An Approach to Novel Fused Triazole or Tetrazole Derivatives Starting from Benzimidazo[1,2-*a*]quinazoline-5(7*H*)-one and 5,7-Dihydro-5-oxopyrido[3',2':5,6]pyrimido[1,2-*a*]benzimidazole

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The synthetic potential of the title compounds benzimidazo[1,2-*a*]quinazoline-5(7*H*)-one **2a** and 5,7-dihydro-5-oxopyrido[3',2':5,6]pyrimido[1,2-*a*]benzimidazole **2b** for the construction of novel polyheterocyclic frameworks is reported. Compounds **2a**,**b**, by conversion into their thio analogues **3a**,**b**, were used for the synthesis of tetrazole (**5a**,**b**) and triazole (**7a**,**b**) derivatives, as well as for an unexpected synthesis of triazoles **8a**,**b**, isomers of **7a**,**b**, resulting from the occurrence of a Dimroth rearrangement.

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Introduction.

In the ongoing search for new effective chemotherapeutic agents, a wide variety of new drugs with completely different chemical structures have been prepared and tested, but until today the development of curative antitumor drugs has been only partially successful. There is still a need to identify and develop clinically effective and well-tolerated antitumor drugs.

DNA replication constitutes the necessary precondition for cell division. Consequently, DNA has become one of the preferred targets for the development of new potential antitumor agents. For these reasons, DNA-binding molecules have been shown to be a highly effective class of anticancer drugs, of which the mechanism of action involves binding in either the major or minor grooves, or intercalation between base pairs of double-stranded DNA. Generally, agents with intercalative properties are characterized by the presence of a planar aromatic or heteroaromatic ring system [1,2].

Our longstanding involvement in the search for new polyheterocyclic compounds with antiproliferative activity has led us to prepare numerous molecules incorporating the benzimidazole, purine and indole moiety [3]. In the continuation of this research program, we have studied the synthetic potential of the benzimidazole derivatives **2a,b** [4,5] for the construction of novel polyheterocyclic frameworks. To the best of our knowledge, compounds **2a,b** have not been adequately investigated from this point of view, although they are readily available. In this paper we show how **2a,b**, by conversion into their thio analogues **3a,b**, can be used for the synthesis of compounds **5a,b** and **7a,b** (Figure 1), as well as for an unexpected synthesis of compounds **8a,b** (Figure 1), all of which are new pentacyclic ring systems.

Results and Discussion.

The benzimidazole derivatives **2a** [4] and **2b** [5], which represented the starting materials for the preparation of the target compounds **5a,b**, **7a,b** and **8a,b**, have already been described. The reported synthesis of compound **2a** involved a two-step procedure: reaction of 2-aminobenzimidazole **1** with 2-chlorobenzoyl chloride to afford the corresponding amide (about 43% yield), which was then cyclized to **2a** (53% yield) by heating at 200-210 °C. Since the overall yield of **2a** (about 23%) was not satisfactory, we obtained **2a** in an essentially quantitative yield (93%) *via* an Ullmann reaction between 2-aminobenzimidazole **1** and 2-bromobenzoic acid, adopting our previously reported procedure [5] for the preparation of **2b** from **1** and 2-chloronicotinic acid (Scheme 1).

