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Potential PFBS and PFHxS Precursors

Literature study and theoretical assessment of abiotic degradation pathways leading to PFBS and PFHxS.

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Preface

Perfluorobutane sulfonic acid (PFBS) and Perfluorohexane sulfonic acid (PFHxS) are today found in the environment and in humans in most parts of the world. The Norwegian Environment Agency is currently evaluating PFBS and assessing the need for risk reduction measures. Furthermore, a proposal to include PFHxS, its salts and related substances in the Stockholm Convention on persistent organic pollutants (POP) has been submitted to the convention.

The overall objective of the present project is to summarize relevant information available in the open literature to provide an overall assessment of relevant precursors including possible grouping, and to evaluate possible routes to provide documentation, where missing, on the potential of abiotic degradation resulting in PFBS and PFHxS.

The present report summarises a classification of potential PFBS and PFHxS precursors and outlines the transformation routes leading to respectively PFBS and PFHxS.

The project has achieved its targets.

The results in this report have been quality controlled according to generally accepted principles for publication in internationally recognised scientific journals.

Oslo, June 2017

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Executive Summary

The open literature related to abiotic environmental degradation of potential PFBS and PFHxS precursors has been reviewed. In addition, the Chemical Abstract Services (CAS) database was searched for commercially available potential PFBS and PFHxS precursors using the "substructure search" method. A total number of 294 such chemicals with commercial sources were located, and 112 of these were tagged with "regulatory information". Interested parties may consult the CAS-database for details in the regulatory information or about the commercial availability of specific substances. This information is outside the scope of the present report.

Experimental and theoretical assessments of abiotic degradation pathways of potential PFBS and PFHxS precursors is summarized by substance class. In general, substances containing the n-$CF_3CF_2CF_2CF_2S(O_2)$- and n-$CF_3CF_2CF_2CF_2CF_2CF_2S(O_2)$- moities may undergo abiotic degradation resulting in the release of respectively PFBS and PFHxS. The abiotic degradation may also result in the release of C_2 – C_6 PFCA´s (perfluoro carboxylic acids).

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1 Literature study on abiotic degradation processes of potential PFBS- and PFHxS precursors

In 2016/2017, the Norwegian Environment Agency collected information about the intrinsic properties, use and exposure of perfluorobutane sulfonic acid (PFBS)[#] to assess the need for risk reduction measures for this substance [*Lassen et al.*, 2017].

The Australian Department of Health has published information on direct and indirect PFBS precursors on the World Wide Web [*Department of Health*, 2017c; 2017b]. The Australian Department of Health has also issued information on the direct perfluorohexane sulfonic acid (PFHxS)[$] precursors [*Department of Health*, 2017a].

The Chemical Abstract Services (CAS) database was searched for potential PFBS and PFHxS precursors using the "substructure search" method. The database contains several thousands compounds containing either the $CF_3CF_2CF_2CF_2S(O_2)$- or the $CF_3CF_2CF_2CF_2CF_2CF_2S(O_2)$- fragment; only those listed with a commercial source are addressed in the present summary. A total number of 285 potential PFBS and PFHxS precursors chemicals are included, and 107 of these are tagged with "regulatory information" in the CAS database.

The scarce scientific literature related to abiotic environmental degradation of potential perfluorobutanesulfonic acid and perfluorohexanesulfonic acid precursors found in the CAS database by 30.05.2017 has been examined.

Terminology, classification and origins of perfluoroalkyl and polyfluoroalkyl substances in the environment was reviewed in 2011 [*Buck et al.*, 2011]. The compound names listed together with the corresponding structures in the present summary are CA index names [*American_Chemical_Society*, 2008].

Reaction with OH radicals is the dominant gas phase loss process for a majority of tropospheric trace gases on a global scale [*Finlayson-Pitts and Pitts*, 1986]. Minor atmospheric oxidants such as ozone, Cl atoms and NO_3 radicals are not considered here. The potential PFBS and PFHxS precursors will with a few exeptions not absorp light in the actinic region (λ> 280 nm) and UV-degradation is generally not important for these compounds.

The atmospheric aqueous phase chemistry, including aqueous surface layer chemistry, of potential PFBS and PFHxS precursors has received little attention. Many potential PFBS and PFHxS precursors are surfactants and even though they are water-repellants, they will be exposed to an aqueous layer having essentially the same features as the atmospheric aerosol and conceivably undergo photo-oxidation. Herrmann and co-workers have reviewed atmospheric aqueous phase chemistry [*Zellner and Herrmann*, 1995; *Herrmann and Zellner*, 1996; *Herrmann*, 2003; 2007]; chemical reactions in the aqueous phase are generally triggered by free radicals such as OH, NO_3 and SO_4^-. Again, OH is the dominat oxidant. The initial step in the aqueous phase OH radical reactions with organics is in most cases the same as in the gas phase.

[#] 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonic acid; CAS RN: 375-73-5 and 59933-66-3 (monohydrate).

[$] 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonic acid, CAS RN: 355-46-4

2 Abiotic degradation pathways of potential PFBS and PFHxS precursors

2.1 PFBS and PFHxS Salts

Table 2.1.1. Commercially available inorganic PFBS salts.

Kation	CAS RN
K^+	* 29420-49-3
Na^+	60453-92-1
Li^+	131651-65-5
NH_4^+	* 68259-10-9
Ag^+	111831-41-5
Mg^{2+}	507453-86-3
Zn^{2+}	502457-69-4

* Substances for which the CAS database contains regulatory information.

Table 2.1.2. Commercially available inorganic PFHxS salts.

Kation	CAS RN
Li^+	* 55120-77-9
Na^+	* 82382-12-5
K^+	* 3871-99-6
NH_4^+	* 68259-08-5

* Substances for which the CAS database contains regulatory information.

Table 2.1.3. Commercially available organic PFBS salts

CAS RN	Kation	Kation CAS RN
* 144317-44-2	Sulfonium, triphenyl-	18393-55-0
194999-82-1	Iodonium, diphenyl-	10182-84-0
* 194999-85-4	Iodonium, bis[4-(1,1-dimethylethyl)phenyl]-	61267-44-5
241806-75-7	Sulfonium, tris[4-(1,1-dimethylethyl)phenyl]-	91815-56-4
108427-52-7	1-Butanaminium, N,N,N-tributyl-	10549-76-5
867373-18-0	Thiophenium, tetrahydro-1-(1-methyl-1H-indol-3-yl)-	867373-17-9
1015420-87-7	Pyridinium, 1-ethyl-3-methyl-	45187-15-3
* 220689-12-3	Phosphonium, tetrabutyl-	15853-37-9
25628-08-4	Ethanaminium, *N*,*N*,*N*-triethyl- (1:1)	66-40-0
* 70225-18-2	Ethanol, 2,2'-iminobis- (1:1)	111-42-2
1001557-05-6	1H-Imidazolium, 3-hexyl-1-methyl-	85100-82-9
905972-83-0	1H-Imidazolium, 1-methyl-3-octyl-	178631-03-3
374571-81-0	2-Propanaminium, N,N-dimethyl-N-(1-methylethyl)-	74747-95-8
857285-80-4	Sulfonium, [4-[2-(1,1-dimethylethoxy)-2-oxoethoxy]phenyl] diphenyl-	180801-54-1
26601-00-3	Pyrrolidinium, 1,1-dimethyl-	15312-12-6
124472-66-8	1-Butanaminium, N,N-dibutyl-N-methyl-	29814-63-9
56773-55-8	1-Pentanaminium, N,N,N-tripropyl-	56773-54-7
503155-89-3	Morpholine (1:1)	110-91-8

* Substances for which the CAS database contains regulatory information.

Table 2.1.4. Commercially available organic PFHxS salts.

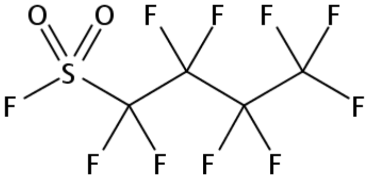
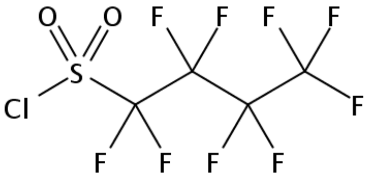
CAS RN	Cation	Cation CAS RN
* 70225-16-0	Ethanol, 2,2'-iminobis-	111-42-2

* Substances for which the CAS database contains regulatory information.

All PFBS and PFHxS salts will eventually dissolve in water resulting in the release of respectively PFBS and PFHxS.

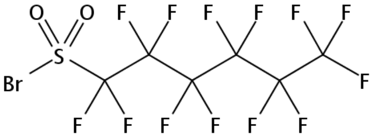
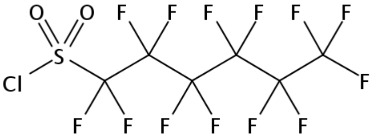
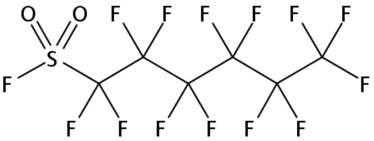
2.2 PFBS and PFHxS sulfonyl halides

Table 2.2.1. Commercially available PFBS sulfonyl halides.

CAS RN	Name	Structure
* 375-72-4	1-Butanesulfonyl fluoride, 1,1,2,2,3,3,4,4,4-nonafluoro-	
2991-84-6	1-Butanesulfonyl chloride, 1,1,2,2,3,3,4,4,4-nonafluoro-	

* Substances for which the CAS database contains regulatory information.

Table 2.2.2. Commercially available PFHxS sulfonyl halides.

CAS RN	Name	Structure
111393-39-6	1-Hexanesulfonyl bromide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
* 55591-23-6	1-Hexanesulfonyl chloride, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
* 423-50-7	1-Hexanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	

* Substances for which the CAS database contains regulatory information.

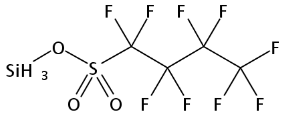
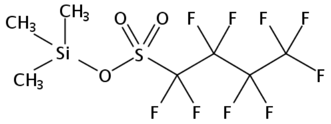
The PFBS and PFHxS sulfonylfluorides do not hydrolyse readily in pure water, but they will eventually do so. The PFBS and PFHxS sulfonylfluorides are reported to hydrolyse reasonably fast in the presence of traces of NH_3 [*Honda and Takano*, 2013]. The PFBS and PFHxS sulfonylchlorides and -bromides readily hydrolyses upon contact with water.

PFBS and PFHxS sulfonyl halides will eventually undergo hydrolysis resulting in the release of respectively PFBS and PFHxS.

2.3 Covalently bonded n-$C_4F_9SO_2O$- and n-$C_6F_{13}SO_2O$- compounds

2.3.1 *Silyl esters*

Table 2.3.1. Commercially available silyl esters of PFBS.

CAS RN	Name	Structure
135524-36-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, silyl ester CAS Name: Methanesulfonic acid, 1,1-difluoro-1-(1,1,2,2,3,3,3-heptafluoro-propyl)-, silyl ester	
68734-62-3	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, trimethylsilyl ester CAS Name: Methanesulfonic acid, 1,1-difluoro-1-(1,1,2,2,3,3,3-heptafluoropropyl)-, trimethylsilyl ester	

No commercially available silyl esters of PFHxS were found in the CAS database.

In the presence of water silanes and silane esters undergo hydrolysis resulting in the corresponding silanols. In the present case hydrolysis will be accompanied by release of the sulfonic acid PFBS as the second hydrolysis product. No relevant information concerning hydrolytic lifetimes of the silyl esters listed was found in the open literature.

The silanes listed have appreciable vapour pressures [*Häbich and Effenberger*, 1978] and may in principle evaporate and undergo photo-oxidation in the atmosphere. Atkinson studied the kinetics of OH reactions with a series of organosilicon compounds including siloxanes and reported atmospheric lifetimes of >10 days [*Roger Atkinson*, 1991]. Tuazon *et al*. have investigated the products formed in the atmospheric degradation of volatile methyl-silicon compounds [*Tuazon et al.*, 2000]. For tetramethylsilane the first steps in the photo-oxidation are reported to be:

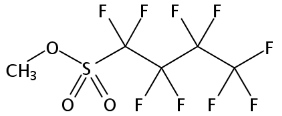
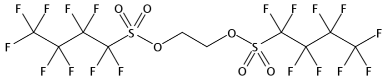
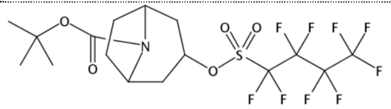
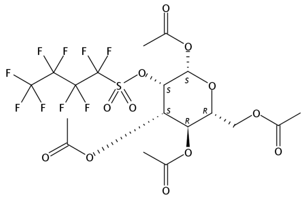
$$Si(CH_3)_4 + OH \rightarrow (CH_3)_3Si\dot{C}H_2 + H_2O$$
$$(CH_3)_3Si\dot{C}H_2 + O_2 \rightarrow [(CH_3)_3SiCH_2(O\dot{O})] \rightarrow (CH_3)_3SiOCH_2\dot{O}$$
$$(CH_3)_3SiOCH_2\dot{O} + O_2 \rightarrow (CH_3)_3SiOCHO + HO_2$$
$$(CH_3)_3SiOCHO + H_2O \rightarrow (CH_3)_3SiOH + HC(O)OH$$

For the above listed silanes the corresponding reactions will lead to release of PFBS.

Silyl esters of PFBS will either undergo atmospheric photo-oxidation or eventually hydrolyse resulting in the release of PFBS.

2.3.2 Alkyl esters

Table 2.3.2. Commercially available alkyl esters of PFBS.

CAS RN	Name	Structure
6401-03-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, methyl ester	
92982-03-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1,2-ethanediyl ester	
1956367-22-8	8-Azabicyclo[3.2.1]octane-8-carboxylic acid, 3-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)-sulfonyl]oxy]-, 1,1-dimethylethyl ester	
480438-48-0	β-D-Mannopyranose, 1,3,4,6-tetraacetate 2-(1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonate)	

No commercially available alkyl esters of PFHxS were found in the CAS database.

