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Tetrahedron
Tetrahedron 60 (2004) 1161–1166

A facile synthesis of pyrrolo[1,2-*a*]benzimidazoles and pyrazolo[3,4:4′,3′]pyrrolo[1,2-*a*]benzimidazole derivatives

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Received 6 August 2003; revised 31 October 2003; accepted 20 November 2003

Abstract—Reaction of 2-cyanomethylbenzimidazole **1** with hydrazonoyl halides **2** led to formation of pyrrolo[1,2-*a*]benzimidazole derivatives **7**. Similar reaction of **1** with halides **3** afforded 5-amino-4-(benzimidazol-2-yl)pyrazole derivatives **11** or 1-amino-2-arylpyrazolo[3,4:4′,3′]pyrrolo[1,2-*a*]benzimidazol-4-one **14** depending on the reaction conditions. The mechanisms of the studied reactions are discussed.

1. Introduction

Hydrazonoyl halides are highly versatile intermediates for the synthesis of a variety of heterocyclic compounds.[1] Also, benzimidazoles represent an important heterocyclic system due to their pharmacological activity.[2] In addition many efforts have been made to develop methods for preparation of pyrrolo[1,2-*a*]benzimidazole.[3–5] This is because derivatives of this ring system proved to have many applications, for example, pyrrolo[1,2-*a*]benzimidazole based antitumor agent system,[6] cytotoxicity against melanoma and renal cancers;[7] cytotoxicity against leukemia and gasteric cancer cell lines,[8] cytotoxicity of various PBI and APBI derivatives,[9] as novel chlain esterase inhibitors,[10] as photochromic compound.[11] Also some pyrrolo[1,2-*a*]benzimidazole derivatives are useful in treating central nervous system disorder,[12] and as topoisomerase inhibitor.[13] In addition, they are used in the synthesis of basic dyes[14] and polymethine dyes.[15]

2. Results and discussion

In continuation of our interest in the synthesis of novel polyfunctionalized heterocycles of biological importance,[16] we report here a facile one-pot synthesis of the title compounds via reaction of hydrazonoyl halides **2** and **3** with 2-cyanomethylbenzimidazole **1**. Thus treatment of hydrazonoyl halides **2a-f** with 2-cyanomethylbenzimidazole **1** in chloroform in the presence of triethylamine under reflux, afforded products identified as 2-arylazo-3-cyano-1-substituted pyrrolo[1,2-*a*]benzimidazoles **7** (Scheme 1). All of the isolated products **7a-f** gave satisfactory elemental analyses and spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS, UV) consistent with their assigned structures. For example, the IR spectra of the products showed conjugated nitrile absorption band near 2200 cm^{-1}, absence of carbonyl absorption and the appearance of NH absorption band in the region 3450–3200 cm^{-1}. Furthermore, the electronic absorption spectra of **7a-f** in dioxane revealed in each case, three intense maxima at λ near 410, 330 and 250 nm assignable to arylazochromophore. The formation of **7a-f** from the reaction of **1** with **2** seems to follow the sequence outlined in Scheme 1 (route a). It is suggested that the reaction starts with nucleophilic substitution of the halogen group in **2** by the carbanion of **1** namely **4** to give **5** which cyclizes via elimination of the elements of water to give **7a-f** as end products.

On the other hand, treatment of hydrazonoyl chlorides **3a-f** with 2-cyanomethylbenzimidazole **1** in ethanolic sodium ethoxide solution at room temperature, afforded a single product in each case, as evidenced by TLC and ^{1}H NMR spectroscopic analyses. The structure of the isolated products was established by analytical and spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS) and identified as alkyl 5-amino-1-aryl-4-(benzimidazol-2-yl)pyrazole-3-carboxylate **11** (Scheme 2). For example, the IR spectra showed the presence of characteristic NH and NH_2 absorption bands in the region 3450–3200 cm^{-1} and the absence of conjugated nitrile absorption band near 2200 cm^{-1} for each product. In addition they revealed the ester carbonyl near 1705 cm^{-1}.

