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The synthesis of two previously unknown heterocyclic ring systems, namely benzo[*h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**1**) and benzo[*f*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**2**) was accomplished *via* photocyclization of the appropriate amides followed by chlorination and catalytic dechlorination. The total assignment of ¹H and ¹³C nmr spectra of **2** was determined utilizing two-dimensional nmr methods, providing unequivocal structural proof of the two novel polycyclic ring systems.

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In the course of our studies [3,4] concerned with nitrogen/sulfur-containing polycyclic aromatic compounds which occur or are suspected of occurring in coal liquids, coal-derived products and shale oils, we synthesized the novel naphtho[2',1':4,5]thieno[2,3-*c*]quinoline ring system and its four monomethyl derivatives [5]. In connection with a continuing study of novel polycyclic heterocyclic ring systems [1] we describe in this paper the synthesis of two previously unknown heterocyclic ring systems, namely, benzo[*h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**1**) and benzo[*f*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**2**) *via* photocyclization.

The synthesis of the key intermediate, 3-chloronaphtho[1,2-*b*]thiophene-2-carbonyl chloride (**3**), has been reported [5,6] by refluxing 3-(2-naphthyl)propenoic acid [7] and thionyl chloride in the presence of pyridine [8,9]. After treatment of **3** with 1-naphthylamine (**4**) in benzene solution, 3-chloro-*N*-(1-naphthyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**5**) was obtained in 80% yield. Irradiation of the amide **5** in cyclohexane solution containing triethylamine with a 450 watt medium pressure mercury vapor lamp gave benzo[*h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**6**) in 93% yield. Phosphorus oxychloride chlorination of **6** produced 6-chlorobenzo[*h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**7**) in 62% yield. Catalytic dechlorination of **7** with 10% Pd-C in 1:1 benzene-methanol solution in the presence of potassium hydroxide at 45 psi and *ca.* 50-55° provided the unsubstituted novel ring system benzo[*h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**1**) in 64% yield (Scheme I).

Similarly, 3-chloro-*N*-(2-naphthyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**9**) was obtained in 73% yield upon treatment of **3** with 2-naphthylamine (**8**). Photocyclization of **9** afforded only one of the two possible isomers, benzo[*f*]naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-8(7*H*)-one (**10**) in 73% yield with no detectable benzo[*g*]naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-7(6*H*)-one (**11**) being formed. These

results are consistent with our previous work [1c,1e]. Chlorination of **10** was performed by refluxing in phosphorus oxychloride to yield 8-chlorobenzo[*f*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**12**) in 60% yield.

