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The synthesis and properties of asymmetrically substituted 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonic acid derivatives as fluorescent brighteners

Joon-Kyun Lee[a], Seong-il Um[a], Yonghan Kang[a,*], Dae-jin Baek[b]

[a]*Department of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do 426-791, South Korea*
[b]*Department of Chemistry, Hanseo University, Soesan, Choongchungnam-do 356-706, South Korea*

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Abstract

Disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives (**9a–i**) which were asymmetrically substituted with various nucleophilic substituents on triazine moiety were prepared. The obtained compounds were characterized by the analysis of the proton NMR spectrum and confirmed by UV spectrum. The physical properties of the derivatives were performed by fastness test and whiteness measurement. The chlorinated water fastness, rubbing fastness, and light fastness of newly synthesized compounds (**9a–i**) were investigated and compared with **CI86**.

Keywords: Fluorescent brightener; Stilbene; Whiteness; Asymmetrical

1. Introduction

Most of the raw materials were treated with the chemical oxidant to remove their colors. But chemical bleaching method could not completely remove a small quantity of yellowness. Fluorescent brighteners were used as functional pigment in the process of the chemical bleaching to the fiber, paper and pulp in order to make them appear brighter. They increased the whiteness by a process of absorption of the light in ultraviolet region (330–380 nm) and emission of the visible blue light (400–450 nm) [1–6]. In 1929, Krais found fluorescent substance in the Esculin solvent, which was used to bleach the linen, and then the concept of fluorescent brightener was introduced from that.

Various disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives which were symmetrically substituted on both triazine moiety were used as fluorescent brighteners for wool and cotton.

We now report the full details of syntheses of the asymmetrically substituted, on triazine moiety, disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives (**9a–i**). The newly synthesized compounds (**9a–i**) were prepared from the 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (**1**) in 7 steps with 75–89% overall yield. The structure of obtained compounds was characterized by analysis of the proton NMR spectrum and confirmed by UV spectrum. The physical properties were performed by fastness test and whiteness measurement.

2. Results and discussions

2.1. Synthesis of dyes

Nine dyes (**9a–i**) were synthesized by the conventional method [7]. Relevant data are given in Tables 1 and 2. The synthetic procedures of 4-amino-4′-(2-amino-4-anilino-1,3,5-triazin-6-yl)aminostilbene-2,2′-disulfonate (**6**) as an intermediate are summarized in Scheme 1.

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* Corresponding author. Tel.: +82-31-400-5495.
E-mail address: yhmkang@hanyang.ac.kr (Y. Kang).

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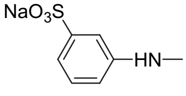
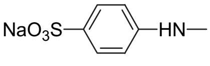
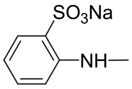
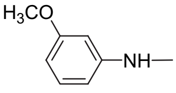
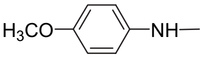
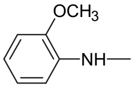
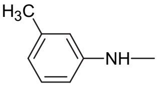
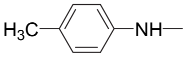
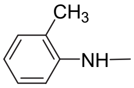
Table 1
Characterization data of the asymmetrically substituted stilbene fluorescent brighteners (**9a–i**)

Entry	R	Yield (%)	UV(λ_{max}) (nm, in MeOH)
9a		86	351, 261
9b		96	352, 268
9c		92	351, 264
9d		80	351, 263
9e		82	351, 267
9f		80	351, 255
9g		95	351, 260
9h		99	351, 262
9i		95	352, 243

