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SYNTHESIS OF OXATHIOLONE FUSED CHALCONES BEARING *O*-AMINOALKYL SIDE CHAIN. COMPARISON OF STABILITY OF ISOMERIC BENZOXATHIOLONES UNDER ALKYLATION REACTION CONDITIONS

Marek T. Konieczny,[a,]* Wojciech Konieczny,[a] Danuta Pirska,[a] Anita Bułakowska,[a] Michał Sabisz,[b] Andrzej Skladanowski,[b] Roland Wakieć,[b] Ewa Augustynowicz-Kopeć,[c] and Zofia Zwolska[c]

[a] Department of Organic Chemistry, Medical University of Gdańsk, 80-416 Gdańsk, Poland; [b] Department of Pharmaceutical Technology and Biochemistry, Gdansk University of Technology, 80-952 Gdańsk, Poland; [c] Department of Microbiology, National Research Institute of Tuberculosis and Lung Diseases, 01-138 Warsaw, Poland

Abstract – Isomeric, oxathiolone fused chalcones bearing *O*-aminoalkyl side chain were synthesized by condensation of suitable benzoxathiolones with substituted benzaldehydes. The starting benzoxathiolones were prepared by *O*-alkylation of corresponding phenols with aminoalkyl chlorides, however, the reaction was often complicated by amino group catalyzed opening of the oxathiolone ring. The obtained chalcones were screened for antimicrobial and cytotoxic activity.

INTRODUCTION

Chalcones have attracted considerable attention because of their interesting biological effects, including anti-inflammatory, anticancer and anti-infective activities.[1-6] Recently, we have described synthesis and biological properties of isomeric chalcones **1A**,[7] **2A**[8] and **3A**[8] bearing oxathiolone ring (Figure 1).

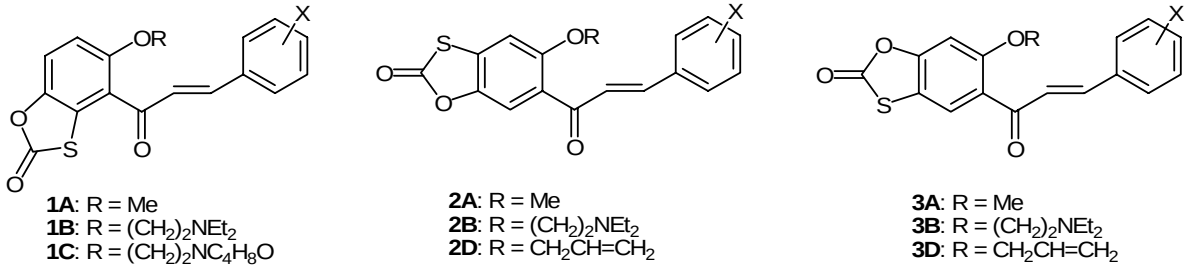


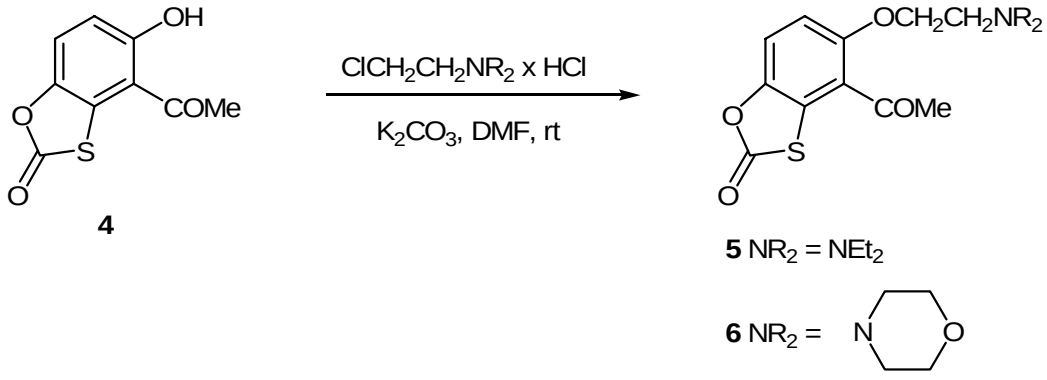
Figure 1

The compounds were tested as cytotoxic and antimicrobial agents, and generally, exhibited rather poor activity. It was found, however, that for compounds **1A** replacement of X = 4'-OMe by X = 4'-$OCH_2CH_2NMe_2$ or X = 4'-$OCH_2CH_2NC_4H_8O$ (morpholinoethoxy) group, significantly increased antimicrobial activity.[7] The observation prompted us to synthesis and activity evaluation of analogs of compounds **1A** – **3A** in which the methoxy substituent in ring A was replaced by diethylaminoethoxy (compounds **B**), morpholinoethoxy (compounds **C**) or allyloxy group (compounds **D**).

RESULTS AND DISCUSSION

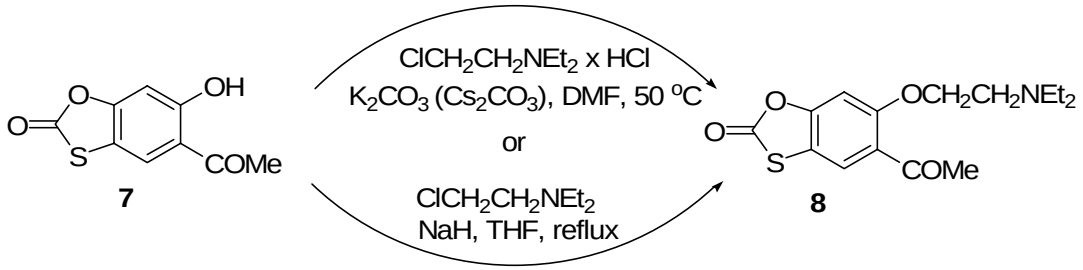
All chalcones were prepared analogously as compounds **1A**, **2A**, **3A**,[7,8] by acid catalyzed condensation of appropriate acetophenones (**5, 6**, **8**, **10**, **11**, **14**) with benzaldehydes. However, synthesis of the starting acetophenones, especially compounds **8** – **14** was found to be more challenging, due to instability of the oxathiolone ring under the reaction conditions. In some cases, even seemingly unimportant differences in the amount of reagents or temperature could be devastating for the yields, due to the ring opening and subsequent reactions of the formed products.

The amino derivatives **5** and **6** were prepared by condensation of hydroxyacetophenone **4**[7,9] with suitable chloroalkylamine hydrochloride in DMF, in the presence of potassium carbonate, at room temperature (Scheme 1).



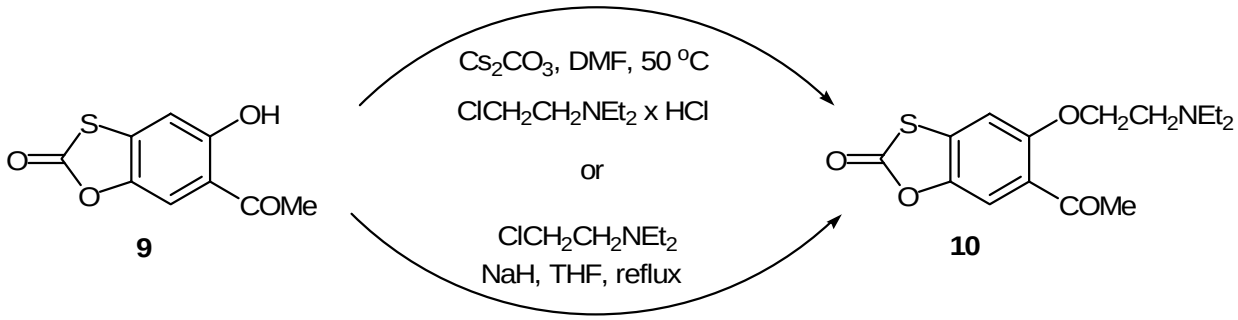
Scheme 1

For isomeric hydroxyacetophenone **7**,[8] analogously run reaction with 2-(diethylamino)ethyl chloride hydrochloride (ratio **7** : amine hydrochloride : potassium carbonate = 1 : 1.5 : 6) lead to complex mixture of products (isolated yield of **8**, 0 %), which apparently were formed by opening of the oxathiolone ring. Simple reduction of the amount of potassium carbonate (ratio **7** : amine hydrochloride : potassium carbonate = 1 : 1.5 : 1.5) and increase of temperature to 50 ^oC gave the desired aminoalkoxy derivative **8** (isolated yield 40 %) (Scheme 2).



Scheme 2

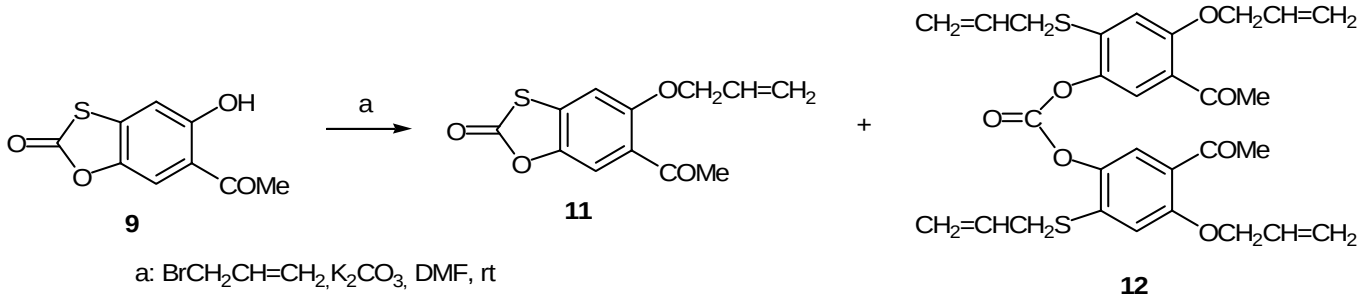
It seems that in the latter case, upon completion of the reaction, the mixture contained essentially potassium bicarbonate which buffered the solution so it was not nucleophilic enough to open the oxathiolone ring. Replacement of the potassium carbonate by cesium carbonate (**7** : amine hydrochloride: cesium carbonate = 1 : 1.5 : 2) gave similar results (yield 30 %). Best yield of **8** (67 %) was obtained in the reaction of **7** with free amine in THF in the presence of sodium hydride (Scheme 2).



