Synthesis of sulfur-containing heterocyclic compounds by cyclo-condensation of acetylenic derivatives of anthraquinone with sodium sulfide

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Dedicated to Professor Boris A. Trofimov on the occasion of his 65th birthday

Abstract

Reaction of *vic*- alkynylchloro- and *vic*- chloro-(1-oxoalk-2-ynyl)-anthraquinones with Na_2S in ethanol, with short heating, has been shown to afford anthrathiophenediones and anthrathiopyrantriones, respectively, generally in good yields. Under the same conditions, 1-alkynylanthraquinones also undergo cyclocondensation to give anthra[2,1-*b*]thiophene-6,11-diones.

Keywords: Acetylenic derivatives of anthraquinone; cyclocondensation; anthrathiophenediones; anthrathiopyrantriones

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,[1–3] reduces side-effects of drugs,[4] or improves the technical characteristics of materials.[5,6] Thus, substituted benzo[*b*]thiophenes are estrogen-receptor modulators, thrombin inhibitors, anti-tumor and anti-inflammation agents.[1,2,7,8] Some of them are currently in pharmaceutical use or development.[7,8]

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

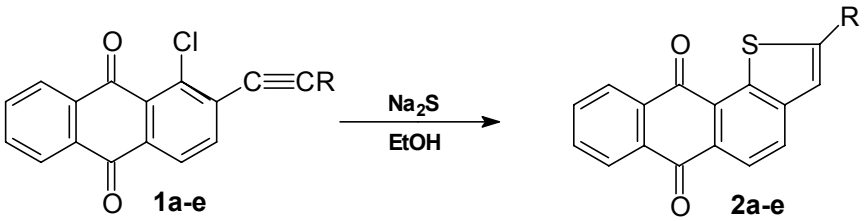
systems based on acetylenic derivatives of quinones as key precursors.[9–18] One would expect that the same "acetylenic" approach will turn out to be fruitful for the construction of an anthrathiophene system as well.

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.[1,19,20] 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.[21–24]

Results and Discussion

In anthraquinone, a chlorine atom, irrespective of its position, possesses a high nucleofugal lability.[25] The triple bond in acetylenic derivatives of quinones has an enhanced electrophilicity and readily adds nucleophiles.[26] 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_2S as the simplest cyclizing agent.

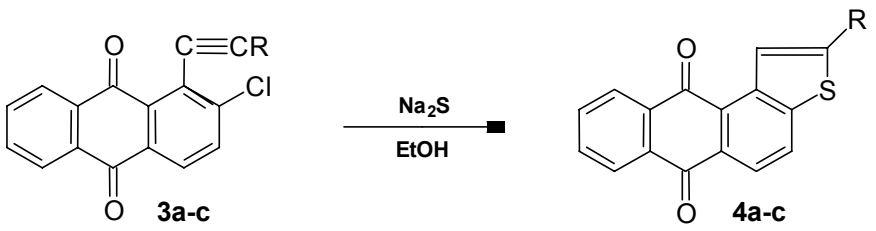
Indeed, 2-alkynyl-1-chloroanthraquinones **1a–e** did react with an excess of Na_2S in 95% ethanol at reflux for 10–20 min to give anthra[1,2-*b*]thiophene-6,11-diones **2a–e** in 57–90 % yields.



a: R = H
b: R = Ph
c: R = CMe_2OH
d: R = CH(OH)Pr - *i*
e: R = CH_2OH

Scheme 1.

The 1-alkynyl-2-chloroanthraquinones **3a–c** bearing the halogen atom in position 2 were condensed with Na_2S in the same way as the chloroacetylenes **1**, and under the same conditions.



a: R = H
b: R = Ph
c: R = CMe_2OH

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 ^{1}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_2S is a simple and convenient method for synthesis of angularly fused anthrathiophenediones.