PFBS alkyl esters (nonaflate esters) and PFHxS alkyl esters will eventually undergo hydrolysis in contact with natural water; no relevant information concerning hydrolytic lifetimes of the alkyl esters listed was found in the open literature. Nonaflate esters are also expected to undergo photo-oxidation in the atmosphere and in the aqueous phase following the same mechanism as suggested for N-methyl perfluorobutane sulfonamidoethanol, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$ [*D'Eon et al.*, 2006], see section 2.3.7 (page 22). The branching between abstraction and addition in the reaction with OH radicals (see below) is not known.

For the methyl ester of PFBS the expected photo-oxidation reactions are:

$CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CH_3 + OH \rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}\dot{C}H_2 + H_2O$ (abstraction)

$\rightarrow CF_3CF_2CF_2CF_2S(O)(OH)\dot{O}\text{-}O\text{-}CH_3$ (addition)

$CF_3CF_2CF_2CF_2S(O)(OH)\dot{O}\text{-}O\text{-}CH_3 \rightarrow \mathbf{CF_3CF_2CF_2CF_2SO_2OH} + CH_3\dot{O}$

$\rightarrow CF_3CF_2CF_2\dot{C}F_2 + CH_3\text{-}O\text{-}S(O_2)OH$

$CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}\dot{C}H_2 + O_2 \rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CH_2O\dot{O}$

$CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CH_2O\dot{O} + NO \rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CH_2\dot{O} + NO_2$

$CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CH_2\dot{O} + O_2 \rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CHO + HO_2$

$CF_3CF_2CF_2\dot{C}F_2 \rightarrow CF_3CF_2CF_2COOH, CF_3CF_2COOH, CF_3COOH$ (see section 2.3.7)

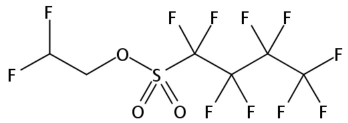
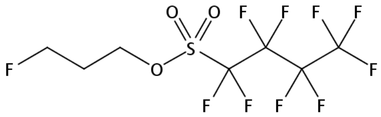
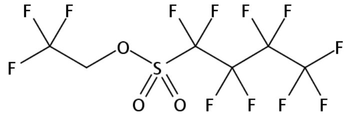
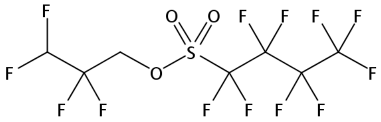
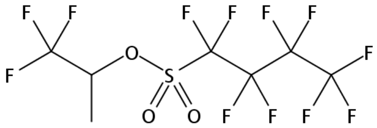
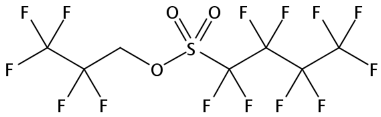
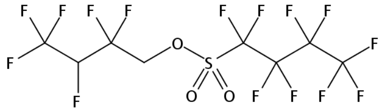
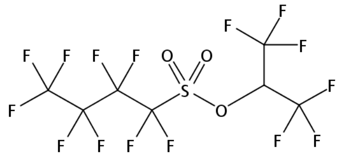
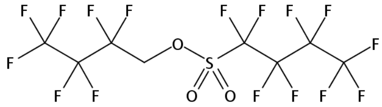
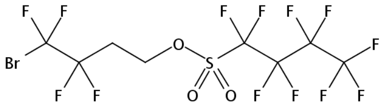
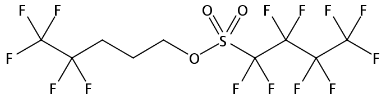
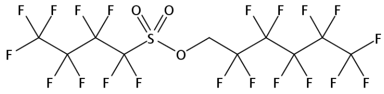
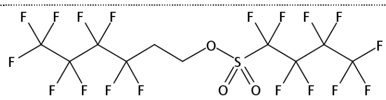
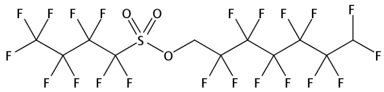
The expected photo-oxidation product resulting from the C-H abstraction reaction in $C_4F_9SO_2\text{-}O\text{-}CH_3$ is the anhydride of PFBS and formic acid. This anhydride will hydrolyse resulting in the release of PFBS:

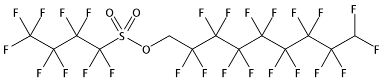
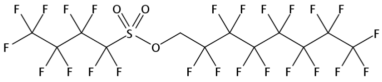
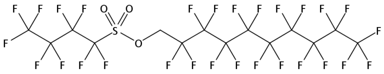
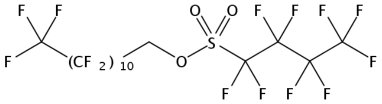
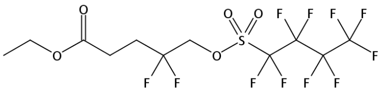
$$CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CHO + H_2O \rightarrow \mathbf{CF_3CF_2CF_2CF_2SO_2OH} + HCOOH$$

Alkyl esters of PFBS and PFHxS will eventually hydrolyse in water / alternatively undergo photo-oxidation in air resulting in the release of respectively PFBS and PFHxS. Photo-oxidation of PFBS and PFHxS alkyl esters will also result in the release of C_2 – C_6 PFCA´s.

2.3.3 Fluoroalkyl esters

Table 2.3.2. Commercially available fluoroalkyl esters of PFBS.

CAS RN	Name	Structure
1036375-28-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2-difluoroethyl	
1346521-48-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 3-fluoropropyl	
# 79963-95-4	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,2-trifluoroethyl ester	
66959-14-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3-tetrafluoropropyl ester	
# 118334-94-4	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,2-trifluoro-1-methylethyl ester	
# 893556-35-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,3-pentafluoropropyl ester	
1205020-79-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,4,4,4-hexafluorobutyl ester	
118334-96-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,2-trifluoro-1-(trifluoromethyl)ethyl ester	
883499-32-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,4,4,4-heptafluorobutyl ester	
1980086-38-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-bromo-3,3,4,4-tetrafluorobutyl ester	
# 1980086-36-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4,4,5,5,5-pentafluoropentyl ester	
# 924894-08-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl ester	
# 1980035-15-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 3,3,4,4,5,5,6,6,6-nonafluorohexyl ester	
1980086-12-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl ester	

1980075-21-5	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorononyl ester	
# 187039-77-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl ester	
# 1363404-12-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecyl ester	
# 924894-11-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-tricosafluorododecyl ester	
1361253-41-9	Pentanoic acid, 4,4-difluoro-5-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl) sulfonyl]oxy]-, ethyl ester	

Compounds containing $CF_3(CF_2)_nCHR^1$-fragment (R^1= H, CH_3,…)

No commercially available fluoro alkyl esters of PFHxS was found in the CAS database. All commercially available PFBS (nonaflate) and PFHxS fluoroalkyl esters (n-$C_4F_9SO_2$-O-R and n-$C_6F_{13}SO_2$-O-R) will eventually undergo hydrolysis; no relevant information concerning hydrolytic lifetimes of the alkyl esters listed was found in the open literature. The vapour pressures available for some of the nonaflate fluoroalkyl esters listed in Table 2.3.2 are relatively high and they are therefore also expected to undergo photo-oxidation in the atmosphere. They all have H-atom(s) in α-position, and they will follow the same mechanism as outlined for the PFBS alkyl esters, see section 2.3.2.

$$\begin{aligned}
CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}CHR^1(CF_2)_nCF_3 + OH &\rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}\dot{C}R^1(CF_2)_nCF_3 + H_2O && \text{(abstraction)}\\
&\rightarrow CF_3CF_2CF_2CF_2S(O)(OH)\dot{O}\text{-}O\text{-}CHR^1(CF_2)_nCF_3 && \text{(addition)}\\
CF_3CF_2CF_2CF_2S(O)(OH)\dot{O}\text{-}O\text{-}CHR^1(CF_2)_nCF_3 &\rightarrow \mathbf{CF_3CF_2CF_2CF_2SO_2OH} + \dot{O}CHR^1(CF_2)_nCF_3\\
&\rightarrow CF_3CF_2CF_2\dot{C}F_2 + CF_3(CF_2)_nR^1CH\text{-}OS(O_2)OH\\
CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}\dot{C}R^1(CF_2)_nCF_3 + O_2 &\rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(O\dot{O})R^1(CF_2)_nCF_3\\
CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(O\dot{O})R^1(CF_2)_nCF_3 + NO &\rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(\dot{O})R^1(CF_2)_nCF_3 + NO_2\\
CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(\dot{O})R^1(CF_2)_nCF_3 &\rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(O)(CF_2)_nCF_3 + \dot{R}^1\\
&\rightarrow CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(O)R^1 + \dot{C}F_2(CF_2)_{n-1}CF_3\\
\dot{O}CHR^1(CF_2)_nCF_3 + O_2 &\rightarrow O{=}CR^1(CF_2)_nCF_3 + HO_2
\end{aligned}$$

The $CF_3CF_2CF_2CF_2SO_2$-O-C(O)R^1 and $CF_3CF_2CF_2CF_2SO_2$-O-C(O)$(CF_2)_nCF_3$ acid anhydrides will eventually hydrolyse resulting in the release of PFBS :

$$\begin{aligned}
CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(O)R^1 + H_2O &\rightarrow \mathbf{CF_3CF_2CF_2CF_2SO_2OH} + R^1COOH\\
CF_3CF_2CF_2CF_2SO_2\text{-}O\text{-}C(O)(CF_2)_nCF_3 + H_2O &\rightarrow \mathbf{CF_3CF_2CF_2CF_2SO_2OH} + CF_3(CF_2)_nCOOH
\end{aligned}$$

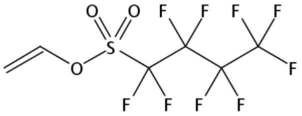
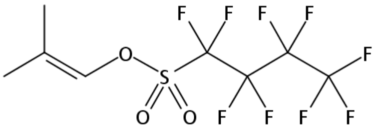
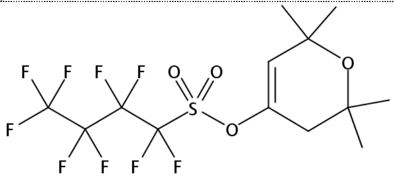
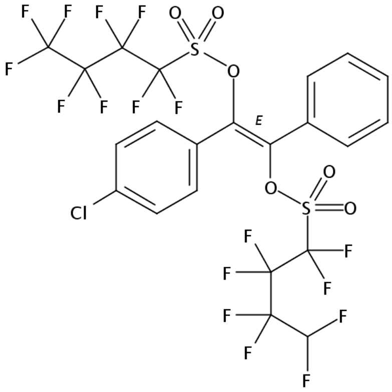
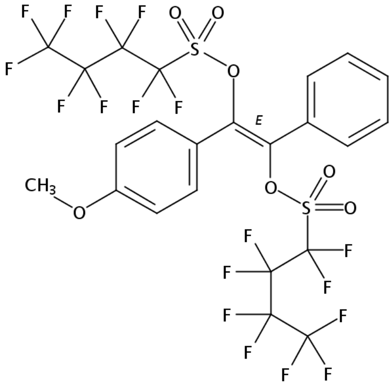
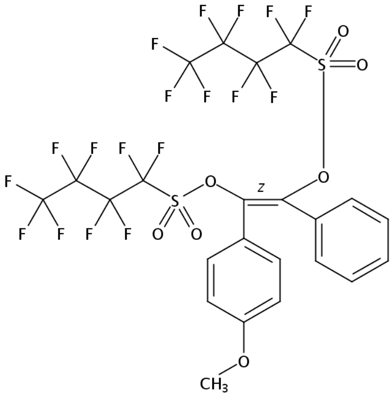
The $CF_3CF_2CF_2\dot{C}F_2$ radical will undergo a series of reactions initiated by O_2 leading to $C_2 – C_4$ PFCA´s, see section 2.3.7 (page 22). $CF_3CF_2CF_2CF_2CF_2\dot{C}F_2$ and $\dot{O}CHR^1(CF_2)_nCF_3$ radicals will also result in PFCA´s.

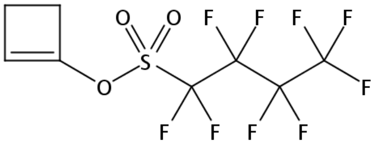
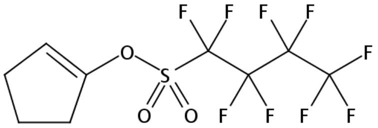
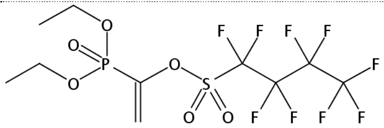
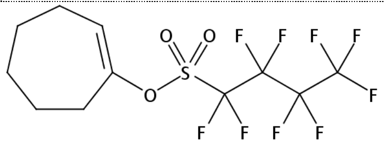
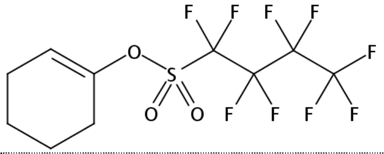
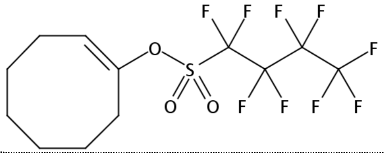
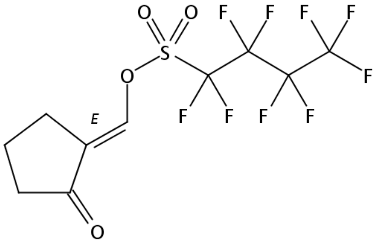
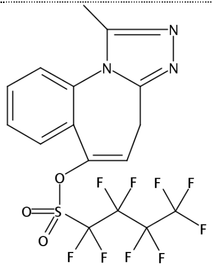
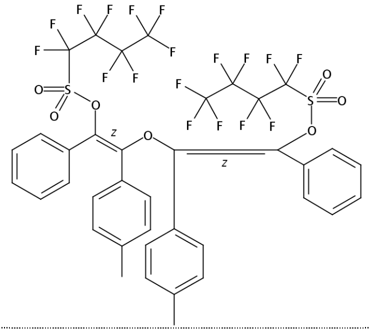
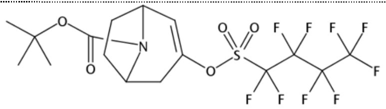
$$CF_3CF_2CF_2\dot{C}F_2 + O_2 \rightarrow CF_3CF_2CF_2COOH,\ CF_3CF_2COOH,\ CF_3COOH \qquad \text{(complex reactions)}$$

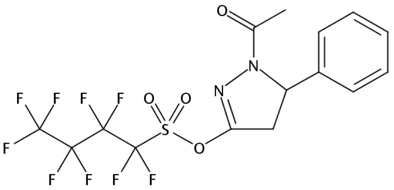
Fluorinated alkyl esters of PFBS and PFHxS will eventually hydrolyse / alternatively undergo photo-oxidation resulting in the release of respectively PFBS and PFHxS. Photo-oxidation of PFBS and PFHxS fluorinated alkyl esters may also result in the release of $C_2 – C_6$ PFCA´s.

