Synthesis of Pyrrolo-, Thienopyrrolo-, Benzothienopyrroloquinolines as well as Triazoloindole Derivatives

S. I. El-Desoky[a,*], E. M. Kandeel[a], A. H. Abd el-Rahman[a], R. R. Shmidt[b]

[a] Chemistry Department, Faculty of Science, Mansoura University, Mansoura, A. R. Egypt
[b] Fakultät für Chemie, Universität Konstanz, Universitätsstraße 10, D-78434 Konstanz, Germany

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Pyrroloquinoline, Triazoloindole Derivatives, NMR Data, IR Data, MS Data

Substituted pyrroloquinoline, thienopyrroloquinoline, benzothieno-pyrroloquinoline and triazoloindole derivatives have been synthesized starting from 6-amino-2,3-diphenylindole. The structures of the newly synthesized compounds were assigned with the help of IR, NMR and MS data.

Indole and its derivatives represent one of the most important classes of compounds which have a wide spectrum of biological activity [1]. Quinoline derivatives related to antitumor alkaloids were synthesized they showed antileukemic and antimalarial activities [2,3]. Significant biological activities are also associated with substituted pyrazoles and triazoles [4,5]. In view of these facts and in continuation of our work on indoles [6–8], it was worthwhile to synthesize new monocyclic or condensed heterocycles containing these structural moieties.

Reaction of 6-amino-2,3-diphenylindole (**1**) [9] with 3-chloro-6-methoxybenzo[b]thiophene-2-carbonyl chloride in benzene afforded 3-chloro-6-methoxy-N-(2',3'-diphenyl-6'-indolyl) benzo[b]thiophene-2-carboxamide (**2**). Oxidative dehydrochlorination of **2** *via* irradiation with a high pressure mercury lamp furnished the lactam **3** which on reaction with phosphorus pentasulphide in pyridine gave the benzothieno[3,2-c]pyrrolo[2,3-f]quinolin-7(6H)thione (**4**). Refluxing **3** in phosphorus oxychloride yielded the 7-chlorobenzothienopyrroloquinoline derivative **5** which was then catalytically dechlorinated to give 10-methoxy-2,3-diphenyl[1]benzothieno[2,3-c]pyrrolo[2,3-f]quinoline (**6**). The structures of compounds **5** and **6** were elucidated from ^{1}H NMR spectrum of compound **5** which showed two douplets at δ 7.9 and δ 9.04 for H-4 and H-5 ($J_{4,5}$ = 9 Hz).

Michael addition of **1** with dimethyl acetylenedicarboxylate proceeded smoothly to give the enamine ester **7**. The signal of the alkenic proton of **7** (at δ = 5.34) lies in the region characteristic of the vinyl resonance of fumarates [10]. Thermal cyclization of **7** to give the pyrrolo[2,3-f]quinolone derivative **8** was best accomplished in triethyleneglycol dimethyl ether (triglyme) rather than with polyphosphoric acid. The quinolone derivative **8** was converted to the required 4-chloro-2-methoxycarbonyl-6,7-diphenylpyrrolo[2,3-f]quinoline (**9**) by refluxing in a phosphorus oxychloride/pyridine mixture. The structures of compounds **8** and **9** were elucidated from ^{1}H NMR spectrum of compound **9** which showed two douplets at δ 8.02 and 8.10 for H-8 and H-9 (J = 9 Hz).

The synthesis of some 4-alicyclicaminopyrroloquinoline derivatives from the reaction of the chloroquinoline derivative **9** with some secondary amines was difficult [11], and instead the corresponding amides **10** were obtained. In the presence of excess amine, the replacement of chlorine by the amine was observed and compound **11** was obtained as a minor product.

The dictamine group of alkaloids which occur widely in Rutaceae have been characterized as derivatives of the furo[2,3]quinoline system [12]. Therefore, we tried to build the thienoquinoline derivative **15** as analogous of these alkaloids. Condensation of γ-chlorobutyroyl chloride with **1** in dry benzene gave 6-amino-N-(γ-chlorobutyroyl)-2,3-diphenylindole (**12**) which was reacted with phosphorus oxychloride in dimethyl formamide to yield pyrroloquinoline derivatives **13** and **14** in a

* Reprint requests to Dr. S. I. El-Desoky.

