

Hirotaka Kudo and Raymond N. Castle* [1]

Department of Chemistry, University of South Florida,
Tampa, Florida 33620

Milton L. Lee

Department of Chemistry, Brigham Young University,
Provo, Utah 84602

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The synthesis of naphtho[1',2':4,5]thieno[2,3-c]quinoline (**11**) and four monomethyl isomers is described.

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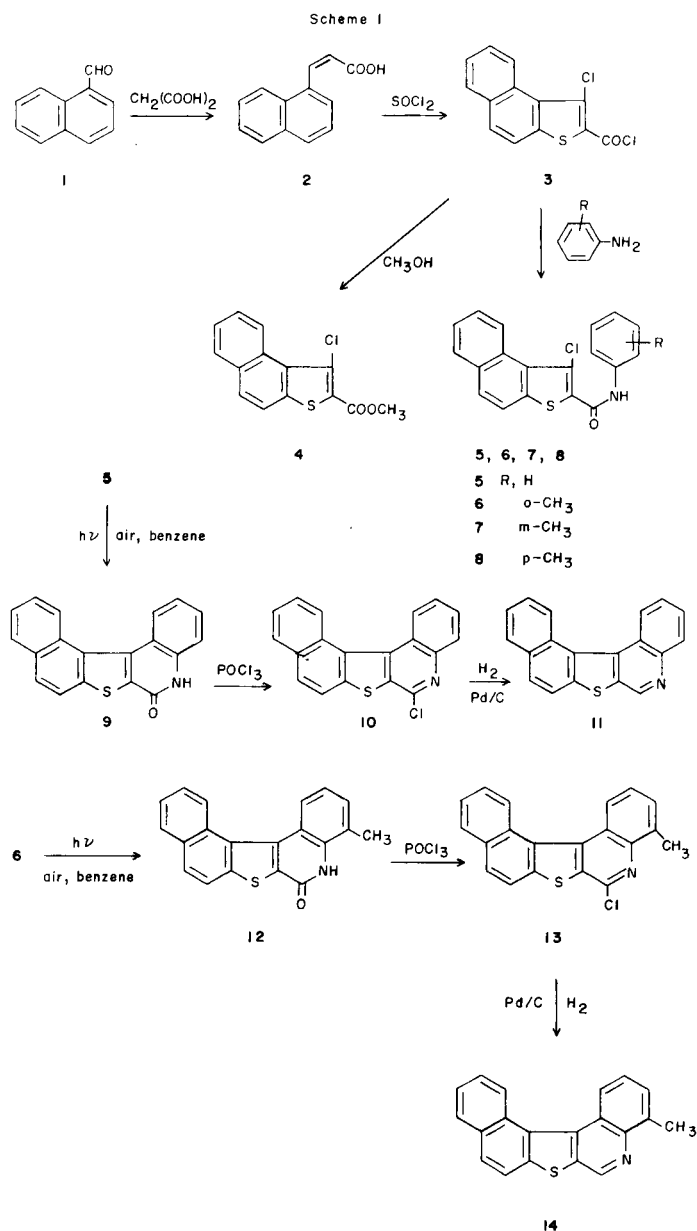
In earlier work from this laboratory [2-21] we have reported the synthesis of a great many polycyclic thiophenes, a number of which have been shown to exist in coal liquids and shale oils [22,23]. Furthermore the mutagenicity of a number of the polycyclic thiophenes has been reported [24,25].

