

# Synthesis of sulfur-containing heterocyclic compounds by cyclocondensation of acetylenic derivatives of anthraquinone with sodium sulfide

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**Dedicated to Professor Boris A. Trofimov on the occasion of his 65<sup>th</sup> birthday**

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## Abstract

Reaction of *vic*-alkynylchloro- and *vic*-chloro-(1-oxoalk-2-ynyl)-anthraquinones with Na<sub>2</sub>S in ethanol, with short heating, has been shown to afford anthrathiophenediones and anthrathiopyrantriones, respectively, generally in good yields. Under the same conditions, 1-alkynylantraquinones also undergo cyclocondensation to give anthra[2,1-*b*]thiophene-6,11-diones.

**Keywords:** Acetylenic derivatives of anthraquinone, cyclocondensation, anthrathiophenediones, anthrathiopyrantriones

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## Introduction

Condensed heterocyclic derivatives of quinones are of interest as biologically active substances and technical materials. A variety of such nitrogen- and oxygen- containing heterocycles has been described. There is much less information about sulfur- containing heterocyclic quinoid compounds. At the same time, the introduction of sulfur- containing rings into the structure of compounds often determines their pharmacological properties,<sup>1-3</sup> reduces side-effects of drugs,<sup>4</sup> or improves the technical characteristics of materials.<sup>5,6</sup> Thus, substituted benzo[*b*]thiophenes are estrogen-receptor modulators, thrombin inhibitors, anti-tumor and anti-inflammation agents.<sup>1,2,7,8</sup> Some of them are currently in pharmaceutical use or development.<sup>7,8</sup>

In this connection, we considered it reasonable to study synthetic pathways to anthraquinones annelated by thiophene and other sulfur- containing rings. To our knowledge, general methods for the synthesis even of anthrathiophenediones have not been described. Earlier we reported the synthesis of a number of condensed N- and O- heterocyclic quinoid

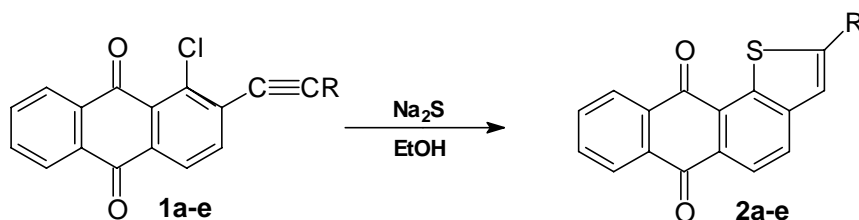
systems based on acetylenic derivatives of quinones as key precursors.<sup>9-18</sup> One would expect that the same “acetylenic” approach will turn out to be fruitful for the construction of an anthrathiophene system as well.

Recently, a method for synthesis of substituted benzo[*b*]thiophenes by cyclization of *ortho*-methylthio- and *ortho*-benzylthio(alkynyl)benzenes under the action of electrophilic agents was elaborated.<sup>1,19,20</sup> However, its expansion to derivatives of anthraquinone is complicated by the limited availability of the corresponding sulfides. Other methods of formation of benzothiophenes from acetylenic precursors are not sufficiently general.<sup>21-24</sup>

## Results and Discussion

In anthraquinone, a chlorine atom, irrespective of its position, possesses a high nucleofugal lability.<sup>25</sup> The triple bond in acetylenic derivatives of quinones has an enhanced electrophilicity and readily adds nucleophiles.<sup>26</sup> When a halogen atom and an acetylenic substituent are arranged in the same ring of anthraquinone, they mutually activate each other. We supposed that the above chemical peculiarities of these anthraquinone derivatives would make it possible to annelate the anthraquinone nuclei with a thiophene ring by using *vic*-alkynylchloroanthraquinones as key acetylenes and Na<sub>2</sub>S as the simplest cyclizing agent.

Indeed, 2-alkynyl-1-chloroanthraquinones **1a-e** did react with an excess of Na<sub>2</sub>S in 95% ethanol at reflux for 10–20 min to give anthra[1,2-*b*]thiophene-6,11-diones **2a-e** in 57–90 % yields.

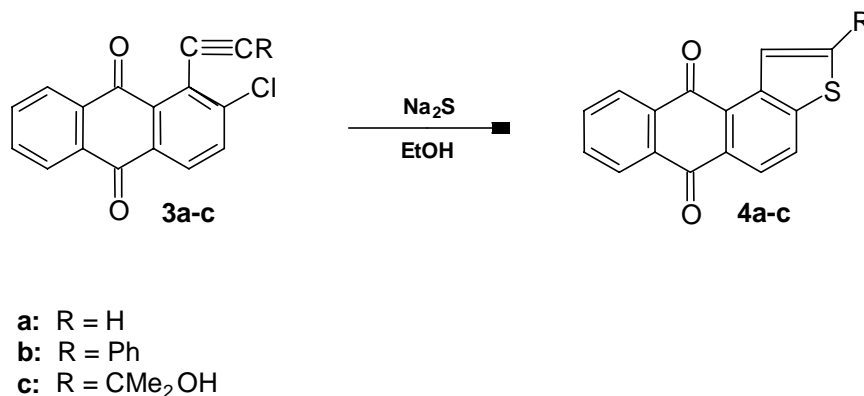


**a:** R = H  
**b:** R = Ph  
**c:** R = CMe<sub>2</sub>OH

**d:** R = CH(OH)Pr - *i*  
**e:** R = CH<sub>2</sub>OH

### Scheme 1

The 1-alkynyl-2-chloroanthraquinones **3a-c** bearing the halogen atom in position 2 were condensed with Na<sub>2</sub>S in the same way as the chloroacetylenes **1**, and under the same conditions.



## Scheme 2

The yields of the anthra[2,1-*b*]thiophene-6,11-diones **4a–c** were 66–97 %. It is noteworthy that in the <sup>1</sup>H NMR spectra of the anthrathiophenediones **4** the signal of the proton in the β-position of the thiophene ring, which is brought together spatially with the carbonyl group, is shifted to a lower field relative to that of the similar proton in spectra of compounds **2** (Δ δ 1.3–1.4 ppm).

Thus, the cyclocondensation of *vic*-alkynylchloroanthraquinones with Na<sub>2</sub>S is a simple and convenient method for synthesis of angularly fused anthrathiophenediones.

