Synthesis of anthrathiopyrantriones by heterocyclization of alkynoyl derivatives of chloroanthraquinones

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A procedure was developed for the synthesis of 2-substituted, including 2-alkenyl-substituted, 4*H*-anthra[1,2-*b*]thiopyran-4,7,12-triones and 4*H*-anthra[2,3-*b*]thiopyran-4,6,11-triones by cyclocondensation of *vic*-alkynoylchloroanthraquinones with Na_2S.

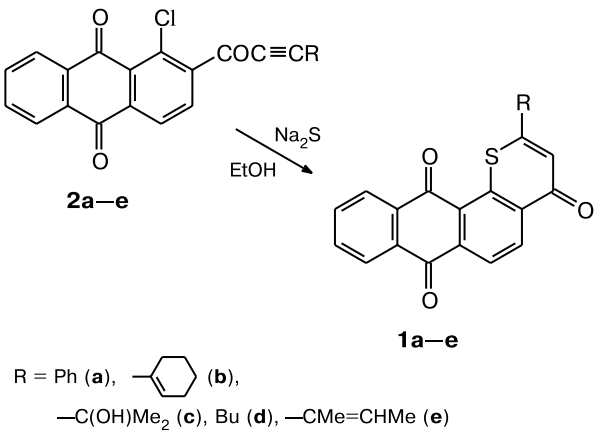
Key words: *vic*-alkynoylchloroanthraquinones, synthesis, cyclocondensation, sodium sulfide, 2-substituted 4*H*-anthra[1,2-*b*]thiopyran-4,7,12-triones, 2-substituted 4*H*-anthra[2,3-*b*]thiopyran-4,6,11-triones.

The cyclic moiety of natural antitumor antibiotics of the kidamycin group is alkynoyl the 4*H*-anthra[1,2-*b*]pyran-4,7,12-trione system.[1] A structural distinguishing feature of these compounds is the presence of unsaturated or other chemically labile substituents at position 2. The introduction of such substituents presents considerable synthetic difficulties. Earlier,[2,3] we have demonstrated that 2-alkenyl-substituted anthrapyrantriones can be synthesized using acetylenic derivatives of anthraquinone as the key intermediates and determined the synthesis conditions. In the present study, we developed a procedure for the preparation of 2-substituted, including 2-alkenyl-substituted, 4*H*-anthra[1,2-*b*]thiopyran-4,7,12-triones within the framework of the same so-called acetylenic approach. The development of rational procedures for the synthesis of sulfur-containing analogs of biologically active pyran compounds is of importance, because the replacement of the heteroatom in a cyclic pharmacophoric structure with the S atom or the introduction of an S-containing heterocycle often makes it possible to reduce the side effects of pharmaceuticals with retention of their main activity or to change the character of their biological activity.[4—6]

2-Alkynoyl-1-mercaptoanthraquinones could seemingly serve as acetylenic precursors in the synthesis of 4*H*-anthra[1,2-*b*]thiopyran-4,7,12-triones **1**. However, these compounds are insufficiently stable and difficultly accessible. Hence, we chose 2-alkynoyl-1-chloroanthraquinones **2** as the key compounds. The Cl atom at position 1 of anthraquinone is labile and can readily be replaced under the action of nucleophiles.[7] In alkynoyl derivatives **2**, this Cl atom is additionally activated by the adjacent substituent. In addition, the triple bond in the substituent is highly electrophilic and can also interact with nucleophiles. Hence, we expected that alkynoylchloroquinones **2** would react with NaHS as a nucleophile under mild conditions, resulting in the thiopyrone-ring closure. The latter fact is of particular importance in the synthesis of heterocycles containing chemically sensitive substituents.

Actually, we found that alkynoylchloroanthraquinones **2** are readily subjected to heterocyclization to form anthrathiopyrans **1** (Scheme 1). It appeared that Na_2S can successfully be used as a cyclizing agent instead of NaHS, whose preparation requires a special procedure.[8] The reaction proceeds rather rapidly in refluxing 95% EtOH in the presence of an excess of Na_2S.

