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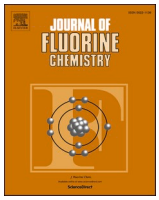

Synthesis of *n*-isomers: Native and deuterium-labelled short-chain perfluoroalkane sulfonamide derivatives

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ABSTRACT

Perfluorooctane sulfonamide derivatives have been extensively used by industry for their surfactant properties and as building blocks for other perfluoroalkyl substances (PFAS). Due to their environmental impact and their potential degradation to other harmful PFAS, short-chain sulfonamide derivatives alternatives were introduced. However, these are now also suspected to be present in different environmental matrices and there is a lack of labelled and unlabelled reference standards to perform analyses. To address this gap, 40 native and deuterium labelled short-chain perfluoroalkane sulfonamide derivatives were synthesized, utilizing commercial perfluoroalkane sulfonyl fluoride as starting materials. All products were synthesized and then purified to obtain linear *n*-isomer reference standards. NMR, GC-FID-MS and LC-MS techniques were used for product identification and purity assessment. Recrystallization method was developed to selectively isolate the *n*-isomer from the isomer mixtures, thereby providing valuable reference and internal standards for environmental and toxicological investigations.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic compounds that are widely used in various consumer and industrial products due to their unique properties, which are mainly attributed to the strong carbon-fluorine bonds found within them. These compounds are employed as surfactants and water, dirt and fat repellants and can be found in a diverse range of products, including aqueous film-forming foams (AFFF), clothing, and food packaging [1,2]. Long-chain PFAS with eight carbon backbone, such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), were extensively utilized by industry for many years [1-3]. However, these long-chain PFAS are persistent and bioaccumulative pollutants and they have been detected in tissues of wildlife and humans [3-5]. Due to their toxicity and environmental impact, several of these compounds (e.g., PFOS and PFOA) have been banned and restrictive regulations on their environmental management have been implemented [6,7]. Perfluorooctane sulfonamide derivatives have also been extensively used in industrial applications, particularly in surface treatment chemicals such as *N*-methyl/ethyl perfluorooctane sulfonamide (Me/Et-FOSA), *N*-methyl/ethyl perfluorooctane sulfonamidoacetic acid (Me/Et--FOSAA), and *N*-methyl/ethyl perfluorooctane sulfonamidoethanol (Me/Et-FOSE) [8]. These compounds are precursors of PFOS and other perfluoroalkyl compounds because they can be degraded to those more stable PFAS during use and in the environment [9-13]. Such compounds (e.g., Me/Et-FOSAA) are relatively polar and are monitored in aqueous environmental matrices [14-18].

In response to the concerns surrounding the use and environmental impact of long-chain PFAS (C_8), industries started to switch to shorter-chain analogues comprising four or six carbon atoms (C_4 and C_6 analogues). For example, *N*-methyl perfluorobutane sulfonamidoacetic acid (MeFBSAA) was first reported by Huset et al. (2011) in landfill leachate with concentrations ranging from 58 to 440 ng/L [19]. The source of MeFBSAA was most likely from discarded items like clothing and paper products treated with PFAS. MeFBSAA has also been detected in aqueous matrices from other sites containing textile waste [20,21]. Moreover, the same compound has been identified in water samples from the US. Newton et al. (2017) reported high concentrations of MeFBSAA in the Tennessee River, downstream from a fluorochemical manufacturing facility near Decatur, Alabama. At one of the sites,

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concentrations exceeded 1 μg/L [22]. MeFBSAA and its C_6 analogue, *N*-methyl perfluorohexane sulfonamidoacetic acid (MeFHxSAA), were also identified in marine life such as whales in Canada [23]. Likewise, *N*-methyl perfluorobutane sulfonamide (MeFBSA) was detected in air samples from the Antarctic peninsula with average concentrations of 3 to 4 pg/m^3 suggesting that there may have been a change from C_8 to short-chain PFAS compared to earlier periods [24]. Regarding sulfonamidoethanol and acrylate derivatives, mainly MeFBSE was investigated [25]. However, C_8 analogues have been studied and reported in air or fabric samples such as carpets [26-32]. Due to its volatility *N*-methyl pefluorooctane sulfonamidoethyl acrylate was only reported in air [33, 34].

Interrelationships between different PFAS structural classes have also been studied. Lange (2017) reported that EtFBSE can degrade into EtFBSAA, then perfluorobutane sulfinic acid (PFBSI) can undergo decomposition exactly like EtFOSE to perfluorooctane sulfinic acid (PFOSI) [8]. Thus, decomposition of perfluorobutane sulfonamide and perfluorohexane sulfonamide derivatives can lead to the detection of PFBS and PFHxS in the environment, comparable to the C_8 analogues decomposing to PFOS [9]. Similarly, methacrylate or acrylate esters may decompose to their respective alcohols via hydrolysis potentially also forming the corresponding sulfonic acid. It has also been shown that EtFOSE itself is the degradation product of fluorinated phosphate diester [35,36]. As such, a single PFAS compound has the potential to generate diverse fluorinated side products with different chemical groups during production, use, environmental release or degradation.

Given the long-term use of perfluorooctane sulfonamide derivatives such as EtFOSAA or MeFOSA, labelled reference standards for these compounds are available but not for the short-chain derivatives which emerged more recently. For the PFAS family that contains thousands of compounds only a few analytical standards exist and even less labelled standards, which limits their determination. The absence of reference standards makes it impossible to accurately and reliably quantify these compounds in environmental samples especially when performing mass spectrometry (MS) analyses [37]. Labelled compounds are used as internal standard in the samples and can for example compensate losses during the extraction of an analyte or fluctuations that could occur during the measurement. Moreover, having specific labelled standards allows a better estimation of the amount of an analyte in a sample instead using other labelled PFAS like for example a labelled PFOS that could under- or overestimate the concentration. It is crucial to obtain pure reference standards of the straight-chain isomers of PFAS compounds, which can be challenging. Indeed, perfluorohexane sulfonyl fluoride, for example, like its C8 analogues, is often sold as a mixture of different isomers and uses for many syntheses as starting material [38-40]. Such mixtures contain a relatively high percentage of branched isomers whose chemical properties are similar to those of the straight isomer. The primary aim of this work, therefore, was first to synthesize unlabelled short-chain perfluoroalkane sulfonamides and then focus on their labelled deuterated analogues since most of them are not yet available, especially the ones containing an ethyl group. We focused on five classes, having a C_4 and C_6 carbon chain length namely *N*-Methyl/Ethyl perfluoroalkane sulfonamide, *N*-Methyl/Ethyl perfluoroalkane sulfonamidoacetic acid, *N*-Methyl/Ethyl perfluoroalkane sulfonamidonamidoethanol, *N*-Methyl/Ethyl perfluoroalkane sulfonamidonamidoethyl acrylate and *N*-Methyl/Ethyl perfluoroalkane sulfonamidonamidoethyl methacrylate and their deuterated analogues, so in total 40 compounds to facilitate accurate and reliable environmental and human analyses, and toxicological studies. N-alkyl perfluoroalkane sulfanomide was a key intermediate to obtain the other derivatives. Recrystallization revealed to be an efficient way to remove isomers at the difference of chromatographic technic used for the C_8 analogues [41].

2. Results and discussion

2.1. Perfluoroakane sulfonamide synthesis

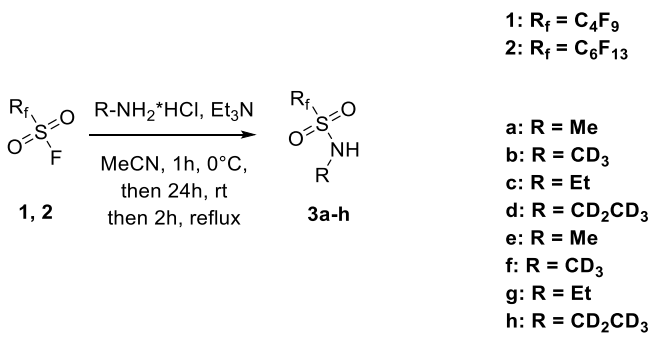
N-methyl or *N*-ethyl perfluoroalkane sulfonamide have been synthesized through the addition of an amine gas to the reaction mixture. This approach was primarily employed for C_8 derivatives and gave a product yield of 24–70 % [41]. However, to synthesize the deuterated analogue compounds with a high yield and good repeatability, the gaseous amine was replaced by its hydrochloride salt, a solid reagent that is more convenient to handle and commercially available. The reaction of the amine HCl salt with perfluoroalkane sulfonyl fluoride was conducted under the presence of triethylamine as a base catalyst. The reaction resulted in improved synthesis yields for both native and deuterated analogues of *N*-methyl/ethyl perfluorobutane/hexane sulfonamides (Scheme 1).

The base was used to release the free methyl/ethylamine or the deuterated analogues from its salt and therefore increase the nucleophilic property in the nucleophilic substitution reaction with the perfluoroalkyl sulfonyl fluoride. For this reason, triethylamine was added in excess to ensure that there is enough base to keep the methyl/ethylamine in its free form and the nucleophilic substitution reaction can proceed efficiently.

The HCl salt was added to the reaction mixture at 0 °C, acetonitrile was used since we thought it could dissolved the complex usually obtained for this reaction but it exhibited poor solubility at room temperature in this solvent. Following the addition of the HCl salt, the suspension mixture was stirred one day at room temperature then the reaction mixture was warmed to reflux for a couple of hours to get a homogeneous solution as suggested by Lehmler et al. (2007) in their protocols for the long-chain analogue, after stirring the reaction mixture between 16 and 24 hours in other solvents [41]. In this procedure, no HCl solution was added at the end of the reaction without modification of the yield [42]. The reaction mixture was purified by flash chromatography on silica gel for the C_4 or C_6 sulfonamides. A yield of around 80 % was obtained after purification, with a good reproducibility.

2.2. Recrystallization method for the isolation of the straight chain n-isomer

Two primary industrial processes, electrochemical fluorination (ECF) and telomerization, have been widely used to manufacture PFAS compounds, resulting in varying isomeric purities in PFAS products. ECF produces a mixture of linear and branched isomers, while telomerization typically yields a higher purity or enriched linear product. In the present study, the C_4 perfluorobutane sulfonyl fluoride was found to be pure upon ^{19}F NMR analysis, while the C_6 perfluorohexane sulfonyl fluoride was a mixture of linear and branched isomers (Fig. 1). The isomeric purity based on ^{19}F NMR of C_4 and C_6 perfluoroalkane sulfonamides remained identical to the starting material used in the synthesis, therefore different purification methods were used to achieve the



Scheme 1. Synthesis of short-chain perfluoroalkane sulfonamides.

