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Reaction of substituted 1-methylthio-4,5-dihydro[1,2]dithiolo[3,4-*c*]-quinolin iodides with arylamines. Synthesis of novel 1,2-dithiolo[3,4-*c*]-quinolin-1-ylidene(aryl)amines and 10-(arylimino)-7,10-dihydro[1,2]dithiolo[3,4-*c*]-pyrrolo[3,2,1-*ij*]quinoline-4,5-diones

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Dedicated to Oleg Alekseevich Rakitin on the occasion of his 65th birthday

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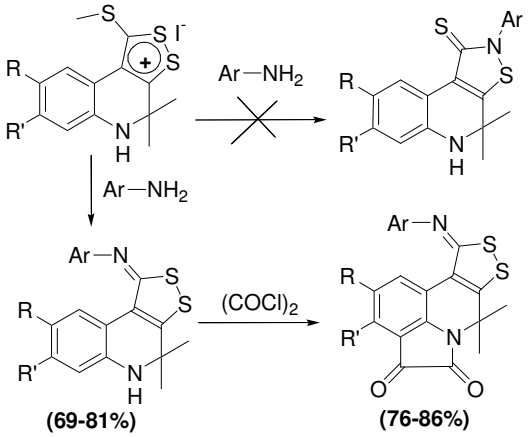
Abstract

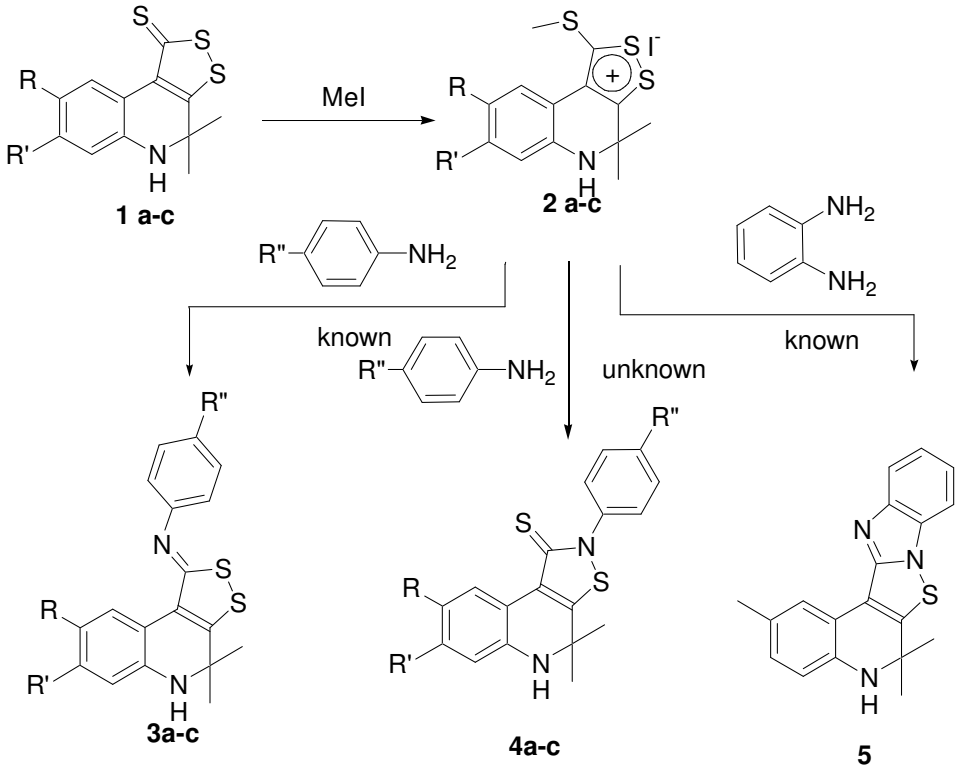
A series of novel (8-R-7-R'-4,4-dimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4(2)-R"-phenyl)amines were synthesized by reaction of 4,4-dimethyl-1-methylthio-4,5-dihydro[1,2]dithiolo[3,4-*c*]quinolin iodides with arylamines in an efficient manner. The Stolle type reaction of the obtained compounds with oxalyl chloride gave 2-R-3-R'-10-[(4(2)-R"-phenyl)imino]-7,7-dimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-diones. The structure of the synthesized compounds were characterized by NMR spectroscopy, mass-spectrometry and elemental analyses.



