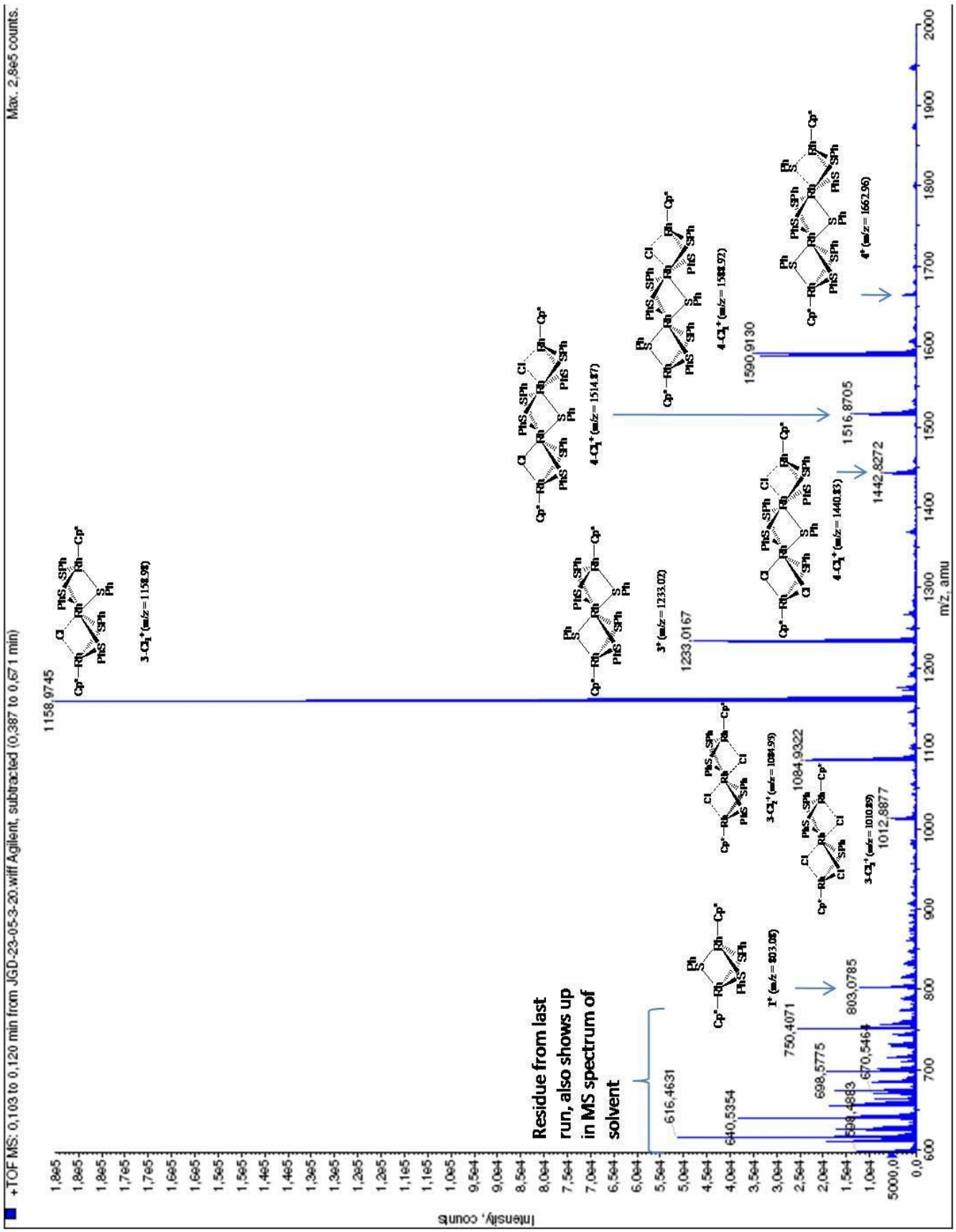
Entry 1



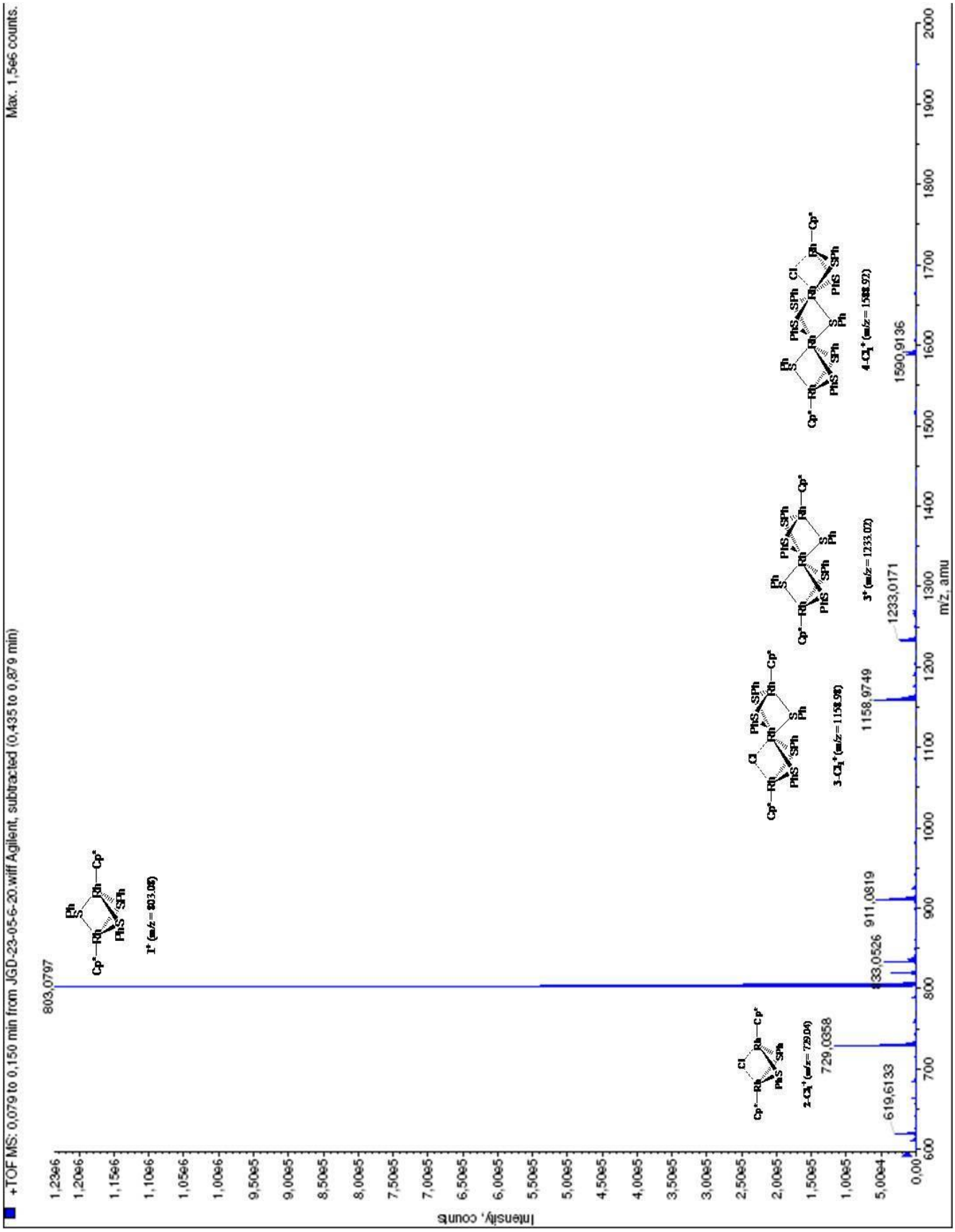
Entry 2


+TOF MS: 0,080 to 0,133 min from JGD-09-07-A-7-63.wiff Agilent, subtracted (0,365 to 0,972 min)
Max. 2,3e6 counts.
Intensity, counts
m/z, amu
1158,9751
654,9942
729,0363
803,0789
1590,9140
3-Cl+ (m/z= 1158.98)
2-Cl+ (m/z= 654.99)
1+ (m/z= 803.08)
2-Cl+ (m/z= 729.04)
3-Cl+ (m/z= 1084.99)
4-Cl+ (m/z= 1514.87)
3+ (m/z= 1233.02)
4-Cl+ (m/z= 1588.92)
5-Cl+ (m/z= 1944.81)
5-Cl+ (m/z= 2018.85)

Entry 3


+TOF MS: 0,103 to 0,120 min from JGD-23-05-3-20.wiff Agilent, subtracted (0,387 to 0,671 min)
Max. 2,8e5 counts.
Intensity, counts
m/z, amu
Residue from last run, also shows up in MS spectrum of solvent
1158,9745
1233,0167
1590,9130
1516,8705
1442,8272
1084,9322
1012,8877
803,0785
750,4071
698,5775
670,5464
640,5354
616,4631
3-Cl+ (m/z = 1158,98)
3+ (m/z = 1233,02)
4-Cl+ (m/z = 1514,87)
4-Cl+ (m/z = 1588,92)
4-Cl+ (m/z = 1440,83)
4+ (m/z = 1662,96)
3-Cl+ (m/z = 1084,99)
3-Cl+ (m/z = 1010,89)
1+ (m/z = 803,08)

Entry 4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Max. 1,5e6 counts.
Intensity, counts
m/z, amu
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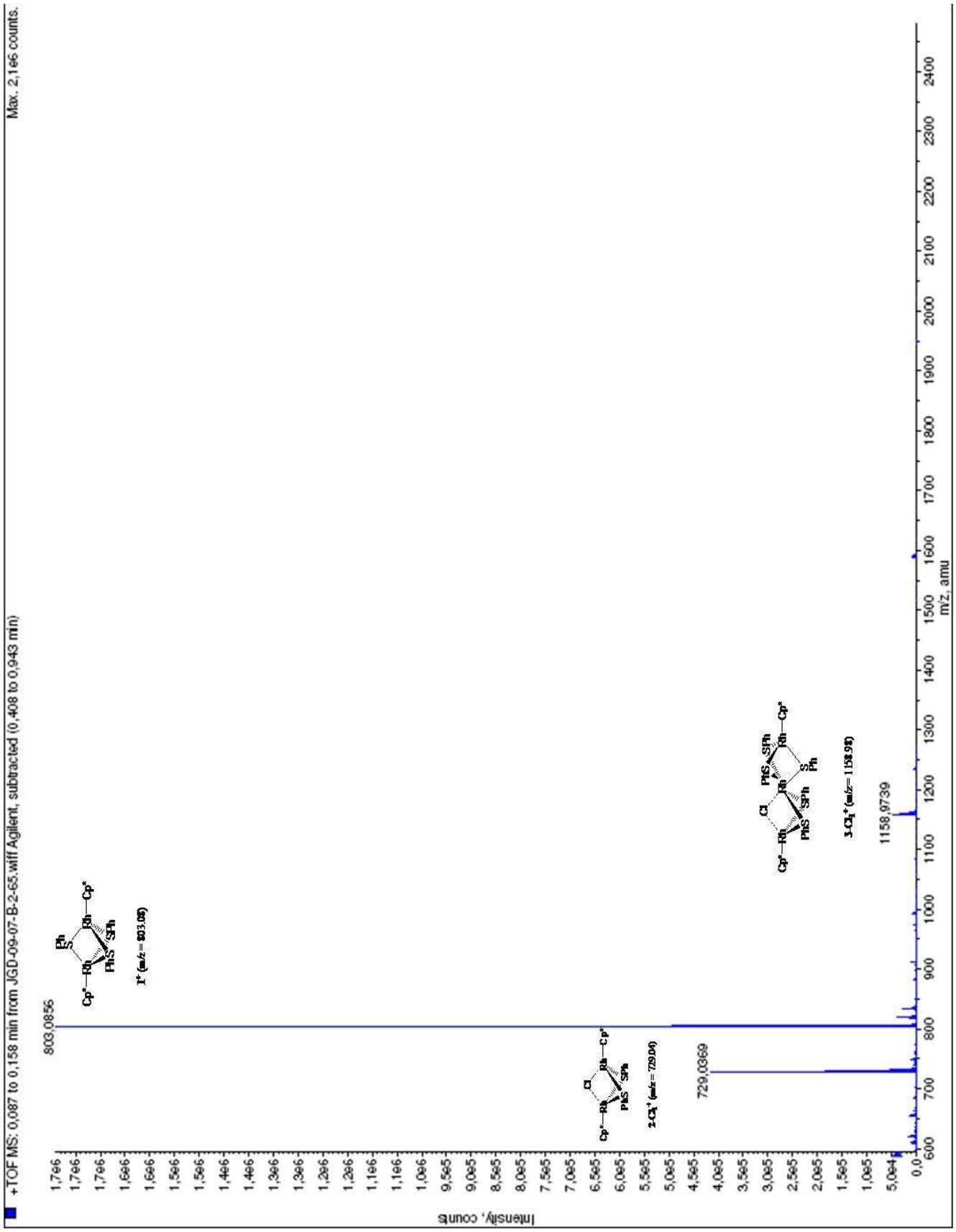
729,0358
619,6133
833,0526
911,0819
1158,9749
1233,0171
1590,9136

