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Perfluoroorganochalcogenyl-ketenes IV. [1]
Bis(perfluoroorganochalcogenyl)ketenes $(R_fE)_2C{=}C{=}O$ $(R_f{=}CF_3,C_6F_5;\ E{=}S,\ Se)$: synthons with a high preparative potential

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Abstract

Chemical reactions of the ketenes $(R_f)_2C{=}C{=}O$ $(R_f{=}CF_3S,\ C_6F_5S,\ CF_3Se)$ with molecules containing reactive hydrogen atoms such as alcohols, secondary amines and thiols are described. Addition across the C=C bond forming the corresponding materials takes place. No insertion is observed with SO_nCl_2 $(n=1,2)$, instead chlorination of the ketenes takes place. Hydrides such as $(n\text{-}C_4H_9)_3SnH$ or $(CH_3)_3SiH$ add to the C=O bond forming enolates. No cycloaddition of the ketenes with olefins containing electron withdrawing substituents, e.g., dimethylmaleate, are observed. With increasing nucleophilicity of the olefinic double bond, reactivity is increased, e.g., styrol forms the corresponding cyclobutanone and ethylvinylether reacts explosively even at low temperatures. Olefins containing allylic H-atoms provide besides [2+2] cycloadducts increasingly unsaturated ketones by ene-reactions as demonstrated with *cis*-2-butene and 2,3-dimethyl-2-butene. Conjugated dienes, e.g., butadiene, form [2+2] in addition to [4+2]-cycloadducts. Supplementary cycloadditions with C=N- and S=N-systems are described. Varying reactivities between perfluorinated and organic ketenes are discussed.

Keywords: Trifluoromethyl; Pentafluorophenyl; Sulfenyl; Selenyl; Ketenes; Nucleophiles; Dienes; Heteroenes and -dienes

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1. Introduction

Efficient synthesis for bis(perfluoroorganylchalcogenyl)ketenes such as $(CF_3S)_2C{=}C{=}O$ [1], $(CF_3Se)_2C{=}C{=}O$ [1] and $(C_6F_5S)_2C{=}C{=}O$ [2] are now available and therefore systematic investigations of typical ketene reactions of these stable compounds became urgently necessary.

In this paper, we shall describe reactions between $(R_f)_2C{=}C{=}O$ $(R = CF_3S,\ CF_3Se$ and $C_6F_5S)$ with nucleophiles, dienes and other double bond-containing systems. Differences in chemical behaviour between these ketenes and normal organic- or dichloroketenes, and $(CF_3)_2C{=}C{=}O$ will be discussed.

2. Addition reactions with protic nucleophiles, hydrides, NOCl, SO_nCl_2 (n=0, 1, 2) and $(CH_3O)_3P$

Ketenes always react with substances containing a hydroxyl group as an acylating agent [3]. As expected bis(perfluoroorganylsulfenyl)- and bis(trifluoromethylselenyl)ketenes (**1a–c**) hydrolyse to the corresponding acetic acids (**2a–c**) [1,2] (Eq. (1)).

$$\underset{\mathbf{1}}{(R_f)_2C{=}C{=}O} + H_2O \rightarrow \underset{\mathbf{2}}{(R_f)_2CHC(O)OH} \qquad (1)$$

R_f=CF_3S,**1a**,**2b**; C_6F_5S,**1b**,**2b**; CF_3Se,**1c**,**2c**

The reactions are carried out under neutral conditions and proceed spontaneously, exothermically and are finished after a few minutes. In moist air, hydrolysis of **1a**, **c** is slow, but hydrolysis of **1b** is very fast and is finished after a few minutes. Similarly, methanolysis to the corresponding acetic methyl ester takes place quantitatively (Eq. (2)).

$$\mathbf{1a\text{–}c} + CH_3OH \rightarrow \underset{\mathbf{3a\text{–}c}}{(R_f)_2CHC(O)OCH_3} \qquad (2)$$

Because of the lower solubility of polyalcohols in ketene solutions, glycerine is only acylated under vigorous conditions according to Eq. (3).

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$$\mathbf{1a}+\begin{array}{l}CH_2OH\\ |\\ CH_2OH\\ |\\ CH_2OH\end{array}\xrightarrow{100^\circ C/40\,h}\begin{array}{l}CH_2OC(O)CH(SCF_3)_2\\ |\\ CHOC(O)CH(SCF_3)_2\\ |\\ CH_2OC(O)CH(SCF_3)_2\end{array}\qquad(3)$$

3d

The ketenes (**1a–c**) react with thiols, especially perfluorinated ones, e.g., CF_3SH and C_6F_5SH, just as fast and exothermic as with primary alcohols. This can be proved by the reactions of **1** with CF_3SH at $-50°C$, C_2H_5SH and C_6F_5SH at 20°C to the corresponding thioacetic acid–*S*-esters (**4a–c**) (Eq. (4)).

$$\mathbf{1a{-}c}+C_2H_5SH \rightarrow (R_f)_2CHC(O)SC_2H_5 \qquad (4)$$

4a–c

$$\mathbf{1a}\rightarrow\begin{cases}+CF_3SH & (CF_3S)_2CHC(O)SCF_3 \quad \mathbf{4d}\\ +C_6F_5SH & (CF_3S)_2CHC(O)SC_6F_5 \quad \mathbf{4e}\end{cases}$$

The higher reactivity of the perfluorinated thiols in comparison to the aliphatic thiols can be explained by the strong inductive effect of the CF_3- and C_6F_5-groups making the S–H bond weaker and therefore more acidic [4,5]. Compared with normal thiols, amines are more reactive. Therefore, acylations of amines with ketenes are very vigorous [3]. The reactivity depends on the basicity of the amines. The reactions studied between **1a–c** and $(C_2H_5)_2NH$ take place immediately, are very exothermic and proceed according to Eq. (5).

$$\mathbf{1a{-}c}+(C_2H_5)_2NH\rightarrow(R_f)_2CHC(O)N(C_2H_5)_2 \qquad (5)$$

5a–c

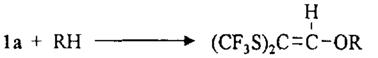
If $(C_2H_5)_2NH$ is replaced by less nucleophilic $(CF_3S)_2NH$ no reaction takes place even on heating. The inductive effect of the CF_3S group lowers the basicity of the amine so strongly that it becomes slightly acidic. In accordance with normal ketenes, **1a** reacts with NOCl to form as the main product chlorobis(trifluoromethylsulfenyl)acetic acid chloride (**6**) besides uncharacterised CF_3S-substituted byproducts. Addition reactions proceed with alkylnitrites. Isoamylnitrite forms with **1a** bis(trifluoromethyl sulfenyl)nitrosoacetic acidisoamylester (**6a**) (Eq. (6)), which shows no tendency to dimerise.

$$\mathbf{1a}\begin{cases}+2NOCl\rightarrow(CF_3S)_2CClC(O)Cl+2NO & \mathbf{6}\\ +(CH_3)_2CH(CH_2)_2ONO \\ \quad\rightarrow(CF_3S)_2C(NO)C(O)O(CH_2)_2CH(CH_3)_2 & \mathbf{6a}\end{cases}\qquad(6)$$

