## Synthesis of novel 3-(1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones

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An efficient method for the synthesis of novel 3-(1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1H,6H)-diones from various 2-dimethylaminomethylidenecyclohexane-1,3-diones, (1,3-thiazol-2-yl)acetonitriles, and dimethylformamide dimethyl acetal was developed. These transformations proceeded through intermediate 2-[2-(4-aryl-1,3-thiazol-2-yl)-2-cyanoethenyl]-3-oxocyclohex-1-en-1-olates. They were isolated as piperidinium salts and used in further heterocyclization reactions with aromatic amines, giving novel 1-aryl-3-(1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1H,6H)-diones. These compounds were also obtained by preparative three-step "one pot" synthesis under controlled microwave irradiation.

**Key words:** 3-(1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones, cyclization, 2-[2-cyano-2-(1,3-thiazol-2-yl)ethenyl]-3-oxocyclohex-1-enolates, aromatic amines, micro-wave irradiation, nuclear Overhauser effect.

An important problem that organic chemists are faced with today is development of methods for the synthesis of compounds with desired properties and creation of combinatorial libraries of compounds with potential biological activity. Some 3-(1,3-thiazol-2-yl)pyridin-2(1*H*)-ones have been found to act as selective GABA<sub>A</sub> antagonists<sup>1</sup> and anxiolytics.<sup>2-4</sup> That is the reason why the synthesis of novel derivatives combining 2-pyridone and 1,3-thiazole fragments is of current interest.

## **Results and Discussion**

One of the methods of constructing the pyridin-2(1H)one ring involves reactive enamines prepared by condensation of various dicarbonyl compounds with dimethylformamide dimethyl acetal (DMFDMA). We used (Scheme 1) 2-dimethylaminomethylidenecyclohexane-1,3-diones 2a-d (prepared from cyclohexane-1,3-diones 1a-d and DMFDMA) as starting materials for our present work. Their structure allows variation of the substituent in the dicarbonyl component, and the dimethylaminomethylidene fragment may be involved in reactions with various active methylene nitriles to form the pyridone ring<sup>5</sup>.

Here we studied transformations of some cyclohexane-1,3-diones 1a-d in reactions with (1,3-thiazol-2-yl)acetonitriles 3a-e.

Reactions of 2-dimethylaminomethylidenecyclohexane-1,3-diones<sup>5</sup> 2a-d with nitriles 3a-d in boiling





1, 2:  $R^1 = R^2 = H$  (a);  $R^1 = R^2 = Me$  (b);  $R^1 = H, R^2 = 4-MeOC_6H_4$  (c);  $R^1 = H, R^2 = 2$ -furyl (d)

Bu<sup>n</sup>OH (method *A*) in the presence of catalytic amounts of piperidine for 10 min yielded 3-(4-aryl-1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones **4** in the individual state (Scheme 2; Tables 1, 2). A previously described microwave-assisted method<sup>6</sup> for the synthesis of various pyridin-2(1*H*)-ones<sup>5</sup> is also applicable for the preparation of these compounds. For instance, irradiation of the reaction mixture in Pr<sup>i</sup>OH at 100 °C for 5 min (method *B*) also gave the target products **4** (see Scheme 2). Their yields were slightly higher (see Table 1) and no

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Scheme 2



**Reagents and conditions:** *i*. Bu<sup>n</sup>OH, piperidine, reflux, 10 min (method *A*). *ii*. Pr<sup>i</sup>OH, piperidine, microwave irradiation, 100 °C, 5 min (method *B*). *iii*. Pr<sup>i</sup>OH, piperidine, 20 °C. *iv*. AcOH, reflux.

