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Synthesis of New Fluoroaliphatic 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.

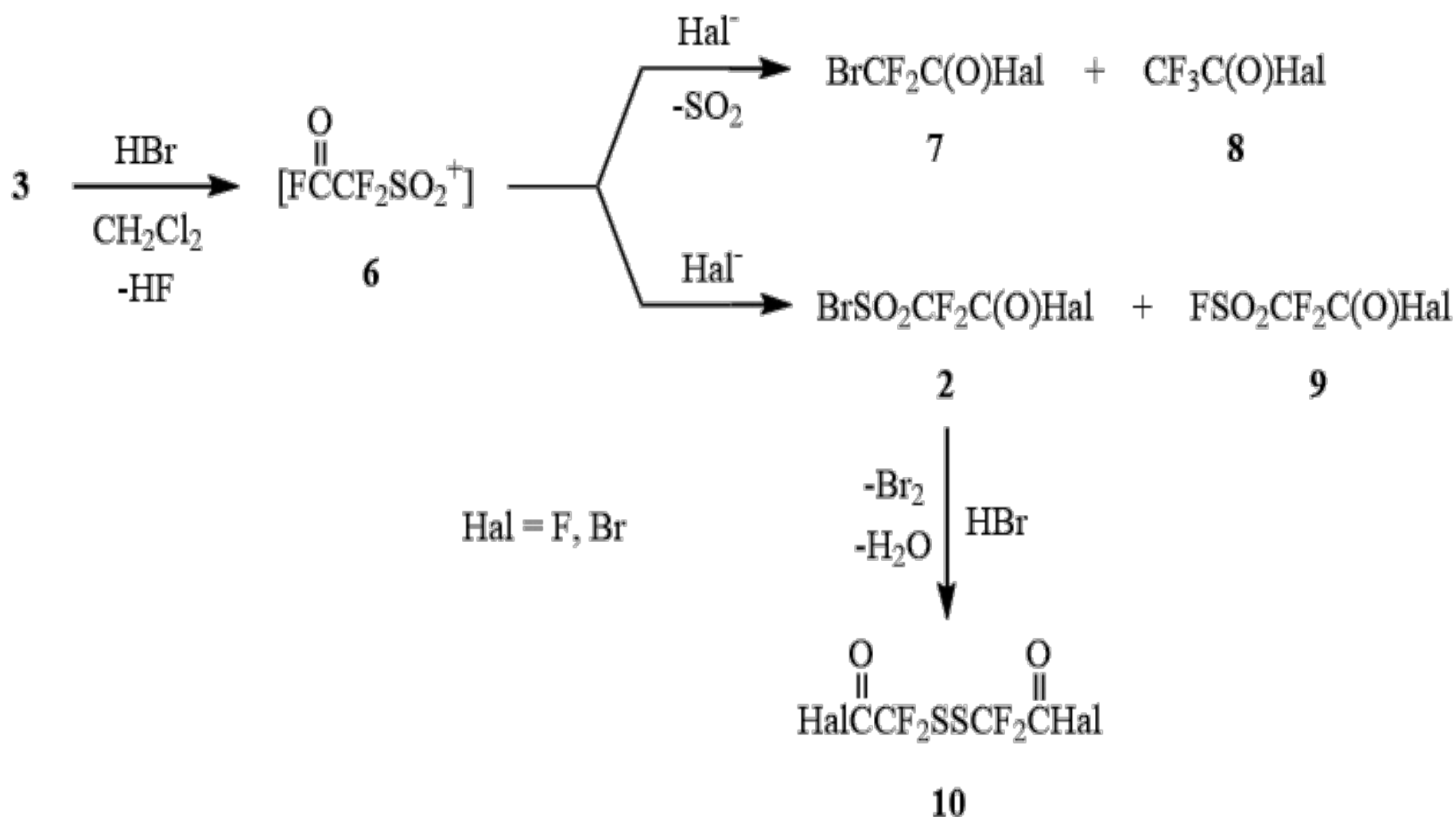
We failed to prepare bromosulfonyl difluoroacetylhalides **2** by the reaction of tetrafluoroethane- β -sultone (**3**) and anhydrous hydrogen bromide by analogy with synthesis of chlorosulfonyl difluoroacetylhalides [6]. The reaction between sultone **3** and anhydrous HBr in ether with the further 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



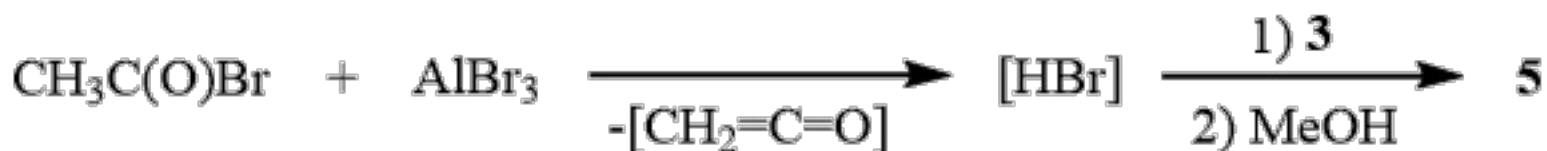
This reaction in CH_2Cl_2 results in formation of a complex mixture of products shown in Scheme 2:

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



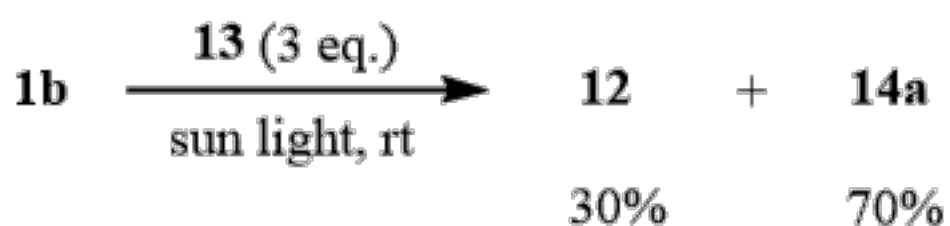
The suggested scheme is supported both by the considerable increase in the yield of sulfonyl bromides 2 (up to 40%) and by the absence of disulfide 10 among the products of the reaction between sultone 3 and HBr in the presence of bromine maintaining the oxidative medium, same as by the composition of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

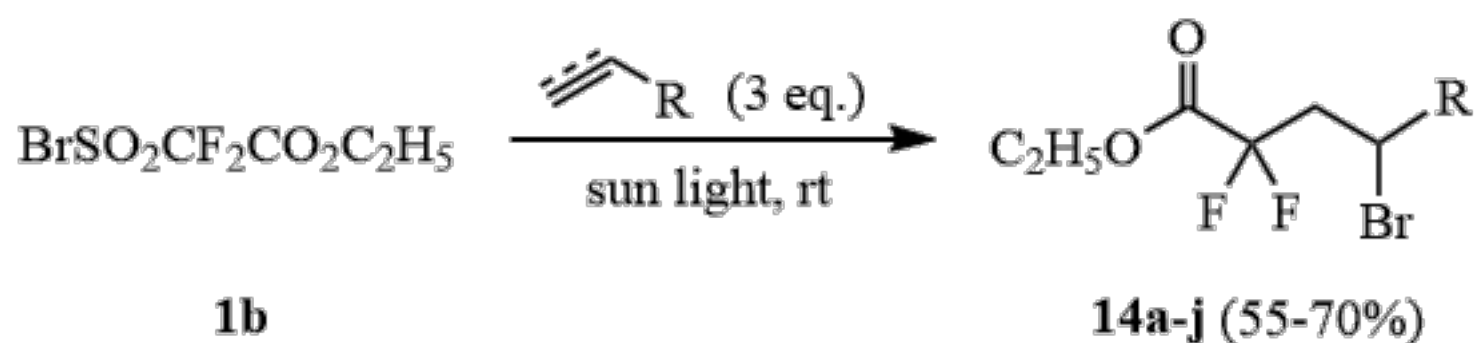


The further studies showed that illumination of the mixture of 1b:13 at the molar ratio of 1:3 by sunlight in a sealed ampoule for 10-12 h results in formation of adduct 14a in the yield of 70%.

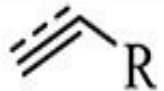
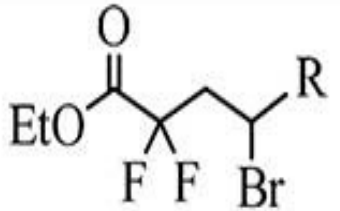
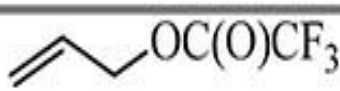
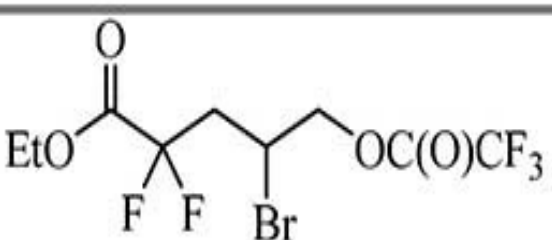
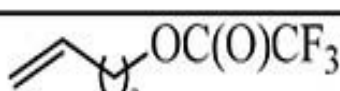
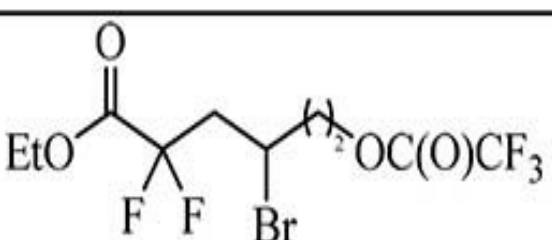

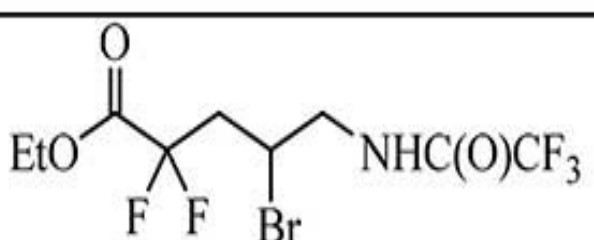
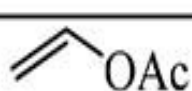
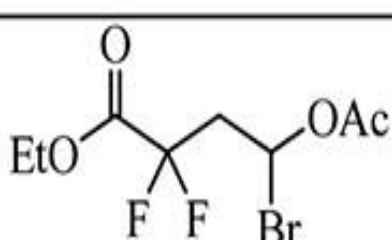
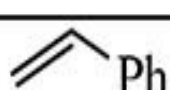
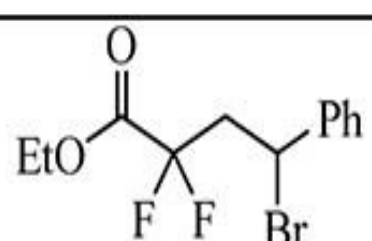
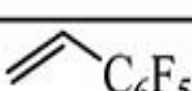
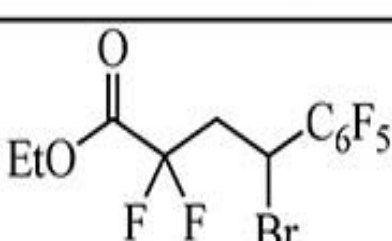


Adducts 14b-j of sulfonyl bromide 1b with other unsaturated hydrocarbon compounds were obtained in a similar way. The structure and yields of the obtained compounds are presented in Table 1.