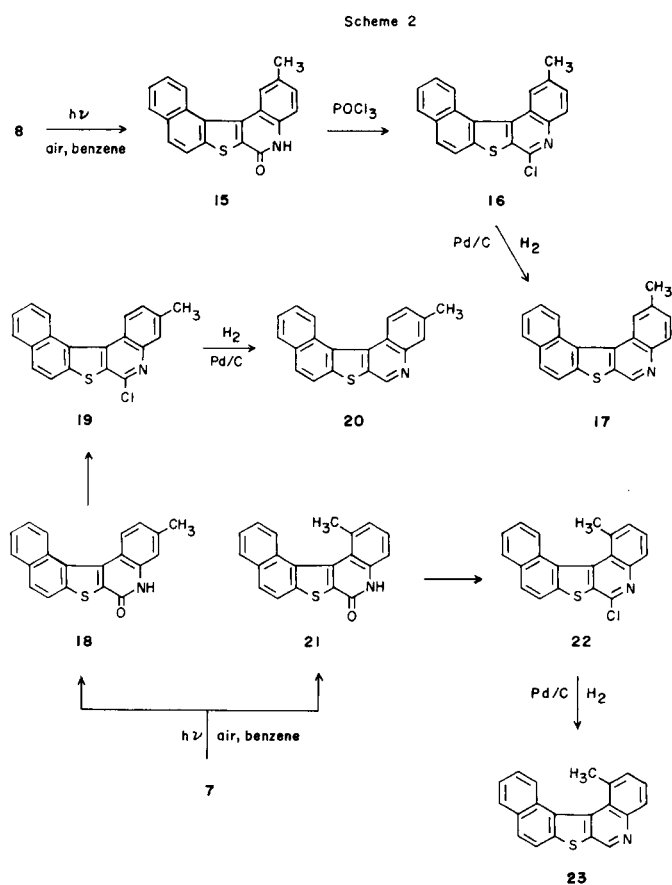
We now have preliminary evidence [26] that heterocycles occur in coal-derived products which contain a sulfur heterocycle fused to a nitrogen heterocycle. We therefore report the synthesis of naphtho[1',2':4,5]thieno[2,3-c]quinoline and four monomethyl isomers.

The reaction of 1-naphthalenecarboxaldehyde (**1**) with malonic acid gave 3-(1-naphthyl)propenoic acid (**2**) (88% yield) [27] which when allowed to react with thionyl chloride produced 1-chloronaphtho[2,1-*b*]thiophene-2-carboxoyl chloride (**3**) (27% yield) [28]. The acid chloride **3**, when treated with methanol, afforded methyl 3-chloronaphtho[2,1-*b*]thiophene-2-carboxylate (**4**) in 97% yield. Reaction of **3** with aniline gave 1-chloro-*N*-phenylnaphtho[2,1-*b*]thiophene-2-carboxamide (**5**) in 99% yield. Likewise when *o*-, *m*- or *p*-toluidine was allowed to react with **3**, the corresponding methyl-substituted carboxamides **6** (94% yield), **7** (97% yield) and **8** (90% yield) were obtained.

Photocyclization of **5**, **6** or **8** in benzene solution with equimolar quantities of triethylamine gave the corresponding pentacyclic compounds **9** (76% yield), **12** (92% yield) and **15** (88% yield). The photocyclization of **7** gave a mixture of **18** and **21** (96% combined yield) which was not readily separated. Compounds **9**, **12** or **15** when allowed to react with phosphorus oxychloride gave respectively: **10** (81% yield), **13** (88% yield) and **16** (88% yield). When the mixture of **18** and **21** was allowed to react with phosphorus oxychloride, a mixture of **19** and **22** was obtained. Crystallization from benzene afforded the more insoluble **22** in 75% yield. The mother liquor contained **19** contaminated with **22** (nmr analysis).

Catalytic dechlorination (Pd-C) of **10**, **13**, **16** or **22** produced respectively **11** (88% yield), **14** (68% yield), **17**





(88% yield) and **23** (88% yield). Catalytic dechlorination of the impure **19** gave **20** which was purified chromatographically (nmr analysis).

The monomethyl derivatives of naphtho[1',2':4,5]thieno[2,3-c]quinoline and the parent ring system are being screened against TA-98 and TA-100 in the Ames test (S9 liver homogenate activation) and these results will be published elsewhere.

EXPERIMENTAL

The melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The ir spectra were obtained on a Perkin Elmer 337 spectrometer. The ^1H nmr spectra were obtained on a Varian EM 360 spectrometer in the solvents indicated using TMS as the internal standard. Mass spectra were obtained on a Hewlett Packard model 5980A mass spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona 85018.

