Electronic Supplementary Material (ESI) for RSC Advances.


Supporting Information for the article:

# Analysis of model Pd- and Pt-containing contaminants in aqueous media using ESI-MS and the fragment partitioning approach

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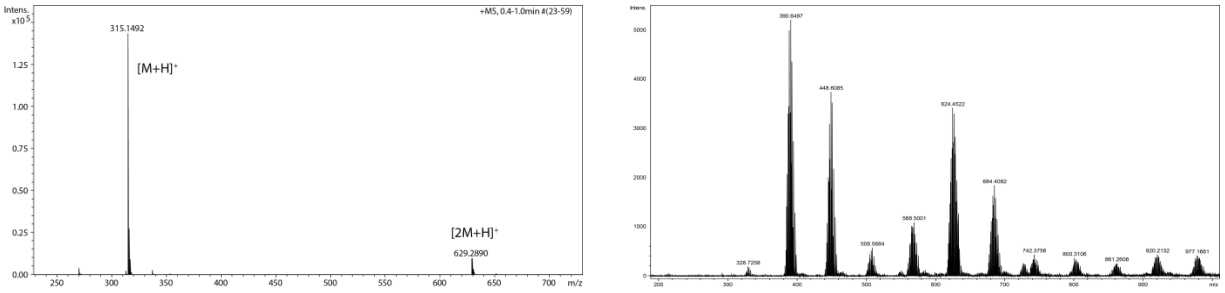
# 1. Program description

The main problem in the analysis of ESI-HRMS-spectra of coordinative compounds is the signal assignment. While an ESI-MS spectrum of a typical organic compound (containing C, H, O, N, S, P etc.) consists of a few signals (usually [M+H], [M+Na], [2M+H] etc.) (Figure S1a), a ESI-MS spectrum of a transition metal complex may consist of hundreds of signals (Figure S1b).




a b

**Figure S1.** a) Typical ESI-MS spectrum of organic compound (antiulcer drug *Ranitidine* $C_{13}H_{23}N_4O_3S$); b) ESI-MS spectrum of aqueous solution of $Na_2PdCl_4$ (negative ion mode).

Very often, in the spectra of transition-metal-containing substances, there are a lot of signals of solvent associates, ligand degradation products, nucleation products with different degrees of nucleation, etc. To assign a signal in mass-spectra of an organic compound, a brutto formula variation procedure by the element exact mass is usually applied. Isotopic distribution acts as a confirmation of the calculated formula. Such an approach is realized in typical HRMS-processing software. Unfortunately, this approach is not convenient for the analysis of mass-spectra of transition metal complexes, especially in the case of ions with high m/z: there are a lot of false "positive" results when the trial-and-error procedure by the element exact mass is applied. At the same time, information about composition (and exact masses) of stable structural fragments of metal complexes (e.g. solvents, ligands or their fragments, counterions, cluster cores, substrate or product molecules in catalytic reactions) is readily available. Utilization of the above-mentioned structural data can substantially facilitate the process of signal assignment in ESI-MS spectra of metal-containing systems, and can significantly decrease the analysis time. For this purpose, a special program tool, which performed the variation procedure by custom structural fragments, was developed.

Input parameters are as follows (Figure S2): fragment name, fragment composition, exact mass (automatically calculated), minimum and maximum fragment coefficients, target mass, and mass tolerance. Because researchers often work with compounds containing similar fragments, it is useful to create a fragment library (*library.csv* file). The file *library.csv* (Figure S3) contains two

columns: names of fragments and their chemical formulae. All fragments from the library are listed in the drop-down list in the field "*Name*". For fragments from the library, it is not necessary to fill in the fields "*Brutto*" and "*Mass*".

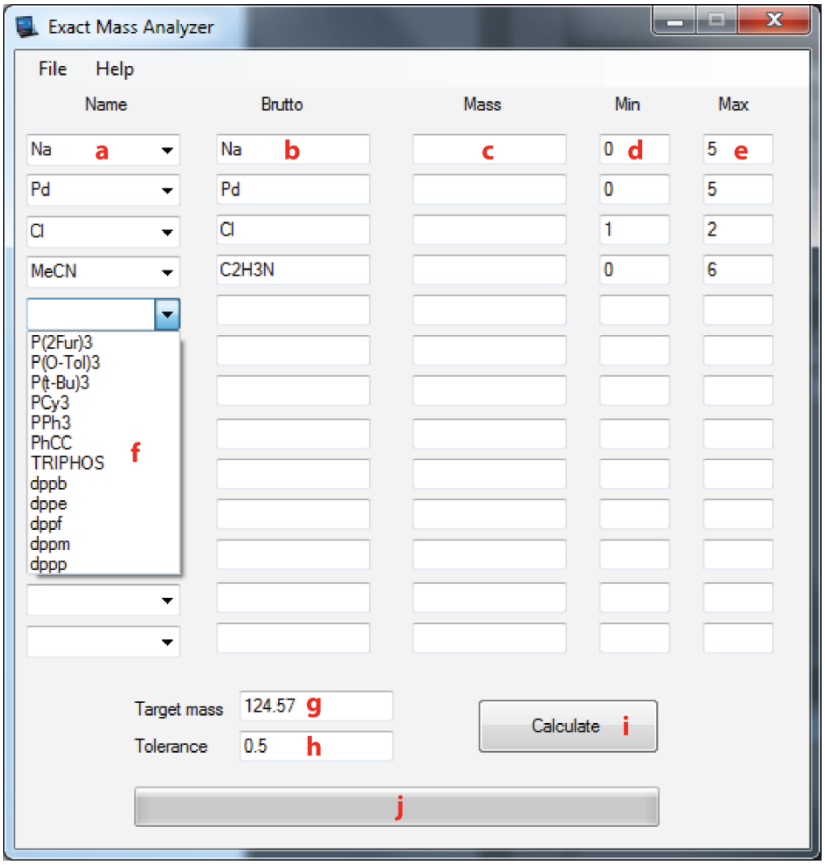



**Figure S2**. Input window of *Exact Mass Analyzer*: a) fragment name field; b) fragment composition; c) fragment exact mass (will be calculated automatically, if empty); d) minimum coefficient of the fragment in the resulting composition (0 if not specified); e) maximum coefficient of the fragment in the resulting composition (unlimited if not specified); f) drop-down list for fragments from the library; g) target mass field (in Da); h) mass tolerance (in Da); i) 'Calculate' button; j) calculation progress bar.

| | A | B |
|---|---|---|
| 1 | dppm | C25H22P2 |
| 2 | dppe | C26H24P2 |
| 3 | dppb | C28H28P2 |
| 4 | PPh3 | C18H15P |
| 5 | P(2Fur)3 | C12H9O3P |
| 6 | P(O-Tol)3 | C21H21P |
| 7 | P(t-Bu)3 | C12H27P |
| 8 | PCy3 | C18H33P |
| 9 | dppp | C27H26P2 |
| 10 | TRIPHOS | C34H33P3 |
| 11 | dppf | C35H28FeP2 |

**Figure S3**. Exemplary library file *library.csv*: a) fragment name; b) fragment composition.

When calculations are finished, the result table appears (Figure S4). This table contains the following columns: component coefficient, mass, difference from target mass ("Delta"), composition. Clicking on the brutto-formula will show the corresponding isotopic pattern. The table can be sorted by each column.

The software may be available at the authors' web-site: http://AnanikovLab.ru

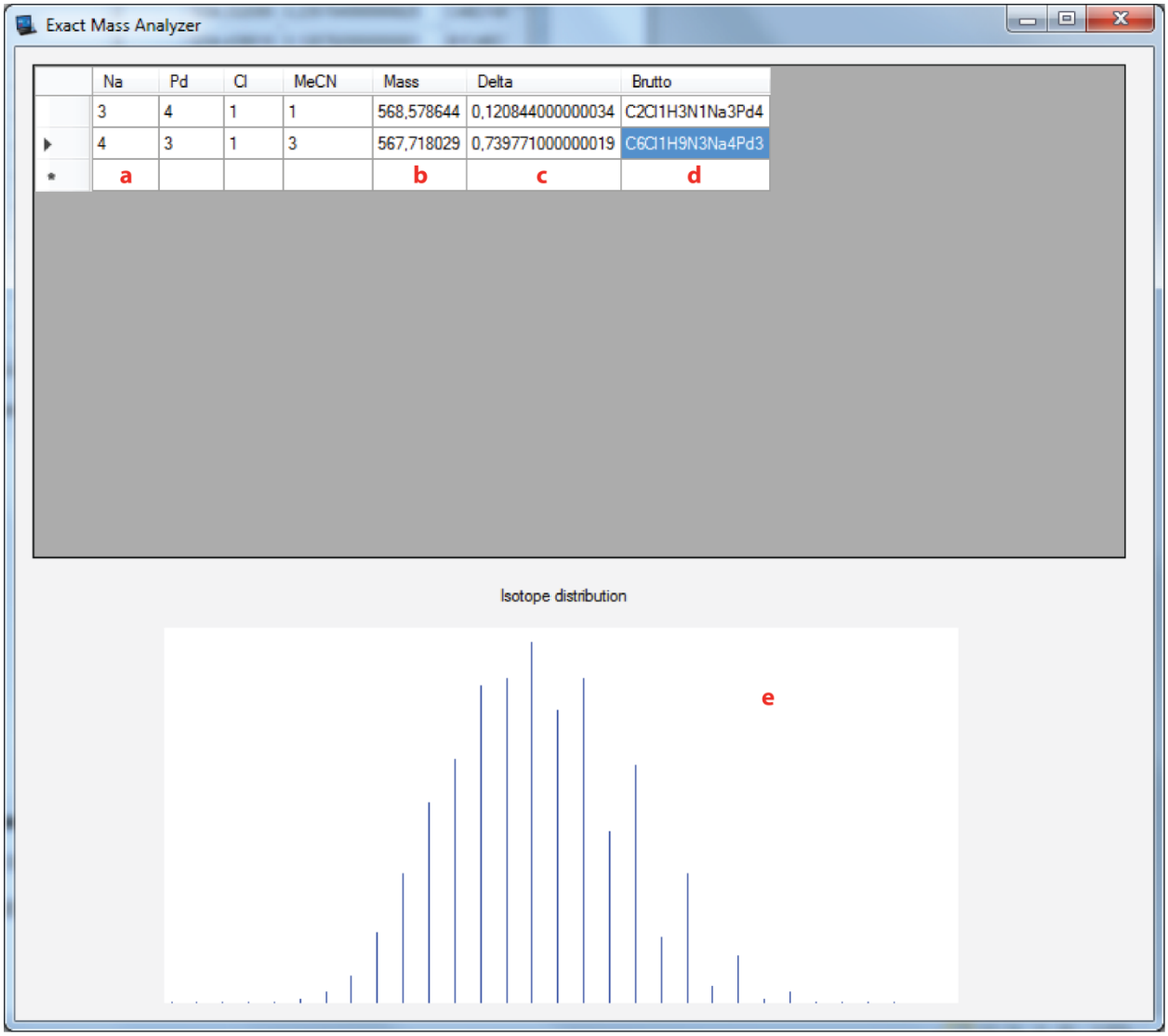



**Figure S4**. Result table of Exact Mass Analyzer: a) fragment coefficients; b) exact mass; c) difference from target mass (in Da); d) composition corresponding to calculated coefficients; e) isotopic pattern.