Scheme 1



2-Substituted anthra[1,2-*b*]thiopyran-4,7,12-triones **1a—e** were prepared in 68—82% yields (Table 1). The possible competitive formation of the five-membered heterocycle was not observed. Due to the mild conditions,

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Table 1. Yields, elemental analysis data, and physicochemical and spectroscopic characteristics of anthrathiopyrantriones **1a—e** and **4a,b**

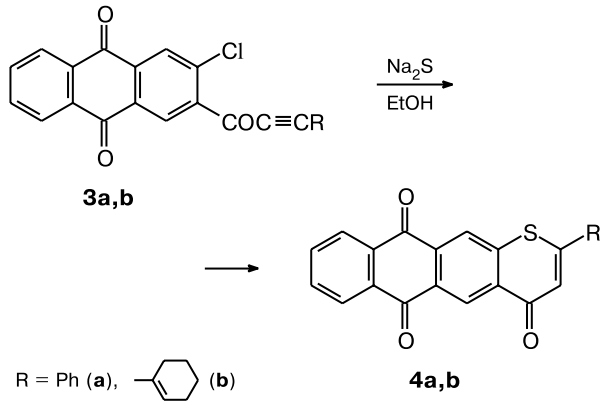
Compound	Yield (%)	M.p.*/°C	Found / Calculated (%)			Molecular formula	^{1}H NMR, δ (*J*/Hz)
			C	H	S		
1a	82	291—292	75.20 74.98	3.43 3.28	8.60 8.70	$C_{23}H_{12}O_3S$	7.30 (s, 1 H, H(3)); 7.50—7.60 (m, 3 H, 3 H_{Ph}); 7.75—7.90 (m, 4 H, 2 H_{Ph}, H(9), H(10)); 8.25—8.40 (m, 2 H, H(8), H(11)); 8.50, 9.07 (both d, 1 H each, H(5), H(6), *J* = 8.3)
1b	81	261—263	74.30 74.17	4.53 4.33	8.40 8.61	$C_{23}H_{16}O_3S$	1.60—1.90 (s, 4 H, C(4′)H_2, C(5′)H_2); 2.30—2.45 (m, 4 H, C(3′)H_2, C(6′)H_2); 6.75—6.80 (m, 1 H, C(2′)H); 6.98 (s, 1 H, H(3)); 7.80—7.90 (m, 2 H, H(9), H(10)); 8.25—8.35 (m, 2 H, H(8), H(11)); 8.40, 8.94 (both d, 1 H each, H(5), H(6), *J* = 8.3)
1c	78	261—262	68.51 68.56	4.30 4.03	9.13 9.15	$C_{20}H_{14}O_4S$	1.75 (s, 6 H, Me); 2.35 (s, 1 H, OH); 7.20 (s, 1 H, H(3)); 7.80—7.90 (m, 2 H, H(9), H(10)); 8.25—8.35 (m, 2 H, H(8), H(11)); 8.45, 8.99 (both d, 1 H each, H(5), H(6), *J* = 8.3)
1d	80	182—183	72.50 72.39	4.73 4.63	9.05 9.20	$C_{21}H_{16}O_3S$	0.97 (t, 3 H, Me, *J* = 7.6); 1.45 (sext, 2 H, γ-CH_2, *J* = 7.6); 1.78 (q, 2 H, β-CH_2, *J* = 7.6); 2.76 (t, 2 H, α-CH_2, *J* = 7.6); 6.94 (s, 1 H, H(3)); 7.80—7.90 (m, 2 H, H(9), H(10)); 8.25—8.35 (m, 2 H, H(8), H(11)); 8.44, 8.99 (both d, 1 H each, H(5), H(6), *J* = 8.3)
1e	68	170—171	72.85 72.81	4.32 4.07	9.13 9.26	$C_{21}H_{14}O_3S$	1.72, 1.92 (both br.d, 3 H each, MeCH=C, *E* isomer, *Z* isomer, *J* = 7.0); 2.10 (br.s, 3 H, MeC=C); 5.80, 6.55 (both br.q, 1 H each, CH=C, *E* isomer, *Z* isomer, *J* = 7.0); 6.87, 7.03 (both s, 1 H each, H(3), *E* isomer, *Z* isomer); 7.80—7.90 (m, 2 H, H(9), H(10)); 8.25—8.40 (m, 2 H, H(8), H(11)); 8.44, 8.99 (both d, 1 H each, H(5), H(6), *Z* isomer, *J* = 8.3); 8.48, 9.05 (both d, 1 H each, H(5), H(6), *E* isomer, *J* = 8.3)
4a	94	338—339	75.05 74.98	3.16 3.28	8.51 8.70	$C_{23}H_{12}O_3S$	7.32 (s, 1 H, H(3)); 7.50—7.60 (m, 3 H, 3 H_{Ph}); 7.70—7.80 (m, 2 H, 2 H_{Ph}); 7.80—7.90 (m, 2 H, H(8), H(9)); 8.35—8.45 (m, 2 H, H(7), H(10)); 8.61, 9.45 (both s, 1 H each, H(5), H(12))
4b	75	290—291	73.68 74.17	4.32 4.33	8.08 8.61	$C_{23}H_{16}O_3S$	1.60—1.90 (m, 4 H, C(4′)H_2, C(5′)H_2); 2.15—2.50 (m, 4 H, C(3′)H_2, C(6′)H_2); 6.65—6.75 (m, 1 H, C(2′)H); 7.02 (s, 1 H, H(3)); 7.80—7.90 (m, 2 H, H(8), H(9)); 8.30—8.45 (m, 2 H, H(7), H(10)); 8.51, 9.37 (both s, 1 H each, H(5), H(12))

