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# Synthesis and Photophysical Characterization of Highly Stable Cyanine Dyes Based on Pyrazolo[5,4-b]pyrido[2,1-c]pyrimidine and Pyrazolo [5,4-b]pyrido[2,1-d][1,3,4] triazepine

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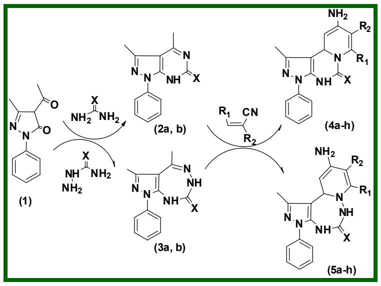
## ABSTRACT

*Outstanding stable cyanine dyes covering the types of monomethine, trimethine, styryl, azastyryl and apocyanines with absorption band reached to 550 nm have been developed and synthesized. These dyes based on high stable N-bridgehead heterocycles namely Pyrazolo[5,4-b]pyrido[2,1-c] pyrimidine*, *pyrazolo[5,4-b]pyrido[2,1-d][1,3,4] triazepines as precursors for the synthesis of the target dyes. The absorption spectra properties of such selected dyes were investigated in 95% ethanol to attempt and throw some light on the influence of such new heterocyclic nuclei and to compare or evaluate spectral behaviors. Such Heterocyclic precursors and related dyes were identified by elemental and spectral analyses.*

## Graphical Abstract



Synthetic Routes of N-Bridge head heterocycles.

**Keywords:** N-Bridgehead heterocycles, cyanine dyes, Spectral behavior.

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## INTRODUCTION

Cyanine dyes are a class of organic compounds that possess two nitrogen containing heterocycles that act as electron donors and acceptors connected by a conjugated methine bridge [1, 2]. Cyanine's were first synthesized from a century ago. They were originally used, and still are, to increase the sensitivity range of photographic emulsions, i.e., to increase the range of wavelengths. This class of dyes has a large application in chemistry, biology and biotechnology [3-5]. N-Bridge head heterocyclic cyanine dyes are an important class of dyes which characterized by the presence unit of aza-heterocyclic compound the nature of nitrogen atom inside the ring. N-Bridge head heterocyclic compound used as precursors possess high site reactivity susceptible to be attack by either electrophile/nucleophile in the substitution/addition reactions which give high stability nature for the dyes [6]. These dyes have many vital general applications this back to their higher stability which can be used as bioactive compounds such as the N-methyl-daspartate antagonists [7]. Furthermore, N-Bridge head heterocyclic cyanine dyes have a wide range of potential applications in fluorescent compounds, DNA-binding dyes [8] and organic materials [9]. According to their bioactivity and structural planarity, it is a reasonable idea to develop functional dyes based on these N-Bridgehead heterocycles. A variety of cyanine dyes incorporating different N-bridgehead heterocyclic moieties have been reported [10-14] heterocycles. In this article, we synthesized novel highly stable N-Bridge head heterocyclic precursors based on pyrazolo[3,4-d]pyrimidine and pyrazolo[5,4-b] pyrido[2,1-d] [1,3,4] triazepine derivatives which directed towards the development of outstanding stable cyanine dyes included the types of monomethine, trimethine, styryl, azastyryl and apocyanines with an expected broad spectrum of biological and industrial applications.

## MATERIALS AND METHODS

**Physical and Chemical Properties Determinations:** All melting points are uncorrected Elemental and spectral analysis was carried out at the microanalytical center-Cairo University. The IR (νKBr) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer. $^1$H-NMR spectra were recorded with a Bruker AMX-250 spectrometer. Mass spectra were recorded on a HpMs 6988 spectrometer. The absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350-700) on 6405 UV/Visible recording spectrophotometers.

**Synthesis:** Analytical data and molecular Properties for all the starting heterocycles and the target dyes involved in this study was obtained and summarized below.

**4-Dimethyl-1-phenyl-1[H]-pyrazolo[3,4-d]pyrimidin-6(7H)-one (thione) (2a,b):** Such compounds were prepared in a way similar to that described in [15].

**3,4-dimethyl-1-phenyl-pyrazolo[3,4-e][1,2,4]triazepin-7-tri-1,6,8[H]-one (3a-h):** An Ethanolic mixture of **(1,** 0.01mol**)** and semi/(thiosemi)-carbazide (0.01mol) was refluxed for 6 h in few drops of piperidine. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol. **(3a, b).**

**5-Amino-3-methyl-1-phenyl-pyrazolo [5,4-b] pyrido [2,1-c] pyrimidine(4a-h) and 5-Amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-d] [1,3,4] triazepine(5a-h):** An ethanolic solution of **(2a, b** or **3a, b,** 0.01mol**)** and arilidine derivatives (0.01 mol) in few drops of piperidine was refluxed for 8-10 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol.

**5-Amino-3-methyl-1-phenyl-pyrazolo [5,4-b] pyrido[2,1-c] pyrimidin-mono-8 [2(4)]methine cyanine dyes (6a-c): Route (A):** An Ethanolic mixture of (**4a, e**, 0.01 mole)**)** and 2-methyl-pyridin [quinolin]-2(4)-ium-ethiodide salts (0.01 mol) in piperidine (1-2 mL) was refluxed for 7-8 h where it gives a deep permanent colour at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products were filtered, washed several times with water, dried and crystallized from ethanol to give the simple cyanine dyes **(6a–c)**, **Route (B):** Fusion of **(4e,** 0.01 mol.**)** with 2-methyl-pyridin[quinolin]-2(4)-ium-ethiodide salts

(0.01 mol) for 30 min, then dissolved in ethanol (30 mL) and refluxed for 5-7 h. The reaction mixture was refluxed for 7-8 h where it gives a deep permanent colour at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products were filtered, washed several times with water, dried and crystallized from ethanol to give the simple cyanine dyes **(6a–c)**.

**5-Amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-d] [1,3,4]triazepin-mono-9[2(4)] methine cyanine dyes(7):** An Ethanolic mixture of **(5a**, 0.01 mol**)** and 2-methyl-pyridin[quinolin]-2(4)-ium-ethiodide salts (0.01 mol) in piperidine (1-2 mL) was refluxed for 6 hours, where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products were filtered, washed several times with water, dried and crystallized from ethanol.

**5-amino-3-methyl-1-phenyl-pyrazolo [5,4-b]pyrido[2,1-c] pyrimidin-2-ium-ethiodide salt (8):** A pure crystallized of **(4b,** 0.01 mol**)** was suspended in excess of ethyl iodide. The reaction mixture was gently refluxed on water bath for 1-2 h. cooled and the precipitates were collected and crystallized from ethanol to give **(8)**.

**5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c] pyrimidin-2-ium-ethiodide salt-mono 8[2(4)] methine cyanine dyes (9):** Fusion of **(8,** 0.01 mol) and 2(4)-methyl-pyridin[quinolin]-2(4)-ium-ethiodide salts (0.01 mol) in few drops of piperidine following refluxed in ethanol for 3-5 h. The reaction mixtures were filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol.

