The Synthesis of Novel Polycyclic Heterocyclic Ring Systems *via* Photocyclization. **16** [1]. [1]Benzothieno[2',3':4,5]thieno[2,3-*c*]quinoline and [1]Benzothieno[2',3':4,5]thieno[2,3-*c*]naphtho[1,2-*f*]quinoline

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The synthesis of two previously unknown polycyclic heterocyclic ring systems *via* photocyclization is described. The unequivocal assignment of their proton and carbon spectra was achieved by utilizing two-dimensional nmr techniques.

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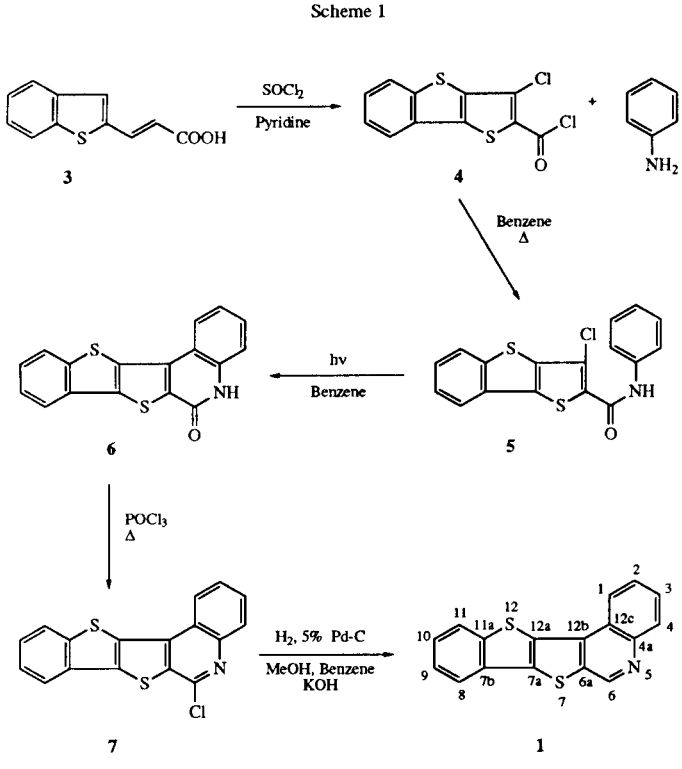
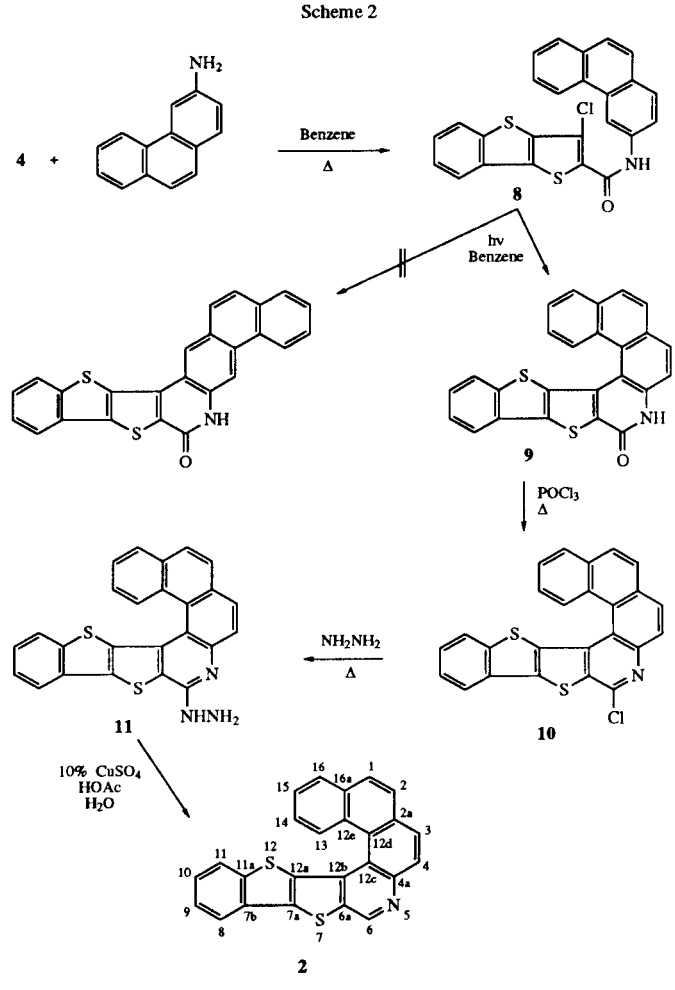
As a continuing study of the synthesis of novel polycyclic heterocyclic ring systems *via* oxidative photocyclization [1] we report in this paper the synthesis of two previously unknown heterocyclic ring systems, namely, [1]benzothieno[2',3':4,5]thieno[2,3-*c*]quinoline (**1**) and [1]benzothieno[2',3':4,5]thieno[2,3-*c*]naphtho[1,2-*f*]-quinoline (**2**).

