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Iron(III) chloride catalysed three-component Grieco condensation: Synthesis of tetrahydropyrido[2′,3′:3,4]pyrazolo [1,5-*a*]pyrimidines/quinazolines

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Abstract

Three-component Grieco condensation reaction of 3-aminopyrazolo[3,4-*b*]pyridine, formaldehyde/benzaldehyde and electron rich alkenes in presence of iron(III) chloride gave tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidines/quinazolines in single pot. The sequence of reactions is formation of di-azadiene in situ and the subsequent regioselective addition of alkenes in aza-Diels Alder type reaction. The structure and stereochemistry of the products were confirmed by spectral data and single crystal X-ray crystallography.

Keywords: Pyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidines/quinazolines; Aza-Diels Alder reaction; Regioselective; Electron rich alkenes and dehydrogenation

1. Introduction

Pyrazole fused pyridines and pyrimidines are known to possess a wide range of biological activity. Specifically pyrazolo pyridines exhibit antitubercular [1], anxiolytic [2] and potent vasodilating activity due to their calcium blocking effect [3], whereas pyrazolo pyrimidines [4,5] are considered to be selective inhibitors of cyclic 3′,5′-adenosine monophosphate (cAMP) phosphodiesterases. The combination pyridine, pyrazole and pyrimidine ring system to form pyrido pyrazolo pyrimidines and their influence on activity is of current interest. Earlier reports on synthesis of pyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidines are mainly by reactions of 3-aminopyrazolo[3,4-*b*]pyridines with symmetrical and unsymmetrical 1,3-diketones [6], β-keto esters [7] and 1,1,1-trifluoro-3-(isobutoxymethylene)-2-propanones.[8] Further Grieco and Bahsas [9] first reported that cyclopentadiene and formaldehyde react with anilines to give tetrahydroquinolines. The same methodology has been applied to build many heterocyclic skeletons from aminoheterocycles in single step, *viz*., synthesis of azasteroids [10] from aminotetralones, polycyclic quinines [11] from aminoanthraquinones, 3,4-dihydro-2*H*-pyrido[1,2-*a*]pyrimidines [12] from 2-aminopyridines and cyclic amidines [13] from aminoheterocycles. These reports have established with different electron rich alkenes that the reaction proceeds via a multi-step pathway. However 3-aminopyrazolo[3,4-*b*]pyridines have not been exploited so far as starting materials for aza-Diels Alder type reactions. Due to our continued interest [14–17] in synthesis of novel ring systems, we report here for the first time synthesis of new pyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidines/quinazolines by formal aza-Diels Alder type reaction of 3-aminopyrazolo[3,4-*b*]pyridine with formaldehyde/benzaldehyde and various electron rich alkenes.

2. Results and discussion

The 6-phenyl-4-(trifluoromethyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (**1**), was reacted with formaldehyde/benzaldehyde followed by electron rich alkene in acetonitrile in presence of one equivalent of $FeCl_3$ under N_2 atmosphere at room temperature for 30–60 min, to result tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidines/quinazolines in single pot. The reaction mixture

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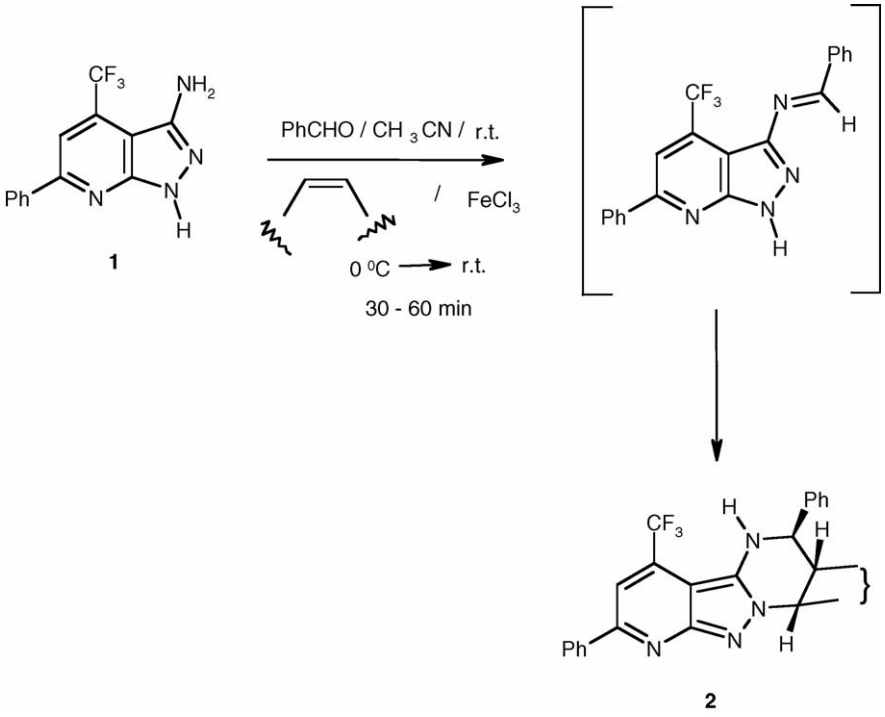
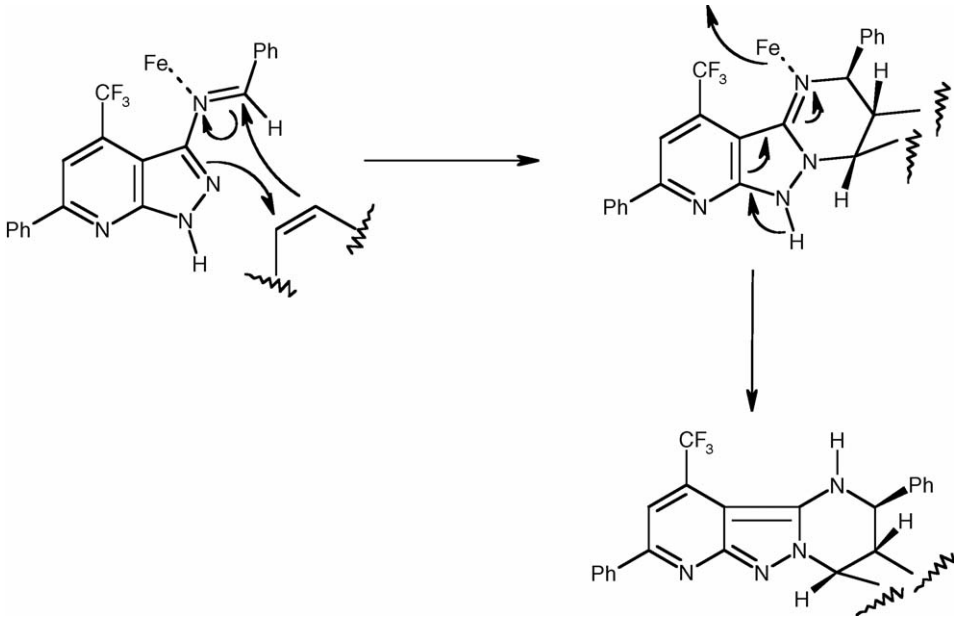


