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Novel efficient synthesis of β-fluoro-β-(trifluoromethyl)styrenes

Aleksey A. Goldberg [a], Vasiliy M. Muzalevskiy [a], Aleksey V. Shastin [b], Elisabeth S. Balenkova [a], Valentine G. Nenajdenko [a,*]

[a] Moscow State University, Department of Chemistry, Leninskie Gory, Moscow 119992, Russia
[b] Institute of Problems of Chemical Physics, Chernogolovka, Moscow Region 142432, Russia

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ABSTRACT

CF_3CFBr_2 was employed in catalytic olefination reactions of aromatic aldehydes. *In situ* prepared hydrazones of aldehydes were transformed to β-fluoro-β-(trifluoromethyl)styrenes by reaction with CF_3CFBr_2 under CuCl catalysis. Based on this reaction, a novel stereoselective approach towards β-fluoro-β-(trifluoromethyl)styrenes was elaborated. Nucleophilic vinylic substitution of fluorine by secondary amines, thiolates and alkoxides in β-fluoro-β-(trifluoromethyl)styrenes was also tested.

1. Introduction

Fluorinated compounds were intensively investigated in recent decades [1,2] due to their unique physical and biological properties caused by the presence of fluorine substituents in the molecules [3–5]. A lot of researchers focused on the elaboration of new synthetic pathways to organofluorine compounds, which afforded an enormous progress in this field [6–8].

It is considered, that freon molecules are involved in ozon layer destruction, which is a challenging and urgent problem to be solved nowadays. On the other hand tremendous stocks of freons were accumulated during last century, which need to be utilized. Several strategies were developed for processing of freons into compounds, which are less destructive for the ozon layer. Among them are the catalytic decomposition or full mineralization [9–11], partial reduction to less harmful fluorohydrocarbons (FHCs) [12–13]; and transformation to useful simple fluorinated synthons [14–15]. The last strategy is very attractive from the economical point of view, because it combines neutralization of environmentally dangerous materials with the elaboration of new perspective synthetic building blocks. Here we would like to present a novel olefination technique of aromatic aldehydes by freon CF_3CFBr_2 as a successful realization of the mentioned strategy.

2. Results and discussion

2.1. Reactions of CF_3CFBr_2 with hydrazones of aromatic aldehydes

About a decade ago, a new catalytic olefination reaction (COR) of aldehydes and ketones was discovered by our research group. It was found, that unsubstituted hydrazones of carbonyl compounds can be efficiently transformed into alkenes by treatment with polyhalogenalkanes in the presence of a base and catalytic amount of copper salts [16–21]. This reaction has a general character and became a reliable technique for stereoselective construction of carbon–carbon double bonds [22]. A range of convenient stereoselective methods for the preparation of various fluorinated alkenes were elaborated using *one-pot* COR protocol for olefination of carbonyl compounds by freons. Thus, employing of CF_3CCl_3, $CF_2ClCFCl_2$, $CFCl_3$, CF_2Cl_2, CF_3CBr_3 and $CFBr_3$ afforded a set of novel approaches towards β-chloro-β-(trifluoromethyl)styrenes [23], β-fluoro-β-(chlorodifluoromethyl)styrenes [23], β-chloro-β-fluorostyrenes [24], *gem*-difluoroalkenes [25], β-bromo-β-(trifluoromethyl)styrenes [26] and β-bromo-β-fluorostyrenes [27]. Additionally, unusual COR direction was found, when the reaction with $BrCF_2CF_2Br$ was investigated. Saturated fluorinated alkane derivatives were isolated instead of expected alkene ones [28].

Having such good background results, we decided to involve CF_3CFBr_2 into COR-type transformation too. In addition, this freon was not thoroughly investigated and only few examples of its reactivity can be found in literature. Addition of CF_3CFBr_2 to the alkene double bond afforded corresponding fluorinated alkanes

* Corresponding author. Tel.: +7 495 9328846; fax: +7 495 9328846.
E-mail address: nen@acylium.chem.msu.ru (V.G. Nenajdenko).

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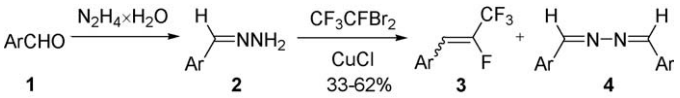


Scheme 1.

[29–33]. Treatment of CF_3CFBr_2 with zinc and magnesium provided an access to 1,2,2-trifluorovinylzinc [34] and 1,2,2-trifluorovinylmagnesium [35]. Reduction of one [36] or both [37] C–Br bonds into C–H was also reported. Finally, CF_3CFBr_2 was also used for the bromination of enolates [38] and organomagnesium compounds [39].