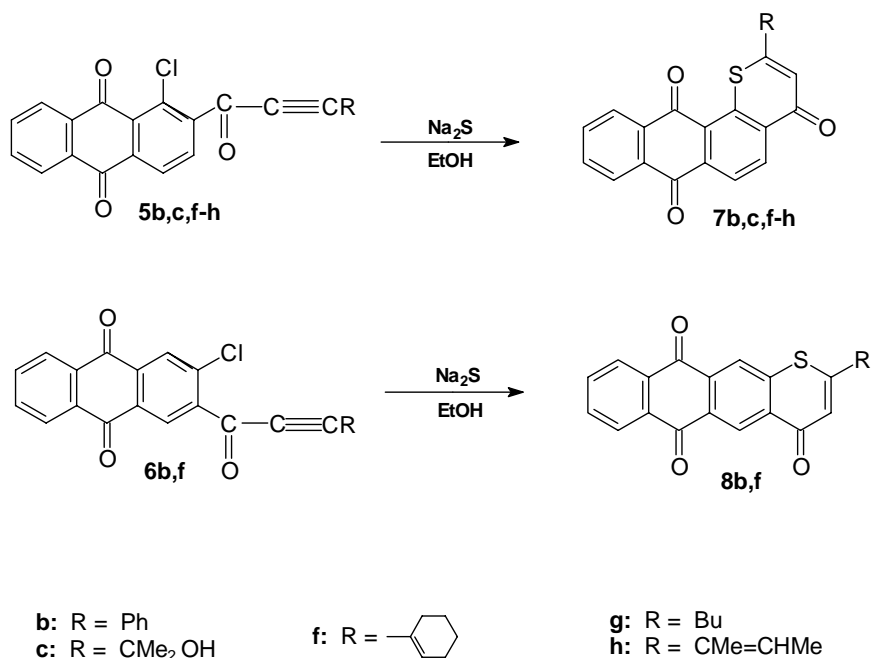
We also applied the cyclocondensation under consideration to annelate anthraquinone with a thiopyran ring. In this case, the 1-chloro-2-(1-oxoalk-2-ynyl)anthraquinones **5b,c,f–h** and the 2-chloro-3-(1-oxoalk-2-ynyl)anthraquinones **6b,f** were used as the acetylenic precursors. These compounds have, like the chloroacetylenes **1,3**, the activated halogen atom and triple bond. Their condensation with Na<sub>2</sub>S proceeds under the same conditions as that of compounds **1,3** and affords the anthra[1,2-*b*]thiopyran-4,7,12-triones **7b,c,f–h** and the anthra[2,3-*b*]thiopyran-4,6,11-triones **8b,f**, respectively, in 68–94 % yields. It is essential to note that the possible competitive cyclization with closure to a 5-membered ring is not observed.

The 4*H*- anthra[1,2-*b*]pyran system provides the cyclic skeleton of the aglycones of the kidamycin group and their biologically active analogs, which are obtained biochemically.<sup>27,28</sup> The synthesized **7b,c,f–h** are thio- analogs of these compounds.

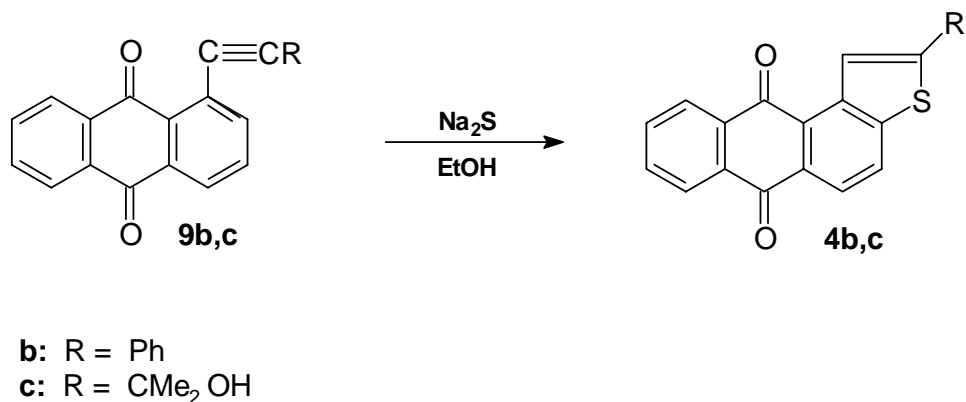
In the synthesis of the kidamycin antibiotics there is a problem in the construction of the heterocycle bearing chemically sensitive substituents (alkenyl, epoxy, etc.).<sup>27</sup> Our cyclocondensation, owing to its mild conditions, gives an opportunity to prepare anthrathiopyrantriones with such labile substituents. The preparation of the alkenylthiopyran **7h** (a mixture of *Z*- and *E*- isomers) from the labile ketone **5h**, as well as of the cyclohexenylthiopyran **7f** demonstrates the applicability of the developed method for the synthesis of thio-analogs of aglycones of anthrapyrane antibiotics.

The initial step of the cyclocondensation of *vic*- acetylenic derivatives of chloroanthraquinones may be not only the substitution of the chlorine atom but also the addition of Na<sub>2</sub>S to the triple bond. However, the intramolecular addition of Na<sub>2</sub>S, or other S-

nucleophiles to alkynylquinones has not been studied. To confirm the possibility of a cyclocondensation pathway beginning with the addition of the cyclizing agent, we carried out the reaction of the 1-alkynylantraquinones **9b,c** with  $\text{Na}_2\text{S}$  under the conditions of the cyclocondensation. The acetylenes **9b,c** were found to react with  $\text{Na}_2\text{S}$ , but the reaction was not limited to the addition of this nucleophile, and was followed by cyclization of the primary adducts to result in the formation of anthra[2,1-*b*]thiophene-6,11-diones **4b,c** prepared before from the chloroacetylenes **3b,c**. The cyclization step of the process seems to be an intramolecular nucleophilic oxidative substitution of the hydrogen atom, the quinone being the oxidant.



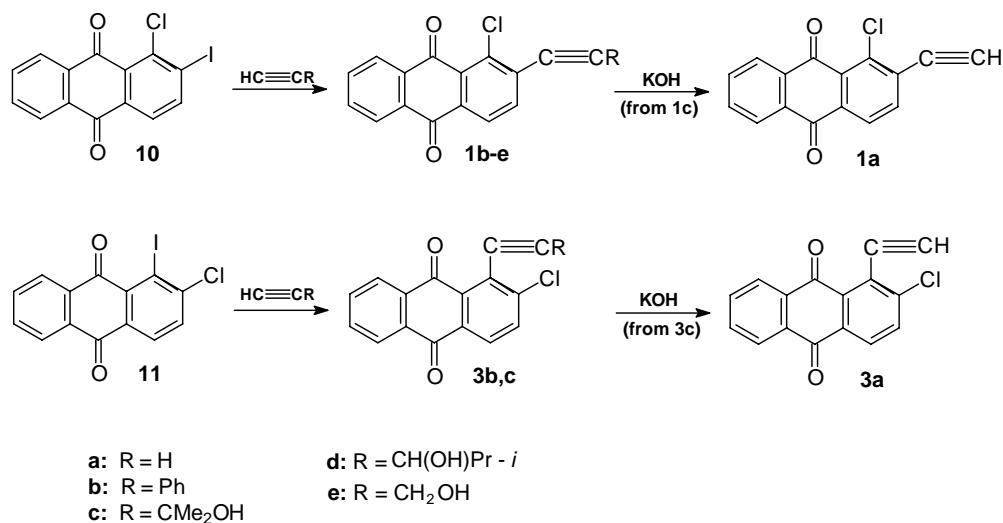
Scheme 3



Scheme 4

The yields of the anthrathiophenediones **4b,c** were 95 %. Our study of the scope and peculiarities of this reaction is in progress.

