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Synthesis of New Floroaliphatic Functionalized Sulfonyl Bromides and Study of Their Chemical Properties

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Abstract: *It is shown that fluoroaliphatic sulfonyl bromides containing terminal functional groups, such as alkoxycarbonyl, trifluorovinyl, or fluorosulfonyl, are convenient agents for radical fluoroalkylation of unsaturated hydrocarbons under photochemical initiation.*

Keywords: *tetrafluoroethane-β-sultone, ethyl bromodifluoroacetate, ethyl bromosulfonyl difluoroacetate, ethoxycarbonyldifluoromethylation, oxaperfluoroalkyl sulfonylbromides.*

It was shown earlier that perfluoroalkyl sulfonylbromides R_FSO_2Br could be used for radical perfluoroalkylation of unsaturated and aromatic hydrocarbons [1-5]. Taking into consideration the literature data we assumed that sulfonylbromides derived from commercially available functionalized fluoroaliphatic bromides, e.g. bromosulfonyl difluoroacetates $BrSO_2CF_2CO_2R$ [R = Me (**1a**), Et (**1b**)], could be used as reagents for radical introduction of the corresponding fluoroaliphatic groups.

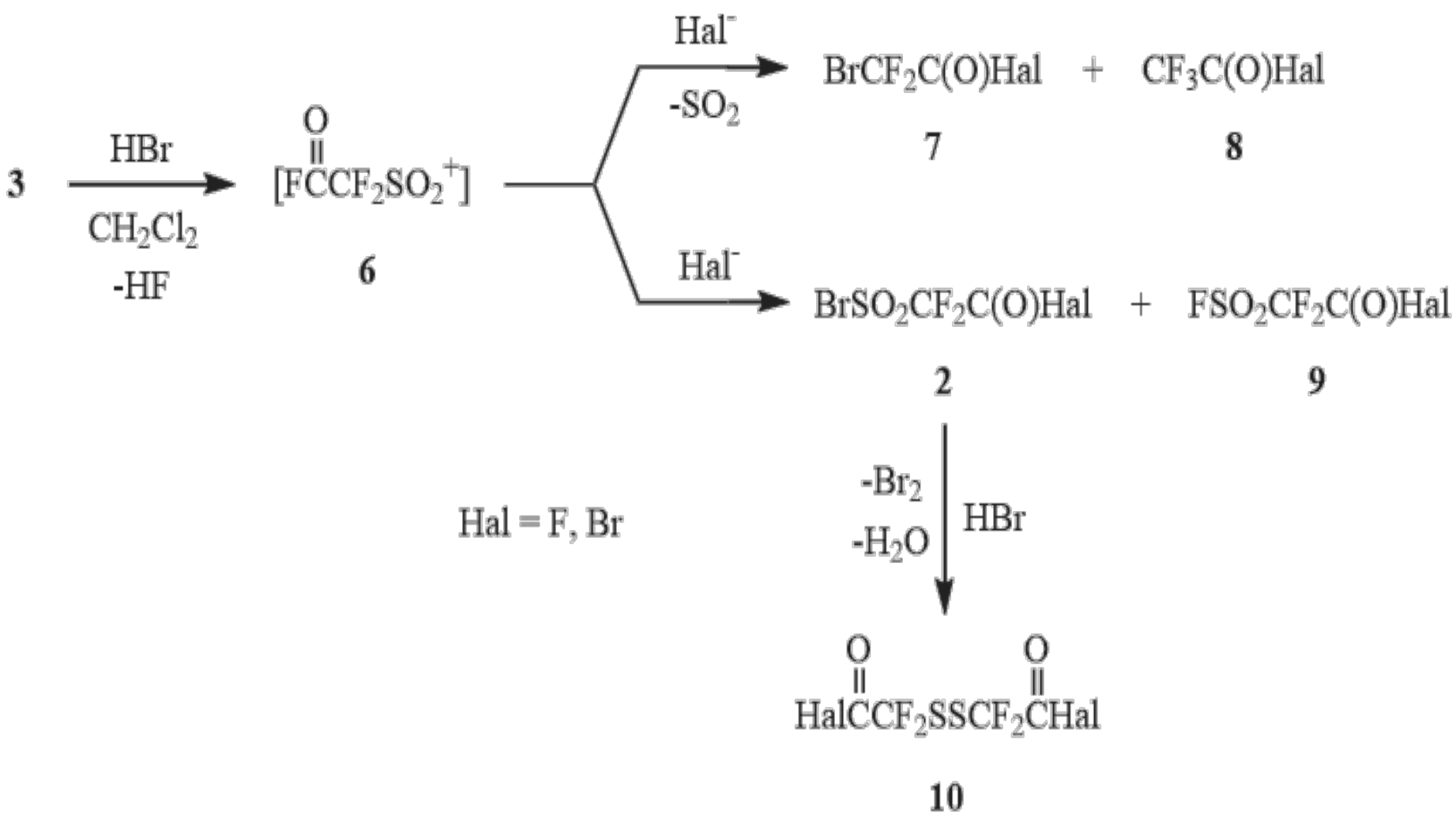
We failed to prepare bromosulfonyl difluoroacetylhalides **2** by the reaction of tetrafluoroethane-β-sultone (**3**) and anhydrous hydrogen bromide by analogy with synthesis of chlorosulfonyl difluoroacetylhalides [6]. The reaction between sultone **3** and anhydrous HBr in ether with the further treatment of the reaction mixture by dry methanol yielded the mixture of methyl bromodifluoroacetate (**4**) and disulfide **5** at the molar ratio of 2:1.

Scheme 1

3 4 5

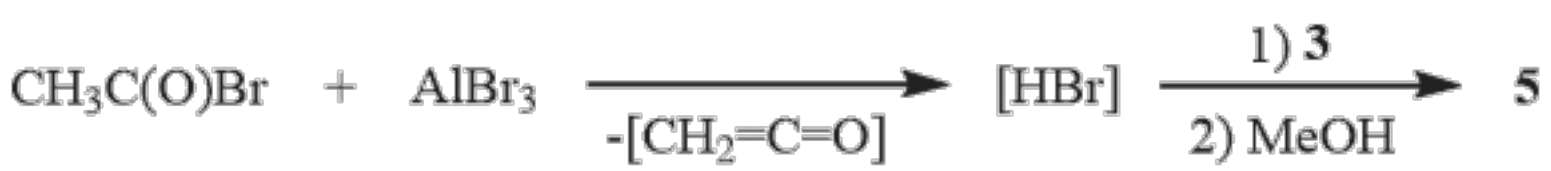
This reaction in CH_2Cl_2 results in formation of a complex mixture of products shown in Scheme 2:

Scheme 2



The difference in the composition of reaction products obviously reflects the effect of the solvent on the mechanism of the opening of sultone **3**. In a nonpolar solvent, methylene chloride, the opening of sultone **3** occurs predominantly according to the electrophilic mechanism with formation of sulfonyl cation **6** that can both attach anions present in the reaction medium (F^-, Br^-) yielding products **2** and **9** and undergo desulfodioxidation with formation of acid halides of bromodifluoroacetic and trifluoroacetic acids **7** and **8**. The assumed formation of disulfide **10** as a result of reduction of sulfonyl bromide **2** by hydrogen bromide was confirmed by high yield of **5** in the reaction between sultone **3** and $AlBr_3$ in acetyl bromide medium.