Accordingly to our previous experience of olefination by freons, CF_3CFBr_2 was expected to be a moderately reactive polyhalogenalkane. So we choose a *one-pot* COR protocol with ethylenediamine as a base in ethanol solution. We found that CF_3CFBr_2 reacted smoothly with prepared *in situ* hydrazones of aromatic aldehydes **2** to form β-fluoro-β-(trifluoromethyl)styrenes **3** in moderate to good yields (Scheme 1, Table 1). According to TLC the only side products of the reaction were corresponding *sym*-azines **4**, which were not isolated and their yields were not determined. The transformation revealed its general character and a wide range of alkenes **3** both with electron-donating and electron-withdrawing substituents were prepared using this method.

The reaction proceeded highly stereoselectively to give mostly the *Z*-isomers of styrenes **3**. The amount of minor *E*-isomers of **3** in a mixture was less than 11% in the case of **3f** and dropped to 3% for **3j**. This result is in a good agreement with the very well known tendency of COR to form the less hindered stereoisomer [22]. Aryl and trifluoromethyl groups are the most bulky ones in compounds **3**, which make the *trans*-arrangement of these groups most favorable. As a result, the *Z*-isomer of **3** dominates in the reaction mixture. The assignment of the configuration of isomers was made by NMR spectroscopy. It is well known, that coupling constants between atoms at double bond in *cis*-position are smaller than in *trans*-position. The configuration of isomers was determined by comparison of $^3J_{H,F}$ coupling constants between fluorine and the vinylic proton in ^1H NMR spectra of fluoroalkenes **3**. The values range from 32.5 to 36.3 Hz for *Z*-isomers and from 18.2 to 21.6 Hz for *E*-isomers (Fig. 1).

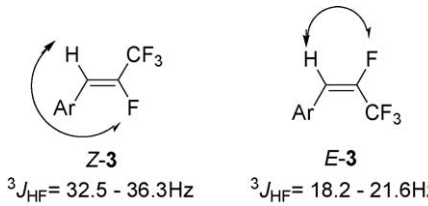


Fig. 1. Assignment of configuration of isomeric alkenes **3**.

We can proudly announce, that the proposed method is a very good alternative to the previously reported approaches to β-fluoro-β-(trifluoromethyl)styrenes. Few publications dealt with synthesis of β-fluoro-β-(trifluoromethyl)styrenes. Thus, reduction of 1-phenylpentafluoropropene with $LiAlH_4$ [40], protonation of β-fluoro-β-trifluoromethyl-α-phenylvinylstannanes [41], reaction of β-fluoro-β-bromostyrenes with trifluoromethyl anion [42], reactions of trifluorovinyllithium [43] and trifluorovinylsilanes [44] with aromatic aldehydes were used for the preparation of these alkenes. In contrast to the mentioned approaches, our method is an extremely simple, straightforward transformation, which does not need to use absolute solvents, expensive or toxic reagents. High stereoselectivity and good yields are other advantages of our method.

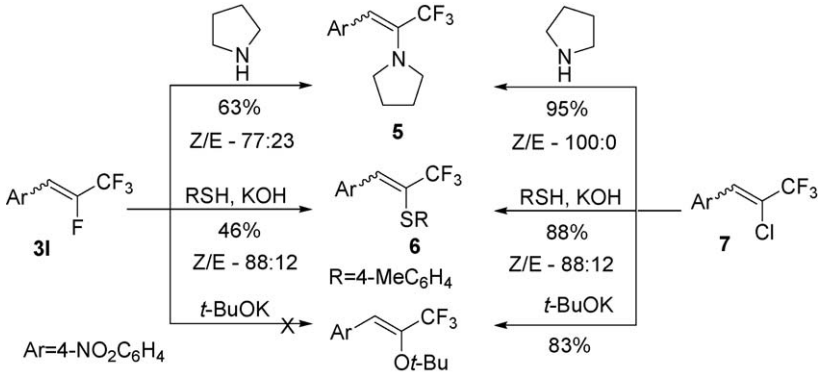
2.2. Reactions of β-fluoro-β-(trifluoromethyl)styrenes 3 with nucleophiles

Previously, in a series of publications we investigated nucleophilic vinylic substitution of β-halogen atom by *C*-, *S*- and *O*-nucleophiles in β-bromo-β-fluorostyrenes, β-chloro- and β-bromo-β-(trifluoromethyl)styrenes. We found that such substitution proceeds easily to give various fluorinated alkenes. Thus, these

Table 1
Synthesis of β-fluoro-β-(trifluoromethyl)styrenes **3**.

