DOI: 10.1002/ejoc.200700125

Synthesis and Photophysical Properties of Some Rigidized Hepta- and Nonamethine Mono- and Bis(merocyanines): Ring-Opening of Quaternized 2-Methylbenzothiazole

Lilia Viteva,[a] Tzveta Gospodova,[a] Jivka Rashkova,[a] Isaac Abrahams,[b] Iliana Timtcheva,[a] Svetlana Simova,[a] Marie Rose Mazieres,[c] and Jean Gérard Wolf*[c]

Keywords: Merocyanine dyes / UV/Vis spectroscopy / Fluorescence spectroscopy / Structure elucidation / Benzothiazole ring cleavage

We have developed a simple and efficient method for the synthesis of rigidized mono- and bis-heptamethine merocyanines that contain one methine unit incorporated into a cyclopentene framework. The synthetic approach is based on C1/C5 regioselective nucleophilic addition of mono- and diketone lithium enolates to readily available pentamethine cyanines with inherent rigidity followed by a Hofmann elimination reaction. The new dyes react easily with heterocyclic benzothiazolium compounds containing an activated methyl group. Depending on the reaction conditions one or two reactive centres can be attacked, thus giving access to new merocyanine derivatives with a lengthened polymethine chain and/or ramified by a second heterocyclic unit. X-ray crystallographic analysis reveals that the second heterocycle is incorporated via a sulfur bridge as a result of the opening of the benzothiazole ring. All new compounds were fully characterized by 1D and 2D NMR spectroscopic techniques (^{1}H, ^{13}C, DEPT, COSY, NOESY, HSQC with and without decoupling, HMBC). Their photophysical properties have been studied and correlated with solvent polarities.

Introduction

Merocyanines or so-called "push-pull" systems are formally uncharged polymethine dyes whose essential structural feature is the presence of both electron-donating and -withdrawing groups. Their practical application ranges from physics to medicine and biology.[1] Merocyanines are extensively used, for example, as non-linear optical (NLO) materials,[2] photosensitizers in the photodynamic treatment of cancer,[3] radiosensitizers in solid tumour treatment,[4] diagnostic agents in medicine,[5] potentiometric sensors.[6] Owing to their pronounced solvatochromic effect, merocyanine dyes have found widespread utilization as probes for solvent polarity.[7]

Depending on the donor and acceptor strengths of the terminal groups, the electronic structure of merocyanines in the ground state changes from a polyene-like type structure (A) through a fully delocalized cyanine type (B) to a zwitterionic structure (C)[1] (Figure 1). The length of the polymethine chain and its flexibility are also of considerable importance in determining their specific properties.

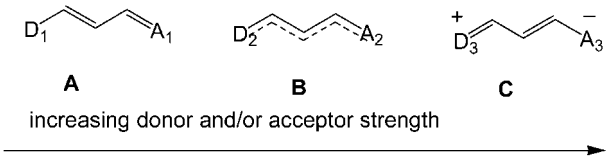


Figure 1. Electronic structures of merocyanines.

The synthesis of merocyanines with desired characteristics is one of the most challenging areas in cyanine chemistry. Much effort has been focused on the search for new preparative variants and reagents for synthesis, the insertion of new or specifically substituted heterocyclic ring systems and the synthesis of dyes with specific substituents in the polymethine chain.[1,8]

In particular, bis-merocyanine dyes contain two merocyanine units that are covalently linked by different types of spacers. Their absorption behaviour is reported to depend on the mutual orientation of the merocyanine moieties.[9] Surprisingly, in spite of the numerous examples of merocyanines reported in the literature, to the best of our knowledge only a few papers deal with the synthesis of bis-merocyanine dyes.[9,10]

In the course of our continued work on the synthesis and reactivity of cyanine dyes,[11] we developed a method for the preparation of substituted merocyanines based on the

[a] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 113 Sofia, Bulgaria
[b] School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London, E1 4NS, UK
[c] Synthèse et Physicochimie de Molécules d'Intérêt Biologique, UMR 5068, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 9, France

hydrolysis of readily available pentamethinium salts under basic conditions.[12] The main advantage of this synthetic strategy is that the starting dyes bear both a cyanine chain and the substitution patterns. Later, in a search for new synthetic applications of organometallics in cyanine chemistry, we elaborated a convenient and high-yielding one-pot experimental procedure for the synthesis of seven-carbon chain merocyanines based on the C1/C5 regioselective nucleophilic addition of lithium enolates of aromatic ketones to non-substituted pentamethine cyanine dyes and subsequent spontaneous Hofmann elimination reaction.[11c]

According to the literature, partial[13] or full[14] incorporation of the methine groups from the polyene chain of merocyanine dyes into a ring system significantly improves their thermal and/or photostability.[13,14]

In this paper, we extend the application of organometallic reagents to the synthesis of rigidized merocyanines and bis(merocyanines) using as key intermediates pentamethinium salts with inherent rigidity. In addition, the presence of a *meso*-chlorine substituent in the polymethine chain reveals the potential for further structural modification by nucleophilic replacement of the chlorine atom.[15]

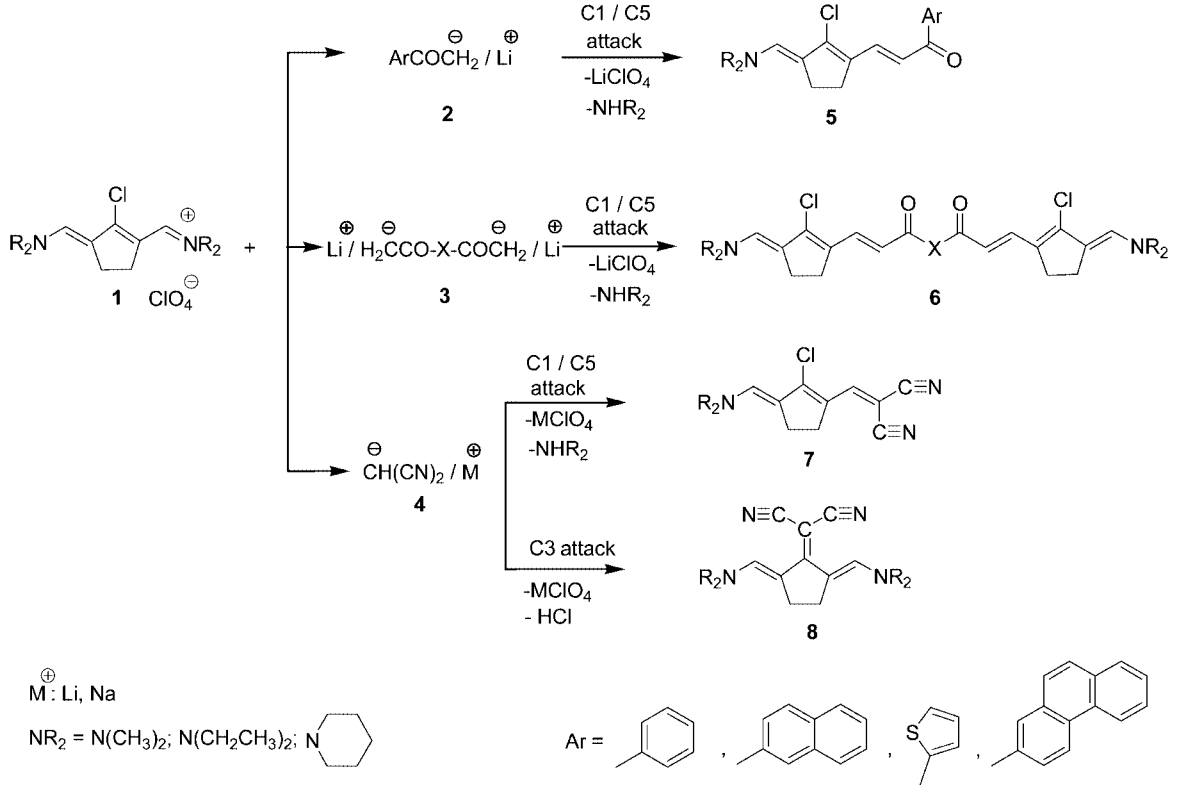
The photophysical behaviour of all the new dyes has been investigated and their spectroscopic characteristics are reported herein. They are compared with those of non-rigid analogues where possible.

Results and Discussion

Synthesis

The synthetic strategy for the preparation of rigidized mono- and bis-merocyanine dyes is shown in Scheme 1. Within the intended scope of this work, the pentamethinium precursors contain one methine unit locked into a cyclopentene framework. They are readily available by the Vilsmeier–Haack–Arnold reaction.[16] The choice of aromatic diketones utilized in the synthesis of bis(merocyanines) was determined by the need for clean generation of bis-enolate species without the occurrence of side-reactions.

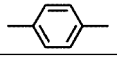
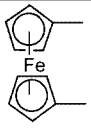
The experimental procedure includes the addition of a cyanine salt to the lithium reagent of the CH-acidic compound prepared at –78 °C. The reaction mixture is then heated to ambient temperature over 3 h. The work up depends on the type of product and is described in the Exptl. Sect. Note the great simplicity of this procedure in the case of bis(merocyanines); the crude reaction mixture is poured into cool water followed by filtration of the separated crystals. This procedure gives direct access to analytically and spectroscopically pure products. Where attempted, the same work up was used in the synthesis of mono-merocyanines and has, in some cases, definite advantages. Thus, flash column chromatography of **5d**, that had up to 80% purity as



Scheme 1. Synthesis of merocyanines **5**, **7** and **8** and bis(merocyanines) **6**. R and X are defined in Tables 1 and 2.

a crude product (^{1}H NMR analysis), resulted in a strong decrease of the reaction yield (6%), evidently due to decomposition on the column. The alternative water purification procedure increased the yield to 44% (see Table 1).

Table 1. Substitution patterns and yields for the synthesis of merocyanines **5** and bis(merocyanines) **6**.

Dye	NR_2	Ar (X)	Yield (%)
5a	NMe_2	Ph	52 (30)[a]
5b	NMe_2	β-naphthyl	46
5c	NMe_2	2-phenanthryl	18
5d	NMe_2	2-thienyl	6 (44)[a]
5e	NEt_2	Ph	68
5f	NEt_2	β-naphthyl	55 (81)[a]
5g	NEt_2	2-phenanthryl	73
5h	NEt_2	2-thienyl	62
5i		β-naphthyl	31 (42)[a]
5j		2-phenanthryl	73[a]
6a	NEt_2		84[a]
6b			80[a]
6c	NEt_2		73[a]
6d	NEt_2		51[a]
6e	NEt_2		67[a]

[a] Water purification procedure.

By using the above-described synthetic approach, a new series of rigidized, seven-carbon-chain merocyanines and bis(merocyanines), with both merocyanine units linked by an aromatic skeleton, were obtained in good-to-excellent yields (Table 1 and Table 2).

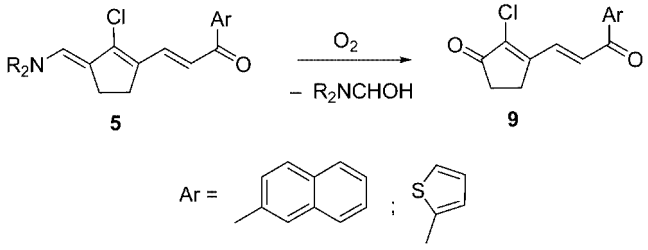
Table 2. Yields and regioselectivity in the synthesis of merocyanines **7**[a] and **8**.

Dye	NR_2	M^+	**7 : 8**	Yield (%)
7a, 8a	NEt_2	Li	100 : 0	66
7a, 8a	NEt_2	Na	100 : 0	63
7b, 8b		Li	86 : 14	92
7b, 8b		Na	38 : 62	68

[a] Me_2N derivative of **7** has already been prepared, see ref.[5c].

