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Reactions of 2-(α-Haloalkyl)thiiranes with Nucleophilic Reagents: IV.* Alkylation of Sulfonamides with 2-Chloromethylthiirane. Synthesis and Properties of 3-(Arylamino)thietanes

V. V. Sokolov, A. N. Butkevich, V. N. Yuskovets, A. A. Tomashevskii, and A. A. Potekhin

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia

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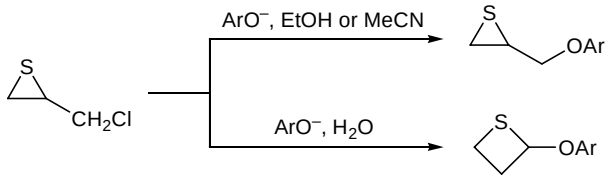
Abstract—Alkylation of primary and secondary sulfonamides with 2-chloromethylthiirane in the presence of alkali gives the corresponding *N*-(thiiran-2-ylmethyl)- and/or *N*-(thietan-3-yl)sulfonamides. The selectivity of the process depends on the solvent: in water, thiirane–thietane rearrangement products are formed exclusively, while ethanol favors Ad–E reaction leading to thiiranylmethyl derivatives. A procedure has been proposed for the synthesis of 3-(arylamino)thietanes which undergo selective acylation at the nitrogen atom. The possibility for synthesizing analogous derivatives of thietane 1-oxide and thietane 1,1-dioxide is considered.

As we showed previously [1], 2-chloromethylthiirane reacts with phenoxide ions along two independent pathways. Polar solvents with a strong ionizing power, such as water or aqueous methanol, favor S_N1 reaction due to effective solvation of intermediate 1-thioniabicyclobutane, and the major products are the corresponding 3-aroxythietanes possessing a less strained heteroring. When the reaction is carried out in anhydrous ethanol or acetonitrile, the only products are 2-(aroxymethyl)thiiranes which are formed as a result of addition–elimination process (opening of the three-membered ring and subsequent recyclization according to the S_N2' mechanism; Scheme 1) .

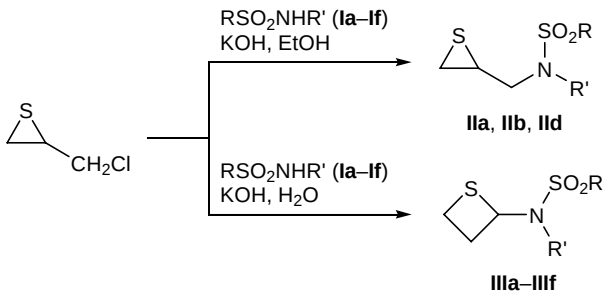
Scheme 1.



Sulfonamides are similar to phenols in their ability to readily undergo alkylation in the presence of bases. The possibility of alkylating sulfonamides with 2-chloromethylthiiranes attracts strong interest from the viewpoints of analogous mechanistic studies and preparation of compounds possessing a sulfonamide fragment and a small sulfur-containing heteroring. Sulfonamides have found wide application in medicine; examples are such medical agents as diuretics of the Chlorothiazide series, non-steroid antiphlogistic agent Piroxicam, Viagra, and arenesulfonamides exhibiting antimicrobial and antihyperglycemic activity [2]. Antibacterial properties of thiirane and thietane derivatives have also become the subject of extensive studies [3]. Taking these data into account, we anticipated useful biological activity of compounds containing both the above structural fragments.

As substrates we selected readily accessible primary and secondary sulfonamides **Ia**–**If**. Preliminary experiments on alkylation of *N*-(4-methoxyphenyl)-benzenesulfonamide (**Ia**) in water and anhydrous ethanol (60–70°C, KOH as base) showed that the desired *N*-(thietane-3-yl)- and *N*-(thiiran-2-ylmethyl)-sulfonamides **IIa** and **IIIa** were actually formed; when

Scheme 2.



R = Ph, R' = 4-$MeOC_6H_4$ (**a**), $PhCH_2$ (**d**), H (**e**), 4-$O_2NC_6H_4$ (**f**);
R = Me, R' = 4-$MeOC_6H_4$ (**b**), 1-naphthyl (**c**).

* For communication III, see [1].

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methanol was used as solvent, a mixture of compounds **IIa** and **IIIa** was obtained at a ratio of 1:5 (Scheme 2).

The reaction was accompanied by strong tarring of thiirane derivatives; therefore, the yield was considerably reduced, and isolation of the products was strongly complicated. Optimization of the reaction conditions allowed us to substantially minimize the contribution of polymerization processes and raise the product yield. By carrying out the reaction at room temperature in the presence of a slight excess of base (~10%) we succeeded in obtaining compounds **IIa** and **IIIa** in 38 and 62% yield, respectively. The use of DMF as solvent turned out to be inappropriate, for it favored oligomerization of thiirane **IIa**.

Replacement of the phenylsulfonyl group by methylsulfonyl had no appreciable effect on the yield of products **IIb** and **IIIb**. By contrast, the effect of the substituent on the nitrogen atom is very strong, and the sensitivity of Ad–E processes to the nature of R' was much greater than that expected for simple combination of charged species with formation of *N*-(thietan-3-yl)sulfonamides. The largest yields of the products were obtained with R' = Ar. Here, donor substituents (e.g., methoxy group) in the *para* position of the aromatic ring increased the yield of compounds having a thietane ring, while acceptor substituents (nitro group) decreased it. Compound **IIf** was not formed at all, and initial sulfonamide **If** was almost quantitatively recovered from the reaction mixture, regardless of whether the reaction was carried out in methanol or in ethanol. The presence of a bulky 1-naphthyl group on the nitrogen also makes the reaction more difficult: the yield of the corresponding *N*-(thietan-3-yl)sulfonamide **IIIc** was as low as 25%, and thiiranylmethyl derivative **IIc** was not obtained. These data are quite consistent with the general relations holding in aliphatic nucleophilic substitution, according to which a bimolecular process is more sensitive to steric factor than unimolecular process.

In going to *N*-alkylsulfonamide **Id** and primary benzenesulfonamide (**Ie**), one more factor was revealed to affect the process, namely NH acidity of the substrate. In fact, *N*-arylsulfonamides are characterized by lower p*K* values than *N*-alkyl and *N*-unsubstituted derivatives; therefore, in the reaction with the latter, the equilibrium concentration of the corresponding anion in the system should be lower, other conditions being equal. As a result, smaller yields of compounds **IId**/**IIId** and **IIe**/**IIIe** might be expected. The alkylation of *N*-benzylbenzenesulfonamide **Id** with 2-chloromethylthiirane both in water and in ethanol gives 10% of compound **IId** and 5% of **IIId**, and in the two cases preparative thin-layer chromatography is necessary to isolate the products. Benzenesulfonamide (**Ie**) undergoes alkylation with 2-chloromethylthiirane only in water, and the yield of monoalkylated product **IIIe** does not exceed 25% even with the use of a large excess of the alkylating agent; however, this reaction is characterized by poor reproducibility. Our attempts to force the reaction by raising the concentration of alkali or increasing the temperature resulted in acceleration of side processes including base-catalyzed polymerization of 2-chloromethylthiirane.

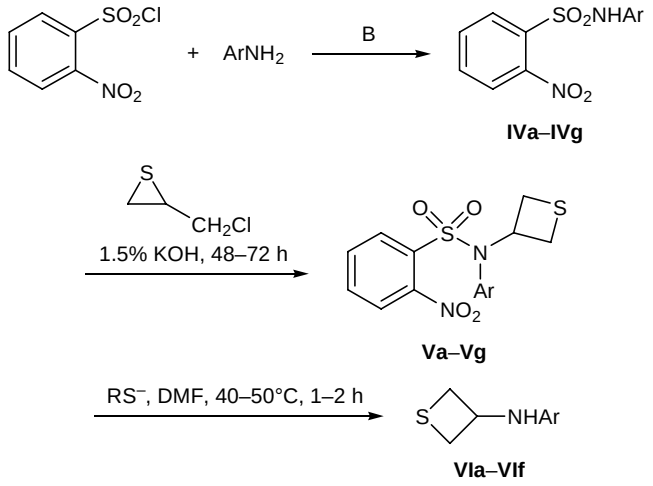
We also examined the possibility for N-alkylation of sulfonamides containing a substituent of a different origin on the nitrogen atom. N'-Phenylsulfonyl-4-methoxybenzohydrazide [4] turned out to be completely inactive in the reaction with 2-chloromethylthiirane. The reaction of 2-chloromethylthiirane with *N*-acetylbenzenesulfonamide attracted interest as an alternative route to *N*-(thietan-3-yl)benzenesulfonamide (**IIIe**) which thus appeared to be difficultly accessible. Unfortunately, we failed to effect N-alkylation of *N*-acetylbenzenesulfonamide, presumably because of strongly reduced nucleophilicity of the nitrogen atom in the substrate (we tried $NaHCO_3$ and KOH as bases, and in both cases only tarry polymerization products of 2-chloromethylthiirane were obtained).

