

Supporting Information - Zipping and Unzipping Monolayers: Switchable Monolayer Oligomerization and Adhesion via Thiol - Disulfide Interconversion. Jian He, Kyle J. Myerson and Matthew B. Zimmt

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ii) Synthesis of **1**

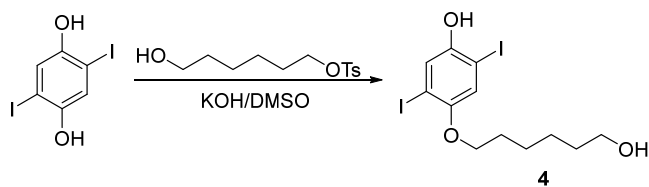
Syntheses and Spectral Characterization of new compounds.

Abbreviations: DCM = dichloromethane; DMAP = 4-dimethylaminopyridine; DMF = dimethylformamide; DTT = dithiothreitol; TTPA = 3-tritylthiopropionic acid; EDC = N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride; Tris = 2-amino-2-(hydroxymethyl)-1,3-propanediol; THAP = 2',4',6'-Trihydroxyacetophenone monohydrate; TEA = triethylamine; THF = tetrahydrofuran; Ts = 4-Toluenesulfonyl.

2,5-Diiodobenzene-1,4-diol, DMAP, 1,6-dibromohexane, 1-octanethiol, DTT, 1-phenyloctane, pentanoic acid, THAP, sodium iodide and cuprous iodide were purchased from Sigma-Aldrich (St. Louis, MO). EDC, TTPA and triphenylphosphine were purchased from Oakwood Chemical (Estill, SC). Iodine was purchased from Alfa Aesar (Ward Hill, MA). Palladium(II) chloride was purchased from Strem Chemicals (Newburyport, MA). Di-tert-butylpyridine was purchased from Combi-Blocks (San Diego, CA). HPLC grade solvents (DCM, chloroform, ethyl acetate, THF, TEA, ethanol, DMSO and DMF), potassium carbonate and potassium hydroxide were purchased from Fisher Scientific (Pittsburgh, PA).

Dry Solvent: Anhydrous and oxygen-free solvents were collected from a solvent column system.¹ All reactions were carried out in flame-dried glass containers under argon atmosphere.

Column Chromatography: Flash column chromatography was run on silica gel (60Å, 230-400 mesh). The eluting solvent was chosen to generate an R_f of 0.15-0.35 of the desired product. Column fractions were analyzed by thin layer chromatography (coated with fluorescent indicator F254) and visualized using a UV lamp (254nm) or phosphomolybdic acid (PMA) as stain.



4-((6-hydroxyhexyl)oxy)-2,5-diiodophenol (4**)**. Into a 5mL microwave tube were added 2,5-diiodobenzene-1,4-diol (208mg, 0.58mmol), potassium hydroxide (40mg, 0.71mmol) and a stirring bar. The tube was sealed with an aluminum cap with septum, degassed under vacuum and refilled with argon a total of three times. Into a sealed 5mL round-bottom flask were added 6-hydroxyhexyl 4-methylbenzenesulfonate² (158mg, 0.58mmol) and DMSO (2mL). The DMSO solution was sparged with argon for 10 minutes and then transferred to the microwave tube using syringes under argon. The mixture was stirred at room temperature for 19 hours. Work-up and purification: The reaction mixture was quenched with 0.5M HCl and extracted with ethyl acetate. The organic layer was washed with

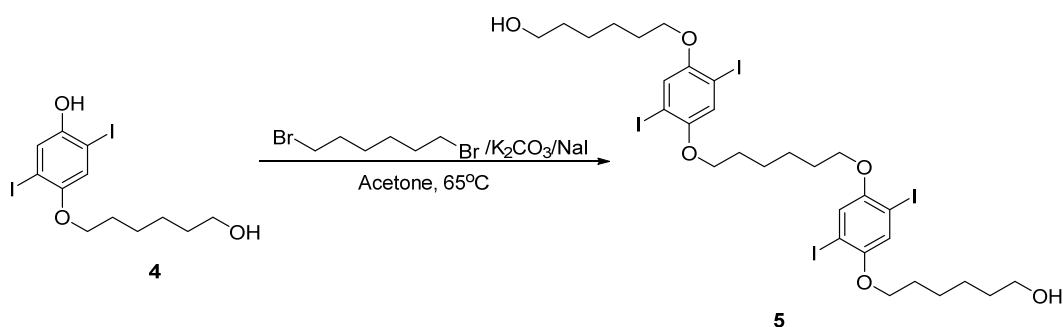
1) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. Timmers, *J. Organometallics*, **1996**, 15, 1518-1520.

2) J. He, C. Fang, R. A. Shelp and M. B. Zimmt, *Langmuir*, **2017**, 33, 459-467.

water, brine and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure. The crude product was purified by a flash column (30% ethyl acetate/hexanes) to afford 4-((6-hydroxyhexyl)oxy)-2,5-diiodophenol; pale solid; Yield: 85mg (32%).

^1H NMR (400MHz, acetone- d_6) δ 8.96 (br, 1H), 7.37 (s, 1H), 7.27 (d, 1H), 4.01 (t, $J = 6.4\text{Hz}$, 2H), 3.58 (t, $J = 6.2\text{Hz}$, 2H), 3.16 (br, 1H), 1.80 (quint, $J = 6.9\text{Hz}$, 2H), 1.60-1.42 (m, 6H).

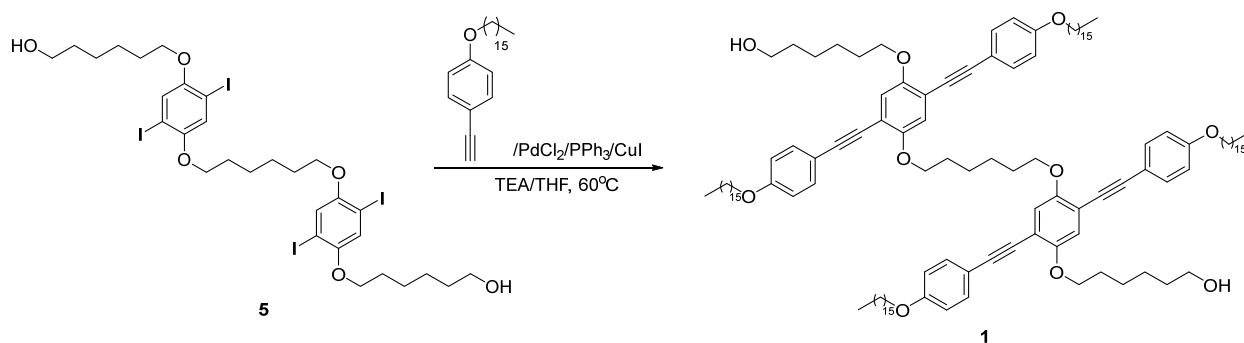
^{13}C NMR (100MHz, acetone- d_6) δ 152.16, 151.71, 124.45, 122.57, 86.19, 83.27, 69.98, 61.60, 32.81, 29.12, 25.84, 25.47.



6,6'-(((hexane-1,6-diylbis(oxy))bis(2,5-diiodo-4,1-phenylene))bis(oxy))bis(hexan-1-ol) (5). Into a 2mL microwave tube were added compound 4 (85mg, 0.18mmol), potassium carbonate (52mg, 0.38mmol) and sodium iodide (4mg, 0.027mmol). The tube was sealed with an aluminum cap with septum, degassed under vacuum and refilled with argon three times. Into a sealed 5mL round-bottom flask were added 1,6-dibromohexanes (21mg, 0.086mmol) and acetone (1mL). The acetone solution was sparged with argon for 5 minutes and then transferred to the microwave tube using syringes under argon. The reaction mixture was stirred at 65°C for 18 hours. Work-up and purification: The reaction mixture was cooled to room temperature, quenched with 0.5M HCl and extracted with ethyl acetate. The organic layer was washed with water, brine and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure. The crude product was purified by a flash column (30% ethyl acetate/DCM) to afford 6,6'-(((hexane-1,6-diylbis(oxy))bis(2,5-diiodo-4,1-phenylene))bis(oxy))bis(hexan-1-ol); white solid; Yield: 58mg (67%).

^1H NMR (400MHz, CDCl_3) δ 7.19 (s, 2H), 7.18 (s, 2H), 3.98 (t, $J = 6.3\text{Hz}$, 4H), 3.95 (t, $J = 6.3\text{Hz}$, 4H), 3.69 (t, $J = 6.5\text{Hz}$, 4H), 1.86 (m, 8H), 1.68-1.43 (m, 16H).

^{13}C NMR (100MHz, CDCl_3) δ 152.83, 152.81, 122.80, 122.74, 86.36, 86.31, 70.18, 69.98, 62.92, 32.69, 29.11, 28.96, 25.91, 25.50, 25.44.



6,6'-(((hexane-1,6-diylbis(oxy))bis(2,5-bis((4-(hexadecyloxy)phenyl)ethynyl)-4,1-phenylene))bis(oxy))bis(hexan-1-ol) (1). Into a 5mL microwave tube were added compound **5** (44mg, 0.044mmol), 1-ethynyl-4-(hexadecyloxy)benzene² (72mg, 0.21mmol), palladium chloride (2mg, 0.01mmol), cuprous iodide (2mg, 0.01mmol) and triphenylphosphine (7mg, 0.03mmol). The tube was sealed with an aluminum cap with septum, degassed under vacuum and refilled with argon three times. THF (2mL) and TEA (0.5mL) were then added to the tube using syringes. The reaction mixture was sparged with argon for 5 minutes and stirred at 60°C for 16 hours. Work-up and purification: The reaction mixture was cooled to room temperature and quenched with saturated NH₄Cl solution. The mixture was extracted with DCM. The organic layer was washed with water, brine and dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure. The crude product was purified by a flash column (2% ethyl acetate/DCM) to afford 6,6'-(((hexane-1,6-diylbis(oxy))bis(2,5-bis((4-(hexadecyloxy)phenyl)ethynyl)-4,1-phenylene))bis(oxy))bis(hexan-1-ol); yellowish solid; Yield: 52mg (63%).

¹H NMR (400MHz, CDCl₃) δ 7.48 (d, *J* = 4.4Hz, 4H), 7.46 (d, *J* = 4.4Hz, 4H), 7.00 (s, 2H), 6.99 (s, 2H), 6.88 (d, *J* = 4.4Hz, 4H), 6.84 (d, *J* = 4.4Hz, 4H), 4.04 (t, *J* = 6.3Hz, 4H), 4.03 (t, *J* = 6.2Hz, 4H), 3.99 (t, *J* = 6.6Hz, 4H), 3.92 (t, *J* = 6.6Hz, 4H), 3.66 (t, *J* = 6.5Hz, 4H), 1.92-1.28 (m, 136H), 0.90 (t, *J* = 6.8Hz, 12H).

¹³C NMR (100MHz, CDCl₃) δ 159.27, 153.50, 153.45, 132.99, 116.87, 115.38, 115.26, 114.53, 114.08, 113.98, 95.06, 94.91, 84.67, 84.61, 69.48, 68.11, 68.07, 62.93, 32.74, 31.95, 29.73, 29.69, 29.66, 29.63, 29.61, 29.46, 29.44, 29.39, 29.37, 29.33, 29.24, 26.05, 25.94, 25.54, 14.15.

MALDI-TOF Mass Spectrum (THAP matrix) 1864.0 (observed [M+H]⁺, expected 1864.4 [M+H]⁺)

iii) TOF-MS and STM Procedures

TOF-MS Procedures

a) Sample air dried then pumped 30 minutes 5 mm Hg prior to THAP application
b) 10-12 μL of 5 mg/mL THAP matrix in 30/70 acetone/hexane applied and allowed to air dry
c) TOF-MS data collected on a Bruker Daltonics Autoflex MALDI-TOF massspectrometer (Billerica, MA) running in linear mode. Sample holder (MTP PAC Frame) modifications to hold the HOPG substrate described in Langmuir 2017, 33, 459–467 (DOI: 10.1021/acs.langmuir.6b03252). HOPG substrates irradiated using the SmartbeamTM-II Nd:YAG laser (355 nm) 6_ultra laser profile operating at 1 kHz. Data was collected in positive ion mode using 500 laser shots at 70% of full laser power (60% for compound **1**), a TOF accelerating voltage of 19.45 kV, a grid voltage of 18.1 kV and pulsed ion extraction time of 90 μs . Instrument calibration for HOPG within the pressure mounted cell was performed using Bruker Daltonics Peptide Calibration Standard II.

STM Procedures

3-5 μL of 12 μM **1** (25% CHCl_3 / phenyloctane) was drop cast on a freshly peeled 12 mm x 12 mm HOPG substrate. After sitting five minutes, the monolayer / graphite was rinsed with 20 μL phenyloctane. For annealed samples (Fig. 2), the graphite was placed monolayer side down in 10 μL of phenyloctane or 10% 1-nonanol / phenyloctane in a sealable chamber and annealed two hours at 60°C. The sample was rinsed with 20 μL phenyloctane before STM or performing reaction chemistry.

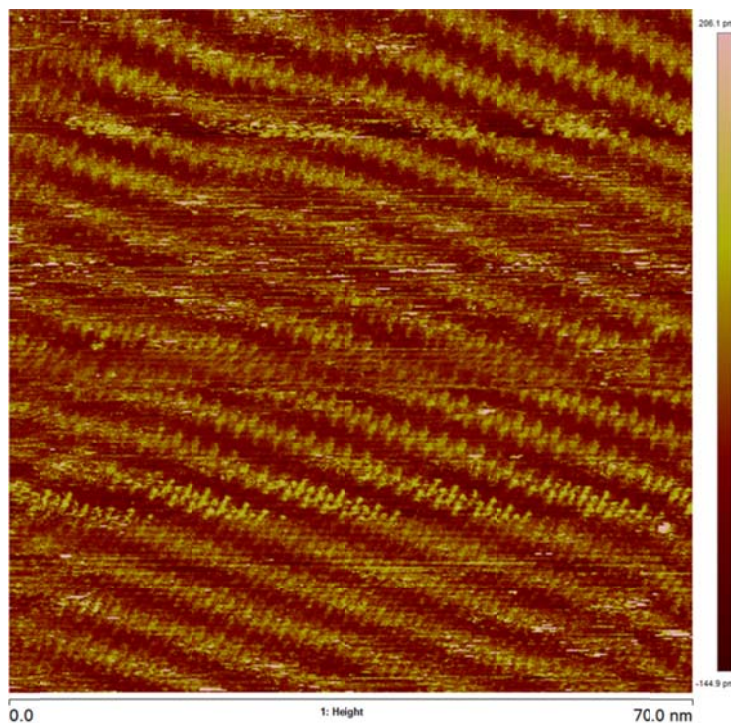
Scanning was initiated using a freshly cut 80/20 Pt/Ir tip (Bias voltage -1.2 V, set current 30 - 35 pA, scan rate, 5 - 7 Hz). All STM data was collected on a VEECO MS-10 STM instrument. Collected images were flattened.

iv) **Fig. S1.** STM image (70nm x 70 nm) of monolayer self-assembled by compound **1**.

(1.4V, 43 pA, 2.77 Hz)

Drop cast 3 μL of 12.5 μM **1** in 25% CHCl_3 / phenyloctane on freshly cleaved HOPG;

Annealed 2 hrs then rinsed rinsed with 20 μL phenyloctane prior to imaging.



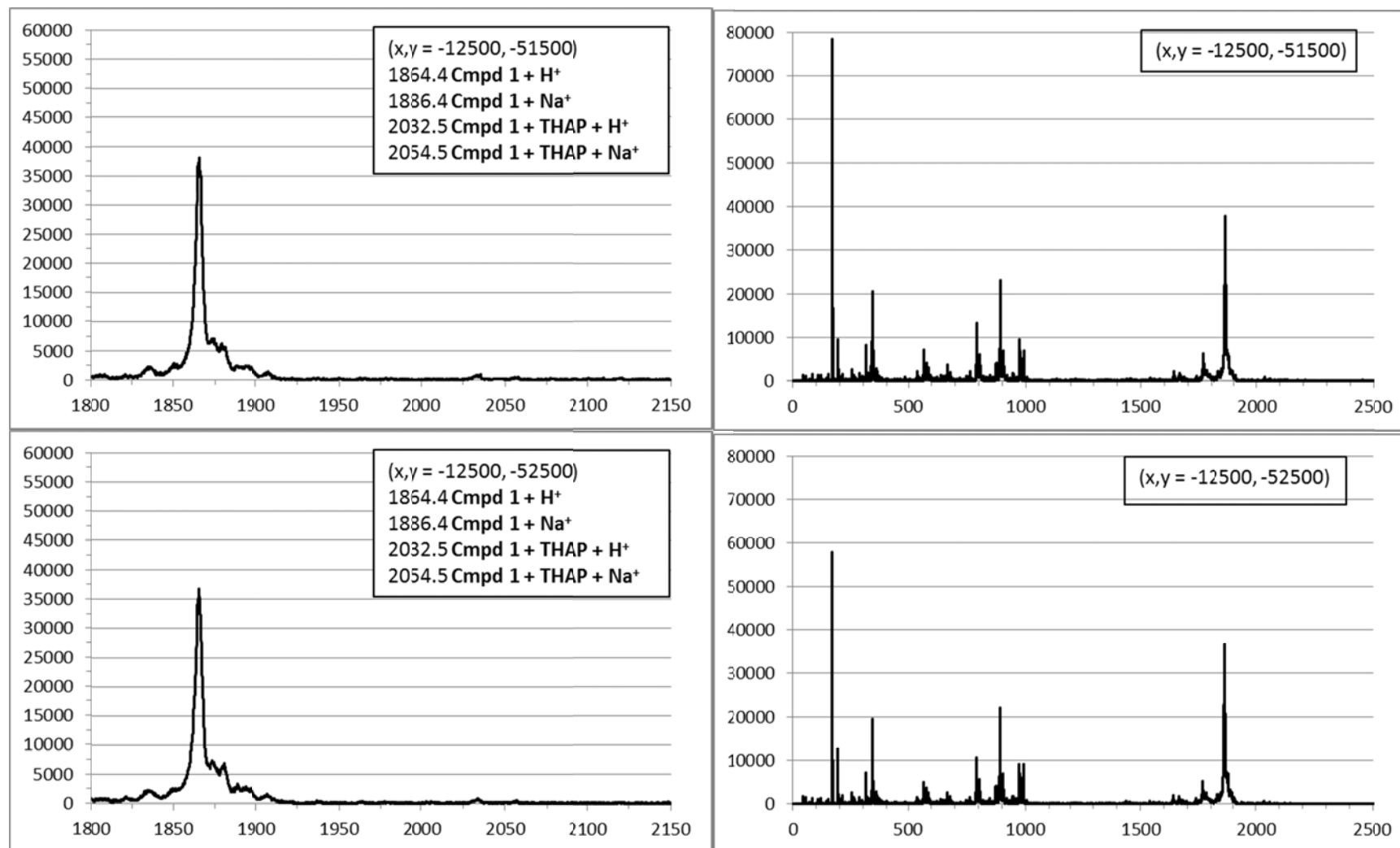
v) Fig. S2. TOF mass spectra from monolayers of **1** on HOPG. a) Statistical analysis of **1** molecular ion and THAP peak intensities from mass spectra collected at 69 spots on four independent samples; b) Individual TOF mass spectra collected from 5 spots used to generate the average spectrum reported in the original manuscript; c) Individual TOF mass spectra collected from 36 spots in a repeat study in December 2017 (see Figs. S4 and S15 for mass spectra at 28 spots measured in these two other studies); d) photo of THAP coated **1** / HOPG substrate after 36 TOF-MS measurements; e) MS peak / fragment assignments.

a) Summary and statistical analysis of mass spectra peak intensities from measurements performed on monolayers assembled from **1**.

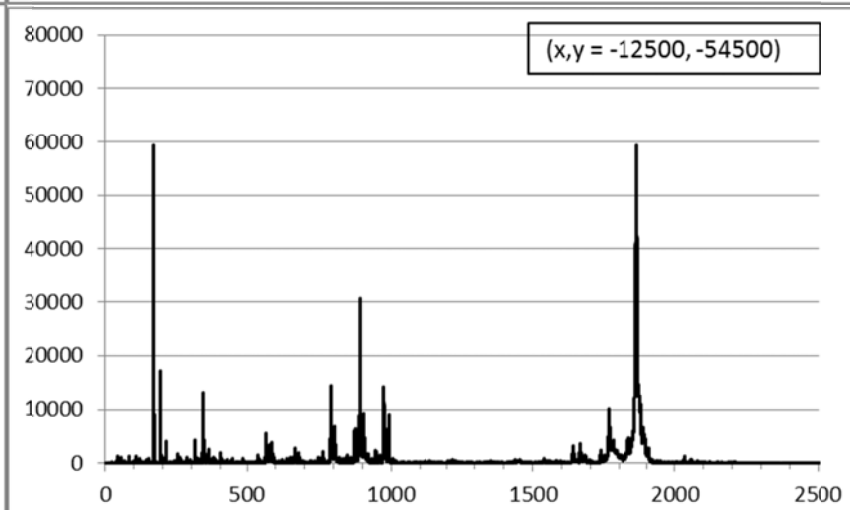
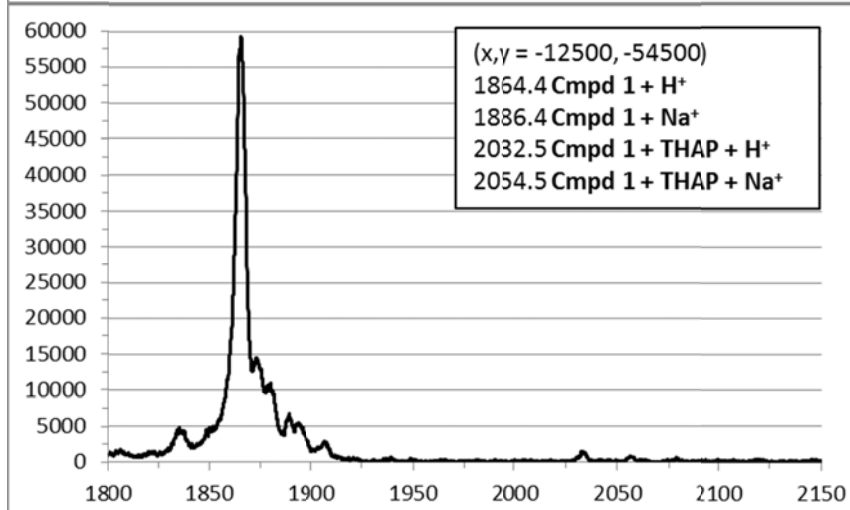
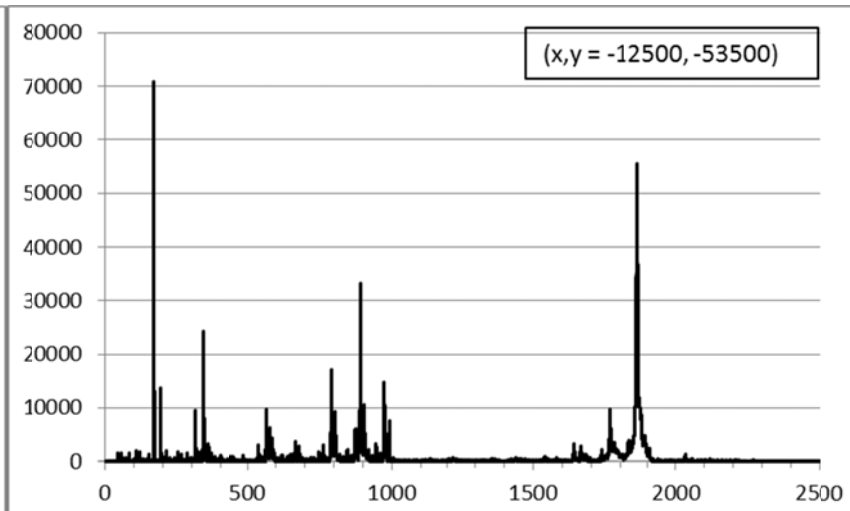
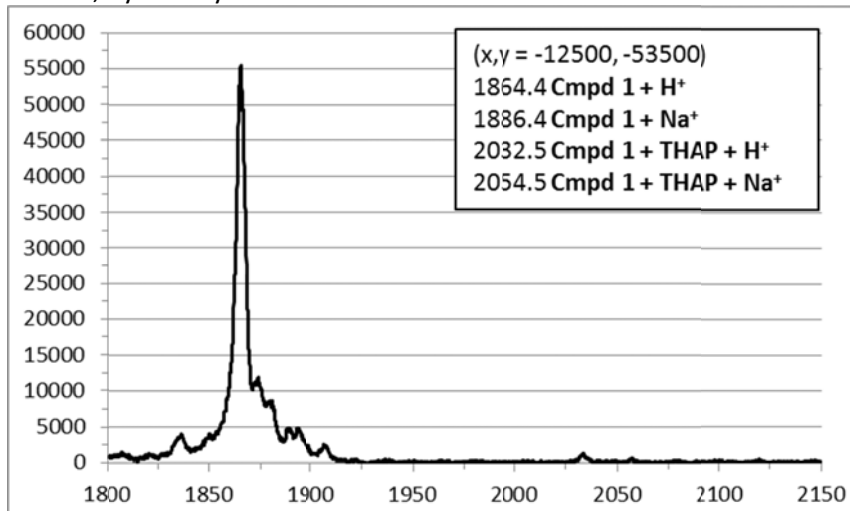
measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
Reported in text	5	169.3	matrix ([THAP+H] ⁺)	58000	78500	65100	9200	0.14
Rinse study (S15)	10	169.3	matrix ([THAP+H] ⁺)	57600	79600	67200	8500	0.13
βTTP control (S4)	18	169.3	matrix ([THAP+H] ⁺)	44800	86600	68000	12000	0.18
Repeat (left)	18	169.3	matrix ([THAP+H] ⁺)	56500	81400	73000	6600	0.09
Repeat (right)	18	169.3	matrix ([THAP+H] ⁺)	57400	85300	72800	8400	0.12
Repeat (l & r)	36	169.3	matrix ([THAP+H] ⁺)	56500	85300	73000	7500	0.10
Original	5	1864	[1 + H] ⁺	28600	59300	43400	13200	0.30
Rinse study (S15)	10	1864	[1 + H] ⁺	20400	59200	39000	11700	0.30
βTTP control (S4)	18	1864	[1 + H] ⁺	28000	57700	38900	10200	0.26
Repeat (left)	18	1864	[1 + H] ⁺	27900	63400	45400	9900	0.22
Repeat (right)	18	1864	[1 + H] ⁺	35600	68900	52700	8800	0.17
Repeat (l & r)	36	1864	[1 + H] ⁺	27900	68900	49000	10000	0.20
4 independently prepared monolayers of 1 on HOPG substrates	69	1864	[1 + H] ⁺	20400	68900	44600	11400	0.26

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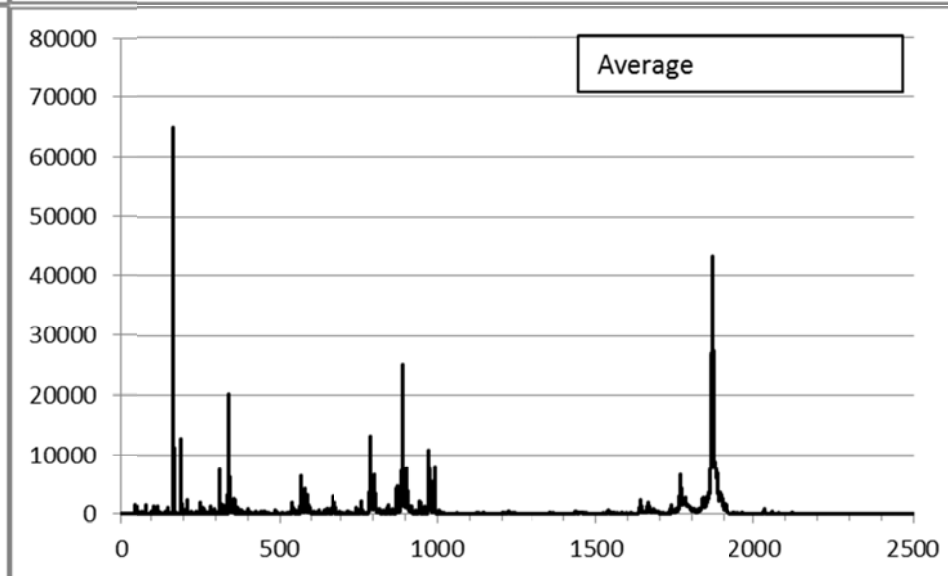
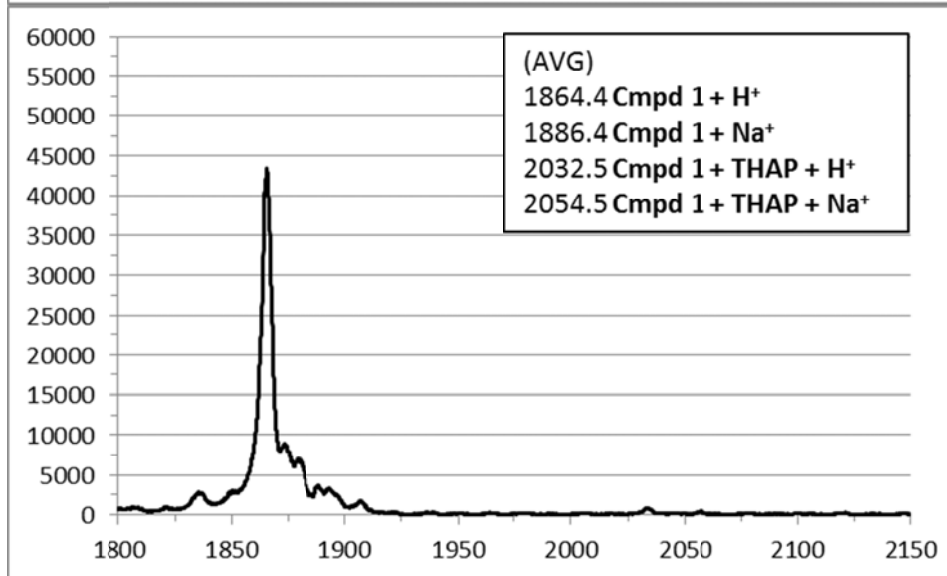
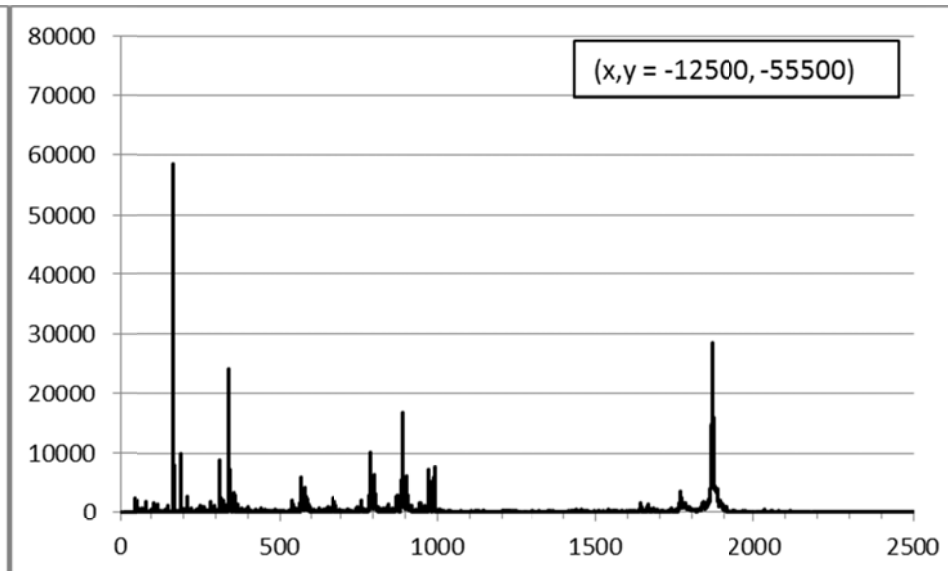
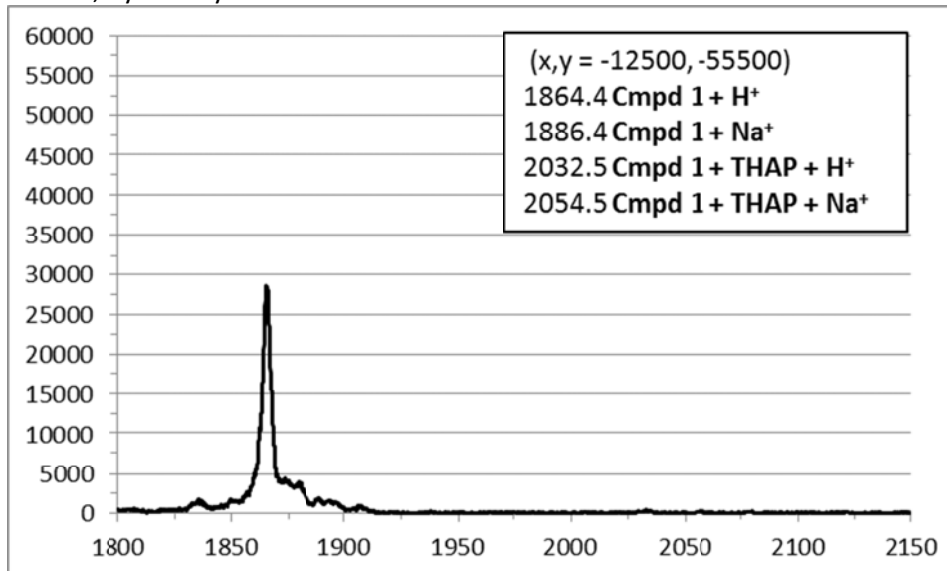
b) TOF mass spectra from monolayer of **1**. TOF-MS molecular ion region (left, Intensity (y) axis scale 0-60000) and 0-2.5kD region (right, intensity (y) axis scale 0-80000) from five locations sampled and then averaged to produce the compound **1** monolayer TOF-MS spectra displayed in the originally submitted manuscript. (x,y) are coordinates in microns at which data was collected (relative to the sample carrier reference position).



