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Synthesis of novel squaraine dyes and their intermediates

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Abstract

We investigate the reactions of mono-substituted squaraines with CH-acidic nucleophiles, heterocyclic methylene bases and thionating reagents. The reactions of mono-substituted squaraines with malononitrile, cyano- and nitroacetic esters, barbituric acid, 1,3-indanedione, NaHS and P_4S_{10} lead to ring-substituted mono-squaraines. These intermediates are useful for the synthesis of novel squaraine dyes with interesting photophysical properties.

Keywords: Dyes; Synthesis; Fluorescence; Squaraines

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1. Introduction

Squaric acid (**1a**) and its dialkyl esters, e.g. 3,4-dibutoxy-3-cyclobutene-1,2-dione (**1b**) are starting materials for the synthesis of the very popular class of long-wavelength squaraine dyes. This class of dyes is used not only as fluorescent probes and labels [1–3], but also as colouring agents for photoelectric conversion elements and photoelectrochemical batteries [4], in electrophotography [5], and optical data storage [6] that utilise the photophysical properties of these dyes.

Symmetrical squaraine dyes are synthesised by reaction of squaric acid with two equivalents of a quaternised methylene base such as 1,2,3,3-tetramethyl-3*H*-indolium iodide **2a** [7–10] (Scheme 1).

Generally, the reaction is carried out in a solvent mixture of 1-butanol and toluene or benzene and azeotropic removal of water in the absence [7] or presence [8,9] of quinoline as catalyst. The reaction is also known to proceed in 1-butanol–pyridine [10], 1-propanol–chlorobenzene [11] or in a mixture of acetic acid, pyridine and acetic anhydride [7].

Law and Bailey [12] and Terpetschnig and Lakowicz [13] proposed the dibutyl-squarate (**1b**) as the reactive intermediate in the synthesis of squaraine dyes.

Squaric acid **1a** or its esters (e.g. **1b**) react with the Fisher base (1,3,3-trimethyl-2-methyleneindoline) **3** or its salts **2a** to symmetrical squaraine dyes **4** [14]. Other CH active compounds such as the quaternised 2-methylbenzothiazole (**2b**), 2-methylquinoline (**2c**), and their derivatives [7,9,15] also react in the same way.

Unsymmetrical squaraine dyes can be synthesised from squaric esters via a multi-step procedure. In the first step, the squaric ester **1b** reacts with an equimolar amount of **3** or quaternised methylene base (**2a–2c**) in ethanol to the mono-squaraines **5a–5c**. Triethylamine (TEA) is used as a catalyst. The hydrolysis of **5a–5c** → **6a–6c** and subsequent reaction of the intermediates **6a–6c** with a second methylene base (**2a–2c**) leads to the corresponding unsymmetrical squaraine dye **7** (Scheme 2) [8,13,15]. While the first substitution step

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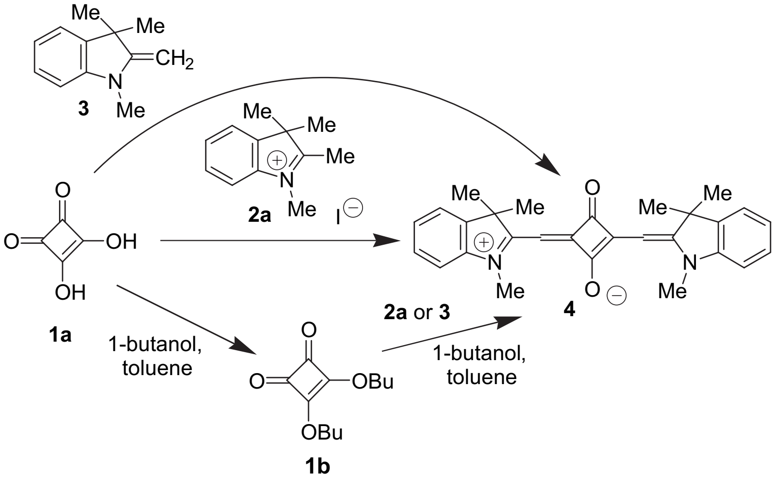


Scheme 1.

proceeds fast at room temperature or at slight heating, the second step requires more vigorous conditions such as heating in butanol–toluene for several hours.

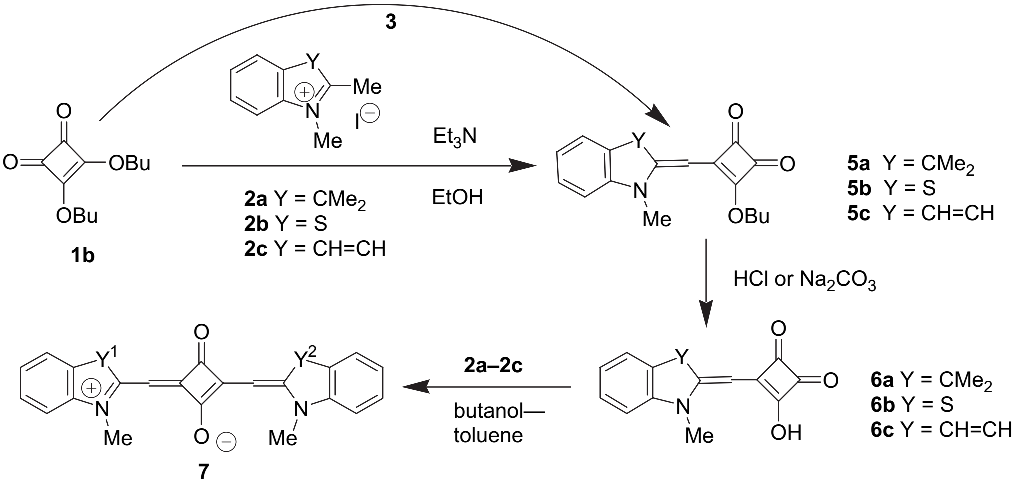
While the reactivity of the quaternised methylene bases **2a**–**2c** towards dibutyl-squarate **1b** seems to be similar, the benzothiazole and quinaldine derivatives **2b**, **2c** do require heating to initiate the reaction.

There are numerous publications on the synthesis of conventional squaraine dyes [1–15], but only a few describe the synthesis of mono-squaraine intermediates [1,13–15] and even less describe squaraine dyes containing a derivatised squaraine moiety [4]. This paper investigates the substitution reactions of mono-squarates **5a**–**5c** with various CH-acidic nucleophiles such as malononitrile, cyano- and nitroacetic esters, barbituric acid, 1,3-indanedione, NH-acidic cyanamide, and thionating reagents. Further, we describe the reaction of these novel intermediates with common heterocyclic methylene bases to ring-modified symmetrical and unsymmetrical squaraine dyes.

