New approach to the synthesis of trifluoromethylvinyl sulfides*

V. M. Muzalevskiy,[a] A. V. Shastin,[b] E. S. Balenkova,[a] and V. G. Nenajdenko[a]★

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation. Fax: +7 (495) 932 8846. E-mail: nen@acylium.chem.msu.ru*
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 142432 Moskovskaya obl., Russian Federation. E-mail: shastin@icp.ac.ru*

Nucleophilic substitution reaction of halogen atom in β-chloro- and β-bromo-β-trifluoromethylstyrenes by thiolates was studied. Stereo- and regioselectivity of the reaction with respect to the electronic and sterical properties of substituents in the aromatic ring of starting styrenes was investigated. Regioisomer with geminal trifluoromethyl and alkyl- or arylthio groups was found to be formed predominantly or exclusively. The reaction proceeds stereoselectively in nearly quantitative yields. On this basis, a new convenient stereoselective method for the synthesis of trifluoromethylvinyl sulfides was elaborated.

Key words: catalytic olefination reaction, β-halo-β-trifluoromethylstyrenes, nucleophilic substitution, regioselectivity, trifluoromethylvinyl sulfides.

Fluoro-containing organic compounds are under the intensive investigation due to their high physiological activity.[1] A large number of works deals with the elaboration of new methods for their synthesis.[2] Earlier, a new reaction of catalytic olefination of aldehydes and ketones was discovered by our research group.[3] It was found that *N*-unsubstituted hydrazones of carbonyl compounds upon treatment with polyhaloalkanes in the presence of a base and catalytic amounts of copper salts are transformed to various substituted alkenes. Inexpensive starting compounds and simplicity of carrying out the experiment and products isolation are the advantages of this method. Thus, this reaction does not require an inert atmosphere and an excess of organometallic or organophosphorus compounds as, for example, in the Wittig reaction.

On the basis of catalytic olefination reaction, we elaborated new methods for the synthesis of various fluoro-containing alkenes.[4] Obtained by these methods β-chloro-β-trifluoromethylstyrenes[4a] and β-bromo-β-trifluoromethylstyrenes[4d] are of particular interest, since the presence of halogen atom gives the opportunity for their further functionalization. Thus, recently we successfully performed a substitution of bromine atom by a nitrile group in β,β-bromofluorostyrenes and β-bromo-β-trifluoromethylstyrenes.[5]

We assumed that in case of thiols the substitution would lead to β-alkylthio- and β-arylthio-β-trifluoromethylstyrenes, which are used for the synthesis of β-alkyl- and β-aryl-β-trifluoromethylstyrenes,[6] potential anti-cancer drugs.[7] By oxidation, sulfides can be easily converted to sulfones $ArC(H)=C(SO_2R)CF_3$ (see Refs 8 and 9), which are of interest as prospective "building blocks" for the synthesis of fluoro-containing compounds and which have been already used in the synthesis of 3-aryl-4-trifluoromethylpyrroles.[9] There are two approaches to the synthesis of such sulfides known from the literature. The first one is based on the Wittig reaction with thioesters of perfluorocarboxylic acids,[10] the second one includes the substitution of halogen atom in β-chloro-β-trifluoromethyl-α-formylstyrenes by alkylthio or arylthio group with subsequent decarbonylation under base treatment.[11] However, both methods have disadvantages. In the first method, the use of expensive starting perfluorothioacetates is required, while the second is a multi-step one.

Results and Discussion

It was found that both β-chloro-β-trifluoromethylstyrenes **1** and β-bromo-β-trifluoromethylstyrenes **2** easily react with ethanethiol in ethanol in the presence of 1.2 equiv. of KOH to form vinyl sulfides **3** and **4** (Scheme 1 and Table 1). In case of electron-withdrawing substituents in aromatic ring, such as nitro or carboxymethyl groups, the reaction is fast and exothermic at room temperature. In all the other cases, a reflux of the reaction mixture for 5—10 min is required for the reaction to come to a full completion. A general nature of the reaction

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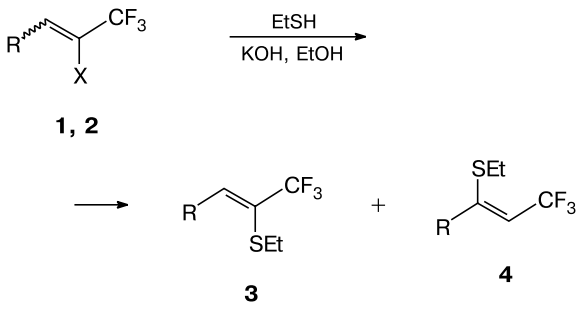
Scheme 1



X = Cl (**1**), Br (**2**)

Table 1. Reaction of β-chloro- and β-bromo-β-trifluoromethylstyrenes with ethanethiol

Compound **1—4**	R	Yield of **3** + **4** (%)		**3** : **4**
		X=Cl	X=Br	
a	4-$NO_2C_6H_4$	96	—[a]	1 : 0
b	3-$NO_2C_6H_4$	95	—[a]	12 : 1
c	2-$NO_2C_6H_4$	76	—[a]	1 : 0
d	2-BrC_6H_4	89	85	1 : 0
e	2-Br-5-$MeOC_6H_3$	—[a]	94	1 : 0
f	4-$MeCO_2C_6H_4$	81[b]	89[b]	1 : 0
g	2-Py	92	—[a]	1 : 0
h	4-ClC_6H_4	90	93	5 : 1
i	4-$MeOC_6H_4$	—[a]	93	0.5 : 1
j	3-$MeOC_6H_4$	—[a]	95	3 : 1
k	2-$MeOC_6H_4$	—[a]	85	7 : 1
l	3,4-$(MeO)_2C_6H_3$	—[a]	89	1 : 1
m	Ph	—[a]	96	2 : 1
n	4-MeC_6H_4	64	76	1 : 1

[a] Reaction was not conducted.
[b] Transesterification to ethyl ester took place.

allows one to obtain trifluoromethylvinyl sulfides, containing both electron-withdrawing and electron-donating substituents. The total yield of vinyl sulfides **3** and **4** was high and in a number of cases was nearly quantitative.

The ratios of regioisomers **3** and **4** were determined by the comparison of the integral intensities for the vinyl protons in ^{1}H NMR spectra. It should be noted that the nature of halogen atom in the starting styrenes does not influence the ratio and total yield of sulfides **3** and **4**. Regioselectivity of the reaction is affected by the nature of substituents in the aromatic ring. The presence of the strong −M electron-withdrawing groups in the aromatic ring in *ortho*- and *para*-positions to the double bond leads to a shift of electron density toward the aromatic ring. In this case, a nucleophile exclusively attacks carbon, bearing a halogen atom, to form a single regioisomer **3**. Similar results are also observed for *ortho*-bromo derivatives with the only difference that, in addition to the electronic factors (−I-effect of bromine atom), steric hindrance, caused by substituent in *ortho*-position, also interfere with the direction of nucleophilic attack. The content of regioisomer **4** increases with the decrease of electron-withdrawing properties of the aromatic substituent, and for donating substrates **2i** and **2l** with *para*-methoxy group, regioisomer **4** becomes predominant. Similarly to the case of styrenes with electron-withdrawing substituents, the steric factors strongly affect the direction of nucleophilic attack in styrenes with electron-donating substituents. For example, for styrene **2k** with *ortho*-methoxy group, the content of regioisomer **4** is 14 times as less as for styrene **2i**. Thus, regioselectivity of the reaction is defined by the electronic and steric properties of aryl (heteroaryl) substituent. In case of electron-withdrawing and sterically hindered substituents, the reaction proceeds with the formation of a single regioisomer **3**.

Despite the fact that the starting substrates **1** and **2** are mixtures of *Z*- and *E*-isomers (with *Z*-isomer being predominant, see Experimental), the formed from them compounds **3** and **4** have *Z*-configuration, and only for styrenes **1c**, **1d**, and **2d** with electron-withdrawing substituents in *ortho*-position to the double bond, formation of admixtures of *E*-isomers are observed. The ratio of *Z*/*E*-isomers in products **3c** and **3d** was 7/1 and 20/1, respectively. Thus, formation of the sulfides proceeds stereoselectively. To assign a configuration of the double bond in sulfides **3**, the spin-spin coupling constant values $^3J_{H,C}$ of carbon atom in trifluoromethyl group and vinylic proton were determined. It was found that they are within the interval 5.9—6.6 Hz, which corresponds to *Z*-isomers.[12] A configuration of regioisomer **4** was determined from the NOE experiment for sulfide **4i**.