1-Chloronaphtho[2,1-b]thiophene-2-carboxoyl Chloride (**3**).

A mixture of compound **2** (9.9 g, 0.05 mole), dry pyridine (0.8 ml, 0.01 mole), thionyl chloride (18 ml, 0.25 mole) and chlorobenzene (50 ml) was heated at reflux for 72 hours. After cooling, the precipitate was collected by filtration to give 2.1 g of tan prisms. The filtrate was concentrated to remove the solvent and the residue was triturated with hexane and filtered giving an additional 1.4 g (total yield 26%). An analytical sample was recrystallized from benzene to give yellow needles, mp 152-153°; nmr ($\text{DMSO}-d_6$): δ 7.01-7.85 (m, 5-H, 6-H, 7-H, 3H, ArH), 7.86-8.22 (m, 8-H, 9-H, 2H, ArH), 9.22-9.64 (m, 4-H, 1H, ArH); ms: m/e 282 ($\text{M}^+ + 2$, 22), 280

(M^+ , 30), 247 (38), 245 ($\text{M}^+ - \text{Cl}$, 100).

Anal. Calcd. for $\text{C}_{13}\text{H}_6\text{Cl}_2\text{OS}$: C, 55.54; H, 2.15; S, 11.40. Found: C, 55.58; H, 2.31; S, 11.15.

Methyl 1-Chloronaphtho[2,1-b]thiophene-2-carboxylate (**4**).

A mixture of **3** (1.4 g, 0.005 mole) and methanol (70 ml) was refluxed for one hour. After evaporation of the methanol, the residue was recrystallized from methanol to give 0.97 g (97%) of tan needles, mp 145-146°; nmr (deuteriochloroform): δ 3.97 (s, COOCH_3 , 3H), 7.43-8.14 (m, 5-H, 6-H, 7-H, 8-H, 9-H, 5H, ArH), 9.44-9.76 (m, 4-H, 1H, ArH); ms: m/e 247 ($\text{M}^+ + 2$, 37), 245 (M^+ , 100), 217 (24), 182 (21).

Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{ClO}_2\text{S}$: C, 60.76; H, 3.28; S, 11.59. Found: C, 60.60; H, 3.44; S, 11.67.

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

A mixture of compound **3** (5.6 g, 0.02 mole), aniline (3.7 g, 0.04 mole) and benzene (100 ml) was heated for one hour on a steam bath. After cooling, the precipitate was collected by filtration, washed with water and recrystallized from ethanol giving yellow prisms (6.3 g, 93%), mp 174-175°; nmr (deuteriochloroform): δ 7.19-7.82 (m, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H, 5H, ArH), 7.83-8.03 (m, 5-H, 6-H, 7-H, 8-H, 9-H, 5H, ArH), 8.9 (bs, NH, 1H), 9.2-9.41 (m, 4-H, 1H, ArH); ms: m/e 339 ($\text{M}^+ + 1$, 10), 337 (25), 247 ($\text{M}^+ - \text{NHC}_6\text{H}_5$, 36), 245 ($\text{M}^+ - \text{NHC}_6\text{H}_4\text{CH}_3$, 100), 182 ($\text{M}^+ - [\text{Cl} + \text{OCNHC}_6\text{H}_4\text{CH}_3]$, 33).

Anal. Calcd. for $\text{C}_{19}\text{H}_{12}\text{ClNOS}$: C, 67.55; H, 3.58; N, 4.15; S, 9.49. Found: C, 67.64; H, 3.77; N, 4.24; S, 9.39.

1-Chloro-N-(2-methylphenyl)naphtho[2,1-b]thiophene-2-carboxamide (**6**).