Satisfactory yields of the corresponding *N*-(thietan-3-yl) derivatives from *N*-arylsulfonamides led us to develop an effective procedure for the synthesis of 3-arylaminothietanes. It should be noted that known methods of synthesis of 3-aminothietanes include complex multistep processes which are characterized by a poor overall yield [5, 6] or are suitable for the preparation of a limited set of compounds with a definite structure. For example, [2+2]-cycloaddition of methylene sulfone $CH_2{=}SO_2$ to enamines *in situ* was reported in [7–9]. 3-Arylaminothietanes were not described previously; it seems to be extremely difficult to introduce an aryl group to the nitrogen atom in the synthesis of 3-aminothietanes by known methods.

The main problem in the synthesis of 3-arylaminothietanes through sulfonyl derivatives includes difficulties in the removal of the sulfonyl protecting group. In this case, the standard procedure is acid hydrolysis under severe conditions, which cannot be applied to labile substrates containing a thietane fragment. However, Kurosawa *et al.* [10] recently showed that 2-nitrophenylsulfonyl group can be removed under

very mild conditions by the action of thiolates. We used a synthetic sequence consisting of three steps: (1) activation of aromatic amine via conversion into the corresponding *N*-aryl-2-nitrobenzenesulfonamides, (2) N-alkylation of the latter with 2-chloromethylthiirane in dilute aqueous alkali to obtain *N*-(thietan-3-yl)sulfonamides, and (3) removal of the 2-nitrophenylsulfonyl protecting group by the action of benzenethiol in the presence of a base (Scheme 3).

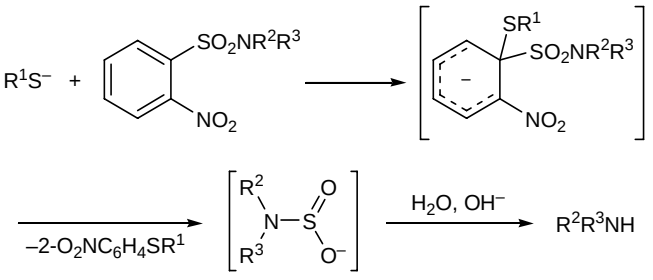
Scheme 3.



Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 2-*i*-PrC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 1-naphthyl (**e**), 3-$O_2NC_6H_4$ (**f**), 4-$O_2NC_6H_4$ (**g**); B = AcONa (1.2–1.3 equiv), 50% EtOH, 25°C (1 h) or $ArNH_2$ (1 equiv), dioxane, reflux (50 h); RS^- = PhSH (2 equiv) + K_2CO_3 (3 equiv) or $HSCH_2CO_2H$ (2 equiv) + K_2CO_3 (4 equiv).

Presumably, the ease of the deprotection step is explained by the fact that thiolate ions do not attack the inert N–S bond in 2-nitrobenzenesulfonamides (Scheme 4).

Scheme 4.



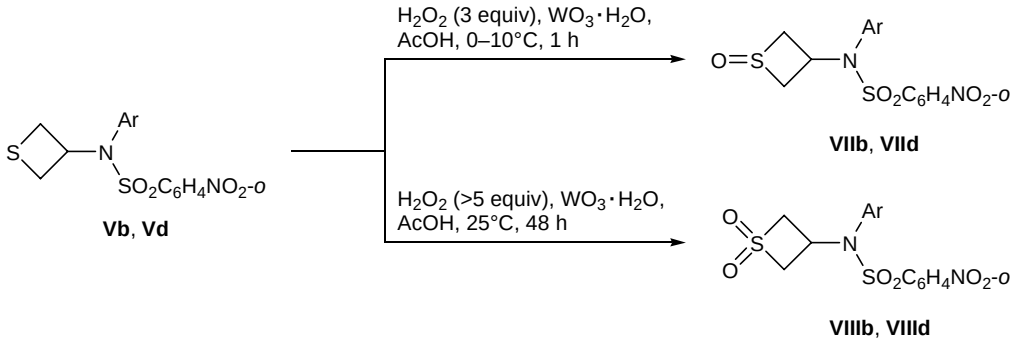
4-Nitrophenylsulfonyl [11, 12] and 2,4-dinitrophenylsulfonyl groups [13] are known as alternative activating groups. 2,4-Dinitrophenylsulfonyl group can be removed under especially mild conditions; moreover, it can be removed with high selectivity from substrates possessing a 2-nitrobenzenesulfonamide fragment [13]. 2-Nitrobenzenesulfonyl chloride is less expensive than its 4-nitro isomer and especially 2,4-dinitrosubstituted analog; therefore, it may be used in enlarged syntheses.

3-Arylaminothietanes **VI** are crystalline substances which are stable to atmospheric oxygen (they do not change on storage for at least several months); they are soluble in most polar organic solvents, poorly soluble in water, and insoluble in hexane. Compounds **VI** are readily soluble in dilute hydrochloric acid [except for 3-(1-naphthylamino)thietane (**VIe**) which gives poorly soluble oily hydrochloride], which facilitates their isolation.

The maximal overall yield, calculated on the three steps, was obtained for anilines having electron-donor substituents in the aromatic ring. The sensitivity of the key alkylation step to steric factor is low: the yields of *N*-(thietan-3-yl)sulfonamides obtained from 1-naphthylamine and 2-isopropylaniline are similar to that of the compound derived from unsubstituted aniline. On the other hand, the sensitivity to electronic factor is very strong, so that preparation of 3-(4-nitrophenylamino)thietane according to Scheme 3 is almost impossible because of the low yield of the corresponding *N*-(thietan-3-yl)sulfonamide **Vg**. Removal of the 2-nitrophenylsulfonyl protecting group from sulfonamide **Vf** by the action of benzenethiolate ion is an unusually slow process which is likely to be accompanied by side reactions. Therefore, the yield of compound **VIf** was as poor as 11%. By using sulfanylacetic or 2-sulfanylbenzoic acid as deprotecting agent in the presence of excess K_2CO_3 we succeeded in raising the yield of **VIf** to 85%.

Compounds **V** are readily oxidized to the corresponding sulfoxides (3-substituted thietane 1-oxides **VII**) or sulfones (3-substituted thietane 1,1-dioxides **VIII**) with excess 30% hydrogen peroxide in glacial acetic acid under catalysis by $WO_3 \cdot H_2O$. These reactions were performed with compounds **Vb** and **Vd** as examples (Scheme 5). Sulfoxides **VIIb** and **VIId** were formed in high yields (>90%) as mixtures of two diastereoisomers when the reactions were carried out at reduced temperature; also, TLC monitoring of the reaction course is necessary to avoid overoxidation. Unlike the corresponding sulfides and sulfones, sulfoxides **VIIb** and **VIId** are readily soluble in glacial acetic acid. Sulfones **VIIIb** and **VIIId** were obtained when the reaction was performed at 25°C for a longer time (25 h) using a larger excess of hydrogen peroxide.

Scheme 5.

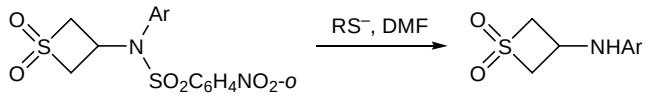


Ar = 4-$MeOC_6H_4$ (**b**), 4-ClC_6H_4 (**d**).

Both thiethanes **V** and sulfoxides **VIIb** can be used as initial compounds, as we showed with compound **VIIb** as an example.

We tried to deprotect compounds **VIIb**, **VIId**, **VIIIb**, and **VIIId** by the action of thiolates under the same conditions as in the synthesis of 3-(arylamino)-thietanes **VI**. From thietane 1,1-dioxides **VIIIb** and **VIIId** we obtained the corresponding 3-(arylamino)-thietane 1,1-dioxides **IX** in moderate to high yields (Scheme 6). Sulfoxides **VII** failed to react under these conditions, presumably because of concurrent reduction of the sulfoxide group to sulfide by thiolate ions (an analogous reaction was described, e.g., in [14]).

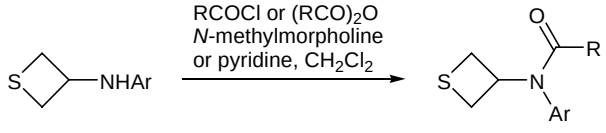
Scheme 6.



Ar = 4-$MeOC_6H_4$ (**b**), 4-ClC_6H_4 (**d**); RS^- = PhSH (2 equiv) + K_2CO_3 (3 equiv), 40–50°C (1 h) (**IXb**, yield 79%); $HSCH_2CO_2H$ (2 equiv) + K_2CO_3 (4 equiv), 70–80°C (4 h) (**IXd**, yield 42%).

We also examined N-acylation of 3-(arylamino)-thietanes **VI** to illustrate the possibility of using these compounds in combinatorial chemistry. The reaction readily occurred to afford the target *N*-acyl derivatives

Scheme 7.



X, Ar = R = Ph (**a**); Ar = 4-$MeOC_6H_4$, R = Ph (**b**); Ar = 4-ClC_6H_4, R = Me (**d**).

X in high yields and was not accompanied by polymerization or thietane ring opening by electrophilic acylating agents (Scheme 7).