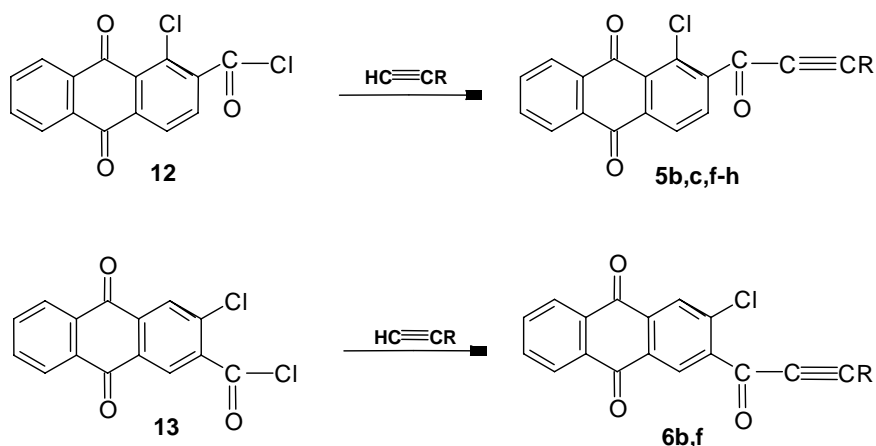
The key chloroacetylenes **1b–e** and **3c** were prepared by cross-coupling of 1-chloro-2-iodoanthraquinone **10** and 2-chloro-1-iodoanthraquinone **11** with the corresponding terminal acetylenes in aqueous dioxane in the presence of  $\text{Na}_2\text{CO}_3$ ,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  and  $\text{CuI}$  in 47–85 % yields. We consider this cross-coupling procedure<sup>12,29</sup> to be the best method for the introduction of acetylenic substituents into quinones. The chloroethynylantraquinones **1a**, **3a** were synthesized from the tertiary acetylenic alcohols **1c**, **3c** by the retro-Favorsky reaction.<sup>29</sup> 2-Chloro-1-phenylethynylantraquinone **3b** was prepared as described earlier.<sup>26</sup>



### Scheme 5

The acetylenic ketones **5b,c,f–h** and **6b,f** were synthesized by acylation of terminal acetylenes with 1-chloroanthraquinonoyl 2-chloride **12** and 2-chloroanthraquinonoyl 3-chloride **13**, respectively, in a system of  $\text{NEt}_3$ – $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ – $\text{CuI}$ –benzene<sup>30</sup> in 49–76 % yields. For the preparation of the vinylacetylenic ketone **5h**, a mixture of geometric isomers of 3-methylpent-3-en-1-yne containing  $\approx 70\%$  of *Z*- isomer was used.

In summary, we have shown that condensation of *vic*- acetylenic derivatives of chloroanthraquinones with  $\text{Na}_2\text{S}$  offers a synthetic pathway to anthraquinones annelated by thiophene and thiopyran rings.



Scheme 6

## Experimental Section

### General procedure for the preparation of *vic*-alkynyl-chloroanthraquinones

**1-Chloro-2-phenylethynylantraquinone (1b).** 1-Chloro-2-iodoanthraquinone **10** (1.90 g, 5.1 mmol) was dissolved in 60 mL of dioxane at 60–70°C under an atmosphere of Ar, and then were added successively phenylacetylene (0.80 g, 0.85 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.040 g), CuI (0.040 g) and 30 mL of aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (0.70 g, 6.6 mmol) heated beforehand to 70–80°C. The mixture was heated at reflux with stirring for 15 min. After complete consumption of the starting iodide **10** (monitoring by TLC), the mixture was cooled, diluted with 200 mL of CHCl<sub>3</sub> and washed with water. The solvent was evaporated under reduced pressure, the residue purified by flash chromatography on silica gel using toluene as the eluent, and recrystallized from toluene–hexane to give 1-chloro-2-phenylethynylantraquinone **1b** (1.50 g, 85 %), m.p. 193.5–194°C.<sup>26</sup>

**1-Chloro-2-(3-hydroxy-3-methylbutynyl)anthraquinone (1c).** The cross-coupling was carried out by the general procedure with 1-chloro-2-iodoanthraquinone **10** (2.50 g, 6.8 mmol) and 3-methylbut-1-yn-3-ol (0.72 g, 0.85 mmol) in 100 mL of dioxane and 50 mL of water in the presence of Na<sub>2</sub>CO<sub>3</sub> (0.72g, 6.8 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.050 g), and CuI (0.025 g). The crude product was chromatographed on silica gel in a benzene–ether mixture to yield 1.84 g (84%) of 1-chloro-2-(3-hydroxy-3-methylbutynyl)anthraquinone **1c**; <sup>17</sup> m.p. 168–168.5°C; IR (CHCl<sub>3</sub>),  $\nu_{\text{max}}$ : 1690 (C=O), 2240 (C≡C), 3605 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.70 (s, 6H, Me), 7.83 (d, 1H, *J* = 8.1 Hz, H-3), 7.75–7.90 (m, 2H, H-6,7), 8.26 (d, 1H, *J* = 8.1 Hz, H-4), 8.20–8.35 (m, 2H, H-5,8); Anal. Calcd for C<sub>19</sub>H<sub>13</sub>O<sub>3</sub>Cl: C, 70.27; H, 4.03; Cl, 10.91. Found: C, 70.40; H, 3.95; Cl, 10.78%.

**1-Chloro-2-(4-methyl-3-hydroxypentynyl)anthraquinone (1d).** The cross-coupling was achieved by the general procedure with 1-chloro-2-iodoanthraquinone **10** (2.00 g, 5.4 mmol) and 4-methylpent-1-yn-3-ol (1.05 g, 10.8 mmol) in 80 mL of dioxane and 40 mL of water in the presence of Na<sub>2</sub>CO<sub>3</sub> (1.00 g, 9.4 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.060 g), and CuI (0.045 g) for 5 min. The yield of 1-chloro-2-(4-methyl-3-hydroxypentynyl)anthraquinone **1d**<sup>17</sup> was 0.87 g (47%); m.p. 160–161.5°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1690 (C=O), 2235 (C≡C), 3400 br., 3615 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.10 (d, 3H, *J* = 6.7 Hz, Me), 1.13 (d, 3H, *J* = 6.7 Hz, Me), 1.95–2.10 (m, 2H, CHMe<sub>2</sub>, OH), 4.45–4.55 (m, 1H, CHO), 7.75–7.85 (m, 2H, H-6,7), 7.83 (d, 1H, *J* = 8.0 Hz, H-3), 8.25 (d, 1H, *J* = 8.0 Hz, H-4), 8.25–8.35 (m, 2H, H-5,8); Anal. Calcd for C<sub>20</sub>H<sub>15</sub>O<sub>3</sub>Cl: C, 70.90; H, 4.46; Cl, 10.46. Found: C, 70.78; H, 4.46; Cl, 10.40%.

**1-Chloro-2-(3-hydroxypropynyl)anthraquinone (1e).** The reaction was carried out by the general procedure with 1-chloro-2-iodoanthraquinone **10** (0.74 g, 2.0 mmol) and propargyl alcohol (0.20 g, 3.57 mmol). The crude product in toluene was filtered through a layer of silica gel (2–3 cm) and crystallized from a toluene–hexane mixture to give 1-chloro-2-(3-hydroxypropynyl)anthraquinone **1e**<sup>17</sup> (0.28 g, 47%); m.p. 197.5–199°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1690 (C=O), 2240 (C≡C), 3400 br., 3620 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  4.67 (s, 2H, CH<sub>2</sub>), 7.75–7.90 (m, 3H, H-3,6,7), 8.20–8.30 (m, 3H, H-4,5,8); Anal. Calcd for C<sub>17</sub>H<sub>9</sub>O<sub>3</sub>Cl: C, 68.82; H, 3.06; Cl, 11.95. Found: C, 68.66; H, 3.02; Cl, 11.79%.

