The Synthesis of Novel Polycyclic Heterocyclic Ring Systems *via* Photocyclization. 6. Naphthothienonaphthyridines

Raymond N. Castle* [1] and Sudabeh Pakray [2]

Department of Chemistry, University of South Florida,
Tampa, FL 33620-5250 USA

Gary E. Martin [3]

Department of Medicinal Chemistry, College of Pharmacy,
University of Houston,
Houston, Texas 77304-5575

Received January 15, 1991

Five novel polycyclic heterocyclic ring systems are reported *via* photocyclization. The specific final products in these ring systems are: naphtho[1',2':4,5]thieno[2,3-*c*][1,8]naphthyridin-6(5*H*)-one (**5**), naphtho[1',2':4,5]thieno[2,3-*c*][1,6]naphthyridin-6(5*H*)-one (**6**), naphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**9**), naphtho[1',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]-1,5-naphthyridine (**12**), and naphtho[2',1':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**17**). The direction of photocyclization to produce **9** was established from a zero quantum two-dimensional nmr spectroscopy experiment (ZQCOSY) using 6-chloronaphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**8**) as the model compound.

J. Heterocyclic Chem., **28**, 1997 (1991).

In continuation of our program [4a-4e] on the synthesis of novel polycyclic heterocyclic ring systems *via* photocyclization we now report the synthesis of five previously unreported ring systems. These are naphtho[1',2':4,5]thieno[2,3-*c*][1,8]naphthyridin-6(5*H*)-one (**5**), naphtho[1',2':4,5]thieno[2,3-*c*][1,6]naphthyridin-6(5*H*)-one (**6**), naphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**9**), naphtho[1',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]-1,5-naphthyridine (**12**), and naphtho[2',1':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**17**).

