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Full Paper

Synthesis of Novel Benzimidazolyl-substituted Acrylonitriles and Amidino-substituted Benzimidazo[1,2-*a*]Quinolines

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Abstract: A series of novel benzimidazole derivatives **3-10** were synthesized. Benzimidazolyl-substituted acrylonitriles **3** and **4** underwent a photochemical dehydro-cyclization reaction to give the corresponding mono- and dicyano-substituted benzimidazo[1,2-*a*] quinolines **5** and **6**. Pinner reaction of these compounds did not give the expected mono- and diamidines, but rather only compounds **7-10**, with amido groups at 6-position were isolated. A mechanism for the reaction is proposed. Acyclic compounds **3** and **4**, as well as cyclic benzimidazo[1,2-*a*]quinolines **5-8**, exhibit interesting spectroscopic properties and are potential biologically active compounds.

Keywords: Benzimidazoles, acrylonitriles, amidines, benzimidazo[1,2-*a*]quinolines, Pinner reaction.

Introduction

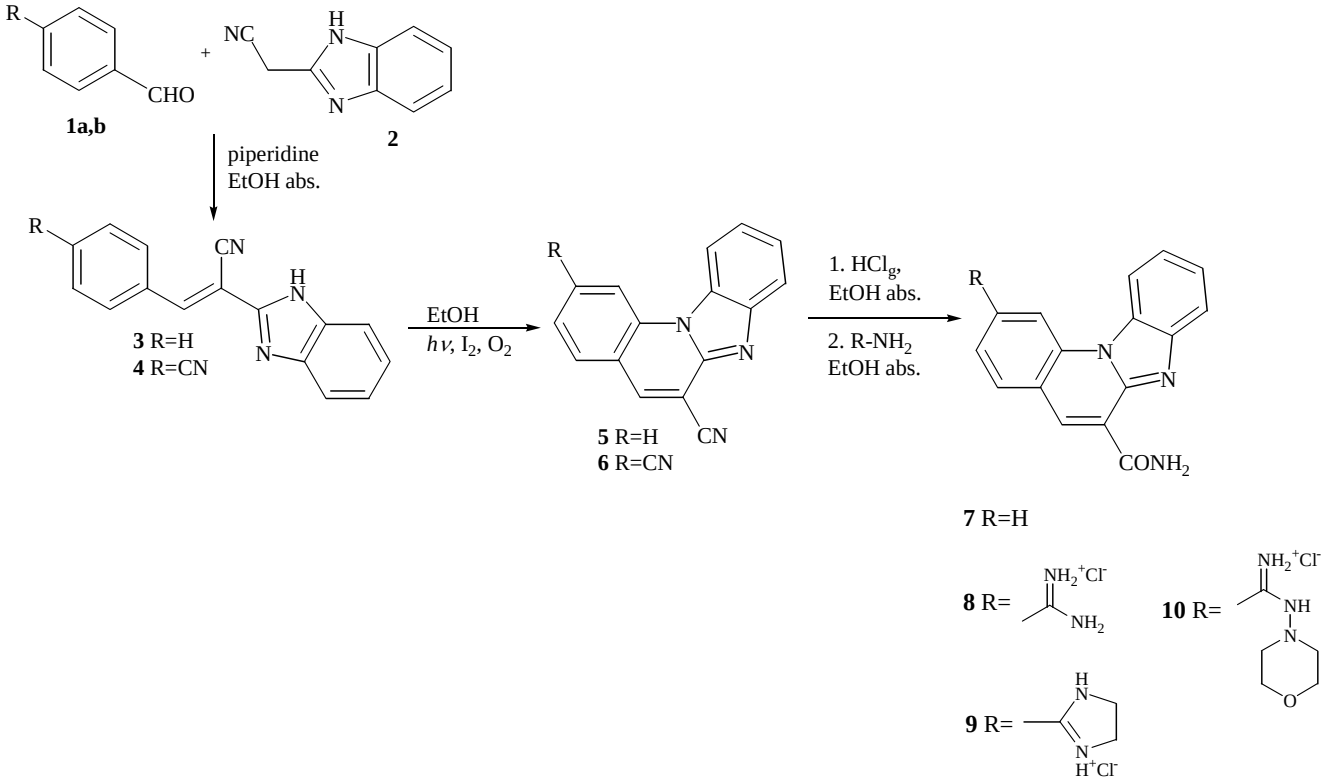
Over the past years substituted benzimidazoles and their azino fused derivatives have been one of the most extensively studied classes of heterocyclic compounds, receiving much attention from synthetic organic chemists because of their applications in several areas such as optical laser and polymer dyes, fluorescent tags in DNA sequencing, cosmetic ingredients, etc. [1-2]. Benzimidazoles

