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Synthetic Potentials of Heptamethine Merocyanine Dyes Containing an Active Chlorine Atom: Reactivity towards Nucleophiles

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The reactivity of heptamethine merocyanine dyes that contain an active chlorine atom at a *meso* position of the polymethine chain towards nucleophiles is investigated for the first time. The reactivity differs completely from that of cationic cyanine dyes and is consistent with a concerted S_NAr addition–elimination mechanism. This mechanism is additionally supported by the performed DFT calculations in the gas phase and in solution. The observed dependence of the reaction on the type of the nucleophilic agents is discussed in terms of Pearson's theory. Additional diversification of and improvement in the stability of the ramified merocyanines is achieved in reactions with methyl-substituted quaternary salts of nitrogen-containing heterocycles. The photophysical characteristics of the novel dyes are reported and compared with those of the parent merocyanine.

Introduction

As a result of the wide use of merocyanines as new organic materials, their structural design and reactivity are in the focus of cyanine dyes chemistry.[1–9] In a recent paper we reported a simple and efficient enolate-based synthetic approach to rigidized mono- and bis(heptamethine) merocyanines with variable donor and acceptor groups possessing a chlorine substituent at a *meso* position.[10] Depending on the reaction conditions, the interaction of the new dyes with 3-ethyl-2-methyl benzothiazol-3-ium iodide afforded products with lengthened and/or ramified polymethine chains. X-ray crystallographic analysis revealed that the ramification occurs through a sulfur bridge as a result of a ring-opening reaction.

Later, we demonstrated that the main product of the basic hydrolysis of 3-ethyl-2-methyl benzothiazol-3-ium iodide, as usually used in the syntheses of dyes, is *N*-(2-mercaptophenyl)-*N*-ethylacetamide, which is the actual species accomplishing the nucleophilic attack.[11]

In this paper, we report a convenient preparation of multifunctional merocyanine dyes by consecutive, two-stage ramification/prolongation of the polymethine chain of the readily available *meso*-chlorine-substituted precursors, employing in each reaction step a different nucleophile. The influence of the substituents at the central and terminal positions of the polymethine chain on the photophysical characteristics of the new dyes is discussed.

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Results and Discussion

Synthesis of Ramified Heptamethine Merocyanine Dyes

As a first stage of this study we examined the possibility for ramification of the merocyanine chain by replacement of the chlorine atom by various nucleophiles. Direct substitution of the nucleofugal chlorine atom in heptamethine cyanines is well recognized and has been used as a common access to functionalized dyes for near-infrared fluorescence labelling. According to the literature, the reaction occurs readily with nucleophiles having good electron-donor ability through a $S_{RN}1$ mechanistic pathway.[12–16] In agreement with the postulated mechanism, the substitution is found to be efficient in solvents promoting the single electron-transfer process (e.g., DMF).[17] Alternatively, in media where such a transfer is not favoured, for example, aqueous alcohol, the substitution is completely suppressed.[18]

Note that although direct functionalization of the chlorine-substituted heptamethine cyanines is well documented,[12–17] surprisingly and to the best of our knowledge no examples are reported for analogous merocyanine dyes.

The reaction was examined by using the readily available merocyanine MC1 with a diethylamino end group and a set of -NH, -OH and -SH nucleophiles. In a single case, the merocyanine MC2 possessing a piperidine moiety at a terminal position was applied.

Our attempts to perform the substitution under $S_{RN}1$ conditions as described for the cyanine dyes series[12–17] completely failed with all tested nucleophiles. On the contrary, in boiling ethanol in the presence of a piperidine base as recently reported,[10] we found dependence of the reaction course on the type of the nucleophilic agent. Thus, the use of -NH (morpholine, piperidine) and -OH (phenol, *p*-aminophenol) nucleophiles did not result in successful ramification. Instead, as proved by ^{1}H NMR spectroscopic analysis, a partial exchange of the terminal diethylamino group by a piperidino one occurred.

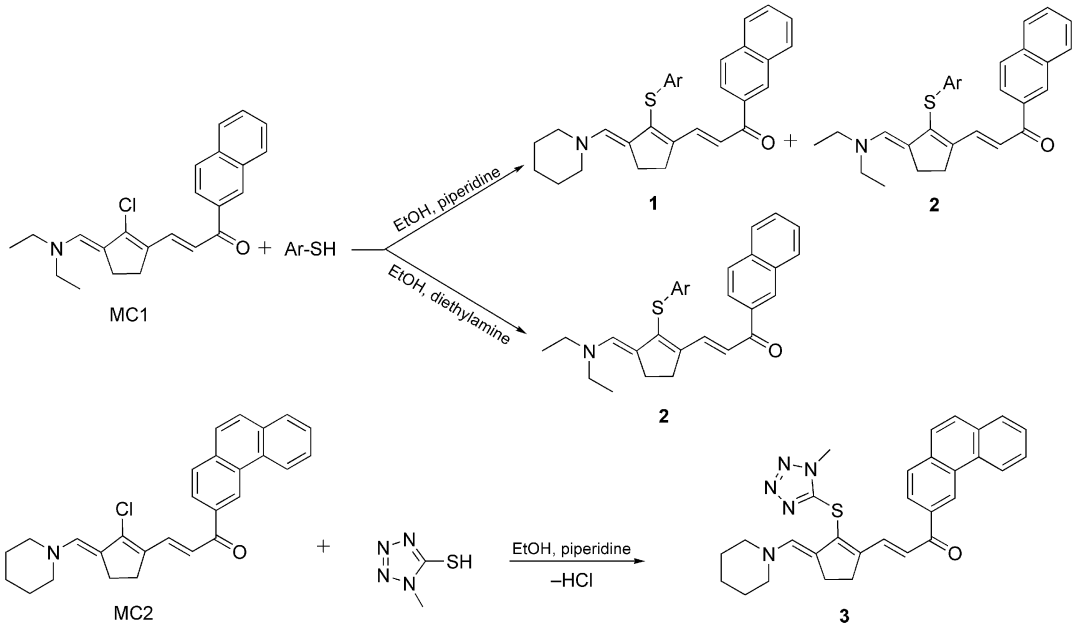
Under identical conditions all tested -SH nucleophiles (Scheme 1, Table 1) replaced the chlorine atom efficiently, and the conversion was complete within 0.5–3 h (TLC monitoring of the reaction). As noted above, the nucleophilic substitution was accompanied by a partial exchange of the end group, thus giving a mixture of products **1** and **2** in different proportions. Our attempt to avoid this side reaction by decreasing the base from 1.5 to 0.3 equivalents was unsuccessful. An exception was observed in the case of **2h**, where the crude target compound was obtained in 96% purity (NMR spectroscopic analysis).

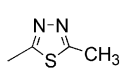
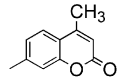
Next, we examined the possibility to direct the reaction entirely to products **1** by increasing the quantity of the piperidine base to 5 equivalents. The ^{1}H NMR spectra of the reaction mixtures demonstrated, however, that although compounds **1** strongly predominated, small proportions of products **2** were still present. Because these proportions did

Table 1. Synthesis of ramified, through a sulfur linker, heptamethine merocyanines.

Compound (ratio)	Base	MC1/ArSH	Time [min]	Yield[d] [%]
1a(**2a**)[a] (86:14)	piperidine	1:5	60	93
1b(**2b**)[a] (91:9)	piperidine	1:5	90	91
1d(**2d**)[a] (80:20)	piperidine	1:5	60	95
1e(**2e**)[a] (90:10)	piperidine	1:5	30	84
1f(**2f**)[a] (86:14)	piperidine	1:5	60	98
1g(**2g**)[a] (80:20)	piperidine	1:5	30	81
2c	diethylamine	1:1	30	80
2d	diethylamine	1:5	30	88
2e	diethylamine	1:5	60	76
2f	diethylamine	1:3	30	89
2g	diethylamine	1:3	30	72
2h[b]	piperidine	1:1	30	95
3[c]	piperidine	1:5	180	63

[a] Compounds were isolated as mixtures of **1** and **2** with a strong predominance of products **1** (^{1}H NMR spectroscopic analysis). [b] Obtained in the presence of piperidine (0.3 equiv.). [c] Starting from merocyanine MC2. [d] Yield after a general workup procedure followed by washing with dry diethyl ether (see Experimental Section).



Compounds 1[a]	1a(2a)	1b(2b)		1d(2d)	1e(2e)	1f(2f)	1g(2g)	
Compounds 2			2c	2d	2e	2f	2g	2h
Ar								

[a] Compounds **1** are obtained as mixtures with compounds **2** with a strong predominance of products **1**. Ratios are given in Table 1.

Scheme 1. Synthesis of ramified merocyanine dyes using -SH nucleophiles.

not change with prolongation of the reaction time indicated in Table 1, they most probably reflect the thermodynamic stability of the products. Unfortunately, our efforts to purify compounds **1** by recrystallization were unsuccessful.

As might be expected, the observed complication due to the end group exchange was prevented by performing the reaction in the presence of an amine, identical with the terminal amino group in the merocyanine precursor. Following this improved protocol, pure samples of compounds **2** were obtained from MC1 in the presence of diethylamine. Alternatively, merocyanine MC2 with a terminal piperidino group gave compound **3** in good yield and purity in the presence of piperidine. The experimental data are summarized in Table 1.

