Mohamed Ali A. Khalil*

Department of Chemistry, Faculty of Science, South Valley University, Aswan 81528, Egypt
*E-mail: khalil_asw@yahoo.com

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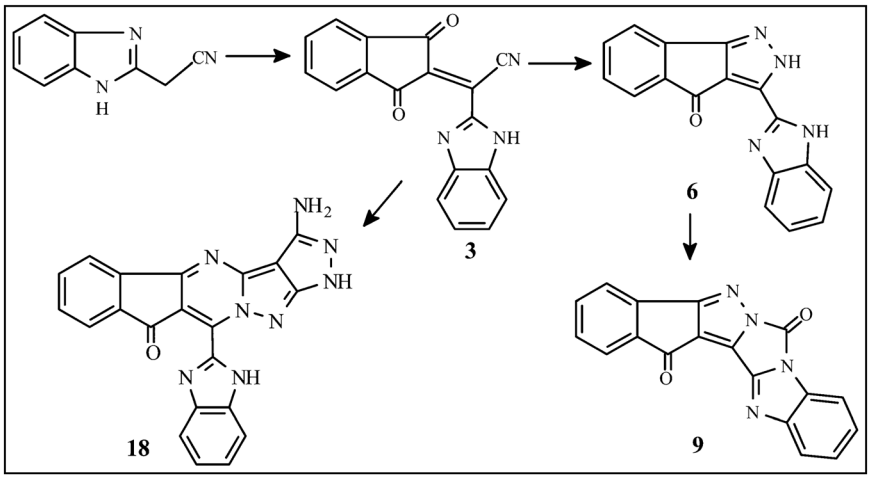

Several (**3**) new benzimidazole based polycyclic compounds of potential pharmaceutical interest have been prepared starting from 2-benzimidazolelyl (1,3-dioxo-2-indenylidene) acetonitrile. Unhypothesized, the C≡N function of the plausible intermediates was released as HCN rather than a classical nucleophilic addition when treated with bidentate reagents such as hydrazines, 5-amino-1*H*-1,2,4-triazole, 5-amino-4-cyano-1*H*-pyrazole and 2-aminobenzimidazole. When compound **3** reacted with active acetonitrile derivatives it afforded new polyfunctional pyridines *via* elimination of HCN in addition to, new pyrimidine, pyrazine and azepine derivatives.

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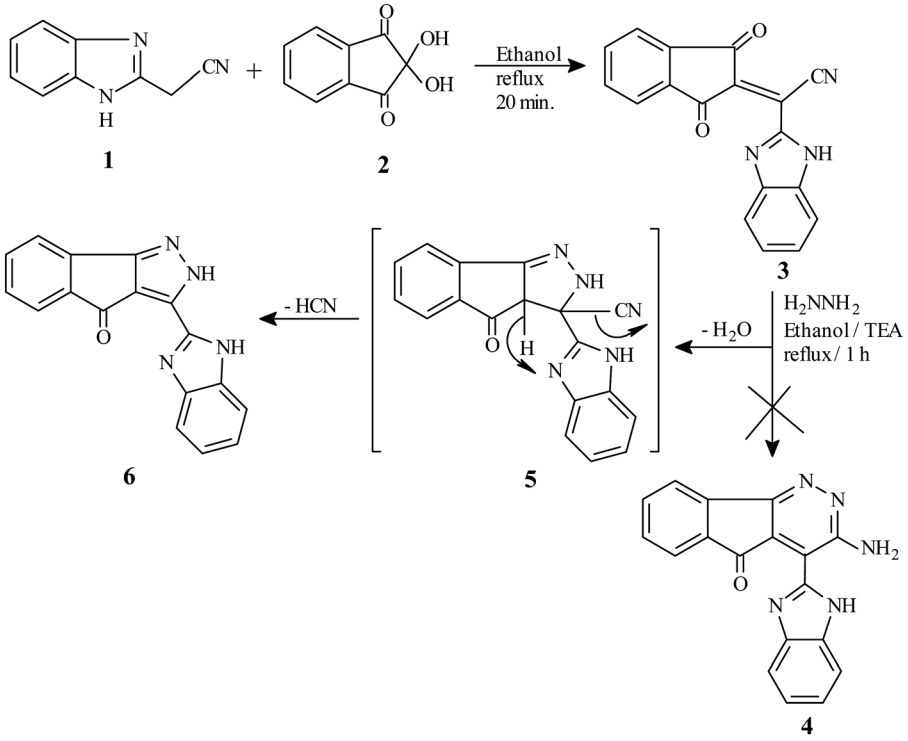
INTRODUCTION

Benzimidazole derivatives are some of the most effective heteroaryl compounds, which are used in the synthesis of many important drugs such as omeprazole and mebendazole [1,2]. Many benzimidazole derivatives have shown evidence of potential anti-inflammatory and analgesic activity [3,4]. Some derivatives also have been found to possess antimicrobial [5], antiviral [6], antifungal [7], antiparasitic [8], pesticidal [9], and herbicidal properties [10]. Furthermore, they also play an important role in anticancer applications [11,12], and cardiovascular diseases treatment [13]. Recently pyridines and pyrimidines synthesis have become the focus in numerous publications [14–17]. Biological applications for pyrazol derivates have been shown considerable interest for their use as muscimol analogs and bacterial metabolites of antipyrine [18–20]. In the pharmaceutical field, pyrazole derivatives serve as antipyretics, analgesics, anti-inflammatories, antireheumatics, antiphlogistics, diuretics, ulcer inhibitors, and cardiovascular agents among others [21–26]. Despite the indan receiving little attention, new indenothiophene derivative has been reported [27]. In conjunction with our previous contributions in the synthesis of new azole and azine derivatives [28–32], it was thought worthwhile to prepare some new azole derivatives annulated benzimidazole core, which might have pharmaceutical action.