According to the NOE data for compound **4i**, the irradiation of vinylic proton showed the nuclear Overhauser effect with *ortho*-protons of phenyl ring, at the same time, interaction with CH_2 protons of the thioalkyl group was not observed, which points out to the same-side position of the vinylic proton and phenyl ring with respect to the double bond. Thus, the configuration of compound **4i** and, most likely, the other sulfides **4** corresponds to *Z*-isomer.

In order to investigate the synthetic potential of the method, we carried out a series of reactions of styrene **1a**, taken as a mixture of isomers, with a number of thiols. It was found that for all the thiols under consideration, similarly to ethanethiol, the substitution reaction of chlorine atom proceeds regio- and stereoselectively with high yields of the target vinyl sulfides, both with alkyl (**5b**, **5d**) and aryl (**5c**, **5e**, **5f**) substituents (Scheme 2 and Table 2).

In conclusion, a nucleophilic substitution reaction of halogen atom in β-chloro- and β-bromo-β-trifluoromethylstyrenes by thiols was investigated. Regio- and stereoselectivity of the reaction was studied. A new con-

Scheme 2

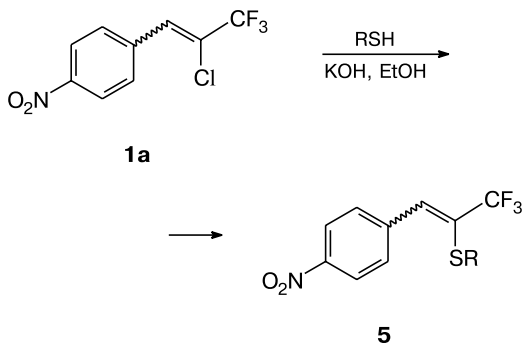


Table 2. Reaction of styrene **1a** with thiols

Compounds	R	Yield of **5** (%)	Ratio *Z*/*E*
a	Et	96	1/0
b	$PhCH_2$	91	1/0
c	$2\text{-}NH_2C_6H_4$	81	1/0
d	$EtCO_2CH_2$	72	12/1
e	$4\text{-}ClC_6H_4$	85	7/1
f	$4\text{-}MeC_6H_4$	88	7/1

venient stereoselective method for the synthesis of trifluoromethylvinyl sulfides was elaborated.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$; Me_4Si was used as the internal standard. IR spectra were recorded on a UR-20 spectrophotometer for neat samples. TLC analysis was carried out on Silufol UV-254 plates with visualization in acidified $KMnO_4$ solution, in a chamber with iodine vapors, or under the UV-light. Column chromatography was performed on Merck silica gel (63—200 mesh). Starting styrenes **1** and **2** were obtained according to the literature procedures.[4a,d]

Synthesis of β-chloro-β-trifluoromethylstyrenes (general procedure). Ethanol (50 mL) and 100% hydrazine hydrate (5 mL, 0.1 mol) were placed in a 500-mL round-bottom flask, and a solution of the corresponding aldehydes (0.1 mol) in ethanol (150 mL) was slowly added to this with vigorous stirring. The reaction mixture was stirred until entire disappearance of the carbonyl compounds (TLC monitoring), 1,2-ethylenediamine (10 mL, 0.15 mol) and CuCl (1 g, 0.01 mol) were added, and this was cooled to 5—10 °C in an ice bath. After this, a solution of CCl_3CF_3 (28 g, 0.15 mol) in ethanol (50 mL) was poured in with caution (vigorous gas emission and foaming!). After the exothermic reaction was over (~0.5—1 h), the ice bath was removed, and this reaction mixture was stirred at room temperature for 16 h. Then the reaction mixture was concentrated to 50—60 mL, the formed precipitate was filtered off, the filtrate was quenched with 0.1 *M* aq. hydrochloric acid (1 L) (in case of 2-pyridinecarbaldehyde, water was used for the quenching), and this was extracted with dichloromethane (3×100 mL). The combined extract was washed with water (100 mL) and brine (100 mL) and dried with Na_2SO_4. Dichloromethane was removed *in vacuo*, the residue was dissolved in hexane or in the appropriate hexane-dichloromethane mixture and run through a short layer of silica gel. Attempted chromatographic separation of *Z*- and *E*-isomers of alkenes failed.

The spectral data for compounds **1a,b,h,i,m,n** agree with those described in the literature.[4a]

1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-nitrobenzene (1a) was obtained from 4-nitrobenzaldehyde. A mixture of *Z*/*E*-isomers (7/1 after purification), the yield was 60%, yellow crystals, m.p. 63—64 °C (Ref. 4a data: m.p. 64—65 °C).

1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-3-nitrobenzene (1b) was obtained from 3-nitrobenzaldehyde. A mixture of *Z*/*E*-isomers (3/1 after purification), the yield was 74%, yellow oil.

1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-2-nitrobenzene (1c) was obtained from 2-nitrobenzaldehyde. A mixture of *Z*/*E*-isomers (5/1 after purification), the yield was 68%, colorless oil. Found (%): C, 42.87; H, 2.05. $C_9H_5ClF_3NO_2$. Calculated (%): C, 42.97; H, 2.00. IR, ν/cm^{-1}: 1330, 1560 (NO_2), 1615 (C=C). ^1H NMR ($CDCl_3$, δ) of *Z*-isomer: 7.60—7.70 (m, 3 H, Ar); 7.78 (s, 1 H, C<u>H</u>=CCF_3); 8.23 (dd, 1 H, Ar, *J* = 8.1 Hz, *J* = 1.0 Hz); *E*-isomer: 7.40 (d, 1 H, Ar, *J* = 7.8 Hz); 7.57 (s, 1 H, C<u>H</u>=CCF_3); 7.58—7.80 (m, 3 H, Ar). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 120.4 (q, CF_3, *J* = 272.3 Hz); 122.6 (q, <u>C</u>—CF_3, *J* = 38.1 Hz); 129.5 (q, <u>C</u>H=CCF_3, *J* = 4.4 Hz); 125.1, 127.5, 130.4, 131.3, 133.9, 147.2 (Ar); *E*-isomer: 120.1 (q, CF_3, *J* = 273.7 Hz); 122.3 (q, <u>C</u>—CF_3, *J* = 37.3 Hz); 133.7 (q, <u>C</u>H=CCF_3, *J* = 2.9 Hz); 124.9, 128.5, 130.1, 131.0, 133.8, 146.3 (Ar).

1-Bromo-2-[2-chloro-3,3,3-trifluoro-1-propenyl]benzene (1d) was obtained from 2-bromobenzaldehyde. A mixture of *Z*/*E*-isomers (3/1 after purification), the yield was 41%, colorless oil. Found (%): C, 38.08; H, 2.01. $C_9H_5BrClF_3$. Calculated (%): C, 37.86; H, 1.77. IR, ν/cm^{-1}: 1620 (C=C). ^1H NMR ($CDCl_3$, δ) of *Z*-isomer: 7.30, 7.43 (both dt, 1 H each, Ar, *J* = 7.8 Hz, *J* = 1.1 Hz); 7.58 (s, 1 H, C<u>H</u>=CCF_3); 7.69, 7.83 (both dd, 1 H each, Ar, *J* = 7.8 Hz, *J* = 1.1 Hz); *E*-isomer: 7.26—7.39 (m, 4 H, Ar and C<u>H</u>=CCF_3); 7.83 (dd, 1 H, Ar, *J* = 8.1 Hz, *J* = 0.8 Hz). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 120.7 (q, CF_3, *J* = 272.3 Hz); 122.2 (q, <u>C</u>—CF_3, *J* = 36.6 Hz); 130.6 (q, <u>C</u>H=CCF_3, *J* = 4.4 Hz); 124.6, 127.3, 130.5, 131.0, 131.9, 133.0 (Ar); *E*-isomer: 120.3 (q, CF_3, *J* = 274.4 Hz); 122.6 (q, <u>C</u>—CF_3, *J* = 36.6 Hz); 136.1 (q, <u>C</u>H=CCF_3, *J* = 2.9 Hz); 124.8, 127.2, 130.3, 130.4, 132.4, 133.5 (Ar).

