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Highly water soluble dyes based on pyrazolone derivatives of carbohydrates

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ABSTRACT

The synthesis of water soluble pyrazolone derivatives dyes was achieved. The pyrazolidin-3,5-dione **5a**,**b** and pyrazolin-5-one **3a**,**b** and **4a**,**b** units were selected as the key building block to prepare the glyco-conjugated H-chromophore **6a**–**d**, **7a**,**b**, azo **8a**–**d**, **9a**,**b** and bisazo **10a**–**d**, **11a**,**b** dyes pyrazolone derivatives based. The water solubility values show that these derivatives require a minimum percentage weight of 50% of the glycidic moiety to be water soluble and the ^{1}H and ^{13}C data confirmed the tendency of pyrazolone derivatives dyes to exist in their OH tautomer form.

1. Introduction

Pyrazolones are a very important class of heterocycles due to their biological and pharmacological activities,[1] which exhibit anti-inflammatory,[2] herbicidal,[3] fungicidal,[4] and bactericidal,[4] plant growth regulating properties,[3] antipyretic[5] and protein kinase inhibitors.[6] Moreover, these heterocycles are used as key starting materials for the synthesis of commercial arylazopyrazolone dyes. Many azopyrazolone dyes have been used as chromogenic reagents for the colorimetric determinations[7] and as indicators for complexometric titrations.[8] It was also demonstrated that some arylazopyrazolone dyes have a potent antimicrobial activity.[9] On the other hand, it is well known that the most important commercial application of pyrazolones is their use as good fastness dyestuffs for wool, cotton, silk, leather, rubber and synthetic polyamides.[10]

The pyrazolin-5-one and pyrazolidine-3,5-dione were chosen for their capacity to form an azo[11] or triazene[12] bond with another pyrazolin-5-one or an aniline derivative. This reactional capacity is due to the presence of hydrogen atom in the alpha position of the carbonyl group of pyrazolin-5-one and pyrazolidine-3,5-dione derivatives (Fig. 1).

Recently, we have developed a new class of water soluble dyes based on the mono or double-glycoconjugation of the starting dyes (azoic, bis-azoic and antraquinonic) with a very common saccharide—lactose and with its components galactose and glucose for dyeing[13–17] and cyanide chemosensing[18–22] applications. The glyco-conjugation of the starting dyes was carried out using the external spacer able to bond the saccharidic moiety to the starting dyes.[13–17]

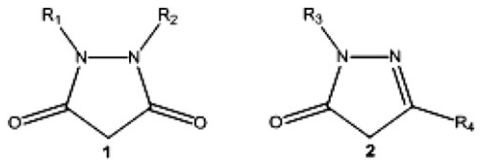

Fig. 1. Structure of pyrazolidine-3,5-dione (**1**) and pyrazolin-5-one (**2**) derivatives.

In this paper, we report a new generation of water soluble synthetic dyes based on heterocyclic derivative carbohydrates. The sugar pyrazolone derivatives (Fig. 2) were used as building blocks to form heterocycle based chromophores including azoic dye classes **9a**–**d**, **10a**,**b**, **11a**–**d** and **12a**,**b**, and H-chromophore dyes **7a**–**d** and **8a**,**b** based on pyrazolidine-3,5-dione and pyrazolin-5-one derivatives.

The glycoconjugation process of the new water soluble heterocyclic dyes does not need an external spacer to bond the sugar and the starting dyes, but the spacer is a part of the dye through the heterocyclic derivative carbohydrates (Fig. 3).

2. Results and discussion

2.1. Synthesis of the sugar pyrazolone derivatives

Saccharides were converted to their hydrazones[23] by treatment with aqueous hydrazine at room temperature as reported in Scheme 1.

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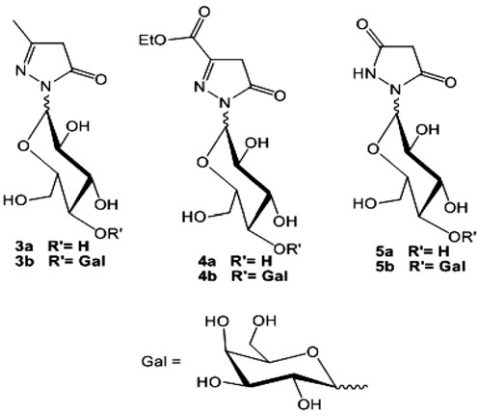
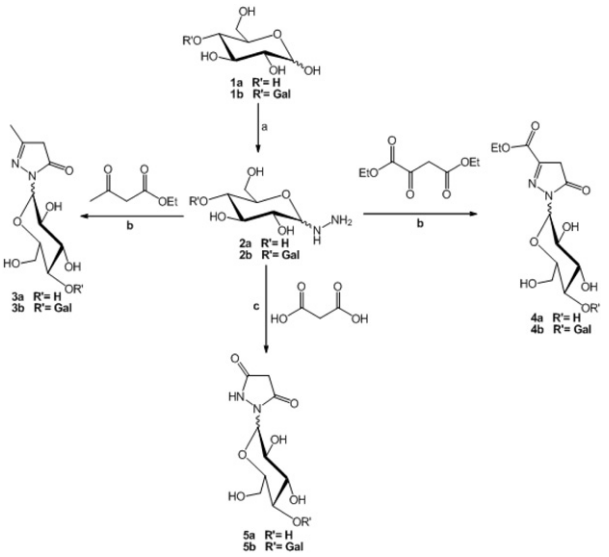


Fig. 2. General structure of the sugar pyrazolone derivatives.



Scheme 1. Synthesis of the sugar pyrazolone derivatives. Reagents and conditions: (a) aqueous hydrazine, rt, 12 h; (b) EtOH/H_2O (pH=6), reflux, 2 h; (c) 1. $SOCl_2$, DCM, 2 h, rt, 2. THF, Et_3N (pH=6), rt, 12 h.

An aldose or ketose hydrazone can exist either in an acyclic hydrazone **A**, or in isomeric cyclic forms such as **B**, **C**, **D**, and **E** forms, which can be considered to be sugar hydrazines (Scheme 2). As previously reported in the literature,[24,25] the aldose hydrazones are formed initially as acyclic hydrazones form **A** that undergo slow cyclization in unbuffered aqueous solution at pH>8. However, at pH<7, the mixture equilibrated more rapidly, forming predominantly β-D-glycopyranosylhydrazine (form **C**), which is likely to be hydrolyzed to the starting saccharide until a small quantity of the isomeric form **C** compounds remained.

The sugar pyrazolidin-5-one derivatives were prepared by addition of ethyl acetoacetate or diethyloxalacetate to freshly prepared aqueous solutions of sugar hydrazone **2a**,**b** (Scheme 1), which produced the coloured mixtures of isomeric heterocyclic derivatives sugar products **3a**,**b** and **4a**,**b**. The conversion of sugar hydrazones to sugar pyrazolidin-5-one derivatives is reported in Scheme 3. The reaction conditions were optimized using different solvents. Thus the reaction of ethyl acetoacetate or diethyloxalacetate with sugar

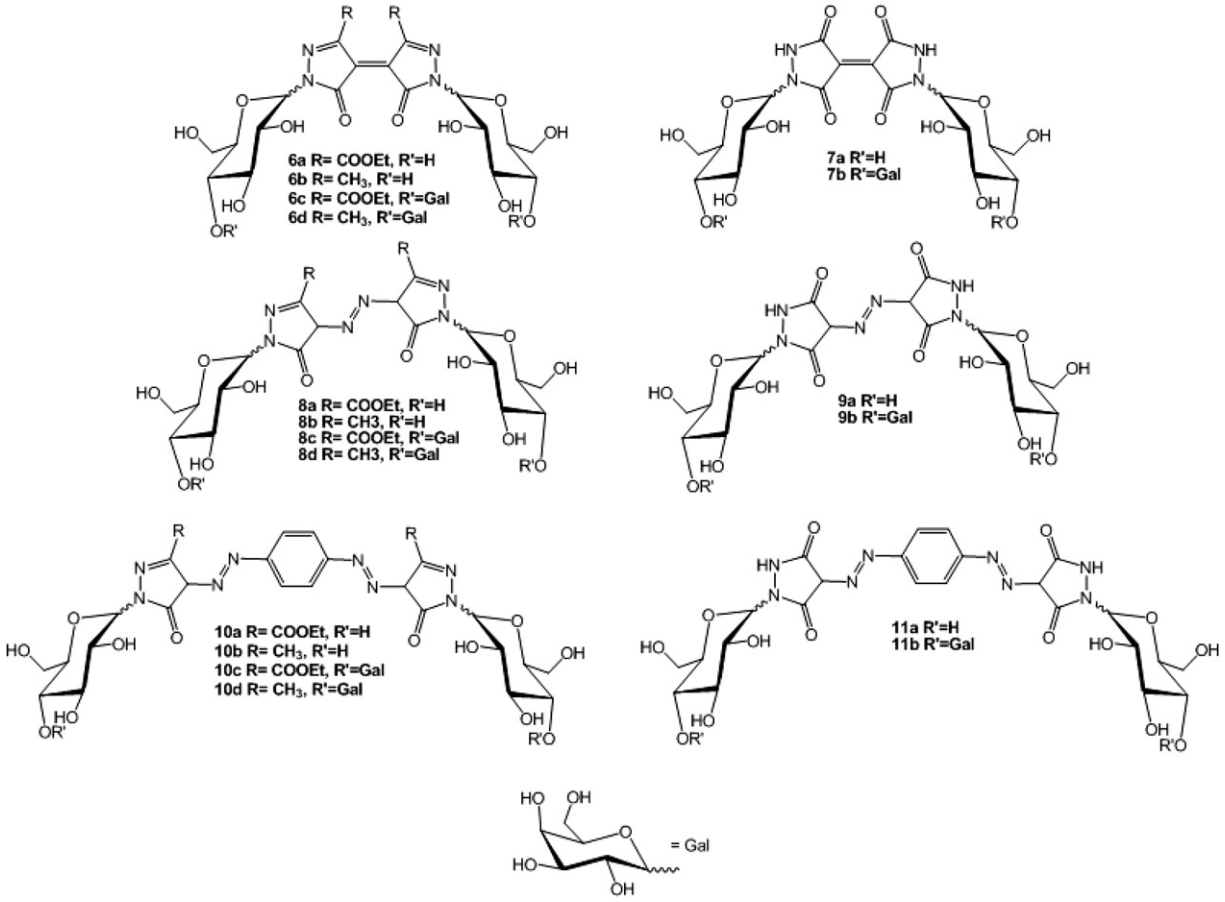
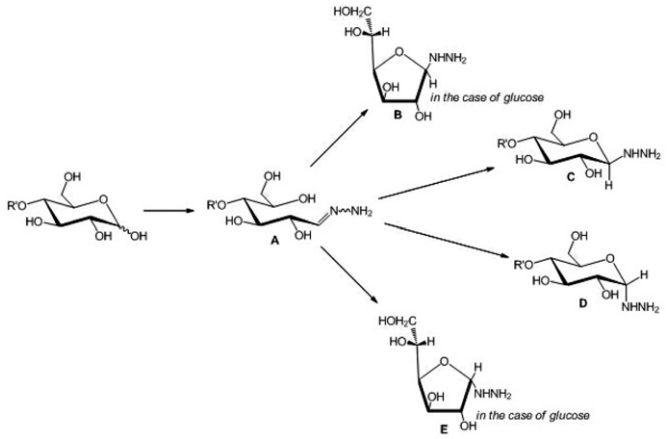