The reactivity of **1a** is different from that of $H_2C{=}C{=}O$ towards SCl_2. While ketene in an inert solvent easily forms thiodiglycolacid dichloride, isolated as its dimethylester, **1a** reacts in CH_2Cl_2 at 50°C (10 d) to chlorosulfenylbis(trifluoromethylsulfenyl)acetic acid chloride (**7**) in only 9% yield. No insertion of **1a** in the S–Cl bond of thionyl dichloride or sulfuryl dichloride is observed. In both cases, only chlorination of **1a** to **6** is accomplished (Eq. (7)).

$$\mathbf{1a}\begin{cases}+SCl_2\rightarrow ClC(O)C(SCF_3)_2SCl & \mathbf{7}\\ +SO_nCl_2\rightarrow\mathbf{6}+SO_2\quad(n=1,2)\end{cases}\qquad(7)$$

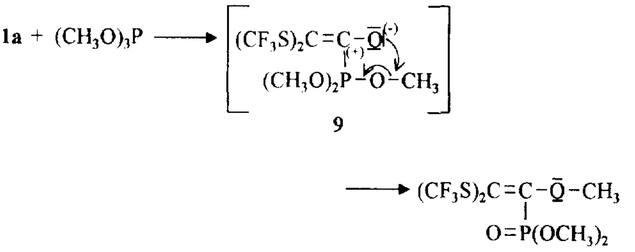
Compounds with a hydrogen–metal bond in which the H-atom has hydride character reduce the carbonyl function of **1a**. This is demonstrated by reactions of **1a** with $(n\text{-}C_4H_9)_3SnH$ and $(CH_3)_3SiH$ proceeding according to Eq. (8).



$$\mathbf{1a}+RH\longrightarrow(CF_3S)_2C{=}\overset{H}{\overset{|}{C}}{-}OR \qquad (8)$$

$R=(n\text{-}C_4H_9)_3Sn$, **8**; $(CH_3)_3Si$, **8a**

Treatment of **1a** with trimethylphosphite provides 1,1-bis(trifluoromethylsulfenyl)-2-dimethylphosphonate-2-methoxy-ethene (**9a**) after a vigorous reaction, contradicting the formation of $(CF_3)_2C{=}C{=}C(CF_3)_2$ from $(CF_3)_2C{=}C{=}O$ and $(C_2H_5O)_3P$. Even with a variation of reaction-parameters, no $(CF_3S)_2C{=}C{=}C(SCF_3)_2$ could be observed while treating **1a** with $(CH_3O)_3P$.



9

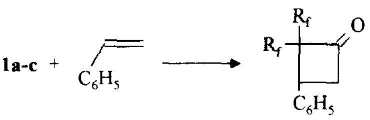
9a

(9)

It can be assumed that this reaction proceeds through nucleophilic attack of phosphorus at the carbonyl carbon forming intermediate **9**, which rearranges according to Michaelis–Arbusow [6] to the final product **9a**.

3. [2 + 2]- and [4 + 2]-cycloaddition-reactions

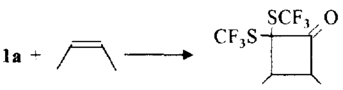
Systems with an electron deficient double bond, e.g., dimethylmaleate, do not react with the perfluorinated ketenes **1a–c**. The two carboxylic groups with an -I-effect deactivate the double bond to such an extent that no [2 + 2]-cycloaddition takes place. If the alkene is activated by a phenyl group as in styrene, cycloaddition occurs at 60 to 80°C (12–24 h) forming 2,2–bis(perfluoroorganylchalcogenyl)-3-phenylcyclobutanone (**10a–c**).



10 (10)

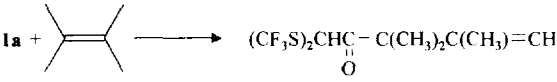
$R_f = CF_3S$, **10a**; C_6F_5S, **10b**; CF_3Se, **10c**

In *cis*-2-butene and in 2,3-dimethyl-2-butene, the double bonds are activated by two and four-methyl functions, respectively, increasing their nucleophilicity compared with styrene, but steric hinderance becomes a significant effect. Therefore, in the reaction of **1a** with *cis*-2-butene, the corresponding cyclobutanone (**11a**) is the major product, but small amounts of a β,γ-unsaturated ketone can also be detected. The latter product was not fully characterised. NMR- and GC/MS-spectroscopical investigations showed that the configuration of *cis*-butene is retained and cycloaddition proceeds stereospecifically as observed in reactions between $Cl_2C{=}C{=}O$ and *cis*-, *trans*-cyclooctene [7] or $(C_6H_5)_2C{=}C{=}O$ and *cis*-, *trans*-2-butene [8]. This observed stereospecificity is a criterion necessary to assign cycloaddition reactions of ketenes as one stage, multicenter reactions [9].



11a (11)

If the olefin contains four methyl groups as in 2,3-dimethyl-2-butene the cyclobutanone can only be detected in traces; the main product is 1,1-bis(trifluoromethylsulfenyl)-3,3,4-trimethyl-4-pentene-2-one (**12a**).

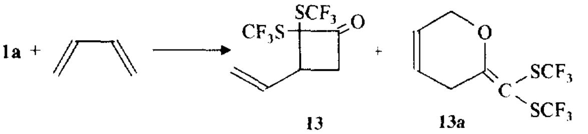


$$\mathbf{1a} + (CH_3)_2C{=}C(CH_3)_2 \longrightarrow (CF_3S)_2CH\overset{}{\underset{\displaystyle O}{\overset{}{C}}}-C(CH_3)_2C(CH_3){=}CH_2 \qquad (12)$$

12a

An analogous behaviour is shown by $(CF_3)_2C{=}C{=}O$, which does not form the cyclobutanone with 2-methylpropene, but the β,γ-unsaturated ketone $(CF_3)_2CHC(O)CH_2C(CH_3){=}CH_2$ [10].

To the peculiarity of ketene-cycloaddition chemistry belongs the preference of ketenes to form with conjugated dienes cyclobutanones [11] instead of Diels–Alder adducts. Only with electron-rich 1,3-dienes could [4+2]-cyclo-additions be accomplished, e.g., $(C_6H_5)_2C{=}C{=}O$ reacts with $(CH_3)_3COCH{=}CH{-}CH{=}CH_2$ or $CH_2{=}C(OSiMe_3){-}CH{=}C(OCH_3)H$ to yield the [4+2]-adduct[12,13]. Similarly $(CF_3)_2C{=}C{=}O$ reacts even with unactivated dienes such as butadiene [10] or cyclooctatetraene [14] to give Diels–Alder adducts. In these cycloadditions, the C=O function of the ketene participates preferably forming an dihydropyran-derivative with an exocyclic methylene group [12,15]. This selectivity of positions is also maintained in the [4+2]-addition of **1a** with butadiene, where, besides [2+2]-, [4+2]-addition products with an exocyclic methylene function are also formed (Eq. (13)).



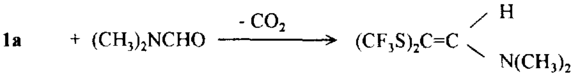
13 **13a** (13)

The isomers **13** and **13a** are obtained in a 1:1 ratio and could be separated by fractional distillation. Attempts to transfer pure **13a** on warming into **13** through a Cope- or Claisen-type rearrangement, respectively, failed [16]. The less nucleophilic hexachlorobutadiene does not react with **1a** even when long reaction times and elevated temperatures are applied.

