Tetrahedron 66 (2010) 8383–8386

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Formation of unexpected products in the attempted aziridination of styrene with trifluoromethanesulfonyl nitrene

Bagrat A. Shainyan [a,*], Mikhail Yu. Moskalik [a], Ines Starke [b], Uwe Schilde [b]

[a] A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Division of Russian Academy of Sciences, 1 Favorsky Street 664033, Irkutsk, Russia
[b] Chemisches Institut der Universität Potsdam, PO Box 69 15 53, D-14415 Potsdam, Germany

ARTICLE INFO

Article history:
Received 25 May 2010
Received in revised form 5 August 2010
Accepted 31 August 2010
Available online 6 September 2010

Keywords:
Aziridination
Sulfonyl nitrenes
Piperazines
X-ray
DFT calculations

ABSTRACT

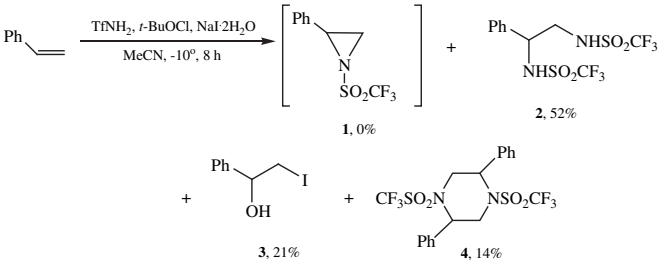
The reaction of styrene with trifluoromethanesulfonyl nitrene generated from trifluoromethanesulfonamide in the system (*t*-BuOCl+NaI) results in the formation of trifluoro-*N*-[2-phenyl-2-(trifluoromethylsulfonyl) aminoethyl]methanesulfonamide, 1-phenyl-2-iodo-ethanol, and 2,5-diphenyl-1,4-bis(trifluoromethyl sulfonyl)piperazine rather than the expected product of aziridination, 2-phenyl-1-(trifluoromethylsulfonyl) aziridine. The mechanism of the reaction is discussed.

1. Introduction

Aziridination of olefins with various precursors of *N*-sulfonylnitrenes, such as *N*-chloro- and *N*-bromoamines RSO_2NNaX,[1–3] *N*-arylsulfonylphenyliodinanes $ArSO_2N{=}IPh$,[4] and sulfonylazides RSO_2N_3,[4,5] as well as with arylsulfonamides $ArSO_2NH_2$ under oxidative conditions has been described;[6–8] the advantages and shortcomings of each method have been reviewed.[9–11] Neither of these methods has been applied to the synthesis of *N*-trifyl aziridines. The only known protocol for the preparation of *N*-trifyl aziridines is dehydration of a β-aminoalcohol with triflic anhydride in the presence of triethylamine.[12] The formation of an *N*-perfluoroalkylsulfonyl aziridine in the reaction of thermally generated nitrene with 2,3-dimethylbut-2-ene has also been reported,[13] although no unambiguous evidence for the structure of the product was given. In view of our interest in *N*-trifyl heterocycles,[14] we tried to apply one of the most recent procedures, the reaction of olefins with *N*-sulfonylnitrenes generated from sulfonamides in the system (*t*-BuOCl+NaI),[8] to the synthesis of *N*-trifyl aziridines, using the reaction of styrene with triflamide $CF_3SO_2NH_2$ as an example.

2. Results and discussion

The reaction with a ratio of triflamide/styrene/*t*-BuOI of 1:2:3 gave a mixture of three products, which were separated by flash chromatography and identified. The major product was found to be trifluoro-*N*-[2-phenyl-2-(trifluoromethylsulfonyl)aminoethyl]methanesulfonamide **2**, which can be formed by the ring opening of the intermediate aziridine **1** by triflamide.