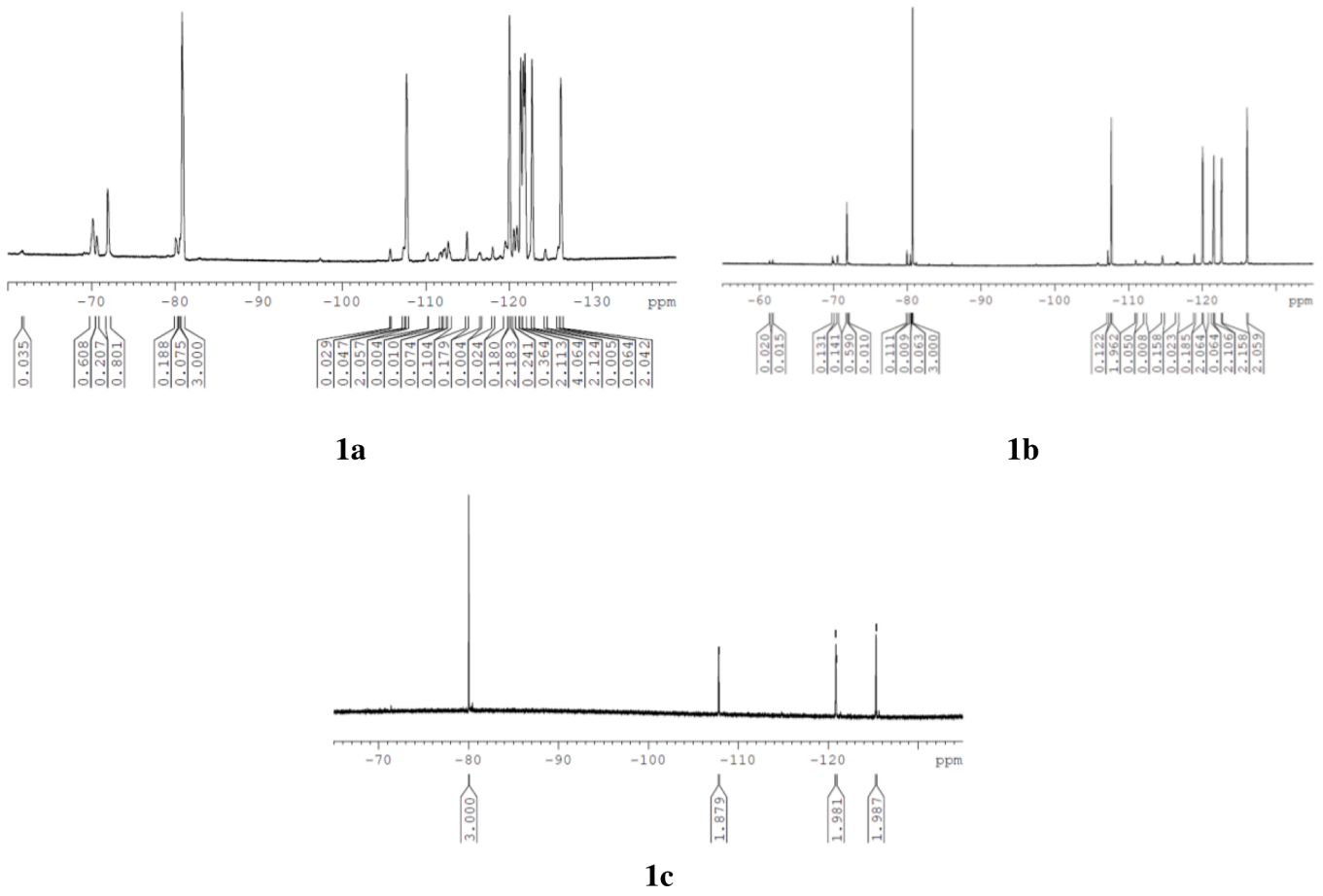


Fig. 1. ^{19}F NMR of perfluoroalkane sulfonyl fluoride. 1a) Perfluorooctane sulfonyl fluoride. 1b) Perfluorohexane sulfonyl fluoride. 1c) Perfluorobutane sulfonyl fluoride.

desired pure *n*-isomer for each compound. In the case of the C_6 sulfonamides, the isomer mixture derived from the commercial perfluorohexane sulfonyl fluoride could not be adequately purified by flash chromatography. Therefore, purification by recrystallization was investigated [41].

Solvents such as acetonitrile, acetone or methanol proved to be too polar for the separation of the sulfonamide derivatives, as they easily dissolved the compounds and therefore no crystals or solid precipitate even at cool temperature. To address this issue, less polar solvents were used. The straight-chain isomer was successfully isolated by repetitive recrystallizations in *n*-hexane and diethyl ether. Ethyl acetate could also be used in a small amount instead of diethyl ether, but diethyl ether was preferred due to easier evaporation between the recrystallizations. *N*-Ethyl perfluorohexane sulfonamide was slightly harder to recrystallize, probably due to a difference in melting point. This purification method resulted in white solid *n*-isomers of MeFHxSA and EtFHxSA with a purity of 98 % based on GC–MS analysis. However, the main drawback of this purification was a yield decrease, ranging from 30 % to 50 % (Table 1).

Lehmler et al. (2007) reported that for the purification of the C_8 *N*-alkyl perfluoroalkane sulfonamide, recrystallization was not a satisfying

Table 1
Comparison between C4 and C6 derivatives of Me- and Et-FBSA and FHxSA.

Entry	Product	Yield (%)	Purification	[c]GC–MS purity (%)	[d]LC-MS purity (%) C18	[e]LC-MS purity (%) (*n*-isomer +branched isomers)
1	MeFBSA	80	[a]A	99.8	n/a	98.1 (96.4 + 1.7)
2	MeFBSA-*d3*	75	A	99.7	99.9	99.1 (98.6 + 0.6)
3	EtFBSA	81	A	99.9	99.9	99.9 (95.8 + 4.2)
4	EtFBSA-*d5*	69	A	99.5	99.8	99.9 (97.2 + 2.8)
5	MeFHxSA	38	[b]B	98.8	95.9	97.2 (88.9 + 8.3)
6	MeFHxSA-*d3*	50	B	99.5	97.4	97.5 (91.0 + 6.5)
7	EtFHxSA	35	B	99.0	99.3	98.9, (91.7 + 7.2)
8	EtFHxSA-*d5*	34	B	99.1	97.3	98.8, (89.4 + 7.4)

[a] Purification A: Flash chromatography + 1 recrystallization.
[b] Purification B: Flash chromatography + multiple recrystallizations.
[c] Purity based on GC-EI-MS analysis.
[d] Purity based on LC-MS with electrospray ionization in negative mode using a Kinetix C18 column.
[e] Purity based on LC-MS with electrospray ionization in negative mode using an Ascentis® Express column.

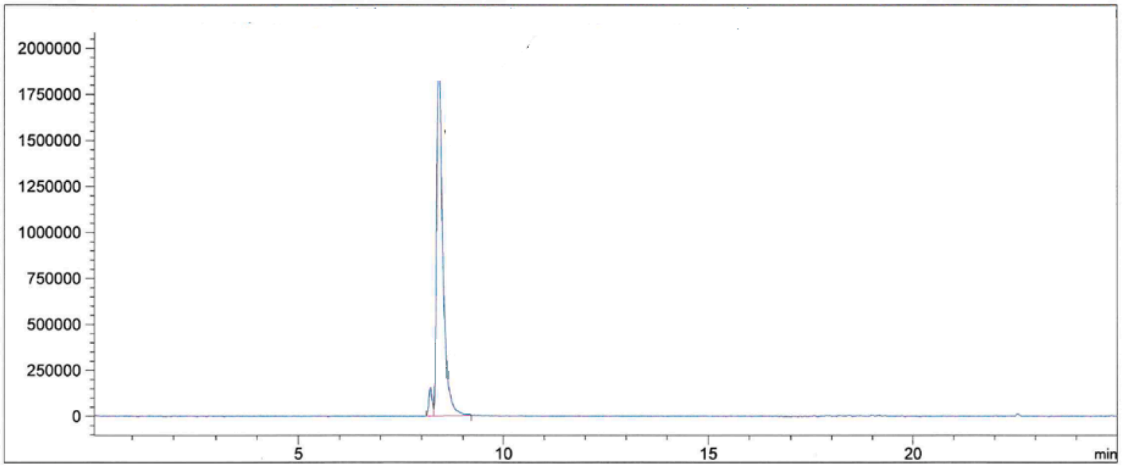
way to isolate the targeted isomer [41]. This further supports the hypothesis that the varying isomeric composition of the starting material could be the reason for this difference in the results obtained in our study. Indeed, commercial sulfonyl fluorides are synthesized by electrochemical fluorination and this process leads to several isomers in the case of the C_8 derivatives. However, when the carbon chain length decreases, a better purity is obtained [43-47]. This is evident in the ^{19}F NMR results of the different sulfonyl fluorides, no extra peaks are observed for the shortest sulfonyl fluoride, but with higher chain lengths, more impurities are being found (Fig. 1).

The successive recrystallization methods developed in our study proved to be an effective approach for purifying the C_6 derivatives. After the purifications, *n*-isomer was isolated in relatively good purity, only trace amounts of a branched isomer were detected on ^{19}F NMR (ca. 1 % to 2 %) for some compounds (see supporting information). GC analysis indicated the presence of the *n*-isomer plus a minor percentage (ca. 2 %) of the other isomer (supporting information). Derivatization of the sulfonamides with BSTFA and analysis by GC–MS did not reveal any further traces of isomers either.

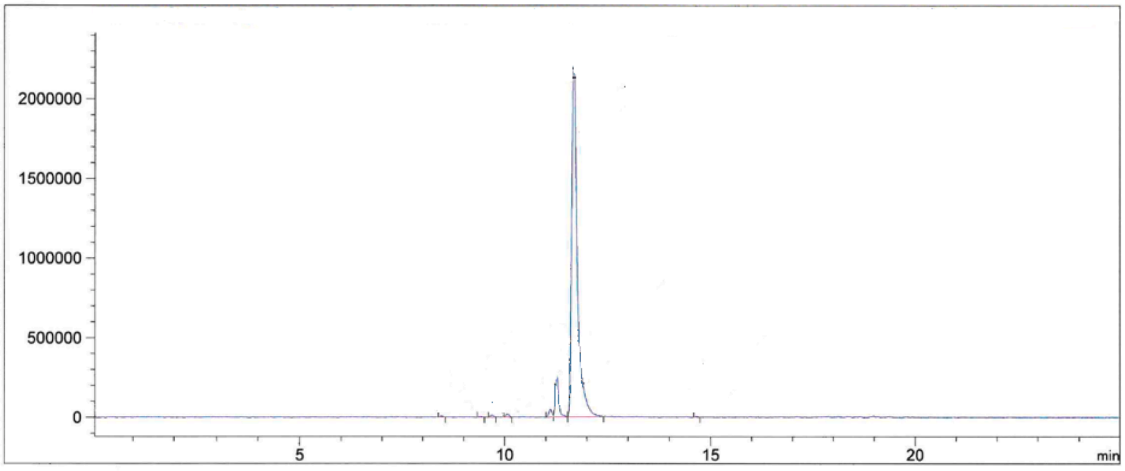
LC analysis was conducted for both C_4 and C_6 sulfonamide derivatives to verify their isomeric purity. Analysis of the C_4 and C_6 *N*-methyl/ethyl perfluoroalkane sulfonamides with a C_{18} column confirmed the purity of the C_4 and C_6 sulfonamides as determined by GC–MS. However, analysis using a specialist PFAS column (Ascentis® Express) able to separate the linear and branched isomers, revealed the presence of branched isomers. In the case of both the C_4 and C_6 analogues, a partially resolved branched isomer peak, not observed previously in previous GC–MS or LC-MS analysis was observed, more significant in the C_6 analogues (Fig. 2a and 2b). In the case of the C_6 derived products, in addition to a higher proportion of branched isomer (s) analysis on the Ascentis® Express column revealed the presence of other analogues (C_7, C_9, C_{10} and C_{11} but with a low percentage (< 0.2 %) which was not detected by ^{19}F NMR (Fig. 2 and supporting information). The comparison between LC analysis and ^{19}F NMR suggests that NMR may overestimate the purity due to the presence of even the branched isomers in a higher percentage (Fig. 2). However, compared to the commercial starting material, the percentage of isomers is reduced in *N*-methyl/ethyl perfluorohexane sulfonamide, demonstrating the effectiveness of the recrystallization process.