# 2. Representative ESI-MS spectra

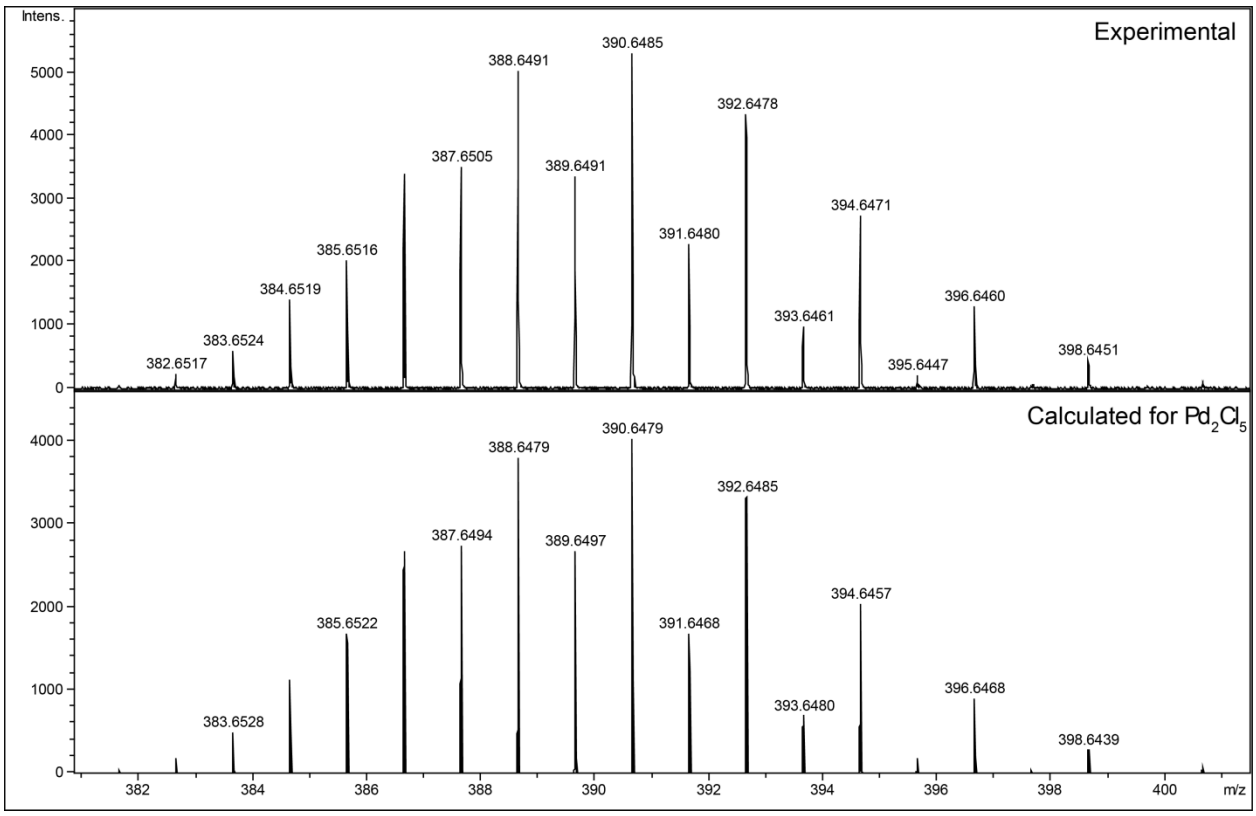



**Figure S5**. $Pd_2Cl_5$ (negative ion mode), $\Delta$ = 1.53 ppm.

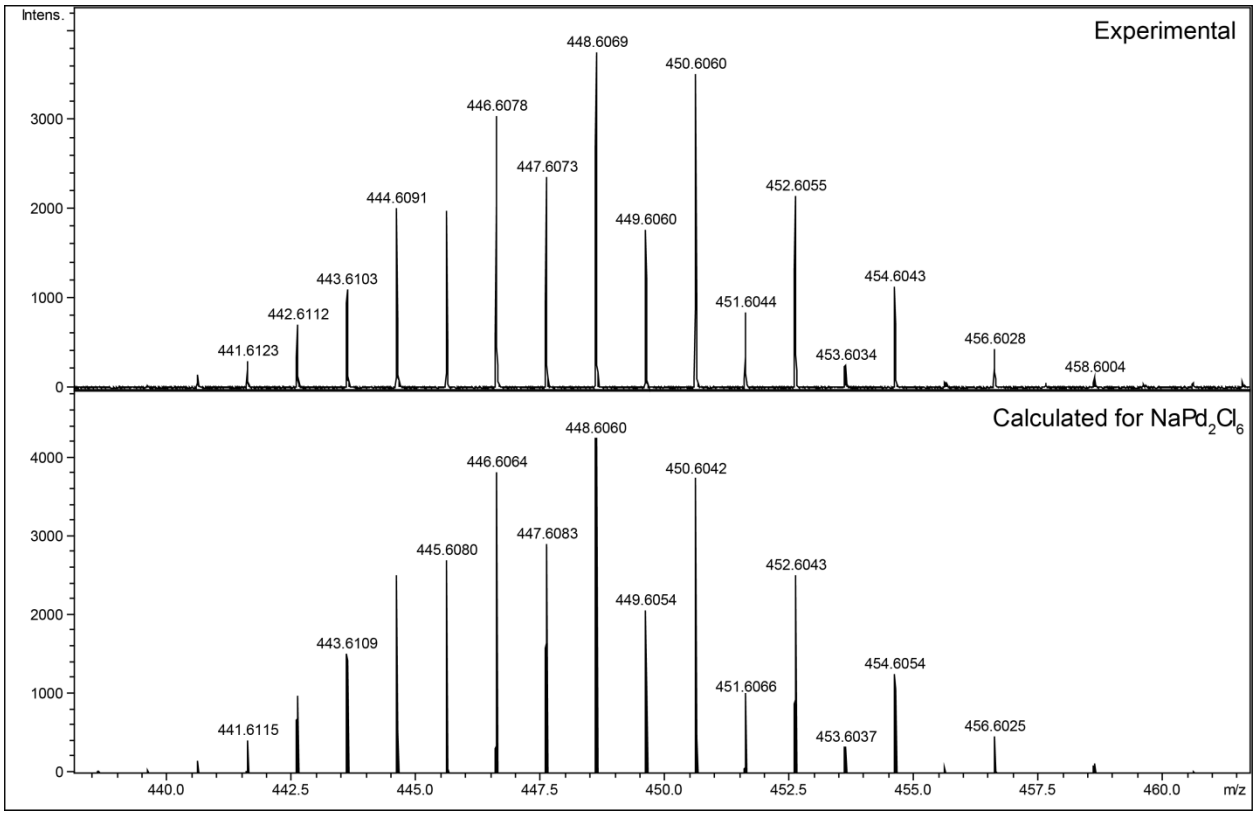



**Figure S6**. $NaPd_2Cl_6$ (negative ion mode), $\Delta$ = 2.01 ppm.

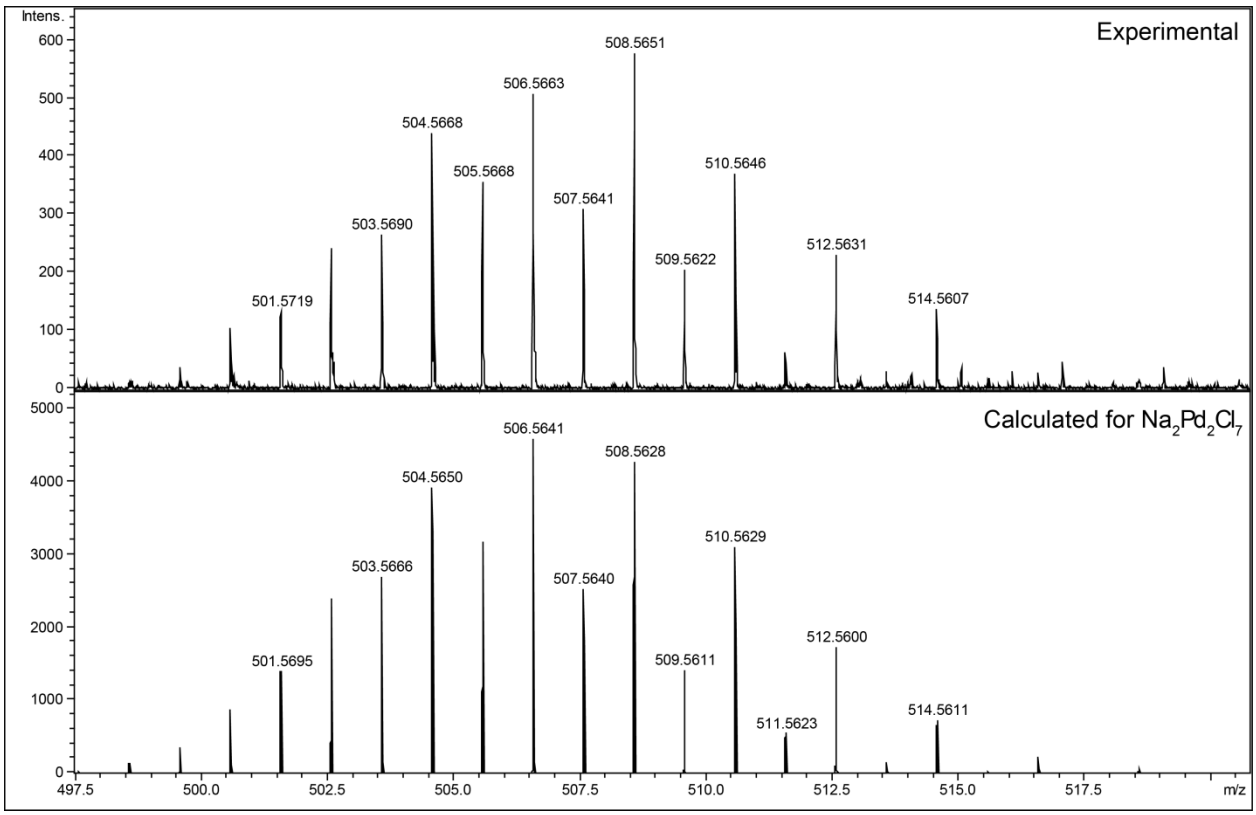



**Figure S7**. $Na_2Pd_2Cl_7$ (negative ion mode), $\Delta = 4.52$ ppm.

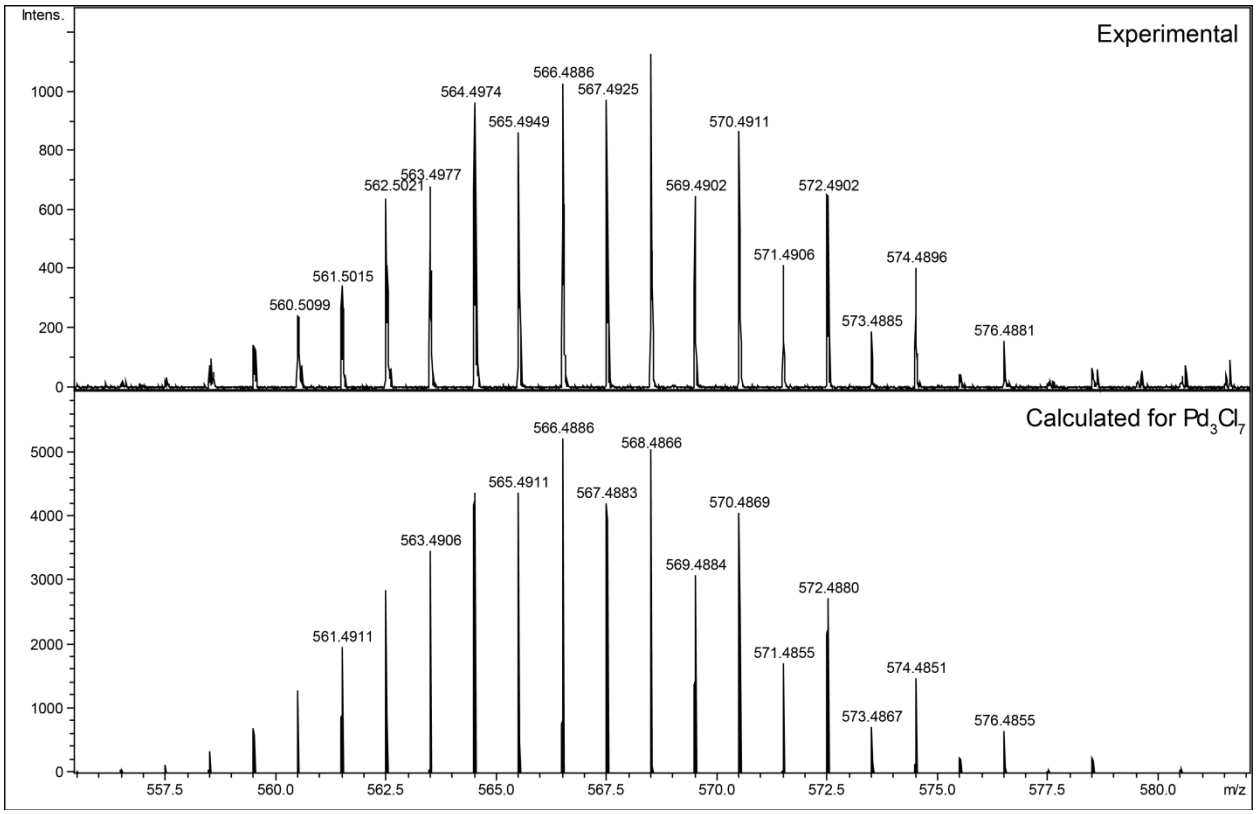



**Figure S8**. $Pd_3Cl_7$ (negative ion mode), $\Delta = 0$ ppm.

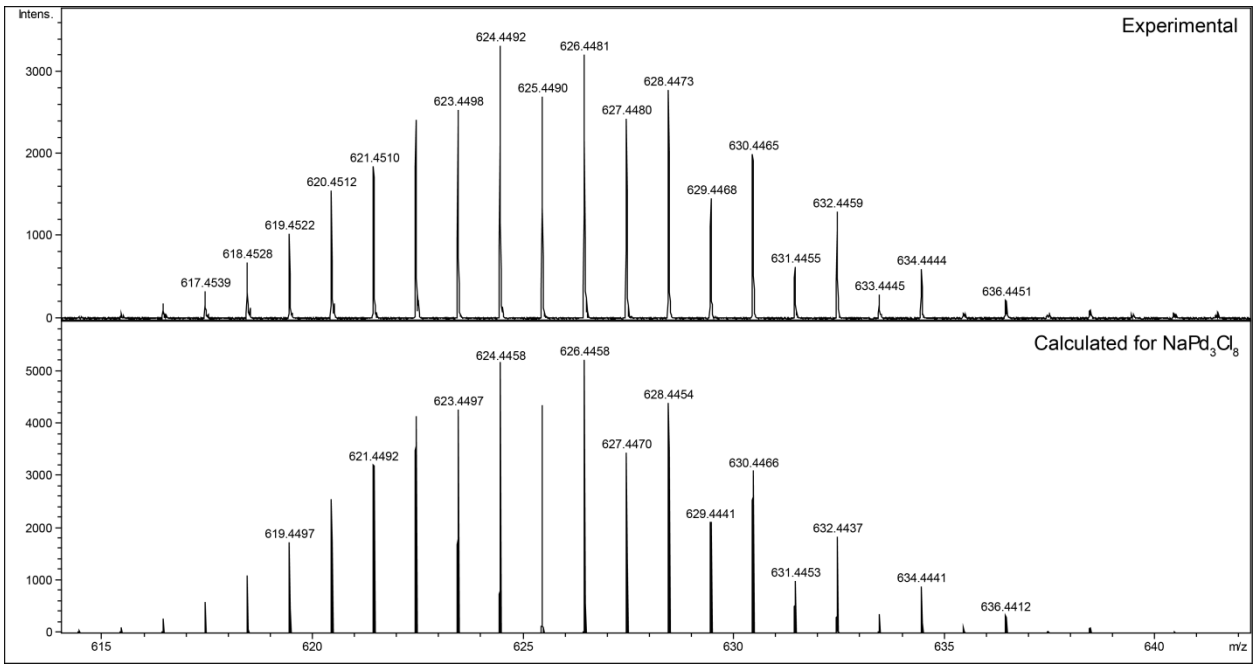