Scheme 3

The reaction of hydroxyacetophenone **9**[8] with 2-(diethylamino)ethyl chloride hydrochloride in the presence of potassium carbonate was messy, despite the amount of the carbonate. However, alkylation in the presence of cesium carbonate gave the desired product **10**. Similarly as for the isomer **7**, best yield (70 %) was obtained under NaH/ THF conditions (Scheme 3).

Reaction of the acetophenone **9** with allyl bromide and potassium carbonate in DMF at room temperature gave a mixture of two products, approximately in 1 : 1 ratio, which were identified as the expected product of allylation **11** and dimer **12** (Scheme 4).



Scheme 4

The result confirmed instability of the oxathiolone ring under the reaction conditions. Lowering of the temperature of the reaction to 0 ^{o}C gave exclusively the desired product **11**. Reaction of the hydroxy derivative **9** with allyl bromide and NaH in THF was sluggish. In comparison with the smooth reaction with 2-(diethylamino)ethyl chloride (Scheme 3) the result was surprising, and suggested that the last reaction took place through aziridinium ion **13**.

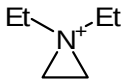


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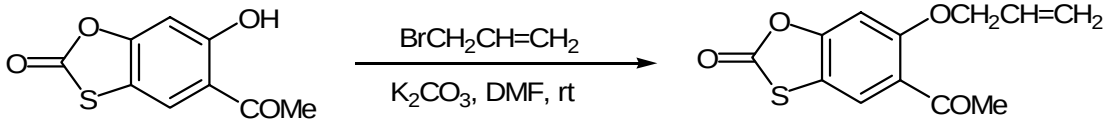
Figure 2

Finally, reaction of the acetophenone **7** with allyl bromide and potassium carbonate in DMF at room temperature gave the expected allyl derivative **14** (Scheme 5).



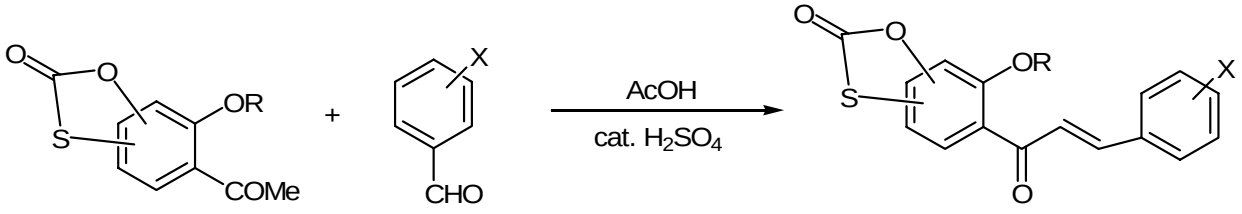
7 **14**

Scheme 5

Comparison of the above results suggests that the order of susceptibility of the benzoxathiolones to nucleophilic ring opening is: **9** > **7** > **4**.

The prepared acetophenones (**5, 6**, **8**, **10**, **11**, **14**) were condensed with suitable benzaldehydes in acetic acid solution, using conc. sulfuric acid as a catalyst (Scheme 6).

The amount of the sulfuric acid was crucial for the course of the reactions. Namely, for reactions of the allyl derivatives **11** and **14** only traces of the catalyst should be used, otherwise acid catalyzed cleavage of the allyl ether became a serious problem, leading to formation of 2'-hydroxychalcones and their cyclization to related flavanones. In contrary, for the amino substrates **5**, **6**, **8**, **10** the amount of the sulfuric acid should be significantly bigger, otherwise the acid was totally bonded as amine sulfate and reactions were sluggish. The obtained compounds are listed in Table 1.

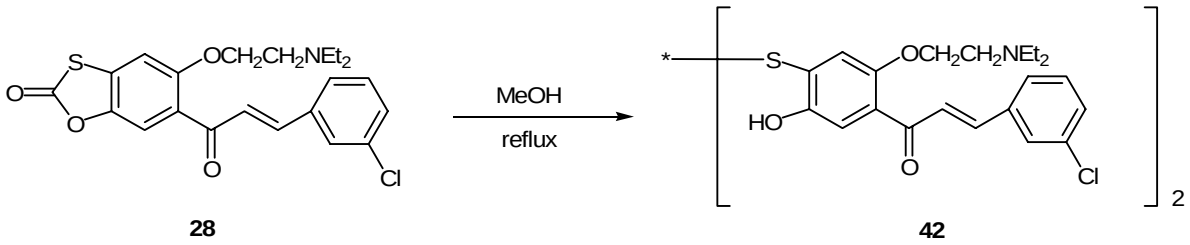


5, **6**, **8**, **10**, **11**, **14** **15 - 41**

Scheme 6

The instability of the oxathiolone ring under alkaline conditions was confirmed by the observed decomposition of chalcones bearing amino side chain, in protic solvents. For example, crystallization of amino derivative **28** from methanol resulted in partial decomposition of the compound to disulfide **42**

(Scheme 7).



28 **42**

Scheme 7

Apparently, the disulfide **42** was formed by amine group catalyzed opening of the oxathiolone ring. However, the chalcones with amino side chain could be safely crystallized from such solvents as acetone, toluene or cyclohexane.

The synthesized compounds (**15 - 41**) were screened for cytotoxic activity using HeLa cells, as well as for antibacterial activity against *Micrococcus luteus*, *Staphylococcus aureus*, *Salmonella typhimurium*, *Escherichia coli*, *Proteus vulgaris*, antifungal activity against *Candida albicans*, and tuberculostatic activity against *Mycobacterium tuberculosis* $H_{37}Rv$ and *Mycobacterium kansasii* strains. The results are given in the Table 1. It appears, that the activity was not influenced significantly by replacement of the methoxy substituent[7,8] with aminoalkyl group. All compound for which the cytotoxic activity against *HeLa* cells could be determined, exhibited weak activity, in the range 2 – 12 μM. Concerning antimicrobial activity, compounds of general formula **2B** and **2D** (except **28**) did not influence growth of any of the tested microorganism, similarly as compounds **2A**.[8] Also, halogenated compounds of general formula **3B** were found to be active only against *Micrococcus luteus* and *Staphylococcus aureus* strains, similarly as **3A**.[8]

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were obtained from KBr pellets on Thermo Mattson Satellite instrument. The ^{1}H NMR spectra were recorded on 200 MHz (Varian Gemini) or 500 MHz (Varian Unity Plus) spectrometers. Mass spectra were recorded on Bruker Biflex III instrument. Elemental analyses were performed on Carlo-Erba 1108 instrument. TLC was carried out on Merck 0.2 mm silica gel 60 F254 aluminum plates. The described reactions were not optimized.

Synthesis of 4-acetyl-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (5)

4-Acetyl-5-hydroxybenzo[1,3]oxathiol-2-one (**4**) (4.2 g, 20 mmol), anhydrous potassium carbonate (16.58 g, 120 mmol) and 2-(diethylamino)ethyl chloride hydrochloride (6.88 g, 40 mmol) in dry DMF (40 mL) were mixed at 0 ^{o}C and next stirred at rt for 2.5 h. The reaction mixture was diluted with cold water, the precipitated solid was filtered off, dried and crystallized from toluene - cyclohexane to give 4-acetyl-5-

Table 1 Activities of the synthesized compounds against tested microorganisms and cell lines[a]