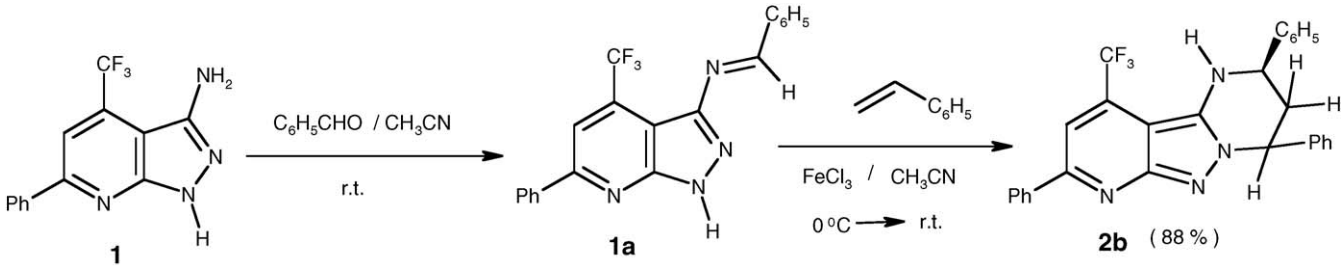
Scheme 1.

after aqueous workup, extraction with dichloromethane and column chromatography gave the corresponding adducts (**2a**–**2o**) in good to excellent yields without side products. The yields of the products with formaldehyde were higher compared to benzaldehyde. This may be attributed to the steric factors. The sequence of reaction is shown in Scheme 1. In case of reaction of compound **1** with benzaldehyde followed by alkenes, the formation of single product unlike the anticipated mixture of regioisomers observed in aza-Diels Alder reactions, indicates that the cyclisation is regioselective.

The mode of reaction is mainly formation of Schiff's base in situ which acts as a diazadiene and iron(III) chloride is complexed with Schiff's base double bond followed by regioselective cyclisation with various electron rich alkenes leading to the corresponding adducts. The regioselectivity in the reaction with benzaldehyde may be due to formation of exclusively one stereo isomer of the Schiff's base, out of the possible E and Z isomers, which undergoes cyclisation with the alkene. It may also be attributed to the steric hindrance of the phenyl group in Schiff's base. The probable mechanism is given in Scheme 2.



Scheme 2.



Scheme 3.

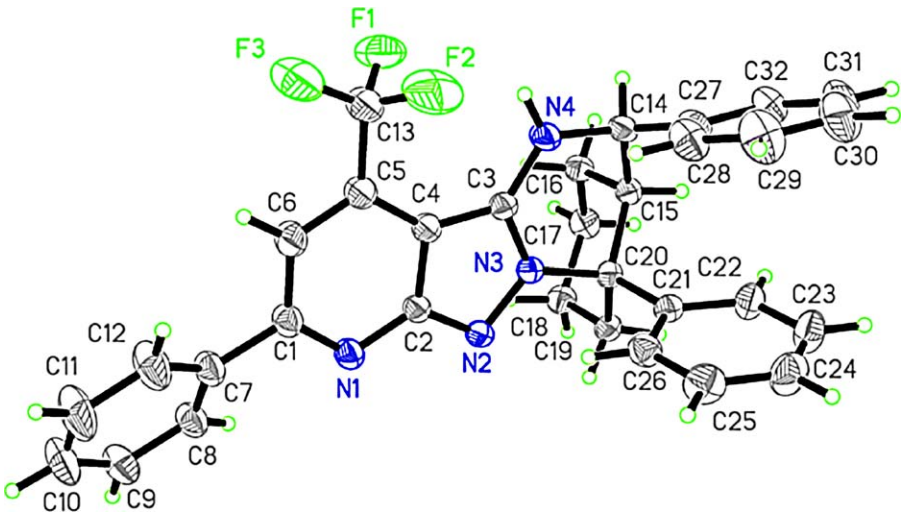


Fig. 1. X-ray crystal structure of **2l**. Displacement ellipsoids are drawn at 30% probability level and H atoms are shown as small spheres of arbitrary radii.

In order to support the mechanism, compound **1** was reacted with benzaldehyde in acetonitrile at room temperature and isolated Schiff's base **1a**. The Schiffs base thus formed was further reacted with styrene in presence of $FeCl_3$ and obtained compound **2b** in 88% yield with stereochemistry identical to the product formed by in situ reaction. Also there were no intermediates isolated in the reaction. This indicates the reaction probably proceeds by concerted mechanism. The reaction is schematically drawn in Scheme 3.

The structure and stereochemistry of all the products were unambiguously confirmed based on ^{1}H NMR, IR, mass spectra and crystal data. The small coupling constant J (**3a**–**11a**) = 7.3 Hz of the ring junction protons in **2c** indicates a *cis* ring junction, supported by crystal structure, is in agreement with earlier reports [12,13]. Similarly regioselectivity in cyclisation is observed whereby only *cis* ring fused adducts are formed. In case of compound **2d** coupling constant J (**3a**–**4**) = 16 Hz indicates anti-reciprocal or *trans* orientation of H-**3a** and H-**4** protons. Single X-ray crystal structure of **2l** (Fig. 1) shows anti-reciprocal or trans orientation of the **5** and **4a** protons as indicated by the large coupling constant (J = 18 Hz). This is possible only when the cyclohexane ring and the phenyl ring are on the opposite sides of the pyrido pyrazolo pyrimidine ring. Reaction of compound **1** with aldehydes and electron deficient alkenes like DMAD or methyl vinyl ketone under similar conditions did not give any product. Other examples of the present cyclisation is summarized in Table 1.

Finally the adducts were dehydrogenated using active MnO_2 at room temperature to give the corresponding pyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidine/quinazolines (**3a**–**j**). The dehydrogenated product was characterized based on ^{1}H

Table 1
Reaction of compound **1** with formaldehyde/benzaldehyde and alkenes

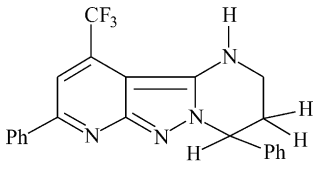
Substrates	Alkenes	Product	Yield (%)
1 + HCHO		 **2a**	90

Table 1 (*Continued*)