As an exception, the lithium reagent of malononitrile reacts with the pentamethine piperidinium salt in a non-regioselective manner, thus producing dyes from both C1/C5 and C3 nucleophilic attack (Table 2). It was found that the proportion of the C3-derived product increases significantly (86:14 vs. 38:62) when the reaction was carried out in pyridine in the presence of CH_3ONa. Surprisingly, use of the diethylaminium salt instead of piperidinium led to regioselective C1/C5 addition. The difference observed is difficult to rationalize. According to our semiempirical AM1 calculations, the replacement of piperidine by a diethylamine residue in the pentamethinium salt does not alter the charge distribution in the polymethine chain. The influence of steric factors seems less probable, although it would favour C3 attack.

The new rigidized merocyanines are stable for months at room temperature. Nevertheless, after a very long time, they undergo photosensitized oxidative cleavage of the terminal enamine double bond to produce the corresponding diketone. Such a transformation is in accord with the chemical reactivity of enamines reported in the literature.[17] In particular, in the course of this work, two diketones **9** were isolated and identified, as shown in the Scheme 2.



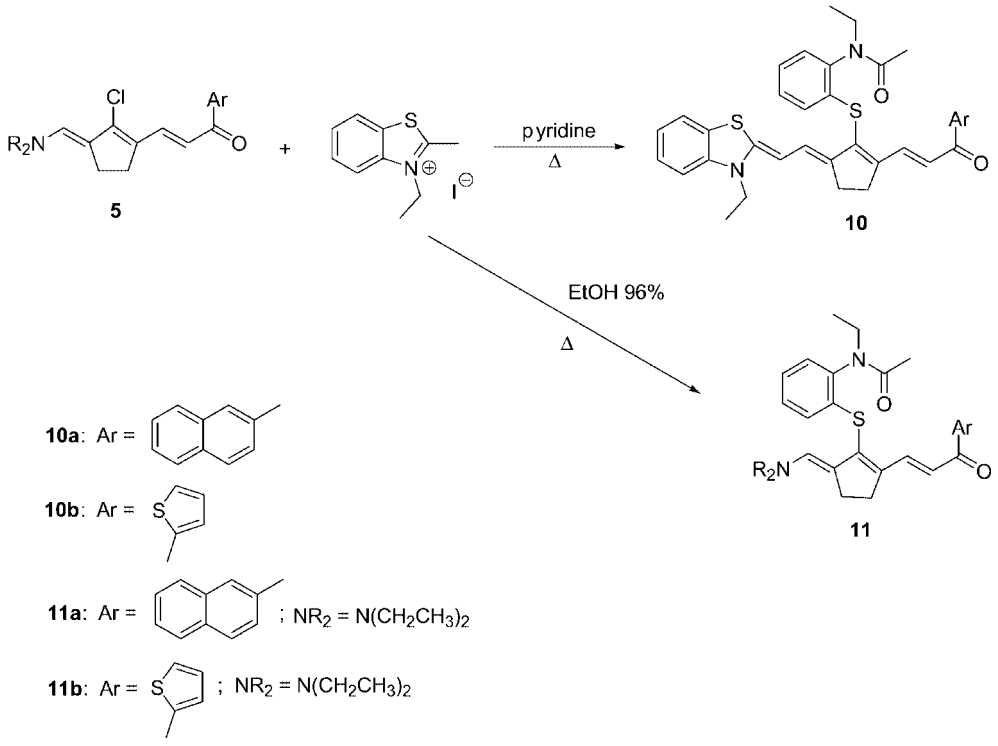
Scheme 2. Oxidation of the merocyanines to diketones.

We next attempted to extend the conjugation between the donor and acceptor systems in the new dyes. The use of a quaternary salt of a heterocyclic compound with an activated methyl group was expected to achieve such an extension, introducing at the same time a heterocyclic moiety as a terminal group.

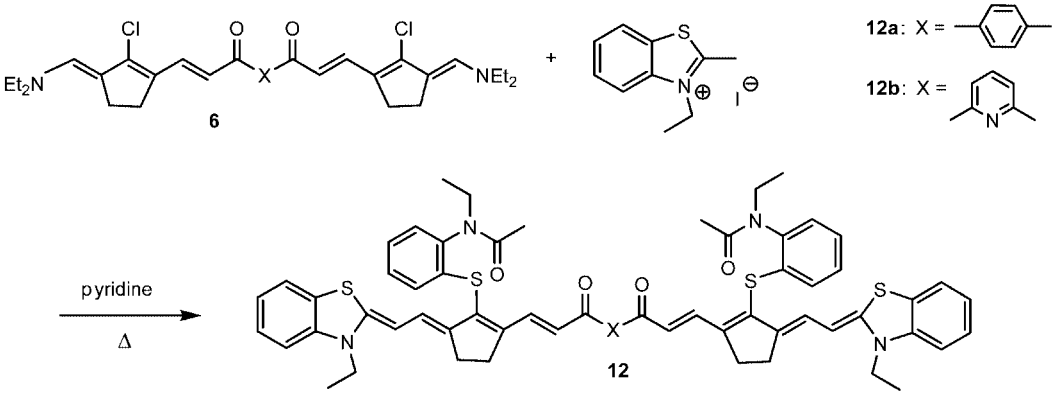
Therefore, merocyanines were subjected to condensation with 3-ethyl-2-methyl-benzothiazolium iodide in pyridine or ethanol in the presence of piperidine. The reaction course was found to depend on the reaction conditions (Scheme 3 and Scheme 4).

In boiling pyridine the chemical transformation affects two reactive centres, the terminal amino group and the *meso*-chlorine substituent, furnishing dyes **10** with both a lengthened and a ramified polymethine chain. Note that the use of one or two molar equivalents of the quaternary salt does not influence the reaction course, but does affect the reaction yield, which increases in the second case. Such an increase was observed when a dimethylamino salt was used instead of a diethylaminopentamethinium salt, probably as a result of the easier elimination of gaseous dimethylamine.[18]

Under the same reaction conditions, bis(merocyanines) **6** (Scheme 4) undergo an analogous transformation with the participation of both merocyanine units, thus giving access to new bis-merocyanine dyes **12**.



Scheme 3. Reaction of the mono-merocyanines with 3-ethyl-2-methylbenzothiazolium iodide.



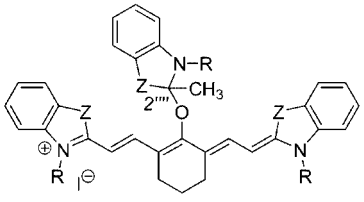
Scheme 4. Reaction of the bis(merocyanines) with 3-ethyl-2-methylbenzothiazolium iodide.

The second synthetic approach, involving condensation in boiling ethanol in the presence of piperidine enables reactions at the two reactive centres to be discriminated. Thus, within 30 min the main reaction products are the ramified, *meso*-substituted merocyanines **11**, whereas the quantity of dyes **10** produced is negligible. The result is the same irrespective of the molar ratios of the quaternary salt and the starting dye. Our attempts to direct the synthesis towards compounds **10** by the use of 2 equivalents of the quaternary salt and prolonged reaction times were unsuccessful.

Structures of Sulfur-Bridged Compounds 10–12

Detailed NMR analysis of the dyes **10**–**12** unexpectedly revealed that their structures exhibit a degree of chirality, as manifested by the observed diastereotopicity of the protons of one methylene group. Unambiguous structural elucidation was not possible. The NMR spectroscopic data closely match those for compounds with general formula **13** published by Ramos et al.,[19] but our analysis of the chemical shifts and of the connectivity between protons and be-

tween proton and carbon atoms in compound **10a** are inconsistent with their suggested chemical structure.



13 Z = CH=CH, O, S, Se

X-ray crystallographic analysis of **10a** provided the solid-state structure of this compound as well as the main structural features of the analogous dyes. One of the benzothiazolium units is located at the terminal position of the starting merocyanine, thus lengthening the polymethine chain by two carbon atoms. The second heterocycle is incorporated at the *meso* position by replacement of the chlorine atom and is attached via a sulfur bridge as a result of the cleavage of the benzothiazole ring. Note that such cleavage is well recognized in the literature and leads in general to the formation of functionalized *o*-aminothiophenols or their derived disulfides.[20]

Figure 2 shows a thermal ellipsoid plot of **10a**; compound **10a** crystallizes with triclinic symmetry with one benzene molecule per formula unit and one water molecule per two formula units. Bond lengths and angles are all within the expected ranges. Relatively large thermal parameters for C26, C23, O2 and C24 indicate some positional disorder at these sites. The structure shows evidence of intramolecular hydrogen bonding between O2 and C24 (O2···C24 1.791 Å, O2···H24a 1.416 Å). In addition, intermolecular hydrogen bonding occurs with the disordered water molecule (Figure 3) with O2···O3 2.715 Å and O2···H3a 1.789 Å.

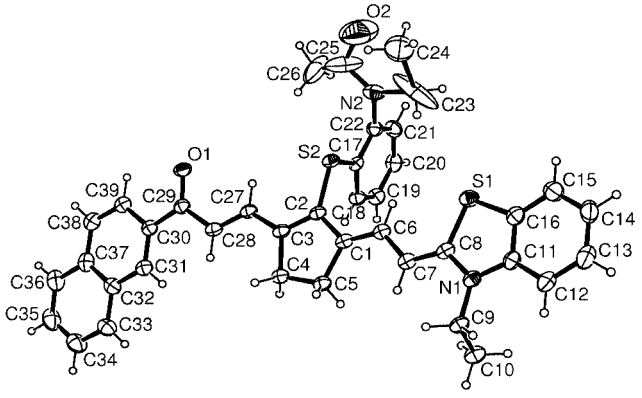


Figure 2. Thermal ellipsoid plot of **10a** (30% probability).

The NMR spectroscopic data for **10a** and **10b** corroborate their structures. Unambiguous assignment of the ^{1}H and ^{13}C spectra, derived using different spectroscopic techniques, COSY, NOESY, HSQC with and without decoupling,[21] and HMBC, are shown in Table 3.

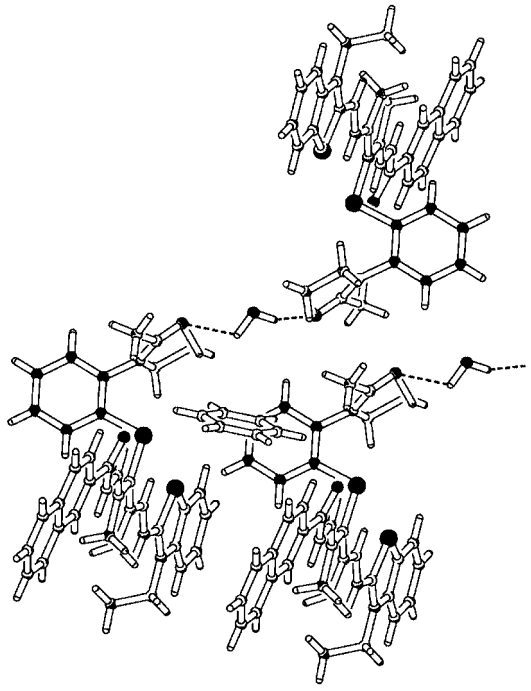


Figure 3. Packing diagram of **10a** showing intermolecular hydrogen bonding. Disorder in the water molecule has been omitted for clarity.

Note that the observed diastereotopicity is not due to the presence of a chiral carbon atom in the molecule. It is a consequence of a hindered rotation around the *ortho*-substituted N–phenyl bond in the acetanilide part of the molecule, analogous to the observations of Rodriguez and coworkers.[22] This phenomenon is not related to the properties of the dyes and will be comprehensively studied separately.

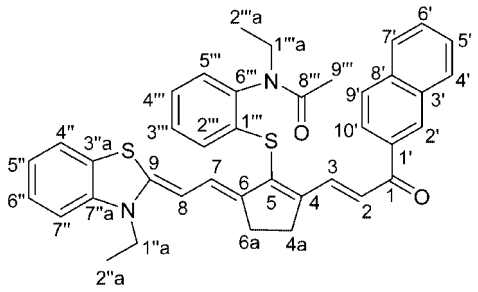
The observed formation of the sulfur-bridged merocyanine dyes by replacement of the nucleophugal *meso*-chlorine atom by a quaternized benzothiazolium unit to the best of our knowledge has not been reported in the literature. This finding is expected to give easy access to various substituted ramified merocyanines by using different quaternized benzothiazolium salts. Work on the elucidation of the mechanistic aspects of the formation of the sulfur-bridged compounds is currently in progress.