Styrene **3**	Ar	*Z*/*E* ratio[a]	Yield, %	Styrene **3**	Ar	*Z*/*E* ratio[a]	Yield, %
a	4-ClC_6H_4	93:7	52	**g**	2-$NO_2C_6H_4$	91:9	48
b	4-BrC_6H_4	92:8	53	**h**	4-(*n*-BuO)C_6H_4	94:6	49
c	2,4-diClC_6H_3	94:6	53	**i**	4-$MeOC_6H_4$	95:5	47
d	4-MeC_6H_4	93:7	61	**j**	4-$MeCO_2C_6H_4$	97:3	62
e	4-EtC_6H_4	94:6	51	**k**	4-$CF_3C_6H_4$	95:5	33
f	3-$NO_2C_6H_4$	89:11	61	**l**	4-$NO_2C_6H_4$	90:10	66

[a] Determined by ^1H and ^{19}F NMR spectroscopy.



Scheme 2. Reactions of β-fluoro-β-(trifluoromethyl)styrene **3l** and β-chloro-β-(trifluoromethyl)styrene **7** with nucleophiles.

reactions resulted in a number of novel convenient approaches to α-fluoro- and α-trifluoromethylacrylonitriles [45], α-fluoro-β-arylvinyl sulfones [46], trifluoromethyl(vinylsulfides) [47], alkoxy-β-(trifluoromethyl)styrenes [48], α-trifluoromethyl-β-aryl enamines and vinylogous guanidium salts [49].

A very interesting fundamental question is: which halogen is more easily substituted in the case of vinylic nucleophilic substitution, fluorine or chlorine? We decided to examine nucleophilic vinylic substitution in β-fluoro-β-(trifluoromethyl)-styrenes **3**. It was found that styrenes **3** are less reactive than β-chloro and β-bromo-β-(trifluoromethyl)styrenes. Thus, the reaction of styrene **3l** with pyrrolidine and 4-methylphenylthiolate gave enamine **5** and vinylsulfide **6** in lower yields, comparing with chlorostyrene **7** [47,49]. In addition, the formation of a mixture of diastereomers of enamine **5** was observed, although chlorostyrene **7** gave only the *Z*-isomer of **5**. In contrast to chlorostyrene **7** [48], the reaction of **3l** with *tert*-BuOK did not afforded any isolatable products at all. We assume, that lower reactivity of **3l** comparing with the corresponding chlorostyrene **7** is explained by different mobility of fluorine and chlorine atoms. Therefore, fluorine is harder to substitute, which results in lower yields of substitution products (Scheme 2).

3. Conclusion

Using *one-pot* COR protocol a novel efficient method for the preparation of β-fluoro-β-(trifluoromethyl)styrenes from aromatic aldehydes and CF_3CFBr_2 was elaborated. High stereoselectivity, good yields and simplicity are advantages of the mentioned method. Nucleophilic vinylic substitution of the fluorine atom in β-fluoro-β-(trifluoromethyl)styrenes was also investigated. We found that β-fluoro-β-(trifluoromethyl)styrenes are less reactive than β-chloro and β-bromo-β-(trifluoromethyl)styrenes.

4. Experimental

NMR spectra were recorded on Bruker AMX Avance 400 spectrometer in $CDCl_3$ with TMS and CCl_3F as internal standards. Mass spectra (ESI-MS) were measured on a MicroTof Bruker Daltonics. IR spectra were recorded on ThermoNicolet IR 200. Bruker TLC was performed using 25-DC-Alufoil with Kieselgel 60 F_{254} (Merck). Fluka Silica gel 60 (0.063–0.200 mm) was used for column chromatography. Commercial reagents and solvents were generally used as received.

4.1. General procedure for synthesis of (2,3,3,3-tetrafluoroprop-1-enyl)arenes (3a–k)

Round bottomed 100 mL flask was charged with hydrazine hydrate (0.5 mL, 10 mmol), EtOH (10 mL) and solution of aromatic aldehyde (10 mmol) in EtOH (20 mL) was added dropwise with stirring. After aldehyde disappeared (overnight, TLC monitoring), freshly purified CuCl [50] (100 mg, 1 mmol) and 1,2-ethylenediamine (2 mL, 30 mmol) were added. The reaction mixture was cooled down to 5–10 °C and CF_3CFBr_2 (2.2 mL, 20 mmol) was added dropwise. After stirring at r.t. for 2 h and at 35 °C for 2 h, the reaction mixture was quenched with 5% aq. HCl (150 mL) and the reaction products were extracted with CH_2Cl_2 (3× 50 mL). Combined extracts were washed with water (50 mL) and dried over Na_2SO_4. CH_2Cl_2 was removed in vacuo and the residue was purified by column chromatography using hexane–CH_2Cl_2 mixture (4:1) as eluent. *E* and *Z* isomers of alkenes could not be separated by column chromatography. ^{13}C NMR spectra of the minor *E*-isomers are not given, because corresponding signals were not found in ^{13}C NMR spectra of the isomeric mixtures due to their low concentration.