Thietanes **III**, **V**, and **VI** were identified on the basis of their ^1H and ^{13}C NMR and mass spectra. In the ^1H NMR spectra of these compounds, protons in the aliphatic three-carbon fragment give rise to a complex *AA'BB'X* spin system which is characterized by similar $^3J_{cis}$ and $^3J_{trans}$ values. As a result, we observe a pseudosimple spectrum consisting of triplets in the δ region 3.0–3.5 ppm with a pronounced "roof" effect and a quintet at δ 4.5–6.0 ppm. In some cases, these signals are additionally split, in particular due to non-zero long-range *W*-coupling constant (^4J). The 3-H proton in 3-(arylamino)thietanes **VIc** and **VIf** appears as a sextet as a result of coupling with the NH proton. Introduction of a bulky substituent into the *ortho* position of the aromatic ring (compound **Vc**) or replacement of the benzene ring by naphthalene system (compounds **IIIc** and **Ve**) hampers free rotation about the C_{Ar}–N bond, thus giving rise to an additional chirality axis. Therefore, the aliphatic region of the ^1H NMR spectra of compounds **IIIc**, **Vc**, and **Ve** becomes more complicated (diastereotopic methylene protons appear as asymmetric multiplets). In the ^{13}C NMR spectra, the thietane fragment gives two or three (if CH_2 protons are diastereotopic) signals in a strong field. These signals are characterized by opposite phases in the DEPT-135 spectrum. The NMR spectra of thietane 1-oxides **VII** and thietane 1,1-dioxides **VIII** and **IX** display analogous patterns differing in the position of the upfield signals. Structural variations affect most strongly the position of the 3-H signal in the ^1H NMR spectra. The chemical shifts of 3-H in compounds **VIIb** and **VIId** are δ 4.8 and 6.2 ppm (the difference in the chemical shifts between two diastereoisomers exceeds 1 ppm), and in **VIIIb** and **VIIId**, 5.2–5.4 ppm.

In going to 3-(arylamino)thietane 1,1-dioxides, the 3-H signal shifts upfield to δ 4.0–4.2 ppm, and the shape of signals from the thietane fragment also changes.

3-Arylaminothietanes **V** and **VI** showed in the mass spectra fragment ion peaks formed by elimination of thioformaldehyde ($[M - 46]^{+\cdot}$) and $C_3H_5S^+$, CHS^+, and/or CH_2S^+ species from the molecular ion {cf. mass spectra of *N*-(thietan-3-yl)-substituted heterocycles [15]}. The electron impact mass spectrum of 3-phenylaminothietane (**VIa**) cannot be interpreted, but in the chemical ionization mass spectrum (using ammonia as reactant gas) we observed strong peaks belonging to quasimolecular ions $[M + H]^{+\cdot}$ and $[M + NH_4]^{+\cdot}$.

In the ^{1}H NMR spectra of thiiranes **II**, protons in the aliphatic three-carbon fragment are nonequivalent, and they give rise to a first- or second-order spin system characterized by the presence of two upfield signals at 2.0–2.5 ppm, which correspond to the endocyclic methylene group. The geminal spin–spin coupling constant for monosubstituted thiiranes is usually close to zero [16]; therefore, the above signals appear as two doublets with different coupling constants ($^3J_{cis} > {}^3J_{trans}$), and the corresponding protons can be identified.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.130 MHz for ^{1}H and 75.03 MHz for ^{13}C; a mixture of DMSO-d_6 with CCl_4 (1:2, by volume) or $CDCl_3$ was used as solvent; the chemical shifts were measured relative to signals from residual protons in the deuterated solvents: δ 7.26 ppm ($CHCl_3$) and 2.50 ppm (DMSO-d_5); δ_C 77.7 ppm ($CDCl_3$) and 39.7 ppm (DMSO-d_6). The coupling constants in the ^{1}H NMR spectra were measured in the first-order approximation. The multiplicities denoted with quotation marks (e.g., "t") refer to signals from protons of the thietane fragment in the pseudofirst-order spectra. Such signals are often characterized by additional splitting. In the description of the DEPT-135 spectra, "+" denotes the positive phase (CH_3 or CH carbon atom), "–" stands for the negative phase (methylene carbon atom), and "q" denotes a missing DEPT signal (quaternary carbon atom). The mass spectra were obtained on a Finnigan MAT Incos 50 instrument (electron impact ionization, 70 eV, unless otherwise stated). The elemental compositions were determined on a Hewlett–Packard HP-185B CHN analyzer. The purity of compounds and the progress of reactions were monitored by thin-layer chromatography on Silufol UV-254 plates.

***N*-(4-Methoxyphenyl)-*N*-(thiiran-2-ylmethyl)-benzenesulfonamide (IIa).** Potassium hydroxide, 0.56 g (10 mmol), and 2-chloromethylthiirane, 1.1 g (10 mmol), were added to a solution of 2.63 g (10 mmol) of *N*-phenyl-4-methoxybenzenesulfonamide (**Ia**) [17] in 30 ml of anhydrous ethanol, and the mixture was stirred for 10 h at room temperature. It was then poured into 200 ml of water and extracted with diethyl ether (3×20 ml), the extract was washed with a 5% solution of sodium hydroxide, water, and a saturated solution of sodium chloride and dried over $MgSO_4$, the solvent was distilled off, and the residue was recrystallized from toluene–hexane (2:1). Yield 1.2 g (38%), mp 103–104°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.95 d (1H, 3'-H, J = 4.9 Hz), 2.31 d (1H, 3'-H, J = 6.1 Hz), 2.88–3.06 m (1H, 2'-H), 3.31 d.d (1H, 1'-H, J = 13.8, 7.9 Hz), 3.73 s (3H, CH_3O), 3.93 d.d (1H, 1'-H, J = 13.8, 3.9 Hz), 6.70–6.96 m (4H), 7.34–7.63 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.5 (–, $C^{3'}$), 31.7 (+, $C^{2'}$), 55.2 (+, CH_3O), 57.3 (–, $C^{1'}$), 114.2 (+, 2C), 127.4 (+, 2C), 128.7 (+, 2C), 130.2 (+, 2C), 131.5 (q), 132.6 (+), 138.6 (q), 159.2 (q). Found, %: C 57.28; H 5.20; N 3.84. $C_{16}H_{17}NO_3S_2$. Calculated, %: C 57.29; H 5.11; N 4.17.

***N*-(4-Methoxyphenyl)-*N*-(thiiran-2-ylmethyl)-methanesulfonamide (IIb)** was synthesized in a similar way from *N*-(4-methoxyphenyl)methanesulfonamide (**Ib**) [18]. Yield 34%, mp 85–86°C (from CH_2Cl_2–hexane, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.01 d (1H, 3'-H, J = 4.6 Hz), 2.40 d (1H, 3'-H, J = 5.8 Hz), 2.89 s (3H, CH_3SO_2), 2.95–3.18 m (1H, 2'-H), 3.50 d.d (1H, 1'-H, J = 13.4, 7.7 Hz), 3.78 s (3H, CH_3O), 4.00 d.d (1H, 1'-H, J = 13.4, 3.6 Hz), 6.84–7.35 m (4H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.3 (–, $C^{3'}$), 31.8 (+, $C^{2'}$), 37.8 (+, CH_3SO_2), 55.2 (+, CH_3O), 57.0 (–, $C^{1'}$), 114.6 (+, 2C), 130.1 (+, 2C), 131.4 (q), 159.3 (q). Found, %: C 48.75; H 5.82; N 5.19. $C_{11}H_{15}NO_3S_2$. Calculated, %: C 48.33; H 5.53; N 5.12.

***N*-Benzyl-*N*-(thiiran-2-ylmethyl)benzenesulfonamide (IId)** was synthesized in a similar way from *N*-benzylbenzenesulfonamide (**Id**) [19]. The product was isolated by preparative thin-layer chromatography on silica gel L 5/40 μm using hexane–diethyl ether (2:1) as eluent. Yield 10%, mp 76–77°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.86 d (1H, 3'-H, J = 5.1 Hz), 2.20 d (1H, 3'-H, J = 6.4 Hz), 2.67–2.85 m

(1H, 2'-H), 3.04 d.d (1H, 1'-H, J = 14.0, 8.1 Hz), 3.53 d.d (1H, 1'-H, J = 14.0, 4.1 Hz), 4.44 s (2H, $PhCH_2$), 7.30 s (5H), 7.50–7.95 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.7 (–, $C^{3'}$), 31.5 (+, $C^{2'}$), 53.6 (–, $PhCH_2$), 56.8 (–, $C^{1'}$), 126.8 (+, 2C), 127.7 (+, 2C), 128.0 (+), 128.4 (+, 2C), 129.0 (+, 2C), 132.5 (+), 135.6 (q), 139.3 (q). Found, %: C 60.82; H 5.52; N 4.39. $C_{16}H_{17}NO_2S_2$. Calculated, %: C 60.17; H 5.37; N 4.39.

***N*-(4-Methoxyphenyl)-*N*-(thietan-3-yl)benzenesulfonamide (IIIa).** A suspension of 2.63 g (10 mmol) of *N*-phenyl-4'-methoxybenzenesulfonamide (**Ia**), 0.56 g (10 mmol) of potassium hydroxide, and 1.1 g (10 mmol) of 2-chloromethylthiirane in 40 ml of water was stirred for 10 h at room temperature. The mixture was extracted with diethyl ether (3×20 ml), the extract was washed with a 5% solution of sodium hydroxide and a saturated solution of sodium chloride and dried over $MgSO_4$, the solvent was distilled off, and the residue was recrystallized from toluene–hexane (2:1). Yield 2.0 g (62%), mp 127–128°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.03 "t" (2H), 3.43 "t" (2H), 3.83 s (3H, CH_3O), 5.36 "quintet" (1H), 6.80–6.90 m (4H), 7.45–7.55 m (2H), 7.57–7.70 m (3H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.5 (–, 2C), 54.7 (+), 55.2 (+, CH_3O), 114.2 (+, 2C), 127.3 (+, 2C), 128.7 (+, 2C), 131.9 (+, 2C), 132.7 (+), 138.6 (q), 159.5 (q). Found, %: C 57.52; H 5.05; N 3.87. $C_{16}H_{17}NO_3S_2$. Calculated, %: C 57.29; H 5.11; N 4.17.