3	R <sup>3</sup>	$R^4$	4	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	$R^4$	5	$R^1$	R <sup>2</sup>	R <sup>3</sup>	$R^4$
а	4-CIC <sub>6</sub> H <sub>4</sub>	Н	а	Н	Н	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Н	а	Me	Me	4-CIC <sub>6</sub> H <sub>4</sub>	Н
b	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Н	b	Me	Me	4-EtOC <sub>6</sub> H <sub>4</sub>	Н	b	Н	4-MeOC <sub>6</sub> H <sub>4</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Н
С	4-EtOC <sub>6</sub> H <sub>4</sub>	Н	С	Н	4-MeOC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	Me					
d	4-MeC <sub>6</sub> H <sub>4</sub>	Me	d	Н	2-Furyl	4-CIC <sub>6</sub> H <sub>4</sub>	Н					

Com- pound	M.p /°C	Yie (2	Yield* (%)		<u>Found</u> (%) Calculated			
		A	В	С	Н	Ν	S	
<b>4</b> a	298-301	52	61	<u>58.79</u> 58.85	<u>3.68</u> 3.57	<u>11.69</u> 11.44	<u>8.83</u> 8.73	$C_{18}H_{13}N_3O_4S$
4b	285—288	51	63	<u>66.66</u> 66.98	<u>5.64</u> 5.62	$\frac{7.31}{7.10}$	<u>7.61</u> 8.13	$C_{22}H_{22}N_2O_3S$
4c	283—285	55	68	<u>71.41</u> 71.03	<u>5.40</u> 5.30	<u>6.42</u> 6.14	<u>6.59</u> 7.02	$C_{27}H_{24}N_2O_3S$
4d	294—296	50	55	<u>62.55</u> 62.49	<u>3.62</u> 3.58	<u>6.81</u> 6.62	<u>7.49</u> 7.58	$C_{22}H_{15}ClN_2O_3S$
5a	278-280	7	8	<u>64.22</u> 64.02	<u>5.75</u> 5.80	<u>9.02</u> 8.96	<u>6.81</u> 6.84	$C_{25}H_{28}ClN_3O_2S$
5b	291-292	7	3	<u>64.34</u> 64.62	<u>5.30</u> 5.24	$\frac{10.33}{10.05}$	<u>5.52</u> 5.75	$C_{30}H_{30}N_4O_5S$
7a	307-309	—	76	<u>61.91</u> 61.79	<u>4.18</u> 4.19	<u>5.60</u> 5.54	<u>6.14</u> 6.34	$C_{26}H_{21}BrN_2O_2S$
7b	297-300	57	79	<u>68.22</u> 68.27	<u>4.92</u> 4.88	<u>6.04</u> 5.90	<u>6.55</u> 6.75	$C_{27}H_{23}ClN_2O_2S$
7c	283-285	—	74	<u>71.10</u> 71.16	<u>5.44</u> 5.33	<u>6.06</u> 5.93	<u>6.19</u> 6.78	$\mathrm{C}_{28}\mathrm{H}_{25}\mathrm{FN}_{2}\mathrm{O}_{2}\mathrm{S}$
7 <b>d</b>	250-251	48	69	<u>64.75</u> 64.86	<u>4.21</u> 4.14	<u>6.13</u> 6.05	<u>6.77</u> 6.93	$C_{25}H_{19}ClN_2O_3S$
7e	284—286	55	73	<u>70.06</u> 70.27	<u>5.06</u> 5.03	<u>4.98</u> 4.82	<u>5.48</u> 5.52	C <sub>34</sub> H <sub>29</sub> ClN <sub>2</sub> O <sub>3</sub> S

Table 1. Selected physicochemical characteristics of compounds 4, 5, and 7

\* With respect to cyclohexane-1,3-dione derivatives.

Table 2. IR and	<sup>1</sup> H NMR spectra	of compounds 4	, <b>5</b> , and <b>7</b>

