Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

SUPPORTING INFORMATION

Per- and polyfluoroalkyl substances (PFAS) in white-tailed sea eagle eggs from Sweden: Temporal trends (1969-2021), spatial variations, fluorine mass balance, and suspect screening

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Experimental Procedure

Chemicals and Reagents

MeOH (99.8%, LiChrosolv®) and ammonium acetate (98%) were purchased from Merck (Darmstadt, Germany). ACN (≥99.9%, Chromasolv™) was obtained from Honeywell (France). Water was purified by a Millipore water purification system and had a resistance <18 MΩ/cm (Milli-Q water). A fluoride standard (1000 mg/L) was obtained from Thermo Scientific. EnviCarb (Supelclean™) was acquired from Sigma Aldrich. Stainless steel beads (4.8 mm) were purchased from Next Advance©. Argon and oxygen gases used for combustion ion chromatography (CIC) analysis were of purity grade 5.0.

Sample Extraction

Initially, 1 g of WTSE egg homogenate was thawed at room temperature. Then, 4 ml ACN was added together with 7-8 beads (stainless steel ø 4.8 mm) followed by homogenization of the samples using a bead blender (SPEX SamplePrep 1600 MiniG®) for 5 min at 1500 rpm. The samples were subsequently centrifuged at 2000 rpm for 5 min (Centrifuge 5810, Eppendorf, Hamburg) before the supernatant was transferred to a new 13 ml PPtube. This extraction procedure was repeated using the remaining precipitate by adding another 4 ml ACN, and vortexing, blending, and centrifuging again. The supernatant was then added to the existing tube with the previous supernatant and the combined extracts were then concentrated to approximately 1 ml under a stream of nitrogen in a water bath at 40 °C (TurboVap LV Evaporator, Biotage). Following concentration of the supernatant, they were then weighed and added to a 1.7 ml Eppendorf tube containing 25mg EnviCarb and 50 µl acetic acid before the tubes were vortexed and centrifuged for 10 min at 10 000 rpm (Galaxy 14D, Microcentrifuge, VWR). 250 µl of supernatant was then transferred to another Eppendorf tube alongside NH_4OAc (4 mM in water) in a 1:1 amount and

stored at -20 ℃. Finally, upon analysis, the extracts were allowed to adjust to room temperature, vortexed, and transferred to LC vial.

LC-MS targeted analysis method (Individual samples)

Targeted analysis of individual samples was carried out on a Waters Acquity UPLC coupled to a Xevo TQ-S triple quadrupole (Waters) mass spectrometer equipped with an electrospray ionization source operated in negative mode. The capillary voltage was set at 1.0 kV, desolvation and source temperatures were set at 350˚C and 150˚C, respectively. The desolvation and cone gas flows were also set at 650 L/h and 150 L/h, respectively. Compound specific parameters provided in Table S6. Extracts (5 µL) were injected onto a BEH C18 column (2.1 × 50 mm, 1.7 µm particle size; Waters) equipped with a guard column BEH C18 (2.1 × 5 mm, 1.7 µm; Waters). In addition, an "isolator column" XBridge™ C18 (2.1 × 50 mm, 3.5µm; Waters) was mounted before the injector. The gradient program is defined in Table S4. Quantification was performed using MassLynx 4.1 (Waters) with 7-point calibration curves ranging from 0.036 to 76.210 pg/µl (linear, 1/x weighting).

LC-HRMS target/suspect screening method (Pooled samples)

Combined target/suspect screening of pooled samples was carried out using a Dionex Ultimate 3000 ultra-high performance liquid chromatograph (UHPLC) coupled to a Q Exactive HF Orbitrap (Thermo Scientific), based on a previously described method.[1,2] The flow rate was held constant at 0.4 ml per minute throughout the run. The mobile phases and eluent program are provided in Table S4. Injection volume was 5 µl. The column temperature was set at 50 ºC and the flow at 0.4 ml/min. The system was operated in negative ion electrospray ionization (ESI-) mode with a capillary voltage of 1.0 kV. The instrument was run in negative ion, full scan (200-1200 m/z) data

dependent acquisition (DDA) MS/MS mode (50-1200 m/z). The resolution was set to 120 000 (15 000 for MS/MS), the automatic gain control (AGC) was set to 3e6. Additional MS parameters are provided in Table S3.

Assigning confidence to suspect identifications

Each suspect was assigned a confidence level (CL; 1-5) according to the Schymanski scale.[33] Briefly, CL 1 was assigned when a reference standard was available, while CL 2a was assigned when there was a library spectrum match of MS2 data. CL 2b was assigned to suspects that formed part of a homologue series containing at least two other homologues with CL 2a or lower, along with a consistent retention time (e.g. falling in-between the retention time of longer and shorter chain-length homologues). CL 3 was assigned to suspects with less than 3 observed fragments and no homologues with CL<3, while CL 4 was given to suspects lacking MS2 fragmentation and no homologues with CL<3 to which an unequivocal molecular formula could be assigned.

Combustion ion chromatography (CIC) method

CIC settings were as follows, samples were combusted at 1100 °C with oxygen (400 mL/min), argon (200 mL/min) and an argon/water vapor mix (100 mL/min) within the combustion unit (HF-210, Mitsubishi) for five minutes. Details of the elution program are given in Table S5. Combustion gases were absorbed in Milli-Q water during the combustion process with use of a gas absorber unit (GA-210, Mitsubishi). Analytes were then separated and analyzed with an ion-chromatograph (Dionex, Thermo Scientific). Quantification was achieved using calibration points at 0.05, 0.1, 0.25, 0.5, and 1 ppm of NaF solution (100 µL) using an unweighted linear calibration curve produced on Chromeleon. All samples were run in triplicate.

Fluorine mass balance calculations

For the purpose of comparisons between LC-HRMS and CIC data, concentrations produced by LC-HRMS analysis must be converted to fluorine concentrations using the following equation:

Equation S1. $$C_{F-PFAS} = \frac{n_F \times MW_F}{MW_{PFAS} \times C_{PFAS}}$$

$C_{F\text{-}PFAS}$ = Corresponding fluoride concentration of individual PFAS
n_F = Total number of fluorine atoms in PFAS
MW_F = Molecular weight of fluorine (19.0)
MW_{PFAS} = Molecular weight of individual PFAS
C_{PFAS} = Measured PFAS concentration using LC-MS/MS analysis

Applying this equation separately to all targeted PFAS will give a total known extractable organofluorine concentration ($\Sigma C_{F\text{-}PFAS}$; ng F/g). This can be combined with the measured concentration of total extractable organofluorine ($C_{F\text{-}EOF}$; ng F/g) obtained through CIC analysis of the sample extract, to calculate the concentration of unidentified, extractable organofluorine ($C_{F\text{-}Unknown}$; ng F/g) using the subsequent equation.

Equation S2. $$C_{F-Unknown} = C_{F-EOF} - \Sigma C_{F-PFAS}$$

The total fluorine concentration ($C_{F\text{-}TF}$; ng F/g) was determined through direct combustion of the eggs using the CIC. This can then be used alongside the total extractable organofluorine concentration ($C_{F\text{-}EOF}$; ng F/g) to equate a concentration for the total non-extractable organofluorine concentration ($C_{F\text{-}Non\ ex.}$; ng F/g) using the equation below.

Equation 3. $$C_{F-Non\,ex} = C_{F-TF} - C_{F-EOF}$$

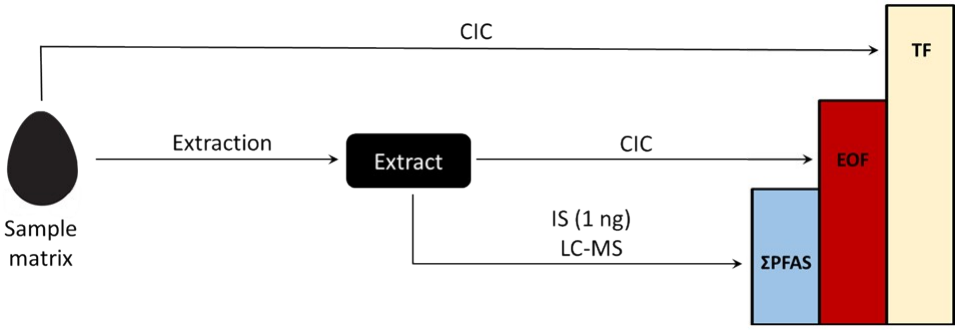

Figure S1. Visual representation of how various analytical approaches are combined to comprise the fluorine mass balance approach.

Table S1. PFAS concentrations in individual samples, before LOQ replacement, after LOQ replacement, and after desiccation index (DI) correction.

Please refer to accompanying Excel work book.

Table S2. Sampling information on pooled samples including the number and sample number (see Table S1) of individuals which made up each pool.

Region	Number of different individuals in pool	Individual sample number in pool
Baltic Proper	4	C2019/07715 C2020/10447 C2020/10442 C2019/07705
Gulf of Bothnia	5	C2020/10449 C2021/02598 C2019/07712 C2019/07713 C2021/02602
Northern Inland	4	C2020/10453 C2020/10454 C2019/07590 C2019/07591

Table S3. Full list of targeted PFAS included in this study alongside their respective internal and recovery standards used for quantification. A standard of PFPeDA was not available, therefore its quantification was based on the calibration curve of PFTeDA. All standards listed were obtained from Wellington Laboratories (Guelph, ON, Canada).

Substance	Abbreviation[#]	Precursor Ion	Quantitative Product ion	Qualitative product ion	Internal standard	IS transition
Perfluorohexanoate	PFHxA	313	269	119	$^{13}C_2$-PFHxA	315>270
Perfluoroheptanoate	PFHpA	363	319	169	$^{13}C_4$-PFHpA	367>322
Perfluorooctanoate	PFOA	413	169	369	$^{13}C_4$-PFOA	417>372
Perfluorononanoate	PFNA	463	419	219	$^{13}C_5$-PFNA	468>423
Perfluorodecanoate	PFDA	513	469	269	$^{13}C_2$-PFDA	515>470
Perfluoroundecanoate	PFUnDA	563	519	269	$^{13}C_2$-PFUnDA	565>520
Perfluorododecanoate	PFDoDA	613	569	169	$^{13}C_2$-PFDoDA	615>570
Perfluorotridecanoate	PFTrDA	663	619	169	$^{13}C_2$-PFDoDA	615>570
Perfluorotetradecanoate	PFTeDA	713	669	169	$^{13}C_2$-PFDoDA	615>570
Perfluoropentadecanoate	PFPeDA*	763	719	169	$^{13}C_2$-PFDoDA	615>570
Perfluorobutane sulfonate	PFBS	299	80	99	$^{18}O_2$-PFHxS	403>84
Perfluorohexane sulfonate	PFHxS	399	80	99	$^{18}O_2$-PFHxS	403>84
Perfluorooctane sulfonate	PFOS	499	80	99	$^{13}C_4$-PFOS	503>80
Perfluorodecane sulfonate	PFDS	599	80	99	$^{13}C_4$-PFOS	503>80
Perfluorooctane sulfonamide	FOSA	498	78	478	$^{13}C_8$-FOSA	506>78

[#]For full chemical names refer to Buck et al[3]

*PFPeDA was semi-quantified using the calibration curve for PFTeDA.

Table S4. LC gradients for Xevo (top) and Orbitrap (bottom)

LC Gradient Program Xevo TQS			***LC Flow Rate***
Time (min)	Mobile phase A (%)[1]	Mobile Phase B (%)[2]	(mL/min)
0.0	90	10	0.4
0.5	90	10	0.4
5.0	20	80	0.4
5.1	0	100	0.4
8.0	0	100	0.4
10.0	90	10	0.4
LC Gradient Program QExactive Orbitrap			***LC Flow Rate***
Time (min)	Mobile phase A (%)[1]	Mobile Phase B (%)[2]	(mL/min)
0.0	90	10	0.4
0.5	90	10	0.4
5.0	20	80	0.4
8.0	1	99	0.4
11.0	1	99	0.4
11.1	90	10	0.4
13	90	10	0.4

[1] Mobile phase A: 90% water and 10% acetonitrile containing 2 mM ammonium acetate.

[2] Mobile phase B: 99% acetonitrile and 1% water containing 2 mM ammonium acetate.

Table S5. Eluent program for combustion ion chromatograph

Time (min)	Concentration OH^- (mM)
0.0	8.0
4.0	8.0
9.9	45.0
10.0	100.0
14.0	100.0
14.1	8.0
20.0	8.0

Table S6. Q-Exactive Orbitrap MS parameters

Scan Parameters		
	Full MS	**dd MS2**
Scan Range / isolation window	200–1200 m/z	0.4 m/z
Fragmentation	-	stepped NCE(30, 80, 120)
Resolution	120 000	15 000
Polarity	Negative	Negative
AGC target	3e6	5e4
Maximum inject time	250	30
HESI Source		
Sheath gas flow rate	30	
Aux gas flow rate	10	
Sweep gas flow rate	0	
Spray voltage (kV)	3.70	
Capillary temp (°C)	350	
S-lens RF level	55.0	
Aux gas heater temp (°C)	350	

Table S7. Suspect screening data
Please refer to accompanying Excel work book.

Table S8. Results of spike/recovery experiments performed as part of ongoing quality control for individual samples (i.e. time series) from 2015-2021. Chicken eggs (n=13) were fortified with 10 or 40 ng of individual linear isomer PFAS standards and then processed in the same manner as real samples. Percent recoveries were determined by subtracting concentrations in unspiked samples from spiked samples and then dividing by the expected concentration. Note that internal standards are fortified prior to extraction, so the percent recoveries shown are corrected for procedural losses.

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS	FOSA
% Recovery	87	76	81	82	88	84	84	63	40	84	84	80	55	77
STDEV	14	9	14	11	12	6	3	24	23	8	8	11	28	5

Table S9. Results of spike/recovery experiments performed as part of ongoing quality control for pooled samples (i.e. fluorine mass balance experiments). Chicken eggs (n=3) were fortified with 10 ng of individual linear isomer PFAS standards and then processed in the same manner as real samples. Percent recoveries were determined by subtracting concentrations in unspiked samples from spiked samples and then dividing by the expected concentration. Note that internal standards were fortified after extraction, so the percent recoveries shown reflect losses during extraction.

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS	FOSA
% Recovery	79	70	79	82	84	82	81	114	108	61	79	86	74	58
STDEV	6	5	6	6	6	6	6	12	9	3	6	12	6	6

Table S10. Averaged fluorine concentrations of targeted PFAS ± standard deviation (from replicate extractions), in regional pooled samples. Concentrations below LOD are marked in italics.