Methyl 4-[2-chloro-3,3,3-trifluoro-1-propenyl]benzoate (1f) was obtained from methyl 4-formylbenzoate. A mixture of *Z*/*E*-isomers (4/1 after purification), the yield was 55%, colorless crystals, m.p. 51—54 °C. Found (%): C, 49.71; H, 3.05. $C_{11}H_8ClF_3O_2$. Calculated (%): C, 49.93; H, 3.05. IR, ν/cm^{-1}: 1610 (C=C), 1720 (C=O, CO_2Et). ^1H NMR ($CDCl_3$, δ) of *Z*-isomer: 3.88 (s, 3 H, $CO_2C\underline{H}_3$); 7.27 (s, 1 H, C<u>H</u>=CCF_3), 7.69, 8.02 (both d, 2 H each, Ar, *J* = 8.5 Hz); *E*-isomer: 3.87 (s, 3 H, $CO_2C\underline{H}_3$); 7.23 (s, 1 H, C<u>H</u>=CCF_3); 7.26, 7.97 (both d, 2 H each, Ar, *J* = 8.3 Hz). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 52.1 ($CO_2\underline{C}H_3$); 120.6 (q, CF_3, *J* = 272.3 Hz); 121.3 (q, <u>C</u>—CF_3, *J* = 37.3 Hz); 129.8 (q, <u>C</u>H=CCF_3, *J* = 5.2 Hz); 129.6, 129.7, 131.2, 135.6 (Ar); 166.1 (<u>C</u>O_2CH_3); *E*-isomer: 52.0 ($CO_2\underline{C}H_3$); 120.3 (q, CF_3, *J* = 274.5 Hz); 122.6 (q, <u>C</u>—CF_3, *J* = 38.1 Hz); 136.0 (q, <u>C</u>H=CCF_3, *J* = 2.9 Hz); 128.3, 129.4, 130.5, 136.8 (Ar); 166.2 (<u>C</u>O_2CH_3).

2-[2-Chloro-3,3,3-trifluoro-1-propenyl]pyridine (1g) was obtained from 2-pyridinecarbaldehyde. A mixture of *Z*/*E*-isomers (5/1 after purification), the yield was 62%, colorless oil. Found (%): C, 46.35; H, 2.47. $C_8H_5ClF_3N$. Calculated (%): C, 46.29; H, 2.43. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 7.07—7.27 (m, 1 H, Py); 7.35 (s, 1 H, C<u>H</u>=CF_3); 7.58—7.66 (m, 1 H, Py); 7.81 (d, 1 H, Py, *J* = 7.8 Hz); 8.53—8.58 (m, 1 H, Py); *E*-isomer: 7.07—7.27 (m, 3 H, Py and C<u>H</u>=CF_3); 7.51—7.58, 8.47—8.51 (both m, 1 H each, Py). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 120.6 (q, CF_3, *J* = 272.3 Hz); 120.8 (q, <u>C</u>—CF_3, *J* = 33.7 Hz); 131.3 (q, <u>C</u>H=CCF_3, *J* = 4.4 Hz); 123.9, 124.6, 136.2, 149.8, 150.8 (Py); *E*-isomer: 120.0 (q, CF_3, *J* = 274.5 Hz); 120.4 (q, <u>C</u>—CF_3, *J* = 37.3 Hz); 136.3 (q, <u>C</u>H=CCF_3, *J* = 2.2 Hz); 123.2, 123.8, 136.1, 149.4, 151.3 (Py).

1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-chlorobenzene (1h) was obtained from 4-chlorobenzaldehyde. A mixture of *Z*/*E*-isomers (3/1 after purification), the yield was 76%, colorless oil.

1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-methoxybenzene (1i) was obtained from 4-methoxybenzaldehyde. A mixture of *Z*/*E*-isomers (10/1 after purification), the yield was 55%, colorless oil.

[2-Chloro-3,3,3-trifluoro-1-propenyl]benzene (1m) was obtained from benzaldehyde. A mixture of *Z*/*E*-isomers (6/1 after purification), the yield was 50%, colorless oil.

1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-methylbenzene (1n) was obtained from 4-methylbenzaldehyde. A mixture of *Z*/*E*-isomers (6/1 after purification), the yield was 59%, colorless oil.

Synthesis of β-bromo-β-trifluoromethylstyrenes (general procedure). DMSO (50 mL) and 100% hydrazine hydrate (5 mL, 0.1 mol) were placed in a 500-mL round-bottom flask, and a solution of the corresponding aldehydes (0.1 mol) in DMSO (150 mL) was slowly added to this with vigorous stirring. The reaction mixture was stirred until entire disappearance of the carbonyl compounds (TLC monitoring), 25% aq. ammonia (8 mL) and CuCl (1 g, 0.01 mol) were added, and this was cooled to 5—10 °C in an ice bath. After this, a solution of CF_3CBr_3 (32 g, 0.1 mol) in DMSO (50 mL) was poured in with caution (vigorous gas emission and foaming!). After the exothermic reaction was over (~0.5 h), the ice bath was removed, and this reaction mixture was stirred at room temperature for 16 h. Then the reaction mixture was quenched with 0.1 *M* aq. hydrochloric acid (1.5 L) and extracted with dichloromethane (3×100 mL). The combined extract was washed with water (100 mL) and brine (100 mL) and dried with Na_2SO_4. Dichloromethane was removed *in vacuo*, the residue was dissolved in hexane or in the appropriate hexane-dichloromethane mixture and run through a short layer of silica gel. Attempted chromatographic separation of *Z*- and *E*-isomers of alkenes failed.

The spectral data for compounds **2f,h,i,n** agree with those described in the literature[4d].

1-Bromo-2-[2-bromo-3,3,3-trifluoro-1-propenyl]benzene (2d) was obtained from 2-bromobenzaldehyde. A mixture of *Z*/*E*-isomers (2/1 after purification), the yield was 46%, colorless oil. Found (%): C, 32.50; H, 1.58. $C_9H_5Br_2F_3$. Calculated (%): C, 32.76; H, 1.53. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 7.34—7.38 (m, 1 H, Ar); 7.43 (td, 1 H, Ar, *J* = 7.7 Hz, *J* = 1.0 Hz); 7.65—7.69 (m, 1 H, Ar); 7.75 (dd, 1 H, Ar, *J* = 7.7 Hz, *J* = 1.0 Hz); 7.78 (s, 1 H, C<u>H</u>=CF_3); *E*-isomer: 7.24—7.35 (m, 3 H, Ar), 7.49 (s, 1 H, C<u>H</u>=CF_3), 7.57—7.62 (m, 1 H, Ar). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 113.0 (q, <u>C</u>—CF_3, *J* = 36.6 Hz); 120.8 (q, CF_3, *J* = 272.3 Hz); 134.6 (q, <u>C</u>H=CCF_3, *J* = 5.1 Hz); 124.0, 127.2, 131.0, 132.1, 132.9, 133.3 (Ar); *E*-isomer: 113.4 (q, <u>C</u>—CF_3, *J* = 38.8 Hz); 120.4 (q, CF_3, *J* = 274.4 Hz); 140.4 (q, <u>C</u>H=CCF_3, *J* = 2.9 Hz); 126.1, 127.3, 130.3, 130.5, 132.4. The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-Bromo-2-[2-bromo-3,3,3-trifluoro-1-propenyl]-4-methoxybenzene (2e) was obtained from 2-bromo-5-methoxybenzaldehyde. A mixture of *Z*/*E*-isomers (4/1 after purification), the yield was 33%, colorless oil. Found (%): C, 33.19; H, 2.02. $C_{10}H_7Br_2F_3O$. Calculated (%): C, 33.37; H, 1.96. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 3.85 (s, 3 H, OC<u>H</u>$_3$); 6.85 (dd, 1 H, Ar, *J* = 8.8 Hz, *J* = 3.0 Hz); 7.31 (d, 1 H, Ar, *J* = 3.0 Hz); 7.52 (d, 1 H, Ar, *J* = 8.8 Hz); 7.74 (s, 1 H, C<u>H</u>=CF_3); *E*-isomer: 3.81 (s, 3 H, OC<u>H</u>$_3$), 6.81 (dd, 1 H, Ar, *J* = 8.6 Hz, *J* = 2.8 Hz); 7.05 (d, 1 H, Ar, *J* = 2.8 Hz); 7.43 (s, 1 H, C<u>H</u>=CF_3); 7.47 (d, 1 H, Ar, *J* = 8.6 Hz). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 55.6 (OCH_3); 112.9 (q, <u>C</u>—CF_3, *J* = 36.6 Hz); 120.8 (q, CF_3, *J* = 272.2 Hz); 134.5 (q, <u>C</u>H=CCF_3, *J* = 5.1 Hz); 114.4, 115.7, 117.1, 133.5, 133.8, 158.6 (Ar); *E*-isomer: 55.8 (OCH_3); 120.3 (q, CF_3, *J* = 273.7 Hz); 140.4 (q, <u>C</u>H=CCF_3, *J* = 2.9 Hz); 114.0, 116.4, 117.2, 133.0, 134.2, 159.2 (Ar).

Methyl 4-[2-bromo-3,3,3-trifluoro-1-propenyl]benzoate (2f) was obtained from methyl 4-formylbenzoate. A mixture of *Z*/*E*-isomers (5/1 after purification), the yield was 63%, colorless oil.

1-[2-Bromo-3,3,3-trifluoro-1-propenyl]-4-chlorobenzene (2h) was obtained from 4-chlorobenzaldehyde. A mixture of *Z*/*E*-isomers (8/1 after purification), the yield was 56%, colorless oil.

