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Synthesis and properties of heterocyclic monoazo dyes derived from 3-cyano-4-trifluoromethyl-6-substituted-2(1*H*)-pyridinethiones

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Abstract

The synthesis and properties of new heterocyclic monoazo dyes derived from polyfunctionally substituted 3-amino-4-trifluoromethyl-thieno[2,3-*b*]pyridines as diazo components are reported. By appropriate selection of substituents in the coupling components, dyes varying in hue from yellow to blue can be obtained. The dyes were applied to polyester; their spectral, fastness properties and colour assessment are reported.

Keywords: Synthesis; 3-Cyano-4-trifluoromethyl-2(1*H*)-pyridinethiones; 3-Amino-4-trifluoromethyl-thieno[2,3-*b*]pyridines; Disperse dyes; Fastness properties; Colour properties

1. Introduction

A number of azo dyes have been prepared from amino heterocycles and several patents describe the synthesis and technical importance of heterocyclic azo disperse dyes [1–6]. Azo disperse dyes derived from heterocyclic ring systems have many advantages, such as colour deepening effect as an intrinsic property of heterocyclic ring and resulting in good sublimation fastness of dyed fibers [7–8]. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afforded very electronegative diazo components and, consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [9–11]. 3-Cyano-2(1*H*)-pyridinethiones are of interest due to use as intermediates for the synthesis of the biologically active deazafolic acid and for deazaaminopterin ring synthesis [12–13]; they are also useful as central nerve depressants and in application in dyes [14–18].

We have previously reported the synthesis of novel heterocyclic systems such as 2-[[4-(arylazo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]-thieno[2,3-*b*]pyridines [19] and 3-(2-methyl-5,7-disubstituted-pyrazolo[1,5-*a*]pyrimidine-3-yl)azo-4,6-disubstituted-thieno[2,3-*b*]pyridine derivatives [20] and their application to polyester fibers as disperse dyes, which gave encouraging results. As a continuation of our previous work, we report here the synthesis of a series of new heterocyclic monoazo dyes derived from novel diazonium components, the polyfunctionally substituted 3-amino-4-trifluoromethyl-thieno[2,3-*b*]pyridines synthesized from 3-cyano-4-trifluoromethyl-6-substituted-2(1*H*)-pyridinethiones and their use as disperse dyes for polyester fibers. The spectral characteristics and dyeing properties of the dyes are also discussed.

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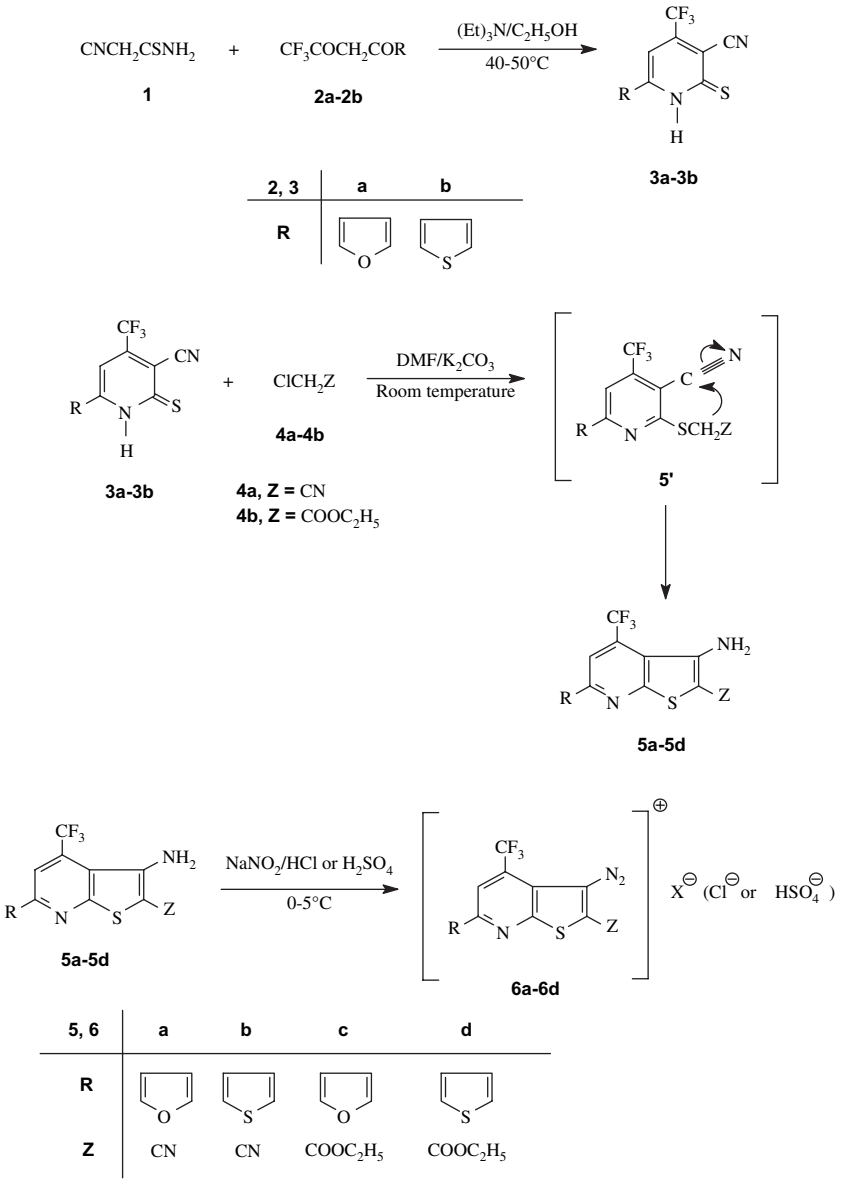
2. Results and discussion

2.1. Synthesis and spectral characteristics

The general route for the synthesis of 3-amino-2,6-disubstituted-4-trifluoromethyl-thieno[2,3-*b*]pyridine derivatives is outlined in Scheme 1. Reaction of 2-cyanothioacetamide **1** with unsymmetrical fluorinated 1,3-ketones such as 2-furoyltrifluoroacetone **2a** and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione **2b** in absolute ethanol in the presence of catalytic amount of triethylamine at 40–50 °C yielded the corresponding 3-cyano-4-trifluoromethyl-6-substituted-2(1*H*)-pyridinethione derivatives **3a** and **3b**, which were cyclized with appropriate alkylating agent **4a–4b** such as chloroacetonitrile and ethyl chloroacetate in DMF in the presence of excess potassium carbonate anhydrous at room temperature to form the nonisolable *S*-alkylated intermediate **5′**, which via nucleophilic substitution and intramolecular cyclocondensation gave the corresponding polyfunctionally substituted 3-amino-2,6-disubstituted-4-trifluoromethyl-thieno[2,3-*b*]pyridines **5a–5d** in good yields.