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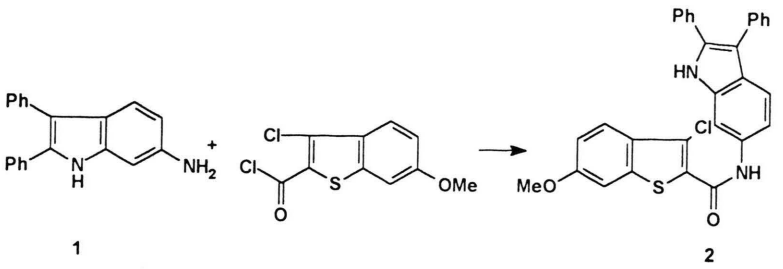

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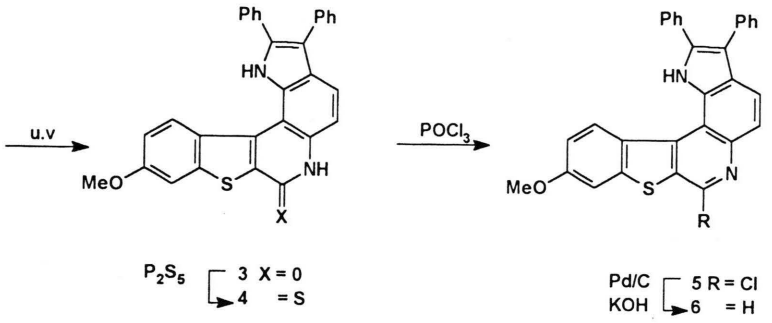
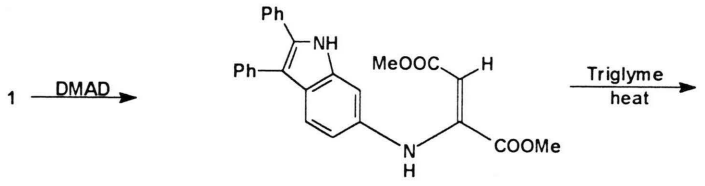


P_2S_5 3 X = 0, 4 = S

Pd/C, KOH 5 R = Cl, 6 = H



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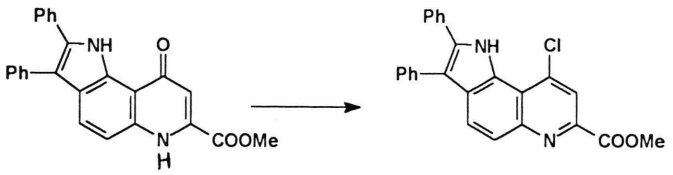

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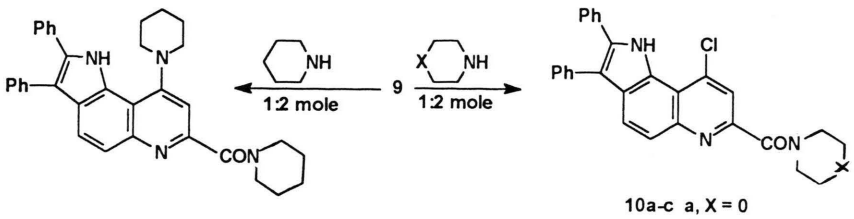

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10a-c a, X = 0
b, = S
c, = CH_2

1:3 ratio. The structures of compounds **13** and **14** were elucidated from ^{1}H NMR spectra which showed for compound **14** two douplets at δ 7.72 and δ 7.98 ppm for the aromatic protons H-8 and H-9, while compound **13** showed two singlets at δ 8.10 and δ 8.17 for H-9 and H-5. Boiling **14** with thiourea in ethanol afforded the desired thienopyrroloquinoline derivative **15**.

Formation of **14** encouraged us to construct a pyrrolo[3,2-g]quinoline system. Therefore, **1** was allowed to react with pentane-2,4-dione in concentrated sulphuric acid, to give 2,4-dimethyl-6,7-diphenylpyrrolo[3,2-g]quinoline (**16**) as the hydrochloride. The ^{1}H NMR spectrum showed two singlet peaks characteristic for H-5 and H-9 at δ 8.12 and 8.09 ppm.