RESULTS AND DISCUSSION

2-Cyanomethylbenzimidazole **1** effortlessly reacted with equimolar amount of 1,2,3-indantrione monohydrate **2** in ethanol at reflux temperature for 20 min affording 2-cyano-2-(1,3-dioxo-2-indenylidene) benzimidazole **3** (Scheme 1). Formation of **3** proceeded *via* an initial condensation reaction of the methylene group of 2-Cyanomethylbenzimidazole and two hydroxyl groups of compound **2.** The IR spectrum (KBr) of **3** illustrated the presence of absorption bands at ν 1680, 1724, and 2220 cm^{-1} due to CO and CN functions, respectively. Accordingly, the ^1H NMR spectrum of **3** illustrated signals as multiplet at δ 7.1–7.9 ppm due to aromatic and NH protons. In addition, its ^{13}C NMR exhibited characteristics signals at δ 95.3 and 115.2 ppm for the methylene, and the carbonitrile carbons,

Scheme 1



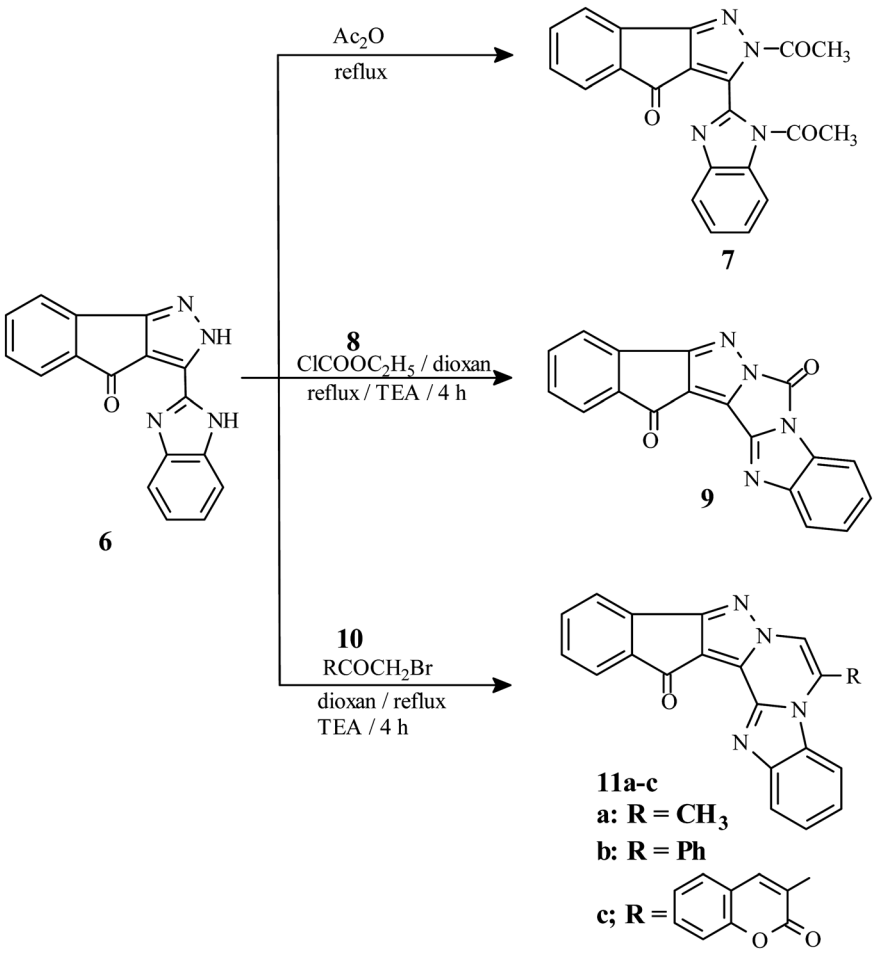
while expected signals of carbonyl carbons at 165.1 and 167.5 ppm have been shown. The MS of compound **3** displayed $[M]^+$ at *m/z* (299, 100%). However, the reactivity of **3** was explored since it contains an active carbonitrile and carbonyl functions, which are easily converted to a variety of other functional groups making it a convenient reactant for the synthesis of various heterocyclic compounds. Thus, benzimidazole **3** reacted easily with hydrazine hydrate in ethanol solution in the presence of few drops of triethylamine at a reflux temperature for 1 h yielding a yellow solid formed during the reflux. The IR spectrum of the product revealed the absence of the absorption band due to CN function, and the presence of bands at 1690, and 3135 cm^{-1}. However, its ^1H NMR spectrum illustrated two singlet signals at δ 9.2 and 9.3 ppm, and a multiplet at 7.1–7.9 ppm integrated for eight protons only. Meanwhile, its MS measurement displayed M^+ at *m/z* 286 (100) and M+1 at 287 (25%). Based on these data, it is concluded that, one of the hydrazine hydrate amine group condensed with the carbonyl oxygen of **3**, while the second amine group of the hydrazine was added to the activated double bond of **3** forming the intermediate **5**, which subsequently released hydrogen cyanide to furnish the unexpected pyrazole compound **6** rather than the pyridazine **4**, which would have been produced as a result of a classical addition of the amine function to the carbonitrile group. (Scheme 1).

