Synthesis of 1,3,5-triazepine-2,4-dione, pyrrolo[3,4-*f*][1,3,5]triazepine-2,4-dione, pyridazino[4,5-*f*][1,3,5]triazepine and 1,3,5,7,9-pentazaheptaline derivatives

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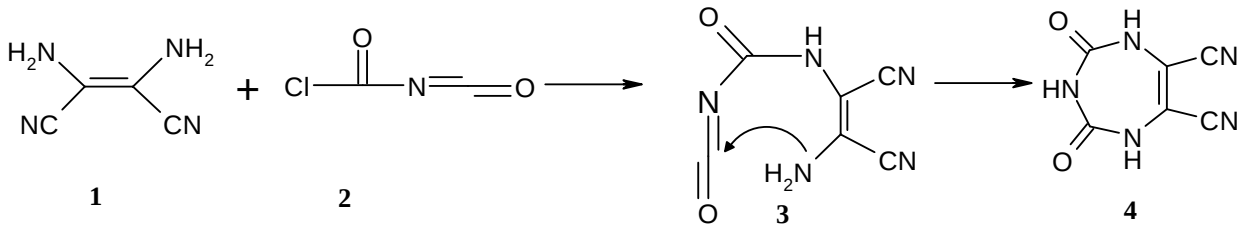
Abstract

The reaction of the enaminonitrile **1** with chlorocarbonyl isocyanate **2** afforded the carbonyl isocyanate derivative **3**. The 1,3,5-triazepine-2,4-dione derivative **4** was synthesized by refluxing **3** with sodium hydroxide. Compound **4** was used in ring formation through reactions with aliphatic-, aromatic-, and heteroaromatic amines, affording pyrrolo[3,4-f][1,3,5]triazepine, pyridazino[4,5-f][1,3,5]triazepine and 1,3,5,7,9-pentazaheptaline derivatives.

Keywords: Enaminonitriles, 1,3,5-triazepine-2,4-dione, pyrrolotriazepine, pyridazinotriazepine, 1,3,5,7,9-pentazaheptaline