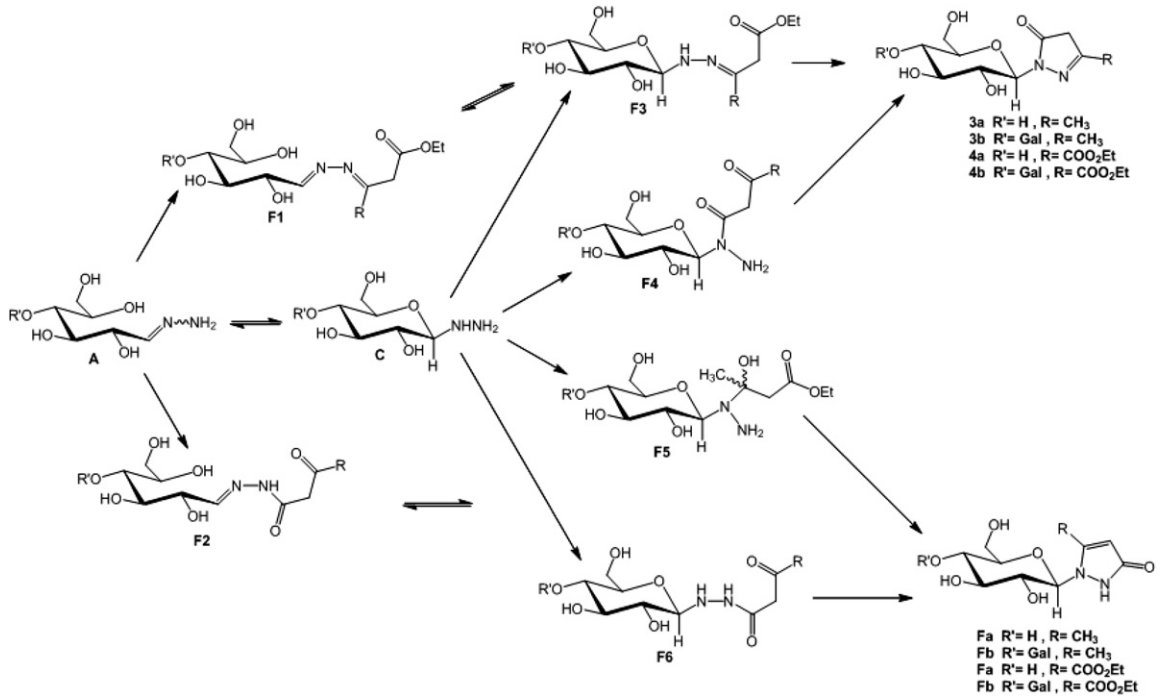
Fig. 3. General structure of the prepared dyes.



Scheme 2. Plausible isomers of the glycosylhydrazines.

Table 1
Optimization of sugar pyrazolidin-5-one derivatives **3a** and **3b** synthesis

Compounds	Entry no.	Solvent/mixture of solvent	Reaction conditions	Yield (%)
3a	1	MeOH	Neutral	33
3a	2	EtOH	Neutral	49
3a	3	EtOH/H_2O	Basic (NaOH/KOH, pH=6)	88
3a	4	DMF	Neutral	29
3a	5	MeOH/DMF (1:1)	Neutral	31
3a	6	EtOH/DMF (1:1)	Neutral	47
3b	7	MeOH	Neutral	35
3b	8	EtOH	Neutral	46
3b	9	EtOH/H_2O	Basic (NaOH/KOH, pH=6)	84
3b	10	DMF	Neutral	31
3b	11	MeOH/DMF (1:1)	Neutral	34
3b	12	EtOH/DMF (1:1)	Neutral	43

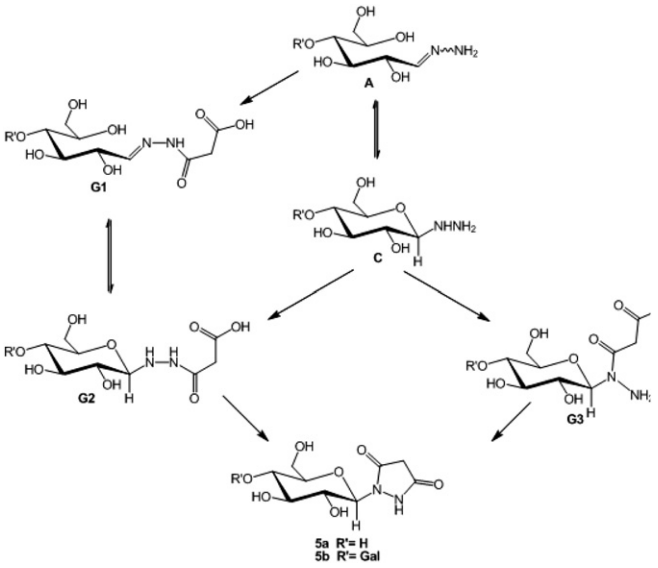


Scheme 3. Reaction pathways for the formation of sugar pyrazolidin-5-one derivatives from sugar hydrazone.

hydrazine using ethanol as solvent resulted in yields of 75–88% of the corresponding sugar-based pyrazole derivatives (Table 1, entry nos. 3, 9). During the course of the reaction, the hydrazone was formed as an intermediate, which then subsequently cyclized and underwent self-oxidation to furnish the expected pyrazole derivatives. Indeed, the intermediates **F1** and **F2**, equilibrate rapidly with **F3** and **F6**, and cyclize irreversibly to **3a**,**b**, **4a**,**b** and **Fa**–**d**, respectively (Scheme 3). The absorption spectra of the sugar pyrazolones separated by HPLC showed that the principal species was the 5-pyrazolone isomer **3a**,**b**, **4a**,**b** as expected (Scheme 3), but small amounts of the 3-pyrazolone isomers, **Fa**–**d** were also present.

Following the results obtained and reported in Table 1, the best sugar—pyrazolin-5-one derivatives synthesis yields were obtained with the polar and protic solvents (EtOH/water) and under basic pH conditions, because the presence of polar and protic solvents helps the hydrazine derivatives to dissolve and the presence of a mineral base (NaOH or KOH) accelerates the condensation reaction between the hydrazine and the ethyl acetoacetate or diethyloxalacetate by the deprotonation of the hydrazine amine, which eases its reaction with the carbonyl group of the ethyl acetoacetate or diethyloxalacetate. On the other hand, hydrazinolysis of the malonyl dichloride with hydrazine derivatives **2a**,**b** in THF at pH 6, affords the respective pyrazolidine-3,5-diones **5a**,**b** in high yields as reported in Scheme 4. The coupling reaction to obtain the corresponding sugar pyrazolone derivatives was carried out at pH=6, to favour one isomer of sugar hydrazine derivative and therefore to obtain predominantly one isomer of sugar pyrazolone derivatives, β-D-glycopyranosylhydrazine as reported below. The proportions of isomeric forms of the glycosylpyrazolones were monitored using reversed-phase HPLC with diode array detection, and the results are reported in Table 2.

The substituted 1*H*-pyrazolin-5-one (Fig. 4) presents three tautomeric forms due to their keto–enolic or lactam–lactim tautomerism, while the full aromatic enol form (OH tautomer) is the predominant one (Fig. 4).



Scheme 4. Reaction pathways for the formation of sugar pyrazolidin-3,5-dione derivatives from sugar hydrazone.

Table 2
Proportions of cyclic isomers of 1-glycosylpyrazolones (%)

	α Furanosyl-	β Furanosyl-	α Pyranosyl-	β Pyranosyl-
3a	2	4	5	89
3b	0	0	11	89
4a	3	5	5	87
4b	0	0	10	90
5a	3	4	4	89
5b	0	0	9	91

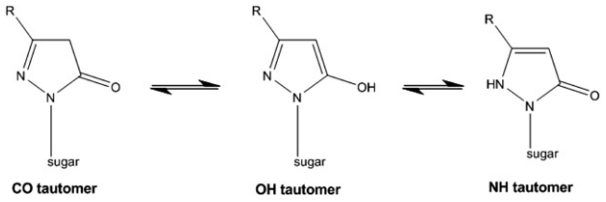


Fig. 4. Tautomerism of the sugar pyrazolin-5-one derivatives.

This phenomenon is confirmed by ^{13}C NMR spectra as reported in Table 3.

All compounds show several signals that correspond to only one tautomer in that solvent. A signal at about 87 ppm, which according to the DEPT spectrum corresponds to a CH group is assigned to C-4. The corresponding proton resonance appears at 6.06 ppm (s, 1H) in the ^1H NMR spectrum. This information rules out the CO tautomer. The signal of about 162 ppm corresponds to C-5, but to assign it as a C=O or C–OH is not straightforward. For this reason, the ^{13}C NMR was carried out at different concentrations in DMSO-d_6 as solvent. For **3a** the ^{13}C NMR spectra in DMSO-d_6 presents 10 downfall signals (for the pyrazolidin-5-onic moiety) that correspond to 2 tautomers. There is one signal at 161.0 ppm (C-5, C=O) and another at 152.5 (C-5, C–OH). According to the areas of the signals in a quantitative ^{13}C spectrum, there is about 92% of the OH tautomer and 8% of the NH tautomer. Consequently, with the information available, the nature of this tautomer cannot be unequivocally established; furthermore, a rapid equilibrium NH/OH could be considered as well. In solid phase sugar pyrazolones exist as either the NH or OH tautomer.

Table 3
^{13}C NMR data of the pyrazolidin-5-onic moiety of compounds **3a**,**b** and **4a**,**b** realized in DMSO-d_6

	C3	C4	C5
3a	147.7	87.2	152.2
3b	147.7	87.1	152.3
4a	142.3	90.5	152.6
4b	142.3	90.4	152.6

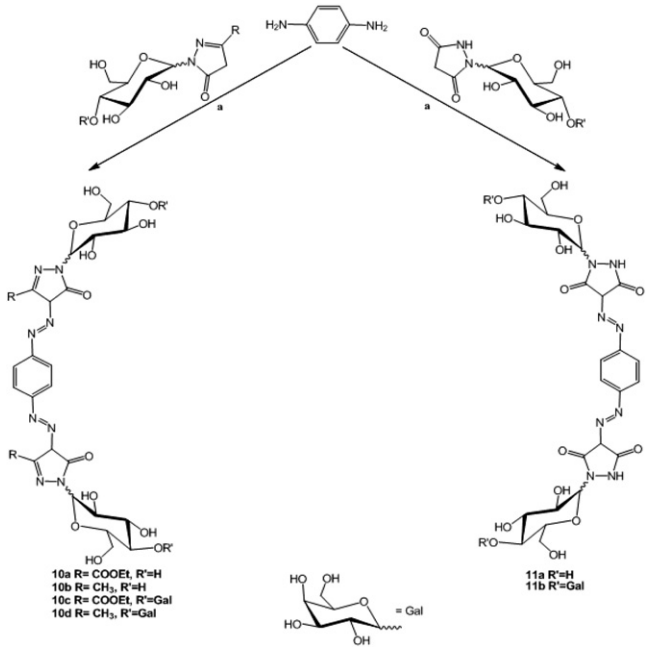
2.2. Synthesis of the sugar pyrazolone based azo dyes

The reaction pathways for the synthesis of the new dyes **10a**–**d** and **11a**,**b** are outlined in Scheme 5.