Entry 5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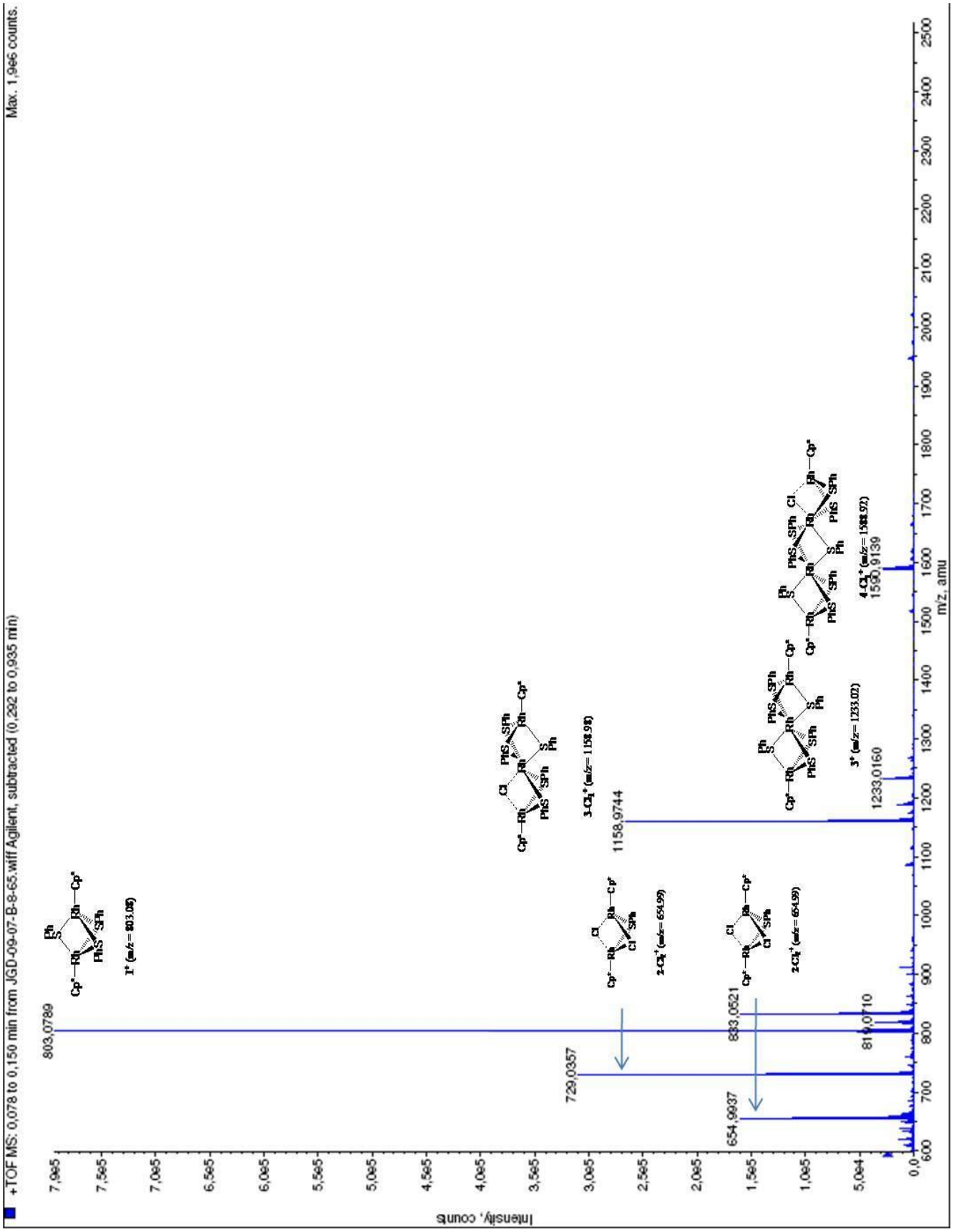
Max. 2,1e6 counts.
Intensity, counts
m/z, amu
803,0856
729,0369
1158,9739
1+ (m/z= 803.08)
2-Cl+ (m/z= 729.04)
3-Cl+ (m/z= 1158.98)

Entry 6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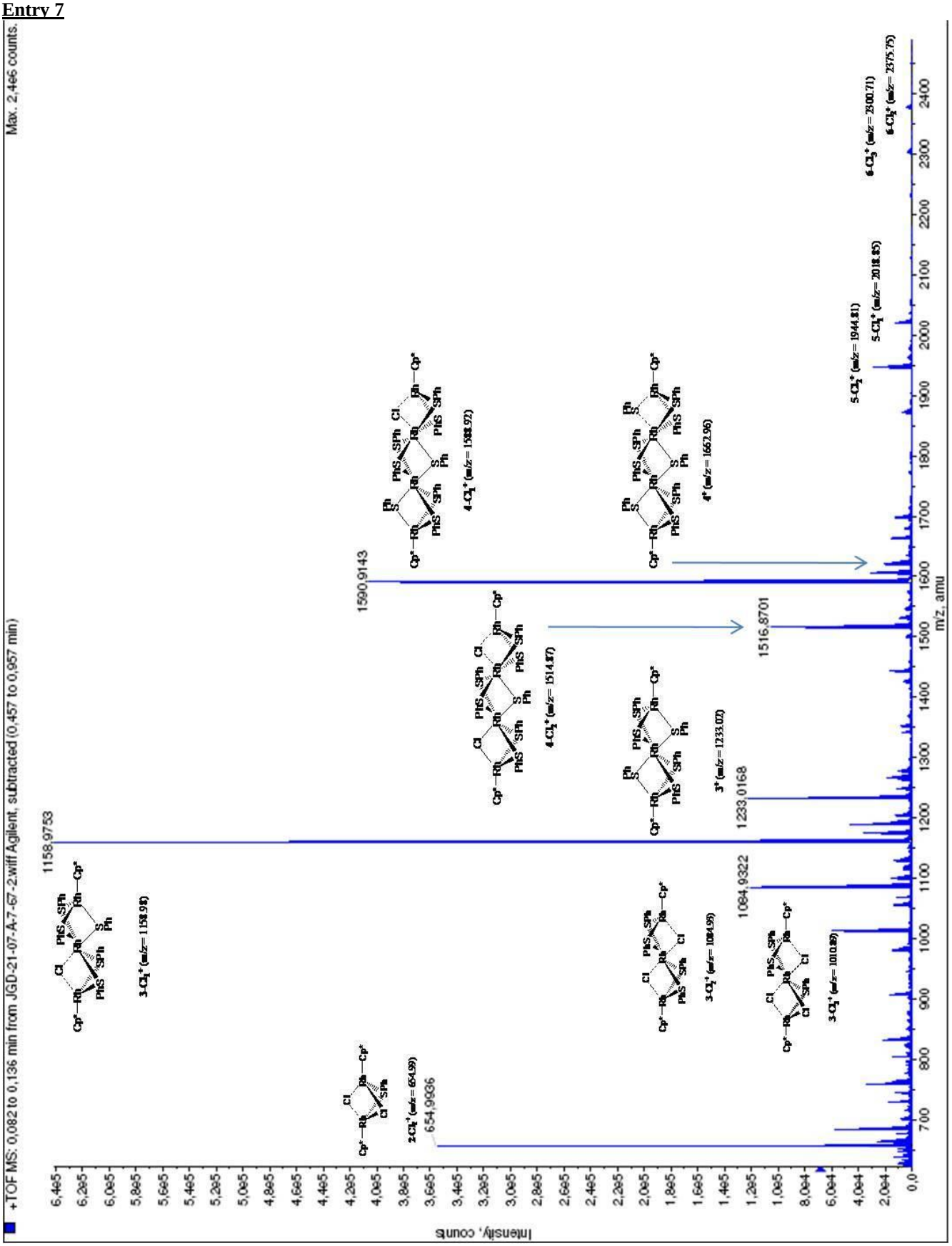
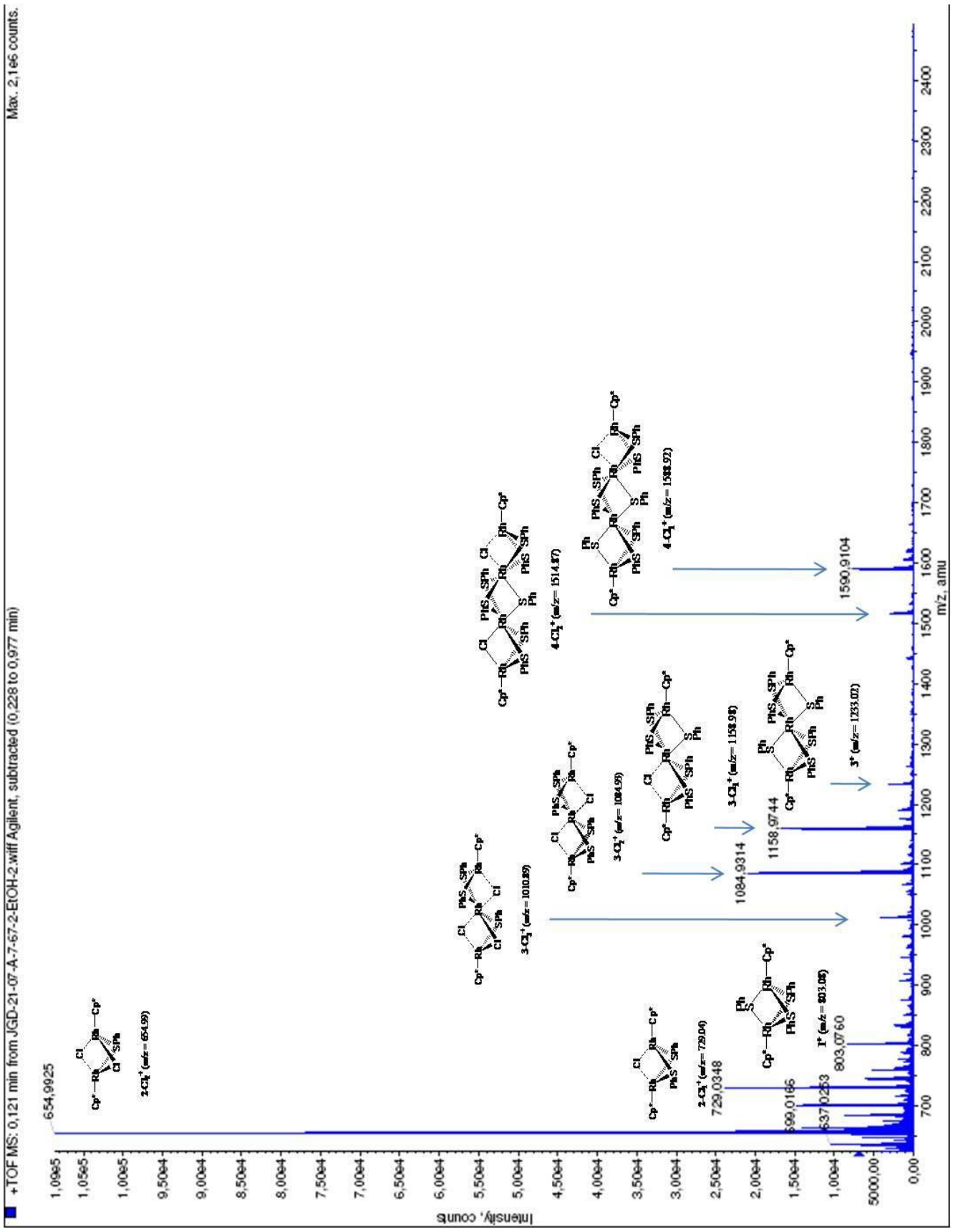
Max. 1,9e6 counts.
Intensity, counts
m/z, amu
803,0789
729,0357
654,9937
833,0521
819,0710
1158,9744
1233,0160
1590,9139