also posses broad spectrum of biological properties such as antiviral (anti-HIV), anticancer, antibacterial, antifungal and many others [3-13]. Benzoannulated benzimidazole analogues such as benzimidazo[1,2-*a*]quinolines or benzimidazo[1,2-*a*]quinazolines, due to their planar chromophore, have the ability to undergo an intercalation process and thus become inserted between adjacent base pairs of a DNA molecule [14-15], or have potential applications as fluorescent probes in homogeneous assays of biological molecules, as well as in optoelectronics [16]. A positive charge is generally needed for activity and it can be provided by quaternization of nitrogen atom or by introduction of substituents containing such a positive charge, such as an amidino group. Amidines, the nitrogen analogues of carboxylic acids, are structural components of numerous compounds of biological interest, including important medical and biochemical agents [17-19]. Herein we present the synthesis and preliminary spectroscopic properties of some novel potentially biologically active acyclic and cyclic benzimidazole derivatives.

Results and Discussion

As part of our medicinal chemistry project aimed at the synthesis of potential biologically active compounds, we synthesized acyclic benzimidazolyl-substituted acrylonitriles **3-4**, as well as their cyclic derivatives, benzimidazo[1,2-*a*]quinolines **5-10** (Scheme 1).

Scheme 1.



Acyclic compounds **3** and **4** were prepared by condensation of the corresponding benzaldehydes **1a,b** and benzimidazole-2-acetonitrile **2** (prepared by a previously described method [20]), in absolute EtOH using piperidine as a catalyst [21-22].

In the photochemical dehydrocyclization reaction of **3** and **4** (ethanolic solution, $c = 1.3 \times 10^{-3}$ mol dm^{-3}) cyclic bezimidazo[1,2-*a*]quinolines **5** and **6** were prepared [23]. Irradiation was performed for about 12-15 h with a 400-W high-pressure mercury lamp using a Pyrex filter under oxidative conditions, with a small amount of iodine as a catalyst. The photochemical dehydrocyclization reaction was followed by UV/Vis spectroscopy. Cyclic derivatives were obtained in good yields (40-50%). In the ^{1}H-NMR spectra of both cyclic compounds it was noted that the cyclization reactions lead to a downfield shift of the signal of the ethylenic proton and most other protons. The proton of the NH group of the benzimidazole ring, as well as one proton of the phenyl ring disappeared, which also confirmed the cyclic nature of the products. In the ^{1}H-NMR spectra of acyclic compound **4** two doublets at 8.11 and 8.04 ppm, corresponding to four phenyl protons, were observed, while in the spectra of compound **6**, due to the cyclization reaction, two doublets and one singlet for three phenyl protons were observed.

Compound **5** had been previously prepared by classic thermal cyclization [24]. In the Pinner reaction [25-26], carried out under acidic conditions and using absolute EtOH as well as carbitol as solvents, compounds **7**-**10** were prepared. The formation of the imino-ester was confirmed by the disappearance of a nitrile band at ~2200 cm^{-1} in the IR spectrum. Attempts to prepare monoamidino- (amidino group at position 6) or diamidino (amidino groups at positions 2 and 6)-substituted benzimidazo[1,2-*a*]quinolines were not successful. Instead of the desired 6-amidino-benzimidazo[1,2-*a*]quinolines, the benzimidazo[1,2-*a*]quinoline-6-carboxamide **7** was unexpectedly isolated [27]. After isolation and identification of the crude imino-ester by NMR and MS, we confirmed that the amido group at the 6-position is formed immediately in the first phase of Pinner reaction. In ^{1}H-NMR spectra of compound **7** two novel singlets can be observed for the amide protons. From the Pinner reaction of dicyano-substituted benzimidazo[1,2-*a*]quinoline **6** only 2-amidino-substituted-benzimidazo[1,2-*a*]-quinoline-6-carboxamides **8**-**10** were isolated. Their structures were confirmed by their NMR and MS spectra. In the ^{1}H-NMR spectrum, singlets for amidine protons can be observed in the 11.63 - 9.60 ppm region. The presence of the corresponding amidine group in compounds **8**, **9** and **10** lead to downfield shifts of most proton signals. In the IR spectrum of amidino compounds **8**, **9** and **10**, bands in the ~3500 cm^{-1} region can be observed.