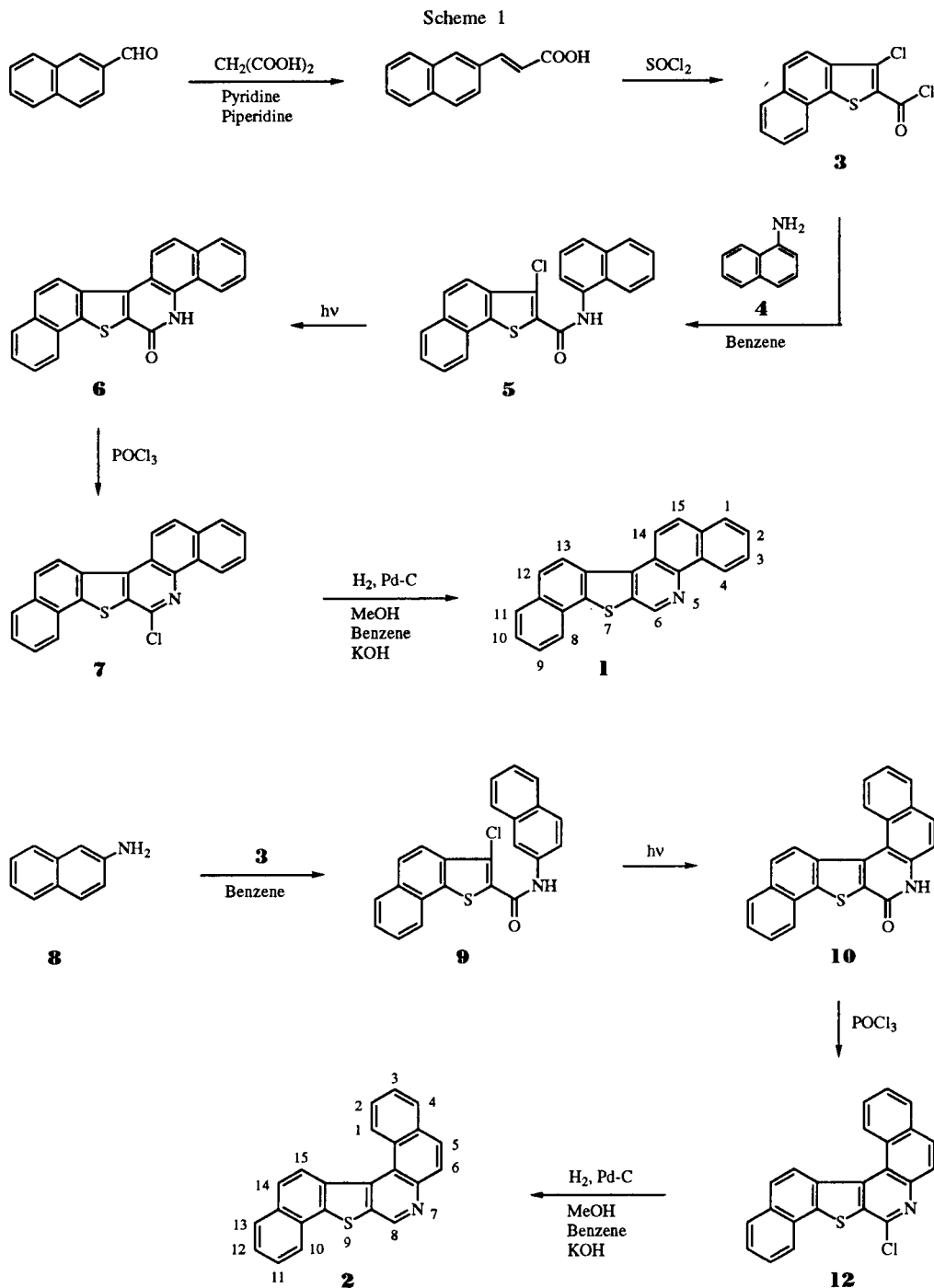
Catalytic dechlorination of **12** with 10% Pd-C in 1:1 benzene-methanol in the presence of potassium hydroxide at 45 psi and *ca.* 50° gave the novel parent ring system benzo[*f*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**2**) in 58% yield after column chromatography (Scheme I).

NMR Spectroscopy.

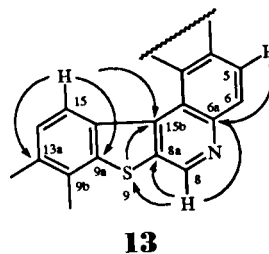
The congested ¹H nmr spectrum of **2** shows two four-spin systems and two two-spin systems which cannot be unambiguously assigned from the COSY spectrum [10] (Figure 1). The well resolved ¹³C nmr spectrum establishes direct heteronuclear correlations from the HMQC spectrum [11] (Figure 2), but unequivocal assignment of the spectrum is not possible without the concerted use of the HMQC and HMBC techniques [11-12].

The key entry point in the long-range heteronuclear chemical shift correlation experiment (Figure 3) is the singlet assigned to H8 at 9.39 ppm on the basis of the lack of coupling and chemical shift. The singlet is directly correlated with the carbon at 144.5 ppm as seen in the HMQC spectrum. Long-range couplings to H8 are observed from three quaternary carbons resonating at 134.3, 137.4 and 145.5 ppm in the HMBC spectrum. By examining the structure of **3**, H8 should correlate to quaternary carbons C6a, C8a and C15b. The correlation at 134.3 ppm is assigned to C8a because it has no other correlations as expected. The carbon resonating at 145.5 ppm is assigned to C6a on the basis of chemical shift. This leaves the correlation at 137.4 ppm, which is assigned to C15b. These correlation pathways are shown in **13**.