Cmpd no	General formula / Substituent X	Antifungal activity IC_{50} (μg/mL)	Bacteriostatic activity IC_{50} (μg/mL)					Cytostatic activity IC_{50} (μM)	Tuberculostatic activity MIC (μg/mL)	
		C.albicans	*M.luteus*	*St.aureus*	*Sal.typh.*	*E.coli*	*Pr. vulgaris*	*HeLa*	*$H_{37}Rv$*	*M.kansasii*
15	1 B / H	>1000	>1000	>1000	>1000	>1000	>1000	10.1	>100	>100
16	1 B /4'-Br	>1000	>1000	>1000	>1000	>1000	>1000	[b]	>100	>100
17	1 B / 4'-Cl	250	31,25	31,25	250	125	125	[b]	50	100
18	1 B / 3'-Cl	125	31,25	31,25	>1000	>1000	>1000	[b]	<25	50
19	1 B / 2'-Cl	125	62,5	62,5	>1000	>1000	>1000	[b]	100	100
20	1 B / 4'-OMe	>1000	>1000	>1000	>1000	>1000	>1000	7.8	50	100
21	1 B / 4'-$O(CH_2)_2NMe_2$	31,25	31,25	31,25	125	62,5	62,5	[b]	50	100
22	1 B / 4'-$(CH_2)_2NC_4H_8O$	31,25	15,62	15,62	>1000	>1000	>1000	[b]	50	>100
23	1 B /3'- $(CH_2)_2NC_4H_8O$	31,25	15,62	15,62	>1000	>1000	>1000	10.8	50	>100
24	1 C / H	>1000	>1000	>1000	>1000	>1000	>1000	[b]	>100	>100
25	2 B / H	>1000	>1000	>1000	>1000	>1000	>1000	6.3	100	100
26	2 B / 4'-Br	>1000	>1000	>1000	>1000	>1000	>1000	[b]	100	>100
27	2 B / 3'-Cl	>1000	>1000	>1000	>1000	>1000	>1000	[b]	100	>100
28	2 B / 4'-OMe	125	7,8	15,6	125,0	62,5	62,5	9.4	100	100
29	2 D / H	>1000	>1000	>1000	>1000	>1000	>1000	11.3	>100	>100
30	2 D / 4'-Br	>1000	>1000	>1000	>1000	>1000	>1000	9.8	>100	>100
31	2 D / 3'-Cl	>1000	>1000	>1000	>1000	>1000	>1000	10.3	>100	>100
32	2 D / 4'-NO_2	>1000	>1000	>1000	>1000	>1000	>1000	12.3	>100	>100
33	2 D / 4'-OMe	>1000	>1000	>1000	>1000	>1000	>1000	[b]	100	>100
34	2 D / 3',4'-diOMe	>1000	>1000	>1000	>1000	>1000	>1000	13.0	100	>100
35	3 B / H	125	31,25	15,62	>1000	>1000	>1000	[b]	100	100
36	3 B / 4'- Br	125	7,81	7,81	>1000	>1000	>1000	2.1	100	>100
37	3 B / 3'-Cl	62,5	15,62	7,81	>1000	>1000	>1000	15.8	<25	100
38	3 B / 4'-OMe	62,5	15,62	7,81	>1000	>1000	>1000	5.8	<25	100
39	3 D / H	>1000	>1000	>1000	>1000	>1000	>1000	[b]	50	>100
40	3 D / 4'-Br	>1000	>1000	>1000	>1000	>1000	>1000	[b]	50	>100
41	3 D / 2'-Cl	125	15,62	7,81	>1000	>1000	>1000	[b]	50	>100

[a] The activities were determined as described before[7,8]

[b] The value could not be determined as the compound precipitated out during incubation

[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**5**) (4.23 g, 68 %) as a beige solid, mp 98 – 99 °C.

Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53; S, 10.34. Found: C, 58.18; H, 6.21; N, 4.52; S, 10.38.

IR (KBr) (cm^{-1}): 1744, 1662, 1460, 1274, 1051.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.72 (d, 1 H, *J* = 9.3 Hz, H-7), 7.31 (d, 1 H, *J* = 9.3 Hz, H-6), 4.23 (t, 2 H, *J* = 5.9 Hz, OCH_2), 2.84 (t, 2 H, *J* = 5.9 Hz, CH_2N), 2.72 (s, 3 H, $COCH_3$), 2.55 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 0.95 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

Synthesis of 4-acetyl-5-[2-(morpholino)ethoxy]benzo[1,3]oxathiol-2-one (6)

4-Acetyl-5-hydroxybenzo[1,3]oxathiol-2-one (**4**) (2.1 g, 10 mmol), anhydrous potassium carbonate (5.53 g, 40 mmol) and 4-(2-chloroethyl)morpholine hydrochloride (2.8 g, 15 mmol) in dry DMF (20 mL) were stirred at 50 °C for 7 h. The reaction mixture was diluted with icy water, the precipitated solid was filtered off, dried and crystallized from toluene - cyclohexane to give 4-acetyl-5-[2-(morpholino)ethoxy]benzo[1,3]oxathiol-2-one (**6**) (1.82 g, 56 %) as a beige solid, mp 157 - 158 °C.

Anal. Calcd for $C_{15}H_{17}NO_5S$: C, 55.71; H, 5.30; N, 4.33; S, 9.92. Found: C, 55.56; H, 4.23; N, 4.45; S, 9.78.

IR (KBr) (cm^{-1}): 1744, 1650, 1459, 1272, 1052.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.73 (d, 1 H, *J* = 9.0 Hz H-7), 7.30 (d, 1 H, *J* = 9.0 Hz, H-6), 4.29 (t, 2 H, *J* = 5.7 Hz, OCH_2), 3.57 (t, 4 h, *J* = 4.7 Hz, CH_2OCH_2), 2.78 (t, 2 H, *J* = 5.7 Hz, CH_2N), 2.74 (s, 3 H, $COCH_3$), 2.5 (m, under DMSO, CH_2NCH_2).

Synthesis of 5-acetyl-6-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (8)

A. 5-Acetyl-6-hydroxybenzo[1,3]oxathiol-2-one (**7**) (4.2 g, 20 mmol), sodium hydride (0.96 g, 40 mmol) and 2-(diethylamino)ethyl chloride (6 mL, 44 mmol) in dry THF (80 mL) were refluxed for 6 h. The reaction mixture was quenched, with cooling, using saturated aqueous potassium bicarbonate solution, the precipitated solid was filtered off, dried and crystallized from cyclohexane to give 5-acetyl-6-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**8**) (4.33 g, 70 %) as a colorless solid, mp 95 - 96 °C.

Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53; S, 10.34. Found: C, 58.14; H, 6.21; N, 4.43; S, 10.18.

IR (KBr) (cm^{-1}): 1759, 1662, 1463, 1273, 1015.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.00 (s, 1 H, H-4), 7.44 (s, 1 H, H-7), 4.19 (t, 2 H, *J* = 5.7 Hz, OCH_2), 2.82 (t, 2 H, *J* = 5.7 Hz, CH_2N), 2.58 (s, 3 H, $COCH_3$), 2.55 (m, under DMSO, 2 x CH_2), 0.95 (t, 6 H, *J* = 7.1 Hz, 2 x CH_3).

B. 5-Acetyl-6-hydroxybenzo[1,3]oxathiol-2-one (**7**) (2.1 g, 10 mmol), anhydrous potassium carbonate (2.07 g, 15 mmol) and 2-(diethylamino)ethyl chloride hydrochloride (2.8 g, 15 mmol) in dry DMF (20

mL) were stirred at 50 °C for 4 h. The reaction mixture was cooled, diluted with icy water, the precipitated solid was filtered off, dried and crystallized from cyclohexane to give 6-acetyl-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**8**) (1.73 g, 56 %) as a beige solid.

C. 5-Acetyl-6-hydroxybenzo[1,3]oxathiol-2-one (**7**) (2.1 g, 10 mmol), anhydrous cesium carbonate (6.52 g, 20 mmol) and 2-(diethylamino)ethyl chloride hydrochloride (2.8 g, 15 mmol) in dry DMF (20 mL) were stirred at 50 °C for 3 h. The reaction mixture was cooled, diluted with icy water, the precipitated solid was filtered off, dried and crystallized from cyclohexane to give 5-acetyl-6-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**8**) (1.48 g, 48 %) as a beige solid.

Synthesis of 6-acetyl-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (10)

A. 6-Acetyl-5-hydroxybenzo[1,3]oxathiol-2-one (**9**) (2.1 g, 10 mmol), sodium hydride (0.48 g, 20 mmol) and 2-(diethylamino)ethyl chloride (3 mL, 22 mmol) in dry THF (40 mL) were refluxed for 5 h. The reaction mixture was quenched, with cooling, using saturated aqueous potassium bicarbonate solution, the precipitated solid was filtered off, dried and crystallized from toluene - cyclohexane to give 6-acetyl-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**10**) (2.1 g, 67 %) as a beige solid, mp 98 - 100 °C.

Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53; S, 10.34. Found: C, 58.07; H, 6.29; N, 4.37; S, 10.23.

IR (KBr) (cm^{-1}): 1773, 1659, 1467, 1261, 1012.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.73 (s, 1 H, H-7), 7.61 (s, 1 H, H-4), 4.16 (t, 2 H, J = 5.8 Hz, OCH_2), 2.85 (t, 2 H, J = 5.8 Hz, CH_2N), 2.62 (s, 3 H, $COCH_3$), 2.55 (m, under DMSO, 2 x CH_2), 0.98 (t, 6 H, J = 7.1 Hz, 2 x CH_3).

B. 6-Acetyl-5-hydroxybenzo[1,3]oxathiol-2-one (**9**) (2.1 g, 10 mmol), anhydrous cesium carbonate (6.52 g, 20 mmol) and 2-(diethylamino)ethyl chloride hydrochloride (2.8 g, 15 mmol) in dry DMF (40 mL) were stirred at 50 °C for 2 h. The reaction mixture was cooled, diluted with icy water, the precipitated solid was filtered off, dried and crystallized from cyclohexane to give 6-acetyl-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**10**) (1.18 g, 38 %) as a beige solid.

Reaction of 6-acetyl-5-hydroxybenzo[1,3]oxathiol-2-one (9) with allyl bromide

Reaction at room temperature

6-Acetyl-5-hydroxybenzo[1,3]oxathiol-2-one (**9**) (2.1 g, 10 mmol), anhydrous potassium carbonate (4.13 g, 30 mmol) and allyl bromide (1.7 mL, 20 mmol) in anhydrous DMF (25 mL) were stirred at rt for 4 h. Next, the mixture was diluted with water and the precipitated solid was filtered, washed with water and dried. The crude product was separated on silica gel column in $CHCl_3$ – cyclohexane 2 : 1 (v/v). The first

fraction was crystallized from toluene – cyclohexane to give 6-acetyl-5-allyloxybenzo[1,3]oxathiol-2-one (**11**) (600 mg, 24 %) as a colorless solid, mp 136 - 138 °C.

Anal. Calcd for $C_{12}H_{10}O_4S$: C, 57.59; H, 4.03; S, 12.81. Found: C, 57,49; H, 3.88; S, 12.65.