**5-Amino-2-ethyl-3-methyl-1-phenyl pyrazolo[5,4-b]pyrido [2,1-c] pyrimidin mono-3[4(1)] methine cyanine dyes (10a-c):** An Ethanolic mixture of **(8,** 0.01 mol) and pyridin[quinolin]-4 (1)-ium-ethiodide salts (0.01 mol) in few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

**5-Amino-3-methyl-1-phenyl pyrazolo[5,4-b] pyrido[2,1-c] pyrimidin-2-ium-ethiodide salt-3-styryl (aza styryl) cyanine dyes (11a-f):** An Ethanolic **(8,** 0.01 mol) and aromatic aldehydes and/or nitrozo aromatic compounds (0.01 mol)] in few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

**5-amino-3-diethoxy ethenyl-3-methyl-1-phenyl pyrazolo [5,4-b]pyrido[2,1-c] pyrimidin-2-ium-ethiodide salt (12):** An Ethanolic of **(8,** 0.01mol) and triethylorthoformate (0.01 mol) in few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

**5-amino-2-ethyl-3-methyl-1-phenyl pyrazolo[5,4-b]pyrido [2,1-c]pyrimidin-tri-3[2(4)] methine cyanine dyes (13a-c):** An Ethanolic solution of (8, 0.01 mol) and 2(4)-methyl-pyridin[quinolin]-2(4)-ium-ethiodide salts (0.01 mol) in few drops of piperidine was refluxed for 3-5 h. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol**.**

**5-Amino-2-ethyl-3-methyl-1-phenyl pyrazolo[5,4-b] pyrido [2,1-c]pyrimidin-bis-mono-3,8[ 4(1), 2(4)] methine cyanine dyes (14a-c): Route-A:** An Ethanolic solution of **(10a-c,** 0.01mol) and 2-methyl-pyridin-2-ium-ethiodide salt (0.01 mol) in few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

**Route-B:** An Ethanolic solution of (**9,** 0.01 mol) and pyridin[quinolin]-4(1)-ium-ethiodide salts (0.01 mol) in the presence of few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

**5-Amino-3-methyl-1-phenyl pyrazolo[5,4-b]pyrido[2,1-c] pyrimidin-2-ium-ethiodide salt-mono-8[2(4)]methine-3-Styryl(Aza-styryl) cyanine dyes (15a-f): Route-A:** An Ethanolic solution of **(11a-f,** 0.01 mol) and 2-methyl-pyridin-2-ium-ethiodide salt (0.01 mol) in few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

**Route-B:** An Ethanolic solution of **(9,** 0.01 mol) and aromatic aldehyde and/or nitrozo aromatic compounds (0.01 mol) in few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

**5-Amino-2-ethyl-3-methyl-1-phenyl-pyrazolo [5,4-b] pyrido [2,1-c] pyrimidin-mono(tri)-8(3) [2(4)] methine cyanine dyes (16a-c): Route-A:** An Ethanolic solution of **(13a-c,** 0.01 mol) and 2-methyl-pyridin-2-ium-ethiodide salt (0.01 mol) in few drops of piperidine was refluxed for 3-5 h. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol.

**Route-B:** An Ethanolic solution of **(17**, 0.01 mol) and 2-methyl-pyridin [quinolin]-2(4)-ium-ethiodide salts (0.01 mol) in few drops of piperidine was refluxed for 3-5 h. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol**.**

**5-amino-3-diethoxy ethenyl-3-methyl-1-phenyl pyrazolo [5,4-b] pyrido [2,1-c] pyrimidin-2-ium-ethiodide salt mono-8[2(4)] methine cyanine (17):** An Ethanolic solution of **(8**, 0.01 mol**)** and triethylorthoformate (0.01 mol) in few drops of piperidine was refluxed for 5-7 h. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water and crystallized from ethanol.

**Characterization of Data:**

**Compound 2a:** Pink crystals, yield 60%, mp 120°C. FT-IR (KBr pellets, cm$^{-1}$): 3064 (Ar), 1496(C=N) and 1708 (C=O). $^1$H NMR (500 MHz, Chloroform-d, δ): 7.88 (t, J = 7.4 Hz, 2H), 7.81 (m, 1H), 7.67 -7.61 (m, 2H), 3.7-3.73(S, 1H, NH), 2.69 (s, 3H), 2.60 (s, 3H). Elemental analysis; Found: C, 64.98; H, 5.01; N, 23.34%; molecular formula $C_{13}H_{12}N_4O$requires C, 65.00; H, 5.00; N, 23.33%. MS; Found: [M$^+$] 238; base peak=65; molecular formula $C_{13}H_{12}N_4O$requires [M$^+$] 240.

**Compound 2b:** Pink crystals yield 60%, mp 160°C. Elemental analysis; Found: C, 60.81; H, 4.67; N, 21.86%; molecular formula $C_{13}H_{12}N_4S$requires C, 60.90; H, 4.68; N, 21.87%. MS; Found: [$M^+$] 256; base peak=69; molecular formula $C_{13}H_{12}N_4S$requires [$M^+$] 256.

**Compound 3a:** Orange crystals yield 65%, mp 135°C. FT-IR (KBr pellets, $cm^{-1}$): 3064 (Ar), 1496 (C=N) and 1708 (C=O). $^1$H NMR (500 MHz, Chloroform-*d,* δ): 9.36 (s, 2H), 7.92-7.84 (m, 2H), 7.81 (m, 1H), 7.63-7.56 (m, 2H), 2.68 (s, 3H), 2.56 (s, 3H). Elemental analysis; Found: C, 65.90; H, 5.01; N, 27.42 %; molecular formula $C_{13}H_{13}N_5O$requires C, 61.11; H, 5.09; N, 27.41 %. MS; Found: [$M^+$] 256; base peak=91; molecular formula $C_{13}H_{13}N_5O$requires [$M^+$] 255.

**Compound 3b:** Brown crystals yield 62%, mp110°C. Elemental analysis; Found: C, 60.81; H, 4.67; N, 21.86%; molecular formula $C_{13}H_{13}N_5S$requires C, 57.50; H, 4.79; N, 25.82%. MS; Found: [$M^+$] 272; base peak=160; molecular formula $C_{13}H_{13}N_5S$requires [$M^+$] 271.

**Compound 4a:** Brown crystals yield 56%, mp 100°C. FT-IR (KBr pellets, $cm^{-1}$): 3344 ($NH_2$), 2202 (CN), 1498 (C=N), 1625(Ar), 1709 for (C=O). $^1$H NMR (500 MHz, Chloroform-*d,* δ): 9.12 (s, 1H), 7.95 (s, 2H), 7.88 (t, *J* = 7.4 Hz, 2H), 7.81 (m, 1H), 7.65-7.58 (m, 2H), 6.04 (d, *J* = 6.2 Hz, 1H), 4.52 (d, *J* = 6.2 Hz, 1H), 2.46 (s, 3H). Elemental analysis; Found: C, 64.07; H, 4.04; N, 26.45%; molecular formula $C_{17}H_{14}N_6O$requires C, 64.08; H, 4.39; N, 26.39%.

**Compound 4b:** Yellow crystals yield 85%, mp 100°C. Elemental analysis; Found: C, 69.91; H, 4.62; N, 22.56%; molecular formula $C_{23}H_{18}N_6O$ requires C, 69.97; H, 4.56; N, 22.29 %. MS; Found: [$M^+$] 395; base peak=302 molecular formula $C_{23}H_{18}N_6O$ requires [$M^+$] 394.

**Compound 4c:** Yellow crystals yield 75%, mp 100°C. Elemental analysis; Found: C, 64.34; H, 4.72; N, 19.51%; molecular formula $C_{23}H_{20}N_6OS$ requires C, 64.41; H, 4.66; N, 19.60%. MS; Found: [$M^+$] 425; base peak=77 molecular formula $C_{23}H_{20}N_6OS$ requires [$M^+$] 428.

