# Polycyclic Fused Phenanthridines: An Alternative Approach from Benzotriazoles



Alan R. Katritzky*, Weihong Du, Yasuhisa Matsukawa, Ion Ghiviriga, and Sergey N. Denisenko

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA

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We describe an alternative approach to polycyclic phenanthridines (**7**) and some of their analogues using conditions much milder than those previously reported. The procedure includes the generation of a benzotriazole stabilized carbanion, oxidation of the resulting anion to a radical, and elimination of nitrogen followed by ring closure to produce phenanthridines.

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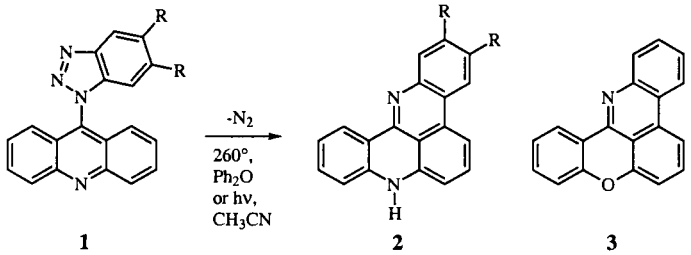
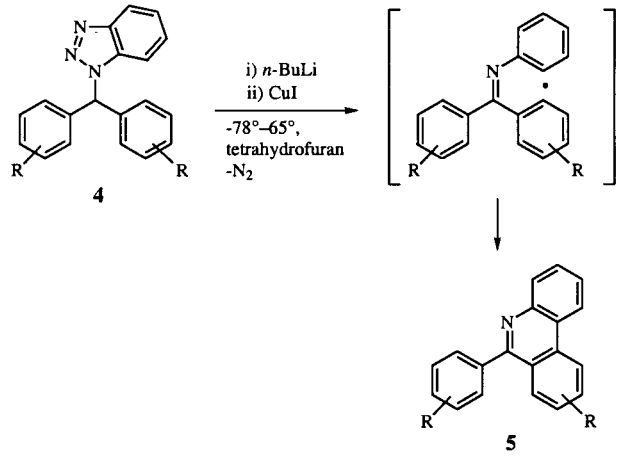
## Introduction.

Stevens and coworkers recently synthesized 7*H*-pyrido[4,3,2-*kl*]acridines **2** by the Graebe-Ulmann thermolysis of substituted 9-(benzotriazol-1-yl)acridines **1** in boiling diphenyl ether. Compounds **1** were obtained from 4,5-disubstituted *N*-(9-acridinyl)-1,2-diaminobenzenes [1]. Acridines **2** are structurally similar to pentacyclic azaaromatic alkaloids isolated from marine organisms and show antiviral and antitumor activity. Pentacycles **2** have also previously been obtained by the photolysis of the corresponding benzotriazoles **1** in acetonitrile [2]. Chromeno-[4,3,2-*gh*]phenanthridine (**3**) was recently described [3] as a by-product (10% yield) of the coupling reaction between benzotriazole, xanthene and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in refluxing toluene.




**1** **2** **3**

Furthermore, our group synthesized 6-arylsubstituted phenanthridines **5** from benzotriazole derivatives **4** of diarylmethanes [4, 5]. Both of those procedures utilized very mild conditions and comprised the generation of a benzotriazole-stabilized carbanion, oxidation of this carbanion by copper iodide [4] or iodine [5] into a radical, and subsequent elimination of nitrogen followed by a ring closure to produce the phenanthridine **5**.




**4** **5**

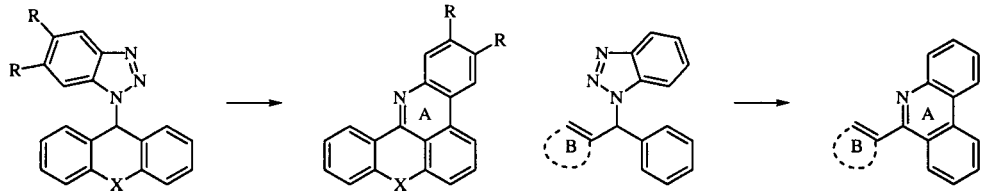
These results stimulated us to determine the accessibility of (a) pentacyclic phenanthridines **7** by the formation of ring **A** starting from benzotriazole derivatives **6** of acridine, xanthene and thioxanthene, and (b) a variety of phenanthridines **9** from benzotriazoles **8** where **B** is a heterocyclic substituent.