The synthesis of the common intermediate, 3-chloro[1]-benzothieno[3,2-*b*]thiophene-2-carbonyl chloride (**4**), for both ring systems was accomplished by refluxing benzo[*b*]-thiophene-2-acrylic acid (**3**) [3] with thionyl chloride in the presence of pyridine and piperidine [4]. When **4** was allowed to react with aniline in refluxing benzene, 3-chloro-*N*-phenyl[1]benzothieno[3,2-*b*]thiophene-2-carboxamide (**5**) was obtained in 77% yield. Irradiation of the amide **5** in benzene solution containing triethylamine with a 450 watt medium pressure mercury vapor lamp yielded [1]benzothieno[2',3':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**6**) in 91% yield. Upon treatment of **6** with phosphorus oxychloride, 6-chloro[1]benzothieno[2',3':4,5]thieno[2,3-*c*]quinoline (**7**) was produced in 80% yield. Catalytic dechlorination of **7** with 5% Pd-C in 1:1 benzene-methanol solution in the presence of potassium hydroxide provided the unsubstituted novel ring system [1]benzothieno[2',3':4,5]thieno[2,3-*c*]-quinoline (**1**) in 79% yield (Scheme 1).

Scheme 1

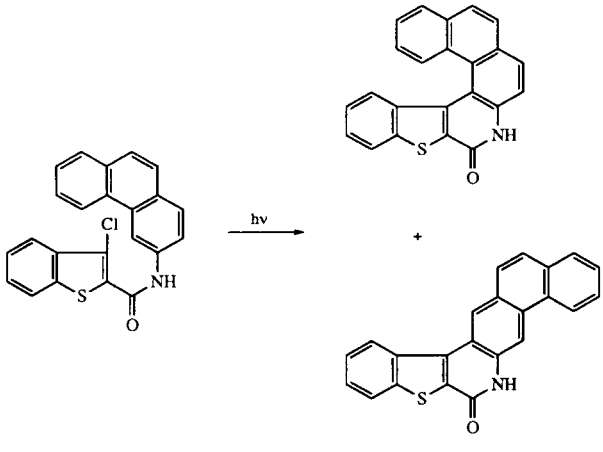


Scheme 2



Similarly, 3-chloro-*N*-(3-phenanthryl)[1]benzothieno-[3,2-*b*]thiophene-2-carboxamide (**8**) was obtained in 62% yield when **4** was treated with 3-aminophenanthrene (Scheme 2). Surprisingly, photocyclization of **8** in 1:2 benzene-cyclohexane solution afforded only one of the two possible isomers, [1]benzothieno[2,3-*c*]naphtho-[1,2-*f*]quinolin-6(5*H*)-one (**9**) in 89% yield. It is worth noting that the photocyclization of 3-chloro-*N*-(3-phenanthryl)benzo[*b*]thiophene-2-carboxamide afforded an isomeric mixture of [1]benzothieno[2,3-*c*]naphtho[1,2-*f*]-quinolin-6(5*H*)-one and [1]benzothieno[2,3-*c*]naphtho-[2,1-*g*]quinolin-7(6*H*)-one [1k] (Scheme 3). It is not clearly understood why upon photocyclization of **8** only **9** was produced. The structural confirmation of **9** was achieved by a complete assignment of proton and carbon spectra of **2** by two-dimensional nmr methods (*vide infra*) after transforming it to chloride **10** followed by