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Dedicated to Full Member of the Russian Academy of Sciences O.N. Chupakhin on his 70th Anniversary

Diels–Alder Reactions with Cyclic Sulfones: VII.* Synthesis of 1-Benzothiophene 1,1-Dioxide Derivatives

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Abstract—5-Arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-diones reacted with 5-isopropenyl-2,3-dihydrothiophene 1,1-dioxide to give the corresponding *ortho*-addition products, 5-aryl-2',2',7-trimethyl-3,3a,5,6-tetrahydro-2*H*-spiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxides. Their aminolysis resulted in opening of the 1,3-dioxane ring and formation of 4-carbamoyl-7-methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxylic acid 1,1-dioxide whose structure was determined by X-ray analysis. Reactions of the spiro adducts with amines and hydrazine hydrate afforded the corresponding mono- or dicarboxylic acid monoamides (hydrazide).

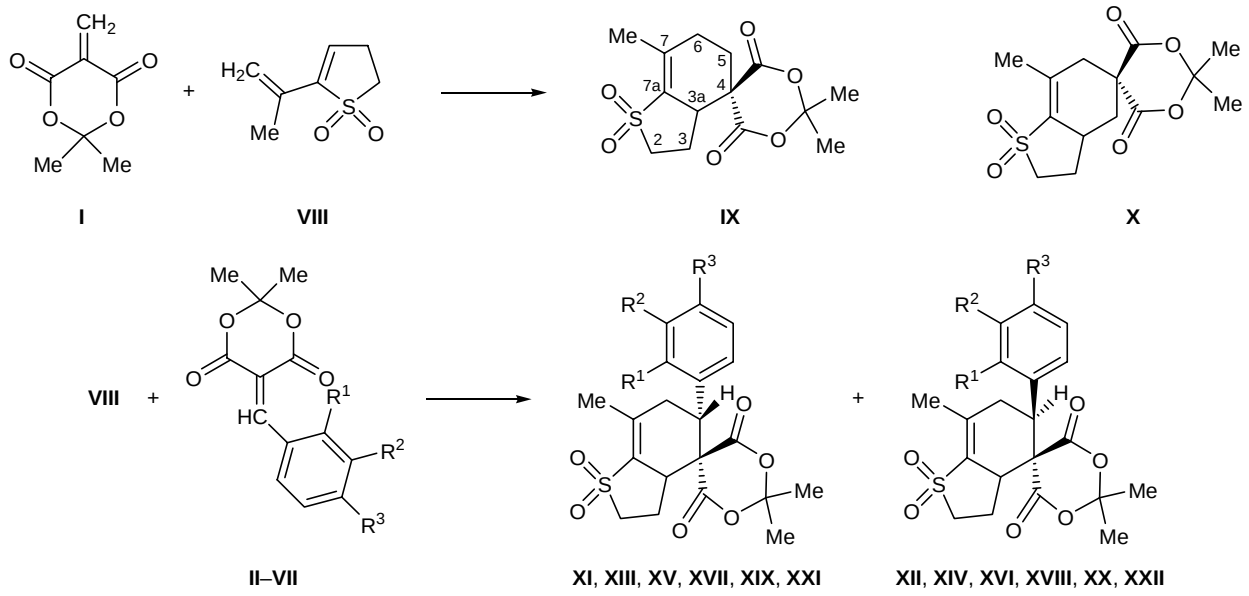
Diels–Alder reactions with 2,3-dihydrothiophene 1,1-dioxide derivatives as dienophiles and dienes were used previously to obtain various tri- and tetracyclic compounds containing a fused tetrahydrothiophene 1,1-dioxide fragment [1–6]. Some of the prepared compounds were found to exhibit a high antiphlogistic, antiulcer, and psychotropic activity together with low toxicity [7–9]. Less attention was given to the synthesis of 1-benzothiophene 1,1-dioxide derivatives. We synthesized such compounds by cycloaddition of 5-methylene-2,2-dimethyl-1,3-dioxane-4,6-dione (**I**) [10] and 5-arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-diones **II**–**VII** to 5-isopropenyl-2,3-dihydrothiophene 1,1-dioxide (**VIII**) [11]. The reaction of diene **VIII** with dienophile **I** was regioselective, and it resulted in formation of 93% of adduct **IX**. The ^{1}H and ^{13}C NMR spectra of the product were consistent with the assumed structure while alternative structure **X** was completely ruled out.

The Diels–Alder reaction of diene **VIII** with cyclic arylmethylenemalonates **II**–**VI**, as well as with compound **VII** generated *in situ*, was regioselective, and the products contained the dioxodioxane moiety spiro-fused at the C^4 atom of the benzothiophene fragment. The stereoselectivity depends on the substituents in the aromatic ring of the dienophile. As a rule, mixtures of (5*R*)- (compounds **XI**, **XIII**, **XV**, **XVII**, **XIX**, and **XXI**) and (5*S*)-diastereoisomers (**XII**, **XIV**, **XVI**, **XVIII**, **XX**, and **XXII**) were formed (Scheme 1). A high stereoselectivity was observed in the addition of 2-methoxy- and 2,3-dimethoxybenzylidene derivatives **III** and **IV**: the ratio of diastereoisomeric products **XIII**/**XIV** and **XV**/**XVI** was about 10:1. The reaction of diene **VIII** with 2,3,4-trimethoxybenzylidene derivative **V** was characterized by lower stereoselectivity. In this case, the ratio of products **XVII** and **XVIII** was the same as in the addition of 5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**II**) having no substituents in the phenyl ring (**XI**:**XII** = 5:1). The reaction of dienophile **VI** with diene **VIII** was not stereoselective, and almost equimolar mixture of isomeric products **XIX** and **XX** was obtained. The Diels–Alder reaction of **VIII** with 4-methoxybenzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**VII**) afforded adducts **XXI** and **XXII** at a ratio of ~0.22:1.

Thus substituents in the aromatic ring strongly affect the stereochemical results of the addition. Presumably, the reaction involves two transition states

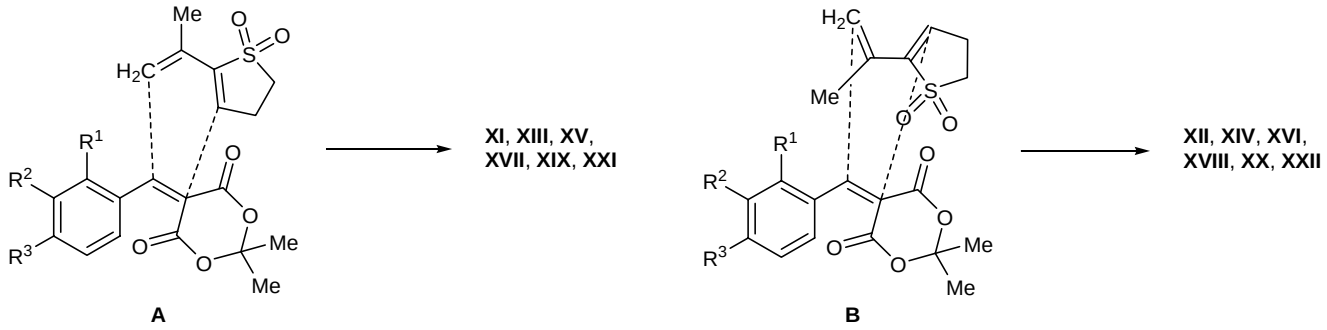
* For communication VI, see [1].

Scheme 1.



II, **XI**, **XII**, $R^1 = R^2 = R^3 = H$; **III**, **XIII**, **XIV**, $R^1 = CH_3O$, $R^2 = R^3 = H$; **IV**, **XV**, **XVI**, $R^1 = R^2 = CH_3O$, $R^3 = H$; **V**, **XVII**, **XVIII**, $R^1 = R^2 = R^3 = CH_3O$; **VI**, **XIX**, **XX**, $R^1 = H$, $R^2 = OH$, $R^3 = CH_3O$; **VII**, **XXI**, **XXII**, $R^1 = R^2 = H$, $R^3 = CH_3O$.

Scheme 2.



A and **B** (Scheme 2) in which the aromatic ring is forced out from the methylenedioxane ring plane. Introduction of a substituent into the *ortho* position of the aromatic ring increases nonequivalence of the transition states, and structure **A** becomes more favorable. In fact, *ortho*-substituted dienophiles **III** and **IV** give rise mainly to adducts **XIII** and **XIV**. *para*-Substituents in the aromatic ring stabilize transition state **B**. It is also possible that in the pre-reaction state diene and dienophile form a transition complex stabilized by hydrogen bonding between the S=O oxygen atoms and substituents in the aromatic ring of the dienophile.

According to published data, the 1,3-dioxane ring in isopropylidene malonates undergoes decomposition with formation of both acetic and malonic acid derivatives [12–15]. Using adducts **IX** and **XI** as examples, we examined opening of the dioxodioxane ring by the action of various reagents. Preliminary deprotection by treatment with potassium hydroxide in methanol gave monomethyl ester **XXIII**. The same mode of the dioxane ring opening was observed in the reaction of compound **IX** with ammonia, which afforded amido acid **XXIV** (Scheme 3). The structure of product **XXIV** was established by X-ray analysis.