**2-Chloro-1-(3-hydroxy-3-methylbutynyl)anthraquinone (3c).** The experiment was carried out by the general procedure with 1.80 g (4.9 mmol) of 2-chloro-1-iodo-anthraquinone **11** and 0.56 g (6.7 mmol) of 3-methylbut-1-yn-3-ol in 60 mL of dioxane and 30 mL of water in the presence of 0.32 g (3.0 mmol) of Na<sub>2</sub>CO<sub>3</sub>, 0.030 g of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 0.015 g of CuI. The crude product was purified by chromatography on silica gel using CHCl<sub>3</sub> as the eluent and recrystallized from a toluene–hexane mixture to yield 1.25 g (79 %) of 2-chloro-1-(3-hydroxy-3-methylbutynyl)-anthraquinone **3c**; m.p. 183.5–184.5°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1690 (C=O), 2240 (C≡C), 3400 br., 3615 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.76 (s, 6H, Me), 2.97 (brs, 1H, OH), 7.70–7.80 (m, 2H, H-6,7), 7.80 (d, 1H, *J* = 8.5 Hz, H-3), 8.20–8.30 (m, 2H, H-5,8), 8.20 (d, 1H, *J* = 8.5 Hz, H-4); Anal. Calcd for C<sub>19</sub>H<sub>13</sub>O<sub>3</sub>Cl: C, 70.27; H, 4.03; Cl, 10.92. Found: C, 70.20; H, 4.04; Cl, 11.03%.

**1-Chloro-2-ethynylantraquinone (1a).** 1-Chloro-2-(3-hydroxy-3-methylbutynyl)anthraquinone **1c** (1.45 g, 4.5 mmol) and powdered KOH (1.00 g, 17.9 mmol) in 100 mL of dry benzene were stirred at 80°C for 45 min and filtered. The product was isolated by column chromatography on Al<sub>2</sub>O<sub>3</sub> using toluene as the eluent and crystallized from a toluene–hexane mixture. The yield of 1-chloro-2-ethynylantraquinone **1a** was 0.90 g (73%); m.p. 211–212°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1690 (C=O), 2130 (C≡C), 3310 (C≡CH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  3.67 (s, 1H, HC≡C), 7.75–7.90 (m, 2H, H-6,7), 7.91 (d, 1H, *J* = 8.1 Hz, H-3), 8.20–8.35 (m, 2H, H-5,8), 8.28 (d, 1H, *J* = 8.1 Hz, H-4); Anal. Calcd for C<sub>16</sub>H<sub>7</sub>O<sub>2</sub>Cl: C, 72.06; H, 2.65; Cl, 13.29. Found: C, 71.98; H, 2.84; Cl, 13.09%.

**2-Chloro-1-ethynylantraquinone (3a).** The retro-Favorsky reaction with 2-chloro-1-(3-hydroxy-3-methylbutynyl)anthraquinone **3c** (1.83 g, 5.6 mmol) and powdered KOH (0.97 g,

17.3 mmol) in 200 mL of benzene (80°C, 20 min), isolation and purification of the product were carried out as described for **1a**, to give 2-chloro-1-ethynylantraquinone **3a** (0.47 g, 31 %); m.p. 244–245°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1690 (C=O), 2120 (C≡C), 3320 (C≡CH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  3.97 (s, 1H, HC≡C), 7.70–7.90 (m, 2H, H-6,7), 7.87 (d, 1H, *J* = 8.4 Hz, H-3), 8.25–8.45 (m, 2H, H-5,8), 8.27 (d, 1H, *J* = 8.4 Hz, H-4); Anal. Calcd for C<sub>16</sub>H<sub>7</sub>O<sub>2</sub>Cl: C, 72.06; H, 2.65; Cl, 13.29. Found: C, 72.18; H, 2.59; Cl, 13.26%.

### General procedure for acylation

**1-Chloro-2-(1-oxo-3-phenylpropynyl)anthraquinone (5b).** To a solution of 1-chloroanthraquinonoyl-2-chloride **12** 1.00 g (3.3 mmol), prepared by refluxing 1-chloroanthraquinone-2-carboxylic acid with SOCl<sub>2</sub> for 4 h, in 50 mL of dry benzene under Ar, were added Et<sub>3</sub>N (1.1 g, 11.0 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.040 g), CuI (0.040 g) and phenylacetylene (0.56 g, 5.5 mmol). The reaction mixture was stirred at r.t. for 20 min, diluted with 300 mL of CHCl<sub>3</sub>, washed with water, dried over MgSO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel in toluene and crystallized from a toluene–hexane mixture to yield 0.85 g (70 %) of 1-chloro-2-(1-oxo-3-phenylpropynyl)anthraquinone **5b**; m.p. 183–183.5°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1670, 1690 (C=O), 2205 (C≡C) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.35–7.55 (m, 3H, 3HPh), 7.60–7.70 (m, 2H, 2HPh), 7.75–7.90 (m, 2H, H-6,7), 8.05 (d, 1H, *J* = 7.9 Hz, H-3), 8.25–8.35 (m, 2H, H-5,8), 8.41 (d, 1H, *J* = 7.9 Hz, H-4); Anal. Calcd for C<sub>23</sub>H<sub>11</sub>O<sub>3</sub>Cl: C, 74.50; H, 2.99; Cl, 9.56. Found: C, 74.48; H, 3.14; Cl, 9.65%.

**1-Chloro-2-(4-hydroxy-4-methyl-1-oxo-pentynyl)anthraquinone (5c).** The reaction of 1-chloro-anthraquinonoyl-2 chloride **12** (0.37g, 1.2 mmol) with 3-methylbut-1-yn-3-ol (0.22 g, 2.6 mmol) in 25 mL of benzene in the presence of Et<sub>3</sub>N (0.36 g, 3.6 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.015 g), CuI (0.015 g) was carried out by the general procedure to afford 1-chloro-2-(4-hydroxy-4-methyl-1-oxo-pentynyl)anthraquinone **5c** (0.28 g, 65%); m.p. 145–146.5°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1670, 1690 (C=O), 2225 (C≡C), 3400 br., 3610 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.62 (s, 6H, Me), 2.20 (brs, 1H, OH), 7.75–7.85 (m, 2H, H-6,7), 7.94 (d, 1H, *J* = 8.0 Hz, H-3), 8.20–8.30 (m, 2H, H-5,8), 8.35 (d, 1H, *J* = 8.0 Hz, H-4); Anal. Calcd for C<sub>20</sub>H<sub>13</sub>O<sub>4</sub>Cl: C, 68.09; H, 3.71; Cl, 10.05. Found: C, 68.23; H, 3.89; Cl, 10.08%.

**1-Chloro-2-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone (5f).** The experiment was carried out by the general procedure with 1-chloroanthraquinonoyl-2 chloride **12** (1.50 g, 4.9 mmol) and 1-ethynylcyclohexene (0.93 g, 8.8 mmol) in 70 mL of benzene in the presence of Et<sub>3</sub>N (1.6 g, 15.7 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.050 g), CuI (0.050 g). The yield of 1-chloro-2-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone **5f** was 1.15 g (63%); m.p. 168–169°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1670, 1690 (C=O), 2195 (C≡C) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.45–1.75 (m, 4H, 4', 5'-CH<sub>2</sub>), 2.10–2.30 (m, 4H, 3', 6'-CH<sub>2</sub>), 6.55–6.60 (m, 1H, 2'-CH), 7.75–7.90 (m, 2H, H-6,7), 7.95 (d, 1H, *J* = 8.0 Hz, H-3), 8.20–8.35 (m, 2H, H-5,8), 8.36 (d, 1H, *J* = 8.0 Hz, H-4); Anal. Calcd for C<sub>23</sub>H<sub>15</sub>O<sub>3</sub>Cl: C, 73.70; H, 4.03; Cl, 9.46. Found: C, 73.80; H, 4.19; Cl, 9.61%.



