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Synthesis, characterization, and dyeing performance of some azo thienopyridine and thienopyrimidine dyes based on wool and nylon

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Abstract

A string of novel heterocyclic mono azo dyes were synthesized and their utilization in dyeing different fabrics as wool and nylon were discussed. Thienopyridine azo dyes **4** and **6**were prepared by reaction of chloro acetamidederivative **2** with diamino compounds to yield **3** and **5**, followed by reaction with $NaNO_2/HCl$ and coupling with nucleophilic reagent. One-pot reaction of chloro acetamide **2** with ammonium thiocyanat in solvent ethanol gave the unexpected thienopyrimidine derivative **7**, which contain two active sites, the former is primary amine that was able to form diazonium salt that coupled with *N*,*N*-dimethylaniline, resorcinol, and/or self-coupling to afford the azo dyes **8-10**, and the latter is active methylene group that underwent coupling with different diazonium salts to give the azo thienopyrimidine derivative dye **11-15**. The dyeing performance of these azo dyes had been investigated in terms of their dyeing behavior and fastness properties on different fabrics. Results showed that the color strength (K/S) values, as well as, washing, rubbing, and resistance to acid, alkali and light showed high efficiency of these heterocyclic mono azo dyes to dye wool rather than nylon fibers.

1 | INTRODUCTION

Azo dyes containing thiophene nucleus generally show a wide range of color, which has definite wavelength similar to aniline-based azo dyes, and characterized by high extinction coefficient.[1–6] Most of azo dyes have raised several environmental concerns owing to their wide spread, which has been enhanced due to the textile industry revolution of synthetic fibers such as polyester.[7] Azo dyes mostly have low solubility in water and to increase its solubility in water it should be minced to a very low particle size using a surfactant (dispersing agent) or by using a carrier, which added during dyeing process.[8–14]

Wool fiber is regarded as an abundant source for structural protein, which is related in general as wool keratin, which are biocompatible[15] and biodegradable.[16] So that, it is used in many biomedical applications or conjugated with bioactive molecules.[17] Wool fiber has high strength, resiliency, and elasticity; moreover, wool has excellent dye ability and comfortability, which gained an incomparable interest in creating novel ideas for wool fibers.[18–20]

Nylon fiber has a number of notable characteristics such as flexibility in surface functionalities and mechanical presentation making it better to many applications and other forms of natural polymeric and/or synthetic materials.[21]

2 | RESULTSAND DISCUSSION

Accordingly, the present study was devoted to synthesis a string of novel heterocyclic mono azo dyes and to investigate their dyeing performance on the fabrics as wool and nylon. 2-Amino-3-cyano thiophene derivative **(1)** was prepared by Gewald reaction.[22] The free amino group of **1** underwent nucleophilic displacement when treated with chloroacetyl chloride to give 2-chloro-*N*-(3-cyano-4,5,6,7-tetrahydrobenzo [b]thiophen-2-yl)ethanamide **(2)** (Scheme 1).

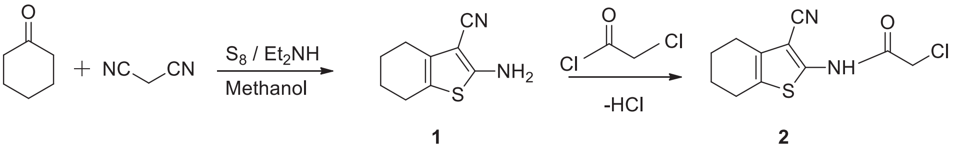
Reaction of acetamide derivative **2** with 1,4-diamino benzene and/or 4,4/–diamino biphenyl in dioxane under reflux conditions afforded thiopheneacetamide derivative**(3)** and 2-((4′-amino-[1,1′-biphenyl]-4-yl)amino)-*N*-(3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)acetamide **(5)**, respectively, (Scheme 2). The structure of compounds **3** and **5** was confirmed by the presence of three absorption signals at chemical shift 8.1, 8.6, and 11.9 ppm for compound **3** and at 7.8, 7.9, and 11.9 ppm for compound **5** in the ^{1}HNMR spectra corresponding to three different protons of NH in addition to protons of aromatic absorption. In continuation of this point, we dissolved compound **3** and/or **5** in HCl then added sodium nitrite solution in order to form the corresponding diazonium salt, which underwent coupling and acid catalyst cyclization when treated with activated aromatic compounds like 2-naphthol in NaOH and/or *N*,*N*-dimethylaniline in acetic acid to obtain orange crystals of azo thienopyridone derivatives **4** and **6** (Scheme 2). The structures of both azo thienopyridones **4** and **6** were proved by disappear of CN band and appearance of enolic hydroxyl and carbonyl bands in IR absorptions, as well as^{1}HNMRsignals.

Treatment of acetamide derivative **(2)** with ammonium thiocyanate in equivalent molar ratio in a mixture of boiling dioxane/ethanol as solvent for 4 hours afforded the unexpected product of ethyl 2-((4-amino-5, 6, 7, 8-tetrahydrobenzo [4,5]thieno[2,3-d] pyrimidin-2-yl) thio)ethanoate **(7)**.