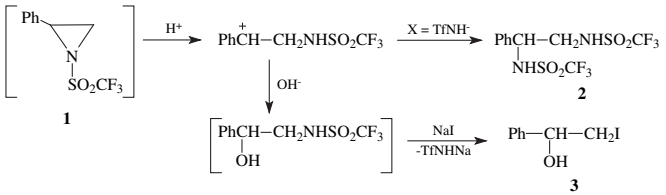
This is consistent with the literature data, which indicate that the $N{-}C^3$ bond is usually cleaved in 2-alkyl substituted aziridines[9,15] while in the 2-Ph substituted aziridines the $N{-}C^2$ bond cleavage predominates.[16–18]

Another isolated product was 1-phenyl-2-iodo-ethanol **3**, whose structure was confirmed by coincidence of its melting point and the IR and NMR spectra with the literature data[19,20] and by the

* Corresponding author. Fax: +7 3952 419346; e-mail address: bagrat@irioch.irk.ru (B.A. Shainyan).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.08.070

proton coupled ^{13}C NMR spectrum, which showed the triplet splitting of the CH_2I signal at 15 ppm and the doublet splitting of the upfield CHOH signal at 74 ppm. Compound **3** could be formed by direct reaction of styrene with *tert*-butyl hypoiodide. To check this possibility, styrene was treated with *t*-BuOCl and $NaI\cdot 2H_2O$ under the reaction conditions but in the absence of triflamide. No signals of compound **3** were observed in the ^1H and ^{13}C NMR spectra of the reaction mixture. This allowed us to conclude that products **2** and **3**, apparently, are formed from the same intermediate aziridine (Scheme 1).



Scheme 1. Formation of the ring-opening products **2** and **3**.

Note, that although the structure of compound **2** itself cannot distinguish between the N–C^2 or N–C^3 bond cleavage, the structure of compound **3** clearly points to the N–C^2 bond cleavage.

The third product gave a ^1H NMR spectrum typical of an ABX spin system, similar to those of compounds **2** and **3**, and the elemental analysis corresponding to compound **1**. Based only on these data, the compound could be assigned to 2-phenyl-1-(trifluoromethylsulfonyl)aziridine, **1**. However, its 2D {^1H–^{13}C} HMBC spectrum showed the direct coupling constant $^1J_{CH}$ of ~148 Hz, which is much lower than should be in aziridines (170–180 Hz[21]). The structure was finally established by X-ray analysis,[22] which showed it to be the *cis*-isomer of 2,5-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine, **4**, that is, the head-to-tail dimer of aziridine **1** (Fig. 1).

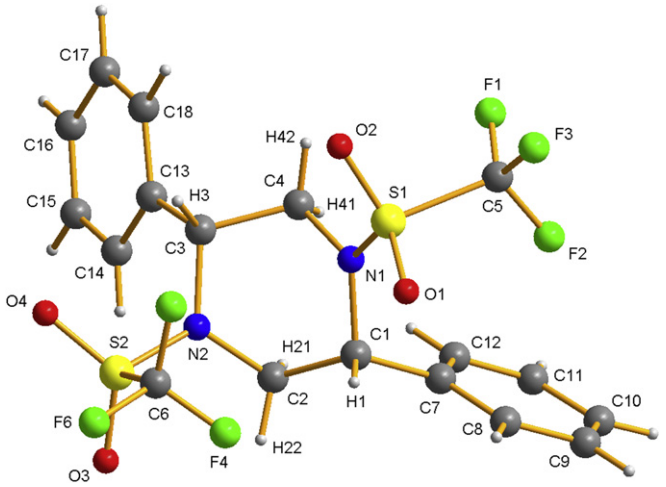


Fig. 1. Crystal structure of 2,5-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine **4**. The picture shows the molecule B with the absolute configuration 2(*R*) and 5(*R*). In the asymmetric unit is a total of three molecules, in the crystal are also the other enantiomers. One of the SO_2CF_3 substituents is disordered; only the major component is drawn.

It should be mentioned that neither the adducts of type **2** nor the product of oxyiodination **3** were detected in the reaction of arenesulfonylnitrenes with various alkenes in the system (*t*-BuOCl+NaI).[8]

The asymmetric unit of the crystal was found to contain three symmetry-independent molecules (labeled with A, B, C) as 2(*S*),5(*S*)-, 2(*S*),5(*S*)-, and 2(*R*),5(*R*)-enantiomers of **4** (Fig. 1). Because the structure is centrosymmetric, the other enantiomer can be found in the crystal, too. The main different geometric features of the molecules A, B, and C are the torsions of the phenyl rings with respect to the piperazine ring system. Otherwise the geometric parameters defining these molecules are very similar (for details see Table S2 of the Supplementary data).