PFAA	Concentration *(ng F/g)*		
	Baltic Proper	*Gulf of Bothnia*	*Northern Inland*
PFOA	0.297 ± 0.0150	0.221 ± 0.0186	*<LOD*
PFNA	11.1 ± 0.552	8.61 ± 0.633	2.06 ± 0.130
PFDA	6.61 ± 0.375	3.37 ± 0.304	1.23 ± 0.103
PFUnDA	10.7 ± 0.532	5.92 ± 0.740	1.87 ± 0.0898
PFDoDA	4.233 ± 0.187	1.82 ± 0.241	0.507 ± 0.0319
PFTrDA	8.24 ± 0.409	6.66 ± 0.726	2.47 ± 0.182
PFTeDA	1.71 ± 0.0576	0.964 ± 0.163	0.343 ± 0.0353
PFPeDA	0.580 ± 0.0313	0.414 ± 0.0504	0.145 ± 0.0437
PFHxS	1.12 ± 0.0242	0.725 ± 0.211	0.196 ± 0.0117
PFOS	164 ± 11.4	66.0 ± 7.77	2.74 ± 0.190
PFDS	0.436 ± 0.0489	*<LOD*	*<LOD*

Table S11. Concentrations of various components comprising the fluorine mass balance, measured in fluorine equivalence (ng F/g) where ΣC_{PFAS} = summed concentration of 15 targeted PFAS, $\Sigma C_{F\text{-}Sus}$ = summed concentrations of semi-quantified suspects, $\Sigma C_{PFAS+Sus}$ = summed concentrations of both targeted PFAS and semi-quantified suspects, $C_{F\text{-}EOF}$ = concentration of extractable organofluorine, $C_{F\text{-}TF}$ = total fluorine concentration of direct combustion of matrix

Region	Concentration *(ng F/g)*				
	ΣC_{PFAS}	**$\Sigma C_{F\text{-}Sus}$**	**$\Sigma C_{PFAS+Sus}$**	**$C_{F\text{-}EOF}$**	**$C_{F\text{-}TF}$**
Baltic Proper	203 ± 13.4	12.4 ± 0.656	215 ± 14.1	213 ± 9.12	402 ± 57.2
Gulf of Bothnia	93.6 ± 11.4	10.2 ± 0.968	104 ± 12.1	116 ± 11.1	301 ± 66.6
Northern Inland	11.2 ± 0.539	3.59 ± 0.264	14.8 ± 0.778	11.3 ± 6.35	32.7 ± 4.38

Table S12. Concentrations of semi-quantified suspects (CL≤2) in each region alongside their native and IS used for semi-quantification measured in fluorine equivalence (ng F/g)

Class	ID	Native	Internal Standard	Avg. concentration *(ng F/g)*		
				BP	GB	LP
n:3 FTCAs	7:3 FTCA	7:3 FTCA	$^{13}C_2$-PFDA	2.272	2.472	0.382
	8:3 FTCA			3.400	3.944	1.431
	9:3 FTCA			2.360	2.914	1.472
	10:3 FTCA			0	0.221	0
	11:3 FTCA			0.008	0	0.038
FASAs	FBSA	FOSA	$^{13}C_8$-FOSA	0	0	0
	FPeSA			0	0	0
	FHxSA			0	0	0
	FOSA			0.021	0.013	0
n:2 FTSAs	6:2 FTSA	6:2 FTSA	$^{18}O_2$-PFHxS	0	0	0
	8:2 FTSA	8:2 FTSA		0	0	0
	10:2 FTSA			0	0	0
Cyclic PFSAs	PFECHS (d/C PFSA, n=8)	PFHxS	$^{13}C_4$-PFOS	3.001	0.389	0
	d/C PFSA, n=9			0.164	0	0
	d/C PFSA, n=10			0.116	0	0
	d/C PFSA, n=11			0.030	0	0
	d/C PFSA, n=12			0.008	0.037	0.037

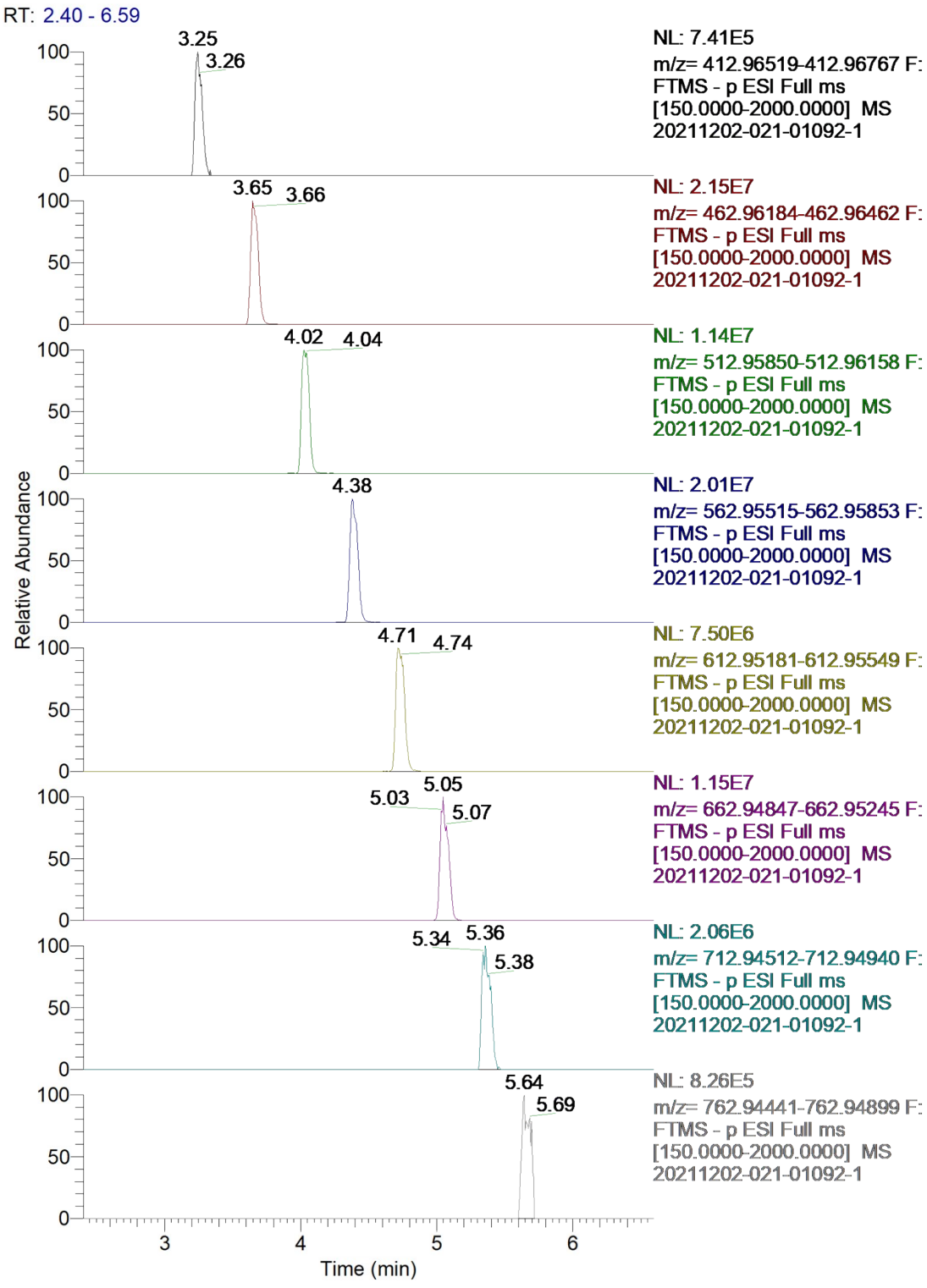

Figure S2. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for PFCAs with n=6-13 (see Table 2 in the main manuscript).

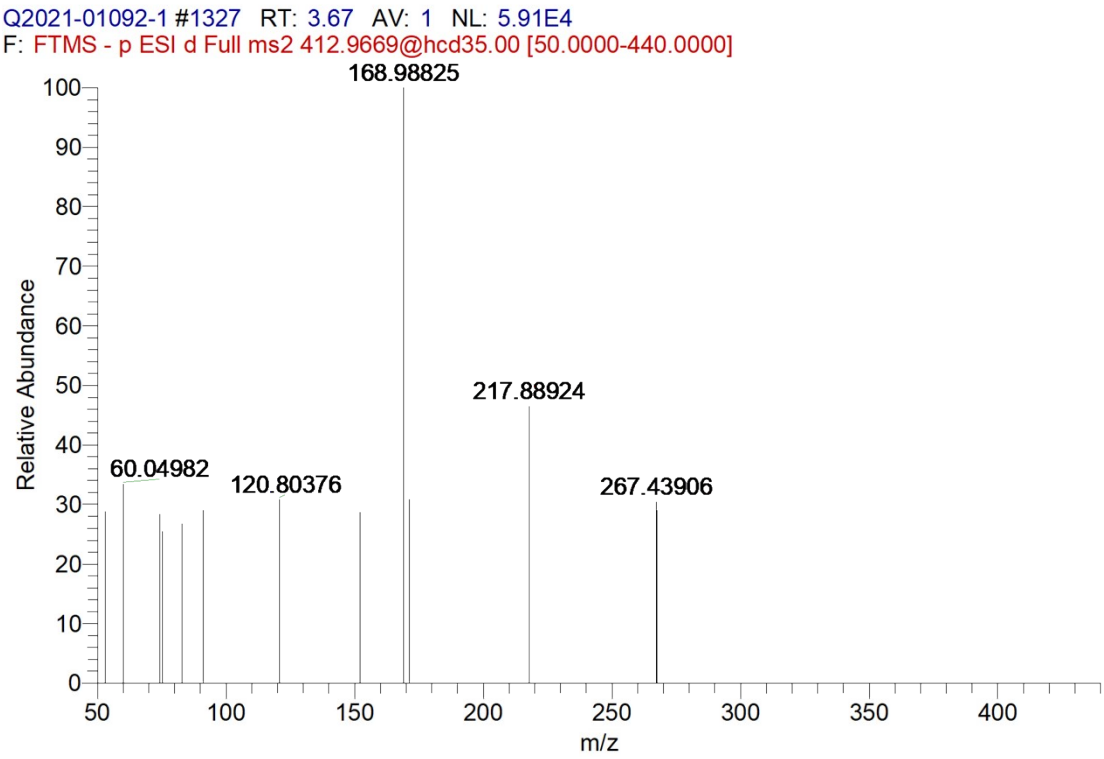

Figure S2a. MS2 spectra recorded for PFOA (n=6). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

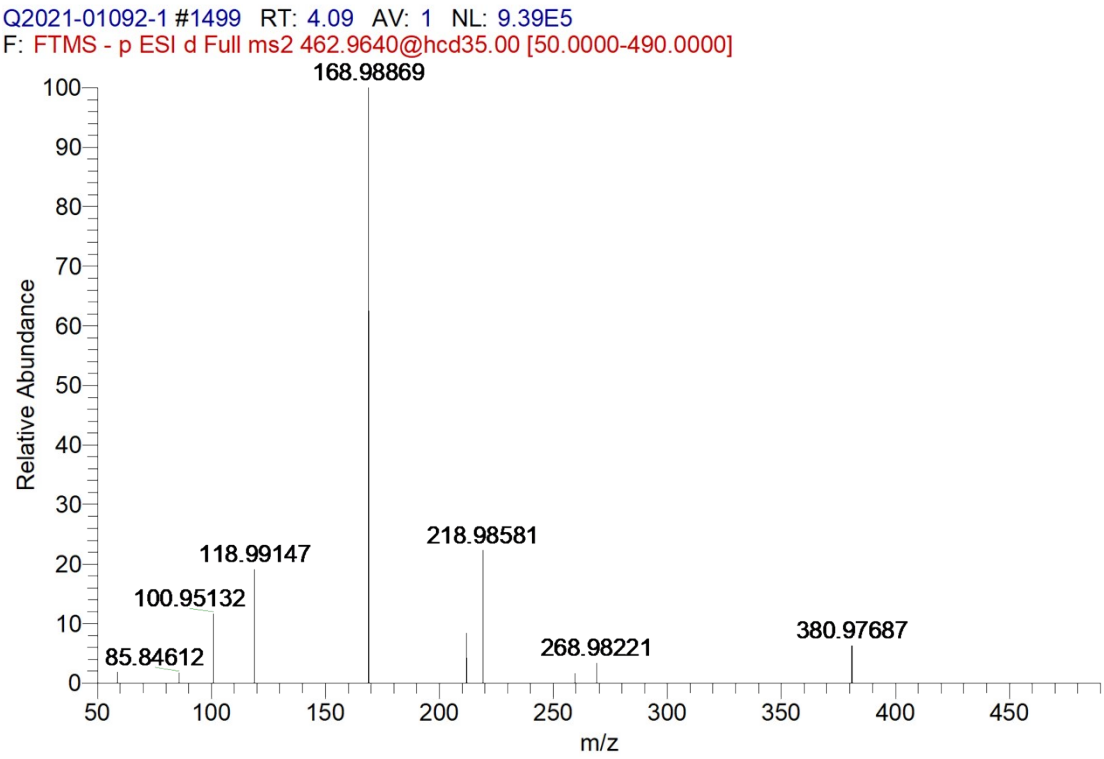

Figure S2b. MS2 spectra recorded for PFNA (n=7). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

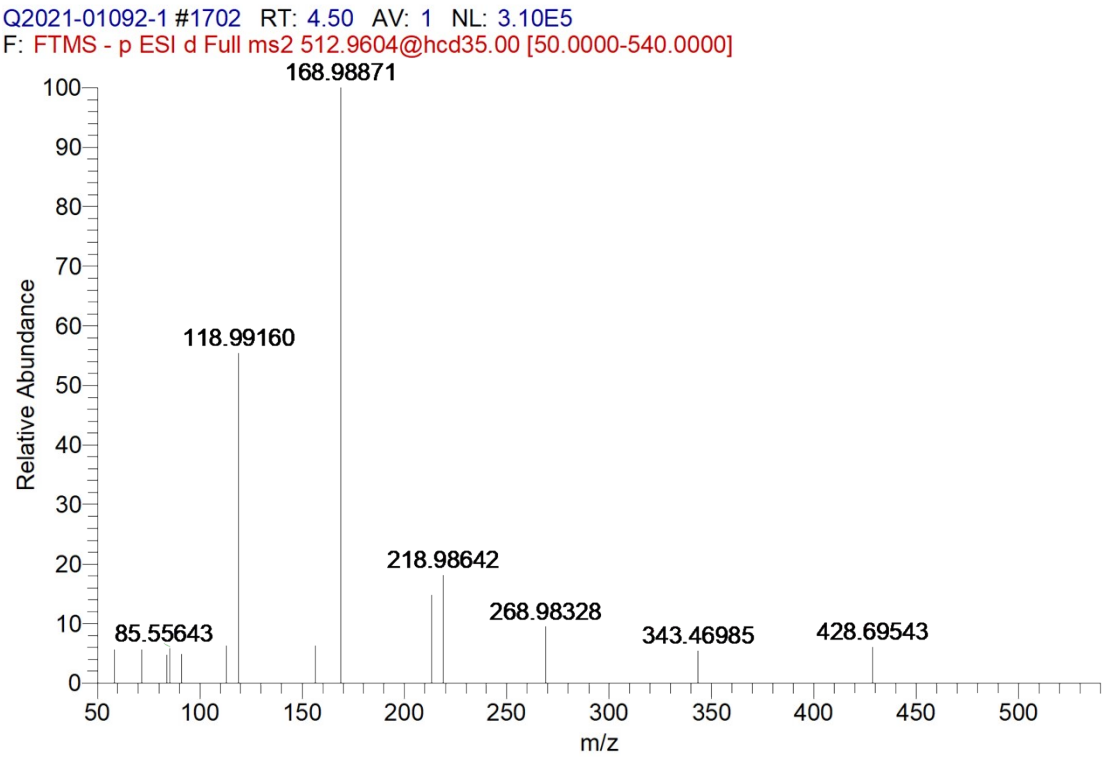

Figure S2c. MS2 spectra recorded for PFDA (n=8). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