2.3. Perfluoroalkane sulfonamidoacetic acid synthesis

Short-chain perfluoroalkane sulfonamidoacetic acid was synthesized in two steps from the different perfluoroalkane sulfonamides (Scheme

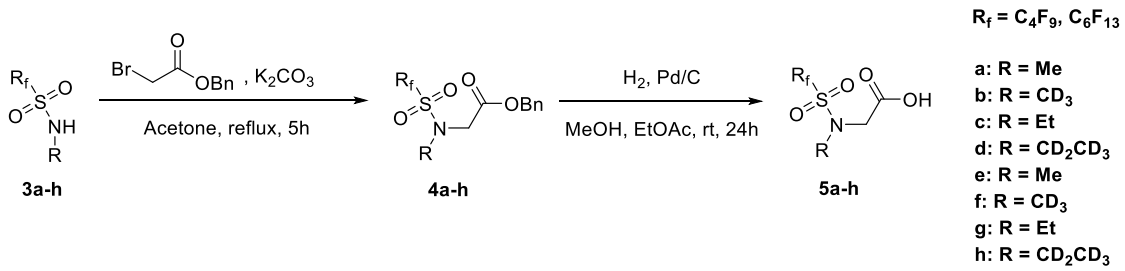


2a



2b

Fig. 2. LC analysis of EtFBSA and EtFHxSA with an Ascentis® Express 90 Å PFAS, 2.7 µm HPLC column on Agilent 1290 UHPLC and simple quadrupole Agilent 6130 using an electrospray ionization (ESI) technique. 1a) Analysis gave a percentage of 95.8 % for the *n*-isomer of EtFBSA. 1b) Analysis gave a percentage of 91.8 % for the *n*-isomer of EtFHxSA by counting isomers and analogues.



Scheme 2. Synthesis of *N*-alkyl perfluoroalkane sulfonamidoacetic acids from *N*-alkyl perfluoroalkane sulfonamides.

2). Direct alkylation using bromo carboxylic acid did not give the expected results. Therefore, a protecting group for the carboxylic acid was employed. The first reaction was an alkylation with benzyl bromoacetate. This benzyl ester was chosen for its ease of deprotection, which are mild conditions. In the literature, the use of methyl esters is reported [41,48,49]. However, Lehmler et al. (2007) reported difficulties to control the deprotection of the ester under basic conditions with potassium hydroxide and the obtention of a complex mixture from this way. They reported moderate yields (not higher than 40 %). Therefore, we privilegeded a benzyl group, especially for the synthesis of the deuterated analogues [41].

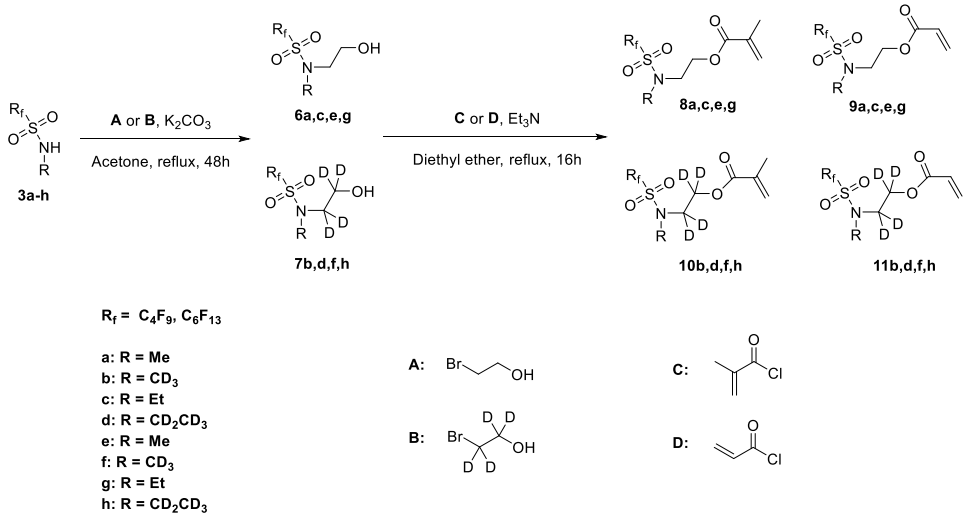
The protecting reaction with benzyl ester gave good yields. However, flash chromatography purification resulted product loss in some cases, since the non-reacted benzyl bromoacetate co-eluted with the reaction product. Finally, the terminal carboxylic acid was obtained by hydrogenation using a palladium-on-carbon catalyst with a reasonable yield after recrystallization in *n*-hexane and diethyl ether or dichloromethane for EtFBSAA. ^{1}H NMR confirmed the carboxylic deprotection. Purity was determined by GC–MS. The masses of the parent molecules were not detectable, due to the CO_2 fragment that is missing, so the final product was derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) to obtain a trimethylsilyl derivative.

2.4. Perfluoroalkane sulfonamidoethanol and perfluoroalkane sulfonamidoethyl (meth)acrylate synthesis

N-alkyl perfluoroalkane sulfonamidoethanol was synthesized from *N*-alkyl perfluoroalkane sulfonamide in good yield via alkylation reactions using 2-bromoethanol or its deuterated analogue (Scheme 3). This direct approach gave a satisfying result (around 80 %). After purification by flash chromatography and acetate protection it was not necessary to get the terminal alcohol [41]. Reported yields for MeFBSE and MeFHxSE were higher than 95 %, but the authors mentioned that yields were affected by the purity of 2-bromoethanol, so the results obtained were acceptable [42]. NMR data generally aligns with published literature data, with the exception of an apparent proton exchange of the alcohol group with NMR solvent.

(Meth)acrylate esters were obtained from the synthesized alcohols by esterification. After the work-up by extraction and washing, the crude products were first purified by flash chromatography. However, because of some remaining impurities, further purification by recrystallization in *n*-hexane using a dry-ice acetone bath had to be used. The yields obtained after the purification were lower than expected, especially for the acrylates. This could be explained by the melting points of some products being below room temperature, hindering the recrystallization process [42]. Additionally, degradation of acryloyl chloride might have contributed to the lower product yields.

Regarding chromatography analysis, the (meth)acrylate compounds could be analysed only on GC–MS as although LC-UV-ESI-MS could provide purity data from the UV spectra (210 nm), confirmation of identity was not possible using the MS. Molecular ions could not be obtained using electron ionization (EI) in full scan mode, due to loss of the methacrylate and acrylate moities due to extensive fragmentation (Fig. 3a). Even in selected ion monitoring (SIM) mode the molecular ion was hardly visible (Fig. 3b). However, identification of the pseudomolecular ion ($[M + H]^+$, *m/z* 519), although minor was possible using positive chemical ionization (PCI) utilizing methane as reactant gas (Fig. 3c). With the exception of the perfluorinated carbon chains, only the ester moieties of the products were confirmed by ^{1}H and ^{13}C NMR.



Scheme 3. Synthesis of native and deuterated *N*-alkyl perfluoroalkane sulfonamidoethanols and *N*-alkyl perfluoroalkane sulfonamidoethyl (meth)acrylates.

3. Conclusions

In summary, a total of 40 short-chain *N*-methyl/ethyl perfluoroalkane sulfonamide derivatives including labelled and unlabelled compounds were synthesized as analytical standards from commercially available perfluoroalkane sulfonyl fluoride. *N*-methyl/ethyl perfluoroalkane sulfonamides were obtained with a good yield through the reaction of the sulfonyl fluoride with native or deuterium labelled methyl or ethylamine hydrochloride. Recrystallization was used to isolate the straight-chain isomer of the *N*-methyl/ethyl perfluohexane sulfonamide and their deuterated analogues. This method led to the targeted product with a satisfactory purity as measured by ^{19}F NMR and GC–MS analysis, with less than 2 % of branched isomers remaining. However, this recrystallization process resulted in a significantly lower product yield due to the product loss in the mother liquor. In addition, LC analysis with a specific PFAS column suggests the presence of traces of longer or shorter analogues. It also indicates that the percentage of the branched isomer decreased compared to the starting material composition, demonstrating the effectiveness of the recrystallization process.

N-methyl/ethyl perfluoroalkane sulfonamidoacetic acids were successfully synthesized in two steps from the *N*-methyl/ethyl perfluoroalkane sulfonamides, using a benzyl ester as a protecting group of the terminal carboxylic acid. The benzyl protecting group was removed via hydrogenation, a milder method than using basic conditions. Recrystallization was used as a final purification step to provide the desired products.

N-methyl/ethyl perfluoroalkane sulfonamidoethanols were also obtained in a satisfactory yield from the *N*-methyl/ethyl perfluoroalkane sulfonamides. Finally, (meth)acrylate esters were synthesized in low to moderate yields from the previous alcohols after recrystallization in *n*-hexane. This lower yield might be explained by the low melting point of these esters, making the recrystallization difficult for some of them.

4. Experimental section

4.1. General information

Unless stated otherwise, all commercially available reagents and solvents were used in the form they were supplied without any further purification. Deuterated reagents were purchased from CDN Isotopes (Pointe-Claire, Canada), perfluorobutane sulfonyl fluoride was purchased from Merck (Darmstadt, Germany) and perfluorohexane sulfonyl fluoride from Synthonix (Wake Forest, United States). Reactions performed under an argon atmosphere are mentioned in the procedures. The stated yields are based on isolated material.

4.2. Characterization

Reactions were followed on a pre-coated thin-layer chromatography sheets ALUGRAM® SIL G/UV$_{254}$ fabricated by Macherey-Nagel (Düren, Germany). Flash column chromatography was performed on silica gel 60 (40 μm) produced by J.T. Baker (Radnor, PE, United States).

^{1}H, ^{13}C and ^{19}F NMR spectra were performed with Bruker 400 MHz Avance III HD equipped with a 5 mm SmartProbe z-gradient probe. Spectra are referenced relatively to the central residual protium solvent resonance in ^{1}H NMR ($CDCl_3$ $\delta_H = 7.26$, acetone-*d6* $\delta_H = 2.05$, DMSO-*d6* $\delta_H = 2.50$) and the central carbon solvent resonance in ^{13}C NMR ($CDCl_3$ $\delta_C = 77.16$, acetone-*d6* $\delta_C = 29.84$, DMSO-*d6* $\delta_C = 39.52$). Chemical shifts (δ) are reported in parts per million (ppm) as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublet (dd), and so on. The coupling constant (*J*) is included for the relevant signals in Hz. In most of the ^{13}C NMR spectra, the signals of CF_3 and/or CF_2 carbons are too weak to be distinguished from the baseline and are not reported [38-42,50]. The recorded NMR spectra were processed with Bruker TopSpin 4.2.0 software.

The products were analyzed using an Agilent 6890 N gas chromatograph equipped with an Agilent 7683B injector and coupled to an Agilent 5975B quadrupole mass spectrometry detector (MSD) and the MSD operated in electron ionization (EI) mode. The carrier gas used was helium with a flow rate of 1 mL/min. Injected volume was 1.0 μl with a split ratio of 20.0:1. An Agilent DB-5MS fused silica WCOT column (30 m x 0.25 mm x 0.25 μm) was used for the separation, running at 50 °C for the first 4 min and the ramped up to 300 °C by a 20 °C/min increase. The acquisition mode was either full-scan mode or selected ion monitoring (SIM) mode. When specified, *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) provided by Aldrich was used for derivatization and analysis of synthesized products using GC–MS. Acrylate and methacrylate products were additionally analyzed using an Agilent 8890 gas chromatograph equipped with an Agilent 7683B injector with the column effluent split between a flame ionization detector (FID) and an Agilent 5977B quadrupole mass spectrometry detector (MSD). The MSD was operated in positive chemical ionization (PCI) mode with methane used as the reactant gas. The carrier gas used was helium with a flow rate of 1 mL/min. Injected volume was 1.0 μl with a split ratio of 20.0:1. An Agilent DB-5MS UI fused silica WCOT column (30 m x 0.25 mm x 0.25 μm) was used for the separation, running at 50 °C for the first 4 min and the ramped up to 300 °C by a 20 °C/min increase. Data acquisition was in full-scan mode.