4.1.1. 1-Chloro-4-(2,3,3,3-tetrafluoroprop-1-enyl)benzene (3a)

Obtained as a 93:7 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.7; IR (nujol) 1590, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.35 (d, J = 35.1 Hz, =CH–, 1H), 7.40 (d, J = 8.6 Hz, 2H, Ar), 7.52 (d, J = 8.6 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −131.12 (dq, J = 35.1 Hz, J = 10.9 Hz, F), −72.13 (d, J = 10.9 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.34, 118.80 (qd, J_{CF} = 271.5 Hz, J_{CF} = 41.0 Hz, CF_3), 128.09 (d, J_{CF} = 3.7 Hz), 128.67, 129.08, 130.85 (d, J_{CF} = 7.3 Hz), 135.68, 145.33 (dq, J_{CF} = 267.9 Hz, J_{CF} = 38.8 Hz, CF); *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, J = 20.5 Hz, 1H, =CH–), 7.22 (d, J = 8.5 Hz, 1H, Ar), 7.37(1H, d, J = 8.5 Hz, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −123.55 (dq, J = 20.5 Hz, J = 9.2 Hz, F), −66.77 (d, J = 9.2 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. ESI-MS (*m*/*z*): calcd. for $C_9H_5ClF_4$ [M^+] 224.0016, found 224.0016.

4.1.2. 1-Bromo-4-(2,3,3,3-tetrafluoroprop-1-enyl)benzene (3b)

Obtained as a 92:8 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.6; IR (nujol) 1590, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.30 (d, J = 35.1 Hz, 1H, =CH–), 7.42 (d, J = 8.3 Hz, 2H, Ar), 7.53 (d, J = 8.3 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −130.73 (dq, J = 35.1 Hz, J = 11.2 Hz, F), −72.13 (d, J = 11.2 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.49, 118.81 (qd, J_{CF} = 272.3 Hz, J_{CF} = 40.5 Hz, CF_3), 125.84 (d, J_{CF} = 3.7 Hz), 129.64, 131.08 (d, J_{CF} = 7.6 Hz), 132.14, 136.51, 145.42 (dq, J_{CF} = 268.1 Hz, J_{CF} = 38.1 Hz, CF); *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, J = 20.5 Hz, 1H, =CH–), 7.13 (d, J = 8.1 Hz, 1H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −123.36 (dq, J = 20.5 Hz, J = 9.2 Hz, F), −66.76 (d, J = 9.2 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. Anal. Calcd. for $C_9H_5BrF_4$: C 40.18; H 1.87. Found: C 40.35; H 1.97.

4.1.3. 2,4-Dichloro-1-(2,3,3,3-tetrafluoroprop-1-enyl)benzene (3c)

Obtained as a 94:6 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.7; IR (nujol) 1600, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, J = 34.6 Hz, 1H, =CH–), 7.32 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H, Ar), 7.48 (d, J = 2.0 Hz, 1H, Ar), 7.77 (d, J = 8.5 Hz, 1H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −129.96 (dq, J = 34.6 Hz, J = 10.6 Hz, F), −72.25 (d, J = 10.6 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.52, 118.54 (qd, J_{CF} = 271.5 Hz, J_{CF} = 41.0 Hz, CF_3), 126.28 (d, J_{CF} = 4.4 Hz), 127.56, 129.75, 131.38 (d, J_{CF} = 12.4 Hz), 134.74, 136.01, 146.35 (dq, J_{CF} = 271.5 Hz, J_{CF} = 38.8 Hz, CF); *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, J = 19.1 Hz, 1H, =CH–); ^{19}F NMR (377 MHz, $CDCl_3$) δ −121.78 (dq, J = 19.1 Hz, J = 9.5 Hz, F), −66.71 (d, J = 9.5 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. Anal. Calcd. for $C_9H_4Cl_2F_4$: C 41.73; H 1.56. Found: C 41.58; H 1.67.

4.1.4. 1-Methyl-4-(2,3,3,3-tetrafluoroprop-1-enyl)benzene (3d)

Obtained as a 93:7 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.6; IR (nujol) 1610, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H, Me), 6.37 (d, J = 36.0 Hz, 1H, =CH-), 7.27 (d, J = 7.8 Hz, 2H, Ar), 7.51 (d, J = 7.8 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −133.16 (dq, J = 36.0 Hz, J = 11.5 Hz, F), −71.94 (d, J = 11.5 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.28, 111.40, 119.04 (qd, J_{CF} = 271.5 Hz, J_{CF} = 41.0 Hz, CF_3), 126.85 (d, J_{CF} = 3.7 Hz), 129.58, 129.62, 129.71 (d, J_{CF} = 7.3 Hz), 139.91, 144.43 (dq, J_{CF} = 265.7 Hz, J_{CF} = 38.8 Hz, CF); *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, J = 21.2 Hz, 1H, =CH–); ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.71 (d, J = 9.8 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. NMR data are in agreement to literature [44].

