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Synthesis of trifluoromethylated heterocycles using partially fluorinated epoxides

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ABSTRACT

Reaction of 2-trifluoromethyl- (**1**) and 2,2-bis(trifluoromethyl)- (**2**) oxiranes with a variety of sulfur nucleophiles proceeds rapidly and under mild conditions. For example, epoxide **2** reacts with aqueous solution of Na_2S, producing $S[CH_2C(CF_3)_2OH]_2$. Reaction of **2** with $Na_2S_2O_3$ leads to the formation of the corresponding Bunte salt. Interaction of **2** with NaSCN in water proceeds exothermically and results in high-yield formation of cyclic imine **5**. Although this material can be isolated, it has limited stability and undergoes cyclotrimerization at ambient temperature, giving the corresponding 1,3,5-triazine. A number of heterocyclic compounds containing pendant $-CH_2C(CF_3)_2OH$ group were prepared by the reaction of the corresponding thio-derivatives, such as pyridine-2-thiole with epoxide **2**. It was found that fluoride anion catalyzes the reaction of epoxides **1** and **2** with isothiocyanates carrying electron withdrawing groups at nitrogen. The reaction results in nucleophilic cyclization and formation of the corresponding exocyclic imines containing a 1,3-oxothiolane moiety. Carbon disulfide was also found to be active in this process, reacting with epoxides **1** and **2** at ambient to give the corresponding trifluoromethylated 1,3-oxathiolane-2-thiones in 58–65% yield.

1. Introduction

2-Trifluoromethyl- (**1**) and 2,2-bis(trifluoromethyl)- (**2**) oxiranes have high reactivity towards nucleophilic reagents and were reported to react under relatively mild conditions with a variety of nucleophilic [1–6] and electrophilic reagents [1,5,7]. Although the epoxide **2** under basic conditions undergoes polymerization [8] and living co-polymerization with $CH_2(O)C(CF_3)CF_2OCH_2CF_3$ [9] it still is able to react with variety of nucleophiles. Sulfur nucleophiles seem to have high reactivity towards this oxirane. For example, **2** was reported to react with $C_6F_{13}(CH_2)_2SH$ in the absence of the catalyst at ambient temperature, producing $C_6F_{13}(CH_2)_2SCH_2C(CF_3)_2OH$ [5].

In this study high reactivity of epoxides **1** and **2** towards sulfur nucleophiles was exploited and was applied for the synthesis of different types of trifluoromethylated heterocycles and compounds containing $-S-CH_2C(CF_3)_2OH$ groups.

2. Results and discussion

2.1. Reaction of 2,2-bis(trifluoromethyl)oxirane (2) with Na_2S, $Na_2S_2O_3$ and thiocyanates salts

The reaction of **2** with aqueous solution of Na_2S proceeds exothermally producing sulfide **3**, isolated in 66% yield after acidification of the reaction mixture (Scheme 1).

Parameters of ^1H and ^{19}F NMR spectral data for sulfide **3** are in a good agreement with data reported by the Shreeve group [10] for the material prepared through the photochemical reaction of hexafluoroacetone and $(CH_3)_2S$ (0 °C, 3d, 52% yield). We found that the melting point of purified **3** (74–75 °C) is higher compared to reported value (52 °C [10]), which may be attributed to higher purity of material prepared in this study. The oxidation of **3** by hydrogen peroxide proceeds under mild conditions, resulting in selective formation of sulfoxide **3a** (Scheme 2).

The fact that the oxidation can be carried out under relatively mild conditions may be attributed to the presence of $-C(CF_3)_2OH$ groups in sulfide **3**, since the accelerating effect of hexafluoro-*iso*-propanol on oxidation of hydrocarbon olefins and β-hydroxy sulfides by H_2O_2 was discovered and studied in details by the Bonnet-Delpon group [11,12].

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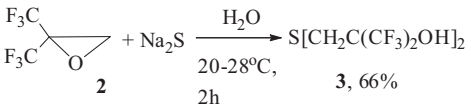
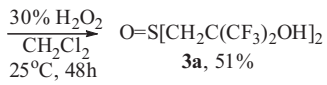
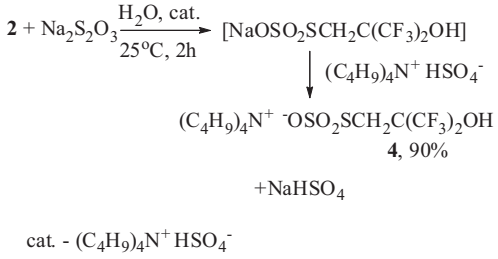


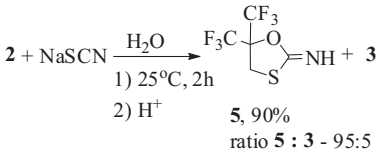
Scheme 1. Reaction of **2** with Na_2S.



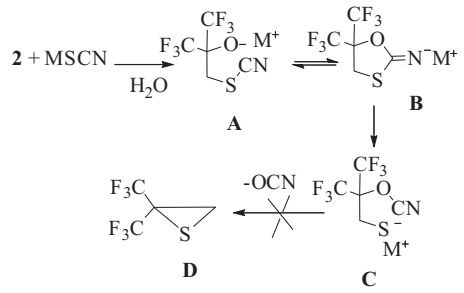
Scheme 2. Preparation of sulfoxide **3a**.



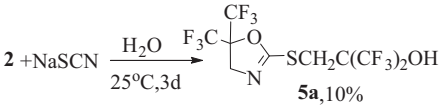
Scheme 3. Reaction of **2** with $Na_2S_2O_3$.



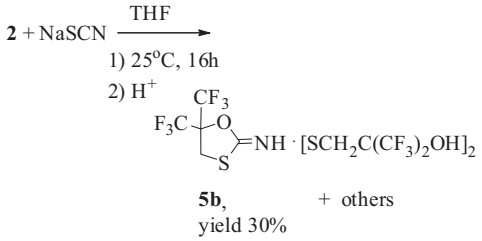
Scheme 4. Reaction of **2** with NaSCN in water (25 °C, 2 h).



Scheme 5. Mechanism of the reaction of **2** with MSCN.



Scheme 6. Reaction of **2** with KSCN in H_2O.



Scheme 7. Reaction of **2** with NaSCN in THF solvent.

Despite low solubility of **2** in water, it is an excellent solvent for the reaction of epoxide **2** with sulfur nucleophiles. For example, the reaction of $Na_2S_2O_3$ with **2** in the presence of phase transfer catalyst proceeds exothermally giving insoluble Bunte salt **4**, (Scheme 3), using the procedure which was employed by Middleton for preparation of Bunte salts of hexafluorothioacetone [13].

The structure of compound **4** was firmly established by single crystal X-ray diffraction data (Fig. 1).

An interesting result was obtained in the reaction of **2** with ambivalent nucleophiles, such as thiocyanate salts. The reaction was explored as a potential route to 2,2-bis(trifluoromethyl)episulfide, since this type of transformation is widely used for the preparation of hydrocarbon thiiranes [14]. The addition of **2** to a water solution of NaSCN was exothermic, resulted in fast disappearance of epoxide layer and the formation of a homogeneous solution. Upon the acidification of the reaction mixture with a saturated aqueous solution of ammonium chloride, followed by extraction with ether or dichloromethane, the product **5** was isolated in 90% yield. The crude product had a typical purity of ~95% and was contaminated by a small amount (~5%) of sulfide **3** (NMR, GC/MS) (Scheme 4).