Com- pound	IR, v/cm <sup>-1</sup>	<sup>1</sup> H NMR, δ ( <i>J</i> /Hz)
4a	3359 (N-H); 2852 (C(sp <sup>3</sup> )-H); 1647 (C=O); 1528 (as-NO <sub>2</sub> ); 1347 (s-NO <sub>2</sub> )	1.96–2.18 (m, 2 H); 2.52, 2.91 (both t, 2 H each, $J = 5.9$ ); 7.75 (t, 1 H, H(5) <sub>Ar(2)</sub> , $J = 8.2$ ); 8.20 (d, 1 H, H(4) <sub>Ar(2)</sub> , $J = 8.2$ ); 8.35–8.56 (m, 2 H, H arom.); 8.80 (s, 1 H); 8.89 (s, 1 H, H(4)); 12.83 (s, 1 H, NH)
4b	3342 (N–H); 2968 (C(sp <sup>3</sup> )–H); 1647 (C=O); 1244 (C <sub>Ar</sub> –O–C)	1.03 (s, 6 H, 2 Me); 1.33 (t, 3 H, $C\underline{H}_3CH_2$ , $J = 7.0$ ); 2.42, 2.80 (both s, 2 H each); 4.05 (q, 2 H, $CH_3C\underline{H}_2$ , $J = 7.0$ ); 6.99 (d, 2 H, $H(3)_{Ar(2)}$ , $H(5)_{Ar(2)}$ , $J = 8.9$ ); 7.81–8.02 (m, 3 H); 8.86 (s, 1 H, H(4)); 12.83 (s, 1 H, NH)
4c	3418 (N–H); 2919 (C(sp <sup>3</sup> )–H); 1650 (C=O); 1514 (C=N)	2.35, 2.56 (both s, 3 H each, Me); 2.61–2.69 (m, 1 H); 2.76–3.18 (m, 3 H); 3.40–3.54 (m, 1 H); 3.72 (s, 3 H, MeO); 6.90 (d, 2 H, $H_{Ar(1)}$ , $J = 8.5$ ); 7.12–7.41 (m, 4 H, H arom.); 7.63 (d, 2 H, $H_{Ar(2)}$ , $J = 7.9$ ); 8.79 (s, 1 H, H(4)); 12.87 (s, 1 H, NH)
4d	3401 (N–H); 2929 (C(sp <sup>3</sup> )–H); 1643 (C=O); 748 (C–Cl)	2.71–2.92, 3.02–3.25 (both m, 2 H each); 3.61–3.80 (m, 1 H); 6.18 (d, 1 H, $J = 2.9$ ); 6.38 (s, 1 H); 7.39–7.69 (m, 3 H, H arom.); 8.07 (d, 2 H, H arom., $J = 8.4$ ); 8.20 (s, 1 H, H <sub>Tz</sub> ); 8.88 (s, 1 H, H(4)); 12.97 (s, 1 H, NH)
5a	2955 (C(sp <sup>3</sup> )—H); 2200 (CN); 1546 (C=O); 1505 (C=N)	0.94 (s, 6 H, 2 Me); 1.32–1.82 (m, 7 H); 2.10–2.18 (m, 3 H); 2.86–3.04 (m, 4 H); 7.47 (d, 2 H, H(3) <sub>Ar(2)</sub> , H(5) <sub>Ar(2)</sub> , $J = 8.7$ ); 7.80 (s, 1 H); 7.95 (d, 2 H, H(2) <sub>Ar(2)</sub> , H(6) <sub>Ar(2)</sub> , $J = 8.7$ ); 8.13 (s, 1 H)
5b	2956 (C(sp <sup>3</sup> )–H); 2220 (CN); 1551 (C=O); 1534 (as-NO <sub>2</sub> ); 1374 (s-NO <sub>2</sub> )	1.30–1.80 (m, 6 H); 2.32–2.45, 2.49–2.65 (both m, 2 H each); 2.88–3.08 (m, 4 H); 3.10–3.24 (m, 1 H); 3.71 (s, 3 H, MeO); 6.84 (d, 2 H, H(3) <sub>Ar(1)</sub> , H(5) <sub>Ar(1)</sub> , $J = 8.6$ ); 7.22 (d, 2 H, H(2) <sub>Ar(1)</sub> , H(6) <sub>Ar(1)</sub> , $J = 8.6$ ); 7.73 (t, 1 H, H(5) <sub>Ar(2)</sub> , $J = 8.1$ ); 8.00–8.28 (m, 3 H, H arom.); 8.38 (d, 1 H, H(6) <sub>Ar(2)</sub> , $J = 8.1$ ); 8.74 (s, 1 H)