2.3.4 Olefinic esters

Table 2.3.3. Commercially available olefinic esters of PFBS.

CAS RN	Name	Structure
42409-05-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, ethenyl ester	
84224-48-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2-methyl-1-propen-1-yl ester	
1142363-55-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 3,6-dihydro-2,2,6,6-tetramethyl-2*H*-pyran-4-yl ester	
101315-44-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-(4-chlorophenyl)-2-[[(1,1,2,2,3,3,4,4-octafluorobutyl)sulfonyl]oxy]-2-phenylethenyl ester, (*E*)-	
101315-35-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-(4-methoxyphenyl)-2-phenyl-1,2-ethenediyl ester, (*E*)-	
101315-36-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-(4-methoxyphenyl)-2-phenyl-1,2-ethenediyl ester, (*Z*)-	

38554-51-7	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-cyclobuten-1-yl ester	
36839-94-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-cyclopenten-1-yl ester	
243137-79-3	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-(diethoxyphosphinyl)ethenyl ester	
42108-79-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-cyclohepten-1-yl ester	
36839-95-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-cyclohexen-1-yl ester	
36839-96-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-cycloocten-1-yl ester	
152485-94-4	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, (2-oxocyclopentylidene)methyl ester, (*E*)-	
1588522-06-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-methyl-4*H*-[1,2,4]triazolo[4,3-*a*][1]benzazepin-6-yl ester	
101315-40-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, oxybis[2-(4-methylphenyl)-1-phenyl-2,1-ethenediyl] ester, (*Z*,*Z*)-	
1206550-28-8	8-Azabicyclo[3.2.1]oct-2-ene-8-carboxylic acid, 3-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)-sulfonyl]oxy]-, 1,1-dimethylethyl ester	

1180009-36-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-acetyl-4,5-dihydro-5-phenyl-1*H*-pyrazol-3-yl ester	

No commercially available olefinic esters of PFHxS were found in the CAS database. They are, however, expected to react the same way as the olefinic nonaflate esters.

The nonaflate olefinic esters ($C_4F_9SO_2\text{-O-}CR^1{=}CR^2R^3$) listed in Table 2.3.3 will eventually undergo hydrolysis; no relevant information concerning hydrolytic lifetimes of the alkyl esters listed was found in the open literature. The vapour pressures for some of the nonaflate fluoroalkyl esters listed in Table 2.3.3 may be sufficiently high to undergo photo-oxidation in the atmosphere. They will follow a slightly more complicated mechanism than that found for N-methyl perfluorobutane sulfonamideethanol, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$ [*D'Eon et al.*, 2006], see section 2.3.2. It has been shown that the gas phase reaction of OH radicals with alkyl vinyl ethers ($CH_2{=}CH\text{-O-}R$; R= CH_3, C_2H_5, C_3H_7) predominantly is an addition reaction [*Perry et al.*, 1977; *Zhou et al.*, 2006]. H-abstraction reactions will also take place from R^1,R^2 and R^3, but this will only result in new oxygen-containing compounds that eventually will hydrolyse. For the sake of simplicity, these reactions are not included below. The PFBS yield in the OH reaction is not know; it is, however, clear that some PFBS will be formed.

$$\begin{array}{rcll}
C_4F_9SO_2\text{-O-}CR^1{=}CR^2R^3 + OH & \rightarrow & C_4F_9SO_2\text{-O-}CR^1(OH)\text{-}\dot{C}R^2R^3 & \text{(addition)} \\
 & \rightarrow & C_4F_9SO_2\text{-O-}\dot{C}R^1\text{-}C(OH)R^2R^3 & \text{(addition)} \\
 & \rightarrow & C_4F_9S(O)(OH)\dot{O}\text{-O-}CR^1{=}CR^2R^3 & \text{(addition)} \\
C_4F_9S(O)(OH)\dot{O}\text{-O-}CR^1{=}CR^2R^3 & \rightarrow & \mathbf{CF_3CF_2CF_2CF_2SO_2OH} + O{=}CR^1\text{-}\dot{C}R^2R^3 & \\
 & \rightarrow & CF_3CF_2CF_2\dot{C}F_2 + R^2R^3C{=}CR^1\text{-O-}S(O_2)OH &
\end{array}$$

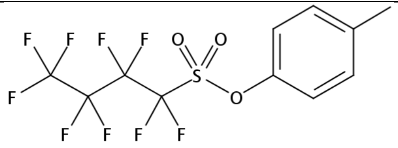
The $CF_3CF_2CF_2\dot{C}F_2$ radical will undergo a series of reactions initiated by O_2 leading to $C_2 – C_4$ PFCA´s, see section 2.3.7 (page 22).

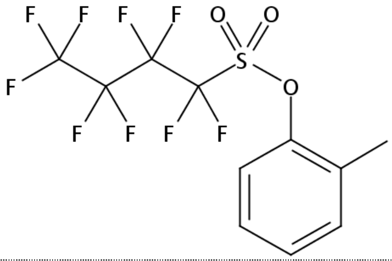
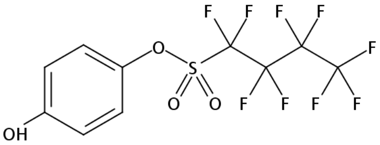
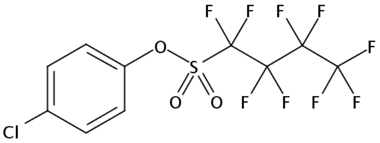
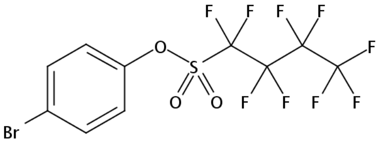
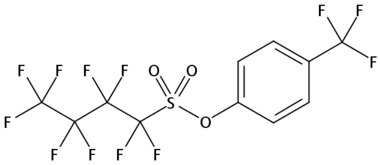
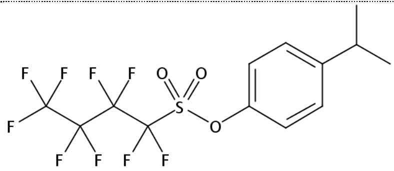
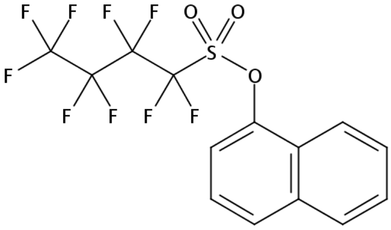
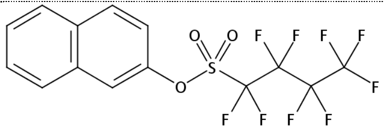
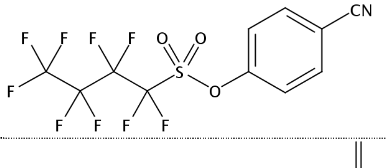
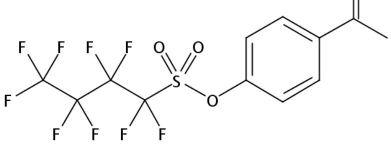
$$CF_3CF_2CF_2\dot{C}F_2 + O_2 \rightarrow CF_3CF_2CF_2COOH,\ CF_3CF_2COOH,\ CF_3COOH \qquad \text{(complex reactions)}$$

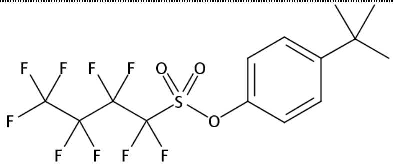
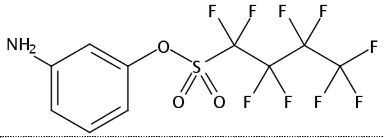
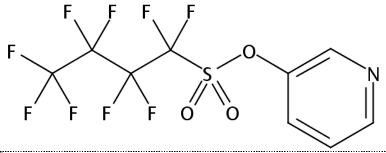
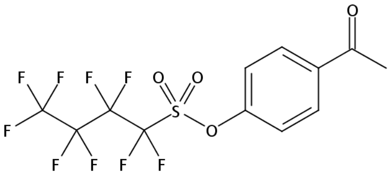
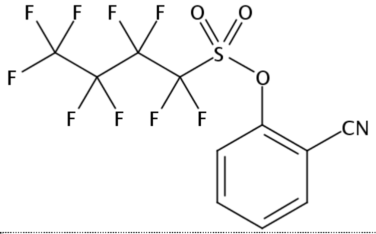
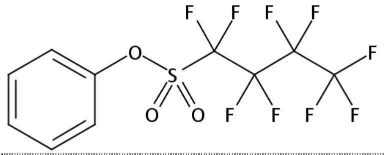
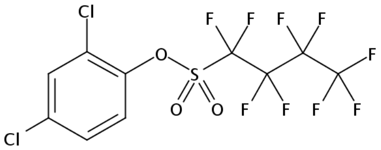
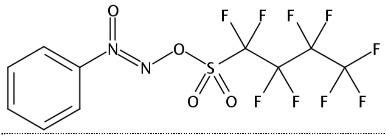
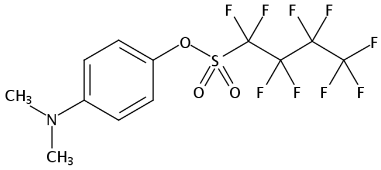
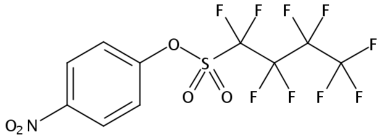
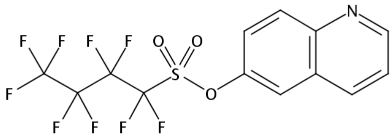
Olefinic esters *of PFBS and PFHxS will eventually hydrolyse / alternatively undergo photo-oxidation resulting in the release of respectively PFBS and PFHxS. Photo-oxidation of PFBS and PFHxS fluorinated alkyl esters may also result in the release of $C_2 – C_6$ PFCA´s.*

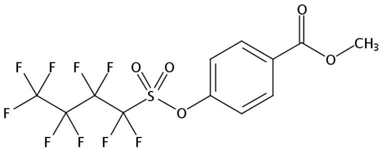
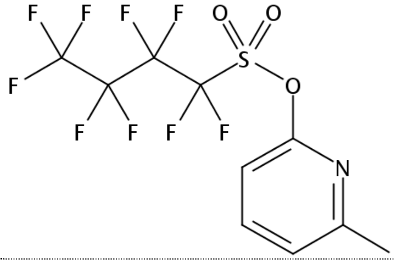
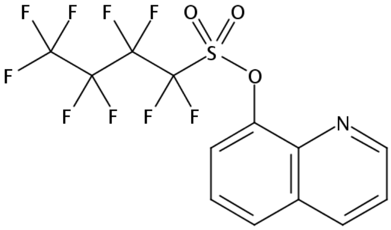
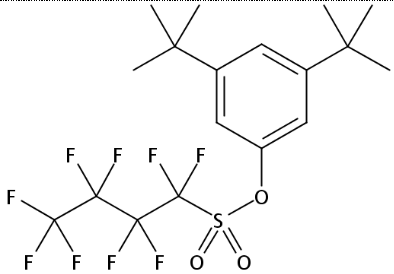
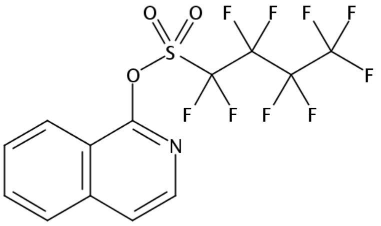
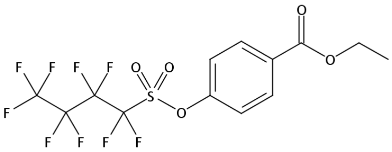
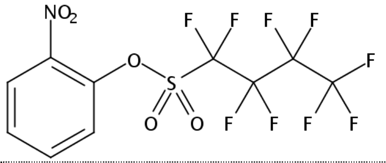
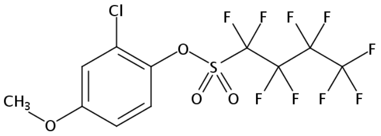
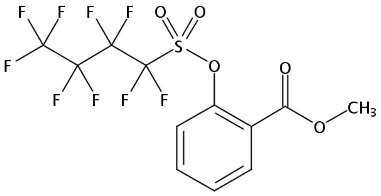
2.3.5 Aryl esters

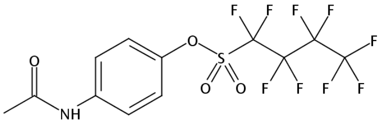
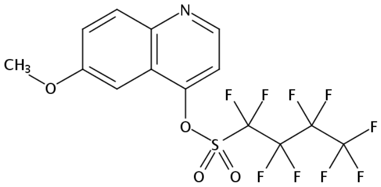
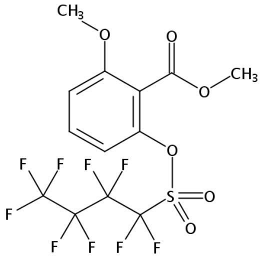
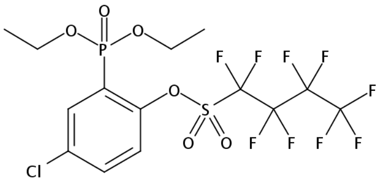
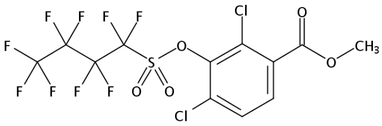
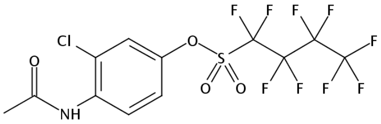
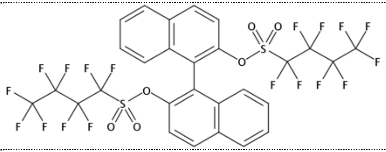
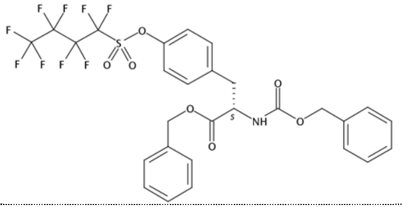
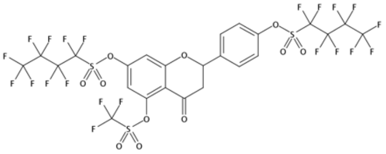
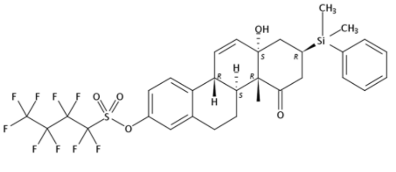
Table 2.3.4. Commercially available aryl esters of PFBS.