IR (KBr) (cm^{-1}): 1784, 1664, 1417, 1253, 1191.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.67 (s, 1 H, H-7), 7.61 (s, 1 H, H-4), 6.10 (m, 1 H, -HC=), 5.46 (dq, 1 H, J_1 = 17.3 Hz, J_2 = 1.6 Hz, =CH_2), 5.33 (dq, 1 H, J_1 = 10.5 Hz, J_2 = 1.4 Hz, =CH_2), 4.70 (d, 2 H, J = 5.3 Hz, OCH_2), 2.57 (s, 3 H, $COCH_3$).

The second fraction was crystallized from cyclohexane to give bis(5-acetyl-4-allyloxy-2-allylthiophenyl)carbonate (**12**) as a colorless solid, mp 136 - 138 °C.

MS MALDI TOF: Calcd for $C_{29}H_{30}O_7S_2$: M = 554.1. Found 592.9 (M + 39), 576.9 (M + 23), 554.9 (M).

IR (KBr) (cm^{-1}): 1779, 1657, 1596, 1399, 1207, 1165.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.63 (s, 2 H, H-6), 7.11 (s, 2 H, H-3), 6.12 (m, 2 H, -HC=), 5.87 (m, 2 H, -HC=), 5.48 (d, 2 H, J = 17.6 Hz, =CH_2), 5.35 (m, 2 x =CH_2), 4.78 (d, 4 H, J = 4.9 Hz, OCH_2), 3.85 (d, 4 H, J = 6.8 Hz, SCH_2), 2.55 (s, 6 H, $COCH_3$).

Reaction at 0 °C

6-Acetyl-5-hydroxybenzo[1,3]oxathiol-2-one (**9**) (2.1 g, 10 mmol), anhydrous potassium carbonate (2.76 g, 20 mmol) and allyl bromide (1.7 mL, 20 mmol) in anhydrous DMF (20 mL) were stirred at 0 °C for 7 h. Next, the mixture was diluted with water and ice, and the precipitated solid was filtered, washed with water and dried. The crude product was crystallized from MeOH to give 6-acetyl-5-allyloxybenzo[1,3]oxathiol-2-one (**11**) (2.6 g, 82 %) as a colorless solid.

Synthesis of 5-acetyl-6-allyloxybenzo[1,3]oxathiol-2-one (14)

5-Acetyl-6-hydroxybenzo[1,3]oxathiol-2-one (**7**) (9.1 g, 43 mmol), anhydrous potassium carbonate (5.94 g, 43 mmol) and allyl bromide (14.7 mL, 172 mmol) in anhydrous DMF (75 mL) were stirred at rt for 1.5 h. Next, the mixture was diluted with water and ice, and the precipitated solid was filtered, washed with water and dried. Crystallization from MeOH gave 5-acetyl-6-allyloxybenzo[1,3]oxathiol-2-one (**14**) (7.1 g, 65 %) as a beige solid, mp 148 – 150 °C.

Anal. Calcd for $C_{12}H_{10}O_4S$: C, 57.59; H, 4.03; S, 12.81. Found: C, 57,48; H, 3.93; S, 12.89.

IR (KBr) (cm^{-1}): 1753, 1662, 1605, 1421, 1271, 1182.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.02 (s, 1 H, H-4), 7.40 (s, 1 H, H-7), 6.10 (m, 1 H, -HC=), 5.47 (dq, 1 H, J_1 = 17.3 Hz, J_2 = 1.6 Hz, =CH_2), 5.33 (dq, 1 H, J_1 = 10.5 Hz, J_2 = 1.4 Hz, =CH_2), 4.75 (dt, 2 H, J_1 = 5.5 Hz, J_2 = 1.4 Hz, OCH_2), 2.55 (s, 3 H, $COCH_3$).

General procedure for condensation of acetylbenzo[1,3]oxathiol-2-ones containing amino group (5, 6, 8, and 10) with benzaldehydes

2-Oxo-benz[1,3]oxathiole derivative (**5**, **6**, **8** or **10**) (1 mmol), suitable benzaldehyde (2 mmol) and conc. sulfuric acid (0.12 mL – 0.2 mL, ~ 2 – 4 mmol) in AcOH (2 - 3 mL) were stirred at 60 - 100 °C until completion of the reaction (2 - 20 h). The cooled mixture was usually poured into saturated aqueous solution of sodium bicarbonate and the precipitated solid was filtered off or extracted, washed with water and purified as given for particular compounds. Alternatively, Et_2O was added to the cooled reaction mixture, the precipitated sulfate of the product was filtered off, washed with ether and either crystallized from EtOH or alkalized with sodium bicarbonate to give the product as a free base.

5-[2-(Diethylamino)ethoxy]-4-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**15**)

Reaction of **5** with benzaldehyde, reaction temp. – 80 °C; time – 20 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), evaporated, and the residue was crystallized from EtOH to give 5-[2-(diethylamino)ethoxy]-4-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**15**) as a yellow solid, yield 30 %, mp 95 - 97 °C.

Anal. Calcd for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52; S, 8.07. Found: C, 66.59; H, 5.87; N, 3.55; S, 8.09.

IR (KBr) (cm^{-1}): 1748, 1597, 1451, 1266, 1049.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.09 (d, 1 H, *J* = 15.7 Hz, H-β), 7.76 – 7.83 (m, 3 H, H-α, H-2', H-6'), 7.72 (d, 1 H, *J* = 9.0 Hz, H-7), 7.44 – 7.50 (m, 3 H, H-3', H-4', H-5'), 7.34 (d, 1 H, *J* = 9.0 Hz, H-6), 4.29 (t, 2 H, *J* = 5.9 Hz, OCH_2), 2.87 (t, 2 H, *J* = 5.9 Hz, NCH_2), 2.54 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 0.90 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

4-[3-(4'-Bromophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**16**)

Reaction of **5** with 4-bromobenzaldehyde, reaction temp. – 100 °C; time – 5 h. Et_2O was added to the cooled mixture and the precipitated solid was filtered off, and washed with Et_2O. The crude product was stirred in cold, saturated aqueous solution of sodium bicarbonate, filtered, washed with water, dried and crystallized from acetone to give 4-[3-(4'-bromophenyl)acryolyl]-5-[2-(diethylamino)-ethoxy]benzo[1,3]oxathiol-2-one (**16**) as a cream solid, yield 59 %, mp 178 – 180 °C.

Anal. Calcd for $C_{22}H_{22}BrNO_4S$: C, 55.47; H, 4.65; N, 2.94; S, 6.73. Found: C, 55.40; H, 4.58; N, 2.81; S, 6.57.

IR (KBr) (cm^{-1}): 1747, 1599, 1418, 1055.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.08 (d, 1 H, *J* = 15.8 Hz, H-β), 7.71 – 7.83 (m, 4 H, H-α, H-2', H-6', H-7), 7.67 (d, 2 H, *J* = 8.5 Hz, H-3', H-5'), 7.36 (d, 1 H, *J* = 9.1 Hz, H-6), 4.30 (t, 2 H, *J* = 5.7 Hz,

OCH_2), 2.85 (t, 2 H, *J* = 5.7 Hz, NCH_2), 2.50 (m, under DMSO, 2 x CH_2), 0.89 (t, 6 H, *J* = 6.9 Hz, 2 x CH_3).

4-[3-(4'-Chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**17**)

Reaction of **5** with 4-chlorobenzaldehyde, reaction temp. – 100 °C; time – 16 h. The cooled mixture was filtered, and the solid was washed with Et_2O. The crude product was stirred in cold, saturated aqueous solution of sodium bicarbonate, filtered, washed with water, dried and crystallized from toluene to give 4-[3-(4'-chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**17**) as an yellow solid, yield 58 %, mp 187 – 190 °C.

Anal. Calcd for $C_{22}H_{22}ClNO_4S$: C, 61.18; H, 5.13; N, 3.24; S, 7.42. Found: C, 60.96; H, 5.01; N, 3.13; S, 7.36.

IR (KBr) (cm^{-1}): 1747, 1599, 1418, 1055.

^1H NMR (500 MHz, DMSO-d_6): δ = 8.09 (d, 1 H, *J* = 15.6 Hz, H-β), 7.84 (d, 2 H, *J* = 8.8 Hz, H-2', H-6'), 7.79 (d, 1 H, *J* = 15.6 Hz, H-α), 7.76 (d, 1 H, *J* = 9.3 Hz, H-7), 7.54 (d, 2 H, *J* = 8.8 Hz, H-3', H-5'), 7.36 (d, 1 H, *J* = 9.3 Hz, H-6), 4.30 (t, 2 H, *J* = 5.8 Hz, OCH_2), 2.85 (t, 2 H, *J* = 5.8 Hz, NCH_2), 2.50 (m, under DMSO, 2 x CH_2), 0.89 (t, 6 H, J = 6.9 Hz, 2 x CH_3).

4-[3-(3'-Chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**18**)

Reaction of **5** with 3-chlorobenzaldehyde, reaction temp. – 100 °C; time – 16 h. The cooled mixture was filtered, and the solid was washed with Et_2O. The crude product was stirred in cold, saturated aqueous solution of sodium bicarbonate, filtered, washed with water and dried. The obtained solid was dissolved in acetone and filtered through short silica gel column. Upon concentration of the filtrate 4-[3-(3'-chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**18**) precipitated as an yellow solid, which was filtered and dried, yield 48 %, mp 130 – 132 °C.

Anal. Calcd for $C_{22}H_{22}ClNO_4S$: C, 61.18; H, 5.13; N, 3.24; S, 7.42. Found: C, 61.03; H, 5.01; N, 3.21; S, 7.29.