Introduction

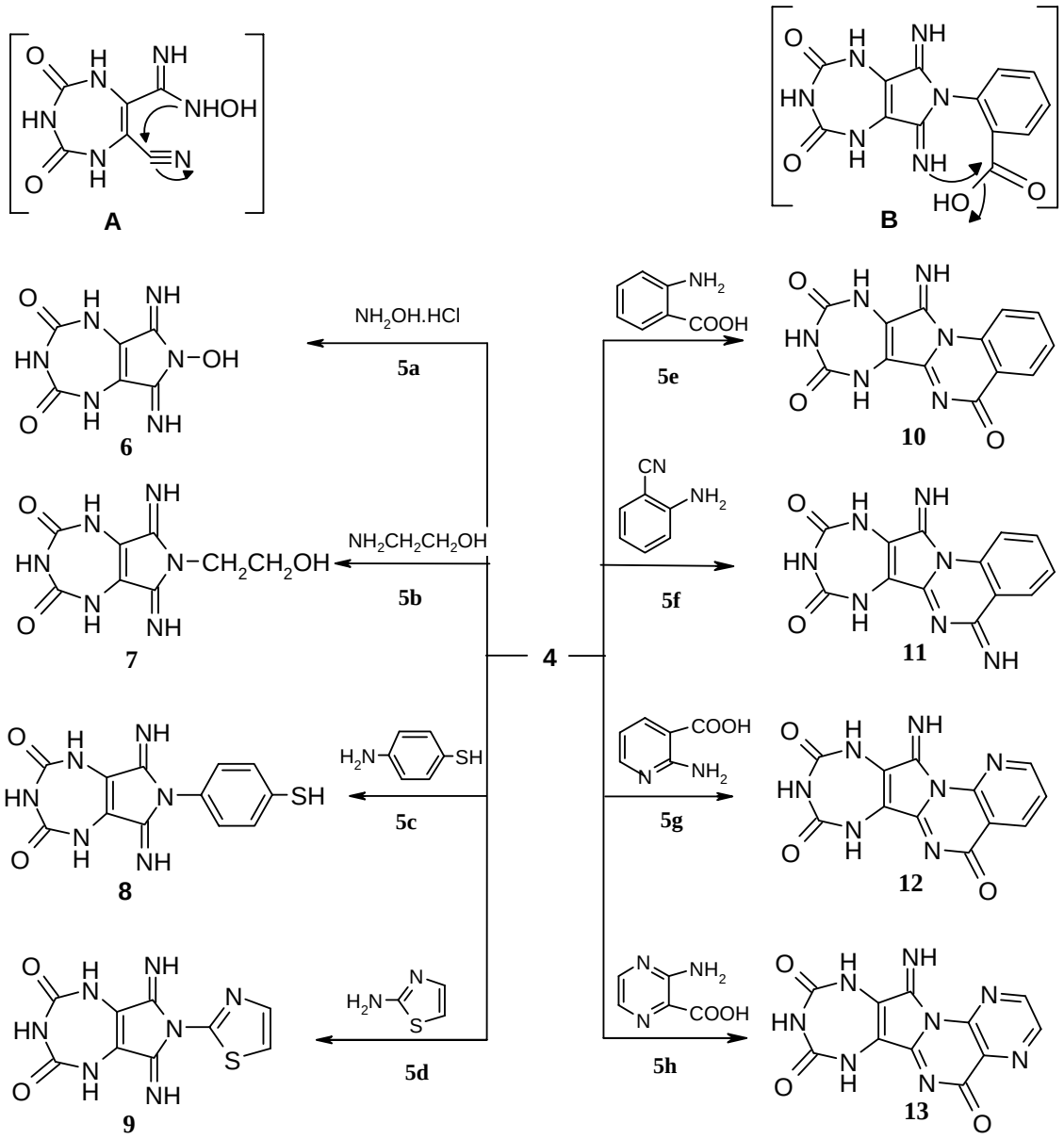
The reactions of diaminomaleonitrile (DAMN) with diones,[1] isocyanates,[2] and phenylacetyl isothiocyanate[3] have been reported. The corresponding dihydro analogues (C6–C7) of the title ring systems have been described.[4–6] Pyrrolo[3,4-*f*][1,3,5]triazepine was synthesized by reaction of the amidine derivative of diaminomaleonitrile with carbonyl compounds.[7,8] Chlorocarbonyl isocyanate **2** was used in the synthesis of heterocyclic compounds.[9–12]



Scheme 1. The reaction of diaminomaleonitrile with chlorocarbonyl isocyanate.

Results and Discussion

The reaction of diaminomaleonitrile **1** with chlorocarbonyl isocyanate **2** in the presence of triethylamine afforded compound **3** whose IR spectra revealed bands at 2265 and 3260 assignable to N=C=O and NH_2 groups respectively. Compound **3** was refluxed in the presence of 10% sodium hydroxide to afford **4** whose IR spectra showed the absence of bands assignable to N=C=O and NH_2 groups, and its structure is in agreement with its elemental analysis and spectral data. (Scheme 1, and Experimental Section).



Scheme 2. Reactions of compound **4** with aliphatic-, aromatic-, and heteroaromatic amines.

Several 7-substituted-6,8-diimino-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2(1*H*),4(3*H*,5*H*)-dione derivatives **6–9** were prepared by reaction of compound **4** with aliphatic-, aromatic-, and heteroaromatic amines **5a–d** (Scheme 2). Thus, compound **4** reacted with hydroxylamine hydrochloride **5a** in boiling ethanol affording **6** through the intermediate **A.** The MS of compound **6** was consistent with a parent peak at $M^+ = 210$. Also, the product showed no CN absorbance but did have an OH absorbance in the IR consistent with **6**. Similarly, compound **4** reacted with ethanolamine **5b** in the presence of pyridine, affording **7**.