Keywords: Condensed 1,2-dithiol-3-thiones, 1,2-dithiolo[3,4-*c*]quinoline-1-thione, arylamines, 1,2-dithiol-3-imines, Stolle reaction, oxalyl chloride

Introduction

Condensed 1,2-dithiol-3-thiones represent an important class of organic compounds due to their wide spectrum of reactivity in diverse reaction types.[1-4] In particular, the 1,2-dithiol-3-thiones (or their salts) react with the N-nucleophiles with cycle cleavage and / or with substitution of one of the exo- or endocyclic sulfur atoms.[1-10] Basically, the reaction with primary aliphatic and aromatic amines tends not to be selective and leads to a mixture of 1,2-dithiol-3-imines and 1,2-thiazol-3-thiones, which exist in the "dynamic isomerism" due to transformation by Dimroth-type rearrangement.[11-16] Although we did not find any information about reactions of 4,5-dihydro-4,4-dimethyl-1*H*-1,2-dithiolo[3,4-*c*]quinoline-1-thiones **1** with amines, the reaction of their methylthio-dithiolium salts **2** with arylamines has been described earlier.[17] According to the author, the salts **2a,b** reacted with *p*-phenetidine in boiling ethanol with loss of a methyl mercaptan molecule to form a substituted 1,2-dithiol-3-imines **3a,b**.[17] As a result of this reaction, only two products were obtained with relatively low yields and their structure only being confirmed by elemental analysis. Later, one more compound **3c** was synthesized by a similar reaction of methylthio-dithiolium salt **2a** with aniline. IR spectroscopy was then used as an additional method in order to prove the structure.[18] However, this data is not sufficient to identify unequivocally the obtained products as 1,2-dithiol-3-imines **3a-c**, and not as isomeric 3-isothiazol-thiones **4a-c** (**Scheme 1**). Moreover, the low yields might be related to non-selectivity of the reaction, proceeding either on the exo-atom of sulfur or on endo-atom. No information about the synthesis of 4,4-dimethyl-2-aryl-4,5-dihydroisothiazolo[5,4-*c*]quinoline-1(2*H*)-thione **4** has been found in the literature. Although the possibility of dithiole cycle's endo-sulfur substitution by a nitrogen atom has been shown,[19] the interaction of methylthio-dithiolium salt **2c** with *o*-phenylenediamine yielding imidazathiazol **5** has been cited as the only example (Scheme 1).



2 R' = H; R = H (a)[17], OEt (b)[17], Me (c)

3 R' = H; R = H, R" = OEt (a)[17]; R = OEt, R" = OEt (b)[17]; R = R" = H (c)[18]

Scheme 1. Examples of methylthio-dithiolium salts **2a-c** reaction with arylamines.

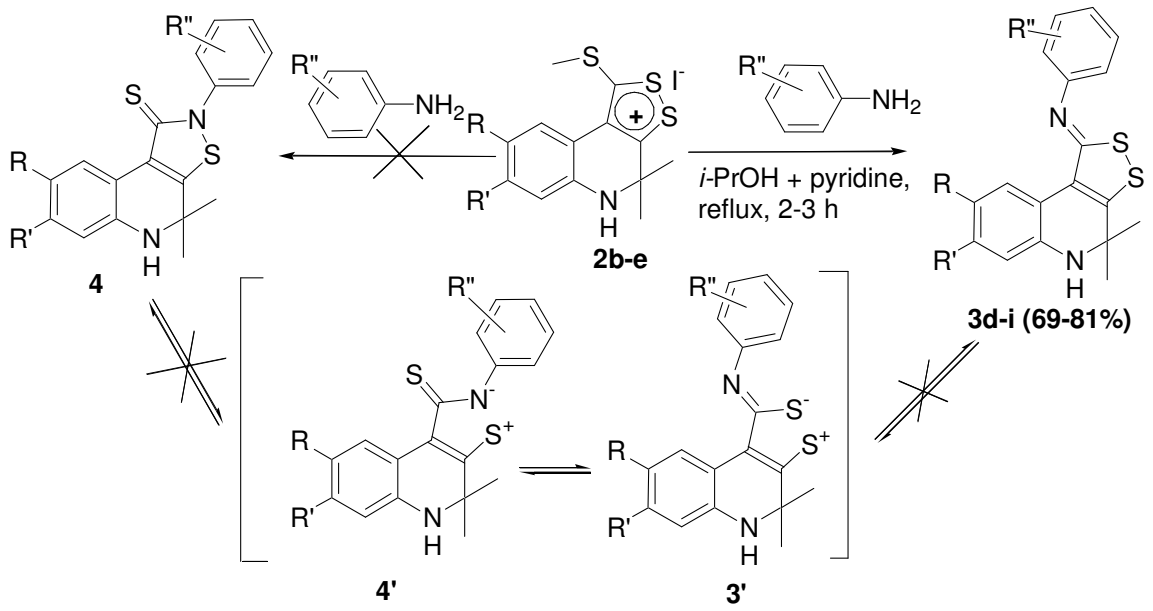
Thus, there is still no conclusive evidence that in the reaction of methylthio-dithiolium salts with arylamines the attack of amino groups targets exclusively the exo-sulfur atom. Therefore, the exact determination of the reaction products structure and chemical properties are of current interest.

Results and Discussion

In order to extend our studies of 1,2-dithiolo[3,4-*c*]quinoline-1-thione chemistry [20-24], we have carried out the reactions of 1,2-dithiolothiones **1** and their methylthiodithiolium salts **2** with arylamines. In addition, we optimized the conditions of the latter reaction, convincingly proved the structure of the resulting products and studied their chemical properties in the reaction of acylation by oxalyl chloride.

