

## Electronic Supporting Information

# A rationally designed perfluorinated host for the extraction of PFOA from water utilising non- covalent interactions

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<b>Characterization data for host 5</b> .....	2
<b>Characterization data for host 6</b> .....	5
<b>Characterisation data for host 8</b> .....	8
<b>NMR spectroscopic data for commercial PFOA used in this study.</b> .....	11
<b>Hirshfeld Surface analysis</b> .....	14
<b>Thermal characterization of hosts and host:guest complexes</b> .....	16
<b><sup>1</sup>H and <sup>19</sup>F NMR titration experiments</b> .....	23
<b><sup>19</sup>F DOSY spectroscopy</b> .....	38
<b>Solid-State NMR spectroscopy of hosts and host:guest complexes</b> .....	40
<b>Computational Chemistry</b> .....	68

## Characterization data for host 5.

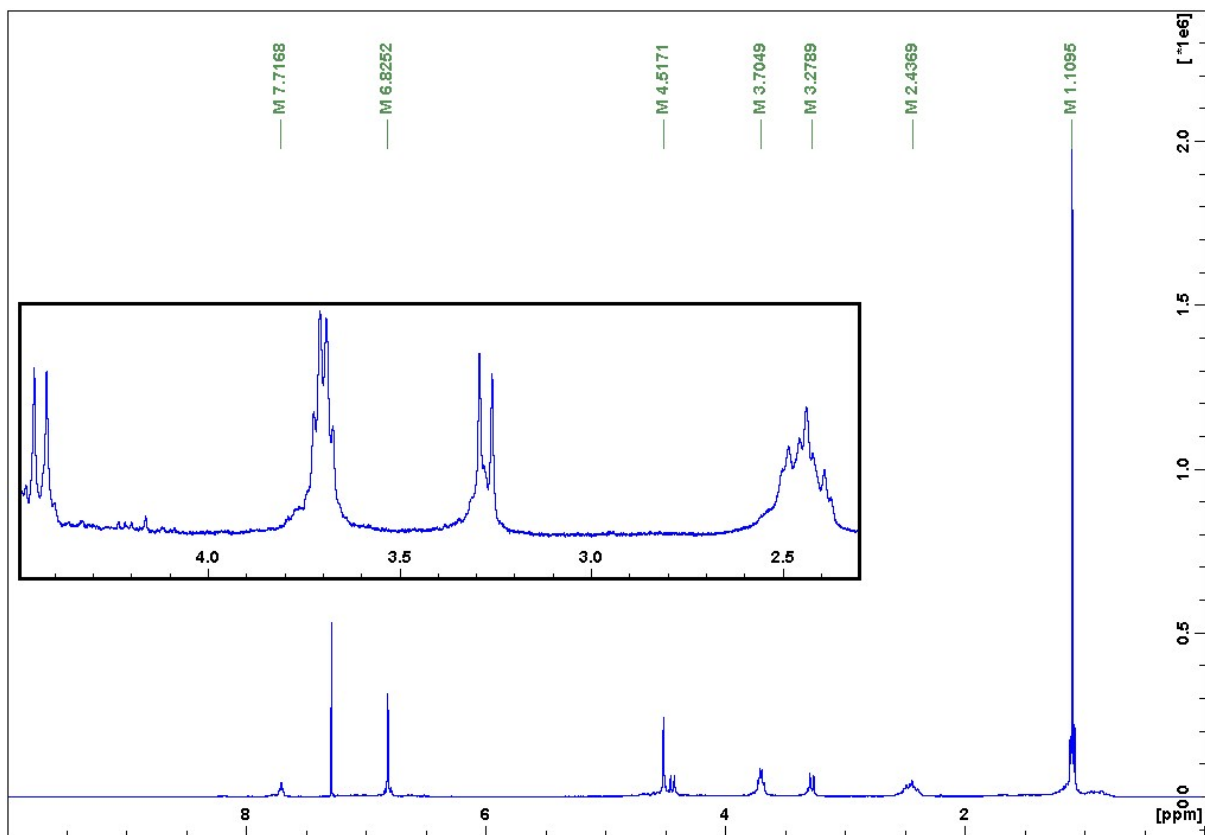


Figure S1.  $^1\text{H}$  NMR spectrum of **5** in  $\text{CDCl}_3$ .

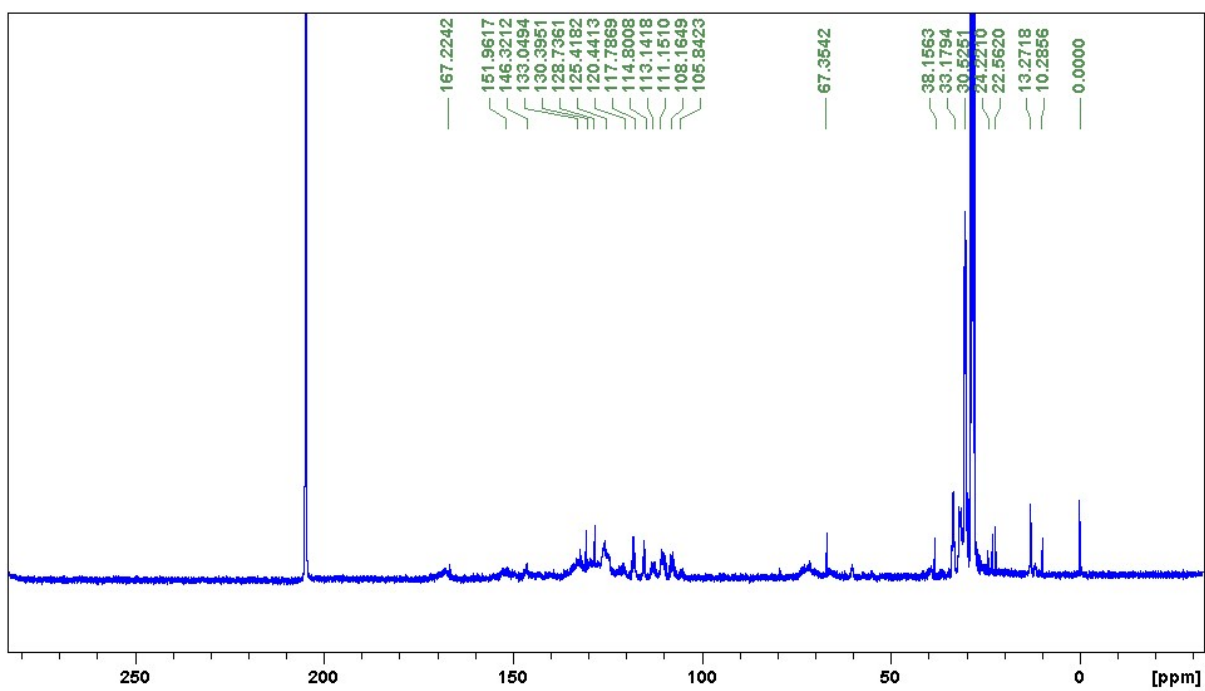
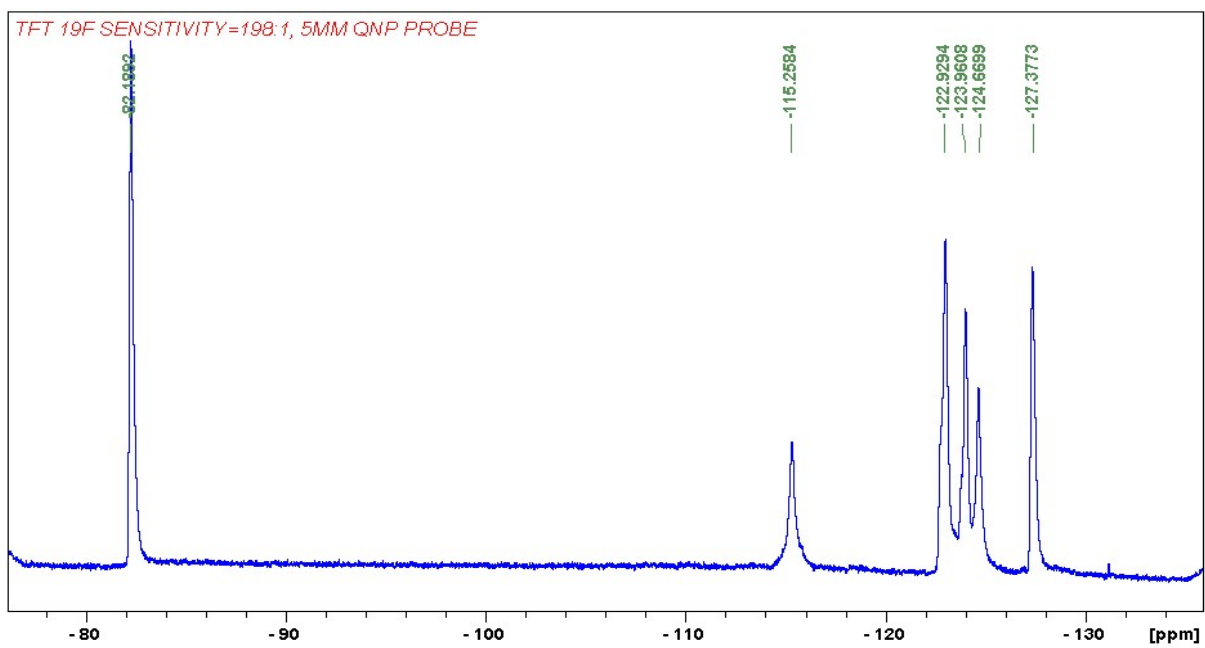


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **5** in  $\text{CDCl}_3$ .



**Figure S3.**  $^{19}\text{F}$  NMR spectrum of **5** in  $\text{CDCl}_3$ .

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 500.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

4674 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)

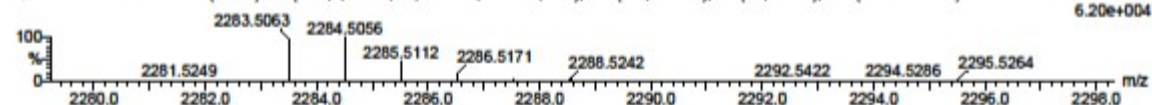
Elements Used:

C: 0-84 H: 0-80 N: 0-4 O: 0-8 F: 0-52 Na: 0-1

Harrison Omorodion (BB), HO\_15N\_C2

Q-TOF20160616MFD05 91 (1.883) AM (Cen,4, 80.00, Ar,10000.0,1570.68,0.70); Sm (SG, 1x5.00); Sb (15,10.00); Cm (19:105-90:92)

TOF MS LD+  
6.20e+004



Minimum: 5.0 5.0 -1.5  
Maximum: 5.0 5.0 500.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
2283.5063	2283.5044	1.9	0.8	20.5	41.6	0.0	C84 H80 N4 O8 F52 Na

Harrison Omorodion (BB), HO\_15N\_C2

Q-TOF20160616MFD05 91 (1.883) AM (Cen,4, 80.00, Ar,10000.0,1570.68,0.70); Sm (SG, 1x5.00); Sb (15,10.00); Cm (19:105-90:92)

TOF MS LD+  
6.20e4

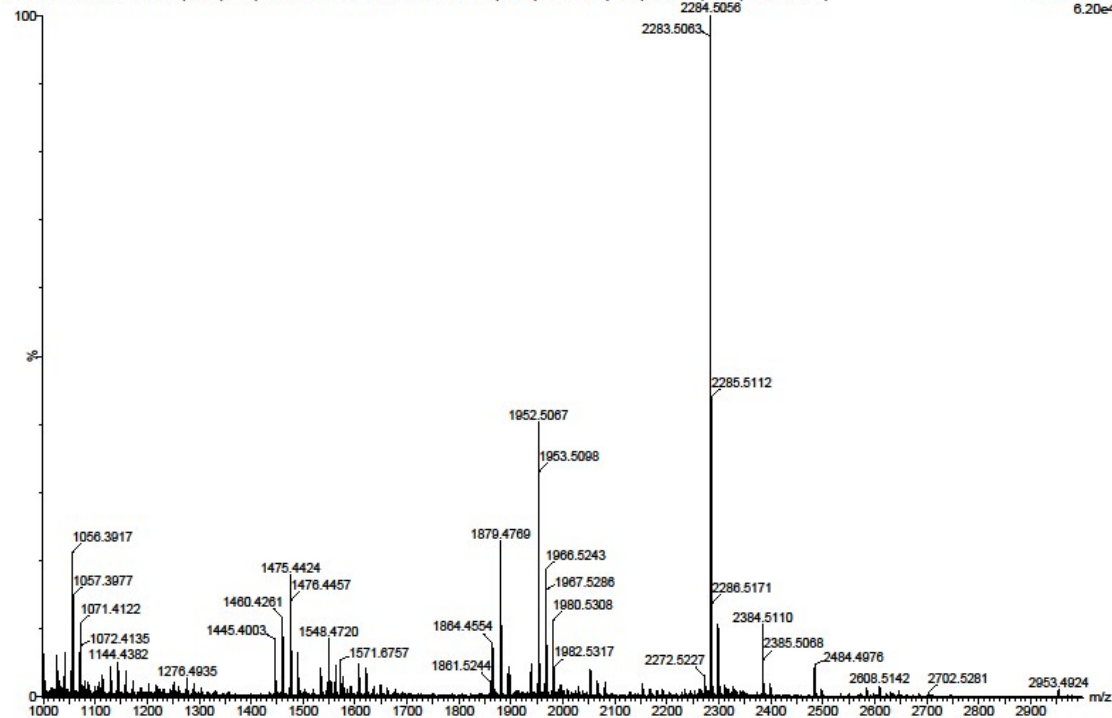
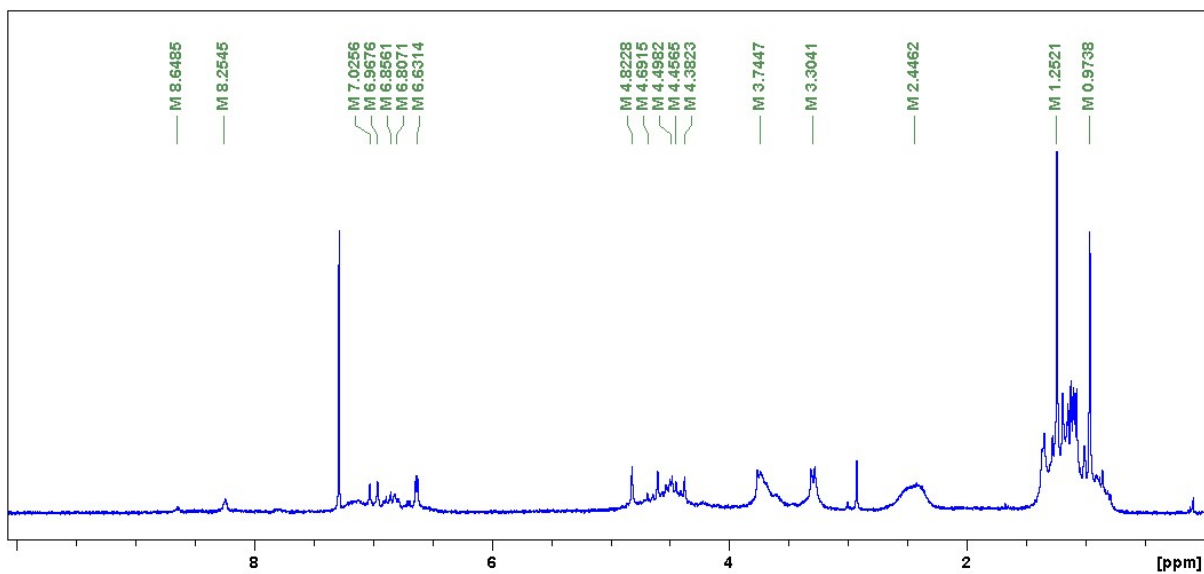
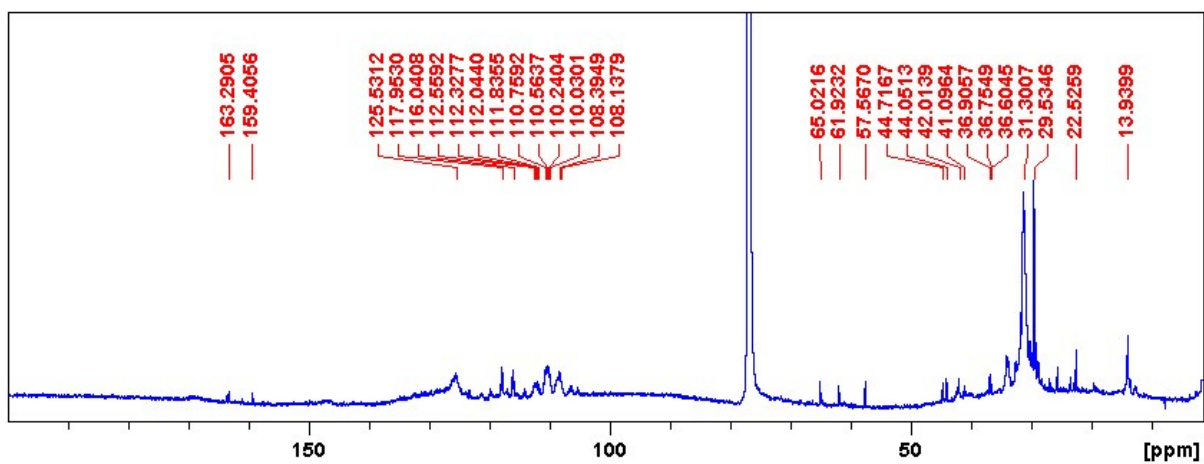


Figure S4. Mass spectrometry and HRMS data for 5.

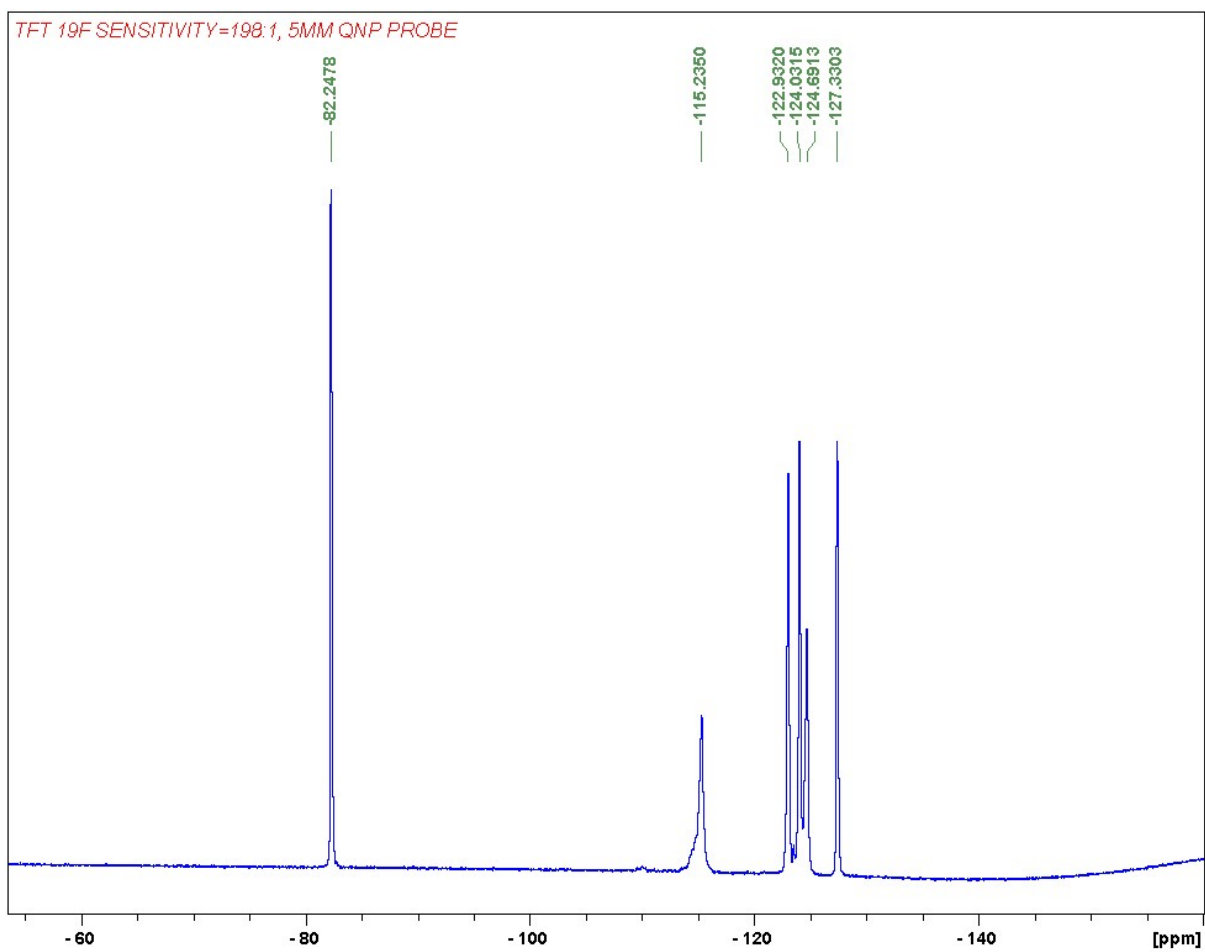
## Characterization data for host 6



**Figure S5.**  $^1\text{H}$  NMR spectrum of **6** in  $\text{CDCl}_3$ .



**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{CDCl}_3$ .



**Figure S7.**  $^{19}\text{F}$  NMR spectrum of **6** in  $\text{CDCl}_3$ .

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 1000.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

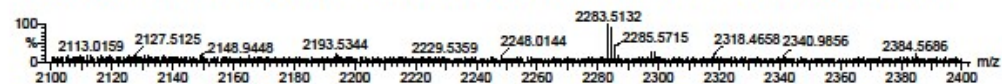
Monoisotopic Mass, Odd and Even Electron Ions

4674 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)

Elements Used:

C: 0-84 H: 0-80 N: 0-4 O: 0-8 F: 0-52 Na: 0-1

Harrison Omorodion (BB), HO-15XXA in DCTB 3.37e+001  
 Q-TOF20140730MF005 77 (1.421) AM (Cen,4, 80.00, Ht,10000.0,1570.68,0.70); Sm (SG, 1x3.00); Sb (15,10.00); Sn (SG, 5x3.00); Cm (5:127-42:100)



Minimum: -1.5  
 Maximum: 5.0 100.0 1000.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
2283.5132	2283.5044	8.8	3.9	20.5	34.4	0.0	C84 H80 N4 O8 F52 Na

Harrison Omorodion (BB), HO 15XXA in DCTB  
 Q-TOF20140730MF005 77 (1.421) AM (Cen,4, 80.00, Ht,10000.0,1570.68,0.70); Sm (SG, 1x3.00); Sb (15,10.00); Sn (SG, 5x3.00); Cm (5:127-42:100) TOF MS LD+ 33.7

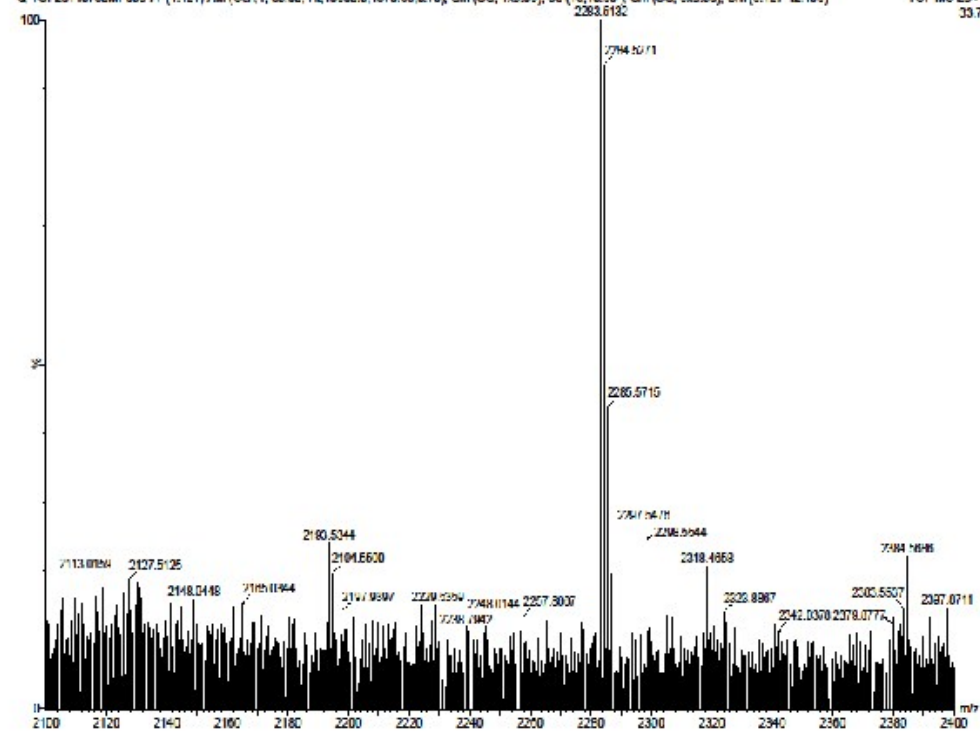


Figure S8. Mass spectrometry and HRMS data for 6.

## Characterisation data for host **8**

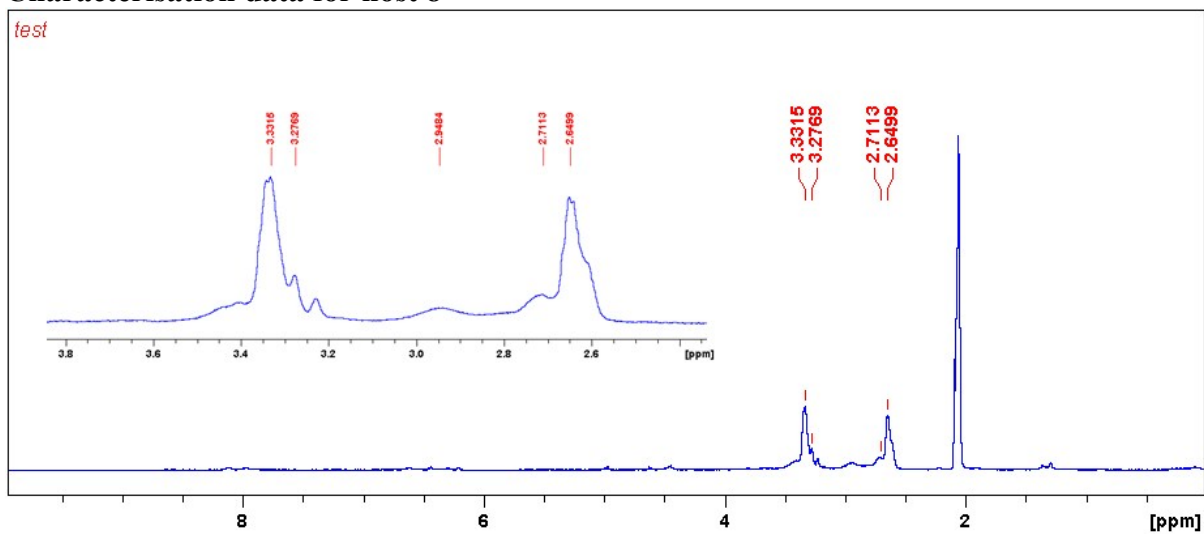


Figure S9.  $^1\text{H}$  NMR spectrum of **8** in  $\text{CDCl}_3$ .

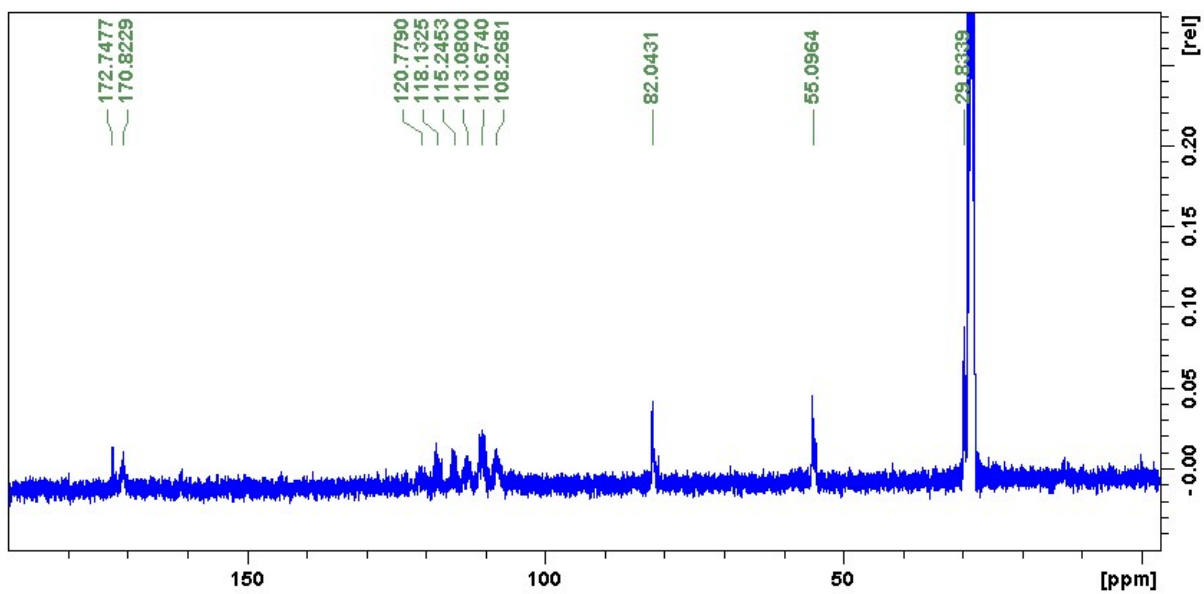


Figure S10.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **8** in  $\text{CDCl}_3$ .



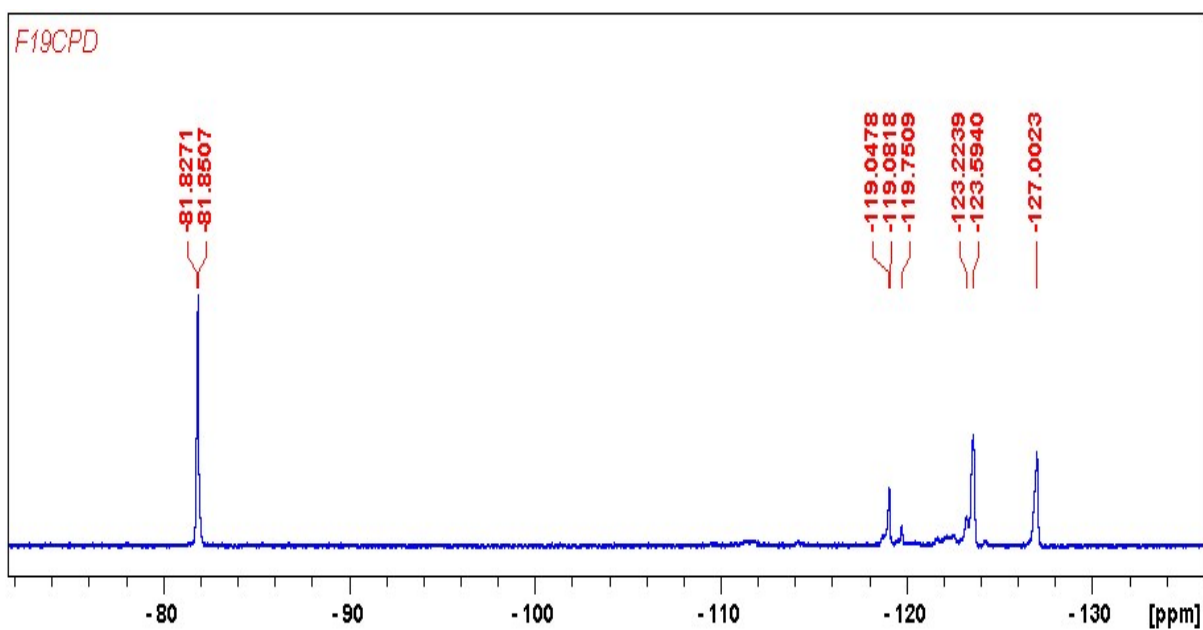


Figure S11.  $^{19}\text{F}$  NMR spectrum of **8** in  $\text{CDCl}_3$ .

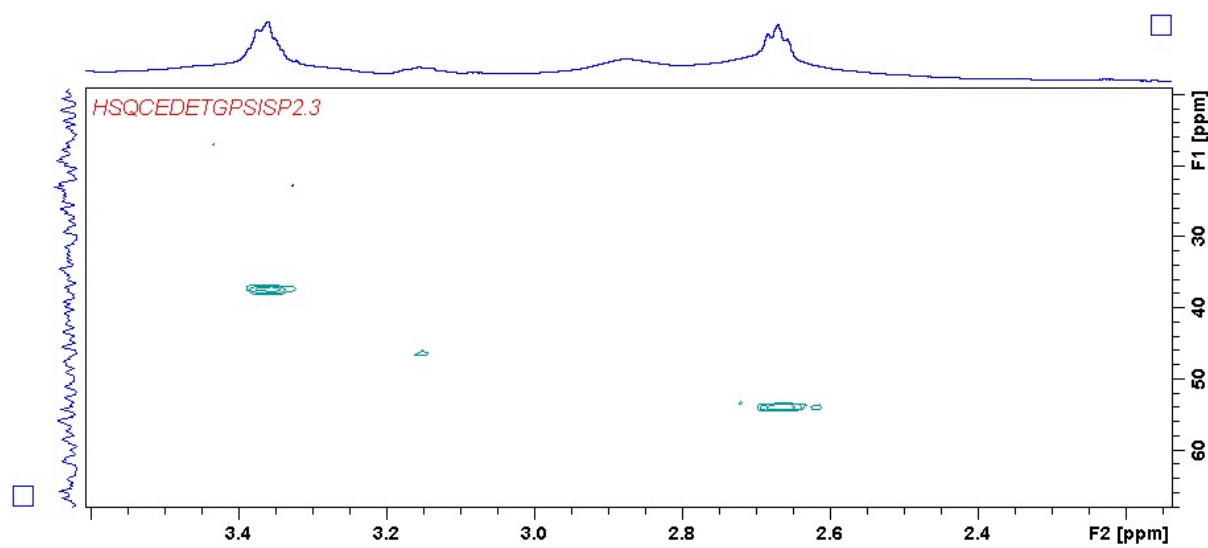


Figure S12. HSQC NMR spectrum of **8** in  $\text{CDCl}_3$ .

