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Synthesis of novel dipyrazolo[3,4-*b*:3,4-*d*]pyridines and study of their fluorescence behavior

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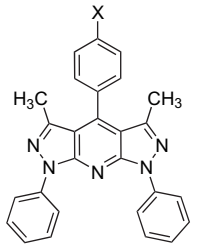
Abstract—A convenient route was successfully developed for the synthesis of novel heterocycles such as pyrazolo[3,4-*h*][1,6]naphthyridine and dipyrazolo[3,4-*b*:3,4-*d*]pyridine (DPP) from pyrazolo[3,4-*b*]pyridine in good yield. The DPP derivatives synthesized were further studied for their fluorescence properties.

1. Introduction

Since the ground-breaking work[1] of Tang and VanSlyke in electroluminescence (EL) devices that use organic molecular materials, the research activity on organic light emitting diodes (OLEDs) has been expanding rapidly and progressed considerably in recent years. The LEDs of this category are of great interest because of their potential applications for making low-cost display products. The continuing efforts include the development of new efficient materials and ingenious device fabrications.[2] There are many activities focused on blue-light emitting OLEDs and a wide variety of organic and organometallic compounds have been utilized for this purpose. Only few compounds like distyrylarylene[3] and silyl substituted ter-(phenylene-vinylene)[4] are significant since the blue emission required is over 10 000 cd/m^2. Thus a suitable blue-light emitting material with high brightness and good thermal stability still remains to be developed.

Derivatives of 3,5-dimethyl-1,7-diphenyl-bis-pyrazolo[3,4-*b*:3,4-*e*]pyridine (DMA-DMPP) with different substituents in position 4 (Fig. 1) show intense fluorescence in the blue-green region and have been considered for applications as fluorescence standards and luminophores in organic light emitting diodes.[5] The derivatives with phenyl and 4-methoxyphenyl substituent (H-DMPP and CH_3O-DMPP, respectively) are characterized by a very intense, solvent independent fluorescence. The nitro derivative (NO_2-DMPP) shows an unexpected photophysical behavior. DMA-DMPP fluoresces with a large quantum yield in nonpolar solvents. The quantum yield decreases in polar solvents, and the emitting state changes its character from a weakly polar to a CT one, confirmed by experimental results.[6–9] In protic solvents dual fluorescence is observed, a phenomenon not often occurring in the case of noncoplanar large donar–acceptor systems.



X-DMPP
X = $N(CH_3)_2$, H, NO_2, OCH_3

Figure 1.

Apart from this, the dipyrazolo[3,4-*b*:3,4-*e*]pyridines are examples of condensed heterocyclic compounds with notable pharmacological activity, e.g., as sedative[10] or anti-asthmatic compounds.[11] Pyrazolopyridines are attractive targets in organic synthesis due to their significant biological and pharmacological activities, such as hypotensive,[12] cytotoxic,[13] and anti-bacterial activity,[14] and found to be potential purine antagonists.[15]

As a part of our ongoing interest in this area [16–18] we have reported the synthesis of pyrazolo[3,4-*b*]pyridines, pyrazolo[3,4-*b*]quinolines, pyrazolonaphthyridines, and pyrazolopyridopyrimidines by *Friedlander* condensation of reactive methylene compounds with 5-aminopyrazole. In our recent communications[19] we reported the synthesis