The structures of the new compounds **3a**, **3b** and **5a–5d** were established on the basis of their elemental analysis and spectral data. The IR spectra of the compounds **3a** and **3b** showed absorption at 2232 and 2225 cm^{-1} for the C≡N group, at 3135 and 3097 cm^{-1} for the NH group and at 1226 and 1202 cm^{-1} for the C=S group, respectively. The ^1H NMR spectra



Scheme 1.

(DMSO-d_6) of compounds **3a** and **3b** showed a broad singlet at δ 14.15–14.10 (b, 1H) assigned for the NH group and a singlet at δ 8.29–8.17 (s, 1H) assigned for the 5-H of the pyridinethione ring. Moreover, compound **3a** showed signal at δ 6.75 (dd, 1H), 7.35 (d, 1H) and 8.02 (d, 1H), which were assigned to the protons 4-H, 3-H and 5-H of furyl moiety and compound **3b** showed signal at δ 7.81 (dd, 1H), 7.84 (d, 1H) and 8.19 (d, 1H), which were assigned to the protons 4-H, 3-H and 5-H of thienyl moiety of the pyridinethione ring, respectively.

The IR spectra of compounds **5a–5d** revealed the absence of NH and C=S bands, and the amino group appears at 3526–3349 cm^{-1} in the form of two bands due to intramolecular association between the 3-NH_2 and 2-C≡N or 2-$COOC_2H_5$ group of compounds **5a–5d**, as observed in other cyclienamino ester [21]. The ^1H NMR spectra (DMSO-d_6) of compounds **5a–5d** showed a broad singlet at δ 6.57–6.21 (b, 2H) assigned for the NH_2 group and a singlet at δ 8.31–7.84 (s, 1H) assigned for the 5-H of the thieno[2,3-*b*]pyridine ring. Furthermore, the IR spectral of the compounds **5c** and **5d** revealed the absence of cyano group and the characteristic absorption band of the carbonyl group at 1684–1676 cm^{-1}. The ^1H NMR spectra (DMSO-d_6) of compounds **5c** and **5d** showed a triplet at δ 1.30 (t, 3H) and a quartet at δ 4.31 (q, 2H) assigned for the ethyl group ($-CH_2CH_3$), was also confirmed by the mass spectrum *m*/*z* 356 and 372 (M^+), respectively. Moreover, compound **5c** showed signals at δ 6.76 (dd, 1H), 7.52 (d, 1H) and 7.99 (d, 1H), which were assigned to the protons 4-H, 3-H and 5-H of furyl moiety and compound **5d** showed signals at δ 7.24 (dd, 1H), 7.84 (d, 1H) and 8.20 (d, 1H), which were assigned to the protons 4-H, 3-H and 5-H of thienyl moiety of the thieno[2,3-*b*]pyridine ring, respectively.

These new polyfunctionally substituted 3-amino-2,6-disubstituted-4-trifluoro-methyl-thieno[2,3-*b*]pyridines **5a–5d** were diazotised with cold hydrochloric acid and sodium nitrite, and with cold nitrosylsulphuric acid to afford the diazonium salts **6a–6d**, respectively (Scheme 1). These diazonium salts **6a–6d**, coupled with a variety of coupling components such as *N*, *N*-dimethylaniline **7**, *N*,*N*-bis(2-hydroxyethyl)aniline **8**, 2-amino-4-phenyl-thiazole **9** and 1-naphthylamine **11** in acidic medium at pH 4–5, as well as with β-naphthol **10** in basic medium at pH 8–9 yielded the corresponding 3-(aryl or hetaryl)azo-2,6-disubstituted-4-trifluoromethyl-thieno[2,3-*b*]pyridine dyes **12a–12j** and **13a–13j**, respectively (Scheme 2).

Dyes **12a–12j** and **13a–13j** were obtained generally in excellent yields (79–93%); the structures of these dyes were verified by elemental analysis and by spectroscopic methods (IR, Mass, and ^1H NMR). Physical and spectral data of dyes **12a–12j** and **13a–13j** are given in Tables 1 and 2.

2.2. Absorption spectral characteristics

The absorption maxima of the dyes **12a–12j** and **13a–13j** were measured in DMF solution and are shown in Table 3. The absorption maxima of the dyes **12a–12j** and **13a–13j** ranged from 465 to 589 nm and from 448 to 465 nm, respectively. It was observed in general that dyes **12a–12j** derived from compounds **6a–6b** were bathochromic when compared with analogous dyes **13a–13j** derived from compounds **6c–6d**. This bathochromic shift is attributed to the stronger electron-acceptor of the cyano group with respect to the electron-donating carboethoxy group at the 2-position of the thieno[2,3-*b*]pyridine ring, thus enhancing electron delocalisation in the dye molecule [22].