Sulfonamides **IIIb**–**IIIf** were synthesized in a similar way.

***N*-(4-Methoxyphenyl)-*N*-(thietan-3-yl)methanesulfonamide (IIIb)** was obtained from *N*-(4-methoxyphenyl)methanesulfonamide (**Ib**). Yield 56%, mp 97–98°C (from CH_2Cl_2–hexane, 2:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.91 s (3H, CH_3SO_2), 3.15 "t" (2H), 3.49 "t" (2H), 3.86 s (3H, CH_3O), 5.45 "quintet" (1H), 6.93–7.02 m (2H), 7.14–7.22 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.7 (–, 2C), 38.8 (+, CH_3SO_2), 54.0 (+), 55.2 (+, CH_3O), 114.6 (+, 2C), 127.3 (q), 132.0 (+, 2C), 159.7 (q). Found, %: C 48.93; H 5.71; N 5.23. $C_{11}H_{15}NO_3S_2$. Calculated, %: C 48.33; H 5.53; N 5.12.

***N*-(1-Naphthyl)-*N*-(thietan-3-yl)methanesulfonamide (IIIc)** was obtained from *N*-(1-naphthyl)-methanesulfonamide (**Ic**) [20]. Yield 25%, mp 103–104°C (from toluene–hexane, 1:1). ^1H NMR spectrum ($CDCl_3$), δ_C, ppm: 2.94 s (3H, CH_3SO_2), 3.06–3.33 m (3H), 3.56 br.t (1H), 5.61 "quintet" (1H), 7.36–8.10 m (7H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.7 (–), 35.3 (–), 39.5 (+, CH_3SO_2), 54.9 (+), 123.4 (+), 125.1 (+), 126.6 (+), 127.3 (+), 128.2 (+), 128.9 (+), 129.9 (+), 131.8 (q), 133.6 (q), 134.6 (q). Found, %: C 57.49; H 5.10; N 4.56. $C_{14}H_{15}NO_2S_2$. Calculated, %: C 57.31; H 5.15; N 4.77.

***N*-Benzyl-*N*-(thietan-3-yl)benzenesulfonamide (IIId)** was isolated by preparative thin-layer chromatography on silica gel L 5/40 μm using hexane–diethyl ether (2:1) as eluent. Yield 5%, mp 79–80°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.85 "t" (2H), 2.88 s (2H, $PhCH_2$), 3.92 "t" (2H), 5.21 "quintet" (1H), 7.20–7.92 m (10H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 34.0 (–, 2C), 48.0 (–, $PhCH_2$), 54.2 (+), 126.7 (+, 2C), 126.9 (+, 2C), 127.4 (+), 128.5 (+, 2C), 129.1 (+, 2C), 132.7 (+), 137.7 (q), 140.5 (q). Found, %: C 60.40; H 5.44; N 4.03. $C_{16}H_{17}NO_2S_2$. Calculated, %: C 60.17; H 5.37; N 4.39.

***N*-(Thietan-3-yl)benzenesulfonamide (IIIe).** Yield 25%, mp 107–108°C (from $CHCl_3$–hexane, 2:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.03 "t" (2H), 3.25 "t" (2H), 4.52 "sextet" (1H), 5.81 br.d (1H, NH), 7.44–8.02 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 36.5 (–, 2C), 50.3 (+), 126.7 (+, 2C), 129.2 (+, 2C), 132.9 (+), 140.5 (q). Found, %: C 47.13; H 5.01; N 6.45. $C_9H_{11}NO_2S_2$. Calculated, %: C 47.14; H 4.48; N 6.11.

***N*-(4-Nitrophenyl)-*N*-(thietan-3-yl)benzenesulfonamide (IIIf)** was synthesized from *N*-(4-nitrophenyl)benzenesulfonamide (**If**) [21]. Yield 30%, mp 188–189°C (from CH_2Cl_2–hexane, 2:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.09 "t" (2H), 3.40 "t" (2H), 5.14 "quintet" (1H), 7.11 d (2H, J = 7.2 Hz), 7.43–7.71 m (5H), 8.20 d (2H, J = 7.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.3 (–, 2C), 54.6 (+), 124.3 (+, 2C), 127.5 (+, 2C), 129.2 (+, 2C), 130.8 (+, 2C), 133.5 (+), 137.1 (q), 142.0 (q), 147.3 (q). Found, %: C 51.89; H 4.11; N 7.88. $C_{15}H_{14}N_2O_4S_2$. Calculated, %: C 51.42; H 4.03; N 8.00.

***N*-Aryl-2-nitrobenzenesulfonamides IVa–IVg (*general procedure*).** *a*. 2-Nitrobenzenesulfonyl chloride, 11.1 g (50 mmol), was added in portions over a period of 30 min under vigorous stirring to a mixture of 62.5 mmol of the corresponding aromatic amine and 67.5 mmol of sodium acetate (anhydrous or trihydrate) in 50 ml of 50% aqueous ethanol. A solid precipitated during the addition. The mixture was then heated to 70–80°C over a period of 30 min, cooled, diluted with water, and acidified with concentrated hydrochloric acid (to adjust the overall volume to 600 ml). The precipitate was filtered off and recrystallized from appropriate solvent.

***N*-Phenyl-2-nitrobenzenesulfonamide (IVa).** Yield 95%, light yellow crystals, mp 118–120°C (from ethanol–water, 4:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.13–7.37 m (6H, Ph, SO_2NH), 7.54–7.63 t.d (1H, *J* = 7.7, 1.5 Hz), 7.66–7.75 t.d (1H, *J* = 7.7, 1.5 Hz), 7.79–7.90 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 123.7 (+, 2C), 125.7 (+), 127.0 (+), 129.9 (+, 2C), 132.2 (+), 132.6 (q), 133.0 (+), 134.4 (+), 135.9 (q), 148.6 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 278 $[M]^+$ (10), 92 (78), 76 (21), 65 (100), 50 (53), 39 (83). Found, %: C 51.78; H 3.67; N 10.14. $C_{12}H_{10}N_2O_4S$. Calculated, %: C 51.79; H 3.62; N 10.07.

***N*-(4-Methoxyphenyl)-2-nitrobenzenesulfonamide (IVb).** Yield 90%, yellow crystals, mp 106–108°C (from ethanol–water, 4:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.76 s (3H, CH_3O), 6.79 d (2H, *J* = 9.2 Hz), 7.09 d (2H, *J* = 9.2 Hz), 7.16 br.s (1H, SO_2NH), 7.57 t.d (1H, *J* = 7.7, 1.5 Hz), 7.65–7.79 m (2H), 7.86 d (1H, *J* = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.8 (+), 115.0 (+, 2C), 125.6 (+), 126.6 (+, 2C), 128.3 (q), 132.3 (+), 132.5 (q), 132.9 (+), 134.4 (+), 148.6 (q), 159.0 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 308 $[M]^+$ (6), 122 (100), 95 (19), 64 (10), 54 (19), 41 (16). Found, %: C 50.87; H 3.95; N 9.06. $C_{13}H_{12}N_2O_5S$. Calculated, %: C 50.64; H 3.92; N 9.09.

***N*-(2-Isopropylphenyl)-2-nitrobenzenesulfonamide (IVc).** Yield 90%, colorless crystals, mp 117–119°C (from ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 d (6H, CH_3, *J* = 6.9 Hz), 3.27 septet (1H, CH, *J* = 6.9 Hz), 7.05–7.35 m (5H, C_6H_4, SO_2NH), 7.63 t (1H, *J* = 7.7 Hz), 7.70–7.84 m (2H), 7.87–7.95 d (1H, *J* = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.8 (+, 2C), 27.8 (+), 125.7 (+), 126.8 (+), 127.0 (+), 127.3 (+), 128.5 (+), 131.8 (+), 132.4 (q), 133.0 (+), 133.8 (q), 134.3 (+), 145.5 (q), 148.4 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 320 $[M]^+$ (12), 132 (95), 118 (65), 106 (61), 91 (94), 77 (64), 65 (67), 50 (100), 39 (95). Found, %: C 56.10; H 4.99; N 8.75. $C_{15}H_{16}N_2O_4S$. Calculated, %: C 56.24; H 5.03; N 8.74.

***N*-(4-Chlorophenyl)-2-nitrobenzenesulfonamide (IVd).** Yield 96%, greenish–yellow crystals, mp 123–124°C (from ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.16 d (2H, *J* = 8.7 Hz), 7.22–7.35 d and br.s (2H, Ar, SO_2NH, *J* = 8.7 Hz), 7.63 t.d (1H, *J* = 7.7, 1.5 Hz), 7.74 t.d (1H, *J* = 7.7, 1.5 Hz), 7.80–7.92 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 125.0 (+, 2C), 125.8 (+), 130.0 (+, 2C), 132.2 (+), 132.7 (q), 133.2 (+), 134.5 (q), 134.7 (+), 148.5 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 312 $[M]^+$ (36), 186 (19), 126 (100), 99 (33), 90 (10), 53 (11), 50 (10). Found, %: C 46.10; H 2.99; N 8.84. $C_{12}H_9ClN_2O_4S$. Calculated, %: C 46.09; H 2.90; N 8.96.