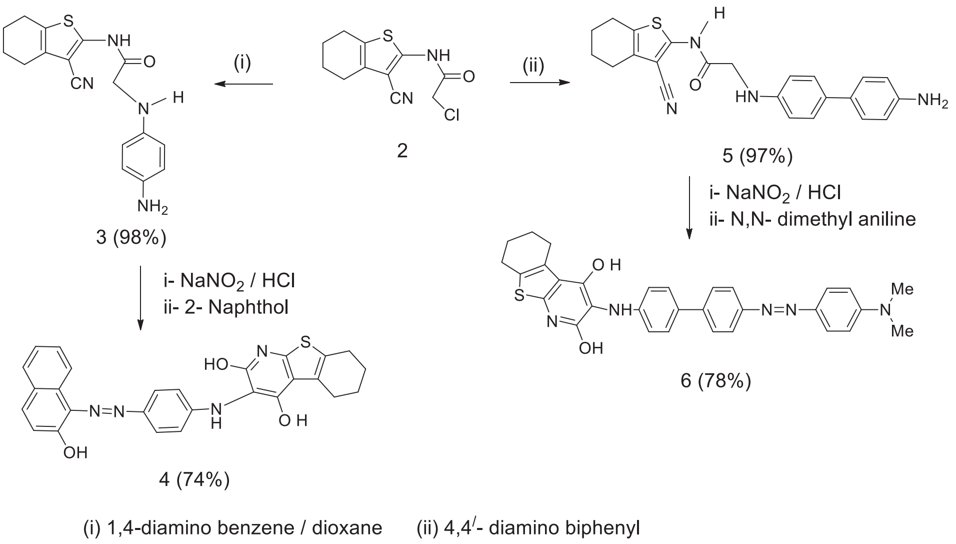
The formation of thienopyrimidine derivative **7** may be explained by the proposed mechanism as shown in Scheme 3. The thiocyanate anion underwent nucleophilic displacement by chloride followed by cyclization to give thiazole intermediate (not isolated) then imino group attack on cyano to forming the unstable second intermediate thiazolopyrimidine (not isolated) and finally thiazole ring opening by ethanol to gives the more stable ester **7**. The ester of **7** was established by IR, which showed a band at 1739 cm^{-1} attributed for C=O of ester group and two bands at 3500 and 3295 cm^{-1} characteristic for NH of NH$_2$. ^{1}HNMR showed signals at chemical shift 1.17 (t), 4.13 (q) attributed to CH$_3$ and CH$_2$ of ester beside peaks of cyclohexene and S-CH$_2$ protons, also MS spectra have peak at m/z 323[M].

Compound **7** contain two active sites able to forming new azo dye, the amino group and active methylene group our work focus on coupling reactions on this two active centers.

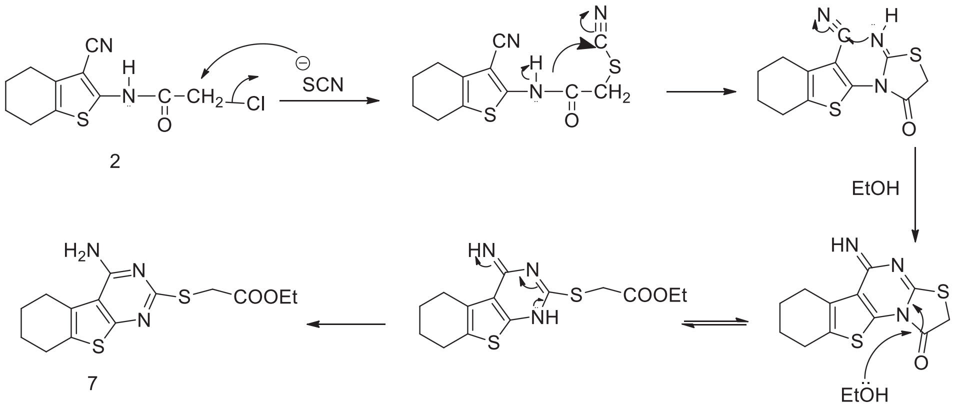
The free amino group on pyrimidine nucleus in thienopyrimidine derivative **7** behaves the same character as primary aromatic amine, which undergoes reaction with sodium nitrite to forming a relatively stable corresponding



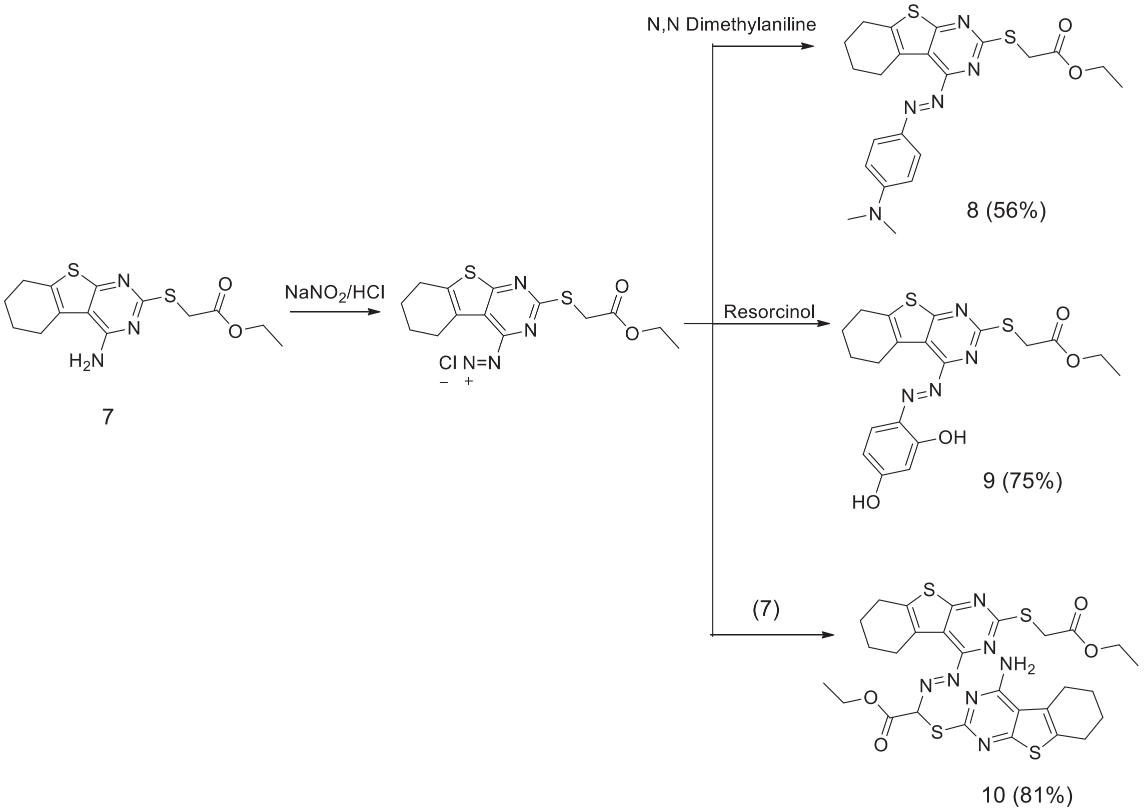
SCHEME 1 Synthesis of thiophenyl amide **2**