Figure 1 shows the structure of molecule **XXIV**. The bond lengths approach the corresponding standard values [16]; they coincide within 3σ with those found for (+)-3-benzyloxy-2,3,4,5,3a,7a-hexahydro-1-benzothiophen-5-one 1,1-dioxide [17] as the closest structural analog deposited to the Cambridge Structural Database [18]. The six-membered ring adopts a *sofa*

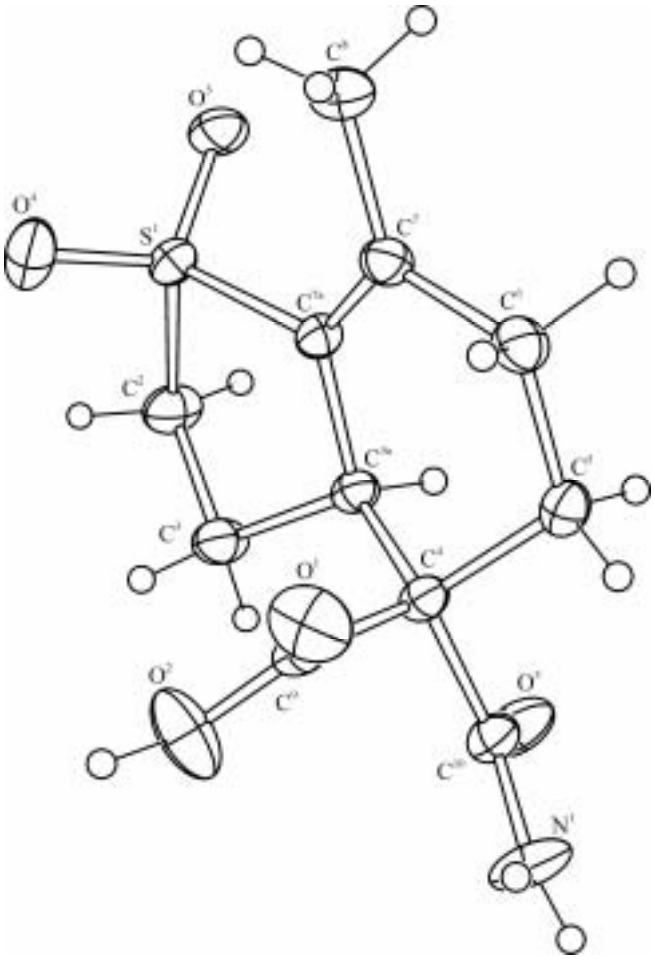


Fig. 1. Structure of the molecule of 4-carbamoyl-7-methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxylic acid 1,1-dioxide (**XXIV**) in crystal**.**

conformation [19] where five carbon atoms (C^5, C^6, C^7, C^{3a}, and C^{7a}) lie in one plane (the mean-square deviation from the plane is 0.019 Å) while the C^4 atom deviates from that plane by 0.688 Å. The sulfur-containing five-membered ring occurs in an *envelope* conformation with the C^3 atom deviating by 0.628 Å from the plane formed by the four remaining atoms.

Parameters of hydrogen bonds in the crystalline structure of amide **XXIV** solvate[a]

DH···A	D–H, Å	H···A, Å	D···A, Å	DH···A, deg
$O^2H\cdots O^{1R}$	0.97(4)	1.62(4)	2.574(3)	166(4)
$O^{1R}H\cdots O^3$	0.87(4)	1.87(4)	2.718(3)	165(4)
$N^1H^A\cdots O^1$	0.90(3)	2.07(3)	2.954(3)	166(3)
$N^1H^B\cdots O^5$	0.83(3)	2.22(3)	3.027(3)	163(3)

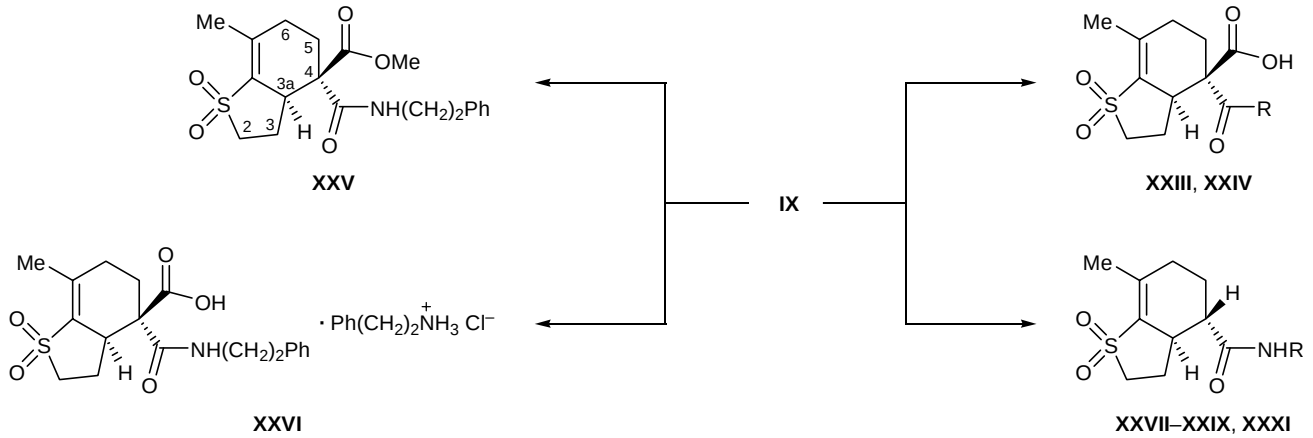
[a] O^{1R} is the oxygen atom in the solvent molecule.

The sulfur atom has a pyramidal configuration: the distances from the O^4 and O^5 atoms to the plane including the C^2, S^1, and C^{7a} atoms are –1.227 and 1.218 Å, respectively. The carboxy and carbamoyl groups are planar, and the dihedral angle between their planes is 79.4°. Molecules of **XXIV** in crystal are linked with solvent molecules by hydrogen bonds (see table), giving rise to layers oriented parallel to the (001) plane (Fig. 2).

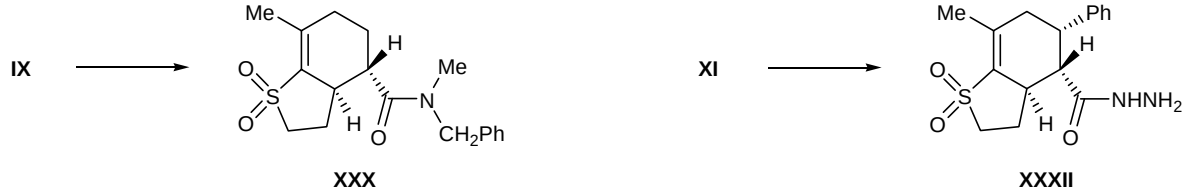
The results of reactions of compound **IX** with amines depend on the amine nature and conditions. The reaction with phenethylamine on heating to 40°C for a short time gave the corresponding amido acid. Methylation of the latter afforded amido ester **XXV**. Opening of the dioxane ring involves intermediate formation of phenethylammonium salt **XXVI** which was isolated as the corresponding hydrochloride. Less basic amines, such as 6-amino-4-hydroxy-2-methylpyrimidine and 2-aminobenzimidazole, reacted with compound **IX** in boiling DMF to give amides **XXVII** and **XXVIII**, respectively. By heating salt **XXVI** in DMF (10 h) we obtained decarboxylation product **XXIX**. The reaction of **IX** with *N*-methylbenzylamine under analogous conditions was also accompanied by decarboxylation leading to *N*-benzyl-*N*-methylamide **XXX** (Scheme 3). Treatment of spiro-dioxanediones **IX** and **XI** with hydrazine hydrate in boiling DMF resulted in formation of 2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carbohydrazide 1,1-dioxides **XXXI** and **XXXII** in high yield.

The structure of the products was determined on the basis of the spectral data. The structure of compound **IX** as the *ortho*-addition product unambiguously follows from its ^{1}H NMR spectrum and X-ray diffraction data for aminolysis product **XXIV**. Four protons at the C^5 and C^6 atoms give complex multiplet signals centered at δ 2.43, 2.33, 2.28, and 2.20 ppm. The 3a-H signal appears at δ 3.50 ppm as a multiplet due to coupling with protons on C^3. The structure of stereoisomeric aryl-substituted adducts **XI**–**XXII** was also deduced from the NMR data. Their configuration was determined by analysis of the vicinal coupling constants for protons at C^5 and C^6. Pseudoequatorial orientation of the aryl substituent in **XII**, **XIV**, **XVI**, **XVIII**, **XX**, and **XXII** follows from the axial–axial coupling constant between 5-H and 6-H ($J \approx 11$ Hz). The ^{1}H NMR spectra of the (5*S*) isomers are characterized by a considerably larger difference between the chemical shifts of the methyl protons in the isopropylidene fragment and by unusually upfield

Scheme 3.



XXIII, R = CH_3O; **XXIV**, R = NH_2; **XXVII**, R = 6-hydroxy-2-methylpyrimidin-4-yl; **XXVIII**, R = 2-benzimidazolyl; **XXIX**, R = $PhCH_2CH_2$; **XXXI**, R = NH_2.



position of one of these signals [cf. δ 0.68, 1.52 ppm (**XII**) and δ 1.62, 1.65 ppm (**XI**)]; this pattern is likely to arise from magnetically anisotropic effect of the phenyl ring. The 6-H and 3a-H signals in the spectra of the adducts with pseudoequatorial aryl substituent at C^5 are displaced downfield [cf. δ 3.62 (**XII**) and 3.31 ppm (**XI**)], and magnetic nonequivalence of the 6-H protons is stronger [cf. δ 2.60, 3.10 ppm (**XII**) and δ 2.66, 2.79 ppm (**XI**)]. The above differences in proton chemical shifts enabled us to estimate the ratio of diastereoisomeric adducts from the ^{1}H NMR spectra of the reaction mixtures. The ^{13}C NMR spectra of the stereoisomers differ by the chemical shifts of the doublet signals from C^5 and C^{3a}. The signals from the (5*R*) isomers are located in a stronger field.

