FUSED 1,2,4-TRIAZOLE HETEROCYCLES. I. SYNTHESIS OF NOVEL [1,2,4]TRIAZOLO[5′,1′: 2,3][1,3]THIAZINO[6,5-*b*]QUINOLINES.

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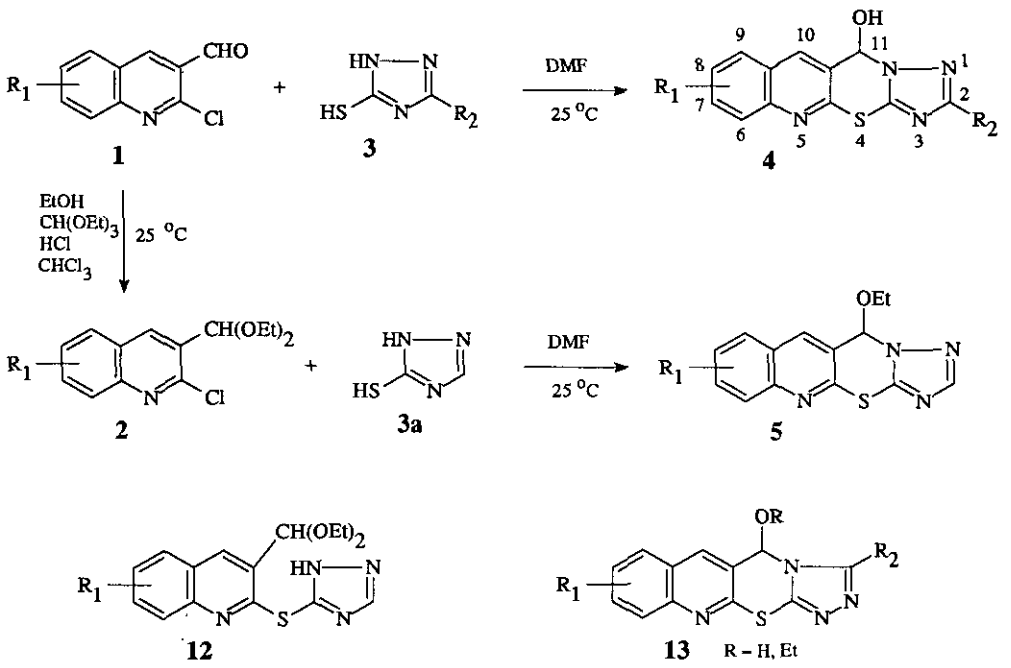
Abstract - Derivatives of a new heterocyclic ring system of [1,2,4]triazolo[5′,1′: 2,3][1,3]thiazino[6,5-*b*]quinolines (**4**, **5**, **6**, **7** and **8**) have been synthesised by the reaction of 2-chloroquinoline-3-carbaldehyde derivatives (**1** and **2**) with 1,2,4-triazole-5-thiols (**3**), and subsequent transformations of the hydroxy group of 11-hydroxy[1,2,4]triazolo[5′,1′: 2,3][1,3]thiazino[6,5-*b*]quinoline (**4a**).

Quinolines condensed with various heterocycles have recently become important compounds because of their affinity to the benzodiazepine receptor.[1,2] On the other hand, condensed triazole heterocycles are also of interest owing to their significant antifungal and antibacterial properties.[3,4,5] In continuation of our work to synthesize new tetracyclic fused heterocycles containing quinoline and 1,2,4-triazole skeletons,[6] now we report on the synthesis of some representatives of the titled new heterocyclic ring system by the condensation reaction of 2-chloroquinoline-3-carbaldehyde derivatives (**1**,**2**) with 1,2,4-triazole-5-thiols (**3**), and subsequent transformations of the hydroxy group of compound (**4a**).

2-Chloroquinoline-3-carbaldehydes (**1**) or their diethyl acetal derivatives (**2**) (obtained from 1 when treated with ethanol and triethyl orthoformate in chloroform in the presence of hydrochloric acid) undergo cyclisation with 1*H*-1,2,4-triazole-5-thiols (**3**) in dimethylformamide at 25 °C to give 11-hydroxy- or 11-ethoxy[1,2,4]triazolo[5′,1′: 2,3][1,3]thiazino[6,5-*b*]quinolines (**4** or **5**) respectively.