IR (KBr) (cm^{-1}): 1748, 1600, 1413, 1054.

^1H NMR (500 MHz, DMSO-d_6): δ = 8.07 (d, 1 H, *J* = 15.6 Hz, H-β), 7.84 (bs, 1 H, H-2'), 7.72 – 7.78 (m, 3 H, H-α, H-7, H-6'), 7.46 – 7.54 (m, 2H, H-4', H-5'), 7.35 (d, 1 H, *J* = 8.8 Hz, H-6), 4.28 (t, 2 H, *J* = 5.9 Hz, OCH_2), 2.86 (t, 2 H, *J* = 5.9 Hz, NCH_2), 2.55 (q, *J* = 7.3 Hz, 2 x CH_2), 0.89 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

4-[3-(2'-Chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**19**)

Reaction of **5** with 2-chlorobenzaldehyde, reaction temp. – 100 °C; time – 24 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), evaporated, and the residue was dissolved in acetone and filtered through short silica gel column. Upon concentration of the filtrate

4-[3-(2'-chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**19**) precipitated as an yellow solid, which was filtered and dried, yield 68 %, mp 153 – 155 °C.

Anal. Calcd for $C_{22}H_{22}ClNO_4S$: C, 61.18; H, 5.13; N, 3.24; S, 7.42. Found: C, 61.10; H, 4.99; N, 3.26; S, 7.33.

IR (KBr) (cm^{-1}): 1748, 1598, 1417, 1055.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.13 (d, 1 H, *J* = 15.6 Hz, H-β), 8.04 (d, 1 H, *J* = 15.6 Hz, H-α), 8.00 (d, 1 H, *J* = 6.8 Hz, H-6'), 7.77 (d, 1 H, *J* = 9.3 Hz, H-7), 7.60 (d, 1 H, *J* = 7.3 Hz, H-3'), 7.50 (t, 1 H, *J* = 7.8 Hz, H-4'), 7.45 (t, 1 H, *J* = 7.3 Hz, H-5'), 7.37 (d, 1 H, *J* = 9.3 Hz, H-6), 4.29 (t, 2 H, *J* = 5.5 Hz, OCH_2), 2.83 (t, 2 H, *J* = 5.5 Hz, NCH_2), 2.50 (m, under DMSO, 2 x CH_2), 0.86 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

5-[2-(Diethylamino)ethoxy]-4-[3-(4'-methoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**20**)

Reaction of **5** with 4-methoxybenzaldehyde, reaction temp. – 100 °C; time – 24 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), evaporated, and the residue was dissolved in acetone and filtered through short silica gel column. The residue was crystallized from toluene – cyclohexane to give 5-[2-(diethylamino)ethoxy]-4-[3-(4'-methoxyphenyl)acryolyl]-benzo[1,3]oxathiol-2-one (**20**) as an yellow solid, yield 35 %, mp 110 – 113 °C.

Anal. Calcd for $C_{23}H_{25}NO_5S$: C, 64.62; H, 5.89; N, 3.28; S, 7.50. Found: C, 64.47; H, 5.72; N, 3.17; S, 7.36.

IR (KBr) (cm^{-1}): 1747, 1593, 1511, 1256, 1172, 1057.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.98 (d, 1 H, *J* = 15.6 Hz, H-β), 7.74 – 7.82 (m, 3 H, H-α, H-2', H-6'), 7.71 (d, 1 H, *J* = 9.3 Hz, H-7), 7.36 (d, 1 H, *J* = 9.3 Hz, H-6), 7.02 (d, 2 H, *J* = 8.3 Hz, H-3', H-5'), 4.29 (t, 2 H, *J* = 5.3 Hz, OCH_2), 3.83 (s, 3 H, OCH_3), 2.87 (t, 2 H, *J* = 5.3 Hz, NCH_2), 2.55 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 0.91 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

5-[2-(Diethylamino)ethoxy]-4-[3-(4'-(2-dimethylamino)ethoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**21**)

Reaction of **5** with 4-[2-(dimethylamino)ethoxy]benzaldehyde, reaction temp. – 100 °C; time – 12 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), evaporated, and the residue was crystallized from acetone to give 5-[2-(diethylamino)ethoxy]-4-[3-(4'-dimethylaminoethoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**21**) as an yellow solid, yield 48 %, mp 133 – 135 °C.

Anal. Calcd for $C_{26}H_{32}N_2O_5S$: C, 64.44; H, 6.66; N, 5.78; S, 6.62. Found: C, 64.34; H, 6.51; N, 5.59; S, 6.47.

IR (KBr) (cm^{-1}): 1744, 1561, 1511, 1256, 1177, 1061.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.99 (d, 1 H, *J* = 15.6 Hz, H-β), 7.79 (d, 1 H, *J* = 15.6 Hz, H-α), 7.76 (d, 2 H, *J* = 8.3 Hz, H-2', H-6'), 7.72 (d, 1 H, *J* = 8.8 Hz, H-7), 7.34 (d, 1 H, *J* = 8.8 Hz, H-6), 7.02 (d, 2 H, *J* = 8.3 Hz, H-3', H-5'), 4.29 (t, 2 H, *J* = 5.3 Hz, OCH_2), 4.12 (t, 2 H, *J* = 5.8 Hz, OCH_2), 2.87 (t, 2 H, *J* = 5.3 Hz, NCH_2), 2.63 (t, 2 H, *J* = 5.8 Hz, NCH_2), 2.56 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 2.21 (s, 6 H, 2 x CH_3), 0.91 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

5-[2-(Diethylamino)ethoxy]-4-[3-(4'-(2-morpholino)ethoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**22**)

Reaction of **5** with 4-[2-(morpholino)ethoxy]benzaldehyde, reaction temp. – reflux; time – 6.5 h. The cooled mixture was treated with Et_2O, the precipitated dark oil was solidified by addition of MeOH and filtered. The crude product was stirred in cold, saturated aqueous solution of sodium bicarbonate, filtered, washed with water, dried, dissolved in acetone in filtered through short silica gel column, and evaporated. The residue was crystallized from acetone to give 5-[2-(diethylamino)ethoxy]-4-[3-(4'-(2-morpholino)ethoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**22**) as an yellow solid, yield 59 %, mp 144 – 145 ^{o}C.

Anal. Calcd for $C_{28}H_{34}N_2O_6S$: C, 63.86; H, 6.51; N, 5.32; S, 6.09. Found: C, 63.67; H, 6.36; N, 5.28; S, 5.95.

IR (KBr) (cm^{-1}): 1742, 1593, 1511, 1254, 1175, 1059.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.00 (d, 1 H, *J* = 15.6 Hz, H-β), 7.80 (d, 1 H, *J* = 15.6 Hz, H-α), 7.76 (d, 2 H, *J* = 8.8 Hz, H-2', H-6'), 7.72 (d, 1 H, *J* = 9.3 Hz, H-7), 7.35 (d, 1 H, *J* = 9.3 Hz, H-6), 7.03 (d, 2 H, *J* = 8.8 Hz, H-3', H-5'), 4.29 (t, 2 H, *J* = 5.4 Hz, OCH_2), 4.16 (t, 2 H, *J* = 5.8 Hz, OCH_2), 3.58 (t, 4 H, *J* = 4.4 Hz, $O(CH_2)_2$, morpholine), 2.87 (t, 2 H, *J* = 5.4 Hz, NCH_2), 2.70 (t, 2 H, *J* = 5.8 Hz, NCH_2), 2.54 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 2.47 (bs, 4 H, $N(CH_2)_2$, morpholine), 0.91 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

5-[2-(Diethylamino)ethoxy]-4-[3-(3'-(2-morpholino)ethoxy)phenylacryolyl]benzo[1,3]oxathiol-2-one (**23**)

Reaction of **5** with 3-[2-(morpholino)ethoxy]benzaldehyde, reaction temp. – reflux; time – 5.5 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), evaporated, and the residue was crystallized from acetone (or toluene) to give 5-[2-(diethylamino)ethoxy]-4-[3-(3'-(2-morpholino)ethoxy)phenylacryolyl]benzo[1,3]oxathiol-2-one (**23**) as an yellow solid, yield 51 %, mp 121 – 122 ^{o}C.

Anal. Calcd for $C_{28}H_{34}N_2O_6S$: C, 63.86; H, 6.51; N, 5.32; S, 6.09. Found: C, 63.62; H, 6.44; N, 5.23; S, 5.90.

IR (KBr) (cm^{-1}): 1745, 1597, 1450, 1268, 1056.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.05 (d, 1 H, *J* = 15.6 Hz, H-β), 7.75 (d, 1 H, *J* = 15.6 Hz, H-α), 7.73 (d, 1 H, *J* = 8.8 Hz, H-7), 7.33 – 7.39 (m, 4 H, H-2', H-5', H-6, H-6'), 7.06 (m, 1 H, H-4'), 4.28 (t, 2 H, *J* = 5.4 Hz, OCH_2), 4.14 (t, 2 H, *J* = 5.8 Hz, OCH_2), 3.58 (t, 4 H, *J* = 4.4 Hz, $O(CH_2)_2$, morpholine), 2.87 (t, 2 H, *J* = 5.4 Hz, NCH_2), 2.70 (t, 2 H, *J* = 5.8 Hz, NCH_2), 2.54 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 2.47 (bs, 4 H, $N(CH_2)_2$, morpholine), 0.90 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

5-[2-(Morpholino)ethoxy]-4-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**24**)

Reaction of **6** with benzaldehyde, reaction temp. – 70 °C; time – 3 h. The cooled mixture was treated with water and the precipitated solid was filtered off. The crude product was stirred for 10 min with saturated aqueous solution of sodium bicarbonate and the solid was filtered off, washed with water and dried. Crystallization from 2-methoxyethanol gave salmon pink needles of 5-[2-(morpholino)ethoxy]-4-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**24**), yield 60 %, mp 214 – 219 °C.