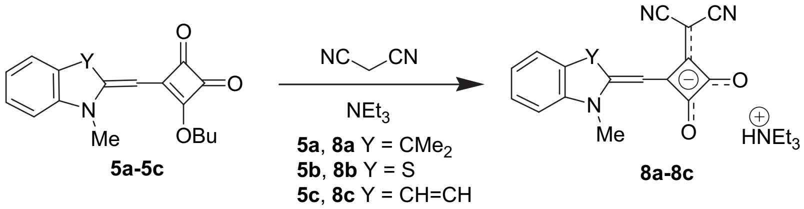
2. Results and discussion

*2.1. Reaction of mono-squarates **5a**–**5c** with CH and NH-acidic compounds, and thionating reagents*

The reaction of mono-squarates **5a** with malononitrile in the presence of TEA was completed at room temperature within 2 h yielding the corresponding dicyanomethylene derivative **8a** at near quantitative amounts (Scheme 3) while **8b** and **8c** were obtained from **5b** and **5c** at lower yields. The structures of **8a**–**8c** were confirmed by ^{1}H NMR. The methine hydrogen signals for **8a**–**8c** were found at 5.73–5.92 ppm (DMSO-d_6) while for **5a**–**5c** they were located between 5.28 and



Scheme 2.



Scheme 3.

5.52 ppm. In addition, the structure of **8a** was confirmed by X-ray analysis (Fig. 1). The data suggest that the negative charge is delocalised within the squaric moiety.

Nitroacetic and cyanoacetic esters appeared to be less reactive than malononitrile. Heating of squarate **5a** under reflux with nitroacetic or cyanoacetic ester in alcohol and TEA gave the corresponding derivatives **9** or **10**, respectively (Scheme 4). The cyclic methylene bases such as barbituric acid and 1,3-indanedione were also found to react and their products **11** and **12** were isolated with low (12%) and satisfactory yield (39%), respectively. Mono-squaraine **5a** was reacted with cyanamide to give the salt **13**. While compounds **8a–8c**, **10**, **11**, and **13** contain a triethylammonium counter ion, **9** and **12** were isolated in their protonated forms. The obtained spectroscopic data (FAB-MS, ^{1}H NMR, IR) and the elemental analysis were in good agreement with the proposed structures for **9–13**. The methine hydrogen signals in ^{1}H NMR spectra were found at 5.85 ppm (for **9**), 6.39 ppm (for **11**) and 7.38 ppm (for **12**). The methine hydrogen signal of **13** split into the two signals at 6.21 and 5.55 ppm with total integral of one proton. Similarly, the methine hydrogen of **10** appears as three signals at 7.00 ppm, 6.19 ppm and 6.02 ppm. This effect can be attributed to the existence of different isomers in compounds **10** and **12**. The OH hydrogen signal could not be observed in the spectra of **9** and **12**.

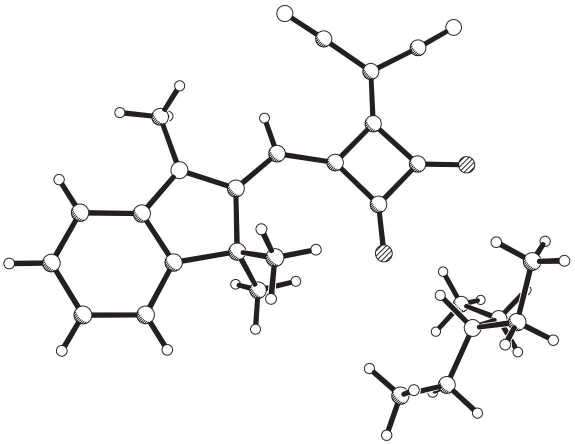


Fig. 1. Structure of **8a** as determined by the X-ray analysis.

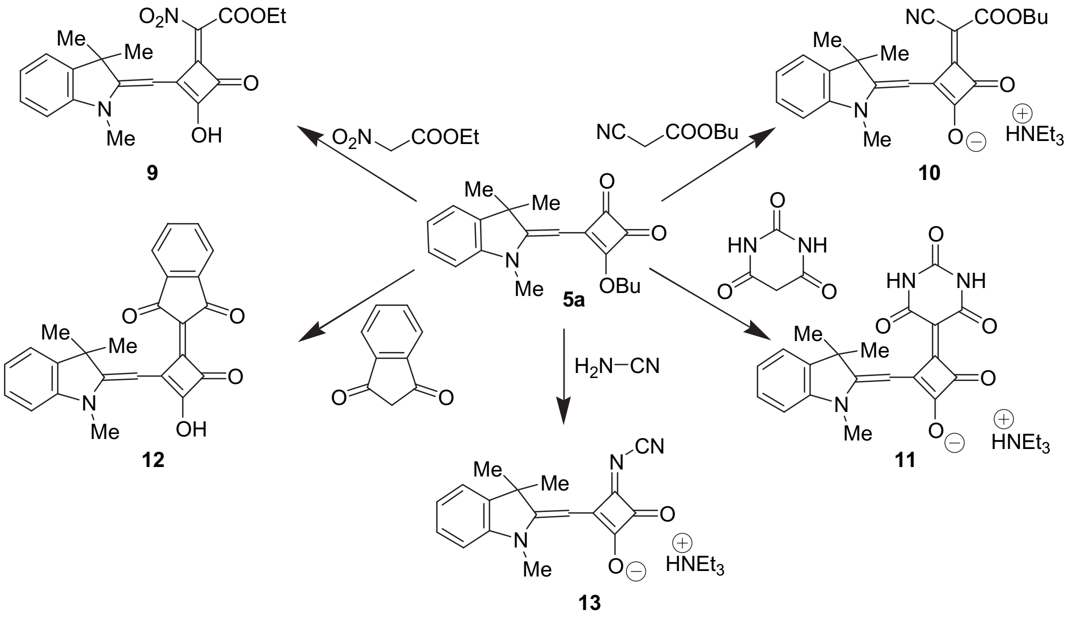
Squarate **5a** was found to react with P_4S_{10} in pyridine at room temperature to yield product **14** as shown in Scheme 5. Refluxing **5a** with NaHS in absolute ethanol for 4 h led to substitution of the butoxy group and yielding the thio-squaraine derivative **15**. The structures of **14** and **15** were confirmed by ^{1}H NMR and IR data. In addition, the structure of **14** was confirmed by X-ray analysis (Fig. 2). The methine CH signals in the ^{1}H NMR spectrum measured in DMSO-d_6 were found at 5.40 ppm for **14** and 5.82 ppm for **15**. Quantum chemical simulations carried out by the AM1 method [16] indicate that the negative charge is delocalised between sulphur and oxygen atoms (Scheme 5).

2.2. Reactions of ring-substituted mono-squarates with methylene bases

We also found that neither **1a** nor **1b** reacted with oxazole-based heterocycles such as 2,3-dimethyl-1,3-benzoxazol-3-ium iodide (**2d**) or 2,3-dimethyl-5-(4-phenylphenyl)-1,3-oxazol-3-ium iodide (**2e**). Nevertheless, compound **5a** readily reacted with these oxazoles in 1-butanol–toluene to give squaraines **16** and **17** with 8% and 15% yields, respectively (Scheme 6). The dicyanomethylene derivatives **8a** and **8b** were found to have even higher reactivity as compared to **5a**. Thus, dyes **18**, **19** and **20** were obtained with 32%, 27% and 45% yields, respectively. Mono-squaraines **8a** and **8b** also reacted with quaternised heterocyclic compounds **2a** and **2b** to squaraines **21–23**.