It appears that the cyano groups at position **2** and **6** reacted quite differently under the "Pinner" conditions used. The cyano group at the 2-position of the cyclic benzimidazo[1,2-*a*]quinoline **6** gave in the first phase an imino-ester, while in the second phase, after reaction with corresponding amine, an amidino-substituted group is obtained. The cyano groups at the 6-position of the cyclic benzimidazo[1,2-*a*]quinolines **5** and **6** gave, in the second phase of the Pinner reaction, an unsubstituted amido group instead of corresponding amidine. The amido group at the 6-position is also formed immediately in the first phase of Pinner reaction. The proposed mechanism of the above-mentioned reaction is presented in Scheme 2. The intermediate protonated imino-ester, formed at the 6-position, underwent an S_N-transformation by ethanol giving an amide.

In order to study the spectroscopic properties of substitued benzimidazo[1,2-*a*]quinolines **5-8** and their acyclic precursors **3-4**, a preliminary investigation of their UV/Vis, fluorescence emission and excitation spectra, recorded in EtOH, was undertaken. The results are shown in Figures 1-2 and summarized in Table 1.

Scheme 2.

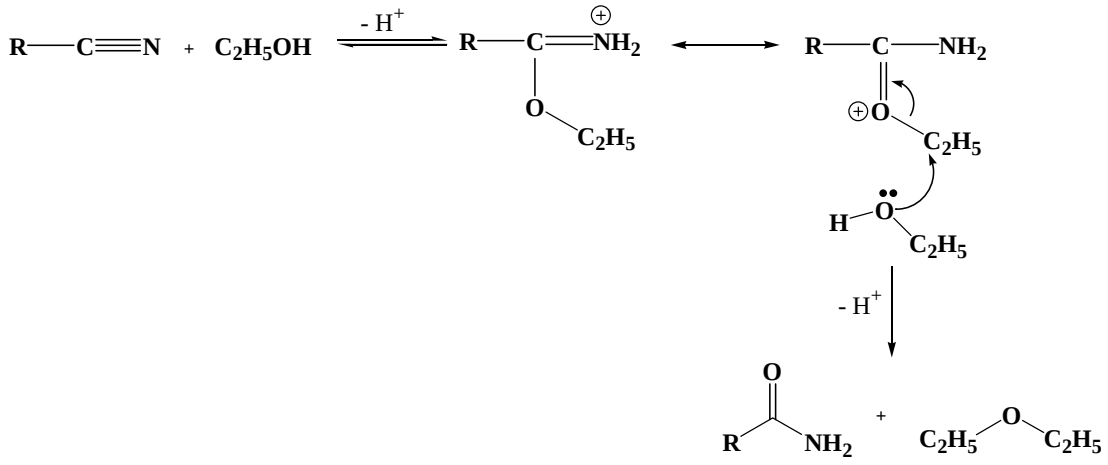


Table 1. Electronic absorption and fluorescence data of compounds **3-8** in EtOH.

Comp.	λ_{max}/nm	ε x 10^3 ($dm^3mol^{-1}cm^{-1}$)	λ_{emiss}/nm	λ_{exc}/nm	Int (arb. un.)
3	355 280	21.7 8.4	445	352 280	28.6
4	371 278	17.6 12.1	490	367 274	570.0
5	387 351 270	6.4 9.9 35.5	469	350 268 245	864.5
6	370 276	7.9 32.5	507	370 274 247	126.3
7	375 344 267	7.8 4.6 28.9	467	345 268 240	469.5
8	374 276	8.1 35.2	507	368 272 249	121.1

Acyclic compound **3** showed an absorption maximum at 355 nm, while dicyano-substituted acyclic compound **4** showed it at 371 nm (batochromic effect). At 280 and 278 nm both compounds showed another absorption band. Cyclic compounds **5-8**, as it can be visualized in Figure 1, showed several absorption bands. Di-substituted benzimidazo[1,2-*a*]quinolines **6** and **8** showed one absorption band in

370 and 374 nm, while mono-substituted benzimidazo[1,2-*a*]quinolines **5** and **7** showed two absorption bands from 344 nm to 387 nm.