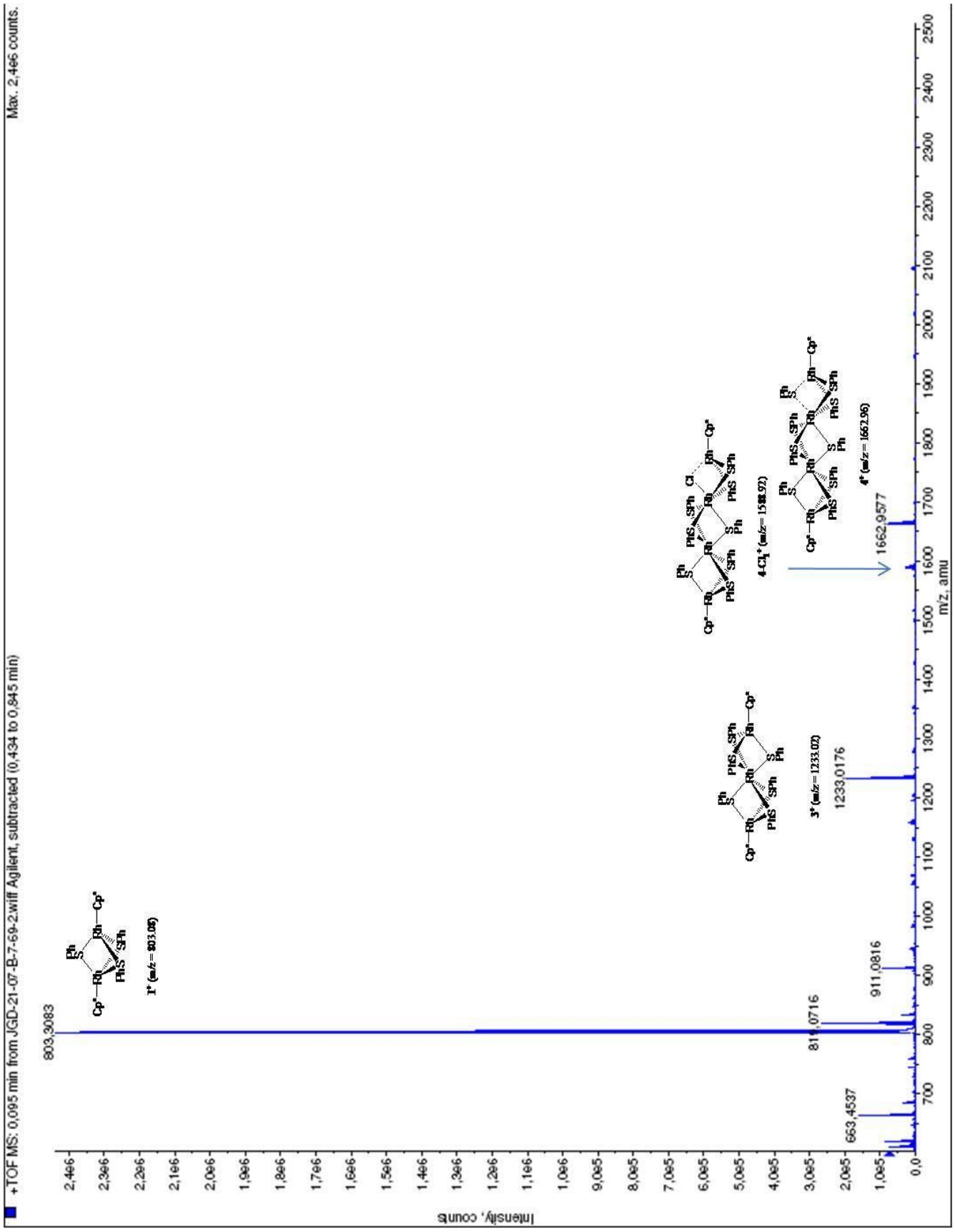
Entry 7


+TOF MS: 0,082 to 0,136 min from JGD-21-07-A-7-67-2.wiff Agilent, subtracted (0,457 to 0,957 min)
Max. 2,4e6 counts.
Intensity, counts
m/z, amu
1158,9753
1590,9143
1516,8701
1233,0168
1084,9322
654,9936
3-Cl+ (m/z= 1158.98)
4-Cl+ (m/z= 1588.92)
4+ (m/z= 1662.96)
4-Cl+ (m/z= 1514.87)
3+ (m/z= 1233.02)
3-Cl+ (m/z= 1084.93)
3-Cl+ (m/z= 1010.89)
2-Cl+ (m/z= 654.99)
5-Cl+ (m/z= 1944.81)
5-Cl+ (m/z= 2018.85)
6-Cl+ (m/z= 2300.71)
6-Cl+ (m/z= 2375.75)

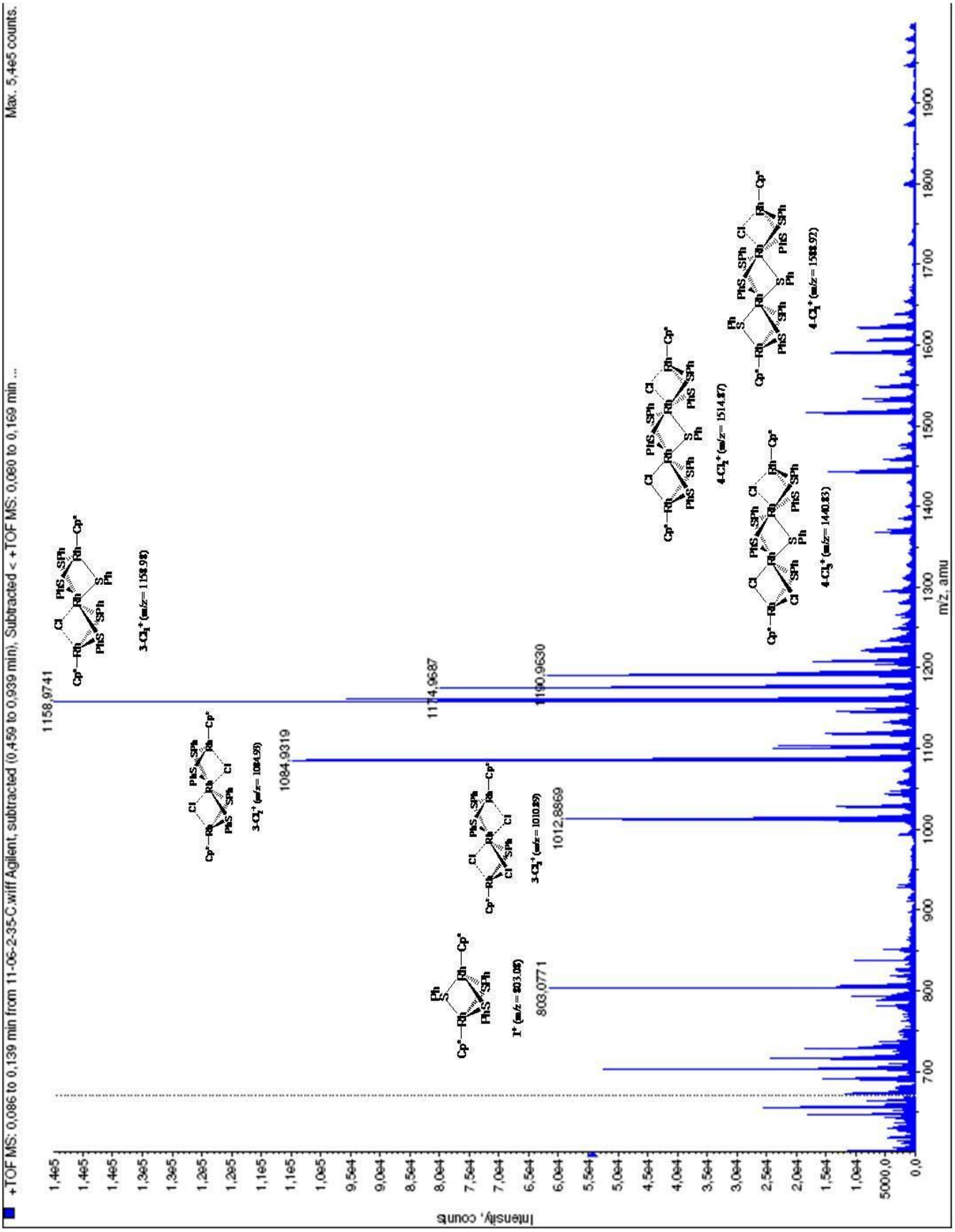
Entry 8


+TOF MS: 0,121 min from JGD-21-07-A-7-67-2-EtOH-2.wiff Agilent, subtracted (0,228 to 0,977 min)
Max. 2,1e6 counts.
Intensity, counts
m/z, amu
654,9925
729,0348
699,0186
637,0253
803,0760
1084,9314
1158,9744
1590,9104

Entry 9


+TOF MS: 0,095 min from JGD-21-07-B-7-69-2.wiff Agilent, subtracted (0,434 to 0,845 min)
Max. 2,4e6 counts.
Intensity, counts
m/z, amu
803,3083
663,4537
811,0716
911,0816
1233,0176
1662,9577

Entry 10


+TOF MS: 0,086 to 0,139 min from 11-06-2-35-C.wiff Agilent, subtracted (0,459 to 0,939 min), Subtracted < +TOF MS: 0,080 to 0,169 min ...
Max. 5,4e5 counts.
Intensity, counts
m/z, amu
1158,9741
1174,9687
1190,9630
1084,9319
1012,8869
803,0771
3-Cl+ (m/z= 1158.98)
3-Cl+ (m/z= 1084.99)
3-Cl+ (m/z= 1010.89)
I+ (m/z= 803.08)
4-Cl+ (m/z= 1514.87)
4-Cl+ (m/z= 1588.92)
4-Cl+ (m/z= 1440.83)

5.3 HPLC-HR-MS characterization

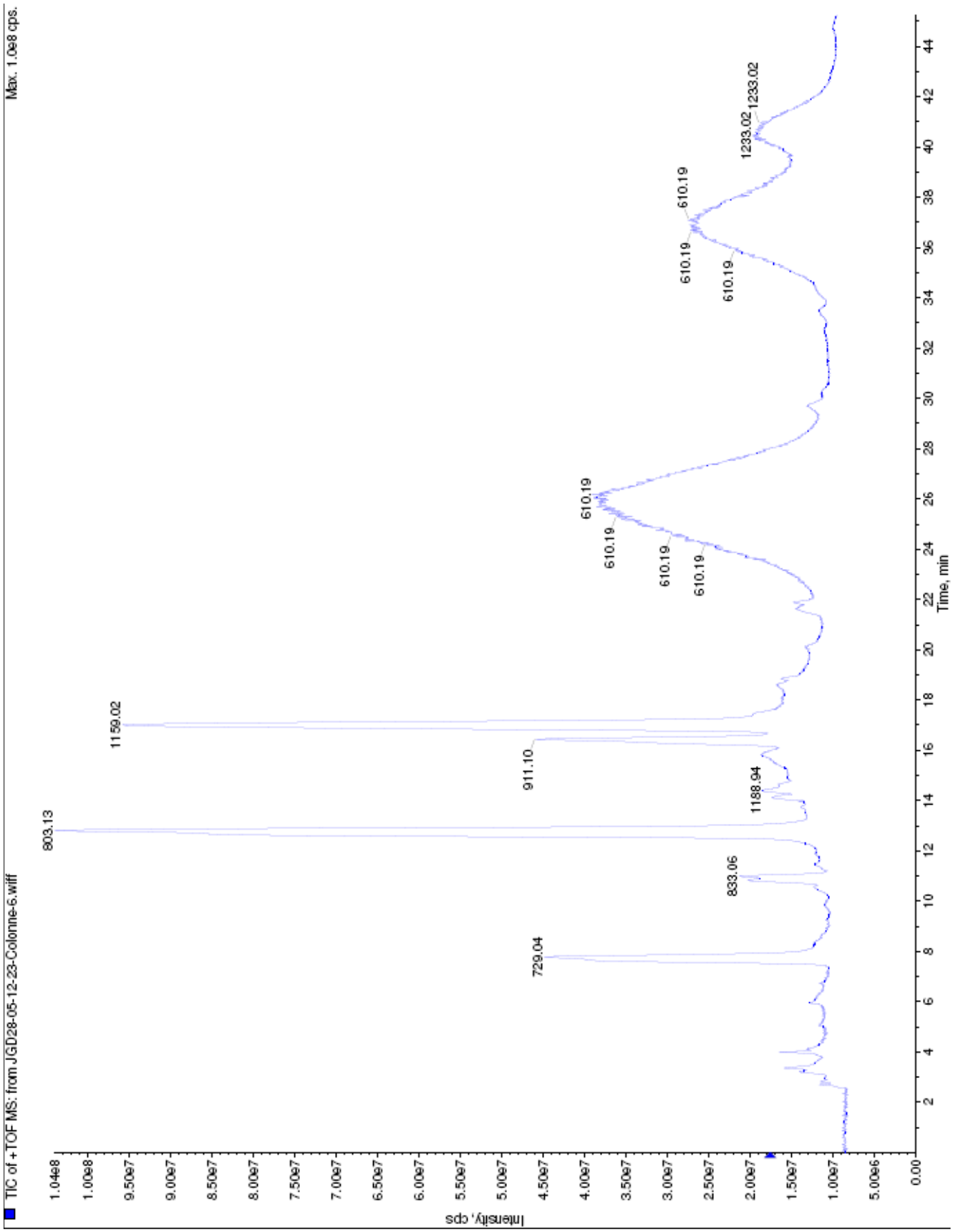
Table S2 – Characterization of homonuclear (Rh) oligomers by HR-MS after separation by HPLC