Scheme 3

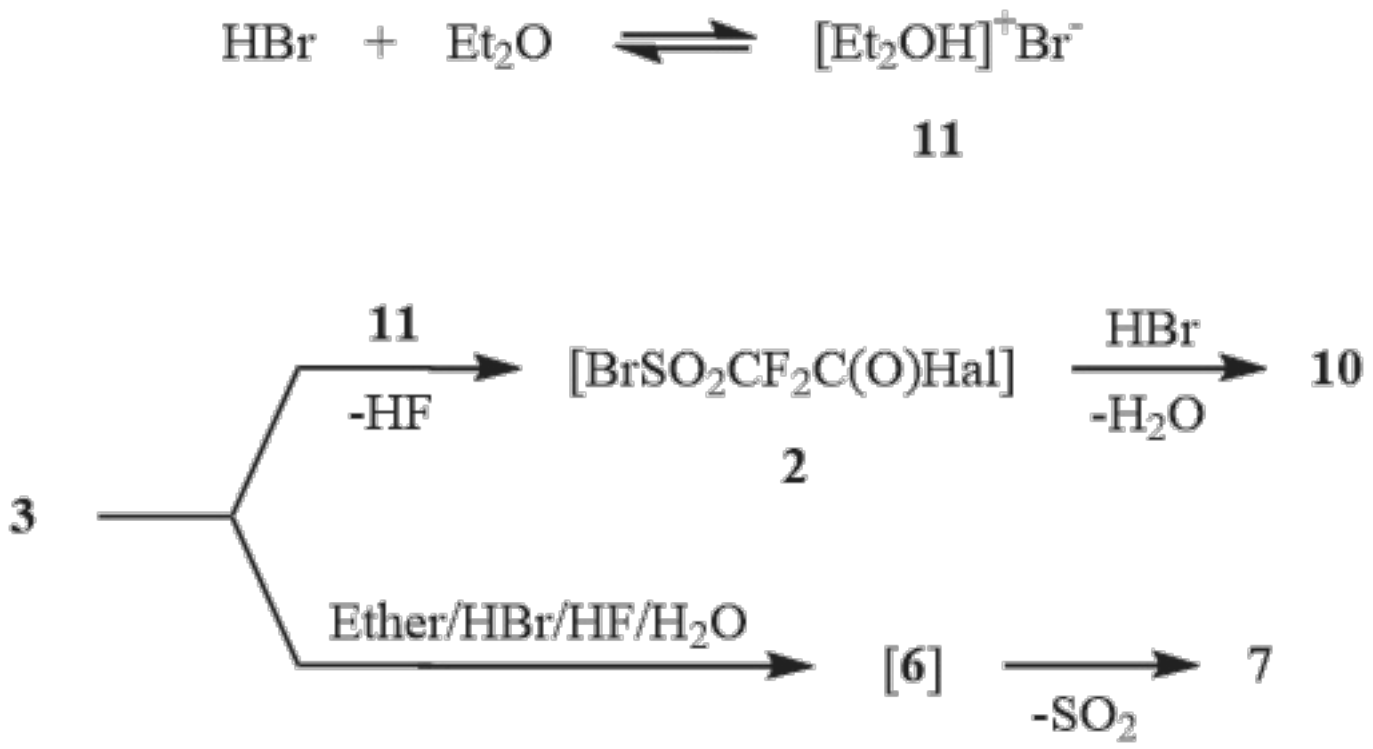


The suggested scheme is supported both by the considerable increase in the yield of sulfonyl bromides **2** (up to 40%) and by the absence of disulfide **10** among the products of the reaction between sultone **3** and HBr in the presence of bromine maintaining the oxidative

medium, same as by the composition of the products of the reaction between **3** and $AlBr_3$ in the medium of benzoyl bromide or dibromomethane, where acid halides **7** and **8** are predominant, but acid halides **2** and **10** are absent.

Formation of comparable amounts of compounds **4** and **5** in the course of the reaction between **3** and HBr in ether reflects in all probability the competition between the nucleophilic and electrophilic opening of the sultone: in the excess of ether HBr yields diethyloxonium bromide **11** that interacts with sultone **3** with intermediate formation of sulfonyl bromides **2** that are further quantitatively reduced to disulfides **10**. At the same time, formation of acid halides of bromodifluoroacetic acid **7** is probably related to accumulation of water and hydrogen fluoride in the reaction mass, which results in generation of sulfonyl cation **6** that eliminates SO_2 in the polar medium with the further formation of bromodifluoroacetyl halides **7**.

Scheme 4

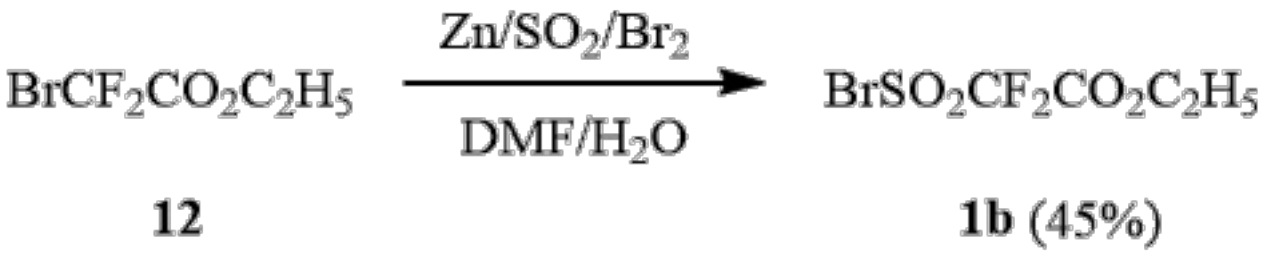


As follows from the above results, synthesis of derivatives of bromosulfonyl dufluoroacetic acid **2** on the basis of sultone **3** can hardly be considered as the preparative method of their synthesis. At the same time, it was shown earlier that perfluoroalkanesulfonyl halides are easily obtained by halogenation of the corresponding metal sulfinates formed in the reaction of sodium dithionite [1] or sulfurous anhydride in the presence of Zn, Al, Mn, or Cd with iodo- or bromoperfluoroalkanes [7].

Taking into account that methyl bromodifluoroacetate (**4**) and ethyl bromodifluoroacetate (**12**) are commercially available products, we attempted to synthesize ethyl bromosulfonyl difluoroacetate (**1b**) according to the method [7].

Indeed, it turned out that the reaction between ethyl bromodifluoroacetate **12** and Zn/SO_2 in DMF with the further bromination of the reaction mixture resulted in formation of **1b** with the yield of 45%.

Scheme 5



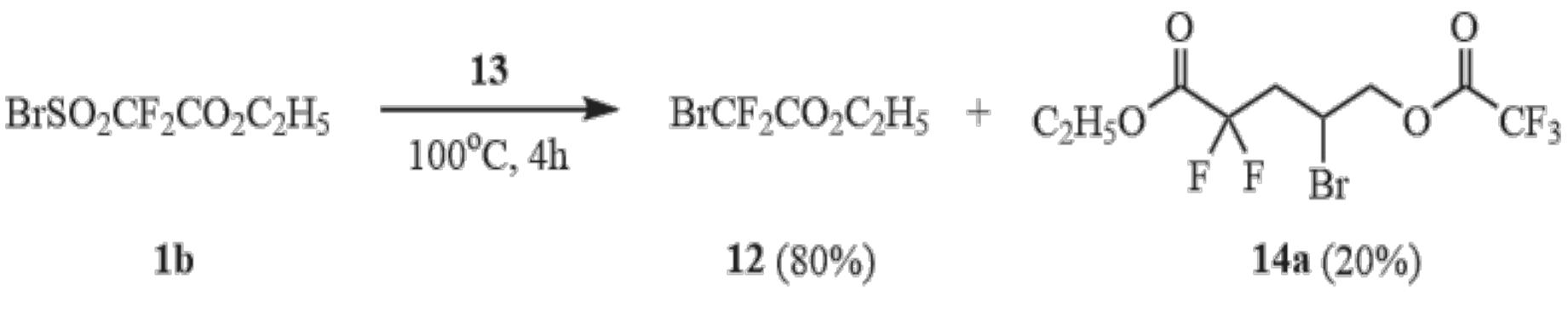
12 **1b** (45%)

The suggested method of synthesis of sulfonyl bromide **1b**, owing to availability of the initial bromodifluoroacetate **12**, is preparatively convenient and can be easily carried out on a large scale, which to a certain extent compensates the low target product yield.

Sulfonyl bromide **1b** is storage-stable in a fridge at 4-8°C; when heated (100°C) or under illumination by sunlight in a sealed ampoule, **1b** undergoes desulfodioxidation by 4% in 4 h and by 5% in 10-12 h, accordingly.

The attempt to add sulfonyl bromide **1b** to allyl trifluoroacetate (**13**) at the molar ratio of **1b**:**13** = 1:1 under the conditions of thermal initiation (100°C/4 h) resulted in predominant desulfodioxidation **1b** with formation of a mixture of ester **12** and adduct **14a**:

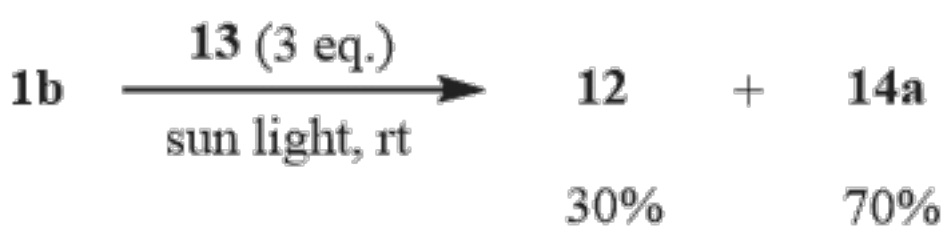
Scheme 6



1b **12** (80%) **14a** (20%)