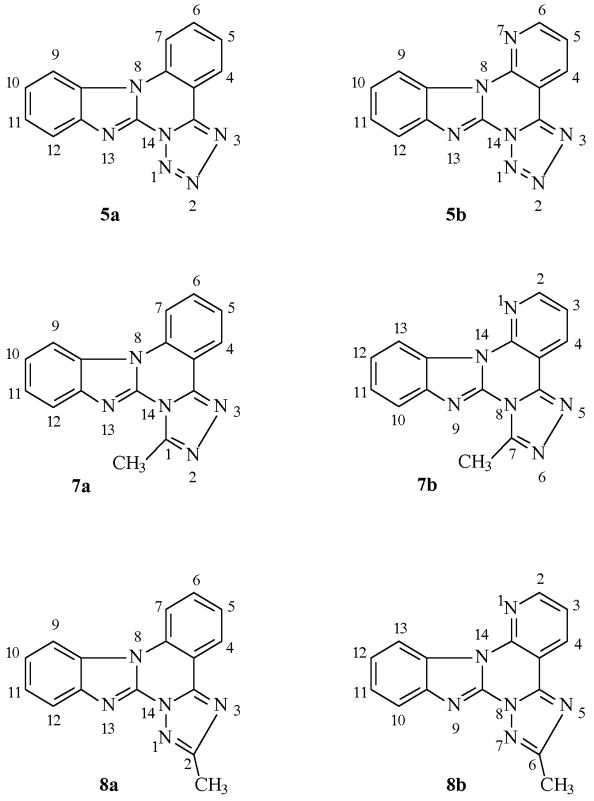


Figure 1

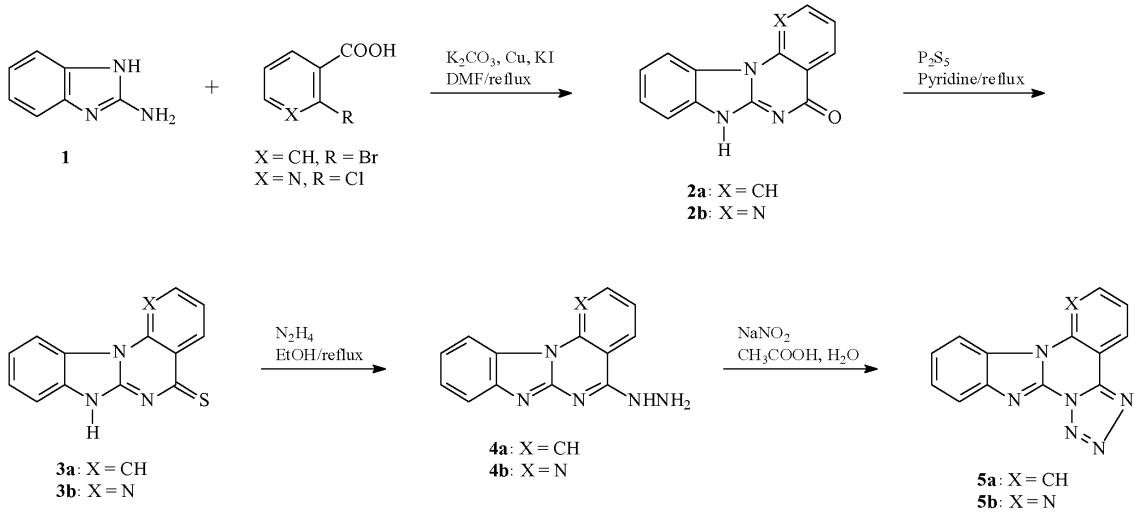
To prepare the key hydrazino intermediates **4a,b** the benzimidazole derivatives **2a,b** were activated by conversion into the thiolactams **3a,b** (Scheme 1). Compounds **3a,b** were obtained essentially pure from the reaction of **2a,b** with phosphorous pentasulfide in refluxing pyridine and were used directly in the following reactions without further purification.

Pure hydrazino derivatives **4a,b** formed upon treatment of compounds **3a,b** with hydrazine monohydrate in refluxing ethanol (Scheme 1). The tetrazole derivatives **5a,b** were easily prepared from **4a,b** by the action of excess sodium nitrite in aqueous acetic acid (Scheme 1). The structural assignment of **5a,b** was confirmed by their ir spectra, which showed absorptions indicative of the tetrazole nucleus in the region between 1110 and 1000 cm^{-1}, while the absence of any azido absorption bands in the 2200-2100 cm^{-1} region excluded the isomeric open-chain azido form [6]. MS spectra of **5a,b** demonstrated that elimination of nitrogen from the tetrazole ring was an important mode of fragmentation of these compounds, since the base peaks were those relative to the molecular weight minus twenty-eight.