The reaction with the tested -SH nucleophiles occurs in high to moderate yields. The reaction time and the excess amount of the nucleophilic agent are specified for each particular case. In general, the target products − individual or as a mixture of compounds **1** and **2** − have up to 95% purity (NMR spectroscopic data) after a common workup procedure followed by trituration with diethyl ether. As mentioned above, attempts at purification by recrystallization or by flash chromatography decreased significantly the reaction yields and in some cases worsened the purities of the products obviously as a result of their chemical instability.

All new compounds are deep-red-coloured substances. Their structures were undoubtedly proven by elemental and spectral analysis (mass, ^{1}H and ^{13}C NMR spectra). Note, whereas the products are stable for months in the solid state, their stability in solution is poor.

Conversion of the Ramified Heptamethine Merocyanines into Nonamethine Dyes

With a series of ramified merocyanines in hand we examined the possibility for elongation of the polyene chain by employing a condensation reaction with methyl-substituted quaternary salts of nitrogen-containing heterocycles. We expected that the successful proceeding of this reaction will contribute both to the synthetic diversity and the stability of the new dyes.[10]

The condensation with benzothiazolium salts bearing different functional groups was carried out in boiling pyridine[10] (Scheme 2, Table 2). ^{1}H NMR spectroscopic analysis of the reaction products revealed however that in some of the cases studied the chain prolongation is accompanied by replacement of the aromatic residue at the central position by the corresponding mercaptan, in situ produced from hydrolysis of the quaternized heterocycle.[11]

Table 2. Conversion of ramified heptamethine merocyanines into their nona analogues.

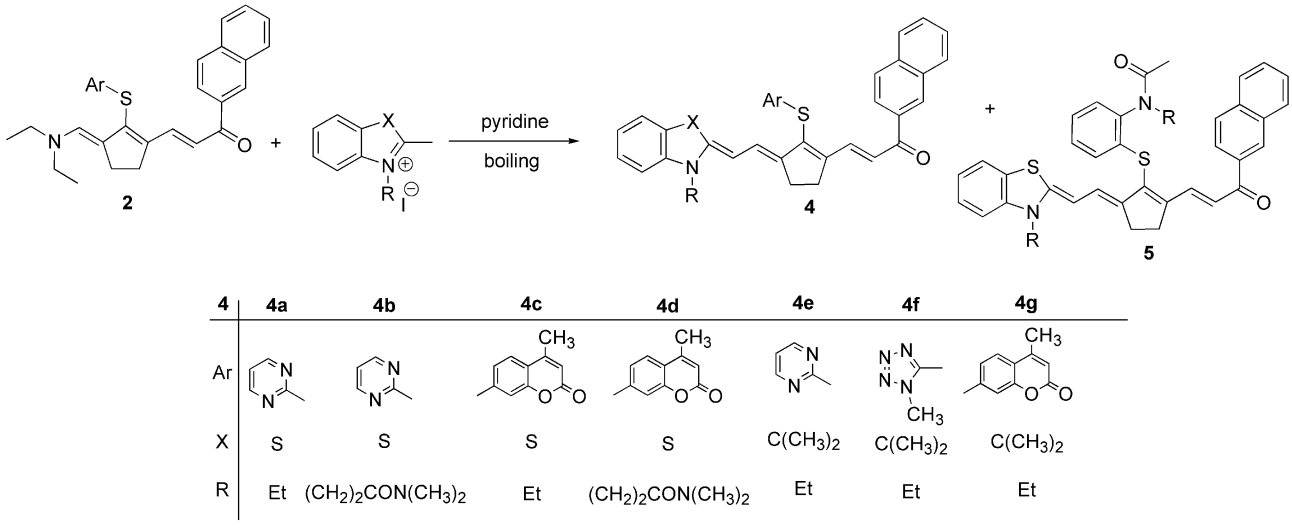
Compound	Ratio **4/5**	Time [min]	Yield [%]
4a[a]	84:26	10	30
4b[a]	63:37	10	32
4c	100:0	10	36
4d	100:0	15	55
4e[b]	100:0	15	54
4f[b]	100:0	25	64
4g	100:0	30	62

[a] Compounds were isolated as mixtures of **4** and **5**. Ratio **4/5** was determined by ^{1}H NMR spectroscopic analysis of the crude products. [b] Two equivalents of the quaternary salt are employed.

The observed side reaction was efficiently avoided by use of quaternary 1-ethyl-2,3,3-trimethyl-3*H*-indolium iodide (compounds **4e**–**g**) where such a competition does not occur. Note that the new dyes with elongated polymethine chains have substantially enhanced stability compared to their ramified precursors. They are purified by column chromatography on silica and are stable both in solution and the solid state.

Photophysical Properties

The absorption and fluorescence characteristics of new dyes **2** and **4** are shown in Table 3. The values for the parent



Scheme 2. Elongation of the polymethine chain of the ramified heptamethine merocyanines.

chlorine-containing merocyanine MC1 are given for comparison. All the studied compounds in ethanol solution at room temperature absorb and fluoresce in the visible region of the spectrum. Their longest wavelength absorption maxima are between 16000 and 19000 cm^{-1} with molar absorptivities in the range 32000–45000 $L\,mol^{-1}\,cm^{-1}$. Correspondingly, the fluorescence Franck–Condon transitions lie between 14200 and 15500 cm^{-1}. The fluorescence quantum yields are uniformly low. Some representative absorption and fluorescence spectra of ramified merocyanines **2** and **4** are shown in Figure 1.

Table 3. Absorption and fluorescence characteristics of the studied compounds at 293 K in ethanol: $\tilde{\nu}_{abs}$ is the energy of the longest wavelength absorption Franck–Condon transition; ε is the molar absorptivity; $\tilde{\nu}_F$ is the energy of the fluorescence Franck–Condon transition; Q_F is the fluorescence quantum yield.

Compound	$\tilde{\nu}_{abs}$ [cm^{-1}]	ε [$L\,mol^{-1}\,cm^{-1}$]	$\tilde{\nu}_F$ [cm^{-1}]	Q_F
MCl	18650	32000	15630	0.03
2c	18830	38600	15410	0.03
2d	18880	39890	15390	0.03
2e	18660	41360	15240	0.02
2f	18970	39320	15460	0.03
2g	18940	41580	15470	0.03
2h	18870	35770	15230	0.03
4a	16780	40780	14080	0.01
4b	16950	38200	14630	0.01
4c	16670	36600	14290	0.02
4d	16720	32230	14710	0.01
4e	17390	43810	14290	0.01
4f	17240	40820	14180	0.01
4g	17300	45280	14180	0.01

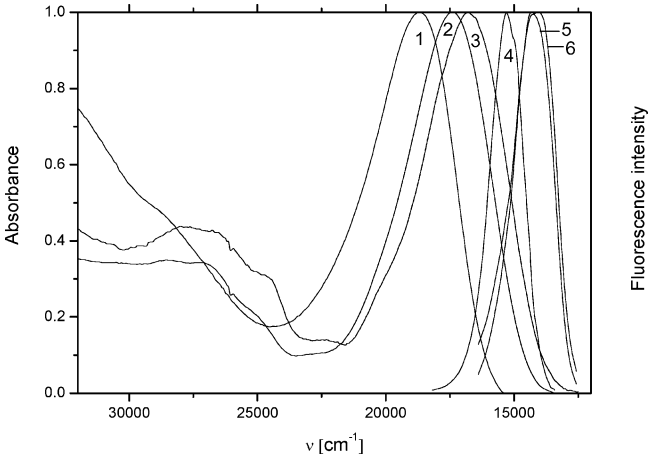


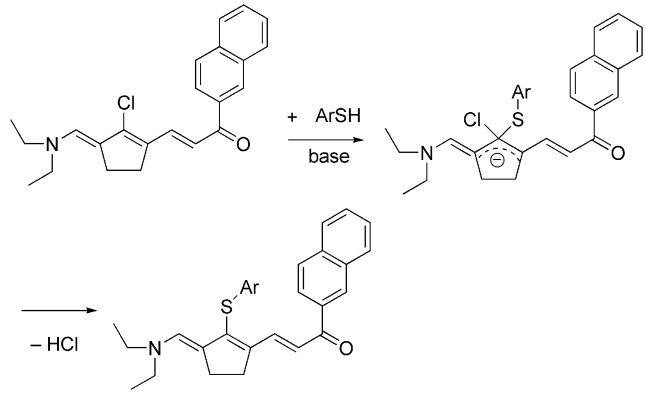
Figure 1. Normalized absorption spectra of compound **2e** (curve 1); **4e** (curve 2) and **4a** (curve 3) and corrected fluorescence spectra of compound **2e** (curve 4); **4e** (curve 5) and **4a** (curve 6) in ethanol (concentration 1×10^{-5} $L\,mol^{-1}$) at room temperature.

As seen from Table 3, ramification of the polymethine chain through a sulfur linkage (compounds **2**) does not appreciably change the basic properties of the parent *meso*-chlorine-substituted dye MC1, independently of the type of residue attached. To the contrary, the prolongation of the conjugated system leads to a bathochromic shift in the longest wavelength absorption Franck–Condon transition with about 2000 cm^{-1} in the case of compounds **4a**–**d** and 1350 cm^{-1} for compounds **4e**–**g**. The effect on the energy of the fluorescence Franck–Condon transition is less pronounced. It is shifted to the red region with approximately 1000 cm^{-1}.

Reaction Mechanism

Finally, we would like to comment on the mechanistic aspects of the reaction under consideration. As reported, the conditions where we achieved a successful nucleophilic replacement of the *meso*-chlorine atom − 96% ethanol in the presence of an organic base − are apparently inconsistent with the $S_{RN}1$ reaction mechanism widely accepted for analogous cationic cyanine dyes.