Single Mass Analysis

Tolerance = 2.0 PPM / DBE: min = -1.5, max = 500.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

789 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

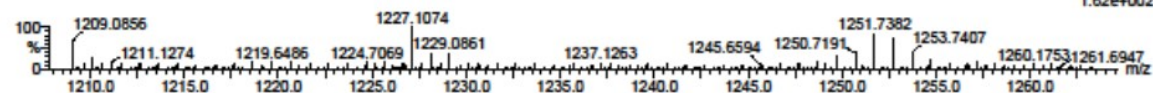
Elements Used:

C: 0-30 H: 0-22 N: 0-4 O: 0-3 F: 0-30

Harrison Omorodion (BB), HO-SC-3 in DCTB

Q-TOF20140714MF002 81 (1.817) AM (Cen,4, 80.00, Ht,10000.0,1570.68,0.70); Sm (SG, 1x5.00); Sb (15,10.00); Cm (15:91-80:82)

TOF MS LD+  
1.62e+002



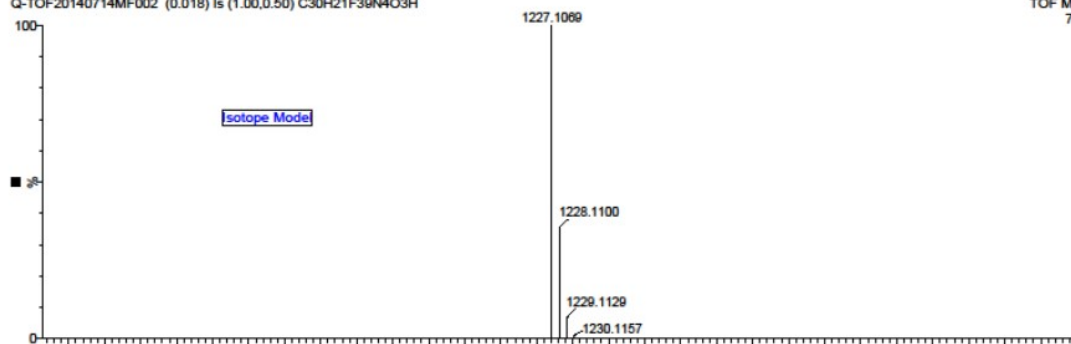
Minimum: -1.5  
Maximum: 5.0 2.0 500.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1227.1074	1227.1069	0.5	0.4	2.5	53.9	0.0	C30 H22 N4 O3 F39

Harrison Omorodion (BB), HO-SC-3 in DCTB

Q-TOF20140714MF002 (0.018) Is (1.00,0.50) C30H21F39N4O3H

TOF MS LD+  
7.00e12



Q-TOF20140714MF002 81 (1.817) AM (Cen,4, 80.00, Ht,10000.0,1570.68,0.70); Sm (SG, 1x5.00); Sb (15,10.00); Cm (15:91-80:82)

TOF MS LD+  
1.16e3

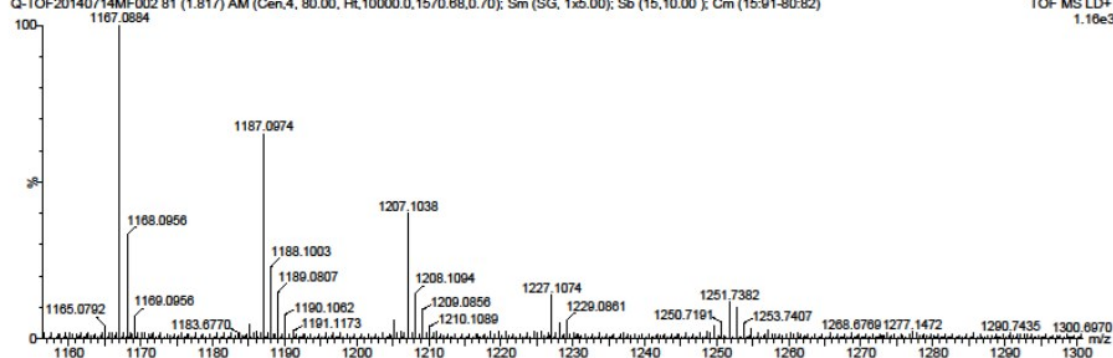
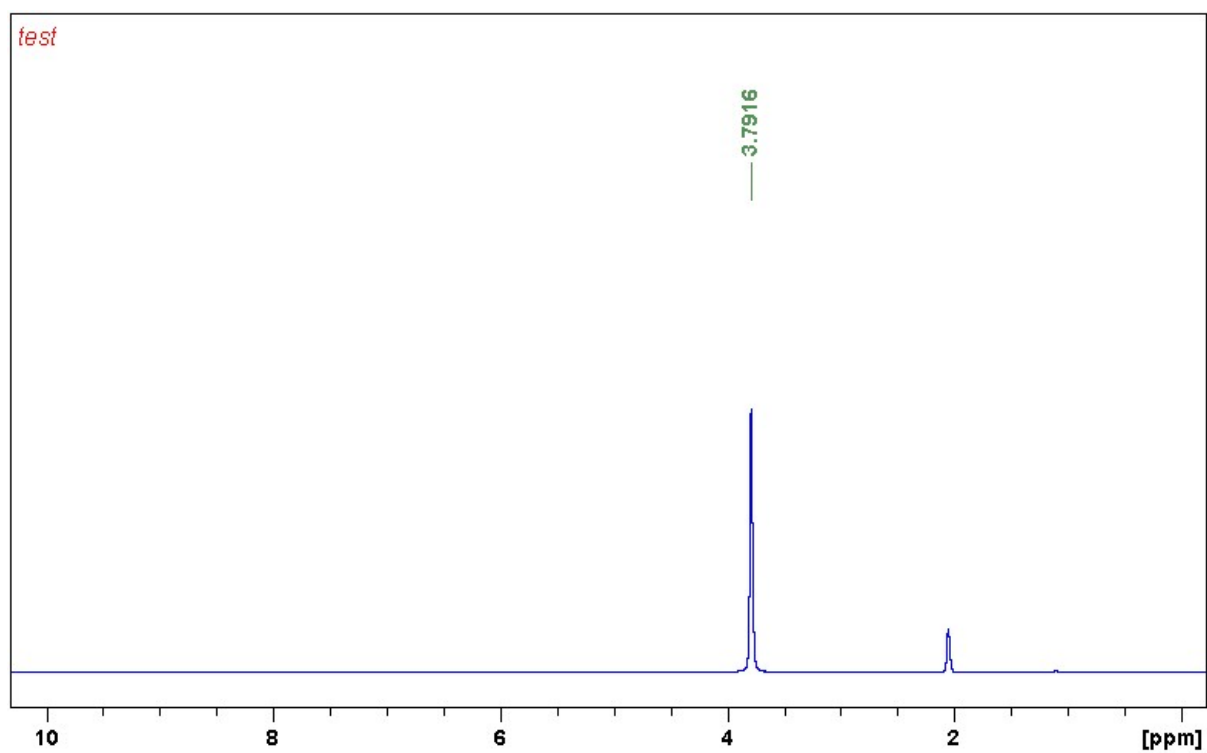
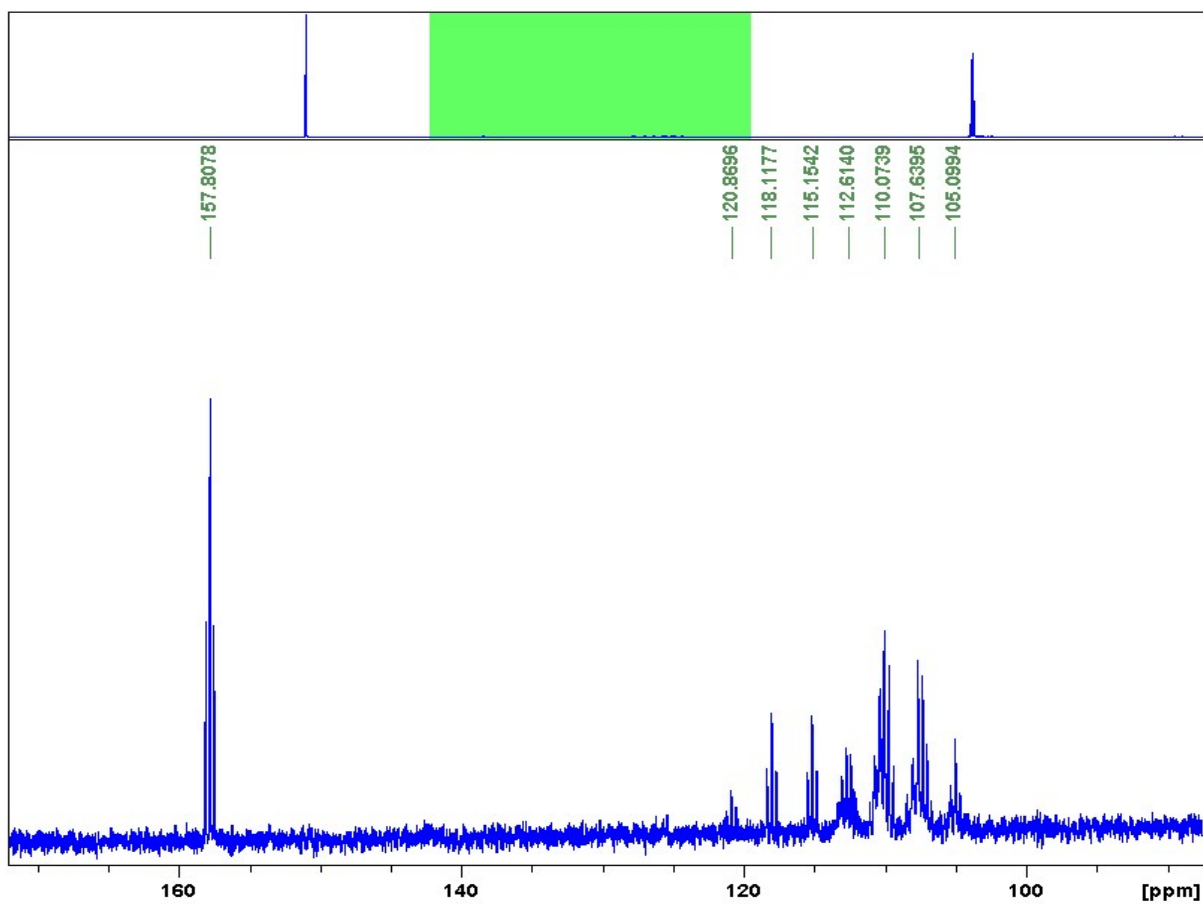


Figure S13. Mass spectrometry and HRMS data for 8.

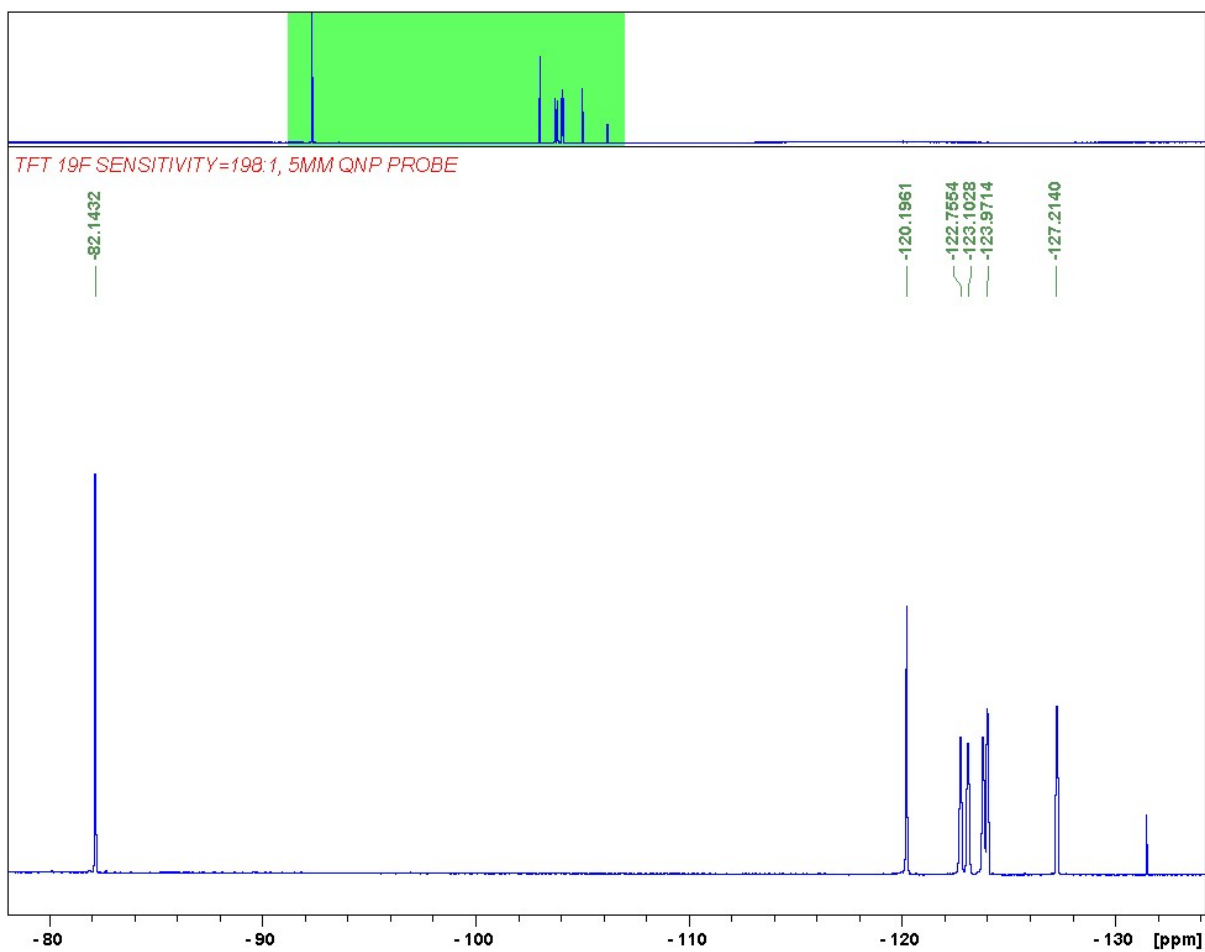
NMR spectroscopic data for commercial PFOA used in this study.



**Figure S14.** <sup>1</sup>H NMR spectrum of **PFOA** in CDCl<sub>3</sub>.

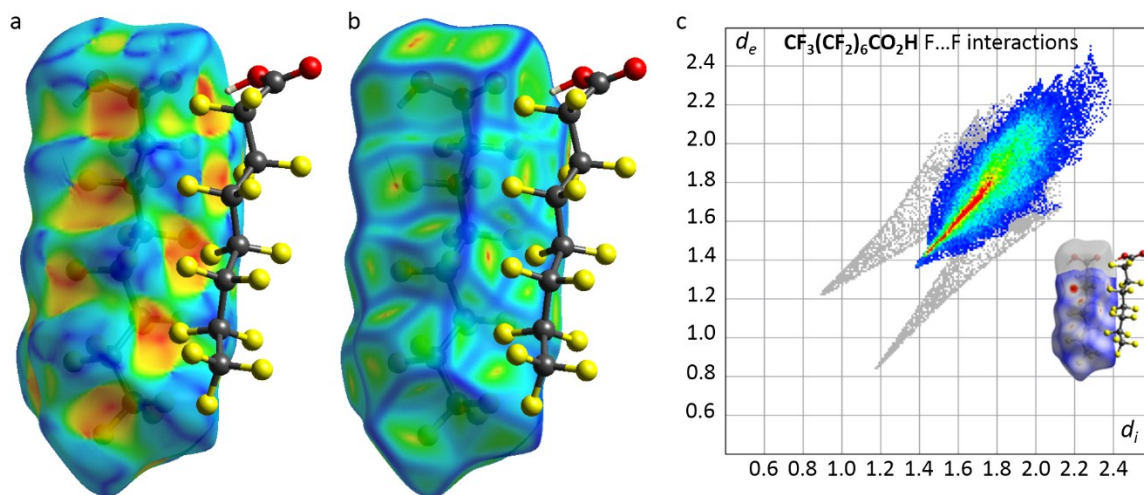


**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of PFOA in  $\text{CDCl}_3$ .

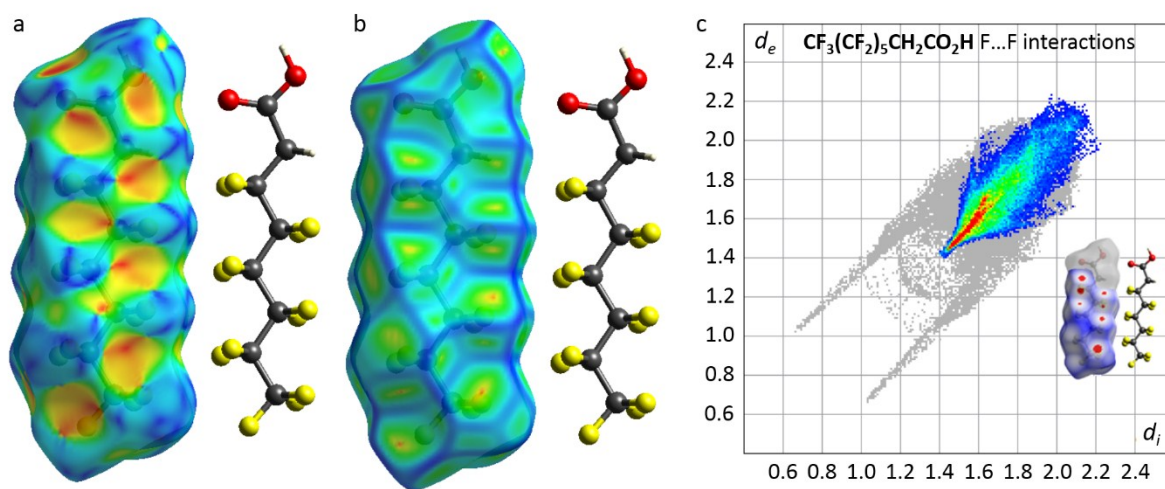


**Figure S16.**  $^{19}\text{F}$  NMR spectrum of PFOA in  $\text{CDCl}_3$ .

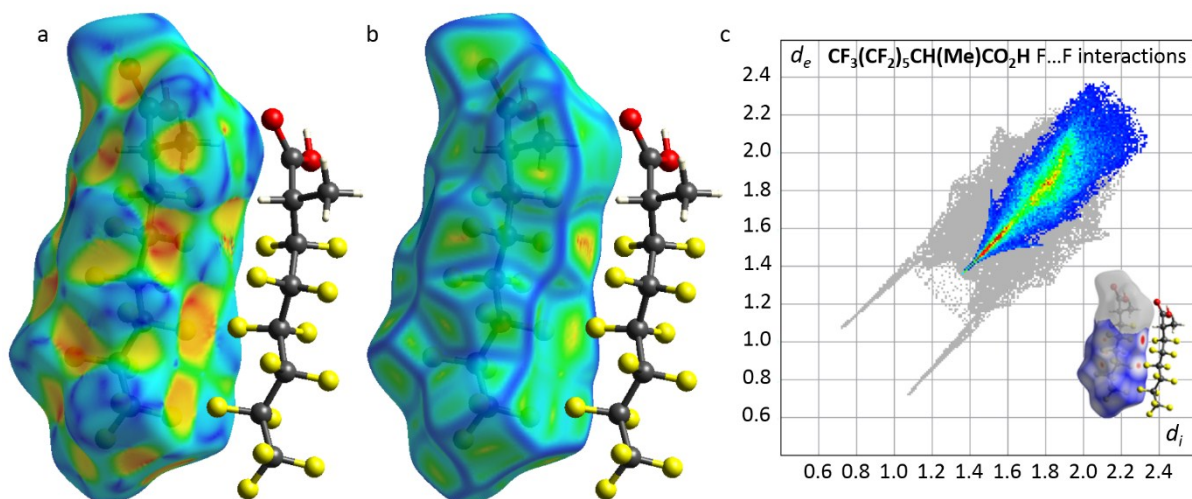
## Hirshfeld Surface analysis



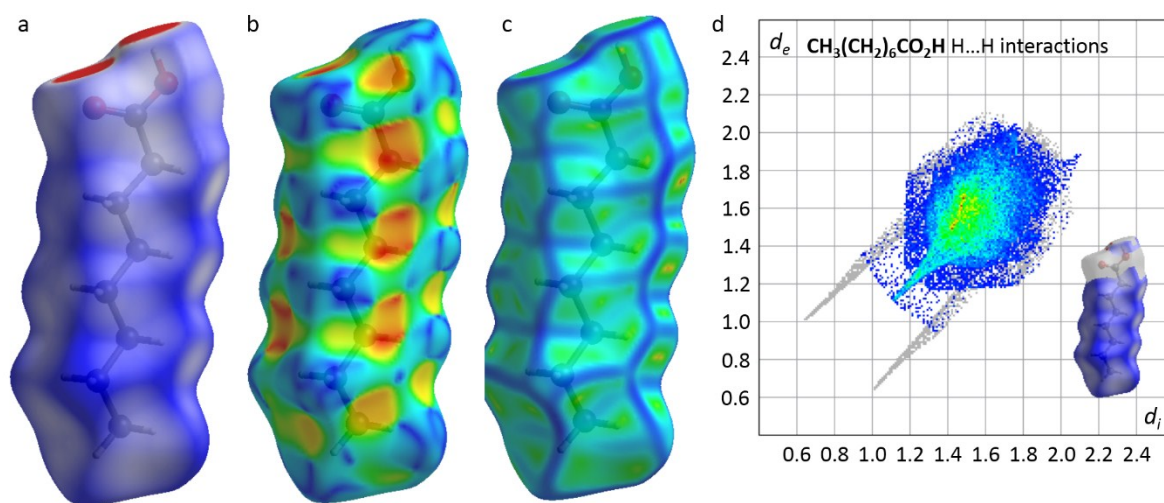
**Figure S17.** Map of (a) shape index (-1 to +1), (b) curvedness (-4 to 0.4) and (c) fingerprint plot showing the F...F interactions for PFOA.



**Figure S18.** Map of (a) shape index (-1 to +1), (b) curvedness (-4 to 0.4) and (c) fingerprint plot showing the F...F interactions for  $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$ .

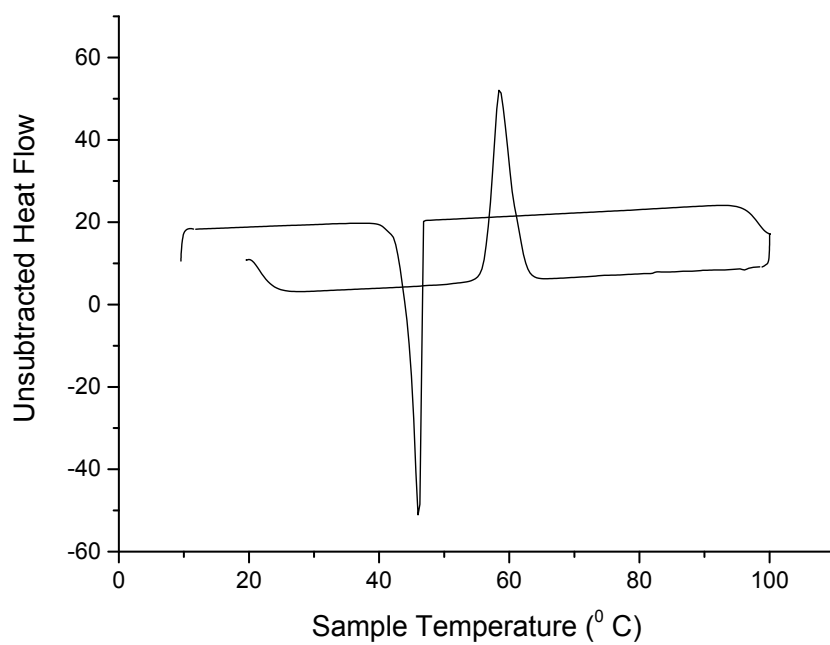


**Figure S19.** Map of (a) shape index (-1 to +1), (b) curvedness (-4 to 0.4) and (c) fingerprint plot showing the F...F interactions for  $\text{CF}_3(\text{CF}_2)_5\text{CH}(\text{Me})\text{CO}_2\text{H}$ .



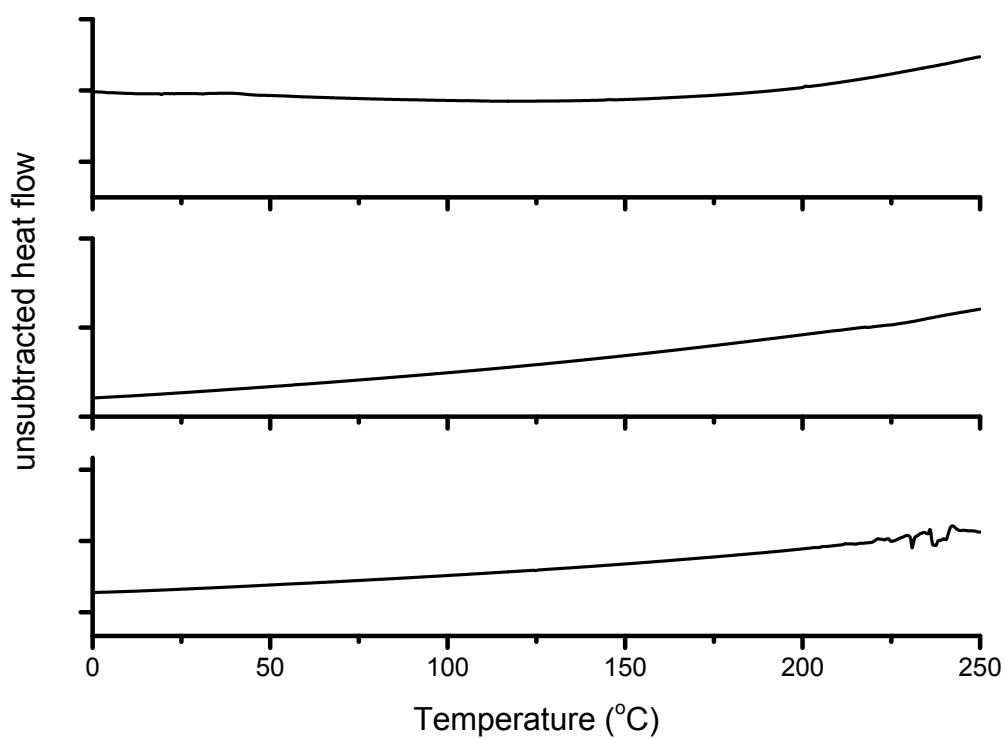
**Figure S20.** Map of (a)  $d_{\text{norm}}$  (-0.1 to 1.0), (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (d) fingerprint plot showing the H...H interactions for  $\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$ .

## Thermal characterization of hosts and host:guest complexes

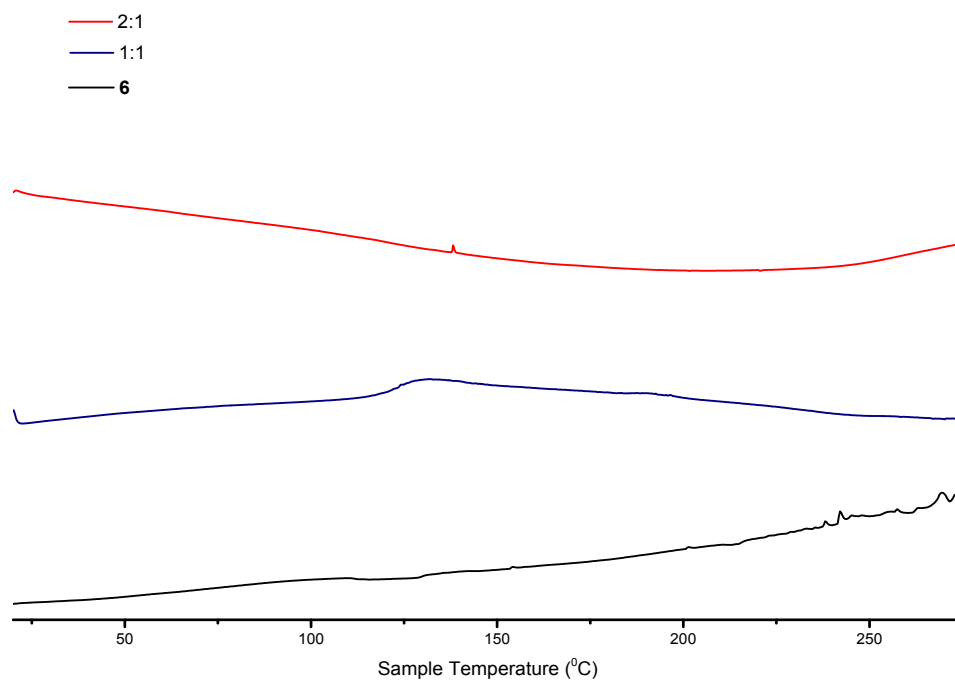


**Figure S21.** DSC Thermogram of PFOA.

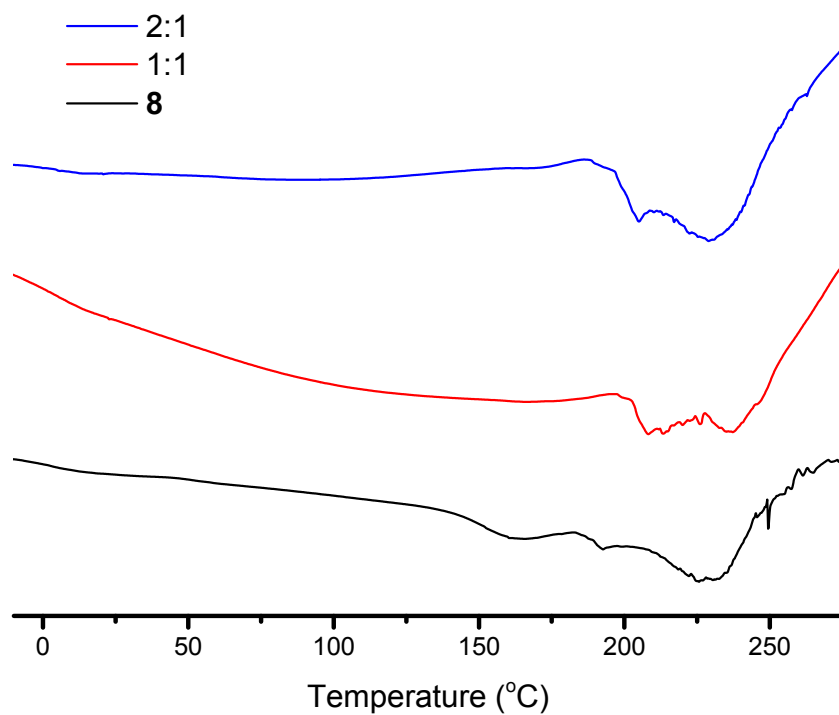




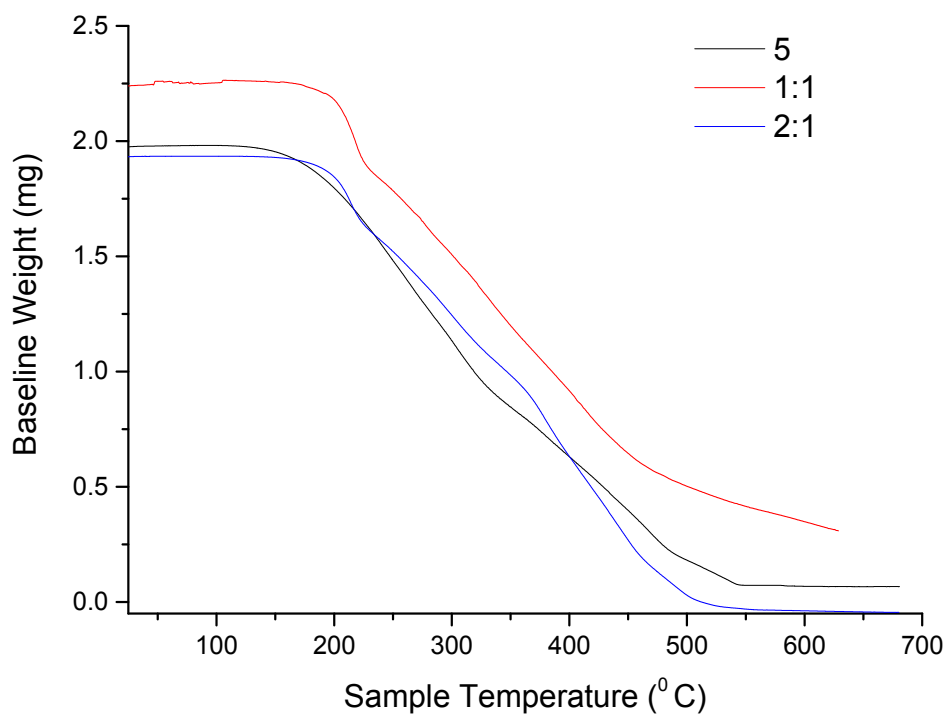
**Figure S22.** DSC Thermograms of **5** (top), 1:1 complex (middle) and 2:1 complex (bottom).