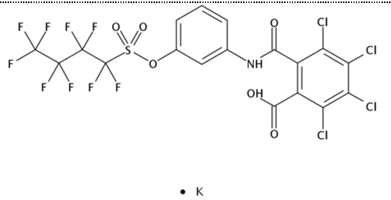
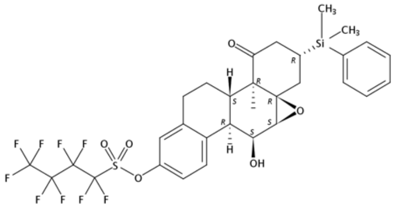
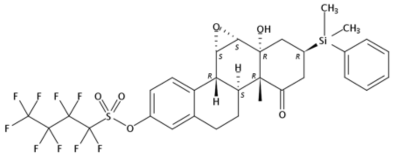
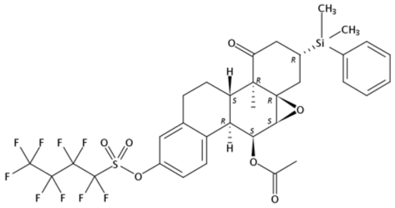
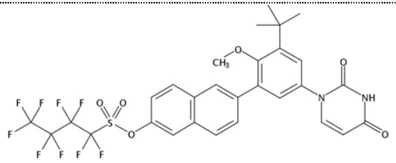
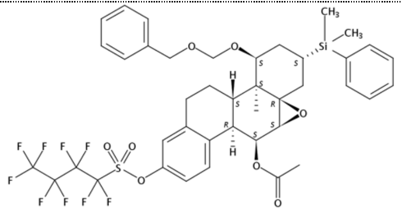
CAS RN	Name	Structure
93131-73-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-methylphenyl ester	

42096-33-3	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2-methylphenyl ester	
1463426-93-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-hydroxyphenyl ester	
41605-52-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-chlorophenyl ester	
321970-34-7	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-bromophenyl ester	
33073-26-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-(trifluoromethyl)phenyl ester	
93131-75-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-(1-methylethyl)phenyl ester	
32848-17-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-naphthalenyl ester	
42096-34-4	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2-naphthalenyl ester	
626201-15-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-cyanophenyl ester	
33073-27-7	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-(1-methylethenyl)phenyl ester	

247018-51-5	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-(1,1-dimethylethyl)phenyl ester	
32848-25-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 3-aminophenyl ester	
32848-20-7	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 3-pyridinyl ester	
264135-62-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-acetylphenyl ester	
873838-37-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2-cyanophenyl ester	
25628-11-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, phenyl ester	
32848-21-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,4-dichlorophenyl ester	
88280-62-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2-oxido-2-phenyldiazenyl ester	
1463426-91-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-(dimethylamino)phenyl ester	
32848-23-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-nitrophenyl ester	
920491-93-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 6-quinolinyl ester	

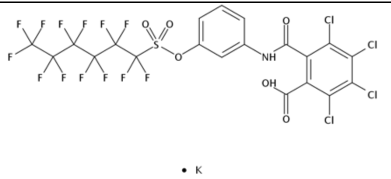
41605-53-2	Benzoic acid, 4-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]oxy]-, methyl ester	
1161941-06-5	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 6-methyl-2-pyridinyl ester	
41605-60-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 8-quinolinyl ester	
93131-76-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 3,5-bis(1,1-dimethylethyl)phenyl ester	
1161941-05-4	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1-isoquinolinyl ester	
32848-24-1	Benzoic acid, 4-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]oxy]-, ethyl ester	
342589-38-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2-nitrophenyl ester	
1131890-97-5	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2-chloro-4-methoxyphenyl ester	
278175-48-7	Benzoic acid, 2-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]oxy]-, methyl ester	

41605-57-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-(acetylamino)phenyl ester	
1161941-02-1	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 6-methoxy-4-quinolinyl ester	
475630-76-3	Benzoic acid, 2-methoxy-6-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]oxy]-, methyl ester	
1227161-30-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-chloro-2-(diethoxyphosphinyl)phenyl ester	
1451750-40-5	Benzoic acid, 2,4-dichloro-3-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]oxy]-, methyl ester	
1428370-26-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 4-(acetylamino)-3-chlorophenyl ester	
232264-15-2	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, [1,1'-binaphthalene]-2,2'-diyl ester	
262603-98-5	L-Tyrosine, *N*-[(phenylmethoxy)carbonyl]-, phenylmethyl ester, 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonate (ester)	
1958068-90-0	INDEX NAME NOT YET ASSIGNED	
303998-33-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, (4b*R*,6a*S*,8*R*,10a*R*,10b*S*)-8-(dimethylphenylsilyl)-4b,6a,7,8,9,10,10a,10b,11,12-decahydro-6a-hydroxy-10a-methyl-10-oxo-2-chrysenyl ester	

* 68568-54-7	Benzoic acid, 2,3,4,5-tetrachloro-6-[[[3-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]oxy]phenyl]amino]carbonyl]-, potassium salt (1:1)	
303998-31-4	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, (6a*S*,6b*R*,9*R*,10a*R*,11a*S*,12*S*,12a*R*)-9-(dimethylphenylsilyl)-5,6a,6b,7,8,9,10,11a,12,12a-decahydro-12-hydroxy-6b-methyl-7-oxo-6*H*-chryseno[6,6a-*b*]oxiren-3-yl ester	
303998-35-8	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, (1a*S*,1b*R*,3*R*,5a*R*,5b*S*,11b*R*,11c*S*)-3-(dimethylphenylsilyl)-1a,1b,2,3,4,5,5a,5b,6,7,11b,11c-dodecahydro-1b-hydroxy-5a-methyl-5-oxochryseno[5,6-*b*]oxiren-9-yl ester	
303998-67-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, (6a*S*,6b*R*,9*R*,10a*R*,11a*S*,12*S*,12a*R*)-12-(acetyloxy)-9-(dimethylphenylsilyl)-5,6a,6b,7,8,9,10,11a,12,12a-decahydro-6b-methyl-7-oxo-6*H*-chryseno[6,6a-*b*]oxiren-3-yl ester	
1355646-97-7	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 6-[5-(3,4-dihydro-2,4-dioxo-1(2*H*)-pyrimidinyl)-3-(1,1-dimethylethyl)-2-methoxyphenyl]-2-naphthalenyl ester	
303998-29-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, (6a*S*,6b*S*,7*S*,9*S*,10a*R*,11a*S*,12*S*,12a*R*)-12-(acetyloxy)-9-(dimethylphenylsilyl)-5,6a,6b,7,8,9,10,11a,12,12a-decahydro-6b-methyl-7-[(phenylmethoxy)methoxy]-6*H*-chryseno[6,6a-*b*]oxiren-3-yl ester	

* Substances for which the CAS database contains regulatory information.

Table 2.3.5. Commercially available aryl esters of PFHxS.

CAS RN	Name	Structure
* 68815-72-5	Benzoic acid, 2,3,4,5-tetrachloro-6-[[[3-[[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]oxy]phenyl]amino]carbonyl]-, potassium salt (1:1)	

The nonaflate aryl esters listed in Table 2.3.4 and the PFHxS esters listed in Table 2.3.5 will undergo slow hydrolysis; no relevant information concerning hydrolytic lifetimes of the alkyl esters listed was found in the open literature. The vapour pressures for some of the nonaflate fluoroalkyl esters listed in Table 2.3.3 may be sufficiently high to undergo photo-oxidation in the atmosphere. It is known that the gas phase reaction of OH radicals with aromatic compounds predominantly is an addition reaction [*R. Atkinson*, 1986]. The photo-oxidation mechanism of PFBS and PFHxS aryl esters will therefore follow a slightly more complicated mechanism than that outlined for the alkyl-, fluoroalkyl-and olefinic esters, see sections 2.3.2 – 2.3.4. H-abstraction reactions will also take place. For the sake of simplicity, these reactions are not included below. The PFBS yield in the OH reaction is not know; it is, however, clear that some PFBS will be formed.

$C_4F_9SO_2\text{-O-Ph} + OH \rightarrow C_4F_9SO_2\text{-O-}\dot{P}hOH$ (addition)
$\rightarrow C_4F_9S(O)(OH)\dot{O}\text{-O-Ph}$ (addition)
$C_4F_9S(O)(OH)\dot{O}\text{-O-Ph} \rightarrow \mathbf{CF_3CF_2CF_2CF_2SO_2OH} + \dot{O}Ph$
$\rightarrow CF_3CF_2CF_2\dot{C}F_2 + \text{Ph-O-}S(O_2)OH$

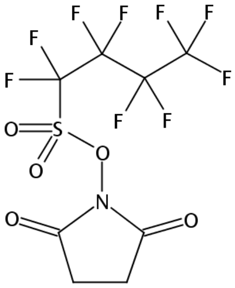
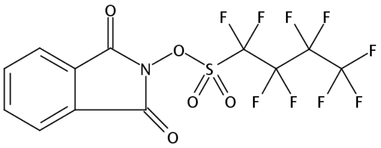
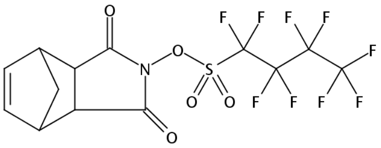
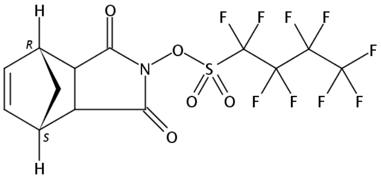
The $CF_3CF_2CF_2\dot{C}F_2$ radical will undergo a series of reactions initiated by O_2 leading to C_2 – C_4 PFCA´s, see section 2.3.7 (page 22). $CF_3CF_2CF_2CF_2CF_2\dot{C}F_2$ radicals from similar $C_6F_{13}SO_2\text{-O-Ph}$ reactions will result in C_2 – C_6 PFCA´s.

$CF_3CF_2CF_2\dot{C}F_2 + O_2 \rightarrow CF_3CF_2CF_2COOH, CF_3CF_2COOH, CF_3COOH$ (complex reactions)

Aryl esters of PFBS and PFHxS will eventually hydrolyse / alternatively undergo photo-oxidation resulting in the release of respectively PFBS and PFHxS. Photo-oxidation of PFBS and PFHxS aryl esters may also result in the release of C_2 – C_6 PFCA´s.

2.3.6 Other PFBS and PFHxS esters

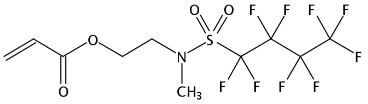
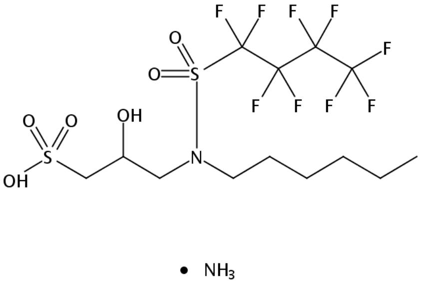
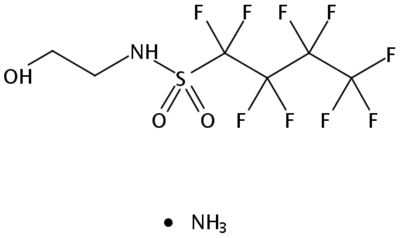
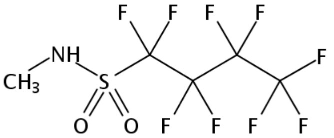
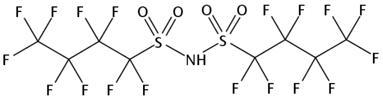
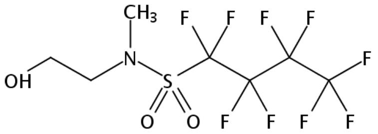
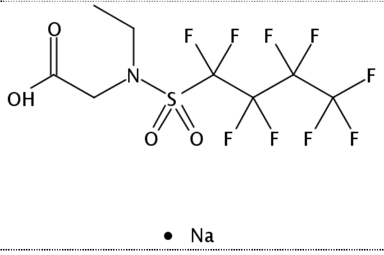
Table 2.3.6. Other commercially available PFBS esters.