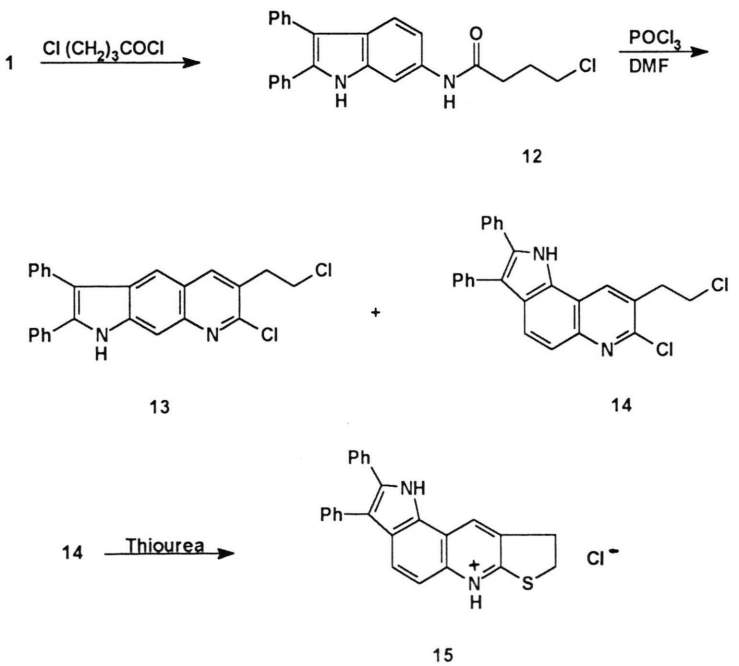
In view of the wide spectrum of activities associated with substituted triazoles, it was planned to synthesize indole derivatives carrying this heterocycle at position **6**. 6-Azido-2,3-diphenylindole (**17**) was generated from compound **1** and then reacted with dienophiles such as dimethylacetylenedicarboxylate and ethyl cyanoacetate to furnish the 1,4,5-trisubstituted triazoles **18** and **19**, respectively. Unsuccessful attempts to eliminate nitrogen from **18** for the synthesis of the pyrrolo[2,3-e]indole derivative **20** were carried out.

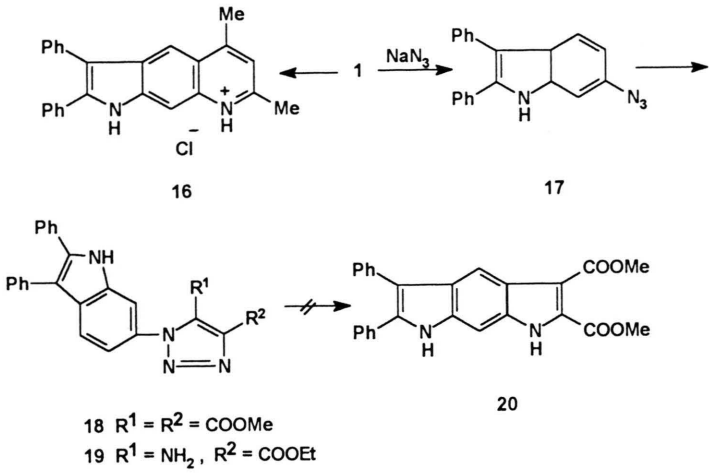
Experimental

Solvents were purified in the usual way; petroleum ether had the boiling range 35–60 °C. Melting points are uncorrected. ^{1}H NMR spectra: Brucker W M 250 Cryospec, Jeol JNM-FX 90; solvents $CDCl_3$, unless noted otherwise, internal standard tetramethylsilane (TMS). Column chromatography: Merck silica gel 60, 0.063–0.200 mm. Flash chromatography: Merck silica gel 60, 0.040–0.063 mm. Medium pressure liquid chromatography (MPLC): Merck silica gel Li Chroprep Si 60, 15–25 μm. Thin layer chromatography (TLC): Merck plates, silica gel 60-F_{254} , layer thickness 0.2 mm. Detection by treatment with a solution of 15% H_2SO_4, followed by heating at 120 C.