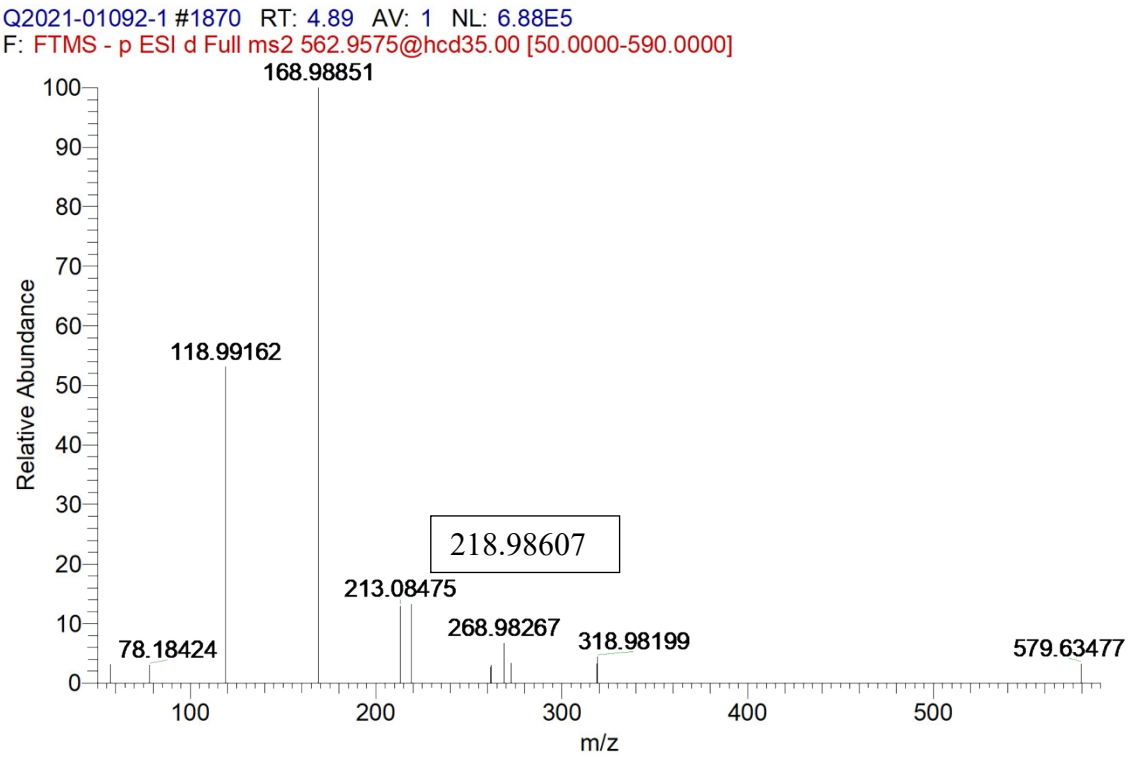

Figure S2d. MS2 spectra recorded for PFUnDA (n=9). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

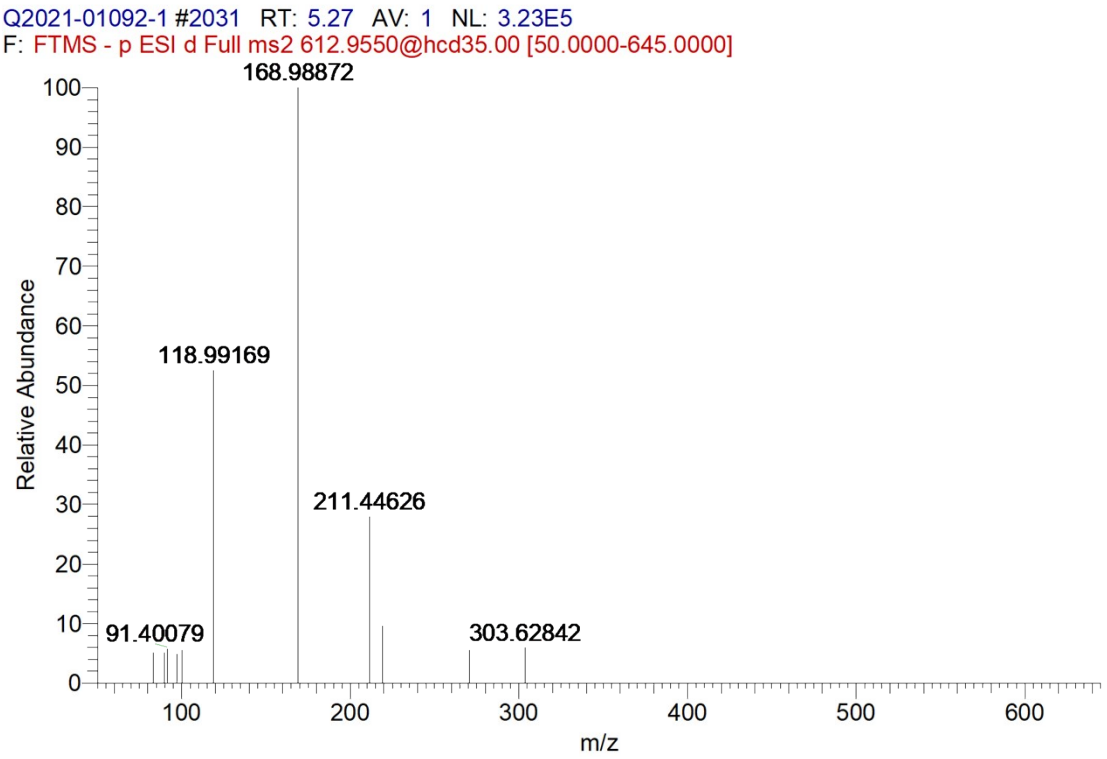

Figure S2e. MS2 spectra recorded for PFDoDA (n=10). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

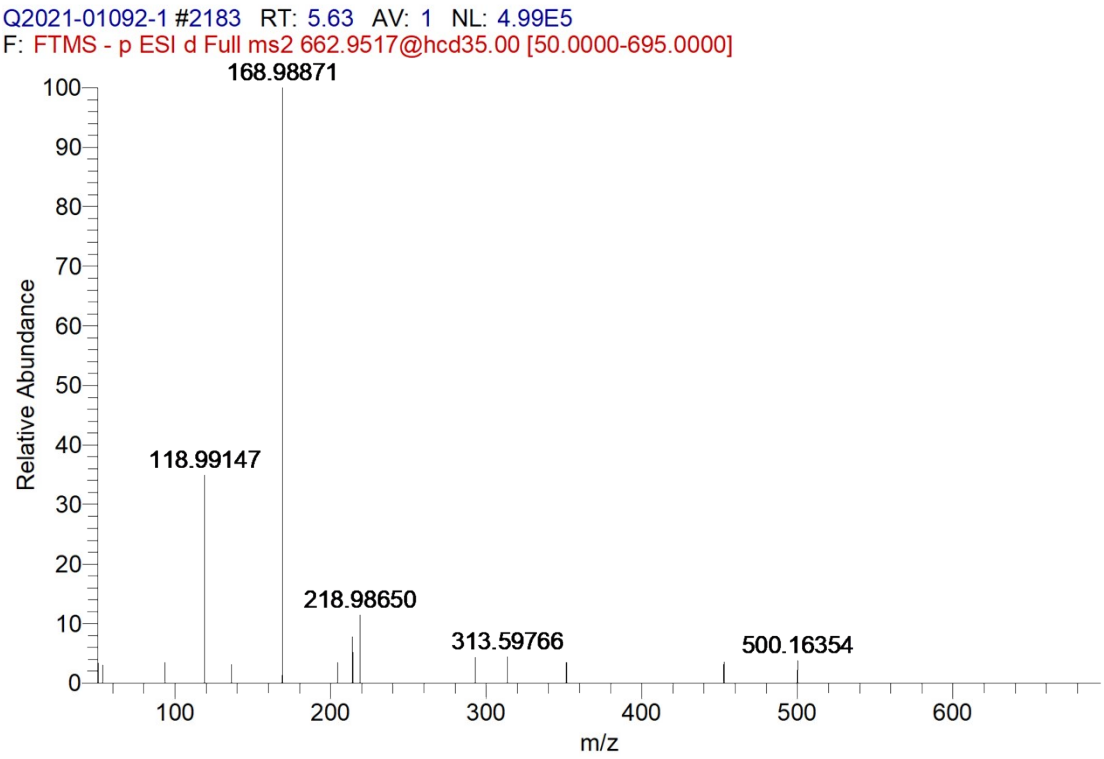

Figure S2f. MS2 spectra recorded for PFTrDA (n=11). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

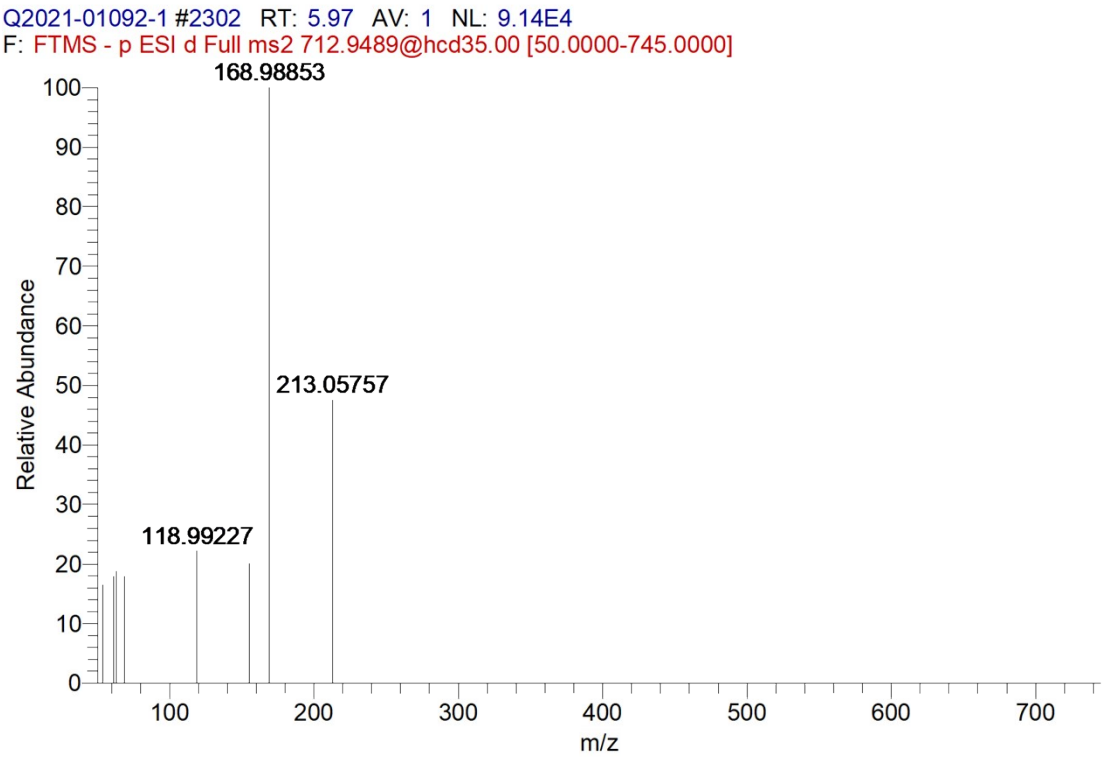

Figure S2g. MS2 spectra recorded for PFTeDA (n=12). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

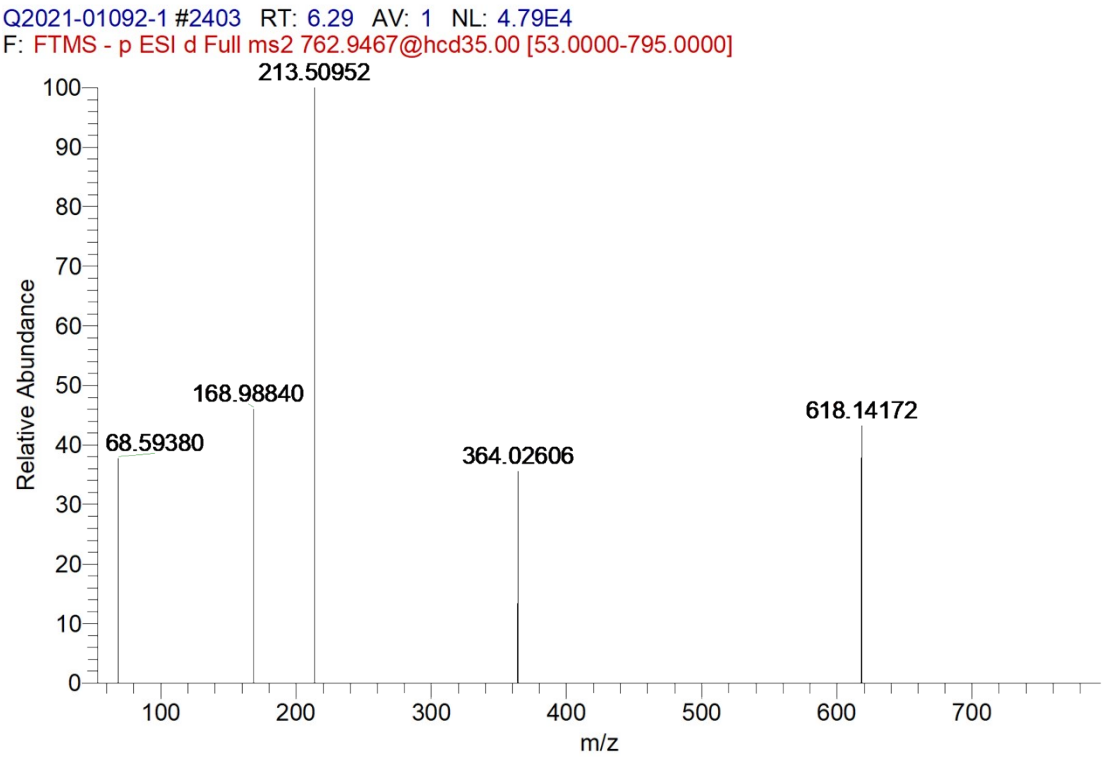

Figure S2h. MS2 spectra recorded for PFPeDA (n=13). The RT does not fit the RT of the peak in Figure S2, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

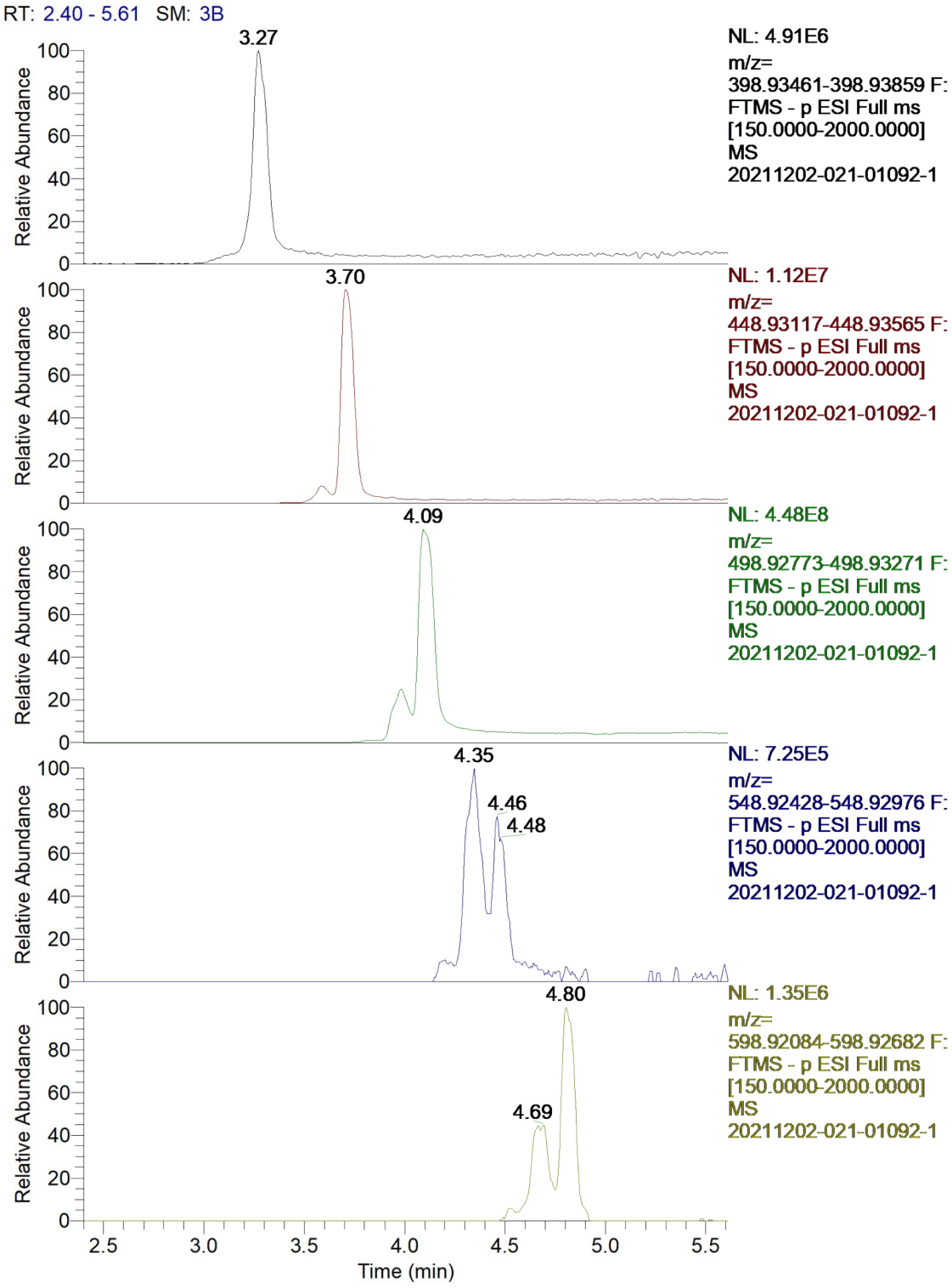

Figure S3. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for PFSAs with n=5-9 (see Table 2 in the main manuscript).