Keywords: 2-Cyanomethylbenzimidazole; Hydrazonoyl halides; Pyrrolo[1,2-*a*]benzimidazole; 5-Amino-4-(benzimidazol-2-yl)pyrazole; 1-Amino-2-arylpyrazolo[3,4:4′,3′]pyrrolo[1,2-*a*]benzimidazol-4-one.
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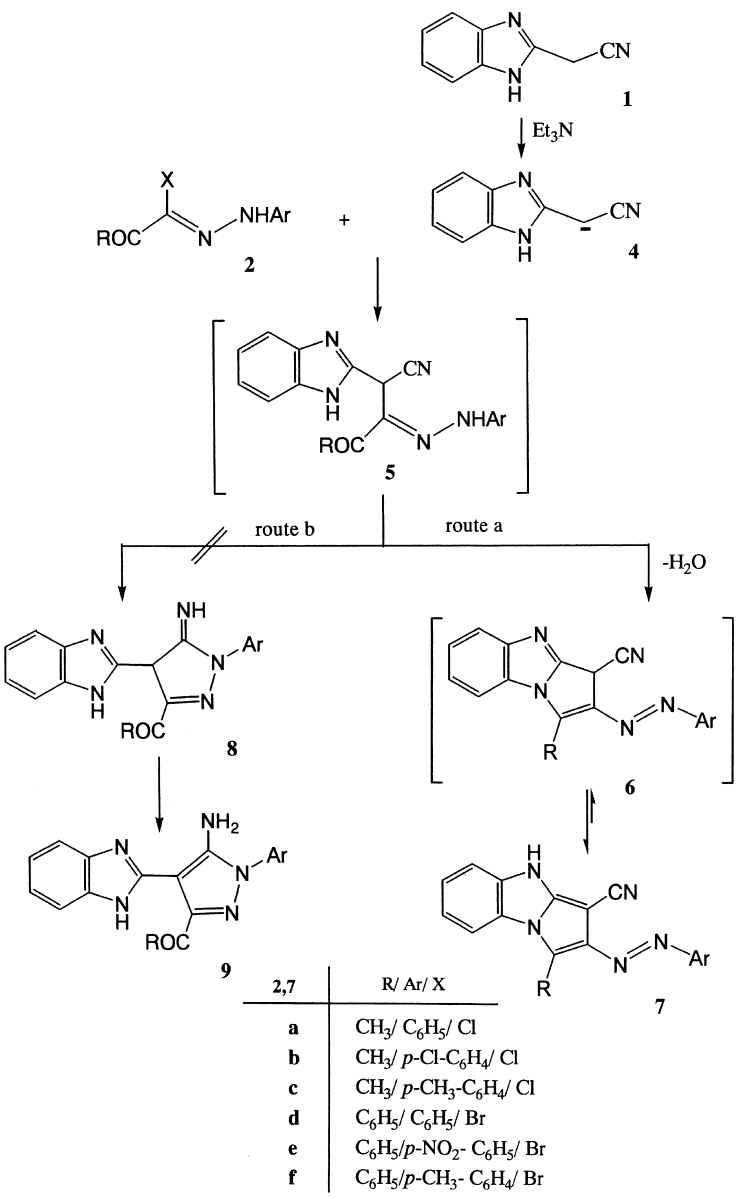
doi:10.1016/j.tet.2003.11.068

