FUSED 1,2,4-TRIAZOLE HETEROCYCLES. III. SYNTHESES AND STRUCTURES OF NOVEL [1,2,4]TRIAZOLO[1,3]THIAZINOQUINOLINES.

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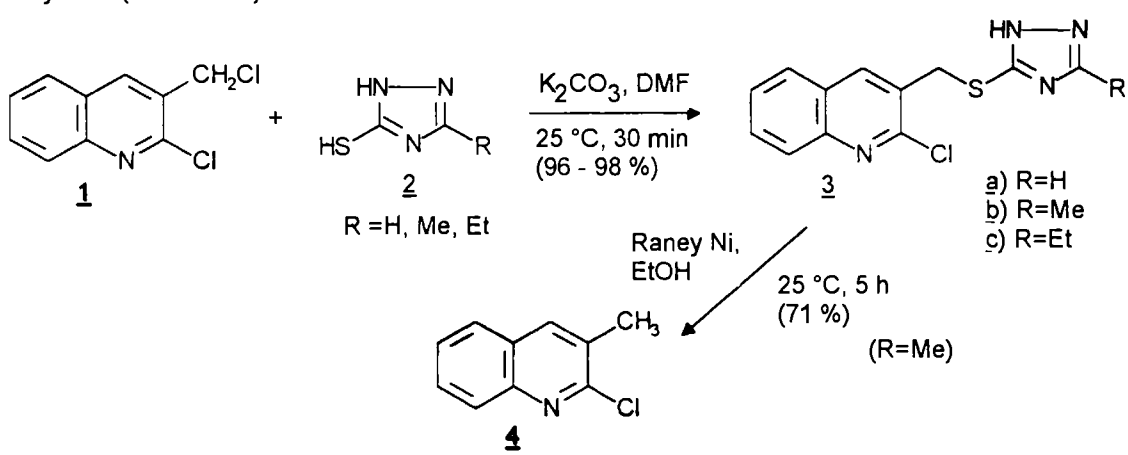
Abstract:
Synthetic methods are described for the preparation of 5*H*-[1,2,4]triazolo[5',1':2,3][1,3]thiazino[4,5-*b*]quinolines 5, 5*H*-[1,2,4]triazolo[3',4':2,3][1,3]thiazino[4,5-*b*]quinolines 6, 11*H*-[1,2,4]triazolo[5',1':2,3][1,3]thiazino[6,5-*b*]quinoline 13 and 11*H*-[1,2,4]triazolo[3',4':2,3][1,3]thiazino[6,5-*b*]quinoline 14 starting from 2-chloro-3-chloromethylquinoline 1 and 1,2,4-triazole-5-thiols 2. Different reactivity of the chlorine atoms of 1 under different reaction conditions, and a new rearrangement were observed during elaboration of these methods. The structures of the products 5, 6, 13, 14 and the intermediates leading to them were confirmed by desulfurisation reactions, unequivocal syntheses and nmr spectroscopy.

Introduction

In the preceding papers of this series we have described the synthesis of 11-substituted-11*H*-[1,2,4]triazolo[5',1':2,3][1,3]thiazino[6,5-*b*]quinolines (1, 2) and some of their [1,2,4]triazolo[3',4':2,3]-condensed isomers (2) by the reaction of 1,2,4-triazole-5-thiols with 2-chloroquinoline-3-carbaldehydes, their diethyl or ethylene acetal derivatives. In this paper we report the synthesis of the derivatives of two new regioisomers 5, 6 of the title heterocycles and new representatives 13, 14 of known (1, 2) heterocyclic ring systems starting from 2-chloro-3-chloromethylquinoline 1 and 1,2,4-triazole-5-thiols 2.

Results and discussion

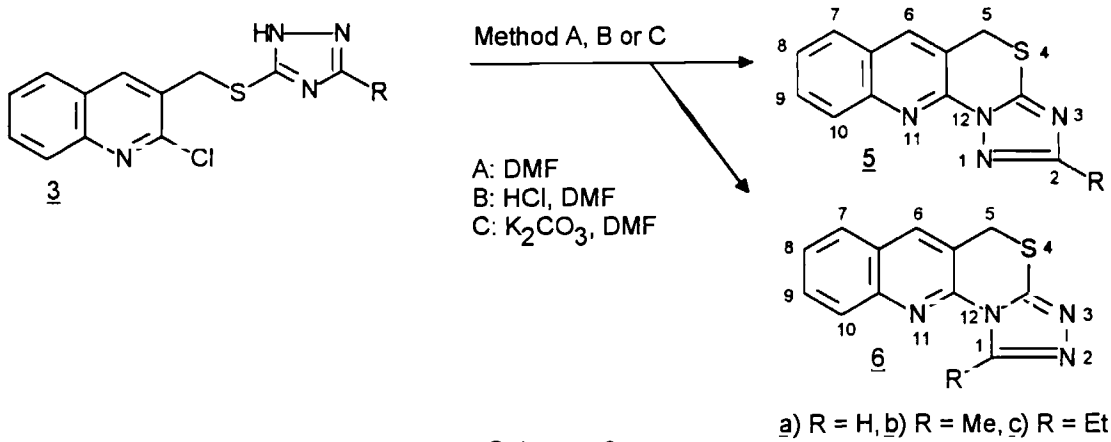
2-Chloro-3-chloromethylquinoline 1 treated with 1,2,4-triazole-5-thiols 2 in the presence of potassium carbonate in dimethylformamide at 25 °C yielded 2-chloro-3-(1,2,4-triazol-5-yl)thiomethylquinolines 3 in excellent yields (Scheme 1).