7a	2956 (C(sp <sup>3</sup> )–H); 1663 (C=O); 1540 (C=N); 1229 (C <sub>Ar</sub> –N)	0.96 (s, 6 H, 2 Me); 2.32–2.45 (m, 4 H); 7.44 (d, 2 H, $H_{Ar(3)}$ , $J = 7.3$ ); 7.51–7.76 (m, 5 H, H arom.); 8.03 (d, 2 H, $H(2)_{Ar(2)}$ , $H(6)_{Ar(2)}$ , $J = 8.2$ ); 8.24 (s, 1 H, $H_{Tz}$ ); 9.06 (s, 1 H, H(4))
7b	2956 (C(sp <sup>3</sup> )–H); 1657 (C=O); 1541 (C=N); 1224 (C <sub>Ar</sub> –N); 758 (C–Cl)	0.94 (s, 6 H, 2 Me); 2.41 (s, 4 H); 2.47 (s, 3 H, Me); 7.28 (d, 2 H, H(3) <sub>Ar(3)</sub> , H(5) <sub>Ar(3)</sub> , $J = 8.3$ ); 7.41 (d, 2 H, H(2) <sub>Ar(3)</sub> , H(6) <sub>Ar(3)</sub> , $J = 8.3$ ); 7.52 (d, 2 H, H(3) <sub>Ar(2)</sub> , H(5) <sub>Ar(2)</sub> , $J = 8.6$ ); 8.07 (d, 2 H, H(2) <sub>Ar(2)</sub> , H(6) <sub>Ar(2)</sub> , $J = 8.6$ ); 8.20 (s, 1 H, H <sub>Tz</sub> ); 9.04 (s, 1 H, H(4))
7c	2955 (C(sp <sup>3</sup> )—H); 1664 (C=O); 1544 (C=N); 1232 (C <sub>Ar</sub> —N)	0.95 (s, 6 H, 2 Me); 2.35 (s, 3 H, Me); 2.42 (s, 4 H); 2.54 (s, 3 H, Me); 7.29 (d, 2 H, H(3) <sub>Ar(2)</sub> , H(5) <sub>Ar(2)</sub> , $J = 8.2$ ); 7.38–7.58 (m, 4 H, H arom.); 7.64 (d, 2 H, H(2) <sub>Ar(2)</sub> , H(6) <sub>Ar(2)</sub> , $J = 8.2$ ); 8.92 (s, 1 H, H(4))
7d	2853 (C(sp <sup>3</sup> )–H); 1654 (C=O); 1540 (C=N); 1274 (C <sub>Ar</sub> –N); 774 (C–Cl)	1.90–2.11 (m, 2 H); 2.49–2.67 (m, 4 H); 3.83 (s, 3 H, MeO); 7.12 (d, 2 H, H(3) <sub>Ar(3)</sub> , H(5) <sub>Ar(3)</sub> , $J = 8.9$ ); 7.35 (d, 2 H, H(2) <sub>Ar(3)</sub> , H(6) <sub>Ar(3)</sub> , $J = 8.9$ ); 7.53 (d, 2 H, H(3) <sub>Ar(2)</sub> , H(5) <sub>Ar(2)</sub> , $J = 8.7$ ); 8.07 (d, 2 H, H(2) <sub>Ar(2)</sub> , H(6) <sub>Ar(2)</sub> , $J = 8.7$ ); 8.20 (s, 1 H, H <sub>Tz</sub> ); 9.04 (s, 1 H, H(4))
7e	2958 (C(sp <sup>3</sup> )—H); 1660 (C=O); 1542 (C=N); 752 (C—Cl)	1.21 (d, 6 H, 2 Me (Pr <sup>i</sup> ), $J = 6.9$ ); 2.33–2.47, 2.53–2.69 (both m, 1 H each, CH); 2.77–3.04 (m, 3 H); 3.38–3.52 (m, 1 H); 3.67 (s, 3 H, MeO); 6.82 (d, 2 H, H(3) <sub>Ar(1)</sub> , H(5) <sub>Ar(1)</sub> , $J = 8.7$ ); 7.15 (d, 2 H, H(2) <sub>Ar(1)</sub> , H(6) <sub>Ar(1)</sub> , $J = 8.7$ ); 7.21–7.48 (m, 4 H); 7.53, 8.09 (both d, 2 H each, H arom., $J = 8.6$ ); 8.23 (s, 1 H, H <sub>Tz</sub> ); 9.08 (s, 1 H, H(4))