4. Reactions with dimethylformamide and cumulated heterodienes

Polarised ketenes such as $Cl_2C{=}C{=}O$ react smoothly with aliphatic and aromatic aldehydes to form β-lactones [17] with the ketene acting as the nucleophile and the aldehyde as the electrophile [18]. The less reactive **1a** reacts with benzaldehyde only in the presence of catalysts and long reaction times to give traces of the corresponding β-lactone detected by $\nu(C{=}O)$ at 1845 cm^{-1} and two $\delta(CF_3S)$ signals at −35.7 and −36.4 ppm showing that the CF_3S-substituents are not magnetically equivalent.

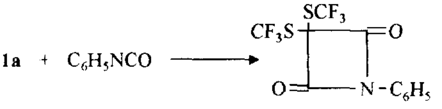
A spontaneous reaction with liberation of CO_2 takes place between **1a** and dimethylformamide yielding $(CF_3S)_2C{=}C(H)N(CH_3)_2$ **14a**.



$$\mathbf{1a} + (CH_3)_2NCHO \xrightarrow{-CO_2} (CF_3S)_2C{=}C\begin{matrix} H \\ N(CH_3)_2 \end{matrix} \qquad (14)$$

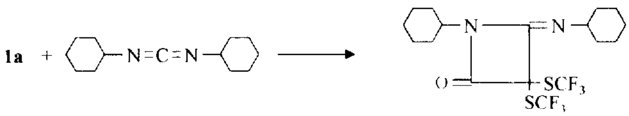
14a

The behaviour of **1a** towards phenyl isocyanate is also rather inert. The [2+2]cycloadduct (**15a**) is formed in only 10% yield after a reaction time and temperature of 14 days and 160°C (Eq. (15)).



15a (15)

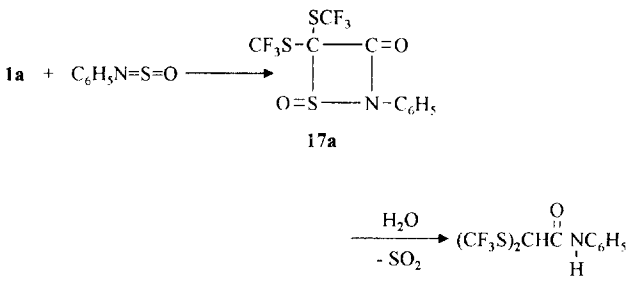
No reaction takes place between **1a** and the less reactive phenyl isothiocyanate. In accordance with the reactivity of ketenes with carbodiimides, **1a** reacts with dicyclohexylcarbodiimide to give the imino-β-lactam (**16a**) (Eq. (16)).



16a

(16)

It could also be shown that **1a** adds to *N*-phenylsulfinylamine to yield the corresponding 1,2-thioazetane-3-one-1-oxide (**17a**) which is sensitive to hydrolysis and is converted in moist air to the acidamide (**17**) (Eq. (17)).

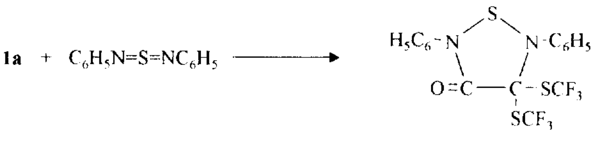


17a

17

(17)

With diphenylsulfur diimide, **1a** forms a red, oily 1:1 adduct at −30°C. Spectroscopic investigations show that the compound has a five-membered ring structure (**18a**) which resulted from a 1,3-cycloaddition (Eq. (18)).



18

(18)

This result is comparable to the reaction between diphenylketene and diphenylsulfur diimide which forms also the corresponding 1,3-cycloadduct [19].

5. Experimental

Air- and moisture-sensitive compounds were handled in a vacuum line with Young valves or in a glove box (M. Braun, München) under argon.

Solvents were distilled before use and dried according to published procedures [20,21]. Microanalyses: Carlo-Erba Elementanalyser model 1106. IR: Bruker FT-IR IFS 85 (4000–400 cm^{-1}), solids as KBr pellets, liquids as capillary films. NMR: $CDCl_3$ solutions unless noted otherwise, Bruker WP 80 PFT, WM 250 PFT and AM 400 PFT, standards used: $Si(CH_3)_4$ (^1H, ^{13}C), $CFCl_3$ (^{19}F) and $(CH_3)_2Se$ (^{77}Se). MS: Varian MAT CH7 (70 eV, emission 10 μA). $(CF_3S)_2C{=}C{=}O$ [1], $(CF_3Se)_2C{=}C{=}O$ [1], $(C_6F_5S)_2C{=}C{=}O$ [2], CF_3SH [22], C_6F_5SH [23], $(CH_3)_3SiH$ [24], PhNSO [25], Ph–NSN–Ph [26] were prepared by published methods. All other substances were commercially available and were used without further treatment.

General procedures for the reactions of the ketenes **1a–c** with various reactants.

(A) Into a 30-ml Carius tube equipped with a Young valve and a Teflon stopcock is placed, a certain amount of the reactant dissolved in a suitable solvent. The Carius tube is evacuated, and the corresponding ketene **1a,c** is condensed in. The mixture is stirred for several hours and the volatile compounds are condensed at 10^{-3} Torr into a trap cooled with liquid nitrogen. The residue is purified by either distillation under reduced pressure or sublimation.

(B) In a 30-ml Carius tube, freshly prepared **1b** is allowed to react with an excess of the reactant in an Ar atmosphere. After stirring for several hours the reaction is stopped, and the excess educt is removed in vacuo. The product is purified by distillation or sublimation.

(C) In a 30-ml Carius tube stoichiometric amounts of **1a** and the reactant are condensed. The mixture is stirred until an IR spectra of the vapor phase indicates that the reactants are consumed. The residue is purified from any by-products by fractional distillation.

Educts, amounts in g (mmol), reaction parameters, yields in g (%), boiling points (melting points), formula (mol.wt.) and elemental analysis for all compounds synthesized by methods A, B or C are given in Table 1. In Table 2, spectroscopical data such as IR-, ^1H-, ^{19}F-, ^{13}C-, ^{77}Se-NMR and mass spectra for the newly prepared substances are provided. ^{13}C-NMR spectroscopical data for permanently appearing moietes such as C_6H_5-bound to carbon or nitrogen, C_6F_5-, CF_3S-, CF_3Se and ^{19}F-NMR values for C_6F_5 including coupling constants are described in the discussion.

2,2-Bis(trifluoromethylsulfenyl)-3-vinylcyclobutane (13) and **6-Bis(trifluoromethylsulfenyl)methyliden-5,6-dihydro-2H-pyran (13a)**: In a 10-ml Carius tube are condensed 0.35 g (6.5 mmol) 1,3-butadiene and 1.8 g (7.4 mmol) of **1a**. After stirring at 70°C for 24 h the colourless mixture changes to yellow. An IR-spectrum of the vapor phase indicates that 1,3 butadiene has been completely consumed. The volatile components are removed in vacuo leaving nearly equal amounts of **13** and **13a**.

The separation of the two isomers is achieved by fractional distillation. The low-boiling fraction at 25°C/10^{-3} Torr contains **13** whereas **13a** distills at 47°C/10^{-3} Torr. Yields: **13** 0.42 g (22%); **13a** 0.53 g (28%).