Keywords: Pyrazolo[3,4-*b*]pyridine; Dipyrazolo[3,4-*b*:3,4-*d*]pyridine; Pyrazolo[3,4-*h*][1,6]naphthyridine; Absorption; Emission.
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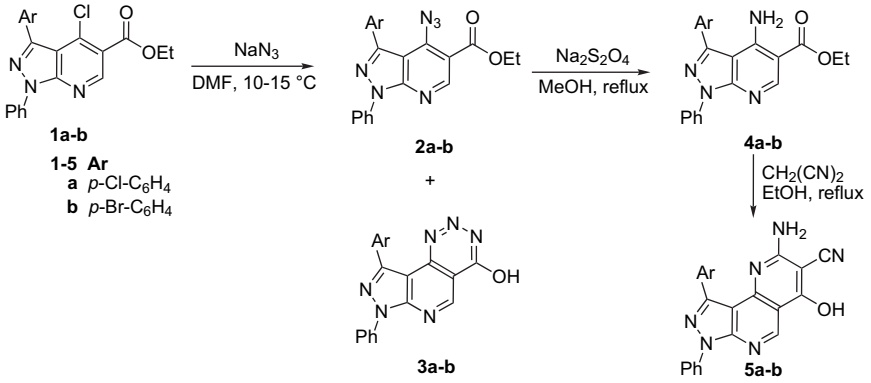
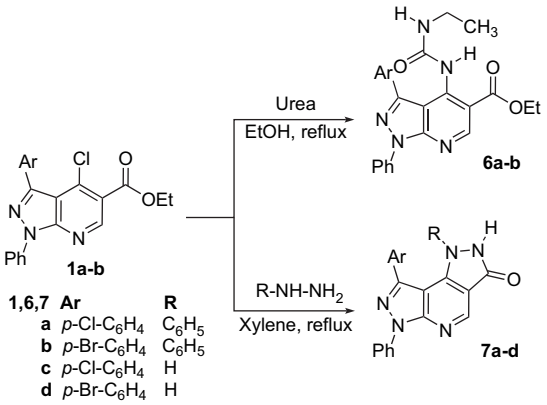


Scheme 1.



Scheme 2.

of fused pyrimidines. These literature reports and our ongoing research in this area prompted us to synthesize DPP and to study their fluorescence behavior (Schemes 1 and 2).

2. Results and discussion

Compounds **1** containing bifunctional groups were used as precursors for the synthesis of tricyclic heterocycles such as dipyrazolo[3,4-*b*:3,4-*d*]pyridine. Thus compound **1** on treatment with sodium azide in DMF at 10–15 °C furnished a mixture of azido pyrazolopyridine derivatives **2** and pyrazolopyridotriazine **3** in 60:20% yield, respectively. The mixture of **2** and **3** were separated by column chromatography using 4:1 toluene/acetone as the eluant. The reduction of N_3 was achieved successfully by refluxing in methanol, containing a catalytic amount of sodium dithionate, for 3 h that yielded the expected 4-aminopyrazolo[3,4-*b*]pyridine derivatives **4** in 60% yield. Despite the proximity of an amine and ester group *ortho* to each other in compounds **4** were unable to form the amide. Moreover, the reaction of **4** with active methylene compounds also proved to be difficult. This might be due to the strong intramolecular hydrogen bond between ester carbonyl and the 4-amino group as reported earlier by Bare et al.[20] in the case pyrazolopyridine (Fig. 2). Only the reaction of **4** with malononitrile in ethanol at reflux for 18 h was successfully carried out to yield the pyrazolonaptharidines **5** in 50% yield.

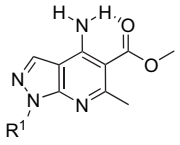


Figure 2.

In continuation of our research on **1** we carried out the reaction with urea and different hydrazines. Thus the reaction of urea with **1** in ethanol containing a catalytic amount of potassium hydroxide furnished an open chain derivative **6** in good yield. Further the reaction of phenylhydrazine or hydrazine hydrate in xylene containing catalytic amount of triethylamine at reflux for 5 h yielded the titled dipyrazolo[3,4-*b*:3,4-*d*]pyridine (DPP) **7** in 60% yield. The structure of all these compounds was confirmed by IR and ^{1}H NMR spectroscopies, and elemental analysis.