Two points are noteworthy when analyzing the crystal structure of **4**. The first is that the piperazine ring has a 2,5-*twist* rather than the usual *chair* conformation. The second point is that the structure with the two phenyl rings in the cis position to each other, at first glance, seems to be more congested and, therefore, less favorable than the one with the *trans* phenyl groups. It was therefore of interest to examine the relative stability of possible conformers of **4** theoretically. DFT calculations (B3LYP/6-311G**) of the two alternatives have shown that neither the *cis* nor the *trans* isomer of piperazine **4** adopts the *chair* conformation. The *trans* isomer has a slightly distorted 3,6-*boat* conformation, whereas the only experimentally observed *cis*-isomer has the 2,5-*twist* conformation. Moreover, the optimized geometry of the *cis*-isomer is 5.7 kcal/mol lower than that of the *trans* isomer. Therefore, theoretical calculations are in excellent agreement with the X-ray structural data (Fig. 2).

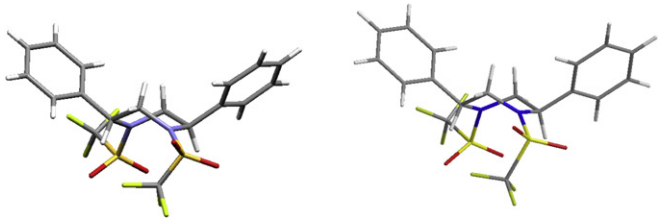


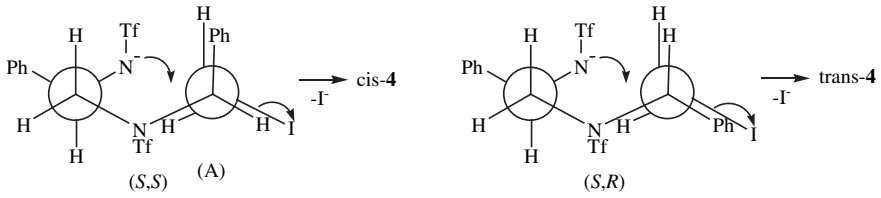
Fig. 2. 2,5-Twist conformation of the piperazine ring of **4** in the experimental X-ray (left) and DFT optimized structure (right).

We failed to find any examples of the direct formation of piperazines in the course of aziridination reactions. Therefore, we believe that compound **4** is also formed from the intermediate aziridine **1**, since the reactions of dimerization of aziridines into piperazines, though rare, are described in the literature.[23,24] In particular, *N*-arylsulfonyl aziridines are dimerized into the corresponding *N*,*N*′-bis(arylsulfonyl)piperazines by the action of iodide ion[23] (which in our case is present in excess in the reaction medium). The general scheme of transformations (using the scheme of the piperazine formation suggested in the literature[23]) can be represented as follows (Scheme 2).

As a mechanistic alternative, the product of aziridine **1** opening by iodide could, after protonation, give rise to compound **2** by nucleophilic substitution of iodine by $TfNH_2$ and to compound **3** by substitution of TfNH by OH. However, in our opinion this is less likely since the nucleophilicity of triflamide is extremely low.

The stereochemistry of product **4** is determined in the step of the aziridine ring opening by the intermediate anion $[CF_3SO_2NCH(Ph)CH_2I]^-$, which occurs stereospecifically leading to intermediate (A) with the same configuration of the two chiral carbon atoms (both *S*,*S* or *R*,*R*).[†] The reasons for this stereospecificity deserve separate consideration but what is important for the present analysis is the fact that the normal 'back-side' intramolecular nucleophilic attack in (A) inevitably affords the product with the *cis*-arrangement of the two phenyl groups (which is the case), whereas the *trans*-product could be formed only from the (*S*,*R*) or (*R*,*S*) precursor, as shown below.

[†] We are grateful to the reviewer who called our attention to the step determining the stereochemistry of the reaction.