Based on combined ^1H and ^{19}F NMR, IR and GC/MS data, the structure of cyclic imine **5** was assigned to the major product of this reaction and the structure was confirmed by single crystal X-ray diffraction data (Fig. 2).

The reaction of **2** with KSCN or NH_4SCN also proceeds under mild conditions and results in the formation of **5** as a principal product, although the reaction with KSCN seems to be slower and less exothermic. It should be also pointed out that the process is limited to epoxide **2**, since the reaction of 2-trifluoromethyloxirane (**1**) and NaSCN resulted in rapid polymerization of epoxide.

The formation of an intermediate, structurally similar to compound **5**, was previously postulated for the reactions of hydrocarbon epoxides with thiocyanate salts [14,15]. However, in this case the intermediate rapidly undergoes conversion into the episulfide. The reaction of **2** with thiocyanates salts stops at stage of cyclic imine salt. The formation of salt **B** (see Scheme 5) is the result of intramolecular attack of alkoxy anion on the carbon of –CN group. The salt **B** probably exists in equilibrium with **A** (see also Scheme 9), however, the reason why **B** it is not converted into episulfide **D** is not clear. It is possible, that the intermediate **B** for some reasons does not undergo isomerization into cyanate **C** or intramolecular attack of sulfide anion on this cyclization of C leading to episulfide **D** for some reason is blocked.[2]

The reaction time has a significant effect on the outcome of this process. When time for the reaction of **2** with aqueous solution of NaSCN was extended to 2d, originally formed salt of **5** (in this experiment the formation of salt **B** (M=Na) was confirmed by NMR) underwent further transformations, leading to a mixture of several products. Compound **5a** was isolated in low yield from the organic layer after ~12 h (see Scheme 9 for mechanism of formation of **5a**). Isolated material was characterized by NMR and IR spectroscopy and the structure **5a** was supported by single crystal X-ray diffraction data (Scheme 6).

The choice of solvent is very important for the reaction of epoxides with thiocyanate salts. While, the reaction of hydrocarbon epoxides with NH_4SCN in CH_3CN proceeds at elevated

[2] The factors preventing the formation of episulfide in this process are not well understood. The explanation involving steric hindrance of the carbon bearing two bulky CF_3-groups towards intramolecular attack of sulfide anion would be tempting intramolecular backside attack by neighboring sulfur nucleophile is presumably one of the most favorable setups for nucleophilic displacement.

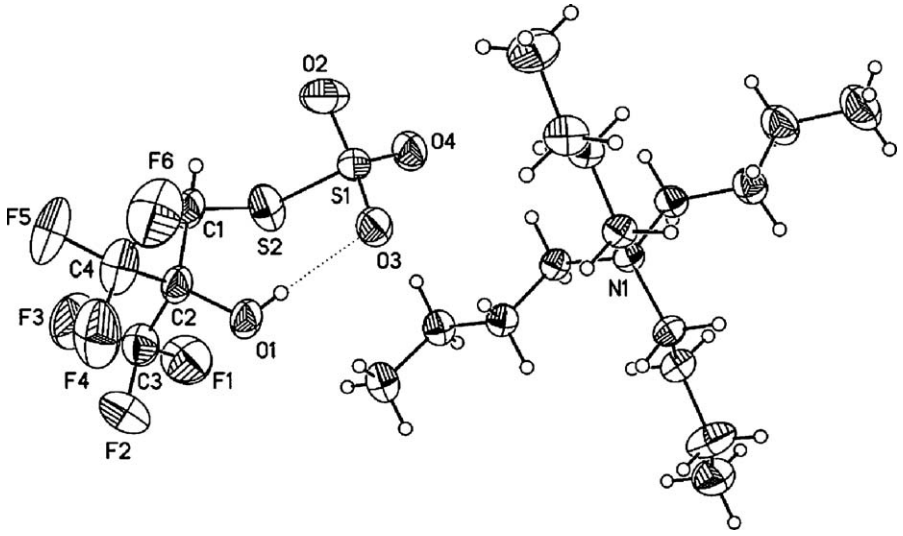


Fig. 1. Thermal ellipsoid drawing of **4** with ellipsoids drawn to the 50% probability level.

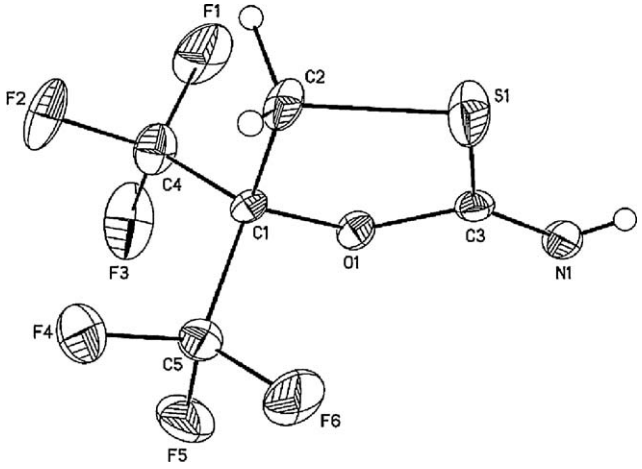


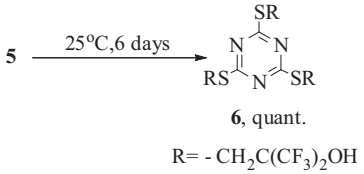
Fig. 2. Thermal ellipsoid drawing of **5** with ellipsoids drawn to the 20% probability level.

temperature and results in clean formation of β-hydroxy thiocyanates [16], the similar process involving **2** and NaSCN in THF or DMF solvent leads to the formation of a rather complex mixture, in which compound **5b** was identified as major component (Scheme 7). The structure of **5b** was established by single crystal X-ray diffraction. The identity of the crystal used for structure determination and the bulk of isolated crystalline material was confirmed by powder X-ray diffraction experiment.

Limited number of complexes between acidic fluoroalcohols is known (see, for example, Refs. [17,18]) and compound **5b** is another example of the stable material formed as the result of relatively strong intermolecular hydrogen bonding between the acidic $-C(CF_3)_2OH$ group and the basic =N–H fragment (O–H···N distance of =2.64 Å). The internal hydrogen bonding in **5b** is depicted in Fig. 3.

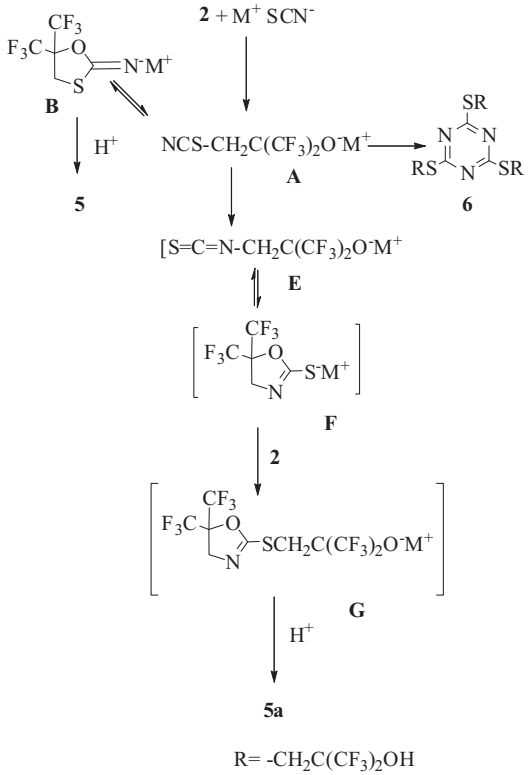
Isolated compound **5** has a limited stability and even at −25 °C slowly undergoes cyclotrimerization. At ambient temperature this process is much faster leading in several days to the quantitative conversion of **5** into **6** (Scheme 8).