**Figure S9**. $NaPd_3Cl_8$ (negative ion mode), $\Delta$ = 3.67 ppm.

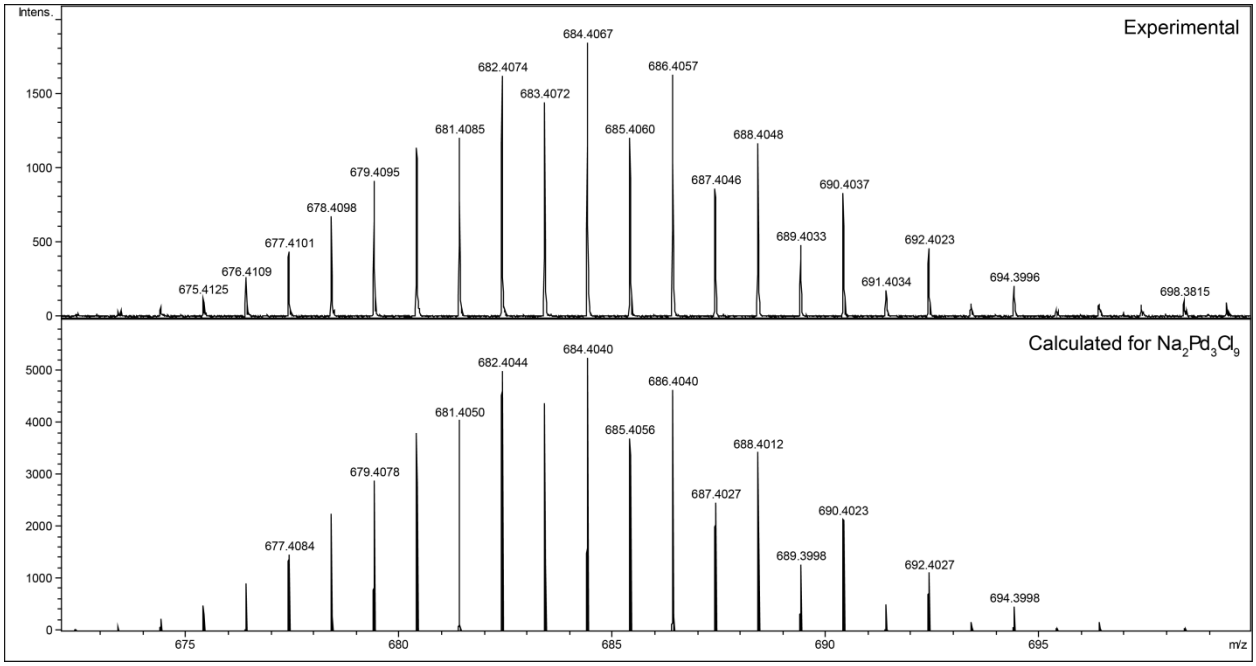



**Figure S10**. $Na_2Pd_3Cl_9$ (negative ion mode), $\Delta$ = 3.94 ppm.

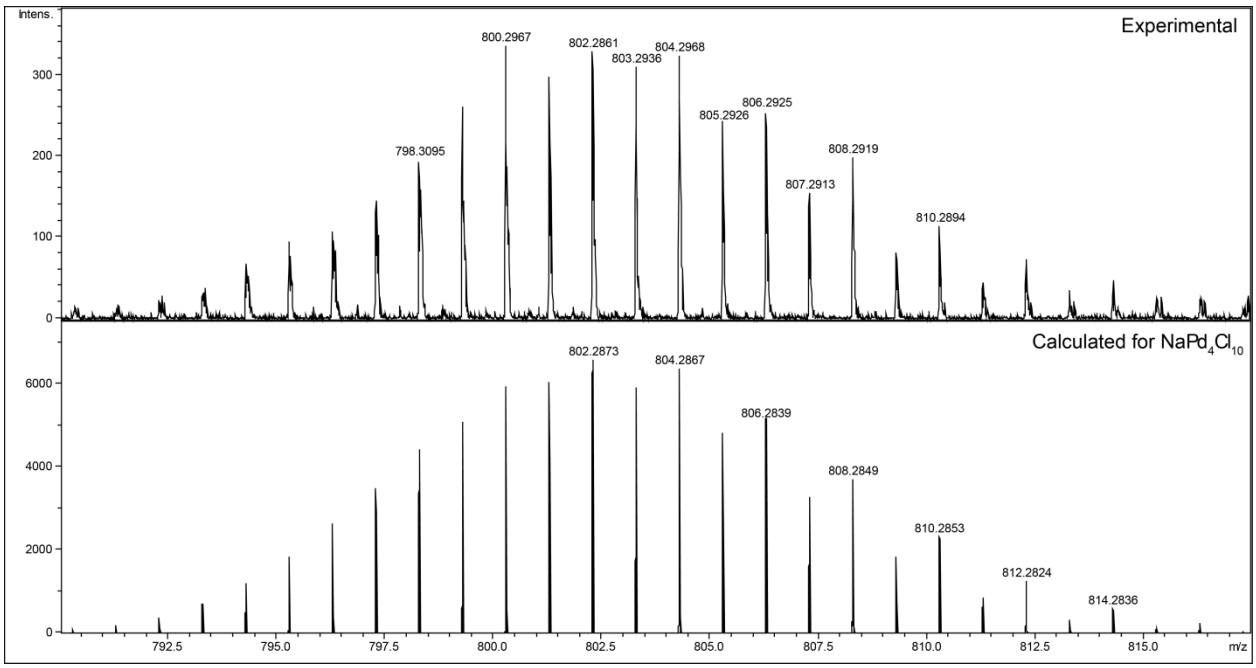



**Figure S11**. $NaPd_4Cl_{10}$ (negative ion mode), $\Delta$ = 1.50 ppm.

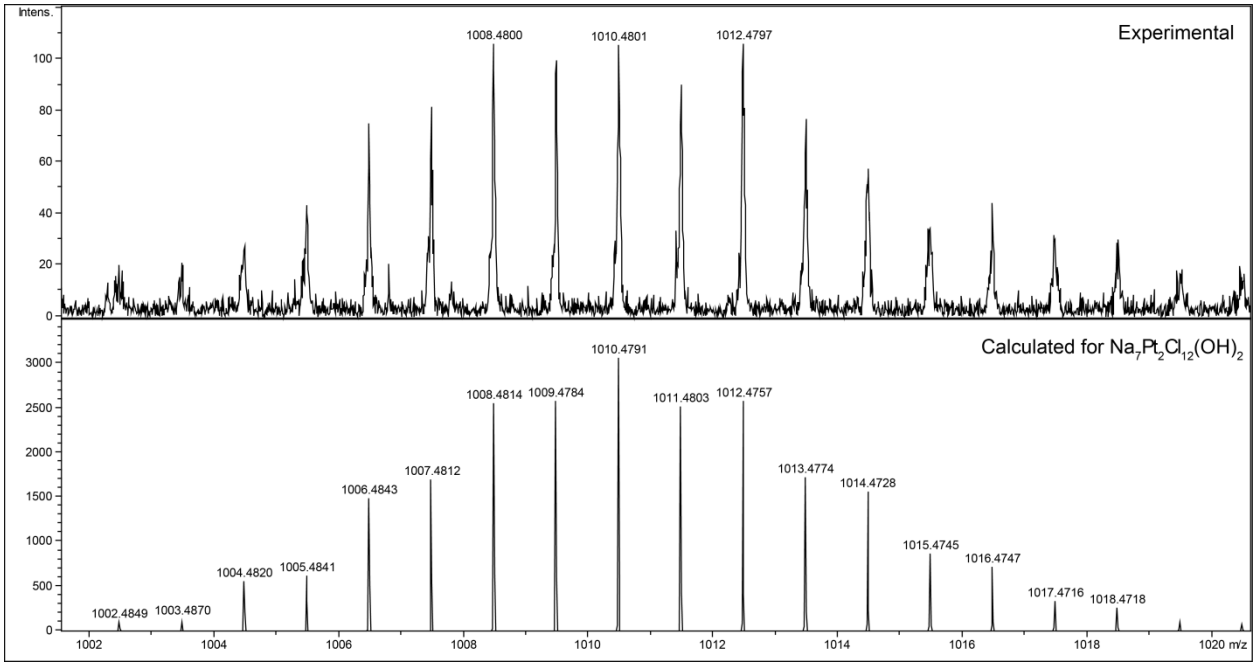



**Figure S12**. $Na_7Pt_2Cl_{12}(OH)_2$ (positive ion mode), $\Delta$ = 0.99 ppm.

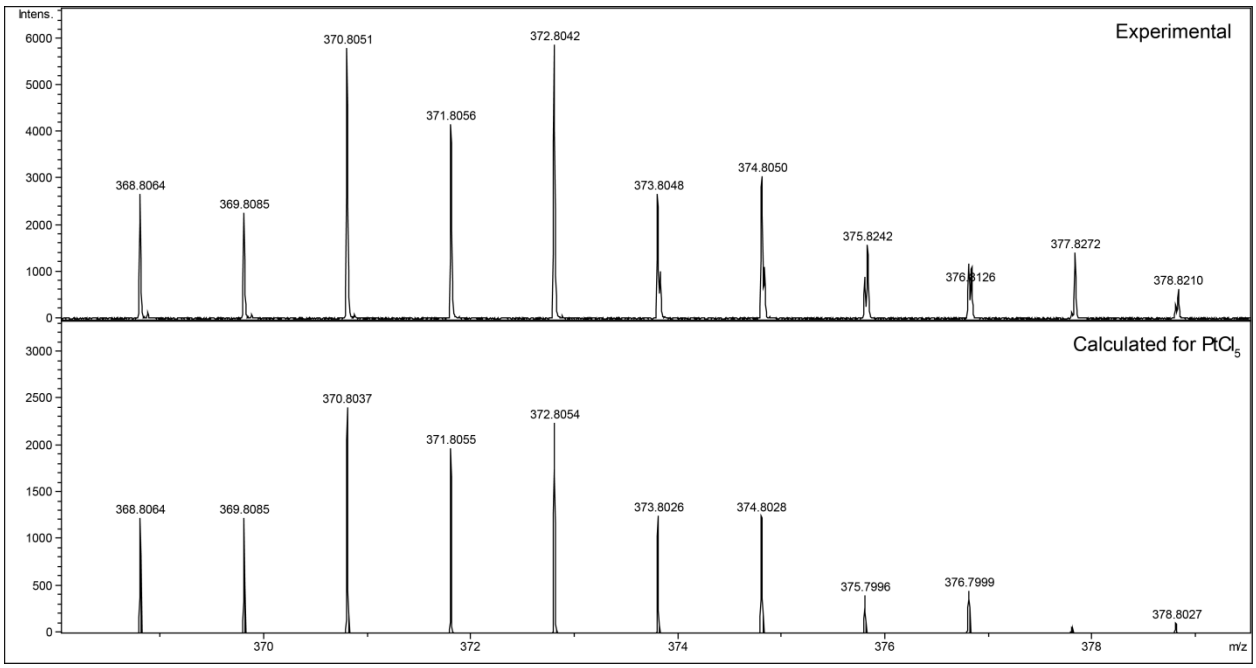



**Figure S13**. $PtCl_5$ (negative ion mode), $\Delta$ = 3.22 ppm.

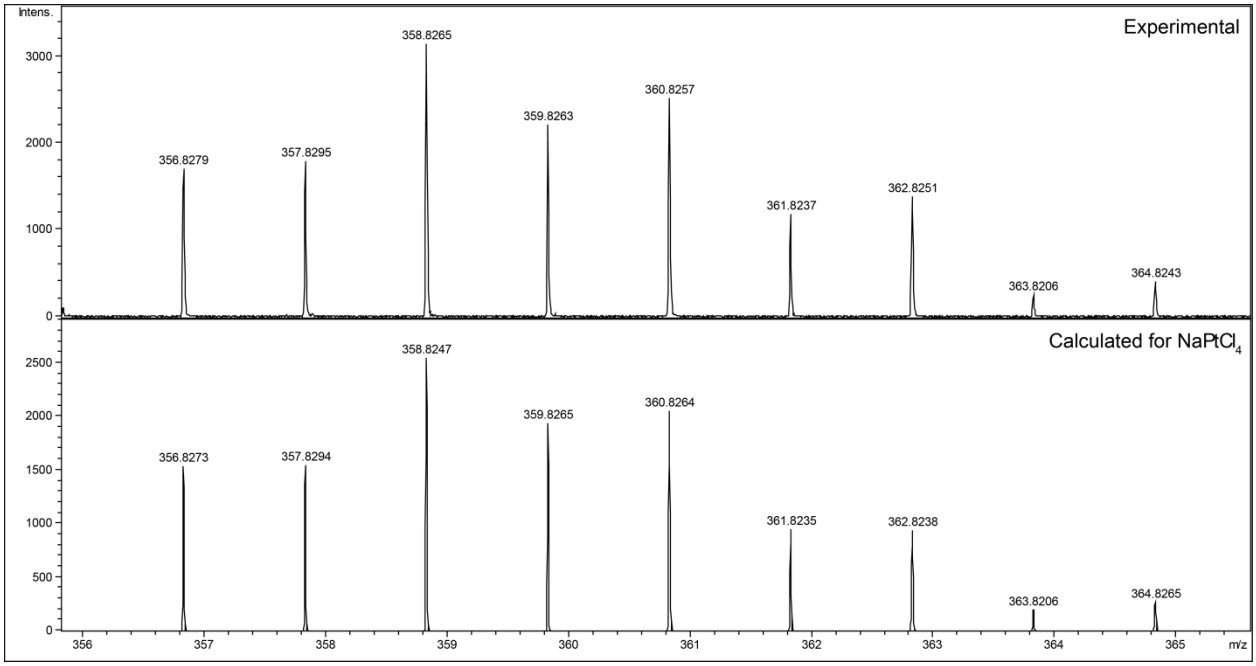