3. Conclusion

It was observed that the dipyrazolo[3,4-*b*:3,4-*d*]pyridine (DPP) **7** showed strong fluorescence, so we further studied the photophysical properties of these compounds. It was noted that DPP **7** showed similar absorption and emission spectra. The DPP **7a**,**b** prepared using phenylhydrazine showed a small peak at the base of strong absorption (a) and emission (b) peaks as shown in (Fig. 3). The appearance of this small characteristic peak might be because of the dual

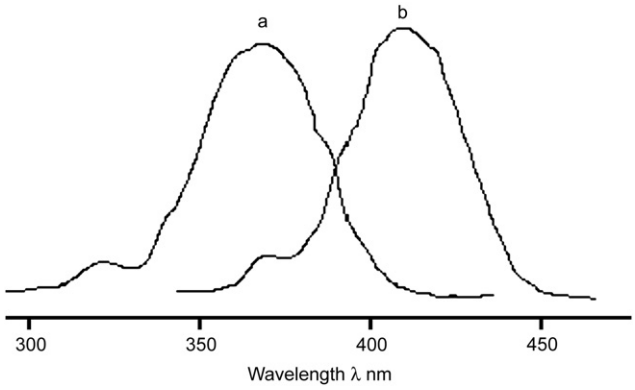


Figure 3. The absorption (a) and emission (b) spectra of **7a** in DMSO.

fluorescence of DPP due to the presence of phenyl ring as it is observed in case of DMA-DMPP. While the absorption and emission spectra of the DPP **7c**,**d** synthesized using hydrazine hydrate does not show any small peak at the base of strong peak (Fig. 4). The DPP **7** showed absorption peaks at 369, 370, 384, and 384.5 nm and emission peaks at 410, 407, 419, and 417 nm.

The spectroscopic data are compiled in Table 1 and the quantum yields calculated are impressive. All these findings reveal that DPP are very useful because of their stability and their photophysical properties. The structures of **7c**–**d** were also characterized by IR and ^{1}H NMR spectroscopies.

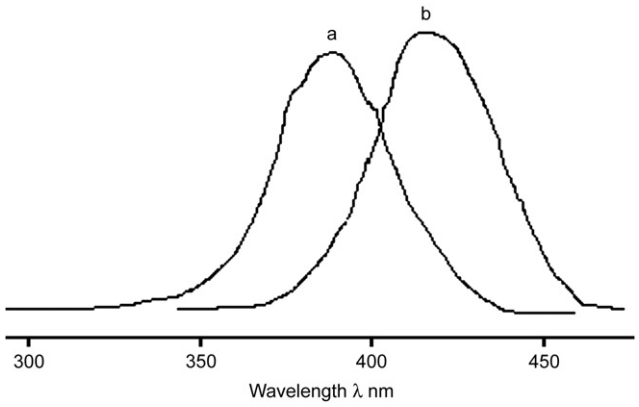


Figure 4. The absorption (a) and emission (b) spectra of **7c** in DMSO.

Table 1. Photophysical data for electronic absorption (abs) and fluorescence (flu) of DPP **7** in DMSO

Compound	λ_{abs} (DMSO)	λ_{flu} (DMSO)	ε (DMSO)	Φ_F (DMSO)
7a	369	410	7325	0.172
7b	370	407	6411	0.173
7c	384	419	5402	0.168
7d	384.5	417	6262	0.166

4. Experimental

4.1. General

Melting points were determined on a Gallenkamp Melting Point Apparatus, Mod. MFB-595 in open capillary tubes and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (300 MHz). Chemical shifts are reported in parts per million using tetramethylsilane as internal standard and are given in δ units. The solvent for NMR spectra was deuteriochloroform unless otherwise stated. Infrared spectra were taken on Shimadzu IR-408, a Shimadzu FTIR instrument in potassium bromide pellets unless otherwise stated. UV spectra were recorded on a Shimadzu UV-1601 UV–vis Spectrophotometer. Compounds for UV scan were dissolved in DMSO. Fluorescence spectra were recorded using RF-5301 PC Spectrofluorophotometer. Compounds for fluorescence measurements were dissolved in DMSO. UV and fluorescence scans were recorded from 200 to 600 nm. Elemental analysis was performed on a Hosli CH-Analyzer and is within ±0.4 of the theoretical percentage. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F_{254} (Merk) plates using UV light (254 and 366 nm) for detection. Common reagents grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

4.2. General procedure for the synthesis of (2a–b), (3a–b)

A solution of **1** (0.01 mol) and sodium azide (0.01 mol) in DMF (15 mL) was stirred at 10–20 °C until the starting material had disappeared (3 h, checked by TLC monitoring). Then the solution was poured into cold water (50 mL) and stirred for 30 min. The obtained solid was filtered, washed with cold water (100 mL), and dried, to afford a mixture of compounds **2** and **3**, which was separated by column chromatography using 4:1 toluene/acetone as the eluant to afford **2** and **3** in 60:20% yield, respectively.