All the new merocyanine dyes are deep-coloured, solid substances. Their structures have been unambiguously determined by elemental and spectral analyses (mass, ^{1}H and ^{13}C NMR spectra). Where necessary for structural elucidation, additional techniques such as DEPT, COSY, NOESY, HMQC, HSQC and HMBC were applied.

Photophysical Properties

Depending on the number of merocyanine moieties and their substitution patterns, the investigated compounds can be divided into three groups as follows: i) merocyanines, ii) bis(merocyanines) and iii) mono- and bis(merocyanines) with ramified polymethine chains.

Table 3. ^1H and ^{13}C NMR chemical shifts [ppm] of compounds **10a** and **10b** ($CDCl_3$, TMS).



10a

No.	δ_H (**10a**)	δ_H (**10b**)	δ_C (**10a**)	δ_C (**10b**)	No.	δ_H (**10a**)	δ_H (**10b**)	δ_C (**10a**)	δ_C (**10b**)
1	–		189.8	181.7	1′′a	3.80	3.76	39.3	39.3
2	7.00	6.73	121.8	121.5	2′′a	1.21	1.26	13.2	13.3
3	8.05	7.99	137.8	136.8	3a′′	–		124.3	124.4
4	–		147.4	147.1	4′′	7.17	7.16	121.3	121.3
4a	3.03	2.92	30.0	29.9	5′′	6.88	6.83	120.9	121.0
5	–		140.9	141.2	6′′	7.11	7.07	126.2	126.2
6	–		137.7	137.7	7′′	6.73	6.68	108.1	108.2
6a	2.90	2.84	26.7	26.7	7′′a			142.1	142.1
7	6.46	6.40	122.7	122.8					
8	5.30	5.25	89.9	89.9					
9	–		148.1	148.2	1′′′a	3.44	3.49	42.4	42.4
						4.24	4.25		
					7′′′	–		170.6	170.6
1′	–		135.8	148.1	2′′′a	1.30	1.26	11.2	11.2
2′	8.38	7.66	129.3	130.8	8′′′	1.95	2.00	22.7	22.7
3′	–		132.4		1′′′			138.8	138.9
4′	7.88	7.05	129.3	128.0	2′′′	7.1	7.10*	129.5	129.5
5′	7.51	7.54	126.4	132.9	3′′′	–	7.11*	125.7	125.7
6′	7.56		127.9		4′′′	7.19	7.16	128.8	128.7
7′	7.86		127.6		5′′′	6.98	6.93	126.9	127.0
8′	–		135.1		6′′′			136.7	136.7
9′	7.84		128.2						
10′	7.98		124.4						

The rigidized heptamethine merocyanines (compounds **5a**–**5j**) in solution at room temperature absorb in the visible region of the spectrum. The longest wavelength absorption bands in ethanol have a maximum of between 19800 and 18500 cm^{-1}, which are shifted to the red by about 2000 cm^{-1} relative to previously studied non-rigidized analogues,[11c] and the molar absorptivity is almost twice the magnitude 35000–70000 cm^{-1} (Table 4, Figure 4).

The solvent polarity and proton-donating ability have a pronounced effect on the energy of the $S_0 \rightarrow S_1$ transition for **5a**–**5j**. Passing from ethanol through acetonitrile to chloroform a hypsochromic shift of up to 800 cm^{-1} is observed (Table 4, Figure 4).

Similar to other merocyanine dyes,[11c,23] the energy of the $S_0 \rightarrow S_1$ transition for **5a**–**5j** depends on the nature of the nitrogen-containing substituent. Replacement of the dimethylamino group (compound **5b**) by a piperidino (compound **5i**) or a diethylamino one (compound **5f**), which increases the electron density on the nitrogen atom, diminishes the energy of the $S_0 \rightarrow S_1$ transition by 600–700 cm^{-1}. The same effect is observed when the phenyl fragment in position 1 is replaced by stronger electron-donating substituents, namely naphthyl (**5b**, **5f**, **5i**), phenanthryl (**5c**, **5j**) or thienyl (**5d**, **5h**). In this case the longest wavelength absorption band is shifted to the red by about 350–500 cm^{-1} (Table 4).

Compounds **7a** and **7b** can also be assigned to the group of rigidized heptamethine merocyanines. Both the carbonyl group and the aryl substituent in position 1 of **5** are replaced by cyano groups. The system remains of the so-called "push–pull" type, but the two cyano groups have a much stronger electron-withdrawing effect than the carbonyl group which leads to a large red shift of the absorption maximum of **7a** of about 700 cm^{-1} compared with that of **5e** (Table 4).

The bis-merocyanine dyes **6a**–**6e** contain two merocyanine units connected by an aromatic spacer. Their longest wavelength absorption maxima are between 17000 and 21000 cm^{-1}. As can be seen from Table 4, they exhibit a red shift of the absorption Franck–Condon transitions of about 1000 cm^{-1} in comparison with the mono analogues **5a**–**5i**.

The third group of investigated compounds are the ramified nonamethine merocyanines (**10a**, **10b**), heptamethine merocyanines (**11a**, **11b**) and bis(merocyanines) (**12a**, **12b**). In these compounds the *meso*-Cl substituent is replaced by

Table 4. Absorption characteristics of the studied merocyanines.[a]

	Absorption parameters					
	Ethanol		Acetonitrile		Chloroform	
	$\tilde{\nu}_{abs}$ [cm^{-1}]	ε [$L\,mol^{-1}\,cm^{-1}$]	$\tilde{\nu}_{abs}$ [cm^{-1}]	ε [$L\,mol^{-1}\,cm^{-1}$]	$\tilde{\nu}_{abs}$ [cm^{-1}]	ε [$L\,mol^{-1}\,cm^{-1}$]
5a	19750	38750	20120	36820	20360	45260
5b	19300	36800	19770	37300	19790	47140
5c	19180	41000	19730	43800	19610	51300
5d	19270	66600	19830	64400	19920	84000
5e	19430	47000	19920	40000	20000	42110
5f	18650	32000	19400	36700	19480	38000
5h	18720	64200	19440	67300	19300	81000
5i	18730	36000	19350	38000	19400	38900
5j	18690	36300	19290	35200	19500	33800
6a	17670	–	18520	–	18350	47270
6b	17490	–	18350	–	18510	56500
6c	18500	–	19200	–	18550	52000
6d	18400	–	19520	–	19280	46000
6e	20750	–	20700	–	20840	65300
	19230		19340		19230	
	sh		sh		sh	
7a	18690	76500	18690	71400	18800	88300
7b	18630	59000	18680	63000	18700	68000
8b	19790	71300	19790	63600	19280	56400
10a	16610	42000	16770	51100	16670	73330
10b	16710	50910	16780	41300	16690	51600
11a	18840	55380	18920	40000	19080	50000
11b	18530	53300	18580	55000	18660	54660
12a	16130	–	16460	–	16200	96000
12b	16250	–	16400	–	16640	92600

[a] ν_{abs} = the energy of the longest wavelength absorption Franck–Condon transitions at 293 K, ε = molar absorptivity, the symbol – denotes very poor solubility.

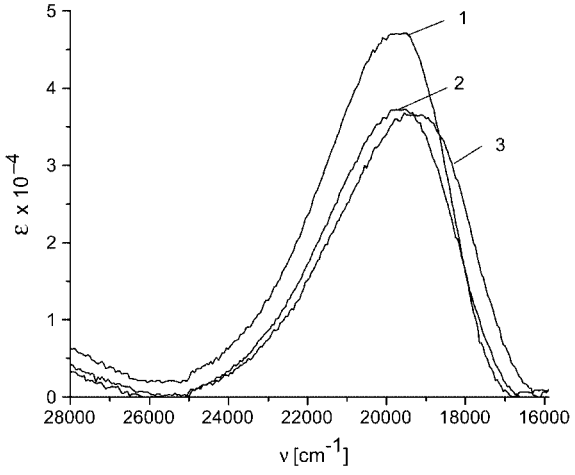


Figure 4. Absorption spectra of compound **5b** at 293 K: curve 1: chloroform; curve 2: acetonitrile; curve 3: ethanol.

a sulfur-bridged acetanilide fragment as a result of the opening of the benzothiazole ring. In addition, in **10a**, **10b**, **12a** and **12b** the terminal amino group is substituted for a second benzothiazolium fragment. As can be seen from Table 4, the ramification of the polymethine chain does not have a pronounced effect on the absorption spectra of the corresponding dyes. Thus, the longest wavelength absorption maxima for compounds **11a** and **11b** are very similar to those of compounds **5f** and **5h**. In contrast, in compounds **10a**, **10b**, **12a** and **12b** a large bathochromic shift of the longest wavelength absorption maxima of approximately 2000 cm^{-1} is observed (Table 4), accompanied by a change in colour of the dyes from red to blue.

Clearly, elongation of the conjugation pathway with two methine units leads to a remarkable decrease in the energy of the absorption Franck–Condon transition.

The longest wavelength absorption maxima of the studied compounds (e.g., **5f**, **5h**, **6b**, **6d**, Table 5) in aprotic solvents move monotonically to the red with increasing solvent polarity. A sharp drop in the energy of the $S_0 \rightarrow S_1$ absorption transition is observed between acetonitrile and 1-butanol despite their similar polarity. The relationship between the orientational polarizability Δf of the solvents, which is a function of the dielectric constant (ε_r), the refractive index (n)[24] and the energy of the absorption maxima, was studied. In protic solvents, no linear correlation between the absorption frequency of these compounds and the Δf (ε_r, n) constants was found, whereas such a correlation exists in aprotic solvents (Figure 5). This indicates that the significant bathochromic shift observed for the absorption maxima of the studied merocyanines in protic solvents cannot be explained only by their higher polarity.

Table 5. Absorption characteristics of compounds **5f**, **5h**, **6b**, **6d**, **10a** and **12a** in solvents with different ET(30) parameters at 293 K.[a]

Solvent	ET(30) [$cal\,mol^{-1}$]	**5f** $\tilde{\nu}_{abs}$ [cm^{-1}]	**5h** $\tilde{\nu}_{abs}$ [cm^{-1}]	**6b** $\tilde{\nu}_{abs}$ [cm^{-1}]	**6d** $\tilde{\nu}_{abs}$ [cm^{-1}]	**10a** $\tilde{\nu}_{abs}$ [cm^{-1}]	**12a** $\tilde{\nu}_{abs}$ [cm^{-1}]
Toluene	33.9	20020	20000	19440	20640	17310	16690
Benzene	34.5	19870	19920	19340	20400	17080	16610
Acetone	42.2	19660	19760	18900	19920	16920	16460
Acetonitrile	46	19400	19440	18350	19520	16770	16460
2-Propanol	48.6	18800	18900	17760	18560	16650	16310
1-Butanol	50.7	18700	18850	17680	18500	16490	16200
Ethanol	51.9	18650	18720	17490	18400	16460	16130
Methanol	55.5	18440	18400	17360	17800	16460	16000

[a] $\tilde{\nu}_{abs}$ = the energy of the absorption maximum.

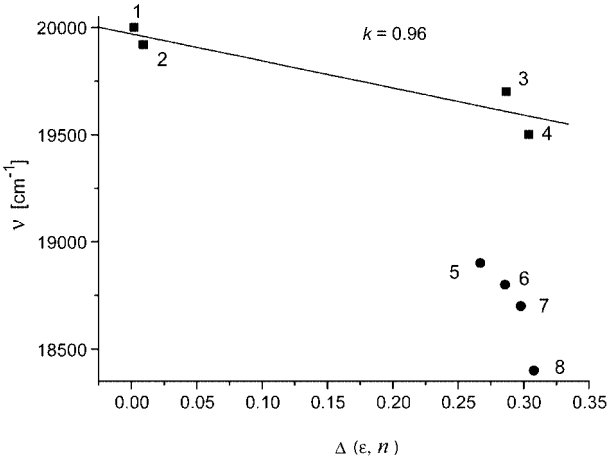


Figure 5. Energy of the absorption maximum $\tilde{\nu}$ of compound **5h** at 293 K versus the Δf constants of the solvents. The numbers of solvents correspond to the order given in Table 5 (1 for toluene to 8 for methanol). The straight line is fitted to the aprotic solvents only.