## Results and Discussion.

### Synthesis of Starting Benzotriazoles.

Two general procedures [6] were used for the preparation of benzotriazoles **17-21** and **26-28.** (i) The sodium

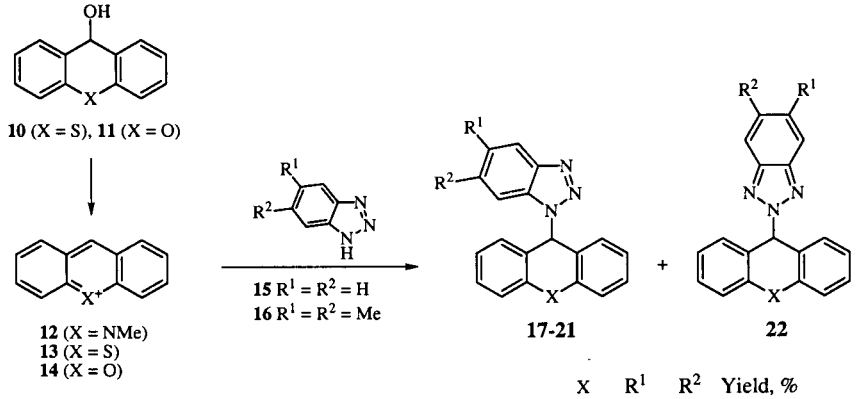
Scheme 1



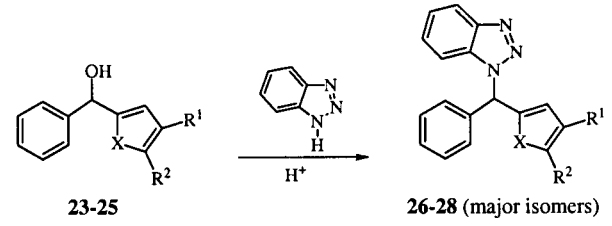
**6** **7** **8** **9**

salts of benzotriazoles **15** and **16** added regiospecifically to *N*-methylacridinium iodide (**12**) [13] in position 9 to give the corresponding benzotriazole addition products **17**, **20** (Scheme 2). (ii) Xanthylium (**14**) and thioxanthylium (**13**) cations were generated *in situ* under acidic catalysis from the corresponding hydroxy derivatives **10** and **11** in the presence of benzotriazoles **15** and **16** to form **18**, **19** and **21** (Scheme 2). The colorless, crystalline *N*-1 isomers **17-21** strongly predominated and were separated from traces of the *N*-2 isomers of general formula **22** by either column chromatography or by crystallization. Secondary alcohols **23-25**, benzotriazole (**15**) and an acid catalyst gave the benzotriazole adducts **26-28** needed for a second series of experiments. However, in this case rather more of the corresponding Bt-2 isomers were formed (approx. 25%), and therefore the target Bt-1 derivatives **26-28**, separated by column chromatography, were obtained in lower yields (Scheme 2). Compounds **17-21** and **26-28** are stable to neutral and basic conditions. However, the furan derivatives **26** and **27** turned red after storage for one month.

Scheme 2



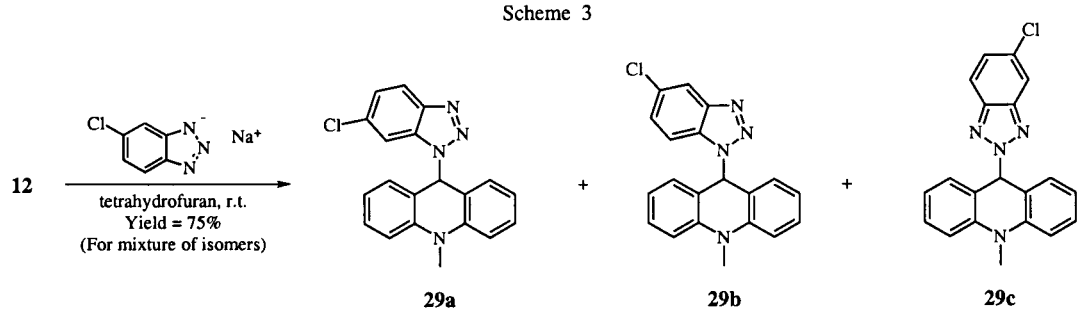

| | X | $R^1$ | $R^2$ | Yield, % |
|---|---|---|---|---|
| **17** | NMe | H | H | 75 |
| **18** | S | H | H | 52 |
| **19** | O | H | H | 79 |
| **20** | NMe | Me | Me | 75 |
| **21** | S | Me | Me | 83 |




| | X | $R^1$ | $R^2$ | Yield, % |
|---|---|---|---|---|
| **23, 26** | O | H | H | 68 |
| **24, 27** | O | H | Me | 55 |
| **25, 28** | S | $(CH)_4$ | | 60 |

The sodium salt of 5-chlorobenzotriazole reacted with *N*-methylacridinium iodide **12** non-selectively to form the crystalline mixture of the three possible adducts **29a-c** in the ratio 44:33:23 (Scheme 3). The isomer ratio was determined by integration of the *N*-Me resonance signals in the proton nmr spectrum. This mixture could not be separated by crystallization or chromatography and was used further as such for the synthesis of phenanthridines. Because of the complex character of the spectra, we failed to assign

Scheme 3



peaks to individual isomers. Nevertheless, a satisfactory CHN analysis was obtained for the mixture of **29a-c**.