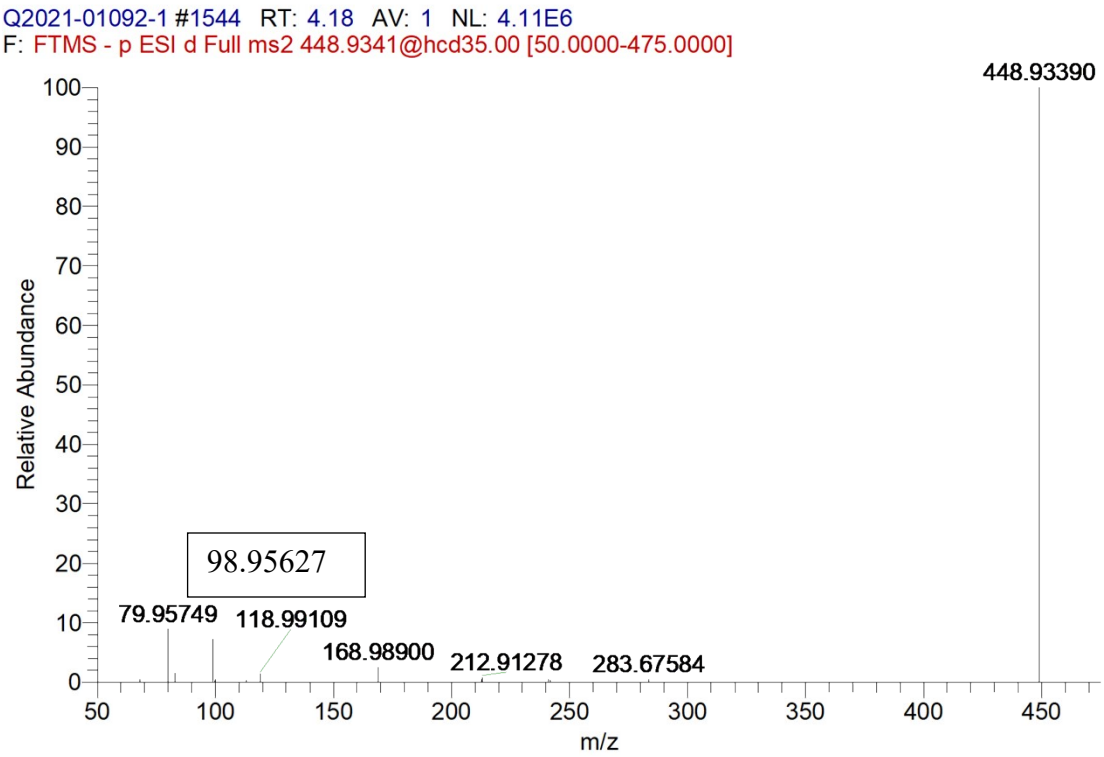

Figure S3a. MS2 spectra recorded for PFHpS (n=6). The RT does not fit the RT of the peak in Figure S3, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

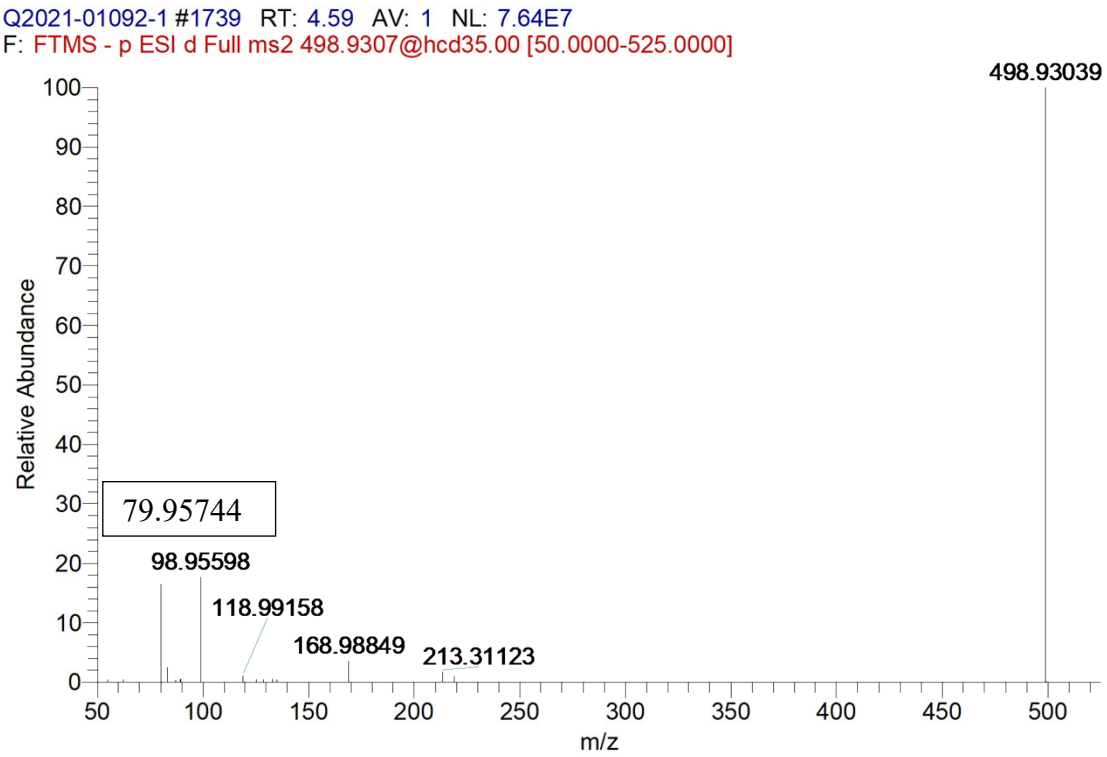

Figure S3b. MS2 spectra recorded for PFOS (n=7). The RT does not fit the RT of the peak in Figure S3, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

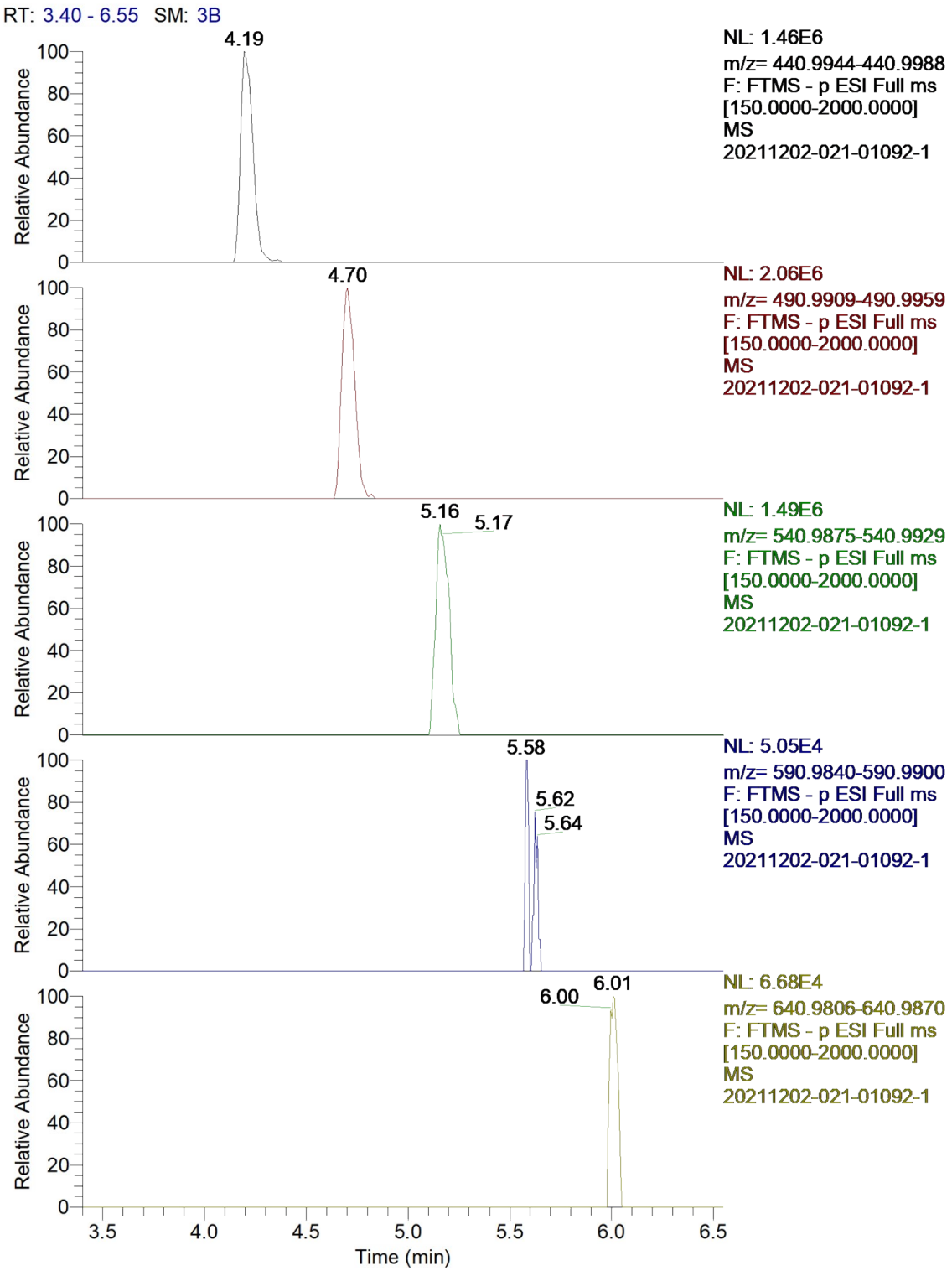

Figure S4. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for n:3 FTCAs with n=6-10 (see Table 2 in the main manuscript).

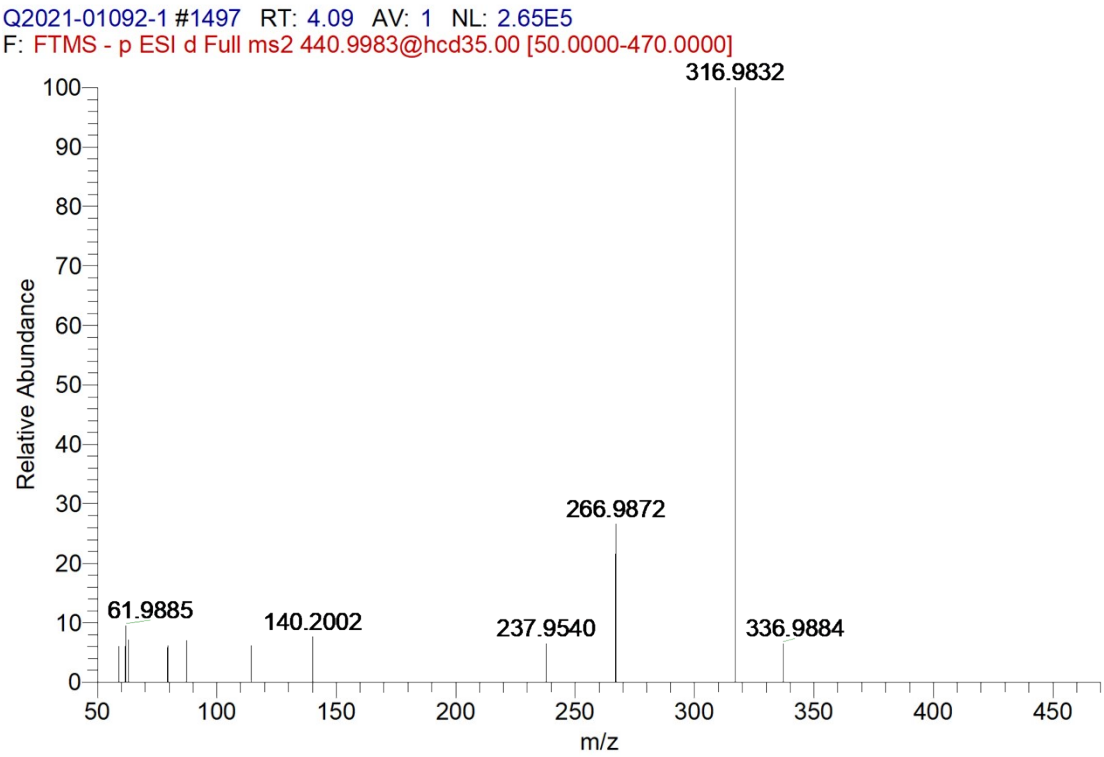

Figure S4a. MS2 spectra recorded for 7:3 FTCA (n=6). The RT does not fit the RT of the peak in Figure S4, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.1 - 0.2 min earlier.

