Removal of Per- and Polyfluoroalkyl Substances (PFAS) from Water by Ceric (IV) Ammonium Nitrate

Jun Sun,[¶a] Sreenu Jennepalli,[¶a] Matthew Lee,[c] Denis M. O'Carroll,[c] Björn Åkermark,[b] Michael J. Manefield,[c] Biswanath Das,[¶*a,b] Naresh Kumar*[a]

[a.] *School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia*

[b.] *Department of Organic Chemistry, Stockholm University, Stockholm 10691, Sweden*

[c.] *School of Civil and Environmental Engineering, Water Research Centre, The University of New South Wales, Sydney, NSW 2052, Australia*

¶ Contributed equally to the experimental work.

Materials and Methods

Materials: Ceric (IV) ammonium nitrate (CAN) (≥98.5%), Cerium (III) chloride heptahydrate, Iron (II) chloride, Ammonium acetate, Methanol (hypergrade for LC-MS) and Acetic Acid (≥99.99% trace metals basis) were purchased from Sigma-Aldrich (https://www.sigmaaldrich.com). Cobalt(II) chloride hexahydrate was purchase from May and Baker. Ammonium nitrate (AN) (>95%) was purchased from Merck (https://www.merckmillipore.com/AU/en). Cerium sulfate was purchased from LabChem (https://www.labchem.com/). Perfluoro-n-octanoic acid (PFOA) (98%) was purchased from Synquest Laboratories (http://www.synquestlabs.com). Potassium salt of perfluorooctanesulfonic acid (PFOS) (98%) (branched isomers is 15% and Linear PFOS is 85% according to LC-MS) was purchased from Matrix Scientific (https://www.matrixscientific.com). Milli Q water was used in all experiments.

Adsorption Experiments: For testing low concentration PFAS system, PFASs were dissolved in Milli Q water as stock solution (30 μM for PFOA, 20 μM for PFOS). $Ce(SO_4)_2$, CAN, AN and other metal salts ($FeCl_2$, $CoCl_2$, $CoCl_2$, $CeCl_3$) were dissolved in Milli Q water to make 6 mM stock solution. 0.5 ml or 0.75 ml PFAS stock solution (0.5 ml for PFOA and 0.75 ml for PFOS), different amount CAN (or $Ce(SO_4)_2$, AN, other metal salts solution) and Milli Q water were mixed to achieve 1 ml system. Then the tubes were shaken 3 minutes at room temperature. After that, all samples were centrifuged at 10000 rpm and 100 μl supernatant was taken out and diluted uniformly (to reach below 100 ppb concentration) before LC-MS testing.

For high concentration PFAS system, PFASs were dissolved in Milli Q water to prepare the stock solutions (3 mM for PFOA, 2 mM for PFOS). CAN was dissolved in Milli Q water to make 0.6 M stock solution. 0.5 ml or 0.75 ml PFAS stock solution (0.5 ml for PFOA, 0.75 ml for PFOS), different amount CAN stock solution and Milli Q water were added to 2 ml centrifuge tube to achieve 1 ml adsorption-complexation system. Then the tubes were shaken by a Vortex for 3 minutes at room temperature. After that, samples were centrifuged at 10000 rpm, then 100 μl supernatant was taken out and diluted uniformly (to reach below 100 ppb concentration) before LC-MS testing.

In order to investigate the effect of time, the tubes were kept for 3 days at room temperature. Then all the samples were centrifuged and 100 µl supernatant was taken out and diluted equally (to reach below 100 ppb concentration) before LCMS testing.

Measurement of PFAS: The concentration of different PFASs including PFOA and PFOS were analyzed by a Shimadzu LCMS-8050 and Nexera X2 LC system (Shimadzu, Kyoto, Japan). Shim-pack XR-ODSIII column was used for separation at 40 ^{0}C using binary gradient of solvent A (methanol) and B (5 mM ammonium acetate in 0.05 % acetic acid). The total flow rate was 0.4 mLmin^{-1}. To identify the PFAS compounds, the electrospray negative ionization mode was used.