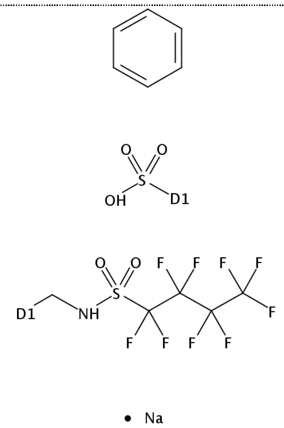
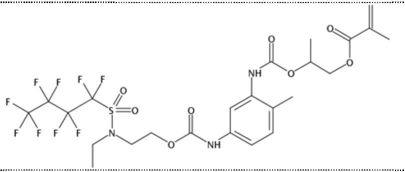
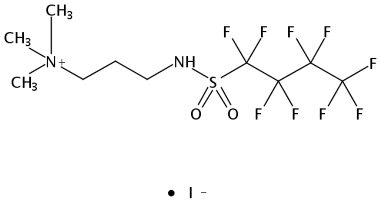
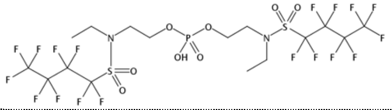
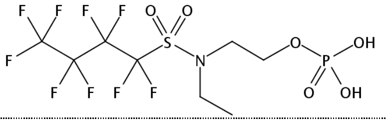
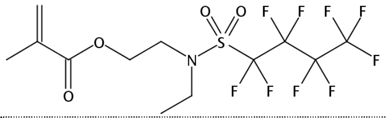
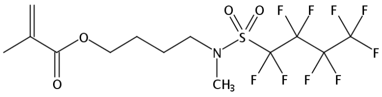
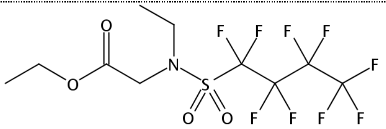
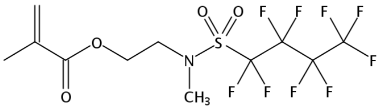
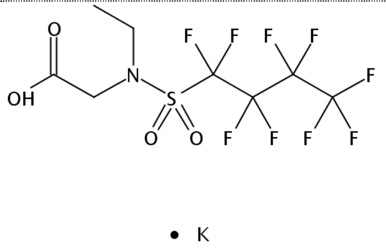
CAS RN	Name	Structure
252937-66-9	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 2,5-dioxo-1-pyrrolidinyl ester	
664329-06-0	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl ester	
307531-76-6	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1,3,3a,4,7,7a-hexahydro-1,3-dioxo-4,7-methano-2*H*-isoindol-2-yl ester	
1404531-60-7	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, (4*S*,7*R*)-1,3,3a,4,7,7a-hexahydro-1,3-dioxo-4,7-methano-2*H*-isoindol-2-yl ester, *rel*-	

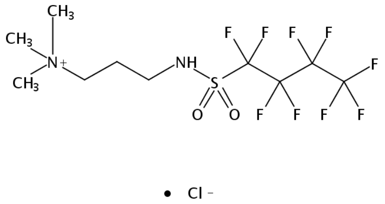
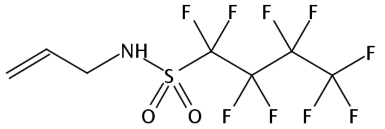
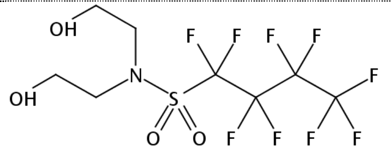
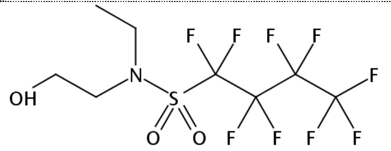
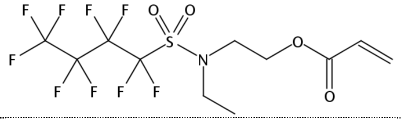
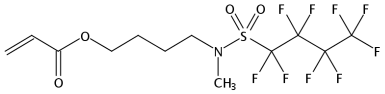
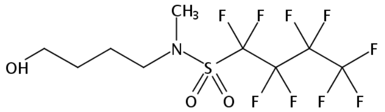
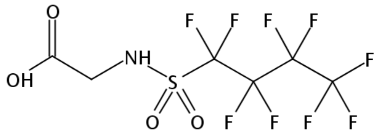
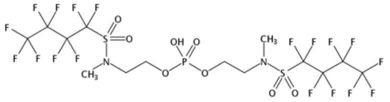
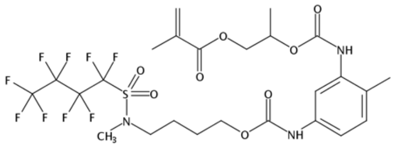
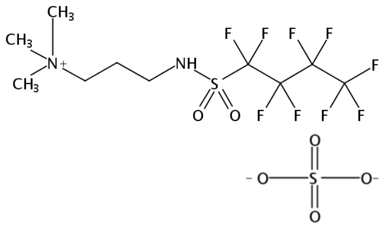
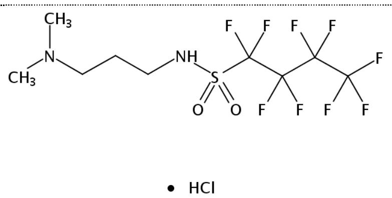
The esters listed in Table 2.3.6 are expected to react similarly to the esters addressed in sections 2.3.2 – 2.3.5. They are expected to eventually hydrolyse / alternatively undergo photo-oxidation resulting in release of PFBS. Photo-oxidation of the compounds may also result in the release of C_2 – C_4 PFCA´s.

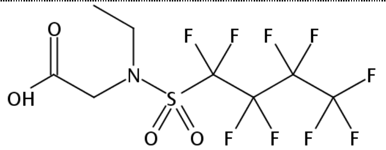
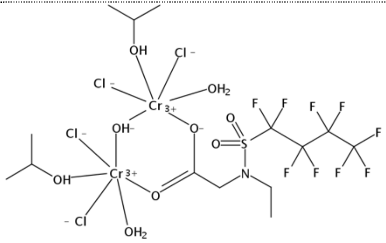
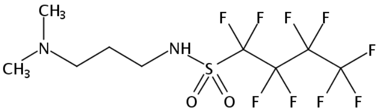
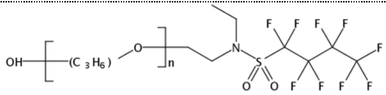
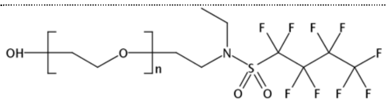
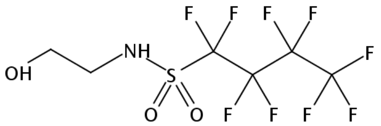
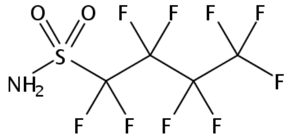
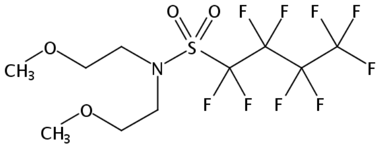
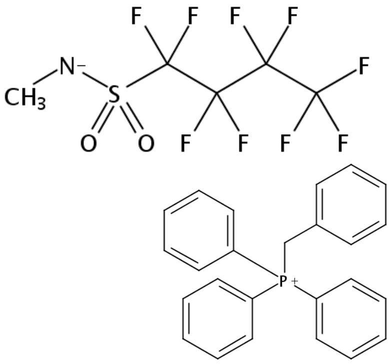
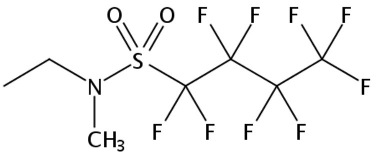
2.3.7 Sulfonamides

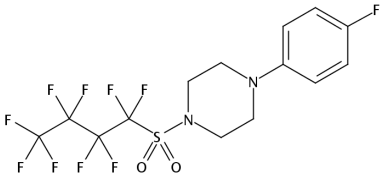
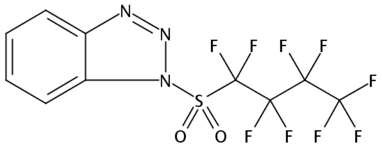
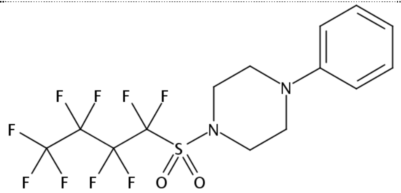
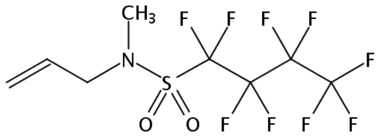
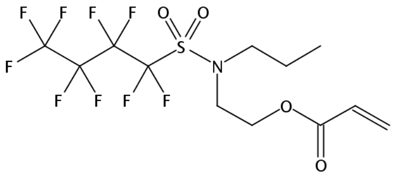
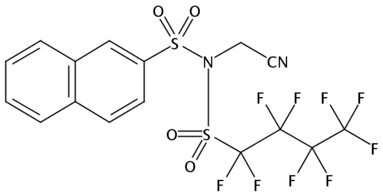
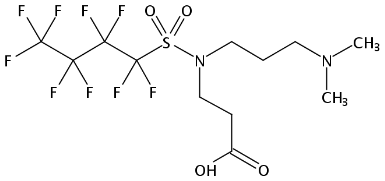
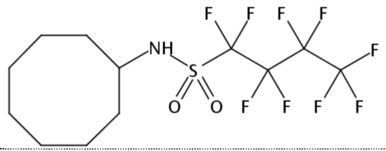
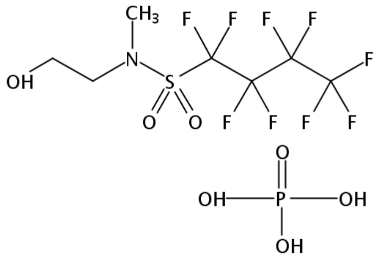
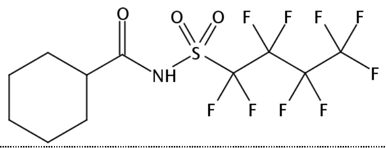
Table 2.3.7. Commercially available PFBS sulfonamides.

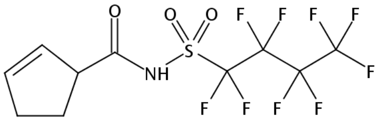
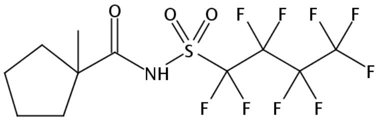
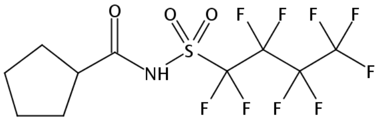
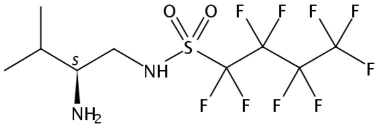
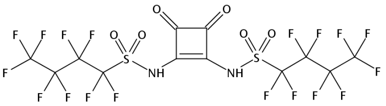
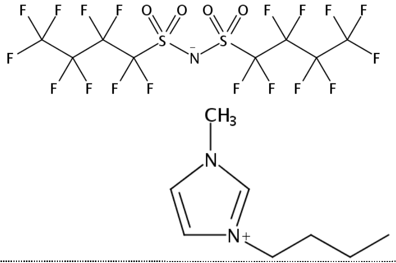
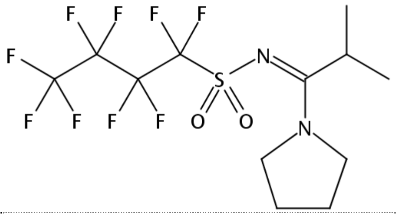
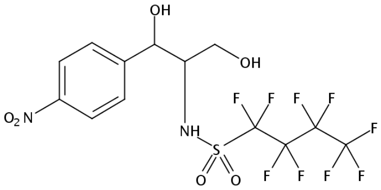
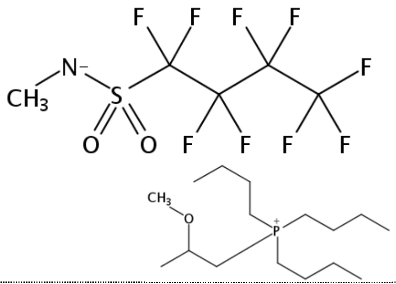
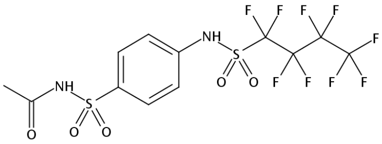
CAS RN	Name	Structure
* 67584-55-8	2-Propenoic acid, 2-[methyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]ethyl ester	
* 606967-06-0	1-Propanesulfonic acid, 3-[hexyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]-2-hydroxy-, ammonium salt (1:1)	
* 484024-67-1	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-, ammonium salt (1:1)	
* 68298-12-4	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-methyl-	
* 39847-39-7	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
* 34454-97-2	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-	
* 68555-68-0	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-, sodium salt (1:1)	

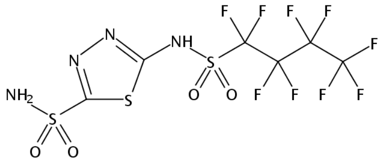
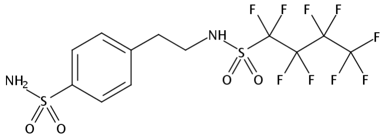
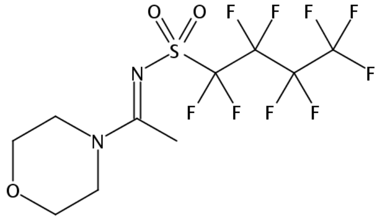
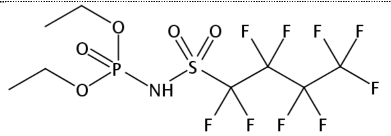
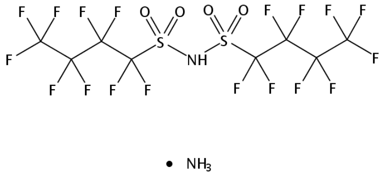
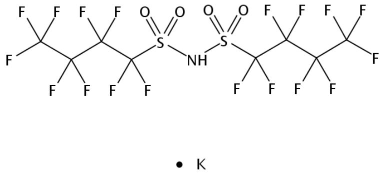
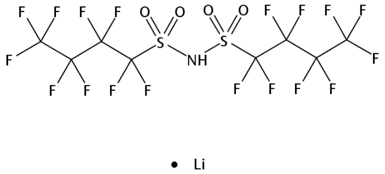
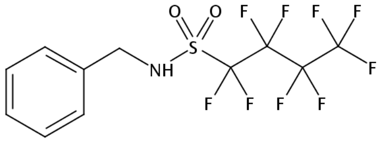
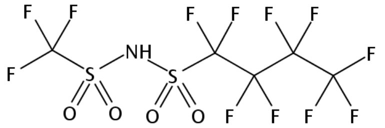
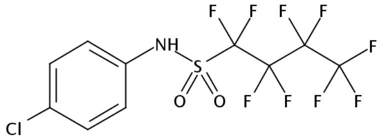
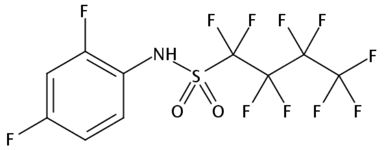
* 68299-19-4	Benzenesulfonic acid, [[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]methyl]-, sodium salt (1:1) **Incompletely Defined Substance**	
* 68298-76-0	2-Propenoic acid, 2-methyl-, 2-[[[[5-[[[2-[ethyl[(nonafluorobutyl)sulfonyl]amino]ethoxy]carbonyl]amino]-2-methylphenyl]amino]carbonyl]oxy]propyl ester	
* 67939-95-1	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]-, iodide (1:1)	
* 67939-91-7	1-Butanesulfonamide, *N*,*N*'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[*N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-	
* 67939-89-3	1-Butanesulfonamide, *N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[2-(phosphonooxy)ethyl]-	
* 67939-33-7	2-Propenoic acid, 2-methyl-, 2-[ethyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]ethyl ester	
* 67906-39-2	2-Propenoic acid, 2-methyl-, 4-[methyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]butyl ester	
* 67584-63-8	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-, ethyl ester	
* 67584-59-2	2-Propenoic acid, 2-methyl-, 2-[methyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]ethyl ester	
* 67584-51-4	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-, potassium salt (1:1)	