This compound was prepared from compound **3** (5.6 g, 0.02 mole), *o*-toluidine (4.2 g, 0.04 mole) and benzene (100 ml) in a manner similar to the preparation of **5** and was obtained as colorless needles, yield 5 g (94%), mp 167-168°; nmr (deuteriochloroform): δ 2.42 (s, CH_3 , 3H), 7.14-7.63 (m, 3'-H, 4'-H, 5'-H, 6'-H, 4H, ArH), 7.64-8.38 (m, 5-H, 6-H, 7-H, 8-H, 9-H, 5H, ArH), 8.88 (bs, NH, 1H), 9.28-9.58 (m, 4-H, 1H, ArH); ms: m/e 247 ($\text{M}^+ - \text{NHC}_6\text{H}_4\text{CH}_3$, 38), 245 ($\text{M}^+ - \text{NHC}_6\text{H}_5$, 100), 217 ($\text{M}^+ - \text{OCNHC}_6\text{H}_4\text{CH}_3$, 18), 182 ($\text{M}^+ - [\text{Cl} + \text{CONHC}_6\text{H}_4\text{CH}_3]$, 182).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{ClNOS}$: C, 68.27; H, 4.01; N, 3.98; S, 9.11. Found: C, 68.36; H, 4.18; N, 4.04; S, 9.00.

1-Chloro-N-(3-methylphenyl)naphtho[2,1-b]thiophene-2-carboxamide (**7**).

This compound was prepared from compound **3** (5.6 g, 0.02 mole), *m*-toluidine (4.2 g, 0.04 mole) and benzene (100 ml) in a manner similar to the preparation of **7** and was obtained as tan prisms giving 6.5 g (97%), mp 117-118°; nmr (deuteriochloroform): δ 2.42 (s, CH_3 , 3H), 6.84-7.22 (m, 4'-H, 5'-H, 2H, ArH), 7.23-7.68 (m, 2'-H, 6'-H, 2H, ArH), 7.69-8.24 (m, 5-H, 6-H, 7-H, 8-H, 9-H, 5H, ArH), 8.95 (bs, NH, 1H), 9.17-9.52 (m, 4-H, 1H, ArH); ms: m/e 274 ($\text{M}^+ - \text{NHC}_6\text{H}_4\text{CH}_3$, 38), 245 ($\text{M}^+ - \text{NHC}_6\text{H}_5$, 100), 217 ($\text{M}^+ - \text{OCNHC}_6\text{H}_4\text{CH}_3$, 25), 217 ($\text{M}^+ - [\text{Cl} + \text{OCNHC}_6\text{H}_4\text{CH}_3]$, 27).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{ClNOS}$: C, 68.27; H, 4.01; N, 3.98; S, 9.11. Found: C, 67.99; H, 4.12; N, 4.00; S, 9.23.

1-Chloro-N-(4-methylphenyl)naphtho[2,1-b]thiophene-2-carboxamide (**8**).

This compound was prepared from compound **3** (5.6 g, 0.02 mole), *p*-toluidine (4.2 g, 0.04 mole) and benzene (100 ml) in a manner similar to the preparation of **7** and was obtained as light tan prisms giving 6 g (90%), mp 155-156°; nmr (deuteriochloroform): δ 2.2 (s, CH_3 , 3H), 6.97-7.3 (m, 3'-H, 5'-H, 2H, ArH), 7.43-7.77 (m, 2'-H, 6'-H, 2H, ArH), 7.78-8.05 (m, 5-H, 6-H, 7-H, 8-H, 9-H, 5H, ArH), 8.9 (bs, NH, 1H), 9.16-9.44 (m, 4-H, 1H, ArH); ms: m/e 247 ($\text{M}^+ - \text{NHC}_6\text{H}_4\text{CH}_3$, 36), 245 ($\text{M}^+ - \text{NHC}_6\text{H}_5$, 100), 217 ($\text{M}^+ - \text{OCNHC}_6\text{H}_4\text{CH}_3$, 18), 182 ($\text{M}^+ - [\text{Cl} + \text{OCNHC}_6\text{H}_4\text{CH}_3]$, 21).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{ClNOS}$: C, 68.27; H, 4.01; N, 3.98; S, 9.11. Found: C, 68.18; H, 4.17; N, 4.00; S, 9.20.

