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Abstract: We report here a synthesis of a new rhodacyanines **7X** analogous to **MKT-077** with quantitative yield using as starting material the thiazolinethione **1**. Merocyanines **4** and their tosylates **5** have been prepared as intermediates for this class of compounds. The reactions leading to rhodacyanine **7X** have been studied under microwave irradiation.

Keywords: condensation, microwave irradiation, rhodacyanine cation, thiazolinethione

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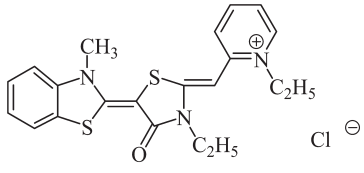
INTRODUCTION

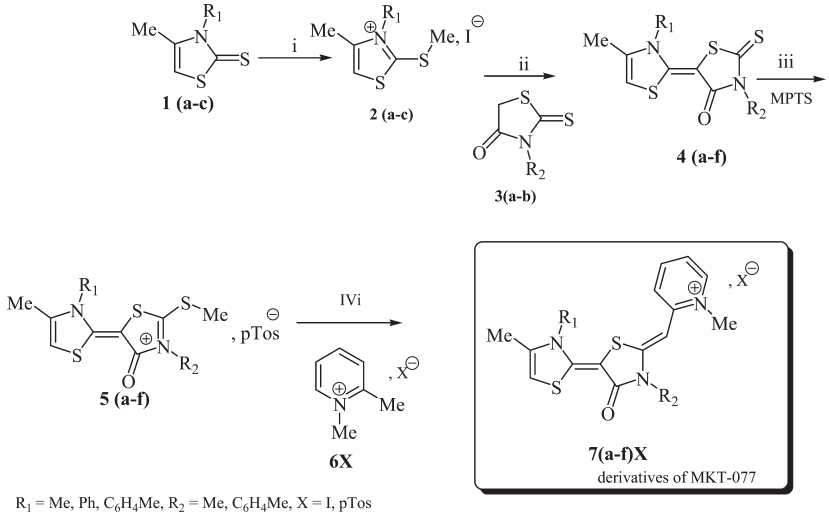
Rhodacyanines dyes and several analogous delocalized lipophilic cation (DLCs) were synthesized and evaluated as novel antitumor agents, and the rhodanine was an essential moiety for antitumor activity.[1,2] Recently, the discovery of the **MKT-077** rhodacyanines[3] opened new prospects in the treatment of malaria.



MKT-077

Knowing this, we found it interesting in this work to synthesize rhodacyanines **7X** (which are DLCs analogous to **MKT-077**) under microwave irradiation. We studied a simple synthesis starting from thiazolinethione **1** because of their known activities,[4–6] according to Scheme 1.

The iodide **2** obtained by alkylation of the thiazolinethione **1**[7] is condensed with the rhodanine **3** in the presence of Et_3N to give in situ the stable merocyanine **4**. This compound is then converted in the corresponding



Scheme 1. Reagents and reaction conditions: (i) MeI (2 eq), acetone, rt, 24 h; (ii) **3** (1 eq), Et_3N (1.5 eq), acetone, rt, 24 h; MW: 50°C, 5–10 min; (iii) MPTS (3 eq), DMF, 110–120°C, 4 h; MW: MPTS (3 eq), 120°C, 20 min (IVi) **6X** (1 eq), Et_3N (1.5 eq), MeCN, reflux, 4 h; MW: **6X** (1 eq), Et_3N (1.5 eq), 85°C, 30 min.

Table 1. Results of merocyanines **4**(**a**–**f**)

Compounds	R_1	R_2	Yields of **4** (%)[a]	Yields of **4** (%)[b]	Time (min) MW	λ_{max} (nm)[c]
4a	Me	Me	95	97	5	432
4b	Ph	Me	88	80	5	428
4c	pC_6H_4Me	Me	95	96	10	432
4d	Me	pC_6H_4Me	70	85	10	434
4e	Ph	pC_6H_4Me	30	62	5	436
4f	pC_6H_4Me	pC_6H_4Me	60	70	5	431

[a]Classical heating (Ch), isolated yield.
[b]Microwave irradiation (MW), isolated yield.
[c]UV-vis spectra were measured in $CHCl_3$ solution.

tosylate **5**, which is also stable, by reaction with an excess of methylparatoluenesulfonate (MPTS). The salt **5** finally reacts with the quaternary pyridinium salt **6X**, which acts as a nucleophile in the presence of Et_3N according to the method of Brooker[8] and gives the desired rhodacyanine **7X**. The results are summarized in Tables 1 to 3.

RESULTS AND DISCUSSION

Satisfactory yield are obtained in both cases (i.e., classical heating, with a small amount of solvent or microwave irradiation at nearly the same temperature without solvent). In the latter case, the purity of the compounds is higher, and obviously the reaction time is reduced.

The structural assignments of **4**, **5**, and **7X** are established by ^1H and ^{13}C NMR. They all exhibit a typical low-field signal for the H_5 proton of the thiazolic cycle around 6.30 to 6.75 ppm (**4**), 6.82–7.12 ppm (**5**), and 6.37–6.93 ppm (**7X**).

Table 2. Results of tosylates **5**(**a**–**f**)

Compounds	R_1	R_2	Yields of **5** (%)[a]	Yields of **5** (%)[b]
5a	Me	Me	72	65
5b	Ph	Me	82	78
5c	pC_6H_4Me	Me	63	72
5d	Me	pC_6H_4Me	92	85
5e	Ph	pC_6H_4Me	75	68
5f	pC_6H_4Me	pC_6H_4Me	66	73

[a]Classical heating (Ch), isolated yield.
[b]Microwave irradiation (MW), isolated yield.

Table 3. Results of the rhodacyanines **7**(**a**–**f**) **X**

Compounds	R_1	R_2	**X**	Yields of **7X** (%)[a]	Yields of **7X** (%)[c]	λ_{max} (nm)[b]
7aT	Me	Me	ptos	78	90	505
7aI	Me	Me	I	70	82	502
7bT	Ph	Me	ptos	72	85	502
7bI	Ph	Me	I	62	79	501.5
7cT	pC_6H_4Me	Me	ptos	60	78	508
7cI	pC_6H_4Me	Me	I	54	76	518
7dT	Me	pC_6H_4Me	ptos	70	88	508
7dI	Me	pC_6H_4Me	I	72	93	516
7eT	Ph	pC_6H_4Me	ptos	65	77	508
7eI	Ph	pC_6H_4Me	I	75	84	506
7fT	pC_6H_4Me	pC_6H_4Me	ptos	72	85	504
7fI	pC_6H_4Me	pC_6H_4Me	I	74	88	520

[a]Classical heating (Ch), isolated yield.
[b]UV-vis spectra were measured in $CHCl_3$ solution.
[c]Yield estimated by ^1H NMR for MW experiments.

The ^{13}C NMR spectra show a signal around 164.93–166.30 ppm (**4**), 160.36–163.30 ppm (**5**), and 163.02–164.80 ppm (**7X**), typical of C_4 of the rhodanine cycle.

All the compounds **7X** exhibit a singlet around 5.19–5.77 ppm for the exocyclic double-bond proton, which shows that Brooker condensation is stereospecific. In all cases, only the (2Z, 5E) stereoisomer is formed (54–78%), in agreement with previous results related to **MKT-077** synthesis.[1–3]

We observed a bathochromic effect for the merocyanine **4** and rhodacyanine **7X**.