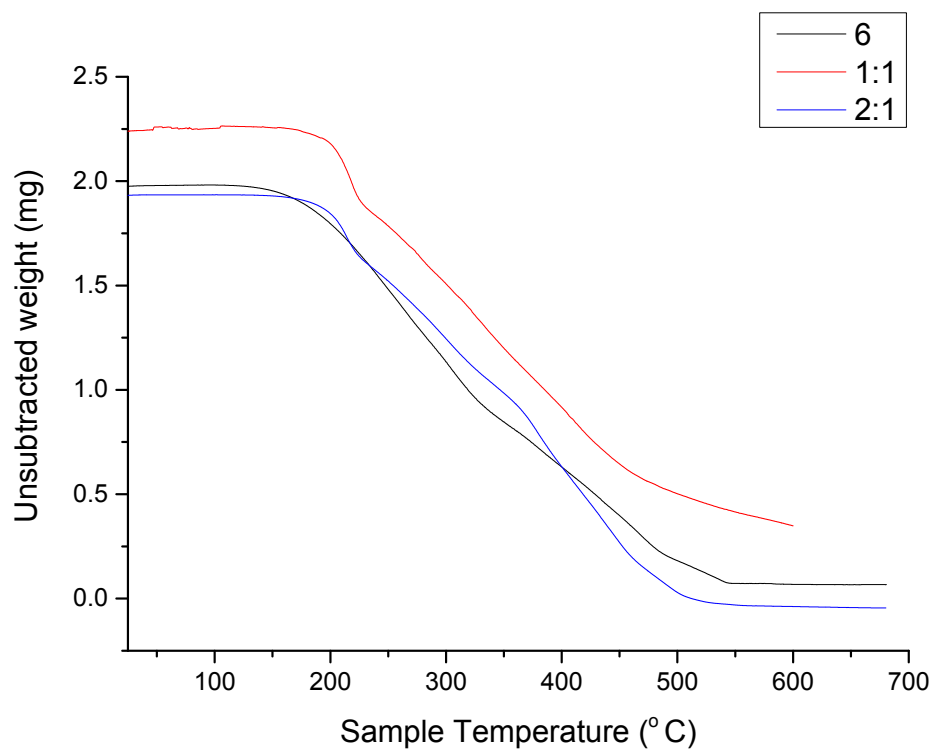
**Figure S23.** DSC Thermograms of **6** (bottom), 1:1 complex (middle) and 2:1 complex (top).



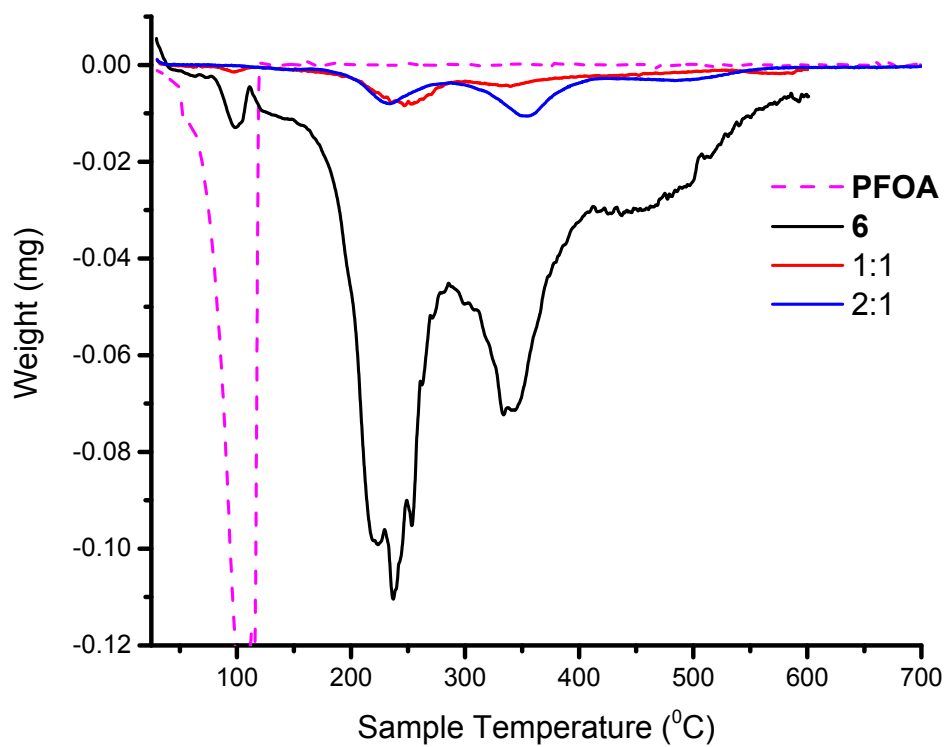
**Figure S24.** DSC Thermograms of **8** (bottom), 1:1 complex (middle) and 2:1 complex (top).



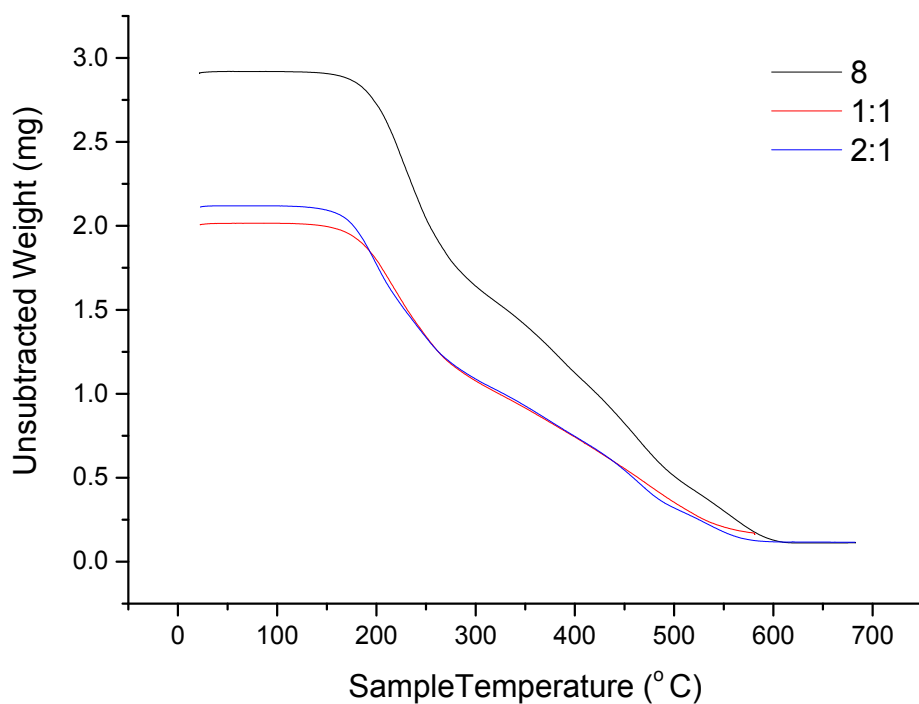
**Figure S25.** TGA of **5** and its 1:1 and 2:1 host:guest complexes.



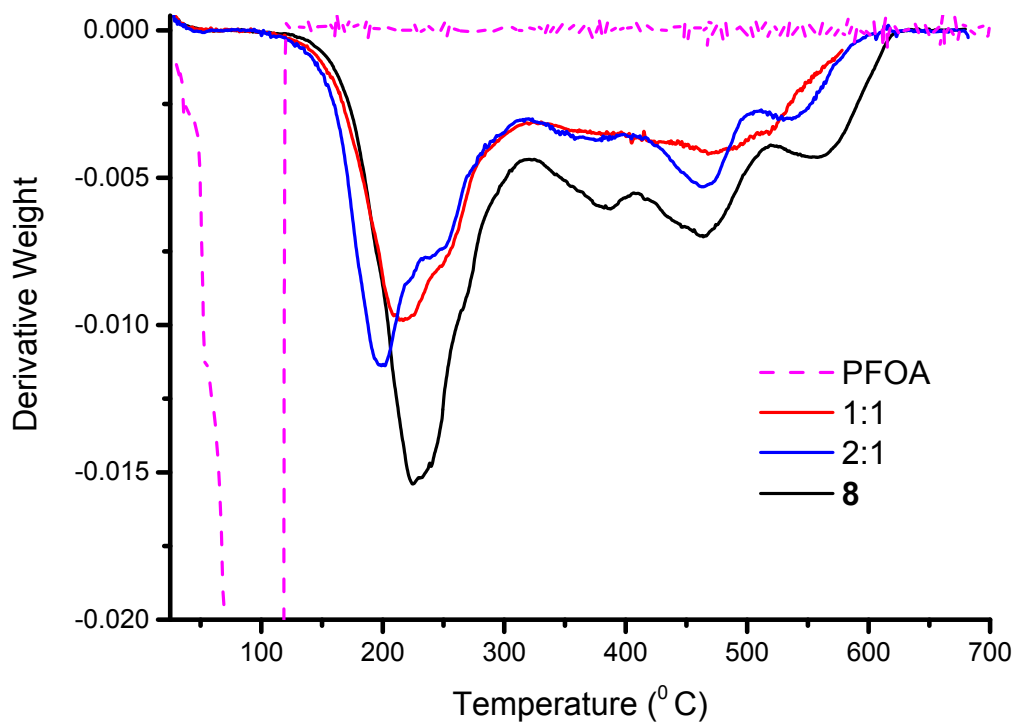
**Figure S26.** TGA of **6** and its 1:1 and 2:1 host:guest complexes.



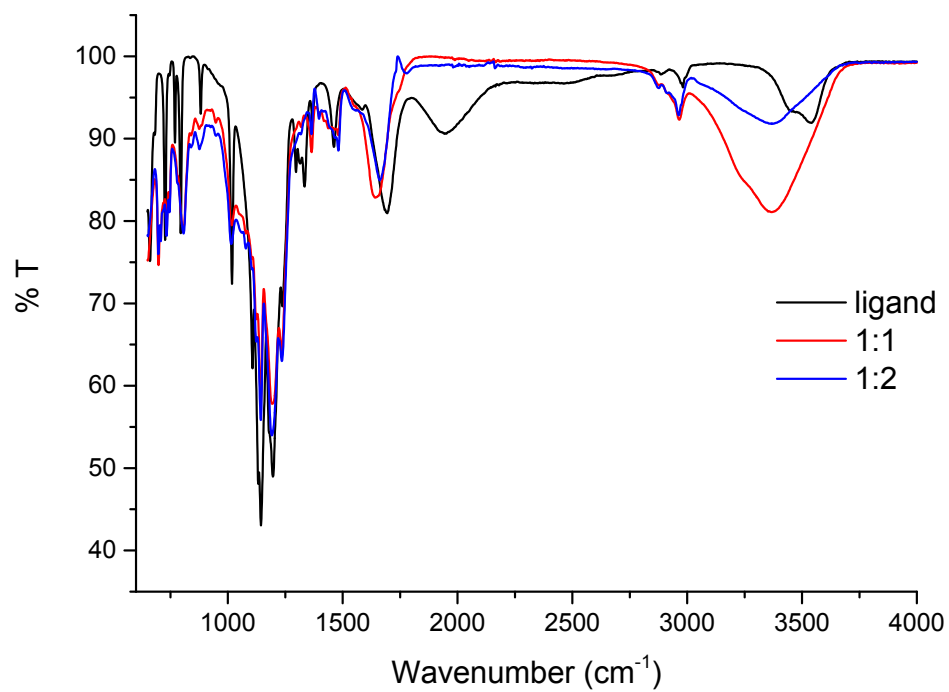
**Figure S27.** TGA (Derivative weight) of **6** and its 1:1 and 2:1 host:guest complexes.



**Figure S28.** TGA of **8** and its 1:1 and 2:1 host:guest complexes.

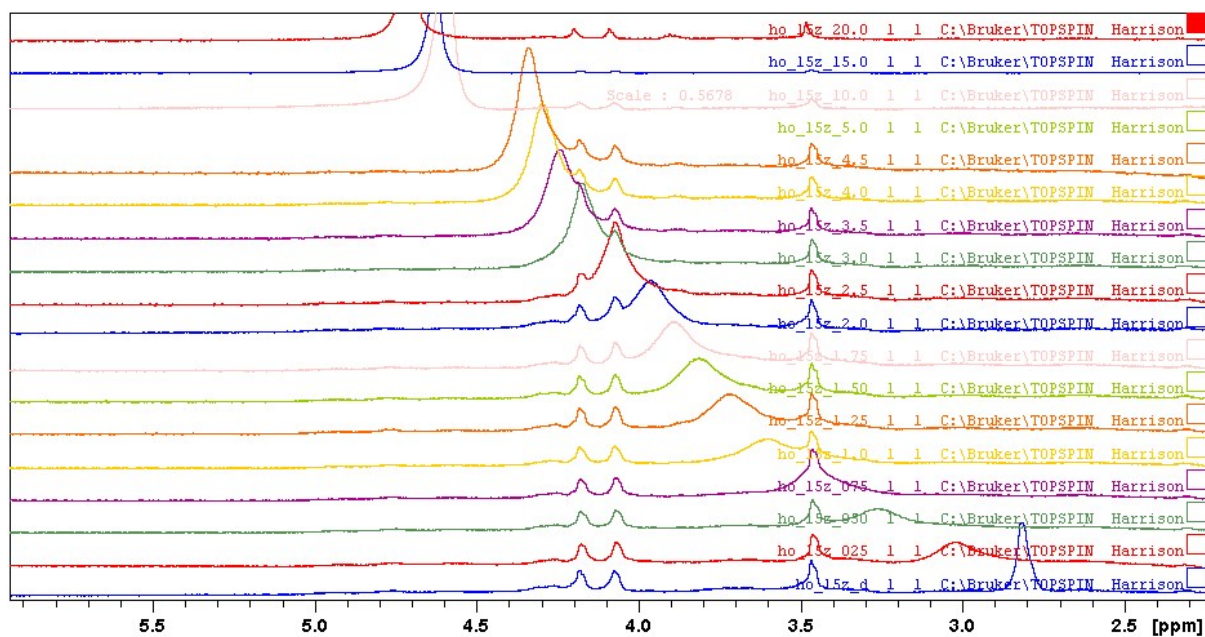


**Figure S29.** Derivative weight TGA of **8** and the 1:1 and 2:1 inclusion complexes.

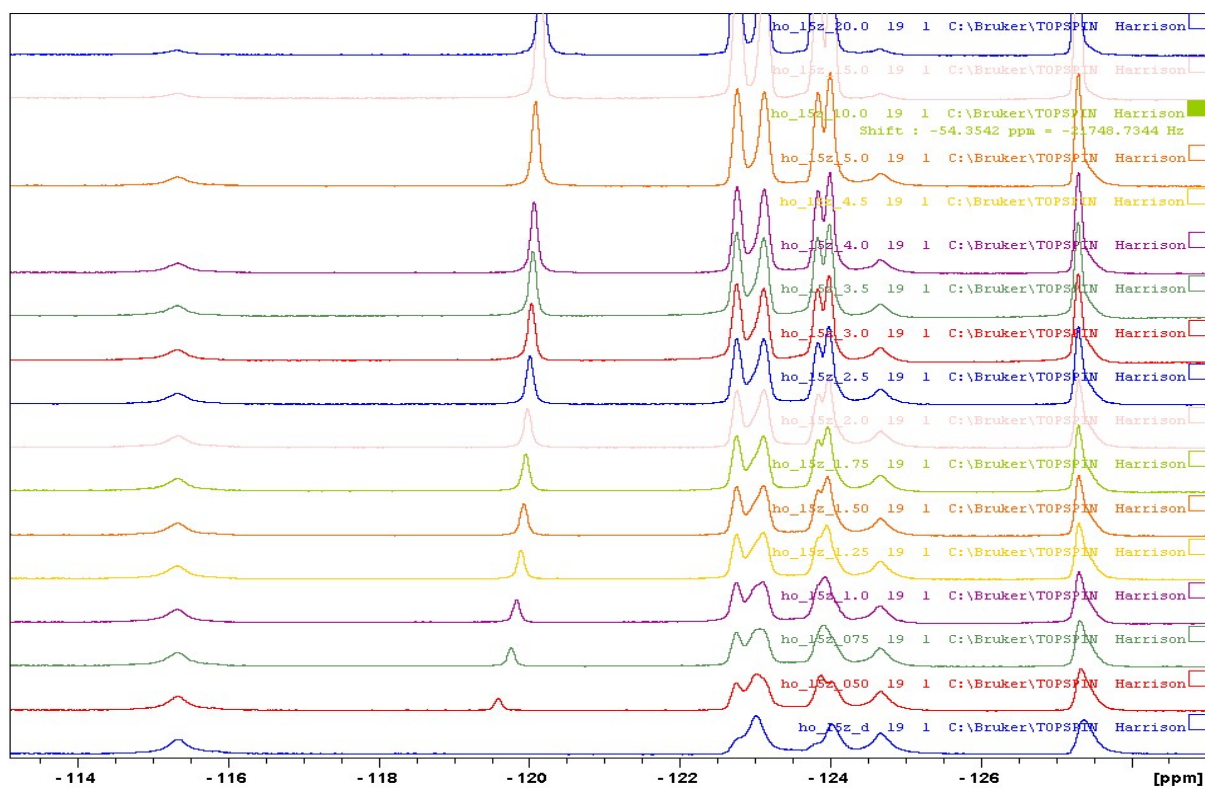


**Figure S30.** IR spectrum of **6** and its PFOA complexes.

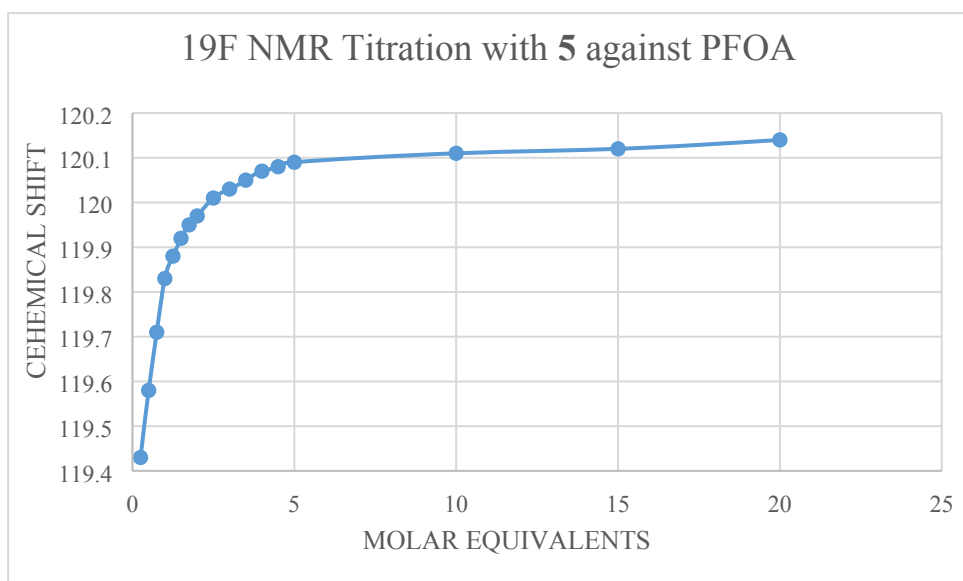
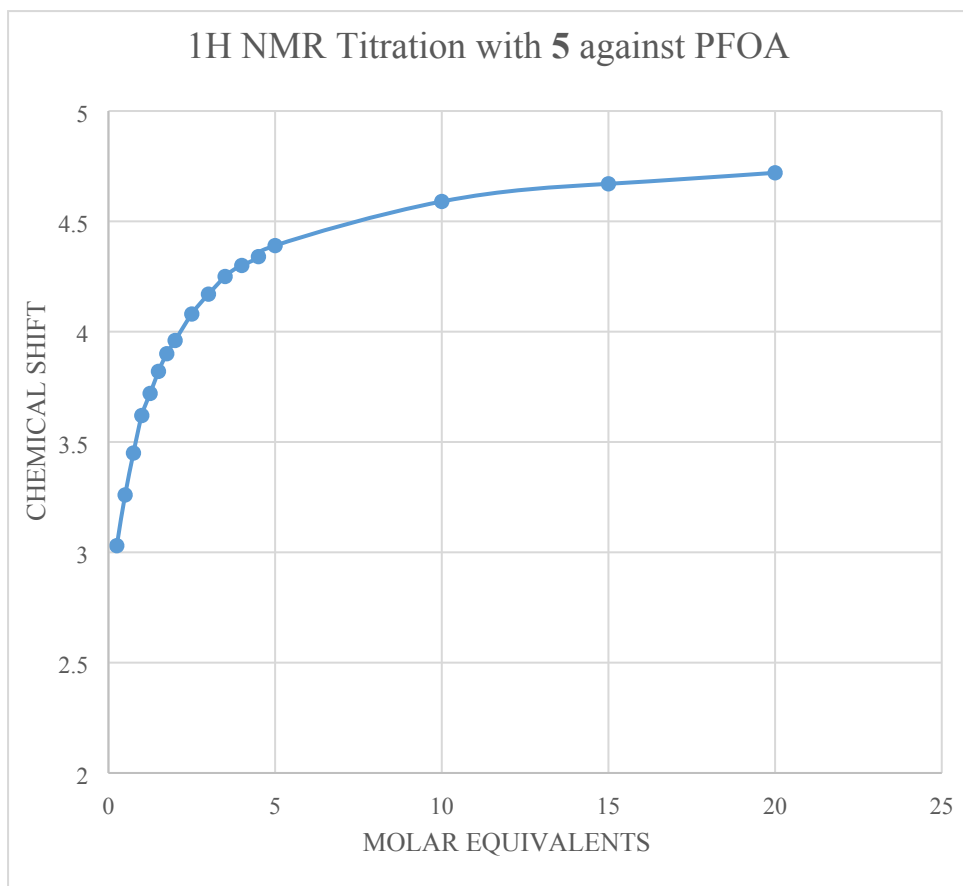
## $^1\text{H}$ and $^{19}\text{F}$ NMR titration experiments



**Figure S31.**  $^1\text{H}$  NMR titration of **5** and varying amounts of PFOA (0 – 20 eq.) in  $d_6$ -acetone at 300 K.

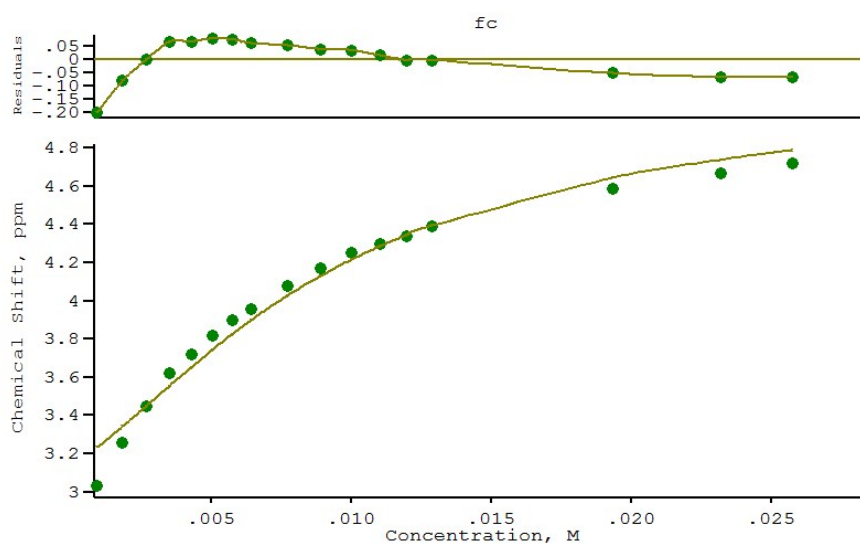


**Figure S32.**  $^{19}\text{F}$  NMR titration of **5** and varying amounts of PFOA (0 – 20 eq.) in  $d_6$ -acetone at 300 K.



**Figure S33.** Plot of  $\delta_H$  (top) and  $\delta_F$  (bottom) changes upon addition of 0-20 equivalents of PFOA.





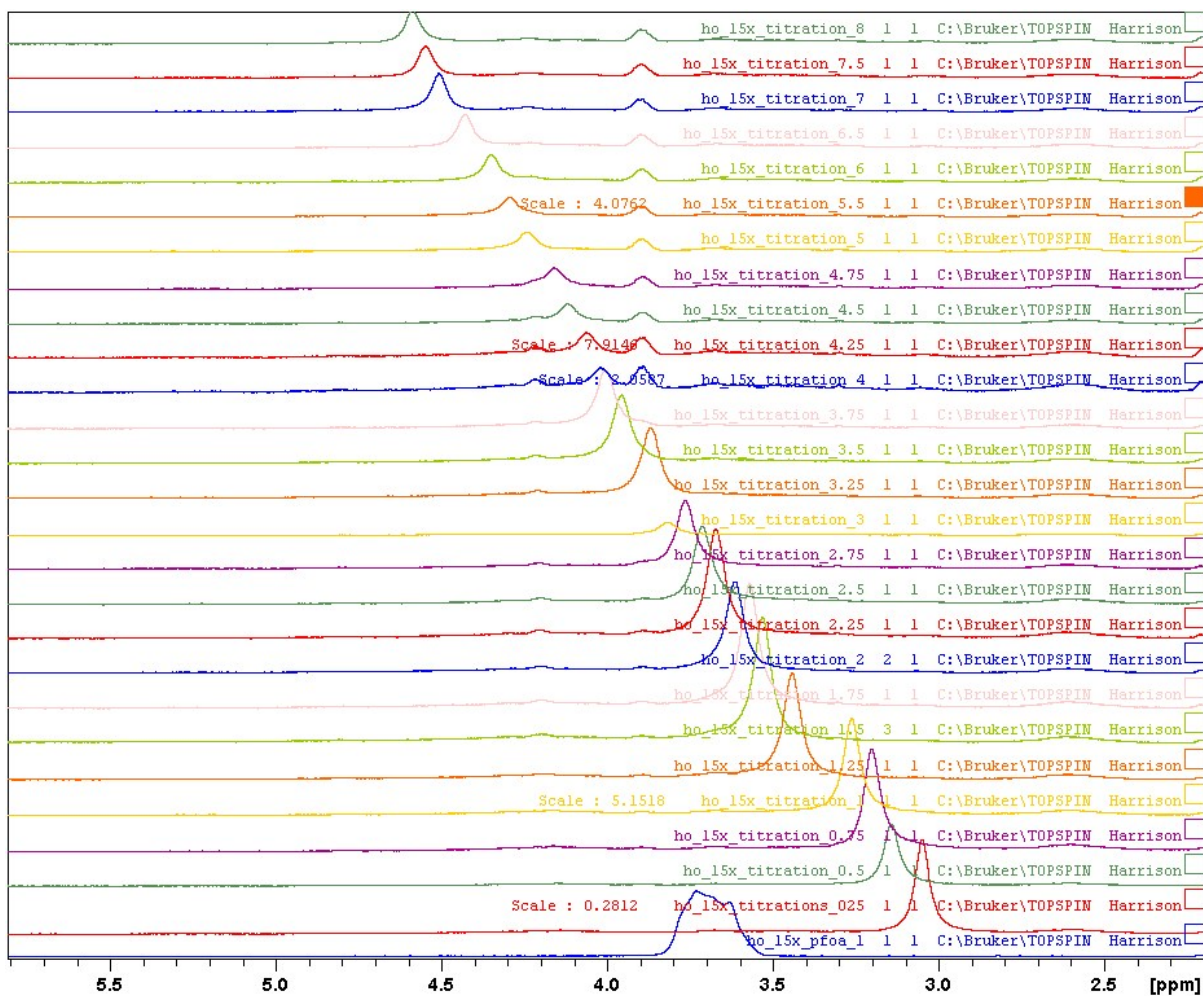
fc  
pfoa  
chemical shift

Equilibrium constants are log10 values

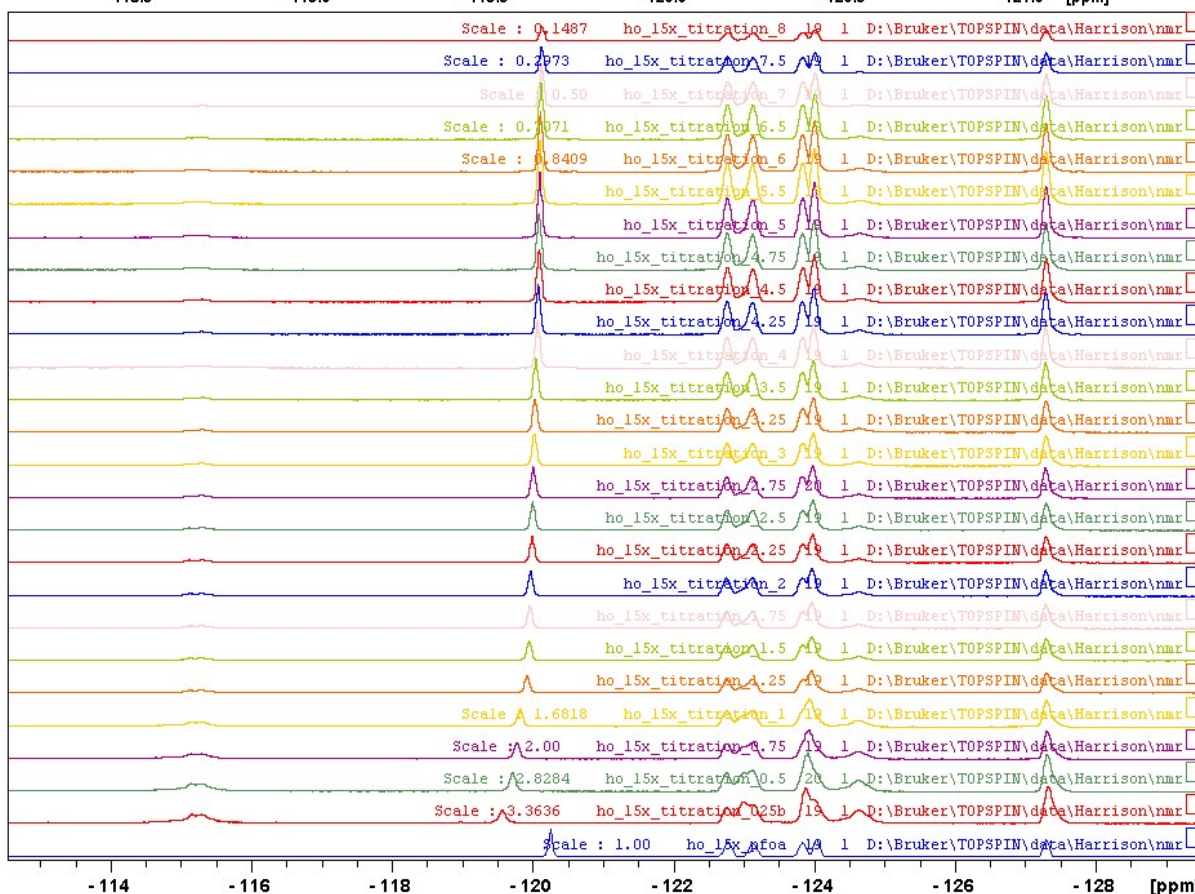
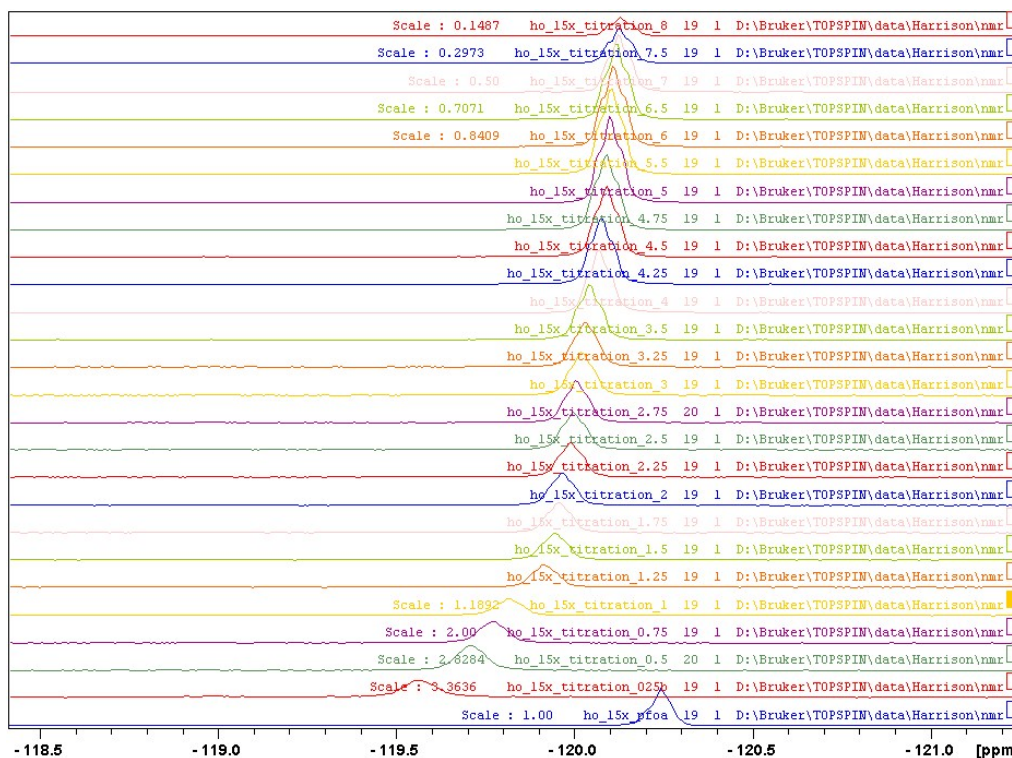
NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	2.66224E+00	1.000E-02	3.497E-01	3.316E+02	stability constant
2	1	2.05479E+00	1.000E-02	1.094E+00	5.446E+02	concentration
3	1	5.28999E+00	1.000E-02	2.063E-01	4.520E+01	chemical shift

ØRMS ERROR = 7.96E-02 MAX ERROR = 2.03E-01 AT OBS.NO. 1  
RESIDUALS SQUARED = 8.87E-02  
RFACTOR = 1.7861 PERCENT

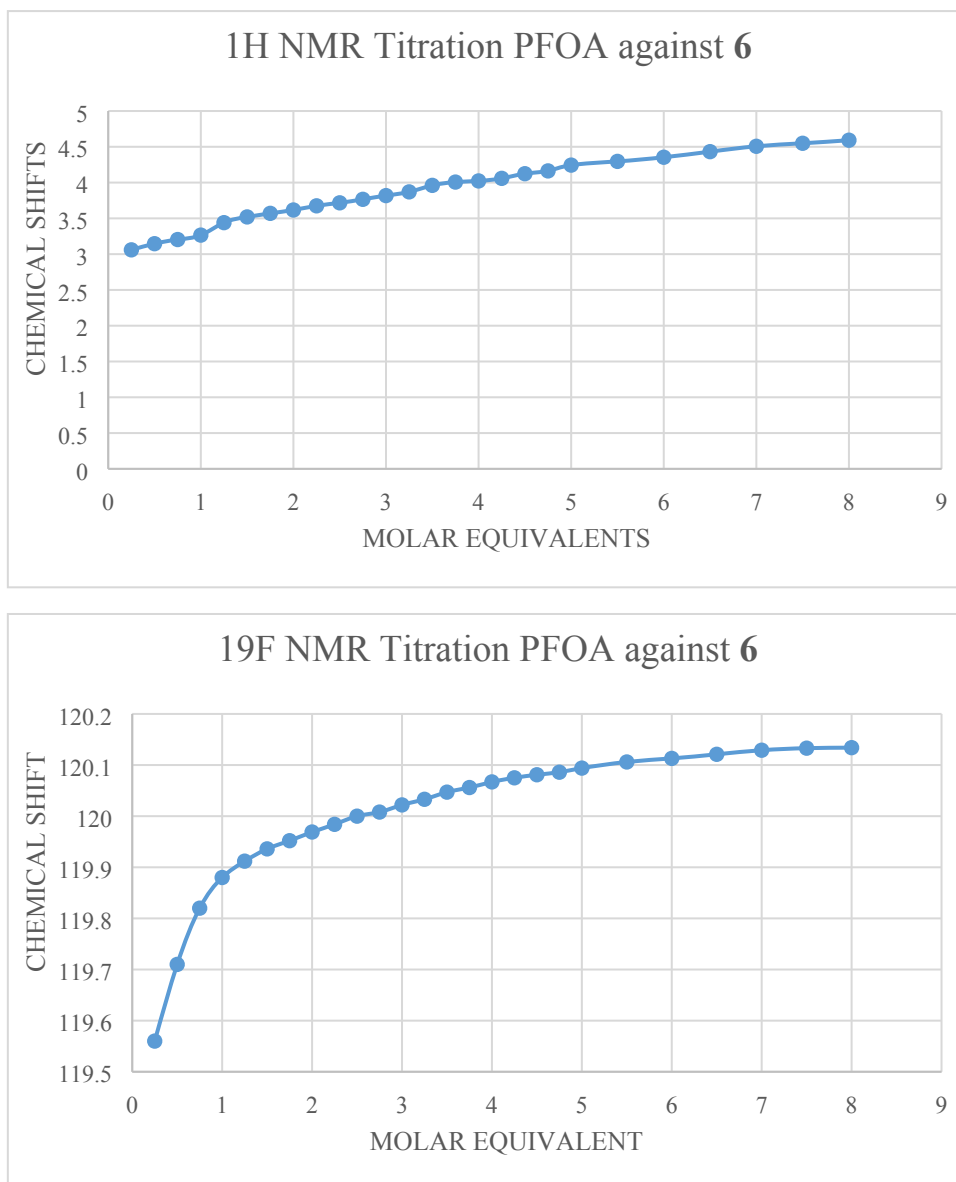
**Figure S34.** Analysis of  $\delta_H$  changes upon addition of 0-20 equivalents of PFOA.