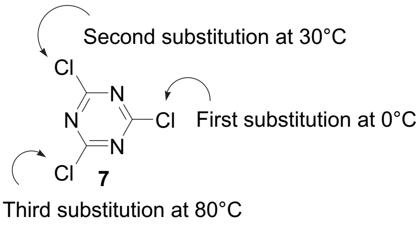
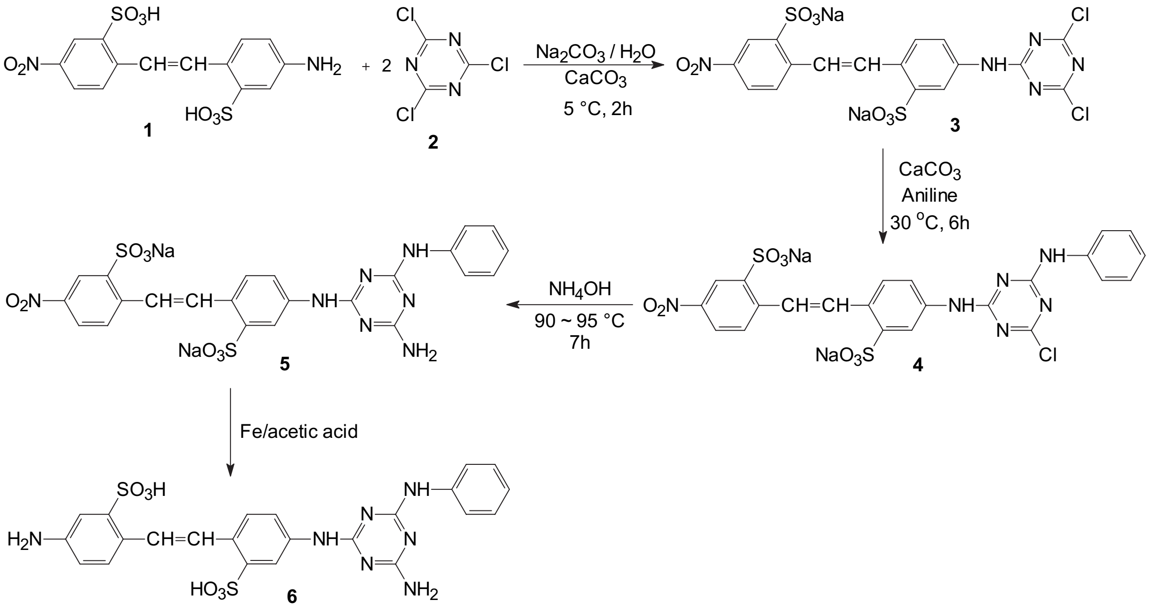


Fig. 1. Differential reactivity of 2,4,6-trichloro-1,3,5-triazine (**2**).

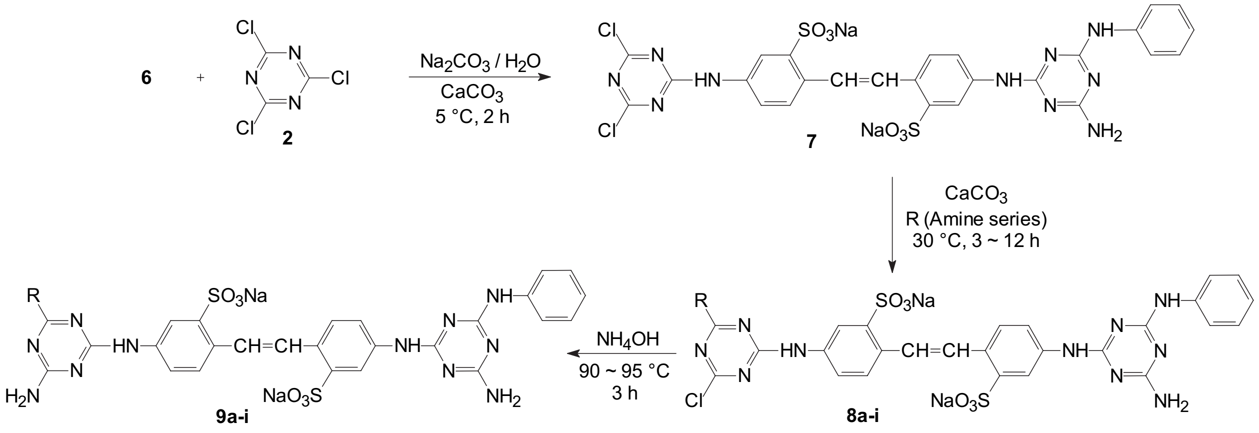
Compound (**6**) was prepared from the reaction of 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (**1**) with 2,4,6-trichloro-1,3,5-triazine (**2**). Three chloro groups showed different chemical reactivities with nucleophiles depending on the reaction temperature [8,9] (Fig. 1).