Cyanoacetic ester, barbituric acid and indanedione derivatives **10–12** readily reacted in 1-butanol–toluene under reflux to squaraine dyes **24–26** with high yields while **13** gave **27** with low yield (Scheme 7).

The monothio derivative **15** reacted with both, the indolenine **2a** or the benzothiazole **2b** by heating in a 1-butanol–toluene mixture and the monothio-squaraines **28** and **29** were isolated (Scheme 8). Thio-squarate **14** on the other hand yielded only a dioxo-squaraine **4**. Surprisingly, no reaction occurred between **9** and indolenine **2a**. It is worth mentioning that small amounts of the dioxo-squaraine **4** were isolated in all reactions of indolenine **2a** with **8a**, **9–13** and **15** despite the fact that the last ones did not contain any impurity of **5a**.



Scheme 4.

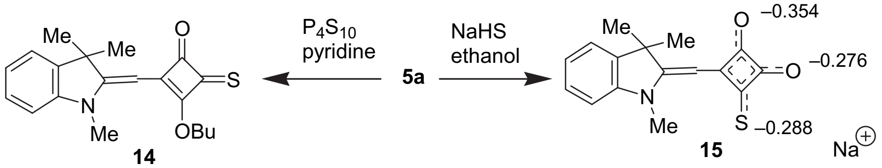
The structure elucidation of the synthesised squaraine dyes was accomplished using ^{1}H NMR, IR and mass spectroscopic tools.

The unsymmetrically substituted squaraines **16–19**, **20**, **23** and **29** show splitting of methine proton signals in the ^{1}H NMR spectra. A closer look at the ^{1}H NMR of **24** and **26** further suggests that the CH (methine) protons form intramolecular hydrogen-bonds with carbonyl-oxygens of the COOBu and indanedione moieties. This is evidenced by a low field shift of the relevant methine proton signal. Thus, the signal of the hydrogen-bonded methine proton of **24** appears at lower field (7.24 ppm) while that not involved in H-bonding can be found at a much higher field (6.64 ppm). Compound **24** has an unsymmetrical structure and only one CH-hydrogen is involved to form an intramolecular H-bond. As a result, **24** not only shows different shifts for the CH signals but also a splitting for all methyl hydrogens in the 1 and 3 positions of the two indolenine moieties. Both CH signals for **26** are low field shifted to 7.59 ppm indicating hydrogen-bonding. The methine-signals of the dicyanomethylene derivative **21** can be found at 6.30 ppm.

Dioxo-squaraine dyes are known to have strong absorption bands in the IR spectrum around 1580–1605 cm^{-1}, indicating a strong bond-delocalization within the four-membered ring system. There is no evidence of carbonyl absorption in the region 1800–1650 cm^{-1} [12–14,17] in dioxo-derivatives, though a weak absorption band appears at 1744 cm^{-1} in **16** and 1736 cm^{-1} for **17**. Noticeably, in dyes **18–23**, **27**, and **28** the intensity of the pseudoaromatic squarate absorption at 1580–1605 cm^{-1} decreases while a new absorption band between 1720 and 1750 cm^{-1} appears. This new band can be attributed to the substitution of the oxygen in the squaraine ring by N–CN, C(CN)$_2$ or S which alters the electron distribution in the ring and renders the C–O bond to appear more like a C=O bond. In addition, the carbonyl-containing substituents (cyanoacetic ester, barbituric acid, and indanedione) show the characteristic carbonyl absorption of these groups.

2.3. Spectral properties of squaraine dyes

The spectral data for the synthesised dyes measured in ethanol and chloroform are given in Tables 1 and 2. When compared to the mono-squaraines **5a–5c**, **8a–8c**, **9–15**, dyes **16–29** exhibit more intense absorption spectra. In addition, the nature of the substituents in



Scheme 5.

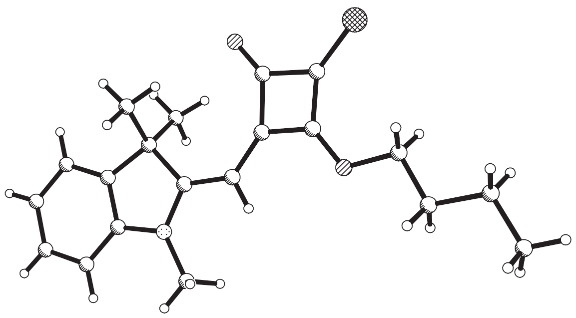


Fig. 2. Structure of **14** as determined by the X-ray analysis.

the squaric ring has strong influence on the spectral properties. All the substitutions of the squaraine ring oxygen by $C(CN)_2$, C(CN)COOR, N–CN, S, etc. are causing red-shifted absorption and emission spectra while the substitution of the indolenine end groups by aryloxazole or benzoxazole moieties results in shorter absorption and emission maxima. The squaraine dyes are suitable for excitation by a red diode laser. Unlike **4**, **16**, **17**, **27**, dyes **18**–**26**, **28**, and **29** exhibit additional absorption bands in the 380–460 nm region with extinction coefficients of about 16–40,000 $M^{-1}\,cm^{-1}$, which makes these dyes also suitable for use with the blue (405 nm) diode laser excitation. A more detailed investigation of these squaraine dyes for use in biological application will follow in a separate paper.

3. Experimental

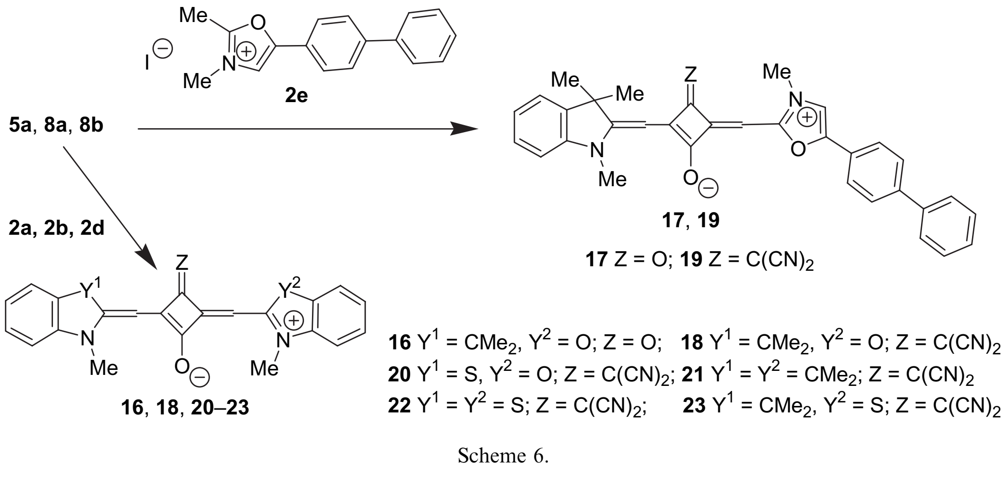
3.1. General

The progress of the chemical reactions and the purity of products were monitored by TLC (Sorbfil TLC Plates, Merck). IR spectra were recorded using KBr pellets on a Specord M80 spectrophotometer. ^1H NMR spectra were measured on a Varian VXP-300 (300 MHz) and Varian Mercury-VX-200 (200 MHz) spectrometers in DMSO-d_6 using TMS as an internal standard. FAB mass spectra were recorded on a SELMI MI-1201E instrument using 3-nitrobenzylalcohol (NBA) or glycerol as a matrix. The crystals for X-ray diffraction analyses were grown in ethanol by slow solvent evaporation (**16**) or crystallisation from 1-propanol (**24**). The X-ray diffraction experiment was carried out using a four-circle automated diffractometer from Siemens P3/PC equipped with graphite monochromator. A MoKα source and the $2\theta/\theta$ scan technique was used for these experiments. Electron absorption spectra and the extinction coefficients were measured in a standard 1 cm quartz cuvette on a LOMO SF-26 spectrophotometer. Fluorescence spectra were taken on a Varian Cary Eclipse spectrofluorometer. Spectral correction was used.