Two different linear correlations are obtained for the relationship between the absorption frequency of **5f**, **5h**, **6b** and **6d** (Table 5) and the ET(30) constants of the sol-

vents:[25] one for protic and another for aprotic solvents (Figure 6). The presence of two correlation lines indicates that the nature of the absorbing states in protic and aprotic solvents is different. These experimental results could be explained, as in the case of other cyanine dyes,[26] by the possible formation of intermolecular hydrogen bonds in the ground state between the substance and the protic solvents.

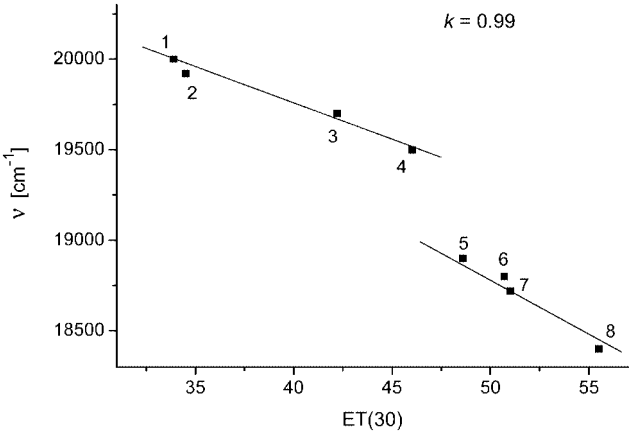


Figure 6. Energy of the absorption maxima $\tilde{\nu}_{abs}$ of compound **5h** at 293 K versus the solvent polarity parameter ET(30) [in kcal mol^{-1}]. The numbers of the solvents correspond to those given in Table 5.

When the amino group at position 7 is replaced by a benzothiazolium fragment no evidence for the formation of intermolecular hydrogen bonds between the merocyanines and the protic solvents is observed (Table 5, Figure 7). The correlation between the absorption frequency of compounds **10a** and **12a** and the ET(30) constants of all the solvents listed in Table 5 is linear with $k = 0.986$. This fact can be explained by the stronger electron-donating properties of the amino group relative to those of the benzothiazolium group. As a result, the partial negative charge on the carbonyl oxygen atom in the amino-substituted merocyanines will be much stronger and the probability of formation of solute–solvent complexes in the ground state will be higher. Similar changes in the spectral behaviour and lack of intermolecular hydrogen bond formation is also observed in other groups of compounds in which the amino group is replaced by other substituents, for example, a methoxy group.[27]

Most of the studied dyes fluoresce in solution at room temperature between 18500 and 15000 cm^{-1} (Table 6). Their fluorescence maxima are bathochromically shifted by less than 1000 cm^{-1} in comparison to those of previously studied merocyanines.[11c] The energy of the fluorescence Franck–Condon transition decreases on passing from chloroform through acetonitrile to ethanol. The fluorescence quantum yields of the rigidized merocyanines (**5a**–**5j**) are a little higher than those of the non-rigidized merocyanines,[11c] bis(merocyanines) (**6a**–**6e**) and the ramified merocyanines **11a** and **11b**. Compounds **10a**, **10b**, **12a** and **12b** do not fluoresce at all. Bearing in mind the structures of the studied merocyanines, heavy fragments connected by a polymethine chain, intramolecular vibrations of great amplitude in the fluorescent excited state are the most probable explanation for the low Φ_F values in solution at room temperature. This assumption is proved by low-temperature measurements at 77 K in ethanol. When the fluorescence spectra of the studied compounds were measured in a frozen matrix at 77 K in ethanol the fluorescence intensity increased by about two-and-a-half orders of magnitude and a blue shift of the fluorescence maxima of 600–800 cm^{-1} was observed.

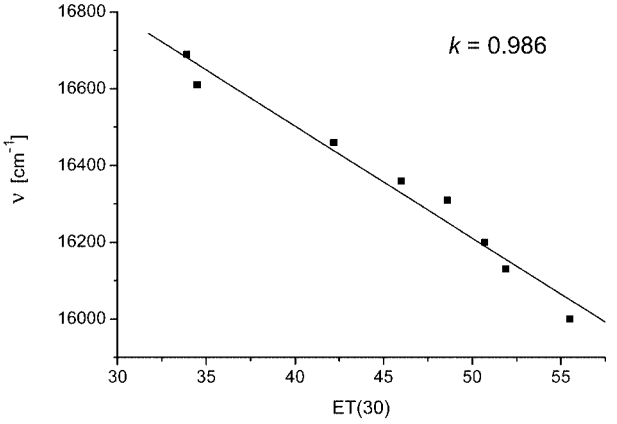


Figure 7. Energy of the absorption maxima $\tilde{\nu}_{abs}$ of compound **12a** at 293 K versus the solvent polarity parameter ET(30) [kcal mol^{-1}]. The numbers of the solvents correspond to those given in Table 5.

Table 6. Fluorescence characteristics of the merocyanines **5a** to **11b** at 293 K.[a]

	Fluorescence					
	Ethanol		Acetonitrile		Chloroform	
	$\tilde{\nu}_F$ [cm^{-1}]	Φ_F	$\tilde{\nu}_F$ [cm^{-1}]	Φ_F	$\tilde{\nu}_F$ [cm^{-1}]	Φ_F
5a	16110	0.03	16280	0.09	17150	0.14
5b	15590	0.04	15850	0.05	16700	0.06
5c	15530	0.04	15700	0.06	16640	0.06
5d	15640	0.02	16090	0.03	16710	0.01
5e	16090	0.08	16240	0.11	17060	0.15
5f	15630	0.03	15930	0.05	16630	0.04
5h	15710	0.03	16110	0.06	16670	0.05
5i	15620	0.02	15870	0.02	16560	0.05
5j	15510	0.03	15720	0.05	16370	0.11
6a	15840	<0.001	16230	<0.001	16060	<0.001
6b	15740	<0.001	16140	<0.001	16340	<0.001
6c	15930	0.03	16180	0.02	16730	0.04
6d	15520	<0.001	15570	<0.001	16120	0.008
6e	15470	0.09	15780	0.03	16200	<0.001
7a	17860	<0.001	17840	<0.001	17850	<0.001
7b	17970	<0.001	17950	<0.001	17840	<0.001
8b	18320	<0.001	18340	<0.001	18190	<0.001
11a	15060	0.03	15380	0.04	15430	0.03
11b	15110	0.02	15600	0.04	16140	0.08

[a] $\tilde{\nu}_F$ = energy of the fluorescence Franck–Condon transitions; Φ_F = fluorescence quantum yield.

Conclusions

We have developed a simple and efficient method for the synthesis of rigidized mono- and bis-heptamethine merocyanines containing one methine unit incorporated into a cy-

clopentene framework. The synthetic approach is based on C1/C5 regioselective nucleophilic addition of mono- and diketone lithium enolates to readily available pentamethine cyanines with inherent rigidity followed by a Hofmann-type elimination reaction. The new dyes react easily with heterocyclic compounds containing an activated methyl group. Depending on the reaction conditions, one or two reactive centres could be affected thus giving access to new merocyanine derivatives with lengthened polymethine chains and/or ramified via a sulfur bridge by a second heterocyclic unit. Such ramification of chlorine-containing polymethine dyes, resulting from the opening of the quaternized benzothiazole ring, to the best of our knowledge has not been reported in the literature and is expected to give a convenient access to new, differently branched merocyanines. The photophysical characteristics of the rigidized mono- and bis-heptamethine merocyanines have been studied in solvents of different polarity and proton-donating ability. The formation of intermolecular hydrogen bonds in the ground state with protic solvents has been observed.

Experimental Section

All reactions involving lithium reagents were carried out under argon using oven-dried flasks equipped with a rubber septum to introduce reagents through a syringe. THF was freshly distilled from $LiAlH_4$. Acetonitrile was dried and distilled from CaH_2 and stored over 3 Å molecular sieves. Pyridine was first dried with KOH, distilled in vacuo and stored over molecular sieves. Ethanol (Fluka UV-spectroscopic, 96%) was commercially available. LDA was prepared from *n*BuLi (1.6 M in hexane, Fluka) and diisopropylamine according to the standard procedure.

All starting materials were commercially available and used without further purification unless otherwise noted. Pentamethinium salts were synthesized according to ref.[16].

Flash chromatography was carried out using Fluka silica gel 60 (0.04–0.063 mm). Analytical thin-layer chromatography (TLC) was performed on Merck 60F-254 plates. Melting points were determined in capillary tubes and are uncorrected. IR spectra were recorded with a Bruker FTR-113 V spectrometer using KBr pellets and only partial data are reported. Mass spectra were recorded with a Hewlett–Packard 5973, a Perkin-Elmer Sciex (API 365) or an Applied Biosystems (Q TRAP) spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX-250 spectrometer using TMS as the internal standard. The chemical shifts are reported in ppm on the δ scale and coupling constants are given in Hz.

Absorption spectra were recorded with a Specord M40 (Carl Zeiss, Jena) UV/Vis spectrophotometer and the corrected fluorescence spectra with a Perkin–Elmer MPF44 spectrofluorimeter. The solvents used were of fluorescence grade. The emission spectra were corrected using a standard tungsten lamp and the excitation spectra were corrected with rhodamine B. The fluorescence quantum yields (Φ_F) were determined relative to that of rhodamine 6G (Φ_F = 0.95 in ethanol)[28] according to Equation (1), where the superscripts X and ST refer to the sample and the standard respectively, n is the refractive index of the solvent, S is the integrated area under the corrected fluorescence spectrum, A denotes the optical density at the excitation wavelength and SS is a characteristic of the spectrofluorimeter.

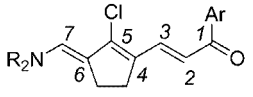
$$\Phi_F^{X} = \frac{\Phi_F^{ST} \cdot (n^X)^2 \cdot \mathbf{S}^X \cdot \mathbf{SS}^{ST} \cdot \mathbf{A}^{ST}}{(n_{ST})^2 \cdot \mathbf{S}^{ST} \cdot \mathbf{SS}^X \cdot \mathbf{A}^X} \quad (1)$$

General Procedure for the Synthesis of Merocyanine and Bis(merocyanine) Dyes: Diisopropylamine (0.18 mL, 1.32 mmol) was added at room temperature to a solution of BuLi (0.7 mL, 1.1 mmol, 1.6 M in hexane) in dry THF (1 mL). After cooling to –78 °C, a solution of the corresponding CH-acidic compound (1 mmol of ketone or malononitrile or 0.5 mmol of diketone) dissolved in THF (2 mL) was added dropwise. The reaction mixture was kept at this temperature for 30 min and then a solution of the desired pentamethinium salt (1 mmol) dissolved in dry acetonitrile (5 mL) was introduced. After stirring for a further 30 min the cooling bath was removed and the reaction mixture was allowed to reach room temperature over 3 h.

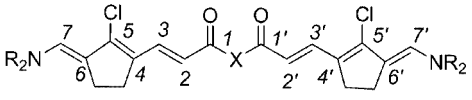
The merocyanine dyes **5**, **7** and **8** were isolated after removal of the solvent under reduced pressure and subsequent purification of the crude products by flash chromatography on silica gel using dichloromethane/methanol, 19:1 (method A).

Alternatively, bis(merocyanines) **6** were isolated by pouring the crude reaction mixture into cold water (150 mL) (method B). Filtration of the precipitated crystals, washing with cold water and drying in the open air gave direct access to analytically and spectroscopically pure **6**. The same procedure was applied in the isolation of merocyanines **5** (see Table 1).

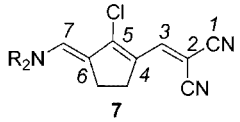
NMR chemical shift assignments of the mono- and bis(merocyanines) follow the numbering system shown below.