*Note.* In the <sup>1</sup>H NMR spectra, Ar(1) is the aryl substituent in position 7 of 7,8-dihydroquinoline-2,5(1*H*,6*H*)-dione, Ar(2) is the aryl substituent in position 4 of the 1,3-thiazole fragment, and Ar(3) is the aryl substituent in position 1 of 7,8-dihydroquinoline-2,5(1*H*,6*H*)-dione.

additional purification was required. It should be emphasized that in all these transformations, it is necessary to prepare firstly 2-dimethylaminomethylidenecyclohexane-1,3-diones 2a-d by condensation of cyclohexane-1,3diones 1a-d with DMFDMA and use them in the following reactions without isolation. At the same time, mixing of all three reaction components (cyclohexane-1,3dione, DMFDMA, and (1,3-thiazol-2-yl)acetonitrile) can result in the formation of nitrile–DMFDMA adducts that are inert to 1,3-dicarbonyl compounds.<sup>5</sup> Interestingly, the room-temperature reaction in the presence of an equivalent amount of piperidine gave piperidinium 2-[2-(4-aryl-1,3-thiazol-2-yl)-2-cyano-ethenyl]-3-oxocyclohex-1-en-1-olates **5a,b** (see Tables 1, 2). Although such salts have been isolated earlier, 5,7-10 we believe that their reaction potential is still to be discovered. Further heating of enolates **5** in acetic acid resulted in their cyclization into 7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones **4**, probably *via* the Dimroth-like rearrangement.<sup>5</sup>



Scheme 3



Reagents and conditions: i. AcOH, 20 °C, 15 min.

In the individual state, salts **5** are sufficiently stable for storage and can be used in reactions with N-nucleophiles. Salts **5** easily react with aromatic amines. For instance, stirring of a mixture of enolate **5a** and aniline **6b** in acetic acid at room temperature for 15 min (method *A*) afforded the target 3-[4-(4-chlorophenyl)-1,3-thiazol-2-yl]-7,7-dimethyl-1-(4-methylphenyl)-7,8-dihydroquinoline-2,5-(1*H*,6*H*)-dione (**7b**) (Scheme 3; see Tables 1, 2).

The conclusion about the formation of 1-aryl-7,8-dihydroquinoline-2,5(1*H*,6*H*)-dione **7b** rather than the alternative 2-(arylimino)-2,6,7,8-tetrahydro-5*H*chromen-5-one **8** (see Scheme 3) was drawn from NOE data. For instance, irradiation of the sample at a resonance frequency of the methylene protons in the cyclohexane fragment ( $\delta$  2.41) gave rise to NOE at the protons of the methyl groups in position 7, the CH groups in the *ortho*-position of the aromatic substituent of the pyridone ring, and the proton in position 4 of 1-aryl-7,8-dihydroquinoline-2,5(1*H*,6*H*)-dione **7b** (see Scheme 3). The nuclear Overhauser effect at the CH groups in the *ortho*-position of the aromatic substituent is possible only for structure **7b**, not for the alternative structure **8**.

*N*-Substituted 3-(1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones 7 can also be obtained in three steps by using a "one pot" procedure (method *B*) without isolation of enamines 2 or intermediate salts 5 (Scheme 4). For instance, stirring of a mixture of 2-dimethylaminomethylidenecyclohexane-1,3-dione 2, nitrile 3, and piperidine in Pr<sup>i</sup>OH at room temperature for 2.5–3 h followed by removal of the solvent *in vacuo* and addition of a solution of aniline **6** in acetic acid gave products **7** in good yields that need no additional purification (see Tables 1, 2). It is worth noting that the total yields of compounds **7** with respect to cyclohexane-1,3-diones **1** were appreciably higher in the case of the "one pot" method *B* (see Table 1).