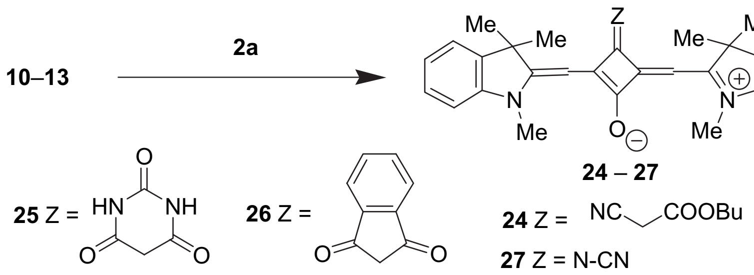
3.2. Synthesis

3.2.1. Preparation of mono-squaraines: general procedure

*3.2.1.1. Triethylammonium 3-dicyanomethylene-4-oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-1-cyclobuten-1-olate (**8a**).* 1 ml (7.14 mmol) of TEA was added dropwise to a mixture of 2 g (6.15 mmol) of **5a**, 440 mg (6.66 mmol) of malononitrile in 35 ml of ethanol and stirred for 2 h at room temperature. Afterwards, the solvent was removed under reduced pressure. The raw product was column purified (Silica gel 60, 0–2% methanol–chloroform) to give (2.52 g, 98%) **8a** as orange crystals, mp 153 °C; Analysis: N, 13.44 $C_{25}H_{30}N_4O_2$ requires N, 13.39%; δ_H (200 MHz, DMSO-d_6) 8.74 (1H, br s, NH^+), 7.29 (1H, d, 7.5 Hz, arom H), 7.20 (1H, t, 7.5 Hz, arom H), 6.95 (1H, d, 8.3 Hz, arom H), 6.93 (1H, t, 7.8 Hz, arom H), 5.92 (1H, s, CH), 3.25 (3H, s, NCH_3), 3.11 (6H, q, 7.3, 14.6 Hz, N(CH_2CH$_3$)$_3$), 1.59 (6H, s, C(CH_3)$_2$), 1.20



Scheme 6.



Scheme 7.

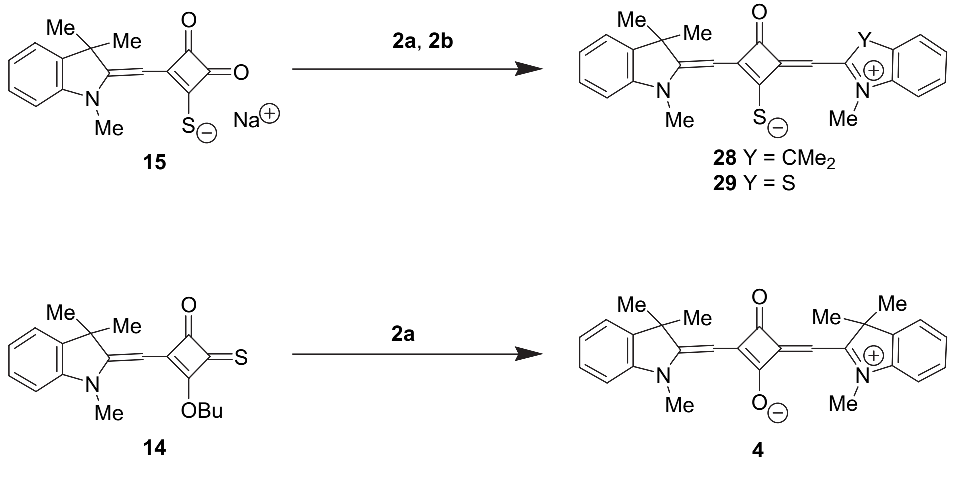
(9H, t, 7.3 Hz, N(CH$_2$C*H*$_3$)$_3$); FAB-MS (glycerol) *m*/*z* 419 (MH$^+$); IR (KBr) 2232 (CN), 2208 (CN), 1744 (CO), 1684, 1652 cm^{-1}.

*3.2.1.2. Triethylammonium 3-dicyanomethylene-2-(3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidenmethyl)-4-oxo-1-cyclobuten-1-olate (**8b**).* This compound was synthesised analogous to **8a** by stirring at 50 °C of **5b**, TEA and malononitrile for 2 h. Yield: 69%; Analysis: N, 13.55; S, 7.96 $C_{22}H_{24}N_4O_2S$ requires N, 13.71; S, 7.85%; δ_H (200 MHz, DMSO-*d*$_6$) 8.82 (1H, br s, N*H*$^+$), 7.61 (1H, d, 8.0 Hz, arom H), 7.29 (1H, td, 7.7, 1.3 Hz, arom H), 7.23 (1H, dd, 8.0, 0.9 Hz, arom H), 7.06 (1H, td, 7.1, 1.6 Hz, arom H), 5.88 (1H, s, C*H*), 3.43 (3H, s, NC*H*$_3$), 3.10 (6H, q, 7.3, 14.6 Hz, N(C*H*$_2$CH$_3$)$_3$), 1.20 (9H, t, 7.4 Hz, N(CH$_2$C*H*$_3$)$_3$); IR (KBr) 2228 (CN), 1748 (CO), 1652 cm^{-1}.

*3.2.1.3. Triethylammonium 3-dicyanomethylene-2-(1-methyl-1,2-dihydro-2-quinolinylidenmethyl)-4-oxo-1-cyclobuten-1-olate (**8c**).* This compound was synthesised analogous to **8a** by stirring at room temperature of **5c**, TEA and malononitrile for 2 h. Yield: 42%, mp 142 °C; Analysis: N, 13.93; $C_{24}H_{26}N_4O_2$ requires N, 13.92%; δ_H (200 MHz, DMSO-*d*$_6$) 8.54 (1H, d, 9.5 Hz, arom H), 7.50–7.34 (3H, m, arom H), 7.26 (1H, d, 9.6 Hz, arom H), 7.10 (1H, t, 6.7 Hz, arom H), 5.73 (1H, br s, C*H*), 3.47 (3H, s, NC*H*$_3$), 3.10 (6H, q, 7.3, 14.6 Hz, N(C*H*$_2$CH$_3$)$_3$), 1.19 (9H, t, 7.2 Hz, N(CH$_2$C*H*$_3$)$_3$); IR (KBr) 2220 (CN), 2200 (CN), 1732 (CO), 1624 cm^{-1}.