Figure 1. UV/Vis absorption spectra of compounds **3-8** in EtOH ($c = 2\times10^{-5}$ mol dm^{-3}).

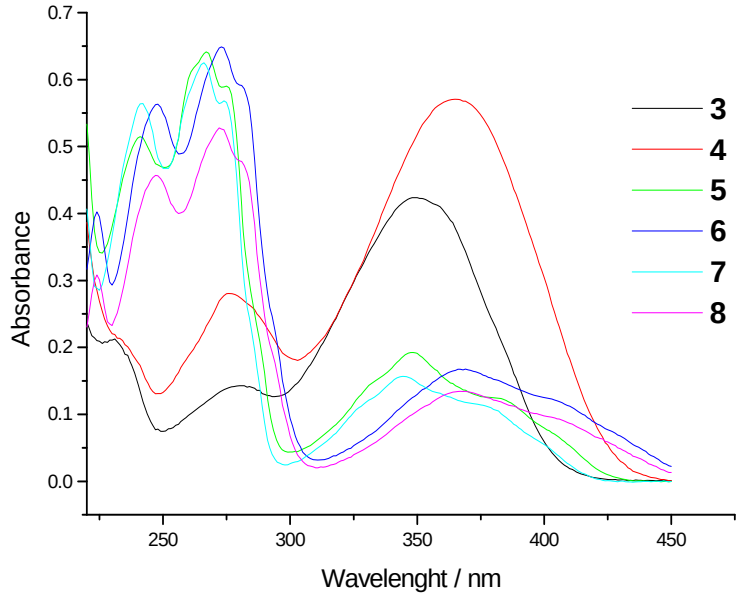
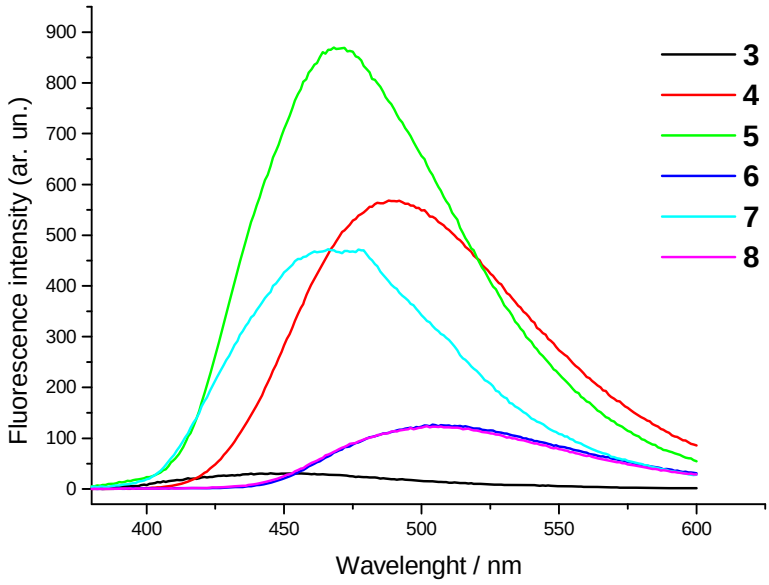


Figure 2. Fluorescence emission spectra of compounds **3-8** in EtOH, excited at $\lambda_{abs.max}$ according to data given in Table 1 ($c = 6.7\times10^{-7}$ mol dm^{-3}).



All the studied compounds showed a single emission band. Acyclic compound **3** exhibited very low fluorescence intensity, while compound **4** exhibited much higher fluorescence intensity and showed a bathochromic shift. Cyclic compound **5** exhibited 30 times higher fluorescence intensity than its acyclic precursor **3**. Interestingly, dicyano-substituted benzimidazo[1,2-*a*]quinoline **6** exhibited ~4.5

times lower fluorescence intensity than its acyclic precursor **4**. Compound **6** also exhibited ~7 times lower fluorescence intensity than the monocyano-substituted benzimidazo[1,2-*a*]quinoline **5**. As it can be visualized from Figure 2, benzimidazo[1,2-*a*]quinoline-6-carboxamide **7** exhibited ~2 times lower fluorescence intensity than 6-cyano-benzimidazo[1,2-*a*]quinoline **5.** The fluorescence intensity of 2-carboxamidine-benzimidazo[1,2-*a*]quinoline-6-carboxamide hydrochloride (**8**) is similar to that of compound **6**. Excitation spectra of all studied compounds are in good agreement with their absorption spectra.

