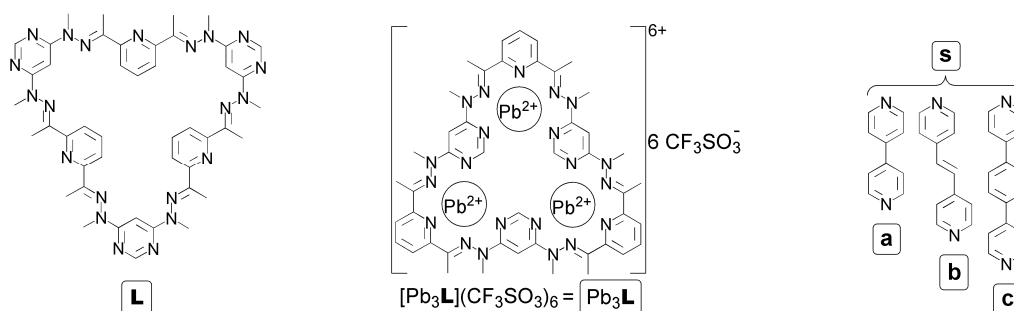


Supporting Information for the paper

Anion-encapsulating, discrete prisms and extended frusta, from trimetallated triangular macrocycles and linkers

A. Synthesis of compounds 1 - 3	page 1
B. Crystal data for compounds 1 - 3	page 2
B1. Table with crystallographic data for compounds 1 - 3	page 2
B2. Collection and refinement.....	page 2
B3. Powder X-ray diffraction.....	page 6
B4. References.....	page 8
B5. Distances and angles in compounds 1 - 3	page 9
B6. Formulae used to calculate several distances and angles.....	page 10
C. Elemental analysis.....	page 11
D. Infrared spectroscopy.....	page 11
E. Mass spectrometry ESI-MS.....	page 13
E1. Compound 1	page 13
E2. Compound 2	page 18
E3. Compound 3	page 25
F. NMR spectroscopy.....	page 33
F1. ¹ H NMR-monitored titrations.....	page 33
F2. ¹ H DOSY NMR.....	page 35
F3. ¹⁹ F NMR.....	page 36
G. Anion exchanges with PF ₆ ⁻	page 39
G1. Table with crystallographic data for compounds 1PF₆ - 3PF₆	page 39
G2. Distances and angles in compounds 1PF₆ - 3PF₆	page 40
H. Change of the solvent used for NMR: CD ₃ CN -> CD ₃ OD.....	page 41
I. Selection.....	page 41

Structural formulae of ligand **L, linkers (connectors) **a - c** and complex [Pb₃L](CF₃SO₃)₆**



A. Synthesis of compounds **1 - 3**

In a typical synthesis, to a suspension of macrocyclic ligand **L** (2.00 mg, 2.26 x 10⁻³ mmol, 1 equiv.) in acetonitrile (0.2 mL) was added a solution of Pb(OTf)₂ (3.42 mg, 6.77 x 10⁻³ mmol, 3 equiv.; OTf = CF₃SO₃⁻) in acetonitrile (0.4 mL) and the mixture was stirred under reflux for about 10-15 min. After cooling, it was added to a mixture of linker **a - c** (3.39 x 10⁻³ mmol, 1.5 equiv.) and acetonitrile (0.3 mL), and the mixture thus obtained was stirred for 20 minutes. After centrifugation, slow diffusion of diethyl ether afforded yellow crystals of macrocyclic complexes with linkers. Average yields (based on recovered, dried crystals): 4.38 mg (≈ 74%, compound **1**), 4.40 mg (≈ 73%, compound **2**) and 4.34 mg (≈ 70%, compound **3**).

B. Crystal data for compounds 1 - 3.

B1. Table 1. Crystallographic data for compounds 1 - 3.

	1	2	3
empirical formulae	C ₁₃₈ H ₁₃₅ F ₃₆ N ₅₁ O ₃₆ Pb ₆ S ₁₂ + [masked solvent]	C ₁₄₁ H ₁₃₂ F ₃₆ N ₄₈ O ₃₆ Pb ₆ S ₁₂ + [masked solvent]	C ₁₅₃ H ₁₄₇ F ₂₇ N ₅₁ O ₂₇ Pb ₆ S ₉ + [masked solvent/counterions]
	C ₁₂₀ H ₁₂₆ N ₄₈ Pb ₆ , 12 CF ₃ O ₃ S, 3 CH ₃ CN + [10.5 CH ₃ CN] where C ₁₂₀ H ₁₂₆ N ₄₈ Pb ₆ = Pb ₆ L ₂ a ₃	C ₁₂₆ H ₁₃₂ N ₄₈ Pb ₆ , 9 CF ₃ O ₃ S, 6 (CF _{1.5} O _{1.5} S _{0.5}) + [16 CH ₃ CN] where C ₁₂₆ H ₁₃₂ N ₄₈ Pb ₆ = Pb ₆ L ₂ b ₃	C ₁₃₈ H ₁₃₈ N ₄₈ Pb ₆ , 9 CF ₃ O ₃ S, 3 CH ₃ CN + [3 CF ₃ O ₃ S, 25 CH ₃ CN] where C ₁₃₈ H ₁₃₈ N ₄₈ Pb ₆ = Pb ₆ L ₂ c ₃
<i>f</i> w [g/mol]	5395.82	5386.80	5176.89
crystal system	hexagonal	trigonal	trigonal
space group	<i>P</i> 6 ₃ / <i>m</i>	<i>R</i> 3̄	<i>R</i> 3̄
Cell <i>a</i> = <i>b</i> [Å]	21.0549(6)	21.1054(2)	21.0331(2)
<i>c</i>	31.7103(14)	51.1319(10)	58.2510(12)
<i>V</i> [Å ³]	12174.1(9)	19724.7(5)	22317.2(6)
<i>Z</i>	2	3	3
<i>T</i> [K]	150(2)	150(2)	150(2)
<i>λ</i> [Å]	GaKα (1.34143)	GaKα (1.34143)	MoKα (0.71073)
<i>d</i> _c [g cm ⁻³]	1.472	1.360	1.156
<i>μ</i> (<i>λ</i>) [mm ⁻¹]	6.457	6.185	3.513
<i>F</i> [000]	5232	7830	7551
2 <i>θ</i> _{max} [°]	128	129	61
meas rflns	51469	93267	107507
unique rflns	9933	11021	14376
<i>R</i> _{int}	0.0964	0.0471	0.0939
<i>R</i> _{sigma}	0.0665	0.0275	0.0633
rflns with <i>I</i> > 2σ(<i>I</i>)	5261	7300	8067
refined params	404	409	399
restraints	13	25	4
<i>R</i> 1(<i>I</i> > 2σ(<i>I</i>)) ^a	0.0696	0.0800	0.0515
<i>wR</i> 2(all data) ^b	0.2213	0.2730	0.1633
largest diff. peak/hole / e Å ⁻³	2.25/-1.68	3.16/-3.42	1.27/-1.53
CCDC number	1436334	2285236	2285239

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^b wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

B2. Collection and refinement

Crystals suitable for single crystal X-ray diffraction (XRD) were selected in perfluoroalkylether oil and mounted on a diffractometer equipped with an Oxford Cryosystem.

Single-crystal X-ray diffraction data of **1** and **2** were collected using GaK α radiation ($\lambda = 1.34143 \text{ \AA}$) generated by an ExcillumGa Metaljet D2 with a Montel multilayer optic on a STOE STADI Vari (DectrisEiger Hybrid Pixel Detector 4M).

Single-crystal X-ray diffraction data of **3** were collected using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) generated by a microfocus sealed X-ray tube (AXO Mo) with a multilayer optic on a STOE STADI Vari (EIGER2 1M CDTE).

Raw intensity data were collected and treated with the STOE X-Area software. All data were corrected for Lorentz and polarization effects.

For **1** – **3** interframe scaling of the dataset was done with the implemented program STOE LANA and a multi-scan absorption correction was applied by scaling of reflection intensities.¹ Absorption corrections by integration based on a crystal description did not lead to better *R* values and a further reduction of the residual electron density found for all datasets close to the Pb atoms.²

Using Olex2,³ the structures were solved with the ShelXT⁴ structure solution program using Intrinsic Phasing and refined with the refinement⁵ package using Least Squares minimization.

Molecular diagrams were prepared using Diamond⁶.

Crystals of **1** – **3** reveal problems when investigated by single crystal X-ray diffraction (SCXRD). Several crystals have been tested and measured for all compounds on different X-ray machines amongst others with a STOE StadiVari equipped with a Ga-metaljet X-ray source and an Eiger 4M pixel detector, which is currently the most powerful laboratory X-ray equipment available.

Although the crystals of **1** – **3** comprise an appropriate size (up to 0.5 mm), nice facets and appear clear when quickly selected from the mother liquor, only freshly separated crystals from the mother liquor display acceptable diffraction patterns indicative for a quick loss of

solvent or non solvent molecules from the crystals accompanied by degradation of the long-range order. Crystals of **1** even show some degradation upon the course of the measurement, even when cooled to 150 K.

Quickly mounted crystals do hardly diffract above 2θ 45° (MoK α) and 85° (GaK α), and $R(\text{Int})$ and $R(\sigma)$ values significantly increase above 20 % for data at higher diffraction angles (**1**: for $d < 0.92 \text{ \AA}$, $R(\text{Int}) > 24.4 \%$ and $I/\sigma < 1.7$; **2**: for $d < 0.83 \text{ \AA}$, $R(\text{Int}) > 24.4 \%$ and $I/\sigma < 3.2$; **3**: for $d < 0.92 \text{ \AA}$, $R(\text{Int}) > 21.4 \%$ and $I/\sigma < 1.5$). This indicates a poor crystallinity i. e. limited long-range order. In addition, for **1**, these R factors distinctly get worse the more data are measured and integrated. Therefore, the integration of **1** was performed only with a minimum of frames required for approximate completeness in hexagonal symmetry.

In compounds **1–3** all Pb, N and C atoms of the cationic cage structure were refined with anisotropic displacement parameters. H atoms were calculated in fixed positions.

Problems arise from the localization and refinement of a part of the trifluoromethanesulfonate (CF_3SO_3^-) anions. For a proper charge balance of the Pb^{2+} ions one expects a dual number of anions (per unit cell for **1**: 24 CF_3SO_3^- , for **2** and **3**: 36 CF_3SO_3^-).

In all three structures, in the asymmetric unit two trifluoromethanesulfonate anions comprising S(1) and S(2) (located on special positions) could be well localized and refined with reasonable anisotropic displacement parameters, although one of the anions is twofold disordered with the S atom lying on an inversion center. Two additional positions (S(3) and S(4)) for such anions could be identified in **1** and **2**. However, these anions could only be refined with restraints and comprise very large thermal displacement parameters when set to full occupancy. This strongly indicates that these anions are distinctly disordered on these positions or even further distributed over the remaining large voids of the structures (see below). For the dataset of **3** only one of these latter anions (S(3)) could be localized and refined leading to the situation that 9 of the 36 expected CF_3SO_3^- anions are missing.

The additional electron density which was identified within large voids of the crystal structures of **1** – **3** was corrected using the solvent masking routine implemented in Olex2, which is based on the method described by van der Sluis and Spek for the PLATON⁷ program. The reaction solvent CH₃CN has been localized in part in the structures, whereas the non solvent (C₂H₅)₂O has been identified by ¹H NMR of shortly dried and redissolved crystals; the incorporation of H₂O is suggested by the elemental analysis. However, as the ratios are unclear, we simply used CH₃CN for the calculation.

Applied corrections:

1 → a total of 448 electrons in a potential solvent accessible area of 3056 Å³.

This is formally consistent with the presence of 10.5 CH₃CN per formula unit, which account for 462 electrons per unit cell.

2 → a total of 1035 electrons in a potential solvent accessible area of 5235 Å³.

This is formally consistent with the presence of 16 CH₃CN per formula unit, which account for 1056 electrons per unit cell.

3 → a total of 2367 electrons in a potential solvent accessible area of 9246 Å³.

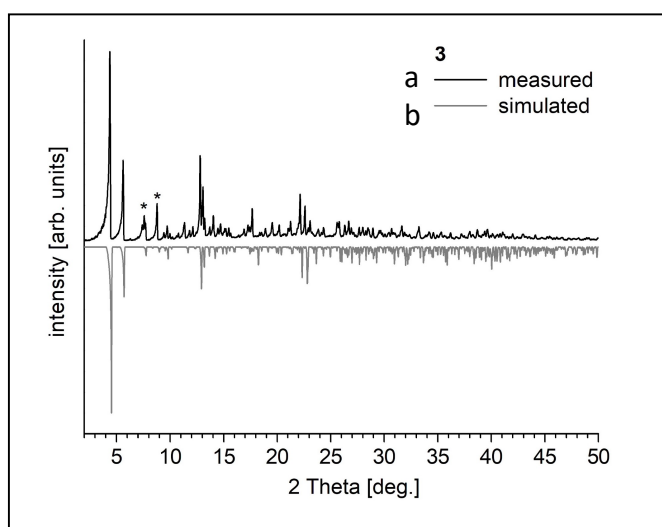
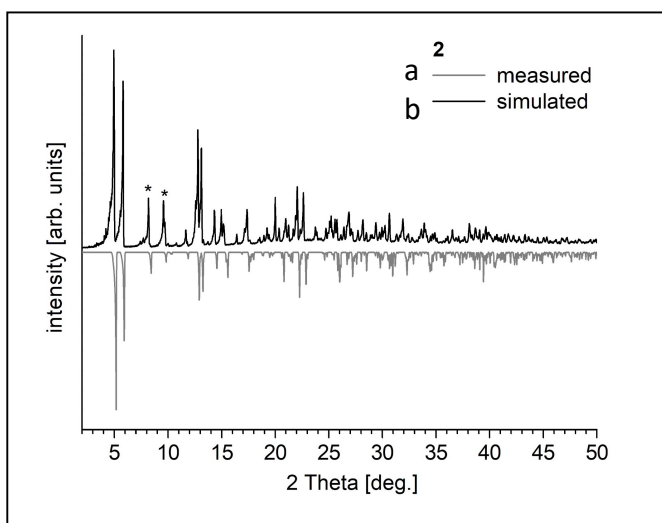
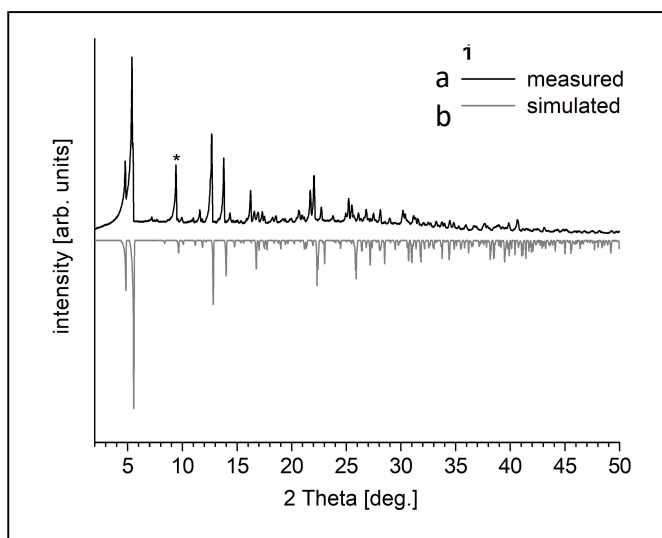
This is formally consistent with the presence of 3 CF₃SO₃ and 18 CH₃CN per formula unit, which account for 2367 electrons per unit cell.

CCDC-1436334 (**1**), 2285236 (**2**) and 2285239 (**3**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (international) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

B3. Powder X-ray diffraction patterns for **1 - 3** (suspension of powder of crystals), were measured at room temperature on a STOE STADI P diffractometer (Cu-K $_{\alpha 1}$ radiation, Germanium primary monochromator, Debye-Scherrer geometry, Mythen 1K detector) in sealed glass capillaries. The theoretical powder diffraction patterns were calculated on the basis of the atom coordinates obtained from single crystal X-ray analysis (150 K) by using the program package STOE WinXPOW.⁸

Most of the main reflection peaks correspond to the simulated patterns of **1 - 3** (see Figure below). Slightly increasing differences in the position of the peaks (like those of **1a** *versus* **1b** and of **2a** *versus* **2b**) with increasing detection angle arise from the temperature difference between data collections (single crystal XRD at 180 K *vs.* powder XRD at room temperature) and / or are indicative for structural changes upon the loss of lattice solvent or non solvent molecules. Differences in the intensity of calculated and measured peaks might arise from absorption effects and / or orientation of plate-like crystals in the glass capillaries. Peaks in the low 2 theta region which deviate strongly from the calculated patterns have been marked with an asterisk and might indicate the existence of a minor impurity compound crystallizing with a much smaller unit cell and could not be identified by single crystal XRD.

Measured (black) and simulated (grey) powder X-ray patterns ($\text{CuK}\alpha_1$) for compounds **1** – **3** (measured as suspension of grinded microcrystals).



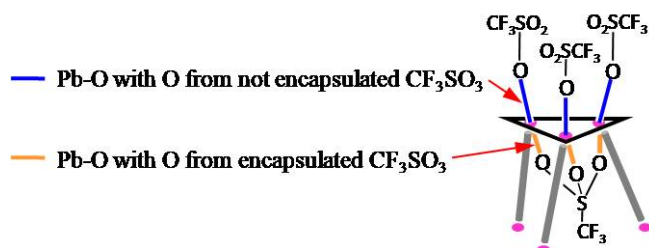
B4. References

- (1) STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis(μ_2 -acetato)-diaqua-di-copper(II)", *Acta Chim. Slovaca* 2016, **9** (2), 136 - 140.
- (2) STOE X-Red32, absorption correction by Gaussian integration, analogous to P. Coppens, "The Evaluation of Absorption and Extinction in Single-Crystal Structure Analysis", published in F. R. Ahmed (Editor), "Crystallographic Computing", Munksgaard, Copenhagen, **1970**, 255 - 270.
- (3) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.
- (4) G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3 - 8.
- (5) G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3 - 8.
- (6) K. Brandenburg, Diamond Version 2.1d, Crystal Impact GbR, 1996-2000.
- (7) A. L. Spek, *Acta Cryst.* 1990, **A46**, C-34.
- (8) STOE, WinXPOW, STOE & Cie GmbH, Darmstadt, 2000.

B5. Table 2. Values of several distances (centroid-to-centroid) and angles in structures **1-3**.

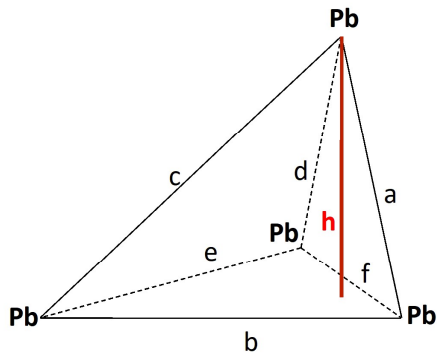
Distance (Å)	1	2	3
Pb-N _{pyrimidine} ¹⁾	2.90(1), 2.778(9), 2.778(7), 2.899(9), 2.899(6), 2.78(1)	2.76(1), 2.764(7), 2.764(9), 2.836(6), 2.836(9), 2.84(1)	2.878(3), 2.878(4), 2.878(6), 2.726(5), 2.726(6), 2.726(9)
Pb-N _{pyridine from ligand L} ¹⁾	2.559(8), 2.56(1), 2.56(1)	2.59(1), 2.59(1), 2.591(8)	2.751(5), 2.751(7), 2.751(9)
Pb-Nsp ² _{hydrazone} ¹⁾	2.64(1), 2.64(1), 2.642(9), 2.70(1), 2.70(1), 2.697(9)	2.66(1), 2.66(1), 2.661(9), 2.70(1), 2.70(1), 2.703(9)	2.681(6), 2.681(7), 2.681(8), 2.656(5), 2.656(7), 2.656(8)
Pb-N _{linker} ¹⁾	2.485(6), 2.485(6), 2.485(7)	2.58(2), 2.58(2), 2.58(2)	2.500(4), 2.500(4), 2.500(4)
Pb-O encapsulated triflate ²⁾	2.929(5), 2.929(7), 2.929(8)	2.94(1), 2.943(5), 2.943(7)	2.903(3), 2.903(4), 2.903(5)
Pb-O _{triflate} (not encapsulated) ²⁾	2.82(1), 2.82(1), 2.82(1)	2.88(1), 2.88(1), 2.878(9)	2.829(7), 2.829(6), 2.829(6)
Pb-Pb (in metallated macrocycle [Pb ₃ L] ⁶⁺) ¹⁾	7.0721(5), 7.0721(6), 7.0721(9)	7.0162(5), 7.0162(6), 7.0162(9)	7.0129(6), 7.0129(7), 7.0129(8)
Pb-Pb (connected through a linker s)	11.960(1)	14.142(1)	16.246(2)
Pb-Pb (in the lower (larger) base of the frustum)	no frustum	14.5927(5), 14.5927(8), 14.5927(8)	14.5162(5), 14.5162(7), 14.5162(9)
Edge of the macrocyclic complex ³⁾	17.772	17.835	17.661
Height of prism or frustum (distance between Pb ₃ planes)	11.960(1)	13.179	15.431
Diameter of the lower (smaller) rim of the calyx-like motif (see paper)	4.683	4.486	4.560
Diameter of the upper (larger) rim of the calyx-like motif (see paper)	12.040	12.213	12.188
Roughly estimated height of anion layer	3.895	3.865	3.986
Angles (°)	1	2	3
Angle between the N-N axis of the linker and the Pb ₃ plane of the macrocycle/larger base of the frustum	90.0	60.9	67.8
Twist angle	0.0	26.5	26.4

Notes

¹⁾ for one subunit [Pb₃LS₃]⁶⁺²⁾ see the figure below:**Charges and real bond type (single/double) were omitted for clarity.**³⁾ centroid-to-centroid distance between H atoms in position 4 of pyridine rings

B6. Formulae used to calculate several distances and angles

- Formula for calculating:
 - the height of a frustum
 - the height of the prism
 - the distance between parallel Pb planes

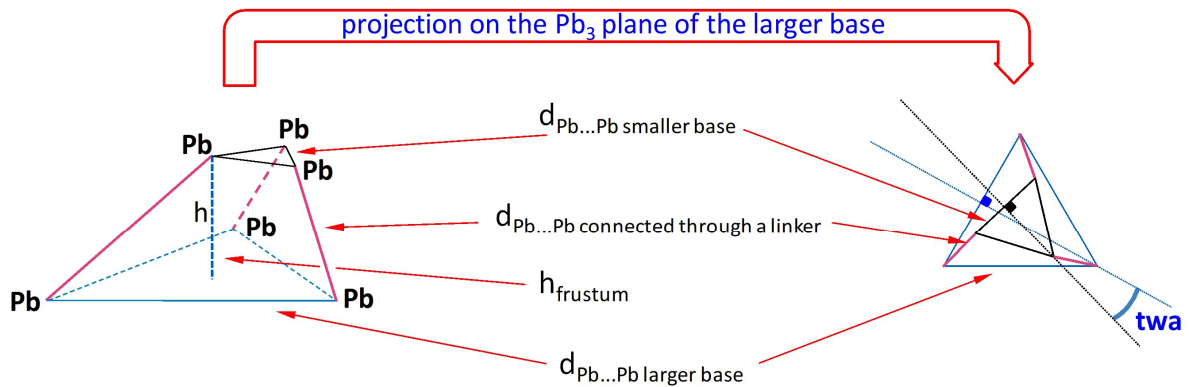


$$g (\text{\AA}) = \frac{[(a+d+f)(-a+d+f)(a-d+f)(a+d-f)]^{1/2}}{2f} \quad (\text{not shown})$$

$$i (\text{\AA}) = \frac{[(a+b+c)(-a+b+c)(a-b+c)(a+b-c)]^{1/2}}{2b} \quad (\text{not shown})$$

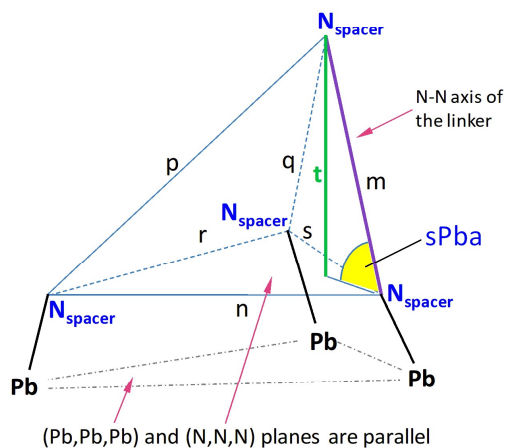
$$h (\text{\AA}) = \left(a^2 - \frac{2a^2 - g^2 - i^2 + \frac{e^2 - b^2 - f^2}{bf} [(a^2 - g^2)(a^2 - i^2)]^{1/2}}{1 - 0.25 \left(\frac{e^2 - b^2 - f^2}{bf} \right)^2} \right)^{1/2}$$

- Formula for calculating the twist angle



$$twa (^{\circ}) = \frac{180}{3,14} \times \arccos \frac{d_{Pb...Pb \text{ larger base}}^2 + d_{Pb...Pb \text{ smaller base}}^2 + 3 h_{\text{frustum}}^2 - 3 d_{Pb...Pb \text{ connected through a linker}}^2}{2 \times d_{Pb...Pb \text{ larger base}} \times d_{Pb...Pb \text{ smaller base}}}$$

3. Formula for calculating the angle between the N-N axis of the linker and the Pb₃ plane of the metallated macrocycle (compound **1**) or the Pb₃ plane of the larger base of the frustum (compounds **2** and **3**)



$$v (\text{\AA}) = \frac{[(m+q+s)(-m+q+s)(m-q+s)(m+q-s)]^{1/2}}{2s} \quad (\text{not shown})$$

$$w (\text{\AA}) = \frac{[(m+n+p)(-m+n+p)(m-n+p)(m+n-p)]^{1/2}}{2n} \quad (\text{not shown})$$

$$t (\text{\AA}) = \left[m^2 - \frac{2m^2 - v^2 - w^2 + \frac{r^2 - n^2 - s^2}{ns} [(m^2 - v^2)(m^2 - w^2)]^{1/2}}{1 - 0.25 \left(\frac{r^2 - n^2 - s^2}{ns} \right)^2} \right]^{1/2}$$

$$sPba (^\circ) = \frac{180}{3,14} \times \arcsin \frac{t}{m}$$

C. Elemental analysis

Table 3. Microanalysis results for compounds **1** - **3**.