13: b.p. 25°C/10^{-3} Torr. IR (film): $\bar{\nu}=2879$ (w), 1805 (s), 1547 (w), 1398 (w), 1304 (w), 1099 (vs), 988 (m), 936 (m), 890 (w), 758 (s), 668 (w) cm^{-1}. ^1H-NMR: $\delta=3.36$–3.80 (3 H, m, CH_2CH), 5.25–5.50 (2 H, m, $CH_2{=}C$), 5.77–6.04 (1 H, m, =CH–). ^{19}F-NMR: $\delta=-36.5$ (6 F, s, CF_3S). ^{13}C-NMR: $\delta=43.9$ [d, ^1J (CH) 144 Hz, CH], 48.0 [t, ^1J (CH) 137 Hz, CH_2CO], 68.3 [s,

Table 1
Educts, conditions, yields, boiling points, formulas and analysis

Educt [amounts (mmol)]	Condition (time, temperature)	Yield (g, %)	Boiling point °C/Torr (m.p. °C)	Formula (mol. weight)	Analysis							
					Found (%)				Calculated (%)			
					C	H	N	S	C	H	N	S
Method A												
1a (0.6 g, 2.5) CH_3OH (0.2 g, 6.3)	2 h, 20°C	3a, 0.6 (88)	$55/10^{-2}$	$C_5H_4F_6O_2S_2$ (274.2)	21.5	1.5		23.8	21.9	1.5		23.4
1c (0.4 g, 1.2) CH_3OH (0.2 g, 6.3)	2 h, 20°C	3c, 0.3 (68)	$65/10^{-2}$	$C_5H_4F_6O_2Se_2$ (368.0)	16.5	1.3			16.3	1.1		
1a (2.5 g, 10.3) $C_3H_8O_3$ (0.3 g, 3.3)	40 h, 100°C	3d, 2.2 (82)	$140/10^{-3}$	$C_{15}H_8F_{18}O_6S_6$ (818.6)	21.5	0.8		22.9	22.0	1.0		23.5
1a (0.6 g, 2.5) C_2H_5SH (0.2 g, 3.2)	2 h, 20°C	4a, 0.58 (77)	$26/10^{-3}$	$C_6H_6F_6OS_3$ (304.3)	24.1	2.0		31.9	23.7	2.0		31.6
1c (0.4 g, 1.2) C_2H_5SH (0.2 g, 3.2)	2 h, 20°C	4c, 0.38 (80)	$35/10^{-2}$	$C_6H_6F_6OSSe_2$ (398.1)	18.0	1.1		8.3	18.1	1.5		8.1
1a (1.1 g, 4.5) C_6F_5SH (0.75 g, 3.8)	3 h, 20°C	4e, 1.4 (84)	$67/10^{-2}$	$C_{10}HF_{11}OS_2$ (442.3)	27.3	0.1		22.0	27.2	0.2		21.8
1a (1.0 g, 4.1) $NH(C_2H_5)_2$ (0.5 g, 6.8)	1 h, 20°C	5a, 0.58 (77)	(35)	$C_8H_{11}F_6NOS_2$ (315.2)	30.5	3.5	4.6	19.7	30.5	3.5	4.4	20.3
1c (0.9 g, 2.7) $NH(C_2H_5)_2$ (0.5 g, 6.8)	1 h, 20°C	5c, 0.73 (67)	$58/10^{-2}$	$C_8H_{11}F_6NOSe_2$ (409.0)	23.5	2.8	3.4	–	23.5	2.7	3.4	–
1a (0.75 g, 3.1) SO_2Cl_2 (0.4 g, 3.0)	7 days, 80°C	6, 0.63 (68)	$29/10^{-2}$	$C_4Cl_2F_6OS_2$ (313.1)	16.0	–	–	21.0	15.3			20.5
1a (0.7 g, 2.9) $(CH_3)_2CHCH_2CH_2O–NO$ (0.26 g, 2.2)	12 h, −50°C → 20°C	6a, 0.71 (89)	$105/10^{-3}$ (dec.)	$C_9H_{11}F_6NO_3S_2$ (359.2)	31.5	3.0	4.0	–	30.1	3.1	3.9	–
1a (1.5 g, 6.2) SCl_2 (0.22 g, 2.1) 5 ml CH_2Cl_2	10 days, 50°C	7, 0.07 (9)	$60/10^{-3}$ (dec.)									
1a (0.8 g, 3.3) $(C_4H_9)_3SnH$ (0.9 g, 3.1) 4 ml C_6H_6	2 days, 20°C	8, 1.35 (82)	$155/10^{-3}$	$C_{16}H_{28}F_6OS_2Sn$ (533.0)	36.3	5.6	–	12.0	36.1	5.3	–	12.0
1a (1.1 g, 4.5) $P(OCH_3)_3$ (0.5 g, 4.0)	12 h, −60°C → 20°C	9a, 1.1 (75)	$77/5\times10^{-2}$	$C_7H_9F_6O_4PS_2$ (366.2)	22.6	2.2	–	17.6	23.0	2.5	–	17.5
1a (0.96 g, 4.0) Ph–$CH=CH_2$ (0.4 g, 3.8)	18 h, 80°C	10a, 1.15 (86)	$110/10^{-3}$	$C_{12}H_8F_6OS_2$ (346.3)	41.1	2.1	–	18.2	41.6	2.3	–	18.5
1c (1.4 g, 4.1) Ph–$CH=CH_2$ (0.4 g, 3.8)	24 h, 80°C	10c, 1.2 (71)	(84)	$C_{12}H_8F_6OSe_2$ (440.0)	32.8	1.8	–	–	32.6	2.1	–	–
1a (0.7 g, 2.9)  (0.7 g, 8.3)	3 days, 80°C	12a, 0.55 (58)	$31/10^{-3}$									
1a (1.9 g, 7.9) $(CH_3)_2NCHO$ (0.55g, 7.5)	24 h, 20°C	14a, 1.85 (78)	$45/10^{-3}$	$C_6H_7F_6NS_2$ (271.2)	26.4	2.6	5.2	23.8	26.6	2.6	5.2	23.7
1a (1.0 g, 4.1) PhNCO (0.4 g, 3.4)	14 days, 160°C	15a, 0.12 (10)	$63/10^{-3}$	$C_{11}H_5F_6NO_2S_2$ (361.3)	36.0	1.2	3.6		36.6	1.4	3.9	

Table 1 (*continued*)