Reaction of 1,2-dithiolothiones 1 and their methylthiodithiolium salts 2 with arylamines. We have found that dithiolothiones **1b-c** do not react with arylamines in the absence of basic catalysts. When an alcoholic or aqueous solution of alkali was used, the reaction mixture turned into black tar. This is probably related to side reactions with the dithiol cycle cleavage.[17] Traces of the condensation product barely appeared in the reaction mixture even after long refluxing (more than 20 hours) of equimolar amounts of reagents in alcohol in the presence of excess pyridine or catalytic amounts of DMAP. Increasing of refluxing time (up to 100 hours) leads to decomposition of the reaction mass. Due to the good leaving group, the side processes for the corresponding iodides **2** were avoided. Thus, the optimal conditions for such interaction were refluxing of the equimolar amounts of reagents in an absolute isopropyl alcohol and in the presence of a two-fold molar excess of pyridine for 2-3 hours. It was found that the reaction proceeds selectively with the substitution of the *exo*-atom of sulfur to form the earlier unknown (8-R-7-R'-4,4-dimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4(2)-R"-phenyl)amines **3d-i** with quantitative yields (Scheme 2). Interestingly, the presence of bulky substituents in aryl amine, the position and the electronic properties of the substituent had no significant effect on the reaction time or product yield. We could not engage the endo-atom of sulfur in the reaction under any conditions. Increasing refluxing time up to 20 hours or using an excess of arylamine (up to 2.5 fold) leads to decomposition of the reaction mass, while increasing the temperature (by changing the solvent to 1-butanol) results in decrease of product yield along with the decomposition of starting iodomethylates **2b-c** to the corresponding 1,2-dithiol-3-thiones **1b-c**.

Our attempts to obtain 7-R'-8-R-4,4-dimethyl-2-(4(2)-R"-phenyl)-4,5-dihydroisothiazolo[5,4-*c*]quinoline-1(*2H*)-thiones **4** by Dimroth-type rearrangement through the formation of intermediate ions **3'**and **4'** were also unsuccessful (**Scheme 2**). We found that the 1,2-dithiol-3-imines fragment of compounds **3d-i** was resistant to a basic environment (treatment with aqueous alkali for 40 h) as well as to an acidic medium (heating at 40-50 °C for 20 h in alcoholic solution with an excess of hydrochloric acid). The stability of the dithiol cycle is obviously related to arylimino group polarity decline due to conjugation with condensed dihydroquinolines cycle.

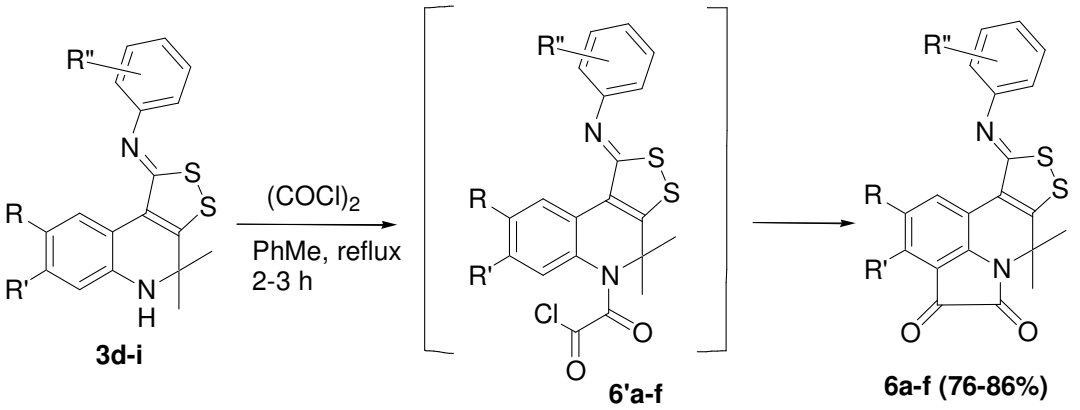


	R	R'
b	OEt	H
2c	Me	H
2d	OMe	H
2e	Me	Me

	R	R'	R"
3d	OEt	H	2-OEt
3e	OEt	H	4-(4-Cl-C_6H_4)CH_2O
3f	Me	H	4-COOEt
3g	Me	H	4-Ph
3h	OMe	H	4-OPentyl
3i	Me	Me	2-Pr

Scheme 2. Preparation of (8-R-7-R'-4,4-dimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4(2)-R"-phenyl)amines **3d-i**.

Reaction of imines 3d-i with oxalyl chloride. Earlier[23, 24] we performed the annelation of pyrroledione fragment to 2,3-dithiol[3,4-*c*]quinolin-1-thione in order to form a new polycondensed heterocyclic system – 10-thioxo-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-dione. In this paper, aiming to obtain new derivatives of this system, we have carried out a Stolle-type reaction[25, 26] of arylamines **3d-i** with oxalyl chloride. The reaction proceeded smoothly, similar to dithiolthiones **1**, by refluxing the substrates in absolute toluene for 1.5 -2 h without any catalyst, although the two-stage Stolle reaction requires the presence of Lewis acids.[25, 26] The hydrogen chloride, generated during acylation, catalyzes further cyclization of intermediate chloroxalylamides **6'a-f**. It was found that the presence of the substituent in position 7 of starting compound **3** does not create any steric hindrances for the cyclization. Thus, the new 2-R-3-R'-10-[(4(2)-R"-phenyl)imino]-7,7-dimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-diones **6a-f** were obtained in high yields (Scheme 3).