* 53518-00-6	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]-, chloride (1:1)	
* 40630-65-7	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-2-propen-1-yl-	
* 34455-00-0	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*,*N*-bis(2-hydroxyethyl)-	
* 34449-89-3	1-Butanesulfonamide, *N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-	
* 17329-79-2	2-Propenoic acid, 2-[ethyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]ethyl ester	
* 1492-87-1	2-Propenoic acid, 4-[methyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]butyl ester	
* 812-94-2	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(4-hydroxybutyl)-*N*-methyl-	
347872-22-4	Glycine, *N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
* 120945-47-3	1-Butanesulfonamide, *N*,*N*'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[1,1,2,2,3,3,4,4,4-nonafluoro-*N*-methyl-	
* 70900-38-8	2-Propenoic acid, 2-methyl-, 2-[[[[2-methyl-5-[[[4-[methyl[(nonafluorobutyl)sulfonyl]amino]butoxy]carbonyl]amino]phenyl]amino]carbonyl]oxy]propyl ester	
* 70225-22-8	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]-, sulfate (2:1)	
* 68957-59-5	1-Butanesulfonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,4-nonafluoro-, hydrochloride (1:1)	

* 68957-33-5	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
* 68900-97-0	Chromium, diaquatetrachloro[μ-[*N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]glycinato-κ*O*:κ*O*']]-μ-hydroxybis(2-propanol)di- Coordination Compound	
* 68555-77-1	1-Butanesulfonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,4-nonafluoro-	
* 68310-18-9	Poly[oxy(methyl-1,2-ethanediyl)], α-[2-[ethyl[(1,1,2,2,3,3,4,4,4-nonafluoro-butyl)sulfonyl]amino]ethyl]-ω-hydroxy- **Incompletely Defined Substance, Polymer**	
* 68298-79-3	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl) sulfonyl]amino]ethyl]-ω-hydroxy- Polymer	
* 34454-99-4	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-	
* 30334-69-1	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-	
1427176-19-9	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*,*N*-bis(2-methoxyethyl)-	
* 332350-93-3	Phosphonium, triphenyl(phenylmethyl)-, salt with 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-methyl-1-butanesulfonamide (1:1) Anion: 332350-89-7 Kation: 15853-35-7	
1427176-16-6	1-Butanesulfonamide, *N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-*N*-methyl-	

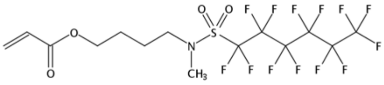
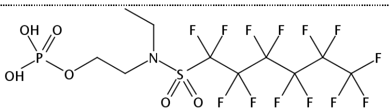
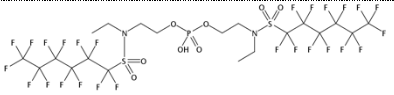
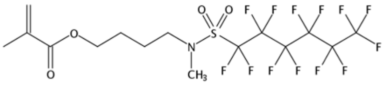
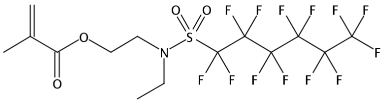
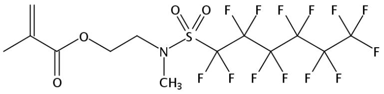
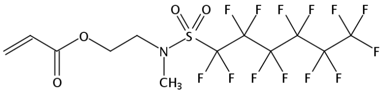
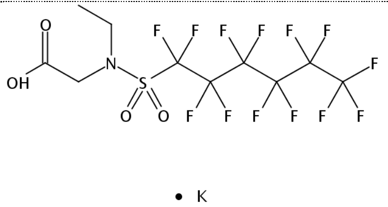
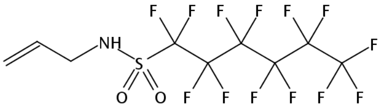
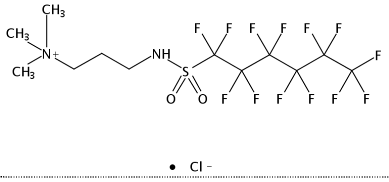
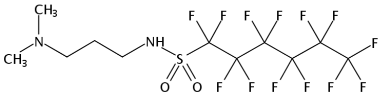
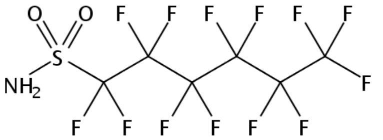
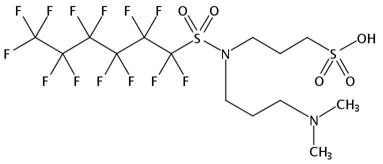
720677-05-4	Piperazine, 1-(4-fluorophenyl)-4-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
681443-29-8	1*H*-Benzotriazole, 1-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
663195-91-3	Piperazine, 1-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-4-phenyl-	
631842-89-2	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-methyl-*N*-2-propen-1-yl-	
499776-70-4	2-Propenoic acid, 2-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]propylamino]ethyl ester	
393122-20-8	2-Naphthalenesulfonamide, *N*-(cyanomethyl)-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
172616-04-5	β-Alanine, *N*-[3-(dimethylamino)propyl]-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
1456900-48-3	1-Butanesulfonamide, *N*-cyclooctyl-1,1,2,2,3,3,4,4,4-nonafluoro-	
* 147545-41-3	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-, phosphate (ester)	
1440968-37-5	Cyclohexanecarboxamide, *N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	

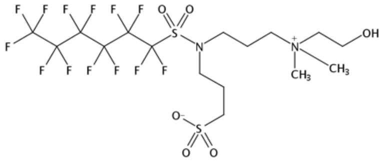
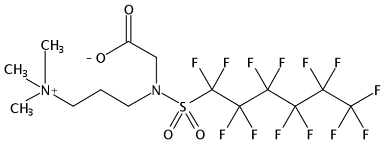
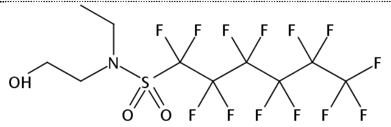
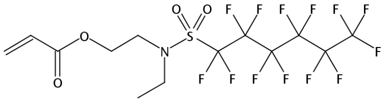
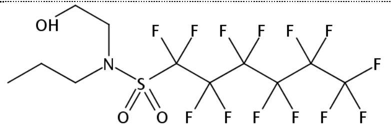
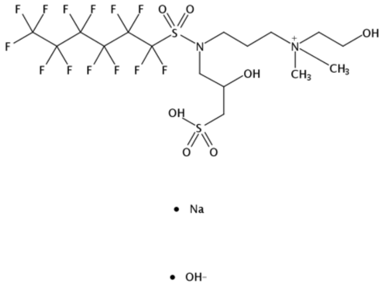
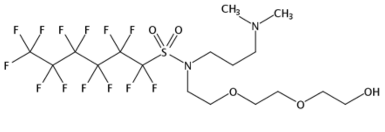
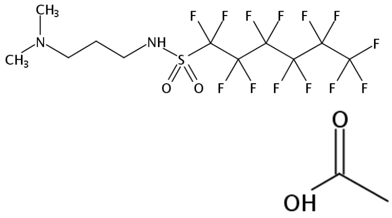
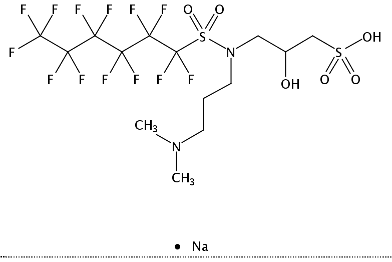
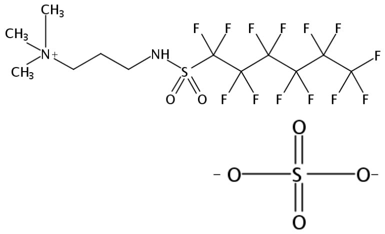
1440968-24-0	2-Cyclopentene-1-carboxamide, *N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
1440968-23-9	Cyclopentanecarboxamide, 1-methyl-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
1440968-21-7	Cyclopentanecarboxamide, *N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-	
1417316-15-4	1-Butanesulfonamide, *N*-[(2*S*)-2-amino-3-methylbutyl]-1,1,2,2,3,3,4,4,4-nonafluoro-	
1234571-87-9	1-Butanesulfonamide, *N*,*N*'-(3,4-dioxo-1-cyclobutene-1,2-diyl)bis[1,1,2,2,3,3,4,4,4-nonafluoro-	
872345-66-9	1*H*-Imidazolium, 3-butyl-1-methyl-, salt with 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-1-butanesulfonamide (1:1) 191101-38-9 + 80432-08-2 kation	
496949-61-2	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[2-methyl-1-(1-pyrrolidinyl) propylidene]-	
401574-88-7	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[2-hydroxy-1-(hydroxymethyl)-2-(4-nitrophenyl)ethyl]-	
* 332350-90-0	Phosphonium, tributyl(2-methoxypropyl)-, salt with 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-methyl-1-butanesulfonamide (1:1) Anion: 332350-89-7 Kation: 126048-99-5	
320599-24-4	Acetamide, *N*-[[4-[[(1,1,2,2,3,3,4,4,4-nonafluoro-butyl)sulfonyl]amino]phenyl]sulfonyl]-	

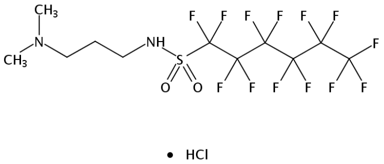
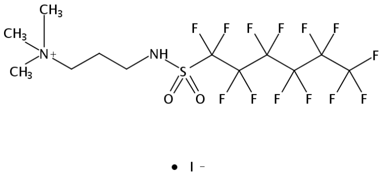
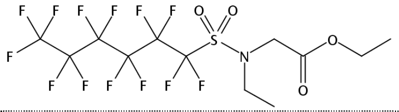
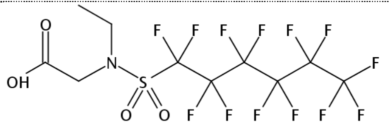
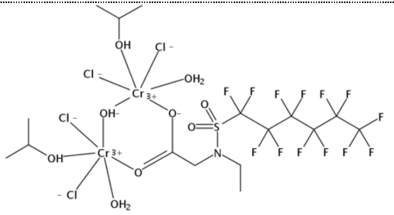
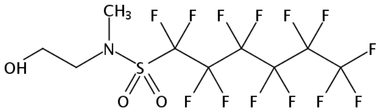
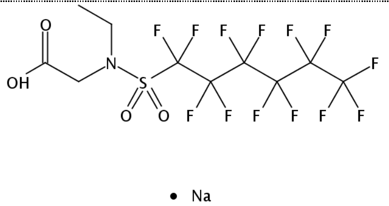
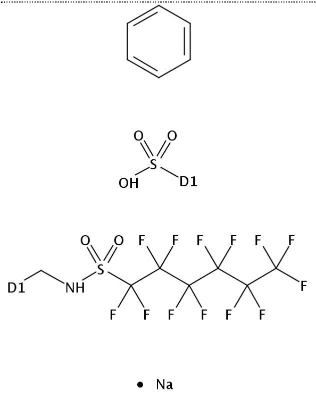
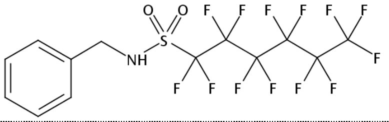
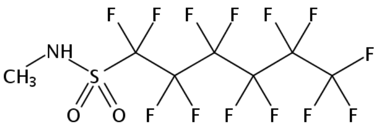
316826-66-1	1,3,4-Thiadiazole-2-sulfonamide, 5-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]-	
316826-59-2	Benzenesulfonamide, 4-[2-[[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]amino]ethyl]-	
292165-43-6	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[1-(4-morpholinyl)ethylidene]-	
181649-25-2	Phosphoramidic acid, [(nonafluorobutyl)sulfonyl]-, diethyl ester (9CI)	
129318-48-5	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-, ammonium salt (1:1)	
* 129135-87-1	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-, potassium salt (1:1)	
119229-99-1	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)sulfonyl]-, lithium salt (1:1)	
* 68298-07-7	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(phenylmethyl)-	
* 39847-37-5	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-[(trifluoromethyl)sulfonyl]-	
23384-05-6	1-Butanesulfonamide, *N*-(4-chlorophenyl)-1,1,2,2,3,3,4,4,4-nonafluoro-	
23375-29-3	1-Butanesulfonamide, *N*-(2,4-difluorophenyl)-1,1,2,2,3,3,4,4,4-nonafluoro-	

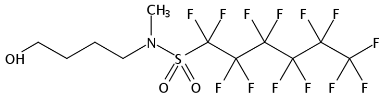
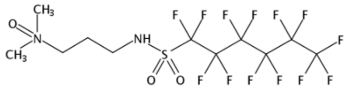
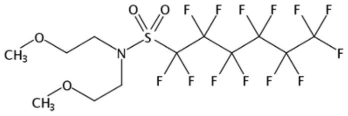
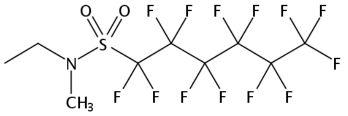
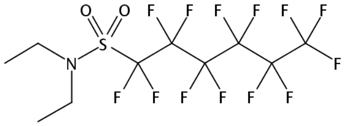
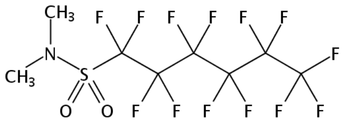
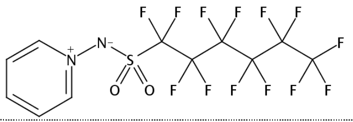
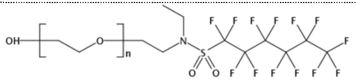
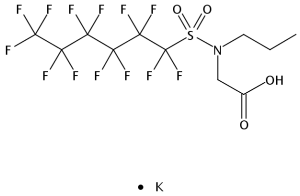
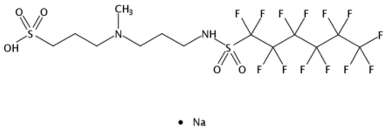
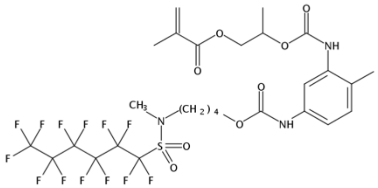
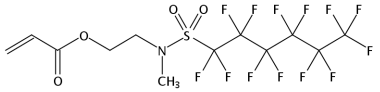
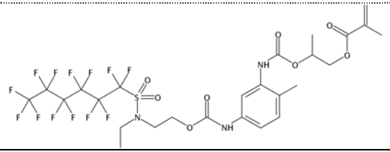
* Substances for which the CAS database contains regulatory information.