5



6



7

Starting from cyanine salts **1** (1 mmol) and the corresponding lithium derivatives **2**, **4** (1 mmol) or **3** (0.5 mmol) and following the general experimental procedure, the following compounds were obtained.

3-{2-Chloro-3-[(dimethylamino)methylene]cyclopent-1-enyl}-1-phenylprop-2-en-1-one (5a): Dark-red solid (method A). Yield: 149 mg (52%). R_f = 0.74 (dichloromethane/methanol, 19:1). M.p. 131–133 °C. $C_{17}H_{18}ClNO$ (287.79): calcd. C 70.95, H 6.30, N 4.87; found C 70.68, H 5.97, N 4.64. MS (EI, 30 eV): *m*/*z* = 287 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1623 (CO) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.67–2.73 (m, 2 H, $CH_{2\ c\text{-pent.}}$), 2.89–2.97 (m, 8 H, 2 CH_3, $CH_{2\ c\text{-pent.}}$), 6.4 (s, 1 H, 7-H), 6.6 (d, J = 14.9 Hz, 1 H, 2-H), 7.4–7.5 (m, 3 H, H_{phenyl}), 7.9–7.99 (m, 2 H, H_{phenyl}, 3-H) ppm. ^{13}C NMR ($CDCl_3$, DEPT,

HMQC): δ = 25.7 (CH_2), 28.5 (CH_2), 42.3 (CH_3), 112.7 (C_q), 117.7 (C-2), 127.7 (C_q), 128.1, 128.3, 131.8 (CH_{phenyl}), 137.7 (C-3, C-7), 139.2, 144.4 (C_q), 190.2 (CO) ppm.

3-{2-Chloro-3-[(dimethylamino)methylene]cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en-1-one (5b): Dark-red solid (method A). Yield: 155 mg (46%). R_f = 0.73 (dichloromethane/methanol, 19:1). M.p. 156–158 °C. $C_{21}H_{20}ClNO$ (337.84): calcd. C 74.66, H 5.97, N 4.15; found C 74.43, H 5.80, N 4.02. MS (EI, 30 eV): *m/z* = 337 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1615 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.61–2.69 (m, 2 H, CH_2), 2.85–2.97 (m, 8 H, 2 CH_3, CH_2), 6.3 (s, 1 H, 7-H), 6.7 (d, *J* = 14.9 Hz, 2-H), 7.9–7.99 (m, 7 H, CH_{naphth}, 3-H), 8.37 (s, 1 H, CH_{naphth}) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 25.7 (CH_2), 28.6 (CH_2), 42.3 (CH_3), 112.8 (C_q), 117.2 (C-2), 124.7, 126.4, 127.7, 127.8, 128.1, 129.1, 129.4 (CH_{naphth}), 132.6, 135.0, 136.6 (C_q), 137.7 (C-7), 137.8 (C-3), 144.4 (C_q), 189.8 (C=O) ppm.

3-{2-Chloro-3-[(dimethylamino)methylene)cyclopent-1-enyl]-1-(phenanthren-2-yl}prop-2-en-1-one (5c): Dark-red solid (method A). Yield: 70 mg (18%). R_f = 0.76 (dichloromethane/methanol, 19:1). M.p. 215–218 °C. $C_{25}H_{22}ClNO$ (387.9): calcd. C 77.41, H 5.72, N 3.61; found C 77.18, H 5.49, N 3.42. MS (EI, 30 eV): *m/z* = 387 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1629 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.79–2.82 (m, 2 H, CH_2), 3.0–3.07 (m, 8 H, 2 CH_3, CH_2), 6.49 (t, *J* = 1.6 Hz, 1 H, 7-H), 6.8 (d, *J* = 14.9 Hz, 1 H, 2-H), 7.64–7.7 (m, 5 H, $CH_{phen.}$), 8.0 (d, *J* = 14.9 Hz, 1 H, 3-H), 8.2–8.76 (m, 4 H, $CH_{phen.}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 25.7 (CH_2), 28.6 (CH_2), 42.4 (CH_3), 112.9 (C_q), 117.8 (C-2), 122.9, 123.2, 125.7, 126.8, 127.4, 127.5, 127.6, 128.6, 129.1 ($CH_{phen.}$), 129.9, 131.5, 132.7, 132.8, 137.2 (C_q), 137.9 (C-3, C-7), 145.6 (C_q), 189.8 (CO) ppm.

3-{2-Chloro-3-[(dimethylamino)methylene]cyclopent-1-enyl}-1-(2-thienyl)prop-2-en-1-one (5d): Dark-red solid (method A). Yield: 128 mg (44%). R_f = 0.76 (dichloromethane/methanol, 19:1). M.p. 205–208 °C. $C_{15}H_{16}ClNOS$ (293.81): calcd. C 61.32, H 5.49, N 4.77; found C 61.01, H 5.13, N 4.38. MS (EI, 30 eV): *m/z* = 293 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1640 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.67–2.73 (m, 2 H, CH_2), 2.99–3.06 (m, 8 H, 2 CH_3, CH_2), 6.48 (t, *J* = 1.7 Hz, 1 H, 7-H), 6.6 (d, *J* = 14.7 Hz, 1 H, 2-H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1 H, H_{thien}), 7.57 (dd, *J* = 4.9, 1.1 Hz, 1 H, H_{thien}), 7.73 (dd, *J* = 3.8, 1.1 Hz, 1 H, H_{thien}), 7.96 (dt, *J* = 14.9, 1.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 25.7 ($CH_{2\ c\text{-}pent.}$), 28.5 ($CH_{2\ c\text{-}pent.}$), 42.4 (CH_3), 112.8 (C_q), 117.3 (C-2), 127.5 (C_q), 127.9, 130.3, 132.3 (CH_{thien}), 136.9 (C-7), 137.9 (C-3), 144.5, 146.7 (C_q), 181.8 (CO) ppm.

3-{2-Chloro-3-[(diethylamino)methylene]cyclopent-1-enyl}-1-phenylprop-2-en-1-one (5e): Dark-red solid (method A). Yield: 215 mg (68%). R_f = 0.82 (dichloromethane/methanol, 19:1). M.p. 110–112 °C. $C_{19}H_{22}ClNO$ (315.84): calcd. C 72.95, H 7.02, N 4.43; found C 72.68, H 6.89, N 4.33. MS (EI, 30 eV): *m/z* = 315 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1626 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.17 (t, *J* = 7.3 Hz, 6 H, 2 CH_3CH_2), 2.68–2.74 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 2.85–2.94 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.3 (q, *J* = 7.3 Hz, 4 H, 2 CH_3CH_2), 6.5 (s, 1 H, 7-H), 6.6 (d, *J* = 14.9 Hz, 1 H, 2-H), 7.43–7.50 (m, 3 H, 3 CH_{phenyl}), 7.93–7.99 (m, 3 H, 2 CH_{phenyl}, 3-H) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.84 (CH_3), 25.78 ($CH_{2\ c\text{-}pent.}$), 28.55 ($CH_{2\ c\text{-}pent.}$), 46.57 (CH_3CH_2), 111.46 (C_q), 117.38 (C-2), 127.15 (C_q), 128.14, 128.3, 131.7 (CH_{phenyl}), 137.9 (C-3, C-7), 139.5, 144.9 (C_q), 190.26 (CO) ppm.

3-{2-Chloro-3-[(diethylamino)methylene]cyclopent-1-enyl}-1-(naphthalen-2-yl)prop-2-en-1-one (5f): Dark-red solid (method A). Yield: 200 mg (55%). R_f = 0.82 (dichloromethane/methanol, 19:1). M.p. 138–140 °C. $C_{23}H_{24}ClNO$ (365.9): calcd. C 75.50, H 6.61, N 3.83; found C 75.22, H 6.27, N 3.59. MS (EI, 30 eV): *m/z* = 365 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1625 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.1 (t, *J* = 7.5 Hz, 6 H, 2 CH_3), 2.76–2.82 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 2.9–2.96 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.2 (q, *J* = 7.5 Hz, 4 H, 2 CH_2CH_3), 6.5 (s, 1 H, 7-H), 6.7 (d, *J* = 14.7 Hz, 1 H, 2-H), 7.52–7.59 (m, 2 H, 2 CH_{naphth}), 7.86–8.08 (m, 5 H, 4 CH_{naphth}, 3-H), 8.45 (s, 1 H, CH_{naphth}) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.85 (CH_3), 25.81 ($CH_{2\ c\text{-}pent.}$), 28.62 ($CH_{2\ c\text{-}pent.}$), 46.59 (CH_3CH_2), 111.52 (C_q), 117.4 (C-2), 124.77, 126.43 (CH_{naphth}), 127.26 (C_q), 127.72, 127.91, 129.37, 129.54 (CH_{naphth}), 132.70, 135.09 (C_q), 136.0 (CH_{naphth}), 136.86 (C_q), 137.86 (C-3, C-7), 145.03 (C_q), 189.99 (CO) ppm.

3-{2-Chloro-3-[(diethylamino)methylene]cyclopent-1-enyl}-1-(phenanthren-2-yl)prop-2-en-1-one (5g): Dark-red solid (method A). Yield: 300 mg (73%). R_f = 0.80 (dichloromethane/methanol, 19:1). M.p. 171–174 °C. $C_{27}H_{26}ClNO$ (415.95): calcd. C 77.96, H 6.30, N 3.37; found C 77.68, H 6.11, N 3.14. MS (EI, 30 eV): *m/z* = 415 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1618 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.18 (t, *J* = 7.1 Hz, 6 H, 2 CH_3CH_2), 2.77–2.83 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 2.91–2.97 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.3 (q, *J* = 7.1 Hz, 4 H, 2 CH_3CH_2), 6.5 (t, *J* = 1.6 Hz, 1 H, 7-H), 6.8 (d, *J* = 14.8 Hz, 1 H, 2-H), 7.63–7.92 (m, 5 H, $CH_{phen.}$), 8.06 (d, *J* = 14.8 Hz, 1 H, 3-H), 8.20–8.75 (m, 4 H, $CH_{phen.}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.9 (CH_3CH_2), 25.8, 28.6 ($CH_{2\ c\text{-}pent.}$), 46.6 (CH_3CH_2), 111.5 (C_q), 117.2 (C-2), 122.8, 123.2, 125.7, 126.8, 127.4, 127.5, 128.6, 129.1 ($CH_{phen.}$), 129.9, 131.5, 132.6, 132.8 (C_q), 136.1 ($CH_{phen.}$), 137.3 (C_q), 137.9 (C-3, C-7), 145.2 (C_q), 189.7 (CO) ppm.

3-{2-Chloro-3-[(diethylamino)methylene]cyclopent-1-enyl}-1-(2-thienyl)prop-2-en-1-one (5h): Dark-red solid (method A). Yield: 200 mg (62%). R_f = 0.77 (dichloromethane/methanol, 19:1). M.p. 118–120 °C. $C_{17}H_{20}ClNOS$ (321.86): calcd. C 63.44, H 6.26, N 4.35; found C 63.22, H 6.01, N 4.12. MS (EI, 30 eV): *m/z* = 321 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1615 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.15 (t, *J* = 7.1 Hz, 6 H, 2 CH_3CH_2), 2.68–2.72 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 2.87–2.93 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.2 (q, *J* = 7.1 Hz, 4 H, 2 CH_3CH_2), 6.5 (d, *J* = 14.8 Hz, 1 H, 7-H), 6.54 (t, *J* = 1.7 Hz, 1 H, 2-H), 7.1 (dd, *J* = 4.9, 3.8 Hz, 1 H, CH_{thien}), 7.54 (dd, *J* = 4.9, 1.1 Hz, 1 H, CH_{thien}), 7.73 (dd, *J* = 3.8, 1.1 Hz, 1 H, CH_{thien}), 7.95 (d, *J* = 14.7 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.8 (CH_3CH_2), 25.7, 28.4 ($CH_{2\ c\text{-}pent.}$), 46.5 (CH_3CH_2), 111.3 (C_q), 116.5 (C-2), 126.8 (C_q), 127.8, 130.2, 132.1 (CH_{thien}), 136.1 (C-7), 136.9 (C-3), 145.3, 146.7 (C_q), 181.7 (CO) ppm.