The positive electrospray ionization mass spectra (ESI-MS) of compound **2** showed the $[M+Na]^+$ ion; the molecular weight was proved by accurate mass measurements. In the negative EIMS of **2** the ion $[M-NHSO_2CF_3]^-$ at *m*/*z* 251 (40%) and $[NHSO_2CF_3]^-$ at *m*/*z* 148 (100%) were found. In the positive EI mass spectrum, the peak at *m*/*z* 331 corresponds to $[M-CF_3]^+$, and the base peak at *m*/*z* 238 corresponds to the fragment ion $[Ph-CH-NHSO_2CF_3]^+$. The EIMS of **3** showed a molecular ion at *m*/*z* 248 and the key fragment ions similar to those described in.[20] The positive ESI-MS of **4** showed the $[M+Na]^+$ ion at *m*/*z* 525; the elemental composition was confirmed by the accurate mass measurements. The positive EIMS of **4** showed the molecular ion at *m*/*z* 502 (15%) and the base peak $[M-SO_2CF_3]^-$ at *m*/*z* 369. The negative EIMS is characterized by the loss of SO_2CF_3 (*m*/*z* 369) and the formation of an intense ion at *m*/*z* 252, that may be resulted from the internal α-cleavage as described for piperazines and piperidines.[25]

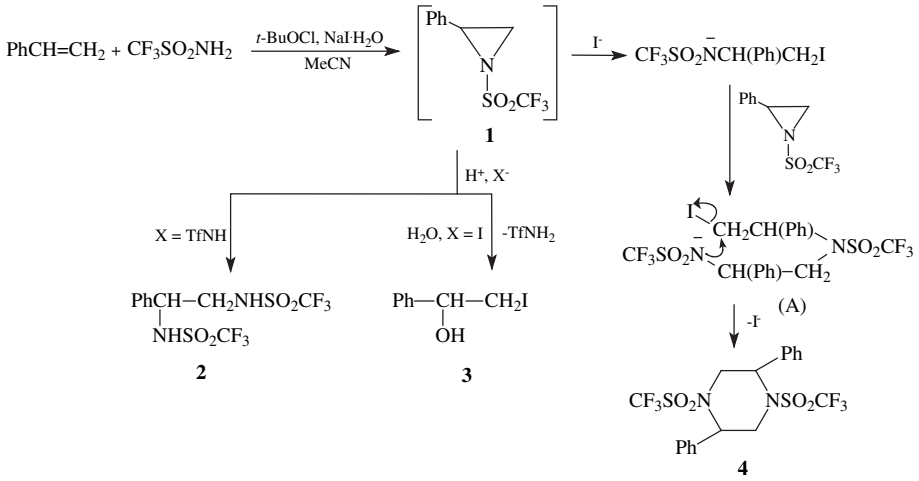
It should be stressed that simple NMR spectroscopy and elemental analysis is insufficient to make a reliable conclusion about the structure of the product(s) of aziridination. To distinguish between the aziridines and their dimers, piperazines, one should obtain the X-ray structure, or, at least, to measure the spin–spin coupling constants $^1J_{CH}$ to approve or exclude the formation of aziridines (note that neither of that was done for the product of the reaction of nitrene R_FSO_2N: with $Me_2C{=}CMe_2$[13]). If aziridine was indeed the product of the reaction of styrene with tosylamide and *t*-BuOI[8] (although neither X-ray nor NMR evidences were given), no aziridine formation with trifluoromethanesulfonamide in the present work may be due to its high acidity, that facilitates the ring opening and further transformations of the originally formed aziridine **1** (Scheme 2).

generated from trifluoromethanesulfonamide in the system (*t*-BuOCl+NaI·2H$_2$O) does not lead to the corresponding product of aziridination, 2-phenyl-1-(trifluoromethylsulfonyl)aziridine but rather results in the formation of trifluoro-*N*-[2-phenyl-2-(trifluoromethylsulfonylaminoethyl]methanesulfonamide, 1-phenyl-2-iodo-ethanol, and *cis*-2,5-diphenyl-1,4-bis(trifluoromethyl sulfonyl)piperazine. The obtained result may be due to strong electronacceptor effect of the trifluoromethanesulfonyl group favoring the ring opening of the intermediate aziridine. The structure of the piperazine is proved by X-ray analysis. The mechanism of the reaction is discussed and the formation of the *cis*-isomer of the product of cyclization rationalized.