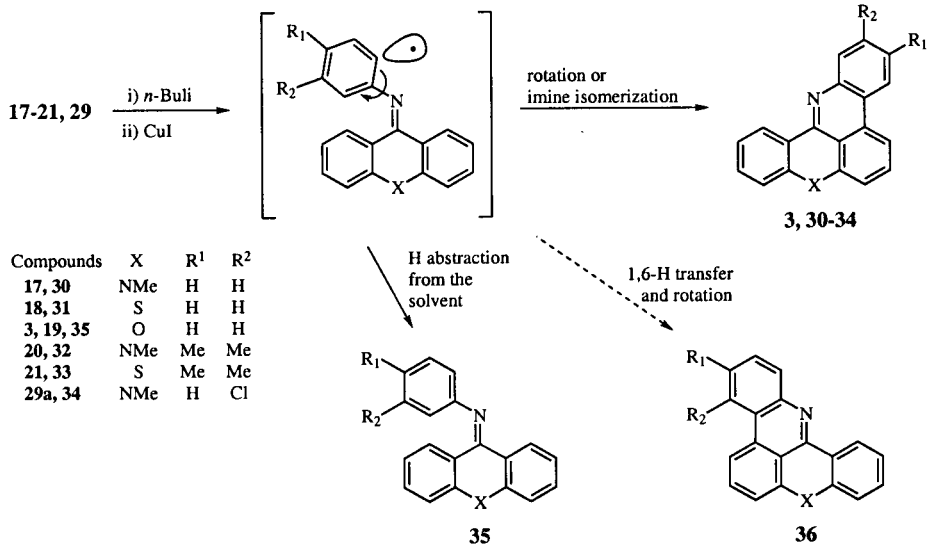
Fused Phenanthridines **7** (**3**, **30-34**).

Compounds **17-21** and mixture **29a-c** on treatment with *n*-BuLi at -78° in tetrahydrofuran gave deep blue colored anions. Oxidation of the anions was achieved by addition of copper iodide to the reaction mixture and heating to reflux for one hour. The isolated yield of the target pentacyclic phenanthridines **3**, **30**, **31** varied from 61% (X = S) to 18% (X = O) from the unsubstituted benzotriazoles (**17-19**) (Scheme 4). The formation of imine (**35**) was the major route for the xanthene derivatives, and probably a competitive side reaction for the other examples.

protons. Regioisomers **32** and **33** are presumed to form from an intermediate radical species following the rotation around a C-N bond or in-plane nitrogen isomerization (Scheme 4), whereas other regioisomers **36** might form as a result of several rotations and 1,6-H exchanges. Byproducts of type **35** or products of their hydrolysis were encountered in the mass spectra of most of the crude reaction mixtures.

5-Chloro-substituted benzotriazoles **29a-c** were used, as mentioned above, without separating the individual isomers. Phenanthridine **34**, derived from **29a**, was isolated from the reaction mixture by column chromatography as the major product (Scheme 4).

Scheme 4




| Compounds | X | $R^1$ | $R^2$ |
|---|---|---|---|
| **17, 30** | NMe | H | H |
| **18, 31** | S | H | H |
| **3, 19, 35** | O | H | H |
| **20, 32** | NMe | Me | Me |
| **21, 33** | S | Me | Me |
| **29a, 34** | NMe | H | Cl |

Interestingly, 5,6-dimethylbenzotriazoles **20**, **21** each formed a single isomer, **32** (X = NMe) and **33** (X = S) respectively (Scheme 4), by $N_2$-elimination/ring closure. This was shown by gc-ms and nmr analyses of the crude products, just as was reported for the thermolysis of benzotriazolylacridines **1** [1]. Compounds **32** and **33** display two singlets corresponding to isolated protons, whereas the other possible isomers of general formula **36** should show two doublets resulting from coupled

The structure of compound **34** was elucidated by means of 2D nmr. The assignments of the $^1H$ and $^{13}C$ chemical shifts is given in Figure 1. The TOCSY [7] spectrum revealed three coupling networks: i) 7.28-7.54-7.23-8.88 for the phenyl ring in acridine which was not involved in the cyclization; ii) 7.06-7.72-7.86 for the phenyl ring in acridine which was involved in the cyclization, and iii) 7.98-7.38-8.23 for the ring bearing the chlorine atom. The proton at 7.98 displays only