The pyrazole **6** directly transformed to the diacetyl compound **7** *via* acylation with acetic anhydride, and cyclized to the corresponding polycyclic compound **9** when it reacted with ethyl chloroformate **8** *via* elimination of HCl, and ethanol (Scheme 2). Both compounds **7** and **9** illustrated no absorption bands due to NH functions. Nevertheless, absorption bands were recorded at *v* 1693–1695 and 1710–1725 cm^{-1} due to CO functions alone. Although the corresponding ^1H NMR spectrum of **7** illustrated one singlet signal assigned for six protons of two methyl groups at 2.1 ppm, the spectrum of compound **9** displayed multiplet due to aromatic protons only. The MS of **7** revealed M^+ at *m/z* at 370 (35%), while of compound **9** *m/z* at 312 (M^+, 100%).

The two hydrogen atoms of pyrazole and imidazole rings of **6** were released when reacted with each of α-bromoacetone **10a**, α-bromo-acetophenone **10b**, and/or 3-(α-bromoacetyl)-coumarin **10c**, respectively yielding pyrazine derivatives **11a**, **11b**, **and 11c**, respectively, (Scheme 2). The IR spectra of **11** illustrated absorption bands at 1692–1712 cm^{-1} assigned for CO functions only, with a complete lack of any absorption bands due to NH functions. The ^1H NMR spectra of **11a** illustrated multiplet at δ 7.1–7.9 ppm due to aromatic protons with an additional two singlet signals at 2.2 and 7.2 ppm for methyl and pyrazine protons; however, the signal of methyl was absent in the spectra of **11b** and **11c**.

As expected, 5-amino-1*H*-1,2,4-triazole **12**, 2-minobenzimidazole **14** and 5-amino-1*H*-3-methylsulfanylpyrazole-4-carbonitrile **16** derivatives reacted under the same

Scheme 2



hypothesis with compound **3.** Annulation of the pyrimidine ring afforded pyrazole derivatives indenopyrimidotriazole **13**, indenopyrimidobenzimidazole **15**, and indenopyrimidopyrazole **17**, respectively. However, the new pyrazole derivative **17** was simply converted to the corresponding new polycyclic pyrazole derivative **18**, when refluxed with hydrazine hydrate in DMF, in the presence of triethylamine for 2 h *via* cycloaddition–elimination reaction, (Scheme 3).

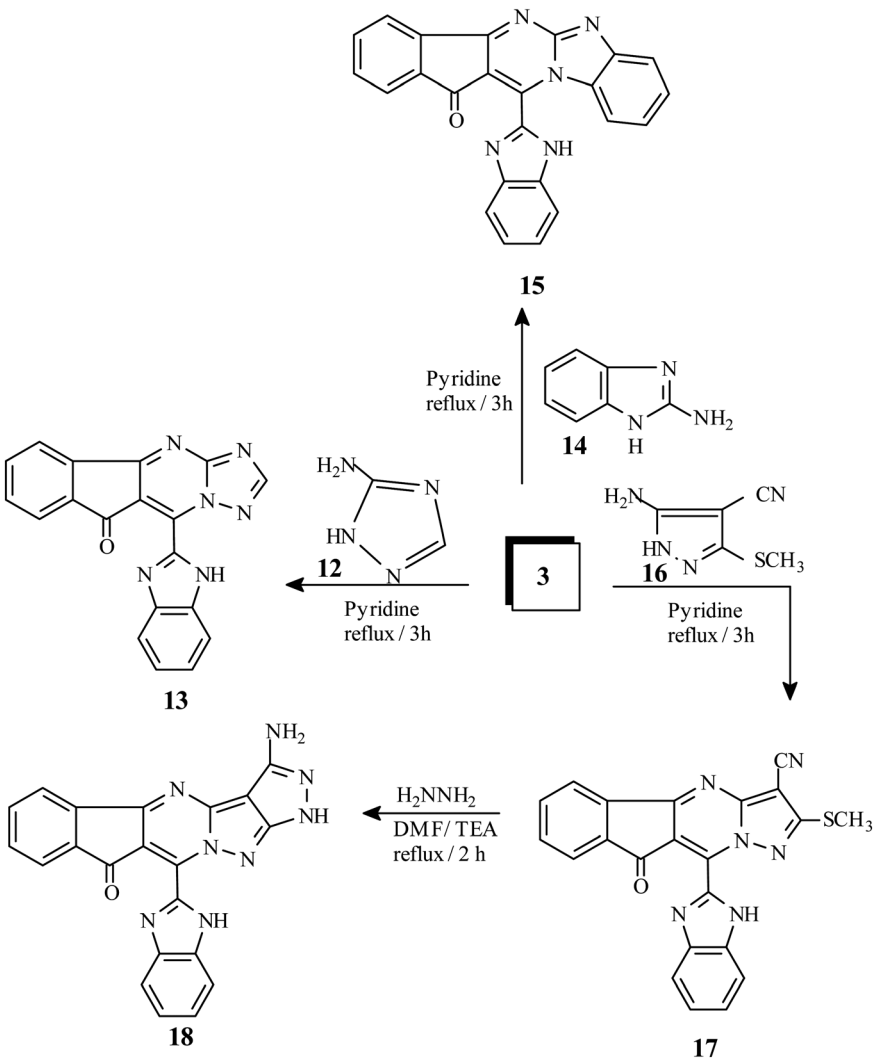
In each reaction, the cyano function was released as HCN and a condensative step led to the stylization product. The chemical structure of the product was established based on the elemental and spectral analysis (Scheme 3). The IR spectra of **13**, **15**, and **18** illustrated no absorption band of CN function whereas, an absorption is recorded as a sharp band in case of compound **17**.