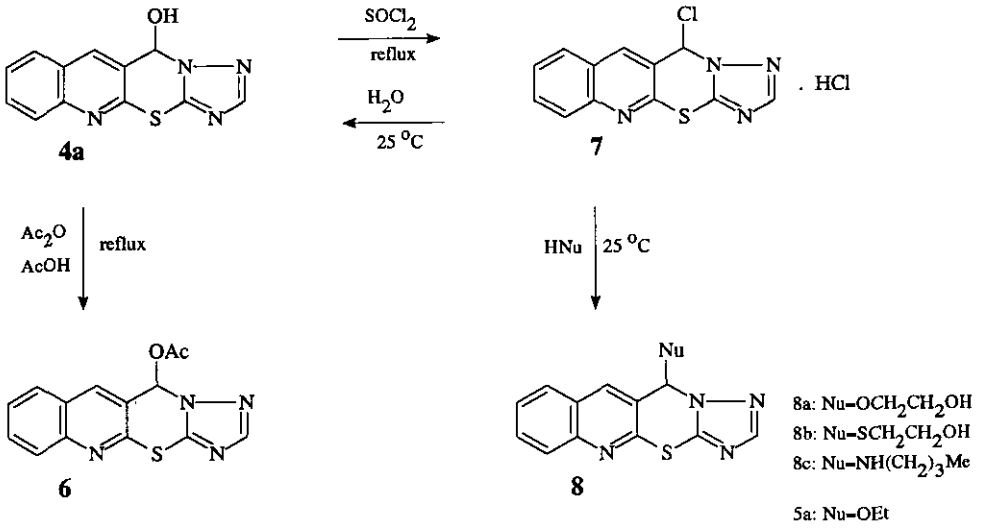
The formation of **4** and **5** involves two reaction steps: the substitution of 2-chloro group of **1** or **2** by the thiol group of **3** followed by an intramolecular addition or substitution reaction leading to **4** or **5** respectively. The initial product from **1** and **3** was not observed, but the formation and subsequent transformation of an intermediate which should have the *S*-arylated structure (**12**) was indicated by tlc monitoring of the

reaction of **2** with **3**. The cyclisation was found to be regiospecific, only one product was isolated in every case. The possible other structure (**13**) of compounds prepared was considered but excluded on the basis of the results derived from the degradation reactions discussed below.