* Benzene—hexane.

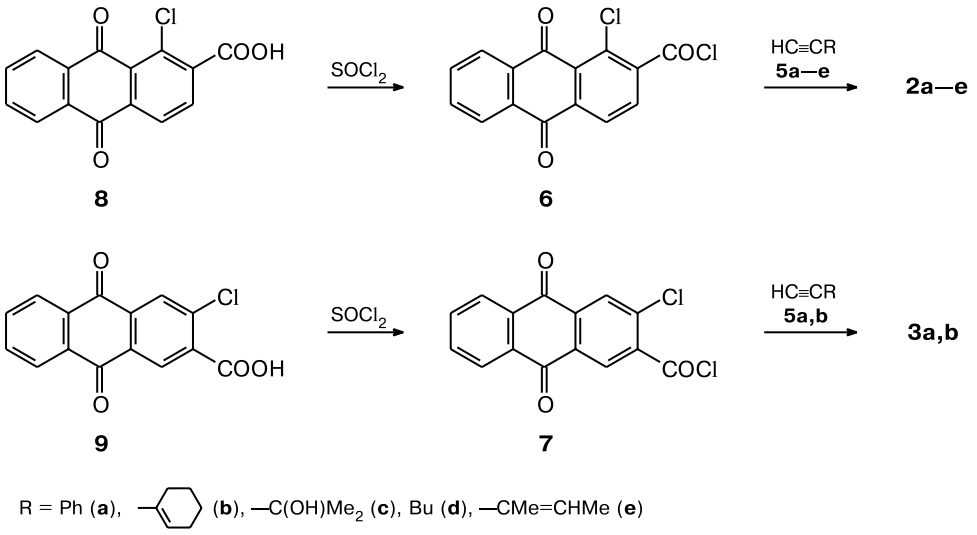
the reaction allows one to prepare anthrathiopyrans containing unsaturated substituents at position 2. The synthesis of alkenylthiopyran **1e** (a mixture of *Z* and *E* isomers) from labile vinylacetylenic ketone **2e**, as well as the preparation of cyclohexenylthiopyran **1b** from ketone **2b**, demonstrates that the proposed method is applicable to the synthesis of thio analogs of aglycones of anthrapyran antibiotics.

The Cl atom in the anthraquinone moiety is characterized by high nucleofugic lability regardless of its position.[7] Hence, there is reason to hope that the new method for the preparation of anthra[1,2-*b*]thiopyran-4,7,12-triones can be extended to the synthesis of compounds in which the thiopyran ring is fused to the anthraquinone moiety in another fashion. We subjected acetylenic ketones **3a,b** containing the Cl atom at position 2 to cyclocondensation with Na_2S. Cyclocondensation of these ketones proceeded under the same conditions as those used in the reactions of their positional isomers **2a,b** and afforded linearly annelated anthra[2,3-*b*]thiopyran-4,6,11-triones **4a,b** (Scheme 2) in 94 and 75% yields, respectively (see Table 1).

Scheme 2



Scheme 3



Acetylenic ketones **2a—e** and **3a,b**, which are precursors of thiopyrans **1a—e** and **4a,b**, respectively, were synthesized by acylation of terminal acetylenes **5** with 1-chloroanthraquinone-2-carboxylic acid chloride (**6**) and 2-chloroanthraquinone-3-carboxylic acid chloride (**7**), respectively, in benzene in the presence of $Pd(PPh_3)_2Cl_2$, CuI, and Et_3N [9] at 20 °C for 10—20 min (Scheme 3).

Acid chlorides **6** and **7** were prepared by heating anthraquinonecarboxylic acids **8** and **9** in $SOCl_2$. After removal of the reagent, acid chlorides **6** and **7** were used without purification (see Scheme 3).

