The Synthesis of Novel Polycyclic Heterocyclic Ring Systems *via* Photocyclization. 9. Phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline, Benzo[*f*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline, and Benzo[*h*]-phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline

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The synthesis of three novel polycyclic heterocyclic ring systems are reported *via* photocyclization. The specific final products in these ring systems are: phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**13**), benzo[*h*]-phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**14**), and benzo[*f*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**15**).

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In a series of related publications [3a-h] eighteen previously unknown polycyclic ring systems have been synthesized by photocyclization of the appropriate amides to afford these ring systems where the new cyclized ring is a condensed pyridine, thus the photocyclization produces the nitrogen heterocyclic moiety of the novel ring systems. We now report the synthesis of three additional heterocyclic ring systems previously unreported. These are phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**13**), benzo[*h*]-phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**14**), and benzo[*f*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**15**).

Commercially available phenanthrene-9-carbaldehyde (**1**) was allowed to react with malonic acid in the presence of pyridine and aniline to afford β-(9-phenanthryl)acrylic acid (**2**) in nearly quantitative yield. Treatment of **2** with thionyl chloride and pyridine in chlorobenzene solution by the method of Wright and Brabander [4] provided 3-chlorophenanthro[9,10-*b*]thiophene-2-carbonyl chloride (**3**) in 42% yield. The reaction of **3** with aniline in benzene solution gave 3-chloro-*N*-phenylphenanthro[9,10-*b*]thiophene-2-carboxamide (**4**) in 87% yield. Photocyclization of **4** provided phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**7**) in 85% yield. Phosphorus oxychloride chlorination of **7** yielded 6-chlorophenanthro[9′,10′:4,5]thieno[2,3-*c*]-quinoline (**10**) in 70% yield. Catalytic dechlorination of **10** with Pd-C and hydrogen afforded the novel unsubstituted ring system phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**13**) in 55% yield.

The reaction of acid chloride **3** with 1-naphthalenamine gave 3-chloro-*N*-(1-naphthyl)phenanthro[9,10-*b*]thiophene-2-carboxamide (**5**) in 70% yield. Photocyclization of **5** provided benzo[*h*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**8**) in 71% yield. Phosphorus oxychloride chlorination of **8** afforded 6-chlorobenzo[*h*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**11**) in 28% yield. Catalytic dechlorination of **11** with 10% Pd-C and hydrogen gave the unsubstituted benzo[*h*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]-quinoline (**14**) in 42% yield.

In like manner **3** was allowed to react with 2-naphthalenamine to afford 3-chloro-*N*-(2-naphthyl)phenanthro[9,10-*b*]thiophene-2-carboxamide (**6**) in 76% yield. Photocyclization of **6** provided benzo[*f*]phenanthro[9′,10′:4,5]thieno-[2,3-*c*]quinoline-8(7*H*)-one (**9**) in 54% yield. Lactam **16** was not obtained [5,6]. Phosphorus oxychloride chlorination of **9** gave 8-chlorobenzo[*f*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]-quinoline (**12**) in 45% yield. Catalytic dechlorination of **12** gave the third novel, unsubstituted ring system benzo[*f*]-phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**15**) in 85% yield. All reactions are outlined in Scheme 1.

These three novel ring systems have been studied by various 2D nmr techniques [5,6] and the final products and intermediates will be used for a study of the reactions of these ring systems.

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. The ^{1}H nmr spectra were obtained on a JEOL FX-90 Q spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and the 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.