Conclusions

We have prepared benzimidazolyl substituted acrylonitriles **3-4**, which were converted into corresponding benzimidazo[1,2-*a*]quinolines **5-6** by a photochemical dehydrocyclization reaction. From the Pinner reaction of compounds **5** and **6** we did not obtain the desired mono- and diamidino-substituted benzimidazo[1,2-*a*]quinolines. The cyano group at the 6-position of both cyclic compounds **5** and **6** gave an unsubstituted amido group, instead of an amidine group. An amido group was formed in the first phase of the Pinner reactions. All the prepared compounds, especially the cyclic benzimidazo[1,2-*a*]quinolines **5-8**, are potential biologically active compounds and may be expected to be DNA intercalators, which will be investigated during the course of our ongoing work in this area.

Acknowledgements

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Experimental

General

Melting points were determinated on a Koffler hot stage microscope and are uncorrected. IR spectra were recorded on Perkin-Elmer 297 spectrophotometer with KBr disks. ^{1}H- and ^{13}C-NMR spectra were recorded in DMSO-d_6 on a Varian Gemini 300 or Bruker Avance DPX 300 spectrometers using TMS as an internal standard. Mass spectra were recorded on an Agilent 1100 series LC/MSD Trap SL. Elemental analysis for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer, Series II, CHNS Analyzer 2400. Where analyses are indicated only as symbols of elements, analytical results obtained are within 0.4% of the theoretical values. All compounds were routinely checked by TLC with Merck silica gel 60F-254 glass plates. The electronic absorption spectra were obtained on Varian Cary 100 spectrometer and fluorescence emission spectra were recorded on Varian Eclipse fluorimeter, in both cases using quartz cuvettes (1 cm).

General method for preparation of **3** *and* **4**.

A solution of equimolar amounts of corresponding benzaldehydes **1a**,**b** and benzimidazole-2-acetonitrile **2** in absolute EtOH (15 mL) was refluxed in the presence of piperidine (0.03 mL) for 4 h. The dark yellow product which separated on cooling was filtered off, washed with petroleum ether and EtOH and recrystallized from EtOH to give the products.

2-(1H-benzimidazol-2-yl)-3-acrylonitrile (**3**)

Compound **3** was prepared as described above from benzaldehyde (1.35 g, 12.72 mmol) and benzimidazole-2-acetonitrile **2** (2.00 g, 12.72 mmol), to obtain after recrystallization from EtOH a yellow powder (2.52 g, yield 80%); mp = 217–218 °C; IR (KBr) υ/cm^{-1}: 3249, 2225, 1621, 1600; ^{1}H-NMR (δ/ppm): 13.20 (brs, 1H, $NH_{benzimidazole}$), 8.34 (s, 1H), 8.00 (d, 2H, *J* = 8.80Hz, $H_{arom.}$), 7-63-7.61 (m, 2H, $H_{arom.}$), 7.60 (d, 1H, *J* = 7.72Hz, $H_{arom.}$), 7.57 (d, 2H, *J* = 8.77Hz, $H_{arom.}$), 7.30-7.24 (m, 2H, $H_{arom.}$); ^{13}C-NMR (δ/ppm): 147.89 (s), 145.86 (d), 139.69 (s), 133.17 (s), 132.14 (d), 130.00 (d, 2C), 129.76 (d, 3C), 123.54 (d), 122.87 (s), 120.99 (d), 118.65 (d), 116.66 (s), 102.90 (s); MS *m/z* 246 (M^{+1}); Anal. Calc. for $C_{16}H_{11}N_3$: C 78.35%, H 4.52%, N 17.13%; found: C 78.13%, H 4.75%, N 17.29%.

