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This paper is dedicated to the memory of Professor Raymond N. Castle

Photocyclization of 3-chloro-*N*-(9-phenanthryl)benzo[*b*]thiophene-2-carboxamide (**3**) and 3-chloro-*N*-(9-phenanthryl)-naphtho[1,2-*b*]thiophene-2-carboxamide (**10**) yielded dibenzo[*f,h*]benzothieno[2,3-*c*]quinolin-10(9*H*)-one (**4**) and dibenzo[*f,h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-10(9*H*)-one (**11**), respectively. Further elaboration of the lactams provided three novel unsubstituted new ring systems.

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We have been interested in the synthesis and nmr spectroscopic properties of nitrogen/sulfur-containing novel heterocycles [2] which occur or are suspected of occurring in coal liquids, coal-derived products and shale oils. To this end, as a continuing study of the synthesis of novel heterocyclic ring systems *via* oxidative photocyclization, we wish to report in this paper the synthesis of three previously unknown heterocyclic ring systems, dibenzo[*f,h*]benzothieno[2,3-*c*]quinoline (**7**), dibenzo[*f,h*]benzothieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (**8**), and dibenzo[*f,h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**14**).

The synthetic pathway to **7** and **8** is illustrated in Scheme 1. The carbonyl chloride **1** was obtained by treatment of cinnamic acid with thionyl chloride in the

presence of pyridine [5]. When **1** was allowed to react with 9-phenanthrenamine (**2**) [6], 3-chloro-*N*-(9-phenanthryl)-benzo[*b*]thiophene-2-carboxamide (**3**) was obtained in 61% yield. Upon irradiation of **3** in benzene solution with a 450 watt medium pressure mercury vapor lamp, dibenzo[*f,h*]benzothieno[2,3-*c*]quinolin-10(9*H*)-one (**4**) was obtained in 95% yield. Chlorination by refluxing the lactam **4** in phosphorus oxychloride provided 10-chloro-dibenzo[*f,h*]benzothieno[2,3-*c*]quinoline (**5**) in 36% yield. Reaction of the chloride **5** with anhydrous hydrazine in a mixture of benzene and ethanol (v/v 7:10) gave 10-hydrazinodibenzo[*f,h*]benzothieno[2,3-*c*]quinoline (**6**) in 94% yield. Upon removal of the hydrazine moiety by refluxing **6** with a 10% copper sulfate solution and

Table 1

¹H and ¹³C NMR Chemical Shift Assignments and Observed Proton Carbon Multiple-Bond Correlations for Compound **7** in Deuteriochloroform at 298 °K at Observation Frequencies of 360.13 and 90.56 MHz, Respectively

Position	δH	δC	Two-Bond Correlation	Three-Bond Correlation
1	8.89	128.9		H3
2	7.51	125.1		H4
3	7.72	128.2		H1
4	8.65	123.6		H2
4a		130.7		H1, H3, H5
4b		131.0		H4, H6, H8
5	8.62	122.3		H7
6	7.77	128.2		H8
7	7.77	127.7		H5
8	9.26	125.3		H6
8a		130.7		H5, H7
8b		143.3		H10
10	9.34	143.4		
10a		136.9	H10	
11a		141.5		H13, H15
12	7.99	123.4		H14
13	7.56	128.2		H15
14	7.38	123.5		H12
15	8.74	126.4		H13
15a		135.0		H12, H14
15b		135.2		H10
15c		121.9		H1
15d		127.6		H2, H4

Table 2

¹H and ¹³C NMR Chemical Shift Assignments and Observed Proton-Carbon Multiple-Bond Correlations for Compound **8** in at 298 °K at Observation Frequencies of 360.13 and 90.56 MHz, Respectively

Position	δH	δC	Three-Bond Correlation
1	8.33	128.4	H3
2	7.37	126.1	H4
3	7.54	127.7	H1
4	8.40	123.3	H2
4a		128.5	H1, H3, H5
4b		130.5	H4, H6, H8
5	8.53	124.0	H7
6	7.63	128.2	H8
7	7.59	127.9	H5
8	8.40	122.1	H6
8a		123.2	H5, H7
8b		130.2	H8
10	9.54	138.0	
12a		146.3	H10
12b		126.5	
13a		140.9	H15, H17
14	7.92	123.3	H16
15	7.39	126.7	H17
16	7.21	124.1	H14
17	7.99	125.9	H15
17a		135.5	H14, H16
17b		125.6	H17
17c		118.1	H1
17d		127.0	H2, H4