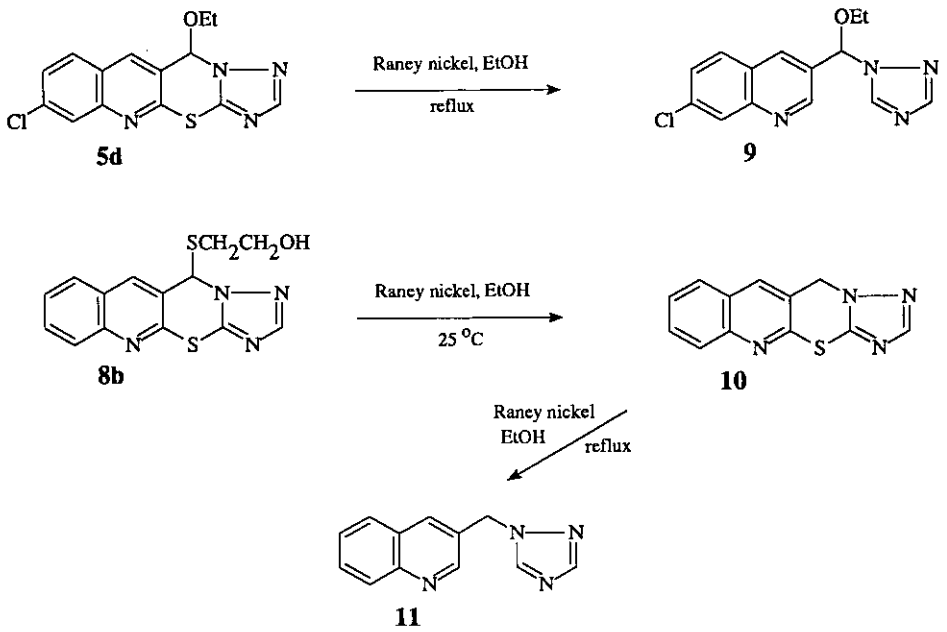
Scheme 1

Some reactions of **4** have been attempted. Alkylation of **4a** with ethyl bromide led to a reaction mixture with many components probably due to the simultaneous alkylation of ring nitrogens, but acylation by heating with acetic anhydride in acetic acid was successful and it furnished the acetoxy derivative (**6**). Heating of **4a** with thionyl chloride afforded the 11-chloro derivative (**7**) of the parent heterocycle. The chloro group of **7** showed high reactivity toward nucleophilic reagents. Thus, stirring of the suspension of **7** in water or ethanol at 25 °C gave **4a** or **5a** respectively. These compounds were identical with that obtained by cyclisation reactions. Furthermore, dissolvation of **7** in ethylene glycol, 2-mercaptoethanol or *n*-butylamine at 25 °C afforded the products (**8a**, **8b** and **8c**) respectively in good yields.



Scheme 2

The ^{1}H-nmr and mass spectral data of all compounds prepared were precisely consistent with the supposed structure of 11-substituted [1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-*b*]quinolines, but these data do not exclude the possibility that the compounds have the isomeric [1,2,4]triazolo[3′,4′:2,3][1,3]thiazino[6,5-*b*]quinoline structure (**13**). For this reason, two of the compounds (**5d** and **8b**) were subjected to desulfurisation. Compound (**5d**), on treatment with Raney nickel in ethanol at reflux temperature gave the desulfurated product (**9**). In the ^{1}H-nmr spectrum of **9** the two triazole protons appeared as two separated singlets (δ 8.10 and 8.93) indicating its triazole-1-yl structure[7] and hence confirming the supposed structure of the starting heterocycle (**5d**). Compound (**8b**) was selectively desulfurated in the side chain when treated with Raney nickel in ethanol at 25 °C to afford the unsubstituted heterocycle (**10**) which was subsequently desulfurated in the ring at reflux temperature to give **11**. The presence of the two separated singlets (δ 8.05 and 8.78) of triazole protons in the ^{1}H-nmr spectrum of **11** is also in agreement only with the supposed [1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-*b*]quinoline structure of the new heterocyclic ring system.



Scheme 3

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. The ^{1}H-nmr spectra were recorded on a Varian Gemini-200 instrument at 200 MHz in deuteriochloroform or DMSO-d_6 solutions using TMS as internal standard and chemical shifts are expressed in ppm. Mass spectra were scanned on a VG TRIO-2 spectrometer in EI mode at 70 eV.

Materials: 2-chloroquinoline-3-carbaldehydes[8] and 1,2,4-triazole-5-thiols[9] were prepared according to previously described procedures.

*Preparation of 2-chloro-3-diethoxymethylquinolines (**2a-d**). General procedure.*

The corresponding 2-chloroquinoline-3-carbaldehyde (1) (0.02 mol) was dissolved in chloroform (20 ml). Dry ethanol (3.86 g, 0.08 mol), distilled triethyl orthoformate (4.44 g, 0.03 mol) and concentrated hydrochloric acid (one drop) was added to this solution, and the reaction mixture was stirred at 25 °C until all the starting 2-chloroquinoline derivative had been consumed (tlc). The reaction mixture was washed with saturated aqueous solution of sodium hydrogen carbonate (5 ml), the organic layer was separated, dried over anhydrous sodium sulfate and evaporated. The residue was purified by crystallisation or by column chromatography.

Table 1. Preparation of 2-chloro-3-diethoxymethylquinolines (**2a-d**).

Compound	R_1	Time (h)	Yield (%)	mp (°C)
2a	H	5	57[a]	46-48 (hexane)
2b	7-Me	10	85[b]	oil
2c	7-OMe	10	72[a]	60-62 (ethanol)
2d	7-Cl	4	79[a]	86-87 (ethanol)

a) Yield of crystallized product; b) Purification was performed by column chromatography (silica gel packing, chloroform eluent).