SCHEME 2 Formation of azo thienopyridones **4** and **6**



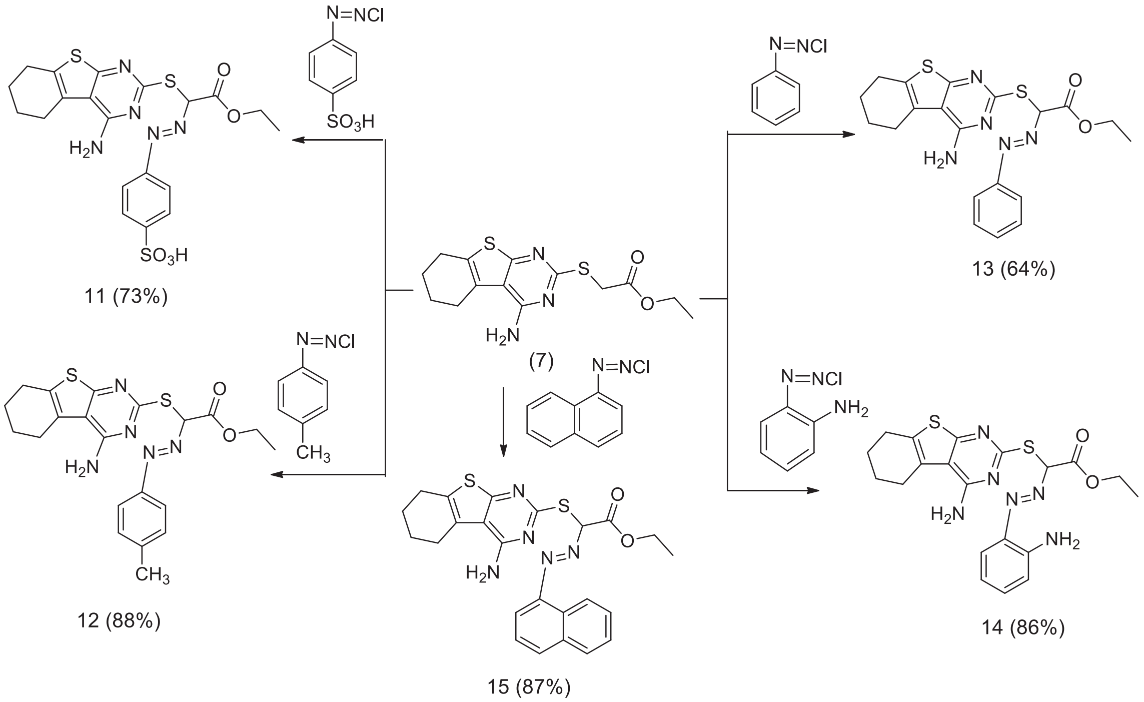
SCHEME 3 The suggested mechanism for the formation of thienopyrimidine derivative **7**



SCHEME 4 Coupling of thienopyrimidine diazonium salt with different nucleophilic reagents

diazonium salt at temperature between 0 and 5°C. This diazonium salt coupled with different activated nucleophilic reagents such as *N,N*-dimethylaniline, resorcinol, and ethyl 2-((4-amino-5,6,7,8-tetrahydrobenzo [4,5]thieno[2,3-d] pyrimidin-2-yl)thio) ethanoate**7**, affording the azo coupling products **(8-10)**, respectively (Scheme 4). The products **8** and **9** accompanied with disappearance of NH_2, while compound **10** still appear in IR as well as^{1}HNMRand ^{13}CNMR.

Thieno pyrimidine derivative **7** contains active methylene group at side chain adjacent to ester group has nucleophalic character, capable to couple with different diazonium salts, that formed from interaction of primary aromatic amines such as *p*-amino benzene sulphonic acid, *p*-toulidine, aniline, *o*-phenylendiamine and finally α-naphthyl amine with HCl and sodium nitrite at 0-5°C for 1 hour, afforded azo coupling products **11-15**, respectively (Scheme 5). All the products accompanied with appearance of NH_2 as present in compound **7** and exist in two tautomeric forms azo-form (**A**) and aryl hydrazones form (**B**) (Figure 1), which was proved by IR showing two absorption bands for carbonyl at 1738 cm^{-1} attributed to azo-form (**A**), at 1673 cm^{-1}qualified for aryl hydrazones conjugated ester (**B**), in addition to ^{1}HNMR and ^{13}CNMR spectra.



SCHEME 5 Coupling of thienopyrimidine **7** with different aromatic diazonium salts

3 | EXPERIMENTAL

All melting points measured on an electric melting point apparatus were uncorrected. The infrared spectra were recorded using potassium bromide disks on a Pye Unicam SP-3-300 infrared spectrophotometer. ^{1}HNMR spectra were run at 300 MHz, on a Varian Mercury VX-300 NMR spectrometer using TMS as an internal standard in deuterated dimethyl sulphoxide (DMSO-d_6). Chemical shifts δ are quoted in ppm and ^{13}CNMR spectra were recorded on the same spectrophotometer at 75 MHz and referenced to solvent signal $\delta = 39.5$ ppm for DMSO-d_6.The mass spectra were recorded on Shimadzu GCMS-QP-1000EX mass spectrometers at 70 eV. All the spectral measurements were carried out at the NMR laboratory of Cairo University, Egypt, the NMR laboratory of Faculty of Pharmacy; Ain shams University, Egypt. The Micro analytical data were measured in Central Lab of Cairo University, Egypt; and the Ministry of Defense Chemical Laboratories, Egypt, and at the Micro Analytical Center of Ain Shams University, Egypt. All the chemical reactions were monitored by TLC.

3.1 | Synthesis of 2-(4-aminophenyl) amino)-*N*-(3-cyano-4,5,6,7-tetrahydrobenzo [b]thiophen-2-yl)acetamide (3)

Heating of chloroacetamide **2** (2.54 g, 0.01 mol) with (0.01 mol) of 1,4-diamino benzene in dioxane (50 mL) for 4 hours under reflux condition, the solid separated was filtered off, dried and crystallized from dioxane, afforded compound **3** as pale yellow crystals, Yield: 3.19 g (98%); m.p: 132-134°C. IR (KBr) showed absorption bands at frequency 3275, 3225 cm^{-1} (NH), 3089 cm^{-1} (Ar—H), 2945 cm^{-1} (Aliph. C—H), 2199 cm^{-1} (CN), 1708 cm^{-1} (C═O).^{1}H-NMR (300 MHz, DMSO-d_6):δ (ppm) 1.83 (t,4H, 2CH$_2$), 2.68-2.71 (m, 2H, CH$_2$), 2.89-2.92 (m, 2H, CH$_2$), 4.31(s,2H, N—CH$_2$), 7.33 (d, *j* = 8 Hz, 2H, Ar-H), 7.52(d, *j* = 7.9 Hz, 2H, Ar-H), 8.1 (s, 1H, NH), D$_2$O exchangeable, 8.6 (s, 1H,NH), D$_2$O exchangeable 11.9 (s,2H,NH$_2$), D$_2$O exchangeable.MS showed the parent peak at m/z (% abundance) 326 (8%). Anal. Calculated for$C_{17}H_{18}N_4OS$ (326.12): C, 62.55; H, 5.56; N, 17.16; Found: C, 62.81; H, 5.78; N, 17.29.