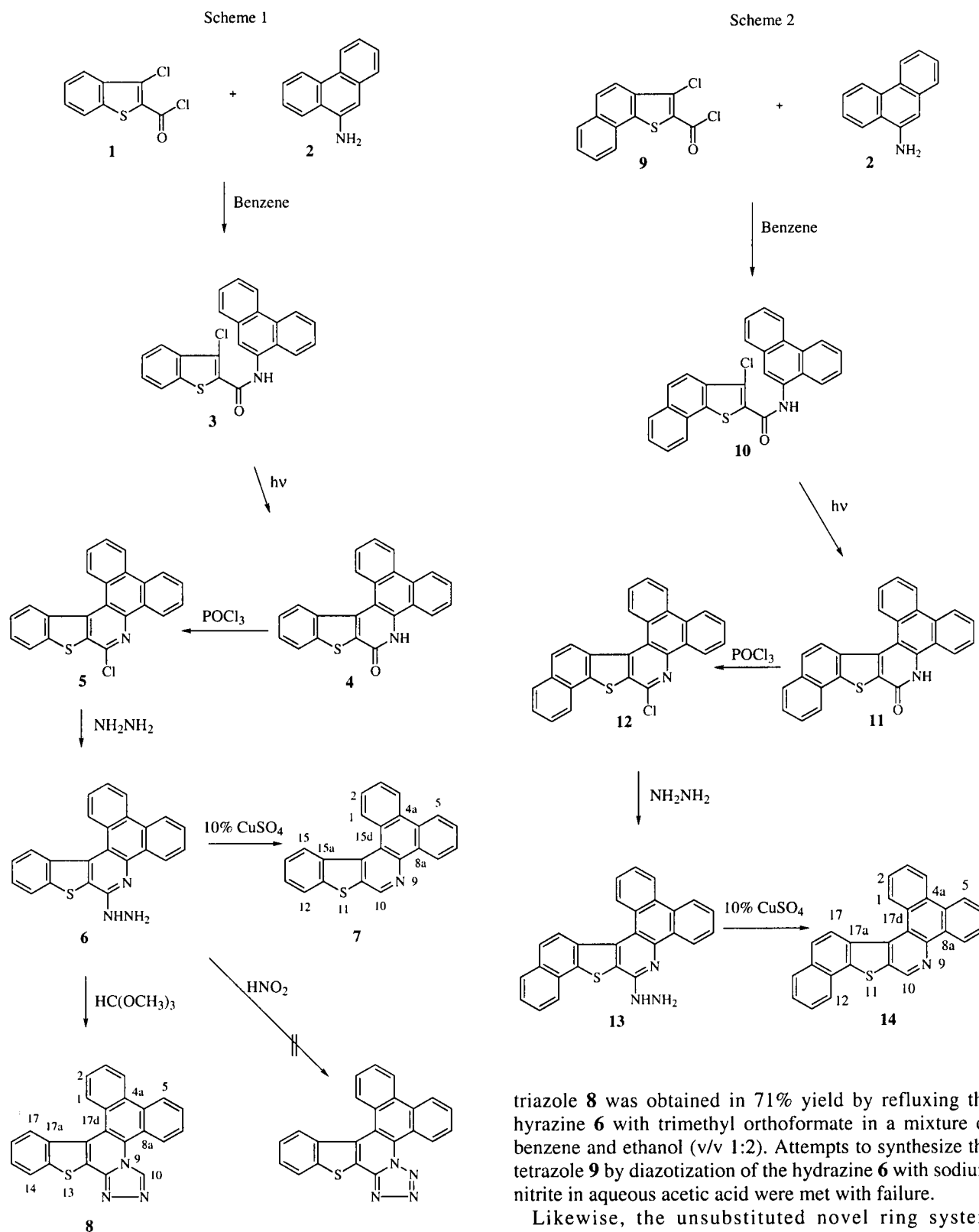


Table 3
¹H and ¹³C NMR Chemical Shift Assignments and Observed Proton Carbon Multiple Bond Correlations for Compound **14** in Deuteriochloroform at 298°K at Observation Frequencies of 360.13 and 90.56 MHz, Respectively

Position	δH	δC	Two-Bond Correlation	Three-Bond Correlation
1	8.75	129.2		H3
2	7.48	125.2		H4
3	7.67	128.1		H1
4	8.60	123.6		H2
4a		130.5		H1, H3, H5
4b		130.6		H4, H6, H8
5	8.57	122.4		H7
6	7.70	128.2		H8
7	7.70	127.6		H5
8	9.23	125.3		H6
8a		131.0		H5, H7
8b		143.1		H10
10	9.33	143.2		
10a		137.7	H10	
11a		141.0		H17
11b		129.0		H13, H15
12	8.19	124.8		H14
13	7.60	127.1		H15
14	7.60	127.6		H12
15	7.90	128.7		H13, H16
15a		132.3		H12, H14, H17
16	7.64	124.4		H15
17	8.46	123.7		
17a		132.3		H16
17b		134.7		H10
17c		121.6		H1
17d		127.7		H2, H4