	Retention time[a] (min)	Exact mass expected (amu)	Mass observed (amu)	Relative error (ppm)
2-Cl$_1$$^+$	7.55	729.0370	729.0395	3.4
4-Cl$_1$$^+$	12.2 to 13.5[†]	1588.9152	1588.9125	-1.7
3-Cl$_2$$^+$	12.42	1084.9338	1084.9319	-1.8
1$^+$	12.99	803.0793	803.0818	3.1
4$^+$	14.11	1662.9575	1662.9522	-3.2
3-Cl$_1$	16.80	1158.9761	1158.9783	1.9
4-Cl$_2$	32.0-34.0[†]	1514.8723	1514.8685	-2.5
3$^+$	40.49	1233.0184	1233.0188	0.3
2-Cl$_2$	*	654.9947	654.9936	-1.7
3-Cl$_3$	*	1010.8914	1010.8917	0.3
4-Cl$_3$	*	1440.8305	1440.8287	-1.2
5-Cl$_2$	*	1944.8114	1944.8071	-2.2
5-Cl$_1$	*	2018.8543	2018.8525	-0.9
6-Cl$_3$	*	2300.7087	2300.7005	-3.6
6-Cl$_2$	*	2375.7544	2375.7438	-4.5

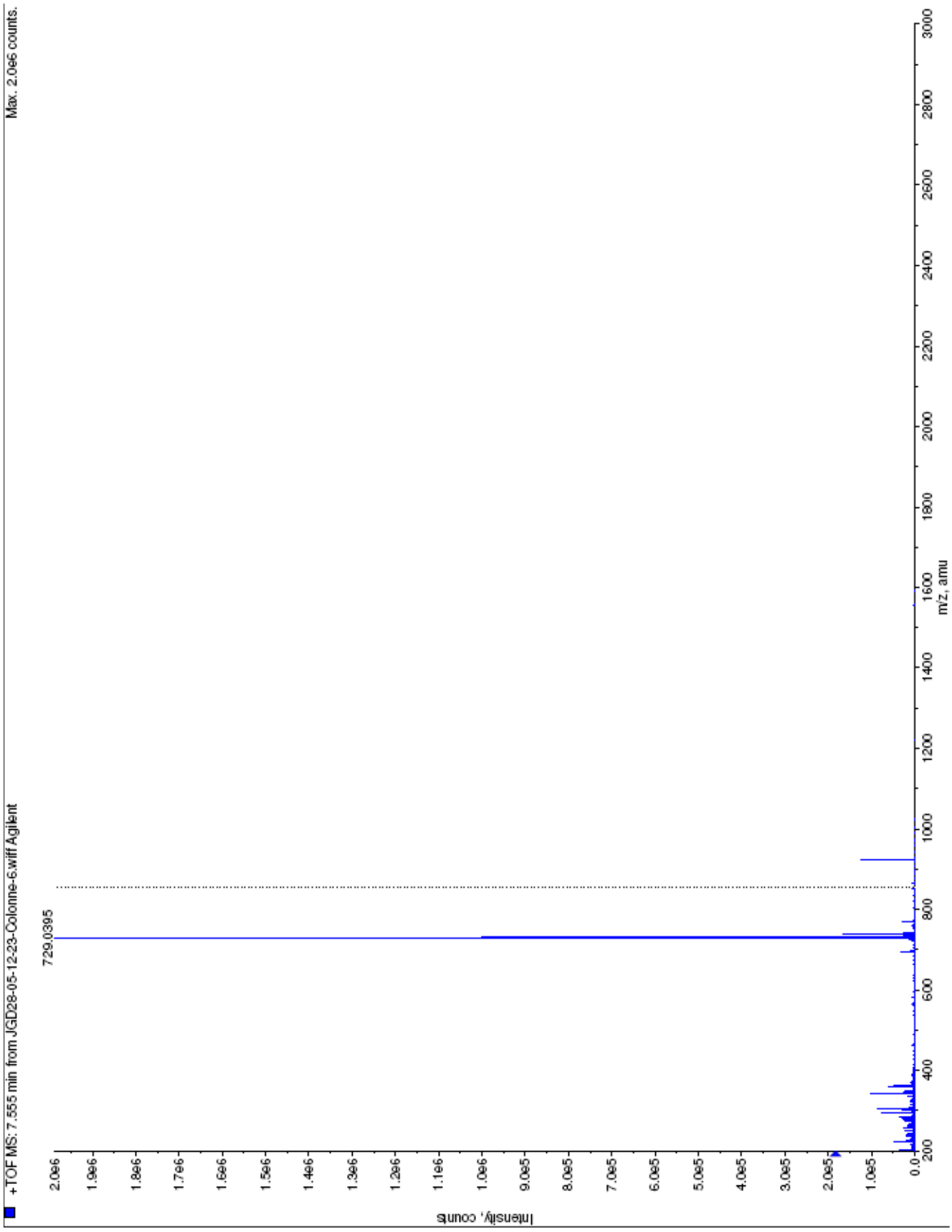
[a] Analyses were done on a Agilent 6210 Time of flight LC/MS, using a Agilent ZORBAX Eclipse XDB-C18 column (1500 x 4.6 mm, 5 μm). Elution conditions are as follows: 20 min using 75:25 methanol:water (5 mM ammonium formate), then a 15 min. gradient to reach 100% acetonitrile which was kept as eluent for the last 10 min. [†] Compound spread out over more than one minute and mass peak of very low intensity. * Species not observed after HPLC separation, masses taken from the HR mass spectrum of the unseparated sample.

5.4 Chromatogram and mass spectra for table S2

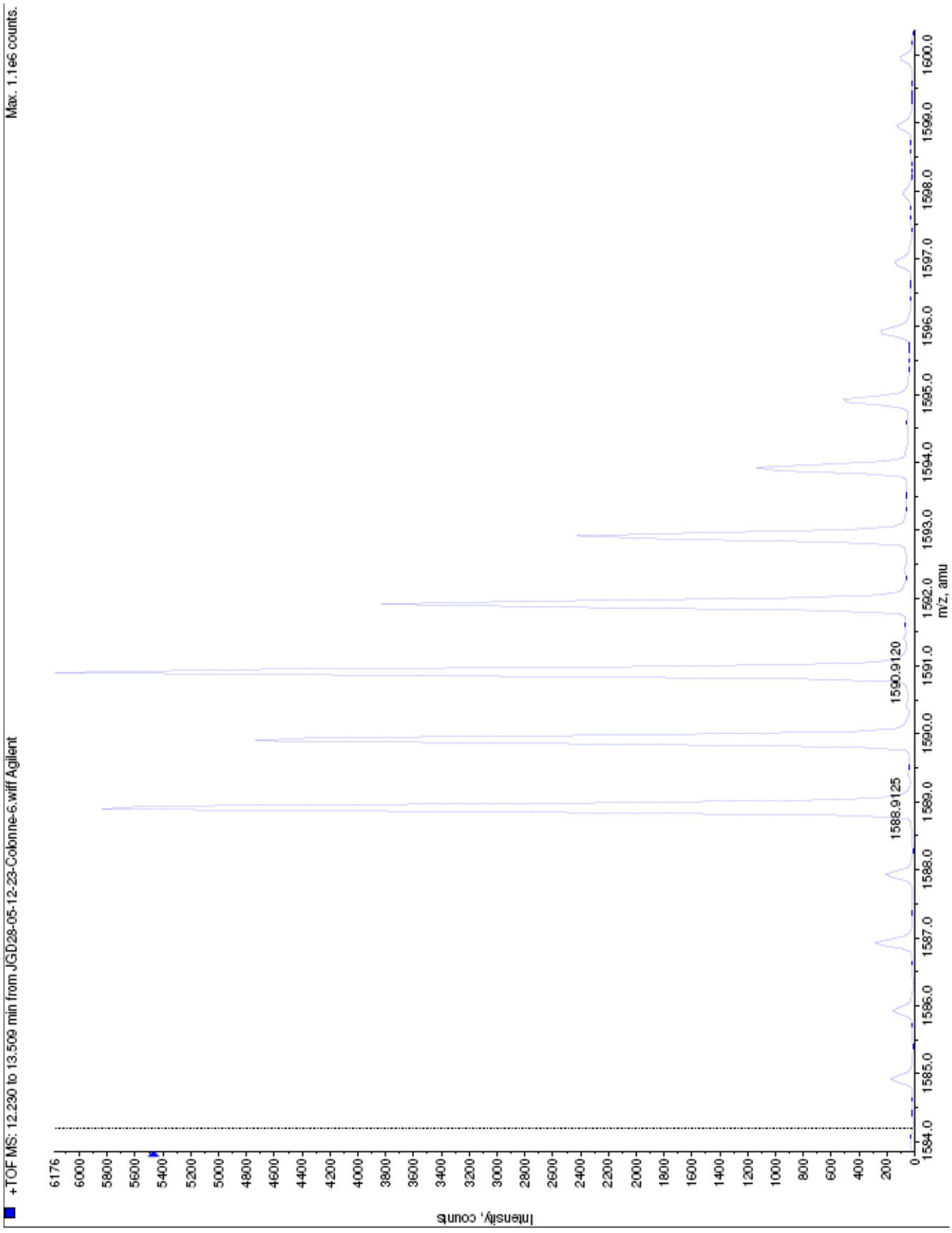
Chromatogram



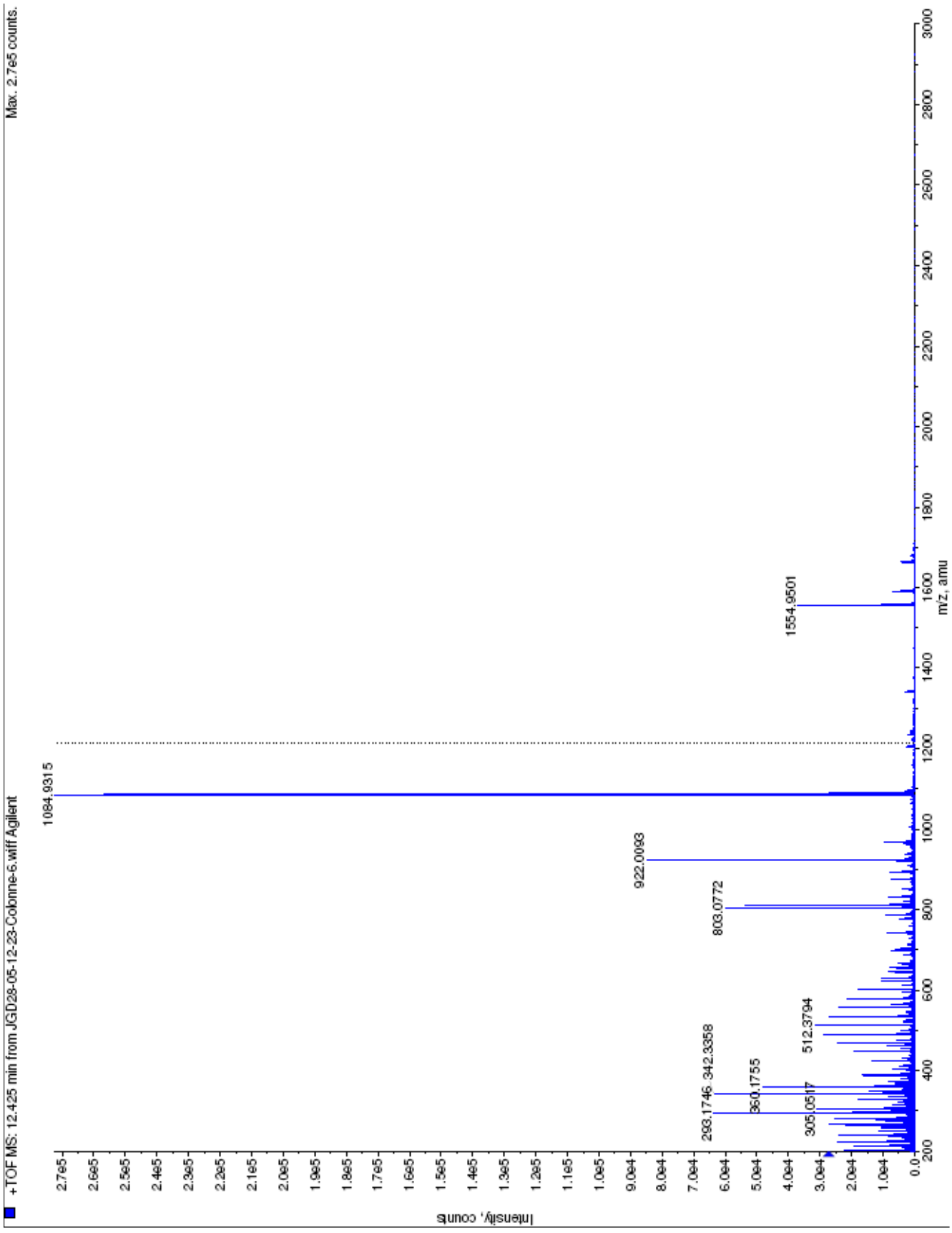
2-Cl$_1$ $^+$ 7.55 min


+TOF MS: 7.555 min from JGD28-05-12-23-Colonne-6.wiff Agilent
Max. 2.0e6 counts.
729.0395
Intensity, counts
m/z, amu