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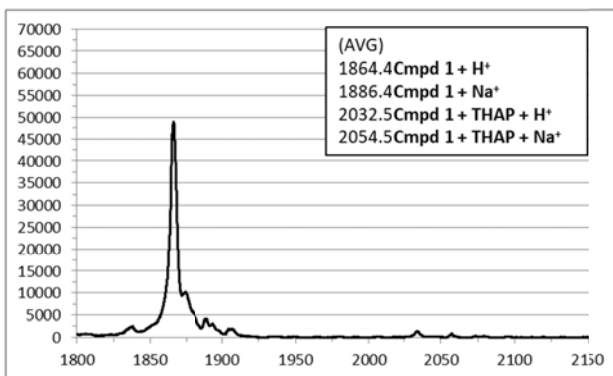
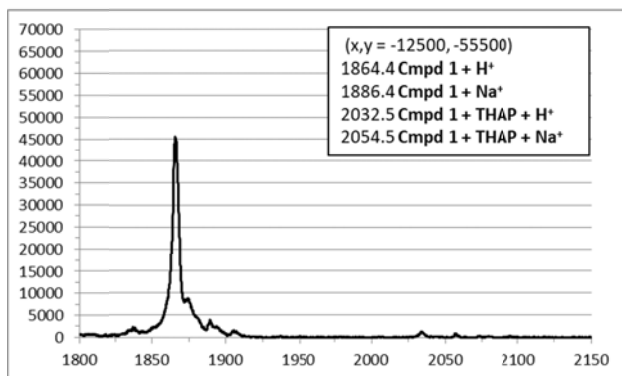
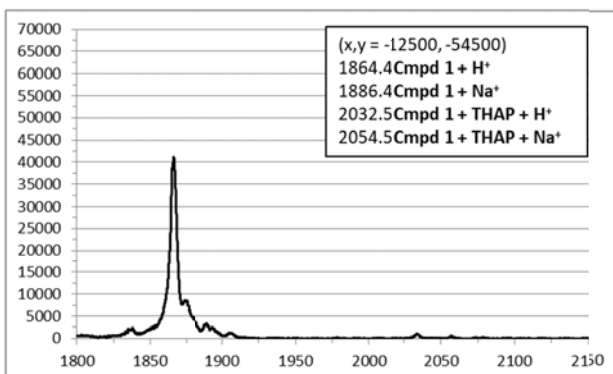
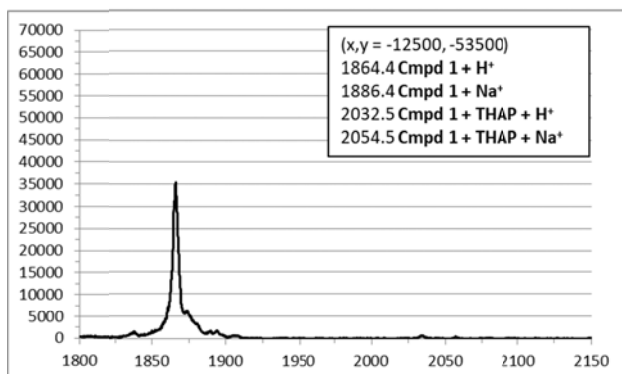
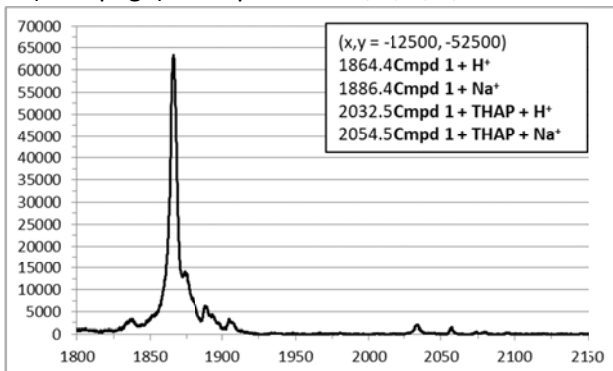
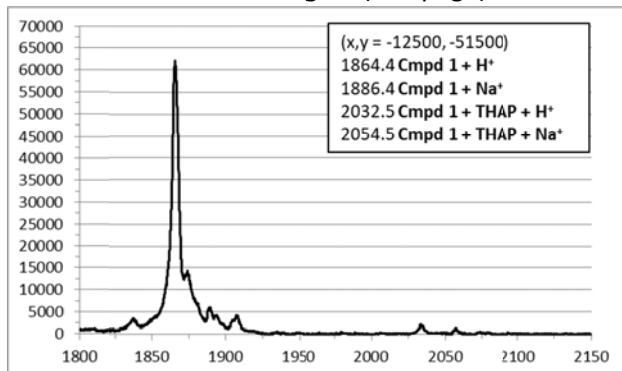


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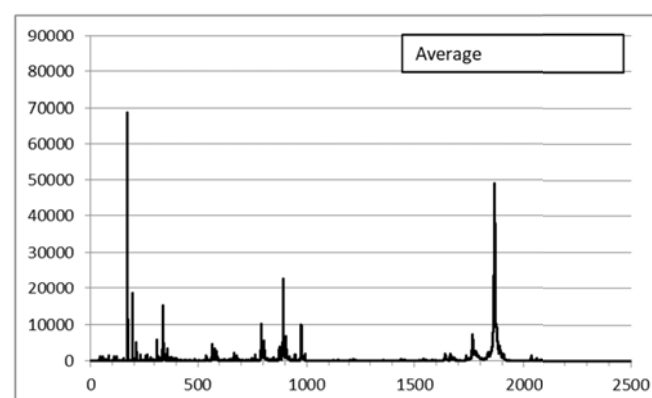
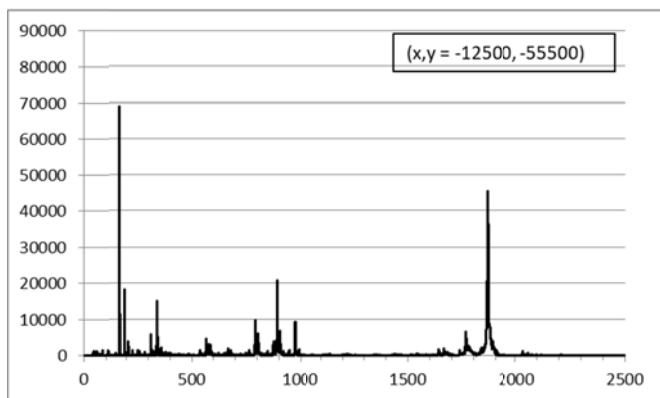
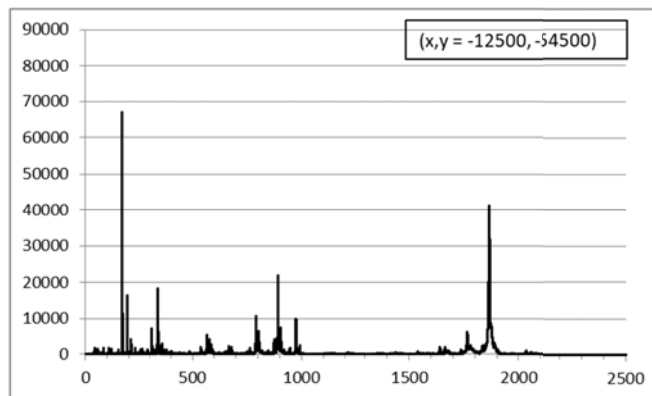
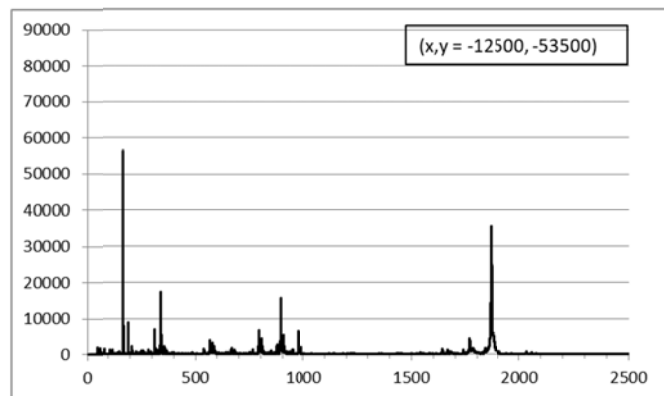
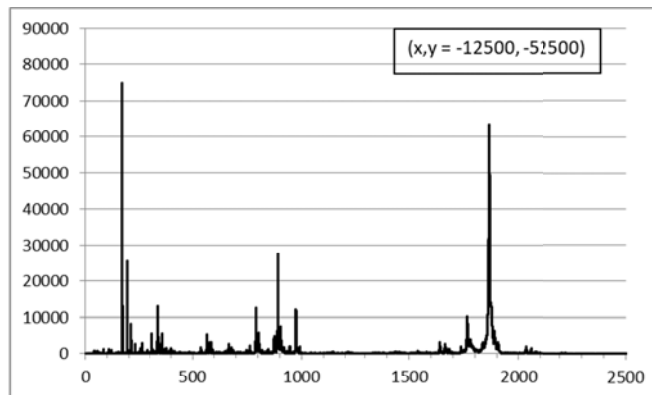
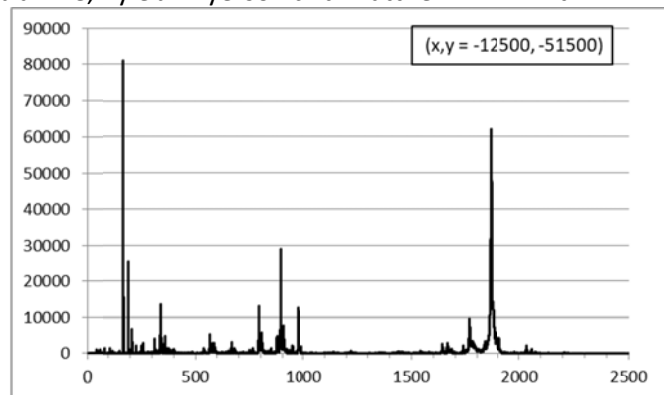
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c) TOF mass spectra from monolayer of **1**. TOF-MS molecular ion regions (Intensity (y) axis scale 0-70000) and 0-2.5kD regions (Intensity (y) axis scale 0-90000) from 36 locations sampled and then averaged (in groups of 5 or 4) for a repeat study of molecular ion intensities generated from a monolayer of compound **1**.

TOF-MS molecular ion region (this page) and 0-2.5 kD region (next page) from positions 1, 3, 5, 7, 9 of the left most column (and their average) of **1** monolayer

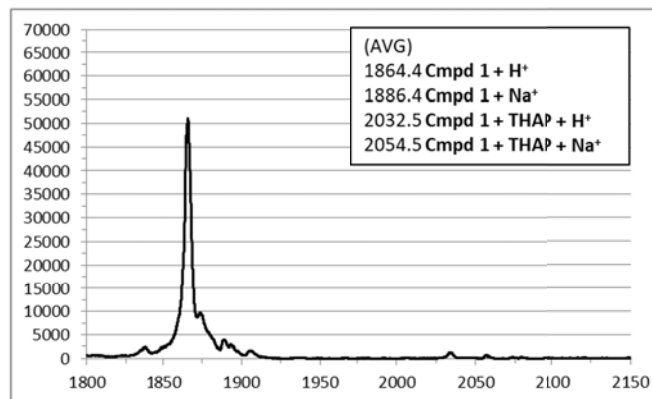
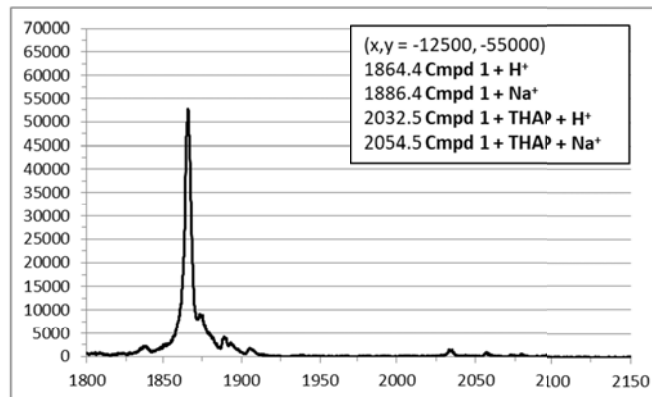
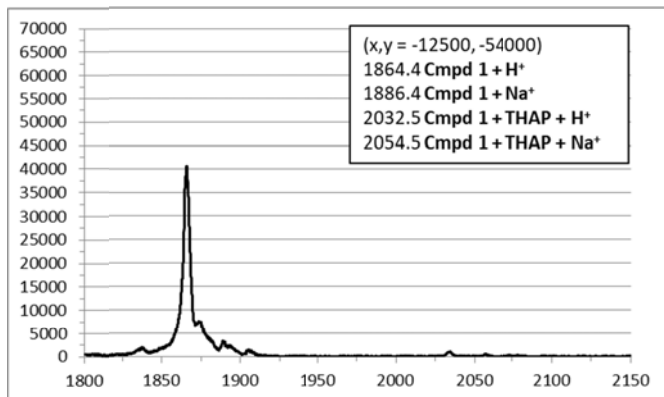
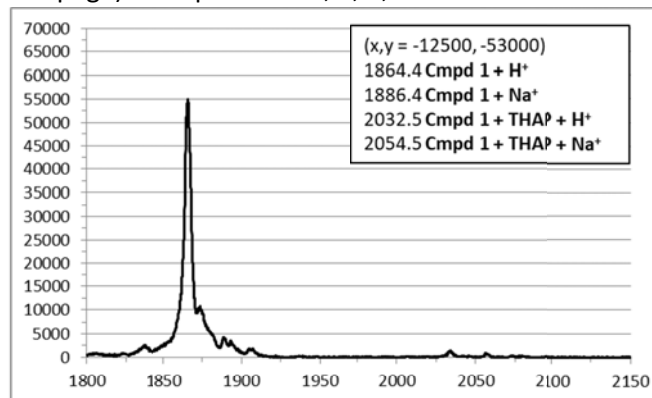
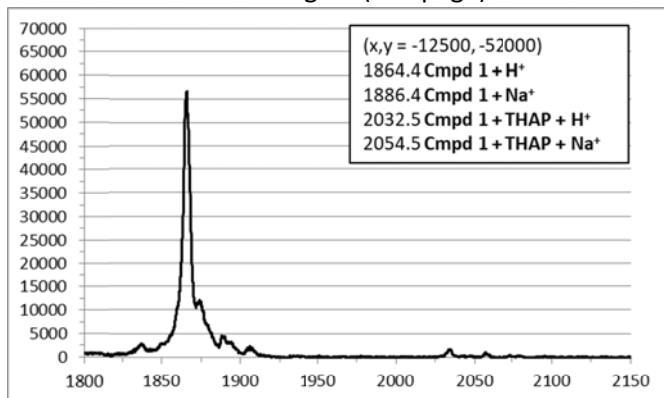


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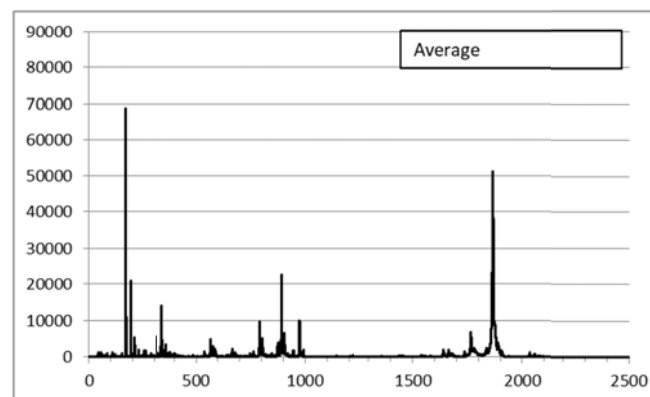
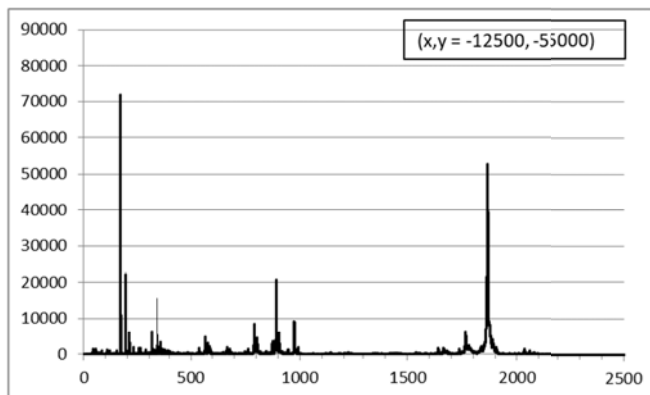
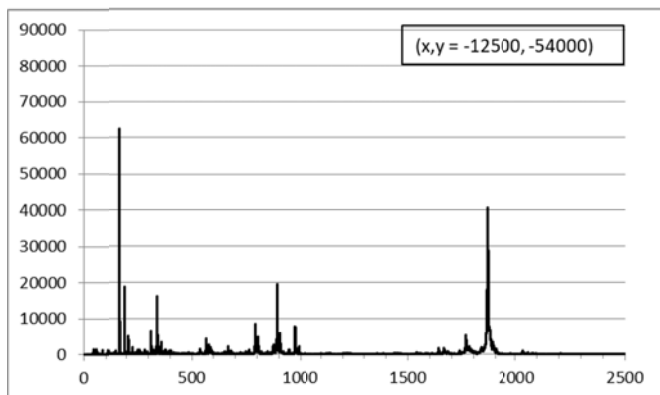
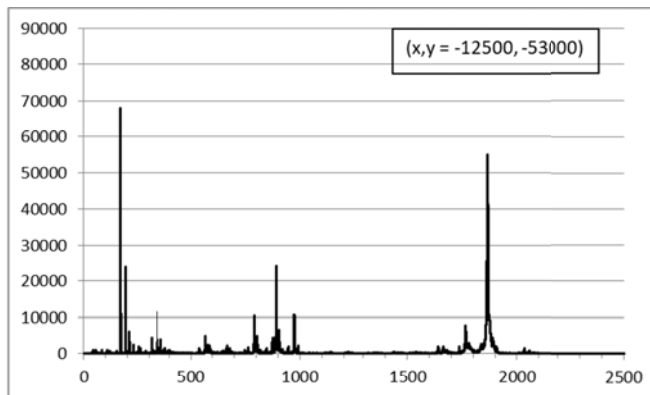
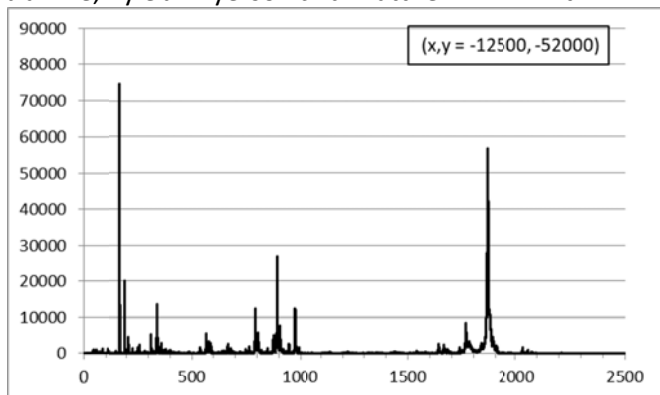


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TOF-MS molecular ion region (this page) and 0-2.5 kD region (next page) from positions 2, 4, 6, 8 of the left most column (and their average) of 1 monolayer