3-Chloro-6-methoxy-N(2',3'-diphenyl-6'-indolyl)-benzo[b]thiophene-2-carboxamide (**2**)

A solution of **1** (7.14 g, 25.1 mmol) and 3-chloro-6-methoxybenzo[b]thiophene-2-carbonyl chloride (2.8 g, 10.72 mmol) in 100 ml dry benzene was heated at 80 C for 1 h. The yellow precipitate formed was filtered off, washed with ethanol and crystallized from ethanol-DMF mixture (8:2) to give colourless crystals, yield 76%, m.p. 266–268 C. ^{1}H NMR (250 MHz, [D_6] DMSO): δ 11.60 (s, br., 1H, CONH), 10.40 (s, br, 1 H, -NH), 8.12 (s, 1H, 7-H), 7.85 (d, 1H, 5'-H), 7.72 (s, 1 H, 7'-H),





7.50–7.25 (m, 13 H, 4, 5, 4′-H, 2Ph), 3.90 (s, 3 H, OCH_3).

$C_{30}H_{21}N_2O_2SCl$ (509)
Calcd C 70.79 H 4.16 N 5.50%,
Found C 70.52 H 4.02 N 5.30%.

10-Methoxy-2,3-diphenyl[1]benzothieno[2,3-c]pyrrolo[2,3-f]-quinoline-7(6H)-one (**3**)

A stirred solution of **2** (3.60 g, 7.07 mmol) and triethyl amine (6 ml) in 500 ml acetone was irradiated with a high pressure mercury lamp for 72 h under nitrogen stream. The solvent was evaporated under reduced pressure and the residue was collected, washed with water, dried and crystallized from ethanol-DMF mixture (8:2) to give yellow crystals, yield 55%, m.p. > 300 C which were used in the next step without further purification.

10-Methoxy-2,3-diphenyl[1]benzothieno[2,3-c]pyrrolo[2,3-f]quinoline-7(6H)-thione (**4**)

A mixture of **3** (0.2 g, 4.2 mmol), phosphorus pentasulphide (0.48 g, 2.12 mmol) in 10 ml pyridine was refluxed for 24 h. The mixture was poured onto 50 ml of boiling water. The solid formed was filtered off and purified by chromatography [petroleum ether/ethyl acetate (7:3)]: $R_f = 0.58$, to give **4** (0.13 g, 63%) as yellow crystals, m.p. 225–227 C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.83 (s, 1 H, NH), 9.13 (d, 1H, 5-H, $J_{5,4} = 9.1$ Hz), 7.98, 7.85 (2d, 2 H, 11, 12-H, $J_{11,12} = 8.9$ Hz), 7.55–7.29 (m, 12 H, 4,9-H, 2Ph), 4.02 (s, 3H, OCH_3). MS: M^+ at *m/e* = 489.9.

$C_{30}H_{20}N_2OS_2$ (488.6)
Calcd C 73.74 H 4.13 N 5.73%,
Found C 73.39 H 3.98 N 5.63%.

7-Chloro-10-methoxy-2,3-diphenyl[1]benzothieno-[2,3-c]pyrrolo [2,3-f]quinoline (**5**)

A mixture of **3** (0.95 g, 2 mmol) and phosphorus oxychloride (10 ml) was refluxed for 3 h. The mixture was evaporated under reduced pressure and the residue was collected by filtration, crystallized from ethanol-DMF mixture (8:2) to furnish yellow crystals, yield 81%, m.p. 220–223 C, TLC (petroleum ether/ethyl acetate (7:3)]: $R_f = 0.58$, ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.38 (s, 1 H, NH), 9.04, 7.90 (2d, 5,4-H, J = 9.0 Hz), 8.0 (d, 1H, 11-H, $J_{12,11}$ = 8.2 Hz), 7.55–7.28 (m, 12 H, 9,12-H, 2Ph), 4.02 (s, 3H, OCH_3) MS: M^+ at *m/e* = 491.4.

$C_{30}H_{19}N_2OSCl.H_2O$ (509)
Calcd C 70.79 H 4.16 N 5.50%,
Found C 70.91 H 4.12 N 5.32%.