3-[2-Chloro-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(naphthalen-2-yl)prop-2-en-1-one (5i): Dark solid (method B). Yield: 158 mg (42%). R_f = 0.67 (dichloromethane/methanol, 19:1). M.p. >320 °C. $C_{24}H_{24}ClNO$ (377.91): calcd. C 76.28, H 6.40, N 3.71; found C 75.99, H 6.11, N 3.48. MS (EI, 30 eV): *m/z* = 377 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1655 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.6 (br., 6 H, 3 $CH_{2\ pip.}$), 2.76–2.83 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 2.90–2.97 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.3 (br., 4 H, 2 $CH_{2\ pip.}$), 6.48 (s, 1 H, 7-H), 6.8 (d, *J* = 14.9, 1 H, 2-H), 7.52–7.57 (m, 2 H, 2 CH_{naphth}), 7.85–8.07 (m, 5 H, 4 CH_{naphth}, 3-H), 8.45 (s, 1 H, CH_{naphth}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.2, 26.1 ($CH_{2\ pip.}$), 26.4, 28.6 ($CH_{2\ c\text{-}pent.}$), 51.5 ($CH_{2\ pip.}$), 112.3 (C_q), 117.5 (C-2), 124.7, 126.4, 127.67, 127.74, 128.1 (CH_{naphth}), 128.7 (C_q), 129.0, 129.3 (CH_{naphth}), 132.6, 135.0, 136.7 (CH_{naphth}), 136.9 (C-7), 137.7 (C-3), 144.8 (C_q), 189.9 (CO) ppm.

3-[2-Chloro-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(phenanthren-2-yl)prop-2-en-1-one (5j): Dark red-blue solid (method B). Yield: 310 mg (73%). R_f = 0.76 (dichloromethane/methanol, 70:1). M.p. 190–193 °C. $C_{28}H_{26}ClNO$ (427.97): calcd. C 78.58, H 6.12, N 3.27; found C 78.44, H 5.84, N 3.07. MS (EI, 30 eV): *m/z* = 427 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1620 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.59

(br., 6 H, 3 $CH_{2\ pip.}$), 2.76–2.83 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 2.90–2.97 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.27–3.35 (br., 4 H, 2 $CH_{2\ pip.}$), 6.46 (s, 1 H, 7-H), 6.8 (d, J = 14.8 Hz, 1 H, 2-H), 7.62–7.88 (m, 5 H, $CH_{phen.}$), 8.05 (d, J = 14.8 Hz, 1 H, 3-H), 8.19–8.73 (m, 4H $CH_{phen.}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 24.2, 26.1 ($CH_{2\ pip.}$), 26.3, 28.6 ($CH_{2\ c\text{-}pent.}$), 51.5 ($CH_{2\ pip.}$), 112.3 (C_q), 117.5 (C-2), 122.8, 123.2, 125.6, 126.8 ($CH_{phen.}$), 127.4 (C_q), 127.5 ($CH_{phen.}$), 127.7 (C_q), 128.6, 129.1 ($CH_{phen.}$), 129.8, 131.5, 132.7 (C_q), 136.9 (C-7), 137.2 (C_q), 137.7 (C-3), 145.0 (C_q), 189.6 (CO) ppm.

1,1′-(1,4-Phenylene)bis(3-{2-chloro-3-[(diethylamino)methylene]-cyclopent-1-enyl}prop-2-en-1-one) (6a): Dark sparkling solid (method B). Yield: 232 mg (84%). R_f = 0.45 (dichloromethane/methanol, 19:1). M.p. 223–225 °C. $C_{32}H_{38}Cl_2N_2O_2$ (553.56): calcd. C 69.43, H 6.92, N 5.06; found C 69.18, H 6.74, N 4.96. MS (EI): m/z = 552 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1612 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.18 (t, J = 7.1 Hz, 12 H, 4 CH_2CH_3), 2.72–2.76 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 2.91–2.96 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 3.3 (q, J = 7.1 Hz, 8 H, 4 CH_2CH_3), 6.57 (s, 2 H, 7-H, 7′-H), 6.6 (d, J = 12.5 Hz, 2 H, 2-H, 2′-H), 7.96 (d, J = 13.7 Hz, 2 H, 3-H, 3′-H), 7.99 (s, 4 H, CH_{phenyl}) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.9 (CH_2CH_3), 25.8 ($CH_{2\ c\text{-}pent.}$), 28.5 ($CH_{2\ c\text{-}pent.}$), 46.6 (CH_2CH_3), 111.6 (C_q), 117.1 (C-2, C-2′), 127.2 (C_q), 128.1 (CH_{phenyl}), 136.4 (C-7, C-7′), 138.4 (C-3, C-3′), 141.9, 145.7 (C_q), 189.7 (CO) ppm.

3-[2-Chloro-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]-1-(4-{3-[2-chloro-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]acryloyl}phenyl)-prop-2-en-1-one (6b): Dark solid (method B). Yield: 230 mg (80%). R_f = 0.56 (dichloromethane/methanol, 19:1). M.p. 236–238 °C. $C_{34}H_{38}Cl_2N_2O_2$ (577.58): calcd. C 70.70, H 6.63, N 4.85; found C 70.48, H 6.39, N 4.62. MS (EI): m/z = 576 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1655 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.6 (br., 12 H, 6 $CH_{2\ pip.}$), 2.71–2.76 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 2.90–2.96 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 3.34 (br., 8 H, 4 $CH_{2\ pip.}$), 6.51 (s, 2 H, 7-H, 7′-H), 6.6 (d, J = 14.9 Hz, 2 H, 2-H, 2′-H), 7.96 (d, J = 15.4 Hz, 2 H, 3-H, 3′-H), 7.99 (s, 4 H, CH_{phenyl}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 24.2 ($CH_{2\ pip.}$), 26.2 ($CH_{2\ pip.}$), 26.3 ($CH_{2\ c\text{-}pent.}$), 28.5 ($CH_{2\ c\text{-}pent.}$), 51.6 ($CH_{2\ pip.}$), 112.3 (C_q), 117.3 (CH-2), 127.6 (C_q), 128.1 (CH_{phenyl}), 137.3 (CH-7), 138.2 (CH-3), 141.8 (C_q), 145.6 (C_q), 189.6 (CO) ppm.

1,1′-(1,3-Phenylene)bis(3-{2-chloro-3-[(diethylamino)methylene]-cyclopent-1-enyl}prop-2-en-1-one) (6c): Dark sparkling solid (method B). Yield: 202 mg (73%). M.p. >330 °C. R_f = 0.57 (dichloromethane/methanol, 19:1). $C_{32}H_{38}Cl_2N_2O_2$ (553.56): calcd. C 69.43, H 6.92, N 5.06; found C 69.24, H 6.69, N 4.88. MS (EI): m/z = 552 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1617 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.19 (t, J = 7.1 Hz, 12 H, 4 CH_2CH_3), 2.72–2.78 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 2.90–2.96 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 3.3 (q, J = 7.1 Hz, 8 H, 4 CH_2CH_3), 6.58 (s, 2 H, 7-H, 7′-H), 6.7 (d, J = 14.7 Hz, 2 H, 2-H, 2′-H), 7.5 (t, J = 7.8 Hz, 1 H, CH_{phenyl}), (d, J = 14.5 Hz, 2 H, 3-H, 3′-H), 8.08 (d, J = 7.8 Hz, 1 H, CH_{phenyl}), 8.1 (d, J = 7.8 Hz, 1 H, CH_{phenyl}), 8.49 (s, 1 H, CH_{phenyl}) ppm. ^{13}C NMR ($CDCl_3$, DEPT): δ = 14.9 (CH_2CH_3), 25.8, 28.5 ($CH_{2\ c\text{-}pent.}$), 46.6 (CH_2CH_3), 111.5 (C_q), 116.8 (CH-2), 127.2 (C_q), 127.6, 128.4, 131.3 (CH_{phenyl}), 136.3 (CH-7), 138.2 (CH-3), 139.6, 145.5 (C_q), 189.5 (CO) ppm.

1,1′-(Pyridine-2,6-diyl)bis(3-{2-chloro-3-[(diethylamino)methylene]-cyclopent-1-enyl}prop-2-en-1-one) (6d): Deep dark-red solid (method B). Yield: 141 mg (51%). R_f = 0.44 (dichloromethane/methanol = 10:1). M.p. 220–222 °C. $C_{31}H_{37}Cl_2N_3O_2$ (554.55): calcd. C 67.14, H 6.73, N 7.58; found C 66.99, H 6.49, N 7.34. MS (ESI): m/z = 553 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1629 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.2 (t, J = 7.1 Hz, 12 H, 4 CH_2CH_3), 2.81–2.87 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 2.92–2.98 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 3.3 (q, J = 7.1 Hz, 8 H, 4 CH_2CH_3), 6.59 (s, 2 H, 7-H, 7′-H), 7.5 (d, J = 15.3 Hz, 2 H, 2-H, 2′-H), 7.96 (t, J = 7.8 Hz, 1 H, $CH_{pyridine}$), 8.13 (d, J = 15.3 Hz, 2 H, 3-H, 3′-H), 8.3 (d, J = 7.6 Hz, 2 H, 2 $CH_{pyridine}$) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.9 (CH_2CH_3), 25.8 ($CH_{2\ c\text{-}pent.}$), 28.4 ($CH_{2\ c\text{-}pent.}$), 46.6 (CH_2CH_3), 111.7 (C_{quat}), 116.1 (2-H, 2′-H), 124.6 ($CH_{pyridine}$), 127.9 (C_q), 136.3 (C-7, C-7′), 137.7 (C-3, C-3′, $CH_{pyridine}$), 145.6, 154.0 (C_q), 188.1 (CO) ppm.

1,1′-(Ferrocene-1,1′-diyl)bis(3-{2-chloro-3-[(diethylamino)methylene]cyclopent-1-enyl}prop-2-en-1-one) (6e): Deep dark-brown solid (method B). The product is purified by chromatographic filtration (dichloromethane) over basic Al_2O_3. Yield: 220 mg (67%). R_f = 0.64 (dichloromethane/methanol, 19:1). M.p. 93–96 °C. $C_{36}H_{42}Cl_2FeN_2O_2$ (661.48): calcd. C 65.37, H 6.40, N 4.23; found C 65.11, H 6.22, N 4.02. MS (EI): m/z = 660 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1625 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.18 (t, J = 7.6 Hz, 12 H, 4 CH_2CH_3), 2.63–2.69 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 2.85–2.90 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 3.2 (q, J = 7.6 Hz, 8 H, 4 CH_2CH_3), 4.5 (t, J = 2.0 Hz, 4 H, $CH_{ferrocene}$), 4.8 (t, J = 2.0 Hz, 4 H, $CH_{ferrocene}$), 6.1 (d, J = 14.9 Hz, 2 H, 2-H, 2′-H), 6.49 (s, 2 H, 7-H, 7′-H), 7.9 (d, J = 14.9 Hz, 2 H, 3-H, 3′-H) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.9 (CH_2CH_3), 25.6 ($CH_{2\ c\text{-}pent.}$), 28.6 ($CH_{2\ c\text{-}pent.}$), 46.5 (CH_2CH_3), 71.2 ($CH_{ferrocene}$), 71.9 ($CH_{ferrocene}$), 111.7 (C_q), 118.6 (C-2, C-2′), 127.3 (C_q), 134.5 (C-3, C-3′), 135.1 (C-7, C-7′), 143.9 (C_q), 191.9 (CO) ppm.