hydrazination/dehydrazination due to the low solubility of **9** in organic solvents. Thus, the lactam **9** was converted to chloride **10** in 63% yield by refluxing in phosphorus oxychloride. Hydrazination of **10** was carried out with anhydrous hydrazine in a refluxing mixture of benzene and ethanol to give 6-hydrazino[1]benzothieno[2',3':4,5]-thieno[2,3-*c*]naphtho[1,2-*f*]quinoline (**11**) in 60% yield. The unsubstituted novel ring system **2** was obtained in 60% yield by refluxing **11** with a 10% solution of copper sulfate and aqueous acetic acid.

Scheme 3



NMR Spectroscopy.

The structure of **1** consists of two four-spin systems and an isolated spin, H6. The congestion of the ^{1}H spectrum of **1** prevents it from being unambiguously assigned from the COSY [5] spectrum. The ^{13}C nmr spectrum of **1** shows fairly good resolution, but unequivocal assignment of the spectrum is not possible by inspection. We chose, as a rapid solution to this assignment problem, the concerted use of HMQC [6], HMBC [7] and HMQC-TOCSY [8] which are in routine use in this laboratory.

The singlet assigned to H6 at 9.23 ppm, on the basis of the lack of coupling and chemical shift, was the obvious entry point to begin the assignment. This singlet has a direct correlation to the carbon at 145.4 ppm as seen in the HMQC spectrum. Long-range couplings to this singlet were observed at 144.6 ppm, 135.0 ppm, and 134.7 ppm in the HMBC spectrum (Figure 1). From the structure of **1**, H6 should correlate to quaternary carbons C4a, C6a and C12b. The correlation response at 134.7 ppm is assigned to C6a, which shows no other correlations as expected. The correlation at 144.6 ppm is assigned to C4a on the basis of chemical shift and two additional proton correlations rather than one, which is expected for C12b resonating at 135.0 ppm. These correlation pathways are shown in **A**.

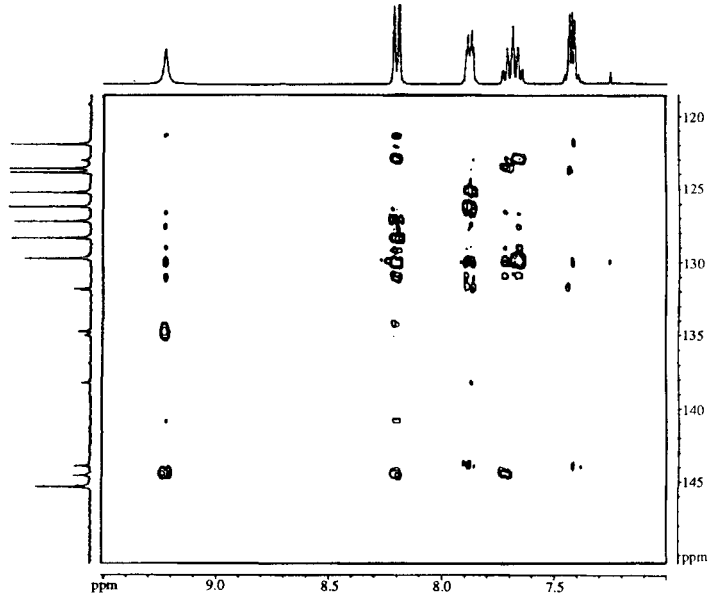


Figure 1. Long-range heteronuclear chemical shift correlation spectrum of **1** recorded in deuteriochloroform at observed frequencies of 360.13/90.56 MHz for ^{1}H and ^{13}C, respectively.