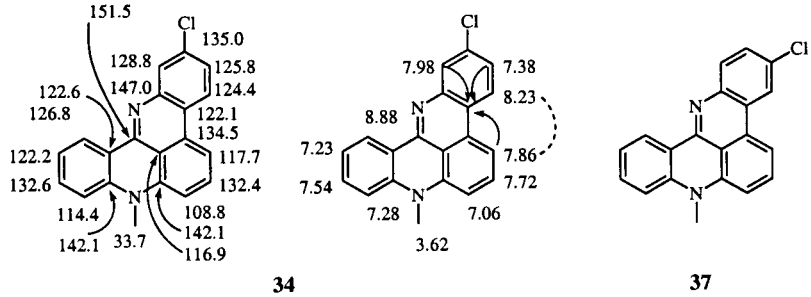
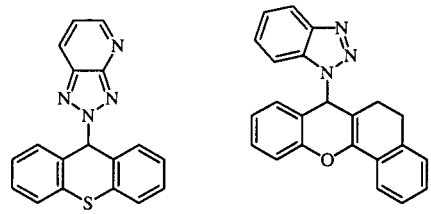



Figure 1.

a small coupling (*ca.* 2 Hz) with 7.38, indicative of 7.98 having no vicinal proton and of a meta relationship between 7.98 and 7.38. The protons at 7.28 and 7.06 displayed positive nOe's when the protons in the *N*-methyl group at 3.62 were irradiated in an nOe difference [8] experiment. These protons were thus identified as being on the acridine next to the *N*-methyl. The proton at 7.86 displayed in the NOESY [9] spectrum an intense cross-peak with the proton at 8.23. This nOe proved that the structure is **34** and not **37**, for which an nOe between 7.86 and 7.98 is to be expected. Further evidence for structure **34** is provided by the long-range couplings of the quaternary carbon at 122.1 ppm with the protons at 7.98, 7.38 and 7.86, observed in the HMBC [10] spectrum. In structure **37**, the quaternary carbon *meta* to 7.98 and 7.38 would be four bonds away from 7.86 and no long-range coupling to this proton is expected; besides, this quaternary carbon would be bound to nitrogen, which does not agree with its chemical shift of 122.1 ppm.

Non-fused Phenanthridines **9, 38, 39.**

Non-fused phenanthridines of type **9** containing a heterocyclic ring as a substituent in the 6-position were also prepared using the procedure described above. For **27** and **28**, cyclization took place selectively on the phenyl ring



**40** **41**

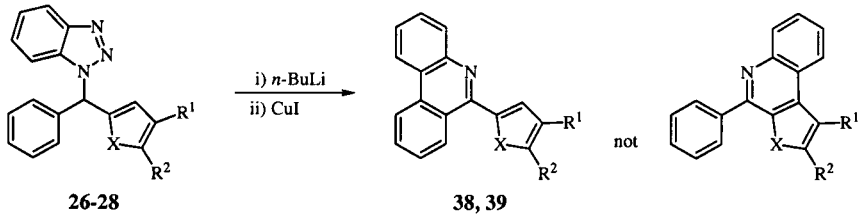
Figure 2.

A second limitation is the formation of imines of type **35** instead of phenathridines. The formation of imine also predominated for 7*H*-(1*H*-benzotriazol-1-yl)-5,6-dihydro(naphtho[1,2-*b*]-1-chromene) (**41**) [11] containing allylic protons (Figure 2). Presumably intramolecular 1,6-hydrogen abstraction followed by quenching of the radical by the solvent leads to the imine.

Conclusions.

We have described an alternative pathway to some fused and heterocyclic substituted phenanthridines. Although the variety of structures that could be used in the key reactions is limited, the present methodology should be useful in cases when reaction components are sensitive to high temperature or irradiation.

Scheme 5




**26-28** **38, 39**

**26**: $R^1 = R^2 = H$, X = O; **27, 38**: $R^1 = H$, $R^2 = Me$, X = O; **28, 39**: $R^1 + R^2 = (CH)_4$, X = S

(Scheme 5) to give the expected phenanthridines **38** and **39** in low yields. Surprisingly, 1-(1*H*-benzotriazol-1-yl)-1-(furan-2-yl)-1-phenylmethane (**26**) (R = R' = H) failed to benzotriazole ring open and we recovered the starting material **26**.

Limitations of the Methodology.