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



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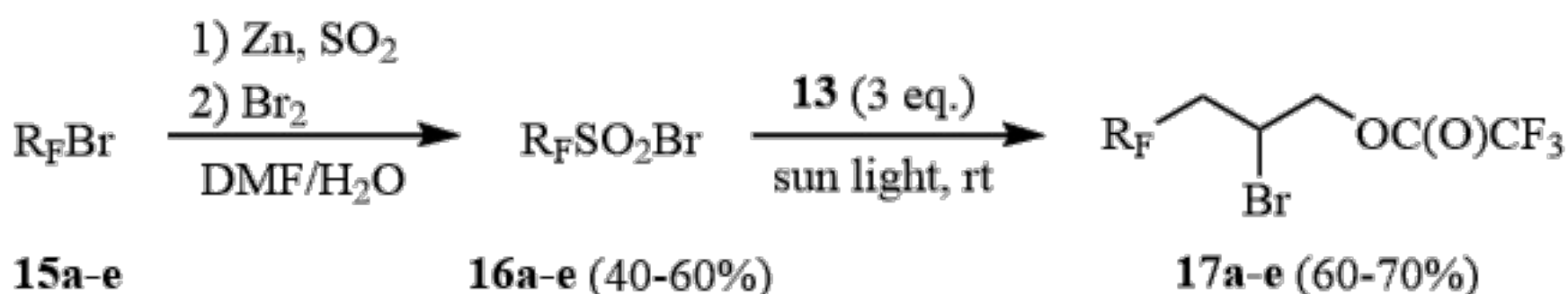
№ п/п			№ в-ва	Выход, %
1			14a	70
2			14b	70
3			14c	60
4			14d	65
5			14e	60
6			14f	60

			14g	65
8			14h	65
9			14i	55
10			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/SO₂ 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