10-Methoxy-2,3-diphenyl[1]benzothieno[2,3-c]pyrrolo[2,3-f]quinoline (**6**)

Compound **5** (0.49 g, 1 mmol) was treated with a mixture of benzene/methanol (100 ml, 1:1) containing 0.07 g potassium hydroxide in the presence of 10% Pd-C (0.1 g) for 24 h at atmospheric pressure and room temperature. The reaction mixture was filtered off and evaporated under reduced pressure. The residue was collected by filtration, washed with water, dried and purified by flash chromatography [petroleum ether/ethyl acetate (3:2)] to give yellow crystals, yield 61%, m.p. 210–213 C. TLC [petroleum ether/ethyl acetate (3:2)]:

R_f = 0.38. ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.40 (s, br, 1 H, NH), 9.10 (m, 2 H, 11, 12-H), 8.0 (s, 1 H, 9-H), 7.60–7.20 (m, 13 H, 4,5,7-H, 2Ph), 4.0 (s, 3 H, OCH_3).

α-Amino-N-(2',3'-diphenylindole-6'-yl)-dimethylfumarate (**7**)

A solution of **1** (5.7 g, 0.02 mole) and dimethylacetylenedicarboxylate (3.55 g, 0.025 mol) in 50 ml methanol was refluxed for 1 h. The precipitate was formed after cooling, filtered off and crystallized from methanol to give golden needles, yield 90%, m.p. 150–152 C. TLC [petroleum ether/ethyl acetate (17:3)]: R_f = 0.62. ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.80 (s, 1 H, NH-enamine), 8.28 (s, 1 H, NH), 7.54 (d, 1 H, 4-H, $J_{4,5}$ = 8.5 Hz), 7.42–7.24 (m, 10 H, 2Ph), 6.98 (d, 1 H, 7-H, $J_{7,5}$ = 1.5 Hz), 6.75 (d, 1 H, 5-H, $J_{5,4}$ = 8.5 Hz), 5.34 (s, 1 H, β-H), 3.74, 3.67 (2s, 6H, 2COOMe).

$C_{26}H_{22}N_2O_4$ (426.5)

Calcd	C 73.21	H 5.20	N 6.57%,
Found	C 73.12	H 5.25	N 6.60%.

2-Methoxycarbonyl-6,7-diphenylpyrrolo[2,3-f]-4[1H]quinolone (**8**)

A solution of dimethylfumarate derivative **7** (1 g, 2.35 mmol) in triethyleneglycol dimethyl ether (triglyme) (10 ml) was refluxed for 1 h. The solid, formed by cooling, was filtered off, washed with cold ether and crystallized from chloroform to give yellow crystals, yield 81%, m.p. 240–243 C. IR (cm^{-1}): 3440, 3360 (2NH), 1740 (COOMe), 1580–1620 (CO, C=C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 11.29 (s, 1 H, NH pyridone), 9.49 (s, 1 H, NH pyrrole), 7.99, 7.20 (2d, 2 H, 8,9-H, $J_{8,9}$ = 9 Hz), 7.54–7.26 (m, 11 H, 3-H, 2Ph), 4.05 (s, 3 H, COOMe), MS: M^+ at *m/e* = 394.

4-Chloro-2-methoxycarbonyl-6,7-diphenylpyrrolo[2,3-f] quinoline (**9**)

A mixture of **8** (1 g, 2.54 mmol), phosphoryl chloride (6 ml), pyridine (1 ml) and water (0.5 ml) was boiled for 1 h. The volatile liquids were removed under reduced pressure and the residue formed was washed with water and purified by chromatography [petroleum ether/ethyl acetate (4:1)] to give yellow crystals, m.p. 166–169 C. TLC [petroleum ether/ethyl acetate (1:1): R_f = 0.66 IR (cm^{-1}): 3460 (NH), 1724 (CO), 1605 (C=C), ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.26 (s, 1 H, NH), 8.34 (s, 1 H, 3-H), 8.10 (d, 1 H, 9-H, $J_{9,8}$ = 9.0 Hz), 8.02 (d, 1 H, 8-H, $J_{8,9}$ = 9.0 Hz), 7.52–7.33 (m, 10 H, 2Ph), 4.10 (s, 3 H, COOMe), MS: M^+ at *m/e* = 412, two fragment ions at *m/e* = 354 and 318.

$C_{25}H_{17}N_2O_2Cl$ (412.9)

Calcd	C 72.72	H 4.15	N 6.79%,
Found	C 72.76	H 4.20	N 6.75%.