Scheme 1

Under these conditions, when *in situ* formation of thiolate anion of 1,2,4-triazolethiols is possible, the substitution of the benzylic chlorine atom took only place but the 2-chlorine atom was found to remain unaffected in terms of both *S*-substitution and cyclisation. The structure of 3 was confirmed by desulfurisation with Raney nickel in ethanol leading to the known (3) 2-chloro-3-methylquinoline 4 .

Cyclocondensation of 3 was performed by different methods: in dimethylformamide without any additional reagent (method **A**), or in the presence of hydrochloric acid (method **B**) or potassium carbonate (method **C**). The mixture of 5*H*-[1,2,4]triazolo[5',1':2,3][1,3]thiazino[4,5-*b*]quinoline 5 and 5*H*-[1,2,4]triazolo[3',4':2,3][1,3]thiazino-[4,5-*b*]quinoline 6 derivatives was formed in every case. These regioisomers were separated by column chromatography but their ratio was determined on the basis of their characteristic signals in the ^{1}H-nmr spectra of the crude products containing the mixture of the two regioisomers. The ratio of the isomers depends on the substituent (R) on the triazole ring and the reaction conditions (Scheme 2, Table 1).



Scheme 2

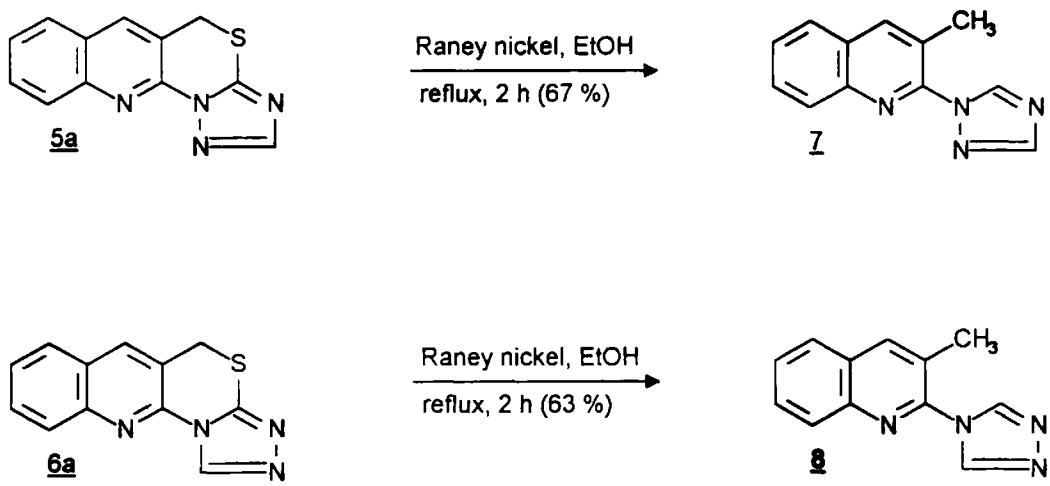
Table1: Cyclisation of 2-Chloro-3-(1,2,4-triazol-5-yl)thiomethylquinolines 3

R	Method	Temperature (°C)	Time (h)	Yield[a] (%)	Ratio of the products[b] (%) 5 : 6
H	A	25	72	88	35 :65
H	B	25	48	88	30 :70
H	A	80	0.5	90	34 : 66
H	C	80	4	90	90 :10
Me	A	80	2	88	55 :45
Me	B	80	1	92	55 :45
Me	C	80	5	89	90 :10
Et	A	80	2	92	72 :28
Et	B	80	1	91	70 :30
Et	C	80	5	93	95 : 5

a) Yield of the crude product containing only the two regioisomers; b) The ratio was determined by ^{1}H-nmr spectroscopy

There are some important points emerging from the data presented: 1) The cyclisation is acid catalyzed due to the activation of 2-chlorine atom toward nucleophilic substitution by protonation of the quinoline ring. 2) In the case of method **A** or **B** (R=H) compound 6 is the main product but the ratio of this product is shifted in favour of 5 by the increasing steric demand of the substituent (R) on the triazole ring. 3) Presence of potassium carbonate inhibits the reaction since it prevents the activation by protonation. In this case, compound 5 predominates over 6 in every case. A possible explanation of this fact may be that potassium carbonate deprotonates the triazole ring and the negative charge localizes mainly to N-1 rather than N-4, so N-1 has the greater nucleophilicity similarly to that was found in alkylation reactions of 1,2,4-triazole (4).