Anal. Calcd for $C_{22}H_{21}NO_5S$: C, 64.22; H, 5.14; N, 3.40; S, 7.79. Found: C, 64.07; H, 5.01; N, 3.27; S, 8.07.

IR (KBr) (cm^{-1}): 1745, 1597, 1414, 1270, 1063.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.08 (d, 1 H, *J* = 15.7 Hz, H-β), 7.72 – 7.82 (m, 4 H, H-α, H-2', H-6', H-7), 7.44 – 7.50 (m, 3 H, H-3', H-4', H-5'), 7.34 (d, 1 H, *J* = 8.8 Hz, H-6), 4.35 (t, 2 H, *J* = 5.2 Hz, OCH_2), 3.47 (t, 4 H, *J* = 4.4 Hz, $O(CH_2)_2$, morpholine), 2.80 (t, 2 H, *J* = 5.2 Hz, NCH_2), 2.40 (bs, 4 H, $N(CH_2)_2$, morpholine).

5-[2-(Diethylamino)ethoxy]-6-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**25**)

Reaction of **10** with benzaldehyde, reaction temp. – 70 °C; time – 4 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), evaporated, and the residue was crystallized from cyclohexane to give 5-[2-(diethylamino)ethoxy]-6-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**25**) as an orange solid, yield 60 %, mp 79 – 82 °C.

Anal. Calcd for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52; S, 8.07. Found: C, 66.41; H, 5.73; N, 3.39; S, 7.97.

IR (KBr) (cm^{-1}): 1761, 1650, 1601, 1587, 1419, 1249, 1161, 1023.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.74 – 7.78 (m, 2 H, H-2', H-6'), 7.73 (s, 1 H, H-7), 7.59 (s, 1 H, H-4), 7.57 (d, 1 H, partly under H-4, H-β), 7.53 (d, 1 H, *J* = 15.6 Hz, H-α), 7.41 – 7.46 (m, 3 H, H-3', H-4', H-5'), 4.14 (t, 2 H, *J* = 5.4 Hz, OCH_2), 2.75 (bs, 2 H, NCH_2), 2.46 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 0.85 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

6-[3-(4'-Bromophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**26**)

Reaction of **10** with 4-bromobenzaldehyde, reaction temp. – reflux; time – 10 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and the precipitate was filtered off, washed with water, dried, and crystallized from cyclohexane to give 6-[3-(4'-bromophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**26**) as an yellow solid, yield 40 %, mp 134 – 138 °C.

Anal. Calcd for $C_{22}H_{22}BrNO_4S$: C, 55.47; H, 4.65; N, 2.94; S, 6.73. Found: C, 55.29; H, 4.60; N, 2.98; S, 6.55.

IR (KBr) (cm^{-1}): 1748, 1613, 1416, 1256, 1069, 1003.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.73 (d, 1 H, *J* = 8.5 Hz, H-2', H-6'), 7.72 (s, 1 H, H-4), 7.63 (d, 2 H, *J* = 8.5 Hz, H-3', H-5'), 7.58 (s, 1 H, H-7), 7.55 (s, 2 H, H-α, H-β), 4.13 (t, 2 H, *J* = 5.8 Hz, OCH_2), 2.73 (d, 2 H, *J* = 5.8 Hz, NCH_2), 2.44 (q, 4 H, *J* = 7.1 Hz, 2 x CH_2), 0.84 (t, 6 H, *J* = 7.1 Hz, 2 x CH_3).

6-[3-(3'-Chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**27**)

Reaction of **10** with 3-chlorobenzaldehyde, reaction temp. – 70 °C; time – 3 h. The solid which precipitated upon cooling, was filtered off, poured into saturated aqueous solution of sodium bicarbonate, and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), and evaporated. The residue was dissolved in acetone, filtered through a silica gel pad, evaporated, and crystallized from MeOH to give 6-[3-(3'-chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]-benzo[1,3]oxathiol-2-one (**27**) as an yellow solid, yield 25 %, mp 105 - 107 °C.

Anal. Calcd for $C_{22}H_{22}ClNO_4S$: C, 61.18; H, 5.13; N, 3.24; S, 7.42. Found: C, 61.04; H, 5.11; N, 3.02; S, 7.31.

IR (KBr) (cm^{-1}): 1764, 1613, 1416, 1258, 1204.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.86 (bs, 1 H, H-2'), 7.71 – 7.75 (m, 2 H, H-6', H-7), 7.61 (d, 1 H, *J* = 16.1 Hz, H-β), 7.60 (s, 1 H, H-4), 7.54 (d, 1 H, *J* = 16.1 Hz, H-α), 7.50 (bd, 1 H, *J* = 8.3 Hz, H-4'), 7.45 (t, 1 H, *J* = 7.8 Hz, H-5'), 4.13 (t, 2 H, *J* = 5.8 Hz, OCH_2), 2.74 (d, 2 H, *J* = 5.8 Hz, NCH_2), 2.46 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 0.85 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

5-[2-(Diethylamino)ethoxy]-6-[3-(4'-methoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**28**)

Reaction of **10** with 4-methoxybenzaldehyde, reaction temp. – 70 °C; time – 2 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and the precipitated solid was filtered off, washed with water and dried. Crystallization from cyclohexane gave 5-[2-(diethylamino)ethoxy]-6-[3-(4'-methoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**28**) as an yellow solid, yield 50 %, mp 78 – 83 °C.

Anal. Calcd for $C_{23}H_{25}NO_5S$: C, 64.62; H, 5.89; N, 3.28; S, 7.50. Found: C, 64.54; H, 5.72; N, 3.20; S, 7.52.

IR (KBr) (cm^{-1}): 1761, 1584, 1512, 1421, 1255.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.72 (d, 2 H, *J* = 8.7 Hz, H-2', H-6'), 7.70 (s, 1 H, H-7), 7.56 (s, 1 H, H-4), 7.53 (d, 1 H, partly under H-4, H-β), 7.37 (d, 1 H, *J* = 15.9 Hz, H-α), 6.99 (d, 2 H, *J* = 8.7 Hz, H-3', H-5'), 4.12 (t, 2 H, *J* = 5.8 Hz, OCH_2), 3.81 (s, 3 H, OCH_3), 2.75 (t, 2 H, *J* = 5.8 Hz, NCH_2), 2.50 (m, under DMSO, 2 x CH_2), 0.86 (t, 6 H, *J* = 7.4 Hz, 2 x CH_3).

6-[2-(Diethylamino)ethoxy]-5-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (35)

Reaction of **8** with benzaldehyde, reaction temp. – 70 °C; time – 2 h. The cooled mixture was poured into saturated solution of sodium bicarbonate, the precipitated solid was filtered off, washed with water and dried. The crude product was purified on silica gel column in $CHCl_3$ – MeOH (20 : 1) solution and crystallized from cyclohexane to give 6-[2-(diethylamino)ethoxy]-5-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**35**) as an yellow solid, yield 24 %, mp 101 - 102 °C.

Anal. Calcd for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52; S, 8.07. Found: C, 66.40; H, 5.66; N, 3.45; S, 7.89.

IR (KBr) (cm^{-1}): 1747, 1651, 1610, 1573, 1463, 1268, 1187, 1021.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7. 59 – 7.78 (m, 4 H), 7.38 – 7.52 (m, 4 H), 7.02 (s, 1 H), 4.24 (bs, 2H, OCH_2), 2.97 (bs, 2 H, NCH_2), 2.66 (bs, 4 H, 2 x CH_2), 1.03 (bs, 6 H, 2 x CH_3).

5-[3-(4'-Bromophenyl)acryolyl]-6-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (36)

Reaction of **8** with 4-bromobenzaldehyde, reaction temp. – 70 °C; time – 2 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and the precipitate was filtered off, washed with water and dried. The crude product was purified on silica gel column in $CHCl_3$ – MeOH (20 : 1) solution, and crystallized from cyclohexane to give 5-[3-(4'-bromophenyl)acryolyl]-6-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**36**) as an yellow solid, yield 25 %, mp 147 – 148 °C.

Anal. Calcd for $C_{22}H_{22}BrNO_4S$: C, 55.47; H, 4.65; N, 2.94; S, 6.73. Found: C, 55.40; H, 4.61; N, 2.87; S, 6.65.

IR (KBr) (cm^{-1}): 1745, 1609, 1268, 1184, 1023.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (s, 1 H, H-4), 7.61 (d, 1 H, *J* = 16.1 Hz, H-β), 7.55 (d, 2 H, *J* = 8.8 Hz, H-2', H-6'), 7.49 (d, 2 H, *J* = 8.8 Hz, H-3', H-5'), 7.46 (d, 1 H, partly under H-3', H-5', H-α), 7.02 (s, 1 H, H-7), 4.25 (bs, 2 H, OCH_2), 2.97 (bs, 2 H, NCH_2), 2.68 (bs, 4 H, 2 x CH_2), 1.05 (bs, 6 H, 2 x CH_3).

5-[3-(3'-Chlorophenyl)acryolyl]-6-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (37)

Reaction of **8** with 3-chlorobenzaldehyde, reaction temp. – 70 °C; time – 2 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and the precipitate was filtered off, washed with water and dried. The crude product was purified on silica gel column in acetone, and crystallized from cyclohexane to give 5-[3-(3'-chlorophenyl)acryolyl]-6-[2-(diethylamino)ethoxy]benzo-[1,3]oxathiol-2-one (**37**) as an yellow solid, yield 56 %, mp 107 - 109 °C.