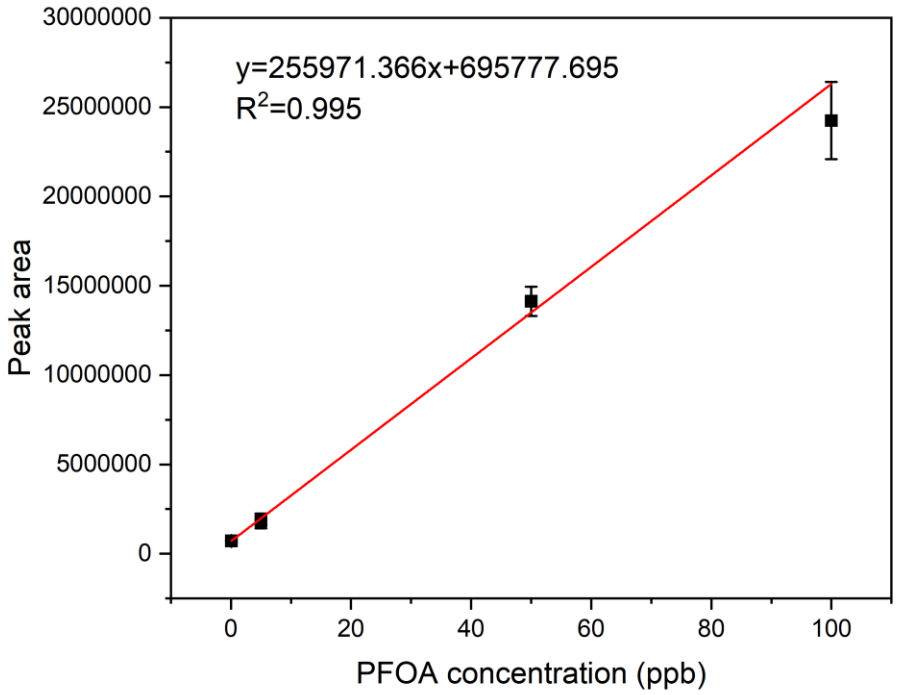

Figure. S1. Standard curve of PFOA

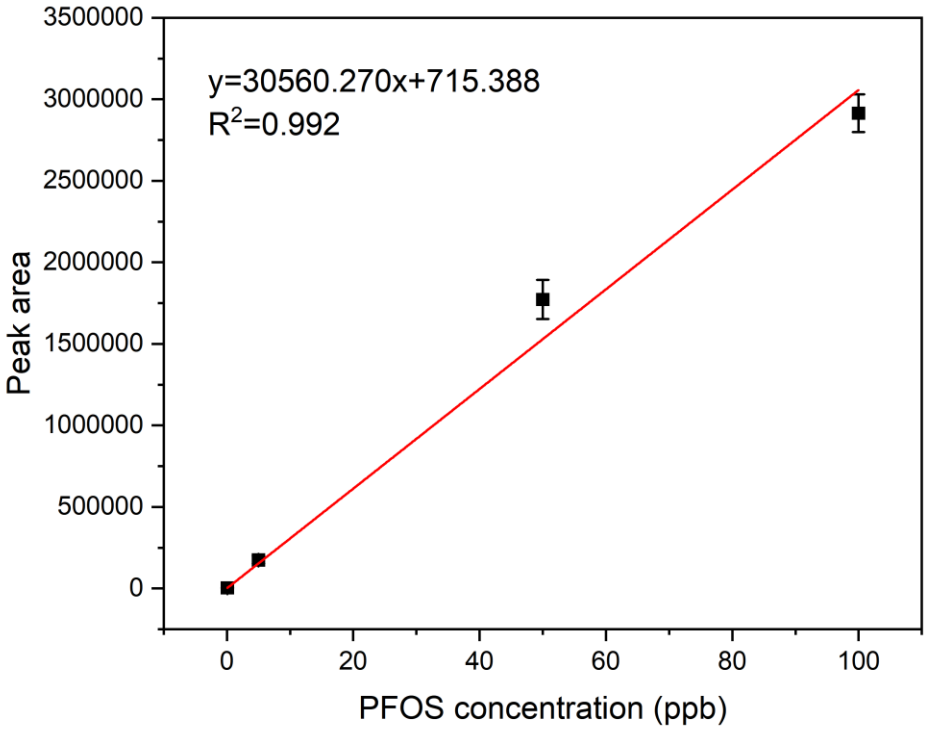

Figure. S2. Standard curve of PFOS

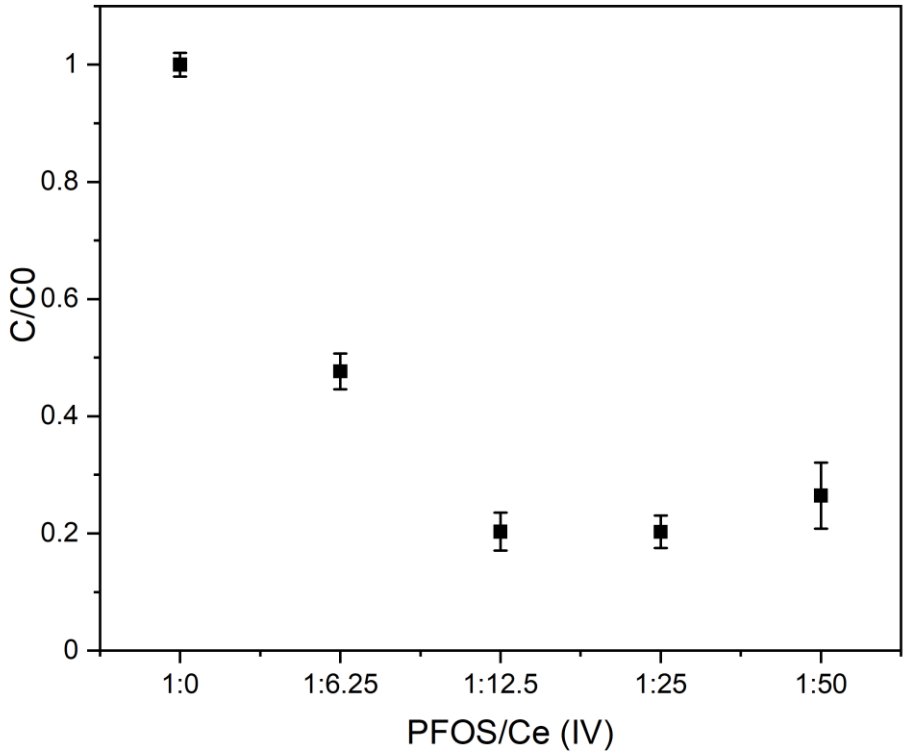

Figure. S3. The LC-MS detected concentrations of 15 µM of PFOS in water before [PFOS:Ce(IV)]=1:0) and after the treatment (3 minutes) with 0.094 mM, 0.19 mM, 0.38 mM and 0.75 mM of CAN.

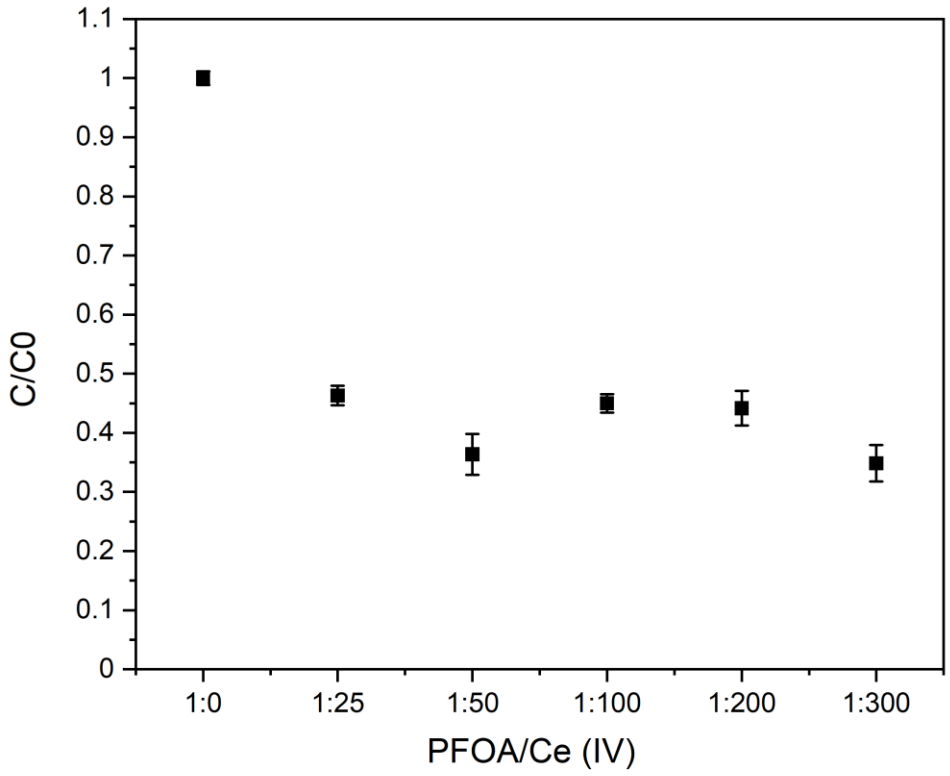

Figure. S4. The LC-MS detected concentrations of 15 µM of PFOA in water before [PFOA:Ce(IV)]=1:0) and after the treatment (3 minutes) with 0.38 mM, 0.75 mM, 1.5 mM, 3 mM and 4.5 mM of CAN.