**1-Chloro-2-(1-oxohept-2-ynyl)anthraquinone (5g).** The acylation was performed by the general procedure with 1-chloroanthraquinonoyl-2 chloride **12** (0.40 g, 1.3 mmol) and 1-hexyne (0.18 g, 2.2 mmol) to result in 1-chloro-2-(1-oxohept-2-ynyl)anthraquinone **5g** (0.30 g, 65 %); m.p. 130–130.5°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1670, 1690 (C=O), 2220 (C≡C) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  0.92 (t, 3H,  $J = 7.2$  Hz, Me), 1.40–1.65 (m, 4H,  $\beta$ -,  $\gamma$ -CH<sub>2</sub>), 2.47 (t, 2H,  $J = 7.0$  Hz,  $\alpha$ -CH<sub>2</sub>), 7.75–7.85 (m, 2H, H-6,7), 7.94 (d, 1H,  $J = 8.0$  Hz, H-3), 8.20–8.30 (m, 2H, H-5,8), 8.36 (d, 1H,  $J = 8.0$  Hz, H-4); Anal. Calcd for C<sub>21</sub>H<sub>15</sub>O<sub>3</sub>Cl: C, 71.90; H, 4.31; Cl, 10.11. Found: C, 71.68; H, 4.22; Cl, 10.19%.

**1-Chloro-2-(4-methyl-1-oxohex-4-en-2-ynyl)anthraquinone (5h).** The reaction of 1-chloroanthraquinonoyl-2 chloride **12** (1.40g, 4.6 mmol) with a mixture of *Z*- and *E*-isomers of 3-methylpent-3-en-1-yne containing  $\approx 70$  % of *Z*-isomer (0.74 g, 9.2 mmol) in 135 mL of benzene in the presence of Et<sub>3</sub>N (1.3 g, 12.8 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.065 g), and CuI (0.065 g), was carried out for 10 min by the general procedure. The reaction mixture was filtered through a layer of silica gel, concentrated under reduced pressure, chromatographed on silica gel using toluene as the eluent and crystallized from a hexane–ether mixture to give 1-chloro-2-(4-methyl-1-oxo-hex-4-en-2-ynyl)anthraquinone **5h** (0.84 g, 52%); which was not sufficiently stable, and was used without further purification; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.75 (d, 3H,  $J = 7.0$  Hz, MeCH=C *E*-isomer), 1.87 (d, 3H,  $J = 7.0$  Hz, MeCH=C *Z*-isomer), 1.92 (brs, 3H, CH<sub>3</sub>-C=C *Z*-isomer), 1.95 (brs, 3H, CH<sub>3</sub>-C=C *E*-isomer), 6.10–6.20 (m, 1H, CH=C *Z*-isomer), 6.35–6.45 (m, 1H, CH=C *E*-isomer), 7.75–7.90 (m, 2H, H-6,7), 7.95 (d, 1H,  $J = 8.0$  Hz, H-3 *E*-isomer), 7.98 (d, 1H,  $J = 8.0$  Hz, H-3 *Z*-isomer), 8.20–8.35 (m, 2H, H-5,8), 8.37 (d, 1H,  $J = 8.0$  Hz, H-4 *E*-isomer), 8.38 (d, 1H,  $J = 8.0$  Hz, H-4 *Z*-isomer).

**2-Chloro-3-(1-oxo-3-phenylpropynyl)anthraquinone (6b).** Phenylacetylene (0.43 g, 4.2 mmol) was acylated by 2-chloroanthraquinonoyl-3 chloride **13** (0.65 g, 2.1 mmol), prepared by refluxing 2-chloroanthraquinone-3-carboxylic acid with SOCl<sub>2</sub> for 4 h, in 40 mL of dry benzene in the presence of Et<sub>3</sub>N (0.72 g, 7.1 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.020 g), and CuI (0.020 g) by the general procedure. The reaction mixture was diluted with hexane (60 mL), cooled and the precipitate was filtered off. It was dissolved in 150 mL of trichloroethene with heating and filtered through a layer of silica gel (3 cm). The solvent was evaporated under reduced pressure and the residue was crystallized from toluene to yield 0.60 g (76 %) of 2-chloro-3-(1-oxo-3-phenylpropynyl)anthraquinone **6b**; m.p. 232–233°C; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1670, 1690 (C=O), 2205 (C≡C) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.40–7.55 (m, 3H, 3HPh), 7.65–7.75 (m, 2H, 2HPh), 7.80–7.90 (m, 2H, H-6,7), 8.30–8.40 (m, 2H, H-5,8), 8.40 (s, 1H, H-1(4)), 8.97 (s, 1H, H-4(1)); Anal. Calcd for C<sub>23</sub>H<sub>11</sub>O<sub>3</sub>Cl: C, 74.50; H, 2.99; Cl, 9.56. Found: C, 74.68; H, 3.09; Cl, 10.06%.

**2-Chloro-3-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone (6f).** The experiment was performed by the general procedure with 2-chloroanthraquinonoyl-3 chloride **13** (0.58 g, 1.9 mmol) and 1-ethynylcyclohexene (0.35 g, 3.3 mmol). The crude product was isolated and purified as described above for **6b** to give 2-chloro-3-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone **6f** (0.35 g, 49 %); which was not sufficiently stable, and was used without further purification; ; IR (CHCl<sub>3</sub>),  $\nu_{\max}$ : 1680, 1690 (C=O), 2230 (C≡C) (CH<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H

NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.55–1.70 (m, 4H, 4', 5'-CH<sub>2</sub>), 2.20–2.35 (m, 4H, 3', 6'-CH<sub>2</sub>), 6.60–6.70 (m, 1H, 2'-CH), 7.80–7.90 (m, 2H, H-6,7), 8.30–8.40 (m, 2H, H-5,8), 8.35 (s, 1H, H-1(4)), 8.85 (s, 1H, H-4(1)).

### General procedure for cyclocondensation

**Anthra[1,2-*b*]thiophene-6,11-dione (2a).** To a suspension of Na<sub>2</sub>S (0.30 g, 3.8 mmol) in ethanol (35 mL) at heating ( $\approx$  60°C) was added 1-chloro-2-ethynylantraquinone **1a** (0.30 g, 1.1 mmol), then stirred at reflux for 15 min (monitoring by TLC). The mixture was poured into 300 mL of water and extracted with CHCl<sub>3</sub> (2 $\times$ 100 mL). The organic layer was washed with water, dried over MgSO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel in benzene and crystallized from a toluene–hexane mixture to yield 0.17 g (57 %) of anthra[1,2-*b*]thiophene-6,11-dione **2a**; m.p. 216–217°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.48 (d, 1H, *J* = 5.5 Hz, H-3), 7.90 (d, 1H, *J* = 5.5 Hz, H-2), 7.75–7.85 (m, 2H, H-8,9), 8.18 (d, 1H, *J* = 8.2 Hz, H-4(5)), 8.30–8.35 (m, 3H, H-5(4),7,10); Anal. Calcd for C<sub>16</sub>H<sub>8</sub>O<sub>2</sub>S: C, 72.71; H, 3.05; S, 12.13. Found: C, 72.52; H, 2.94; S, 11.86%.

**2-Phenylantra[1,2-*b*]thiophene-6,11-dione (2b).** 1-Chloro-2-phenylethynylantraquinone **1b** (0.30 g, 0.9 mmol) was condensed with Na<sub>2</sub>S (0.30 g, 3.8 mmol) in 65 mL of ethanol for 20 min by the general procedure. The crude product was purified by flash chromatography on silica gel in CHCl<sub>3</sub> and recrystallized from toluene to give 0.27 g (90 %) of 2-phenylantra[1,2-*b*]thiophene-6,11-dione **2b**; m.p. 287–288°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.40–7.55 (m, 3H, 3HPh), 7.65 (s, 1H, H-3), 7.80–7.90 (m, 4H, 2HPh, H-8,9), 8.12 (d, 1H, *J* = 8.2 Hz, H-4(5)), 8.30–8.40 (m, 3H, H-5(4),7,10); Anal. Calcd for C<sub>22</sub>H<sub>12</sub>O<sub>2</sub>S: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.60; H, 3.69; S, 9.40%.