**Figure S14**. $NaPtCl_4$ (negative ion mode), $\Delta$ = 5.02 ppm.

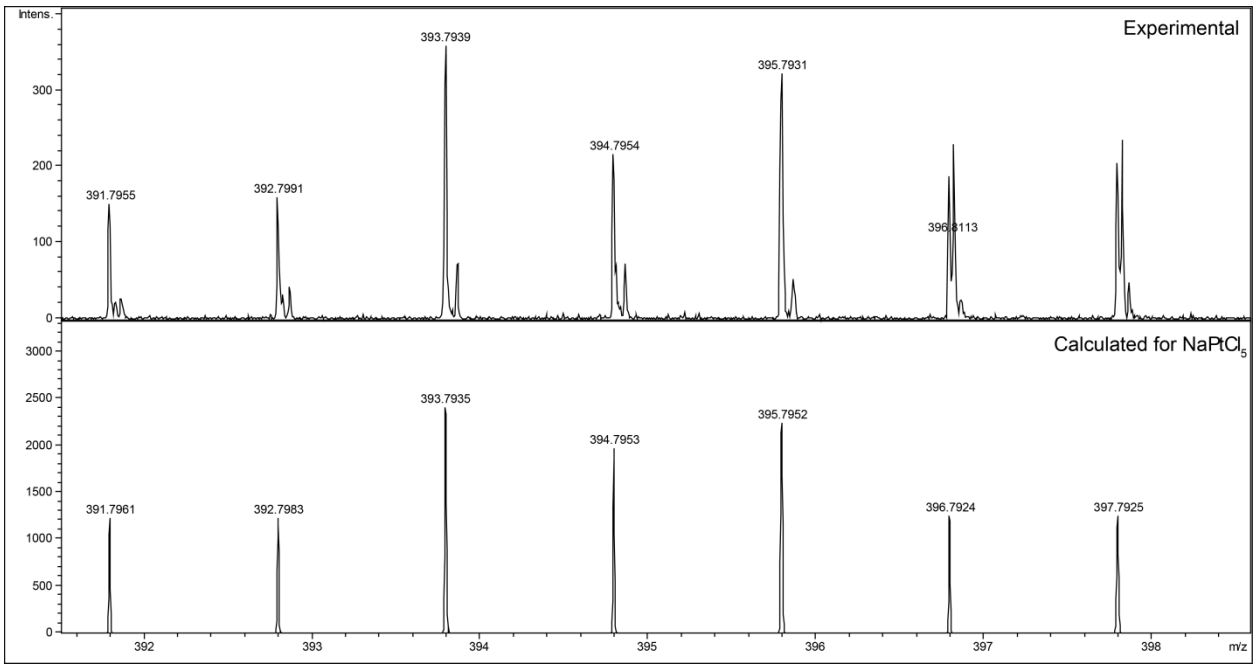



**Figure S15**. $NaPtCl_5$ (negative ion mode), $\Delta$ = 1.02 ppm.

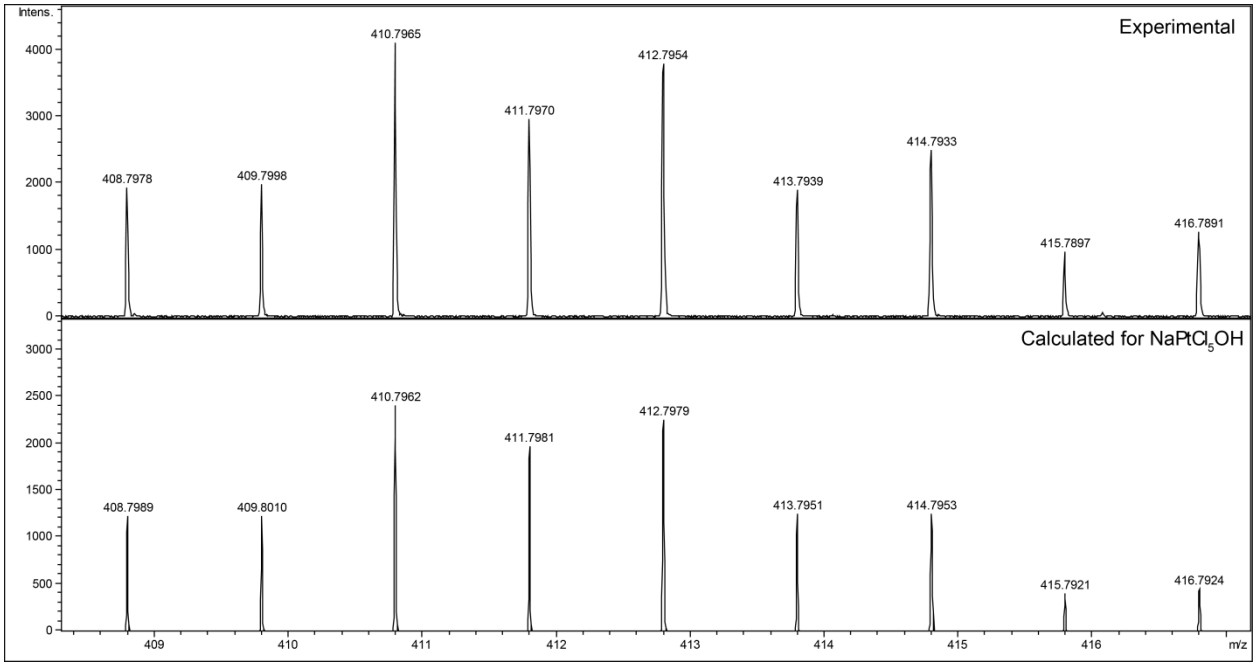



**Figure S16**. $NaPtCl_5OH$ (negative ion mode), $\Delta$ = 0.73 ppm.

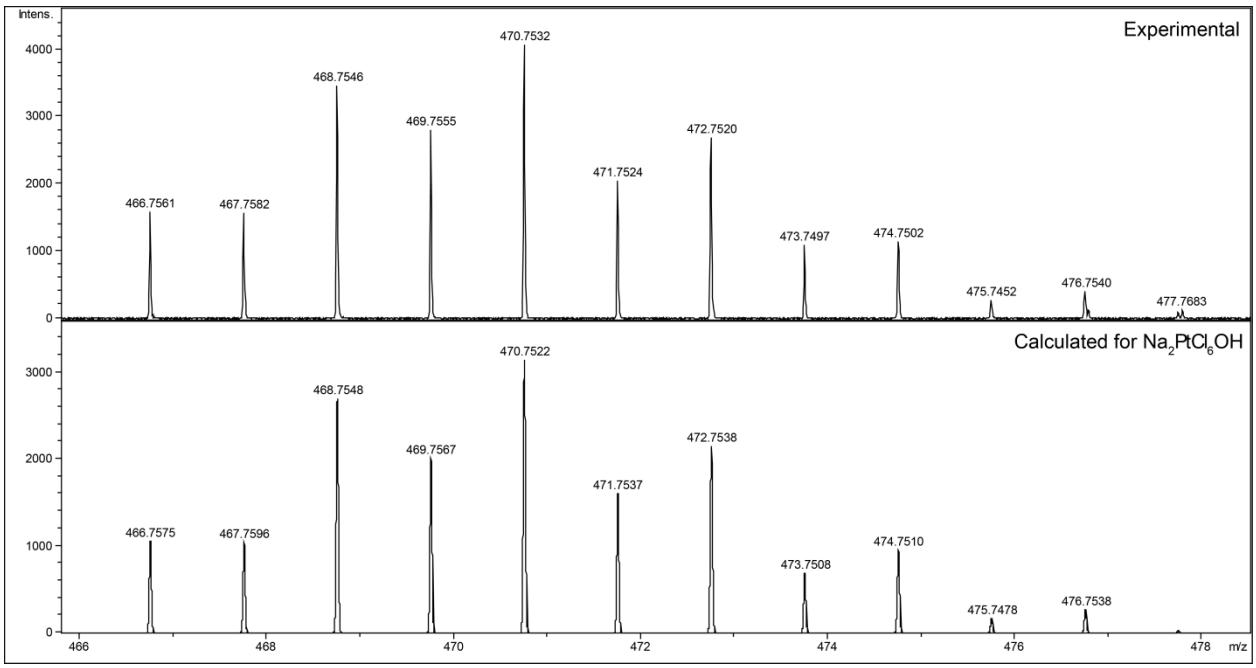



**Figure S17**. $Na_2PtCl_6OH$ (negative ion mode), $\Delta$ = 2.43 ppm.

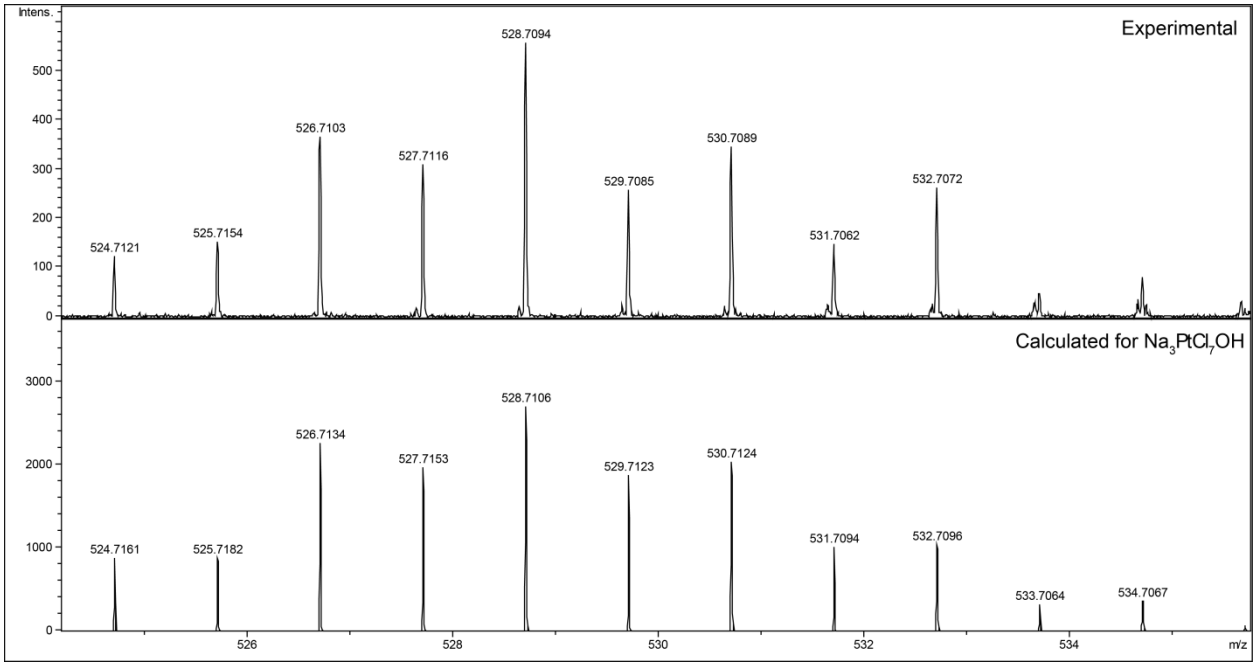



**Figure S18**. $Na_3PtCl_7OH$ (negative ion mode), $\Delta$ = 2.27 ppm.

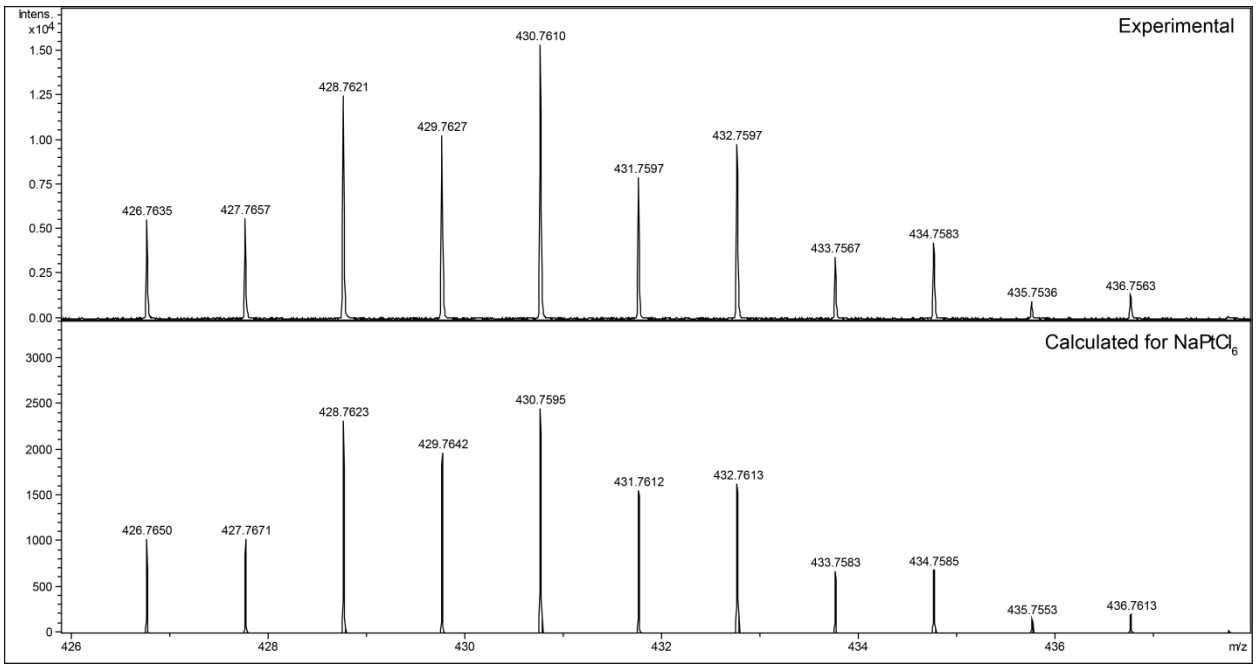