Compound	Formula with x molecules of water	x	C (%)		H (%)		N (%)	
			found	calcd.	found	calcd.	found	calcd.
1	$\text{Pb}_6\text{L}_2\mathbf{a}_3(\text{OTf})_{12}(\text{H}_2\text{O})_x$	9	29.29	29.17	2.67	2.67	12.34	12.37
2	$\{\text{Pb}_6\text{L}_2\mathbf{b}_3(\text{OTf})_{12}(\text{H}_2\text{O})_x\}_n$	10	30.12	29.97	2.76	2.77	12.10	12.16
3	$\{\text{Pb}_6\text{L}_2\mathbf{c}_3(\text{OTf})_{12}(\text{H}_2\text{O})_x\}_n$	9	31.51	31.81	2.62	2.78	11.70	11.87

The crystals were dried for about four days under vacuum at room temperature and for about half an hour under vacuum at 45-50°C.

D. Infrared spectra of crystals of complexes **1** - **3**

1) A selection of main peaks; for IR spectra (Nicolet IS50 FT-IR), see below.

Compound **1**, wavenumbers: 514, 572, 634, 808, 1022, 1153, 1220, 1236, 1483, 1584 cm⁻¹.

Compound **2**, wavenumbers: 514, 634, 811, 1022, 1152, 1220, 1237, 1482, 1584 cm⁻¹.

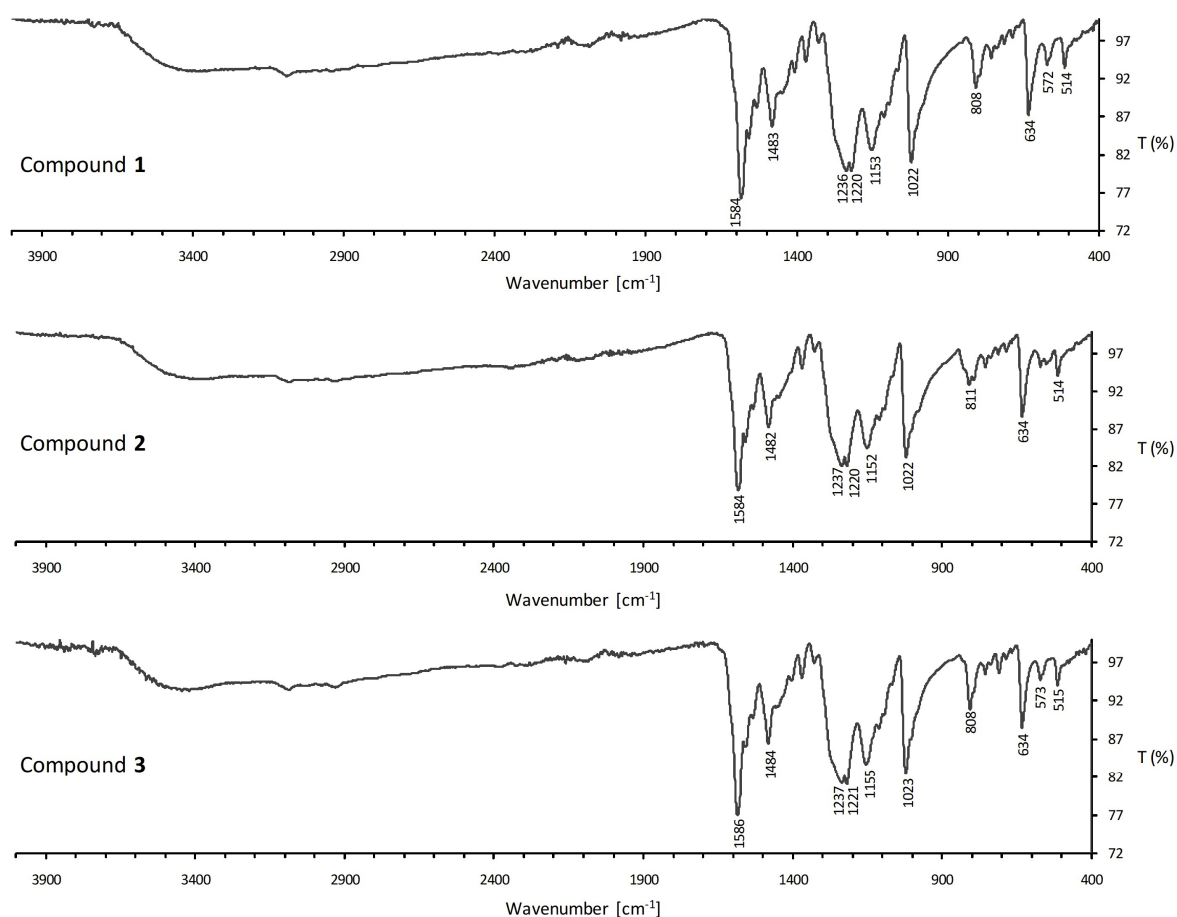
Compound **3**, wavenumbers: 515, 573, 634, 808, 1023, 1155, 1221, 1237, 1484, 1586 cm⁻¹.

2) Triflate anions give infrared (IR) bands which include those corresponding to symmetric group angle deformation $\delta_s\text{SO}_3$ (about 633 cm^{-1}), symmetric stretching $\nu_s\text{SO}_3$ (about 1022 cm^{-1}), and symmetric stretching $\nu_s\text{CF}_3$ (about 1237 cm^{-1}).

3) References: a) M. G. Miles, G. Doyle, R. P. Cooney, R. S. Tobias, *Spectrochim. Acta*, 1969, **25A**, 1515-1526; b) D. H. Johnston, D. F. Shiver, *Inorg. Chem.* 1993, **32**, 1045-104.

4) IR spectra of dried crystals of complexes 1 - 3 (Nicolet IS50 FT-IR).

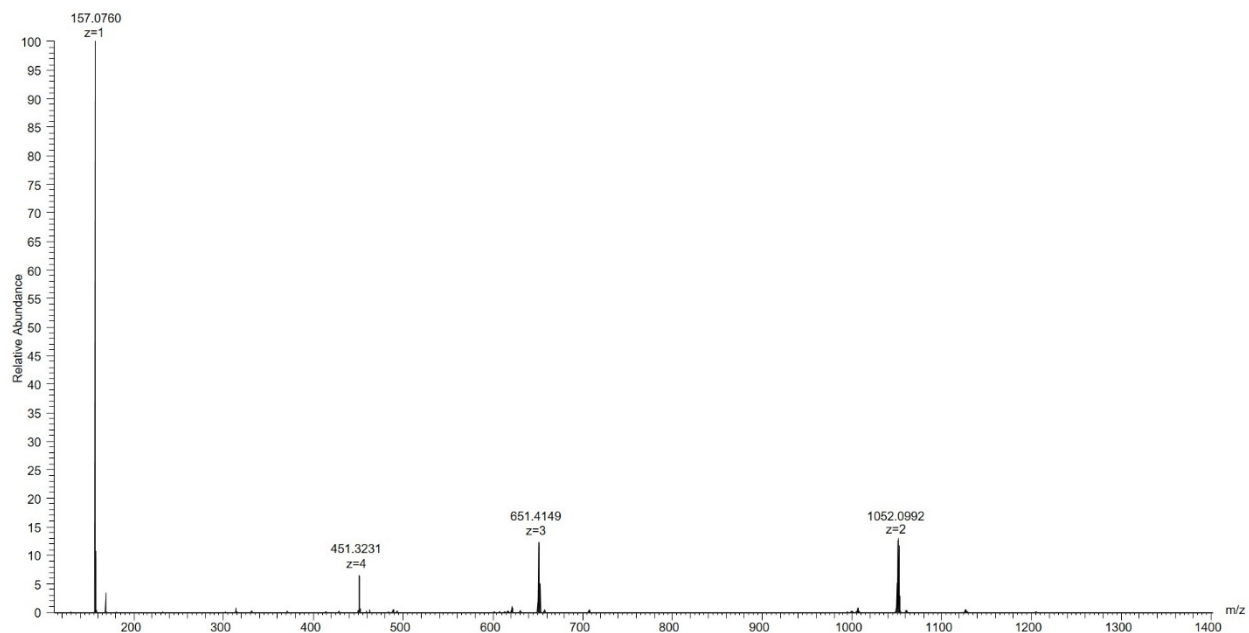
T = transmittance



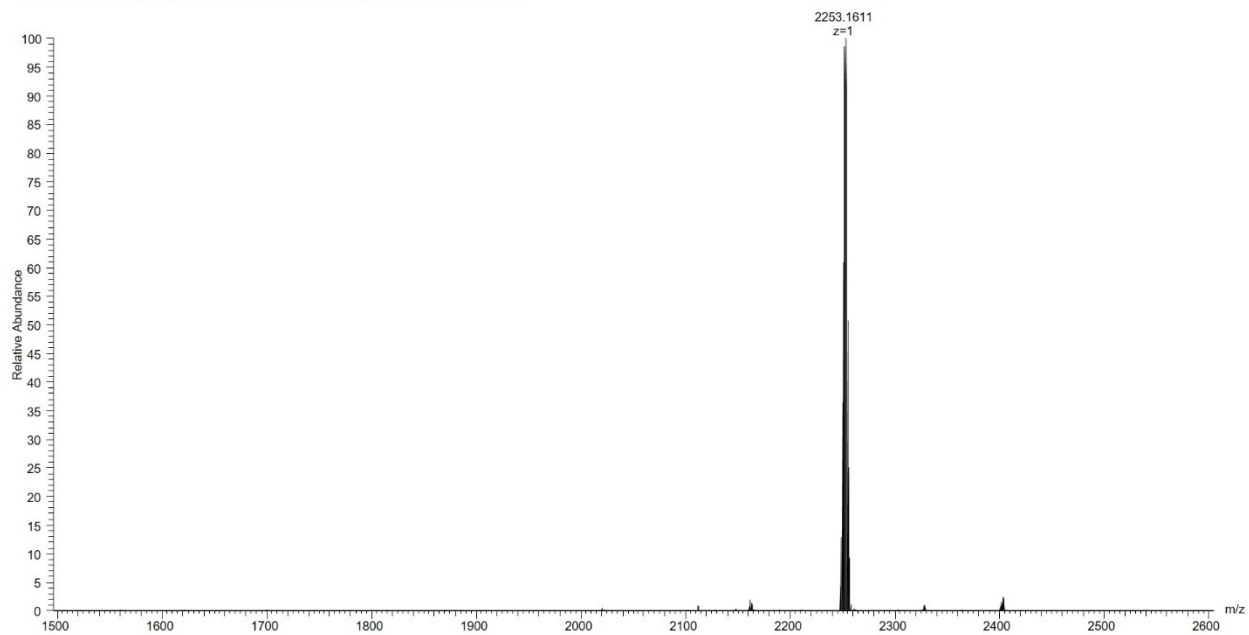
E. ESI-MS of redissolved crystals of complexes 1 – 3.

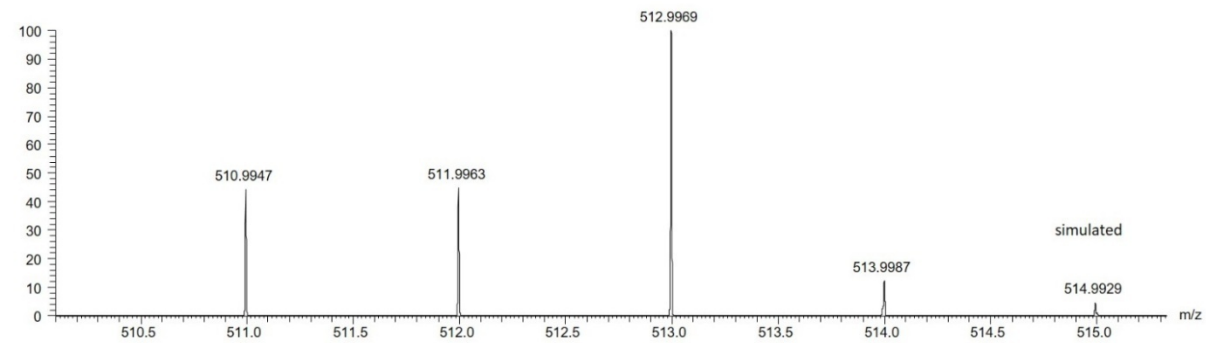
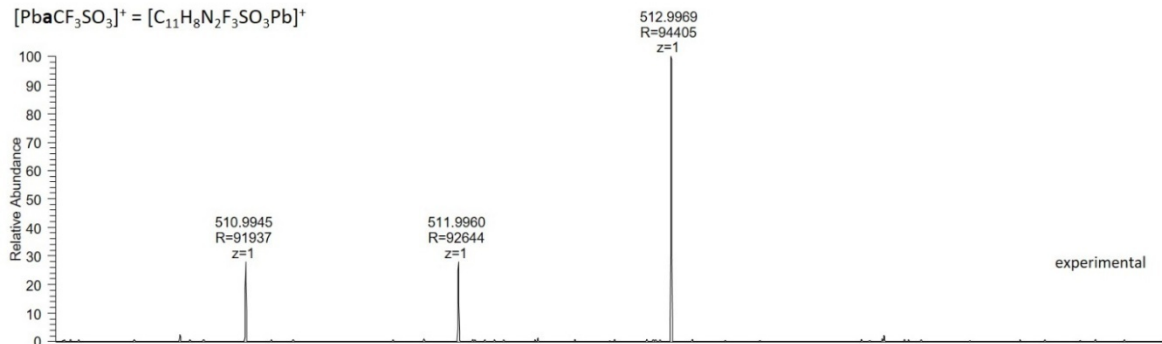
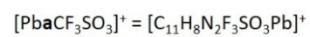
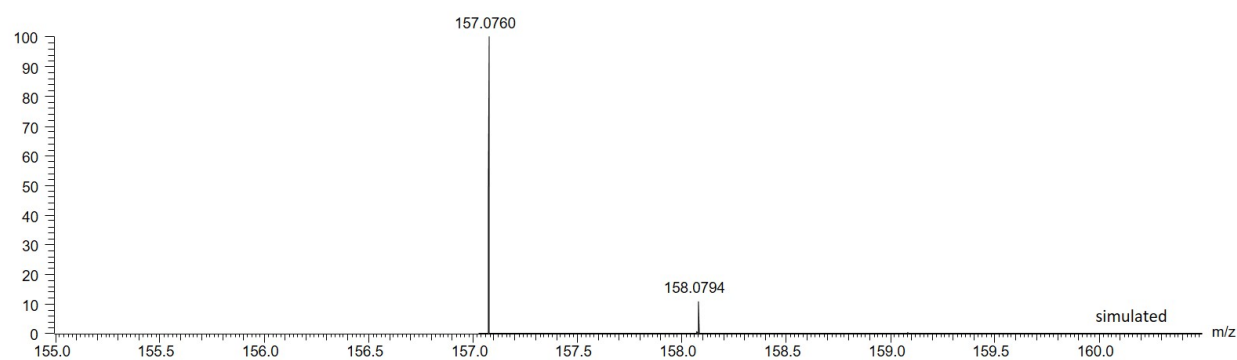
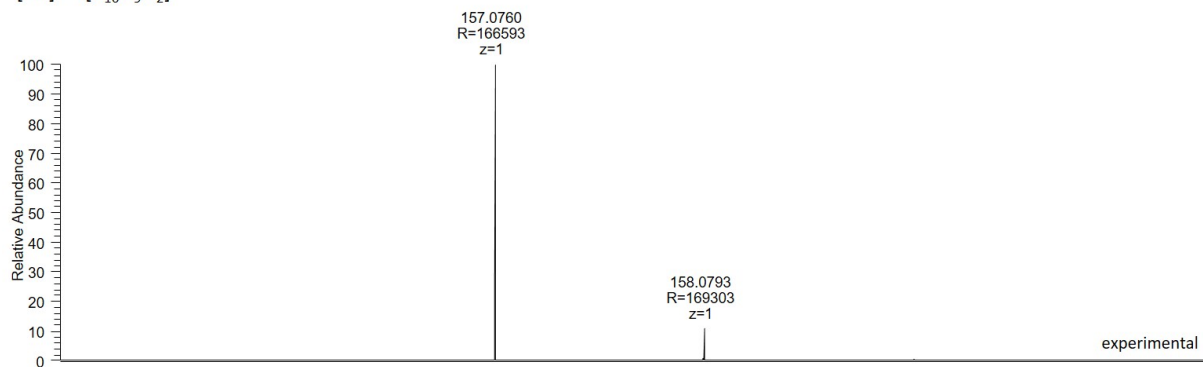
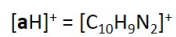
E1. Compound 1

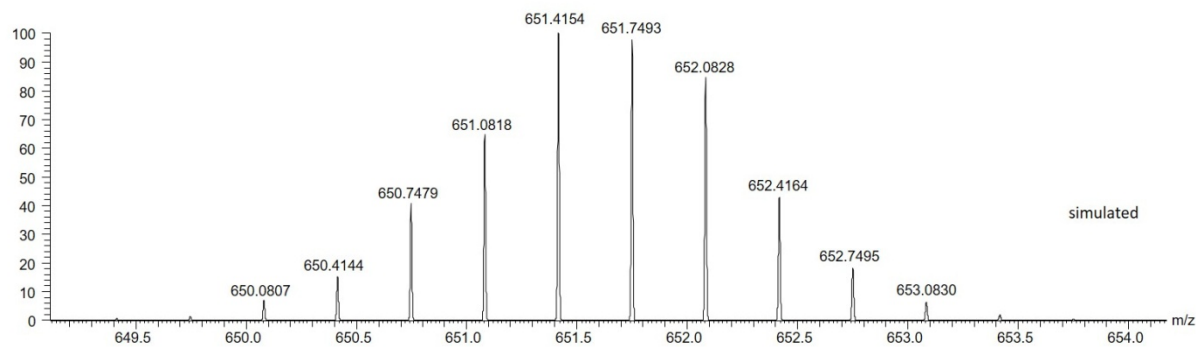
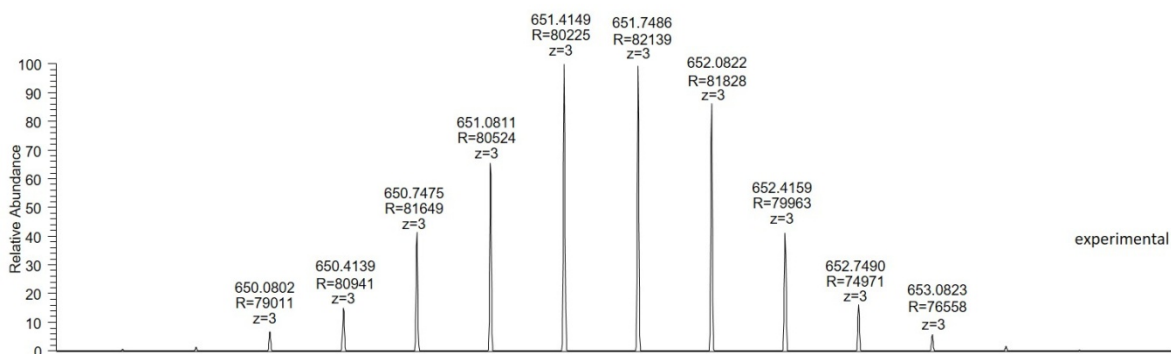
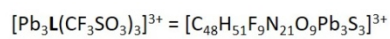
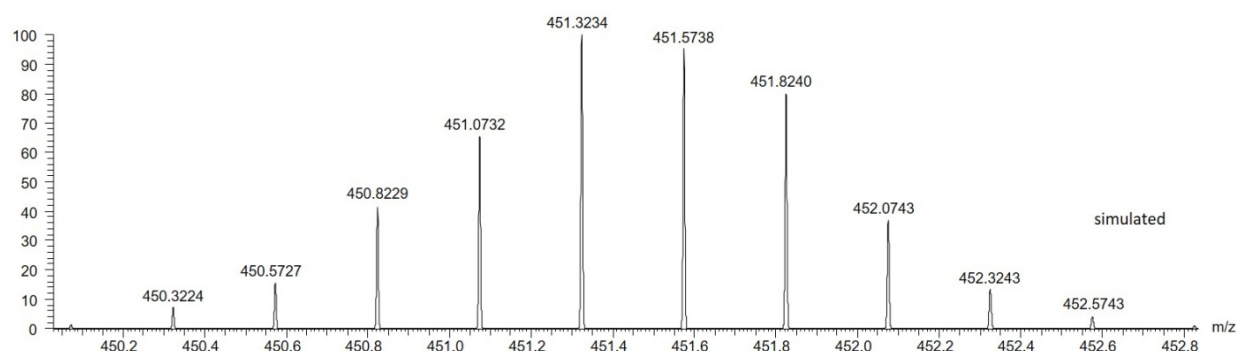
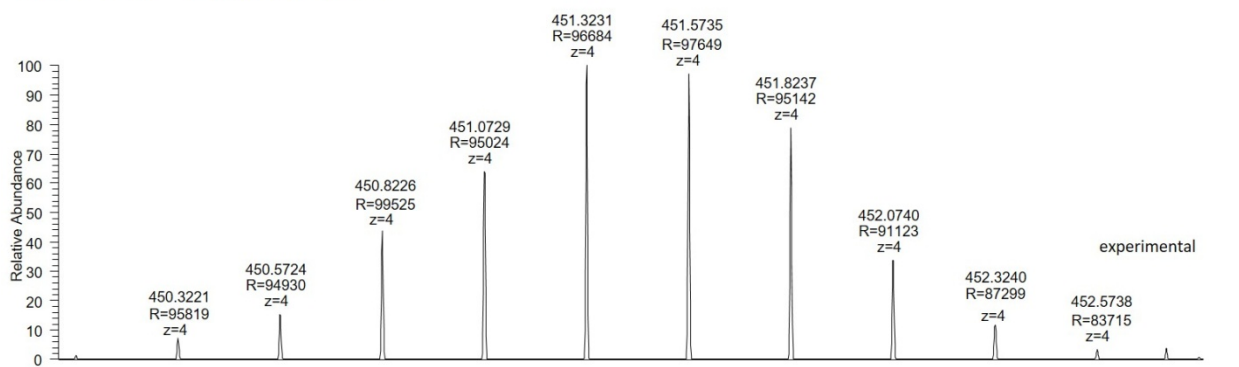
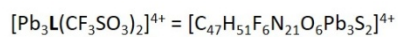
Part of the ESI-MS spectrum of redissolved crystals of compound 1