*3.2.1.4. Ethyl 2-[3-hydroxy-4-oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-2-cyclobutenyliden]-2-nitroacetate (**9**).* This compound was synthesised analogous to **8a** by refluxing of **5a**, TEA and ethyl 2-nitroacetate for 10 h. Yield: 21%, mp 221 °C; Analysis: N, 7.03; $C_{20}H_{20}N_2O_6$ requires N, 7.29%; δ_H (200 MHz, DMSO-*d*$_6$) 7.34 (1H, d, 7.3 Hz, arom H), 7.23 (1H, t, 7.7 Hz, arom H), 7.02 (1H, d, 8.5 Hz, arom H), 6.94 (1H, t, 6.6 Hz, arom H), 5.82 (1H, s, C*H*), 4.06 (2H, q, 6.8, 13.9 Hz, COOC*H*$_2$CH$_3$), 3.24 (3H, s, NC*H*$_3$), 1.59 (6H, s, (C*H*$_3$)$_2$), 1.16 (3H, t, 7.2 Hz, COOCH$_2$C*H*$_3$).

*3.2.1.5. Triethylammonium 3-butyloxycarbonyl(cyano)-methylene-4-oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-1-cyclobuten-1-olate (**10**).* This compound was synthesised analogous to **8a** by stirring at room temperature for 4 h and at 50 °C for 0.5 h of **5a**, TEA and butyl 2-cyanoacetate in 1-butanol. Yield: 42%; Analysis: N, 13.93; $C_{29}H_{39}N_3O_4$ requires N, 8.51%; δ_H (200 MHz, DMSO-*d*$_6$) 8.84 (1H, br s,



Scheme 8.

Table 1
Spectral properties and extinction coefficients of mono-squaric acid precursors in ethanol

Compound	λ_{max}(abs) [nm]	ε [M^{-1} cm^{-1}]
5a	425	66,100
5b	442	82,000
5c	465	62,600
8a	460	50,100
8b	481	63,200
8c	515	n.d.
9	475	n.d.
10	462	37,600
11	457	33,500
12	492	26,500
13	436	42,000
14	500	116,100
15	446	47,300

NH^+), 7.27 (1H, d, 7.3 Hz, arom H), 7.18 (1H, t, 7.5 Hz, arom H), 6.91 (1H, d, 7.3 Hz, arom H), 7.00 (0.55 H, br s, C*H*), 6.88 (1H, t, 7.4 Hz, arom H), 6.19 (0.25 H, br s, C*H*), 6.02 (0.20 H, br s, C*H*), 4.00 (2H, t, 6.1 Hz, $COOCH_2$ (Bu)), 3.25 (3H, s, NCH_3), 3.10 (6H, q, 7.4, 14.6 Hz, $N(CH_2CH_3)_3$), 1.57 (6H, s, $(CH_3)_2$), 1.64–1.26 (4H, m), 1.17 (9H, t, 7.3 Hz, $N(CH_2CH_3)_3$), 0.90 (3H, t, 7.2 Hz, $COO(CH_2)_3CH_3$); IR (KBr) 2212 (CN), 1748 (CO), 1684, 1652 cm^{-1}.

Table 2
Spectral properties and extinction coefficients of squaraine dyes in chloroform

Compound	λ_{max}(abs) [nm]	ε [M^{-1} cm^{-1}]	λ_{max}(em) [nm]
4	635	219,000	643
16	608	214,000	619
17	606	112,000	625
18	655	177,000	673
	390	39,000	
19	648	104,000	n.d.
	385	43,000	
20	664	n.d.	682
	395		
21	684	196,000	700
	380	38,000	
22	703	n.d.	723
	375		
23	691	159,000	708
	380	34,000	
24	691	134,000	708
	393	32,000	
25	644	103,000[a]	665
	430	27,000	
26	675	128,000	699
	460	42,000	
27	655	n.d.	665
28	650	100,000	663
	367	21,000	
29	661	87,000	676
	370	16,000	

[a] Measured in DMF.

*3.2.1.6. Triethylammonium 4-oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-3-(2,4,6-trioxohexahydro-5-pyrimidinyliden)-1-cyclobuten-1-olate (**11**).* This compound was synthesised as described for **8a** by refluxing in ethanol of **5a**, TEA and barbituric acid for 15 h. Yield: 12%, mp >300 °C; Analysis: N, 11.48 $C_{26}H_{32}N_4O_5$ requires N, 11.66%; δ_H (200 MHz, DMSO-d_6) 9.66 (2H, s, N*H*), 7.32 (1H, d, 7.1 Hz, arom H), 7.22 (1H, td, 6.7, 1.1 Hz, arom H), 6.97 (1H, d, 7.3 Hz, arom H), 6.95 (H, t, 7.1 Hz, arom H), 6.53–6.26 (1H, br s, C*H*), 3.29 (3H, s, NCH_3), 3.00 (6H, q, 7.3, 14.4 Hz, $N(CH_2CH_3)_3$), 1.57 (6H, s, $(CH_3)_2$), 1.15 (9H, t, 7.2 Hz, $N(CH_2CH_3)_3$); IR (KBr) 1760 (CO), 1700 (CO), 1652, 1600 cm^{-1}.

*3.2.1.7. 2-[3-Hydroxy-4-oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-2-cyclobutenyliden]-1,3-indanedione (**12**).* This compound was synthesised analogous to **8a** by refluxing in ethanol of **5a**, TEA and 1,3-indanedione for 4 h. Yield: 39%; mp >300 °C; Analysis: N, 3.49 $C_{25}H_{19}NO_4$ requires N, 3.52%; δ_H (300 MHz, DMSO-d_6) 7.47 (4H, m, arom H (indanedione)), 7.38 (1H, br s, C*H*), 7.34 (1H, d, 7.5 Hz, arom H), 7.23 (1H, t, 7.6 Hz, arom H), 7.01 (1H, d, 7.3 Hz, arom H), 6.95 (1H, t, 7.3 Hz, arom H), 3.43 (3H, s, NCH_3), 1.60 (6H, s, $(CH_3)_2$); IR (KBr) 1748 (CO), 1668, 1652, 1616 cm^{-1}.

*3.2.1.8. Triethylammonium 3-cyanoimino-4-oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-1-cyclobuten-1-olate (**13**).* This compound was synthesised analogous to **8a** by refluxing in ethanol of **5a**, TEA and cyanamide for 12 h. Oiled yellow solid was obtained. Yield: 78%; Analysis: N, 14,32 $C_{23}H_{30}N_4O_2$ requires N, 14.20%; δ_H (300 MHz, DMSO-d_6) 8.88 (1H, br s, NH^+), 7.31 (1H, d, 7.4 Hz, arom H), 7.20 (1H, t, 7.8 Hz, arom H), 6.99 (1H, d, 7.7 Hz, arom H), 6.91 (1H, t, 7.3 Hz, arom H), 6.21 (0.5H, br s, C*H*), 5.55 (0.5H, br s, C*H*), 3.25 (3H, s, NCH_3), 3.10 (6H, $N(CH_2CH_3)_3$, m), 1.56 (6H, s, $(CH_3)_2$), 1.18 (9H, t, 7.3 Hz, $N(CH_2CH_3)_3$); FAB-MS (NBA) *m/z* 394 ($M^{+\cdot}$), 395 (MH^+); IR (thin film) 2288 (CN), 2184 (CN), 1756 (CO), 1664, 1616 cm^{-1}.