1-[2-Bromo-3,3,3-trifluoro-1-propenyl]-4-methoxybenzene (2i) was obtained from 4-methoxybenzaldehyde. A mixture of *Z*/*E*-isomers (8/1 after purification), the yield was 73%, colorless oil.

1-[2-Bromo-3,3,3-trifluoro-1-propenyl]-3-methoxybenzene (2j) was obtained from 3-methoxybenzaldehyde. A mixture of *Z*/*E*-isomers (6/1 after purification), the yield was 68%, colorless oil. Found (%): C, 42.68; H, 2.85. $C_{10}H_8BrF_3O$. Calculated (%): C, 42.73; H, 2.87. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 3.88 (s, 3 H, OC<u>H</u>$_3$); 7.03 (dd, 1 H, Ar, *J* = 7.9 Hz, *J* = 1.8 Hz); 7.31 (d, 1 H, Ar, *J* = 7.9 Hz); 7.63 (s, 1 H, C<u>H</u>=CF_3); 7.36 (s, 1 H, Ar); 7.31 (t, 1 H, Ar, *J* = 7.9 Hz); *E*-isomer: 3.85 (s, 3 H, OCH_3); 6.86 (s, 1 H, C<u>H</u>=CF_3); 6.91 (d, 1 H, Ar, *J* = 8.0 Hz); 6.95 (dd, 1 H, Ar, *J* = 8.0 Hz, *J* = 2.2 Hz). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 55.2 (O<u>C</u>H$_3$); 109.6 (q, <u>C</u>—CF_3, *J* = 36.6 Hz); 121.1 (q, CF_3, *J* = 271.5 Hz); 134.4 (q, <u>C</u>H=CCF_3, *J* = 5.1 Hz); 114.7, 115.9, 122.3, 129.6, 133.6, 159.6 (Ar); *E*-isomer: 55.2 (O<u>C</u>H$_3$); 141.5 (q, <u>C</u>=CHCF_3, *J* = 2.2 Hz); 117.1, 117.6, 120.7, 129.8, 135.0, 159.4 (Ar). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-[2-Bromo-3,3,3-trifluoro-1-propenyl]-2-methoxybenzene (2k) was obtained from 2-methoxybenzaldehyde. A mixture of *Z*/*E*-isomers (7/1 after purification), the yield was 43%, colorless oil. Found (%): C, 42.85; H, 2.96. $C_{10}H_8BrF_3O$. Calculated (%): C, 42.73; H, 2.87. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 3.91 (s, 3 H, OC<u>H</u>$_3$); 6.97 (d, 1 H, Ar, *J* = 7.9 Hz); 7.08 (t, 1 H, Ar, *J* = 7.9 Hz); 7.40 (td, 1 H, Ar, *J* = 7.9 Hz, *J* = 1.3 Hz); 7.95 (s, 1 H, C<u>H</u>=CF_3); 7.98 (dd, 1 H, Ar, *J* = 7.9 Hz, *J* = 1.3 Hz); *E*-isomer: 3.89 (s, 3 H, OCH_3); 6.94

(d, 1 H, Ar, J = 7.8 Hz); 7.00 (t, 1 H, Ar, J = 7.8 Hz); 7.31 (d, 1 H, Ar, J = 7.8 Hz); 7.41 (td, 1 H, Ar, J = 7.8 Hz, J = 1.3 Hz); 7.60 (s, 1 H, CH=CCF$_3$). ^{13}C NMR (CDCl$_3$, δ) of *Z*-isomer: 55.5 (O<u>C</u>H$_3$); 109.7 (q, <u>C</u>—CF$_3$, J = 36.6 Hz); 121.2 (q, CF$_3$, J = 270.8 Hz); 110.6, 120.1, 121.5, 129.4, 131.5, 157.7 (Ar); *E*-isomer: 55.5 (OCH$_3$); 120.7 (q, CF$_3$, J = 273.0 Hz); 138.0 (q, <u>C</u>=CHCF$_3$, J = 2.9 Hz); 110.4, 120.3, 122.6, 129.8, 130.9, 156.7 (Ar). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-[2-Bromo-3,3,3-trifluoro-1-propenyl]-1,2-dimethoxybenzene (2l) was obtained from 1,2-dimethoxybenzaldehyde. A mixture of *Z*/*E*-isomers (8/1 after purification), the yield was 54%, colorless oil. Found (%): C, 42.38; H, 3.20. $C_{11}H_{10}BrF_3O_2$. Calculated (%): C, 42.47; H, 3.24. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR (CDCl$_3$, δ) of *Z*-isomer: 3.89 (s, 6 H, 2 OCH$_3$); 6.88 (d, 1 H, Ar, J = 8.5 Hz); 7.29 (dd, 1 H, Ar, J = 8.5 Hz, J = 1.8 Hz); 7.41 (d, 1 H, Ar, J = 1.8 Hz); 7.49 (s, 1 H, C<u>H</u>=CCF$_3$); *E*-isomer: 3.86 (s, 6 H, OCH$_3$); 7.15 (dd, 1 H, Ar, J = 8.6 Hz, J = 1.5 Hz). ^{13}C NMR (CDCl$_3$, δ) of *Z*-isomer: 55.9 (2 OCH$_3$); 106.5 (q, <u>C</u>—CF$_3$, J = 36.6 Hz); 121.2 (q, CF$_3$, J = 270.8 Hz); 133.8 (q, <u>C</u>H=CCF$_3$, J = 5.9 Hz); 110.8, 112.1, 124.1, 124.9, 148.7, 150.7 (Ar); *E*-isomer: 55.9 (OCH$_3$); 141.5 (q, <u>C</u>=CHCF$_3$, J = 2.9 Hz); 111.0, 111.5, 122.1, 125.3, 148.6, 150.0 (Ar). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

[2-Bromo-3,3,3-trifluoro-1-propenyl]benzene (2m) was obtained from benzaldehyde. A mixture of *Z*/*E*-isomers (6/1 after purification), the yield was 73%, colorless oil. Found (%): C, 43.27; H, 2.38. $C_9H_6BrF_3$. Calculated (%): C, 43.06; H, 2.41. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR (CDCl$_3$, δ) of *Z*-isomer: 7.49—7.54 (m, 3 H, Ar); 7.69 (s, 1 H, CH=CCF$_3$); 7.77—7.83 (m, 2 H, Ar); *E*-isomer: 7.34—7.83 (m, 2 H, Ar); 7.42—7.47 (m, 3 H, Ar); 7.60 (s, 1 H, C<u>H</u>=CCF$_3$). ^{13}C NMR (CDCl$_3$, δ) of *Z*-isomer: 109.6 (q, <u>C</u>—CF$_3$, J = 36.6 Hz); 121.1 (q, CF$_3$, J = 271.5 Hz); 134.5 (q, <u>C</u>H=CCF$_3$, J = 5.1 Hz); 128.6, 129.7, 130.2, 132.5 (Ar); *E*-isomer: 128.4, 129.1, 128.3, 133.9 (Ar); 141.7 (q, <u>C</u>H=CCF$_3$, J = 2.9 Hz). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-[2-Bromo-3,3,3-trifluoro-1-propenyl]-4-methylbenzene (2n) was obtained from 4-methylbenzaldehyde. A mixture of *Z*/*E*-isomers (9/1 after purification), the yield was 72%, colorless oil.

The synthesis of trifluoromethylvinyl sulfides (general procedure). Ethanol (5 mL), KOH (0.34 g, 5.5 mmol), and thiol (6 mmol) were placed in a 25-mL round-bottom flask, and this was stirred for 5 min until complete dissolution of KOH. Then, a solution of the corresponding styrenes **1** or **2** (5 mmol) in ethanol (5 mL) was added with vigorous stirring, and the reaction mixture was refluxed for 5—10 min (TLC monitoring). The reaction mixture was poured in water (100 mL), extracted with dichloromethane (3×100 mL). The combined extract was washed with brine and dried with Na_2SO_4. Dichloromethane was removed *in vacuo*, the residue was dissolved in hexane or in the appropriate hexane-dichloromethane mixture and run through a short layer of silica gel. Attempted chromatographic separation of isomeric of alkenes failed.

Regioisomers **3**, **4** and *E-, Z*-stereoisomers failed to be isolated by chromatography.