From **13** one can see that C15b provides a link between the singlet, H8, and the two-spin system H14 and H15 and that C6a furnishes a link between H8 and the other two-



spin systems, H5 and H6. The quaternary C15b should exhibit only two correlations: one to H8 as assigned previously; the other to H15 as a doublet observed at 8.63 ppm in the HMBC spectrum. Given the unequivocal assignment of the resonance at 8.63 ppm as H15, the response at 141.0 ppm is attributed to C9a on the basis of chemical shift and our past experience [1f,13,14] and thus the quaternary carbon resonating at 132.5 ppm must be C13a. In addition H14 may be unequivocally assigned to the doublet observed at 7.74 ppm on the basis of COSY connecti-



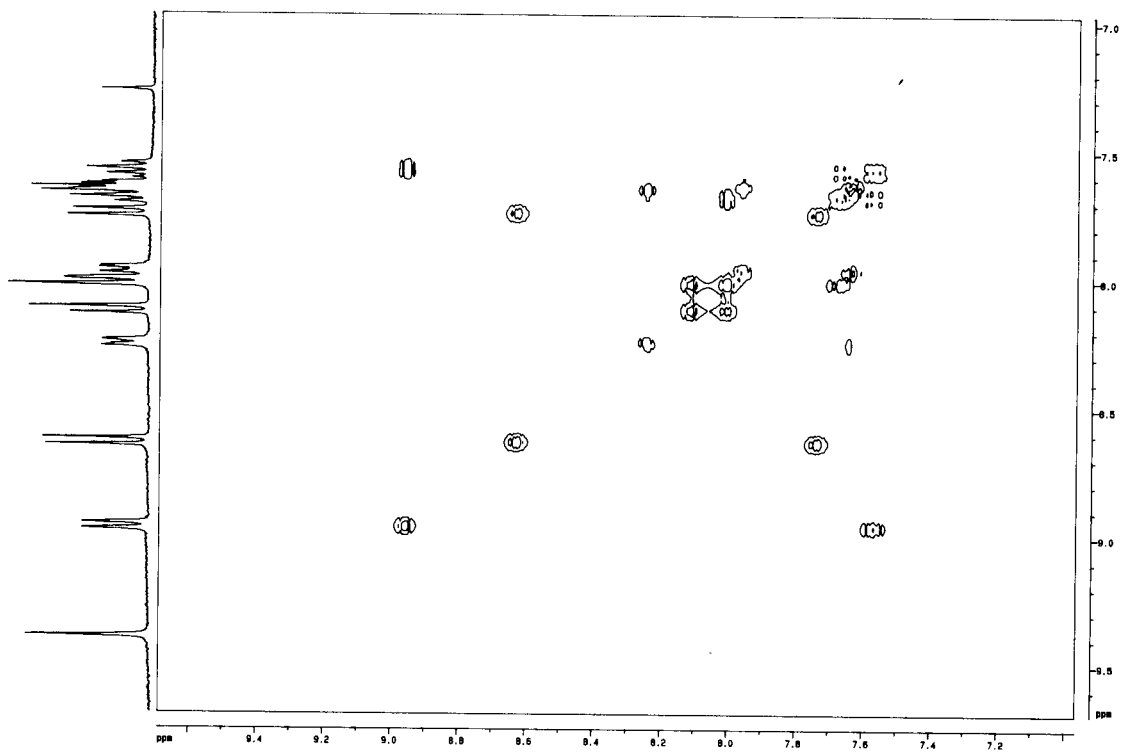


Figure 1. Two-dimensional autocorrelated (COSY) homonuclear nmr spectrum of **2** in deuteriochloroform at observation frequency of 360.13 MHz for ^1H .