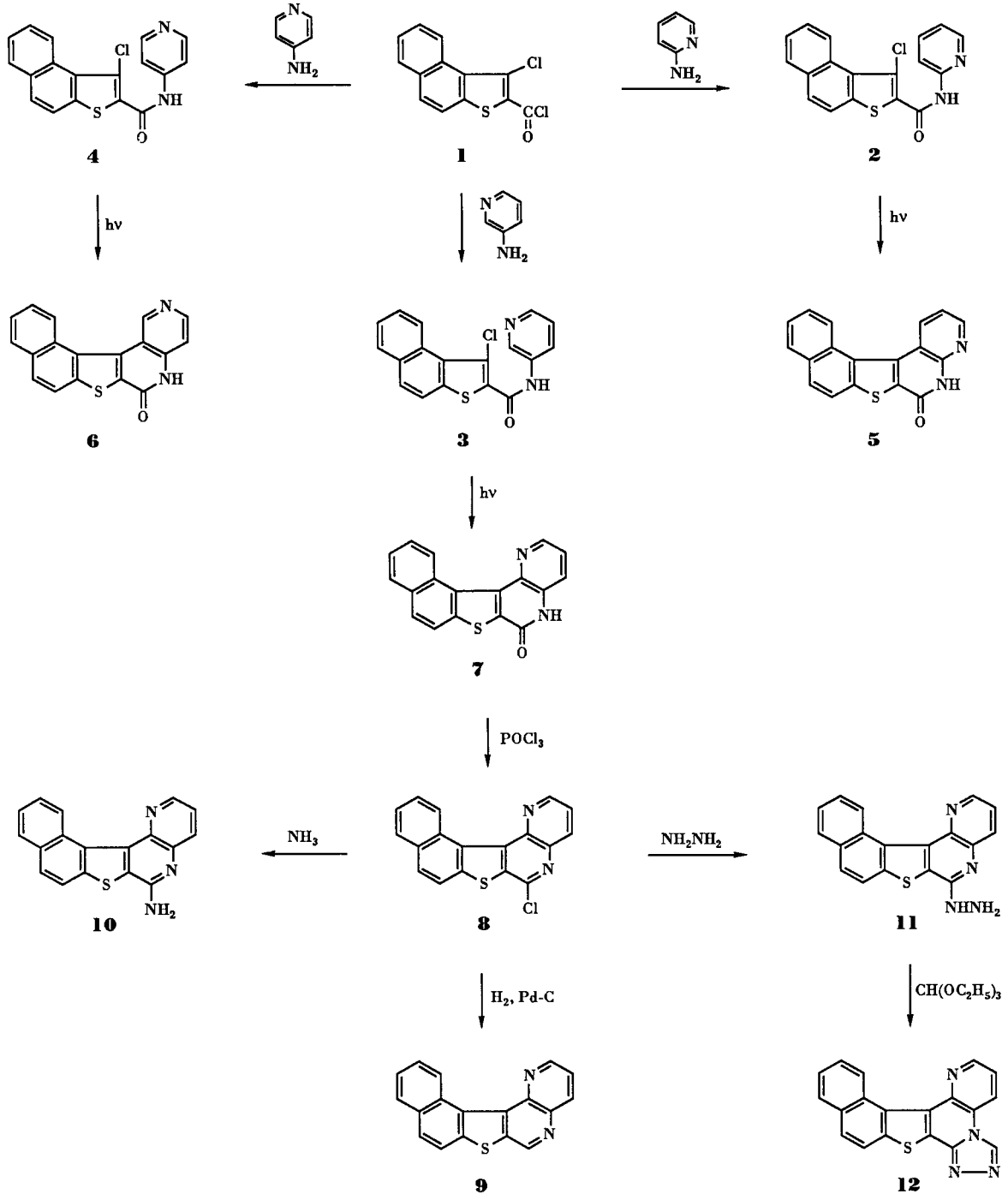
1-Chloronaphtho[2,1-*b*]thiophene-2-carbonyl chloride (**1**) [5] served as the starting material for the synthesis of the naphtho[1',2':4,5]thieno[2,3-*c*]naphthyridines. When **1** was allowed to react with 2-aminopyridine, 1-chloro-*N*-(2'-pyridyl)naphtho[2,1-*b*]thiophene-2-carboxamide (**2**) was obtained in 66% yield. Likewise **1** and 3-aminopyridine provided 1-chloro-*N*-(3'-pyridyl)naphtho[2,1-*b*]thiophene-2-carboxamide (**3**) in 43% yield and **1** with 4-aminopyridine afforded 1-chloro-*N*-(4'-pyridyl)naphtho[2,1-*b*]thiophene-2-carboxamide (**4**) in 75% yield. Photocyclization of **2** gave naphtho[1',2':4,5]thieno[2,3-*c*][1,8]naphthyridin-6(5*H*)-one (**5**) in 22% yield while photocyclization of **4** provided naphtho[1',2':4,5]thieno[2,3-*c*][1,6]naphthyridin-6(5*H*)-one (**6**) in 35% yield. Photocyclization of **3** could produce either the 1,5- or the 1,7-naphthyridine isomers. In our hands only one lactam was obtained, namely, naphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridin-6(5*H*)-one (**7**) in 66% yield. Treatment of **7** with phosphorus oxychloride afforded 6-chloronaphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**8**) in 51% yield. Catalytic dechlorination of **8** yielded the unsubstituted ring system naphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**9**) in 56% yield. Furthermore when **8** was allowed to react with methanolic ammonia 6-aminonaphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**10**) was obtained in 53% yield. Likewise the reaction of **8** with hydrazine afforded 6-hydrazinonaphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**11**) in 29% yield. Cyclization of **11** with triethyl orthoformate provided another novel ring system, namely, naphtho[1',2':4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]-1,5-naphthyridine (**12**) in 72% yield. The above reactions are outlined in Schme 1.

3-Chloronaphtho[1,2-*b*]thiophene-2-carbonyl chloride (**13**) [6] when allowed to react with 3-aminopyridine gave 3-chloro-*N*-(3'-pyridyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**14**) in 55% yield. Photocyclization of **14** afforded naphtho[2',1':4,5]thieno[2,3-*c*]-1,5-naphthyridin-6(5*H*)-one (**15**) in 83% yield. Chlorination of **15** produced 6-chloronaphtho[2',1':4,5]theino[2,3-*c*]-1,5-naphthyridine (**16**) in 57% yield which upon catalytic dechlorination gave the novel unsubstituted ring system naphtho[2',1':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**17**) in 23% yield. The methanolic ammonia reaction of **16** afforded 6-aminonaphtho[2',1':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**18**) in 43% yield. These transformations are outlined in Scheme 2.

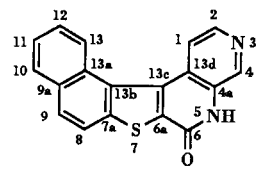
Structure Proof of 6-Chloronaphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridine (**8**).

The photocyclization of **3** could have produced the alternate lactam naphtho[1',2':4,5]thieno[2,3-*c*][1,7]naphthyridin-6(5*H*)-one (**19**). Since in our hands only the lactam **7** was obtained, we have used two-dimensional nmr techniques to establish the direction of photocyclization using the more soluble chloro compound **8**.