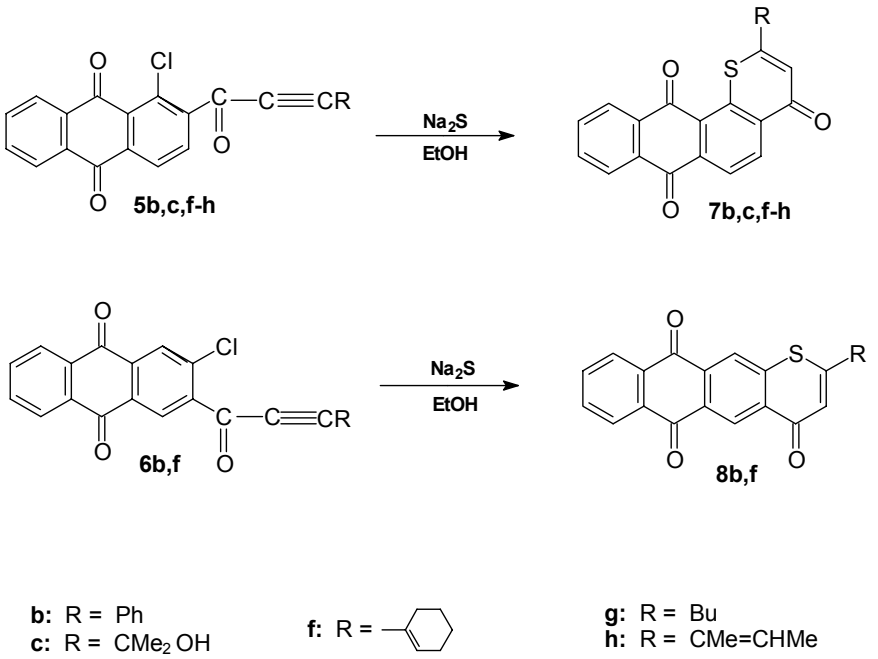
We also applied the cyclocondensation under consideration to annelate anthraquinone with a thiopyran ring. In this case, the 1-chloro-2-(1-oxoalk-2-ynyl)anthraquinones 5**b,c,f–h** and the 2-chloro-3-(1-oxoalk-2-ynyl)anthraquinones **6b,f** were used as the acetylenic precursors. These compounds have, like the chloroacetylenes **1,3**, the activated halogen atom and triple bond. Their condensation with Na_2S 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 natural antitumor antibiotics of the kidamycin group and their biologically active analogs, which are obtained biochemically.[27,28] 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.).[27] 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.

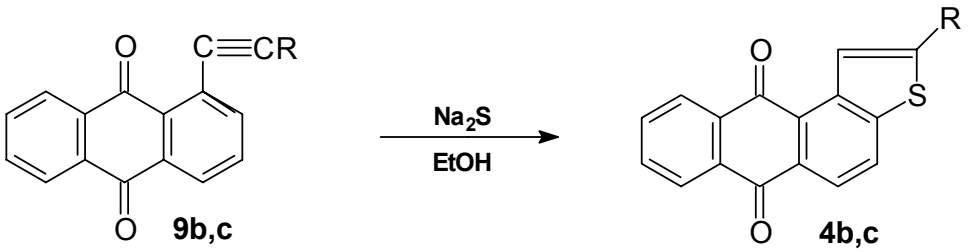
The initial step of the cyclocondensation of *vic*- acetylenic derivatives of chloroanthraquinones may be not only the substitution of the chlorine atom but also the addition

of Na_2S to the triple bond. However, the intramolecular addition of Na_2S, 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-alkynylanthraquinones **9b,c** with Na_2S under the conditions of the cyclocondensation. The acetylenes **9b,c** were found to react with Na_2S, 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.



b: R = Ph
c: R = CMe_2OH
f: R =
g: R = Bu
h: R = CMe=CHMe

Scheme 3.