The structure of the separated products 5, 6 has been determined by desulfurisation with Raney nickel in case of R=H (Scheme 3).



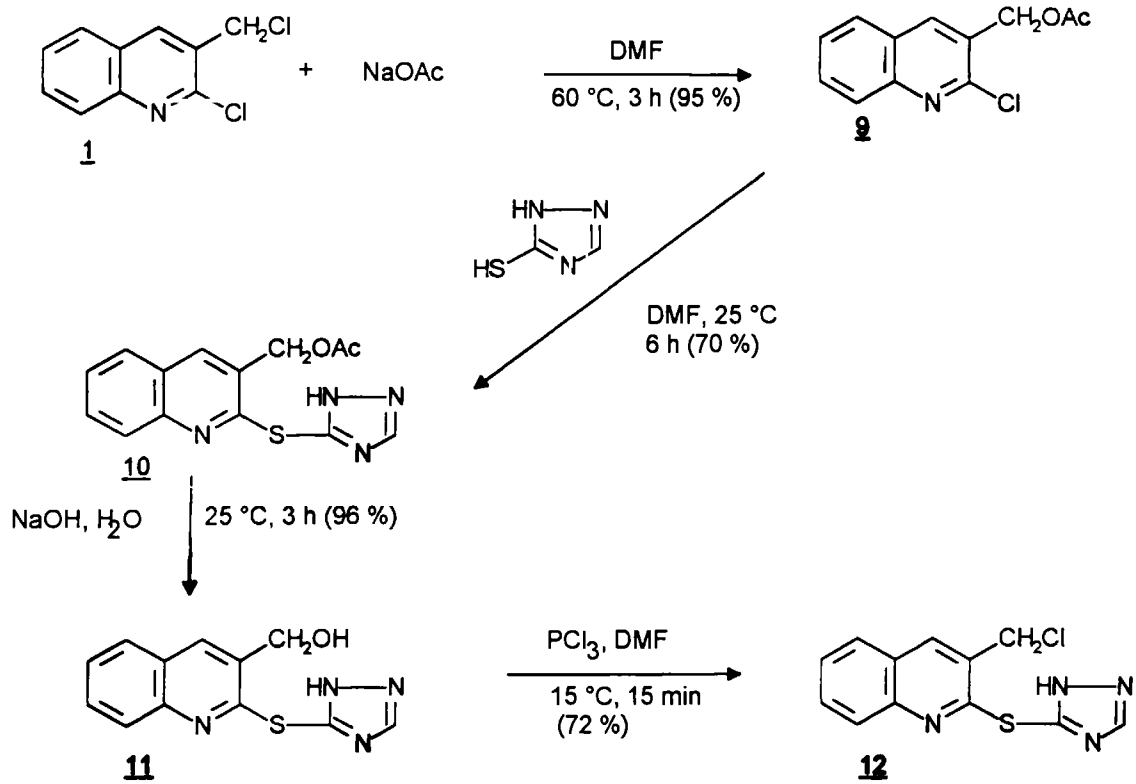
Scheme 3

Desulfurisation of 5a and 6a led to different products 7 and 8 which could be distinguished easily by nmr spectroscopy. The ^{1}H-nmr spectrum of 7 showed two separated triazole singlets, whereas triazole protons of 8 were equivalent and appeared as one two-proton signal confirming the structure of the starting heterocycles.

In the case of R=Me and Et, the structure of 5 and 6 has been confirmed by nmr spectroscopy on the basis of general rules concerning the chemical shifts of both the methylene protons of the thiazino ring and the triazole carbons as well as one bond triazole proton-carbon couplings. These rules have been drawn from the ^{1}H- and ^{13}C-nmr study of a large number of [1,2,4]triazolo[5,1]- and [1,2,4]triazolo[3,4][1,3]thiazinoquinoline regioisomers included 5 and 6, and have been reported recently (5).