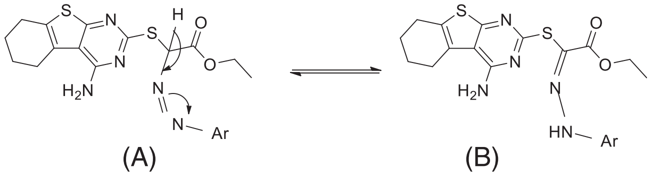


FIGURE 1 The two tautomeric forms azo-form (A) and aryl hydrazones form (B) of compound 7

3.2 | Synthesis of 2-hydroxy-3-((4-((2-hydroxynaphthalen-1-yl)diazenyl) phenyl)-amino)-5,6,7,8-tetrahydrobenzo[4,5]thieno [2,3-b] pyridin −4(3H)-one (4)

Solution of compound **3** (3.26 g, 0.01 mol) in dil HCl (20 mL, 10%) was added to sodium nitrite solution

(30 mL, 0.01 mol), the reaction mixture was stirred for 1 hour in ice bath to form the diazonium salt of compound **3**. A solution of 0.01 mol of 2-naphthol in NaOH (10 mL, 10%) was cooled and kept the temperature between 0 and 5°C for 45 minute, the diazonium salt of compound **3** was added drop wise in a period of half hour, stirring well for 4 hours in ice bath, filtered off the solid obtained, washed with water (100 mL) then washed with diethyl ether (20 mL) crystallized from ethanol to obtain **4** as orange crystals. Yield: 3.37 g (74%); m.p: 240-242°C. (UV-vis) λ maxwas 438 nm. IR spectrum (KBr) showed absorption bands at frequency at 3449 cm^{-1} (OH), 3249 cm^{-1} (NH), 2925 cm^{-1} (Aliph. C—H), 1715 cm^{-1} (C═O) and absent of (CN) absorption band. ^{1}HNMR (300 MHz, DMSO-d_6): δ(ppm) 1.82 (t, 4H, 2CH$_2$), 2.74-2.81 (m, 2H, CH$_2$,), 2.89-2.93 (m, 2H, CH$_2$), 6.86 (d, *j* = 8 Hz, 2H, Ar-H), 7.31 (d, *j* = 8 Hz, 1H, Ar-H), 7.42 (d, *j* = 8 Hz, 2H, Ar-H), 7.41-7.66 (m, 5H, Ar-H), 7.8 (s, 1H, NH), D$_2$O exchangeable, 7.9 (s, 2H,2OH), D$_2$O exchangeable, 10.1 (s, 1H, OH),D$_2$O exchangeable. ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 160.2, 155.6, 150.3, 148.0, 146.3, 142.3, 137.6, 129.5, 128.5, 126.6, 125.3, 120.8, 118.5, 116.9, 112.6, 109.3, 105.6101.3, 99.3, 90.8, 25.4, 23.6, MS showed the parent peak at m/z (% abundance) 482 (2%). Anal. Calculated for $C_{27}H_{22}N_4O_3S$ (482.14): C, 67.20; H, 4.60; N, 11.61; Found: C, 67.222; H, 4.65; N, 11.67.

3.3 | Synthesis of 2-((4′-amino-[1,1′-biphenyl]-4-yl)amino)-*N*-(3-cyano-4,5,6,7-tetrahydro benzo[b]-thiophen-2-yl) acetamide (5)

Chloroacetamide **2** (2.54 g, 0.01 mol) and 4,4′–diamino biphenyl (0.01 mol) in dioxane (30 mL) was heated under reflux conditions for 4 hours, the solid formed was filtered off, dried and crystallized from dioxane to gives compound **5**, as green crystals, Yield: 3.89 g (97%); m.p:128-130°C. IR (KBr): showed absorption bands at frequency at 3416, 3345, 3226 cm^{-1} (NH), 2928 cm^{-1} (Aliph. C—H), 2217 cm^{-1} (CN), 1685 cm^{-1} (C═O). ^{1}HNMR (300 MHz, DMSO-d_6): δ(ppm) 1.9 (t, 4H, 2CH$_2$), 2.72-2.76 (m, 2H, CH$_2$), 2.90-2.94 (m, 2H, CH$_2$), 4.2 (s,2H, N—CH$_2$) 6.9 (d, *j* = 8.1 Hz, 2H, Ar-H), 7.4 (*d*, *j* = 8 Hz, 2H, Ar-H), 7.51-7.74 (m, 4H, Ar-H), 7.81(s, 1H, NH), D$_2$O exchangeable, 7.9(s, 1H, NH), D$_2$O exchangeable, 11.9 (s, 2H, NH$_2$), D$_2$O exchangeable. MS showed the parent peak at m/z (% abundance) 402 (4%). Anal calculated for $C_{23}H_{22}N_4OS$ (402.15): C, 68.63; H, 5.51; N, 13.92; Found: C, 68.75; H, 5.62; N, 14.05.