R_F =

a: -CF₂CF₂OCF=CF₂

b: -CF₂CF₂OCF(CF₃)CO₂Me

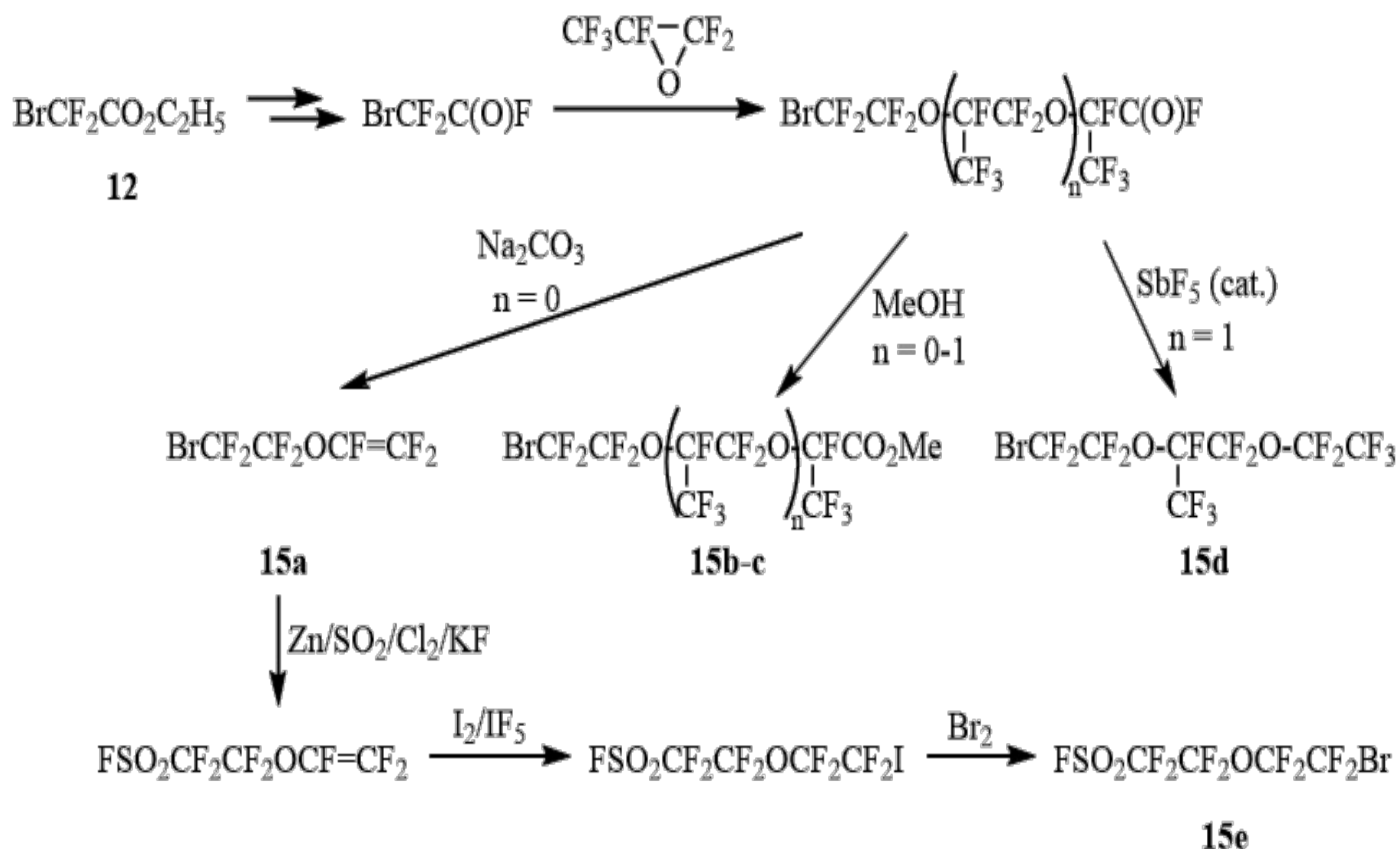
c: -CF₂CF₂OCF(CF₃)CF₂OCF(CF₃)CO₂Me

d: -CF₂CF₂OCF(CF₃)CF₂OCF₂CF₃

e: -CF₂CF₂OCF₂CF₂SO₂F

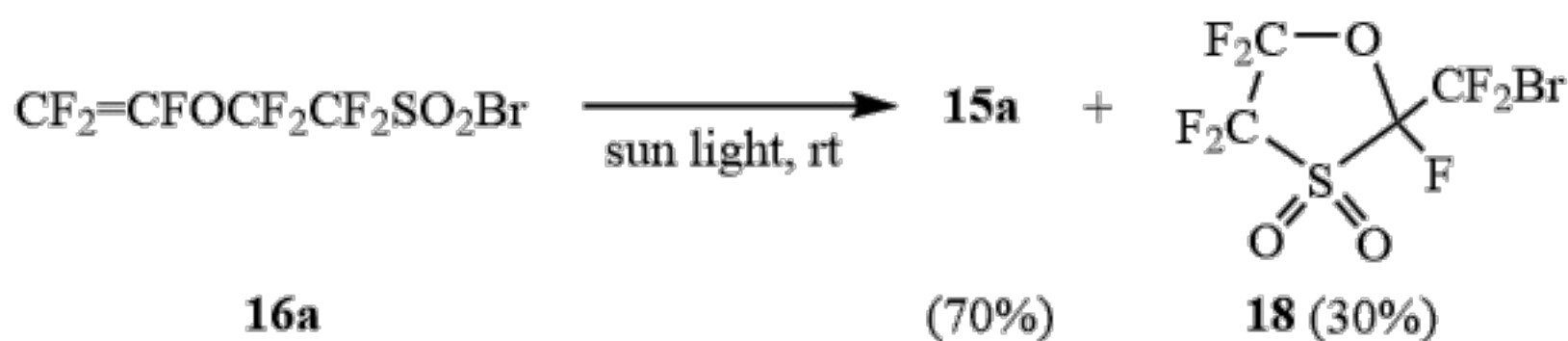
The initial bromides **15a-e** are obtained on the basis of bromodifluoroacetate **12** through a series of transformations shown in Scheme 9 [8-11]:

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 SO₂ across C-Br bond in fluoroaliphatic bromides can be considered as a latent form of its activation, which allows to compensate the relatively low reactivity of fluoroaliphatic bromides in the reactions of radical addition.

Experimental

¹H, ¹⁹F NMR spectra were recorded using a Bruker AVANCE-300 spectrometer at 300 and 282 MHz, accordingly; the external standard was CDCl₃. 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 ¹⁹F spectra are given in ppm vs. CFCl₃. 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 ^1H , ^{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 ^1H and ^{19}F NMR data, the esters 5 and 4. The mass spectrum of bis(methoxycarbonyl difluoromethyl)disulfide (5) (M/Z, reference): 297[M+CH₃]⁺, 282[M]⁺, 263[M-F]⁺, 235[C₅H₃F₄O₂S₂]⁺, 218[M-2S]⁺(100%), 195[C₅H₆FO₂S₂]⁺, 181[C₅H₆FO₄S]⁺, 154[C₃H₃FO₂S₂]⁺, 141[C₃HF₂OS]⁺, 124[C₂HFOS₂]⁺, 121[C₃H₂FO₂S]⁺, 114[CF₂S₂]⁺, 109[C₃F₃O]⁺, 93[C₃F₃]⁺, 82[CF₂S]⁺, 81[C₂F₃]⁺, 64[S₂]⁺, 63[CFS]⁺, 59[C₂H₃O₂]⁺, 45[CHS]⁺.

Reaction of Tetrafluoroethane- β -Sultone (3) with HBr in CH₂Cl₂.

Tetrafluoroethane- β -sultone (3) (18 g, 0.1 mol) is added dropwise to the solution of anhydrous HBr (24 g, 0.3 mol) in CH₂Cl₂ (100 ml) at -50°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 NaHCO₃ solution to give 12.4 g of a mixture of esters 1a, 4, 5, FSO₂CF₂CO₂Me, and CF₃CO₂Me identified by GLC, ^{19}F NMR and chromatomass spectrometry methods.

Reaction of Tetrafluoroethane- β -Sultone (3) with AlBr₃ in CH₃C(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°C, stirred for 30 min, then dry methanol is added dropwise; the whole is heated to 20÷25°C, the reaction mass is poured onto ice, the organic layer is separated, washed with dilute aqueous NaHCO₃ solution to give 12.7 g of ester 5 (90%).