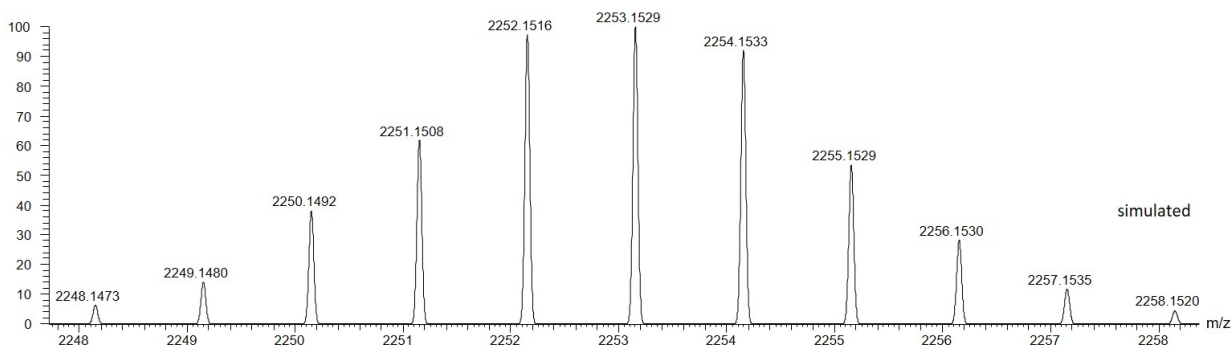
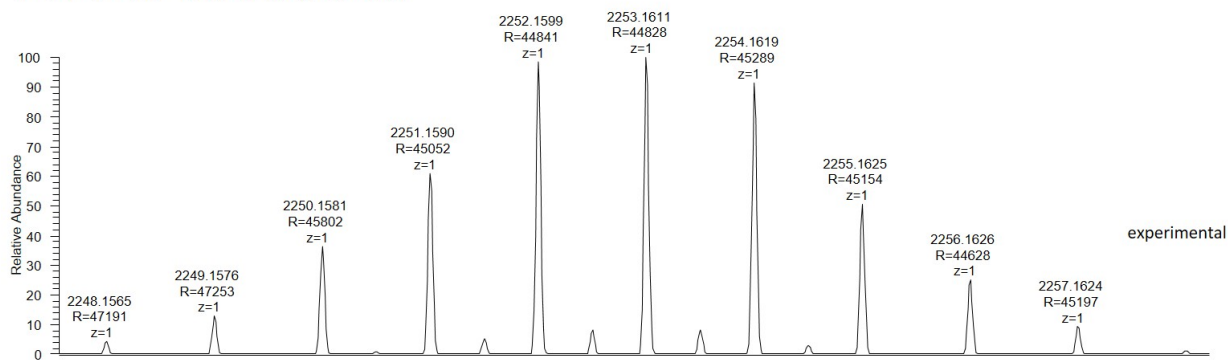
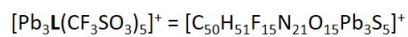
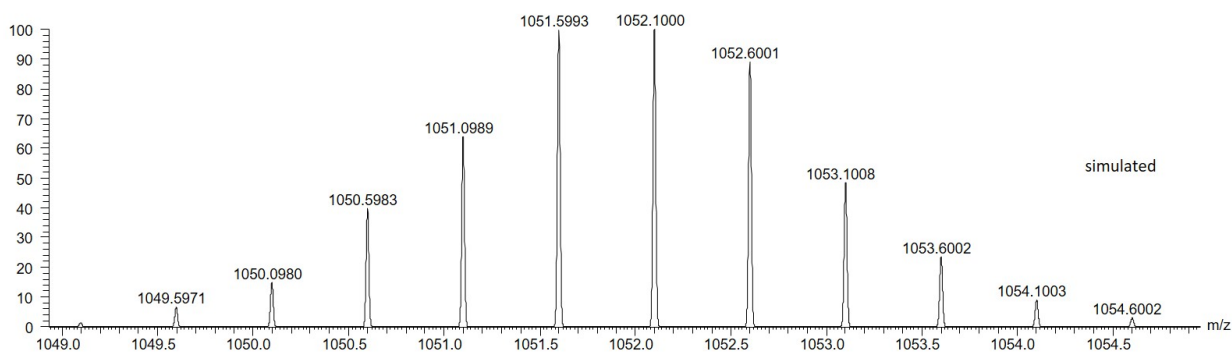
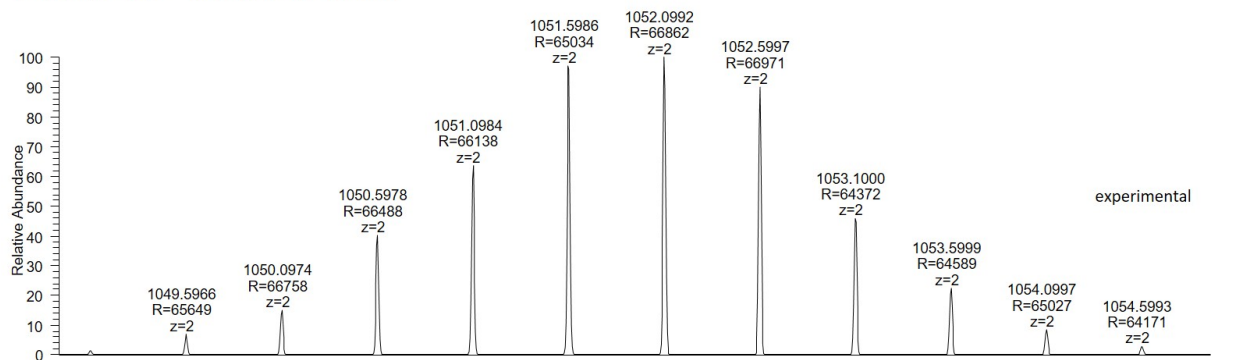
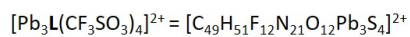


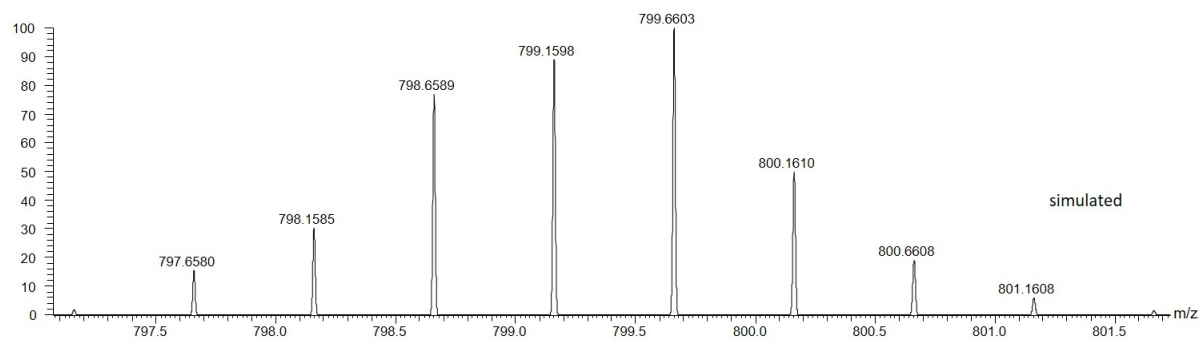
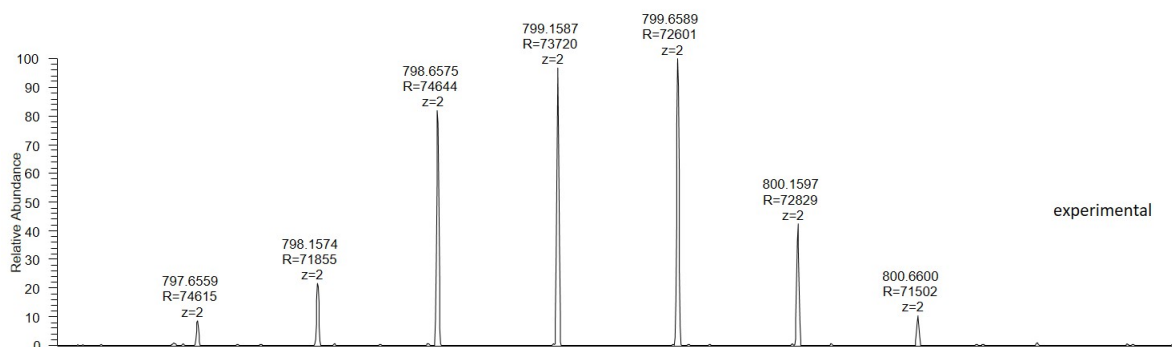
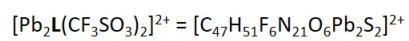
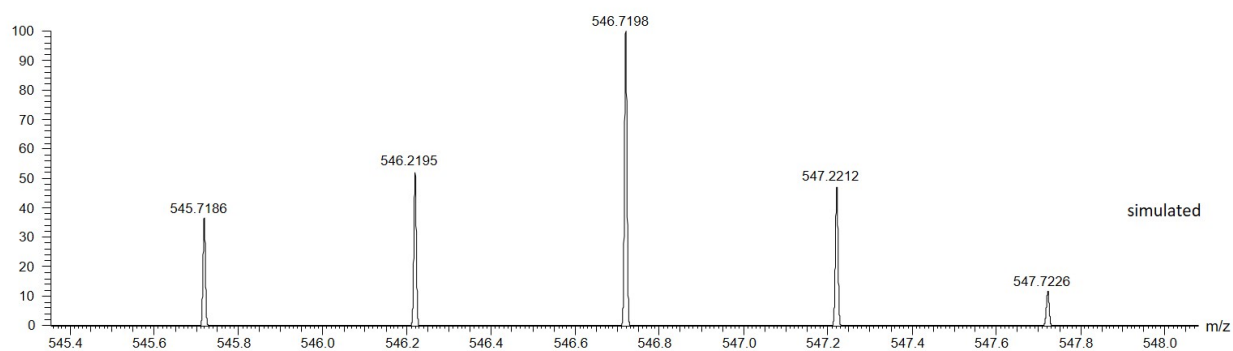
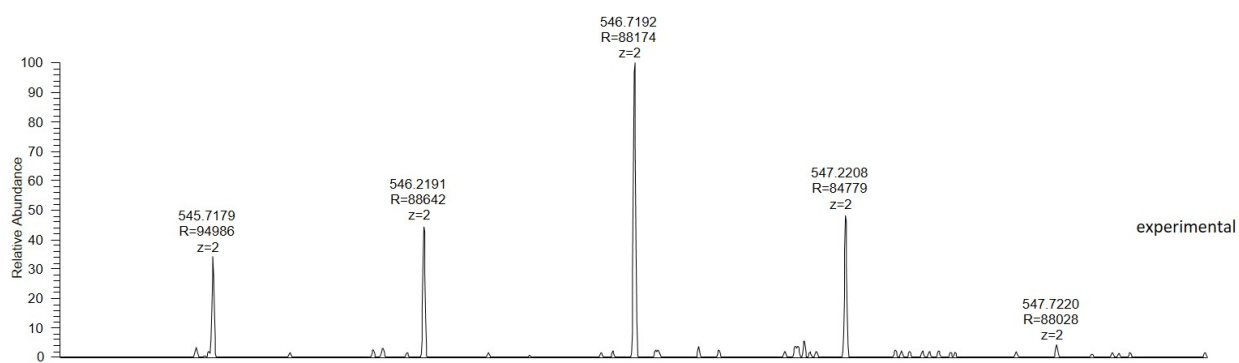
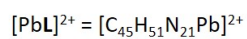
Part of the ESI-MS spectrum of redissolved crystals of compound 1

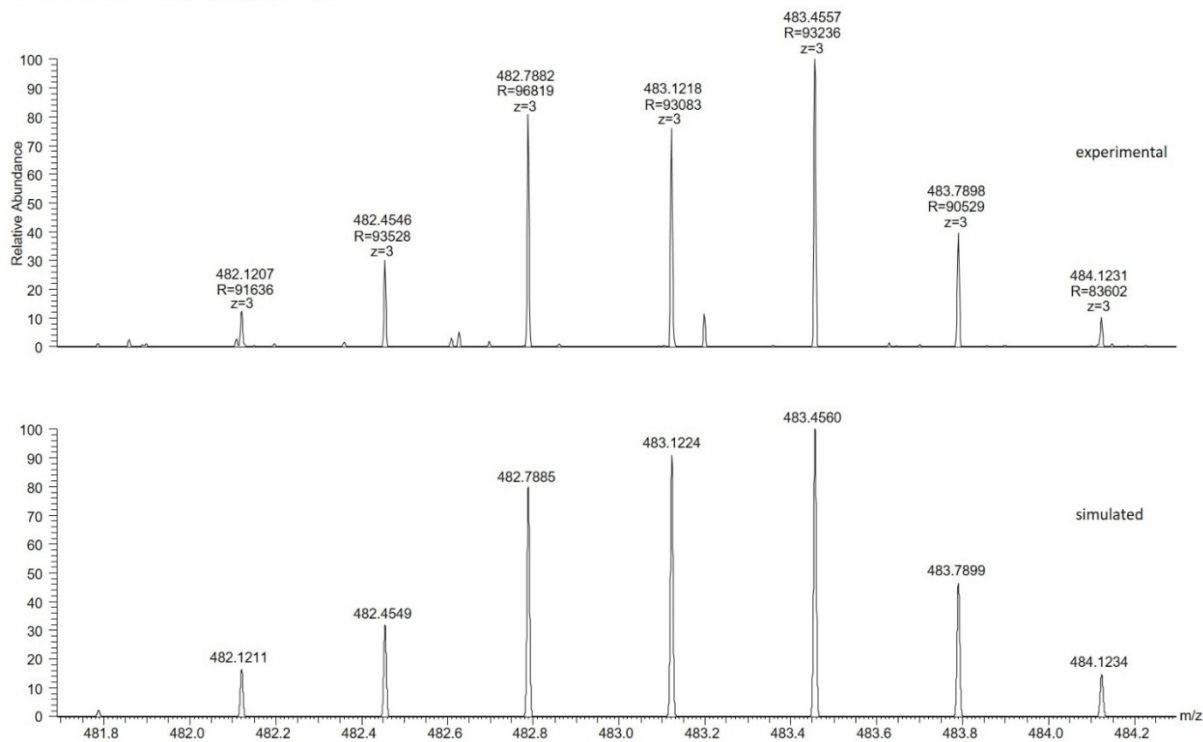
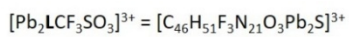






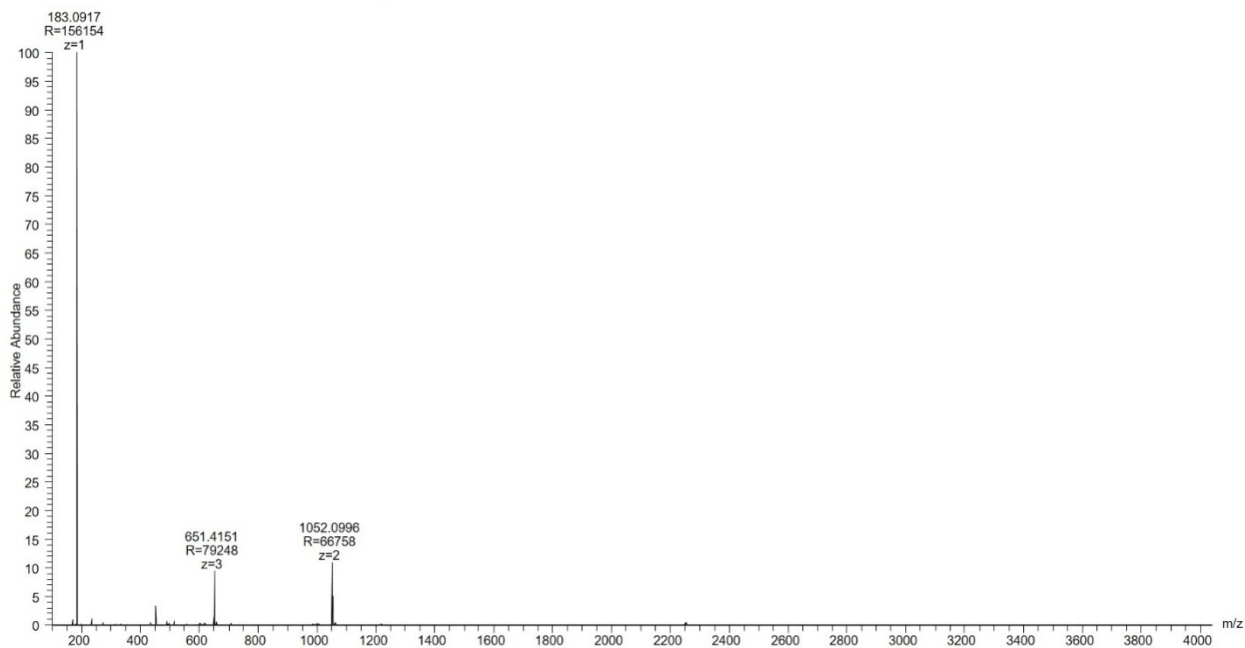




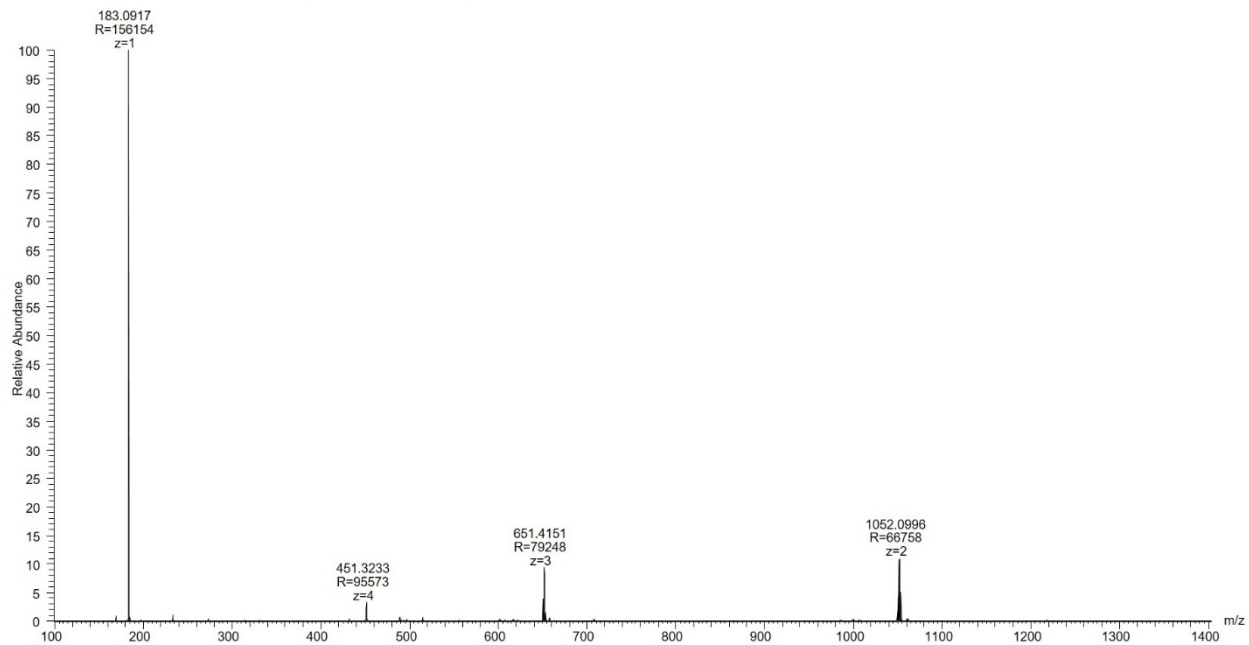


E2. Compound 2

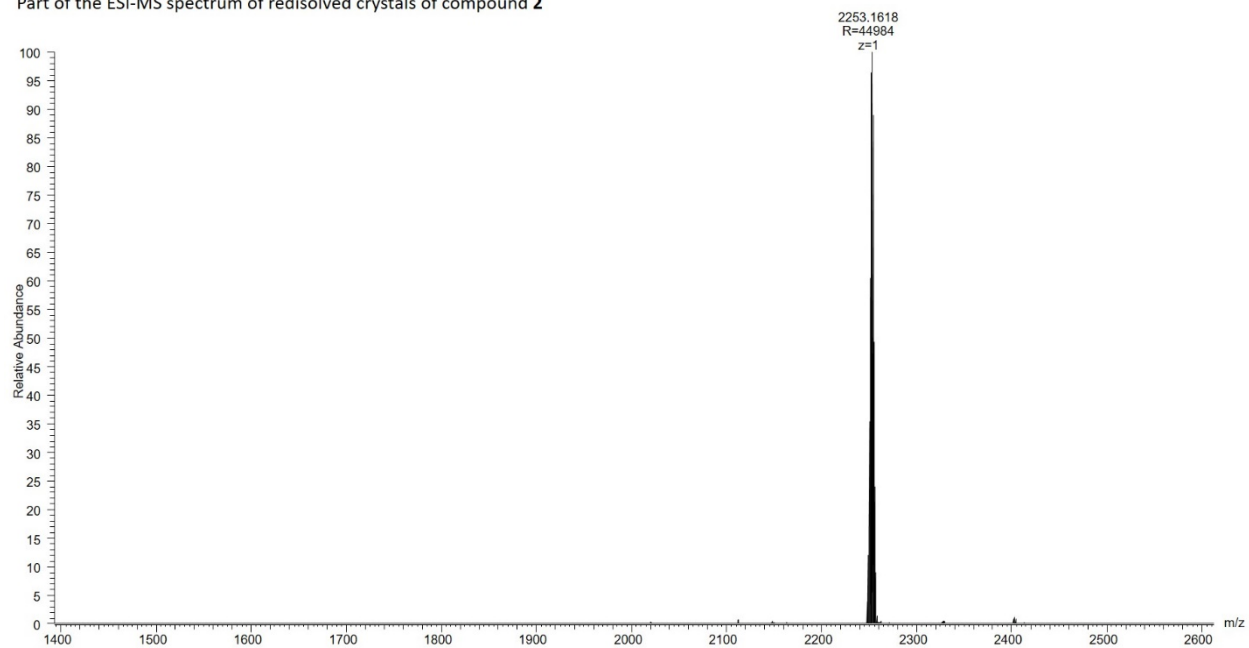
ESI-MS spectrum of redissolved crystals of compound 2