Educt [amounts (mmol)]	Condition (time, temperature)	Yield (g, %)	Boiling point °C/Torr (m.p. °C)	Formula (mol. weight)	Analysis							
					Found (%)				Calculated (%)			
					C	H	N	S	C	H	N	S
1a (0.5 g, 2.1) C_6H_{11}–NCN–C_6H_{11} (0.4 g, 1.9) 5 ml hexane	3 days, 60°C	16a, 0.65 (75)	(62)	$C_{17}H_{22}F_6N_2OS_2$ (448.3)	44.7	4.8	5.9	14.3	45.5	4.9	6.2	14.3
1a (1.3 g, 5.4) PhNSO (0.6 g, 4.3)	5 days, 20°C	17a, 1.2 (73)	(42)	$C_{10}H_5F_6NO_2S_3$ (381.3)	31.9	1.1	3.6	25.1	31.5	1.3	3.7	25.2
1a (1.5 g, 3.9) H_2O 5 ml	2 days, 20°C	17, 1.2 (91)	(73)	$C_{10}H_7F_6NOS_2$ (335.2)	36.1	1.9	4.0	18.8	35.8	2.1	4.2	19.1
1a (0.4 g, 1.7) Ph–NSN–Ph (0.35 g, 1.6)	2 h, −30°C	18, 0.7 (94)	> 150/10^{-3} (dec.)									
Method B												
1b (0.6 g, 1.4) CH_3OH (0.1 g, 3.1)	2 h, 20°C	3b, 0.45 (70)	165/10^{-3}	$C_{15}H_4F_{10}O_2S_2$ (470.3)	38.0	0.9	–	13.1	38.3	0.9	–	13.6
1b (0.6 g, 1.4) C_2H_5SH (0.2 g, 3.2)	2 h, 20°C	4b, 0.45 (66)	(55)	$C_{16}H_6F_{10}OS_3$ (500.4)	38.0	0.9	–	18.6	38.4	1.2	–	19.2
1b (0.6 g, 1.4) $NH(C_2H_5)_2$ (0.3 g, 4.1)	1 h, 20°C	5b, 0.5 (71)	(126)	$C_{18}H_{11}F_{10}NOS_2$ (511.3)	42.3	2.1	3.1	13.4	42.3	2.2	2.7	12.5
1b (0.8 g, 1.8) Ph–CH=CH_2 (0.2 g, 1.9)	12 h, 60°C	10b, 0.65 (66)	(135)	$C_{22}H_8F_{10}OS_2$ (542.4)	48.8	1.7	–	11.8	48.7	1.5	–	11.8
Method C												
1a (1.1 g, 4.5) CF_3SH (0.55 g, 5.4)	18 h, −50°C → 20°C	4d, 1.4 (90)	27/10^{-2}	$C_5HF_9OS_3$ (344.3)	16.6	0.4	–	28.7	17.4	0.3	–	27.9
1a (1.0 g, 4.1) $(CH_3)_3SiH$ (0.3 g, 4.0)	12 h, −30°C → 20°C	8a, 0.95 (74)	28/10^{-2}	$C_7H_{10}F_6OS_2Si$ (316.3)	26.4	3.3	–	19.7	26.6	3.3	–	20.3
1a (1.8 g, 7.4)  **(0.54 g, 9.6)**	24 h, 70°C	11a, 1.6 (72)	30/10^{-3}	$C_8H_8F_6OS_2$ (298.2)	31.9	2.4	–	21.6	32.2	2.7	–	21.5

Table 2
Spectroscopical data

	IR-frequency (cm^{-1}	^{13}C-NMR (ppm) (^{77}Se-NMR)	^{19}F-NMR (ppm) (^{1}H-NMR)	Mass-spectra: *m*/*z* (%)
3a	2963 (m), 1755 (vs), 1439 (s), 1302 (vs), 1096 (vs), 996 (m), 900 (m), 759 (s), 722 (w), 543 (w), 474 (w)	46.4 [d, ^{1}J (CH) 162 Hz, CH(SCF$_3$)$_2$], 54.3 [q, ^{1}J (CH) 149 Hz, CH$_3$], 166.3 [s, CO]	-41.6 (6 F, s, CF$_3$S) [5.09 (1 H, s, CH)]	274 (12, M$^+$), 215 (4), 173 (22), 145 (25), 115 (6), 69 (61), 63 (12), 59 (76), 45 (74), 32 (20), 28 (100)
3b	2962 (w), 1744 (s), 1640 (m), 1516 (vs), 1489 (vs), 1439 (w), 1403 (w), 1291 (m), 1147 (m), 1094 (s), 1017 (w), 983 (vs), 863 (s), 808 (w), 634 (w), 515 (w)	53.9 [q, ^{1}J (CH) 149 Hz, CH$_3$], 54.8 [d, ^{1}J (CH) 160 Hz, CH(SC$_6$F$_5$)$_2$], 167.2 [d, ^{2}J (CH) 4 Hz, CO]	[4.89 (1 H, s, CH)]	470 (36, M$^+$), 411 (22), 398 (13), 271 (100), 243 (84), 211 (38), 199 (88), 168 (16), 155 (46), 117 (6), 69 (10), 59 (20), 45 (71), 29 (10)
3c	3005 (w), 2961 (w), 1738 (s), 1439 (m), 1296 (s), 1141 (vs), 1101 (vs), 1070 (vs), 1017 (w), 997 (w), 896 (w), 741 (s)	30.5 [d, ^{1}J (CH) 164 Hz, CH (SeCF$_3$)$_2$], 54.2 [q, ^{1}J (CH) 149 Hz, CH$_3$], 168.6 [s, CO] [580 (m)]	-35.3 (6 F, s, CF$_3$Se) [5.24 (1 H, s, CH]	370 (23, M$^+$), 311 (15), 242 (7), 221 (81), 193 (71), 149 (6), 124 (34), 93 (78), 80 (11), 69 (100), 59 (34), 29 (35)
3d	2988 (w), 1759 (s), 1594 (w), 1454 (w), 1284 (m), 1095 (vs), 817 (w), 759 (m), 543 (w), 475 (w)	46.0 [d, ^{1}J (CH) 160 Hz, CH(SCF$_3$)$_2$], 63.9 [t, ^{1}J (CH) 151 Hz, CH$_2$], 71.2 [d, ^{1}J (CH) 151 Hz, CH], 165.2 [d, ^{2}J (CH) 11 Hz, CO]	-41.5 (18 F, s, CF$_3$S) [4.38 - 4.51 (5 H, m), 5.11 (3 H, s, CH)]	717 (57, M$^+$-CF$_3$S), 616 (46), 559 (100), 458 (18), 389 (12), 317 (23), 242 (8), 215 (95), 142 (54), 115 (21), 101 (4), 57 (50), 45 (58), 29 (12)