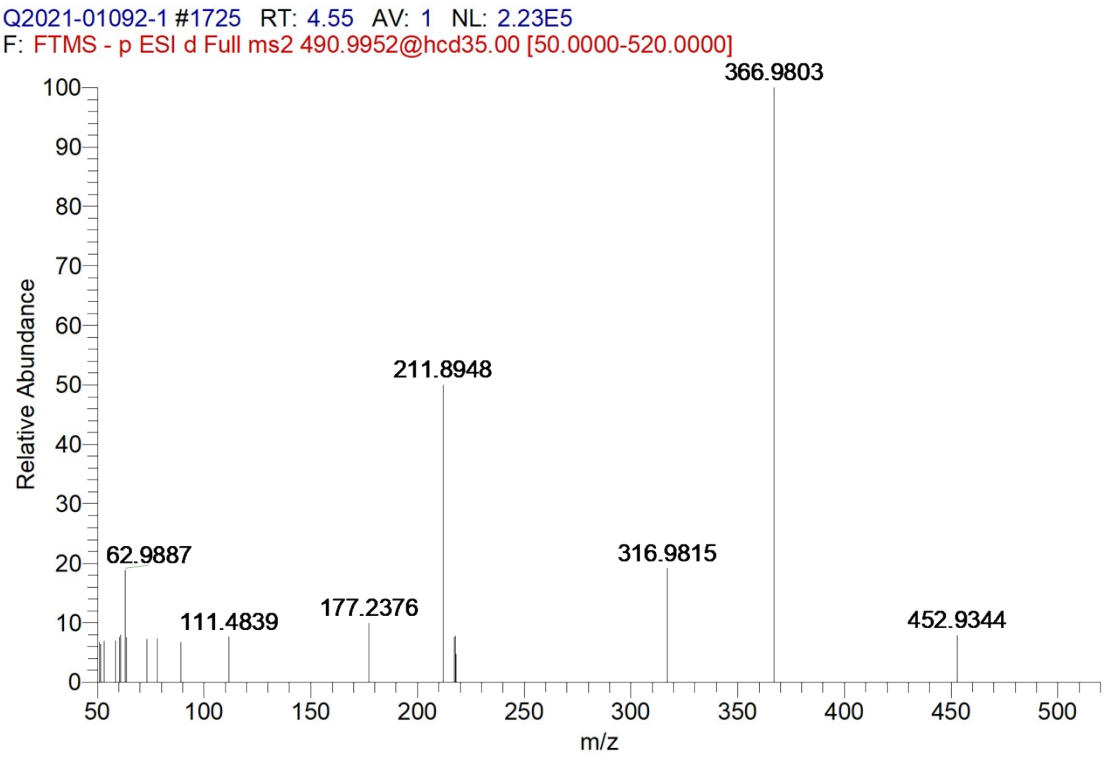

Figure S4b. MS2 spectra recorded for 8:3 FTCA (n=7). The RT does not fit the RT of the peak in Figure S4, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.1 - 0.2 min earlier.

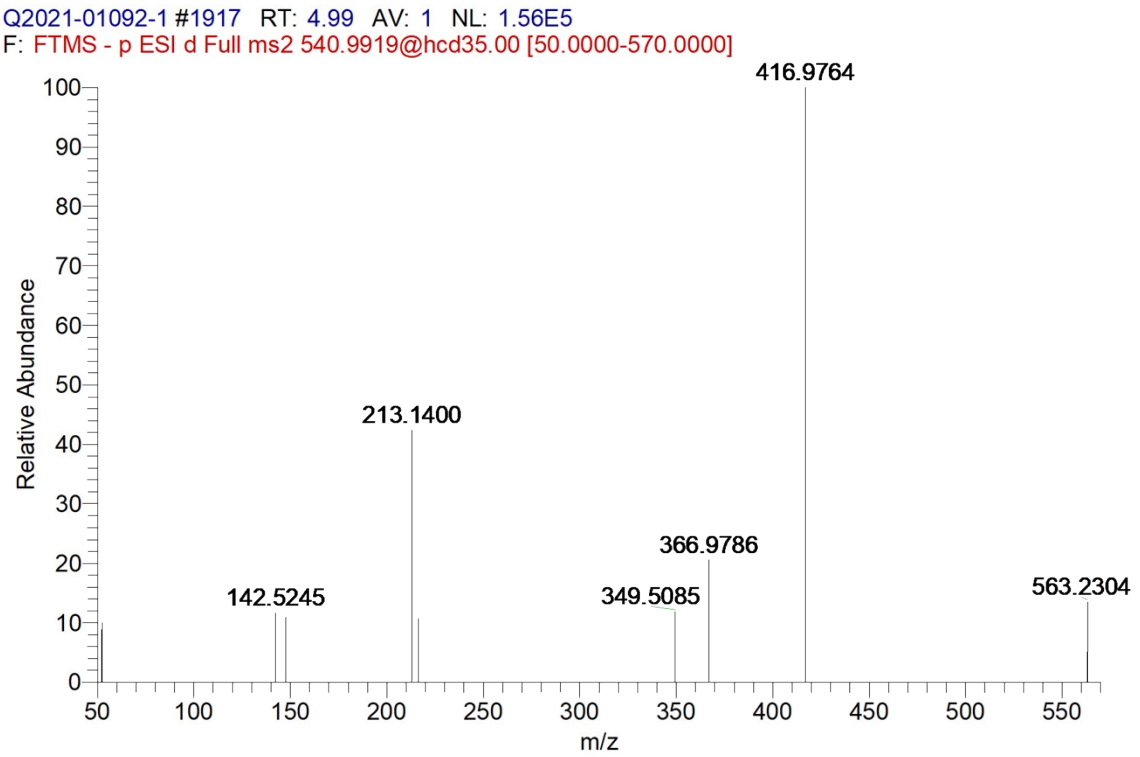

Figure S4c. MS2 spectra recorded for 9:3 FTCA (n=7). The RT does not fit the RT of the peak in Figure S4, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.1 - 0.2 min earlier.

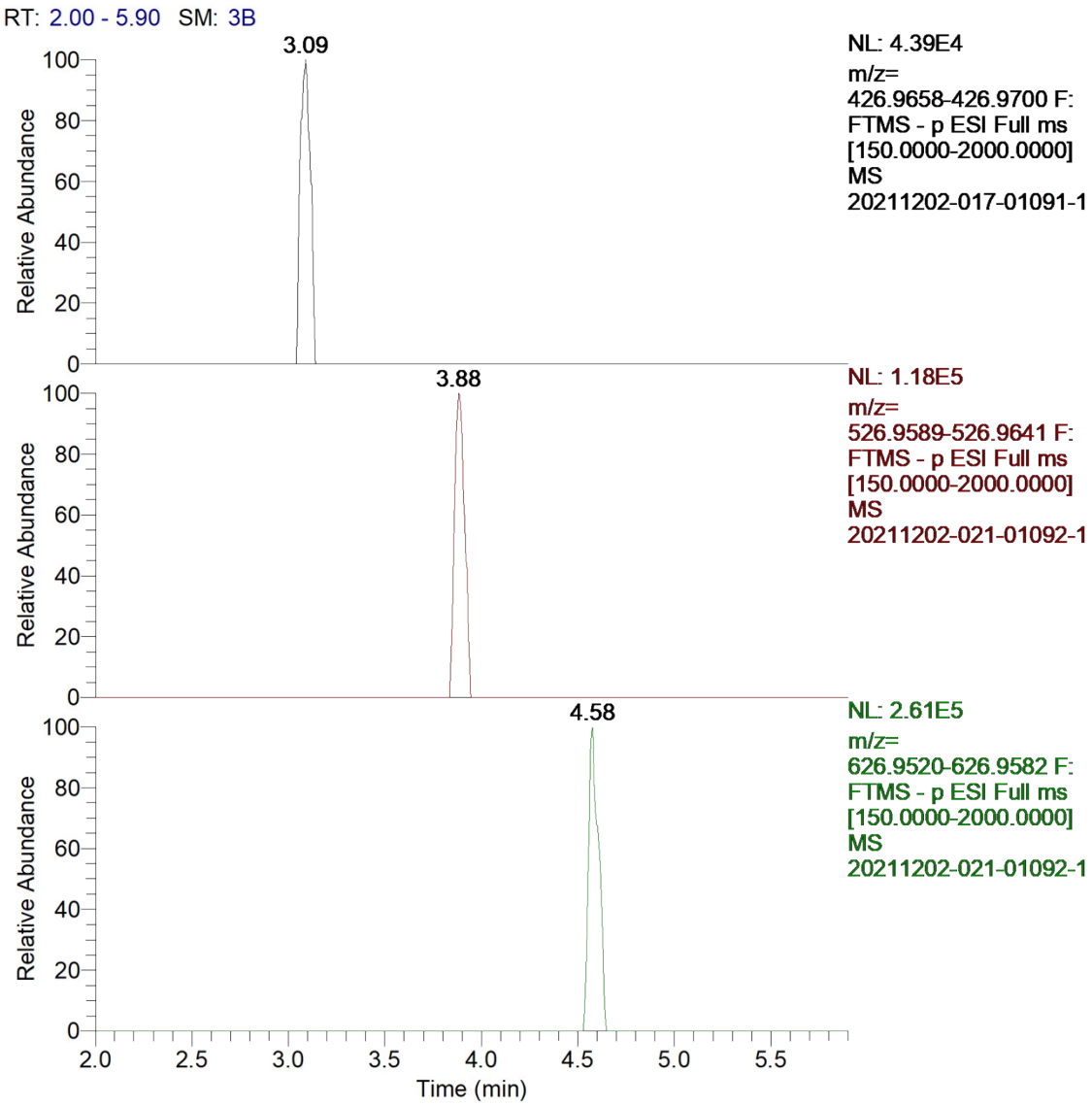

Figure S5. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for n:2 FTSAs with n=3,5,7 (see Table 2 in the main manuscript).

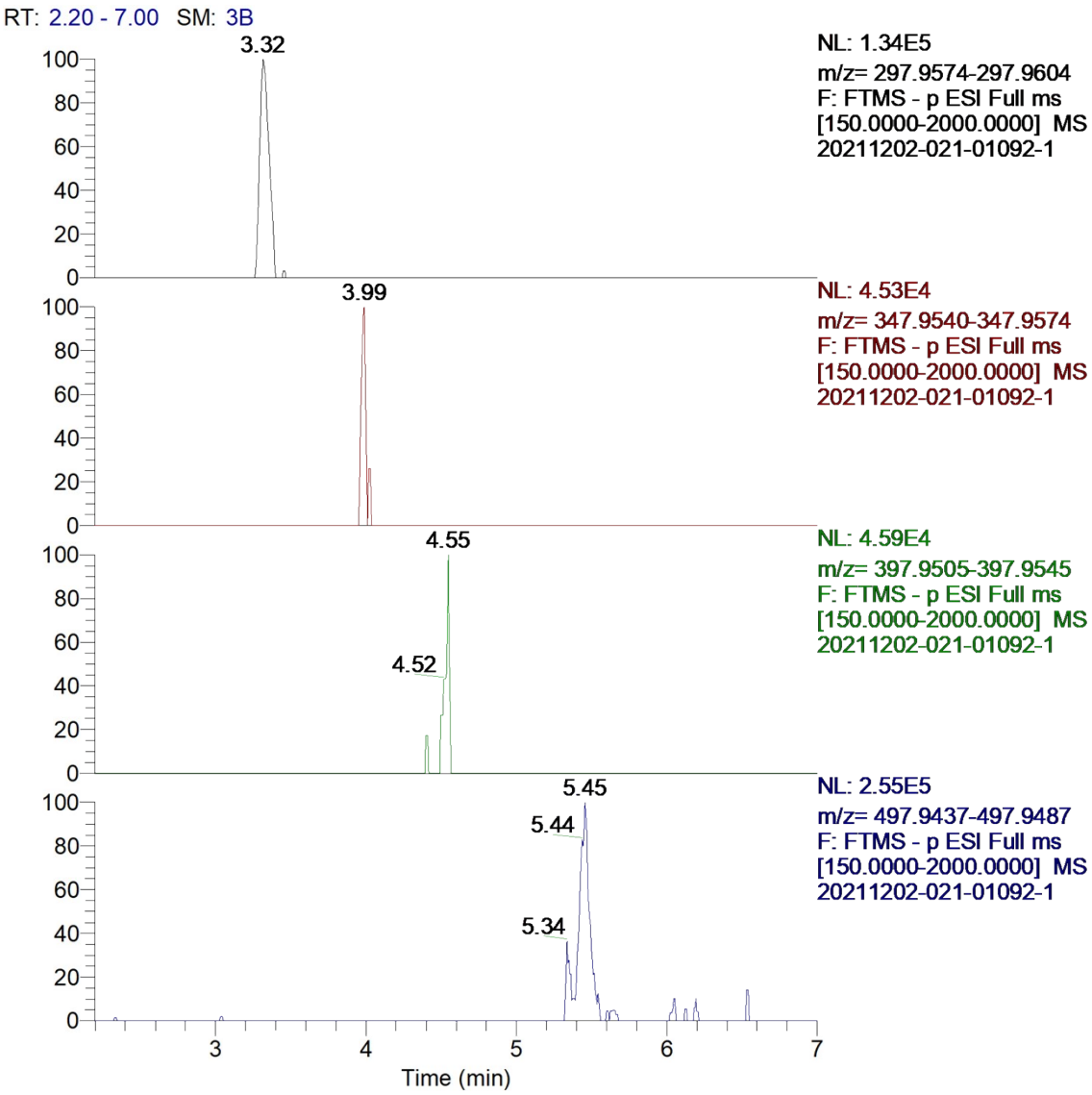

Figure S6. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for FASAs with n=3,4,5,7 (see Table 2 in the main manuscript).

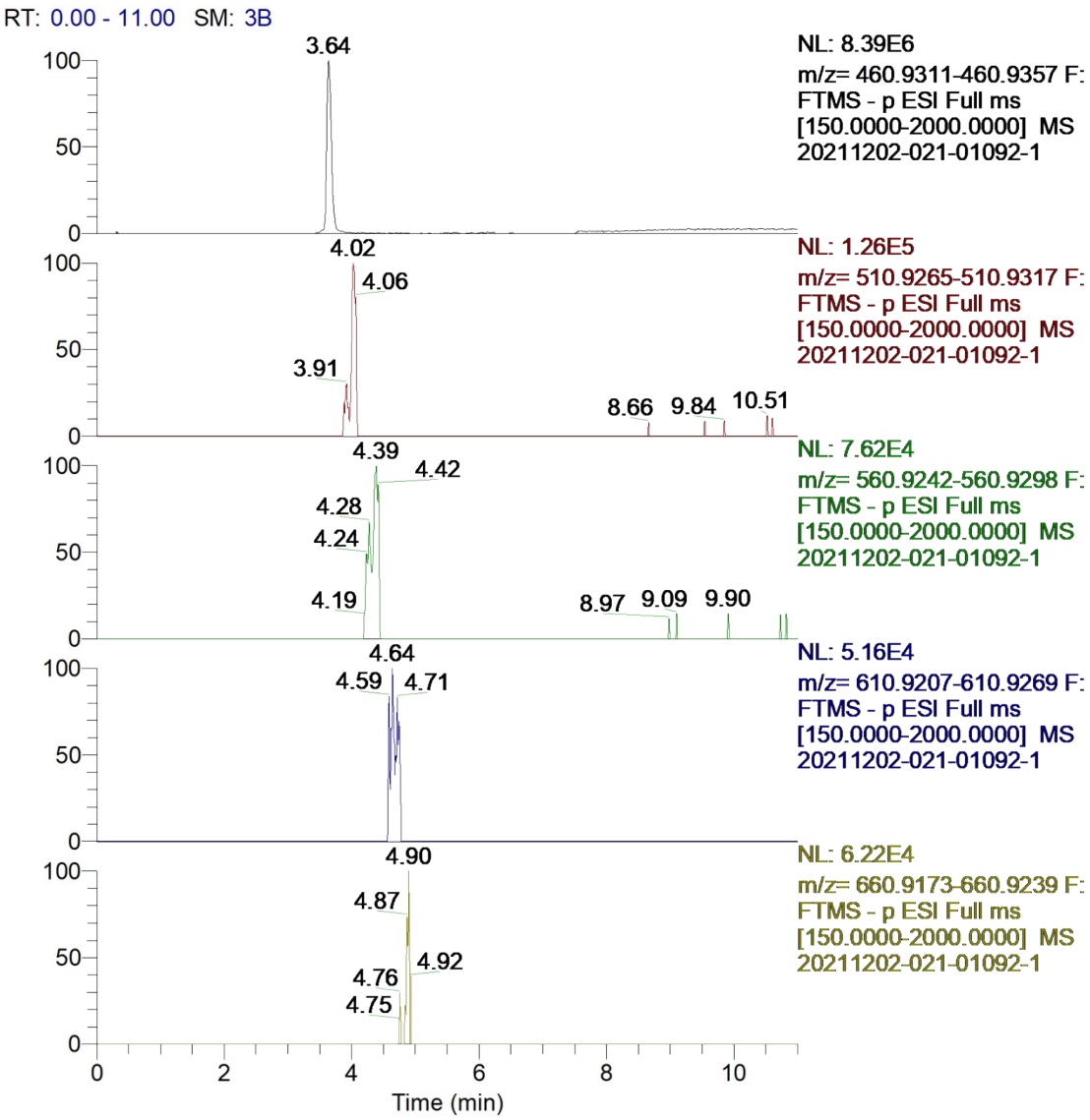

Figure S7. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for Cyclic/unsaturated PFSAs with n=1-5 (see Table 2 in the main manuscript).