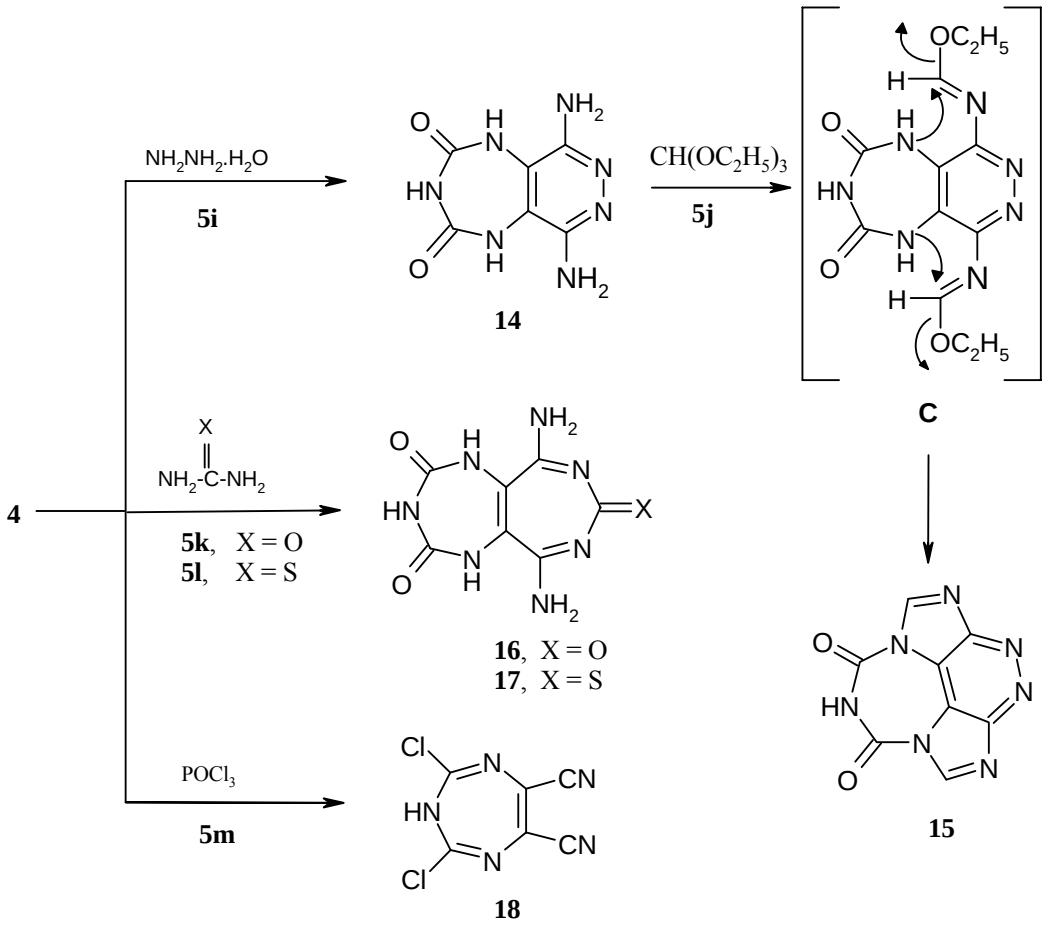
Compound **4** reacted with 4-aminothiophenol, **5c**, in the presence of pyridine/water to give **8**. Also, the reaction of **4** with 2-aminothiazole **5d** afforded **9**. The structures of the prepared compounds are in agreement with their spectral data (Scheme 2, *c.f.* Experimental Section).

On the other hand, the tetracyclic derivatives **10**–**13** containing pyrrolo[3,4-*f*][1,3,5]triazepine-2(1*H*),4(3*H*,5*H*)-dione were synthesized by reaction of **4** with the aromatic and heteroaromatic amines **5e–h**. Thus, compound **4** reacted with anthranilic acid, **5e** affording **10** through the intermediate **B**. The ^{1}H NMR spectra of compound **10** revealed two signals as a pair of doublets at δ = 7.68 (*J* = 6.65, 6.65 Hz) and δ = 7.78 (*J* = 7.7, 7.7 Hz) and two signals as doublets at δ = 7.84 (*J* = 7, 5 Hz) and δ = 8.35 (*J* = 8, 7 Hz) for aromatic hydrogens. Similarly, compound **4** reacted with 2-aminobenzonitrile **5f** affording **11**. Also, compound **4** reacted with 2-aminopyridine-2-carboxylic acid **5g** to yield **12** for which ^{1}H NMR spectra revealed one signal as pair of doublets at δ = 7.62 (*J* = 5, 7 Hz) and two signals as doublet quartet at δ = 8.90 (*J* = 5, 2 Hz) and δ = 8.75 (*J* = 7, 2 Hz) as a result of meta coupling of pyridine ring hydrogens. Compound **4** reacted with 3-aminopyrazine-2-carboxylic acid **5h** affording **13** whose structure is in agreement with its elemental analysis and spectral data (Scheme 2, cf. Experimental).