4.3. Synthesis of ethyl 4-amino-3-aryl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (4a–b)

A solution of **2** (0.01 mol) and sodium dithionate (0.01 mol) in methanol (15 mL) was refluxed for 3 h. Then the solution was allowed to cool, and poured into cold water (30 mL) and stirred for 30 min, the solid separated out was filtered, dried, and recrystallized from the proper solvent to afford **4** in good yield.

4.4. Synthesis of 2-amino-9-aryl-4-hydroxy-7-phenyl-7*H*-pyrazolo[3,4-*h*][1,6]naphthyridine-3-carbonitrile (5a–b)

A solution of **4** (0.01 mol) and malononitrile (0.01 mol) in ethanol (15 mL) containing catalytic amount of piperidine was refluxed for 18 h. Then the solution was allowed to cool and the solid separated out was filtered, dried, and recrystallized from proper solvent to afford **5** in good yield.

4.5. Synthesis of ethyl 3-aryl-4-{[(ethylamino)-carbonyl]amino}-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (6a–b)

A solution of compound **1** (0.01 mol) and ethyl urea (0.02 mol) in ethanol (15 mL) containing catalytic amount of potassium hydroxide was refluxed for 5 h. Then the solution was allowed to cool, and poured into cold water (25 mL) and stirred for 20 min. The solid separated was filtered, washed with water (100 mL), and dried to afford **6** in good yield.

4.6. Synthesis of 8-aryl-1,6-diphenyl-1,6-dihydrodi-pyrazolo[3,4-*b*:3′,4′-*d*]pyridin-3(2*H*)-one (7a–d)

A solution of compound **1** (0.01 mol) and phenylhydrazine or hydrazine hydrate (0.01 mol) in xylene (15 mL) containing a catalytic amount of triethylamine (0.5 mL) was refluxed for 3–5 h. The excess solvent was removed by reduced pressure. The solid obtained was stirred in ethanol (20 mL), filtered, dried, and recrystallized from proper solvent to afford **7** in good yield.

4.6.1. Ethyl 4-azido-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (2a). Recrystallized from ethanol to afford colorless needles; mp 187–188 °C. IR (KBr): 2991, 2922, 2854, 2144, 1706, 1585, 1498, 1269, 1134, 910 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.43 (t, J=6.9 Hz, 3H, CH_3), 4.45 (q, J=7.5 Hz, 2H, OCH_2), 7.23–7.55 (m, 5H, Ar-H), 7.80 (d, J=8.4 Hz, 2H, Ar-H), 8.21 (d, J=8.4 Hz, 2H, Ar-H), 9.07 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 14.1, 60.8, 105.3, 120.2, 125.4, 126.2, 128.4, 128.7, 129.3, 129.4, 134.2, 135.7, 139.7, 144.2, 148.9, 150.2, 167.6. Anal. Calcd for $C_{21}H_{15}ClN_6O_2$: C, 60.22; H, 3.61; N, 20.07. Found: C, 60.40; H, 3.44; N, 20.30.