New pyridine derivatives were prepared when compound **3** reacted with cyanoacetamide **19a**, cyanothioacetamide **19b**, cyanoacetanilides **22a**,**b**, and 2-cyanomethylbenzimidazole **1**. An initial condensation step of the active methylene center and the carbonyl oxygen at position 3 of compound **3** followed by elimination of HCN resulted in the pyridine annulated products **20a**,**b**, **23** and **25**, respectively (Scheme 4).

Furthermore, the pyridines **20** easily reacted with ethyl chloroformate **8** in DMF in the presence of triethylamine yielding new imidazolone derivatives **21a**,**b**. The IR spectra of **20a**,**b** demonstrated absorption bands at ν 1320, 1692, 1695, and 2220 and 3154–3127 cm^{-1} assigned for CS, CO, CN, and NH functions, respectively. Furthermore, the IR spectra of the **21a**,**b** revealed intense absorption bands at ν 1315, 1682, 1694 and 2221 cm^{-1} due to CS, CO, and CN functions, respectively, while the bands of NH was absent. Meanwhile, an intense absorption bands appeared at ν 3345–3355 cm^{-1} for the generated amino group of compounds **24a**,**b** with the lack of cyano absorption bands at ν 2222–2225 cm^{-1} in the IR spectrum of **23.**

The ^{1}H NMR spectra of the products demonstrated general features for aromatic protons as multiplet at δ 7.1–7.9 ppm. The MS of **20a**,**b** illustrated *m/z* at 338 (100) and at 354 (87%), as for compounds **21a**,**b** M^+ was displayed at *m/z* 468 (85) and 380 (100).

Scheme 3



Seven-membered benzimidazole based compounds **28a–c** were prepared *via* boiling compound **3** with an equimolar amounts of 2-aminophenol derivatives **26a–c** for about 3 h, plausibly *via* formation of the condensative intermediate **27**, which subsequently afforded **28**a–c after losing HCN (Scheme 5).

The compound **28a** isolated during reflux was found insoluble in most organic solvents. The IR spectra of **28a–c** revealed absorption bands at υ 1672–1685 and 3219–3215 cm^{-1} assigned for CO and NH functions. ^1H NMR spectra of **28b, c** illustrated multiplet signals at δ 7.1–7.8 ppm due to the aromatic and NH protons. The MS of **28a–c** was displayed at *m/z* 363 (78), 379 (100), and 362 (100%), respectively.

Nevertheless, the new benzimidazole annulated polycyclic azoles and azines have been prepared using inexpensive laboratory chemicals through facile and convenient reactions.

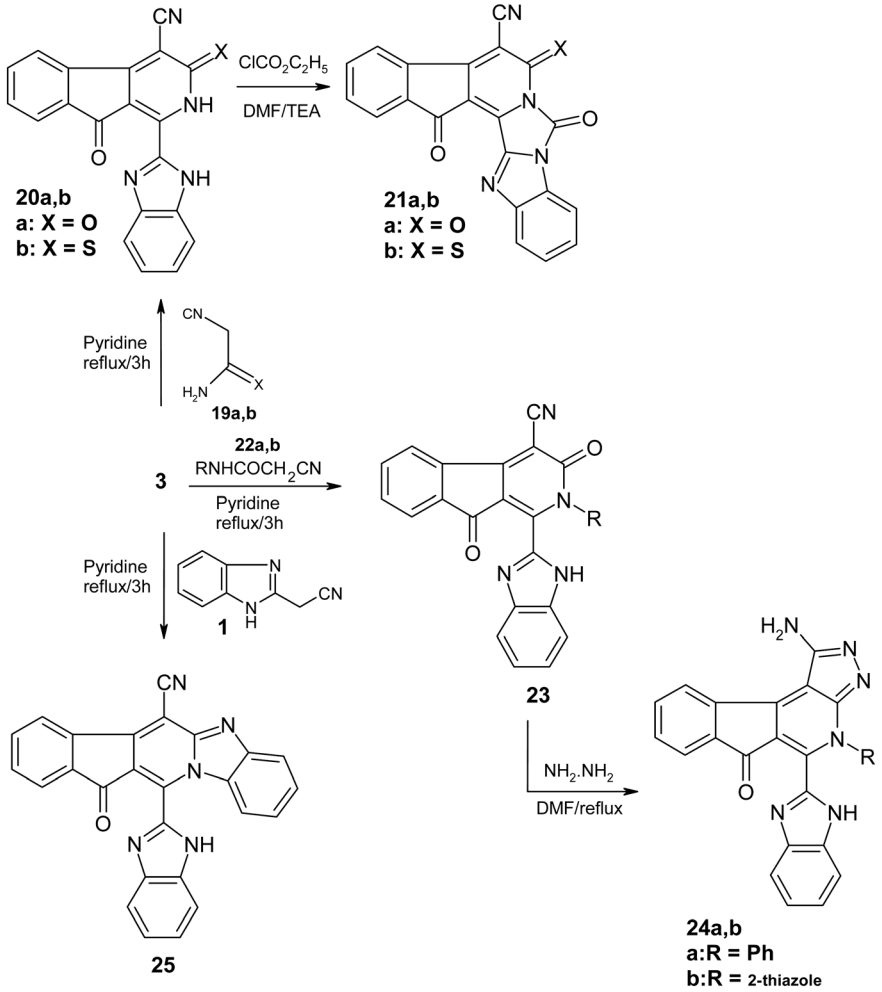
EXPERIMENTAL

All melting points are measured using Galenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Micro analytical Center of Cairo University. IR (KBr pellets $\upsilon = cm^{-1}$) spectra were determined in 1650 FTIR instrument (Cairo University). ^1H NMR and ^{13}C NMR spectra (δ = ppm) (DMSO-*d*) were accomplished using 300 MHz NMR spectrometer and mass spectroscopy were recorded on GCMS-QP-1000 EX spectrometer (Cairo University).