	R	R’	R”
6a	OEt	H	2-OEt
6b	OEt	H	4-(4-Cl-C_6H_4)CH_2O
6c	Me	H	4-COOEt
6d	Me	H	4-Ph
6e	OMe	H	4-OPentyl
6f	Me	Me	2-Pr

Scheme 3. Preparation of 2-R-3-R’-10-[(4(2)-R”-phenyl)imino]-7,7-dimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-diones **6a-f**.

Structure confirmation. The structure of compounds **3** and **6** were unambiguously proved by ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry. In ^{1}H NMR spectra of compounds **3d-l**, the signals of gem-dimethyl and secondary amino group protons appear in their respective fields.[20-22] The protons of arylimino fragments along with the protons of quinoline cycle show their signals in the aromatic field of spectrum. It should be noted that the arylimino-group, like thio-keto group of 2,3-dithiol[3,4-*c*]quinolin-1-thiones,[23, 24] exerts the anisotropic effect on the C(9)-H proton, shifting the corresponding signal in the weak field – up to 8.2-8.4 ppm. The presence of the characteristic signal of the imino group carbon atom [12, 27] at 166-168 ppm in the ^{13}C NMR spectra of the obtained compounds and the absence of peaks in the region of 183-185 ppm, corresponding to the signals of the thiocarbonyl group carbon atom [12, 27], have allowed us to assign them the structure of 1,2-dithiol-3-imines **3d-i** instead of isomeric isothiazol-3-thiones **4**. The peaks of molecular ion-radicals of medium and high intensity are observed in the mass spectra (EI) of imines **3d-i**. The fragment ions of compounds **3d, f-i**, formed by cleavage of methyl radical from molecular ion-radicals, are the peaks possessing maximum intensity (I_{rel} =100%). This kind of elimination is characteristic for disintegration of molecular ions of hydroquinoline derivatives with gem-dimethyl group in the second position. [28] As for compound **3e**, it is the fragment ion, formed by elimination of methyl and substituted benzyl radicals, which has the maximal intensity (I_{rel} =100%), and not the molecular ion-radical (I_{rel} =87%). It is interesting to note that the spectra of all synthesized compounds contain ion peaks of varying intensity (from I_{rel}=5% to I_{rel}=14%), formed by sequential elimination of methyl radical and corresponding aryl-isocyanide molecule from molecular ion-radicals, which confirms additionally the assigned structure. No secondary amino group proton signal is found in the ^{1}H NMR spectra of pyrroldiones **6a-f** (comparing to starting compounds **3d-i**), while a characteristic set of aromatic protons signals (though reduced by one proton) is still observed in the corresponding area. The ^{13}C-NMR spectra contain the signals of two carbon atoms (from carbonyl groups) at 161-164 ppm and 182-183

ppm. The mass spectra of compounds **6a-f** reveal the peaks of molecular ion-radicals with intensity from low (for **6a-e**) to maximal (for **6f**) (I_{rel}=14-100%). Their fragmentation occurs mostly by simultaneous elimination of methyl radical and CO molecule (for compounds **6a, c-f**), preceded by substituted benzyl radical elimination in the case of the compound **6b**.

Conclusions

4,4-Dimethyl-4,5-dihydro-1*H*-[1,2] dithiolo[3,4-*c*]quinoline-1-thiones react with arylamines only in the form of methylthiodithiolium salts at reflux in an alcoholic medium in the presence of pyridine, the reaction proceeds selectively with the substitution of exo-atom of sulfur to give (8-R-7-R'-4,4-dimethyl-4,5-dihydro-1H-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4(2)-R"-phenyl)amines. 1,2-Dithiol-3-imine fragment of latest retains stability and in the basic and in an acid medium at the expense of conjugation with a condensed dihydroquinoline cycle, making it impossible isomerizing these compounds into 7-R'-8-R-4,4-dimethyl-2-(4(2)-R"-phenyl)-4,5-dihydroisothiazolo[5,4-*c*]quinoline-1(2*H*)-thiones by the type Dimroth rearrangement. Reacting the resulting compounds with oxalyl chloride proceeds by Stolle type reaction without additional catalyst and leads to the formation of 2-R-3-R'-10-[(4(2)-R"-phenyl)imino]-7,7-dimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-diones in high yields even if there is of steric hindrance.