Condensation of **9** *with different amines "General procedure"*

The corresponding amine (3 mmol) was added to a solution of **9** (0.4 g, 1 mmol) in 10 ml dry toluene and the reaction mixture was stirred at 100 °C. When TLC showed complete conversion of the starting material, the liquids were evaporated *in vacuo* and the residue was washed with water and purified with the suitable method as follows to give compounds **10a-c**:

4-Chloro-6,7-diphenyl-2-(N-morpholinocarbonyl)-pyrrolo[2,3-f]quinoline (**10a**)

Flash chromatography of the residue [petroleum ether/ethyl acetate (1:1)] gives pale yellow crystals, yield 77%, m.p. 230–232 C. TLC [petroleum ether/ethyl acetate (1:1)]: R_f = 0.34, ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.23 (s, 1 H, NH), 8.09, 7.82 (2d, 2 H, 8,9-H, $J_{8,9}$ = 9Hz), 8.00 (s, 1 H, 3-H), 7.57–7.33 (m, 10 H, 2Ph), 3.98–3.74 (m, 8 H, $4CH_2$).

$C_{28}H_{22}N_3O_2Cl$ (468)

Calcd	C 71.85	H 4.74	N 8.98%,
Found	C 71.46	H 4.75	N 8.77%.

4-Chloro-6,7-diphenyl-2-(N-thiomorpholinocarbonyl)pyrrolo[2, 3-f]quinoline (**10b**)

Medium pressure chromatography [toluene/acetone (12:1)] of the residue gave yellow crystals, yield 62%, m.p. 232–235 C. TLC [toluene/acetone (12:1)]: R_f = 0.44, ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.39 (s, 1 H, NH), 8.11, 7.87 (2d, 2 H, 8,9-H, $J_{8,9}$ = 9.0 Hz), 7.98 (s, 1 H, 3-H), 7.63–7.38 (m, 10 H, 2Ph), 4.28–4.09 (2 m, 4 H, CH_2-S-CH_2), 2.98–2.85 (m, 4 H, CH_2-N-CH_2).

$C_{28}H_{22}N_3OClS$ (484)

Calcd	C 69.48	H 4.58	N 8.68%,
Found	C 69.26	H 4.70	N 8.34%.

4-Chloro-6,7-diphenyl-2-(N-piperidinocarbonyl)-pyrrolo[2,3-f] quinoline (**10c**)

Medium pressure chromatography of the residue [toluene/acetone (14:1)] gave colourless crystals, m.p. 118–120 C, TLC (toluene/acetone 14:1) R_f = 0.30. ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.21 (s, 1 H, NH), 8.04, 7.83 (2d, 2 H, 8,9-H, $J_{8,9}$ = 8.9 Hz), 7.86 (s, 1 H, H-3), 7.52–7.34 (m, 10 H, 2Ph), 3.87–

3.67 (2m, 4 H, CH_2NCH_2), 1.74–1.60 (m, 6 H, $2CH_3$).

$C_{29}H_{24}N_3OCl$ (466)
Calcd C 74.75 H 5.19 N 9.02%,
Found C 74.39 H 5.05 N 8.81%.

6,7-Diphenyl-4(N-piperidino)-2-N-piperidinocarbonyl)pyrrolo (2,3-f)quinoline (**11**)

Compound **11** was separated as a by product in the synthesis of **10c**, TLC [toluene/acetone (14:1)]: R_f = 0.2, ^{1}H NMR [250 MHz, $CDCl_3$): δ 10.76 (s, 1 H, NH), 7.99, 7.78 (2d, 2 H, 8,9-H), 7.67–7.32 (m, 11 H, 3-H, 2Ph), 3.88–3.42 (m, 8 H, $2CH_2NCH_2$), 2.90, 2.10, 1.20 (3 m, 12 H, $6CH_2$), MS: M^+ at *m/e* 514.5 an elemental analysis could not be obtained.