**2-(1-Hydroxy-1-methylethyl)anthra[1,2-*b*]thiophene-6,11-dione (2c).** The experiment was carried out by the general procedure with 1-chloro-2-(3-hydroxy-3-methylbutynyl)anthraquinone **1c** (0.48 g, 1.5 mmol) and Na<sub>2</sub>S (0.48 g, 6.1 mmol) in 80 mL of ethanol, the reaction time was 15 min. The crude product was chromatographed on silica gel using CHCl<sub>3</sub>–ether as the eluent and recrystallized from toluene to yield 0.40 g (83 %) of 2-(1-hydroxy-1-methylethyl)anthra[1,2-*b*]thiophene-6,11-dione **2c**; m.p. 184–184.5°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  1.78 (s, 6H, Me), 2.30 (brs, 1H, OH), 7.28 (s, 1H, H-3), 7.75–7.85 (m, 2H, H-8,9), 8.01 (d, 1H, *J* = 8.2 Hz, H-4(5)), 8.20–8.35 (m, 3H, H-5(4),7,10); Anal. Calcd for C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>S: C, 70.79; H, 4.38; S, 9.95. Found: C, 70.90; H, 4.54; S, 9.91%.

**2-(1-Hydroxymethylpropyl)anthra[1,2-*b*]thiophene-6,11-dione (2d).** The condensation of 1-chloro-2-(3-hydroxy-4-methylpentynyl)anthraquinone **1d** (0.28 g, 0.8 mmol) with Na<sub>2</sub>S (0.30 g, 3.8 mmol), isolation and purification of the crude product were carried out by the general procedure to give 2-(1-hydroxymethylpropyl)anthra[1,2-*b*]thiophene-6,11-dione **2d** (0.21 g, 75 %); m.p. 162–163°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  0.99 (d, 3H, *J* = 6.7 Hz, Me), 1.07 (d, 3H, *J* = 6.7 Hz, Me), 2.10–2.25 (m, 1H, CHMe<sub>2</sub>), 2.30 (brs, 1H, OH), 4.82 (d, 1H, *J* = 4.7 Hz, CHO), 7.28 (s, 1H, H-3), 7.75–7.85 (m, 2H, H-8,9), 8.03 (d, 1H, *J* = 8.2 Hz, H-4(5)), 8.25–8.35 (m, 3H,

H-5(4),7,10); Anal. Calcd for C<sub>20</sub>H<sub>16</sub>O<sub>3</sub>S: C, 71.41; H, 4.79; S, 9.53. Found: C, 71.27; H, 4.71; S, 9.38%.

**2-Hydroxymethylanthra[1,2-*b*]thiophene-6,11-dione (2e).** The reaction of 1-chloro-2-(3-hydroxy-propynyl)anthraquinone **1e** (0.30 g, 1.0 mmol) with Na<sub>2</sub>S (0.30 g, 3.8 mmol), isolation, and purification of the crude product were carried out by general procedure to give 2-hydroxymethylanthra[1,2-*b*]thiophene-6,11-dione **2e** (0.26 g, 87 %); m.p. 212–213°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 2.23 (brs, 1H, OH), 5.00 (s, 2H, CH<sub>2</sub>), 7.33 (s, 1H, H-3), 7.75–7.85 (m, 2H, H-8,9), 8.05 (d, 1H, *J* = 8.2 Hz, H-4(5)), 8.25–8.35 (m, 3H, H-5(4),7,10); Anal. Calcd for C<sub>17</sub>H<sub>10</sub>O<sub>3</sub>S: C, 69.37; H, 3.42; S, 10.89. Found: C, 69.26; H, 3.65; S, 10.81%.

**Anthra[2,1-*b*]thiophene-6,11-dione (4a).** The experiment was carried out by the general procedure with 2-chloro-1-ethynylantraquinone **3a** (0.17g, 0.6 mmol) and Na<sub>2</sub>S (0.25 g, 3.2 mmol) in 35 mL of ethanol during 15 min. The crude product was purified by flash chromatography on Al<sub>2</sub>O<sub>3</sub> in toluene and recrystallized from a toluene–hexane mixture to yield anthra[2,1-*b*]thiophene-6,11-dione **4a** (0.11 g, 66 %); m.p. 182–183.5°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.75–7.85 (m, 2H, H-8,9), 7.81 (d, 1H, *J* = 5.5 Hz, H-2(1)), 8.20–8.35 (m, 4H, H-4,5,7,10), 8.81 (d, 1H, *J* = 5.5 Hz, H-1(2)); Anal. Calcd for C<sub>16</sub>H<sub>8</sub>O<sub>2</sub>S: C, 72.71; H, 3.05; S, 12.13. Found: C, 72.54; H, 3.01; S, 11.93%.

**2-Phenylanthra[2,1-*b*]thiophene-6,11-dione (4b).** a) 2-Chloro-1-phenylethynylantraquinone **3b**<sup>26</sup> (0.20 g, 5.8 mmol) was condensed with Na<sub>2</sub>S (0.30 g, 3.8 mmol) in 40 mL of ethanol for 20 min by the general procedure. The crude product was chromatographed on silica gel using toluene as the eluent and recrystallized from toluene to yield 2-phenylanthra[2,1-*b*]thiophene-6,11-dione **4b** (0.17g, 84%); m.p. 246.5–247.5°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.40–7.55 (m, 3H, 3HPh), 7.75–7.90 (m, 4H, 2HPh, H-8,9), 8.19 (d, 1H, *J* = 8.4 Hz, H-4(5)), 8.25–8.35 (m, 3H, H-5(4),7,10), 9.08 (s, 1H, H-1); Anal. Calcd for C<sub>22</sub>H<sub>12</sub>O<sub>2</sub>S: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.67; H, 3.61; S, 9.50%.

b) The condensation of 1-phenylethynylantraquinone **9b**<sup>26</sup> (0.20 g, 0.7 mmol) with Na<sub>2</sub>S (0.20 g, 2.6 mmol) in 25 mL of ethanol under the same conditions afforded **4b** (0.21 g, 95 %).

**2-(1-Hydroxy-1-methylethyl)anthra[2,1-*b*]thiophene-6,11-dione (4c).** a) The reaction of 2-chloro-1-(3-hydroxy-3-methylbutynyl)anthraquinone **3c** (0.25 g, 0.8 mmol) with Na<sub>2</sub>S (0.30 g, 3.8 mmol) in 30 ml of ethanol was carried out by the general procedure. The crude product was chromatographed on silica gel in CHCl<sub>3</sub> and recrystallized from a toluene–hexane mixture to give 2-(1-hydroxy-1-methylethyl)anthra[2,1-*b*]thiophene-6,11-dione **4c** (0.24 g, 97 %); m.p. 171–172°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 1.77 (s, 6H, Me), 2.32 (brs, 1H, OH), 7.75–7.85 (m, 2H, H-8,9), 8.14 (d, 1H, *J* = 8.4 Hz, H-4(5)), 8.24 (d, 1H, *J* = 8.4 Hz, H-5(4)), 8.25–8.30 (m, 2H, H-7,10), 8.59 (s, 1H, H-1); Anal. Calcd for C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>S: C, 70.79; H, 4.38; S, 9.95. Found: C, 70.80; H, 4.20; S, 9.81%.

b) 1-(3-Hydroxy-3-methylbutynyl)anthraquinone **9c**<sup>29</sup> (0.20 g, 0.7 mmol) was condensed with Na<sub>2</sub>S (0.20 g, 2.6 mmol) in 25 mL of ethanol for 15 min under the same conditions to give **4c** (0.21 g, 95 %).