Preparation of 2-cyano-2-(1,3-dioxo-2-indenylidene) benzimidazole (3). A mixture of 1,2,3-indan-trione monohydrate **2** (0.18 g, 0.001 mol) and 2-cyanomethylbenzimidazole **1** (0.16 g, 0.001 mol) in 40 mL of ethanol was refluxed for 20 min. A red crystalline product that was formed, filtered, washed with ethanol, and recrystallized from dimethylformamide.

Yield: 0.25 g (83%). mp 295–97°C. IR: υ 1680 (CO), 1724 (CO), 2220 (CN). ^1H NMR: δ 7.1–7.9 (*m*, 8H, Ar-H+NH). ^{13}C NMR: 95.3 (*C*—CN), 115.2 (CN), 121.1, 124.4, 125.8, 130.1

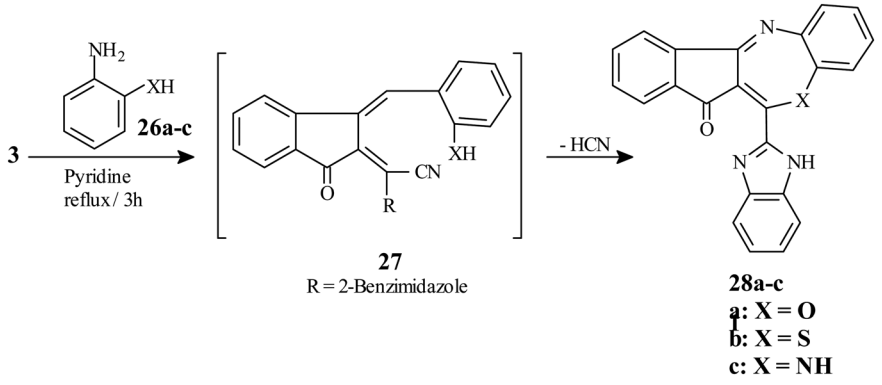
Scheme 4



(Ph), 122.5, 126.9, 128.7, 132.6 (Ph), 140.1 (C-2-inden), 142.2 (C-2-benzimid.), 165.1 (CO), 167.5 (CO). Ms: *m/z* 299 (M^+, 100%). *Anal*. Calcd for $C_{18}H_9N_3O_2$ (299.29): C 72.24, H 3.03, N 14.04. Found: C 72.35, H 3.11, N 14.17.

Preparation of 3-(1*H*-benzimidazol-2-yl)-2*H*-indeno[3,2-*c*] pyrazole-4-one (6). A mixture of **1** (0.8 g, 0.003 mol) and 40 mL of ethanol was warmed for 5 min, then 0.1 mL (excess) of hydrazine hydrate was added whereupon the suspension was

Scheme 5



turned to a clear yellow solution and was refluxed for 1 h. A yellow crystalline product that precipitated during the reflux was filtered, washed with ethanol, and recrystallized from dioxane.

Yield: 0.6 g (78%). mp 320–22°C. IR: υ 1690 (CO), 3135 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 8H, Ar-H), 9.2 (*s*, 1H, NH), 9.3 (*s*, 1H, NH). ^{13}C NMR: 121.1, 124.4, 125.8, 130.1 (Ph), 121.5, 124.9, 126.7, 131.6 (Ph), 167.5 (CO). MS: *m/z* 286 (M^+, 100%). *Anal*. Calcd for $C_{17}H_{10}N_4O$ (286.28): C 71.32, H 3.52, N 19.57. Found: C 71.46, H 3.67, N 19.79.

Preparation of 2-acetyl-3-(1-acetyl-benzimidazole-2-yl) indeno[1,2-*c*]pyrazol-4(2*H*)-one (7). A mixture of **6** (0.8 g, 0.003 mol) and 20 mL of acetic anhydride was refluxed for 1 h, the acetic anhydride was evaporated under vacuum. The residue was washed thoroughly with cold water several times (25 mL each), and was extracted with hot 10 mL methanol three times. The combination of the methanol was concentrated whereupon a colorless product was isolated, filtered, washed with ethanol, and recrystallized from dioxane.

Yield: 0.5 g (50%). mp 283–84°C. IR: υ 1693, 1715 (CO). ^{1}H NMR: δ 2.1 (s, 6H, 2 CH_3), 7.1–7.9 (*m*, 8H, Ar-H). MS: *m/z* 370 (M^+, 35%). *Anal*. Calcd for $C_{21}H_{14}N_4O_3$ (370.37): C 68.81, H 3.81, N 15.13. Found: C 68.98, H 3.90, N 15.40.

Preparation of benzimidazo[1″,2″:5′,1′]imidazo[4′,3′:1,5] pyrazolo[4,3-*b*]- indene-3,12-dione (9). A mixture of **6** (0.8 g, 0.003 mol) and ethyl chloroformate **8** (0.33 g, 0.003 mol) was refluxed for 3 h in 20 mL of dioxane in the presence of 0.1 mL of triethylamine. The mixture was evaporated under vacuum, and the residue was triturated with 15 mL cold methanol, forming a colorless product, which was filtered, washed with methanol, and crystallized from ethanol.