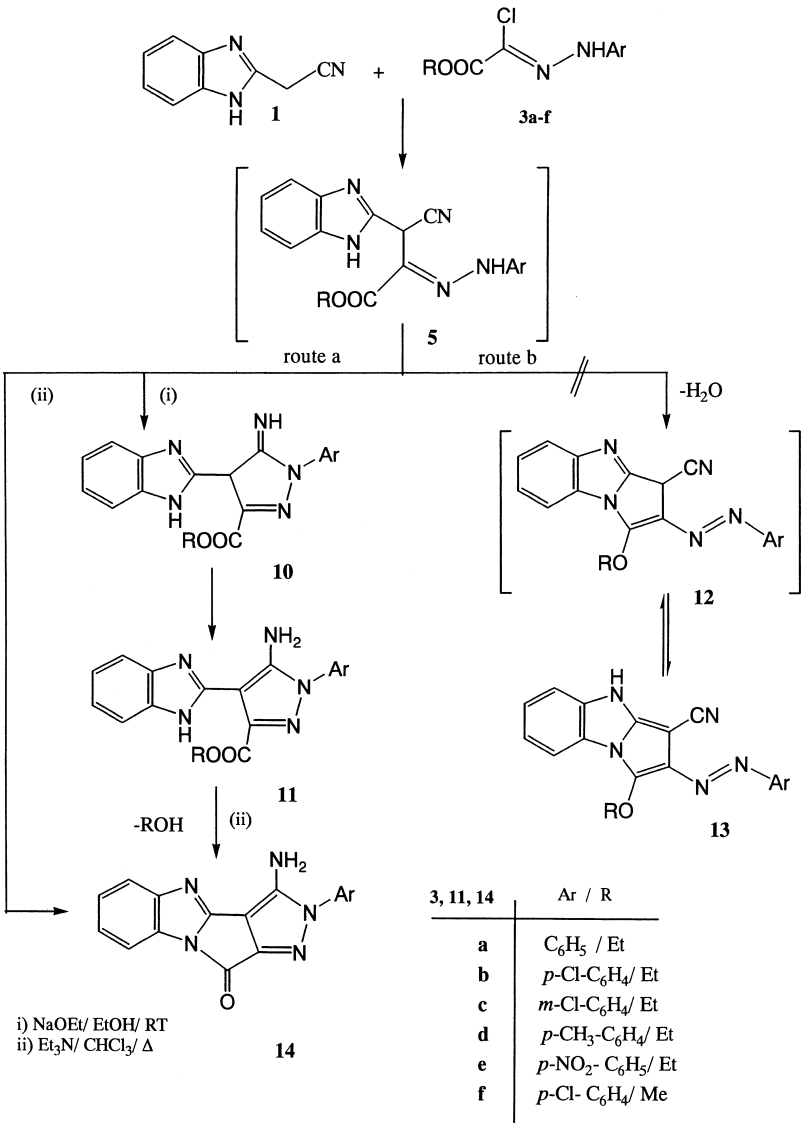


Scheme 1.

The assigned structures were further supported by their chemical reactions. Thus heating **11b** or **11f** in chloroform in the presence of triethylamine yielded the same product **14b**. Also, treatment of 2-cyanomethylbenzimidazole **1** with hydrazonoyl chlorides **3a-d** in chloroform in the presence of triethylamine under reflux, afforded, in each case, one single product **14a-d** as evidenced by TLC and ^{1}H NMR spectroscopy of the reaction products (Scheme 2). The mass spectra of the products exhibited in each case a molecular ion peak with high intensity. ^{1}H NMR spectra were devoid of signals characteristic of an ethyl group. The latter structure was firmly established for the reaction products by alternate synthesis of the product **14b** via reaction of methyl *N*-(*p*-chlorophenyl)hydrazonochloroacetate **3f** with **1** in chloroform in the presence of triethylamine under reflux to afford a product, which proved to be identical in all respects (mp, mixed mp, spectral data) with **14b**. An attempt to cycle **11e** to get **14e** by the same method was not successful. However, **14e** was obtained in small yield (30%) by heating **11e** in refluxing xylene for 48 h.

3. Experimental

Melting points were recorded on Gallenkamp apparatus and are uncorrected. Infrared spectra (KBr) were determined on a Pye Unicam SP-3000 infrared spectrophotometer. ^{1}H NMR and ^{13}C spectra were determined on a Varian Gemini 200 spectrometer (200 MHz) in DMSO-d_6 with TMS as an internal standard. Mass spectra were recorded on a GCMS-QP 1000EX Schimadzu spectrometer. The electronic spectra were recorded using Perkin–Elmer Lambda 4B UV–VIS spectrophotometer. Elemental analyses were carried out at the microanalytical center, University of Cairo, Giza, Egypt. The starting 2-cyanomethybenzimidazole **1**[17] and hydrazonoyl halides **2** and **3**[18–21] were



Scheme 2.

prepared as previously described. Due to the limited solubility of products **7**, **11** and **14** in common ^{13}C NMR solvents, the ^{13}C NMR spectra were recoded for **7a-c**, **7e**, **11d**, **e**, **14a-c** and **14e** only as representative examples of the series prepared.