High-resolution mass spectrometry (HRMS) data were obtained with a high-resolution quadrupole time-of-flight (qTOF) mass spectrometer (MS) (Compact, Bruker Daltonics Bremen, Germany) connected to a LC 1260 HPLC (Agilent Technologies, Amstelveen, the Netherlands) using a XBridge BEH C18 XP column (2.5 μm, 2.1 mm x 100 mm) from Waters (Mildred, Massachusetts, USA) and a delay/isolator column (2.1 mm x 100 mm) also from Waters. The mobile phase was a gradient between MeOH and a 20 mmol/L ammonium acetate aqueous solution. The injection volume was 5 μl. QTOF-MS parameters are given in the supporting information file.

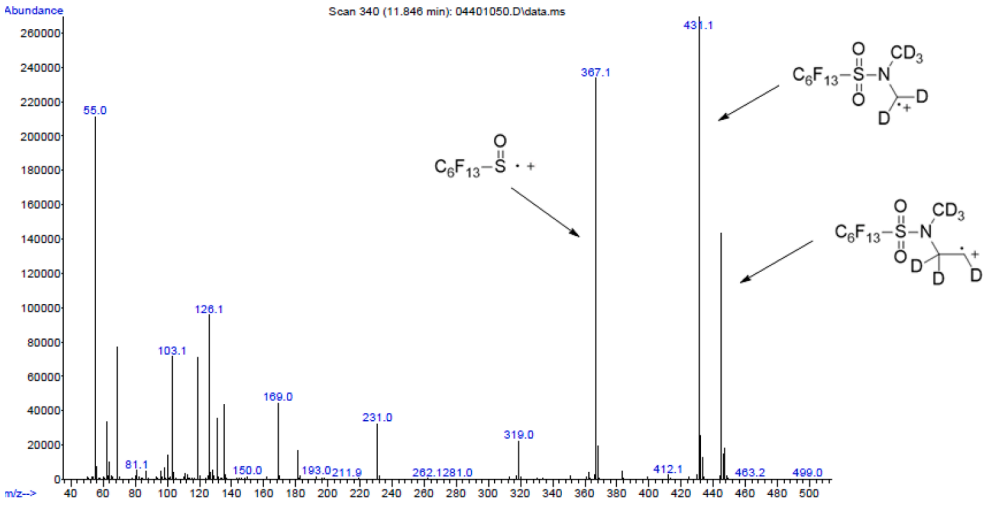
Analyses on liquid chromatography were performed either with a, a Kinetix C18 (1.7 μm, 2.1 × 100 mm) HPLC column (Phenomenex) or an Ascentis® Express 90 Å PFAS, 2.7 μm HPLC (Supelco) column using an Agilent 1290 ultra-high performance liquid chromatography (UHPLC) (eluent A was a 2 mM ammonium formate solution in water, 0.1 % (v/v) formic acid and eluent B was a 2 mM ammonium formate solution in MeOH, 0.1 % (v/v) formic acid, flow rate used was 0.55 mL/min) coupled with a single quadrupole Agilent 6130 in electrospray ionization (ESI) mode.

4.3. General procedure for synthesis of N-alkyl perfluoroalkane sulfonamide

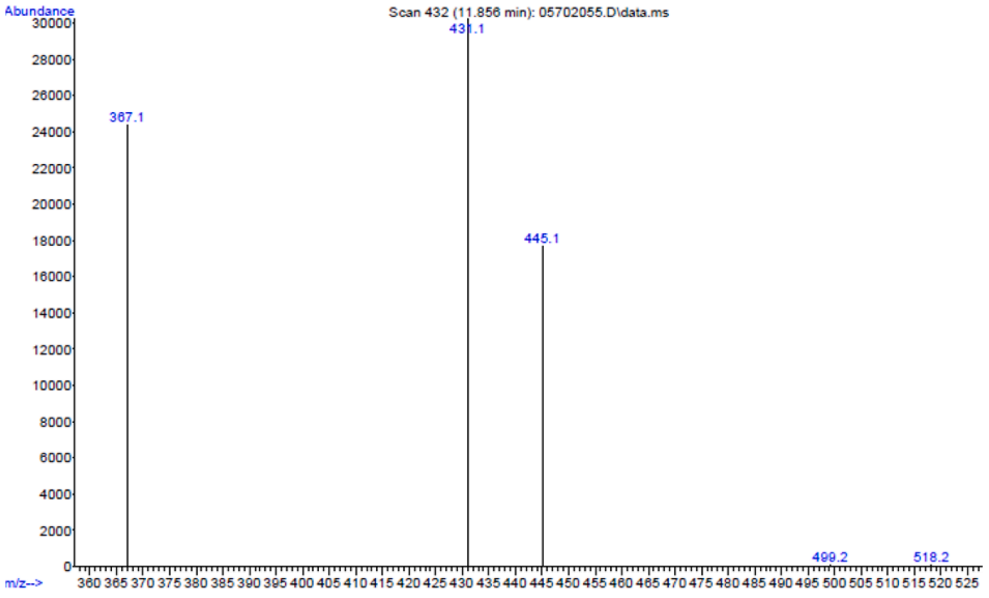
Short-chain perfluoroalkane sulfonamides (C_4 and C_6) were synthesized from commercial perfluoroalkane sulfonyl fluoride in an one-step reaction (Scheme 1). The protocols for both *N*-alkyl perfluorobutane sulfonamide (C_4) and *N*-alkyl perfluorohexane sulfonamide (C_6) are largely identical, with the exception of the purification process. This difference is elaborated in the subsequent sections.

4.3.1. Synthesis of N-alkyl perfluorobutane sulfonamide

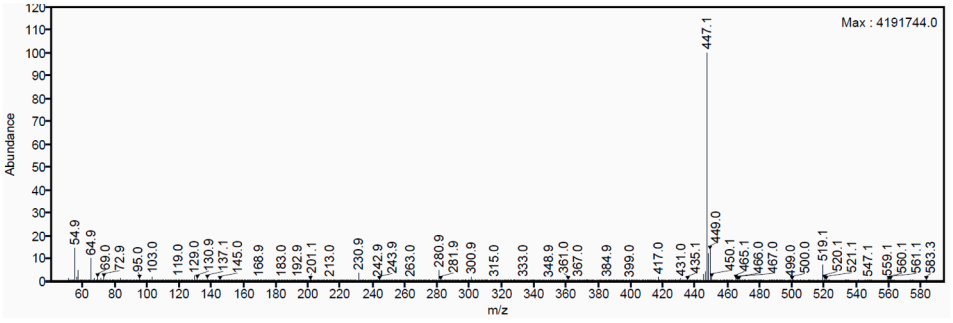
Perfluorobutane sulfonyl fluoride (1.0 eq) and triethylamine (4.0 eq) were dissolved in dry acetonitrile (2.5 mL per 1 mmol of perfluoroalkane sulfonyl fluoride) under an inert argon atmosphere. Alkylamine hydrochloride (1.2 eq) was added to the mixture in portions over a period of 1 hour at a temperature of 0–5 °C (ice bath), and the reaction was allowed to warm to room temperature and stirred for 24 h. After this period, the reaction mixture was refluxed for 2 h and then cooled down to room temperature. The solvent was then evaporated under reduced pressure. The residue was purified by flash column chromatography using a gradient of 15 % to 30 % ethyl acetate in petroleum ether. The resulting fractions were collected and checked on thin-layer chromatography (TLC) plates spotted with a revealing stain of $KMnO_4$ to visually identify the desired product. The product was further purified by



3a



3b



3c

Fig. 3. GC-MS spectra of MeFHxSEA-*d7* (m/z 518) using different MS ionization modes. 3a) Full scan spectra in Electron Ionization (EI) mode showing fragments with loss of the deuterium atoms and the acrylate fragment. 3b) Selection Ion Monitoring spectra in EI mode. 3c) Full scan spectra in Positive Chemical Ionisation (PCI) mode showing the molecular ion $[M+H]^+$ (m/z 519) and the main fragment containing all the deuterium atoms (m/z 447.1).

recrystallization using a mixture of *n*-hexane and a few drops of diethyl ether to isolate the *n*-isomer product. The synthesized *N*-methyl/ethyl-perfluorobutane sulfonamides were characterized by NMR and HRMS spectra analysis, the chemical purity of what was assumed to be the *n*-isomer was determined by GC–MS analysis.

***N*-methyl perfluorobutane sulfonamide (3a)**

Perfluorobutane sulfonyl fluoride (9.5 g, 5.35 mL, 31.4 mmol), triethylamine (17.4 mL, 125.8 mmol), methylamine hydrochloride (2.54 g, 37.7 mmol), acetonitrile (65 mL). Yield: 80%. White solid, mp 42-43°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 3.04 (3H, s, CH_3), 4.92 (1H, br s, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 30.7 (NCH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.75 (CF_3), -112.16 (α-CF_2), -121.38 (β-CF_2), -125.96 (γ-CF_2). HRMS (ESI), m/z: calcd for $C_5H_3F_9NO_2S$ 311.9741 [M-H]$^-$, found 311.9743 (err: 0.8 ppm).

***N*-methyl perfluorobutane sulfonamide-*d3* (3b)**

Perfluorobutane sulfonyl fluoride (3.5 g, 1.97 mL, 11.5 mmol), triethylamine (6.42 mL, 46.3 mmol), methyl-*d3*-amine hydrochloride (0.98 g, 13.9 mmol), acetonitrile (25 mL). Yield: 75%. White solid, mp 43°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 4.88 (1H, br s, NH). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.74 (CF_3), -112.18 (α-CF_2), -121.37 (β-CF_2), -125.95 (γ-CF_2). HRMS (ESI), m/z: calcd for $C_5D_3F_9NO_2S$ 314.9929 [M-H]$^-$, found 314.9936 (err: 2.3 ppm).

***N*-ethyl perfluorobutane sulfonamide (3c)**

Perfluorobutane sulfonyl fluoride (7.8 g, 4.4 mL, 25.8 mmol), triethylamine (14.3 mL, 103.2 mmol), ethylamine hydrochloride (2.52 g, 30.9 mmol), acetonitrile (55 mL). Yield: 81 %. White solid, mp 41–42 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.28 (3H, t, J = 7.4 Hz, CH_3), 3.41 (2H, m, CH_2), 5.03 (1H, br s, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 16.1 (CH_2CH_3), 40.3 (NCH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −80.77 (CF_3), −112.69 (α-CF_2), −121.33 (β-CF_2), −126.01 (γ-CF_2). HRMS *m/z* 325.9908 [M-H]$^-$, calculated 325.9897 (err: 3.3 ppm).

***N*-ethyl perfluorobutane sulfonamide-*d5* (3d)**

Perfluorobutane sulfonyl fluoride (2.9 g, 1.6 mL, 9.6 mmol), triethylamine (5.3 mL, 38.4 mmol), ethyl-*d5*-amine hydrochloride (1 g, 11.5 mmol), acetonitrile (20 mL). Yield: 69 %. White solid, mp 41 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 4.96 (1H, br s, NH). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −80.74 (CF_3), −112.67 (α-CF_2), −121.28 (β-CF_2), −125.97 (γ-CF_2). HRMS *m/z* 331.0219 [M-H]$^-$, calculated 331.0211 (err: 2.4 ppm).