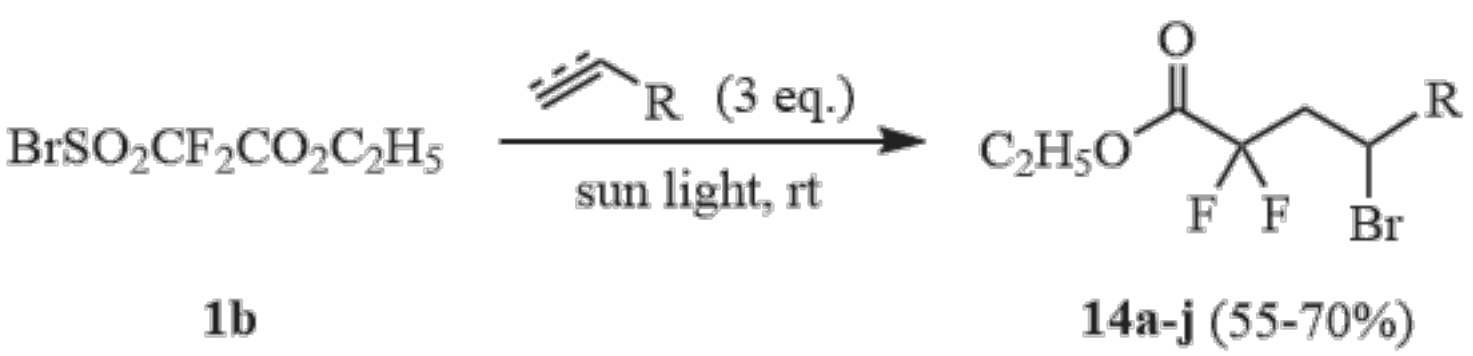
The further studies showed that illumination of the mixture of **1b**:**13** at the molar ratio of 1:3 by sunlight in a sealed ampoule for 10-12 h results in formation of adduct **14a** in the yield of 70%.

Scheme 7

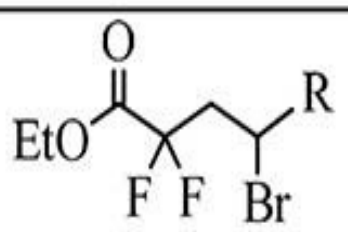
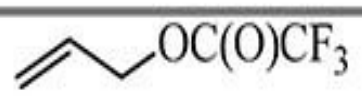
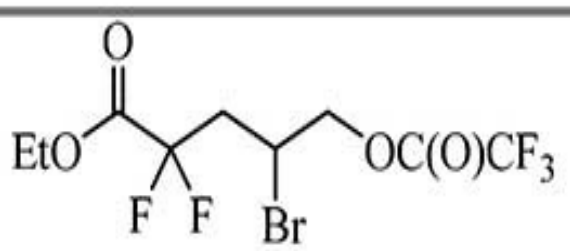
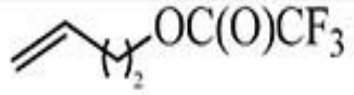
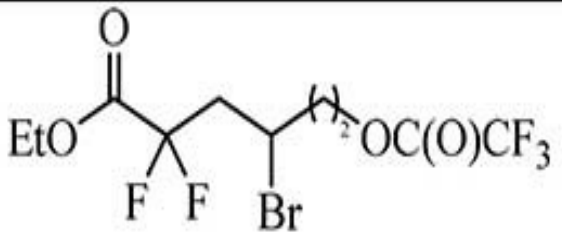
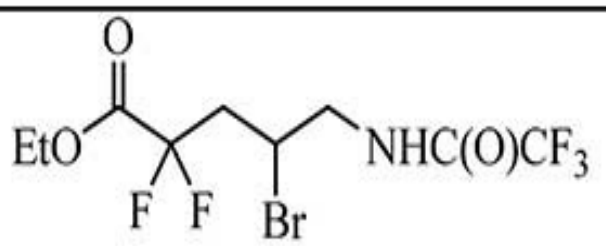
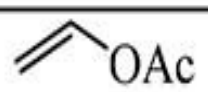
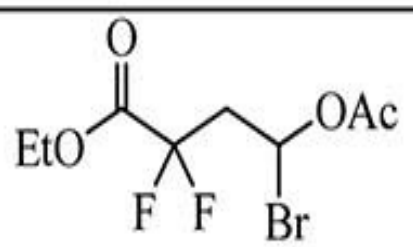
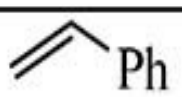
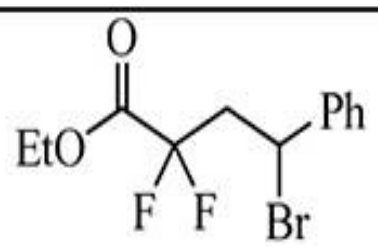
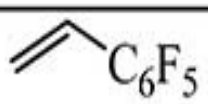
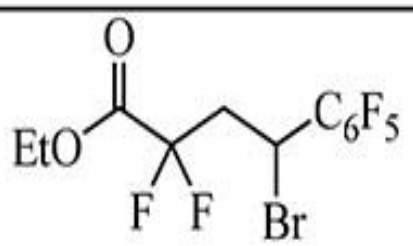
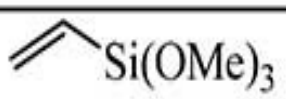
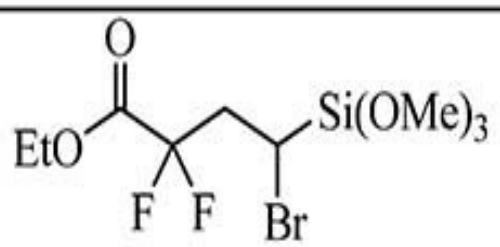
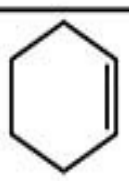
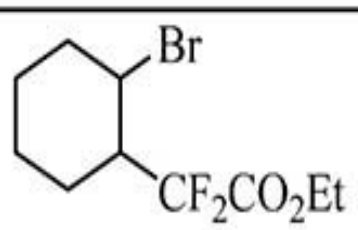


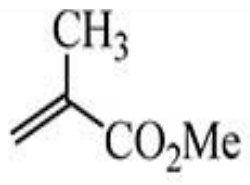
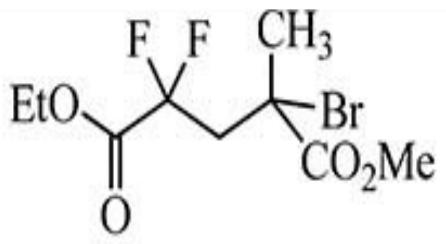
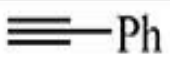
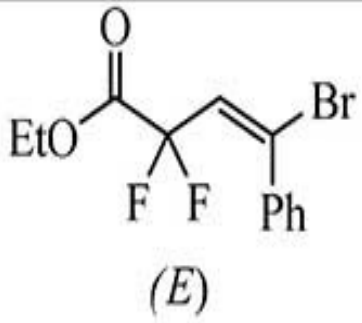
Adducts **14b-j** of sulfonyl bromide **1b** with other unsaturated hydrocarbon compounds were obtained in a similar way. The structure and yields of the obtained compounds are presented in Table 1.

Table 1. Reactions of ethyl bromosulfonyl difluoroacetate 1b with unsaturated compounds.



1b **14a-j** (55-70%)

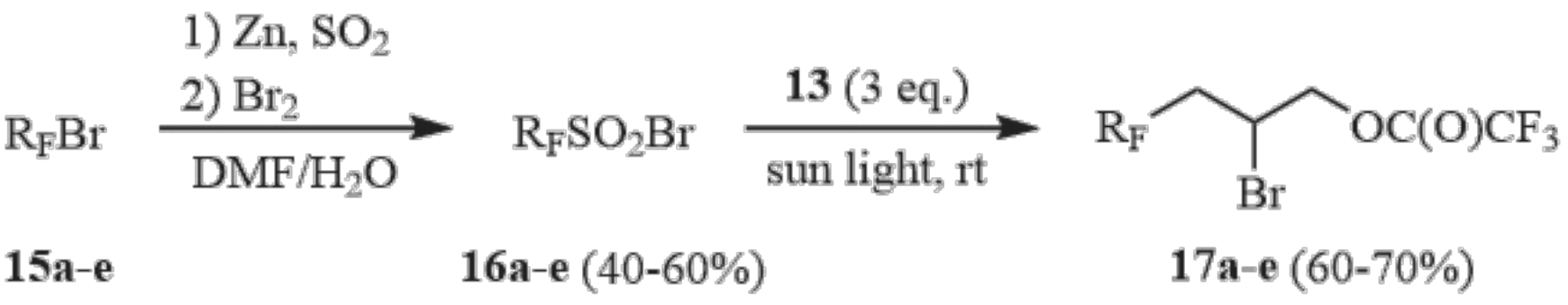
№ п/п			№ в-ва	Выход, %
1			**14a**	70
2			**14b**	70
3			**14c**	60
4			**14d**	65
5			**14e**	60
6			**14f**	60
7			**14g**	65
8		 (*Z*/*E*=1:1)	**14h**	65

9			**14i**	55
10		 (*E*)	**14j**	55

The performed experiments showed that ethyl bromosulfonyl difluoroacetate **1b** adds to unsaturated compounds under mild conditions under exposure to sunlight and can be used for the embedding the ethoxycarbonyl difluoromethyl group into the hydrocarbon chain.