From **A** one can see that C4a and C12b provide links between the isolated singlet, H6, and the four-spin system H1, H2, H3, and H4. The quaternary C4a should show three correlations, *i.e.* H1, H3 and H6 and C12b should show only one correlation to H1. Thus, the doublet at 8.21 ppm exhibiting correlation to both C4a and C12b in the HMBC spectrum is assigned to H1 and the multiplet at 7.72 ppm to H3 with direct correlation to C3 at 128.4 ppm in the HMQC spectrum. Although the COSY spectrum provides the vicinal ^{1}H-^{1}H connectivities between H2/H3 and H3/H4 leading to the assignment of H2 and H4 at 7.67 and 8.21 ppm, respectively, the overlapped doublets at 8.21 ppm assigned to H1 and H4 leave the assignment

of C1 and C4 with uncertainty. However, on the basis of chemical shift considerations, HMBC and the HMQC-TOCSY spectra it is clear that C1 resonates at 123.6 ppm and C4 at 129.7 ppm.

In addition to the congestion of the proton spectrum, the breaks of long-range coupling between quinoline (**A**) and benzo[*b*]thiophene (**B**) moieties and the absence of nOe between H1 and H11 of **1** make the determination of the orientation of the four-spin system H8, H9, H10, and H11 a difficult task. Fortunately, inspection of benzo[*b*]thiophene moiety (**B**) reveals that H8 should exhibit three long-range correlations with C7a, C10, and C11a, whereas H11 should show only two, *i.e.* C9 and C7b. Indeed, these connectivities are observed in the HMBC spectrum of **1**. Thus, the proton resonating at 7.87 ppm showing three long-range responses is assigned as H8 and the resonance at 7.88 ppm displaying two long-range correlations is assigned as H11. Given that C7a exhibits only one long-range correlation with H8, the quaternary carbon resonanting at 138.2 ppm can thus be assigned as C7a, whereas the resonance at 143.9 ppm is identified as C7b by correlations to both H9 and H11; C11a is assigned at 131.8 ppm *via* correlations to both H8 and H10. The remaining two protonated carbons, C9 and C10 are identified by their long-range correlations to H11 and H8, respectively. By elimination the resonance at 131.9 ppm which shows no correlations to any protons is identified as C12a. Final chemical shift assignments are presented in Table 1.

Table 1

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

Position	δ H	δ C	Long-Range Correlation
1	8.21	123.6	H3
2	7.67	127.2	H4
3	7.72	128.4	H1
4	8.21	129.7	H2
4a		144.6	H1, H3, H6
6	9.23	145.4	
6a		134.7	H6
7a		138.2	H8
7b		143.9	H9, H11
8	7.87	123.9	H10
9	7.41	126.2	H11
10	7.44	125.3	H8
11	7.88	121.9	H9
11a		131.8 [a]	H8, H10
12a		131.9 [a]	
12b		135.0	H1, H6
12c		123.0	H2, H4

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

Table 2

The ^{1}H 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	δ H	δ C	Long-Range Correlation
1	8.15	128.6	H16
2	8.01	125.9	H3
2a		131.3	H1, H4
3	8.13	128.8	H2
4	8.31	128.3	
4a		145.6	H3, H6
6	9.56	145.2	
6a		136.7	H6
7a		137.3	
7b		143.4	H9, H11
8	7.68	123.4	H10
9	7.43	126.0	H11
10	7.50	124.7	H8
11	8.04	121.8	H9
11a		131.1	H8, H10
12a		135.3	
12b		136.2	H6
12c		118.8	H4
12d		126.0	H2, H3, H13
12e		129.6	H1, H14, H16
13	8.28	129.2	H15
14	7.34	126.1	H16
15	7.63	126.6	H13
16	8.18	127.8	H14
16a		132.8	H2, H13, H15