Scheme 1



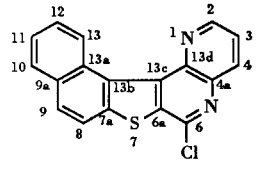
We have found proton zero quantum nmr (ZQCOSY) spectroscopy to be extremely useful in the case of the congested proton nmr spectra of polynuclear aromatic/heteroaromatic systems [7-10]. For example, in a recent comparative study, we were able to demonstrate the clear superiority of ZQCOSY over the more conventional and familiar



19

COSY and double quantum nmr (DQCOSY) experiments in the case of dinaphtho[1,2-*b*:1′,2′-*d*]thiophene [9]. In the present case, a ZQCOSY spectrum was used to irrefutably establish the cyclization to afford a 1,5-naphthyridine system.

The identification of the structure of 6-chloronaphtho-[1′,2′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**8**) hinges upon the assignment of the proton nmr spectrum of the molecule. Reaction of 3-aminopyridine with **1** provides the

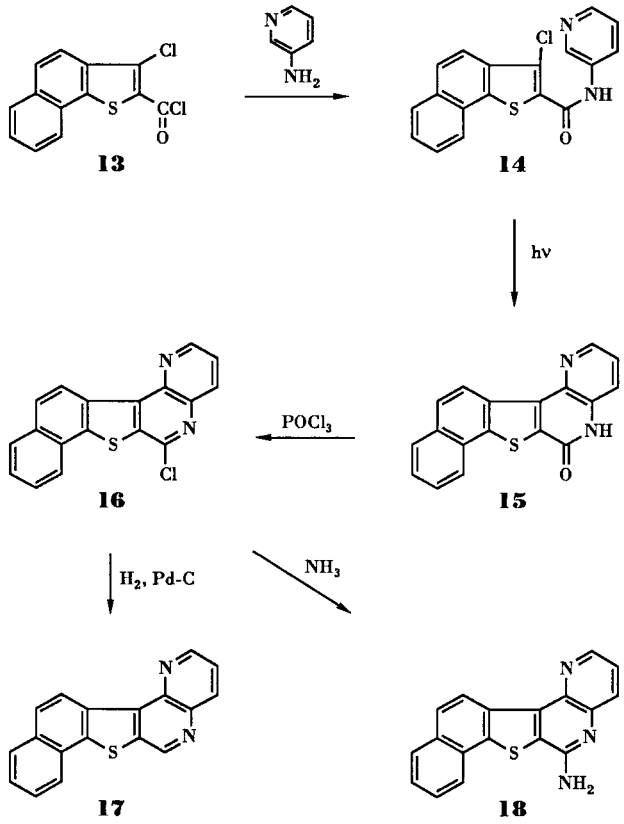


8

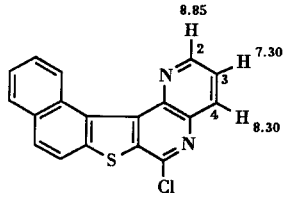
possibility of photocyclization to afford either a 1,5- or a 1,7-naphthyridine system **19**. In the case of the 1,5-naphthyridine, which requires photocyclization at the 2-position of the pyridine ring, we would end up with the pyridine nitrogen in the bay region of the resultant pentacyclic system with H2, H3 and H4 comprising a linear system of spins which could range from ABX through AMX. In contrast, the 1,7-naphthyridine system which would be formed if photocyclization took place at the 4-position of the pyridine ring, would have an isolated proton at the 4-position and a pair of protons comprised of H1 and H2. These would normally, in the absence of the balance of the pentacyclic molecular framework, constitute an AX pair, H1 resonating substantially upfield of H2. However, because of the balance of the pentacyclic system, H1 in the case of the 1,7-naphthyridine system would, since it was in a bay region, be expected to resonate significantly downfield, at least as far downfield as H2, possibly further.