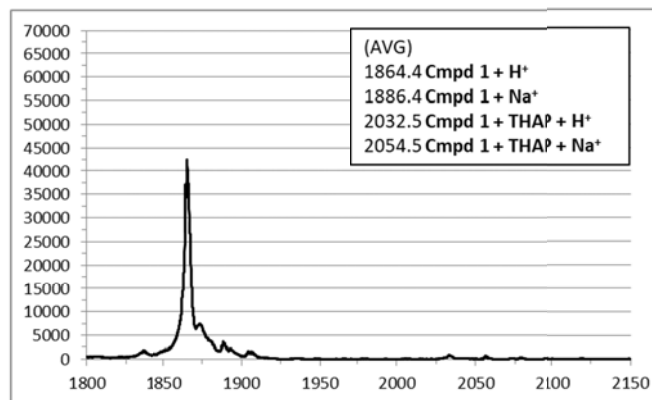
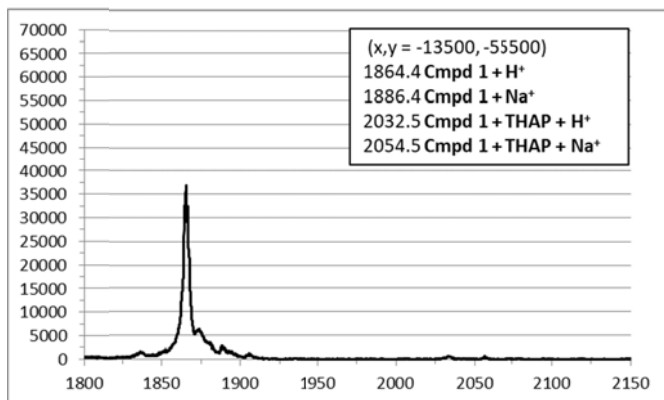
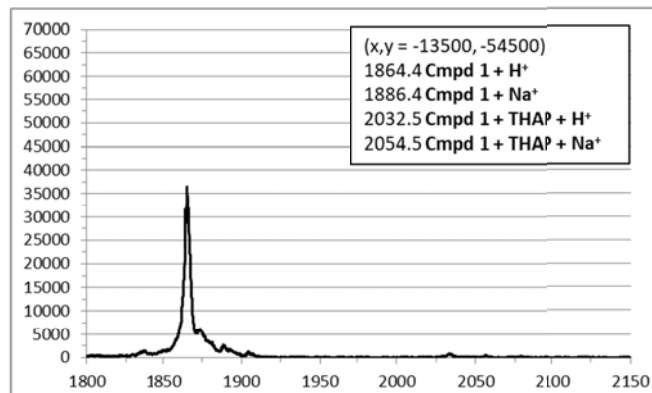
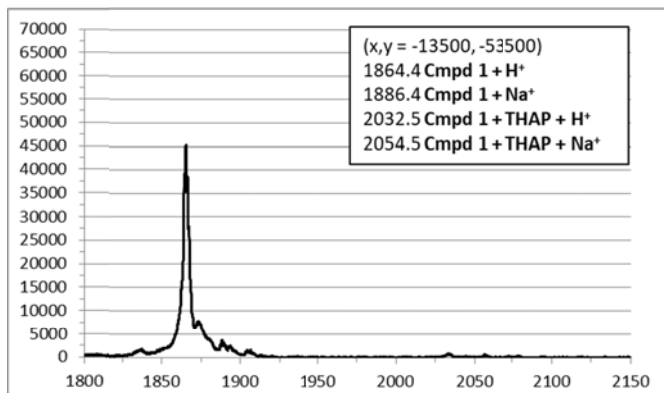
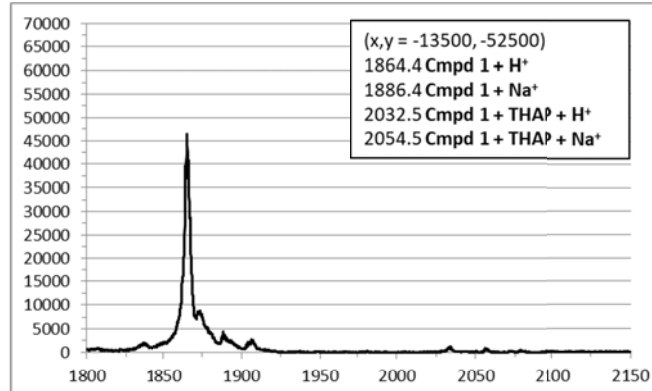
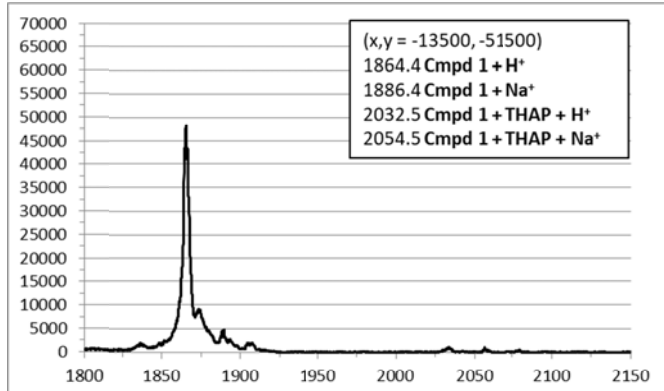
Supporting Information - Zipping and Unzipping Monolayers: Switchable Monolayer Oligomerization and Adhesion via Thiol - Disulfide Interconversion.
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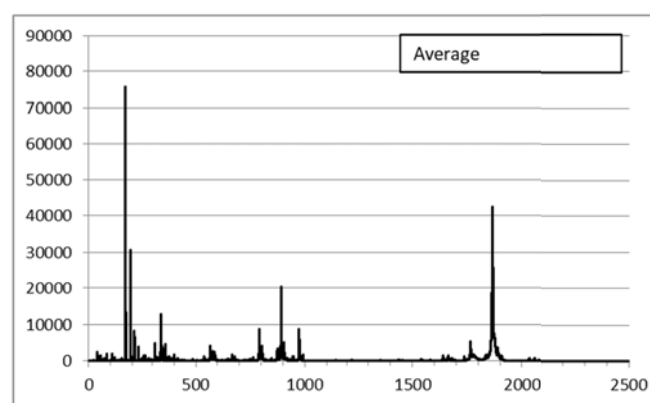
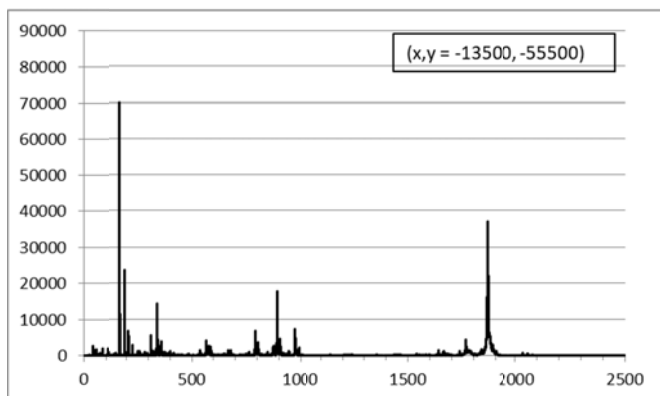
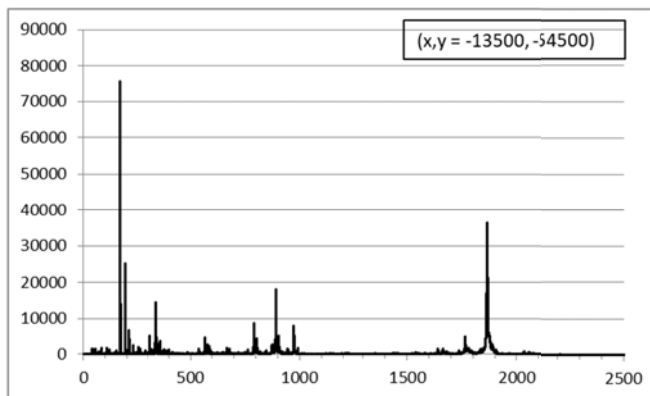
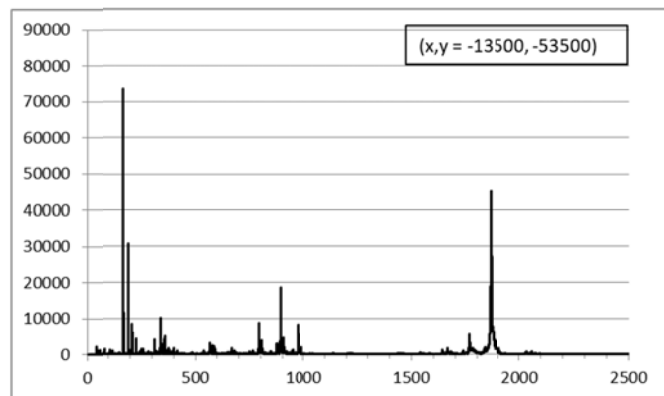
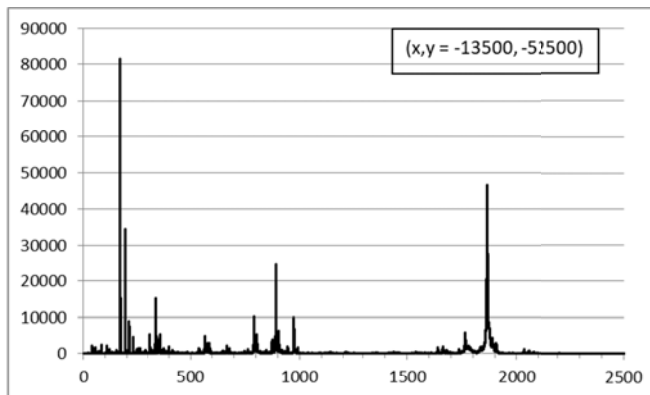
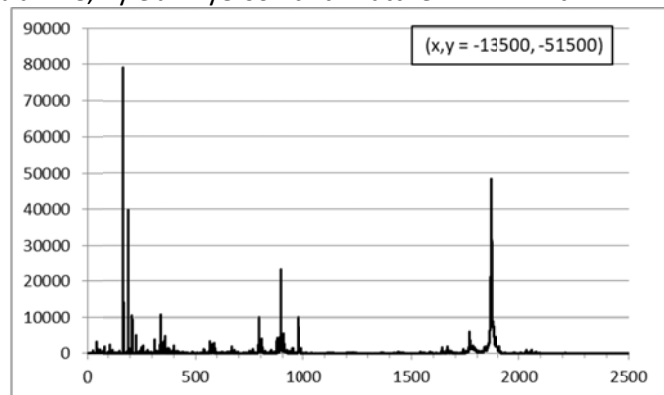
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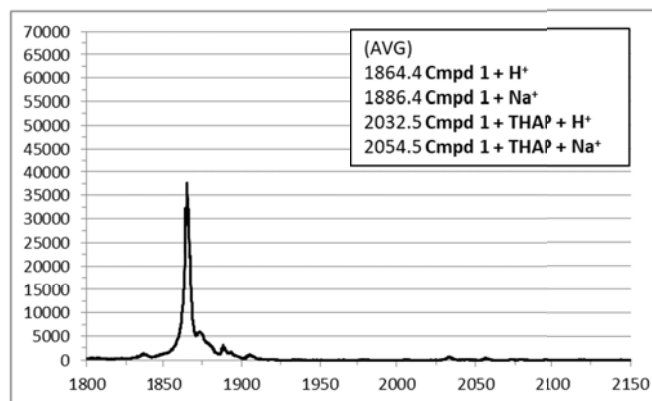
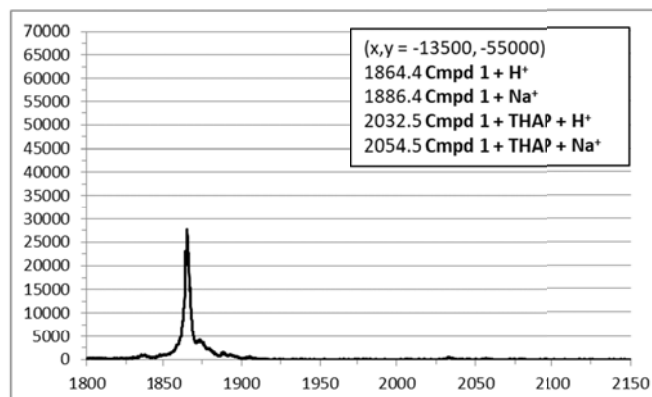
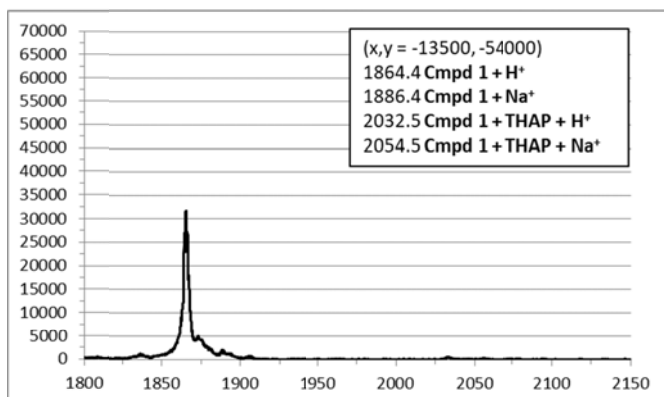
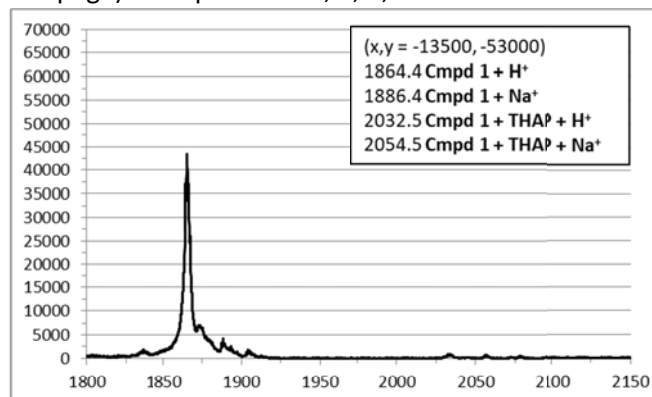
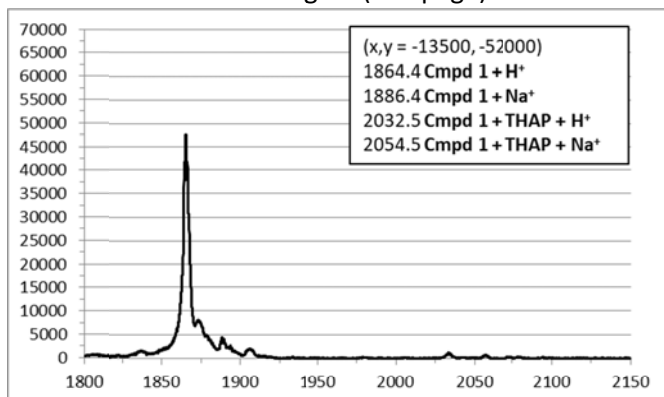
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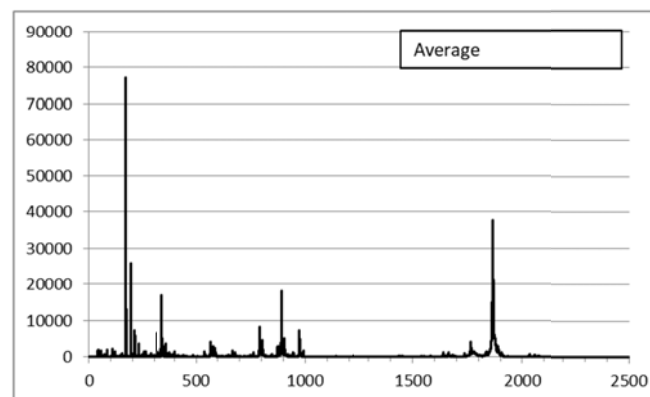
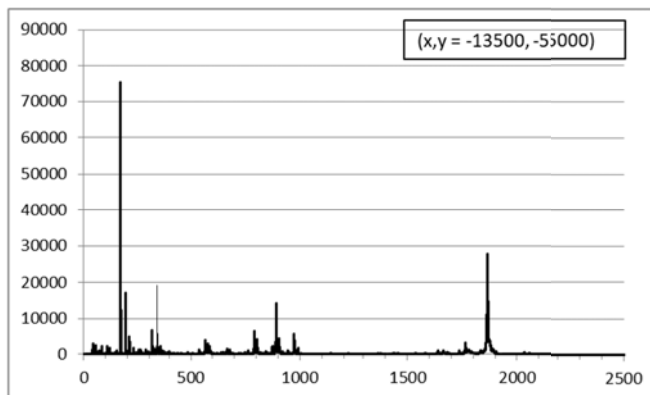
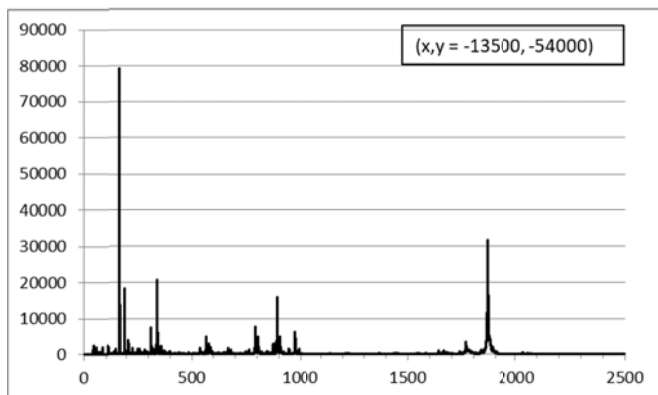
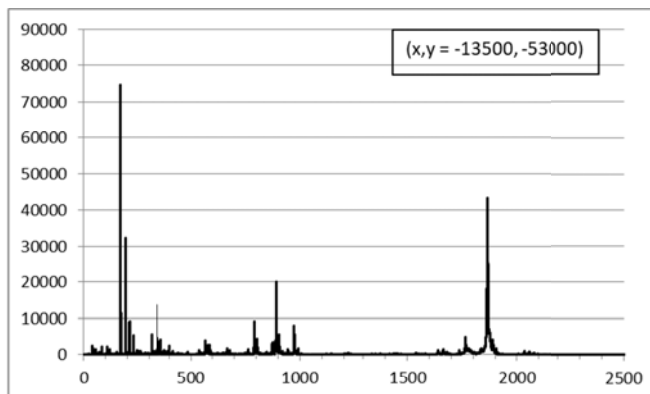
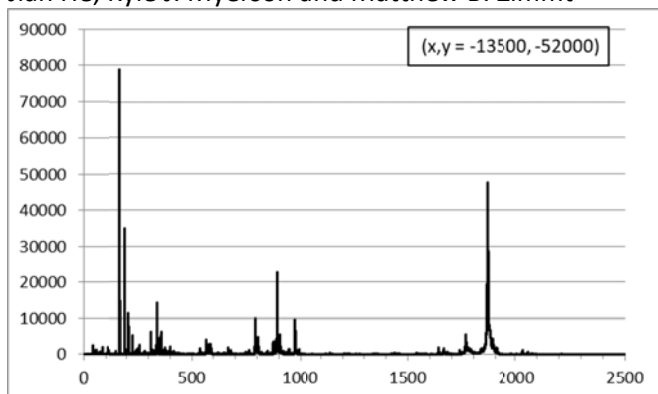
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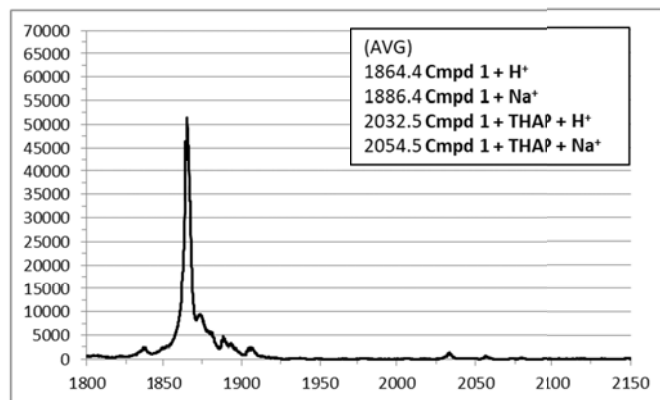
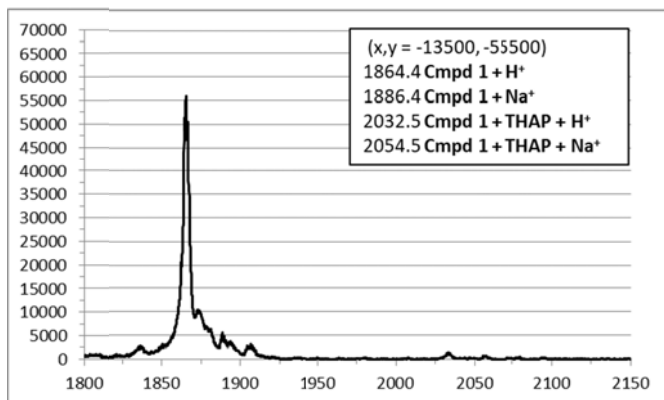
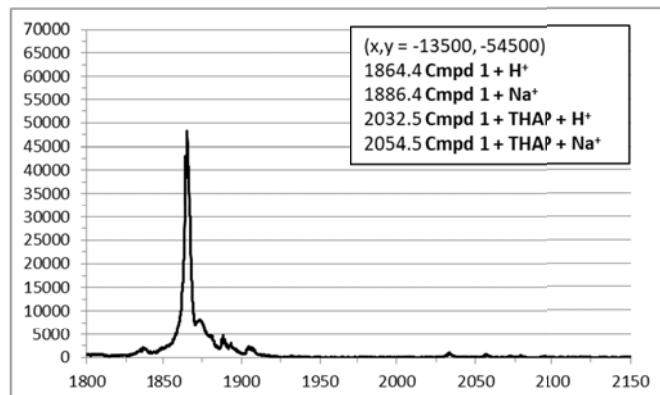
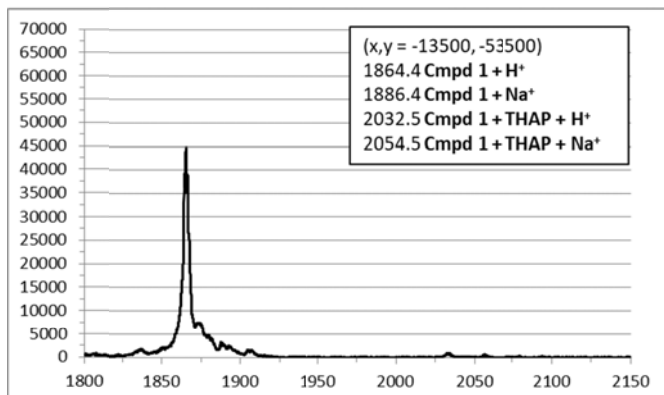
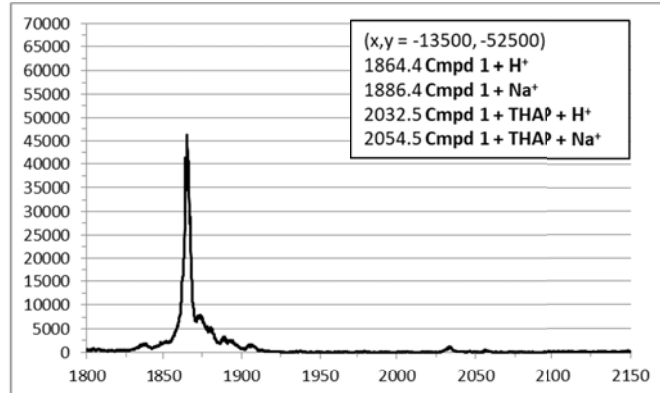
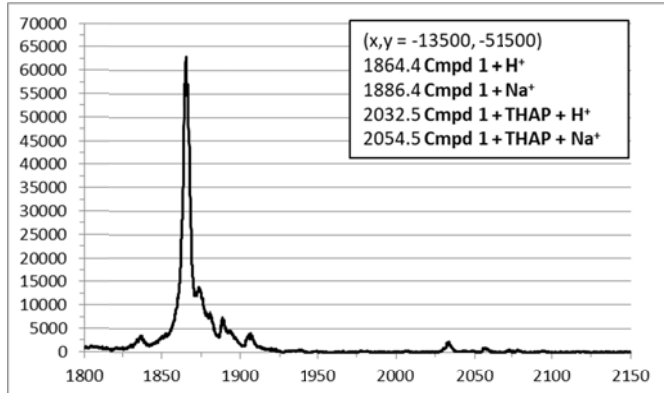
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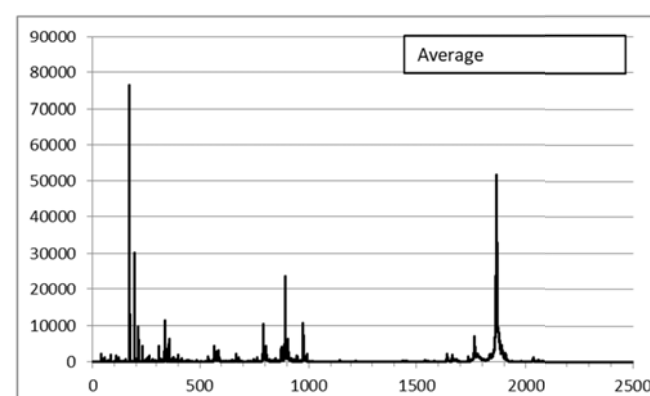
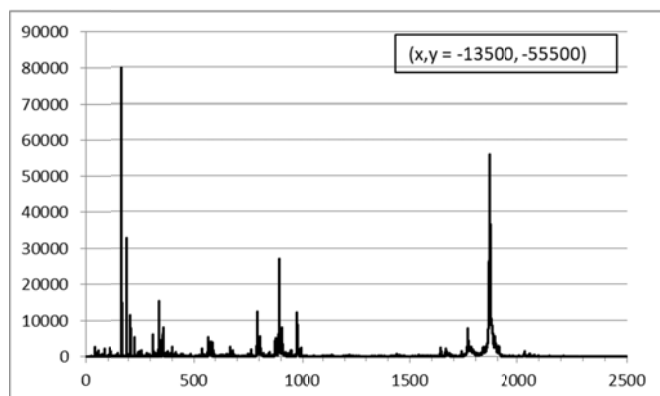
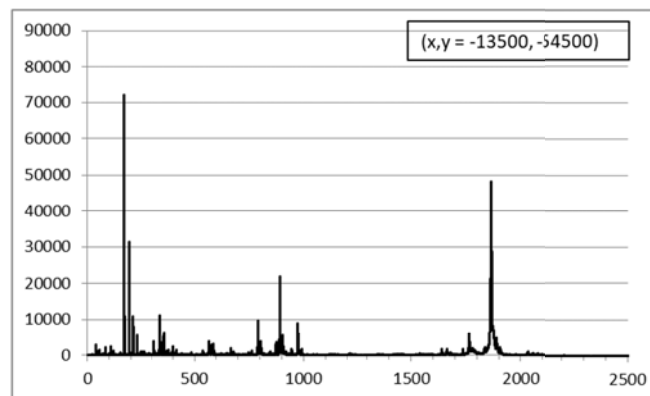
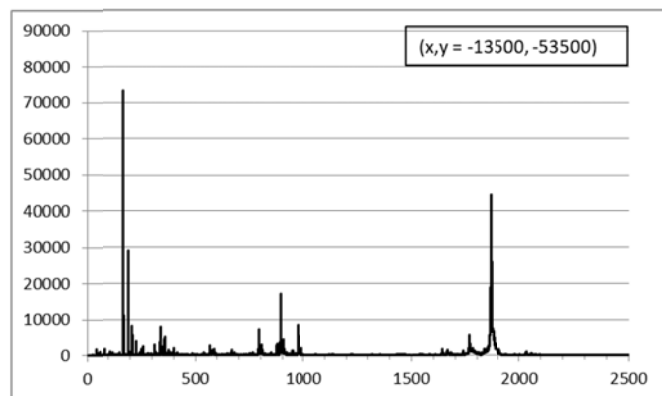
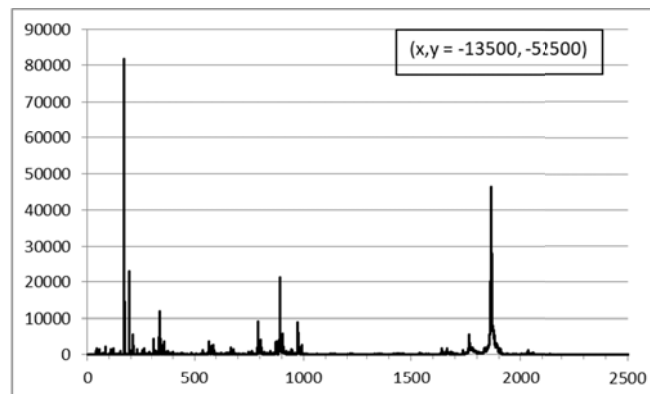
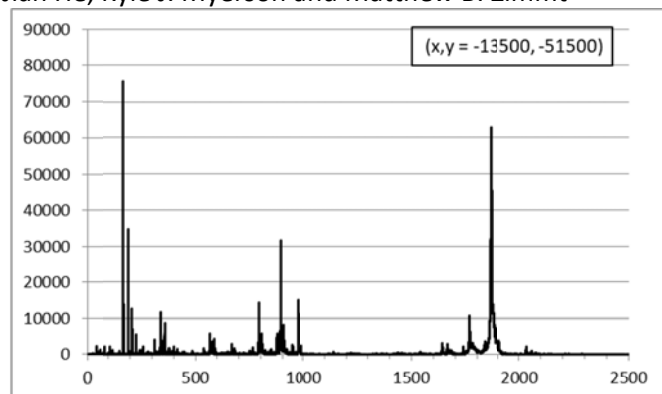
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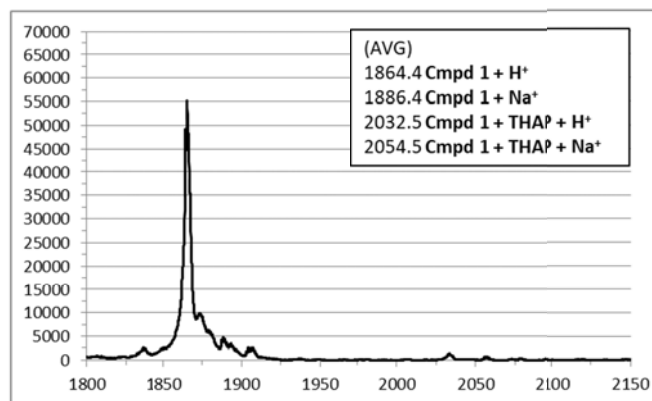
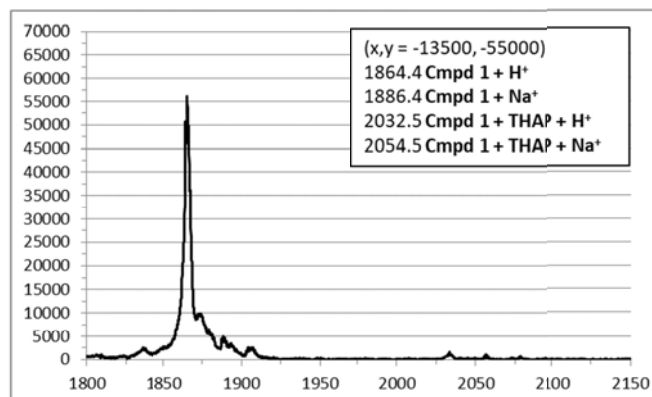
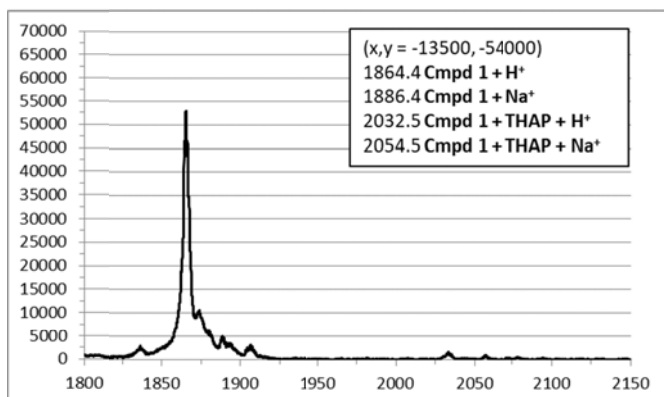
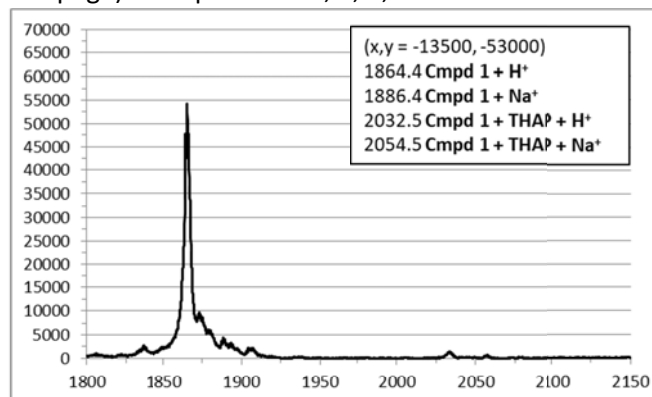
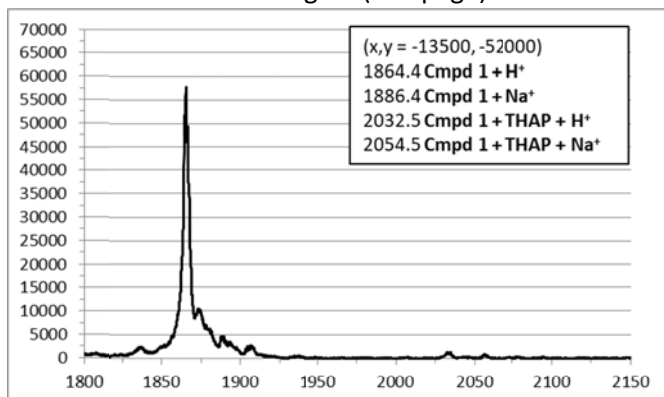
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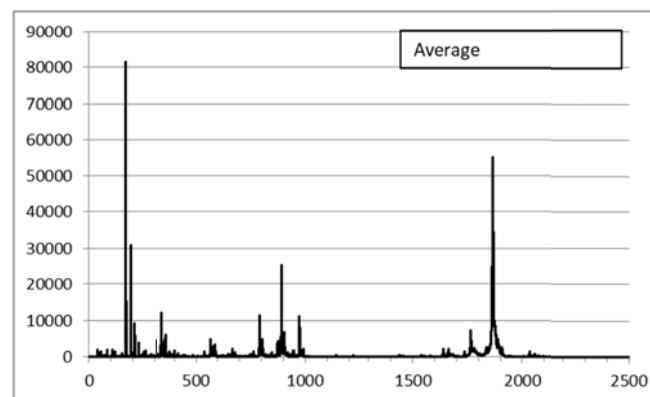
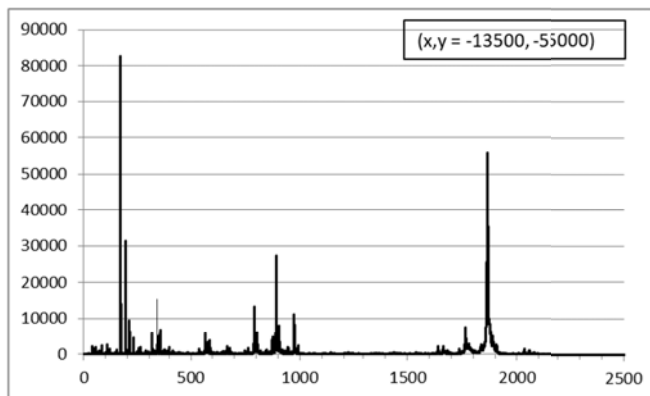
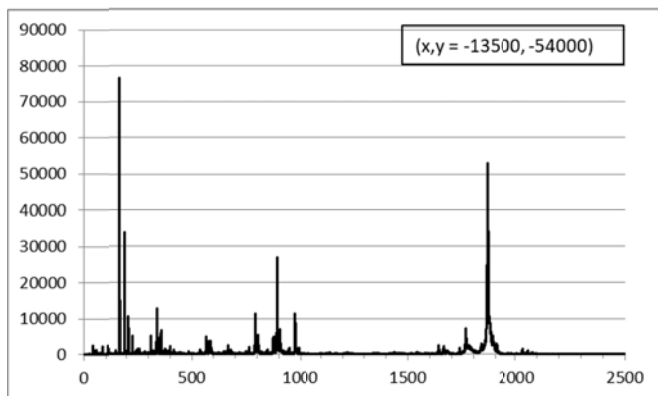
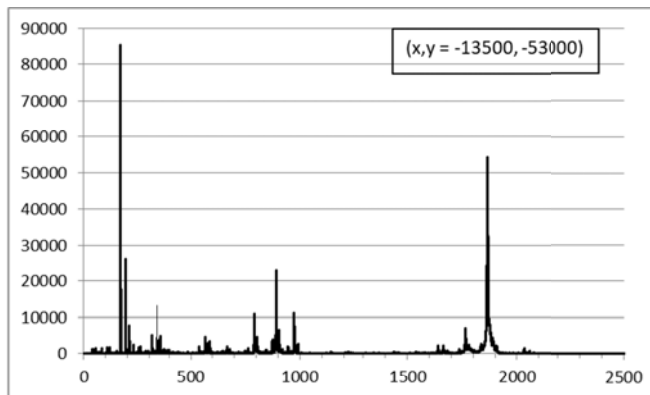
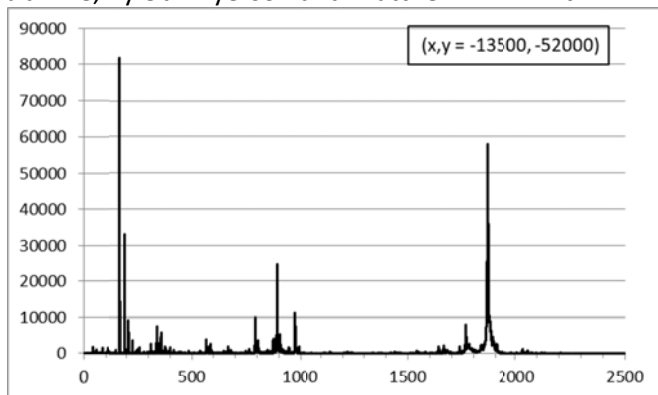
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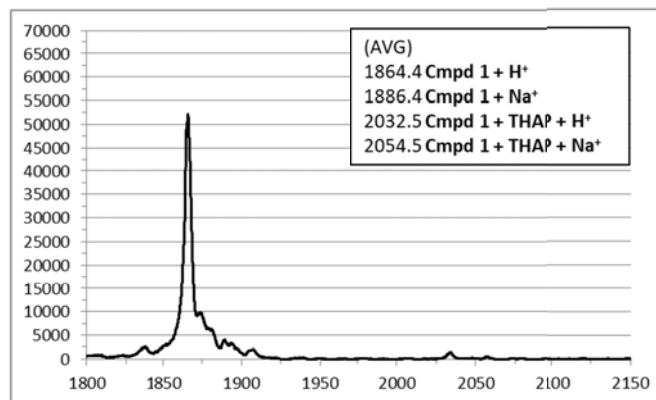
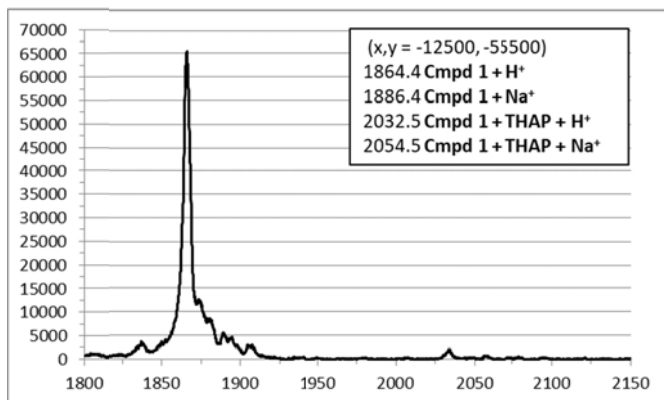
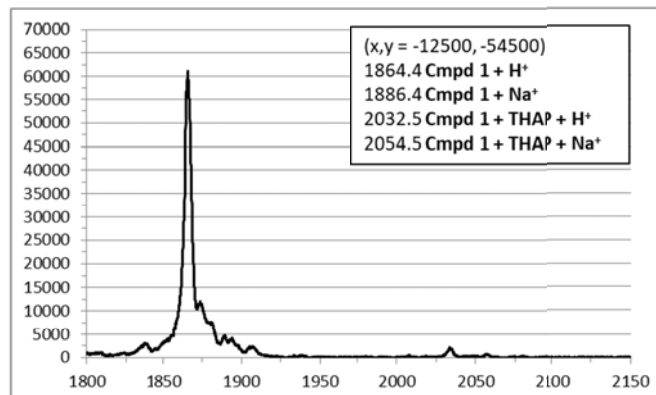
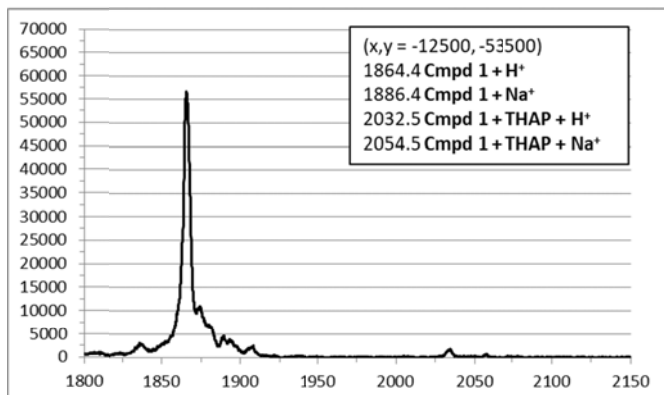
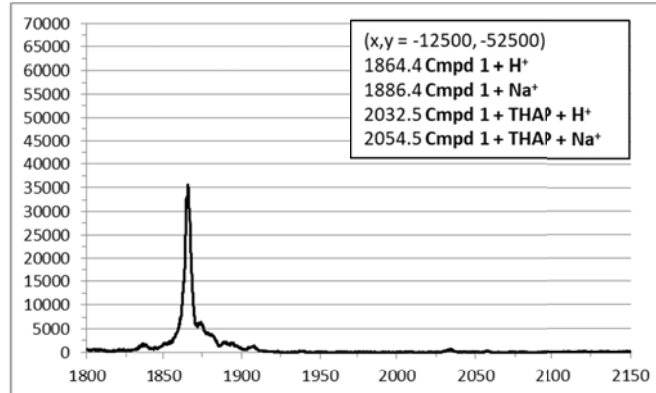
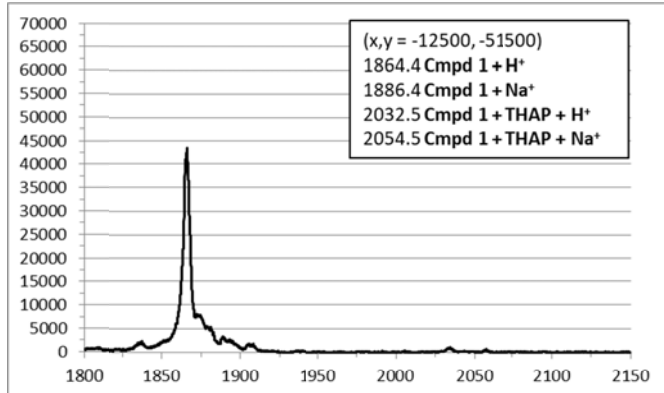
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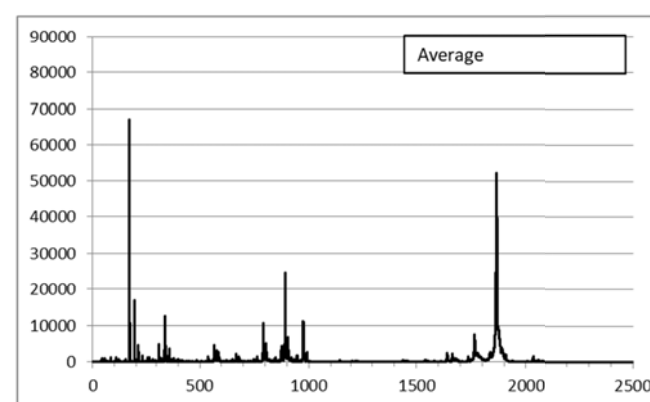
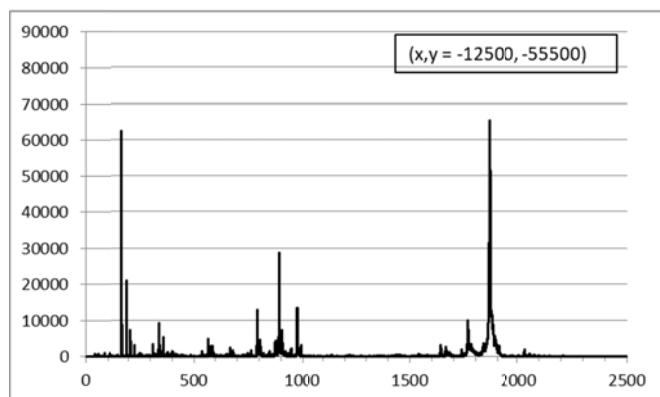
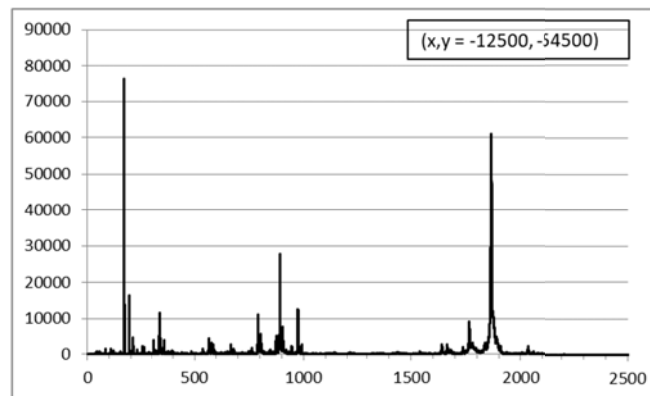
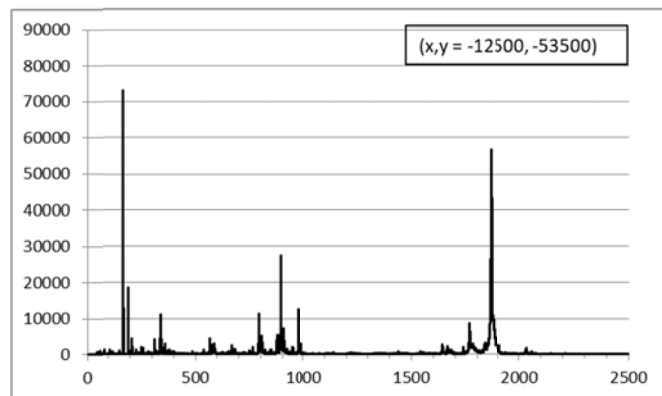
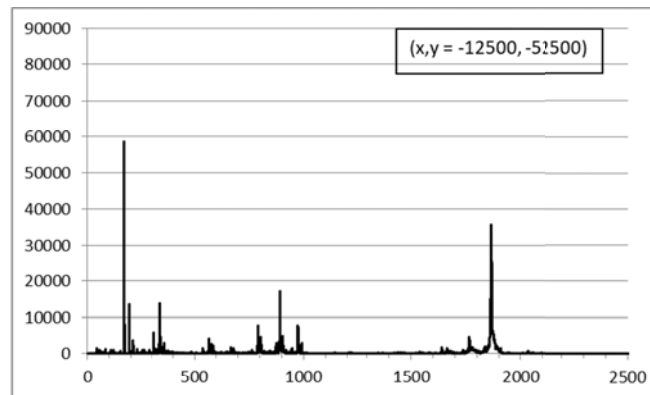
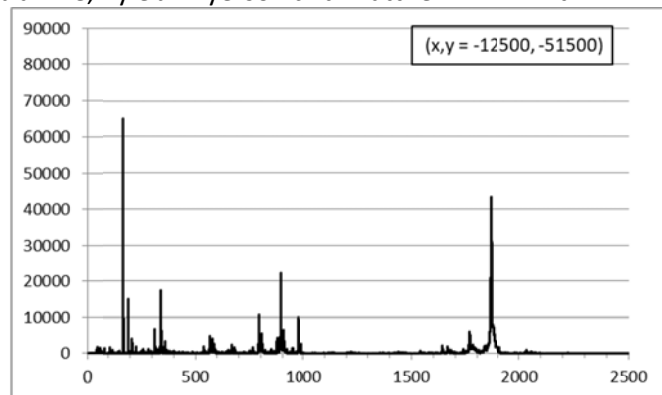
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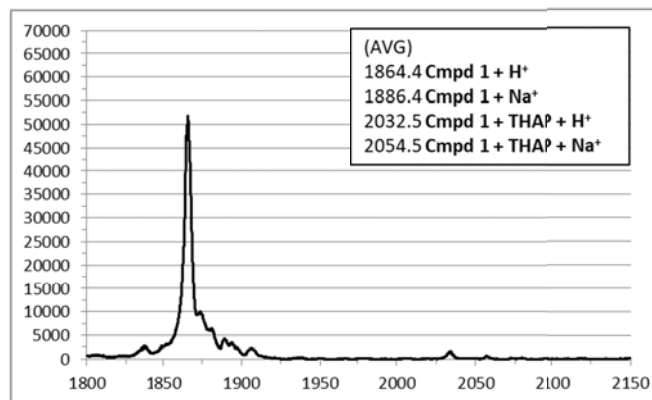
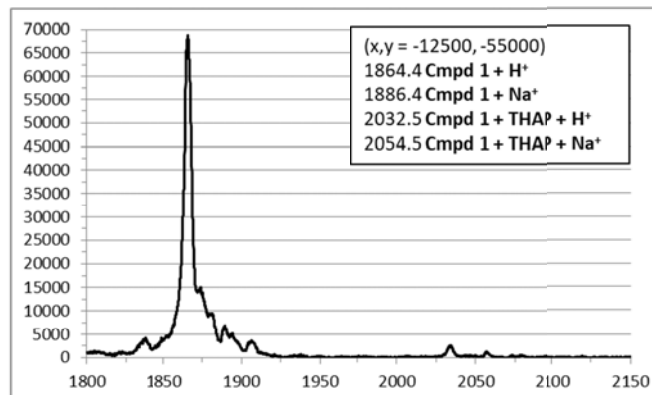
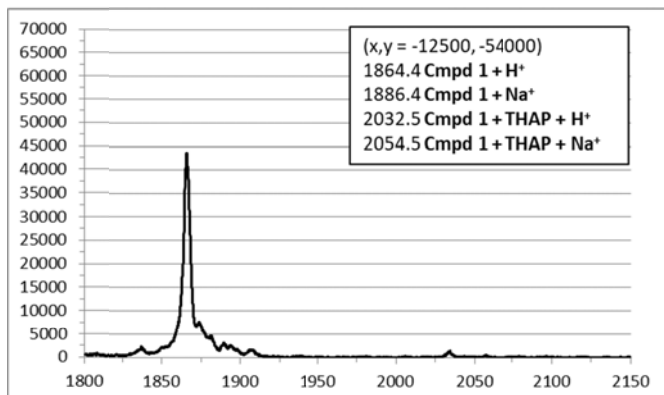
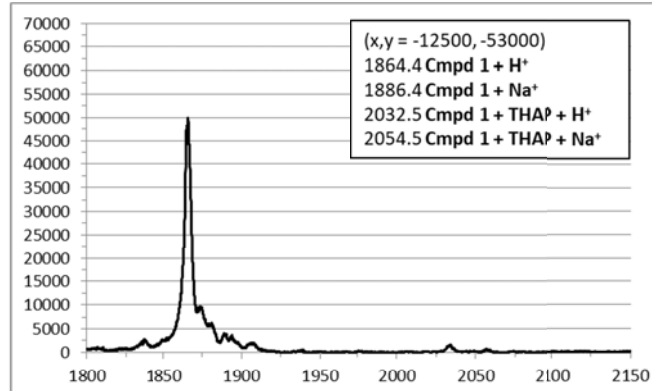
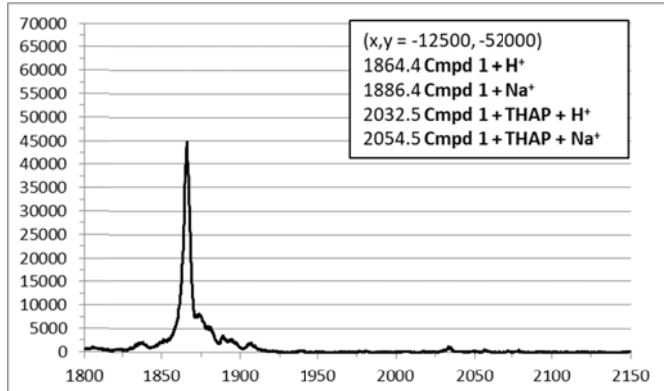
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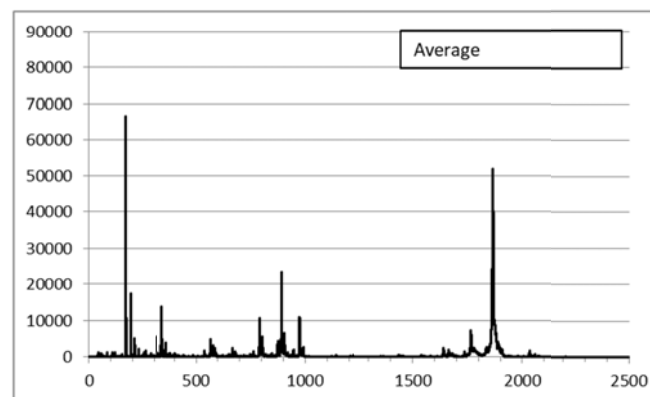
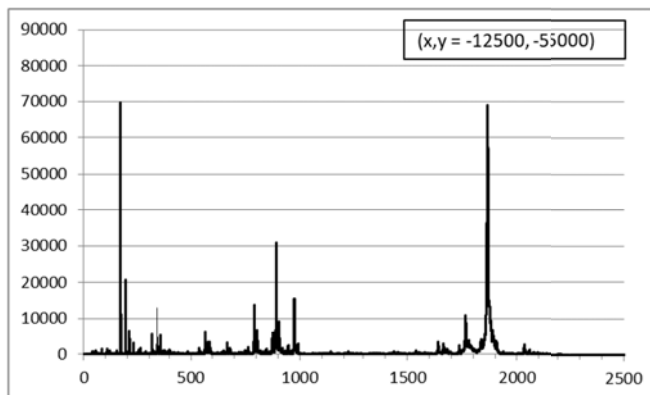
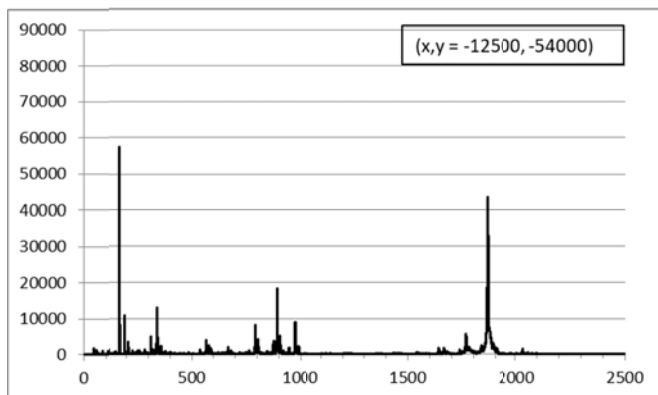
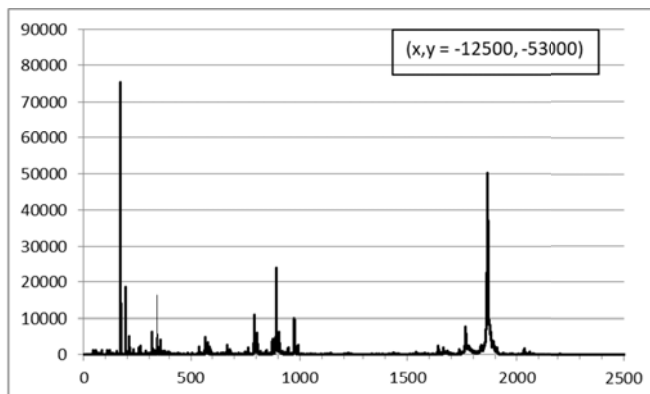
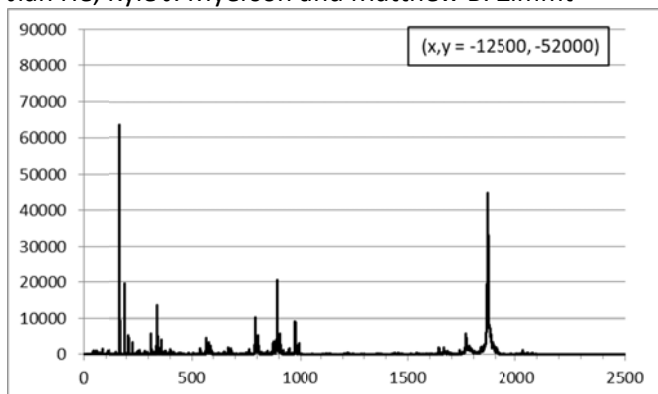
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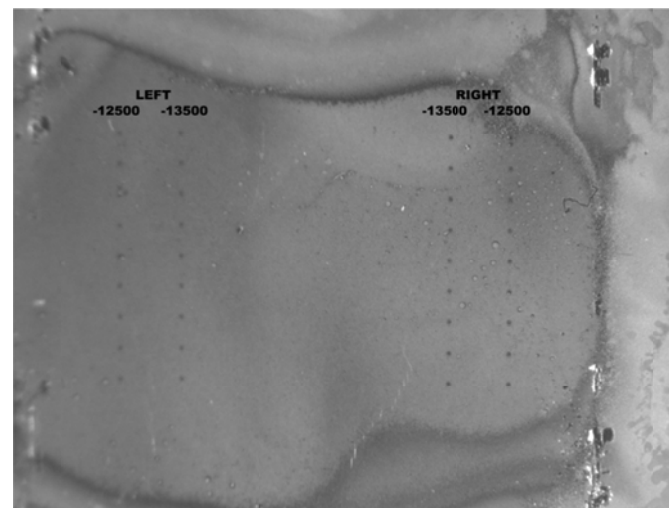
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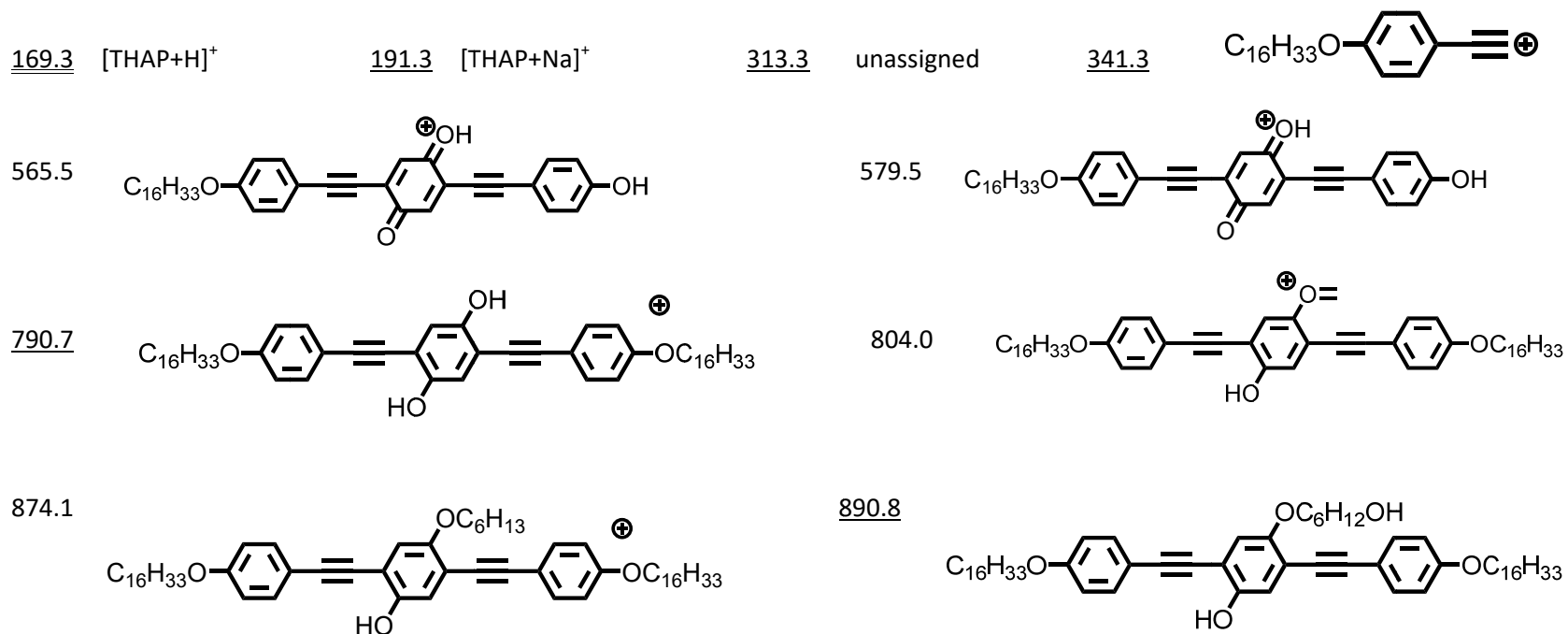