Compound **5** was distilled under reduced pressure, but the isolated yield did not exceed 40%, due to competitive formation of **6** at elevated temperature. ^{1}H and ^{19}F NMR of **5** and **6** are virtually identical, although in ^{13}C spectra of **6** the resonance of the carbon of triazine ring is shifted substantially downfield (δ = 180.0 ppm *vs.*



Scheme 8. Trimerization of imine **5**.

δ = 165.3 ppm in **5**). The IR spectrum of **6** exhibits a strong absorption at 1661 cm^{-1}. Data of ^{13}C and IR-spectroscopy of **6** are in good agreement with values reported for hydrocarbon triazines of similar structure [19]. Final proof of the structure comes from single crystal X-ray diffraction (see Fig. 4).



Scheme 9. Mechanism of formation compounds **5a** and **6**.

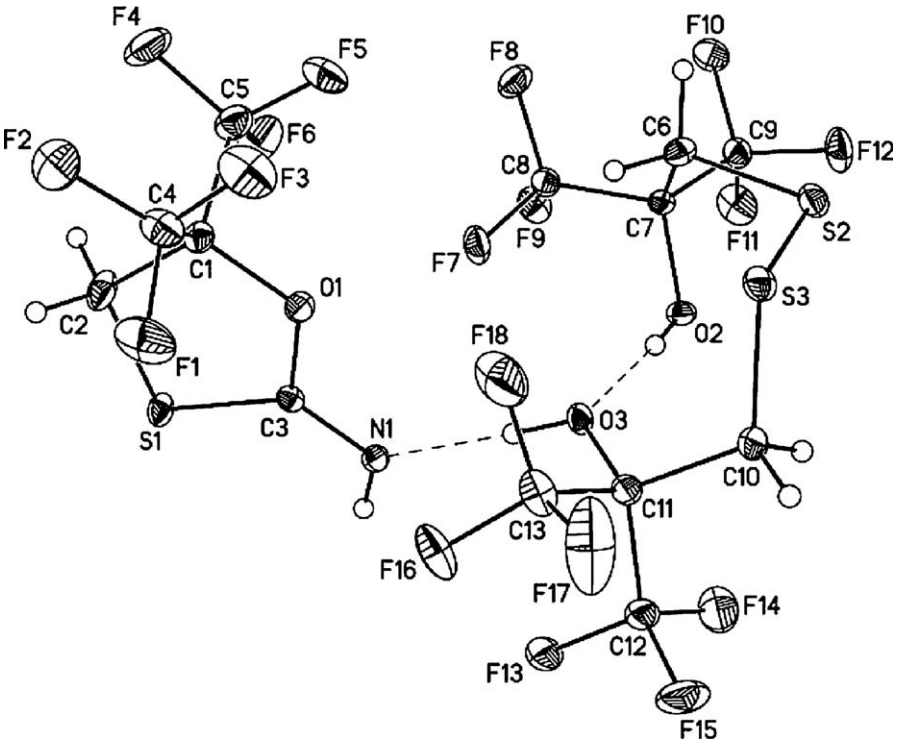


Fig. 3. Thermal ellipsoid drawing of **5b** with ellipsoids drawn to the 20% probability level.

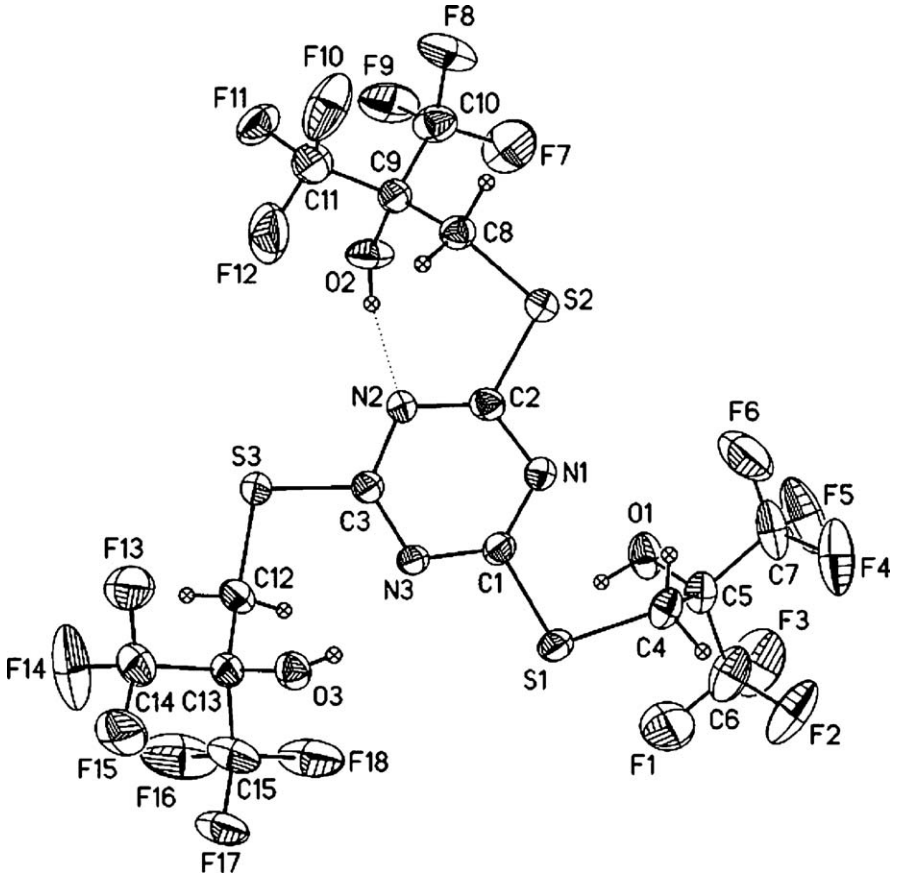


Fig. 4. Thermal ellipsoid drawing of **6** with ellipsoids drawn to the 50% probability level.

The reaction of **2** with HSCN (generated by reaction of KSCN with sulphuric acid [15] in ether) proceeds in the absence of catalyst (0–25 °C, 16 h) leading to the formation of a mixture containing compounds **3**, **5** and **6** as major components (ratio 17:54:27, NMR, GC/MS).

The formation of compounds **5**, **5a** and **6** in reaction of **2** with thiocyane salts can be explained by the existence of equilibrium between salts **A** and **B** (Scheme 9).

Obviously, the trimerization of thiocyanate **A** is responsible for the formation of triazine **6**. The formation of compound **5a** is the result of consecutive transformations including thiocyanate–isothiocyanate rearrangement of **A** into **E**, followed by reversible intramolecular cyclization of **E** into **F** and the reaction of **F** with a second mole of **2** leading to adduct **G**, which is getting converted into **5a** after acidification. The difference in the yields and rates of formation of compounds **5** and **5a** (2 h *vs.* 3 days) suggests that the formation of salts **A** and **B**, is fast but the rate of the formation **5a** is, limited by relatively slow thiocyanate–isothiocyanate rearrangement of **A** into **E**.