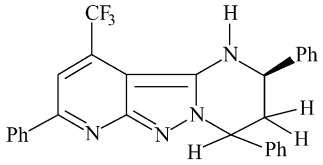
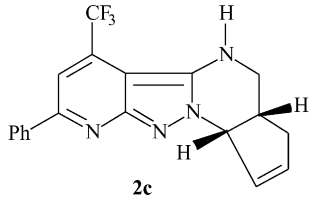
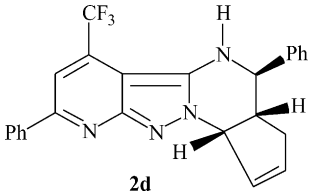
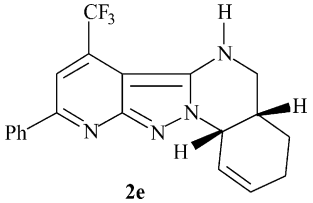
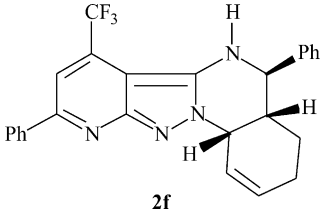
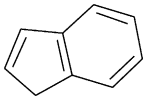
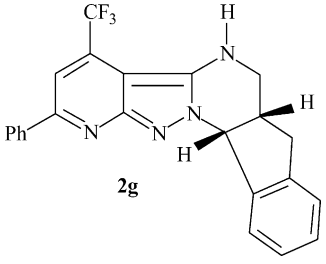
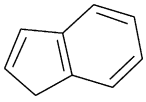
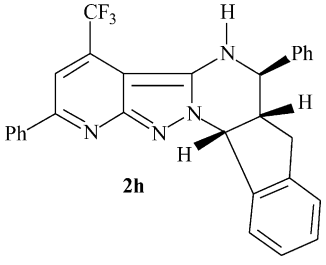
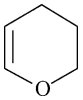
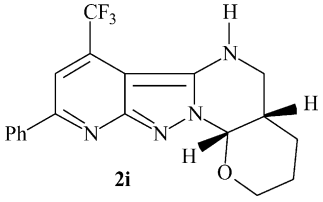
Substrates	Alkenes	Product	Yield (%)
1 + PhCHO		 **2b**	82
1 + HCHO		 **2c**	94
1 + PhCHO		 **2d**	80
1 + HCHO		 **2e**	89
1 + PhCHO		 **2f**	81
1 + HCHO		 **2g**	85
1 + PhCHO		 **2h**	76
1 + HCHO		 **2i**	80

Table 1 (*Continued*)

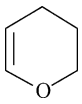
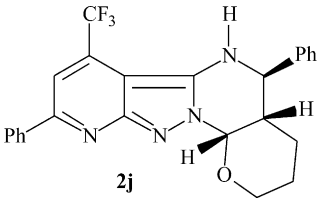
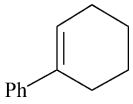
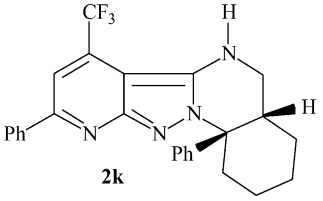
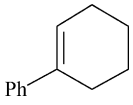
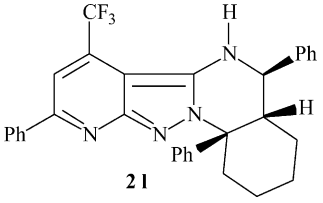
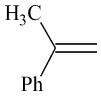
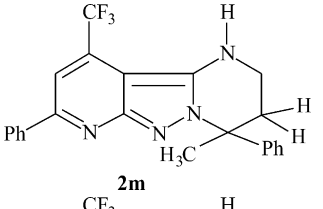
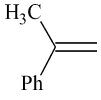
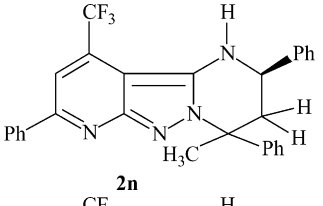
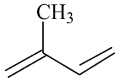
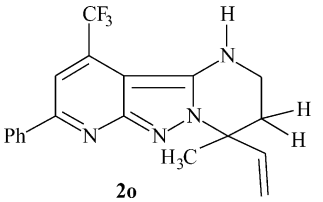
Substrates	Alkenes	Product	Yield (%)
1 + PhCHO		 **2j**	68
1 + HCHO		 **2k**	87
1 + PhCHO		 **2 l**	82
1 + HCHO		 **2m**	89
1 + PhCHO		 **2n**	65
1 + HCHO		 **2o**	72

Table 2
Dehydrogenation of compound **2** with active MnO_2

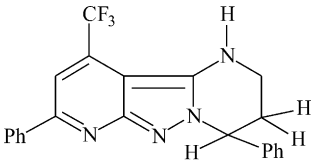
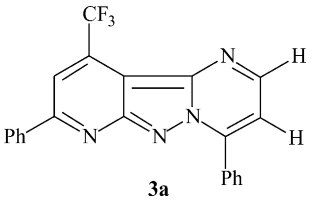
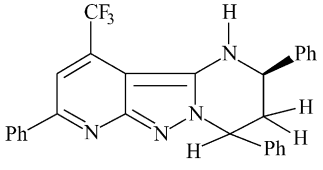
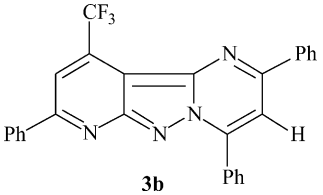
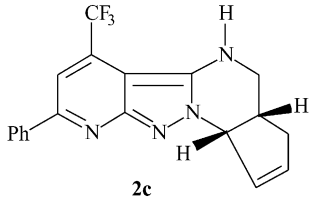
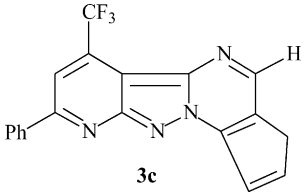
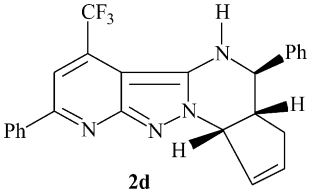
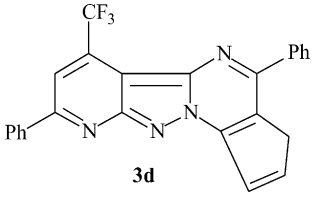
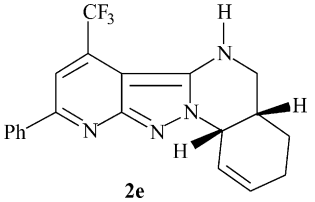
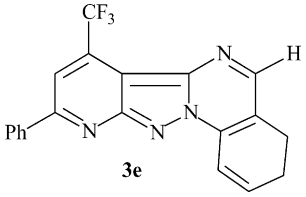
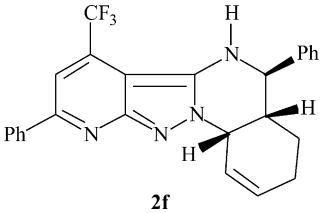
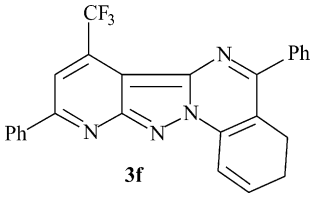
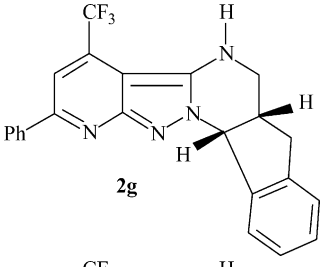
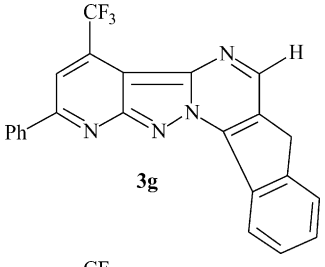
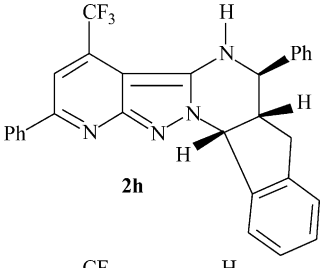
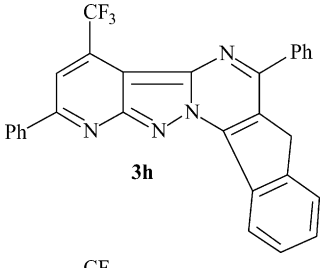
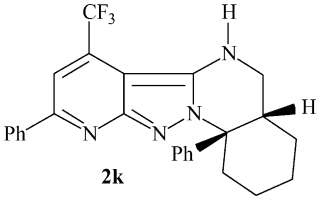
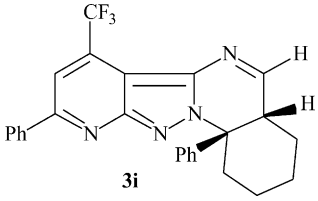
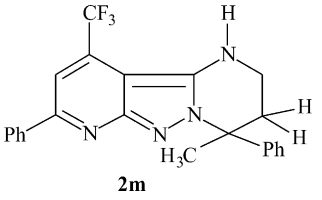
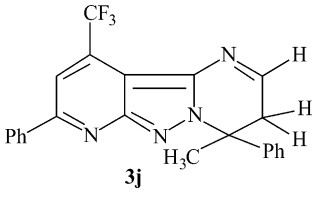
Substrate	Product	Yield (%)
 **2a**	 **3a**	85
 **2b**	 **3b**	78