3.4 | Synthesis of 3-((4′-((4-(dimethylamino)phenyl)diazenyl)-[1,1′-biphenyl]-4-yl)amino)-2-hydroxy-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-b] pyridin-4(3H)-one (6)

Dissolve (4.02 g, 0.01 mol) of acetamide derivative **5** in dil. HCl (20 mL, 10%) then add (0.01 mol) of sodium nitrite solution, stirring for 1 hour in ice bath to forming the diazonium salt of compound **5**, dissolve (0.01 mol) of *N*,*N*-dimethyl aniline in 10 mL of acetic acid the solution was cooled for 45 minute at 0-5°C, the diazonium salt of compound **5** was added drop wise in a period of half hour, stirring well for 4 hours in ice bath, the solid obtained was filtered off, washed with water (100 mL) then washed with diethyl ether (50 mL), crystallized from dioxane to gives **6** as orange crystals. Yield: 4.16 g(78%); m.p: 221-223°C. (UV -vis) λ max was 441 nm. IR (KBr) showed absorption bands at frequency at 3441 cm^{-1}(OH), 3180 cm^{-1} (NH), 2924 cm^{-1}(Aliph. C—H), 1744 cm^{-1} (C═O),^{1}HNMR (300 MHz, DMSO-d_6):δ(ppm) 1.7(t, 4H, 2CH$_2$), 2.76-2.78 (m, 4H, 2CH$_2$), 3.01 (s, 6H, 2CH$_3$), 6.85 (d, *j* = 7.8 Hz, 2H, Ar-H), 7.31 (d, *j* = 6.8 Hz, 2H, Ar-H), 7.52 (d, *j* = 7.6 Hz, 2H, Ar-H), 7.63-7.81 (m,6H,Ar-H),8.1 (s, 1H, NH), D$_2$Oexchangeable, 9.6(s, 2H, 2OH), D$_2$O exchangeable. MS showed the parent peak at m/z (% abundance) 535 (8%). Anal. Calculated for $C_{31}H_{29}N_5O_2S$ (534.22): C, 69.51; H, 5.46; N, 13.07; Found: C, 69.78; H, 5.68; N, 13.21.

3.5 | Synthesis of ethyl 2-((4-amino-5, 6, 7, 8-tetrahydrobenzo [4,5] thieno[2,3-d] pyrimidin-2-yl)thio) ethanoate (7)

Refluxing 2-chloroacetamide **2** (2.54 g, 0.01 mol) with ammonium thiocyanate (0.76 g, 0.01 mol) in a mixture of 1:1 dioxane-ethanol (100 mL) for 4 hours. The reaction mixture was poured in ice water (200 mL), the precipitate formed was filtered off, dried and crystallized from butanol, afforded ethanoate **7** as pale yellow crystals. Yield: 3.1 g (96%); m.p: 123-125°C. IR (KBr) showed absorption bands at frequency 3296, 3134 cm^{-1}characteristic for primary amino group (NH$_2$), 1739 cm^{-1} (C═O ester), as well as disappearance the absorption band for CN, ^{1}HNMR (300 MHz, DMSO-d_6):δ(ppm) 1.17 (t.3H, CH$_3$), 1.79-1.81 (m,4H, 2CH$_2$), 2.70-2.72 (m, 4H, 2CH$_2$), 3.9 (s.2H, SCH$_2$), 4.13 (q, *j* = 6.1 Hz, 2H, OCH$_2$), 6.9 (s, 2H, NH$_2$) D$_2$O exchangeable, MS showed the parent peak at m/z (% abundance): 323 (35%). Anal. Calculated for $C_{14}H_{17}N_3O_2S_2$ (323.43): C, 51.99; H, 5.30; N, 12.99 Found: C, 52.11; H, 5.21; N, 13.11.

3.6 | General procedure for azo coupling; preparation of diazonium salt of compound 7: Synthesis of compounds 8-10

Dissolve 3.23 g (0.01 mol) of compound **7** in 20 mL of HCl (10%) then add (0.01 mol) of sodium nitrite solution, stirring well for 1 hour, the solution was cooled at temperature between 0 and 5°C, the diazonium salt was formed is added drop wise in a period of half hour to a solution of different nucleophilic reagent such as *N*,*N*-dimethyl analine (0.01 mol) in 10 mL of acetic acid, resorcinol (0.01 mol) in 10 mL of NaOH (10%), and/or active methylene compound as ethyl 2-((4-amino-5,-6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl) thio) acetate (**7**) (0.01 mol) in acetic acid (10 mL), the precipitated was formed, filtered off, washed with water (100 mL) then washed with diethyl ether (50 mL ×2 times), which affording the azo dyes compounds **8-10**, respectively.

3.7 | Ethyl 2-((4-((4-(dimethylamino)phenyl)diazenyl)-5,6,7,8-tetrahydrobenzo[4,5]thieno [2,3-d]pyrimidin-2-yl)thio)acetate (8)

Crystallized from ethanol as yellowish green crystals. Yield: 2.55 g(56%); m.p: 186-188°C.(UV -vis) λ max was 397 nm. IR(KBr) no absorption band for NH but showed absorption bands at frequency 3063 cm^{-1}(Ar C—H), 2936 cm^{-1}(Aliph C—H), 1669 cm^{-1}(C=O), 1615 cm^{-1} (C=N), 1540 cm^{-1}(N=N). ^{1}HNMR (300 MHz, DMSO-d_6): δ(ppm) 1.2 (t.3H, CH_3), 1.69-1.71(m, 4H, $2CH_2$), 2.70-2.72 (m,2H,CH_2), 2.80-2.82 (m, 2H,CH_2), 2.9 (s, 6H, $N[CH_3]_2$), 3.7 (s.2H, SCH_2),4.2 (q, *j* = 6.8 Hz,2H, CH_2), 7.61 (d, 2H, *j* = 7.6 Hz ,Ar-H), 7.81(d, 2H, *j* = 7.6 Hz, Ar-H). Anal. Calculated for $C_{22}H_{25}N_5O_2S_2$ (455.60): C, 58.00; H, 5.53; N, 15.37 Found: C, 58.15; H, 5.68; N, 15.49.