Yield: 0.72 g (82%). m.p. 265–67°C. IR: υ 1693, 1695, (CO). ^{1}H NMR: δ 7.1–7.9 (*m*, 8H, Ar-H). MS: *m/z* 312 (M^+, 100%). *Anal*. Calcd for $C_{18}H_8N_4O_2$ (312.29): C 69.23, H 2.58, N 17.94. Found: C 69.35, H 2.73, N 18.11.

General procedure for preparation of 4-methylbenzimidazo [1″,2″:1′,2′]-pyrazino[3′,4′:1,5]pyrazolo[4,3-*b*]indene-12-one (11a) and its derivatives (11b,c). A mixture of **6** (0.8 g, 0.003 mol) and bromoacetone **10a** (0.41 g ,0.003 mol) was refluxed for 4 h. in 20 mL of dioxane in the presence of triethylamine (0.1 mL). A colorless crystalline product was isolated during reflux, filtered, washed with dioxane, and recrystallized from DMF. In analogy, equimolar amounts of compound **6** and 2-bromo-acetophenone **10b** (0.59 g), and 3-(bromoacetyl)coumarin **10c** (0.8 g) reacted under the same reaction conditions affording **11b** and **11c**, respectively.

Compound 11a. Yield: 0.65 g (72%). mp 310–12°C. IR: υ 1693 (CO). ^{1}H NMR: δ 2.2 (*s*, 3H, CH_3),7.2 (*s*, 1H, pyrazine-H), 7.1–7.9 (*m*, 8H, Ar-H). MS: *m/z* 324 (M^+, 75%). *Anal.* Calcd for $C_{20}H_{12}N_4O$ (324.34): C 74.06, H 3.73, N 17.27. Found: C 74.21, H 3.89, N 17.41.

Compound 11b. Yield: 0.8 g (74%). mp 280–81°C. IR: υ 1695 (CO). ^{1}H NMR: δ 7.1–7.9 (*m*, 14H, Ar-H). MS: *m/z* 386 (M^+, 85%). *Anal*. Calcd for $C_{25}H_{14}N_4O$ (386.41): C 77.71, H 3.65, N 14.50. Found: C 77.84, H 3.78, N 14.65.

Compound 11c. Yield: 0.65 g (50%). mp 340–42°C. IR: υ 1698, 1705 (CO). ^{1}H NMR: δ 7.1–7.9 (*m*, 14H, Ar-H). MS: *m/z* 454 (M^+, 77%). *Anal*. Calcd for $C_{28}H_{14}N_4O_3$ (454.43): C 74.01, H 3.10, N 12.33. Found: C 74.12, H 3.26, N 12.48.

General procedure for the reaction with amino compounds. A mixture of **6** (0.4 g, 0.004 mol) and 5-amino-1,2,4–1*H*-triazole **12** (0.28 g, 0.004 mol) was refluxed for 3 h in 10 mL of pyridine. The pyridine solution was evaporated under vacuum, and the residue was washed with methanol producing a brownish powder, which was isolated by filtration, washed, and crystallized from DMF furnishing compound **13**. Accordingly, equimolar amounts of compound **6** reacted with 0.22 g of 2-aminobenzimidazole **14** and 0.26 g of 5-amino-3-methylsulfanyl-1*H*-pyrazole-4-carbonitrile **16** under the same reaction conditions affording **15** and **1**7, respectively.

10-(1H-Benzimdazole-2-yl)indeno[1,2:4,5]pyrimido[1,2-b] [1,2,4] triazole-9-one (13). Yield: 0.3 g (65%), mp 265–67°C. IR: υ 1698 (CO), 3214 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 8H, Ar-H), 8.1 (*s*, 1H, triazole-*H*), 9.6 (*s*, 1H, NH). MS: *m/z* 337 (M^+, 55%). *Anal*. Calcd for $C_{19}H_9N_6O$ (337.32): C 67.65, H 2.69, N 24.9. Found: C 67.78, H 2.80, N 25.1.

12-(1H-Benzimidazole-2-yl)indeno[1,2:4,5]pyrimido[1,2-a] benz-imidazole-11-one (15). Yield: 0.16 g (62%), mp 285–87°C, pale yellow (DMF). IR: υ 1695 (CO), 3222 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 12H, Ar-H), 9.2 (*s*, 1H, NH). MS: *m/z* 387 (M^+, 75%). *Anal*. Calcd for $C_{24}H_{13}N_5O$ (387.40): C 74.41, H 3.38, N 18.08. Found: C 74.56, H 3.49, N 18.15.

4-(1H-Benzimdazole-2-yl)-1-methylsulfanyl-5-oxo-indeno [1,2:4,5] pyrimido-[1,2-b]pyrazole-11-carbonitrile (17). Yield: 0.16 g (62%), mp 280°C, pale yellow (DMF). IR: υ 1692 (CO), 2225 (CN), 3222 (NH). ^{1}H NMR: δ 3.4 (s, 3H, SCH_3), 7.1–7.9 (*m*, 8H, Ar-H), 9.6 (*s*, 1H, NH). MS: *m/z* 408 (M^+, 100%). *Anal.* Calcd for $C_{22}H_{12}N_6OS$ (408.44): C 64.69, H 2.96, N 20.57, S 7.85. Found: C 64.81, H 3.11, N 20.69, S 7.94.

3-Amino-10-(1H-benzimdazole-2-yl)indeno[1,2:4,5]pyrimido [1,2: 5,1]- pyrazolo[3,4-c]pyrazol-11-one (18).. A mixture of **10** (0.5 g, 0.0013 mol) and hydrazine hydrate 0.1 g, (excess) was refluxed for 2 h in 10 mL of DMF in the presence of few drops of triethylamine. The solution was evaporated under vacuum, and the residue was washed with methanol resulting in a pale yellow powder that was isolated by filtration, washed, and crystallized from DMF.