**Figure S35.** <sup>1</sup>H NMR titration of **6** and varying amounts of PFOA (0 – 8 eq.) in d<sub>6</sub>-acetone at 300 K.

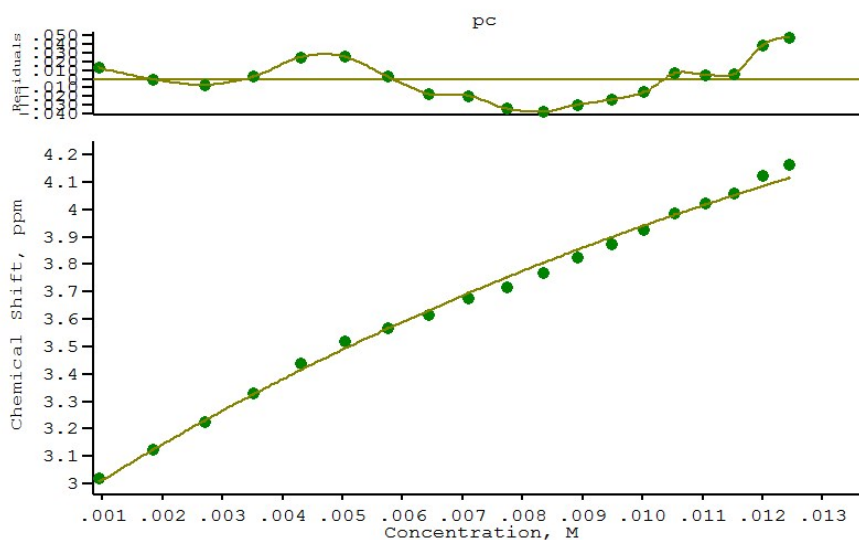


**Figure S36.**  $^{19}\text{F}$  NMR titration of **6** and varying amounts of PFOA (0 – 8 eq.) in  $\text{d}_6$ -acetone at 300 K.



**Figure S37.** Plot of  $\delta_H$  (top) and  $\delta_F$  (bottom) changes upon addition of 0-8 equivalents of PFOA.





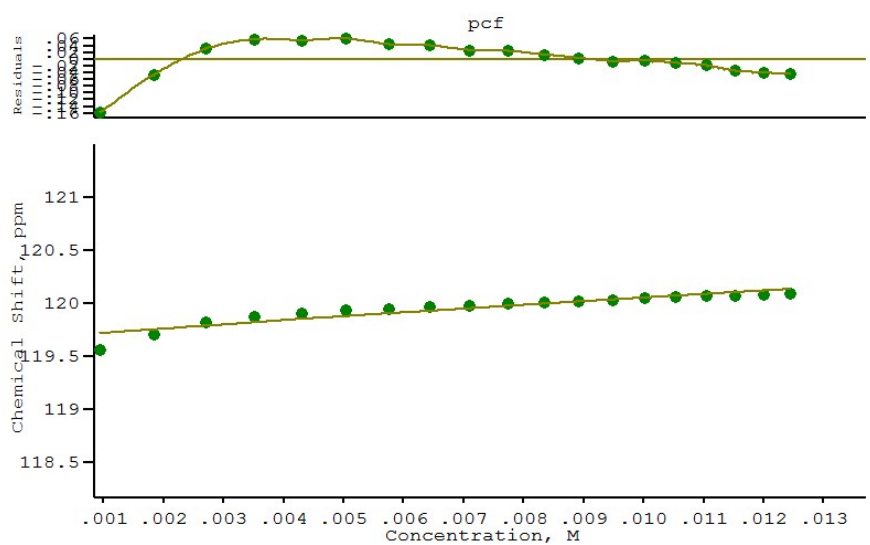
pc  
pfoa  
chemical shift

Equilibrium constants are log10 values

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	1.90154E+00	1.000E-02	2.181E-01	1.640E+04	stability constant
2	1	-6.39419E+00	1.000E-02	6.270E+00	4.585E+04	concentration
3	1	6.12742E+00	1.000E-02	6.402E-01	7.795E+03	chemical shift

ØRMS ERROR = 2.54E-02 MAX ERROR = 4.75E-02 AT OBS.NO. 19  
RESIDUALS SQUARED = 1.03E-02  
RFACOR = 0.6300 PERCENT

**Figure S38.** Analysis of  $\delta_H$  changes upon addition of 0-8 equivalents of PFOA.



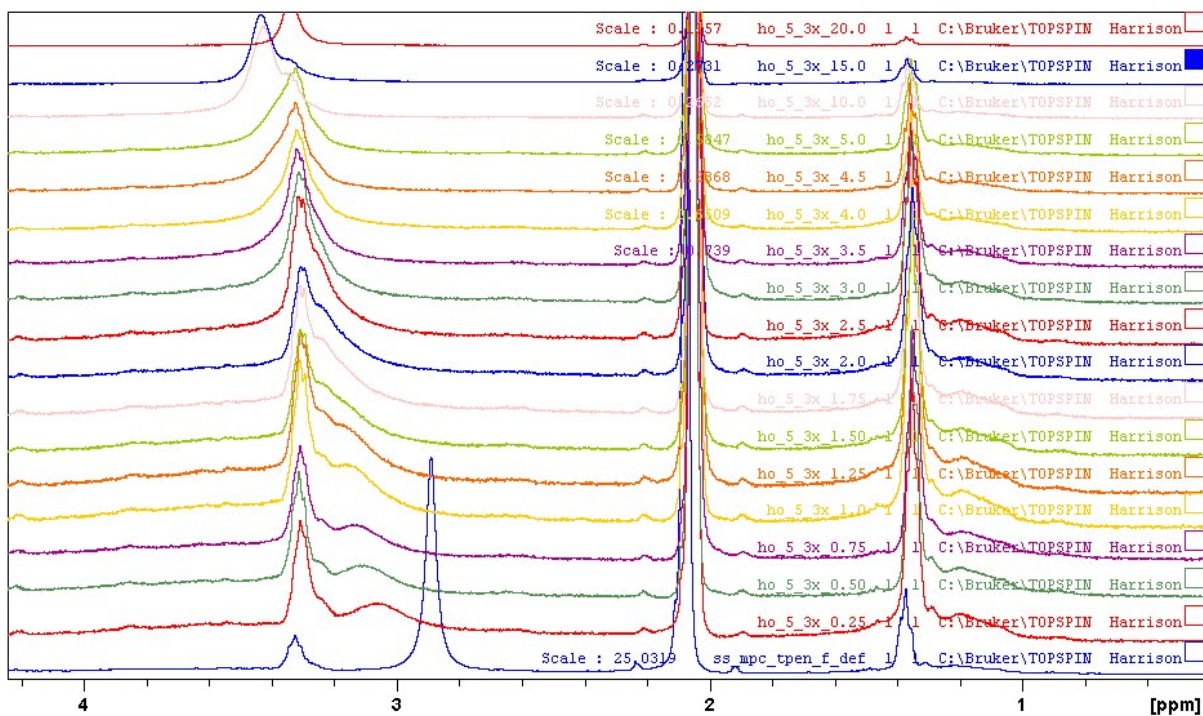
pcf  
pfoa  
chemical shift

Equilibrium constants are log10 values

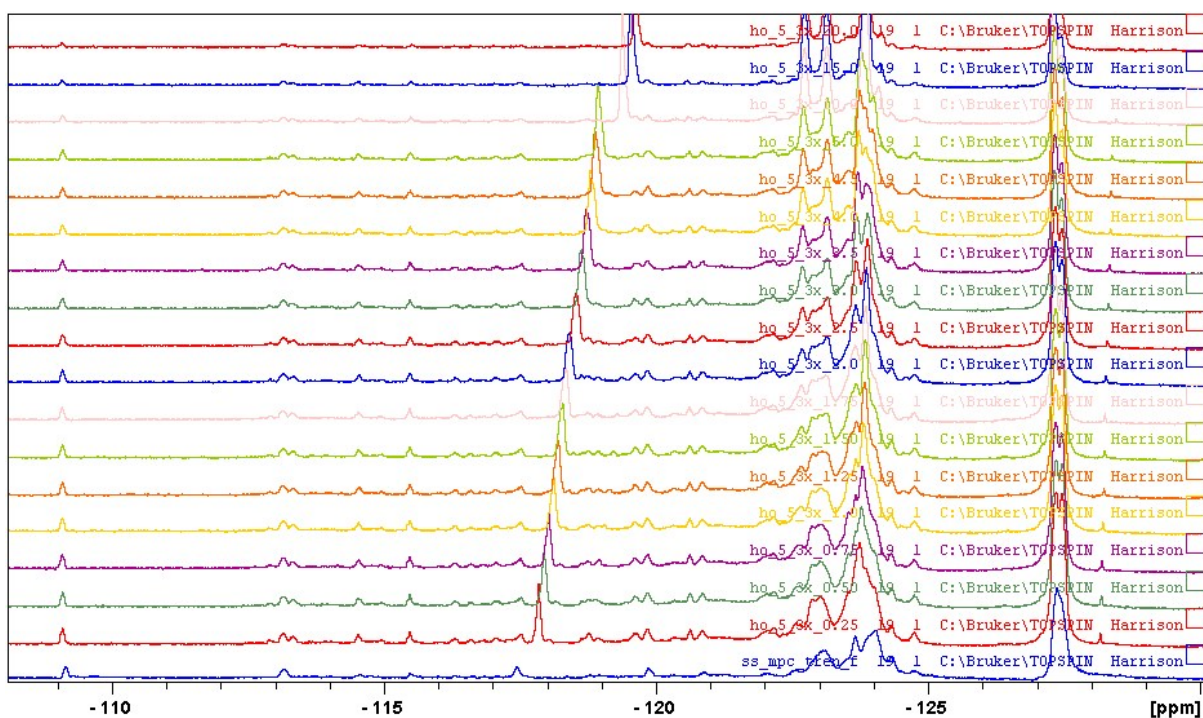
NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	1.14118E+00	1.000E-02	1.991E-01	1.070E+04	stability constant
2	1	6.21818E+01	1.000E-02	4.527E+01	3.535E+04	concentration
3	1	1.23168E+02	1.000E-02	1.155E+00	7.467E+03	chemical shift

ØRMS ERROR = 5.52E-02 MAX ERROR = 1.59E-01 AT OBS.NO. 1  
RESIDUALS SQUARED = 4.88E-02  
RFACOR = 0.0422 PERCENT

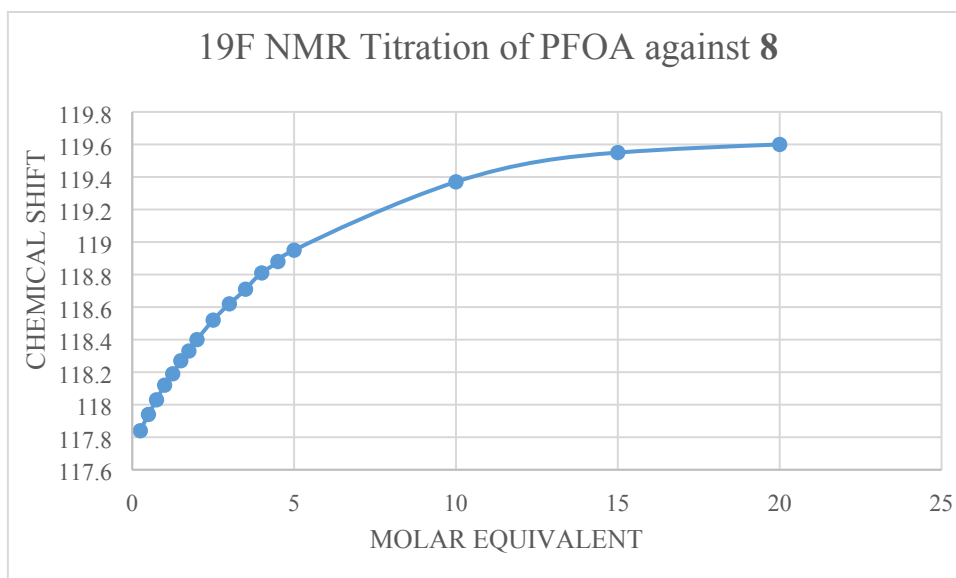
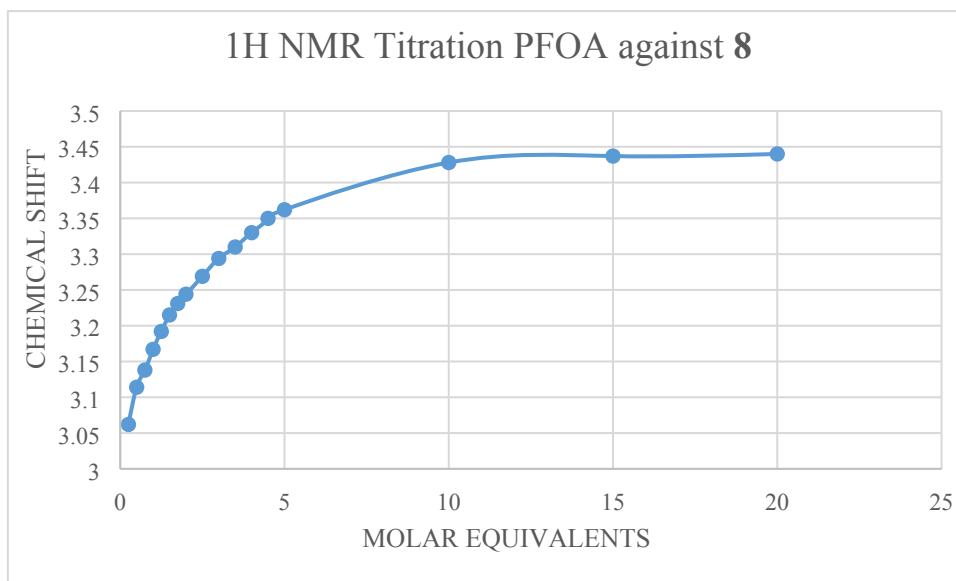
**Figure S39.** Analysis of  $\delta_F$  changes upon addition of 0-8 equivalents of PFOA.



**Figure S40.**  $^1\text{H}$  NMR titration of **8** and varying amounts of PFOA (0 – 20 eq.) in  $\text{d}_6$ -acetone at 300 K.

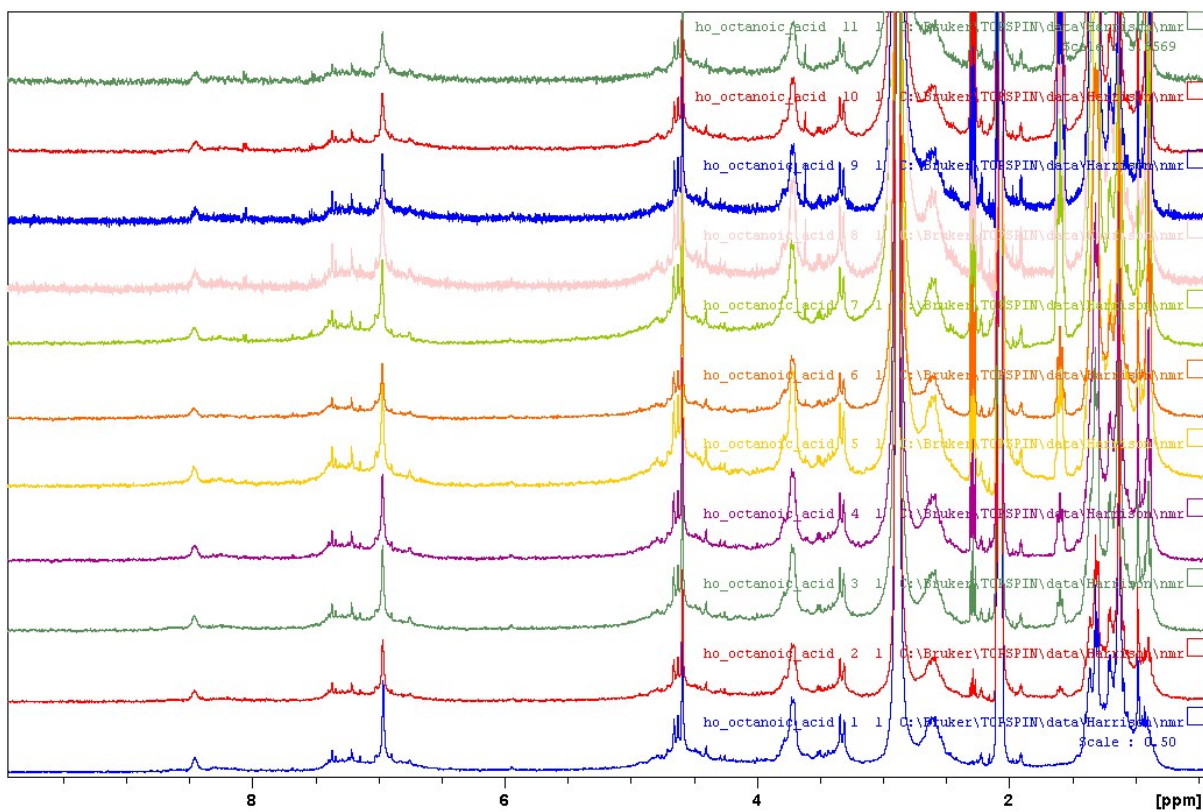


**Figure S41.**  $^{19}\text{F}$  NMR titration of **8** and varying amounts of PFOA (0 – 20 eq.) in  $\text{d}_6$ -acetone at 300 K.

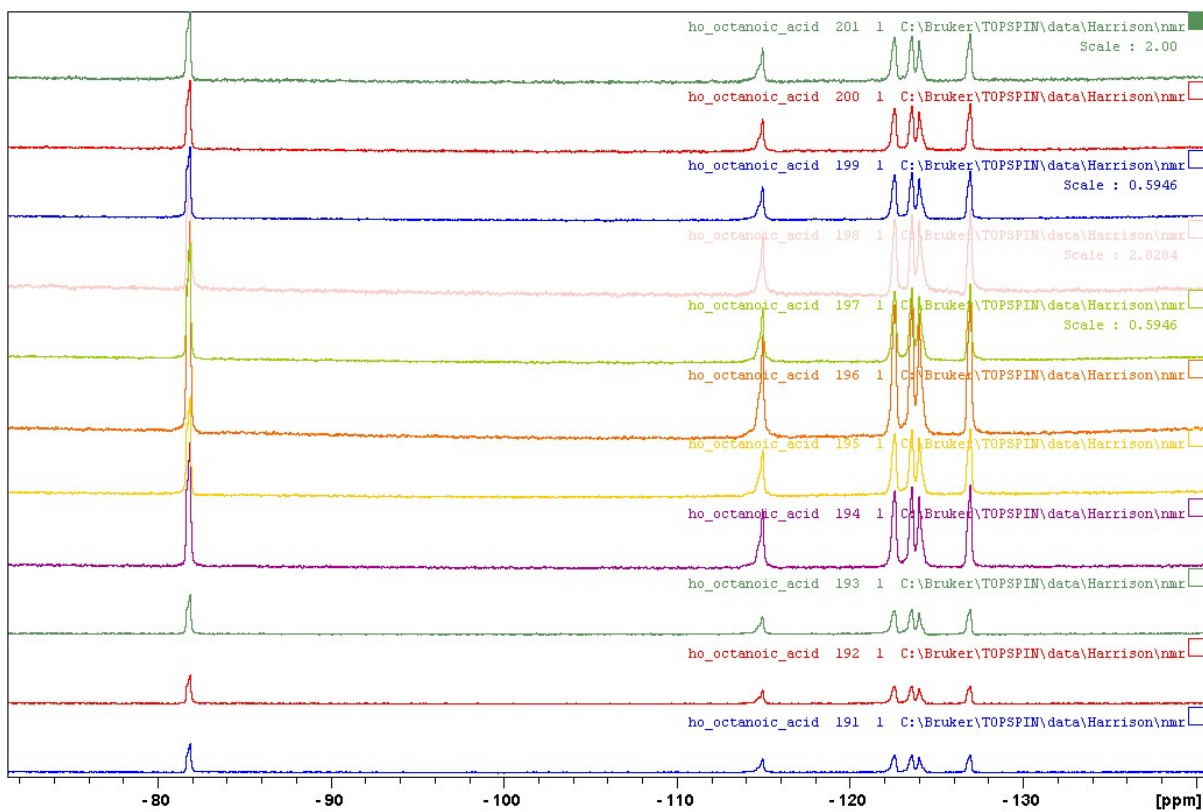


**Figure S42.** Plot of  $\delta_H$  (top) and  $\delta_F$  (bottom) changes upon addition of 0-20 equivalents of PFOA.

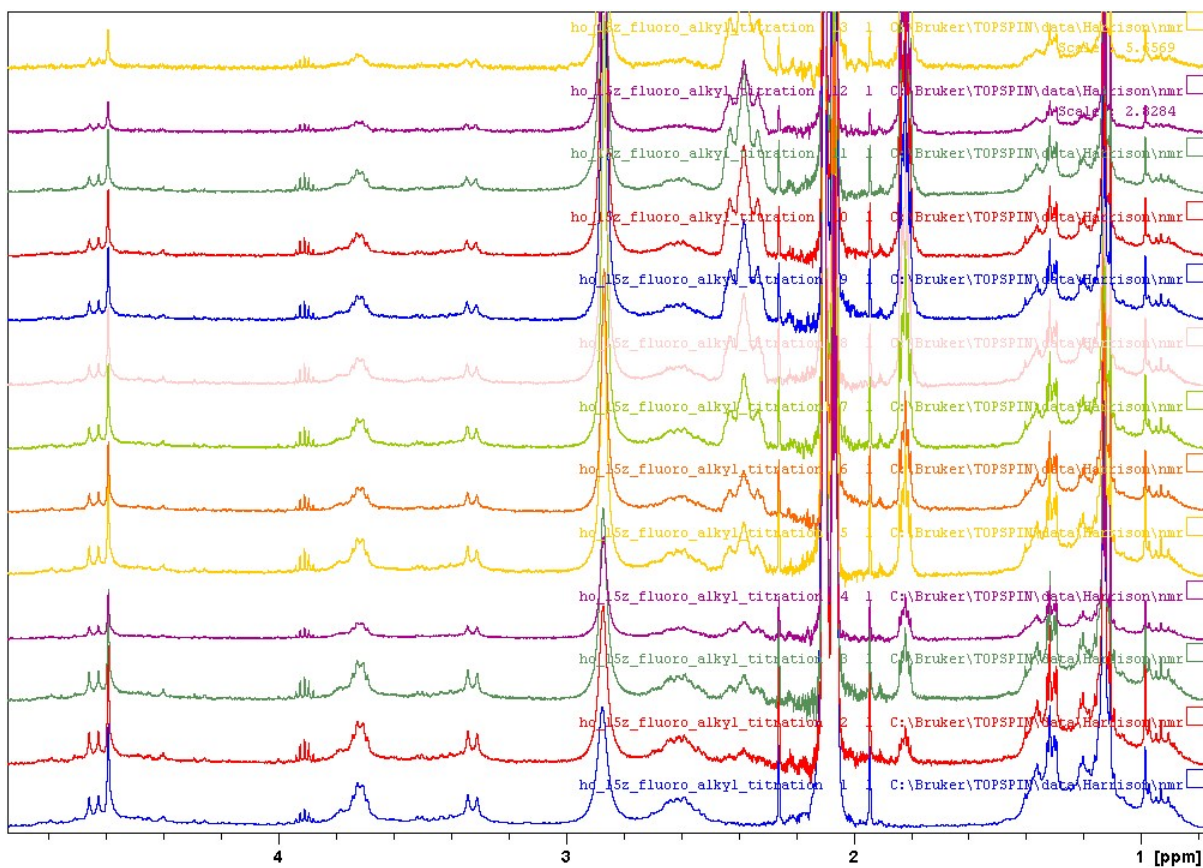




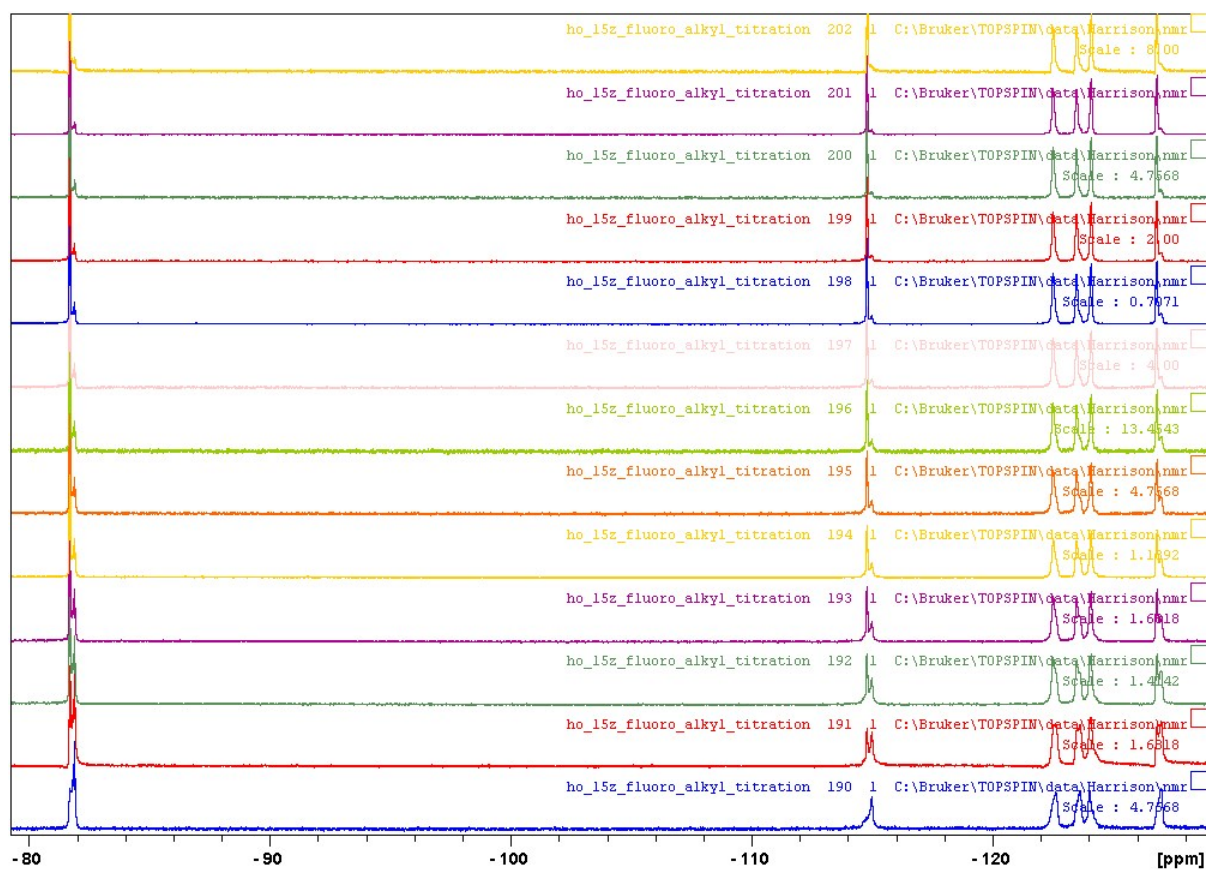
**Figure S43.**  $^1\text{H}$  NMR titration of **5** and varying amounts of octanoic acid (0 – 10 eq.) in  $d_6$ -acetone at 300 K.



**Figure S44.**  $^{19}\text{F}$  NMR titration of **5** and varying amounts of octanoic acid (0 – 10 eq.) in  $d_6$ -acetone at 300 K.

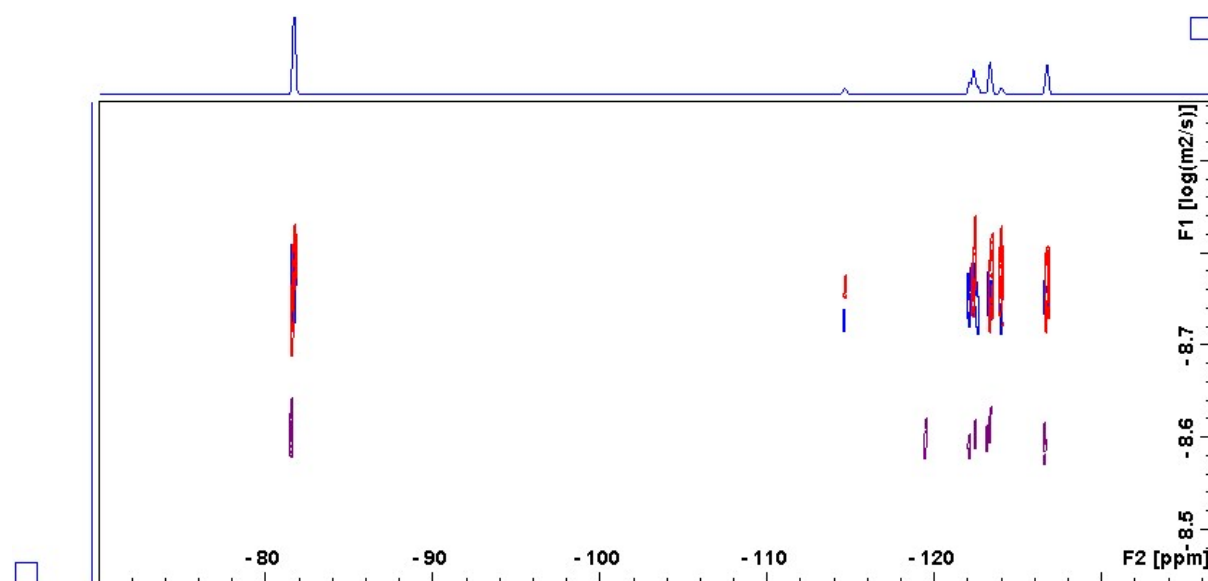


**Figure S45.**  $^1\text{H}$  NMR titration of **5** and varying amounts of  $\{\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\}_2$  (0 – 20 eq.) in  $d_6$ -acetone at 300 K.

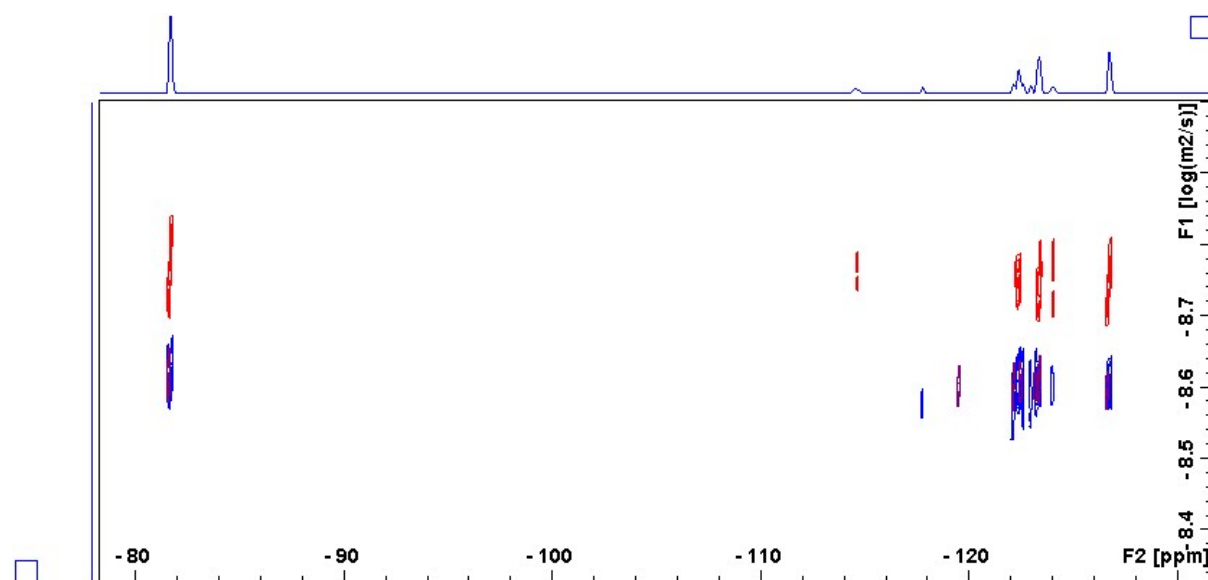


**Figure S46.**  $^{19}\text{F}$  NMR titration of **5** and varying amounts of  $\{\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\}_2$  (0 – 20 eq.) in  $d_6$ -acetone at 300 K.