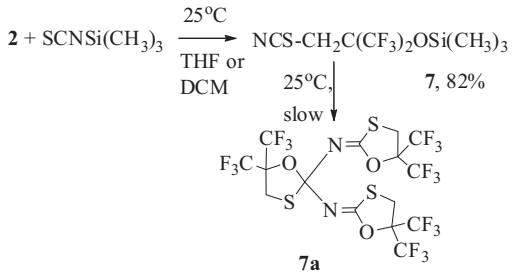
Indirect evidence for possible formation of the intermediate **A** was obtained in a reaction of **2** and trimethylsilylisothiocyanate. The reaction proceeds slowly at ambient temperature in the absence of solvent, leading to a clean and selective formation of *thiocyanate* **7** (see Scheme 10).

The structure of thiocyanate **7** is consistent with data of both IR (sharp absorption at 2163 cm^{-1} *cf.* 2140 cm^{-1} for alkyl thiocyanates [20]) and ^{13}C NMR, spectroscopy (**7**, –S–**C**N, δ = 110.16 ppm, *cf.* δ = 112.1 and 127.8 ppm for C_2H_5S**C**N and C_2H_5N**C**S, respectively [21,22]). Interestingly, compound **7** has significantly higher stability compared to compound **5**. It can be handled and stored at ambient temperature and distilled under reduced pressure without any signs of trimerization. A liquid sample of **7**, stored in a glass sample vial at ambient temperature for ~6 months underwent a partial conversion (~10 wt.% of sample) into a solid material, which was filtered and identified by single crystal X-ray diffraction as **7a**, but was not further characterized.

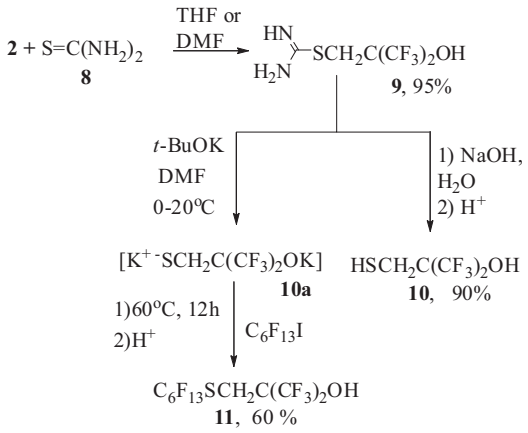
Remarkably rapid conversion of isolated **5** into **6** probably, should involve isomerization of **5** into $CNSCH_2C(CF_3)_2OH$, followed by its trimerization to form **6**. It should be pointed out, that trimerization of hydrocarbon thiocyanates usually requires a catalysis. For example, as it was reported [19] CH_3SCN undergoes trimerization in the presence of triflic anhydride catalyst. It is possible that the conversion of **5** into **6** is catalyzed by an acidic –$C(CF_3)_2OH$ group which is present in intermediate $CNSCH_2C(CF_3)_2OH$. Significantly higher stability of $CNSCH_2C(CF_3)_2OSi(CH_3)_3$ (**7**) towards trimerization agrees well with this hypothesis.

Perfluorinated epoxides were reported to react with thiourea (**8**) to form heterocyclic products [23–27]. Epoxide **2** reacts with **8** in a different fashion, giving linear adduct **9** in 95% yield (Scheme 11).

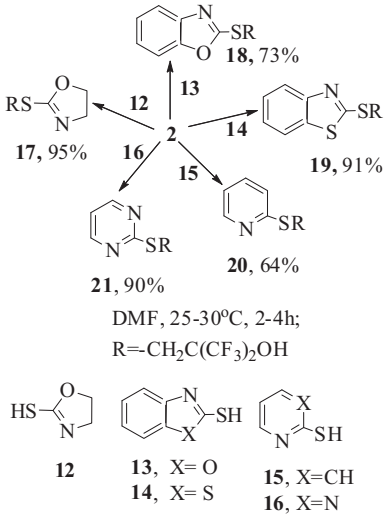
As expected the basic hydrolysis of **9** leads to thiol **10**. The treatment of **9** by *t*-BuOK in DMF solvent followed by reaction with $C_6F_{13}I$ at 50–80 °C results in perfluoroalkylation of intermediate



Scheme 10. Reaction of **2** with $(CH_3)_3SiNCS$.



Scheme 11. Reaction of **2** with thiourea.



Scheme 12. Preparation of heterocycles containing pendant $–SCH_2C(CF_3)_2OH$ group.

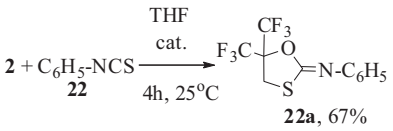
10a and selective formation of sulfide **11**. The mechanism of perfluoroalkylation probably involves a single electron transfer step, a process which is well established for the reaction of thiols with R_FI [28].

Epoxide **2** rapidly reacts with other sulfur nucleophiles. For example, oxazolidine **12**, benzoxa- (**13**) benzthia- (**14**) azoles, pyridine **15** and pyrimidine **16** all react with epoxide **2** in the absence of catalyst to form the corresponding sulfides **17–21** (Scheme 12).

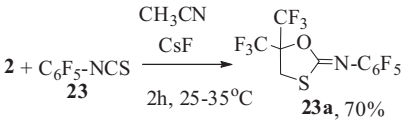
2.2. Reactions of epoxides 1 and 2 with aryl-, fluoroalkenyl-isothiocyanates and carbon disulfide

Epoxides **1** or **2** were found to be inert towards aryl- and alkyl-isothiocyanates in the absence of the catalyst at ambient temperature. However, when the reaction of **2** and phenyl isothiocyanate (**22**) was carried out in the presence of tetrabutylammonium fluoride catalyst, it resulted in high yield formation of imine **22a** (Scheme 13).

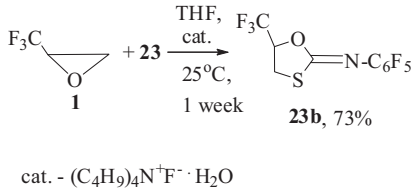
The outcome of the reaction depends strongly on the choice of the catalyst and the reactivity of isothiocyanate. While the use of tetrabutylammonium fluoride catalyst led to a reasonable yield of **22a** in the reaction of **2** with **22**, – either triethylamine or CsF catalyst caused rapid polymerization of epoxide **2**. On the other



Scheme 13. Reaction of **2** with C_6H_5NCS.



Scheme 14. Reaction of **2** with C_6F_5NCS catalyzed by CsF.



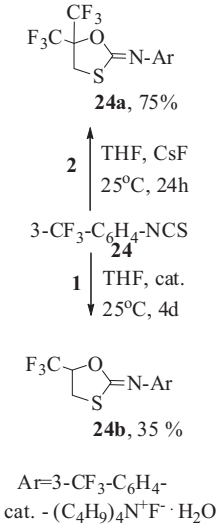
Scheme 15. Reaction of **1** with pentafluorophenylisothiocyanate.

hand, for the reaction of more electrophilic C_6F_5NCS (**23**) with **2** CsF was found to an effective catalyst (Scheme 14).