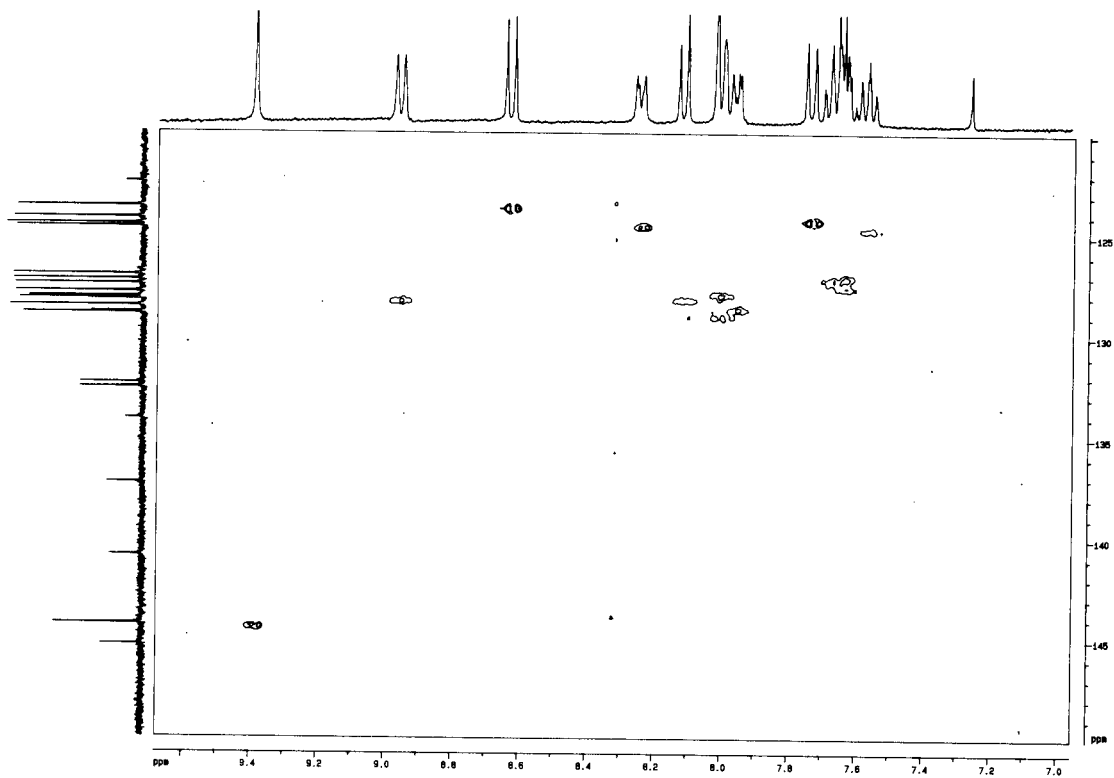


Figure 2. Heteronuclear proton-carbon chemical shift correlation spectrum of **2** in deuteriochloroform at observation frequencies of 360.13/90.56 MHz for ^1H and ^{13}C , respectively.

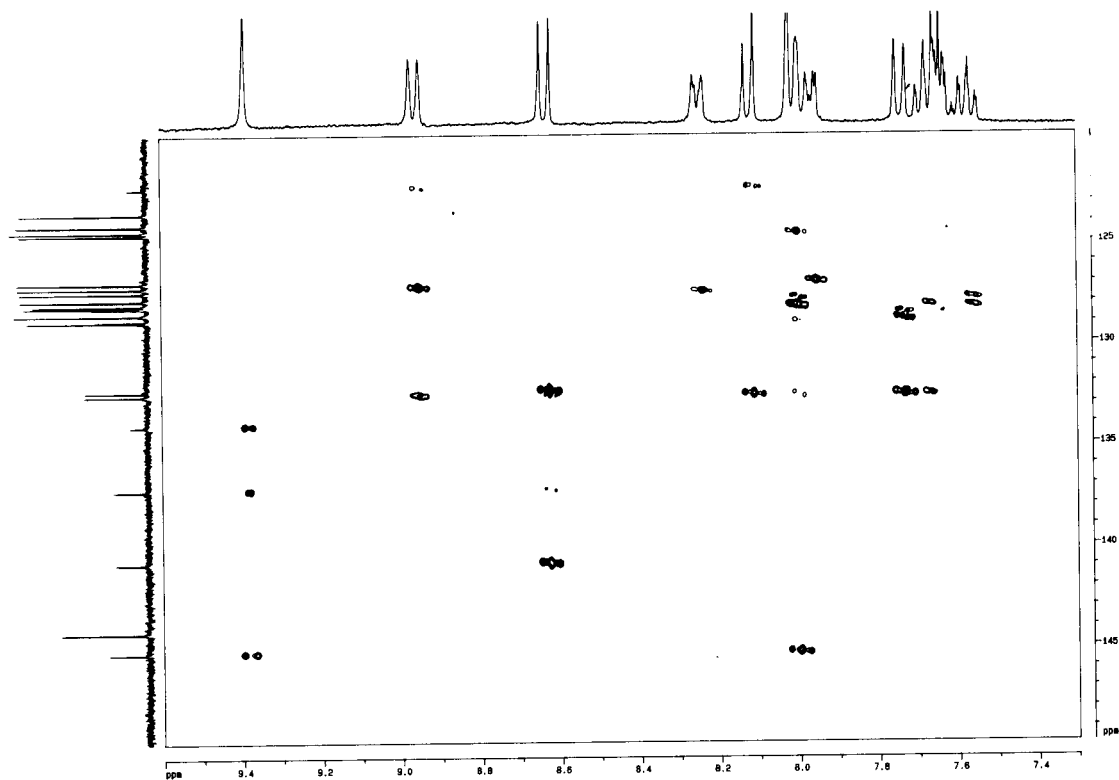
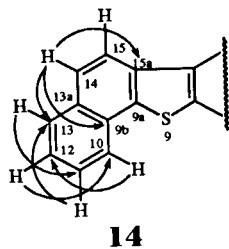