1-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-4-nitrobenzene (3a) was obtained from **1a.** The yield was 96%, yellow oil. Found (%): C, 47.94; H, 3.69. $C_{11}H_{10}F_3NO_2S$. Calculated (%): C, 47.65; H, 3.64. IR, ν/cm^{-1}: 1340, 1520 (NO$_2$), 1620 (C=C). ^{1}H NMR (CDCl$_3$), δ: 1.21 (t, 3 H, SCH$_2$C<u>H</u>$_3$, J = 7.4 Hz); 2.80 (q, 2 H, SC<u>H</u>$_2$CH$_3$, J = 7.4 Hz); 7.49 (s, 1 H, C<u>H</u>=CCF$_3$); 7.92, 8.24 (both d, 2 H each, Ar, J = 7.4 Hz). ^{13}C NMR (CDCl$_3$), δ: 14.4 (SCH$_2$<u>C</u>H$_3$); 28.5 (S<u>C</u>H$_2$CH$_3$); 123.0 (q, CF$_3$, J = 275.2 Hz); 128.5 (q, <u>C</u>—CF$_3$, J = 32.2 Hz); 136.0 (q, <u>C</u>H=CCF$_3$, J = 5.1 Hz); 123.5, 130.9, 140.0, 147.7 (Ar).

1-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-3-nitrobenzene (3b) was obtained as a 12/1 mixture with **1-[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]-3-nitrobenzene (4b)** from **1b**. The yield was (**3** + **4**) 95%, yellow oil. Found (%): C, 47.60; H, 3.51. $C_{11}H_{10}F_3NO_2S$. Calculated (%): C, 47.65; H, 3.64. IR, ν/cm^{-1}: 1340, 1530 (NO$_2$), 1620 (C=C). ^{1}H NMR (CDCl$_3$, δ) of regioisomer **3b**: 1.24 (t, 3 H, SCH$_2$C<u>H</u>$_3$, J = 7.4 Hz); 2.82 (q, 2 H, SC<u>H</u>$_2$CH$_3$, J = 7.4 Hz); 7.51 (s, 1 H, C<u>H</u>=CCF$_3$); 7.62 (t, 1 H, Ar, J = 8.0 Hz); 8.07 (d, 1 H, Ar, J = 8.0 Hz); 8.22 (dd, 1 H, Ar, J = 8.0 Hz, J = 1.4 Hz); 8.70 (s, 1 H, Ar); regioisomer **4b**: 1.11 (t, 3 H, SCH$_2$C<u>H</u>$_3$, J = 7.4 Hz); 2.44 (q, 2 H, SC<u>H</u>$_2$CH$_3$, J = 7.4 Hz); 6.00 (q, 1 H, C<u>H</u>CF$_3$, J = 7.8 Hz); 7.87 (d, 1 H, Ar, J = 8.1 Hz); 8.28 (dd, 1 H, Ar, J = 8.1 Hz, J = 1.3 Hz); 8.63 (s, 1H, Ar). ^{13}C NMR (CDCl$_3$, δ) of regioisomer **3b**: 14.4 (SCH$_2$<u>C</u>H$_3$); 28.7 (S<u>C</u>H$_2$CH$_3$); 123.1 (q, CF$_3$, J = 275.2 Hz); 123.2 (q, <u>C</u>—CF$_3$, J = 32.2 Hz); 136.4 (q, <u>C</u>H=CCF$_3$, J = 5.9 Hz); 123.9, 124.8, 129.4, 135.2, 136.0, 148.2 (Ar); regioisomer **4b**: 14.8 (SCH$_2$<u>C</u>H$_3$); 26.8 (S<u>C</u>H$_2$CH$_3$); 120.8 (q, C=<u>C</u>HCF$_3$, J = 34.4 Hz); 121.5 (q, CF$_3$, J = 270.8 Hz); 123.2, 124.4, 129.5, 137.9, 139.3, 148.1 (Ar). The rest of the signals of **4b** are overlapped with those of regioisomer **3b**.

1-[2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-2-nitrobenzene (3c) was obtained from **1c.** A mixture of *Z*/*E*-isomers (7/1 after purification), the yield was 76%, yellow oil. Found (%): C, 46.86; H, 3.08. $C_{11}H_{10}F_3NO_2S$. Calculated (%): C, 47.65; H, 3.64. IR, ν/cm^{-1}: 1330, 1560 (NO$_2$); 1615 (C=C). ^{1}H NMR (CDCl$_3$, δ) of *Z*-isomer: 1.11 (t, 3 H, SCH$_2$C<u>H</u>$_3$, J = 7.4 Hz); 2.61 (q, 2 H, SC<u>H</u>$_2$CH$_3$, J = 7.4 Hz); 7.56—7.79 (m, 3 H, Ar); 7.85 (s, 1 H, C<u>H</u>=CCF$_3$); 8.20 (d, 1 H, Ar, J = 8.3 Hz); *E*-isomer: 1.32 (t, 3 H, SCH$_2$C<u>H</u>$_3$, J = 7.3 Hz); 2.71 (q, 2 H, SC<u>H</u>$_2$CH$_3$, J = 7.3 Hz); 8.24 (d, 1 H, Ar, J = 8.3 Hz). ^{13}C NMR (CDCl$_3$, δ) of *Z*-isomer: 14.3 (SCH$_2$<u>C</u>H$_3$); 28.4 (S<u>C</u>H$_2$CH$_3$); 123.1 (q, CF$_3$, J = 273.7 Hz); 126.7 (q, <u>C</u>—CF$_3$, J = 32.2 Hz); 137.8 (q, <u>C</u>H=CCF$_3$, J = 5.9 Hz); 124.7, 129.8, 130.1, 131.8, 133.5, 147.3 (Ar); *E*-isomer: 14.4 (SCH$_2$<u>C</u>H$_3$); 32.9 (S<u>C</u>H$_2$CH$_3$); 126.7 (q, <u>C</u>—CF$_3$, J = 38.1 Hz); 129.5 (q, <u>C</u>H=CCF$_3$, J = 4.4 Hz); 125.1, 127.5, 130.4, 131.3, 133.8, 147.2 (Ar). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-Bromo-2-[2-(ethylthio)-3,3,3-trifluoro-1-propenyl]benzene (3d) was obtained from **1d** and **2d.** A mixture of *Z*/*E*-isomers (20/1 after purification), the yield was 89% (from **1d**), 85% (from **2d**), colorless oil. Found (%): C, 42.47; H, 3.14. $C_{11}H_{10}BrF_3S$. Calculated (%): C, 42.46; H, 3.24. IR, ν/cm^{-1}: 1625 (C=C). ^{1}H NMR (CDCl$_3$, δ) of *Z*-isomer: 1.18 (t, 3 H, SCH$_2$C<u>H</u>$_3$, J = 7.4 Hz); 2.68 (q, 2 H, SC<u>H</u>$_2$CH$_3$, J = 7.4 Hz); 7.26 (td, 1 H, Ar, J = 7.6 Hz, J = 1.2 Hz); 7.39 (td, 1 H, Ar, J = 7.6 Hz, J = 0.9 Hz); 7.63 (s, 1 H, C<u>H</u>=CCF$_3$); 7.65 (dd, 1 H, Ar, J = 7.6 Hz, J = 1.2 Hz); 7.77 (dd, 1 H, Ar, J = 7.6 Hz, J = 0.9 Hz); *E*-isomer: 1.45 (t, 3 H, SCH$_2$C<u>H</u>$_3$, J = 7.4 Hz); 2.95 (q, 2 H, SC<u>H</u>$_2$CH$_3$, J = 7.4 Hz). ^{13}C NMR (CDCl$_3$, δ) of *Z*-isomer: 14.3 (SCH$_2$<u>C</u>H$_3$); 28.2 (S<u>C</u>H$_2$CH$_3$); 123.3 (q, CF$_3$, J = 274.5 Hz); 126.7 (q, <u>C</u>—CF$_3$, J = 31.5 Hz); 138.7 (q, <u>C</u>H=CCF$_3$, J = 5.9 Hz); 124.2, 127.1, 130.4, 131.1, 132.6, 134.3 (Ar); *E*-isomer: 15.3 (SCH$_2$<u>C</u>H$_3$); 29.8 (S<u>C</u>H$_2$CH$_3$); 129.8 (q,

C<u>H</u>=CCF$_3$, J = 5.1 Hz). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-Bromo-2-[(1*Z*)-2-(ethylthio)-3,3,3-trifluoro-1-propenyl]-4-methoxybenzene (3e) was obtained from **2e.** The yield was 94%, colorless oil. Found (%): C, 42.33; H, 3.42. $C_{12}H_{12}BrF_3OS$. Calculated (%): C, 42.24; H, 3.55. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.19 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.69 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 3.84 (s, 3 H, $OC\underline{H}_3$), 6.82 (dd, 1 H, Ar, J = 8.8 Hz, J = 2.9 Hz); 7.38 (d, 1 H, Ar, J = 2.9 Hz); 7.50 (d, 1 H, Ar, J = 8.8 Hz); 7.58 (s, 1H, C<u>H</u>=CCF$_3$). ^{13}C NMR ($CDCl_3$), δ: 14.4 ($SCH_2\underline{C}H_3$); 28.3 ($S\underline{C}H_2CH_3$); 55.6 (OCH_3); 123.3 (q, CF_3, J = 273.7 Hz); 126.7 (q, <u>C</u>—CF$_3$, J = 31.5 Hz); 138.5 (q, <u>C</u>H=CCF$_3$, J = 5.6 Hz); 114.7, 116.2, 116.8, 133.2, 134.7, 158.5 (Ar).