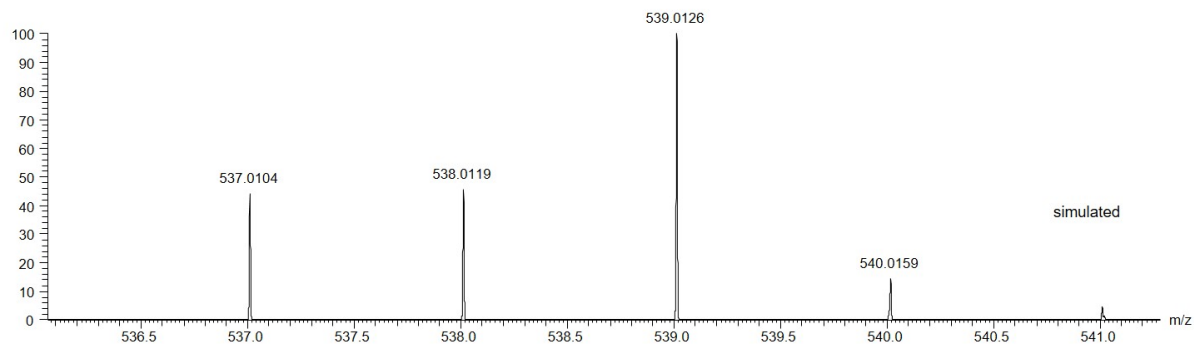
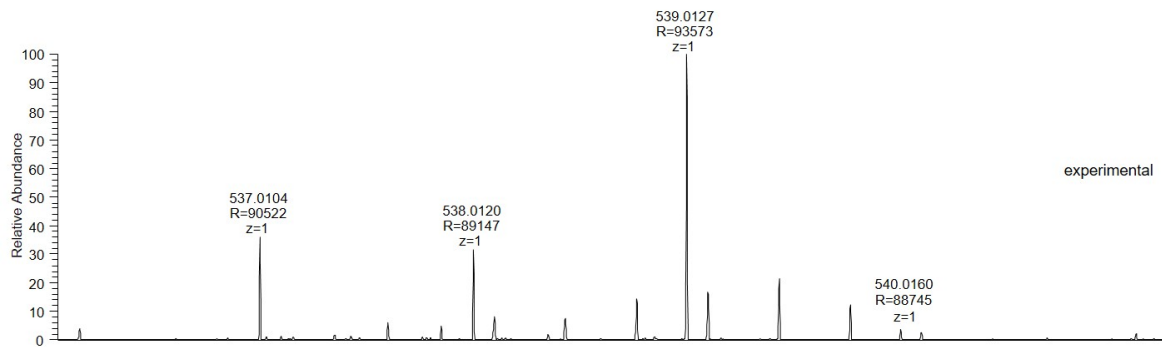
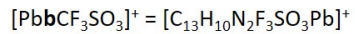
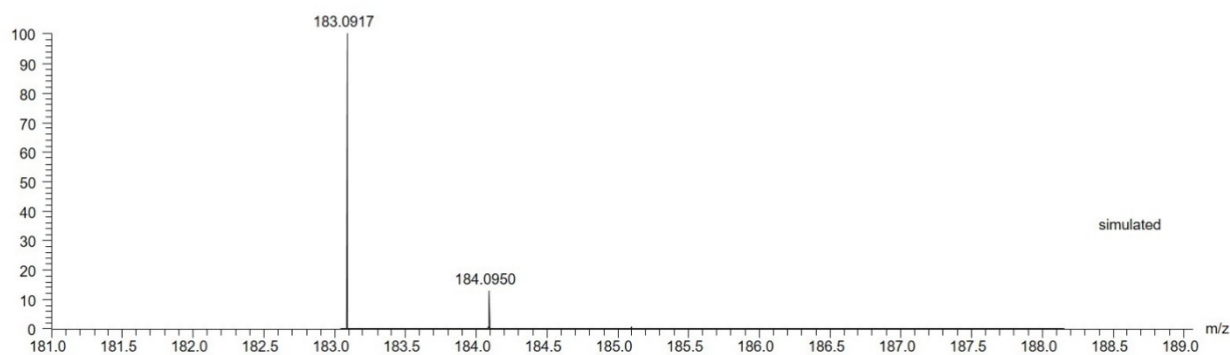
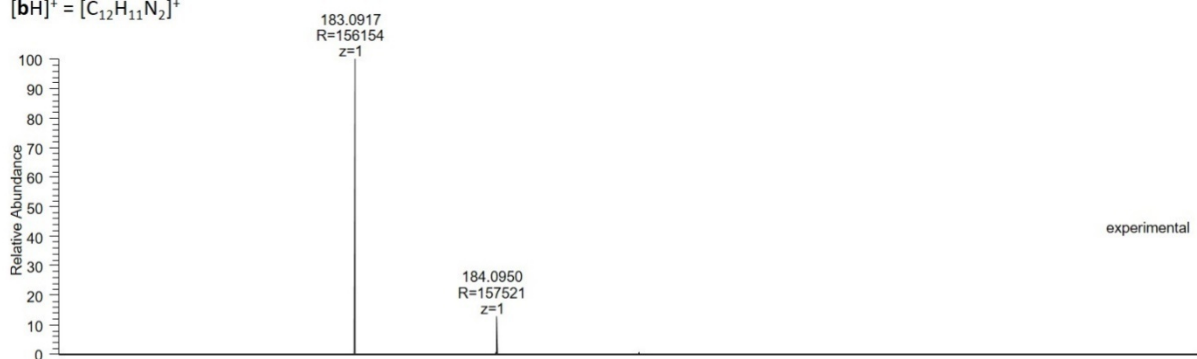
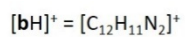


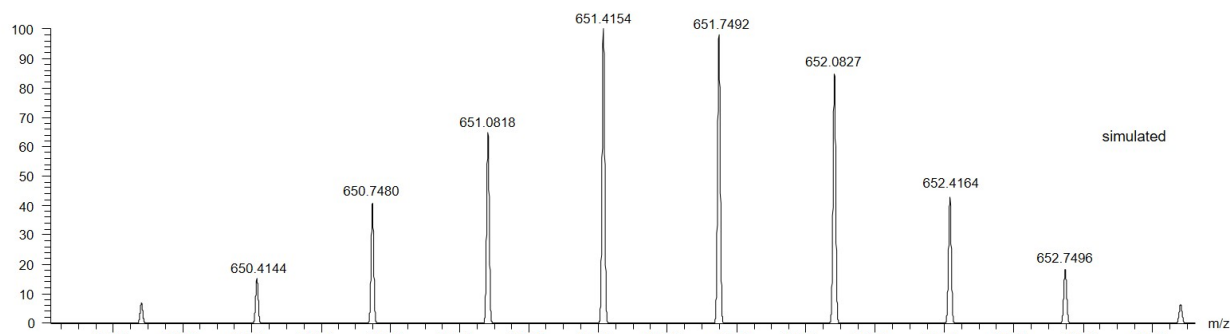
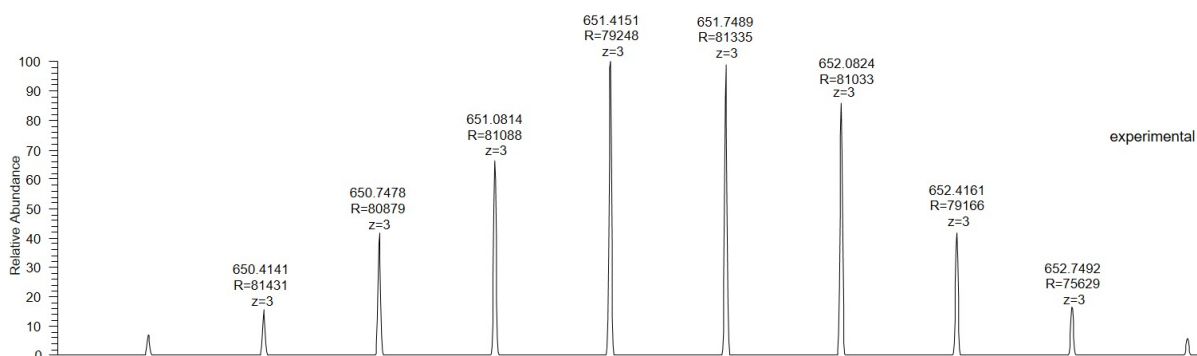
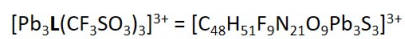
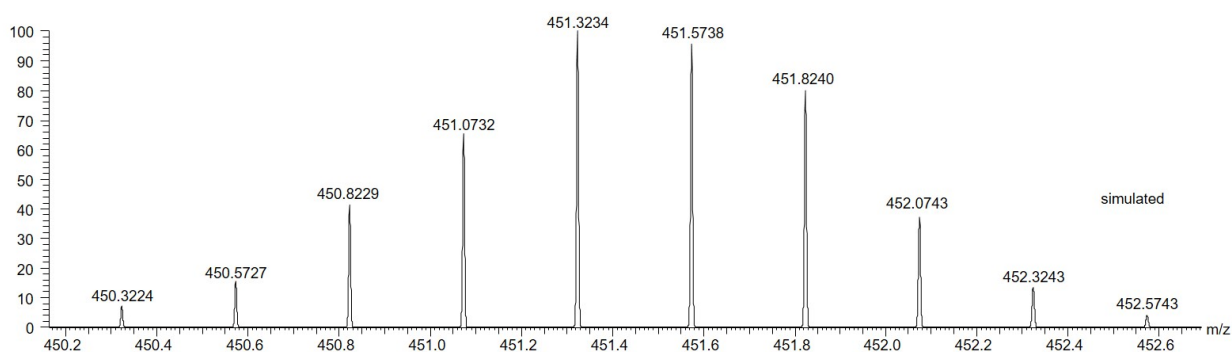
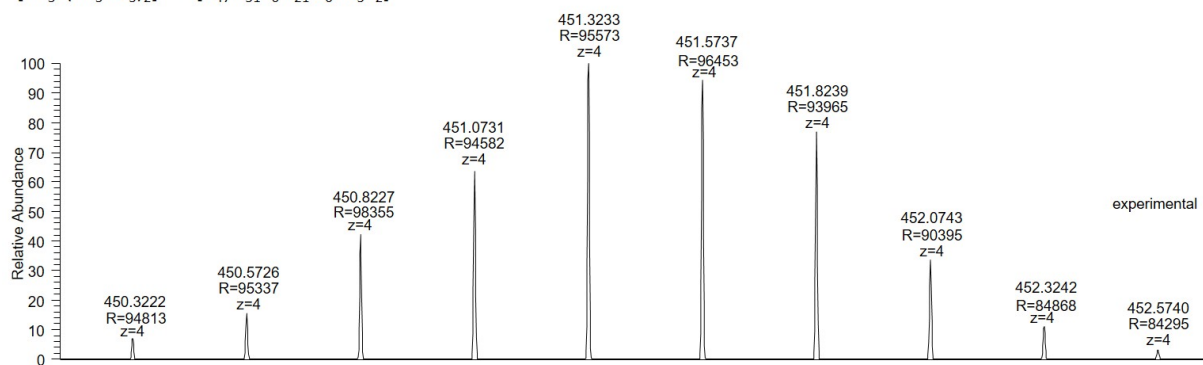
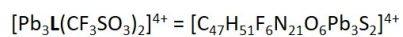
Part of the ESI-MS spectrum of redissolved crystals of compound 2

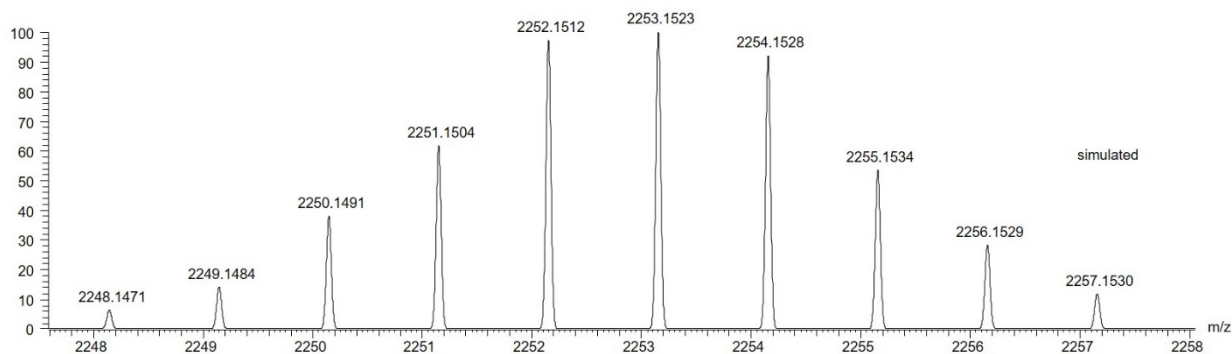
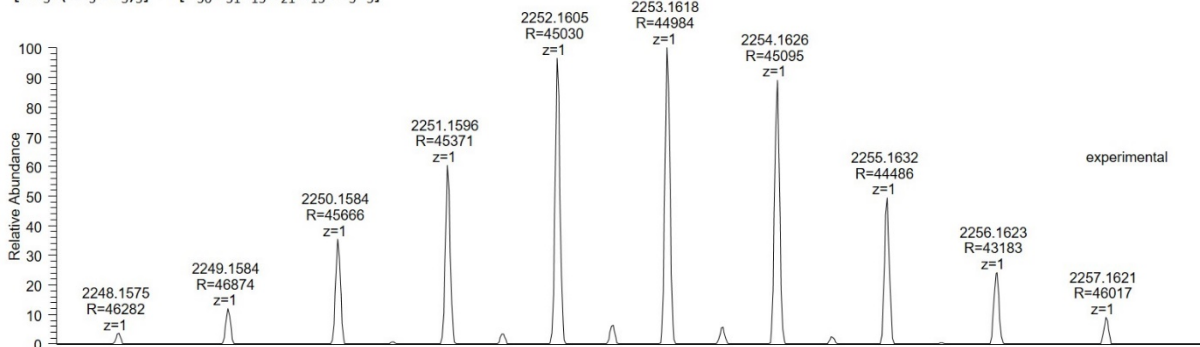
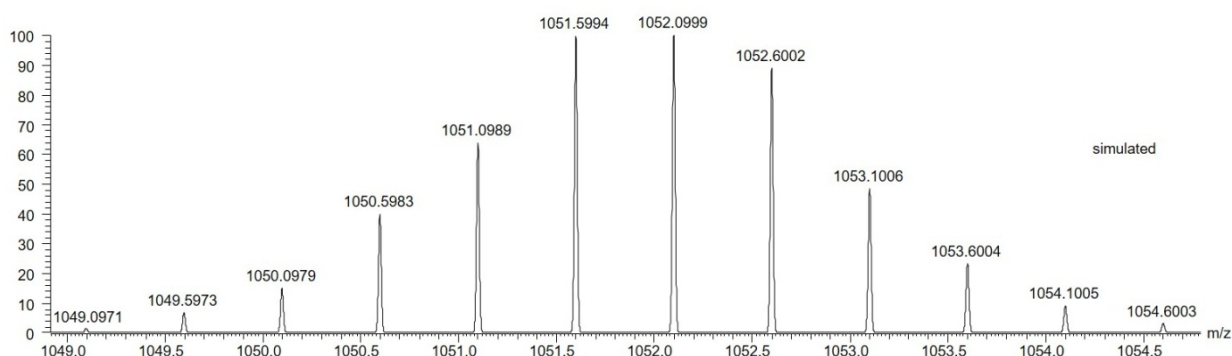
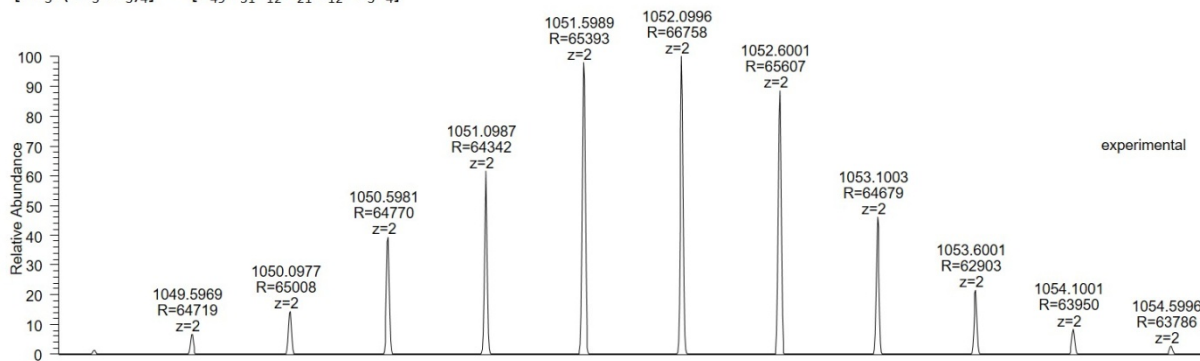
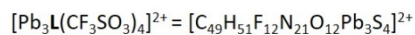


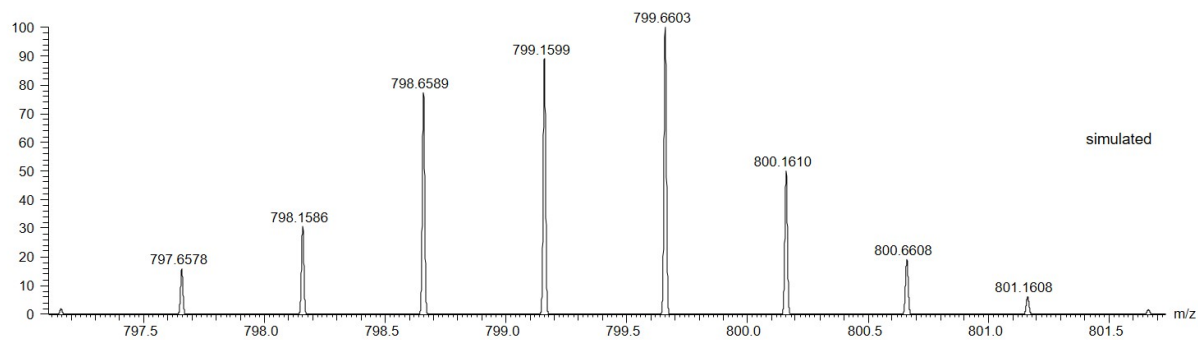
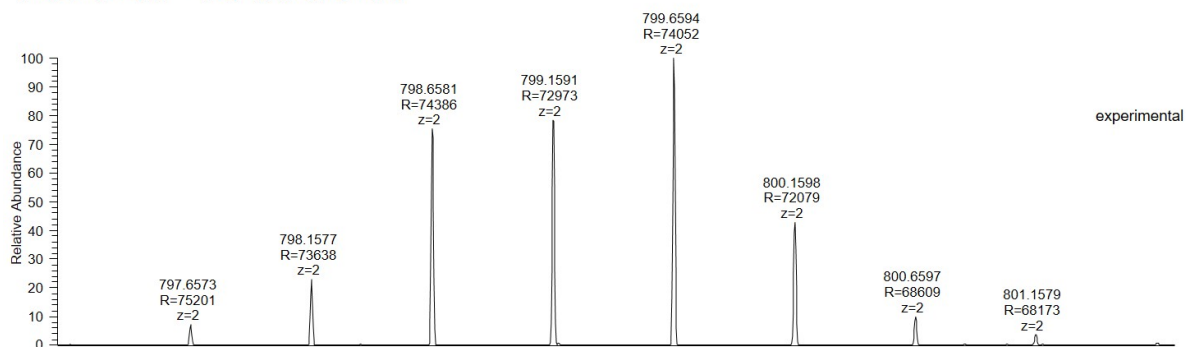
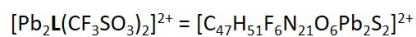
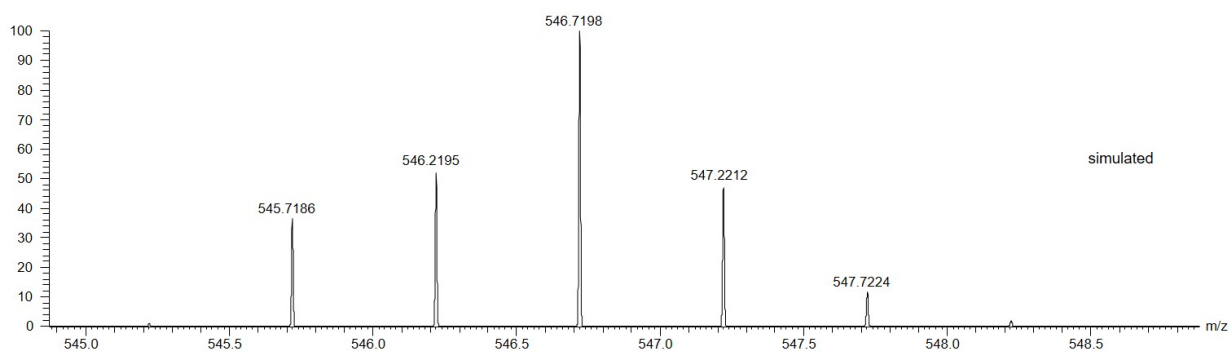
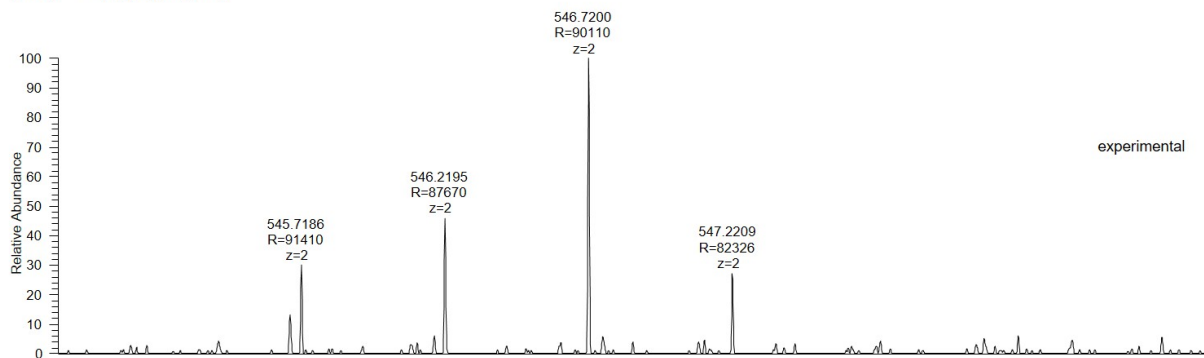
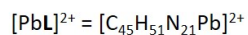
Part of the ESI-MS spectrum of redissolved crystals of compound 2