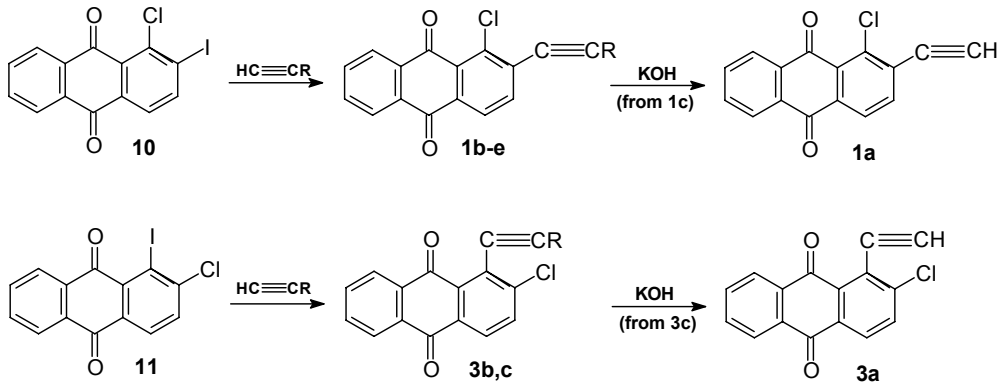


b: R = Ph
c: R = CMe_2OH

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-iodo-anthraquinone **10** and 2-chloro-1-iodoanthraquinone **11** with the corresponding terminal acetylenes in aqueous dioxane in the presence of Na_2CO_3, $Pd(PPh_3)_2Cl_2$ and CuI in 47–85 % yields. We consider this cross-coupling procedure[12,29] to be the best method for the introduction of acetylenic substituents into quinones. The chloroethynylanthraquinones **1a**, **3a** were synthesized from the tertiary acetylenic alcohols **1c**, **3c** by the retro- Favorsky reaction.[29] 2-Chloro-1-phenylethynylanthraquinone **3b** was prepared as described earlier.[26]

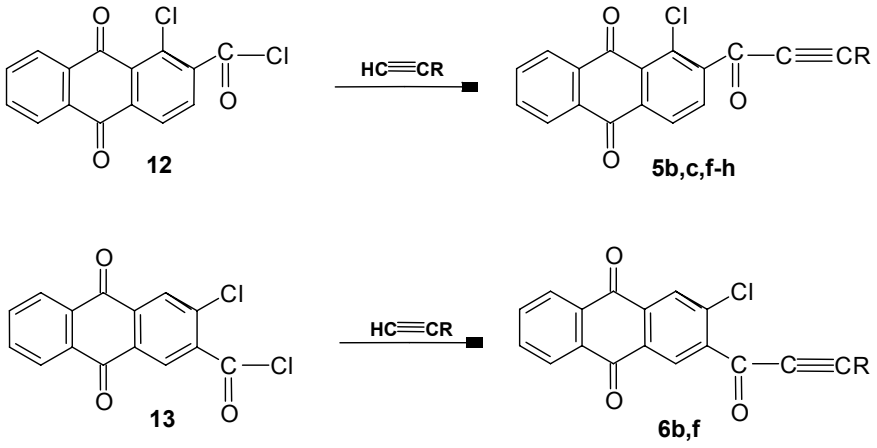


a: R = H
b: R = Ph
c: R = CMe_2OH
d: R = CH(OH)Pr - *i*
e: R = CH_2OH

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 NEt_3–$Pd(PPh_3)_2Cl_2$–CuI–benzene[30] 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 ≈70% of Z- isomer was used.

In summary, we have shown that condensation of *vic*- acetylenic derivatives of chloroanthraquinones with Na_2S 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-phenylethynylanthraquinone 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), $Pd(PPh_3)_2Cl_2$ (0.040 g), CuI (0.040 g) and 30 mL of aqueous solution of Na_2CO_3 (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 $CHCl_3$ 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-phenylethynylanthraquinone **1b** (1.50 g, 85 %), m.p. 193.5–194°C.[26]

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_2CO_3 (0.72g, 6.8 mmol), $Pd(PPh_3)_2Cl_2$ (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**; [17] m.p. 168–168.5°C; IR ($CHCl_3$), ν_{max}: 1690 (C=O), 2240 (C≡C), 3605 (OH) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{19}H_{13}O_3Cl$: 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_2CO_3 (1.00 g, 9.4 mmol), $Pd(PPh_3)_2Cl_2$ (0.060 g), and CuI (0.045 g) for 5 min. The yield of 1-chloro-2-(4-methyl-3-hydroxypentynyl)anthraquinone **1d**[17] was 0.87 g (47%); m.p. 160–161.5°C; IR ($CHCl_3$), ν_{max}: 1690 (C=O), 2235 (C≡C), 3400 br., 3615 (OH) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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$_2$, 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 $C_{20}H_{15}O_3Cl$: 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**[17] (0.28 g, 47%); m.p. 197.5–199°C; IR ($CHCl_3$), ν_{max}: 1690 (C=O), 2240 (C≡C), 3400 br., 3620 (OH) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.67 (s, 2H, CH_2), 7.75–7.90 (m, 3H, H-3,6,7), 8.20–8.30 (m, 3H, H-4,5,8); Anal. Calcd for $C_{17}H_9O_3Cl$: 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_2CO_3, 0.030 g of $Pd(PPh_3)_2Cl_2$, 0.015 g of CuI. The crude product was purified by chromatography on silica gel using $CHCl_3$ 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 ($CHCl_3$), ν_{max}: 1690 (C=O), 2240 (C≡C), 3400 br., 3615 (OH) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{19}H_{13}O_3Cl$: C, 70.27; H, 4.03; Cl, 10.92. Found: C, 70.20; H, 4.04; Cl, 11.03%.