The total assignments of the proton and carbon-13 nmr spectra of **7**, **8**, and **14** were achieved by the concerted usage of two-dimensional nmr techniques. The ¹H and ¹³C chemical shifts of **7**, **8**, and **14** are summarized in Table 1, 2 and 3.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting apparatus and are uncorrected. The ¹H nmr were obtained on a Bruker AMX360 MHz NMR spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and J values in Hz. Analysis (tlc) were performed on Sigma precoated silica gel plates containing a fluorescent indicator. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

The ¹H and ¹³C spectra of **7**, **8** and **14** were acquired on a Bruker AMX360 MHz NMR spectrometer operating at an observation frequency of 360.13 MHz for ¹H and 90.56 for ¹³C. All experiments were performed using an inverse-geometry 5 mm broad band probe. Pulse widths (90°) for ¹H and ¹³C were 8.0 and 16.0 μsec, respectively. The COSY spectra were recorded using the Bruker pulse program (COSY90) [7]. The NOESY experiments were performed using the Bruker pulse program (noesytp) [8]. The HMQC experiments were performed using the Bruker pulse program (invbdgtp) with the BIRD sequence

optimized for direct couplings (165 Hz ¹J_{CH}) [9]. The HMQC-TOCSY were obtained using the Bruker pulse program (invbmltp) [10] with decoupling and acquisition initiated simultaneously. The HMBC spectra were obtained using the Bruker pulse program (inv4lplrnd) [11] optimized for 10 Hz ³J_{CH} couplings.

3-Chloro-N-(9-phenanthryl)benzo[b]thiophene-2-carboxamide (**3**).

A mixture of 2.08 g (9.0 mmoles) of carbonyl chloride **1** [5], and 1.74 g (9.0 mmoles) of 9-phenanthrenamine (**2**) [6] in 80 ml of benzene was heated under reflux for 4 hours. After cooling to room temperature, the mixture was evaporated to dryness *in vacuo*. The solid was recrystallized from benzene to afford 2.12 g (5.47 mmoles, 61%) of amide **3** as off-white crystals, mp 218-219°; tlc (benzene) R_f 0.47; ¹H nmr (deuteriochloroform): δ 7.55 (m, 2H, ArH), 7.62 (m, 2H, ArH), 7.72 (m, 2H, ArH), 7.90 (m, 2H, ArH), 7.96 (dd, 1H, ArH), 8.15 (dd, 1H, ArH), 8.59 (s, 1H, H-10'), 8.65 (dd, 1H, ArH), 8.78 (dd, 1H, ArH), 9.39 (br s, 1H, NH).

Anal. Calcd. for C₂₃H₁₄ClNOS: C, 71.22; H, 3.64; N, 3.61; S, 8.27. Found: C, 70.90; H, 3.92; N, 3.50; S, 8.00.

Dibenzo[f,h]benzothieno[2,3-c]quinolin-10(9H)-one (**4**).

A mixture of 0.20 g (0.52 mmole) of amide **3**, 0.052 g of triethylamine in 460 ml of benzene was irradiated with a 450 watt Hanovia medium pressure mercury vapor lamp. A slow stream of air was passed through the solution during the course of the reaction. The precipitate was collected by filtration and washed with water to afford 0.18 g (0.51 mmole, 99%) of lactam **4**, mp >300°. This compound was used in the next step without further purification because of its low solubility.

10-Chlorodibenzo[f,h]benzothieno[2,3-c]quinoline (**5**).

A mixture of 1.70 g (4.84 mmoles) of lactam **4** and 100 ml of phosphorus oxychloride was heated at 100-110° for 4 hours. After cooling to room temperature the mixture was poured into 1000 ml of ice water with vigorous stirring. The precipitate was collected by filtration, washed with water and dried. The solid was recrystallized from benzene to yield 0.65 g (1.76 mmoles, 36%) of **5** as yellowish feather-like crystals, mp 251-253°; tlc (benzene) R_f 0.95; ¹H nmr (deuteriochloroform): δ 7.40 (t, J = 7.8 Hz, 1H, ArH), 7.52 (t, J = 7.8 Hz, 1H, ArH), 7.59 (t, J = 7.8 Hz, 1H, ArH), 7.74 (m, 3H, ArH), 8.00 (d, J = 7.8 Hz, 1H, ArH), 8.60 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H, ArH), 8.65 (d, J = 7.8 Hz, 1H, ArH), 8.71 (d, J = 7.8 Hz, 1H, ArH), 8.83 (d, J = 7.8 Hz, 1H, H-1), 9.19 (dd, 1H, J = 7.8 Hz, J = 1.3 Hz, 1H, H-8).