d) Photograph of THAP coated **1** / HOPG substrate after 36 TOF-MS measurements in c).

A thin film of THAP was applied to the monolayer **1** / HOPG substrate using 10 μL of 5 mg/mL THAP in 30/70 acetone/hexane and allowed to air dry. Regions irradiated to collect mass spectra appear as dark spots ($\sim 50\mu\text{m}$ diameter). The horizontal spacing between spots in the left (right) two columns is 1000 μm . The vertical spacing between spots in a column is 500 μm .

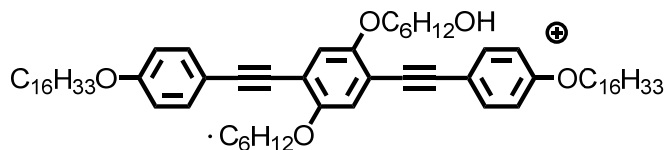


e) TOF MS m/z peaks with proposed structural assignments: monolayer of **1** on HOPG with applied THAP (underlined m/z intensities $> 0.05 \times \text{Int}(\text{THAP})$)

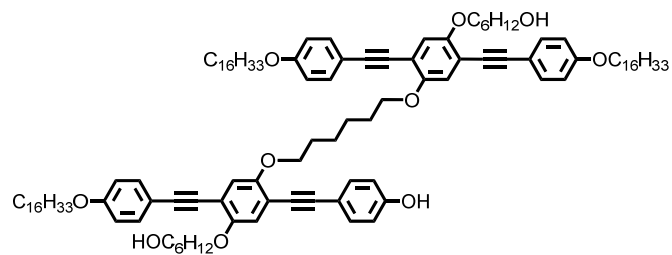


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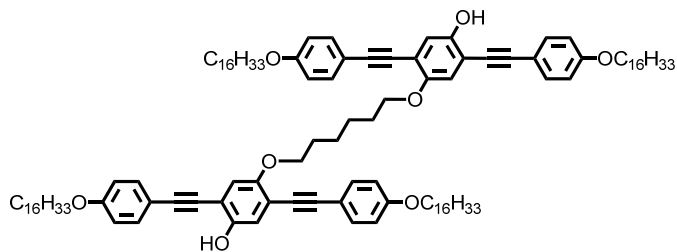
973.4



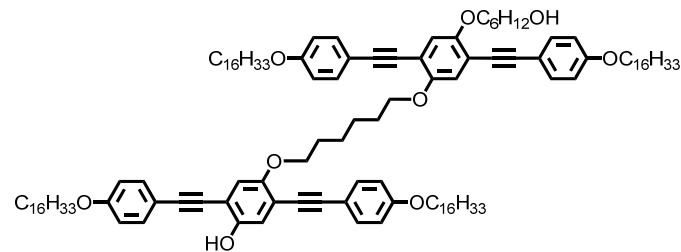
1639.4



1663.9



1764.5



1835.1 unassigned

1864.4 [1 + H]⁺

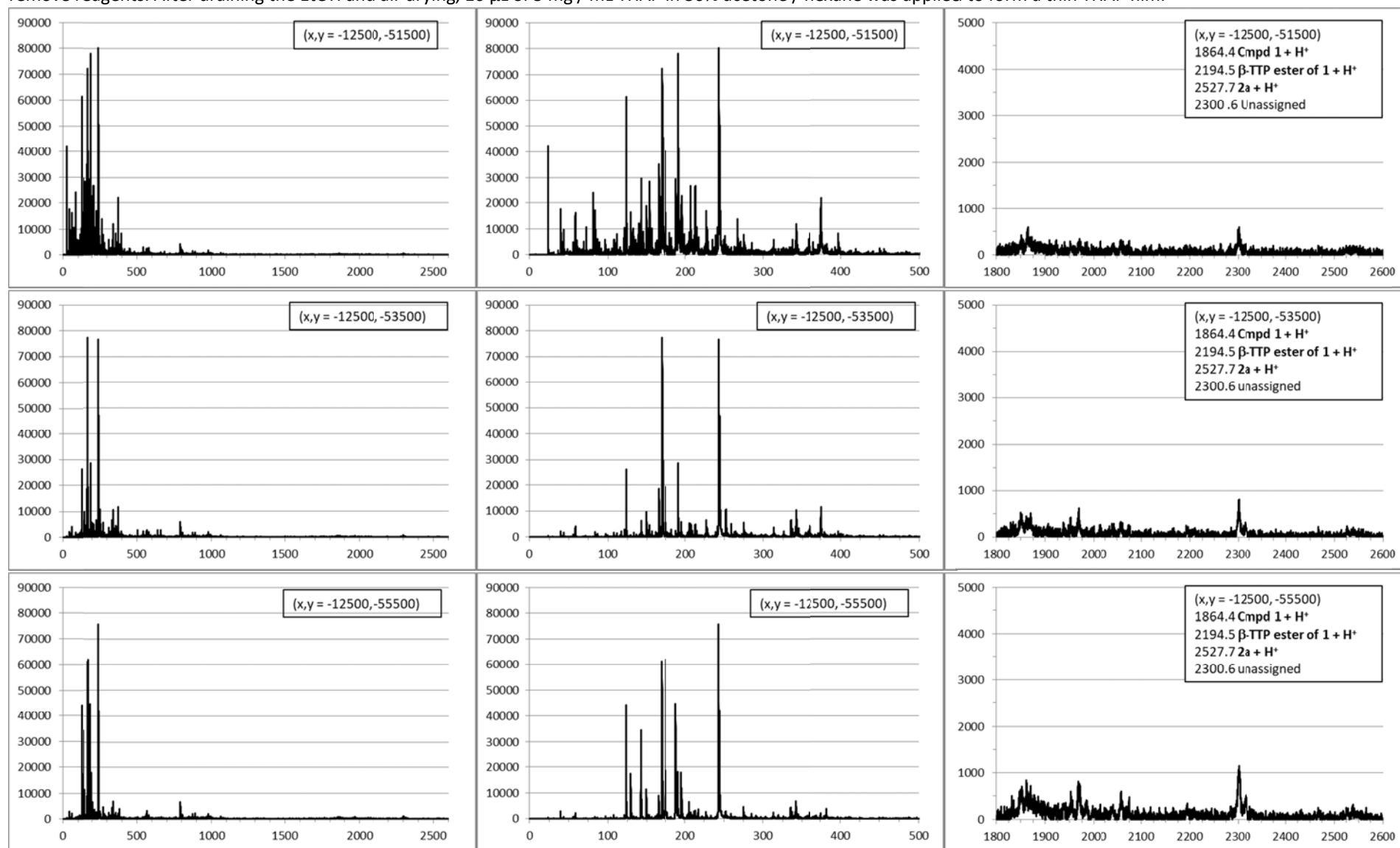
1886 [1 + Na]⁺

2032.8 [1 + THAP + H]⁺

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vi) Fig. S3. TOF mass spectra following in-situ reaction of monolayer **1** to form monolayer **2a**. Three spectral regions are presented for each spot sampled: the 0-2.5kD region, the 0-0.5kD region (Intensity (y) axis scales 0-90000) and the 1.8-2.6 kD region (Intensity (y) axis scale 0-5000).

Procedure: monolayer of **1** immersed in DCM containing 40mM β -tritylthiopropionic acid, 40 mM EDC and 40 mM DMAP for 0.5 hr. Monolayer was rinsed with 0.1 mL EtOH to remove reagents. After draining the EtOH and air drying, 10 μ L of 5 mg / mL THAP in 30% acetone / hexane was applied to form a thin THAP film.



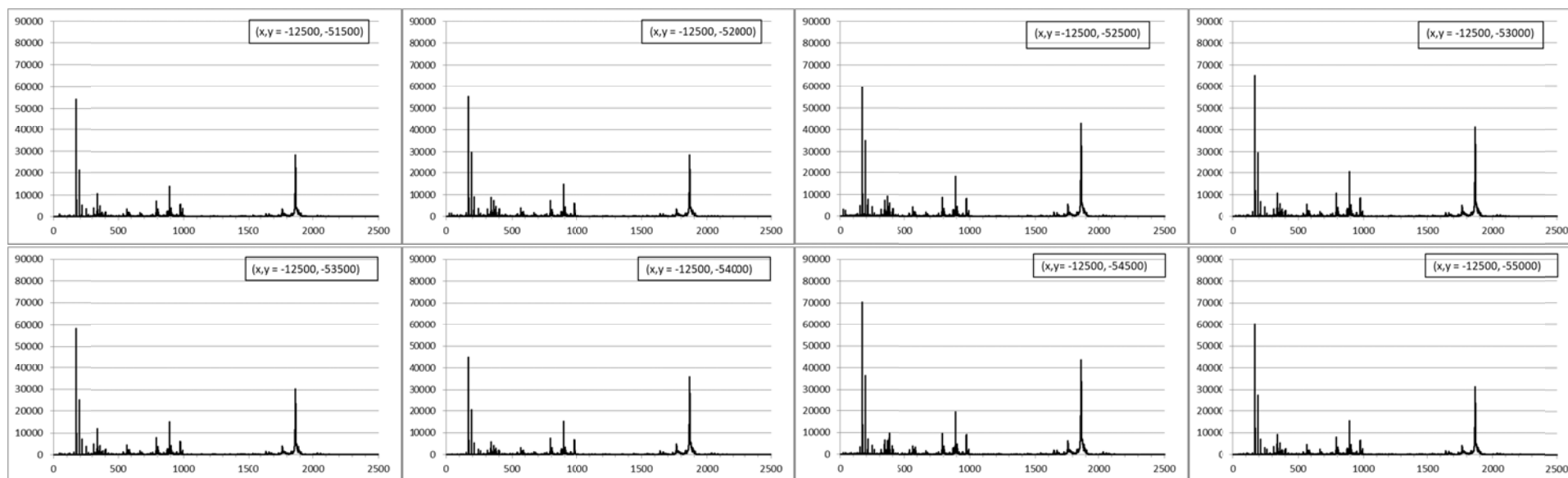
vii) Fig. S4. TOF mass spectra following incubation of monolayer **1** with DCM containing 40mM β -TTP but lacking EDC and DMAP. Three spectral regions are presented for each spot sampled: the 0-2.5kD region, the 0-0.5kD region and 1.8-2.5 kD region.

Procedure: monolayer of **1** immersed in DCM containing 40mM β -tritylthiopropionic acid for 0.5 hr. Monolayer was rinsed with 0.1 mL EtOH to remove reagents. After draining the EtOH and air drying, 10 μ L of 5 mg / mL THAP in 30% acetone / hexane was applied to form a thin THAP film.

a) Summary and statistical analysis of mass spectra peak intensities from incubating a monolayer of **1** with β -TTP solution lacking EDC and DMAP.

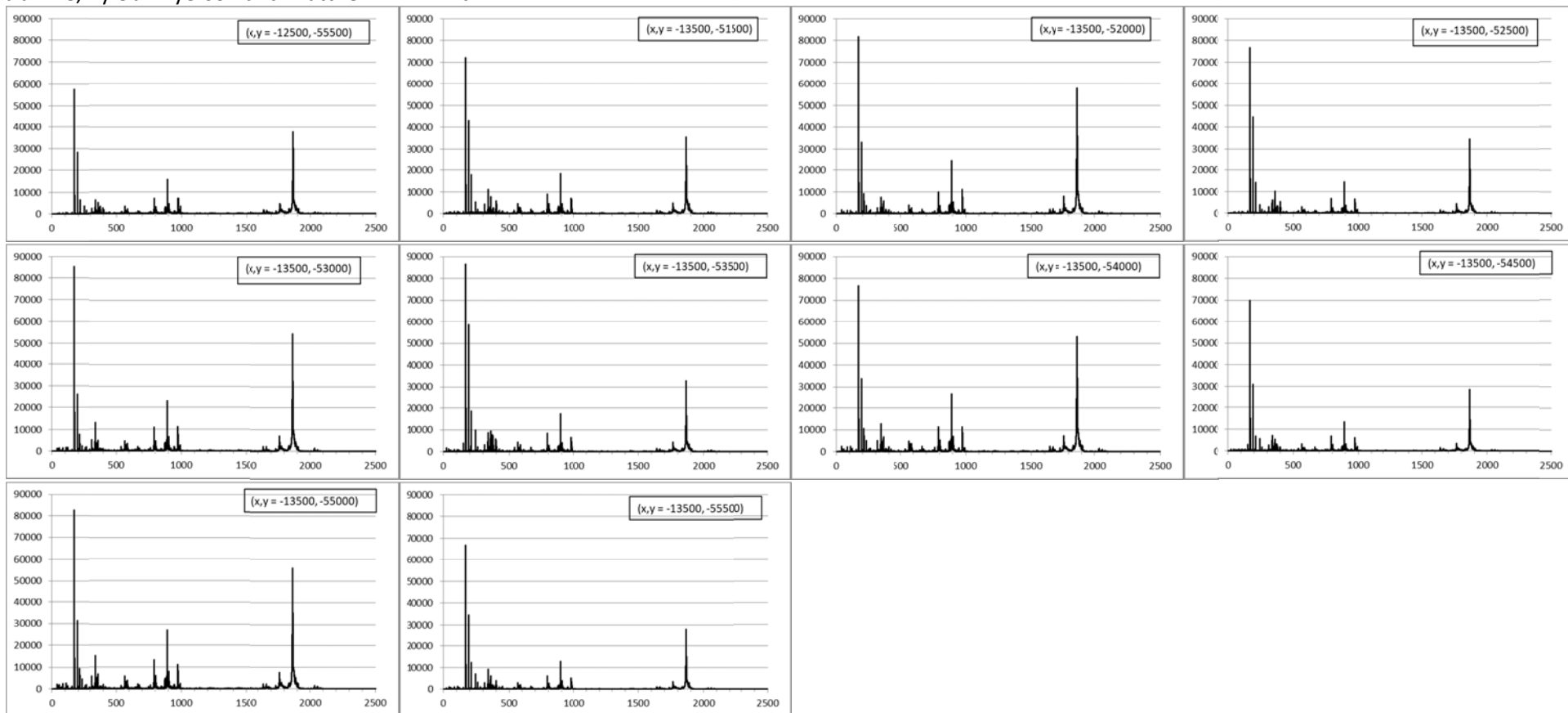
<u>samples</u>	<u>m/z</u>	<u>assignment</u>	<u>Int. minimum</u>	<u>Int. maximum</u>	<u>Intensity average</u>	<u>Intensity st.dev.</u>	<u>st.dev. / < Int. ></u>
18	169.3	matrix ([THAP+H] ⁺)	44800	86600	68000	12000	0.18
18	243.1	Trityl cation	520	10000	3800	2300	0.61
18	1864.4	[1 + H] ⁺	28000	57700	38900	10200	0.26

b) TOF mass spectra 0-2.5 kD region (**1** + β -TTP only): 18 samples (Intensity (y) axis scale 0-90000)

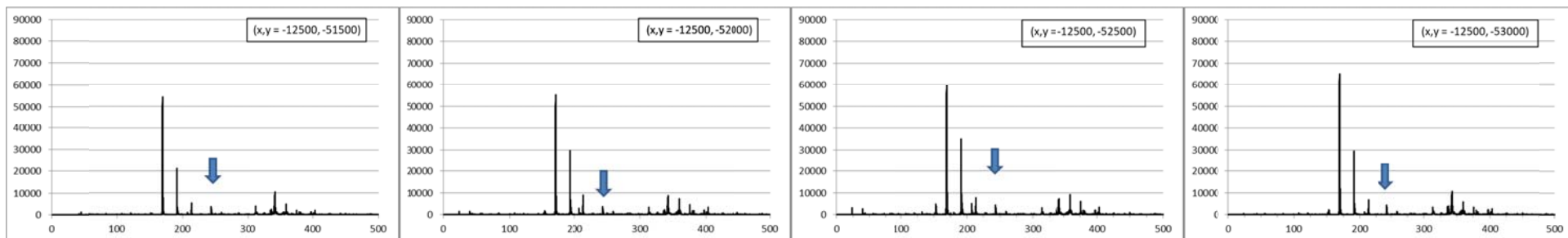


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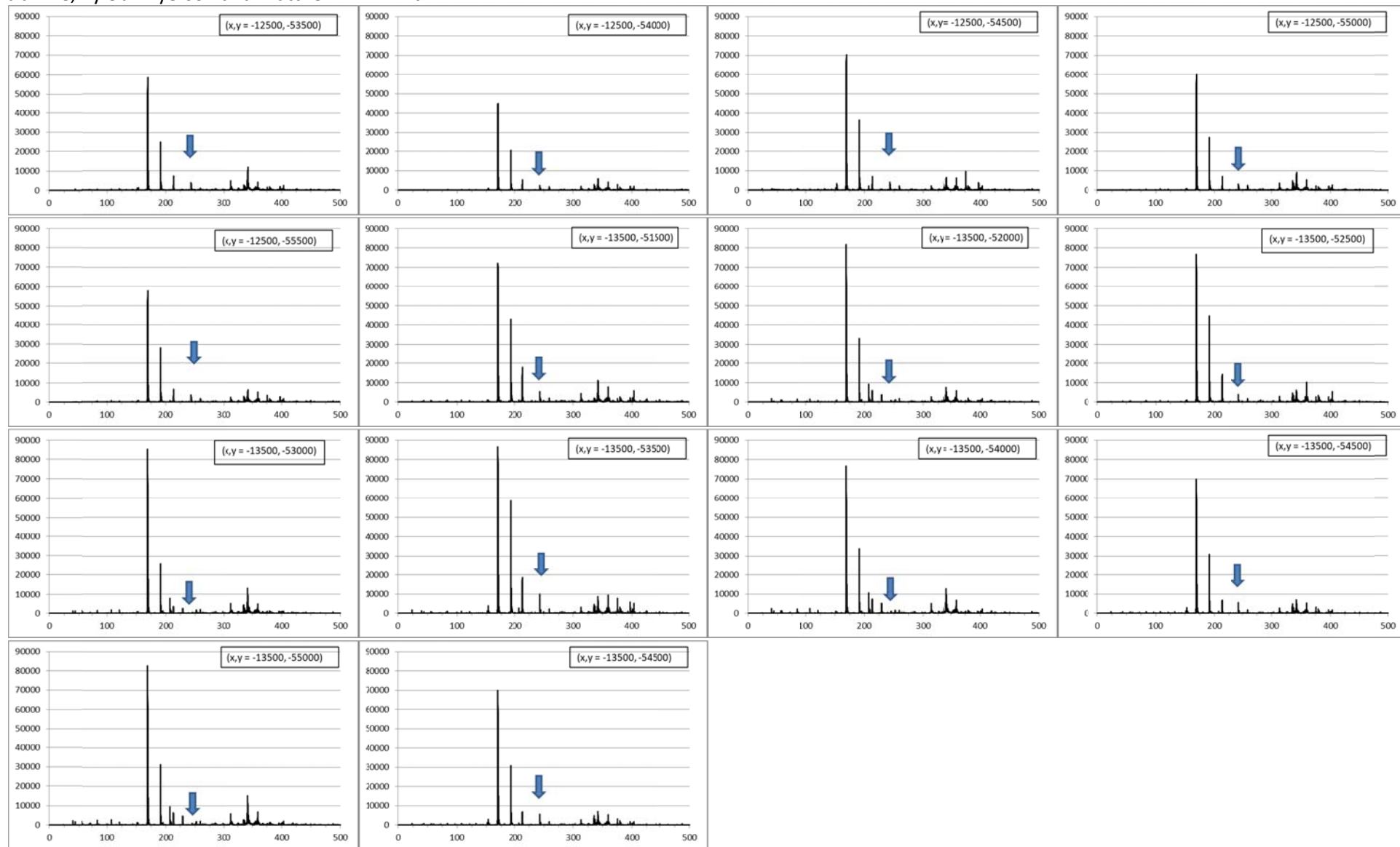


c) TOF mass spectra 0-0.5 kD region ($1 + \beta$ -TTP only): 18 samples (Intensity (y) axis scale 0-90000, arrow points to trityl cation peak at $m/z = 243$)