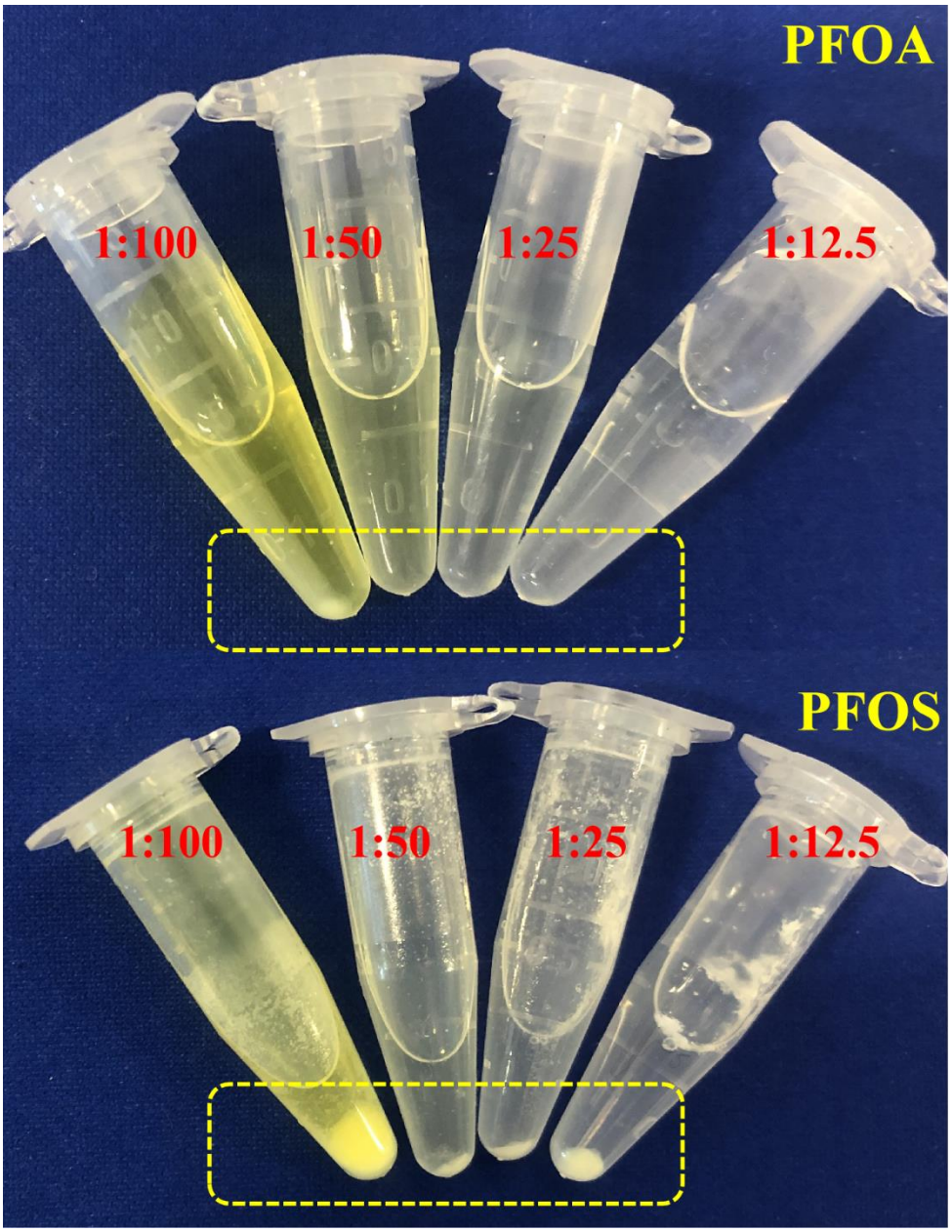

Figure. S5. Precipitates for 1.5 mM PFAS (PFOA and PFOS) in water after treatment with 0.15 M, 0.075 M, 0.038 M, and 0.019 M of CAN for three days.

^{19}F-NMR and HRMS experiments:

^{19}F NMR spectra were recorded in the solvents specified using a Bruker Avance 400 MHz spectrometer as designated. Chemical shifts are quoted in parts per million (ppm), to the nearest 0.01 ppm and internally referenced relative to the solvent nuclei. High-resolution mass spectrometry was performed by the Bioanalytical Mass Spectrometry facility, UNSW.