In conclusion, we showed that microwave irradiation without solvent was suitable for this type of synthesis, leading to higher yield in quite short reaction times (5 to 30 min) and is a more ecofriendly process.[9]

EXPERIMENTAL

General

Melting points were determined on a Kofler melting-point apparatus and are uncorrected. IR spectra were taken with a Perkin-Elmer 1420 spectrometer. ^1H NMR spectra were recorded on Bruker ARX 200 (200 MHz) and Bruker AC 300P (300 MHz) spectrometers, and ^{13}C NMR spectra were measured on a Bruker AC 300P (75 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. The mass spectra (MS) were measured on a Variant MAT 311 at a ionizing

potential of 70 eV in the Centre de Mesures Physiques de l'Ouest (CRMPO, Rennes). The sources are electronic impact (EI) and electrospray (ESI). Elemental analysis was performed at the Centre de Mesures Physiques de l' Ouest (CRMPO, Rennes). The UV-vis spectra were recorded on a UV-vis Spectrometer Pye Unicam at Tiaret University. Reactions under microwave irradiation were performed in a Prolabo Synthewave 402 (2.45-GHz) microwave reactor with a single focused system. All solvents and reagents were purchased from Acros Organics and Aldrich Chemic and used without further purification unless otherwise stated.

Compound 1

The preparation of the compounds 1 was obtained according to the literature[7] from disulfide carbon, amine in aqueous ammonia, and chloro acetone by Hantzsch's cyclization.

3,4-Dimethyl-1,3-thiazole-2(3*H*)-thione (1a). Beige crystals; yield = 80%; mp = 115°C (lit. 119–114°C). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 6.30 (s, 1H); 3.68 (s, 3H); 2.31 (s, 3H). ^{13}C NMR (50 MHz $CDCl_3$) δ: 187.8; 139.9; 105.9; 34.1; 15.7.

4-Methyl-3-phenyl-1,3-thiazole-2(3*H*)-thione (1b). White crystals; yield = 80%; mp = 150°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.20–7.65 (m, 5Har); 6.39 (s, 1H); 1.99 (s, 3H); ^{3}C NMR (50 MHz, $CDCl_3$): δ = 190.2; 140.1; 137.8; 130.7; 128.1, 127. 5, 106.3; 16.1.

4-Methyl-3-(4-methylphenyl)-1,3-thiazole-2-(3H)-thione (1c). Beige crystals; yield = 95%; mp = 110°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.30 (d, 2H); 7.12 (d, 2H) 6.34 (s, 1H); 2.42 (s, 3H); 1.95 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 190.1; 10.3; 139.7; 135.1; 130.6; 127.8; 127.7; 127.7; 106.2; 21.3; 16.1.

Compound 2

3,4-Dimethyl-2-(methylthio)-1,3-thiazol-3ium Iodide (2a). The alkylation of **1a** (4.35 g; 30 mmol) with iodomethane (8.52 g; 60 mmol) gave **2a** (6.45 g; 75%).

2a: pale yellow needles; mp = 162°C; ^{1}H NMR (200 MHz, $CDCl_3$ + TFA) δ: 7.59 (s, 1H); 3.92 (s, 3H); 2.98 (s, 3H); 2.59 (s, 3H).

4-Methyl-3phenyl-2-(methylthio)-1,3-thiazol-3ium Iodide (2b). The alkylation of **1b** (4.14 g; 20 mmol) with iodomethane (5.68 g; 40 mmol) gave **2b** (5.16 g; 74%).

2b: pale pink needles; yield: 74%; mp = 193°C; ^{1}H NMR (200 MHz, $CDCl_3$ + TFA) δ: 7.47–7.79 (m, 5Har); 7.46 (s, 1H); 2.93 (s, 3H,); 2.30 (s, 3H).

4-Methyl-3-(4-methylphényl)-2-(methylthio)-1,3-thiazol-ium (2c). The alkylation of **1c** (4.40 g; 20 mmol) with iodomethane (5.68 g; 40 mmol) gave **2c** (5.87 g; 81%).

2c: bricked crystals; yield = 81%; mp = 160°C; ^{1}H NMR (200 MHz, $CDCl_3$ + TFA) δ: 8.22 (s, 1H); 7.7 (m, 4H); 2.95 (s, 3H); 2.50 (s, 3H); 2.27 (s, 3H).

Compound 3

The preparation of the compounds 3 was obtained according to the literature[10a] from disulfide carbon, amine in aqueous ammonia, and chloroacetic acid by Hantzsch's cyclization.

3-Methyl-2-thioxo-1,3-thiazolidin-4-one (3a). Yellow crystals; yield = 75%; mp = 71°C (lit. 69–71°C); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.10 (s, 2H); 3.40 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 201.1; 173.3; 35.6; 31.2.

3-(4-Methylphényl)-2-thioxo-1,3-thiazolidin-4-one (3b). Yellow crystals; yield = 68%; mp = 152°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.33 (d, 2H, J = 6.0 Hz); 7.07 (d, 2H, J = 6.1 Hz); 4.17 (s, 2H); 2.40 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 201.3; 173.5; 140.0; 132.2; 130.2; 128.0; 125.5; 120.7; 36.3; 21.3.

General Process for Merocyanine 4

Classical Heating (Ch)

In a 250-ml round-bottomed flask, 10 mmol of salt **2**, 10 mmol of rhodanine **3**, 20 ml of acetone, and 2 ml of triethylamine are placed. After stirring at room temperature during one night or at reflux during 1 h, a yellow-green solid is formed. It is filtered off and washed several time with aceton.

Microwave Irradiation (MW)

In a cylindrical quartz reactor (Φ = 1.5 cm), 1.39 mmol of the iodide **2**, rhodanine **3** (1.39 mmol), and 0.28 ml of triethylamine are placed. Microwave irradiation under stirring is applied at 50°C for 5 to 10 min (by monitoring the temperature). After cooling to room temperature, the yellow product is washed with acetone and then dried under vacuum.

(5E)-3-Methyl-5-(3,4-dimethylthiazol-2(3H)-ylidene)-2-thioxothiazolidin-4-one (4a). The condensation of **2a** (2.87 g; 10 mmol) with **3a** (1.47 g; 10 mmol) gave **4a** (2.45 g; 95%) in classical heating, and the condensation of **2a** (400 mg; 1.39 mmol) with **3a** (204 mg; 1.39 mmol) gave **4a** (358 mg; 97%) in MW.

4a: yellow-green powder; mp $> 260^{\circ}$C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.30 (s, 1H, H_5); 3.78 (s, 3H, CH_3Nthiazol); 3.55 (s, 3H; CH_3rhod); 2.30 (s, 3H, CH_3-C_4). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.3 (C═S); 164.9 (C═O); 157.3 (C_2thiazol); 137.3 (C_4thiazol); 109.8 (C_5thiazol, d, $J = 186.1$ Hz); 84.9 (C_5rhod); 34.8 (q, $J = 140.0$ Hz, CH$_3$Nthiazol); 31.3 (q, $J = 142.1$ Hz, CH$_3$rhod); 14.6 (qd, $J = 130.2$ Hz, $J = 2.2$ Hz, CH$_3$C$_4$). HRMS (EI) M+for $C_9H_{10}N_2OS_3$ calcd.: 257.99553; found: 257.995.

(5E)-3-Methyl-5-(4-methyl-3-phenylthiazol-2(3H)-ylidene)-2-thioxothiazolidin-4-one (4b). The condensation of **2b** (3.49 g; 10 mmol) with **3a** (1.47 g; 10 mmol) gave **4b** (2.82 g; 88%) in classical heating, and the condensation of **2b** (485 mg; 1.39 mmol) with **3a** (204 mg; 1.39 mmol) gave **4b** (360 mg; 80%) in MW.