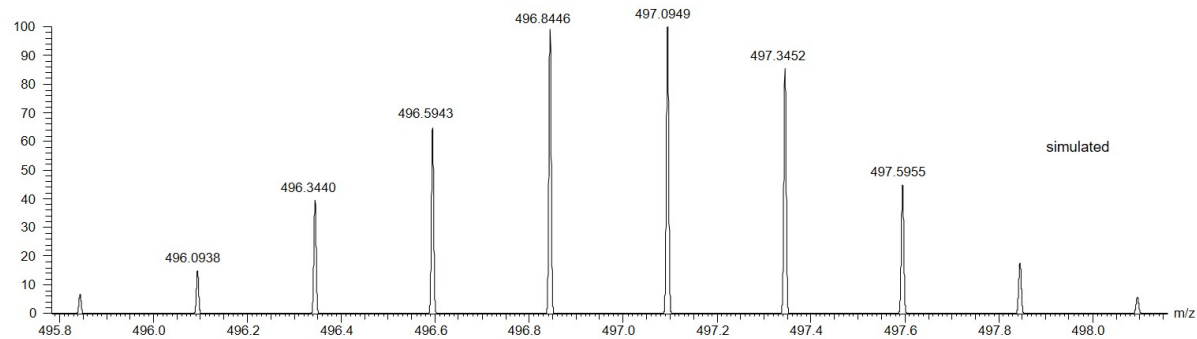
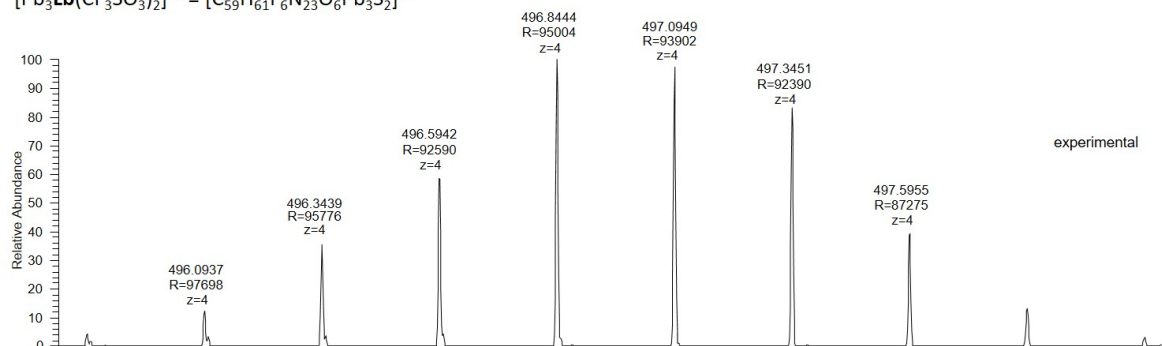
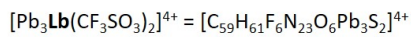
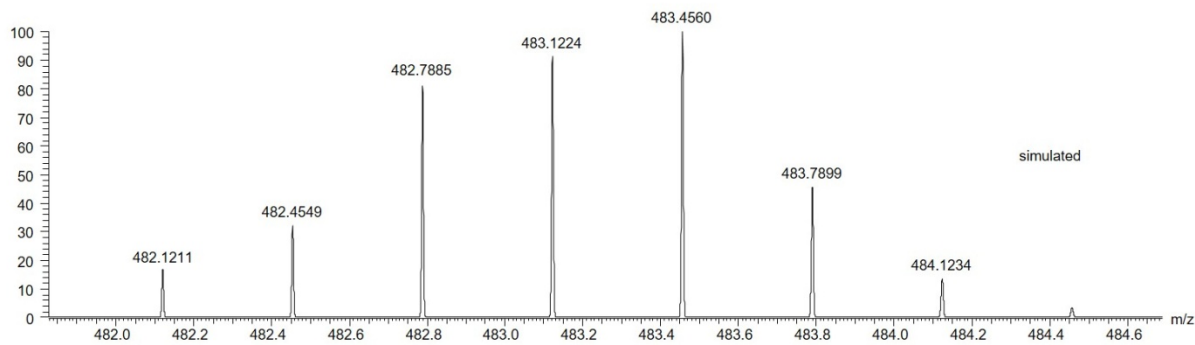
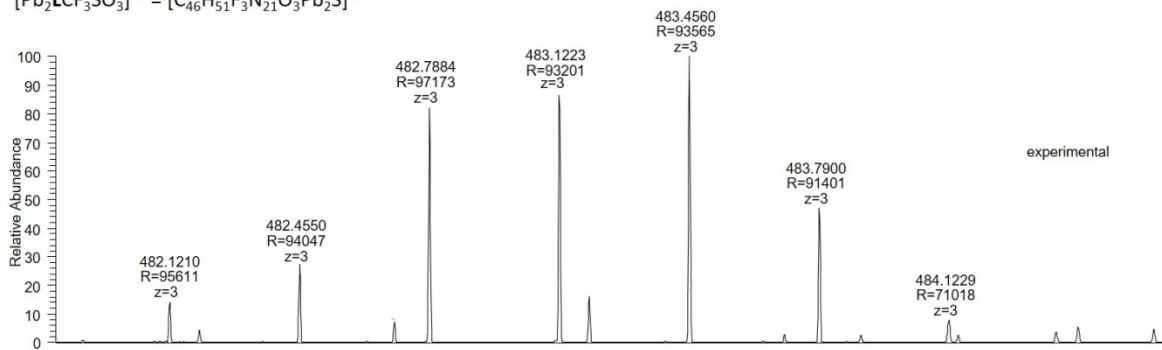
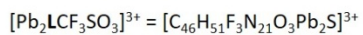


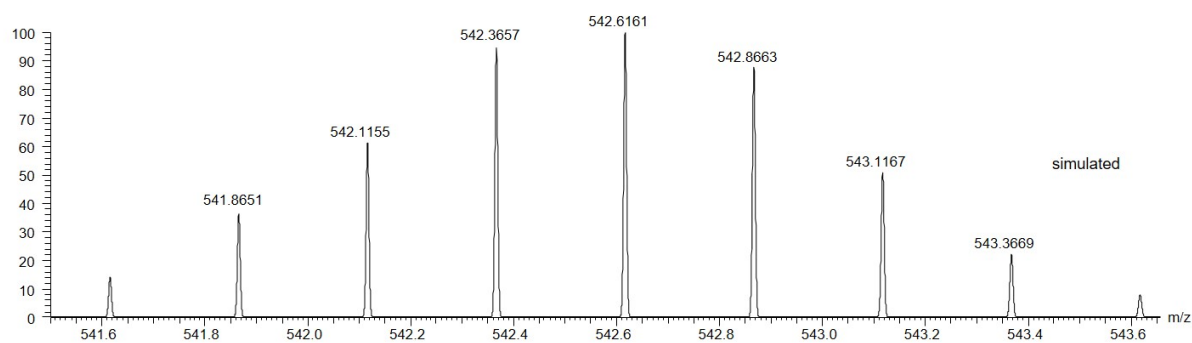
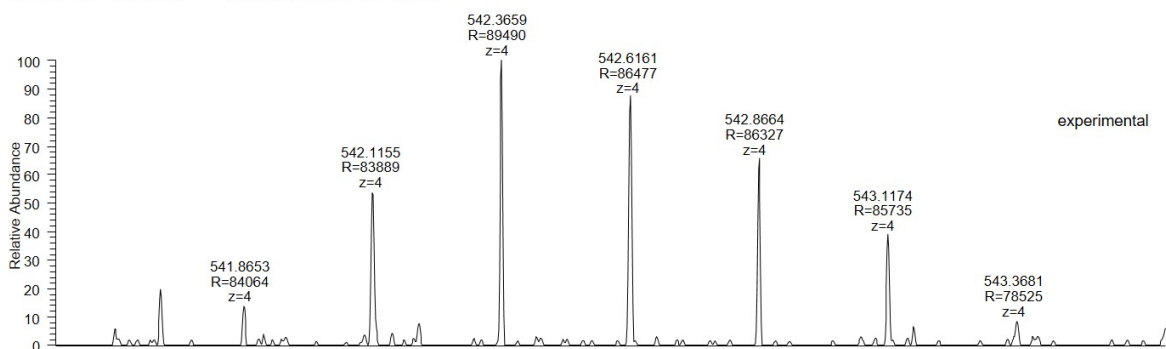
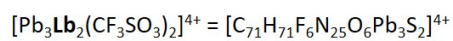






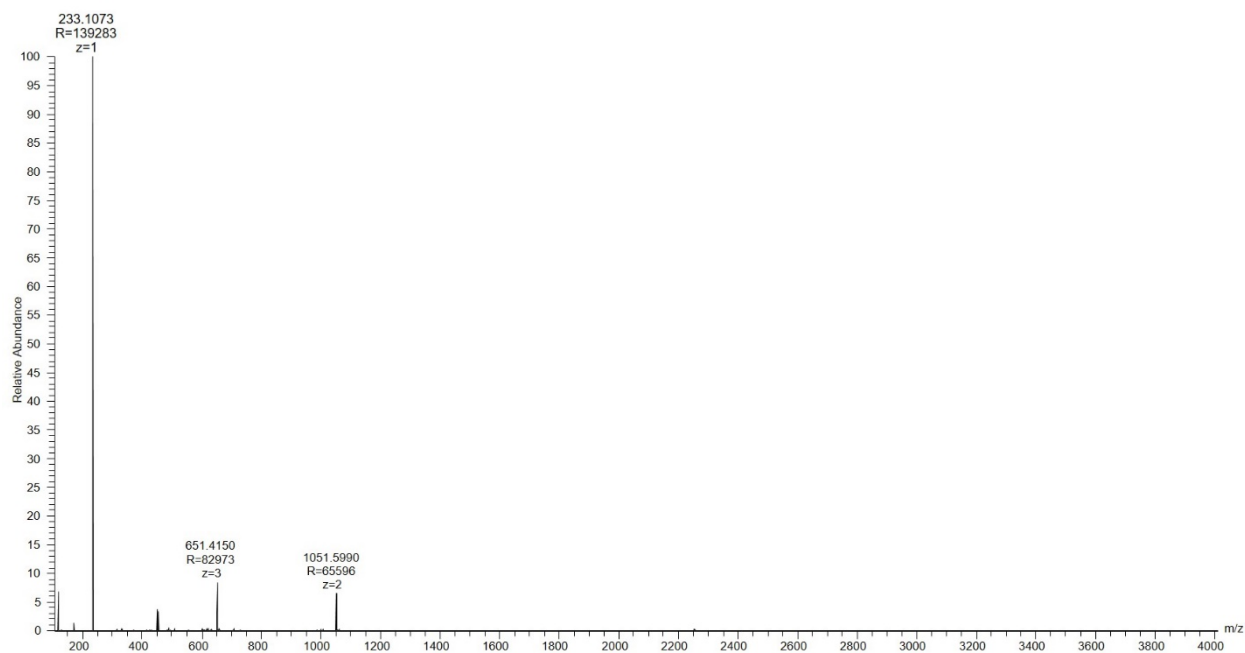




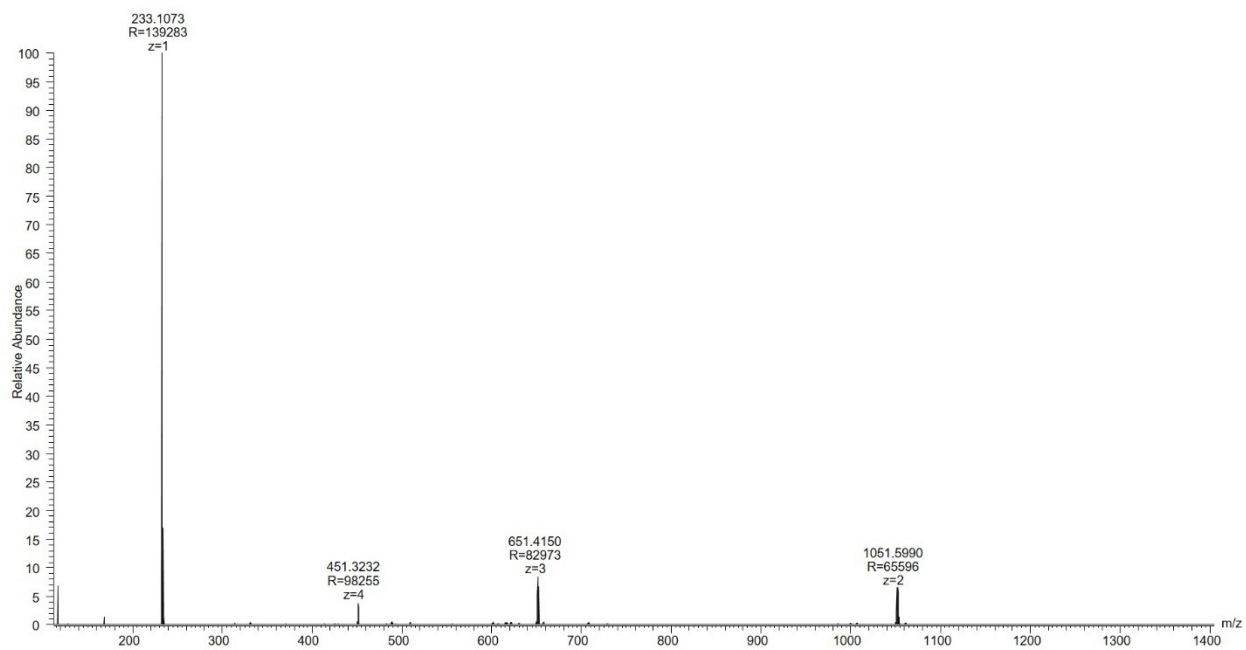


E3. Compound 3

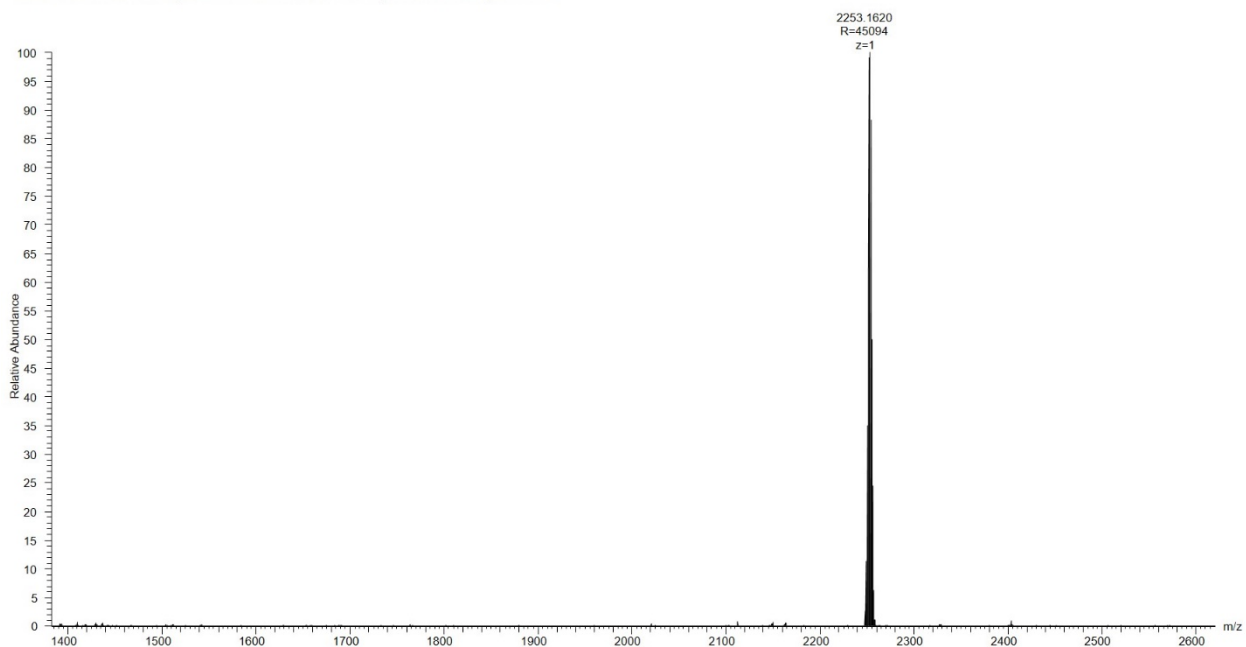
ESI-MS spectrum of redissolved crystals of compound **3**

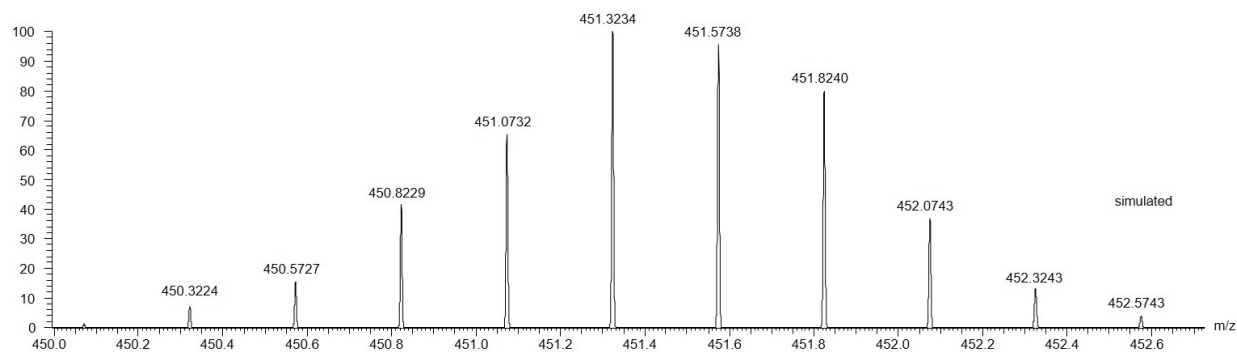
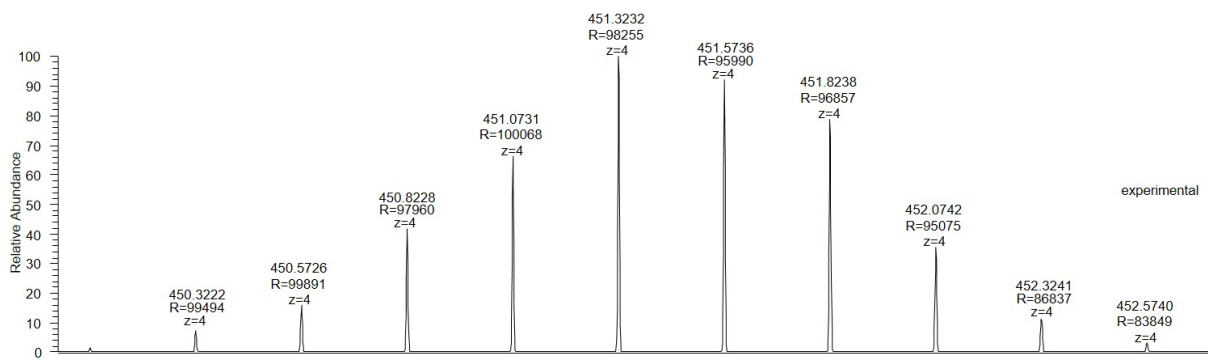
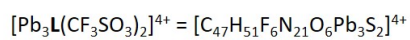
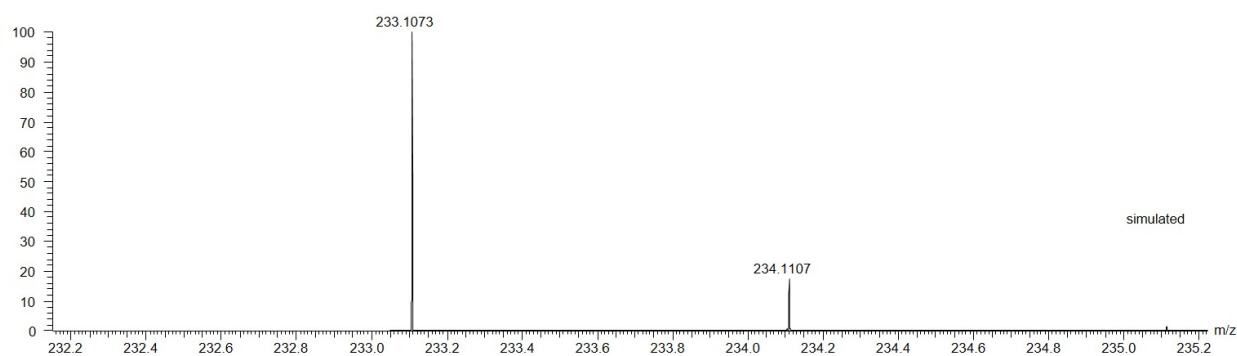
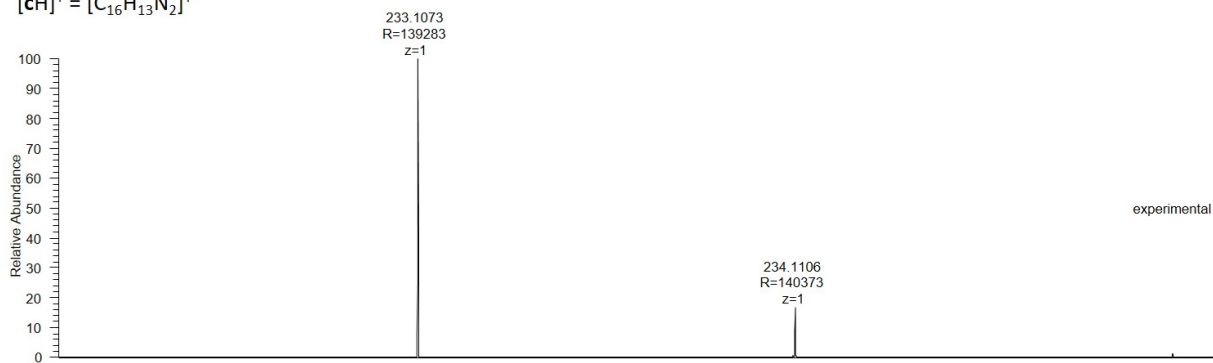
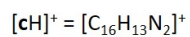