***N*-(1-Naphthyl)-2-nitrobenzenesulfonamide (IVe).** The crude product was purified by heating in boiling ethanol, followed by recrystallization from $CHCl_3$–hexane (3:1). Yield 72%, pale violet crystals, mp 165–167°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.34–7.96 m (11H, Ar, SO_2NH), 8.05–8.15 m (1H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 122.3 (+), 124.6 (+), 125.6 (+), 125.7 (+), 126.9 (+), 127.4 (+), 128.7 (+), 128.8 (+), 130.2 (q), 131.3 (q), 131.8 (+), 133.0 (+), 133.4 (q), 134.2 (+), 134.7 (q), 148.5 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 328 $[M]^+$ (12), 142 (83), 115 (100), 89 (10), 76 (12), 63 (17), 50 (27), 39 (17). Found, %: C 58.73; H 3.77; N 8.41. $C_{16}H_{12}N_2O_4S$. Calculated, %: C 58.53; H 3.68; N 8.53.

b. A mixture of 144 mmol of the corresponding aromatic amine and 72 mmol of 2-nitrobenzenesulfonyl chloride in 100 ml of dioxane (preliminarily dried over KOH) was heated for 30–50 h under reflux. The yield of the product increased on prolonged heating. The resulting dark brown mixture was poured into a solution of 25 g of sodium hydroxide in 700 ml of water, stirred for 20 min, and filtered from undissolved material. The filtrate was acidified with concentrated hydrochloric acid and was left to stand for crystallization. The precipitate (sulfonamide **IVf** or **IVg**) was recrystallized from aqueous ethanol.

***N*-(3-Nitrophenyl)-2-nitrobenzenesulfonamide (IVf).** Yield 91%, light brown crystals, mp 165–166°C. ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 7.45–7.63 m (2H), 7.73–7.93 m (4H), 7.98–8.11 m (2H), 11.14 br.s (1H, SO_2NH). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ_C, ppm: 114.9 (1C, +), 119.3 (1C, +), 125.5 (1C, +), 126.2 (1C, +), 131.0 (1C, +), 131.1 (1C, +), 132.3 (q), 133.1 (1C, +), 135.4 (1C, +), 139.2 (q), 148.7 (q), 149.1 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 323 $[M]^+$ (37), 186 (100), 91 (9), 63 (15). Found, %: C 44.51; H 2.74; N 13.19. $C_{12}H_9N_3O_6S$. Calculated, %: C 44.58; H 2.81; N 13.00.

***N*-(4-Nitrophenyl)-2-nitrobenzenesulfonamide (IVg).** Yield 75%, light brown (from aqueous ethanol) or golden brown crystals (from $CHCl_3$), mp 173–175°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.42 d (2H, *J* = 9 Hz), 7.60–7.84 m (3H, Ar, SO_2NH), 7.92 d (1H, *J* = 7.7 Hz), 8.02 d (1H, *J* = 7.7 Hz), 8.20 d (2H, *J* = 9 Hz). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ_C, ppm: 119.1 (+, 2C), 125.6 (+), 125.7 (+, 2C), 131.3 (+), 132.2 (q), 133.2 (+), 135.5 (+), 143.8 (q), 144.1 (q), 148.7 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 323 $[M]^+$

(9), 186 (100), 92 (27), 76 (43), 63 (100), 50 (96), 39 (73). Found, %: C 44.51; H 2.86; N 12.96. $C_{12}H_9N_3O_6S$. Calculated, %: C 44.58; H 2.81; N 13.00.

***N*-Aryl-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamides Va–Vd, Vf, and Vg (*general procedure*).** *N*-Aryl-2-nitrobenzenesulfonamide, 20 mmol, was added under stirring to a solution of 1.3 g (23 mmol) of KOH in 80 ml of water. The initial sulfonamide dissolved (when Ar = 4-ClC_6H_4 or 4-$NO_2C_6H_4$, abundant precipitate of the sulfonamide potassium salt separated). 2-Chloromethylthiirane, 2.4 g (22 mmol), was then added, and the mixture was stirred for 48 h at room temperature. During this time, the intensely yellow mixture paled, and a solid precipitated. The product was filtered off, washed with water, and dissolved in 100 ml of methylene chloride. The organic solution was washed with a 5% solution of sodium hydroxide (3×50 ml), water (2×50 ml), and a saturated solution of sodium chloride (50 ml), dried over $MgSO_4$ or K_2CO_3, and filtered through a 1.5-cm layer of silica gel. The sorbent was washed with methylene chloride to adjust the filtrate to a volume of 300 ml. The solvent was evaporated to dryness on a rotary evaporator, and the residue was washed with diethyl ether or recrystallized from appropriate solvent.

***N*-Phenyl-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide (Va).** Yield 35%, colorless crystals, mp 109–111°C (from CH_2Cl_2–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.23–3.34 m (2H), 3.43–3.54 m (2H), 5.66–5.81 m (1H), 7.04–7.12 m (2H), 7.34–7.54 m (5H), 7.64–7.73 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 35.7 (–, 2C), 54.7 (+), 124.5 (+), 130.0 (+, 2C), 130.1 (+), 131.7 (+), 132.5 (q), 132.7 (+), 132.9 (+, 2C), 134.0 (q), 134.3 (+), 148.2 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 350 $[M]^+$ (2), 304 (63), 118 (85), 104 (71), 91 (100), 77 (85), 73 (80), 65 (27), 51 (56), 45 (56), 39 (34). Found, %: C 51.33; H 4.05; N 8.09. $C_{15}H_{14}N_2O_4S_2$. Calculated, %: C 51.41; H 4.03; N 7.99.

***N*-(4-Methoxyphenyl)-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide (Vb).** Yield 41%, colorless crystals, mp 101–102°C (no recrystallization was necessary). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.28 "t" (2H), 3.48 "t" (2H), 3.84 s (3H), 5.72 "quintet" (1H), 6.88 d (2H, *J* = 9.3 Hz), 6.98 d (2H, *J* = 9.3 Hz), 7.44–7.58 m (2H), 7.63–7.73 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 35.6 (–, 2C), 54.7 (+), 55.9 (+), 115.1 (+, 2C), 124.5 (+), 126.1 (q), 131.8 (+), 132.6 (q), 132.7 (+), 134.1 (+, 2C), 134.2 (+), 148.2 (q), 160.7 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 334 (10), 194 (46), 148 (71), 133 (48), 117 (35), 105 (32), 92 (24), 77 (39), 73 (100), 64 (34), 50 (27), 45 (39), 39 (15). Found, %: C 50.36; H 4.21; N 7.21. $C_{16}H_{16}N_2O_5S_2$. Calculated, %: C 50.51; H 4.24; N 7.36.

***N*-(2-Isopropylphenyl)-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide (Vc).** Yield 27%, colorless crystals, mp 168–169°C (from CH_2Cl_2–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 d (3H, *J* = 6.9 Hz), 1.26 d (3H, *J* = 6.9 Hz), 3.12–3.21 "t.d" (1H), 3.23–3.52 m (4H), 5.64–5.78 m (1H), 6.75 d (1H, *J* = 7.7 Hz), 7.06–7.15 m (1H), 7.35–7.56 m (4H), 7.64–7.74 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.3 (+), 24.9 (+), 28.0 (+), 35.1 (–), 36.5 (–), 55.6 (+), 124.4 (+), 126.6 (+), 128.4 (+), 130.5 (+), 131.65 (+), 131.68 (q), 132.4 (+), 132.7 (q), 133.0 (+), 134.3 (+), 148.6 (q), 151.6 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 346 (26), 160 (100), 144 (17), 130 (18), 118 (46), 91 (24), 77 (15), 73 (32), 51 (12), 45 (26). Found, %: C 55.08; H 5.19; N 7.06. $C_{18}H_{20}N_2O_4S_2$. Calculated, %: C 55.08; H 5.14; N 7.14.

***N*-(4-Chlorophenyl)-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide (Vd).** Yield 31%, colorless crystals, mp 140–141°C (from CH_2Cl_2–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.29 "t" (2H), 3.45 "t" (2H), 5.71 "quintet" (1H), 7.03 d (2H), 7.38 d (2H), 7.48–7.59 m (2H), 7.66–7.75 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 35.6 (–, 2C), 54.7 (+), 124.7 (+), 130.3 (+, 2C), 131.9 (+), 132.2 (q), 132.6 (+), 134.1 (+, 2C), 134.5 (+), 136.3 (q), 148.2 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 338 (54), 152 (38), 117 (100), 73 (38). Found, %: C 47.07; H 3.37; N 7.29. $C_{15}H_{13}ClN_2O_4S_2$. Calculated, %: C 46.81; H 3.40; N 7.28.