4b: yellow powder; yield = mp $> 260^{\circ}$C. ^{1}H NMR (300 MHz, $CDCl_3 + CF_3$-COOH) δ: 7.76–7.33 (m, 5Har); 6.75 (s, 1H, H_5); 3.46 (s, 3H, CH_3rod); 1.98 (s, 3H, CH_3C$_4$). ^{13}C NMR (75 MHz, $CDCl_3 + CF_3COOH$) δ: 187.4 (C═S); 165.2 (C═O); 157.0 (C_2thiazol); 138.8 (C_4thiazol); 132.2; 130.8; 129.0; 116.6; 112.8 (Car); 109.0 (C_5thiazol, dq, $J = 186.1$ Hz, $J = 5.0$ Hz); 85.0 (C_5rhod); 31.5 (q, $J = 142.0$ Hz, CH$_3$ rhod); 14.3 (qd, $J = 130.5$ Hz; $J = 2.1$ Hz; CH$_3$-C$_4$). HRMS (EI) M+. for $C_{14}H_{12}N_2OS_3$ calcd.: 320.01118; found: 320.0124.

(5E)-3-Methyl-5-(4-methyl-3-p-tolylthiazol-2(3H)-ylidene)-2-thioxothiazolidin-4-one (4c). The condensation of **2c** (3.63 g; 10 mmol) with **3a** (1.47 g; 10 mmol) gave **4c** (3.18 g; 95%) in classical heating, and the condensation of **2c** (504 mg; 1.39 mmol) with **3a** (204 mg; 1.39 mmol) gave **4c** (464 mg; 96%) in MW.

4c: brown yellow powder; mp $>260^{\circ}$C. ^{1}H NMR (300 MHz, $CDCl_3 + CF_3$-COOH) δ: 7.43 (d, 2H, $J = 8.07$ Hz); 7.18 (d, 2H, $J = 8.25$ Hz); 6.58 (s, 1H, H_5); 3.48 (s, 3H, CH_3Nrhod); 2.30 (s, 3H, pCH_3); 1.98 (s, 3H, CH_3C$_4$). ^{13}C NMR (75 MHz, $CDCl_3 + CF_3COOH$) δ: 186.2 (C═S); 166.3 (C═O); 157.2 (C_2thiazol); 143.0 (C_4thiazol); 131.8; 128.5; 120.3; 116.5; 106.0 (dq, $J = 188.0$ Hz, $J = 5.1$ Hz); 84.2 (C_5rhod); 31.6 (q, $J = 142.6$ Hz, CH$_3$rhod); 21.5 (qt, $J = 127.2$ Hz, $J = 4.2$ Hz, pCH_3thiazol); 14.4 (qd, $J = 130.6$ Hz, $J = 2.1$ Hz; CH$_3$C$_4$). HRMS (EI) M+ for $C_{15}H_{14}N_2OS_3$ calcd.: 334. 02683; found: 334.0273.

(5E)-5-(3,4-Dimethylthiazol-2(3H)-ylidene)-2-thioxo-3-p-tolylthiazolidin-4-one (4d). The condensation of **2a** (2.87 g; 10 mmol) with **3b** (2.23 g; 10 mmol) gave **4d** (2.30 g; 70%) in classical heating, and the condensation of **2a** (400 mg; 1.39 mmol) with **3b** (310 mg; 1.39 mmol) gave **4d** (390 mg; 85%) in MW.

4d: powder; mp = 266°C. ^{1}H NMR (300 MHz, $CDCl_3 + CF_3COOH$ F) δ: 7.38 (d, 2H, $J = 7.9$ Hz); 7.21 (d, 2H, $J = 2.2$ Hz); 6.7 (s, 1H, H_5); 3.87 (s, 3H, CH_3Nthiazol); 2.44 (s, 3H, pCH_3); 2.34 (s, 3H, CH_3C$_4$). ^{13}C NMR (75 MHz, $CDCl_3 + CF_3COOH$) δ: 187.6 (C═S); 165.3 (C═O); 158.7 (C_2thiazol); 140.1 (C_4thiazol); 133.5; 130.6; 128.5 (Car); 106.7 (dq, $J = 190.7$ Hz, $J = 5.2$ Hz, C_5thiazol); 83.2 (C_5rhod); 35.6 (q, $J = 141.0$ Hz, CH$_3$-Nthiazol); 21.7 (qt, $J = 126.5$ Hz, $J = 4.3$ Hz, pCH$_3$); 15.1 (qd, $J = 130.2$ Hz, $J = 2.3$ Hz, CH$_3$C$_4$). HRMS (EI) M+. for $C_{15}H_{14}N_2OS_3$ calcd.: 334.02683; found: 334.0273.

(5E)-5-(4-Methyl-3-phenylthiazol-2(3H)-ylidene)-2-thioxo-3-p-tolylthiazolidin-4-one (4e). The condensation of **2b** (3.49 g; 10 mmol) with **3b** (2.23 g; 10 mmol) gave **4e** (1.18 g; 30%) in classical heating, and the condensation of **2b** (485 mg; 1.39 mmol) with **3b** (310 mg; 1.39 mmol) gave **4e** (340 mg; 62%) in MW.

4e: green power; mp > 260°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72–7.13 (m, 9Har); 6.36 (s, 1H, H_5); 2.38 (s, 3H, pCH_3); 1.98 (s, 3H, CH_3C$_4$).^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.1 (C═S); 165.5 (C═O); 155.6 (C_2 thiazol); 139.0 (C_4thiazol); 137.5; 135.0; 133.4; 131.7; 130.5; 129.9; 129.2; 128.0 (Car); 104.2 (dq, $J = 191.0$ Hz, $J = 5.2$ Hz, C_5thiazol); 84.6 (C_5rhod); 21.3 (qt, $J = 126.1$ Hz, $J = 4.3$ Hz, pCH$_3$); 14.4 (qd, $J = 130.2$ Hz, $J = 2.2$ Hz, CH_3C$_4$). HRMS (EI) M+ for $C_{20}H_{16}N_2OS_3$ calcd.: 396.0422248; found: 396.0412.

(5E)-5-(4-Methyl-3-p-tolylthiazol-2(3H)-ylidene)-2-thioxo-3-p-tolylthiazolidin-4-one (4f). The condensation of **2c** (3.63 g; 10 mmol) with **3b** (2.23 g; 10 mmol) gave **4f** (2.46 g; 60%) in classical heating, and the condensation of **2c** (504 mg; 1.39 mmol) with **3b** (310 mg; 1.39 mmol) gave **4f** (400 mg; 70%) in MW.

4f: yellow crystals; mp > 260°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.70–7.17 (m, 8Har); 6.40 (s, 1H, H_5); 2.56 (s, 3H, pCH_3thiazol); 2.20 (s, 3H, p CH_3rhod); 1.97 (s, 3H, CH_3C$_4$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.6 (C═S); 165.9 (C═O); 156.3 (C_2thiazol); 142.6 (C_4thiazol); 139.4; 138.1; 133.9; 132.7; 131.5; 130.4; 129.3; 128.4 (Car); 104.5 (qd, $J = 191.0$ Hz, $J = 5.3$ Hz, rhod); 84.9 (C_5rhod); 22.0 (qt, $J = 127.3$ Hz, $J = 4.2$ Hz, CH$_3$ thiazol); 21.7 (qt, $J = 126.7$ Hz, $J = 4.5$ Hz, pCH_3rhod); 14.8 (qd, $J = 130.3$ Hz, $J = 2.1$ Hz, CH$_3$C$_4$). HRMS (EI) M+ for $C_{21}H_{18}N_2OS_3$ calcd.: 410.05813; found: 410.0598.

General Procedure for Salts Tosylates 5

Classical Heating (Ch)

A mixture of **4** (5 mmol), 15 mmol of MPTS (methyl paratoluensulfonate), and 5 ml of DMF is stirred at 110–120°C during 4 h. The reaction mixture is cooled down to 40°C, and 50 ml of acetone is added. After completion, the mixture is cooled down to room temperature and then refrigerated for one night. The resulting salt is filtered off and dried under vacuum.