Reactivity close to that of sulfonyl bromide **1b** is also specific for sulfonyl bromides **16a-e** obtained by the reaction of primary fluoroaliphatic bromides **15a-e** with Zn/SO_2 with the further bromination of the forming zinc sulfinates (Scheme 8). Sulfonyl bromides **16a-e** adds to allyl trifluoroacetate (**13**) under exposure to sunlight and form adducts **17a-e** in 60-70% yield:

Scheme 8



15a-e **16a-e** (40-60%) **17a-e** (60-70%)

$\mathbf{R_F}$ =

a: $-CF_2CF_2OCF{=}CF_2$

b: $-CF_2CF_2OCF(CF_3)CO_2Me$

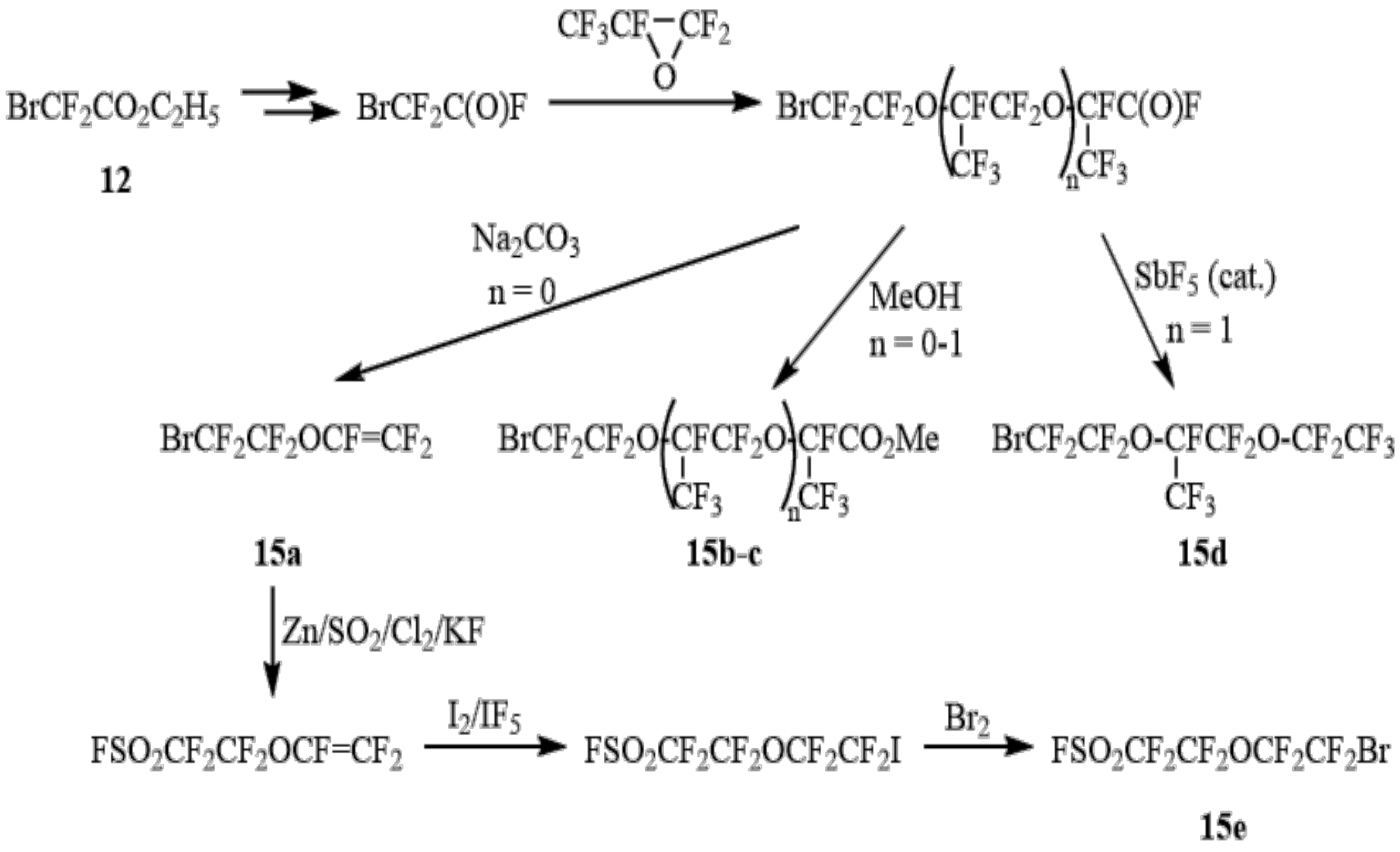
c: $-CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)CO_2Me$

d: $-CF_2CF_2OCF(CF_3)CF_2OCF_2CF_3$

e: $-CF_2CF_2OCF_2CF_2SO_2F$

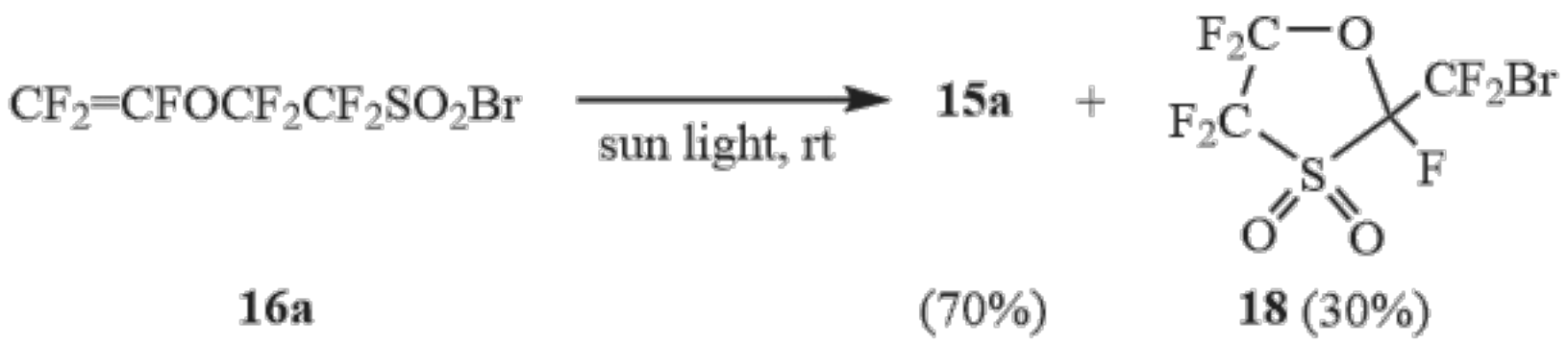
The initial bromides **15a-e** are obtained on the basis of bromodifluoroacetate **12** through a series of transformations shown in Scheme 9 [8-11]:

Scheme 9



As opposed to sulfonyl bromides **1a-b** and **16b-e** that undergo desulfodioxidation under exposure to sunlight with formation of bromides **12** and **15b-e**, sulfonyl bromide **16a** yields in sunlight a mixture of bromide **15a** and cyclic bromide **18**:

Scheme 10



Thus the embedding of SO_2 across C-Br bond in fluoroaliphatic bromides can be considered as a latent form of its activation, which allows to compensate the relitavely low reactivity of fluoroaliphatic bromides in the reactions of radical addition.

Experimental

^1H, ^{19}F NMR spectra were recorded using a Bruker AVANCE-300 spectrometer at 300 and 282 MHz, accordingly; the external standard was $CDCl_3$. Chemical shifts for ^1H spectra are presented vs. the residual signal of the solvent (δ 7.26) and are given in ppm vs. tetramethylsilane. Chemical shifts in ^{19}F spectra are given in ppm vs. $CFCl_3$. Downfield shifts are positive. Raman spectra are recorded on a Jobin Yvon LabRam spectrometer. Mass spectra are recorded using a Finnigan Polaris Q mass spectrometer (Trace GC ultra).

The method of synthesis of sultone **3** has been described earlier in [12-13].

Reaction of Tetrafluoroethane-β-Sultone (3) with HBr in Ether.

Tetrafluoroethane- β-sultone (**3**) (14.55 g, 0.081 mol) is added dropwise to the ether solution of dry HBr (18.36 g, 0.227 mol, in 100 g of dry ether) under stirring at the temperature of -50÷-45°C. Then, the temperature of the reaction mixture is increased to 20÷25°C and the mixture is stirred at this temperature for 30 min. Further, the mixture is cooled to -20÷-15°C and dry methanol (15 ml) is added under stirring; the mixture temperature is increased to 20÷25°C and the mixture is stirred at this temperature for 30 min. Then the volatile components are distilled in vacuum (10-15 torr) into a trap (-78°C). The obtained liquid residue (10.6 g) is analyzed using ^{1}H, ^{19}F NMR.