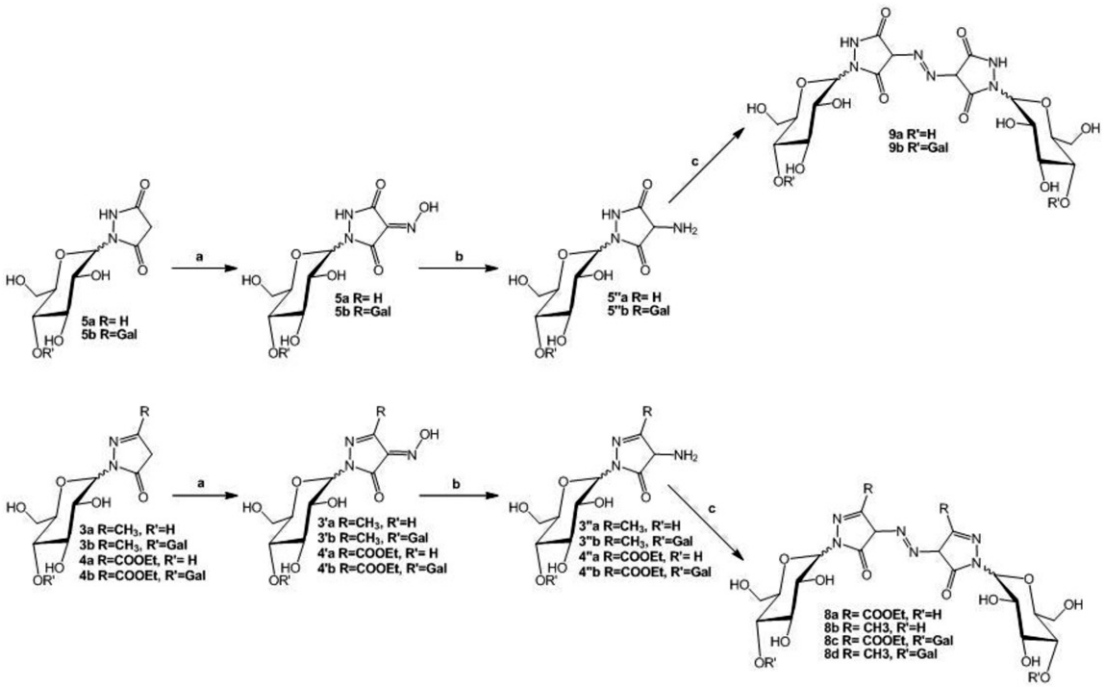
The diazotization reaction of 4-amino aniline in the presence of $NaNO_2$, and aqueous solution of HCl 1 N as solvent at 0 °C gives the corresponding bis-diazonium salts, which treated with sugar pyrazolidine-5-one **3a**,**b** and **4a**,**b** or sugar pyrazolidine-3,5-dione **5a**,**b**, already treated by sodium acetate affords the new azoic dyes **10a**–**d** and **11a**,**b** in 90–94% yield.

On the other side, the treatment of the sugar pyrazolone derivatives **3a**,**b**, **4a**,**b** and **5a**,**b** with sodium nitrite in aqueous solution of concentrated HCl at 0 °C affords the corresponding oxime derivatives **3′a**,**b**, **4′a**,**b** and **5′a**,**b**. The reduction of the oxime group of compounds **3′a**,**b**, **4′a**,**b** and **5′a**,**b** to the corresponding 4-amino pyrazolones **3″a**,**b**, **4″a**,**b** and **5″a**,**b** is carried out in the presence of zinc dust and ammonium chloride in methanol and under reflux for several hours. Finally, the dyes **8a**–**d** and **9a**,**b** are prepared in one step from sugar pyrazolones **3a**,**b**, **4a**,**b** and **5a**,**b** and the prepared sugar 4-amino pyrazolones derivatives **3″a**,**b**, **4″a**,**b** and **5″a**,**b** in high yields via diazotization reaction in the presence of sodium nitrite in HCl solution (1 N) (Scheme 6).

The dyes **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b** can exist as three tautomers, azoketo form **A**, azo-enol form **B** and hydrazone-keto form **C** as reported in our previous study.[11] ^1H NMR spectroscopy of the dyes **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b** shows only peaks of aryl protons (8.14–7.77 ppm), and a highly characteristic destabilized proton at 12.77 ppm for the hydrogen bond N–H peaks and there are no signals in the 4–6 ppm region corresponding to the proton that bears in the position C-4. These NMR data proved that the hydrazo-keto tautomers form **C** are the synthesized dyes due to their stabilization by intramolecular hydrogen bond, where the hydrogen



Scheme 5. Synthetic sequences for dyes **10a**–**d** and **11a**,**b**. Reagents and conditions: (a) 1. sodium acetate, THF/H_2O, 2. $NaNO_2$, HCl 1 N, H_2O, 0 °C, rt, 12 h, 90–94%.



Scheme 6. Synthetic sequences for dyes **8a**–**d** and **9a**,**b**. Reagents and conditions: (a) $NaNO_2$, HCl 1 N, H_2O, 0 °C, 10 h; (b) Zn, MeOH, NH_4Cl, reflux, 4 h; (c) $NaNO_2$, HCl 37%, H_2O, 0 °C, rt, 12 h.

bears by the N–H bond is stabilized by the oxygen of one of both carbonyl groups present in the pyrazolone moiety, which confirms our previous results[11] (Fig. 5).

2.3. Synthesis of the H-chromophore dyes 6a–d and 7a,b

The H-chromophore dyes are C=C double bond substituted by two opposing donor and acceptor groups. These donor–acceptor systems are called 'H-chromophore' due to its structural geometry.[26] The synthesis of the H-chromophore dyes **6a**–**d** and **7a**,**b** is showed in Scheme 7.

To obtain the desired merocyanine dyes **6a**–**d** and **7a**,**b** (Fig. 3), glycoconjugated pyrazolidine-3,5-dione (**1**) and pyrazolin-5-one (**2**) derivatives **3a**,**b**, **4a**,**b** and **5a**,**b** (Fig. 2) were chosen as the building

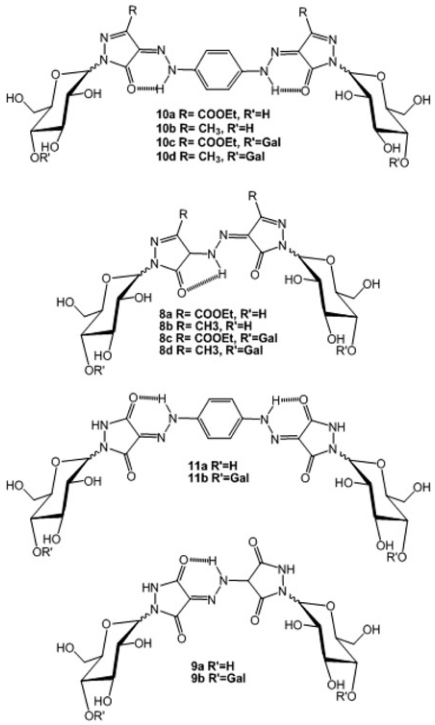
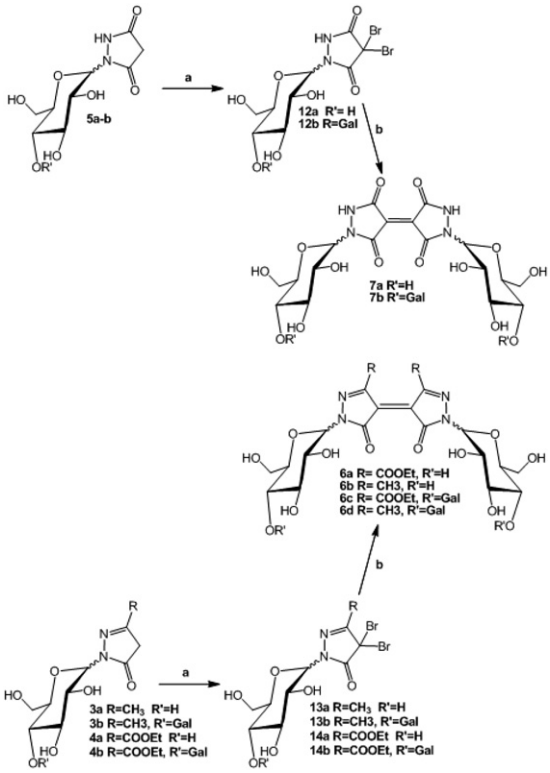


Fig. 5. Stable tautomer form of the **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b**.



Scheme 7. Synthesis for the H-chromophore dyes 1**6a**–**d** and **7a**,**b**. Reagents and conditions: (a) AcOH, Br_2, 0 °C, rt, 12 h; (b) NaH, THF, rt, 0.5 h.

blocks. The pyrazolidin-3,5-dione **5a**,**b** and pyrazolin-5-one **3a**,**b** and **4a**,**b** units were activated by the treatment of these compounds by 2 equiv of sodium hydride to deprotonate the *C*4 of these derivatives, to form their corresponding enolate ions as an electron donor. On the other hand, the di-bromination of the same pyrazolidin-3,5-dione **5a**,**b** and pyrazolin-5-one **3** and **4a**,**b** with Br_2 under acidic conditions yield the di-bromo-pyrazolidine-3,5-dione **12a**,**b** and di-bromo-pyrazolidine-5-dione **13a**,**b** and **14a**,**b** as electron acceptors. Finally, the new H-chromophore dyes **6a**–**d** and **7a**,**b** were synthesized by the coupling step of the bis-carbanions with the 4,4-dibrominated derivatives as shown in Scheme 7 in high yields.

2.4. Water solubility of the prepared dyes

With all these sugar pyrazolone based azo dyes **6a**–**d**, **7a**,**b**, **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b**, we can compare their solubility in water and their glycidic content (Table 4).

The water solubility is immediate with the all dyes except the dyes **10a** and **11a**, which are insoluble and poorly soluble, respectively, in water. Therefore we can conclude that for these derivatives to be soluble, a minimum percentage weight of 50% of the glycidic moiety is required, whereas at 42% they are completely insoluble.