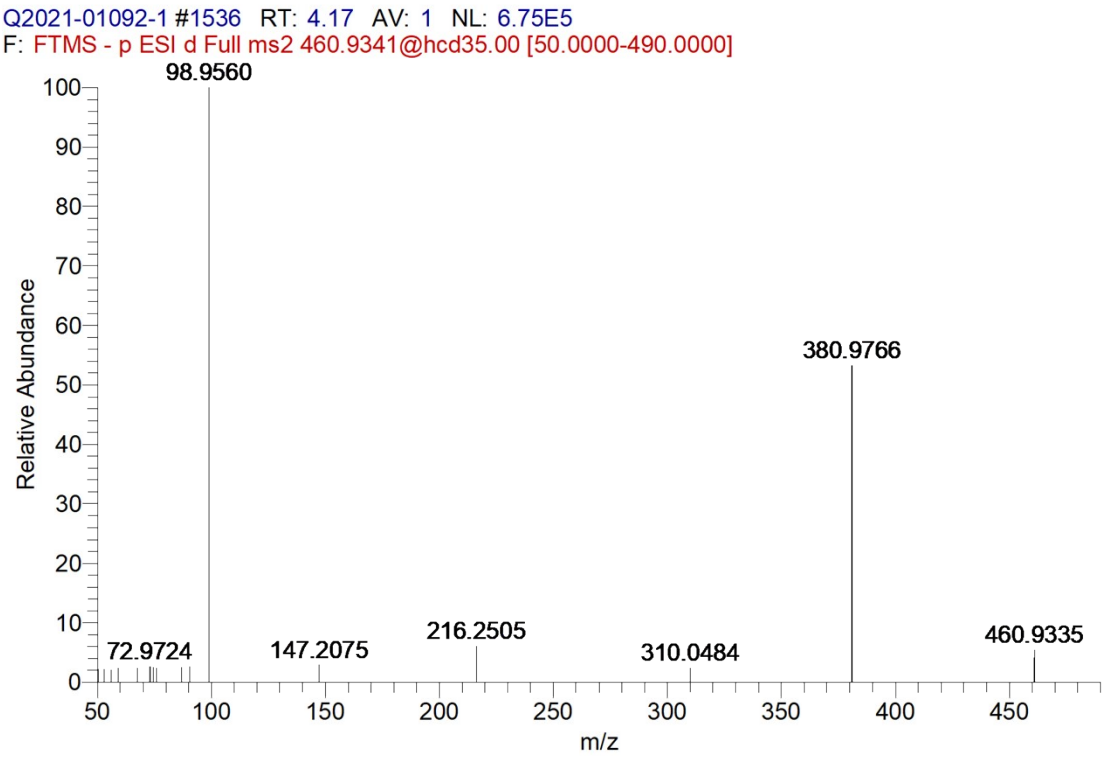

Figure S7a. MS2 spectra recorded for d/C PFSA (PFECHS, n=1). The RT does not fit the RT of the peak in Figure S6, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

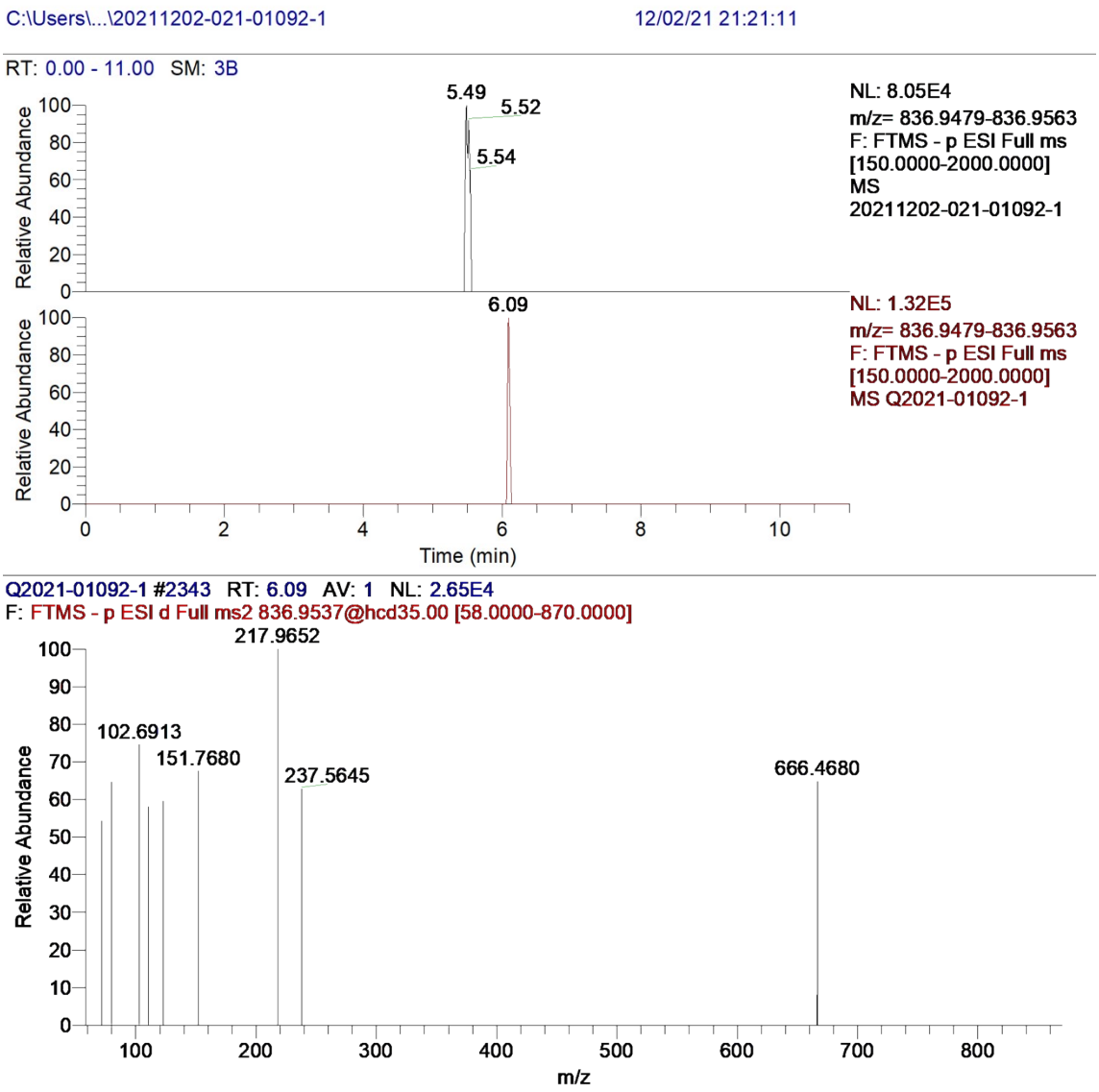

Figure S8. Upper part: Extracted ion chromatograms of the exact mass (mass deviation 5 ppm) for PFNhcs (see Table 2 in the main manuscript) in the first and the rerun. Lower part: MS2 spectra recorded in rerun.

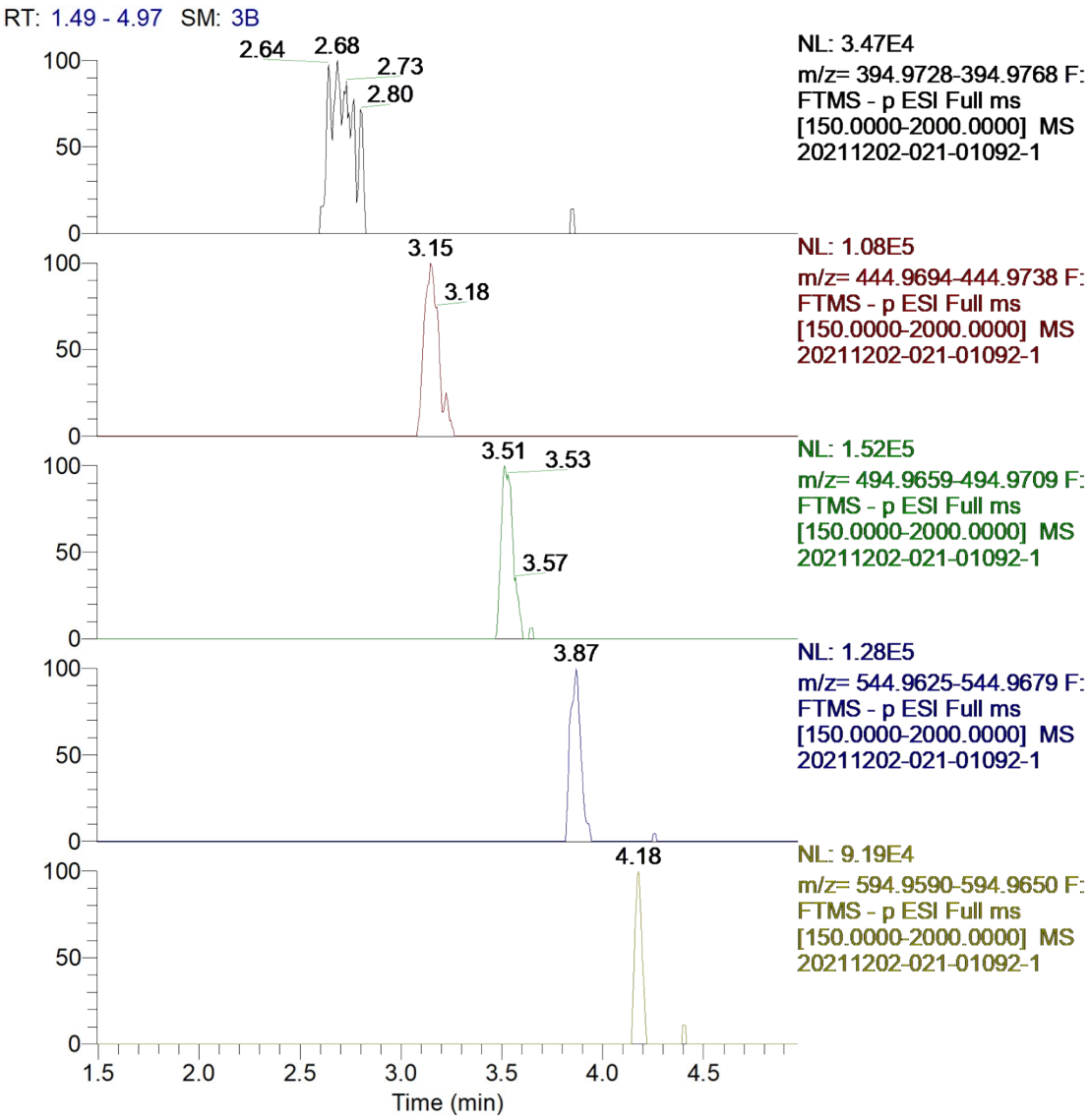

Figure S9. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for H-PFCAs with n=5-9 (see Table 2 in the main manuscript).

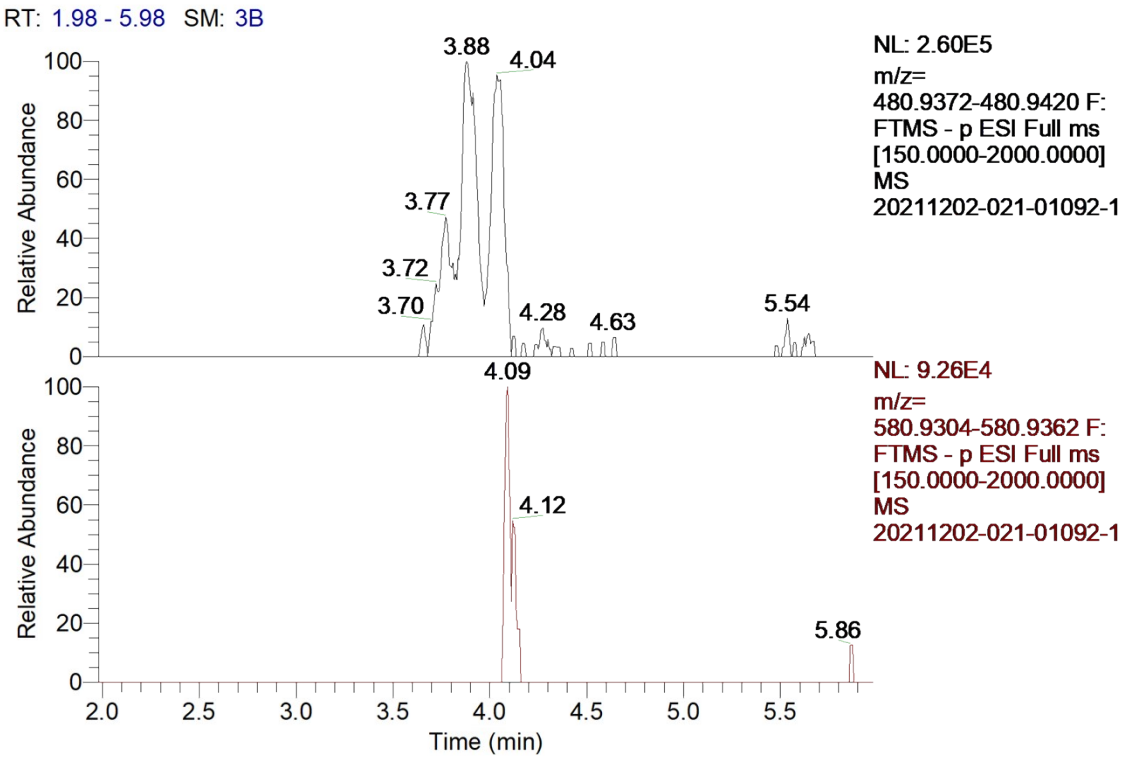

Figure S10. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for H-PFSAs with n=6,8 (see Table 2 in the main manuscript).