*3.2.1.9. 3-Butoxy-4-thioxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-2-cyclobuten-1-one (**14**).* 500 mg (1.54 mmol) of **5a** was dissolved in 10 ml of pyridine and added 700 mg of P_4S_{10}. The colour of the solution darkened during the reaction and an intense red solution was obtained. The mixture was stirred for another 6.5 h at room temperature, diluted by adding 20 ml of water, extracted with dichloromethane. The dichloromethane was removed under reduced pressure and the residue was purified by a column chromatography (Silica gel 60, dichloromethane) to give **14** (220 mg, 42%), mp 134 °C; Analysis: N, 4.12; S, 9.64 $C_{20}H_{23}NO_2S$ requires N, 4.10; S, 9.39%; δ_H (200 MHz, DMSO-d_6) 7.52 (1H, d, 7.3 Hz, arom H), 7.45–7.29 (2H, m, arom H), 7.29–7.14 (1H, m, arom H), 5.40 (1H, s, C*H*), 5.18 (2H, t, 6.6 Hz, OCH_2), 3.55 (3H, s, NCH_3), 1.95–1.70 (2H, m, CH_2), 1.59 (6H, (CH_3)$_2$, s), 1.55–1.31 (2H, m, CH_2), 0.95 (3H, t, 7.3 Hz, CH_3); FAB-MS (NBA) *m*/*z* 342 (MH^+); IR (KBr) 1752 (CO), 1616, 1584 cm^{-1}.

*3.2.1.10. Sodium 3,4-dioxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-1-cyclobutene-1-thiolate (**15**).* A mixture of 500 mg (1.54 mmol) of **5a** and 250 mg (4.46 mmol) of NaHS was refluxed with stirring for 4 h in 20 ml of absolute ethanol. The reaction mixture was allowed to cool in a refrigerator and the formed orange-yellow crystals were collected by filtration, washed and recrystallised from ethanol to yield (250 mg, 53%) **15**, mp 264 °C (dec); Analysis: N, 4.41; S, 10.60 $C_{16}H_{14}NNaO_2S$ requires N, 4.56; S, 10.43%; δ_H (200 MHz, DMSO-d_6) 7.28 (1H, d, 7.5 Hz, arom H), 7.19 (1H, td, 7.5, 1.2 Hz, arom H), 6.94 (1H, d, 7.9 Hz, arom H), 6.89 (1H, t, 7.4 Hz, arom H), 5.82 (1H, s, C*H*), 3.27 (3H, s, NCH_3), 1.57 (6H, s, (CH_3)$_2$); FAB-MS (glycerol) *m*/*z* 308 (MH^+), 330 (MNa^+); IR (KBr) 1724 (CO), 1664, 1616 cm^{-1}.

3.2.2. Preparation of squaraine dyes: general procedure

*3.2.2.1. 2-(3-Methyl-2,3-dihydro-1,3-benzoxazol-2-ylidenmethyl)-3-oxo-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**16**).* 150 mg (0.46 mmol) of **5a** and 130 mg (0.47 mmol) of **2d** were heated under reflux in a mixture of 18 ml of a 1-butanol–toluene mixture (1:1 v/v) with a Dean-Stark trap for 8 h. The solvent was removed under reduced pressure by a rotary evaporator. The residue was purified by a column chromatography (Silica gel 60, 0–2% methanol–chloroform) to give product **16** (14 mg, 8%) as the dark violet crystals, R_f 0.56 (Sorbfil, chloroform–methanol, 10:1); Analysis: N, 6.94 $C_{25}H_{22}N_2O_3$ requires N, 7.03%; δ_H (300 MHz, DMSO-d_6) 7.69 (1H, d, 8.1 Hz, arom H), 7.64 (1H, d, 7.7 Hz, arom H), 7.46 (1H, td, 7.6, 0.9 Hz, arom H), 7.43 (1H, d, 7.3 Hz, arom H), 7.38 (1H, td, 7.9, 1.0 Hz, arom H), 7.29 (1H, t, 7.9 Hz, arom H), 7.17 (1H, d, 8.1 Hz, arom H), 7.05 (1H, t, 7.4 Hz, arom H), 5.54 (1H, s, C*H*), 5.53 (1H, s, C*H*), 3.77 (3H, s, NCH_3), 3.44 (3H, s, NCH_3), 1.66 (6H, s, (CH_3)$_2$); FAB-MS (glycerol) *m*/*z* 398 ($M^{+\cdot}$), 399 (MH^+); IR (KBr) 1744 (w), 1576 cm^{-1}.

*3.2.2.2. 2-[3-Methyl-5-(4-phenylphenyl)-2,3-dihydro-1,3-oxazol-2-ylidenmethyl]-3-oxo-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**17**).* The title dye was prepared as described for compound **16** from **5a** and **2e**. Yield: 15%; R_f 0.50, (Sorbfil, chloroform–methanol, 10:1); Analysis: N, 5.45 $C_{33}H_{28}N_2O_3$ requires N, 5.60%; δ_H (200 MHz, DMSO-d_6) 8.06 (2H, d, 8.4 Hz, arom H), 7.87 (2H, d, 8.4 Hz, arom H), 7.78 (2H, d, 8.0 Hz, arom H), 7.69 (1H, d, 2.5 Hz, C*H* (oxazole)), 7.51 (2H, t, 7.3 Hz, arom H), 7.44 (1H, t, 6.6 Hz, arom H), 7.34 (1H, d, 7.3 Hz, arom H), 7.22 (1H, t, 7.6 Hz, arom H), 7.02 (1H, d, 8.2 Hz, arom H), 6.95 (1H, t, 7.4 Hz, arom H), 5.55 (1H, s, C*H*), 5.44 (1H, s, C*H*), 3.73 (3H, s, NCH_3), 3.33 (3H, s, NCH_3), 1.66 (6H, s, (CH_3)$_2$); FAB-MS (NBA) *m*/*z* 500 ($M^{+\cdot}$), 501 (MH^+); IR (KBr) 1736 (w), 1576 cm^{-1}.