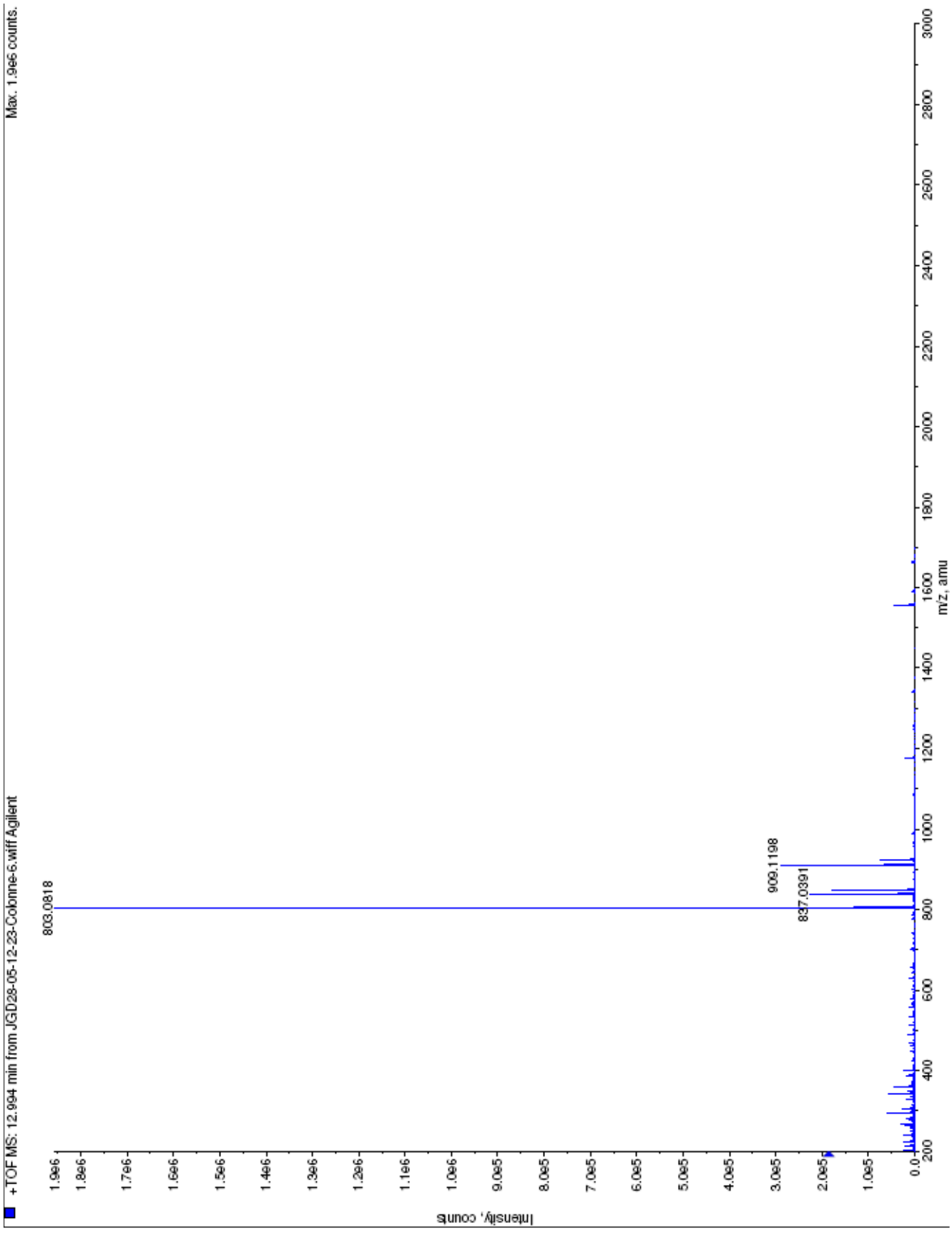
4-Cl_1^+ 12.23 to 15.51 min



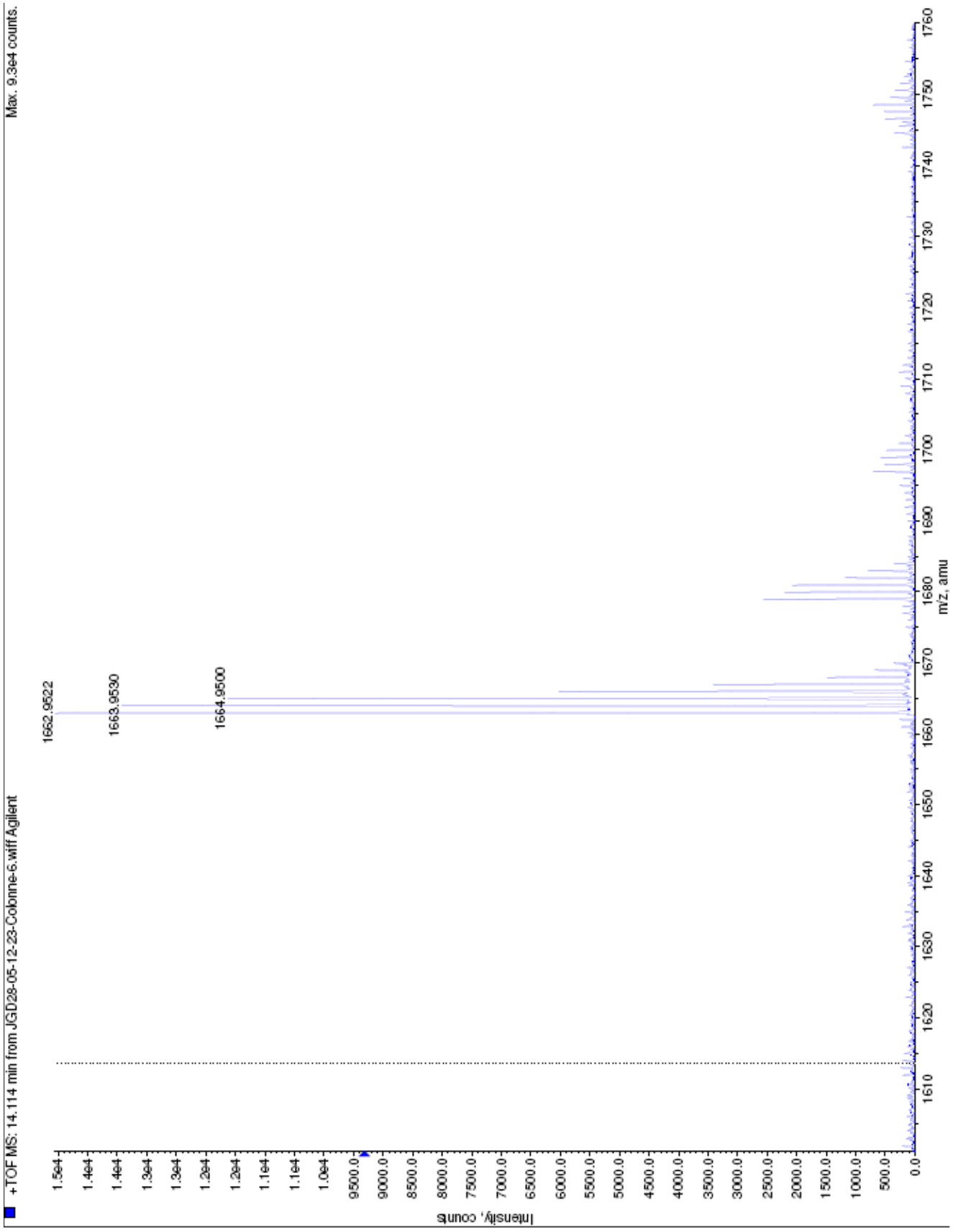
3-Cl_2^+ 12.42 min



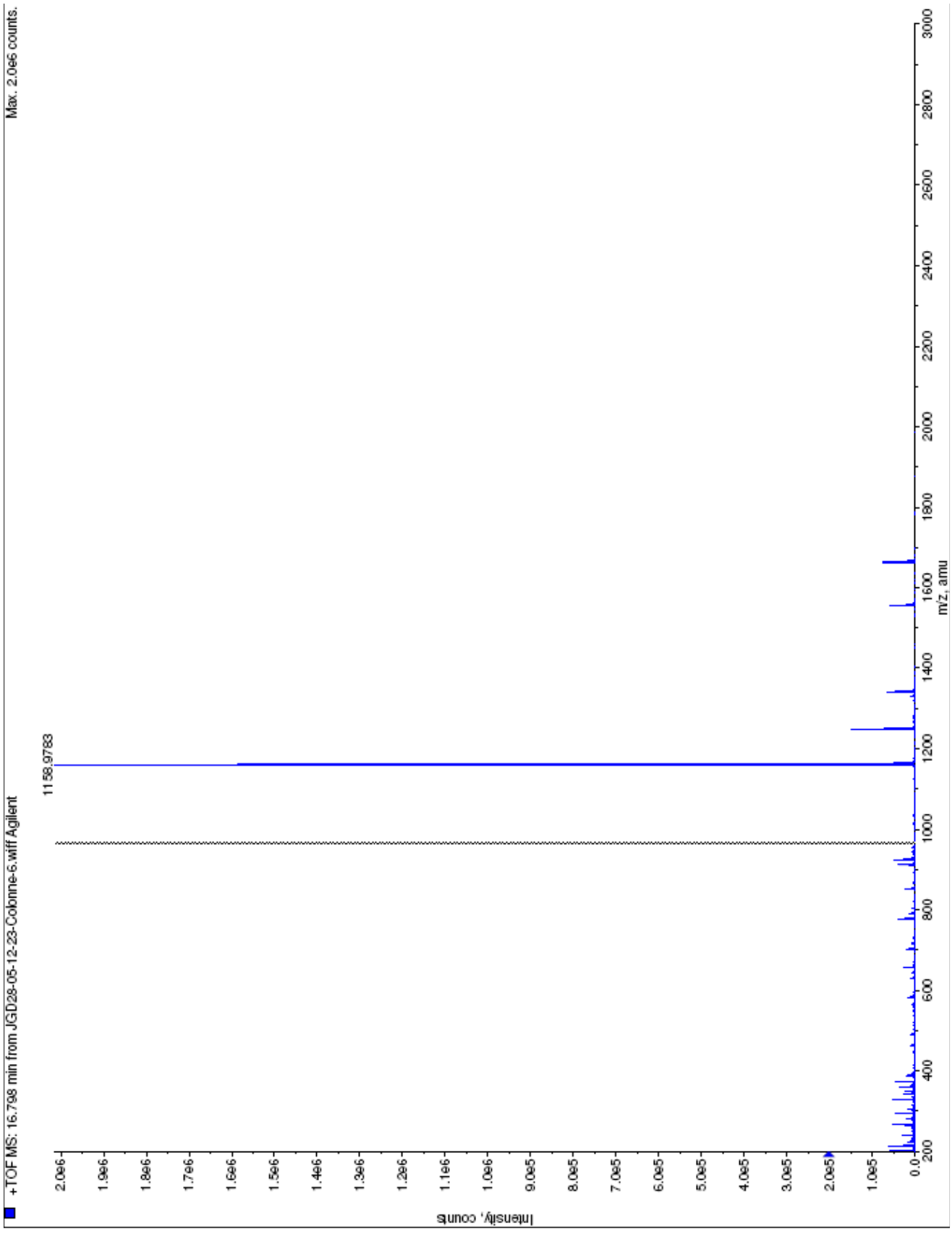
1^{+} 12.99 min


+TOF MS: 12.994 min from JGD28-05-12-23-Colonne-6.wiff Agilent
Max. 1.9e6 counts.
803.0818
909.1198
837.0391
Intensity, counts
m/z, amu