2-({2-Chloro-3-[(diethylamino)methylene]cyclopent-1-enyl}methylene)malononitrile (7a): Dark-red solid (method A). Yield: 173 mg (66%). R_f = 0.68 (dichloromethane/methanol, 19:1). M.p. 161–163 °C. $C_{14}H_{16}ClN_3$ (261.75): calcd. C 64.24, H 6.16, N 16.05; found C 63.01, H 5.98, N 15.93. MS (EI, 30 eV): m/z = 261 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2189, 2202 (CN) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.28 (t, J = 7.2 Hz, 6 H, 2 CH_3CH_2), 2.96–3.0 (m, 2 H, $CH_{2cyclopenl}$), 3.10–3.13 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.43 (q, J = 7.2 Hz, 4 H, 2 CH_3CH_2), 7.05 (s, 1 H, 1-H), 7.43 (s, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 14.9 (CH_3CH_2), 26.8, 27.4 ($CH_{2\ c\text{-}pent.}$), 47.7 (CH_3CH_2), 112.4 (C_q), 116.8 (CN), 118.2, 124.7 (C_q), 144.0 (C-7), 146.2 (C-3), 154.7 (C_q) ppm.

2-{[2-Chloro-3-(piperidin-1-ylmethylene)cyclopent-1-enyl]methylene}malononitrile (7b): Dark solid (method A, dichloromethane/methanol, 50:1). Yield: 70 mg (26%). R_f = 0.6 (dichloromethane/methanol, 50:1). M.p. 222–225 °C. $C_{15}H_{16}ClN_3$ (273.76): calcd. C 65.81, H 5.89, N 15.35; found C 65.54, H 5.61, N 15.26. MS (EI, 30 eV): m/z = 273 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2183, 2199 (CN) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.7 (s, 6 H, 3 $CH_{2\ pip.}$), 2.90–2.98 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.05–3.12 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.53 (s, 4 H, 2 $CH_{2\ pip.}$), 7.01 (s, 1 H, 7-H), 7.40 (s, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 23.8 ($CH_{2\ pip.}$), 26.6 ($CH_{2\ pip.}$), 27.5, 27.6 ($CH_{2\ c\text{-}pent.}$), 52.7 ($CH_{2\ pip.}$), 112.1 (C_q), 116.4, 116.9 (CN), 118.2, 124.7 (C_q), 143.8 (C-7), 146.3 (C-3), 154.7 (C_q) ppm.

2-[2,5-Bis(piperidin-1-ylmethylene)cyclopentylidene]malononitrile (8b): Dark-orange oil (method A, dichloromethane/methanol, 50:1). Yield: 135 mg (42%). R_f = 0.65 (dichloromethane/methanol = 19:1). $C_{20}H_{26}N_4$ (322.45): calcd. C 74.50, H 8.13, N 17.38; found C 74.24, H 7.89, N 17.27. MS (EI, 30 eV): m/z = 322 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2197 (CN) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.67 (br., 12 H, 6 $CH_{2\ pip.}$), 2.58–2.63 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 2.83–2.88 (m, 2 H, $CH_{2\ c\text{-}pent.}$), 3.38 (br., 4 H, 2 $CH_{2\ pip.}$), 3.53 (br., 4 H, 2 $CH_{2\ pip.}$), 6.71 (s, 1 H, CH), 7.07 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 23.8, 24.4, 26.4, 27.5 ($CH_{2\ pip.}$), 28.9 ($CH_{2\ c\text{-}pent.}$), 52.2 ($CH_{2\ pip.}$), 52.6 (C_q), 55.7 ($CH_{2\ pip.}$), 108.5, 116.2 (C_q), 119.9, 121.7 (CN), 144.1, 144.9 (CH), 174.9 (C_q) ppm.

General Experimental Procedure for the Synthesis of Ramified Nonamethine Merocyanines 10 and Bis-nonamethine Merocyanines 12 in Pyridine: A mixture of 3-ethyl-2-methylbenzothiazolium iodide (610 mg, 2 mmol) and the corresponding merocyanine **5** (1 mmol) or bis-merocyanine **6** (0.5 mmol) in dry pyridine (6 mL) was refluxed for 10 min. The reaction mixture changed from deep red to dark blue. The solution was allowed to reach room temperature and then was poured into cold water. The dark-blue crystals were filtered and dried in the open air. The crude products were purified by flash chromatography or by recrystallization from an appropriate solvent. The NMR spectroscopic data for compounds **10a** and **10b** are presented in Table 3.

***N*-Ethyl-*N*-[2-(5-{2-[3-ethylbenzothiazol-2(3*H*)-ylidene]ethylidene}-2-[3-(naphthalen-2-yl)-3-oxoprop-1-enyl]cyclopent-1-enylthio)phenyl]acetamide (10a):** Sparkling dark-blue crystals (method A). Yield: 200 mg (63%). R_f = 0.4 (dichloromethane/methanol, 35:1). M.p. 176–178 °C. $C_{39}H_{36}N_2O_2S_2$ (628.85): calcd. C 74.49, H 5.77, N 4.45; found C 74.16, H 5.52, N 4.27. MS (ESI): *m*/*z* = 629 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 1536, 1659 (CO) cm^{-1}.

Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a benzene solution of the compound at room temperature over a period of 2 days. $C_{39}H_{36}N_2O_2S_2 \cdot C_6H_6 \cdot 0.5H_2O$ (715.97). Note that no proton or carbon signals due to from the benzene molecule were observed in the NMR spectra, indicating that benzene and water were included in the crystals during crystallization.

***N*-Ethyl-*N*-[2-(5-{2-[3-ethylbenzothiazol-2(3*H*)-ylidene]ethylidene}-2-[3-oxo-3-(2-thienyl)prop-1-enyl]cyclopent-1-enylthio)phenyl]acetamide (10b):** Sparkling dark-blue crystals (method A). Yield: 117 mg (40%). R_f = 0.35 (dichloromethane/methanol, 40:1). M.p. 91–94 °C. $C_{33}H_{32}N_2O_2S_3$ (584.81): calcd. C 67.77, H 5.52, N 4.79; found C 67.50, H 5.28, N 4.50. MS (EI, 30 eV): *m*/*z* = 584 [M]$^+$.

General Experimental Procedure for the Synthesis of Ramified Heptamethine Merocyanines 11 in Ethanol: Piperidine (8 drops) was added to 3-ethyl-2-methylbenzothiazolium iodide (305 mg, 1 mmol) and the corresponding merocyanine **5** (1 mmol) dissolved in 96% EtOH (70 mL) and the reaction was refluxed for 30 min. The reaction mixture was then allowed to reach room temperature, concentrated in vacuo and poured into cold water. The dark-red crystals were collected by filtration and dissolved in dichloromethane. After drying with $MgSO_4$, the solvent was removed to give compounds **11** with satisfactory analytical and spectral purity. Further attempts to purify the crude products by column chromatography or recrystallization were unsuccessful.

***N*-(2-{5-[(Diethylamino)methylene]-2-[3-(naphthalen-2-yl)-3-oxoprop-1-enyl]cyclopent-1-enylthio}phenyl)-*N*-ethylacetamide (11a):** Dark-red gum. Yield: 385 mg (73%) after trituration with dry diethyl ether (2 × 3 mL). R_f = 0.5 (dichloromethane/methanol, 19:1). $C_{33}H_{36}N_2O_2S$ (524.72): calcd. C 75.54, H 6.92, N 5.34; found C 75.28, H 6.66, N 5.20. ^{1}H NMR ($CDCl_3$): δ = 1.05–1.19 (m, 9 H, 3 CH_2CH_3), 1.8 (s, 3 H, CH_3), 2.96–3.0 (m, 4 H, 2 $CH_{2\ c\text{-}pent.}$), 3.18 (q, *J* = 7.1 Hz, 4 H, 2 CH_2CH_3), 3.24–3.35 (m, 1 H, $N^+CH_aH_bCH_3$), 4.10–4.18 (m, 1 H, $N^+CH_aH_bCH_3$), 6.6 (s, 1 H, 7-H), 6.82 (d, *J* = 15.2 Hz, 1 H, 2-H), 6.99–7.21 (m, 4 H, CH_{arom}), 7.49–7.55 (m, 2 H, CH_{arom}), 7.82–7.98 (m, 4 H, CH_{arom}), 8.0 (d, *J* = 15.1 Hz, 1 H, 3-H), 8.35 (s, 1 H, CH_{arom}) ppm. ^{13}C NMR ($CDCl_3$, DEPT, HMQC): δ = 13.0 (CH_2CH_3), 14.8 (CH_2CH_3), 22.3 (CH_3), 26.7 ($CH_{2\ c\text{-}pent.}$), 30.4 ($CH_{2\ c\text{-}pent.}$), 42.2 ($N^+CH_aH_bCH_3$), 46.6 (CH_2CH_3), 114.7 (C_q), 119.0 (C-2), 124.7, 125.6, 126.4, 126.8, 127.6, 127.7, 128.1, 128.7, 129.1, 129.3, 129.4 (CH_{arom}), 132.5, 134.9, 136.41 (C_q), 136.4 (C-7), 137.0, 138.68, 138.74 (C_q), 138.9 (C-3), 144.1 (C_q), 170.3 (CH_3-*C*-O), 190.6 (CO) ppm.

***N*-(2-{5-[(Diethylamino)methylene]-2-[3-oxo-3-(2-thienyl)prop-1-enyl]cyclopent-1-en-ylthio}phenyl)-*N*-ethylacetamide (11b):** Dark-red gum. Yield: 400 mg (85%) after trituration with dry diethyl ether (2 × 3 mL). R_f = 0.6 (dichloromethane/methanol, 19:1). $C_{27}H_{32}N_2O_2S_2$ (480.69): calcd. C 67.46, H 6.71, N 5.83; found C 67.23, H 6.58, N 5.66. ^{1}H NMR ($CDCl_3$): δ = 1.04–1.30 (m, 9 H, 3 CH_3CH_2), 1.90 (s, 3 H, CH_3), 2.87–3.01 (m, 4 H, $CH_{2\ c\text{-}pent.}$), 3.03–3.32 (m, 4 H, 2 CH_3CH_2), 3.34–3.40 (m, 1 H, $N^+CH_aH_bCH_3$), 4.12–4.26 (m, 1 H, $CH_aH_bCH_3$), 6.51 (s, 1 H, 7-H), 6.6 (d, *J* = 14.9 Hz, 1 H), 6.96–7.19 (m, 5 H), 7.55–7.90 (m, 2 H), 8.02 (d, *J* = 14.9 Hz, 1 H) ppm.

***N*,*N*′-[2,2′-(5*E*,5′*E*)-2,2′-[(1*E*,1′*E*)-3,3′-(1,4-Phenylene)bis(3-oxoprop-1-ene-3,1-diyl)]bis(5-{2-[3-ethylbenzothiazol-2(3*H*)-ylidene]ethylidene}cyclopent-1-ene-2,1-diyl)bis(sulfanediyl)bis(2,1-phenylene)]bis(*N*-ethylacetamide) (12a):** Dark-blue crystals (method B). Yield: 329 mg (61%) after recrystallization from CH_3CN. R_f = 0.64 (dichloromethane/methanol, 10:1). M.p. >320 °C. MS (ESI): *m*/*z* = 1078 [M]$^+$. ^{1}H NMR ($CDCl_3$): δ = 1.22–1.34 (m, 12 H, 4 CH_2CH_3), 2.0 (s, 6 H, 2 CH_3), 2.90–2.96 (m, 8 H, 4 $CH_{2\ c\text{-}pent.}$), 3.40–3.53 (m, 2 H, $N^+CH_aH_bCH_3$), 3.80–3.83 (m, 4 H, 2 CH_2CH_3), 4.17–4.28 (m, 2 H, $N^+CH_aH_bCH_3$), 5.3 (d, *J* = 11.5 Hz, 2 H), 6.5 (d, *J* = 11.5 Hz, 2 H), 6.72–8.03 (m, 23 H) ppm.