In the IR spectra of the aminolysis products we observed absorption bands belonging to stretching vibrations of the amide carbonyl (ν 1628–1690 cm^{-1}) and N–H groups (ν 3348–3446 cm^{-1}). Ammonium salt **XXVI** showed in the IR spectrum absorption bands from the amide (1627 and 1674 cm^{-1}) and carboxylate groups (1747 cm^{-1}), bands typical of ammonium group (ν 2059, 2599, and 2726 cm^{-1}) [20], narrow bands at 3300 and 3458 cm^{-1} [ν(NH_2), ν(OH)], and bands corresponding to stretching vibrations of the sulfonyl group (ν 1120 and 1295 cm^{-1}). In the IR spectra of hydrazides **XXXI** and **XXXII**, the carbonyl absorption band is displaced to lower frequencies (ν 1628–1633 cm^{-1}), and vibrations of the NH–NH_2 group appear at 3430–3480 cm^{-1}.

The ^{1}H NMR spectrum of adduct **XXVI** contained signals from protons in the hexahydro-1-benzothiophene fragment, 10 aromatic protons, and protons of four methylene groups, the latter being located at δ, ppm: 3.36 m (1H), 3.30 m (1H, CH_2N), 3.00 m (CH_2N), 2.93 m (CH_2Ph), 2.74 t (CH_2Ph).

The *trans* arrangement of the substituents at C^{3a} and C^4 in amides **XXVII**–**XXX** follows from the ^{1}H NMR data, specifically from the vicinal coupling constants between 3a-H and 4-H (^3J = 10.2–11.4 Hz). Mutual orientation of the substituents on C^{3a}, C^4, and C^5 in molecule **XXXII** was confirmed by the NOESY spectrum: NOE was observed for the 3a-H signal while suppressing resonance of the 6-H proton (δ 2.33 ppm), as well as of the *ortho* protons in the aryl substituent at C^5. The 4-H signal showed NOE with the downfield 6-H proton (δ 2.76 ppm).

Thus cycloaddition of 5-arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-diones to 5-isopropenyl-2,3-dihydrothiophene 1,1-dioxide gives the corresponding spiro adducts which react with amines and hydrazine to afford derivatives of hexahydro-1-benzothiophene-4-mono- and 4,4-dicarboxylic acid 1,1-dioxides.

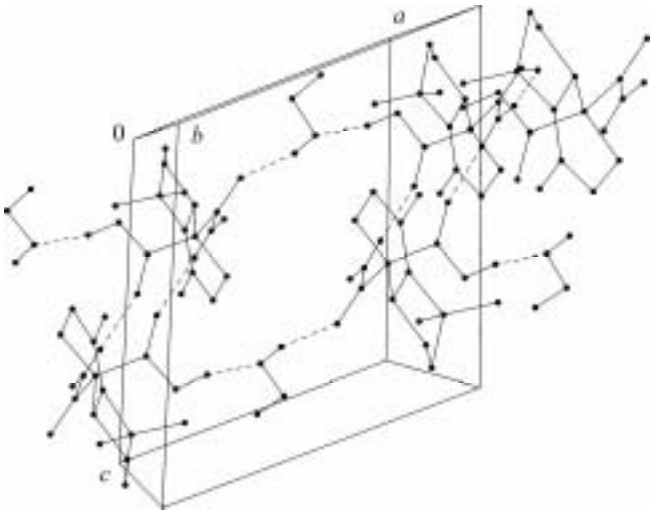


Fig. 2. Packing of molecules **XXIV** and solvent molecules in crystal along the *b* axis (hydrogen atoms are not shown, except for those in the NH_2 and OH groups).

EXPERIMENTAL

The IR spectra were recorded on a Vector-22 spectrometer from samples prepared as KBr pellets. The electron absorption spectra were measured on an HP 8453 UV Vis spectrophotometer from solutions in ethanol ($c = 10^{-4}$ M). The NMR spectra were obtained on Bruker AC-200 (200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C) and Bruker DRX-500 spectrometers (500.13 MHz for ^{1}H and 125.7 MHz for ^{13}C) from solutions in $CDCl_3$, CD_3OD, or DMSO-d_6. The signals were assigned using various proton–proton and carbon–proton shift correlation techniques (COSY, COLOC, CORRD) and ^{1}H 2D-NOESY spectroscopy. The mass spectra (electron impact, 70 eV) were run on a Finnigan MAT-8200 high-resolution mass spectrometer (vaporizer temperature 200–300°C). The melting points were determined on a Koefler device.

X-Ray diffraction experiment was performed on a Bruker P4 diffractometer (MoK_α-irradiation, graphite monochromator, $2\theta/\theta$ scanning to $2\theta < 50°$).

The progress of reactions was monitored by TLC on Silufol UV-254 plates. The products were isolated from the reaction mixtures by crystallization or by column chromatography on KSK silica gel (0–70 μm) using chloroform and chloroform–ethanol (100:1, 100:5, or 10:1) as eluents with subsequent recrystallization.

Meldrum's acid was synthesized by the procedure reported in [21].

5-Benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (II) was synthesized by the procedure described in [21]. Yield 72%, mp 84–85°C; published data [22]: mp 85°C. UV spectrum, λ_{max}, nm (logε): 227 (3.88), 264 (3.93), 321 (4.16). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.76 s (6H, $2CH_3$), 7.46 m (3H, Ph), 8.01 m (2H, Ph), 8.38 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 27.40 q ($2CH_3$), 104.33 s (C^2), 114.75 s (C^5), 128.50 d ($C^{2'}$, $C^{6'}$), 131.55 s ($C^{1'}$), 133.36 d ($C^{3'}$, $C^{4'}$, $C^{5'}$), 157.79 d (CH=), 159.47 s and 162.98 s (C=O).

5-Isopropenyl-2,3-dihydrothiophene 1,1-dioxide (**VIII**) was synthesized as described in [11], and diazomethane was prepared by known method [23].

5-Arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-diones (III–VI). To a solution of 2.30 g (16 mmol) of Meldrum's acid in 25 ml of benzene we added 24 mmol of the corresponding aldehyde, 0.10 ml of piperidine, and 0.30 ml of acetic acid. The mixture was heated under reflux in a flask equipped with a Dean–Stark trap until water no longer separated (~1 h). The solvent was distilled off under reduced pressure, and the residue was recrystallized from ethyl acetate.

5-(2-Methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (III). Yield 60%, mp 98–100°C; published data [20]: mp 100°C. IR spectrum, ν, cm^{-1}: 754, 801, 925, 1290, 1573, 1610 (C=C), 1027, 1163, 1192 (C–O–C), 1728, 1765 (C=O). UV spectrum, λ_{max}, nm (logε): 257 (3.94), 317 (3.85), 374 (3.83). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.77 s (6H, $2CH_3$), 3.85 s (3H, OCH_3), 6.92 m (2H, 5'-H, 6'-H), 7.45 d.t (1H, 3'-H, J = 7.8 Hz), 7.90 d.d (1H, 4'-H, J = 7.8, 8.1 Hz), 8.68 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 27.38 q ($2CH_3$), 55.54 q (OCH_3), 104.17 s (C^2), 110.93 d ($C^{3'}$), 115.44 s (C^5), 120.23 d ($C^{6'}$), 121.55 s ($C^{1'}$), 132.26 d ($C^{4'}$), 134.58 d ($C^{5'}$), 152.60 d (CH=), 159.42 s ($C^{2'}$), 159.50 s (C=O), 162.85 s (C=O).

5-(2,3-Dimethoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (IV). Yield 74%, yellow crystals, mp 98–100°C. IR spectrum, ν, cm^{-1}: 741, 797, 926, 974, 1574, 1590 (C=C), 1080 (C–O–C), 1204, 1265, 1727, 1763 (C=O). UV spectrum, λ_{max}, nm (logε): 204 (4.30), 259 (3.89), 330 (3.99). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.77 s (6H, $2CH_3$), 3.86 s (3H, 2'-OCH_3), 3.93 s (3H, 3'-OCH_3), 7.07 d (2H, 4'-H, 6'-H, J = 8.1, 8.2 Hz), 7.43 t (1H, 5'-H, J = 8.1, 8.2 Hz), 8.63 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 27.45 q ($2CH_3$), 55.90 q (OCH_3), 61.60 q (OCH_3), 104.34 s (C^2), 116.48 s (C^5), 117.08 d ($C^{4'}$), 123.01 d and 123.31 d ($C^{5'}$, $C^{6'}$), 126.26 s ($C^{1'}$), 149.74 s ($C^{2'}$), 152.27 s ($C^{3'}$), 152.96 d (CH=), 159.38 s (C=O),

162.62 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 292 (23), 234 (100), 203 (80), 162 (55). Found: $[M]^+$ 292.09445. $C_{15}H_{16}O_6$. Calculated: *M* 292.09468.

2,2-Dimethyl-5-(2,3,4-trimethoxybenzylidene)-1,3-dioxane-4,6-dione (V). Yield 82%, yellow crystals, mp 123–124°C. IR spectrum, ν, cm^{-1}: 796, 894, 957, 1586, 1615 (C=C), 1007, 1097 (C–O–C), 1199, 1286, 1724, 1760 (C=O). UV spectrum, λ_{max}, nm (logε): 205 (4.32), 256 (3.98), 375 (4.15). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.77 s (6H, $2CH_3$), 3.83 s (3H, 3'-OCH_3), 3.93 s and 3.98 s (3H each, 2'-OCH_3, 4'-OCH_3), 6.71 d (1H, 5'-H, *J* = 7.9 Hz), 8.16 d (1H, 6'-H, *J* = 7.9 Hz), 8.72 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 27.43 q ($2CH_3$), 56.14 q (OCH_3), 60.82 q (OCH_3), 61.99 q (OCH_3), 104.00 s (C^2), 106.85 d ($C^{5'}$), 112.28 s ($C^{1'}$), 119.00 s (C^5), 129.08 d ($C^{6'}$), 141.40 s ($C^{2'}$), 152.43 d (CH=), 155.91 s ($C^{3'}$), 159.11 s ($C^{4'}$), 160.39 s (C=O), 163.53 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 322 (18), 264 (51), 232 (100). Found: $[M]^+$ 322.10520. $C_{16}H_{18}O_7$. Calculated: *M* 322.10524.