4. Experimental section

4.1. General

IR spectra were taken on a Bruker Vertex 70 spectrophotometer in KBr. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H), 100 (^{13}C), and 376 (^{19}F) MHz; ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield to TMS, and ^{19}F NMR in parts per million downfield to $CFCl_3$. The low resolution EI mass spectra were obtained using a GC–MS TRACE DSQ II mass spectrometer (Thermo Fisher Scientific Dreieich, Germany) with an electron energy of 70 eV, and source temperature of 425 K, using a direct insertion probe with DEP filament for positive and for negative ionization modus. The HRMS ESI spectra were recorded using a Micromass Q-TOF$_{micro}$ mass spectrometer in positive electrospray mode. All samples were injected (10 μL/min) with a Harvard syringe pump.



Scheme 2. General scheme of transformations in the system styrene+$CF_3SO_2NH_2$+*t*-BuCl+NaI.

3. Conclusions

Therefore, as distinct from reactions with other sulfonyl nitrenes, the reaction of styrene with trifluoromethanesulfonyl nitrene

The capillary voltage was set to 3.2 kV, with a cone voltage between 20 and 25 V. Elemental compositions were determined by accurate mass measurement with standard deviation <5 ppm. H_3PO_4 was used as a reference compound.

4.2. Synthesis

4.2.1. Reaction of trifluoromethanesulfonamide with styrene. To the mixture of trifluoromethanesulfonamide (2.3 g, 15.4 mmol), styrene (3.18 g, 30.5 mmol), and $NaI\cdot 2H_2O$ (8.5 g, 46 mmol) in acetonitrile (90 mL) *t*-BuOCl (5 g, 46 mmol) was added dropwise, stirred in the dark at −10 °C for 8 h, removed solvent in vacuum without heating, the residue dissolved in chloroform, washed with sodium thiosulfate solution, dried ($MgSO_4$), and the solvent removed in vacuum to yield 3 g of the crude product. About one third part of it was dissolved in benzene and allowed to stay overnight. The precipitate formed was filtered off and crystallized from chloroform to give compound **4**. The tarry residue of the crude product (2 g) was chromatographed on a column with silica gel/60 0.063–0.200, using ether–hexane (1:5, 1:2) and pure ether successively as eluents. Elution with ether–hexane (1:5) gave the mixture of compounds **2** and **3**, and final elution with ether gave pure piperazine **4** (0.54 g, 14%). The mixture of **2** and **3** was further purified on a column with fine-pore granulated silica gel of 0.015–0.040 mm granule size using ether–hexane 1:1 as the eluent to give the mixture of oily compound **3** and crystalline compound **2**. 1-Phenyl-2-iodo-ethanol **3** (0.86 g, 21%) was separated from compound **2** by dissolving in hexane with small amount of ether and removal of solvent, the remaining crystals of trifluoro-*N*-[2-phenyl-2-(trifluoromethylsulfonyl)aminoethyl] methanesulfonamide **2** (1.6 g, 52%) were filtered off.

*4.2.2. Trifluoro-N-[2-phenyl-2-(trifluoromethylsulfonyl)aminoethyl]-methanesulfonamide, **2**.* Mp 94–96 °C; ν_{max} (KBr) 3331 (NH), 3307 (NH), 1461, 1442, 1373, 1231, 1201, 1141, 1062, 1050, 982, 891 cm^{-1}; δ_H (CD_3CN) 7.42 (5H, m, *Ph*), 7.2 (2H, br s, N*H*), 4.76 (1H, d, *J* 6.9 Hz, PhC*H*), 3.60 (2H, d, *J* 7.1 Hz, PhCHCH_2); δ_H (C_6D_6) 7.10 (5H, m, *Ph*), 5.5 (2H, br s, N*H*), 4.61 (1H, dd, *J* 8.4, 4.5 Hz, PhC*H*), 3.19 (1H, dd, *J* 14.2, 8.4 Hz, PhCHCH^B), 3.09 (1H, dd, *J* 14.2, 4.5 Hz, PhCHCH^A); δ_C (CD_3CN) 138.1 (C_i), 130.1 (C_o), 129.8 (C_p), 127.8 (C_m), 120.8 (q, *J* 320.7 Hz, 2-CF_3), 120.6 (q, *J* 320.4 Hz, 1-CF_3), 60.8 (CH), 49.8 (CH_2). ^{19}F NMR, δ_F, ppm: −78.80 (1-CF_3), −78.58 (2-CF_3). HRMS (ESI): $[M+Na]^+$, found 422.9865. $C_{10}H_{10}F_6N_2O_4S_2Na$ requires 422.9884.