4.1.5. 1-Ethyl-4-(2,3,3,3-tetrafluoroprop-1-enyl)benzene (3e)

Obtained as a 94:6 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.7; IR (nujol) 1610, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.6 Hz, 3H, Me), 2.73 (q, J = 7.6 Hz,

2H, $-CH_2-$), 6.38 (d, J = 36.0 Hz, 1H, =CH–), 7.30 (d, J = 8.1 Hz, 2H, Ar), 7.55 (d, J = 8.1 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −133.17 (dq, J = 36.0 Hz, J = 11.5 Hz, F), −71.94 (d, J = 11.5 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.26, 28.78, 111.45, 119.10 (qd, J_{CF} = 270.8 Hz, J_{CF} = 41.0 Hz, CF_3), 127.14 (d, J_{CF}b = 3.7 Hz), 128.44, 129.84 (d, J_{CF} = 7.3 Hz), 145.33 (dq, J_{CF} = 265.7 Hz, J_{CF} = 38.8 Hz, CF), 146.29; *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 21.5 Hz, 1H, =CH–); ^{19}F NMR (377 MHz, $CDCl_3$) δ −125.58 (dq, J = 21.4 Hz, J = 9.8 Hz, F), −66.72 (d, J = 9.8 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. Anal. Calcd for $C_{11}H_{10}F_4$: C 60.55; H 4.62. Found: C 60.67; H 4.53.

4.1.6. 1-Nitro-3-(2,3,3,3-tetrafluoropropen-1-yl)benzene (3f)

Obtained as a 89:11 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane–CH_2Cl_2 2:1) 0.5; IR (nujol) 1350, 1540 (NO_2); 1610, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.40 (d, J = 34.0 Hz, 1H, =CH–), 7.61 (t, J = 8.0 Hz, 1H, Ar), 7.89 (d, J = 8.0 Hz, 1H, Ar), 8.23 (ddd, J = 8.0 Hz, J = 2.1 Hz, J = 0.9 Hz, 1H, Ar), 8.41 (s, 1H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −127.81 (dq, J = 34.0 Hz, J = 10.6 Hz, F), −72.33 (d, J = 10.6 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.61, 118.39 (qd, J_{CF} = 272.3 Hz, J_{CF} = 41.0 Hz, CF_3), 124.21, 124.31 (d, J_{CF} = 8.1 Hz), 130.02, 131.14 (d, J_{CF} = 2.9 Hz), 135.22 (d, J_{CF} = 7.3 Hz), 146.71 (dq, J_{CF} = 271.5 Hz, J_{CF} = 38.8 Hz, CF), 148.48; *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, J = 19.4 Hz, 1H, =CH–); ^{19}F NMR (377 MHz, $CDCl_3$) δ −120.95 (dq, J = 19.4 Hz, J = 9.2 Hz, F), −66.83 (d, J = 9.2 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. ESI-MS (*m*/*z*): calcd. for $C_9H_5F_4NNaO_2$ [M^+] 258.0154, found 258.0149.

4.1.7. 1-Nitro-2-(2,3,3,3-tetrafluoropropen-1-yl)benzene (3g)

Obtained as a 91:9 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane–CH_2Cl_2, 2:1) 0.5; IR (nujol) 1610, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 32.5 Hz, 1H, =CH–), 7.59 (td, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.72 (td, J = 7.7 Hz, J = 1.1 Hz, 1H, Ar), 7.78 (dd, J = 8.0 Hz, J = 1.1 Hz, 1H, Ar), 8.14 (d, J = 8.1 Hz, 1H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −131.30 (dq, J = 32.5 Hz, J = 10.7 Hz, F), −72.46 (dd, J = 10.7 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.76, 118.41 (qd, J_{CF} = 272.3 Hz, J_{CF} = 41.0 Hz, CF_3), 124.14, 125.15, 130.21, 131.64 (d, J_{CF} = 8.0 Hz), 133.60, 146.30 (dq, J_{CF} = 269.3 Hz, J_{CF} = 38.8 Hz, CF), 147.71; *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 18.2 Hz, 1H, =CH–), 7.42 (d, J = 7.8 Hz, 2H, Ar), 8.22 (d, J = 7.8 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −123.61 (dq, J = 18.1 Hz, J = 9.7 Hz, F), −66.90 (d, J = 9.7 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. ESI-MS (*m*/*z*): calcd. for $C_9H_5F_4NNaO_2$ [M^+] 258.0154, found 258.0149.