Taking into account our experimental data and the electronic structure of the merocyanines, delocalized π electronic systems,[3] we presumed that the examined nucleophilic substitution follows a S_NAr addition–elimination pathway as depicted in Scheme 3.



Scheme 3. Probable mechanism of the nucleophilic replacement of the *meso*-chlorine atom.

We further performed DFT calculations to study the mechanism by using the B3PW91 functional as implemented in Gaussian 03, which show somewhat different mechanistic pictures for "hard" and "soft" nucleophiles. The "hard" -OH and -NH reagents do not form any intermediate adduct, and the nucleophilic attack occurs concertedly on the "front side"[19] of a tetrahedral transition structure. In contrast, attack of the "soft" -SH nucleophiles (Figure 2) leads to formation of two transition structures with close geometry parameters, separated by a shallow intermediate. However, account for solvent in the DFT calculations indicates concertedness and front-side substitution also by "soft" -SH nucleophiles. Details of these calculations will be published elsewhere.

The observed dependence of the reactivity on the type of the nucleophilic agent could be rationalized in terms of Pearson's theory.[20] Most probably -NH and -OH nucleophiles failed to react owing to their "harder" character than the -SH reagents. It the latter case, the better fit between the "soft" nucleophilic centre – sulfur atom – and the "soft" electrophile – delocalized merocyanine chain – seems to be of crucial importance for a successful reaction.

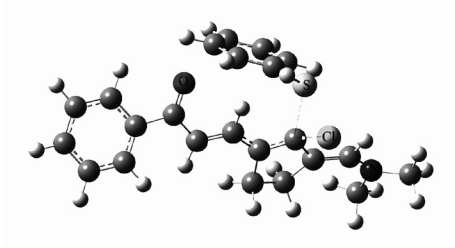


Figure 2. Transition structure for the attack of thiophenol on a model merocyanine MC1, optimized at the B3PW91/6-31G* level of theory in the gas phase.

Conclusions

In this paper we investigated for the first time the reactivity of rigidized heptamethine merocyanine dyes containing a nucleofugal chlorine atom at a *meso* position of the polymethine chain. Our experimental data clearly demonstrated that the reactivity towards nucleophiles differs completely from that reported for analogous cationic cyanine dyes and is consistent with a front-side S_NAr addition–elimination mechanism. This mechanism is further supported by the performed DFT calculations. Additional diversification of the ramified merocyanine dyes concerning both the length of the polymethine chain and its functionality was achieved by employing a condensation reaction with methyl-substituted quaternary salts of nitrogen-containing heterocycles. This structural modification improves significantly the stability of the ramified precursors both in solution and in the solid state.

Our study reveals the synthetic utility of the chlorine-substituted merocyanine dyes and contributes to their design and synthetic diversity. It offers an easy and general approach to the ramified, through a sulfur linker, and rigidized analogues.

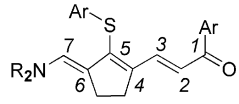
As a result of the present investigation a new series of merocyanine dyes, differently functionalized at the central and the terminal positions, were synthesized in good to moderate yields.

Experimental Section

General: The starting merocyanines were synthesized as reported.[10] All other reagents are commercially available and were used without further purification. Thin-layer chromatography (TLC) of the reaction mixtures and determination of the R_f values of the products were performed on aluminum sheets precoated with silica gel 60 F_{254} (Merck). Melting points were determined with a Kofler apparatus and are uncorrected. NMR spectra were recorded at ambient temperature (300 K) in $CDCl_3$ solutions with a Bruker Avance DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C nuclei or with an Avance 600 II+ spectrometer, operating at 600.13 and 150.92 MHz for ^1H and ^{13}C nuclei, respectively, with TMS as internal standard for chemical shifts. Mass spectra (MS) were recorded with Hewlett–Packard 5973A, Perkin–Elmer Sciex (API 365) or Applied Biosystems (Q TRAP) spectrometers. Elemental analysis were performed by the Microanalytical service Laboratory of the Institute of Organic Chemistry, Bulgarian Academy of Sciences. Absorption spectra were scanned with a UV/Vis Spectrophotometer Perkin–Elmer Lambda 25. The corrected fluorescence spectra were measured with a Perkin–Elmer LS 55 spectrofluorimeter (photomultiplier R928). The fluorescence quantum yield (Q_F) was determined relative to that of the dye Rhodamine 6G (Q_F = 0.58 in ethanol)[21] and Cresyl Violet (Q_F = 0.53 in methanol).[22]

General Experimental Procedure for the Synthesis of Ramified Heptamethine Merocyanines 1–3: The optimized reaction parameters − ratio between the reactants and the reaction time − for each particular case are shown in Table 1. To a solution of the starting merocyanine MC (1 mmol) and the corresponding thiol (ArSH) in 96% EtOH (35 mL) was dropwise added the organic base (piperidine or diethylamine, 5 mmol). The reaction was kept under reflux for the time indicated and then cooled to room temperature. After removal of the solvent in vacuo the residue was dissolved in dichloromethane (50 mL) and washed consecutively with 10% NaOH (5 mL) and water (2 × 20 mL). The organic layer was dried with Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. Trituration of the crude products with dry ethyl ether (1 × 10 mL) afforded the ramified merocyanines as mixtures of **1** and **2** (synthesis in the presence of piperidine) or as individual compounds **2** and **3** (synthesis in the presence of diethylamine). All new products (mixtures or individual adducts) have satisfactory purity according to ^1H NMR and elemental analysis (for individual compounds).

NMR chemical shift assignments of the new merocyanines follow the numbering system shown below:



The ^1H and ^{13}C NMR chemical shifts of compounds **1** are taken from the spectra of the corresponding mixtures with compounds **2**, where products **1** strongly predominate (see Table 1). Compounds **2a** and **2b** were detected as minor impurities of compounds **1a** and **1b** and are not described. The ratios **1/2**, indicated in Table 1, were determined by integration of the signals for the 7-H protons, having sufficiently different chemical shifts.

1-(Naphthalen-2-yl)-3-[2-(phenylthio)-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]prop-2-en-1-one (1a): Starting from merocyanine MC1 (365 mg, 1 mmol) and benzenethiol (550 mg, 5 mmol), the general procedure afforded a spectroscopically pure mixture of **1a**/**2a** (86:14) as a dark-red solid. Yield: 420 mg (93%). R_f = 0.45 (diethyl ether/hexane, 1:1). MS (EI, 9 eV): m/z = 451 $[M]^+$. ^1H NMR ($CDCl_3$): δ = 1.53 (br., 6 H, 3 CH_{2pip}), 2.93–3.06 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.27 (br., 4 H, 2 CH_{2pip}), 6.66 (s, 1 H, 7-H), 6.87 (d, J = 15 Hz, 1 H, 2-H), 7.19–7.21 (m, 5 H, H_{arom}), 7.51–7.63 (m, 2 H, H_{arom}), 7.87–8.07 (m, 4 H, H_{arom}), 8.25 (d, J = 15 Hz, 1 H, 3-H), 8.42 (s, 1 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.25, 26.06 (CH_{2pip}), 27.27, 30.52 ($CH_{2c\text{-}pent}$), 51.61 (CH_{2pip}), 116.06 (C_q), 118.9, 124.77, 125.40, 126.37, 127.35, 127.67, 128.08, 128.82, 129.10, 129.35 (CH) 132.58, 134.99, 136.67, 136.78 (C_q), 138.26 (CH), 138.43 (C_q), 139.27 (CH), 146.77 (C_q), 190.50 (CO) ppm.

3-[2-(4-Chlorophenylthio)-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(naphthalen-2-yl)prop-2-en-1-one (1b): Starting from merocyanine MC1 (365 mg, 1 mmol) and 4-chlorobenzenethiol (723 mg, 5 mmol), the general procedure afforded a spectroscopically pure mixture of **1b/2b** (91:9) as a dark-red solid. Yield: 442 mg (91%). R_f = 0.55 (diethyl ether/hexane, 1:1). MS (EI, 70 eV): m/z = 485 $[M]^+$. ^1H NMR ($CDCl_3$): δ = 1.59 (br., 6 H, 3 CH_{2pip}), 2.9–3.06 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.28 (m, 4 H, 2 CH_{2pip}), 6.61 (s, 1 H, 7-H),

6.88 (d, J = 15 Hz, 1 H, 2-H), 7.11–7.25 (m, 4 H, H_{arom}), 7.52–7.63 (m, 2 H, H_{arom}), 7.88–8.05 (m, 4 H, H_{arom}), 8.2 (d, J = 15 Hz, 1 H, 3-H), 8.42 (s, 1 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.22, 26.09 (CH_{2pip}), 27.25, 30.51 ($CH_{2c\text{-}pent}$), 51.63 (CH_{2pip}), 115.70 (C_q), 119.13, 124.71, 126.42, 127.69, 127.77, 128.14, 128.49, 128.93, 129.13 (CH), 129.27 (C_q), 129.36 (CH), 131.18, 132.58, 135.03, 135.41, 136.59 (C_q), 138.09 (CH), 138.58 (C_q), 138.89 (CH), 145.99 (C_q), 190.41 (CO) ppm.