Microwave Irradiation (MW)

In the previous quartz reactor, 3.1 mmol of merocyanine **4** and 9.3 mmol of MPTS are added. After irradiation at 120°C during 20 min the tosylate **5** is collected and washed with acetone.

(5E)-3-Methyl-5(3,4-dimethyl-1,3-thiazol-2-ylidene)-2-(methylthio)-4-oxo-1, 3-thiazolium p-toluenesulfonate (5a). The alkylation of **4a** (1.29 g; 5 mmol) with MPTS (2.79 g; 15 mmol) gave **5a** (1.59 g; 72%) in classical heating, and the alkylation of **4a** (800 mg; 3.1 mmol) with MPTS (1.73 g; 9.3 mmol) gave **5a** (894 mg; 65%) in MW.

5a: yellow-green powder; mp = 252°C. ^{1}H NMR (300 MHz, $CDCl_3 + CF_3$ COOH) δ: 7.90 (d, 2H, $J = 8.0$ Hz); 7.18 (d, 2H, $J = 8.0$ Hz); 7.02 (s, 1H, H_5); 4.12 (s, 3H, CH_3Nthiazol); 3.73 (s, 3H, CH_3N^+); 2.99 (s, 3H, CH_3-S); 2.50 (s, 3H, CH_3tos); 2.11 (s, 3H, CH_3C_4). ^{13}C NMR (75 MHz, $CDCl_3 + CF_3$ COOH) δ: 174.0 (C-S); 160.3 (C═O); 159.5 (C_2thiazol); 142.6 (C_4thiazol); 141.4; 130.3; 129.3; 126.2 (Car); 106.2 (qd, $J = 196.1$ Hz, $J = 5.2$ Hz, C_5); 84.9 (C_5rhod); 37.0 (q, $J = 144.1$ Hz, CH_3 Nthiazol); 33.8 (q, $J = 143.8$ Hz, CH_3N^+); 21.6 (qt, $J = 126.4$ Hz, $J = 4.4$ Hz, CH_3tos); 16.2 (q, $J = 145.0$ Hz, CH_3-S); 14.1 (qd, $J = 129.1$ Hz, $J = 2.2$ Hz, CH_3C_4). HRMS (ESI) M+ for $C_{10}H_{13}N_2OS_3$ calcd.: 273.01900; found: 273.0186. The ionization clusters $(2C^+, Tos^-)^+$ are found at m/z 717.

(5E)-3-Methyl-5(4-methyl-3-phenyl-1,3-thiazol-2-ylidene)-2-(methylthio) -4-oxo-1,3-thiazolium p-toluenesulfonate (5b). The alkylation of **4b** (1.60 g; 5 mmol) with MPTS, (2.79 g; 15 mmol) gave **5b** (2.07 g; 82%) in classical heating, and the alkylation of **4b** (1.00 g; 3.1 mmol) with MPTS (1.73 g; 9.3 mmol) gave **5b** (1.22 g; 78%) in MW.

5b: deep green crystals; mp = 205°C. ^{1}H NMR (300 MHz, $CDCl_3 + CF_3$ COOH) δ: 7.79–7.74 (m, 5Har); 7.72 (d, 2H, $J = 8.0$ Hz); 7.69 (d, 2H, $J = 8.0$ Hz); 7.12 (s, 1H, H_5); 3.50 (s, 3H, CH_3N^+); 2.6 (s, 3H, CH_3-S); 2.29 (s, 3H, CH_3tos); 2.08 (s, 3H, CH_3C_4). ^{13}C NMR (75 MHz, $CDCl_3 + CF_3$ COOH) δ: 175.9 (C-S); 162.4 (C═O); 160.9 (C_2thiazol); 143.2 (C_4thiazol);

140.4; 139.2; 134.9; 132.9; 131.1; 128.8; 128.4; 126.1 (Car); 109.2 (dq, $J = 196.0$ Hz, $J = 5.1$ Hz, C_5); 84.6 (C_5rhod); 32.6 (q, $J = 143.8$ Hz, CH_3N^+); 21.3 (qt, $J = 126.4$ Hz, $J = 4.4$ Hz, CH_3tos); 15.9 (q, $J = 145.0$ Hz, CH_3-S); 14.2 (qd, $J = 130.1$ Hz, $J = 2.1$ Hz, CH_3thiazol). HRMS (ESI) M+ for $C_{15}H_{15}N_2OS_3$ calcd.: 335.0365; found: 335.035. The ionization cluster $(2C^+, Tos^-)^+$ is found at m/z 841.

(5E)-3-Methyl-5[4-Methyl-3-(4-methylphenyl)-1,3-thiazol-2-ylidene]-2-(methylthio)-4-oxo-1,3-thiazolium p-toluenesulfonate (5c). The alkylation of **4c** (1.67 g; 5 mmol) with MPTS, (2.79 g; 15 mmol) gave **5c** (1.63 g; 63%) in classical heating, and the alkylation of **4c** (1.04 g; 3.1 mmol) with MPTS (1.73 g; 9.3 mmol) gave **5c** (1.16 g; 72%) in MW.

5c: deep green crystals; mp = 198°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76 (d, 2H, $J = 8.0$ Hz); 7.57 (d, 2H, $J = 8.1$ Hz); 7.32 (d, 2H, $J = 8.2$ Hz); 7.11 (d, 2H, $J = 8.0$ Hz); 7.05 (s, 1H, H_5); 3.56 (s, 3H, CH_3N^+); 2.73 (s, 3H, CH_3S); 2.48 (s, 3H, pCH_3thiazol); 2.32 (s, 3H, CH_3tos); 2.11 (s, 3H, CH_3C_4 CH_3tos). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.8 (C-S); 162.2 (C═O); 160.4 (C_2thiazol); 143.8 (C_4thiazol); 143.6; 141.6; 140.7; 138.8; 133.0; 131.5; 129.3; 129.0; 126.8 (Car); 109.3 (dq, $J = 191.3$ Hz, $J = 5.3$ Hz, C_5thiazol); 85.5(C_5rhod); 32.5 (q, $J = 144.2$ Hz, CH_3N^+); 21.5 (qt, $J = 127.6$ Hz, $J = 4.2$ Hz, pCH_3thiazol); 21.2 (qt, $J = 126.4$ Hz, $J = 5.0$ Hz, CH_3tos); 15.9 (qt, $J = 126..4$ Hz, $J = 4.5$ Hz, pCH_3tos); 14.4 (q, $J = 144.9$ Hz, CH_3-S); 14.2 (qd, $J = 131.1$ Hz, $J = 2.1$ Hz, CH_3C_4). HRMS (ESI) M+for $C_{16}H_{17}N_2OS_3$ calcd.: 349.05030; found: 349.0509. The ionization clusters $(2C^+, Tos^-)^+$ are found at m/z 869.

(5E)-3-(4-Methylphenyl)-5-(3,4-dimethyl-1,3-thiazol-2-ylidene)-2-(methyl thio)-4-oxo-1,3-thiazolium p-toluenesulfonate (5d). The alkylation of **4d** (1.67 g; 5 mmol) with MPTS (2.79 g; 15 mmol) gave **5d** (2.39 g; 92%) in cl assical heating, and the alkylation of **4d** (1.05 g; 3.1 mmol) with MPTS (1.73 g; 9.3 mmol) gave **5d** (1.37 g; 85%) in MW.