**Compound 4d:** Reddish crystals yield 50%, mp 110°C. MS; Found: [$M^+$] 330; base peak=77 molecular formula $C_{18}H_{16}N_6O$ requires [$M^+$] 332.

**Compound 4e:** Brown crystals yield 70%, mp 180°C. Elemental analysis; Found: C, 61.04; H, 4.22; N, 25.11%; molecular formula $C_{17}H_{14}N_6S$ requires C, 61.07; H, 4.19; N, 25.15%. MS; Found: [$M^+$] 330; base peak=77 molecular formula $C_{17}H_{14}N_6S$ requires [$M^+$] 334.

**Compound 4f:** Green crystals yield 78%, mp 110°C. Elemental analysis; Found: C, 66.65; H, 11.61; N, 20.23%; molecular formula $C_{23}H_{18}N_6S$requires C, 66.69; H, 11.56; N, 20.38%.

**Compound 4g:** Green crystals yield 78%, mp 110°C. Elemental analysis; Found: C, 62.18; H, 4.52; N, 18.56%; molecular formula $C_{17}H_{14}N_6S$ requires C, 62.08; H, 4.50; N, 18.89%.

**Compound 4h:** Brown crystals yield 90%, mp 108°C. FT-IR (KBr pellets, $cm^{-1}$): 3314 ($NH_2$), 2102(CN), 1495 (C=N), 1625(Ar). $^1$H NMR (500 MHz, Chloroform-*d,* δ): 9.24 (s, 1H), 7.94-7.85 (m, 5H), 7.64 – 7.58 (m, 2H), 6.13 (d, *J* = 6.2 Hz, 1H), 4.52 (d, *J* = 6.2 Hz, 1H), 2.47 (d, *J* = 4.9 Hz, 6H).

**Compound 5a:** Brown crystals yield 76%, mp 160°C. FT-IR (KBr pellets, $cm^{-1}$): 3370 ($NH_2$), 2197 (CN), 1497.5 (C=N), at 1730 (C=O). $^1$H NMR (500 MHz, Chloroform-*d,* δ): 7.87 (d, *J* = 6.0 Hz, 4H), 7.81 (m, 1H), 7.61 – 7.54 (m, 2H), 5.50 (d, *J* = 6.2 Hz, 1H), 5.42 (s, 2H), 4.52 (d, *J* = 6.2 Hz, 2H), 2.43 (s, 3H). MS; Found: [$M^+$] 334; base peak=330 molecular formula $C_{17}H_{15}N_7O$ requires [$M^+$] 333.

**Compound 5b:** Yellow crystals yield 75%, mp 110°C. Elemental analysis; Found: C, 67.34; H, 4.62; N, 23.12%; molecular formula $C_{23}H_{19}N_7O$ requires C, 67.40; H, 4.64; N, 23.93 %. MS; Found: [$M^+$] 415; base peak=77 molecular formula $C_{23}H_{19}N_7O$ requires [$M^+$] 409.

**Compound 5c:** Red crystals yield 82%, mp 100°C. Elemental analysis; Found: C, 62.21; H, 4.76; N, 22.10 %; molecular formula $C_{23}H_{21}N_7OS$ requires C, 62.22; H, 4.73; N, 22.09 %.

**Compound 5d:** Green crystals yield 85 %, mp120°C. Elemental analysis; Found: C, 62.19; H, 4.90; N, 28.22%; molecular formula $C_{18}H_{17}N_7O$ requires C, 62.18; H, 4.89; N, 28.21%.

**Compound 5e:** Red crystals yield 82%, mp 140°C. Elemental analysis; Found: C, 58.39; H, 4.19; N, 28.19%; molecular formula $C_{17}H_{15}N_7S$ requires C, 58.38; H, 4.29; N, 28.04%.

**Compound 5f**: Red crystals yield 80%, mp 110°C. Elemental analysis; Found: C, 64.99; H, 4.48; N, 23.01 %; molecular formula $C_{23}H_{19}N_7S$ requires C, 64.87; H, 4.46; N, 23.03%.

**Compound 5g:** Yellow crystals yield 79%, mp 92°C. Elemental analysis; Found: C, 60.09; H, 4.51; N, 21.19%; molecular formula $C_{23}H_{21}N_7S_2$ requires C, 60.06; H, 4.56; N, 21.32%.

**Compound 5h:** Brown crystals yield 67%, mp 125°C. Elemental analysis; Found: C, 59.41; H, 4.53; N, 26.90%; molecular formula $C_{18}H_{17}N_7S$requires C, 59.43; H, 4.67; N, 26.96%.

**Compound 6a:** Red crystals yield 78%, mp 190°C. Elemental analysis; Found: C, 54.66; H, 4.39; N, 17.81%; molecular formula $C_{25}H_{24}IN_7$requires C, 54.65; H, 4.40; N, 17.85%. Uv-Vis: $\lambda_{max}$ (EtOH) 520 nm and molar extinction coefficient $\varepsilon_{max}$ 2550 $M^{-1}cm^{-1}$.

**Compound 6b:** Violet crystals yield 82%, mp 140°C. FT-IR (KBr pellets, $cm^{-1}$): 3429.5 ($NH_2$), 2195.9 (CN), 1496.5 (C=N), 1620.8 (C=C) conjugated. $^1$H NMR (500 MHz, Chloroform-d, δ): 0.843 (S, 3H, $CH_3$), 1.22 (q, 2H, $CH_2$), 1.55 (t, 3H, $CH_3$), 2.5 (S, 2H, $NH_2$), 3.4 (S, 1H, NH), 7.4-7.9 (16H, m). MS; Found: [$M^+$] 599; base peak=271 molecular formula $C_{29}H_{26}IN_7$requires [$M^+$] 599. UV-Vis: $\lambda_{max}$ (EtOH) 550 nm and molar extinction coefficient $\varepsilon_{max}$ 2660 $M^{-1}cm^{-1}$.

**Compound 6c:** Red crystals yield 75%, mp 160°C. Elemental analysis; Found: C, 54.36; H, 4.31; N, 17.91 %; molecular formula $C_{25}H_{24}IN_7$ requires C, 54.65; H, 4.40; N, 17.85%. Uv-Vis: $\lambda_{max}$ (EtOH) 525 nm and molar extinction coefficient $\varepsilon_{max}$ 2580 $M^{-1}cm^{-1}$.

**Compound 7:** Red crystals, yield 87%, mp 185°C. FT-IR (KBr pellets, $cm^{-1}$): 3423.99 ($NH_2$), 2202.31 (CN), 1496.49 (C=N), 1600.63 (C=C) conjugated and 2925.48 (heterocyclic quaternary salt).MS; Found: [$M^+$] 565; base peak=231 molecular formula $C_{25}H_{25}IN_8$ requires [$M^+$] 564. UV-Vis: $\lambda_{max}$ (EtOH) 545 nm and molar extinction coefficient $\varepsilon_{max}$ 2125 $M^{-1}cm^{-1}$.

**Compound 8:** Pale brown crystals, yield 82 %, mp 160°C. Elemental analysis; Found: C, 46.51; H, 3.83; N, 17.16%; molecular formula $C_{19}H_{19}IN_6S$ requires C, 46.49; H, 3.87; N, 17.13%.

**Compound 9:** Brown crystals yield 85%, mp 135°C. Elemental analysis; Found: C, 45.54; H, 4.23; N, 13.96 %; molecular formula $C_{27}H_{29}I_2N_7$requires C, 45.97; H, 4.14; N, 13.90%.