*Preparation of 11-hydroxy[1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-b]quinolines (**4a-k**). General procedure.*

The mixture of the corresponding 2-chloroquinoline-3-carbaldehyde (**1**) (0.01 mol) and the 1,2,4-triazole-5-thiol (**3**) (0.012 mol) derivatives in dimethylformamide (10 ml) was stirred at 25 °C. When the reaction had been completed, the reaction mixture was poured into water (50 ml), the precipitated product was collected, washed with water and dried. The raw product was crystallized from DMSO - ethanol (1:2, v/v) mixture.

Table 2. Preparation of 11-Hydroxy[1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-*b*]quinolines (**4a-k**).

Compound	R_1	R_2	Time (h)	Yield (%)[a]	mp (°C)
4a	H	H	3	84	228-229
4b	H	Me	9	79	306-307
4c	H	Et	3	83	220-221
4d	8-Me	H	3	69	252-253
4e	7-Me	H	6	69	245-246
4f	6-Me	H	24	91	260-261
4g	8-OMe	H	10	90	272-273
4h	7-OMe	H	10	84	258-259
4i	6-OMe	H	24	91	250-251
4j	8-Cl	H	48	79	291-292
4k	7-Cl	H	24	94	263-264

a) Yield of crystallized product.

*Preparation of 11-ethoxy-[1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-b]quinolines (**5a-d**). General procedure.* The corresponding 2-chloro-3-diethoxymethylquinoline derivative (**2**) (0.01 mol) was treated with 1,2,4-triazole-5-thiol (**3a**) (1.21 g, 0.012 mol) in dimethylformamide (10 ml) at 25 °C. After completion, the reaction mixture was worked up in a manner similar to that described above for the preparation of compounds (**4**). The raw product was crystallized from DMSO - ethanol (1:2, v/v) mixture.

Table 3. Preparation of 11-Ethoxy[1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-*b*]quinolines (**5a-d**).

Compound	R_1	$Time_1$[a] (h)	$Time_2$[b] (h)	Yield[c] (%)	mp (°C)
5a	H	30	72	77	153-154
5b	7-Me	30	72	75	136-137
5c	7-OMe	24	48	80	152-153
5d	7-Cl	36	81	76	147-148

a) Time required to the consumption of the starting material (**2**); b) Time required to the consumption of the intermediate (**12**); c) Yield of crystallized product.

*11-Acetoxy[1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-b]quinoline (**6**).*
Compound (**4a**) (2.56 g, 0.01 mol) was refluxed for 1 h in the mixture of glacial acetic acid (10 ml) and acetic anhydride (5 ml). The reaction mixture was cooled to room temperature and diluted with water. The precipitate formed was collected, dried and then crystallized from dimethylformamide-acetone (1:3, v/v) mixture to provide **6**, 1.58 g (53 %), mp 193-195 °C; ^{1}H-nmr (DMSO-d_6): δ 2.02 (s, 3H), 7.70 (m, 1H), 7.93 (m, 1H), 8.03(m, 1H), 8.18 (m, 1H), 8.40 (m, 2H), 8.82 (s, 1H); ms: m/z 298 (M^+,11), 239 (100).

*11-Chloro[1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-b]quinoline hydrochloride (**7**).*
Compound (**4a**) (2.56 g, 0.01 mol) was treated with thionyl chloride (30 ml, 0.41 mol) at reflux temperature for 3 h. By that time all the starting material had gone to solution. The reaction mixture was diluted with chloroform (30 ml), cooled to room temperature, and the precipitated material was collected, washed three times with dry chloroform to afford **7** (a raw product pure enough for further syntheses), 2.93 g (94 %), mp 187-188 °C (decomp.); ^{1}H-nmr (DMSO-d_6): δ 7.67 (m, 1H), 7.90 (m, 1H), 8.07 (m, 2H), 8.28 (s, 1H), 8.59 (s, 1H), 8.85 (s, 1H); ms: m/z 274 (M^+, 6), 239 (100).