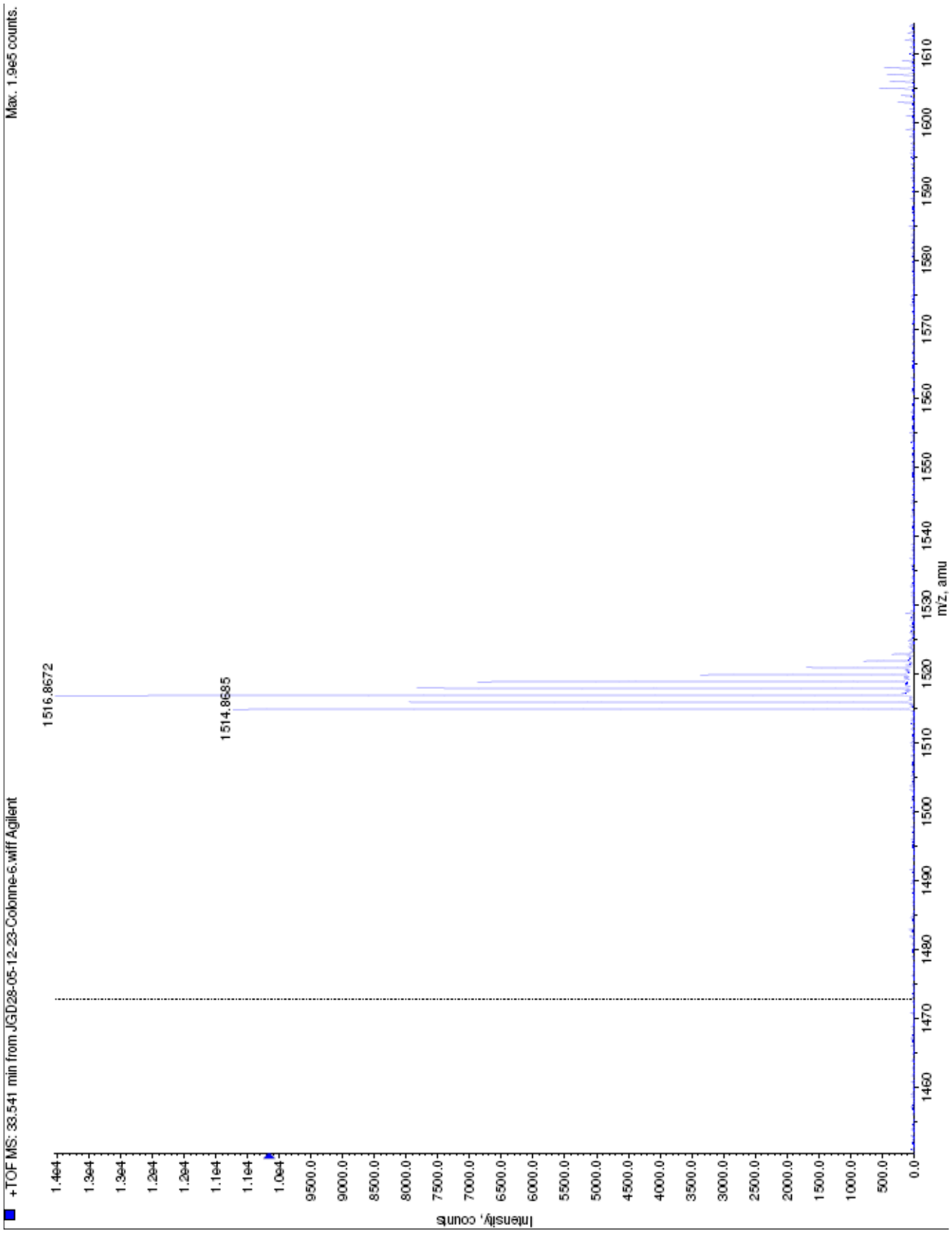
4^{+} 14.11 min


+TOF MS: 14.114 min from JGD28-05-12-23-Colonne-6.wiff Agilent
Max. 9.3e4 counts.
1662.9522
1663.9530
1664.9500
Intensity, counts
m/z, amu

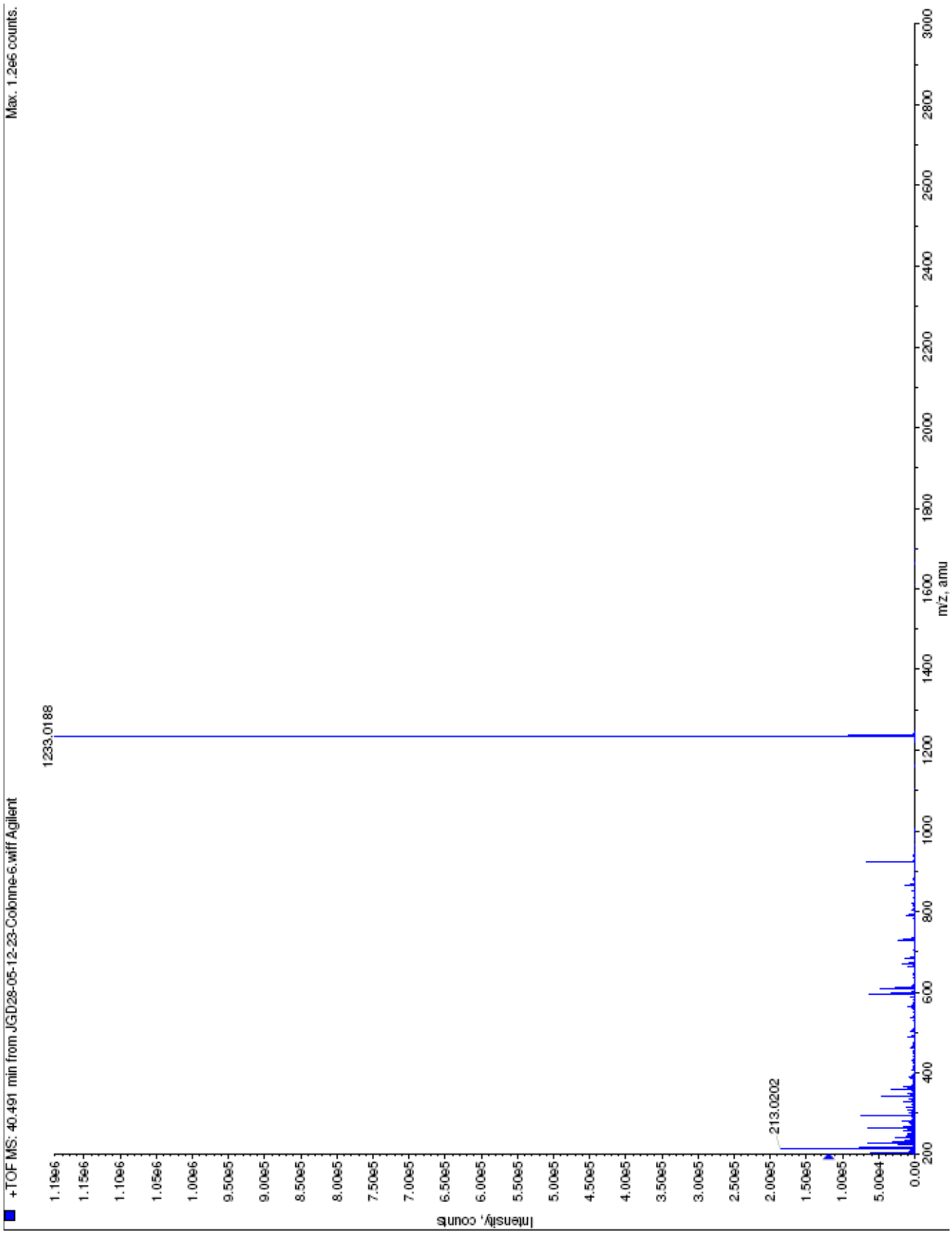
3-Cl$_1$ 16.80 min



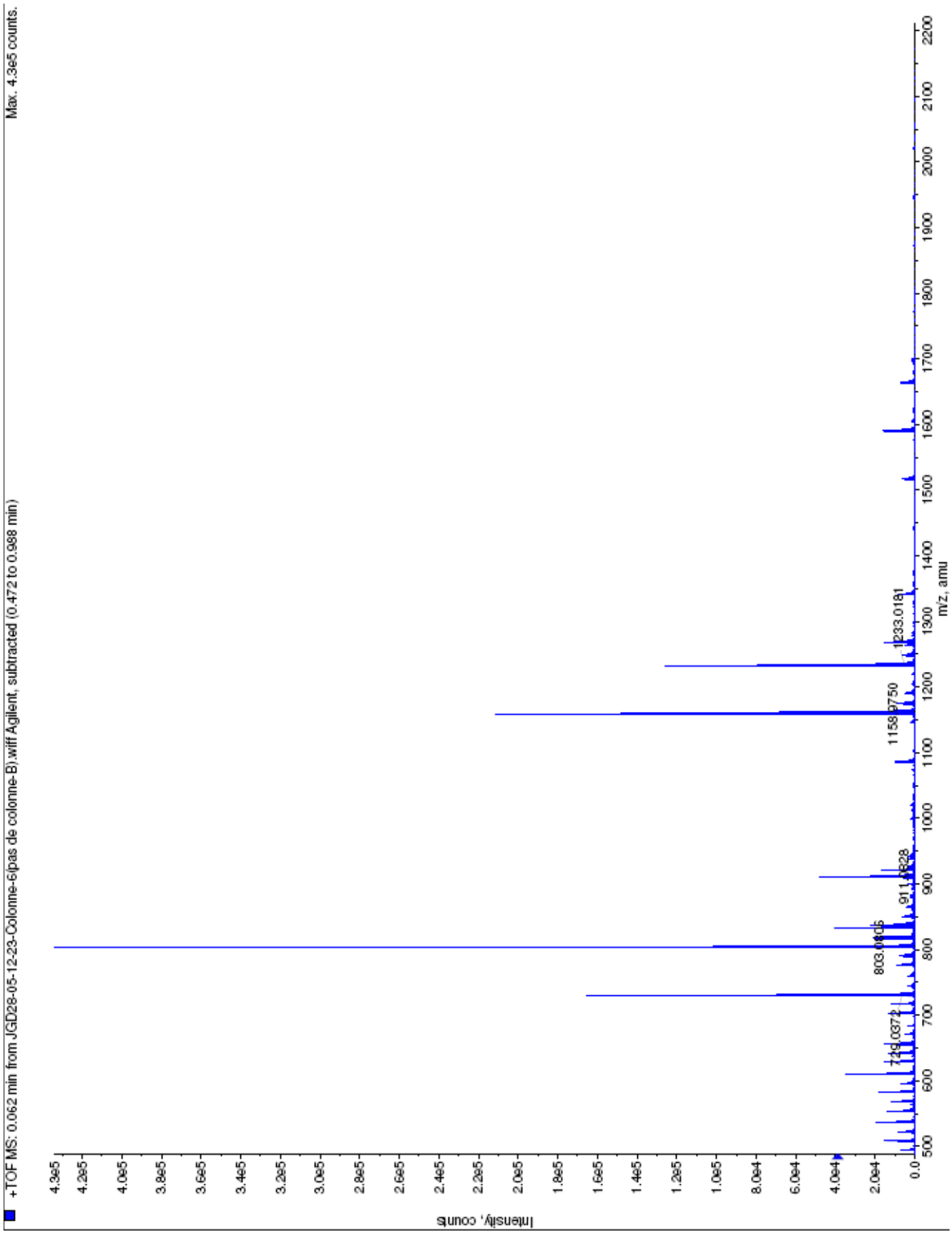
4-Cl_2 33.54 min



3^{+} 40.49 min


+TOF MS: 40.491 min from JGD28-05-12-23-Colonne-6.wiff Agilent
Max. 1.2e6 counts.
1233.0188
213.0202
Intensity, counts
m/z, amu