Experimental Section

General. Melting points were determined on a PTP-M apparatus. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer in DMSO-*d*6 at 400 and 100 MHz, respectively. TMS was used as the internal standard. Mass spectra were recorded on a Finnigan MAT Incos 50 instrument with direct introduction of sample into the ion source at 100-150 °C, with EI ionization and accelerating voltage of 70 eV. The results of elemental analysis for the obtained compounds correspond to calculated data (Perkin Elmer 2400). The reactions were monitored and the purity of the products were checked by TLC with Silufol UV-254 (silica gel STC-1A as the sorbent) using chloroform as the mobile phase. The starting 8-R-7-R'-4,4-dimethyl-1-methylthio-4,5-dihydro[1,2]dithiolo[3,4-*c*]quinoline iodides **2b-e** were synthesized according to known procedures.[17]

General procedure for the synthesis of (8-R-7-R'-4,4-dimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4(2)-R"-phenyl)amines (3d-i). A solution of iodides **2b-e** (1 mmol) and arylamine (1 mmol) was refluxed in a mixture of absolute isopropyl alcohol (10 mL) and pyridine (1.6 mL) for 2-3 hours until no more evolution methyl mercaptan was observed. The solvent was removed using the rotary evaporator, the solid product was crystallized from isopropyl alcohol.

(8-Ethoxy-4,4-dimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(2-ethoxyphenyl)amine (3d). Yellow crystals (0.284 g, 69%); mp 145-146 °C (isopropyl alcohol); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.20 (t, 3 H, *J* 7.3 Hz, $\underline{CH_3}CH_2O_{quinol}$), 1.24 (t, 3 H, *J* 6.9 Hz, CH_3), 1.38 (s, 6 H, $2CH_3$), 3.86 (q, 2 H, *J* 7.3 Hz, CH_2O_{quinol}), 4.02 (q, 2 H, *J* 6.9 Hz, CH_2O), 5.90 (br s, 1 H, NH), 6.66 (d, 1 H, *J* 8.4 Hz, H-6_{quinol}), 6.70 (d, 1 H, *J* 8.4 Hz, H-7_{quinol}), 6.92 - 6.95 (m, 2 H, Ar-H), 7.07 – 7.10 (m, 2 H, Ar-H), 8.33 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 15.2, 15.3, 27.7, 55.9, 64.05, 64.6, 111.3, 115.1, 115.2, 115.8, 119.2, 120.3, 122.0, 123.2, 126.2, 137.4, 141.9, 149.5, 151.0, 161.3, 167.5; MS (EI) *m/z* (%): 412 (M^+, 65), 397 (100), 275 (10), 222 (6), 168 (17), 154 (10). *Anal*. Calcd. for $C_{22}H_{24}N_2O_2S_2$ (412.57): C, 64.05; H, 5.86; N, 6.79; S, 15.54 %. Found: C, 63.92; H, 5.72; N, 6.93; S, 12.68 %.

(8-Ethoxy-4,4-dimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)[4-[(4-chlorobenzyl)oxy-phenyl]amine (3e). Yellow crystals (0.372 g, 73%); mp 153-154 °C (isopropyl alcohol); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.22 (t, 3 H, *J* 7.0 Hz, CH_3), 1.37 (s, 6 H, $2CH_3$), 3.84 (q, 2 H, *J* 7.0 Hz, CH_2O), 5.08 (s, 2 H, CH_2), 5.90 (br s, 1 H, NH), 6.65 (d, 1 H, *J* 8.4 Hz, H-6_{quinol}), 6.70 (d, 1 H, *J* 8.4 Hz, H-7_{quinol}), 6.96 (d, 2 H, *J* 8.0 Hz, Ar-H), 7.05 (d, 2, *J* 8.3 Hz, Ar-H), 7.42 (d, 2 H, *J* 8.0 Hz, Ar-H), 7.47 (d, 2, *J* 8.3 Hz, Ar-H), 8.24 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 15.35, 27.7, 55.8, 64.0, 69.4, 111.1, 115.1, 115.8, 116.8, 119.1, 121.4, 123.3, 128.95, 129.95, 133.0, 136.8, 137.4, 146.2, 150.95, 156.0, 161.1, 167.2; MS (EI) *m/z* (%): 509 (M^+, 87), 494 (88), 397 (7), 384 (9), 369 (100), 319 (6), 244 (60), 228 (14), 216 (13), 199 (10), 173 (10). *Anal*. Calcd. for $C_{27}H_{25}ClN_2O_2S_2$ (509.08): C, 63.70; H, 4.95; N, 5.50; S, 12.60 %. Found: C, 63.59; H, 5.62; N, 5.38; S, 12.74 %.