Ethyl 4-[(1*Z*)-2-(ethylthio)-3,3,3-trifluoro-1-propenyl]benzoate (3f) was obtained from **1f** and **2f**. The yield was 81% (from **1f**), 89% (from **2f**), colorless oil. Found (%): C, 53.85; H, 4.47. $C_{14}H_{15}F_3O_2S$. Calculated (%): C, 55.25; H, 4.97. IR, ν/cm^{-1}: 1610 (C=C), 1720 (C=O, CO_2Et). ^{1}H NMR ($CDCl_3$), δ: 1.16 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 1.39 (t, 3 H, $CO_2CH_2C\underline{H}_3$, J = 7.1 Hz); 2.73 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 4.38 (q, 2 H, $CO_2C\underline{H}_2CH_3$, J = 7.1 Hz); 7.46 (s, 1 H, C<u>H</u>=CCF$_3$); 7.81, 8.06 (both d, 2 H each, Ar, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.2, 14.3 (both CH_3); 28.5 ($S\underline{C}H_2CH_3$); 61.1 ($CO_2\underline{C}H_2CH_3$); 123.3 (q, CF_3, J = 275.2 Hz); 126.3 (q, <u>C</u>—CF$_3$, J = 30.7 Hz); 137.3 (q, <u>C</u>H=CCF$_3$, J = 5.9 Hz); 129.5, 130.0, 131.0, 137.9 (Ar); 165.9 (<u>C</u>O$_2$CH$_2$CH$_3$).

2-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]pyridine (3g) was obtained from **1g.** The yield was 92%, colorless oil. Found (%): C 51.29; H 4.33. $C_{10}H_{10}F_3NS$. Calculated (%): C, 51.49; H 4.32. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.19 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.81 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 7.21—7.24 (m, 1 H, Py); 7.47 (s, 1 H, C<u>H</u>=CCF$_3$); 7.70 (td, 1 H, Py, J = 7.7 Hz, J = 1.7 Hz); 7.95 (d, 1 H, Py, J = 7.7 Hz); 8.64—8.67 (m, 1 H, Py). ^{13}C NMR ($CDCl_3$), δ: 14.2 ($SCH_2\underline{C}H_3$); 28.2 ($S\underline{C}H_2CH_3$); 123.2 (q, CF_3, J = 274.4 Hz); 127.9 (q, <u>C</u>—CF$_3$, J = 31.5 Hz); 136.7 (q, <u>C</u>H=CCF$_3$, J = 5.9 Hz); 123.3, 125.3, 136.1, 149.5, 152.9 (Py).

1-Chloro-4-[(1*Z*)-2-(ethylthio)-3,3,3-trifluoro-1-propenyl]benzene (3h) was obtained as a 5/1 mixture with **1-chloro-4-[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]benzene (4h)** from **1h** and **2h**. The yield was (**3** + **4**) 90% (from **1h**), 93% (from **2h**), colorless oil. Found (%): C, 49.62; H, 3.73. $C_{11}H_{10}ClF_3S$. Calculated (%): C, 49.54; H, 3.78. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of regioisomer **3h**: 1.23 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.79 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 7.41 (d, 2 H, Ar, J = 8.6 Hz); 7.45 (s, 1 H, C<u>H</u>=CCF$_3$); 7.79 (d, 2 H, Ar, J = 8.6 Hz); regioisomer **4h**: 1.11 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.3 Hz); 2.44 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.3 Hz); 5.91 (q, 1 H, C<u>H</u>CF$_3$, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$, δ) of regioisomer **3h**: 14.4 ($SCH_2\underline{C}H_3$); 28.6 ($S\underline{C}H_2CH_3$); 123.5 (q, CF_3, J = 274.4 Hz); 124.5 (q, <u>C</u>—CF$_3$, J = 31.5 Hz); 137.9 (q, <u>C</u>H=CCF$_3$, J = 5.1 Hz); 128.7, 131.6, 132.1, 135.5 (Ar); regioisomer **4h**: 14.9 ($SCH_2\underline{C}H_3$); 26.7 ($S\underline{C}H_2CH_3$); 119.2 (q, C=<u>C</u>HCF$_3$, J = 34.4 Hz); 129.0, 129.4, 135.7, 136.0 (Ar). The rest of the signals of **4h** are overlapped with those of regioisomer **3h**.

1-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-4-methoxybenzene (3i) was obtained as a 0.5/1 mixture with **1-[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]-4-methoxybenzene (4i)** from **2i**. The yield was (**3** + **4**) 93%, colorless oil. Found (%): C, 54.88; H, 4.93. $C_{12}H_{13}F_3OS$. Calculated (%): C, 54.95; H, 5.00. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of regioisomer **3i**: 1.26 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.80 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 3.87 (s, 3 H, OCH_3); 6.97 (d, 2 H, Ar, J = 8.7 Hz); 7.46 (s, 1 H, C<u>H</u>=CCF$_3$); 7.92 (d, 2 H, Ar, J = 8.7 Hz); regioisomer **4i**: 1.11 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.3 Hz); 2.48 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.3 Hz); 3.87 (s, 3 H, $OC\underline{H}_3$); 5.88 (q, 1 H, C<u>H</u>CF$_3$, J = 8.6 Hz); 6.97, 7.47 (both d, 2 H each, Ar, J = 8.9 Hz). ^{13}C NMR ($CDCl_3$, δ) of regioisomer **3i**: 14.4 ($SCH_2\underline{C}H_3$); 28.7 ($S\underline{C}H_2CH_3$); 55.3 ($O\underline{C}H_3$); 120.5 (q, <u>C</u>—CF$_3$, J = 31.5 Hz); 124.0 (q, CF_3, J = 274.5 Hz); 139.3 (q, <u>C</u>H=CCF$_3$, J = 5.1 Hz); 113.8, 126.2, 132.4, 160.8 (Ar); regioisomer **4i**: 14.9 ($SCH_2\underline{C}H_3$); 26.8 ($S\underline{C}H_2CH_3$); 55.3 ($O\underline{C}H_3$); 117.5 (q, C=<u>C</u>HCF$_3$, J = 34.4 Hz); 123.0 (q, CF_3, J = 270.8 Hz); 151.0 (q, <u>C</u>=CHCF$_3$, J = 5.1 Hz); 114.1, 126.2, 129.5, 160.8 (Ar).

1-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-3-methoxybenzene (3j) was obtained as a 3/1 mixture with **1-[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]-3-methoxybenzene (4j)** from **2j**. The yield was (**3** + **4**) 95%, colorless oil. Found (%): C, 54.48; H, 4.85. $C_{12}H_{13}F_3OS$. Calculated (%): C, 54.95; H, 5.00. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR ($CDCl_3$, δ) of regioisomer **3j**: 1.26 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.81 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 3.87 (s, 3 H, OCH_3); 6.95—7.02 (m, 1 H, Ar); 7.34—7.39 (m, 2 H, Ar); 7.49 (s, 1 H, C<u>H</u>=CCF$_3$); 7.64 (s, 1 H, Ar); regioisomer **4j**: 1.14 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.3 Hz); 2.49 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.3 Hz); 3.87 (s, 3 H, OCH_3); 5.94 (q, 1 H, C<u>H</u>CF$_3$, J = 8.1 Hz); 7.05—7.12 (m, 2 H, Ar); 7.28—7.34, 7.35—7.39 (both m, 1 H each, Ar). ^{13}C NMR ($CDCl_3$, δ) of regioisomer **3j**: 14.4 ($SCH_2\underline{C}H_3$); 28.6 ($S\underline{C}H_2CH_3$); 55.2 (OCH_3); 123.7 (q, CF_3, J = 273.7 Hz); 124.0 (q, <u>C</u>—CF$_3$, J = 31.5 Hz); 139.1 (q, <u>C</u>H=CCF$_3$, J = 5.1 Hz); 115.2, 115.6, 123.1, 129.4, 134.9, 159.5 (Ar); regioisomer **4j**: 15.0 ($SCH_2\underline{C}H_3$); 26.8 ($S\underline{C}H_2CH_3$); 55.3 ($O\underline{C}H_3$); 118.4 (q, C=<u>C</u>HCF$_3$, J = 34.4 Hz); 122.9 (q, CF_3, J = 270.8 Hz); 151.4 (q, <u>C</u>=CHCF$_3$, J = 5.1 Hz); 113.6, 120.5, 129.7, 138.9, 159.9 (Ar). The rest of the signals are overlapped with those of regioisomer **3j**.