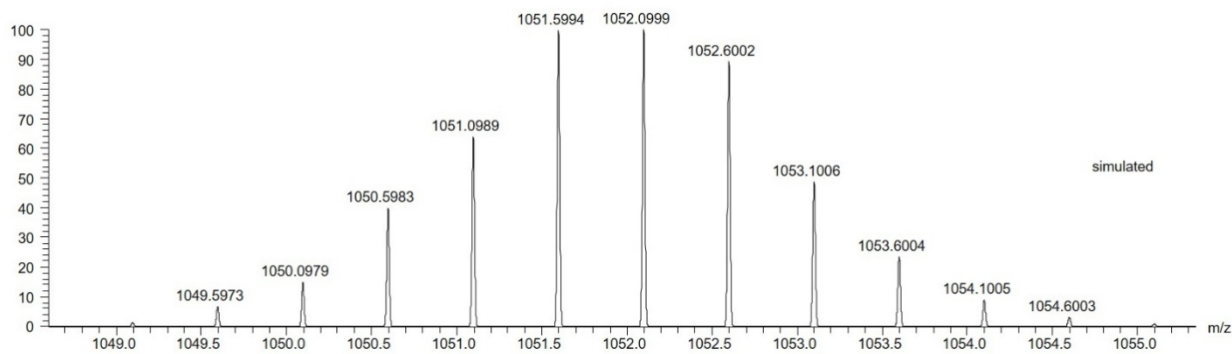
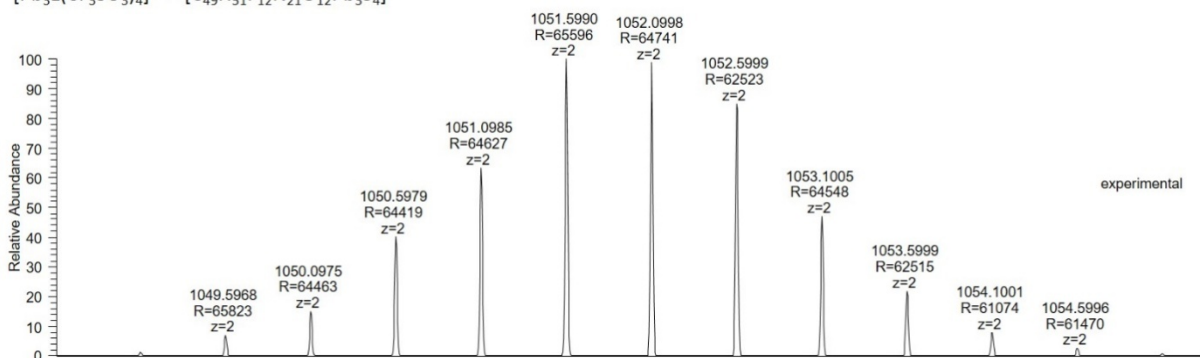
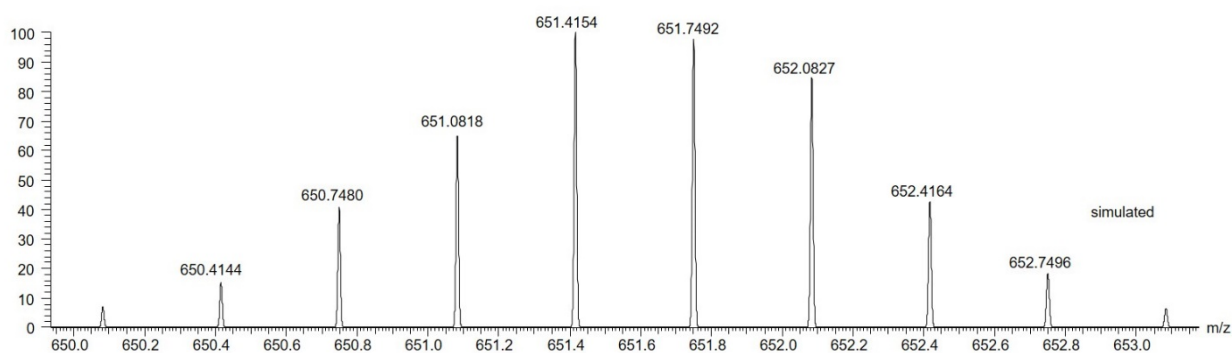
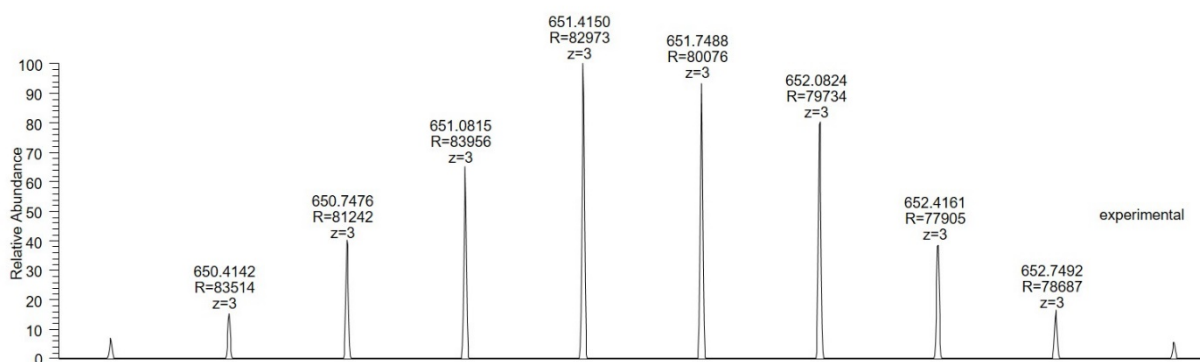
Part of the ESI-MS spectrum of redissolved crystals of compound **3**

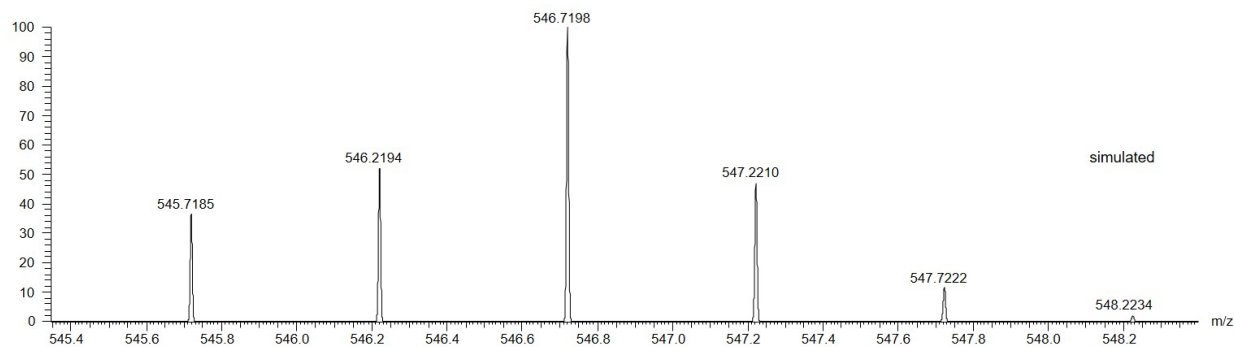
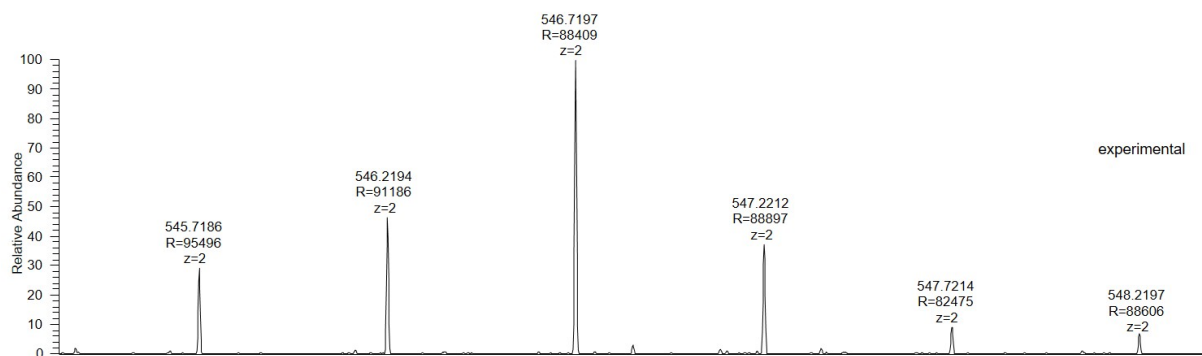
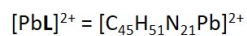
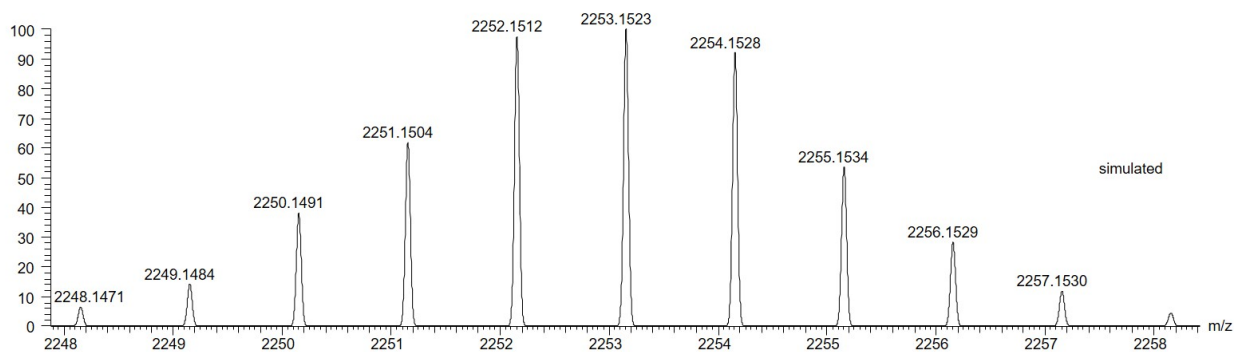
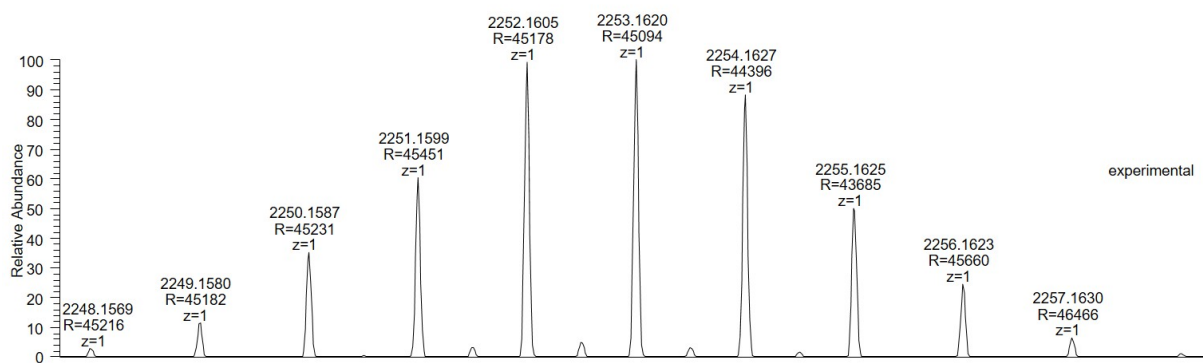
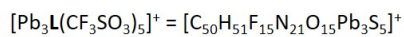


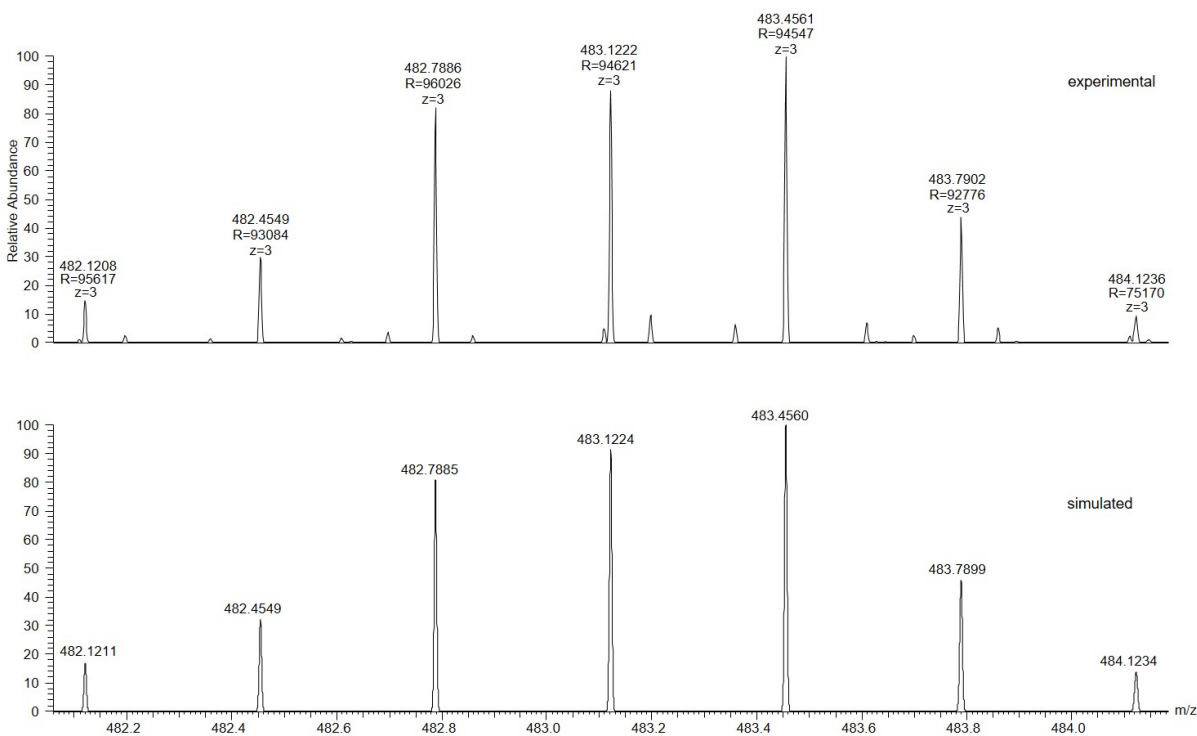
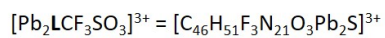
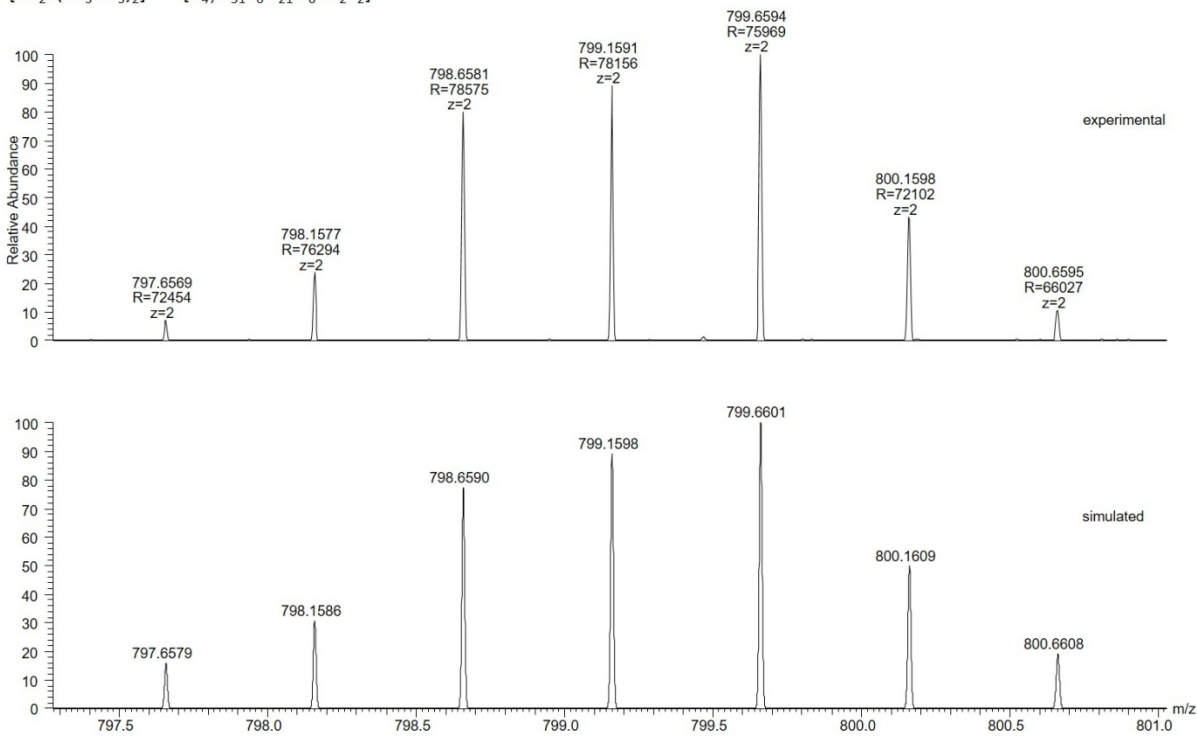
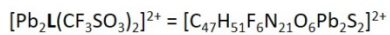
Part of the ESI-MS spectrum of redissolved crystals of compound **3**

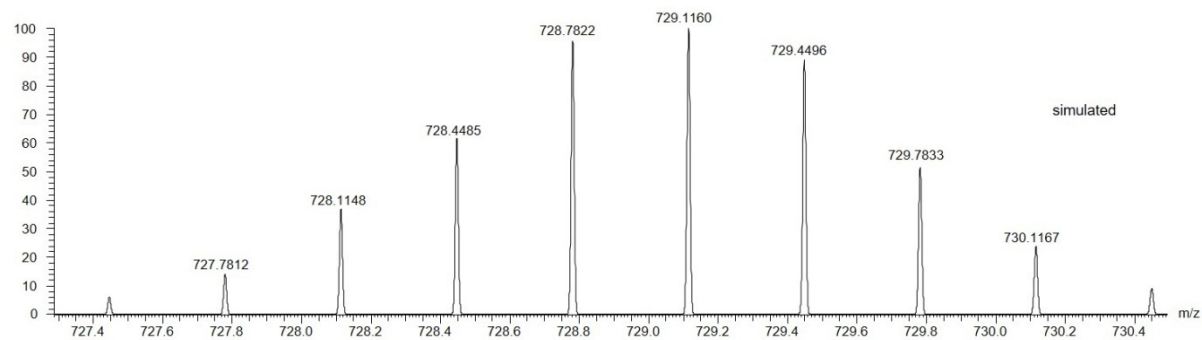
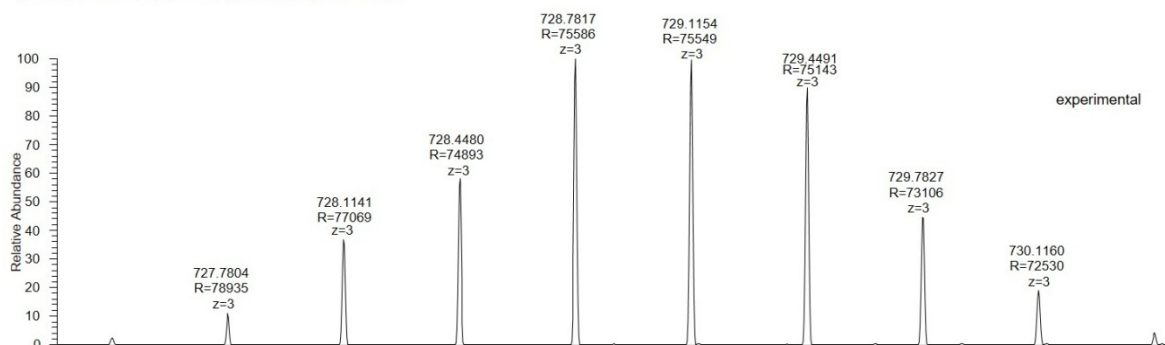
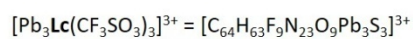
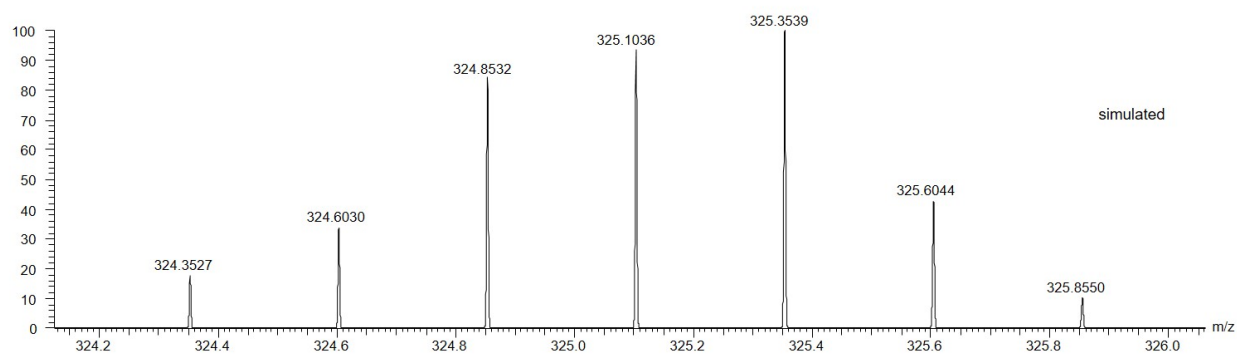
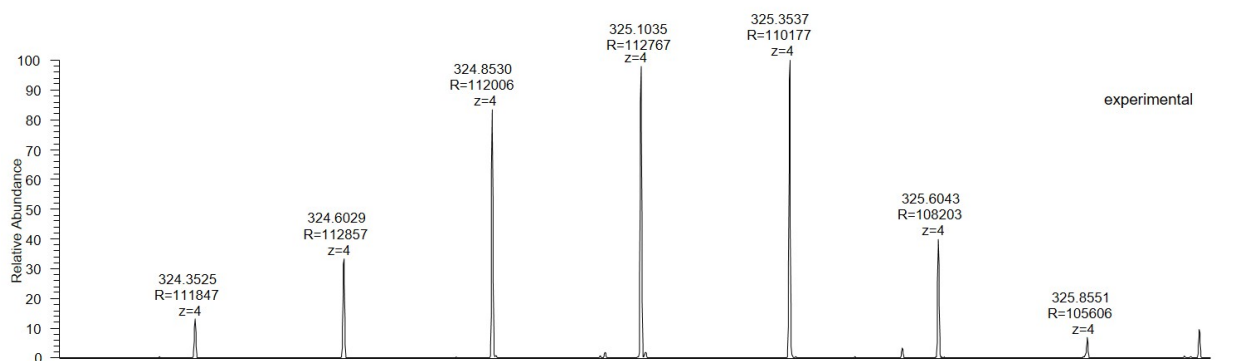
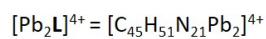