*3.2.2.3. 3-Dicyanomethylene-2-(3-methyl-2,3-dihydro-1,3-benzoxazol-2-ylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**18**).* The title dye was prepared similar to compound **16** from **8a** and **2d**. Yield: 32%; R_f 0.32 (Sorbfil, chloroform–methanol, 50:1); Analysis: N, 12.41 $C_{28}H_{22}N_4O_2$ requires N, 12.55%; δ_H (200 MHz, DMSO-d_6) 7.81 (1H, dd, 7.0, 1.7 Hz, arom H), 7.74 (1H, dd, 6.7, 1.6 Hz, arom H), 7.55 (1H, td, 7.4, 1.5 Hz, arom H), 7.47 (1H, dd, 7.5, 0.9 Hz, arom H), 7.46 (1H, td, 7.5, 1.5 Hz, arom H), 7.34 (1H, td, 7.6, 0.9 Hz, arom H), 7.24 (1H, d, 7.5 Hz, arom H), 7.14 (1H, td, 7.2, 1.0 Hz, arom H), 6.09 (1H, s, C*H*), 5.87 (1H, s, C*H*), 3.77 (3H, s, NCH_3), 3.49 (3H, s, NCH_3), 1.66 (6H, s, (CH_3)$_2$); FAB-MS (NBA) *m*/*z* 446 ($M^{+\cdot}$), 447 (MH^+); IR (KBr) 2224 (CN), 2200 (CN), 1728, 1632 cm^{-1}.

*3.2.2.4. 3-Dicyanomethylene-2-[3-methyl-5-(4-phenylphenyl)-2,3-dihydro-1,3-oxazol-2-ylidenmethyl]-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**19**).* The title dye was prepared in a manner similar to **16** from **8a** and 2,3-dimethyl-5-(4-phenylphenyl)-1,3-oxazol-3-ium iodide (**2e**). Yield: 27%; R_f 0.72 (Sorbfil, chloroform–methanol, 40:1); Analysis: N, 10.11 $C_{36}H_{28}N_4O_2$ requires N, 10.21%; δ_H (200 MHz, DMSO-d_6) 8.41 (1H, d, 2.5 Hz, C*H* (oxazole)), 8.01 (2H, d, 8.3 Hz, arom H), 7.91 (2H, d, 8.5 Hz, arom H), 7.80 (2H, d, 7.6 Hz, arom H), 7.51 (2H, t, 7.6 Hz, arom H), 7.42 (2H, m, arom H), 7.28 (1H, t, 7.8 Hz, arom H), 7.11 (1H, d, 7.8 Hz, arom H), 7.04 (1H, t, 7.3 Hz, arom H), 5.92 (1H, broad s, C*H*), 5.84 (1H, s, C*H*), 3.71 (3H, s, NCH_3), 3.32 (3H, s, NCH_3), 1.66 (6H, s, (CH_3)$_2$); FAB-MS (NBA) *m*/*z* 548 ($M^{+\cdot}$), 549 (MH^+).

*3.2.2.5. 3-Dicyanomethylene-4-(3-methyl-1,3-benzoxazol-3-ium-2-ylmethylene)-2-(3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidenmethyl)-1-cyclobuten-1-olate (**20**).* The title dye was prepared similar to compound **16** from **8b** and **2d**. Yield: 45%; R_f 0.47 (Sorbfil, chloroform–methanol, 50:1); Analysis: N, 12.98; S, 7.23 $C_{25}H_{16}N_4O_2S$ requires N, 12.84; S, 7.35%; δ_H (200 MHz, DMSO-d_6) 7.92 (1H, d, 7.5 Hz, arom H), 7.70–7.54 (3H, m, arom H), 7.51 (1H, d, 7.3 Hz, arom H), 7.44 (1H, d, 6.2 Hz, arom H), 7.41–7.25 (2H, m, arom H), 6.14 (1H, s, C*H*), 5.52 (1H, s, C*H*), 3.72 (3H, s, NC*H*$_3$), 3.64 (3H, s, NC*H*$_3$); FAB-MS (NBA) *m*/*z* 436 ($M^{+\cdot}$), 437 (MH^+); IR (KBr) 2224 (CN), 2200 (CN), 1732, 1636 cm^{-1}.

*3.2.2.6. 3-Dicyanomethylene-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**21**).* The title dye was synthesised in a manner similar to **16**, vide supra, from **8a** and **2a**. Yield: 46%; R_f 0.47 (Sorbfil, chloroform–methanol, 50:1); Analysis: N, 11.73 $C_{31}H_{28}N_4O$ requires N, 11.86%; δ_H (200 MHz, DMSO-d_6) 7.54 (2H, d, 7.4 Hz, arom H), 7.47–7.37 (4H, m, arom H), 7.32–7.18 (2H, m, arom H), 6.30 (2H, s, C*H*), 3.61 (6H, s, NC*H*$_3$), 1.68 (12H, s, (C*H*$_3$)$_2$); FAB-MS (NBA) *m*/*z* 472 ($M^{+\cdot}$), 473 (MH^+); IR (KBr) 2228 (CN), 2208 (CN), 1724, 1624, 1604 cm^{-1}.

*3.2.2.7. 3-Dicyanomethylene-4-[(E)-1-(3-methyl-1,3-benzothiazol-3-ium-2-yl)methylidene]-2-(3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidenmethyl)-1-cyclobuten-1-olate (**22**).* The title dye was synthesised in a manner similar to **16**, vide supra, from **8b** and **2b**. Yield: 34%; R_f 0.52 (Sorbfil, chloroform–methanol, 50:1); Analysis: N, 12.53; S, 14.00 $C_{25}H_{16}N_4OS_2$ requires N, 12.38; S, 14.17%; δ_H (300 MHz, DMSO-d_6) 7.90 (2H, d, 7.8 Hz, arom H), 7.61 (2H, d, 8.1 Hz, arom H), 7.51 (2H, t, 7.7 Hz, arom H), 7.34 (2H, t, 7.5 Hz, arom H), 6.18 (2H, s, C*H*), 3.73 (6H, s, NC*H*$_3$); FAB-MS (NBA) *m*/*z* 452 ($M^{+\cdot}$), 453 (MH^+); IR (KBr) 2228 (CN), 2200 (CN), 1724, 1616 cm^{-1}.

*3.2.2.8. 3-Dicyanomethylene-2-(3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**23**).* The title dye was synthesised in a manner similar to **16**, vide supra, from **8a** and **2b**. Yield: 40%, R_f 0.70 (Sorbfil, chloroform–methanol, 7:1); Analysis: N, 12.34; S, 6.92 $C_{28}H_{22}N_4OS$ requires N, 12.11; S, 6.93%; δ_H (200 MHz, DMSO-d_6) 8.10 (1H, d, 7.8 Hz, arom H), 7.81 (1H, d, 8.3 Hz, arom H), 7.61 (1H, t, 7.5 Hz, arom H), 7.47 (1H, d, 7.2 Hz, arom H), 7.46 (1H, t, 7.4 Hz, arom H), 7.33 (1H, t, 7.6 Hz, arom H), 7.23 (1H, d, 7.8 Hz, arom H), 7.13 (1H, t, 7.3 Hz, arom H), 6.42 (1H, s, C*H*), 6.06 (1H, s, C*H*), 3.87 (3H, s, NC*H*$_3$), 3.47 (3H, s, NC*H*$_3$), 1.64 (6H, s, (C*H*$_3$)$_2$); FAB-MS (NBA) *m*/*z* 462 ($M^{+\cdot}$), 463 (MH^+); IR (KBr) 2232 (CN), 2204 (CN), 1720, 1624 cm^{-1}.