Table 4
Formulae of the prepared dyes and the molecular weights of their lipophilic (chromophore) and glycidic moieties (saccharide) and their molecular weight ratios and solubility

Dyes	Chromophore (formula weight)	Saccharide (formula weight)	MW [g/mol]	Ratio saccharide /MW [%]	Solubility [*a*][g/L][a]
6a	$C_{12}H_{10}N_4O_6$	$C_{12}H_{22}O_{10}$	$C_{24}H_{32}N_4O_{16}$	51.58	45.4
6b	$C_8H_6N_4O_2$	$C_{12}H_{22}O_{10}$	$C_{20}H_{28}N_4O_{12}$	63.17	45.8
6c	$C_{12}H_{10}N_4O_6$	$C_{24}H_{42}O_{20}$	$C_{36}H_{52}N_4O_{26}$	67.99	57.6
6d	$C_8H_6N_4O_2$	$C_{24}H_{42}O_{20}$	$C_{32}H_{48}N_4O_{22}$	77.38	57.1
7a	$C_6H_2N_4O_4$	$C_{12}H_{22}O_{10}$	$C1_8H_{24}N_4O_{14}$	62.69	43.3
7b	$C_6H_2N_4O_4$	$C_{24}H_{42}O_{20}$	$C_{30}H_{44}N_4O_{24}$	70.01	43.9
8a	$C_{12}H_{12}N_6O_6$	$C_{12}H_{22}O_{10}$	$C_{24}H_{34}N_6O_{16}$	49.24	42.2
8b	$C_8H_8N_6O_2$	$C_{12}H_{22}O_{10}$	$C_{20}H_{30}N_6O_{12}$	59.69	42.4
8c	$C_{12}H_{12}N_6O_6$	$C_{24}H_{42}O_{20}$	$C_{36}H_{54}N_6O_{26}$	65.99	55.6
8d	$C_8H_8N_6O_2$	$C_{24}H_{42}O_{20}$	$C_{32}H_{50}N_6O_{22}$	74.71	55.3
9a	$C_6H_4N_6O_4$	$C_{12}H_{22}O_{10}$	$C_{18}H_{26}N_6O_{14}$	59.27	37.5
9b	$C_6H_4N_6O_4$	$C_{24}H_{42}O_{20}$	$C_{30}H_{46}N_6O_{24}$	74.37	46.2
10a	$C_{18}H_{16}N_8O_6$	$C_{12}H_{22}O_{10}$	$C_{30}H_{38}N_8O_{16}$	42.55	Insoluble
10b	$C_{14}H_{12}N_8O_2$	$C_{12}H_{22}O_{10}$	$C_{26}H_{34}N_8O_{12}$	50.15	31.4
10c	$C_{18}H_{16}N_8O_6$	$C_{24}H_{42}O_{20}$	$C_{42}H_{58}N_8O_{26}$	59.63	38.9
10d	$C_{14}H_{12}N_8O_2$	$C_{24}H_{42}O_{20}$	$C_{38}H_{54}N_8O_{22}$	66.73	39.1
11a	$C_{12}H_8N_8O_4$	$C_{12}H_{22}O_{10}$	$C_{24}H_{30}N_8O_{14}$	49.84	Poorly soluble
11b	$C_{12}H_8N_8O_4$	$C_{24}H_{42}O_{20}$	$C_{36}H_{50}N_8O_{24}$	66.42	40.4

[a] The solubility was measured at rt.

2.5. UV/vis study

UV/vis absorption spectra of the newly generated water soluble dye based on carbohydrates **6a**–**d**, **7a**,**b**, **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b** were studied and compared to their corresponding dyes without carbohydrates **15a**,**b**, **16**, **17a**,**b**, **18**, **19a**,**b**, **20** (Fig. 6) because the glycoconjugated dyes should display the same colour as the no glycoconjugated materials **15a**,**b**, **16**, **17a**,**b**, **18**, **19a**,**b**, **20** if the chromophore is not affected by the glycoconjugation process. The UV/vis spectra of the dyes **15a**,**b**, **16**, **17a**,**b**, **18**, **19a**,**b**, **20** and the glycoconjugated dyes **6a**–**d**, **7a**,**b**, **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b** in diluted MeOH solutions (10^{-5} M) are reported in Table 4.

The results reported in Table 5 show that λ_{max} does not exhibit any significant shift between the no glycoconjugated dyes and the glycoconjugated derivatives with glycide units. Also, molar

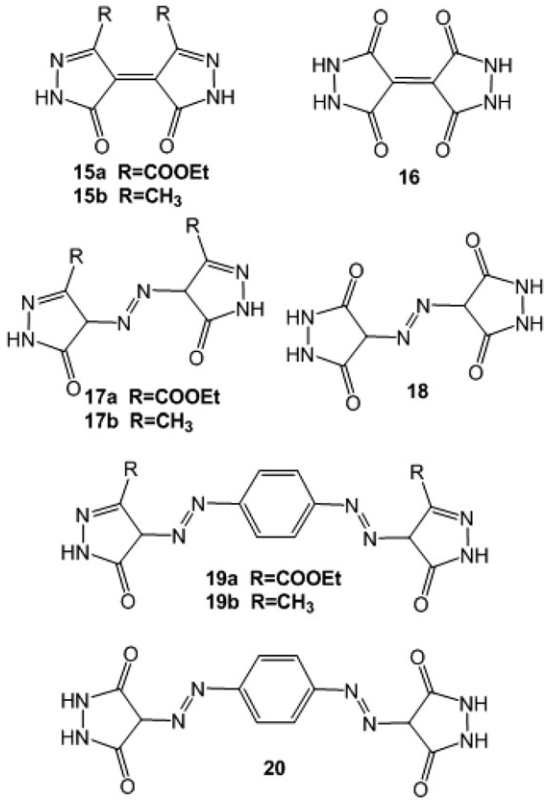


Fig. 6. General structure of the in-glycoconjugated dyes **15a**,**b**, **16**, **17a**,**b**, **18**, **19a**,**b**, **20**.

extinction coefficient values can be considered almost constant, only very small differences being detected. Thus, the presence of the carbohydrates on the dyes **6a**–**d**, **7a**,**b**, **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b** does not affect the UV/vis spectrum as these carbohydrates are far from the chromophore. Very small changes are apparent in the spectra of compounds.

Table 5
UV/vis absorption spectra of the dyes **6a**–**d**, **7a**,**b**, **8a**–**d**, **9a**,**b**, **10a**–**d** and **11a**,**b** and of their not glycoconjugated **15a**,**b**, **16**, **17a**,**b**, **18**, **19a**,**b**, **20**

Dyes	λ_{max} (MeOH) [nm]	$\varepsilon_{(max)}/M^{-1}\ cm^{-1}$
6a	506	32,745
6b	494	31,698
6c	507	32,739
6d	494	31,701
7a	511	35,615
7b	511	35,608
8a	424	29,467
8b	401	28,043
8c	424	29,455
8d	401	28,011
9a	456	30,613
9b	455	30,598
10a	396	27,264
10b	371	25,736
10c	396	27,241
10d	370	25,699
11a	416	30,156
11b	415	30,129
15a	505	32,754
15b	495	31,672
16	510	35,622
17a	425	29,412
17b,	400	28,009
18	456	30,624
19a	397	27,257
19b	372	25,747
20	416	30,169

3. Conclusion

A convenient approach to water soluble pyrazolone derivative based dyes has been reported by using the glycoconjugated pyrazolone derivatives as a building block to form the desired dyes. The glycoconjugation process of the new water soluble heterocyclic dyes does not need an external spacer to bond the carbohydrates and the starting dyes, but the spacer is a part of the dye through the heterocyclic derivative carbohydrates. The final glycoconjugated species were quite water soluble and the water solubility of dyes depends on the molecular weight of the lipophilic portion in the final molecule, The pyrazolones presented offer the opportunity to introduce two units of carbohydrates, as we recently reported for commercial disperse dyes.[16] Currently, tinctorial tests of these new dyes are under investigation on synthetic and natural textiles. But the glyconjugation process here illustrated can be usefully applied to the pyrazolone-based derivatives in general, so that the property of water solubility can be easily reached with this kind of derivatives.

4. Experimental section

4.1. Chemicals and materials

All chemicals were reagent grade (Aldrich Chemical Co.) and were used as purchased without further purification. Thin layer chromatography (TLC) analysis was performed using Fluka aluminium foils coated with 25 mm particle size silica gel matrix F254. TLC development involved either UV (254 and 366 nm) or visible light inspection, followed by either treatment with an acid solution of *p*-anisaldehyde or a basic solution of $KMnO_4$ and heating. Flash column chromatography was performed on Merck silica gel 60 (particle size 0.040–0.063 nm, 230–400 mesh ASTM) according to the procedure of Still.[27] Melting points were recorded on a Melting Point Apparatus SMP3-STUART SCIENTIFIC. Optical rotations were measured on a Jasco DIP-370 polarimeter using a 100 mm path-length cell at 589 nm. UV/vis spectra were recorded on a Cary-4000 Varian spectrophotometer, using either 0.1 or 1 cm quartz cuvette. Infrared spectra were recorded in a KBr disk on a Perkin Elmer-Spectrum BX FTIR system. Absorptions are quoted in wavenumbers (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded at 200 MHz ^1H (50.0 MHz ^{13}C) on a Varian Gemini spectrometer. Spin resonances are reported as chemical shifts (δ) in parts per million (ppm) and referenced to the residual peak as an internal standard of the solvent employed, as follows: $CDCl_3$ 7.27 ppm (^1H NMR), 77 ppm (^{13}C NMR, central band), DMSO-d_6 2.50 ppm (^1H NMR, central band), 39.5 ppm (^{13}C NMR, central band). Spin multiplicity is showed by s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Coupling constants *J* are reported in hertz (Hz). Mass spectra were recorded on a ThermoScientific LCQ-Fleet mass spectrometer under electrospray ionization (ESI, +c or −c technique). High resolution mass spectra (HRMS) were recorded on an LTP-Orbitrap mass spectrometer from Thermo Electron Corporation under ESI (+c) technique. Mass spectrometric analysis is quoted in the *m*/*z* form. Preparative reversed-phase high-performance liquid chromatographic (RP-HPLC) purification of compounds was carried out using a Jordi divinylbenzene column (100×10 mm, Alltech, Deerfield, USA) with detection at 220 and 240 nm using a Shimadzu series 10 HPLC system. The elution conditions were adjusted to suit each monosaccharide. For example, monosaccharide pyrazoles were separated by elution at 1.5 mL/min with 13:87 acetonitrile/water for 8 min, a gradient to 25:75 over 12 min, then to 60:40 over 6 min. Disaccharide pyrazoles were fractionated by normal-phase HPLC on a 5/μm aminopropylsilica column (220×4.6 mm, Brownlee, Foster City, USA), eluted isocratically at 1 mL/min with 84:16 acetonitrile/water. Elemental analyses were recorded on a Perkin Elmer 240 C Elemental Analyzer. The sugar hydrazone was prepared following the procedure reported in the literature.[23]

4.2. General procedure A: synthesis of the sugar pyrazolidin-5-dione derivatives (3a,b and 4a,b)

The freshly prepared sugar hydrazone **2a**,**b** (1 equiv) was dissolved in 1:3 MeCN/water (20 mL) then purged with argon, and ethyl acetoacetate or diethyloxalacetate (1 equiv) was added. Argon is bubbled through the mixture for a further 3 h, and the sample was lyophilized to yield **3a**,**b** or **4a**,**b** as a yellow powder.