^{19}F NMR δ: -84, s, (**5**) (*cf*. [14]), -62, s, (**4**), the molar ratio of **5**:**4**=1:2.

The obtained mixture is twice washed with cold water; the lower layer contains, according to ^{1}H and ^{19}F NMR data, the esters **5** and **4**. The mass spectrum of bis(methoxycarbonyl difluoromethyl)disulfide (**5**) (M/Z, reference): 297$[M+CH_3]^+$, 282$[M]^+$, 263$[M-F]^+$, 235$[C_5H_3F_4O_2S_2]^+$, 218$[M-2S]^+$(100%), 195$[C_5H_6FO_2S_2]^+$, 181$[C_5H_6FO_4S]^+$, 154$[C_3H_3FO_2S_2]^+$, 141$[C_3HF_2OS]^+$, 124$[C_2HFOS_2]^+$, 121$[C_3H_2FO_2S]^+$, 114$[CF_2S_2]^+$, 109$[C_3F_3O]^+$, 93$[C_3F_3]^+$, 82$[CF_2S]^+$, 81$[C_2F_3]^+$, 64$[S_2]^+$, 63$[CFS]^+$, 59$[C_2H_3O_2]^+$, 45$[CHS]^+$.

Reaction of Tetrafluoroethane-β-Sultone (3) with HBr in CH_2Cl_2.

Tetrafluoroethane- β-sultone (**3**) (18 g, 0.1 mol) is added dropwise to the solution of anhydrous HBr (24 g, 0.3 mol) in CH_2Cl_2 (100 ml) at -50^{o}C; at the end of addition, the reaction mixture is stirred for 30 min, then dry methanol is added dropwise; the whole is heated to the room temperature, the reaction mass is poured onto crashed ice, the organic layer is separated, washed with dilute aqueous $NaHCO_3$ solution to give 12.4 g of a mixture of esters **1a**, **4**, **5**, $FSO_2CF_2CO_2Me$, and CF_3CO_2Me identified by GLC, ^{19}F NMR and chromato-mass spectrometry methods.

Reaction of Tetrafluoroethane-β-Sultone (3) with $AlBr_3$ in $CH_3C(O)Br$.

Tetrafluoroethane- β-sultone (**3**) (18 g, 0.1 mol) is added dropwise to the solution of aluminum bromide (5.4 g, 0.02 mol) in acetyl bromide (75 g, 0.61 mol) at -50^{o}C, stirred for 30 min, then dry methanol is added dropwise; the whole is heated to 20÷25^{o}C, the reaction mass is poured onto ice, the organic layer is separated, washed with dilute aqueous $NaHCO_3$ solution to dive 12.7 g of ester **5** (90%).

Sulfodioxidation of Ethyl Bromodifluoroacetate (12).

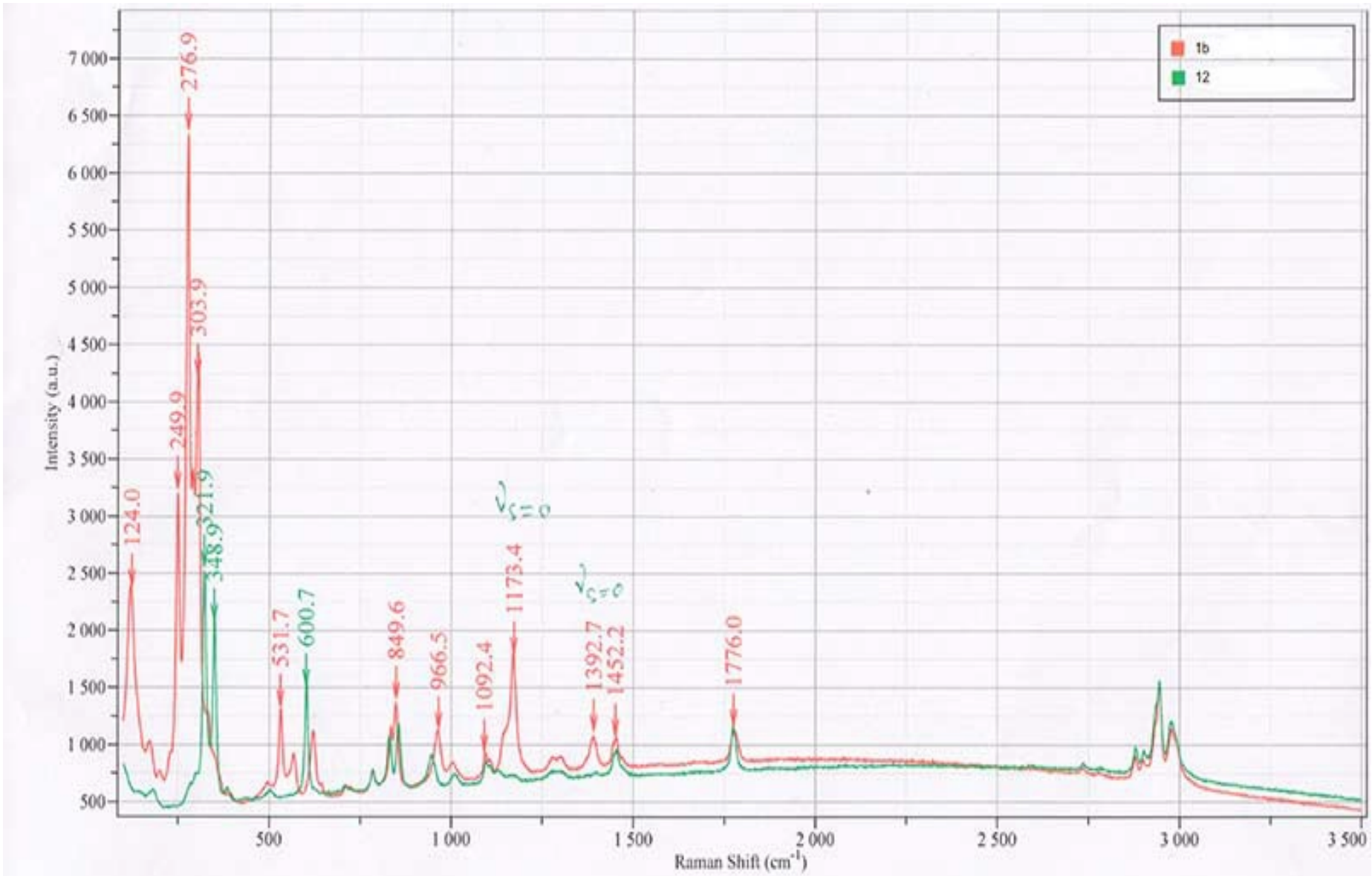
Ethyl Bromosulfonyldifluoroacetate (1b).

Zn powder (14.65 g, 0.224 mol) and water (4 ml) are added under stirring to the solution of ethyl bromodifluoroacetate (**12**) (100 g, 0.49 mol) and SO_2 (57.4 g, 0.896 mol) in DMF (350 ml) cooled to 5°C; upon that, the mixture temperature increases to 35÷45°C. The reaction mixture is cooled to 25÷30°C, stirred at this temperature for 1 h, cooled to 10÷15°C, Zn powder (14.65 g, 0.224 mol) and water (4 ml) are added; meanwhile, the mixture temperature rises to 30÷35°C. Then the reaction mixture is cooled to 25÷30°C, stirred at this temperature for 3 h, cooled to -15÷-10°C and bromine (115 g, 0.72 mol) is added dropwise under stirring. The temperature mixture is increased to 5÷10°C; the reaction mixture is poured into ice water (500 ml), hydrochloric acid (100 ml) is added under

stirring, the lower layer is separated, washed with dilute hydrochloric acid and distilled over P_2O_5 in vacuum; the fraction at 55-115°C/10 torr is collected.

Further rectification yields 47 g (45% with account for conversion of **12**), b.p. 65-66°C/1.5 torr. Found (%): C, 17.93; H, 1.90; B, 30.18; F, 14.20; S, 11.78. $C_4H_5BrF_2O_4S$. Calculated (%): C, 17.99; H, 1.89; B, 29.92; F, 14.23; S, 12.01. ^{1}H NMR δ: 1.6 (t, 3H, CH_3), 4.7 (q, 2H, CH_2); ^{19}F NMR δ: -101 (s, CF_2). The mass spectrum (M/Z, reference): 267$[M+H]^+$, 239$[C_2H_2BrF_2O_4S]^+$, 203$[C_4H_6BrF_2O_2]^+$, 175$[C_3H_6BrF_2O]^+$, 59$[C_2H_3O_2]^+$(100%), 51$[CF_2H]^+$, 29$[C_2H_5]^+$.