4a	2979 (w), 2973 (w), 2937 (w), 1686 (s), 1453 (w), 1380 (w), 1301 (w), 1268 (w), 1183 (vs), 1119 (vs), 1040 (w), 983 (m), 966 (m), 758 (s), 473 (w)	14.0 [q, ^{1}J (CH) 128 Hz, CH$_3$], 25.1 [t, ^{1}J (CH) 143 Hz, CH$_2$], 53.5 [d, ^{1}J (CH) 158 Hz, CH(SCF$_3$)$_2$], 191.5 [d, ^{2}J (CH) 4 Hz, CO]	-41.2 (6 F, s, CF$_3$S) [1.29 (3 H, t, CH$_3$), 3.0 (2 H, q, CH$_2$), 5.18 (1 H, s, CH)]	304 (3, M$^+$), 215 (34), 183 (10), 89 (100), 69 (27), 59 (8), 45 (50), 29 (88)
4b	2958 (w), 1661 (s), 1639 (m), 1514 (vs), 1488 (vs), 1294 (w), 1267 (w), 1220 (w), 1164 (w), 1088 (s), 981 (vs), 863 (s), 838 (w), 755 (w), 733 (w), 704 (w)	14.1 [q, ^{1}J (CH) 126 Hz, CH$_3$], 24.8 [t, ^{1}J (CH) 137 Hz, CH$_2$], 61.3 [d, ^{1}J (CH) 160 Hz, CH(SC$_6$F$_5$)$_2$], 192.2 [d, ^{2}J (CH) 4 Hz, CO]	[1.24 (3 H, t, CH$_3$), 2.92 (2 H, q, CH$_2$), 4.96 (1 H, s, CH)]	500 (12, M$^+$), 411 (100), 273 (78), 211 (31), 199 (24), 168 (8), 155 (13), 117 (8), 89 (16), 63 (6), 45 (58)
4c	2975 (w), 2935 (w), 1684 (s), 1457 (w), 1400 (w), 1267 (w), 1131 (vs), 1100 (vs), 1074 (s), 1000 (m), 740 (m), 676 (w), 638 (w)	14.1 [q, ^{1}J (CH) 128 Hz, CH$_3$], 25.2 [t, ^{1}J (CH) 143 Hz, CH$_2$], 39.5 [d, ^{1}J (CH) 162 Hz, CH(SeCF$_3$)$_2$], 193.4 [s, CO] [597 (m)]	-35.0 (6 F, s, CF$_3$Se) [1.26 (3 H, t, CH$_3$), 2.94 (2 H, q, CH$_2$), 3.89 (1 H, s, CH)]	311 (2, M$^+$-C$_2$H$_5$SCO), 252 (43), 210 (16), 191 (22), 163 (72), 141 (10), 89 (63), 69 (72), 61 (37), 45 (61), 29 (100)
4d	2925 (w), 1739 (s), 1160 (vs), 1096 (vs), 1030 (s), 967 (m), 760 (s), 728 (w), 704 (w)	53.8 [d, ^{1}J (CH) 156 Hz, CH(SCF$_3$)$_2$], 184.0 [d, ^{2}J (CH) 6 Hz, CO]	-40.5 (3 F, s, CF$_3$S), -40.8 (3 F, s, CF$_3$S) [5.19 (1 H, s, CH)]	215 (1, M$^+$-CF$_3$SCO), 145 (1), 69 (10), 45 (11), 32 (35), 28 (100)
4e	2924 (w), 1723 (s), 1641 (m), 1516 (vs), 1498 (vs), 1413 (w), 1379 (w), 1299 (w), 1149 (vs), 1120 (vs), 1095 (vs), 1037 (m), 985 (vs), 867 (s), 759 (s)	53.0 [d, ^{1}J (CH) 156 Hz, CH(SCF$_3$)$_2$], 186.3 [s, CO]	-40.7 (6 F, s, CF$_3$S), [5.33 (1 H, s, CH)]	442 (1, M$^+$), 398 (1), 313 (10), 215 (75), 199 (36), 155 (20), 143 (11), 117 (6), 69 (63), 63 (8), 45 (87), 28 (100)
5a	2983 (m), 2942 (m), 2880 (w), 1654 (vs), 1487 (m), 1463 (s), 1437 (s), 1386 (m), 1363 (m), 1311 (m), 1282 (m), 1217 (s), 1097 (vs), 800 (m), 757 (s), 668 (w), 463 (m)	12.2 [q, ^{1}J (CH) 128 Hz, CH$_3$], 14.3 [q, ^{1}J (CH) 126 Hz, CH$_3$], 41.6 [t, ^{1}J (CH) 135 Hz, CH$_2$], 43.1 [t, ^{1}J (CH) 137 Hz, CH$_2$], 46.9 [d, ^{1}J (CH) 155 Hz, CH(SCF$_3$)$_2$], 164.2 [s, CO]	-41.2 (6 F, s, CF$_3$S) [1.15 (6 H, m, CH$_3$), 3.36 (4 H, m, CH$_2$), 5.41 (1 H, m, CH)]	316 (31, M$^+$+1), 300 (4), 215 (32), 195 (12), 130 (9), 100 (100), 72 (92), 58 (47), 44 (59), 29 (61)
5b	2994 (w), 1630 (vs), 1514 (vs), 1489 (s), 1463 (m), 1451 (m), 1387 (w), 1306 (w), 1292 (w), 1130 (w), 1095 (s), 984 (s), 861 (s)	12.2 [q, ^{1}J (CH) 124 Hz, CH$_3$], 14.1 [q, ^{1}J (CH) 128 Hz, CH$_3$], 41.3 [t, ^{1}J (CH) 134 Hz, CH$_2$], 42.6 [t, ^{1}J (CH) 135 Hz, CH$_2$], 55.8 [d, ^{1}J (CH) 155 Hz, CH(SC$_6$F$_5$)], 164.2 [d, ^{2}J (CH) 4 Hz, CO]	[1.09 (3 H, t, CH$_3$), 1.29 (3 H, t, CH$_3$), 3.34 (2 H, q, CH$_2$), 3.45 (2 H, q, CH$_2$), 5.39 (1 H, s, CH)]	512 (17, M$^+$+1), 411 (10), 312 (63), 284 (100), 256 (8), 211 (32), 199 (37), 168 (5), 155 (20), 117 (8), 100 (73), 72 (82), 44 (34)