*4.2.1. 3-Methyl-1-((3S,4S,5S)-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-yl)-1H-pyrazol-5(4H)-one (**3a**).* The product **3a** was prepared following the general procedure A using the following amounts: ethyl acetoacetate (1.00 g, 7.96 mmol), 1-glucosyl hydrazine (1.49 g, 7.96 mmol) to yield **3a** (1.88 g, 94% yield) as a yellow solid as a mixture of α- and β-pyranosic anomers. ^1H NMR (200 MHz, Me_2SO): δ=11.48 (s, O*H*), 6.12 (s, 1H, pyrC4*H*), 5.28–5.22 (d, 1H), 3.81–3.60 (m, 4H), 3.48–3.34 (m, 2H), 2.32 (s, 3H, pyrCH_3). ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=152.2, 147.7, 87.2, 13.9 ppm. MS (ESI): *m*/*z*=261.31 $[M+1]^+$. $C_{10}H_{16}N_2O_6$ (260.10): calcd C, 46.15; H, 6.20; N, 10.76; found: C, 46.31; H, 6.39; N, 10.81.

*4.2.2. (2S,3R,4S,5R,6R)-2-((3S,4R,5S)-4,5-Dihydroxy-6-(5-hydroxy-3-methyl-1H-pyrazol-1-yl)-2-(hydroxymethyl)tetrahydro-2H-pyran-3-yloxy)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol (**3b**).* The product **3b** was prepared following the general procedure A using the following amounts: ethyl acetoacetate (1.00 g, 7.96 mmol), 1-lactosyl hydrazine (2.82 g, 7.96 mmol) to yield **3b** (3.12 g, 93% yield) as a yellow solid as a mixture of α- and β-pyranosic anomers. ^1H NMR (200 MHz, Me_2SO): δ=11.51 (s, O*H*, both anomers), 6.14 (s, 1H, pyrC4*H*, both anomers), 5.10–4.55 (m, 2H, both anomers), 4.31–4.16 (m, 4H, both anomers), 3.88–3.79 (m, 6H, both anomers), 3.44–3.41 (m, 2H, both anomers), 2.31 (s, 3H, pyrCH_3). ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=152.3, 147.7, 87.1, 13.7 ppm. MS (ESI): *m*/*z*=423.27 $[M+1]^+$. $C_{16}H_{26}N_2O_{11}$ (422.15): calcd C, 45.50; H, 6.20; N, 6.63; found: C, 45.61; H, 6.27; N, 6.77.

*4.2.3. Ethyl 5-hydroxy-1-((3S,4S,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)-1H-pyrazole-3-carboxylate (**4a**).* The product **4a** was prepared following the general procedure A using the following amounts: diethyloxalacetate (1.00 g, 5.32 mmol), 1-glucosyl hydrazine (1.03 g, 5.32 mmol) to yield **4a** (1.59 g, 94% yield) as a yellow solid as a mixture of α- and β-pyranosic anomers. ^1H NMR (200 MHz, Me_2SO): δ=11.46 (s, O*H*), 7.07 (s, 1H, pyrC4*H*), 5.28–5.21 (d, 1H), 4.28 (q, *J*=7.00 Hz, 2H, CH_2), 3.81–3.61 (m, 4H), 3.47–3.34 (m, 2H), 1.28 (t, *J*=7.00 Hz, 3H, CH_3). ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=161.3, 152.6, 142.3, 90.5, 60.1, 14.2 ppm. MS (ESI): *m*/*z*=319.22 $[M+1]^+$. $C_{12}H_{18}N_2O_8$ (318.11): calcd C, 45.28; H, 5.70; N, 8.80; found: C, 45.36; H, 5.79; N, 8.88.

*4.2.4. Ethyl 1-((3S,4R,5S)-3,4-dihydroxy-6-(hydroxymethyl)-5-((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)tetrahydro-2H-pyran-2-yl)-5-hydroxy-1H-pyrazole-3-carboxylate (**4b**).* The product **4b** was prepared following the general procedure A using the following amounts: diethyloxalacetate (1.00 g, 5.32 mmol), 1-lactosyl hydrazine (1.89 g, 5.32 mmol) to yield **4b** (2.42 g, 95% yield) as a yellow solid as a mixture of α- and β-pyranosic anomers. ^1H NMR (200 MHz, Me_2SO): δ=11.52 (s, O*H*, both anomers), 7.14 (s, 1H, pyrC4*H*, both anomers), 5.11–4.55 (m, 2H, both anomers),

4.29 (q, J=6.8 Hz, 2H, CH_2), 4.25–4.14 (m, 4H, both anomers), 3.88–3.78 (m, 6H, both anomers), 3.44–3.40 (m, 2H, both anomers), 1.28 (t, J=6.8 Hz, 3H, CH_3). ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=161.2, 152.6, 142.3, 90.4, 60.2, 14.2 ppm. MS (ESI): m/z=481.26 $[M+1]^+$. $C_{18}H_{28}N_2O_{13}$ (480.15): calcd C, 45.00; H, 5.87; N, 5.83; found: C, 45.16; H, 5.94; N, 5.89.

4.3. General procedure B: synthesis of the sugar pyrazolidine-3,5-dione derivatives (5a,b)

Malonic acid (1 equiv) and sugar hydrazine derivative (1 equiv) were suspended in methanol (approximate concn 0.2 M) under argon atmosphere and stirred for 2 h at 80 C. Afterwards, the solution was lyophilized to yield **5a**,**b** as a yellow powder.

*4.3.1. 1-((3S,4S,5S)-3,4,5-Trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)pyrazolidine-3,5-dione (**5a**).* The product **5a** was prepared following the general procedure B using the following amounts: malonic acid (2.00 g, 19.23 mmol), glucose hydrazine (3.73 g, 19.23 mmol) to yield **5a** (4.73 g, 94% yield) as a yellow solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.21 (d, 1H), 3.81–3.61 (m, 4H), 3.47–3.34 (m, 2H), 3.08 (s, 2H, CH_2). ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=170.1, 169.2, 46.9 ppm. MS (ESI): m/z=263.28 $[M+1]^+$. $C_9H_{14}N_2O_7$ (262.06): calcd C, 41.22; H, 5.38; N, 10.68; found: C, 41.31; H, 5.44; N, 10.78.

*4.3.2. 1-((3S,4R,5S)-3,4-Dihydroxy-6-(hydroxymethyl)-5-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-yloxy)tetrahydro-2H-pyran-2-yl) pyrazolidine-3,5-dione (**5b**).* The product **5b** was prepared following the general procedure **B** using the following amounts: malonic acid (2.00 g, 19.23 mmol), lactose hydrazine (6.84 g, 19.23 mmol) to yield **5b** (7.74 g, 95% yield) as a yellow solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.11–4.55 (m, 2H, both anomers), 4.25–4.14 (m, 4H, both anomers), 3.88–3.78 (m, 6H, both anomers), 3.44–3.40 (m, 2H, both anomers), 3.09 (s, 2H, CH_2). ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=170.2, 169.2, 47.0 ppm. MS (ESI): m/z=425.33 $[M+1]^+$. $C_{15}H_{24}N_2O_{12}$ (424.12): calcd C, 42.45; H, 5.70; N, 6.60; found: C, 42.53; H, 5.76; N, 6.68.

4.4. General procedure C: synthesis of the 4,4-dibromo pyrazolidine-3,5-dione and pyrazolidin-5-dione derivatives (12a,b, 13a,b, 14a,b)

To a suspension of sugar pyrazolidine-3,5-dione or sugar pyrazolidine-5-dione derivatives (1 mmol) in acetic acid (10 mL), Br_2 (2 mmol) was added at 0 °C and the resulting mixture was stirred at room temperature for 2 h. Excess of the bromine and the acetic acid were removed under reduced pressure and the resulting colourless oil was dried for 10 min by vacuum suction and used as-is without purification.

*4.4.1. 4,4-Dibromo-1-((3R,5S)-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-yl)pyrazolidine-3,5-dione (**12a**).* The product **12a** was prepared according to the general procedure C using the following amounts: **5a** (1.00 g, 3.80 mmol), bromine (0.44 mL, 7.60 mmol) in acetic acid (15 mL) to afford **12a** (1.03g, 95%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.22 (d, 1H), 3.82–3.61 (m, 4H), 3.47–3.31 (m, 2H). ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=170.3, 168.7, 93.9 ppm. MS (ESI): m/z=418.94 $[M+1]^+$. $C_9H_{12}Br_2N_2O_7$ (417.82): calcd C, 25.74; H, 2.88; N, 6.67; found: C, 25.81; H, 2.95; N, 6.77.

*4.4.2. 4,4-Dibromo-1-((3R,5S)-3,4-dihydroxy-6-(hydroxymethyl)-5-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-yloxy) tetrahydro-2H-pyran-2-yl) pyrazolidine-3,5-dione (**12b**).* The product **12b** was prepared according to the general procedure C using the following amounts: **5b** (1.00 g, 2.35 mmol), bromine (0.27 mL, 4.70 mmol) in acetic acid (15 mL) to afford **12b** (1.28 g, 94%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.11–4.55 (m, 2H, both anomers), 4.30–4.16 (m, 4H, both anomers), 3.88–3.79 (m, 6H, both anomers), 3.44–3.41 (m, 2H, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=170.4, 168.7, 93.8 ppm. MS (ESI): m/z=581.11 $[M+1]^+$. $C_{15}H_{22}Br_2N_2O_{12}$ (579.94): calcd C, 30.95; H, 3.81; N, 4.81; found: C, 31.08; H, 3.93; N, 4.97.

*4.4.3. 4,4-Dibromo-3-methyl-1-((3R,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)-1H-pyrazol-5(4H)-one (**13a**).* The product **13a** was prepared according to the general procedure C using the following amounts: **3a** (1.00 g, 2.41 mmol), bromine (0.25 mL, 4.82 mmol) in acetic acid (15 mL) to afford **13a** (0.95 g, 95%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.29–5.21 (d, 1H), 3.81–3.61 (m, 4H), 3.47–3.30 (m, 2H), 2.01 (s, 3H, CH_3–Pyr) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=171.6, 156.7, 75.6, 17.4 ppm. MS (ESI): m/z=416; 13 $[M+1]^+$. $C_{10}H_{14}Br_2N_2O_6$ (415; 91): calcd C, 28.73; H, 3.38; N, 6.70; found: C, 28.86; H, 3.44; N, 6.81.