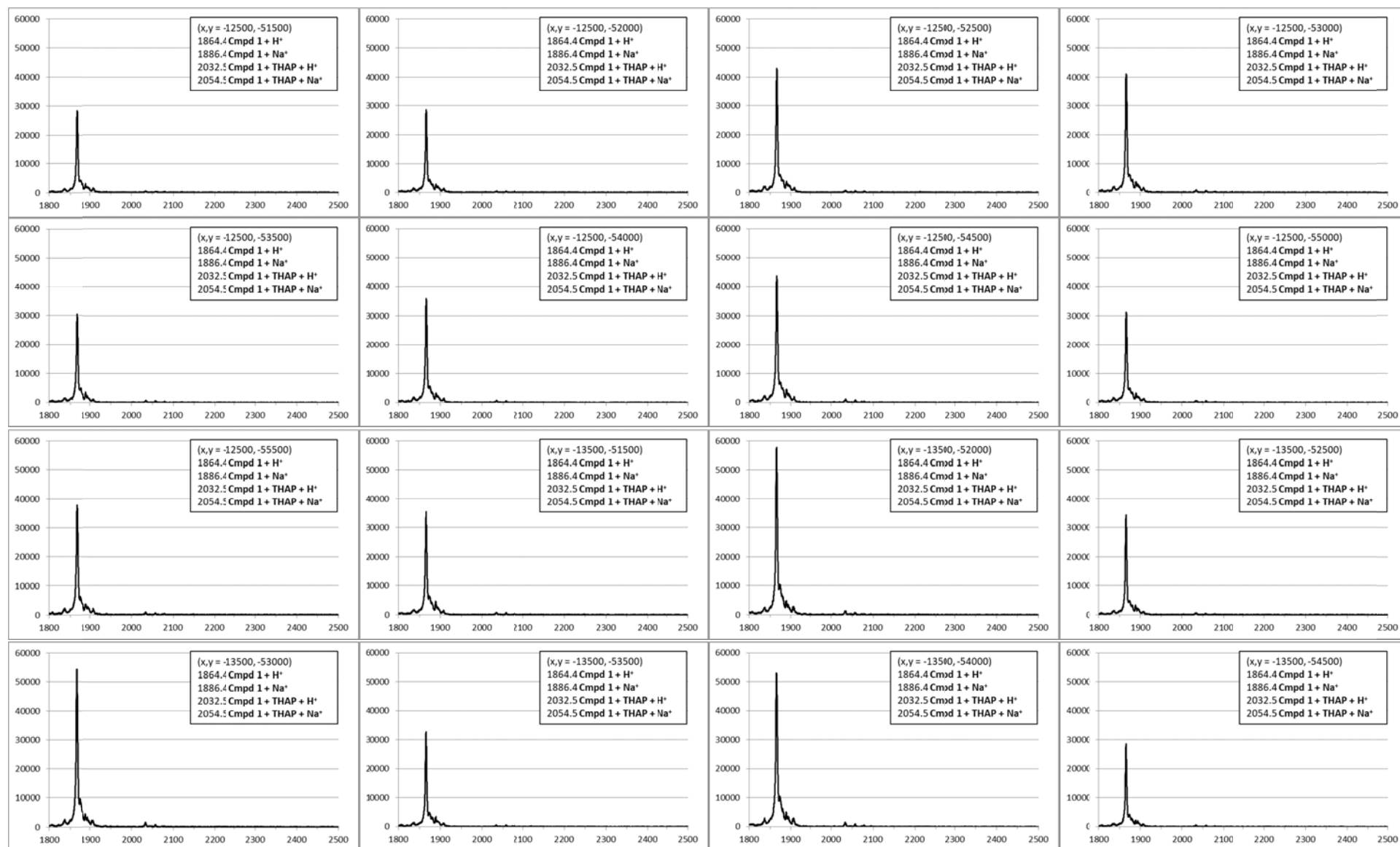
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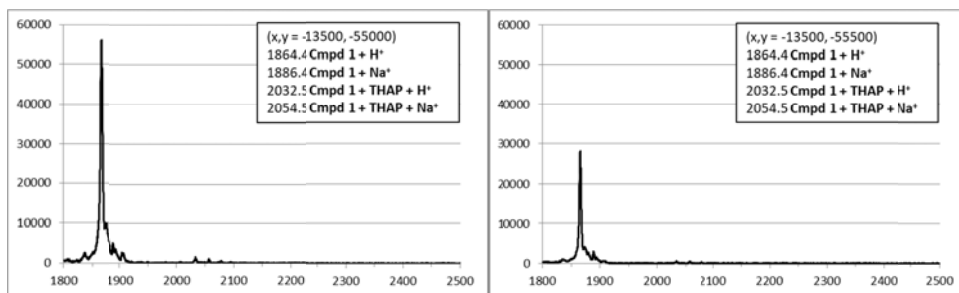
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d) TOF mass spectra 1.8-2.5 kD region (1 + β -TTP only): 18 samples (Intensity (y) axis scale 0-60000)





viii) **Fig. S5.** TOF mass spectra following in-situ reaction of monolayer **1** to form monolayer **2b**

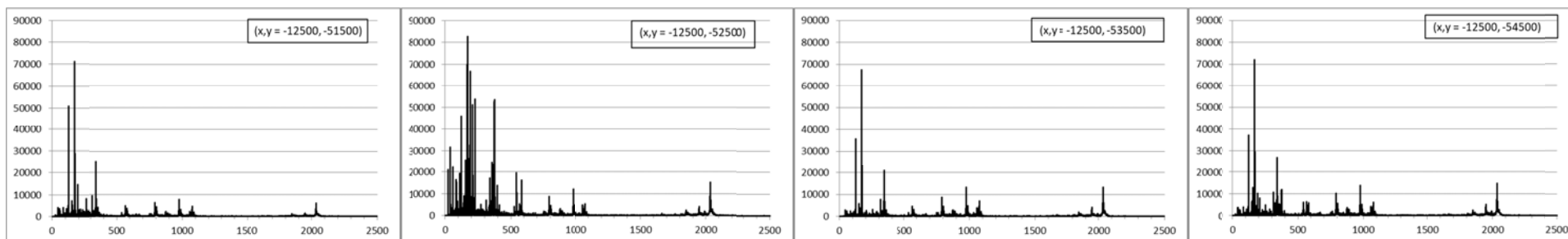
TOF mass spectra after immersing a monolayer of **1** on HOPG in a DCM solution with 40 mM valeric acid, 40 mM EDC and 40 mM EDC for 30 minutes. Two spectral regions are presented for each spot sampled: the 0-2.5kD region and the 1.8-2.5 kD region.

Procedure: monolayer of **1** immersed in DCM containing 40 mM valeric acid, 40 mM EDC and 40 mM EDC for 0.5 hr. Monolayer was rinsed with 0.1 mL EtOH to remove reagents. After draining the EtOH and air drying, 10 μ L of 5 mg / mL THAP in 30% acetone / hexane was applied to form a thin THAP film.

a) Summary and statistical analysis of mass spectra peak intensities from incubating a monolayer of **1** with valenic acid / EDC / DMAP solution.

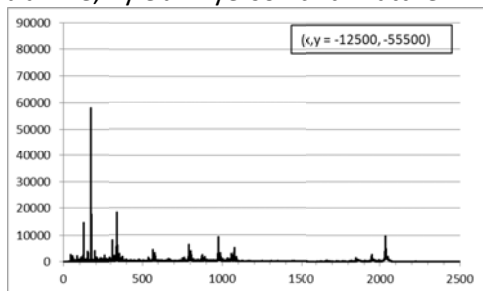
<u>samples</u>	<u>m/ z</u>	<u>assignment</u>	<u>Int. minimum</u>	<u>Int. maximum</u>	<u>Intensity average</u>	<u>Intensity st.dev.</u>	<u>st.dev. / < Int. ></u>
5	169.3	matrix ([THAP+H] ⁺)	58200	82600	70300	8800	0.13
5	1864.4	[1 + H] ⁺	780	1600	1200	370	0.30
5	1948.5	[1 valerate ester + H] ⁺	1630	5100	3300	1400	0.42
5	2032.6	[2b + H] ⁺	6000	15400	11400	3900	0.35

b) TOF mass spectra 0-2.5 kD region (**2b**): 5 samples (Intensity (y) axis scale 0-90000)

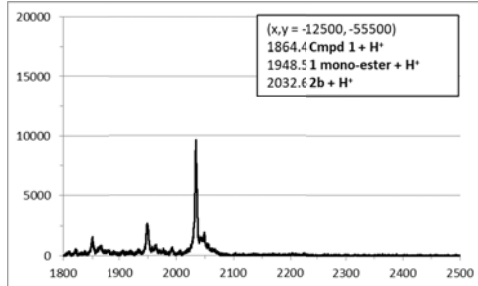
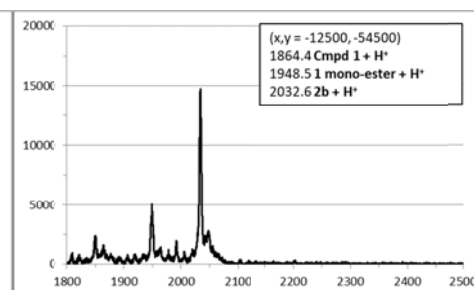
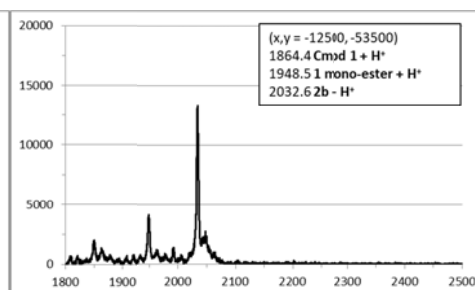
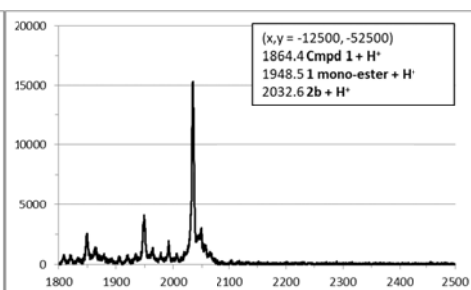
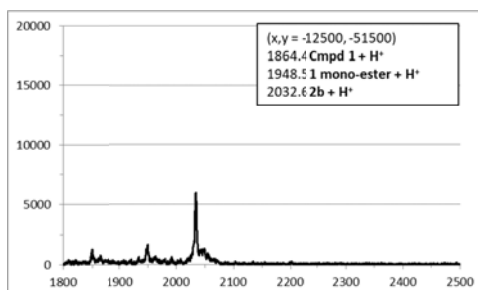


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c) TOF mass spectra 1.8-2.5 kD region (**2b**): 5 samples (Intensity (y) axis scale 0-20000)



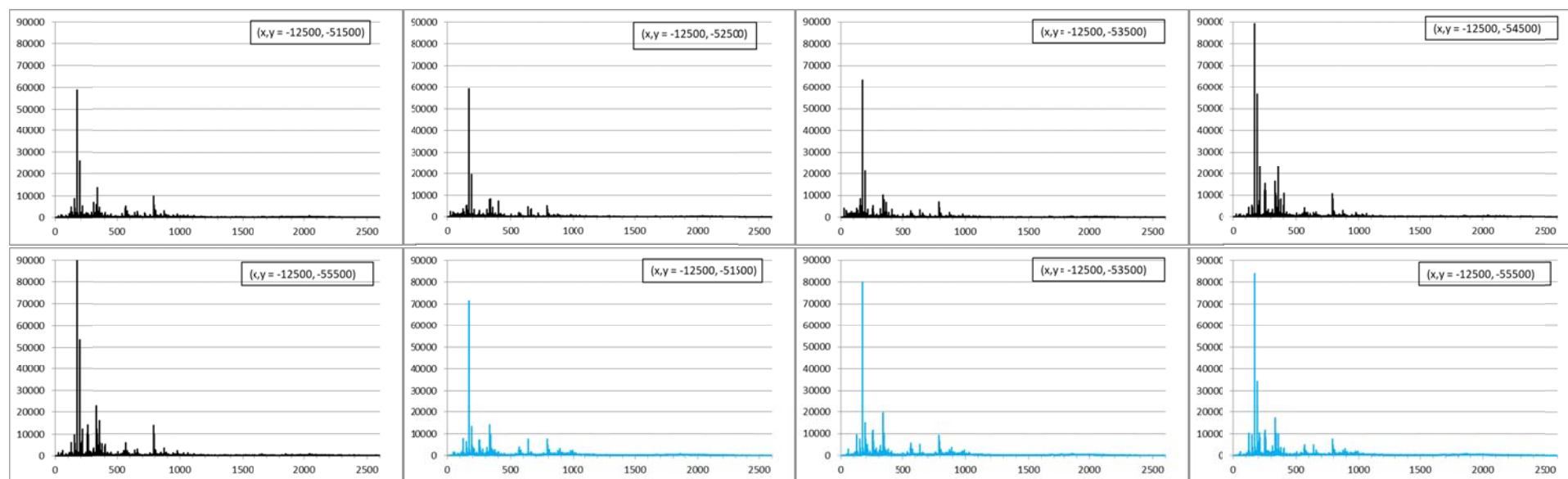
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ix) Fig. S6. TOF mass spectra following in-situ reaction of monolayer **2a** with I₂ in DMF to form monolayer **(3)_x**. Three spectral regions are presented for each spot sampled: the 0-2.6kD region, the 0-0.5kD region and the 1.8-2.6 kD region Mass spectra from the independent sample are displayed in blue.

a) Summary and statistical analysis of mass spectra peak intensities from independent experiments.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
Manuscript	5	169.3	matrix ([THAP+H] ⁺)	58900	95700	73200	17800	0.24
Independent	3	169.3	matrix ([THAP+H] ⁺)	71300	83900	78400	6400	0.08
Manuscript	5	243.1	Trityl cation	950	2300	1460	620	0.43
Independent	3	243.1	Trityl cation	990	1020	1010	20	0.02
Manuscript	5	1864	[1 + H] ⁺	270	480	350	90	0.26
Independent	3	1864	[1 + H] ⁺	880	950	920	30	0.03
Manuscript	5	2040	[3 + H] ⁺	650	900	750	100	0.13
Independent	3	2040	[3 + H] ⁺	460	540	500	40	0.08

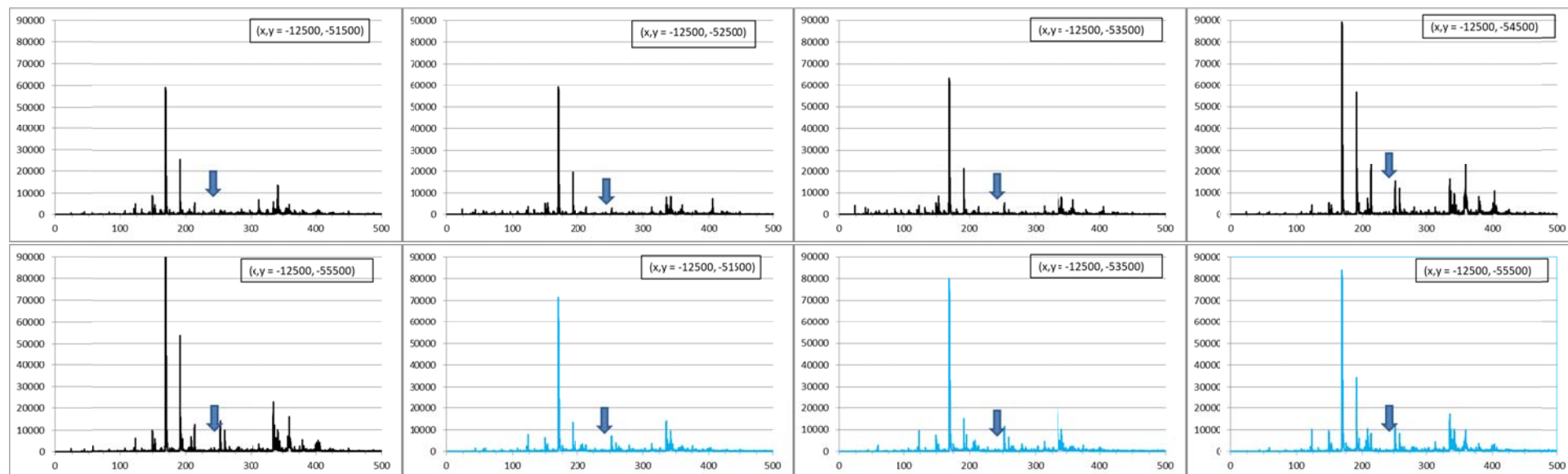
b) TOF mass spectra 0-2.6 kD region (**(3)_x**): 5 samples and 3 samples (Intensity (y) axis scale 0-90000)



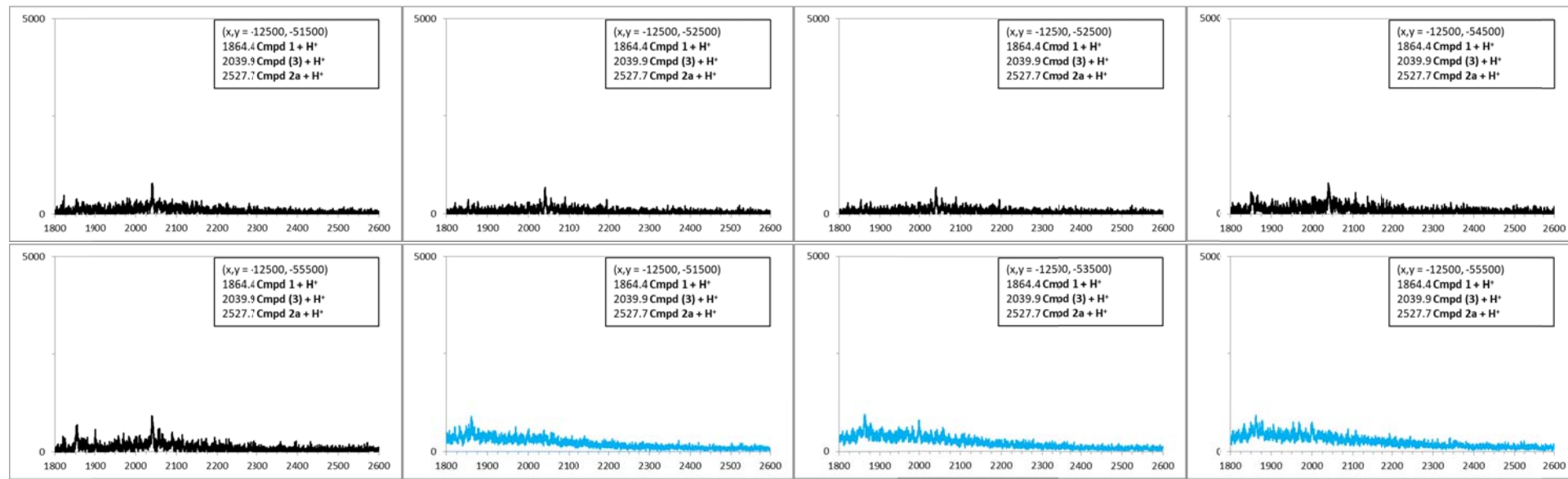
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c) TOF mass spectra 0-0.5 kD region ((**3**)_x): 5 samples and 3 samples (Intensity (y) axis scale 0-90000, arrow points to trityl cation peak at m/z = 243)

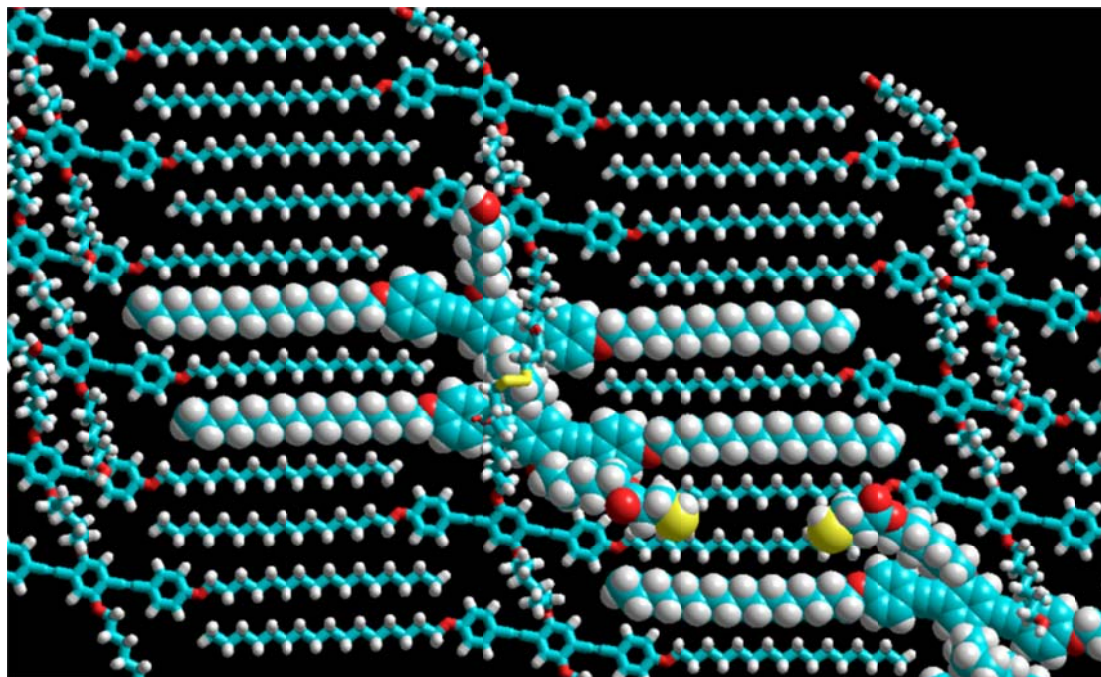


d) TOF mass spectra 1.8-2.6 kD region ((**3**)_x): 5 samples and 3 samples (Intensity (y) axis scale 0-5000)

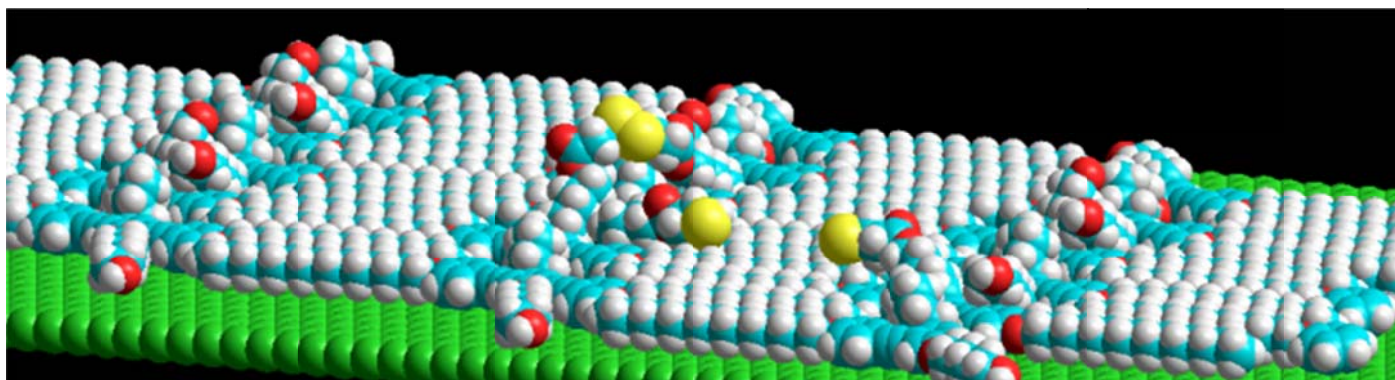


(x) Fig. S7. Alternative views of molecular mechanics minimized model showing next-nearest neighbor TPE₂ disulfide cross-link within one aryl column and thiol side chain approach in different aryl columns.

a) (right) Molecular mechanics model of a monolayer section with a disulfide cross-link between next-nearest neighbor TPE₂ molecules in one aryl column. The closest (O(CH₂)₆O₂C(CH₂)₂SH) chains from TPE₂ molecules in different aryl columns (CPK) are not long enough to form an inter-column disulfide link.



b) (below) Side view of the modeled monolayer section containing a disulfide cross-link (yellow, center) between next-nearest neighbor TPE₂ molecules in one aryl column. The sulfur atoms (yellow) on (O(CH₂)₆O₂C(CH₂)₂SH) chains from TPE₂ molecules in different aryl columns are separated by 1.3 nm.



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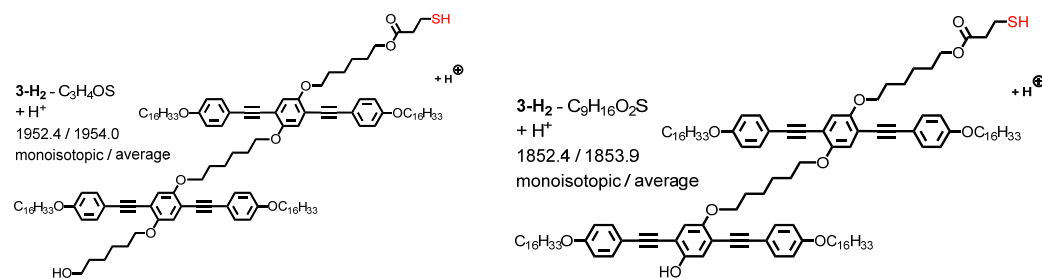
(xi) Fig. S8. TOF mass spectra following in-situ reduction of monolayer **(3)_x** with DTT to form monolayer **3H₂** (one cycle)

a) Summary and statistical analysis of mass spectra peak intensities from independent experiments.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
Manu Study-1	10	169.3	matrix ([THAP+H] ⁺)	75900	112000	86700	11600	0.13
Manu Study-2	10	169.3	matrix ([THAP+H] ⁺)	66200	99900	82500	11600	0.14
Repeat 1	10	169.3	matrix ([THAP+H] ⁺)	67900	105000	93700	10100	0.11
Repeat 2	10	169.3	matrix ([THAP+H] ⁺)	50800	102000	86900	15300	0.18
Average	40	169.3	matrix ([THAP+H]⁺)			87400±12100		
Manu Study-1	10	2040	[3-H₂ + H] ⁺	2400	8200	5900	1800	0.31
Manu Study-2	10	2040	[3-H₂ + H] ⁺	7900	14700	10400	2300	0.22
Repeat 1	10	2040	[3-H₂ + H] ⁺	3200	13700	8900	3500	0.39
Repeat 2	10	2040	[3-H₂ + H] ⁺	5600	13900	11100	2300	0.20
Average	40	2040	[3-H₂ + H]⁺			9100±2500		
Manu Study-1	10	2088	[3-H(O₃H) + H] ⁺	330	610	500	100	0.20
Manu Study-2	10	2088	[3-H(O₃H) + H] ⁺	300	830	520	170	0.33
Repeat 1	10	2088	[3-H(O₃H) + H] ⁺	200	1100	730	270	0.37
Repeat 2	10	2088	[3-H(O₃H) + H] ⁺	160	690	470	160	0.33
Average	40	2088	[3-H(O₃H) + H]⁺			550±180		
Manu Study-1	10	2136	[3-(O₃H)₂ + H] ⁺	120	440	280	110	0.39
Manu Study-2	10	2136	[3-(O₃H)₂ + H] ⁺	120	1200	330	320	0.99
Repeat 1	10	2136	[3-(O₃H)₂ + H] ⁺	80	470	290	120	0.41
Repeat 2	10	2136	[3-(O₃H)₂ + H] ⁺	470	1260	870	310	0.35
Average	40	2136	[3-(O₃H)₂ + H]⁺			440±220		

b) Structures of TPE₂ fragment ions observed at (left) m/z = 1952.4 / 1954.0 and (right) 1852.4 / 1853.9 in mass spectra of **3-H₂** monolayers.

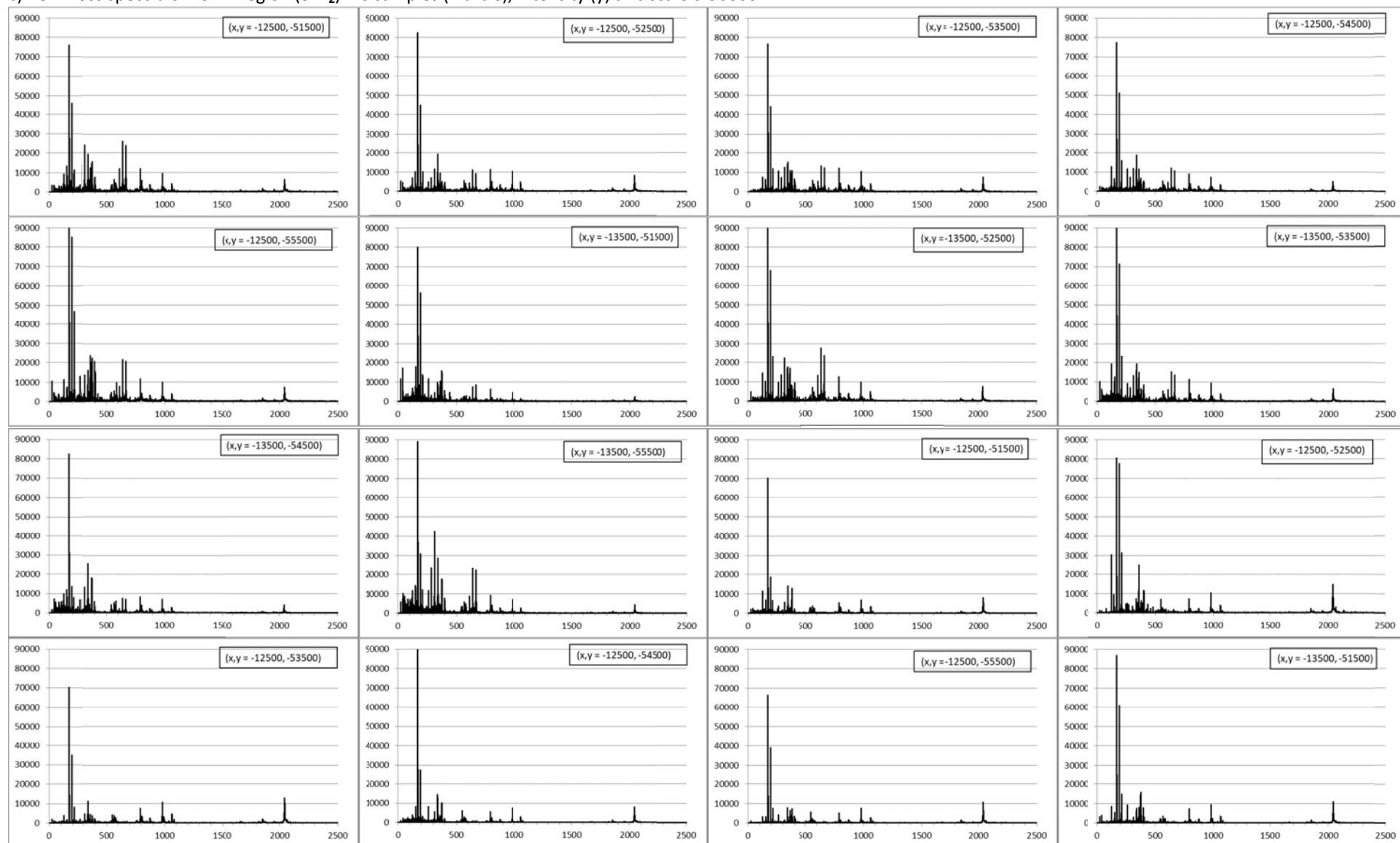
The numbers (before / after) are the monoisotopic / average ion m/z values.