Anal. Calcd for $C_{22}H_{22}ClNO_4S$: C, 61.18; H, 5.13; N, 3.24; S, 7.42. Found: C, 59.99; H, 5.01; N, 3.12; S, 7.31.

IR (KBr) (cm^{-1}): 1763, 1610, 1568, 1512, 1255, 1182, 1007.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.96 (s, 1 H, H-4), 7.85 (bs, 1 H, H-2'), 7.72 (d, 1 H, *J* = 6.8 Hz, H-6'), 7.62 (d, 1 H, *J* = 16.1 Hz, H-β), 7.54 (d, 1 H, *J* = 16.1 Hz, H-α), 7.40 – 7.51 (m 3 H, H-4', H-5', H-7), 4.19 (t, 2 H, *J* = 5.8 Hz, OCH_2), 2.74 (d, 2 H, *J* = 5.8 Hz, NCH_2), 2.46 (q, 4 H, *J* = 6.8 Hz, 2 x CH_2), 0.85 (t, 6 H, *J* = 6.8 Hz, 2 x CH_3).

6-[2-(Diethylamino)ethoxy]-5-[3-(4'-methoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**38**)

Reaction of **8** with 4-methoxybenzaldehyde, reaction temp. – 70 °C; time – 2 h. The cooled mixture was poured into saturated aqueous solution of sodium bicarbonate and the precipitate was filtered off, washed with water and dried. The crude product was purified on silica gel column in acetone, and crystallized from cyclohexane to give 6-[2-(diethylamino)ethoxy]-5-[3-(4'-methoxy)phenylacryolyl]benzo-[1,3]oxathiol-2-one (**38**) as an yellow solid, yield 60 %, mp 106 – 109 °C.

Anal. Calcd for $C_{23}H_{25}NO_5S$: C, 64.62; H, 5.89; N, 3.28; S, 7.50. Found: C, 64.49; H, 5.81; N, 3.13; S, 7.36.

IR (KBr) (cm^{-1}): 1767, 1749, 1611, 1268, 1187, 1031, 995.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.91 (s, 1 H, H-4), 7.71 (d, 2 H, *J* = 8.5 Hz, H-2', H-6'), 7.53 (d, 1 H, *J* = 15.8 Hz, H-β), 7.46 (s, 1 H, H-7), 7.39 (d, 1 H, *J* = 15.8 Hz, H-α), 6.99 (d, 2 H, *J* = 8.5 Hz, H-3', H-5'), 4.17 (t, 2 H, *J* = 5.8 Hz, OCH_2), 3.81 (s, 3 H, OCH_3), 2.74 (t, 2 H, *J* = 5.8 Hz, NCH_2), 2.47 (q, 4 H, *J* = 7.3 Hz, 2 x CH_2), 0.86 (t, 6 H, *J* = 7.3 Hz, 2 x CH_3).

General procedure for condensation of acetylbenzo[1,3]oxathiol-2-ones containing allyl group (11, 14) with benzaldehydes

2-Oxo-benz[1,3]oxathiole derivative (**11** or **14**) (1 mmol), suitable benzaldehyde (2 mmol) and conc. sulfuric acid (traces) in AcOH (2 - 3 mL) were stirred at 60 - 100 °C until completion of the reaction (2 - 20 h). The cooled mixture was usually diluted with MeOH or water, and the precipitate was filtered off or extracted, washed with water and purified as given for particular compounds.

5-(Allyloxy)-6-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**29**)

Reaction of **11** with benzaldehyde, reaction temp. – 70 °C; time – 3 h. The cooled mixture was diluted with water and the precipitate was filtered off. The crude product was purified on silica gel column in CH_2Cl_2 – cyclohexane (2 : 1) solution, and crystallized from 2-methoxyethanol to give 5-(allyloxy)-6-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**29**) as a cream solid, yield 15 %, mp 155 – 156 °C.

Anal. Calcd for $C_{19}H_{14}O_4S$: C, 67.44; H, 4.17; S, 9.48. Found: C, 67.33; H, 4.05; S, 9.24.

IR (KBr) (cm^{-1}): 1754, 1648, 1588, 1419, 1169, 1086.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.71 – 7.75 (m, 2 H, H-2', H-6'), 7.70 (s, 1 H, H-7), 7.61 (s, 1 H, H-4), 7.57 (d, 1 H, J = 16.1 Hz, H-β), 7.47 (1 H, partly under the next multiplet, H-α), 7.42 – 7.46 (m, 3 H, H-3', H-4', H-5'), 5.98 – 6.07 (m, 1 H, -HC=), 5.40 (dd, 1 H, J_1 = 17.1 Hz, J_2 = 1.5 Hz, =CH_2), 5.22 (dd, 1 H, J_1 = 10.7 Hz, J_2 = 1.5 Hz, =CH_2), 4.68 (d, 2 H, J = 4.9 Hz, OCH_2).

5-(Allyloxy)-6-[3-(4'-bromophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**30**)

Reaction of **11** with 4-bromobenzaldehyde, reaction temp. – 70 °C; time – 3 h. The cooled mixture was diluted with water and the precipitate was filtered off, and washed with MeOH. The crude product was purified on silica gel column in CH_2Cl_2 – cyclohexane (1 : 1) solution to give 5-(allyloxy)-6-[3-(4'-bromophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**30**) as an yellow solid, yield 23 %, mp 179 – 180 °C.

Anal. Calcd for $C_{19}H_{13}BrO_4S$: C, 54.69; H, 3.14; S, 7.68. Found: C, 54.47; H, 3.26; S, 7.47.

IR (KBr) (cm^{-1}): 1771, 1648, 1612, 1581, 1414.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.70 (s, 1 H, H-7), 7.69 (d, 2 H, partly under H-7, H-2', H-6'), 7.64 (d, 2 H, J = 8.8 Hz, H-3', H-5'), 7.61 (s, 1 H, H-4), 7.55 (d, 1 H, J = 16.1 Hz, H-β), 7.48 (d, 1 H, J = 16.1 Hz, H-α), 5.96 – 6.06 (m, 1 H, -HC=), 5.38 (d, 1 H, J = 17.6 Hz, =CH_2), 5.22 (d, 1 H, J = 10.7 Hz, =CH_2), 4.66 (d, 2 H, J = 4.9 Hz, OCH_2).

5-(Allyloxy)-6-[3-(3'-chlorophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**31**)

Reaction of **11** with 3-chlorobenzaldehyde, reaction temp. – 70 °C; time – 3 h. The cooled mixture was diluted with water and the precipitate was filtered off, and washed with MeOH. The crude product was purified on silica gel column in CH_2Cl_2 – cyclohexane (2 : 1) solution and crystallized from 2-methoxyethanol to give 5-(allyloxy)-6-[3-(3'-chlorophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**31**) as a cream solid, yield 15 %, mp 130 – 132 °C.

Anal. Calcd for $C_{19}H_{13}ClO_4S$: C, 61.21; H, 3.51; S, 8.60. Found: C, 61.09; H, 3.37; S, 8.48.

IR (KBr) (cm^{-1}): 1772, 1656, 1592, 1421, 1090.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.84 (bs, 1 H, H-2'), 7.71 (m, 2 H, H-6', H-7), 7.62 (s, 1 H, H-4), 7.56 (d, 1 H, J = 16.6 Hz, H-β), 7.53 (d, 1 H, J = 16.6 Hz, H-α), 7.50 (bd, 1 H, J = 8.3 Hz, H-4'), 7.46 (t, 1 H, J = 7.9 Hz, H-5'), 5.98 – 6.08 (m, 1 H, -HC=), 5.40 (dd, 1 H, J_1 = 17.6 Hz, J_2 = 1.4 Hz, =CH_2), 5.23, (dd, 1 H, J_1 = 10.7 Hz, J_2 = 1.4 Hz, =CH_2), 4.68 (d, 2 H, J = 4.9 Hz, OCH_2).

5-(Allyloxy)-6-[3-(4'-nitrophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**32**)

Reaction of **11** with 4-nitrobenzaldehyde, reaction temp. – 70 °C; time – 3 h. The cooled mixture was diluted with water and the precipitate was filtered off, and washed with MeOH. The crude product was purified on silica gel column in CH_2Cl_2 – cyclohexane (1 : 1) solution and crystallized from 2-methoxyethanol to give 5-(allyloxy)-6-[3-(4'-nitrophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**32**) as an yellow solid, yield 26 %, mp 159 – 162 °C.

Anal. Calcd for $C_{19}H_{13}NO_6S$: C, 59.52; H, 3.42; N, 3.65; S, 8.36. Found: C, 59.38; H, 3.31; N, 3.58; S, 8.21.

IR (KBr) (cm^{-1}): 1773, 1613, 1516, 1422, 1350, 1085.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.27 (d, 2 H, J = 8.8 Hz, H-3', H-5'), 8.01 (d, 2 H, J = 8.8 Hz, H-2', H-6'), 7.73 (s, 1 H, H-7), 7.68 (d, 1 H, J = 16.3 Hz, H-β), 7.64 (d, 1 H, J = 16.3 Hz, H-α), 7.64 (s, 1 H, H-4), 5.98 – 6.07 (m, 1 H, -HC=), 5.39 (dd, 1 H, J_1 = 17.1 Hz, J_2 = 1.5 Hz, =CH_2), 5.23, (dd, 1 H, J_1 = 10.7 Hz, J_2 = 1.5 Hz, =CH_2), 4.68 (d, 2 H, J = 4.9 Hz, OCH_2).