On examination of the 300 MHz proton reference spectrum plotted beneath the zero quantum spectrum shown in Figure 1, we note that there is a doublet resonating furthest downfield at about 11.3 ppm. Proceeding upfield, we observe a doublet of doublets resonating at 8.85 ppm. Correlations in a ZQCOSY spectrum are normally observed with a slope of +2 and are associated with pairs of responses at the respective F_2 frequencies separated in the zero quantum or F_1 frequency domain by ± the algebraic difference of the F_2 offsets of the coupled spins relative to the transmitter frequency, F_2 = 0 Hz. Thus, the double doublet observed at 8.85 ppm is correlated with another resonating at 8.3 ppm to which the former is weakly coupled (response labeled 2-4) and to a well resolved double doublets to which both of the aforementioned protons are coupled resonating at 7.3 ppm (see responses labeled 2-3 and 3-4). Clearly, this pattern of chemical shifts is entirely inconsistent with cyclization to afford a 1,7-naphthyridine

Scheme 2



nucleus. In contrast, cyclization to give a 1,5-naphthyridine system, **9**, is entirely consistent with this pattern of chemical shifts and coupling constants. Thus, H2 may be assigned as the proton resonating at 8.85 ppm, H3 at 7.30 ppm and finally, H4 at 8.30 ppm (see **8a**).



8a

Next we must turn our attention to the doublet resonating extremely far downfield at 11.3 ppm. Based upon the structure of the molecule as **8**, we may account for this unusual deshielding for the H13 resonance when it is in the bay region in proximity to N1 of the naphthyridine moiety on the other side of the bay. This contention is substantiated when the chemical shift of the bay region proton of quino[5′,6′:5,6]quinoline is compared with the chemical shift of benzo[*c*]phenanthrene. Here, the presence of a nitrogen atom from the quinoline in one ring induces a 2.27 ppm downfield shift relative to benzo[*c*]phen-

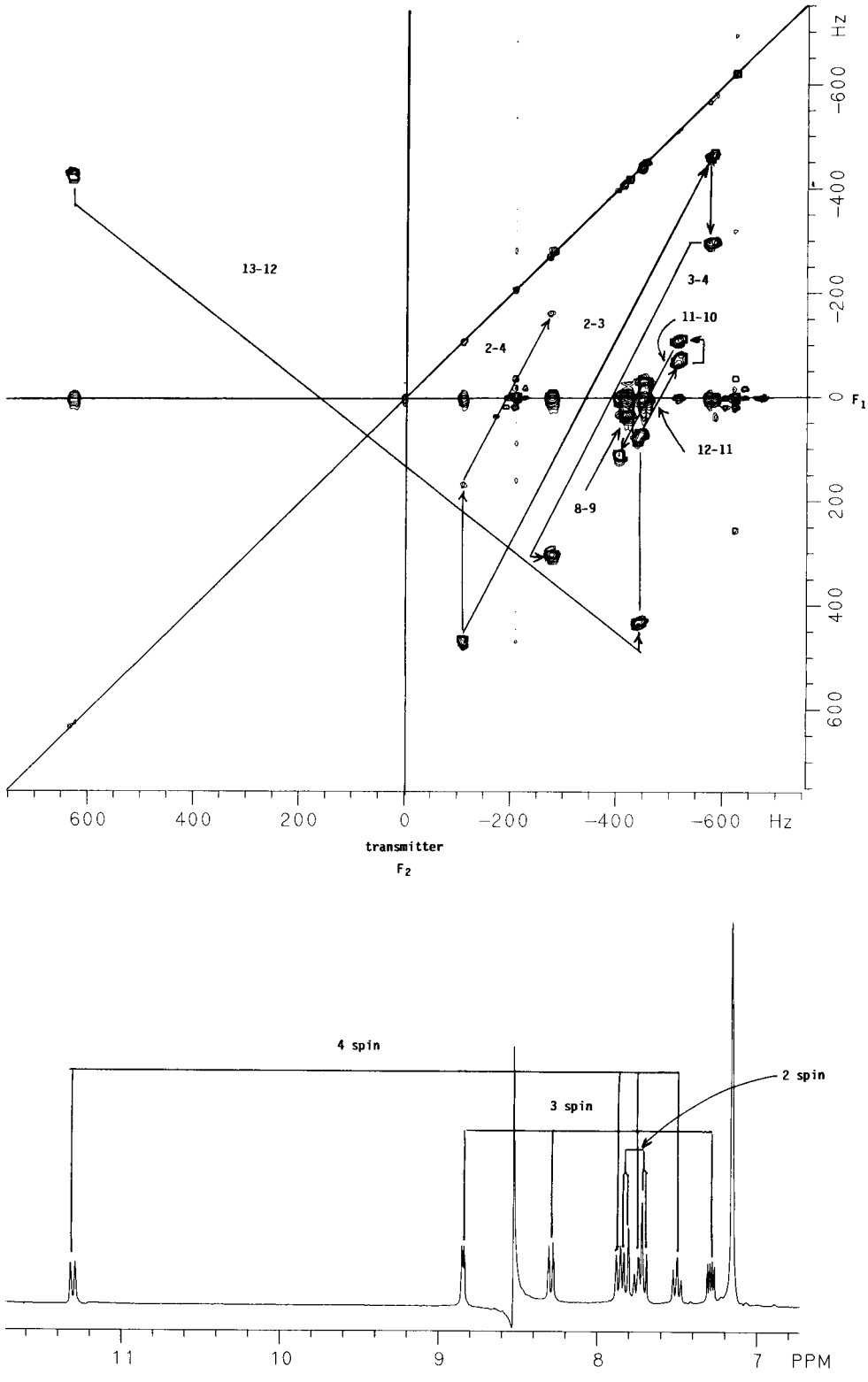
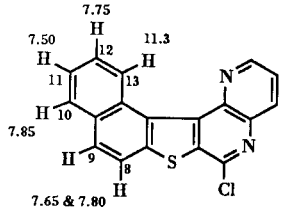