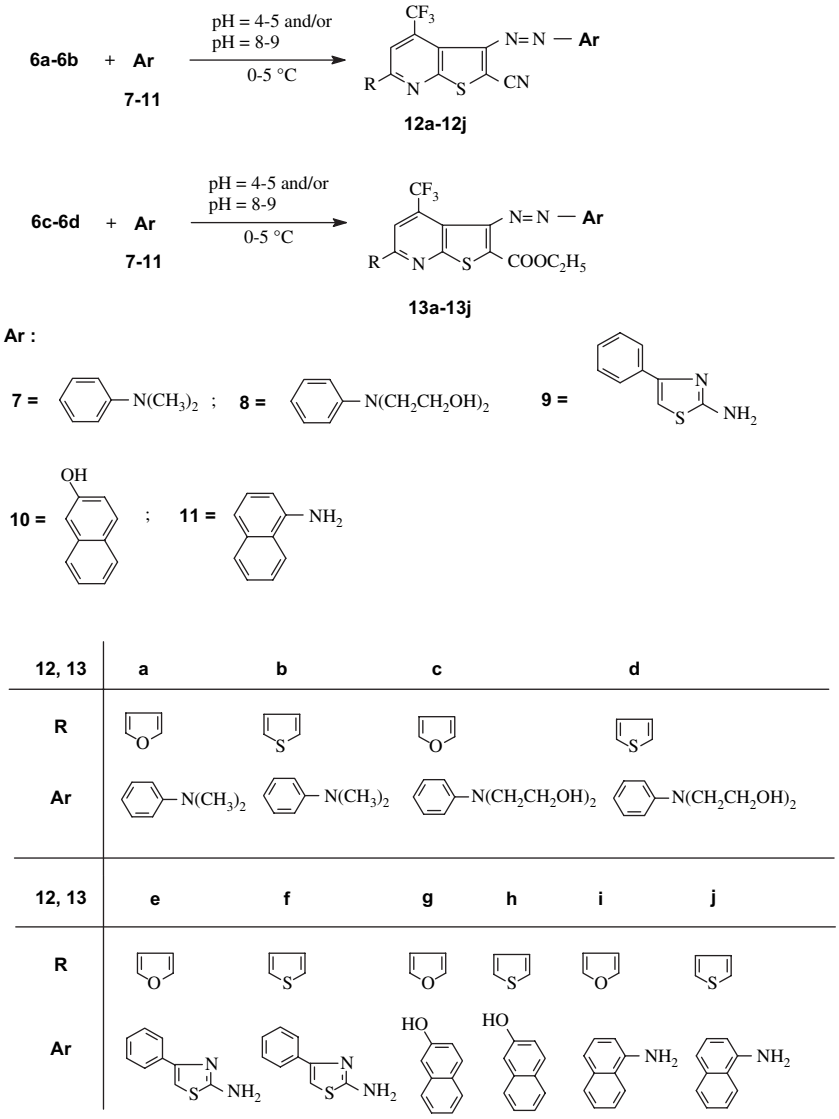
Colour shifts are in accord with variations resulting from changes in substituents in the coupling component observed in these dyes. Moreover, the introduction of further electron-donor substituents into the coupling component results in additional colour shifts. Thus, the introduction of the naphthylamine coupler into dyes **12i** (λ_{max} 589 nm) and **12j** (λ_{max} 587 nm) resulted in bathochromic shifts of 124 and 122 nm, respectively, compared to the dyes **12g** (λ_{max} 465 nm) and **12h** (λ_{max} 465 nm). The spectroscopic data also demonstrate that the dye **12b** (λ_{max} 528 nm) containing the thienyl moiety show a small bathochromic effect in comparison with the dye **12a** (λ_{max} 525 nm) containing the furyl moiety. The same effect is also observed in those of dyes. On the other hand, the inductive influence of substituent in the hydroxyethyl coupler gives bathochromic shifts (**12c** and **12a**, $\Delta\lambda$, 8 nm; **12d** and **12b**, $\Delta\lambda$, 5 nm) relatable to polarisation effects [8].

2.3. Dyeing and fastness properties

The dyes **12a–12j** and **13a–13j** were applied to polyester fiber at 1% shade by high-temperature–pressure techniques and gave hues ranged from yellow to reddish-blue. The fastness properties of the dyes are shown in Table 3. The lightfastness was determined using standard procedures [27]. For sublimation fastness determinations, the dyed polyester fibers were stitched between two pieces of undyed polyester fibers (stained cloth) and treated at 200 °C for 1 min. Any staining on the undyed piece, change in tone, or loss in depth was assessed on a 1 (poor) to 5 (very good) rating. The dyeing on polyester fiber showed good lightfastness (in most cases 4–5) and good sublimation fastness (mostly between 3 and 5).

2.4. Colour assessment

The colour parameters of the dyed polyester fabrics were measured using the Applied Colour System, CS-5 chroma-sensor, model 502 using D_{65} source and



Scheme 2.

ultraviolet radiation [26]. Each fabric sample was folded twice so as to realise a total of four thicknesses of fabric. The assessment of colour-dyed fabrics was made in terms of tristimulus colorimetry [23]. The CIELAB attributes of lightness (L^*), chroma (C^*), and hue (a^* value represents the degree of redness (positive) and greenness (negative) and b^* represents the degree of yellowness (positive) and blueness (negative)) are calculated in the present work. Figs. 1 and 2 show a graph of CIELAB coordinates a^* versus b^* for dyes **12a–12j** and **13a–13j**, respectively. The values of the CIELAB coordinate (L^*, h° and C^*) are listed in Table 4. According to Richter [24] and McLaren [25], the position of the colour is distributed in the yellow–blue area with hue angle h° 5.64–356.09° and radial chroma C^* of length 30.39–47.14. Table 4 shows that, in general, the dyeing obtained using dye **12d** was redder (as evidenced by the lower b^* values and lower h° values) and duller (as shown by the lower C^* values) than the dye **12b**; the dyeing obtained using dye **12d** was redder (as evidenced by the higher a^* values, lower b^* values and lower h° values) and brighter (as shown by the higher C^* values) than the dye **12c**. Similarly, the dyeing obtained using dye **12f** was more violet (as evidenced by the lower b^* values and higher h° values) than the dye **12e**; on the other hand, the dyeing obtained using dye **12h** was more orange (as shown by the higher a^* values, higher b^* values and lower h° values) and brighter (as shown by the higher C^* values) than the dye **12g**. Furthermore, the dyeing obtained using dyes **13b** and **13d** was more greenish-yellow (as evidenced by the lower a^* values and higher h° values) than the dyes **13a** and **13c**; the dyeing obtained using dye **13j** was more orange–yellow (as shown by the higher a^* values,

Table 1
Physical and analytical data of 3-(aryl or hetaryl)azo-2,6-disubstituted-4-trifluoromethyl-thieno[2,3-*b*]pyridine derivatives (**12a–12j** and **13a–13j**)