*4.2.3. 1-Phenyl-2-iodo-ethanol, **3**.* Oil with crystals; lit. mp 34 °C;[20] δ_H (CD_3CN) 7.40 m (5H, m, *Ph*), 4.78 (1H, ddd, *J* 7.4, 4.5, 3.9 Hz, PhC*H*), 3.76 (1H, d, *J* 3.9 Hz, O*H*), 3.52 (1H, dd, *J* 10.1, 4.5 Hz, PhCHCH^B), 3.42 (1H, dd, *J* 10.1, 7.4 Hz, PhCHCH^A); δ_C (CD_3CN) 143.6 (C_i), 129.2 (C_m), 128.6 (C_p), 126.7 (C_o), 73.8 (d, *J* 146.0 Hz, CH), 15.6 (t, J_{CH} 151.1 Hz, CH_2I).

*4.2.4. 2,5-Diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine, **4**.* Mp 130.5 °C; ν_{max} (KBr) 3070, 3038, 2929, 1628, 1499, 1457, 1399, 1229, 1201, 1140, 1122, 1056, 1028, 954, 909, 875, 698 cm^{-1}; δ_H (CD_3CN) 7.46m (5H, Ph), 5.32 (1H, dd, *J* 11.2, 6.8 Hz, PhC*H*), 4.40 (1H, dd, *J* 15.5, 6.8 Hz, PhCHCH^B), 4.01 (1H, dd, *J* 15.5, 11.2 Hz, PhCHCH^A); δ_C (CD_3CN) 137.7 (C_i), 130.2 (C_p), 130.0 (C_m), 127.5 (C_o), 120.5 q (CF_3, J_{CF} 321.1 Hz), 61.7 (CH, $^1J_{CH}$ 148.4 Hz), 48.6 (CH_2, $^1J^A_{CH}$ 146.7, $^1J^B_{CH}$ 148.8 Hz). ^{19}F NMR, δ_F, ppm: −77.34. HRMS (ESI): $[M+Na]^+$, found 525.0347. $C_{18}H_{16}F_6N_2O_4S_2Na$ requires 525.0353.

Acknowledgements

We gratefully acknowledge supporting of this work by the Russian Foundation for Basic Research and Deutsche Forschungsgemeinschaft (Grants RFBR 10-03-00110 and RFBR-DFG 08-03-91954). We also thank Dr. Regine Herbst-Irmer (Institut für Anorganische Chemie, Universität Göttingen) for her very useful comments.