Compound **6** was easily cyclized to **7b** by heating at 250 °C in Dowtherm A for 0.5 hour (Scheme 2).

To obtain compound **7b** directly, the thione **3b**, acetohydrazide and *N*,*N*-dimethylformamide were again reacted in a sealed tube for 7 hours, raising the temperature from 100 to 200 °C. Unexpectedly, the crude product proved to be a 1:1 mixture (ratio based on the methyl groups in the ^1H nmr spectrum) of compound **7b** and its isomer **8b**. It was not possible to separate **7b** from **8b** by either chromatography, due to their low solubility in organic solvents, or fractional recrystallization.

Scheme 1

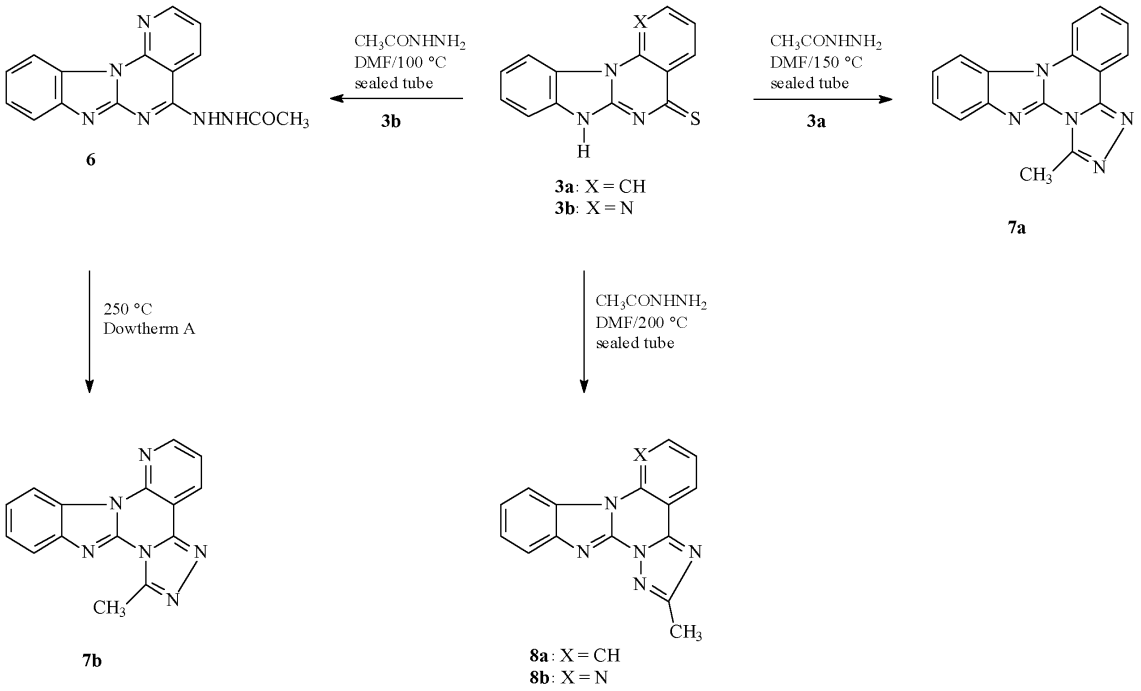


To further explore the synthetic scope and reactivity of thione derivatives **3a,b** for the obtainment of new polyheterocyclic compounds, condensation of **3a,b** with acetohydrazide was investigated.

By heating a suspension of **3b** and acetohydrazide in *N*,*N*-dimethylformamide at reflux for 24 hours, only the unreacted starting material could be recovered. Accordingly, adopting more drastic conditions, this suspension was heated in a sealed tube for 7 hours, at 100 °C, to afford the acetylhydrazino intermediate **6** with a low yield, together with some starting material (Scheme 2). The ^1H nmr spectrum of **6** showed two signals for the CH_3 group at 2.02 and 2.21 ppm, which were in the ratio of 1:1, and three deuterium oxide-exchangeable signals for the NHNHCO protons at 9.35, 10.10 and 12.00 ppm, which were in the ratio of 1:1:2. These data indicated that in solution (dimethylsulfoxide-d_6) the product was a mixture of tautomeric forms: the existence of a keto-enol tautomers was confirmed by the presence of two singlets for both the CH_3 group and the NHCO proton [7], while the broad singlet centered at 12.00 ppm resulted from the tautomerization of the other hydrazino proton on the N-6 and N-7 atoms.