The method now proposed for phenanthridine synthesis has some limitations. Difficulties arise in the preparation of the starting benzotriazole adducts, especially when unsymmetrically substituted benzotriazole are used, as was demonstrated for **29**. The reaction of pyrido[*b,d*]triazole with thioxanthen-9-ol formed the *N*-2 isomer **40** unsuitable for $N_2$-elimination/ring close. The structure **40** assigned for this product was supported by nOe experiment which shows no interaction between the protons in pyrido[*b,d*]triazole and thioxanthene moieties (Figure 2).

## EXPERIMENTAL

Melting points were determined on a Koefler hot stage apparatus and are uncorrected. $^1H$ and $^{13}C$ nmr spectra were recorded at 300 MHz and 75 MHz respectively in deuteriochloroform or dimethyl-$d_6$ sulfoxide, and referenced to tetramethylsilane for the $^1H$ spectra and deuteriochloroform or dimethyl-$d_6$ sulfoxide, for the $^{13}C$ spectra. The spectra of compound **34** were recorded on a Varian Unity 500, ($^1H$ at 500 MHz, $^{13}C$ at 125 MHz) equipped with an indirect detection probe. Microanalyses were performed on a Carlo Erba 1106 elemental analyzer. Tetrahydrofuran was distilled under nitrogen from sodium-benzophenone immediately before use. All reactions with moisture-sensitive compounds were carried out in a dry nitrogen atmosphere. Compounds **10** [12], **12** [13], **17-19, 28** [6], and **41** [11] were prepared according to previously reported procedures.

General Procedure for the Preparation of **21, 23, 24.**

A mixture of benzotriazole 7.26 g (61 mmoles) and the appropriate carbinol (55.6 mmoles) was stirred for 8 hours in benzene (200 ml) at reflux in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate. The water formed during the reaction was azeotropically removed using a Dean-Stark apparatus. The reaction mixture was washed with sodium carbonate (10%), dried (magnesium sulfate), and concentrated to give a mixture of the benzotriazol-1-yl and -2-yl isomers. The benzotriazol-l-yl isomer was separated by flash column chromatography or crystallization.

9*H*-9-(5,6-Dimethyl-1,2,3-benzotriazol-1-yl)thioxanthene (**21**).

The product was isolated by recrystallization from ethanol/ethyl acetate (yield 83%), mp 178-180°; $^1$H nmr δ 2.23 (s, 3H), 2.34 (s, 3H), 6.87 (s, 1H), 7.04 (d, 2H, J = 7.8 Hz), 7.14 (t, 2H, J = 7.4 Hz), 7.29 (t, 2H, J = 8.3 Hz), 7.35 (s, 1H), 7.48 (d, 2H, J = 7.7 Hz), 7.80 (s, 1H); $^{13}$C nmr: δ 20.3, 20.9, 62.0, 110.4, 119.2, 126.4, 126.8, 128.5, 128.8, 129.9, 130.9, 131.8, 133.8, 137.8, 145.9.

*Anal.* Calcd. for $C_{21}H_{17}N_3S$: C, 73.43; H, 5.00; N, 12.44. Found: C, 73.34; H, 5.00; N, 12.22.

1-(2-Furyl)-1-phenyl-1-(1*H*-1,2,3-benzotriazol-1-yl)methane (**23**).

The compound was isolated by column chromatography on silica gel using ethyl acetate/hexanes (ethyl acetate was 10%, 15%, and 20% in 200 ml portions) as eluent to yield white crystals (yield 68%), mp 77-78°; $^1$H nmr: δ 6.31 (d, 1H, J = 2.8 Hz), 6.41 (s, 1H), 7.14-7.27 (m, 3H, 7.28-7.47 (m, 6H), 7.46 (s, 1H), 8.07 (dd, 1H, J = 3.6 Hz, J = 2.0 Hz); $^{13}$C nmr: δ 61.2, 110.5, 111.2, 119.9, 123.8, 127.3, 127.4, 128.6, 128.7, 132.5, 136.0, 143.4, 146.3, 150.1.

*Anal.* Calcd. for $C_{17}H_{13}N_3O$: C, 74.17; H, 4.76; N, 15.26. Found: C, 74.34; H, 4.73; N, 15.37.

1-(5-Methyl-2-furyl)-1-phenyl-1-(1*H*-1,2,3-benzotriazol-1-yl)methane (**24**).