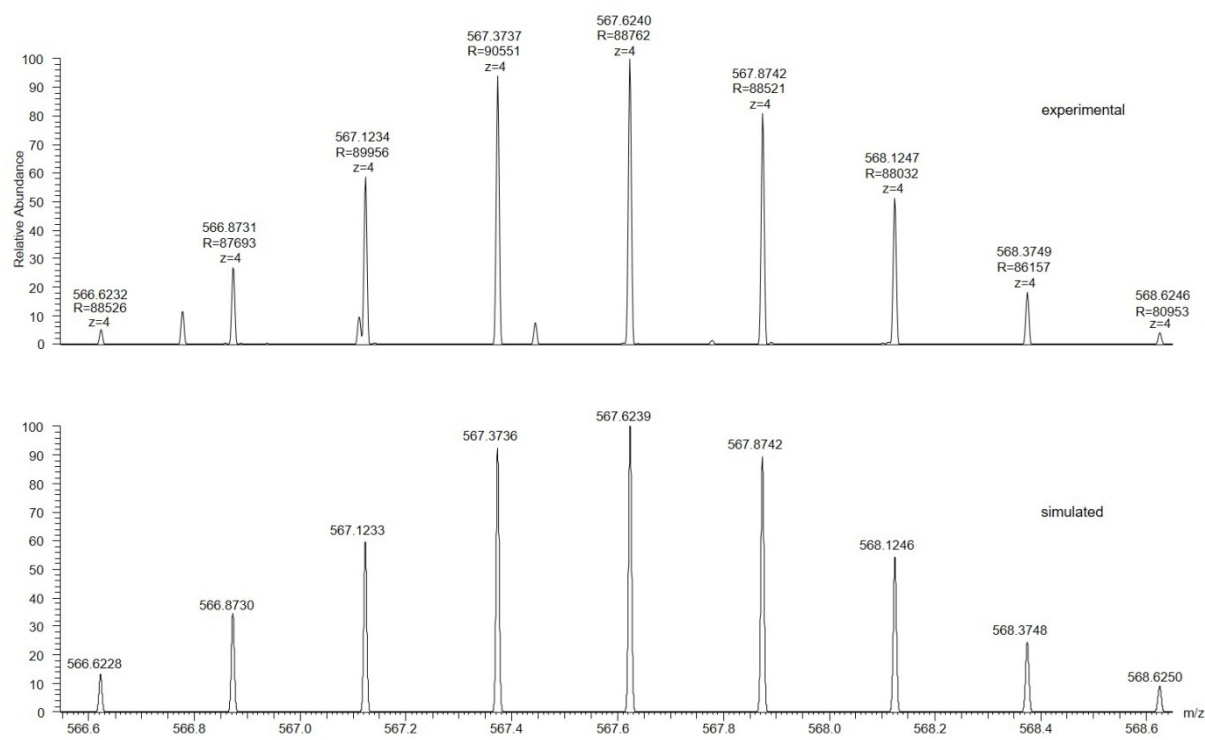
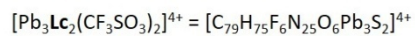
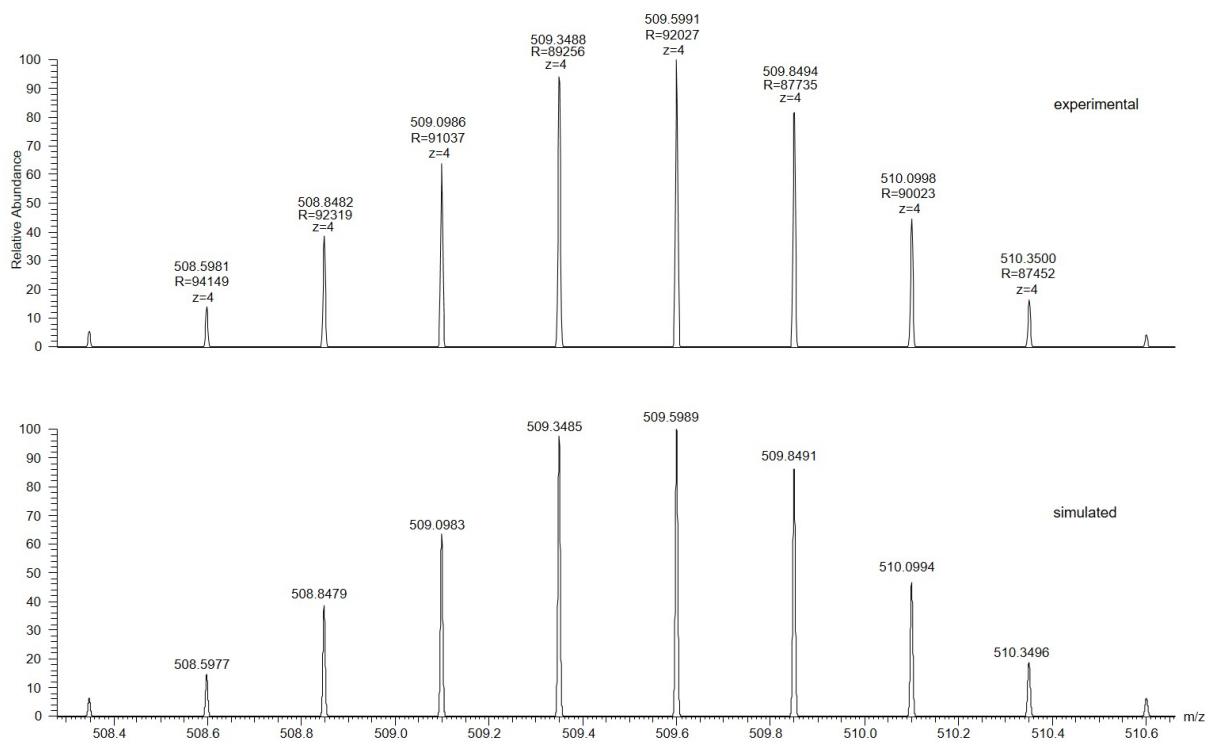
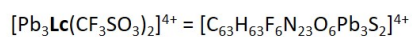








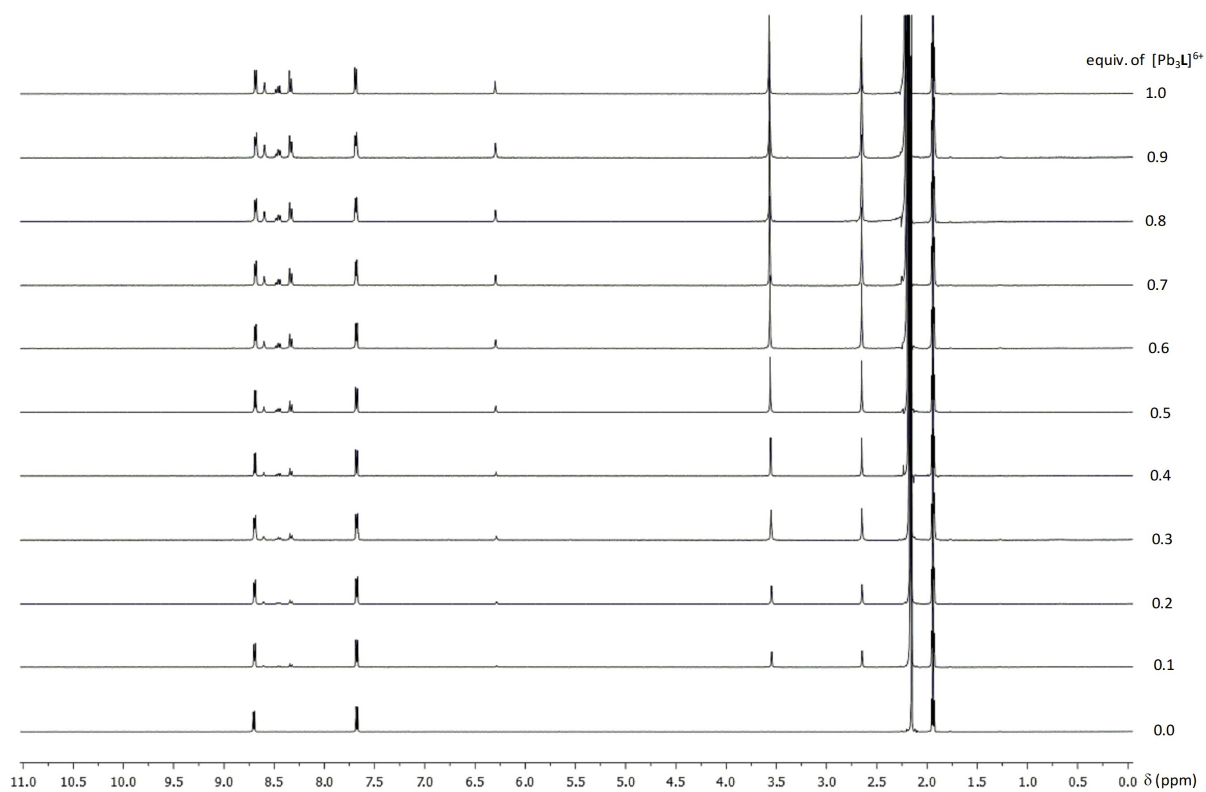




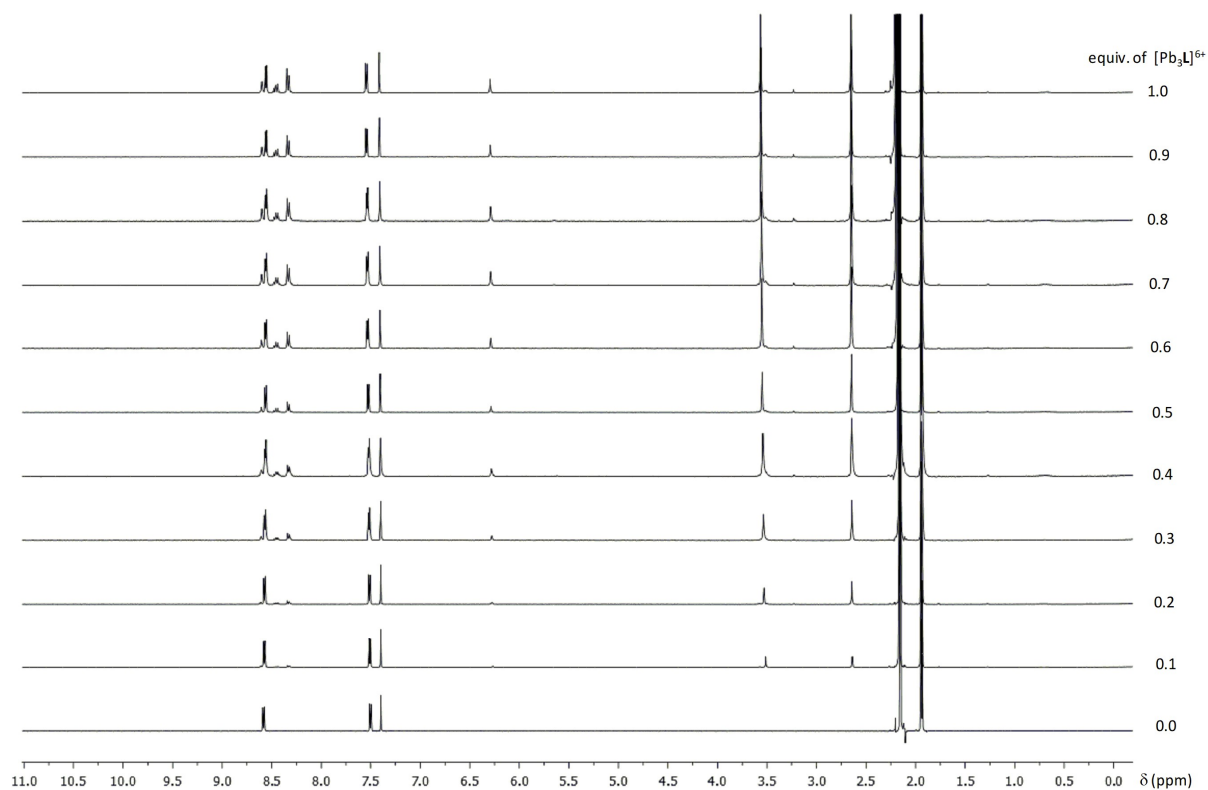
F. NMR spectroscopy

F1. ^1H NMR-monitored titrations

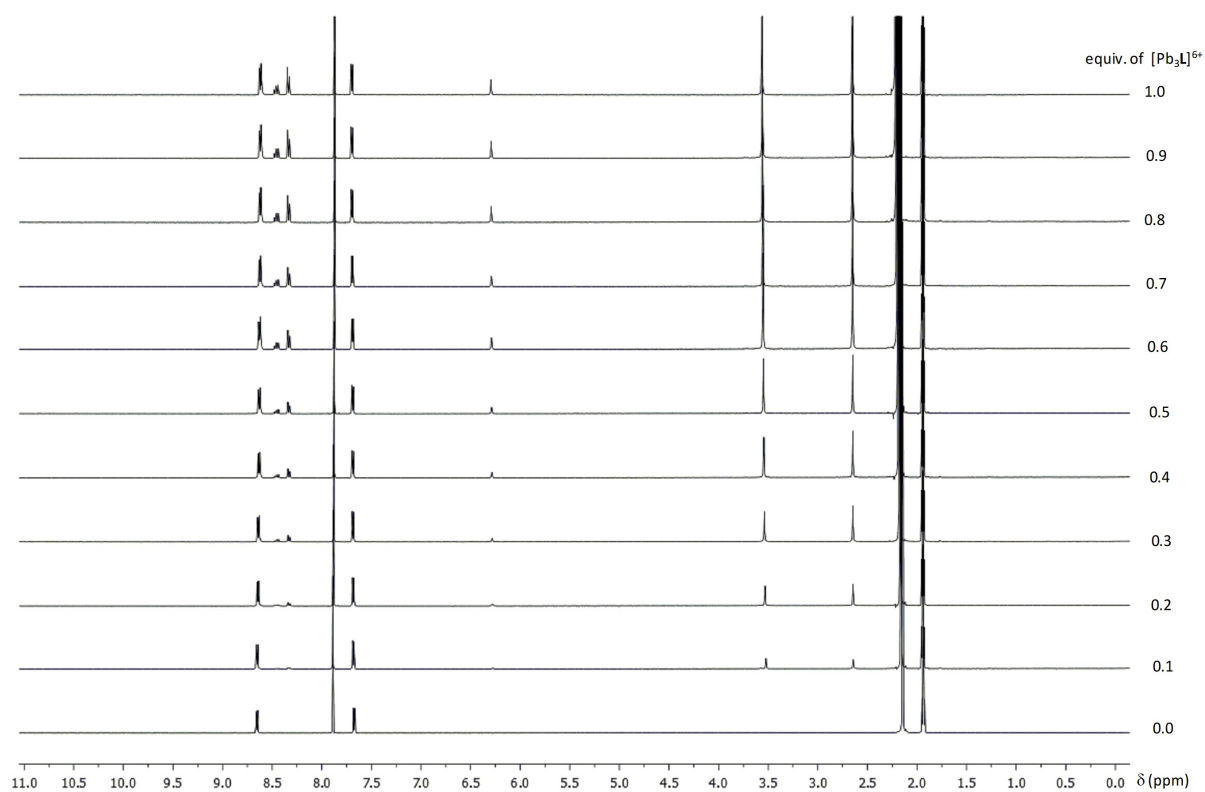
1) ^1H NMR (CD_3CN , 400 MHz)-monitored titration of compound **a** (1.5 equiv.) with compound $[\text{Pb}_3\text{L}](\text{OTf})_6$ (1 equiv.).



2) ^1H NMR (CD_3CN , 400 MHz)-monitored titration of compound **b** (1.5 equiv.) with compound $[\text{Pb}_3\text{L}](\text{OTf})_6$ (1 equiv.).



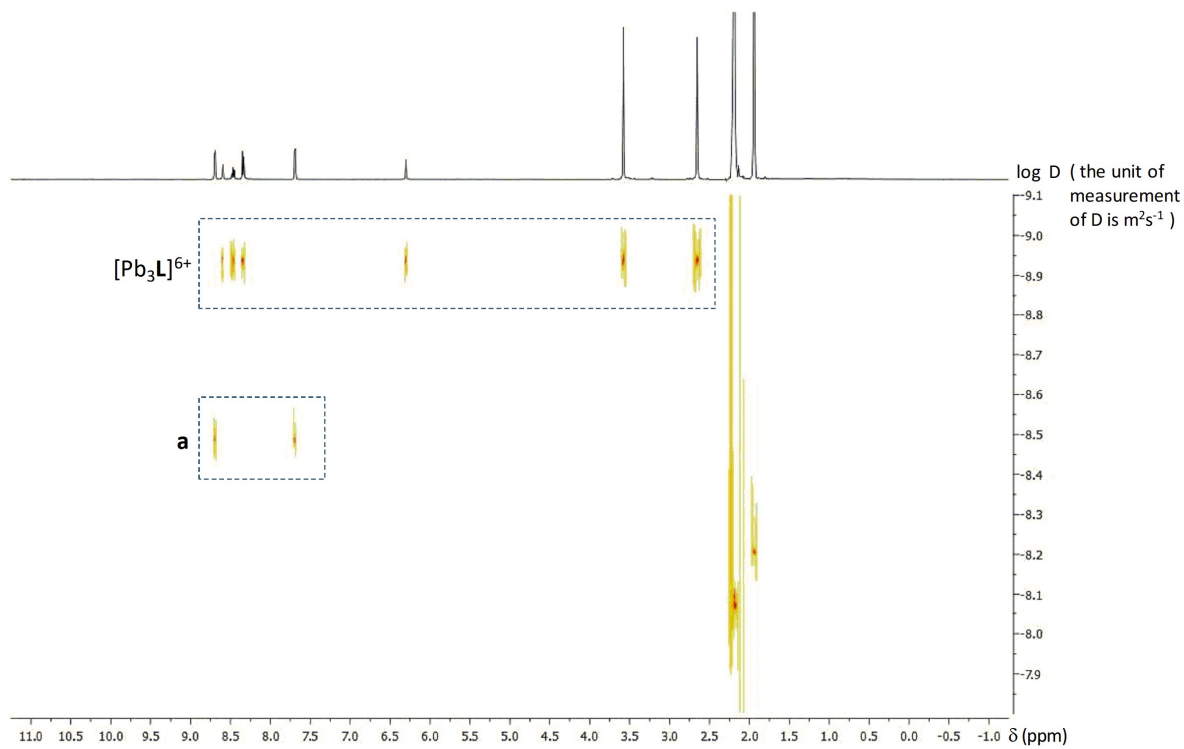
3) ^1H NMR (CD_3CN , 400 MHz)-monitored titration of compound **c** (1.5 equiv.) with compound $[\text{Pb}_3\text{L}](\text{OTf})_6$ (1 equiv.).



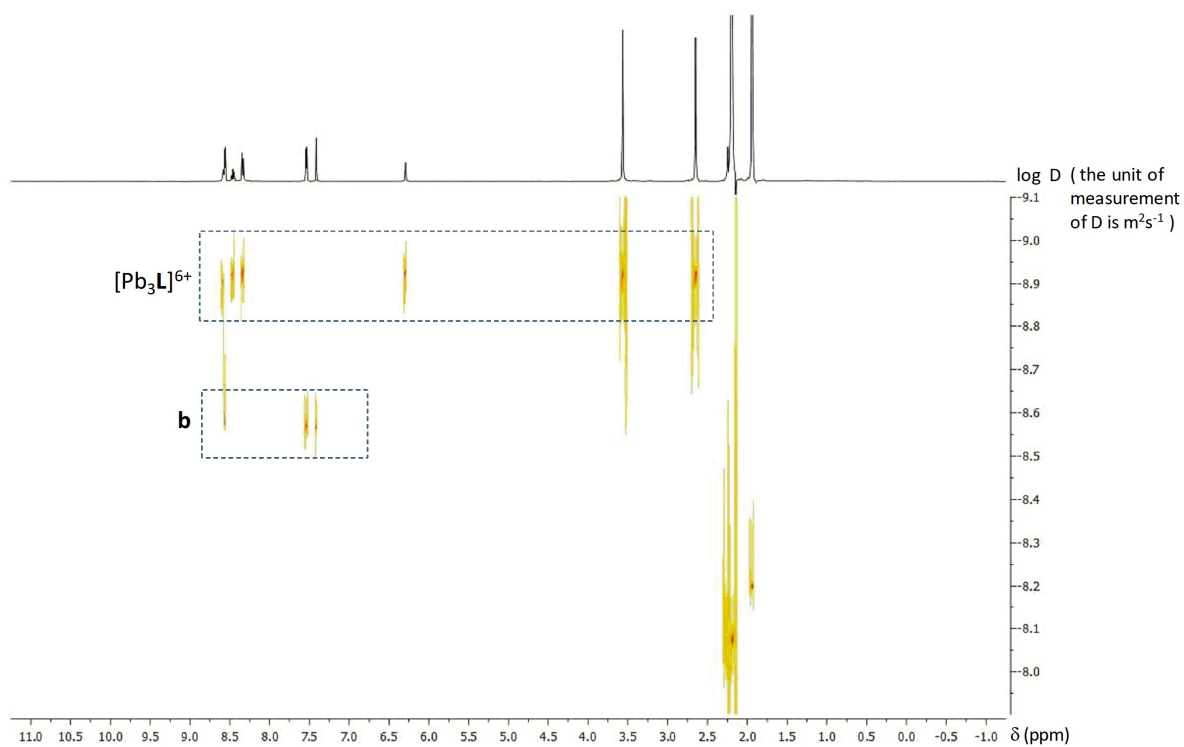
F2. ^1H DOSY NMR

DOSY = Diffusion-Ordered Spectroscopy

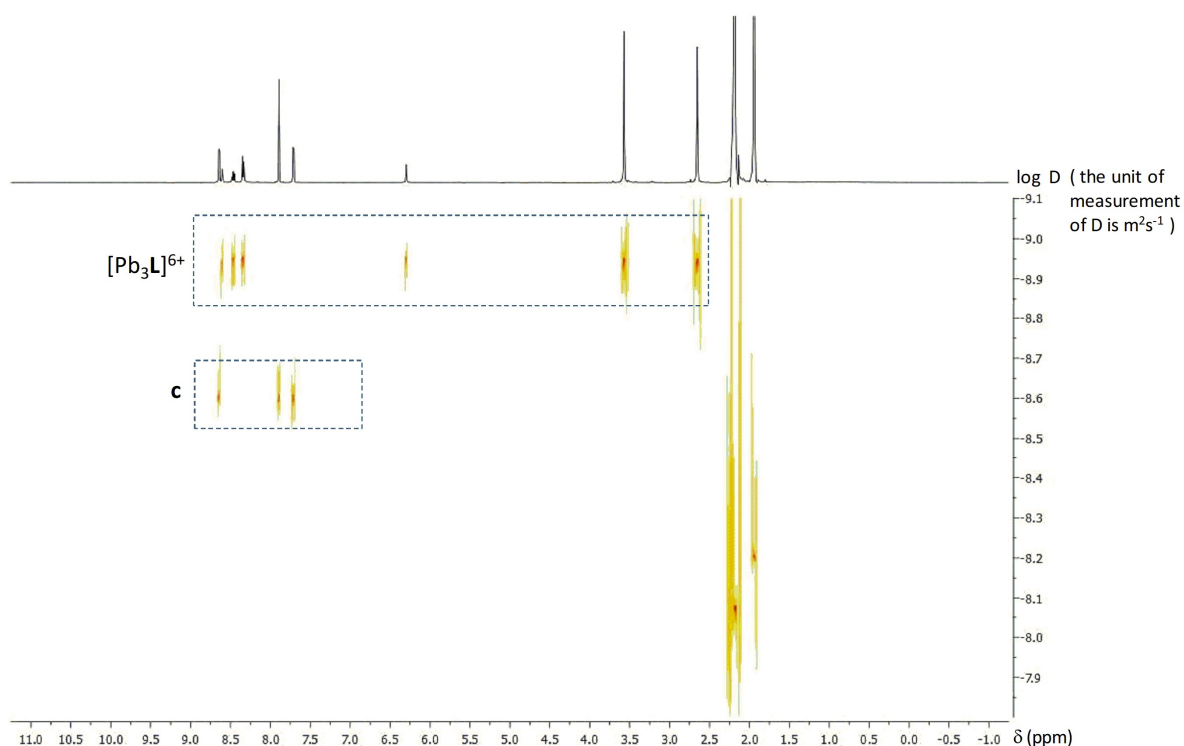
1) ^1H DOSY NMR (CD_3CN , 500 MHz) of redissolved crystals of compound **1**.



2) ^1H DOSY NMR (CD_3CN , 500 MHz) of redissolved crystals of compound **2**.



3) ^1H DOSY NMR (CD_3CN , 500 MHz) of redissolved crystals of compound **3**.