It appeared that a Dimroth rearrangement partially occurred under the above-mentioned conditions, while no isomerization took place during the thermal cyclization of the intermediate **6** in Dowtherm A. This assumption was confirmed by a comparison between the ^1H nmr spectrum of compound **7b** and that of the mixture. The former showed the triazole methyl as a singlet at 3.06 ppm; the latter exhibited two methyl singlets: one at 2.61 ppm, the other at 3.06 ppm. In agreement with literature reports on fused 1,2,4-triazoles [8], the methyl protons at 2.61 ppm could be assigned to the isomer **8b**, as the methyl groups in the rearranged products are more upfield than the corresponding ones in the unrearranged compounds.

Scheme 2



The isomer **8b** was isolated after heating compound **3b**, acetohydrazide and *N*,*N*-dimethylformamide at 200 °C in a sealed tube for 24 hours (Scheme 2). However, the Dimroth rearrangement was not complete under these conditions, either, since the first solid that precipitated from the mother liquors contained only **8b** (its ^{1}H nmr spectrum did not show the methyl singlet due to **7b**), but the second fraction collected was a 1:2 mixture (ratio based on the methyl groups in the ^{1}H nmr spectrum) of **7b** and **8b**.

On the basis of the above-mentioned observations, a suspension of the thione derivative **3a** and acetohydrazide in *N*,*N*-dimethylformamide was heated in a sealed tube for 7 hours, at 100 °C, with the aim of isolating a type **6** acetylhydrazino intermediate to be cyclized to compound **7a**. Unexpectedly, under these conditions **3a** did not react. When the reaction was run at a higher temperature (150 °C), the first solid obtained consisted of a small amount of compound **7a** (Scheme 2), while the second fraction proved to be a 1:1 mixture (ratio based on the methyl groups in the ^{1}H nmr spectrum) of **7a** and its isomer **8a**. The structure assigned to **7a** was supported by the ^{1}H nmr spectrum, which showed a methyl singlet at 3.06 ppm, that is to say in the same position as the methyl protons of **7b**. In this case, too, the obtainment of **8a** could be explained by admitting that the initially formed **7a** had partially undergone a Dimroth rearrangement. This assumption was confirmed by an examination of the ^{1}H nmr spectrum of the mixture, which exhibited two methyl singlets resonating at 2.59 ppm (**8a**) and 3.06 ppm (**7a**), respectively. Compounds **7a** and **8a** could not be separated by either chromatography, due to their low solubility in organic solvents, or fractional recrystallization.

Pure **8a** was produced directly from the thione derivative **3a** and acetohydrazide by heating their suspension in *N*,*N*-dimethylformamide at 200 °C in a sealed tube for 24 hours, that is to say under the same conditions as those used to synthesize compound **8b** from **3b** (Scheme 2). In this case, investigation of the ^{1}H nmr spectrum of the final product revealed the presence of only one methyl singlet at 2.59 ppm.

It is interesting to note that the two isomeric pairs of triazole derivatives **7a-8a** and **7b-8b** did not show any considerable differences in the fragmentation patterns of their ms spectra, although products **7a,b**, which did not rearrange, were characterized by an intense peak corresponding to the molecular weight minus forty. Further, the uv spectra of compounds **7a,b** were characterized by two absorption maxima in the 300-330 nm region, whilst the rearranged ones **8a,b** showed only one maximum in the same region.

Conclusions.