1-Chloro-2-ethynylanthraquinone 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_2O_3 using toluene as the eluent and crystallized from a toluene–hexane mixture. The yield of 1-chloro-2-ethynylanthraquinone **1a** was 0.90 g (73%); m.p. 211—212°C; IR ($CHCl_3$), ν_{max}: 1690 (C=O), 2130 (C≡C), 3310 (C≡CH) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{16}H_7O_2Cl$: C, 72.06; H, 2.65; Cl, 13.29. Found: C, 71.98; H, 2.84; Cl, 13.09%.

2-Chloro-1-ethynylanthraquinone 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-ethynylanthraquinone **3a** (0.47 g, 31 %); m.p. 244–245°C; IR ($CHCl_3$), ν_{max}: 1690 (C=O), 2120 (C≡C), 3320 (C≡CH) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{16}H_7O_2Cl$: C, 72.06; H, 2.65; Cl, 13.29. Found: C, 72.18; H, 2.59; Cl, 13.26%.

General procedure for the 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 $SOCl_2$ for 4 h, in 50 mL of dry benzene under Ar, were added Et_3N (1.1 g, 11.0 mmol), $Pd(PPh_3)_2Cl_2$ (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 $CHCl_3$, washed with water, dried over $MgSO_4$ 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 ($CHCl_3$), ν_{max}: 1670, 1690 (C=O), 2205 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{23}H_{11}O_3Cl$: 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_3N (0.36 g, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (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 ($CHCl_3$), ν_{max}: 1670, 1690 (C=O), 2225 (C≡C), 3400 br., 3610 (OH) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{20}H_{13}O_4Cl$: 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_3N (1.6 g, 15.7 mmol), $Pd(PPh_3)_2Cl_2$ (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 ($CHCl_3$), ν_{max}: 1670, 1690 (C=O), 2195 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.45–1.75 (m, 4H, 4', 5'-CH_2), 2.10–2.30 (m, 4H, 3', 6'-CH_2), 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 $C_{23}H_{15}O_3Cl$: 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 ($CHCl_3$), ν_{max}: 1670, 1690 (C=O), 2220 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.92 (t, 3H, *J* = 7.2 Hz, Me), 1.40–1.65 (m, 4H, β-, γ-CH_2), 2.47 (t, 2H, *J* = 7.0 Hz, α-CH_2), 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 $C_{21}H_{15}O_3Cl$: 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-chloroanthra- quinonoyl-2 chloride **12** (1.40g, 4.6 mmol) with a mixture of *Z*- and *E*-isomers of 3-methylpent-3-en-1-yne containing ≈ 70 % of *Z*-isomer (0.74 g, 9.2 mmol) in 135 mL of benzene in the presence of Et_3N (1.3 g, 12.8 mmol), $Pd(PPh_3)_2Cl_2$ (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; ^1H NMR ($CDCl_3$, 200 MHz) δ 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_3-C=C *Z*-isomer), 1.95 (brs, 3H, CH_3-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 $SOCl_2$ for 4 h, in 40 mL of dry benzene in the presence of Et_3N (0.72 g, 7.1 mmol), $Pd(PPh_3)_2Cl_2$ (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 ($CHCl_3$), ν_{max}: 1670, 1690 (C=O), 2205 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{23}H_{11}O_3Cl$: 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 ($CHCl_3$), ν_{max}: 1680, 1690 (C=O), 2230 (C≡C) (CH_2) cm^{-1}; ^1H

NMR ($CDCl_3$, 200 MHz) δ 1.55–1.70 (m, 4H, 4', 5'-CH_2), 2.20–2.35 (m, 4H, 3', 6'-CH_2), 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 the cyclocondensation.