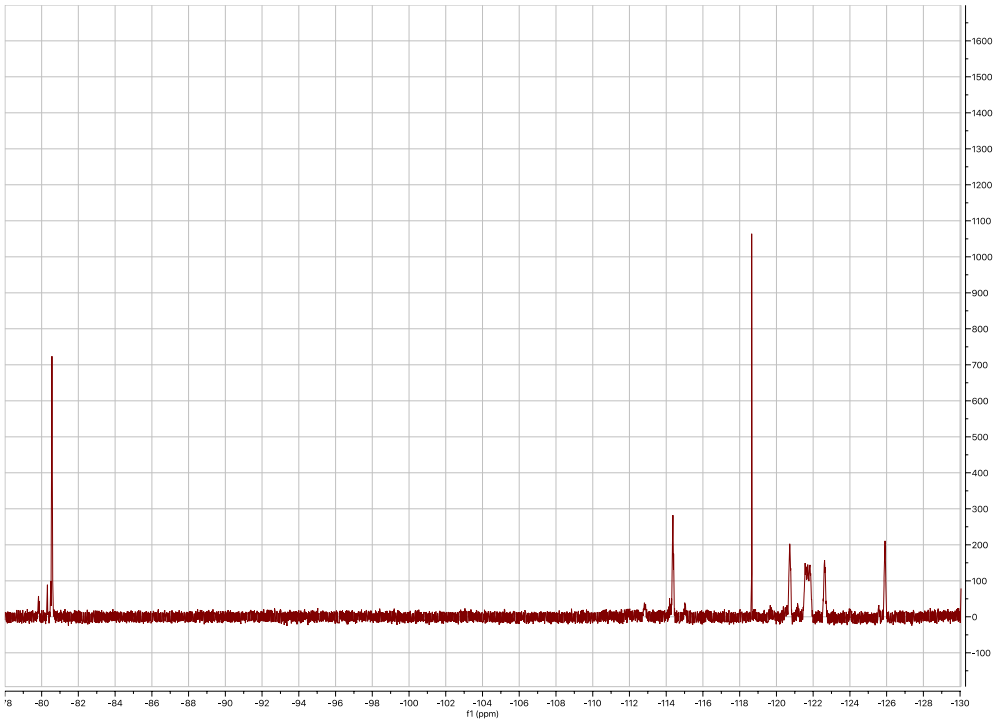

Figure. S6. ^{19}F NMR of PFOS dissolved in DMSO-d6

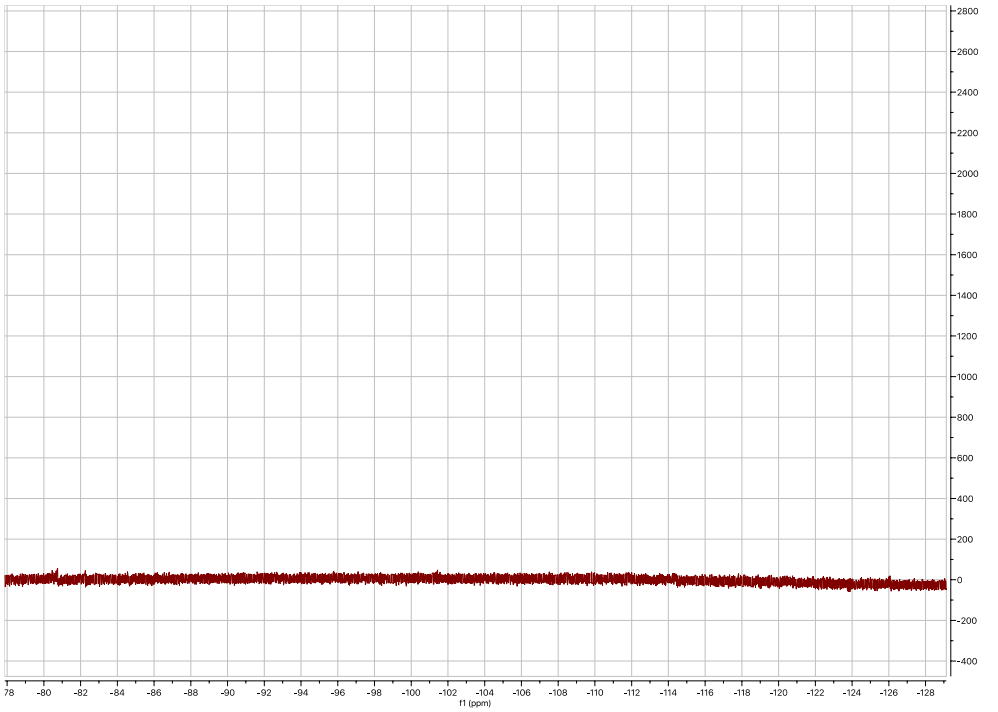

Figure. S7. ^{19}F NMR of PFOS filtrate from the PFOS and CAN reaction

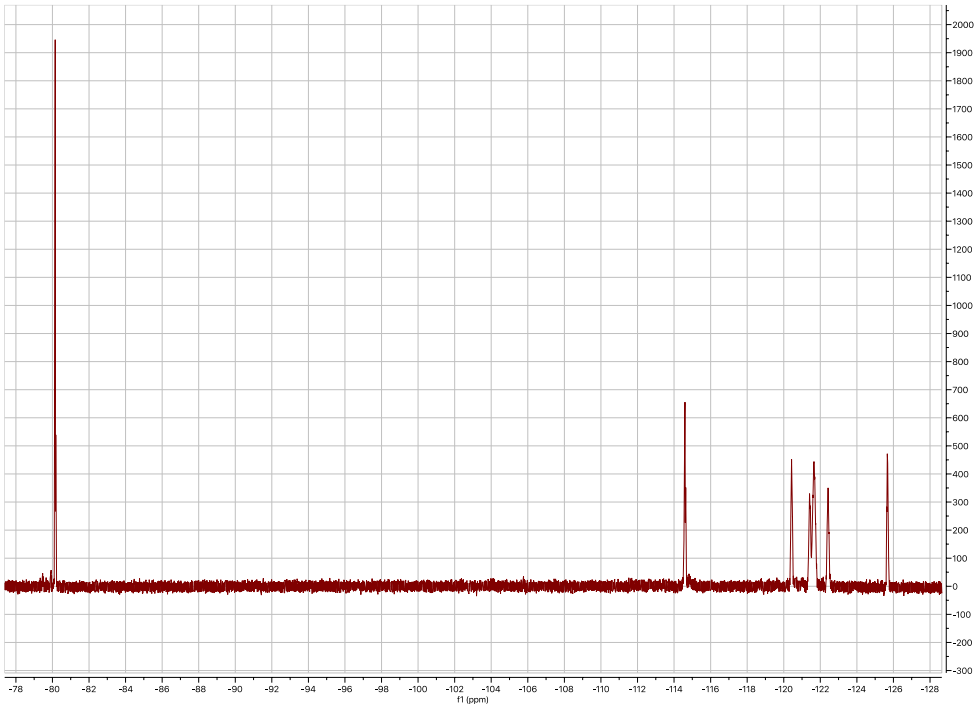

Figure. S8. ^{19}F NMR of PFOS precipitate after the CAN reaction

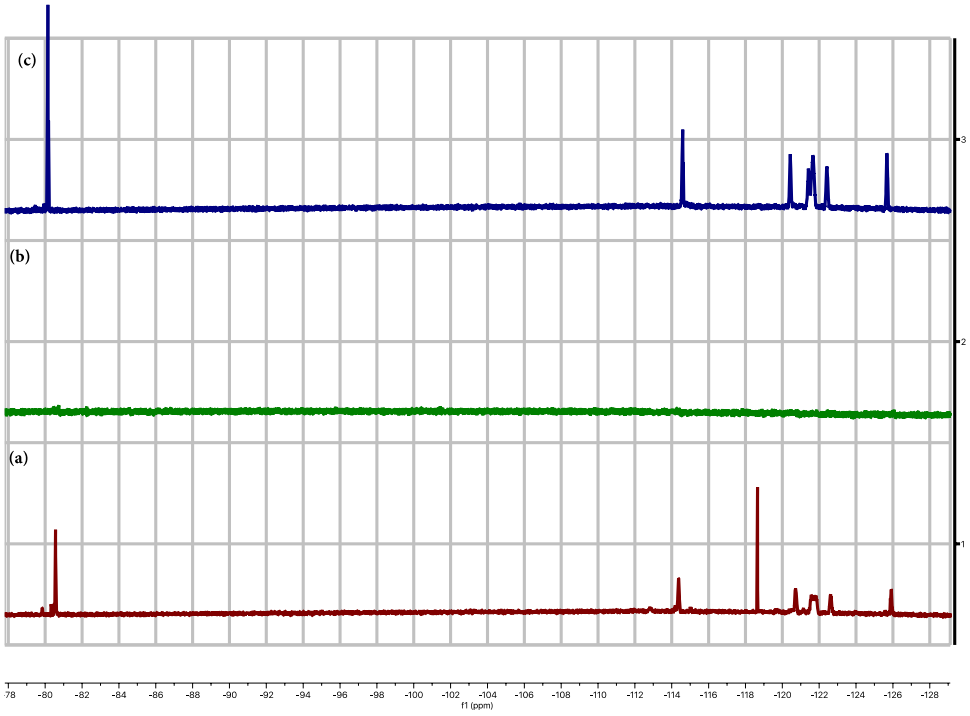

Figure. S9. Stacked ^{19}F NMR of PFOS (a) PFOS dissolved in DMSO-d6 (b) The filtrate from the PFOS and CAN reaction (c). PFOS precipitate after the CAN reaction.