3-[2-(Benzothiazol-2-ylthio)-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(naphthalen-2-yl)prop-2-en-1-one (1d): Reaction between MC1 (365 mg, 1 mmol) and benzothiazole-2-thiol (835 mg, 5 mmol) afforded a pure mixture of **1d/2d** (80:20) as a dark-red solid. Yield: 483 mg (95%). R_f = 0.86 (dichloromethane/MeOH, 19:1). MS (EI, 70 eV): m/z = 508 $[M]^+$. ^{1}HNMR ($CDCl_3$): δ = 1.59 (br., 6 H, 3 CH_{2pip}), 2.98–3.15 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.32 (br., 4 H, 2 CH_{2pip}), 6.79 (s, 1 H, 7-H), 6.94 (d, J = 15 Hz, 1 H, 2-H), 7.27–7.32 (m, 1 H, H_{arom}), 7.4–7.6 (m, 3 H, H_{arom}), 7.7 (d, J = 8.7 Hz, 1 H, H_{arom}), 7.82–7.92 (m, 4 H, H_{arom}), 8.02 (d, J = 8.7 Hz, 1 H, H_{arom}), 8.20 (d, J = 15 Hz, 1 H, 3-H), 8.42 (s, 1 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.23, 26.20 (CH_{2pip}), 27.43, 30.63 ($CH_{2c\text{-}pent}$), 51.66 (CH_{2pip}), 115.27 (C_q), 120.31, 120.80, 121.78, 124.24, 124.73, 126.07, 126.49, 127.73, 127.88, 128.23, 129.36 (CH), 132.58, 135.14, 135.72, 136.38 (C_q), 137.61, 138.17 (CH), 139.33, 142.71, 153.89 (C_q), 190.48 (CO) ppm.

(*E*)-1-(Naphthalen-2-yl)-3-[(*Z*)-3-(piperidin-1-ylmethylene)-2-(pyrimidin-2-ylthio)cyclopent-1-enyl]prop-2-en-1-one (1e): Reaction between MC1 (365 mg, 1 mmol) and pyrimidine-2-thiol (560 mg, 5 mmol) afforded a pure mixture of **1e/2e** (90:10) as a dark-red solid. Yield: 381 mg (84%). R_f = 0.35 (dichloromethane/methanol, 100:2). MS (EI, 9 eV): m/z = 453 $[M]^+$. ^{1}H NMR ($CDCl_3$): δ = 1.59 (br., 6 H, 3 CH_{2pip}), 2.95–3.13 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.29 (br., 4 H, 2 CH_{2pip}), 6.66 (s, 1 H, 7-H), 6.9 (d, J = 15 Hz, 1 H, 2-H), 6.98 (t, J = 5 Hz, 1 H, H_{pyrim}), 7.5–7.61 (m, 2 H, H_{arom}), 7.87–8.05 (m, 4 H, H_{arom}), 8.16 (d, J = 15 Hz, 1 H, 3-H), 8.44 (s, 1 H, H_{arom}), 8.50 (d, J = 5 Hz, 2 H, H_{pyrim}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.28, 26.14 (CH_{2pip}), 27.45, 30.68 ($CH_{2c\text{-}pent}$), 51.59 (CH_{2pip}), 116.93 (C_q), 117.07, 118.96, 124.72, 126.44, 127.73, 127.77, 128.12, 129.11, 129.38 (CH) 132.65, 135.07, 136.72 (C_q), 137.37 (CH), 138.98 (C_q), 139.02 (CH), 143.22 (C_q), 157.66 (CH), 171.69 (C_q), 190.16 (CO) ppm.

2-[(5-Methyl-1,3,4-thiadiazol-2-ylthio)-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(naphthalen-2-yl)prop-2-en-1-one (1f): Reaction of MC1 (365 mg, 1 mmol) with 5-methyl-1,3,4-thiadiazole-2-thiol (660 mg, 5 mmol) gave a pure mixture of **1f/2f** (86:14) as a dark-red solid. Yield: 464 mg (97%). R_f = 0.36 (dichloromethane/methanol, 19:1). MS (EI, 9 eV): m/z = 473 $[M]^+$. ^{1}HNMR ($CDCl_3$): δ = 1.59 (br., 6 H, 3 CH_{2pip}), 2.65 (s, 3 H, CH_3), 2.90–3.10 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.31 (br., 4 H, 2 CH_{2pip}), 6.72 (s, 1 H, 7-H), 6.92 (d, J = 15 Hz, 1 H, 2-H), 7.52–7.58 (m, 2 H, H_{arom}), 7.85–8.05 (m, 4 H, H_{arom}), 8.1 (d, J = 15 Hz, 1 H, 3-H), 8.21 (s, 1 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 15.75 (CH_3), 24.22, 26.23 (CH_{2pip}), 27.32, 30.54 ($CH_{2c\text{-}pent}$), 51.69 (CH_{2pip}), 114.75 (C_q), 119.92, 124.65, 126.58, 127.78, 127.98, 128.29, 129.30, 129.42 (CH), 135.21, 136.38 (C_q), 137.69, 137.90 (CH), 138.42, 143.70, 166.01, 167.13 (C_q), 190.02 (CO) ppm.

(*E*)-3-[(*E*)-2-(1-Methyl-1*H*-tetrazol-5-ylthio)-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(naphthalen-2-yl)prop-2-en-1-one (1g): Starting from merocyanine MC1 (365 mg, 1 mmol) and 1-methyl-1*H*-tetrazole-5-thiol (348 mg, 3 mmol), the general procedure afforded a spectroscopically pure mixture of **1g/2g** (80:20) as a dark-red solid. Yield: 370 mg (81%). R_f = 0.6 (dichloromethane/MeOH, 30:1). MS (EI, 9 eV): m/z = 457 $[M]^+$. ^{1}H NMR ($CDCl_3$): δ = 1.58 (br., 6 H, 3 CH_{2pip}), 2.9–3.05 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.29 (br., 4 H, 2 CH_{2pip}), 3.99 (s, 3 H, CH_3), 6.65 (s, 1 H, 7-H), 6.93 (d, J = 15 Hz, 1 H, 2-H), 7.53–7.58 (m, 2 H, H_{arom}), 7.86–8.06 (m, 4 H, H_{arom}), 8.21 (d, J = 15 Hz, 1 H, 3-H), 8.45 (s, 1 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.17, 26.17 (CH_{2pip}), 27.25, 30.58 ($CH_{2c\text{-}pent}$), 34.44 (CH_3), 51.68 (CH_{2pip}), 114.69 (C_q), 119.55, 124.56, 126.61, 127.78, 128.03, 128.34, 129.27, 129.43 (CH), 132.66, 135.25, 136.35 (C_q), 137.07 (CH), 138.22 (C_q), 138.60 (CH), 139.45, 151.04 (C_q), 189.78 (CO) ppm.

3-{2-(4-Bromophenylthio)-3-[(diethylamino)methylene]cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en-1-one (2c): Starting from merocyanine MC1 (365 mg, 1 mmol) and 4-bromobenzenethiol (189 mg, 1 mmol), the general procedure afforded spectroscopically and analytically pure **2c** as a dark-red viscous oil. Yield: 414 mg (80%). R_f = 0.86 (dichloromethane/MeOH, 19:1). $C_{29}H_{28}BrNOS$ (518.51): calcd. C 67.18, H 6.30, N 2.70, S 6.18; found C 67.23, H 6.07, N 2.63, S 6.11. MS (EI, 9 eV): m/z = 519 $[M]^+$. ^{1}H NMR ($CDCl_3$): δ = 1.07 (t, J = 7 Hz, 6 H, 2 CH_3), 2.88–3.02 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.19 (q, J = 7 Hz, 4 H, 2 CH_2CH_3), 6.6 (s, 1 H, 7-H), 6.84 (d, J = 15 Hz, 1 H, 2-H), 7.03–7.09 (m, 2 H, H_{arom}), 7.29–7.36 (m, 2 H, H_{arom}), 7.49–7.59 (m, 2 H, H_{arom}), 7.83–8.04 (m, 4 H, H_{arom}), 8.19 (d, J = 15 Hz, 1 H, 3-H), 8.39 (s, 1 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 14.84 (2 CH_3), 26.81, 30.49 ($CH_{2c\text{-}pent}$), 46.69 (2 CH_3CH_2), 114.34 (C_q), 118.70 (CH), 119.03 (C_q), 124.80, 126.45, 127.74, 128.16, 128.88, 129.13, 129.40, 131.82, 132.24 (CH), 132.64, 135.06, 136.23, 136.75 (C_q), 137.26 (CH), 137.97 (C_q), 139.02 (CH), 146.24 (C_q) 190.47 (CO) ppm.

(*E*)-3-{(*E*)-2-(Benzo[*d*]thiazol-2-ylthio)-3-[(diethylamino)methylene]-cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en-1-one (2d): Starting from merocyanine MC1 (365 mg, 1 mmol) and benzothiazole-2-thiol (836 mg, 5 mmol), the general procedure afforded pure **2d** as a dark-red solid. Yield: 437 mg (88%). R_f = 0.24 (diethyl ether/hexane, 1:1). M.p. 154–156 °C. $C_{30}H_{28}N_2OS_2$ (496.69): calcd. C 72.55, H 5.68, N 5.64, S 12.91; found C 72.71, H 5.95, N 5.49, S 12.80. MS (EI, 9 eV): m/z = 496 $[M]^+$. ^{1}HNMR ($CDCl_3$): δ = 1.12 (t, J = 7.1 Hz, 6 H, 2 CH_3CH_2), 2.97–3.1 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.24 (q, J = 7.1 Hz, 4 H, 2 CH_3CH_2), 6.84 (s, 1 H, 7-H), 6.89 (d, J = 15 Hz, 1 H, 2-H), 7.24–7.30 (m, 1 H, H_{arom}), 7.36–7.58 (m, 3 H, H_{arom}), 7.80–7.97 (m, 4 H, H_{arom}), 7.98–8.01 (m, 1 H, H_{arom}), 8.18 (d, J = 15 Hz, 1 H, 3-H), 8.39 (s, 1 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 14.95 (CH_3CH_2), 26.92, 30.54 ($CH_{2c\text{-}pent}$), 46.73 (CH_3CH_2), 114.34 (C_q), 119.80, 120.81, 121.77, 124.26, 124.75, 126.07, 126.50, 127.74, 127.86, 128.22, 129.32, 129.36 (CH), 132.59, 135.12, 135.74, 136.47 (C_q), 136.92, 138.28 (CH), 138.59, 143.00, 153.82 (C_q), 190.46 (CO) ppm.