Table 2 (*Continued*)

Substrate	Product	Yield (%)
 **2c**	 **3c**	80
 **2d**	 **3d**	72
 **2e**	 **3e**	88
 **2f**	 **3f**	79
 **2g**	 **3g**	77
 **2h**	 **3h**	67
 **2k**	 **3i**	89
 **2m**	 **3j**	66

NMR data and mass spectra. Disappearance of NH and methylene protons and appearance of protons in aromatic region established the products structure. The number of compounds synthesized are tabulated in Table 2.

3. Conclusion

In conclusion novel pyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidines/quinazolines were synthesized from 3-aminopyrazolo[3,4-*b*]pyridine in presence of iron(III) chloride in a single pot through aza-Diels Alder type reaction at room temperature in good to excellent yields.

4. Experimental

Melting points were recorded on Casia-siamia (VMP-AM) melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240 C spectro photometer using KBr disks. ^{1}H NMR spectra were recorded on Gemini varian 200 MHz, Bruker AV 300 MHz and Unity 400 MHz spectro meter in $CDCl_3$ using TMS as an internal standard. LSIMS mass spectra were recorded on a VG 7070 H instrument at 70 eV. All reactions were monitored by thin layer chromatography (TLC) on precoated silicagel 60 F_{254} (mesh); spots were visualized with UV light. Merck silicagel (60–120 mesh) was used for chromatography. CHN analyses were recorded on a Vario EL analyser.

4.1. General procedure

4.1.1. Preparation of N-[1-phenylmethylidene]-N-[6-phenyl-4-(trifluoromethyl)-1H-pyrazolo[3,4-b]pyridin-3-yl]amine (*1a*)

To a solution of 6-phenyl-4-(trifluoromethyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (**1**) (1.0 g, 3.6 mmol) in acetonitrile (8 mL), benzaldehyde (0.58 g, 5.47 mmol) and catalytic amount of acetic acid was added and the reaction mixture was stirred for 20 min, at room temperature. Acetonitrile was removed under vacuum and the reaction mixture was diluted with cold water. The separated solid was collected by filtration, washed with water and dried. The crude product was purified by column chromatography using 60–120 mesh silica gel and the desired product was eluted with 50% $CHCl_3$/hexane mixture.

Yield: 1.18 g (90%); reddish brown coloured solid; mp 172 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 7.4–7.6 (6H, m, Ar–H), 7.9 (1H, s, Ar–H), 8.0–8.2 (4H, m, Ar–H), 9.2 (1H, s, HC=N). IR (KBr) (cm^{-1}): 3469 (N–H), 1607 (C=N). LSIMS; *m/z*: 367 (*M*H$^+$). Anal. Calcd. for $C_{20}H_{13}F_3N_4$: C, 65.75%; H, 3.58%; N, 15.29%. Found: C, 65.53%; H, 3.39%; N, 15.44%.

4.1.2. Preparation of (2R)-2,4,8-triphenyl-10-(trifluoromethyl)-1,2,3,4-tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (*2b*)

To cooled solution of **1a** (0.5 g, 1.36 mmol) in acetonitirile, $FeCl_3$ (0.22 g, 1.36 mmol) and styrene (0.28 g, 2.7 mmol) were added and the reaction mixture was stirred for 1 h under N_2 atmosphere at room temperature. Acetonitrile was removed under vacuo and the reaction mixture was diluted with water, extracted with dichloromethane and dried over sodium sulphate. The dichloromethane extract was concentrated to give the crude product which was purified by column chromatography using 60–120 mesh silica gel and desired product was eluted with 20% EtOAc/hexane mixture.

Yield: 0.73 g (88%); bright yellow coloured solid; mp 203 °C. IR (KBr) (cm^{-1}): 3356 (N–H), 1610 (C=N). ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.45–2.65 (2H, m, CH_2), 4.85 (1H, d, *J* 20 Hz, NHC*H*Ph), 5.4 (1H, br, s, N*H*), 5.7 (1H, q, *J* 8.5 Hz, N–C*H*–Ph), 7.2–7.4 (7H, m, Ar–H), 7.4–7.6 (6H, m, Ar–H), 8.0–8.1 (3H, m, Ar–H), LSIMS; *m/z*: 471 (*M*H$^+$). Anal. Calcd. for $C_{28}H_{21}F_3N_4$: C, 71.84%; H, 4.50%; N, 11.91%. Found: C, 71.55%; H, 4.28%; N, 11.66%.