Dye	Appearance	m.p.[a] (°C)	Yield (%)	Molecular formula	Elemental analysis (%) Calcd/Found		
					C	H	N
12a	Red needles	156	83	$C_{21}H_{14}N_5F_3OS$	57.14 57.21	3.17 3.21	15.87 15.88
12b	Red needles	152	91	$C_{21}H_{14}N_5F_3S_2$	55.14 55.14	3.06 3.10	15.31 15.33
12c	Red needles	130	84	$C_{23}H_{18}N_5F_3O_3S$	55.08 55.12	3.59 3.62	13.97 13.99
12d	Red needles	142	89	$C_{23}H_{18}N_5F_3O_2S_2$	53.38 53.40	3.48 3.44	13.53 13.55
12e	Red–violet needles	132	87	$C_{22}H_{11}N_6F_3OS_2$	53.22 53.36	2.21 2.25	16.93 16.89
12f	Violet needles	190	84	$C_{22}H_{11}N_6F_3S_3$	51.56 51.61	2.14 2.23	16.40 16.45
12g	Orange–yellow needles	164	89	$C_{23}H_{11}N_4F_3O_2S$	59.48 59.58	2.37 2.41	12.06 12.12
12h	Orange–yellow needles	185	83	$C_{23}H_{11}N_4F_3OS_2$	57.50 57.48	2.29 2.28	11.66 11.78
12i	Blue needles	126	79	$C_{23}H_{12}N_5F_3OS$	59.61 59.67	2.59 2.64	15.11 15.35
12j	Blue needles	192	85	$C_{23}H_{12}N_5F_3S_2$	57.62 57.65	2.50 2.50	14.61 14.69
13a	Yellow needles	108	88	$C_{23}H_{19}N_4F_3O_3S$	56.55 56.52	3.89 3.92	11.47 11.51
13b	Yellow needles	100	89	$C_{23}H_{19}N_4F_3O_2S_2$	54.76 54.55	3.77 3.68	11.11 11.14
13c	Yellow needles	102	87	$C_{25}H_{23}N_4F_3O_5S$	54.74 54.77	4.19 4.23	10.21 10.33
13d	Yellow needles	98	90	$C_{25}H_{23}N_4F_3O_4S_2$	53.19 53.17	4.07 4.12	9.92 10.01
13e	Yellow needles	130	86	$C_{24}H_{16}N_5F_3O_3S_2$	53.03 53.12	2.94 3.01	12.89 12.91
13f	Yellow needles	126	92	$C_{24}H_{16}N_5F_3O_2S_3$	51.52 51.63	2.86 2.94	12.52 12.52
13g	Yellow needles	105	87	$C_{25}H_{16}N_3F_3O_4S$	58.70 58.77	3.13 3.25	8.21 8.25
13h	Yellow needles	147	93	$C_{25}H_{16}N_3F_3O_3S_2$	56.92 57.02	3.03 3.15	7.96 8.03
13i	Yellow needles	112	87	$C_{25}H_{17}N_4F_3O_3S$	58.82 58.98	3.33 3.56	10.98 10.99
13j	Yellow needles	115	87	$C_{25}H_{17}N_4F_3O_2S_2$	57.03 57.12	3.23 3.25	10.64 10.56

[a] Recrystallization from ethanol.

higher b^* values and lower h° values) and brighter (as shown by the higher C^* values) than the dye **13i**. Similarly, the dyeing obtained using dye **13g** was also more greenish-yellow (as evidenced by the lower a^* values, lower b^* values and higher h° values) and duller (as shown by the lower C^* values) than the dye **13h**.

3. Experimental

3.1. General

All melting points are uncorrected and in degree Celsius. IR spectra were recorded on a JASCO FTIR-3

Table 2
Spectral data of 3-(aryl or hetaryl)azo-2,6-disubstituted-4-trifluoromethyl-thieno[2,3-*b*]pyridine derivatives (**12a–12j** and **13a–13j**)