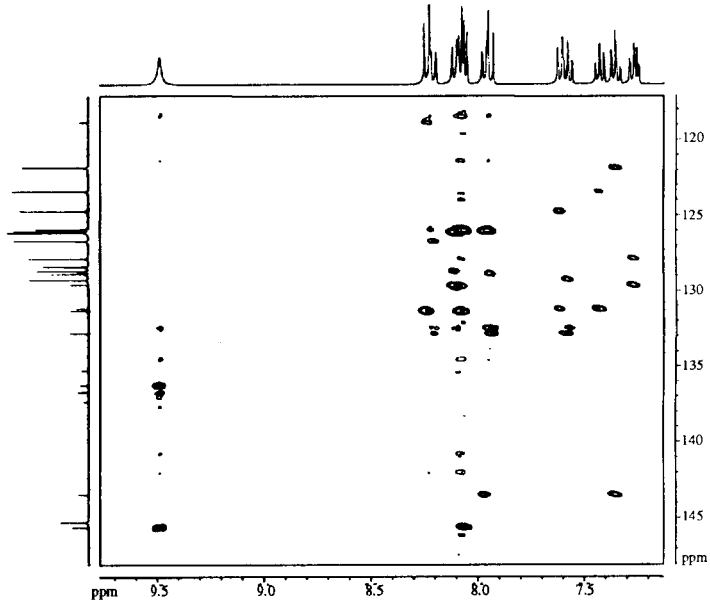
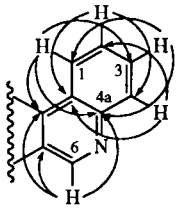
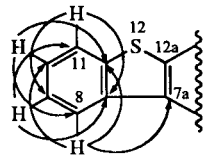


Figure 2. Long-range heteronuclear chemical shift correlation spectrum of **2** recorded in deuteriochloroform at observed frequencies of 360.13/90.56 MHz for ^{1}H and ^{13}C, respectively.

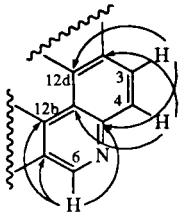
The complete assignment of ^{1}H and ^{13}C nmr spectra of **2** was analyzed and achieved in a fashion identical to that described in the assignment of the spectra of **1**. The only



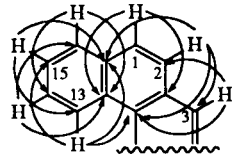
A



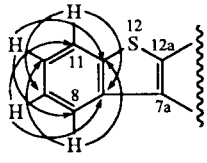
B



C



D



E

singlet resonating at 9.56 ppm assigned as H6 provides the key entry leading to the assignment of quinoline moiety (**C**) of **2**, which in turn affords the assignment of the naphthalene moiety (**D**) through long-range coupling responses between H4/C2a and H3/C2 in the HMBC spectrum (Figure 2). The remaining four-spin system H8, H9, H10 and H11 in the benzo[*b*]thiophene moiety (**E**) is assigned on the basis of chemical shifts of **1** elucidated as above, because there is no nOe observed between H11 and H14 in the NOESY [9] spectrum of **2**, nor is there a long-range coupling response between H8 and C7a at a different level of the slice in the HMBC spectrum. The ^1H and ^{13}C nmr chemical shifts of **2** are presented in Table 2.

Thus, we have synthesized two previously unknown heterocyclic ring systems. Total assignments of their ^1H and ^{13}C spectra were accomplished by concerted usage of COSY, HMQC, HMBC, NOESY and HMQC-TOCSY two-dimensional nmr methods and this confirms our structural identification of **2**.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting 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 or 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. Analyses (tlc) were performed on Sigma precoated silica gel plates containing a fluorescent indicator. The mass spectra were determined on a Hewlett-Packard model 5980A mass spectrometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