Pyridazino[4,5-*f*][1,3,5]triazepine-2(1*H*),4(3*H*,5*H*)-dione **14** was synthesized by treatment of **4** with hydrazine hydrate **5i**. Compound **14** was treated with triethyl orthoformate **5j** yielding the imidate derivative **C** which cyclizes under the reaction condition to yield **15**.

Compound **4** reacted with urea **5k** and thiourea **5l** to yield 1,3,5,7,9-pentazaheptaline derivatives **16** and **17** respectively.

Compound **4** reacted with $POCl_3$ **5m** to yield 3-hydro-2,4-dichloro-6,7-dicyano-1,3,5-triazepine **18** for which IR spectra revealed a characteristic nitrile absorption at 2230 cm^{-1} besides an absorption band at 698 cm^{-1} for (C–Cl) and its elemental analysis and spectral data revealed a molecular formula $C_6HN_5Cl_2$ ($M^+ = 214$).



Scheme 3. New compounds derived from compound **4**.

Experimental Section

General Procedures. Melting points were determined on a Gallenkamp Electrothermal apparatus and are uncorrected. IR spectra were recorded on a Pye-Unicam SP 110 spectrophotometer, in KBr disks. The ^{1}H- and ^{13}C- NMR spectra were recorded on a Varian Gemini NMR spectrometer 300 (300 MHz for ^{1}H, 75.5 MHz for ^{13}C) using Me_4Si as an internal reference, and are given as δ/ppm. Mass spectra were measured on a Hitachi 80-B spectrometer at 70 eV. The progress of the reaction was monitored by TLC using precoated silica gel plates (F254, Merck, Darmstadt). Methylene chloride was dried over molecular sieves, 80–100 mesh, and distilled by refluxing over calcium hydride.

Preparation of carbonyl isocyanate derivative 3. An equimolar mixture of diaminomaleonitrile **1** (1.08g, 0.01mole) and chlorocarbonyl isocyanate **2** (1.05 g, 0.01 mole) in dry methylene chloride (30 mL) was stirred in the presence of triethylamine (1.5 mL) at 0 °C for

2h, then for 1 h at 25 °C and the reaction mixture was left to stand overnight at room temperature. Water (3 mL) was added and the solid product was collected by filtration and crystallized from ethanol. **3**: 1.57 g (94 %), m.p. = 276 °C; IR ν/ cm^{-1}: 2226 (CN), 1670 (CO), 3430 (NH), 3260 (NH_2) 1660 (C=C), 2265 (N=C=O); ^{1}H NMR ($CDCl_3$) δ: 8.2 (br, s, 1H, NH), 6.4 (br, s, 2H, NH_2), D_2O-exchangeable; ^{13}C NMR ($CDCl_3$) δ: 117.2 (CN), 117.3 (CN), 144.5 (C), 144.7 (C), 165.8 (CO), 168.2 (CO); m/z: 177 (M^+, 82 %). Anal. Calc. for $C_6H_3N_5O_2$ (MW = 177.12): C 40.69, H 1.71, N 39.54. Found: C 40.64, H 1.67, N 39.48 %.