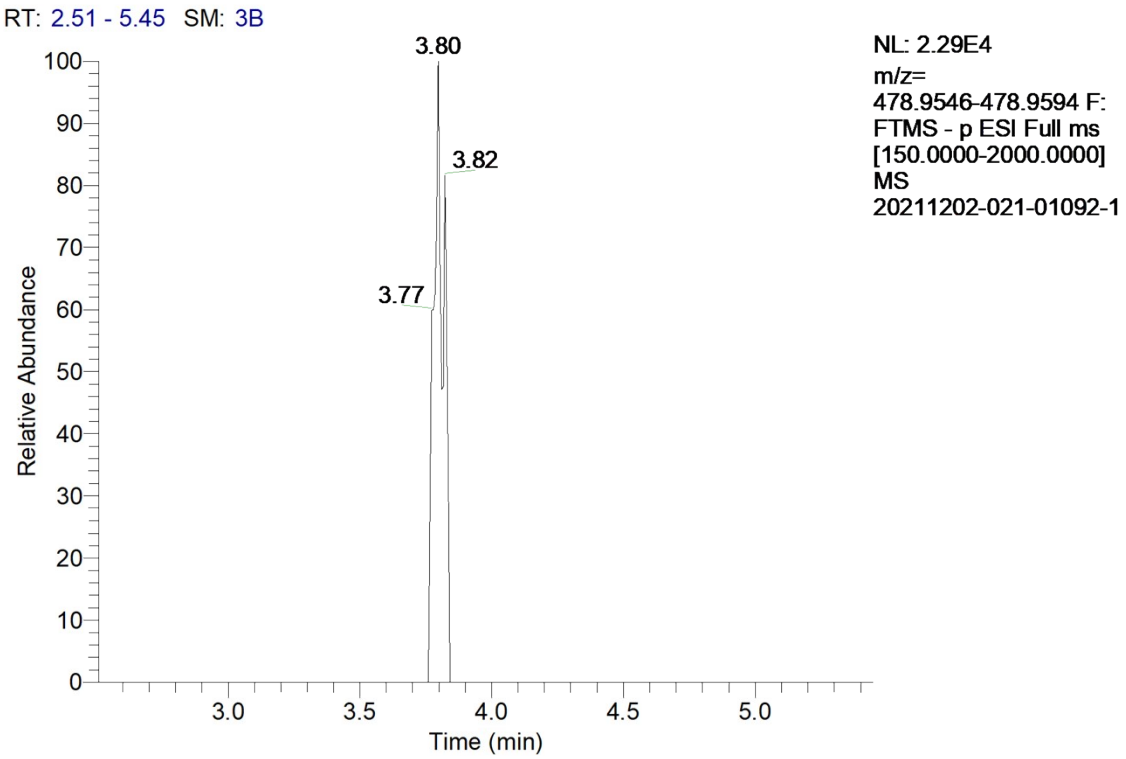

Figure S11. Extracted ion chromatogram of the exact mass (mass deviation 5 ppm) for PFECA with n=6 (see Table 2 in the main manuscript).

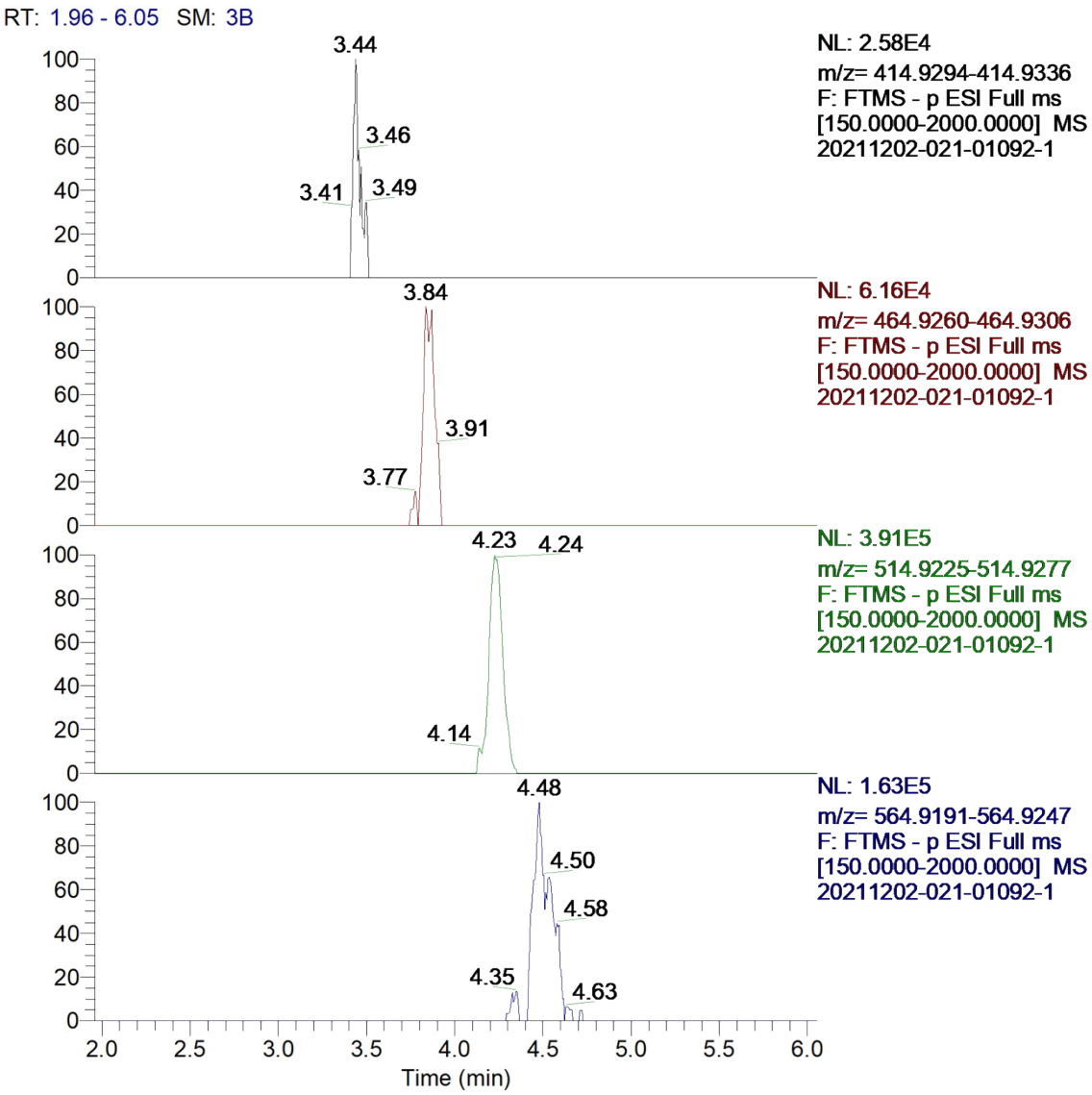

Figure S12. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for ether PFSAs with n=4-7 (see Table 2 in the main manuscript).

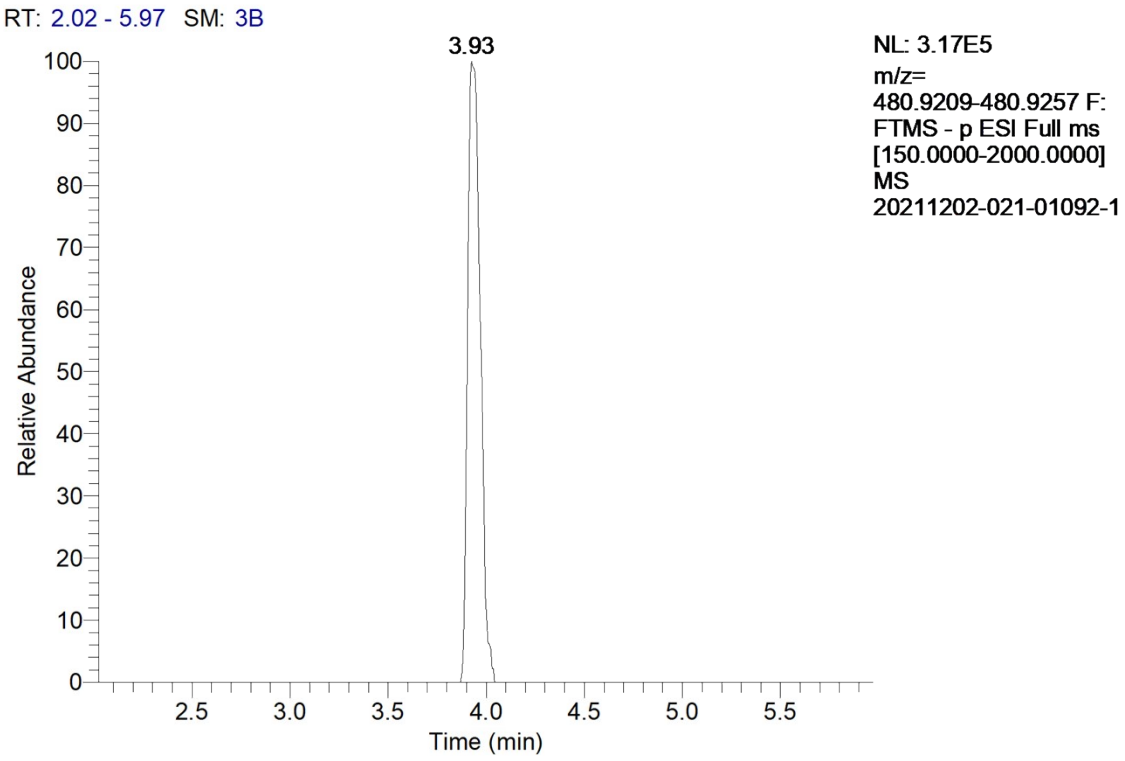

Figure S13. Extracted ion chromatogram of the exact mass (mass deviation 5 ppm) for mOPFSA with n=3 (see Table 2 in the main manuscript).

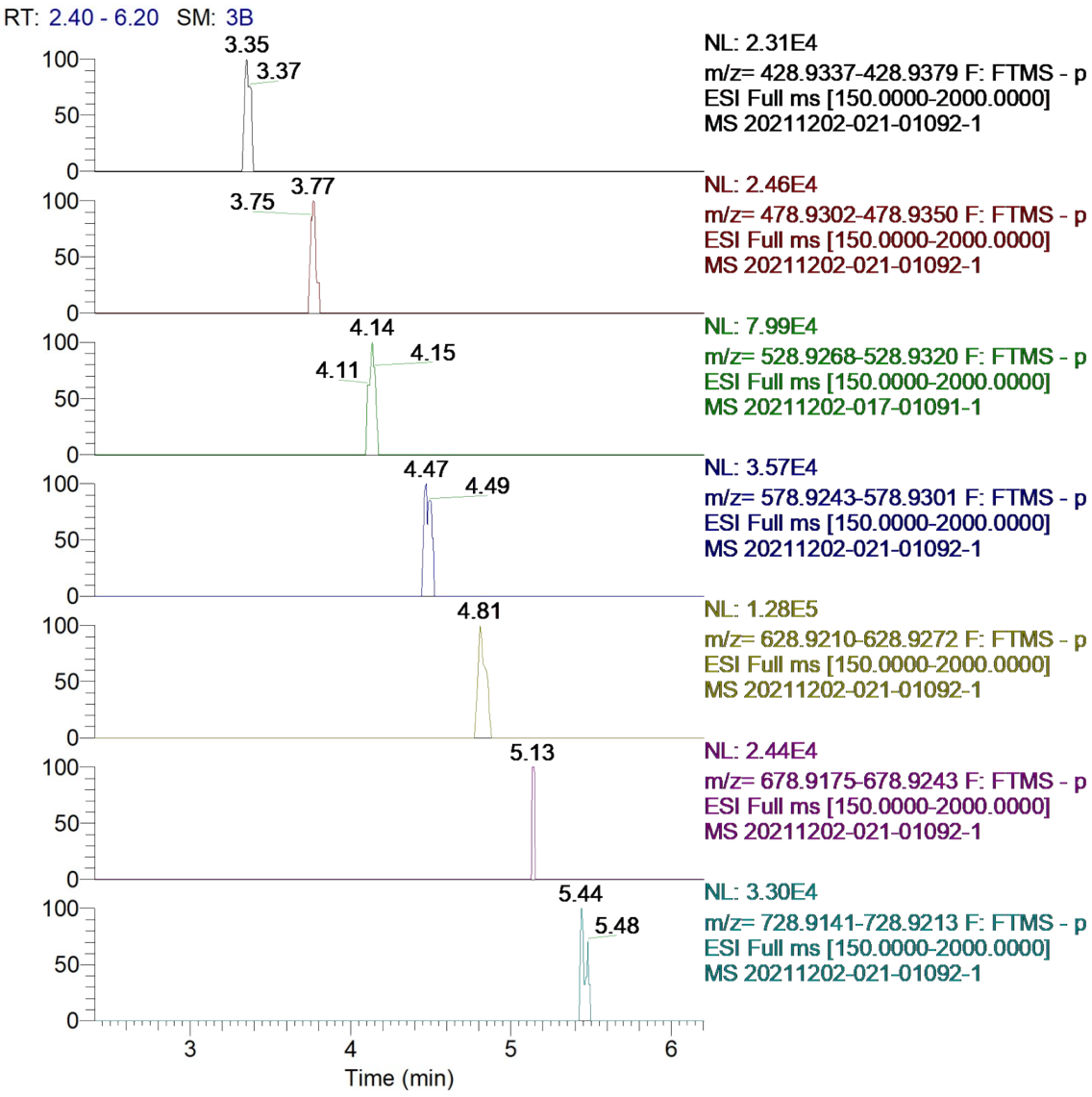

Figure S14. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for Cl substituted PFCAs with n=4-8 (see Table 2 in the main manuscript).

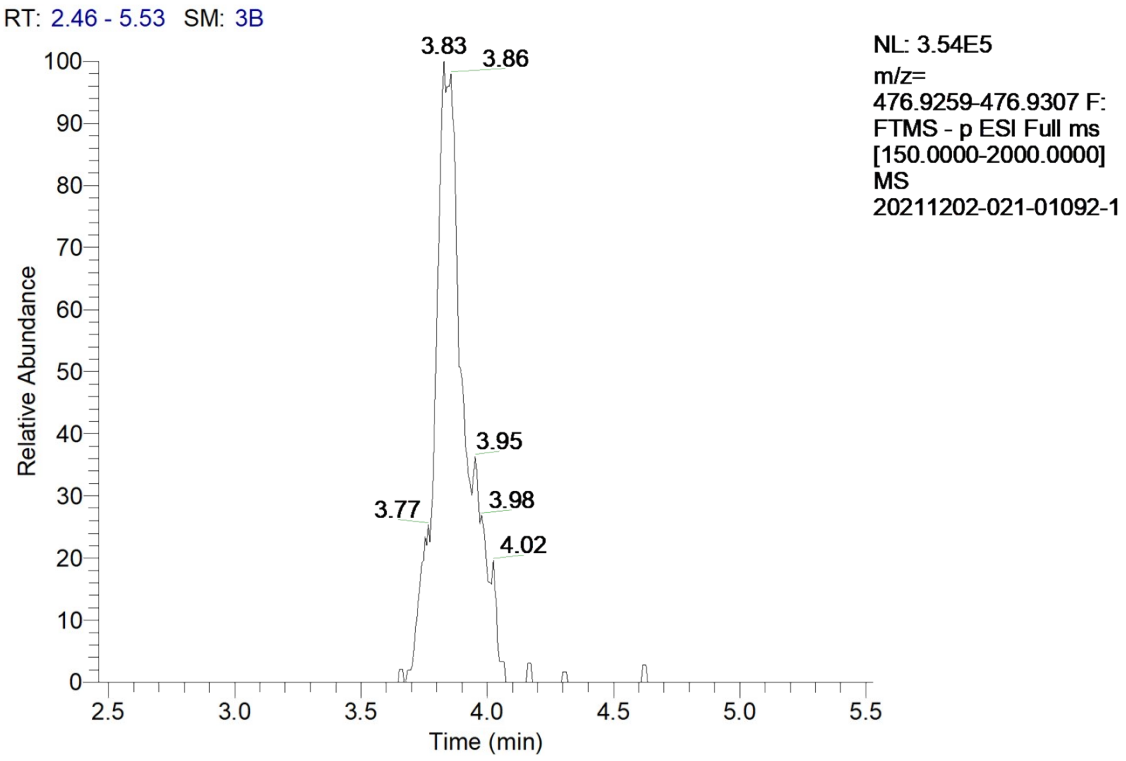

Figure S15. Extracted ion chromatogram of the exact mass (mass deviation 5 ppm) for eecec PFSA with n=2 (see Table 2 in the main manuscript).