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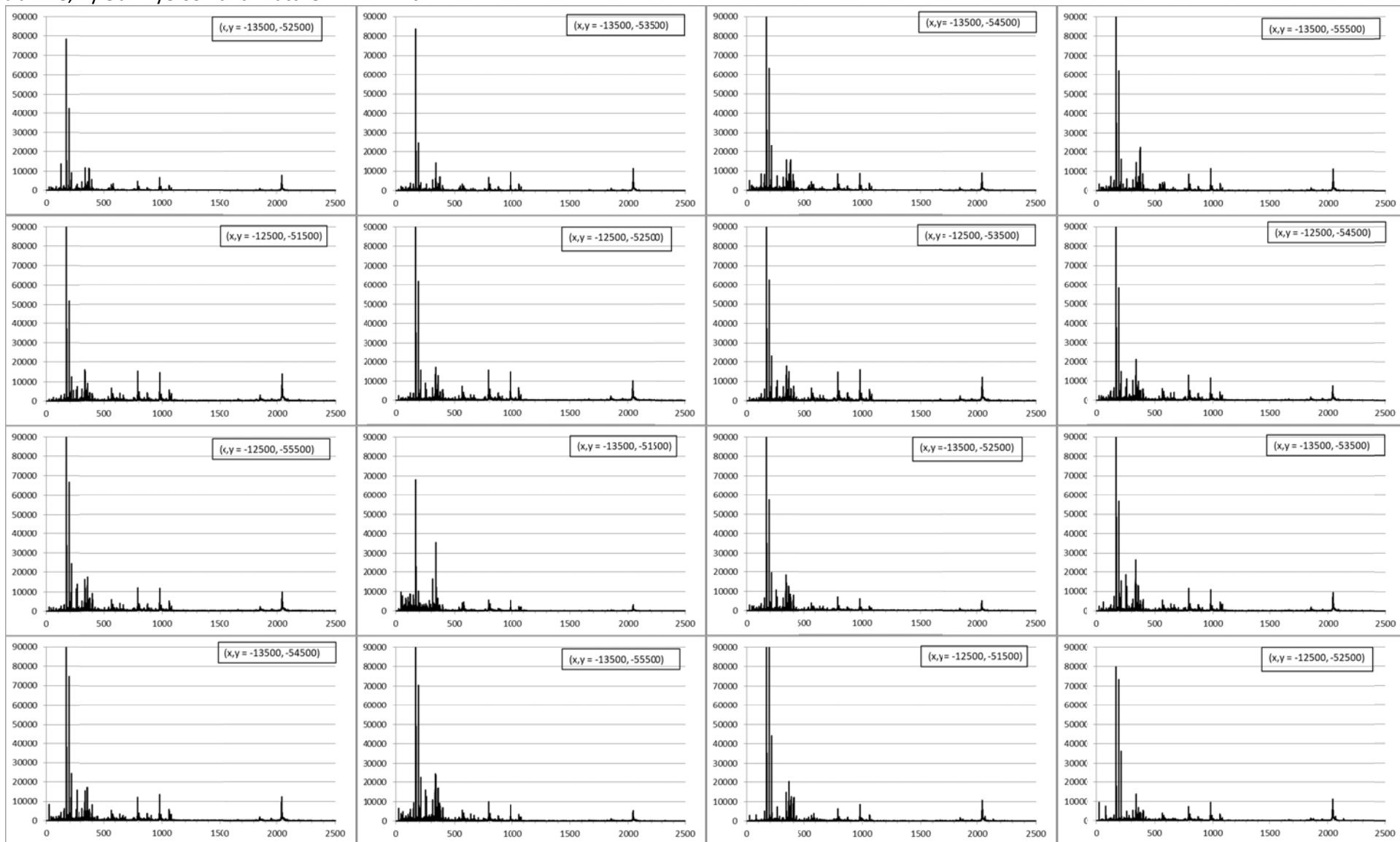
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c) TOF mass spectra 0-2.5 kD region (3-H_2): 40 samples (4 trials), intensity (y) axis scale 0-90000.



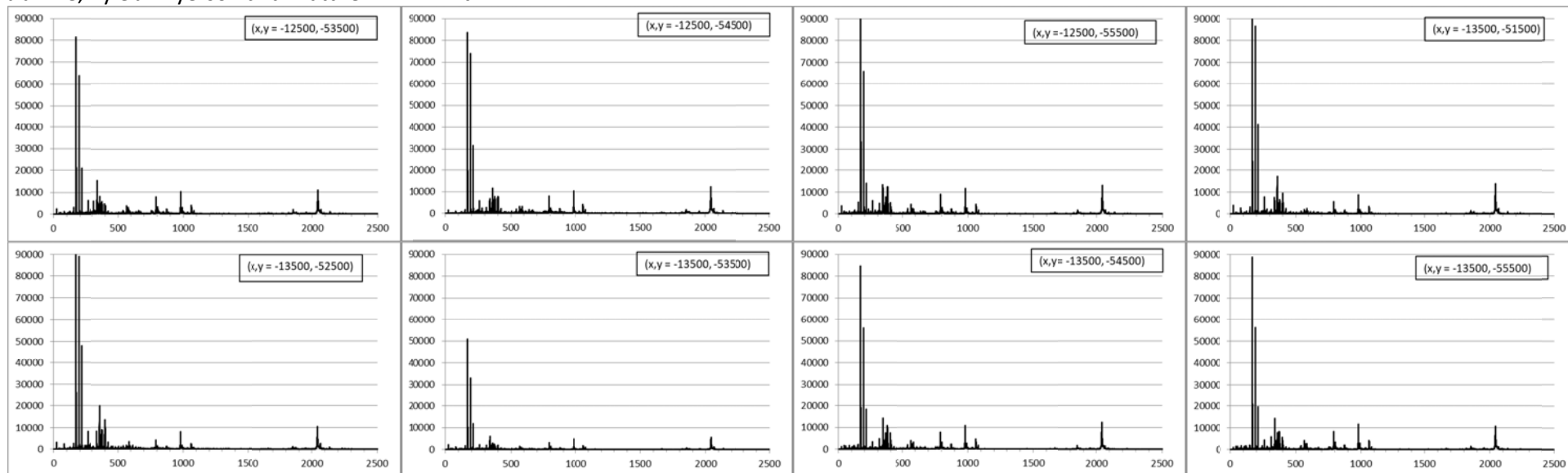
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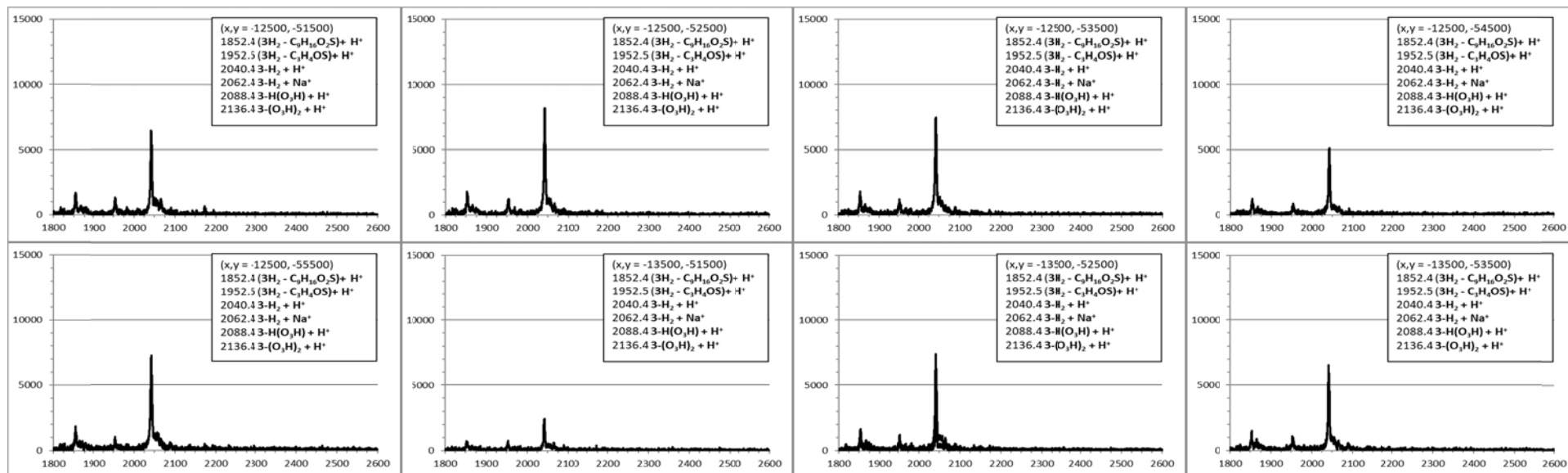


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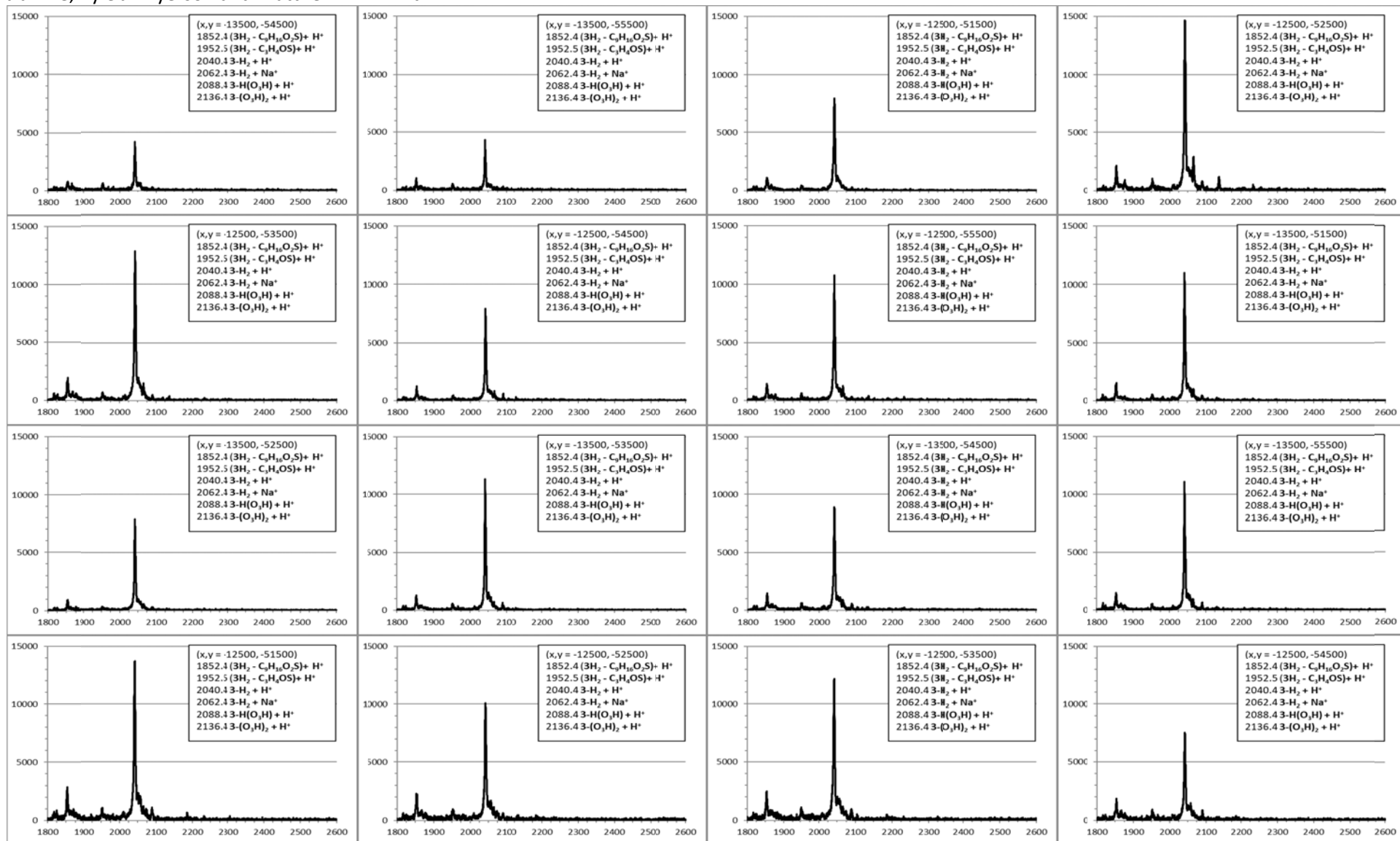


d) TOF mass spectra 1.8-2.6 kD region (**3-H₂**): 40 samples (4 trials), intensity (y) axis scale 0-15000



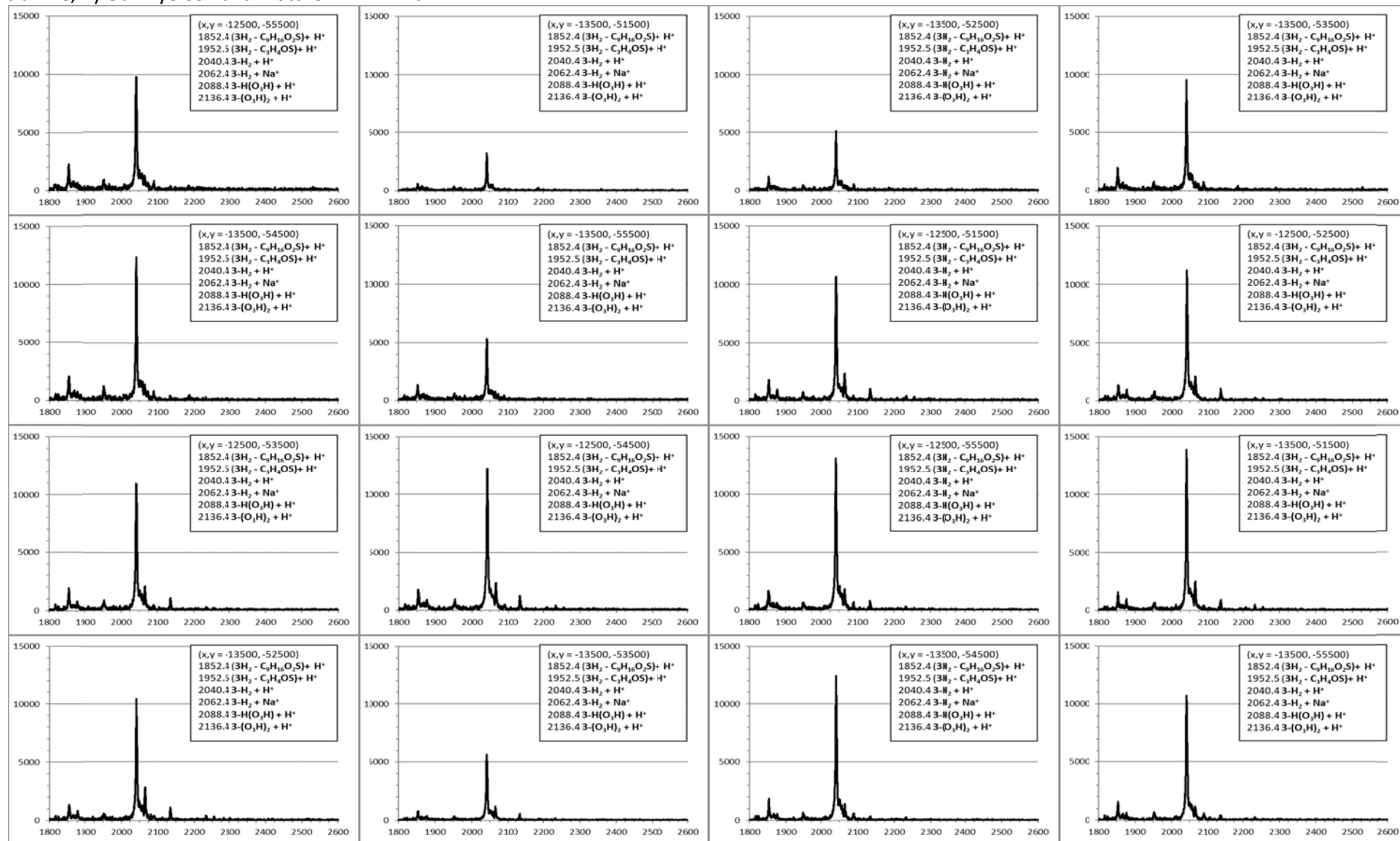
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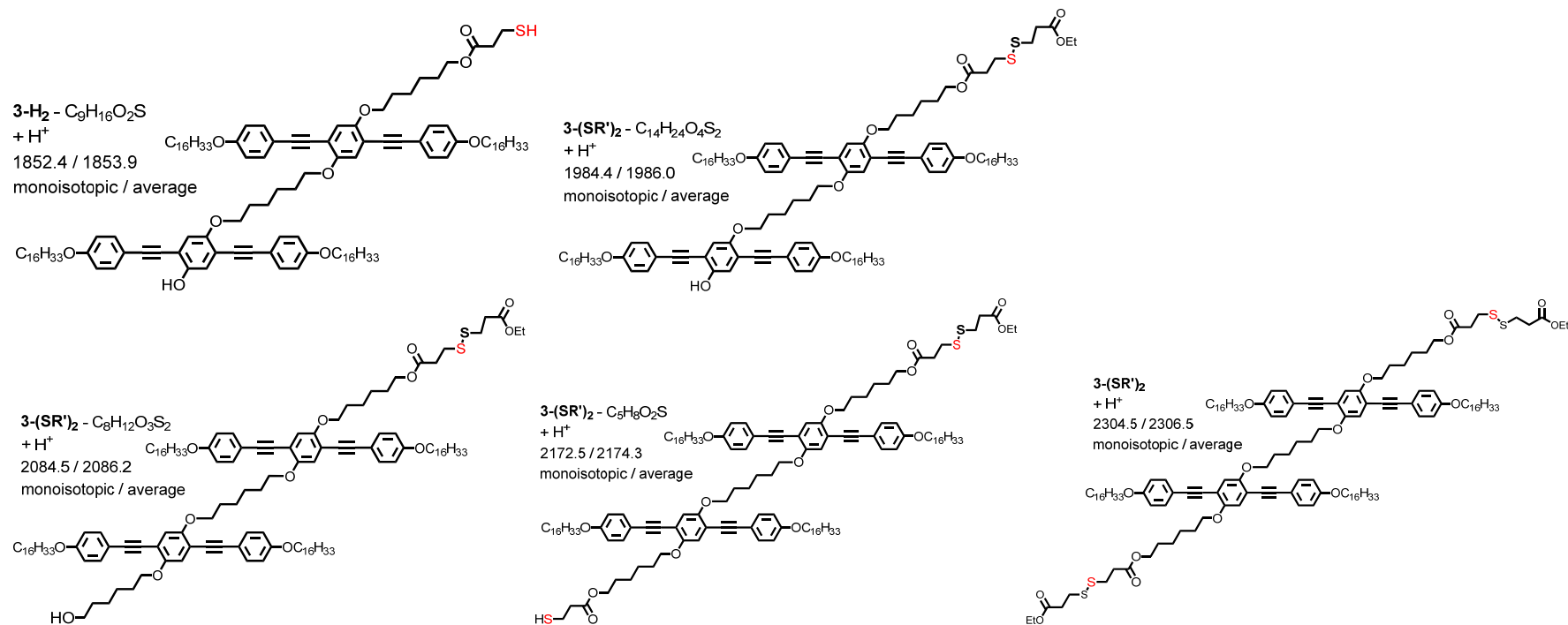


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(xii) Fig. S9. TOF mass spectra of **3-H₂** monolayer formed by DTT reduction of **3-(SR')**₂ monolayer (SR' = S(CH₂)₂CO₂Et).

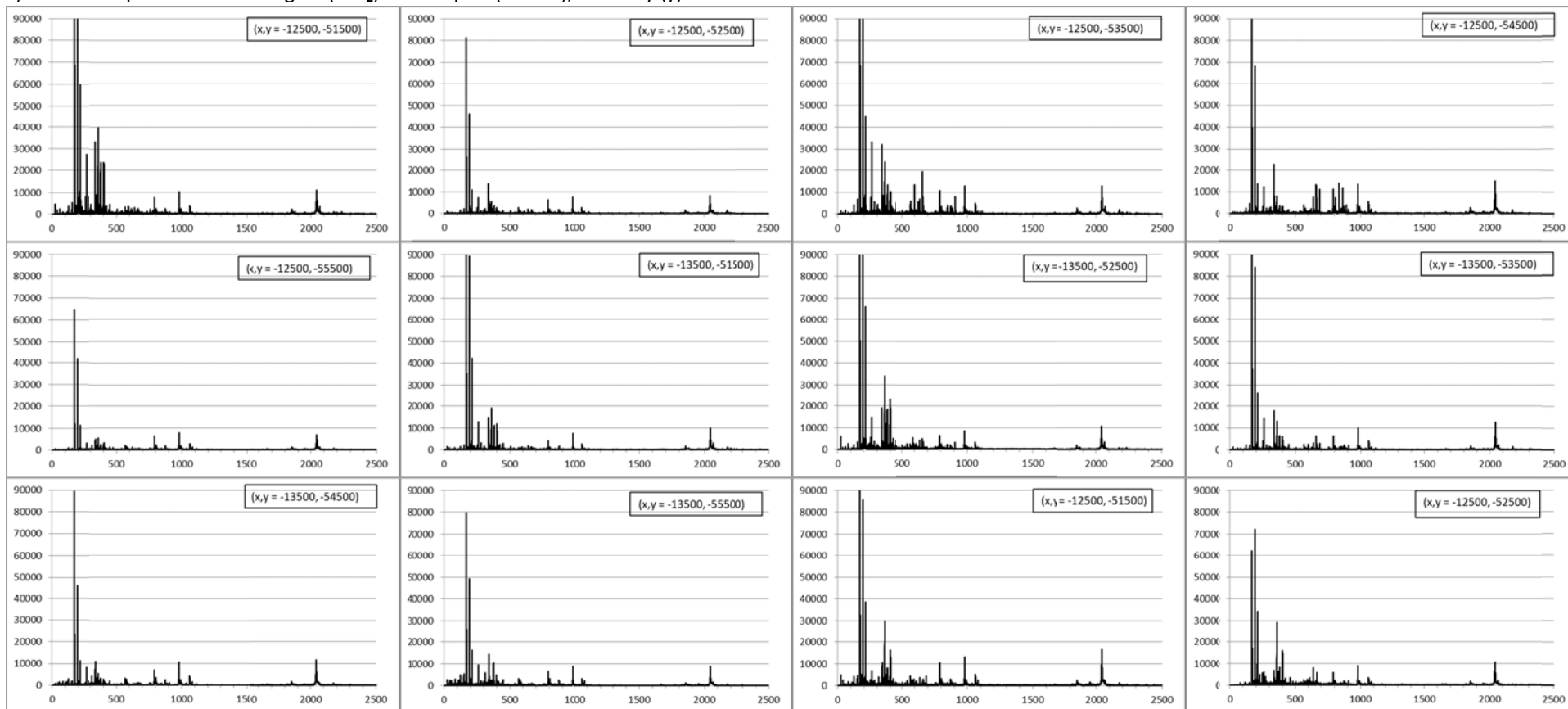
a) Summary and statistical analysis of mass spectra peak intensities.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
3-(SR') ₂ +DTT #1	10	169.3	matrix ([THAP+H] ⁺)	32100	112000	84800	22900	0.27
3-(SR') ₂ +DTT #2	10	169.3	matrix ([THAP+H] ⁺)	64600	121000	98500	18600	0.19
3-(SR') ₂ +DTT #1	10	2040	[3-H₂ + H] ⁺	6500	16400	11000	3400	0.31
3-(SR') ₂ +DTT #2	10	2040	[3-H₂ + H] ⁺	6900	15100	10800	2400	0.23
3-(SR') ₂ +DTT #1	10	2085	[3-(SR') ₂ - C ₈ H ₁₂ O ₃ S ₂ + H] ⁺	220	560	390	140	0.35
3-(SR') ₂ +DTT #2	10	2085	[3-(SR') ₂ - C ₈ H ₁₂ O ₃ S ₂ + H] ⁺	270	630	450	120	0.27
3-(SR') ₂ +DTT #1	10	2173	[3-(SR') ₂ - C ₅ H ₈ O ₂ S + H] ⁺	260	1600	760	420	0.56
3-(SR') ₂ +DTT #1	10	2173	[3-(SR') ₂ - C ₅ H ₈ O ₂ S + H] ⁺	570	1900	1200	440	0.36
3-(SR') ₂ +DTT #1	10	2305	[3-(SR') ₂ + H] ⁺	130	360	250	90	0.34
3-(SR') ₂ +DTT #2	10	2305	[3-(SR') ₂ + H] ⁺	160	630	350	150	0.42

b) Structures of TPE₂ ions observed after DTT reduction of **3-(SR')**₂ monolayer

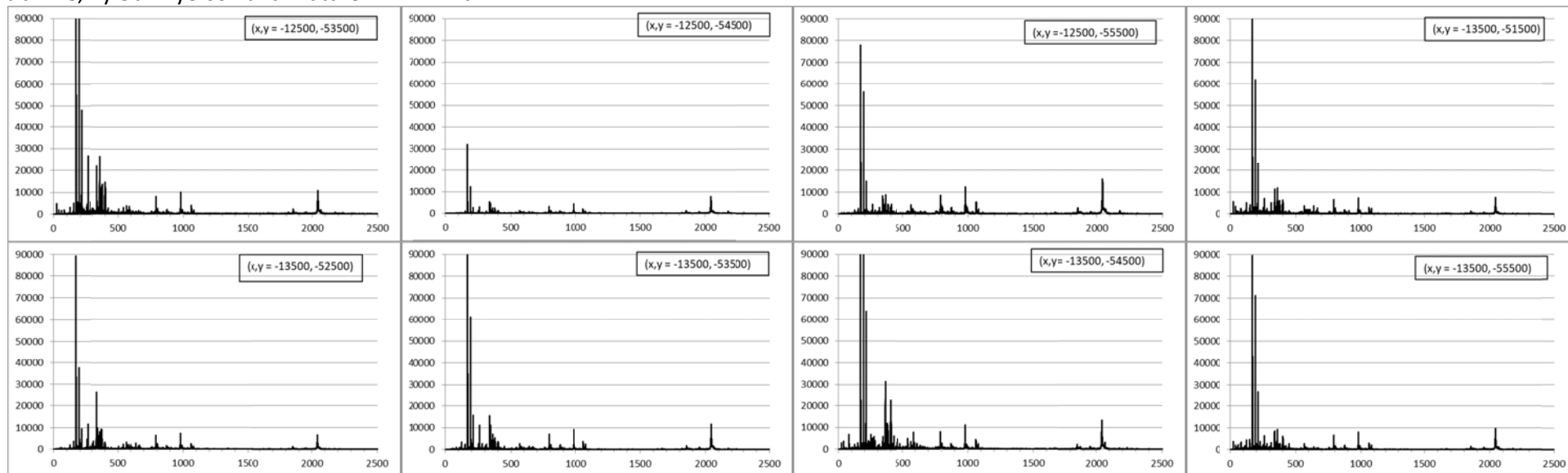
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c) TOF mass spectra 0-2.5 kD region (**3-H₂**): 20 samples (2 trials), intensity (y) axis scale 0-90000.

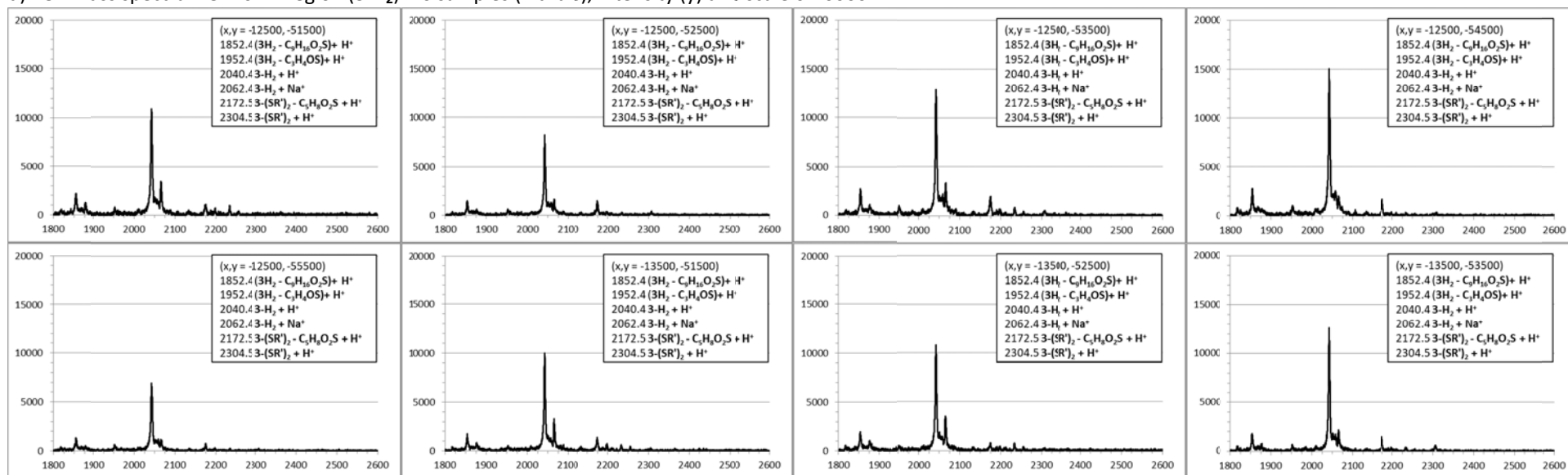


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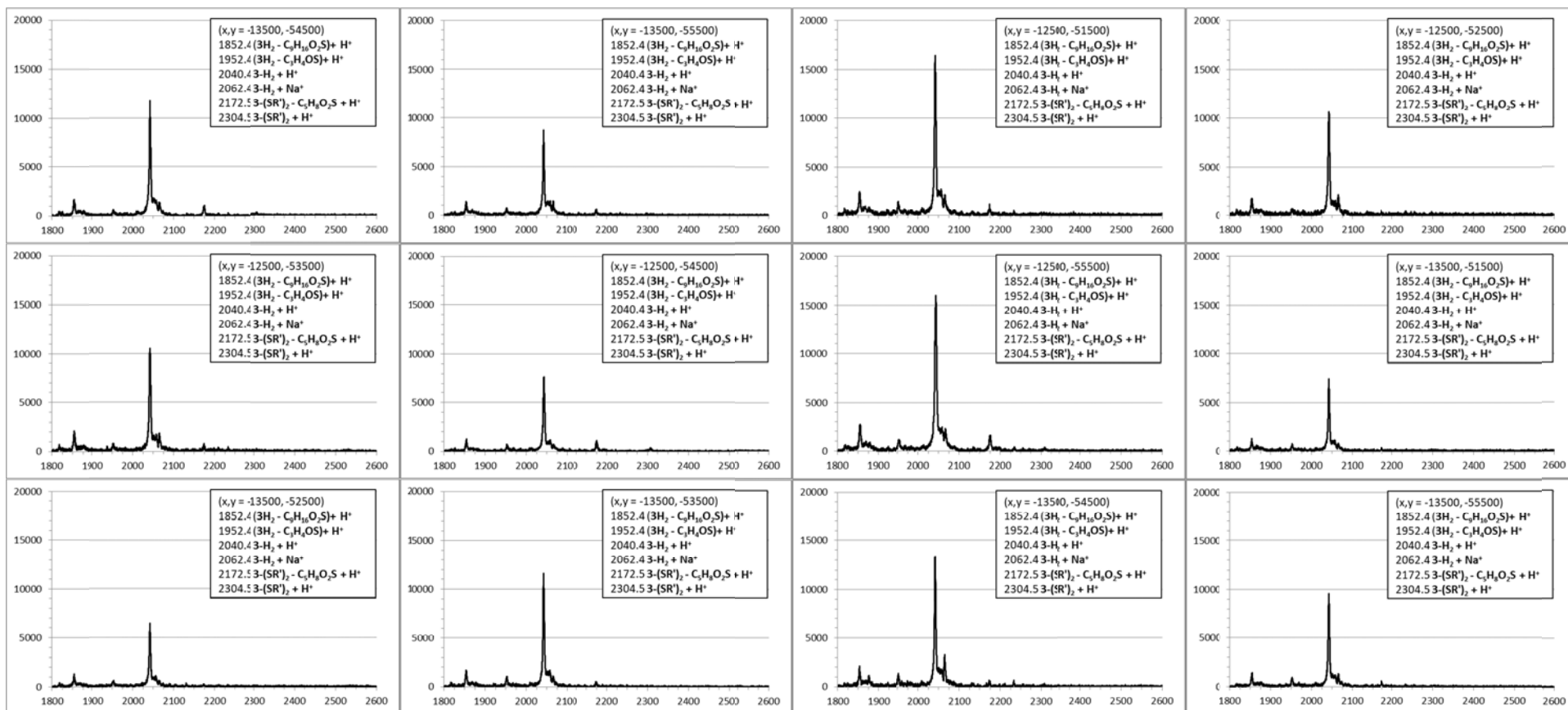
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d) TOF mass spectra 1.8-2.6 kD region (3-H_2): 20 samples (2 trials), intensity (y) axis scale 0-20000.