Table 2.3.8. Commercially available PFHxS sulfonamides.

CAS RN	Name	Structure
* 68227-98-5	2-Propenoic acid, 4-[methyl[(1,1,2,2,3,3,4,4,5,5,-6,6,6-tridecafluorohexyl)sulfonyl]amino]butyl ester	
* 67969-65-7	2-Propenoic acid, 4-[methyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]butyl ester	
* 67939-92-8	1-Hexanesulfonamide, *N*,*N*'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
* 67939-61-1	2-Propenoic acid, 2-methyl-, 4-[methyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]butyl ester	
* 67906-70-1	2-Propenoic acid, 2-methyl-, 2-[ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester	
* 67584-61-6	2-Propenoic acid, 2-methyl-, 2-[methyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester	
* 67584-57-0	2-Propenoic acid, 2-[methyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester	
* 67584-53-6	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, potassium salt (1:1)	
* 67584-48-9	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-2-propen-1-yl-	
* 52166-82-2	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, chloride (1:1)	
* 50598-28-2	1-Hexanesulfonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
* 41997-13-1	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
* 38850-60-1	1-Propanesulfonic acid, 3-[[3-(dimethylamino)propyl][(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-	

* 38850-58-7	1-Propanaminium, *N*-(2-hydroxyethyl)-*N*,*N*-dimethyl-3-[(3-sulfopropyl)[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, inner salt	
* 38850-52-1	1-Propanaminium, 3-[(carboxymethyl)[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-*N*,*N*,*N*-trimethyl-, inner salt	
* 34455-03-3	1-Hexanesulfonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(2-hydroxyethyl)-	
* 1893-52-3	2-Propenoic acid, 2-[ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester	
* 85665-64-1	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(2-hydroxyethyl)-*N*-propyl-	
* 81190-38-7	1-Propanaminium, *N*-(2-hydroxyethyl)-3-[(2-hydroxy-3-sulfopropyl)[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-*N*,*N*-dimethyl-, hydroxide, sodium salt (1:1:1)	
* 73772-34-6	1-Hexanesulfonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-[2-[2-(2-hydroxyethoxy)ethoxy]ethyl]-	
* 73772-33-5	1-Hexanesulfonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, acetate (1:1)	
* 73772-32-4	1-Propanesulfonic acid, 3-[[3-(dimethylamino)propyl][(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-2-hydroxy-, sodium salt (1:1)	
* 70248-52-1	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, sulfate (2:1)	

* 68957-61-9	1-Hexanesulfonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, hydrochloride (1:1)	
* 68957-58-4	1-Propanaminium, *N*,*N*,*N*-trimethyl-3-[[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, iodide (1:1)	
* 68957-53-9	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, ethyl ester	
* 68957-32-4	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-	
* 68891-98-5	Chromium, diaquatetrachloro[μ-[*N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]glycinato-κ*O*:κ*O*']]-μ-hydroxybis(2-propanol)di- Coordination Compound	
* 68555-75-9	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-	
* 68555-70-4	Glycine, *N*-ethyl-*N*-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, sodium salt (1:1)	
* 68299-21-8	Benzenesulfonic acid, [[[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]methyl]-, sodium salt (1:1) **Incompletely Defined Substance**	
* 68298-09-9	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(phenylmethyl)-	
* 68259-15-4	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-methyl-	

* 68239-74-7	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(4-hydroxybutyl)-*N*-methyl-	
* 30295-56-8	1-Hexanesulfonamide, *N*-[3-(dimethyloxidoamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
1427176-20-2	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*,*N*-bis(2-methoxyethyl)-	
1427176-17-7	1-Hexanesulfonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-methyl-	
1270179-93-5	1-Hexanesulfonamide, *N*,*N*-diethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
1270179-82-2	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*,*N*-dimethyl-	
254889-10-6	Pyridinium, 1-[[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, inner salt	
* 56372-23-7	Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl]-ω-hydroxy-	
* 85665-66-3	Glycine, *N*-propyl-*N*-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, potassium salt (1:1)	
* 80621-17-6	1-Propanesulfonic acid, 3-[methyl[3-[[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]propyl]amino]-, sodium salt (1:1)	
* 70900-36-6	2-Propenoic acid, 2-methyl-, 2-[[[[2-methyl-5-[[[4-[methyl[(tridecafluorohexyl)sulfonyl]amino]butoxy]carbonyl]amino]phenyl]amino]carbonyl]oxy]propyl ester	
* 70776-36-2	Polymer based on 67584-57-0	
* 68298-74-8	2-Propenoic acid, 2-methyl-, 2-[[[[5-[[[2-[ethyl[(tridecafluorohexyl)sulfonyl]amino]ethoxy]carbonyl]amino]-2-methylphenyl]amino]carbonyl]oxy]propyl ester	

The commercially available PFBS- and PFHxS-sulfonamides listed in Tables 2.3.6 and 2.3.7 will undergo slow hydrolysis resulting in release of PFBS and PFHxS, respectively. No experimental information concerning solubility or hydrolytic lifetimes of the sulfonamides listed was found in the open literature; the compounds are predicted to be "sparingly soluble" by the Advanced Chemistry Development (ACD/Labs) Software V11.02, i.e. their solubility is < 1 g L^{-1}. The vapour pressures for some of the compounds listed Tables 2.3.6 and 2.3.7 are likely high enough to make atmospheric photo-oxidation relevant as shown for N-methyl perfluorobutane sulfonamideethanol, $C_4F_9SO_2$-$N(CH_3)CH_2CH_2OH$ [*D'Eon et al.*, 2006] (note that the similar investigation of N-ethyl perfluorobutanesulfonamide, $C_4F_9SO_2$-$N(H)CH_2CH_3$, did not include a product study of the OH initiated photo-oxidation because the OH radical experiments proceeded too slowly to produce discernable amounts of secondary products [*Martin et al.*, 2006]). $C_4F_9SO_2$-$NHCH_3$ and $C_4F_9SO_2$-$N(CH_3)CH_2CHO$ were reported as major primary products in the OH initiated $C_4F_9SO_2$-$N(CH_3)CH_2CH_2OH$ photo-oxidation, whereas PFBS and PFCA´s accounted for respectively 1% and 10% of $C_4F_9SO_2$-$N(CH_3)CH_2CH_2OH$ reacted [*D'Eon et al.*, 2006]. The mechanism proposed for the $C_4F_9SO_2$-$N(CH_3)CH_2CH_2OH$ + OH reaction is outlined below; the branching between the abstraction and addition is only approximately known for $C_4F_9SO_2$-$N(CH_3)CH_2CH_2OH$.

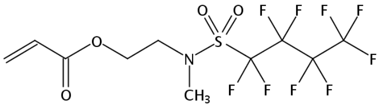
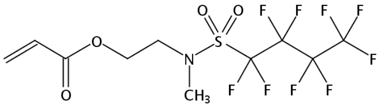
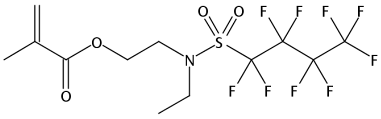
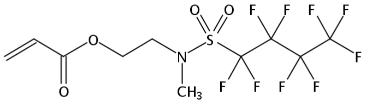
$C_4F_9SO_2O\text{-}N(CH_3)CH_2CH_2OH + OH \rightarrow C_4F_9SO_2O\text{-}NHCH_3 + ??$ (unknown mechanism)
$\rightarrow C_4F_9SO_2O\text{-}N(CH_3)CH_2\dot{C}HOH + H_2O$ (H-abstraction)
$\rightarrow C_4F_9S(\dot{O})OH\text{-}O\text{-}N(CH_3)CH_2CH_2OH$ (addition)
$C_4F_9S(\dot{O})OHO\text{-}N(CH_3)CH_2CH_2OH \rightarrow \mathbf{C_4F_9SO_2OH} + \dot{N}(CH_3)CH_2CH_2OH$
$\rightarrow CF_3CF_2CF_2\dot{C}F_2 + HOS(O_2)N(CH_3)CH_2CH_2OH$
$C_4F_9SO_2O\text{-}N(CH_3)CH_2\dot{C}HOH + O_2 \rightarrow C_4F_9SO_2O\text{-}N(CH_3)CH_2CHO + HO_2$
$CF_3CF_2CF_2\dot{C}F_2 + O_2 \rightarrow \mathbf{CF_3CF_2CF_2COOH}$ (complex mechanism)
$\rightarrow \mathbf{CF_3CF_2COOH}$
$\rightarrow \mathbf{CF_3COOH}$

$CF_3CF_2CF_2CF_2CF_2\dot{C}F_2$ radicals from similar $C_6F_{13}SO_2O\text{-}NR^1R^2$ reactions will result in $C_2 – C_6$ PFCA´s.

Sulfonamides of PFBS and PFHxS will eventually hydrolyse / alternatively undergo photo-oxidation resulting in the release of respectively PFBS and PFHxS. Photo-oxidation of PFBS and PFHxS sulfonamides will also result in the release of $C_2 – C_6$ PFCA´s.

2.3.8 Polymers

Table 2.3.9. Polymers containing the n-$C_4F_9SO_2$- fragment.

CAS RN	Name	Structure
* 70776-36-2	Polymer based on 67584-55-8	
* 1017237-78-3	Polymer based on 67584-55-8	
* 68877-32-7	Polymer based on 67939-73-4	
* 68586-14-1	Polymer based on 67584-55-8	

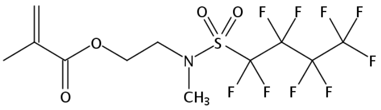
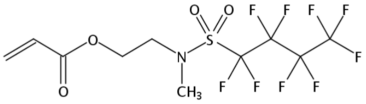
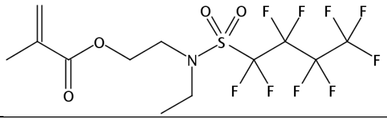
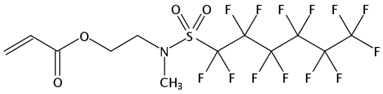
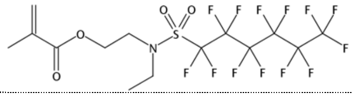
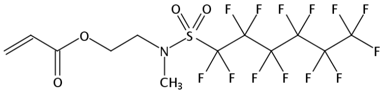
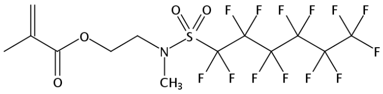
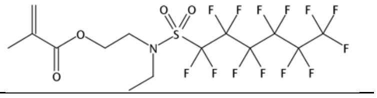
* 68555-92-0	Polymer based on 67584-59-2	
* 68555-90-8	Polymer based on 67584-55-8	
* 67939-34-8	Polymer based on 67939-73-4	

Table 2.3.10. Polymers containing the n-$C_6F_{13}SO_2$- fragment.

CAS RN	Name	Structure
* 68555-90-8	Polymer based on 67584-57-0	
* 68877-32-7	Polymer based on 67906-70-1	
* 68586-14-1	Polymer based on 67584-57-0	
* 68555-92-0	Polymer based on 67584-61-6	
* 68555-91-9	Polymer based on 67906-70-1	

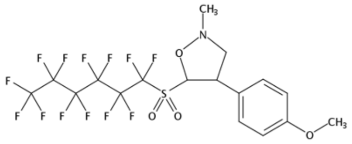
In the environment polymers will be exposed to an aqueous layer having essentially the same features as the atmospheric aerosol. That is OH-initiated photo-oxidation will take place. The sulfonamide building blocks will eventually undergo reactions similar to those experimentally observed for gaseous sulfonamides, see section 2.3.7 (page 23).