(4,4,8-Trimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4-ethoxycarbonylphenyl)amine (3f). Yellow crystals (0.312 g, 76%); mp 220-221 °C (isopropyl alcohol); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.29 (t, 3 H, *J* 7.2 Hz, $\underline{CH_3}CH_2$), 1.39 (s, 6 H, $2CH_3$), 2.13 (s, 3 H, CH_3), 4.28 (q, 2 H, *J* 7.2 Hz, CH_2), 6.10 (br s, 1 H, NH), 6.65 (d, 1 H, *J* 8.1 Hz, H-6_{quinol}), 6.87 (d, 1 H, *J* 8.1 Hz, H-7_{quinol}), 7.12 (d, 2 H, *J* 7.8 Hz, Ar-H), 7.98 (d, 2, *J* 7.8 Hz, Ar-H), 8.34 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.7, 22.2, 27.8, 55.8, 61.05, 114.6, 118.0, 120.4, 123.6, 124.3, 125.8, 126.6, 129.8, 131.9, 141.2, 156.6, 161.6, 165.9, 168.4; MS (EI) *m/z* (%): 410 (M^+, 37), 395 (100), 367 (28), 321 (4), 183 (6), 175 (15), 156 (15). *Anal*. Calcd. for $C_{22}H_{22}N_2O_2S_2$ (410.55): C, 64.36; H, 5.40; N, 6.82; S, 15.64 %. Found: C, 64.21; H, 5.51; N, 6.74; S, 15.50 %.

(4,4,8-Trimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4-phenylphenyl)amine (3g). Yellow crystals (0.335 g, 81%); mp 209-210 °C (isopropyl alcohol); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.39 (s, 6 H, $2CH_3$), 2.15 (s, 3 H, CH_3), 6.10 (br s, 1 H, NH), 6.67 (d, 1 H, *J* 8.1 Hz, H-6_{quinol}), 6.88 (d, 1 H, *J* 8.1 Hz, H-7_{quinol}), 7.10 (d, 2 H, *J* 7.7 Hz, Ar-H), 7.32 (t, 1 H, *J* 7.4 Hz, Ph-H), 7.43 (t, 2 H, *J* 7.4 Hz, Ph-H), 7.65 (t, 2 H, *J* 7.4 Hz, Ph-H), 7.65 (d, 2 H, *J* 7.4 Hz, Ph-H),7.71 (d, 2, *J* 7.7 Hz, Ar-H), 8.42 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 27.9, 55.75, 114.5, 118.2, 120.8, 123.5, 124.4, 125.8, 126.9, 127.7, 128.7, 129.4, 129.7, 137.1, 140.3, 141.2, 152.0, 160.8, 167.7; MS (EI) *m/z* (%): 414 (M^+, 23), 399 (100), 220 (14), 213 (9), 199 (8), 156 (6). *Anal*. Calcd. for $C_{25}H_{22}N_2S_2$ (414.59): C, 72.43; H, 5.35; N, 6.76; S, 15.47 %. Found: C, 72.56; H, 5.41; N, 6.63; S, 15.61 %.

(8-Methoxy-4,4-dimethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(4-pentyloxyphenyl)amine (3h). Yellow crystals (0.312 g, 71%); mp 154-155 °C (isopropyl alcohol); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (t, 3 H, *J* 7.3 Hz, $\underline{CH_3}$), 1.30 – 1.35 (m, 4 H, $2CH_2$), 1.37 (s, 6 H, $2CH_3$), 1.65 – 1.70 (m, 2 H, $\underline{CH_2}CH_2O$), 3.32 (s, 3 H, CH_3O), .3.91 (t, 2 H, *J* 6.6 Hz, CH_2O), 5.91 (br s, 1 H, NH), 6.67 (d, 1 H, *J* 8.4 Hz, H-6_{quinol}), 6.71 (d, 1 H, *J* 8.4 Hz, H-7_{quinol}), 6.93 - 6.97 (m, 4 H, Ar-H), 8.29 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.3, 22.3, 27.6, 27.7. 28.3, 29.0, 55.8, 56.0, 68.4, 110.3, 115.0, 115.1, 116.3, 119.1, 121.4, 123.3, 137.5, 145.6, 151.8, 156.6, 161.0, 166.8; MS (EI) *m/z* (%): 440 (M^+, 35), 425 (100), 365 (7), 236 (8), 230 (22). *Anal*. Calcd. for $C_{24}H_{28}N_2O_2S_2$ (440.62): C, 65.42; H, 6.41; N, 6.36; S, 14.55 %. Found: C, 65.28; H, 6.52; N, 6.24; S, 14.61 %.

(4,4,7,8-Tetramethyl-4,5-dihydro-1*H*-[1,2]dithiolo[3,4-*c*]quinolin-1-ylidene)(2-propoxyphenyl)amine (3i). Yellow crystals (0.303 g, 74%); mp 165-166 °C (isopropyl alcohol); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3 H, *J* 7.7 Hz, $\underline{CH_3}CH_2$), 1.37 (s, 6 H, $2CH_3$), 1.59 – 1.62 (m, 2 H, CH_2), 2.04 (s, 3 H, CH_3-7), 2.10 (s, 3 H, CH_3-8), 3.91 (t, 2 H, *J* 6.3 Hz, CH_2O), 5.96 (br s, 1 H, NH), 6.53 (s, 1 H, H-6_{quinol}), 6.92 - 6.94 (m, 2 H, Ar-H), 7.06 – 7.09 (m, 2 H, Ar-H), 8.41 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 10.8, 19.5, 20.2, 22.6, 27.8, 55.7, 70.2, 114.9, 115.6, 116.1, 120.35, 122.0, 123.2, 124.55, 125.0, 126.2, 137.0, 141.5, 142.1, 149.4, 159.3, 168.1; MS (EI) *m/z* (%): 410 (M^+, 40), 395 (100), 352 (5), 319 (5), 288 (14), 234 (9), 170 (8), 160 (15). *Anal*. Calcd. for $C_{23}H_{26}N_2OS_2$ (410.60): C, 67.28; H, 6.38; N, 6.82; S, 15.62 %. Found: C, 67.14; H, 6.51; N, 6.93; S, 15.75 %.