**Compound 10a:** Red crystals yield 65%, mp 220°C. Elemental analysis; Found: C, 52.34; H, 4.43; N, 16.46 %; molecular formula $C_{26}H_{26}IN_7S$requires C, 52.39; H, 4.33; N, 16.45%. MS; Found: [$M^+$] 595; base peak=91 molecular formula $C_{26}H_{26}IN_7S$ requires [$M^+$] 595Uv-Vis: $\lambda_{max}$ (EtOH) 395 nm and molar extinction coefficient $\varepsilon_{max}$ 2396 $M^{-1}cm^{-1}$.

**Compound 10b:** Red crystals yield 75%, mp 190°C. FT-IR (KBr pellets, $cm^{-1}$): 1494 (C=N), 1599.66 conjugated (C=C), 2200.3 (CN)), 3409.5 ($NH_2$). $^1$H NMR (500 MHz, Chloroform-d, δ): 0.9 (t, 6H, $2CH_3$), 1.6 (q, 4H, $2CH_2$), 3.3 (S, 2H, $NH_2$), 7.3-8.1(13H, Aromatic).MS; Found: [$M^+$] 646; base peak=60 molecular formula $C_{30}H_{28}IN_7S$ requires [$M^+$] 645. UV-Vis: $\lambda_{max}$ (EtOH) 495 nm and molar extinction coefficient $\varepsilon_{max}$ 2389 $M^{-1}cm^{-1}$.

**Compound 10c:** Red crystals yield 80%, mp 180°C. UV-Vis: $\lambda_{max}$ (EtOH) 455 nm and molar extinction coefficient $\varepsilon_{max}$ 2368 $M^{-1}cm^{-1}$.

**Compound 11a:** Red crystals yield 63%, mp 155°C. UV-Vis: $\lambda_{max}$ (EtOH) 460 nm and molar extinction coefficient $\varepsilon_{max}$ 1694 $M^{-1}cm^{-1}$.

**Compound 11b:** Reddish crystals yield 88%, mp 120°C. FT-IR (KBr pellets, $cm^{-1}$): 1494 (C=N), 1598.4 conjugated (C=C), 2230.3 (CN)), 3410.5 ($NH_2$).MS; Found: [$M^+$] 621; base peak=305 molecular formula $C_{28}H_{28}IN_7S$ requires [$M^+$] 621. UV-Vis: $\lambda_{max}$ (EtOH) 390 and 465 nm, molar extinction coefficient $\varepsilon_{max}$2479 and 2469 $M^{-1}cm^{-1}$.

**Compound 11c:** Orange crystals yield 81%, mp 140°C. UV-Vis: $\lambda_{max}$ (EtOH) 390 nm and molar extinction coefficient $\varepsilon_{max}$1591 $M^{-1}cm^{-1}$.

**Compound 11d:** Dark red crystals yield 83%, mp200°C.MS; Found: [$M^+$] 596; base peak=374 molecular formula $C_{25}H_{22}IN_7OS$ requires [$M^+$] 595.UV-Vis: $\lambda_{max}$ (EtOH) 440 nm and molar extinction coefficient $\varepsilon_{max}$1792$M^{-1}cm^{-1}$.

**Compound 11e:** Brown crystals yield 72%, mp 185°C. FT-IR (KBr pellets, $cm^{-1}$): 1493.7 (C=N), 1592.91 conjugated (C=C), 2194.6 (CN), 3376.75 ($NH_2$).MS; Found: [$M^+$] 648; base peak=92 molecular formula $C_{29}H_{24}IN_7OS$ requires [$M^+$] 645. UV-Vis: $\lambda_{max}$ (EtOH) 390 and 460 nm, molar extinction coefficient $\varepsilon_{max}$1720 and 1604$M^{-1}cm^{-1}$.

**Compound 11f:** Brown crystals yield 76%, mp 190°C. UV-Vis: $\lambda_{max}$ (EtOH) 390 and 500 nm, molar extinction coefficient $\varepsilon_{max}$2401 and 2264$M^{-1}cm^{-1}$.

**Compound 12:** Brown crystals yield 85%, mp 200°C. Elemental analysis; Found: C, 48.59; H, 4.80; N, 14.51 %; molecular formula $C_{24}H_{29}IN_6O_2S$ requires C, 48.60; H, 4.89; N, 14.17%.

**Compound 13a:** Dark red crystals yield 63 %, mp 260°C. UV-Vis: $\lambda_{max}$ (EtOH) 475 nm and molar extinction coefficient $\varepsilon_{max}$1625 $M^{-1}cm^{-1}$.

**Compound 13b:** Violet crystals yield 70%, mp 230°C. FT-IR (KBr pellets, $cm^{-1}$): 1493.9 (C=N), 1596 conjugated (C=C), 2232.4(CN), 3411 ($NH_2$). $^1H$ NMR (500 MHz, Chloroform-d, δ): 1.23 (t, 6H, $2CH_3$), 2.26 (q, 4H, $2CH_2$), 2.497 (S, 2H, $NH_2$), 2.65 (S, 1H, CH), 3.34 (S, NH, H), 7.32-7.82 (m, 15H). UV-Vis: $\lambda_{max}$ (EtOH) 535 nm and molar extinction coefficient $\varepsilon_{max}$1871 $M^{-1}cm^{-1}$. MS; Found: [$M^+$] 672; base peak=298 molecular formula $C_{32}H_{30}IN_7S$ requires [$M^+$] 671.

**Compound 13c:** Brown crystals yield 66 %, mp 237°C. UV-Vis: $\lambda_{max}$ (EtOH) 495 nm and molar extinction coefficient $\varepsilon_{max}$1792 $M^{-1}cm^{-1}$.

**Compound 14a:** Violet crystals yield 74 %, mp 160°C. UV-Vis: $\lambda_{max}$ (EtOH) 540 nm and molar extinction coefficient $\varepsilon_{max}$2500 $M^{-1}cm^{-1}$.

**Compound 14b:** Violet crystals yield 69 %, mp 165°C. $^1H$ NMR (500 MHz, Chloroform-d, δ): 1.2 (t, 6H, $2CH_3$),1.55 (q, 4H, $2CH_2$), 2.27 (S, 2H, $NH_2$), 3.34 (S,1H, NH), 7.4-7.9(16H; m).MS; Found: [$M^+$] 860; base peak=207 molecular formula $C_{40}H_{40}I_2N_8$ requires [$M^+$] 886.Uv-Vis: $\lambda_{max}$ (EtOH) 550 nm and molar extinction coefficient $\varepsilon_{max}$2654 $M^{-1}cm^{-1}$.

**Compound 14c:** Red violet crystals yield 78 %, mp 170°C.UV-Vis: $\lambda_{max}$ (EtOH) 545nm and molar extinction coefficient $\varepsilon_{max}$2522$M^{-1}cm^{-1}$.

**Compound 15a:** Yellow crystals yield 62 %, mp 150°C.UV-Vis: $\lambda_{max}$ (EtOH) 495 nm and molar extinction coefficient $\varepsilon_{max}$2354 $M^{-1}cm^{-1}$.

**Compound 15b:** Orange crystals yield 67 %, mp 182°C.UV-Vis: $\lambda_{max}$ (EtOH) 500 nm and molar extinction coefficient $\varepsilon_{max}$2588 $M^{-1}cm^{-1}$.