4.1.8. 1-Butoxy-4-(2,3,3,3-tetrafluoropropen-1-yl)benzene (3h)

Obtained as a 94:6 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.4; IR (nujol) 1610, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, J = 7.4 Hz, 3H, Me), 1.56 (m, 2H, $-CH_2-$), 1.83 (m, 2H, $-CH_2-$), 4.03 (t, J = 6.5 Hz, 2H, O–CH_2-), 6.32 (d, J = 36.3 Hz, 1H, =CH–), 6.95 (d, J = 8.5 Hz, 2H, Ar), 7.54 (d, J = 8.5 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −135.53 (dq, J = 36.3 Hz, J = 11.8 Hz, F), −71.79 (d, J = 11.8 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.77, 19.23, 31.23, 67.76, 111.15, 114.79, 119.20 (qd, J_{CF} = 270.8 Hz, J_{CF} = 41.0 Hz, CF_3), 122.02 (d, J_{CF} = 3.7 Hz), 131.31 (d, J_{CF} = 7.3 Hz), 146.71 (dq, J_{CF} = 263.5 Hz, J_{CF} = 38.8 Hz, CF), 160.17; *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, J = 21.6 Hz, 1H, =CH–), 7.24 (d, J = 8.4 Hz, 1H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −126.71 (dq, J = 21.6 Hz, J = 9.7 Hz, F), −66.77 (d, J = 9.7 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. Anal. Calcd. for $C_{13}H_{14}OF_4$: C 59.54; H 5.38. Found: C 59.75; H 5.49.

4.1.9. 1-Methoxy-4-(2,3,3,3-tetrafluoropropen-1-yl)benzene (3i)

Obtained as a 95:5 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.3; IR (nujol) 1610, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H, O-Me), 6.30 (d, J = 36.2 Hz, 1H, =CH–), 6.93 (d, J = 8.8 Hz, 2H, Ar), 7.52 (d, J = 8.8 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −135.31 (dq, J = 36.2 Hz, J = 11.7 Hz, F), −71.81 (d, J = 11.7 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.04, 111.13, 114.27, 119.26 (qd, J_{CF} = 270.8 Hz, J_{CF} = 41.0 Hz, CF_3), 122.26 (d, J_{CF} = 3.7 Hz), 131.34 (d, J_{CF} = 7.3 Hz), 143.62 (dq, J_{CF} = 263.5 Hz, J_{CF} = 38.0 Hz, CF), 160.64; *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, J = 21.5 Hz, 1H, =CH–); ^{19}F NMR (377 MHz, $CDCl_3$) δ −126.49 (dq, J = 21.5 Hz, J = 9.7 Hz, F), −66.71 (d, J = 9.7 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. Anal. Calcd. for $C_{10}H_8OF_4$: C 54.55; H 3.66. Found: C 54.68; H 3.74.

4.1.10. Methyl 4-(2,3,3,3-tetrafluoropropen-1-yl)benzoate (3j)

Obtained as a 97:3 mixture of *Z*/*E* isomers. White solid, m.p. 59.3–59.5 °C; R_f (hexane–CH_2Cl_2 2:1) 0.5; IR (nujol) 1610, 1700 (C=C) cm^{-1}; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H, O–Me), 6.39 (d, J = 35.0 Hz, 1H, =CH–), 7.61 (d, J = 7.8 Hz, 2H, Ar), 8.05 (d, J = 7.8 Hz, 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −128.75 (dq, J = 35.0 Hz, J = 10.9 Hz, F), −72.24 (d, J = 10.9 Hz, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.12, 110.57, 118.60 (qd, J_{CF} = 272.3 Hz, J_{CF} = 41.0 Hz, CF_3), 129.54 (d, J_{CF} = 7.3 Hz), 129.94, 130.88, 133.80 (d, J_{CF} = 3.7 Hz), 146.11 (dq, J_{CF} = 270.8 Hz, J_{CF} = 38.0 Hz, CF), 166.20; *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, J = 20.1 Hz, 1H, =CH–); ^{19}F NMR (377 MHz, $CDCl_3$) δ −122.36 (dq, J = 20.10 Hz, J = 9.5 Hz, F), −66.82 (d, J = 9.5 Hz, CF_3); the other signals are identical to those of the *Z*-isomer. ESI-MS (*m*/*z*): calcd. for $C_{11}H_8F_4NaO_2$ [M^+]: 271.0358, found 271.0353.

4.1.11. 1-(2,3,3,3-Tetrafluoropropen-1-yl)-4-(trifluoromethyl)benzene (3k)

Obtained as a 95:5 mixture of *Z*/*E* isomers. Colorless oil; R_f (hexane) 0.5; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.40 (d, J = 34.8 Hz, 1H, =CH–), 7.66 (m, 4H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$) δ −128.85 (dq, J = 34.8 Hz, J = 10.8 Hz, F), −72.31 (d, J = 10.8 Hz, CF_3), −63.05 (s, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.12, 118.55 (qd, J_{CF} = 272.3 Hz, J_{CF} = 41.3 Hz, CF_3), 123.7 (q, J_{CF} = 272.3 Hz, CF_3), 125.7, 129.82 (d, J_{CF} = 7.6 Hz), 131.05, 133.04, 146.40 (dq, J_{CF} = 270.6 Hz, J_{CF} = 38.0 Hz, CF); *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, J = 20.2 Hz, 1H, =CH–); ^{19}F NMR (377 MHz, $CDCl_3$) δ −122.05 (dq, J = 20.2 Hz, J = 9.4 Hz, F), −66.84 (d, J = 9.4 Hz, CF_3), −62.95 (s, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ; the other signals are identical to those of the *Z*-isomer. Anal. Calcd. for $C_{10}H_5F_7$: C 46.53; H 1.95. Found: C 46.65; H 2.09.