4.2. General procedure

4.2.1. Preparation of tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidines (*2a–o*)

To a solution of 6-phenyl-4-(trifluoromethyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (**1**) (0.5 g, 1.8 mmol) in acetonitrile (8 mL), 40% formaldehyde solution (3 mL) or benzaldehyde (0.29 g, 2.7 mmol) was added and the reaction mixture was stirred for 15–20 min under N_2 atmosphere at room temperature. The solution was cooled to 0 °C and $FeCl_3$ (0.3 g, 1.8 mmol) was added followed by the addition of corresponding alkene (2 equiv.). The total mixture was stirred for 30–60 min, under N_2 atmosphere at room temperature. Acetonitrile was removed under vacuo and the reaction mixture was diluted with water, extracted with dichloromethane and dried over sodium sulphate. The dichloromethane extract was concentrated to give the crude product which was purified by column chromatography using 60–120 mesh silica gel and desired product was eluted with 20% EtOAc/hexane mixture.

4.2.2. 4,8-Diphenyl-10-(trifluoromethyl)-1,2,3,4-tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (*2a*)

Yield: 0.63 g (90%); bright yellow coloured solid; mp 166 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.2–2.3 (2H, m, CH_2), 2.5–2.6 (2 H, m, CH_2–N), 5.7 (1H, br, s, NH), 5.8 (1H, t, *J* 8.2 Hz, C*H*–Ph), 7.0 (2H, d, *J* 17 Hz, Ar–H), 7.2–7.3 (3H, m, Ar–H), 7.4–7.5 (4H, m, Ar–H), 8.05 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3469 (N–H), 1607 (C=N). LSIMS; *m/z*: 395 (*M*H$^+$), 291 (*M*$^+$−CH_2Ph). Anal. Calcd. for $C_{22}H_{17}F_3N_4$: C, 67.31%; H, 4.34%; N, 14.21%. Found: C, 67.52%; H, 4.58%; N, 14.41%.

4.2.3. (2R)-2,4,8-Triphenyl-10-(trifluoromethyl)-1,2,3,4-tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (*2b*)

Yield: 0.69 g (82%); bright yellow coloured solid; mp 203 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.45–2.65 (2H, m, CH_2), 4.85 (1H, d, *J* 16 Hz, NHC*H*Ph), 5.4 (1H, br, s, N*H*), 5.7 (1H, q, *J* 8.5 Hz, N–C*H*–Ph), 7.2–7.4 (7H, m, Ar–H), 7.4–7.6 (6H, m, Ar–H), 8.0–8.1 (3H, m, Ar–H). IR (KBr) (cm^{-1}): 3356 (N–H), 1610 (C=N). LSIMS; *m/z*: 471 (*M*H$^+$), 367

(M^+-CH_2Ph). Anal. Calcd. for $C_{28}H_{21}F_3N_4$: C, 71.84%; H, 4.50%; N, 11.91%. Found: C, 71.62%; H, 4.31%; N, 11.72%.

*4.2.4. (3aS,11aS)-8-Phenyl-6-(trifluoromethyl)-3a,4,5,11a-tetrahydro-3H-cyclopenta[e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2c**)*

Yield: 0.6 g (94%); yellow coloured solid; mp 217 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.4–2.9 (2H, m, CH_2), 3.2–3.5 (3H, m, CH_2–N and C*H*), 5.4 (1H, d, *J* 7.3 Hz, *H*C–N), 5.65 (1H, br, s, N*H*), 6.0 (1H, d, *J* 17.3 Hz, *H*C=CH), 6.25 (1H, d, *J* 17.3 Hz, HC=C*H*), 7.6–7.7 (4H, m, Ar–H), 8.1–8.2 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3352 (N–H), 1605 (C=N), 2926 (C–H). LSIMS; *m/z*: 357 (*M*H$^+$), 291 ($M^+-C_5H_4$). Anal. Calcd. for $C_{19}H_{15}F_3N_4$: C, 64.04%; H, 4.24%; N, 15.72%. Found: C, 64.24%; H, 4.43%; N, 15.54%.

*4.2.5. (3aS,4R,11aS)-4,8-Diphenyl-6-(trifluoromethyl)-3a,4,5,11a-tetrahydro-3H-cyclopenta[e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2d**)*

Yield: 0.62 g (80%); bright yellow coloured solid; mp 249 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.8–2.0 (1H, m, CH_2), 2.5–2.7 (1H, m, CH_2), 3.05–3.15 (1H, m, C*H*), 5.0 (1H, d, *J* 16 Hz, *H*C–Ph), 5.1 (1H, br, s, N*H*), 5.45 (1H, d, *J* 8.2 Hz, C*H*–N), 6.0 (1H, d, *J* 18 Hz, *H*C=CH), 6.25 (1H, d, *J* 17.3 Hz, HC=C*H*), 7.3–7.5 (9H, m, Ar–H), 8.0–8.1 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3355 (N–H), 1605 (C=N), 2926 (C–H). LSIMS; *m/z*: 433 (*M*H$^+$), 367 ($M^+-C_5H_4$). Anal. Calcd. for $C_{25}H_{19}F_3N_4$: C, 69.44%; H, 4.43%; N, 12.96%. Found: C, 69.21%; H, 4.25%; N, 12.72%.

*4.2.6. (4aS,12aS)-9-Phenyl-7-(trifluoromethyl)-1,2,4a,5,6,12a-hexahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**2e**)*

Yield: 0.59 g (89%); yellow coloured solid; mp 188 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.9–2.0 (2H, m, CH_2–CH_2–HC=CH), 2.15–2.3 (2H, m, CH_2–HC=CH), 2.5–2.6 (1H, m, C*H*), 3.4–3.5 (2H, m, CH_2–N), 5.1 (1H, s, *H*C–N), 5.5 (1H, br, s, N*H*), 5.9 (1H, d, *J* 18 Hz, *H*C=CH), 6.25 (1H, d, *J* 17 Hz, HC=C*H*), 7.4–7.5 (4H, m, Ar–H), 8.1–8.2 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3406 (N–H), 1607 (C=N), 2932 (C–H). LSIMS; *m/z*: 371 (*M*H$^+$). Anal. Calcd. for $C_{20}H_{17}F_3N_4$: C, 64.86%; H, 4.63%; N, 15.13%. Found: C, 64.63%; H, 4.41%; N, 15.35%.

*4.2.7. (4aS,5R,12aS)-5,9-Diphenyl-7-(trifluoromethyl)-1,2,4a,5,6,12a-hexahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**2f**)*

Yield: 0.65 g (81%); yellow coloured solid; mp 218 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.4–1.5 (2H, m, CH_2–CH_2–HC=CH), 1.9–2.05 (2H, m, CH_2–HC=CH), 2.35–2.4 (1H, m, C*H*), 5.0 (1H, m, *H*C–Ph), 5.1 (1H, br, s, N*H*), 5.2 (1H, t, *J* 9.2 Hz, *H*C–N), 6.0 (1H, d, *J* 18 Hz, *H*C=CH), 6.5 (1H, d, *J* 18 Hz, HC=C*H*), 7.2–7.5 (9H, m, Ar–H), 8.0–8.1 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3437 (N–H), 1607 (C=N), 2932 (C–H). LSIMS; *m/z*: 447 (*M*H$^+$). Anal. Calcd. for $C_{26}H_{21}F_3N_4$: C, 69.94%; H, 4.74%; N, 12.55%. Found: C, 69.72%; H, 4.55%; N, 12.32%.