2-(1H-benzimidazol-2-yl)-3-(4-cyanophenyl)-acrylonitrile (**4**)

Compound **4** was prepared from 4-cyanobenzaldehyde (1.60 g, 12.72 mmol) and benzimidazole-2-acetonitrile **2** (2.00 g, 12.72 mmol), using the described general method, to give, after recrystallization from EtOH, a yellow powder (2.60 g, yield 75%); mp = 290–291 °C; IR (KBr) υ/cm^{-1}: 3332, 2225, 2214, 1641, 1619; ^{1}H-NMR (δ/ppm): 13.32 (s, 1H, $NH_{benzimidazole}$), 8.40 (s, 1H), 8.11 (d, 2H, *J* = 8.64Hz, $H_{arom.}$), 8.04 (d, 2H, *J* = 8.52Hz, $H_{arom.}$), 7.68 (brs, 1H, $H_{arom.}$), 7.63 (d, 1H, *J* = 7.70Hz, $H_{arom.}$), 7.27 (brs, 2H, $H_{arom.}$); ^{13}C-NMR (δ/ppm): 147.28 (s), 147.27 (s), 143.68 (d), 137.44 (s), 133.48 (d, 2C), 130.42 (d, 2C), 118.79 (s), 124.55 (d), 123.18 (d), 119.20 (d), 118.79 (s), 116.07 (s), 113.58 (s), 112.09 (d), 105.99 (s); MS *m/z* 271 (M^{+1}); Anal. Calc. for $C_{17}H_{10}N_4$: C 75.54%, H 3.73%, N 20.73%; found: C 75.77%, H 3.98%, N 20.44%.

General method for preparation of **5** *and* **6**

A solution of 2-(1*H*-benzimidazol-2-yl)-3-acrylonitrile **3** or 2-(1*H*-benzimidazol-2-yl)-3-(4-cyano phenyl)acrylonitrile **4** and small amount of iodine (5%) in EtOH (c = 1.3 × 10^{-3} moldm^{-3}) was irradiated at room temperature with a 400-W high-pressure mercury lamp, using a Pyrex filter, for about 12-15 h, until the UV spectra shown that the dehydrocyclization reaction was finished. Air was bubbled through the solution, which was then concentrated under reduced pressure to give the product.

Benzimidazo[1,2-a]quinoline-6-carbonitrile (**5**)

Compound **5** was prepared using above described method from 2-(1*H*-benzoimidazol-2-yl)-3-acrylonitrile **3** (1.40 g, 5.71 mmol) after irradiation for 12 h, to give a yellow powder (0.67 g, yield 50%); mp = 256–258 °C (Lit [24] mp = 261 °C); IR (KBr) υ/cm^{-1}: 3056, 2225, 1608, 1572; ^{1}H-NMR (δ/ppm): 8.77 (d, 1H, *J* = 8.40Hz, $H_{arom.}$), 8.74 (s, 1H, $H_{quinoline}$), 8.66 (d, 1H, *J* = 8.10Hz, $H_{arom.}$), 8.06 (d, 1H, *J* = 7.68Hz, $H_{arom.}$), 7.95 (d, 1H, *J* = 8.00Hz, $H_{arom.}$), 7.93 (t, 1H, *J* = 8.10Hz, $H_{arom.}$), 7.59 (t, 1H, *J* = 7.44Hz, $H_{arom.}$), 7.55-7.51 (m, 2H, $H_{arom.}$); ^{13}C-NMR (δ/ppm): 144.44 (s), 143.74 (s), 140.67 (d), 135.80 (s), 133.65 (d), 131.21 (s), 125.19 (d), 123.64 (d), 121.20 (s), 120.26 (d), 115.97 (s), 115.38 (s), 114.86 (d); MS *m/z* 244 (M^{+1}); Anal. Calc. for $C_{16}H_9N_3$: C 79.00%, H 3.73%, N 17.27%; found: C 79.17%, H 3.89%, N 17.60%.