**Compound 15c:** Red crystals yield 73 %, mp 190°C. FT-IR (KBr pellets, $cm^{-1}$): 3425.9 ($NH_2$), 2198.5(CN), 1494.56 (C=N), 1370.2 ($NO_2$), 1623.8 (C=C) conjugated. UV-Vis: $\lambda_{max}$ (EtOH) 425 nm and molar extinction coefficient $\varepsilon_{max}$2321 $M^{-1}cm^{-1}$.

**Compound 15d:** Brownish crystals yield 75 %, mp 123°C. UV-Vis: $\lambda_{max}$ (EtOH) 485 nm and molar extinction coefficient $\varepsilon_{max}$2611 $M^{-1}cm^{-1}$.

**Compound 15e:** Red crystals yield 72%, mp 120°C. FT-IR (KBr pellets, $cm^{-1}$): 3383.5 ($NH_2$), 2198.5 (CN), 1499.4(C=N), 1617.98 (C=C) conjugated. UV-Vis: $\lambda_{max}$ (EtOH) 490 nm and molar extinction coefficient $\varepsilon_{max}$2661 $M^{-1}cm^{-1}$.

**Compound 15f:** Brownish crystals yield 69%, mp 153°C. UV-Vis: $\lambda_{max}$ (EtOH) 500 nm and molar extinction coefficient $\varepsilon_{max}$2710 $M^{-1}cm^{-1}$.

**Compound 16a:** Red crystals yield 67%, mp 147°C. UV-Vis: $\lambda_{max}$ (EtOH) 555 nm and molar extinction coefficient $\varepsilon_{max}$2510 $M^{-1}cm^{-1}$.

**Compound 16b:** Red crystals, yield 72%, mp 150°C.$^1$H NMR (500 MHz, Chloroform-d, δ): 1.2-1.6 (t, 6H, 2$CH_3$), 2.2-2.4 (q, 4H, 2$CH_2$), 2.5 (S, 2H, $NH_2$), 3.34 (S, 1H, NH), 7.38-7.67 (16H, m).UV-Vis: $\lambda_{max}$ (EtOH) 580 nm and molar extinction coefficient $\varepsilon_{max}$2770 $M^{-1}cm^{-1}$.

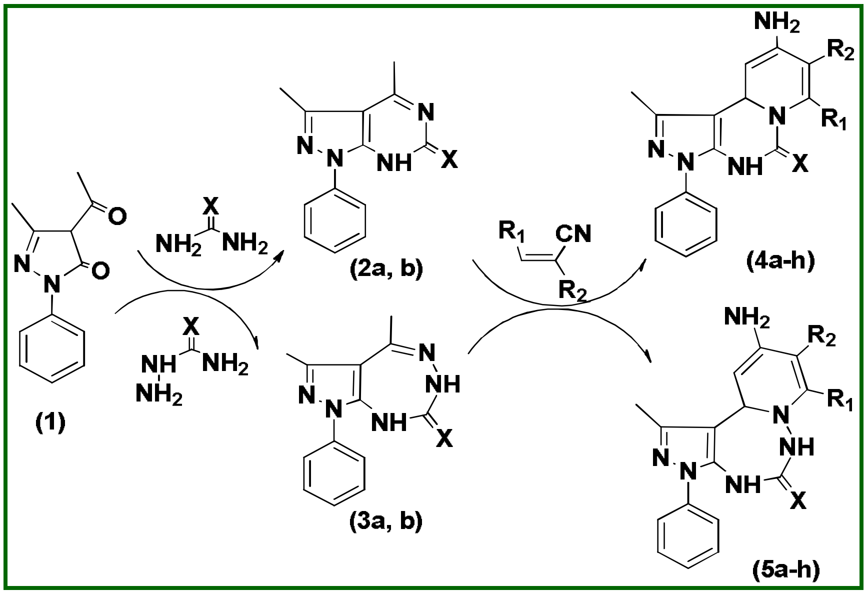
**Compound 16c:** Pale red crystals yield 65%, mp 155°C. UV-Vis: $\lambda_{max}$ (EtOH) 560nm and molar extinction coefficient $\varepsilon_{max}$2600 $M^{-1}cm^{-1}$.

**Compound 17:** Pale brown crystals yield 70%, mp 155°C. UV-Vis: $\lambda_{max}$ (EtOH) 560 nm and molar extinction coefficient $\varepsilon_{max}$2600 $M^{-1}cm^{-1}$. Elemental analysis; Found: C, 47.61; H, 4.86; N, 12.31 %; molecular formula $C_{24}H_{29}IN_6O_2S$ requires C, 47.60; H, 4.87; N, 12.14%.

## RESULTS AND DISCUSSION

**Synthesis:** The target dyes synthesized started by cycloaddition reaction of **(2a, b** and **3a, b)** with arilyidine derivatives such as methylidene propane dinitrile, benzilidine malononitrile, 2-cyano-3-phenylprop-2-ene-thioamide and ethylidene propane dinitrile, in equimolar amount, under piperidine catalysis to afford 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidine derivatives **(4a-h)** and 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-d][1,3,4]triazepine derivatives **(5a-h)** respectively, **Scheme (1A).**

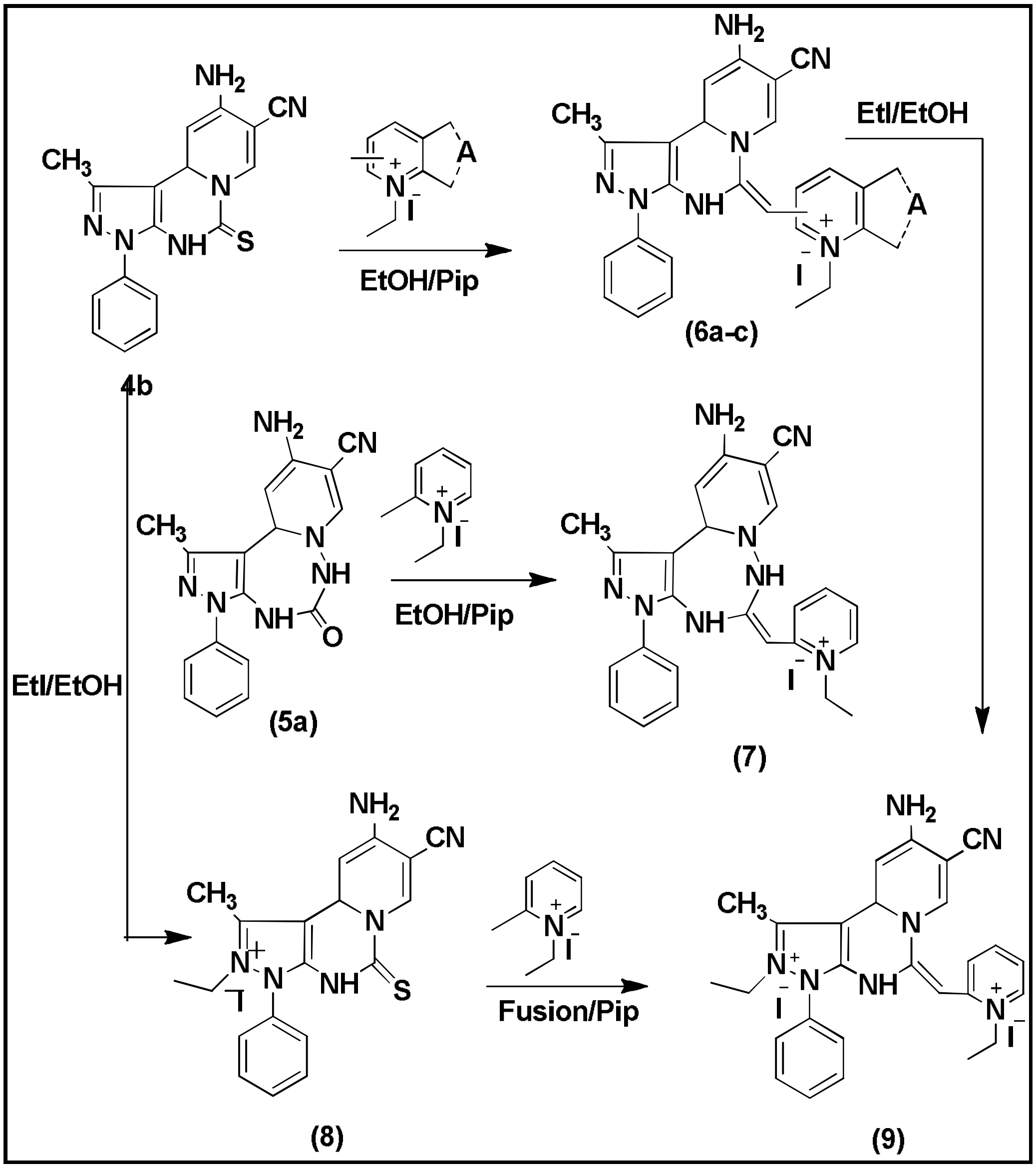
5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b] pyrido [2,1-c] pyrimidine and 5-amino-6-cyano-3-methyl-1-phenyl-pyrazolo[3,4-f]pyrido[1,2-d][1,2,4]triazepine **(4b** and **5a)** reacted with 2-methyl-pyridin (quinolin)-2(4)-ium-ethiodide salts inequimolar amount, under piperidine catalysis afforded pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-mono-8[2(4)]methine **(6a-c)** and 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-d][1,3,4] triazepin-mono-9[2(4)]methine **(7)** respectively**.** Selective quaternization of 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidine **(4b)** using