Preparation of 6,7-dicyano-1,3,5-triazepine-2(1*H*),4(3*H*,5*H*)-dione (**4).** To a suspension of compound **3** (1.77 g, 0.01 mol) in methylene chloride was added 10 % NaOH (20 mL). The reaction mixture was refluxed for 2 h and then cooled to room temperature. Water (3 mL) was added and the solid product was collected by filtration and crystallized from ethanol. **4:** 1.57 g (89 %), m.p. > 300 °C (ethanol); IR (KBr) ν/ cm^{-1}: 2228 (CN), 1675 (CO), 3445 (NH), 1652 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.8, 8.0 (br, s, 3H, NH) D_2O exchangeable; ^{13}C NMR ($CDCl_3$) δ: 117.8 (CN), 144.3 (2 x C), 163.8 (CO); m/z: 177 (M^+, 66 %). Anal. Calc. for $C_6H_3N_5O_2$ (MW = 177.12): C 40.69, H 1.71, N 39.54, Found: C 40.64, H 1.67, N 39.48 %

Preparation of 7-substituted-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2(1*H*),4-(3*H*,5*H*)-diones, 6–13

A mixture of **4** (1.77 g, 0.01 mole) and an aliphatic or heteroaromatic amine **5a – h** (0.01 mole) in 50 mL of (ethanol for **6**, pyridine/water for **8**, pyridine for **7**, **9–13**) containing triethylamine (1.5 mL) was refluxed for 3 h. The reaction mixture was cooled. Water was added and the product was filtered, washed with water and crystallized from the appropriate solvent.

7-Hydroxy-6,8-diimino-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2-(1*H*), 4-(3*H*,5*H*)-dione (6). Yield 1.78 g (85 %), m.p. = 293 °C (ethanol); IR ν/ cm^{-1}: 1674 (CO), 3448 (NH), 3350 (C=NH), 1640 (C=C), 3590 (OH); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.8, 7.3 (br, s, 3H, NH), 5.3 (s, 2H, -C=NH) D_2O exchangeable, 6.7 (s, H, OH); ^{13}C NMR ($CDCl_3$) δ: 136.8 (C), 137.6 (C), 142.6 (C), 143.3 (C), 162.4 (CO), 162.9 (CO); m/z: 210 (M^+, 77 %). Anal. Calc. for $C_6H_6N_6O_3$ (MW = 210.15): C 34.29, H 2.88, N 39.99, Found: C 34.23, H 2.86, N 39.95 %.

7-(2-Hydroxyethyl)-6,8-diimino-2*H*,5*H*-pyrrolo-[3,4-*f*][1,3,5]triazepine-2(1*H*),4-(3*H*,5*H*)-dione (7). Yield 1.89 g (77 %), m.p. = 281 °C (ethanol); IR (KBr) ν/ cm^{-1}: 1680 (CO), 3452 (NH), 3346 (C=NH), 1644 (C=C), 3470 (OH); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.7, 7.3 (br, s, 3H, NH), 5.5 (s, 2H, -C=NH), 2.3 (dd, *J* = 4.1 Hz, *J* = 8.7 Hz, H, OH) D_2O exchangeable, 2.30-2.33 (m, 2H, CH_2), 3.45 (tt, *J* = 7.3 Hz, 1.0 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ: 17.4 (-CH_2), 18.6 (-CH_2), 134.4 (C), 135.8 (C), 142.9 (C), 143.5 (C), 162.3 (CO), 162.5 (CO); m/z: 208 (M^+, 85 %). Anal. Calc. for $C_7H_8N_6O_2$ (MW = 208.18): C 40.39, H 3.87, N 40.37, Found: C 40.32, H 3.79, N 40.33 %.

7-(*p*-Mercaptophenyl)-6,8-diimino-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2(1*H*),4-(3*H*,5*H*)-dione (8). Yield 2.5 g (83 %), m.p. > 300 °C (ethanol); IR (KBr) ν/ cm^{-1}: 1682 (CO), 3454 (NH), 3348 (C=NH), 2570 (SH), 1642 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.8, 7.2 (br, s, 3H, NH), 5.4 (s, 2H, -C=NH), D2O exchangeable, 7.78 (d, *J* = 7.7 Hz, 1H, Ph), 7.84 (d, *J* = 7.5 Hz, 1H, Ph), 8.35