The ^1H and ^{13}C spectra of **1** and **2** were acquired on a Bruker AMX360 MHz NMR spectrometer operating at an observation frequency of 360.13 MHz for ^1H and 90.56 for ^{13}C. All experiments were performed using an inverse-geometry 5 mm broad band probe. Pulse widths (90°) for ^1H and ^{13}C were 7.2 and 14.4 μsec, respectively, for compound **1** and 6.8 and 13.6 μsec, respectively, for compound **2**. The COSY spectra were recorded using the Bruker pulse program (*COSY90*) [5]. The HMQC experiments were performed using the Bruker pulse program (*invbdgtp*) with the BIRD sequence optimized for direct couplings (165 Hz $^1J_{CH}$) [6]. The HMBC spectra were obtained using the Bruker pulse program (*inv4lplrnd*) [7] optimized for 10 Hz $^3J_{CH}$ couplings. The HMQC-TOCSY were obtained using the Bruker pulse program (*invbmltp*) [8]. The NOESY experiments were performed using the Bruker pulse program (*noesytp*) acquired with a mixing time of 500 μsec [9].

3-Chloro[1]benzothieno[3,2-*b*]thiophene-2-carbonyl Chloride (**4**).

To a mixture of 4.0 g (19.6 mmoles) of benzo[*b*]thiophene-2-acrylic acid (**3**) [3], 0.3 ml of pyridine, and 20 ml of chlorobenzene in an ice bath was added dropwise 7.3 ml of thionyl chloride [4]. The resulting mixture was heated at 120-125° for 48 hours. The solvent and thionyl chloride were removed by distillation under reduced pressure. The residue was triturated with hexane and filtered. The solid was recrystallized from cyclohexane to afford 3.0 g (10.4 mmoles, 53%) of chloride **4** as yellowish crystals, mp 180-181°; ^1H nmr (deuteriochloroform): δ 7.46-7.62 (m, 2H, H-6 and H-7), 7.82-7.97 (m, 2H, H-5 and H-8); ms: m/z 286 (M^+, 23), 253 (43), 251 (M^+ -Cl, 100), 223 (M^+ -COCl, 33). This compound was converted to its methyl ester for elemental analysis. Thus, a mixture of 1.0 g (3.48 mmoles) of **4** and 50 ml of methanol was refluxed for an hour. Upon removal of excess solvent the residue was recrystallized from a benzene-methanol mixture to give 0.9 g (3.18 mmoles, 91%) of yellowish crystals, mp 182-183°; ir (potassium bromide): 3070 (aromatic CH stretching), 2998, 2954, 2836 (aliphatic CH stretching), 1725 (C=O stretching), 1368 (CH bending of CH_3), 1232, 1090 (C-O stretching); ^1H nmr (deuteriochloroform): δ 3.90 (s, 3H, CH_3), 7.56-7.60 (m, 2H, H-6 and H-7), 8.16-8.20 (m, 2H, H-5 and H-8); ms: m/z 284 (M^+ +2, 42), 282 (M^+, 100), 253 (43), 251 (M^+ -OCH_3, 99).

Anal. Calcd. for $C_{12}H_7ClO_2S_2$: C, 50.97; H, 2.50; S, 22.68. Found: C, 50.72; H, 2.70; S, 22.59.

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

A mixture of 4.1 g (14.3 mmoles) of **4** and 1.4 g (15.0 mmoles) of aniline in 100 ml of benzene was heated under reflux for four hours. After cooling to room temperature the precipitate was collected by filtration and recrystallized from benzene to afford 4.0 g (11.6 mmoles, 81%) of **5** as colorless crystals, mp 201-202°; ir (potassium bromide): 3389 (NH stretching),

3055 (aromatic CH stretching), 1648 (C=O stretching); ^{1}H nmr (deuteriochloroform): δ 7.17 (t, $J_{3',4'} = J_{4',5'} = 7.3$ Hz, 1H, H-4'), 7.34-7.48 (m, 4H, ArH), 7.65 (d, $J_{5,6} = J_{7,8} = 8.0$ Hz, 2H, H-5 and H-8), 7.85-7.90 (m, 2H, H-2' and H-6'), 8.69 (br s, 1H, NH); ms: m/z 345 (M^+ +2, 11), 343 (M^+, 25), 253 (42), 251 (M^+ -NHC_6H_5, 100), 223 (M^+ -$CONHC_6H_5$, 23).