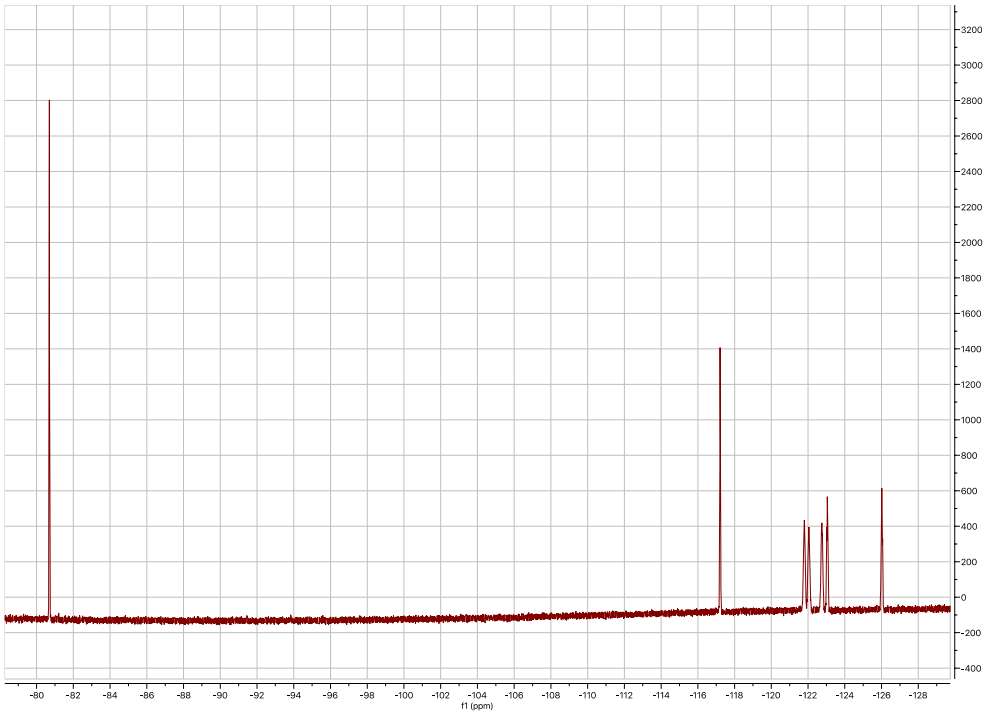

Figure. S10. ^{19}F NMR of PFOA dissolved in DMSO-d6

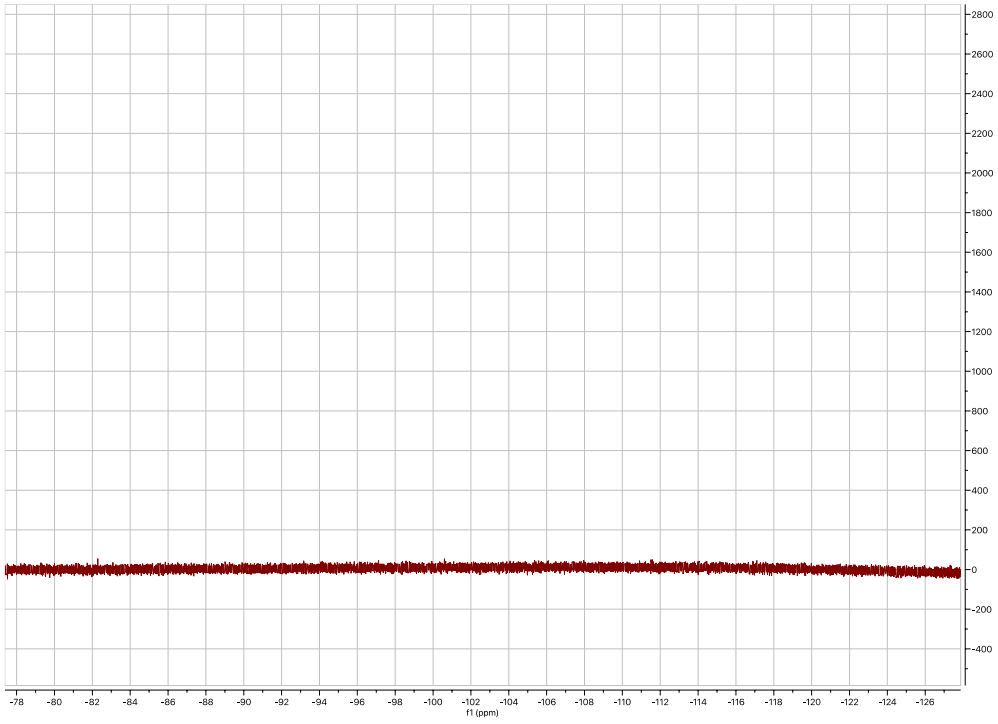

Figure. S11. ^{19}F NMR of PFOA filtrate from the PFOA and CAN reaction

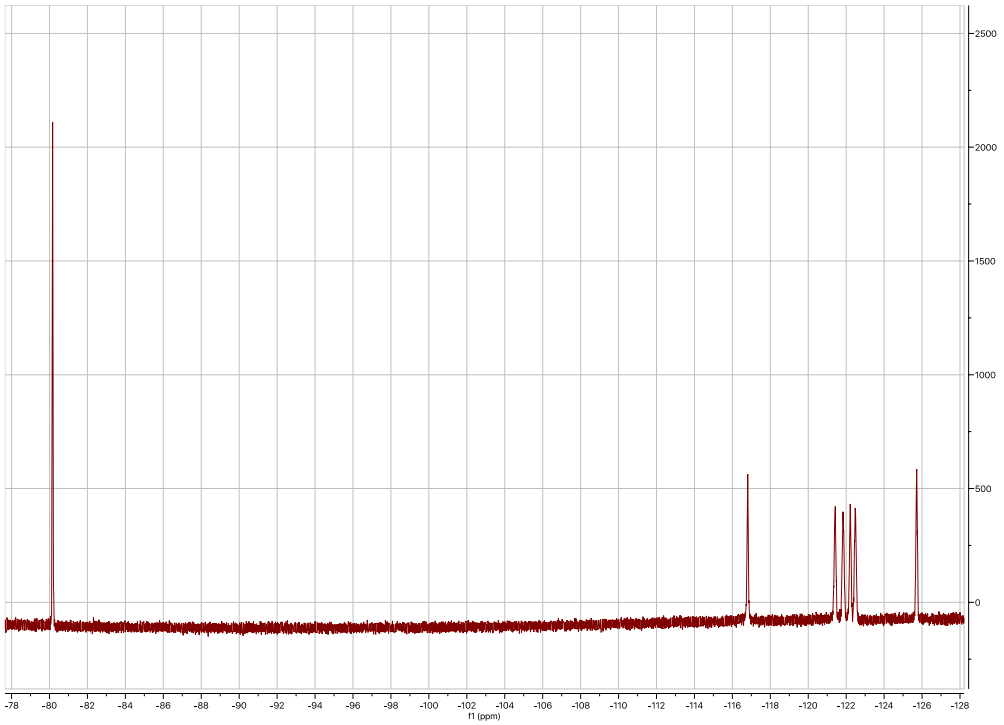

Figure. S12. ^{19}F NMR of PFOA precipitate after the CAN reaction

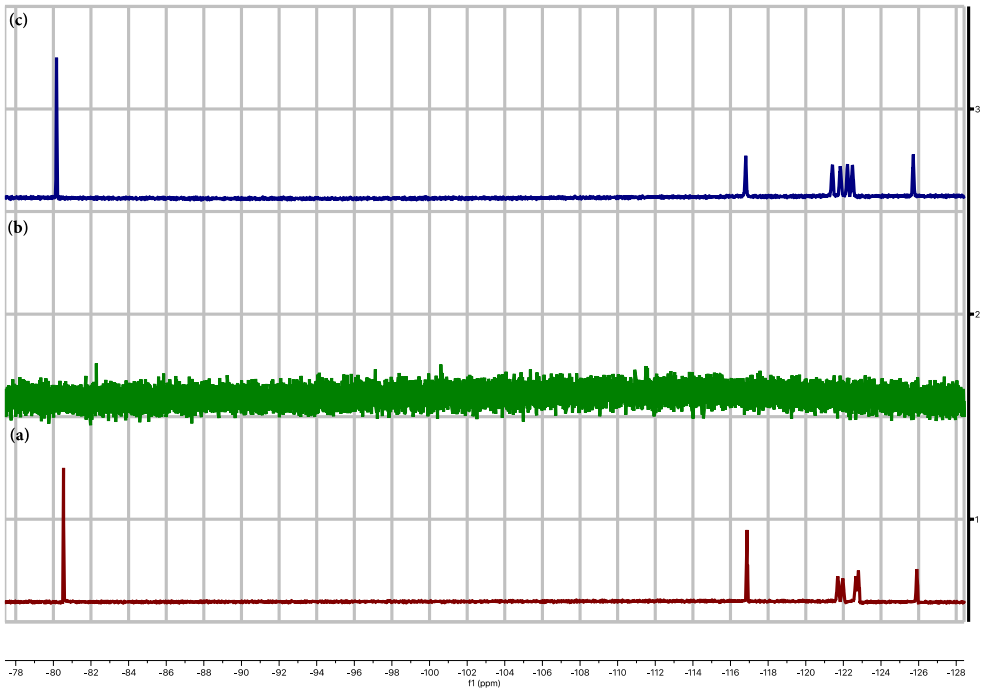