After stirring 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (**1**) with 2,4,6-trichloro-1,3,5-triazine (**2**) at 5 °C, the resulting disodium 4-(2,4-dichloro-1,3,5-triazin-6-yl) amino-4′-nitrostilbene-2,2′-disulfonate (**3**) was treated with aniline at 30 °C without separation. Finally, ammonia water was added in situ to the reaction mixture. The third substitution reaction occurred when the temperature reached 80 °C and the intermediate (**4**), disodium 4-(2-anilino-4-chloro-1,3,5-triazin-6-yl)amino-4′-nitrostilbene-2,2′-disulfonate, was converted into 4-(2-amino-4-anilino-1,3,5-triazin-6-yl)amino-4′-nitrostilbene-2,2′-disulfonate (**5**). The reduction of 4′-nitro group of compounds (**5**) to amino group by using the iron powder in acidic medium afforded 4′-amino-4-(2-amino-4-anilino-1,3,5-triazin-6-yl)aminostilbene-2,2′-disulfonic acid (**6**) with 88% overall yield from the starting material (**1**).

The synthetic pathways of the final products (**9a–i**) from the intermediate (**6**) are shown in Scheme 2, yield and their photophysical properties are presented in Table 1. According to the procedure previously



Scheme 1.



Scheme 2.

announced for the synthesis of (**6**), the final products (**9a–i**) were obtained.

2.2. Dyeing procedure

Dyeing of cotton was carried out precisely at 80 °C for 1 h. It was prepared with a paste of finely powdered dye, 0.1% aq. NaOH and water at 40 °C and the temperature was raised to 80 °C for cotton at the rate of 1 °C/min.

2.3. Fastness properties

The washing fastness was assessed by using multi-specimen (acetate, cotton, nylon, polyester, acryl, wool) in accordance with ISO 105-C01. The light fastness test was assessed by using Xenon arc lamp method in accordance with ISO 105-B02, the rubbing fastness test was carried out using crock meter method in accordance with ISO 105-X12 and chlorinated water fastness test in accordance with KS K 0725.

2.4. Color assessment

Characteristics of the compounds (**9a–i**) were compared with **CI86** which are used for commercial purpose. The structures of **CI86** are shown in Fig. 2. The compounds (**9a–i**) were applied at a concentration of 0.05%, 0.1%, 0.3%, 0.5%, and 1.0% to 100% cotton by the previously described dyeing procedure. Color strength value (K/S) [10] of these compounds was highest at 0.1% concentration. The degree of the whiteness and the CIE $L^*a^*b^*$ coordinates were determined. The data obtained are presented in Table 2. It is apparent that most of the compounds impart a high degree of whiteness at 0.1% concentration with a series of the very pale purple. Their effect of whiteness increased in the order: **9c** < **9b** < **9a** < **9h** < **9d** < **9f** < **9i** < **9g** < **9e**. The data obtained are given in Table 2.

The compounds (**9a–i**) showed the same light fastness, lower fastness in the chlorinated water, and higher rubbing fastness than the corresponding values of **CI86**. The fastness data of the compounds (**9a–i**) are presented in Table 3. The washing fastness results are given in Table 4 and the compounds (**9a–i**) showed higher washing fastness than **CI86**.

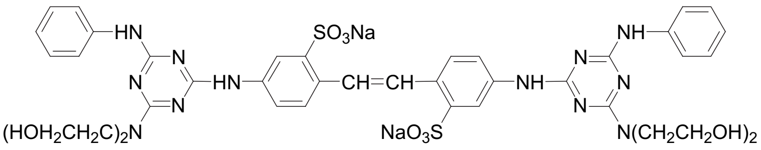
3. Conclusions

As the derivatives of **CI86**, asymmetrically substituted 1,3,5-triazinylstilbene derivatives were synthesized by using 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (**1**) as a starting material in 7 steps with 75–89% overall yield. Generally, the newly prepared compounds showed higher dyeing properties than **CI86**.

4. Experimental

4.1. Materials and analysis

All chemicals were used as purchased from commercial sources (Aldrich, Merck, Duksan, Yakuri, Junsei),



CI86

Fig. 2. The structure of **CI86**.

Table 2
Degree of whiteness and color data for 100% cotton treated with the compounds (**9a–i**)