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

A solution of **5** (1 g, 0.003 mole), triethylamine (0.3 g, 0.003 mole) in dry benzene (500 ml) was irradiated for 2 hours with a 450 watt Hanovia

medium pressure mercury lamp. During the course of the reaction, a slow stream of air was passed through the solution. The resulting precipitate was collected by filtration and used for the next reaction without further purification, white prisms, 0.76 g (76%), mp > 290°; ir (nujol): 1660 (NHCO); nmr (deuteriochloroform): 7.21-7.94 (m, 2-H, 3-H, 9-H, 11-H, 12-H, 5H, ArH), 7.95-8.34 (m, 4-H, 8-H, 10-H, 3H, ArH), 8.63-9.11 (m, 1-H, 13-H, 2H, ArH); ms: m/e 299 (M⁺ + 2, 12), 283 (21), 282 (M⁺, 100), 272 (M⁺ - 1, -[CO⁺ + H⁺], 21), 270 (M⁺ - 2, -[CO⁺ + H⁺], 14).

6-Chloronaphtho[1',2':4,5]thieno[2,3-c]quinoline (10).

A mixture of compound **9** (1.5 g, 0.0015 mole) and phosphorus oxychloride (40 ml) was gently refluxed for 3.5 hours on an oil bath. The residue obtained upon removal of the excess of oxychloride was poured into ice water (200 ml). The solid which separated was collected by filtration and washed with water, recrystallized from benzene giving colorless prisms 1.3 g (81%), mp 177-178°; nmr (deuteriochloroform): δ 7.18-7.82 (m, 2-H, 3-H, 9-H, 11-H, 12-H, 5H, ArH), 7.83-8.39 (m, 4-H, 8-H, 10-H, 3H, ArH), 8.53-8.92 (m, 1-H, 13-H, 2H, ArH); ms: m/e 321 (M⁺ + 1, 36), 320 (M⁺, 53), 319 (M⁺ - 1, 99), 318 (M⁺ - 2, 100).

Anal. Calcd. for C₁₉H₁₀ClNS: C, 71.36; H, 3.15; N, 4.38; S, 10.02. Found: C, 71.13; H, 3.45; N, 4.45; S, 9.84.

Naphtho[1',2':4,5]thieno[2,3-c]quinoline (11).

A solution of compound **10** (0.64 g, 0.002 mole) and potassium hydroxide (0.11 g, 0.002 mole) in methanol (80 ml) and benzene (80 ml) was reduced catalytically using a palladium catalyst (5% palladium on carbon, 0.5 g) at atmospheric pressure and room temperature. After the uptake of an equimolar amount of hydrogen, the catalyst was filtered and the solvent was removed under reduced pressure. The product was treated with water and extracted with benzene. The benzene solution was dried over anhydrous sodium sulfate and evaporated. The residue was recrystallized from benzene to give colorless prisms, 0.5 g (88%), mp 229-230°; nmr (deuteriochloroform): δ 7.26-7.74 (m, 2-H, 3-H, 9-H, 11-H, 12-H, 5H, ArH), 7.83-8.45 (m, 4-H, 8-H, 10-H, 3H, ArH), 8.67-9.03 (m, 1-H, 13-H, 2H, ArH), 9.27 (s, 6-H, 1H, ArH); ms: m/e 286 (M⁺ + 1, 19), 284 (M⁺ - 1, 100), 285 (M⁺, 75), 283 (M⁺ - 2, 22).

Anal. Calcd. for C₁₉H₁₁NS: C, 79.95; H, 3.89; N, 4.93; S, 11.23. Found: C, 80.15; H, 3.97; N, 5.10; S, 11.14.

4-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinolin-6(5H)-one (12).