Figure. S13. Stacked ^{19}F NMR of PFOA (a) PFOA dissolved in DMSO-d6 (b) The filtrate from the PFOA and CAN reaction (c). PFOA precipitate after the CAN reaction

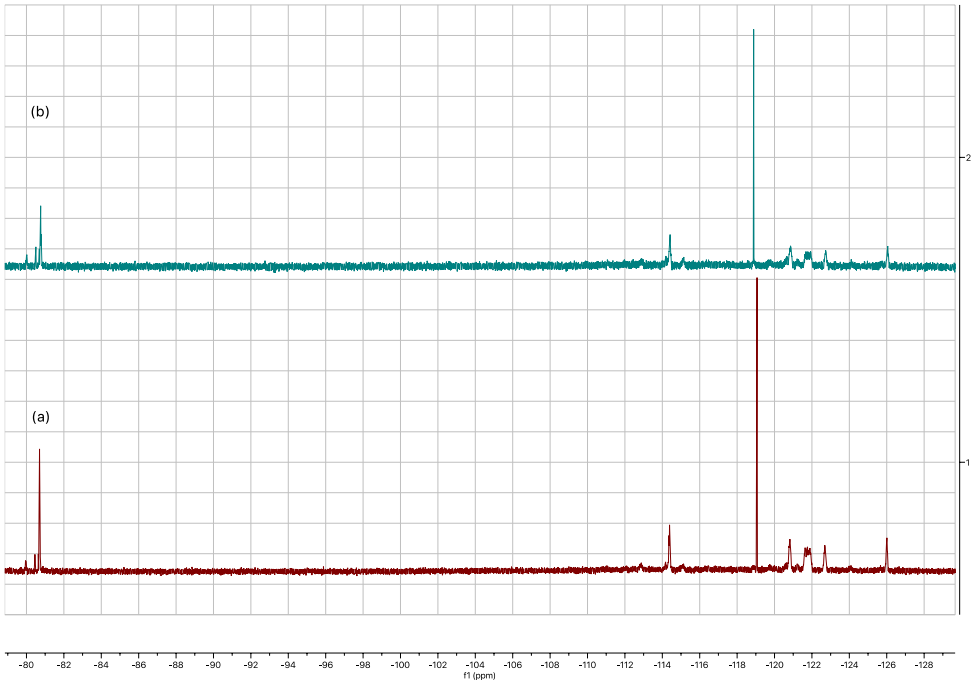

Figure. S14. Stacked ^{19}F NMR of PFOS (a) PFOS dissolved in DMSO-d6 (b) The filtrate from the PFOS and Ammonium Nitrate (NH_4NO_3) reaction.