***N*,*N*′-[2,2′-(5*E*,5′*E*)-2,2′-[(1*E*,1′*E*)-3,3′-(Pyridine-2,6-diyl)bis(3-oxoprop-1-ene-3,1-diyl)]bis(5-{(*Z*)-2-[3-ethylbenzothiazol-2(3*H*)-ylidene]ethylidene}cyclopent-1-ene-2,1-diyl)bis(sulfanediyl)bis(2,1-phenylene)]bis(*N*-ethylacetamide) (12b):** Dark-blue crystals (method B). Yield: 220 mg (40%) after recrystallization from CH_3CN. R_f = 0.7 (dichloromethane/methanol = 10:1). M.p. >320 °C. MS (ESI): *m*/*z* = 1079 [M]$^+$. ^{1}H NMR ($CDCl_3$): δ = 1.2 (m, 12 H, 4 CH_2CH_3), 2.04 (s, 6 H, 2 CH_3), 2.96–3.13 (m, 8 H, 4 $CH_{2\ c\text{-}pent.}$), 3.45–3.59 (m, 2 H, $N^+CH_aH_bCH_3$), 3.78–3.87 (m, 4 H, 2 CH_2CH_3), 4.25–4.39 (m, 2 H, $N^+CH_aH_bCH_3$), 5.37 (d, *J* = 11.8 Hz, 2 H), 6.5 (d, *J* = 11.8 Hz, 2 H), 6.49–8.22 (m, 23 H) ppm.

X-ray Crystallography: Single-crystal X-ray diffraction data were collected using an Enraf-Nonius Kappa CCD area detector on an Enraf-Nonius FR591 rotating anode generator at 120(2) K. Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used throughout. The crystal-to-detector distance was 30 mm and &πηι; and Ω scans (2.0° increments, 12 s exposure time) were carried out to fill the Ewald sphere. Data collection, cell refinement and data reduction were carried out using the DENZO[29] and COLLECT[30] packages. Absorption correction was carried out by multiple scans using SORTAV.[31] The structure was solved by direct methods using the SHELXS-97 program[32] and developed by difference Fourier techniques with subsequent refinement on F^2 by full-matrix least-squares using SHELXL-97.[32] The hydrogen atoms were calculated geometrically and isotropic thermal parameters were refined using a riding model. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Molecular graphics were obtained using ORTEP-3[33] and Platon.[34] WinGX[35] was used to prepare material for publication. The final refinement yielded *R* factors of R_1 = 0.0867, wR_2 = 0.2209 for 6052 reflections with $F_{obs} > 4\sigma(F_{obs})$ and R_1 = 0.1194, wR_2 = 0.2435 for all 8593 reflections. CCDC-631663 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors gratefully acknowledge the EPSRC National Crystallography Service at the University of Southampton, UK, for X-ray data collection.

[1] a) G. Bach, S. Daehne, "Cyanine dyes and related compounds" in *Rodd's Chemistry of Carbon Compounds* (Ed.: M. Sainsbury), Elsevier, Amsterdam, **1997**, vol. IVb, chapter 15, pp. 383–481; b) R. Raue, *Methine dyes and pigments* in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Wiley-VCH, Weinheim, **1990**, vol. A16, pp. 487–534; c) A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, G. B. Behera, *Chem. Rev.* **2000**, *100*, 1973–2011.

[2] a) A. Ulman, *Introduction to Ultrathin Organic Films*, Academic Press, San Diego, **1991**, p. 133; b) S. R. Marder, J. W. Perry, B. G. Tiemann, C. B. Gorman, S. Gilmour, S. L. Biddle, G. Bourhill, *J. Am. Chem. Soc.* **1993**, *115*, 2524–2526; c) S. R. Marder, C. B. Gorman, B. G. Tiemann, L. T. Cheng, *J. Am. Chem. Soc.* **1993**, *115*, 3006–3007; d) S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J. L. Bredas, B. M. Pierce, *Science* **1994**, *265*, 632–635; e) J. Cabrera, O. Althoff, H.-T. Man, H. Y. Yoon, *Adv. Mater.* **1994**, *6*, 43–45.

[3] a) C. J. Gomer, *Photochem. Photobiol.* **1991**, *54*, 1093–1107; b) R. W. Redmond, M. B. Srichai, J. M. Bilitz, D. D. Schlomer, M. Krieg, *Photochem. Photobiol.* **1994**, *60*, 348–355.

[4] A. Harriman, L. C. T. Shoute, P. Neta, *J. Phys. Chem.* **1991**, *95*, 2415–2420.

[5] a) N. S. Dixit, R. A. Mackay, *J. Am. Chem. Soc.* **1983**, *105*, 2928–2929; b) G. Salama, M. Morad, *Science* **1976**, *191*, 485–487; c) M. A. Kessler, O. S. Wolfbeis, *Anal. Biochem.* **1992**, *200*, 254–259.

[6] F. Sieber, *Photochem. Photobiol.* **1987**, *46*, 1035–1042.

[7] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358, and references cited therein.

[8] N. Tyutulkov, J. Fabian, A. Mehlhorn, F. Dietz, A. Tadjer, *Polymethine Dyes: Structure and Properties*, St. Kliment Ohridsky University Press, Sofia, **1991**.

[9] a) K. Katoh, Y. Inagaki, R. Okazaki, *J. Am. Chem. Soc.* **1998**, *120*, 3623–3628; b) L. Lu, R. J. Lachicotte, T. L. Penner, D. G. Whitten, *J. Am. Chem. Soc.* **1999**, *121*, 8146–8156; c) S. Yao, U. Beginn, T. Gress, M. Lysetska, F. Würthner, *J. Am. Chem. Soc.* **2004**, *126*, 8336–8348.

[10] a) M. Kusser, H. Balli, *Helv. Chim. Acta* **1989**, *72*, 638–647; b) M. Dabrowska-Przybylska, J. Swiderski, W. Markocki, *Rocz. Chem.* **1969**, *43*, 1499–1511.

[11] a) L. Viteva, Y. Stefanovsky, T. Gospodova, M. R. Mazières, J. G. Wolf, *Tetrahedron Lett.* **2000**, *41*, 2541–2544; b) L. Viteva, T. Gospodova, Y. Stefanovsky, M. R. Mazières, J. G. Wolf, *Tetrahedron Lett.* **2001**, *42*, 7945–7949; c) L. Viteva, T. Gospodova, Y. Stefanovsky, K. Petrova, I. Timtcheva, M. R. Mazières, J. G. Wolf, *Eur. J. Org. Chem.* **2004**, 385–394.

[12] Z. Voitenko, M. R. Mazières, M. Sanchez, J. G. Wolf, *Tetrahedron* **2001**, *57*, 1059–1066.

[13] a) C. F. Shu, W. J. Tsai, A. K. Y. Jen, *Tetrahedron Lett.* **1996**, *37*, 7055–7058; b) C. F. Shu, W. J. Tsai, J. Y. Chen, A. K. Y. Jen, Y. Zhang, T. A. Chen, *Chem. Commun.* **1996**, 2279–2280; c) Y. C. Shu, Z. H. Gong, C. F. Shu, *Chem. Mater.* **1999**, *11*, 1628–1632; d) C. Zhang, A. S. Ren, F. Wang, J. Zhu, L. R. Dalton, *Chem. Mater.* **1999**, *11*, 1966–1968; e) F. Würthner, S. Yao, J. Schilling, R. Wortmann, M. Redi-Abshiro, E. Mecher, F. Gallego-Gomes, K. Meerholz, *J. Am. Chem. Soc.* **2001**, *123*, 2810–2824; f) A. J. Kay, A. D. Woolhouse, G. J. Gainsford, T. G. Haskell, T. H. Barnes, I. T. McKinnie, C. P. Wyss, *J. Mater. Chem.* **2001**, *11*, 996–1002; g) A. J. Kay, A. D. Woolhouse, G. J. Gainsford, T. J. Haskell, C. P. Wyss, S. M. Giffin, I. T. McKinnie, T. H. Barnes, *J. Mater. Chem.* **2001**, *11*, 2271–2281; h) A. J. Kay, A. D. Woolhouse, Y. Zhao, K. Clays, *J. Mater. Chem.* **2004**, *14*, 1321–1330.

[14] a) U. Lawrentz, W. Grahn, I. Dix, P. G. Jones, *Acta Crystallogr., Sect. C* **1999**, *55*, 446–450; b) U. Lawrentz, W. Grahn, K. Lukaszuk, C. Klein, R. Wortmann, A. Feldner, D. Scherer, *Chem. Eur. J.* **2002**, *8*, 1573–1590; c) C. F. Shu, Y. Ch. Shu, Z. H. Gong, *Chem. Mater.* **1998**, *10*, 3284–3286.

[15] a) L. Strekowski, M. Lipowska, G. Patonay, *Synth. Commun.* **1992**, *22*, 2593–2598; b) L. Strekowski, M. Lipowska, G. Patonay, *J. Org. Chem.* **1992**, *57*, 4578–4580; c) M. Lipowska, G. Patonay, L. Strekowski, *Synth. Commun.* **1993**, *23*, 3087–3094; d) N. Narayanan, L. Strekowski, M. Lipowska, G. Patonay, *J. Org. Chem.* **1995**, *60*, 2391–2395; e) L. Strekowski, T. Gorecki, J. C. Mason, H. Lee, G. Patonay, *Heterocycl. Commun.* **2001**, *7*, 117–122.

[16] J. Žemlička, Z. Arnold, *Collect. Czech. Chem. Commun.* **1961**, *26*, 2852–2864.

[17] P. W. Hickmott, *Tetrahedron* **1975**, *38*, 1975–2050.

[18] Y. L. Slominskii, I. D. Radchenko, C. V. Popov, A. I. Tolmachev, *Zh. Org. Kkim.* **1983**, *19*, 2134–2142.

[19] S. S. Ramos, P. F. Santos, L. V. Reis, P. Almeida, *Dyes Pigm.* **2002**, *53*, 143–152.

[20] a) M. R. Chedekel, D. E. Sharp, G. A. Jeffery, *Synth. Commun.* **1980**, *10*, 167–173; b) F. Babudri, G. Bartoli, F. Ciminale, S. Florio, *Tetrahedron Lett.* **1984**, *25*, 2047–2050; c) S. Florio, *Tetrahedron* **1984**, *4*, 4527–4533; d) F. Babudri, S. Florion, *Synthesis* **1986**, *8*, 638–640; e) M. Aresta, C. F. Nobile, *J. Chem. Soc., Dalton Trans.* **1976**, *13*, 1203–1207.

[21] S. Simova, *Magn. Reson. Chem.* **1998**, *36*, 505–510.

[22] a) J. Rodriguez, L. Canoira, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1393–1396; b) J. Rodriguez, L. Canoira, C. Calderon, M. Martinez-Ripoll, S. Blanco, *J. Chem. Soc., Perkin Trans. 2* **1986**, 199–203; c) J. Rodriguez, L. Canoira, F. Temporano, *J. Chem. Soc., Perkin Trans. 2* **1986**, 1193–1196.

[23] C. D. Gabbutt, J. D. Hepworth, B. M. Heron, S. M. Partington, D. A. Thomas, *Dyes Pigm.* **2001**, *49*, 65–74.

[24] E. Lippert, *Z. Elektrochem.* **1957**, *61*, 962–975.

[25] K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, *Justus Liebigs Ann. Chem.* **1963**, *661*, 1.

[26] B. K. Mishra, M. Kuanar, A. Mishra, G. B. Behera, *Bull. Chem. Soc. Jpn.* **1966**, *69*, 2581–2584.

[27] P. Nikolov, I. Timtcheva, *J. Photochem. Photobiol. A* **2000**, *131*, 23–26.

[28] C. Zander, K. H. Drexhage, *Adv. Photochem.* **1995**, *20*, 59–78.

[29] DENZO Data collection and processing software: Z. Otwinowski, W. Minor, *Methods in Enzymology*, vol. 276: *Macromolecular Crystallography*, part A, p. 307–326, **1997** (Eds.: C. W. Carter Jr, R. M. Sweet), Academic Press.

[30] R. Hooft, B. V. Nonius, COLLECT Data collection and processing user interface, Collect: data collection software, **1998**.

[31] SORTAV absorption correction software package: a) R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–37; b) R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426.

[32] G. M. Sheldrick, *SHELX-97*, *Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[33] ORTEP-3 for Windows: L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[34] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

[35] L. J. Farrugia, *WinGX – A Windows Program for Crystal Structure Analysis*, University of Glasgow, **1998**.

Received: February 12, 2007
Published Online: May 22, 2007