This compound was prepared from compound **6** (0.5 g, 0.0014 mole), triethylamine (0.15 g, 0.0014 mole) and dry benzene (500 ml) in a manner similar to the preparation of **9** and was obtained as colorless prisms (0.4 g, 91%), mp > 280° and used for the next reaction without further purification; ir (nujol): 1665 (NHCO); nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 2.72 (s, CH₃, 3H), 7.31 (d, J = 2 Hz, 9-H, 1H, ArH), 7.34-7.84 (m, 2-H, 3-H, 11-H, 12-H, 4H, ArH), 7.85-8.18 (m, 8-H, 10-H, 2H, ArH), 8.43-8.78 (m, 1-H, 13-H, 2H, ArH); ms: m/e 316 (M⁺ + 1, 24), 315 (M⁺, 100), 314 (M⁺ - 1, 40), 300 (M⁺ - CH₂, 79).

4-Methyl-6-chloronaphtho[1',2':4,5]thieno[2,3-c]quinoline (13).

This compound was prepared from compound **12** (1.5 g, 0.0048 mole) and phosphorus oxychloride (40 ml) in a manner similar to the preparation of **10** and was obtained as pale yellow needles (1.4 g, 88%), mp 166-167°; nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 2.95 (s, CH₃, 3H), 7.29-8.09 (m, 2-H, 3-H, 9-H, 11-H, 12-H, 5H, ArH), 8.10-8.49 (m, 8-H, 10-H, 2H, ArH), 8.58-9.18 (m, 1-H, 13-H, 2H, ArH); ms: m/e 335 (M⁺ + 2, 28), 334 (M⁺ + 1, 23), 333 (M⁺, 71), 320 (M⁺ - CH, 36), 318 (M⁺ - 2, 100).

Anal. Calcd. for C₂₀H₁₂ClNS: C, 71.96; H, 3.62; N, 4.20; S, 9.60. Found: C, 71.77; H, 3.71; N, 4.12; S, 9.71.

4-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinoline (14).

This compound was prepared from compound **13** (0.67 g, 0.002 mole), potassium hydroxide (0.16 g, 0.002 mole) and palladium on carbon (5%, 0.5 g) in methanol (80 ml) and benzene (80 ml) in a manner similar to the

preparation of **11** and colorless prisms were obtained, 0.41 g (68%), mp 210-211°; nmr (deuteriochloroform): δ 2.92 (s, CH₃, 3H), 7.26-7.79 (m, 2-H, 9-H, 11-H, 12-H, 4H, ArH), 7.86-8.14 (m, 3-H, 8-H, 10-H, 3H, ArH), 8.53-9.05 (m, 1-H, 13-H, 2H, ArH), 9.35 (s, 6-H, 1H, ArH); ms: m/e 300 (M⁺ + 1, 18), 299 (M⁺, 73), 284 (100), 283 (32), 142 (23).

Anal. Calcd. for C₂₀H₁₃NS: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 80.23; H, 4.40; N, 4.77; S, 10.65.

2-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinolin-6(5H)-one (15).

This compound was prepared from compound **8** (0.5 g, 0.0014 mole), triethylamine (0.15 g, 0.0014 mole) and dry benzene (500 ml) in a manner similar to the preparation of **9**. It was obtained as colorless prisms (0.38 g, 88%) mp > 270° and was used without further purification in the next step; ir (nujol): 1660 (NHCO); nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 2.5 (s, CH₃, 3H), 7.15-7.79 (m, 3-H, 4-H, 9-H, 3H, ArH), 7.87-8.21 (m, 8-H, 10-H, 11-H, 12-H, 4H, ArH), 8.46-8.82 (m, 1-H, 13-H, 2H, ArH); ms: m/e 315 (M⁺, 100), 301 (M⁺ - CH₂, 17), 300 (M⁺ - CH₃, 89), 282 (34).

2-Methyl-6-chloronaphtho[1',2':4,5]thieno[2,3-c]quinoline (16).