Figure 3. Long-range heteronuclear chemical shift correlation spectrum of **2** recorded in deuteriochloroform at observation frequencies of 360.13/90.56 MHz for ^1H and ^{13}C , respectively.

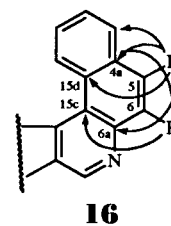
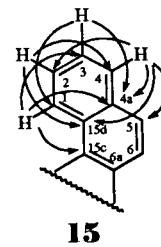
ities and thus C14 is at 124.3 ppm in HMQC spectrum. Although both C9a and C13a show no connectivities to the four-spin system H10, H11, H12 and H13, fortunately H14 reveals long-range correlations to a protonated carbon assigned as C13 at 128.7 ppm and two quaternary carbons observed at 129.0 and 132.7 ppm. The observed correlation at 132.7 ppm is assigned to C15a on the basis of chemical shift and the precedents [1f,13,14]. Therefore the correlation at 129.0 ppm must be C9b. Having established the assignment of H13 and C13, the balance of the proton and carbon resonances in the four-spin system containing H13 can be readily assigned through concerted usage of COSY, HMQC and HMBC spectra. These correlation pathways are shown in **14**.



At this point one can complete the assignment of the ^1H nmr spectrum using the data from the COSY spectrum by assuming that H1, as the other bay region proton, is the

doublet resonating at 8.96 ppm. With the proton spectrum assigned, the remaining quaternary carbons can be easily assigned in similar fashion described as above.

These correlation pathways are shown in **15** and **16**. The ^1H and ^{13}C nmr chemical shifts of **2** are presented in Table 1.



In conclusion, we have synthesized two previously unknown novel heterocyclic ring systems. Total assignments of ^1H and ^{13}C spectra of **2** were achieved by concerted

Table 1

The ^1H and ^{13}C -NMR Chemical Shift Assignments and Observed Proton-Carbon Multiple-Bond Correlations for Compound **2** in Deuteriochloroform at Observation Frequencies of 360.13 and 90.56 MHz, Respectively

Position	δH	δC	Two-Bond Correlation	Three-Bond Correlation
1	8.96	128.3		H-3
2	7.57	124.8		H-4
3	7.68	127.4		H-1
4	8.01	128.0		H-2, H-5
4a		132.8 [a]	H-4, H-5	H-1, H-3, H-6
5	8.01	129.1		H-4
6	8.12	128.3		
6a		145.5		H-5, H-8
8	9.39	144.5		
8a		134.3	H-8	
9a		141.0		H-15
9b		129.0		H-14
10	8.25	124.6		H-12
11	7.64	127.2		H-13
12	7.64	127.6		H-10
13	7.96	128.7		H-11, H-14
13a		132.5		H-15
14	7.74	124.3		
15	8.63	123.8		
15a		132.7 [a]		H-14
15b		137.4		H-8, H-15
15c		122.5		H-1, H-6
15d		128.4		H-2, H-4, H-5

[a] Assignments for the resonances noted may be interchanged. Unequivocal assignment could not be made with the digital resolution available.

usage of COSY, HMQC and HMBC two-dimensional nmr methods and this confirms our structural identification of **2** [15].

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The ir spectra were recorded on a Beckman FT1100 spectrometer as potassium bromide pellets and frequencies are expressed in cm^{-1} . The ^1H nmr spectra of the intermediates were obtained on a JEOL FX-90Q spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and J values in Hz. Column chromatography was performed utilizing Aldrich silica gel, 70-230 mesh. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