3.8 | Ethyl 2-((4-((2,4-dihydroxyphenyl)diazenyl)-5,6,7,8-tetrahydrobenzo [4,5]thieno[2,3-d]pyrimidin-2-yl)thio)acetate (9)

Crystallized from methanol as yellowish brown crystals, Yield: 3.32 g(75%); m.p:184-186°C. (UV -vis) λ max was 488 nm IR (KBr) showed absorption bands at frequency 3497 cm^{-1} (OH),3050 cm^{-1}(Ar C—H), 2934 cm^{-1} (Aliph C—H), 1735 cm^{-1} (C=O), 1652 cm^{-1}(C=N), 1567 cm^{-1} (N=N).^{1}HNMR (300 MHz, DMSO-d_6):δ(ppm) 1.2 (t.3H, CH_3), 1.79-1.81 (m,4H, $2CH_2$), 2.66-2.68 (m, 2H, CH_2), 2.87-2.89 (m, 2H, CH_2), 3.7 (s.2H, S—CH_2), 4.1 (q, *j* = 6.8 Hz, 2H, OCH_2), 6.91 (s, 1H, Ar-H), 7.18 (d, 1H, *j* = 7.6 Hz, Ar-H) 7.30 (d, 1H, *j* = 7.6 Hz, Ar-H), 12.6 (s, 2H, 2OH) D_2O exchangeable. Anal. Calculated for $C_{20}H_{20}N_4O_4S_2$ (444.53): C, 54.04; H, 4.53; N, 12.60; Found: C, 54.06; H, 4.55; N, 12.63.

3.9 | Ethyl 2-((4-amino-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl)thio)-2-((2-((2-ethoxy-2-oxoethyl)thio)-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-4-yl)diazenyl)acetate (10)

Crystallized from ethanol as yellow crystal. Yield: 5.32 g (81%); m.p: above 300°C.(UV -vis) λ max was 453 nm. IR (KBr) showed absorption bands at frequency: 3299, 3160 cm^{-1}(NH_2), 2933 cm^{-1} (Aliph. C—H), 1737, 1669 cm^{-1} (C=O of two ester), 1547.36 cm^{-1} (N=N). ^{1}HNMR (300 MHz, DMSO-d_6):δ(ppm):1.21 (t, 3H, CH_3), 1.28 (t, 3H, CH_3), 1.81-1.83 (m,8H, $4CH_2$), 2.68-2.71 (m, 8H, $4CH_2$), 3.72 (s.1H, S—CH), 3.83 (s,2H, S—CH_2), 4.12(q, *j* = 6.9 Hz, 2H, OCH_2), 4.23(q, *j* = 6.9 Hz, 2H, OCH_2), 7.0 (s, 2H,NH_2) D_2O exchangeable. ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 180.5, 176.2, 174.6, 174.5, 170.3, 162.3, 160.5, 156.3, 140.3, 130.9, 122.3, 115.8, 78.6, 62.3, 42.5, 28.6, 24.6, 22.8, 21.7, 20.8, 18.6, 15.4. Anal. Calculated for $C_{28}H_{31}N_7O_4S_4$ (657.85): C, 51.12; H, 4.75; N, 14.90; Found: C, 51.24; H, 4.88; N, 15.11.

3.10 | General procedure for azo coupling of compound 7 with different diazonium salts: Synthesis of compounds 11-15

A solution of (0.01 mol) primary aromatic amines, namely *p*-amino benzene sulphonic acid, *p*-toluidine, aniline, *o*-phenylene diamine, and/or 1-naphthyl amine in 20 mL of HCl (10%) was added to (0.015 mol) of sodium nitrite solution, the reaction mixture was stirred well in ice bath at temperature between 0 and 5°C for 1 hour until the diazonium salt is formed, then added a solution of acetate derivative **7** (3.23 g, 0.01 mol) in 10 mL of acetic acid; dropwise in a period of 30 minutes; the reaction was done in ice bath 0-5°C with stirring for 4 hours, the formed precipitated was filtered off, dried and washed by 100 mL of water, then washed by diethyl ether (50 mL × 2 times) afforded the azo coupling compounds **11-15**, respectively.

3.11 | 4-((1-((4-Amino-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl)thio)-2-ethoxy-2-oxoethyl)diazenyl)benzenesulfonic acid (11)

Crystallized from ethanol as orange crystal. Yield: 3.7 g (73%); m.p:183-185°C. (UV-vis) λ max was 442 nm. IR (KBr) showed absorption bands at frequency 3297, 3122 cm^{-1} (NH_2), 3064 cm^{-1} (Ar, C—H), 2932 cm^{-1} (Aliph. C—H), 1737, 1669 cm^{-1} (C=O), 1551 cm^{-1} (N=N). ^{1}H-NMR (300 MHz, DMSO-d_6): δ(ppm) 1.22 (t,3H, CH_3),1.78-1.81 (m.4H, $2CH_2$), 2.89 (m,4H, $2CH_2$) 3.58 (s, 1H, SCH), 4.21 (q, *j* = 6.8 Hz, 2H, OCH_2), 7.01 (broads, 2H,NH_2) D_2O exchangeable, 7.80 (d, *j* = 9 Hz, 2H, Ar-H), 7.83(d, *j* = 9.1 Hz, 2H, Ar-H), 8.35 (broads, 1H,SO_3H) D_2O exchangeable, MS showed the parent peak at m/z (% abundance):: 507 (9.3%). Anal. Calculated for $C_{20}H_{21}N_5O_5S_3$ (507.07): C, 47.32; H, 4.17; N, 13.80; Found: C, 47.63; H, 4.36; N, 13.46.

3.12 | Ethyl −2-((4-amino-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl)thio)-2-(*p*-tolyldiazenyl)acetate (12)

Crystallized from dioxane as pale yellow. Yield: 3.88 g (88%); m.p: 190-192°C. (UV-vis) λ max was 409 nm. IR (KBr) showed absorption bands at frequency 3509, 3449 cm^{-1}(NH_2), 3124 cm^{-1} (NH), 3064 cm^{-1}(Ar. C—H), 2975 cm^{-1} (Aliph C—H), 1738, 1662 cm^{-1} (C=O), 1556 cm^{-1} (N=N). ^{1}HNMR1 (300 MHz, DMSO-d_6):δ (ppm):1.21 (t.3H, CH_3), 1.85 (m,4H, $2CH_2$), 2.1 (s,3H, CH_3), 2.69-2.71 (m, 2H, CH_2), 2.82-2.84 (m, 2H, CH_2), 3.74 (s.1H, S—CH), 4.12 (q, *j* = 6.9 Hz, 2H, OCH_2), 5.51 (broads, 2H,NH_2) D_2O exchangeable, 7.45 (d, *j* = 8.4 Hz, 2H, Ar-H), 7.62 (*d*, *j* = 8.4 Hz, 2H, Ar-H). ^{13}C NMR (75 MHz, DMSO-*d6*) δ (ppm): 174.2, 170.5, 160.5, 155.4, 148.2, 142.3, 137.9, 130.1, 128.3, 123.5, 115.6, 76.3, 62.3, 25.3, 23.6, 19.5, 14.9. MS showed the parent peak at m/z (% abundance):: 441 (7%). Anal. Calculated for $C_{21}H_{23}N_5O_2S_2$ (441.13): C, 57.12; H, 5.25; N, 15.86; Found: C, 57.25; H, 5.17; N, 16.12.