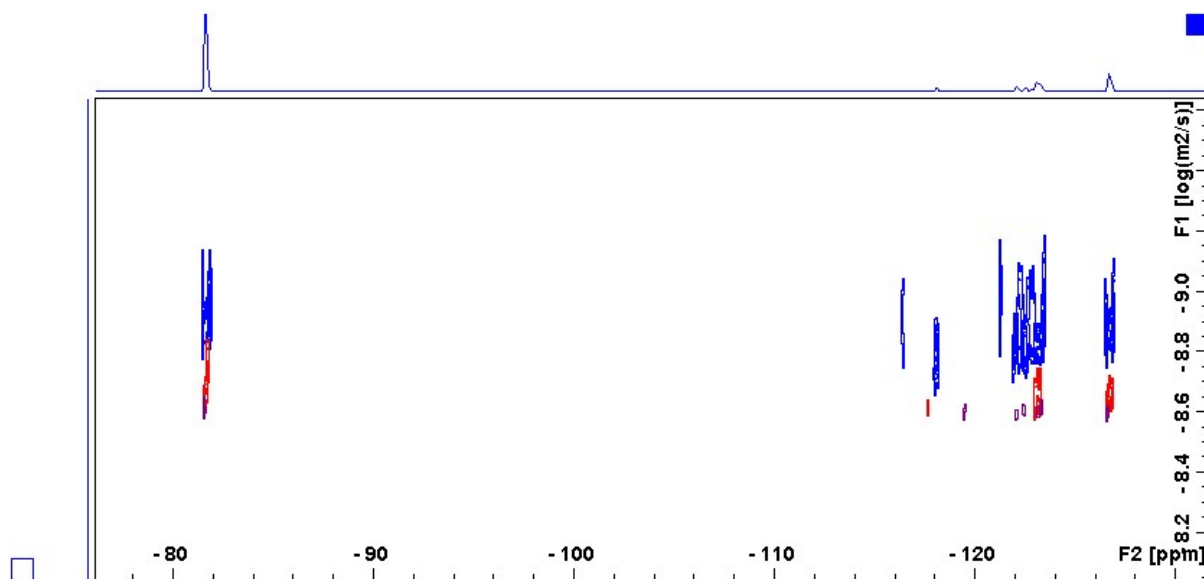
## $^{19}\text{F}$ DOSY spectroscopy



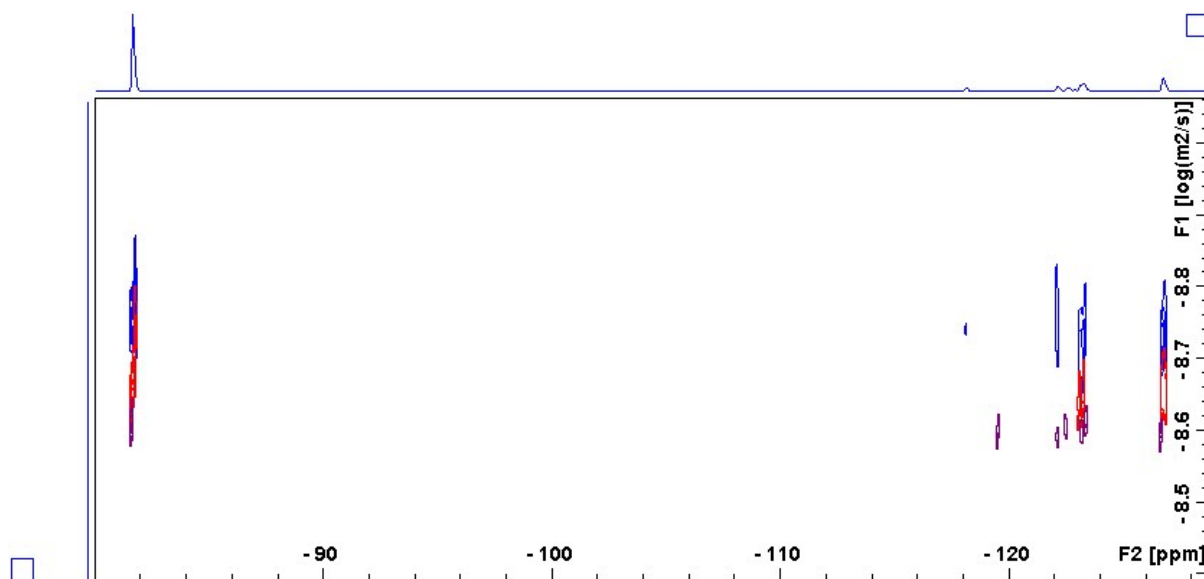
**Figure S47.**  $^{19}\text{F}$  DOSY spectra of **5** (red) the 2:1 complex (blue) and PFOA (purple) in  $d_6$ -Acetone at 300 K.



**Figure S48.**  $^{19}\text{F}$  DOSY spectra of **6** (red) the 2:1 complex (blue) and PFOA (purple) in  $d_6$ -Acetone at 300 K.



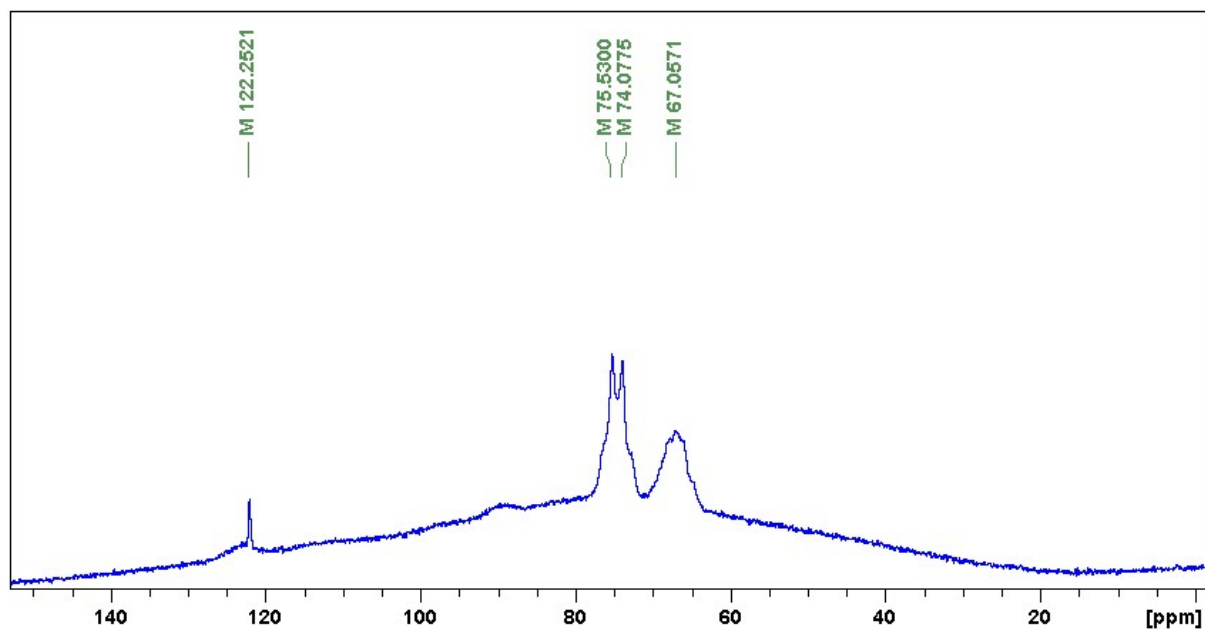
**Figure S49.**  $^{19}\text{F}$  DOSY spectra of **8** (red) the 1:1 complex (blue) and PFOA (purple) in  $\text{d}_6$ -Acetone at 300 K.



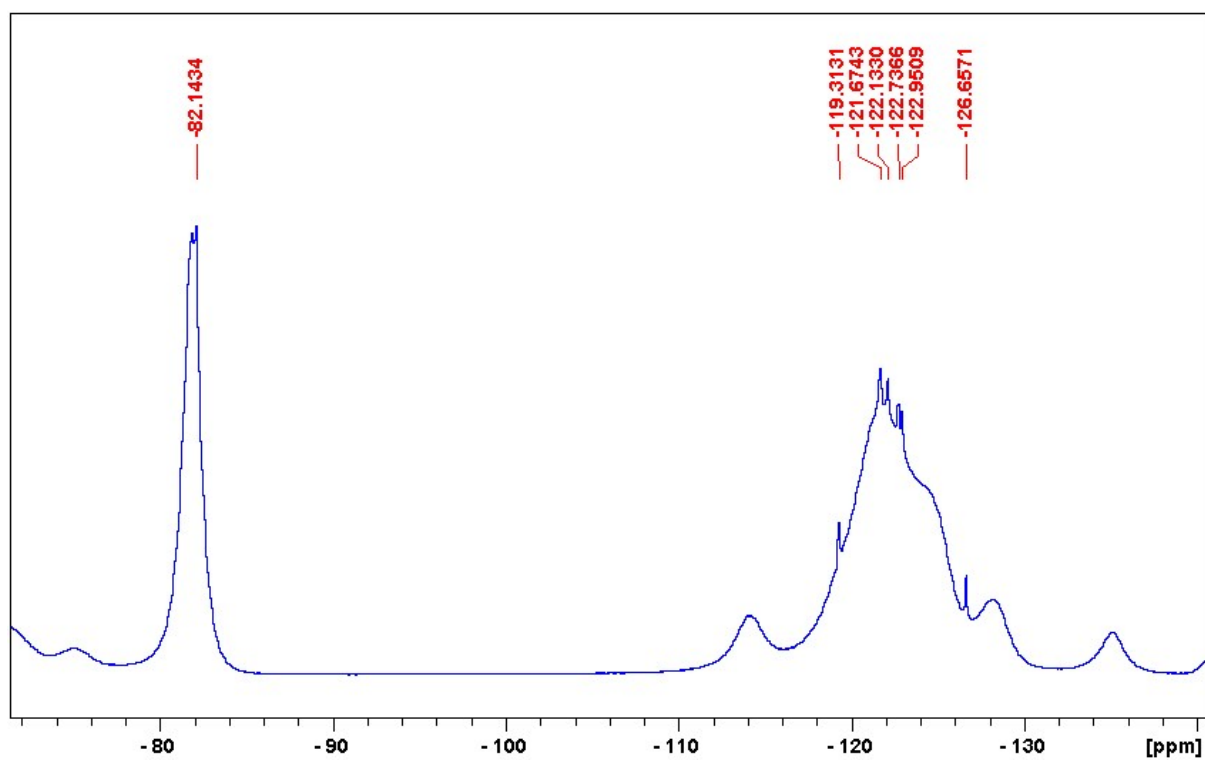
**Figure S50.**  $^{19}\text{F}$  DOSY spectra of **8** (red) the 2:1 complex (blue) and PFOA (purple) in  $\text{d}_6$ -Acetone at 300 K.



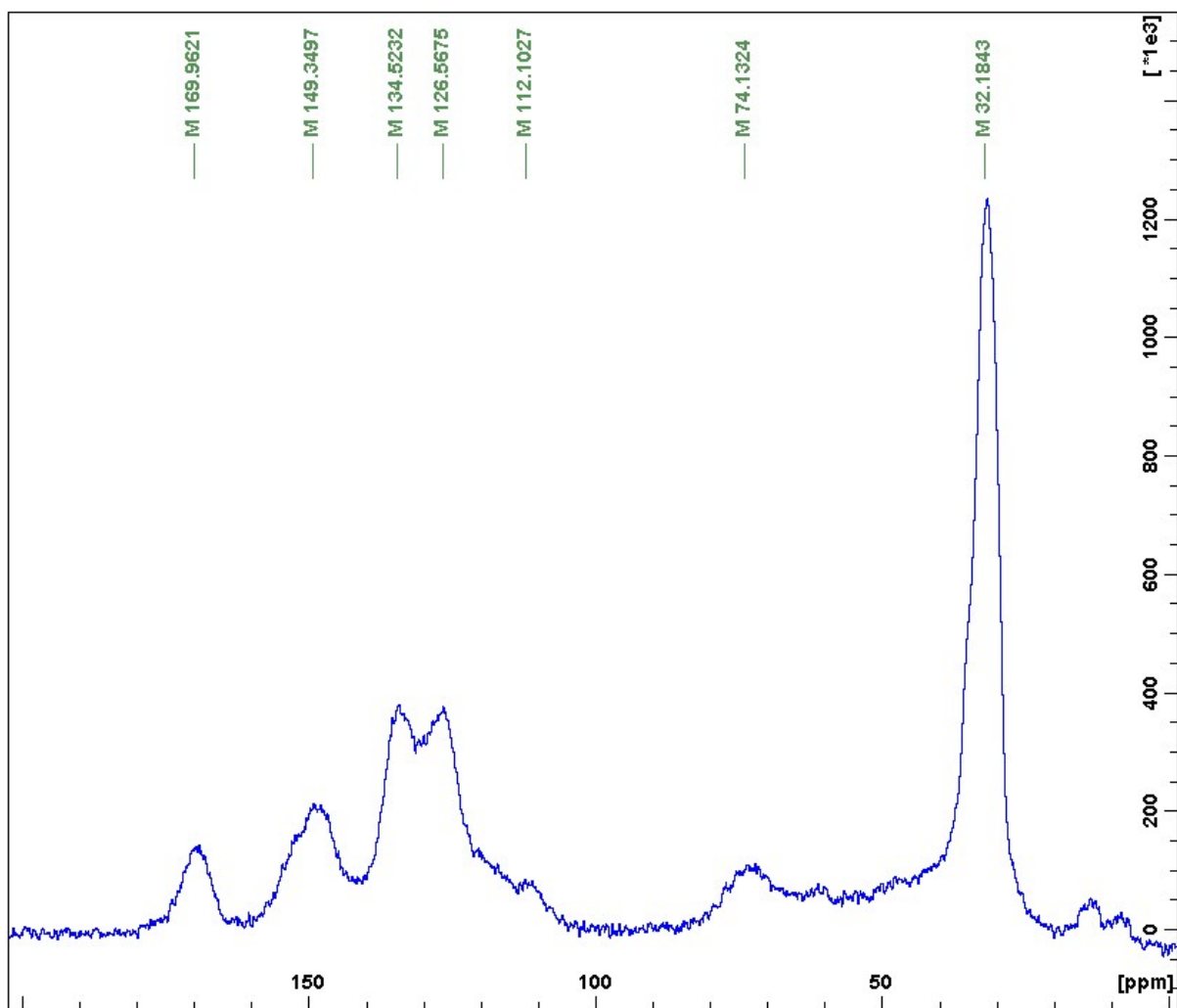
## Solid-State NMR spectroscopy of hosts and host:guest complexes



**Figure S51.**  $^{13}\text{C}\{^{19}\text{F}\}$  MAS NMR spectrum of **PFOA** at 20 kHz spin rate and 298 K.

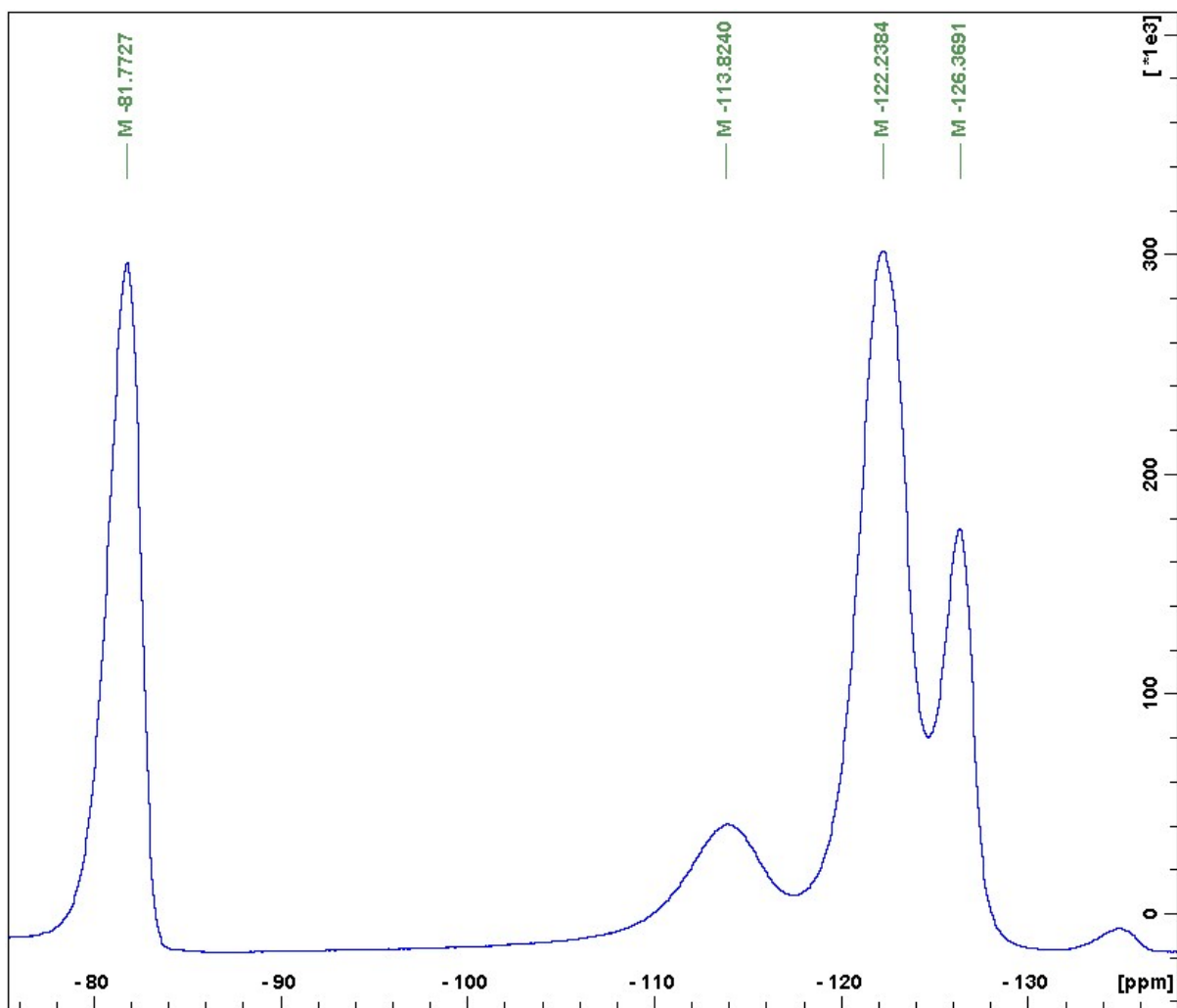


**Figure S52.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **PFOA** at 20 kHz spin rate and 298 K.

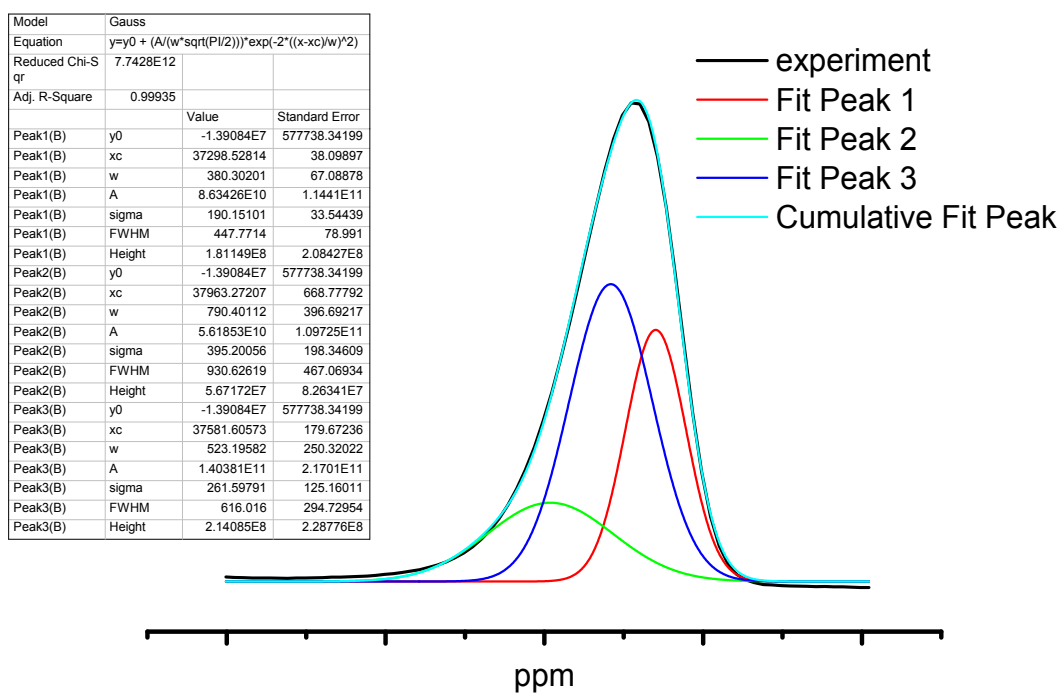


**Figure S53.**  $^{13}\text{C}\{^{19}\text{F}\}$  MAS NMR spectrum of **5** at 10 kHz spin rate and 298 K.

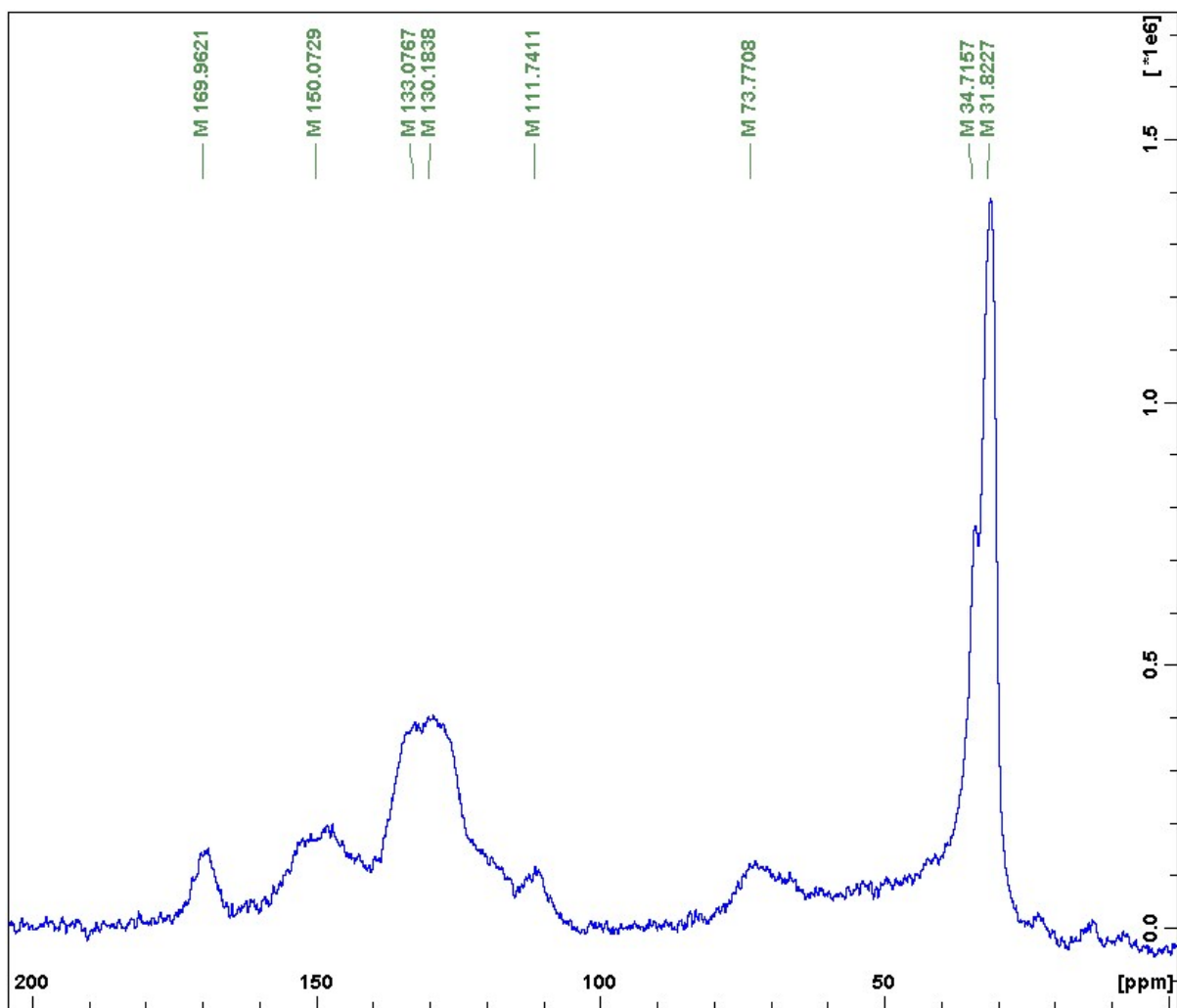




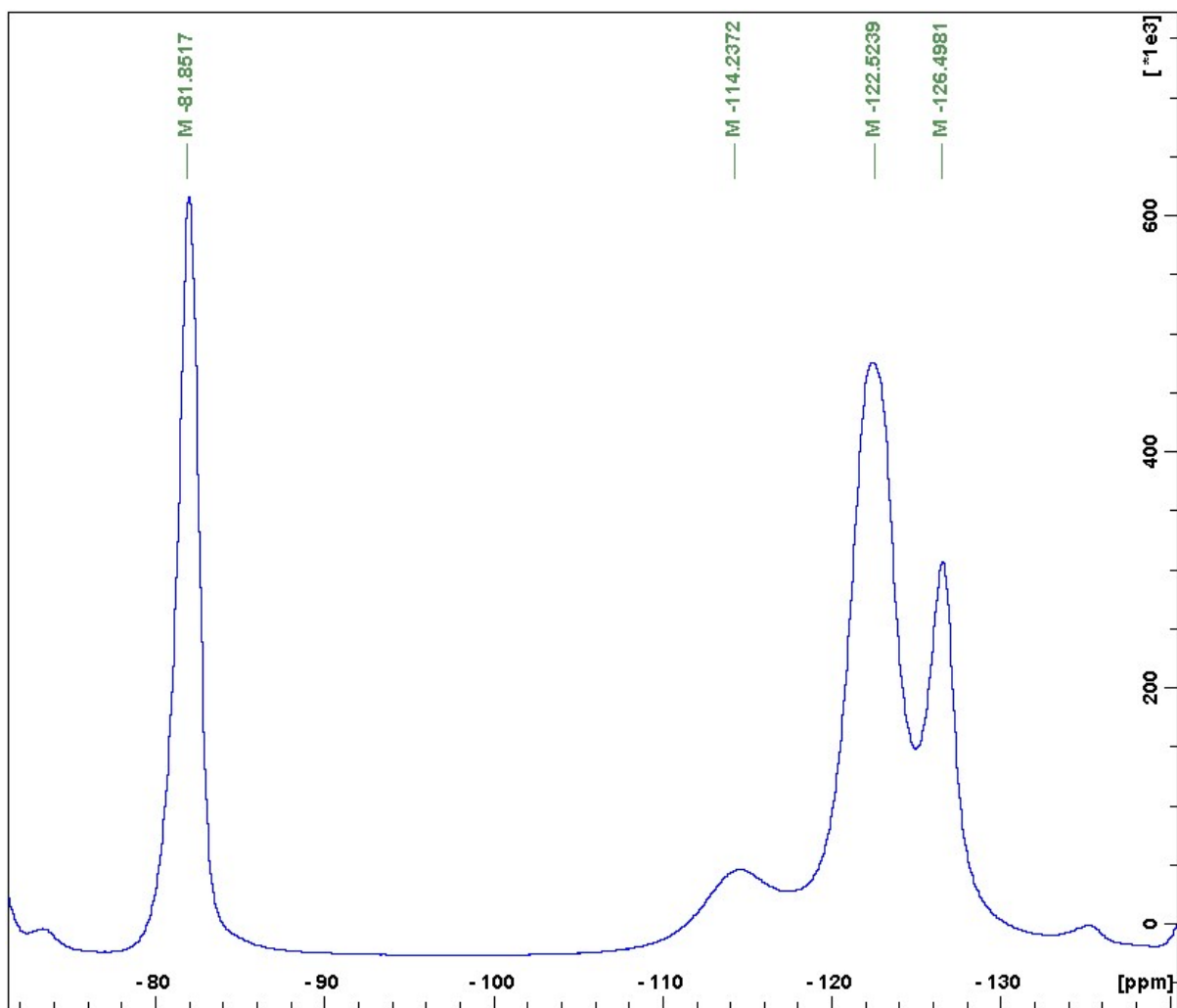
**Figure S54.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **5** at 20 kHz spin rate and 298 K.



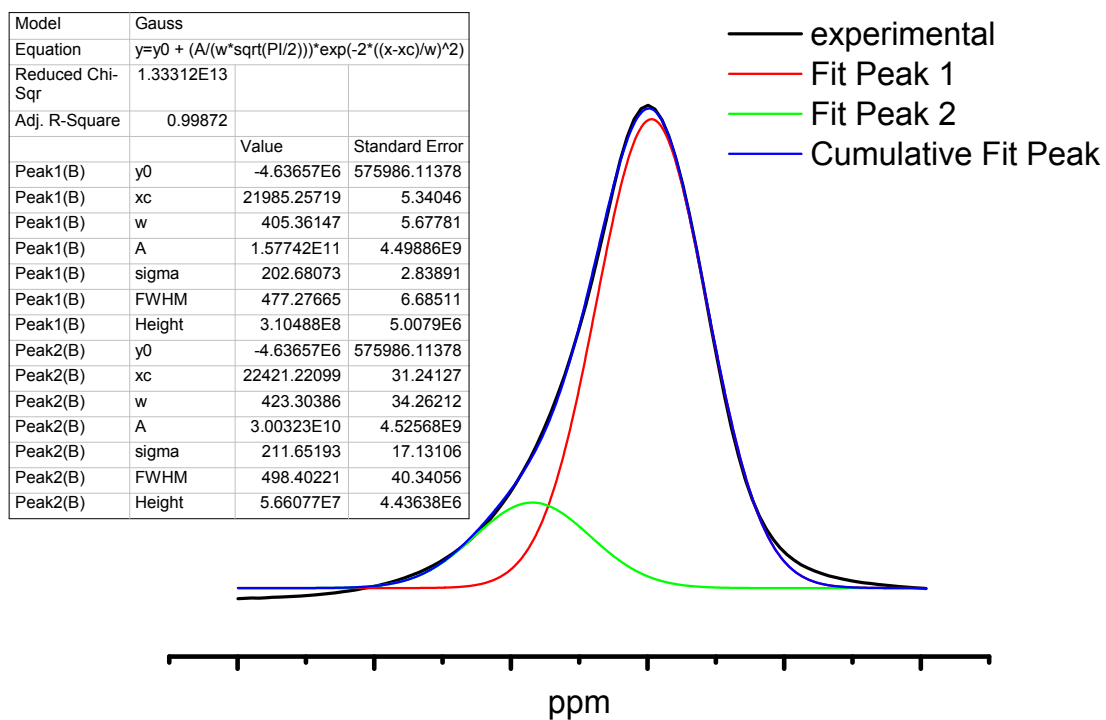
**Figure S55.** Deconvolution of  $\text{CF}_3$  resonance from the  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **5**.



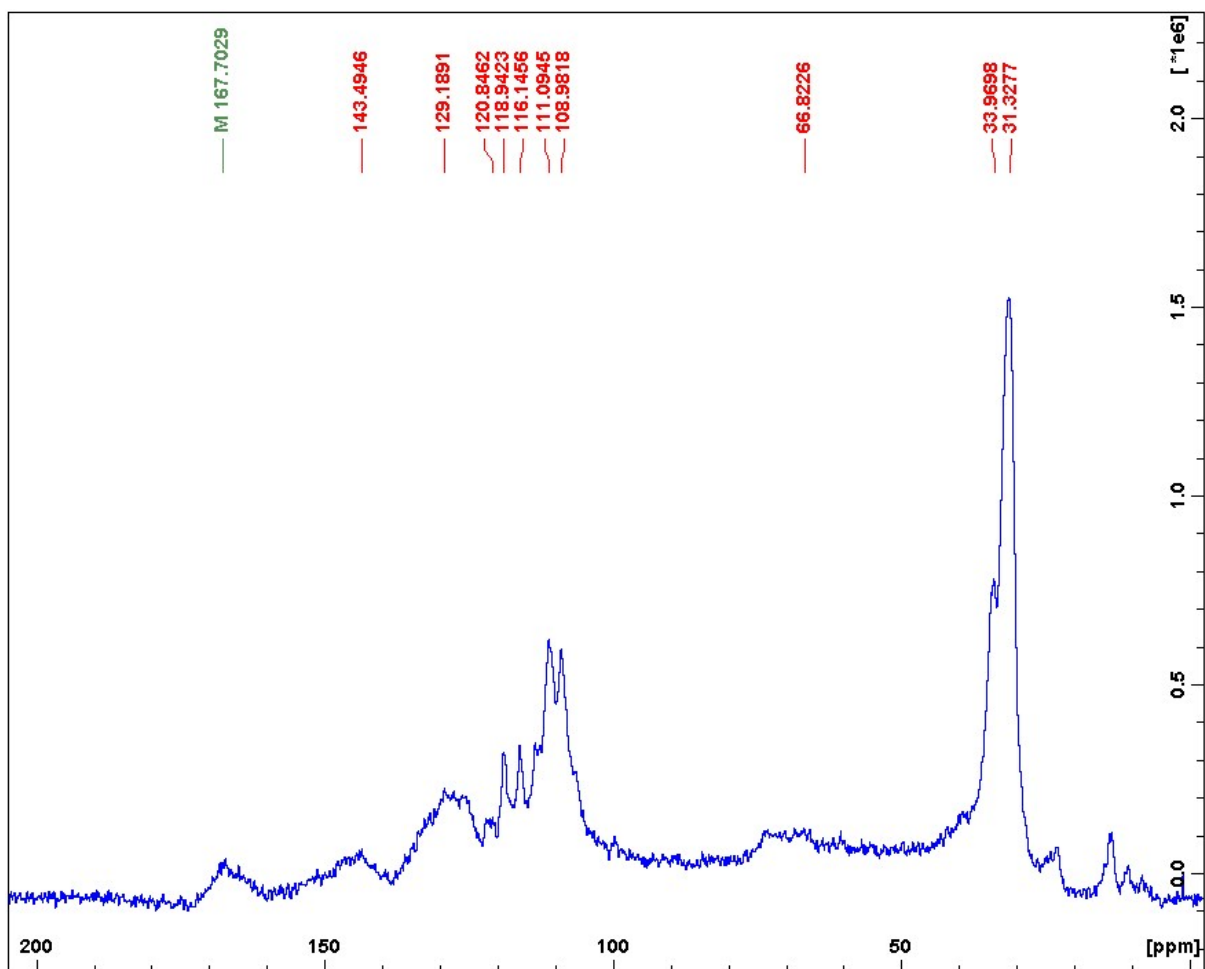
**Figure S56.**  $^{13}\text{C}\{^{19}\text{F}\}$  MAS NMR spectrum of **5:1PFOA** at 10 kHz spin rate and 298 K.