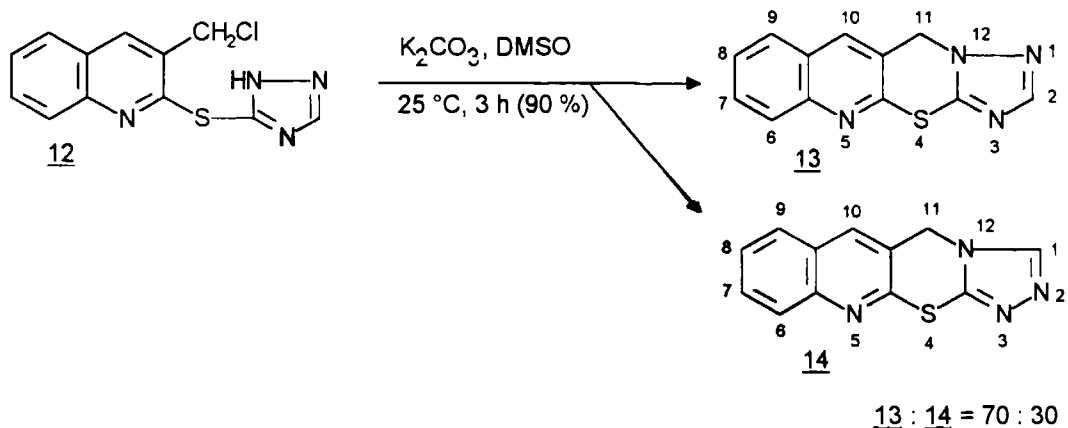
3-Chloromethyl-2-(1,2,4-triazol-5-yl)thioquinoline 12 , the regioisomer of 3a was prepared by an unequivocal route starting from 1 via 9, 10, and 11 (Scheme 4).

The cyclocondensation of 12 was studied under different reaction conditions. When it was treated with potassium carbonate in dimethylsulfoxide at 25 °C, formation of two products 13, 14 was observed (Scheme 5) in a cyclocondensation involving the nucleophilic substitution of the benzylic chlorine atom by the triazole ring nitrogen atom.



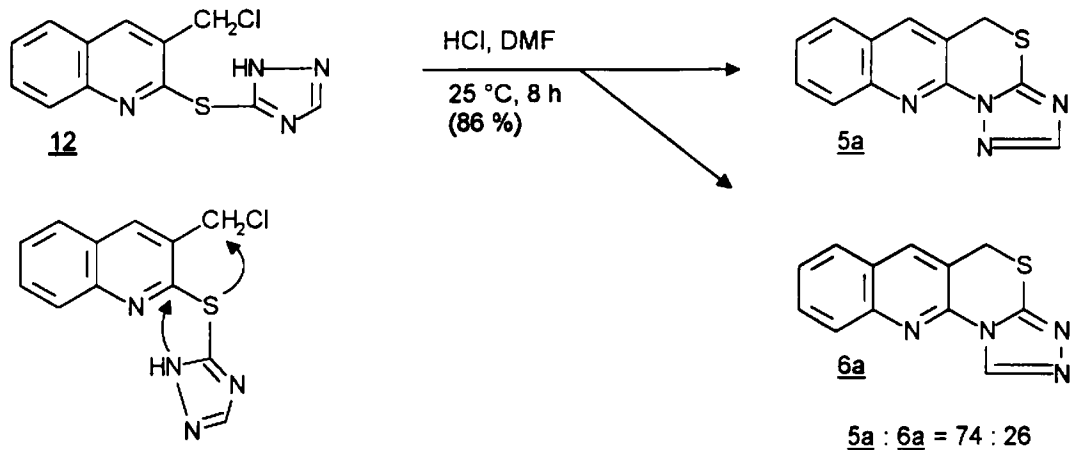
Scheme 4

Compound 13 was identical with that prepared by selective desulfurisation of its 11-(2-hydroxyethyl)thio derivative (1); the structure of 14 was confirmed by homonuclear NOE difference spectroscopy (5).