Anal. Calcd. for C₂₃H₁₂ClNS: C, 74.69; H, 3.27; N, 3.79; S, 8.67. Found: C, 74.54; H, 3.12; N, 3.54; S, 8.42.

10-Hydrazinodibenzo[f,h]benzothieno[2,3-c]quinoline (**6**).

To a boiling solution of 0.57 g (1.54 mmoles) of chloride **5** in 35 ml of benzene and 50 ml of absolute ethanol, was added dropwise 10 ml of anhydrous hydrazine over a period of 30 minutes. The resulting solution was heated under reflux for 18 hours. After cooling to room temperature the solid was collected by filtration and washed with ice-chilled absolute ethanol to obtain 0.53 g (1.45 mmoles, 94%) of hydrazine **6** as yellow crystals after recrystallization from ethanol/benzene mixture, mp 257-260° dec; tlc (benzene) R_f 0.57. There is no nmr spectrum of **6** available due to its low solubility and thermal instability.

Anal. Calcd. For $C_{23}H_{15}N_3S$: C, 75.59; H, 4.14; N, 11.50. Found: C, 75.40; H, 4.34; N, 11.46.

Dibenzo[*f,h*]benzothieno[2,3-*c*]quinoline (7).

To a mixture of 0.15 g (0.41 mmole) of hydrazine **6** in 10 ml of glacial acetic acid and 5 ml of water, was added dropwise 10 ml of a 10% copper sulfate solution. The resulting mixture was heated under reflux for 20 hours. After cooling to room temperature the mixture was basified with a 2*N* sodium hydroxide solution. The solid was collected by filtration and washed with water. The solid was dissolved in 10 ml of chloroform and applied to a column eluted with benzene. The fractions containing the product were pooled and evaporated to dryness *in vacuo*. The solid was recrystallized from cyclohexane/benzene mixture (1:1) to give 0.091 g (0.27 mmole, 66%) of the unsubstituted product **7** as yellowish fine needles, mp 207-209°, tlc (benzene) R_f 0.74.

Anal. Calcd. for $C_{23}H_{13}NS$: C, 82.36; H, 3.91; N, 4.18. Found: C, 82.15; H, 4.15; N, 4.01.

Dibenzo[*f,h*]benzothieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]quinoline (8).

A mixture of 0.18 g (0.49 mmole) of hydrazine **6** in 50 ml of absolute ethanol and 25 ml of benzene was heated under reflux. To the boiling mixture, 15 ml of trimethyl orthoformate was added and the mixture was heated under reflux for 16 hours. After cooling to room temperature the mixture was evaporated to dryness *in vacuo*. The solid was dissolved in 10 ml of chloroform and applied to a column chromatography eluted with chloroform/ethyl acetate (4:1) mixture. The fractions containing the product were pooled and evaporated to dryness *in vacuo*. The solid was recrystallized from benzene to give 0.13 g (0.35 mmole, 71%) of triazole **8** as colorless granules, mp > 284-285°; tlc (dichloromethane:ethyl acetate, 4:1) R_f 0.41.

Anal. Calcd. for $C_{24}H_{13}N_3S$: C, 76.78; H, 3.49; N, 11.19. Found: C, 76.55; H, 3.71; N, 10.95.

3-Chloro-*N*-(9-phenanthryl)naphtho[1,2-*b*]thiophene-2-carboxamide (10).

A mixture 2.53 g (9.0 mmoles) of 3-chloronaphtho[1,2-*b*]thiophene-2-carbonyl chloride (**9**) [12,13] and 1.74 g (9.0 mmoles) of 9-phenanthrenamine (2) (**6**) was heated under reflux for 4 hours. After cooling to room temperature, the solid was collected by filtration and recrystallized from benzene to afford 2.61 g (5.96 mmoles, 66%) of amide **10** as off-white crystals, mp 276-279°; tlc (benzene) R_f 0.78; 1H nmr (deuteriochloroform): 47°, δ 7.61-7.76 (m, 7H, ArH), 7.90 (s, 1H, H-10'), 7.93-8.00 (m, 2H, ArH), 8.23 (m, 2H, ArH), 8.64 (d, $J = 5.6$ Hz, 1H, ArH), 8.68 (d, $J = 7.8$ Hz, 1H, ArH), 8.79-8.82 (m, 1H, ArH), 9.39 (br s, 1H, NH).