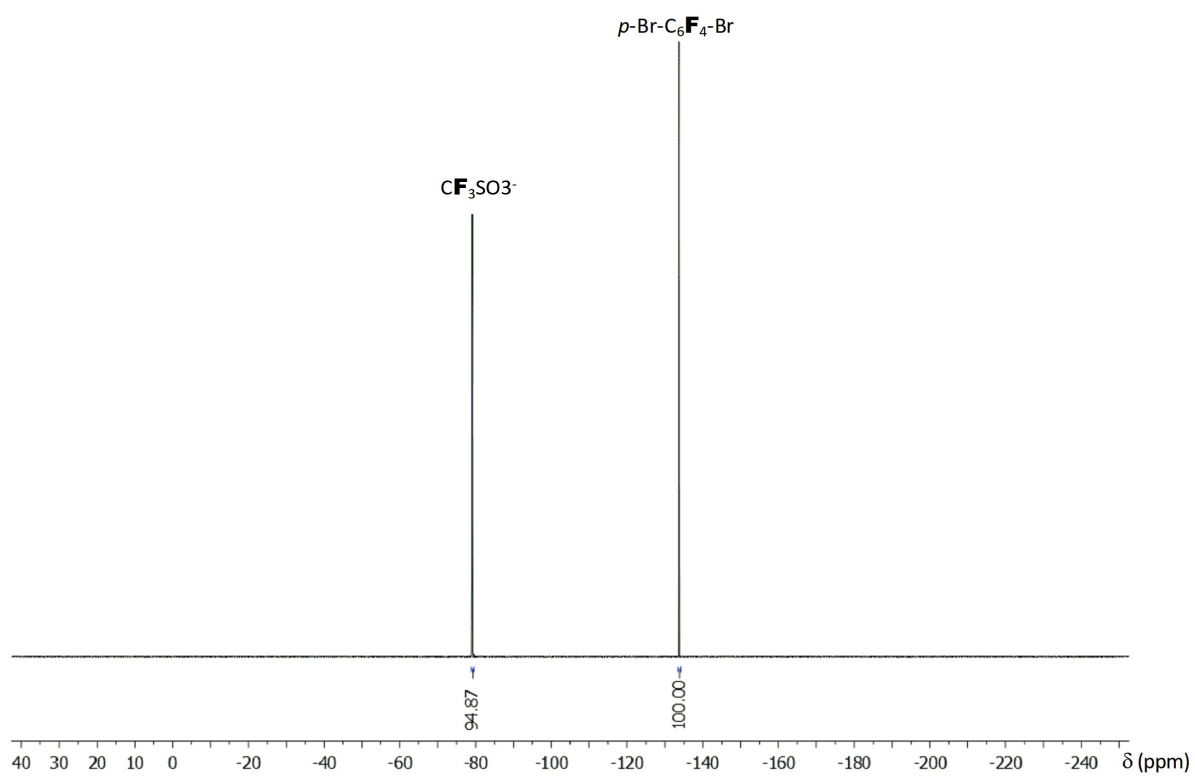
F3. ^{19}F NMR (CD_3CN , 471 MHz) spectra of redissolved crystals of complexes **1 - 3**.

In each tube was added (as an internal standard) an amount of $p\text{-Br-C}_6\text{F}_4\text{-Br}$ which corresponds to the theoretical amount of fluorine in complexes, calculated with the formula

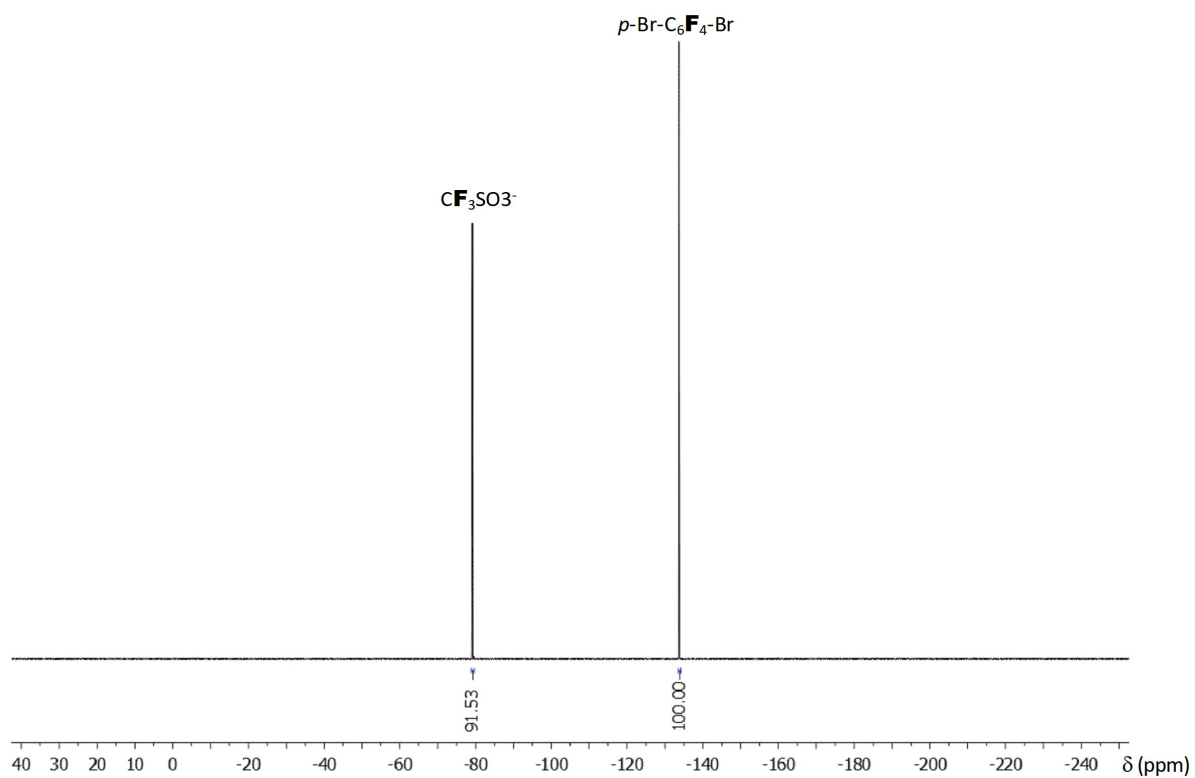
$$m_{p\text{-Br-C}_6\text{F}_4\text{-Br}} = 9 \times m_{\text{Pb}_6\text{L}_2\text{S}_3(\text{CF}_3\text{SO}_3)_{12}} \times \frac{\text{MW}_{p\text{-Br-C}_6\text{F}_4\text{-Br}}}{\text{MW}_{\text{Pb}_6\text{L}_2\text{S}_3(\text{CF}_3\text{SO}_3)_{12}}}, \text{ where } \mathbf{s} = \mathbf{a}, \mathbf{b} \text{ or } \mathbf{c}.$$

The integration of the peaks corresponding to F atoms from $p\text{-Br-C}_6\text{F}_4\text{-Br}$ was fixed at 100.

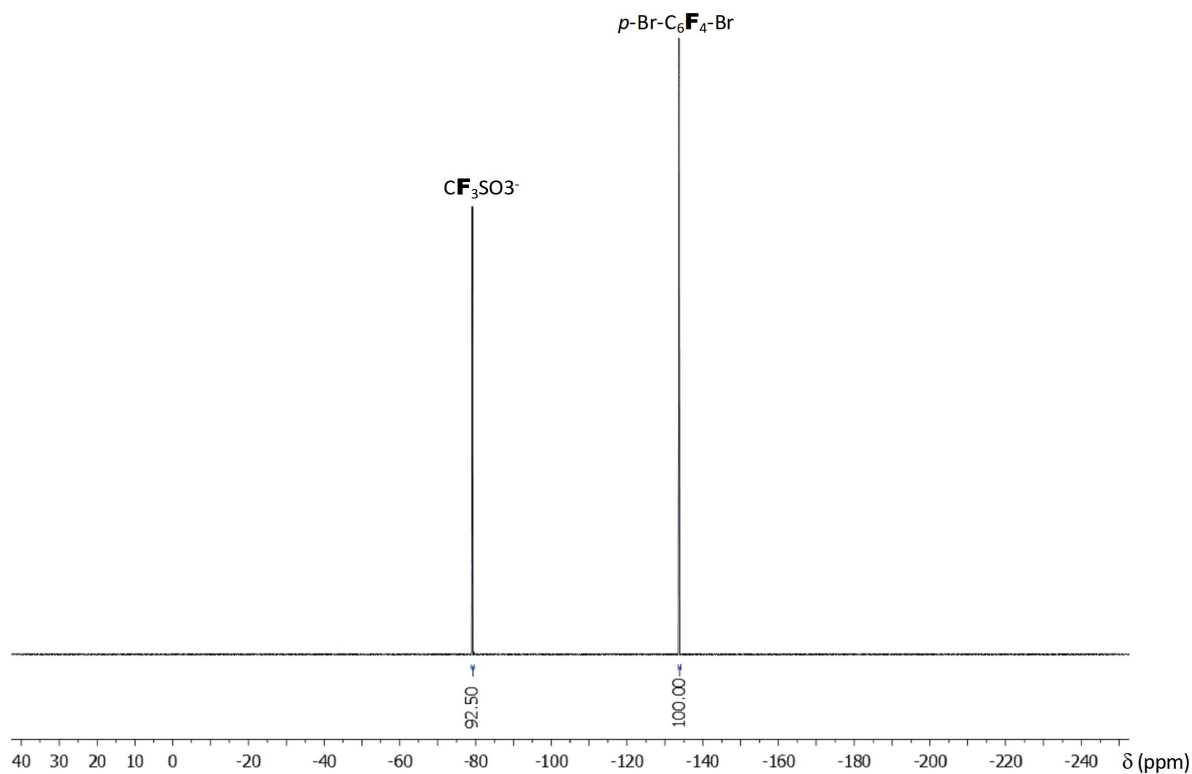
1) ^{19}F NMR (CD_3CN , 471 MHz) spectra of redissolved crystals of compound **1**.



2) ^{19}F NMR (CD_3CN , 471 MHz) spectra of redissolved crystals of compound **2**.



3) ^{19}F NMR (CD_3CN , 471 MHz) spectra of redissolved crystals of compound **3**.



4) **Table 4.** ^{19}F NMR results

Compound	Theoretical mass percentage of CF_3SO_3^- in $\text{Pb}_6\text{L}_2\text{S}_3(\text{OTf})_{12}$ (%)	Integral of F from spectra of compounds 1 - 3 , when that corresponding to 9 equiv. of $p\text{-BrC}_6\text{F}_4\text{Br}$ is 100	Mass percentage of CF_3SO_3^- found in the sample (%) ($\pm 10.0\%$ of the values)	Number of CF_3SO_3^- anions (with respect to the formula $\text{Pb}_6\text{L}_2\text{S}_3(\text{OTf})_{12}$) according to the percentage found in the sample ($\pm 10.0\%$ of the values)	Theoretical number of CF_3SO_3^- anions
	<i>pOTft</i>	<i>l</i>	<i>pOTff</i>	<i>nOTff</i>	<i>nOTft</i>
1 (s =a)	33.9	94.9	32.2	11.4	12.0
2 (s =b)	33.4	91.5	30.6	11.0	12.0
3 (s =c)	32.5	92.5	30.1	11.1	12.0

Notations and formulae:

$$pOTff = pOTft \times l \times 0.01$$

$$nOTff = 12 \times l \times 0.01 = 0.12 \times l$$

G. Anion exchanges with PF₆⁻

To reaction mixtures prepared as described before (section A), but starting from 1.0 mg of ligand **L**, was added an excess of NBu₄PF₆ (7-9 equiv.; Bu = CH₃CH₂CH₂CH₂). Slow diffusion of diethyl ether into the solution afforded yellow-orange crystals (1.8 - 2.5 mg). Only 1-2 single crystals per sample were analyzed through X-ray diffraction.

G1. Table 5. Crystallographic data for compounds **1PF₆**, **2PF₆** and **3PF₆**.

	1PF₆	2PF₆	3PF₆
empirical formulae	C ₁₃₁ H ₁₂₆ F ₃₉ N ₄₈ O ₃₃ PPb ₆ S ₁₁ [+ solvent] = Pb ₆ L ₂ a ₃ (OTf) ₁₁ PF ₆ [+ solvent]	C ₁₃₄ H ₁₃₂ F ₃₀ N ₄₈ O ₂₄ PPb ₆ S ₈ [+ solvent] = Pb ₆ L ₂ b ₃ (OTf) ₈ PF ₆ [+ solvent]	C ₁₄₆ H ₁₃₈ F ₃₀ N ₄₈ O ₂₄ PPb ₆ S ₈ [+ solvent] = Pb ₆ L ₂ c ₃ (OTf) ₈ PF ₆ [+ solvent]
<i>fw</i> [g/mol]	5268.56	4899.46	5049.63
crystal system	hexagonal	trigonal	Trigonal
space group	P63/m	R-3:H	R-3:H
Cell <i>a</i> = <i>b</i> [Å]	21.0367(9)	21.1133(6)	21.0435(6)
<i>c</i>	31.8231(16)	51.250(3)	58.507(3)
<i>V</i> [Å ³]	12196.3(12)	19784.9(15)	22437.5(16)
<i>Z</i>	2	3	3
<i>T</i> [K]	120(2)	120(2)	120(2)
<i>λ</i> [Å]	0.71073	0.71073	0.71073
<i>d_c</i> [g cm ⁻³]	1.435	1.234	1.121
<i>μ</i> (<i>λ</i>) [mm ⁻¹]	4.317	3.957	3.491
<i>F</i> [000]	5092	7107	7341
2 θ _{max} [°]	56	56	56
meas rflns	216465	117507	70808
unique rflns	9913	10519	11923
<i>R</i> _{int}	0.0821	0.0421	0.0314
<i>R</i> _{sigma}	0.0263	0.0208	0.0224
rflns with <i>I</i> > 2 σ (<i>I</i>)	7225	8716	10039
refined params	365	370	376
restraints	29	35	18
<i>R</i> 1(<i>I</i> > 2 σ (<i>I</i>))	0.0789	0.0395	0.0403
<i>wR</i> 2(all data)	0.2101	0.1158	0.1220
largest diff. peak/hole / e Å ⁻³	1.90/-2.09	2.52/-1.21	2.43/-2.16
CCDC number	2293672	2293677	2293673

Comments to structure 1PF₆. 1) Due to high thermal agitation, two CF₃SO₃⁻ anions were left as isotropic, a fact that produced an alert of level B in the checkCIF report (F2, F3, F4, O1, O2 etc). 2) The squeeze tool has been used and the residual electron density was assigned to four molecules of CH₃CN per asymmetric unit.

Comments to structure 2PF₆. 1) Three negative charges are required for the formula C₁₃₄H₁₃₂F₃₀N₄₈O₂₄PPb₆S₈ = Pb₆L₂b₃(OTf)₈PF₆ to be neutral. 2) The squeeze tool has been used; the residual electron density was assigned to 14 molecules of acetonitrile (solvent) and 0.50 CF₃SO₃⁻ anion; 2131/6 ≈ 355 e per asymmetric unit; 14 molecules of acetonitrile CH₃CN (solvent) and 0.50 CF₃SO₃⁻ anion would give 345 e. 3) Some atoms were left as isotropic due to high thermal agitation: S1, O1, O2, O3, C21, F1, F2, F3, C21, AF1, AF2, AF3.

Comments to structure 3PF₆. 1) Three negative charges are required for the formula C₁₄₆H₁₃₈F₃₀N₄₈O₂₄PPb₆S₈ = Pb₆L₂c₃(OTf)₈PF₆ to be neutral. 2) The squeeze tool has been used; the residual electron density was assigned to 18 molecules of acetonitrile (solvent) and 0.50 CF₃SO₃⁻

anion; $2695/6 \approx 449$ e per asymmetric unit; 18 molecules of acetonitrile CH_3CN (solvent) and 0.50 CF_3SO_3^- anion would give 433 e. 3) Some atoms were left as isotropic due to high thermal agitation: C24, F1, F2, F3, C24, AF1, AF2, AF3.

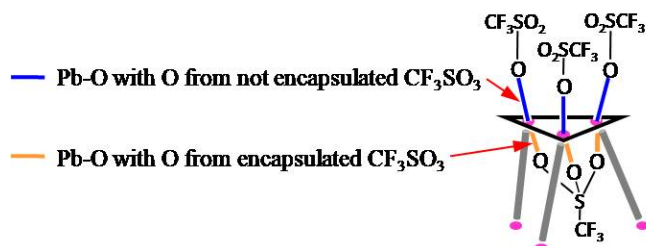
G2. Table 6. Values of several distances (centroid-to-centroid) and angles in structures 1PF_6 - 3PF_6 .

Distance (Å)	1PF_6	2PF_6	3PF_6
Pb-N _{pyrimidine} ¹⁾	2.87(1), 2.87(2), 2.869(8), 2.757(8), 2.76(1), 2.76(1)	2.735(5), 2.735(3), 2.735(6), 2.820(5), 2.820(5), 2.820(6)	2.718(4), 2.718(5), 2.718(6), 2.866(3), 2.866(4), 2.866(6)
Pb-N _{pyridine from ligand L} ¹⁾	2.57(1), 2.57(1), 2.57(1)	2.609(5), 2.609(5), 2.609(6)	2.601(4), 2.601(5), 2.601(6)
Pb-Nsp ² _{hydrazone} ¹⁾	2.64(1), 2.64(2), 2.644(8), 2.68(1), 2.68(1), 2.678(8)	2.668(4), 2.668(7), 2.668(3), 2.692(7), 2.692(4), 2.692(4)	2.710(3), 2.710(5), 2.710(6), 2.674(3), 2.674(5), 2.674(6)
Pb-N _{linker} ¹⁾	2.49(1), 2.49(1), 2.49(1)	2.476(5), 2.476(5), 2.476(5)	2.494(4), 2.494(4), 2.494(4)
Pb-O encapsulated triflate ²⁾	2.905(9), 2.90(1), 2.90(1)	2.940(4), 2.940(5), 2.940(6)	2.894(5), 2.894(3) 2.894(4)
Pb-O _{triflate} (not encapsulated) ²⁾	2.838(9), 2.84(1), 2.84(1)	2.809(5), 2.809(5), 2.809(6)	2.796(7), 2.796(7), 2.796(8)
Pb-Pb (in metallated macrocycle $[\text{Pb}_3\text{L}]^{6+}$) ¹⁾	7.0369(6), 7.0369(8), 7.0369(9)	6.9862(6), 6.9862(8), 6.9862(9)	6.9792(6), 6.9792(8), 6.9792(9)
Pb-Pb (connected through a linker s)	11.995(1)	14.122(2)	16.248(2)
Pb-Pb (in the lower (larger) base of the frustum)	no frustum	14.5786(9), 14.5786(9), 14.5786(6)	14.5091(6), 14.5091(9), 14.5091(9)
Edge of the macrocyclic complex ³⁾	17.775	17.818	17.725
Height of prism or frustum (distance between Pb_3 planes)	11.995(1)	13.184	15.452
Diameter of the lower (smaller) rim of the calyx-like motif (see paper)	4.536	4.472	4.533
Diameter of the upper (larger) rim of the calyx-like motif (see paper)	12.158	12.238	12.216
Roughly estimated height of anion layer	3.916	3.900	4.050
Angles (°)	1PF_6	2PF_6	3PF_6
Angle between the N-N axis of the linker and the Pb_3 plane of the macrocycle/larger base of the frustum	90.0	62.5	68.0
Twist angle	0.0	25.1	25.0

Notes

¹⁾ for one subunit $[\text{Pb}_3\text{Ls}_3]^{6+}$

²⁾ see the figure below:



Charges and real bond type (single/double) were omitted for clarity.

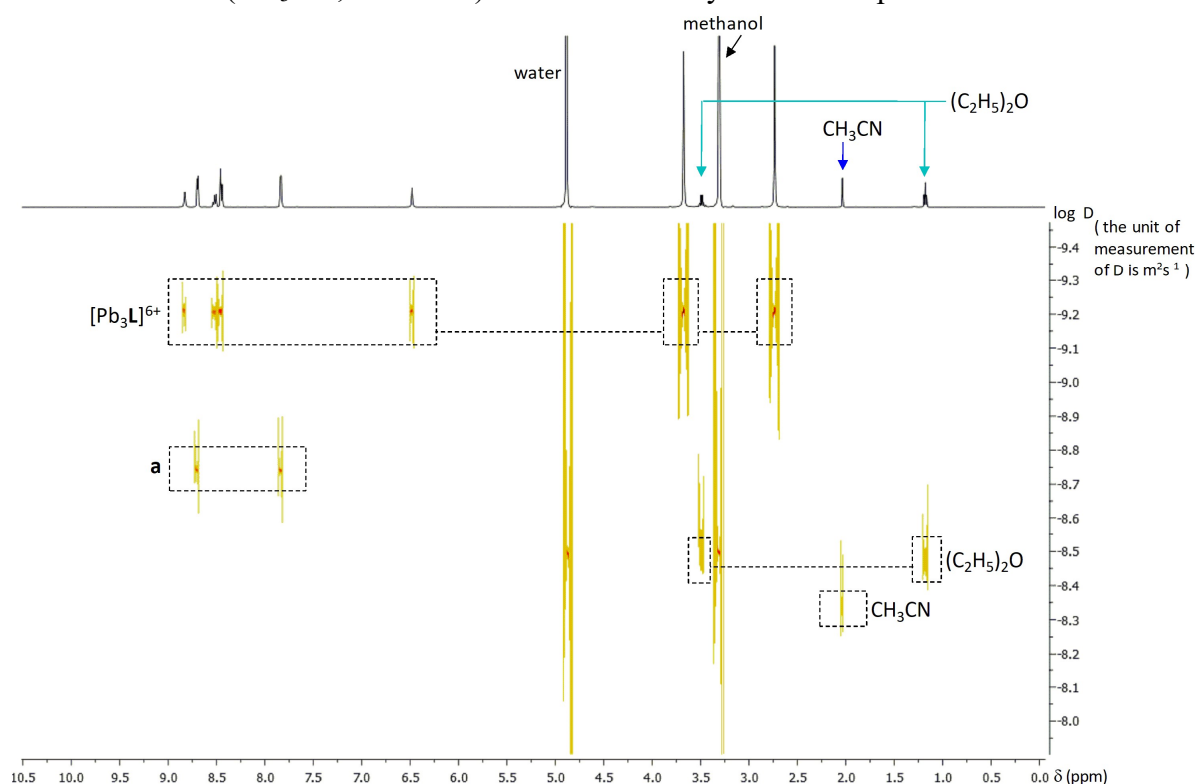
³⁾ centroid-to-centroid distance between H atoms in position 4 of pyridine rings

H. Change of the solvent used for NMR: CD₃CN -> CD₃OD

Crystals of compound **1**, dried for about 20-30 min under vacuum at room temperature, were redissolved in CD₃OD. It can be seen that:

- peaks corresponding to (C₂H₅)₂O and CH₃CN are present;
- dissociation of [Pb₆L₂a₃]¹²⁺ occurs in CD₃OD too.

¹H DOSY NMR (CD₃OD, 500 MHz) of redissolved crystals of compound **1**.



I. Selection

To a suspension of macrocyclic ligand **L** (1.00 mg, 1.13×10^{-3} mmol, 1 equiv.) in acetonitrile (0.1 mL) was added a solution of Pb(CF₃SO₃)₂ (1.71 mg, 3.39×10^{-3} mmol, 3 equiv.) in acetonitrile (0.2 mL) and the mixture was refluxed for about 10 min. The mixture was cooled to room temperature, then treated with 1.5 equiv. (1.69×10^{-3} mmol) of linker **a** in 26.4 μL solution of concentration 1 mg/100 μL , 1.5 equiv. (1.69×10^{-3} mmol) of linker **b** in 30.8 μL solution of concentration 1 mg/100 μL and 1.5 equiv. (1.69×10^{-3} mmol) of linker **c** in 157.3 μL solution of concentration 1 mg/400 μL . The mixture thus obtained was stirred for 10 minutes at room temperature, after which it was centrifuged. Slow diffusion of diethyl

ether into the solution afforded yellow crystals, which were dried under vacuum at room temperature (yield: 2.40 mg).

^1H DOSY NMR (CD_3CN , 500 MHz) of redissolved crystals obtained from a mixture of 1 equiv. of $[\text{Pb}_3\text{L}](\text{OTf})_6$, 1.5 equiv. of linker **a**, 1.5 equiv. of linker **b** and 1.5 equiv. of linker **c**.