13-12
2-4
2-3
3-4
11-10
12-11
8-9
600
400
200
0
-200
-400
-600
Hz
F1
transmitter
F2
4 spin
3 spin
2 spin
11
10
9
8
7
PPM

Figure 1

anthrene [11]. In the present case, the angular influence of the thiophene ring would tend to bring H13 and N1 into even closer proximity than would be encountered in the case of quino[5',6':5,6]quinoline hence contributing to an even greater downfield shift of H13. Because of the wide range of frequencies in F_2 and the desire to maximize digital resolution in the F_1 frequency domain of the spectrum shown in Figure 1, we elected to set the dwell time to cause responses associated with the proton resonating at 11.3 ppm to fold in the F_1 frequency domain. As a result of this, the correlation of H13 with it's vicinal neighbor, H12 (labeled 13-12), is observed along an axis with a negative slope rather than the normal slope of +2. Given this entry point into the four spin system, H12 is easily identified as a proton resonating at 7.75 ppm, one of four protons in the cluster between 7.65 and 7.85 ppm. The H12 resonance is, in turn, coupled to a clearly resolved doublet of doublets (apparent triplet) resonating at 7.47 ppm (correlation response labeled 12-11) which we may thus assign as H11. Finally, the H11 resonance is coupled to the H10 doublet resonating at 7.85 ppm (correlation response labeled 10-11) (see **8b**).



8b

At this point, we are left with only the H8-H9 two spin system to be assigned. These protons constitute an AB spin system (7.65 and 7.80 ppm) which cannot be assigned unequivocally at this point due to a lack of any long range coupling responses which would correctly orient this spin system relative to the four spin system. Normally, a five bond epi-zig-zag coupling would be expected between H9 and H13 but this was not observed in this case. Alternatively, a four bond peri coupling between H9 and H10 would also serve to orient the AB spin system. Regretably, this correlation response was also not observed. Solubility limitations also precluded the use of long range heteronuclear shift correlation [12] to orient the AB system through the $^3J_{CH}$ coupling response between H9 and C7a. Hence these protons may only be tentatively assigned and the assignment should be considered reversible.

EXPERIMENTAL

All melting points (uncorrected) were taken on a Thomas-Hoover capillary melting point apparatus. The ^{1}H-nmr spectra were recorded on either a Varian EM-360 or JEOL FX-90Q spectrometer in deuteriochloroform or DMSO-d_6 and are reported in ppm relative to TMS. All elemental analyses were preformed by MHW laboratories, Phoenix, Arizona.

1-Chloro-*N*-(2'-pyridyl)naphtho[2,1-*b*]thiophene-2-carboxamide (**2**).

1-Chloronaphtho[2,1-*b*]thiophene-2-carbonyl chloride (**1**) (8.2 g, 0.029 mole), 2-aminopyridine (5.4 g, 0.058 mole) and benzene (300 ml) was heated for an hour on a water bath. After cooling the resulting solid was collected by filtration and the filtrate was evaporated under reduced pressure. The residue was recrystallized from ethanol to give 6.50 g (66% yield) of pale yellow crystals, mp 189-190°; ^{1}H nmr (deuteriochloroform): 7.12-8.62 (m, 10H, ArH), 9.17-9.61 (m, 1H, NH).

Anal. Calcd. for $C_{18}H_{11}ClN_2OS$: C, 63.81; H, 3.27; Cl, 10.46; S, 9.46. Found: C, 63.65; H, 3.37; Cl, 10.49; S, 9.33.