The compound was isolated by column chromatography on silica gel using ethyl acetate/hexanes (ethyl acetate was 10%, 15%, and 20% in 200 ml portions) as an eluent to give white crystals (yield 89%), mp 106-107°; $^1$H nmr: δ 2.25 (s, 3H), 5.99 (d, 1H, J =1.8 Hz), 6.16 (d, 1H, J = 2.7 Hz), 7.16-7.27 (m, 3H), 7.29-7.40 (m, 6H), 8.08 (d, 1H, J = 8.4 Hz); $^{13}$C nmr: δ 13.6, 61.4, 106.6, 110.8, 112.2, 120.0, 123.8, 127.3, 128.6, 128.8, 132.7, 136.3, 146.4, 148.1, 153.5.

*Anal.* Calcd. for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.73; H, 5.27; N, 14.65.

General Procedure for the Preparation of **20**, **29a-c**.

A mixture of the corresponding benzotriazole **15** or **16** (10 mmoles), sodium hydride (0.40 g of 60% solution in mineral oil, 10 mmoles) and 10-methylacridinium iodide (**12**) (10 mmoles) was stirred for 1 hour in dry tetrahydrofuran (50 ml) at rt. The reaction mixture was washed with sodium carbonate (10%), dried (magnesium sulfate), and concentrated to give a mixture of the benzotriazol-1-yl and -2-yl isomers. The benzotriazol-1-yl isomer was separated by crystallization.

9,10-Dihydro-10-methyl-9-(5,6-dimethyl-1,2,3-benzotriazol-1-yl)acridine (**20**).

The benzotriazol-1-yl isomer was separated by crystallization from ethyl acetate to give white crystals (yield 75%), mp 164-166°; $^1$H nmr: δ 2.16 (s, 3H), 2.26 (s, 3H), 3.65 (s, 3H), 6.67 (s, 1H), 6.90 (t, 2H, J = 7.1 Hz), 7.11 (d, 2H, J = 8.2 Hz), 7.21 (d, 2H, J = 7.4 Hz), 7.34 (t, 2H, J = 7.3 Hz), 7.55 (s, 1H), 7.69 (s, 1H); $^{13}$C nmr: δ 20.2, 21.1, 33.3, 59.6, 110.1, 113.0, 118.6, 118.9, 121.0, 129.6, 130.2, 133.3, 137.0, 141.6, 146.1.

*Anal.* Calcd. for $C_{22}H_{20}N_4$: N, 16.46. Found: N, 16.21.

9,10-Dihydro-10-methyl-9-(6-(or 5)-chloro-1,2,3-benzotriazolyl)acridines **29a-c**.

The mixture of three benzotriazolyl isomers was obtained as white crystals (yield 75%); the nmr spectra were too complex for interpretation.

*Anal.* Calcd. for $C_{20}H_{15}ClN_4$: N, 16.15. Found: N, 15.63.

General Procedure for the Preparation of Phenanthridines **3**, **30-34**, **38**, **39.**

To a solution of the corresponding benzotriazole derivative (2 mmoles) in dry tetrahydrofuran (30 ml) was added *n*-BuLi (1.6 ml, 1.4 M, 2.2 mmoles) at -78° under nitrogen. The reaction mixture was stirred at this temperature for 30 minutes before copper (I) iodide (0.42 g, 2.2 mmoles) was added through a finger tube. The suspension was stirred for 2 hours at -78°, then slowly heated (during 2 hours) to room temperature and finally raised to reflux for 1 hour. After the reaction mixture was cooled, water (5 ml) was added. The mixture was filtered, and the filter cake was washed several times with ethyl acetate (40 ml total). The filtrate was washed with saturated ammonium hydroxide solution and water, and then dried over magnesium sulfate. After removing the solvent, the residue was purified by crystallization from ethyl acetate to give the phenanthridine compound.

Chromeno[4,3,2-*gh*]phenanthridine (**3**) and *N*-(9*H*-xanthen-9-ylidene)aniline (**35**).

The gc/ms indicated that a pentacyclic compound **3** (22%) and an *N*-phenylimine **35** (51%) were produced. Compound **3** was obtained by recrystallization of the residue from ethyl acetate (yield 18%), mp 189-191°; $^1$H nmr: δ 7.44-7.60 (m, 3H), 7.66-7.78 (m, 2H), 7.86 (t, 1H, J = 7.2 Hz), 8.01 (t, 1H, J = 8.2 Hz), 8.25 (d, 1H, J = 8.1 Hz), 8.45 (d, 1H, J = 7.9 Hz), 8.71 (d, 1H, J = 8.1 Hz), 8.80 (d, 1H, J = 7.5 Hz); $^{13}$C nmr: δ 112.3, 113.9, 115.2, 117.2, 120.7, 122.9, 123.1, 124.1, 124.6, 126.2, 129.4 (2C), 132.4, 132.5, 133.4, 144.8, 146.6, 152.1, 153.5.