5d: orange crystals; mp = 244°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.75 (d, 2H, $J = 8.0$ Hz); 7.43 (d, 2H, $J = 8.0$ Hz); 7.28 (d, 2H, $J = 8.1$ Hz); 7.0 (d, 2H, $J = 7.5$ Hz); 6.82 (s, 1H, H_5); 4.30 (s, 3H, CH_3thiazol); 3.03 (s, 3H, CH_3-S); 2.48 (s, 3H, pCH_3tos); 2.44 (s, 3H, CH_3rhod); 2.34 (s, 3H, CH_3-C_4). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.7 (C-S); 163.3 (C═O); 161.5 (C_2thiazol); 144.0 (C_4thiazol); 142.3; 141.7; 140.5; 139.5; 132.9; 132.2; 131.3; 128.9; 126.3 (Car); 109.7 (dq, $J = 196.2$ Hz, $J = 5.3$ Hz, C_5thiazol); 86.2 (C_5rhod); 38.0 (q, $J = 144.1$ Hz, CH_3thiazol); 21.8 (qt, $J = 127.1$ Hz, $J = 3.0$ Hz, pCH_3rhod); 21.6 (qt, $J = 126.6$ Hz, $J = 4.5$ Hz, CH_3tos); 16.8 (q, $J = 14.8$ Hz, CH_3S); 15.0 (qd, $J = 131.2$ Hz, $J = 2.3$ Hz, CH_3C_4). HRMS (ESI) M+ for $C_{16}H_{17}N_2OS_3$ calcd.: 349.05030; found: 349.0512. The ionization clusters $(2C^+, Tos^-)^+$ are found at m/z 869.

(5E)-3(4-Methylphenyl)-5(4-methyl-3-phenyl-1,3-thiazol-2-ylidene)-2-(methylthio)-4-oxo-1,3-thiazolium p-toluenesulfonate (5e). The alkylation of **4e** (1.98 g; 5 mmol) with MPTS (2.79 g; 15 mmol) gave **5e** (2.17 g; 75%) in classical heating, and the alkylation of **4d** (1.24 g; 3.1 mmol) with MPTS (1.73 g; 9.3 mmol) gave **5e** (1.22 g; 68%) in MW.

5e: green crystals; mp = 234°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.80–7.06 (m, 13Har); 7.03 (s, 1H, H_5); 2.52 (s, 3H, pCH_3rhod); 2.41 (s, 3H, CH_3-S); 2.28 (s, 3H, CH_3tos); 2.06 (s, 3H, CH_3thiazol). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 177.3 (C-S); 162.6 (C═O); 161.0 (C_2thiazol); 143.8 (C_4thiazol); 141.7; 140.5; 138.8; 134.2; 132.9; 132.0; 130.7; 129.13; 128.6; 128.4; 127.2; 126.6 (Car); 109.3 (dq, J = 196.5 Hz, J = 5.4 Hz, C_5thiazol); 86.0 (C_5rhod); 21.4 (qt, J = 127.2 Hz, J = 3.0 Hz, pCH$_3$rhod); 21.2 (qt, 126.8 Hz, J = 4.5 Hz, CH$_3$tos); 15.8 (q, J = 1.8 Hz, CH$_3$-S); 14.2 (qd, J = 131.1 Hz, J = 2.3 Hz, CH$_3$C$_4$). HRMS (ESI) M+ for $C_{21}H_{19}N_2OS_3$ calcd.: 411.06595; found: 411.0656. The ionization cluster $(2C^+, Tos^-)^+$ is not seen.

(5E)-3(4-Methylphenyl)-5-[4-methyl-3-(4-methylphenyl)-1,3-thiazol-2-ylidene]2(methylthio)-4-oxo-1,3-thiazolium p-toluenesulfonate (5f). The alkylation of **4f** (2.06 g; 5 mmol) with MPTS (2.79 g; 15 mmol) gave **5f** (1.98 g; 66%) in classical heating, and the alkylation of **4f** (1.30 g; 3.1 mmol) with MPTS (1.73 g; 9.3 mmol) gave **5f** (1.35 g; 73%) in MW.

5f: deep green crystals; mp = 216°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.75 (d, 2H, J = 8.0 Hz); 7.59 (d, 2H, J = 8.1 Hz); 7.35 (d, 2H, J = 6.5 Hz); 7.31 (d, 2H, J = 7.2 Hz); 7.25 (d, 2H, J = 8.3 Hz); 7.09 (d, 2H, J = 8.3 Hz); 7.03 (s, 1H, H_5); 2.60 (s, 3H, CH_3-S, pCH_3rhod); 2.55 (s, 3H, pCH_3thiazol); 2.43 (s, 3H, pCH_3rhod); 2.29 (s, 3H, CH_3tos); 2.08 (s, 3H, CH_3C$_4$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 177.5 (C-S); 162.6 (C═O); 160.1 (C_2thiazol); 144.3 (C_4thiazol); 141.7; 140.7; 138.5; 134.2; 132.1; 131.9; 130.9; 130.6; 129.1; 128.2; 126.6; 126.1 (Car); 109.1 (qd, J = 196.1 Hz, J = 5.2 Hz, C_5thiazol); 86.0 (C_2rhod); 21.5 (qt, J = 127.1 Hz, J = 4.2 Hz, pCH$_3$thiazol); 21.4 (qt, J = 127.2 Hz, J = 4.3 Hz, pCH$_3$rhod); 21.2 (qt, J = 126.2 Hz, J = 4.0 Hz, pCH$_3$tos); 15.9 (q, J = 14.8 Hz, CH$_3$-S); 14.2 (qd, J = 131.0 Hz, J = 2.1 Hz, CH$_3$C$_4$). HRMS (ESI) M+ for $C_{22}H_{21}N_2OS_3$ calcd.: 425.08160; found: 425.0816. The ionization clusters $(2C^+, Tos^-)^+$ is found at m/z 1021.

General Process for Pyridinium Salts 6X Preparations

A mixture of 50 mmol of 2-methylpyridine and 100 ml of iodomethane or MPTS is stirred in acetonitrile (50 ml) for 24 h at room temperature. The resulting salt is filtered off and washed with aceton.

1,2-Dimethylpyridinium iodide (6I). The alkylation of 2-methylpyridine (4.65 g; 50 mmol) with iodomethane (14.2 g; 100 mmol) gave **6I** (7.64 g; 65%).

6I: white crystals; mp = 244°C; ^{1}H NMR (200 MHz, D_2O) δ: 8.61 (d, 1H, J = 6.2 Hz); 8.28 (t, 1H, J = 7.9 Hz); 7.83 (d, 1H, J = 8.0 Hz); 7.74 (t, 1H, J = 7.0 Hz); 4.15 (s, 3H); 2.71 (s, 3H).

1,2-Dimethylpyridinium p-toluenesulfonate (6T). The alkylation of 2-methylpyridine (4.65 g; 50 mmol) with MPTS (18.62 g; 100 mmol) gave **6T** (9.77 g; 70%).

6T: white crystals; mp = 173°C. ^{1}H NMR(200 MHz, D_2O) δ: 8.45 (d, 1H, J = 6.2 Hz); 8.16 (t, 1H, J = 7.8 Hz); 7.67 (d, 1H, J = 8,1 Hz); 7.58 (t, 1H, J = 6.7 Hz); 7.49 (d, 2H, J = 8.2 Hz); 7.15 (d, 2H, J = 8.3 Hz); 4.01 (s, 3H); 2.58 (s, 1H); 2.21 (s, 3H).

General Procedure for Rhodacyanines 7X

Classical Heating (Ch)

In a round-bottom flask, 25 ml of acetonitrile are introduced and then 5 mmol of **5**, 5 mmol of the 1,2-dimethyl pyridinium salt **6X**, and 1 ml of Et_3N are added after reflux under stirring for 4 h or 24 h at room temperature. The red reaction mixture is concentrated, and the residue is precipitated by a minimum ethanol or EtOH/Et_2O mixture.

Microwave Irradiation (MW)

In the quartz reactor, 0.53 mmol of tosylate **5** and 0.53 mmol of salt **6X** are placed in the presence of two drops of Et_3N. After irradiation for 30 min at 85°C, a deep red solid is obtained, which is analyzed by ^{1}H NMR.