11-Hydroxy[1,2,4]triazolo[5',1':2,3][1,3]thiazino[6,5-b]quinoline (4a).

Compound (**7**) (3.11 g, 0.01 mol) was suspended in water (20 ml), and the suspension was stirred at 25 °C for 8 h, then the solid material was collected, washed with water and crystallized from DMSO-ethanol (1:2, v/v) to give **4a**, 1.59 g (62 %), mp 227-228 °C. The ^{1}H-nmr and mass spectra of this compound are identical with that of prepared by general procedure described above.

11-Ethoxy[1,2,4]triazolo[5',1':2,3][1,3]thiazino[6,5-b]quinoline (5a).

Compound (**7**) (1.55 g, 0.005 mol) was suspended in dry ethanol (10 ml) and the suspension was stirred at 25 °C for 8 h, then the reaction mixture was neutralized with 15 % aqueous ammonia solution, the solid material was collected and washed with ethanol than crystallized from DMSO - ethanol (1:2, v/v) to give **5a**, 0.85 g (60 %), mp 152-154 °C. The ^{1}H-nmr and mass spectra of this compound are identical with that of prepared by general procedure described above.

11-(2-Hydroxyethyl)oxy[1,2,4]triazolo[5',1':2,3][1,3]thiazino[6,5-b]quinoline (8a).

Compound (**7**) (1.55 g, 0.005 mol) was suspended in dry ethylene glycol (10 ml) and the suspension was stirred at 25 °C until all the solid material had gone to solution (6 h). The reaction mixture was diluted with water (50 ml), cooled in a refrigerator overnight, and the precipitate was collected , washed with water and crystallized from ethanol to provide **8a**, 0.95 g (63 %), mp 152-153 °C; ^{1}H-nmr (DMSO-d_6): δ 3.47 (m, 2H), 3.63 (m, 1H), 3.80 (m, 1H), 4.75 (br, 1H), 7.20 (s, 1H), 7.70 (m, 1H), 7.82 (m, 1H), 8.02 (m, 1H), 8.12 (m, 1H), 8.36 (s, 1H), 8.83 (s, 1H); ms: m/z 300 (M^+,41), 255 (100).

11-(2-Hydroxyethyl)thio [1,2,4]triazolo[5',1':2,3][1,3]thiazino[6,5-b]quinoline (8b).

Compound (**7**) (1.55 g, 0.005 mol) was stirred in 2-mercaptoethanol (10 ml) at 25 °C until all the starting material had been dissolved (1 h), then the reaction mixture was worked up in a manner similar to that described for the prepration of **8a**, and the raw product was crystallized from ethanol to produce **8b**, 1.07 g (68 %), mp 176-178 °C; ^{1}H-nmr (DMSO-d_6): δ 2.77 (m, 1H), 2.98 (m, 1H), 3.58 (m, 2H), 5.00 (br, 1H), 7.60 (s, 1H), 7.70 (m, 1H), 7.88 (m, 1H), 8.00 (m, 1H), 8.10 (m, 1H), 8.32 (s, 1H), 8.70 (s, 1H); ms: m/z 316 (M^+, 8), 239 (100).

11-Butylamino[1,2,4]triazolo[5',1':2,3][1,3]thiazino[6,5-b]quinoline (8c).

Compound (**7**) (1.55 g, 0.005 mol) was stirred with cooling in *n*-butylamine (5 ml) at 25 °C for 1h. The

reaction mixture was evaporated and the residue was crystallized from ethanol to give **8c**, 1.06 g (68 %), mp 126-128 °C; ^{1}H-nmr (DMSO-d_6): δ 0.75 (t, J = 7 Hz, 3H), 1.25 (m, 4H), 2.43 (m, 2H), 3.63 (m, 1H, exchangable with deuterium oxide), 6.72 (d, J = 7 Hz, 1H), 7.67 (m, 1H), 7.87 (m, 1H), 8.00 (m, 1H), 8.12 (m, 1H), 8.27 (s, 1 H), 8.70 (s, 1H); ms: m/z 311 (M^+, 35), 239 (100).

3-[1-(1H-1,2,4-triazol-1-yl)-1-ethoxy]methyl-7-chloroquinoline (9).