(*E*)-3-{(*Z*)-3-[(Diethylamino)methylene]-2-(pyrimidin-2-ylthio)cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en-1-one (2e): Reaction between merocyanine MC1 (365 mg, 1 mmol) and pyrimidine-2-thiol (560 mg, 5 mmol) afforded pure **2e** as a dark-red solid. Yield: 335 mg (76%). R_f = 0.23 (dichloromethane/methanol, 100:2). M.p. 168–170 °C. $C_{27}H_{27}N_3OS$ (441.59): calcd. C 73.44, H 6.16, N 9.52, S 7.26; found C 73.29, H 6.02, N 9.29, S 7.03. MS (EI, 70 eV): m/z = 441 $[M]^+$. ^{1}HNMR ($CDCl_3$): δ = 1.1 (t, J = 7.1 Hz, 6 H, 2 CH_3CH_2), 2.88–3.02 (m, 4 H, 2 $CH_{2c\text{-}pent}$), 3.20 (q, J = 7.1 Hz, 4 H, 2 CH_3CH_2), 6.69 (s, 1 H, 7-H), 6.86 (d, J = 14.9 Hz, 1 H, 2-H), 6.95 (t, J = 4.8 Hz, 1 H, H_{pyrim}), 7.48–7.58 (m, 2 H, H_{arom}), 7.48–8.02 (m, 4 H, H_{arom}), 8.15 (d, J = 14.9 Hz, 1 H, 3-H), 8.41 (s, 1 H, H_{arom}), 8.48 (d, J = 4.8 Hz, 2 H, CH_{pyrim}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 14.79 (CH_3CH_2), 26.89, 30.52 ($CH_{2c\text{-}pent}$), 46.53 (CH_3CH_2), 115.78 (C_q), 116.97, 118.47 (CH), 124.71, 126.36, 127.66, 128.03, 128.99, 129.32 (CH), 132.61, 135.00 (C_q), 136.47 (CH), 136.79, 138.18 (C_q), 139.07 (CH), 143.53 (C_q), 157.55, 157.85 (CH), 171.70 (C_q), 190.14 (CO) ppm.

(*E*)-3-{(*E*)-3-[(Diethylamino)methylene]-2-(5-methyl-1,3,4-thiadiazol-2-ylthio)cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en-1-one (2f): Reaction of merocyanine MC1 (365 mg, 1 mmol) with 5-methyl-1,3,4-thiadiazole-2-thiol (396 mg, 3 mmol) afforded **2f** as a dark-red solid. Yield: 410 mg (89%). R_f = 0.45 (dichloromethane/methanol, 19:1). M.p. 76–77 °C. $C_{26}H_{27}N_3OS_2$ (461.64): calcd. C 67.65, H 5.90, N 9.10, S 13.89; found C 67.38, H 5.73, N 9.00, S 13.71. MS (EI, 9 eV): *m*/*z* = 461 [M] $^+$. ^{1}H NMR ($CDCl_3$): δ = 1.12 (t, *J* = 7.1 Hz, 6 H, 2 C*H*$_3$CH$_2$), 2.64 (s, 3 H, CH$_3$), 2.88–3.00 (m, 4 H, 2 CH$_{2c\text{-pent}}$), 3.24 (q, *J* = 7.1 Hz, 4 H, 2 CH$_3$C*H*$_2$), 6.78 (s, 1 H, 7-H), 6.9 (d, *J* = 14.9 Hz, 1 H, 2-H), 7.52–7.57 (m, 2 H, H$_{arom}$), 7.85–8.05 (m, 4 H, H$_{arom}$), 8.19 (d, *J* = 14.9 Hz, 1 H, 3-H), 8.44 (s, 1 H, H$_{arom}$) ppm ^{13}C NMR ($CDCl_3$, DEPT): δ = 14.95 (2 *C*H$_3$CH$_2$), 15.74 (CH$_3$), 26.83 (CH$_{2c\text{-pent}}$), 30.46 (CH$_{2c\text{-pent}}$), 46.74 (2 CH$_3$*C*H$_2$), 113.82 (C$_q$), 119.15, 124.68, 126.55, 127.77, 127.94, 128.27, 129.24, 129.40 (CH), 132.65, 135.18, 136.48 (C$_q$), 137.13 (CH), 137.77 (C$_q$), 137.81 (CH), 143.95, 166.05, 167.12 (C$_q$), 190.04 (CO) ppm.

(*E*)-3-{(*E*)-3-[(Diethylamino)methylene]-2-(1-methyl-1*H*-tetrazol-5-ylthio)cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en-1-one (2g): Reaction of merocyanine MC1 (365 mg, 1 mmol) with 1-methyl-tetrazole-5-thiol (348 mg, 3 mmol) gave pure **2g** as a dark-red gum. Yield: 320 mg (72%). R_f = 0.28 (dichloromethane/methanol, 100:2). $C_{25}H_{27}N_5OS$ (445.58): calcd. 67.39, H 6.11, N 15.72, S 7.20; found C 67.12, H 5.93, N 15.49, S 7.03. MS (EI, 9 eV): *m*/*z* = 445 [M]$^+$. ^{1}HNMR ($CDCl_3$) δ = 1.16 (t, *J* = 7.1 Hz, 6 H, 2 C*H*$_3$CH$_2$), 2.8–3.05 (m, 4 H, 2 CH$_{2c\text{-pent}}$), 3.26 (q, *J* = 7.1 Hz, 4 H, 2 CH$_3$C*H*$_2$), 4.02 (s, 3 H, CH$_3$), 6.76 (s, 1 H, 7-H), 6.96 (d, *J* = 14.8 Hz, 1 H, 2-H), 7.55–7.64 (m, 2 H, H$_{arom}$), 7.92–8.10 (m, 4 H, H$_{arom}$), 8.28 (d, *J* = 14.8 Hz, 1 H, 3-H), 8.49 (s, 1 H, H$_{arom}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 14.89 (2*C*H$_3$CH$_2$), 26.77, 30.49 (CH$_{2c\text{-pent}}$), 34.50 (CH$_3$), 46.74 (2CH$_3$*C*H$_2$), 113.73 (C$_q$), 119.12, 124.57, 126.61, 127.78, 128.02, 128.33, 129.23, 129.43 (CH), 132.65, 135.23, 136.42, (C$_q$), 137.17 (CH), 137.61 (C$_q$), 137.93 (CH), 139.78, 150.94 (C$_q$), 189.75 (CO) ppm.

7-{(*E*)-5-[(Diethylamino)methylene]-2-[(*E*)-3-(naphthalen-2-yl)-3-oxoprop-1-enyl]cyclopent-1-enylthio}-4-methyl-2*H*-chromen-2-one (2h): Reaction of merocyanine MC1 (365 mg, 1 mmol) and 7-mercapto-4-methyl-2*H*-chromen-2-one (192 mg, 1 mmol) produced pure **2h** as a dark-red solid. Yield: 495 mg (95%). R_f = 0.84 (dichloromethane/methanol, 19:1). M.p. 125–128 °C. $C_{33}H_{31}NO_3S$ (521.67): calcd. C 75.98, H 5.99, N 2.68, S 6.15; found C 75.73, H 5.77, N 2.48, S 6.00. MS (EI, 9 eV): *m*/*z* = 521 [M]$^+$. ^{1}HNMR ($CDCl_3$): δ = 1.1 (t, *J* = 7 Hz, 6 H, 2 CH$_2$C*H*$_3$), 2.38 (d, *J* = 1.2 Hz, 3 H, CH$_3$), 2.95–3.1 (m, 4 H, 2 CH$_{2c\text{-pent}}$), 3.21 (q, *J* = 7 Hz, 4 H, 2 C*H*$_2$CH$_3$), 6.17 (d, *J* = 1.2 Hz, 1 H), 6.67 (s, 1 H, 7-H), 6.89 (d, *J* = 15 Hz, 1 H, 2-H), 7.03 (d, *J* = 1.8 Hz, 1 H, CH$_{coum}$), 7.16 (d, *J* = 1.8 Hz, 1 H, CH$_{coum}$), 7.42 (d, *J* = 8, 1H Hz, CH$_{coum}$), 7.51–7.56 (m, 2 H, CH$_{napht}$), 7.84–7.93 (m, 4 H, CH$_{napht}$), 8.00 (dd, *J* = 8, 1.8 Hz, 1 H, CH$_{coum}$), 8.14 (d, *J* = 15 Hz, 1 H, 3-H), 8.41 (s, 1 H, CH$_{napht}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 14.83 (*C*H$_3$CH$_2$), 18.54 (CH$_{3coum}$), 26.79, 30.47 (CH$_{2c\text{-pent}}$), 46.61 (CH$_3$*C*H$_2$), 113.65, 113.87 (CH), 114.54, 117.15 (C$_q$), 118.93, 122.36, 124.54, 124.65, 126.42, 127.69, 127.79, 128.12, 129.11, 129.34 (CH), 132.61, 135.08, 136.62 (C$_q$), 136.79, 138.37 (CH), 138.47, 143.29, 144.14, 152.22, 153.91 (C$_q$), 160.69 (CO$_{coum}$), 190.05 (CO$_{merocyanine}$) ppm.