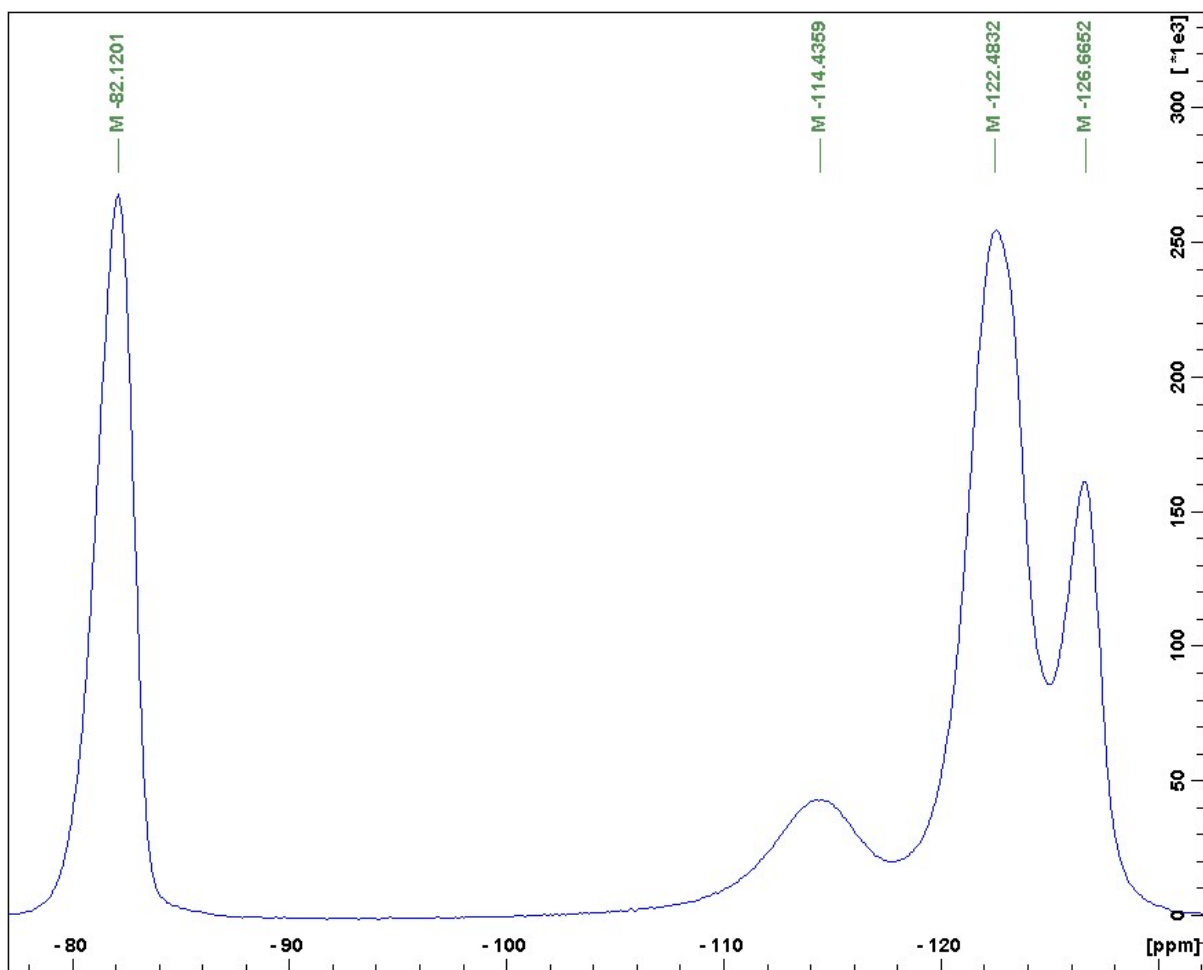
**Figure S57.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **5:1PFOA** at 20 kHz spin rate and 298 K.



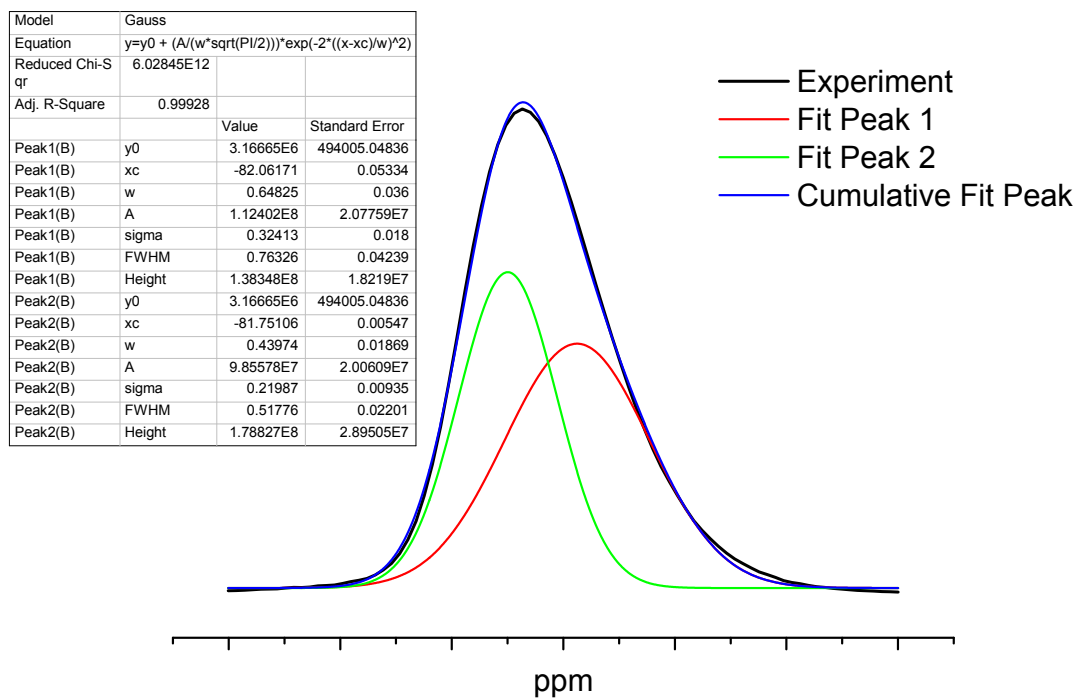
**Figure S58.** Deconvolution of  $\text{CF}_3$  resonance from the  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of 5:1PFOA.



**Figure S59.**  $^{13}\text{C}\{^{19}\text{F}\}$  MAS NMR spectrum of **6** at 10 kHz spin rate and 298 K.

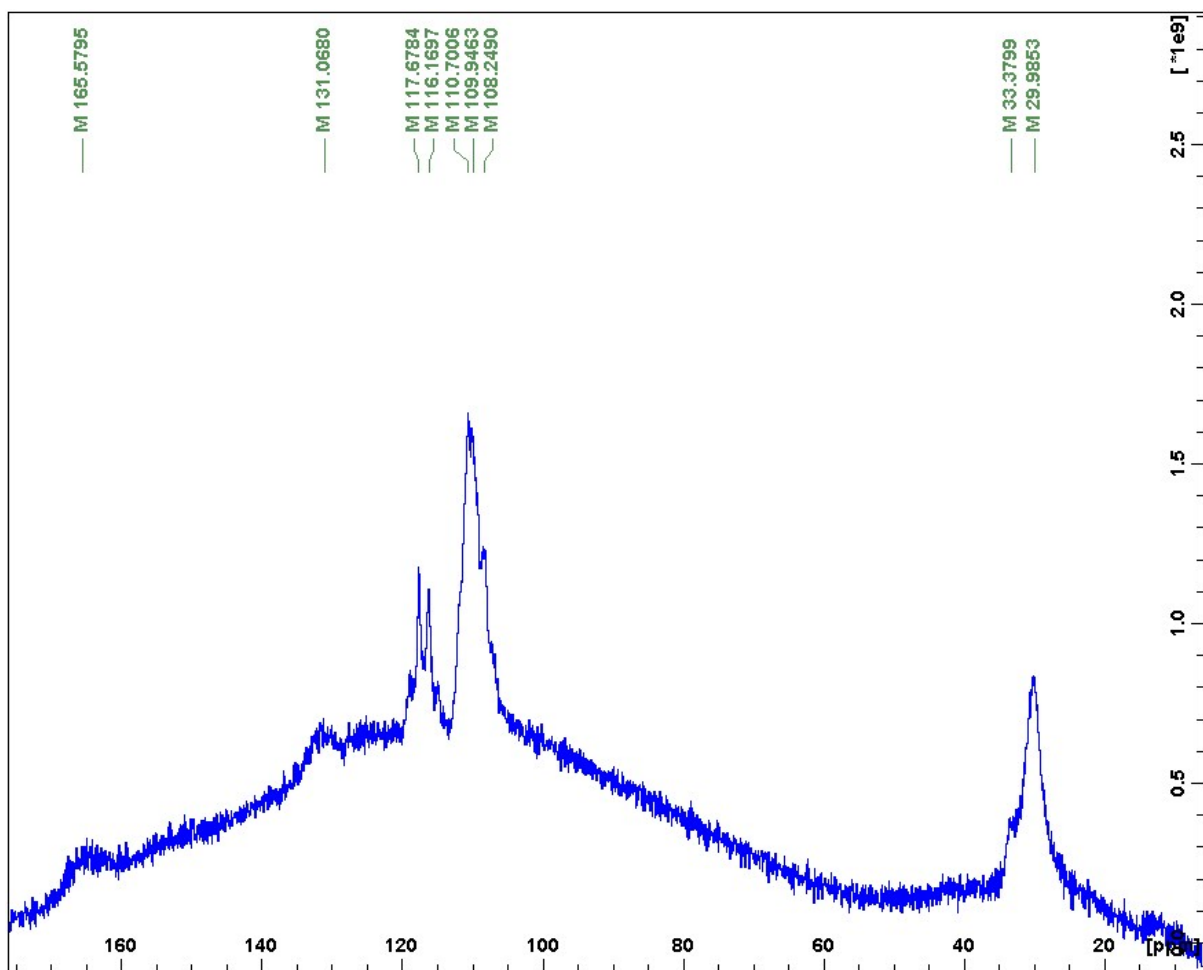


**Figure S60.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **6** at 20 kHz spin rate and 298 K.

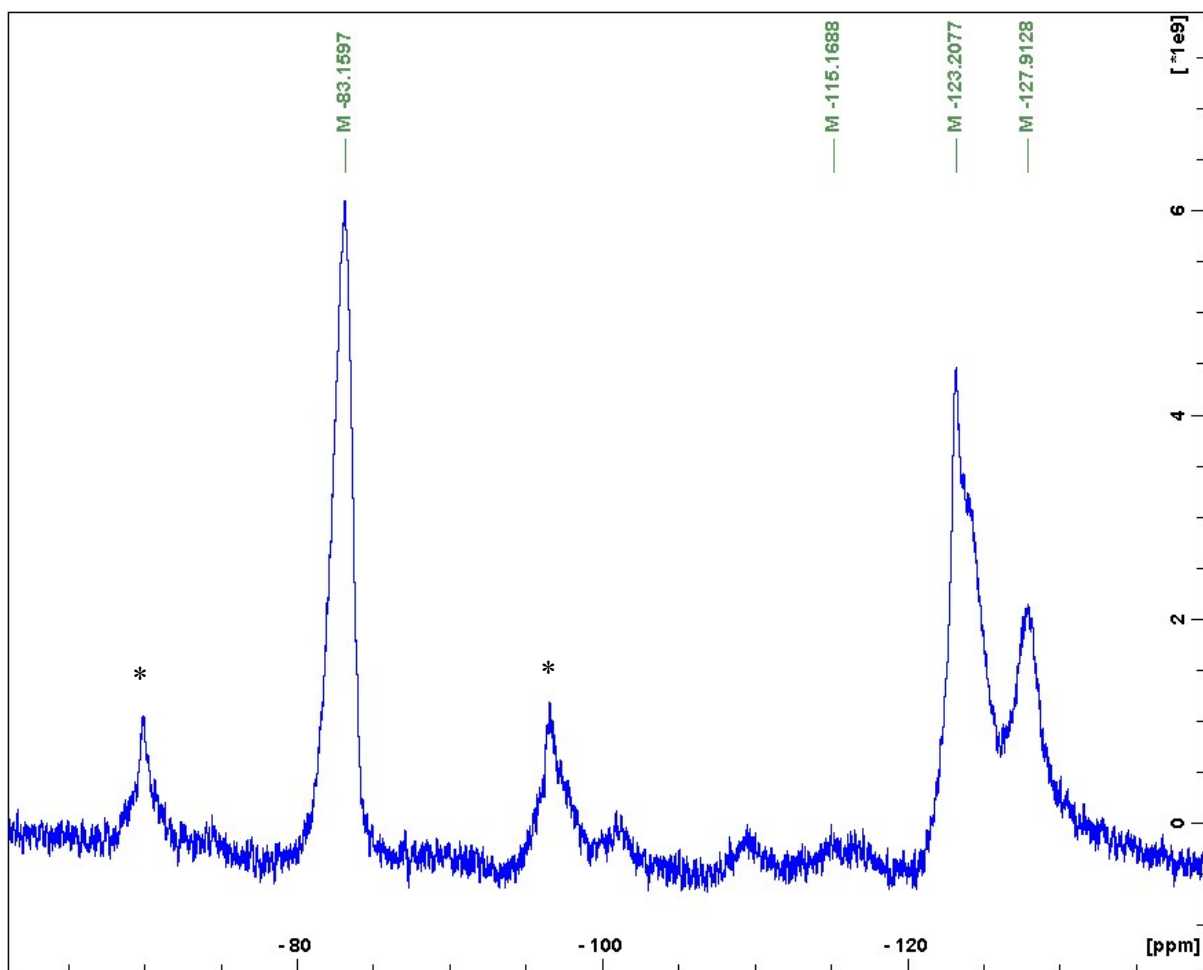


**Figure S61.** Deconvolution of  $\text{CF}_3$  resonance from the  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **6**.

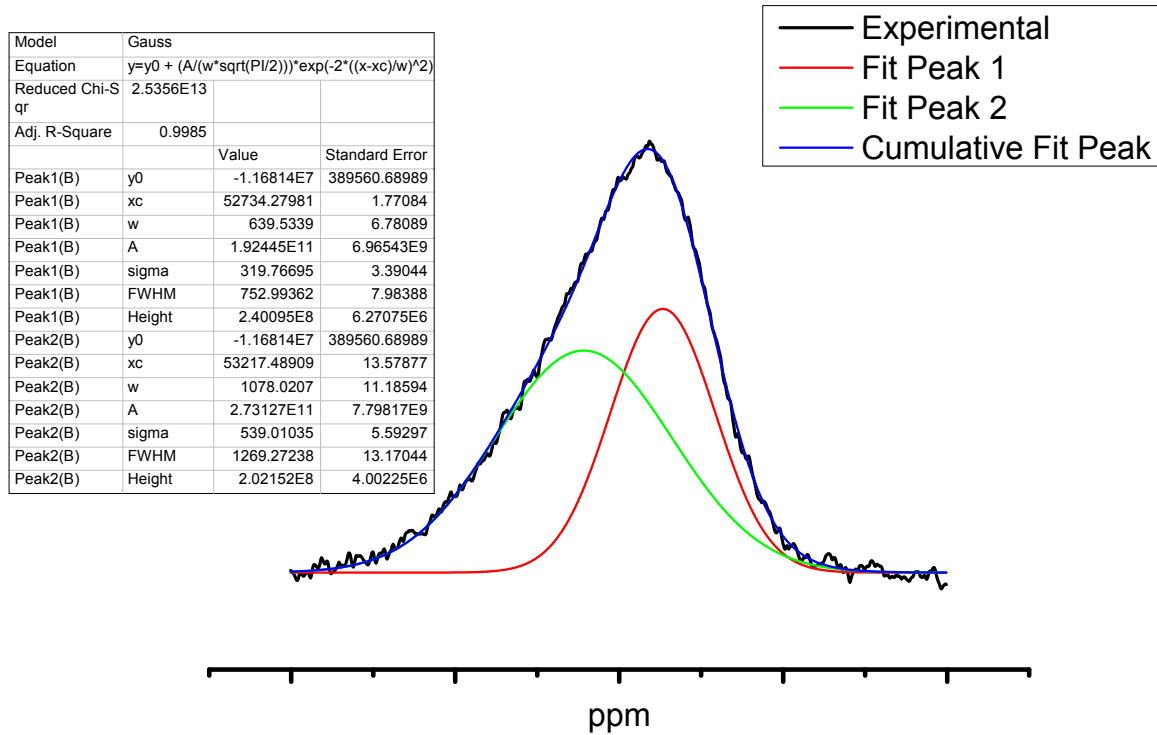




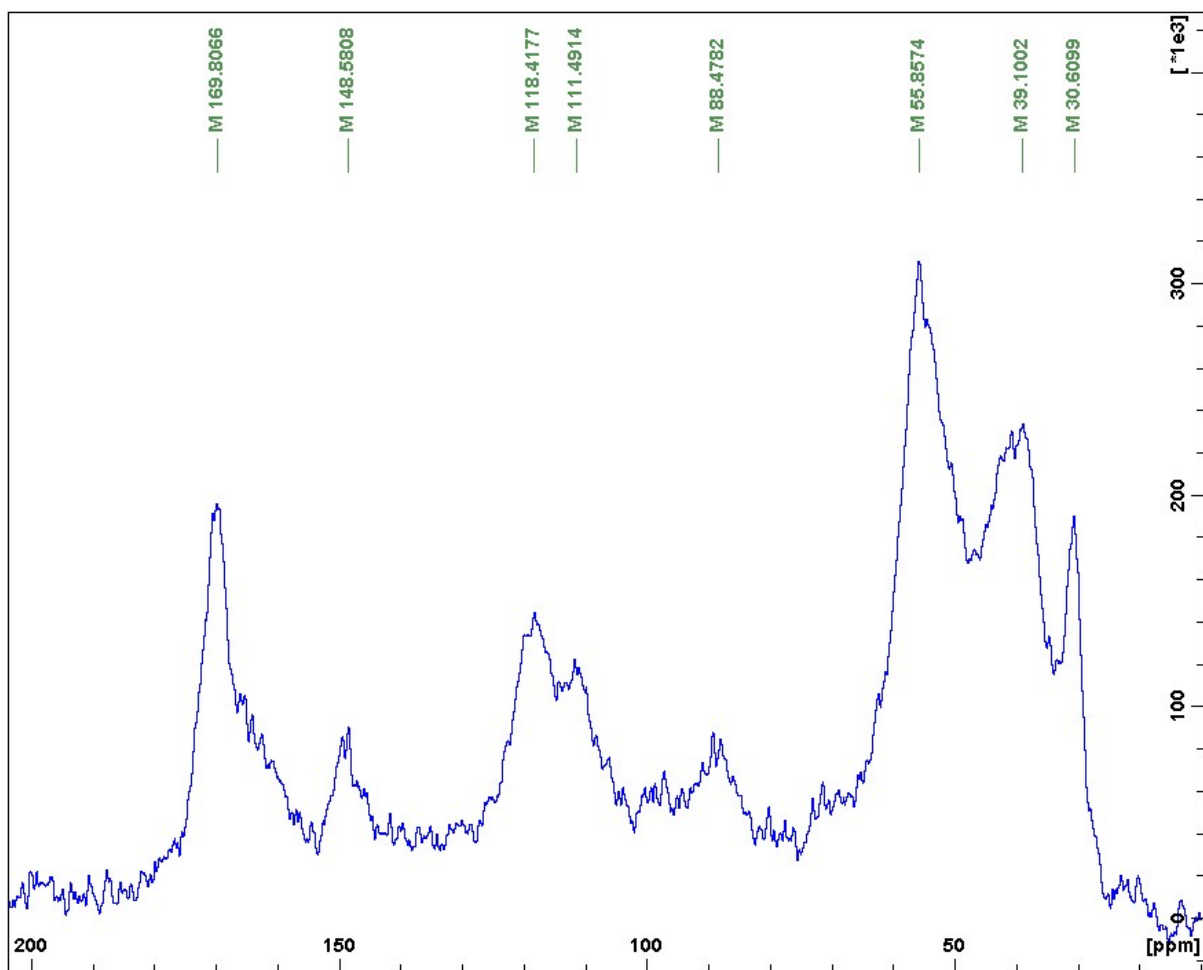
**Figure S62.**  $^{13}\text{C}\{^{19}\text{F}\}$  MAS NMR spectrum of 6:1PFOA at 10 kHz spin rate and 298 K.



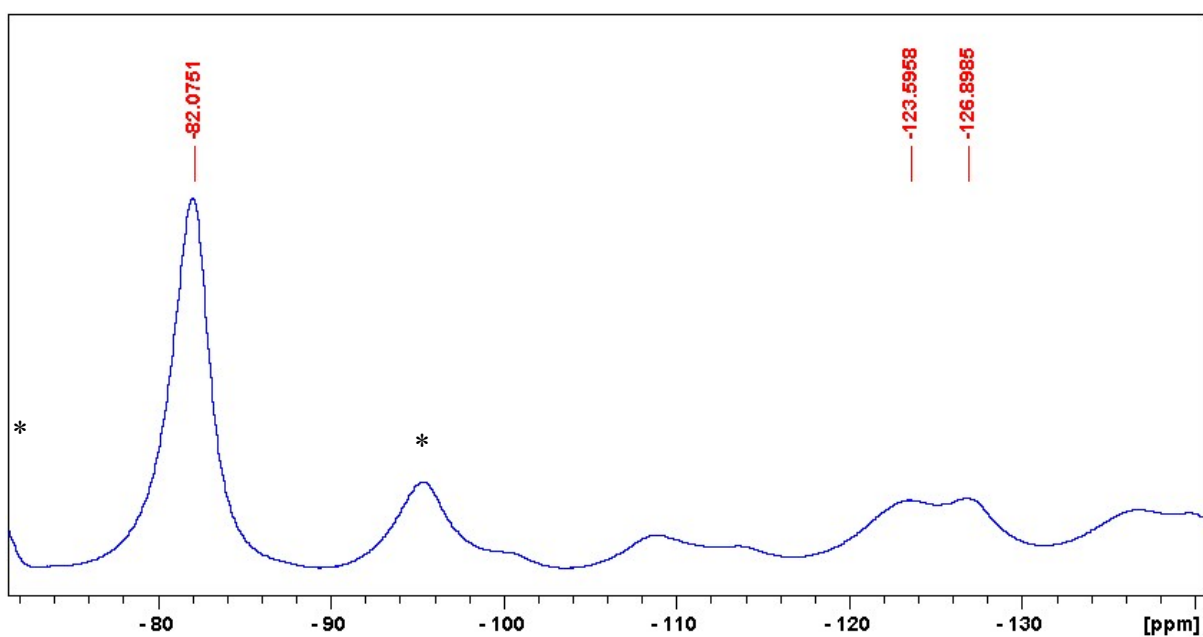
**Figure S63.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of 6:1PFOA at 20 kHz spin rate and 298 K (\* indicates spinning side bands).



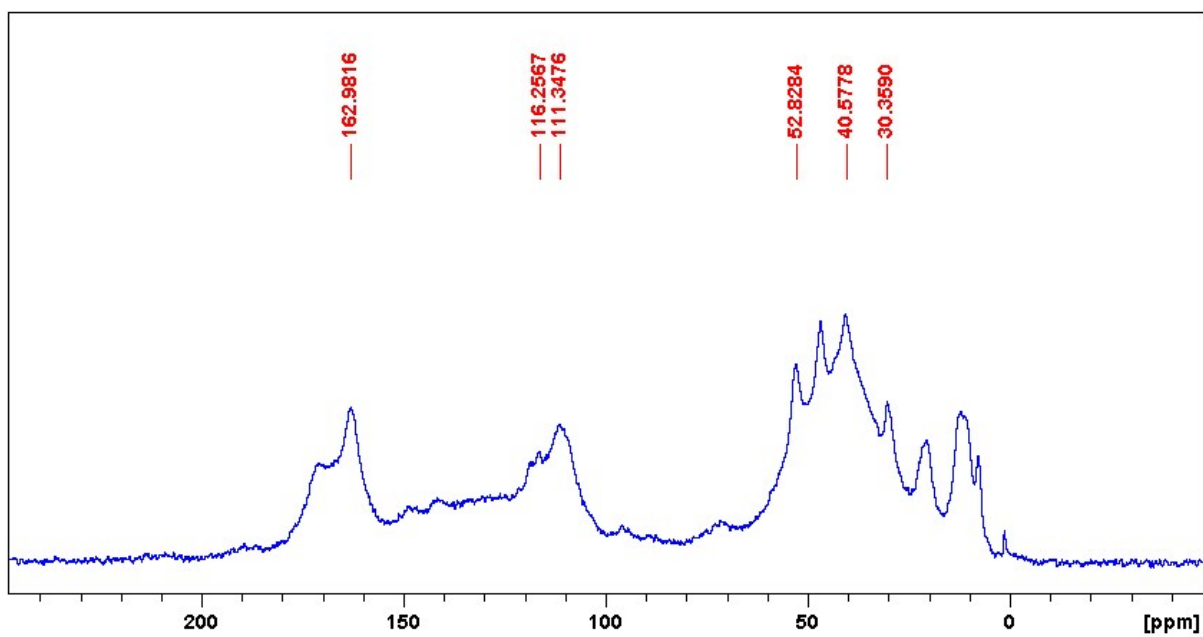
**Figure S64.** Deconvolution of  $\text{CF}_3$  resonance from the  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **6:1PFOA**.



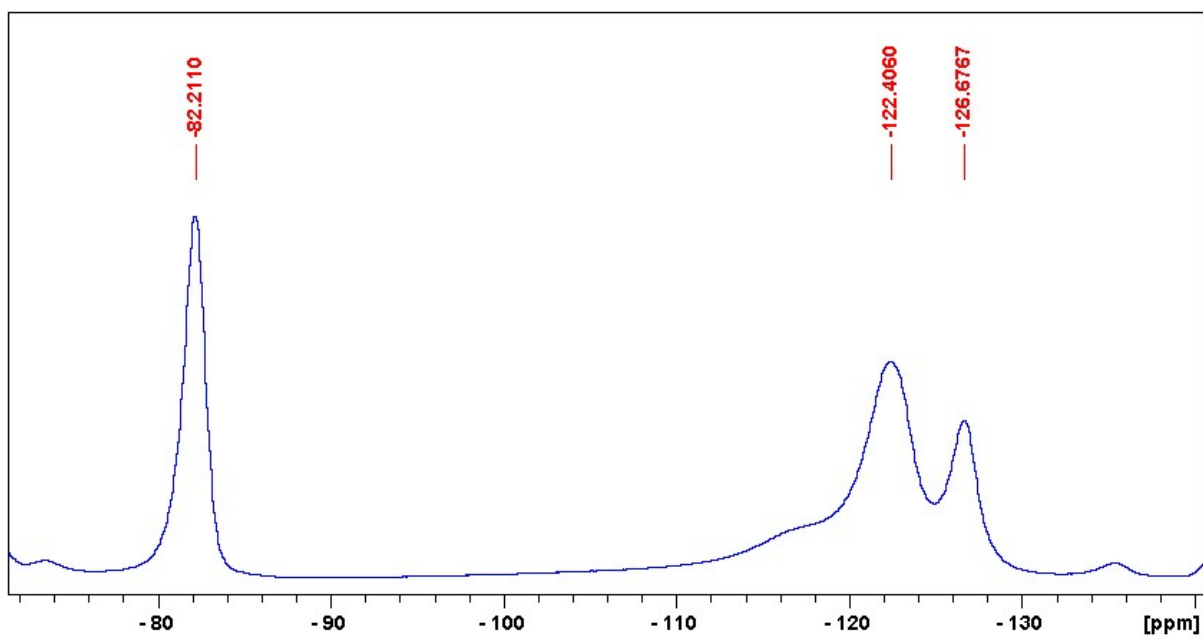
**Figure S65.**  $^{13}\text{C}\{^{19}\text{F}\}$  MAS NMR spectrum of **8** at 5 kHz spin rate and 298 K.



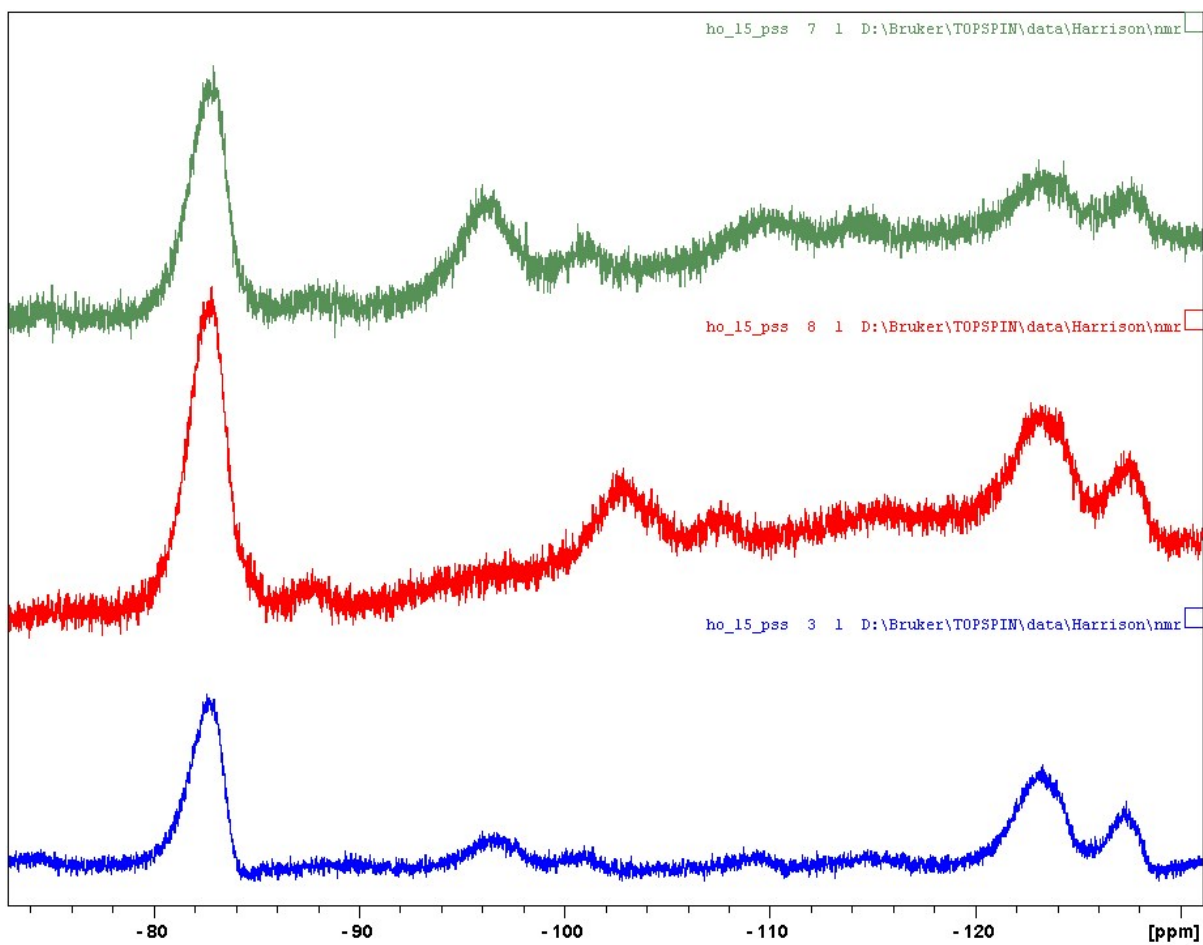
**Figure S66.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **8** at 5 kHz spin rate and 298 K (\* indicates spinning side bands).