Compound (**5d**) (0.80 g, 0.002 mol) and Raney nickel (5.0 g wet paste, washed with ethanol) were stirred at reflux temperature in ethanol (25 ml) under nitrogen. After 1 h fresh portion of Raney nickel (5 g) was added to the reaction mixture and the heating was continued for 2 h. The catalyst was separated by filtration, and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel column using chloroform-acetone (8:2, v/v) eluent to yield **9**, 0.43 g (60 %), mp 81-82 °C (ethanol); ^{1}H-nmr (DMSO-d_6): δ 1.22 (t, J = 7 Hz, 3H), 3.50 (m, 1H), 3.73 (m, 1H), 7.04 (s, 1H), 7.70 (dd, J_1 = 9 Hz, J_2 = 2 Hz, 1H), 8.10 (s, 1H), 8.12 (d, J = 2 Hz, 1H), 8.16 (d, J = 9 Hz, 1H), 8.50 (d, J = 2 Hz, 1H), 8.93 (s, 1H), 8.96 (d, J = 2 Hz, 1H); ms: m/z 288 (M^+, 12), 192 (100).

[1,2,4]Triazolo[5',1':2,3][1,3]thiazino[6,5-b]quinoline (10).

Compound (**8b**) (0.78 g, 0.0025 mol) and Raney nickel (5 g wet paste, washed with ethanol) were stirred in ethanol (25 ml) at 25 °C under nitrogen. After 1 h fresh portion of Raney nickel (5 g) was added to the reaction mixture and the stirring was continued for 1 h. The catalyst was separated by filtration, washed with ethanol, and the filtrate was concentrated (5 ml). The product precipitated on cooling in a refrigerator was collected, washed with ethanol and dried. Yield of **10**, 0.37 g (62 %), mp 197-199 °C; ^{1}H-nmr (DMSO-d_6): δ 5.80 (s, 2H), 7.65 (m, 1H), 7.83 (m, 1H), 8.00 (m, 2H), 8.22 (s, 1H), 8.50 (s, 1H); ms: m/z 240 (M^+, 100).

3-(1H-1,2,4-triazol-1-yl)methylquinoline (11).

Compound (**10**) was treated in the same way and in the same scale described above for the preparation of **9**. The evaporation residue was crystallized from ether to afford **11**, 0.34 g (64 %), mp 118-120 °C; ^{1}H-nmr (DMSO-d_6): δ 5.68 (s, 2H), 7.63 (m, 1H), 7.78 (m, 1H), 8.02 (m, 2H), 8.05 (s, 1H), 8.26 (d, J = 2 Hz, 1H), 8.78 (s, 1H), 8.92 (d, J = 2 Hz, 1H); ms: m/z 210 (M^+, 59), 142 (100).

Table 4. ^{1}H-Nmr and Mass Spectral Data of Compounds (**2**, **4** and **5**).