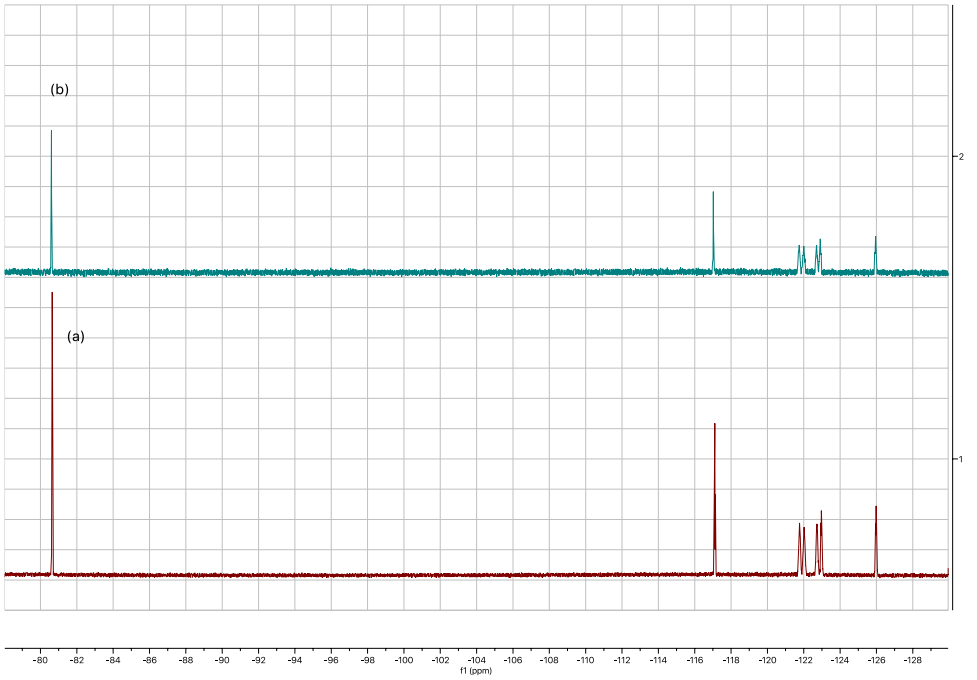

Figure. S15. Stacked ^{19}F NMR of PFOA (a) PFOA dissolved in DMSO-d6 (b) The filtrate from the PFOA and Ammonium Nitrate (NH_4NO_3) reaction.

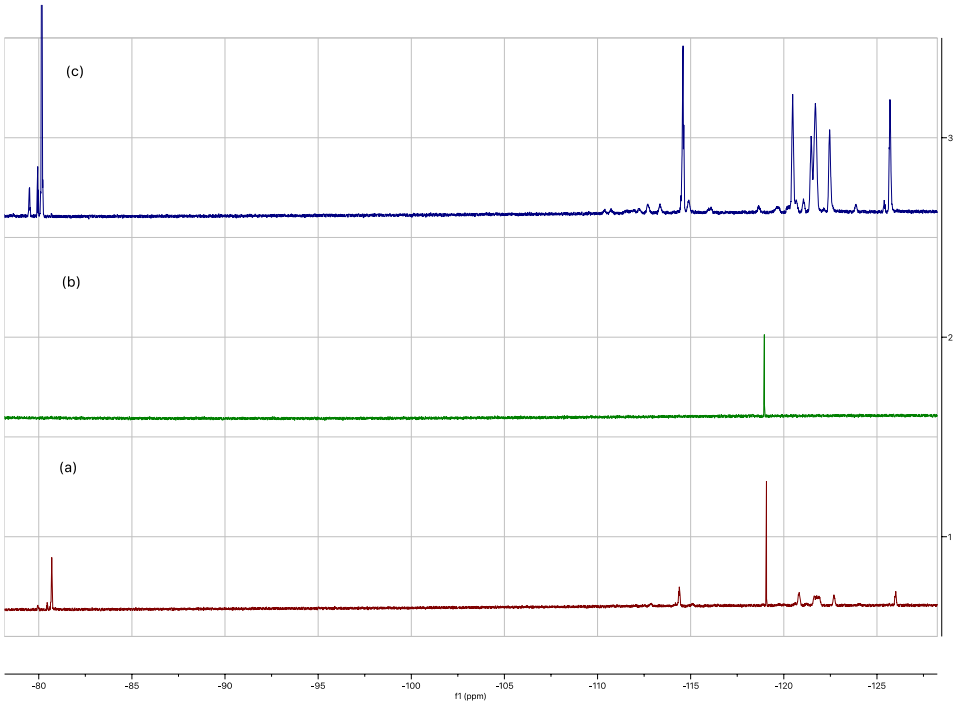

Figure. S16. Stacked ^{19}F NMR of PFOS (a) PFOS dissolved in DMSO-d6 (b) The filtrate from the PFOS and $Ce(SO_4)_2$ reaction (c). PFOS precipitate after the $Ce(SO_4)_2$ reaction

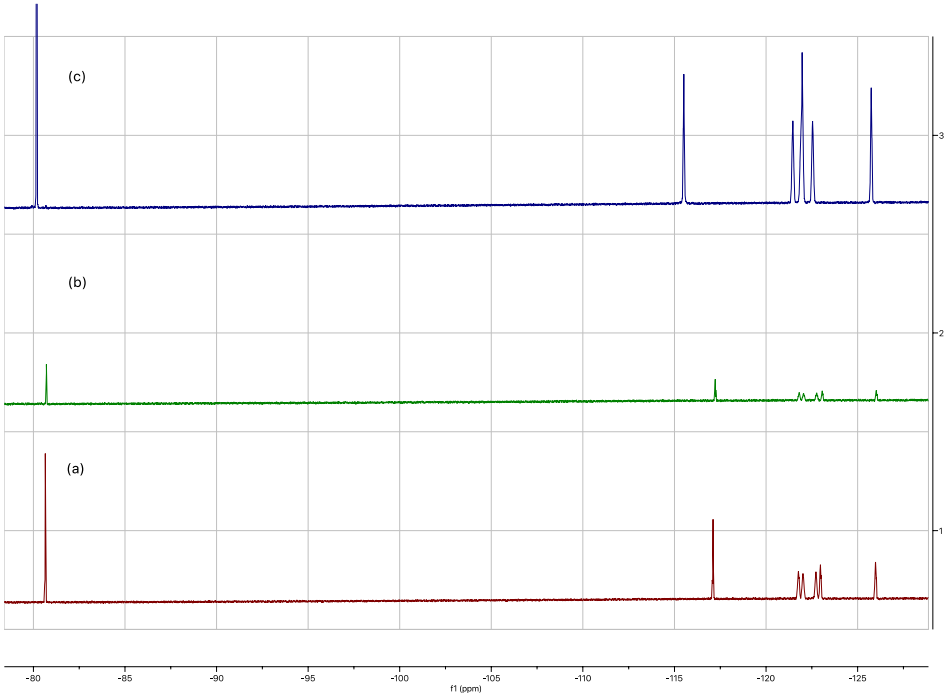

Figure. S17. Stacked ^{19}F NMR of PFOA (a) PFOA dissolved in DMSO-d6 (b) The filtrate from the PFOA and $Ce(SO_4)_2$ reaction (c) PFOA precipitate after the $Ce(SO_4)_2$ reaction.