4.6.2. Ethyl 4-azido-3-(4-bromophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (2b). Recrystallized from ethanol to afford colorless needles; mp 191–192 °C. IR (KBr): 2958, 2912, 2314, 1700, 1515, 1445, 1134, 912 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.42 (t, J=6.9 Hz, 3H, CH_3), 4.43 (q, J=7.2 Hz, 2H, OCH_2), 7.21–7.51 (m, 5H, Ar-H), 7.81 (d, J=8.4 Hz, 2H, Ar-H), 8.22 (d, J=8.4 Hz, 2H, Ar-H), 9.07 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 14.2, 60.0, 106.3, 120, 125, 126.2, 128, 128.4, 129, 129.1, 133.6, 134.3, 138.5, 144.1, 147.5, 152, 168.6. Anal. Calcd for $C_{21}H_{15}BrN_6O_2$: C, 54.44; H, 3.26; N, 18.14. Found: C, 54.40; H, 3.22; N, 18.30.

4.6.3. 9-(4-Chlorophenyl)-7-phenyl-7*H*-pyrazolo[4′,3′:5,6]-pyrido[4,3-*d*][1,2,3]triazin-4-ol (3a). Recrystallized from ethanol to afford colorless needles; mp 201–203 °C. IR (KBr): 3416, 3044, 2926, 2855, 2762, 1538, 1456, 1287, 1136, 922 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.24 (m, 5H, Ar-H), 7.67 (d, J=8.4 Hz, 2H, Ar-H), 8.18 (d, J=8.4 Hz, 2H, Ar-H), 9.24 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 108, 119, 123.6, 124.8, 125.4, 127.5, 129.9, 130, 132.8, 135, 139, 145, 148.2, 149.1, 155. Anal. Calcd for $C_{19}H_{11}ClN_6O$: C, 60.89; H, 2.96; N, 22.42. Found: C, 60.90; H, 2.92; N, 22.49.

4.6.4. 9-(4-Bromophenyl)-7-phenyl-7*H*-pyrazolo[4′,3′:5,6]pyrido[4,3-*d*][1,2,3]triazin-4-ol (3b). Recrystallized from ethanol to afford colorless needles; mp 211–212 °C. IR (KBr): 3452, 3125, 3012, 2906, 2812, 2760, 1507, 1344, 1227, 1134, 920 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.23 (m, 5H, Ar-H) 7.68 (d, J=8.4 Hz, 2H, Ar-H), 8.19 (d, J=8.4 Hz, 2H, Ar-H), 9.23 (s, 1H, Ar-H). Anal. Calcd for $C_{19}H_{11}BrN_6O$: C, 54.43; H, 2.64; N, 20.05. Found: C, 54.47; H, 2.70; N, 20.09.

4.6.5. Ethyl 4-amino-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (4a). Recrystallized from ethanol to afford colorless needles; mp 161–162 °C. IR (KBr): 2916, 2848, 1678, 1598, 1552, 1468, 1406, 1163, 723.3 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.38 (t, J=6.9 Hz, 3H, CH_3), 4.33 (q, J=7.2 Hz, 2H, OCH_2), 5.50 (br s, 1H, NH), 7.24–8.14 (m, 9H, Ar-H) 8.41 (br s, 1H, NH), 8.97 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 14.1, 60.9, 104.6, 105.0, 120.2, 126.3, 128.8, 128.9, 129.4, 130.2, 131.3, 134.3, 145.9, 149.1, 151.3, 155.0, 166.0. Anal. Calcd for $C_{21}H_{17}ClN_4O_2$: C, 64.21; H, 4.36; N, 14.26. Found: C, 64.37; H, 4.40; N, 14.09.

4.6.6. Ethyl 4-amino-3-(4-bromophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (4b). Recrystallized from ethanol to afford colorless needles; mp 172–173 °C. IR (KBr): 3101, 2948, 1688, 1598, 1525, 1368, 1406, 1155, 769 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.39 (t, J=6.9 Hz, 3H, CH_3), 4.35 (q, J=7.2 Hz, 2H, –OCH_2), 5.53 (br s, 1H, NH), 7.26–8.01 (m, 9H, Ar-H) 8.45 (br s, 1H, NH), 8.97 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 14.4, 60, 106.5, 107.2, 121.6, 126, 128, 128.8, 129, 130, 131.6, 133.1, 144.5, 147, 152.4, 154.3, 169. Anal. Calcd for $C_{21}H_{17}BrN_4O_2$: C, 57.68; H, 3.92; N, 12.81. Found: C, 57.67; H, 3.99; N, 12.90.