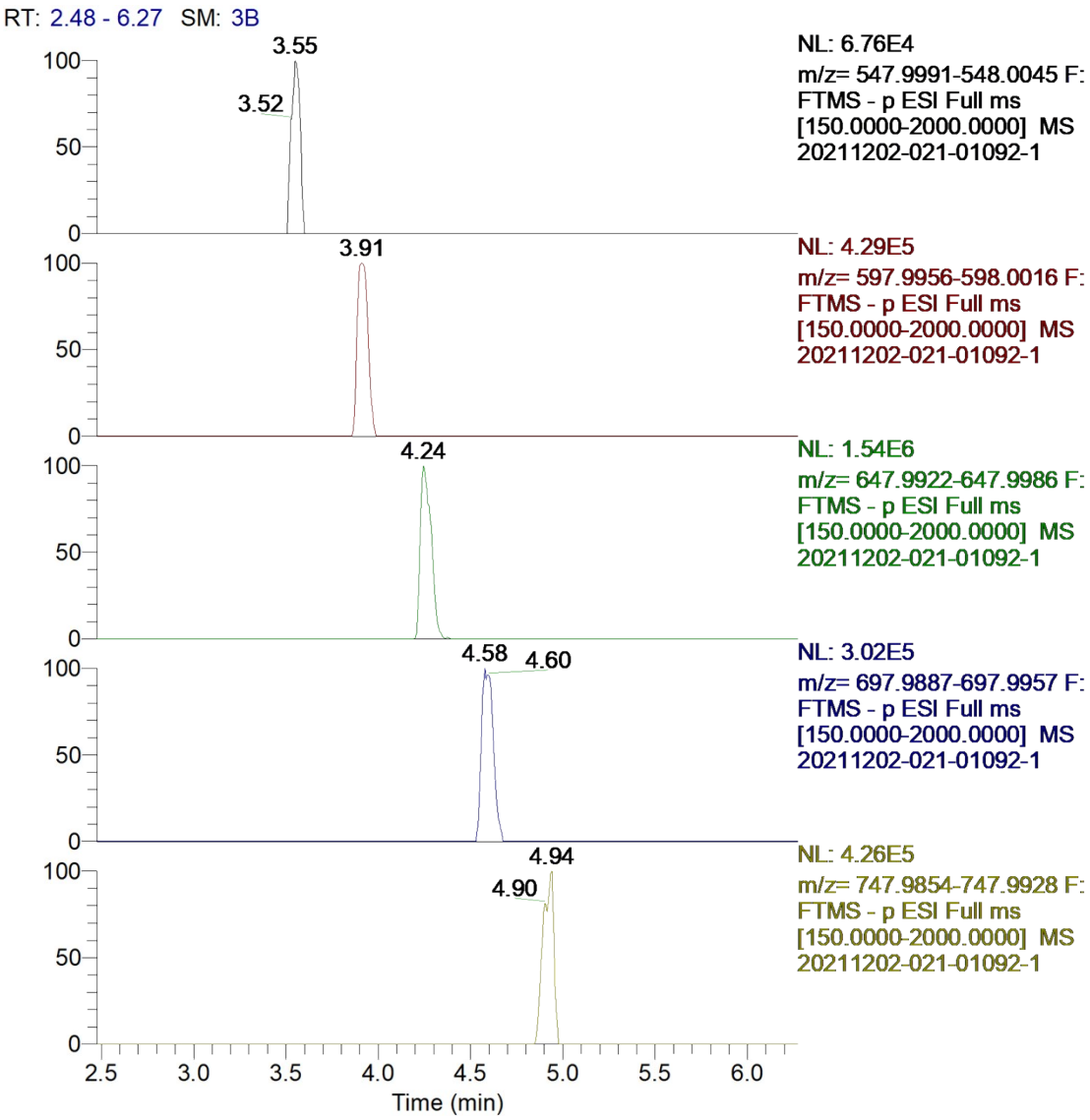

Figure S16. Extracted ion chromatograms of the exact masses (mass deviation 5 ppm) for Unknown group with n=12-16 (see Table 2 in the main manuscript).

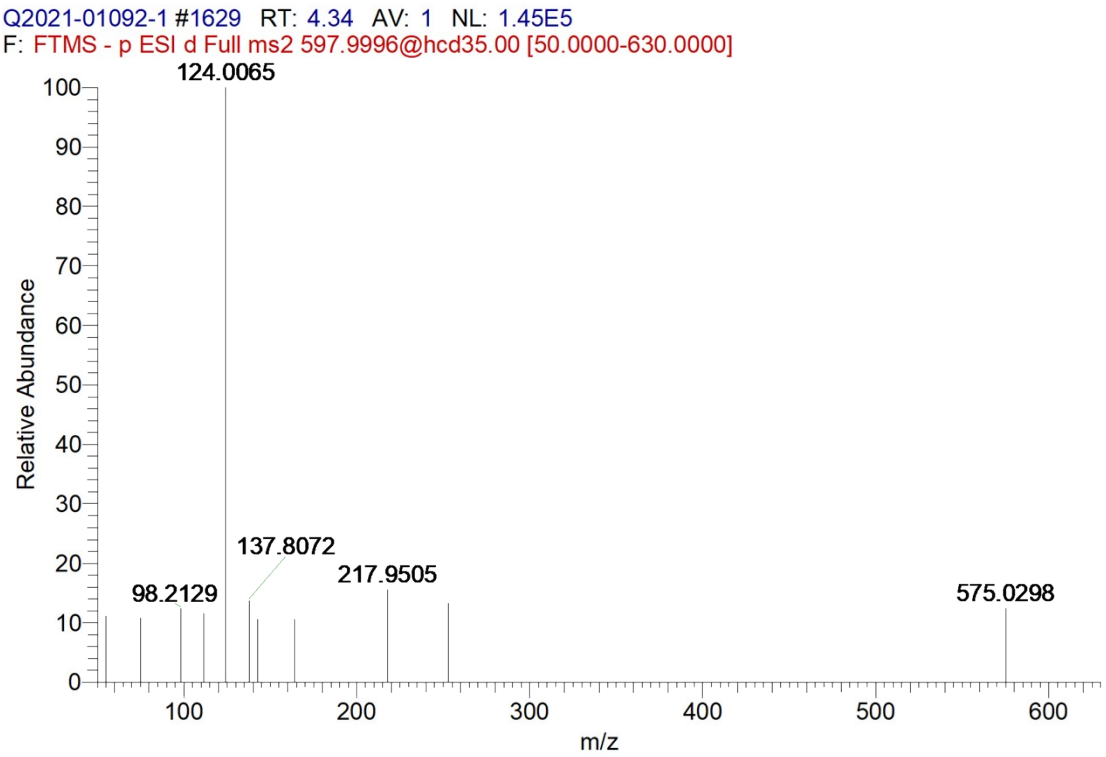

Figure S16a. MS2 spectra recorded for C13F17H9NO4SH. The RT does not fit the RT of the peak in Figure S16, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

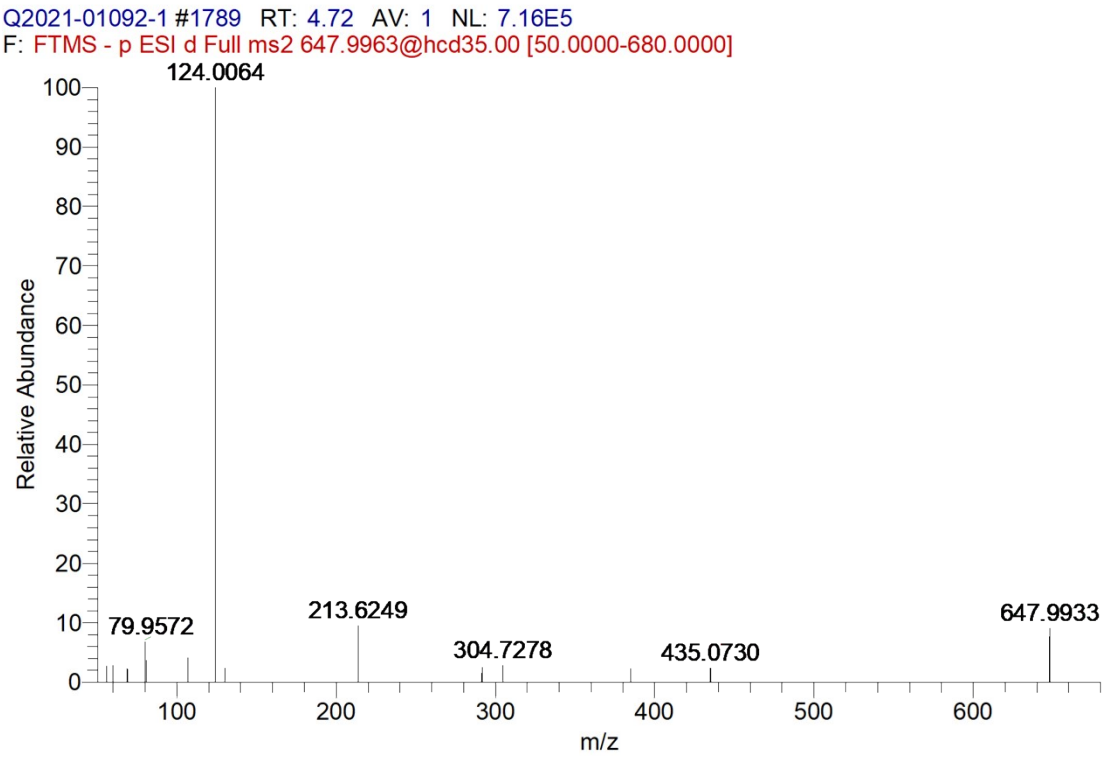

Figure S16b. MS2 spectra recorded for C14F19H9NO4SH. The RT does not fit the RT of the peak in Figure S16, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

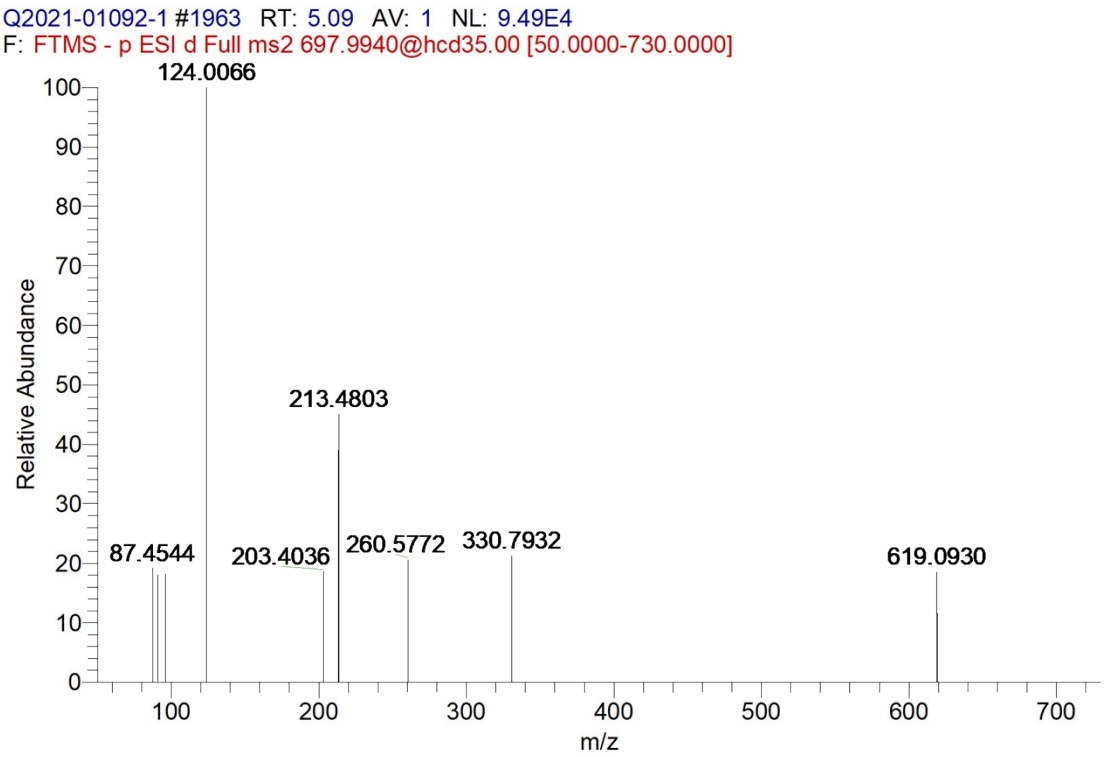

Figure S16c. MS2 spectra recorded for C15F21H9NO4SH. The RT does not fit the RT of the peak in Figure S16, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

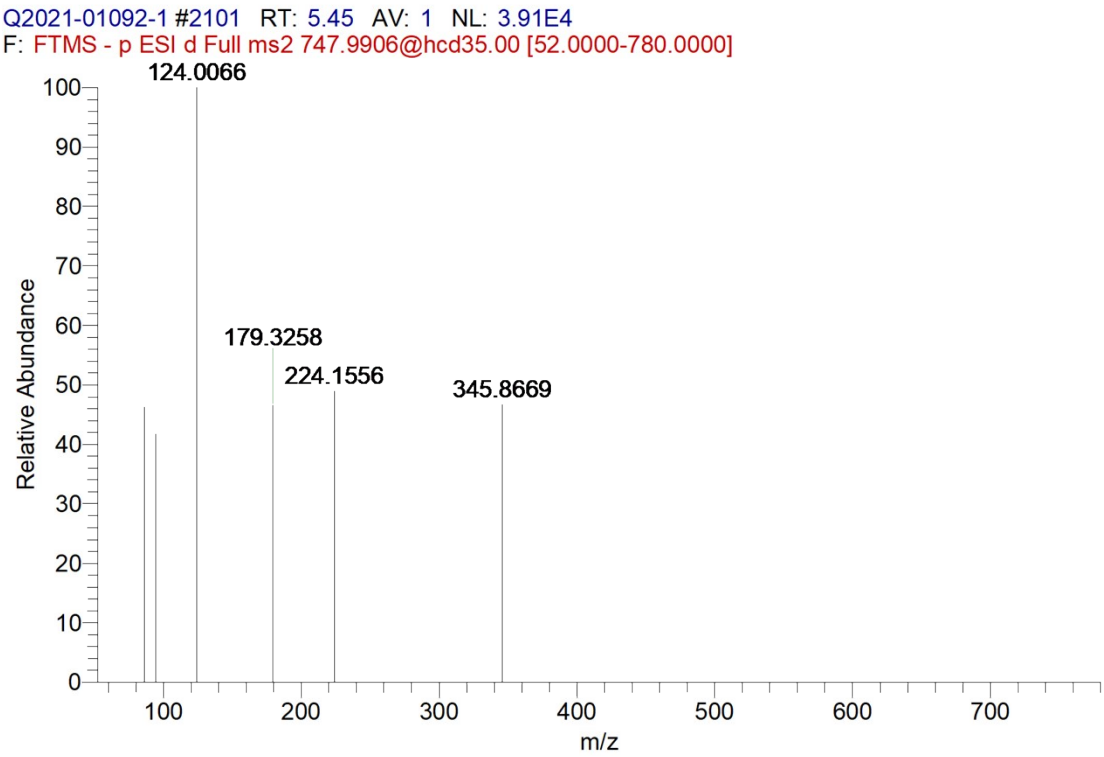

Figure S16d. MS2 spectra recorded for C16F23H9NO4SH. The RT does not fit the RT of the peak in Figure S16, as this MS2 is from a rerun of the same sample with a CE of 35 (while the first run was using a stepped CE of 30, 80 and 120, which did not result in any good fragment data), where RTs were about 0.4 - 0.5 min later.

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