Anal. Calcd. for $C_{17}H_{10}ClNOS_2$: C, 59.38; H, 2.93; N, 4.07; S, 18.65. Found: C, 59.18; H, 3.13; N, 4.08; S, 18.47.

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

A solution of 0.5 g (1.45 mmoles) of **5** and 0.15 g of triethylamine in 500 ml of benzene was irradiated with a 450 watt Hanovia medium pressure mercury vapor lamp for four 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 (1.37 mmoles, 94%) of lactam **6**, mp >270°; ir (potassium bromide): 3145 (NH stretching), 3062 (aromatic CH stretching), 1671 (C=O stretching); ^{1}H nmr (DMSO-d_6): δ 7.46-7.65 (m, 5H, ArH), 8.03 (d, J = 7.8 Hz, 1H, ArH), 8.25-8.29 (m, 2H, ArH), 12.15 (br s, 1H, NH); ms: m/z 251 (100), 223 (13), 222 (29). This compound was used in the next step without further purification because of low solubility.

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

A mixture of 1.3 g (4.23 mmoles) of **6** and 30 ml of phosphorus oxychloride was heated under reflux for four hours. After cooling in an ice bath, the mixture was poured into 600 ml of ice water very slowly with vigorous stirring. The precipitate was collected by filtration and washed with water, and then recrystallized from benzene to yield 1.1 g (3.38 mmoles, 80%) of **7** as colorless crystals, mp 245-247°; ^{1}H nmr (deuteriochloroform/trifluoroacetic acid-d): δ 7.50-7.75 (m, 2H, ArH), 7.90-8.30 (m, 4H, ArH), 8.35-8.65 (m, 2H, ArH).

Anal. Calcd. for $C_{17}H_8ClNS_2$: C, 62.66; H, 2.48; N, 4.30. Found: C, 63.08; H, 2.80; N, 4.35.

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

A mixture of 0.54 g (1.66 mmoles) of chloride **7**, 0.11 g of potassium hydroxide, 0.5 g of 5% Pd-C in 80 ml of methanol and 80 ml of benzene was hydrogenated at atmospheric pressure and room temperature until the uptake of hydrogen ceased. The catalyst was removed by filtration. The filtrate was evaporated to dryness *in vacuo*. The solid was recrystallized from benzene to afford 0.38 g (1.31 mmoles, 79%) of **1** as colorless crystals, mp 220-221°; ir (potassium bromide): 3060 (aromatic CH stretching).

Anal. Calcd. for $C_{17}H_9NS_2$: C, 70.07; H, 3.11; N, 4.81. Found: C, 69.71; H, 3.40; N, 4.79.

3-Chloro-*N*-(3-phenanthryl)[1]benzothieno[3,2-*b*]thiophene-2-carboxamide (**8**).

A mixture of 2.44 g (8.50 mmoles) of carbonyl chloride **4** and 1.64 g (8.50 mmoles) of 3-phenanthrenamine in 100 ml of benzene was heated under reflux for four hours. After cooling the solid was collected by filtration. The solid was recrystallized from benzene to afford 2.34 g (5.28 mmoles, 62%) of amide **8** as off-white crystals, mp 252-254°; ir (potassium bromide): 3404 (NH stretching), 3047 (aromatic CH stretching), 1656 (C=O stretching); ^{1}H nmr (DMSO-d_6): 120°, δ 7.49-7.77 (m, 6H, ArH), 7.90-8.15 (m, 4H, ArH), 8.61-8.72 (m, 1H, H-2'), 9.15 (d, $J_{2',4'} = 2.0$ Hz, 1H, H-4').

Anal. Calcd. for $C_{25}H_{14}ClNOS_2$: C, 67.63; H, 3.18; N, 3.16; S, 14.44. Found: C, 67.78; H, 3.41; N, 3.05; S, 14.27.

[1]Benzothieno[2',3':4,5]thieno[2,3-*c*]naphtho[1,2-*f*]quinolin-6(5*H*)-one (**9**).