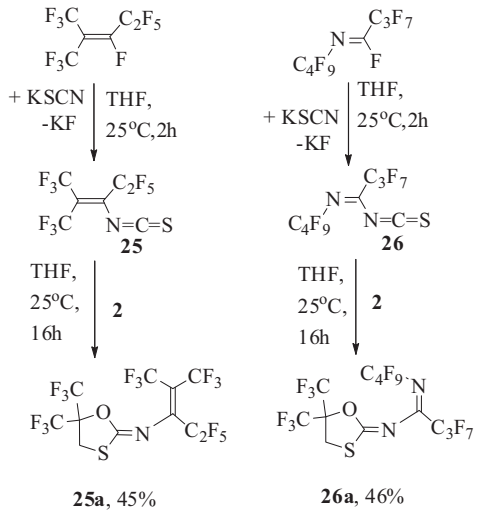
Despite its lower nucleophilicity epoxide **1** reacts with **23** giving imine **23b** ($Bu_4N^+F^-$ catalyst, Scheme 15).

This reaction although was significantly slower (1 week at 25 °C) compared to similar process involving epoxide **2** (see Scheme 14). The same trend was observed in the reaction of epoxides **1** and **2** with isothiocyanate **24** (Scheme 16). While product **24a** was isolated in moderate yield after 24 h, analogous process involving **1** took ~4 days.

Perfluorinated isothiocyanates **25** [29–31] and **26** [32] readily prepared by the reaction of perfluoro(2-methyl)pentene-2 [33,34] or perfluoro-4-aza-nonene-3 [35,36] with sodium thiocyanate were used for the synthesis of a variety of fluorinated heterocycles (see Refs. [37–48] and [32] for reactions of **25** for **26**, respectively). In this study it was shown that both **25** and **26** (generated *in situ* by



Scheme 16. Reaction of **1** and **2** with 3-(trifluoromethyl)phenylisothiocyanate.



Scheme 17. Reaction of **2** with isothiocyanates **25** and **26**.

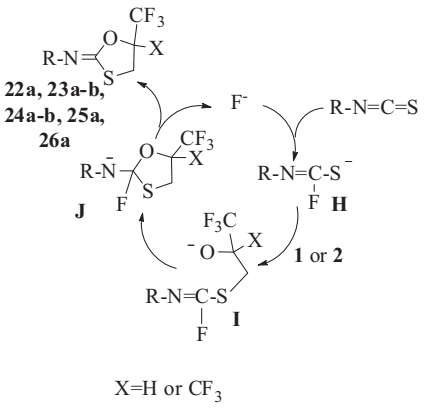
reaction with KSCN in DMF, Scheme 17) rapidly react with **2** giving of the corresponding cyclic imines **25a** and **26a**, respectively.

The reactions were carried out as one-pot process, in the absence of added catalyst, since required for this reaction KF was generated in the first step of the process.

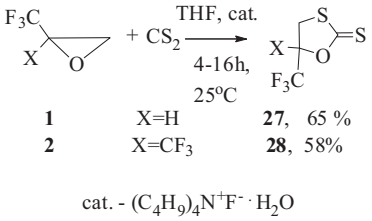
The possible mechanism of the reaction of isothiocyanates **22a**, **23a**, **b**, **24a**, **b**, **25** and **26** with fluorinated epoxides (Scheme 18) involves attack of fluoride anion on isothiocyanate resulting in the formation of delocalized anion **H**. The reaction of **H** with epoxide **1** or **2** leads to alkoxy anion **I** and is followed by its intramolecular cyclization into **J**. The elimination of fluoride anion leads to the formation of cyclic imines **22a**, **23a**, **b**, **24a**, **b**, **25a** or **26a**. Fluoride anion released at this step drives another catalytic cycle.

Experimental data indicate that the electrophilicity of the starting isothiocyanate plays an important role since only relatively electron deficient aryl- or fluoroalkenyl-isothiocyanates were found to be active in this process. All attempts to involve **2** in reaction with *alkyl* isothiocyanates failed.

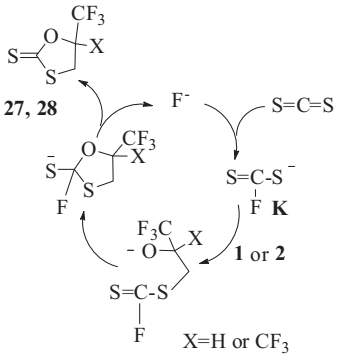
Carbon disulfide been previously shown to undergo [3 + 2] cycloaddition with hydrocarbon epoxides. These reactions usually carried out either in organic solvent or water and are catalyzed by alkoxides [49], aluminium complexes [50] or tertiary amines [51]. We have demonstrated that fluorinated epoxides **1** and **2** react with CS_2 selectively forming the corresponding cycloadducts **27** and **28**. The reaction proceeds under mild conditions and is catalyzed by fluoride anion. The addition of CS_2 to a solution of



Scheme 18. Mechanism of reaction of epoxides **1** and **2** with isothiocyanates.



Scheme 19. Fluoride anion catalyzed reaction of **1** and **2** with CS_2.



Scheme 20. Mechanism of reaction of epoxides **1** and **2** with CS_2.

tetrabutylammonium fluoride in THF results in immediate appearance of deep red colour, which rapidly disappears after addition of epoxide. The reaction of epoxide **2** with CS_2 is fast and typically is completed within 2–3 h, but it takes >12 h under similar conditions with epoxide **1** (Scheme 19).

The mechanism of fluoride anion catalyzed reaction of CS_2 with fluorinated epoxides similar to the mechanism suggested for analogous process reported for hydrocarbon epoxides and catalyzed by sodium methoxide [49] is depicted by Scheme 20.

3. Conclusion

The fluoride anion catalyzed reaction of 2-trifluoromethyl- (**1**) and 2,2-bis(trifluoromethyl)- (**2**) oxiranes with sulfur nucleophiles provides a simple and efficient method for the preparation of a variety of heterocycles containing a variable number of trifluoromethyl or a pendant $S–CH_2C(CF_3)_2OH$ group(s). Most of these reactions proceed under mild conditions, selectively producing the corresponding materials in acceptable yields.

4. Experimental

^1H NMR and ^{19}F NMR spectra were recorded on a Bruker DRX-500 (499.87 MHz) instrument using $CFCl_3$ or TMS as internal standards. Unless stated otherwise, $CDCl_3$ was used as a lock solvent. IR spectra were recorded on a PerkinElmer 1600 FT spectrometer (KCl plates, liquid film or in KBr for solids). Moisture sensitive materials were handled in a glove box, under nitrogen atmosphere. GC and GC/MS analyses were carried out on a HP-6890 instrument, using HP FFAP capillary column and TCD (GC) or mass selective (GS/MS) detectors, respectively. KSCN, NaSCN, NH_4SCN, $Na_2S·9H_2O$, CS_2, $Na_2S_2O_3$, phenyl-, pentafluorophenyl-, 3-CF_3-phenyl-isothiocyanates, thiourea, $(CH_3)_3SiNCS$, $(C_4H_9)_4N^+F^-·H_2O$, $(C_4H_9)_4N^+·HSO_4^-$, compounds **12–16**, THF, CH_3CN (Aldrich), $(CF_3)_2C{=}CFC_2F_5$, 2-(trifluoromethyl)oxirane (**1**, Synquest), $C_6F_{13}I$, 2,2-bis(trifluoromethyl)oxirane (**2**, DuPont) were obtained from commercial sources and used without further purification. CsF (Aldrich) was dried at 100–120 °C under dynamic vacuum for 4–8 h and was stored and handled inside of the dry box. $C_4F_9N{=}CFC_3F_7$ was prepared using literature procedure [36]. Due to a high ratio of sulfur to fluorine, elemental analysis was not attempted for new materials prepared in this study. The purity of all isolated compounds was established by GC/MS and NMR spectroscopy and it was at least 97%.