6-Amino-N(γ-chlorobutyroyl)-2,3-diphenylindole (**12**)

To a solution of **1** (14.2 g, 0.05 mol) in 150 ml anhydrous benzene, γ-chlorobutyroyl chloride (10.58 g, 0.075 mol) in 100 ml benzene was added dropwisely at room temperature within 30 min. After heating for 3 h at 80 °C, the reaction mixture was filtered and the filtrate was stirred vigorously into 200 ml of sodium carbonate solution (20%). The organic layer was separated, washed with water and dried with sodium sulphate. Flash chromatography [petroleum ether/ethyl acetate (3:2)] gave colourless crystals, yield 76%, m.p. 168 C, TLC [petroleum ether/ethyl acetate (3:2)]: R_f = 0.42. ^{1}H NMR (80 MHz, $CDCl_3$): δ 8.80 (s, 1 H, CONH), 8.30 (s, 1 H, NH), 7.75 (s, 1 H, 7-H), 7.70–7.30 (m, 10 H, 2Ph), 7.00 (d, 1 H, 4-H), 6.90 (d, 1 H, 5-H, 5-H), 3.70 (t, 2 H, $COCH_2$), 2.70–2.10 (m, 4 H, $2CH_2$).

$C_{24}H_{21}N_2OCl$ (388.9)
Calcd C 74.12 H 5.44 N 7.20%,
Found C 74.02 H 5.46 N 7.15%.

2-Chloro-3-(2'-chloroethyl)-6,7-diphenylpyrrolo-[3,2-g]quinoline (**13**) *and 2-chloro-3-(2'-chloroethyl)-6,7-diphenylpyrrolo[2,3-f]-quinoline* (**14**)

To a solution of **12** (3.89 g, 10 mmol) in DMF (4 ml) was added 4.4 ml (7.65 g, 50 mmol) of $POCl_3$ within 1 h (the temperature should not increase above 20 °C). The reaction mixture was stirred at room temperature for 1 h, then for 4 h at 75 C. After cooling, the reaction mixture was poured into crushed ice to give a yellow residue. Flash chromatography [petroleum ether/ethyl acetate (7:3)] gave yellow crystals (**13**) and white crystals (**14**) in a ratio of about 1:3.

Compound **13**: TLC [petroleum ether/ethyl acetate (4:1): R_f = 0.51, m.p. 205–207 C, ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.95 (s, 1 H, NH), 8.17 (s, 1 H, 5-H), 8.10 (s, 1 H, 9-H), 7.60–7.40 (m, 11 H, 4-H, 2Ph), 3.85 (t, 2 H, β-CH_2, J = 7.6 Hz), 3.18 (t, 2 H, α-CH_2, J = 6.7 Hz).

$C_{25}H_{18}N_2Cl_2$ (417.3)
Calcd C 71.95 H 4.35 N 6.71%,
Found C 72.07 H 4.17 N 6.49%.

Compound **14**: TLC [petroleum ether/ethyl acetate (4:1)]: R_f = 0.56, m.p. 210–212 C, ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.09 (s, br, 1 H, NH), 8.35 (s, 1 H, 4-H), 7.95, 7.72 (2d, 2 H, 8,9-H, $J_{8,9}$ = 9.0 Hz) 7.51–7.26 (m, 10 H, 2Ph), 3.93 (t, 2 H, β-CH_2, J = 6.7 Hz), 3.41 (t, 2 H, α-CH_2, J = 6.7 Hz).

$C_{25}H_{18}N_2Cl_2$ (417.3)
Calcd C 71.95 H 4.35 N 6.71%,
Found C 71.71 H 4.40 N 6.35%.

2,3-Diphenyl-8,9-dihydrothieno[2,3-b]pyrrolo-[2,3-f]quinolinium hydrochloride (**15**)

Compound **14** (0.42 g, 1 mmol) was refluxed with thiourea (0.1 g, 1.3 mmol) in 20 ml ethanol for 12 h. The residue obtained after cooling was filtered off and washed with ethanol. Chromatography [petroleum ether/ethyl acetate (3:7)] gave yellow crystals, yield 94%, m.p. > 300 C, TLC [petroleum ether/ethyl acetate (3:7)]: R_f = 0.47, ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.11 (s, br, 1 H, NH), 8.01 (s, 1 H, 10-H), 7.76 (d, 1 H, 9-H, $J_{8,9}$ = 8.8 Hz), 7.75, 7.60 (2d, 2 H, 5,6-H, $J_{5,6}$ = 8.9 Hz), 7.45–7.29 (m, 10 H, 2 Ph), 3.37 (m, 4 H, 8–2H, 9–2H).