4.1.12. 1-Nitro-4-(2,3,3,3-tetrafluoropropen-1-yl)benzene (3l)

Obtained as a 90:10 mixture of *Z*/*E* isomers. Colorless solid, m.p. 60.5–61.3 °C; R_f (hexane–CH_2Cl_2 2:1) 0.4; *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, J = 34.0 Hz, 1H, =CH–), 7.76 (d, J = 8.8 Hz, 2H, Ar), 8.29 (d, J = 8.9 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.66, 118.34 (qd, J_{CF} = 271.5 Hz, J_{CF} = 40.5 Hz, CF_3), 123.91, 130.39 (d, J_{CF} = 7.6 Hz), 135.76, 147.96 (dq, J_{CF} = 273.2 Hz, J_{CF} = 38.8 Hz, CF), 147.90; *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 19.5 Hz, 1H, =CH–); the other signals are identical to those of the *Z*-isomer. Anal. Calcd. for $C_9H_5NO_2F_4$: C 45.97; H 2.14. Found: C 45.85; H 2.03.

4.2. Reactions of styrene 3l with nucleophiles

Reactions with nucleophiles were carried out according to our previously reported procedures for the substitution of chlorine in styrene **7** by pyrrolidine [49], 4-methylphenylthiolate [47] and potassium *tert*-butoxide [48]. Identification of the reaction products were performed by comparison with spectroscopic data reported in mentioned references.