4.3.2. Synthesis of N-alkyl perfluorohexane sulfonamide

Perfluorohexane sulfonyl fluoride used as the starting material consists as an isomer mixture containing both straight and branched isomers. After the flash chromatography, the *n*-isomer was isolated by multiple recrystallizations in boiling *n*-hexane, where diethyl ether is added until al solid was dissolved. The solution was then slowly cooled under stirring to induce crystal formation, followed by filtration to isolate the crystals. This procedure was repeated on the mother liquor to obtain a purity higher than 98 % based on GC–MS and to increase the yield of the straight chain *n*-isomer.

***N*-methyl perfluorohexane sulfonamide (3e)**

Perfluorohexane sulfonyl fluoride (9 g, 5.04 mL, 22.4 mmol), triethylamine (12.4 mL, 89.5 mmol), methylamine hydrochloride (1.81 g, 89.5 mmol), acetonitrile (45 mL). Yield: 38%. White solid, mp 79°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 3.04 (3H, s, CH_3), 4.96 (1H, br s, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 30.7 (NCH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.72 (CF_3), -111.95 (α-CF_2), -120.37 (β-CF_2), -121.72 (γ-CF_2), -122.67 (δ-CF_2), -126.07 (ε-CF_2). HRMS (ESI), m/z: calcd for $C_7H_3F_{13}NO_2S$ 411.9677 [M-H]$^-$, found 411.9688 (err: 2.8 ppm).

***N*-methyl perfluorohexane sulfonamide-*d3* (3f)**

Perfluorohexane sulfonyl fluoride (4.7 g, 2.6 mL, 11.7 mmol), triethylamine (6.5 mL, 46.7 mmol), methyl-*d3*-amine hydrochloride (1 g, 14 mmol), acetonitrile (25 mL). Yield: 50%. White solid, mp 78-79°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 4.90 (1H, br s, NH). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.71 (CF_3), -111.97 (α-CF_2), -120.36 (β-CF_2), -121.71 (γ-CF_2), -122.66 (δ-CF_2), -126.06 (ε-CF_2). HRMS (ESI), m/z: calcd for $C_7D_3F_{13}NO_2S$ 414.9865 [M-H]$^-$, found 414.9872 (err: 1.7 ppm).

***N*-ethyl perfluorohexane sulfonamide (3g)**

Perfluorohexane sulfonyl fluoride (9.5 g, 5.35 mL, 31.4 mmol), triethylamine (17.4 mL, 125.8 mmol), ethylamine hydrochloride (2.54 g, 37.7 mmol), acetonitrile (65 mL). Yield: 35 %. White solid, mp 68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.29 (3H, t, J = 7.3 Hz, CH_3), 3.42 (2H, q, J = 7.2 Hz, CH_2), 4.91 (1H, br s, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 16.1 (CH_2CH_3), 40.2 (NCH_2CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −80.73 (CF_3), −111.42 (α-CF_2), −120.28 (β-CF_2), −121.74 (γ-CF_2), −122.68 (δ-CF_2), −126.08 (ε-CF_2). HRMS (ESI), *m/z*: calcd for $C_8H_5F_{13}NO_2S$ 425.9833 [M-H]$^-$, found 425.9847 (err: 3.2 ppm).

***N*-ethyl perfluorohexane sulfonamide-*d5* (3h)**

Perfluorohexane sulfonyl fluoride (3.9 g, 2.18 mL, 19.8 mmol), triethylamine (5.3 mL, 38.7 mmol), ethyl-*d5*-amine hydrochloride (1 g, 11.6 mmol), acetonitrile (20 mL). Yield: 34 %. White solid, mp 68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 4.86 (1H, br s, NH). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −80.71 (CF_3), −112.43 (α-CF_2), −120.28 (β-CF_2), −121.73 (γ-CF_2), −122.66 (δ-CF_2), −126.07 (ε-CF_2). HRMS (ESI), *m/z*: calcd for $C_8D_5F_{13}NO_2S$ 431.0147 [M-H]$^-$, found 431.0158 (err: 2.6 ppm).

4.3.3. General procedure for synthesis of N-alkyl perfluoroalkanesulfonamido acetic acid

N-alkyl perfluoroalkane sulfonamide (1.0 eq), benzyl bromoacetate (1.1 eq) and potassium carbonate (2.0 eq) were refluxed in acetone (90 mL) for 5 h. After cooling to room temperature, the inorganic solid was filtered off and the filtrate was evaporated to obtain a crude yellow solid. The crude product was purified by flash column chromatography (ethyl acetate/petroleum ether, revealing stain – $KMnO_4$) providing benzyl *N*-Alkyl-*N*-((perfluoroalkyl)sulfonyl)glycinate. The benzyl *N*-Alkyl-*N*-((perfluoroalkyl)sulfonyl)glycinate was dissolved in a mixture of methanol/ethyl acetate (3:2, v/v) and Pd/C was added to the reaction mixture. The mixture was stirred under hydrogen atmosphere (balloon) for 24 h, and then palladium on carbon was filtered on celite and solid was washed with methanol, the filtrate was evaporated, under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (20 % to 30 % ethyl acetate in petroleum ether, revealing stain – $KMnO_4$), followed by recrystallization in n-hexane and diethyl ether or DCM to remove the last traces of impurities to provide the targeted N-alkyl perfluoroalkane sulfonamidoacetic acid. The sulfonamidoacetic acid was derivatized with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) to obtain a more volatile compound for GC–MS analysis. In a 1.5 mL vial, 1 mg of *N*-alkyl perfluoroalkane sulfonamidoacetic acid was added, followed by 20 drops of BSTFA. Acetonitrile was then added (0.5 mL), and the vial was placed on a heated shaker for 1 hour at 70 °C. The vial was cooled to room temperature. Acetonitrile (1 mL) was added and the sample was analysed by GC–MS.

***N*-methyl perfluorobutane sulfonamidoacetic acid (5a)**

N-methyl perfluorobutane sulfonamide (5.962 g, 12.9 mmol), benzyl bromoacetate (3.32 mL, 21 mmol), potassium carbonate (5.28 g, 38.2 mmol), acetone (90 mL). Yield: 66%. Benzyl *N*-methyl-*N*-((perfluorobutyl)sulfonyl)glycinate (5.81 g, 12.6 mmol), Pd/C (1.5 g), methanol (120 mL), ethyl acetate (80 mL). Yield: 48%. White solid, mp 96°C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 3.12 (3H, s, CH_2), 4.20 (2H, s, CH_2COOH), 13.32 (1H, br s, COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 37.1 (NCH_3), 51.2 (CH_2COOH), 168.9 (C=O). ^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm -80.27 (CF_3), -112.82 (α-CF_2), -121.25 (β-CF_2), -125.68 (γ-CF_2). HRMS (ESI), m/z: calcd for $C_7H_5F_9NO_4S$ 369.9796 [M-H]$^-$, found 369.9799 (err: 1.0 ppm).

***N*-methyl perfluorobutane sulfonamidoacetic acid-*d3* (5b)**

N-methyl perfluorobutane sulfonamide-*d3* (2.34 g, 5.6 mmol), benzyl bromoacetate (0.97 mL, 6.2 mmol), potassium carbonate (1.55 g, 11.2 mmol), acetone (30 mL). Yield: 65%. Benzyl *N*-methyl-*N*-((perfluorobutyl)sulfonyl)glycinate-*d3* (1.68 g, mmol), Pd/C (0.7 g),

methanol (60 mL), ethyl acetate (40 mL). Yield: 42%. White solid, mp 95-96°C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 4.19 (2H, s, CH_2COOH), 13.10 (1H, br s, COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 51.1 (CH_2COOH), 168.9 (C=O). ^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm -80.31 (CF_3), -112.89 (α-CF_2), -121.29 (β-CF_2), -125.72 (γ-CF_2). HRMS (ESI), m/z: calcd for $C_7H_2D_3F_9NO_4S$ 372.9984 [M-H]$^-$, found 372.9985 (err: 0.3 ppm).

***N*-ethyl perfluorobutane sulfonamidoacetic acid (5c)**

N-ethyl perfluorobutane sulfonamide (5.04 g, 15.4 mmol), benzyl bromoacetate (2.68 mL, 16.9 mmol), potassium carbonate (4.25 g, 30.7 mmol), acetone (85 mL). Yield: 59 %. Benzyl *N*-ethyl-*N*-((perfluorobutyl)sulfonyl)glycinate (4.3 g, 12.6 mmol), Pd/C (0.8 g), methanol (100 mL), ethyl acetate (60 mL). Yield: 45 %. White solid, mp 130 °C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 1.17 (3H, t, $J = 7.2$ Hz, CH_3), 3.55 (2H, m, CH_2CH_3), 4.19 (2H, m, CH_2COOH), 13.24 (1H, br s, COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 13.3 (CH_2CH_3), 45.5 (NCH_2CH_3), 48.3 (NCH_2COOH), 169.3 (C = O). ^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm −80.42 (CF_3), −113.09 (α-CF_2), −121.21 (β-CF_2), −125.77 (γ-CF_2). HRMS (ESI), *m/z*: calcd for $C_7H_5F_9NO_4S$ 383.9952 [M-H]$^-$, found 383.9953 (err: 0.3 ppm).

***N*-ethyl perfluorobutane sulfonamidoacetic acid-*d5* (5d)**

N-ethyl perfluorobutane sulfonamide-*d5* (1.275 g, 3.8 mmol), benzyl bromoacetate (0.7 mL, 4.2 mmol), potassium carbonate (1.06 g, 7.6 mmol), acetone (20 mL). Yield: 66 %. Benzyl *N*-ethyl-*N*-((perfluorobutyl)sulfonyl)glycinate-*d5* (0.954 g, 2 mmol), Pd/C (0.2 g), methanol (40 mL), ethyl acetate (25 mL). Yield: 40 %. White solid, mp 128–129 °C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 4.18 (2H, m, CH_2COOH), 13.23 (1H, br s, COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 48.2 (CH_2COOH), 169.3 (C = O). ^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm −80.28 (CF_3), −113.10 (α-CF_2), −121.15 (β-CF_2), −125.67 (γ-CF_2). HRMS (ESI), *m/z*: calcd for $C_7H_2D_3F_9NO_4S$ 389.0266 [M-H]$^-$, found 389.0268 (err: 0.6 ppm).

***N*-methyl perfluorohexane sulfonamidoacetic acid (5e)**

N-methyl perfluorohexane sulfonamide (2.71 g, 6.5 mmol), benzyl bromoacetate (1.1 mL, 7.2 mmol), potassium carbonate (1.81 g, 13.1 mmol), acetone (35 mL). Yield: 63%. Benzyl *N*-methyl-*N*-((perfluorohexyl)sulfonyl)glycinate (2.3 g, 4.1 mmol), Pd/C (0.7 g), methanol (60 mL), ethyl acetate (40 mL). Yield: 49%. White solid, mp 125°C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 3.12 (3H, s, CH_3), 4.12 (2H, s, CH_2COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 37.1 (NCH_3), 51.2 (CH_2CCOH), 168.9 (C=O). ^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm -80.21 (CF_3), -112.65 (α-CF_2), -120.29 (β-CF_2), -121.61 (γ-CF_2), -122.48 (δ-CF_2), -125.73 (ε-CF_2). HRMS (ESI), m/z: calcd for $C_9H_5F_{13}NO_4S$ 469.9732 [M-H]$^-$, found 469.9739 (err: 1.6 ppm).