***N*-(3-Nitrophenyl)-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide (Vf).** Yield 26%, yellowish crystals, mp 140–142°C (from CH_2Cl_2–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.32 "t" (2H), 3.43 "t" (2H), 5.72 "quintet" (1H), 7.48–7.61 m (3H), 7.62–7.70 t (1H, *J* = 8 Hz), 7.71–7.81 m (2H), 7.88–7.94 m (1H), 8.33 br.d (1H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.5 (–, 2C), 54.9 (+), 124.95 (+), 125.0 (+), 127.4 (+), 130.9 (+), 131.7 (q), 132.1 (+), 132.3 (+), 135.0 (+), 135.8 (q), 139.1 (+), 148.3 (q), 149.1 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 395 $[M]^+$ (4), 349 (96), 186 (100), 162 (21), 149 (32), 117 (48), 89 (24), 76 (23), 73 (33), 63 (15), 50 (13), 45 (25), 39 (11). Found, %: C 45.67; H 3.37; N 10.52. $C_{15}H_{13}N_3O_6S_2$. Calculated, %: C 45.56; H 3.31; N 10.63.

***N*-(4-Nitrophenyl)-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide (Vg).** Yield 1.3%, light yellow crys-

tals, mp 178–179°C (from $CHCl_3$–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.31 "t" (2H), 3.43 "t" (2H), 5.71 "quintet" (1H), 7.33 d (2H, *J* = 8.7 Hz), 7.50–7.62 m (2H), 7.68–7.80 m (2H), 8.28 d (2H, *J* = 8.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 35.5 (–, 2C), 54.9 (+), 124.9 (+), 125.2 (+, 2C), 131.7 (q), 132.1 (+), 132.4 (+), 133.5 (+, 2C), 135.0 (+), 140.4 (q), 148.5 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 395 $[M]^+$ (4), 349 (93), 319 (29), 239 (18), 186 (100), 117 (88), 90 (65), 83 (43), 76 (76), 73 (68), 63 (59), 50 (80), 45 (100), 39 (66), 35 (56). Found, %: C 45.39; H 3.39; N 10.43. $C_{15}H_{13}N_3O_6S_2$. Calculated, %: C 45.56; H 3.31; N 10.63.

***N*-(1-Naphthyl)-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide (Ve).** Compound **IVe**, 9.8 g (30 mmol), was added under stirring to a solution of 2.6 g (46 mmol) of potassium hydroxide in 160 ml water. During the addition, pale yellow flaky sulfonamide **IVe** potassium salt precipitated. 2-Chloromethylthiirane, 3.6 g (33 mmol), was added, the mixture was vigorously stirred for 72 h, 150 ml of methylene chloride and 150 ml of a 5% solution of sodium hydroxide were added, the mixture was thoroughly shaken in a separatory funnel, and initial sulfonamide potassium salt was filtered off. The organic phase was separated, washed with 100 ml of a 5% solution of sodium hydroxide, two 100-ml portions of water, and 100 ml of a saturated solution of sodium chloride, dried over K_2CO_3, and filtered through a 1.5-cm layer of silica gel. The sorbent was washed with methylene chloride to adjust the filtrate to a volume of 250 ml. The solvent was distilled off to dryness on a rotary evaporator, and the residue was recrystallized from CH_2Cl_2–hexane (2:1). Yield 5.33 g (44%), colorless crystals, mp 160–161°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.20–3.40 m (3H), 3.62 "t" (1H), 6.00 "quintet" (1H), 7.23–7.39 m (4H), 7.42–7.55 m (2H), 7.56–7.66 m (1H), 7.70 d (1H, *J* = 7.7 Hz), 7.78 d (1H, *J* = 8.5 Hz), 7.88 d (1H, *J* = 7.7 Hz), 7.97 d (1H, *J* = 8.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.9 (–), 36.2 (–), 55.8 (+), 123.8 (+), 124.4 (+), 125.7 (+), 127.0 (+), 127.5 (+), 128.7 (+), 130.5 (q), 130.9 (+), 131.7 (+), 132.3 (+), 132.5 (+), 132.6 (q), 133.9 (q), 134.2 (+), 135.1 (q), 148.2 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 400 $[M]^+$ (9), 354 (63), 214 (18), 168 (100), 141 (37), 127 (37), 115 (27), 73 (78), 45 (45). Found, %: C 56.96; H 4.11; N 7.02. $C_{19}H_{16}N_2O_4S_2$. Calculated, %: C 56.98; H 4.03; N 7.00.

3-Arylaminothietanes VIa–VIg. Deprotection in the system PhSH–K_2CO_3–DMF (*general procedure*). A mixture of 4 mmol of *N*-aryl-*N*-(thietan-3-yl)-2-nitrobenzenesulfonamide, 8 mmol of benzenethiol, and 12 mmol of anhydrous K_2CO_3 in 25 ml of DMF was stirred for 1–1.5 h at 40–50°C. The progress of the reaction was monitored by TLC using methylene chloride as eluent; the initial compound disappeared, and two new spots appeared, yellow with $R_f \approx 1$ (2-nitrodiphenyl sulfone) and colorless with $R_f < 0.5$ (target product); the latter spot disappeared on treatment with dilute hydrochloric acid of a sample dissolved in diethyl ether. The mixture was poured into 150 ml of water and extracted with diethyl ether (3× 50 ml). The extract was washed with water (2×100 ml) and treated with 3 N hydrochloric acid (3×50 ml) to transfer the amine into the aqueous phase. The aqueous phase was washed with diethyl ether (2×50 ml; the ether extracts were discarded) and was made alkaline by adding 15% aqueous sodium hydroxide (in doing so, a solid precipitated). The mixture was extracted with diethyl ether (3×50 ml), the extract was washed with 100 ml of water and a saturated solution of sodium chloride and dried over K_2CO_3, the solvent was distilled off to dryness on a rotary evaporator, and the residue was recrystallized from aqueous ethanol.

3-Phenylaminothietane (VIa). Yield 80%, colorless leaflets, mp 56–57°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.32 "t" (2H), 3.48 "t" (2H), 3.9–4.3 br.s (1H), 4.86 "quintet" (1H), 6.61 d (2H, *J* = 7.7 Hz), 6.79 t (1H, *J* = 7.7 Hz), 7.22 t (2H, *J* = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 36.9 (–, 2C), 52.4 (+), 113.6 (+, 2C), 118.9 (+), 129.9 (+, 2C), 145.8 (q). Mass spectrum (chemical ionization, NH_3), *m*/*z* (I_{rel}, %): 166 $[M + H]^+$ (90), 183 $[M + NH_4]^+$ (100). Found, %: C 65.68; H 6.69; N 8.46. $C_9H_{11}NS$. Calculated, %: C 65.41; H 6.71; N 8.48.

3-(4-Methoxyphenylamino)thietane (VIb). Yield 86%, colorless needles, mp 81–82°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.28 "t" (2H), 3.46 "t" (2H), 3.76 s (3H), 3.6–4.1 br.s (1H), 4.77 "quintet" (1H), 6.58 d (2H), 6.80 d (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 36.9 (–, 2C), 53.4 (+), 56.1 (+), 115.2 (+, 2C), 115.5 (+, 2C), 139.9 (q), 153.3 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 195 $[M]^+$ (13), 149 (100), 134 (77), 122 (26), 107 (38), 95 (10), 91 (9), 77 (28), 73 (29), 63 (26), 52 (44), 45 (100), 39 (55). Found, %: C 61.54; H 6.82; N 7.05. $C_{10}H_{13}NOS$. Calculated, %: C 61.50; H 6.71; N 7.17.

3-(2-Isopropylphenylamino)thietane (VIc). Yield 71%, colorless leaflets, mp 67–69°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 d (6H), 2.90 septet (1H),

3.33 "t" (2H), 3.52 "t" (2H), 3.9–4.2 br.s (1H), 4.8–5.0 "br.sextet" (1H), 6.58 d (1H), 6.81 t (1H), 7.06–7.24 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 22.8 (+, 2C), 27.6 (+), 37.1 (–, 2C), 52.6 (+), 111.7 (+), 119.0 (+), 125.8 (+), 127.2 (+), 133.1 (q), 142.6 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 207 $[M]^+$ (5), 161 (18), 146 (100), 130 (21), 118 (18), 91 (33), 77 (27), 73 (16), 65 (24), 51 (26), 46 (94), 39 (52). Found, %: C 69.58; H 8.23; N 6.81. $C_{12}H_{17}NS$. Calculated, %: C 69.51; H 8.26; N 6.76.

3-(4-Chlorophenylamino)thietane (VId). Yield 60%, colorless leaflets, mp 57–58°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.28 "t" (2H), 3.46 "t" (2H), 3.9–4.3 br.s (1H), 4.78 "quintet" (1H), 6.51 d (2H), 7.15 d (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 36.6 (–, 2C), 52.4 (+), 114.7 (+, 2C), 123.5 (q), 129.7 (+, 2C), 144.4 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 199 $[M]^+$ (13), 153 (100), 117 (35), 111 (11), 99 (10), 91 (31), 75 (17), 73 (18), 63 (11), 46 (31), 40 (20). Found, %: C 53.88; H 5.00; N 7.21. $C_9H_{10}ClNS$. Calculated, %: C 54.13; H 5.05; N 7.01.