(*E*)-3-[(*E*)-2-(1-Methyl-1*H*-tetrazol-5-ylthio)-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(phenanthren-3-yl)prop-2-en-1-one (3): Reaction of merocyanine MC2 (428 mg, 1 mmol) and 1-methyl-1*H*-tetrazole-5-thiol (580 mg, 5 mmol) gave pure **3** as a dark-red solid. Yield: 320 mg (63%). R_f = 0.28 (dichloromethane/methanol, 100:2). M.p. 178–180 °C. $C_{30}H_{29}N_5OS$ (507.65): calcd. C 70.98, H 5.76, N 13.80, S 6.32; found C 70.73, H 5.59, N 13.72, S 6.09. MS (EI, 9 eV): *m*/*z* = 507 [M]$^+$. ^{1}H NMR ($CDCl_3$) δ = 1.62 (br., 6 H, 3 CH$_{2pip}$), 2.90–3.05 (m, 4 H, 2 CH$_{2c\text{-pent}}$), 3.33 (br., 4 H, 2 CH$_{2pip}$), 4.03 (s, 3 H, CH$_3$), 6.69 (s, 1 H, 7-H), 6.98 (d, *J* = 15 Hz, 1 H, 2-H), 7.65–7.80 (m, 2 H, H$_{arom}$), 7.84–7.89 (m, 2 H, H$_{arom}$), 7.93–7.97 (m, 1 H, H$_{arom}$), 8.22–8.30 (m, 2 H, H$_{arom}$, 3-H), 8.51- 8.52 (m, 1 H, H$_{arom}$), 8.73–8.80 (m, 2 H, H$_{arom}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.17, 26.19 (3CH$_{2pip}$), 27.27, 30.57 (CH$_{2c\text{-pent}}$), 34.45 (CH$_3$), 51.69 (CH$_{2pip}$), 114.73 (C$_q$), 119.46, 123.06, 125.60, 126.95, 127.41, 127.57, 127.73, 128.69, 129.25 (CH), 131.55, 132.89, 136.84 (C$_q$), 137.14 (CH), 138.21 (C$_q$), 138.66 (CH), 139.43, 139.58 (C$_q$), 189.52 (CO) ppm.

General Experimental Procedure for the Conversion of Ramified Heptamethine Merocyanines into Nonamethine Merocyanines Dyes: A solution of the corresponding ramified merocyanine **2** (1 mmol) and benzazolium salt (1 or 2 mmol) in dry pyridine (10 mL) was kept under reflux for the time indicated in Table 2. The mixture was allowed to cool to room temperature and then poured onto cold water. The separated fine crystals were collected by filtration. Pure compounds **4a**–**4g** were obtained after column chromatography purification on silica gel.

(*E*)-3-{(*E*)-3-[(*Z*)-2-(3-Ethylbenzo[*d*]thiazol-2(3*H*)-ylidene)ethylidene]-2-(pyrimidin-2-ylthio)cyclopent-1-enyl}-1-(naphthalen-2-yl)-prop-2-en-1-one (4a): The general experimental procedure followed by separation of the crude product, a mixture of **4a/5b** (84:26), by column chromatography (silica; CH_2Cl_2/CH_3OH, 30:1) afforded pure **4a** as a dark-blue solid. Yield: 164 mg (30%). M.p. 205–208 °C. $C_{33}H_{27}N_3OS_2$ (545.16): calcd. C 72.63, H 4.99, N 7.70, S 11.75; found C 72.81, H 5.15, N 7.47, S 11.92. MS (ESI): *m*/*z* (%) = 546.2 (25) [M + 1]$^+$. ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, *J* = 7.0 Hz, 3 H, CH$_3$), 2.93–2.97 (m, 2 H, CH$_{2c-pent}$), 3.05–3.09 (m, 2 H, CH$_{2c\text{-pent}}$), 3.84 (q, *J* = 7.0 Hz, 2 H, CH$_3$C*H*$_2$), 5.38 (d, *J* = 11.6 Hz, 1 H, 8-H), 6.57 (d, *J* = 11.6 Hz, 1 H, 7-H), 6.76 (d, *J* = 8.07 Hz, 1 H, CH$_{arom}$), 6.92 (t, *J* = 7.6 Hz, 1 H, CH$_{arom}$), 6.99 (t, *J* = 4.8 Hz, 1 H, CH$_{arom}$), 7.09 (d, *J* = 15.1 Hz, 1 H, 2-H), 7.17 (t, *J* = 7.8 Hz, 1 H, CH$_{arom}$), 7.25 (d, *J* = 7.6 Hz, 1 H, CH$_{arom}$), 7.56 (t, *J* = 7.6 Hz, 1 H, CH$_{arom}$), 7.60 (t, *J* = 7.8 Hz, 1 H, CH$_{arom}$), 7.90 (t, *J* = 8.5 Hz, 2 H, CH$_{arom}$), 7.96 (d, *J* = 7.6 Hz, 1 H, CH$_{arom}$), 8.05 (d, *J* = 7.3 Hz, 1 H$_{arom}$), 8.17 (d, *J* = 15.1 Hz, 1 H, 3-H), 8.46 (s, 1 H, CH$_{arom}$), 8.53 (d, *J* = 4.8 Hz, 2 H, CH$_{pyrim}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 11.34 (CH$_3$), 26.94 (CH$_{2c\text{-pent}}$), 30.12 (CH$_{2c\text{-pent}}$), 39.28 (*C*H$_2$CH$_3$), 90.20, 108.06, 117.13, 120.93, 121.46, 121.89, 122.42, 124.65, (CH), 124.84 (C$_q$), 126.22, 126.57, 127.78, 128.02, 128.30, 129.44, 129.47 (CH), 132.61, 135.23, 136.25 (C$_q$), 138.38 (CH), 138.83, 140.57, 142.40, 146.72, 147.79 (C$_q$), 157.66 (CH),171.55 (C$_q$), 190.10 (CO) ppm. Compound **5a**, isolated from the same separation procedure (56 mg, 9%), was previously described.[10]

***N*,*N*-Dimethyl-3-{(*Z*)-2-[(*E*)-2-{3-[(*E*)-3-(naphthalen-2-yl)-3-oxoprop-1-enyl]-2-(pyrimidin-2-ylthio)cyclopent-2-enylidene}ethylidene]benzo[*d*]thiazol-3(2*H*)-yl}propanamide (4b):** Pure **4b** was isolated from the crude mixture of **4b**/**5b** (63:37) by column chromatography (silica; CH_2Cl_2/CH_3OH, 40:1) as a dark-blue solid. Yield: 197 mg (36%). M.p. 175–178 °C. $C_{36}H_{32}N_4O_2S_2$ (616.20): calcd. C 70.10, H 5.23, N 9.08, S 10.40; found C 70.39, H 5.01, N 9.32, S 10.23. MS (ESI): *m*/*z* (%) = 617.2 (100) [M + 1]$^+$. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.71 (t, *J* = 7.2 Hz, 2 H, CH$_2$CO), 2.94–2.96 (m, 2 H, CH$_{2c\text{-pent}}$), 2.97 [s, 3 H, CON(CH$_3$)$_2$], 2.98 [s, 3 H, CON(CH$_3$)$_2$], 3.05–3.08 (m, 2 H, CH$_{2c\text{-pent}}$), 4.17 (t, *J* = 7.6 Hz, 2 H, NCH$_2$), 5.41 (d, *J* = 11.6 Hz, 1 H, 8-H), 6.54 (d, *J* = 11.6 Hz, 1 H, 7-H), 6.84 (d, *J* = 7.9 Hz, 1 H, CH$_{arom}$), 6.91 (dt, *J* = 7.6, 0.9 Hz, 1 H, CH$_{arom}$), 6.99 (t, *J* = 4.8 Hz, 1 H, CH$_{arom}$),

7.11 (d, J = 15.1 Hz, 1 H, 2-H), 7.16 (t, J = 8.2 Hz, 1 H, CH_{arom}), 7.24 (dd, J = 7.6, 0.9 Hz, 1 H, CH_{arom}), 7.54–7.62 (m, 2 H, CH_{arom}), 7.89 (d, J = 7.3 Hz, 1 H, CH_{arom}), 7.90 (d, J = 8.5 Hz, 1 H, CH_{arom}), 7.97, (d, J = 7.9 Hz, 1 H, CH_{arom}), 8.04 (dd, J = 8.5, 1.8 Hz, 1 H, CH_{arom}), 8.15 (d, J = 15.1 Hz, 1 H, 3-H), 8.46 (s, 1 H, CH_{arom}), 8.53 (d, J = 4.8 Hz, 2 H, CH_{pyrim}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 27.03 ($CH_{2c\text{-}pent}$), 29.36 (CH_2CO), 30.17 ($CH_{2c\text{-}pent}$), 35.43, 37.18 [$CON(CH_3)_2$], 40.58 (NCH_2), 90.49, 108.39, 117.15, 121.18, 121.47, 122.00, 122.20, 124.60 (CH), 124.62 (C_q), 126.35, 126.60, 127.79, 128.08, 128.33, 129.48 (CH), 132.60, 135.26, 136.18 (C_q), 138.30 (CH), 139.41, 140.35, 142.33, 147.20, 147.43 (C_q), 157.66 (CH),170.29 (C_q), 171.50, 190.10 (CO) ppm.