Supplementary data

Supplementary data include the details of X-ray structural analysis, NMR, and IR spectra of the products, energy and geometry of the diastereomers of 2,5-diphenyl-1,4-bis (trifluoromethylsulfonyl)piperazine, **4**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.08.070. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. Gontcharov, A. V.; Liu, H.; Sharpless, K. B. *Org. Lett.* **1999**, *1*, 783.
2. Vyas, R.; Chanda, B. M.; Bedekar, A. V. *Tetrahedron Lett.* **1998**, *39*, 4715.
3. Chanda, B. M.; Vyas, R.; Bedekar, A. V. *J. Org. Chem.* **2001**, *66*, 30.
4. Albone, D. P.; Aujla, P. S.; Taylor, P. C. *J. Org. Chem.* **1998**, *63*, 9569.
5. Ruppel, J. V.; Jones, J. E.; Huff, C. A.; Kamble, R. M.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2008**, 1995.
6. Han, H.; Park, S. B.; Kim, S. K.; Chang, S. *J. Org. Chem.* **2008**, *73*, 2862.
7. Nadir, U. K.; Singh, A. *Synth. Commun.* **2004**, *34*, 1337.
8. Minakata, S.; Morino, Y.; Oderaotoshi, Y.; Komatsu, M. *Chem. Commun.* **2006**, 3337.
9. Sweeney, J. B. *Chem. Soc. Rev.* **2002**, *31*, 247.
10. Singh, G. S.; D'hooghe, M.; De Kimpe, N. *Chem. Rev.* **2007**, *107*, 2080.
11. Minakata, S. *Acc. Chem. Res.* **2009**, *42*, 1172.
12. Nelson, S. G.; Mills, P. M. *Org. Synth.* **2005**, *82*, 170.
13. Zhu, S.-Z. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2077.
14. (a) Shainyan, B. A.; Meshcheryakov, V. I. *Russ. J. Org. Chem.* **2001**, *37*, 1797; (b) Mescheryakov, V. I.; Albanov, A. I.; Shainyan, B. A. *Russ. J. Org. Chem.* **2005**, *41*, 1381; Mescheryakov, V. I.; Shainyan, B. A.; Zavodnik, V. E.; Bel'skii, V. K. *Russ. J. Org. Chem.* **2006**, *42*, 1254; Mescheryakov, V. I.; Danilevich, Y. S.; Moskalik, M. Y.; Stetsjura, N. Y.; Zavodnik, V. E.; Bel'skii, V. K.; Shainyan, B. A. *Russ. J. Org. Chem.* **2007**, *43*, 793; Mescheryakov, V. I.; Moskalik, M. Y.; Kelling, A.; Schilde, U.; Ushakov, I. A.; Shainyan, B. A. *Russ. J. Org. Chem.* **2008**, *44*, 311; Shainyan, B. A.; Meshcheryakov, V. I. *Mini-Rev. Org. Chem.* **2009**, *6*, 66.
15. Lake, F.; Moberg, C. *Eur. J. Org. Chem.* **2002**, 3179.
16. Pandey, M. K.; Bisai, A.; Singh, V. K. *Tetrahedron Lett.* **2000**, *45*, 9661.
17. Kumar, M.; Gandhi, S.; Kalra, S. S.; Singh, V. K. *Synth. Commun.* **2008**, *38*, 1527.
18. Wu, J.; Sun, X.; Xia, H.-G. *Eur. J. Org. Chem.* **2005**, 4769.
19. Golumbic, C.; Cottle, D. L. *J. Am. Chem. Soc.* **1939**, *61*, 996.
20. Villegas, R. A. S.; Santo, J. L. E., Jr.; de Mattos, M. C. S.; de Aguiar, M. R. M. P.; Guarino, A. W. S. *J. Braz. Chem. Soc.* **2005**, *16*, 565.
21. Knipe, A. C.; Khandelwal, Y.; McAuley, I. E.; Brown, N. M. D. *Magn. Reson. Chem.* **1985**, *23*, 177; Forni, A.; Moretti, I.; Mucci, A.; Prati, F.; Schenetti, L. *Chem. Heterocycl. Comp.* **1995**, *31*, 1071; Joly, G. J.; Peeters, K.; Mao, H.; Brossette, T.; Hoornaert, G. J.; Compernolle, F. *Tetrahedron Lett.* **2000**, *41*, 2223.
22. Crystal data for **4**: $3(C_{18}H_{16}F_6N_2O_4S_2)\cdot C_2H_5OH$, M_r=1553.56 g mol^{-1}, crystal dimensions 0.25×0.25×0.15 mm, monoclinic, space group $P2_1/n$, a=18.3378 (13), b=11.6748(5), c=32.096(2) Å, V=6870.4(7) $Å^3$, Z=4, ρ_{calcd}=1.485 g cm^{-1}; μ(Mo Kα)=0.31 mm^{-1} (λ=0.71073 Å), T=210 K; $2\Theta_{max}$=49.16°, 40,714 reflections measured, 11,520 unique (R_{int}=0.0960), R=0.0581, wR=0.1232 ($I>2\sigma(I)$) For details of the data collection and the structure solution and refinement see Supplementary data. CCDC-766328 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
23. Heine, H. W.; Canyon, W. G.; Johnson, E. M. *J. Am. Chem. Soc.* **1961**, *83*, 2570.
24. Okada, I.; Itoh, N.; Sudo, R. *Bull. Chem. Soc.* **1969**, *42*, 547.
25. Porter, Q. N. *Mass Spectrometry of Heterocyclic Compounds*; John Wiley: New York, NY, 1985.