**2-Phenylanthra[1,2-*b*]thiopyran-4,7,12-trione (7b).** The reaction of 1-chloro-2-(1-oxo-3-phenyl-propynyl)anthraquinone **5b** (0.52 g, 1.4 mmol) with Na<sub>2</sub>S (0.50 g, 6.4 mmol) in 90 mL of ethanol was carried out by the general procedure. The crude product was purified by crystallization from a toluene–hexane mixture to yield 2-phenylanthra[1,2-*b*]thiopyran-4,7,12-trione **7b** (0.42 g, 82 %); m.p. 291–292°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.30 (s, 1H, H-3), 7.50–7.60 (m, 3H, 3HPh), 7.75–7.90 (m, 4H, 2HPh, H-9,10), 8.25–8.40 (m, 2H, H-8,11), 8.50 (d, 1H, *J* = 8.3 Hz, H-5(6)), 9.07 (d, 1H, *J* = 8.3 Hz, H-6(5)); Anal. Calcd for C<sub>23</sub>H<sub>12</sub>O<sub>3</sub>S: C, 74.98; H, 3.28; S, 8.70. Found: C, 75.20; H, 3.43; S, 8.60%.

**2-(1-Hydroxy-1-methylethyl)anthra[1,2-*b*]thiopyran-4,7,12-trione (7c).** 1-Chloro-2-(4-hydroxy-4-methyl-1-oxo-pentynyl)anthraquinone **5c** (0.40 g, 1.1 mmol) was condensed with Na<sub>2</sub>S (0.40 g, 5.1 mmol) in 60 mL of ethanol for 15 min by the general procedure. The crude product was purified by flash chromatography on silica gel in CHCl<sub>3</sub> and recrystallized from a toluene–hexane mixture to yield 2-(1-hydroxy-1-methylethyl)anthra[1,2-*b*]thiopyran-4,7,12-trione **7c** (0.31 g, 78 %); m.p. 261–262°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 1.75 (s, 6H, Me), 2.35 (s, 1H, OH), 7.20 (s, 1H, H-3), 7.80–7.90 (m, 2H, H-9,10), 8.25–8.35 (m, 2H, H-8,11), 8.45 (d, 1H, *J* = 8.3 Hz, H-5(6)), 8.99 (d, 1H, *J* = 8.3 Hz, H-6(5)); Anal. Calcd for C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>S: C, 68.56; H, 4.03; S, 9.15. Found: C, 68.51; H, 4.30; S, 9.13%.

**2-(1-Cyclohexenyl)anthra[1,2-*b*]thiopyran-4,7,12-trione (7f).** The condensation of 1-chloro-2-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone **5f** (0.40 g, 1.1 mmol) with Na<sub>2</sub>S (0.45 g, 5.8 mmol) was performed by the general procedure. The crude product was purified by crystallization from a toluene–hexane mixture to give 2-(1-cyclohexenyl)anthra[1,2-*b*]thiopyran-4,7,12-trione **7f** (0.32 g, 81 %); m.p. 261–263°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 1.60–1.90 (m, 4H, 4', 5'-CH<sub>2</sub>), 2.30–2.45 (m, 4H, 3', 6'-CH<sub>2</sub>), 6.75–6.80 (m, 1H, 2'-CH), 6.98 (s, 1H, H-3), 7.80–7.90 (m, 2H, H-9,10), 8.25–8.35 (m, 2H, H-8,11), 8.40 (d, 1H, *J* = 8.3 Hz, H-5(6)), 8.94 (d, 1H, *J* = 8.3 Hz, H-6(5)); Anal. Calcd for C<sub>23</sub>H<sub>16</sub>O<sub>3</sub>S: C, 74.17; H, 4.33; S, 8.61. Found: C, 74.30; H, 4.53; S, 8.40%.

**2-Butylanthra[1,2-*b*]thiopyran-4,7,12-trione (7g).** The experiment was performed by the general procedure with 1-chloro-2-(1-oxohept-2-ynyl)anthraquinone **5g** (0.50 g, 1.4 mmol) and Na<sub>2</sub>S (0.50 g, 6.4 mmol). The crude product was chromatographed on silica gel in toluene and crystallized from a toluene–hexane mixture to yield 0.40 g (80 %) of 2-butylanthra[1,2-*b*]thiopyran-4,7,12-trione **7g**; m.p. 182–183°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 0.97 (t, 3H, *J* = 7.6 Hz, Me), 1.45 (sextet, 2H, *J* = 7.6 Hz, γ-CH<sub>2</sub>), 1.78 (quintet, 2H, *J* = 7.6 Hz, β-CH<sub>2</sub>), 2.76 (t, 2H, *J* = 7.6 Hz, α-CH<sub>2</sub>), 6.94 (s, 1H, H-3), 7.80–7.90 (m, 2H, H-9,10), 8.25–8.35 (m, 2H, H-8,11), 8.44 (d, 1H, *J* = 8.3 Hz, H-5(6)), 8.99 (d, 1H, *J* = 8.3 Hz, H-6(5)); Anal. Calcd for C<sub>21</sub>H<sub>16</sub>O<sub>3</sub>S: C, 72.39; H, 4.63; S, 9.20. Found: C, 72.50; H, 4.73; S, 9.05%.

**2-(1-Methylprop-1-enyl)anthra[1,2-*b*]thiopyran-4,7,12-trione (7h).** The reaction of a mixture of *Z*- and *E*- isomers of 1-chloro-2-(4-methyl-1-oxo-hex-4-en-2-ynyl)anthraquinone **5h** (0.40 g, 1.1 mmol) with Na<sub>2</sub>S (0.40 g, 5.1 mmol) was run by the general procedure. The crude product was purified by flash chromatography on silica gel in toluene and crystallized from a toluene–hexane mixture to yield 0.27 g (68 %) of 2-(1-methylprop-1-enyl)anthra[1,2-*b*]thiopyran-4,7,12-

trione **7h** (a mixture of *Z*- and *E*-isomers); m.p. 170–171 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 1.72 (brd, 3H, *J* = 7.0 Hz, MeCH=C *E*-isomer), 1.92 (brd, 3H, *J* = 7.0 Hz, MeCH=C *Z*-isomer), 2.10 (brs, 3H, CH<sub>3</sub>-C=C), 5.80 (brq, 1H, *J* = 7.0 Hz, CH=C *E*-isomer), 6.55 (brq, 1H, *J* = 7.0 Hz, CH=C *Z*-isomer), 6.87 (s, 1H, H-3 *E*-isomer), 7.03 (s, 1H, H-3 *Z*-isomer), 7.80–7.90 (m, 2H, H-9,10), 8.25–8.40 (m, 2H, H-8,11), 8.44 (d, 1H, *J* = 8.3 Hz, H-5(6) *Z*-isomer), 8.48 (d, 1H, *J* = 8.3 Hz, H-5(6) *E*-isomer), 8.99 (d, 1H, *J* = 8.3 Hz, H-6(5) *Z*-isomer); 9.05 (d, 1H, *J* = 8.3 Hz, H-6(5) *E*-isomer); Anal. Calcd for C<sub>21</sub>H<sub>14</sub>O<sub>3</sub>S: C, 72.81; H, 4.07; S, 9.26. Found: C, 72.85; H, 4.32; S, 9.13%.