This compound was prepared from compound **15** (1.5 g, 0.0048 mole) and phosphorus oxychloride (40 ml) in a manner similar to the preparation of **10** and was obtained as yellow needles, (1.4 g, 88%), mp 164-165°; nmr (deuteriochloroform): δ 2.45 (s, CH₃, 3H), 7.23-7.63 (m, 3-H, 4-H, 9-H, 3H, ArH), 7.81-8.09 (m, 8-H, 10-H, 11-H, 12-H, 4H, ArH), 8.42 (s, 1-H, 1H, ArH), 8.5-8.75 (m, 13-H, 1H, ArH); ms: m/e 334 (M⁺, 27), 333 (M⁺ - 1, 99), 318 (100), 283 (37).

Anal. Calcd. for C₂₀H₁₂ClNS: C, 71.96; H, 3.62; N, 4.20; S, 9.60. Found: C, 72.04; H, 3.62; N, 4.12; S, 9.49.

2-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinoline (17).

This compound was prepared from compound **16** (0.67 g, 0.002 mole) and potassium hydroxide (0.16 g, 0.002 mole) in methanol (80 ml) and benzene (80 ml) in a manner similar to the preparation of **11** and was obtained as colorless prisms (0.51 g, 85%), mp 171-172°; nmr (deuteriochloroform): δ 2.55 (s, CH₃, 3H), 7.42 (d, J = 2 Hz, 9-H, 1H, ArH), 7.47 (d, J = 2 Hz, 3-H, 4-H, 2H, ArH), 7.82-8.21 (m, 8-H, 10-H, 11-H, 12-H, 4H, ArH), 8.62 (s, 1-H, 1H, ArH), 8.72-9.09 (m, 3-H, 1H, ArH); ms: m/e 299 (M⁺, 30), 294 (100), 283 (30), 142 (60).

Anal. Calcd. for C₂₀H₁₃NS: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 80.27; H, 4.60; N, 4.85; S, 10.66.

3-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinolin-6(5H)-one (18) and 1-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinolin-6(5H)-one (21).

These compounds were prepared from compound **7** (0.5 g, 0.0014 mole), triethylamine (0.15 g, 0.0014 mole) and dry benzene (500 ml) in a manner similar to the preparation of **9**. The resulting precipitate (compound **21**) was collected by filtration and used for the next reaction without further purification, colorless prisms (0.3 g, 68%), mp > 270°; ir (nujol): 1660 (NHCO); nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 2.33 (s, CH₃, 3H), 7.11-7.52 (m, 2-H, 3-H, 4-H, 9-H, ArH), 7.53-7.74 (m, 8-H, 10-H, 11-H, 12-H, 4H, ArH), 7.92-8.41 (m, 1-H, 13-H, 2H, ArH); ms: m/e 301 (M⁺ - CH₂, 23), 300 (M⁺ - CH₃, 100), 282 (55), 150 (21).

The mother liquor of the above benzene solution was evaporated at reduced pressure and the residue (compound **18**) was obtained and used in the next reaction without further purification, colorless prisms (0.12 g, 27%), mp > 270°; nmr (deuteriochloroform): δ 2.6 (s, CH₃, 3H), 7.19-7.85 (m, 2-H, 3-H, 4-H, 3H, ArH), 7.86-8.33 (m, 9-H, 10-H, 11-H, 12-H, 4H, ArH), 8.44-8.87 (m, 8-H, 13-H, 2H, ArH).

3-Methyl-6-chloronaphtho[1',2':4,5]thieno[2,3-c]quinoline (19).

This compound was prepared from compound **18** (1.5 g, 0.005 mole) and phosphorus oxychloride (40 ml) in a manner similar to the preparation of **10**. Compound **19** was recrystallized from benzene to give 1.2 g (75%) of colorless needles, mp 217-218°; nmr (deuteriochloroform): δ 2.2 (s, CH₃, 3H), 7.27-7.74 (m, 2-H, 4-H, 9-H, 3H, ArH), 7.75-8.14 (m, 8-H, 10-H, 11-H, 12-H, 4H, ArH), 8.15-8.47 (m, 1-H, 13-H, 2H, ArH); ms: m/e

334 ($M^+ + 1$, 35), 333 (M^+ , 100), 332 ($M^+ - 1$, 48), 318 ($M^+ - CH_3$, 68).