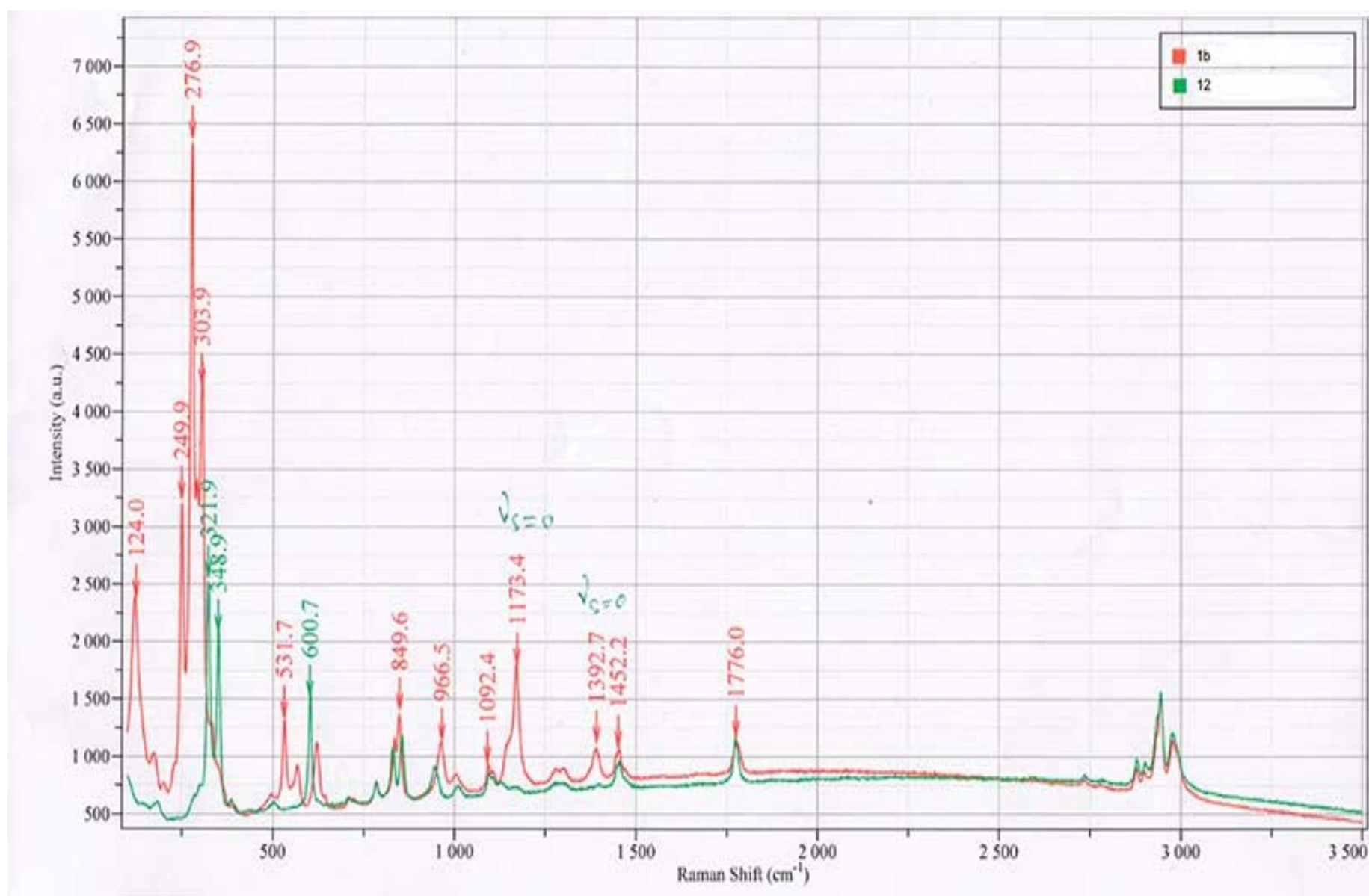
Sulfodioxidation of Ethyl Bromodifluoroacetate (12).

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 SO₂ (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 P₂O₅ 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; Br, 30.18; F, 14.20; S, 11.78. C₄H₅BrF₂O₄S. Calculated (%): C, 17.99; H, 1.89; Br, 29.92; F, 14.23; S, 12.01. ^1H NMR δ : 1.6 (t, 3H, CH₃), 4.7 (q, 2H, CH₂); ^{19}F NMR δ : -101 (s, CF₂). The mass spectrum (M/Z, reference): 267[M+H]⁺, 239[C₂H₂BrF₂O₄S]⁺, 203[C₄H₆BrF₂O₂]⁺, 175[C₃H₆BrF₂O]⁺, 59[C₂H₃O₂]⁺(100%), 51[CF₂H]⁺, 29[C₂H₅]⁺.

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. 1H NMR δ : 1.3 (t, 3H, CH_3), 2.8 (dt, 2H, CH_2CF_2), 4.3 (q, 2H, CH_2CH_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, CF_2CO_2Et), -77 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 357[M+H]⁺, 277[M-Br]⁺, 249[C₇H₆F₅O₄]⁺, 243[C₇H₁₀BrF₂O₂]⁺, 215[C₆H₁₀BrF₂O]⁺, 195[C₅H₂BrF₂O]⁺, 169[C₄H₄BrF₂]⁺, 163[C₇H₉F₂O₂]⁺, 135[C₅H₅F₂O₂]⁺(100%), 115[C₅H₄FO₂]⁺, 107[C₄H₅F₂O]⁺, 91[C₄H₅F₂]⁺, 90[C₄H₄F₂]⁺, 71[C₄H₄F]⁺, 69[CF₃]⁺, 51[CF₂H]⁺.

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

B.p. 145-147°C/10 torr. 1H NMR δ : 1.3 (t, 3H, CH_3), 2.1-2.5 (m, 2H, CH_2CH_2O), 2.6-3 (m, 2H, CH_2CF_2), 4.3 (m, 3H, $CHBr$, CH_2CH_3), 4.6 (m, 2H, CH_2O); ^{19}F NMR δ : -107.7, -103.3 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, CF_2CO_2Et), -77 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 371[M+H]⁺, 370[M]⁺, 291[M-Br]⁺, 263[C₉H₁₂F₅O₃]⁺, 177[C₈H₁₁F₂O₂]⁺, 149[C₆H₇F₂O₂]⁺(100%), 129[C₆H₃F₂O]⁺, 103[C₅H₇F₂]⁺, 69[CF₃]⁺.