General procedure for the synthesis of 2-R-3-R'-10-[(4(2)-R"-phenyl)imino]-7,7-dimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-diones (6a-f). Oxalyl chloride (1,1 mmol) was added

to a solution of 1,2-dithiol-3-imine **3d-i** (1 mmol) in absolute toluene (50 mL) and refluxed for 1,5-2 hours while the reaction progress was monitored by TLC. The solvent was removed using the rotary evaporator; the solid product was crystallized from toluene.

2-Ethoxy-10-[(2-ethoxyphenyl)imino]-7,7-dimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-dione (6a). Dark red crystals (0.354 g, 76%); mp 166-167 °C (toluene); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.21 (t, 3 H, *J* 7.2 Hz, $\underline{CH_3}CH_2O_{quinol}$), 1.24 (t, 3 H, *J* 7.0 Hz, CH_3), 1.95 (s, 6 H, $2CH_3$), 3.96 (q, 2 H, *J* 7.2 Hz, CH_2O_{quinol}), 4.03 (q, 2 H, *J* 7.0 Hz, CH_2O), 6.98 – 7.02 (m, 3 H, 2 Ar-H + 1 H-7_{quinol}), 7.06 – 7.13 (m, 2 H, Ar-H), 8.64 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 15.0, 15.2, 27.9, 61.05, 64.7, 64.8, 108.4, 115.2, 116.2, 117.0, 119.7, 119.9, 120.0, 121.95, 126.9, 140.9, 141.7, 149.7, 155.6, 158.3, 163.8, 166.0, 182.5 ; MS (EI) *m/z* (%): 466 (M^+, 67), 433 (28), 423 (100), 405 (8), 368 (7), 309 (5), 273 (8), 212 (21), 181 (15), 167 (20). *Anal*. Calcd. for $C_{24}H_{22}N_2O_4S_2$ (466.57): C, 61.78; H, 4.75; N, 6.00; S, 13.75 %. Found: C, 61.56; H, 4.62; N, 6.11; S, 13.52 %.

10-({4-[(4-Chlorobenzyl)oxy]phenyl}imino)-2-ethoxy-7,7-dimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo-[3,2,1-*ij*]quinoline-4,5-dione (6b). Dark red crystals (0.456 g, 81%); mp 165-166 °C (toluene); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.25 (t, 3 H, *J* 7.0 Hz, CH_3), 1.94 (s, 6 H, $2CH_3$), 3.97 (q, 2 H, *J* 7.0 Hz, CH_2O), 5.09 (s, 2 H, CH_2), 6.99 (s, 1 H, H-7_{quinol}), 7.01 (d, 2 H, *J* 8.0 Hz, Ar-H), 7.06 (d, 2, *J* 8.4 Hz, Ar-H), 7.42 (d, 2 H, *J* 8.0 Hz, Ar-H), 7.47 (d, 2, *J* 8.4 Hz, Ar-H), 8.53 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 15.0, 27.9, 40.9, 61.0, 64.8, 69.5, 108.5, 116.3, 116.9, 119.4, 120.05, 121.4, 128.95, 129.9, 133.0, 136.7, 141.6, 145.4, 153.6, 155.5, 156.4, 158.3, 163.8, 165.9, 182.5; MS (EI) *m/z* (%): 563 (M^+, 26), 437 (87), 395 (10), 366 (8), 253 (25), 125 (100). *Anal*. Calcd. for $C_{29}H_{23}ClN_2O_4S_2$ (563.09): C, 61.86; H, 4.12; N, 4.97; S, 11.39 %. Found: C, 62.00; H, 4.21; N, 5.10; S, 11.43 %.

10-[(4-Ethoxycarbonylphenyl)imino]-2,7,7-trimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]-quinoline-4,5-dione (6c). Dark red crystals (0.399 g, 86%); mp 232-233 °C (toluene); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.30 (t, 3 H, *J* 7.4 Hz, $\underline{CH_3}CH_2$), 1.96 (s, 6 H, $2CH_3$), 2.24 (s, 3 H, CH_3), 4.29 (q, 2 H, *J* 7.4 Hz, CH_2), 7.19 (d, 2 H, *J* 8.8 Hz, Ar-H), 7.28 (s, 1 H, H-7_{quinol}), 8.02 (d, 2 H, *J* 8.8 Hz, Ar-H), 8.69 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.7, 21.2, 27.95, 61.0, 61.2, 100.0, 115.6, 116.1, 120.4, 120.5, 124.2, 127.2, 131.55, 131.9, 132.95, 145.3, 155.9, 158.4, 164.3, 165.8, 167.6, 182.5; MS (EI) *m/z* (%): 464 (M^+, 14), 420 (100), 393 (5), 363 (6), 211 (5), 197 (5), 188 (11). *Anal*. Calcd. for $C_{24}H_{20}N_2O_4S_2$ (464.56): C, 62.05; H, 4.34; N, 6.03; S, 13.80 %. Found: C, 62.19; H, 4.37; N, 6.14; S, 13.68 %.