**Figure S19**. $NaPtCl_6$ (negative ion mode), $\Delta = 3.48$ ppm.

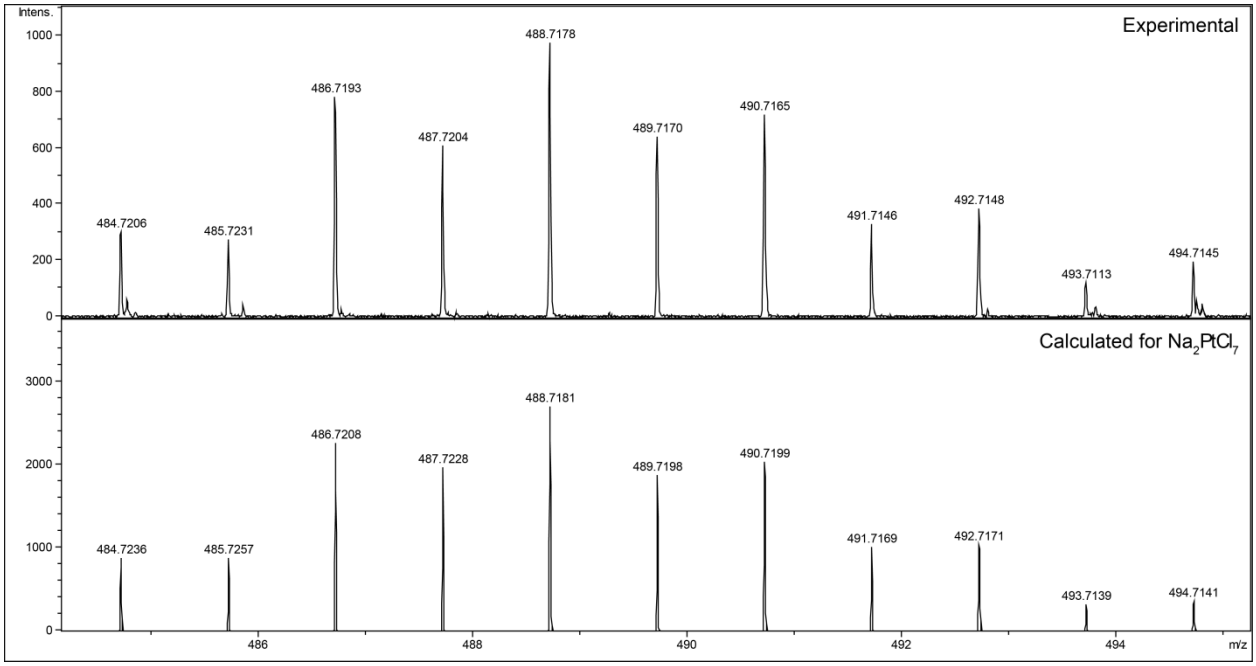



**Figure S20**. $Na_2PtCl_7$ (negative ion mode), $\Delta = 0.61$ ppm.

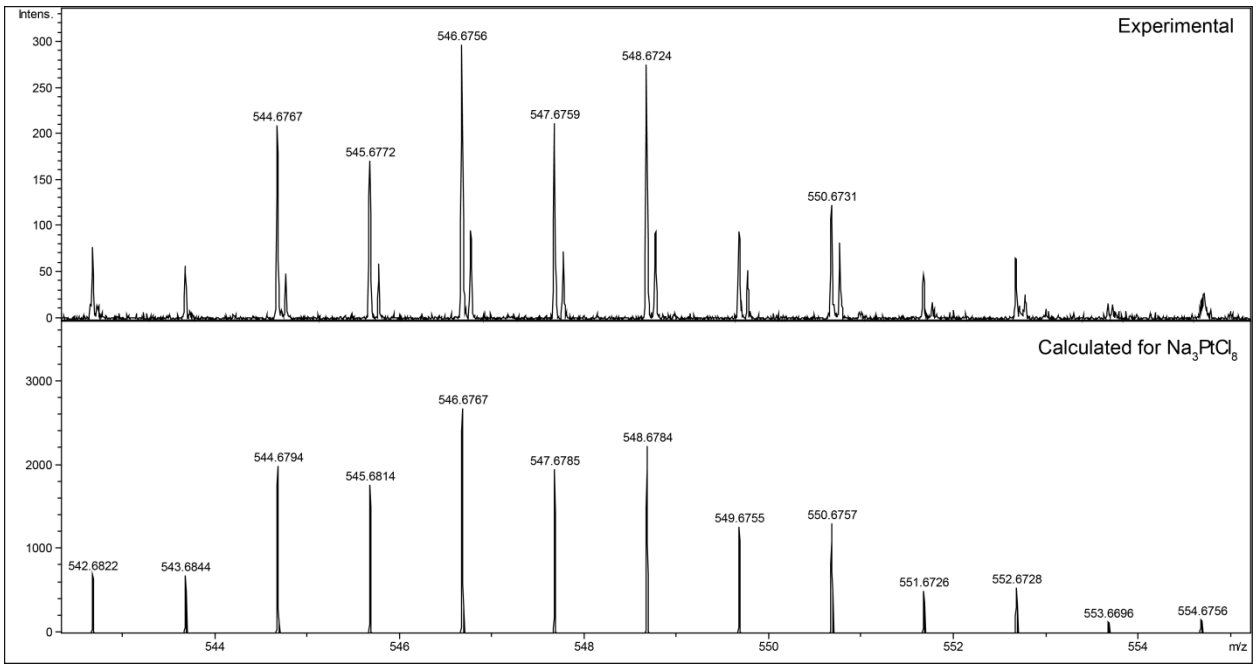



**Figure S21**. $Na_3PtCl_8$ (negative ion mode), $\Delta$ = 2.01 ppm.

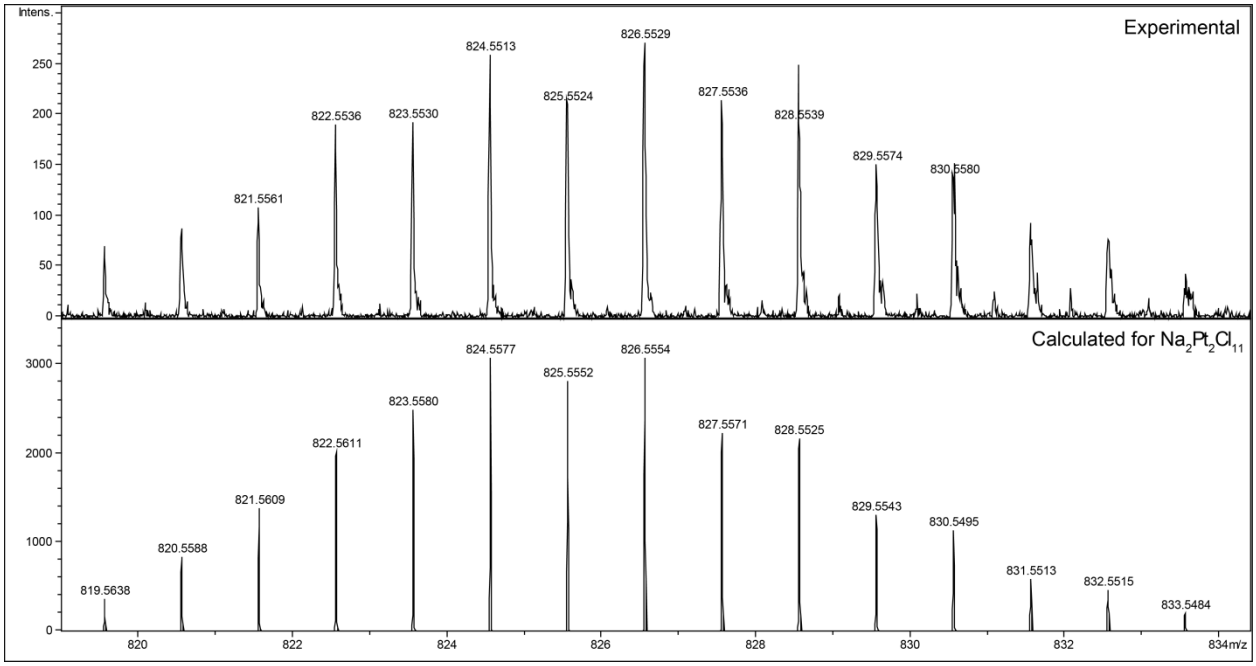



**Figure S22**. $Na_2Pt_2Cl_{11}$ (negative ion mode), $\Delta$ = 3.02 ppm.

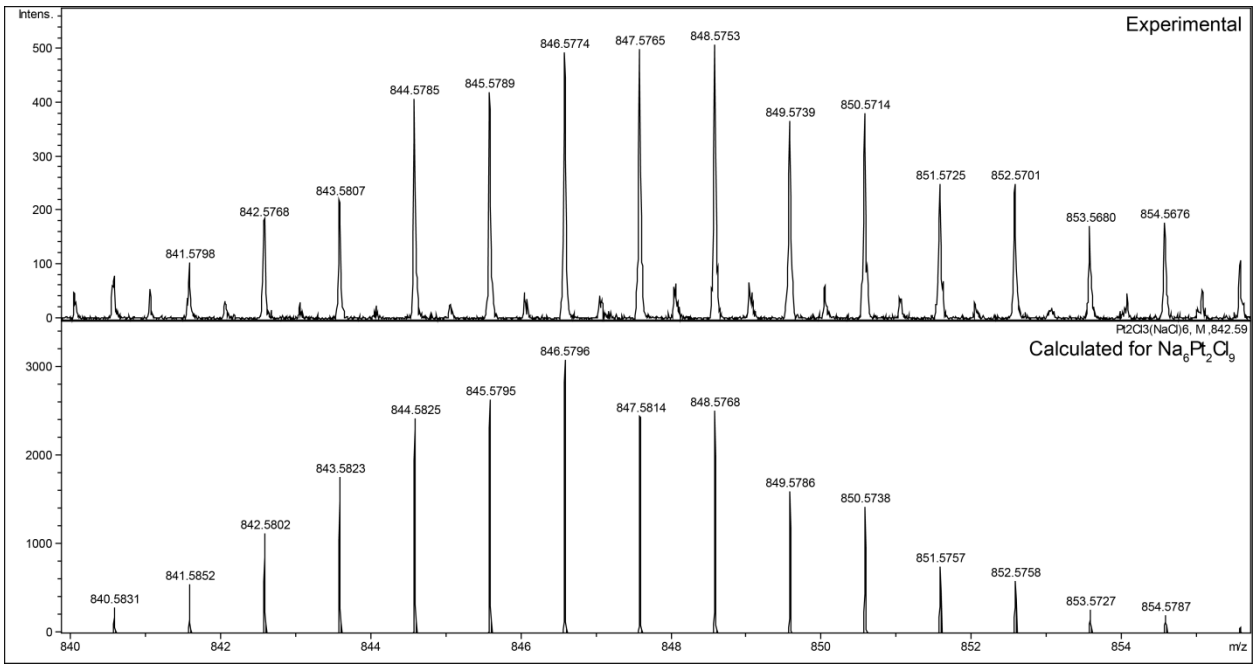



**Figure S23**. $Na_6Pt_2Cl_9$ (negative ion mode), $\Delta$ = 3.89 ppm.

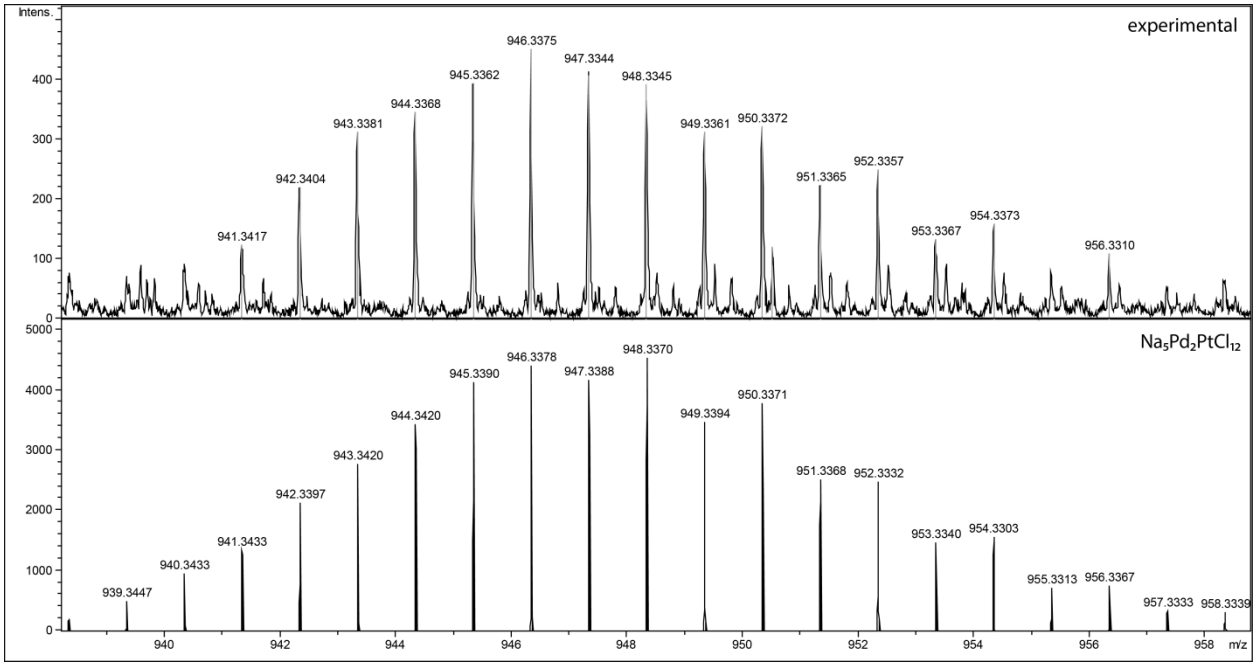