In conclusion, the easily available benzimidazole derivatives **2a,b** proved to be a useful tool for the obtainment of novel fused triazole or tetrazole derivatives, with DNA-intercalating properties. The occurrence of the Dimroth rearrangement has been exploited to synthesize two new triazole derivatives, which should otherwise be prepared by more elaborate routes.

EXPERIMENTAL

General.

Melting points were uncorrected. IR spectra were obtained in Nujol mulls. ^{1}H nmr spectra (200 MHz) were recorded in dimethylsulfoxide-d_6 solution. ^{1}H nmr chemical shifts were referenced to tetramethylsilane. MS spectra were obtained by direct injection using electron impact ionization mode (EI, 70 eV). UV spectra were recorded in ethanol solution. Evaporations were performed *in vacuo* (rotary evaporator). TLC was carried out on Merck aluminium sheets, silica gel 60 F_{254}. Elemental analyses were performed by our Analytical Laboratory.

5,7-Dihydro-5-oxopyrido[3',2':5,6]pyrimido[1,2-*a*]benzimidazole **2b** was prepared in accordance with our previously reported method [5].

Benzimidazo[1,2-*a*]quinazoline-5(7*H*)-one (**2a**) [4].

2-Aminobenzimidazole **1** (2.194 g, 16 mmol) and 2-bromobenzoic acid (3.418 g, 16 mmol) were thoroughly mixed with anhydrous potassium carbonate (2.7 g, 19.56 mmol), 0.08 g of Ullmann copper, a trace of potassium iodide and 50 mL of *N*,*N*-dimethylformamide. The stirred suspension was refluxed for 5 hours. After cooling, the reaction mixture was diluted with water and acidified to pH 1 with 10% hydrochloric acid. The solid was collected, washed with water and suspended in boiling *N*,*N*-dimethylformamide to give 3.62 g (93% yield) of pure **2a**; yellow solid, mp > 300 °C (lit. [4] mp 348-350 °C); ir (cm^{-1}): 1680 (C=O); ^{1}H nmr: δ 7.29-7.42 (m, 2H), 7.51-7.65 (m, 2H), 7.93-8.00 (m, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.35 (d, *J* = 7.6 Hz, 1H), 8.49 (d, *J* = 8.3 Hz, 1H), 12.80 (s, 1H, exchangeable with deuterium oxide); ms (*m/z*, %): 235 (M^+, 100), 207 (M^+-CO, 27).

Anal. Calcd. for $C_{14}H_9N_3O$: C, 71.49; H, 3.83; N, 17.87. Found: C, 71.13; H, 3.66; N, 17.79.

General Procedure for the Preparation of Compounds **3a,b.**

Pyridine (25 mL) was added to a mixture of compound **2a** or **2b** (5.1 mmol) and phosphorous pentasulfide (2.41 g, 10.85 mmol). The resulting suspension was refluxed for 24 h under stirring. After cooling, the solid was collected, washed with water and used without further purification.

Benzimidazo[1,2-*a*]quinazoline-5(7*H*)-thione (**3a**). Yellow-orange solid, 1.09 g (85% yield); mp > 300 °C; ir (cm^{-1}): 1215 (C=S); ^{1}H nmr: δ 7.42-7.74 (m, 4H), 7.96-8.06 (m, 1H), 8.44-8.50 (m, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.80-8.86 (m, 1H); ms (*m/z*, %): 251 (M^+, 100), 207 (M^+-CS, 21).

Anal. Calcd. for $C_{14}H_9N_3S$: C, 66.93; H, 3.58; N, 16.73. Found: C, 66.62; H, 3.64; N, 16.71.

Pyrido[3',2':5,6]pyrimido[1,2-*a*]benzimidazole-5(7*H*)-thione (**3b**). Yellow solid, 1.13 g (88% yield); mp > 300 °C; ir (cm^{-1}): 1215 (C=S); ^{1}H nmr: δ 7.43-7.48 (m, 2H), 7.62-7.70 (m, 2H), 8.69-8.74 (m, 1H), 8.96-9.04 (m, 2H); ms (*m/z*, %): 252 (M^+, 100), 208 (M^+-CS, 21).