3.13 | Ethyl −2-((4-amino-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl)thio)-2-(phenyldiazenyl)acetate (13)

Crystallized from ethanol as pale yellow. Yield: 3.58 g (84%); m.p: 173-175°C. (UV-vis) λ max was 431 nm IR (KBr) showed absorption bands at frequency 3297.9, 3124.8 cm^{-1}(NH_2), 3064.98 cm^{-1} (Ar. C—H), 2976.9 cm^{-1} (Aliph, C—H), 1736.2, 1662.6 cm^{-1} (C=O).1555.3 cm^{-1} (N=N). ^{1}H-NMR (300 MHz, DMSO-d_6): δ(ppm) 1.29 (t,3H, CH_3), 1.79-1.81 (m.4H, $2CH_2$), 2.88-2.91 (m,4H, $2CH_2$) 3.6 (s, 1H, SCH), 4.1 (q, *j* = 6.9 Hz,2H, OCH_2), 5.51 (broads, 2H,NH_2) D_2O exchangeable, 7.22-7.43 (m, 5H, Ar-H), MS showed the parent peak at m/z (% abundance):: 427 (12%). Anal. Calculated for $C_{20}H_{21}N_5O_2S_2$ (427.11): C, 56.19; H, 4.95; N, 16.38; Found: C, 56.32; H, 5.23; N, 16.43.

3.14 | Ethyl −2-((4-amino-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl)thio)-2-((2-aminophenyl)diazenyl)acetate (14)

Crystallized from acetic acid as pale yellow crystal. Yield: 3.8 g(86%); m.p: 242-244°C. (UV-vis) λ max was 404 nm. IR (KBr) showed absorption bands at frequency 3513, 3451, 3212, 3190 cm^{-1} ($2NH_2$), 3064 cm^{-1} (Ar.C—H), 2976 cm^{-1} (Aliph. C—H), 1738, 1674 cm^{-1} (C=O), 1556 cm^{-1} (N=N), ^{1}H-NMR (300 MHz, DMSO-d_6): δ(ppm) 1.25 (t,3H, CH_3), 1.85-1.87 (m.4H, $2CH_2$), 2.89-2.91 (m,4H, $2CH_2$) 3.6 (s, 1H, SCH), 4.1 (q, *j* = 6.8 Hz, 2H, OCH_2), 5.21 (broads, 2H,NH_2) D_2O exchangeable, 6.78-7.12 (m, 4H, Ar-H), 7.42(broads, 2H,NH_2) D_2O exchangeable,^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 175.2, 171.2, 159.3, 155.6, 144.3, 138.6, 134.3, 128.9, 126.3, 122.8, 120.8, 115.6, 112.7, 77.5, 64.3, 24.9, 22.2, 20.3, 14.9. MS showed the parent peak at m/z (% abundance): 442 (11%). Anal. Calculated for $C_{20}H_{22}N_6O_2S_2$ (442.12): C, 54.28; H, 5.01; N, 18.99; Found: C, 54.32; H, 5.33; N, 18.43.

3.15 | Ethyl −2-((4-amino-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl)thio)-2-(naphthalen-1-yldiazenyl)acetate (15)

Crystallized from ethanol as brownish orange. Yield: 4.14 g (87%); m.p:174-176°C. (UV-vis) λ max was 469 nm. IR (KBr) showed absorption bands at frequency 3299, 3156 cm^{-1}(NH_2), 3055 cm^{-1} (Ar. C—H), 2978 cm^{-1} (Aliph. C—H), 1735, 1665 cm^{-1} (C=O), 1547 cm^{-1} (N=N). ^{1}HNMR (300 MHz, DMSO-d_6):δ (ppm) 1.31(t, 3H, CH_3), 1.79-1.81 (m.4H, $2CH_2$), 2.81-2.83 (m, 4H, $2CH_2$), 3.6(s, H, SCH), 4.1 (q, *j* = 6.4 Hz, 2H, OCH_2), 7.12-8.21 (m, 7H Aromatic) 10.11(s, 2H, NH_2). MS showed the parent peak at m/z (% abundance):: 477 (6%). Anal. Calculated for $C_{24}H_{23}N_5O_2S_2$ (477.13): C, 60.36; H, 4.85; N, 14.66; Found: C, 60.28; H, 5.15; N, 14.31.

3.16 | Fabrics

Wool fabric was supplied from Misr for Spinning and Weaving Company (Mahalla El-Kobra, Egypt) weight 205 g^{-2}, 72 ends per inch, 64 picks per inch. Polyamide fabric (100% nylon 66) of 110 g/m^2 supplied by private sector Co was scoured. Before using, the fabric was treated with nonionic detergent at 50°C, washed several time with water, bleached and dried thoroughly.

3.17 | Dyeing of nylon and wool procedures

Dyeing of wool and nylon fibers was performed by using concentrations of 2% o.w.f (on the weight of fabric). The wool and/or nylon was added to dying bath containing dyes components that dissolve in water at PH = 5 (accustomed by dil. acetic acid) at temperature 40°C. The temperature was raised to 100°C with a rate 2°C/min and kept at 100°C for 60 minutes. The fibers were next cooled and rinsed in a raw tap water, and then washed in a bath of L.R. 50:1 using 2 g/L of nonionic detergent at 50°C for 30 minutes. Finally, the dyed samples were dried at ambient temperature.

3.18 | Color measurements and color fastness

Color of the dyed nylon and wool fabrics is a key importance due to the effect of the colored fabrics on the production demands and customer consumption.[23] In the current work, of nylon and wool fabrics were our main objective. To examine the color properties of the dyed fabrics, the colorimetric data were measured for the dyed nylon and wool fabrics using synthesized dyes.