(d, *J* = 8.7 Hz, 1H, Ph), 8.36 (d, *J* = 8.2 Hz, 1H, Ph), 3.7 (s, 1H, SH); ^{13}C NMR ($CDCl_3$) δ: 129.6, 130.4, 131.5, 132.8 (CH), 134.9, 135.2, (C) 142.4 (C), 143.2 (C), 144.6 (C), 144.9 (C), 162.8, 163.2 (2 x CO); m/z: 302 (M^+, 62 %). Anal. Calc. for $C_{12}H_{10}N_6O_2S$ (MW = 302.32): C 47.68, H 3.33, N 27.80, Found: C 47.59, H 3.28, N 27.71 %.

7-(2'-Thiazolyl)-6,8-diimino-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2(1*H*),4-(3*H*,5*H*)-dione (9). Yield 2.19 g (79 %), m.p. = 274 °C (ethanol); IR (KBr) ν/ cm^{-1}: 1688 (CO), 3356 (NH), 3351 (C=NH), 1610 (C=N), 1644 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.8, 7.4 (br, s, 3H, NH), 5.2 (s, 2H, -C=NH) D_2O exchangeable, 3.2 (d, *J* = 3.4 Hz, 1H, thiazole ring), 3.5(d, *J* = 3.7 Hz, 1H, thiazole ring); ^{13}C NMR ($CDCl_3$) δ: 134.8 (-CH), 135.3 (-CH), 136.4 (C), 137.2 (C), 139.5 (C), 143.7 (C), 144.4 (C), 163.4 (CO), 164.5 (CO); m/z: 277 (M^+, 73 %). Anal. Calc. for $C_9H_7N_7O_2S$ (MW = 277.27): C 38.99, H 2.54, N 35.36, Found: C 38.94, H 2.48, N 35.27 %.

6-Imino-(quinazolin-4-oxo-yl)[1',2':7,8]-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine 2(1*H*),4(3*H*,5*H*)-dione (10). Yield 2.25 g (76 %), m.p. = 258 °C (dilute acetic acid); IR (KBr) ν/ cm^{-1}: 1687 (CO), 3348 (NH), 3338 (C=NH), 1615 (C=N), 1645 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.6, 7.3 (br, s, 3H, NH), 5.4 (s, H, -C=NH) D_2O exchangeable, 7.68 (1H, dd, *J* = 6.65, 6.65 Hz), 7.78 (1H, dd, *J* = 7.7, 7.7 Hz), 7.84 (1H, d, *J* = 7.5 Hz), 8.35 (1H, d, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ: 129.3 (-CH), 130.4 (-CH), 131.6 (-CH), 132.4 (-CH), 134.5 (C), 136.7 (C), 138.2 (C), 142.8 (C), 143.4 (C), 145.7 (C), 161.8, 162.2, 164.0 (3 x CO); m/z: 296 (M^+, 48 %). Anal. Calc. for $C_{13}H_8N_6O_3$ (MW = 296.25): C 52.71, H 2.72, N 28.37, Found: C 52.64, H 2.69, N 28.29 %.

6-Imino-(quinazolin-4-imino-yl)[1',2':7,8]-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2(1*H*),4(3*H*,5*H*)- dione (11). Yield 2.39 g (81 %), m.p. = 261 °C (dilute acetic acid); IR (KBr) ν/ cm^{-1}: 1682 (CO), 3360 (NH), 3350 (C=NH), 1615 (C=N), 1644 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.7, 7.4 (br, s, 3H, NH), 5.0 (s, 2H, 2x C=NH) D_2O exchangeable, 7.84 (1H, dd, *J* = 6.30, 6.30 Hz), 7.66 (1H, dd, *J* = 7.3, 7.3 Hz), 7.60 (1H, d, *J* = 6.9 Hz), 8.34 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ: 129.8 (-CH), 130.2 (-CH), 131.7 (-CH), 132.5 (-CH), 134.5 (C), 136.7 (C), 138.2 (C), 142.7 (C), 143.4 (C), 144.2 (C), 145.8 (C), 161.7, 162.6 (2x CO); m/z: 295 (M^+, 79 %). Anal. Calc. for $C_{13}H_9N_7O_2$ (MW = 295.26): C 52.88, H 3.07, N 33.21, Found: C 52.83, H 3.01, N 33.17 %.