3-(1-Naphthylamino)thietane (VIe). A mixture of 4 g (10 mmol) of compound **Ve**, 2.2 g (20 mmol) of benzenethiol, and 4.14 g (30 mmol) of anhydrous potassium carbonate in 50 ml of DMF was stirred for 1 h at 40–50°C (TLC). The mixture was poured into 150 ml of water and extracted with diethyl ether (3× 50 ml). The extract was washed with water (2×100 ml) and treated with 200 ml of 3 N hydrochloric acid under vigorous shaking. The precipitate (amine hydrochloride) was filtered off and washed with diethyl ether. The organic phase was separated from the filtrate and discarded, and the aqueous phase was washed with diethyl ether (2×50 ml). The precipitate of amine hydrochloride was added to the aqueous solution under stirring, and the mixture was made alkaline by adding a 15% aqueous solution of sodium hydroxide. The mixture was extracted with diethyl ether (4×50 ml), the combined extracts were washed with water (2× 100 ml) and a saturated solution of sodium chloride (100 ml) and dried over K_2CO_3, the solvent was distilled off to dryness on a rotary evaporator, and the residue was recrystallized from aqueous ethanol. Yield 1.71 g (80%), light yellow needles, mp 124–125°C; hydrochloride: colorless crystals, mp 155–160°C. The product showed an intense blue fluorescence under UV light both in crystal and in solution. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.43 "t" (2H), 3.62 "t" (2H), 4.5–4.9 br.s (1H), 5.04 quintet (1H), 6.52–6.63 m (1H), 7.29–7.40 m (2H), 7.44–7.55 m (2H), 7.78–7.88 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 36.7 (–, 2C), 52.7 (+), 106.1 (+), 119.2 (+), 120.3 (+), 123.9 (q), 125.5 (+), 126.4 (+), 126.8 (+), 129.2 (+), 134.9 (q), 141.0 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 215 $[M]^+$ (28), 168 (100), 154 (12), 141 (18), 127 (18), 115 (38), 73 (17), 45 (31), 39 (17). Found, %: C 72.53; H 6.22; N 6.44. $C_{13}H_{13}NS$. Calculated, %: C 72.52; H 6.09; N 6.51.

3-(3-Nitrophenylamino)thietane (VIf). A mixture of 880 mg (2.2 mmol) of compound **Vf**, 460 mg (4.4 mmol) of 2-sulfanylacetic acid, and 1.23 g (8.9 mmol) of anhydrous K_2CO_3 in 20 ml of DMF was stirred for 4 h at 70–80°C (TLC, diethyl ether–hexane, 1:1). The mixture was poured into 400 ml of water containing 10 g of NaOH and extracted with diethyl ether (4×50 ml). The ether extract was washed with a 5% solution of NaOH (2×75 ml), water (100 ml), and a saturated solution of NaCl (100 ml) and dried over $MgSO_4$. The solvent was distilled off to dryness on a rotary evaporator, and the residue was recrystallized from aqueous ethanol. Yield 85%, orange–yellow needles, mp 124–125°C. A solution of compound **VIf** in diethyl ether (but not in CH_2Cl_2 or acetone) exhibits a yellow–green fluorescence upon irradiation with UV light (λ = 366 nm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.33 "t" (2H), 3.51 "t" (2H), 4.40–4.55 br.d (1H), 4.88 "sextet" (1H), 6.87 d.d (1H, *J* = 7.7, 2.3 Hz), 7.32 t (1H, *J* = 8.5 Hz), 7.38 t (1H, *J* = 2.3 Hz), 7.59 d.d (1H, *J* = 8.5, 2.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 36.3 (–, 2C), 51.9 (+), 107.2 (+), 113.4 (+), 119.4 (+), 130.5 (+), 146.7 (q), 149.8 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 210 $[M]^+$ (10), 164 (100), 147 (27), 117 (84), 91 (30), 73 (18), 65 (15), 63 (13), 45 (29), 39 (13). Found, %: C 51.27; H 4.78; N 13.14. $C_9H_{10}N_2O_2S$. Calculated, %: C 51.41; H 4.79; N 13.32.

***N*-(4-Methoxyphenyl)-*N*-(1-oxothietan-3-yl)-2-nitrobenzenesulfonamide (VIIb).** Compound **Vb**, 3 g (7.9 mmol), was dissolved in 50 ml of acetic acid on heating. A mixture of 20 mg of $WO_3 \cdot H_2O$, 2 ml of water, and one drop of a 50% aqueous solution of sodium hydroxide was stirred until it became homogeneous, and the resulting solution of sodium tungstate was added to the solution of **Vb**. The mixture was cooled to 0–10°C with an ice bath (a solid precipitated), and a mixture of 2.6 g of 30% hydrogen peroxide and 10 g of acetic acid was added dropwise over a period of 20 min. During the addition, the precipitate dissolved. The mixture was stirred for an additional 30 min at 0–10°C (TLC, eluent CH_2Cl_2). When the initial compound disappeared, the mixture was diluted with water under stirring to adjust the overall volume to 400 ml. An oily material separated,

and it slowly crystallized to give a colorless solid. The product was filtered off and washed with water (no recrystallization was necessary). Yield 2.91 g (93%), colorless crystals, mp 107–109°C. The product was a mixture of two diastereoisomers at a ratio of 63:37. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.05–3.19 m (0.7H), 3.21–3.35 m (1.3H), 3.48–3.62 m (1.3H), 3.84 s (3H), 4.02–4.18 m (0.7H), 4.75–4.93 m (0.37H), 6.17 "quintet" (0.63H), 6.84–6.94 m (2H), 6.95–7.06 m (2H), 7.47–7.62 m (2H), 7.66–7.76 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 42.2, 53.7, 55.96, 55.98, 56.3, 60.6, 115.4, 115.6, 124.4 (q), 124.7, 125.4 (q), 131.9, 132.1, 132.2 (q), 132.5 (q), 132.8, 133.0, 133.9, 134.50, 134.55, 134.61, 148.2 (q), 161.1 (q), 161.2 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 396 $[M]^+$ (9), 334 (11), 307 (14), 162 (20), 148 (100), 135 (23), 133 (28), 121 (17), 117 (15), 105 (16), 77 (14). Found, %: C 48.52; H 4.10; N 7.17. $C_{16}H_{16}N_2O_6S_2$. Calculated, %: C 48.47; H 4.07; N 7.07.

***N*-(4-Chlorophenyl)-*N*-(1-oxothietan-3-yl)-2-nitrobenzenesulfonamide (VIId)** was synthesized in a similar way from compound **Vd**. Yield 97%, colorless crystals, mp 168–175°C (sintered above 150°C). The product was a mixture of two diastereoisomers at a ratio of 63:37. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.00–3.13 m (0.7H), 3.15–3.27 m (1.3H), 3.47–3.60 m (1.3H), 4.06–4.17 m (0.7H), 4.76–4.93 m (0.37H), 6.18 "quintet" (0.63H), 6.99–7.11 m (2H), 7.34–7.45 m (2H), 7.49–7.61 m (2H), 7.69–7.79 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 42.4, 53.9, 56.0, 60.6, 124.9, 130.6, 130.7, 131.1, 131.7, 132.0, 132.1, 132.3, 132.7, 132.9, 133.8, 134.6, 134.87, 134.92, 136.9, 137.2, 148.0, 148.3. Mass spectrum, *m*/*z* (I_{rel}, %): 400 $[M]^+$ (33), 351 (35), 338 (88), 312 (18), 186 (51), 152 (63), 138 (57), 117 (100), 111 (48). Found, %: C 45.05; H 3.34; N 6.96. $C_{15}H_{13}ClN_2O_5S_2$. Calculated, %: C 44.94; H 3.27; N 6.99.

***N*-(1,1-Dioxothietan-3-yl)-*N*-(4-methoxyphenyl)-2-nitrobenzenesulfonamide (VIIIb).** Compound **VIIb**, 2.8 g (7.1 mmol), was dissolved in 50 ml of acetic acid, a solution of sodium tungstate (prepared as described above) was added, and a solution of 3 g of 30% H_2O_2 in 10 ml of acetic acid was then added dropwise. The mixture was stirred for 2 h at room temperature. During this time, a solid precipitated. The mixture was kept for 24 h, and the precipitate was filtered off, washed with diethyl ether, and recrystallized from CH_2Cl_2–hexane (3:1). Yield 1.98 g (68%), colorless very light silky crystals, mp 184–185°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 s (3H), 4.10–4.23 m (2H), 4.37–4.50 m (2H), 5.39 "quintet" (1H), 6.90 d (2H), 7.03 d (2H), 7.46–7.59 m (2H), 7.68–7.79 m (2H). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 40.9 (+), 56.0 (+), 70.3 (–, 2C), 115.5 (+, 2C), 125.2 (+), 126.4 (q), 130.7 (q), 132.45 (+), 132.53 (+), 133.6 (+), 135.8 (+), 148.4 (q), 160.8 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 412 $[M]^{+\cdot}$ (2), 226 (100), 162 (33), 148 (24), 134 (58), 105 (30), 77 (33), 39 (28). Found, %: C 46.64; H 3.86; N 6.69. $C_{16}H_{16}N_2O_7S_2$. Calculated, %: C 46.59; H 3.91; N 6.79.