Anthra[1,2-*b*]thiophene-6,11-dione 2a. To a suspension of Na_2S (0.30 g, 3.8 mmol) in ethanol (35 mL) at heating (≈ 60°C) was added 1-chloro-2-ethynylanthraquinone **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 $CHCl_3$ (2×100 mL). The organic layer was washed with water, dried over $MgSO_4$ 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; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{16}H_8O_2S$: C, 72.71; H, 3.05; S, 12.13. Found: C, 72.52; H, 2.94; S, 11.86%.

2-Phenylanthra[1,2-*b*]thiophene-6,11-dione 2b. 1-Chloro-2-phenylethynylanthraquinone **1b** (0.30 g, 0.9 mmol) was condensed with Na_2S (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 $CHCl_3$ and recrystallized from toluene to give 0.27 g (90 %) of 2-phenylanthra[1,2-*b*]thiophene-6,11-dione **2b**; m.p. 287–288°C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{22}H_{12}O_2S$: 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_2S (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 $CHCl_3$–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; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 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 $C_{19}H_{14}O_3S$: 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_2S (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; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 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$_2$), 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 $C_{20}H_{16}O_3S$: 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_2S (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; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.23 (brs, 1H, OH), 5.00 (s, 2H, CH_2), 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 $C_{17}H_{10}O_3S$: 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-ethynylanthraquinone **3a** (0.17g, 0.6 mmol) and Na_2S (0.25 g, 3.2 mmol) in 35 mL of ethanol during 15 min. The crude product was purified by flash chromatography on Al_2O_3 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; ^{1}H NMR ($CDCl_3$, 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 $C_{16}H_8O_2S$: 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-phenylethynylanthraquinone **3b**[26] (0.20 g, 5.8 mmol) was condensed with Na_2S (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; ^{1}H NMR ($CDCl_3$, 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 $C_{22}H_{12}O_2S$: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.67; H, 3.61; S, 9.50%.

b) The condensation of 1-phenylethynylanthraquinone **9b**[26] (0.20 g, 0.7 mmol) with Na_2S (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_2S (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 $CHCl_3$ 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; ^{1}H NMR ($CDCl_3$, 200 ^{1}H NMR ($CDCl_3$, 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 $C_{19}H_{14}O_3S$: 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**[29] (0.20 g, 0.7 mmol) was condensed with Na_2S (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** (0.52g, 1.4 mmol) with Na_2S (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; ^{1}H NMR ($CDCl_3$, 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 $C_{23}H_{12}O_3S$: 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_2S (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 $CHCl_3$ 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; ^{1}H NMR ($CDCl_3$, 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 $C_{20}H_{14}O_4S$: 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_2S (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; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.60–1.90 (m, 4H, 4', 5'-CH_2), 2.30–2.45 (m, 4H, 3', 6'-CH_2), 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 $C_{23}H_{16}O_3S$: 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** (0.50g, 1.4 mmol) and Na_2S (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; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.97 (t, 3H, J = 7.6 Hz, Me), 1.45 (sextet, 2H, *J* = 7.6 Hz, γ-CH_2), 1.78 (quintet, 2H, *J* = 7.6 Hz, β-CH_2), 2.76 (t, 2H, *J* = 7.6 Hz, α-CH_2), 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 $C_{21}H_{16}O_3S$: 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_2S (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; ^{1}H NMR ($CDCl_3$, 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_3-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 $C_{21}H_{14}O_3S$: 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_2S (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; ^{1}H NMR ($CDCl_3$, 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 $C_{23}H_{12}O_3S$: 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_2S (0.30g, 3.8 mmol). The crude product was chromatographed on silica gel in $CHCl_3$ 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; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.60–1.90 (m, 4H, 4', 5'-CH_2), 2.15–2.50 (m, 4H, 3', 6'-CH_2), 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 $C_{23}H_{16}O_3S$: C, 74.17; H, 4.33; S, 8.61. Found: C, 73.68; H, 4.32; S, 8.08%.

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