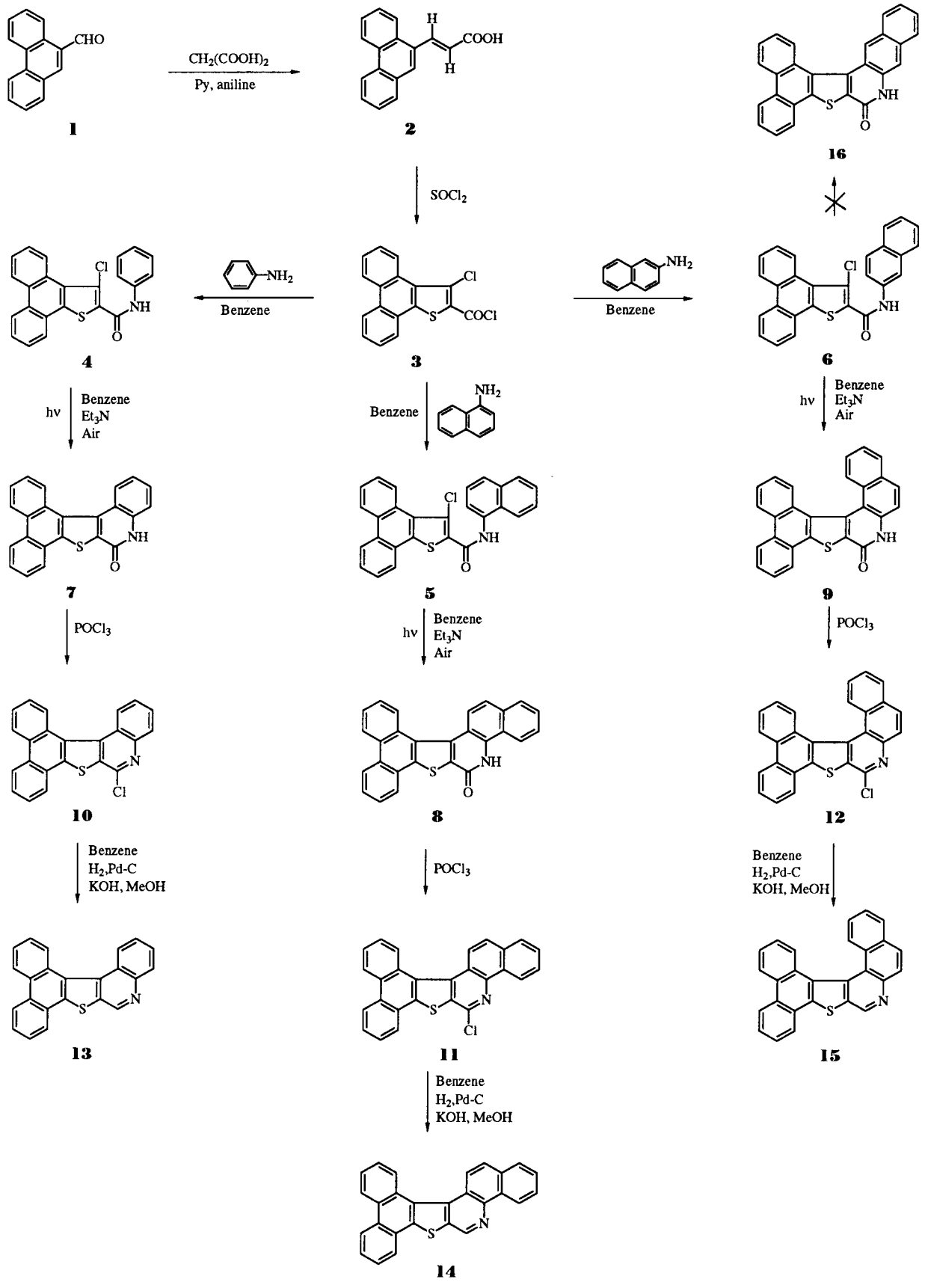
β-(9-Phenanthryl)acrylic Acid (**2**).

Compound **2** was prepared in almost quantitative yield after recrystallization from ethanol, mp 231-232° following the procedure of Bachmann and Kloetzel [7], lit mp 231-233.5°.

3-Chlorophenanthro[9,10-*b*]thiophene-2-carbonyl Chloride (**3**).