Benzimidazo[1,2-a]quinoline-2,6-dicarbonitrile (**6**)

Compound **6** was prepared using the above described method from 2-(1*H*-benzimidazol-2-yl)-3-(4-cyano phenyl)-acrylonitrile **4** (1.04 g, 3.86 mmol) to give after irradiation for 15 h a yellow powder (0.42 g, yield 40%); mp >295 °C; IR (KBr) υ/cm^{-1}: 3058, 2231, 2224, 1609, 1600; ^{1}H-NMR (δ/ppm): 8.99 (s, 1H), 8.75 (d, 1H, $H_{arom.}$, *J* = 8.34Hz), 8.73 (s, 1H, $H_{quinoline}$), 8.17 (d, 1H, *J*= 8.10Hz, $H_{arom.}$), 7.93 (d, 1H, *J* = 8.10Hz, $H_{arom.}$), 7.89 (d, 1H, *J* = 7.86Hz, $H_{arom.}$), 7.53-7.47 (m, 2H, $H_{arom.}$); ^{13}C-NMR (δ/ppm): 144.10 (s), 143.97 (s), 139.97 (d), 135.80 (s), 132.51 (d), 130.83 (s), 128.47(d), 126.03 (d), 124.82 (s), 124.78 (d), 120.85 (d), 119.96 (d), 118.44 (s), 115.74 (d), 115.35 (s), 115.28 (s), 104.62 (s); MS *m/z* 269 (M^{+1}); Anal. Calc. for $C_{17}H_8N_4$: C 76.11%, H 3.08%, N 20.88%; found: C 75.87%, H 3.10%, N 21.14%.

General method for preparation of benzimidazo[1,2-a]quinoline-6-carboxamide **7** *and 2-amidino-benzimidazo[1,2-a]quinoline-6-carboxamides* **8-10**

A stirred suspension of compounds **5** and **6** in absolute EtOH was cooled in an ice-salt bath and then saturated with HCl gas. The flask was then tightly stoppered and the mixture was maintained at room temperature for 20 days until the nitrile band disappeared (monitored by IR analysis at 2200 cm^{-1}). The reaction mixture was purged with N_2 gas and diluted with diethyl ether (50 mL). The crude imidate was filtered off and was immediately suspended in absolute EtOH (10 mL). The corresponding amine was added and the mixture was stirred for one to three days at room temperature. The crude product was then filtered off and washed with diethyl ether.

Benzimidazo[1,2-a]quinoline-6-carboxamide (**7**)

Compound **7** was obtained from **5** (0.20 g, 0.82 mmol) as the main product of the above described Pinner reaction, instead of the corresponding amidine, as a light yellow powder (0.07 g, yield 35%); mp >295 °C; IR (KBr) υ/cm^{-1}: 3180, 1719, 1644, 1621, 1571; ^{1}H-NMR (δ/ppm): 9.89 (brs, 1H), 8.91 (d, 1H, *J* = 8.49 Hz, $H_{arom.}$), 8.80 (s, 1$H_{quinoline}$), 8.77 (d, 1H, *J* = 8.30Hz, $H_{arom.}$), 8.30 (d, 1H, *J* = 7.80Hz, $H_{arom.}$), 8.19 (brs, 1H), 8.03 (d, 1H, *J* = 7.80Hz, $H_{arom.}$), 7.97 (d, 1H, *J* = 8.20Hz, $H_{arom.}$), 7.68-

7.55 (m, 2H, $H_{arom.}$); ^{13}C-NMR (δ/ppm): 163.86 (s), 146.46 (s), 143.21 (s), 136.03 (s), 135.93 (d), 132.96 (d), 132.13 (d), 130.56 (s), 125.63 (d), 125.54 (d), 123.93 (d), 122.28 (s), 120.68 (s), 120.24 (d), 116.23 (d), 115.42 (d); MS *m/z* 262 (M^{+1}); Anal. Calc. for $C_{16}H_{11}N_3O$: C 73.55%, H 4.24%, N 16.08%; found: C 73.81%, H 4.55%, N 16.14%.

2-Carboxamidine-benzimidazo[1,2-a]quinoline-6-carboxamide hydrochloride (**8**)

Compound **8** was prepared as a yellow powder (0.11 g, yield 43%) using above described Pinner method from **6** (0.20 g, 0.75 mmol) and NH_3 gas; mp >295 °C; IR (KBr) υ/cm^{-1}: 3480, 3220, 1715, 1655, 1627, 1589; ^{1}H-NMR (δ/ppm): 9.92 (s, 1H), 9.60 (brs, 4H, $H_{amidine}$), 9.14 (s, 1H), 8.89 (s, 1H), 8.77 (d, 1H, *J* = 7.60Hz), 8.56 (d, 1H, *J* = 8.65Hz), 8.20 (s, 1H), 8.11 (d, 1H, *J* = 7.65Hz), 8.03 (d, 1H, *J* = 8.60Hz), 7.72-7.65 (m, 2H); ^{13}C-NMR (δ/ppm): 164.01 (s), 162.11 (s), 146.26 (s), 144.23 (s), 136.33 (d), 136.02 (s), 132.99 (d), 131.01 (s), 129.68 (s), 127.02 (d), 125.89 (s), 125.67 (d), 124.12 (d), 122.56 (s), 120.51 (d), 118.76 (d), 116.28 (d); MS *m/z* 304 (M^{+1}); Anal. Calc. for $C_{17}H_{14}N_5OCl$: C 60.09%, H 4.15%, N 20.61%; found: C 60.24%, H 4.33%, N 20.88%.