Unseparated sample

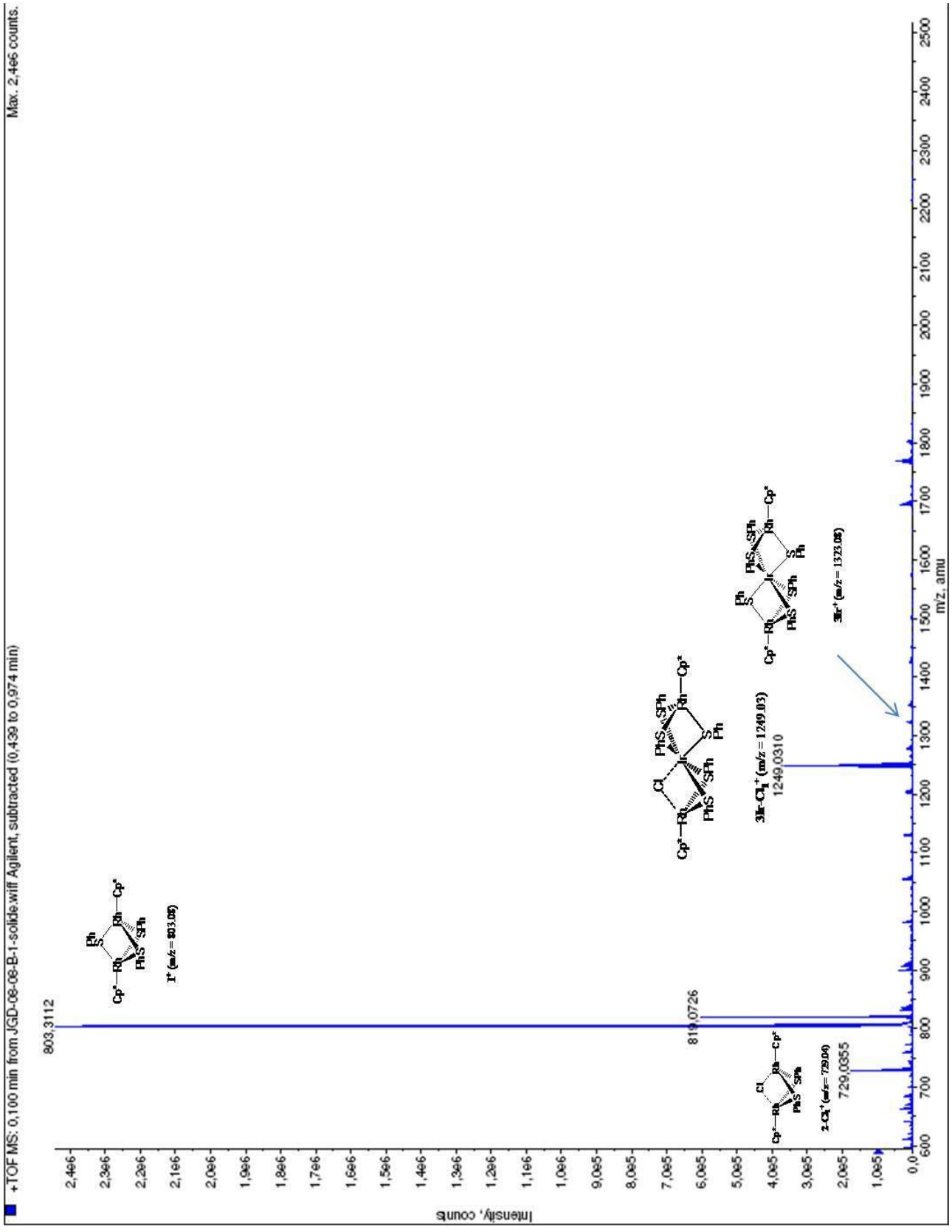


6. Formation of heteronuclear (Rh-Ir) oligomers

6.1 Experimental

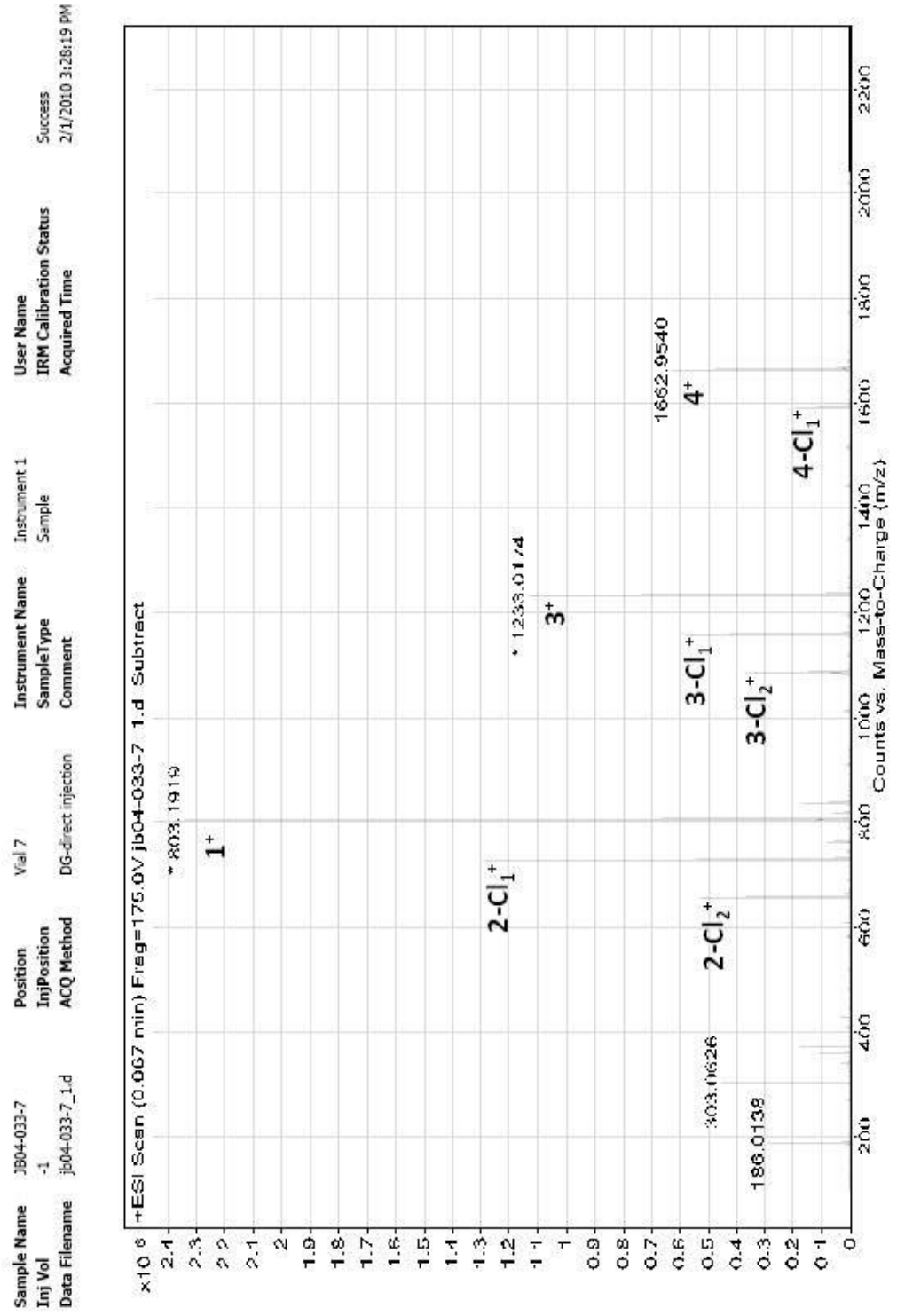
$IrCl_3.3H_2O$ (4.2 mg, 0.012 mmol) and HSPh (3.6 µL, 0.012 mmol) and HCl 2% in ether (65 µL, 0.036 mmol) were added to [**1**$^+$]**Cl** (10 mg, 0.012 mmol) in toluene (10 mL) in a round bottom flask, which was heated at 110 ºC for 48 hours.