A mixture of 0.49 g (1.10 mmoles) of **8** and 0.12 g of triethylamine in 160 ml of benzene and 320 ml of cyclohexane was irradiated with a 450 watt Hanovia medium pressure mercury vapor lamp for four 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 yield 0.40 g (0.98 mmole) of lactam **9**, mp >280°; ir (potassium bromide): 3150 (NH stretching), 3044 (aromatic CH stretching), 1635 (C=O stretching); ^{1}H nmr (DMSO-d_6): δ 7.16-8.21 (m, ArH). This compound was used in the next step without further purification because of its low solubility.

6-Chloro[1]benzothieno[2',3':4,5]thieno[2,3-*c*]naphtho[1,2-*f*]-quinoline (**10**).

A mixture of 1.51 g (3.71 mmoles) of **9** and 60 ml of phosphorus oxychloride was heated under reflux for four hours. After cooling to room temperature the mixture was poured slowly into 500 ml of ice water with vigorous stirring. The solid was collected by filtration and washed with water. It was recrystallized from benzene to give 1.0 g (2.35 mmoles, 63%) of **10** as yellowish crystals, mp >300°; tlc (benzene) R_f 0.58; ir (potassium bromide): 3060, 3050 (aromatic CH stretching); ^{1}H nmr (deuteriochloroform): 50°, δ 7.17-7.67 (m, 5H, ArH), 7.85-8.23 (m, 7H, ArH).

Anal. Calcd. for $C_{25}H_{12}ClNS_2$: C, 70.49; H, 2.84; N, 3.29; S, 15.05. Found: C, 70.66; H, 2.61; N, 3.26; S, 14.89.

6-Hydrazino[1]benzothieno[2',3':4,5]thieno[2,3-*c*]naphtho-[1,2-*f*]quinoline (**11**).

To a boiling mixture of 0.96 g (2.25 mmoles) of **10** in 25 ml of benzene and 25 ml of absolute ethanol was added dropwise 15 ml of anhydrous hydrazine over a period of one hour. The mixture was refluxed for 48 hours. After cooling the solid was collected by filtration and washed with ethanol to give 0.57 g (1.35 mmoles, 60%) of **11** as a yellow powder, mp 267-270° dec; tlc (benzene) R_f 0.021; ir (potassium bromide): 3358, 3188 (NH stretching), 3044 (aromatic CH stretching); ^{1}H nmr (DMSO-d_6): δ 5.03 (br s, 2H, NH_2), 7.24 (t, J = 7.6 Hz, 1H, ArH), 7.38 (t, J = 7.4 Hz, 1H, ArH), 7.47 (t, J = 7.5 Hz, 1H, ArH), 7.56 (t, J = 7.4 Hz, 1H, ArH), 7.80 (d, J = 8.4 Hz, 2H, ArH), 7.96-8.14 (m, 6H, ArH), 8.90 (s, 1H, NH). Attempts to purify this compound for an elemental analysis resulted in darkening of the sample. Therefore, this compound was used in the next step without further purification.

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

To a boiling mixture of 0.2 g (0.47 mmole) of **11** in 7 ml of water and 10 ml of glacial acetic acid was added 10 ml of 10% copper sulfate solution. The mixture was heated under reflux for 24 hours. After cooling to room temperature the mixture was basified with 2*N* sodium hydroxide solution. The mixture was extracted with chloroform (50 ml x 3) and the organic extracts were dried over anhydrous magnesium sulfate. After removal of solvent the solid was recrystallized from a cyclohexane-benzene mixture (1:1) to afford 0.11 g (0.28 mmole, 60%) of **2** as yellowish crystals, mp 264-266° dec; tlc (benzene) R_f 0.096; ir (potassium bromide): 3050 (aromatic CH stretching).

Anal. Calcd. for $C_{25}H_{13}NS_2$: C, 76.70; H, 3.35; N, 3.58. Found: C, 76.59; H, 3.47; N, 3.66.

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