**Scheme 1A.** Synthetic Routes of N-Bridgehead heterocycles. Where, **(2,3 a, b):** X=O (a), X=S (b), **(4, 5a-h):** X=O, $R_1$= H, $R_2$= CN (a), X=O, $R_1$= Ph, $R_2$= CN(b), X=O, $R_1$= Ph, $R_2$= $CSNH_2$ (c), X=O, $R_1$= $CH_3$, $R_2$= CN (d), X=S, $R_1$= H, $R_2$= CN (e), X=S, $R_1$= Ph, $R_2$= CN (f), X=S, $R_1$= Ph, $R_2$= $CSNH_2$ (g), X=S, $R_1$= $CH_3$, $R_2$= CN (h).

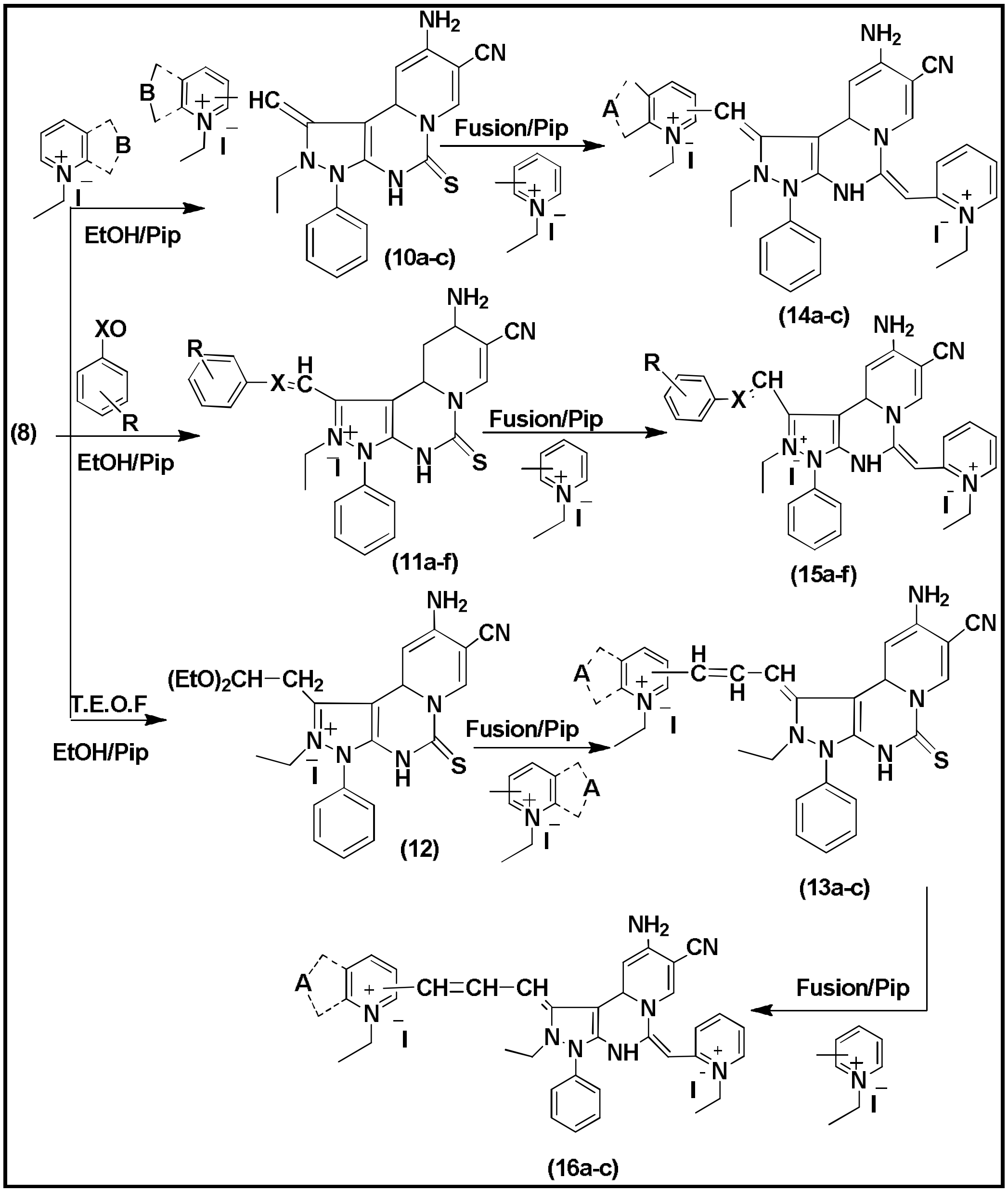
ethyl iodide afforded 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-2-ium-ethiodide salt **(8)** which reacted with 2-methyl-pyridin -2(4)-ium-ethiodide salt in, equimolar amount, under piperidine catalysis to give pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-2-ium-ethiodide salt-mono 8[2(4)] methine cyanine dye **(9).** The later dye **(9)** was chemically confirmed by the direct selective quaternization of 1-phenyl-3-methyl-5-amino-6-cyano-9-hydro-pyrazolo[4,3-e]pyrido[1,2-c] [1,3] pyrimidin-8-mono [2(4)] methine cyanine dyes **(8)** using ethyl iodide, **Scheme (1B)**.