Therefore, cyclocondensation of *vic*-alkynoylchloroanthraquinones with Na_2S provides a rather general method for the synthesis of 2-substituted anthrathiopyrantriones.

Experimental

The ^1H NMR spectra were recorded on a Bruker DPX-200 instrument (200 MHz) in $CDCl_3$ at 25 °C. The IR spectra were measured on a UR-20 spectrometer in $CHCl_3$. The course of the reactions and purity of the compounds were monitored by TLC on Silufol UV 254 plates.

1-Chloroanthraquinone-2-carboxylic acid chloride (6). A solution of 1-chloroanthraquinone-2-carboxylic acid (**8**) (3.70 g, 1.3 mmol) in $SOCl_2$ (13 mL) was refluxed for 4 h and an excess of $SOCl_2$ was removed under argon. The residue was washed with hexane, brought to reflux in dry toluene (10—15 mL), and cooled. The precipitate was filtered off and washed with hexane. Acid chloride **6** was obtained in a yield of 3.35 g (85.0%) and used without additional purification.

1-Chloro-2-(1-oxo-3-phenylpropynyl)anthraquinone (2a). Triethylamine (1.10 g, 11.0 mmol), $Pd(PPh_3)_2Cl_2$ (40 mg), CuI (40 mg), and phenylacetylene (**5a**) (0.56 g, 5.5 mmol) were successively added to a solution of acid chloride **6** (1.00 g, 3.3 mmol) in anhydrous benzene (50 mL) under argon. The reaction mixture was stirred at 20 °C for 20 min, diluted with $CHCl_3$ (300 mL), washed with water, and dried with $MgSO_4$. The solvent was removed *in vacuo*. Ketone **2a** was isolated by chromatography on SiO_2 in toluene and crystallization from a toluene—hexane mixture. The yield was 0.85 g (Table 2).

1-Chloro-2-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone (2b). Acetylenic ketone **2b** was prepared analogously to ketone **2a** from acid chloride **6** (1.50 g, 4.9 mmol) and 1-ethynylcyclohexene (**5b**) (0.93 g, 8.8 mmol) in benzene (70 mL) in the presence of Et_3N (1.60 g, 15.7 mmol), $Pd(PPh_3)_2Cl_2$ (50 mg), and CuI (50 mg). The yield was 1.15 g (see Table 2).

1-Chloro-2-(4-hydroxy-4-methyl-1-oxopent-2-ynyl)anthraquinone (2c) was prepared analogously to ketone **2a** from acid chloride **6** (0.37 g, 1.2 mmol) and 2-methylbut-3-yn-2-ol (**5c**) (0.22 g, 2.6 mmol) in benzene (25 mL) in the presence of Et_3N (0.36 g, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg), and CuI (15 mg). The yield was 0.28 g (see Table 2).

1-Chloro-2-(1-oxohept-2-ynyl)anthraquinone (2d) was synthesized analogously to ketone **2a** by acylation of hex-1-yne (**5d**) (0.18 g, 2.2 mmol) with acid chloride **6** (0.40 g, 1.3 mmol). The yield was 0.30 g (see Table 2).

1-Chloro-2-(4-methyl-1-oxohex-4-en-2-ynyl)anthraquinone (2e). The reaction of acid chloride **6** (1.40 g, 4.6 mmol) with 3-methylpent-3-en-1-yne (**5e**) (0.74 g, 9.2 mmol) (a mixture of *Z* and *E* isomers, the percentage of the *Z* isomer was ~70%) in benzene (135 mL) in the presence of Et_3N (1.30 g, 12.8 mmol), $Pd(PPh_3)_2Cl_2$ (65 mg), and CuI (65 mg) was carried out as described for ketone **2a**. The condensation time was 10 min. The reaction mixture was filtered through a thin SiO_2 layer under pressure, concentrated *in vacuo*, and chromatographed on SiO_2 in toluene. After crystallization from a hexane—diethyl ether mixture, vinylacetylenic ketone **2e** was isolated in a yield of 0.84 g (see Table 2).