Anal. Calcd. for $C_{13}H_8N_4S$: C, 61.90; H, 3.17; N, 22.22. Found: C, 61.71; H, 3.01; N, 22.44.

General Procedure for the Preparation of Compounds **4a,b.**

A stirred suspension of **3a** or **3b** (1.98 mmol) in ethanol (20 mL) and hydrazine monohydrate (2 mL, 41.2 mmol) was refluxed for 7 h. After cooling, the solid was collected, washed with water and ethanol, and used without further purification.

5-Hydrazinobenzimidazo[1,2-*a*]quinazoline (**4a**).

This compound was obtained as a yellow ochre solid, 0.374 g (76% yield); mp > 300 °C; ir (cm^{-1}): 3267, 3192, 3051 ($NHNH_2$); ^{1}H nmr: δ 4.80-6.60 (br s, 3H, exchangeable with deuterium oxide), 7.22-7.37 (m, 2H), 7.47-7.61 (m, 2H), 7.85-7.94 (m, 1H), 8.28-8.34 (m, 2H), 8.53 (d, *J* = 8.3 Hz, 1H); ms (*m/z*, %): 249 (M^+, 100).

Anal. Calcd. for $C_{14}H_{11}N_5$: C, 67.47; H, 4.42; N, 28.11. Found: C, 67.14; H, 4.38; N, 27.83.

5-Hydrazinopyrido[3',2':5,6]pyrimido[1,2-*a*]benzimidazole (**4b**).

This compound was obtained as a yellow solid, 0.388 g (78% yield); mp 267-269 °C dec; ir (cm^{-1}): 3267, 3192, 3051 ($NHNH_2$); ^{1}H nmr: δ 4.60-6.40 (br s, 3H, exchangeable with deuterium oxide), 7.19-7.33 (m, 2H), 7.50-7.55 (m, 2H), 8.55-8.64 (m, 2H), 8.83 (m, 1H); ms (*m/z*, %): 250 (M^+, 100).

Anal. Calcd. for $C_{13}H_{10}N_6$: C, 62.40; H, 4.00; N, 33.60. Found: C, 62.17; H, 4.10; N, 33.25.

General Procedure for the Preparation of Compounds **5a,b**.

A solution of sodium nitrite (0.414 g, 6 mmol) in water (2 mL) was added dropwise to a stirred solution of **4a** or **4b** (1.2 mmol) in acetic acid (3 mL) and water (2 mL). After the completion of the addition, the resulting suspension was stirred at room temperature for 1 hour. The solid was then collected, washed with water and recrystallized from *N*,*N*-dimethylformamide.

Benzimidazo[1,2-*a*]tetrazolo[1,5-*c*]quinazoline (**5a**).

This compound was obtained as a yellow solid, 0.20 g (64% yield); mp 240-241 °C dec; ir (cm^{-1}): 1102, 1093, 1009 (tetrazole); ^{1}H nmr: δ 7.56-7.68 (m, 2H), 7.74-7.82 (m, 1H), 8.00-8.15 (m, 2H), 8.63-8.73 (m, 2H), 8.86 (d, *J* = 8.5 Hz, 1H); ms (*m/z*, %): 260 (M^+, 18), 232 (M^+-N_2, 100). uv: λ_{max} nm (log ε) 324 (3.76), 254 (4.39), 238 (4.36), 217 (4.28), 202 (4.28).

Anal. Calcd. for $C_{14}H_8N_6$: C, 64.61; H, 3.08; N, 32.31. Found: C, 64.66; H, 3.09; N, 32.66.

Pyrido[3',2':5,6]tetrazolo[1',5':3,4]pyrimido[1,2-*a*]benzimidazole (**5b**).