*4.4.4. 4,4-Dibromo-1-((3R,5S)-3,4-dihydroxy-6-(hydroxymethyl)-5-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)tetrahydro-2H-pyran-2-yl)-3-methyl-1H-pyrazol-5(4H)-one (**13b**).* The product **13b** was prepared according to the general procedure C using the following amounts: **3b** (1.00 g, 2.36 mmol), bromine (0.24 mL, 4.72 mmol) in acetic acid (15 mL) to afford **13b** (1.30 g, 96%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.55 (m, 2H, both anomers), 4.31–4.15 (m, 4H, both anomers), 3.89–3.79 (m, 6H, both anomers), 3.44–3.40 (m, 2H, both anomers), 2.02 (s, 3H, CH_3–Pyr) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=171.7, 156.7, 75.5, 17.6 ppm. MS (ESI): m/z=579.17 $[M+1]^+$. $C_{16}H_{24}Br_2N_2O_{11}$ (577.97): calcd C, 33.12; H, 4.17; N, 4.83; found: C, 33.18; H, 4.25; N, 4.93.

*4.4.5. Ethyl 4,4-dibromo-5-oxo-1-((3R,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)-4,5-dihydro-1H-pyrazole-3-carboxylate (**14a**).* The product **14a** was prepared according to the general procedure C using the following amounts: **4a** (1.00 g, 3.14 mmol), bromine (0.32 mL, 6.28 mmol) in acetic acid (15 mL) to afford **14a** (0.95 g, 95%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.22 (d, 1H), 4.26 (q, J=6.9 Hz, 2H, CH_2), 3.82–3.61 (m, 4H), 3.47–3.30 (m, 2H), 1.28 (t, J=6.9 Hz, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=171.9, 164.1, 149.6, 69.2, 60.6, 14.3 ppm. MS (ESI): m/z=475.16 $[M+1]^+$. $C_{12}H_{16}Br_2N_2O_8$ (473.93): calcd C, 30.27; H, 3.39; Br, 33.57; N, 5.88; found: C, 30.33; H, 3.43; Br, 33.64; N, 5.95.

*4.4.6. Ethyl 4,4-dibromo-1-((3R,5S)-3,4-dihydroxy-6-(hydroxymethyl)-5-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)tetrahydro-2H-pyran-2-yl)-5-oxo-4,5-dihydro-1H-pyrazole-3-carboxylate (**14b**).* The product **14b** was prepared according to the general procedure C using the following amounts: **4b** (1.00 g,

2.08 mmol), bromine (0.21 mL, 4.16 mmol) in acetic acid (15 mL) to afford **14b** (1.70 g, 97%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.55 (m, 2H, both anomers), 4.25 (q, J=6.6 Hz, 2H, CH_2), 4.32–4.16 (m, 4H, both anomers), 3.87–3.77 (m, 6H, both anomers), 3.44–3.41 (m, 2H, both anomers), 1.27 (t, J=6.6 Hz, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=171.6, 164.3, 149.8, 69.4, 60.6, 14.5 ppm. MS (ESI): m/z=637.23 $[M+1]^+$. $C_{18}H_{26}Br_2N_2O_{13}$ (635.98): calcd C, 33.87; H, 4.11; N, 4.39; found: C, 33.94; H, 4.11; N, 4.46.

4.5. General procedure D: synthesis of the 4-amino pyrazolidine-3,5-dione and pyrazolidine-5-dione derivatives

To a solution of **3a**,**b**, **4a**,**b**, **5a**,**b** (1 mol) in HCl 1 N/water (1:10) and cooled to 0 °C in an ice-bath. With stirring, sodium nitrite (1.2 mol) was added portion wise over 1 h, while maintaining the internal temperature near 0 °C. After that, the flask was removed from ice-bath and the resulting mixture was stirred at room temperature. After 3 h, the water was removed under reduced pressure to yield the oxime derivatives. To a solution of the oxime derivatives (1 mol) in DMSO (10 mL), ammonium chloride (4 mol) and zinc dust (2 mol) were added and the resulting mixture was stirred under reflux. After the completion of the reaction, the reaction mixture was filtered through Celite. The filtrate was evaporated under vacuum and the residue was purified by precipitation with ethanol to yield the corresponding 4-amino-pyrazolidine-3,5-dione and 4-amino-pyrazolidine-5-dione derivatives.

*4.5.1. 4-Amino-1-((3R,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)pyrazolidine-3,5-dione (**5″a**).* The product **5″a** was prepared according to the general procedure D using the following amounts: **5a** (1.00 g, 3.80 mmol) to afford **5″a** (1.00g, 95%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.22 (d, 1H), 4.52 (s, 1H), 3.82–3.61 (m, 4H), 3.47–3.31 (m, 2H). ^{13}C NMR (50 MHz, Me_2SO): see Table 5 for the glycidic part and δ=170.6, 168.9, 77.5 ppm. MS (ESI): m/z=278.25 $[M+1]^+$. $C_9H_{15}N_3O_7$ (277.08): calcd C, 38.99; H, 5.45; N, 15.16; found: C, 39.21; H, 5.53; N, 15.22.

*4.5.2. 4-Amino-1-((3R,5S)-3,4-dihydroxy-6-(hydroxymethyl)-5-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-yloxy)tetrahydro-2H-pyran-2-yl)pyrazolidine-3,5-dione (**5″b**).* The product **5″b** was prepared according to the general procedure C using the following amounts: **5b** (1.00 g, 2.35 mmol) to afford **5″b** (0.99 g, 93%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=5.11–4.55 (m, 2H, both anomers), 4.52 (s, 1H), 4.30–4.15 (m, 4H, both anomers), 3.88–3.79 (m, 6H, both anomers), 3.45–3.42 (m, 2H, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=170.9, 168.4, 76.4 ppm. MS (ESI): m/z=440.29 $[M+1]^+$. $C_{15}H_{25}N_3O_{12}$ (439.14): calcd C, 41.00; H, 5.74; N, 9.56; found: C, 41.12; H, 5.83; N, 9.64.

*4.5.3. 4-Amino-3-methyl-1-((3R,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)-1H-pyrazol-5(4H)-one (**3″a**).* The product **3″a** was prepared according to the general procedure C using the following amounts: **3a** (1.00 g, 2.41 mmol) to afford **3″a** (0.97 g, 94%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=11.54 (s, 1H, OH), 5.29–5.21 (d, 1H), 3.81–3.61 (m, 4H), 3.47–3.30 (m, 2H), 2.71 (s, 3H, CH_3–Pyr) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=147.2, 140.4, 123.8, 12.4 ppm. MS (ESI): m/z=276; 31 $[M+1]^+$. $C_{10}H_{17}N_3O_6$ (275.11): calcd C, 43.63; H, 6.23; N, 15.27; found: C, 43.72; H, 6.31; N, 15.34.

*4.5.4. 4-Amino-1-((3R,5S)-3,4-dihydroxy-6-(hydroxymethyl)-5-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)tetrahydro-2H-pyran-2-yl)-3-methyl-1H-pyrazol-5(4H)-one (**3″b**).* The product **3″b** was prepared according to the general procedure C using the following amounts: **3b** (1.00 g, 2.36 mmol) to afford **3″b** (0.98 g, 96%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=11.50 (s, 1H), 5.11–4.56 (m, 2H, both anomers), 4.31–4.16 (m, 4H, both anomers), 3.88–3.79 (m, 6H, both anomers), 3.44–3.40 (m, 2H, both anomers), 2.70 (s, 3H, CH_3–Pyr) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=147.4, 140.7, 123.4, 12.6 ppm. MS (ESI): m/z=438.32 $[M+1]^+$. $C_{16}H_{27}N_3O_{11}$ (437:17): calcd C, 43.93; H, 6.22; N, 9.61; found: C, 44.12; H, 6.35; N, 9.73.

*4.5.5. Ethyl 4-amino-5-oxo-1-((3R,5S)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)-4,5-dihydro-1H-pyrazole-3-carboxylate (**4″a**).* The product **4″a** was prepared according to the general procedure C using the following amounts: **4a** (1.00 g, 3.14 mmol), bromine (0.32 mL, 6.28 mmol) in acetic acid (15 mL) to afford **4″a** (0.99 g, 96%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=11.49 (s, 1H), 5.28–5.22 (d, 1H), 4.25 (q, J=7.1 Hz, 2H, CH_2), 3.83–3.62 (m, 4H), 3.47–3.30 (m, 2H), 1.30 (t, J=7.0 Hz, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=160.9, 144.3, 136.4, 126.6, 60.9, 14.7 ppm. MS (ESI): m/z=334.32 $[M+1]^+$. $C_{12}H_{19}N_3O_8$ (333.13): calcd C, 43.24; H, 5.75; N, 12.61; found: C, 43.32; H, 5.86; N, 12.70.

*4.5.6. Ethyl 4-amino-1-((3R,5S)-3,4-dihydroxy-6-(hydroxymethyl)-5-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)tetrahydro-2H-pyran-2-yl)-5-oxo-4,5-dihydro-1H-pyrazole-3-carboxylate (**4″b**).* The product **4″b** was prepared according to the general procedure C using the following amounts: **4b** (1.00 g, 2.08 mmol) to afford **4″b** (1.70 g, 97%) as a coloured solid as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=11.52 (s, 1H), 5.10–4.55 (m, 2H, both anomers), 4.24 (q, J=6.9 Hz, 2H, CH_2), 4.32–4.16 (m, 4H, both anomers), 3.87–3.77 (m, 6H, both anomers), 3.44–3.41 (m, 2H, both anomers), 1.28 (t, J=6.9 Hz, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=160.7, 144.5, 136.4, 126.5, 60.7, 14.8 ppm. MS (ESI): m/z=496.29 $[M+1]^+$. $C_{18}H_{29}N_3O_{13}$ (495.17): calcd C, 43.64; H, 5.90; N, 8.48; found: C, 43.73; H, 5.96; N, 8.54.

4.6. General procedure E: synthesis of the azoic dyes 10a–d and 11a,b

To a solution of 4-amino aniline (1 mol) in 15 mL of water/HCl 1 N 15:1.5, a solution of $NaNO_2$ (2.4 mmol) in water (2 mL) was added drop wise at 0 C° and the resulting mixture was stirred for 30 min. The diazonium salt solution previously prepared was added drop wise to the solution of sugar pyrazolidine-3,5-dione **5a**,**b** sugar pyrazolidine-5-dione **3a**,**b**, **4a**,**b** derivatives (2 mmol) in water (3 mL) and the combined solution was maintained at 0 C° for 6 h with stirring. After this time the resulting mixture was filtered and the resulting solution was purified by precipitation with ethanol to yield the corresponding azo dyes **10a**–**d** and **11a**,**b**.

*4.6.1. Synthesis of the dye **10a**.* The product **10a** was prepared according to the general procedure E using the following amounts: 4-amino aniline (0.50 g, 4.63 mmol), **4a** (2.95 g, 9.26 mmol), $NaNO_2$ (0.77 g, 11.11 mmol), in HCl 1 N/water (10 mL), to afford **10a** (3.26 g,

92%) as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=6.42 (m, 4H), 5.28–5.21 (d, 2H), 4.25 (q, J=7.0 Hz, 4H, CH_2), 3.82–3.61 (m, 8H), 3.47–3.30 (m, 4H), 1.27 (t, J=7.0 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=168.9, 164.3, 136.2, 133.6, 120.6, 60.8, 14.5 ppm. MS (ESI): m/z=767.37 $[M+1]^+$. $C_{30}H_{38}N_8O_{16}$ (766.24): calcd C, 47.00; H, 5.00; N, 14.62; found: C, 47.13; H, 5.16; N, 14.73.