$C_{25}H_{19}N_2SCl$ (415)
Calcd C 72.35 H 4.61 N 6.75%,
Found C 72.16 H 4.38 N 6.66%.

2,4-Dimethyl-6,7-diphenylpyrrolo[3,2-g]-quinolinium hydrochloride (**16**)

A mixture of **1** (7.1 g, 25 mmol), pentandione (6 g, 100 mmol) and concentrated hydrochloric acid (35%, 4 drops) was heated on a steam bath for 30 min, then boiled at 140 C for 1 h. The cooled mixture was dissolved in concentrated sulphuric acid, left at room temperature for 24 h, poured onto crushed ice and made basic using ammonium hydroxide. The solid formed was extracted with dichloromethane and the extract was washed with acetic acid then basified with ammonium hydroxide. Crystallization from dichloromethane gave pale yellow crystals, yield 41%, m.p. > 300 C, ^{1}H NMR (250 MHz, DMSO [D_6]): δ = 12.05 (s, br, 1

H, NH), 8.12 (s, 1 H, 5-H), 8.09 (s, 1 H, 9-H), 7.55–7.34 (m, 10 H, 2Ph), 7.26 (s, 1 H, 3-H), 2.71–2.70 (2 singlets, 6 H, 2Me).

$C_{25}H_{21}N_2Cl$ (384.9)

Calcd	C 78.01	H 5.50	N 7.28%,
Found	C 78.22	H 5.68	N 7.31%.

6-Azido-2,3-diphenylindole (**17**)

Compound **17** was prepared following a known procedure [13], m.p. 110 C.

4,5-Dimethoxycarbonyl-1-(2',3'-diphenyl-6'-indolyl)triazole (**18**)

To a solution of **17** (3.1 g, 0.01 mmol) in toluene was added dimethyl acetylenedicarboxylate (1.71 g, 0.012 mmol) and the mixture was boiled for 40 h. The solvent was evaporated *in vacuo* and the residue was collected by filtration, crystallized from dichloromethane/petroleum ether (1:1) to give colourless needles, yield 82%, m.p. 180–183 C. TLC [petroleum ether/ethyl acetate (3:2)]: R_f = 0.41, ^{1}H NMR (80 MHz, $CDCl_3$): δ 9.15 (s, br, 1 H, NH), 7.90 (d, 1 H, 4'-H), 7.60–7.30 (m, 12 H, 5',7'-H, 2Ph), 3.95 (s, 6 H, 2 COOMe).

$C_{26}H_{20}N_4O_4$ (452.5)

Calcd	C 69.01	H 4.46	N 12.38%,
Found	C 68.87	H 4.63	N 12.36%.

5-Amino-4-ethoxycarbonyl-1-(2',3'-diphenyl-6'-indolyl)triazole (**19**)

To a solution of **17** (3.5 g, 11.28 mmol) in ethanol (20 ml) was added ethyl cyanoacetate (1.28 g, 11.32 mmol), sodium ethoxide (2 g sodium in 10 ml ethanol) and the mixture was heated at 100 C. After 1 h, a colourless precipitate was filtered off, washed with water, dried and crystallized from ethanol to give colourless needles, yield 78%, m.p. 251–253 C, ^{1}H NMR (250 MHz, DMSO-D_6): δ 11.68 (s, 1 H, NH), 7.85 (s, 1 H, 7'-H) 7.72 (d, 1 H, 4-H, $J_{4',5'}$ = 8.2), 7.63–7.20 (m, 10 H, 2Ph), 7.17 (d, 1 H, 5'-H, $J_{5',6'}$ = 8.2 Hz, $J_{5',7'}$ = 1.8 Hz), 6.15 (s, br, 2 H, NH_2), 4.40 (q, 2H, CH_2), 1.41 (t, 3 H, Me) (disappearance of the signals at 11.68 and 6.15 after adding deutrated methanol [D_4], MS: M^+ at *m/e* = 423.9.

$C_{25}H_{21}N_5O_2$ (423.5)

Calcd	C 70.90	H 5.00	N 16.54%,
Found	C 70.97	H 5.05	N 16.50%.

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