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References

[1] P. Kirsch, Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications, Wiley-VCH, Weinheim, 2004.
[2] K. Uneyama, Organofluorine Chemistry, Blackwell, Oxford, 2006.
[3] G. Theodoridis, Fluorine-containing agrochemicals: an overview of recent developments, in: A. Tressaud (Ed.), Advances in Fluorine Science, vol. 2, Elsevier, Amsterdam, 2006, pp. 121–175.
[4] J.P. Bégué, D. Bonnet-Delpon, Bioorganic and Medicinal Chemistry of Fluorine, John Wiley & Sons, Hoboken, 2008.
[5] A. Tressaud, G. Haufe (Eds.), Fluorine and Health. Molecular Imaging, Biomedical Materials and Pharmaceuticals, Elsevier, Amsterdam, 2008, pp. 553–778.
[6] M. Hudlický, A.P. Pavlath, Chemistry of Organic Fluorine Compounds II, ACS Symposium Series 187, American Chemical Society, Washington, 1995.
[7] V.A. Soloshonok (Ed.), Fluorine-Containing Synthons, ACS Symposium Series 911American Chemical Society, Washington, 2005.
[8] V.A. Soloshonok, K. Mikami, T. Yamazaki, J.T. Welch, J.F. Honek (Eds.), Current Fluoroorganic Chemistry. New Synthetic Directions, Technologies, Materials, and Biological Applications, ACS Symposium Series 949American Chemical Society, Washington, 2006.
[9] I.N. Martyanov, K.J. Klabunde, J. Catal. 224 (2004) 340–346.
[10] Z. Ma, W.M. Hua, Y. Tang, Z. Gao, J. Mol. Catal. A: Chem. 159 (2000) 335–345.
[11] P. Hohener, D. Werner, C. Balsiger, G. Pasteris, Crit. Rev. Environ. Sci. Technol. 33 (2003) 1–29.
[12] V.V. Lunin, E.S. Lokteva, Russ. Chem. Bull. 45 (1996) 1519–1534.
[13] F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 102 (2002) 4009–4091.
[14] K.I. Petko, L.M. Yagupolskii, Synth. Commun. 36 (2006) 1967–1972.
[15] V.G. Koshechko, V.D. Pokhodenko, Russ. Chem. Bull. 50 (2001) 1929–1935.
[16] A.V. Shastin, V.N. Korotchenko, V.G. Nenajdenko, E.S. Balenkova, Russ. Chem. Bull. 48 (1999) 2184–2185.
[17] A.V. Shastin, V.N. Korotchenko, V.G. Nenajdenko, E.S. Balenkova, Tetrahedron 56 (2000) 6557–6563.
[18] A.V. Shastin, V.N. Korotchenko, V.G. Nenajdenko, E.S. Balenkova, Synthesis (2001) 2081–2084.
[19] V.N. Korotchenko, A.V. Shastin, V.G. Nenajdenko, E.S. Balenkova, J. Chem. Soc., Perkin Trans. 1 (2002) 883–887.
[20] A.V. Shastin, V.N. Korotchenko, V.G. Nenajdenko, E.S. Balenkova, Russ. Chem. Bull. 50 (2001) 1401–1404.
[21] V.N. Korotchenko, A.V. Shastin, V.G. Nenajdenko, E.S. Balenkova, Org. Biomol. Chem. 1 (2003) 1906–1908.
[22] V.G. Nenajdenko, V.N. Korotchenko, A.V. Shastin, E.S. Balenkova, Russ. Chem. Bull. 53 (2004) 1034–1064.
[23] V.N. Korotchenko, A.V. Shastin, V.G. Nenajdenko, E.S. Balenkova, Tetrahedron 57 (2001) 7519–7527.
[24] V.G. Nenajdenko, A.V. Shastin, V.N. Korotchenko, G.N. Varseev, E.S. Balenkova, Eur. J. Org. Chem. (2003) 302–308.
[25] V.G. Nenajdenko, G.N. Varseev, V.N. Korotchenko, A.V. Shastin, E.S. Balenkova, J. Fluorine Chem. 124 (2003) 115–118.
[26] V.G. Nenajdenko, G.N. Varseev, A.V. Shastin, E.S. Balenkova, J. Fluorine Chem. 126 (2005) 907–913.
[27] A.V. Shastin, V.M. Muzalevsky, E.S. Balenkova, V.G. Nenajdenko, Mendeleev Commun. 16 (2006) 179–180.
[28] V.G. Nenajdenko, G.N. Varseev, V.N. Korotchenko, A.V. Shastin, E.S. Balenkova, J. Fluorine Chem. 125 (2004) 1339–1345.
[29] W. Peng, S. Zhu, G. Jin, Tetrahedron 57 (2001) 5781–5784.
[30] X.-Q. Tang, C.-M. Hu, J. Chem. Soc., Perkin Trans. 1 (1994) 2161–2163.
[31] E. Bosone, F. Gozzo, Ger. Offen. DE 3244641 (1983).
[32] G. Caprara, F. Gozzo, G. Paparatto, L. Roberti, Fr. Demande FR 2499070 (1982).
[33] P. Piccardi, F. Corda, F. Gozzo, A. Menconi, A. Longoni, Belg. BE 874515 (1979).
[34] S. Peng, F.-L. Qing, J. Chem. Soc., Perkin Trans. 1 (1999) 3345–3348.
[35] X. Tang, C. Hu, Chin. Chem. Lett. 5 (1994) 183–186.
[36] W. Huang, Y. Xie, Faming Zhuanli Shenqing Gongkai Shuomingshu CN 1097190 (1995).
[37] C. Hu, M. Tu, F. Qing, Faming Zhuanli Shenqing Gongkai Shuomingshu CN 1056864 (1991).
[38] W. Fu, X. Zhang, X. Jiang, Sci. Chin. Ser. B: Chem. 44 (2001) 337–343.
[39] I. Hemer, A. Posta, V. Dedek, J. Fluorine Chem. 26 (1984) 467–479.
[40] W. Dmowski, J. Fluorine Chem. 29 (1985) 273–286.
[41] I.H. Jeong, Y.S. Park, M.S. Kim, Y.S. Song, J. Fluorine Chem. 120 (2003) 195–209.
[42] G.E. Carr, R.D. Chambers, T.F. Holmes, D.G. Parker, J. Chem. Soc., Perkin Trans. 1 (1988) 921–926.
[43] W.R.J. Dolbier, T.A. Gray, K. Onishi, Synthesis (1987) 956–958.
[44] N.V. Kirij, D.A. Dontsova, N.V. Pavlenko, Y.L. Yagupolskii, H. Scherer, W. Tyrra, D. Naumann, Eur. J. Org. Chem. (2008) 2267–2272.
[45] V.G. Nenajdenko, V.M. Muzalevskiy, A.V. Shastin, E.S. Balenkova, G. Haufe, J. Fluorine Chem. 128 (2007) 818–826.
[46] A.V. Shastin, V.M. Muzalevskiy, E.S. Balenkova, V.G. Nenajdenko, R. Fröhlich, G. Haufe, Tetrahedron 64 (2008) 9725–9732.
[47] V.M. Muzalevskiy, A.V. Shastin, E.S. Balenkova, V.G. Nenajdenko, Russ. Chem. Bull. 56 (2007) 1526–1533.
[48] V.M. Muzalevskiy, V.G. Nenajdenko, A.V. Shastin, E.S. Balenkova, G. Haufe, Synthesis (2009) 2249–2259.
[49] V.M. Muzalevskiy, V.G. Nenajdenko, A.V. Shastin, E.S. Balenkova, G. Haufe, Tetrahedron 65 (2009) 6991–7000.
[50] D.D. Perrin, W.L.F. Armaredo, Purification of Laboratory Chemicals, Pergamon Press, New York, 1988, p. 322.