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

1H NMR δ : 1.4 (t, 3H, CH_3CH_2), 2.85 (dt, 2H, CH_2CF_2), 3.85 (m, 1H, $CHBr$), 4 (m, 2H, CH_2NH), 4.4 (q, 2H, CH_3CH_2), 8.5 (m, 1H, NH); ^{19}F NMR δ : -107.95, -103.05 (AB_q, 2F, $^2J_{FF}$ = 282 Hz, CF_2CO_2Et), -77.5 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 356[M+H]⁺, 276[C₉H₁₁F₅O₃N]⁺, 248[C₈H₁₁F₅O₂N]⁺, 230[C₇H₅F₅O₃N]⁺, 214[C₇H₅BrO₂N]⁺, 202[C₆H₃F₅ON]⁺(100%), 182 [C₆H₂F₄ON]⁺, 163[C₆H₂F₃ON]⁺, 135[C₄H₄F₃]⁺, 126[C₃H₃F₃ON]⁺, 112[C₂HF₃ON]⁺, 69[CF₃]⁺, 51[CHF₂]⁺.

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

B.p. 125-127°C/10 torr. ^1H NMR δ : 1.5 (t, 3H, CH_3CH_2), 2.25 (s, 3H, CH_3), 3.1-3.6 (m, 2H, CH_2CF_2), 4.6 (q, 2H, CH_3CH_2), 7 (m, 1H, CHBr); ^{19}F NMR δ : -107.4, -105.6 (AB_q , 2F, $^2J_{\text{FF}} = 282$ Hz, $\text{CF}_2\text{CO}_2\text{Et}$). The mass spectrum (M/Z, reference): 289[M+H] $^+$, 209[C₈H₁₀F₂O₄] $^+$, 167[C₆H₈F₂O₃] $^+$ (100%), 147[C₆H₇FO₃] $^+$, 51[CHF₂] $^+$, 43[C₂H₃O] $^+$.

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

^1H NMR δ : 0.9 (t, 3H, CH_3CH_2), 2.8-3.1 (m, 2H, CH_2CF_2), 3.75 (q, 2H, CH_3CH_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, $^2J_{\text{FF}} = 282$ Hz, $\text{CF}_2\text{CO}_2\text{Et}$). The mass spectrum (M/Z, reference): 227[M-Br] $^+$, 207[C₁₂H₁₂FO₂] $^+$, 187[C₁₂H₁₁O₂] $^+$, 169[C₇H₆Br] $^+$, 159[C₁₀H₄FO] $^+$, 153[C₉H₇F₂] $^+$, 133[C₉H₆F] $^+$, 131[C₆H₈FO₂] $^+$ (100%), 115[C₉H₇] $^+$, 104[C₈H₈] $^+$, 103[C₈H₇] $^+$, 51[CHF₂] $^+$.

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

B.p. 95°C/1.5 torr. ^1H NMR δ : 1.1 (t, 3H, CH_3), 2.8-3.1 (m, 2H, CH_2CF_2), 4 (q, 2H, CH_3CH_2), 5.3 (m, 1H, CHBr); ^{19}F NMR δ : -164 (m, 2F, m- $\text{F}_{\text{C}_6\text{F}_5}$), -156 (m, 1F, p- $\text{F}_{\text{C}_6\text{F}_5}$), -143 (m, 2F, o- $\text{F}_{\text{C}_6\text{F}_5}$), -109.4, -106.6 (AB_q , 2F, $^2J_{\text{FF}} = 282$ Hz, $\text{CF}_2\text{CO}_2\text{Et}$). The mass spectrum (M/Z, reference): 397[M+H] $^+$, 317[M-Br] $^+$ (100%), 297[C₁₂H₇F₆O₂] $^+$, 271[C₁₀H₂F₇O] $^+$, 269[C₁₀F₇O] $^+$, 259[C₇HBrF₅] $^+$, 249[C₁₁H₆F₅O] $^+$, 241[C₇H₂BrF₄] $^+$, 221[C₉F₆] $^+$, 194[C₈H₃F₅] $^+$, 174[C₈H₂F₄] $^+$, 161[C₇F₄] $^+$, 143[C₇HF₃] $^+$, 105[C₄H₃F₂O] $^+$, 51[CHF₂] $^+$.

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

^1H NMR δ : 1.4 (t, 3H, CH_3CH_2), 2.6-2.9 (m, 2H, CH_2CF_2), 3.4 (m, 1H, CHBr), 3.75 (s, 9H, $\text{Si}(\text{OCH}_3)_3$), 4.4 (q, 2H, CH_3CH_2); ^{19}F NMR δ : -108.95, -104.05 (AB_q , 2F, $^2J_{\text{FF}} = 282$ Hz, $\text{CF}_2\text{CO}_2\text{Et}$). The mass spectrum (M/Z, reference): 319[C₈H₁₄BrF₂O₄Si] $^+$ (100%), 299[C₈H₁₃BrFO₄Si] $^+$, 271[C₉H₁₇F₂O₅Si] $^+$, 251[C₉H₁₆BrFO₅Si] $^+$, 122[C₅H₂O₂Si] $^+$, 103[C₄HF₂O] $^+$, 91[C₃HF₂O] $^+$.

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

^1H NMR δ : 1.25 (m, 3H, CH_3CH_2), 1.6-2.6 (m, 8H, Cy), 4 (dt, 1H, CHCF_2), 4.2-4.3 (m, 2H, CH_3CH_2), 4.5 (s, 1H, CHBr); ^{19}F NMR δ : -116.5, -107.5 (AB_q , 2F, $^2J_{\text{FF}} = 282$ Hz, Z-isomer), -111.31, -110.19 (AB_q , 2F, $^2J_{\text{FF}} = 282$ Hz, $\text{CF}_2\text{CO}_2\text{Et}$, E-isomer). The mass spectrum (M/Z, reference): 285[M+H] $^+$, 233[C₈H₇BrFO₂] $^+$, 205[M-Br] $^+$ (100%), 185[C₁₀H₁₄FO₂] $^+$, 177[C₈H₁₁F₂O₂] $^+$, 157[C₈H₁₀FO₂] $^+$, 131[C₇H₉F₂] $^+$, 109[C₆H₂FO] $^+$, 91[C₆H₃O] $^+$, 81[C₆H₉] $^+$, 77[C₅HO] $^+$, 51[CHF₂] $^+$.