*4.2.8. (6aS,11bR)-2-Phenyl-4-(trifluoromethyl)-6,6a,7,11b-tetrahydro-5H-indeno[2,1-e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2g**)*

Yield: 0.62 g (85%); bright yellow coloured solid; mp 159 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.95–3.3 (2H + 1H + 1H, m, CH_2, C*H*, CH_2–N), 3.5–3.6 (1H, m, CH_2–N), 5.5 (1H, br, s, NH), 5.8 (1H, d, *J* 8.8 Hz, *H*C–N), 7.1–7.3 (3H, m, Ar–H), 7.35–7.5 (4H, m, Ar–H), 7.95 (1H, m, Ar–H), 8.1–8.2 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3358 (N–H), 1605 (C=N), 2926 (C–H). LSIMS; *m/z*: 407 (*M*H$^+$). Anal. Calcd. for $C_{23}H_{17}F_3N_4$: C, 67.97%; H, 4.22%; N, 13.79%. Found: C, 67.74%; H, 4.46%; N, 13.93%.

*4.2.9. (6R,6aS,11bR)-2,6-Diphenyl-4-(trifluoromethyl)-6,6a,7,11b-tetrahydro-5H-indeno[2,1-e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2h**)*

Yield: 0.66 g (76%); bright yellow coloured solid; mp 192 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 3.25–3.35 (2H, dd, CH_2), 3.9–3.95 (1H, m, C*H*–C), 5.45 (1H, br, s, N*H*), 5.6 (1H, m, N–C*H*Ph), 6.05 (1H, d, *J* 8.8 Hz, *H*C–N), 6.9–7.25 (7H, m, Ar–H), 7.3–7.45 (6H, m, Ar–H), 8.4–8.45 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3352 (N–H), 1602 (C=N), 2926 (C–H). LSIMS; *m/z*: 483 (*M*H$^+$). Anal. Calcd. for $C_{29}H_{21}F_3N_4$: C, 72.19%; H, 4.39%; N, 11.61%. Found: C, 72.38%; H, 4.58%; N, 11.40%.

*4.2.10. (4aS,12aS)-9-Phenyl-7-(trifluoromethyl)-3,4,4a,5,6,12a-hexahydro-2H-pyrano[3,2-e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2i**)*

Yield: 0.54 g (80%); yellow coloured solid; mp 202 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.55–1.6 (1H, m, OCH$_2$CH_2), 1.9–2.1 (1H + 2H, m, OCH$_2$CH_2, CH_2–CH), 2.3–2.4 (1H, m, C*H*), 3.3–3.4 (1H, m, CH_2–N), 3.6–3.8 (1H + 2H, m, CH_2–O, CH_2–N), 3.9–4.0 (1H, m, CH_2–O), 5.6 (1H, d, *J* 9.6 Hz, *H*C–O), 5.85 (1H, br, s, N*H*), 7.35–7.5 (4H, m, Ar–H), 8.0–8.1 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3381 (N–H), 1607 (C=N), 2933 (C–H). LSIMS; *m/z*: 375 (*M*H$^+$), 291 ($M^+-C_6H_7$). Anal. Calcd. for $C_{19}H_{17}F_3N_4O$: C, 60.96%; H, 4.58%; N, 14.97%. Found: C, 60.71%; H, 4.79%; N, 14.69%.

*4.2.11. (4aS,5R,12aS)-5,9-Diphenyl-7-(trifluoromethyl)-3,4,4a,5,6,12a-hexahydro-2H-pyrano[3,2-e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2j**)*

Yield: 0.55 g (68%); yellow coloured solid; mp 228 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.2–1.3 (1H, m, CH_2CH$_2$–O), 1.6–1.8 (2H + 1H, m, HC–CH_2, CH_2CH$_2$–O), 2.4–2.5 (1H, m, C*H*), 3.4–3.65 (1H, m, CH_2–O), 3.8 (1H, m, CH_2–O), 4.8 (1H, d, *J* 16 Hz, *H*C–Ph), 5.1 (1H, br, s, N*H*), 6.3 (1H, s, *H*C–O), 7.25–7.6 (8H, m, Ar–H), 8.05–8.15 (3H, m, Ar–H). IR (KBr) (cm^{-1}): 3388 (N–H), 1600 (C=N), 2930 (C–H). LSIMS; *m/z*: 451 (*M*H$^+$), 367 ($M^+-C_6H_7$). Anal. Calcd. for $C_{25}H_{21}F_3N_4O$: C, 66.66%; H, 4.70%; N, 12.44%. Found: C, 66.42%; H, 4.51%; N, 12.67%.

*4.2.12. (4aS,12aS)-9,12a-Diphenyl-7-(trifluoromethyl)-1,2,3,4,4a,5,6,12a-octahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**2k**)*

Yield: 0.7 g (87%); bright yellow coloured solid; mp 237 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.5–1.6 (2H + 1H, m,

CH_2CH$_2$–CH, CH_2CH$_2$–CPh), 1.7–1.85 (2H + 1H, m, CH_2–HC, CH_2CH$_2$–CPh), 1.95–2.05 (1H, m, CH_2–CPh), 2.55 (1H, d, *J* 16 Hz, C*H*), 3.0–3.1 (1H, m, CH_2–CPh), 3.2–3.4 (2H, m, CH_2–N), 4.8 (1H, br, s, N*H*), 6.75–6.8 (2H, m, Ar–H), 7.2–7.3 (3H, m, Ar–H), 7.4–7.5 (4H, m, Ar–H), 8.2–8.3 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3322 (N–H), 1601 (C=N), 2932 (C–H). LSIMS; *m/z*: 449 (*M*H$^+$). Anal. Calcd. for $C_{26}H_{23}F_3N_4$: C, 69.63%; H, 5.17%; N, 12.38%. Found: C, 69.88%; H, 5.37%; N, 12.65%.

4.2.13. (4aS,5R,12aS)-5,9,12a-Triphenyl-7-(trifluoromethyl)-1,2,3,4,4a,5,6,12a-octahydro pyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**2l**)

Yield: 0.77 g (82%); yellow coloured solid; mp 283 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.6–1.7 (2H + 1H, m, CH_2CH$_2$ CH, CH_2CH$_2$CPh), 1.75–1.9 (1H + 2H, m, CH_2CH$_2$CPh, CH_2–CH), 2.05–2.15 (1H, m, CH_2–CPh), 2.65 (1H, d, *J* 14 Hz, C*H*), 3.1–3.2 (1H, m, CH_2–CPh), 4.7 (1H, br, s, N*H*), 5.3 (1H, d, *J* 18 Hz N–C*H*Ph), 6.4–6.5 (2H, m, Ar–H), 6.7–6.9 (8H, m, Ar–H), 7.5–7.6 (4H, m, Ar–H), 8.2–8.3 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3482 (N–H), 1612 (C=N), 2938 (C–H). LSIMS; *m/z*: 525 (*M*H$^+$). Anal. Calcd. for $C_{32}H_{27}F_3N_4$: C, 72.27%; H, 5.19%; N, 10.68%. Found: C, 72.42%; H, 5.33%; N, 10.87%.