No.	o.w.f (%)	Whiteness	L^*	a^*	b^*	No.	o.w.f (%)	Whiteness	L^*	a^*	b^*
CI86	0.05	123.69	91.91	2.55	−9.06	**9e**	0.05	110.72	91.59	2.07	−6.49
	0.1	132.07	91.77	2.78	−10.75		0.1	115.95	91.82	2.40	−7.44
	0.3	141.05	92.52	2.17	−12.00		0.3	107.85	90.82	2.63	−6.01
	0.5	142.28	92.85	1.52	−11.90		0.5	96.50	90.54	2.76	−3.69
	1	138.00	93.02	0.22	−10.56		1	73.50	89.56	3.36	0.68
9a	0.05	91.14	90.65	1.45	−2.83	**9f**	0.05	109.48	91.34	2.14	−6.35
	0.1	98.77	91.28	1.85	−4.16		0.1	112.45	90.88	2.54	−7.12
	0.3	99.44	90.92	2.66	−4.44		0.3	112.04	91.26	2.85	−6.74
	0.5	95.47	90.62	3.00	−3.70		0.5	103.79	91.10	3.03	−5.04
	1	81.91	89.98	3.72	−1.24		1	81.71	89.82	3.55	−0.95
9b	0.05	85.12	90.88	0.90	−1.45	**9g**	0.05	112.09	91.07	2.27	−6.95
	0.1	91.19	90.65	1.42	−2.84		0.1	113.82	91.48	2.56	−7.09
	0.3	99.99	91.11	2.30	−4.47		0.3	99.88	91.03	2.97	−4.20
	0.5	94.85	90.75	2.68	−3.53		0.5	84.47	90.22	3.22	−1.31
	1	87.40	90.14	3.31	−2.22		1	56.50	88.68	4.39	3.73
9c	0.05	78.51	90.57	0.44	−0.16	**9h**	0.05	104.18	91.27	1.90	−5.26
	0.1	84.24	90.34	0.93	−1.46		0.1	107.61	91.39	2.19	−5.89
	0.3	93.31	90.64	1.78	−3.21		0.3	101.35	91.05	2.57	−4.62
	0.5	94.03	90.71	2.19	−3.32		0.5	92.42	90.50	2.87	−2.96
	1	87.37	90.07	2.98	−2.19		1	68.00	89.22	3.6	1.54
9d	0.05	107.42	91.58	1.83	−5.76	**9i**	0.05	108.98	91.31	2.13	−6.25
	0.1	109.59	91.39	2.04	−6.22		0.1	113.36	91.37	2.42	−7.08
	0.3	101.24	90.56	2.22	−4.64		0.3	110.56	91.13	2.70	−6.42
	0.5	93.76	90.67	2.19	−2.97		0.5	101.13	90.53	2.76	−4.62
	1	68.39	89.58	2.53	1.87		1	79.76	89.86	3.27	−0.42

which were of analytical grade. The solvents were purified by distillation and the other reagents were used without further purification. The ^{1}H NMR spectra were measured at 300 MHz using a Varian Mercury 300. The UV spectra were obtained on a Shimadzu UV-2401PC. TLC was carried out by using Merck silica gel plates (F_{254}) with distilled solvents by using a mixture of $MEK:DEA:NH_4OH = 3:3:1$ (v/v) as an eluent. Light fastness results were obtained on a Xenotest 150S. Washing fastness and chlorinated water fastness results were obtained on an Atras LP2. Rubbing fastness was measured on an Atras CM-5. The computer color matching (CCM) data were obtained on a SF600 Data color.

Table 3
Various fastness data of 100% cotton fiber dyed with the compounds (**9a–i**)

Compound	Chlorinated water fastness	Light fastness	Rubbing fastness	
			Dry	Wet
CI86	3	2	3–4	2
9a	2	2	4	3
9b	2–3	2	4	3
9c	2–3	2	4–5	4
9d	1–2	2	4–5	3
9e	2	2	4	3
9f	2	2	4	3
9g	2	2	4	2–3
9h	2	2	4–5	3
9i	2–3	2	4	3

4.2. Synthesis of the compounds

*4.2.1. Synthesis of 4′-amino-4-(2-amino-4-anilino-1,3,5-triazin-6-yl)aminostilbene-2,2′-disulfonic acid (**6**)*

To a stirred suspension of cyanuric chloride (**2**, 7.6 g, 40 mmol), $CaCO_3$ (2 g, 20 mmol) and small amounts of dispersant agent in water (40 mL) was added a solution of 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (**1**, 24.6 g, 40 mmol, 66.4%) and Na_2CO_3 (4.24 g, 40 mmol) in water (400 mL) at 0 °C. After addition was completed, the reaction mixture was stirred for 2 h below 5 °C. To the reaction mixture were added $CaCO_3$ (2 g, 20 mmol), antifoaming agent and aniline (3.72 mL, 40 mmol) and then allowed to warm to 30 °C. After being stirred at 30 °C for 6 h, ammonium water (30 mL,

Table 4
The washing fastness of 100% cotton fiber dyed with the compounds (**9a–i**)