Fig. 1. Raman spectra of compounds 1b and 12.



Synthesis of Compounds 14a-j (Typical Experiment).

A mixture of ethyl bromosulfonyldifluoroacetate (**1b**) (2 g, 7.5 mmol) and olefin or phenyl acetylene (22.5 mmol) (Table 1) is placed into a tube of molybdenum glass (the loading factor is 10%) sealed by a stopper and conditioned for 24 h under sunlight irradiation (the temperature is 25-30°C, cloudy weather produces no significant effect on the reaction).

Volatile mixture components are evacuated at 25÷50°C/15-0.1 torr into a trap (-78°C) to give a residue containing adducts **14a-j**. The yields are presented in Table 1.

Ethyl 4-bromo-2,2-difluoro-5-(2,2,2-trifluoroacetoxy)valerate (14a).

B.p. 124-125°C/10 torr. Found (%): C, 30.24; H, 2.94; F, 26.49. $C_9H_{10}BrF_5O_4$. Calculated (%): C, 30.27; H, 2.82; F, 26.60. ^{1}H NMR δ: 1.3 (t, 3H, CH_3), 2.8 (dt, 2H, CH_2CF_2), 4.3 (q, 2H, $\underline{CH_2}CH_3$), 4.4 (m, 1H, CHBr), 4.6 (d, 2H, CH_2O); ^{19}F NMR δ: -108, -104 (AB_q, 2F, $^2J_{FF}$ =

282 Hz, $\underline{CF_2}CO_2Et$), -77 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 357$[M+H]^+$, 277$[M-Br]^+$, 249$[C_7H_6F_5O_4]^+$, 243$[C_7H_{10}BrF_2O_2]^+$, 215$[C_6H_{10}BrF_2O]^+$, 195$[C_5H_2BrF_2O]^+$, 169$[C_4H_4BrF_2]^+$, 163$[C_7H_9F_2O_2]^+$, 135$[C_5H_5F_2O_2]^+$(100%), 115$[C_5H_4FO_2]^+$, 107$[C_4H_5F_2O]^+$, 91$[C_4H_5F_2]^+$, 90$[C_4H_4F_2]^+$, 71$[C_4H_4F]^+$, 69$[CF_3]^+$, 51$[CF_2H]^+$.

Ethyl 4-bromo-2,2-difluoro-5-(2,2,2-trifluoroacetoxy)caproate (14b).

B.p. 145-147°C/10 torr. ^{1}H NMR δ: 1.3 (t, 3H, CH_3), 2.1-2.5 (m, 2H, $\underline{CH_2}CH_2O$), 2.6-3 (m, 2H, $\underline{CH_2}CF_2$), 4.3 (m, 3H, CHBr, $\underline{CH_2}CH_3$), 4.6 (m, 2H, CH_2O); ^{19}F NMR δ: -107.7, -103.3 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, $\underline{CF_2}CO_2Et$), -77 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 371$[M+H]^+$, 370$[M]^+$, 291$[M-Br]^+$, 263$[C_9H_{12}F_5O_3]^+$, 177$[C_8H_{11}F_2O_2]^+$, 149$[C_6H_7F_2O_2]^+$ (100%), 129$[C_6H_3F_2O]^+$, 103$[C_5H_7F_2]^+$, 69$[CF_3]^+$.

Ethyl 4-bromo-2,2-difluoro-5-(2,2,2-trifluoroacetamido)valerate (14c).

^{1}H NMR δ: 1.4 (t, 3H, $\underline{CH_3}CH_2$), 2.85 (dt, 2H, $\underline{CH_2}CF_2$), 3.85 (m, 1H, CHBr), 4 (m, 2H, $\underline{CH_2}NH$) 4.4 (q, 2H, $CH_3\underline{CH_2}$), 8.5 (m, 1H, NH); ^{19}F NMR δ: -107.95, -103.05 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, $\underline{CF_2}CO_2Et$), -77.5 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 356$[M+H]^+$, 276$[C_9H_{11}F_5O_3N]^+$, 248$[C_8H_{11}F_5O_2N]^+$, 230$[C_7H_5F_5O_3N]^+$, 214$[C_7H_5BrO_2N]^+$, 202$[C_6H_3F_5ON]^+$(100%), 182 $[C_6H_2F_4ON]^+$, 163$[C_6H_2F_3ON]^+$, 135$[C_4H_4F_3]^+$, 126$[C_3H_3F_3ON]^+$, 112$[C_2HF_3ON]^+$, 69$[CF_3]^+$, 51$[CHF_2]^+$.

Ethyl 4-acetoxy-4-bromo-2,2-difluorobutyrate (14d).

B.p. 125-127°C/10 torr. ^{1}H NMR δ: 1.5 (t, 3H, $\underline{CH_3}CH_2$), 2.25 (s, 3H, CH_3), 3.1-3.6 (m, 2H, $\underline{CH_2}CF_2$), 4.6 (q, 2H, $CH_3\underline{CH_2}$), 7 (m, 1H, CHBr); ^{19}F NMR δ: -107.4, -105.6 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, $\underline{CF_2}CO_2Et$). The mass spectrum (M/Z, reference): 289$[M+H]^+$, 209$[C_8H_{10}F_2O_4]^+$, 167$[C_6H_8F_2O_3]^+$(100%), 147$[C_6H_7FO_3]^+$, 51$[CHF_2]^+$, 43$[C_2H_3O]^+$.

Ethyl 4-bromo-2,2-difluoro-4-phenylbutyrate (14e).

^{1}H NMR δ: 0.9 (t, 3H, $\underline{CH_3}CH_2$), 2.8-3.1 (m, 2H, $\underline{CH_2}CF_2$), 3.75 (q, 2H, $CH_3\underline{CH_2}$), 5 (m, 1H, CHBr), 6.9-7.2 (m, 5H, C_6H_5); ^{19}F NMR δ: -105.23, -104.57 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, $\underline{CF_2}CO_2Et$). The mass spectrum (M/Z, reference): 227$[M-Br]^+$, 207$[C_{12}H_{12}FO_2]^+$, 187$[C_{12}H_{11}O_2]^+$, 169$[C_7H_6Br]^+$, 159$[C_{10}H_4FO]^+$, 153$[C_9H_7F_2]^+$, 133$[C_9H_6F]^+$, 131$[C_6H_8FO_2]^+$(100%), 115$[C_9H_7]^+$, 104$[C_8H_8]^+$, 103$[C_8H_7]^+$, 51$[CHF_2]^+$.

Ethyl 4-bromo-2,2-difluoro-4-(pentafluorophenyl)butyrate (14f).

B.p. 95°C/1.5 torr. ^{1}H NMR δ: 1.1 (t, 3H, CH_3), 2.8-3.1 (m, 2H, $\underline{CH_2}CF_2$), 4 (q, 2H, $CH_3\underline{CH_2}$), 5.3 (m, 1H, $\underline{CH}$Br); ^{19}F NMR δ: -164 (m, 2F, m-F_{C6F5}), -156 (m, 1F, p-F_{C6F5}), -143 (m, 2F, o-F_{C6F5}), -109.4, -106.6 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, $\underline{CF_2}CO_2Et$). The mass spectrum (M/Z, reference): 397$[M+H]^+$, 317$[M-Br]^+$(100%), 297$[C_{12}H_7F_6O_2]^+$, 271$[C_{10}H_2F_7O]^+$, 269$[C_{10}F_7O]^+$, 259$[C_7HBrF_5]^+$, 249$[C_{11}H_6F_5O]^+$, 241$[C_7H_2BrF_4]^+$, 221$[C_9F_6]^+$, 194$[C_8H_3F_5]^+$, 174$[C_8H_2F_4]^+$, 161$[C_7F_4]^+$, 143$[C_7HF_3]^+$, 105$[C_4H_3F_2O]^+$, 51$[CHF_2]^+$.

Ethyl 4-bromo-2,2-difluoro-4-(trimethoxysilyl)butyrate (14g).

^{1}H NMR δ: 1.4 (t, 3H, $\underline{CH_3}CH_2$), 2.6-2.9 (m, 2H, $\underline{CH_2}CF_2$), 3.4 (m, 1H, CHBr), 3.75 (s, 9H, $Si(OCH_3)_3$), 4.4 (q, 2H, $CH_3\underline{CH_2}$); ^{19}F NMR δ: -108.95, -104.05 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, $\underline{CF_2}CO_2Et$). The mass spectrum (M/Z, reference): 319$[C_8H_{14}BrF_2O_4Si]^+$(100%), 299$[C_8H_{13}BrFO_4Si]^+$, 271$[C_9H_{17}F_2O_5Si]^+$, 251$[C_9H_{16}BrFO_5Si]^+$, 122$[C_5H_2O_2Si]^+$, 103$[C_4HF_2O]^+$, 91$[C_3HF_2O]^+$.