Scheme 5

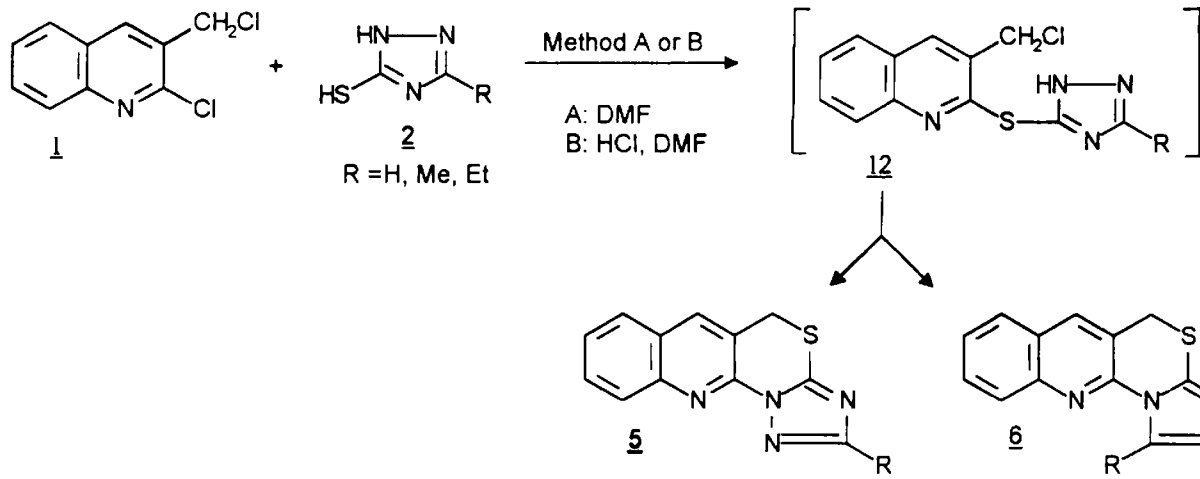
When the solution of 12 in dimethylformamide was stirred at 25 °C, no reaction occurred at all, but in the presence of hydrochloric acid unexpected formation of the mixture of 5a and 6a was observed (Scheme 6) in a ratio totally different from that observed in cyclocondensation of 3a. Compounds 13 and 14 could not be detected in the crude product by tic and nmr spectroscopy.



Scheme 6

This unexpected observation can be explained by assuming an acid catalyzed rearrangement via a four-membered cyclic system at the transition state as shown in Scheme 6. This rearrangement consists of two quasi-simultaneous nucleophilic steps: the acid catalyzed nucleophilic attack of the triazole ring nitrogen atom to the C-2 atom of the quinoline ring and the nucleophilic attack of the sulfur atom to the benzylic carbon atom. This type of rearrangement has not been observed so far in the cyclocondensation reactions of 1,2,4-triazolethiols but some similarities can be found with the mechanism of the *Newman - Kwart* rearrangement of thionocarbamates to thiolcarbamates (6).

Results derived from the study of the reaction of 1 with 2 in the absence of potassium carbonate (method **A**) or in the presence of hydrochloric acid (method **B**) were also unexpected. Under these conditions the reaction led to the formation of the mixture of 5 and 6 immediately, however, the presence of an intermediate was monitored by tlc. In the case of method **A** a quasi-simultaneous consumption of the starting material 1 and the intermediate was observed, while in case of method **B** the formation of the intermediate was faster (Table 2), so the first step of the reaction should be acid catalyzed. The ratio of the isomers (Table 2) was totally different from that was observed in the cyclisation of 3, but was very similar (R=H) to that was observed in cyclisation of 12. This result, in agreement with the acid catalytic nature of the formation of the intermediate, suggested that the reaction should proceed mainly via intermediate 12 rather than 3. Thus it seems to be very probable that the first step of the reaction of 1 with 2 under the reaction conditions of methods **A** and **B** should be the formation of 12 which undergoes a rearrangement to give the mixture of 5 and 6.



Scheme 7

Table 2: Reaction of 2-Chloro-3-chloromethylquinoline 1 with 1,2,4-Triazole-5-thiols 2 According to the Methods A and B

R	Method	Temperature (°C)	Time[a] (h)	Yield[c] (%)	Ratio of the isomers[d] (%) 5 : 6
H	A	25	9	94	70 :30
H	A	80	0.5	93	61 :39
H	B	25	8 (4)[b]	91	70 :30
Me	A	25	10	91	95 : 5
Me	A	80	0.5	90	90 :10
Et	A	25	9	90	100 : 0

a) Time required to the consumption of the starting material 1 and the intermediate; b) Time required to the consumption of the starting material 1 ; c) Yield of the crude product containing only the two regioisomers; d) The ratio of the regioisomers in the crude product was determined by ^{1}H-nmr spectroscopy

In conclusion, the results of our work presented in this paper can be summarized in the followings:

(1) Starting from 2-chloro-3-chloromethylquinoline 1 and 1,2,4-triazole-5-thiols 2 , all the four possible heterocyclic ring systems are accessible by the methods presented.

(2) These methods are based partly on our original observation that under acid catalytic or autocatalytic reaction conditions, the 2-chlorine atom, whereas in the presence of a strong base or towards an anionic nucleophile the benzylic chlorine atom of 1 has greater reactivity.