Dye	MS (m/e M^+)	IR (KBr) ν (cm^{-1})	^1H NMR[a] (DMSO-d_6) δ (ppm)
12a	441	2118 (C≡N)	3.11 (s, 6H, $N(CH_3)_2$), 6.67 (dd, 1H, J = 1.0, 1.0 Hz 4-H of furyl), 6.86 (d, 2H, J = 1.5 Hz, 3,5-H of phenyl), 7.56 (s, 1H, 5-H), 7.76 (d, 1H, J = 1.0 Hz, 3-H of furyl), 8.02 (d, 2H, J = 1.0 Hz, 2,6-H of phenyl), 8.50 (d, 1H, J = 1.0 Hz, 5-H of furyl)
12b	457	2143 (C≡N)	2.83 (s, 6H, $N(CH_3)_2$), 6.62 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of thienyl), 6.75 (d, 2H, J = 1.0 Hz, 3,5-H of phenyl), 7.37 (s,1H, 5-H), 7.53 (d, 1H, J = 1.0 Hz, 3-H of thienyl), 7.95 (d, 2H, J = 1.0 Hz, 2,6-H of phenyl), 8.11 (d, 1H, J = 1.0 Hz, 5-H of thienyl)
12c	501	3178 (OH), 2216 (C≡N)	3.87–3.62, 4.89 (m, 8H, CH_2), 6.77 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 6.94 (d, 2H, J = 1.5 Hz, 3,5-H of phenyl), 7.55 (s, 1H, 5-H), 7.76 (d, 1H, J = 1.0 Hz, 3-H of furyl), 8.00 (d, 2H, J = 1.5 Hz, 2,6-H of phenyl), 8.48 (d, 1H, J = 1.0 Hz, 5-H of furyl)
12d	517	3198 (OH), 2216 (C≡N)	4.89–3.62 (m, 8H, CH_2), 6.93 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of thienyl), 7.23 (d, 2H, J = 1.0 Hz, 3,5-H of phenyl), 7.74 (d, 2H, J = 1.0 Hz, 2,6-H of phenyl), 7.84 (s, 1H, 5-H), 8.19 (d, 1H, J = 1.0 Hz, 3-H of thienyl), 8.42 (d, 1H, J = 1.0 Hz, 5-H of thienyl)
12e	496	3530, 3354 (NH_2), 2202 (C≡N)	3.87 (b, 2H, NH_2), 6.56 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 7.56–7.41 (m, 6H, 5-H and phenyl-H), 7.76 (d, 1H, J = 1.0 Hz, 3-H of furyl), 8.48 (d, 1H, J = 1.0 Hz, 5-H of furyl)
12f	512	3612, 3473 (NH_2), 2223 (C≡N)	3.56 (b, 2H, NH_2), 6.91 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of thienyl), 7.90–7.67 (m, 6H, 5-H and phenyl-H), 8.21 (d, 1H, J = 2.0 Hz, 3-H of thienyl), 8.53 (d, 1H, J = 2.0 Hz, 5-H of thienyl)
12g	464	3306 (OH), 2218 (C≡N)	6.76 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 7.44 (s, 1H, 5-H), 8.48–7.53 (m, 7H, 3-H of furyl and naphthyl-H), 8.50 (d, 1H, J = 1.0 Hz, 5-H of furyl)
12h	480	3326 (OH), 2219 (C≡N)	6.91 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of thienyl), 7.46 (s, 1H, 5-H), 8.52–7.49 (m, 7H, 3-H of thienyl and naphthyl-H), 8.59 (d, 1H, J = 1.0 Hz, 5-H of thienyl)
12i	463	3540, 3387 (NH_2), 2213 (C≡N)	6.66 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 8.47–7.03 (m, 8H, 3-H of furyl, 5-H and naphthyl-H), 8.84 (d, 1H, J = 1.0 Hz, 5-H of furyl)
12j	479	3543, 3359 (NH_2), 2212 (C≡N)	6.86 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of thienyl), 8.09 (s, 1H, 5-H), 8.87–7.21 (m, 8H, 3,5-H of thienyl and naphthyl-H)
13a	488	1705 (C=O)	1.31 (t, 3H, J = 4.0 Hz, CH_3), 2.83 (s, 6H, $N(CH_3)_2$), 4.36 (q, 2H, J = 1.0 Hz, CH_2), 6.62 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 6.75 (d, 2H, J = 1.0 Hz, 3,5-H of phenyl), 7.37 (s, 1H, 5-H), 7.53 (d, 1H, J = 1.0 Hz, 3-H of furyl), 7.95 (d, 2H, J = 1.0 Hz, 2,6-H of phenyl), 8.11 (d, 1H, J = 1.0 Hz, 5-H of furyl)
13b	504	1715 (C=O)	1.27 (t, 3H, J = 2.5 Hz, CH_3), 2.94 (s, 6H, $N(CH_3)_2$), 4.65 (q, 2H, J = 3.3 Hz, CH_2), 6.68 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of thienyl), 7.19 (d, 2H, J = 1.0 Hz, 3,5-H of phenyl), 7.96 (d, 1H, J = 1.0 Hz, 3-H of thienyl), 8.02 (d, 2H, J = 1.0 Hz, 2,6-H of phenyl), 8.18 (s, 1H, 5-H), 8.25 (d, 1H, J = 1.0 Hz, 5-H of thienyl)
13c	548	3165 (OH), 1707 (C=O)	1.29 (t, 3H, J = 5.0 Hz, CH_3), 4.81–3.47 (m, 10H, CH_2), 6.54 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 6.68 (d, 2H, J = 1.5 Hz, 3,5-H of phenyl), 7.33 (s, 1H, 5-H), 7.68 (d, 1H, J = 1.5 Hz, 3-H of furyl), 7.89 (d, 2H, J = 2.0 Hz, 2,6-H of phenyl), 7.97 (d, 1H, J = 1.5 Hz, 5-H of furyl)
13d	564	3198 (OH), 1702 (C=O)	1.27 (t, 3H, J = 2.5 Hz, CH_3), 4.73–3.42 (m, 10H, CH_2), 6.54 (dd, 1H, J = 2.0, 2.0 Hz, 4-H of thienyl), 6.63 (d, 2H, J = 2.0 Hz, 3,5-H of phenyl), 7.19 (d, 1H, J = 3.0 Hz, 3-H of thienyl), 7.56 (s, 1H, 5-H), 7.96 (d, 2H, J = 1.0 Hz, 2,6-H of phenyl), 8.02 (d, 1H, J = 2.0 Hz, 5-H of thienyl)
13e	543	3573, 3304 (NH_2), 1705 (C=O)	1.11 (t, 3H, J = 1.5 Hz, CH_3), 4.14 (q, 2H, J = 1.0 Hz, CH_2), 6.76 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 7.47–7.10 (m, 5H, phenyl-H), 7.55 (s, 1H, 5-H), 7.74 (b, 2H, NH_2), 7.93 (d, 1H, J = 1.0 Hz, 3-H of furyl), 8.11 (d, 1H, J = 1.0 Hz, 5-H of furyl)
13f	559	3597, 3387 (NH_2), 1694 (C=O)	1.11 (t, 3H, J = 2.0 Hz, CH_3), 4.14 (q, 2H, J = 2.5 Hz, CH_2), 7.48–7.10 (m, 6H, 4-H of thienyl and phenyl-H), 7.75 (d, 1H, J = 2.0 Hz, 3-H of thienyl), 7.84 (s, 1H, 5-H), 8.02 (d, 1H, J = 2.0 Hz, 5-H of thienyl)
13g	511	3198 (OH), 1705 (C=O)	1.29 (t, 3H, J = 2.5 Hz, CH_3), 4.30 (q, 2H, J = 2.5 Hz, CH_2), 6.66 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 8.21–7.09 (m, 9H, 5-H, 3,5-H of furyl and naphthyl-H)

continued on next page

Table 2 (*continued*)