(*continued*)

Table 2 (*continued*)

	IR-frequency (cm^{-1}	^{13}C-NMR (ppm) (^{77}Se-NMR)	^{19}F-NMR (ppm) (^{1}H-NMR)	Mass-spectra: *m/z* (%)
5c	2979 (m), 2940 (w), 1635 (s), 1537 (w), 1484 (w), 1463 (m), 1438 (m), 1384 (w), 1363 (w), 1311 (w), 1283 (w), 1219 (w), 1103 (vs), 1070 (s), 738 (m), 613 (w)	12.2 [q, ^1J (CH) 128 Hz, CH_3], 14.3 [q, ^1J (CH) 126 Hz, CH_3], 33.9 [d, ^1J (CH) 158 Hz, $CH(SCF_3)_2$], 41.6 [t, ^1J (CH) 139 Hz, CH_2], 43.4 [t, ^1J (CH) 137 Hz, CH_2], 166.6 [s, CO] [600 (m)]	-34.9 (6 F, s, CF_3Se) [1.17 (6 H, m, CH_3), 3.52 (4 H, m, CH_2), 4.03 (1 H, s, CH)]	411 (3, M^+), 311 (1), 262 (3), 234 (5), 163 (6), 114 (18), 100 (100), 72 (84), 58 (42), 44 (36), 29 (58)
6	1795 (m), 1773 (s), 1169 (vs), 1011 (vs), 981 (s), 783 (m), 760 (s), 712 (s), 611 (w), 468 (w)	80.6 [s, $(CF_3S)_2C$], 166.7 [s, CO]	-38.7 (6 F, s, CF_3S)	249 (80, M^+-COCl), 242 (4), 214 (8), 176 (4), 145 (36), 79 (54), 76 (13), 72 (8), 69 (100), 63 (7)
6a	2964 (m), 2876 (w), 1751 (s), 1591 (m), 1466 (w), 1389 (w), 1371 (w), 1223 (s), 1165 (vs), 1087 (vs), 943 (w), 758 (m), 464 (w)	22.2 [q, ^1J (CH) 126 Hz, CH_3], 24.8 [d, ^1J (CH) 126 Hz, CH], 36.3 [t, ^1J (CH) 124 Hz, CH_2], 68.5 [t, ^1J (CH) 151 Hz, CH_2], 73.4 [s, $(CF_3S)_2C$], 163.3 [s, CO]	-37.4 (6 F, s, CF_3S) [0.93 (6 H, d, CH_3), 1.56-1.68 (3 H, m), 4.29 (2 H, t, OCH_2)]	329 (92, M^+-NO), 314 (4), 259 (6), 242 (11), 215 (25), 157 (4), 145 (43), 71 (92), 69 (94), 55 (51), 43 (100), 41 (57), 29 (35)
7	1792 (m), 1761 (s), 1167 (vs), 1093 (vs), 1000 (s), 760 (s), 731 (m), 702 (m), 544 (w), 466 (w)	78.9 [s, $(CF_3S)_2C$], 166.7 [s, CO]	-37.1 (6 F, s, CF_3S)	277 (20, M^+-SCl), 249 (21), 242 (7), 145 (60), 76 (22), 69 (100), 63 (25), 44 (10), 28 (58)
8	2961 (m), 2927 (m), 2875 (w), 2857 (w), 1552 (vs), 1466 (m), 1379 (w), 1320 (m), 1269 (m), 1106 (vs), 950 (w), 877 (w), 752 (w), 677 (w), 575 (w), 539 (w), 510 (w)	13.5 [q, ^1J (CH) 124 Hz, CH_3], 17.3 [t, ^1J (CH) 130 Hz, CH_2], 27.0 [t, ^1J (CH) 120 Hz, CH_2], 27.4 [t, ^1J (CH) 118 Hz, CH_2], 81.9 [d, ^2J (CH) 20 Hz, $(CF_3S)_2C$], 175.4 [d, ^1J (CH) 174 Hz, CH-OR]	-44.2 (3 F, s, CF_3S), -47.8 (3 F, s, CF_3S) [0.86-1.63 (27 H, m, C_4H_9), 7.74 (1 H, s, CH)]	534 (2, M^+), 477 (10), 291 (71), 253 (31), 234 (58), 205 (98), 177 (79), 139 (20), 121 (43), 69 (31), 57 (58), 41 (82), 29 (100)
8a	2965 (m), 2817 (w), 1581 (vs), 1272 (s), 1261 (vs), 1104 (vs), 963 (s), 847 (vs), 755 (s), 743 (m), 639 (m), 611 (w), 583 (w), 515 (w)	-0.6 [q, ^1J (CH) 120 Hz, CH_3], 91.0 [s, $(CF_3S)_2C$], 165.3 [d, ^1J (CH) 183 Hz, CH]	-43.1 (3 F, s, CF_3S), -46.3 (3 F, s, CF_3S) [0.32 (9 H, s, CH_3), 7.51 (1 H, s, CH)]	316 (30, M^+), 247 (8), 224 (12), 205 (17), 155 (11), 123 (4), 89 (13), 77 (35), 73 (100), 69 (33), 59 (8), 45 (53)
9a	2961 (w), 2857 (w), 1751 (w), 1526 (w), 1460 (w), 1276 (m), 1142 (s), 1103 (vs), 1032 (s), 841 (w), 800 (w), 756 (m), 574 (w), 491 (w)	53.7 [qd, ^1J (CH) 149 Hz, ^2J (CP) 6 Hz, COP(O)], 61.7 [q, ^1J (CH) 149 Hz, CH_3], 112.3 [d, ^2J (CP) 38 Hz, $(CF_3S)_2C$], 167.1 [d, ^1J (CP) 208 Hz, CP(O)]	-40.1 (3 F, s ,CF_3S), -41.9 (3 F, s, CF_3S) [3.75 (3 H, s, CH_3), 3.92 (6 H, d, OCH_3)]	366 (51, M^+), 347 (10), 297 (60), 269 (43), 242 (7), 215 (40), 145 (48), 109 (98), 93 (100), 78 (49), 69 (98), 59 (44), 47 (10), 29 (31)
10a	3035 (m), 1810 (s), 1604 (w), 1524 (w), 1497 (m), 1452 (m), 1399 (m), 1096 (vs), 1053 (vs), 984 (m), 757 (s), 728 (m), 696 (s), 585 (w), 475 (w)	43.5 [d, ^1J (CH) 141 Hz, CH], 45.9 [t, ^1J (CH) 137 Hz, CH_2CO], 71.6 [s, $(CF_3S)_2C$], 190.4 [s, CO]	-36.2 (3 F, s, CF_3S), -36.6 (3 F, s, CF_3S) [3.48-4.24 (3 H, m, $CHCH_2$), 7.39 (5 H, m, C_6H_5)]	346 (10, M^+), 304 (10), 277 (66), 235 (21), 215 (31), 191 (10), 147 (28), 131 (100), 115 (40), 104 (73), 77 (50), 69 (65), 51 (26), 45 (32)
10b	1794 (s), 1639 (m), 1609 (w), 1515 (vs), 1486 (vs), 1451 (m), 1401 (m), 1297 (w), 1095 (vs), 1077 (m), 1024 (w), 980 (vs), 860 (s), 765 (m), 726 (w), 696 (m)	43.3 [d, ^1J (CH) 141 Hz, CH], 45.5 [t, ^1J (CH) 137 Hz, CH_2CO], 193.7 [d, ^2J (CH) 6 Hz, CO] [550 (m), 602 (m)]	[3.16-4.23 (3 H, m, $CHCH_2$), 7.48 (5 H, m, C_6H_5)]	500 (83, M^+-C_2H_2O), 438 (8), 411 (8), 301 (71), 281 (9), 243 (20), 211 (72), 199 (29), 181 (17), 168 (11), 155 (22), 131 (20), 115 (68), 104 (100), 91 (31), 77 (31), 69 (11), 51 (20), 45 (40), 39 (11)
10 c	3072 (w), 3031 (w), 2950 (w), 1799 (vs), 1601 (w), 1580 (w), 1498 (m), 1449 (m), 1397 (m), 1158 (vs), 1131 (vs), 1098 (vs), 1069 (vs), 1051 (vs), 965 (m), 930 (m), 763 (s), 739 (s), 703 (s), 488 (m)	42.8 [d, ^1J (CH) 145 Hz, CH], 45.3 [t, ^1J (CH) 140 Hz, CH_2CO], 61.9 [s, $CF_3Se)_2C$], 192.4 [s, CO]	-30.0 (3 F, s, CF_3Se), -31.5 (3 F, s, CF_3Se) [3.45-4.31 (3 H, m, $CHCH_2$), 7.39 (5 H, m, C_6H_5)]	442 (1, M^+), 400 (8), 373 (44), 331 (5), 240 (8), 195 (12), 182 (81), 131 (28), 115 (96), 104 (100), 91 (36), 77 (40), 69 (78), 63 (36), 51 (40), 39 (23), 28 (30)

(*continued*)

Table 2 (*continued*)