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

B.p. 110/1 torr. ^1H NMR δ : 0.9 (t, 3H, CH_3CH_2), 3.8 (q, 2H, CH_3CH_2), 6.5 (t, 1H, CHCF_2), 7.15 (m, 3H, m,p- $\text{H}_{\text{C}_6\text{H}_5}$), 7.3 (m, 2H o- $\text{H}_{\text{C}_6\text{H}_5}$); ^{19}F NMR δ : -94.5 (d, 2F, $^3J_{\text{FH}} = 11$ Hz, $\text{CF}_2\text{CO}_2\text{Et}$). The mass spectrum (M/Z, reference): 305[M+H] $^+$, 285[M-F] $^+$, 265[C₁₂H₁₀BrO₂] $^+$, 231[C₉H₆BrF₂] $^+$, 225[C₁₂H₁₁F₂O₂] $^+$, 213[C₉H₇BrF] $^+$ (100%), 197[C₁₁H₁₁F₂O] $^+$, 169[C₉H₇F₂O] $^+$, 151[C₉H₅F₂] $^+$, 133[C₉H₆F] $^+$, 102[C₈H₆] $^+$, 91[C₃HF₂O] $^+$, 76[C₃H₂F₂] $^+$, 75[C₃HF₂] $^+$, 63[C₂HF₂] $^+$, 50[CF₂] $^+$.

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 SO₂ (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 P₂O₅ 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°C/10 torr. Found (%): C, 14.10; F, 39.04; S, 9.05. C₄BrF₇O₃S. Calculated (%): C, 14.09; F, 39.00; S, 9.40. ^{19}F NMR δ : -137.1 (dd, 1F, $^3J_{\text{FF-trans}} = 112$ Hz, $^3J_{\text{FF-cis}} = 68$ Hz, OCF), -123.3 (dd, 1F, $^2J_{\text{FF}} = 90$ Hz, =CF-trans), -115.8 (dd, 1F, $^2J_{\text{FF}} = 90$ Hz, =CF-cis), -109.9 (s, 2F, CF₂SO₂Br), -82.9 (s, 2F, OCF₂).

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

Yield 60%, b.p. 52°C/1 torr. ^1H NMR δ : 4.1 (s, 3H, CH_3); ^{19}F NMR δ : -133.1 (m, 1F, CF), -110.2 (s, 2F, CF₂SO₂Br), -84.2 (s, 3F, CF₃), -83.4, -75.2 (AB_q , 2F, $^2J_{\text{FF}} = 143$ Hz, CF₂O).

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). ^1H NMR spectrum of 16c δ : 4.0 (s, 3H, CH_3); ^{19}F NMR δ : -146.5 (m, 1F, CF_2CF_2), -133.6 (m, 1F, $\text{CF}_2\text{CO}_2\text{Me}$), -110.3 (s, 2F, $\text{CF}_2\text{SO}_2\text{Br}$), -84.7 (m, 6F, CF_3), -88÷-80 (m, 2F, $\text{CF}_2\text{CF}_2\text{O}$), -78 (m, 2F, $\text{CF}_2\text{CF}_2\text{O}$).

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, $\text{CF}_2\text{SO}_2\text{Br}$), -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. ^{19}F NMR δ : -114.1 (m, 2F, $\text{CF}_2\text{SO}_2\text{F}$), -110.4 (s, 2F, $\text{CF}_2\text{SO}_2\text{Br}$), -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-trifluorovinylloxypentyl trifluoroacetate (17a).

Yield 70%. ^1H NMR δ : 2.75 (m, 2H, CH_2CF_2), 4.4 (m, 1H, CHBr), 4.6 (d, 2H, CH_2O); ^{19}F NMR δ : -137.6 (dd, 1F, $^3J_{\text{FF-trans}} = 112$ Hz, $^3J_{\text{FF-cis}} = 68$ Hz, OCF), -125.2 (dd, 1F, $^2J_{\text{FF}} = 90$ Hz, =CF-trans), -118.9 (m, 2F, CF_2), -117.3 (dd, 1F, $^2J_{\text{FF}} = 90$ Hz, =CF-cis), -92.5 (s, 2F, CF_2O), -77.5 (s, 3F, CF_3). The mass spectrum (M/Z, reference): 351[M-Br] $^+$, 333[C₇H₅BrF₇O₂] $^+$, 313[C₇H₄BrF₆O₂] $^+$, 297[C₇H₄BrF₆O] $^+$, 279[C₇H₃BrF₅O] $^+$, 269[C₇HBrF₃O₃] $^+$, 249[C₇BrF₂O₃] $^+$, 219[C₅H₄BrF₄] $^+$, 199[C₅H₃BrF₃] $^+$, 189[C₅H₅F₄O₃] $^+$, 169[C₄H₄BrF₂] $^+$, 157[C₅H₅F₄O] $^+$, 155[C₃H₂BrF₂] $^+$, 145[C₄H₅F₄O] $^+$, 139[C₅H₃F₄] $^+$, 109[C₄H₄F₃] $^+$, 95[C₃H₅F₂O] $^+$, 77[C₃H₃F₂] $^+$, 69[CF₃] $^+$ (100%), 51[CHF₂] $^+$.