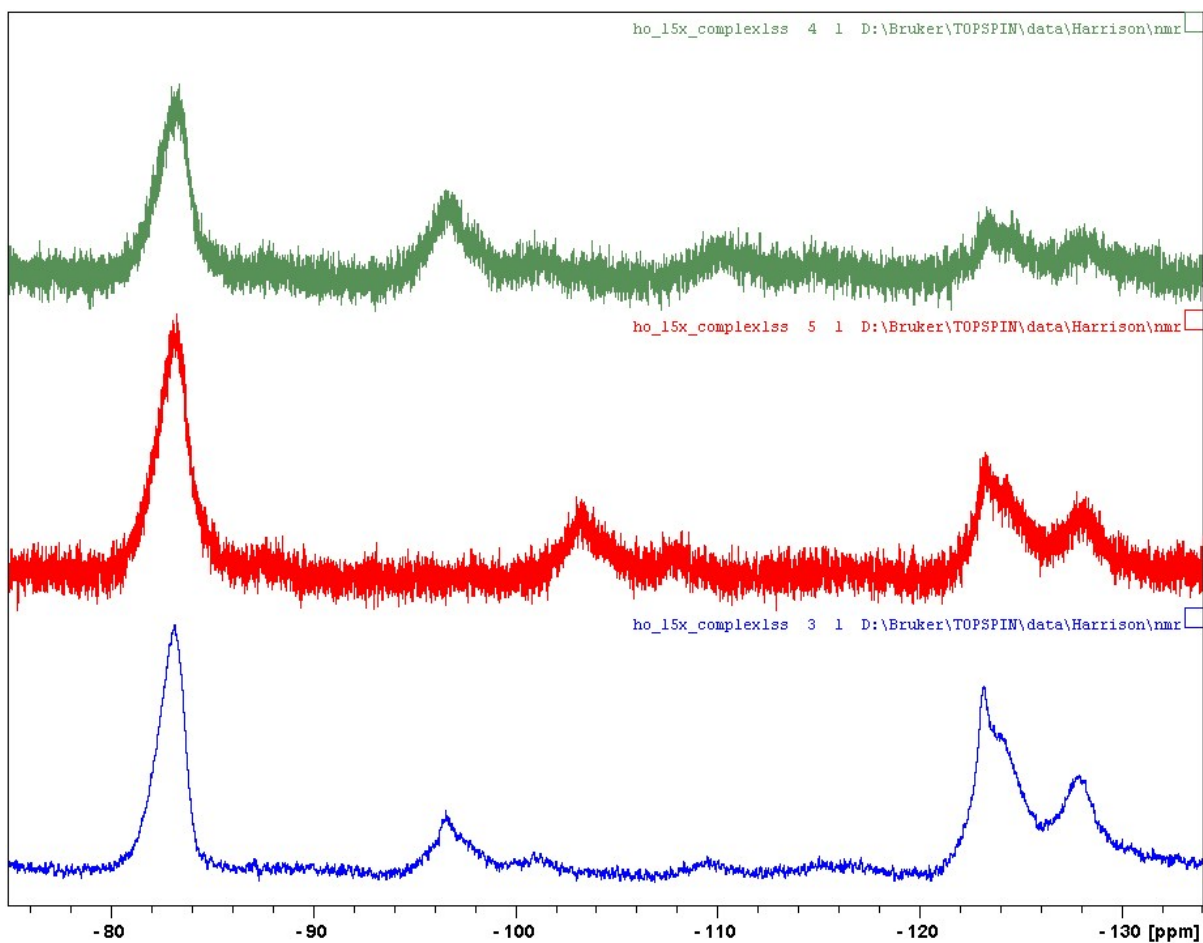
**Figure S67.**  $^{13}\text{C}\{^{19}\text{F}\}$  MAS NMR spectrum of **8:1PFOA** at 10 kHz spin rate and 298 K.



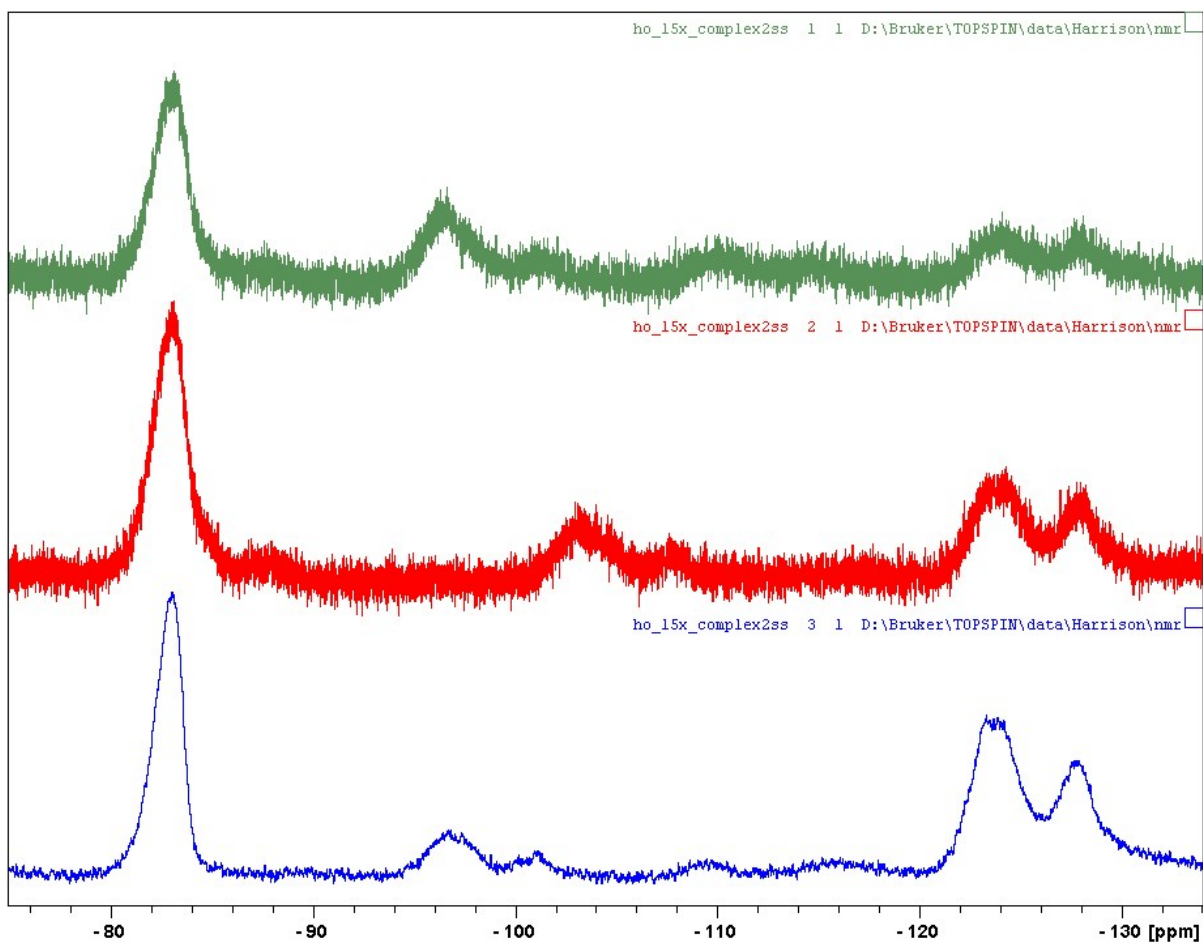
**Figure S68.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **8:2PFOA** at 20 kHz spin rate and 298 K.



**Figure S69.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of **6** at variable spin rates 10, 15, 20 kHz (top to bottom) and 298 K.

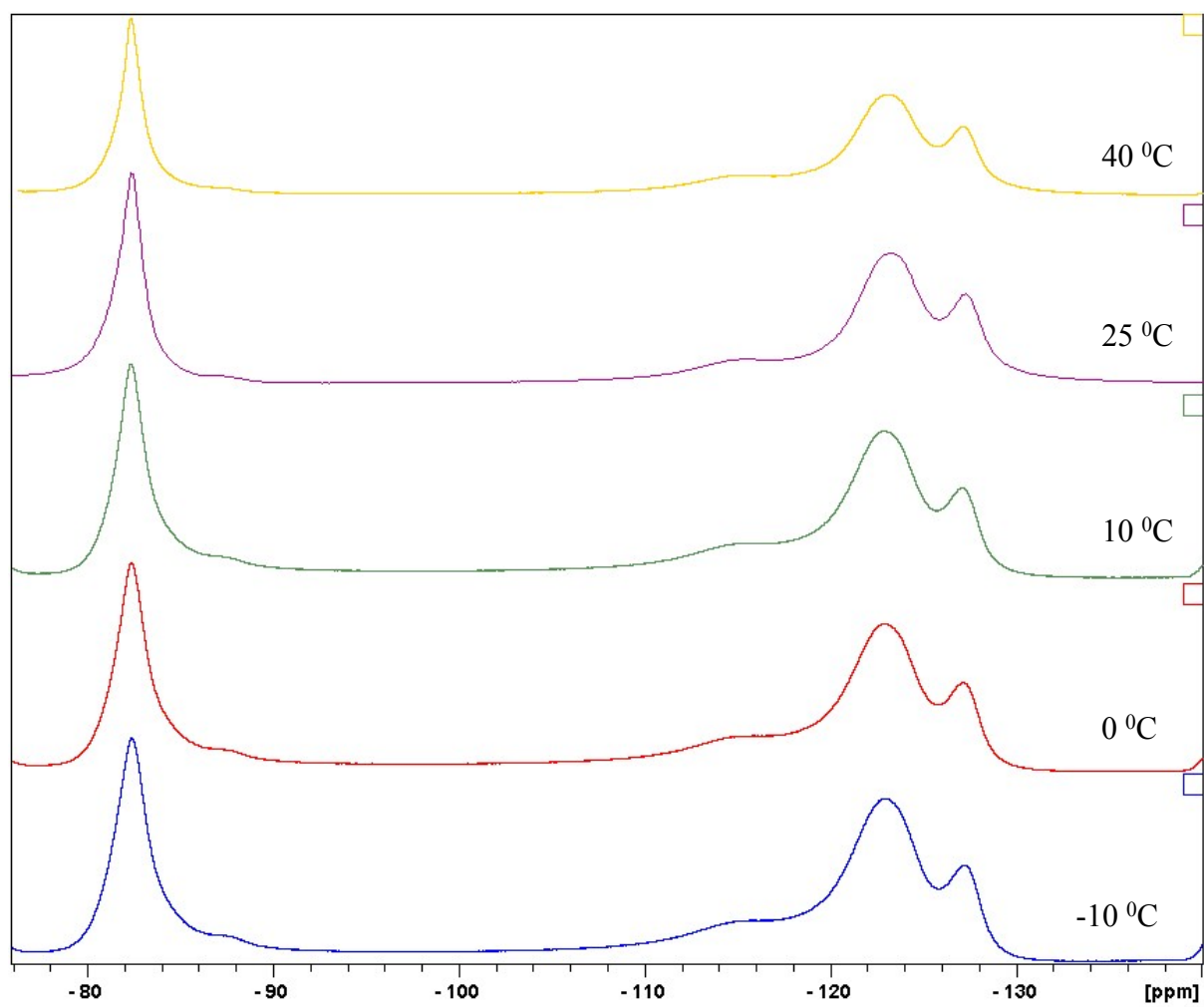


**Figure S70.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of 6:PFOA at variable spin rates 10, 15, 20 kHz (top to bottom) and 298 K.

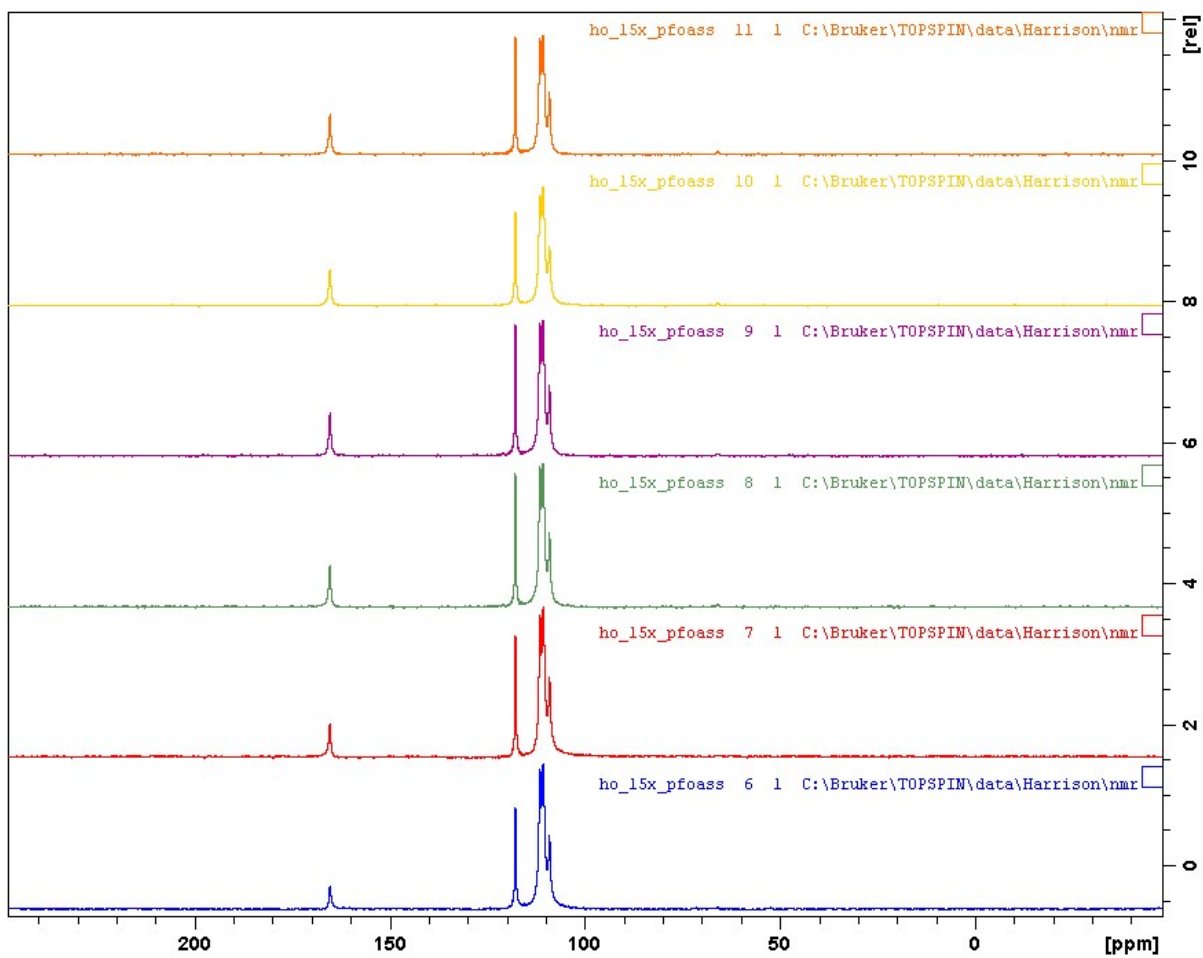


**Figure S71.**  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectrum of 6:2PFOA at variable spin rates 10, 15, 20 kHz (top to bottom) and 298 K.

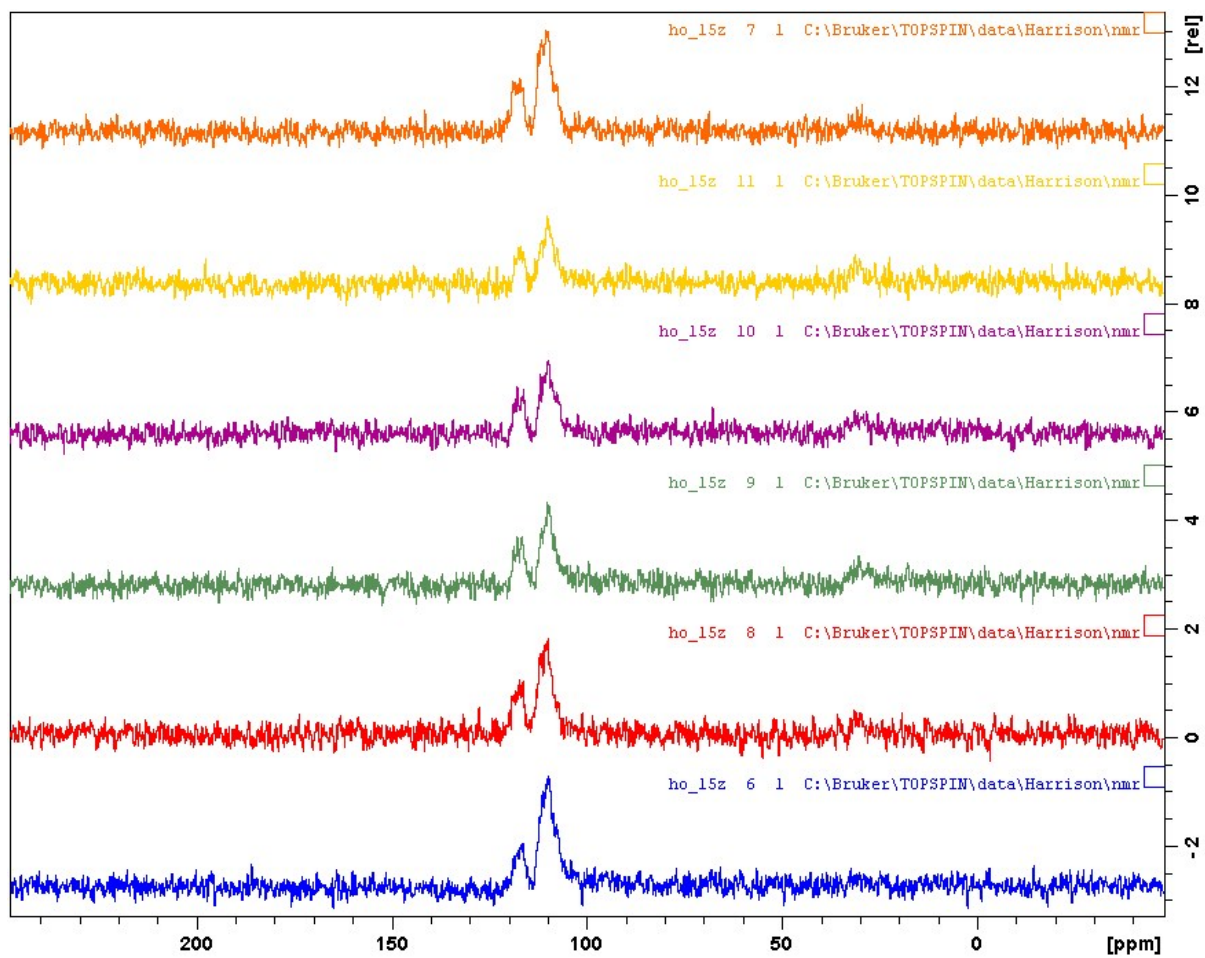




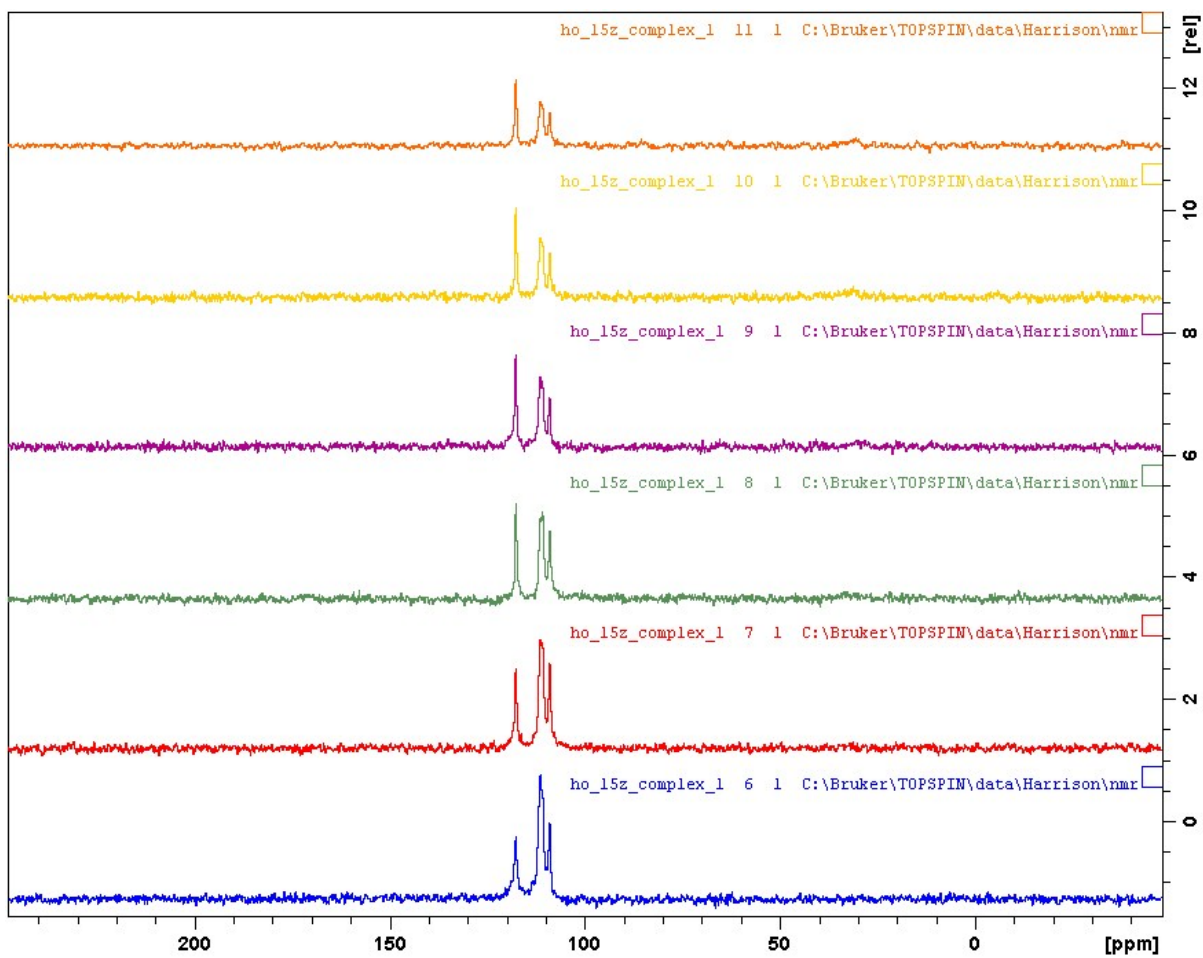
**Figure S72.** Variable temperature  $^{19}\text{F}\{^{13}\text{C}\}$  MAS NMR spectra of 5:1PFOA.



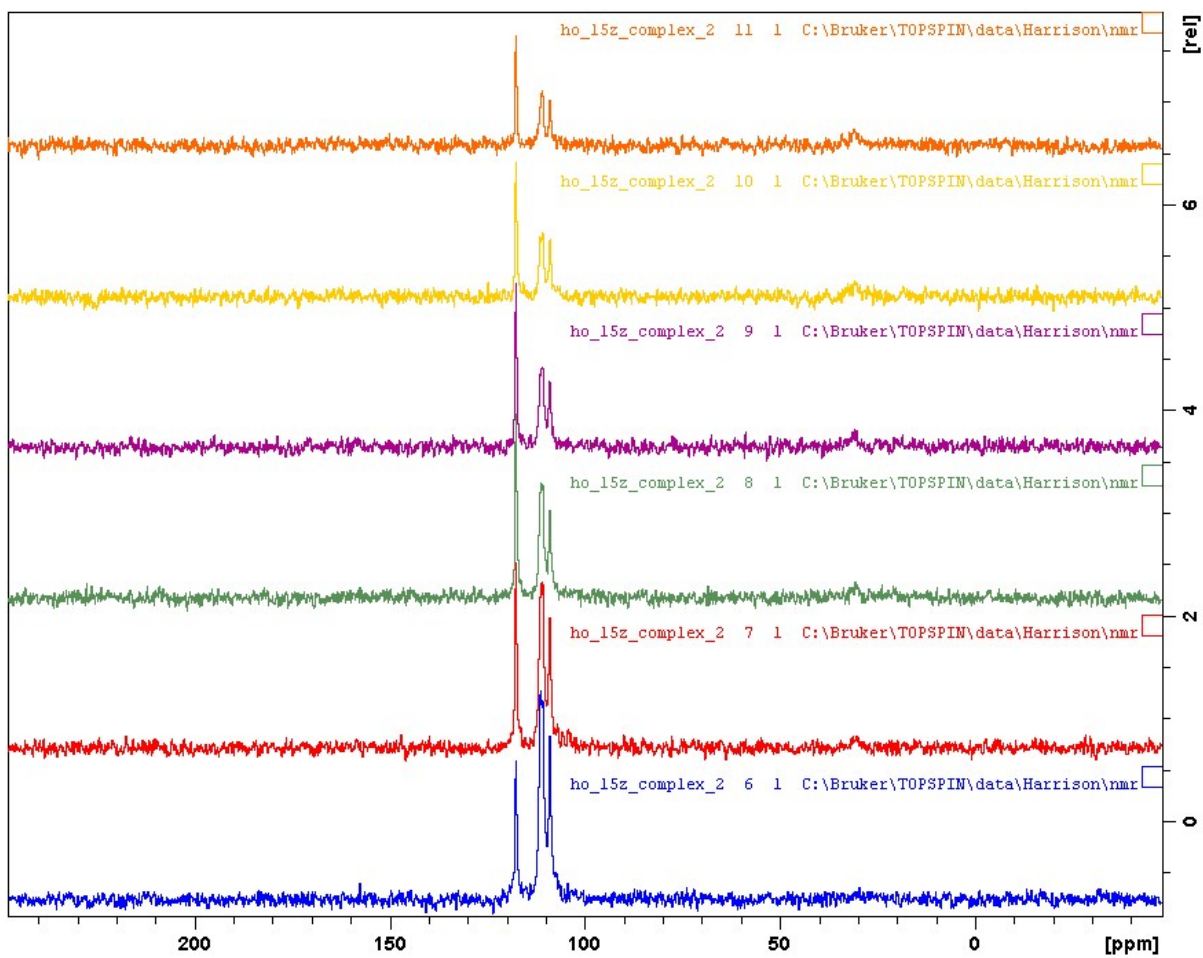
**Figure S73.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of PFOA with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).



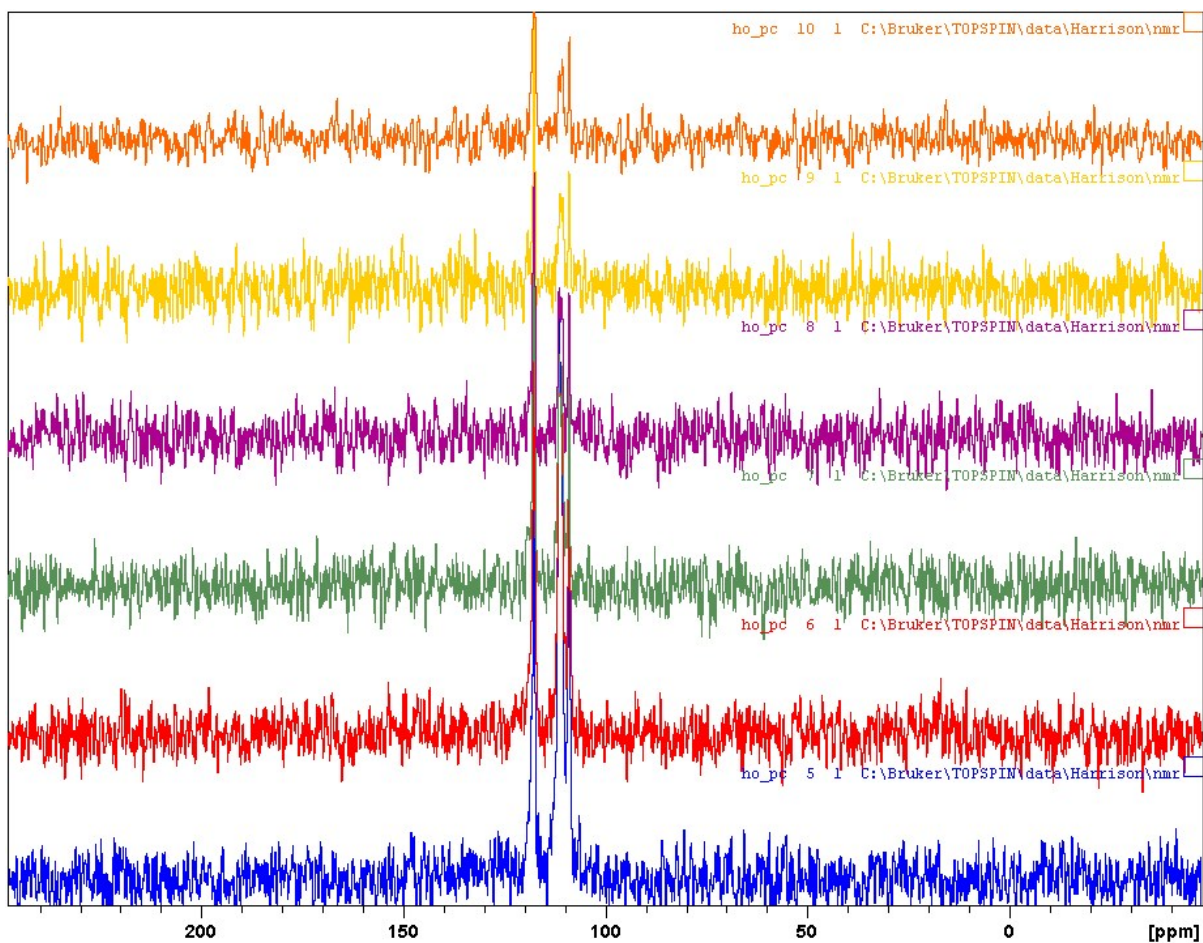
**Figure S74.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of **5** with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).



**Figure S75.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of 5:1PFOA with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).

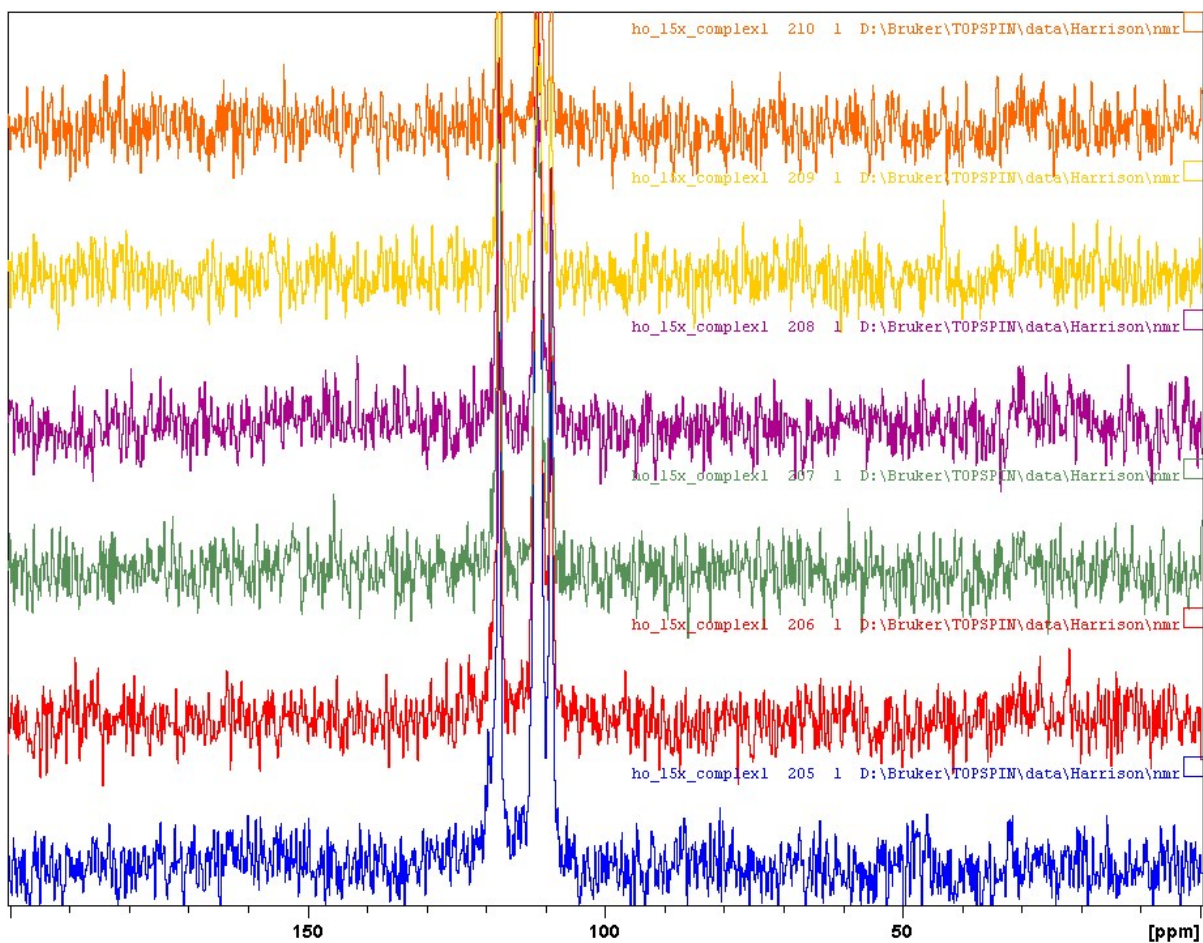


**Figure S76.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of 5:2PFOA with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).



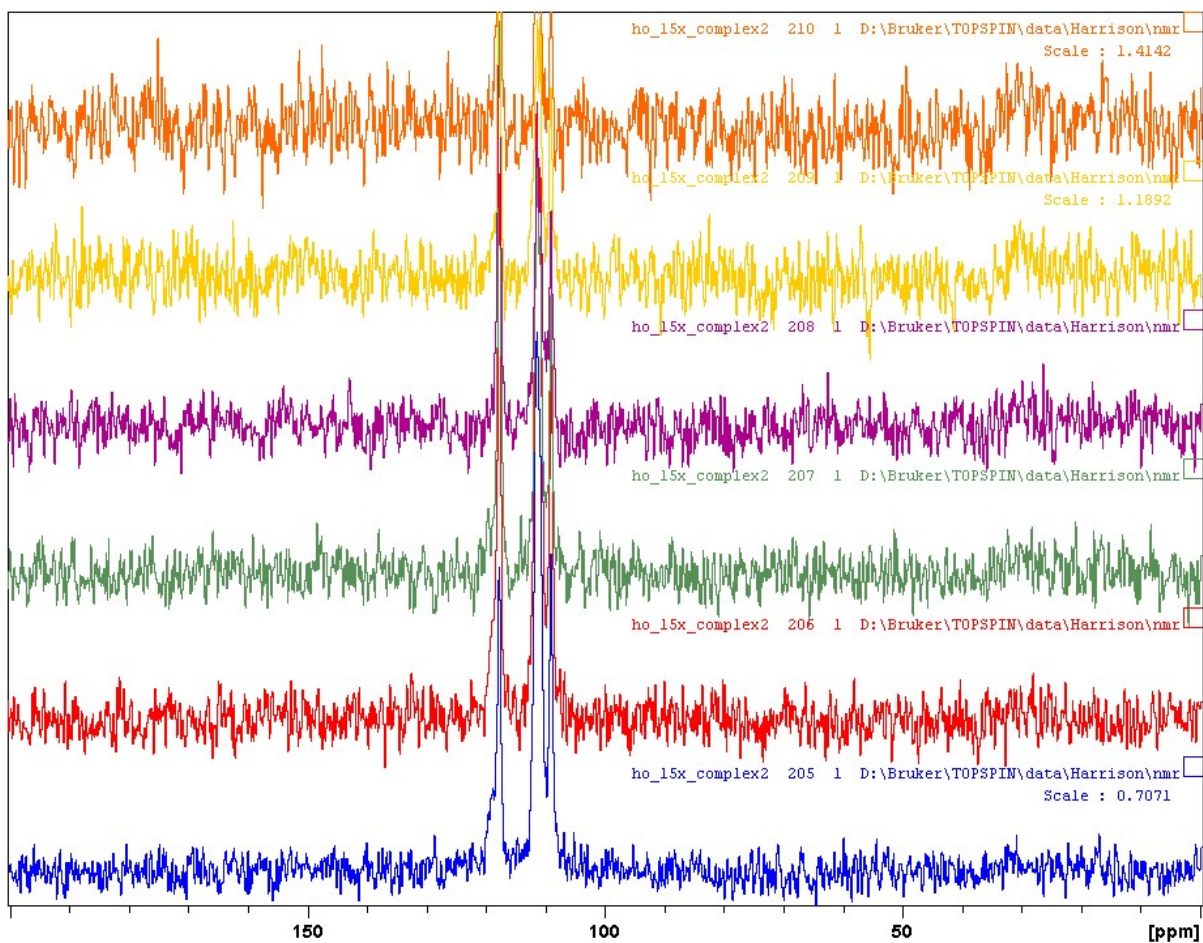
**Figure S77.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of **6** with a contact times 1, 2, 4, 6, 8, 10 ms.