5-(3-Hydroxy-4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (VI). Yield 75%, yellow crystals, mp 130–131°C. IR spectrum, ν, cm^{-1}: 798, 811, 928, 959, 974, 1507, 1574 (C=C); 1017, 1114 (C–O–C); 1160, 1283, 1718, 1750 (C=O), 3116 (OH). UV spectrum, λ_{max}, nm (logε): 204 (4.33), 261 (3.99), 380 (3.95), 391.0 (4.26). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.75 s (6H, $2CH_3$), 3.96 s (3H, OCH_3), 5.86 br.s (1H, OH), 6.90 d (1H, 6'-H, *J* = 7.5 Hz), 7.67 d.d (1H, 5'-H, *J* = 7.5, 1.8 Hz), 7.89 d (1H, 2-H, *J* = 1.8 Hz), 8.27 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 27.34 q ($2CH_3$), 56.06 q (OCH_3), 104.06 s (C^2), 110.19 d ($C^{2'}$), 111.56 d ($C^{6'}$), 119.50 s (C^5), 125.36 s ($C^{1'}$), 129.98 d ($C^{5'}$), 145.33 s ($C^{3'}$), 151.79 s ($C^{4'}$), 157.86 d (CH=), 160.08 s (C=O), 163.80 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 278 (30), 220 (76), 175 (100), 161 (78). Found: $[M]^+$ 278.07927. $C_{14}H_{14}O_6$. Calculated: *M* 278.07903.

2',2',7-Trimethyl-2,3,3a,4,5,6-hexahydrospiro-[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (IX). To a solution of 1.44 g (15 mmol) of Meldrum's acid in 20 ml of acetonitrile we added 0.01 g of L-proline and 20 ml of a 40% formaldehyde solution. The mixture was stirred for 5 min, and 1.58 g (10 mmol) of diene **VIII** was added in portions over a period of 20 min. The mixture was stirred for 2 h at room temperature and was poured into 20 ml of ice water. The precipitate was filtered off, washed with water, dried in air, and recrystallized from ethyl acetate. Yield 2.92 g (93%), mp 193–195°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 750, 1640 (C=C), 1131, 1292, 1312 (CO_2), 1681, 1732, 1772 (C=O). UV spectrum, λ_{max}, nm (logε): 207 (3.99). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.70 s (3H, CH_3), 1.73 s (3H, CH_3), 1.81 m (1H, 3-H), 2.10 d (3H, CH_3, *J* = 2.1 Hz), 2.15 m (1H, 3-H), 2.20 m (1H, 6-H), 2.28 m (1H, 6-H), 2.33 m (1H, 5-H), 2.43 m (1H, 5-H), 2.93 m (1H, 2-H), 3.13 m (1H, 2-H), 3.50 m (1H, 3a-H). ^{13}C NMR spectrum, δ_C, ppm: 17.85 q (4-CH_3), 22.16 t (C^3), 28.84 q (CH_3), 29.14 q (CH_3), 29.80 t (C^5), 30.94 t (C^6), 42.96 d (C^{3a}), 50.18 t (C^2), 50.67 s (C^4), 105.27 s ($C^{2'}$), 130.92 s (C^{7a}), 140.83 s (C^7), 164.15 s (C=O), 169.22 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 314 (5), 256 (25), 228 (41), 212 (36), 184 (33), 120 (94), 105 (45), 921 (44), 91 (100). Found: $[M]^+$ 314.08187. $C_{14}H_{18}O_6S$. Calculated: *M* 314.08240.

5-Aryl-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxides XI–XX (*general procedure*). A mixture of 9 mmol of 5-arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-dione **II**–**VI**, 1.42 g (9 mmol) of diene **VIII**, and 0.09 g of L-proline in aqueous benzene (10 ml + 1 ml) was heated for 24–40 h under reflux (TLC). The mixture was cooled, and the precipitate was filtered off and recrystallized from ethyl acetate to isolate compounds **XI**, **XIII**, **XV**, **XVII**, and **XIX**. The mother liquor was evaporated, and the residue was subjected to column chromatography. In the order of elution, we isolated unreacted dienophile **II**–**VI**, diene **VIII**, (5*R*) isomers **XI**, **XIII**, **XV**, **XVII**, and **XIX**, and (5*S*) isomers **XII**, **XIV**, **XVI**, **XVIII**, and **XX**. Compounds **XIV** (yield 5%, according to the ^{1}H NMR spectrum of a mixture of diastereoisomers) and **XVI** (yield 5%, according to the ^{1}H NMR spectrum of a mixture of diastereoisomers **XV** and **XVI**) were not isolated as individual products. The ^{1}H NMR data for compound **XVI** were obtained from the spectrum of diastereoisomer mixture **XV**/**XVI**.

(5'*R*)-2',2',7-Trimethyl-5-phenyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XI). Yield 60%, mp 165–168°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 702, 736, 1497 (Ph), 1125, 1294 (SO_2), 1678, 1725, 1746, 1780 (C=O). UV spectrum, λ_{max}, nm (logε): 258 (3.41). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62 s (3H, CH_3), 1.65 s (3H, CH_3), 2.09 m (2H, 3-H), 2.23 d (3H, CH_3, *J* = 2.9 Hz), 2.66 d.d.d (1H, 6-H, *J* = 18.0, 6.2, 4.4 Hz), 2.79 d.d.d (1H, 6-H, *J* = 18.0, 6.1, 1.8 Hz), 3.00 m (1H, 2-H), 3.23 m (1H,

2-H), 3.32 m (1H, 3a-H), 3.54 d.d (1H, 5-H, J = 6.1, 4.4 Hz), 7.10 m (2H, Ph), 7.30 m (3H, Ph). ^{13}C NMR spectrum, δ, ppm: 18.37 q (4-CH_3); 22.60 t (C^3); 27.86 q (CH_3); 30.33 q (CH_3); 36.22 t (C^6); 37.70 d (C^{3a}); 46.52 d (C^5); 50.65 t (C^2); 57.40 s (C^4); 105.87 s ($C^{2'}$); 132.04 s (C^{7a}); 137.48 s ($C^{1'}$); 128.97 d, 128.50 d, 127.97 d ($C^{2''}$, $C^{3''}$, $C^{4''}$, $C^{5''}$, $C^{6''}$); 140.53 s (C^7), 164.94 s (C=O), 166.36 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 390 (5), 332 (29), 314 (35), 304 (50), 287 (22), 250 (53), 235 (32), 225 (25), 222 (49), 196 (93), 195 (89), 181 (58), 118 (85), 91 (84), 31 (100). Found: $[M]^+$ 390.11290. $C_{20}H_{22}O_6S$. Calculated: *M* 390.11370.

(5*S*)-2',2',7-Trimethyl-5-phenyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XII). Yield 12%, mp 194–195°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 707, 896, 1498, 1602 (C=C_{arom}), 1133, 1291 (SO_2), 1680, 1726, 1759 (C=O). UV spectrum, λ_{max}, nm (logε): 206 (4.56), 280 (2.60). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.68 s (3H, CH_3), 1.52 (3H, CH_3), 1.85 m (1H, 3-H), 2.10 m (1H, 3-H), 2.21 d (3H, CH_3, J = 2.2 Hz), 2.60 d.d.d (1H, 6-H, J = 19.0, 6.0, 1.5 Hz), 2.98 m (1H, 2-H), 3.10 m (1H, 6-H, J = 19.0, 11.8 Hz), 3.20 m (1H, 2-H), 3.64 m (1H, 3a-H), 3.70 d.d (1H, 5-H, J = 11.8, 6.0 Hz), 7.20 m (2H, Ph), 7.30 (3H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 18.00 q (4-CH_3); 22.78 t (C^3); 28.36 q (CH_3); 29.58 q (CH_3); 36.89 t (C^6); 46.16 d (C^5); 46.36 d (C^{3a}); 50.71 t (C^2); 56.88 s (C^4); 106.04 s ($C^{2'}$); 127.99 d, 128.68 d, 129.00 d, 129.06 d ($C^{2''}$, $C^{3''}$, $C^{4''}$, $C^{5''}$, $C^{6''}$); 130.11 s (C^{7a}); 137.07 s ($C^{1'}$); 142.42 s (C^7); 163.15 s (C=O); 168.46 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 390 (15), 332 (60), 314 (62), 304 (33), 288 (47), 259 (34), 250 (92), 235 (42), 222 (43), 195 (65), 181 (46), 174 (46), 167 (47), 165 (64), 118 (92), 102 (56), 91 (80), 77 (40), 43 (100). Found: $[M]^+$ 390.113977. $C_{20}H_{22}O_6S$. Calculated: *M* 390.11370.