Anal. Calcd. for $C_{27}H_{16}ClNOS$: C, 74.05; H, 3.68; N, 3.20; S, 7.32. Found: C, 74.18; H, 3.80; N, 3.20; S, 7.3

Dibenzo[*f,h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-10(9*H*)-one (11).

A mixture of 0.5 g (1.17 mmoles) of amide **10** and 0.12 g of triethylamine in 500 ml of benzene was irradiated with a 450 watt Hanovia medium pressure mercury vapor lamp for 4 hours. A slow stream of air was passed through the solution during the course of the reaction. The solid was collected by filtration and washed with water to afford 0.40 g (1.0 mmole, 85%) of lactam **11** as yellowish powder, mp > 300°. The compound was used

without further purification due to its low solubility. The low solubility keeps us from measuring a meaningful proton nmr spectrum of **11**.

10-Chlorodibenzo[*f,h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (12).

A mixture of 1.60 g (3.99 mmoles) of lactam in 80 ml of phosphorus oxychloride was heated at 110-120° for 4 hours. After cooling to room temperature the mixture was poured into 600 ml of ice-water with vigorous stirring. The precipitate was collected by filtration and washed with water. The dried solid was recrystallized from benzene to afford 0.85 g (2.02 mmoles, 51%) of chloride **12** as yellowish feather-like crystals, mp > 300°; tlc (benzene) R_f 0.92; 1H (deuteriochloroform and two drops of deuterated trifluoroacetic acid): δ 7.71 (t, $J = 7.6$ Hz, 1H, ArH), 7.83-8.03 (m, 6H, ArH), 8.09 (dd, $J = 7.0$ Hz, $J = 1.5$ Hz, 1H, ArH), 8.38 (dd, $J = 7.0$ Hz, $J = 1.5$ Hz, 1H, ArH), 8.52 (d, $J = 9.1$ Hz, 1H, ArH), 8.77 (d, $J = 8.4$ Hz, 1H, ArH), 8.80 (d, $J = 8.4$ Hz, 1H, ArH), 8.87 (d, $J = 8.2$ Hz, 2H, ArH).

Anal. Calcd. for $C_{27}H_{14}ClNS$: C, 77.22; H, 3.36; N, 3.34; S, 7.64. Found: C, 77.08; H, 3.33; N, 3.32; S, 7.72.

10-Hydrazinodibenzo[*f,h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (13).

A mixture of 1.18 g (2.81 mmoles) of chloride **12** in 20 ml of absolute ethyl alcohol and 15 ml of benzene was heated to boiling. To the above boiling mixture 10 ml of anhydrous hydrazine was added dropwise over a period of 30 minutes. The resulting mixture was heated under reflux for 48 hours. After cooling to room temperature, the solid was filtrated and washed with ethanol to give 0.54 g (1.3 mmoles, 46%) of hydrazine **13** as yellow crystals, mp > 280°; 1H nmr (DMSO- d_6): 7.58-7.88 (m, 6H, ArH), 8.11 (d, $J = 7.0$ Hz, 1H, ArH), 8.35-8.41 (m, 2H, ArH), 8.54 (d, $J = 7.6$ Hz, 1H, ArH), 8.71-8.80 (m, 3H, ArH), 9.17 (d, $J = 6.0$ Hz, 1H, ArH). The compound was used for the next reaction without further purification due to its low solubility and thermal instability.

Dibenzo[*f,h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (14).

To a boiling mixture of 0.15 g (0.36 mmole) of hydrazine **13** in 15 ml of glacial acetic acid, was added dropwise 10 ml of 10% aqueous copper sulfate solution. The mixture was heated under reflux for 30 hours. After cooling to room temperature the mixture was neutralized with 2*N* sodium hydroxide solution. The solid was collected by filtration and washed with water. The dried solid was dissolved in 10 ml of benzene and the solution was subjected to column chromatography eluted with benzene. The fractions containing the product were pooled and the solvent was removed under reduced pressure. The solid was recrystallized from benzene/cyclohexane (1:4) to give 0.09 g (0.23 mmole, 64%) of **14** as yellow crystals, mp > 280°, tlc (benzene) R_f 0.70.

Anal. Calcd. for $C_{27}H_{15}NS$: C, 84.13; H, 3.92; N, 3.63. Found: C, 84.01; H, 4.03; N, 3.89.

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