(3) In addition, we have observed an unexpected rearrangement of 3-chloromethyl-2-(1,2,4-triazol-5-yl)thioquinoline 12 . A possible mechanism of this rearrangement has been suggested, however, investigation of this phenomenon is in progress in our laboratory.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. Nmr spectra were recorded on a Varian Gemini-200 instrument at 200 MHz in DMSO-d_6 solution using TMS as internal standard and chemical shifts are expressed in ppm. The NOE experiments along with the total ^{1}H- and ^{13}C-nmr assignation of compounds 5, 6, 13 and 14 have already been published (5). Mass spectra were scanned on a VG TRIO-2 spectrometer in EI mode at 70 eV except for compounds 3 which cyclize to 5 or 6 in these conditions, but they gave molecular ion peak investigated by thermospray technique. The purification and separation of some products was performed by column chromatography using Kieselgel 60 (0.063 - 0.2 mm) (Reanal, Hungary) packing and chloroform - ethanol (95:5, v/v) eluent.

Materials: 2-chloro-3-chloromethylquinoline 1 (7) and 1,2,4-triazole-5-thiols 2 (8) were prepared according to previously described procedures.

Preparation of 2-chloro-3-(1,2,4-triazol-5-yl)thiomethylquinolines 3 . General procedure:

The mixture of the corresponding 2 (12 mmol) and potassium carbonate (1.66 g, 12 mmol) was stirred in dimethylformamide at 25 °C for 15 min. Compound 1 (2.12 g, 10 mmol) was then added to the mixture and it was stirred at the same temperature for 30 min then was poured into ice-water (50 ml). The precipitated product was collected, washed with water and ethanol and dried at room temperature.

Using this general procedure the following compounds were prepared:

3a (R=H), 2.65 g (96 %), mp 148 -150 °C (decomp); ^{1}H-nmr: δ 4.57 (s, 2H), 7.64 (m, 1H), 7.80 (m, 1H), 7.90 - 8.00 (m, 2H), 8.42 (s, 1H), 8.59 (s, 1H), 14.15 (br, 1H); ms (TSP): m/z (%) 277 (MH^+, 61), 241 (100).

3b (R=Me), 2.85 g (98 %), mp 154 - 156 °C (decomp); ^{1}H-nmr: δ 2.32 (s, 3H), 4.53 (s, 2H), 7.62 (m, 1H), 7.80 (m, 1H), 7.89 - 8.00 (m, 2H), 8.43 (s, 1H), 13.72 (br, 1H); ms (TSP): m/z (%) 291 (MH^+, 48), 255 (100).

3c (R=Et), 2.98 g (98 %), mp 143 - 145 (decomp); ^{1}H-nmr: δ 1.21 (t, 3H, J=7.5 Hz,), 2.68 (q, 2H, J=7.5 Hz), 4.53 (s, 2H), 7.64 (m, 1H) 7.80 (m, 1H), 7.92 - 7.99 (m, 2H), 8.43 (s, 1H), 13.25 (br, 1H); ms (TSP): m/z (%) 305 (MH^+, 40), 269 (100).

Desulfurisation of compound 3b:

Compound 3b (0.58 g, 2 mmol) and Raney nickel (5 g wet paste washed with ethanol) were stirred at 25 °C in ethanol (20 ml) for 5 h. The catalyst was separated by filtration and the filtrate was evaporated to dryness. The residue was crystallized from chloroform - ethanol (1:3, v/v) to yield 2-chloro-3-methylquinoline (4), 0.25 g (70 %), mp 81-82 °C (lit (3) mp 84°C); ^{1}H-nmr ($CDCl_3$): δ 2.51 (s, 3H), 7.50 (m, 1H), 7.67 (m, 1H), 7.74 (m, 1H), 7.95 (s, 1H), 8.00 (m, 1H); ms: m/z (%) 177 (M^+, 100).

Cyclisation of compounds 3. General procedure for the preparation of 5H-[1,2,4]triazolo[5',1':2,3][1,3]thiazino[4,5-b]quinolines 5 and 5H-[1,2,4]triazolo[3',4':2,3][1,3]thiazino[4,5-b]quinolines 6 :

The corresponding 3 (10 mmol) was stirred in dimethylformamide (10 ml) without any additional reagent (method **A**), in the presence of hydrochloric acid (10 mmol) (method **B**) or potassium carbonate (10 mmol) (method **C**) at the temperature indicated in Table 1 until all the starting material had been consumed (tic). The reaction mixture was then diluted with water (50 ml), neutralized with 15 % aqueous ammonia solution (methods **A** and **B**), the solid material was collected, washed with water and dried. The yields of the crude products and the ratio of the isomers 5, 6 determined by ^{1}H-nmr spectroscopy are indicated in Table1. The crude products obtained by method **A** at 80 °C were subjected to column chromatography to give compounds 5 as a firts crop and 6 as a second crop in every case. The isolated yields and the melting points (DMSO - ethanol = 1:2) of the compounds are the followings:

5a (R=H): 0.70 g (29 %), mp 259 - 261 °C; 6a (R=H): 1.31 g (55 %), mp 231 - 232 °C;

5b (R=Me): 1.20 g (47 %), mp 240 - 242 °C; 6b (R=Me): 0.97 g (38 %), mp 211 - 213 °C;
5c (R=Et): 1.72 g (64 %), mp 133 - 135 °C; 6c (R=Et): 0.65 g (24 %), mp 173 - 175 °C.
The microanalysis and mass spectral data of the compounds 5 and 6 are assembled in Table 3.