*4.6.2. Synthesis of the dye **10b**.* The dye **10a** was prepared according to the general procedure E using the following amounts: 4-amino aniline (0.50 g, 4.63 mmol), **3a** (2.40 g, 9.26 mmol), $NaNO_2$ (0.77 g, 11.11 mmol), in HCl 1 N/water (10 mL), to afford **10b** (2.82 g, 94%) as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=6.44 (m, 4H), 5.28–5.20 (d, 2H), 3.82–3.62 (m, 8H), 3.48–3.30 (m, 4H), 2.27 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=168.6, 148.3, 133.4, 128.6, 120.5, 13.3 ppm. MS (ESI): m/z=651.45 $[M+1]^+$. $C_{26}H_{34}N_8O_{12}$ (650.23): calcd C, 48.00; H, 5.27; N, 17.22; found: C, 48.14; H, 5.34; N, 17.31.

*4.6.3. Synthesis of the dye **10c**.* The product **10c** was prepared according to the general procedure E using the following amounts: 4-amino aniline (0.50 g, 4.63 mmol), **4b** (4.45 g, 9.26 mmol), $NaNO_2$ (0.77 g, 11.11 mmol), in HCl 1 N/water (10 mL), to afford **10c** (4.49 g, 92%) as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=6.42 (m, 4H), 5.11–4.55 (m, 4H, both anomers), 4.31–4.16 (m, 12H, both anomers), 3.88–3.79 (m, 12H, both anomers), 3.44–3.41 (m, 4H, both anomers), 1.28 (t, J=7.4 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 5 for the glycidic part and δ=168.7, 164.5, 136.3, 133.6, 120.5, 60.9, 14.8 ppm. MS (ESI): m/z=1091.54 $[M+1]^+$. $C_{42}H_{58}N_8O_{26}$ (1090.35): calcd C, 46.24; H, 5.36; N, 10.27; found: C, 46.33; H, 5.43; N, 10.37.

*4.6.4. Synthesis of the dye **10d**.* The dye **10d** was prepared according to the general procedure E using the following amounts: 4-amino aniline (0.50 g, 4.63 mmol), **3b** (4.44 g, 9.26 mmol), $NaNO_2$ (0.77 g, 11.11 mmol), in HCl 1 N/water (10 mL), to afford **10d** (4.77 g, 93%) as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=6.44 (m, 4H), 5.11–4.54 (m, 4H, both anomers), 4.32–4.16 (m, 8H, both anomers), 3.87–3.77 (m, 12H, both anomers), 3.45–3.41 (m, 4H, both anomers), 2.28 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=168.5, 148.5, 133.4, 128.4, 120.4, 13.4 ppm. MS (ESI): m/z=975.53 $[M+1]^+$. $C_{38}H_{54}N_8O_{22}$ (974.34): calcd C, 46.82; H, 5.58; N, 11.49; found: C, 46.94; H, 5.64; N, 11.53.

*4.6.5. Synthesis of the dye **11a**.* The product **11a** was prepared according to the general procedure E using the following amounts: 4-amino aniline (0.50 g, 4.63 mmol), **5a** (2.43 g, 9.26 mmol), $NaNO_2$ (0.77 g, 11.11 mmol), in HCl 1 N/water (10 mL), to afford **11a** (2.88 g, 96%) as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=6.55 (m, 4H), δ=5.28–5.21 (d, 2H), 3.82–3.61 (m, 8H), 3.47–3.30 (m, 4H) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=168.2, 159.4, 136.7, 133.1, 120.2 ppm. MS (ESI): m/z=655.35 $[M+1]^+$. $C_{24}H_{30}N_8O_{14}$ (654.19): calcd: C, 44.04; H, 4.62; N, 17.12; found: C, 44.17; H, 4.72; N, 17.23.

*4.6.6. Synthesis of the dye **11b**.* The product **11b** was prepared according to the general procedure E using the following amounts: 4-amino aniline (0.50 g, 4.63 mmol), **5b** (2.42 g, 9.26 mmol), $NaNO_2$ (0.77 g, 11.11 mmol), in HCl 1 N/water (10 mL), to afford **11a** (4.16 g, 92%) as a mixture of α- and β-pyranosic anomers. ^{1}H NMR (200 MHz, Me_2SO): δ=6.56 (m, 4H), 5.10–4.55 (m, 4H, both anomers), 4.31–4.16 (m, 8H, both anomers), 3.88–3.79 (m, 12H, both anomers), 3.44–3.41 (m, 4H, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=168.4, 159.4, 136.5, 133.6, 120.4 ppm. MS (ESI): m/z=978.29 $[M+1]^+$. $C_{36}H_{50}N_8O_{24}$ (979.36): calcd C, 44.17; H, 5.15; N, 11.45; found: C, 44.22; H, 5.25; N, 11.64.

4.7. General procedure F: synthesis of the azoic dyes 8a–d and 9a,b

To a solution of sugar 4-amino-pyrazolidine-3,5-dione **5″a**,**b** or sugar 4-amino-pyrazolidine-5-dione **3″a**,**b**, **4″a**,**b** derivatives (1 mol) in 15 mL of water/HCl 1 N 15:1.5, a solution of $NaNO_2$ (1.2 mol) in water (2 mL) was added drop wise at 0 C° and the resulting mixture was stirred for 30 min. The diazonium salt solution previously prepared was added drop wise to the solution of sugar pyrazolidine-3,5-dione derivatives or sugar pyrazolidine-5-dione derivatives (1 mmol) in water (3 mL) and the combined solution was maintained at 0 C° for 6 h with stirring. After this time the resulting mixture was filtered and the resulting solution was purified by precipitation with ethanol to yield the corresponding azo dyes **8a**–**d** and **9a**,**b**.

*4.7.1. Synthesis of the dye **8a**.* The product **8a** was prepared according to the general procedure F using the following amounts: **4″a** (1.00 g, 2.99 mmol), **4a** (0.95 g, 2.99 mmol), $NaNO_2$ (0.24 g, 3.60 mmol), in HCl 1 N/water (10 mL), to afford **8a** (1.86 g, 94%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.20 (d, 2H), 4.27 (q, J=7.2 Hz, 4H, CH_2), 3.82–3.61 (m, 9H), 3.47–3.31 (m, 4H), 1.31 (t, J=7.2 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=171.2, 168.5, 163.6, 149.6, 135.9, 61.4, 60.2, 14.3 ppm. MS (ESI): m/z=663.35 $[M+1]^+$. $C_{24}H_{34}N_6O_{16}$ (662.21): calcd C, 43.51; H, 5.17; N, 12.68; found: C, 43.58; H, 5.27; N, 12.75.

*4.7.2. Synthesis of the dye **8b**.* The product **8b** was prepared according to the general procedure F using the following amounts: **3″a** (1.00 g, 3.62 mmol), **3a** (0.94 g, 3.62 mmol), $NaNO_2$ (0.28 g, 4.34 mmol), in HCl 1 N/water (10 mL), to afford **8b** (1.83 g, 93%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.21 (d, 2H), 3.82–3.61 (m, 9H), 3.47–3.31 (m, 4H), 2.33 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=171.6, 168.7, 155.7, 148.4, 128.6, 66.9, 19.5, 13.4 ppm. MS (ESI): m/z=547.34 $[M+1]^+$. $C_{20}H_{30}N_6O_{12}$ (546.19): calcd C, 43.96; H, 5.53; N, 15.38; found: C, 44.08; H, 5.63; N, 15.44.

*4.7.3. Synthesis of the dye **8c**.* The product **8c** was prepared according to the general procedure F using the following amounts: **4″b** (1.00 g, 2.01 mmol), **4b** (0.95 g, 2.01 mmol), $NaNO_2$ (0.16 g, 2.41 mmol), in HCl 1 N/water (10 mL), to afford **8c** (1.83 g, 94%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.55 (m, 4H, both anomers), 4.31–4.16 (m, 12H, both anomers), 3.88–3.79 (m, 13H, both anomers), 3.44–3.41 (m, 4H, both anomers), 1.31 (t, J=6.6 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=171.4, 168.5, 163.7, 149.9, 135.8, 61.4, 60.2, 14.1 ppm. MS (ESI): m/z=987.46 $[M+1]^+$. $C_{36}H_{54}N_6O_{26}$ (986.31): calcd C, 43.82; H, 5.52; N, 8.52; found: C, 43.98; H, 5.64; N, 8.66.

*4.7.4. Synthesis of the dye **8d**.* The product **8d** was prepared according to the general procedure F using the following amounts: **3″b** (1.00 g, 2.28 mmol), **3b** (0.94 g, 2.28 mmol), $NaNO_2$ (0.17 g, 2.74 mmol), in HCl 1 N/water (10 mL), to afford **8d** (1.83 g, 93%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.54 (m, 4H, both anomers), 4.32–4.16 (m, 8H, both anomers), 3.88–3.79 (m, 13H, both anomers), 3.43–3.40 (m, 4H, both anomers), 2.35 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the

glycidic part and δ=171.7, 168.7, 155.5, 148.5, 128.8, 66.8, 19.8, 13.6 ppm. MS (ESI): *m*/*z*=871.48 $[M+1]^+$. $C_{32}H_{50}N_6O_{22}$ (870.30): calcd C, 44.14; H, 5.79; N, 9.65; found: C, 44.22; H, 5.84; N, 9.75.

*4.7.5. Synthesis of the dye **9a**.* The product **9a** was prepared according to the general procedure F using the following amounts: **5′′a** (1.00 g, 3.59 mmol), **5a** (0.95 g, 3.59 mmol), $NaNO_2$ (0.28 g, 4.31 mmol), in HCl 1 N/water (10 mL), to afford **8d** (1.88 g, 95%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.21 (d, 2H), 4.48 (s, 1H), 3.82–3.62 (m, 8H), 3.47–3.31 (m, 4H) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=170.4, 168.6, 168.2, 159.5, 136.7, 83.8 ppm. MS (ESI): *m*/*z*=551.32 $[M+1]^+$. $C_{18}H_{26}N_6O_{14}$ (550.15): calcd C, 39.28; H, 4.76; N, 15.27; found: C, 39.33; H, 4.84; N, 15.34.

*4.7.6. Synthesis of the dye **9b**.* The product **9b** was prepared according to the general procedure F using the following amounts: **5′′b** (1.00 g, 2.28 mmol), **5b** (0.94 g, 2.28 mmol), $NaNO_2$ (0.28 g, 2.74 mmol), in HCl 1 N/water (10 mL), to afford **8d** (1.77 g, 95%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.55 (m, 4H, both anomers), 4.46 (s, 1H), 4.31–4.16 (m, 8H, both anomers), 3.88–3.78 (m, 12H, both anomers), 3.44–3.40 (m, 4H, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=170.5, 168.6, 168.1, 159.6, 136.8, 83.7 ppm. MS (ESI): *m*/*z*=875.37 $[M+1]^+$. $C_{30}H_{46}N_6O_{24}$ (874.26): calcd C, 41.19; H, 5.30; N, 9.61; found: C, 41.26; H, 5.38; N, 9.72.