Sample submission report

Sample Analysis Request #	**3092932**
Samples submitted by	**Jun Sun**
Date run	2020-12-08
Operator	Chowdhury Sarowar
Report prepared by	Chowdhury Sarowar

Notes:

Sample: 7

Full spectrum

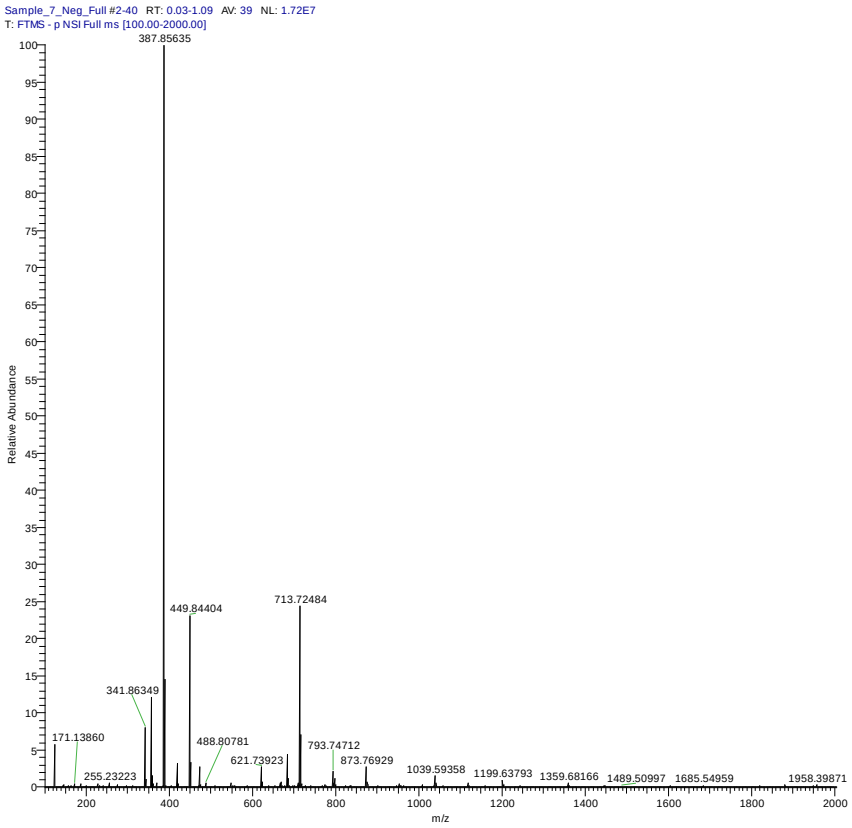

Figure. S18. HRMS data for PFOA precipitate (dissolved in 1:20 DMSO:Water) formed after the reaction of PFOA and CAN.

Sample submission report

Sample Analysis Request #	**3092932**
Samples submitted by	**Jun Sun**
Date run	2020-12-08
Operator	Chowdhury Sarowar
Report prepared by	Chowdhury Sarowar

Notes:

Sample: 9

Full spectrum

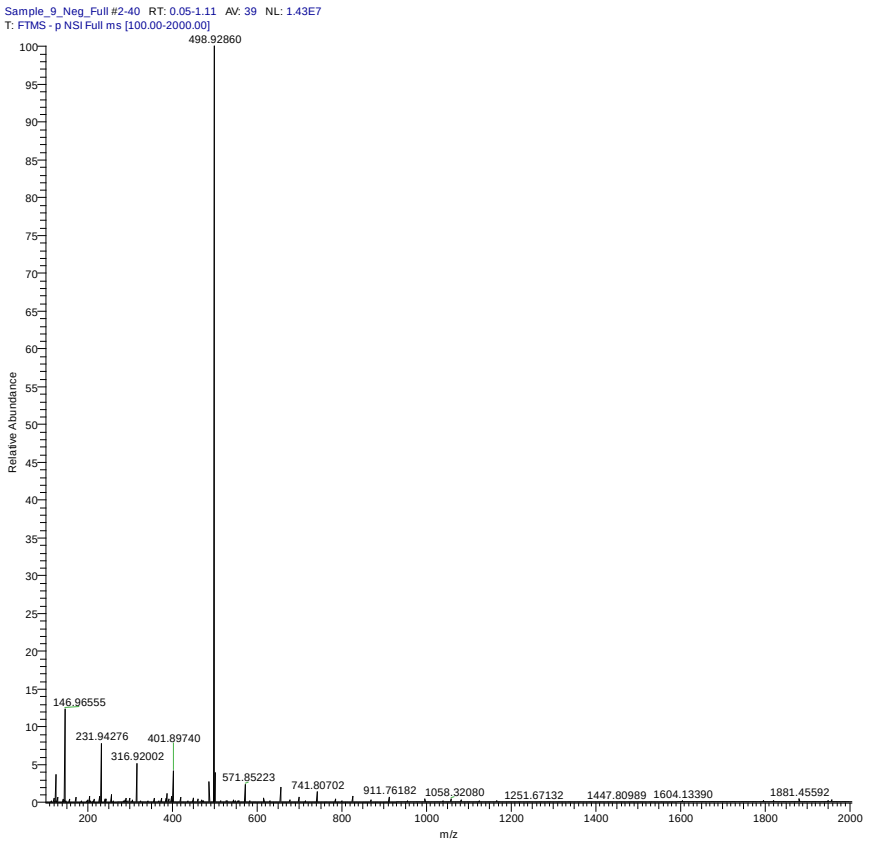

Figure. S19. HRMS data for PFOS precipitate (dissolved in 1:20 DMSO:Water) formed after the reaction of PFOS and CAN.