3-{(*Z*)-2-[(*E*)-2-{2-(2-{*N*-[3-(Dimethylamino)-3-oxopropyl]acetamido}phenylthio)-3-[(*E*)-3-(naphthalen-2-yl)-3-oxoprop-1-enyl]cyclopent-2-enylidene}ethylidene]benzo[*d*]thiazol-3(2*H*)-yl}-*N*,*N*-dimethylpropanamide (5b): The above described experiment gave access to pure **5b** as a dark-blue solid. Yield: 123 mg (16%). M.p. 193–196 °C. $C_{45}H_{46}N_4O_4S_2$ (770.30): calcd. C 70.10, H 6.01, N 7.27, S 8.32; found C 70.36, H 5.87, N 7.11, S 8.49. MS (ESI): m/z (%) = 771 (100) $[M + 1]^+$. ^{1}H NMR (600 MHz ($CDCl_3$): δ = 1.98 (s, 3 H, $COCH_3$), 2.69 (t, J = 7.5 Hz, 2 H, CH_2CO), 2.79–2.86 (m, 1 H, CH_2CO), 2.90–2.93 (m, 3 H, $CH_{2c\text{-}pent}$, 1 H, CH_2CO), 2.93 [s, 3 H, $CON(CH_3)_2$], 2.94 [s, 3 H, $CON(CH_3)_2$], 2.97 [s, 3 H, $CON(CH_3)_2$], 3.05–3.08 (m, 2 H, $CH_{2c\text{-}pent}$), 3.11 [s, 3 H, $CON(CH_3)_2$], 3.88–3.93 (m, 1 H, NCH_2), 4.15 (t, J = 7.5 Hz, 2 H, NCH_2), 4.25–4.30 (m, 1 H, NCH_2), 5.35 (d, J = 11.7 Hz, 1 H, 8-H), 6.47 (d, J = 11.7 Hz, 1 H, 7-H), 6.82 (d, J = 8.1 Hz, 1 H, CH_{arom}), 6.92 (dt, J = 7.6, 0.9 Hz, 1 H, CH_{arom}), 7.00 (dd, J = 7.2, 1.9 Hz, 1 H, CH_{arom}), 7.10 (d, J = 15.1 Hz, 1 H, H-2), 7.14–7.23 (m, 4 H, CH_{arom}), 7.33 (dd, J = 7.8, 1.0 Hz, 1 H, CH_{arom}), 7.54 (dt, J = 8.1, 1.2 Hz, 1 H, CH_{arom}), 7.59 (dt, J = 6.7, 1.2 Hz, 1 H, CH_{arom}), 7.88 (t, J = 8.9 Hz, 2 H, CH_{arom}) 7.92 (d, J = 8.1 Hz, 1 H, CH_{arom}), 8.01 (dd, J = 8.5, 1.8 Hz, 1 H, CH_{arom}), 8.08 (d, J = 15.1 Hz, 1 H, H-3), 8.43 (s, 1 H, CH_{arom}). ^{13}C NMR ($CDCl_3$, DEPT): δ = 22.62 (CH_3CO), 26.89 ($CH_{2c\text{-}pent}$), 29.39 (CH_2CO), 30.18 ($CH_{2c\text{-}pent}$), 32.31 (CH_2CO), 35.31, 35.43, 37.18, 37.49 [2 × $CON(CH_3)_2$], 40.60, 45.50 (2 × NCH_2), 89.92, 108.43, 121.43, 121.81, 122.49, 122.80, 124.55, 126.25, 126.38, 126.65, 127.15, 127.78, 128.14, 128.39, 128.98 (CH), 129.40 (C_q), 129.45, 129.51 (CH), 132.54, 135.25, 136.01, 136.52 (C_q), 137.72 (CH), 137.95, 139.55, 140.95, 142.19, 147.80, 148.60 (C_q), 170.21, 170.80, 171.24, 190.10 (CO) ppm.

7-{(*E*)-5-[(*Z*)-2-{3-Ethylbenzo[*d*]thiazol-2(3*H*)-ylidene}ethylidene]-2-[(*E*)-3-(naphthalen-2-yl)-3-oxoprop-1-enyl]cyclopent-1-ylthio}-4-methyl-2*H*-chromen-2-one (4c): Following the general procedure, purification of the crude product by column chromatography (silica; CH_2Cl_2/CH_3OH, 50:1) afforded pure **4c** as a dark-blue solid. Yield: 225 mg (36%). M.p. 172–175 °C. $C_{39}H_{31}NO_3S_2$ (625.17): calcd. C 74.84, H 4.99, N 2.24, S 10.25; found C 74.53, H 5.11, N 2.18, S 10.40. MS (ESI): m/z (%) = 626.2 (100) $[M + 1]^+$. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 2.43 (d, J = 1.0 Hz, 3 H, CH_{3coum}), 2.91–2.96 (m, 2 H, $CH_{2c\text{-}pent}$), 3.05–3.09 (m, 2 H, $CH_{2c\text{-}pent}$), 3.84 (q, J = 7.1 Hz, 2 H, CH_3CH_2), 5.34 (d, J = 11.7 Hz, 1 H, 8-H), 6.19 (d, J = 1.0 Hz, 1 H CH_{coum}), 6.55 (d, J = 11.7 Hz, 1 H, 7-H), 6.77 (d, J = 8.0 Hz, 1 H, CH_{arom}), 6.92 (t, J = 7.1 Hz, 1 H, CH_{arom}), 7.11–7.19 (m, 3 H, CH_{arom}, 2-H), 7.22–7.25 (m, 2 H, CH_{arom}), 7.47 (d, J = 8.5 Hz, 1 H, CH_{arom}), 7.55–7.61 (m, 2 H, CH_{arom}), 7.90 (t, J = 11.7 Hz, 2 H, CH_{arom}), 7.96 (d, J = 7.9 Hz, 1 H, CH_{arom}), 8.05 (dd, J = 8.6, 1.7 Hz, 1 H, CH_{arom}), 8.18 (d, J = 15.1 Hz, 1 H, 3-H), 8.47 (s, 1 H, CH_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 11.38 (CH_3CH_2), 18.66 (CH_{3cum}), 26.82 ($CH_{2c\text{-}pent}$), 30.05 ($CH_{2c\text{-}pent}$), 39.36 (CH_2CH_3), 89.95, 108.23, 113.78, 114.59 (CH), 117.42 (C_q), 121.14, 121.48, 122.23, 122.94, 123.39, 124.59, 124.67 (CH), 124.70 (C_q), 126.32, 126.63, 127.78, 128.12, 128.37, 129.47, 129.50 (CH), 132.60, 135.15, 137.45 (C_q), 137.66 (CH), 141.59, 142.32, 142.79, 146.87, 148.66, 152.34, 153.85, 160.82 (C_q), 190.00, 207.10 (CO) ppm.

***N*,*N*-Dimethyl-3-{(*Z*)-2-[(*E*)-2-{2-(4-methyl-2-oxo-2*H*-chromen-7-ylthio)-3-[(*E*)-3-(naphthalen-2-yl)-3-oxoprop-1-enyl]cyclopent-2-enylidene}ethylidene]benzo[*d*]thiazol-3(2*H*)-yl}propanamide (4d):** Pure **4d** was obtained after purification of the crude mixture by column chromatography (silica; CH_2Cl_2/CH_3OH, 20:1). Yield: 383 mg (55%). M.p. 157–160 °C. $C_{42}H_{36}N_2O_4S_2$ (696.21): calcd. C 72.39, H 5.21, N 4.02, S 9.20; found C 72.61, H 5.45, N 4.37, S 9.68. MS (ESI): m/z (%) = 697.3 (100) $[M + 1]^+$. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_{3coum}), 2.71 (t, J = 7.5 Hz, 2 H, CH_2CO), 2.88–2.95 (m, 2 H, $CH_{2c\text{-}pent}$), 2.96 [s, 3 H, $CON(CH_3)_2$], 2.98 [s, 3 H, $CON(CH_3)_2$], 3.04–3.09 (m, 2 H, $CH_{2c\text{-}pent}$), 4.17 (t, J = 7.5 Hz, 2 H, NCH_2), 5.37 (d, J = 11.5 Hz, 1 H, 8-H), 6.19 (s, 1 H, CH_{coum}), 6.51 (d, J = 11.5 Hz, 1 H, 7-H), 6.85 (d, J = 11.5 Hz, 1 H, CH_{arom}), 6.92 (t, J = 7.5 Hz, 1 H, CH_{arom}), 7.08–7.19 (m, 3 H, C H_{arom}, 2-H), 7.23 (d, J = 7.3 Hz, 2 H, CH_{arom}), 7.47 (d, J = 8.5 Hz, 1 H, CH_{arom}), 7.54–7.63 (m, 2 H, CH_{arom}), 7.90 (t, J = 9.7 Hz, 2 H, CH_{arom}), 7.97 (d, J = 7.9 Hz, 1 H), 8.05 (d, J = 9.1 Hz, 1 H, CH_{arom}), 8.17 (d, J = 15.1 Hz, 1 H, 3-H), 8.47 (s, 1 H, CH_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 18.67 (CH_{3coum}), 26.89 ($CH_{2c\text{-}pent}$), 29.37 (CH_2CO), 30.10 ($CH_{2c\text{-}pent}$), 35.44, 37.21 [$CON(CH_3)_2$], 40.59 (NCH_2), 90.23, 108.55, 113.76, 114.53 (CH), 117.41 (C_q), 121.36, 121.47, 122.49, 122.94, 122.97 (CH), 124.47 (C_q), 124.55, 124.67, 126.44, 126.65, 127.78, 128.16, 128.40, 129.49, 129.55 (CH), 132.59, 135.31, 136.06 (C_q), 137.55 (CH), 138.03, 141.36, 142.24, 142.78, 147.39, 148.27, 152.38, 153.85 (C_q), 160.81, 170.19, 189.95 (CO) ppm.