(*Z, E*)-Ethyl (2-bromocyclohexyl)-2,2-difluoroacetate (14h).

^{1}H NMR δ: 1.25 (m, 3H, $\underline{CH_3}CH_2$), 1.6-2.6 (m, 8H, Cy), 4 (dt, 1H, $\underline{CH}CF_2$), 4.2-4.3 (m, 2H, $CH_3\underline{CH_2}$), 4.5 (s, 1H, CHBr); ^{19}F NMR δ: -116.5, -107.5 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, *Z*-isomer), -111.31, -110.19 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, $\underline{CF_2}CO_2Et$, *E*-isomer). The mass spectrum (M/Z, reference): 285$[M+H]^+$, 233$[C_8H_7BrFO_2]^+$, 205$[M\text{-}Br]^+$(100%), 185$[C_{10}H_{14}FO_2]^+$, 177$[C_8H_{11}F_2O_2]^+$, 157$[C_8H_{10}FO_2]^+$, 131$[C_7H_9F_2]^+$, 109$[C_6H_2FO]^+$, 91$[C_6H_3O]^+$, 81$[C_6H_9]^+$, 77$[C_5HO]^+$, 51$[CHF_2]^+$.

(*E*)-Ethyl 4-bromo-2,2-difluoro-4-phenylbut-3-enoate (14j).

B.p. 110/1 torr. ^{1}H NMR δ: 0.9 (t, 3H, $\underline{CH_3}CH_2$), 3.8 (q, 2H, $CH_3\underline{CH_2}$), 6.5 (t, 1H, $\underline{CH}CF_2$), 7.15 (m, 3H, m,p-H_{C6H5}), 7.3 (m, 2H o-H_{C6H5}); ^{19}F NMR δ: -94.5 (d, 2F, $^3J_{FH}$ = 11 Hz, $\underline{CF_2}CO_2Et$). The mass spectrum (M/Z, reference): 305$[M+H]^+$, 285$[M\text{-}F]^+$, 265$[C_{12}H_{10}BrO_2]^+$, 231$[C_9H_6BrF_2]^+$, 225$[C_{12}H_{11}F_2O_2]^+$, 213$[C_9H_7BrF]^+$(100%), 197$[C_{11}H_{11}F_2O]^+$, 169$[C_9H_7F_2O]^+$, 151$[C_9H_5F_2]^+$, 133$[C_9H_6F]^+$, 102$[C_8H_6]^+$, 91$[C_3HF_2O]^+$, 76$[C_3H_2F_2]^+$, 75$[C_3HF_2]^+$, 63$[C_2HF_2]^+$, 50$[CF_2]^+$.

General Method of Synthesis of Sulfonyl bromides 16a-c and 16e.

Zn powder (9.8 g, 0.15 mol) and water (2.7 ml) are added under stirring to the solution of bromide **15a-c** or **15e** (0.33 mol) and SO_2 (38.4 g, 0.6 mol) in DMF (300 ml) cooled to 5°C; upon that, the mixture temperature increases to 35÷45°C. The reaction mixture is cooled to 25÷30°C; stirred at this temperature for 1 h, cooled to 10÷15°C, Zn powder (9.8 g, 0.15 mol) and water (4 ml) are added; meanwhile, the mixture temperature rises to 30÷35°C. Then the reaction mixture is cooled to 25÷30°C, stirred for 3 h, cooled to -15÷-10°C and bromine (76.8 g, 0.48 mol) is added dropwise under stirring, the temperature is increased to 5÷10°C. The reaction mixture is poured into ice water (500 ml), hydrochloric acid (100 ml) is added under stirring, the lower layer is separated, washed with dilute hydrochloric acid and distilled over P_2O_5 in vacuum; further rectification is used to separate sulfonyl bromides **16a-c** and **16e**.

2-(Trifluorovinyloxy)tetrafluoroethane sulfonyl bromide (16a).

Yield 60%, b.p. 33-34^{o}C/10 torr. Found (%): C, 14.10; F, 39.04; S, 9.05. $C_4BrF_7O_3S$. Calculated (%): C, 14.09; F, 39.00; S, 9.40. ^{19}F NMR δ: -137.1 (dd, 1F, $^3J_{FF\text{-}trans}$ = 112 Hz, $^3J_{FF\text{-}cis}$ = 68 Hz, OCF), -123.3 (dd, 1F, $^2J_{FF}$ = 90 Hz, =CF-trans), -115.8 (dd, 1F, $^2J_{FF}$ = 90 Hz, =CF-cis), -109.9 (s, 2F, CF_2SO_2Br), -82.9 (s, 2F, OCF_2).

Methyl 3-oxa-5-bromosulfonylperfluoro-2-methylvalerate (16b).

Yield 60%, b.p. 52°C/1 torr. ^{1}H NMR δ: 4.1 (s, 3H, CH_3); ^{19}F NMR δ: -133.1 (m, 1F, CF), -110.2 (s, 2F, CF_2SO_2Br), -84.2 (s, 3F, CF_3), -83.4, -75.2 (AB_q, 2F, $^2J_{FF}$ = 143 Hz, CF_2O).

Methyl 3,6-dioxa-8-bromosulfonylperfluoro-2,5-dimethylcaprylate (16c).

Sulfonylbromide was synthesized according to the general procedure in 450 ml of DMF per 0.33 mol of ester **15c**. The rectification of organic layer resulted in separation of a fraction (70-95°C/0.5 torr) that contained 70% **16c** and 30% **15c**, yield 50% (based on **15c** entered the reaction). ^{1}H NMR spectrum of **16c** δ: 4.0 (s, 3H, CH_3); ^{19}F NMR δ: -146.5 (m, 1F, $\underline{CF}CF_2$), -133.6 (m, 1F, $\underline{CF}CO_2Me$), -110.3 (s, 2F, CF_2SO_2Br), -84.7 (m, 6F, CF_3), -88÷-80 (m, 2F, $CF\underline{CF_2}O$), -78 (m, 2F, $CF_2\underline{CF_2}O$).

3,6-Dioxaperfluoro-4-methyloctane Sulfonyl Bromide (16d).

Zn powder (9.8 g, 0.15 mol) and water (2.7 ml) are added under stirring to the solution of SO_2 (38.4 g, 0.6 mol) in DMF (450 ml) cooled to 5°C; upon that, the mixture temperature increases to 35÷45°C. The reaction mixture is cooled to 10÷15°C; Zn powder (9.8 g, 0.15 mol) and water (2.7 ml) are added; meanwhile, the mixture temperature rises to 30÷35°C. Then bromide **15d** (96.2 g, 0.2 mol) is added into the reaction mixture, the whole is stirred vigorously at 55÷60°C for 3-4 h, cooled to -15÷-10°C and bromine (76.8 g, 0.48 mol) is added dropwise under stirring. The temperature mixture is increased to 5÷10°C; the reaction mixture is poured into ice water (500 ml), hydrochloric acid (100 ml) is added under stirring, the lower layer is separated, washed with dilute hydrochloric acid and distilled over P_2O_5 in vacuum; further rectification is used to separate sulfonyl bromide **16d**.

Yield 60%, b.p. 57-58°C/15 torr. ^{19}F NMR δ: -147.1 (m, 1F, CF), -110.7 (s, 2F, CF_2SO_2Br), -90.9 (m, 2F, CF_2O), -89.7 (m, 3F, CF_3), -85.2 (m, 2F, CF_2O), -82.4 (m, 3F, CF_3), -78.4 (m, 2F, CF_2O).

3-Oxa-5-bromosulfonylperfluoropentane sulfonyl fluoride (16e).

Yield 40%. b.p. 72-73°C/15 torr. ЯМР ^{19}F δ: -114.1 (m, 2F, CF_2SO_2F), -110.4 (s, 2F, CF_2SO_2Br), -83.5 (m, 2F, CF_2O), -80.7 (m, 2F, CF_2O), 43.9 (m, 1F, SO_2F).

The synthesis of compounds 17a-e.

The adducts **17a-e** are prepared from sulfonylbromides **16a**-**e** and allyl trifluoroacetate (**13**) under the conditions of preparing compounds **14a**-**j**.

2-Bromo-4,4,5,5-tetrafluoro-5-trifluorovinyloxypentyl trifluoroacetate (17a).