Proton and carbon nmr spectra of compound **2** were acquired using a Bruker AMX360 spectrometer operating at a proton frequency of 360.13 MHz and a carbon frequency of 90.56 MHz. The proton spectra were obtained using a 5 μsecond (48.6°) pulse and 5 seconds between transients to insure accurate integrals. All two-dimensional experiments were acquired using a Bruker inverse-geometry probe. Spectral width for all proton and proton correlation experiments was 992.06 Hz. A one-dimensional carbon spectrum was obtained with a spectral width of 15001.5 Hz with 2 seconds between transients. The COSY spectrum was ob-

tained using the standard COSY pulse sequence [10] with 512 t_1 increments of 504 μs used to encode a second dimension of 992.06 Hz. Proton-carbon correlation experiments were acquired using the proton-detected techniques of Bax and Subramanian [11]. Mixing times of 3.0 ms and 47.0 ms were used for direct and long-range methods, respectively. For the phase-sensitive direct correlation technique, 256 t_1 increments of 156 μs were used to encode a spectral width of 3205.13 Hz. The HMBC spectrum was obtained using the pulse sequence described by Bax and Summers [12] using 256 t_1 increments of 312 μs to encode a spectral width of 3205.13 Hz.

3-Chloro-*N*-(1-naphthyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**5**).

A mixture of 5.0 g (17.8 mmoles) of 3-chloronaphtho[1,2-*b*]thiophene-2-carbonyl chloride (**3**) [5,6] and 2.55 g (17.8 mmoles) of 1-naphthylamine (**4**) in 150 ml of benzene was heated under reflux for 2 hours. After cooling the mixture was evaporated to dryness *in vacuo*. The solid was washed with water and then recrystallized from benzene to give 5.50 g (14.2 mmoles, 80%) of **5** as an off-white powder, mp 200-202°; ir (potassium bromide): 3417 (NH stretching), 3050 (aromatic CH stretching), 1653 (C=O stretching); ^1H nmr (DMSO- d_6): δ 7.46-8.34 (m, 13H, ArH), 10.25 (br s, 1H, NH).

Anal. Calcd. for $\text{C}_{23}\text{H}_{14}\text{ClNOS}$: C, 71.22; H, 3.64; N, 3.61; S, 8.27. Found: C, 71.18; H, 3.82; N, 3.55; S, 8.06.

Benzo[*h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**6**).

A mixture of 0.5 g (1.29 mmoles) of **5**, 0.15 g of triethylamine, and 500 ml of cyclohexane 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 give 0.42 g (1.20 mmoles, 93%) of **6**, mp > 280°; ir (potassium bromide): 3163 (NH stretching), 3050 (aromatic CH stretching), 1653 (C=O stretching); ^1H nmr (DMSO- d_6): 150° δ 7.43-8.37 (m, 11H, ArH), 8.84 (dd, $J_{3,4} = 9.1$ Hz, $J_{2,4} = 3.8$ Hz, 1H, H-4), 9.95 (br s, 1H, NH). The compound was used for the next step without further purification because of low solubility.

6-Chlorobenzo[*h*]naphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**7**).

A mixture of 1.23 g (3.50 mmoles) of **6** and 25 ml of phosphorus oxychloride was heated at 110-120° for 4 hours. After cooling, the mixture was poured into 400 ml of ice-water with caution. The solid was collected by filtration and recrystallized from benzene to afford 0.80 g (2.16 mmoles, 62%) of **7** as golden needles, mp > 300°; ir (potassium bromide): 3047 (aromatic CH stretching); ^1H nmr (DMSO- d_6): 150° δ 7.69-7.82 (m, 4H, ArH), 8.04-8.39 (m, 5H, ArH), 8.91-9.24 (m, 3H, ArH).

Anal. Calcd. for $\text{C}_{23}\text{H}_{12}\text{ClNS}$: C, 74.69; H, 3.27; N, 3.79; S, 8.67. Found: C, 74.78; H, 3.24; N, 3.95; S, 8.55.

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

A mixture of 0.26 g (0.70 mmole) of **7**, 0.1 g of 10% Pd-C, 100 ml of benzene, 100 ml of methanol, and 0.040 g (0.71 mmole) of potassium hydroxide was hydrogenated in a Parr hydrogenator at 45 psi and ca. 50-55° until the uptake of hydrogen ceased. The catalyst was removed by filtration while the mixture was boiling. The filtrate was evaporated to dryness *in vacuo*. The solid was recrystallized from benzene to yield 0.15 g (0.45 mmole, 64%) of **1** as colorless cubes [16], mp 267-269°; ir (potassium bromide): 3052 (aromatic CH stretching); ^1H nmr (deuteriochloroform): 50°

δ 7.60-8.10 (m, 8H, ArH), 8.23-8.34 (m, 1H, H-8), 8.87 (d, $J_{1,2,13} = 9.0$ Hz, 1H, H-13), 8.92 (d, $J_{1,15} = 9.3$ Hz, 1H, H-14), 9.40-9.49 (m, 1H, H-4), 9.52 (s, 1H, H-6).