(2Z,5E)-1-Methyl-2-[{3-methyl-5-(3,4-dimethyl-1,3-thiazol-2-ylidene)-4-oxo -1,3-thiazolidin-2-ylidene}] methyl] pyridinium p-toluenesulfonate (7aT). The condensation of **5a** (2.20 g; 5 mmol) with **6T** (1.39 g; 5 mmol) gave **7aT** (1.96 g; 78%) in classical heating.

7aT: garnet red crystals; mp = 249°C. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 8.55 (d, 1H, J = 6.4 Hz); 8.18 (t, 1H, J = 7.8 Hz); 7.86 (d, 1H, J = 8.7 Hz); 7.50 (d, 2H, J = 7.9 Hz); 7.25 (t, 1H, J = 6.6 Hz); 7.15 (d, 2H, J = 7.8 Hz); 6.78 (s, 1H, H_5); 5.73 (s, 1H, C*H*=C_2rhod); 4.06 (s, 3H, CH_3N^+); 3.85 (s, 3H, CH_3N); 2.50 (s, 3H, CH_3Nrhod); 2.30 (s, 3H, CH_3tos); 2.26 (s, 3H, CH_3C_4). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 163.0 (C=O); 158.1 (C_2thiazol); 152.4 (C_2rhod); 150.5; 146.0; 145.1; 142.3; 138.9; 137.9; 131.1; 128.4 (Car + pyridine); 105.2 (C_5thiazol); 83.1 (*C*H=C_2); 77.8 (C_5rhod); 45.1 (*C*H_3N^+); 35.5 (*C*H_3Nthiazol); 30.6 (*C*H_3Nrhod); 21.1

(CH$_3$tos); 14.2 (CH$_3$C$_4$). HRMS (ESI) M+ for $C_{16}H_{18}N_3OS_2$ calcd.: 332.08913; found: 332.0896.

(2Z,5E)-1-Methyl-2-[{3-methyl-5-(3,4-dimethyl-1,3-thiazol-2-ylidene)-4-oxo -1,3-thiazolidin-2-ylidene}]methyl]Pyridinium Iodide (7aI). The condensation of **5a** (2.20 g; 5 mmol) with **6I** (1.17 g; 5 mmol) gave in classical heating **7aI** (1.60 g; 70%).

7aI: deep red powder; mp = 260°C. ^{1}H NMR (200 MHz, DMSO-d$_6$) δ: 8.55 (d, 1H, J = 6.2 Hz); 8.20 (t, 1H, J = 7.0 Hz); 7.89 (d, 1H, J = 8. 3 Hz); 7.30 (t, 1H, J = 7.1 Hz); 6.82 (s, 1H, H$_5$); 5.77 (s, 1H, CH=C$_2$rhod); 4.20 (s, 3H, CH_3N$^+$); 3.99 (s, 3H, CH_3Nthiazol); 3.70 (s, 3H, CH_3Nrhod); 2.30 (s, 3H, CH_3C$_4$). HRMS (ESI) M+ for $C_{16}H_{18}N_3OS_2$ calcd.: 332.08913; found: 332.0896. The ionization cluster (2C$^+$, I$^-$)$^+$ is not seen. Anal. calcd. for $C_{16}H_{18}N_3OIS_2$: C, 41.83; H, 3.95; N, 9.15; S, 13.96. Found: C, 41.56; H, 3.92; N, 9.54; S, 14.63.

(2Z,5E)-1-Methyl-2-[{3-methyl-5-(4-methyl-3-phenyl-1,3-thiazol-2-ylidene)-4-oxo-1,3-thiazolidine-2-ylidene}methyl] pyridinium p-Toluenesulfonate (7bT). The condensation of **5b** (2.53 g; 5 mmol) with **6T** (1.39 g; 5 mmol) gave in classical heating **7bT** (2.03 g; 72%).

7bT: red powder; mp > 260°C. ^{1}H NMR (200 MHz, DMSO-d$_6$) δ: 8.53 (d, 1H, J = 6.4 Hz); 8.06 (t, 1H, J = 7.5 Hz); 7.82 (d, 1H, J = 6.9 Hz); 7.77–7.65 (m, 5Har); 7.49 (d, 2H, J = 7.5 Hz); 7.33 (d, 2H, J = 7.8 Hz); 7.27 (t, 1H, J = 6.6 Hz); 6.93 (s, 1H, H$_5$); 5.63 (s, 1H, CH=C$_2$rhod); 4.00 (s, 3H, CH$_3$N$^+$); 2.53 (s, 3H, CH$_3$Nrhod); 2.31 (s, 3H, CH$_3$tos); 1.96 (s, 3H, CH_3C$_4$). ^{13}C NMR (50 MHz, DMSO-d$_6$) δ: 163.6 (C=O); 158.5 (C$_2$thiazol); 152.3 (C$_2$rhod); 148.8; 147.8; 146.8; 143.6; 137.1; 133.6; 132.2; 129.5; 127.8; 127.3; 125.4; 119.8; 116.0; 112.8; 112.3 (Car + Cpyriddine); 105.5 (C$_5$thiazol); 82.5 (CH=C$_2$rhod); 77.1 (C$_5$rhod); 46.5 (CH$_3$N$^+$); 33.6 (CH$_3$Nrhod); 20.7 (CH$_3$tos); 13.6 (CH$_3$C$_4$). HRMS (ESI) M+ for $C_{21}H_{20}N_3OS_2$ calcd.: 394.10478; found: 394.1043. The ionization clusters (2C$^+$, Tos$^-$)$^+$ are found at m/z 959.

(2Z,5E)-1-Methyl-2-[{3-methyl-5-(4-methyl-3-phenyl-1,3-thiazol-2-ylidene) -4-oxo-1,3-thiazolidine-2-ylidene}methyl] pyridinium Iodide (7bI). The condensation of **5b** (2.53 g; 5 mmol) with **6I** (1.17 g; 5 mmol) gave in classical heating **7bI** (1.61 g; 62%).

7bI: red crystals; mp > 260°C. ^{1}H NMR (200 MHz, DMSO-d$_6$) δ: 8.58 (d, 1H, J = 6.6 Hz); 8.08 (t, 1H, J = 8.1 Hz); 7.79–7.69 (m, 5Har); 7.33 (t, 1H, J = 6.1 Hz); 7.15 (d, 1H, J = 7.2 Hz); 6.92 (s, 1H, H$_5$); 5.28 (s, CH=C$_2$rhod); 4.00 (s, 3H, CH_3N$^+$); 2.54 (s, 3H, CH_3Nrhod); 1.96 (s, 3H, CH_3C$_4$). HRMS (ESI) M+ for $C_{21}H_{20}N_3OS_2$ calcd.: 394.10478;

found: 394.1043. The ionization cluster $(2C^+, I^-)^+$ for $C_{42}H_{40}N_6O_2IS_4$ calcd.: 915.11404; found: 915.1185. Anal. calcd. for $C_{21}H_{20}N_3OIS_2$: C, 48.37; H, 3.87; N, 8.06; S, 12.30. Found: C, 47.75; H, 3.82; N, 8.25; S,13.45.

(2Z,5E)-1-Methyl-2[{3-methyl-5-[4-methyl-3-(4-methylphenyl)-1,3-thiazol-2-ylidene]-4-oxo-1,3-thiazolidine-2-ylidene}methyl] pyridinium p-Toluenesulfonate (7cT). The condensation of **5c** (2.60 g; 5 mmol) with **6T** (1.39 g; 5 mmol) gave in classical heating **7cT** (1.80 g; 60%).