3.1. Synthesis of pyrrolo[1,2-*a*]benzimidazoles 7a-f

General method. To a solution of 2-cyanomethylbenzimidazole **1** (0.79 g, 5 mmol) and the appropriate hydrazonoyl halide **2** (5 mmol) in chloroform (40 mL) was added triethylamine (0.7 mL, 5 mmol) at room temperature. The reaction mixture was refluxed for 8 h and the solvent was then evaporated and the residue was treated with methanol. The solid that formed was collected and crystallized from dimethylformamide to give **7a-f** in needle form.

3.1.1. 3-Cyano-1-methyl-2-phenylazo-4*H*-pyrrolo[1,2-*a*]-benzimidazole 7a. The compound was obtained in 80% yield, orange, mp 264 °C; IR (KBr) ν 3394 (NH), 2200 (CN) cm^{-1}; ^1H NMR (DMSO) δ 2.7 (s, 3H), 7.2–7.5 (m, 5H), 7.6–7.9 (m, 2H), 8.0–8.2 (m, 1H), 8.6–8.8 (m, 1H), 13.2 (s, 1H); ^{13}C NMR (DMSO) δ 13.6, 113.8, 117.2, 118.4, 122.5, 126.2, 126.4, 128.5, 129.6, 130.4, 134.2, 137.1, 145.6, 155.4, 164.1, 177.7 ppm; MS, *m/z* (%): 300 (21.9), 299 (100), 207 (25.4), 194 (26.6), 92 (64.6), 77 (48.4), 65 (72.1); UV (dioxane), λ_{max} (nm): 438, 354, 256. Anal. Calcd for $C_{18}H_{13}N_5$: C, 72.22; H, 4.38; N, 23.40. Found: C, 72.45; H, 4.23; N, 23.75%.

3.1.2. 3-Cyano-1-methyl-2-(*p*-chlorophenylazo)-4*H*-pyrrolo[1,2-*a*]benzimidazole 7b. The compound was obtained in 82% yield, red, mp 280 °C; IR (KBr) ν 3170 (NH), 2206 (CN) cm^{-1}; ^1H NMR (DMSO) δ 2.7 (s, 3H), 7.2–7.7 (m, 5H), 7.8–8.0 (m, 2H), 8.6–8.7 (m, 1H), 13.2 (s, 1H); ^{13}C NMR (DMSO) δ 13.5, 110.0, 112.6, 115.4, 116.9, 117.8, 121.8, 123.1, 125.3, 127.6, 129.9, 132.9, 143.4, 146.3, 153.1, 162.9 ppm; MS, *m/z* (%): 335 (35.4), 334 (27.7), 333 (100), 207 (45.4), 126 (53.8), 90 (39.9), 75 (26.0), 64 (32), 63 (43.5); UV (dioxane), λ_{max} (nm): 447, 359, 256. Anal. Calcd for $C_{18}H_{12}ClN_5$: C, 64.77; H, 3.63; N, 20.98. Found: C, 64.91; H, 3.85; N, 20.86%.

3.1.3. 3-Cyano-1-methyl-2-(*p*-methylphenylazo)-4*H*-pyrrolo[1,2-*a*]benzimidazole 7c. The compound was obtained in 78% yield, orange, mp 274 °C; IR (KBr) ν 3163 (NH), 2206 (CN) cm^{-1}; ^1H NMR (DMSO) δ 2.3 (s, 3H), 2.5 (s, 3H), 7.2–7.5 (m, 5H), 7.6–7.7 (m, 2H), 8.5–8.6 (m, 1H), 13.2 (s, 1H); ^{13}C NMR (DMSO) δ 13.6, 23.2, 113.4, 117.1, 118.5 122.2, 126.1, 126.3, 128.2, 131.6 134.0, 136.9, 139.8, 145.1, 153.1, 163.5, 177.6; MS, *m/z* (%): 314 (20.1), 313 (100), 207 (26.1), 106 (70.2); UV (dioxane), λ_{max} (nm): 440, 350, 255. Anal. Calcd for $C_{19}H_{15}N_5$: C, 72.82; H, 4.83; N, 22.35. Found: C, 73.01; H, 4.55; N, 22.60%.