***N*-(4-Chlorophenyl)-*N*-(1,1-dioxothietan-3-yl)-2-nitrobenzenesulfonamide (VIIId).** Compound **Vd**, 2 g (5.2 mmol), was dissolved in 50 ml of acetic acid, a solution of sodium tungstate (see above) was added, and a solution of 6 g of 30% H_2O_2 in 20 ml of acetic acid was then added dropwise. The mixture was stirred for 2 h at room temperature, and a solid began to separate from the solution. The mixture was kept for 48 h, and the precipitate was filtered off and washed with diethyl ether. Blue inorganic impurities were removed by washing with water. The product was then recrystallized from CH_2Cl_2–hexane, 3:1. Yield 1.78 g (82%), colorless very light silky crystals, mp 198–200°C. ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 4.02–4.20 m (2H), 4.36–4.54 m (2H), 5.17 "quintet" (1H), 7.23 d (2H, *J* = 8.7 Hz), 7.42 d (2H, *J* = 8.7 Hz), 7.59 d (1H), 7.66–7.78 m (1H), 7.85–7.98 m (2H). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 41.1 (+), 70.5 (–, 2C), 125.3 (+), 130.0 (q), 130.4 (+, 2C), 132.3 (+), 132.7 (+), 133.7 (+, 2C), 133.9 (q), 135.7 (q), 136.1 (+), 148.6 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 416 $[M]^+$ (4), 338 (20), 186 (30), 166 (39), 152 (37), 151 (37), 138 (59), 130 (39), 117 (100), 111 (55), 75 (36), 39 (34). Found, %: C 43.20; H 3.22; N 6.73. $C_{15}H_{13}ClN_2O_6S_2$. Calculated, %: C 43.22; H 3.14; N 6.72.

3-(4-Methoxyphenylamino)thietane 1,1-dioxide (IXb). Anhydrous K_2CO_3, 1.5 g (10.9 mmol), and benzenethiol, 800 mg (7.3 mmol), were added to a solution of 1.5 g (3.6 mmol) of compound **VIIIb** in 25 ml of DMF, and the mixture was stirred for 1 h at 40–50°C. The mixture turned yellow, and a colorless solid precipitated. The progress of the reaction was monitored by TLC using CH_2Cl_2 as eluent (until the initial compound disappeared). The mixture was poured into 150 ml of water and treated with methylene chloride (4×50 ml CH_2Cl_2; the product is almost insoluble in diethyl ether). The organic phase was washed with water (2×100 ml) and treated with 3 N hydrochloric acid (3×80 ml) to transfer the product into the aqueous phase. The aqueous phase was washed with diethyl ether (2×50 ml) and was made alkaline by adding 20%

aqueous sodium hydroxide on cooling with cold water. In doing so, a solid precipitated. The product was extracted into methylene chloride (4×50 ml), the combined extracts were washed with 100 ml of water and 100 ml of a saturated solution of sodium chloride and dried over $MgSO_4$, the solvent was distilled off to dryness on a rotary evaporator, and the residue was recrystallized from CH_2Cl_2–hexane (3:1). Yield 654 mg (79%), colorless crystals, mp 167–168°C. ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 3.68 s (3H), 3.90–4.02 m (2H), 4.07–4.20 m (1H), 4.43–4.57 m (2H), 5.3–6.3 br.s (1H), 6.49 d (2H, J = 8.7 Hz), 6.70 d (2H, J = 8.7 Hz). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ_C, ppm: 35.1 (+), 55.9 (+), 71.3 (–, 2C), 114.8 (+, 2C), 115.4 (+, 2C), 141.1 (q), 152.7 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 227 $[M]^+$ (15), 149 (100), 134 (39), 77 (22), 52 (20), 41 (47), 39 (51). Found, %: C 52.91; H 5.88; N 6.19. $C_{10}H_{13}NO_3S$. Calculated, %: C 52.85; H 5.77; N 6.16.

3-(4-Chlorophenylamino)thietane 1,1-dioxide (IXd). A mixture of 1.58 g (3.8 mmol) of compound **VIIId**, 700 mg (7.6 mmol) of 2-sulfanylacetic acid, and 2.1 g (15.2 mmol) of anhydrous K_2CO_3 in 50 ml of DMF was stirred for 4 h at 70–80°C. The mixture was poured into 400 ml of water containing 1–2 g of NaOH and extracted with methylene chloride (4×50 ml), the extract was washed with a 5% solution of sodium hydroxide (2×75 ml), water (100 ml), and a saturated solution of sodium chloride (100 ml) and dried over $MgSO_4$, the solvent was distilled off on a rotary evaporator, and the residue (a yellow oily substance) was diluted with hexane and cooled to –15°C. The crystals were filtered off and washed with hexane and a small amount of ether. Yield 370 mg (42%), colorless crystals, mp 178–180°C. ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 3.91–4.04 m (2H), 4.08–4.24 m (1H), 4.48–4.63 m (2H), 6.42–6.58 m (3H, $2H_{arom}$, NH), 7.07 d (2H, J = 8.7 Hz). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ_C, ppm: 34.5 (+), 71.3 (–, 2C), 114.8 (+, 2C), 122.0 (q), 129.4 (+, 2C), 146.0 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 231 $[M]^+$ (34), 153 (100), 118 (10), 117 (11), 91 (10), 39 (12). Found, %: C 46.63; H 4.44; N 6.11. $C_9H_{10}ClNO_2S$. Calculated, %: C 46.65; H 4.35; N 6.05.

***N*-(Thietan-3-yl)-*N*-phenylbenzamide (Xa).** *N*-Methylmorpholine, 650 mg (5.6 mmol), and benzoyl chloride, 520 mg (3.7 mmol), were added to a solution of 610 mg (3.7 mmol) of 3-phenylaminothietane (**VIa**) in 25 ml of methylene chloride. The mixture was heated to the boiling point and slowly evaporated by half, and a colorless solid precipitated. The mixture was kept for 12 h at room temperature and was then evaporated to dryness on a rotary evaporator. The residue was dissolved in 30 ml of methylene chloride, and the solution was washed with 20 ml of dilute hydrochloric acid, two 20-ml portions of a dilute solution of sodium hydroxide, and two 20-ml portions of water. The organic phase was evaporated to dryness, and the residue was recrystallized from methylene chloride–hexane (2:1). Yield 610 mg (61%), slightly colored crystals, mp 75–76°C. ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 3.19 "t" (2H), 3.52 "t" (2H), 5.74 "quintet" (1H), 7.05–7.35 m (10H). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 34.0 (–, 2C), 54.3 (+), 128.2 (+, 2C), 128.4 (+), 128.8 (+, 2C), 129.8 (+, 2C), 130.0 (+), 130.9 (+, 2C), 136.9 (q), 140.1 (q), 170.0 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 269 $[M]^+$ (2), 223 (23), 197 (39), 180 (4), 105 (100), 91 (5), 77 (46), 51 (10), 45 (5). Found, %: C 70.96; H 5.50; N 5.33. $C_{16}H_{15}NOS$. Calculated, %: C 71.34; H 5.61; N 5.20.

***N*-(4-Methoxyphenyl)-*N*-(thietan-3-yl)benzamide (Xb)** was synthesized in a similar way from 3-(4-methoxyphenylamino)thietane (**VIb**). Yield 83%, colorless crystals, mp 97–98°C (from CH_2Cl_2–hexane, 2:1). ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 3.16 "t" (2H), 3.47 "t" (2H), 3.75 s (3H), 5.74 "quintet" (1H), 6.80 d (2H, J = 8.7 Hz), 7.02 d (2H, J = 8.7 Hz), 7.11–7.28 m (5H). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 33.9 (–, 2C), 54.0 (+), 55.8 (+), 114.9 (+, 2C), 128.2 (+, 2C), 128.7 (+, 2C), 129.8 (+), 132.1 (+, 2C), 132.3 (q), 137.0 (q), 159.2 (q), 170.1 (q). Mass spectrum, *m*/*z* (I_{rel}, %): 299 $[M]^+$ (9), 253 (21), 227 (53), 210 (20), 105 (100), 77 (46), 73 (9), 51 (8), 45 (8). Found, %: C 68.15; H 5.62; N 4.79. $C_{17}H_{17}NO_2S$. Calculated, %: C 68.20; H 5.72; N 4.68.

***N*-(4-Chlorophenyl)-*N*-(thietan-3-yl)acetamide (Xd).** Acetic anhydride, 700 mg (6.9 mmol), and pyridine, 500 mg (6.3 mmol), were added to a solution of 800 mg (4 mmol) of 3-(4-chlorophenylamino)thietane (**VId**) in 20 ml of methylene chloride. The mixture was heated to the boiling point, kept for 12 h at room temperature, and evaporated to dryness on a rotary evaporator. The residue was dissolved in 50 ml of methylene chloride, the solution was washed with a dilute solution of sodium hydroxide (2×30 ml), water (30 ml), dilute hydrochloric acid (2×30 ml), and water again (30 ml) and dried over Na_2SO_4, and the solvent was distilled off to dryness on a rotary evaporator. Yield 916 mg (96%), colorless crystals, mp 92–94°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.76 s (3H),

3.12 “t” (2H), 3.34 “t” (2H), 5.87 “quintet” (1H), 7.07 d (2H, J = 8.5 Hz), 7.46 d (2H, J = 8.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.7 (+), 34.0 (–, 2C), 52.2 (+), 130.6 (+, 2C), 131.6 (+, 2C), 135.3 (q), 137.9 (q), 170.2 (q). Mass spectrum, m/z (I_{rel}, %): 241 $[M]^+$ (6), 195 (15), 169 (46), 153 (66), 127 (28), 117 (45), 111 (22), 91 (13), 75 (26), 73 (38), 63 (11), 50 (10), 45 (29), 43 (100), 39 (20). Found, %: C 54.70; H 5.06; N 5.77. $C_{11}H_{12}ClNOS$. Calculated, %: C 54.65; H 5.00; N 5.79.

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