7cT: red powder; mp = 234°C. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 8.51 (d, 1H, J = 6.2 Hz); 8.01 (t, 1H, J = 7.9 Hz); 7.60 (d, 1H, J = 6.1 Hz); 7.52 (m, 4Har); 7.40 (d, 2H, J = 8.0 Hz); 7.23 (t, 1H, J = 6.6 Hz); 7.09 (d, 2H, J = 7.6 Hz); 6.88 (s, 1H, H_5); 5.59 (s, 1H, C*H*=C_2); 3.97 (s, 3H, CH_3N^+); 3.35 (s, 3H, pCH_3rhod); 2.52 (s, 3H, pCH_3); 2.26 (s, 3H, CH_3tos); 1.93 (s, 3H, CH_3C_4). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 164.1 (C=O); 157.1 (C_2thiazol); 153.7 (C_2rhod); 151.5; 146.6; 145.9; 142.4; 138.2; 133.0; 131.2; 130.9; 128.7; 126.0; 122.0; 118.1 (Car + Cpyridine); 104.1 (C_5thiazol); 83.5 (*C*H=C_2rhod); 78.7 (C_5rhod); 45.1 (*C*H_3N^+); 29.7 (*C*H_3Nrhod); 20.8 (pCH_3); 20.7 (p*C*H_3tos); 13.78 (*C*H_3C_4). HRM (ESI) M+ for $C_{22}H_{22}N_3OS_2$ calcd.: 408.12043; found: 408.1209. The ionization cluster $(2C^+, Tos^-)^+$ is not seen.

(2Z,5E)-1-Methyl-2[{3-methyl-5-[4-methyl-3-(4-methylphenyl)-1,3-thiazol-2-ylidene]-4-oxo-1,3-thiazolidine-2-ylidene}methyl]pyridinium iodide (7cI). The condensation of **5c** (2.60 g; 5 mmol) with **6I** (1.17 g; 5 mmol) gave in classical heating, **7cI** (1.44 g; 54%).

7cI: garnet red crystals; mp > 260°C. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 8.53 (d, 1H, J = 6.7 Hz); 8.04 (t, 1H, J = 7.2 Hz); 7.51 (m, 4H, J = 7.9 Hz); 7.27 (t, 1H, J = 7.1 Hz); 7.15 (d, 1H, J = 8.4 Hz); 6.92 (s, 1H, H_5); 5.62 (s, 1H, C*H*=C_2); 4.02 (s, 3H, CH_3N^+); 3.36 (s, 3H, pCH_3rhod); 2.52 (s, 3H, pCH_3); 1.96 (s, 3H, CH_3C_4). HRMS (ESI) M+ for $C_{22}H_{22}N_3OS_2$ calcd.: 408.12043; found: 408.1209. The ionization cluster $(2C^+, I^-)^+$ for $C_{44}H_{44}N_6O_2IS_4$ calcd.: 943.14534; found: 943.1478.

(2Z,5E)-1-Methyl-2-[{3-(4-methylphenyl)-5-(3,4-dimethyl-1,3-thiazol-2-ylidene)-4-oxo-1,3-thiazolidine-2-ylidene}methyl] pyridinium p-toluenesulfonate (7dT). The condensation of **5d** (2.60 g; 5 mmol) with **6T** (1.39 g; 5 mmol) gave in classical heating **7dT** (2.10 g; 70%).

7dT: brick red powder; mp = 258°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.58 (d, 1H, J = 6.3 Hz); 8.19 (t, 1H, J = 7.9 Hz); 7.98 (d, 1H, J = 8.6 Hz); 7.76 (t, 1H, J = 7.9 Hz); 7.38 (d, 2H, J = 8.0 Hz); 7.20 (d, 2H, J = 8.1 Hz; 7.08 (d, 2H, J = 7.8 Hz); 7.01 (d, 2H, 6.7 Hz); 6.39 (s, 1H, H_5); 5.27 (s, 1H, C*H*=C_2rhod); 4.02 (s, 3H, CH_3N^+); 3.70 (s, 3H, CH_3Nthizol); 3.02 (s, 3H,

CH_3Nrhod); 2.40 (s, 3H, CH_3tos); 2.29 (s, 3H, CH_3C$_4$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 164.7 (C═O); 159.9 (C$_2$thiazol); 155.5 (C$_2$rhod); 151.6; 145.6; 143.4; 142.5; 141.1; 138.9; 138.6; 131.9; 131.1; 128.4; 127.9; 125.9; 123.7; 117.9 (Car + Cpyridine); 106.2 (C$_5$thiazol); 83.2 (*C*H═C$_2$rhod); 78.2 (C$_2$rhod); 44.8 (*C*H$_3$N$^+$); 36.3 (*C*H$_3$Nthiazol); 21.4 (p*C*H$_3$rhod); 21.3 (p*C*H$_3$tos); 14.7 (*C*H$_3$C$_4$). HRMS (ESI) M+ for $C_{22}H_{22}N_3OS_2$ calcd.: 408.12043; found: 408.119. The ionization clusters (2C$^+$, Tos$^-$)$^+$ is found to be m/z 987.

(2Z,5E)-1-Methyl-2-[{3-(4-methylphenyl)-5-(3,4-dimethyl-1,3-thiazol-2-ylidene)-4-oxo-1,3-thiazolidine-2-ylidene}methyl]pyridinium iodide (7dI). The condensation of **5d** (2.60 g; 5 mmol) with **6I** (1.17 g; 5 mmol) gave in classical heating **7dI** (1.90 g; 72%).

7dI: garnet red crystals; mp = 192°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.57 (d, 1H, J = 6.5 Hz); 8.13 (t, 1H, J = 7.9 Hz); 7.92 (d, 1H, J = 8.5 Hz); 7.76 (d, 1H, J = 8.0 Hz); 7.38 (d, 2H, J = 8.1 Hz); 7.19 (d, 2H, J = 8.2 Hz); 7.02 (t, 1H, J = 6.6 Hz); 6.37 (s, 1H, H$_5$); 528 (s, 1H, C*H*═C$_2$rhod); 3.97 (s, 3H, CH_3N$^+$); 3.70 (s, 3H, CH_3Nthiazol); 2.45 (s, 3H, CH_3rhod); 2.30 (s, 3H, CH_3C$_4$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 163.7 (C═O); 159.0 (C$_2$thiazol); 154.5 (C$_2$rhod); 150.5; 144.0; 142.3; 140.3; 139.0; 132.5; 128.5; 127.9; 117.4 (Car + Cpyridine); 105.4 (C$_5$thiazol); 83.9 (*C*H═C$_2$rhod); 79.0 (C$_5$rhod); 44.7 (*C*H$_3$N$^+$); 35.8 (*C*H$_3$Nrhod); 21.3 (p*C*H$_3$rhod); 14.6 (*C*H$_3$C$_4$). HRMS (ESI) for $C_{22}H_{22}N_3OS_2$ calcd.: 408.12043; found: 408.119. The ionization cluster (2C$^+$, I$^-$)$^+$ for $C_{44}H_{44}N_6O_2IS_4$ calcd.: 943.14534; found: 943.1446.

(2Z,5E)-1-Methyl-2-[{3-(4-methylphenyl)-5-(4-methyl-3-phenyl-1,3-thiazol-2-ylidene)-4-oxo-1,3-thiazolidine-2-ylidene}methyl]pyridinium p-toluenesulfonate (7eT). The condensation of **5e** (3.00 g; 5 mmol) with **6T** (1.39 g; 5 mmol) gave in classical heating **7eT** (2.00 g; 65%).