The structures of the compounds obtained were unambiguously determined from their <sup>1</sup>H NMR and IR spectra and elemental analysis data, as well as from an analysis of the literature data. For instance, the <sup>1</sup>H NMR spectra of 7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones **4** show a singlet at  $\delta$  8.79–8.88 for the CH proton in position 4 of the pyridine fragment, a singlet at  $\delta$  8.00–8.80 (depending on the aryl substituent in the thiazole fragment) for the proton in position 5 of the thiazole ring (for R<sup>4</sup> = H), and a broadened signal at  $\delta$  12.83–12.97 for the NH proton. This low-field signal is absent from the spectra of *N*-substituted derivatives **7**; instead, they contain the corresponding set of signals for the aryl substituent.

The IR spectra of compounds **4** show absorption bands at 3318–3401 (N–H stretching vibrations), 2852–2968 (C–H stretching vibrations in the aliphatic system), and 1643–1650 cm<sup>-1</sup> (C=O vibrations). The nitro group in derivatives **4a** and **5b** is represented by two bands at 1347 ( $v_s$ ) and 1528 cm<sup>-1</sup> ( $v_{as}$ ). In the case of salts **5**, the v(C=O) band is substantially shifted to the shorter wavelengths because of delocalization of the negative charge over the enolate anion of the 1,3-dicarbonyl fragment (1546–1551 cm<sup>-1</sup>) and a signal for the cyano group appears at 2200–2220 cm<sup>-1</sup>. When passing from 7,8-dihydroquinoline-2,5(1*H*,6*H*)-







**3e:** R<sup>3</sup> = 4-BrC<sub>6</sub>H<sub>4</sub>, R<sup>4</sup> = H; **6:** R<sup>5</sup> = H (**a**), 4-Me (**b**), 3-F (**c**), 4-OMe (**d**), 4-Pr<sup>i</sup> (**e**)

7	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>
а	Me	Me	4-BrC <sub>6</sub> H <sub>4</sub>	Н	Н
b	Me	Me	4-CIC <sub>6</sub> H <sub>4</sub>	Н	4-Me
С	Me	Me	4-MeC <sub>6</sub> H <sub>4</sub>	Me	3-F
d	Н	Н	4-CIC <sub>6</sub> H <sub>4</sub>	Н	4-OMe
е	Н	4-MeOC <sub>6</sub> H <sub>4</sub>	4-CIC <sub>6</sub> H <sub>4</sub>	Н	4-Pr <sup>i</sup>

diones 4 to *N*-substituted derivatives 7, the absorption band at  $3318-3401 \text{ cm}^{-1}$  (N-H group of the pyridin-2-one) disappears from the IR spectra.

To sum up, we developed both stepwise (with isolation of intermediate 2-[2-(4-arylthiazol-2-yl)-2-cyanoethenyl]-3-oxocyclohex-1-en-1-olates**5**) and "one pot"methods for the synthesis of <math>3-(1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones **4** and 1-aryl-3-(1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)diones **7**. The methods proposed for isolation of intermediate enolates **5** as piperidinium salts provide the possibility to apply them in the further synthesis of novel heterocycles.

## Experimental

Substituted 5-R-cyclohexane-1,3-diones were prepared according to a known procedure.<sup>11</sup> (1,3-Thiazol-2-yl)acetonitriles were synthesized by the Hantzsch reaction of  $\omega$ -bromoaceto-phenones with 2-cyanothioacetamide.<sup>12</sup> The other starting com-

pounds were commercial chemicals. Melting points were determined on a Kofler hot stage. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury VX-200 instrument in DMSO-d<sub>6</sub> (200 MHz). IR spectra were recorded on a Specord M-82 instrument (pellets with KBr). Elemental analysis was carried out on an EuroVector EA-3000 instrument. All the microwave-assisted reactions were carried out in an Emryse<sup>TM</sup> Creator EXP microwave system (Biotage, Uppsala) in hermetically sealed vessels for microwave synthesis (initial radiation power 300 W (Normal option). The reaction time corresponded to the period of time during which the reaction mixture was kept at a given temperature.