4.2.14. Crystal data for (4aS,5R,12aS)-5,9,12a-triphenyl-7-(trifluoromethyl)-1,2,3,4,4a,5,6,12a-octahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**2l**)

$C_{32}H_{27}F_3N_4$: M_w = 524.58, colorless needle crystal 0.19 mm × 0.11 mm × 0.09 mm, a = 9.1338(7) Å, b = 13.2004(10) Å, c = 22.0747(16) Å, β = 101.659(1)°, V = 2606.6(3) Å^3, monoclinic, space group $P2_1/c$, ρ_{calc} = 1.337 mg m^{-3}, λ = 0.71073 Å, μ(Mo Kα) = 0.095 mm^{-1}, F_{000} = 1096, T = 273(2) K. Data collection yielded 24,529 reflection resulting in 4581 unique, averaged reflection, 3897 with $I > 2\sigma(I)$, θ range: 1.81–25.00°. Full-matrix least-squares refinement led to a final R = 0.0512, R_w = 0.1370 and GOF = 1.026. Intensity data were measured on Bruker Smart Apex with CCD area detector. CCDC 283727 contains supplementary crystallographic data for the structure **2l**.

4.2.15. 4-Methyl-4,8-diphenyl-10-(trifluoromethyl)-1,2,3,4-tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2m**)

Yield : 0.6 g (89%); yellow coloured solid; mp 167 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.2 (3H, s, CH_3), 2.4–2.65 (2H, m, C–CH_2), 3.1–3.25 (1H, m, CH_2–N), 3.3–3.4 (1H, m, CH_2–N), 4.85 (1H, br, s, N*H*), 6.8–6.9 (2H, m, Ar–H), 7.2–7.3 (3H, m, Ar–H), 7.4–7.6 (4H, m, Ar–H), 8.15–8.25 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3396 (N–H), 1606 (C=N). ESIMS; *m/z*: 409 (*M*H$^+$). Anal. Calcd. for $C_{23}H_{19}F_3N_4$: C, 67.64%; H, 4.69%; N, 13.72%. Found: C, 67.87%; H, 4.85%; N, 13.95%.

4.2.16. (2R)-4-Methyl-2,4,8-triphenyl-10-(trifluoromethyl)-1,2,3,4-tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2n**)

Yield: 0.56 g (65%); yellow coloured solid; mp 227 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.3 (3H, s, CH_3), 2.5–2.6 (2H, m, C–CH_2), 4.6–4.65 (1H, m, *H*C–Ph), 4.85 (1H, br, s, N*H*), 6.9–7.1 (2H, m, Ar–H), 7.15–7.25 (3H, m, Ar–H), 7.3–7.4 (5H, m, Ar–H), 7.5–7.65 (4H, m, Ar–H), 8.25–8.4 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3422 (N–H), 1601 (C=N), 2930 (C–H). ESI MS; *m/z*: 485 (*M*H$^+$). Anal. Calcd. for $C_{29}H_{23}F_3N_4$: C, 71.89%; H, 4.78%; N, 11.56%. Found: C, 71.65%; H, 4.52%; N, 11.77%.

4.2.17. 4-Methyl-8-phenyl-10-(trifluoromethyl)-4-vinyl-1,2,3,4-tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**2o**)

Yield: 0.46 g (72%); yellow coloured solid; mp 213 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.9 (3H, s, CH_3–C), 2.1–2.3 (2H, m, CH_2), 3.5–3.6 (2H, m, CH_2–NH), 4.75 (1H, d, *J* 18 Hz, HC=CH_2), 5.2 (1H, d, *J* 18 Hz, HC=CH_2), 5.4 (1H, br, s, N*H*), 5.95–6.15 (1H, m, *H*C=CH$_2$), 7.4–7.6 (4H, m, Ar–H), 8.1–8.2 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 3396 (N–H), 1608 (C=N), 2930 (C–H). LSIMS; *m/z*: 359 (*M*H$^+$). Anal. Calcd. for $C_{19}H_{17}F_3N_4$: C, 63.68%; H, 4.78%; N, 15.63%. Found: C, 63.85%; H, 4.92%; N, 15.81%.

4.3. Procedure for the preparation of pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidines (**3a–j**)

Tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-*a*]pyrimidines (0.35 g) and 10-fold excess of active MnO_2 were taken in dichloromethane and the reaction mixture was stirred at for 12–24 h under N_2 atmosphere at room temperature. The reaction mixture was diluted with dichloromethane and MnO_2 was separated by filteration using Celite filtration aid. The filtrate was concentrated under vacuo to give crude product which was purified by column chromatography using 60–120 mesh silica gel and desired product was eluted 30% $CHCl_3$ in hexane mixture.

4.3.1. 4,8-Diphenyl-10-(trifluoromethyl)pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**3a**)

Yield: 0.3 g (85%); green coloured solid; mp 232 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 7.4–7.6 (7H, m, Ar–H), 7.95–8.05 (2H, m, Ar–H), 8.2–8.3 (3H, m, Ar–H), 8.9 (1H, d, *H*C=N). IR (KBr) (cm^{-1}): 1605 (C=C), 1590 (C=N). LSIMS; *m/z*: 391 (*M*H$^+$). Anal. Calcd. for $C_{22}H_{13}F_3N_4$: C, 67.69%; H, 3.36%; N, 14.35%. Found: C, 67.45%; H, 3.13%; N, 14.52%.

4.3.2. 2,4,8-Triphenyl-10-(trifluoromethyl)pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**3b**)

Yield: 0.27 g (78%); pale green coloured solid; mp 254 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 7.5–7.7 (9H, m, Ar–H), 8.0–8.1 (2H, m, Ar–H), 8.25–8.4 (6H, m, Ar–H). IR (KBr) (cm^{-1}): 1622 (C=C), 1595 (C=N). LSIMS; *m/z*: 467 (*M*H$^+$). Anal. Calcd. for $C_{28}H_{17}F_3N_4$: C, 72.10%; H, 3.67%; N, 12.01%. Found: C, 72.34%; H, 3.73%; N, 12.23%.