1-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-2-methoxybenzene (3k) was obtained as a 7/1 mixture with **1-[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]-2-methoxybenzene (4k)** from **2k**. The yield was (**3** + **4**) 85%, colorless oil. Found (%): C, 55.37; H, 5.03. $C_{12}H_{13}F_3OS$. Calculated (%): C, 54.95; H, 5.00. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of regioisomer **3k**: 1.21 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.75 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 3.89 (s, 3 H, $OC\underline{H}_3$); 6.95 (d, 1 H, Ar, J = 8.0 Hz); 7.04 (t, 1 H, Ar, J = 7.6 Hz); 7.40 (td, 1 H, Ar, J = 8.0 Hz, J = 1.1 Hz); 7.81 (s, 1 H, C<u>H</u>=CCF$_3$); 8.05 (dd, 1 H, Ar, J = 7.6 Hz, J = 1.1 Hz); regioisomer **4k**: 1.11 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.3 Hz); 2.37 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.3 Hz); 3.88 (s, 3 H, OCH_3); 5.71 (q, 1 H, C<u>H</u>CF$_3$, J = 8.5 Hz); 6.98 (d, 1 H, Ar, J = 8.8 Hz); 7.26 (dd, 1 H, Ar, J = 7.6 Hz, J = 1.5 Hz). ^{13}C NMR ($CDCl_3$, δ) of regioisomer **3k**: 14.2 ($SCH_2\underline{C}H_3$); 28.3 ($S\underline{C}H_2CH_3$); 55.5 (OCH_3); 123.4 (q, <u>C</u>—CF$_3$, J = 30.7 Hz); 123.8 (q, CF_3, J = 273.7 Hz); 134.9 (q, <u>C</u>H=CCF$_3$, J = 5.9 Hz); 110.5, 120.1, 122.5, 130.3, 131.0, 157.8 (Ar); regioisomer **4k**: 14.5 ($SCH_2\underline{C}H_3$); 26.1 ($S\underline{C}H_2CH_3$); 55.6 ($O\underline{C}H_3$); 116.0 (q, C=<u>C</u>HCF$_3$, J = 34.4 Hz); 123.2 (q, CF_3, J = 270.8 Hz); 148.7 (q, <u>C</u>=CHCF$_3$, J = 5.9 Hz); 111.1, 120.6, 126.2, 130.2, 130.4, 156.3 (Ar). The rest of the signals of **4k** are overlapped with those of regioisomer **3k**.

4-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-1,2-dimethoxybenzene (3l) was obtained as a 1/1 mixture with **4-[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]-1,2-dimethoxybenzene (4l)** from **2l**. The yield was (**3** + **4**) 89%, colorless oil. Found (%): C, 53.37; H, 5.28. $C_{13}H_{15}F_3O_2S$. Calculated (%): C, 53.41; H, 5.17. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR ($CDCl_3$, δ) of regioisomer **3l**: 1.21 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.76 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 3.89 (s, 6 H, $OC\underline{H}_3$); 6.87 (d, 1 H, Ar, J = 8.3 Hz); 7.31 (dd, 1 H, Ar, J = 8.3 Hz, J = 1.8 Hz); 7.38 (s, 1 H, C$\underline{H}$=CCF_3); 7.80 (d, 1 H, Ar, J = 1.8 Hz); regioisomer **4l**: 1.07 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.3 Hz); 2.44 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.3 Hz); 3.89 (s, 6 H, OCH_3); 5.86 (q, 1 H, $CHCF_3$, J = 8.1 Hz); 6.87 (d, 1 H, Ar, J = 8.3 Hz); 7.01 (d, 1 H, Ar, J = 2.0 Hz); 7.04 (dd, 1 H, Ar, J = 8.3 Hz, J = 2.0 Hz). ^{13}C NMR ($CDCl_3$, δ) of regioisomer **3l**: 14.5 ($SCH_2\underline{C}H_3$); 28.8 ($S\underline{C}H_2CH_3$); 55.8, 56.0 (both OCH_3); 120.4 (q, $\underline{C}$—CF_3, J = 30.7 Hz); 123.9 (q, CF_3, J = 273.7 Hz); 139.4 (q, $\underline{C}$H=CCF_3, J = 5.1 Hz); 111.0, 112.6, 125.2, 130.0, 150.3, 150.4 (Ar); regioisomer **4l**: 15.0 ($SCH_2\underline{C}H_3$); 26.8 ($S\underline{C}H_2CH_3$); 55.8, 55.9 (both OCH_3); 117.7 (q, C=$\underline{C}HCF_3$, J = 34.4 Hz); 122.9 (q, CF_3, J = 270.8 Hz); 150.0 (q, $\underline{C}$=$CHCF_3$, J = 5.9 Hz); 110.6, 111.0, 120.9, 126.3, 148.6, 149.0 (Ar).

[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]benzene (3m) was obtained as a 2/1 mixture with **[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]benzene (4m)** from **2m.** The yield was (**3** + **4**) 96%, colorless oil. Found (%): C, 56.69; H, 4.81. $C_{11}H_{11}F_3S$. Calculated (%): C, 56.88; H, 4.77. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR ($CDCl_3$, δ) of regioisomer **3m**: 1.29 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.84 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 7.43—7.52 (m, 3 H, Ar); 7.58 (s, 1 H, C$\underline{H}$=CCF_3); 7.91 (d, 2 H, Ar, J = 6.8 Hz); regioisomer **4m**: 1.16 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.3 Hz); 2.51 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.3 Hz); 5.96 (q, 1 H, C$\underline{H}CF_3$, J = 8.1 Hz); 7.54—7.59 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$, δ) of regioisomer **3m**: 14.4 ($SCH_2\underline{C}H_3$); 28.6 ($S\underline{C}H_2CH_3$); 123.8 (q, CF_3, J = 273.7 Hz); 123.9 (q, $\underline{C}$—CF_3, J = 31.5 Hz); 139.3 (q, $\underline{C}$H=CCF_3, J = 5.1 Hz); 128.4, 129.7, 130.4, 133.7 (Ar); regioisomer **4m**: 14.9 ($SCH_2\underline{C}H_3$); 26.7 ($S\underline{C}H_2CH_3$); 118.5 (q, C=$\underline{C}HCF_3$, J = 34.4 Hz); 123.0 (q, CF_3, J = 270.8 Hz); 151.6 (q, $\underline{C}$=$CHCF_3$, J = 5.1 Hz); 128.2, 128.8, 129.7, 137.6 (Ar). The rest of the signals of **4m** are overlapped with those of regioisomer **3m**.

1-[(1*Z*)-2-(Ethylthio)-3,3,3-trifluoro-1-propenyl]-4-methylbenzene (3n) was obtained as a 1/1 mixture with **1-[(1*Z*)-1-(ethylthio)-3,3,3-trifluoro-1-propenyl]-4-methylbenzene (4n)** from **1n** and **2n**. The yield was (**3** + **4**) 64% (from **1n**), 76% (from **2n**), colorless oil. Found (%): C, 58.33; H, 4.99. $C_{12}H_{13}F_3S$. Calculated (%): C, 58.52; H, 5.32. IR, ν/cm^{-1}: 1610 (C=C). ^{1}H NMR ($CDCl_3$, δ) of regioisomer **3n**: 1.27 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.45 (s, 3 H, CH_3); 2.82 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.4 Hz); 7.28 (d, 2 H, Ar, J = 7.7 Hz); 7.51 (s, 1 H, C$\underline{H}$=CCF_3); 7.81 (d, 2 H, Ar, J = 7.7 Hz); regioisomer **4n**: 1.13 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.3 Hz); 2.46 (s, 3 H, CH_3); 2.49 (q, 2 H, $SC\underline{H}_2CH_3$, J = 7.3 Hz); 5.92 (q, 1 H, C$\underline{H}CF_3$, J = 8.1 Hz); 7.28, 7.43 (both d, 2 H each, Ar, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, δ) of regioisomer **3n**: 14.2 ($SCH_2\underline{C}H_3$); 21.4 (CH_3); 28.6 ($S\underline{C}H_2CH_3$); 122.1 (q, $\underline{C}$—CF_3, J = 30.7 Hz); 123.8 (q, CF_3, J = 273.0 Hz); 139.4 (q, $\underline{C}$H=CCF_3, J = 5.1 Hz); 129.2, 130.5, 130.9, 140.1 (Ar); regioisomer **4n**: 14.9 ($SCH_2\underline{C}H_3$); 21.2 (CH_3); 26.7 ($S\underline{C}H_2CH_3$); 118.0 (q, C=$\underline{C}HCF_3$, J = 34.4 Hz); 123.0 (q, CF_3, J = 270.8 Hz); 151.4 (q, $\underline{C}$=$CHCF_3$, J = 5.1 Hz); 128.0, 129.4, 134.6, 139.8 (Ar).