Compound	^{1}H-nmr[a] δ (ppm), J (Hz)	ms m/z (%)
2a	1.30 (t, J=7, 6H), 3.70 (m, 4H), 5.82 (s, 1H), 7.57 (m, 1H), 7.73 (m, 1H), 7.88 (m, 1H), 8.02 (m,1H), 8.45 (s, 1H).	265 (M^+, 8), 220 (100).
2b	1.30 (t, J=7, 6H), 2.55 (s, 3H), 3.70 (m, 4H), 5.80 (s, 1H), 7.40 (dd, J_1=8, J_2=1.5, 1H), 7.75 (d, J=8, 1H), 7.80 (d, J=1.5, 1H), 8.40 (s, 1H).	279 (M^+, 9), 234 (100).
2c	1.30 (t, J=7, 6H), 3.70 (m, 4H), 3.85 (s, 3H), 5.80 (s, 1H), 7.20 (dd, J_1=9, J_2=2.5, 1H), 7.35 (d, J=2.5, 1H), 7.75 (d, J=9, 1H), 8.35 (s, 1H).	295 (M^+, 11), 250 (100).
2d	1.30 (t, J=7, 6H), 3.70 (m, 4H), 5.80 (s, 1H), 7.55 (dd, J_1=9, J_2=2, 1H), 7.82 (d, J=9, 1H), 8.02 (d, J=2, 1H), 8.45 (s, 1H).	299 (M^+, 6), 254 (100).
4a	7.17 (d, J=7, 1H), 7.67 (m, 1H), 7.90 (m, 1H), 7.95 (d, J=7, 1H)[b], 8.02 (m, 1H), 8.12 (m, 1H), 8.30 (s, 1H), 8.75 (s, 1H).	256 (M^+, 100), 239 (56).
4b	2.37 (s, 1H), 7.05 (d, J=7, 1H), 7.67 (m, 1H), 7.85 (d, J=7, 1H)[b], 7.90 (m, 1H, 8.00 (m, 1H), 8.10 (m, 1H), 8.75 (s, 1H).	270 (M^+, 100), 253 (65).
4c	1.27 (t, J=7, 3H), 2.72 (q, J=7, 2H), 7.07 (d, J=7, 1H), 7.67 (m, 1H), 7.85 (d, J=7, 1H)[b], 7.90 (m, 1H), 8.00 (m, 1H), 8.10 (m, 1H), 8.72 (s, 1H).	284 (M^+, 100), 267 (56).
4d	2.50 (s, 3H), 7.10 (d, J=7, 1H), 7.65 (dd, J_1=8, J_2=2, 1H), 7.80 (d, J=2, 1H), 7,85 (d, J=8, 1H), 7.90 (d, J=7, 1H)[b], 8.25 (s, 1H), 8.57 (s, 1H).	270 (M^+, 100), 253 (50).
4e	2.55 (s, 3H), 7.15 (d, J=7, 1H), 7.50 (dd, J_1=8, J_2=2, 1H), 7.80 (d, J=2, 1H), 7.90 (d, J=7, 1H)[b], 8.00(d, J=8, 1H), 8.30 (s, 1H), 8.65 (s, 1H).	270 (M^+, 100), 253 (68).
4f	2.67 (s, 3H), 7.15 (d, J=7, 1H), 7.55 (m, 1H), 7.70 (m, 1H), 7.90 (m, 1H), 7.95 (d, J=7, 1H)[b], 8.32 (s, 1H), 8.67 (s, 1H).	270 (M^+, 100), 253 (27).
4g	3.95 (s, 3H), 7.15 (d, J=7, 1H), 7.50 - 7.57 (m, 2H), 7.90 (d, J=2.5, 1H), 7.95 (d, J=7, 1H)[b], 8.30 (s, 1H), 8.57 (s, 1H).	286 (M^+, 100), 269 (31).
4h	3.97 (s, 3H), 7.10 (d, J=7, 1H), 7.30 (dd, J_1=9, J_2=2, 1H), 7.40 (d, J=2, 1H), 7.90 (d, J=7, 1H)[b], 8.00 (d, J=9, 1H), 8.30 (s, 1H), 8.60 (s, 1H).	286 (M^+, 84), 269 (100).
4i	4.00 (s, 3H), 7.15 (d, J=7, 1H), 7.27 (d, J=8, 1H), 7.58 (m, 2H), 7. 97 (d, J=7, 1H)[b], 8.35 (s, 1H), 8.65 (s, 1H).	286 (M^+, 100), 269 (24).
4j	7.15 (d, J=7, 1H), 7.90 (dd, J_1=9, J_2=2, 1H), 8.00 (d, J=7, 1H)[b], 8.03 (d, J=9, 1H) 8.30 (m, 2H), 8.70 (s, 1H).	290 (M^+, 100), 273 (46).
4k	7.15 (d, J=7, 1H), 7.70 (dd, J_1=9, J_2=2, 1H), 7.97 (d, J=7, 1H)[b], 8.10 (d, J=2, 1H), 8.17 (d, J=9, 1H), 8.30 (s, 1H), 8.72 (s, 1H).	290 (M^+, 100), 273 (68).
5a	1.10 (t, J=7, 3H), 3.75 (m, 2H), 7.17 (s, 1H), 7.70 (m, 1H), 7.90 (m, 1H), 8.03 (m,1H), 8.15 (m, 1H), 8.35 (s, 1H), 8.82 (s, 1H).	284 (M^+, 16), 239 (100).
5b	1.07 (t, J=7, 3H), 2.55 (s, 3H), 3.20 (m, 2H), 7.13 (s, 1H), 7.55 (dd, J_1=8, J_2=2, 1H), 7.82 (d, J=2, 1H), 8.05 (d, J=8, 1H), 8.32 (s, 1H), 8.75 (s, 1H).	298 (M^+, 14), 253 (100).
5c	1.07 (t, J=7, 3H), 3.72 (m, 2H), 3.95 (s, 3H), 7.10 (s, 1H), 7.35 (dd, J_1=9, J_2=2, 1H) 7.42 (d, J=2, 1H), 8.03 (d, J=9, 1H), 8.33 (s, 1H), 8.70 (s, 1H).	314 (M^+, 14), 269(100).
5d	1.10 (t, J=7, 3H), 3.75 (m, 2H), 7.17 (s, 1H), 7.70 (dd, J_1=9, J_2=2, 1H), 8.07 (d, J=2, 1H), 8.17 (d, J=9, 1H), 8.37 (s, 1H), 8.85 (s, 1H).	318 (M^+, 11), 273 (100).