(5*R*)-5-(2-Methoxyphenyl)-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XIII). Yield 50.5%, mp 217–218°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 738, 756, 1491, 1600 (C=C_{arom}), 1117, 1132, 1298 (SO_2), 1738, 1774 (C=O). UV spectrum, λ_{max}, nm (logε): 220 (2.51), 276 (2.55), 283 (2.51). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.72 s (3H, CH_3), 1.97 m (1H, 3-H), 1.98 s (3H, CH_3), 2.02 m (1H, 3-H), 2.24 d (3H, CH_3, J = 2.8 Hz), 2.48 d.d.d (1H, 6-H, J = 19.0, 2.8, 2.0 Hz), 2.84 m (1H, 6-H, ^2J = 19.0 Hz), 2.9 m (1H, 2-H), 3.15 m (1H, 2-H), 3.31 m (1H, 3a-H), 3.74 s (3H, OCH_3), 4.10 d.d (1H, 5-H, J = 6.2, 2.8 Hz), 6.83 d.d (1H, 3"-H, J = 8.0, 1.5 Hz), 6.97 d.t (1H, 4"-H, J = 8.0, 1.8 Hz), 7.12 d.d (1H, 6"-H, J = 7.5, 1.8 Hz), 7.29 d.t (1H, 5"-H, J = 7.5, 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.96 q (4-CH_3), 21.66 t (C^3), 28.40 q (CH_3), 29.84 q (CH_3), 37.69 t (C^6), 37.74 d (C^{3a}), 39.00 d (C^5), 50.27 t (C^2), 54.63 q (OCH_3), 54.98 s (C^4), 105.35 s ($C^{2'}$), 110.22 d ($C^{3''}$), 121.45 d ($C^{5''}$), 126.45 s ($C^{1''}$), 127.23 d and 129.45 d ($C^{4''}$, $C^{5''}$), 131.64 s (C^{7a}), 140.57 s (C^7), 156.69 s ($C^{2''}$), 164.71 s (C=O), 165.20 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 420 (4), 289 (22), 148 (38), 108 (100). Found: $[M]^+$ 420.12191. $C_{21}H_{24}O_7S$. Calculated: *M* 420.12426.

(5*R*)-5-(2,3-Dimethoxyphenyl)-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XV). Yield 60%, mp 219–220°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 721, 759, 1482, 1584 (C=C_{arom}), 1133, 1289, 1310 (SO_2), 1737, 1774 (C=O). UV spectrum, λ_{max}, nm (logε): 203 (4.57), 281 (3.24). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.70 s (3H, CH_3), 1.86 m (1H, 3-H), 1.94 s (3H, CH_3), 2.05 m (1H, 3-H), 2.23 d (3H, CH_3, J = 2.9 Hz), 2.46 d.d (1H, 6-H, J = 18.4, 2.9, 2.0 Hz), 2.87 m (1H, 6-H, ^2J = 18.4 Hz), 2.93 m (1H, 2-H), 3.16 m (1H, 2-H), 3.40 m (1H, 3a-H), 3.81 s (3H, OCH_3), 3.82 s (3H, OCH_3), 4.02 d.d (1H, 5-H, J = 6.0, 2.9 Hz), 6.76 d.d (1H, 4"-H, J = 8.0, 2.0 Hz), 6.88 d.d (1H, 6"-H, J = 8.0, 2.0 Hz), 7.03 t (1H, 5"-H, J = 8.0). ^{13}C NMR spectrum, δ_C, ppm: 17.97 q (4-CH_3), 21.55 t (C^3), 28.39 q (CH_3), 29.74 q (CH_3), 37.48 d (C^{3a}), 37.59 t (C^6), 39.96 d (C^5), 50.16 t (C^2), 54.96 s (C^4), 55.61 q (OCH_3), 60.19 q (OCH_3), 105.34 s ($C^{2'}$), 112.48 d ($C^{4''}$), 118.78 d ($C^{5''}$), 124.37 d ($C^{6'}$), 131.51 s (C^{7a}), 132.04 s ($C^{1'}$), 140.59 s (C^7), 146.79 s ($C^{2''}$), 151.82 s ($C^{3''}$), 164.64 s (C=O), 165.16 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 450 (2), 364 (4), 319 (16), 138 (100). Found: M^+ 450.13479. $C_{22}H_{26}O_8S$. Calculated; *M* 450.13483.

(5*S*)-5-(2,3-Dimethoxyphenyl)-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XVI). Yield 5%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.09 s (3H, CH_3), 1.56 s (3H, CH_3), 1.75 m (1H, 3-H), 1.98 m (1H, 3-H), 2.16 d (3H, CH_3, J = 2.9 Hz), 2.50 m (1H, 6-H, ^2J = 19.0 Hz), 2.88 m (1H, 2-H), 3.12 m (1H, 6-H), 3.20 m (1H, 2-H), 3.67 m (1H, 3a-H), 3.70 m (1H, 5-H, J = 11.5, 6.0 Hz), 3.85 s (3H, OCH_3), 3.87 s (3H, OCH_3), 6.78 d.d (1H, 4"-H, J = 7.8, 1.8 Hz), 6.90 d.d (1H, 6"-H, J = 7.8, 1.8 Hz), 7.05 t (1H, 5"-H, J = 7.8 Hz).

(5*R*)-2',2',7-Trimethyl-5-(2,3,4-trimethoxyphenyl)-2,3,3a,4,5,6-hexahydrospiro[1-benzothio-

phene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XVII). Yield 58%, mp 202–204°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 720, 748, 1498, 1600 (C=C_{arom}), 1098, 1119, 1290 (SO_2), 1736, 1774 (C=O). UV spectrum, λ_{max}, nm (logε): 205 (4.60), 270 (3.20), 285 (3.42). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.71 s (3H, CH_3), 1.87 m (1H, 3-H), 1.94 s (3H, CH_3), 2.04 m (1H, 3-H), 2.22 d (3H, CH_3, *J* = 2.2 Hz), 2.43 d.d.d (1H, 6-H, *J* = 18.8, 2.8, 1.6 Hz), 2.85 m (1H, 6-H, ^2J = 18.8 Hz), 2.92 m (1H, 2-H), 3.16 (1H, 2-H), 3.34 m (1H, 3a-H), 3.78 s (3H, OCH_3), 3.83 s (3H, OCH_3), 3.88 s (3H, OCH_3), 3.94 d.d (1H, 5-H, *J* = 6.2, 2.8 Hz), 6.63 d (1H, 5"-H, *J* 7.2 Hz), 6.82 d (1H, 6"-H, *J* = 7.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.85 q (4-CH_3); 21.39 t (C^3); 28.27 q (CH_3); 29.75 q (CH_3); 37.67 d (C^5); 37.70 t (C^6); 38.73 d (C^{3a}); 50.14 t (C^2); 55.20 s (C^4); 55.65 q (OCH_3); 60.23 q and 60.48 q (OCH_3); 105.21 s ($C^{2'}$); 106.95 d ($C^{5"}$); 121.52 d ($C^{6"}$); 123.14 s ($C^{1"}$); 132.03 s (C^{7a}); 140.43 s (C^7); 151.44 s and 153.68 s ($C^{2"}$, $C^{3"}$, $C^{4"}$); 164.56 s (C=O); 165.27 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 480 (15), 337 (28), 195 (24), 168 (100). Found: $[M]^+$ 480.14680. $C_{23}H_{28}O_9S$. Calculated: *M* 480.14539.

(5*S*)-2',2',7-Trimethyl-5-(2,3,4-trimethoxyphenyl)-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XVIII). Yield 13%, mp 169–170°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 727, 770, 1516, 1611 (C=C_{arom}), 1133, 1280, 1288, 1300, 1331 (SO_2), 1730, 1763 (C=O). UV spectrum, λ_{max}, nm (logε): 279 (3.31). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.57 s (3H, CH_3), 1.84 s (3H, CH_3), 1.87 m (1H, 3-H), 2.16 d (3H, CH_3, *J* = 2.5 Hz), 2.19 m (1H, 3-H), 2.42 d.d.d (1H, 6-H, *J* = 18.6, 3.2, 2.0 Hz), 2.8 m (1H, 2-H), 3.02 m (1H, 6-H), 3.22 m (1H, 2-H), 3.76 m (1H, 3a-H), 3.86 m (1H, 5-H), 3.78 s (3H, OCH_3), 3.80 s (3H, OCH_3), 3.87 s (3H, OCH_3), 6.58 d (1H, 5"-H), 6.83 d (1H, 6"-H); in DMSO-d_6: 1.12 s (3H, CH_3), 1.59 s (3H, CH_3), 1.65 m (1H, 3-H), 2.05 d (3H, CH_3, *J* = 2.5 Hz), 2.21 m (1H, 3-H), 2.49 m (1H, 6-H), 2.52 m (1H, 2-H), 2.70 m (1H, 2-H), 3.20 m (1H, 6-H), 3.70 m (1H, 3a-H), 3.73 s (3H, OCH_3), 3.78 s (3H, OCH_3), 3.79 (3H, OCH_3), 4.03 d.d. (1H, 5-H, *J* = 11.6, 6.1 Hz), 6.68 s (2H, 5"-H, 6"-H). ^{13}C NMR spectrum, δ_C, ppm: 17.95 q (4-CH_3), 22.72 t (C^3); 28.32 q (CH_3); 30.39 q (CH_3); 38.20 t (C^6); 45.26 d (C^5); 45.34 d (C^{3a}); 50.81 t (C^2); 55.78 s (C^4); 55.90 q (OCH_3); 60.54 q (OCH_3); 61.37 q (OCH_3); 105.76 s ($C^{2'}$); 106.75 d ($C^{5"}$); 122.00 d ($C^{6"}$); 130.46 s (C^{7a}, $C^{1"}$); 130.49 s, 152.21 s, 153.75 s ($C^{2"}$, $C^{3"}$, $C^{4"}$); 141.92 s (C^7); 163.90 s (C=O); 167.95 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 480 (24), 422 (51), 208 (35), 195 (68), 192 (24), 168 (100), 59 (26), 43 (36). Found: $[M]^+$: 480.14571. $C_{23}H_{28}O_9S$. Calculated: *M* 480.14539.