3.1.4. 3-Cyano-1-phenyl-2-phenylazo-4*H*-pyrrolo[1,2-*a*]-benzimidazole 7d. The compound was obtained in 77% yield, orange, mp 254 °C; IR (KBr) ν 3340 (NH), 2129 (CN) cm^{-1}; ^1H NMR (DMSO) δ 7.3–8.0 (m,14H), 8.7–8.8 (m,1H); MS, *m/z* (%): 361 (75.8), 360 (100), 333 (22.1), 257 (44.7), 127 (15.2), 92 (48.1), 77 (72.6), 65 (60.3); UV (dioxane), λ_{max} (nm): 451, 324, 276. Anal. Calcd for $C_{23}H_{15}N_5$: C, 76.44; H, 4.18; N, 19.38. Found: C, 76.24; H, 4.50; N, 19.62%.

3.1.5. 3-Cyano-1-phenyl-2-(*p*-nitrophenylazo)-4*H*-pyrrolo[1,2-*a*]benzimidazole 7e. The compound was obtained in 80% yield, reddish brown, mp 170 °C; IR (KBr) ν 3425 (NH), 2183 (CN) cm^{-1}; ^1H NMR (DMSO) δ 7.2–7.5 (m, 12H), 8.0 (d, *J*=9.1 Hz, 1H), 8.8 (d, *J*=9.1 Hz, 1H); ^{13}C NMR (DMSO) δ 108.2, 115.3, 117.6, 119.5, 126.2, 126.3, 126.9, 127.2, 127.6, 127.9, 128.2, 129.0, 129.2, 130.3, 130.5, 131.0, 132.3, 134.8, 138.6, 140.3, 177.3 ppm; MS, *m/z* (%): 407 (5.3), 406 (17.7), 105 (100), 77 (78.4); UV (dioxane), λ_{max} (nm): 400, 320, 268. Anal. Calcd for $C_{23}H_{14}N_6O_2$: C, 67.97; H, 3.47; N, 20.68. Found: C, 68.10; H, 3.52; N, 21.01%.

3.1.6. 3-Cyano-1-phenyl-2-(*p*-methylphenylazo)-4*H*-pyrrolo[1,2-*a*]benzimidazole 7f. The compound was obtained in 78% yield, reddish brown, mp 185 °C; IR (KBr) ν 3425 (NH), 2175 (CN) cm^{-1}; ^1H NMR (DMSO) δ 2.3 (s, 3H); 6.8–7.8 (m, 11H), 8.0–8.2 (m, 2H), 9.9 (s, 1H); MS, *m/z* (%): 376 (10.2), 375 (51.4), 374 (100), 268 (11.5), 77 (54.8), 64 (19.3); UV (dioxane), λ_{max} (nm): 416, 328, 258. Anal. Calcd for $C_{24}H_{17}N_5$: C, 76.78; H, 4.57; N, 18.66. Found: C, 76.80; H, 4.23; N, 18.76%.

3.2. Synthesis of alkyl 5-amino-1-aryl-4-(benzimidazol-2-yl)pyrazole-3-carboxylate derivatives 11a-f

General method. To an ethanolic sodium ethoxide solution, prepared from sodium metal (0.1 g, 5 mmol) and absolute ethanol (30 mL), was added 2-cyanomethylbenzimidazole **1** (0.79 g, 5 mmol) with stirring. To the resulting solution, the appropriate hydrazonoyl chloride **3** (5 mmol) was added at room temperature. The mixture was stirred for 12 h at room temperature. During this time the hydrazonoyl chloride dissolved and the crude product precipitated. The latter was filtered, washed with water, dried and finally crystallized from the proper solvent to give the respective product **11a-f** as polycrystalline materials.

3.2.1. Ethyl 5-amino-1-phenyl-4-(benzimidazol-2-yl)pyrazole-3-carboxylate 11a. The compound was obtained in 70% yield, yellow, mp 203 °C (methanol); IR (KBr) ν 3440, 3178, 3062 (NH_2, NH), 1705 (CO) cm^{-1}; ^1H NMR (DMSO) δ 1.3 (t, *J*=7 Hz, 3H); 4.2 (q, *J*=7 Hz, 2H), 4.3 (s, 2H), 7.0–7.3 (m, 8H), 8.0–8.1 (m, 1H), 11.0 (s, 1H); MS, *m/z* (%): 348 (5.9), 347 (25.7), 273 (10.1), 156 (13.9), 92 (69.3), 91 (100).Anal. Calcd for $C_{19}H_{17}N_5O_2$: C, 65.69; H, 4.93; N, 20.16. Found: C, 65.74; H, 5.22; N, 20.00%.