6-Imino-(pyrido[2',3':4,5]pyrimidine-6-one-yl)[2',3':7,8]-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2 (1*H*),4-(3*H*,5*H*)-dione (12). Yield 2.52 g (85%), m.p. = 255 °C (dilute acetic acid); IR (KBr) ν/ cm^{-1}: 1685 (CO), 3358 (NH), 3341 (C=NH), 1620 (C=N), 1642 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.7, 7.3 (br, s, 3H, NH), 4.3 (s, H, C=NH) D_2O exchangeable, 8.90 (dq, *J* = 5, 2 Hz, 1H, pyridine ring), 7.25 (dd, *J* = 5, 7 Hz, 1H, pyridine ring), 8.75 (dq, *J* = 7, 2 Hz, 1H, pyridine ring); ^{13}C NMR ($CDCl_3$) δ: 130.6 (-CH), 131.6 (-CH), 132.4 (-CH), 134.5 (C), 136.7 (C), 138.2 (C), 142.8 (C), 143.4 (C), 145.7 (C), 161.8, 162.3, 164.2 (3 x CO); m/z: 297 (M^+, 49 %). Anal. Calc. for $C_{12}H_7N_7O_3$ (MW = 297.23): C 48.49, H 2.37, N 32.99, Found: C 48.47, H 2.32, N 32.91 %.

6-Imino-(pteridin-4(1*H*)-one-yl)[1',2':7,8]-2*H*,5*H*-pyrrolo[3,4-*f*][1,3,5]triazepine-2(1*H*),4(3*H*,5*H*)- dione (13). Yield 2.29 g (77 %), m.p. = 246 °C (dilute acetic acid); IR (KBr)

ν/ cm^{-1}: 1685 (CO), 3358 (NH), 3344 (C=NH), 1618 (C=N), 1642 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.8, 7.2 (br, s, 3H, NH), 4.5 (s, H, C=NH) D_2O exchangeable, 8.65 (d, *J* = 6.8 Hz, 1H, pyrazine ring), 8.36 (d, *J* = 6.8 Hz, 1H, pyrazine ring); ^{13}C NMR ($CDCl_3$) δ: 131.5 (-CH), 132.6 (-CH), 134.5 (C), 136.7 (C), 138.2 (C), 142.8 (C), 143.4 (C), 145.4 (C), 161.6, 162.4, 164.1 (3 x CO); m/z: 298 (M^+, 33 %). Anal. Calc. for $C_{11}H_6N_8O_3$ (MW = 298.22): C 44.30, H 2.03, N 37.57, Found: C 44.25, H 1.98, N 37.52 %.

Preparation of 6,9-diamino-2*H*,5*H*-pyridazino[4,5-*f*][1,3,5]triazepine-2(1*H*), 4-(3*H*,5*H*)-dione (14). Compound **4** (1.77 g, 0.01 mol) and hydrazine hydrate (0.01 mole) were refluxed in ethanol with triethylamine (0.5 mL) for 4 h. The solvent was then evaporated in vacuo and the remaining product was triturated with a little of water and then acidified with HCl acid. The resulting solid product was collected by filtration and crystallized from ethanol. **14**: 1.52 g (73 %), m.p. = 264 °C (ethanol); IR (KBr) ν/ cm^{-1}: 1672 (CO), 3352 (NH), 3248 (NH_2), 1620 (C=N), 1638 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.1, 7.3 (br, s, 3H, NH), 6.3 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$) δ: 140.6, 141.5, 142.3 (C), 143.8 (C), 161.8, 162.2 (2xCO); m/z: 209 (M^+, 66 %). Anal. Calc. for $C_6H_7N_7O_2$ (MW = 209.17): C 34.45, H 3.37, N 46.87, Found: C 34.39, H 3.32, N 46.80 %.