**Figure S24**. $Na_5Pd_2PtCl_{12}$ (positive ion mode), $\Delta$ = 0.32 ppm.

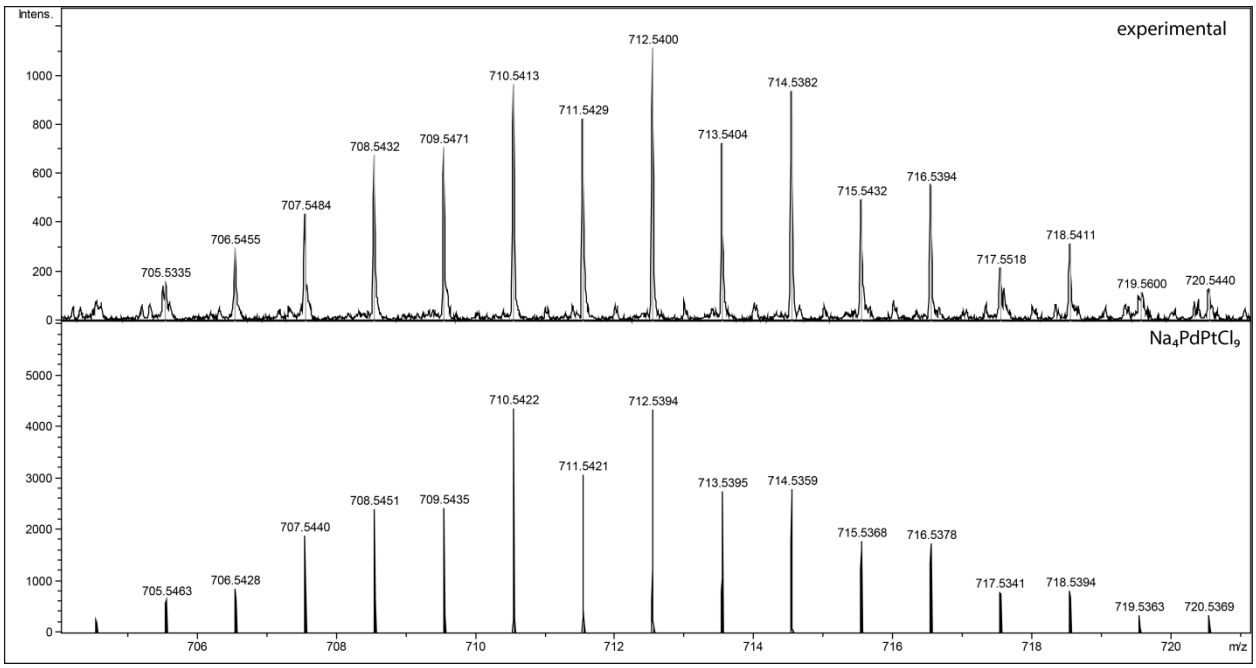



**Figure S25**. $Na_4PdPtCl_9$ (positive ion mode), $\Delta = 0.84$ ppm.

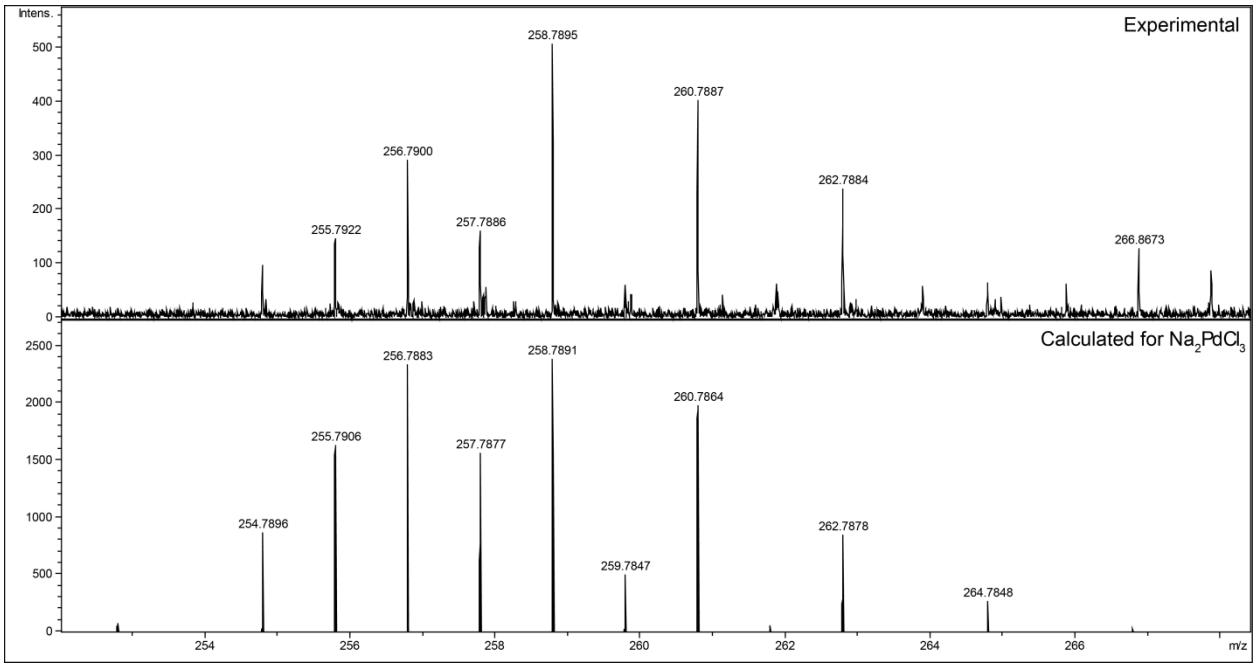



**Figure S26**. $Na_2PdCl_3$ (positive ion mode), $\Delta = 1.55$ ppm.

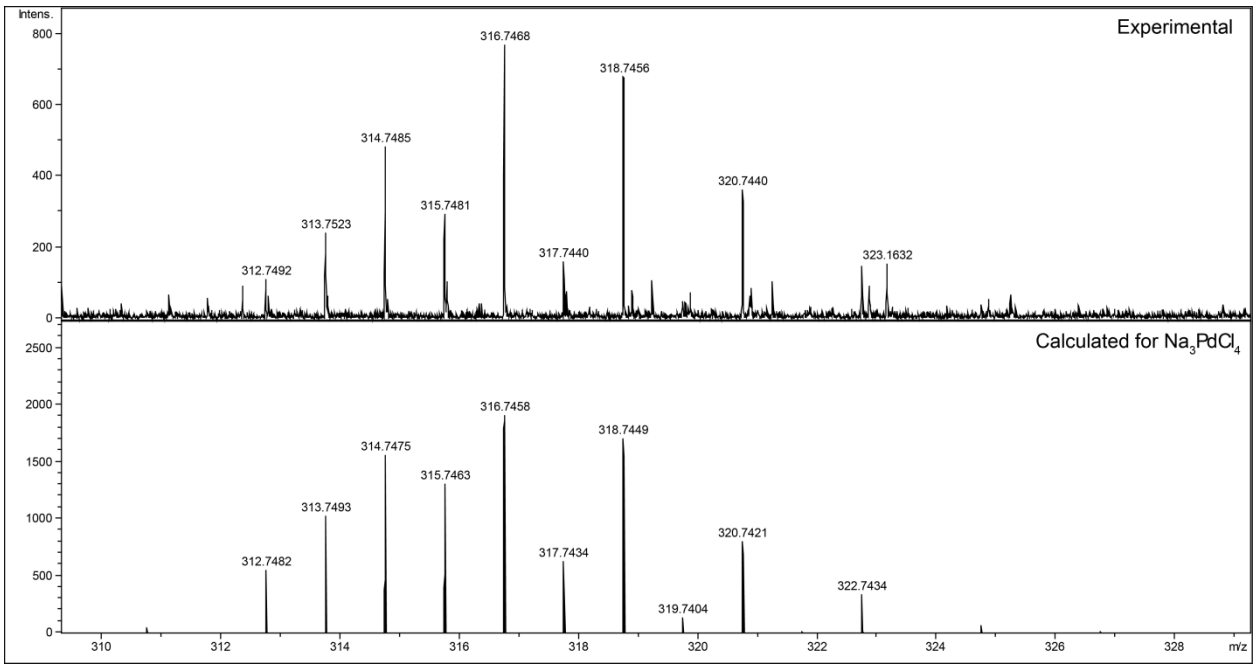



**Figure S27**. $Na_3PdCl_4$ (positive ion mode), $\Delta$ = 3.16 ppm.

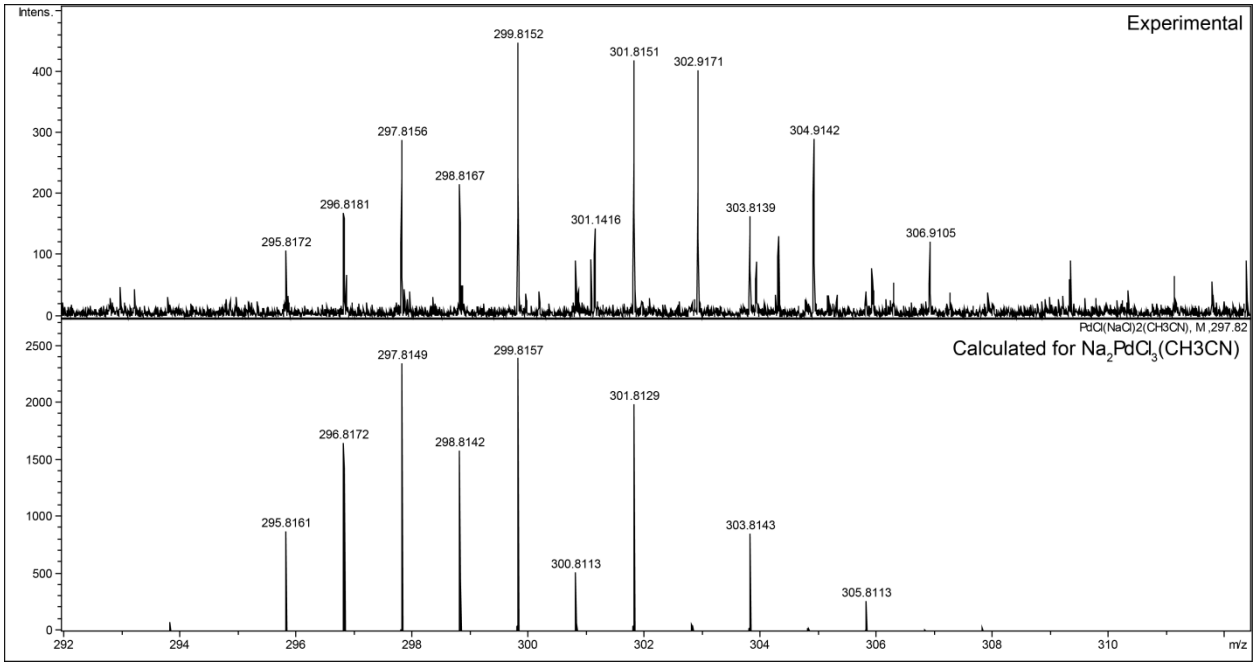



**Figure S28**. $Na_2PdCl_3(CH_3CN)$ (positive ion mode), $\Delta$ = 1.67 ppm.

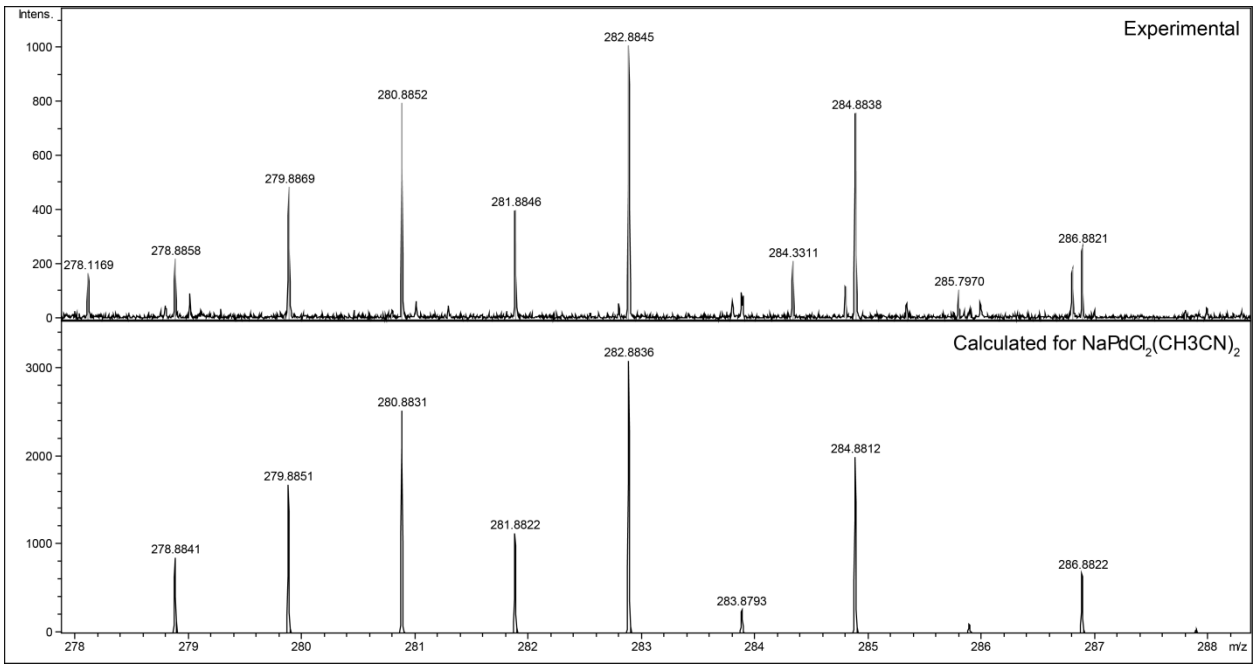