Dye	MS (m/e M^+)	IR (KBr) ν (cm^{-1})	^1H NMR[a] (DMSO-d_6) δ (ppm)
13h	527	3198 (OH), 1705 (C=O)	1.12 (t, 3H, J = 2.0 Hz CH_3), 4.18 (q, 2H, J = 2.5 Hz, CH_2), 6.81 (dd, 1H, J = 2.0, 2.0 Hz, 4-H of thienyl), 8.30–7.01 (m, 8H, 5-H, 3-H of thienyl and naphthyl-H), 8.58 (d, 1H, J = 2.0 Hz, 5-H of thienyl)
13i	510	3582, 3445 (NH_2), 1680 (C=O)	1.29 (t, 3H, J = 2.5 Hz, CH_3), 4.30 (q, 2H, J = 2.5 Hz, CH_2), 6.59 (dd, 1H, J = 1.0, 1.0 Hz, 4-H of furyl), 8.31–7.29 (m, 9H, 5-H, 3,5-H of furyl and naphthyl-H)
13j	526	3599, 3387 (NH_2), 1693 (C=O)	1.09 (t, 3H, J = 2.0 Hz, CH_3), 4.19 (q, 2H, J = 2.5 Hz, CH_2), 6.83 (dd, 1H, J = 2.0, 2.0 Hz, 4-H of thienyl), 8.40–7.11 (m, 8H, 5-H, 3-H of thienyl and naphthyl-H), 8.60 (d, 1H, J = 2.0 Hz, 5-H of thienyl)

[a] Abbreviations: s, singlet; d, doublet; q, quartet; m, multiplet.

spectrometer (KBr); ^1H NMR spectra were obtained on a Bruker AM-300 WB FI-NMR spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Electron impact mass spectra were obtained at 70 eV using a Finingan Mat TSQ-46C spectrometer. Microanalyses for C, H, and N were performed on a Perkin–Elmer 240 Elemental Analyzer. Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in DMF at a concentration of 1×10^{-5} mol l^{-1}.

3.2. Synthesis of 3-amino-2,6-disubstituted-4-trifluoromethyl-thieno[2,3-b]pyridine derivatives

*3.2.1. 3-Cyano-6-furyl-4-trifluormethyl-2-(1H)-pyridinethione (**3a**)*

To a mixture of cyanothioacetamide **1** (5.0 g, 0.05 mol) and 2-furoyltrifluoroacetone **2a** (10.3 g, 0.05 mol) in absolute ethanol (60 ml), a few drops of triethylamine was added. The reaction mixture was stirred at 40–50 °C for 2 h. After cooling, the precipitate was filtered, washed with water, and recrystallized from acetic acid/ethanol to give 12.0 g of deep red needles (89% yield), m.p. 192 °C; IR: ν 3135 (NH), 2232 (C≡N), 1226 (C=S) cm^{-1}; ^1H NMR (DMSO-d_6): δ 6.75 (dd, 1H, 4-H of furyl), 7.35 (d, 1H, 3-H of furyl), 8.02 (d, 1H, 5-H of furyl), 8.17 (s, 1H, 5-H), 14.15 (b, NH); MS: 270 (M^+).

Anal. Calcd. for $C_{11}H_5N_2F_3OS$: C, 48.88; H, 1.85; N, 10.37. Found: C, 48.68; H, 1.90; N, 10.32%.

*3.2.2. 3-Cyano-6-thienyl-4-trifluoromethyl-2(1H)-pyridinethione (**3b**)*

This compound was synthesized from cyanothioacetamide 1 (5.0 g, 0.05 mol) and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione **2b** (11.1 g, 0.05 mol) in a manner similar to that described for the preparation **3a**. It was recrystallized from acetic acid/ethanol to give 11.4 g of orange needles (80% yield); m.p. 168 °C; IR: ν 3097 (NH), 2225 (C≡N), 1202 (C=S) cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.81 (dd, 1H, 4-H of thienyl), 7.84 (d, 1H, 3-H of thienyl), 8.19 (d, 1H, 5-H of thienyl), 8.29 (s, 1H, 5-H), 14.10 (b, NH); MS: 286 (M^+).

Table 3
Absorption spectra and dyeing properties of 3-(aryl or hetaryl)azo-2,6-disubstituted-4-trifluoromethyl-thieno[2,3-*b*]pyridine derivatives (**12a–12j** and **13a–13j**)

Dye	Absorption λ_{max} nm (in DMF)	Log ε	Lightfastness	Sublimation fastness
12a	525	3.98	5	4
12b	528	4.34	5	3
12c	533	4.11	5	4
12d	533	4.56	5	4
12e	548	4.48	4–5	3
12f	544	4.18	4	4
12g	465	4.54	4–5	3
12h	465	4.02	4	5
12i	589	4.10	4–5	4
12j	587	4.33	4–5	3–4
13a	448	4.65	5	3
13b	451	4.41	4–5	3–4
13c	448	4.38	4–5	3
13d	454	4.43	4–5	4
13e	452	4.23	4–5	3
13f	456	4.42	4–5	3
13g	453	4.34	4–5	3
13h	452	4.41	4	4
13i	452	4.43	5	3
13j	465	3.90	5	3

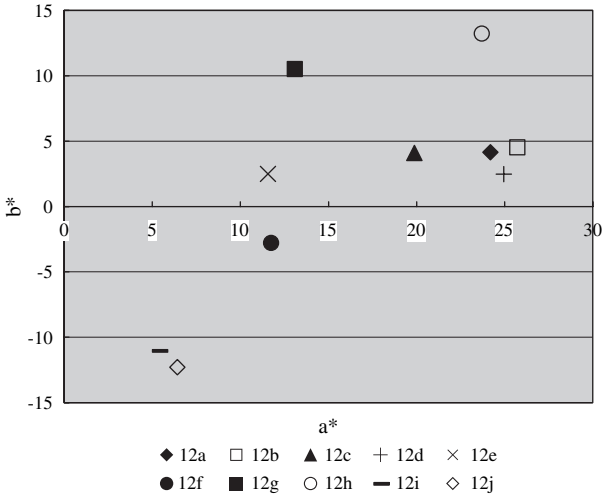


Fig. 1. Graph of CIE a^* versus b^* for dyes **12a–12j**.