Preparation of diimidazolyl[3',4',5',3,4,5][*e*,*f*]pyridazino[4,5-*f*][1,3,5]triazepine-2,4-dione (15). A mixture of **14** (2.09 g, 0.01 mol), an equimolar amount of triethyl orthoformate and acetic anhydride (16 mL) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting solid product was crystallized from benzene/petroleum ether (1:1). **15**: 1.74 g (71%), m.p. = 193 °C (benzene/petroleum); IR (KBr) ν/ cm^{-1}: 1675 (CO), 3345 (NH), 1622 (C=N), 1638 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 8.0 (br, s, H, NH) D_2O exchangeable, 8.15 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 136.2 (CH), 137.4 (-CH), 138.7 (C), 139.4 (C), 144.1 (C), 144.7 (C), 162.9, 163.2 (2 x CO); m/z: 245 (M^+, 76 %). Anal. Calc. for $C_9H_7N_7O_2$ (MW = 245.20): C 44.09, H 2.88, N 39.99, Found: C 44.02, H 2.83, N 39.95 %.

Preparation of 6,10-diamino-1,3,5,7,9-pentazaheptalin-2,4,8-trione, 16 and 6,10-diamino-8-thioxo-1,3,5,7,9-pentazaheptaline-2,4-dione (17). Compound **4** (1.77 g, 0.01 mol) and urea **5j** or thiourea **5k** (0.01 mole) were refluxed in ethanol (50 mL) containing triethylamine (0.5 mL) for 3 h. The mixture was then collected by filtration then recrystallized from ethanol. **16**: 1.61 g (68 %), m.p. > 300 °C (ethanol); IR (KBr) ν/ cm^{-1}: 1683 (CO), 3355 (NH), 3252 (NH_2), 1620 (C=N), 1642 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.7, 7.5 (br, s, 3H, NH), 6.8 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$) δ: 137.6 (C), 138.4 (C), 144.3 (C), 145.8 (C), 163.3, 163.5, 165.2 (3 x CO); m/z: 237 (M^+, 82 %). Anal. Calc. for $C_7H_7N_7O_3$ (MW = 237.17): C 35.45, H 2.97, N 41.34, Found: C 35.37, H 2.94, N 41.29 %. **17**: 1.87 g (74 %), m.p. = 286 °C (ethanol); IR (KBr) ν/ cm^{-1}: 1683 (CO), 1195 (CS), 3354 (NH), 3250 (NH_2), 1620 (C=N), 1642 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.8, 7.3 (br, s, 3H, NH), 6.6 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$) δ: 139.6 (C), 140.4 (C), 144.3 (C), 145.8 (C), 163.8, 164.1 (2 x CO), 181.4 (CS); m/z: 253 (M^+, 82 %).

Anal. Calc. for $C_7H_7N_7O_2S$ (MW = 253.24): C 33.17, H 2.78, N 38.71, Found: C 33.09, H 2.72, N 38.66 %.

Preparation of 3-hydro-2,4-dichloro-6,7-dicyano-1,3,5-triazepine (18). A mixture of **4** (1.77 g, 0.01 mole), phosphorus oxychloride (20 mL) and *N*,*N*-dimethylaniline (2 mL) was

refluxed for 3 h. After removal of the excess of phosphorus oxychloride, the residue was added 200 mL of ice water. The precipitate was collected by filtration and recrystallized from chloroform. **18**: 1.64 g (77 %), m.p. = 183 ^{o}C (chloroform); IR (KBr) ν/ cm^{-1}: 2230 (CN), 698 (C – Cl), 1660 (C=C); ^{1}H NMR ($CDCl_3$) δ/ppm: 7.2 (br, s, H, NH) D_2O exchangeable; ^{13}C NMR ($CDCl_3$) δ: 117.6, 117.8 (2 x CN), 141.2 (C), 141.6 (C), 144.3 (C), 145.8 (C); m/z: 214 (M^+, 12 %). Anal. Calc. for $C_6HN_5Cl_2$ (MW = 214.01): C 33.67, H 0.47, N 32.72, Found: C 33.58, H 0.42, N 32.65 %.

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