10-(Biphenyl-4-ylimino)-2,7,7-trimethyl-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-dione (6d). Dark red crystals (0.393 g, 84%); mp 227-228 °C (toluene); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.96 (s, 6 H, $2CH_3$), 2.25 (s, 3 H, CH_3), 7.15 (d, 2 H, *J* 8.0 Hz, Ar-H), 7.28 (s, 1 H, H-7_{quinol}), 7.35 (t, 1 H, *J* 7.7 Hz, Ph-H), 7.45 (t, 2 H, *J* 7.7 Hz, Ph-H), 7.68 (t, 2 H, *J* 7.7 Hz, Ph-H), 7.75 (d, 2 H, *J* 8.0 Hz, Ph-H), 8.76 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 27.9, 61.1, 115.8, 116.1, 120.4, 120.7, 124.1, 126.95, 127.8, 128.8, 129.5, 131.7, 132.9, 137.7, 140.1, 145.3, 151.15, 158.4, 163.5, 166.6, 182.6; MS (EI) *m/z* (%): 468 (M^+, 73), 425 (100), 396 (8), 363 (6), 348 (6), 213 (14), 152 (33). *Anal*. Calcd. for $C_{27}H_{20}N_2O_2S_2$ (468.59): C, 69.20; H, 4.30; N, 5.98; S, 13.69 %. Found: C, 69.33; H, 4.43; N, 6.11; S, 13.58 %.

2-Methoxy-7,7-dimethyl-10-{[4-(pentyloxy)phenyl]imino}-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-dione (6e). Dark red crystals (0.390 g, 79%); mp 189-190 °C (toluene); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.87 (t, 3 H, *J* 7.8 Hz, $\underline{CH_3}$), 1.30 – 1.35 (m, 4 H, $2CH_2$), 1.65 – 1.70 (m, 2 H, $\underline{CH_2}CH_2O$), 1.94 (s, 6 H, $2CH_3$), 3.71 (s, 3 H, CH_3O), .3.94 (t, 2 H, *J* 6.8 Hz, CH_2O), 6.93 – 7.07 (m, 5 H, 4 Ar-H + 1 H-7_{quinol}), 8.57 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.3, 22.3, 27.85, 28.2, 28.9, 56.6, 61.0, 68.5, 107.8, 116.3, 116.45, 117.0, 118.8, 120.05, 121.45, 141.7, 144.8, 156.4, 157.0. 158.3, 163.6, 165.4, 182.5; MS (EI) *m/z* (%): 494 (M^+, 72), 451 (100), 422 (5), 274 (5), 239 (5), 190 (7). *Anal*. Calcd. for $C_{26}H_{26}N_2O_4S_2$ (494.63): C, 63.13; H, 5.30; N, 5.66; S, 12.97 %. Found: C, 63.01; H, 5.17; N, 5.79; S, 13.11 %.

2,3,7,7-Tetramethyl-10-[(2-propoxyphenyl)imino]-7,10-dihydro[1,2]dithiolo[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4,5-dione (6f). Dark red crystals (0.362 g, 78%); mp 145-146 °C (toluene); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3 H, *J* 7.3 Hz, $\underline{CH_3}CH_2$), 1.59 – 1.62 (m, 2 H, CH_2), 1.92 (s, 6 H, $2CH_3$), 2.10 (s, 3 H, CH_3-8), 2.35 (s, 3 H, CH_3-8), 3.92 (t, 2 H, *J* 6.3 Hz, CH_2O), 6.95 – 7.01 (m, 2 H, Ar-H), 7.08 – 7.14 (m, 2 H, Ar-H), 8.77 (s, 1 H, H-9_{quinol}); ^{13}C NMR (100 MHz, DMSO-d_6): δ 10.7, 14.6, 18.8, 22.7, 27.7, 60.9, 70.65, 113.3, 114.6, 115.4, 120.1, 120.2, 122.0, 126.7, 131.7, 132.0, 138.1, 141.4, 145.3, 149.65, 158.2, 161.7, 166.7, 183.3; MS (EI) *m/z* (%): 464 (M^+, 100), 431 (50), 420 (92), 379 (17), 350 (18), 317 (28), 285 (18), 244 (10), 173 (10). *Anal*. Calcd. for $C_{25}H_{24}N_2O_3S_2$ (464.60): C, 64.63; H, 5.21; N, 6.03; S, 13.80 %. Found: C, 64.50; H, 5.31; N, 6.14; S, 13.94 %.

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