Table 1 shows that all the dyed nylon and wool fabrics using synthesized dyes showed relatively moderate to very good color strength (K/S) values, in compared with blank selective Society2-(2-(3-Methyl-5-oxo-1-phenyl-1H-pyrazol-4[5H]ylidene)hydrazinyl)-4,5,6,7-tetrahydro benzo[b] thiophene-3-carbonitrile,[24] the dyed nylon and wool fabrics shows brilliant good to very good K/S values ranging between 2 and 2.86 for the dyed nylon fabric and 1.64-5.47 for the dyed wool fabric using synthesized dyes.

TABLE 1 The color strength (K/S) values and colorimetric data of nylon and wool fabrics dyed with synthesized dyes

Nu	Fabric	L*	a*	b*	K/S
Blank	Nylon	92.48	2.12	−8.91	1.61
	Wool	83.57	0.16	14.47	1.45
4	Nylon	89.66	3.31	−4.6	2
	Wool	82.91	0.35	17.12	1.77
6	Nylon	69.73	6.53	9.07	2.61
	Wool	50.30	−2.94	0.76	4.99
8	Nylon	74.3	3.34	−3.97	2.17
	Wool	80.38	−0.29	19.65	1.94
9	Nylon	75.36	7.7	10.34	2.59
	Wool	82.32	−0.02	13.9	1.74
10	Nylon	85.9	3.4	0.67	2.28
	Wool	61.98	3.29	23.39	5.47
11	Nylon	75.28	6.28	7.98	2.86
	Wool	80.92	1.01	11.26	1.64
12	Nylon	84.6	3.96	4.83	2.74
	Wool	80.20	1.03	16.97	1.86
13	Nylon	86.19	2.62	0.31	2.6
	Wool	82.07	0.97	15.64	1.66
14	Nylon	84.16	4.98	9.05	2.57
	Wool	80.98	1.35	15.34	1.75
15	Nylon	67.9	14.3	19.5	2.66
	Wool	68.02	−4.32	8.86	2.81

3.19 | Color measurements

The colorimetric measurement of the dyed samples was measured using a Hunter Lab ultra Scan PRO spectrophotometer. The analogous color strength value (K/S) was assessed by applying the KubelkaMunk[6] equation (1) as follows:

$$K/S = (1-R)^2/2R - (1-R_o)^2/2R_o \quad (1)$$

where R is the decimal fraction of the reflectance of the dyed fabric, R_o is the decimal fraction of the reflectance of the undyed fabric, K is the absorption coefficient, and S is the scattering coefficient.

3.20 | CIE lab difference

Color measurements of treated textile, were made according to the CIE (L*, a*, b*) system to evaluate the color coordinates. In this system, L* refers to lightness/darkness values from 100 to 0 representing white to black, a* values run from negative (green) to positive (red), and b* values run from negative (blue) to positive (yellow).

3.21 | Fastness properties

Fastness properties were measured according to ISO 105-X12(1987), ISO 105-CO4 (1989), ISO105-EO4 (1989),

TABLE 2 Fastness properties of nylon and wool fabrics dyed with synthesized dyes

							Perspiration						
		Washing			Rubbing		Acidic			Alkaline			
Nu	**Fabric**	**St.***	**St.****	**Alt.**	**Dry**	**Wet**	**St.***	**St.* ***	**Alt.**	**St.***	**St.****	**Alt.**	**Light**
4	Nylon	4	4	4	4	4	4	4	4	4	4	4	3-4
	Wool	4	4	4	4	4	4	4	4	4	4	4	3-4
6	Nylon	3	3	2-3	2-3	2	3	3	2-3	3	3	2-3	2
	Wool	2-3	2-3	2-3	2-3	2	2-3	2-3	2	2-3	2-3	2	2
8	Nylon	3	3	2-3	2-3	2	3	3	2-3	3	3	2-3	2
	Wool	4	4	4	4	4	4	4	4	4	4	4	4
9	Nylon	3	3	2-3	2-3	2	3	3	2-3	3	3	2-3	2
	Wool	4	4	4	4	4	4	4	4	4	4	4	4
10	Nylon	3-4	3-4	3	3-4	3	3-4	3-4	3	3-4	3-4	3	3-4
	Wool	2-3	2-3	2-3	2-3	2	2-3	2-3	2	2-3	2-3	2	2
11	Nylon	2-3	2-3	2-3	2-3	2	2-3	2-3	2	2-3	2-3	2	2
	Wool	3-4	3-4	3	3-4	3	3-4	3-4	3	3-4	3-4	3	3-4
12	Nylon	3	3	3-4	3	2-3	3-4	3-4	3	3-4	3-4	3	2-3
	Wool	4	4	4	4	4	4	4	4	4	4	4	3-4
13	Nylon	3	3	3-4	3	2-3	3-4	3-4	3	3-4	3-4	3	2-3
	Wool	4	4	4	4	4	4	4	4	4	4	4	3-4
14	Nylon	3	3	3-4	3	2-3	3-4	3-4	3	3-4	3-4	3	2-3
	Wool	3-4	3-4	3	3-4	3	3-4	3-4	3	3-4	3-4	3	3-4
15	Nylon	3	3	2-3	2-3	2	3	3	2-3	3	3	2-3	2
	Wool	2-3	2-3	2-3	2-3	2	2-3	2-3	2	2-3	2-3	2	2

Abbreviations: Alt., alteration in color; St.*, staining on cotton; St.**, staining on wool.

ISO 105-BO2 (1988) corresponding to color fastness to rubbing, washing, acid and alkali perspiration, respectively. For the fastness assessment, a rating scale of 1 (poor) to 5 (excellent) was used.

It can be seen from Table 2 that all the dyed nylon and wool fabrics using synthesized dyes showed relatively poor to very good fastness properties to washing, rubbing, acid and alkali perspiration, ranging between 2 and 4 relative to the blank selective thiophene azodye. On the other hand, light fastness tests were carried out for 4 hours irradiation to the dyed samples using a XENOTEST 1200 apparatus at a relative air humidity of 65% and 50°C with duration 4 hours. The prepared synthesized dyes show poor to good as 1-2 to 3-4 and 4 light fastness.

4 | CONCLUSIONS

The present work demonstrates the synthesis of 10 novel azo thienopyridine and thieno pyrimidine dyes and testing their dying abilities on wool and nylon fabrics. The color strength (K/S) values, as well as washing, rubbing, and resistance to acid, alkali and light showed high efficiency of these heterocyclic mon azo dyes to dyeing wool rather than nylon fibers.

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