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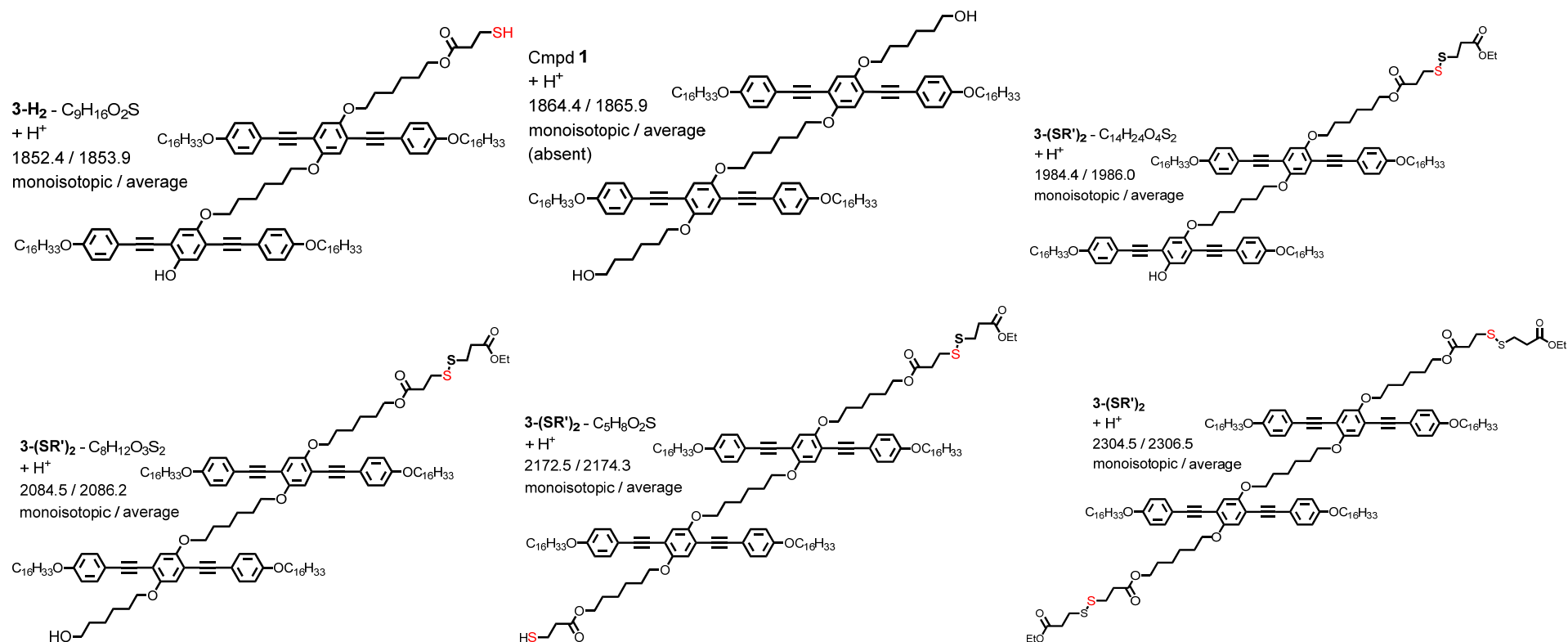


(xiii) Fig. S10. TOF mass spectra of **3-(SR')**₂ monolayer (SR' = S(CH₂)₂CO₂Et) formed via esterification of **1** monolayer with HO₂C(CH₂)₂SSR' /EDC / DMAP.

a) Summary and statistical analysis of mass spectra peak intensities.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
3-(SR') ₂ prep	10	169.3	matrix ([THAP+H] ⁺)	57500	85300	67800	7600	0.11
3-(SR') ₂ prep	10	1864	[1 + H] ⁺	190	510	330	100	0.33
3-(SR') ₂ prep	10	2085	[3-(SR') ₂ - C ₈ H ₁₂ O ₃ S ₂ + H] ⁺	670	1200	1000	180	0.18
3-(SR') ₂ prep	10	2173	[3-(SR') ₂ - C ₅ H ₈ O ₂ S + H] ⁺	820	2000	1500	400	0.26
3-(SR') ₂ prep	10	2305	[3-(SR') ₂ + H] ⁺	4800	9200	7100	1600	0.23

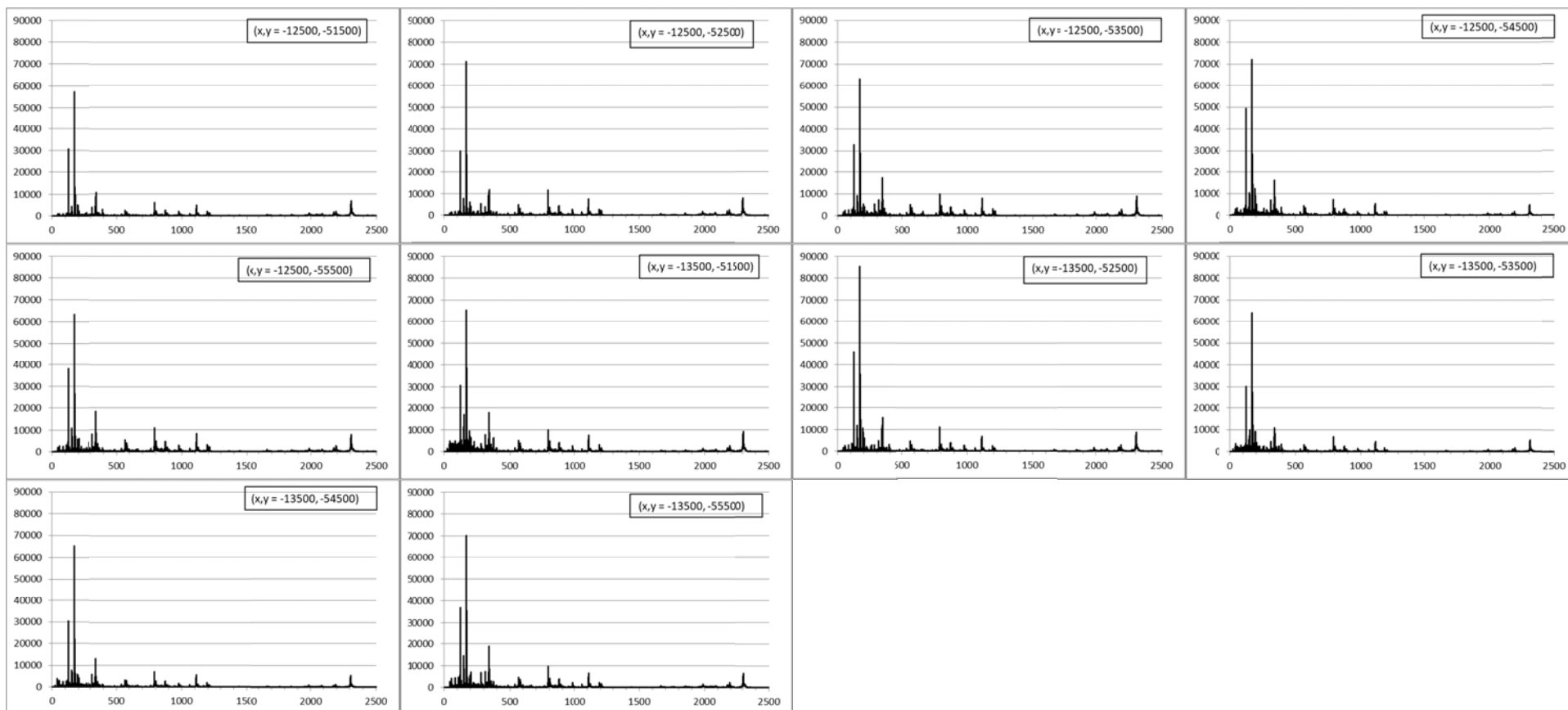
b) Structures of TPE₂ ions observed after esterification of **1** monolayer with HO₂C(CH₂)₂SSR' /EDC / DMAP.



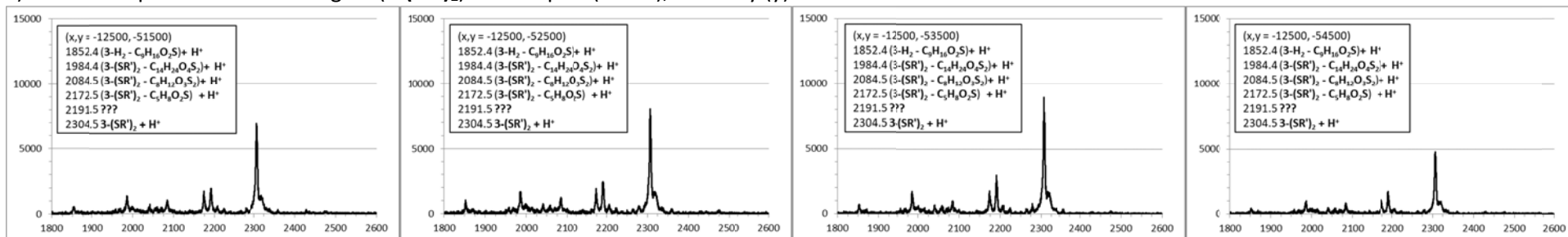
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c) TOF mass spectra 0-2.5 kD region ($3\text{-}(\text{SR}')_2$): 10 samples (1 trial), intensity (y) axis scale 0-90000.

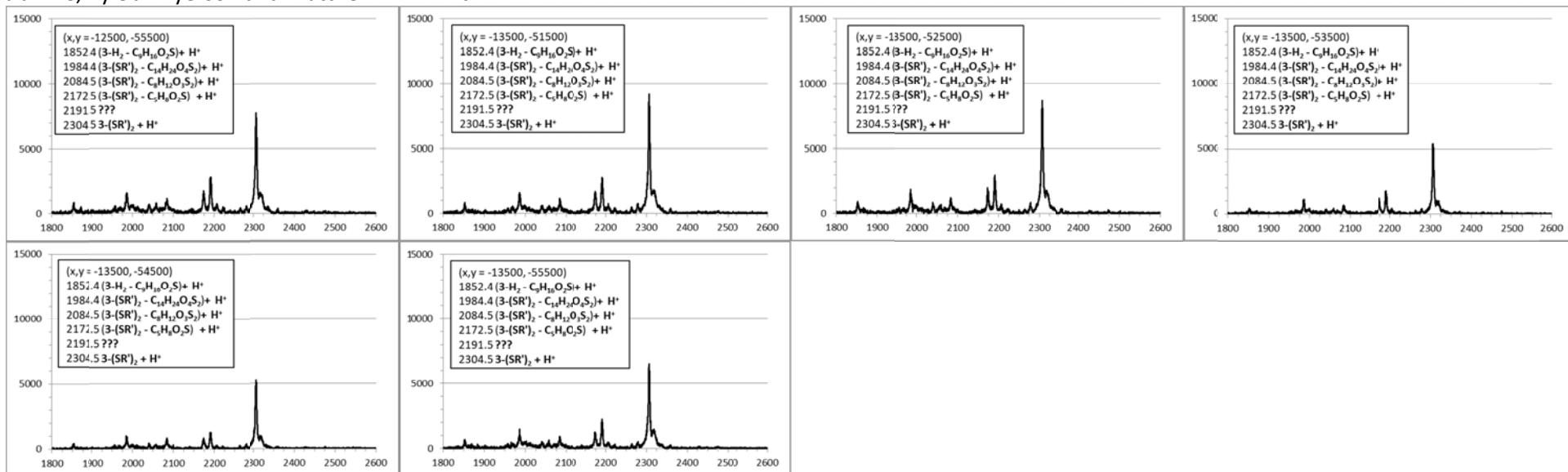


c) TOF mass spectra 1.8-2.6 kD region ($3\text{-}(\text{SR}')_2$): 10 samples (1 trial), intensity (y) axis scale 0-15000.



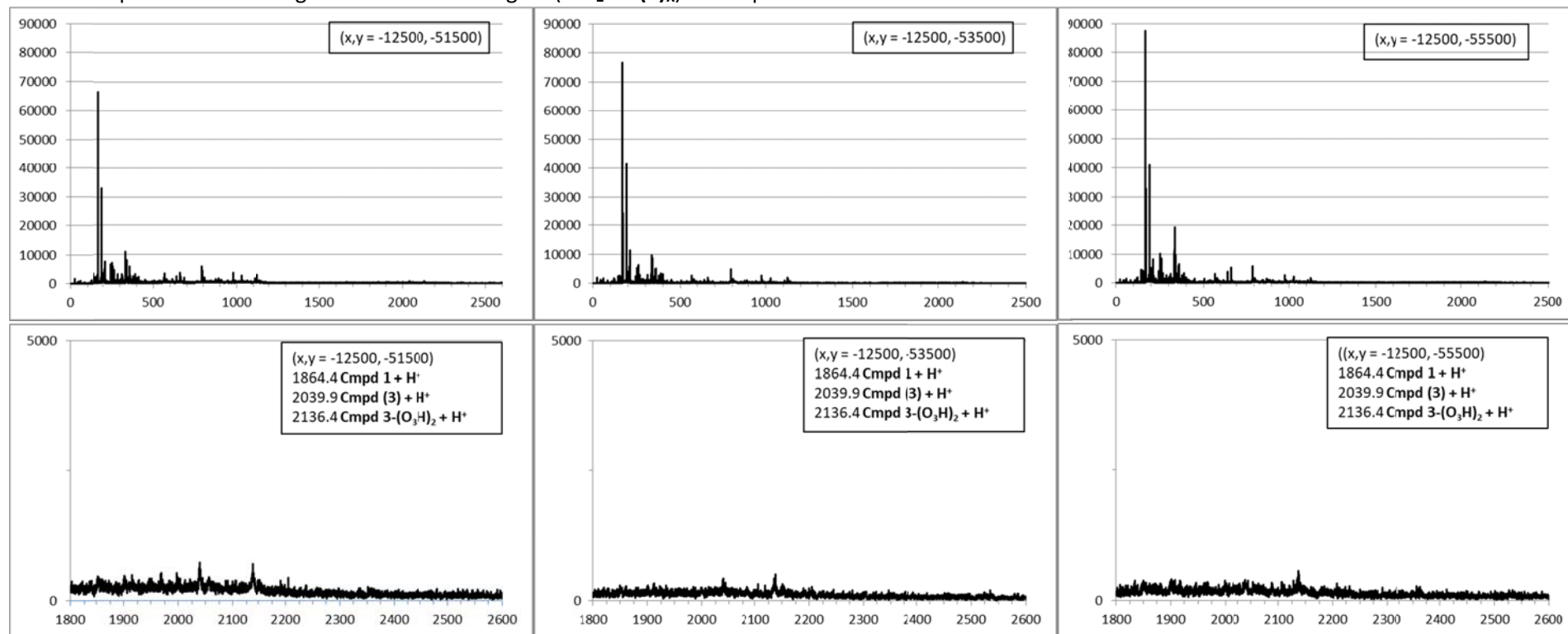
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(xiv) Fig. S11. TOF mass spectra following in-situ reaction of monolayer **3-H₂** with I₂ in DMF to form monolayer **(3)_x**

TOF mass spectra 0-2.6 kD region and 1.8-2.6kD region (**3-H₂** → **(3)_x**): 3 samples

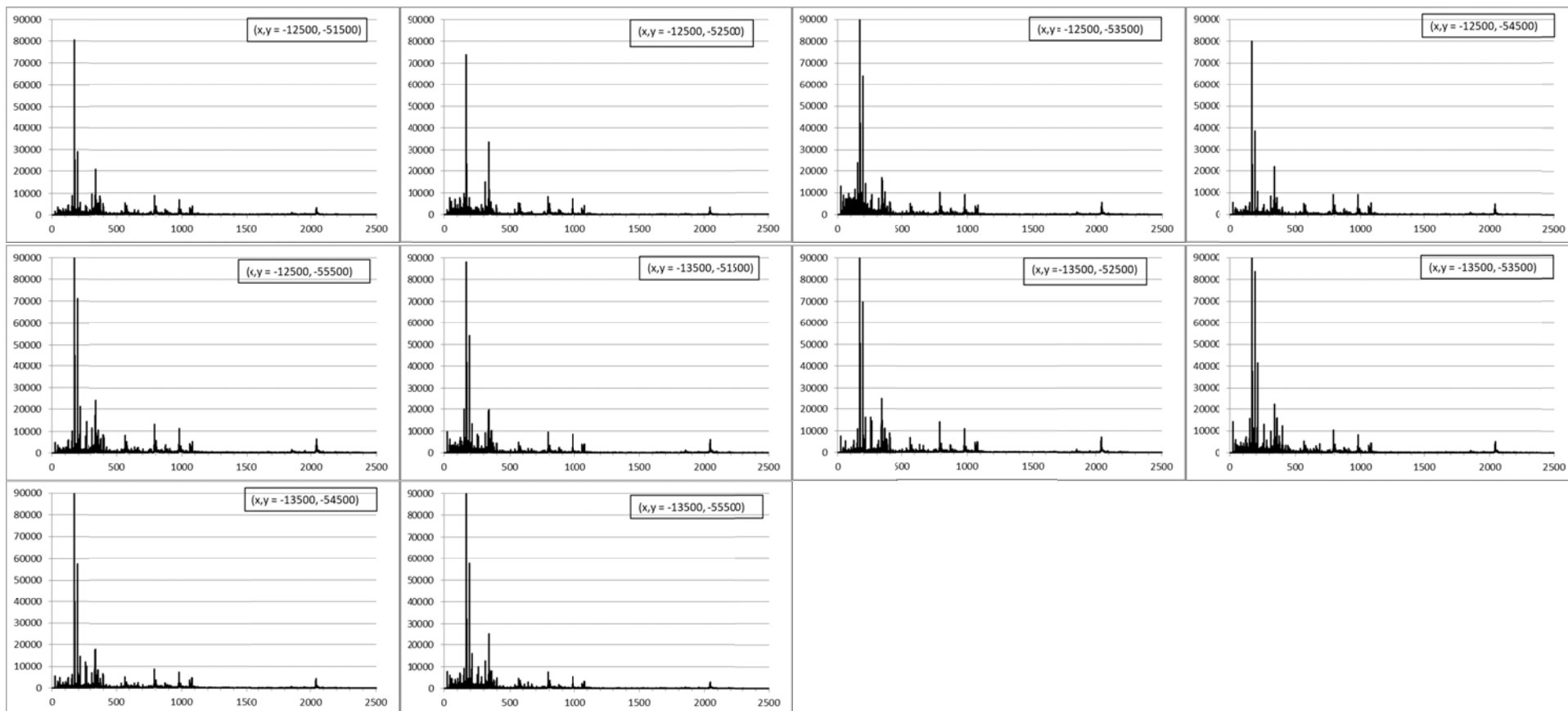


(xv). Fig. S12. TOF mass spectra of **3-H₂** monolayer formed by treatment of **2a** monolayer with two (2) cycles of oxidation (I₂) / reduction (DTT).

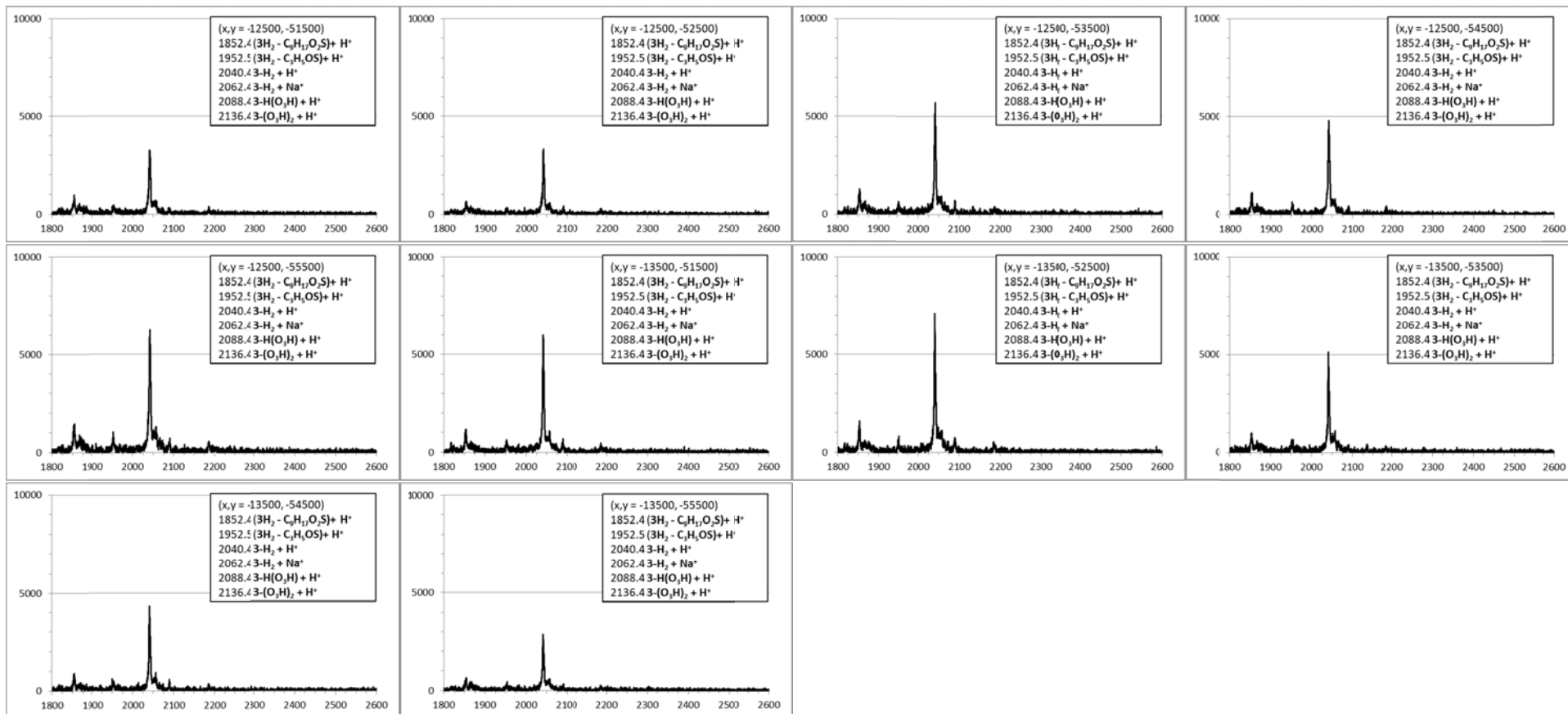
a) Summary and statistical analysis of mass spectra peak intensities.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
2a (ox/red) ₂	10	169.3	matrix ([THAP+H] ⁺)	73700	108000	92000	11400	0.12
2a (ox/red) ₂	10	2040	[3-H₂ + H] ⁺	2900	7100	4900	1400	0.29
2a (ox/red) ₂	10	2088	[3-H(O₃H) + H] ⁺	330	750	540	170	0.31
2a (ox/red) ₂	10	2136	[3-(O₃H)₂ + H] ⁺	140	410	250	90	0.36

b) TOF mass spectra 0-2.5 kD region of **3-H₂** monolayer: 10 samples (Intensity (y) axis scale 0-90000).



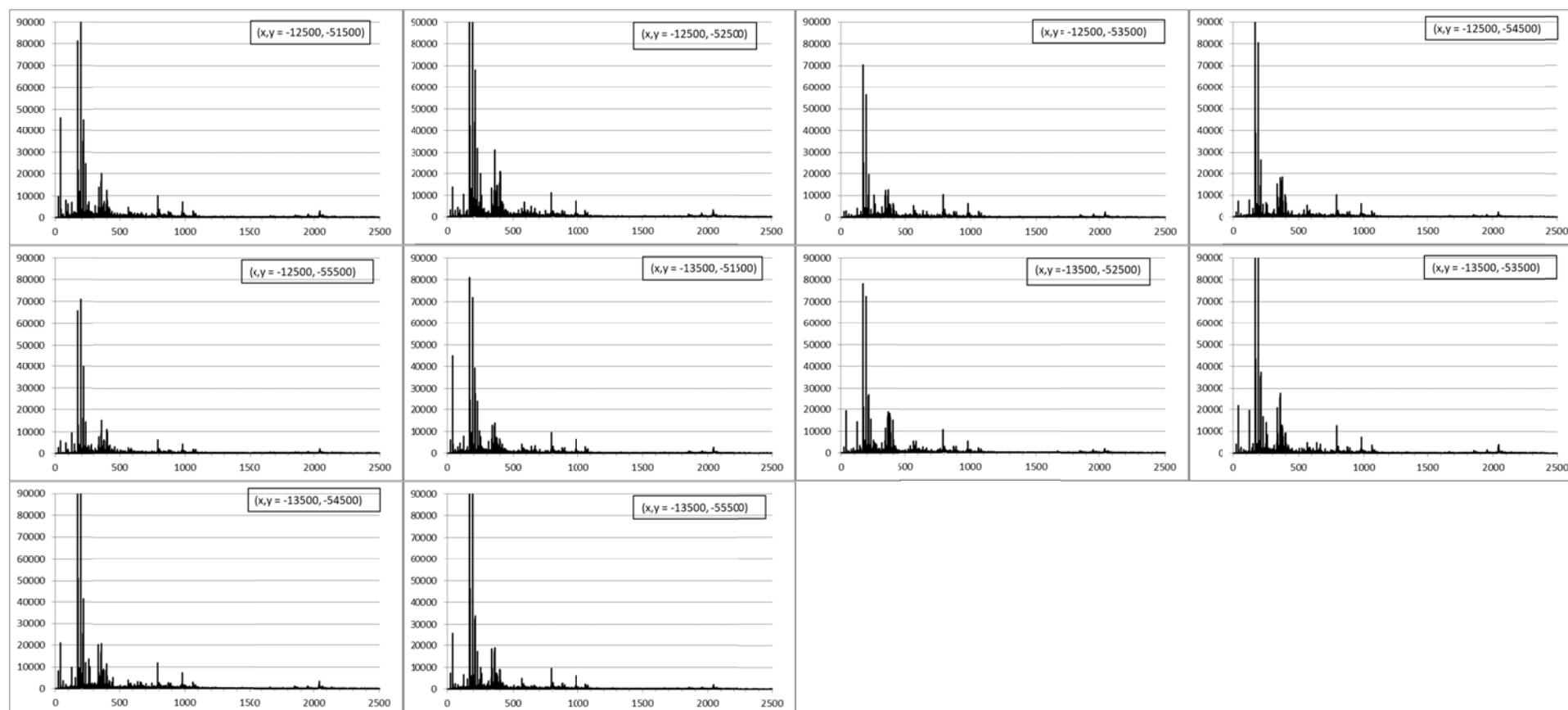
c) TOF mass spectra 1.8-2.6 kD region of **3-H₂** monolayer after 2 ox/red cycles: 10 samples (Intensity (y) axis scale 0-10000).



(xvi). **Fig. S13.** TOF mass spectra of **3-H₂** monolayer formed by treatment of **2a** monolayer with three (3) cycles of oxidation (I₂) / reduction (DTT).

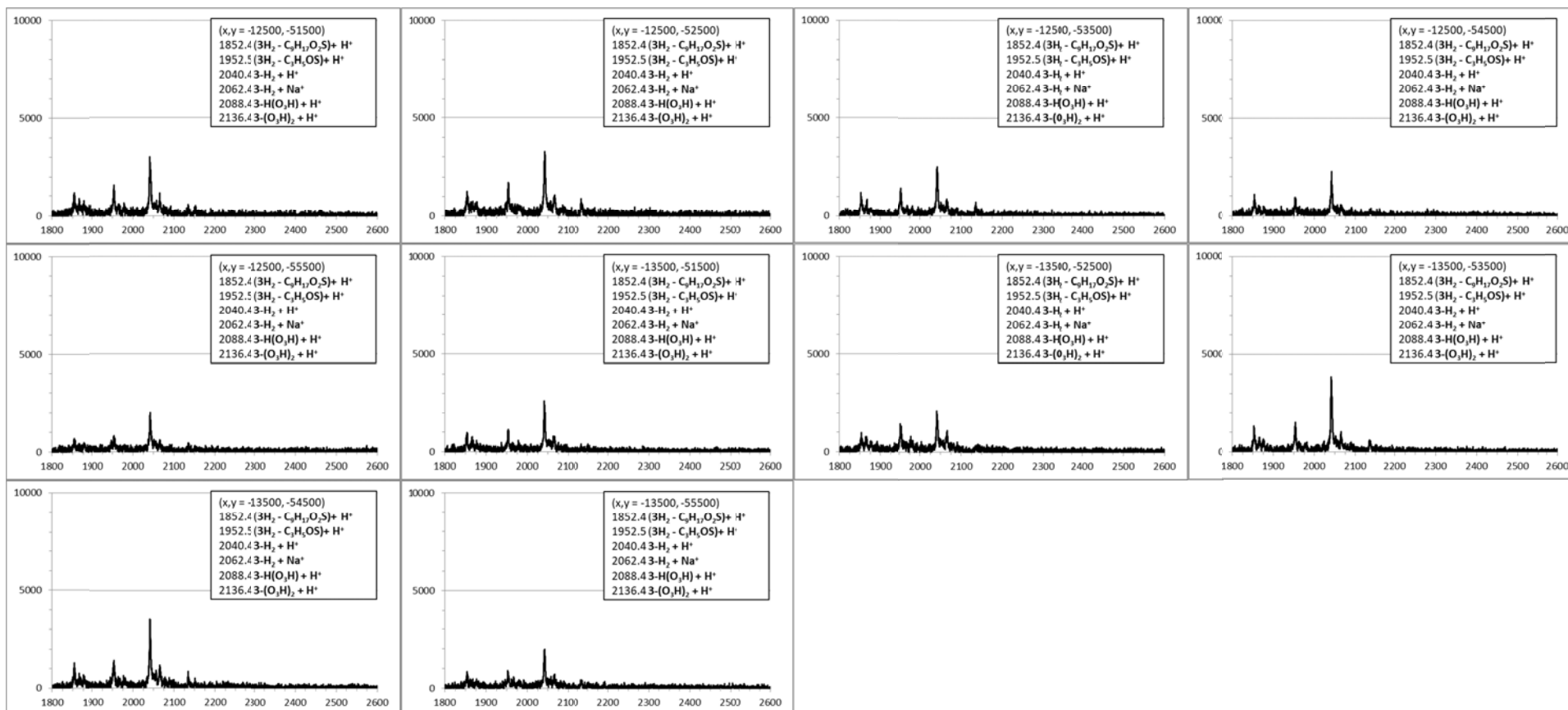
a) Summary and statistical analysis of mass spectra peak intensities.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
2a (ox/red) ₃	10	169.3	matrix ([THAP+H] ⁺)	65800	107000	89500	15800	0.18
2a (ox/red) ₃	10	2040	[3-H₂ + H] ⁺	1970	3900	2720	670	0.25
2a (ox/red) ₃	10	2088	[3-H(O₃H) + H] ⁺	330	530	430	70	0.15
2a (ox/red) ₃	10	2136	[3-(O₃H)₂ + H] ⁺	380	900	570	190	0.33

b) TOF mass spectra 0-2.5 kD region of **3-H₂** monolayer after 3 ox/red cycles: 10 samples (Intensity (y) axis scale 0-90000).

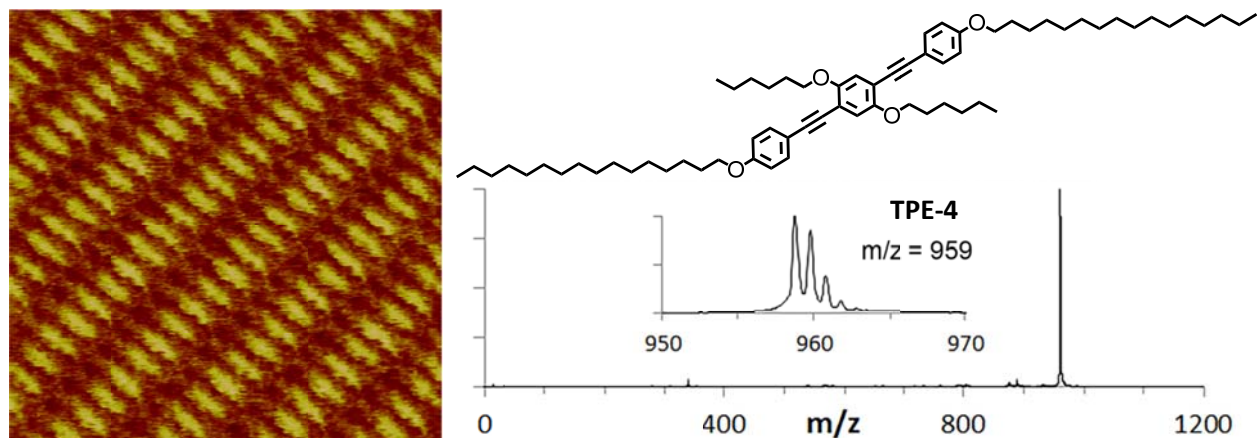
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c) TOF mass spectra 1.8-2.6 kD region of **3-H₂** monolayer after 3 ox/red cycles: 10 samples (Intensity (y) axis scale 0-10000).