**Figure S29**. $NaPdCl_2(CH_3CN)_2$ (positive ion mode), $\Delta$ = 3.18 ppm.

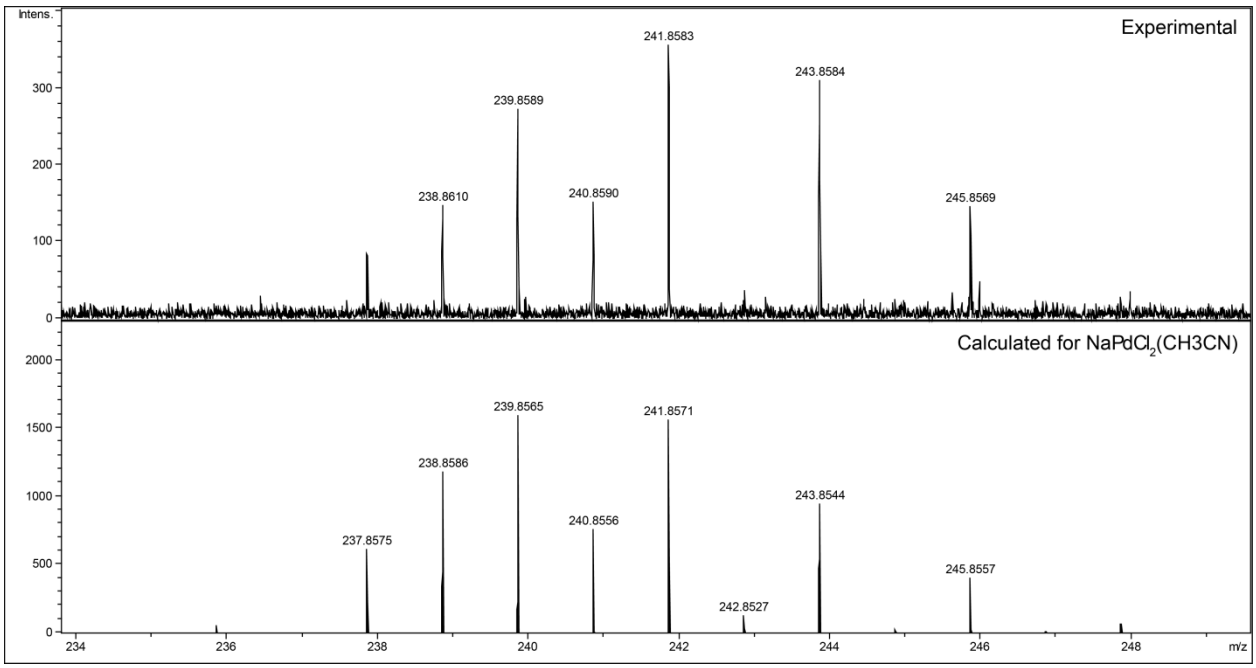



**Figure S30**. $NaPdCl_2(CH_3CN)$ (positive ion mode), $\Delta$ = 4.96 ppm.

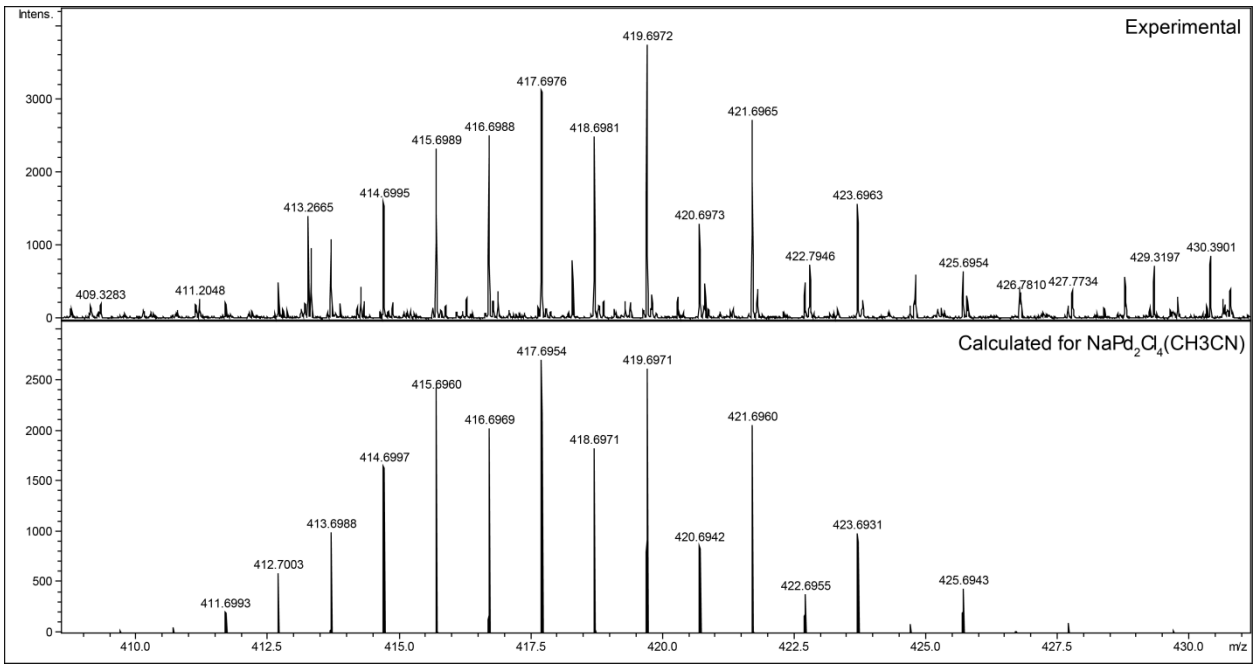



**Figure S31**. $NaPd_2Cl_4(CH_3CN)$ (positive ion mode), $\Delta$ = 0.24 ppm.

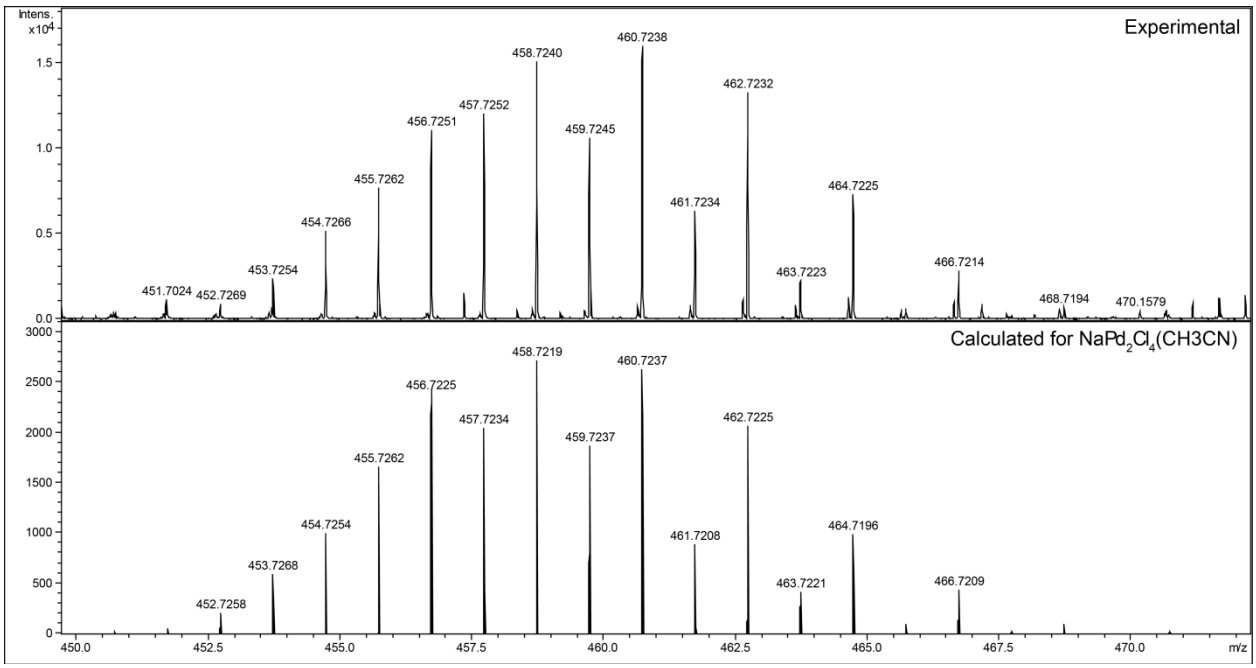



**Figure S32**. $NaPd_2Cl_4(CH_3CN)$ (positive ion mode), $\Delta$ = 2.86 ppm.

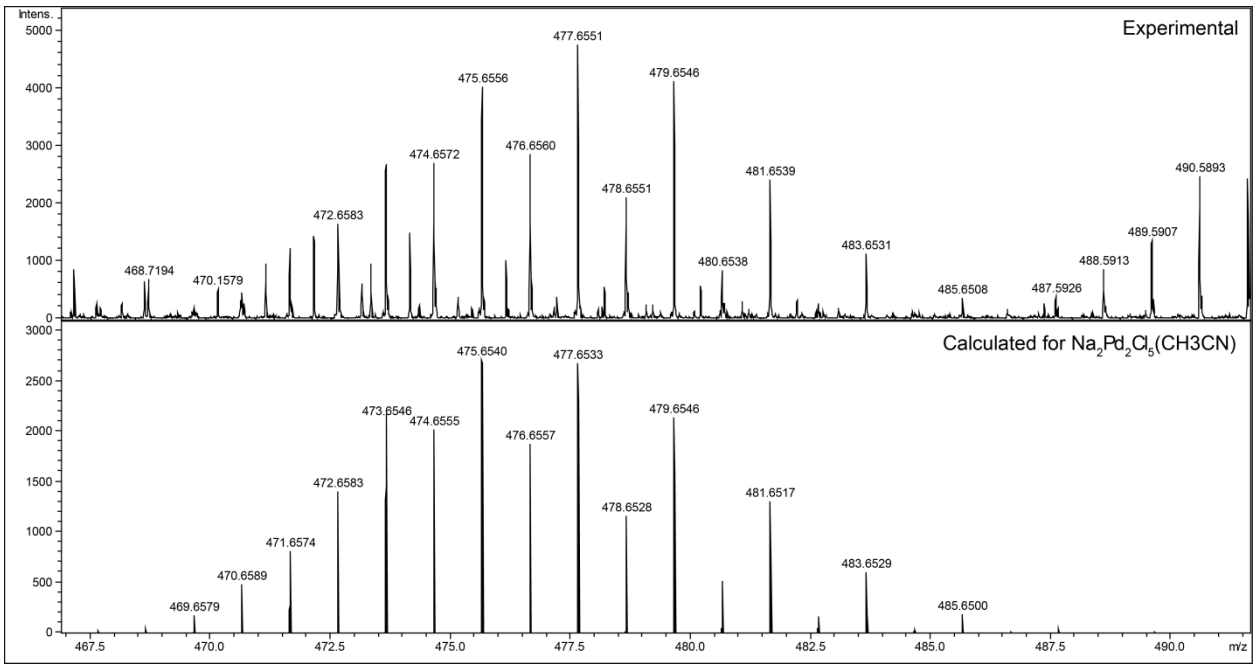



**Figure S33**. $Na_2Pd_2Cl_5(CH_3CN)$ (positive ion mode), $\Delta$ = 3.78 ppm.

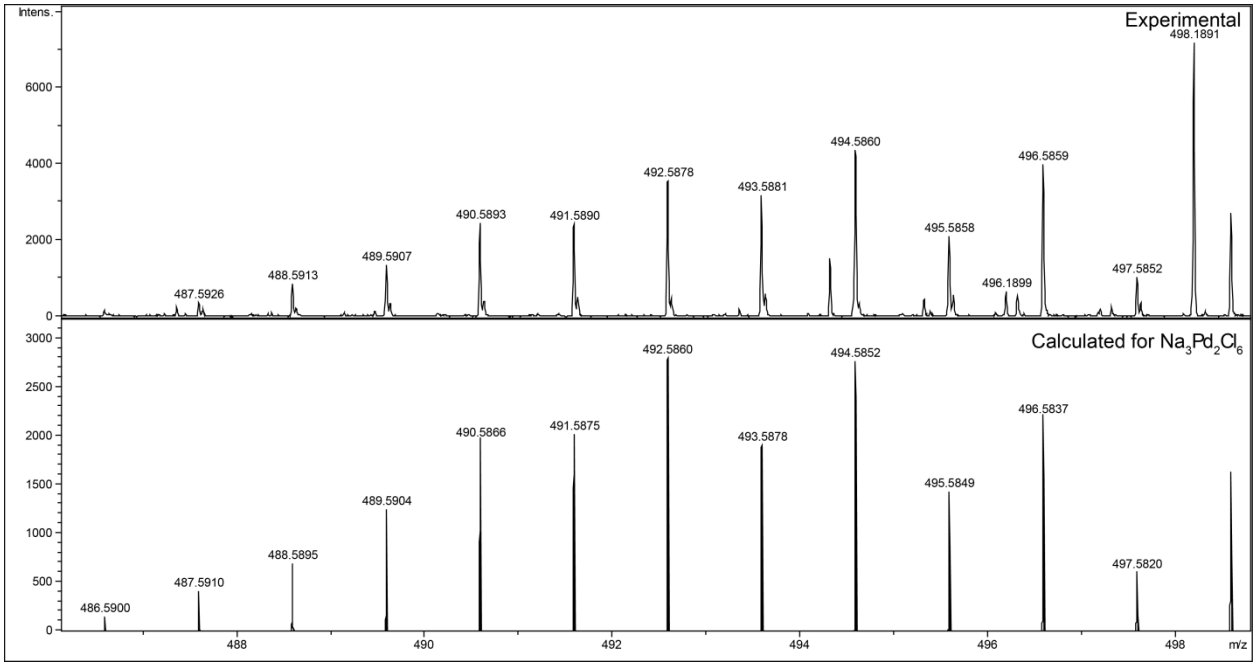