Thionyl chloride (40 ml, 0.55 mole) was added dropwise to an ice cooled suspension of **2** (20 g, 0.08 mole) in 60 ml of chlorobenzene containing 0.65 ml (0.09 mole) of pyridine. The mixture was refluxed for 72 hours, the excess solvent was removed under reduced pressure and the residual material was suspended in hot hexane (100 ml). While hot the solids were removed by filtration and the filtrate treated with charcoal. After standing at room tem-

Scheme 1


CHO
1
CH2(COOH)2
Py, aniline
COOH
2
SOCl2
Cl
COCl
3
NH2
Benzene
Cl
NH
S
O
4
hv
Benzene
Et3N
Air
7
POCl3
10
Benzene
H2,Pd-C
KOH, MeOH
13
Benzene
NH2
5
hv
Benzene
Et3N
Air
8
POCl3
11
Benzene
H2,Pd-C
KOH, MeOH
14
NH2
Benzene
6
hv
Benzene
Et3N
Air
9
POCl3
12
Benzene
H2,Pd-C
KOH, MeOH
15
16
N
Cl

perature overnight, the precipitate was collected by filtration to give after recrystallization from benzene 11.2 g (42%) of **3**, mp 202° (lit [8] 174-175°); ir (potassium bromide): 1740, 878, 775, 740, 710, 673, 660, 650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.34-7.83 (m, 4H, ArH), 8.05-9.15 (m, 1H, ArH), 8.54-9.37 (m, 2H, ArH), 9.41-9.48 (m, 1H, ArH).

3-Chloro-*N*-phenylphenanthro[9,10-*b*]thiophene-2-carboxamide (**4**).

A mixture of 1.66 g (5 mmoles) of **3** and 0.93 g (10 mmoles) of aniline in 30 ml of benzene was heated for two hours on a steam bath. The solvent was removed by distillation under reduced pressure and the resulting solid was suspended in ice water and then filtered. This solid was recrystallized from benzene (charcoal) to afford 1.70 g (87%) of **4**, mp 217-218°; ir (potassium bromide): 3312, 1635, 1527, 748 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.27-7.76 (m, 9H, ArH), 7.77-8.20 (m, 1H, ArH), 8.22-8.72 (m, 2H, ArH), 8.75 (br s, 1H, NH), 9.33-9.44 (m, 1H, ArH).

Anal. Calcd. for $C_{23}H_{14}ClNOS$: C, 71.22; H, 3.64; N, 3.63. Found: C, 71.19; H, 3.73; N, 3.63.

3-Chloro-*N*-(1-naphthyl)phenanthro[9,10-*b*]thiophene-2-carboxamide (**5**).

This compound was prepared from **3** (2.32 g, 7 mmoles) and 1-naphthalenamine (2.00 g, 1.4 mmoles) in 40 ml of benzene in a manner similar to that described for the synthesis of **4** and 2.15 g (70%) of **5** was obtained after recrystallization from benzene, mp 258-259°; ir (potassium bromide): 3414, 3229, 3052, 1653, 1630, 1543, 770, 755 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.34-8.02 (m, 12H, ArH), 8.11-8.66 (m, 2H, ArH), 8.71-9.36 (m, 1H, ArH), 9.51 (br s, 1H, NH).

Anal. Calcd. for $C_{27}H_{16}ClNOS$: C, 74.05; H, 3.65; N, 3.20; S, 7.31. Found: C, 74.29; H, 3.89; N, 3.18; S, 7.50.

3-Chloro-*N*-(2-naphthyl)phenanthro[9,10-*b*]thiophene-2-carboxamide (**6**).

This compound was prepared from **3** (3.31 g, 10 mmoles) and 2-naphthalenamine (2.86 g, 20 mmoles) in 50 ml of benzene in a manner similar to that described for the synthesis of **4** and 3.30 g (76%) of **6** was obtained after recrystallization from benzene, mp 218-219°; ir (potassium bromide): 3368, 3127, 1648, 1540, 1499, 1265, 815, 748, 727 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.39-7.88 (m, 10H, ArH), 8.06-8.16 (m, 1H, ArH), 8.36-8.51 (m, 1H, ArH), 8.53-8.78 (m, 2H, ArH), 9.09 (br s, 1H, NH), 9.28-9.38 (m, 1H, ArH).

Anal. Calcd. for $C_{27}H_{16}ClNOS$: C, 74.05; H, 3.65; N, 3.20. Found: C, 73.88; H, 3.46; N, 3.24.

Phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**7**).