Crystallography. X-ray data for **4**, **5**, **5b**, **6** and **7a** were collected at −100°C using a Bruker 1K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator.

The structures were solved and refined using the Shelxtl [52] software package, refinement by full-matrix least squares on F^2, scattering factors from Int. Tab. Vol. C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #787678–787682. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.1. Preparation of compound 3

24 g (0.1 mol) of $Na_2S·9H_2O$ was dissolved in 150 mL of DI water. The solution was placed in 250 mL flask equipped with thermocouple, addition funnel, dry-ice condenser and magnetic stir bar. Epoxide **2** (36 g, 0.1 mol) was slowly added to vigorously agitated solution (mildly exothermic), at sufficient rate to maintain an internal temperature <30 °C. The reaction mixture was cooled down to ambient temperature and was agitated for an additional 2 h. It was poured into 300 mL of aqueous saturated solution of NH_4Cl. The precipitate was filtered off and air dried. 26 g (66%) of slightly yellow solid was isolated and identified as sulfide **3**. The isolated material had a limited solubility in acetone, chloroform, acetonitrile, but was readily soluble in basic water. Data for compound **3** are given in Tables 1 and 2.

4.2. Preparation of compound 3a

Compound **3** (1 g, 0.026 mol) was dissolved in 100 mL of CH_2Cl_2 and 5 mL of 30% H_2O_2 was added. The reaction mixture was agitated for 48 h at ambient temperature. Organic layer was separated and washed by 1 N aqueous solution of sodium thiosulfate (3× 200 mL, peroxide test was negative), dried over $MgSO_4$ and solvent was removed under vacuum to leave 0.51 g (51%) of white solid identified as **3a**. Data for compound **3a** are given in Tables 1 and 2.

4.3. Preparation of compound 4

To an agitated mixture of sodium thiosulfate (16 g, 0.1 mol), 0.1 g of $(C_4H_9)_4N^+\ HSO_4^-$ (phase transfer catalyst) and 100 mL of DI water (placed in a flask equipped with thermocouple, addition funnel, dry ice condenser and magnetic stir bar) 18 g (0.1 mol) of **2** was added at a rate, that maintained an internal temperature at 25–30 °C. After the separate layer of **2** completely dissolved, the reaction mixture was agitated for 1 h and then it was poured into an aqueous solution of $(C_4H_9)_4N^+\ HSO_4^-$ (34 g (0.1 mol) in 200 mL of H_2O). The thick reaction mixture was agitated for 10 min, water was drained, and the semi-sold residue was dissolved in 200 mL of acetone. The solution was dried over $MgSO_4$ and the solvent was removed to leave 48 g (90%) of **4**, which crystallized upon storage at ambient temperature. Data for compound **4** are given in Tables 1 and 2.

4.4. Preparation of compound 5

To an agitated solution of 5 g (0.052 mol) KSCN in 50 mL of DI water 10 g (0.55 mol) of **2** was slowly added at 25–28 °C (slightly exothermic). After 2 h the organic phase disappeared and reaction

Table 1
Yields, melting (boiling) points, IR and MS data for new materials.

Entry no.	Comp.	Yield (%)	M.p. (°C) (b.p., °C/mm Hg)	IR (cm^{-1})	MS (*m*/*z*)
1	**3**[a]	66	73–75	–	394 (M^+, $C_8H_6F_{12}O_2S^+$)
2	**3a**[a]	51	113–114[b]	–	410 (M^+, $C_8H_6F_{12}O_3S^+$)
3	**4**[a]	90	195–197[b]	–	–
4	**5**[a]	95[c]	~20[d] (46–47/2)[c]	3228, 1667[e] (C=N)	239 (M^+, $C_5H_3F_6NOS^+$
5	**5a**[a]	10	46–48[b]	1627[f] (C=N)	420 [(M+1)$^+$, $C_9H_6F_{12}NO_2S^+$]
6	**5b**[a]	30	–	3330[f] (OH), 3011 (NH), 1652 (C=N)	–
7	**6**[a]	100	119–120[b]	3227[f] (OH), 1490 (C=N, triazine)	–
8	**7**	82	(94–95/15)	2163[e] (SCN)	238[($M-C_3H_9Si$)$^+$, $C_5H_2F_6NSO^+$)
9	**9**	95	196–197[b]	–	256 (M^+, $C_5H_6F_6N_2OS^+$)
10	**10**	90	–	–	214(M^+, $C_4H_4F_6OS^+$)
11	**11**	60	(95–97/0.5)	–	532 (M^+, $C_{10}H_3F_{19}OS^+$)
12	**17**	95[g]	62–64[b]	–	283, (M^+, $C_8H_9F_6NO_2S^+$)
13	18[a]	73[h]	54–56[b]	–	331 (M^+, $C_{11}H_7F_6NO_2S^+$)
14	**19**	91[h]	100–101[b]		347 (M^+, $C_{11}H_7F_6NOS_2^+$)
15	**20**[a]	64	36–37[b]	–	291 (M^+, $C_9H_7F_6NOS^+$)
16	**21**	90	198–200[b]	–	292 (M^+, $C_8H_6F_6N_2OS^+$)
17	**22a**[a]	67	32–33[b] (80/0.9)		315(M^+, $C_{11}H_7F_6NOS^+$)
18	**23a**[a]	70	50–52	1683, 1675[f] (C=N)	405 (M^+, $C_{11}H_2F_{11}NOS^+$)
19	**23b**[a]	73	50–52[b]		337 (M^+, $C_{10}H_3F_8NOS^+$)
20	**24a**	75	39–40[b]	1676[f] (C=N)	383 (M^+, $C_{12}H_6F_9NOS^+$)
21	**24b**[a]	35			315 (M^+, $C_{11}H_7F_6NOS^+$)
22	**25a**	45	81–82[b] (50–52/0.7)	1627[f] (C=N), 1694 (C=C)	519 (M^+, $C_{11}H_2F_{17}NOS^+$)
23	**26a**	46	(67–68/0.5)	1559,[f] 1649, 1704 (br.)	633 [($M-F$)$^+$, $C_{13}H_2F_{21}N_2OS^+$)
24	**27**[a]	65	(63–64/0.5)[i]		188 (M^+, $C_4H_3F_3OS_2^+$)
25	**28**[a,j]	58	(75–78/25)[i]	–	256 (M^+, $C_5H_2F_6OS_2^+$)

[a] Structure established by single crystal X-ray diffraction.
[b] From hexane.
[c] Yield of crude product; purity 95%, contaminated by 5% of **3**. Freshly prepared **5** was free of **6**, but it underwent partial trimerization during distillation; compound **6** (purity >95%, NMR) was found in distillation pot.
[d] Sample of crude **5** crystallized on storage in refrigerator at −25 °C.
[e] Neat, KCl plate.
[f] In CH_2Cl_2.
[g] Yield of crude product, purity 97%, contaminated by 3% of **12**.
[h] Yield of crude product, purity >98%.
[i] From CCl_4.
[j] Purity of distilled material was 98%.

mixture became homogeneous. The reaction mixture was diluted with 300 mL of saturated aqueous solution of NH_4Cl, extracted with CH_2Cl_2 (3× 50 mL) and the combined organic solution was dried over $MgSO_4$ (~20 min). Solvent was removed under reduced pressure to leave 12.6 g of crude **5**, contaminated by 5% of **3** (NMR). Sample of **5** crystallized on storage in refrigerator. The distillation of crude product gave a fraction of **5** (b.p. 46–47 °C/2 mm Hg, purity >98%) and high boiling point residue in pot of distillation column (~50% of sample by weight), which was found to be almost pure **6** (purity 98% NMR and GC/MS). Data for compound **5** are given in Tables 1 and 2.