3.2.2. Ethyl 5-amino-1-(*p*-chlorophenyl)-4-(benzimidazol-2-yl)pyrazole-3-carboxylate 11b. The compound was obtained in 80% yield, yellow, mp 390 °C (ethanol); IR (KBr) ν 3417, 3240, 3200 (NH_2, NH), 1710 (CO) cm^{-1}; ^1H NMR (DMSO) δ 1.2 (t, *J*=7 Hz, 3H); 4.2 (q, *J*=7 Hz, 2H), 4.3 (s, 2H), 7.1–7.5 (m, 7H), 7.6–7.8 (m, 1H), 11.1 (s, 1H); MS, *m/z* (%): 383 (12.0), 382 (7.7), 381 (29.9), 307 (10.1), 157 (12.7), 156 (23.3), 127 (51.4), 125 (100), 99 (41.5), 90 (33.4). Anal. Calcd for $C_{19}H_{16}ClN_5O_2$: C, 59.76; H, 4.22; N, 18.34. Found: C, 59.55; H, 4.34; N, 18.60%.

3.2.3. Ethyl 5-amino-1-(*m*-chlorophenyl)-4-(benzimidazol-2-yl)pyrazole-3-carboxylate 11c. The compound was obtained in 78% yield, yellow, mp 200 °C (ethanol); IR (KBr) ν 3417, 3155, 3070 (NH_2, NH), 1705 (CO) cm^{-1}; ^1H NMR (DMSO) δ 1.2 (t, *J*=7 Hz, 3H); 4.3 (q, *J*=7 Hz, 2H), 4.5 (s, 2H), 7.0–7.4 (m, 7H), 7.6–7.8 (m, 1H), 11.0 (s, 1H); MS, *m/z* (%): 383 (10.8), 382 (8.1), 381 (37.4), 307 (12.2),242 (15.5), 157 (24.2), 156 (27.8), 127 (17.7), 125 (100), 99 (61.3). Anal. Calcd for $C_{19}H_{16}ClN_5O_2$: C, 59.76; H, 4.22; N, 18.34. Found: C, 59.87; H, 4.26; N, 18.58%.

3.2.4. Ethyl 5-amino-1-(*p*-methylphenyl)-4-(benzimidazol-2-yl)pyrazole-3-carboxylate 11d. The compound was obtained in 73% yield, yellow, mp 200 °C (methanol); IR (KBr) ν 3447, 3170, 3100 (NH_2, NH), 1705 (CO) cm^{-1}; ^1H NMR (DMSO) δ 1.3 (t, *J*=7 Hz, 3H); 2.3 (s, 3H), 4.2 (q, *J*=7 Hz, 2H), 4.4 (s, 2H), 7.1–7.5 (m, 8H); 9.9 (s, 1H); ^{13}C NMR (DMSO) δ 15.8, 22.1, 63.1, 112.0, 116.7, 116.9, 117.3, 118.4, 121.3, 124.7, 125.5, 131.4, 131.6, 133.9, 136.4, 144.3, 147.6, 162.6 ppm; MS, *m/z* (%): 362 (7.4), 361 (30.2), 156 (11.1), 107 (23.0), 106 (63.1), 105 (100), 77 (46.3). Anal. Calcd for $C_{20}H_{19}N_5O_2$: C, 66.47; H, 5.30; N, 19.38. Found: C, 66.65; H, 5.43; N, 19.24%.