**2-Phenylanthra[2,3-*b*]thiopyran-4,6,12-trione (8b)**. The experiment was carried out by the general procedure with 2-chloro-3-(1-oxo-3-phenylpropynyl)anthraquinone **6b** (0.30g, 0.8 mmol) and Na<sub>2</sub>S (0.45g, 5.8 mmol) in 80 mL of ethanol. The product was purified by crystallization from toluene to give 0.28 g (94 %) of 2-phenylanthra[2,3-*b*]thiopyran-4,6,12-trione **8b**; m.p.338–339°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.32 (s, 1H, H-3), 7.50–7.60 (m, 3H, 3HPh), 7.70–7.80 (m, 2H, 2HPh), 7.80–7.90 (m, 2H, H-8,9), 8.35–8.45 (m, 2H, H-7,10), 8.61 (s, 1H, H-5(12)), 9.45 (s, 1H, H-12(5)); Anal. Calcd for C<sub>23</sub>H<sub>12</sub>O<sub>3</sub>S: C, 74.98; H, 3.28; S, 8.70. Found: C, 75.05; H, 3.16; S, 8.51%.

**2-(1-Cyclohexenyl)anthra[2,3-*b*]thiopyran-4,6,12-trione (8f)**. The experiment was carried out by the general procedure with 2-chloro-3-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone **6f** (0.20g, 0.5 mmol) and Na<sub>2</sub>S (0.30g, 3.8 mmol). The crude product was chromatographed on silica gel in CHCl<sub>3</sub> and recrystallized from toluene to yield 0.15 g (75 %) of 2-(1-cyclohexenyl)anthra[2,3-*b*]thiopyran-4,6,12-trione **8d**; m.p. 290–291 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 1.60–1.90 (m, 4H, 4', 5'-CH<sub>2</sub>), 2.15–2.50 (m, 4H, 3', 6'-CH<sub>2</sub>), 6.65–6.75 (m, 1H, 2'-CH), 7.02 (s, 1H, H-3), 7.80–7.90 (m, 2H, H-8,9), 8.30–8.45 (m, 2H, H-7,10), 8.51 (s, 1H, H-5(12)), 9.37 (s, 1H, H-12(5)); Anal. Calcd for C<sub>23</sub>H<sub>16</sub>O<sub>3</sub>S: C, 74.17; H, 4.33; S, 8.61. Found: C, 73.68; H, 4.32; S, 8.08%.

## References

1. Yue, D.; Larock, R.C. *J. Org. Chem.* **2002**, *67*, 1905.
2. McDonald, F.E.; Burova, S.A.; Huffman, L.G. *Synthesis* **2000**, 970.
3. Tolstikova, T. G.; Davydova, V. A.; Shul'ts, E. E.; Vafina, G. F.; Safarova, G. M.; Zarudii, F. A.; Lazareva, D. N.; Tolstikov, G. A. *Khim.-Farm. Zh.* **1990**, *24*, 27 (Russ.).
4. Kita, Y.; Kirihara, M.; Sekihachi, J.; Okunaka, R.; Sasho, M.; Mohri, Sh.; Honda, T.; Akai, Sh.; Tamura, Y.; Shimooka, K. *Chem. Pharm. Bull.* **1990**, *38*, 1836.
5. Ohba, Y.; Murakami, Y.; Sone, T.; Awano, H. *J. Heterocycl. Chem.* **1997**, *34*, 781.
6. Deng, X.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 7703.
7. Sall, D.J.; Bastian, J.A.; Briggs, S.L.; Buben, J.A.; Chirgadze, N.Y.; Clawson, D.K.; Denney, M.L.; Giera, D.D.; Gifford-Moore, D.S.; Harper, R.W.; Hauser, K.L.; Klimkowski, V.J.; Kohn, T.J.; Lin, H. Sh.; McCowan, J.R.; Palkowitz, A.D.; Smith, G.F.; Takeuchi, K.;

- Thrasher, K.J.; Tinsley, J.M.; Utterback, B.G., Yan, S.-Ch. B.; Zhang, M. *J. Med. Chem.* **1997**, *40*, 3489.
8. Bradley, D.Y., Godfrey, A.G., Schmid, C.R. *Tetrahedron Lett.* **1999**, *40*, 5155.
  9. Piskunov, A.V.; Shvartsberg, M.S. *Mendeleev Commun.* **1995**, 155.
  10. Shvartsberg, M.S.; Ivanchikova, I.D.; Lebedeva, N.I. *Tetrahedron Lett.* **2000**, *41*, 5757.
  11. Shvartsberg, M.S.; Piskunov, A.V.; Mzhelskaya, M.A.; Moroz, A.A. *Izv. Akad. Nauk, Ser. Khim.* **1993**, 1423; *Russ. Chem. Bull.* **1993**, *42*, 1357.
  12. Shvartsberg, M.S.; Barabanov, I.I.; Fedenok, L.G. *Mendeleev Commun.* **1997**, 98.
  13. Shvartsberg, M.S.; Ivanchikova, I.D.; Vasilevsky, S.F. *Tetrahedron Lett.* **1994**, *35*, 2077.
  14. Mzhelskaya, M.A.; Moroz, A.A.; Shvartsberg, M.S. *Izv. Akad. Nauk Ser. Khim.* **1991**, 1656; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1991**, *40*, 1469.
  15. Shvartsberg, M.S.; Ivanchikova, I.D.; Fedenok, L.G. *Tetrahedron Lett.* **1994**, *35*, 6749.
  16. Shvartsberg, M.S.; Ivanchikova, I.D. *Tetrahedron Lett.* **2000**, *41*, 771.
  17. Barabanov, I.I.; Ivanchikova, I.D.; Shvartsberg, M.S. *Mendeleev Commun.* **2000**, 188.
  18. Fedenok, L.G.; Barabanov, I.I.; Ivanchikova, I.D. *Tetrahedron* **2001**, *57*, 1331.
  19. Larock, C.R.; Yue, D. *Tetrahedron Lett.* **2001**, *42*, 6011.
  20. Flynn, B.L.; Verdier-Pinard, P.; Hamel, E. *Org. Lett.* **2001**, *5*, 651.
  21. Malte, A.M.; Castro, C.E. *J. Am. Chem. Soc.* **1967**, *89*, 6770.
  22. Lendel, V.G.; Pakh, V. J.; Petrus, V.V.; Kijak, M.Yu.; Migalina, Yu.V. *Khim. Geterotsikl. Soedin.* **1990**, 1331 (Russ.).
  23. Smirnov-Zamkov I.V.; Zborovsky, Yu.L. *Zh. Organ. Khim.* **1977**, 667 (Russ).
  24. Sakamoto, T.; Kondo, Y.; Watanabe, R.; Yamanaka, H. *Chem. Pharm. Bull.* **1986**, *34*, 2719.
  25. Gorelik, M.V. *Chemistry of Anthraquinones and Their Derivatives*; Khimiya: Moscow, 1983, pp 296.
  26. Piskunov, A.V.; Moroz, A.A.; Shvartsberg, M.S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 864; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *35*, 785.
  27. Hauser, F. M.; Rhee, R. P. *J. Org. Chem.* **1980**, *45*, 3061.
  28. JP 61/224992. JPN. – *Chem. Abstr.* **1987**, *106*, 137013h.
  29. Piskunov, A.V.; Moroz, A.A.; Shvartsberg, M.S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 828; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, *36*, 755.
  30. Zanina, A.S.; Shergina, S.I.; Sokolov, I.E.; Kotlyarevsky, I.L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1158 (Russ.).