Ox / Red Cycles	<THAP>	< [3-H ₂ + H ⁺] >	< [3-H(O ₃ H) + H ⁺] >	< [3- (O ₃ H) ₂ + H ⁺] >
1	87400	9100	550	440
2	92000	4900	540	250
3	89500	2720	430	570

(xvii) **Fig. S14.** Single core molecule **TPE-4** structure, monolayer STM image and resistance to o-dichlorobenzene (oDCB) rinsing determined by laser desorption and ionization (LDI) TOF mass spectroscopy.

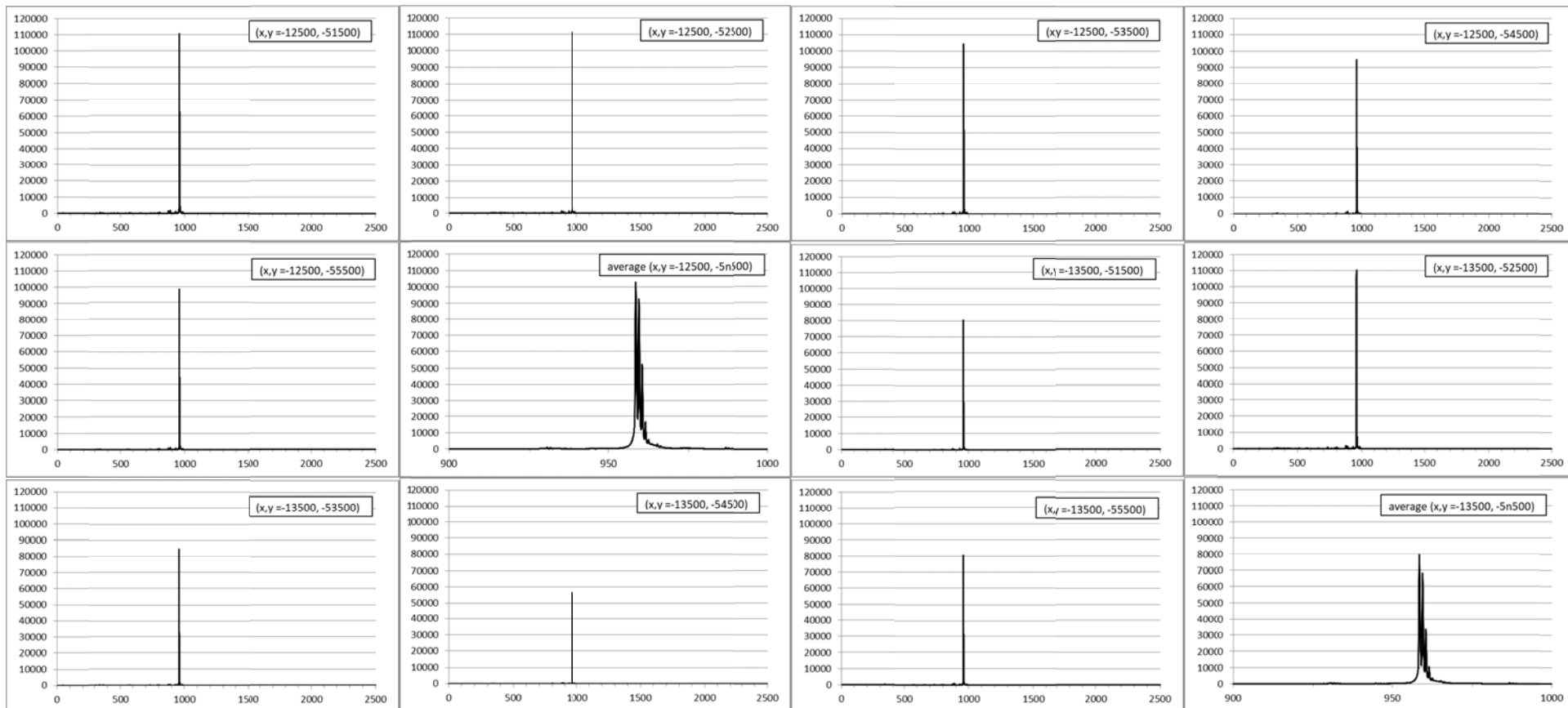


STM scan: 20nm x 20 nm

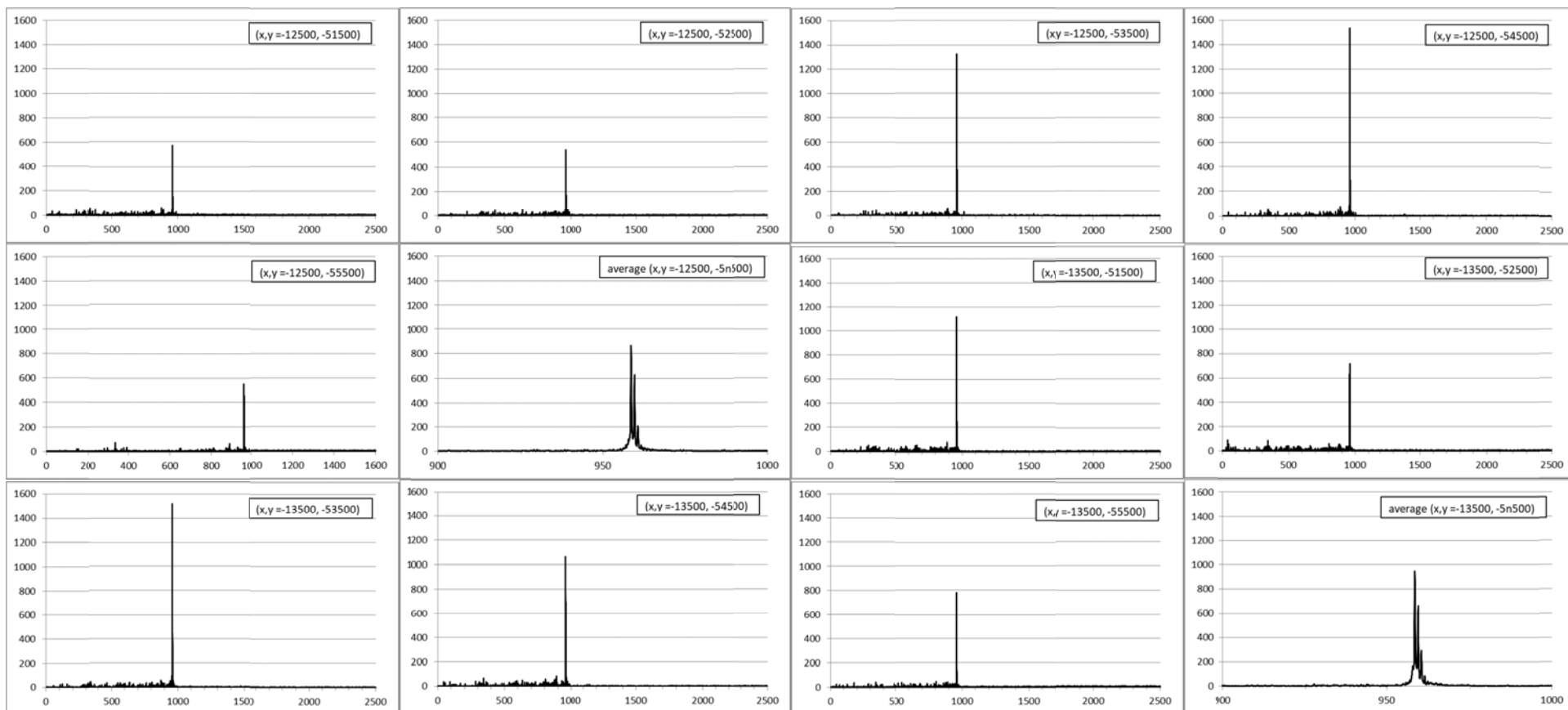
a) Summary and statistical analysis of mass spectra peak intensity prior and after 20 μ L oDCB rinse of **TPE-4** monolayer.

<u>measurement</u>	<u>samples</u>	<u>m/ z</u>	<u>assignment</u>	<u>Int. minimum</u>	<u>Int. maximum</u>	<u>Intensity average</u>	<u>Intensity st.dev.</u>	<u>st.dev. / < Int. ></u>
Before rinse	10	958.5	[TPE-4] ⁺	56500	111000	93200 (1.00)	17600	0.19
After 20 μ L	10	958.5	[TPE-4] ⁺	490	1500	970 (0.01)	390	0.41

b) LDI-TOF mass spectra of **TPE-4** monolayer prior to oDCB rinse: 10 sampled spots. 0-2.5 kD region and 0.9-1.0 kD region of the average spectrum collected from five spots at x = -12500 and at x = -13500 (Intensity (y) axis scale 0 - 120000)



c) LDI-TOF mass spectra of **TPE-4** monolayer after 20 μ L oDCB rinse: 10 sampled spots. 0-2.5 kD region and 0.9-1.0 kD region of the average spectrum collected from five spots at x = -12500 and at x = -13500 (Intensity (y) axis scale 0 - 1600)

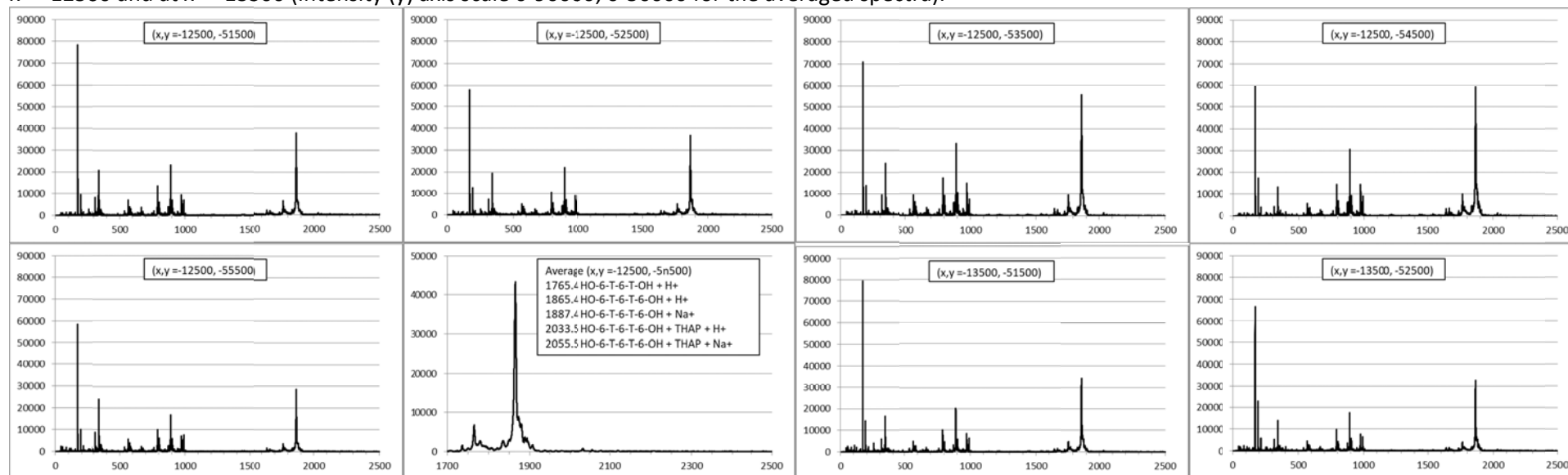


(xviii) Fig. S15. Resistance of TPE₂ monolayer **1** to incubation in oDCB determined by mass spectra.

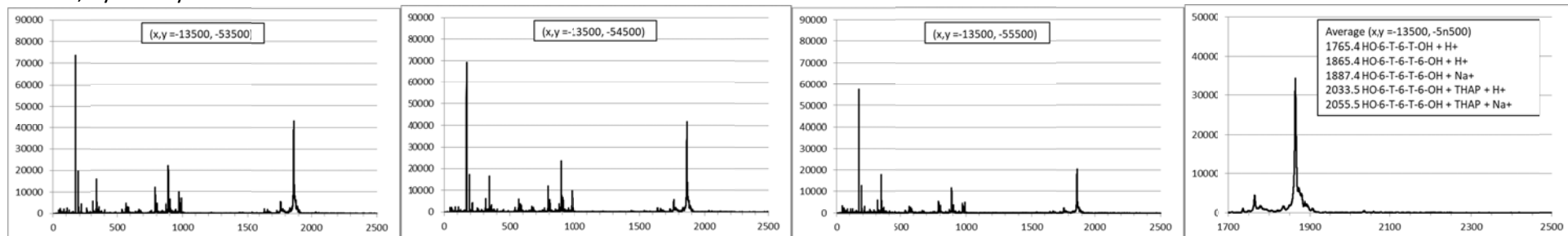
a) Summary and statistical analysis of mass spectra peak intensity prior to, after 3 hr and after 18 hr incubation in oDCB at 19°C.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
Before	10	169.3	matrix ([THAP+H] ⁺)	57600	79600	67200	8500	0.13
3 hr in oDCB	10	169.3	matrix ([THAP+H] ⁺)	32100	59000	45500	7700	0.17
18 hr in oDCB	10	169.3	matrix ([THAP+H] ⁺)	61100	80700	70700	6000	0.08
Before	10	1864	[1 + H] ⁺	20400	59300	39000 (1.00)	11700	0.30
3 hr in oDCB	10	1864	[1 + H] ⁺	6200	18700	10300 (0.26)	3700	0.36
18 hr in oDCB	10	1864	[1 + H] ⁺	1500	4900	2400 (0.06)	1000	0.42

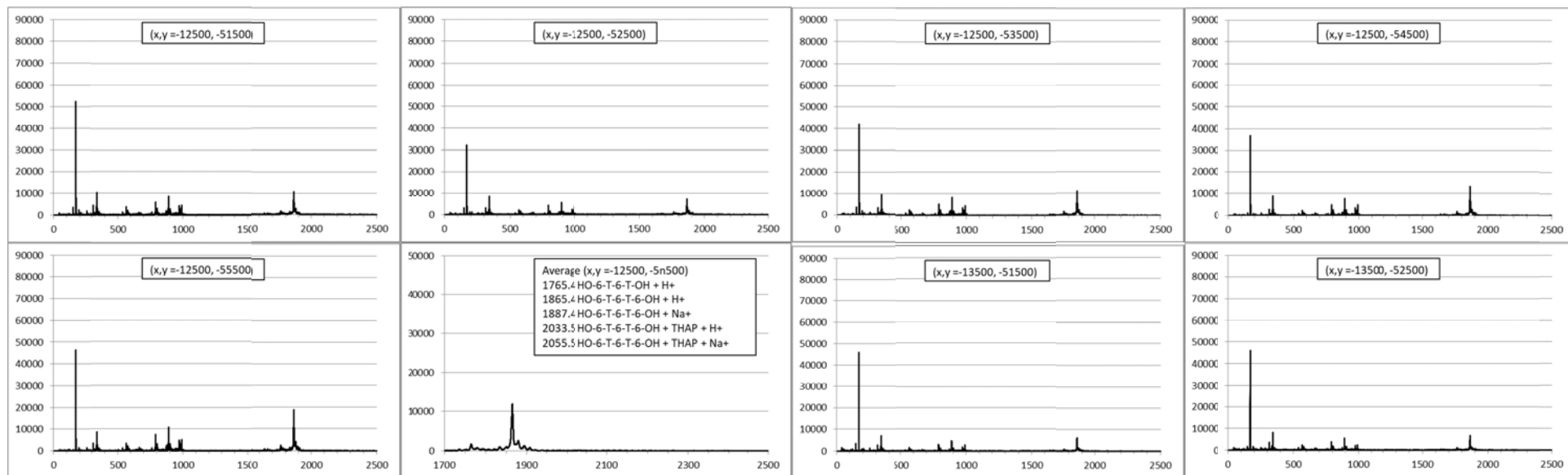
b) **1** Monolayer on HOPG - prior to oDCB incubation: 10 sampled spots. 0-2.5kD region and 1.7-2.5 kD region of the average spectrum collected from five spots at x = -12500 and at x = -13500 (Intensity (y) axis scale 0-90000; 0-50000 for the averaged spectra).



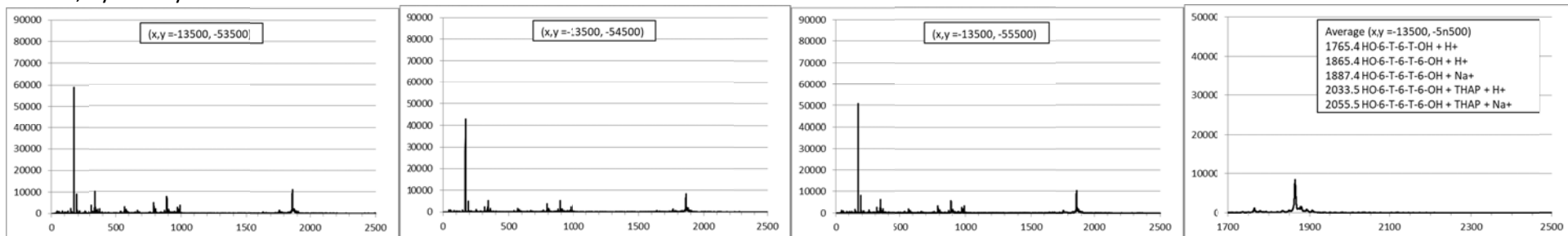
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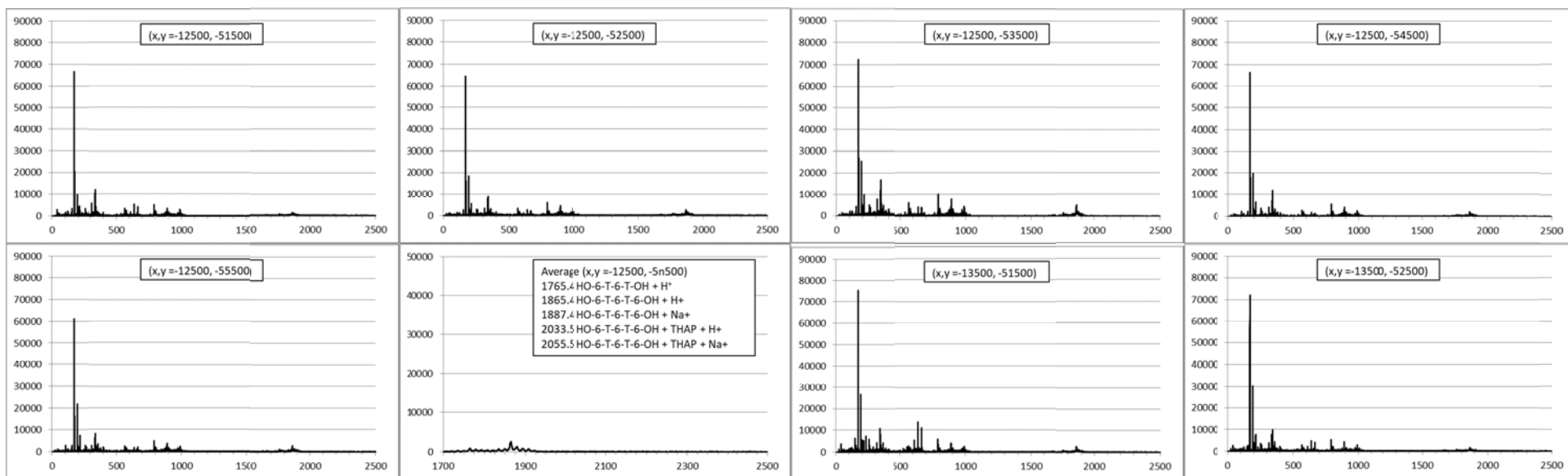
c) **1** Monolayer on HOPG after 3 hr oDCB incubation: 10 sampled spots. 0-2.5kD region and 1.7-2.5 kD region of the average spectrum collected from five spots at x = -12500 and x = -13500 (Intensity (y) axis scale 0-90000; 0-50000 for the averaged spectra).



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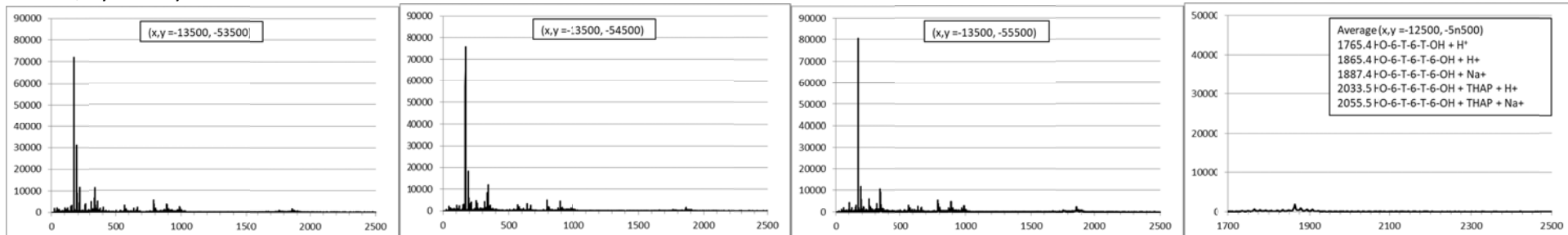


d) **1** Monolayer on HOPG after 18 hr oDCB incubation: 10 sampled spots. 0-2.5kD region and 1.7-2.5 kD region of the average spectrum collected from five spots at x = -12500 and x = -13500 (Intensity (y) axis scale 0-90000; 0-50000 for the averaged spectra).



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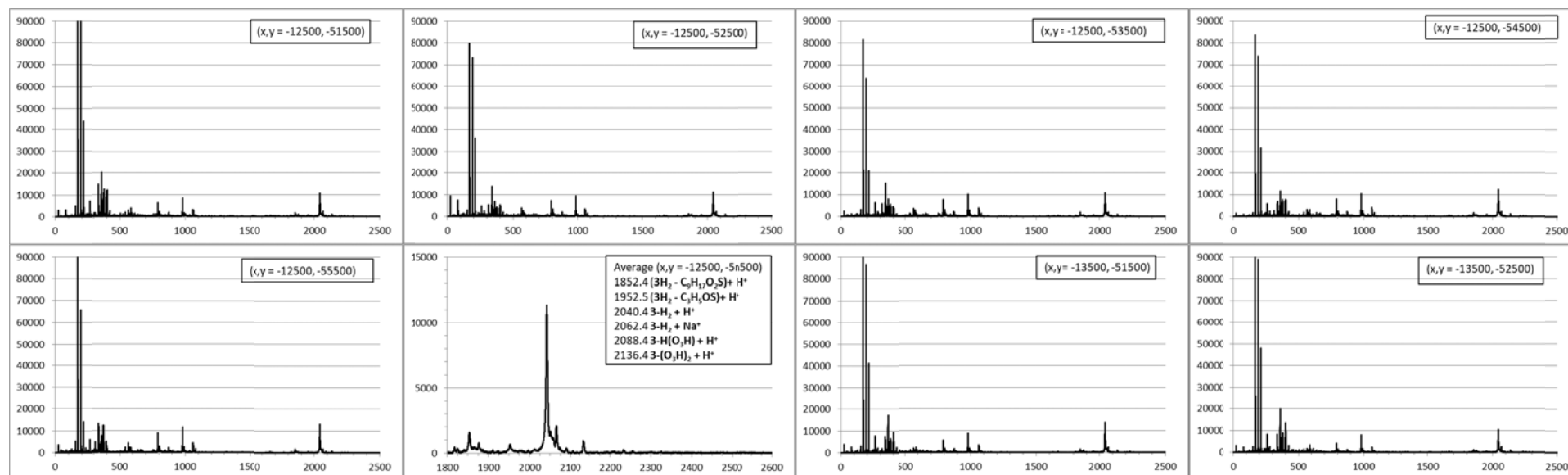
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(xix) Fig. S16. Resistance of **(3)_x** monolayer to 19°C and 60°C oDCB evaluated as the TOF MS intensity after reduction to **3-H₂**.

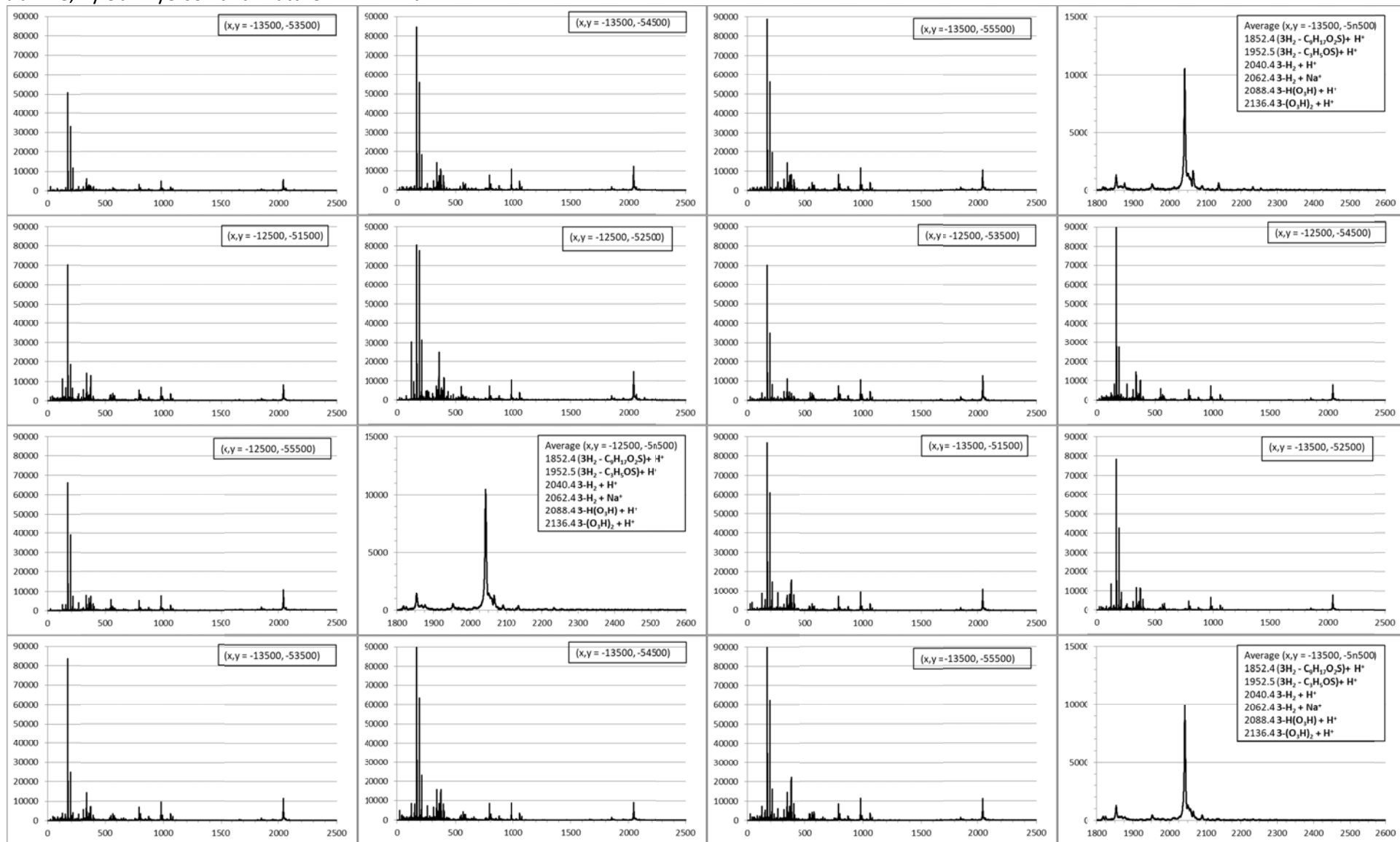
a) Summary and statistics of mass spectra peak intensity prior to, after 20 hr incubation at 19°C in oDCB and after 21 hr incubation at 60°C in oDCB.

measurement	samples	m/z	assignment	Int. minimum	Int. maximum	Intensity average	Intensity st.dev.	st.dev. / < Int. >
Before	20	169.3	matrix ([THAP+H] ⁺)	50800	102000	84700	13400	0.16
20 hr 19°C oDCB	10	169.3	matrix ([THAP+H] ⁺)	67600	107000	81700	13500	0.17
21 hr 60°C oDCB	10	169.3	matrix ([THAP+H] ⁺)	81400	115000	96900	9800	0.10
Before	20	2040	[3-H₂ + H] ⁺	5600	14700	10200 (1.00)	2300	0.23
20 hr 19°C oDCB	10	2040	[3-H₂ + H] ⁺	5800	14200	9400 (0.92)	2800	0.29
21 hr 60°C oDCB	10	2040	[3-H₂ + H] ⁺	6400	9700	8400 (0.82)	1300	0.15

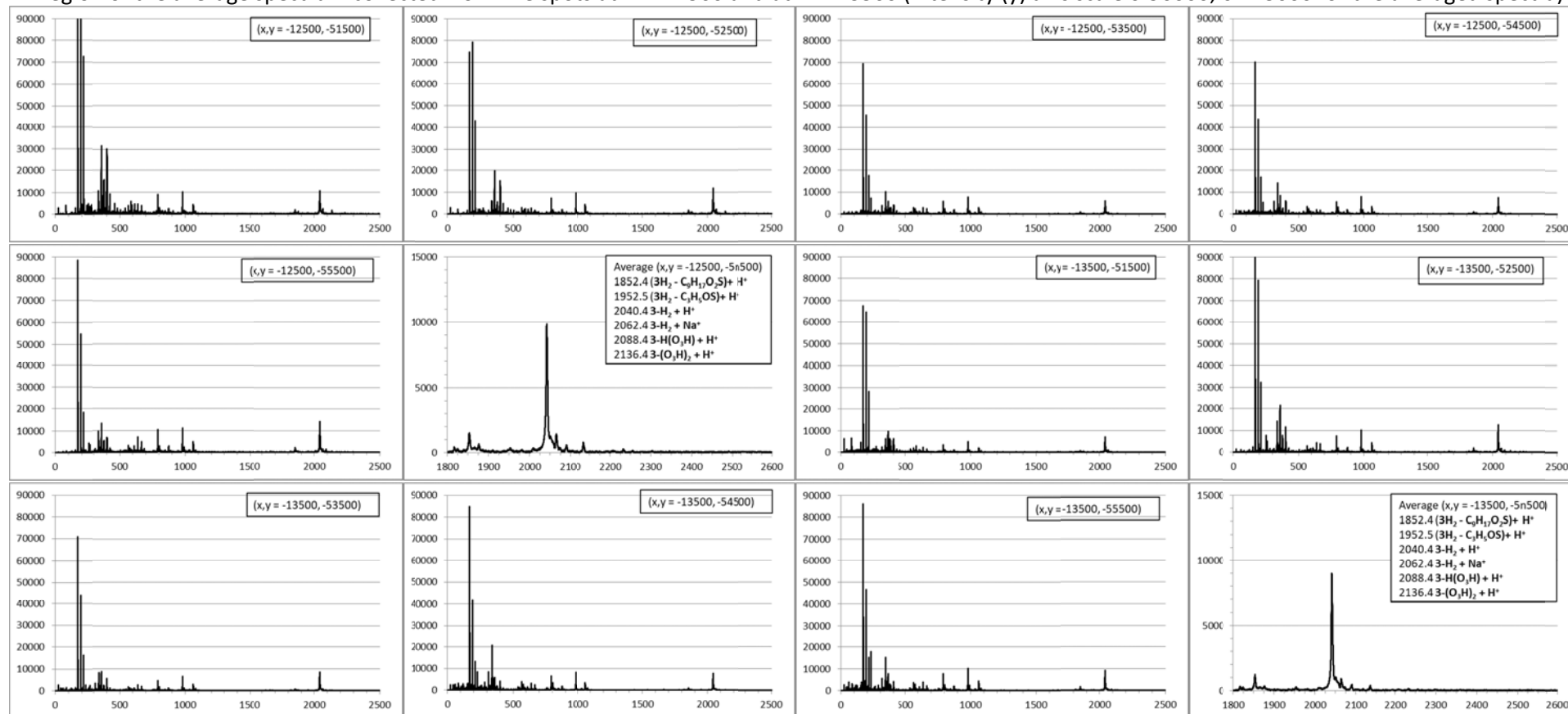
b) Freshly prepared **3-H₂** monolayer on HOPG without oDCB incubation of **(3)_x** precursor: 20 sampled spots. 0-2.5kD region and 1.8-2.6 kD region of the average spectrum collected from five spots at x = -12500 and at x = -13500 from two sides of HOPG (Intensity (y) axis scale 0-90000; 0-15000 for the averaged spectra).

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c) **3-H₂** monolayer on HOPG prepared by DTT reduction after (**3**)_x monolayer incubation for 20 hours in 19°C oDCB: 10 sampled spots. 0-2.5kD region and 1.8-2.6 kD region of the average spectrum collected from five spots at x = -12500 and at x = -13500 (Intensity (y) axis scale 0-90000; 0 - 15000 for the averaged spectra).



d) **3-H₂** monolayer on HOPG prepared by DTT reduction after (**3**)_x monolayer incubation for 21 hours in 60°C oDCB: 10 sampled spots. 0-2.5kD region and 1.8-2.6 kD region of the average spectrum collected from five spots at x = -12500 and at x = -13500 (ntensity (y) scale 0-90000; 0 - 15000 for the averaged spectra).