This compound was obtained as gold crystals, 0.30 g (96% yield); mp 244-245 °C dec; ir (cm^{-1}): 1102, 1093, 1009 (tetrazole); ^{1}H nmr: δ 7.56-7.68 (m, 2H), 7.83 (ddd, *J* = 8.1, 4.9, 1.2 Hz, 1H), 7.99-8.04 (m, 1H), 8.93-8.98 (m, 1H), 9.02-9.13 (m, 2H); ms (*m/z*, %): 261 (M^+, 15), 233 (M^+-N_2, 100). uv: λ_{max} nm (log ε) 317 (4.01), 253 (4.52), 228 (4.40), 202 (4.43).

Anal. Calcd. for $C_{13}H_7N_7$: C, 59.77; H, 2.68; N, 37.55. Found: C, 59.87; H, 2.75; N, 37.92.

5-Acetylhydrazinopyrido[3',2':5,6]pyrimido[1,2-*a*]benzimidazole (**6**).

A suspension of compound **3b** (0.5 g, 1.98 mmol) and 90% acetohydrazide (0.5 g, 6.08 mmol) in *N*,*N*-dimethylformamide (10 mL) was heated in a sealed tube at 100 °C for 7 hours. Unreacted **3b** was removed by filtration of the hot suspension. After cooling, the solid that precipitated from the filtrate was collected and suspended in boiling ethanol to give 0.083 g (14% yield) of pure **6**; yellow-orange solid, mp > 300 °C; ir (cm^{-1}): 3301, 3088 (NHNH), 1638 (C=O); ^{1}H nmr: δ 2.02, 2.21 (2s, 3H, CH_3), 7.20-7.60 (m, 4H), 8.40-8.84 (m, 3H), 9.35, 10.10, 11.40-12.20 (2s, 1br s, 2H, exchangeable with deuterium oxide); ms (*m/z*, %): 292 (M^+, 68), 274 (M^+-H_2O, 92), 250 (M^+-CH_2CO, 49), 221 (86), 43 (CH_3CO^+, 100).

Anal. Calcd. for $C_{15}H_{12}N_6O$: C, 61.64; H, 4.11; N, 28.77. Found: C, 61.30; H, 3.80; N, 28.91.

1-Methylbenzimidazo[1,2-*a*][1,2,4]triazolo[4,3-*c*]quinazoline (**7a**).

A suspension of compound **3a** (0.5 g, 1.99 mmol) and 90% acetohydrazide (0.5 g, 6.08 mmol) in *N*,*N*-dimethylformamide (10 mL) was heated in a sealed tube at 150 °C for 7 hours. After cooling, the solid that precipitated from the resulting solution was collected, washed with ethanol and recrystallized from *N*,*N*-dimethylformamide to give 0.066 g (12% yield) of pure **7a**; cream solid, mp 274-276 °C; ir (cm^{-1}): ν_{max} 1633, 1611, 1585, 1572, 1549, 1527, 1488, 1267, 741; ^{1}H nmr: δ 3.06 (s, 3H, CH_3), 7.49-7.54 (m, 2H), 7.60-7.68 (m, 1H), 7.84-7.94 (m, 2H), 8.49 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.54-8.59 (m, 1H), 8.67 (d, *J* = 8.5 Hz, 1H); ms (*m/z*, %): 273 (M^+, 100), 233 (83); uv: λ_{max} nm (log ε) 319 (3.88), 307 (3.96), 260 (4.62), 249 (4.65), 204 (4.46).

Anal. Calcd. for $C_{16}H_{11}N_5$: C, 70.33; H, 4.03; N, 25.64. Found: C, 70.71; H, 3.95; N, 25.84.

7-Methylpyrido[3',2':5,6][1,2,4]triazolo[4',3':3,4]pyrimido-[1,2-*a*]benzimidazole (**7b**).