4.5. Preparation of compound 5a

The reaction was carried out on same scale as in Section 4.4, but the reaction mixture was left at ambient temperature for 4 days. The precipitated dark organic layer (~3.5 g) was separated, left under a flow of nitrogen overnight and crystallized. Crystalline material (2.3 g, 10% yield) was identified as **5a** based on combined data of NMR, IR spectroscopy, MS spectrometry and single crystal X-ray diffraction data. A small sample of **5a** for melting point measurement was obtained by crystallization from hexane (white needles). Data for compound **5a** are given in Tables 1 and 2.

4.6. Preparation of compound 5b

A mixture of KSCN (10 g, 0.1 mol), **2** (36 g, 0.2 mol) and 200 mL of water was agitated at ambient temperature for 4d. Precipitated organic layer (7.5 g, mostly **5a**) was removed and the remaining reaction mixture was diluted by saturated aqueous solution of NH_4Cl, extracted by ether (3× 75 mL). Combined ether extract was dried over $MgSO_4$, and solvent was removed under reduced pressure to leave 18 g of black, oily material. It was dissolved in 300 mL of hexane and put through short silica gel column. After solvent removal 9.5 g (30%) of tan crystalline solid was isolated and identified as **5b** (NMR, IR, GC/MS, purity 98%). Crystals for X-ray diffraction experiment were obtained by crystallization of small sample from hexane at −25 °C. Data for compound **5b** are given in Tables 1 and 2.

4.7. Preparation of compound 6

Sample of crude **5** (liquid, 12 g, 0.05 mol) stored at ambient temperature crystallized after 6 days. Crystalline material was identified as **6**, 99% purity (NMR, GC/MS). Yield of **6** was quantitative. A small sample for melting point measurement was obtained by crystallization from hexane. Data for compound **6** are given in Tables 1 and 2.

4.8. Preparation of compounds 7 and 7a

(a) A mixture of 3.9 g (0.03 mol) $(CH_3)_3SiNCS$, and 6 g (0.033 mol) of **2** was kept at ambient temperature for 5d. The thick, clear reaction mixture was distilled under reduced pressure to give 7.7 g (82%) of **7**, b.p. 94–95 °C /15 mm Hg. Data for compound **7** are given in Tables 1 and 2.
(b) A mixture of 2.6 g (0.02 mol) $(CH_3)_3SiNCS$, 3.6 g (0.02 mol) **2**, 1 drop of triethylamine and 20 mL of dry THF was agitated at ambient temperature for 24 h. The solvent was removed under vacuum to leave 6.4 g of clear slightly yellow oil, was identified as compound **7** (NMR, IR, GC/MS), containing 5% of THF and 5% of two unknown products.

Table 2
^{1}H, ^{13}C and ^{19}F NMR spectra of new materials.

Compound no.	^{1}H NMR (δ, ppm, J, Hz)[a]	^{19}F NMR (δ, ppm, J, Hz)[a]	^{13}C NMR (δ, ppm, J, Hz)[a,b]
3[c]	3.24 (2H, s), 4.26 (1H, s)	−76.83 (s)	
3a[c]	3.82 (2H, AB quartet, 16), 7.75 (1H, br.s)	−77.12 (3F, q, 10.1), −77.93 (3F, q, 10.1)	52.37, 75.80 (sept, 29.7), 122.46 (q, 288.0), 122.87 (q, 288.0)
4[c]	0.98 (12H, t, 7.4), 1.44 (8H, m, 7.4), 1.82 (8H, m, 7.7), 3.43 (8H, m), 3.66 (2H, s)	−77.44 (s)	
5	3.78 (2H, s), 6.58 (1H, br.s)	−77.50 (s)	31.60, 83.98 (sept, 29.9), 121.13 (q, 286), 165.29
5a	3.50 (2H, s), 4.45 (2H, s), 4.60 (1H, br.s)	−77.20 (3F, s), −78.10 (3F, s)	
5b	3.50 (4H, s), 4.85 (2H, s), 5.90 (1H, br.s)	−76.30 (6F, s), −77.30 (3F, s)	30.84, 42.70, 75.55 (sept, 29.5), 84.64 (sept, 33), 121.00 (q, 284), 122.41 (q, 286), 167.72
6	3.78 (2H, s), 5.30 (1H, br.s)	−77.04 (s)	30.84, 76.84 (sept, 29.0), 124.36 (q, 284), 179.93
7	0.14 (9H, s), 3.35 (2H, sept, 0.6)	−74.86 (s)	0.04, 34.90, 76.26 (sept, 30.5), 110.16, 121.33 (q, 292.0)
9[d]	3.50 (s)[c], 6.42 (br.s)	−76.98 (s)[c]	31.90, 77.19 (sept, 27.6), 123.66 (q, 292.0), 167.51[c]
10	3.51 (s)	−76.20 (s)	
11	3.49 (s)	−76.49 (6F, s), −80.86 (3F, tt, 10.0, 2.0), −119.57 (2F, m), −121.37 (2F, m), −122.73 (2F, m), −126.12 (2F, m)	
17	3.51 (2H, s), 3.54 (2H, t, 8.1), 4.18 (2H, t, 8.1)	−76.40 (s)	33.87 (sept, 1.3), 37.36, 62.15, 77.09 (sept, 27.8), 129.12 (q, 288.0), 172.68
18	3.78 (2H, s), 7.38 (2H, m), 7.52 (1H, m), 7.62 (1H, m)	−76.81	
19	3.76 (2H, s), 7.39 (1H, t, 7.5), 7.48 (1H, t, 7.5), 7.77 (1H, d, 7.5), 7.86 (1H, d, 7.5), 9.93 (1H, br.s)	−76.32	
20	3.58 (2H, s), 7.18 (1H, ddd, 7.4, 5.6, 1.0), 7.41 (1H, dt, 8.2, 1.3), 7.63 (1H, td, 7.8, 1.8), 8.37 (1H, dm, 5.3), 9.82 (1H, s)	−76.32 (s)	
21[c]	3.94 (2H, sept, 0.6), 7.38 (1H, t, 4.9), 8.28 (1H, br.s), 8.72 (2H, d, 4.9)[c]	−76.80[c]	
22a[e]	3.19 (2H, s), 6.98 (2H, t, 7.5), 7.17 (1H, t, 7.5), 7.35 (2H, t, 7.4)	Major: −76.78 (s) Minor: −77.17 (s)	31.04, 82.68 (sept, 32.9), 120.66 (q, 292), 120.62, 121.54, 125.65, 129.45, 147.45, 159.32
23a[f]	3.89 (s), 3.92 (s)	−76.88 (s), −77.11 (s)	
23b[g]	Major: 3.68, 3.74 (2H, m), 5.11 (1H, m) Minor: 3.68, 3.74 (2H, m), 5.04 (1H, m)	Major: −77.51 (3F, d, 5.4), −151.01 (2F, d), −162.51 (2F, t), −163.81 (1F, t) Minor: −77.86 (3F, d, 5.4), −150.21 (2F, d), −160.91 (2F, t), −162.23 (1F, t)	
24a[h]	3.8 (2H, s), 7.15 (1H, m), 7.23 (1H, m), 7.43 (1H, m), 7.47 (1H, m)	Major: −62.88 (3F, s), −76.88 (6F, s) Minor: −63.06 (3F, s), −77.23 (6F, s)	
24b[i]	Major: 3.62 (2H, m), 4.98 (1H, m), 7.14 (1H, d), 7.22 (1H, s), 7.41 (1H, d), 7.46 (1H, m) Minor: 3.22 (2H, m), 5.64 (2H(m)	Major: −62.77 (3F, s), −77.38 (3F, d, 5.4) Minor: −62.55 (3F, dd, 6.1, 1.8), −79.26 (3F, d, 6.1)	
25a	4.0 (s)	−58.62 (3F, m), −63.00 (3F, m), −80.51 (6F, s), −84.12 (3F, m), −114.72 (2F, m)	
26a	3.96 (s)	−77.58 (6F, s), −80.76 (3F, t, 7.6), −81.39 (3F, t, 9.5), −94.48 (2F, m), −116.65 (2F, q, 8.9), −125.97 (2F, m), −126.25 (2F, m), −126.35 (2F, m)	
27	3.78 (dd), 3.87 (dd), (2H, AB quartet), 5.36 (1H, m)	−77.57 (d, 6.1)	33.45 (sept, 1.7), 83.30 (sept, 33.8), 122.00 (q, 280), 208.44
28	3.94 (s)	−77.10 (s)	34.33 (sept, 1.4), 89.99 (sept, 33.2), 120.87 (q, 287), 204.21