3-(4-Aryl-1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones 4a-d (general procedure *A*). A mixture of cyclohexane-1,3-dione 1 (2 mmol) and DMFDMA (2 mmol) was stirred at room temperature for 5 min. The resulting 2-dimethylaminomethylidenecyclohexane-1,3-dione 2 was refluxed with 2-(4-aryl-1,3-thiazol-2-yl)acetonitrile 3 (2 mmol), four drops (~0.15 mL) of piperidine, and Bu<sup>n</sup>OH (2.0 mL) for 10 min. The reaction was accompanied by the formation of a voluminous precipitate. After cooling, the crystalline precipitate was filtered off, washed with ethanol (1.0 mL), and dried at 80 °C. The yields and physicochemical characteristics of compounds 4a-d are given in Tables 1 and 2.

**General procedure** *B*. A mixture of cyclohexane-1,3-dione **1** (2 mmol) and DMFDMA (2 mmol) was stirred at room temperature for 5 min in a vessel for microwave synthesis (for the reaction mixture volumes V = 0.5-2.5 mL). 2-(4-Aryl-1,3-thiazol-2-yl)acetonitrile **3** (2 mmol), four drops (~0.15 mL) of piperidine, and Pr<sup>i</sup>OH (1.0 mL) were added to the resulting 2-dimethylaminomethylidenecyclohexane-1,3-dione **2**. The vessel was sealed and the reaction mixture was subjected to microwave irradiation at 100 °C for 5 min, the gage pressure of the reaction mixture being 8–9 atm. On cooling, the crystalline precipitate that formed was filtered off, washed with Pr<sup>i</sup>OH (1.0 mL), and dried at 80 °C. The physicochemical characteristics of the products obtained were identical with those of compounds **4a**–**d** synthesized according to method *A* (see Tables 1, 2).

Piperidinium 2-[2-(4-aryl-1,3-thiazol-2-yl)-2-cyanoethenyl]-3-oxocyclohex-1-enolates 5a,b (general procedure). A mixture of cyclohexane-1,3-dione 1 (10 mmol) and DMFDMA (10 mmol) was stirred at room temperature for 5 min. 2-(4-Aryl-1,3-thiazol-2-yl)acetonitrile 3 (10 mmol), piperidine (10 mmol), and  $Pr^{i}OH$ (10.0 mL) were added to the resulting 2-dimethylaminomethylidenecyclohexane-1,3-dione 2. The reaction mixture was stirred at room temperature for 2.5–3 h. The yellow crystalline precipitate that formed was filtered off and dried at room temperature. The yields and physicochemical characteristics of compounds 5a,b are given in Tables 1 and 2.

1-Aryl-3-(4-aryl-1,3-thiazol-2-yl)-7,8-dihydroquinoline-2,5(1*H*,6*H*)-diones 7a—e (general procedure *A*). Piperidinium 2-[2-(4-aryl-1,3-thiazol-2-yl)-2-cyanoethenyl]-3-oxocyclohex-1-enolate 5 (2 mmol) was added to a solution of aromatic amine 6 (2.2 mmol) in acetic acid (2 mL). The reaction mixture was stirred at room temperature for 15 min. The white precipitate that formed was filtered off, washed with water (2×2 mL), and dried at 80 °C. The yields and physicochemical and spectroscopic characteristics of compounds 7a—e are given in Tables 1 and 2.

**General procedure** *B*. A mixture of cyclohexane-1,3-dione **1** (2 mmol) and DMFDMA (2 mmol) was stirred at room temperature for 5 min. 2-(4-Aryl-1,3-thiazol-2-yl)acetonitrile **3** 

(2 mmol), piperidine (2 mmol), and Pr<sup>i</sup>OH (5.0 mL) were added to the resulting 2-dimethylaminomethylidenecyclohexane-1,3-dione **2**. The reaction mixture was stirred at room temperature for 2.5–3 h. The solvent was removed *in vacuo*. The resulting crystalline precipitate was stirred with a solution of aniline **6** (2 mmol) in acetic acid at room temperature for 15 min. The precipitate that formed was filtered off, washed with water (2×2 mL), and dried at 80 °C. The physicochemical characteristics of the products obtained were identical with those of compounds **7a**–**e** synthesized according to method *A* (see Tables 1, 2).

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