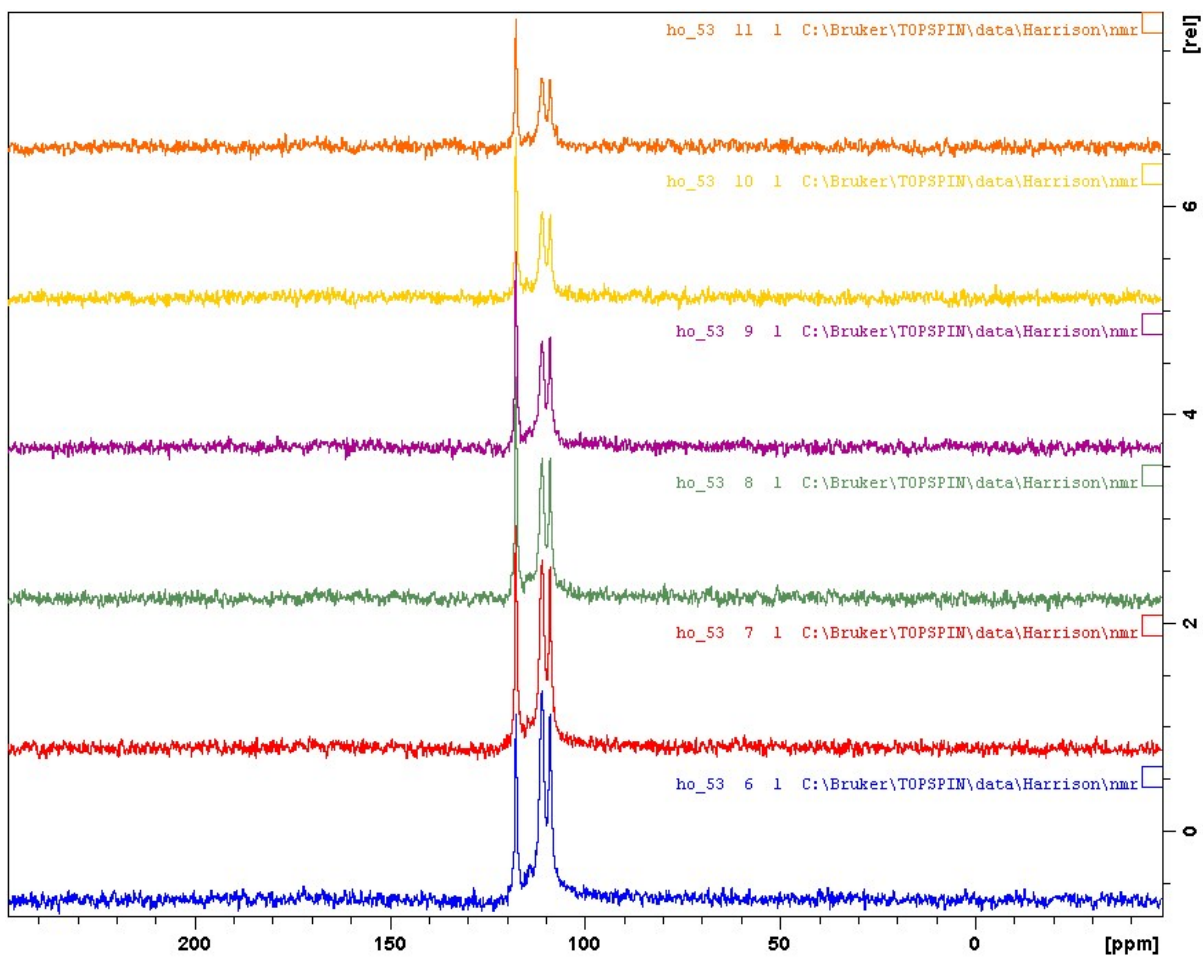


**Figure S78.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of 6:PFOA with a contact times 1, 2, 4, 6, 8, 10 ms.

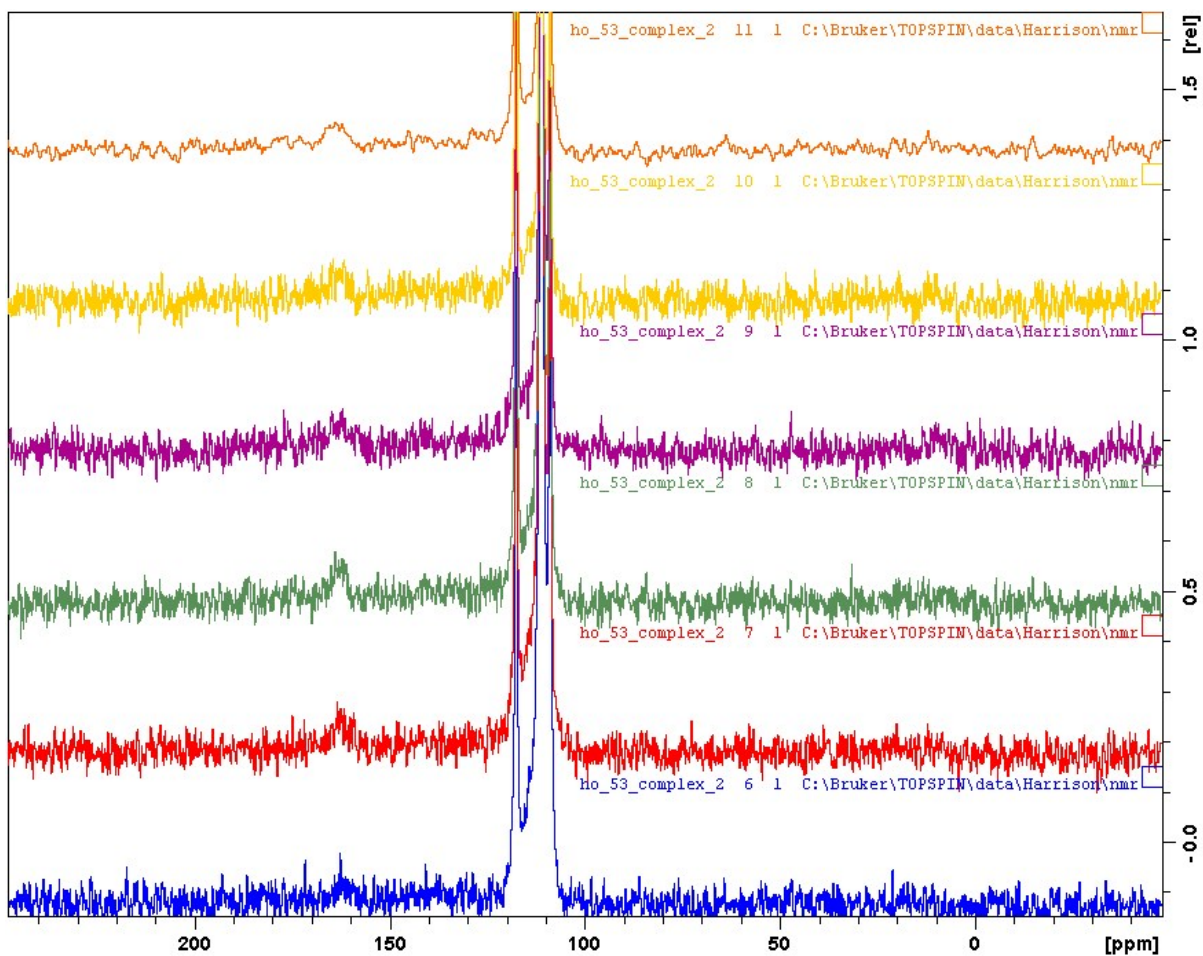




**Figure S79.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of **6:2PFOA** with a contact times 1, 2, 4, 6, 8, 10 ms.



**Figure S80.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of **8** with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).



**Figure S81.**  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP/MAS NMR spectrum of 8:2PFOA with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).

**Table S1.** Partition coefficient of PFOA in water:solvent measured by  $^{19}\text{F}$  NMR spectroscopy.

Solvent	FC-72	1,3- Bis(trifluoromethyl)benzene	Chloroform	DCM	Toluene
Partition coefficient	96:4	31:69	53:47	68:32	85:16

## Computational Chemistry

**Table S2.** Coordinates for host **5**.

C	1.193200	3.020900	0.591200
C	2.659700	2.715200	0.231200
H	3.134800	3.621700	-0.121000
H	3.184700	2.391900	1.137900
C	0.376000	3.919600	-0.139300
C	0.863800	5.377400	-0.414500
C	-0.265400	6.437700	-0.242600
H	0.146700	7.452300	-0.169200
H	-0.845500	6.257400	0.669900
H	-0.955800	6.498200	-1.081500
C	1.457400	5.469500	-1.816800
H	1.722200	6.499800	-2.077900
H	0.760500	5.095600	-2.567800
H	2.360000	4.863500	-1.902300
C	1.924800	5.868300	0.619700
H	2.121700	6.942200	0.507200
H	2.904000	5.403800	0.514500
H	1.580300	5.704900	1.647800
C	-0.973100	3.514800	-0.347900
C	-1.554700	2.601200	0.564400
H	-2.607200	2.354400	0.450500
C	-0.793500	1.995900	1.558400
O	-1.234500	1.107200	2.496200
C	-2.619200	1.088900	2.793600
H	-2.715600	0.757400	3.834200
H	-3.064200	2.090200	2.744800
C	0.584200	2.173600	1.534600
H	1.197900	1.562700	2.195700
C	2.630900	-0.142900	-2.991300
H	2.494100	-0.827100	-3.823500
C	3.491200	0.972200	-3.109400
C	4.077900	1.277100	-4.494600
H	4.873900	0.552800	-4.707900
H	4.544100	2.246800	-4.428500

C	3.790900	1.736500	-1.930800
C	5.200900	2.402800	-1.709100
C	6.340000	1.633100	-2.443000
H	7.330200	1.948100	-2.090200
H	6.364200	1.819800	-3.517800
H	6.264500	0.552300	-2.277000
C	5.656700	2.345700	-0.219000
H	6.724900	2.575500	-0.115500
H	5.496000	1.352000	0.214400
H	5.158600	3.089300	0.406100
C	5.252200	3.873000	-2.149900
H	6.235400	4.310300	-1.937700
H	4.513300	4.484400	-1.628400
H	5.085600	3.988300	-3.221200
C	2.844100	1.652100	-0.865000
C	2.016900	0.513300	-0.794400
H	1.436400	0.354000	0.101800
C	1.944400	-0.413900	-1.816300
O	1.239700	-1.585200	-1.765200
C	0.169800	-1.658000	-0.832500
H	-0.491100	-2.458800	-1.184800
H	-0.429000	-0.738900	-0.848500
C	0.901500	0.991000	-7.368500
H	-0.010700	0.825900	-7.940700
C	1.807500	-0.054900	-7.246600
O	1.480900	-1.178000	-7.950700
C	2.494000	-2.151900	-8.145900
H	2.284800	-2.639700	-9.105100
H	3.491900	-1.705500	-8.232300
C	2.848800	0.076400	-6.334200
H	3.473900	-0.777800	-6.087300
C	3.094300	1.305500	-5.676200
C	2.345900	2.449800	-6.072100
C	2.973600	3.878000	-6.142700
C	4.504100	3.853800	-6.435300
H	4.866900	4.840400	-6.751000
H	4.744600	3.148500	-7.239300
H	5.122400	3.613900	-5.572500
C	2.701400	4.628900	-4.842900
H	3.212500	5.597500	-4.819900
H	3.025200	4.051400	-3.976400
H	1.634800	4.814400	-4.711200
C	2.431500	4.720700	-7.339400
H	3.006400	5.647300	-7.465000
H	1.402400	5.056900	-7.223300
H	2.501800	4.162400	-8.280500
C	1.084700	2.196800	-6.667300
C	-0.179800	3.024000	-6.367000
H	-0.859200	2.951600	-7.224600
H	0.095900	4.064300	-6.250300
C	-1.798700	1.615600	-2.631800
H	-2.088300	1.205700	-1.668500
C	-1.559100	0.722900	-3.666300
O	-1.824900	-0.595600	-3.419400
C	-1.210100	-1.558100	-4.264900
H	-1.215900	-2.500100	-3.703500
H	-0.154100	-1.315100	-4.438000
C	-1.073500	1.225700	-4.857900
H	-0.813200	0.539900	-5.650300
C	-0.931800	2.608000	-5.091600

C	-1.499000	3.516300	-4.146500
C	-2.127500	4.882600	-4.614100
C	-2.623900	4.832100	-6.091400
H	-3.279100	5.680700	-6.325700
H	-3.193700	3.918100	-6.294600
H	-1.810300	4.910400	-6.815200
C	-1.158000	6.067500	-4.493500
H	-1.618900	6.989300	-4.869300
H	-0.244300	5.911100	-5.070000
H	-0.871900	6.262200	-3.459500
C	-3.427700	5.234400	-3.830000
H	-3.985000	6.043800	-4.318500
H	-3.236500	5.607600	-2.822500
H	-4.100100	4.371500	-3.762100
C	-1.689900	3.012100	-2.815300
C	-1.816500	3.905500	-1.573600
H	-2.872600	3.955000	-1.280600
H	-1.526200	4.899400	-1.873800
C	0.506600	-2.010900	0.622800
O	-0.217500	-1.660100	1.554900
N	1.623600	-2.800800	0.782900
C	2.050600	-3.291900	2.082800
H	3.018100	-3.778800	1.925400
C	1.021600	-4.234600	2.718300
C	1.686200	-5.468000	3.314400
F	2.413200	-6.054900	2.318900
C	0.682800	-6.481200	3.855300
F	-0.225300	-6.750600	2.865700
F	-0.019500	-5.941100	4.884800
C	1.353300	-7.782200	4.279700
F	2.092900	-8.265900	3.237600
C	0.335800	-8.844700	4.658200
F	-0.466900	-9.080700	3.576500
F	-0.479600	-8.387300	5.642700
C	0.966500	-10.159400	5.076200
F	1.805600	-10.615200	4.100000
C	-0.109500	-11.200000	5.323900
F	-0.806600	-11.464900	4.186600
F	-1.008600	-10.799900	6.251400
F	0.421800	-12.370700	5.749500
F	1.727600	-9.991900	6.190100
F	2.216000	-7.558200	5.300900
F	2.565000	-5.094800	4.276400
H	0.296000	-4.555800	1.961100
H	0.469600	-3.694200	3.496000
H	2.213600	-2.424900	2.732900
H	2.178700	-3.025700	-0.038800
C	-3.437500	0.113000	1.957100
O	-4.622000	0.322300	1.703000
N	-2.767400	-1.028100	1.576200
C	-3.408800	-2.096100	0.836000
H	-2.616000	-2.688600	0.368600
H	-4.008400	-1.643500	0.038200
C	-4.279200	-2.977200	1.730400
C	-4.941800	-4.080200	0.915000
F	-5.604600	-3.513100	-0.127800
C	-5.899800	-4.941900	1.727500
F	-6.836000	-4.158600	2.327600
F	-5.204300	-5.519600	2.745700
C	-6.578400	-6.003400	0.873400

F	-7.326100	-5.418300	-0.100800
C	-7.446300	-6.947400	1.682400
F	-8.461500	-6.263600	2.273100
F	-6.709800	-7.468000	2.702800
C	-7.994700	-8.080700	0.846300
F	-8.844900	-7.596000	-0.101500
C	-8.710400	-9.092700	1.710400
F	-9.729700	-8.535600	2.404500
F	-7.878900	-9.670600	2.609100
F	-9.243500	-10.089700	0.962600
F	-6.988200	-8.710000	0.167400
F	-5.620300	-6.725300	0.216700
F	-3.968800	-4.861400	0.361300
H	-5.046200	-2.361000	2.213400
H	-3.660100	-3.413800	2.523000
H	-1.766100	-1.130200	1.805300
C	-1.877200	-1.884100	-5.611600
O	-1.292500	-2.553500	-6.465200
N	-3.172600	-1.424300	-5.735200
C	-3.999900	-1.653800	-6.912200
H	-4.910200	-1.064300	-6.765600
C	-4.309400	-3.137100	-7.100800
H	-3.521000	-3.595900	-7.709400
C	-5.676300	-3.392900	-7.736800
F	-5.724000	-2.849200	-8.975200
F	-6.611300	-2.754200	-6.986700
C	-5.976600	-4.885700	-7.779800
F	-5.086800	-5.495600	-8.617300
C	-7.406000	-5.272800	-8.146700
F	-7.709400	-4.855800	-9.400300
F	-8.286800	-4.663200	-7.309400
C	-7.550400	-6.782800	-8.023200
F	-6.620400	-7.392400	-8.816500
C	-8.902600	-7.355300	-8.325700
F	-9.258700	-7.079200	-9.609000
F	-9.851400	-6.784100	-7.535700
C	-8.877600	-8.858600	-8.098600
F	-7.941400	-9.477600	-8.861400
F	-10.073600	-9.421200	-8.396300
F	-8.587200	-9.181400	-6.812200
F	-7.221500	-7.151000	-6.744800
F	-5.694200	-5.397700	-6.537500
H	-4.284100	-3.623300	-6.117200
H	-3.562500	-0.885800	-4.964500
C	2.501400	-3.253900	-7.095400
H	-3.472100	-1.259600	-7.787400
O	3.515300	-3.895600	-6.823400
N	1.273600	-3.527000	-6.529100
C	1.114400	-4.566300	-5.540500
H	0.180600	-4.359300	-5.008400
H	1.936200	-4.494400	-4.818500
C	1.083000	-5.950000	-6.182300
C	0.773400	-6.994400	-5.133000
F	1.726600	-6.992700	-4.169100
C	0.620600	-8.404500	-5.677100
F	1.766900	-8.870400	-6.223000
F	-0.308200	-8.429200	-6.669400
C	0.162100	-9.362300	-4.602500
F	1.047100	-9.508300	-3.589200
C	-0.139100	-10.743600	-5.090600

F	0.973200	-11.298400	-5.641200
F	-1.070200	-10.694200	-6.076500
F	-0.546800	-11.437600	-4.035100
F	0.495600	-11.789000	-3.299100
C	-1.147300	-12.574000	-4.396900
F	-0.418400	-13.318600	-5.264600
F	-2.366300	-12.374200	-4.958900
F	-1.355400	-13.366900	-3.310000
F	-1.408500	-10.851500	-3.232000
F	-0.985000	-8.928100	-4.016700
F	-0.387700	-6.653900	-4.506000
H	2.044500	-6.168800	-6.660000
H	0.314300	-5.964100	-6.964500
H	0.448300	-2.972800	-6.801100

**Table S3.** Coordinates for host:guest complex.

C	-8.458200	-1.055800	2.366000
C	-8.741700	0.445900	2.509600
H	-9.742800	0.710200	2.159300
H	-8.689300	0.706600	3.584500
C	-8.942500	-1.836800	1.261900
C	-10.441900	-1.739900	0.828800
C	-10.979900	-3.087700	0.259600
H	-12.084900	-3.082600	0.312200
H	-10.607400	-3.950200	0.842200
H	-10.725300	-3.245800	-0.801100
C	-10.720400	-0.642500	-0.203500
H	-11.802900	-0.585100	-0.433500
H	-10.182600	-0.867400	-1.134800
H	-10.389100	0.344800	0.145900
C	-11.304900	-1.507600	2.107300
H	-12.374600	-1.508800	1.822300
H	-11.102600	-0.553900	2.618900
H	-11.138000	-2.322500	2.836300
C	-8.056400	-2.854700	0.800900
C	-7.076600	-3.387100	1.670400
H	-6.471700	-4.228500	1.316800
C	-6.890900	-2.843700	2.952400
O	-6.095800	-3.383600	3.924100
C	-5.539500	-4.669400	3.676100
H	-5.192500	-5.036800	4.660600
H	-6.295200	-5.374400	3.278800
C	-7.507000	-1.609500	3.239700
H	-7.197500	-1.066300	4.140800
C	-5.649600	2.345200	0.095400
H	-4.875300	2.688100	-0.599300
C	-6.943800	2.908700	0.036000
C	-7.131700	3.920800	-1.124500
H	-6.561000	4.841000	-0.895400
H	-8.172000	4.211900	-1.194100
C	-7.967000	2.502100	0.972700
C	-9.190000	3.413300	1.377100
C	-9.047700	4.898000	0.924900
H	-9.722600	5.519300	1.542200
H	-9.349000	5.070100	-0.120700
H	-8.016900	5.269400	1.063600



C	-9.231000	3.506400	2.933400
H	-10.012300	4.230200	3.233800
H	-8.260100	3.861300	3.328000
H	-9.477500	2.551800	3.418300
C	-10.570400	2.910100	0.880400
H	-11.336800	3.686200	1.071700
H	-10.901300	1.998200	1.403900
H	-10.561000	2.691700	-0.199400
C	-7.697500	1.297600	1.716800
C	-6.392200	0.787500	1.756600
H	-6.210500	-0.081200	2.384400
C	-5.352400	1.342000	1.016700
O	-4.041600	0.885900	1.128400
C	-3.842100	-0.318100	1.871500
H	-2.884800	-0.741100	1.535600
H	-4.614100	-1.074700	1.647900
C	-5.304600	1.961800	-4.483100
H	-4.729200	1.361800	-5.198100
C	-4.733900	3.143900	-3.980100
O	-3.581400	3.575800	-4.575400
C	-3.077100	4.845100	-4.179800
H	-2.370100	5.148400	-4.975400
H	-3.879700	5.605200	-4.112500
C	-5.354100	3.760300	-2.880100
H	-4.856700	4.562900	-2.324900
C	-6.649000	3.366700	-2.470000
C	-7.369200	2.393900	-3.224700
C	-8.920200	2.297600	-3.260700
C	-9.653900	3.602400	-2.833300
H	-10.690800	3.572700	-3.216900
H	-9.158500	4.499800	-3.247700
H	-9.739600	3.713700	-1.743700
C	-9.396600	1.161100	-2.349400
H	-10.496900	1.052200	-2.388900
H	-9.103300	1.376700	-1.308300
H	-8.939500	0.195600	-2.611000
C	-9.400600	2.117100	-4.736600
H	-10.502700	2.013000	-4.745000
H	-8.984300	1.249200	-5.265800
H	-9.136800	3.016300	-5.325300
C	-6.577400	1.540600	-4.065100
C	-6.946200	0.088900	-4.390300
H	-6.470800	-0.189400	-5.349900
H	-8.023900	-0.041800	-4.516300
C	-5.737300	-2.189500	-0.912300
H	-5.462000	-2.618800	0.054700
C	-4.835300	-1.324500	-1.542600
O	-3.575100	-1.193700	-0.987100
C	-2.803000	-0.065200	-1.372900
H	-2.025000	0.047500	-0.600900
H	-3.402200	0.862400	-1.391300
C	-5.265300	-0.599400	-2.654700
H	-4.656800	0.210800	-3.059800
C	-6.498300	-0.884300	-3.270300
C	-7.294200	-1.985700	-2.811200
C	-8.303500	-2.728400	-3.767200
C	-7.825700	-2.641300	-5.250500
H	-8.381800	-3.383500	-5.852600
H	-6.746600	-2.869900	-5.331100
H	-8.011200	-1.663500	-5.716700

C	-9.755300	-2.203000	-3.695000
H	-10.401900	-2.797400	-4.370000
H	-9.824800	-1.145600	-4.004100
H	-10.164900	-2.285100	-2.673400
C	-8.319100	-4.262600	-3.475000
H	-8.788600	-4.788000	-4.327200
H	-8.899900	-4.539500	-2.583500
H	-7.290800	-4.651100	-3.354100
C	-6.980800	-2.489900	-1.498800
C	-7.996600	-3.309900	-0.657700
H	-7.739900	-4.385700	-0.697800
H	-8.971100	-3.187300	-1.130500
C	-3.744900	-0.112800	3.389300
O	-3.700500	-1.080400	4.154700
N	-3.662400	1.171700	3.819700
C	-3.386900	1.500100	5.212300
H	-3.640700	2.561400	5.377100
C	-1.929100	1.214900	5.630400
C	-0.928100	2.247100	5.117700
F	-1.073700	2.435500	3.762600
C	0.555500	1.811600	5.419200
F	0.764200	0.605500	4.831900
F	0.653200	1.661600	6.766100
C	1.700000	2.793200	4.943900
F	1.473400	3.164900	3.664400
C	3.141400	2.126200	5.010200
F	3.258100	1.264600	3.974100
F	3.267300	1.438200	6.168700
C	4.325200	3.165900	4.933700
F	4.075400	4.064900	3.957300
C	5.729800	2.508500	4.640100
F	5.775700	1.999500	3.403400
F	5.976900	1.531200	5.526700
F	6.677900	3.449600	4.757200
F	4.414800	3.810600	6.119200
F	1.676000	3.890400	5.734400
F	-1.141600	3.462900	5.702600
H	-1.639700	0.215300	5.267400
H	-1.849800	1.212900	6.731200
H	-4.042400	0.879200	5.848100
H	-3.658700	1.913100	3.125900
C	-4.337100	-4.684100	2.705700
O	-4.151400	-5.642800	1.956300
N	-3.512200	-3.607700	2.800400
C	-2.266900	-3.528800	2.053400
H	-1.819400	-2.543900	2.260400
H	-2.463200	-3.606100	0.967400
C	-1.279900	-4.640400	2.473600
C	0.092900	-4.452700	1.849100
F	-0.006700	-4.366500	0.484500
C	1.071100	-5.643700	2.189200
F	0.565900	-6.761000	1.607700
F	1.071500	-5.819300	3.537300
C	2.570000	-5.441200	1.728900
F	2.583900	-5.118500	0.414800
C	3.500300	-6.706400	1.925600
F	3.008700	-7.736700	1.200100
F	3.499200	-7.044700	3.236600
C	4.997000	-6.475800	1.466300
F	5.017500	-6.297000	0.126800

C	5.972000	-7.671600	1.796100
F	5.520200	-8.819200	1.271300
F	6.114700	-7.820100	3.119900
F	7.171800	-7.394900	1.262600
F	5.506100	-5.379900	2.074100
F	3.091000	-4.426100	2.455300
F	0.655800	-3.286800	2.292500
H	-1.681000	-5.621600	2.171900
H	-1.151400	-4.634600	3.569500
H	-3.736400	-2.821700	3.429500
C	-2.056500	-0.180300	-2.705700
O	-1.640200	0.831500	-3.278300
N	-1.809400	-1.436900	-3.151300
C	-0.931500	-1.662300	-4.293700
H	-1.066300	-2.696900	-4.650500
C	0.537400	-1.386700	-3.909400
H	0.589300	-0.416700	-3.392700
C	1.455000	-1.300600	-5.121800
F	1.030400	-0.313200	-5.968400
F	1.434300	-2.476100	-5.821400
C	2.946100	-0.992900	-4.709500
F	2.934400	0.039000	-3.824700
C	3.915200	-0.613000	-5.896800
F	3.547700	0.591700	-6.392100
F	3.792700	-1.551400	-6.863200
C	5.441000	-0.526100	-5.477400
F	5.559000	0.242600	-4.371400
C	6.366200	0.104500	-6.594000
F	6.138400	1.435600	-6.647900
F	6.079200	-0.444300	-7.797500
C	7.908900	-0.106800	-6.335700
F	8.235300	0.271800	-5.090800
F	8.598300	0.640200	-7.211300
F	8.249500	-1.390600	-6.508200
F	5.887100	-1.773500	-5.199600
F	3.433900	-2.097700	-4.090700
H	0.923900	-2.163300	-3.229700
H	-2.139200	-2.218600	-2.589100
C	-2.309300	4.848100	-2.843900
H	-1.227500	-0.968400	-5.099700
O	-2.218900	5.879600	-2.179400
N	-1.710200	3.670700	-2.527700
C	-0.804400	3.548200	-1.400000
H	-0.482900	2.496900	-1.355600
H	-1.322400	3.794300	-0.453600
C	0.419600	4.480500	-1.546400
C	1.534200	4.097200	-0.591100
F	1.077700	4.044400	0.700900
C	2.753000	5.086100	-0.634000
F	2.288600	6.355100	-0.503500
F	3.339700	4.967900	-1.854200
C	3.830500	4.848900	0.503200
F	3.328400	5.354500	1.652800
C	5.219200	5.544600	0.197600
F	4.993600	6.811400	-0.222800
F	5.837800	4.851500	-0.787500
C	6.191000	5.605300	1.438600
F	5.685600	6.455400	2.359300
C	7.652400	6.093900	1.099700
F	7.621300	7.275400	0.466000

F	8.292200	5.201000	0.334000
F	8.330300	6.236500	2.249200
F	6.299100	4.368900	1.978100
F	4.051700	3.524000	0.663500
F	2.009600	2.858200	-0.920200
H	0.113600	5.523400	-1.370300
H	0.831800	4.407100	-2.568300
H	-1.852900	2.832000	-3.099200
C	-0.305600	0.375700	1.814700
C	1.199800	0.148400	1.458100
F	1.862700	1.325200	1.411400
C	1.337500	-0.579000	0.063600
F	1.104100	0.301200	-0.933400
F	0.361800	-1.533100	-0.006100
C	2.707200	-1.327600	-0.206000
F	2.813200	-2.327300	0.687400
C	4.012100	-0.451600	-0.143000
F	4.222700	-0.081400	1.139900
F	3.832200	0.655000	-0.897100
C	5.340300	-1.144600	-0.683800
F	5.233300	-1.303200	-2.018600
C	5.718200	-2.538200	-0.053100
F	4.896400	-3.477400	-0.576900
F	5.555300	-2.492300	1.287400
C	7.202000	-2.992500	-0.340800
F	7.478200	-2.885400	-1.649000
F	7.346600	-4.273800	0.028600
F	8.067800	-2.245400	0.355200
F	6.340200	-0.266100	-0.426600
F	2.606600	-1.866800	-1.447900
F	1.738600	-0.625600	2.418000
O	-0.866400	-0.280700	2.654800
O	-0.847900	1.329300	1.051200
H	-1.801100	1.424200	1.266700

**Table S4.** Table of  $\rho_{\text{bcp}}$  for 5:PFOA

BCP #	Atom1	No1	Atom2	No2	Rho
313	F	225	F	233	0.009
314	F	225	F	231	0.008
248	F	166	F	236	0.008
349	F	196	F	250	0.007
241	F	155	F	236	0.007
352	F	187	F	241	0.006
236	F	167	F	236	0.006
363	F	196	F	241	0.006
219	F	167	F	234	0.006
343	F	127	F	251	0.006
223	F	150	F	234	0.006
370	F	160	F	243	0.006
344	F	167	F	251	0.006
317	F	208	F	231	0.005
191	F	127	F	231	0.005
346	F	225	F	239	0.005

199	F	125	F	231	0.005
372	F	165	F	247	0.005
374	F	165	F	244	0.004
285	F	182	F	250	0.004
237	F	155	F	243	0.004
371	F	160	F	247	0.003
275	F	182	F	239	0.003
358	F	224	F	239	0.002
378	F	166	F	244	0.001
192	F	127	F	238	0.001
357	F	132	F	238	0.001
202	F	122	O	252	0.008
167	F	120	O	252	0.008
387	F	208	O	253	0.002
384	F	167	O	252	0.002
291	H	197	F	250	0.008
261	H	177	F	233	0.005
307	H	204	F	233	0.004
125	H	90	F	234	0.003
157	H	55	O	252	0.013
74	H	90	O	253	0.011
213	H	146	O	252	0.008
296	H	204	O	253	0.006
200	H	138	O	252	0.005
58	O	53	H	254	0.011

**Table S5.** Table of  $\rho_{\text{bcp}}$  for 5:octanoic acid

BCP	Atom1	No1	Atom2	No2	Rho
314	F	225	H	242	0.010
278	F	182	H	245	0.009
245	F	167	H	243	0.009
235	F	155	H	243	0.008
237	F	155	H	245	0.007
344	F	224	H	246	0.007
343	F	224	H	247	0.007
350	F	166	H	244	0.007
194	F	225	H	240	0.007
222	F	150	H	243	0.006
330	F	225	H	247	0.006
354	F	187	H	249	0.006
200	F	125	H	240	0.005
199	F	127	H	240	0.004
353	F	160	H	253	0.004
358	F	216	H	248	0.003

276	F	160	H	245	0.003
366	F	192	H	251	0.003
195	F	127	H	246	0.002
365	F	187	H	251	0.002
349	F	224	H	240	0.002
376	F	216	H	247	0.002
359	F	223	H	248	0.002
356	F	132	H	254	0.001
357	F	132	H	246	0.001
380	F	164	H	251	0.000
347	F	122	O	237	0.008
169	F	120	O	237	0.008
309	F	225	O	238	0.006
348	F	167	O	237	0.006
264	H	177	H	242	0.002
158	H	55	O	237	0.013
302	H	204	O	238	0.010
74	H	90	O	238	0.010
214	H	146	O	237	0.010
202	H	138	O	237	0.006
70	O	53	H	239	0.007