**Figure S34**. $Na_3Pd_2Cl_6$ (positive ion mode), $\Delta$ = 3.65 ppm.

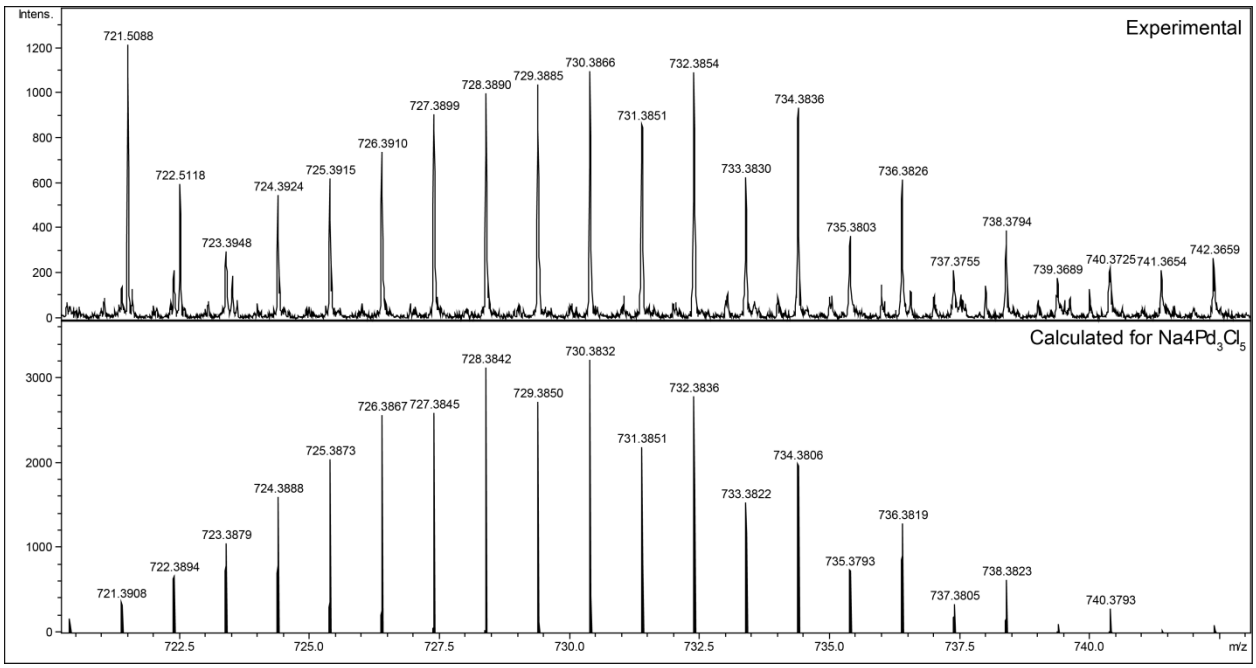



**Figure S35**. $Na_4Pd_3Cl_5$ (positive ion mode), $\Delta$ = 4.66 ppm.

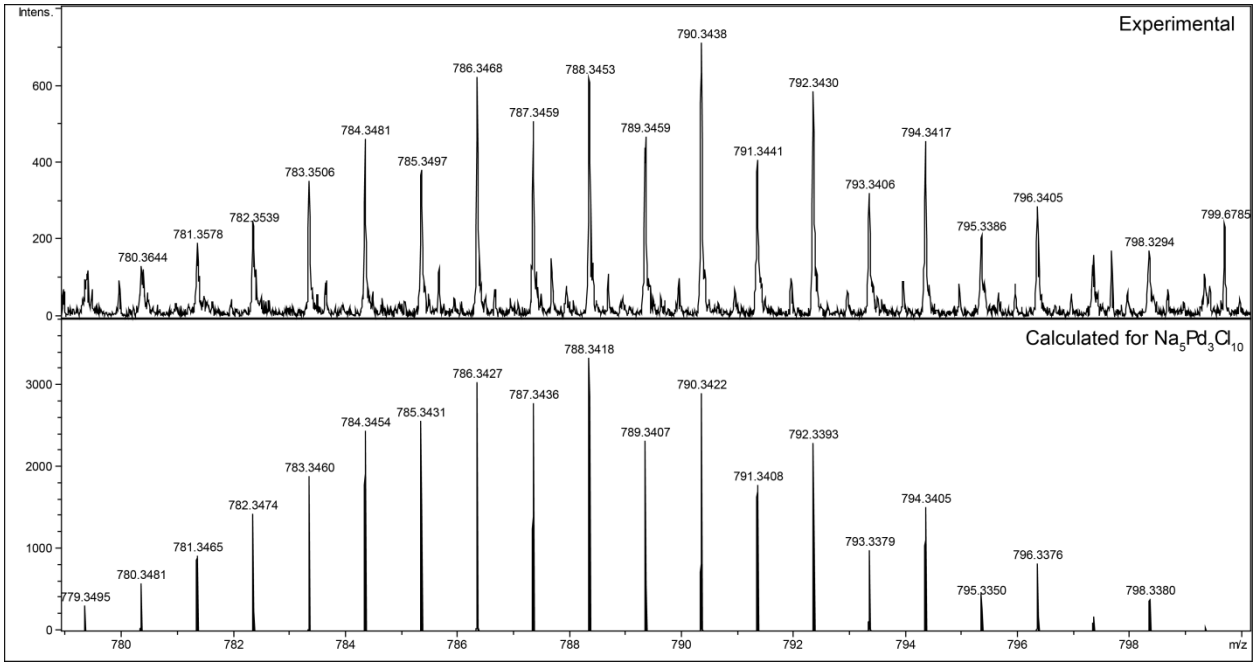



**Figure S36**. $Na_5Pd_3Cl_{10}$ (positive ion mode), $\Delta$ = 4.44 ppm.

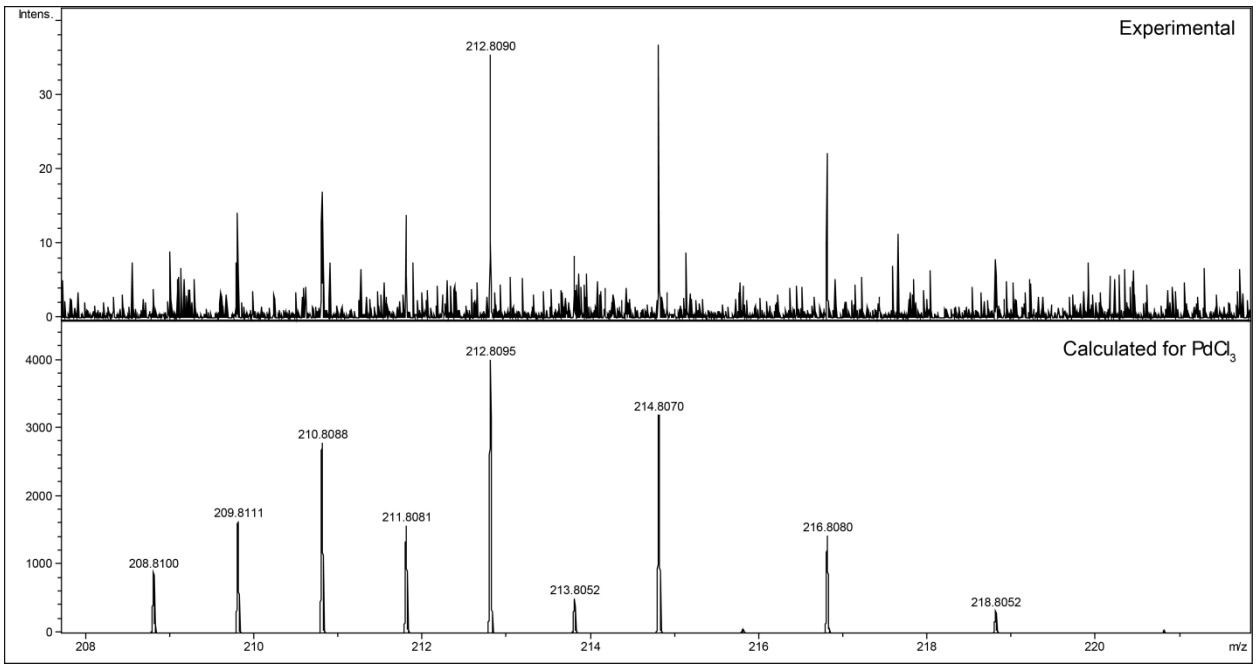



**Figure S37**. $PdCl_3$ (negative ion mode), $\Delta$ = 2.35 ppm.

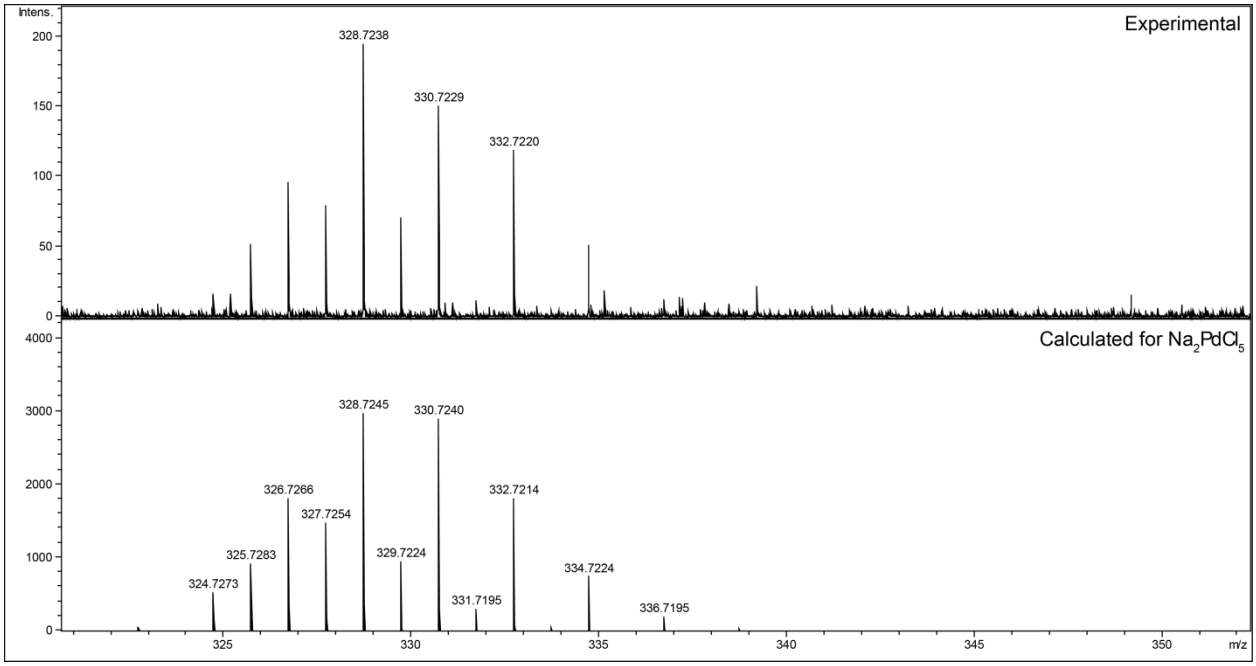



**Figure S38**. $Na_2PdCl_5$ (negative ion mode), $\Delta$ = 2.13 ppm.