***N*-methyl perfluorohexane sulfonamidoacetic acid-*d3* (5f)**

N-methyl perfluorohexane sulfonamide-*d3* (2.168 g, 5.2 mmol), benzyl bromoacetate (0.91 mL, 5.7 mmol), potassium carbonate (1.44 g, 10.4 mmol), acetone (25 mL). Yield: 54%. Benzyl *N*-methyl-*N*-((perfluorohexyl)sulfonyl)glycinate-*d3* (1.58 g, 2.8 mmol), Pd/C (0.55 g), methanol (60 mL), ethyl acetate (40 mL). Yield: 55%. White solid, mp 128°C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 4.19 (2H, s, CH_2COOH), 13.31 (1H, br s, COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 51.1 (CH_2COOH), 168.9 (C=O). ^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm -80.23 (CF_3), -112.68 (α-CF_2), -120.30 (β-CF_2), -121.64 (γ-CF_2), -122.50 (δ-CF_2), -125.76 (ε-CF_2). HRMS (ESI), m/z: calcd for $C_9H_2D_3F_{13}NO_4S$ 472.9920 [M-H]$^-$, found 472.9926 (err: 1.3 ppm).

***N*-ethyl perfluorohexane sulfonamidoacetic acid (5g)**

N-ethyl perfluorohexane sulfonamide (2.57 g, 6 mmol), benzyl bromoacetate (1 mL, 6.6 mmol), potassium carbonate (1.66 g, 12 mmol), acetone (25 mL). Yield: 64 %. Benzyl *N*-ethyl-*N*-((perfluorohexyl)sulfonyl)glycinate (2.21 g, 3.8 mmol), Pd/C (0.4 g), methanol (50 mL), ethyl acetate (30 mL). Yield: 68 %. White solid, mp 147 °C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 1.17 (3H, br t, $J = 7.2$ Hz, CH_3), 3.54 (2H, m, CH_2CH_3), 4.18 (2H, m, CH_2COOH), 13.25 (1H, br s, COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 13.3 (CH_2CH_3), 45.5 (NCH_2CH_3), 48.3 (CH_2COOH), 169.3 (C = O). ^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm −79.95 (CF_3), −112.93 (α-CF_2), −120.27 (β-CF_2), −121.83 (γ-CF_2), −122.60 (δ-CF_2), −125.98 (ε-CF_2). HRMS (ESI), *m/z*: calcd for $C_{10}H_7F_{13}NO_4S$ 483.9888 [M-H]$^-$, found 483.9893 (err: 1.0 ppm).

***N*-ethyl perfluorohexane sulfonamidoacetic acid-*d5* (5h)**

N-ethyl perfluorohexane sulfonamide-*d5* (1.3 g, 3 mmol), benzyl bromoacetate (0.52 mL, 3 mmol), potassium carbonate (0.813 g, 12 mmol), acetone (15 mL). Yield: 69 %. Benzyl *N*-ethyl-*N*-((perfluorohexyl)sulfonyl)glycinate-*d5* (1.17 g, 3.8 mmol), Pd/C (0.3 g), methanol (40 mL), ethyl acetate (25 mL). Yield: 40 %. White solid, mp 147 °C. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ ppm 4.19 (2H, m, CH_2COOH), 13.23 (1H, br s, COOH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 48.2 (CH_2COOH), 169.3 (C = O).^{19}F NMR (DMSO-*d6*, 376 MHz): δ ppm −80.25 (CF_3), −112–94 (α-CF_2), −120.20 (β-CF_2), −121.64 (γ-CF_2), −122.50 (δ-CF_2), −125.77 (ε-CF_2). HRMS (ESI), *m/z*: calcd for $C_{10}H_2D_5F_{13}NO_4S$ 489.0202 [M-H]$^-$, found 489.0212 (err: 2.1 ppm).

4.3.4. General procedure for synthesis of N-alkyl perfluoroalkane sulfonamidoethanol

A mixture of *N*-methyl/ethyl perfluoroalkane sulfonamide (1.0 eq), 2-bromoethanol (**A**) or 2-bromoethanol-d4 (**B**) (1.1 eq), potassium carbonate (2.0 eq) and potassium iodide (catalytic amount) was refluxed in acetone for 48 h, then the mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (30 % to 70 % ethyl acetate in petroleum ether, revealing stain – $KMnO_4$). Pure fractions were combined and evaporated to give N-methy/ethyl perfluroalkane sulfoamidoethanols or their deuterated analogues.

***N*-methyl perfluorobutane sulfonamidoethanol (6a)**

N-methyl perfluorobutane sulfonamide (5.8 g, 18.5 mmol), K_2CO_3 (5.11 g, 37 mmol), 2-bromoethanol (1.42 mL, 20.3 mmol), KI (catalytic), acetone (90 mL). Yield: 83%. White solid, mp 61-62°C. ^{1}H NMR (acetone-*d6*, 400 MHz): δ ppm 3.23 (3H, s, CH_3), 3.42 (1H, m, CH_2CH_2), 3.78 (3H, m, CH_2CH_2), 4.12 (1H, t, CH_2OH). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ ppm 37.2 (NCH_3), 54.1 (NCH_2), 60.6 (60.5) (CH_2OH). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm -81.73 (CF_3), -112.98 (α-CF_2), -122.09 (β-CF_2), -126.65 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 326 (100) [M-CH_3O]$^+$, 262 (21) [M-$C_3H_8FO_3$]$^+$.

***N*-methyl perfluorobutane sulfonamidoethanol-*d7* (7b)**

N-methyl perfluorobutane sulfonamide-*d3* (2.59 g, 8.2 mmol), K_2CO_3 (2.26 g, 16.4 mmol), 2-bromoethanol-1,1,2,2-*d4* (0.65 mL, 9 mmol, eq), KI (catalytic), acetone (40 mL). Yield: 68%. White solid, mp 61-62°C. ^{1}H NMR (acetone-*d6*, 400 MHz): δ ppm 4.07 (1H, s, CD_2OH). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm -81.72 (CF_3), -113.06 (α-CF_2), -122.10 (β-CF_2), -126.65 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 331 (100) [M-CHD_2O]$^+$, 267 (25) [M-$C_3HD_7NO_3$]$^+$.

***N*-ethyl perfluorobutane sulfonamidoethanol (6c)**

N-ethyl perfluorobutane sulfonamide (5.86 g, 17.9 mmol), K_2CO_3 (1.66 g, 13.2 mmol), 2-bromoethanol (0.47 mL, 7.2 mmol), KI (catalytic), acetone (30 mL). Yield: 73%. Orange liquid. ^{1}H NMR (acetone-*d6*, 400 MHz): δ ppm, 1.29 (3H, t, $J = 7.1$ Hz, CH_3), 3.52 (1H, m, CH_2CH_2), 3.67 (3H, m, CH_2CH_2), 3.79 (2H, q, $J = 5.5$ Hz, CH_2CH_3), 4.10 (1H, t, CH_2OH). ^{13}C NMR (acetone-*d6*, 100 MHz): δ ppm 14.4 (CH_3), 45.7 (NCH_2CH_3), 51.0 (NCH_2), 61.0 (60.9) (CH_2OH). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm -81.74 (CF_3), -113.37 (α-CF_2), -121.94 (β-CF_2), -126.65 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 340 (100) [M-CH_3O]$^+$, 248 (12) [M-$C_4H_{10}FNO_3$]$^+$.

***N*-ethyl perfluorobutane sulfonamidoethanol-*d9* (7d)**

N-ethyl perfluorobutane sulfonamide-*d5* (2 g, 6.6 mmol), K_2CO_3 (4.95 g, 35.8 mmol), 2-bromoethanol-1,1,2,2-d4 (1.37 mL, 19.7 mmol), KI (catalytic), acetone (90 mL). Yield: 66%. Colorless liquid. ^{1}H NMR (acetone-*d6*, 400 MHz): δ ppm 4.05 (1H, s, CD_2OH). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm -81.72 (CF_3), -113.41 (α-CF_2), -121.93 (β-CF_2), -126.64 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 347 (100) [M-CHD_2O]$^+$, 251 (12) [M-$C_4HD_9NO_4$]$^+$.

***N*-methyl perfluorohexane sulfonamidoethanol (6e)**

N-methyl perfluorohexane sulfonamide (3.8 g, 9.2 mmol, 1 eq),

K_2CO_3 (2.55 g, 18.4 mmol, eq), 2-bromoethanol (0.7 mL, 10.1 mmol, eq), KI (catalytic) acetone (45 mL). Yield: 77%. White solid, mp 87°C. ^{1}H NMR (acetone-*d6*, 400 MHz): δ ppm 3.23 (3H, s, CH_3), 3.42 (1H, m, CH_2CH_2), 3.78 (3H, m, CH_2CH_2), 4.12 (1H, t, CH_2OH). ^{13}C NMR (acetone-*d6*, 100 MHz): δ ppm 37.2 (CH_3), 54.1 (NCH_2), 60.6 (60.5) (CH_2OH). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm -81.65 (CF_3), -112.77 (α-CF_2), -121.06 (β-CF_2), -122.32 (γ-CF_2), -123.26 (δ-CF_2), -126.73 (ε-CF_2). GC-MS, 70 eV, m/z (rel. int.): 426 (100) $[M\text{-}CH_2O]^+$, 362 (43) $[M\text{-}C_3H_8FO_3]^+$.

***N*-methyl perfluorohexane sulfonamidoethanol-*d7* (7f)**

N-methyl perfluorohexane sulfonamide-*d3* (2.24 g, 5.3 mmol, 1 eq), K_2CO_3 (1.48 g, 10.7 mmol, eq), 2-bromoethanol-1,1,2,2-*d4* (0.43 mL, 5.9 mmol, eq), KI (catalytic), acetone (30 mL). Yield: 88%. White solid, mp 88°C. ^{1}H NMR (d6-acetone, 400 MHz): δ ppm 4.07 (1H, s, CH_2OH). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm -81.65 (CF_3), -112.84 (α-CF_2), -121.09 (β-CF_2), -122.34 (γ-CF_2), -123.27 (δ-CF_2), -126.73 (ε-CF_2). GC-MS, 70 eV, m/z (rel. int.): 431 (100) $[M\text{-}CHD_2O]^+$, 367 (43) $[M\text{-}C_3HD_7NO_2]^+$.

***N*-ethyl perfluorohexane sulfonamidoethanol (6g)**

N-ethyl perfluorohexane sulfonamide (3.33 g, 7.8 mmol), K_2CO_3 (2.15 g, 15.6 mmol), 2-bromoethanol (0.6 mL, 8.6 mmol), KI (catalytic), acetone (90 mL). Yield: 70 %. White solid, mp 54 °C. ^{1}H NMR (acetone-*d6*, 400 MHz): δ ppm 1.30 (3H, t, J = 7.2 Hz, CH_3), 3.53 (1H, m, CH_2CH_2), 3.67 (3H, m, CH_2CH_2), 3.79 (2H, q, J = 5.6 Hz, CH_2CH_3), 4.11 (1H, t, J = 5.5 Hz, CH_2OH). ^{13}C NMR (acetone-*d6*, 100 MHz): δ ppm 14.6 (CH_2CH_3), 45.7 (NCH_2CH_3), 51.0 (NCH_2CH_2), 60.9 (CH_2OC). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm −81.66 (CF_3), −113.16 (α-CF_2), −120.93 (β-CF_2), −122.32 (γ-CF_2), −123.26 (δ-CF_2), −126.73 (ε-CF_2). GC–MS, 70 eV, *m/z* (rel. int.): 440 (100) $[M\text{-}CH_2OH]^+$, 348 (23) $[M\text{-}C_4H_{10}FNO_2]^+$.