*Anal.* Calcd. for $C_{19}H_{11}NO$: C, 84.73; H, 4.13; N, 5.20. Found: C, 84.39; H, 4.23; N, 5.28.

*N*-(9*H*-Xanthen-9-ylidene)aniline (**35**) [14].

The compound was detected by gc/ms in the crude reaction mixture along with cyclic product **3**; ms: m/z (%) 271 (80, M$^+$), 270 (100, M$^+$ - 1), 241 (10), 206 (10), 180 (5), 152 (20), 151 (20), 139 (18), 135 (20).

8-Methyl-8*H*-quino[4,3,2-*kl*]acridine (**30**).

This compound was purified by recrystallization from ethanol/ethyl acetate (1:1), yield (48%), mp 204-206°; $^1$H nmr: δ 3.90 (s, 3H), 7.42-7.52 (m, 2H), 7.57-7.69 (m, 2H), 7.82-7.98 (m, 3H), 8.01 (d, 2H, J = 4.4 Hz), 8.25 (d, 1H, J = 8.0 Hz), 8.73 (d, 1H, J = 8.3 Hz); $^{13}$C nmr: δ 35.1, 112.0, 112.2, 113.2, 116.8, 119.5, 121.2, 123.2, 123.5, 124.8, 126.9, 131.0, 132.5, 133.8, 135.8, 136.3, 140.7, 146.1, 158.3, 158.8.

*Anal.* Calcd. for $C_{20}H_{14}N_2$: C, 85.07; H, 5.01; N, 9.92. Found: C, 84.64; H, 5.24; N, 9.89.

Thiochromeno[4,3,2-*gh*]phenanthridine (**31**).

The product was purified by column chromatography on silica gel using ethyl acetate/hexanes (1:19) (yield 52%), mp 173-175°; $^1$H nmr: δ 7.28-7.35 (m, 1H), 7.35-7.44 (m, 2H), 7.45-7.58 (m, 2H), 7.59-7.73 (m, 2H), 8.08 (d, 1H, J = 8.0 Hz), 8.27 (d, 1H, J = 8.2 Hz), 8.38 (d, 1H, J = 8.4 Hz), 9.02-9.11 (m, 1H); $^{13}$C nmr: δ 118.2, 121.0, 122.1, 122.6, 123.9, 125.4, 126.3, 126.5, 128.4, 129.3, 129.7, 130.0, 130.4, 133.1, 133.9, 135.1, 144.5, 149.7.

*Anal.* Calcd. for $C_{19}H_{11}NS$: C, 79.96; H, 3.89; N, 4.91. Found: C, 79.75; H, 3.65; N, 4.91.

2,3,8-Trimethyl-8*H*-quino[4,3,2-*kl*]acridine (**32**).

The product was purified twice by column chromatography on silica gel using ethyl acetate/hexanes (1:1) and then by recrystallization from hexanes/ethyl acetate/chloroform (yield 13%), mp 256-257°; $^1$H nmr: δ 2.46 (s, 3H), 2.47 (s, 3H), 3.57 (s, 3H), 6.95 (d, 1H, J = 8.2 Hz), 7.19 (dd, 1H, J = 8.5 Hz, J = 7.6 Hz), 7.24 (d, 1H, J = 8.6 Hz), 7.48 (t, 1H, J = 8.6 Hz), 7.65 (t, 1H, J = 8.5 Hz), 7.81 (s, 1H), 7.86 (d, 1H, J = 8.2 Hz), 8.08 (s, 1H), 8.89 (d, 1H, J = 7.6 Hz); $^{13}$C nmr: δ 20.1, 20.2, 33.7, 107.3, 111.0, 113.7, 116.4, 121.1, 121.3, 122.5, 122.6, 122.7, 125.9, 129.1, 131.3, 134.2, 134.3, 138.6, 141.4, 141.7, 144.2, 149.0.

*Anal.* Calcd. for $C_{22}H_{18}N_2$: N, 9.02. Found: N, 8.67.

2,3-Dimethylthiochromeno[4,3,2-*gh*]phenanthridine (**33**).

The product was purified by column chromatography on silica gel using ethyl acetate/hexanes (1:19) (yield 52%), mp 171-173°; $^1$H nmr: δ 2.42 (s, 3H), 2.45 (s, 3H), 7.22-7.31 (m, 1H), 7.31-7.42 (m, 3H), 7.54 (t, 1H, J = 7.8 Hz), 7.79 (s, 1H), 8.03 (s, 1H), 8.15 (d, 1H, J = 8.2 Hz), 8.96-9.04 (m, 1H); $^{13}$C nmr: δ 20.0, 20.3, 117.9, 121.9, 122.2, 125.3, 126.3, 128.1, 129.3, 129.7, 129.9, 130.6, 132.8, 133.6, 134.7, 135.7, 138.8, 143.1, 148.7.