Compound	Acetate	Cotton	Nylon	PET	Acrylic	Wool
CI86	4–5	1	3	4–5	4–5	4–5
9a	4–5	1–2	4	4–5	4–5	4–5
9b	4	2	4–5	4–5	4–5	4–5
9c	4–5	2	4–5	4–5	4–5	4–5
9d	4	1	4–5	4–5	4–5	4–5
9e	4	1	4–5	4–5	4–5	4–5
9f	4	1–2	4–5	4–5	4–5	4–5
9g	4–5	1	4–5	4–5	4–5	4–5
9h	4–5	1–2	4–5	4–5	4–5	4–5
9i	4	1–2	4–5	4–5	4–5	4–5

25%) was added to a reaction mixture and then heated at 90–95 °C for 7 h. The resulting 4-(2-amino-4-anilino-1,3,5-triazin-6-yl)amino-4-nitrostilbene-2,2′-disulfonate (**5**) was transferred to a 2 L beaker containing the iron powder (10 g) without further purification. The reaction mixture was stirred at 90 °C and acidified by addition of acetic acid. After the reduction was completed, the reaction mixture was adjusted to pH 10 by slow addition of 1 N NaOH solution. The insoluble solid was filtered off through Celite 545. The filtrate was adjusted to pH 4 with acetic acid and then heated till a clear solution was obtained. After being cooled to room temperature, the precipitate was filtered and dried to provide 4′-amino-4-(2-amino-4-anilino-1,3,5-triazin-6-yl)aminostilbene-2,2′-disulfonic acid (**6**, 18.9 g, 85%) as an orange powder.

*4.2.2. General method for the synthesis of disodium 4′-(2-amino-4-substituted-1,3,5-triazin-6-yl)amino-4-(2-amino-4-anilino-1,3,5-triazin-6-yl)aminostilbene-2,2′-disulfonate (**9a–i**)*

To a stirred suspension of cyanuric chloride (**2**, 4.43 g, 24 mmol), $CaCO_3$ (1.2 g, 12 mmol) and small amounts of dispersant agent in water (40 mL) was added a solution of 4′-amino-4-(2-amino-4-anilino-1,3,5-triazin-6-yl)aminostilbene-2,2′-disulfonic acid (**6**, 13.35 g, 24 mmol) and Na_2CO_3 (2.55 g, 24 mmol) in water (400 mL) at 0 °C. After addition was completed, the reaction mixture was stirred for 2 h below 5 °C. To the reaction mixture were added $CaCO_3$ (1.2 g, 20 mmol), antifoaming agent and amine derivative (24 mmol) and then allowed to warm to 30 °C. After being stirred at 30 °C for 6 h, ammonium water (30 mL, 25%) was added to a reaction mixture and then heated at 90–95 °C for 7 h. To the reaction mixture was added sodium chloride (45 g) and then allowed to cool to room temperature. The precipitate was filtered and dried to provide the compound (**9a–i**) as a sodium salt.

*4.2.2.1. Synthesis of the compound **9a***

Yields 86%; UV (351, 261 nm); ^{1}H NMR[DMSO] δ 6.70 (s, 2H, $-NH_2$), 6.96 (t, 1H, ArH), 7.27 (m, 5H, ArH), 7.59 (d, 2H, ArH), 7.64 (s, 1H, ArH), 7.79 (s, 2H, $-CH{=}CH-$), 7.83 (d, 3H, ArH), 8.02 (s, 3H, ArH), 8.18 (s, 2H, $-NH_2$), 9.35 (m, 3H, $-NH$), 11.17 (s, 1H, $-NH$).

*4.2.2.2. Synthesis of the compound **9b***

Yields 96%; UV (352, 268 nm); ^{1}H NMR[DMSO] δ 6.66 (d, 2H, $-NH_2$), 6.92 (t, 1H, ArH), 7.25 (t, 5H, ArH), 7.48 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.78 (s, 2H, $-CH{=}CH-$), 7.86 (d, 2H, ArH), 8.00 (s, 2H, ArH), 8.34 (d, 2H, $-NH_2$), 9.11 (m, 3H, $-NH$).

*4.2.2.3. Synthesis of the compound **9c***

Yields 92%; UV (351, 264 nm), ^{1}H NMR[DMSO] δ 6.59 (s, 2H, $-NH_2$), 6.92 (m, 4H, ArH), 7.25 (m, 5H, ArH), 7.58 (d, 2H, ArH), 7.77 (s, 2H, $-CH{=}CH-$), 7.86 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.24 (s, 2H, $-NH_2$), 9.05 (m, 3H, $-NH$).