Anal. Calcd. for $C_{20}H_{12}ClNS$: C, 71.96; H, 3.62; N, 4.20; S, 9.60. Found: C, 72.14; H, 3.77; N, 4.28; S, 9.53.

3-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinoline (**20**).

This compound was prepared from compound **19** (0.7 g, 0.002 mole), potassium hydroxide (0.1 g, 0.002 mole) and palladium on carbon (5%, 0.5 g) in methanol (80 ml) and benzene (80 ml) in a manner similar to the preparation of **11** and was obtained as colorless prisms (0.5 g, 88%), mp 205-206°; nmr (deuteriochloroform): δ 2.13 (s, CH_3 , 3H), 7.13-7.63 (m, 2-H, 9-H, 2H, ArH), 7.63-8.04 (m, 4-H, 10-H, 11-H, 12-H, 4H, ArH), 8.05-8.39 (m, 1-H, 8-H, 13-H, 3H, ArH), 9.23 (s, 6-H, 1H, ArH); ms: m/e 300 ($M^+ + 1$, 29), 285 (23), 284 (100), 142 (25).

Anal. Calcd. for $C_{20}H_{13}NS$: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 80.49; H, 4.50; N, 4.84; S, 10.44.

1-Methyl-6-chloronaphtho[1',2':4,5]thieno[2,3-c]quinoline (**22**).

This compound was prepared from compound **21** (1 g, 0.0032 mole) and phosphorus oxychloride (30 ml) in a manner similar to the preparation of **10**. Compound **22** was recrystallized from benzene-hexane (1:1) to give 0.2 g (14%) of colorless prisms, mp 191-192°; nmr (deuteriochloroform): δ 2.57 (s, CH_3 , 3H), 7.2 (d, $J = 2$ Hz, 9-H, 1H, ArH), 7.33-7.69 (m, 2-H, 3-H, 4-H, 11-H, 12-H, 5H, ArH), 7.73-8.03 (m, 10-H, 1H, ArH), 8.5-8.95 (m, 8-H, 13-H, 2H, ArH); ms: m/e 335 ($M^+ + 1$, 35), 334 (M^+ , 26), 333 ($M^+ - 1$, 88), 320 (36), 318 (100), 282 (42).

Anal. Calcd. for $C_{20}H_{12}ClNS$: C, 71.96; H, 3.62; N, 4.20; S, 9.60. Found: C, 71.94; H, 3.78; N, 4.12; S, 9.69.

1-Methylnaphtho[1',2':4,5]thieno[2,3-c]quinoline (**23**).

This compound was prepared from compound **22** (0.3 g, 0.009 mole), potassium hydroxide (0.05 g, 0.0009 mole) and palladium on carbon (5%, 0.3 g) in methanol (40 ml) and benzene (40 ml) in a manner similar to the preparation of **11**. Compound **23** was obtained as colorless prisms (0.2 g, 67%), mp 180-181°; nmr (deuteriochloroform): δ 2.6 (s, CH_3 , 3H), 7.2 (d, $J = 2$ Hz, 9-H, 1H, ArH), 7.41-7.72 (m, 2-H, 3-H, 4-H, 11-H, 12-H, 5H, ArH), 8.07 (d, $J = 2$ Hz, 10-H, 1H, ArH), 8.53-9.04 (m, 8-H, 13-H, 2H, ArH), 9.3 (s, 6-H, 1H, ArH); ms: m/e 300 ($M^+ + 1$, 25), 299 (M^+ , 100), 298 ($M^+ - 1$, 66), 294 (79), 283 (33).

Anal. Calcd. for $C_{20}H_{13}NS$: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 80.13; H, 4.18; N, 4.74; S, 10.44.

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- [1] To whom correspondence regarding this work should be addressed at the University of South Florida.
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