2-Chloro-3-(1-oxo-3-phenylpropynyl)anthraquinone (3a). Condensation of acid chloride **7** (0.65 g, 2.1 mmol), which was

Table 2. Yields, elemental analysis data, and physicochemical and spectroscopic characteristics of acetylenic ketones **2a—e** and **3a,b**

Compound	Yield (%)	M.p.*/°C	Found / Calculated (%)			Molecular formula	^{1}H NMR, δ (*J*/Hz)	IR, ν/cm^{-1}
			C	H	Cl			
2a	70	183—183.5	74.48 / 74.50	3.14 / 2.99	9.65 / 9.56	$C_{23}H_{11}ClO_3$	7.35—7.55 (m, 3 H, 3 H_{Ph}); 7.60—7.70 (m, 2 H, 2 H_{Ph}); 7.75—7.90 (m, 2 H, H(6), H(7)); 8.05 (d, 1 H, H(3), *J* = 7.9); 8.25—8.35 (m, 2 H, H(5), H(8)); 8.41 (d, 1 H, H(4), *J* = 7.9)	1670, 1690 (C=O); 2205 (C≡C)
2b	63	168—169	73.80 / 73.70	4.19 / 4.03	9.61 / 9.46	$C_{23}H_{15}ClO_3$	1.45—1.75, 2.10—2.30 (both m, 4 H each, C(4′)H_2, C(5′)H_2, C(3′)H_2, C(6′)H_2); 6.55—6.60 (m, 1 H, C(2′)H); 7.75—7.90 (m, 2 H, H(6), H(7)); 7.95 (d, 1 H, H(3), *J* = 8.0); 8.20—8.35 (m, 2 H, H(5), H(8)); 8.36 (d, 1 H, H(4), *J* = 8.0)	1670, 1690 (C=O); 2195 (C≡C)
2c	65	145—146.5	68.23 / 68.09	3.89 / 3.71	10.08 / 10.05	$C_{20}H_{13}ClO_4$	1.62 (s, 6 H, Me); 2.20 (br.s, 1 H, OH); 7.75—7.85 (m, 2 H, H(6), H(7)); 7.94 (d, 1 H, H(3), *J* = 8.0); 8.20—8.30 (m, 2 H, H(5), H(8)); 8.35 (d, 1 H, H(4), *J* = 8.0)	1670, 1690 (C=O); 2225 (C≡C); 3400 br, 3610 (OH)
2d	65	130—130.5	71.68 / 71.90	4.22 / 4.31	10.19 / 10.11	$C_{21}H_{15}ClO_3$	0.92 (t, 3 H, Me, *J* = 7.2); 1.40—1.65 (m, 4 H, β-CH_2, γ-CH_2); 2.47 (t, 2 H, α-CH_2, *J* = 7.0); 7.75—7.85 (m, 2 H, H(6), H(7)); 7.94 (d, 1 H, H(3), *J* = 8.0); 8.20—8.30 (m, 2 H, H(5), H(8)); 8.36 (d, 1 H, H(4), *J* = 8.0)	1670, 1690 (C=O); 2220 (C≡C)
2e	52	177—178.5	73.29 / 72.32	3.40 / 3.76	10.00 / 10.16	$C_{21}H_{13}ClO_3$	1.75, 1.87 (both d, 3 H each, MeCH=C, *E* isomer, *Z* isomer, *J* = 7.0); 1.92, 1.95 (both br.s, 3 H each, MeC=C, *Z* isomer, *E* isomer); 6.10—6.20, 6.35—6.45 (both m, 1 H each, CH=C, *Z* isomer, *E* isomer); 7.75—7.90 (m, 2 H, H(6), H(7)); 7.95, 7.98 (both d, 1 H each, H(3), *E* isomer, *Z* isomer, *J* = 8.0); 8.20—8.35 (m, 2 H, H(5), H(8)); 8.37, 8.38 (both d, 1 H each, H(4), *E* isomer, *Z* isomer, *J* = 8.0)	1670, 1690 (C=O); 2200 (C≡C)
3a	76	232—233	74.68 / 74.50	3.09 / 2.99	10.06 / 9.56	$C_{23}H_{11}ClO_3$	7.40—7.55 (m, 3 H, 3 H_{Ph}); 7.65—7.75 (m, 2 H, 2 H_{Ph}); 7.80—7.90, 8.30—8.40 (both m, 2 H each, H(6), H(7), H(5), H(8)); 8.40, 8.97 (both s, 1 H each, H(1), H(4))	1670, 1690 (C=O); 2205 (C≡C)
3b	49	149.5—150.5	73.76 / 73.70	4.25 / 4.03	9.56 / 9.46	$C_{23}H_{15}ClO_3$	1.55—1.70, 2.20—2.35 (both m, 4 H each, C(4′)H_2, C(5′)H_2, C(3′)H_2, C(6′)H_2); 6.60—6.70 (m, 1 H, C(2′)H); 7.80—7.90, 8.30—8.40 (both m, 2 H each, H(6), H(7), H(5), H(8)); 8.35, 8.85 (both s, 1 H each, H(1), H(4))	1680, 1690 (C=O); 2230 (C≡C)