3.2.5. Ethyl 5-amino-1-(*p*-nitrophenyl)-4-(benzimidazol-2-yl)pyrazole-3-carboxylate 11e. The compound was obtained in 71% yield, yellow, mp 243 °C (DMF–ethanol); IR (KBr) ν 3394, 3170, 3055 (NH_2, NH), 1705 (CO) cm^{-1}; ^1H NMR (DMSO) δ 1.3 (t, *J*=7 Hz, 3H); 4.2 (q, *J*=7 Hz, 2H), 4.3 (s, 2H), 7.0–7.6 (m, 8H), 11.0 (s, 1H); ^{13}C NMR (DMSO) δ 16.0, 63.9, 112.1, 116.6, 116.9, 117.3, 121.3, 122.7, 124.9, 125.8, 127.2, 127.3, 143.8, 144.1, 147.3, 150.1, 162.1 ppm; MS, *m/z* (%): 393 (22.5), 392 (100), 352 (48.5), 346 (25.7), 242 (23.3), 168 (20.7), 157 (53.5), 136 (45.6), 122 (17.9), 91 (22.2), 90 (70.9). Anal. Calcd for $C_{19}H_{16}N_6O_4$: C, 58.16; H, 4.11; N, 21.42. Found: C, 58.32; H, 4.05; N, 21.68%.

3.2.6. Methyl 5-amino-1-(*p*-chlorophenyl)-4-(benzimidazol-2-yl)pyrazole-3-carboxylate 11f. The compound was obtained in 83% yield, yellow, mp 232 °C (DMF–ethanol); IR (KBr) ν 3394, 3170, 3055 (NH_2, NH), 1710 (CO) cm^{-1}; ^1H NMR (DMSO) δ 3.4 (s, 3H), 4.7 (s, 2H), 7.1–7.6 (m, 7H), 8.2–8.3 (m, 1H), 12.0 (s, 1H); MS, *m/z* (%): 369 (25.1), 368 (20.3), 367 (10.0), 168 (28.1), 125 (100). Anal. Calcd

for $C_{18}H_{14}ClN_5O_2$: C, 58.78; H, 3.84; N, 19.04. Found: C, 59.01; H, 3.65; N, 19.33%.

3.3. Synthesis of 1-amino-2-arylpyrazolo[3,4:4′,3′]-pyrrolo[1,2-*a*]benzimidazole-4-ones 14a-d

Method A. To a solution of 2-cyanomethylbenzimidazole **1** (0.79 g, 5 mmol) and the appropriate hydrazonoyl chloride **3a-d** (5 mmol) in chloroform (40 mL) was added triethylamine (0.7 mL, 5 mmol) at room temperature. The reaction mixture heat at reflux for (12 h). The solvent was evaporated and the residue was treated with methanol. The solid that formed was collected and crystallized from DMF–ethanol to give **14** as polycrystalline materials.

Method B. Compound **14b** was prepared by the same method described for the synthesis of **14** using methyl *N*-(*p*-chlorophenyl)hydrazonochloroacetate **3f** instead of **3b**. The solid that formed was collected and crystallized from ethanol. The product was identical in all respects (mp, mixed mp, IR, MS, ^{1}H and ^{13}C NMR) with that obtained by method A.

Method C. Compound **14b** was prepared by heating of **11b** or **11f** (5 mmol) in chloroform (40 mL) at reflux in the presence of triethylamine (0.7 mL, 5 mmol) for (8 h). The solid that formed was collected and crystallized from ethanol. The product is identical in all respects (mp, mixed mp, IR, MS, ^{1}H and ^{13}C NMR) with that obtained by methods A and B.

3.3.1. 1-Amino-2-phenylpyrazolo[3,4:4′,3′]pyrrolo[1,2-*a*]-benzimidazol-4-one 14a. The compound was obtained in 72% yield, yellow, mp 261 °C; IR (KBr) ν 3390, 3184 (NH_2), 1710 (CO) cm^{-1}; ^{1}H NMR (DMSO) δ 4.3 (s, 2H), 6.9–7.0 (m, 1H), 7.2–7.4 (m, 3H), 7.5–7.8 (m, 4H), 8.1–8.2 (m,1H); ^{13}C NMR (DMSO) δ 116.3, 117.0, 117.8, 119.3, 124.3, 124.9, 128.9, 129.0, 131.0, 131.2, 138.6, 139.6, 144.2, 151.6, 162.2 ppm; MS, *m*/*z* (%): 301 (25.8), 300 (22.5), 142 (11.3), 77 (100). Anal. Calcd for $C_{17}H_{11}N_5O$: C, 67.76; H, 3.68; N, 23.25. Found: C, 67.89; H, 3.57; N, 23.47%.