4.8. General procedure G: synthesis of the H-chromophore dyes 6a–d and 7a,b

To a solution of sugar pyrazolidine-3,5-dione **5a**,**b** or sugar pyrazolidine-5-one derivatives **3a**,**b**, **4a**,**b** (1 mol) in DMSO (15 mL), a solution of NaH (2 mol) in THF (2 mL) was added drop wise at 0 C° and the resulting mixture was stirred for 30 min sugar 4,4-dibromo-pyrazolidine-3,5-dione **12a**–**d** or sugar 4,4-dibromo-pyrazolidine-5-one **13a**–**d**, **14a**–**d** derivatives (1 mmol) was dissolved in DMSO (3 mL) and added to the first solution and the resulting mixture was stirred at room temperature for 12 h. After this time, the resulting mixture was filtered and the resulting solution was purified by precipitation with ethanol to yield the corresponding H-chromophore dyes **6a**–**d** and **7a**,**b**.

*4.8.1. Synthesis of the dye **6a**.* The product **6a** was prepared according to the general procedure G using the following amounts: **14a** (1.00 g, 2.10 mmol), **4a** (0.67 g, 2.10 mmol), NaH (0.06 g, 2.10 mmol) to afford **6a** (1.26 g, 95%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.29–5.21 (d, 2H), 4.24 (q, *J*=7.2 Hz, 4H, CH_2), 3.82–3.61 (m, 8H), 3.47–3.30 (m, 4H), 1.30 (t, *J*=7.2 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=165.4, 163.2, 143.9, 137.3, 61.8, 14.1 ppm. MS (ESI): *m*/*z*=633.29 $[M+1]^+$. $C_{24}H_{32}N_4O_{16}$ (632.18): calcd C, 45.57; H, 5.10; N, 8.86; found: C, 45.63; H, 5.17; N, 8.94.

*4.8.2. Synthesis of the dye **6b**.* The product **6b** was prepared according to the general procedure G using the following amounts: **13a** (1.00 g, 2.40 mmol), **3a** (0.67 g, 2.40 mmol), NaH (0.06 g, 2.40 mmol) to afford **6b** (1.18 g, 97%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.29–5.21 (d, 2H), 3.82–3.61 (m, 8H), 3.47–3.30 (m, 4H), 2.32 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=165.6, 147.7, 143.4, 13.8 ppm. MS (ESI): *m*/*z*=517.31 $[M+1]^+$. $C_{20}H_{28}N_4O_{12}$ (516.18): calcd C, 46.51; H, 5.46; N, 10.85; found: C, 46.58; H, 5.52; N, 10.94.

*4.8.3. Synthesis of the dye **6c**.* The product **6c** was prepared according to the general procedure **G** using the following amounts: **14b** (1.00 g, 1.56 mmol), **4b** (0.67 g, 1.56 mmol), NaH (0.04 g, 1.56 mmol) to afford **6a** (1.40 g, 94%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.55 (m, 4H, both anomers), 4.31–4.16 (m, 12H, both anomers), 3.88–3.79 (m, 12H, both anomers), 3.44–3.41 (m, 4H, both anomers), 1.28 (t, *J*=7.0 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=165.5, 1632, 148.7, 137.6, 61.7, 14.0 ppm. MS (ESI): *m*/*z*=957.36 $[M+1]^+$. $C_{36}H_{52}N_4O_26$ (956.29): calcd C, 45.19; H, 5.48; N, 5.86; found: C, 45.25; H, 5.54; N, 5.94.

*4.8.4. Synthesis of the dye **6d**.* The product **6d** was prepared according to the general procedure G using the following amounts: **13b** (1.00 g, 1.73 mmol), **3b** (0.73 g, 1.73 mmol), NaH (0.04 g, 1.73 mmol) to afford **6d** (1.18 g, 97%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.54 (m, 4H, both anomers), 4.31–4.15 (m, 8H, both anomers), 3.88–3.78 (m, 12H, both anomers), 3.44–3.41 (m, 4H, both anomers), 2.30 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=165.7, 147.8, 143.6, 13.7 ppm. MS (ESI): *m*/*z*=840.39 $[M+1]^+$. $C_{32}H_{48}N_4O_{22}$ (840.28): calcd C, 45.71; H, 5.75; N, 6.66; found: C, 45.78; H, 5.84; N, 6.76.

*4.8.5. Synthesis of the dye **7a**.* The product **7a** was prepared according to the general procedure G using the following amounts: **12a** (1.00 g, 2.39 mmol), **5a** (0.62 g, 2.39 mmol), NaH (0.05 g, 2.39 mmol) to afford **7a** (1.26 g, 95%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.28–5.21 (d, 1H), 3.82–3.61 (m, 4H), 3.47–3.30 (m, 2H), ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 6 in Supplementary data for the glycidic part and δ=163.9, 163.1, 149.3 ppm. MS (ESI): *m*/*z*=521.31 $[M+1]^+$. $C_{18}H_{24}N_4O_{14}$ (520.13): calcd C, 41.54; H, 4.65; N, 10.77; found: C, 41.63; H, 4.73; N, 10.83.

*4.8.6. Synthesis of the dye **7b**.* The product **7b** was prepared according to the general procedure G using the following amounts: **12b** (1.00 g, 1.72 mmol), **5b** (0.73 g, 1.72 mmol), NaH (0.04 g, 1.72 mmol) to afford **7a** (1.26 g, 95%). ^{1}H NMR (200 MHz, Me_2SO): δ=5.10–4.55 (m, 2H, both anomers), 4.31–4.16 (m, 4H, both anomers), 3.88–3.79 (m, 6H, both anomers), 3.44–3.41 (m, 2H, both anomers) ppm. ^{13}C NMR (50 MHz, Me_2SO): see Table 7 in Supplementary data for the glycidic part and δ=163.7, 163.3, 149.3 ppm. MS (ESI): *m*/*z*=845.41 $[M+1]^+$. $C_{30}H_{44}N_4O_{24}$ (844.23): calcd C, 42.66; H, 5.25; N, 6.63; found: C, 42.74; H, 5.32; N, 6.70.

*4.8.7. Synthesis of dye **15a**.* The product **15a** was prepared according to the general procedure G. ^{1}H NMR (200 MHz, Me_2SO): 4.24 (q, *J*=7.2 Hz, 4H, CH_2), 1.30 (t, *J*=7.2 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=174.5, 163.6, 143.7, 137.6, 61.4, 14.2 ppm. MS (ESI): *m*/*z*=309.22 $[M+1]^+$. $C_{12}H_{12}N_4O_6$ (308.08): calcd C, 46.76; H, 3.92; N, 18.18; found: C, 46.83; H, 4.12; N, 18.23.

*4.8.8. Synthesis of dye **15b**.* The product **15b** was prepared according to the general procedure G. ^{1}H NMR (200 MHz, Me_2SO): 2.34 (s, –H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=174.3, 147.8, 143.6, 13.8 ppm. MS (ESI): *m*/*z*=337.22 $[M+1]^+$. $C_8H_8N_4O_2$ (192.06): calcd C, 50.00; H, 4.20; N, 29.15; found: C, 50.11; H, 4.28; N, 29.23.

*4.8.9. Synthesis of dye **16**.* The product **16** was prepared according to the general procedure G. ^{1}H NMR (200 MHz, Me_2SO): 2.34 (s, –H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=163.5, 149.5 ppm. MS (ESI): *m*/*z*=197.19 $[M+1]^+$. $C_6H_4N_4O_4$ (196.02): calcd C, 36.74; H, 2.06; N, 28.57; found: C, 36.82; H, 2.11; N, 28.62.

4.9. Synthesis of dye 17a

The product **17a** was prepared according to the general procedure F. ^{1}H NMR (200 MHz, Me_2SO): 4.45 (s, 1H), 4.25 (q, *J*=6.9 Hz,

4H, CH_2), 1.30 (t, J=6.9 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=173.3, 163.3, 161.2, 149.4, 136.5, 136.7, 62.8, 61.4, 14.1 ppm. MS (ESI): m/z=339.28 $[M+1]^+$. $C_{12}H_{14}N_6O_6$ (338.10): calcd C, 42.61; H, 4.17; N, 24.84; found: C, 42.75; H, 4.22; N, 24.94.

4.10. Synthesis of dye 17b

The product **17b** was prepared according to the general procedure F. ^{1}H NMR (200 MHz, Me_2SO): 4.46 (s, 1H), 2.33 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=173.4, 161.5, 155.3, 148.8, 128.5, 69.8, 14.2 ppm. MS (ESI): m/z=223.26 $[M+1]^+$. $C_8H_{10}N_6O_2$ (222.09): calcd C, 43.24; H, 4.54; N, 37.82; found: C, 43.33; H, 4.62; N, 37.93.

4.11. Synthesis of dye 18

The product **18** was prepared according to the general procedure F. ^{1}H NMR (200 MHz, Me_2SO): 4.49 (s, 1H) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=170.4, 168.4, 136.3, 85.1 ppm. MS (ESI): m/z=227.22 $[M+1]^+$. $C_6H_6N_6O_4$ (226.05): calcd C, 31.87; H, 2.67; N, 37.16; found: C, 31.95; H, 2.76; N, 37.25.

4.12. Synthesis of dye 19a

The product **19a** was prepared according to the general procedure E. ^{1}H NMR (200 MHz, Me_2SO): 6.91 (m, 4H), 4.26 (q, J=6.6 Hz, 4H, CH_2), 1.28 (t, J=6.6 Hz, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=163.6, 161.1, 136.1, 133.7, 120.6, 60.9, 13.8 ppm. MS (ESI): m/z=443.28 $[M+1]^+$. $C_{18}H_{18}N_8O_6$ (442.13): calcd C, 48.87; H, 4.10; N, 25.33; found: C, 48.94; H, 4.21; N, 25.43.

4.13. Synthesis of dye 19b

The product **19b** was prepared according to the general procedure E. ^{1}H NMR (200 MHz, Me_2SO): 6.90 (m, 4H), 2.29 (s, 6H, CH_3) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=161.4, 148.4, 133.6, 128.7, 120.3, 13.2 ppm. MS (ESI): m/z=327.31 $[M+1]^+$. $C_{14}H_{14}N_8O_2$ (326.12): calcd C, 51.53; H, 4.32; N, 34.34; found: C, 51.63; H, 4.42; N, 34.47.

4.14. Synthesis of dye 20

The product **20** was prepared according to the general procedure E. ^{1}H NMR (200 MHz, Me_2SO): 6.88 (m, 4H) ppm. ^{13}C NMR (50 MHz, Me_2SO): δ=168.9, 136.6, 133.3, 120.6 ppm. MS (ESI): m/z=331.27 $[M+1]^+$. $C_{12}H_{10}N_8O_4$ (330.08): calcd C, 43.64; H, 3.05; N, 33.93; found: C, 43.77; H, 3.17; N, 34.11.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.01.038.

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