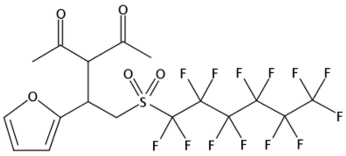
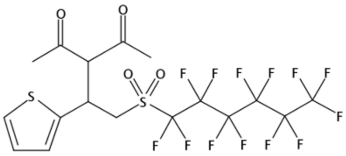
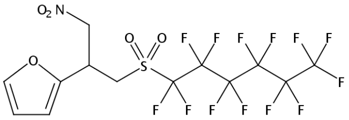
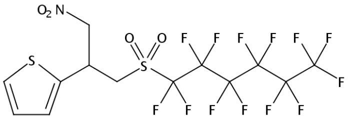
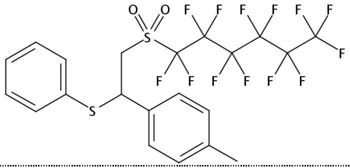
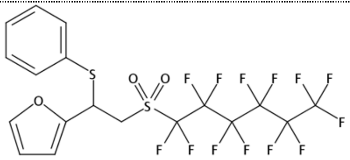
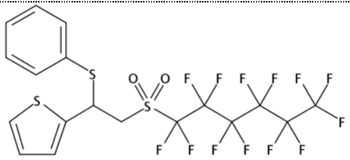
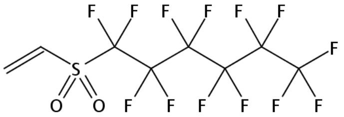
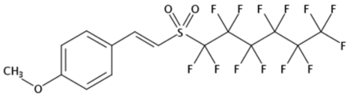
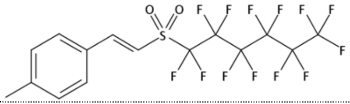
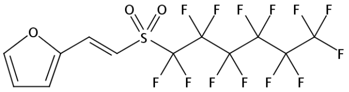
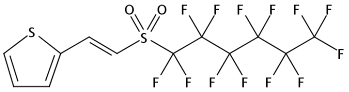
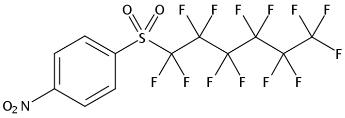
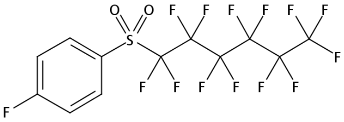
The polymers listed in Tables 2.3.9 and 2.3.10 will eventually hydrolyse / undergo aqueous phase photo-oxidation resulting in the release of PFBS and PFHxS. The polymers may also contain some unreacted monomers. It is also plausible that C_2 – C_6 PFCA´s may be released.

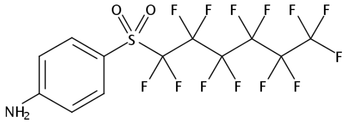
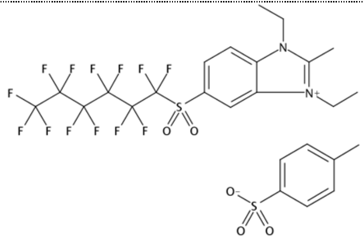
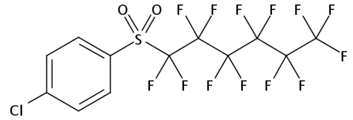
2.4 Other potential PFBS and PFHxS precursors

2.4.1 Sulfones

Table 2.4.1. Commercially available PFHxS sulfones.

CAS RN	Name	Structure
93416-31-0	Isoxazolidine, 4-(4-methoxyphenyl)-2-methyl-5-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-	

89863-64-9	2,4-Pentanedione, 3-[1-(2-furanyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-	
89863-63-8	2,4-Pentanedione, 3-[1-(2-thienyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-	
89863-56-9	Furan, 2-[1-(nitromethyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-	
89863-55-8	Thiophene, 2-[1-(nitromethyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-	
89863-50-3	Benzene, 1-methyl-4-[1-(phenylthio)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-	
89863-49-0	Furan, 2-[1-(phenylthio)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-	
89863-48-9	Thiophene, 2-[1-(phenylthio)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-	
680187-86-4	Hexane, 1-(ethenylsulfonyl)-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-	
86525-52-2	Benzene, 1-methoxy-4-[2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethenyl]-	
86525-51-1	Benzene, 1-methyl-4-[2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethenyl]-	
86525-48-6	Furan, 2-[2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethenyl]-	
86525-43-1	Thiophene, 2-[2-[(tridecafluorohexyl)sulfonyl]ethenyl]-	
171561-95-8	Benzene, 1-nitro-4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-	
149652-30-2	Benzene, 1-fluoro-4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-	

147029-28-5	Benzenamine, 4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-	
76848-68-5	1*H*-Benzimidazolium, 1,3-diethyl-2-methyl-5-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, 4-methylbenzenesulfonate (1:1)	
76848-59-4	Benzene, 1-chloro-4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-	

Dimethylsulfone, $(CH_3)_2SO_2$, is the only sulfone for which there is relevant data available in the literature. No products were observed in the gas phase reaction with OH [*Falbe-Hansen et al.*, 2000], and in the similar aqueous phase reaction [*Zhu et al.*, 2003]. This was interpreted in terms of C-H abstraction being the major route. Dimethylsulfone is a major product in the OH radical reaction with dimethylsulfoxide, $(CH_3)_2SO$, in the gas phase [*Arsene et al.*, 2002] and in the aqueous phase [*Bardouki et al.*, 2002] suggesting that at least some OH addition will also take place in the OH reaction with dimethylsulfone:

$(CH_3)_2SO + OH \rightarrow (CH_3)_2S(\dot{O})OH$ (addition)
$\rightarrow CH_3S(O)\dot{C}H_2 + H_2O$ (abstraction)
$(CH_3)_2S(\dot{O})OH + O_2 \rightarrow (CH_3)_2SO_2 + HO_2$

$(CH_3)_2SO_2 + OH \rightarrow (CH_3)_2SO(OH)\dot{O}$ (addition)
$\rightarrow (CH_3)S(O_2)\dot{C}H_2 + H_2O$ (abstraction)
$(CH_3)_2SO(OH)\dot{O} \rightarrow CH_3S(O_2)OH + \dot{C}H_3$

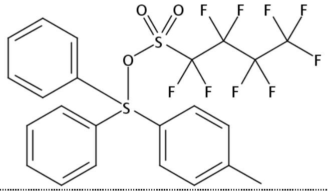
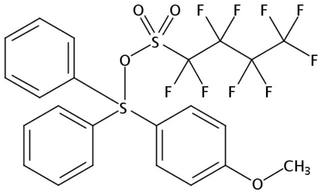
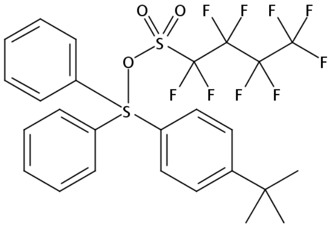
PFBS and PFHxS sulfones will likely follow the same reaction routes. Taking $CF_3CF_2CF_2CF_2SO_2CH_3$ as example:

$CF_3CF_2CF_2CF_2SO_2CH_3 + OH \rightarrow CF_3CF_2CF_2CF_2SO_2\dot{C}H_2 + H_2O$ (abstraction)
$\rightarrow CF_3CF_2CF_2CF_2S(O)(\dot{O})(OH)CH_3$ (addition)
$CF_3CF_2CF_2CF_2S(O)(\dot{O})(OH)CH_3 \rightarrow \mathbf{CF_3CF_2CF_2CF_2S(O_2)OH} + \dot{C}H_3$
$\rightarrow CF_3CF_2CF_2\dot{C}F_2 + CH_3\text{-}O\text{-}S(O_2)OH$

PFBS and PFHxS sulfones may undergo photo-oxidation resulting in the release of respectively PFBS and PFHxS. The amounts of PFBS and PFHxS formed are very uncertain. Photo-oxidation of PFBS and PFHxS sulfones may also result in the release of C_2 – C_6 PFCA´s.

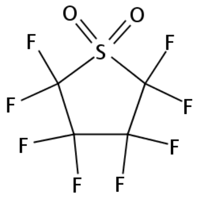
2.4.2 Other compounds

Table 2.4.2. Sulfaneyl sulfonates.

CAS RN	Name	Structure
1029635-28-6	INDEX NAME NOT YET ASSIGNED	
1029635-01-5	INDEX NAME NOT YET ASSIGNED	
1029635-05-9	INDEX NAME NOT YET ASSIGNED	

The PFBS sulfonates listed in Table 2.4.2 are expected to react similarly to other sulfonates, see e.g. section 2.3.2.

The PFBS sulfonates included in Table 2.4.2 will eventually hydrolyse / alternatively undergo photo-oxidation resulting in the release of PFBS.

CAS RN	Name	Structure
42060-64-0	Thiophene, 2,2,3,3,4,4,5,5-octafluorotetrahydro- , 1,1-dioxide	

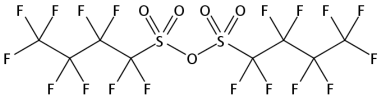
Perfluorosulfolane, 2,2,3,3,4,4,5,5-octafluorotetrahydro-thiophene 1,1-dioxide, will eventually either hydrolyse in the environment or undergo atmospheric photo-oxidation. Hydrolysis will result in 1,1,2,2,3,3,4,4-octafluoro-1-butanesulfonic acid (CAS RN 70259-86-8):

$$\text{c-}C_4F_8S(O_2)_{aq} + H_2O_{aq} \rightarrow HCF_2CF_2CF_2CF_2S(O_2)OH_{aq}$$

Atmospheric photo-oxidation will result in a perfluoroalkyl radical:

$$\begin{aligned}
\text{c-}C_4F_8S(O_2) + OH &\rightarrow \dot{C}F_2CF_2CF_2CF_2S(O_2)OH \\
\dot{C}F_2CF_2CF_2CF_2S(O_2)OH + O_2 &\rightarrow \dot{O}OCF_2CF_2CF_2CF_2S(O_2)OH \\
\dot{O}OCF_2CF_2CF_2CF_2S(O_2)OH + NO &\rightarrow \dot{O}CF_2CF_2CF_2CF_2S(O_2)OH + NO_2 \\
\dot{O}CF_2CF_2CF_2CF_2S(O_2)OH &\rightarrow \dot{C}F_2CF_2CF_2S(O_2)OH + CF_2O \\
&\vdots
\end{aligned}$$

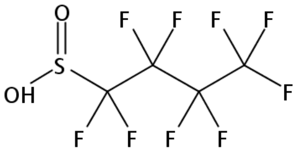
Perfluorosulfolane is not a PFBS precursor.

CAS RN	Name	Structure
* 36913-91-4	1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, 1,1'-anhydride	

The PFBS-anhydride, 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonic acid, 1,1'-anhydride, will eventually hydrolyse resulting in PFBS:

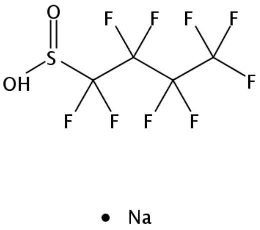
$$C_4F_9S(O_2)\text{-}O\text{-}(O_2)SC_4F_{9aq} + H_2O_{aq} \rightarrow 2\ C_4F_9S(O_2)OH_{aq}$$

PFBS-anhydride is a PFBS precursor

CAS RN	Name	Structure
* 34642-43-8	1-Butanesulfinic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-	

Sulfinic acids will undergo oxidation to sulfonic acids by H_2O_2, which is a natural oxidant found in water and aqueous aerosols [*van Bergen et al.*, 2014]. $CH_3S(O)OH$ is also found to be very reactive towards OH leading to $CH_3S(O_2)OH$ [*Bardouki et al.*, 2002].

The compound is a PFBS precursor.

CAS RN	Name	Structure
* 102061-82-5	1-Butanesulfinic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, sodium salt (1:1)	

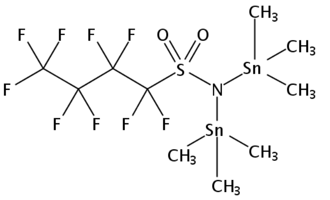
The sulfinic acid salt will dissolve in water resulting in the sulfinic acid, see above.

The compound is a PFBS precursor.

CAS RN	Name	Structure
* 90268-45-4	Butanesulfonyl fluoride, nonafluoro-, branched	

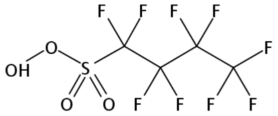
This is a blend of $C_4F_9S(O_2)OH$ isomers and may contain various amounts of n-$C_4F_9S(O_2)OH$ (PFBS).

CAS RN	Name	Structure

41006-34-2	Methanesulfonamide, 1,1-difluoro-1-(1,1,2,2,3,3,3-heptafluoropropyl)-*N*,*N*-bis(trimethylstannyl)- Other name: 1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-N,N-bis(trimethylstannyl)-	

The metalorganic sulfonamide will eventually follow the same reactions as outlined for other sulfonamides, see section 2.3.6.

The compound is a potential PFBS and PFCA precursor

CAS RN	Name	Structure
85963-79-7	1-Butanesulfonoperoxoic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-	

In aqueous solution peroxy acids are in equilibrium with the corresponding acid. Peroxy-acids are also oxidizing agents and will, at least in part, be reduced to the corresponding acid.

The PFBS-peroxy acid is a PFBS precursor

2.5 Summary/Conclusion

The open literature related to abiotic environmental degradation of potential PFBS and PFHxS precursors has been reviewed. In addition, the Chemical Abstract Services (CAS) database was searched for commercially available potential PFBS and PFHxS precursors using the "substructure search" method. A total number of 294 such chemicals with commercial sources were located, and 112 of these were tagged with "regulatory information".

The hydrolysis rates of PFBS and PFHxS sulfonates, sulfones and sulphonamides are known to be slow, but no information on "how slow/fast" was found in the open literature. In general, these classes of compounds are not very water soluable. However, they will eventually hydrolyse.

The literature on gas phase and aqueous phase photo-oxidation of PFBS and PFHxS sulfonates, sulfones and sulphonamides is very scarce. The general mechanistic principles for photo-oxidation are, however, relatively well established allowing an extrapolation to these compounds.

Based on best estimates of reaction mechanisms, it can be concluded that compounds containing the F-$(CF_2)_nS(O_2)N$- fragment (sulphonamides) will undergo abiotic degradation in the environment resulting in the release of C_2 – C_n PFCA´s as well as minor amounts of the corresponding sulfonic acids. Compounds containing the F-$(CF_2)_nS(O_2)O$-fragment (sulfonates) will undergo abiotic degradation in the environment resulting in the release of the corresponding sulfonic acids and likely also of C_2 – C_n PFCA´s. Compounds containing the F-$(CF_2)_nS(O_2)$-fragment (sulfones) will likely undergo abiotic degradation in the environment resulting in some release of the corresponding sulfonic acids and likely also of C_2 – C_n PFCA´s.

The extremely scarce literature on abiotic degradation of compounds such as $CF_3(CF_2)_nS(O_2)N$-R, $CF_3(CF_2)_nS(O_2)O$-R and $CF_3(CF_2)_nS(O_2)$-R, warrants that systematic research on these classes of compounds is undertaken such that their fate in the environment can be modelled in a scientific manner.

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