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

This compound was prepared from **1** (7.50 g, 0.026 mole), 3-aminopyridine (5.0 g, 0.053 mole) and benzene (150 ml) in a manner similar to the preparation of **2** and was obtained as beige crystals, 3.80 g (43% yield), mp 169-170°; ^{1}H nmr (deuteriochloroform): 7.24-8.45 (m, 10H, ArH), 9.24-9.52 (bs, 1H, NH).

Anal. Calcd. for $C_{18}H_{11}ClN_2OS$: C, 63.81; H, 3.27; N, 8.27; S, 9.46. Found: C, 63.76; H, 3.23; N, 8.25; S, 9.41.

1-Chloro-*N*-(4'-pyridyl)naphtho[2,1-*b*]thiophene-2-carboxamide (**4**).

This compound was prepared from **1** (10 g, 0.035 mole), 4-aminopyridine (6.6 g, 0.070 mole), and benzene (200 ml) in a manner similar to the preparation of **2**. Recrystallization from ethanol afforded 9.0 g (75% yield) of off white crystals, mp 188-189°; ^{1}H nmr (deuteriochloroform): 7.23-8.16 (m, 10H, ArH), 9.25-9.54 (m, 1H, NH).

Anal. Calcd. for $C_{18}H_{11}ClN_2OS$: C, 63.81; H, 3.27; Cl, 10.46; S, 9.46. Found: C, 64.34; H, 3.53; Cl, 10.29; S, 9.61.

Naphtho[1',2':4,5]thieno[2,3-*c*][1,8]naphthyridin-6(5*H*)-one (**5**).

A mixture of compound **2** (0.50 g, 0.00147 mole) and triethylamine (0.5 ml) in 1% methanol-benzene solution (500 ml) was irradiated with a 450 watt Hanovia medium pressure mercury lamp for three hours. The resulting solid was collected, washed with water, dried and recrystallized from ethanol to give 0.1 g (22% yield) of white flakes, mp >250°; ^{1}H nmr (DMSO-d_6): 6.85-7.23 (m, 6*H*, ArH), 8.15-8.35 (d, 2H, ArH), 9.25-9.55 (m, 2H, ArH and NH).

Anal. Calcd. for $C_{18}H_{10}N_2OS$: C, 71.50; H, 3.33; S, 10.60. Found: C, 71.39; H, 3.50; S, 10.42.

Naphtho[1',2':4,5]thieno[2,3-*c*]-1,5-naphthyridin-6(5*H*)-one (**7**).

A stirred solution of **3** (0.5 g, 0.00147 mole) and triethylamine (0.5 ml) in 1% methanol-benzene solution (500 ml) was irradiated for three hours. The resulting white solid was collected by filtration, washed with water and dried. The material obtained was pure enough to take on to the next step without any further treatment, 0.2 g (66% yield), mp >250°; ^{1}H nmr (DMSO-d_6): 7.82-9.12 (m, 8H, ArH), 9.31 (s, 1H, C-4), 10.93-10.96 (m, 1H, NH).

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

A mixture of **4** (0.5 g, 0.00147 mole) triethylamine (0.5 ml) and 1% methanol-benzene (500 ml) was irradiated for three hours. The resulting solid was collected by filtration, washed with water,

dried, and recrystallized from ethanol to afford 0.15 g (35% yield) of the lactam, mp >250°; ^{1}H nmr (DMSO-d_6): 6.71-7.83 (m, 6H, ArH), 8.22-8.81 (m, 2H, ArH), 9.12-9.35 (m, 2H, ArH, and NH).

Anal. Calcd. for $C_{18}H_{10}N_2OS$: C, 71.50; H, 3.33; S, 10.60. Found: C, 71.46; H, 3.22; S, 10.51.

6-Chloronaphtho[1′,2′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**8**).

A mixture of lactam **7** (0.20 g, 0.00066 mole) and phosphorus oxychloride (20 ml) was refluxed for three hours. The residue which was obtained upon distillation of the phosphorus oxychloride was poured into ice-water and the resulting solid was collected by filtration. Recrystallization from benzene furnished 0.1 g (51% yield) of yellow crystals, mp 190-191°; ^{1}H nmr (deuteriochloroform): 7.77-8.26 (m, 6H, ArH), 8.45-8.57 (dd, 1H, J = 1.2 Hz, J′ = 6 Hz), 9.12-9.18 (dd, 1H, J = 1.2 Hz, J′ = 2.4 Hz), 10.85 (s, 1H, C4).

Anal. Calcd. for $C_{18}H_9ClN_2S$: C, 67.39; H, 2.80, N, 8.73; S, 9.98. Found: C, 67.23; H, 3.03; N, 8.70; S, 9.95.