A suspension of compound **6** (0.25 g, 0.86 mmol) in Dowtherm A (3 mL) was heated at 250 °C for 0.5 hour. After cooling, the solid was collected, washed with petroleum ether 60-80 °C and recrystallized from *N*,*N*-dimethylformamide to give 0.168 g (71% yield) of pure **7b**; red-orange solid, mp > 300 °C; ir (cm^{-1}): ν_{max} 1638, 1605, 1587, 1568, 1544, 1488, 1446, 1253, 821, 764, 755, 741; ^{1}H nmr: δ 3.06 (s, 3H, CH_3), 7.47-7.52 (m, 2H), 7.68 (dd, *J* = 8.0, 4.9 Hz, 1H), 7.85-7.90 (m, 1H), 8.80-8.90 (m, 3H); ms (*m/z*, %): 274 (M^+, 100), 234 (62); uv: λ_{max} nm (log ε) 324 (3.89), 313 (3.92), 258 (4.32), 237 (4.32), 208 (4.32).

Anal. Calcd. for $C_{15}H_{10}N_6$: C, 65.69; H, 3.65; N, 30.66. Found: C, 65.31; H, 3.70; N, 31.04.

2-Methylbenzimidazo[1,2-*a*][1,2,4]triazolo[1,5-*c*]quinazoline (**8a**).

A suspension of compound **3a** (0.5 g, 1.99 mmol) and 90% acetohydrazide (0.5 g, 6.08 mmol) in *N*,*N*-dimethylformamide (10 mL) was heated in a sealed tube at 200 °C for 24 hours. After cooling, the solid that precipitated from the resulting solution was collected and washed with ethanol to give 0.212 g of crude **8a**. The mother liquors were then concentrated to small volume to yield another 0.113 g of crude **8a**. The combined solids were recrystallized from *N*,*N*-dimethylformamide to give 0.217 g (40% yield) of pure **8a**; cream solid, mp 286-287 °C; ir (cm^{-1}): ν_{max} 1638, 1610, 1591, 1568, 1474, 1446, 1403, 1309, 1253, 1201, 760, 750, 731; ^{1}H nmr: δ 2.59 (s, 3H, CH_3), 7.49-7.56 (m, 2H), 7.63-7.71 (m, 1H), 7.86-8.00 (m, 2H), 8.44 (d, *J* = 7.8 Hz, 1H), 8.57-8.62 (m, 1H), 8.75 (d, *J* = 8.5 Hz, 1H); ms (*m/z*, %): 273 (M^+, 100); uv: λ_{max} nm (log ε), 312 (4.15), 252 (4.75), 242 (4.76), 213 (4.57).

Anal. Calcd. for $C_{16}H_{11}N_5$: C, 70.33; H, 4.03; N, 25.64. Found: C, 69.98; H, 3.86; N, 25.44.

6-Methylpyrido[3',2':5,6][1,2,4]triazolo[1',5':3,4]pyrimido-[1,2-*a*]benzimidazole (**8b**).

A suspension of compound **3b** (0.5 g, 1.98 mmol) and 90% acetohydrazide (0.5 g, 6.08 mmol) in *N*,*N*-dimethylformamide (10 mL) was heated in a sealed tube at 200 °C for 24 hours. After cooling, the solid that precipitated from the resulting solution was collected, washed with ethanol and recrystallized from *N*,*N*-dimethylformamide to give 0.216 g (40% yield) of pure **8b**; pale orange solid, mp 288-290 °C; ir (cm^{-1}): ν_{max} 1638, 1602, 1580, 1466, 1430, 1351, 1307, 1258, 829, 768, 759, 746; ^{1}H nmr: δ 2.61 (s, 3H, CH_3), 7.48-7.57 (m, 2H), 7.70-7.77 (m, 1H), 7.85-7.90 (m, 1H), 8.76-9.01 (m, 3H); ms (*m/z*, %): 274 (M^+, 100); uv: λ_{max} nm (log ε) 318 (4.16), 241 (4.61), 208 (4.54).

Anal. Calcd. for $C_{15}H_{10}N_6$: C, 65.69; H, 3.65; N, 30.66. Found: C, 65.62; H, 3.46; N, 31.00.

The initial filtrate was concentrated to a small volume to afford 0.077 g of a 1:2 mixture (^{1}H nmr analysis) of **7b** and **8b**.

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