A stirred solution of **4** (0.50 g, 1.28 mmoles) and triethylamine (0.18 ml, 1.28 mmoles) in benzene (500 ml) was irradiated for 5 hours with a 450 watt Hanovia medium pressure mercury vapor lamp under a slow stream of air. The solid was collected by filtration and then washed with water to give 0.39 g (85%) of **7**, mp >280°; ir (potassium bromide): 3173, 3124, 2988, 2852, 1671, 1653, 1586, 743, 722, 643 cm^{-1}; ^1H nmr (DMSO-d_6): 140° δ 7.50-7.88 (m, 6H, ArH), 8.23-8.33 (m, 2H, ArH), 8.41-8.90 (m, 4H, ArH). This compound was used without further purification in the next reaction due to its low solubility.

Benzo[*h*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**8**).

This compound was prepared from **5** (0.50 g, 1.14 mmoles) in a manner similar to that described for the synthesis of **7**, to give 0.33 g (71%), mp >280°; ir (potassium bromide): 3162, 3052, 1653, 1635, 750 cm^{-1}; ^1H nmr (DMSO-d_6): 100° δ 7.35-8.10 (m, 8H, ArH), 8.30-8.43 (m, 2H, ArH), 8.56-8.65 (m, 1H, ArH), 8.88-9.06 (m, 3H, ArH). This compound was used without further purification in the next reaction due to its low solubility.

Benzo[*f*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinolin-8(7*H*)-one (**9**).

This compound was obtained in 54% yield from **6** (0.50 g, 1.14 mmoles) in exactly the same manner as described for the synthesis of **7**, mp >280°; ir (potassium bromide): 3139, 3067, 3008, 2857, 1666, 1620, 1484, 1422, 815, 753, 743, 725, 650, 591 cm^{-1}; ^1H nmr (DMSO-d_6): 100° δ 6.96-7.13 (m, 2H, ArH), 7.33-8.37 (m, 9H, ArH), 8.39-8.45 (m, 1H, ArH), 8.80-8.99 (m, 2H, ArH). This compound was used without further purification in the next reaction due to its low solubility.

6-Chlorophenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**10**).

A mixture of 0.60 g (1.7 mmoles) of **7** and 30 ml of phosphorus oxychloride was refluxed for 5 hours. Excess phosphorus oxychloride was removed under reduced pressure and the residual material was treated with ice water. The precipitate was collected by filtration, washed with water and dried. Recrystallization from benzene furnished 0.44 g (70%), mp 226-227°; ir (potassium bromide): 3142, 1558, 1481, 1401, 1259, 746, 723 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.34-7.83 (m, 6H, ArH), 8.16-8.65 (m, 2H, ArH), 8.68-8.81 (m, 4H, ArH).

Anal. Calcd. for $C_{23}H_{12}ClNS$: C, 74.69; H, 3.24; N, 3.72; S, 8.66. Found: C, 74.88; H, 3.13; N, 3.77; S, 8.81.

6-Chlorobenzo[*h*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**11**).

A mixture of 0.50 g (1.24 mmoles) of lactam **8** and phosphorus oxychloride (30 ml) was refluxed for 24 hours. The work-up procedure was similar to the preparation of **10**. Recrystallization from benzene afforded 0.15 g (28%), mp >300°; ir (potassium bromide): 3260, 3075, 2926, 1563, 1506, 1435, 1008, 967, 751, 728, 726 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.35-8.14 (m, 9H, ArH), 8.17-8.76 (m, 4H, ArH), 8.83-8.85 (m, 1H, ArH).

Anal. Calcd. for $C_{27}H_{14}ClNS$: C, 77.23; H, 3.36; N, 3.34. Found: C, 77.42; H, 3.58; N, 3.33.

8-Chlorobenzo[*f*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**12**).

A mixture of 0.40 g (1 mmole) of lactam **9** and phosphorus oxychloride (30 ml) was refluxed for 12 hours. The work-up procedure was similar to the preparation of **10**. Recrystallization from benzene gave 0.19 g (45%), mp 261-262°; ir (potassium bromide): 3368, 3127, 1648, 1540, 1499, 1265, 815, 748, 727 cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.99-8.33 (m, 12H, ArH), 8.59-8.76 (m, 2H, ArH).