Desulfurisation of compounds 5a and 6a:
The mixture of compounds 5a or 6a (0.48 g, 2 mmol) and Raney nickel (5 g wet paste, washed with ethanol) was stirred in ethanol (25 ml) at reflux temperature for 2 h. The catalyst was separated by filtration, the filtrate was concentrated (5 ml), then water (5 ml) was added. The product precipitated on cooling in a refrigerator was collected, washed with the mixture of ethanol - water (1:1, v/v) and dried.
Product obtained from 5a: 3-methyl-2-(1,2,4-triazol-1-yl)quinoline (7), 0.28 g (67 %), mp 87 - 89 °C; ^{1}H-nmr: δ 2.54 (s, 3H), 7.68 (m, 1H), 7.81 (m, 1H), 7.98 - 8.07 (m, 2H), 8.35 (s, 1H), 8.50 (s,1H), 9.24 (s, 1H); ms: m/z (%) 210 (M^+, 100).
Product obtained from 6a: 3-methyl-2-(1,2,4-triazol-4-yl)quinoline (8), 0.26 g (62 %), mp 144 - 145 °C; ^{1}H-nmr: δ 2.46 (s, 3H), 7.69 (m, 1H), 7.82 (m, 1H), 7.98 - 8.09 (m, 2H), 8.54 (s, 1H), 9.12 (s, 2H); ms: m/z (%) 210 (M^+, 100).

3-Acetoxymethyl-2-chloroquinoline 9:
The mixture of 1 (10.6 g, 50 mmol) and anhydrous sodium acetate (6.15 g, 75 mmol) was stirred in dimethylformamide (50 ml) at 60 °C for 3 h. The reaction mixture was poured into water (250 ml) and the precipitated material was collected, washed with water and dried. Yield of 9 (a crude product pure enough for further syntheses), 11.2 g (95 %), mp 69 - 70 °C (71 - 72 °C recryst. from ethanol); ^{1}H-nmr: δ 2.16 (s, 3H), 5.28 (s, 2H), 7.68 (m,1H), 7.83 (m,1H), 7.97 (m,1H), 8.07 (m,1H), 8.50 (s, 1H); ms: m/z (%) 235 (M^+,16), 200 (37), 193 (20), 176 (33), 158 (61), 140 (90), 43 (100).

3-Acetoxymethyl-2-(1,2,4-triazol-5-yl)thioquinoline 10:
Compound 9 (4.71 g, 20 mmol) was treated with 2a (2.4 g, 24 mmol) in dimethylformamide (20 ml) at 25 °C for 6 h. The reaction mixture was poured into water (100 ml), neutralized with 15 % aqueous ammonia solution, the precipitated product was collected, washed with water and dried. The crude product was recrystallized from DMSO - ethanol (1:2, v/v) to give 10, 4.2 g (70 %), mp 154 -155 °C; ^{1}H-nmr: δ 2.16 (s, 3H), 5.30 (s, 2H), 7.52 - 7.78 (m, 3H), 8.00 (m, 1H), 8.39 (s, 1H), 8.78 (s, 1H), 14.50 (br, 1H); ms: m/z (%) 300 (M^+, 2), 257 (17), 43 (100).

3-Hydroxymethyl-2-(1,2,4-triazol-5-yl)thioquinoline 11:
Compound 10 (12.0 g, 40 mmol) was treated with 2 M aqueous sodium hydroxide solution (40 ml) at 25 °C for 3 h. By that time all the starting material had gone to solution. The reaction mixture was then neutralized with 2 M aqueous hydrochloric acid solution, the precipitated material was collected, washed with water and dried. Yield of 11 (a crude product pure enough for further syntheses), 9.91 g (96 %), mp 181 - 183 °C (183 - 184 °C recryst. from DMSO - ethanol = 1:2); ^{1}H-nmr: δ 4.68 (s, 2H), 7.50 - 7.70 (m, 3H), 7.98 (m, 1H), 8.30 (s, 1H), 8.56 (s, 1H), 14.45 (br, 1H); ms: m/z (%) 258 (M^+, 4), 239 (5), 227 (16), 189 (24), 161(100).