* Benzene—hexane.

prepared from 2-chloroanthraquinone-3-carboxylic acid (**9**) analogously to acid chloride **6**, with phenylacetylene (**5a**) (0.43 g, 4.2 mmol) was carried out under the conditions used in the synthesis of ketone **2a** in the presence of Et_3N (0.72 g, 7.1 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), and CuI (20 mg) in benzene (40 mL). The reaction mixture was diluted with hexane (60 mL) and cooled. The precipitate that formed was filtered off, dissolved in trichloroethylene (150 mL) with heating, and filtered through a thin SiO_2 layer under pressure. The solvent was distilled off *in vacuo* and the residue was recrystallized from toluene. The yield of ketone **3a** was 0.60 g (see Table 2).

2-Chloro-3-[3-(1-cyclohexenyl)-1-oxopropynyl]anthraquinone (3b) was prepared analogously to ketone **3a** from acid chloride **7** (0.58 g, 1.9 mmol) and 1-ethynylcyclohexene (**5b**) (0.35 g, 3.3 mmol). The yield was 0.35 g (see Table 2).

2-Phenylanthra[1,2-*b*]thiopyran-4,7,12-trione (1a). Chloroanthraquinone **2a** (0.52 g, 1.4 mmol) was added to a suspension of Na_2S (0.50 g, 6.4 mmol) in 95% EtOH (90 mL) with heating (~60 °C). The reaction mixture was refluxed with stirring for 15 min, cooled, poured into water (500 mL), and extracted with $CHCl_3$ (3×100 mL). The chloroform solution was washed with water and dried with $MgSO_4$. The solvent was removed *in vacuo*. The crude product was purified by chromatography on SiO_2 in $CHCl_3$ and crystallization from a toluene—hexane mixture. The yield of anthrathiopyrantrione **1a** was 0.42 g (see Table 1).

2-(1-Cyclohexenyl)anthra[1,2-*b*]thiopyran-4,7,12-trione (1b) was prepared analogously to compound **1a** from ketone **2b** (0.40 g, 1.1 mmol) and Na_2S (0.45 g, 5.8 mmol). The yield of thiopyran **1b** was 0.32 g (see Table 1).

2-(1-Hydroxy-1-methylethyl)anthra[1,2-*b*]thiopyran-4,7,12-trione (1c) was prepared analogously to compound **1a** from ketone **2c** (0.40 g, 1.1 mmol) and Na_2S (0.40 g, 5.1 mmol) in 95% EtOH (60 mL). The yield of thiopyran **1c** was 0.31 g (see Table 1).

2-Butylanthra[1,2-*b*]thiopyran-4,7,12-trione (1d). Condensation of ketone **2d** (0.50 g, 1.4 mmol) with Na_2S (0.50 g, 6.4 mmol) in 95% EtOH (80 mL) was carried out under the conditions of synthesis of thiopyran **1a**. The crude product was chromatographed on SiO_2 in toluene and crystallized from a toluene—hexane mixture. The yield of anthrathiopyrantrione **1d** was 0.40 g (see Table 1).

2-(1-Methylprop-1-enyl)anthra[1,2-*b*]thiopyran-4,7,12-trione (1e) was prepared from vinylacetylenic ketone **2e** (a mixture of *Z* and *E* isomers) (0.40 g, 1.1 mmol) and Na_2S (0.40 g, 5.1 mmol) analogously to thiopyran **1d**. The yield was 0.27 g (see Table 1).

2-Phenylanthra[2,3-*b*]thiopyran-4,6,11-trione (4a) was prepared from chloroanthraquinone **3a** (0.30 g, 0.8 mmol) and Na_2S (0.45 g, 5.8 mmol) in 95% EtOH (80 mL) under the conditions of synthesis of compound **1a**. Compound **4a** was purified by crystallization from toluene. The yield was 0.28 g (see Table 1).

2-(1-Cyclohexenyl)anthra[2,3-*b*]thiopyran-4,6,11-trione (4b) was prepared from ketone **3b** (0.20 g, 0.5 mmol) and Na_2S (0.30 g, 3.8 mmol) analogously to thiopyran **1a**. The yield was 0.15 g (see Table 1).

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