Subsequent reaction of 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c] pyrimidin-2-ium-ethiodide salt **(8)** with pyridin[quinolin]-4(1)-ium-ethiodide salts in, equimolar amount, under piperidine catalysis afforded 5-amino-2-ethyl-3-methyl-1-phenyl Pyrazolo [5,4-b] pyrido [2,1-c]pyrimidin-mono-3[4(1)]methine cyanine dyes **(10a-c).**The interaction of **(8)** and aromatic aldehydes and/or aromatic Nitroso compounds in, equimolar amount, under piperidine catalysis afforded5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-2-ium -ethiodide salt-3-styryl (aza-styryl) cyanine dyes **(11a-f).** Interaction of **(8)** and tri-ethyl ortho-format in, equimolar amount, under piperidine catalysis gives 5-amino-3-diethoxy-ethenyl-3-methyl-1-phenyl-Pyrazolo[5,4-b]pyrido[2,1-c] pyrimidin-2-ium-ethiodide salt **(12)**. Further reaction of **(12)**with pyridin [quinolin]-2(4)-ium-1-ethiodide salts in, equimolar amount, under piperidine catalysis produced 5-amino-2-ethyl-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido [2,1-c] pyrimidin-tri-3[2(4)]methine cyanine dyes **(13a-c)**.Thermal piperidine catalysis of 5-amino-2-ethyl-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-mono-3[4(1)]methine **(10a-c)** and 2-methyl-pyridin(quinolin)-2(4)-ium-ethiodide saltsin, equimolar amount, under piperidine catalysis afforded 5-amino-2-ethyl-3-methyl-1-phenyl pyrazolo [5,4-b] pyrido[2,1-c]pyrimidin-bis-mono-3,8[4(1), 2(4)] methine cyanine dyes **(14a-c)**. Thermal piperidine catalysis of 3-styryl (azastyryl) cyanine dyes **(11a-f)** and 2-methyl-pyridine ethiodide saltsunder piperidine catalysis afforded 5-amino-3-methyl-1-phenyl-pyrazolo [5,4-b]pyrido[2,1-c]pyrimidin-2-ium-ethiodide-salt-mono-8[2(4)]methine-3-styrylcyanine dyes **(15a-f)**. Thermal piperidine catalysis of pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-tri-3[2(4)]methine cyanine dyes **(13a-c)** and 2-methyl-pyridine ethiodide salts in piperidine afforded 5-amino-2-ethyl-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-mono(tri)-8(3) [2(4)] methine cyanine dyes **(16a-c), Schemes (2A).**



**Scheme 1B:** Synthetic routes of dyes **(6a-c), (7),** and **(9).** where,A = 1-ethyl pyridin-2-ium salt (a); A=1-ethyl-quinolin-2-ium salt (b); A= 1-ethyl-pyridin-4-ium salt (c).

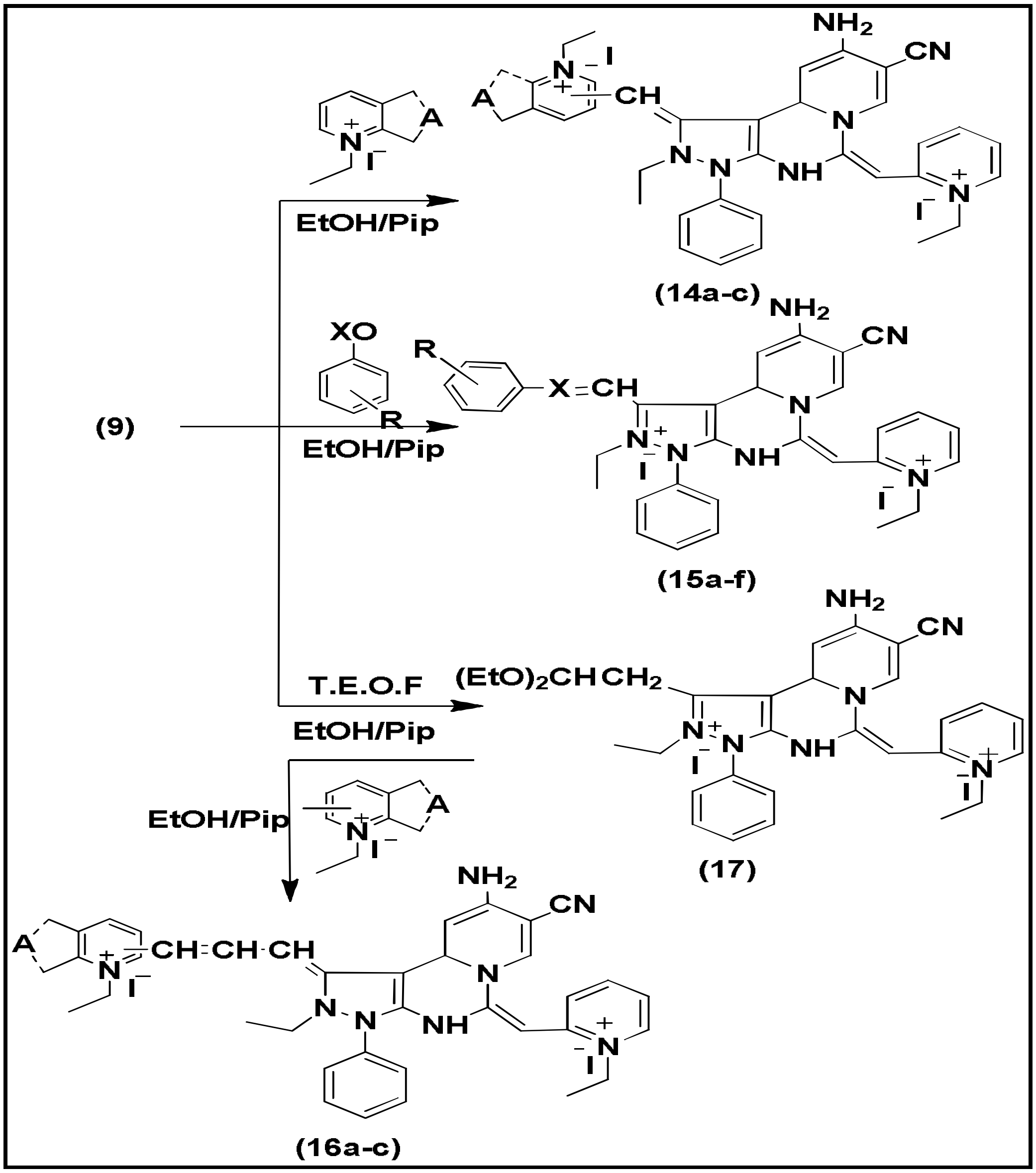
Where, **(10a-c):** B = 1-ethyl pyridin-4-ium salt (a); 1-ethyl-quinolin-4-ium salt (b); 2-ethyl-quinolin-1-ium salt (c),; **(11a-f):** R = H, X= CH (a); R=p-N $(CH_3)_2$, X=CH (b); R=p-$NO_2$, X=CH (c); R= 4-OH, X=N (d); R= 2-OH, 5, 6- $C_4H_4$-, X=N (e); R= 2-OH; 3, 4-$C_4H_4$-, X=N (f); **(13a – c):** A=1-ethyl pyridin-2-ium salt (a); 1-ethyl-quinolin-2-ium salt (b); 1-ethyl-pyridin-4-ium salt (c); **(14a-c):** A=1-ethyl pyridin-2-ium salt (a); 1-ethyl-quinolin-2-ium salt (b); 1-ethyl-pyridin-4-ium salt (c); **(15a-f):** R = H, X= CH (a); R=p-N $(CH_3)_2$, X=CH (b); R=p-$NO_2$, X=CH (c); R= 4-OH, X=N (d); R= 2-OH, 5, 6-$C_4H_4$-, X=N (e); R= 2-OH; 3, 4-$C_4H_4$-, X=N (f) and **(16a-c):** A=1-ethyl pyridin-4-ium salt (a); 1-ethyl-quinolin-4-ium salt (b); 2-ethyl-quinolin-1-ium salt (c).