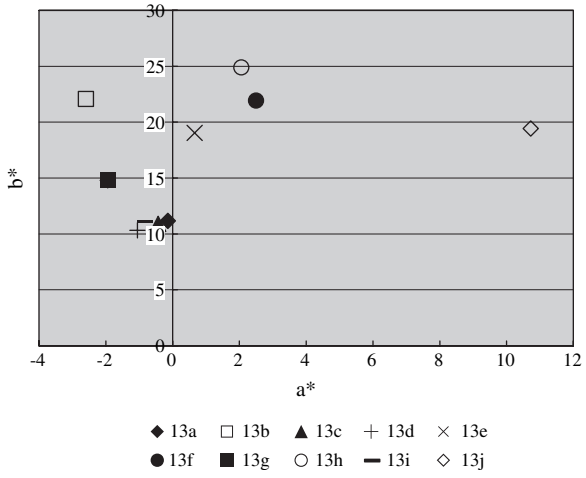


Fig. 2. Graph of CIE a^* versus b^* for dyes **13a–13j**.

Anal. Calcd. for $C_{11}H_5N_2F_3S_2$: C, 46.15; H, 1.74; N, 9.79. Found: C, 46.48; H, 1.70; N, 9.72%.

*3.2.3. 3-Amino-2-cyano-6-furyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**5a**)*

To a solution of pyridinethione **3a** (2.7 g, 0.01 mol) in DMF (50 ml), potassium carbonate anhydrous (2.76 g, 0.02 mol) and chloroacetonitrile (0.64 g, 0.01 mol) were added. The reaction mixture was stirred at a room temperature for 4 h and then diluted with cold water (50 ml). The resulting solid product was collected by filtration, washed with water and recrystallized from dioxane/ethanol to give 2.56 g (83%) of yellow needles; m.p. 259 °C; IR (KBr): ν 3511, 3350 (NH_2), 2204 (CN) cm^{-1}; ^1H NMR (DMSO-d_6): δ 6.22 (b, 2H, NH_2), 6.77 (dd, 1H, 4-H of furyl), 7.55 (d, 1H, 3-H of furyl), 8.01 (d, 1H, 5-H of furyl), 7.84 (s, 1H, 5-H); MS: 309 (M^+).

Anal. Calcd. for $C_{13}H_6N_3F_3OS$: C, 50.48; H, 1.94; N, 13.59. Found. C, 50.44; H, 1.90; N, 13.52%.

The above procedure was also used to synthesize compounds **5b–5d**.

Table 4
CIELAB of dyes **12a–12j** and **13a–13j** on polyester

Dye	L^*	a^*	b^*	C^*	h°
12a	36.53	24.19	4.14	44.45	9.72
12b	33.50	25.72	4.51	46.11	9.93
12c	40.68	19.87	4.10	40.29	11.67
12d	35.52	24.95	2.47	45.07	5.64
12e	40.95	11.56	2.50	31.57	13.48
12f	33.37	11.75	−2.80	31.78	356.09
12g	48.94	13.10	10.51	36.80	38.74
12h	40.37	23.71	13.22	47.14	29.14
12i	33.31	5.44	−11.06	32.32	296.19
12j	31.25	6.42	−12.29	33.87	297.60
13a	66.43	−0.14	11.17	31.17	90.74
13b	67.75	−2.59	22.07	42.22	96.70
13c	66.19	−0.43	10.90	30.91	92.28
13d	66.93	−1.05	10.33	30.39	95.80
13e	64.55	0.66	19.03	39.04	88.02
13f	62.99	2.50	21.92	42.07	83.48
13g	66.33	−1.94	14.79	34.92	97.47
13h	63.27	2.06	24.90	44.99	85.28
13i	66.09	−0.82	11.07	31.10	94.25
13j	58.18	10.72	19.44	44.20	61.12

*3.2.4. 3-Amino-2-cyano-6-thienyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**5b**)*

Crystallized from ethyl acetate/ethanol as yellow needles (86%); m.p. 237 °C; IR (KBr): ν 3504, 3349 (NH_2), 2205 (CN) cm^{-1}; ^1H NMR (DMSO-d_6): δ 6.21 (b, 2H, NH_2), 7.25 (dd, 1H, 4-H of thienyl), 7.86 (d, 1H, 3-H of thienyl), 8.23 (d, 1H, 5-H of thienyl), 8.31 (s, 1H, 5-H); MS: 325 (M^+).

Anal. Calcd. for $C_{13}H_6N_3F_3S_2$: C, 48.00; H, 1.84; N, 12.92. Found. C, 48.05; H, 1.90; N, 12.92%.

*3.2.5. 3-Amino-2-ethoxycarbonyl-6-furyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**5c**)*

Crystallized from ethyl acetate as yellow needles (84%); m.p. 169 °C; IR (KBr): ν 3508, 3366 (NH_2), 1676 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.30 (3H, t, CH_3), 4.31 (q, 2H, OCH_2), 6.32 (b, 2H, NH_2), 6.77 (dd, 1H, 4-H of furyl), 7.52 (d, 1H, 3-H of furyl), 7.99 (d, 1H, 5-H of furyl), 8.01 (s, 1H, 5-H); MS: 356 (M^+).

Anal. Calcd. for $C_{15}H_{11}N_2F_3O_3S$: C, 50.56; H, 3.08; N, 7.86. Found. C, 50.68; H, 3.00; N, 7.99%.

*3.2.6. 3-Amino-2-ethoxycarbonyl-6-thienyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**5d**).*

Crystallized from ethyl acetate/ethanol as yellow needles (75%); m.p. 182 °C; IR (KBr): ν 3526, 3366 (NH_2), 1684 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.30 (3H, t, CH_3), 4.31 (q, 2H, OCH_2), 6.57 (b, H, NH_2), 7.24 (dd, 1H, 4-H of thienyl), 7.84 (d, 1H, 3-H of thienyl), 8.20 (d, 1H, 5-H of thienyl), 8.26 (s, 1H, 5-H); MS: 372 (M^+).

Anal. Calcd. for $C_{15}H_{11}N_2F_3O_2S_2$: C, 48.38; H, 2.95; N, 7.52. Found. C, 48.68; H, 2.90; N, 7.99%.