Yield 70%. ^{1}H NMR δ: 2.75 (m, 2H, $\underline{CH_2}CF_2$), 4.4 (m, 1H, CHBr), 4.6 (d, 2H, CH_2O); ^{19}F NMR δ: -137.6 (dd, 1F, $^3J_{FF\text{-trans}}$ = 112 Hz, $^3J_{FF\text{-cis}}$ = 68 Hz, OCF), -125.2 (dd, 1F, $^2J_{FF}$ = 90 Hz, =CF-trans), -118.9 (m, 2F, CF_2), -117.3 (dd, 1F, $^2J_{FF}$ = 90 Hz, =CF-cis), -92.5 (s, 2F, CF_2O), -77.5 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 351$[M\text{-}Br]^+$, 333$[C_7H_5BrF_7O_2]^+$, 313$[C_7H_4BrF_6O_2]^+$, 297$[C_7H_4BrF_6O]^+$, 279$[C_7H_3BrF_5O]^+$, 269$[C_7HBrF_3O_3]^+$, 249$[C_7BrF_2O_3]^+$, 219$[C_5H_4BrF_4]^+$, 199$[C_5H_3BrF_3]^+$, 189$[C_5H_5F_4O_3]^+$, 169$[C_4H_4BrF_2]^+$, 157$[C_5H_5F_4O]^+$, 155$[C_3H_2BrF_2]^+$, 145$[C_4H_5F_4O]^+$, 139$[C_5H_3F_4]^+$, 109$[C_4H_4F_3]^+$, 95$[C_3H_5F_2O]^+$, 77$[C_3H_3F_2]^+$, 69$[CF_3]^+$(100%), 51$[CHF_2]^+$.

Methyl 3-oxa-7-bromo-8-trifluoroacetoxy-2-trifluoromethyl-2,4,4,5,5-pentafluorocaprilate (17b).

Yield 70%. ^{1}H NMR δ: 2.8 (m, 2H, $\underline{CH_2}CF_2$), 3.95 (s, 3H, CH_3), 4.5 (m, 1H, CHBr), 4.65 (m, 2H, CH_2O); ^{19}F NMR δ: -134.1 (m, 1F, CF), -118.8 (m, 2F, $\underline{CF_2}CH_2$), -93.4, -86.0 (AB_q, 2F, $^{2}J_{FF}$ = 143 Hz, CF_2O), -84.7 (s, 3F, $CF\underline{CF_3}$), -77.5 (s, 3F, $\underline{CF_3}CO_2$). The mass spectrum (M/Z, reference): 523$[M+CH_3]^+$, 449$[C_9H_5BrF_{11}O_3]^+$, 429$[M-Br]^+$, 409$[C_{11}H_7F_{10}O_5]^+$, 375$[C_{10}H_4BrF_{11}O_4]^+$, 355$[C_{10}H_3BrF_{10}O_4]^+$, 335$[C_{10}H_2BrF_9O_4]^+$, 315$[C_9H_7F_8O_3]^+$, 295$[C_9H_6F_7O_3]^+$(100%), 275$[C_9H_5F_6O_3]^+$, 233$[C_7H_4F_6O_2]^+$, 199$[C_5H_3BrF_3]^+$, 169$[C_4H_4BrF_2]^+$, 151$[C_4H_5BrF]^+$, 131$[C_4H_4Br]^+$, 89$[C_4H_3F_2]^+$, 69$[CF_3]^+$, 59$[C_2H_3O_2]^+$.

Methyl 3,6-dioxa-10-bromo-11-trifluoroacetoxy-2,5-di(trifluoromethyl)-2,4,4,5,7,7,8,8-octafluoroundecanoate (17c).

Mixture of stereoisomers, yield 60%. ^{1}H NMR δ: 3.1 (m, 2H, $\underline{CH_2}CF_2$), 4.2 (m, 3H, CH_3), 4.7 (m, 1H, CHBr), 4.9 (m, 2H, CH_2O); ^{19}F NMR δ: -147.1 (m, 1F, $\underline{CF}CF_2$), -133.5 (m, 1F, $\underline{CF}CO_2Me$), -118.8 (m, 2F, $\underline{CF_2}CH_2$), -88÷-80 (m, 4F, $\underline{CF_2}OCF\underline{CF_2}O$), -84.5 (s, 3F, CF_3), -81.8 (s, 3F, CF_3), -77.4 (m, 3F, $\underline{CF_3}CO_2$). The mass spectrum (M/Z, reference): 595$[M-Br]^+$, 540$[C_{12}H_6BrF_{13}O_4]^+$, 521$[C_{12}H_6BrF_{12}O_4]^+$, 461$[C_{12}H_6F_{13}O_4]^+$, 441$[C_{12}H_5F_{12}O_4]^+$, 325$[C_7H_3F_{10}O_3]^+$, 297$[C_9H_5F_8O_2]^+$, 199$[C_5H_3BrF_3]^+$, 150$[C_3F_6]^+$, 131$[C_3F_5]^+$(100%), 119$[C_5H_2F_3]^+$, 81$[C_2F_3]^+$, 69$[CF_3]^+$, 59$[C_2H_3O_2]^+$, 51$[CHF_2]^+$, 39$[C_3H_3]^+$.

6,9-Dioxa-2-Bromo-7-trifluoromethyl-4,4,5,5,7,8,8,10,10,11,11,11-dodecafluoroundecyl trifluoroacetate (17d).

Yield 65%. ^{1}H NMR δ: 3.1 (m, 2H, $\underline{CH_2}CF_2$), 4.9 (m, 1H, CHBr), 5.1 (m, 2H, CH_2O); ^{19}F NMR δ: -147.1 (m, 1F, CF), -118.9 (m, 2F, $\underline{CF_2}CH_2$), -90.5 (m, 2F, CF_2O), -89.1 (s, 3F, CF_3), -87.6 (m, 2F, CF_2O), -84.9 (s, 2F, CF_2O), -82.0 (m, 3F, $CF\underline{CF_3}$), -77.4 (s, 3F, $\underline{CF_3}CO_2$). The mass spectrum (M/Z, reference): 615$[M-F]^+$, 555$[M-Br]^+$, 521$[C_{10}H_5BrF_{15}O_2]^+$, 501$[C_{10}H_5BrF_{14}O_2]^+$, 419$[C_{10}H_2F_{14}O_2]^+$, 255$[C_7H_3F_8O]^+$, 219$[C_5H_4BrF_4]^+$, 199$[C_5H_3BrF_3]^+$, 169$[C_4H_4BrF_2]^+$, 155$[C_3H_2BrF_2]^+$, 139$[C_5H_3F_4]^+$, 119$[C_5H_2F_3(C_2F_5)]^+$, 95$[C_3H_2F_3]^+$, 89$[C_4H_3F_2]^+$, 77$[C_3H_3F_2]^+$, 69$[CF_3]^+$(100%), 51$[CHF_2]^+$.

3-Oxa-7-bromo-8-trifluoroacetoxy-1,1,2,2,4,4,5,5-octafluorooctane sulfonyl fluoride (17e).

Yield 60%. ^{1}H NMR δ: 3.1 (m, 2H, $\underline{CH_2}CF_2$), 4.9 (m, 1H, CHBr), 5.1 (m, 2H, CH_2O); ^{19}F NMR δ: -118.9 (m, 2F, $\underline{CF_2}CH_2$), -114.1 (s, 2F, CF_2SO_2F), -89.7 (m, 2F, CF_2O), -83.9 (m, 2F, CF_2O), -77.2 (s, 3F, $\underline{CF_3}CO_2$), 43.2 (m, 1F, SO_2F). The mass spectrum (M/Z, reference): 453$[M-Br]^+$, 418$[C_7H_4BrF_9O_3S]^+$, 398$[C_7H_3BrF_8O_3S]^+$, 379$[C_7H_3BrF_7O_3S]^+$, 335$[C_7H_4BrF_8O]^+$, 317$[C_7H_4BrF_7O]^+$, 273$[C_7H_5F_8O_2]^+$, 253$[C_7H_4F_7O_2]^+$, 233$[C_7H_3F_6O_2]^+$, 213$[C_7H_2F_5O_2]^+$, 199$[C_5H_3BrF_3]^+$, 183$[C_2F_5O_2S]^+$, 169$[C_4H_4BrF_2]^+$, 155$[C_3H_2BrF_2]^+$, 139$[C_5H_3F_4]^+$(100%), 119$[C_5H_2F_3]^+$, 117$[C_3H_2Br]^+$, 109$[C_4H_4F_3]^+$, 100$[C_2F_4]^+$, 95$[C_3H_2F_3]^+$, 89$[C_4H_3F_2]^+$, 69$[CF_3]^+$, 67$[C_4F]^+$, 51$[CHF_2]^+$, 39$[C_3H_3]^+$.

2,4,4,5,5-Pentafluoro-2-(bromodifluoromethyl)-3-oxathiolane-1,1-dioxide (18).

^{19}F NMR δ: -128.1, -125.2 (AB_q, 2F, $^2J_{FF}$ = 214 Hz, CF_2SO_2), -126.8 (s, 1F, CFO), -87.4, -83.3 (AB_q, 2F, $^2J_{FF}$ = 90 Hz, CF_2O), -68.2, -67.3 (AB_q, 2F, $^2J_{FF}$ = 14 Hz, CF_2Br).

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