Anal. Calcd. for $C_{23}H_{13}NS$: C, 82.36; H, 3.91; N, 4.18. Found: C, 82.38; H, 4.07; N, 4.21.

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

A mixture of 2.95 g (10.5 mmoles) of 3-chloronaphtho[1,2-*b*]thiophene-2-carbonyl chloride (**3**) [5,6] and 1.50 g (10.5 mmoles) of 2-naphthylamine (**8**) in 150 ml of benzene was heated under reflux for 2 hours. After cooling the mixture was evaporated to dryness *in vacuo*. The solid was recrystallized from ethyl acetate to afford 2.99 g (7.71 mmoles, 73%) of **9** as an off-white powder, mp 207-210°; ir (potassium bromide): 3392 (NH stretching), 3050 (aromatic CH stretching), 1653 (C=O stretching); ¹H nmr (deuteriochloroform): δ 7.37-8.19 (m, 12H, ArH), 8.38 (d, $J_{1,3'} = 2.1$ Hz, 1H, H-1'), 9.05 (br s, 1H, NH).

Anal. Calcd. for $C_{23}H_{14}ClNOS$: C, 71.22; H, 3.64; N, 3.61; S, 8.27. Found: C, 71.21; H, 3.64; N, 3.50; S, 8.20.

Benzo[*f*]naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-8(7*H*)-one (**10**).

A mixture of 0.5 g (1.29 mmoles) of **9**, 0.15 g of triethylamine, and 500 ml of cyclohexane 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 give 0.36 g (1.02 mmoles, 79%) of **10** as an off-white powder, mp >300°; ir (potassium bromide): 3150 (NH stretching), 3044 (aromatic CH stretching), 1653 (C=O stretching); ¹H nmr (DMSO-*d*₆): 150° δ 7.45-8.40 (m, 11H, ArH), 8.57 (m, 1H, H-1). The compound was used for the next step without further purification because of low solubility.

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

A mixture of 0.99 g (2.82 mmoles) of **10** and 35 ml of phosphorus oxychloride was heated at 110-120° for 4 hours. After cooling the mixture was poured into 400 ml of ice-water with caution. The solid was collected by filtration and recrystallized from benzene to give 0.63 g (1.70 mmoles, 60%) of **12** as off-white crystals, mp 266-268°; ir (potassium bromide): 3047 (aromatic CH stretching); ¹H nmr (deuteriochloroform): 50° δ 7.50-8.08 (m, 9H, ArH), 8.32 (m, 1H, H-10), 8.62 (d, $J_{1,15} = 8.8$ Hz, 1H, H-15), 8.94 (dd, $J_{1,2} = 7.3$ Hz, $J_{1,3} = 2.2$ Hz, 1H, H-1).

Anal. Calcd. for $C_{23}H_{12}ClNS$: C, 74.69; H, 3.27; N, 3.79; S, 8.67. Found: C, 74.73; H, 3.28; N, 3.80; S, 8.49.

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

A mixture of 0.50 g (1.35 mmoles) of **12**, 0.1 g of 10% Pd-C, 0.075 g of potassium hydroxide, 80 ml of methanol, and 80 ml of benzene was hydrogenated in a Parr hydrogenator at 45 psi and *ca.* 50° until the uptake of hydrogen ceased. The catalyst was removed by filtration while the mixture was boiling. The filtrate was evaporated to dryness *in vacuo*. The solid was dissolved in 20

ml of dichloromethane and the solution was chromatographed on silica gel eluting with dichloromethane to recover 0.10 g of the starting material **12** and to give 0.21 g (0.63 mmole, 58%) of **2** as yellow crystals after recrystallization from cyclohexane, mp 219-221°; ir (potassium bromide): 3050 (aromatic CH stretching).

Anal. Calcd. for $C_{23}H_{13}NS$: C, 82.36; H, 3.91; N, 4.18. Found: C, 82.49; H, 4.11; N, 4.02.

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- [16] Needles were formed at the beginning but changed to cubes after a few days in the solvent.