3.3. Preparation of dyes

*3.3.1. 3-[4-(Dimethylamino)phenylazo]-2-cyano-6-furyl-4-trifluoromethyl-thieno-[2,3-b]pyrdine (**12a**)*

3-Amino-2-cyano-6-furyl-4-trifluoromethyl-thieno[2,3-*b*]pyridine **5a** (3.09 g, 0.01 mol) was dissolved in hydrochloric acid (10 ml conc. hydrochloric acid in 10 ml water) by warming, and the solution was then cooled to 0–5 °C with stirring. Sodium nitrite (0.70 g, 0.01 mol) in water (5 ml) was gradually added to this solution over 15 min period at 0–5 °C with stirring. The reaction mixture was stirred for an additional 30 min while maintaining a temperature of 0–5 °C. Excess nitrous acid was destroyed by the addition of urea, and

the solution was filtered to obtain a clear diazonium salt solution **6a**.

N,*N*-Dimethylaniline **7** (1.21 g, 0.01 mol) was dissolved in sulphuric acid (1.1 g sulphuric acid in 5 ml water). The solution was cooled to 0–5 °C by external cooling. To this cooled solution, the prepared diazonium salt **6a** was added slowly so that the temperature did not rise above 5 °C, while maintaining the pH at 4–5 by addition of solid sodium acetate. The mixture was further stirred for 4 h at 0–5 °C and filtered, and the presscake washed with water, dried, and recrystallized from ethanol.

The above procedure was also used to synthesize dyes **12b–12d**. Physical and spectral data of the **12a–12d** are recorded in Tables 1 and 2.

*3.3.2. 3-[4-(Dimethylamino)phenylazo]-2-ethoxycarbonyl-6-furyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**13a**)*

3-Amino-2-ethoxycarbonyl-6-furyl-4-trifluoromethyl-thieno[2,3-*b*]pyridine **5c** (3.56 g, 0.01 mol) in glacial acetic acid (10 ml) was added in portions during 30 min to a cooled mixture of nitrosylhydrogensulphate prepared from sodium nitrite (0.70 g, 0.01 mol) and concentrated sulphuric acid (10 ml) at 0 °C. The mixture was stirred for an additional 30 min at 0 °C, then added to an ice–water mixture under stirring. Excess nitrous acid was destroyed by the addition of urea and the solution was filtered to obtain a clear diazonium salt solution **6c**.

N,*N*-Dimethylaniline **7** (1.21 g, 0.01 mol) was dissolved in sulphuric acid (1.1 g sulphuric acid in 5 ml water). The solution was cooled to 0–5 °C by external cooling. To this cooled solution, the prepared diazonium salt **6c** was added slowly so that the temperature did not rise above 5 °C, while maintaining the pH at 4–5 by addition of solid sodium carbonate. The mixture was further stirred for 4 h at 0–5 °C and filtered, and the presscake washed with water, dried and recrystallized from ethanol.

The above procedure was also used to synthesize dyes **13b–13d**. Physical and spectral data of the **13a–13d** are recorded in Tables 1 and 2.

*3.3.3. 3-[(2-Amino-4-phenyl-thiazoly-5-yl)azo]-2-cyano-6-furyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**12e**)*

2-Amino-4-phenyl-thiazole **9** (1.76 g, 0.01 mol) was dissolved in ethanol (sodium acetate 2.0 g dissolved in 10 ml of 50% aqueous ethanol). The solution was cooled to 0–5 °C by external cooling. To this cooled solution, the prepared diazonium salt **6a** was added slowly so that the temperature did not rise above 5 °C, while maintaining the pH at 4–5 by addition of solid sodium acetate. The mixture was further stirred for 4 h at 0–5 °C and filtered, and the presscake washed with water, dried, and recrystallized from ethanol.

The above procedure was also used to synthesize dyes **12f** and **12i–12j**. Physical and spectral data of the **12e–12f** and **12i–12j** are recorded in Tables 1 and 2.

*3.3.4. 3-[(2-Amino-4-phenyl-thiazoly-5-yl)azo]-2-ethoxycarbonyl-6-furyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**13e**)*

Dye **13e** was synthesized from 2-amino-4-phenyl-thiazole **9** (1.76 g, 0.01 mol) and the diazonium salt **6c** in a manner similar to that described for the preparation of dye **12e**. It was crystallized from ethanol.

The above procedure was also used to synthesize dyes **13f** and **13i–13j**. Physical and spectral data of the **13e–13f** and **13i–13j** are recorded in Tables 1 and 2.

*3.3.5. 3-[(2-Hydroxynaphthyl-1-yl)azo]-2-cyano-6-furyl-4-trifluoromethyl-thieno-[2,3-b]pyridine (**12g**)*

β-Naphthol **10** (1.44 g, 0.01 mol) was dissolved in dilute sodium bicarbonate. The solution was cooled to 0–5 °C by external cooling. To this cooled solution, the prepared diazonium salt **6a** was added slowly so that the temperature did not rise above 5 °C, while maintaining the pH at 8–9 by addition of solid sodium carbonate. The mixture was further stirred for 4 h at 0–5 °C and the partially separated dye was completely precipitated by neutralizing with dilute hydrochloric acid (5%). It was filtered, washed with water, dried, and recrystallized from ethanol.

The above procedure was also used to synthesize dyes **12h**. Physical and spectral data of the **12g–12h** are recorded in Tables 1 and 2.

*3.3.6. 3-[(2-Hydroxynaphthyl-1-yl)azo]-2-ethoxycarbonyl-6-furyl-4-trifluoromethyl-thieno[2,3-b]pyridine (**13g**)*

Dye **13g** was synthesized from β-naphthol **10** (1.44 g, 0.01 mol) and the diazonium salt **6c** in a manner similar to that described for the preparation of dye **12g**. It was crystallized from ethanol.

The above procedure was also used to synthesize dyes **13h**. Physical and spectral data of the **13g–13h** are recorded in Tables 1 and 2.

4. Conclusions

The 3-cyano-4-trifluoromethyl-6-substituted-2(1*H*)-pyridinethiones were obtained by cyclocondensation of cyanothioacetamide with unsymmetrical fluorinated 1,3-ketones. Cyclization of 3-cyano-4-trifluoromethyl-6-substituted-2(1*H*)-pyridine-thiones with appropriate alkylating agent afforded the corresponding polyfunctionally substituted 3-amino-4-trifluoromethyl-thieno[2,3-*b*]pyridines, which has been shown to be a useful diazo

components for the synthesis of some new azo disperse dyes. These dyes showed good fastness properties on polyester fibers.

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