***N*-ethyl perfluorohexane sulfonamidoethanol-*d9* (7h)**

N-ethyl perfluorohexane sulfonamide-*d5* (1.58 g, 3.6 mmol, 1 eq), K_2CO_3 (1.01 g, 7.3 mmol, eq), 2-bromoethanol-1,1,2,2-*d4* (0.29 mL, 4 mmol, eq), KI (catalytic), acetone (20 mL). Yield: 75 %. White solid, mp 52–53 °C. ^{1}H NMR (acetone-*d6*, 400 MHz): δ ppm 4.05 (1H, s, CH_2OH). ^{19}F NMR (acetone-*d6*, 376 MHz): δ ppm −81.64 (CF_3), −113.21 (α-CF_2), −120.93 (β-CF_2), −122.31 (γ-CF_2), −123.26 (δ-CF_2), −126.73 (ε-CF_2). GC–MS, 70 eV, *m/z* (rel. int.): 447 (100) $[M\text{-}CD_2OH]^+$, 351 (26) $[M\text{-}C_4HD_9NO_3]^+$.

4.3.5. General procedure for synthesis of N-alkyl perfluoroalkane sulfonamidoethyl (meth)acrylate

N-alkyl perfluoroalkane sulfonamidoethanol (1.0 eq), triethylamine (1.3 eq), and hydroquinone (catalytic amount) were dissolved in diethyl ether at 0 °C under inert atmosphere in an oven-dried two-necked flask. At 0 °C, (meth)acryloyl chloride **C** or **D** (1.3 eq) were added. After the addition, the reaction mixture was warmed and stirred under reflux conditions for 16 h The reaction mixture was cooled to room temperature, then washed with water (10 mL/mmol of alcohol), hydrochloric acid (1 N, 10 mL/mmol of alcohol), and saturated aqueous sodium bicarbonate (10 mL/mmol of alcohol). The organic phase was separated and dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by flash chromatography (50 % ethyl acetate in petroleum ether, revealing stain - $KMnO_4$). Pure fractions were combined, evaporated, and recrystallized in *n*-hexane with a dry ice-acetone bath to obtain the targeted (meth)acrylate compounds.

***N*-methyl perfluorobutane sulfonamidoethyl methacrylate (8a)**

N-methyl perfluorobutane sulfonamidoethanol (0.6 g, 1.6 mmol), triethylamine (0.3 mL, 2.2 mmol), hydroquinone (catalytic), diethyl ether (15 mL), methacryloyl chloride (0.21 mL, 2.2 mmol). Yield: 19%. White solid, mp 48-49°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.96 (3H, s, CH_2=CCH_3), 3.17 (3H, s, CH_2CH_2), 3.44 (1H, m, CH_2CH_2), 3.96 (1H, m, CH_2CH_2), 4.35 (2H, m, CH_2CH_2), 5.63 (1H, br s, CH_2=C), 6.16 (1H, br s, CH_2=C). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 18.4 (CH_3), 36.7 (NCH_3), 50.1 (NCH_2CH_3), 61.4 (CH_2OCO), 126.8 (CH_2=C), 135.7 (CH_2=C), 167.1 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.72 (CF_3), -111.83 (α-CF_2), -121.39 (β-CF_2), -125.92 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 339 (84) $[M\text{-}C_4H_6O_2]$, 326 (100) $[M\text{-}C_5H_7O_2]$, 262 (36) $[M\text{-}C_7H_{10}FO_3]^+$.

***N*-methyl perfluorobutane sulfonamidoethyl methacrylate-*d7* (10b)**

N-methyl perfluorobutane sulfonamidoethanol-d7 (0.8 g, 2.2 mmol), triethylamine (0.39 mL, 2.8 mmol), hydroquinone (catalytic), diethyl ether (20 mL), methacryloyl chloride (0.27 mL, 2.8 mmol). Yield: 21%. White solid, mp 50°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.96 (3H, s, CH_2=CCH_3), 5.63 (1H, s, CH_2=C), 6.16 (1H, s, CH_2=C). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 18.3 (CH_3), 126.7 (CH_2=C), 135.8 (CH_2=C), 167.1 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.73 (CF_3), -111.93 (α-CF_2), -121.39 (β-CF_2), -125.92 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 345 (81) $[M\text{-}C_4H_5DO_2]^+$, 331 (100) $[M\text{-}C_5H_5D_2O_2]^+$, 267 (38) $[M\text{-}C_7H_5D_7NO_3]^+$.

***N*-ethyl perfluorobutane sulfonamidoethyl methacrylate (8c)**

N-ethyl perfluorobutane sulfonamidoethanol (1.6 g, 4.3 mmol), triethylamine (0.77 mL, 5.6 mmol), hydroquinone (catalytic), diethyl ether (45 mL), methacryloyl chloride (0.53 mL, 5.6 mmol). Yield: 16%. White solid, mp 33-34°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.30 (3H, t, J = 7.3 Hz, CH_2CH_3), 1.95 (3H, s, CH_2=CCH_3), 3.58 (3H, m, CH_2CH_2), 3.87 (1H, m, CH_2CH_2), 4.34 (2H, t, J = 5.7 Hz, CH_2CH_3), 5.63 (1H, s, CH_2=C), 6.15 (1H, s, CH_2=C). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 13.4 (NCH_2CH_3), 18.3 (CH_3), 44.6 (NCH_2CH_3), 46.5 (NCH_2CH_2), 61.8 (CH_2OCO), 126.7 (CH_2=C), 135.8 (CH_2=C), 167.1 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.73 (CF_3), -112.45 (α-CF_2), -121.24 (β-CF_2), -125.92 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 353 (35) $[M\text{-}C_4H_6O_2]^+$, 340 (100) $[M\text{-}C_5H_7O_2]^+$, 248 (21) $[M\text{-}C_8H_{14}FNO_3]^+$.

***N*-ethyl perfluorobutane sulfonamidoethyl methacrylate-*d9* (10d)**

N-ethyl perfluorobutane sulfonamidoethanol-d9 (0.6 g, 1.5 mmol), triethylamine (0.28 mL, 2 mmol), hydroquinone (catalytic), diethyl ether (15 mL), methacryloyl chloride (0.19 mL, 2 mmol). Yield: 29%. White solid, mp 33°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.95 (3H, s, CH_2=C-CH_3), 5.62 (1H, s, C=CH2), 6.15 (1H, s, C=CH2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 18.4 (CH_3), 126.7 (CH_2=C), 135.8 (CH_2=C), 167.1 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.74 (CF_3), -112.49 (α-CF_2), -121.24 (β-CF_2), -125.93 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 361 (17) $[M\text{-}C_4H_5DO_2]^+$, 347 (100) $[M\text{-}C_5H_5D_2O_2]^+$, 251 (17) $[M\text{-}C_8H_5D_9NO_4]^+$.

***N*-methyl perfluorohexane sulfonamidoethyl methacrylate (8e)**

N-methyl perfluorohexane sulfonamidoethanol (1.2 g, 2.6 mmol), triethylamine (0.47 mL, 3.4 mmol), hydroquinone (catalytic), diethyl ether (26 mL), methacryloyl chloride (0.33 mL, 3.4 mmol). Yield: 28%. White solid, mp 74°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.96 (3H, s, CH_2=CCH_3), 3.17 (3H, s, NCH_3), 3.43 (1H, m, CH_2CH_2), 3.96 (1H, m, CH_2CH_2), 4.35 (2H, m, CH_2CH_2), 5.63 (1H, s, CH_2=C), 6.17 (1H, m, C=CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 18.4 (CH_3) 36.7 (NCH_2CH_3), 50.1 (NCH_2CH_2), 61.4 (CH_2OCO), 126.8 (CH_2=CH), 135.7 (CH_2=CH), 167.1 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.71 (CF_3), -111.69 (α-CF_2), -120.39 (β-CF_2), -121.71 (γ-CF_2), -122.67 (δ-CF_2), -126.06 (ε-CF_2). GC-MS, 70 eV, m/z (rel. int.): 439 (88) $[M\text{-}C_4H_6O_2]^+$, 426 (100) $[M\text{-}C_5H_7O_2]^+$, 362 (83) $[M\text{-}C_7H_{12}FO_3]^+$.

***N*-methyl perfluorohexane sulfonamidoethyl methacrylate-*d7* (10f)**

N-methyl perfluorohexane sulfonamidoethanol-d7 (0.7 g, 1.5 mmol), triethylamine (0.27 mL, 1.9 mmol), hydroquinone (catalytic), diethyl ether (15 mL), methacryloyl chloride (0.19 mL, 1.9 mmol). Yield: 45%. White solid, mp 75°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.96 (3H, s, CH_2=CCH_3), 5.63 (1H, s, CH_2=C), 6.16 (1H, s, C=CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 18.4 (CH_3), 126.7 (CH_2=CH), 135.7 (CH_2=CH), 167.1 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.71 (CF_3), -111.75 (α-CF_2), -120.40 (β-CF_2), -121.71 (γ-CF_2), -122.65 (δ-CF_2), -126.05 (ε-CF_2). GC-MS, 70 eV, m/z (rel. int.): 445 (90) $[M\text{-}C_4H_5O_2]^+$, 431 (100) $[M\text{-}C_5H_5DO_2]^+$, 367 (75) $[M\text{-}C_7H_5D_7NO_3]^+$.

***N*-ethyl perfluorohexane sulfonamidoethyl methacrylate (8g)**

N-ethyl perfluorohexane sulfonamidoethanol (0.6 g, 1.2 mmol),

triethylamine (0.23 mL, 1.6 mmol), hydroquinone (catalytic), diethyl ether (15 mL), methacryloyl chloride (0.15 mL, 1.6 mmol) Yield: 16 %. White solid, mp 46 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.30 (3H, t, J = 7.3 Hz, CH_2CH_3), 1.96 (3H, s, CH_2═CCH_3), 3.58 (3H, m, CH_2CH_2), 3.85 (1H, m, CH_2CH_2), 4.34 (2H, m, CH_2CH_3), 5.63 (1H, m, C═CH_2), 6.15 (1H, s, C═CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 14.0 (CH_2CH_3), 18.4 (CH_2═CCH_3), 44.6 (NCH_2CH_3), 46.4 (NCH_2CH_2), 61.8 (CH_2OCO), 126.7 (CH_2═C), 135.8 (CH_2═C), 167.1 (C = O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −80.71 (CF_3), −112.26 (α-CF_2), −120.25 (β-CF_2), −121.71 (γ-CF_2), −122.66 (δ-CF_2), −126.07 (ε-CF_2). GC–MS, 70 eV, *m/z* (rel. int.): 454 (37) [M-$C_4H_6O_2$]$^+$, 440 (100) [M-$C_5H_7O_2$]$^+$, 348 (38) [M-$C_8H_{14}FNO_4$]$^+$.

_N_-ethyl perfluorohexane sulfonamidoethyl methacrylate-*d9* (10h)

N-ethyl perfluorohexane sulfonamidoethanol-*d9* (0.6 g, 1.2 mmol), triethylamine (0.23 mL, 1.6 mmol), hydroquinone (catalytic), diethyl ether (12 mL), methacryloyl chloride (0.16 mL, 1.6 mmol). Yield: 19 %. White solid, mp 44 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.95 (3H, s, CH_2═CCH_3), 5.63 (1H, br s, C═CH_2), 6.15 (1H, m, C═CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 18.3 (CH_2═CCH_3), 126.7 (CH_2═C), 135.8 (CH_2═C), 171.1 (C = O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −81.71 (CF_3), −112.31 (α-CF_2), −120.26 (β-CF_2), −121.71 (γ-CF_2), −122.66 (δ-CF_2), −126.04 (ε-CF_2). GC–MS, 70 eV, *m/z* (rel. int.): 463 (33) [M-$C_4H_5DO_2$]$^+$, 447 (100) [M-$C_5H_5D_2O_2$]$^+$, 351 (34) [M-$C_8H5D_9NO_4$]$^+$.