*4.3.3. 8-Phenyl-6-(trifluoromethyl)-1H-cyclopenta[e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**3c**)*

Yield: 0.28 g (80%); pale green coloured solid; mp 226 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 3.95–4.2 (2H, m, CH_2), 6.75 (1H, d, *J* 18 Hz, *H*C=CH), 7.35 (1H, d, HC=C*H*), 7.25–7.4 (4H, m, Ar–H), 8.2–8.35 (2H, m, Ar–H), 9.05 (1H, s, *H*C=N). IR (KBr) (cm^{-1}): 1588 (C=N). LSIMS; *m*/*z*: 353 (*M*H$^+$). Anal. Calcd. for $C_{19}H_{11}F_3N_4$: C, 64.77%; H, 3.15%; N, 15.90%. Found: C, 64.94%; H, 3.37%; N, 15.72%.

*4.3.4. 4,8-Diphenyl-6-(trifluoromethyl)-1H-cyclopenta[e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**3d**)*

Yield: 0.25 g (72%); green coloured solid; mp 248 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 3.9–4.15 (2H, m, CH_2), 6.6 (1H, d, *J* 19 Hz, *H*C=CH), 7.25 (1H, d, *J* 19 Hz, HC=C*H*), 7.3–7.6 (7H, m, Ar–H), 7.85–7.95 (2H, m, Ar–H), 8.2–8.4 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 1592 (C=N). LSIMS; *m*/*z*: 429 (*M*H$^+$). Anal. Calcd. for $C_{25}H_{15}F_3N_4$: C, 70.09%; H, 3.53%; N, 13.08%. Found: C, 70.27%; H, 3.36%; N, 13.22%.

*4.3.5. 9-Phenyl-7-(trifluoromethyl)-1,4-dihydropyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**3e**)*

Yield: 0.3 g (88%); pale green coloured solid; mp 262 °C. ^{1}H (200 MHz, $CDCl_3$), δ = 2.6–2.8 (2H, m, CH_2), 3.0–3.2 (2H, m, CH_2), 6.8–6.9 (1H, m, *H*C=CH), 7.4–7.6 (3H, m, Ar–H), 7.7 (1H, d, *J* 19 Hz, HC=C*H*), 8.0 (1H, s, Ar–H), 8.2–8.3 (2H, m, Ar–H), 8.6 (1H, s, *H*C=N). IR (KBr) (cm^{-1}): 1588 (C=N). LSIMS; *m*/*z*: 367 (*M*H$^+$). Anal. Calcd. for $C_{20}H_{13}F_3N_4$: C, 66.57%; H, 3.58%; N, 15.22%. Found: C, 66.32%; H, 3.77%; N, 15.45%.

*4.3.6. 5,9-Diphenyl-7-(trifluoromethyl)-1,4-dihydropyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**3f**)*

Yield: 0.27 g (79%); green coloured solid; mp 227 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 3.0–3.15 (4H, m, CH_2), 6.7–6.75 (1H, m, *H*C=CH), 7.3–7.45 (6H, m, Ar–H), 7.55 (1H, d, *J* 17 Hz, HC=C*H*), 7.8–8.1 (5H, m, Ar–H). IR (KBr) (cm^{-1}): 1598 (C=N). LSIMS; *m*/*z*: 443 (*M*H$^+$). Anal. Calcd. for $C_{26}H_{17}F_3N_4$: C, 70.58%; H, 3.87%; N, 12.68%. Found: C, 70.32%; H, 3.61%; N, 12.43%.

*4.3.7. 2-Phenyl-4-(trifluoromethyl)-11H-indeno[1,2-e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**3g**)*

Yield: 0.26 g (77%); green coloured solid; mp 189 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 4.25–4.35 (2H, m, CH_2), 6.8–7.2 (3H, m, Ar–H), 7.25–7.5 (4H, m, Ar–H), 8.2–8.3 (3H, m, Ar–H), 9.15 (1H, s, *H*C=N). IR (KBr) (cm^{-1}): 1580 (C=N). LSIMS; *m*/*z*: 403 (*M*H$^+$). Anal. Calcd. for $C_{23}H_{13}F_3N_4$: C, 68.66%; H, 3.26%; N, 13.92%. Found: C, 68.83%; H, 3.47%; N, 13.71%.

*4.3.8. 2,6-Diphenyl-4-(trifluoromethyl)-11H-indeno[1,2-e]pyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**3h**)*

Yield: 0.23 g (67%); pale green coloured solid; mp 194 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 4.15–4.25 (2H, m, CH_2), 7.3–7.4 (2H, m, Ar–H), 7.45–7.65 (7H, m, Ar–H), 7.7–7.8 (4H, m, Ar–H), 8.2–8.3 (2H, m, Ar–H). IR (KBr) (cm^{-1}): 1594 (C=N). LSIMS; *m*/*z*: 479 (*M*H$^+$). Anal. Calcd. for $C_{29}H_{17}F_3N_4$: C, 72.51%; H, 3.43%; N, 11.89%. Found: C, 72.72%; H, 3.66%; N, 11.65%.

*4.3.9. 9,12a-Diphenyl-7-(trifluoromethyl)-1,2,3,4,4a,12a-hexadropyrido[2′,3′:3,4]pyrazolo[1,5-a]quinazoline (**3i**)*

Yield: 0.31 g (89%); pale green coloured solid; mp 222 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 1.51–1.65 (2H + 1H, m, CH_2–CH$_2$–CH, CH_2–CH$_2$–CPh), 1.8–1.85 (1H + 2H, m, CH_2–CH$_2$–CPh, CH$_2$–CH_2–CH), 1.90–2.0 (1H, m, CH_2–CPh), 3.2 (1H + 1H, m, CH_2–CPh, C*H*), 6.95–7.05 (2H, m, Ar–H), 7.2–7.3 (2H, m, Ar–H), 7.4–7.7 (4H, m, Ar–H), 8.2–8.3 (3H, m, Ar–H), 8.7 (1H, s, HC=N). IR (KBr) (cm^{-1}): 1590 (C=N). LSIMS; *m*/*z*: 447 (*M*H$^+$). Anal. Calcd. for $C_{26}H_{21}F_3N_4$: C, 69.61%; H, 4.83%; N, 12.46%. Found: C, 69.83%; H, 4.61%; N, 12.69%.

*4.3.10. 4-Methyl-4,8-diphenyl-10-(trifluoromethyl)-3,4-dihydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidine (**3j**)*

Yield: 0.23 g (66%); green coloured solid; mp 276 °C. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 2.15 (3H, s, CH_3), 2.6–2.65 (2H, m, CH_2), 6.9–7.0 (2H, m, Ar–H), 7.2–7.35 (3H, m, Ar–H), 7.5–7.7 (4H, m, Ar–H), 8.2–8.3 (2H, m, Ar–H), 8.6 (1H, s, *H*C=N). IR (KBr) (cm^{-1}): 1596 (C=N). LSIMS; *m*/*z*: 407 (*M*H$^+$). Anal. Calcd. for $C_{23}H_{17}F_3N_4$: C, 67.61%; H, 3.59%; N, 13.41%. Found: C, 67.85%; H, 3.38%; N, 13.63%.

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