*Anal.* Calcd. for $C_{21}H_{15}NS$: C, 80.48; H, 4.82; N, 4.47. Found: C, 80.62; H, 5.05; N, 4.50.

2-Chloro-8-methyl-8*H*-quino[4,3,2-*kl*]acridine (**34**).

The compound was isolated by column chromatography on silica gel using ethyl acetate/hexanes (5:95) as eluent (yield 44%), mp 209-211°; $^1$H nmr: δ 3.63 (s, 3H), 7.05 (d, 1H, J = 8.2 Hz), 7.17-7.33 (m, 2H), 7.38 (1H, dd, J = 7.2 Hz, J = 1.90 Hz), 7.54 (t, 1H, J = 6.9 H z), 7.71 (t, 1H, J = 8.2 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.98 (d, 1H, J = 1.9 Hz), 8.23 (d, 1H, J = 8.7 Hz), 8.87 (d, 1H, J = 7.9 Hz); $^{13}$C nmr: δ 33.7, 108.8, 111.7, 114.4, 116.4, 122.1, 122.2, 124.4, 125.8, 126.6, 126.8, 128.8, 132.4, 132.6, 134.5, 135.0, 142.1, 142.1, 147.0, 151.5.

*Anal.* Calcd. for $C_{20}H_{13}ClN_2$: C, 75.83; H, 4.14; N, 8.84. Found: C, 75.17; H, 4.21; N, 8.76.

6-(5-Methyl-2-furyl)phenanthridine (**38**).

The compound was isolated as a red oil by column chromatography on silica gel using ethyl acetate/hexanes (1:19) as eluent (yield 14%) (compound unstable at room temperature); $^1$H nmr: δ 2.52 (s, 3H), 6.25 (s, 1H), 7.14 (d, 1H, J = 3.0 Hz), 7.54-7.75 (m, 3H), 7.80 (t, 1H, J = 7.2 Hz), 8.21 (d, 1H, J = 8.0 Hz), 8.51 (d, 1H, J = 8.2 Hz), 8.61 (d, 1H, J = 8.2 Hz), 8.79 (d, 1H, J = 8.2 Hz); $^{13}$C nmr: δ 14.1, 108.1, 114.8, 121.8, 122.1, 123.4, 124.1, 126.7, 127.4, 127.8, 128.7, 130.2, 130.4, 133.6, 143.8, 149.6, 151.6, 154.3.

hrms: Calcd. for $C_{18}H_{14}NO$ (M+1): 260.1075. Found: 260.1050.

6-(1-Benzothiophen-2-yl)phenanthridine (**39**).

The compound was isolated by column chromatography on silica gel using ethyl acetate/hexanes (1:19) as eluent (yield 55%), mp 158-159°; $^1$H nmr: 7.42 (d, 2H, J = 3.0 Hz), 7.62-7.79 (m, 3H), 7.81-7.95 (m, 4H), 8.24 (d, 1H, J = 7.9 Hz), 8.55 (d, 1H, J = 7.5 Hz), 8.65 (dd, 2H, J = 9.0 Hz, J = 10.0 Hz); δ $^{13}$C nmr: δ 121.9, 122.2, 122.4, 123.6, 124.3, 124.5, 124.7, 125.1, 126.0, 127.3, 127.5, 127.9, 128.9, 130.3, 130.7, 133.6, 134.0, 140.7, 142.6, 143.6, 154.0.

*Anal.* Calcd. for $C_{21}H_{13}NS$: C, 81.00; H, 4.21; N, 4.50. Found: C, 79.96; H, 4.44; N, 4.48.

9*H*-9-(Pyrido[4,5-*b*]benzotriazol-2-yl)thioxanthene (**40**).

The product was synthesized by the general procedure for reaction of 9-hydroxythioxanthene with benzotriazoles and isolated as yellow crystals by crystallization from ethyl acetate/hexanes (yield 45%), mp 150°; $^1$H nmr δ 7.40-7.12 (m, 5H), 7.43 (d, 2H, J = 7.9 Hz), 7.52 (d, 2H, J = 8.2 Hz), 8.36 (d, 1H, J = 8.3 Hz), 8.72 (d, 1H, J = 4.5 Hz); $^{13}$C nmr δ 60.20, 119.87, 126.50, 126.80, 128.56, 129.48, 130.49, 133.89, 136.71, 150.27.

*Anal.* Calcd. for $C_{18}H_{12}N_4S$: C, 68.33; H, 3.82; N, 17.71. Found: C, 68.16; H, 3.81; N, 17.40.

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