(5*R*)-5-(3-Hydroxy-4-methoxyphenyl)-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XIX). Yield 30%, mp 186–188°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 736, 767, 1512, 1590 (C=C_{arom}), 1120, 1297 (SO_2), 1743, 1774 (C=O), 3456 (OH). UV spectrum, λ_{max}, nm (logε): 206 (4.39), 283 (3.54). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.65 s (3H, CH_3), 1.67 s (3H, CH_3), 2.07 m (2H, 3-H), 2.21 d (3H, CH_3, *J* = 2.9 Hz), 2.69 m (1H, 6-H, ^2J = 18.8 Hz), 2.98 d.d.d (1H, 6-H, *J* = 18.8, 6.2, 2.6 Hz), 3.04 m (1H, 2-H), 3.21 m (1H, 2-H), 3.35 m (1H, 3a-H), 5.46 d.d (1H, 5-H, *J* = 6.2, 4.2 Hz), 3.85 s (3H, OCH_3), 5.60 s (1H, OH), 6.61 d.d (1H, 6"-H, *J* = 7.8, 2.0 Hz), 6.68 d.d. (1H, 2"-H, *J* = 2.0 Hz), 6.77 d (1H, 5"-H, *J* = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.37 q (4-CH_3), 22.54 t (C^3), 28.04 q (CH_3), 30.42 q (CH_3), 36.70 t (C^6), 37.65 d (C^{3a}), 46.25 d (C^5), 50.74 t (C^2), 56.00 q (OCH_3), 57.75 s (C^4), 105.90 s ($C^{2'}$), 110.91 d ($C^{5"}$), 114.41 d ($C^{2"}$), 119.64 d ($C^{6"}$) 130.71 s (C^{7a}), 132.11 s ($C^{1'}$), 140.38 s (C^7), 145.83 s, 146.65 s ($C^{3"}$, $C^{4"}$), 165.06 s (C=O), 166.37 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 436 (3), 350 (14), 149 (16), 86 (76), 84 (100). Found: $[M]^+$ 436.11909. $C_{21}H_{24}O_8S$. Calculated: *M* 436.11918.

(5*S*)-5-(3-Hydroxy-4-methoxyphenyl)-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XX). Yield 30%, mp 207–209°C (from ethyl acetate). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.83 s (3H, CH_3), 1.56 s (3H, CH_3), 1.83 m (1H, 3-H), 2.16 m (1H, 3-H), 2.21 d.d (3H, CH_3, *J* = 2.8 Hz), 2.52 d.d.d (1H, 6-H, *J* = 18.6, 5.8, 2.0 Hz), 2.98 m (1H, 2-H), 3.02 d.d.d (1H, 6-H, *J* = 18.6, 11.8, 3.8 Hz), 3.20 m (1H, 2-H), 3.61 d.d (1H, 5-H, *J* = 11.8, 5.8 Hz), 3.63 m (1H, 3a-H), 3.85 s (3H, OCH_3), 6.68 d.d (1H, 4"-H, *J* = 8.0, 2.0 Hz), 6.75 d (1H, 5"-H, *J* = 8.0 Hz), 6.78 d (1H, 2"-H, *J* = 2.0 Hz), 5.6 br.s (1H, OH, halfwidth 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.05 q (4-CH_3), 22.82 t (C^3), 28.75 q (CH_3), 29.55 q (CH_3), 37.34 t (C^6), 45.74 d (C^{3a}), 46.51 d (C^5), 50.76 t (C^2), 55.89 q (OCH_3), 56.98 s (C^4), 105.88 ($C^{2'}$), 110.68 d ($C^{5"}$), 114.89 d ($C^{2"}$), 120.82 d ($C^{6"}$), 130.15 s and 130.36 s (C^{7a}, $C^{1"}$), 142.47 (C^7), 145.99 s and 146.58 s ($C^{2"}$, $C^{3"}$), 163.13 s (C=O), 168.49 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 436 (57), 378 (72), 350 (38), 334 (25), 333 (31), 322 (22). Found: $[M]^+$ 436.11916. $C_{21}H_{24}O_8S$. Calculated: *M* 436.11918.

(5'*R*)- and (5*S*)-5-(4-Methoxyphenyl)-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxides XXI and XXII. Cetyltrimethylammonium bromide, 0.54 g, and L-proline, 0.15 g, were added to a solution of 2.04 g (15 mmol) of 4-methoxybenzaldehyde, 0.87 g (6 mmol) of Meldrum's acid, and 0.95 g (6 mmol) of diene **VIII** in 30 ml of distilled water. The mixture was stirred for 24 h at 20°C, heated for 36 h under reflux, and extracted with chloroform. The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography to isolate (in the order of elution) 1.70 g of 4-methoxybenzaldehyde, 0.66 g of dienophile **VII** [23], 0.06 g of diene **VIII**, 0.37 g (14.7%) of adduct **XXI**, and 1.27 g (50.04%) of adduct **XXII**. The ratio **XXI**:**XXII** was 0.22:1.0. Compound **XXI** was not isolated in the pure state. ^{1}H NMR spectrum of **XXI** ($CDCl_3$), δ, ppm (from the spectrum of a mixture with **XXII**): 1.65 s (6H, $2CH_3$), 2.10 m (2H, 3-H), 2.23 d (3H, CH_3, J = 2.8 Hz), 2.58 d.d (1H, 6-H, J = 19.0, 6.2 Hz), 2.70 m (1H, 6-H), 3.0 m (1H, 2-H), 3.22 m (2H, 2-H, 3a-H), 3.52 d.d (1H, 5-H, J = 6.2, 4.3 Hz), 3.75 s (3H, OCH_3), 6.81 d (2H, 3"-H, 5"-H, J = 8.0 Hz), 7.18 d (2H, 2"-H, 6"-H, J = 8.0 Hz).

(5*S*)-5-(4-Methoxyphenyl)-2',2',7-trimethyl-2,3,3a,4,5,6-hexahydrospiro[1-benzothiophene-4,5'-[1,3]dioxane]-4',6'-dione 1,1-dioxide (XXII). mp 240–241°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 727, 770, 1516, 1611 ($C{=}C_{arom}$), 1133, 1280, 1288, 1300, 1331 (SO_2), 1730, 1763 (C=O). UV spectrum, λ_{max}, nm (logε): 224 (4.12), 277 (3.22), 282 (3.35). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.76 s (3H, CH_3), 1.54 s (3H, CH_3), 1.82 m (1H, 3-H), 2.16 m (1H, 3-H), 2.20 d (3H, CH_3, J = 2.8 Hz), 2.52 d.d.d (1H, 6-H, J = 18.8, 6.2, 1.8 Hz), 3.0 m (2H, 2-H, 6-H), 3.20 m (1H, 2-H), 3.63 m (1H, 3a-H), 3.66 d.d (1H, 5-H, J = 11.8, 6.2 Hz), 3,74 s (3H, OCH_3), 6.81 d (2H, 3"-H, 5"-H, J = 7.8 Hz), 7.12 d (2H, 2"-H, 6"-H, J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.93 q (4-CH_3), 22.81 t (C^3), 28.56 q (CH_3), 29.55 q (CH_3), 37.22 t (C^6), 45.71 d (C^{3a}), 46.17 d (C^5), 50.76 t (C^2), 55.21 q (OCH_3), 57.15 s (C^4), 105.97 s ($C^{2'}$), 114.33 d ($C^{3"}$, $C^{5"}$), 129.08 s ($C^{1"}$), 130.03 s ($C^{2"}$, $C^{6"}$), 130.17 s (C^{7a}), 142.44 s (C^7), 159.72 c ($C^{4"}$), 168.59 s (C=O), 163.26 s (C=O). Mass spectrum, m/z (I_{rel}, %): 420 (12), 362 (100), 277 (28), 226 (64), 148 (69), 135 (38). Found: $[M]^+$ 420.12399. $C_{21}H_{24}O_7S$. Calculated: M 420.12426.

4-Methoxycarbonyl-7-methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxylic acid 1,1-dioxide (XXIII). Adduct **IX**, 0.63 g (2 mmol), was added under stirring to a solution of 0.011 g (0.2 mmol) of potassium hydroxide in 20 ml of methanol. The mixture was stirred for 7 h at 20°C and evaporated, 0.1 ml of dilute (1:1) hydrochloric acid and 5 ml of methanol were added to the residue, and the precipitate was filtered off and recrystallized from methanol. Yield 0.51 g (52%), mp 160–163°C. UV spectrum, λ_{max}, nm (logε): 209 (4.01), 275 (2.28), 288 (2.30). IR spectrum, ν, cm^{-1}: 1128, 1287 (SO_2); 1715, 1732 (CO); 3200, 3480 (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.88 m (1H, 3-H), 2.06 d (3H, CH_3, J = 2.8), 2.40 m (4H, 3-H, 5-H, 6-H), 2.95 m (1H, 2-H), 3.20 m (3H, 2-H, 3a-H, 6-H), 3.78 s (3H, OCH_3), 8.1 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 17.81 q (CH_3), 22.51 t (C^3), 28.95 t and 29.96 t (C^5, C^6), 41.29 d (C^{3a}), 50.68 t (C^2), 52.91 q (CH_3), 55.33 s (C^4), 131.72 s (C^{7a}), 141.47 s (C^7), 170.60 s (CO), 171.31 s (CO). Mass spectrum, m/z (I_{rel}, %): 288 (1), 242 (6), 184 (16), 119 (17), 91 (20), 84 (100). Found: $[M]^+$ 288.06713. $C_{12}H_{16}O_6S$. Calculated: M 288.06675.