	IR-frequency (cm^{-1}	^{13}C-NMR (ppm) (^{77}Se-NMR)	^{19}F-NMR (ppm) (^1H-NMR)	Mass-spectra: *m/z* (%)
11a	2983 (m), 2944 (m), 2879 (w), 1790 (s), 1465 (m), 1451 (w), 1389 (m), 1326 (w), 1142 (vs), 1109 (vs), 1073 (s), 1004 (m), 871 (m), 795 (m), 758 (s), 730 (w), 466 (w)	8.8 [qd, ^1J (CH) 130 Hz, ^2J (CH) 6 Hz, CH_3], 12.0 [qd, ^1J (CH) 130 Hz, ^2J (CH) 6 Hz, CH_3], 38.1 [d, ^1J (CH) 148 Hz, CH], 54.8 [d, ^1J (CH) 141 Hz, CHCO], 72.1 [s, $(CF_3S)_2C$], 195.5 [d, ^2J (CH) 8 Hz, CO]	-36.0 (3 F, s, CF_3S), -38.4 (3 F, s, CF_3S) [1.17 (6 H, d, CH_3), 2.8 (1 H, dq, CH), 4.27 (1 H, dq, CH)]	298 (2, M^+), 242 (12), 229 (95), 215 (20), 173 (30), 169 (31), 145 (30), 129 (20), 85 (10), 69 (43), 56 (100), 41 (20), 28 (48)
	1254 (m), 1143 (s), 1100 (s), 1043 (m), 1001 (m), 907 (m), 893 (m), 881 (m), 757 (m), 690 (w), 668 (w), 466 (w)	160.8 [s, CO]	3.51-3.60 (2 H, m)]	(43), 242 (16), 227 (4), 215 (45), 183 (6), 163 (9), 145 (26), 123 (13), 97 (8), 83 (97), 69 (38), 55 (100), 41 (90), 29 (38)
17a	3075 (w), 1771 (s), 1594 (m), 1498 (m), 1458 (m), 1324 (s), 1169 (vs), 1099 (vs), 1004 (m), 994 (m), 947 (m), 901 (w), 757 (s), 686 (m), 658 (m), 599 (m), 571 (m)	87.0 [s, $(CF_3S)_2C$], 155.4 [s, CO]	-34.5 (3 F s, CF_3S), -35.6 (3 F, s, CF_3S) [7.46 (5 H, m, C_6H_5)]	381 (28, M^+), 365 (8), 280 (11), 242 (26), 232 (5), 145 (82), 139 (100), 119 (51), 101 (5), 91 (47), 77 (27), 69 (88), 64 (44), 51 (24), 45 (18), 39 (22), 27 (6)
17	3287 (s), 3144 (w), 3059 (w), 2958 (w), 1667 (vs), 1602 (s), 1538 (s), 1500 (m), 1466 (m), 1335 (m), 1094 (vs), 819 (w), 758 (s), 716 (m), 690 (s), 655 (w), 465 (w)	49.4 [d, ^1J (CH) 156 Hz, $CH(SCF_3)_2$], 163.2 [s, CO]	-41.0 (6 F, s, CF_3S) [5.38 (1 H, s, CH), 7.30 (5 H, m, C_6H_5), 8.77 (1 H, s, NH)]	335 (60, M^+), 334 (7), 215 (11), 120 (100), 104 (13), 92 (60), 77 (63), 65 (38), 51 (14), 45 (33), 39 (19)
18	3064 (w), 1697 (s), 1629 (m), 1591 (m), 1485 (s), 1448 (s), 1297 (m), 1222 (m), 1153 (vs), 1101 (vs), 1027 (w), 994 (w), 940 (w), 758 (s), 691 (s), 531 (w)	53.3 [s, $(CFS)_2C$], 148.2 [s, CO]	-44.3 (6 F, s, CF_3S) [7.25-7.43 (10 H, m, C_6H_5)]	456 (7, M^+), 355 (38), 236 (19), 214 (40), 204 (100), 166 (10), 135 (90), 119 (51), 91 (31), 77 (72), 69 (32), 51 (24), 28 (11)

$(CF_3S)_2C$]. 122.2 [td, ^1J (CH) 156 Hz, ^2J (CH) 4 Hz, CH_2=CH], 130.9 [d, ^1J (CH) 156 Hz, CH=CH_2], 190.0 [s, CO]. MS, *m/z* (%): 296 (21, M^+), 242 (12), 227 (94), 215 (13), 199 (8), 185 (100), 167 (37), 145 (57), 125 (10), 97 (38), 84 (42), 79 (19), 69 (79), 58 (19), 54 (44), 45 (24), 39 (8), 27 (25). $C_8H_6F_6OS_2$ (296.2): calcd. C 32.4, H 2.0, S 21.7; found C 31.8, H 1.8, S 20.8.

13a: b.p. 47°C/10^{-3} Torr. IR (film): $\bar{\nu}$ = 3065 (w), 2936 (w), 2888 (w), 1548 (s), 1464 (m), 1401 (m), 1380 (w), 1309 (m), 1257 (s), 1105 (vs), 988 (m), 956 (m), 892 (m), 822 (m), 753 (s), 670 (m), 626 (w), 541 (w), 479 (w) cm^{-1}. ^1H-NMR: δ = 3.51 (2 H, m, CH_2), 4.77 (2 H, m, CH_2–O), 6.03 (2 H, m, CH=CH). ^{19}F-NMR: $\delta = -44.2$ (3 F, s, CF_3S), -45.5 (3F, s, CF_3S). ^{13}C-NMR: δ = 28.3 [tt, ^1J (CH) 134 Hz, ^2J (CH) 6 Hz, CH_2–CH], 68.3 [tt, ^1J (CH) 151 Hz, ^2J (CH) 6 Hz, CH_2–O], 81.0 [s, $(CF_3S)_2C$], 122.6 [dt, ^1J (CH) 176 Hz, ^2J (CH) 6 Hz, CH=], 124.2 [dt, ^1J (CH) 174 Hz, ^2J (CH) 6 Hz, CH=], 176.5 [s, O–C=]. MS, *m/z* (%): 296 (95, M^+), 242 (20), 227 (98), 195 (7), 185 (9), 167 (7), 145 (100), 125 (17), 97 (12), 69 (84), 54 (15), 39 (10), 27 (4). $C_8H_6F_6OS_2$ (296.2): calcd. C 32.4, H 2.0, S 21.7; found C 32.0, H 1.8, S 21.0.

6. Characteristics of phenyl, pentafluorophenyl and trifluoromethylchalcogenyl groups

Characteristic spectroscopic data (^{13}C-, ^{19}F-NMR) can be attributed to the following groups: C_6H_5-, C_6F_5-, CF_3S-, CF_3Se- in the large number of compounds synthesized. The ^{13}C-NMR chemical shifts δ and the ^1J(CH) or ^1J(CF) coupling constants are observed to be within very narrow limits and are given as mean values.

For C_6H_5-groups linked to carbon: δ(C-1) = 133.8 ± 0.9 ppm, δ(C-2,6) = 128.9 ± 0.2 ppm, δ(C-3,5) = 128.7 ± 0.2 ppm, δ(C-4) = 127.7 ± 0.5 ppm: ^1J(CH) = 162.9 ± 8.8 Hz.

For C_6H_5-groups linked to nitrogen: δ(C-1) = 133.6 ± 2.4 ppm, δ(C-2,6) = 121.3 ± 1.5 ppm, δ(C-3,5) = 129.6 ± 0.4 ppm, δ(C-4) = 128.3 ± 2.2 ppm: ^1J(CH) = 161.9 ± 3.2 Hz.

For C_6F_5-groups: δ(C-1) = 104.3 ± 3.3 ppm, δ(C-2,6) = 147.9 ± 0.9 ppm, δ(C-3,5) = 137 ± 80.2 ppm, δ(C-4) = 143.1 ± 0.4 ppm; ^1J(CF) = 254.4 ± 12.2 Hz.

For CF_3S-groups: $\delta(CF_3S)$ = 128.5 ± 2.0 ppm; ^1J(CF) = 311.5 ± 3.2 Hz.

For CF_3Se-groups: $\delta(CF_3Se)$ = 123.0 ± 0.8 ppm; ^1J(CF) = 333.8 ± 2.0 Hz.

^{19}F-NMR data for the C_6F_5-group: $\delta(F_o) = -130.0 \pm 2.8$ ppm, $\delta(F_p) = -148.3 \pm 1.4$ ppm, $\delta(F_m) = -160.0 \pm 0.9$ ppm; $^3J(FF_m) = 21 \pm 1.3$ Hz. Additional spectroscopic data are provided in Table 2.

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