7eT: brown crystals; mp = 258°C. ^{1}H NMR (200 MHz, DMSO-d$_6$) δ: 8.46 (d, 1H, J = 6.1 Hz); 8.06 (t, 1H, J = 7.8 Hz); 7.73 (m, 5H); 7.47 (d, 2H, J = 8.0 Hz); 7.41 (d, 2H, J = 8.2 Hz); 7.37 (d, 1H, J = 7.9 Hz); 7.25 (m, 4Har); 7.12 (t, 1H, J = 8.2 Hz); 6.91 (s, 1H, H$_5$); 5.14 (s, 1H, C*H*═C$_2$rhod); 3.59 (s, 3H, CH_3N$^+$); 2.40 (s, 3H, pCH_3); 2.28 (s, 3H, CH_3tos); 1.95 (s, 3H, CH_3C$_4$).^{13}C NMR (50 MHz, DMSO-d$_6$) δ: 163.3 (C═O); 156.0 (C$_2$thiazol); 153.2 (C$_2$rhod); 151.2; 146.6; 140.0; 138.3; 138.1; 135.6; 135.1; 133.2; 132.1; 131.3; 130.9; 128.9; 128.7; 126.2; 122.0; 113.5; 112.6 (Car + Cpyridine); 104.8 (C$_5$thiazol); 84.9 (*C*H═C$_2$thiazol); 76.5 (C$_2$rhod); 44.5 (*C*H$_3$N$^+$); 20.8 (p*C*H$_3$tos); 20.7 (p*C*H$_3$rhod); 13.8 (*C*H$_3$C$_4$). HRMS (ESI) M+ for $C_{27}H_{24}N_3OS_2$ calcd.: 470.13608; found: 470.1358. The ionization cluster (2C$^+$, Tos$^-$)$^+$ is not seen. Anal. calcd. for $C_{34}H_{31}N_3O_4S_3$: C, 63.63; H, 4.87; N, 6.55; S, 14.99. Found: C, 63.29; H, 4.86; N, 6.64; S, 15.07.

(2Z,5E)-1-Methyl-2-[{3-(4-methylphenyl)-5-(4-methyl-3-phenyl-1,3-thiazol-2-ylidene)-4-oxo-1,3-thiazolidine-2-ylidene}methyl]pyridinium iodide (7eI). The condensation of **5e** (3.00 g; 5 mmol) with **6I** (1.17 g; 5 mmol) gave in classical heating **7eI** (2.25 g; 75%).

7eI: brick red crystals; mp $>$ 260°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.88 (d, 1H, $J = 6.2$ Hz); 7.90 (t, 1H, $J = 8.0$ Hz); 7.77 (t, 1H, $J = 8.0$ Hz); 7.74–7.68 (m, 5Har); 7.42 (d, 2H, $J = 8.0$ Hz); 7.28 (d, 2H, $J = 7.6$ Hz); 7.20 (d, 1H, $J = 8.6$ Hz); 6.4 (s, 1H, H_5); 5.16 (s, 1H, C*H*=C_2rhod); 3.7 (s, 3H, CH_3N^+); 2.3 (s, 3H, pCH_3); 2.29 (s, 3H, CH_3C_4). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 164.3 (C=O); 156.8 (C_2thiazol); 154.5 (C_2rhod); 150.6; 146.2; 143.6; 141.2; 137.2; 132.1; 130.1; 129.9; 128.7; 127.7; 121.8; 118.3 (Car + Cpyridine); 104.5 (C_5thizol); 84.4 (*C*H=C_2rhod); 78.2 (C_5rhod); 44.8 (*C*H_3N^+); 21.3 (pCH_3); 14.4 (*C*H_3C_4). HRMS (ESI) M+ for $C_{27}H_{24}N_3OS_2$ calcd.: 470.13608; found: 470.1358. The ionization cluster $(2C^+, I^-)^+$ for $C_{54}H_{48}N_6O_2IS_4$ calcd.: 1067.17664; found: 1067.1763. Anal. calcd. for $C_{27}H_{24}N_3OIS_2$: C, 54.27; H, 4.05; N, 7.03; S, 10.73. Found: C, 53.92; H, 4.10; N, 7.27; S, 10.70.

(2Z,5E)-1-Methyl-2-[{3-(4-methylphenyl)-5-(4-methyl-3-(4-methylphenyl)-1,3-thiazol-2-ylidene)-4-oxo-1,3-thiazolidine-2-ylidene}methyl] pyridinium p-toluenesulfonate (7fT). The condensation of **5f** (3.00 g; 5 mmol) with **6T** (1.39 g; 5 mmol) gave in classical heating **7fT** (2.34 g; 72%).

7fT: garnet red crystals; mp = 255°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.9 (d, 1H, $J = 6.2$ Hz); 7.8 (d, 2H, $J = 8.0$ Hz); 7.7 (t, 1H, $J = 8.2$ Hz); 7.5 (d, 2H, $J = 8.2$ Hz); 7.38 (d, 2H, $J = 8.5$ Hz); 7.30 (d, 2H, $J = 8.0$ Hz); 7.25 (d, 1H, $J = 6.3$ Hz); 7.17 (d, 2H, $J = 8.1$ Hz); 7.13 (t, 1H, $J = 7.1$ Hz); 6.45 (s, 1H, H_5); 5.23 (s, 1H, C*H*=C_2rhod); 3.85 (s, 3H, CH_3N^+); 2.62 (s, 3H, pCH_3rhod); 2.48 (s, 3H, pCH_3thiazol); 2.35 (s, 3H, CH_3tos); 2.17 (s, 3H, CH_3C_4). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 164.3 (C=O); 156.5 (C_2thiazol); 154.5 (C_2rhod); 150.7; 146.5; 143.6; 142.2; 140.7; 140.4; 139.0; 137.3; 132.4; 132.1; 131.1; 130.9; 129.9; 128.4; 127.7; 126.0; 121.7; 118.2 (Car + Cpyridine); 104.3 (C_5thiazol); 84.3 (*C*H=C_2rhod); 79.8 (C_2rhod); 44.9 (*C*H_3N^+); 30.9 (p*C*H_3thiazo); 21.4 (p*C*H_3rhod); 21.3 (*C*H_3tos); 14.4 (*C*H_3C_4). HRMS (ESI) M+ for $C_{28}H_{26}N_3OS_2$ calcd.: 484.15173; found: 484.1520. The ionization cluser $(2C^+, Tos^-)^+$ is not seen.

(2Z,5E)-1-Methyl-2-[{3-(4-methylphenyl)-5-(4-methyl-3-(4-methylphenyl)-1,3-thiazol-2-ylidene)-4-oxo-1,3-thiazolidine-2-ylidene}methyl]pyridinium iodide (7fI). The condensation of **5f** (3.00 g; 5 mmol) with **6I** (1.17 g; 5 mmol) gave in classical heating **7fI** (2.24 g; 74%).

7fI: red crystals; mp = 216°C. ^{1}H NMR (200 MHz, CDCl3) δ: 9.04 (d, 1H, $J = 6.0$ Hz); 7.7 (t, 1H, $J = 8.2$ Hz); 7.57 (d, 1H, $J = 7.8$ Hz); 7.30

(d, 4Har); 7.20 (t, 1H, $J = 8.2$ Hz); 7.15 (d, 4Har); 6. 47 (1H, H_5); 5.21 (s, 1H, C*H*=C_2rhod); 3.84 (s, 3H, CH_3N^+); 2.48 (s, 3H, pCH_3thiazol); 2.35 (s, 3H, pCH_3rhod); 2.04 (s, 3H, CH_3C_4). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 163.5 (C=O); 159.9 (C_2thiazol); 154.3 (C_4thiazol); 150.9; 145.5; 142.3; 140.9; 138.5; 137.5; 131.1; 129.9; 122.0; 117.8 (Car + Cpyridine); 104.5 (C_5thiazol); 84.2 (*C*H = C_2rhod); 79.5 (C_2rhod); 45.3 (*C*H_3N^+); 31.0 (p*C*H_3-thiazol); 21.5 (p*C*H_3rhod); 14.4 (*C*H_3C_4). HRMS (ESI) M+ for $C_{28}H_{26}N_3OS_2$ calcd.: 484.15173; found: 484.1520. The ionization cluster $(2C^+, I^-)^+$ for $C_{56}H_{52}N_6O_2IS_4$ calcd.: 1095.2079; found: 1095.2061.

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