3.3.2. 1-Amino-2-(*p*-chlorophenyl)pyrazolo[3,4:4′,3′]-pyrrolo[1,2-*a*]benzimidazol-4-one 14b. The compound was obtained in 75% yield, yellow, mp 348 °C; IR (KBr) ν 3402, 3147 (NH_2), 1710 (CO) cm^{-1}; ^{1}H NMR (DMSO) δ 4.6 (s, 2H), 7.2–7.6 (m, 7H), 7.9–8.0 (m, 1H); ^{13}C NMR (DMSO) δ 116.7, 120.5, 120.7, 122.1, 127.1, 129.3, 129.7, 131.7, 133.9, 134.2, 134.5, 134.6, 136.3, 155.4, 156.1; MS, *m*/*z* (%): 337 (31.4), 336 (48.5), 335 (100), 309 (35.4), 150 (13.3), 131 (22.2), 111 (37,2), 77 (16.1), 75 (53.2). Anal. Calcd for $C_{17}H_{10}ClN_5O$: C, 60.81; H, 3.00; N, 20.86. Found: C, 60.9; H, 3.12; N, 21.01%.

3.3.3. 1-Amino-2-(*m*-chlorophenyl)pyrazolo[3,4:4′,3′]-pyrrolo[1,2-*a*]benzimidazole-4-one 14c. The compound was obtained in 71% yield, yellow, mp 363 °C; IR (KBr) ν 3449, 3237 (NH_2), 1710 (CO) cm^{-1}; ^{1}H NMR (DMSO) δ 4.6 (s, 2H), 6.9–7.0 (m, 1H), 7.2–7.5 (m, 6H), 7.7–7.8 (m, 1H); ^{13}C NMR (DMSO) δ 113.5, 114.0, 114.6, 115.0, 115.9, 123.6, 125.8, 126.1, 127.9, 130.3, 132.4, 135.7, 136.0, 146.1, 156.6; MS, *m*/*z* (%): 337 (24.0), 336 (17.0), 335 (58.9), 183 (100), 102 (44.0), 63 (37.2). Anal. Calcd for $C_{17}H_{10}ClN_5O$: C, 60.81; H, 3.00; N, 20.86. Found: C, 61.11; H, 2.92; N, 20.90%.

3.3.4. 1-Amino-2-(*p*-methylphenyl)pyrazolo[3,4:4′,3′]-pyrrolo[1,2-*a*]benzimidazol-4-one 14d. The compound was obtained in 70% yield, yellow, mp 280 °C; IR (KBr) ν 3401, 3209 (NH_2), 1712 (CO) cm^{-1}; ^{1}H NMR (DMSO) δ 1.2 (s, 3H), 4.5 (s, 2H), 7.1–8.0 (m, 7H), 8.1–8.2 (m, 1H); MS, *m*/*z* (%): 316 (25.0), 315 (28.3), 132 (18.0), 91 (100), 77 (33.6). Anal. Calcd for $C_{18}H_{13}N_5O$: C, 68.56; H, 4.15; N, 22.21. Found: C, 68.46; H, 4.34; N, 22.41%.

3.3.5. Synthesis of 14e. A solution of **11e** (3 mmol) in xylene (15 mL) was refluxed for 48 h. The reaction mixture was cooled. The crude product was collected and crystallized from DMF to give **14e**. The compound was obtained in 30% yield, yellow, mp 298 °C; IR (KBr) ν 3407, 3235 (NH_2), 1710 (CO) cm^{-1}; ^{1}H NMR (DMSO) δ 4.6 (s, 2H), 7.2–7.6 (m, 6H), 7.8–8.1 (m, 2H); MS, *m*/*z* (%): 346 (13.2), 242 (23.3), 207 (10.6), 168 (26.4), 157 (64.6), 136 (62.7), 131 (33.1), 103 (38.9), 90 (100), 76 (34.7), 64 (59.8), 52 (28.3). Anal. Calcd for $C_{17}H_{10}N_6O_3$: C, 58.96; H, 2.91; N, 24.27. Found: C, 59.01; H, 2.74; N, 24.36%.

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