*4.2.2.4. Synthesis of the compound **9d***

Yields 80%; UV (351, 263 nm); ^{1}H NMR[DMSO] δ 3.75 (s, 3H, $-CH_3$), 6.62 (s, 2H, $-NH_2$), 6.92 (t, 1H, ArH), 7.32 (t, 1H, ArH), 7.24 (m, 5H, ArH), 7.39 (d, 1H, ArH), 7.52 (d, 1H, ArH), 7.62 (d, 2H, ArH), 7.78 (s, 2H, $-CH{=}CH-$), 7.86 (d, 2H, ArH), 8.01 (s, 2H, $-NH_2$), 9.02 (m, 2H, $-NH$), 9.15 (s, 1H, $-NH$), 11.17 (s, 1H, $-NH$).

*4.2.2.5. Synthesis of the compound **9e***

Yields 82%; UV (351, 267 nm); ^{1}H NMR[DMSO] δ 3.74 (s, 3H, $-CH_3$), δ 6.60 (s, 2H, $-NH_2$), 6.89 (m, 5H, ArH), 7.25 (t, 2H, ArH), 7.51 (d, 1H, ArH), 7.61 (d, 1H, ArH), 7.71 (d, 2H, ArH), 7.83 (s, 2H, $-CH{=}CH-$), 7.85 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.24 (s, 2H, $-NH_2$), 8.89 (s, 1H, $-NH$), 9.04 (s, 1H, $-NH$), 9.16 (s, 1H, $-NH$), 10.06 (s,1H, $-NH$).

*4.2.2.6. Synthesis of the compound **9f***

Yields 80%; UV (351, 255 nm); ^{1}H NMR[DMSO] δ 3.87 (s, 3H, $-CH_3$), 6.73 (s, 2H, $-NH_2$), 7.01 (m, 5H, ArH), 7.25 (t, 2H, ArH), 7.49 (d, 2H, ArH), 7.58 (t, 2H, ArH), 7.78 (s, 2H, $-CH{=}CH-$), 7.86 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.24 (m, 2H, $-NH_2$), 9.05 (s, 2H, $-NH_2$), 9.16 (s, 1H, $-NH$), 9.28 (s, 1H, $-NH$).

*4.2.2.7. Synthesis of the compound **9g***

Yields 95%; UV (351, 260 nm); ^{1}H NMR[DMSO] δ 2.29 (s, 3H, $-CH_3$), 6.63 (s, 2H, $-NH_2$), 6.76 (d, 2H, ArH), 6.93 (t, 2H, ArH), 7.25 (m, 5H, ArH), 7.63 (d, 2H, ArH), 7.83 (s, 2H, $-CH{=}CH-$), 7.85 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.24 (s, 2H, $-NH_2$), 8.99 (m, 3H, $-NH$), 9.07 (s, 1H, $-NH$), 9.17 (s, 1H, $-NH$).

*4.2.2.8. Synthesis of the compound **9h***

Yields 99%; UV (351, 262 nm); ^{1}H NMR[DMSO] δ 2.28 (s, 3H, $-CH_3$), 6.66 (s, 2H, $-NH_2$), 7.07 (m, 5H, ArH), 7.25 (t, 1H, ArH), 7.52 (s, 1H, ArH), 7.58 (d, 2H, ArH), 7.71 (d, 2H, ArH), 7.78 (d, 2H, $-CH{=}CH-$), 7.85 (d, 2H, ArH), 8.01 (s, 2H, ArH), 8.23 (S, 2H, $-NH_2$) 8.97 (s, 1H, NH), 9.06 (s, 1H, NH), 9.18 (s, 1H, NH), 11.18 (s, 1H, NH).

*4.2.2.9. Synthesis of the compound **9i***

Yields 95%; UV (352, 243.5 nm); ^{1}H NMR[DMSO] δ 2.23 (s, 3H, $-CH_3$), 6.62 (s, 2H, $-NH_2$), 7.18 (m, 5H, ArH), 7.44 (d, 2H, ArH), 7.60 (d, 2H, ArH), 7.74 (d, 2H, ArH), 7.78 (d, 2H, $-CH{=}CH-$), 7.85 (d, 2H, ArH), 7.98 (s, 2H, ArH), 8.18 (s, 2H, $-NH_2$), 9.05 (s, 1H, NH), 9.16 (s, 1H, NH), 9.46 (s, 1H, NH).

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