Anal. Calcd. for $C_{27}H_{14}ClNS$: C, 77.23; H, 3.36; N, 3.34; S, 7.62. Found: C, 77.48; H, 3.56; N, 3.29; S, 7.75.

Phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**13**).

A solution of 0.20 g (0.54 mmole) of **10**, 0.10 g of 10% Pd-C, 30 mg of potassium hydroxide, 100 ml of benzene and 100 ml of methanol was hydrogenated at atmospheric pressure at room temperature for 3 days. The catalyst was removed by filtration through a celite pad and the filtrate was evaporated to dryness under reduced pressure. The solid was chromatographed on a silica gel column using benzene as the eluent to give after recrystallization from methylene chloride and *n*-hexane 0.10 g

(55%) of **13**, mp 186-187°; ir (potassium bromide): 3147, 3075, 1563, 1496, 1401, 1229, 748, 722 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.52-7.58 (m, 2H, ArH), 7.62-7.75 (m, 4H, ArH), 8.13-8.16 (d, 1H, ArH, J = 7.7 Hz), 8.28-8.30 (d, 1H, ArH, J = 8.2 Hz), 8.65-8.68 (m, 2H, ArH), 8.74-8.77 (m, 2H, ArH), 9.35 (s, 1H, ArH).

Anal. Calcd. for $C_{23}H_{13}NS$: C, 82.38; H, 3.88; N, 4.17; S, 9.55. Found: C, 82.55; H, 3.99; N, 4.17; S, 9.41.

Benzo[*h*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**14**).

This compound was prepared from **11** (0.090 g, 0.214 mmole), 10% Pd-C (0.10 g), potassium hydroxide (12 mg), benzene (150 ml) and methanol (150 ml) in a manner similar to that described for the synthesis of **13** and 35 mg (42%) of **14** was obtained after recrystallization from benzene, mp 180-181°; ir (potassium bromide): 3152, 3121, 1399, 1383, 751, 720 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.56-7.83 (m, 7H, ArH), 7.93-7.95 (d, 1H, ArH, J = 7.8 Hz), 8.16-8.19 (d, 1H, ArH, J = 7.8 Hz), 8.56-8.59 (d, 1H, ArH, J = 9.0 Hz), 8.68-8.72 (m, 3H, ArH), 9.40-9.42 (d, 1H, ArH, J = 8.0 Hz), 9.46 (s, 1H, ArH).

Anal. Calcd. for $C_{27}H_{15}NS$: C, 84.15; H, 3.89; N, 3.63; S, 8.31. Found: C, 84.30; H, 4.00; N, 3.41; S, 8.16.

Benzo[*f*]phenanthro[9′,10′:4,5]thieno[2,3-*c*]quinoline (**15**).

This compound was prepared from **12** (0.11 g, 0.26 mmole), 10% Pd-C (0.10 g), potassium hydroxide (14.6 mg), benzene (150 ml) and methanol (150 ml) in a manner similar to that described for the synthesis of **13** and 85 mg (85%) of **15** was obtained after recrystallization from benzene, mp 264-265°; ir (potassium bromide): 3140, 1399, 820, 750, 730, 720 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.00-7.07 (m, 2H, ArH), 7.42-7.53 (m, 3H, ArH), 7.68-7.78 (m, 2H, ArH), 7.83-7.85 (d, 1H, ArH, J = 8.3 Hz), 7.98-8.00 (d, 1H, ArH, J = 7.8 Hz), 8.07-8.09 (d, 1H, ArH, J = 8.8 Hz), 8.20-8.26 (m, 2H, ArH), 8.64-8.66 (d, 1H, ArH, J = 8.2 Hz), 8.71-8.73 (d, 1H, ArH, J = 8.0 Hz), 9.43 (s, 1H, ArH).

Anal. Calcd. for $C_{27}H_{15}NS$: C, 84.15; H, 3.89; N, 3.63; S, 8.31. Found: C, 84.31; H, 4.00; N, 3.51; S, 8.46.

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