4.6.7. 2-Amino-9-(4-chlorophenyl)-4-hydroxy-7-phenyl-7*H*-pyrazolo[3,4-*h*][1,6]naphthyridine-3-carbonitrile (5a). Recrystallized from ethanol to afford colorless needles; mp 215–216 °C. IR (KBr): 3435, 3315, 3126, 2234, 1470, 1160, 945 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.74 (br s, 2H, NH_2), 7.18–8.35 (m, 9H, Ar-H), 8.63 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 82.4, 100.8, 106.3, 117.0, 120.2, 120.4, 128.3, 128.6, 129.2, 129.4, 134.3, 134.4, 145.9, 148.1, 148.3, 149.1, 162.8, 171.2. Anal. Calcd for $C_{22}H_{13}ClN_6O$: C, 64.01; H, 3.17; N, 20.36. Found: C, 64.07; H, 3.19; N, 20.40.

4.6.8. 2-Amino-9-(4-bromophenyl)-4-hydroxy-7-phenyl-7*H*-pyrazolo[3,4-*h*][1,6]naphthyridine-3-carbonitrile (5b). Recrystallized from ethanol to afford colorless needles; mp 221–222 °C. IR (KBr): 3456, 3341, 3221, 2244, 1461, 1162, 948 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.73 (br s, 2H, NH_2), 7.17–8.36 (m, 9H, Ar-H), 8.65 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 83, 101.4, 105.2, 116.1, 120.3, 120.4, 128, 128.5, 129, 129.9, 133.8, 135.9, 145, 148.3, 148.8, 149.5, 162.6, 171. Anal. Calcd for $C_{22}H_{13}BrN_6O$: C, 57.78; H, 2.87; N, 18.38. Found: C, 57.70; H, 2.89; N, 18.40.

4.6.9. Ethyl 3-(4-chlorophenyl)-4-{[(ethylamino)carbonyl]-amino}-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (6a). Recrystallized from ethanol to afford colorless needles; mp 235–236 °C. IR (KBr): 3315, 3245, 2966, 1738, 1618, 1455, 1136, 915 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.00 (t, J=6.9 Hz, 3H, CH_3), 1.39 (t, J=6.8 Hz, 3H, CH_3), 2.83 (q, J=7.2 Hz, 2H, CH_2), 4.33 (q, J=7.2 Hz, 2H, OCH_2), 7.24 (m, 9H, Ar-H), 8.72 (br s, 1H, –NH), 8.95 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 14.1, 14.5, 36.5, 60.4, 104.3, 105.8, 120, 126, 128.3, 129.4, 129.6, 131.8, 134.6, 139.8, 145.9, 149.3, 151.3, 154, 155, 166. Anal. Calcd for $C_{24}H_{22}ClN_5O_3$: C, 62.14; H, 4.78; N, 15.10. Found: C, 62.20; H, 4.84; N, 15.30.

4.6.10. Ethyl 3-(4-bromophenyl)-4-{[(ethylamino)carbonyl]amino}-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate (6b). Recrystallized from ethanol to afford colorless needles; mp 239–240 °C. IR (KBr): 3328, 3215, 2926, 1734, 1628, 1465, 1160, 930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.00 (t, J=6.9 Hz, 3H, CH_3), 1.37 (t, J=6.8 Hz, 3H, CH_3), 2.82 (q, J=7.2 Hz, 2H, CH_2), 4.34 (q, J=7.2 Hz, 2H, OCH_2), 7.23 (m, 9H, Ar-H), 8.71 (br s, 1H, –NH), 8.95 (s, 1H, C_6-H). ^{13}C NMR ($CDCl_3$): δ 14.1, 14.6, 36.3, 60, 103.8, 106.5, 121, 125.2, 128.3, 129, 129.7, 131, 133.4, 138.9, 145, 149, 151.6, 155, 155.8, 167. Anal. Calcd for $C_{24}H_{22}BrN_5O_3$: C, 56.70; H, 4.36; N, 13.78. Found: C, 56.75; H, 4.34; N, 13.80.