4-Carbamoyl-7-methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxylic acid 1,1-dioxide (XXIV). Aqueous ammonia, 15 ml, was added dropwise over a period of 10 min to a solution of 0.63 g (2 mmol) of adduct **IX** in 13 ml of dioxane. The mixture was stirred for 7 h at 20°C, the solvent was removed under reduced pressure, 5 ml of water was added to the residue, and the solution was acidified with 6 N hydrochloric acid to pH ≈ 2. The precipitate was filtered off to obtain 0.04 g of compound **XXIV**. The filtrate was evaporated, and the residue was dried by azeotropic distillation with isopropyl alcohol and dissolved in ethanol. The precipitate was filtered off. Yield 0.45 g (83%), mp 198–201°C. IR spectrum, ν, cm^{-1}: 1118, 1122, 1275, 1292 (SO_2); 1639, 1673, 1718 (C=O); 2970, 3147, 3446 (NH_2, OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.03 m (1H, 5-H), 2.05 d (3H, CH_3, J = 2.2 Hz), 2.40 m (3H, 3-H, 6-H), 2.52 m (2H, 3a-H, 6-H), 2.95 m (1H, 2-H), 3.19 s (1H, 2-H), 3.35 m (1H, 5-H), 6.06 br.s and 6.82 br.s (NH, OH). ^{13}C NMR spectrum, δ_C, ppm: 17.86 q (CH_3), 21.91 t (C^3), 30.61 t (C^5), 32.14 t (C^6), 41.13 d (C^{3a}), 50.65 t (C^2), 55.77 s (C^4), 132.46 s (C^{7a}), 140.16 s (C^7), 171.91 s (C=O), 172.61 s (C=O). Mass spectrum, m/z (I_{rel}, %): 257 $[M - 16]^+$ (2), 229 (23), 184 (100), 119 (36), 105 (49), 91 (48).

Methyl 7-methyl-4-phenethylcarbamoyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxylate 1,1-dioxide (XXV). Adduct **IX**, 0.31 g (1 mmol), was dissolved in 1 ml of phenethylamine, and the solution

was heated for 3 h at 40°C and was then diluted with 0.5 ml of cold 10% hydrochloric acid. The aqueous phase was extracted with chloroform, the extract was dried over $MgSO_4$ and evaporated, and the oily residue was treated with a saturated solution of diazomethane in diethyl ether. When the reaction was complete (nitrogen no longer evolved), the mixture was evaporated, and the residue was purified by column chromatography on silica gel. Yield 0.20 g (50%). IR spectrum, ν, cm^{-1}: 702, 752, 1498, 1600 ($C=C_{arom}$); 1127, 1291 (SO_2); 1532, 1657, 1740 (C=O); 3375, 3500 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.88 m (1H, 6-H), 1.93 d (3H, CH_3, J = 2.1 Hz), 2.15 m (4H, 3-H, 6-H, 3a-H), 2.30 m (1H, 5-H), 2.74 t (2H, CH_2, J = 7.2 Hz), 2.79 m (1H, 2-H), 3.05 m (1H, 2-H), 3.14 m (1H, 5-H), 3.46 m (2H, CH_2), 3.57 s (3H, OCH_3), 6.59 t (1H, NH), 7.09 m (2H, Ph), 7.13 m (1H, Ph), 7.21 m (2H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 17.42 q (CH_3), 21.67 t (C^3), 30.23 t (CH_2), 31.14 t (C^6), 34.74 (C^5), 40.57 t (CH_2), 41.14 d (C^{3a}), 50.34 (C^2), 52.34 q (OCH_3), 55.89 s (C^4), 126.17 d ($C^{4'}$), 128.18 d and 128.34 d ($C^{2'}$, $C^{3'}$, $C^{5'}$, $C^{6'}$), 132.44 (C^{7a}), 138.04 s ($C^{1'}$), 139.29 (C^7), 168.44 s (C=O), 170.74 s (C=O). Mass spectrum, m/z (I_{rel}, %): 391 (100), 332 (89), 243 (30), 211 (74), 105 (52), 91 (44). Found: $[M]^+$ 391.14547. $C_{20}H_{25}NO_5$. Calculated: M 391.14533.

Phenethylammonium hydrochloride–7-methyl-4-phenethylcarbamoyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxylic acid 1,1-dioxide (XXVI). A mixture of 1.13 g (3.6 mmol) of adduct **IX** and 4 ml of phenethylamine was heated for 3 h at 40°C, 0.5 ml of cold 10% hydrochloric acid was added, and the aqueous phase was extracted with chloroform. The combined extracts were dried over $MgSO_4$ and evaporated, the residue was treated with a saturated solution of hydrogen chloride in ether, and the precipitate was filtered off. Yield 1.23 g (83%), mp 142–144°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 745, 940, 1498, 1602 ($C=C_{arom}$); 1120, 1295 (SO_2); 1674, 1747 (C=O); 2059 (NH_3^+); 1627, 2525, 2599, 2726, 3300, 3458 (NH_2). UV spectrum, λ_{max}, nm (log ε): 207 (3.29), 252 (2.08), 258 (2.08), 264 (2.04). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.83 m (1H, 6-H), 1.89 d (3H, CH_3, J = 2.4 Hz), 2.03 m (1H, 3-H), 2.17 m (1H, 6-H), 2.21 m (2H, 6-H, 5-H), 2.32 m (1H, 3a-H), 2.73 t (2H, CH_2, J = 7.2 Hz), 2.87 m (1H, 2-H), 2.92 m (1H, 5-H), 2.93 m (2H, CH_2), 3.00 m (2H, CH_2), 3.12 m (1H, 2-H), 3.30 m, 3.37 m (2H, CH_2), 7.16 m (3H, Ph), 7.26 m (5H, Ph), 7.30 m (2H, Ph), 7.88 br.s and 8.22 br.s (NH, NH_2, OH). ^{13}C NMR spectrum, δ_C, ppm: 17.50 q (CH_3); 22.17 t (C^3); 29.45 t (CH_2); 30.19 t (CH_2); 32.97 t (C^6); 34.85 t (CH_2); 40.60 t (CH_2); 41.26 d (C^{3a}); 50.61 t (C^2); 55.74 s (C^4); 126.11 d, 126.76 d ($C^{4''}$); 128.31 d, 128.66 d, 128.68 d, 128.72 d, 128.73 d, 128.74 d, 128.78 d, 128.79 d ($C^{2'}$, $C^{3'}$, $C^{5'}$, $C^{6'}$); 133.27 s (C^7); 137.45 s (C^3); 138.94 s, 139.39 s (C^1, C^{7a}); 169.73 s (C=O); 171.04 s (C=O). Found, %: C 59.9; H 6.7; Cl 6.6; N 4.5; S 7.4. $C_{25}H_{33}N_2O_5S \cdot HCl$. Calculated, %: C 58.9; H 6.7; Cl 6.9; N 5.5; S 6.3.

***N*-(6-Hydroxy-2-methylpyrimidin-4-yl)-7-methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxamide 1,1-dioxide (XXVII).** A solution of 0.94 g (3 mmol) of adduct **IX** and 0.41 g (3.6 mmol) of 4-amino-6-hydroxy-2-methylpyrimidine in 10 ml of DMF was heated for 14 h at 130°C (TLC). The mixture was cooled, and the precipitate, 0.70 g, was filtered off. The filtrate was evaporated, the residue was dissolved in ethyl acetate, the solution was cooled, and an additional portion of amide **XXVII**, 0.22 g, was filtered off. Overall yield 91%, mp 152–154°C. IR spectrum, ν, cm^{-1}: 806, 1457, 1500, 1610, 1629 (C=C); 1125, 1285 (SO_2); 1629, 3167, 3349, 3505 (C–N, OH); 1680 (CO). UV spectrum, λ_{max}, nm (log ε): 211 (4.33), 259 (3.80). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.72 m (2H, 3-H, 5-H), 2.10 s (3H, CH_3), 2.15 m (1H, 4-H, J = 2.0, 10.2 Hz), 2.31 m (3H, 3-H, 5-H, 6-H), 2.51 m (1H, 6-H), 2.87 m (1H, 3a-H, $J_{3a,4}$ = 10.2 Hz), 2.99 m (1H, 2-H), 3.20 m (1H, 2-H), 6.12 s (1H, 5'-H), 7.4 br.s and 9.6 br.s (2H, OH, NH). ^{13}C NMR spectrum, δ_C, ppm: 17.82 q (CH_3), 20.86 q (CH_3), 26.15 t and 26.16 t (C^3, C^5), 31.86 t (C^6), 43.67 d and 46.99 d (C^{3a}, C^4), 50.94 t (C^2), 82.87 d ($C^{5'}$), 135.42 s (C^{7a}), 140.00 s (C^7), 156.13 s and 158.76 s ($C^{2'}$, $C^{6'}$), 163.34 s and 168.20 s ($C^{4'}$, C=O). Mass spectrum, m/z (I_{rel}, %): 184 $[M - 153]^+$ (53), 125 (100), 105 (32), 97 (46), 68 (49), 42 (64).