**Scheme (2A):** Synthetic routes of dyes **(10a-c)**, **(11a-f)**, **(13a-c)**, **(14a-c)**, **(15a-f)** and **(16a-c):**

Dyes**(13a-c)**, **(14a-c), (15a-f) and (16a-c)**. have been experimentally confirmed by the interaction of 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido [2,1-c] pyrimidin-2-ium-ethiodide salt-mono-8[2(4)] methine cyanine dye **(9)** with pyridin[quinolin]-4(1)-ium-ethiodide salts in equimolar amount, under piperidine catalysis afforded 5-amino-2-ethyl-3-methyl-1-phenyl pyrazolo [5,4-b] pyrido[2,1-c]pyrimidin-bis-mono-3,8 [4(1), 2(4)] methine cyanine dyes **(14a-c)**.The reaction of 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b] pyrido[2,1-c]pyrimidin-2-ium-ethiodide salt-mono-8[2(4)] methine cyanine dye **(9)** and aromatic (aldehydes and/or Nitroso) compounds in equimolar amount, under piperidine catalysis afforded 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-2-ium-ethiodide-salt-mono-8[2(4)] methine-3-styryl cyanine dyes **(15a-f)**. the Interaction of 5-amino-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-2-ium-ethiodide salt-mono-8[2 (4)] methine cyanine dye **(9)** and tri-ethyl ortho-format in equimolar amount, under piperidine catalysis achieve 5-

amino-3-diethoxy-ethenyl-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c]pyrimidin-2-ium-ethiodide salt mono-8[2(4)] methine cyanine **(17)** followed by the reaction with 2-methyl-pyridin(quinolin)-2(4)-ium-ethiodide salts in piperidine afforded 5-amino-2-ethyl-3-methyl-1-phenyl-pyrazolo[5,4-b]pyrido[2,1-c] pyrimidin-mono(tri)-8(3) [2(4)] methine cyanine dyes **(16a-c)**, **Scheme (2B).**



**Schemes (2B):** Synthetic routes of dyes **(14a-c), (15a-f)** and **(16a-c)**

**Color and Spectral behaviour:** The Synthesized mono (tri) methine and (aza) styryl cyanine dyes**(6a-c), (7),(10a-c), (11a-f), (13a-c),(14a-c)(15a-f)**and**(16a-c)** are highly colored compounds. Their color in ethanolic solution are ranging from (reddish brown to red), (reddish brown to reddish) and (red to violet) in color respectively, easily (partially) soluble in polar (non) organic solvents exhibiting colored solutions (reddish/red/violet) concomitant with slight or intense greenish-red fluorescence depending upon the solvent used. They are soluble in concentrated $H_2SO_4$ acid liberating iodine vapour on warming. Their ethanolic solutions gave permanent colors in basic media which reversibly discharged on acidification. The absorption spectra of the dyes in 95% ethanol showed absorption bands batho underwent (hypso) chromically shifted depending upon the nature of heterocyclic quaternary residue A, B and their linkage position. Thus, the visible absorb-maximum of dye**6b**showed absorption band at which bathochromically shifted to dyes **6a, 6c**concomitant with the increasing number of absorption bands. This is attributed to the more extensive π- delocalization and extra conjugation in the quinoline ring than pyridine. Additionally, changing the linkage position of pyridinium from 2-ium salt in**6a** to the 4-ium analogue salt in**6c** showed bathochromically shifted band by $\Delta\lambda_{max}$ = 5 nm. This is due to the extended of π-delocalization within pyridine-4-ium ethiodide in **6c.** Also, substituting of heterocyclic pyrazolo[5,4-b]pyrido[2,1-c]pyrimidine in dye**6a** by pyrazolo [5, 4-b]pyrido[2,1-d][1,2,4]triazepines in dye **10** showed bathochromic shift by $\Delta\lambda_{max}$ = 25 nm. This is due to increasing the ring size in dye7compared to dye**6a.** The same behavior observed for dyes**(10a-c), (13a-c), (14a-c)**and **(16a-c)**. Moreover, the absorption spectra of dyes **11a-f** in 95% ethanol consists of different absorption bands, their position and molar extinction coefficient being influenced by the nature of aryl substituent's. Thus, the absorption spectra **11b** achieved bathochromic shift by $\Delta\lambda_{max}$=5nm. This is attributed to the partial mixing of the lone pair orbitals of nitrogen with π system of the heterocyclic ring leading to a modified set of energy levels and this moves the band to the longer wavelength and hypsochromic shift to **11c**by $\Delta\lambda_{max}$= 75nm. This is due to an electron withdrawing character of $NO_2$ group which leads to decreasing the charge transfer on pyrazolo [5,4-b]pyrido[1,2-c] pyrimidin-2-ium-quaternary salt residue. On the other hand, dye **11e**achieved bathochromic shift by $\Delta\lambda_{max}$= 20 nm compared to **11d**, this is due to the more extensive π-delocalization in naphthalene ring. While **11f** achieved bathochromic shift compared to **11e** by $\Delta\lambda_{max}$=40 nm, this can be explained by the fact that dye **11e** is of angular type but dye **11f** the antagonism is performed by stronger interaction between the n-electrons of the nitrogen atom and the more extended conjugation of the naphthyl ring, this is due to the planarity of dye **11f**.Thesame spectral behavior observed for **(15a-f). We** noticed that, yes **(14a-c)** and **(15a-c)** are bathochromically shifted compared to dyes (**10a-c)** and **(11a-c)** respectively. This is due to dyes **(14a-c)** and **(15a-c)** have two π-delocalization conjugations while, **(10a-c)** and **(11a-c)** have just one π-conjugation.

## APPLICATION

Novel unsymmetrical bis-monomethine and apomethine cyanine dyes based on N-bridgehead heterocycles have been developed and characterized. These dyes have many vital general applications this back to the high stability of that type of dyes. These dyes have a wide range of potential applications in energy conversion, as laser dyes, as optoelectronic devices, perovskite, nucleic acids labelling, fluorescence sensors, electro-, chemo-, and photoluminescent devices.

## CONCLUSIONS

Highly panchromatic monomethine, trimethine, styryl, azastyryl and apocyanine dyes which may have a large use in biological and industrial applications have been synthesized with absorption wavelength bands in the region of 400-550 nm. The easier of dye formation is due to that N-bridge head heterocyclic compound used as precursors possess high site reactivity susceptible to be attack by either Electrophile/Nucleophile in the substitution/ addition reactions. The color of the fluorescence intensity of all dyes depends basically upon the type of dye and solvent used. the UV-Vis absorption spectra of the synthesized cyanine dyes give bathochromic or hypsochromic shifted bands depending on the following factors:a) Increasing and/or decreasing л-delocalization conjugation in the dye molecule b) Presence of electron pushing and/or electron pulling groups c) Higher and/or lower planarity of the dye molecule d) The intensity of the color of the synthesized cyanine dyes is due to two suggested mesomeric structures producing a delocalized positive charge over the conjugated system.

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