Yield: 0.3 g (64%), mp 188–90°C. IR: υ 1699 (CO), 3222 (NH), 3326 (NH_2). ^{1}H NMR: δ 6.4 (*s*, 2H, NH_2), 7.1–7.9 (*m*, 9H, Ar-H + NH), 8.6 (*s*, 1H, NH). MS: *m/z* 390 (M^+, 80%). *Anal*. Calcd for $C_{21}H_{12}N_8O$ (392.38): C 64.28, H 3.08, N 28.56. Found: C 64.43, H 3.25, N 28.72.

Reaction of compound 3 with the active methylene compounds: Preparation of 9-(1*H*-benzimd-azole-2-yl)-1,2(*H*)-oxo-pyrido [2,1-*c*]indene-3-carbonitrile (20a) and its 2-thioxo derivative (20b). A mixture of **3** (0.5 g, 0.002 mol) and cyanoacetamide **19a** (0.14 g, 0.002 mol) was refluxed for 3 h in 10 mL of pyridine. The solution was evaporated under vacuum, and the residue was washed with acidified cold water several times, and triturated with methanol producing a pale brown powder that was isolated by filtration, washed, and crystallized from DMF. Similarly, compound **3** reacted with 0.17 g of cyanothioacetamide **19b** (0.002 mol) under the same reaction conditions affording thioxopyridine **20b**.

Compound 20a. Yield: 0.35 g (61%), mp 280–81°C. IR: υ 1685, 1692 (CO), 2220 (CN), 3223, 3225 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 9H, Ar-H + NH), 9.3 (*s*, 1H, NH). MS: *m/z* 338 (M^+, 100%). *Anal*. Calcd for $C_{20}H_{10}N_4O_2$ (338.33): C 71.00, H 2.98, N 16.56. Found: C 71.14, H 3.13, N 16.69.

Compound 20b. Yield: 0.45 g (75%), mp 292°C, brownish yellow (DMF). IR: υ 1320 (CS), 1695 (CO), 2220 (CN), 3154, 3227 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 9H, Ar-H + NH), 8.7 (*s*, 1H, NH). MS: *m/z* 354 (M^+, 87%). *Anal*. Calcd for $C_{20}H_{10}N_4OS$ (354.39): C 67.78, H 2.84, N 15.81, S 9.05. Found: C 67.91, H 3.1, N 15.96, S 9.16.

General method for the reaction of 20a,b with ethyl chloroformate. An equivalent amounts of **20a** (0.5 g, 0.0015 mol) and ethyl chloroformate (**8**) (0.16 g, 0.0015 mol) were refluxed for 2 h in 10 mL of DMF in the presence of few drops of triethylamine. The solution was evaporated under vacuum, and the residue was triturated with methanol resulting in a yellowish powder (**21a**). The yellowish powder was isolated by filtration, washed, and crystallized from DMF. Similarly, of compound **20b** (0.5 g) reacted with ethyl chloroformate (**8**) (0.15 g, 0.0015 mol) under the same reaction conditions affording the thioxo derivative **21b**.

2,4,12-Trioxo-benzimidazo[1″,2″:5′,1′]imidazo[4′,3′:1,2]pyrido [3,4-b]-indene-1-carbonitrile (21a). Yield: 0.45 g (83%), mp 223–25°C. IR: υ 1682, 1685, 1692 (CO), 2221(CN). ^{1}H NMR: δ 7.1–7.9 (*m*, 8H, Ar-H). MS: *m/z* 470 (M+2, 100), 468 (M^+, 65%). *Anal*. Calcd for $C_{21}H_8N_4O_3$ (364.32): C 69.23, H 2.21, N 15.38. Found: C 69.41, H 2.36, N 15.55.

Compound 21b. Yield: 0.48 g (86%), mp 275–77°C. IR: υ 1315 (CS), 1688, 1694 (CO), 2221(CN). ^{1}H NMR: δ 7.1–7.9 (*m*, 8H, Ar-H). MS: *m/z* 380 (M^+, 100%). *Anal*. Calcd for $C_{21}H_8N_4O_2S$ (380.38): C 66.31, H 2.12, N 14.73, S 8.43. Found: C 66.48, H 2.38, N 14.90, S 8.59.

General procedure for preparation of 9-(1*H*-benzimdazole-2-yl)-1,2(*H*)-2-oxo-indeno[2,1-*c*]-1-phenyl-pyridine-3-carbonitrile (23a) and its 1-thiazolyle derivative (23b). An equivalent amounts of **3** (0.6 g, 0.002 mol) and of cyanoacetanilide **22a** (0.32 g, 0.002 mol) were refluxed for 3 h in 10 mL of pyridine solution. The solution was evaporated under vacuum, the residue was washed thoroughly with acidified cold water, and triturated with methanol, producing a brownish powder. The brownish powder was isolated by filtration, washed, and crystallized from DMF. Under same reaction conditions, the thiazolyl derivative **22b** was prepared.

Compound 23a. Yield 0.54g (77%), mp 320–22°C. IR: υ 1690, 1694 (CO), 2225 (CN), 3134 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 14H, Ar-H+NH). MS: *m/z* 414 (M^+, 100%). *Anal.* Calcd for $C_{26}H_{14}N_4O_2$ (414.42): C 75.35, H 3.40, N 13.52. Found: C 75.52, H 3.56, N 13.69.