_N_-methyl perfluorobutane sulfonamidoethyl acrylate (9a)

N-methyl perfluorobutane sulfonamidoethanol (0.6 g, 1.6 mmol), triethylamine (0.3 mL, 2.2 mmol), hydroquinone (catalytic), diethyl ether (16 mL), acryloyl chloride (0.17 mL, 2.2 mmol). Yield: 6%. White solid, mp 56°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 3.17 (3H, s, CH_3), 3.47 (1H, m, CH_2CH_2), 3.92 (1H, m, CH_2CH_2), 4.36 (2H, m, CH_2CH_2), 5.90 (1H, br dd, J = 1.1 and 10.4 Hz, CH_2=CH), 6.14 (1H, dd, J = 10.4 and 17.3 Hz, CH_2=CH), 6.46 (1H, br dd, J = 1.1 and 17.3 Hz, CH_2=CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 36.7 (NCH_3), 50.1 (NCH_2CH_2), 61.3 (CH_2OCO), 127.8 (CH_2=C), 132.1 (CH_2=C), 165.8 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.73 (CF_3), -111.84 (α-CF_2), -121.39 (β-CF_2), -125.92 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 339 (50) [M-$C_3H_4O_2$]$^+$, 326 (100) [M-$C_4H_5O_2$]$^+$, 262 (36) [M-$C_6H_{10}FO_3$]$^+$.

_N_-methyl perfluorobutane sulfonamidoethyl acrylate-*d7* (11b)

N-methyl perfluorobutane sulfonamidoethanol-d7 (0.350 g, 0.96 mmol), triethylamine (0.17 mL, 1.2 mmol), hydroquinone (catalytic), diethyl ether (10 mL), acryloyl chloride (0.10 mL, 1.2 mmol). Yield: 8%. White solid, mp 56°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 5.90 (1H, dd, J = 1.1 and 10.5 Hz, CH2=CHCO), 6.14 (1H, dd, J = 10.5 and 17.3 Hz, CH2=CHCO), 6.46 (1H, dd, J = 1.4 and 17.4 Hz, C=CHCO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 127.8 (CH_2=C), 132.1 (CH_2=C), 165.8 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.72 (CF_3), -111.89 (α-CF_2), -121.39 (β-CF_2), -125.91 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 344 (71) [M-$C_3H_3DO_2$]$^+$, 331 (100) [M-$C_4H_3D_2O_2$]$^+$, 267 (50) [M-$C_6H_3D_7NO_3$]$^+$.

_N_-ethyl perfluorobutane sulfonamidoethyl acrylate (9c)

N-ethyl erfluorobutame sulfonamidoethanol (1.6 g, 4.3 mmol), triethylamine (0.77 mL, 5.6 mmol), hydroquinone (catalytic), diethyl ether (43 mL), acryloyl chloride (0.45 mL, 5.6 mmol). Yield: 8%. White semi-solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.29 (3H, t, J = 7.2 Hz, CH_2CH_3), 3.59 (3H, m, CH_2CH_2), 3.84 (1H, m, CH_2CH_2), 4.35 (2H, t, J = 5.7 Hz, CH_2CH_3), 5.90 (1H, dd, J = 1.2 and 10.5 Hz, CH_2=CH), 6.13 (1H, dd, J = 10.4 and 17.3 Hz, CH_2=CH), 6.45 (1H, dd, J = 1.2 and 17.4 Hz, CH_2=CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 14.0 (NCH_2CH_3), 44.7 (NCH_2CH_3), 46.5 (NCH_2CH_2), 61.7 (CH_2OCO), 127.8 (CH_2=C), 132.1 (CH_2=C), 165.8 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.74 (CF_3), -112.36 (α-CF_2), -121.24 (β-CF_2), -125.92 (γ-CF_2). GC-MS, 70 eV, m/z (rel. int.): 353 (17) [M-$C_3H_4O_2$]$^+$, 340 (100) [M-$C_4H_5O_2$]$^+$, 248 (18) [M-$C_7H_{12}FNO_3$]$^+$.

_N_-ethyl perfluorobutane sulfonamidoethyl acrylate-*d9* (11d)

N-ethyl perfluorobutane sulfonamidoethanol-*d9* (0.6 g, 1.5 mmol), triethylamine (0.28 mL, 2 mmol), hydroquinone (catalytic), diethyl ether (16 mL), acryloyl chloride (0.16 mL, 2 mmol). Yield: 11%. White semi-solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 5.90 (1H, dd, J = 1.4 and 10.6 Hz, CH2=CHCO), 6.13 (1H, dd, J = 10.6 and 17.4 Hz, CH2=CHCO), 6.46 (1H, dd, J = 1.3 and 17.3 Hz, C=CHCO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 127.8 (CH_2=CH), 132.1 (CH_2=CH), 165.8 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -125.92 (CF_3), -121.26 (CF_2), -112.42 (CF_2), -80.73 (CF_2). GC-MS, 70 eV, m/z (rel. int.): 361 (17) [M-$C_3H_3DO_2$]$^+$, 347 (100) [M-$C_4H_3D_2O_2$]$^+$, 251 (18) [M-$C_7H_3D_9NO_4$]$^+$.

_N_-methyl perfluorohexane sulfonamidoethyl acrylate (9e)

N-methyl perfluorohexane sulfonamidoethanol (1 g, 2.2 mmol), triethylamine (0.39 mL, 2.8 mmol), hydroquinone (catalytic), diethyl ether (20 mL), acryloyl chloride (0.23 mL, 2.8 mmol). Yield: 19%. White solid, mp 73°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 3.17 (3H, s, NCH_3), 3.46 (1H, m, NCH_2), 3.92 (1H, m, CH_2), 4.35 (2H, m, CH_2OCO), 5.90 (1H, dd, J = 1.0 and 10.4 Hz, CH_2=CHCO), 6.15 (1H, dd, J = 10.5 and 17.6 Hz, CH_2=CHCO), 6.46 (1H, dd, J = 1.0 and 17.4 Hz, C=CHCO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 36.7 (NCH_3), 50.1 (NCH_2CH_2), 61.3 (CH_2OCO), 127.8 (CH_2=CH), 132.1 (CH_2=CH), 165.8 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.72 (CF_3), -111.66 (α-CF_2), -120.40 (β-CF_2), -121.71 (γ-CF_2), -122.67 (δ-CF_2), -126.08 (ε-CF_2). GC-MS, 70 eV, m/z (rel. int.): 440 (51) [M-$C_3H_4O_2$]$^+$, 426 (100) [M-$C_4H_5O_2$]$^+$, 362 (87) [M-$C_6H_{10}FO_3$]$^+$.

_N_-methyl perfluorohexane sulfonamidoethyl acrylate-*d7* (11d)

N-methyl perfluorohexane sulfonamidoethanol-*d7* (0.9 g, 1.9 mmol), triethylamine (0.34 mL, 2.5 mmol), hydroquinone (catalytic), diethyl ether (20 mL), acryloyl chloride (0.2 mL, 2.5 mmol). Yield: 10%. White solid, mp 73°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 5.90 (1H, dd, J = 1.2 and 10.5 Hz, CH_2=CHCO), 6.13 (1H, dd, J = 10.5 and 17.3 Hz, CH_2=CHCO), 6.45 (1H, dd, J = 1.2 and 17.5 Hz, C=CHCO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 127.8 (CH_2=CH), 132.1 (CH_2=CH), 165.8 (C=O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm -80.71 (CF_3), -111.72 (α-CF_2), -120.37 (β-CF_2), -121.72 (γ-CF_2), -122.66 (δ-CF_2), -126.05 (ε-CF_2). GC-MS, 70 eV, m/z (rel. int.): 361 (17) [M-$C_3H_3DO_2$]$^+$, 347 (100) [M-$C_4H_3D_2O_2$]$^+$.

_N_-ethyl perfluorohexane sulfonamidoethyl acrylate (9g)

N-ethyl perfluorohexane sulfonamidoethanol (0.6 g, 1.2 mmol), triethylamine (0.23 mL, 1.6 mmol), hydroquinone (catalytic), diethyl ether (12 mL), acryloyl chloride (0.13 mL, 1.6 mmol). Yield: 9 %. White solid, mp 33 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.30 (3H, t, J = 7.2 Hz, CH_2CH_3), 3.57 (3H, m, C═CH_2), 3.82 (1H, m, CH_2CH_2), 4.35 (2H, t, J = 5.6 Hz, CH_2CH_2), 5.90 (1H, dd, J = 1.3 and 10.6 Hz, CH_2═CH), 6.12 (1H, dd, J = 10.5 and 17.4 Hz, CH_2═CH), 6.46 (1H, dd, J = 1.3 and 17.3 Hz, CH_2═CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 14.0 (CH_3), 44.7 (NCH_2CH_3), 46.5 (NCH_2CH_2), 61.8 (CH_2O), 127.8 (CH_2═CH), 132.1 (CH_2═CH), 165.8 (C = O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −81.71 (CF_3), −112.16 (α-CF_2), −120.27 (β-CF_2), −121.71 (γ-CF_2), −122.66 (δ-CF_2), −126.05 (ε-CF_2). GC–MS, 70 eV, *m/z* (rel. int.): 454 (16) [M-$C_3H_4O_2$]$^+$, 440 (100) [M-$C_4H_5O_2$]$^+$, 348 (40) [M-$C_7H_{12}FNO_3$]$^+$.

_N_-ethyl perfluorohexane sulfonamidoethyl acrylate-*d9* (11h)

N-ethyl perfluorohexane sulfonamidoethanol-*d9* (0.6 g, 1.2 mmol), triethylamine (0.22 mL, 1.6 mmol), hydroquinone (catalytic), diethyl ether (15 mL), acryloyl chloride (0.13 mL, 1.6 mmol) Yield: 14 %. White solid, mp 33–34 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 5.90 (1H, dd, J = 1.4 and 10.6 Hz, CH_2═CH), 6.13 (1H, dd, J = 10.5 and 17.3 Hz, CH_2═CH), 6.45 (1H, dd, J = 1.3 and 17.4 Hz, CH_2═CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 127.8 (CH_2═C), 132.1 (CH_2═C), 165.8 (C = O). ^{19}F NMR ($CDCl_3$, 376 MHz): δ ppm −80.71 (CF_3), −112.22 (α-CF_2), −120.25 (β-CF_2), −121.70 (γ-CF_2), −122.66 (δ-CF_2), −126.05 (ε-CF_2). GC–MS, 70 eV, *m/z* (rel. int.): 463 (22) [M-$C_3H_3DO_2$]$^+$, 447 (100) [$C_4H_3D_2O_2$]$^+$, 351 (34) [M-$C_7H_3D_9NO_4$]$^+$.

The description of the other compounds is described in the supporting information file.

Associated content

Data availability statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

^{1}H, ^{19}F and ^{13}C NMR spectra and GC-MS chromatograms of the synthesized perfluoroalkane sulfonamide derivatives.

CRediT authorship contribution statement

D. Jérémy Liwara: Investigation, Conceptualization. **Anton Pavlov:** Conceptualization. **Craig Mckenzie:** Formal analysis. **Jon E. Johansen:** Writing – review & editing, Supervision. **Pim E.G. Leonards:** Writing – review & editing, Supervision. **Sicco Brandsma:** Writing – review & editing, Project administration. **Jacob de Boer:** Writing – review & editing, Supervision. **Huiling Liu:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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