2-(1H-imidazol-2-yl)-benzimidazo[1,2-a]quinoline-6-carboxamide Hydrochloride (**9**)

Compound **9** was prepared as a yellow powder (0.180 g, yield 66%) from **6** (0.20 g, 0.75 mmol) and ethylenediamine (0.121 mL, 1.80 mmol) using above described Pinner method; mp >295 °C; IR (KBr) υ/cm^{-1}: 3456, 3212, 1730, 1651, 1634, 1593; ^{1}H-NMR (δ/ppm): 11.29 (s, 2H, $H_{amidine}$), 9.78 (s, 1H), 9.09 (s, 1H), 9.06 (d, 1H, *J* = 7.45Hz), 8.87 (s, 1H), 8.44 (d, 1H, *J* = 8.40Hz), 8.37 (s, 1H), 8.20 (d, 1H, *J* = 8.37Hz), 8.06 (d, 1H, *J* = 7.50Hz), 7.71-7.64 (m, 2H), 4.11 (brs, 2H, CH_2), 3.09 (brs, 2H, CH_2); ^{13}C NMR (δ/ppm): 163.98 (s), 162.14 (s), 145.96 (s), 144.40 (s), 136.88 (s), 136.34 (d), 133.10 (d), 131.33 (s), 129.61 (s), 127.41 (d), 126.10 (s), 125.89 (d), 124.24 (d), 122.44 (s), 120.58 (d), 118.76 (d), 116.02 (d), 46.45 (t), 39.88 (t); MS *m/z* 330 (M^+); Anal. Calc. for $C_{19}H_{16}N_5OCl$: C 62.38%, H 4.41%, N19.14%; found: C 62.54%, H 4.26%, N 18.89%.

N-Morpholin-4-yl-benzimidazo[1,2-a]quinoline-6-carboxamide hydrochloride (**10**)

Compound **10** was prepared as a yellow powder (0.20 g, yield 63 %) from **6** (0.20 g, 0.75 mmol) and 4-aminomorpholine (0.360 mL, 1.80 mmol) using above described Pinner method; mp >295 °C; IR (KBr) υ/cm^{-1}: 3480, 3256, 1726, 1639, 1624, 1591; ^{1}H-NMR (δ/ppm): 11.63 (s, 1H, $H_{amidine}$), 10.20 (s, 1H, $H_{amidine}$), 9.82 (s, 1H), 9.45 (s, 1H, $H_{amidine}$), 9.08 (s, 1H), 8.92 (d, 1H, *J* = 7.10Hz), 8.86 (s, 1H), 8.54 (d, 1H, *J* = 8.16Hz), 8.32 (s, 1H), 8.10 (d, 1H, *J* = 7.11Hz), 7.98 (d, 1H, *J* = 8.25Hz), 7.69-7.64 (m, 2H), 3.83 (brs, 4H, $2CH_2$), 3.20 (brs, 2H, $2CH_2$); ^{13}C-NMR (δ/ppm): 163.54 (s), 161.84 (s), 145.87 (s), 144.08 (s), 135.10 (s), 135.03 (d), 132.36 (d), 130.23 (s), 129.63 (s), 126.31 (d), 125.76 (s), 125.20 (d), 124.53 (d), 122.75 (s), 120.08 (d), 116.55 (d), 116.13 (d), 66.01 (t, 2C), 54.42 (t, 2C); MS *m/z* 389 (M^{+1}); Anal. Calc. for $C_{21}H_{21}N_6O_2Cl$: C 59.36%, H 4.98%, N 19.78%; found: C 59.56%, H 5.11%, N 20.03%.

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