Compound 23b. Yield 0.5g (71%), mp 340–42°C, green (DMF). IR: υ 1320 (CS), 1695, 1715 (CO), 2222 (CN), 3134 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 14H, Ar-H+NH). MS: *m/z* 421 (M^+, 94%). *Anal*. Calcd for $C_{23}H_{11}N_5O_2S$ (421.44): C 65.55, H 2.63, N 16.62, S 7.61. Found: C 65.72, H 2.80, N 16.80, S 7.77.

Reaction of 23a,b with hydrazine hydrate: Preparation of 1-amino-5(1H-benzimidazole-2-yl)-4(*N*)-phenyl-indeno [2,3:3,4] pyrido[6,5-*c*]pyrazole-6-one 24a and its 2-thiazolyl derivative 24b. An equivalent amounts of **23a** and hydrazine hydrate 0.1 g (excess) were refluxed for 2 h in 15 mL of DMF. The solution was evaporated under vacuum, the residue was triturated with methanol producing a yellow powder of **24a**, which was isolated by filtration, washed, and crystallized from DMF. Similarly, compound **23b** reacted with hydrazine hydrate under the same reaction conditions.

Compound 24a. Yield: 0.4 g (75%), mp. 215–17 ^{0}C. IR: ν 1693 (CO), 3115 (NH), 3355 (NH_2). ^{1}H NMR: δ 6.3 (*s*, 2H, NH_2), 7.1–7.9 (*m*, 14 H, Ar-H + NH). MS: *m/z* 428 (M^+, 67%). *Anal*. Calcd. for $C_{26}H_{16}N_6O$ (428.46): C 72.89, H 3.76, N 19.61. Found: C 73.08, H 3.81, N 19.83.

Compound 24b. Yield: 0.35 g (66%), mp. 246–66 ^{0}C. IR: ν 1696 (CO), 3117 (NH), 3345 (NH_2). ^{1}H NMR: δ 6.4 (*s*, 2H, NH_2), 6.8 (*d*, 2H, thiazole), 7.1–7.9 (*m*, 14 H, Ar-H + NH). MS: *m/z* 435 (M^+, 75%). *Anal*. Calcd. for $C_{23}H_{13}N_7OS$ (435.47): C 63.43, H 3.01, N 22.52, S 7.37. Found: C 63.62, H 3.15, N 22.67, S 7.52.

12-(1-H-Benzimidazole-2-yl)-11-oxo-benzimidazo[1′,2′:1,2]pyrido [4,5-b]-indene-6-carbonitrile (25). An equivalent amounts of **3** (0.5 g, 0.002 mol) and 2-cyanomethylbenz-imidazole (**1**) (0.26 g, 0.002 mol) were refluxed for 3 h in 15 mL of pyridine. The solution was evaporated under vacuum, the residue was washed several time with acidified cold water, and triturated with 20 mL hot methanol producing a brown powder ultimately isolated by filtration, washed, and crystallized from DMF.

Yield: 0.4 g (58%), m.p. 320–22°C. IR: υ 1690 (CO), 2223 (CN), 3115 (NH). ^{1}H NMR : δ 7.1–7.9 (*m*, 13H, Ar-H + NH). MS: *m/z* 411 (M^+, 72%). *Anal*. Calcd for $C_{26}H_{13}N_5O$ (411.42): C 75.90, H 3.18, N 17.20. Found: C 76.07, H 3.37, N 17.37.

General procedure for preparation of 6-(1H-benzimidazole-2-yl)indeno-[1,2-*b*][1,5]-benzoxazepine-7-one (28a) and its derivatives (28b and 28c). An equivalent amounts of **3** (0.5 g, 0.002 mol) and of 2-aminophenol **26a** (0.18 g, 0.002 mol) were refluxed for 3 h in 15 mL of pyridine. The solution was evaporated under vacuum, and the residue was washed several times with acidified cold water, and triturated with methanol producing a brown powder (**28a**). In due course, the brown powder was isolated by filtration from the hot solution and found insoluble in most organic solvents.

Each of 2-aminothiophenol **26b** (0.2 g) and 2-phenylenediamine **26c** (0.18 g) reacted similarly with compound **3** to yield the corresponding 1,5-benzothiazepine **28b** and 1,5-benzodiazepine **28c**, respectively.

Compound 28a. Yield: 0.4 g (67%), mp 340–42°C. IR: υ 1672 (CO), 3215 (NH). MS: *m/z* 363 (M^+, 78%). *Anal*. Calcd for $C_{23}H_{13}N_3O_2$ (363.37): C 76.02, H 3.60, N 11.56. Found: C 76.18, H 3.76, N 11.73.

Compound 28b. Yield: 0.5 g (83%), mp 352–45°C. IR: υ 1680 (CO), 3222 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 13H, Ar-H + NH). MS: *m/z* 379 (M^+, 100%). *Anal*. Calcd for $C_{23}H_{13}N_3OS$ (379.44): C 72.80, H 3.45, N 11.07, S 8.45. Found: C 72.97, H 3.67, N 11.23, S 8. 63.

Compound 28c. Yield: 0.38 g (63%), mp 330–32°C. IR: υ 1685 (CO), 3215, 3213 (NH). ^{1}H NMR: δ 7.1–7.9 (*m*, 14H, Ar-H + NH). MS: *m/z* 362 (M^+, 100%). *Anal*. Calcd for $C_{23}H_{14}N_4O$ (362.39): C 76.28, H 3.89, N 15.46. Found: C76.42, H 4.08, N 15.63.

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