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

Yield 70%. ^1H NMR δ : 2.8 (m, 2H, CH_2CF_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, CF_2CH_2), -93.4, -86.0 (AB_q, 2F, $^2J_{\text{FF}} = 143$ Hz, CF_2O), -84.7 (s, 3F, CF_3), -77.5 (s, 3F, CF_3CO_2). The mass spectrum (M/Z, reference): 523[M+CH₃] $^+$, 449[C₉H₅BrF₁₁O₃] $^+$, 429[M-Br] $^+$, 409[C₁₁H₇F₁₀O₅] $^+$, 375[C₁₀H₄BrF₁₁O₄] $^+$, 355[C₁₀H₃BrF₁₀O₄] $^+$, 335[C₁₀H₂BrF₉O₄] $^+$, 315[C₉H₇F₈O₃] $^+$, 295[C₉H₆F₇O₃] $^+$ (100%), 275[C₉H₅F₆O₃] $^+$, 233[C₇H₄F₆O₂] $^+$, 199[C₅H₃BrF₃] $^+$, 169[C₄H₄BrF₂] $^+$, 151[C₄H₅BrF] $^+$, 131[C₄H₄Br] $^+$, 89[C₄H₃F₂] $^+$, 69[CF₃] $^+$, 59[C₂H₃O₂] $^+$.

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

Mixture of stereoisomers, yield 60%. ^1H NMR δ : 3.1 (m, 2H, CH_2CF_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, CF_2CF_2), -133.5 (m, 1F, $\text{CF}_2\text{CO}_2\text{Me}$), -118.8 (m, 2F, CF_2CH_2), -88÷-80 (m, 4F, $\text{CF}_2\text{OCF}_2\text{CF}_2\text{O}$), -84.5 (s, 3F, CF_3), -81.8 (s, 3F, CF_3), -77.4 (m, 3F, CF_3CO_2). The mass spectrum (M/Z, reference): 595[M-Br] $^+$, 540[C₁₂H₆BrF₁₃O₄] $^+$, 521[C₁₂H₆BrF₁₂O₄] $^+$, 461[C₁₂H₆F₁₃O₄] $^+$, 441[C₁₂H₅F₁₂O₄] $^+$, 325[C₇H₃F₁₀O₃] $^+$, 297[C₉H₅F₈O₂] $^+$, 199[C₅H₃BrF₃] $^+$, 150[C₃F₆] $^+$, 131[C₃F₅] $^+$ (100%), 119[C₅H₂F₃] $^+$, 81[C₂F₃] $^+$, 69[CF₃] $^+$, 59[C₂H₃O₂] $^+$, 51[CHF₂] $^+$, 39[C₃H₃] $^+$.

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

Yield 65%. ^1H NMR δ : 3.1 (m, 2H, CH_2CF_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, CF_2CH_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_3CO_2), -77.4 (s, 3F, CF_3CO_2). The mass spectrum (M/Z, reference): 615[M-F] $^+$, 555[M-Br] $^+$, 521[C₁₀H₅BrF₁₅O₂] $^+$, 501[C₁₀H₅BrF₁₄O₂] $^+$, 419[C₁₀H₂F₁₄O₂] $^+$, 255[C₇H₃F₈O] $^+$, 219[C₅H₄BrF₄] $^+$, 199[C₅H₃BrF₃] $^+$, 169[C₄H₄BrF₂] $^+$, 155[C₃H₂BrF₂] $^+$, 139[C₅H₃F₄] $^+$, 119[C₅H₂F₃(C₂F₅)] $^+$, 95[C₃H₂F₃] $^+$, 89[C₄H₃F₂] $^+$, 77[C₃H₃F₂] $^+$, 69[CF₃] $^+$ (100%), 51[CHF₂] $^+$.

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

Yield 60%. ^1H NMR δ : 3.1 (m, 2H, CH_2CF_2), 4.9 (m, 1H, CHBr), 5.1 (m, 2H, CH_2O); ^{19}F NMR δ : -118.9 (m, 2F, CF_2CH_2), -114.1 (s, 2F, $\text{CF}_2\text{SO}_2\text{F}$), -89.7 (m, 2F, CF_2O), -83.9 (m, 2F, CF_2O), -77.2 (s, 3F, CF_3CO_2), 43.2 (m, 1F, SO_2F). The mass spectrum (M/Z, reference): 453[M-Br] $^+$, 418[C₇H₄BrF₉O₃S] $^+$, 398[C₇H₃BrF₈O₃S] $^+$, 379[C₇H₃BrF₇O₃S] $^+$, 335[C₇H₄BrF₈O] $^+$, 317[C₇H₄BrF₇O] $^+$, 273[C₇H₅F₈O₂] $^+$, 253[C₇H₄F₇O₂] $^+$, 233[C₇H₃F₆O₂] $^+$, 213[C₇H₂F₅O₂] $^+$, 199[C₅H₃BrF₃] $^+$, 183[C₂F₅O₂S] $^+$, 169[C₄H₄BrF₂] $^+$, 155[C₃H₂BrF₂] $^+$, 139[C₅H₃F₄] $^+$ (100%), 119[C₅H₂F₃] $^+$, 117[C₃H₂Br] $^+$, 109[C₄H₄F₃] $^+$, 100[C₂F₄] $^+$, 95[C₃H₂F₃] $^+$, 89[C₄H₃F₂] $^+$, 69[CF₃] $^+$, 67[C₄F] $^+$, 51[CHF₂] $^+$, 39[C₃H₃] $^+$.

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, $^2J_{\text{FF}} = 214$ Hz, CF_2SO_2), -126.8 (s, 1F, CFO), -87.4, -83.3 (AB_q, 2F, $^2J_{\text{FF}} = 90$ Hz, CF_2O), -68.2, -67.3 (AB_q, 2F, $^2J_{\text{FF}} = 14$ Hz, CF_2Br).

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