6.2 HR-MS characterization

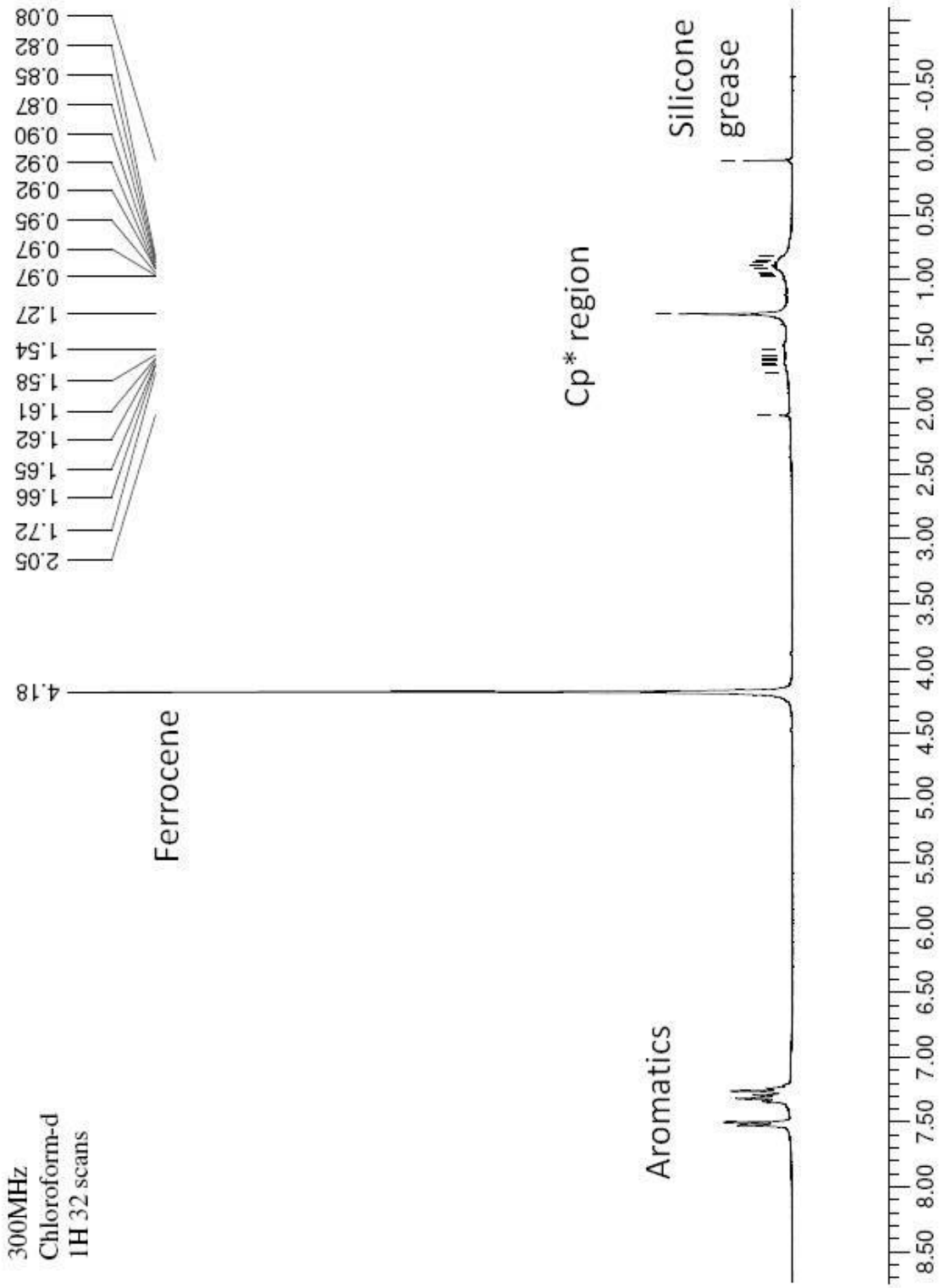


7. ^{1}H and $^{13}C\{^{1}H\}$ NMR characterization of oligomers

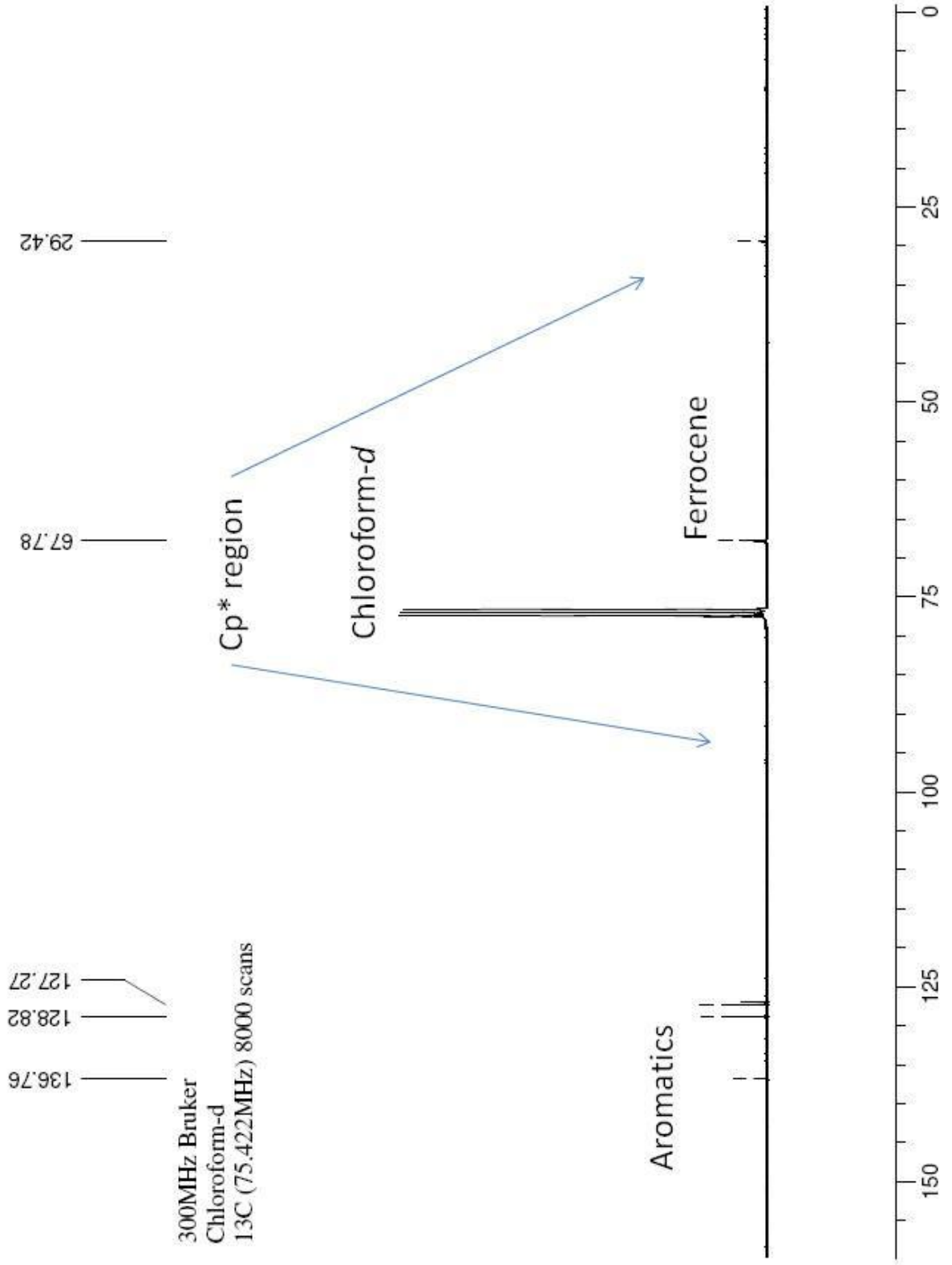
7.1. HR-MS spectrum



7.2. ^{1}H NMR spectrum

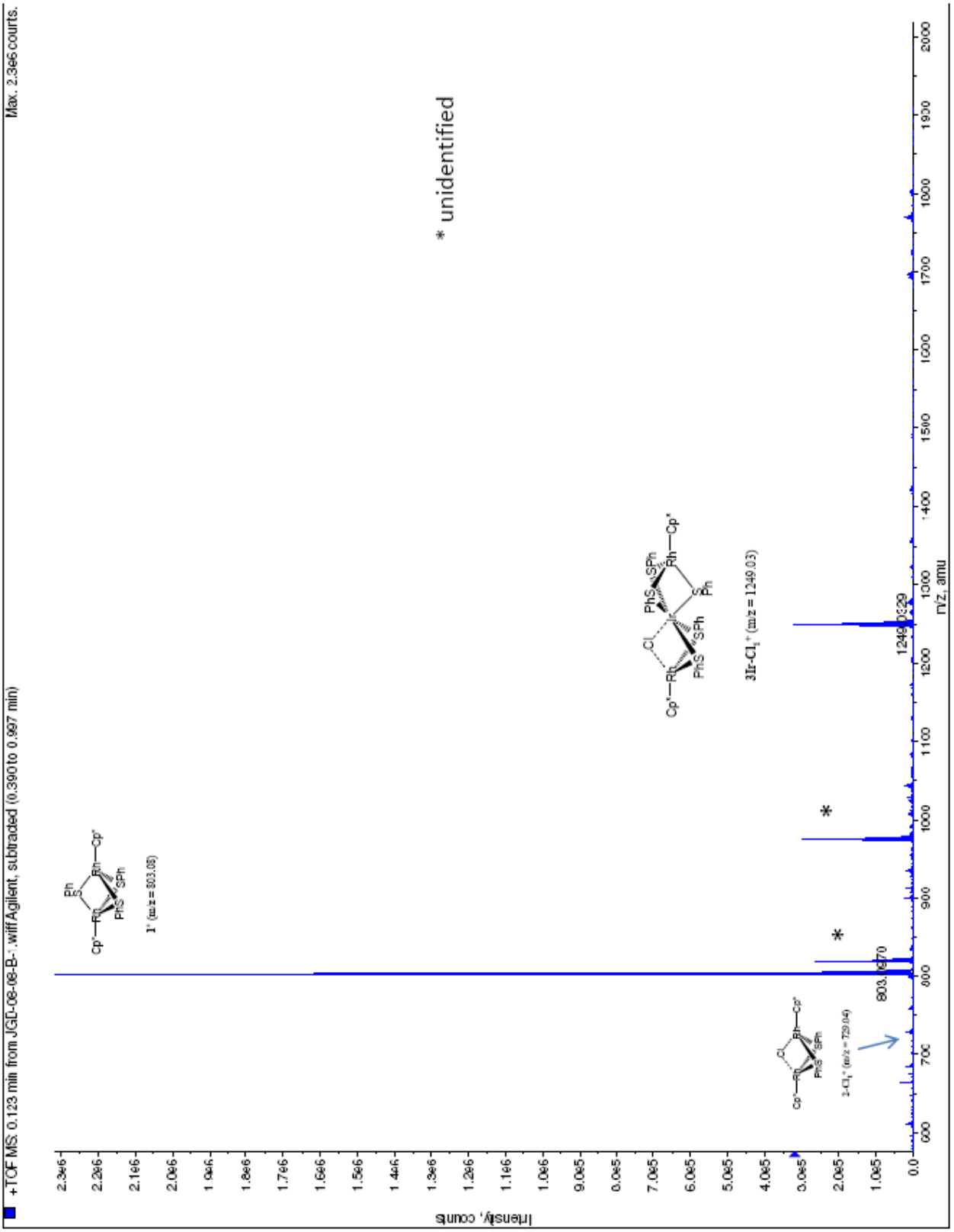


7.3. $^{13}C\{^{1}H\}$ NMR spectrum

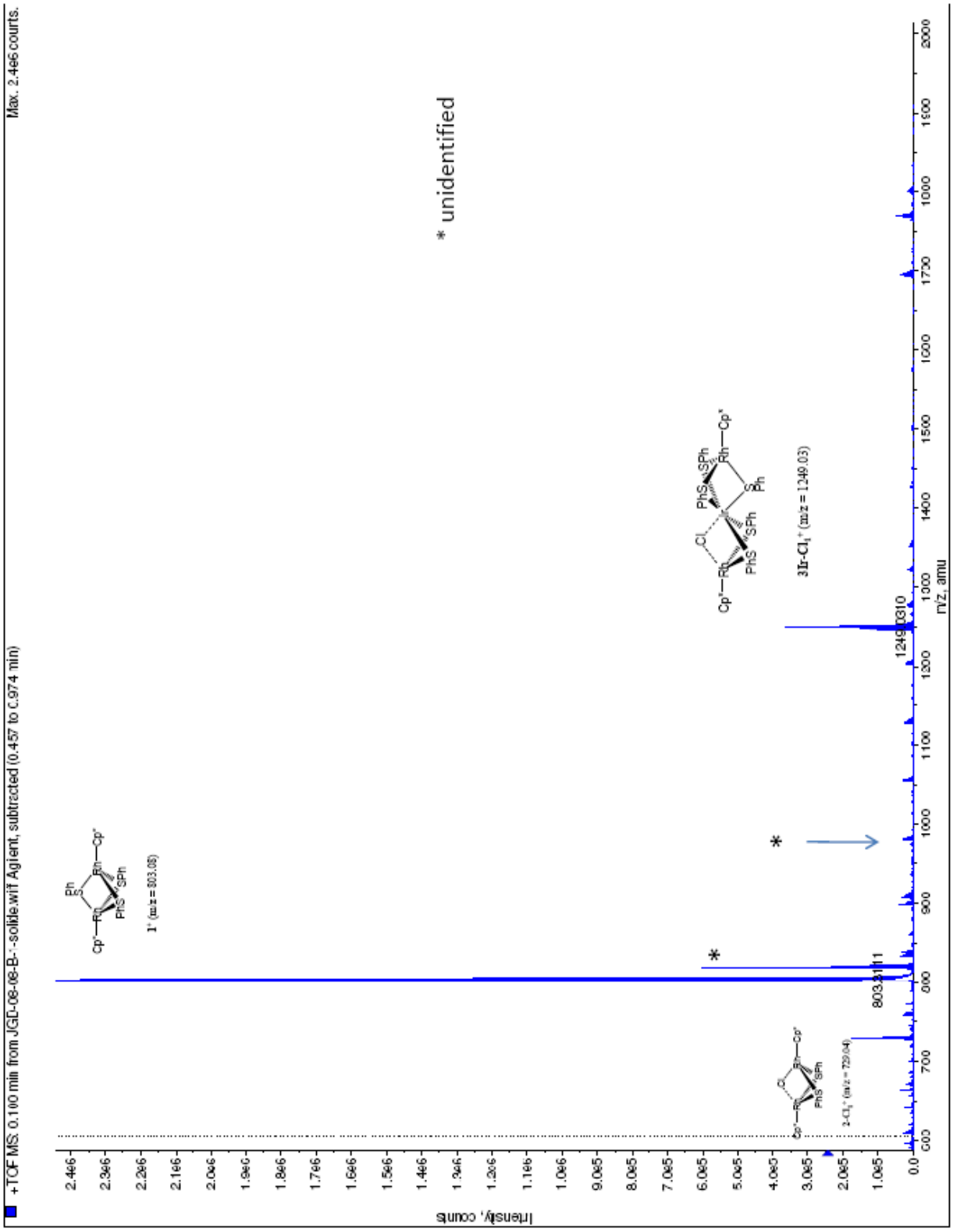


8. Distribution of oligomers in toluene solution *vs* precipitate for the formation of heteronuclear (Rh-Ir) oligomers

8.1 Sample of toluene solution in dichloromethane



8.2 Sample of precipitate in dichloromethane



9. Crystallographic data for [3$^+$]Cl

9.1 Experimental details

Data Collection

A red crystal having approximate dimensions of 0.05 x 0.05 x 0.02 mm was mounted on a cryoloop using Paratone N hydrocarbon oil. Measurements were made at 200(2)K on a Bruker APEX II area detector diffractometer equipped with graphite monochromated MoKα radiation. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.5º counted for a total of 30 seconds per frame.

An orientation matrix corresponding to cell constants listed in Table S3 was obtained from a least-squares refinement using the measured positions of 1385 centered reflections in the range 2.38º < θ < 14.44º. The program used for retrieving cell parameters and data collection was APEX 2.[1]

Data Reduction

Data were integrated using the program SAINT.[2] The data were corrected for Lorentz and polarization effects. Face-indexed and multiscan absorption corrections were both performed, respectively using the XPREP[3] and SADABS[4] programs.

Structure Solution and Refinement

The structure was solved and refined using SHELXS-97 and SHELXL-97.[5] All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions. All calculations and drawings were performed using the SHELXTL package.[6] The crystal structure gave a satisfactory chekcif report and the data have been deposited with CCDC (CCDC No. 757796). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the internet at www.ccdc.cam.ac.uk.

Table S3- Crystal data and structure refinement for **[3$^+$]Cl**.

Empirical formula	C56 H60 Cl1 Rh3 S6	
Formula weight	1269.64	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.593(4) Å	α= 90°.
	b = 13.798(3) Å	β= 113.975(14)°.
	c = 23.592(5) Å	γ = 90°.
Volume	5233(2) Å^3	
Z	4	
Density (calculated)	1.612 Mg/m^3	
Absorption coefficient	1.263 mm^{-1}	
F(000)	2576	
Crystal size	0.05 x 0.05 x 0.02 mm^3	
θ range for data collection	1.80 to 23.50°.	
Reflections collected	44110	
Independent reflections	7746 [R(int) = 0.2009]	
Observed Reflections	3894 [I>2σ(I)]	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2σ(I)]	R1 = 0.0596, wR2 = 0.0939	
R indices (all data)	R1 = 0.1567, wR2 = 0.1255	
Largest diff. peak and hole	0.674 and -0.672 e.Å^{-3}	

10. SI references

[1] Bruker. *APEX 2* Version 2.0.2 **2005,** Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker, *SAINT* Version 7.07a, **2003,** Bruker AXS Inc., Madison, Wisconsin, USA.

[3] Bruker, *XPREP* Version 2005/2, **2005,** Bruker AXS Inc., Madison, Wisconsin, USA.

[4] G.M. Sheldrick, *SADABS* Version 2004/1, **2004,** Bruker AXS Inc., Madison, Wisconsin, USA.

[5] G.M. Sheldrick, *SHELXS-97 and SHELXL-97* Programs for the refinement of crystal structures. **1997,** University of Gottingen, Germany.

[6] Bruker, *SHELXTL* Version 6.12 **2001,** Bruker AXS, Madison, Wisconsin, USA.