Naphtho[1′,2′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**9**).

Compound **8** (0.1 g, 0.00031 mole) was catalytically dechlorinated in 60 ml of benzene-methanol (1:1) containing 0.1 g of potassium hydroxide in the presence of 10% Pd-C at atmospheric pressure and room temperature for 24 hours. The catalyst was removed by filtration and the solvent was evaporated. The residue was washed with water, dried, and recrystallized from benzene to afford 0.05 g (56% yield) of white prisms, mp 141-142°; ^{1}H nmr (deuteriochloroform): 7.66-8.07 (m, 6H, ArH), 8.62-9.10 (dd, J = 8 Hz, 1H), 9.18-9.32 (dd, J = 2 Hz, 1H), 10.42 (s, 1H, H6), 11.15 (m, 1H, H4).

Anal. Calcd. for $C_{18}H_{10}N_2S$: C, 75.50: H, 3.52; N, 9.78; S, 11.20. Found: C, 75.75; H, 3.75; N, 9.86; S, 11.31.

6-Aminonaphtho[1′,2′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**10**).

A sealed tube containing compound **8** (0.14 g, 0.00143 mole) in ammonia-saturated methanol (30 ml at 0°) was heated at 180° for 24 hours. After cooling, the methanol was removed *in vacuo* and the remaining solid was recrystallized from benzene to afford 0.07 g, (53% yield) of the product, mp 243-244°; ^{1}H nmr (deuteriochloroform): 5.65 (bs, 2H, NH_2), 7.66-8.24 (m, 6H, ArH), 8.43-8.52 (dd, 1H, J = 2.9 Hz, J′ = 4.6 Hz), 9.06-9.15 (dd, 1H, J = 1.1 Hz, J′ = 2.3 Hz), 11.48 (s, 1H, H4).

Anal. Calcd. for $C_{18}H_{11}N_3S$: C, 71.74; H, 3.68; N, 13.94; S, 10.64. Found: C, 71.88; H, 3.83; N, 14.09; S, 10.72.

6-Hydrazinonaphtho[1′,2′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**11**).

A mixture of **8** (0.415 g, 0.00129 mole), anhydrous hydrazine (5 ml), and pyridine (30 ml) was refluxed for three days. The excess of pyridine was removed *in vacuo* and the remaining solid was recrystallized from chloroform to give 0.12 g (29% yield) of the product mp 212-214°; ^{1}H nmr (deuteriochloroform): 1.15-2.31 (bs, 2H, NH_2), 4.24-4.60 (1H, bs, NH), 7.34-7.98 (m, 6H, ArH), 8.23-8.34 (dd, 1H, J = 1.3 Hz, J′ = 5.6 Hz), 8.88-8.95 (dd, 1H, J = 1.3 Hz, J′ = 2.9 Hz), 10.48 (s, 1H, H4).

Anal. Calcd. for $C_{18}H_{12}N_4S$: C, 68.33; H, 3.82; N, 17.71; S, 10.13. Found: C, 68.21; H, 3.88; N, 17.54; S, 9.96.

Naphtho[1′,2′:4,5]thieno[2,3-*c*][1,2,4]triazolo[4,3-*a*]-1,5-naphthyridine (**12**).

A mixture of **11** (0.1 g, 0.00031 mole), and triethyl orthoformate (20 ml) was refluxed for 6 hours. The excess of triethyl orthoformate was removed *in vacuo* and the residue was recrystallized from benzene to give 0.073 g (72% yield) of the product, mp >280°; ^{1}H nmr (DMSO-d_6): 7.50-8.47 (m, 6H, ArH), 9.10-9.22 (m, 2H, ArH), 10.22 (s, 1H), 10.34 (s, 1H).

Anal. Calcd. for $C_{19}H_{10}N_4S$: C, 69.92; H, 3.09; N, 17.17; S, 9.82. Found: C, 70.13; H, 3.21; N, 17.15; S, 9.80.

3-Chloro-*N*-(3′-pyridyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**14**).

3-Chloronaphtho[1,2-*b*]thiophene-2-carbonyl chloride (**13**) [6] (20.0 g, 0.071 mole), 3-aminopyridine (13.5 g, 0.142 mole), and benzene (250 ml) was refluxed for one hour following the procedure for the preparation of **2**. There was obtained 13.3 g (55% yield) of product, mp 208-210°; ^{1}H nmr (deuteriochloroform): 6.78-8.43 (m, 10H, ArH), 8.85-8.89 (m, 1H, NH).