a) Spectra were recorded in deuteriochloroform (compounds **2**) or DMSO-d_6 (compounds **4** and **5**); b) Signals are exchangable with deuterium oxide.

Table 5. Analytical Data for [1,2,4]triazolo[5′,1′:2,3][1,3]thiazino[6,5-*b*]quinolines synthesised.

Compound	Formula	Elemental analysis (%)					
		Calculated			Found		
		C	H	N	C	H	N
4a	$C_{12}H_8N_4OS$	56.24	3.15	21.86	56.36	3.12	21.79
4b	$C_{13}H_{10}N_4OS$	57.76	3.73	20.73	57.89	3.79	20.73
4c	$C_{14}H_{12}N_4OS$	59.14	4.25	19.70	58.98	4.26	19.56
4d	$C_{13}H_{10}N_4OS$	57.76	3.73	20.73	57.78	3.81	20.68
4e	$C_{13}H_{10}N_4OS$	57.76	3.73	20.73	57.83	3.75	20.70
4f	$C_{13}H_{10}N_4OS$	57.76	3.73	20.73	57.61	3.74	20.89
4g	$C_{13}H_{10}N_4O_2S$	54.54	3.52	19.57	54.50	3.51	19.66
4h	$C_{13}H_{10}N_4O_2S$	54.54	3.52	19.57	54.72	3.52	19.61
4i	$C_{13}H_{10}N_4O_2S$	54.54	3.52	19.57	54.65	3.44	19.69
4j	$C_{12}H_7N_4OSCl$	49.58	2.43	19.27	49.51	2.40	19.21
4k	$C_{12}H_7N_4OSCl$	49.58	2.43	19.27	49.73	2.42	19.19
5a	$C_{14}H_{12}N_4OS$	59.14	4.25	19.70	59.12	4.25	19.75
5b	$C_{15}H_{14}N_4OS$	60.38	4.73	18.78	60.59	4.69	18.80
5c	$C_{15}H_{14}N_4O_2S$	57.31	4.49	17.82	57.28	4.50	17.93
5d	$C_{14}H_{11}N_4OSCl$	52.75	3.48	17.58	52.91	3.52	17.65
6	$C_{14}H_{10}N_4O_2S$	56.37	3.38	18.78	56.33	3.43	18.89
7	$C_{12}H_8N_4SCl_2$	46.32	2.59	18.00	46.05	2.52	17.79
8a	$C_{14}H_{12}N_4O_2S$	55.99	4.03	18.65	56.16	4.01	18.74
8b	$C_{14}H_{12}N_4OS_2$	53.15	3.82	17.71	53.18	3.80	17.69
8c	$C_{16}H_{17}N_5S$	61.71	5.50	22.49	61.79	5.55	22.51
10	$C_{12}H_8N_4S$	59.98	3.36	23.32	59.95	3.30	23.24

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