4.6.11. 8-(4-Chlorophenyl)-1,6-diphenyl-1,6-dihydrodi-pyrazolo[3,4-*b*:3′,4′-*d*]pyridin-3(2*H*)-one (7a). Recrystallized from DMF/ethanol (2:8) to afford yellow needles; mp 220–221 °C. IR (KBr): 3216, 2912, 1632, 1553, 1435, 1162, 936 cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.19–7.65 (m,

10H, Ar-H), 7.95 (d, J=8.4 Hz, 2H, Ar-H), 8.18 (d, J=8.4 Hz, 2H, Ar-H), 8.50 (s, 1H, C_6-H), 8.62 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 104.6, 115.8, 120.1, 121.2, 123.4, 125.6, 125.7, 126.1, 126.2, 129.1, 129.2, 130.1, 134.2, 134.3, 145.9, 149.1, 154.6, 156.6, 167.3. Anal. Calcd for $C_{25}H_{16}ClN_5O$: C, 68.57; H, 3.66; N, 15.99. Found: C, 68.67; H, 3.69; N, 15.80.

4.6.12. 8-(4-Bromophenyl)-1,6-diphenyl-1,6-dihydrodipyrazolo[3,4-*b*:3′,4′-*d*]pyridin-3(2*H*)-one (7b). Recrystallized from DMF/ethanol (2:8) to afford yellow needles; mp 226–227 °C. IR (KBr): 3217, 2933, 1622, 1511, 1415, 1162, 935 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.18–7.64 (m, 10H, Ar-H), 7.91 (d, J=8.4 Hz, 2H, Ar-H), 8.19 (d, J=8.4 Hz, 2H, Ar-H), 8.51 (s, 1H, C_6-H), 8.63 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 106, 114, 121.5, 121.8, 123, 124, 125.9, 126.8, 126.9, 129, 129.8, 130, 133.2, 134.5, 141, 146, 152.6, 158.6, 169.2. Anal. Calcd for $C_{25}H_{16}BrN_5O$: C, 62.25; H, 3.34; N, 14.52. Found: C, 62.27; H, 3.39; N, 14.66.

4.6.13. 8-(4-Chlorophenyl)-6-phenyl-1,6-dihydrodipyrazolo[3,4-*b*:3′,4′-*d*]pyridin-3(2*H*)-one (7c). Recrystallized from DMF/ethanol (2:8) to afford yellow needles; mp 242–243 °C. IR (KBr): 3315, 3128, 2926, 1612, 1535, 1456, 1228, 936 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.22–8.16 (m, 9H, Ar-H), 8.53 (s, 1H, C_6-H), 8.62 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 105.2, 115, 121.6, 124, 126.7, 128.5, 129, 129.3, 130, 130.2, 145, 149, 154, 156, 167.3. Anal. Calcd for $C_{19}H_{12}ClN_5O$: C, 63.08; H, 3.34; N, 19.36. Found: C, 63.17; H, 3.44; N 19.56.

4.6.14. 8-(4-Bromophenyl)-6-phenyl-1,6-dihydrodipyrazolo[3,4-*b*:3′,4′-*d*]pyridin-3(2*H*)-one (7d). Recrystallized from DMF/ethanol (2:8) to afford yellow needles; mp 248–249 °C. IR (KBr): 3328, 3216, 2927, 1624, 1545, 1416, 1229, 912 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.21–8.14 (m, 9H, Ar-H), 8.54 (s, 1H, C_6-H), 8.61 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 107.2, 117, 121, 124.8, 126.3, 128.4, 129.5, 129.9, 130.2, 130.3, 142, 148, 151, 154, 168. Anal. Calcd for $C_{19}H_{12}BrN_5O$: C, 56.18; H, 2.98; N, 17.24. Found: C, 56.27; H, 2.77; N, 17.36.

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