1-[(1*Z*)-2-(Benzylthio)-3,3,3-trifluoro-1-propenyl]-4-nitrobenzene (5b) was obtained from **1a**. The yield was 91%, yellow oil. Found (%): C, 54.89; H, 3.50. $C_{16}H_{12}F_3NO_2S$. Calculated (%): C, 56.63; H, 3.56. IR, ν/cm^{-1}: 1350, 1530 (NO_2), 1620 (C=C). ^{1}H NMR ($CDCl_3$), δ: 3.97 (s, 2 H, CH_2); 7.11—7.17 (m, 2 H, Ph); 7.19—7.24 (m, 3 H, Ph); 7.54 (s, 1 H, C$\underline{H}$=CCF_3); 7.59, 8.20 (both d, 2 H each, 4-$NO_2C_6\underline{H}_4$, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 39.1 (CH_2); 123.4 (q, CF_3, J = 275.2 Hz); 127.1 (q, $\underline{C}$—CF_3, J = 31.5 Hz); 139.1 (q, $\underline{C}$H=CCF_3, J = 5.1 Hz); 123.2, 127.7, 128.6, 129.2, 130.8, 136.0, 139.6, 147.7 (Ar).

2-{(*Z*)-[2-(4-Nitrophenyl)-1-(trifluoromethyl)vinyl]thio}phenylamine (5c) was obtained from **1a**. The yield was 81%, orange crystals, m.p. 81—82 °C. Found (%): C, 52.97; H, 3.48. $C_{15}H_{11}F_3N_2O_2S$. Calculated (%): C, 52.94; H, 3.26. IR, ν/cm^{-1}: 1350, 1510 (NO_2), 1620 (C=C), 2950 br. (NH). ^{1}H NMR ($CDCl_3$), δ: 4.07 (s, 2 H, NH_2); 6.60—6.67 (m, 2 H, 2-$NH_2C_6H_4$); 7.11 (td, 1 H, 2-$NH_2C_6H_4$, J = 7.7 Hz, J = 1.5 Hz); 7.23 (dd, 1 H, 2-$NH_2C_6H_4$, J = 7.7 Hz, J = 1.2 Hz); 7.55 (s, 1 H, C$\underline{H}$=CCF_3); 7.80 (d, 2 H, 4-$NO_2C_6H_4$, J = 8.8 Hz); 8.25 (d, 2 H, 4-$NO_2C_6H_4$, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 122.5 (q, CF_3, J = 275.2 Hz); 128.7 (q, $\underline{C}$—CF_3, J = 31.5 Hz); 135.3 (q, $\underline{C}$H=CCF_3, J = 5.1 Hz); 112.4, 115.5, 118.8, 123.5, 130.7, 131.0, 135.6, 139.6, 147.8, 148.1 (Ar).

Ethyl [(2-(4-nitrophenyl)-1-(trifluoromethyl)vinyl)thio]acetate (5d) was obtained from **1a**. A mixture of *Z*/*E*-isomers (12/1 after purification), the yield was 72%, yellow oil. Found (%): C, 46.48; H, 3.75. $C_{13}H_{12}F_3NO_4S$. Calculated (%): C, 46.57; H, 3.61. IR, ν/cm^{-1}: 1360, 1530 (NO_2), 1620 (C=C), 1740 (C=O, CO_2Et). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 1.19 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1 Hz); 3.52 (s, 2 H, $SC\underline{H}_2$); 4.07 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.1 Hz); 7.55 (s, 1 H, C$\underline{H}$=CCF_3); 7.97, 8.26 (both d, 2 H each, Ar, J = 8.9 Hz); *E*-isomer: 1.30 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.63 (s, 2 H, $SC\underline{H}_2$); 4.24 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.2 Hz); 7.45 (s, 1 H, C$\underline{H}$=CCF_3); 7.45, 8.21 (both d, 2 H each, Ar, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 14.0 ($OCH_2\underline{C}H_3$); 35.3 (SCH_2); 61.9 ($O\underline{C}H_2CH_3$); 122.9 (q, CF_3, J = 275.2 Hz); 126.5 (q, $\underline{C}$—CF_3, J = 32.2 Hz); 138.3 (q, $\underline{C}$H=CCF_3, J = 5.1 Hz); 123.6, 131.1, 139.4, 148.0, (Ar); 168.1 ($\underline{C}O_2C_2H_5$); *E*-isomer: 14.2 ($OCH_2\underline{C}H_3$); 35.3 (SCH_2); 61.9 ($O\underline{C}H_2CH_3$); 123.5 (Ar); 129.3 (q, $\underline{C}$H=CCF_3, J = 2.2 Hz). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-Chloro-4-[(2-(4-nitrophenyl)-1-(trifluoromethyl)vinyl)thio]benzene (5e) was obtained from **1a**. A mixture of *Z*/*E*-isomers (7/1 after purification), the yield was 85%, yellow oil. Found (%): C, 50.04; H, 2.33. $C_{15}H_9ClF_3NO_2S$. Calculated (%): C, 50.08; H, 2.52. IR, ν/cm^{-1}: 1350, 1530 (NO_2), 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 7.19—7.26 (m, 4 H, 4-ClC_6H_4); 7.73 (s, 1 H, C$\underline{H}$=CCF_3); 7.88, 8.24 (both d, 2 H each, 4-$NO_2C_6\underline{H}_4$, J = 8.7 Hz); *E*-isomer: 7.01 (s, 1 H, C$\underline{H}$=CCF_3); 7.41 (d, 2 H, 4-$ClC_6\underline{H}_4$, J = 8.6 Hz); 7.45 (d, 2 H, 4-$NO_2C_6\underline{H}_4$, J = 8.7 Hz); 7.49 (d, 2 H, 4-$ClC_6\underline{H}_4$, J = 8.6 Hz); 8.21 (d, 2 H, 4-$NO_2C_6\underline{H}_4$, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 122.7 (q, CF_3, J = 275.2 Hz); 127.1 (q, $\underline{C}$—CF_3, J = 32.2 Hz); 139.6 (q, $\underline{C}$H=CCF_3, J = 5.1 Hz); 123.6, 129.5, 130.7, 130.9, 131.0, 134.0, 139.0, 148.2 (Ar); *E*-isomer: 129.3 (q, $\underline{C}$H=CCF_3, J = 2.2 Hz); 123.5, 130.1, 134.0, 137.7 (Ar). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

1-Methyl-4-[(2-(4-nitrophenyl)-1-(trifluoromethyl)vinyl)thio]benzene (5f) was obtained from **1a**. A mixture of *Z*/*E*-isomers (7/1 after purification), the yield was 88%, yellow oil. Found (%): C, 56.71; H, 3.63. $C_{16}H_{12}F_3NO_2S$. Calculated (%): C, 56.63, H, 3.56. IR, ν/cm^{-1}: 1350, 1530 (NO_2), 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ) of *Z*-isomer: 2.31 (s, 3 H, CH_3); 7.08, 7.20 (both d, 2 H each, 4-$CH_3C_6H_4$, J = 8.1 Hz); 7.67 (s, 1 H, C<u>H</u>=CCF_3); 7.89, 8.22 (both d, 2 H each, 4-$NO_2C_6H_4$, J = 8.7 Hz); *E*-isomer: 2.41 (s, 3 H, CH_3); 6.72 (s, 1 H, C<u>H</u>=CCF_3); 7.27 (d, 2 H, 4-$CH_3C_6H_4$, J = 8.0 Hz); 7.41 (d, 2 H, 4-$NO_2C_6H_4$, J = 8.7 Hz); 7.49 (d, 2 H, 4-$CH_3C_6H_4$, J = 8.0 Hz); 8.18 (d, 2 H, 4-$NO_2C_6H_4$, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, δ) of *Z*-isomer: 21.0 (CH_3); 122.8 (q, CF_3, J = 275.2 Hz); 128.2 (q, <u>C</u>—CF_3, J = 32.2 Hz); 138.2 (q, <u>C</u>H=CCF_3, J = 5.1 Hz); 123.5, 128.4, 130.1, 130.2, 130.9, 138.1, 139.4, 148.0 (Ar); *E*-isomer: 21.3 (CH_3); 129.3 (q, <u>C</u>H=CCF_3, J = 1.5 Hz); 123.4, 130.8, 134.0, 140.0, 141.1, 147.4 (Ar). The rest of the signals of *E*-isomer are overlapped with those of *Z*-isomer.

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