*3.2.2.9. 3-Cyano(butyloxycarbonyl)methylene-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**24**).* The title dye was prepared in a manner similar to **16**, vide supra, from **10** and **2a**. Yield: 52%; R_f 0.73 (Sorbfil, chloroform); Analysis: N, 7.50 $C_{35}H_{37}N_3O_3$ requires N, 7.67%; δ_H (200 MHz, DMSO-d_6) 7.53 (1H, d, 7.1 Hz, arom H), 7.51 (1H, d, 7.1 Hz, arom H), 7.45–7.30 (4H, m, arom H), 7.27 (1H, s, C*H*), 7.30–7.14 (2H, m, arom H), 6.64 (1H, s, C*H*), 4.10 (2H, t, 6.4 Hz, COOC*H*$_2$ (Bu)), 3.62 (3H, s, NC*H*$_3$), 3.59 (3H, s, NC*H*$_3$), 1.67 (6H, s, (C*H*$_3$)$_2$), 1.65 (6H, s, (C*H*$_3$)$_2$), 1.70–1.24 (4H, m), 0.93 (3H, t, 7.2 Hz, COO(CH$_2$)$_3$C*H*$_3$); FAB-MS (NBA) *m*/*z* 547 ($M^{+\cdot}$), 548 (MH^+); IR (KBr) 2212 (CN), 1720, 1672, 1620 (w), 1600 (w) cm^{-1}.

*3.2.2.10. 2-(1,3,3-Trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-3-(2,4,6-trioxohexahydro-5-pyrimidinyliden)-1-cyclobuten-1-olate (**25**).* The title dye was prepared as described for compound **16** from **11** and **2a**. Yield: 39%; R_f 0.48 (Sorbfil, chloroform–methanol, 10:1); Analysis: N, 10.27 $C_{32}H_{30}N_4O_4$ requires N, 10.48%; δ_H (200 MHz, DMSO-d_6) 10.07 (2H, s, N*H*), 7.56 (2H, d, 7.5 Hz, arom H), 7.47–7.33 (4H, m, arom H), 7.25 (2H, t, 6.8 Hz, arom H), 6.44 (2H, s, C*H*), 3.58 (6H, s, NC*H*$_3$), 1.67 (12H, s, (C*H*$_3$)$_2$); FAB-MS (NBA) *m*/*z* 535 (MH^+); IR (KBr) 1716 (CO), 1592 cm^{-1}.

*3.2.2.11. 3-(1,3-Dioxo-2,3-dihydro-1H-2-indenyliden)-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**26**).* The title dye was prepared as described for compound **16** from **12** and **2a**. Yield: 51%; R_f 0.46 (Sorbfil, chloroform–methanol, 100:1); Analysis: N, 5.14 $C_{37}H_{32}N_2O_3$ requires N, 5.07%; δ_H (300 MHz, DMSO-d_6) 7.60 (4H, d, 6.8 Hz, arom H), 7.59 (2H, s, C*H*), 7.56 (2H, d, 7.8 Hz, arom H), 7.45–7.35 (4H, m, arom H), 7.24 (2H, td, 6.3, 1.9 Hz, arom H), 3.72 (6H, s, NC*H*$_3$), 1.70 (12H, s, (C*H*$_3$)$_2$); FAB-MS (NBA) *m*/*z* 552 ($M^{+\cdot}$), 553 (MH^+); IR (KBr) 1724 (CO), 1624, 1580 cm^{-1}.

*3.2.2.12. 3-Cyanoimino-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobuten-1-olate (**27**).* The title dye was prepared as described for compound **16** from **13** and **2a**. Yield: 5.6%; R_f 0.39 (Sorbfil, chloroform–methanol, 50:1); Analysis: N, 12.26 $C_{29}H_{28}N_4O$ requires N, 12.49%; δ_H (300 MHz, DMSO-d_6) 7.49 (2H, d, 7.5 Hz, arom H), 7.41–7.31 (4H, m, arom H), 7.24–7.15 (2H, m, arom H), 3.61 (6H, s, NC*H*$_3$), 1.70 (12H, s, (C*H*$_3$)$_2$) (the −CH= protons do not appear); FAB-MS (NBA) *m*/*z* 448 ($M^{+\cdot}$), 449 (MH^+); IR (KBr) 2192 (CN), 2156 (CN), 1720 (broad) (CO), 1624, 1604 cm^{-1}.

*3.2.2.13. 3-Oxo-2-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidenmethyl)-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobutene-1-thiolate (**28**).* The title dye was prepared as described for compound **16** from **15** and **2a**. Yield: 31%; R_f 0.36 (Sorbfil, chloroform); Analysis: N, 6.19; S, 7.15 $C_{28}H_{28}N_2OS$ requires N, 6.36; S, 7.28%; δ_H (200 MHz, DMSO-d_6) 7.53 (2H, d, 7.0 Hz, arom H), 7.43–7.31 (4H, m, arom H), 7.30–7.08 (2H, m, arom H), 6.13 (2H, s, C*H*), 3.63 (6H, s, NC*H*$_3$), 1.71 (12H, s, (C*H*$_3$)$_2$); FAB-MS (NBA) *m*/*z* 440 ($M^{+\cdot}$), 441 (MH^+); IR (KBr) 1748, 1696, 1616 (w), 1600 (w) cm^{-1}.

*3.2.2.14. 2-(3-Methyl-2,3-dihydro-1,3-benzothiazol-2-ylidenmethyl)-3-oxo-4-(1,3,3-trimethyl-3H-2-indoliumylmethylene)-1-cyclobutene-1-thiolate (**29**).* The title dye was prepared as described for compound **16** from **15** and **2b**. Yield: 19%; R_f 0.44 (Sorbfil, chloroform); Analysis: N, 6.34; S, 14.60 $C_{25}H_{22}N_2OS_2$ requires N, 6.51; S, 14.89%; δ_H (200 MHz, DMSO-d_6) 8.05 (1H, d, 7.6 Hz, arom H), 7.78 (1H, d, 8.2 Hz, arom H), 7.57 (1H, td, 7.6, 1.2 Hz, arom H), 7.47 (1H, d, 7.1 Hz, arom H), 7.41 (1H, t, 7.6 Hz, arom H), 7.33 (1H, t, 7.6 Hz, arom H), 7.24 (1H, d, 7.3 Hz, arom H), 7.11 (1H, td, 7.1, 0.9 Hz, arom H), 6.14 (1H, CH, s), 5.90 (1H, CH, s), 3.91 (3H, NCH_3, s), 3.50 (3H, NCH_3, s), 1.65 (6H, $(CH_3)_2$, s); FAB-MS (NBA) *m*/*z* 430 ($M^{+\cdot}$), 431 (MH^+).

4. Conclusion

The reactions of mono-substituted squaraines with malononitrile, cyano- and nitroacetic esters, barbituric acid, 1,3-indanedione, NaHS and P_4S_{10} lead to ring-substituted mono-squaraines. These intermediates are useful for the synthesis of novel squaraine dyes that exhibit high molar absorptivity and long-wavelength absorption and emission. The high reactivity of the mono-squarate intermediates also allows to synthesise benzoxazole and aryloxazole type squaraine dyes which has not been possible using the conventional squaraine synthesis route.

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