Anal. Calcd. for $C_{18}H_{11}ClN_2OS$: C, 63.81; H, 3.27; Cl, 10.46; S, 9.46. Found: C, 63.21; H, 3.24; Cl, 10.34; S, 9.43.

Naphtho[2′,1′:4,5]thieno[2,3-*c*]-1,5-naphthyridin-6(5*H*)-one (**15**).

This compound was prepared from **14** (0.5 g, 0.00147 mole), and triethylamine (0.5 ml) in 1% methanol-benzene solution (500 ml) in a manner similar to the preparation of **5**. This material was pure enough to be used in the next step without further treatment, (0.35 g, 83% yield), mp >250°; ^{1}H nmr (DMSO-d_6): 6.65-9.15 (m, 9H, ArH), 9.27-9.32 (m, 1H, NH).

6-Chloro[2′,1′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**16**).

A solution of **15** (0.5 g, 0.00165 mole), and phosphorus oxychloride (15 ml) was refluxed for four hours in a manner similar to the preparation of **8** and there was obtained 0.3 g (57% yield) of yellow crystals, mp 245-246°; ^{1}H nmr (DMSO-d_6): 7.46-8.70 (m, 8H, ArH), 9.52-9.56 (m, 1H, C4).

Anal. Calcd. for $C_{18}H_9ClN_2S$: C, 67.39; H, 2.80; N, 8.73; S, 9.98. Found: C, 67.20; H, 3.04; N, 8.82; S, 9.61.

Napththo[2′,1′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**17**).

This compound was prepared from **16** in a manner similar to the preparation of **9** and was obtained as white crystals (23% yield), mp 236-237°; ^{1}H nmr (deuteriochloroform): 7.51-8.22 (m, 6H, ArH), 8.41-8.52 (dd, 1H, ArH, J = 5.8 Hz, J′ = 4.0 Hz), 9.00-9.07 (dd, 1H, ArH, J = 1.8 Hz, J′ = 2.9 Hz), 9.35 (s, 1H, H-6), 9.54-9.64 (d, 1H, ArH).

Anal. Calcd. for $C_{18}H_{10}N_2S$: C, 75.50; H, 3.52; S, 11.20. Found: C, 75.46; H, 3.65; S, 11.08.

6-Aminonaphtho[2′,1′:4,5]thieno[2,3-*c*]-1,5-naphthyridine (**18**).

Compound **16** (0.17 g, 0.00053 mole) in ammonia-saturated methanol was heated at 180° for 24 hours. After cooling, the solvent was removed and the remaining solid was recrystallized from benzene to afford 0.067 g (42% yield) of product, mp 280°; ^{1}H nmr (DMSO-d_6): 7.05 (s, 2H, NH_2), 7.35 (s, 1H, ArH), 7.58-8.32 (m, 6H, ArH), 8.74-8.81 (dd, 1H, ArH), 9.60-9.70 (d, 1H, ArH).

Anal. Calcd. for $C_{18}H_{11}N_3S$: C, 71.74; H, 3.68; N, 13.94; S, 10.64. Found: C, 71.66; H, 3.61; N, 13.88; S, 10.48.

NMR Data Acquistion.

The ZQCOSY spectral data was acquired using a sample of approximately 10 mg of **8** dissolved in 0.4 ml of deuteriochloroform and was recorded at 300.068 MHz using a Nicolet NT-300 wide bore spectrometer equipped with a dual tuned ^{1}H/^{13}C probe. The pulse sequence used was that of Müller [13] which combined a 30

msec homospoil pulse with a sixteen step phase cycle as described in our previous work [7,14]. The data were taken as 256 x 1K complex points. The sample was not spun and four accumulations were discarded prior to the accumulation of the sixteen transients/block which were actually stored. Fixed delays during the excitation of zero quantum coherence were optimized for 7 Hz (35.7 msec). Spectral width in both frequency domains was ±750 Hz, causing the response correlating H13 to H12 to fold (the algebraic difference in F_2 shifts in this case was 1050 Hz). Data were processed using sinusoidal multiplication prior to both Fourier transformations to afford a final matrix consisting of 512 x 512 points.

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[1] To whom correspondence should be directed at the Department of Chemistry, University of South Florida, Tampa, FL 33620-5250 USA.

[2] Present address: Schering Plough, Bloomfield, NJ 07003.

[3] Present address: Division of Organic Chemistry, Burroughs Wellcome Company, 3030 Cornwallis Road, Research Triangle Park, NC 27709.

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