[a] In $CDCl_3$ solvent, unless stated otherwise.
[b] ^{13}C {H} NMR spectrum.
[c] In actone-d_6.
[d] In acetonitrile-d_3.
[e] Mixture of two isomers, ratio 90:10.
[f] Mixture of two isomers, ratio 50:50.
[g] Mixture of two isomers, ratio 1.5:1.
[h] Mixture of two isomers, ratio 4:1.
[i] Mixture of two isomers, ratio 5:1.

A sample of crude **7** was left at ambient temperature and after ~6 months the formation of crystalline solid (needles) was observed in the sample. Crystals were filtered and identified as compound **7a** by single crystal X-ray diffraction.

4.9. Preparation of compounds 9, 10 and 11

Compound **2** (12 g, 0.11 mol) was slowly added to an agitated solution of thiourea (**8**, 7.6 g, 0.1 mol) in 100 mL of dry THF, at a rate that maintained internal temperature at 25–28 °C. The reaction mixture was agitated at 25 °C for 2 h and the solvent was removed under vacuum to leave 26 g of white solid material, identified as **9**.

To a solution of 5 g of *t*-BuOK in 30 mL of dry DMF was added a solution of **9** (5 g in 20 mL of DMF) at 5–10 °C. The reaction mixture was warmed to 25 °C (~1 h) and diluted with 300 mL of saturated aqueous solution of NH_4Cl. Precipitated organic layer was separated, washed with water (3× 30 mL), dried over $MgSO_4$ and identified as thiol **9** (NMR spectroscopy).

The reaction of **9** with *t*-BuOK was run as described above (same scale), but after the addition of the solution of *t*-BuOK in DMF, the reaction mixture was agitated at 25 °C for 1 h, and then 13 g of $C_3F_{13}I$ was added. The agitation was continued for another 6 h at 60 °C. The reaction mixture was diluted with 300 mL of 10% hydrochloric acid, extracted by hexane (3× 50 mL), combined extract was washed with water (2× 100 mL), dried over $MgSO_4$ and the solvent was removed under vacuum. The residue (10 g) was distilled under reduced pressure to give 6 g of compound **11**, b.p. 95–97 °C/0.5 mm Hg. Data for compound **9**, **10** and **11** are given in Tables 1 and 2.

4.10. Preparation of compounds 17–21 (typical procedure)

To an agitated solution of 0.1 mol of substrate **12**,**13**,**14**,**15** or **16** in 100 mL of dry THF (placed in the flask equipped with thermocouple, dry-ice condenser and addition funnel), the epoxide **2** (20 g, 0.11 mol) was added slowly at 25–30 °C (mildly exothermic). The reaction mixture was agitated at ambient temperature for 4–16 h and the solvent was removed under vacuum to leave products **17–21** (typical purity 97–98%, NMR). Small samples for melting point measurement were prepared by crystallization of crude material from hexane. Data for compound **17–21** are given in Tables 1 and 2.

4.11. Preparation of compounds 22a, 23a, b, 24a, b (typical procedure)

To a mixture of 0.2–0.5 g of catalysts ($Bu_4N^+F^-\cdot H_2O$ was used for the preparation of **22a**, **23b**, **24b** and CsF for synthesis of **23a** and **24a**) and arylisothiocyanate (0.02 mol) in 50 mL THF (for reaction of **22**, **23**, **24** with the epoxides **1**, **2**) or 50 mL CH_3CN (preparation of **23a**) the epoxide **2** or **1** (0.025 mol) was added slowly. The reactions involving more reactive **2** were exothermic, the epoxide addition was carried out at 25–30 °C and they typically were completed within 2–24 h. The reactions involving less reactive **1** require 4–7 days at 25 °C for completion (monitored by GC). After the conversion of epoxide reached >90%, the reaction mixture was diluted with water, extracted with hexane (3× 50 mL), hexane layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to leave crude crystalline material or oil. Pure samples were obtained by crystallization from hexane. Data for compounds **22a**, **23a**, **b**, **24a**, **b** are given in Tables 1 and 2.

4.12. Preparation of compounds 25a and 26a (typical procedure)

To a solution of 4 g (0.04 mol) KSCN in 100 mL of dry THF, the olefin **25** (10.5 g, 0.035 mol) or imidoyl fluoride **26** (15.1 g, 0.035 mol) was added slowly at 25–30 °C. The orange-brown reaction mixture was agitated for 2 h at 25 °C and the epoxide **2** (6.3 g, 0.035 mol) was added drop wise at 25–30 °C (slightly exothermic). The reaction mixture was agitated for 16 h at ambient temperature, diluted with water (200 mL), extracted with hexane (3× 50 mL). Combined organic layer was washed with water, dried over $MgSO_4$ and solvent was removed under vacuum. The residue was distilled under reduce pressure to give compound **25a** or **26a** (purity 97–98%). Data for compounds **25a**, **26a** are given in Tables 1 and 2.

4.13. Preparation of compounds 27 and 28 (typical procedure)

The epoxide **1** or **2** or (0.05–0.1 mol) was added slowly at 25–30 °C to agitated mixture of CS_2 (4.0–7.5 mL, 0.05–0.1 mol) and 0.1–0.3 g of $Bu_4N^+F^-\cdot H_2O$ catalyst and dry THF (50–100 mL). The reaction mixture was agitated at 25 °C for 4–16 h and the solvent was removed under reduced pressure. The residue was distilled under vacuum to give compound **27** or **28** (purity >98%). Data for both compounds are given in Tables 1 and 2.

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