***N*-(2-Benzimidazolyl)-7-methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxamide 1,1-dioxide (XXVIII).** A solution of 0.94 g (3 mmol) of adduct **IX** and 0.48 g (3.6 mmol) of 2-aminobenzimidazole in 10 ml of DMF was heated for 14 h at 130°C (TLC). The mixture was cooled, and 0.12 g of compound **XXVIII** was filtered off. The filtrate was evaporated, the residue was dissolved in ethyl acetate, the solution was cooled, and an additional portion of amide **XXVIII**, 0.81 g, was filtered off. Overall yield 89%. IR spectrum, ν, cm^{-1}: 699, 719, 779, 1500, 1552 (C=C, C=N); 1651, 1667 (C=O, C=N); 2366, 2604, 2734, 3449, 3500 (NH). UV spectrum, λ_{max}, nm (log ε): 206 (4.21), 251 (2.50), 257 (2.59), 262 (2.50), 268

(2.44). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.68 m (1H, 3-H), 1.86 m (2H, 5-H, 6-H), 1.97 d (3H, CH_3, J = 2.9 Hz), 2.0–2.6 m (5H, 3a-H, 3-H, 4-H, 5-H, 6-H), 3.0–3.5 m (2H, 2-H), 5.8 br.s (2H, NH), 7.02–7.12 m (2H, 4'-H, 7'-H), 7.36–7.46 m (2H, 5'-H, 6-H). ^{13}C NMR spectrum, δ_C, ppm: 17.62 q (CH_3), 25.30 t (C^3), 25.98 t (C^5), 28.17 t (C^6), 36.28 d, 45.88 d (C^{3a}, C^4), 50.76 t (C^2), 121.17 d ($C^{5'}$, $C^{6'}$), 124.88 s and 126.61 s ($C^{3a'}$, $C^{7a'}$), 128.54 d and 129.66 d ($C^{4'}$, $C^{7'}$), 134.64 s (C^{7a}), 140.28 s (C^7), 146.34 s ($C^{2'}$), 173.29 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 345 (7), 184 (28), 160 (27), 134 (24), 133 (100), 105 (41), 91 (43), 77 (30). Found: $[M]^+$ 345.11701. $C_{17}H_{19}N_3O_3S$. Calculated: *M* 345.11470.

***N*-Phenethyl-7-methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxamide 1,1-dioxide (XXIX).** A mixture of 0.59 g (1.2 mmol) of hydrochloride **XXVI** and 5 ml of DMF was heated for 12 h at 160°C. The solvent was distilled off under reduced pressure, and the residue was subjected to column chromatography to isolate 0.18 g (53%) of compound **XXIX**, mp 144–146°C (from diethyl ether). IR spectrum, ν, cm^{-1}: 720, 725, 753 (Ph); 1126, 1298 (SO_2); 1549, 1658, 1666 (CONH); 3312, 3352, 3385 (NH). UV spectrum, λ_{max}, nm (logε): 253 (2.20), 259 (2.30). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.52 m (1H, 3-H), 1.80 m (3H, 3-H, 5-H), 2.05 d (3H, CH_3), 2.20 m (2H, 4-H, 6-H), 2.83 m (3H, CH_2, 6-H), 2.92 m (1H, 2-H), 3.06 m (1H, 2-H), 3.55 m (3H, CH_2, 3a-H), 7.20 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 18.08 q (CH_3); 25.04 t (C^3); 25.51 t (CH_2); 31.95 t (C^6); 35.45 t (C^5); 39.54 d (C^{3a}); 40.30 t (CH_2); 47.34 s (C^4); 50.92 t (C^2); 126.47 d, 128.52 d, 128.57 d ($C^{2'}$, $C^{3'}$, $C^{5'}$, $C^{6'}$); 134.57 s (C^{7a}); 138.46 s ($C^{4'}$); 140.86 s (C^7); 172.68 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 333 (43), 185 (32), 119 (26), 105 (100), 93 (25), 79 (38), 77 (39), 55 (32). Found: $[M]^+$ 333.13920. $C_{18}H_{23}NO_3S$. Calculated: *M* 333.13985.

***N*-Benzyl-7,*N*-dimethyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carboxamide 1,1-dioxide (XXX).** A mixture of 0.63 g (2 mmol) of adduct **IX** and 1.8 ml of *N*-methylbenzylamine was heated for 9 h at 100°C. The mixture was cooled, 5 ml of diethyl ether was added, and the precipitate was filtered off and recrystallized from ethyl acetate. Yield 0.51 g (76%), mp 153–155°C. IR spectrum, ν, cm^{-1}: 726, 749, 1517 (Ar); 1126, 1138, 1287 (SO_2); 1577, 1634, 1691 (CO). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.47 m (2H, 3-H, 5-H), 1.90 m (1H, 4-H), 1.93 d (3H, CH_3, J = 2.9 Hz), 1.95 m (1H, 5-H), 2.18 m (2H, 6-H), 2.33 m (1H, 3-H), 2.40 s (3H, CH_3), 2.66 m (1H, 3a-H, $J_{3a,4}$ = 11.5 Hz), 2.95 (1H, 2-H), 3.12 m (1H, 2-H), 3.92 s (2H, CH_2), 7.31 (3H, Ph), 7.43 m (2H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 17.84 q (CH_3), 26.19 t (C^3, C^5), 31.91 t (C^6), 32.84 q (NCH_3), 40.01 d (C^{3a}), 47.35 d (C^4), 50.95 t (C^2), 52.28 t (CH_2), 128.09 d ($C^{4'}$), 128.49 d and 129.34 d ($C^{2'}$, $C^{3'}$, $C^{5'}$, $C^{6'}$), 134.97 s and 135.50 s ($C^{1'}$, C^{7a}), 139.93 s (C^7), 176.92 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 333 (0.5), 230 (12), 184 (100), 120 (36), 93 (59), 105 (46). Found: $[M]^+$ 333.13920. $C_{18}H_{23}NO_3S$. Calculated: *M* 333.13985.

7-Methyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carbohydrazide 1,1-dioxide (XXXI). Hydrazine hydrate, 1.5 ml, was added to a solution of 0.63 g (2 mmol) of compound **IX** in 5 ml of DMF, and the mixture was heated for 12 h under reflux. The solvent was distilled off under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.42 g (86%), mp 260–261°C. IR spectrum, ν, cm^{-1}: 702, 733, 1500, 1580 (C=C); 1119, 1120, 1287 (SO_2); 1554, 3438, 3486 ($NHNH_2$); 1660, 1670 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.50 m (2H, 3-H, 5-H), 1.93 d (3H, CH_3, J = 3.0 Hz), 1.99 m (1H, 4-H), 2.20 m (2H, 5-H, 6-H), 2.35 m (2H, 3-H, 6-H), 2.70 m (1H, 3a-H, $J_{3a,4}$ = 11.2 Hz), 2.90 m (1H, 2-H), 3.05 m (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 17.72 q (CH_3), 23.47 t (C^3, C^5), 31.91 t (C^6), 39.79 d (C^{3a}),46.99 d (C^4), 50.92 t (C^2), 135.37 s (C^{7a}), 139.70 s (C^7), 176.09 s (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 229 $[M - 15]^+$ (7), 184 (100), 105 (73), 93 (56), 92 (45), 91 (63), 79 (36).

7-Methyl-5-phenyl-2,3,3a,4,5,6-hexahydro-1-benzothiophene-4-carbohydrazide 1,1-dioxide (XXXII) was synthesized as described above using compound **XI**. Yield 81%, mp 156–158°C (from ethanol). UV spectrum, λ_{max}, nm (logε): 252 (2.39), 258 (2.41), 265 (2.33). IR spectrum, ν, cm^{-1}: 702, 733, 1500, 1580 (C=C); 1119, 1120, 1287 (SO_2); 1554, 3438, 3486 ($NHNH_2$); 1660, 1670 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.42 m (1H, 3-H), 2.08 d (3H, CH_3, J = 2.4, 1.2 Hz), 2.25 d.d (1H, 4-H, J = 3.8 Hz, 11.0), 2.36 d.d (1H, 6-H, J = 19.2, 2.5 Hz), 2.40 m (1H, 3a-H, $J_{3a,4}$ = 11.0 Hz), 2.51 m (1H, 3-H), 2.77 d.d.d.d (1H, 6-H, J = 19.2, 7.0, 4.4, 1.2 Hz), 2.93 m (1H, 2-H), 3.11 m (1H, 2-H), 3.60 d.d (1H, 5-H, J = 7.0, 3.8 Hz), 7.03 m (2H, *o*-H), 7.16 m (1H, *o*-H), 7.20 m (2H, *m*-H). ^{13}C NMR spectrum, δ_C, ppm: 17.86 q (7-CH_3), 26.36 t (C^3), 34.36 d (C^{3a}), 38.60 t (C^6), 40.00 d (C^5), 50.91 t (C^2), 51.53 d (C^4), 126.28 d ($C^{4'}$), 127.73 d and 127.87 d ($C^{2'}$, $C^{3'}$, $C^{5'}$, $C^{6'}$), 136.23 s (C^{7a}), 139.75 s ($C^{1'}$), 142.79 s (C^7), 174.76 s (C=O).

Mass spectrum, *m*/*z* (I_{rel}, %): 306 $[M - 15]^+$ (7), 260 (95), 181 (41), 168 (28), 104 (41), 91 (38), 44 (100).

X-Ray diffraction study of compound (XXIV). A 0.80×0.40×0.16-mm single crystal was selected. Triclinic system with the following unit cell parameters: a = 8.6915(7), b = 10.058(1), c = 10.346(1) Å; α = 103.998(7), β = 111.127(7), γ = 103.748(8)°; V = 764.05(14) Å^3; space group P-1; Z = 2; $C_{11}H_{15}NO_5S_1$ + C_2H_5OH; d_{calc} = 1.388 g/cm^3; μ = 0.238 mm^{-1}. Intensities of 2597 independent reflections were measured. A correction for absorption was introduced empirically by psi-curves (transmission 0.79–0.84). The structure was solved by the direct method using SHELXS-97 program. Hydrogen atoms in molecule **XXIV** and in the hydroxy group of the solvent molecule were localized by the difference synthesis of electron density. The positions of hydrogen atoms attached to carbon atoms of the solvent were calculated at each refinement cycle from coordinates of the respective carbon atoms, and they were not refined. The final refinement of the structure parameters was performed by the least-squares procedure in full-matrix anisotropic approximation (isotropic for hydrogen atoms) using SHELXL-97 program with respect to all F^2 to wR_2 = 0.1188, S = 1.030; 260 parameters were refined (R = 0.0431 for 2340 $F > 4\sigma$).

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