(*E*)-3-{(*E*)-3-[(*E*)-2-(1-Ethyl-3,3-dimethylindolin-2-ylidene)ethylidene]-2-(pyrimidin-2-ylthio)cyclopent-1-enyl}-1-(naphthalen-2-yl)-prop-2-en-1-one (4e): Pure **4e** was obtained after purification of the crude mixture by column chromatography (silica; CH_2Cl_2/CH_3OH, 160:1). Yield: 301 mg (54%). M.p. 108–110 °C. $C_{36}H_{33}N_3OS$ (555.23): calcd. C 77.80, H 5.99, N 7.56, S 5.77; found C 77.53, H 5.68, N 7.87, S 5.58. MS (ESI): m/z (%) = 556.3 (28) $[M + 1]^+$. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.0 Hz, 3 H, CH_2CH_3), 1.58 [s, 6 H, $C(CH_3)_2$], 2.93–2.97 (m, 2 H, $CH_{2c\text{-}pent}$), 3.34–3.38 (m, 2 H, $CH_{2c\text{-}pent}$), 3.66 (q, J = 7.0 Hz, 2 H, CH_2CH_3), 5.32 (d, J = 12.6 Hz, 1 H, 8-H), 6.59 (d, J = 7.8 Hz, 1 H), 6.83 (t, J = 7.3 Hz, 1 H, CH_{arom}), 6.96 (t, J = 7.3 Hz, 1 H, CH_{arom}), 7.04–7.09 (m, 2 H, CH_{arom}), 7.10 (d, J = 15.1 Hz, 1 H, 2-H), 7.15 (dt, J = 7.6, 1.2 Hz, 1 H, CH_{arom}), 7.53–7.57 (m, 1 H, CH_{arom}), 7.57–7.61 (m, 1 H, CH_{arom}), 7.87 (d, J = 8.1 Hz, 1 H, CH_{arom}), 7.89 (d, J = 8.8 Hz, 1 H, CH_{arom}), 7.96 (d, J = 7.4 Hz, 1 H, CH_{arom}), 8.04 (dd, J = 8.6, 1.6 Hz, 1 H, CH_{arom}), 8.23 (d, J = 15.1 Hz, 1 H, 3-H), 8.46 (s, 1 H, CH_{arom}), 8.51 (d, J = 4.8 Hz, 2 H, CH_{pyrim}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 11.14 (CH_2CH_3), 26.19 ($CH_{2c\text{-}pent}$), 27.96 ($C(CH_3)_2$), 30.17 ($CH_{2c\text{-}pent}$), 36.86 (CH_2CH_3), 45.78 (C_q), 77.24, 94.03, 105.99, 117.05, 119.77, 121.59, 121.67, 122.20, 124.66, 126.61, 127.71, 127.81, 128.08, 128.36, 129.49 (CH), 132.63, 135.27, 136.24 (C_q), 138.29 (CH), 138.69, 139.19, 141.15, 144.05, 146.89, 156.86 (C_q), 157.68 (CH), 171.55 (C_q), 190.25 (CO) ppm.

(*E*)-3-{(*E*)-3-[(*E*)-2-(1-Ethyl-3,3-dimethylindolin-2-ylidene)ethylidene]-2-(1-methyl-1*H*-tetrazol-5-ylthio)cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en1-one (4f): Pure **4f** was isolated after purification of the crude mixture by column chromatography (silica; CH_2Cl_2/CH_3OH, 70:1). Yield: 357 mg (64%). M.p. 92–95 °C. $C_{34}H_{33}N_5OS$ (559.24): calcd. C 72.96, H 5.94, N 12.51, S 5.73; found C 72.56, H 5.71, N 12.78, S 5.97. MS (ESI): m/z (%) = 560.2 (100) $[M + 1]^+$. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.2 Hz, 3 H, CH_2CH_3), 1.50 [s, 6 H, $C(CH_3)_2$], 2.86–2.90 (m, 2 H,

$CH_{2c\text{-pent}}$), 2.99–3.02 (m, 2 H, $CH_{2c\text{-pent}}$), 3.67 (q, J = 7.2 Hz, 2 H, CH_2CH_3), 4.01 (s, 3 H, $CH_{3\text{tetrazole}}$), 5.23 (d, J = 12.4 Hz, 1 H, 8-H), 6.64 (d, J = 7.8 Hz, 1 H), 6.89 (t, J = 7.3 Hz, 1 H, CH_{arom}), 7.04 (d, J = 12.4 Hz, 1 H, 7-H), 7.13–7.20 (m, 3 H, CH_{arom}), 7.55–7.58 (m, 1 H, CH_{arom}), 7.59–7.63 (m, 1 H, CH_{arom}), 7.89 (d, J = 12.4 Hz, 1 H, CH_{arom}), 7.93 (d, J = 8.7 Hz, 1 H, CH_{arom}), 7.99 (d, J = 7.9 Hz, 1 H, CH_{arom}), 8.07 (dd, J = 8.5, 1.7 Hz, 1 H, CH_{arom}), 8.26 (d, J = 15 Hz, 1 H, 3-H), 8.49 (s, 1 H, CH_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 11.15 (CH_2CH_3), 26.20 ($CH_{2c\text{-pent}}$), 28.06 [$C(CH_3)_2$], 29.97 ($CH_{2c\text{-pent}}$), 34.49 ($CH_{3\text{tetrazole}}$) 36.94 (CH_2CH_3), 46.16 (C_q), 93.78, 106.32, 120.36, 121.82, 122.87, 123.18, 124.49, 126.79, 127.74, 127.86, 128.34, 128.56, 129.53, 129.67 (CH), 132.61, 135.42, 135.87 (C_q), 136.42 (CH), 136.88, 137.05, 139.46, 143.74, 146.54, 150.76, 158.63 (C_q), 189.72 (CO) ppm.

7-{(*E*)-5-[(*E*)-2-(1-Ethyl-3,3-dimethylindolin-2-ylidene)ethylidene]-2-[(*E*)-3-(naphthalen-2-yl)-3-oxoprop-1-enyl]cyclopent-1-enylthio}-4-methyl-2*H*-chromen-2-one (4g): Product **4g** was isolated after purification of the crude reaction mixture by column chromatography (silica, CH_2Cl_2). Yield: 394 mg (62%). M.p. 123–126 °C. $C_{42}H_{37}NO_3S$ (635.25): calcd. C 79.34, H 5.87, N 2.20, S 5.04; found C 79.52, H 5.49, N 2.59, S 4.87. MS (ESI): m/z (%) = 636.3 (100) $[M + 1]^+$. ^{1}H NMR ($CDCl_3$): δ = 1.26 [t, J = 7.2 Hz, 6 H, $C(CH_3)$ overlapped with CH_2CH_3], 1.63 [s, 3 H, $C(CH_3)$], 2.36 (d, J = 1.0 Hz, 3 H, $CH_{3\text{coum}}$), 2.93–2.98 (m, 2 H, $CH_{2c\text{-pent}}$), 3.05–3.10 (m, 2 H, $CH_{2c\text{-pent}}$), 3.67 (q, J = 7.2 Hz, 2 H, CH_3CH_2), 5.30 (d, J = 12.7 Hz, 1 H, 8-H), 6.19 (d, J = 1 Hz, 1 H, CH_{coum}), 6.63 (d, J = 7.7 Hz, 1 H, CH_{arom}), 6.85 (t, J = 7.5 Hz, 1 H, CH_{arom}), 7.00 (d, J = 12.7 Hz, 1 H, 7-H), 7.07 (d, J = 6.8 Hz, 1 H, CH_{arom}), 7.15–7.19 (m, 3 H, CH_{arom}), 7.24 (dd, J = 8.4, 1.8 Hz, 1 H, CH_{arom}), 7.48 (d, J = 8.5 Hz, 1 H, CH_{arom}), 7.55–7.60 (m, 1 H, CH_{arom}), 7.60–7.65 (m, 1 H, CH_{arom}), 7.91 (d, J = 8.0 Hz, 1 H, CH_{arom}), 7.93 (d, J = 8.7 Hz, 1 H, CH_{arom}), 8.00 (d, J = 7.0 Hz, 1 H, CH_{arom}), 8.08 (dd, J = 8.5, 1.6 Hz, 1 H), 8.25 (d, J = 15.1 Hz, 1 H, 3-H), 8.50 (s, 1 H, CH_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 11.18 (CH_3CH_2), 18.62 ($CH_{3\text{cum}}$), 26.09 ($CH_{2c\text{-pent}}$), 27.80 [$C(CH_3)_2$], 30.11 ($CH_{2c\text{-pent}}$), 36.91 (CH_2CH_3), 45.79 (C_q), 93.78, 106.16 (CH), 109.11 (C_q), 113.85, 114.77, 119.97, 121.64, 122.40, 122.75, 122.97, 124.59, 124.69, 126.67, 127.75, 127.82, 128.17, 128.42, 129.50, 129.56 (CH), 132.61, 135.33, 136.12, 136.70, 137.28 (C_q), 137.59 (CH), 139.13, 141.91, 142.57, 143.88, 147.25, 152.17 (C_q), 153.88, 190.07, (CO) ppm.

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