5-(Allyloxy)-6-[3-(4'-methoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**33**)

Reaction of **11** with 4-methoxybenzaldehyde, reaction temp. – 70 °C; time – 3 h. The cooled mixture was diluted with water and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), and evaporated. The residue was purified on silica gel column in CH_2Cl_2 – cyclohexane (1 : 1) solution and crystallized from 2-methoxyethanol to give 5-(allyloxy)-6-[3-(4'-methoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**33**) as an yellow solid, yield 21 %, mp 166 - 169 °C.

Anal. Calcd for $C_{20}H_{16}O_5S$: C, 65.20; H, 4.38; S, 8.70. Found: C, 65.01; H, 4.33; S, 8.59.

IR (KBr) (cm^{-1}): 1747, 1584, 1509, 1421, 1249, 1146.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.69 (d, 2 H, J = 8.8 Hz, H-2', H-6'), 7.69 (s, 1 H, H-7), 7.58 (s, 1 H, H-4), 7.53 (d, 1 H, J = 15.8 Hz, H-β), 7.31 (d, 1 H, J = 15.8 Hz, H-α), 7.00 (d, 2 H, J = 8.8 Hz, H-3', H-5'), 5.98 – 6.06 (m, 1 H, -HC=), 5.40 (dd, 1 H, J_1 = 17.1 Hz, J_2 = 1.4 Hz, =CH_2), 5.23, (dd, 1 H, J_1 = 10.7 Hz, J_2 = 1.4 Hz, =CH_2), 4.66 (d, 2 H, J = 4.9 Hz, OCH_2), 3.80 (s, 3 H, OCH_3).

5-(Allyloxy)-6-[3-(3',4'-dimethoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**34**)

Reaction of **11** with 3,4-dimethoxybenzaldehyde, reaction temp. – 70 °C; time – 3 h. The cooled mixture was diluted with water and extracted with EtOAc. The organic layer was washed with water and brine, dried (magnesium sulfate), and evaporated. The residue was purified on silica gel column in $CHCl_3$ – cyclohexane (2 : 1) solution and crystallized from 2-methoxyethanol to give 5-(allyloxy)-6-[3-(3',4'-dimethoxyphenyl)acryolyl]benzo[1,3]oxathiol-2-one (**34**) as an yellow solid, yield 16 %, mp 160 - 163 °C.

Anal. Calcd for $C_{21}H_{18}O_6S$: C, 63.30; H, 4.55; S, 8.05. Found: C, 63.13; H, 4.32; S, 7.91.

IR (KBr) (cm^{-1}): 1753, 1562, 1514, 1420, 1275, 1142. 1022.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.69 (s, 1 H, H-7), 7.58 (s, 1 H, H-4), 7.50 (d, 1 H, J = 16.1 Hz, H-β), 7.36 (d, 1 H, J = 16.1 Hz, H-α), 7.33 (s, 1 H, H-2'), 7.29 (dd, 1 H, J_1 = 8.3 Hz, J_2 = 1.9 Hz, H-6'), 7.01 (d, 1 H, J = 8.3 Hz, H-5'), 5.98 – 6.07 (m, 1 H, -HC=), 5.40 (dd, 1 H, J_1 = 17.1 Hz, J_2 = 1.5 Hz, =CH_2), 5.22, (dd, 1 H, J_1 = 10.7 Hz, J_2 = 1.5 Hz, =CH_2), 4.66 (d, 2 H, J = 4.9 Hz, OCH_2), 3.81 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3).

6-(Allyloxy)-5-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**39**)

Reaction of **14** with benzaldehyde, reaction temp. – 70 °C; time – 2 h. The mixture was cooled and the precipitate was filtered off, and washed with water. The crude product was purified on silica gel column in $CHCl_3$ – cyclohexane (2 : 1) solution, and crystallized from 2-methoxyethanol to give 6-(allyloxy)-5-(3-phenylacryolyl)benzo[1,3]oxathiol-2-one (**39**) as a cream solid, yield 20 %, mp 130 – 134 °C.

Anal. Calcd for $C_{19}H_{14}O_4S$: C, 67.44; H, 4.17; S, 9.48. Found: C, 67.39; H, 4.11; S, 9.34.

IR (KBr) (cm^{-1}): 1756, 1610, 1267, 1190.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.96 (s, 1 H, H-4), 7.73 (m, 2 H, H-2', H-6'), 7.59 (d, 1 H, J = 16.0 Hz, H-β), 7.40 – 7.48 (m, 5 H, H-α, H-3', H-4', H-5', H-7), 5.92 – 6.14 (m, 1 H, -HC=), 5.40 (dd, 1 H, J_1 = 17.2 Hz, J_2 = 1.8 Hz, =CH_2), 5.22 (dd, 1 H, J_1 = 10.2 Hz, J_2 = 1.8 Hz, =CH_2), 4.74 (d, 2 H, J = 4.8 Hz, OCH_2).

6-(Allyloxy)-5-[3-(4'-bromophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**40**)

Reaction of **14** with 4-bromobenzaldehyde, reaction temp. – 70 °C; time – 2 h. The cooled mixture was diluted with water and the precipitate was filtered off, and washed with water and EtOH. The crude product was crystallized from $CHCl_3$ to give 6-(allyloxy)-5-[3-(4'-bromophenyl)-acryolyl]benzo[1,3]oxathiol-2-one (**40**) as a colorless solid, yield 35 %, mp 197 – 200 °C.

Anal. Calcd for $C_{19}H_{13}BrO_4S$: C, 54.69; H, 3.14; S, 7.68. Found: C, 54.60; H, 3.11; S, 7.59.

IR (KBr) (cm^{-1}): 1758, 1666, 1611, 1189, 1016.

^{1}H NMR (500 MHz, acetone-d_6): δ = 7.53 (s, 1 H, H-4), 7.25 (d, 2 H, J = 7.8 Hz, H-2', H-6'), 7.20 (d, 2 H, J = 7.8 Hz, H-3', H-5'), 7.11 (d, 1 H, J = 19.0 Hz, H-β), 7.05 (d, 1 H, partly under H-7, H-α), 7.03 (s, 1 H, H-7), 5.52 – 5.64 (m, 1 H, -HC=), 4.95 (d, 1 H, J = 17.1 Hz, =CH_2), 4.78 (d, 1 H, J = 10.7 Hz, =CH_2), 4.29 (s, 2 H, OCH_2).

6-(Allyloxy)-5-[3-(2'-chlorophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**41**)

Reaction of **14** with 2-chlorobenzaldehyde, reaction temp. – 70 °C; time – 2 h. The mixture was cooled and the precipitate was filtered off, washed with AcOH, and crystallized from 2-methoxyethanol to give 6-(allyloxy)-5-[3-(3'-chlorophenyl)acryolyl]benzo[1,3]oxathiol-2-one (**41**) as a cream solid, yield 45 %, mp 173 – 175 °C.

Anal. Calcd for $C_{19}H_{13}ClO_4S$: C, 61.21; H, 3.51; S, 8.60. Found: C, 61.10; H, 3.45; S, 8.53.

IR (KBr) (cm^{-1}): 1760, 1662, 1609, 1270, 1191.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.03 (s, 1 H, H-4), 7. 96 (m, 1 H, H-6'), 7.88 (d, 1 H, J = 16.2 Hz, H-β), 7.40 – 7.63 (m, 5 H, H-α, H-3', H-4', H-5', H-7), 5.95 – 6.17 (m, 1 H, -HC=), 5.42 (dd, 1 H, J_1 = 17.3 Hz, J_2 = 1.6 Hz, =CH_2), 5.25, (dd, 1 H, J_1 = 10.6 Hz, J_2 = 1.6 Hz, =CH_2), 4.78 (d, 2 H, J = 5.1 Hz, OCH_2).

Synthesis of di[3-chloro-2'-(N,N-diethylamino)ethoxy-5'-hydroxychalcone-4'-yl] disulfide (42)

6-[3-(3'-Chlorophenyl)acryolyl]-5-[2-(diethylamino)ethoxy]benzo[1,3]oxathiol-2-one (**27**) (216 mg, 0.5 mmol) in MeOH (5 mL) was refluxed for 10 h. The solvent was evaporated and the residue separated on silica gel column in $CHCl_3$ – MeOH (3 : 1) solution. The yellow fraction was evaporated and crystallized from toluene to give di[3-chloro-2'-(N,N-diethylamino)ethoxy-5'-hydroxychalcone-4'-yl] disulfide (**42**) as an yellow solid, yield 59 mg (29 %), mp 142 – 144 ^{o}C.

MS MALDI TOF:. Calcd for $C_{19}H_{13}NO_4S$: M = 808.2. Found (809.2 (M + 1), 593.1, 549.2, 406.2.

IR (KBr) (cm^{-1}): 3287, 1649, 1603, 1572, 1408, 1199, 1176.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 10.3 (bs, 1 H, OH), 7.78 (bs, 1 H, H-2), 7.68 (d, 1 H, *J* = 7.8 Hz, H-6), 7.63 (d, 1 H, *J* = 16.1 Hz, H-β), 7.52 (d, 1 H, *J* = 16.1 Hz, H-α), 7.47 (bd, 1 H, *J* = 8.3 Hz, H-4), 7.43 (t, 1 H, *J* = 7.8 Hz, H-5), 7.22 (s, 1 H, H-6'), 7.10 (s, 1 H, H-3'), 3.97 (t, 2 H, *J* = 5.8 Hz, OCH_2), 2.62 (bs, 2 H, NCH_2), 2.37 (q, 4 H, *J* = 7.0 Hz, 2 x CH_2), 0.77 (t, 6 H, *J* = 7.0 Hz, 2 x CH_3).

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