3-Chloromethyl-2-(1,2,4-triazol-5-yl)thioquinoline *12:*
Phosphorus trichloride (5.13 g, 37 mmol) was added dropwise to the solution of compound 11 (7.74 g, 30 mmol) in dimethylformamide (30 ml) at 15 °C and the solution was stirred at the same temperature for 15 min. The mixture was then poured into ice-water (150 ml) and the precipitated product was collected, washed with water and dried. The crude product was dissolved in dimethylformamide (40 ml), ethanol (80 ml) was added to this solution and

the crystalline product precipitated on cooling in a refrigerator overnight was collected, washed with ethanol and dried. Yield of 12, 5.97 g (72 %), mp 159 - 161 °C; ^{1}H-nmr: δ 5.05 (s, 2H), 7.50 - 7.80 (m, 3H), 7.97 (m, 1H), 8.50 (s, 1H), 8.65 (s, 1H), 14.25 (br, 1H); ms (TSP): m/z (%) 277 (M^+, 9), 241 (100).

Cyclisation of compound 12 in the presence of potassium carbonate:
Compound 12 (1.38 g, 5 mmol) was treated with potassium carbonate (0.69 g, 5 mmol) in dimethylsulfoxide (5 ml) at 25 °C for 3 h. After consumption of 12 (tlc), the reaction mixture was diluted with water (25 ml), the precipitated material was collected, washed with water and dried. The weight of the crude product (consist of the mixture of 13 (70 %) and 14 (30 %) determined by ^{1}H-nmr) was 1.08 g (90 %). The two products were separated by column chromatography. The first crop obtained from the column was 11*H*-[1,2,4]triazolo[5',1':2,3]1,3]thiazino[6,5-*b*]quinoline 13 , 0.69 g (58 %), mp 196 - 198 °C; identical with an authentic specimen obtained from its 11-(2-hydroxyethyl)thio-derivative (1). The second crop was 11*H*-[1,2,4]triazolo[3',4':2,3]1,3]thiazino[6,5-*b*]quinoline 14 , 0.30 g (25 %), mp 286 - 288 °C. The microanalysis and mass spectral data are incorporated in Table 3.

Cyclisation of compound 12 in the presence of hydrochloric acid:
Compound 12 (1.38 g, 5 mmol) was suspended in dimethylformamide (4 ml) and was treated with 5 M hydrochloric acid in dimethylformamide solution (1 ml) at 25 °C for 8 h. The reaction mixture was diluted with water (25 ml), neutralized with 15 % aqeous ammonia solution, the precipitated material was collected, washed with water and dried. The weight of the crude product (consists of the mixture of 5a (74 %) and 6a (26 %) determined by ^{1}H-nmr) was 1.03 g (86 %).

Reaction of 1 with 2 in the absence of potassium carbonate or in the presence of hydrochloric acid. General procedures:
The mixture of 1 (2.12 g, 10 mmol) and the corresponding 2 (12 mmol) was stirred in dimethylformamide (10 ml) without any additional reagent (method **A**) or in the presence of hydrochloric acid (10 mmol) (method **B**) at the temperature indicated in Table 2 until completion of the reaction (tlc). The reaction mixture was diluted with water (50 ml), neutralized with 15 % aqueous ammonia solution, the precipitated material was collected and dried. The yields of the crude products and the ratio of the isomers 5, 6 determined by ^{1}H-nmr spectroscopy are indicated in Table 2.

Table 3: Analytical and Mass Spectral Data of Compounds 5, 6, and 14.

Compound	Formula	Elemental analysis (%) Calculated [Found] C	H	N	ms m/z (%)
5a	$C_{12}H_8N_4S$	59.98 [59.77]	3.36 [3.29]	23.32 [23.34]	240 (M^+, 100)
6a	$C_{12}H_8N_4S$	59.98 [59.74]	3.36 [3.35]	23.32 [23.30]	240 (M^+, 100)
5b	$C_{13}H_{10}N_4S$	61.40 [61.59]	3.96 [3.87]	22.03 [22.24]	254 (M^+, 100)
6b	$C_{13}H_{10}N_4S$	61.40 [61.58]	3.96 [4.02]	22.03 [22.29]	254 (M^+, 100)
5c	$C_{14}H_{12}N_4S$	62.67 [62.65]	4.51 [4.50]	20.88 [21.13]	268 (M^+, 100)
6c	$C_{14}H_{12}N_4S$	62.67 [62.91]	4.51 [4.43]	20.88 [20.95]	268 (M^+, 100)
14	$C_{12}H_8N_4S$	59.98 [60.13]	3.36 [3.47]	23.32 [23.06]	240 (M^+, 100)

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